Lunes 24 de Enero

Hora	Duración	Ponencia	Título	Ponente
9:15	15’	Organización Encuentro		
9:30	15’	Sistemas Acuosos I – Clatratos: Presentación del Moderador		Olga Prieto Ballesteros
9:45	2x15’	Ponencias Sistemas Acuosos I	*Clatratos en el Sistema Solar*	Mª Victoria Muñoz Iglesias
			Análisis cualitativo y cuantitativo del CO_2 en salmueras	Laura Jiménez Bonales
10:15	45’	Conferencia Invitada	*Emerging risks related to food technology*	Jean Claude Cheftel
11:00	15’	Sistemas Acuosos II – Disoluciones: Presentación del Moderador		Pedro D. Sanz Martínez
11:15	3x15’	Ponencias Sistemas Acuosos II	*Efectos inducidos por la presión sobre agregados en medio acuoso. Estudio del dodecanoato de sodio mediante medidas de velocidad del sonido*	Eduardo Hidalgo Baltasar
			Efectos inducidos por la presión sobre agregados en medio acuoso. Aplicación de técnicas volumétricas al estudio de la asociación de caseínas	Bérengère Guignon
			Influencia de la presión en la simulación del plegamiento de proteínas	Ramiro Perezzan Rodríguez
12:00	Pausa			
12:30	15’	Sistemas Acuosos III – Microbiología y T. Alimentos: Presentación		Buenaventura Guamis
12:45	4x15’	Ponencias Sistemas Acuosos III	*Muerte y daño subletal causados por alta presión*	Jordi Saldo Periago
			Nanoencapsulación por Ultra Alta Presión Homogenización (UHPH)	Roger Escriu Justo
			Incorporación de Sensores Ópticos al procesado de alimentos	Manuel Castillo Zambudio
			Modelización matemática de procesos a alta presión	Nadia A. S. Smith
13:45	15’	Sistemas Acuosos - Resumen, Discusión y Perspectivas		
14:15	Comida			
15:30	Sesiones 3M – Round Tables 1-8			
16:30	45	Conferencia Invitada	*Magnetism in oxygen under pressure*	Stefan Klotz
17:15	15’	Sistemas Moleculares I – Materiales NOCH: Presentación del Moderador		Mercedes Taravillo Corralo
17:30	3x15’	Ponencias Sistemas Moleculares I	*Caracterización de yunques de zafiro y moissanita a alta presión*	Elena del Corro García
			Presión interna de disoluciones acuosas	Nubia J. Mendoza Lugo
			Síntesis de Resinas Fósiles a alta presión. Resina, copal y ámbar	Óscar R. Montoro
18:15	Pausa			
18:45	15’	Sistemas Moleculares II – Enlace y Reactividad: Presentación		Víctor Luaña Cabal
19:00	4x15’	Ponencias Sistemas Moleculares II	*Funciones de distribución del número de electrones (EDF)*	Evelio Francisco Miguélez
			Enlace químico en moléculas heterodiatómicas bajo la perspectiva de Átomos Cuánticos Interaccionantes	Aurora Costales Castro
			Modelización de la alta presión con métodos de función de onda	José Tortajada Pérez
			Desarrollo de técnicas híbridas QM/MM y dinámica molecular para el estudio de la estructura y reactividad	José Javier Ruiz Pernía
20:00	15’	Sistemas Moleculares - Resumen, Discusión y Perspectivas		
20:15	45’	Conferencia Invitada	*Nanociencia Molecular y Alta Presión*	Eugenio Coronado Miralles
21:00	Cena			
22:30	Sesiones 3M – Round Tables 9-16			

Martes 25 de Enero

Hora	Duración	Ponencia		Ponente
9:30	10'	Infraestructuras MALTA-Consolider: Presentación del Moderador		Óscar R. Montoro
9:40	20'	*Infraestructura I – Servidor MALTA*		José Manuel Menéndez Montes
10:00	20'	*Infraestructura II – Difracción de Rayos X*		David Santamaría Pérez
10:20	20'	*Infraestructura III – Raman Confocal*		Jesús González Gómez
10:40	20'	*Infraestructura IV – FTIR*		Vinod Panchal
11:00	20'	*Infraestructura V – Sistema de Calentamiento Láser*		Daniel Errandonea
11:20	20'	*Infraestructura VI – Prensa de Gran Volumen*		Ramón Gervilla Fernández
11:40	20'	*Infraestructura VII – Centro de Mecanizado*		Samuel Gilliland
12:00	Pausa			
12:30	15'	Edición del Libro Especializado en Altas Presiones		Rafael Valiente Barroso
12:45	15'	V Escuela de Altas Presiones – La Laguna 2011		Alfonso Muñoz/Víctor Lavín
13:00	15'	Resumen Reunión Sociedad Francesa de Alta Presión		Jesús A. González Gómez
13:15	15'	Organización Congreso AIRAPT/EHPRG Madrid 2015		Fernando Rodríguez González
14:00	Comida			
15:30	Sesiones 3M –Cross-Link Round Tables A			
16:30	Sesión Monográfica: Instrumentación a Alta Presión			
16:30	30'	Homenaje a Jean-Claude Chervin		Alfredo Segura García del Río Jesús A. González Gómez
17:00	45'	Conferencia Invitada	*Desarrollo de Dispositivos de Alta Presión*	Jean-Claude Chervin
17:45	Pausa			
18:00	20'	*Celdas París-Edimburgo*		Domingo Martínez García
18:20	20'	*Status of the High Pressure end-station at Alba*		Inmaculada Peral Alonso
18:40	20'	*Desarrollo en celdas de alta presión para medidas de propiedades magnéticas*		Javier Sánchez Benítez
19:00	20'	*Simulación de Procesos a alta presión*		Ángel Ramos del Olmo
19:20	Resumen Tercer Año MALTA-Evaluación MICINN			
20:30	Salida Cena Oficial			
21:00	Cena Oficial de la Reunión			
23:30	Regreso Cena Oficial a la Sede			

Miércoles 26 de Enero

Hora	Duración	Ponencia		Ponente
9:30	15’	Óxidos y Minerales I –Estructura y Reactividad 1: Presentación del Moderador		Alfredo Segura García del Río
9:45	4x15’	Ponencias Óxidos y Minerales I – 1	*Aplicación de la absorción de rayos X al estudio de las delafositas bajo presión*	Julio Pellicer Porres
			Estudio estructural de la distorsión Jahn-Teller del $CuWO_4$ bajo presión	Javier Ruiz Fuertes
			Transiciones de fase en Rb_2S a alta presión. Comparación estructural de los sulfuros alcalinos y sus óxidos correspondientes	David Santamaría Pérez
			Estudio bajo altas presiones de la estructura de minerales de la corteza y de la capa superior del manto	Daniel Errandonea
10:45	45’	Conferencia Invitada	*Difracción de Neutrones en Condiciones Extremas: XTREMED*	Javier Campo Ruiz
11:30	15’	Óxidos y Minerales I – Estructura y Reactividad 2: Presentación del Moderador		Alfonso Muñoz González
11:30	4x15’	Ponencias Óxidos y Minerales I – 2	*$HgWO_4$ under pressure*	Javier López Solano
			Estudio del $MnGa_2Se_4$ bajo presión	Eduardo Pérez González
			Materiales de alta presión como electrodo para baterías de litio	Elena Arroyo y de Dompablo
12:30	Pausa			
13:00	15’	Óxidos y Minerales I – Estructura y Reactividad 3: Presentación del Moderador		José Manuel Recio Muñiz
13:15	5x12’	Ponencias Óxidos y Minerales I – 3	*Rigorous treatment of first principles data for quasiharmonic thermodynamics of solids*	Alberto Otero de la Roza
			Más allá del modelo de Debye. Nuevo módulo de cálculo de efectos térmicos en cristales	David Abassi Pérez
			Estudio sistemático de las ecuaciones de estado en las perovskitas KMF_3	José Manuel Menéndez Montes
			Estudio de polimorfos de TiO_2. DFT+U	Ángel Morales García
			Metales alcalinos a alta presión	Miriam Marqués Arias
14:30	Comida			
16:00	Sesiones 3M –Cross-Link Round Tables B			
17:00	15’	Óxidos y Minerales I – Estructura y Reactividad 4: Presentación del Moderador		Armando Beltran Flors
17:15	4x15’	Ponencias Óxidos y Minerales I – 4	*Modelización de transiciones de fase inducidas por presión en compuestos ABO_4 y A_2BO_4*	Lourdes Gracia Edo
			Comportamiento estructural de perovskitas sometidas a condiciones extremas	Fernando Aguado Menéndez
			Estudio teórico (y experimental) del efecto de la presión sobre TiO_2 y $SbPO_4$	Marcilene Cristina Gomes
			Síntesis y caracterización de perovskitas complejas derivadas del $CaCu_3Mn_4O_{12}$	Paula Kayser González
18:15	15’	Óxidos y Minerales I –Estructura y Reactividad – Resumen, Discusión y Perspectivas		
18:30	Pausa			
19:00	30’	Miguel Álvarez Blanco – Recuerdo/Homenaje		Ángel Martín Pendás
19:30	90’	Reunión Comités MALTA-Consolider		
21:00	Cena			
22:30	Sesiones 3M –Round Table Final			

Jueves 27 de Enero

Hora	Duración	Ponencia		Ponente
9:30	15’	Óxidos y Minerales II – Espectroscopia 1: Presentación del Moderador		Fernando Rodríguez González
9:45	5x15’	Ponencias Óxidos y Minerales II – Espectroscopia 1	*Metastability of wurtzite and rock-salt phases in ZnCoO nanoparticles investigated by optical absorption*	Rosa Martín Rodríguez
			Transiciones de spin en sistemas Jahn-Teller de Mn^{3+}, Ni^{3+}, Co^{3+}	Marta N. Sanz Ortiz
			Luminescence dependence of $NaYF4:Er^{3+}$, Yb^{3+} with pressure	Carlos Renero Lecuna
			Absorción óptica bajo presión del compuesto multiferroico $BiFeO_3$. Estudio del momento dipolar eléctrico	Susana Gómez Salces
			Medidas ópticas, magnéticas y vibracionales en películas de ZnO:Co co-dopadas con Ga	Gloria Almonacid Caballer
11:00	15’	Óxidos y Minerales II – Espectroscopia 2: Presentación del Moderador		Fco. Javier Manjón Herrera
11:15	2x15’	Ponencias Óxidos y Minerales II – Espectroscopia 2	*High-pressure study of YVO_4 nanoboxes*	Óscar Gomis Hilario
			High-Pressure Raman Scattering in AB_2X_4 compounds	Rosario Vilaplana Cerdá
12:00	Pausa			
11:45	15’	Óxidos y Minerales II – Espectroscopia 3: Presentación del Moderador		Víctor Lavín della Ventura
12:30	4x15’	Ponencias Óxidos y Minerales II – Espectroscopia 3	*Espectroscopia a alta presión en granates nanocristalinos*	Ulises Rodríguez Mendoza
			Desarrollo de nuevos materiales prácticamente activos para sensores de presión	Sergio F. León Luis
			Seguimiento de cambios estructurales bajo presión mediante campo cristalino	Juan E. Muñoz Santiuste
			Desarrollo de materiales ópticamente activos como sensores de temperatura	Inocencio R. Martín Benenzuela
13:30	15’	Óxidos y Minerales II – Espectroscopia - Resumen, Discusión y Perspectivas		
13:45	Entrega Certificados Simposio y Sesiones 3M Clausura del Simposio			
14:00	Comida			
16:00	Salida Autobús			

SISTEMAS ACUOSOS –I

AGUA Y SISTEMAS RELACIONADOS CON LA VIDA

www.malta-consolider.com

CONSOLIDER MALTA

Matter at High Pressure

Programa Ingenio 2010

Grupo: Centro de Astrobiología

Felipe Gómez
Laura Jiménez Bonales
José Antonio R. Manfredi
Victoria Muñoz Iglesias
Olga Prieto Ballesteros

I. AGUA Y SISTEMAS RELACIONADOS CON LA VIDA

a. Síntesis, propiedades y estabilidad de clatratos

b. Efectos de la alta presión en soluciones acuosas de agregados supramoleculares y proteinas

c. Microbiología en condiciones extremas de presión y temperatura

I. AGUA Y SISTEMAS RELACIONADOS CON LA VIDA

a. Síntesis, propiedades y estabilidad de clatratos de gas

Preguntas científicas

- Cinética de la formación y descomposición de clatratos
- Estudio de las propiedades físico-químicas de los clatratos bajo condiciones de las cortezas de los satélites de hielo
- Rango de estabilidad de clatratos, incluyendo las posibles transiciones de fase que cambiarían sus propiedades físicas y químicas

Metas específicas

- Síntesis de clatratos en celdas de gran volumen diseñadas específicamente
- Raman, IR y ultrasonidos
- Propiedades ópticas, eléctricas y dieléctricas
- Formación de clatratos desde salmueras a presiones del océano de Europa
- Determinación de diagramas PTx

I. AGUA Y SISTEMAS RELACIONADOS CON LA VIDA

b. Efectos de alta presión sobre soluciones acuosas: sales, agregados supramoleculares y proteinas

Preguntas científicas:

- Efectos de la presión en la constante de equilibrio de las soluciones acuosas
- Efectos de la presión en las propiedades físico-químicas de los hidratos en las condiciones de las cortezas de los satélites de hielo
- Experimentos y simulaciones de soluciones de proteínas

Metas específicas:

- Sistemas acuosos con sulfatos de Mg2+, Na+, Fe2+/3+; los sistemas multi-componente son de interés para las ciencias de la Tierra y del Espacio.
- Diagramas pH, eH en función de la presión
- Propiedades reological and termodinámicas (densidad y coeficientes de expansión) de fases ultra-hidratadasof ultra hydrated phases of these ions will be studied to several GPa.
- Pressure effects on cyclodextrine-based host-guest systems
- Micelle formation and stability: caseine and other systems of interest in food science and technology
- Studying the conformational changes in proteins under pressure

I. AGUA Y SISTEMAS RELACIONADOS CON LA VIDA

c. Microbiología en condiciones extremas de presión y temperatura

Preguntas científicas

- Adaptación de los organismos vivos bajo presión como campo de interés de biología y tecnología de los alimentos
- Identificación de los factores clave que determinan la piezorresistencia en arqueas y eubacterias extremófilas, especialmente la piezorresistencia de proteínas y los genes relacionados
- Influencia de los factores previos en el origen de la vida (básica) y procesamiento de alimentos (aplicado)

Metas específicas

- Estudio de procesos de oxidación lipídica en membranas celulares bajo presión
- Estudio de integridad y funcionalidad de las membranas celulares bajo presión
- Modelización de comportamiento de las membranas celulares bajo presión como liposomas de composición simple
- Identificación de proteínas responsables de piezoresistencia y genes relacionados

Clatratos en Europa

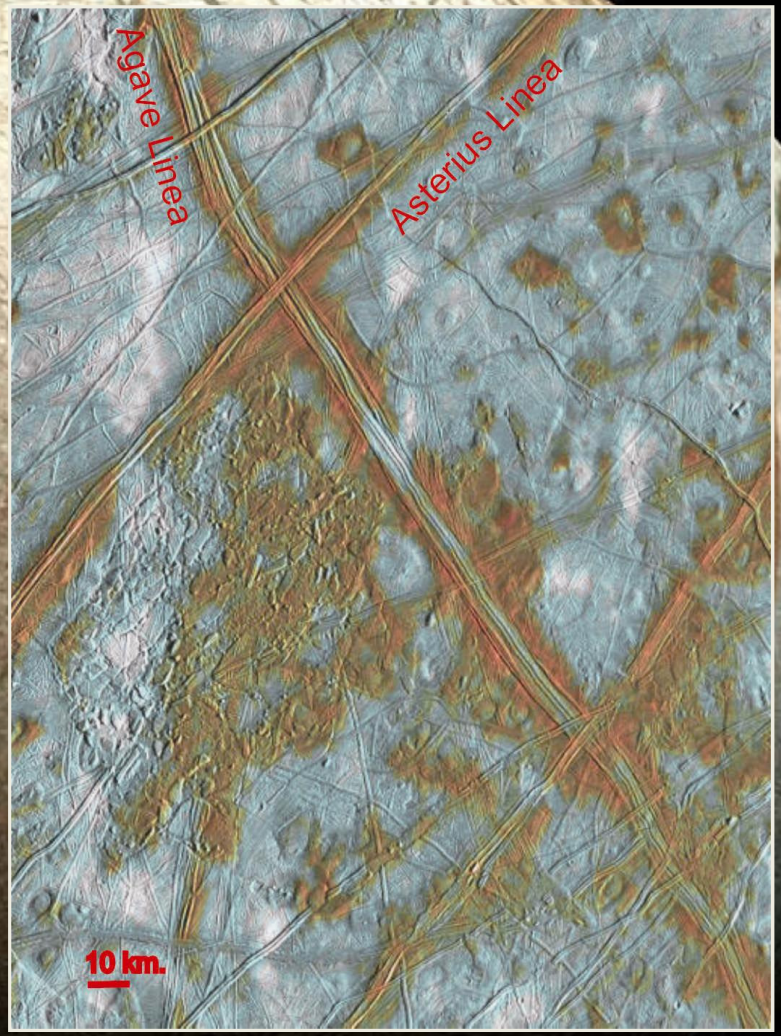
Master de tesis de Vicky – Octubre 2010
Clatratos en Europa, satélite de Júpiter

En el sistema solar exterior se dan las condiciones y los materiales necesarios para que se formen clatratos de gas, tanto en los satélites de hielo como en los cometas

- agua
- volátiles
- P y T

Manifestaciones geológicas observadas en los satélites de hielo pueden ser producto de la descomposición de los clatratos de gas

- estructuras de terrenos caóticos
- actividad de géiseres



EUROPA

Europa es un satélite especialmente interesante para Astrobiología debido a que parece albergar en su interior un océano de agua líquida en contacto con un substrato rocoso.

Actualmente Europa tiene una superficie de hielo dominada por H_2O, sales hidratadas y/o hidratos de ácido sulfúrico, CO_2, SO_2 y H_2S.
El océano de agua líquida está en contacto con la capa rocosa probablemente afectada por actividad hidrotermal, cuyas fumarolas liberan gases.

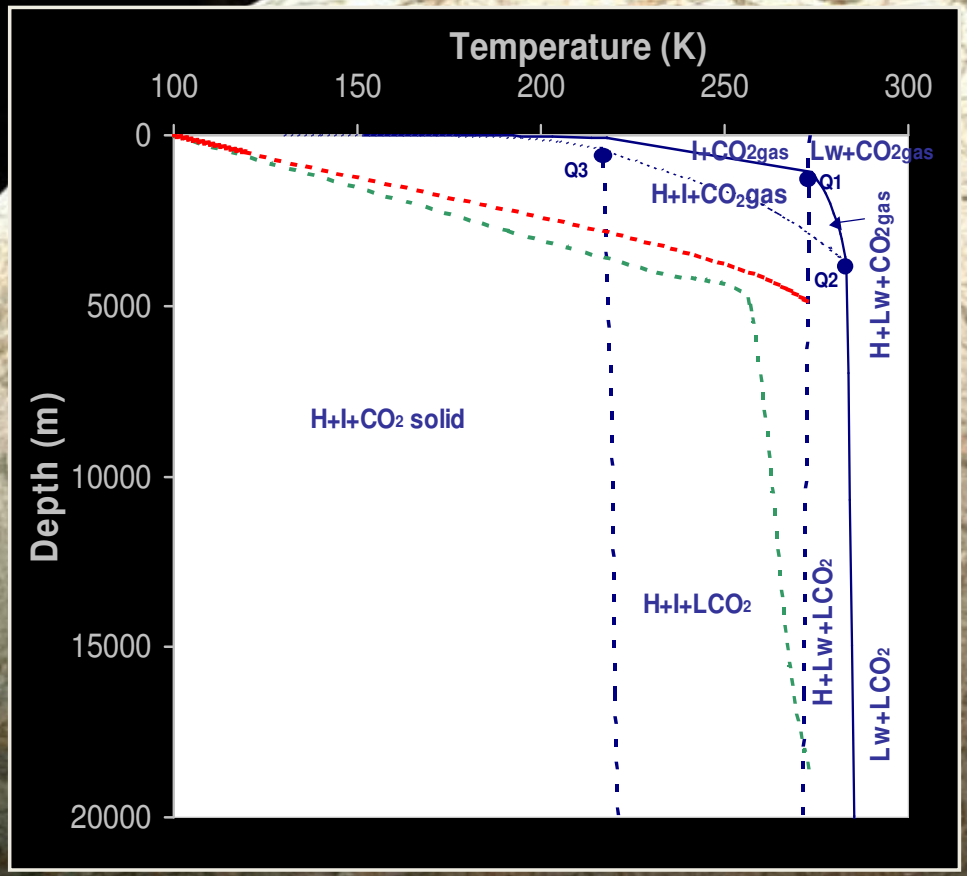
Clatratos de gases volcánicos en el interior. De oxidantes radiogénicos en la subsuperficie.

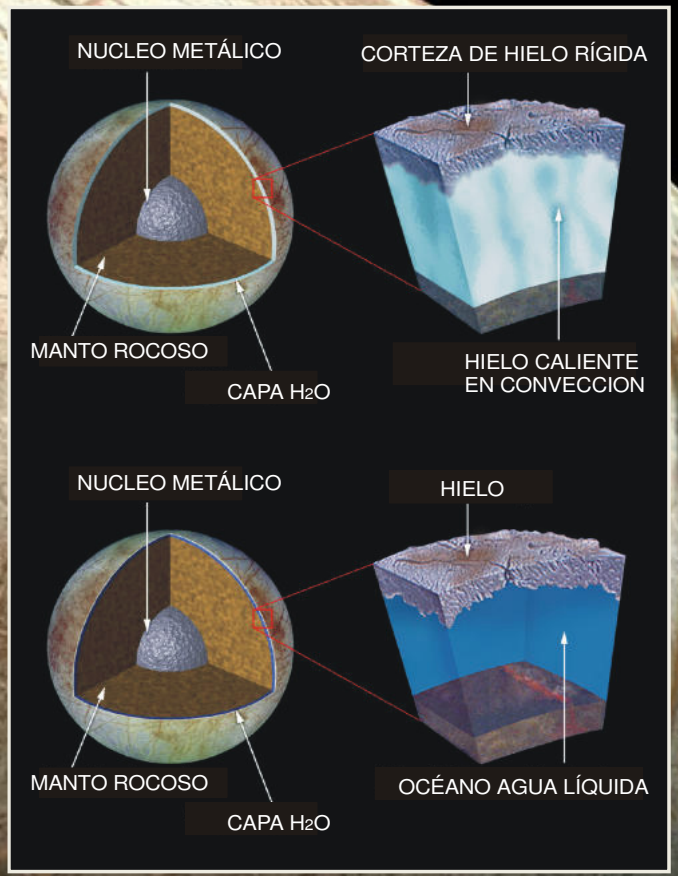
APLICACIONES:

Terrenos caóticos

Diferenciación criomagmática

ESTABILIDAD CLATRATOS





CO_2 → Estabilidad desde 0.05-0.5 mm de profundidad hasta el océano

H_2S → Estabilidad desde 0.25-1.5 mm de profundidad hasta el océano

www.malta-consolider.com

CONSOLIDER MALTA

Matter at High Pressure

INGENIO 2010

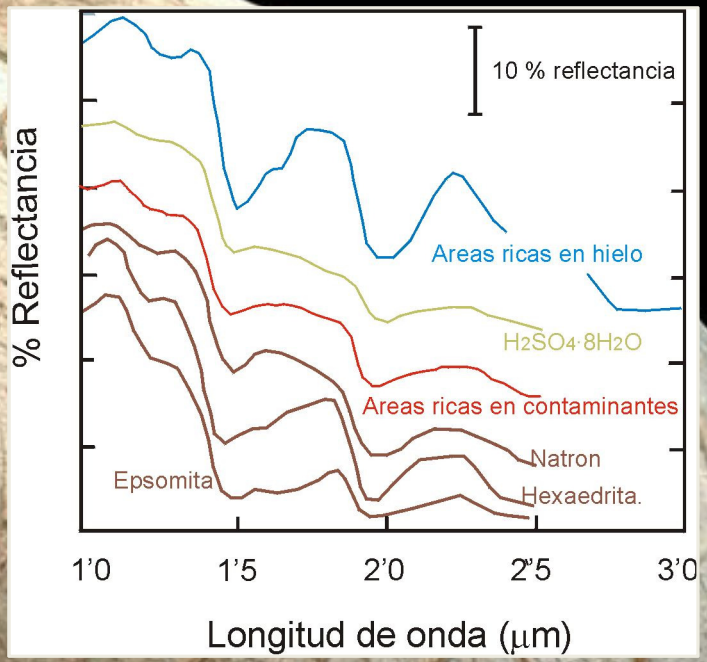
CLATRATOS VS. SALMUERAS

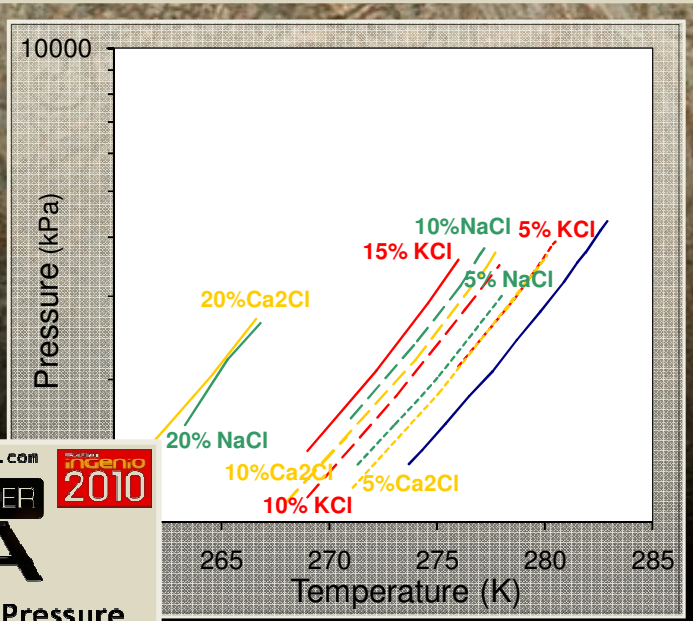
Tradicionalmente los electrolitos en solución se han descrito como inhibidores de formación de clatratos debido a:

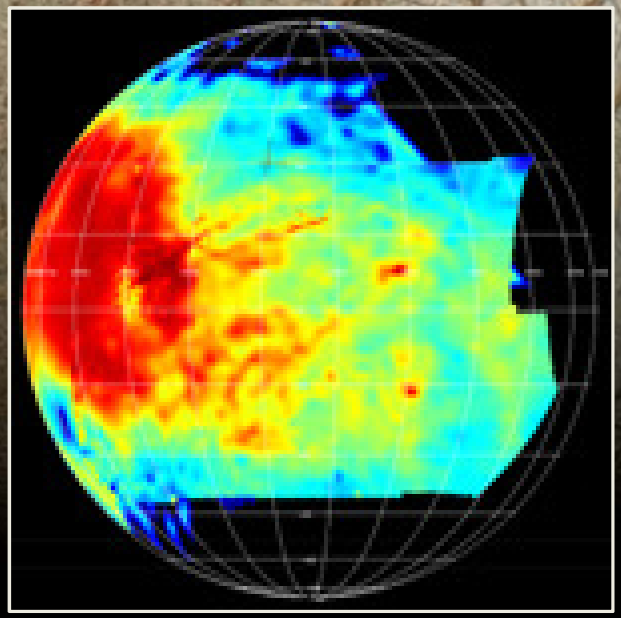
-La fuerte atracción del agua hacia los electrolitos.

-El efecto "*salting-out*": descenso de la solubilidad del gas en la salmuera debido al enlace del agua con los iones.

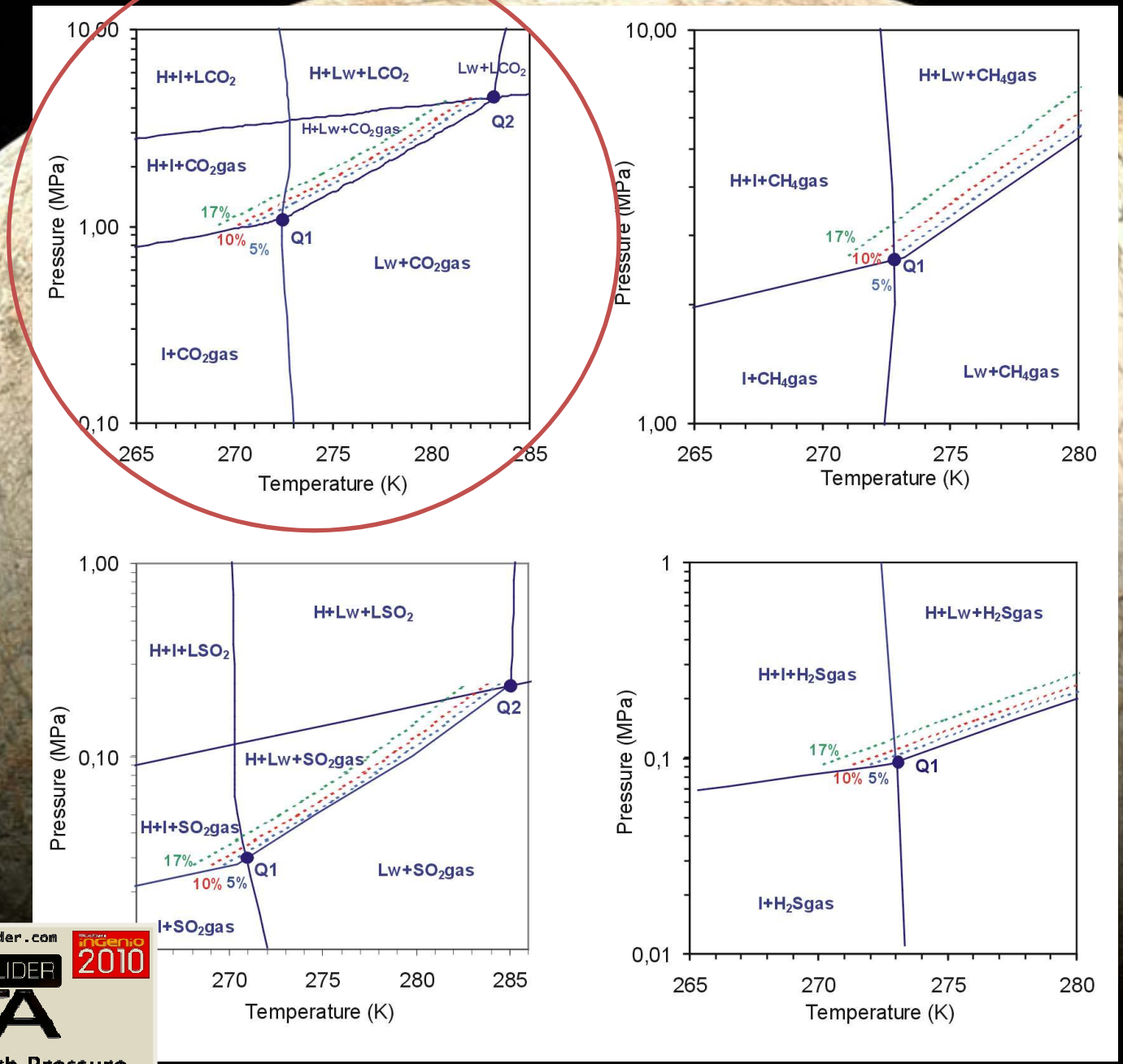
Inhibidores típicos: metanol, cloruros. Muy estudiados debido a sus aplicaciones técnicas y su aplicación en el análisis de inclusiones fluidas.







www.malta-consolider.com
CONSOLIDER MALTA
Ingenio 2010
Matter at High Pressure



www.malta-consolider.com

CONSOLIDER MALTA

Ingenio 2010

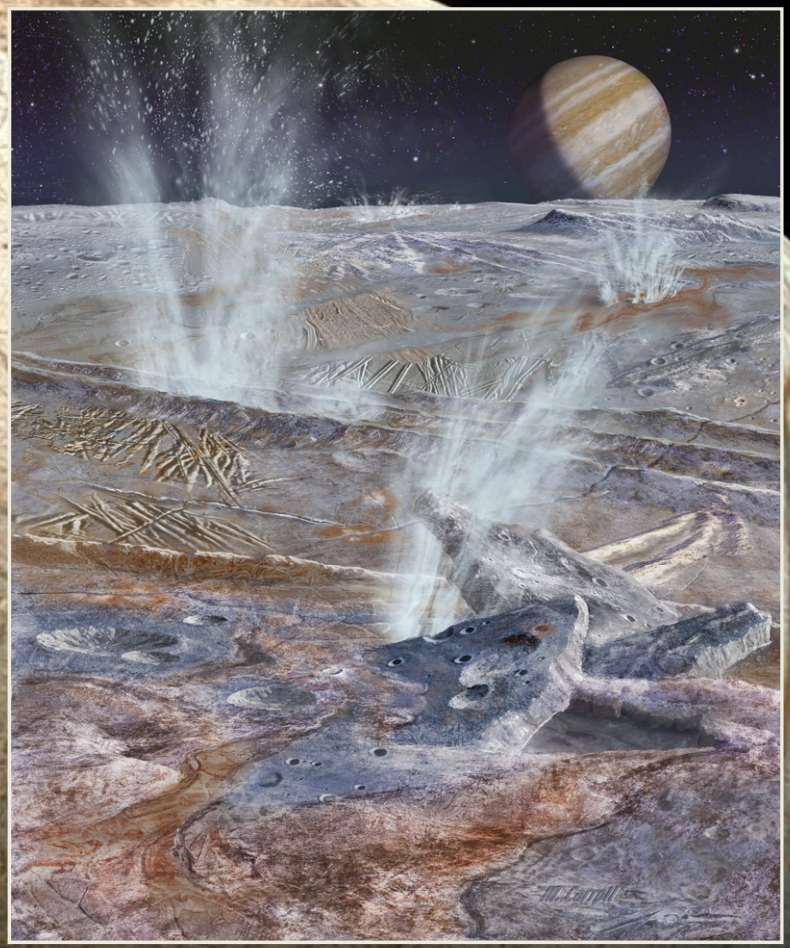
Matter at High Pressure

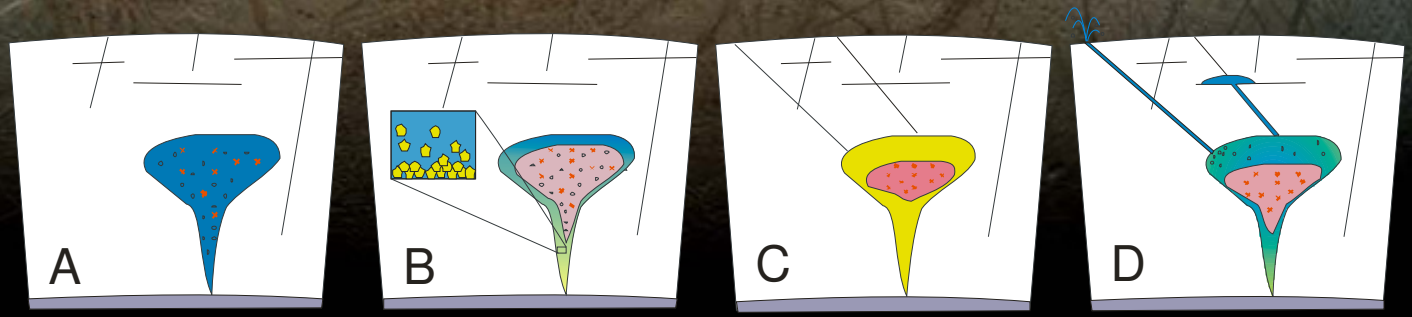
DIFERENCIACIÓN POR CLATRATIZACIÓN

La formación de clatratos desde un magma enriquecido en gases e iones disueltos puede producir la diferenciación de la cámara magmática en los satélites de hielo.

Durante el proceso, las sales disueltas pueden precipitar y separarse por su mayor densidad, permitiendo a la solución con gases cristalizar en clatratos de gas.

Si los clatratos se desestabilizan por descompresión, los criomagmas ricos en volátiles podrán ascienden a la superficie, e incluso erupcionar explosivamente.





CO_2 en disoluciones acuosas planetarias

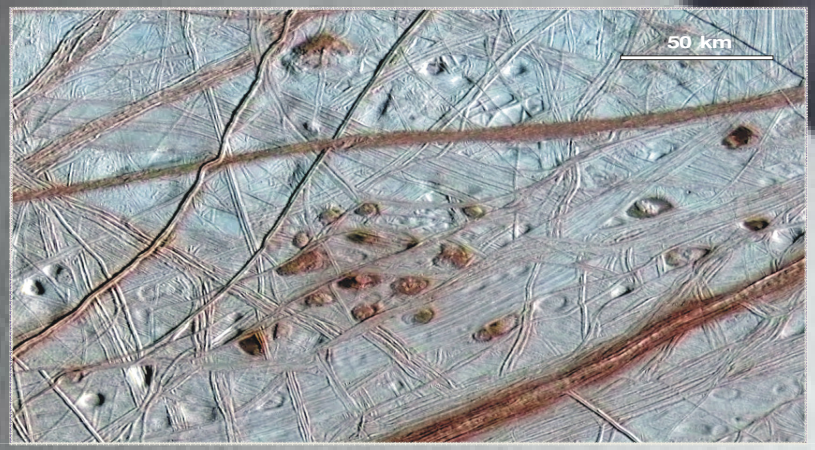
(desarrollo de Laura)

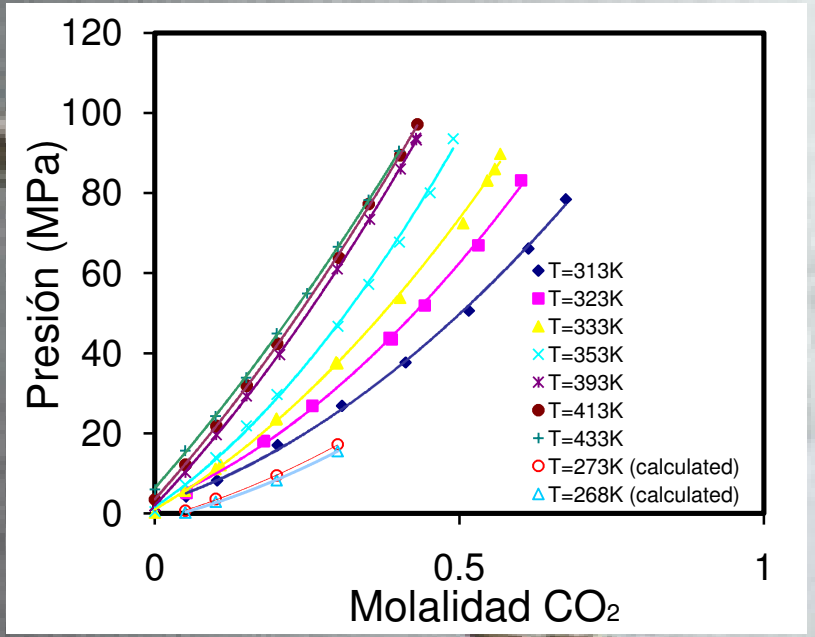
- CO_2 en soluciones sulfatadas a alta presión

Aplicación en criomagmatismo. Flotabilidad. Explosividad de las erupciones de criomagmas. Diferenciación por clatratización

- CO_2 y carbonatos

Aplicación en la formación de carbonatos en épocas tempranas de la Tierra y Marte





www.malta-consolider.com
CONSOLIDER
MALTA
Matter at High Pressure
Ingenio 2010

Carbonatos en Tierra y Marte primitivos

Los Carbonatos pueden ser precipitados inorgánicamente o ser biomediados

Las calizas en la Tierra desempeñan un papel muy importante en el ciclo del C, fijan el carbonato y liberan CO_2

Actualmente los carbonatos precipitan en mares someros en donde el agua está cargada de CO_2 según la reacción:

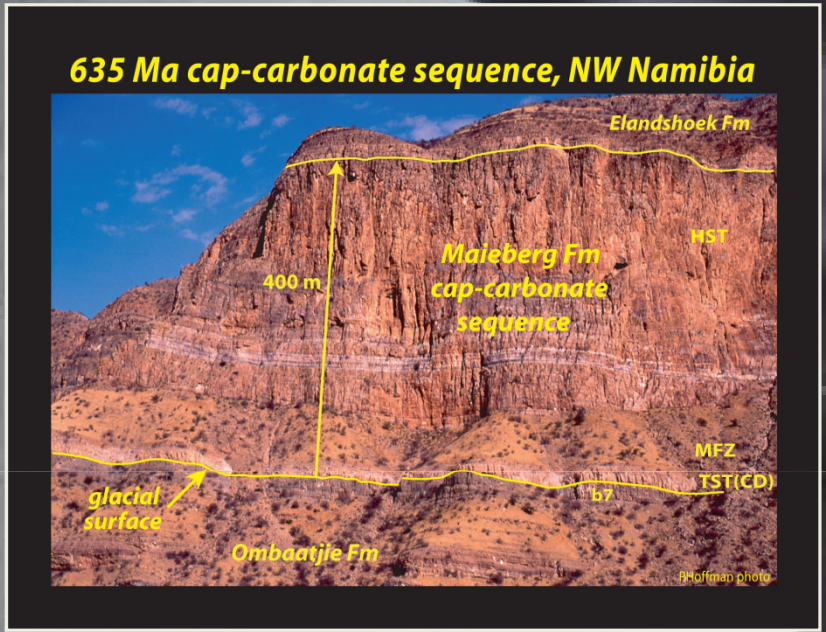
$$Ca^{2+} + 2\,(HCO_3^-) = CaCO_3 + H_2O + CO_2$$

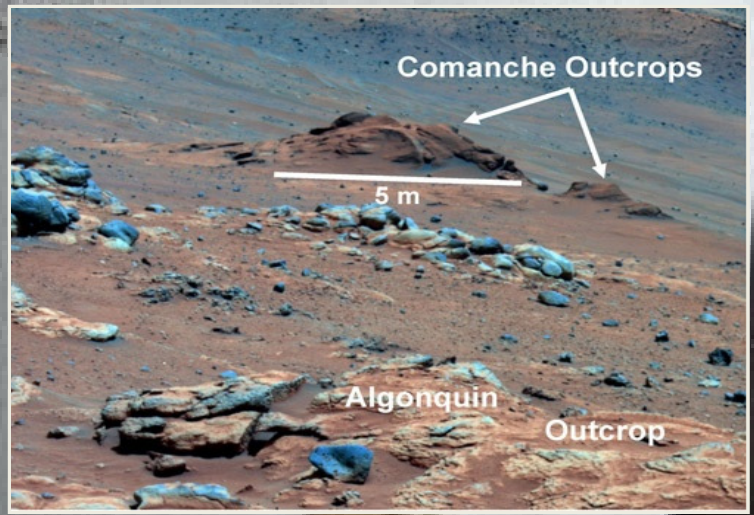
Los carbonatos son geomarcadores de unas condiciones ambientales particulares. Y pueden ser biomarcadores

Existen periodos en la historia de la Tierra con carbonatos particulares ¿Cómo precipitan?

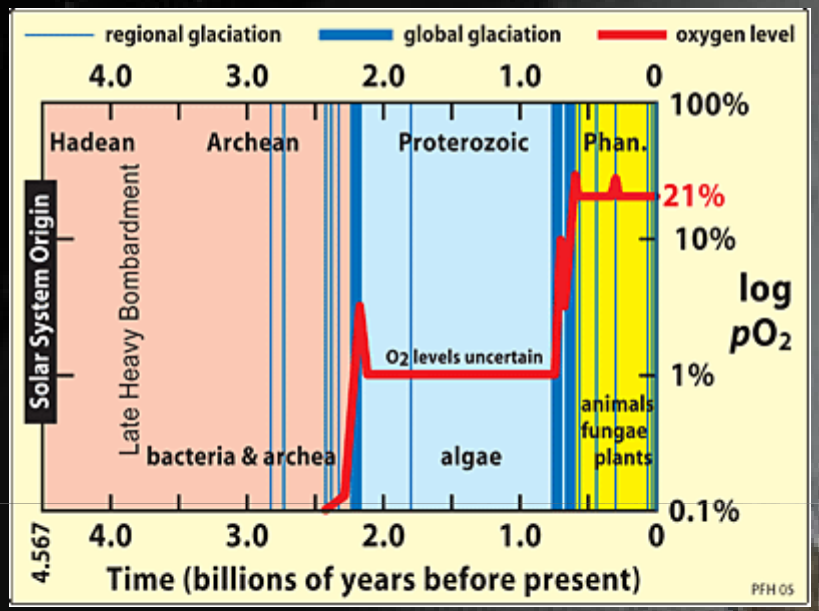
- Carbonatos arcaicos
- CAP Carbonates

¿Dónde están los carbonatos en Marte?





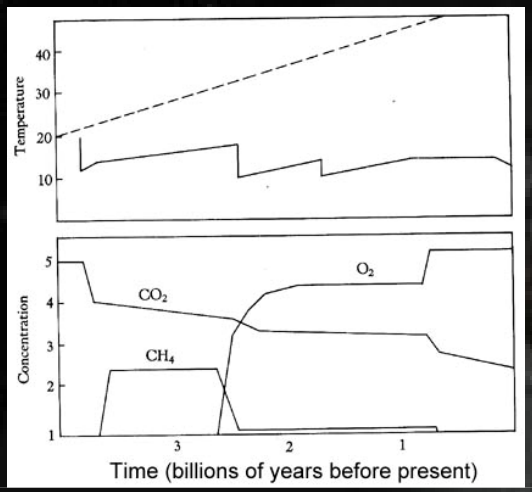
Tierra primitiva-carbonatos vs. Alta P

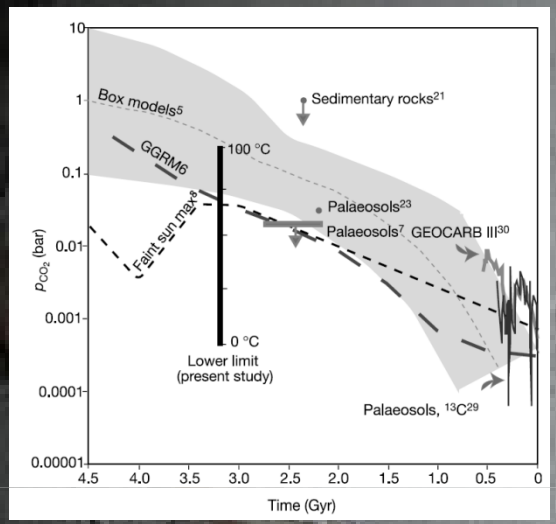


Arcaico-atmósfera más densa. Hasta 200 bares de presión de CO_2

Proterozoico- los "*cap carbonates*" son calizas y dolomías que aparecen por encima de los depósitos glaciares proterozoicos (Makganyene ~ 2220 M.a., Sturtian ~700 M.a. o Marinoan 635 M.a.). Tienen características especiales en relación a carbonatos de otras épocas: cementos bien desarrollados, ondulaciones gigantes, barita diagenética, relación isotópica deficitaria en ^{13}C etc.

Carbonatos Arcaicos





Los carbonatos de más de 2400 m.a. No son frecuentes en la Tierra. Son peculiares:

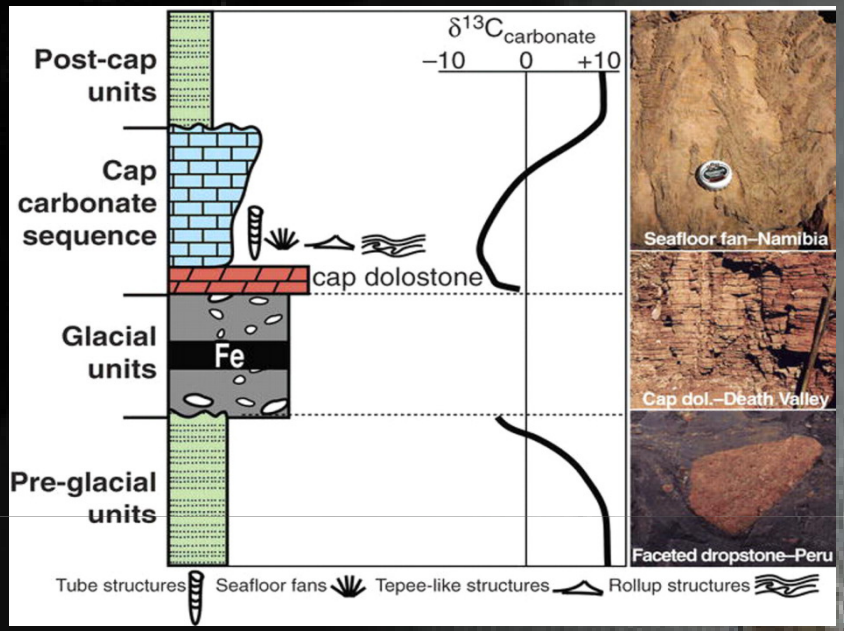
- Asociaciones de caliza y ortocuarcitas (sedimentarias o volcanicas)
- Carbonatos asociados a esquistos o cherts
- Carbonatos en asociaciones volcánicas
- Sedimentos clásticos-carbonatados

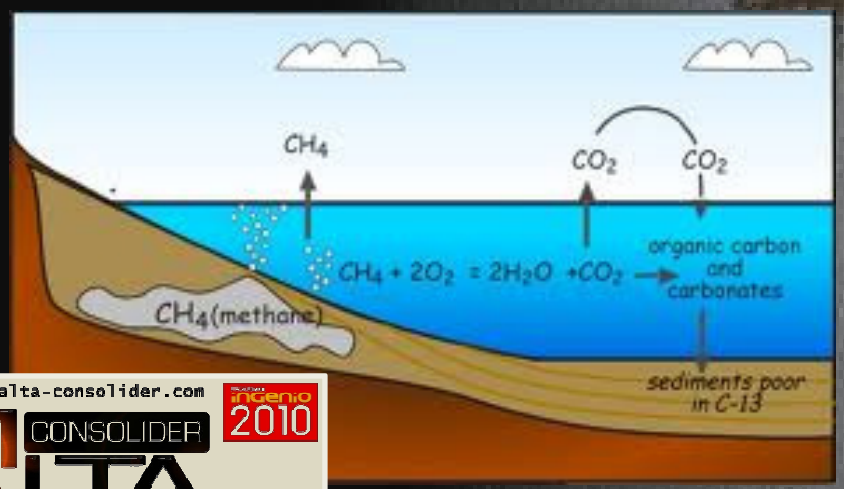
La atmósfera del Arcaico fue muy rica en CO2. Esto pudo acidificar los océanos

Los datos muestran que la alteración de las rocas igneas liberó Ca^{2+} a los océanos

La corteza era delgada e inestable, con pocos lugares aptos para la precipitación masiva de carbonatos. Solo en partes profundas con favorable contenido en CO_2 (fáciles de destruir posteriormente por tectónica)

Carbonatos Proterozoicos. *Cap carbonates*





Carbonatos que están en contacto limpio con facies periglaciares. Son dolomias microcristalinas que aparecen por todo el globo, con calizas post-glaciares por encima

Se han propuesto 3 modelos que relacionan una deglaciación abrupta y el evento de precipitación de carbonatos (alcalinidad extrema)

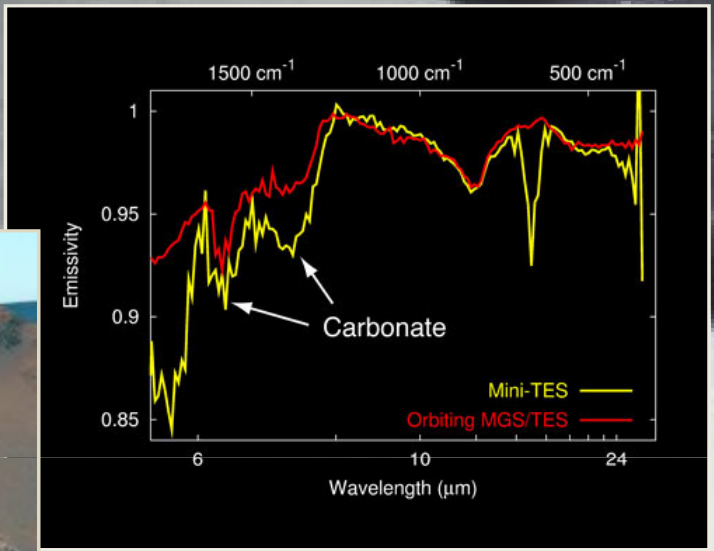
- **cambio brusco de los océanos** anóxicos profundos, desgasificación de CO_2, subsecuente liberación de la alcalinidad en nuevas cuencas subsumergidas y precipitación de $CaCO_3$
- **Snow Ball Earth**: alto grado de alteración química debido a condiciones de un super efecto invernadero seguidas de una glaciación global. Deglaciación catastrófica cuando el nivel de pCO_2 fue crítico (0.12 bares)
- liberación masiva de la alcalinidad por desestabilización **de clatratos de metano,** debido a la oxidación anaeróbica por sulfato-reducción

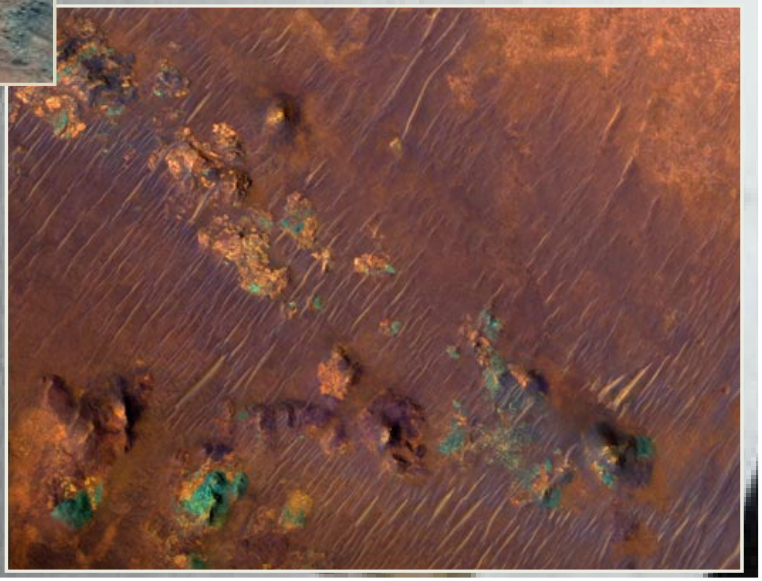
Experimentos de precipitación de carbonatos para determinar las condiciones en las que ocurrió: P, T, acidez, redox??? Validación de alguna de las hipótesis mencionadas. La dolomita no cristaliza directamente en columnas de agua en condiciones de la superficie terrestre.

Marte primitivo-carbonatos vs. Alta P

Si Marte tuvo agua y una atmósfera mas densa podría haber formado carbonatos

El rover Spirit ha identificado carbonatos Mg-Fe (16 - 34 peso%) en Columbia Hills del cráter Gusev. Podrían haber precipitado de soluciones carbonatadas en condiciones hidrotermales a pH casi neutro en asociación con la actividad volcánica del periodo Noico





www.malta-consolider.com
CONSOLIDER
MALTA
Matter at High Pressure
Ingenio 2010

Modelling High Pressure Processes in Food Engineering

Nadia Smith, Ángel Manuel Ramos del Olmo

Research Group MOMAT - Universidad Complutense de Madrid - Spain
http://www.mat.ucm.es/momat

Reunión MALTA-CONSOLIDER 2011

Madrid, January 24th, 2010

Consumers needs

Consumers want food in **good conditions**.

- **Problem**: Food decomposition due to microorganisms and enzymes.
- **Goal**: Prolong food shelf life, preserving organoleptic (flavour, colour, etc...) and nutritional properties.
- Minimally processed and additive-free products.

$\longrightarrow$ **Food processing**

- **Classical Industrial Methods**: Freezing, Sterilization, Pasteurization...
- Disadvantages: Loss of nutritional properties, change in flavour, oxidation (for process that use high temperatures) and non homogeneous crystallization (for classical freezing methods).

Consumers needs

Consumers want food in **good conditions**.

- **Problem**: Food decomposition due to microorganisms and enzymes.
- **Goal**: Prolong food shelf life, preserving organoleptic (flavour, colour, etc...) and nutritional properties.
- Minimally processed and additive-free products.

$\longrightarrow$ **Food processing**

- **Classical Industrial Methods**: Freezing, Sterilization, Pasteurization...
- Disadvantages: Loss of nutritional properties, change in flavour, oxidation (for process that use high temperatures) and non homogeneous crystallization (for classical freezing methods).

Nowadays technology

New emerging technology $\longrightarrow$ **High Pressure (HP) processes**

- Combination of HP and moderate temperatures inactivates microorganisms and enzymes ..... preserving many nutritional and organoleptic properties.
- additive-free products!
- HP can also be used for freezing: uniform nucleation and crystallization

Our goal as mathematicians

Modelling of different kinds of HP processes for **simulation** and **optimization** purposes

- Mathematical modelling of enzymatic and microbial inactivation
- Heat Transfer modelling for HP-moderate temperature process and also for HP-freezing processes.

Nowadays technology

New emerging technology $\longrightarrow$ **High Pressure (HP) processes**

- Combination of HP and moderate temperatures inactivates microorganisms and enzymes ..... preserving many nutritional and organoleptic properties.
- additive-free products!
- HP can also be used for freezing: uniform nucleation and crystallization

Our goal as mathematicians

Modelling of different kinds of HP processes for **simulation** and **optimization** purposes

- Mathematical modelling of enzymatic and microbial inactivation
- Heat Transfer modelling for HP-moderate temperature process and also for HP-freezing processes.

Nowadays technology

New emerging technology $\longrightarrow$ **High Pressure (HP) processes**

- Combination of HP and moderate temperatures inactivates microorganisms and enzymes ..... preserving many nutritional and organoleptic properties.
- additive-free products!
- HP can also be used for freezing: uniform nucleation and crystallization

Our goal as mathematicians

Modelling of different kinds of HP processes for **simulation** and **optimization** purposes

- Mathematical modelling of enzymatic and microbial inactivation
- Heat Transfer modelling for HP-moderate temperature process and also for HP-freezing processes.

Nowadays technology

New emerging technology $\longrightarrow$ **High Pressure (HP) processes**

- Combination of HP and moderate temperatures inactivates microorganisms and enzymes ..... preserving many nutritional and organoleptic properties.
- additive-free products!
- HP can also be used for freezing: uniform nucleation and crystallization

Our goal as mathematicians

Modelling of different kinds of HP processes for **simulation** and **optimization** purposes

- Mathematical modelling of enzymatic and microbial inactivation
- Heat Transfer modelling for HP-moderate temperature process and also for HP-freezing processes.

Definition (Inactivation)

Reduction of undesired biological activity, such as enzymatic catalysis and microbial contamination.

The enzymatic activity of a particular enzyme can usually be described by the first-order kinetic model

$$\begin{cases} \dfrac{\mathrm{d}A(t;T,P)}{\mathrm{d}t} = -k(T,P)A(t;T,P) \\ A(0;T,P) = A_0 \end{cases}$$

$A(t;T,P)$: enzymatic activity at time t, when the food sample follows a process at temperature T and pressure P; A_0: initial enzy. act.; k: *inactivation rate*

- Isothermal/Isobaric process $\Rightarrow A(t;T,P) = A_0 \exp\left(-k(T,P)t\right)$
- General process $\Rightarrow A(t;T,P) = A_0 \exp\left(-\int_0^t k(T(s),P(s))\mathrm{d}s\right)$

Definition (Inactivation)

Reduction of undesired biological activity, such as enzymatic catalysis and microbial contamination.

The enzymatic activity of a particular enzyme can usually be described by the first-order kinetic model

$$\begin{cases} \dfrac{\mathrm{d}A(t;T,P)}{\mathrm{d}t} = -k(T,P)A(t;T,P) \\ A(0;T,P) = A_0 \end{cases}$$

$A(t;T,P)$: enzymatic activity at time t, when the food sample follows a process at temperature T and pressure P; A_0: initial enzy. act.; k: *inactivation rate*

- Isothermal/Isobaric process $\Rightarrow A(t;T,P) = A_0 \exp\left(-k(T,P)t\right)$
- General process $\Rightarrow A(t;T,P) = A_0 \exp\left(-\int_0^t k(T(s),P(s))\mathrm{d}s\right)$

Modelling HP-T on microorganisms and enzymes

Model for enzymatic inactivation

Definition (Inactivation)

Reduction of undesired biological activity, such as enzymatic catalysis and microbial contamination.

The enzymatic activity of a particular enzyme can usually be described by the first-order kinetic model

$$\begin{cases} \dfrac{\mathrm{d}A(t;T,P)}{\mathrm{d}t} = -k(T,P)A(t;T,P) \\ A(0;T,P) = A_0 \end{cases}$$

$A(t;T,P)$: enzymatic activity at time t, when the food sample follows a process at temperature T and pressure P; A_0: initial enzy. act.; k: *inactivation rate*

- Isothermal/Isobaric process $\Rightarrow A(t;T,P) = A_0 \exp\left(-k(T,P)t\right)$
- General process $\Rightarrow A(t;T,P) = A_0 \exp\left(-\int_0^t k(T(s),P(s))\mathrm{d}s\right)$

Modelling HP-T on microorganisms and enzymes

Model for bacterial inactivation

To describe the evolution of a microbial population, we can follow the above model, just by changing enzymatic activity $A(t; T, P)$ by microbial population $N(t; T, P)$.

Or this other model

$$\begin{cases} \dfrac{\mathrm{d}N(t; T, P)}{\mathrm{d}t} = -\dfrac{\ln(10)}{D(T, P)} N(t; T, P) \\ N(0; T, P) = N_0 \end{cases}$$

$D(T, P)$: *decimal reduction time*, or time required for a 1-log-cycle reduction in the microbial population.

- Isothermal/Isobaric process $\Rightarrow N(t; T, P) = N_0\, 10^{-\frac{t}{D(T,P)}}$
- General process $\Rightarrow N(t; T, P) = N_0\, 10^{-\int_0^t \frac{1}{D(T(s),P(s))} \mathrm{d}s}$

Modelling HP-T on microorganisms and enzymes

Model for bacterial inactivation

To describe the evolution of a microbial population, we can follow the above model, just by changing enzymatic activity $A(t; T, P)$ by microbial population $N(t; T, P)$.
Or this other model

$$\begin{cases} \dfrac{\mathrm{d}N(t; T, P)}{\mathrm{d}t} = -\dfrac{\ln(10)}{D(T, P)} N(t; T, P) \\ N(0; T, P) = N_0 \end{cases}$$

$D(T, P)$: *decimal reduction time*, or time required for a 1-log-cycle reduction in the microbial population.

- Isothermal/Isobaric process $\Rightarrow N(t; T, P) = N_0\, 10^{-\frac{t}{D(T,P)}}$
- General process $\Rightarrow N(t; T, P) = N_0\, 10^{-\int_0^t \frac{1}{D(T(s),P(s))} \mathrm{d}s}$

Modelling HP-T on microorganisms and enzymes

Model for bacterial inactivation

To describe the evolution of a microbial population, we can follow the above model, just by changing enzymatic activity $A(t; T, P)$ by microbial population $N(t; T, P)$.
Or this other model

$$\begin{cases} \dfrac{\mathrm{d}N(t; T, P)}{\mathrm{d}t} = -\dfrac{\ln(10)}{D(T, P)} N(t; T, P) \\ N(0; T, P) = N_0 \end{cases}$$

$D(T, P)$: *decimal reduction time*, or time required for a 1-log-cycle reduction in the microbial population.

- Isothermal/Isobaric process $\Rightarrow N(t; T, P) = N_0\, 10^{-\frac{t}{D(T,P)}}$
- General process $\Rightarrow N(t; T, P) = N_0\, 10^{-\int_0^t \frac{1}{D(T(s),P(s))} \mathrm{d}s}$

Modelling HP-T on microorganisms and enzymes

Model for bacterial inactivation

To describe the evolution of a microbial population, we can follow the above model, just by changing enzymatic activity $A(t; T, P)$ by microbial population $N(t; T, P)$.
Or this other model

$$\begin{cases} \dfrac{\mathrm{d}N(t; T, P)}{\mathrm{d}t} = -\dfrac{\ln(10)}{D(T, P)} N(t; T, P) \\ N(0; T, P) = N_0 \end{cases}$$

$D(T, P)$: *decimal reduction time*, or time required for a 1-log-cycle reduction in the microbial population.

- Isothermal/Isobaric process $\Rightarrow N(t; T, P) = N_0\ 10^{-\frac{t}{D(T,P)}}$
- General process $\Rightarrow N(t; T, P) = N_0\ 10^{-\int_0^t \frac{1}{D(T(s),P(s))} \mathrm{d}s}$

Identification of kinetic parameters

Identification of the inactivation rate constants $k(T,P)$ and $D(T,P)$

For general (T,P)–dependent processes we may use

- A combination of Eyring's and Arrhenius' equations:

$$k(T,P) = k_{T_{\text{ref}},P_{\text{ref}}} \exp\left(-B\left(\frac{1}{T} - \frac{1}{T_{\text{ref}}}\right)\right) \exp(-C(P - P_{\text{ref}}))$$

- A more complex choice given by

$$k(P,T) = k_{\text{ref}} \exp\left(\frac{-\Delta V_{\text{ref}}}{RT}(P - P_{\text{ref}})\right) \exp\left(\frac{\Delta S_{\text{ref}}}{RT}(T - T_{\text{ref}})\right)$$

$$\exp\left(\frac{-\Delta\kappa}{2RT}(P - P_{\text{ref}})^2\right) \exp\left(\frac{-2\Delta\zeta}{RT}(P - P_{\text{ref}})(T - T_{\text{ref}})\right)$$

$$\exp\left(\frac{\Delta C_p}{RT}\left(T(\ln\frac{T}{T_{\text{ref}}} - 1) + T_{\text{ref}}\right)\right) + \text{high order terms},$$

- For the microbial decimal reduction time $D(T,P)$ we have not found any formula in the literature. By construction $k = \frac{\ln(10)}{D}$

Identification of kinetic parameters

Identification of the inactivation rate constants $k(T,P)$ and $D(T,P)$

For general (T,P)–dependent processes we may use

- A combination of Eyring's and Arrhenius' equations:

$$k(T,P) = k_{T_{\text{ref}},P_{\text{ref}}} \exp\left(-B\left(\frac{1}{T} - \frac{1}{T_{\text{ref}}}\right)\right) \exp(-C(P - P_{\text{ref}}))$$

- A more complex choice given by

$$\begin{aligned} k(P,T) = \quad & k_{\text{ref}} \exp\left(\frac{-\Delta V_{\text{ref}}}{RT}(P - P_{\text{ref}})\right) \exp\left(\frac{\Delta S_{\text{ref}}}{RT}(T - T_{\text{ref}})\right) \\ & \exp\left(\frac{-\Delta\kappa}{2RT}(P - P_{\text{ref}})^2\right) \exp\left(\frac{-2\Delta\zeta}{RT}(P - P_{\text{ref}})(T - T_{\text{ref}})\right) \\ & \exp\left(\frac{\Delta C_p}{RT}\left(T(\ln\frac{T}{T_{\text{ref}}} - 1) + T_{\text{ref}}\right)\right) + \text{high order terms,} \end{aligned}$$

- For the microbial decimal reduction time $D(T,P)$ we have not found any formula in the literature. By construction $k = \frac{\ln(10)}{D}$

Identification of kinetic parameters

Identification of the inactivation rate constants $k(T,P)$ and $D(T,P)$

For general (T,P)–dependent processes we may use

- A combination of Eyring's and Arrhenius' equations:

$$k(T,P) = k_{T_{\text{ref}},P_{\text{ref}}} \exp\left(-B\left(\frac{1}{T} - \frac{1}{T_{\text{ref}}}\right)\right) \exp(-C(P - P_{\text{ref}}))$$

- A more complex choice given by

$$\begin{aligned} k(P,T) = \quad & k_{\text{ref}} \exp\left(\frac{-\Delta V_{\text{ref}}}{RT}(P - P_{\text{ref}})\right) \exp\left(\frac{\Delta S_{\text{ref}}}{RT}(T - T_{\text{ref}})\right) \\ & \exp\left(\frac{-\Delta\kappa}{2RT}(P - P_{\text{ref}})^2\right) \exp\left(\frac{-2\Delta\zeta}{RT}(P - P_{\text{ref}})(T - T_{\text{ref}})\right) \\ & \exp\left(\frac{\Delta C_p}{RT}\left(T(\ln\frac{T}{T_{\text{ref}}} - 1) + T_{\text{ref}}\right)\right) + \text{high order terms,} \end{aligned}$$

- For the microbial decimal reduction time $D(T,P)$ we have not found any formula in the literature. By construction $k = \frac{\ln(10)}{D}$

Solving the inactivation models

- We identify the parameters ($k_{T,P}$, T_{ref}, P_{ref}, $k_{T_{\text{ref}},P_{\text{ref}}}$,$B$, C, z_T, z_P, $\cdots$) by using experimental data and regression techniques.
- We can now model enzymatic inactivation or microbial population for $HP{-}T$ processes, using the models for $A(t;T,P)$ or $N(t;T,P)$. For this you need **temperature** and **pressure** curves.
- The pressure is known a priori, but the temperature changes during the process (adiabatic heating effect, cooling or heating on the walls of the chamber, etc...)

$\longrightarrow$ **Heat Transfer models**

Solving the inactivation models

- We identify the parameters ($k_{T,P}$, T_{ref}, P_{ref}, $k_{T_{\text{ref}},P_{\text{ref}}}$,$B$, C, z_T, z_P, $\cdots$) by using experimental data and regression techniques.
- We can now model enzymatic inactivation or microbial population for HP–T processes, using the models for $A(t; T, P)$ or $N(t; T, P)$. For this you need **temperature** and **pressure** curves.
- The pressure is known a priori, but the temperature changes during the process (adiabatic heating effect, cooling or heating on the walls of the chamber, etc...)

$\longrightarrow$ **Heat Transfer models**

Solving the inactivation models

- We identify the parameters ($k_{T,P}$, T_{ref}, P_{ref}, $k_{T_{\text{ref}},P_{\text{ref}}}$,$B$, C, z_T, z_P, $\cdots$) by using experimental data and regression techniques.
- We can now model enzymatic inactivation or microbial population for HP–T processes, using the models for $A(t; T, P)$ or $N(t; T, P)$. For this you need **temperature** and **pressure** curves.
- The pressure is known a priori, but the temperature changes during the process (adiabatic heating effect, cooling or heating on the walls of the chamber, etc...)

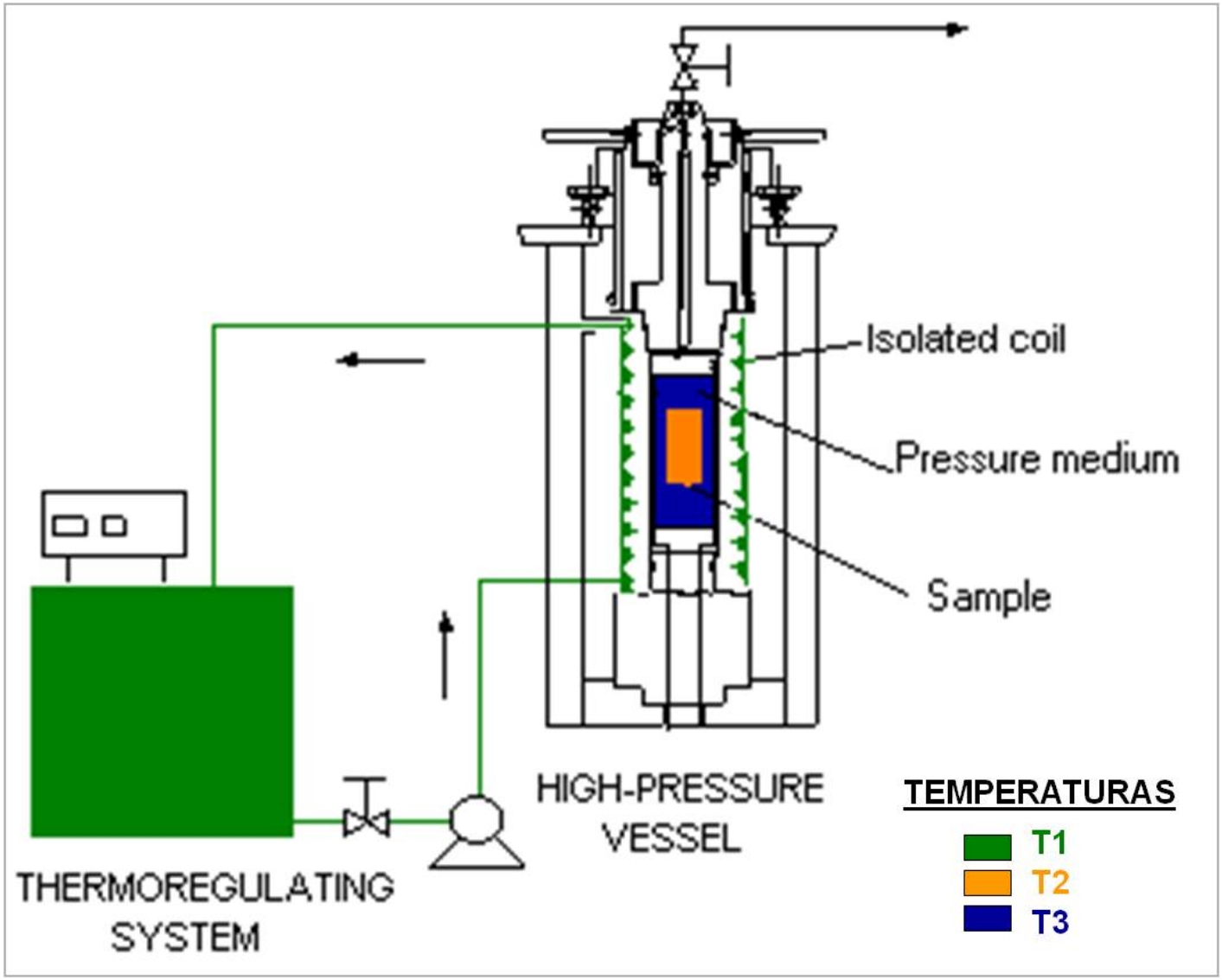
$\longrightarrow$ **Heat Transfer models**

Solving the inactivation models

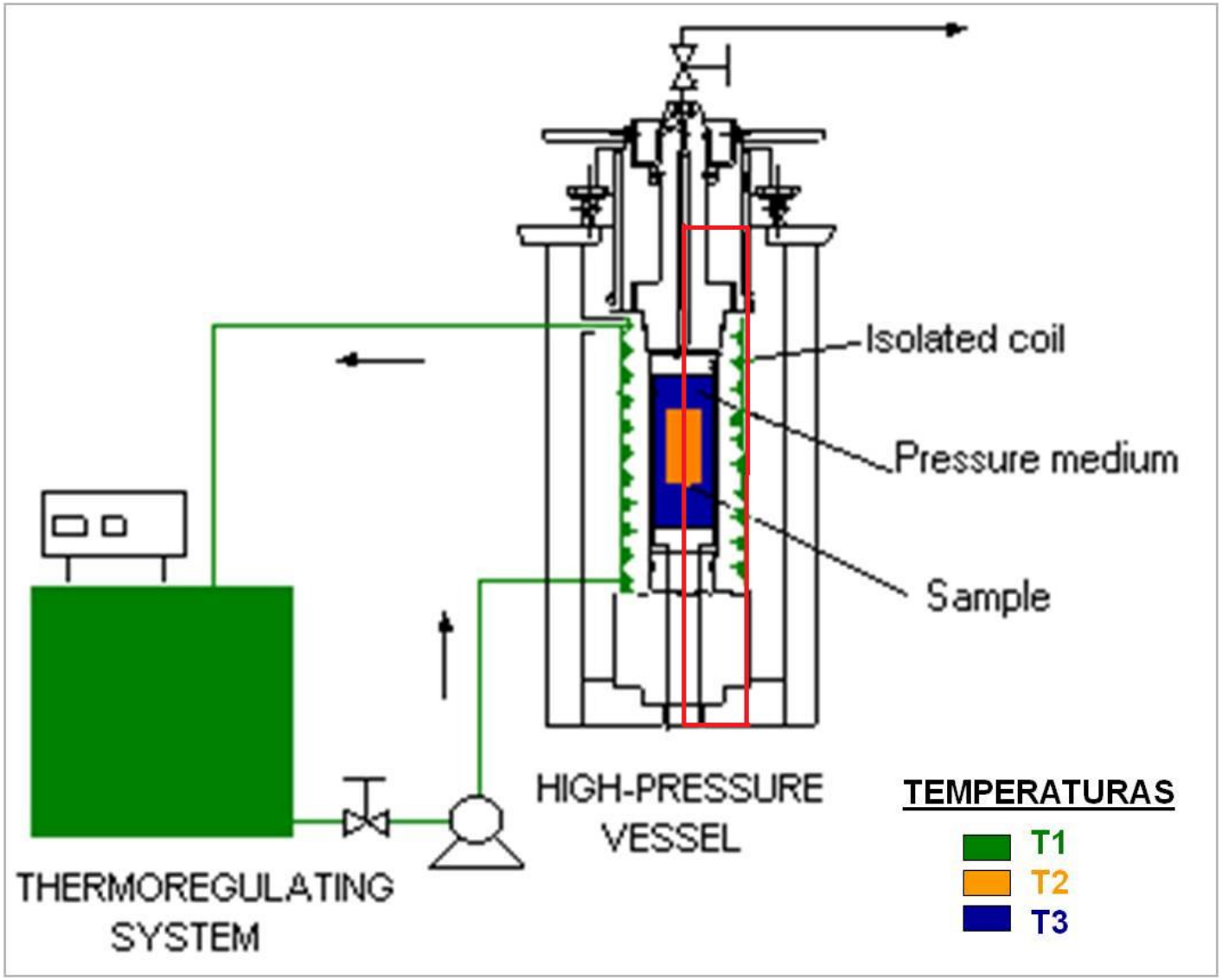
- We identify the parameters ($k_{T,P}$, T_{ref}, P_{ref}, $k_{T_{\text{ref}},P_{\text{ref}}}$,$B$, C, z_T, z_P, $\cdots$) by using experimental data and regression techniques.
- We can now model enzymatic inactivation or microbial population for HP–T processes, using the models for $A(t; T, P)$ or $N(t; T, P)$. For this you need **temperature** and **pressure** curves.
- The pressure is known a priori, but the temperature changes during the process (adiabatic heating effect, cooling or heating on the walls of the chamber, etc...)

$\longrightarrow$ **Heat Transfer models**

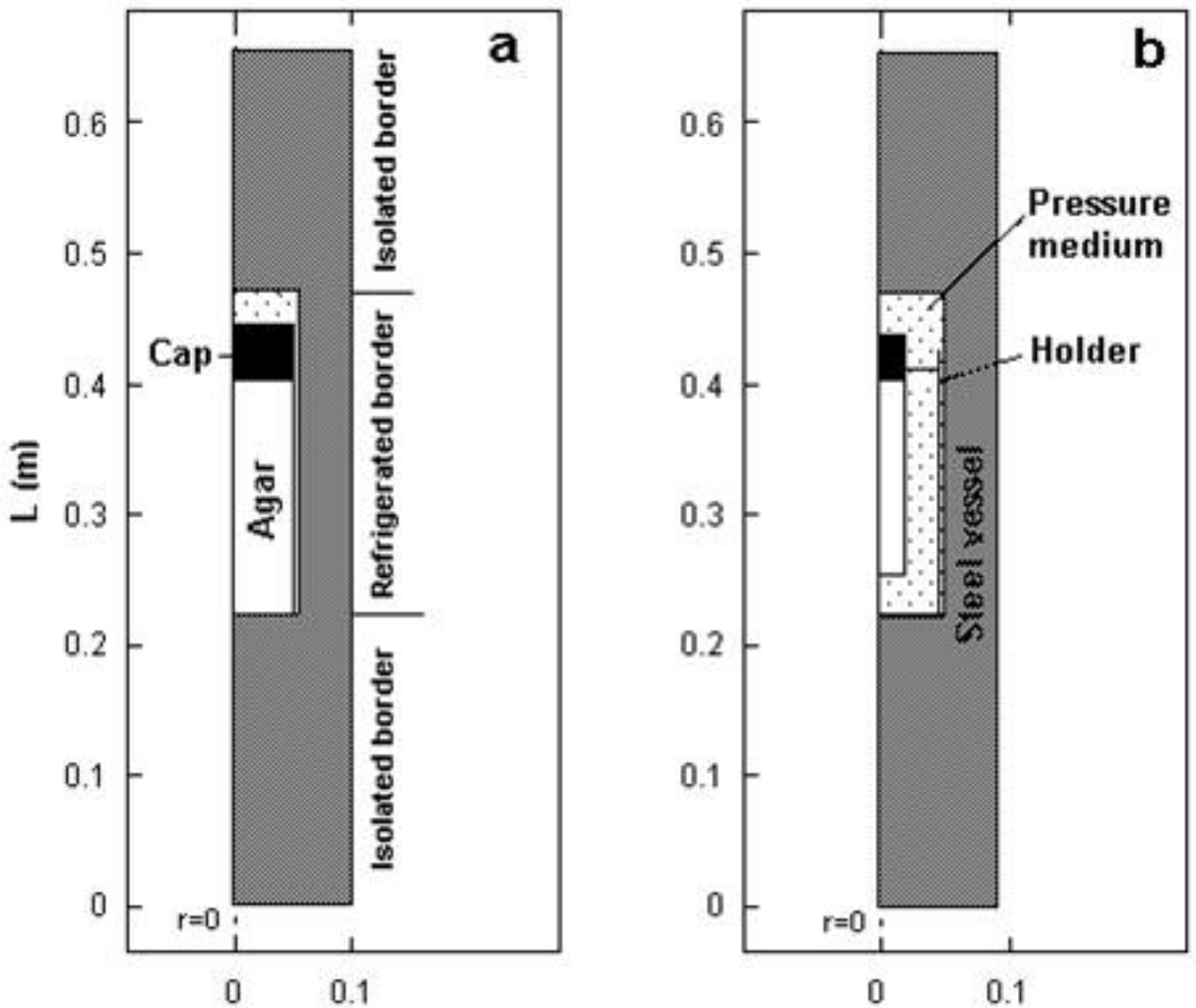
Graphical description of the HP Equipment



Graphical description of the HP Equipment



2D model (r,z) - Computational domain (big and small food sample)



Different heat transfer models

During a *HP–T* process the temperature of the processed food may change with time and with space. There are many models that describe the evolution of temperature of the processed food

- **ODE models:** when temperature only depends on time

$$\frac{\mathrm{d}T}{\mathrm{d}t} = H(T^{\mathrm{e}} - T) + \alpha T \frac{\mathrm{d}P}{\mathrm{d}t}$$

- **PDE models:** when temperature depends on time and space. Different models depending on type of food sample
  - **Heat transfer by conduction: For solid type foods (big sample)**
  - Heat transfer by conduction and convection (only in the pressurizing fluid): For solid type foods (small sample)
  - Heat transfer by conduction and convection (in food and fluid): For liquid type foods

Different heat transfer models

During a *HP–T* process the temperature of the processed food may change with time and with space. There are many models that describe the evolution of temperature of the processed food

- **ODE models:** when temperature only depends on time

$$\frac{\mathrm{d}T}{\mathrm{d}t} = H(T^{\mathrm{e}} - T) + \alpha T \frac{\mathrm{d}P}{\mathrm{d}t}$$

- **PDE models:** when temperature depends on time and space. Different models depending on type of food sample
  - **Heat transfer by conduction: For solid type foods (big sample)**
  - Heat transfer by conduction and convection (only in the pressurizing fluid): For solid type foods (small sample)
  - Heat transfer by conduction and convection (in food and fluid): For liquid type foods

Different heat transfer models

During a *HP–T* process the temperature of the processed food may change with time and with space. There are many models that describe the evolution of temperature of the processed food

- **ODE models:** when temperature only depends on time

$$\frac{\mathrm{d}T}{\mathrm{d}t} = H(T^{\mathrm{e}} - T) + \alpha T \frac{\mathrm{d}P}{\mathrm{d}t}$$

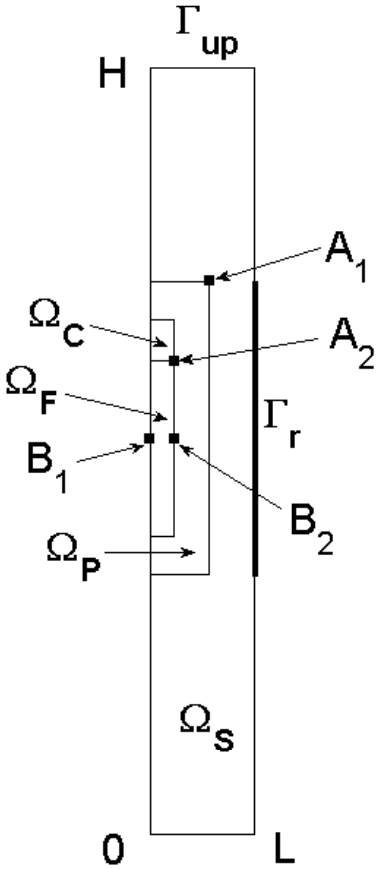
- **PDE models:** when temperature depends on time and space. Different models depending on type of food sample
  - **Heat transfer by conduction: For solid type foods (big sample)**
  - Heat transfer by conduction and convection (only in the pressurizing fluid): For solid type foods (small sample)
  - Heat transfer by conduction and convection (in food and fluid): For liquid type foods

Heat transfer by conduction

Solid type foods. Big sample

By using cylindrical coordinates and taking into account axial symmetry, our starting point is the **(r,z) 2D-model**

$$
\begin{cases}
\rho C_p \dfrac{\partial T}{\partial t} - \dfrac{1}{r}\dfrac{\partial}{\partial r}\left(rk\dfrac{\partial T}{\partial r}\right) - \dfrac{\partial}{\partial z}\left(k\dfrac{\partial T}{\partial z}\right) = \alpha \dfrac{\mathrm{d}P}{\mathrm{d}t} T & \\
k\dfrac{\partial T}{\partial \mathbf{n}} = 0 & \text{on } \left(\Gamma \setminus (\Gamma_{\mathrm{r}} \cup \Gamma_{\mathrm{up}})\right), \\
k\dfrac{\partial T}{\partial \mathbf{n}} = h(T_{\mathrm{env}} - T) & \text{on } \Gamma_{\mathrm{up}}, \\
T = T_{\mathrm{r}} & \text{on } \Gamma_{\mathrm{r}}, \\
T(0) = T_0 & \text{in } \Omega.
\end{cases}
$$



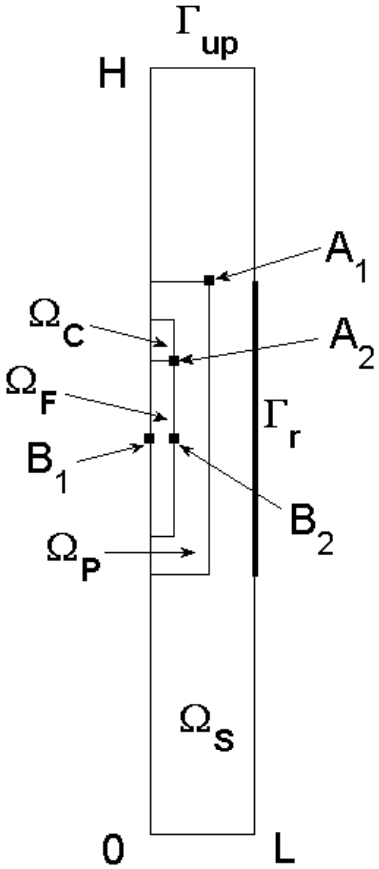
⟶ **Can we simplify this model?**

Heat transfer by conduction

Solid type foods. Big sample

By using cylindrical coordinates and taking into account axial symmetry, our starting point is the **(r,z) 2D-model**

$$
\begin{cases}
\rho C_p \dfrac{\partial T}{\partial t} - \dfrac{1}{r}\dfrac{\partial}{\partial r}\left(rk\dfrac{\partial T}{\partial r}\right) - \dfrac{\partial}{\partial z}\left(k\dfrac{\partial T}{\partial z}\right) = \alpha \dfrac{\mathrm{d}P}{\mathrm{d}t} T & \\
k\dfrac{\partial T}{\partial \mathbf{n}} = 0 & \text{on } \left(\Gamma \setminus (\Gamma_{\mathrm{r}} \cup \Gamma_{\mathrm{up}})\right), \\
k\dfrac{\partial T}{\partial \mathbf{n}} = h(T_{\mathrm{env}} - T) & \text{on } \Gamma_{\mathrm{up}}, \\
T = T_{\mathrm{r}} & \text{on } \Gamma_{\mathrm{r}}, \\
T(0) = T_0 & \text{in } \Omega.
\end{cases}
$$



$\longrightarrow$ **Can we simplify this model?**

Dimensional analysis

Non-dimensionalization (ˆ denote non-dimensional variables):

$$\hat{r} = \frac{r}{R}, \quad \hat{z} = \frac{z}{Z}, \quad \hat{t} = \frac{t}{\tau}, \quad \hat{T} = \frac{T - T_{\mathrm{r}}}{\Delta T}$$

Consider

$$\frac{\mathrm{d}P}{\mathrm{d}t}(t) = \begin{cases} \dfrac{\gamma}{t_p}, & 0 < t \leq t_p, \\ 0, & t > t_p \end{cases}$$

Dropping the ˆ symbol:

$$\frac{\partial T}{\partial t} - \frac{k\tau}{R^2 \rho C_p} \frac{\partial}{\partial r}\left(r \frac{\partial T}{\partial r}\right) - \frac{k\tau}{Z^2 \rho C_p} \frac{\partial^2 T}{\partial z^2} = \frac{\alpha\gamma\tau}{\rho C_p t_p} T + \frac{\alpha\gamma\tau}{\rho C_p t_p} \frac{T_{\mathrm{r}}}{\Delta T}$$

Choose scales: $R =$ width food sample, $Z =$ height food sample,

$$\Delta T = \max\{|T_0 - T_{\mathrm{r}}|, \frac{\alpha\gamma T_0}{\rho C_p}\}, \quad \tau = \frac{\rho C_p t_p}{\alpha\gamma} \min\left\{1, \frac{\Delta T}{T_{\mathrm{r}}}\right\}$$

Dimensional analysis

Non-dimensionalization (ˆ denote non-dimensional variables):

$$\hat{r} = \frac{r}{R}, \quad \hat{z} = \frac{z}{Z}, \quad \hat{t} = \frac{t}{\tau}, \quad \hat{T} = \frac{T - T_{\mathrm{r}}}{\Delta T}$$

Consider

$$\frac{\mathrm{d}P}{\mathrm{d}t}(t) = \begin{cases} \dfrac{\gamma}{t_p}, & 0 < t \leq t_p, \\ 0, & t > t_p \end{cases}$$

Dropping the ˆ symbol:

$$\frac{\partial T}{\partial t} - \frac{k\tau}{R^2 \rho C_p} \frac{\partial}{\partial r}\left(r \frac{\partial T}{\partial r}\right) - \frac{k\tau}{Z^2 \rho C_p} \frac{\partial^2 T}{\partial z^2} = \frac{\alpha\gamma\tau}{\rho C_p t_p} T + \frac{\alpha\gamma\tau}{\rho C_p t_p} \frac{T_{\mathrm{r}}}{\Delta T}$$

Choose scales: $R =$ width food sample, $Z =$ height food sample,

$$\Delta T = \max\{|T_0 - T_{\mathrm{r}}|, \frac{\alpha\gamma T_0}{\rho C_p}\}, \quad \tau = \frac{\rho C_p t_p}{\alpha\gamma} \min\left\{1, \frac{\Delta T}{T_{\mathrm{r}}}\right\}$$

Dimensional analysis

Non-dimensionalization (ˆ denote non-dimensional variables):

$$\hat{r} = \frac{r}{R}, \quad \hat{z} = \frac{z}{Z}, \quad \hat{t} = \frac{t}{\tau}, \quad \hat{T} = \frac{T - T_{\mathrm{r}}}{\Delta T}$$

Consider

$$\frac{\mathrm{d}P}{\mathrm{d}t}(t) = \begin{cases} \dfrac{\gamma}{t_p}, & 0 < t \leq t_p, \\ 0, & t > t_p \end{cases}$$

Dropping the ˆ symbol:

$$\frac{\partial T}{\partial t} - \frac{k\tau}{R^2 \rho C_p} \frac{\partial}{\partial r}\left(r \frac{\partial T}{\partial r}\right) - \frac{k\tau}{Z^2 \rho C_p} \frac{\partial^2 T}{\partial z^2} = \frac{\alpha\gamma\tau}{\rho C_p t_p} T + \frac{\alpha\gamma\tau}{\rho C_p t_p} \frac{T_{\mathrm{r}}}{\Delta T}$$

Choose scales: $R =$ width food sample, $Z =$ height food sample,

$$\Delta T = \max\{|T_0 - T_{\mathrm{r}}|, \frac{\alpha\gamma T_0}{\rho C_p}\}, \quad \tau = \frac{\rho C_p t_p}{\alpha\gamma} \min\left\{1, \frac{\Delta T}{T_{\mathrm{r}}}\right\}$$

Dimensional analysis

Non-dimensionalization (ˆ denote non-dimensional variables):

$$\hat{r} = \frac{r}{R}, \quad \hat{z} = \frac{z}{Z}, \quad \hat{t} = \frac{t}{\tau}, \quad \hat{T} = \frac{T - T_{\mathrm{r}}}{\Delta T}$$

Consider

$$\frac{\mathrm{d}P}{\mathrm{d}t}(t) = \begin{cases} \dfrac{\gamma}{t_p}, & 0 < t \leq t_p, \\ 0, & t > t_p \end{cases}$$

Dropping the ˆ symbol:

$$\frac{\partial T}{\partial t} - \frac{k\tau}{R^2 \rho C_p} \frac{\partial}{\partial r}\left(r \frac{\partial T}{\partial r}\right) - \frac{k\tau}{Z^2 \rho C_p} \frac{\partial^2 T}{\partial z^2} = \frac{\alpha\gamma\tau}{\rho C_p t_p} T + \frac{\alpha\gamma\tau}{\rho C_p t_p} \frac{T_{\mathrm{r}}}{\Delta T}$$

Choose scales: $R =$ width food sample, $Z =$ height food sample,

$$\Delta T = \max\{|T_0 - T_{\mathrm{r}}|, \frac{\alpha\gamma T_0}{\rho C_p}\}, \quad \tau = \frac{\rho C_p t_p}{\alpha\gamma} \min\left\{1, \frac{\Delta T}{T_{\mathrm{r}}}\right\}$$

Dimensional analysis

Non-dimensionalization (ˆ denote non-dimensional variables):

$$\hat{r} = \frac{r}{R}, \quad \hat{z} = \frac{z}{Z}, \quad \hat{t} = \frac{t}{\tau}, \quad \hat{T} = \frac{T - T_{\mathrm{r}}}{\Delta T}$$

Consider

$$\frac{\mathrm{d}P}{\mathrm{d}t}(t) = \begin{cases} \dfrac{\gamma}{t_p}, & 0 < t \leq t_p, \\ 0, & t > t_p \end{cases}$$

Dropping the ˆ symbol:

$$\frac{\partial T}{\partial t} - \underbrace{\frac{k\tau}{R^2 \rho C_p}}_{\mathbf{a}} \frac{\partial}{\partial r}\left(r \frac{\partial T}{\partial r}\right) - \underbrace{\frac{k\tau}{Z^2 \rho C_p}}_{\mathbf{b}} \frac{\partial^2 T}{\partial z^2} = \underbrace{\frac{\alpha\gamma\tau}{\rho C_p t_p}}_{\mathbf{c}} T + \underbrace{\frac{\alpha\gamma\tau}{\rho C_p t_p} \frac{T_{\mathrm{r}}}{\Delta T}}_{\mathbf{d}}$$

Choose scales: $R =$ width food sample, $Z =$ height food sample,

$$\Delta T = \max\{|T_0 - T_{\mathrm{r}}|, \frac{\alpha\gamma T_0}{\rho C_p}\}, \quad \tau = \frac{\rho C_p t_p}{\alpha\gamma} \min\left\{1, \frac{\Delta T}{T_{\mathrm{r}}}\right\}$$

Non-dimensional system

With all the previously chosen scales, we can now rewrite the system in a simplified non-dimensional form:

$$\begin{cases} \dfrac{\partial T}{\partial t} - \mathbf{a}\dfrac{1}{r}\dfrac{\partial}{\partial r}\left(\dfrac{\partial T}{\partial r}\right) - \mathbf{b}\dfrac{\partial^2 T}{\partial z^2} = (\mathbf{c}T + \mathbf{d})\chi_{(0,\frac{t_p}{\tau})}(t) & \text{in } \hat{\Omega} \\ \dfrac{\partial T}{\partial \mathbf{n}} = 0 & \text{on } \left(\hat{\Gamma} \setminus (\hat{\Gamma}_{\mathrm{r}} \cup \hat{\Gamma}_{\mathrm{up}})\right) \\ \dfrac{\partial T}{\partial \mathbf{n}} = -\dfrac{hZ}{k}T & \text{on } \hat{\Gamma}_{\mathrm{up}}, \\ T = 0 & \text{on } \hat{\Gamma}_{\mathrm{r}}, \\ T(0) = \dfrac{T_0 - T_{\mathrm{r}}}{\Delta T} & \text{in } \hat{\Omega}. \end{cases}$$

The values of the parameters **a, b, c, d** depend on the food sample, the pressurizing fluid, the dimensions of the holder, the pressure profile, the process time, etc...

Example of a HP process

The pressure profile is given by Process P (360 MPa):

$$T_0 = 40^\circ\mathrm{C} \text{ in } \Omega, \quad \frac{dP}{dt} = \begin{cases} \dfrac{120}{61} \text{ MPa s}^{-1}, & 0 < t \leq 183 \\ 0 \text{ MPa s}^{-1}, & t > 183. \end{cases}$$

Using thermophysical data of **tylose** as the food simile, **water** as the pressurizing medium, and for a **900 seconds** process, the values of the parameters are

	a	b	c	d
$\hat{\Omega}_F$	0.02	0.00126	0.07	1
$\hat{\Omega}_P$	0.023	0.0014	0.05	0.7
$\hat{\Omega}_C$	0.013	0.00081	0	0
$\hat{\Omega}_S$	2.423	0.148	0	0

Key point: Conductivity height coefficient (**b**) was smaller than the radial one.

Is it reasonable to neglect that term? $\longrightarrow$ 1D model ?

Example of a HP process

The pressure profile is given by Process P (360 MPa):

$$T_0 = 40^\circ\mathrm{C} \text{ in } \Omega, \quad \frac{dP}{dt} = \begin{cases} \dfrac{120}{61} \text{ MPa s}^{-1}, & 0 < t \leq 183 \\ 0 \text{ MPa s}^{-1}, & t > 183. \end{cases}$$

Using thermophysical data of **tylose** as the food simile, **water** as the pressurizing medium, and for a **900 seconds** process, the values of the parameters are

	a	b	c	d
$\hat{\Omega}_F$	0.02	0.00126	0.07	1
$\hat{\Omega}_P$	0.023	0.0014	0.05	0.7
$\hat{\Omega}_C$	0.013	0.00081	0	0
$\hat{\Omega}_S$	2.423	0.148	0	0

Key point: Conductivity height coefficient (**b**) was smaller than the radial one.

Is it reasonable to neglect that term? $\longrightarrow$ 1D model ?

Example of a HP process

The pressure profile is given by Process P (360 MPa):

$$T_0 = 40^\circ\mathrm{C} \text{ in } \Omega, \quad \frac{dP}{dt} = \begin{cases} \dfrac{120}{61} \text{ MPa s}^{-1}, & 0 < t \leq 183 \\ 0 \text{ MPa s}^{-1}, & t > 183. \end{cases}$$

Using thermophysical data of **tylose** as the food simile, **water** as the pressurizing medium, and for a **900 seconds** process, the values of the parameters are

	a	b	c	d
$\hat{\Omega}_F$	0.02	0.00126	0.07	1
$\hat{\Omega}_P$	0.023	0.0014	0.05	0.7
$\hat{\Omega}_C$	0.013	0.00081	0	0
$\hat{\Omega}_S$	2.423	0.148	0	0

Key point: Conductivity height coefficient (**b**) was smaller than the radial one.

Is it reasonable to neglect that term? $\longrightarrow$ 1D model ?

Example of a HP process

The pressure profile is given by Process P (360 MPa):

$$T_0 = 40^\circ\mathrm{C} \text{ in } \Omega, \quad \frac{dP}{dt} = \begin{cases} \dfrac{120}{61} \text{ MPa s}^{-1}, & 0 < t \leq 183 \\ 0 \text{ MPa s}^{-1}, & t > 183. \end{cases}$$

Using thermophysical data of **tylose** as the food simile, **water** as the pressurizing medium, and for a **900 seconds** process, the values of the parameters are

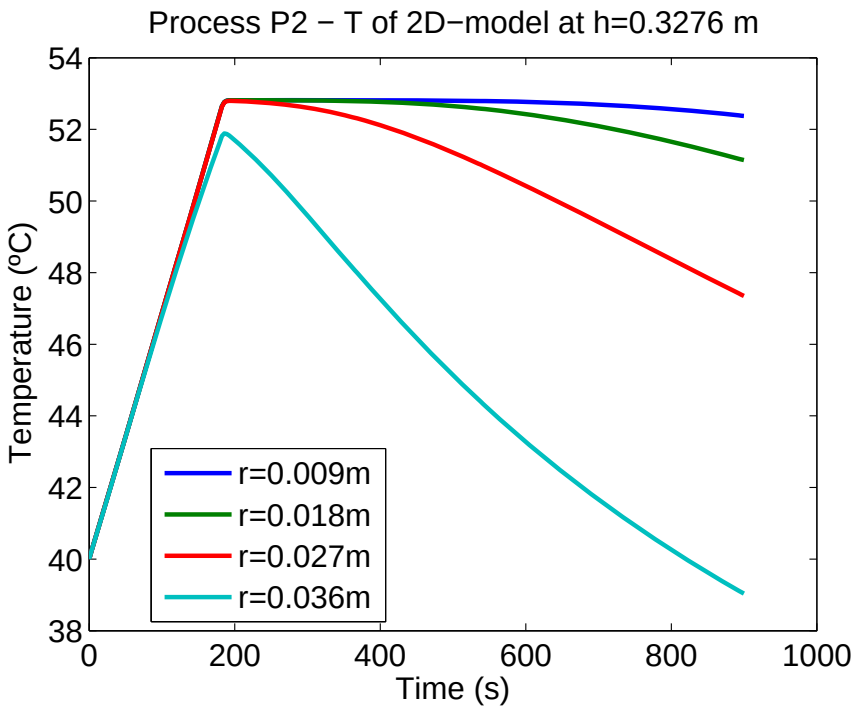
	a	b	c	d
$\hat{\Omega}_F$	0.02	0.00126	0.07	1
$\hat{\Omega}_P$	0.023	0.0014	0.05	0.7
$\hat{\Omega}_C$	0.013	0.00081	0	0
$\hat{\Omega}_S$	2.423	0.148	0	0

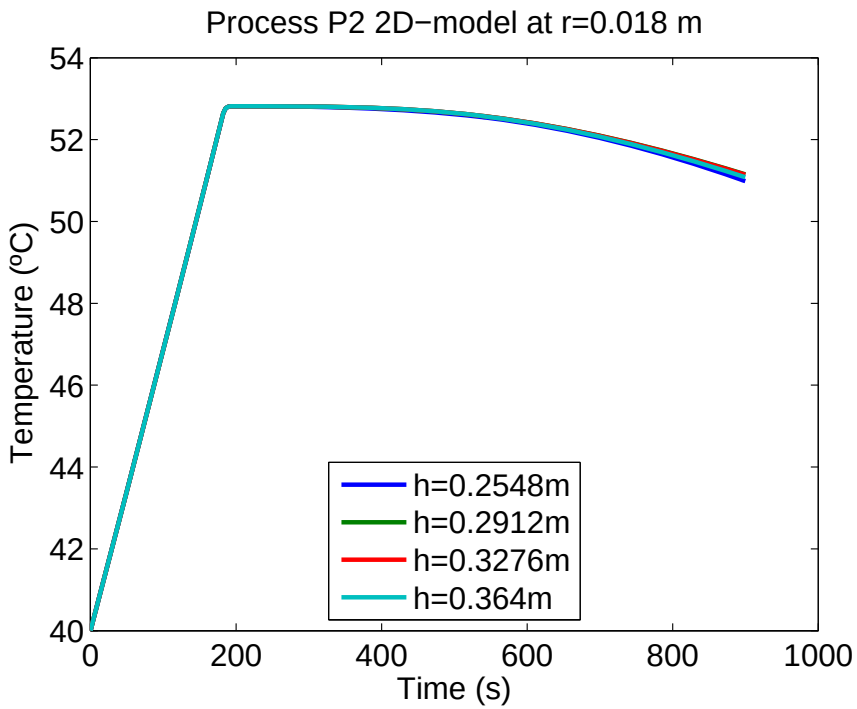
Key point: Conductivity height coefficient (**b**) was smaller than the radial one.

Is it reasonable to neglect that term? $\longrightarrow$ 1D model ?

Graphical results of the 2D-model

Solution of 2D model inside the food during process P at different heights and different radius





1D Heat transfer model

$$\begin{cases} \dfrac{\partial T}{\partial t} - a\dfrac{1}{r}\dfrac{\partial}{\partial r}\left(r\dfrac{\partial T}{\partial r}\right) = (c\,T + d)\chi_{(0,0,56)}(t) & \text{in} \quad (0,2)\times(0,2{,}76), \\ \dfrac{\partial T}{\partial r} = 0 & \text{on} \quad \{0\}\times(0,2{,}76), \\ T = 0 & \text{on} \quad \{2\}\times(0,2{,}76), \\ T(0) = 1 & \text{in} \quad (0,2), \end{cases}$$

- This model is much faster to solve computationally than the 2D-model.
- But even better: we can find an **analytic solution** for the temperature inside the food!

$$T_{\mathrm{F}}(r,t) = \begin{cases} t+1, & t \le 0{,}56, \\ \displaystyle\sum_{n=1}^{\infty} C_n J_0(\lambda_n r)\exp(-0{,}02\lambda_n^2(t-0{,}56)), & t > 0{,}56, \end{cases}$$

1D Heat transfer model

$$\begin{cases} \dfrac{\partial T}{\partial t} - a\dfrac{1}{r}\dfrac{\partial}{\partial r}\left(r\dfrac{\partial T}{\partial r}\right) = (c\,T + d)\chi_{(0,0,56)}(t) & \text{in} \quad (0,2)\times(0,2{,}76), \\ \dfrac{\partial T}{\partial r} = 0 & \text{on} \quad \{0\}\times(0,2{,}76), \\ T = 0 & \text{on} \quad \{2\}\times(0,2{,}76), \\ T(0) = 1 & \text{in} \quad (0,2), \end{cases}$$

- This model is much faster to solve computationally than the 2D-model.
- But even better: we can find an **analytic solution** for the temperature inside the food!

$$T_{\mathrm{F}}(r,t) = \begin{cases} t+1, & t \le 0{,}56, \\ \displaystyle\sum_{n=1}^{\infty} C_n J_0(\lambda_n r)\exp(-0{,}02\lambda_n^2(t-0{,}56)), & t > 0{,}56, \end{cases}$$

1D Heat transfer model

$$\begin{cases} \dfrac{\partial T}{\partial t} - a\dfrac{1}{r}\dfrac{\partial}{\partial r}\left(r\dfrac{\partial T}{\partial r}\right) = (c\,T + d)\chi_{(0,0,56)}(t) & \text{in} \quad (0,2)\times(0,2{,}76), \\ \dfrac{\partial T}{\partial r} = 0 & \text{on} \quad \{0\}\times(0,2{,}76), \\ T = 0 & \text{on} \quad \{2\}\times(0,2{,}76), \\ T(0) = 1 & \text{in} \quad (0,2), \end{cases}$$

- This model is much faster to solve computationally than the 2D-model.
- But even better: we can find an **analytic solution** for the temperature inside the food!

$$T_{\mathrm{F}}(r,t) = \begin{cases} t+1, & t \le 0{,}56, \\ \displaystyle\sum_{n=1}^{\infty} C_n J_0(\lambda_n r)\exp(-0{,}02\lambda_n^2(t-0{,}56)), & t > 0{,}56, \end{cases}$$

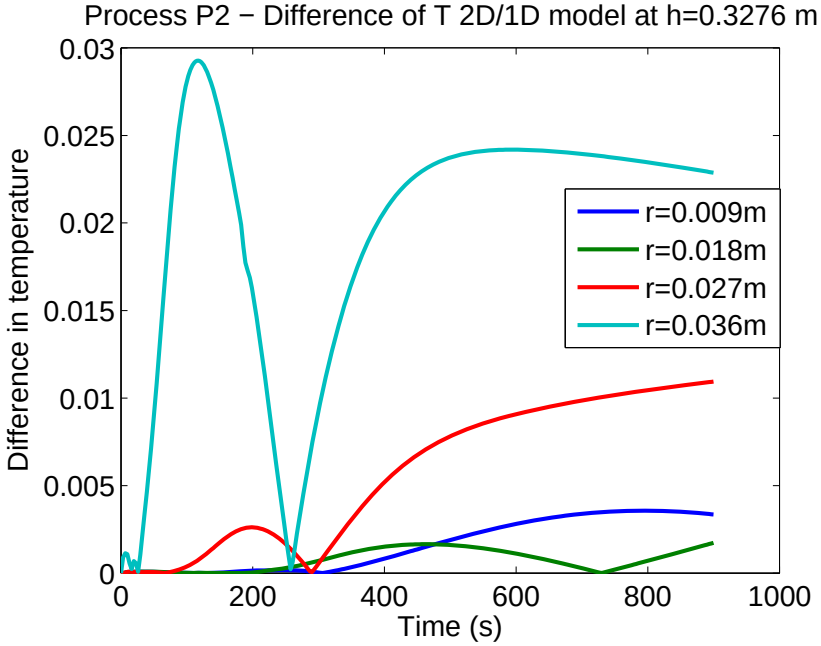
1D Heat transfer model

$$\begin{cases} \dfrac{\partial T}{\partial t} - a\dfrac{1}{r}\dfrac{\partial}{\partial r}\left(r\dfrac{\partial T}{\partial r}\right) = (c\,T + d)\chi_{(0,0,56)}(t) & \text{in} \quad (0,2)\times(0,2{,}76), \\ \dfrac{\partial T}{\partial r} = 0 & \text{on} \quad \{0\}\times(0,2{,}76), \\ T = 0 & \text{on} \quad \{2\}\times(0,2{,}76), \\ T(0) = 1 & \text{in} \quad (0,2), \end{cases}$$

- This model is much faster to solve computationally than the 2D-model.
- But even better: we can find an **analytic solution** for the temperature inside the food!

$$T_{\mathrm{F}}(r,t) = \begin{cases} t+1, & t \le 0{,}56, \\ \displaystyle\sum_{n=1}^{\infty} C_n J_0(\lambda_n r)\exp(-0{,}02\lambda_n^2(t-0{,}56)), & t > 0{,}56, \end{cases}$$

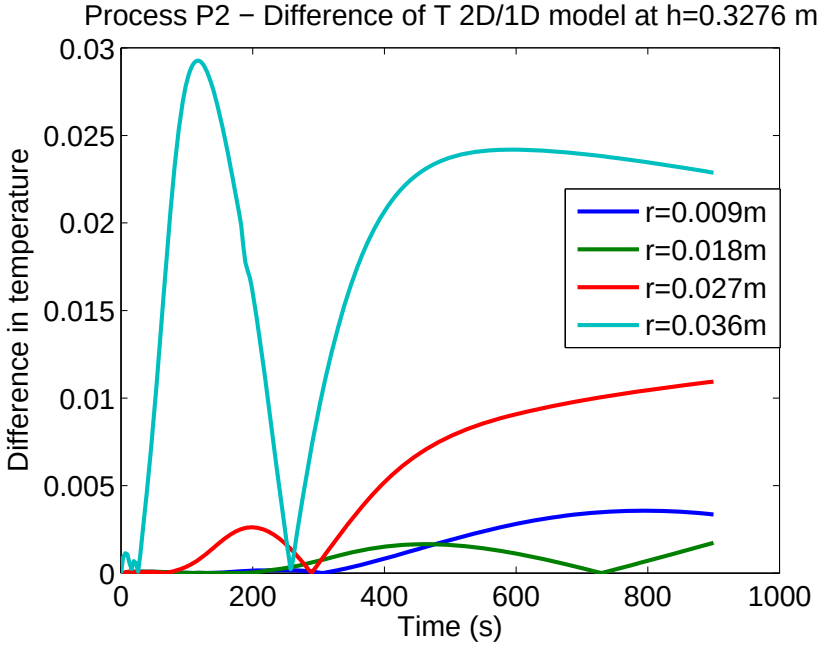
Pros and cons of the simplifications



Temperature differences between 2D and 1D model at the same radial points inside the food. Mid height. Process P.

We have tried with different pressure curves and conditions $\longrightarrow$ Very small differences for nearly every point inside food sample, except for points very close to the top (Rubber cap) or bottom (Steel) $\longrightarrow$ Studying possibility of **boundary layers** . Working on **asymptotic expansion** right now.

Pros and cons of the simplifications



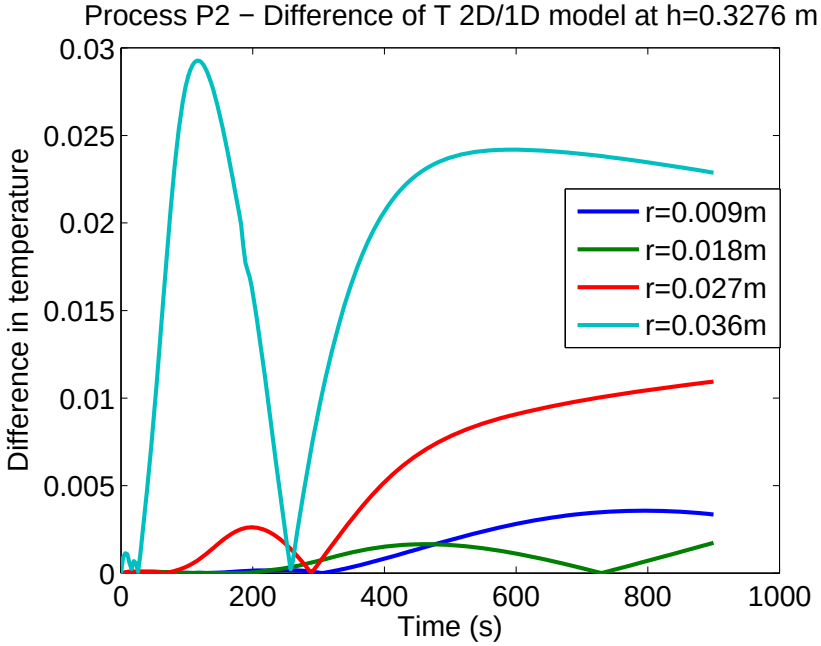
Temperature differences between 2D and 1D model at the same radial points inside the food. Mid height. Process P.

We have tried with different pressure curves and conditions $\longrightarrow$

Very small differences for nearly every point inside food sample, except for points very close to the top (Rubber cap) or bottom (Steel) $\longrightarrow$

Studying possibility of **boundary layers** . Working on **asymptotic expansion** right now.

Pros and cons of the simplifications



Temperature differences between 2D and 1D model at the same radial points inside the food. Mid height. Process P.

We have tried with different pressure curves and conditions $\longrightarrow$ Very small differences for nearly every point inside food sample, except for points very close to the top (Rubber cap) or bottom (Steel) $\longrightarrow$ Studying possibility of **boundary layers** . Working on **asymptotic expansion** right now.

Coupling of Enzymatic Inactivation and Heat Transfer Simplified Models

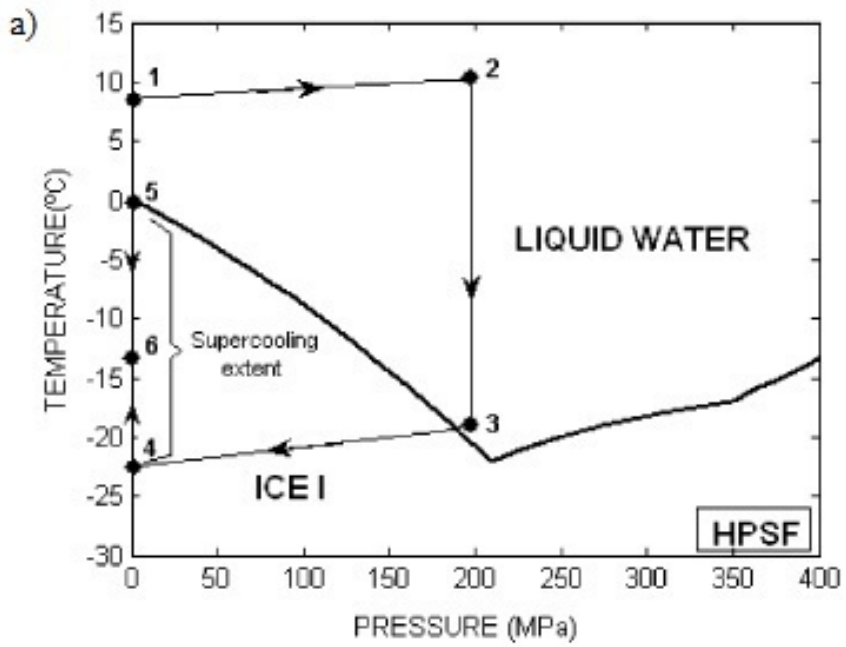
We can now couple the heat transfer models with kinetic equation for enzymatic activity $A(t; T, P)$. We compare the **resulting enzymatic activity** distribution that we obtain using the 2D heat transfer models versus the 1D models.

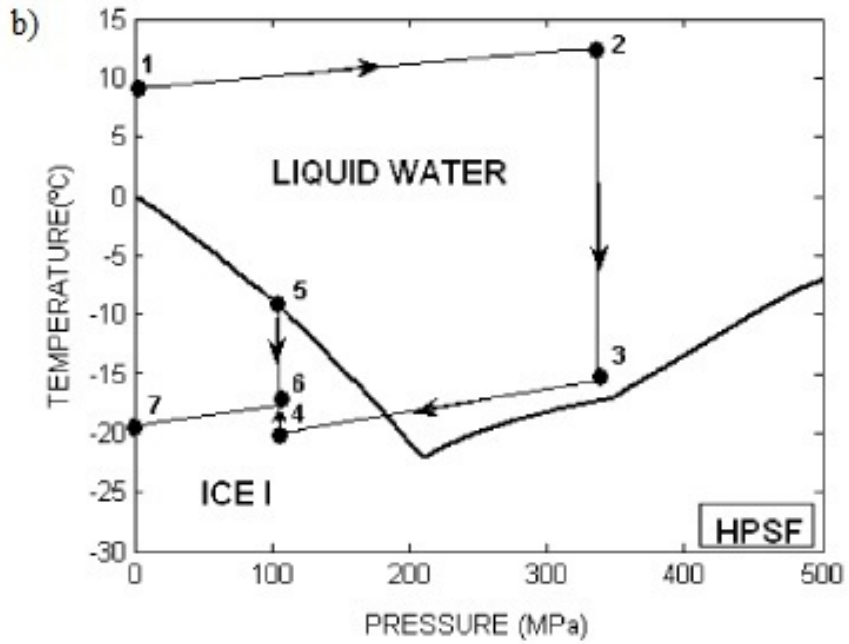
Model (for T)	BSAA	LOX	CPE
1D	26.92	68.66	93.88
2D-mid height	25.77	67.06	93.76
2D-full	26.43	67.18	93.86

Mean activity at final time for the 3 models considered and for BSAA (Bacillus Subtilis α-Amylase), LOX (Lipoxygenase) and CPE (Carrot Pectin Methyl-Esterase) enzymes.

- J. A. Infante, B. Ivorra, Á. M. Ramos and J. M. Rey, *On the Modelling and Simulation of High Pressure Processes and Inactivation of Enzymes in Food Engineering.* Mathematical Models and Methods in Applied Sciences (M3AS), Vol. 19, No. 12, (2009) pp. 2203–2229.

Modelling freezing processes with High pressure. HPSF processes





We are developing a heat transfer model for HPSF processes with rapid (a) or slow (b) expansions. For rapid expansion the **phase transition** occurs at atmospheric pressure conditions and for slow expansions under pressure.

The enthalpy formulation

Voller and Swaminathan (1990): g_l (liquid volume fraction) and g_s (solid volume fraction). "Mixture enthalpy":

$$e = g_s \int_{T_{\text{ref}}}^{T} \rho_s C_{p_s} \mathrm{d}\theta + g_l \int_{T_{\text{ref}}}^{T} \rho_l C_{p_l} \mathrm{d}\theta + \rho_l g_l \lambda,$$

where T_{ref} is a reference temperature (it is the temperature at which all the latent heat has been released) and λ is the latent heat.
"Mixture conductivity":

$$k = g_s k_s + g_l k_l.$$

Energy equation in enthalpy formulation

$$\frac{\partial e}{\partial t} = \nabla \cdot (k \nabla T).$$

Defining $C_{\text{vol}} = g_s \rho_s C_{p_s} + g_l \rho_l C_{p_l}$, and $\delta e = \int_{T_{\text{ref}}}^{T} (\rho_l C_{p_l} - \rho_s C_{p_s}) \mathrm{d}\theta + \rho_l \lambda$,

$$\frac{\partial e}{\partial t} = C_{\text{vol}} \frac{\partial T}{\partial t} + \delta e \frac{\partial g_l}{\partial t}.$$

The enthalpy formulation: Source based method

Now it is possible to give the equation in a formulation for temperature:

$$C_{\mathrm{vol}}\frac{\partial T}{\partial t} - \nabla\cdot(k\nabla T) = \alpha\frac{\mathrm{d}P}{\mathrm{d}t}T - \delta e\frac{\partial g_l}{\partial t}$$

More convenient: only one variable and easier to adapt the algorithms to existing numerical codes.

Problems: How to calculate the liquid fraction as a function of time $g_l(t)$. How to release the exact amount of latent heat λ for the temperature to increase up to the corresponding freezing point at atmospheric conditions.

We assume that the phase transition occurs at atmospheric pressure conditions (rapid expansion) and over a short period of time.

The enthalpy formulation: Source based method

Now it is possible to give the equation in a formulation for temperature:

$$C_{\mathrm{vol}}\frac{\partial T}{\partial t} - \nabla\cdot(k\nabla T) = \alpha\frac{\mathrm{d}P}{\mathrm{d}t}T - \delta e\frac{\partial g_l}{\partial t}$$

More convenient: only one variable and easier to adapt the algorithms to existing numerical codes.

Problems: How to calculate the liquid fraction as a function of time $g_l(t)$. How to release the exact amount of latent heat λ for the temperature to increase up to the corresponding freezing point at atmospheric conditions.

We assume that the phase transition occurs at atmospheric pressure conditions (rapid expansion) and over a short period of time.

The enthalpy formulation: Source based method

Now it is possible to give the equation in a formulation for temperature:

$$C_{\mathrm{vol}}\frac{\partial T}{\partial t} - \nabla\cdot(k\nabla T) = \alpha\frac{\mathrm{d}P}{\mathrm{d}t}T - \delta e\frac{\partial g_l}{\partial t}$$

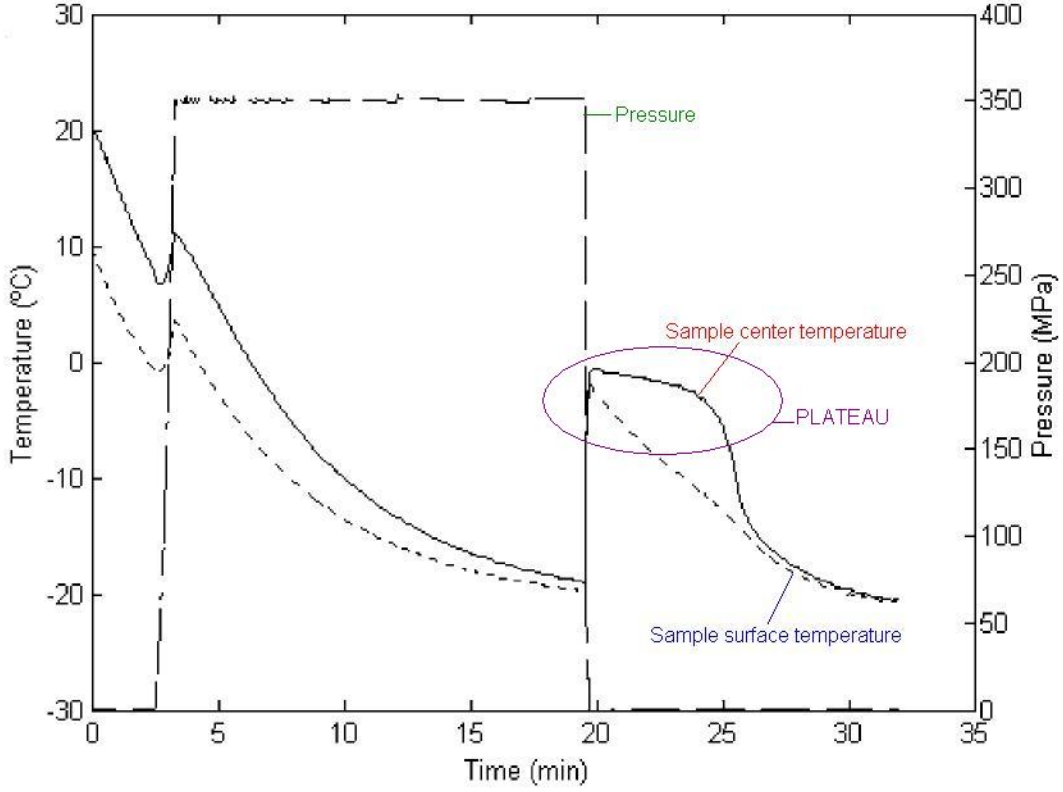
More convenient: only one variable and easier to adapt the algorithms to existing numerical codes.

Problems: How to calculate the liquid fraction as a function of time $g_l(t)$. How to release the exact amount of latent heat λ for the temperature to increase up to the corresponding freezing point at atmospheric conditions.

We assume that the phase transition occurs at atmospheric pressure conditions (rapid expansion) and over a short period of time.

Experimental results of HPSF

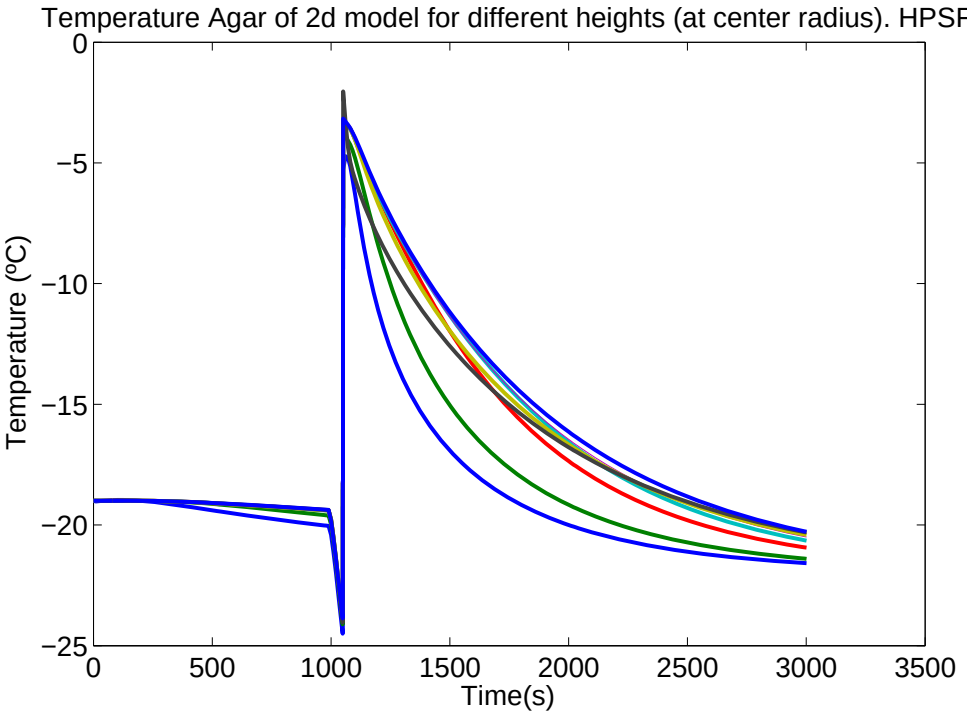
Pressure and temperature experimental evolution in a gelatin sample during a High-pressure shift freezing process.

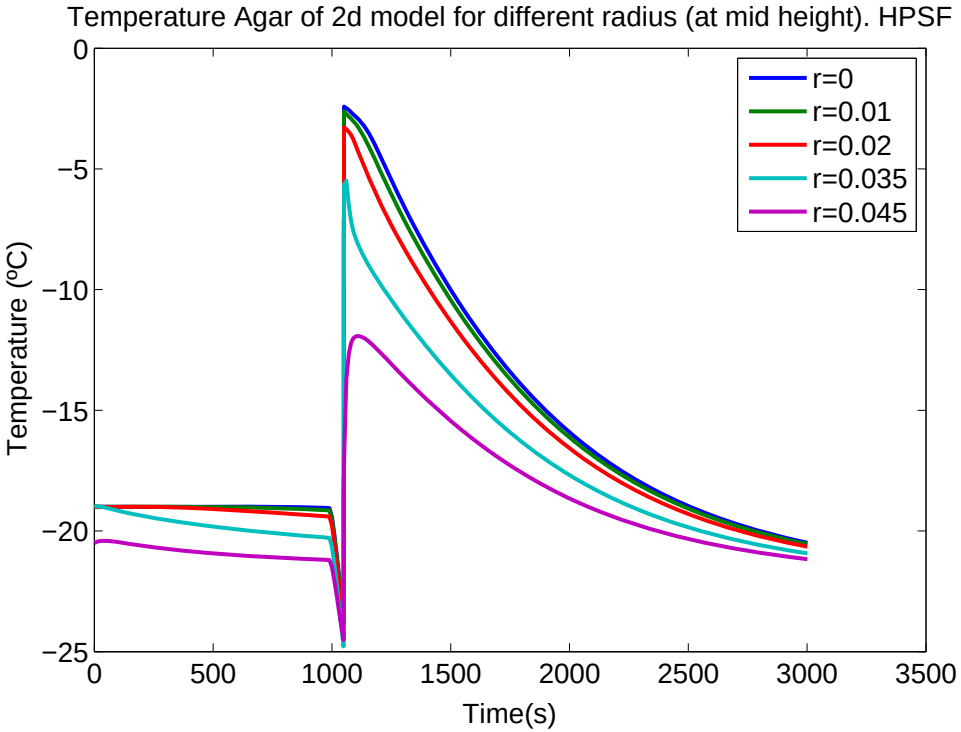


- P. P. Fernández, L. Otero, B. Guignon, P. D. Sanz, *High-pressure shift freezing versus high-pressure assisted freezing: Effects on the microstructure of a food model.* Food Hydrocolloids 20 (2006), pp. 510–522.

Numerical results when modelling HPSF

Example of HPSF process with rapid expansion of agar gel.

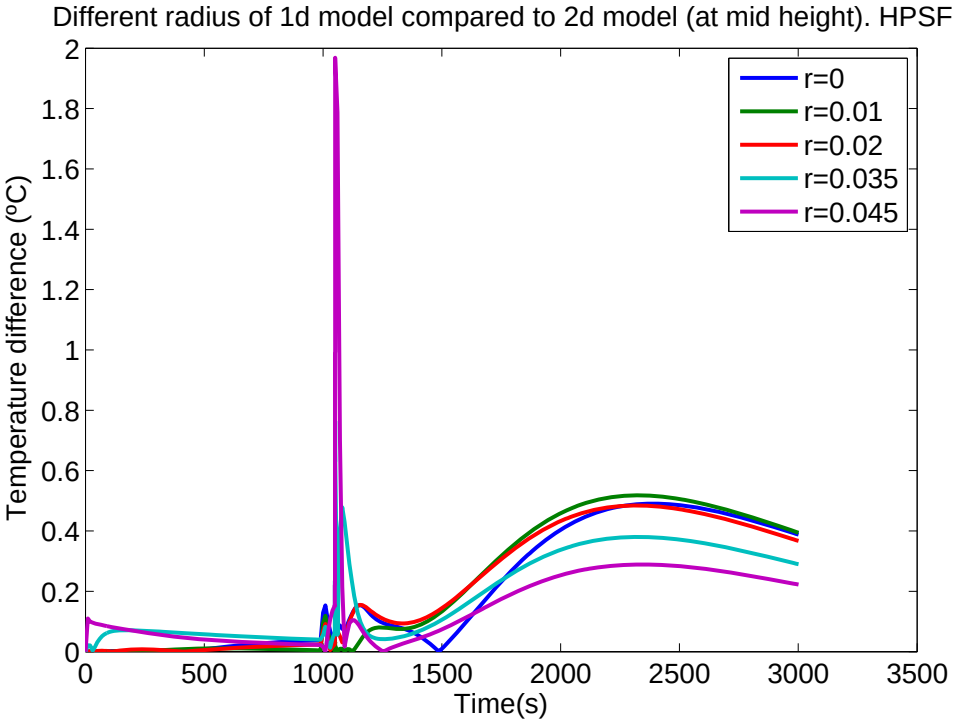


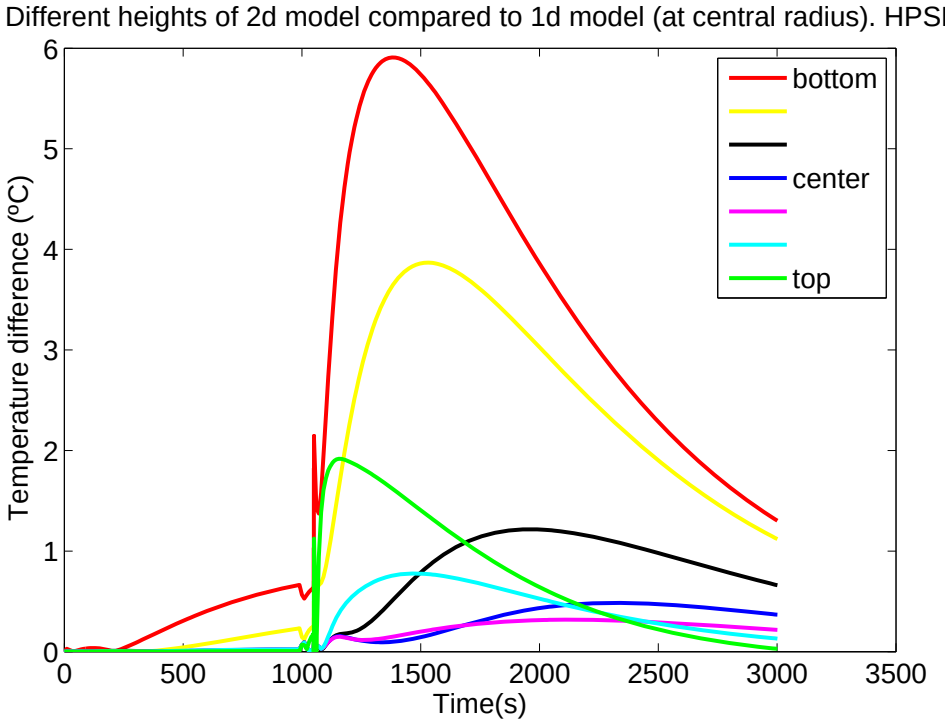


Evolution of the temperature inside food during HPSF process for 2D model, for different heights (left) and radial points (right).

Numerical examples when modelling HPSF

We again perform dimensional analysis and try to go to a 1D model.





Difference of temperatures of 2D model and 1D model inside food during HPSF process for different heights (left) and radial points (right).

Concluding Remarks

- The combination of high pressure with moderate temperatures inactivates microorganisms and enzymes without damaging the food significantly.
- We are able to predict the bacterial and enzymatic inactivation for high pressure processes in foods.
- These models are a very useful tool for equipment design and for optimization of the inactivation processes.
- Simplification of the models is convenient for quick simulations and for optimization purposes.
- Analytic solutions allow a qualitative study of the temperature profile
- **... a lot of research is still to be done in this area**

Concluding Remarks

- The combination of high pressure with moderate temperatures inactivates microorganisms and enzymes without damaging the food significantly.
- We are able to predict the bacterial and enzymatic inactivation for high pressure processes in foods.
- These models are a very useful tool for equipment design and for optimization of the inactivation processes.
- Simplification of the models is convenient for quick simulations and for optimization purposes.
- Analytic solutions allow a qualitative study of the temperature profile
- **... a lot of research is still to be done in this area**

Concluding Remarks

- The combination of high pressure with moderate temperatures inactivates microorganisms and enzymes without damaging the food significantly.
- We are able to predict the bacterial and enzymatic inactivation for high pressure processes in foods.
- These models are a very useful tool for equipment design and for optimization of the inactivation processes.
- Simplification of the models is convenient for quick simulations and for optimization purposes.
- Analytic solutions allow a qualitative study of the temperature profile
- **... a lot of research is still to be done in this area**

Concluding Remarks

- The combination of high pressure with moderate temperatures inactivates microorganisms and enzymes without damaging the food significantly.
- We are able to predict the bacterial and enzymatic inactivation for high pressure processes in foods.
- These models are a very useful tool for equipment design and for optimization of the inactivation processes.
- Simplification of the models is convenient for quick simulations and for optimization purposes.
- Analytic solutions allow a qualitative study of the temperature profile
- **... a lot of research is still to be done in this area**

Concluding Remarks

- The combination of high pressure with moderate temperatures inactivates microorganisms and enzymes without damaging the food significantly.
- We are able to predict the bacterial and enzymatic inactivation for high pressure processes in foods.
- These models are a very useful tool for equipment design and for optimization of the inactivation processes.
- Simplification of the models is convenient for quick simulations and for optimization purposes.
- Analytic solutions allow a qualitative study of the temperature profile
- **... a lot of research is still to be done in this area**

Concluding Remarks

- The combination of high pressure with moderate temperatures inactivates microorganisms and enzymes without damaging the food significantly.
- We are able to predict the bacterial and enzymatic inactivation for high pressure processes in foods.
- These models are a very useful tool for equipment design and for optimization of the inactivation processes.
- Simplification of the models is convenient for quick simulations and for optimization purposes.
- Analytic solutions allow a qualitative study of the temperature profile
- **... a lot of research is still to be done in this area**

Emerging Risks in the Food Supply Chain

claude.j.cheftel@orange.fr

Honorary Professor of Food Biochemistry & Technology
Université de Montpellier, France

www.cheftel.com

MALTA-CONSOLIDER
Miraflores de la Sierra, 24 Jan. 2011

Emerging Risks

An emerging risk can be defined as (EFSA, 2007):

- **a risk resulting from a newly identified hazard to which a significant exposure may occur**
- **or from an unexpected increased significant exposure and/or susceptibility to a known hazard.**

Main Categories of Food Hazards & Risks

Types of Hazards	Manifestations	Populations at risk
Pathogenic Micro-organisms	**Acute, Immediate**	**General** (individual & group vulnerability)
Toxic chemicals	**Mainly chronic diseases after prolonged exposure** (often masked by influence of other factors)	**General** (individual & group vulnerability)
Food allergens	**Acute, Immediate** (individual control is uncertain)	**Small proportion** (individual sensitivity)
Under-nutrition, Over-eating & Malnutrition	**Immediate or progressive**	**General or Groups**

Burden of Foodborne Illnesses (USA)

48 million Americans become sick due to foodborne illness each year
128,000 are hospitalized. Estimated annual deaths: 3000.
(CDC estimations, 2010)

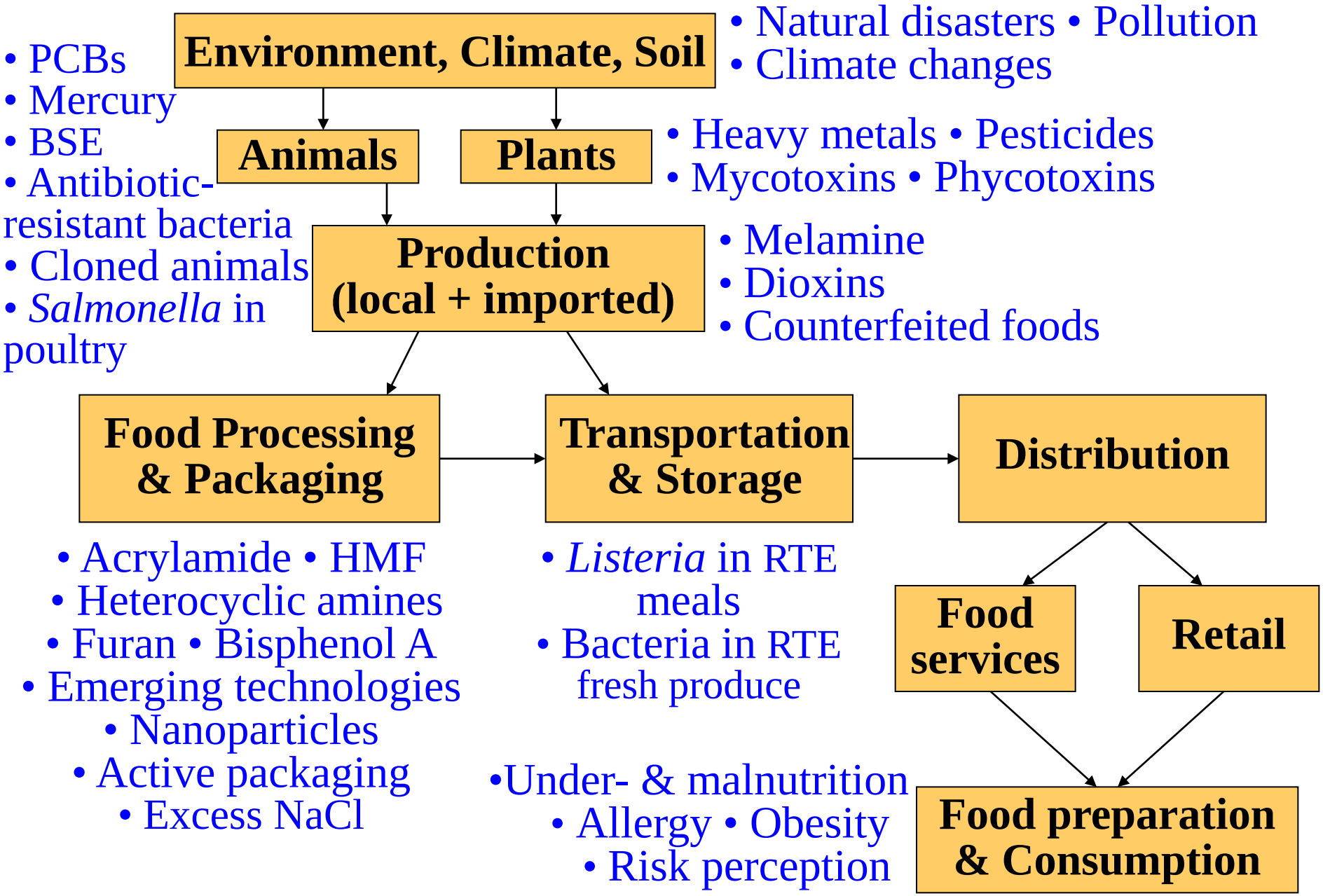
Pathogens that cause the most illnesses: Norovirus: 58%; non-typhoidal *Salmonella* spp: 11%; *Clostridium perfringens*: 10%; *Campylobacter*: 9%.

Leading causes of death: non-typhoidal *Salmonella* spp: 28%; *Toxoplasma gondii*: 24%; *Listeria monocytogenes*: 19%; Norovirus: 11%.

Of 33,625 *Salmonella* isolates from animals & foods (BfR, 2000-08), **48% were resistant to at least one class of antibiotics** and 35% were resistant to more. Similar data for *Escherichia coli* & *Campylobacter*.

~203,000 visits/year to hospitals emergency depts for **food allergies** (including ~90,000 cases of anaphylaxis).

Foodborne illness costs $152 B/year ($39 B due to fresh produce)
("Health-Related Costs from Foodborne Illness in the United States"
by Robert L. Scharff, Produce Safety Project, 2010).
Obesity estimated at $160 B/year in medical costs (Mc Kinsey Office)



Safety Hazards & Risks in the Food Supply Chain

Drivers for Emerging Risks in Food Safety & Security

Overview (7 slides)

Driver 1: Globalisation

Growing global trade, migration & travel accelerate the spread of dangerous pathogens & contaminants in food.

Complex international supply chains or networks with long transit distances & time increase exposure to contaminants & complicate food safety management

Such supply chains are vulnerable to agro/bio-terrorist attacks.

One single contaminated food ingredient can lead to the recall of tons of food products in several countries, with high economic losses, possible import bans, damage to the tourist industry…

However, globalisation has many advantages:
Year-round supply of fresh food at competitive prices; wide commercial opportunities with total annual exports of agricultural & food products exceeding US$ 1000 billion

Driver 2: Potential for Climate Changes

Water shortages cause quantity & quality problems with irrigation, process or ingredient water, + possible shifts in production areas & cultured crops, and increased uses of agrochemicals.

Flooding may cause increased contamination of crops in the field, or increased exposure of food animals to zoonotic agents.

Changes in temperatures & humidity are expected to affect the distribution of plant & animal diseases, the production of mycotoxins, the spread of food pathogens.

Changes in the oceans & coastal environments may affect marine resources & seafood (warming, algal toxins, acidification, pollution…)

FAO Monthly Food Price Index:
213.5 (June 2008); 206 (Nov. 2010); 214.7 (Dec. 2010)

Driver 3: Agriculture & Animal Breeding

Intensive agriculture & use of agro-chemicals will further impact on soil, water & energy supplies, with a high risk of contamination of water, food & feed crops by fertilisers & pesticides

Rising oil prices & the demand for agrofuels impact food prices

Animal breeding (FAO, 2010) uses:
~75% of world agricultural areas (including pastures & feed crops), ~8% of the world water consumption, produces ~18% of total greenhouse gases.

The huge current increase in intensive production of eggs, milk & meat threatens the livelihoods of million of small breeders.

Large farms & herd size with enhanced contacts between animals, & their location near cities, increase the risk of zoonotic diseases.
3/4 of emerging human infectious diseases are due to animal pathogens (SARS, BSE, avian Flu, Q fever, parasitic diseases…)

Antimicrobials given to animals as growth promoters & drugs contribute to induce antimicrobial-resistant micro-organisms

Driver 4: Trends in Food Processing

The trends for mildly preserved foods (minimal heating, cold pasteurisation, "natural" preservatives, "hurdle" technology)

& for lower salt or sugar contents increase the risk of surviving pathogenic micro-organisms, possibly stress-resistant, & of microbial spoilage of foods.

Ready-to-eat foods with long refrigerated shelf-life enhance risks:

- **Some manufacturers, especially SMEs, do not use appropriate product & process design, nor HACCP;**
- **Consumers do not always treat such foods as perishable items requiring refrigeration and/or specific conditions of preparation. Under-cooking is frequent.**

Refrigerated storage has created niches for psychrotrophs: *Listeria*, *Yersinia*… & noroviruses.

Reduced packaging may also increase microbial risks & food wastes

Driver 5: Changes in Demographics

Global population is predicted to rise from 6.6 billion people in 2008 to 7.4-7.8 billion in 2020. The world food demand is further enhanced by increasing affluent urban population and diet changes in emerging countries (China, India…)

Many countries with insufficient production capacity will become net food importers.

Globally, due to climate changes & environmental constraints (water scarcity, risks of deforestation, loss of biodiversity…), **the main sustainable solution is to raise crop productivity on fertile land**

Overfishing has already decreased seafood resources

These trends will tend to increase food prices and reduce the global availability of certain foods. Food choices will be affected,
depending on country & income level, towards foods requiring less land & resources (e.g. less beef, more poultry & pork)

Driver 6: Consumer Behaviour

Life expectancy & the proportion of elderly people will increase, with a higher vulnerability to foodborne diseases.

Changes in food composition motivated by consumer health
(less salt, sugar or anti-microbial agents)
may enhance microbial growth.

Increased consumption of fresh, pre-packaged produce or other food eaten without heating has already caused pathogen outbreaks.

Exotic food & ingredients, unusual animal species, small restaurants & catering, street vendors, also enhance risks & errors.

Organic food production & animal welfare (outdoor access) may lead to reintroduction of pathogens with wildlife reservoirs (*Trichinella*, *Toxoplasma*) or increased prevalence (*Campylobacter*).

WHO estimated the number of overweight & obese persons, to increase to 2,300 & 700 million in 2015, with major health, social & economic impacts.
In the EU: overweight persons = 50% of adults, including 15% obese

Driver 7: Socio-Economic Changes

Cost is a major criterion for consumer's food selection, and manufacturers' margins of profits on food products are low, making it difficult for firms to target investment to food safety, & possibly enhancing fraud.

Poverty, city overpopulation, economic crises, increasing food prices, compromise food security, but also food safety and quality:

- **Food producers & processors may comply less with regulations** (use sick animals, recycle foods, do not recall contaminated foods, neglect factory maintenance…)

- **Low cost imports (e.g. from aquaculture & seafood, fresh produce) may originate from regions with poor sanitary practices.**

- Consumers may reduce the consumption of nutritious protein-rich animal foods, use foods past their expiry date. People with reduced immunity will be particularly vulnerable

Social & economic inequalities, conflicts, migrants, natural disasters disrupt food security, and require large emergency operations (with complex logistics) that do not solve the development problems

Some Food Risk Management Tools

Risk Analysis

Risk assessment (structured, scientific process)

Risk management

Risk communication

Select policy & control options to prevent, eliminate or reduce the risk to acceptable level. Change HACCP rules?

Interactive exchange of information & opinions on risks among stakeholders

Hazard identification

Hazard characterization (dose/response assessment)

Exposure assessment

combines data on the concentration of a chemical substance or a biological agent in foods with data on the quantity of those foods consumed across a region

Risk characterization

Risk = f (probability + severity) of adverse health impact of a hazard

Quantitative Risk Assessment (QRA)

Proposals for Allergen Management in the Food Supply Chain

QRA implies the determination of "action levels", i.e. maximum dose of an allergen present in a food portion which would not elicit severe reactions in the vast majority of allergic individuals

(for ex. ~ 8 mg of whole peanut elicit a **mild** reaction in only **10%** of the at-risk population).

With proper management of cross-contamination in the food industry (segregation, cleaning, traceability…),
3 categories of foods could then be offered:

1) **"Free from…"** (allergen not detectable)

2) **"Suitable for…"** (allergen below "action level")

3) **"May contain…" or "not suitable for…"** (above "action level")

Quantitative Microbial Risk Assessment

Risk pathway for *Salmonella* in chicken (T.P. Oscar, 2010)

Post-processing food handling unit operations	Associated pathogen events	Incidence (%) (**data collection**)
• Packaging (in the plant)	Low "initial" contamination level. Strain of high or lesser virulence. (= initial hazard identification **by microbiological testing**)	**a**
• Distribution	Growth (if temperature and/or time abuse)	**b**
• Washing	Incomplete removal	**c**
• Cooking	Survival (if undercooking)	**d**
• Serving	Cross-contamination	**e**
Host demographics	Host vulnerability (aged, ill, on anti-acid medication)	**f**

(response doses for given virulence strains)

→ ASSESSMENT OF PATHOGEN EXPOSURE & RISK

Risk/Benefit Health Assessment of Food

For instance when the same food contains substances with adverse effects & substances with beneficial health effects.

The balance can shift towards benefit or risk depending on concentrations, intakes, subgroup of population.

Example**: the potential benefit of eating fish & seafood in adults versus the potential risk of neuro-toxicity in infants and children due to methyl-mercury & persistent organic pollutants**

When health risks do not clearly outweigh health benefits or vice-versa, the calculation becomes complex

Identification & Notification of Food Safety Risks

Rapid Alert Systems

Rapid Identification & Alert Systems

When food safety issues are first detected
(by public controls, food companies, consumers…)

they are usually related to specific hazard(s) and to given food chain(s).

To make these data available to risk managers as soon as possible, public authorities have created rapid reactive systems for identification & notification of food hazards & health risks:

- **WHO International Food Safety Authorities Network (INFOSAN)**
- **US Foodborne Diseases Active Surveillance Network (FoodNet)**
  (& US PulseNet for DNA fingerprinting)
- **EU Rapid Alert System for Food & Feed (RASFF)**

These are essential for risk & crisis management.
Their retrospective statistical analysis indicate trends,
but they are not predictive.

The EU Rapid Alert System for Food and Feed (RASFF)

lists food safety hazards (presence of illegal substances or unacceptable concentrations of chemicals or pathogenic organisms) on its database, on a public weekly basis.

Each Member State identifies hazards, in country or at EU borders, & must report them rapidly to RASFF, including measures taken regarding food safety
(e.g. food recalls, rejection of not complying imports…)

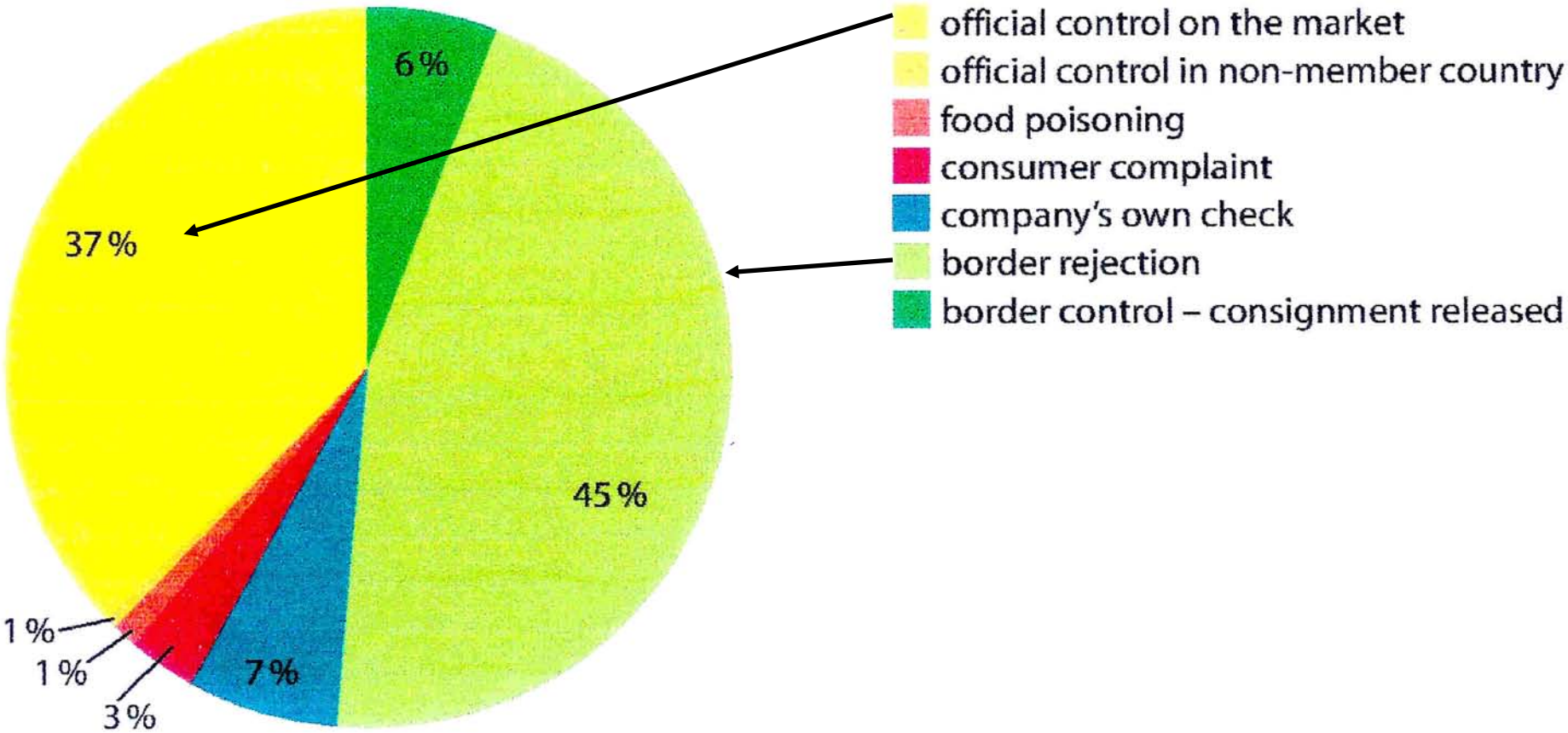
RASSF sorts out the information and further transmits it to all M.S.

RASFF acts as a notification, communication & alert platform

RASFF has 34 members + 60 connected non-member countries.

http://ec.europa.eu/rasff
https://webgate.ec.europa.eu/rasff-window/portal/index.cfm?event=notificationsList

RASFF Annual Report 2009: Basis for Notification



~ 8000 notifications in 2009

including:

1796 "market notifications"

(**578 "alert"** + 1218 "information")

(~ 50% from 3rd country products)

& 1484 "border rejections"

TABLE 1: ALERT NOTIFICATIONS

Notifications in blue typeface concern feed, all other notifications concern food.

DATE	NOTIFIED BY	REF.	REASON FOR NOTIFYING	NOTIFICATION BASIS	STATUS
30/06/2009	Italy	2009.0831	mercury (2.63 mg/kg - ppm) in smoked swordfish (Xiphias gladius) from Denmark	official control on the market	distribution on the market (possible) / product (to be) seized
30/06/2009	Hungary	2009.0833	deoxynivalenol (DON) (1464; 1613; 1398; 819; 2002; 1507; 2150; 1302 µg/kg - ppb) in durum groats from Hungary	company's own check	distribution on the market (possible) / product (to be) withdrawn from the market
02/07/2009	Poland	2009.0845	histamine (1433.5; 959.7 mg/kg - ppm) in frozen tuna steak from Spain	official control on the market	distribution on the market (possible) / product (to be) withdrawn from the market
02/07/2009	Germany	2009.0847	aflatoxins (B1 = 11.3; Tot. = 11.3 µg/kg - ppb) in groundnut kernels from Sudan, via the Netherlands	company's own check	distribution on the market (possible) / product (to be) returned to dispatcher
02/07/2009	France	2009.0848	Diarrhoeic Shellfish Poisoning (DSP) toxins (positive) in frozen cooked mussels without shell from Germany	official control on the market	distribution on the market (possible)
03/07/2009	France	2009.0849	Escherichia coli O157:H7 in frozen beef from Germany, via the Netherlands	company's own check	distribution on the market (possible) / product (to be) returned to dispatcher
03/07/2009	Austria	2009.0850	undeclared milk ingredient (casein: 1300 mg/kg - ppm) in dark chocolate bars from Italy	official control on the market	distribution on the market (possible) / product (to be) withdrawn from the market
03/07/2009	Austria	2009.0851	undeclared milk ingredient (casein: 810 mg/kg - ppm) in soybeans, roasted in the Netherlands, coated with dark chocolate manufactured in Belgium and packaged in Austria	official control on the market	distribution on the market (possible) / product (to be) withdrawn from the market
03/07/2009	Finland	2009.0854	norovirus (genogroup 2) in frozen raspberries from Poland	food poisoning	distribution on the market (possible) / product (to be) withdrawn from the market
03/07/2009	the Slovak Republic	2009.0858	undeclared nuts (134.10 mg/kg - ppm) in wafers with cocoa cream from Bulgaria	official control on the market	distribution on the market (possible) / product (to be) relabelled
03/07/2009	the Netherlands	2009.0860	benzo(a)pyrene (16.6 µg/kg - ppb) in food supplement from Germany	official control on the market	distribution on the market (possible) / product (to be) withdrawn from the market

RASFF Annual Report 2009

Alert Notifications

Risks most frequently reported from:

pathogenic micro-organisms *Listeria m*. (fish, dairy prod.)
Salmonella (feeds, meats & poultry…)
allergens (↑ undeclared milk ingredients or sulphites)
heavy metals (Hg in fish; Cd, in crustaceans & cephalopods)
mycotoxins (↓) (mainly in nuts, seeds, dried fruit & veg., spices).

55 recorded/notified cases of food poisoning, with 5 large outbreaks:

- Norovirus in frozen raspberries from Poland (2x)
- Histamine in tuna from Sri Lanka
- *Salmonella* from Spanish eggs
- *Salmonella* from US peanut products

54 recorded cases of fraud (most for food of animal origin)
41 cases being from 3rd countries:
• Illegal imports • False health certificates • Unauthorised establishments

An alert notification commands immediate action, e.g. product withdrawal from the market

RASFF Annual Report 2009

1484 EU Border Rejections

Products frequently rejected	Main rejection causes
1) Nuts & seeds	Mycotoxins
2) Fish & fishery products	Insufficient controls; parasites; heavy metals; microbiological hazards; biocontaminants
3) Fruits & vegetables	Mycotoxins, moulds, pesticides, pathogens, foreign bodies

The control frequency of food imports is risk-based & frequently adjusted

Prediction (& Prevention) of Emerging Food Safety Risks

Predictive Early Warning Systems

“Expecting the unexpected”

Assessment of emerging risks requires early detection or prediction
allowing preventive measures, before they become real risks

Predictive early warning systems

Focused on specific food hazards:

Predictive microbiology

Ex.: Early warning systems for molds & mycotoxins in maize or wheat:
Computer models **based on weather variables**

Focused on food imports:

Predictive Risk-Based Evaluation for Import Compliance Targeting
(PREDICT) **automatically scans & screens many databases for information that may affect admissibility of food imports:**

• a product's inherent risk rating (e.g., raw seafood); • if a company or product is subject to an import alert • the compliance history of relevant companies and product, including recalls, inspection results, analyses… • open source intelligence. PREDICT then issues a risk score for each entry line. Based on the score, the system may flag the entry as risky and send it to FDA

Vulnerability assessment:

CARVER-shock approach, for Food Defence against attacks

Vulnerable points in the food supply chain where the introduction of (intentional) hazards is most likely to occur.

shield the food supply against threats of terrorist attacks & new dangers. "Critical nodes" are identified, rather than specific hazards. Multidisciplinary experts focus on the production chain & flow diagram for a specific sector or product.

Predictive Early Warning Systems

Moderately focused: Data recording + expert or stakeholder opinion:

Sharing of information & knowledge to overcome problems of misinterpretation of data and ignorance of emerging risk signals.
EFSA's Stakeholder Consultative Platform, with web-based posting of documents, for feedback.

Broadly oriented: Combining food safety with other data:

Eurostat (EU Statistical Office): **database "from farm to fork"** which can show trends & developments associated with various steps in the production-trade-consumption chain in Europe.

FAO Global Information and Early Warning System on Food & Agriculture (GIEWS): preventive measures.
For ex.: **Satellite observations for agricultural land status & forecast crop harvest yields**.

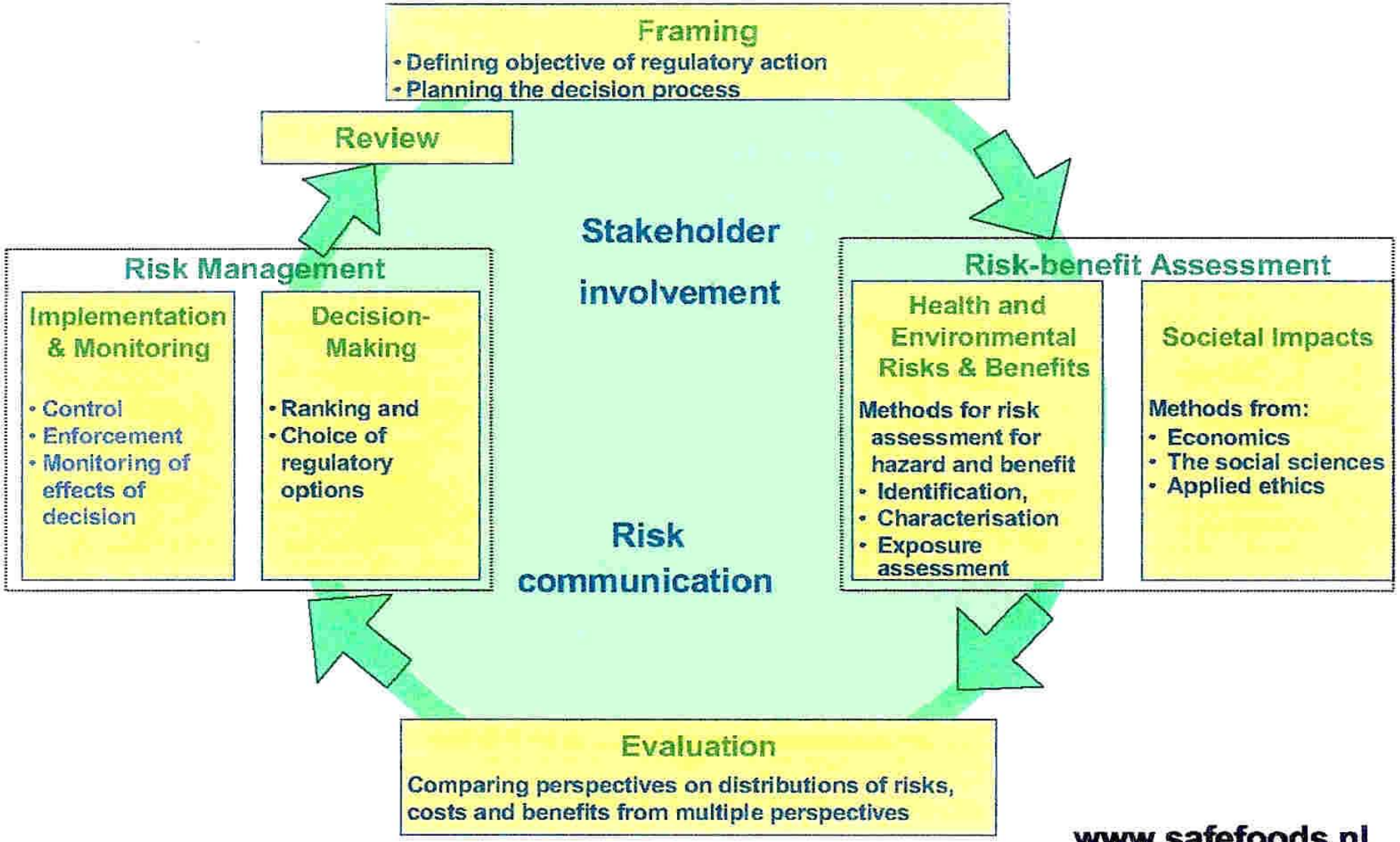
Strategic foresight by experts and stakeholders:

Horizon scanning: systematic exploration of potential threats, opportunities & future developments
What policy changes are required to reach desirable scenarios?
EC Scientific Committee for emerging & newly identified health risks.

Safety prediction systems based on a holistic approach

Framework of the EU Project SAFE FOOD

Structured Approach



www.safefoods.nl

Predictive systems based on a holistic approach

(after Marvin et al., 2009)

The EU project SAFE FOOD attempts to expand the scope of risk assessment & consider many sectors in & out the food production chain

science, technology, industry & innovation; international trade; nature & environment; government & policies; consumer behaviour; culture & demography; public health & welfare; agriculture; economy; information

Also attempts to identify specific indicators from these sectors:

Indicator = reliable & sensitive element informing on hazard & source of risk

Signal = change in such indicator, which may result in the development of a risk.

Multidisciplinary experts are asked to select critical indicators for a specific food supply chain and to score possible change in each indicator & subsequent consequences on food safety

Safety Risks in Food Production & Processing

Potential Safety Risks of Food Processing

Under-processing (including non homogeneity of treatment)

- Incomplete physical removal of contaminants
- Incomplete inactivation of micro-organisms, spores, viruses, parasites (special risks for the chilled storage of foods of animal origin)
  + microbial recovery & adaptation of stress-resistant microbial strains
- Incomplete inactivation of natural toxicants, anti-nutrients, allergens

Over-processing (including non homogeneous treatment)

- Nutrient losses (& decrease in nutrient bioavailability)
- Formation of toxic molecules (acrylamide, heterocyclic amines, HMF..)
- Enhancement of microbial growth (slicing, grinding, long storage…)
- Migration of chemicals from package into food (including inks…)

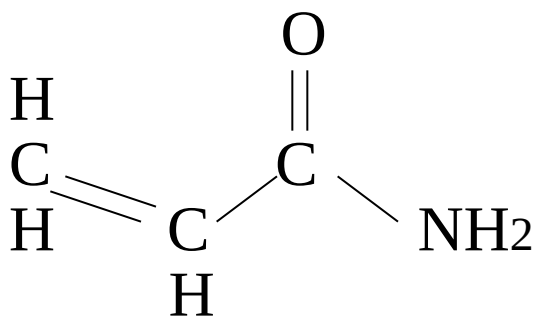
Intentional addition of unsafe substances

some food additives, nanoparticles, adulteration products, antibiotic-resistance genes, pathogens…

Acrylamide in Foods (discovered in 2002)

Acrylamide may be formed in carbohydrate-rich foods: potatoes & cereal-based products (chips, French fries, bread, crispbreads, biscuits, breakfast cereals, coffee) during cooking processes such as frying, baking, roasting, microwaving at ≥ 120°C (not boiling)
(up to 5 mg/kg potato chips and 2 mg/kg biscuits).
It may also form in heated (oxidised?) fat-rich dry foods such as nuts.

Exact mechanisms of formation are unsure, but involve Maillard reactions between asparagine & reducing sugars/reactive carbonyls



prop-2-enamide (C_3H_5NO)

Acrylamide is also a highly reactive industrial chemical used for the production of plastics & materials.

Acrylamide is a genotoxic carcinogen to experimental animals, EU listed as Substance of Very High Concern, thus exposure from all sources, including diet, should be minimized.
Its primary metabolite, glycidamide, is also toxic.

Reducing Acrylamide Formation

CIAA "Toolbox" to show how recipes & processes can be modified (use low sugar varieties & mixes, avoid overheating & brown colour, add asparaginase or amino acids or an asparagine-degrading yeast).

From 2003 to 06, the acrylamide levels of EU bread & potato chips has decreased, but not that of biscuits, breakfast cereals, French fries, cereal-based baby foods (EFSA).

The link between acrylamide & cancer risk in humans is uncertain. People have been exposed to acrylamide in their diet for a long time.

Recent studies suggest that tolerable daily intakes of acrylamide for carcinogenic levels should be set at 2.6 µg/kg b.w.,
while the TDI for neurotoxicity is higher, at 40 µ/kg b.w.
Canadian, Swedish & US studies estimate the average exposure of adults to acrylamide in food as 0.3, 0.5 & 0.4 µg/kg b.w. per day, respectively.

This example shows how even long-used processes can suddenly reveal unsuspected risks (frying & grilling of meat & fish may form carcinogenic heterocyclic amines. HMF, furan, acetaldehyde -potential carcinogens- may also be formed in various foods upon heating)

"Margins of Exposure" (MoEs) to Carcinogens in Foods

Attempt to quantify risks by calculating the ratio:

Dose that produces a certain frequency of cancer in animals/ divided by the **dose that humans are exposed to**.

Low value MoEs are probably dangerous

Genotoxic carcinogens	**MoE** (JEFCA, 2005) (for median human intakes)
Acrylamide	300
Ethyl carbamate	20,000
Polycyclic aromatic hydrocarbons (PAHs)	25,000

Although the risk from acrylamide is much larger than that from the 2 other (regulated) carcinogens (but less than from smoking), **there are no regulations concerning acrylamide in foods.**

Hormonal Disruptors from Food Packaging & Containers

Chemicals used as plasticizers in food packaging and various plastics, such as **phtalates, bisphenol A**… are suspected of causing increasing numbers of anomalies.

Bisphenol A (BPA) **is used in polycarbonate bottles, infant feeding bottles & in epoxy resins serving as protective coatings for food & drink cans & vats**

During storage, BPA migrates in small amounts into food & drinks.

EFSA (2007) indicates that the intake is 5 to 500 fold below the "tolerable daily intake", and that BPA is metabolised & eliminated.

BPA is permitted in food contact materials in the EU, USA, Japan.

Canada and the EU have banned its use for infant food bottles (2010)

Frauds & Adulterated Foods

Profit-motivated frauds, often criminal, have caused many food crises
(e.g. direct or indirect addition of toxic substances to foods or feeds):

Examples	Impact	Fraud (& error)
Spanish oil syndrome (1981)	**20,000 persons affected >800 deaths**	**Denatured oil sold as olive oil**
Ukrainian sunflower oil (2008)	**Exported to EU Late withdrawal & ban**	**Mineral oil added**
Bovine spongiform encephalopathy (UK, 1984, then EU)	**>100 deaths >1 million cows culled ↘ meat consumption Huge economic losses Loss of consumer trust Changes in regulations**	**Prion-infected meat & bone flours fed to cows. Milder flour process. Ban on flours not respected**
Belgian chicken (1999)	**Economic losses**	**Dioxin in feeds (from electric transformer oil)**

Frauds & Adulterated Foods (2)

Examples	Impact	Fraud (& error)
Irish pigs & pork meat products (2008)	Large trace & recall from 54 countries	PCB & dioxin in feeds 100 fold legal limit. Dried/contaminated fuel
German feeds, pigs, chicken, eggs (2010)	~150,000 T feeds, 6000 farms affected	Dioxin-rich industrial fatty acids added to feeds
Chinese gluten, milk, infant milk formulae (2007-2010)	Grave kidney problems for >300,000 infants & children	Melamine addition to fake higher N content + long denial from authorities

Non authorised food or feed additives are frequently used in some countries (with corruption, official silence, opaque supply & export channels).

In 2007, some 2000 Chinese producers & 1000 retailers had exported food ingredients & additives worth US$ 4 billion (including vitamins & amino acids); Food & pharmaceutical companies worldwide used these ingredients & additives without sufficient traceability or quality control.

Counterfeited Foods & Drinks

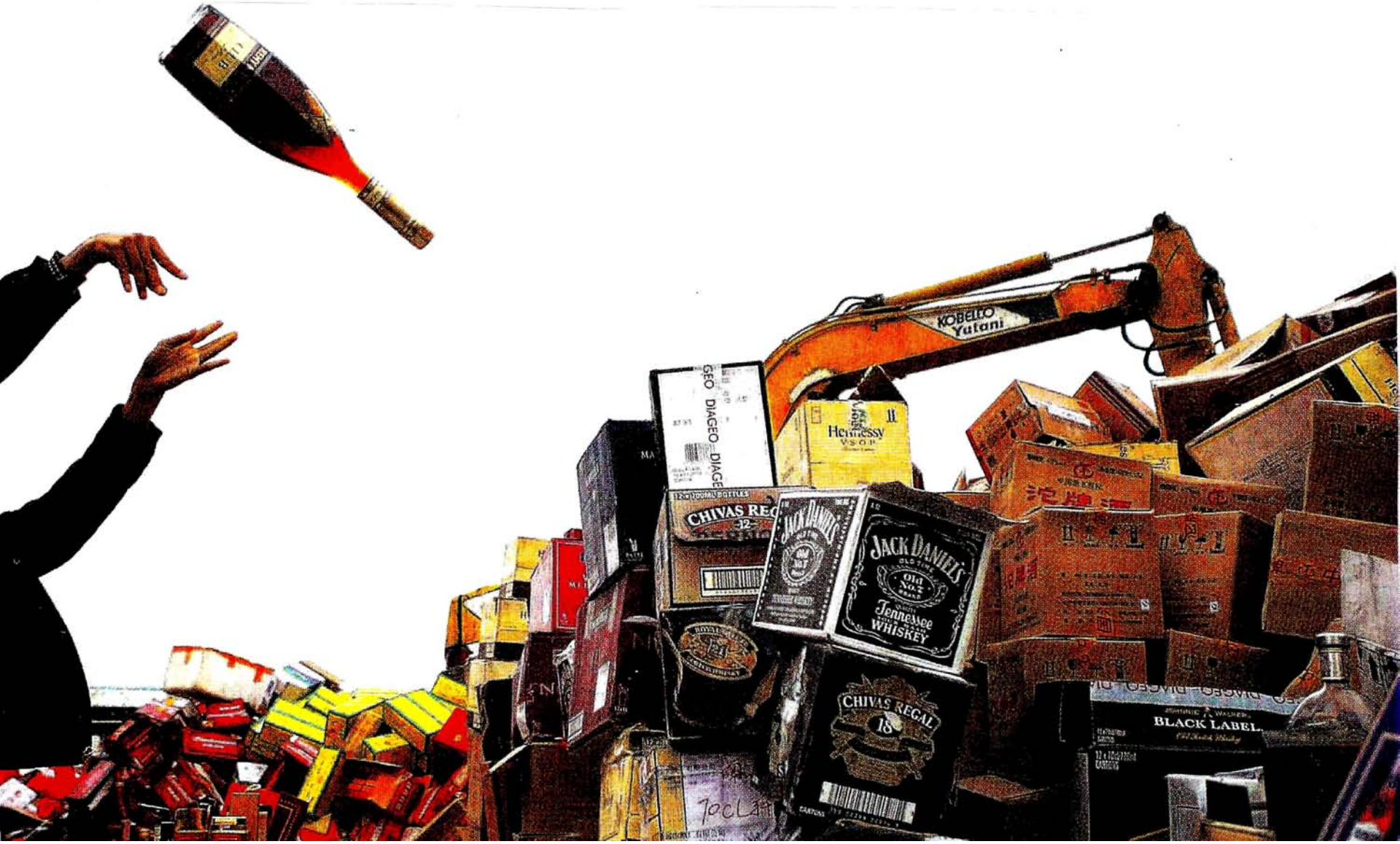
The global level of fraud as counterfeiting in the food & drink industry is estimated at ~ $50 bn/year.
Global trade & high food prices increase fraud opportunities

High losses for food firms through damage to brands & spending on security measures. Also health risks for consumers.

Security measures on packaging include: holograms, microdots, data codes, use-by dates, lot numbers, markers… are not always efficient

The EU plus 10 countries (Japan, USA, Korea, New Zealand, Canada, Australia, Switzerland, Morocco, Mexico, Singapore)
have been negotiating an **anti-counterfeiting trade agreement (ACTA)**

Counterfeited Foods & Drinks



Destruction of faked whiskies & cognacs at Zhuliao (Guangdong province)

Potential Food, Feed or Drink Targets for Bioterrorism

(intentional addition of toxic chemicals or biological agents)

Those with easy access, large volumes, wide diffusion, short shelf-life, able to reach a maximum of people, or a specific group of people

- **Water: rivers, ponds, city reservoirs, tanks, sea salt ponds (although protected by water treatments, controls & dilution effect)**

- **Liquid foods: milk, fruit juices, beer, wine… Liquids facilitate an uniform diffusion of contaminants**

- **Ingredients (possibly "foreign") which are sourced globally, at low prices, undergo less controls, are less visible and reach multiple end-products: flours, milk powder, salt, sugar, tomato paste, peanut butter..**

- **Counterfeited foods with faked known & trusted brands: Coca Cola, Nescafé, baby foods brands…**

- **Food Animals (& animal feeds), which can transmit zoonotic diseases to man through consumption of animal products.**

Safety of “Innovative” Food Technologies

"New" Preservation Technologies: Potential Food Safety Risks

Physical treatments
(often minimal, or low temperature)

High pressure pasteurisation: **incomplete microbial inactivation, no spore inactivation, microbial recovery; some chemical reactions**

Pulsed electric fields: **no spore inactivation, non homogeneity & arcing; electrochemical reactions; metal transfer from electrodes?**

Cold plasma (dielectric barrier discharge at atmospheric pressure and ~30°C). OK for surface disinfection, but free radicals, oxidations?

Light pulses & UV: **non homogeneity (surface only); photo-oxidative reactions.**

Ultrasounds: **safe cleaning but low efficiency/microbial inactivation**

Ohmic heating: **under/overheating, metal transfer from electrodes?**

Microwaves: **non homogeneity (cold spots) & power reduction over time of domestic MW ovens?**

Ionising radiations: **free radicals, oxidative reactions, consumer distrust** (US petition for surface irradiation of meat carcasses)

Chemical or combined treatments

Modified atmospheres, anti-microbial agents, "hurdle" processing (often minimal or low temperature processing)

- **Incomplete microbial inactivation**
- **Growth only delayed in storage**
- **Inciting to over-extend shelf-life**
- **Sub-lethally injured cells may give antimicrobial-resistant, acid-resistant, osmotic-resistant or virulent strains, through adaptation.**
- Potential reactivity or toxicity of antimicrobial agents
- Possible use to conceal poor hygiene practices

Decontamination of poultry, pork or beef carcasses by washing/spraying with solutions of Cl_2, ClO_2, hypochlorite, acidified Na chlorite, trisodium phosphate, organic acids (lactic), H_2O_2, O_3, electrolysed H_2O, lactoferrin…
Only some of these antimicrobials are authorised in the EU.

Fresh-cut bagged fruit & vegetable: Norovirus, *Salmonella*, *E. coli* O157 (18 major outbreaks in the US 1998-2006, mostly due to leafy greens).
Initial contamination through irrigation water & fertilizers.
Increased surfaces from cut or peeled tissues release liquids & nutrients, enhance microbial attachment & growth, and interfere with disinfectant washes (NaOCl, Cl_2) or CO_2 M.A.

Nanotechnologies

Use of engineered substances on a very small scale: 1-100 nm (obtained by assembly of molecules or downsizing).

Nanoparticles have specific physico-chemical properties:
Small size increases diffusivity. High surface area (>60 m^2/cm^3) **enhances reactivity, binding, recognition…**
Structure, size distribution, chemical composition, & surface charge may also confer **unique functionalities for food uses:**

1) As food ingredients & additives: increased solubility, dispersion; stable emulsions without emulsifier; low fat emulsions

2) As encapsulation & delivery systems for bioactive compounds: **molecular traps** (e.g. emulsion droplets) **for protection & targeted delivery** (lycopene, phytosterol); **higher nutrient availability** (Fe, Zn)

3) As more protective or intelligent packaging: in polymer or biopolymer films & coatings, **nanoparticules act as "fillers" to enhance barrier properties & resistance to mechanical or thermal stress**.
Reactive nanoprobes alerting of use-by date, temperature, pathogens, toxins;
Anti-bacterial coating (silver particles) for food-contact surface (refrigerator)

Safety of using nanoparticules in foods? & health implications of exposure

(EFSA Draft Opinion, 2008)

Existing risk assessment methods can be applied, on a case/case basis

Data on non nano chemicals cannot be extrapolated to their nano equivalents, since formulation to the nanosize may change properties

There are considerable limitations & uncertainties: 1) on detecting, characterising & "dosing" ENM; 2) on their absorption, distribution (in fatty tissues, bone, brain?), **accumulation, metabolism & excretion; 3) on their toxicity**

Small size increases their ability to move unexpectedly in the body. Adhesive & reactive surfaces may cause various interactions.

Main other challenges (many other uses of nanoparticles):

workplace safety; distinction of natural & engineered nanoparticles; cost; impact on the environment: biodegradation/persistence/accumulation in soil, water, air, food chain; consumer uncertainty & suspicion; labelling & legislation.

Active & Intelligent Food Packaging: Safety Concerns

While "classic" packaging should be as inert as possible**, these new packaging intentionally interact with the food or its environment**, **1) either ("active) to extend shelf-life** with maintenance of quality, **or 2) ("intelligent") to give indication & monitor the food freshness** (time-temperature indicators, ripeness indicator, biosensors, tamper-proof or identity-ensuring systems, nano-chips in smart inks…).

Active packaging contain deliberately incorporated components intended to release or absorb substances into or from the food or its environment (release antimicrobials, antioxidants; absorb O_2, C_2H_4)

Highly promising, these new packaging are not yet widely used

The main safety issue (as for classic packaging) is migration of chemicals (& their degradation products) **into the food**. Nano sizes could increase risks.

A recent Regulation (450/2009/EC) specific to A&I packaging introduces safety evaluation by EFSA, with an authorisation scheme, focusing on migration data of chemicals & their toxicological properties

Active & Intelligent Food Packaging: Safety Concerns (2)

Their efficiency to perform the claimed function should be demonstrated in real foods. This is critical when they should prevent microbial growth or reveal the presence of pathogenic bacteria or toxic contaminants.

Their proper use should be explained to consumers by way of labelling.

Their acceptance may be limited since Consumers may perceive systems for the extension of shelf-life as detrimental to food freshness,

while **Retailers** fear that they may induce consumers to select only recently displayed items,
and convey a negative carbon footprint image.

RFID tags printed on food packages (no direct interaction with food) may change food sales & marketing, allow cell phones to indicate food composition, nutritional adequacy; refrigerators to signal expiry dates & send automatic reorders…
with some risks of "neuromarketing" & intrusion into private life!

Citizens' Perception of Risks in Food Technologies

Technologies which tend to elicit consumer suspicion & rejection
(& strong political debates):

- **Ionising irradiation of foods**
- **Hormonal (& antibiotic) treatment of animals to hasten growth & increase meat or milk production (banned in the EU)**
- **Genetically modified food crops & food ingredients (in the EU)**
- **Genetically modified animals (cloned animals & their offspring)**
- **Various food additives (consumers' request for "clean labels")**

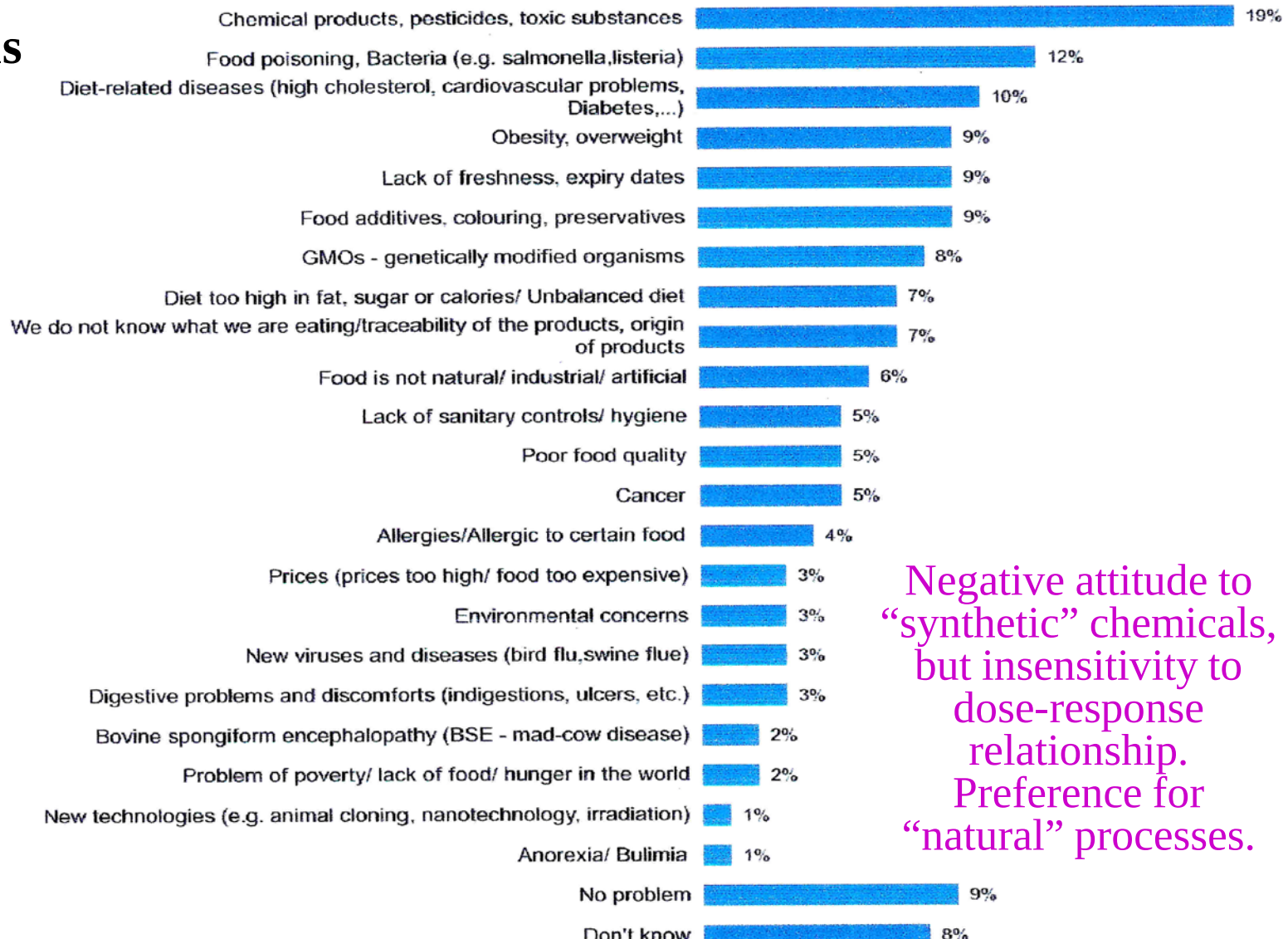
The consumer right to informed choice is well established in the EU:

Mandatory labelling for irradiated foods and GM foods have discouraged manufacturers & retailers to place such foods on the market, in spite of their potential advantages.

Survey on How European Citizens Perceive Food-Related Risks
EFSA 2010 - Eurobarometer 354 - TNS Opinion & Social, Brussels

Face to face interviews with 27,000 individuals >15, in 27 M.S.

Spontaneous responses



Negative attitude to "synthetic" chemicals, but insensitivity to dose-response relationship. Preference for "natural" processes.

Eurobarometer Survey 354 (EFSA, 2010) (2)

• **Trust in information sources:**

Doctors & health professionals: 84%
Family & friends: 82%
Consumer organisations: 76%
Scientists: 73%
Environmental protection groups 71%
Food safety agencies: 64%
European Institutions 57%
National governments 47%

• **The role of public authorities is perceived as effective, but**
1 in 2 consider that they are not independent from producers' interests.

According to the EU Commissioner for Health,
conditions necessary to support acceptance of innovation are:

1) Clear benefits perceived for consumers & society

2) Predictable regulatory environment & legal certainty (+ safety assurance & control)

3) Science behind risk assessment made more credible

4) Improved transparency & dialogue with the public

Thank you for your attention

Future EU Regulation on Novel Foods & Novel Ingredients

Disagreements and delays

The **E. Council** wants **"nanofoods"** included. The **E. Parliament** wants a moratorium until safety is established, and asks for indicating any nanomaterial on the food label.

The **Council** supports including food from the **offspring of cloned animals**, while **Parliament** wants to ban such food, and asks for a new law covering ethical & safety issues of animal cloning.

The **E. Commission** proposed (Oct. 2010) a 5 year ban on the use of cloned farm animals and on the marketing of food from cloned offspring, although it supports **EFSA**'s opinion on the lack of food safety problems.

The **E. Commission** recognises the problems of animal welfare and ethics.

ENDORSED FOR PUBLIC CONSULTATION

DRAFT SCIENTIFIC OPINION

Guidance on risk assessment concerning potential risks arising from applications of nanoscience and nanotechnologies to food and feed[1]

EFSA Scientific Committee[2, 3]

January 2011

www.efsa.europa.eu/en/consultations/call/scaf110114.pdf

The EU Food Legislation on Novel Foods & Ingredients (1)

Protection against Food Safety Risks or Barrier to Innovation & Trade?

Regulation 97/258/EC on Novel Foods & Food Ingredients subjects each novel food to a severe pre-market safety assessment & authorisation procedure. Also edicts **specific labelling rules to inform the consumer** of any characteristics making the novel food no longer "equivalent" to an existing food, or having health or ethical implications.

Categories of Novel Foods:

1) a food not used significantly for humans in the EU before 1997

2) a new or modified molecular structure or ingredient isolated from animals, plants, micro-organisms, fungi, algae

3) a food or ingredient subjected to a new process, or issued from a new production or breeding process, resulting in significant changes in composition, structure, nutritive value, metabolic effect and/or level of undesirable substances.

Includes "functional foods", also subject to an Health Claim Regulation

Excluded from the Regulation (because other rules apply): food additives, flavourings, enzymes, extraction solvents, vitamins & minerals, GM foods.

Future EU Regulation on Novel Foods & Novel Ingredients (2)

Regulation 97/258/EC on Novel Foods & Food Ingredients exerts strong detrimental constraints on innovation & trade (cost, delays), as much as a protection against food safety risks.

A revised proposal (of 14 Jan. 2008) is discussed, to:

1) Promote a more favourable legislative environment for technological innovation & industrial competition

2) Consider the particular needs of traditional foods from 3rd countries (a "notification procedure" may be sufficient)

3) Clarify & facilitate implementation, with a single EU harmonised, centralised & shorter procedure for assessment & authorisation

4) Give a wider choice of safe novel foods to the consumers.

Food Safety Management Tools

- **Food legislation & standards**
- **GAP, GHP, GMP & HACCP certifications**
- **Food quality & safety management systems** (ISO 9001 & 22000)
- **Risk analysis**

Others:

- Traceability
- Food operators' responsibility & auto-controls
- Third party certification
- National food inspections & controls, including at borders
- Risk-based controls
- Mandatory transparency & reporting of food incidents
- Mandatory collaboration with authorities
- Withdrawal & recall procedures
- Prior notice of imported food shipments
- Registration of food facilities
- Food defence plans of individual food companies

Selection of critical factors for identifying emerging food safety risks in dynamic food production chains

(Van Asselt et al., Food Control, 2010, 21, 919-926)

Endogenous indicators

Factors 1-6 relate to the **Food chain complexity:** the higher possibility of errors in complex systems results in food safety risks.

Factors 7-10 are linked to the **Producers' attitude towards food safety**.

Factors 11-13 show **Producers' compliance to food safety regulations**.

Factors 14-18 correspond to **Technical innovations** in the food chain.

Exogenous indicators

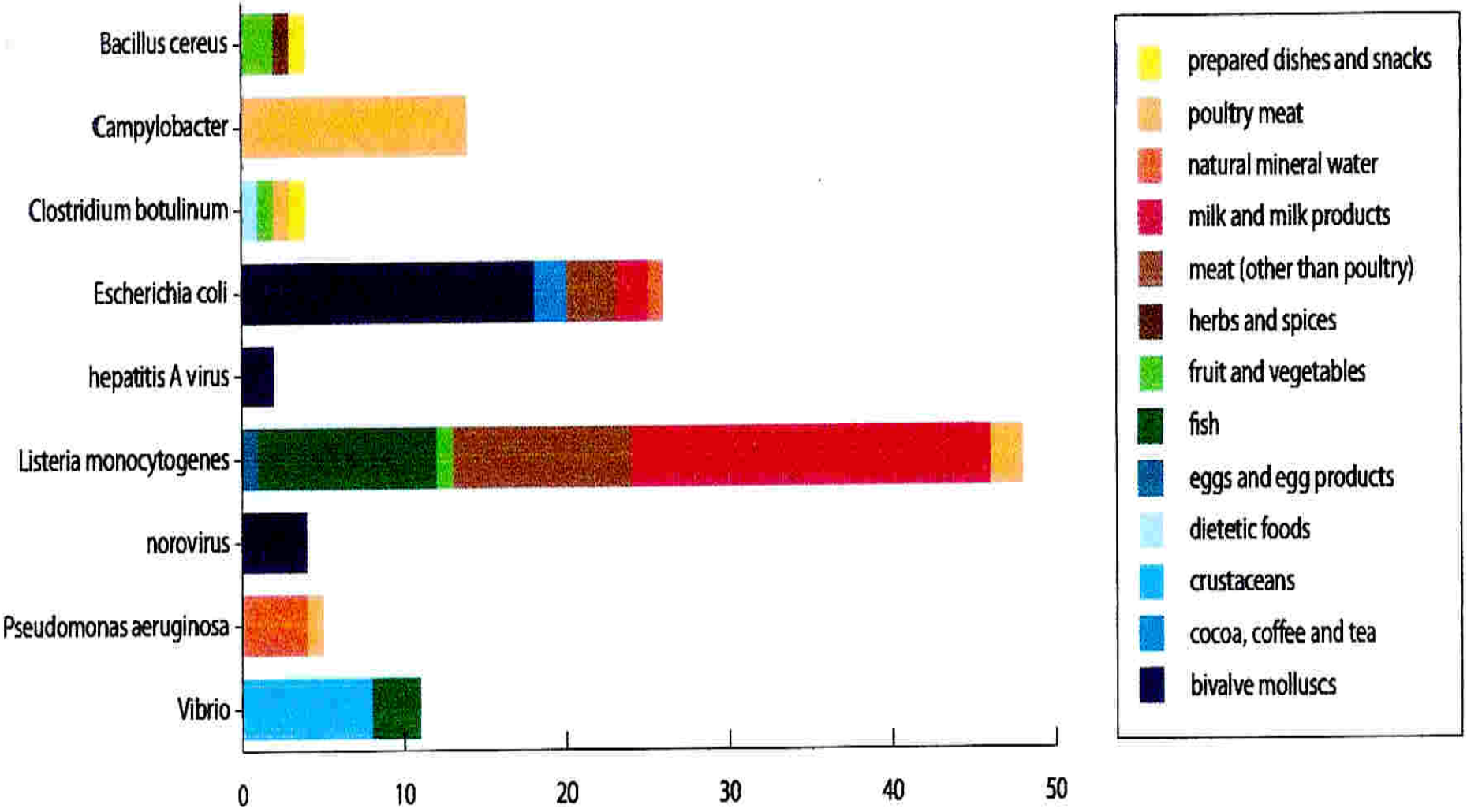
Factors 19-22 include **Origin of raw materials; Legal requirements; Climate change; & Economic status**.

Factors 23-29 are related to **Consumers**: **Size of demand; Demand for convenience or quality; Consumer concern for health**

Multidisciplinary experts were asked to select critical indicators for each specific case, rank them (individually) and detect & analyse their signals.

RASFF 2008

(POTENTIALLY) PATHOGENIC MICRO-ORGANISMS



Number of notifications (2008)

	Classification	Date of case	Last change	Reference	Country	Subject	Product Category
1.	alert	20/12/2010	07/01/2011	2010.1725	FR	suspicion of phytohaemagglutinin in chilli con carne from France	prepared dishes and snacks
2.	alert	28/12/2010	07/01/2011	2010.1769	IT	parasitic infestation with Anisakis of anglerfish (Lophius piscatorius) from the United Kingdom	fish and fish products
3.	alert	28/12/2010	07/01/2011	2010.1771	DE	dioxins (in fat used for the feed: 123; 124 pg WHO TEQ/g) in vegetable feed fat for pigs and poultry from Germany	feed materials
4.	information	06/01/2011	06/01/2011	2011.0024	HU	unauthorised substance pseudovardenafil (suspected) in food supplement from Malaysia	dietetic foods, food supplements, fortified foods
5.	information	06/01/2011	06/01/2011	2011.0026	PT	prohibited substance nitrofuran (metabolite) nitrofurazone (SEM) (3.3 µg/kg - ppb) in frozen beef from Brazil	meat and meat products (other than poultry)
6.	alert	26/11/2010	06/01/2011	2010.1624	NL	hepatitis A virus (present) in dates from Algeria, via Belgium	fruit and vegetables
7.	border rejection	23/12/2010	06/01/2011	2010.CIC	GB	aflatoxins (B1 = 5.0; Tot. = 5.9 µg/kg - ppb) in peanut butter from Sierra Leone	nuts, nut products and seeds
8.	alert	06/01/2011	06/01/2011	2011.0025	DK	deoxynivalenol (DON) (1000 µg/kg - ppb) in organic oat meal from Denmark, with raw material from Sweden	cereals and bakery products
9.	alert	06/01/2011	06/01/2011	2011.0023	IE	undeclared soya in white bread flour from the United Kingdom	cereals and bakery products
10.	border rejection	06/01/2011	06/01/2011	2011.AAP	NL	aflatoxins (B1 = 16.6; Tot. = 18.8 / B1 = 5.7; Tot. = 6.4 µg/kg - ppb) in groundnut kernels from Argentina	nuts, nut products and seeds
11.	alert	23/12/2010	06/01/2011	2010.1752	IT	mercury (1.7 mg/kg - ppm) in swordfish loins from Spain	fish and fish products
12.	alert	06/01/2011	06/01/2011	2011.0022	IE	undeclared soya in batter mix from the United Kingdom	cereals and bakery products
						Salmonella Derby (3 out of 11 samples /25g), Salmonella enteritidis (FT1 + FT14b: 7 out of	

Risk/Benefit Health Assessment of Food

J. Hoekstra et al., Food & Chemical Toxicology, 2010, in press

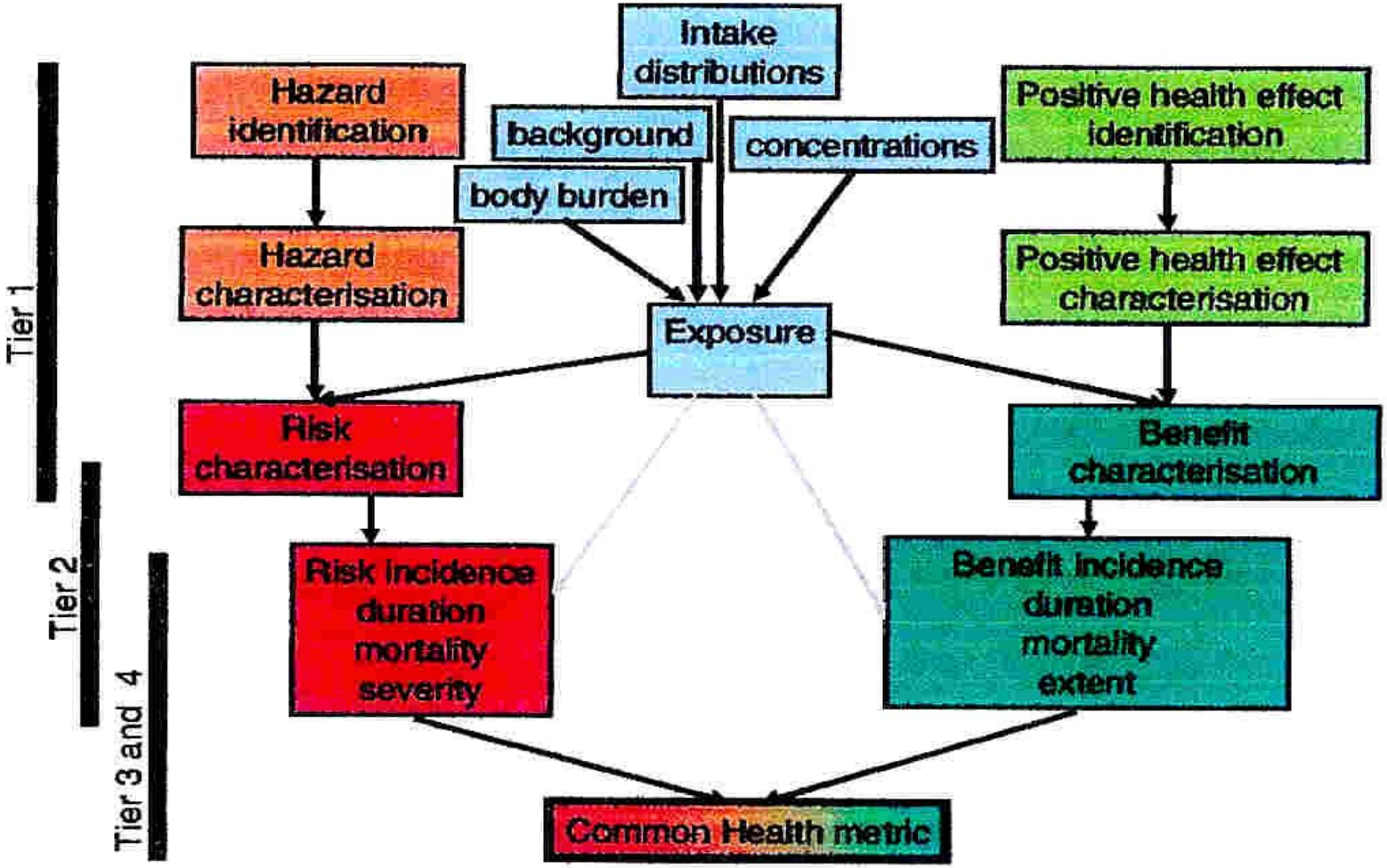


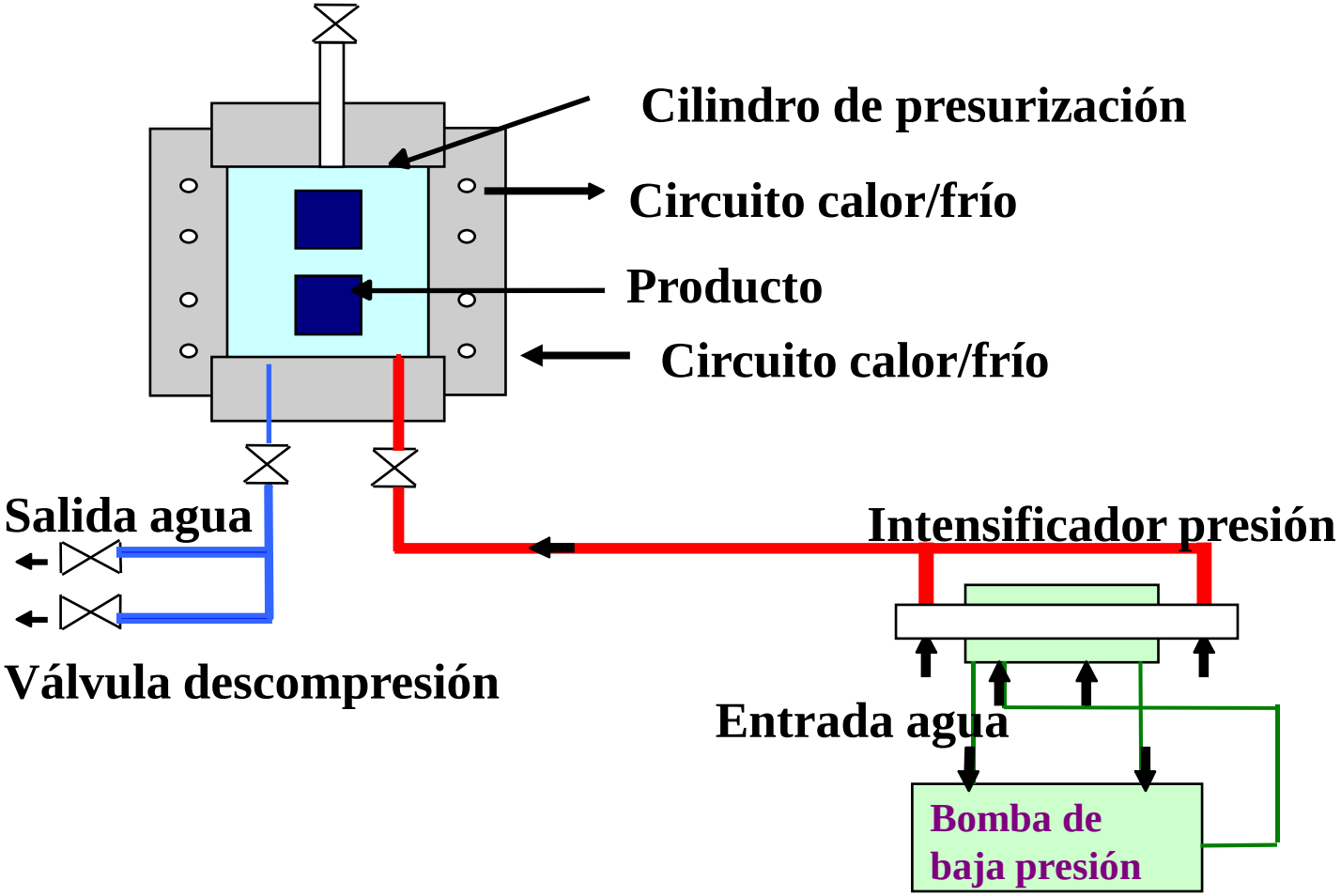
Fig. 2. A schematic description of the steps within each tier.

CERPTA

Necesidades en Tecnología Alimentaria

- Conservación de alimentos
  - Destrucción patógenos
  - Destrucción otros microorganismoa alterantes
  - Inactivación de enzimas
  - No toxicidad
  - Compatibilidad de los envases con el alimento y el proceso
  - Nuevas emulsiones, nuevas texturas
  - Sistemas de control-uniformidad

Equipos de alta presión hidrostática



Economical analysis for novel process technology: High Pressure Processing

NC Hyperbaric
Carole Tonello, PhD

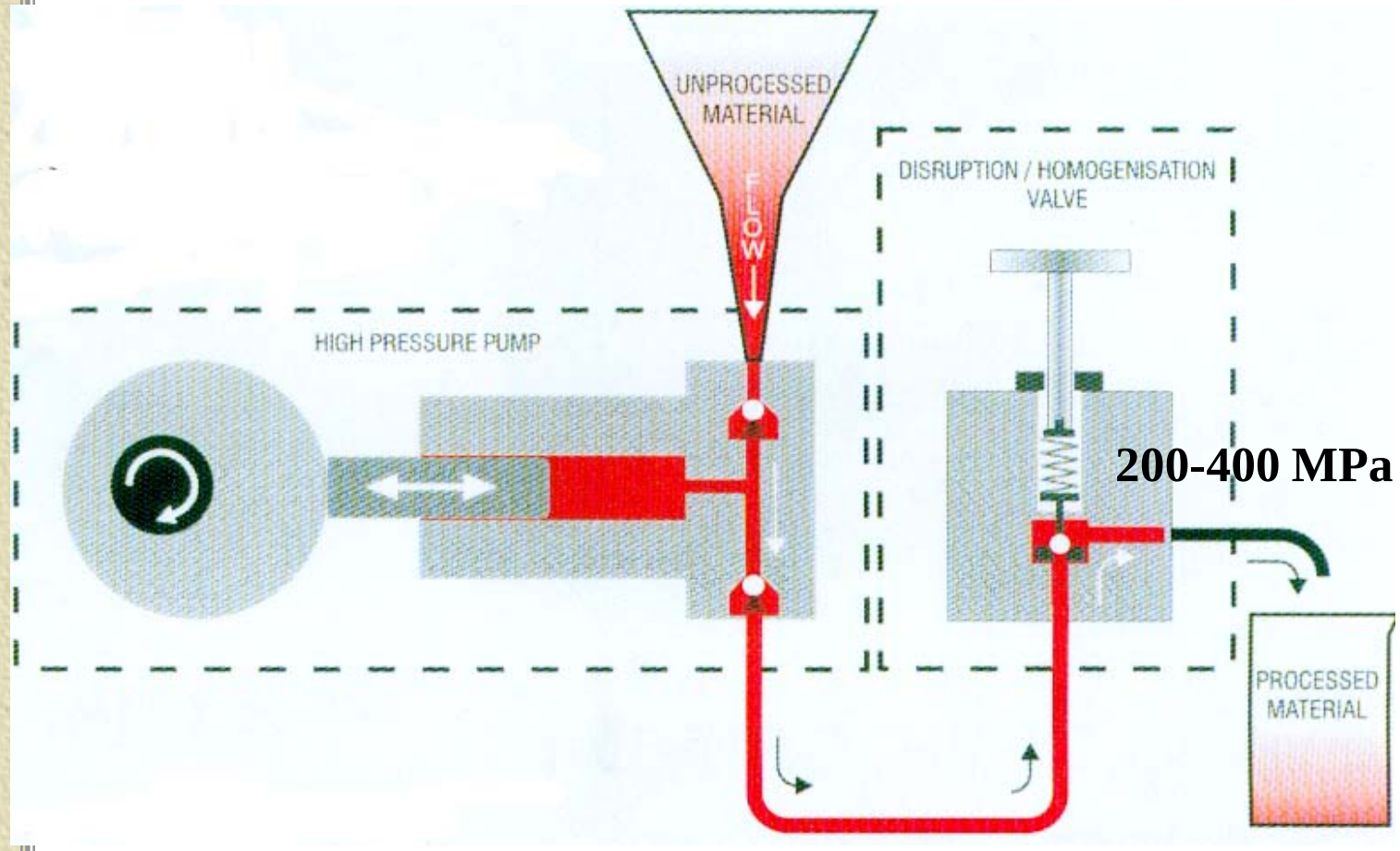
NovelQ – Sept 6, 2007

Instalaciones

Línea de alta presión

Línea de alta presión homogenización

Ultra alta presión homogenización

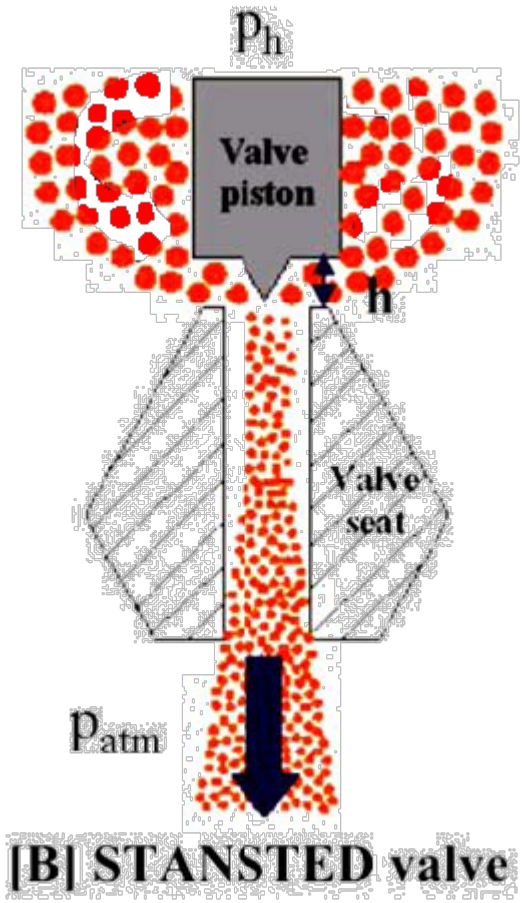


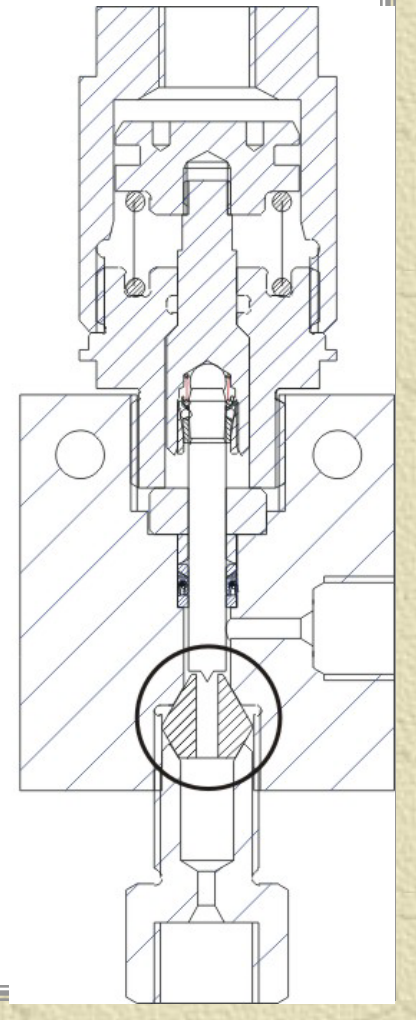
Ultra alta presión homogenización

- Alta presión
- Impacto
- Cizalla
- Cavitación
- Turbulencia

Stansted Fluid Power

- Redesigned ceramic valve, changing its geometry
- On 92-340 MPa treatments flow speed reach 75-100 m/s before exiting the valve and 120-200 m/s after
- It’s possible withstand up to 400 MPa





Patente EU solicitada UAB

- CONTINUOUS SYSTEM AND PROCEDURE OF STERILIZATION AND PHYSICAL STABILIZATION OF PUMPABLE FLUIDS BY MEANS OF ULTRA-HIGH PRESSURE HOMOGENIZATION
- Pat nº 10380094.2-1221
- Explotación. EBT YPSICON

Nuevo equipo UHPH 400 MPa 125 l/h. CERPTA-UAB (Pat nº 10380094.2-1221)

DISEÑO Y PRODUCCIÓN DE ALIMENTOS FUNCIONALES

Diferencia alimento funcional-medicamento

- El medicamento cura o cronifica una enfermedad
- El alimento funcional tomado regularmente puede reducir el riesgo de tener una determinada enfermedad

Tecnofuncionalidad

- Aplicación de procesos tecnológicos incluidas las nuevas tecnologías para mantener o mejorar la funcionalidad de un alimento, por las modificaciones que se producen a nivel conformacional o estructural

Tipos de alimentos funcionales

- Origen natural
- Alimentos funcionales de diseño

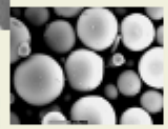

CONCURSO
NACIONAL
DE QUESOS
de cabra
PREMIOS
TARETE
FUERTEVENTURA
239
CABILDO DE FUERTEVENTURA

The Scale of Objects

Natural Objects

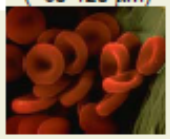
Ant
~ 5 mm

Dust mite
~200 µm

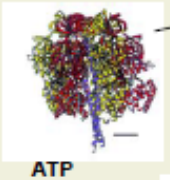


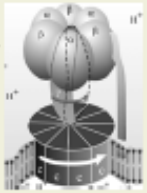
Fly ash
~ 10-20 µm

Human Hair
(~60-120 µm)

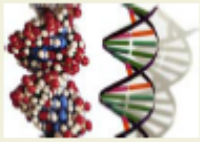


Red blood cells
(~7-8 µm)

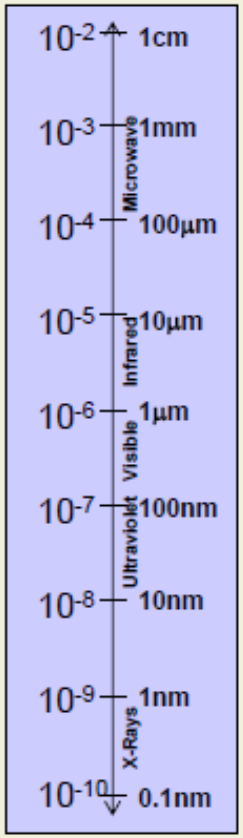




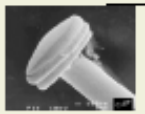
ATP
Synthase
~10 nm



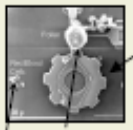
DNA
~2-1/2 nm



Manufactured Objects



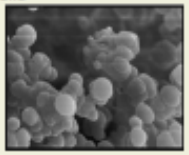
Head of a pin
1-2 mm



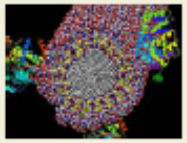
MicroElectroMechanical
(MEMS) devices
10 -100 mm wide

Red blood
cells

Pollen grain

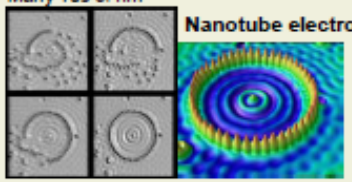


Globular Protein
Aggregate
Many 10's of nm



Self-assembled,
structure
Many 10s of nm

Nanotube electrode



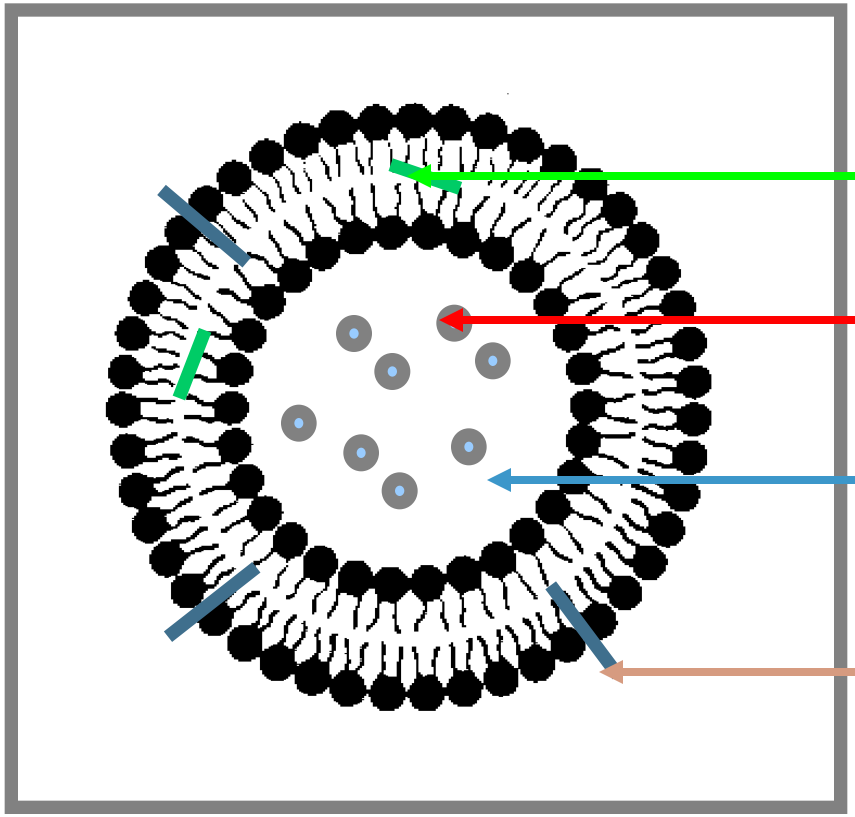
Carbon nanotube
~1.3 nm diameter

Weiss, IFT. 2007

Productos en función del tamaño de la protección

- Microproductos: Cápsulas entre 1 y 3 micras
- Submicroproductos: Submicrocápsulas entre 100 y 1000 nm
- Nanoproductos: Nanocápsulas inferiores a 100 nm (Engineering Nanomatherials-EN)

Liposomas



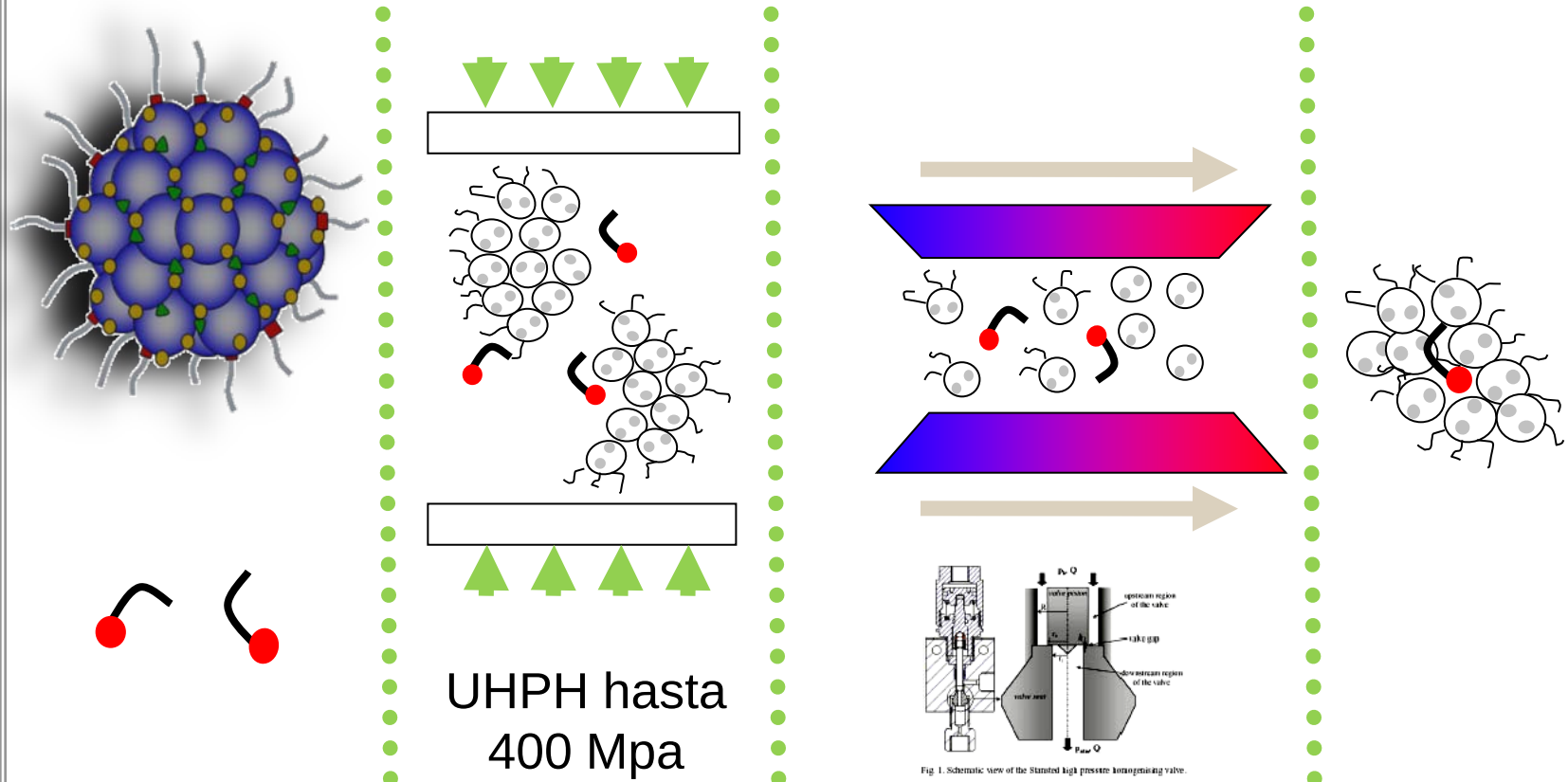
Molécula lipofila

Molécula hidrófila

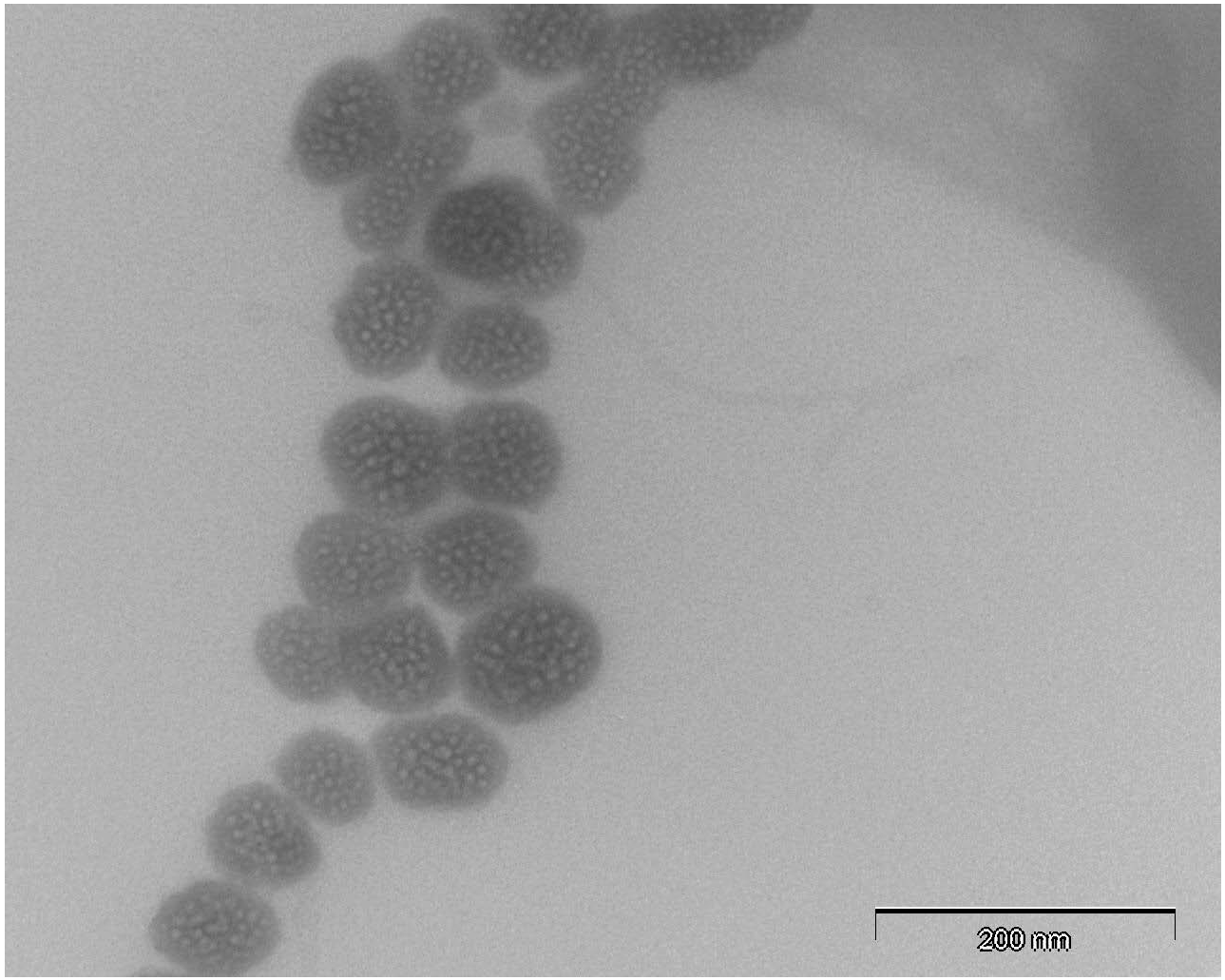
Fase acuosa interna

Molécula amfifílica

Nanoencapsulación



ImagenTEM de submicrocapsulas



UITA UNIDAD DE INNOVACIÓN EN TECNOLOGÍA DE ALIMENTOS

CONSOLIDER ALTA

CERPTA

PARC DE RECERCA UAB

GRACIAS POR SU ATENCIÓN

XaRTA
Xarxa de Referència en Tecnologia dels Aliments de la Generalitat de Catalunya

TECNIO
Be tech. Be competitive

SISTEMAS ACUOSOS –I

AGUA Y SISTEMAS RELACIONADOS CON LA VIDA

www.malta-consolider.com

CONSOLIDER MALTA

Matter at High Pressure

PROGRAMA INGENIO 2010

Grupo: Centro de Astrobiología

Felipe Gómez
Laura Jiménez Bonales
José Antonio R. Manfredi
Victoria Muñoz Iglesias
Olga Prieto Ballesteros

I. AGUA Y SISTEMAS RELACIONADOS CON LA VIDA

a. Síntesis, propiedades y estabilidad de clatratos

b. Efectos de la alta presión en soluciones acuosas de agregados supramoleculares y proteinas

c. Microbiología en condiciones extremas de presión y temperatura

Clatratos en Europa

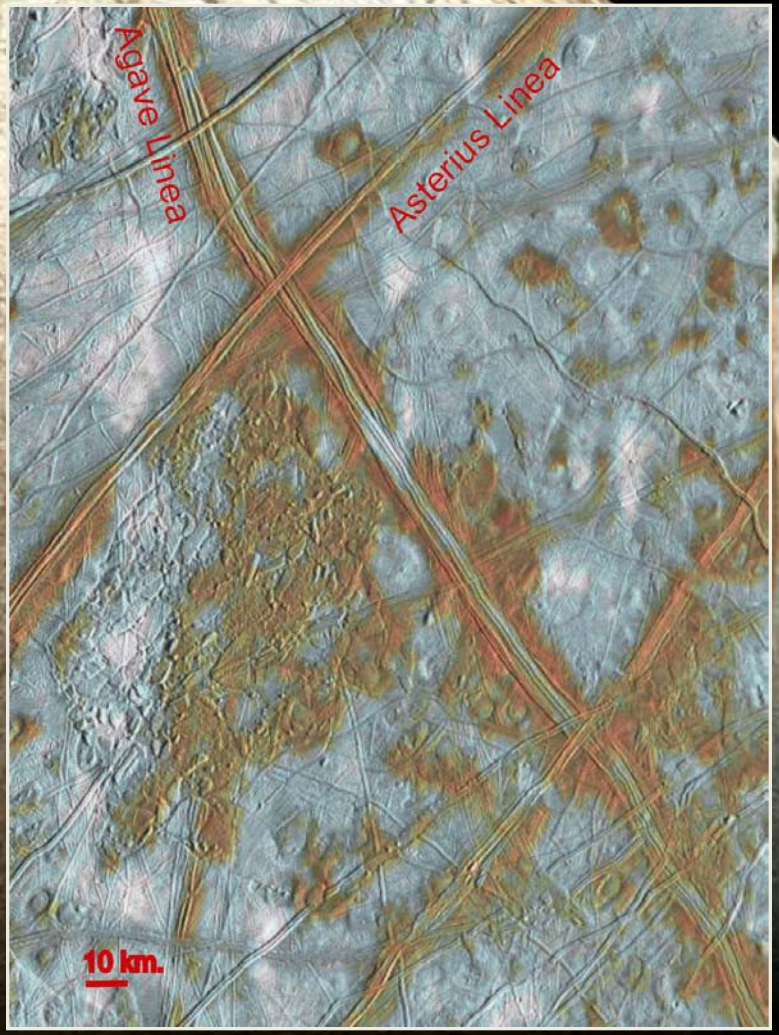
Master de tesis de Vicky – Octubre 2010
"Clatratos en Europa, satélite de Júpiter"

En el sistema solar exterior se dan las condiciones y los materiales necesarios para que se formen clatratos de gas, tanto en los satélites de hielo como en los cometas

- agua
- volátiles
- P y T

Manifestaciones geológicas observadas en los satélites de hielo pueden ser producto de la descomposición de los clatratos de gas

- estructuras de terrenos caóticos
- actividad de géiseres



EUROPA

Europa es un satélite especialmente interesante para Astrobiología debido a que parece albergar en su interior un océano de agua líquida en contacto con un substrato rocoso.

Actualmente Europa tiene una superficie de hielo dominada por H_2O, sales hidratadas y/o hidratos de ácido sulfúrico, CO_2, SO_2 y H_2S.

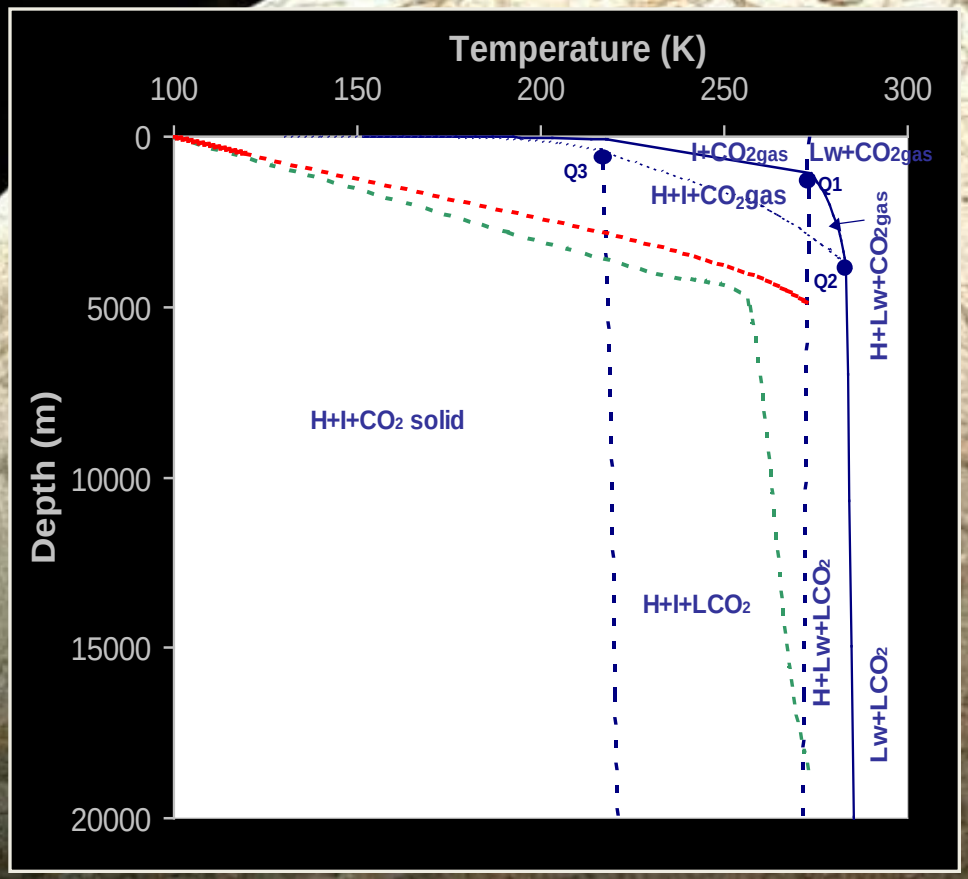
El océano de agua líquida está en contacto con la capa rocosa probablemente afectada por actividad hidrotermal, cuyas fumarolas liberan gases.

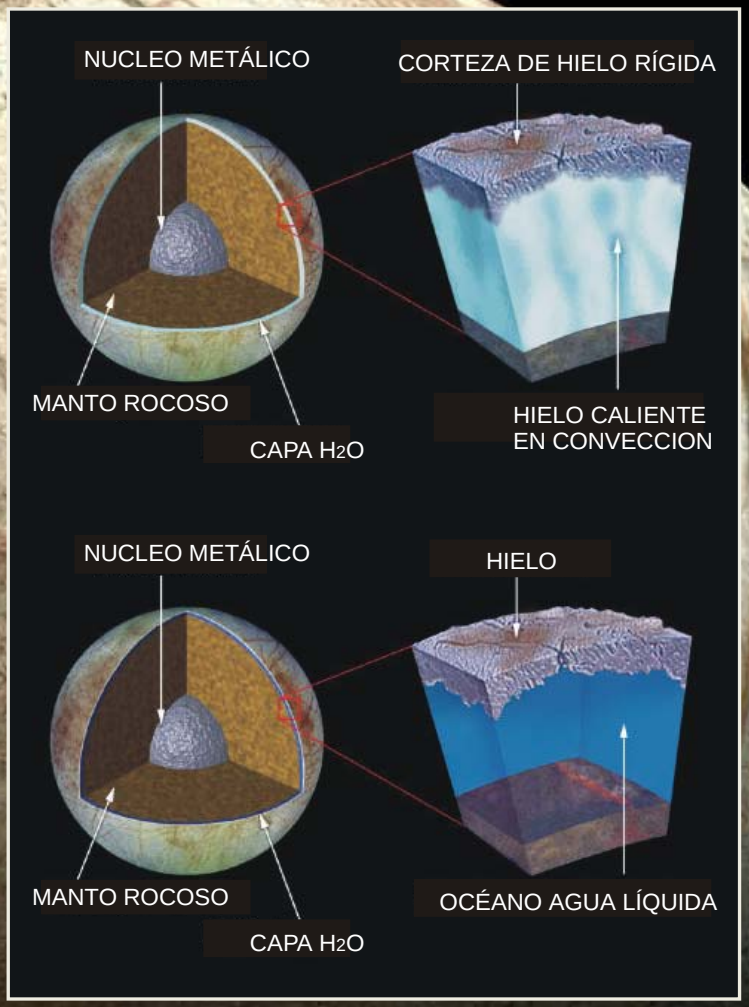
Estabilidad de los clatratos de gases volcánicos en el interior del satélite. De oxidantes radiogénicos en la subsuperficie.

APLICACIONES:

- Terrenos caóticos
- Diferenciación criomagmática

ESTABILIDAD CLATRATOS de CO_2





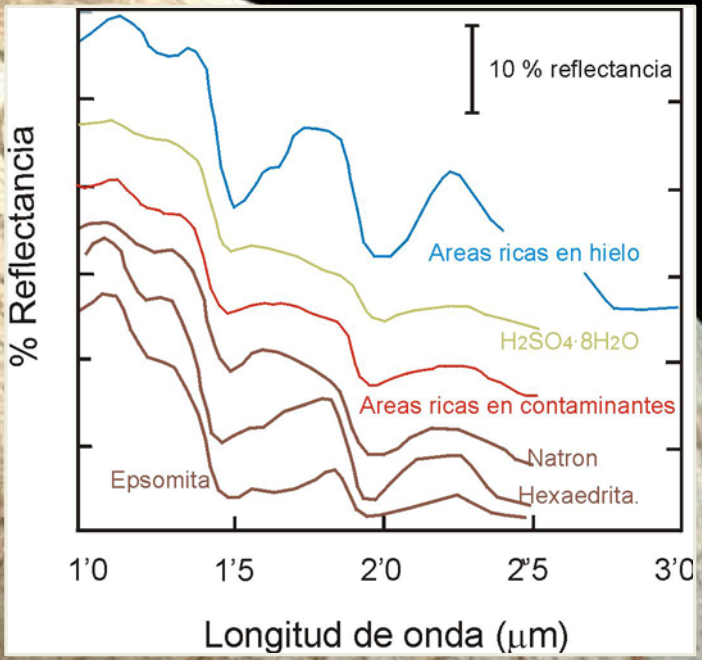
CO_2 → Estabilidad desde 0.05-0.5 mm de profundidad hasta el océano

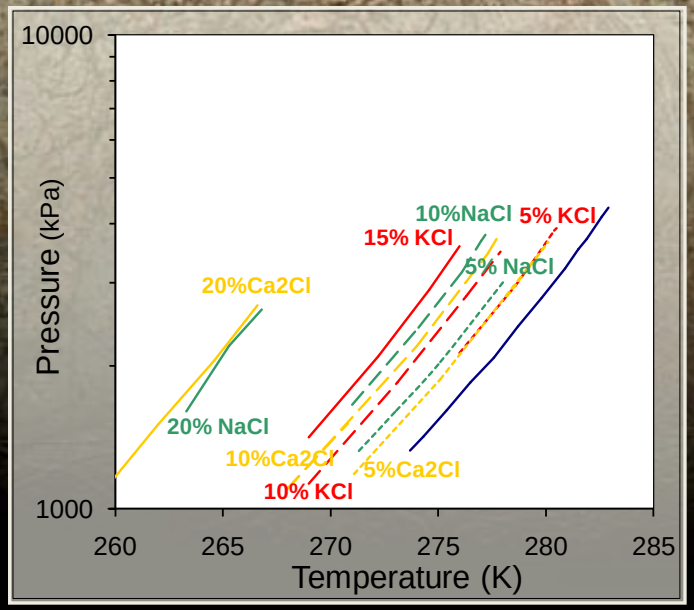
CLATRATOS VS. SALMUERAS

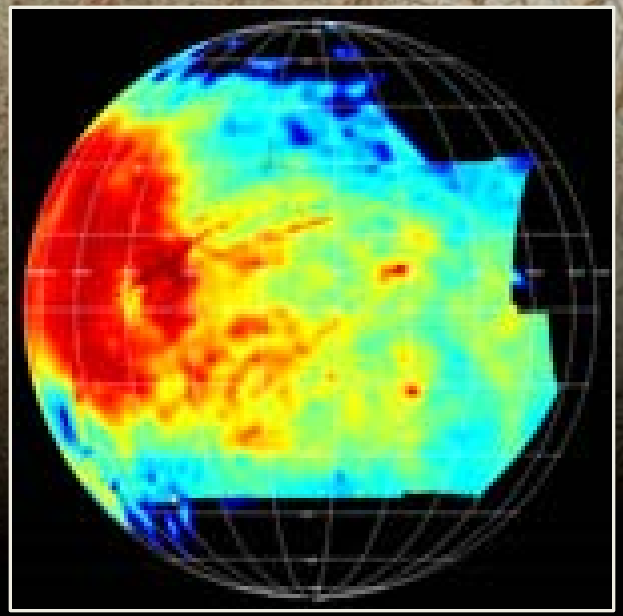
Las áreas superficiales no dominadas por el hielo de agua, son ricas en hidratos de sales y de ácido sulfúrico.

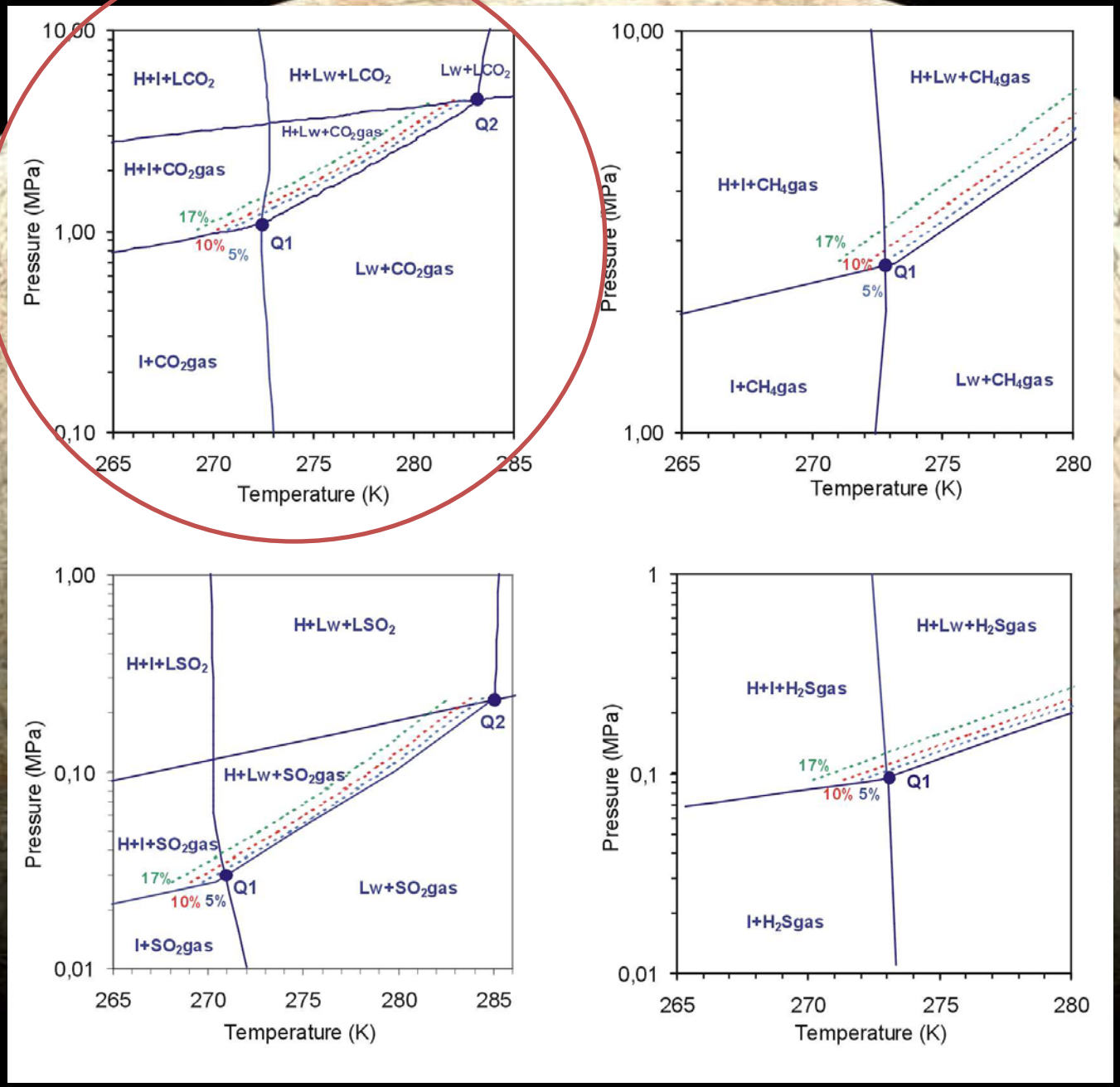
Se cree que estos materiales tienen origen endógeno por su relación estructural con las fracturas y la presencia de un campo magnético autoinducido.

Tradicionalmente los electrolitos en solución se han descrito como inhibidores de formación de clatratos debido a:
-La fuerte atracción del agua hacia los electrolitos.
-El efecto "*salting-out*": descenso de la solubilidad del gas en la salmuera debido al enlace del agua con los iones.







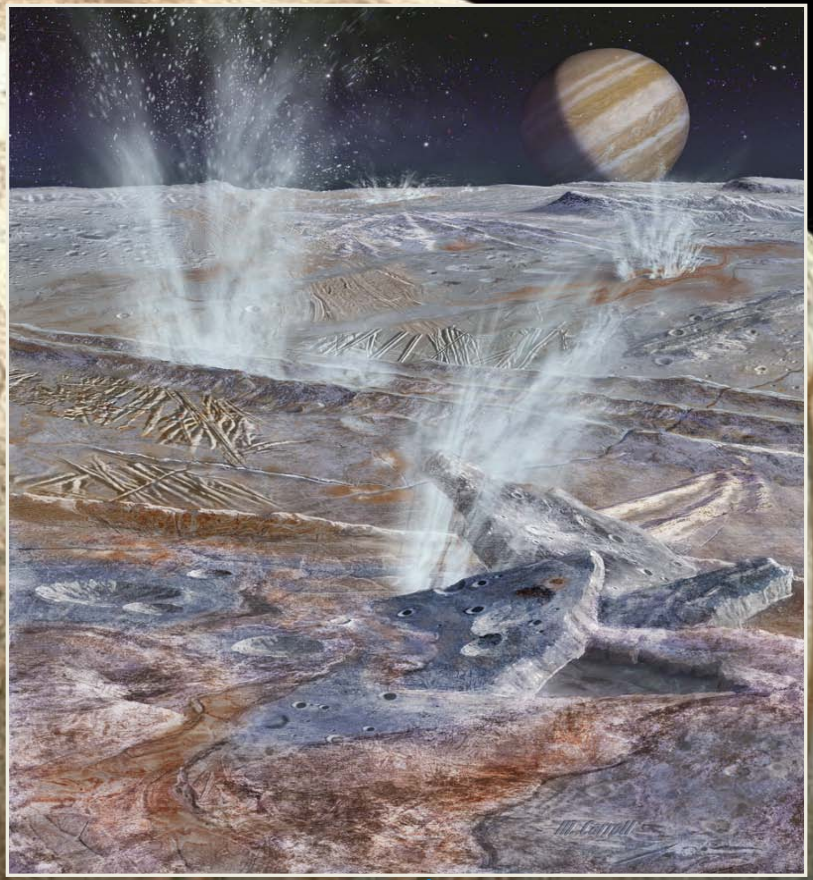

10,00
1,00
0,10
Pressure (MPa)
265
270
275
280
285
Temperature (K)
H+I+LCO2
H+Lw+LCO2
Lw+LCO2
H+Lw+CO2gas
Q2
H+I+CO2gas
17%
10%
5%
Q1
Lw+CO2gas
I+CO2gas
10,00
1,00
Pressure (MPa)
265
270
275
280
Temperature (K)
H+Lw+CH4gas
H+I+CH4gas
17%
10%
5%
Q1
I+CH4gas
Lw+CH4gas
1,00
0,10
0,01
Pressure (MPa)
265
270
275
280
285
Temperature (K)
H+Lw+LSO2
H+I+LSO2
Q2
H+Lw+SO2gas
H+I+SO2gas
17%
10% 5%
Q1
Lw+SO2gas
I+SO2gas
1
0,1
0,01
Pressure (MPa)
265
270
275
280
Temperature (K)
H+Lw+H2Sgas
H+I+H2Sgas
17%
10% 5%
Q1
I+H2Sgas

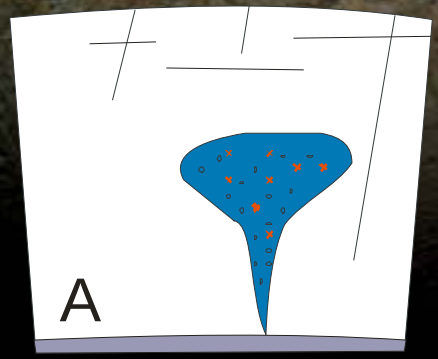
DIFERENCIACIÓN POR CLATRATIZACIÓN

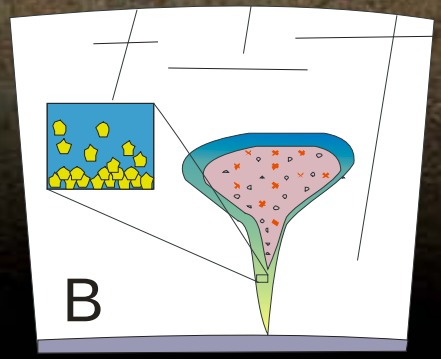
La formación de clatratos desde un magma enriquecido en gases e iones disueltos puede producir la diferenciación de la cámara magmática en los satélites de hielo.

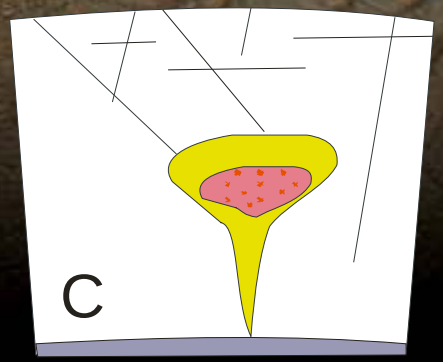
Durante el proceso, las sales disueltas pueden precipitar y separarse por su mayor densidad, permitiendo a la solución con gases cristalizar en clatratos de gas.

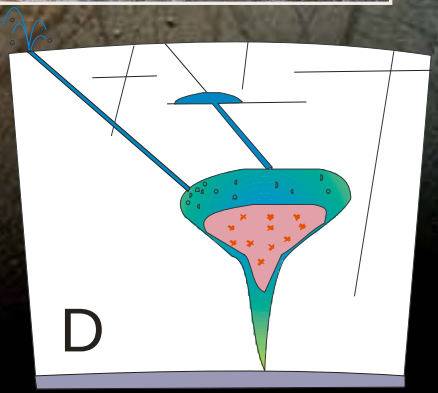
Si los clatratos se desestabilizan por descompresión, los criomagmas ricos en volátiles podrán ascienden a la superficie, e incluso erupcionar explosivamente.











CO_2 en disoluciones acuosas planetarias

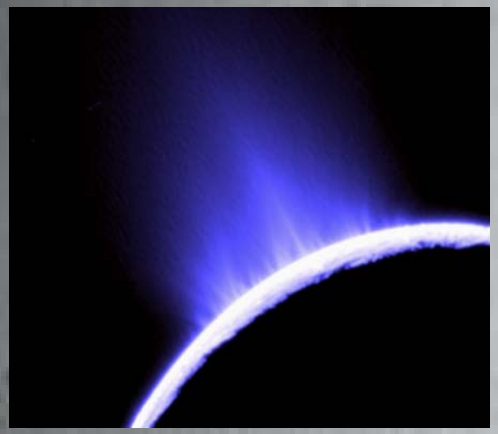
(desarrollo de Laura)

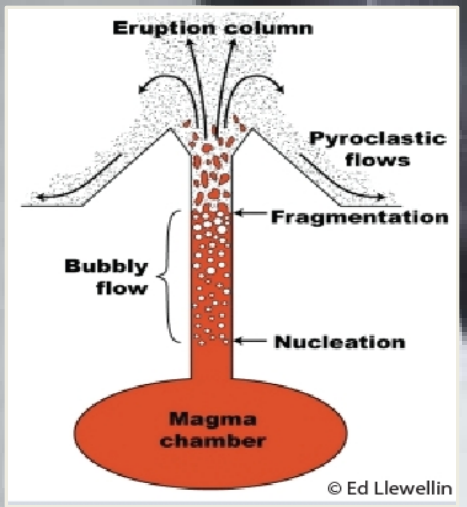
- CO_2 en soluciones sulfatadas a alta presión

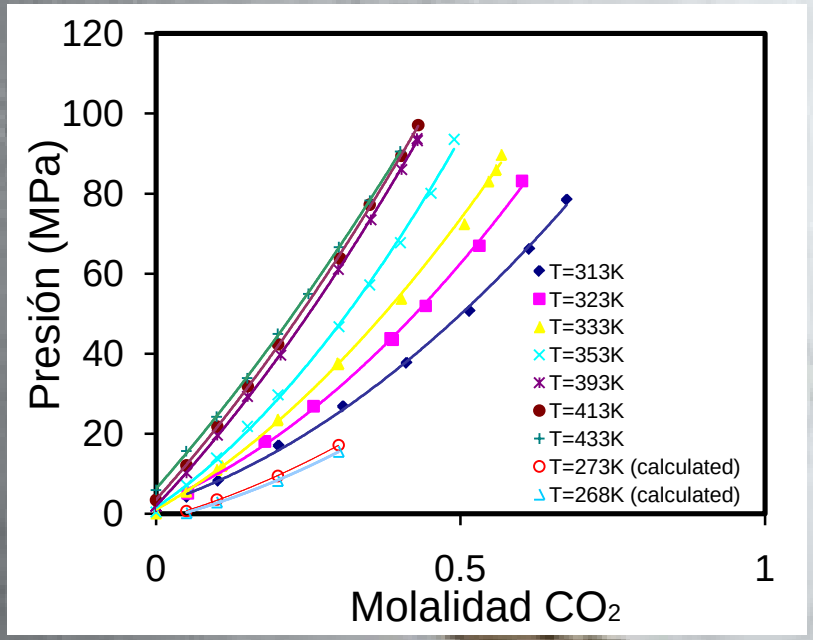
Aplicación en modelos de criomagmatismo del SSE. Explicación de la flotabilidad de los criomagmas. Explosividad de las erupciones de criomagmas. Diferenciación por clatratización

- CO_2 y carbonatos

Aplicación en la formación de carbonatos en épocas tempranas de la Tierra y Marte







www.malta-consolider.com
CONSOLIDER MALTA
Matter at High Pressure
PROGRAMA INGENIO 2010

Carbonatos en Tierra y Marte primitivos

Los carbonatos en la Tierra desempeñan un papel muy importante en el ciclo del C, fijan y liberan CO_2

Pueden ser precipitados inorgánicamente o ser biomediados

Actualmente los carbonatos precipitan en mares someros, según la reacción:

$$Ca^{2+} + 2\,(HCO_3^-) = CaCO_3 + H_2O + CO_2$$

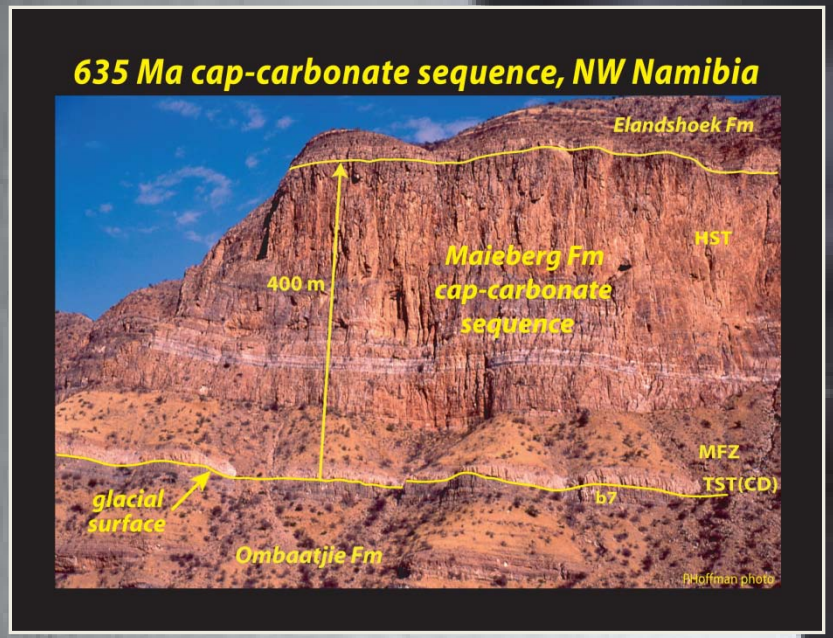
Los carbonatos son geomarcadores de unas condiciones ambientales particulares. Y pueden ser biomarcadores

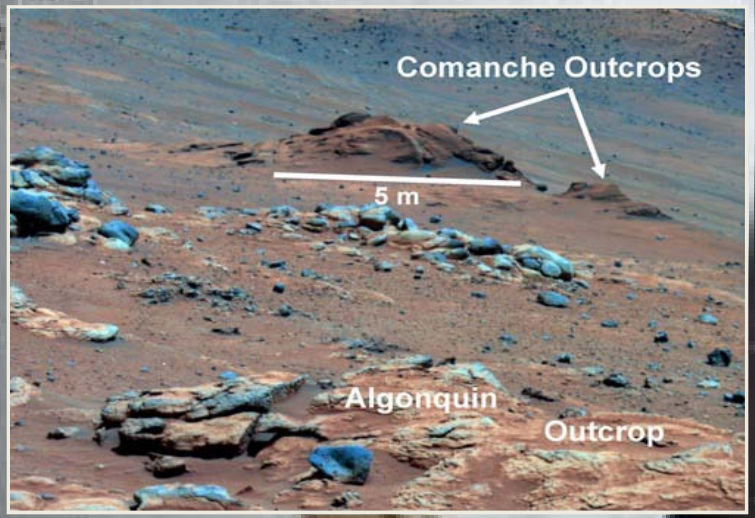
Existen periodos en la historia de la Tierra con carbonatos particulares **¿Cómo precipitan?**

- **Carbonatos arcaicos**
- **Carbonatos proterozoicos**

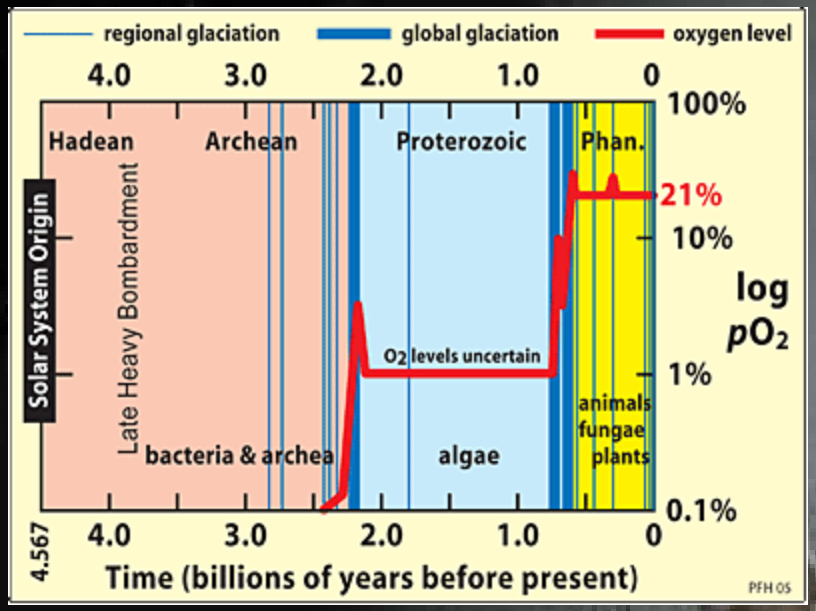
¿Dónde están los carbonatos en Marte?

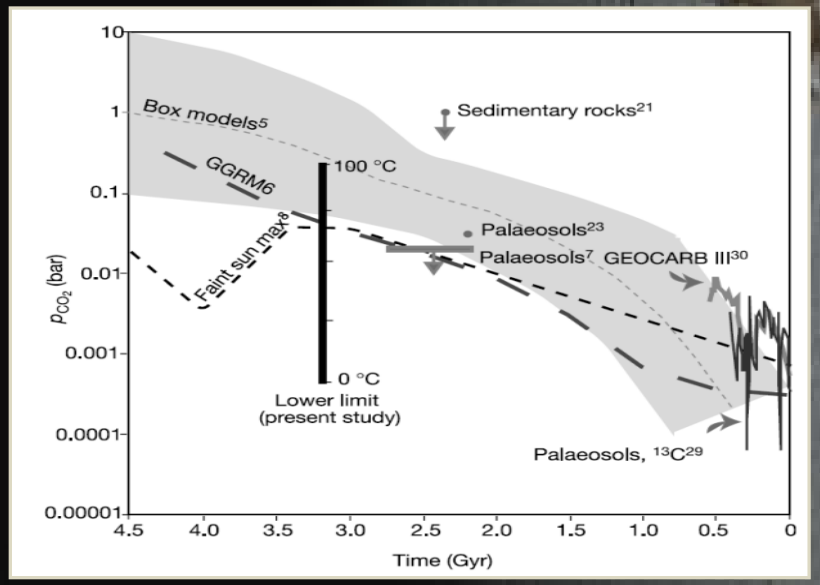
¿Se puede precipitar la dolomita inorgánicamente en condiciones de la corteza terrestre?





Tierra primitiva-carbonatos vs. Alta P





Proterozoico- los *"cap carbonates"* son calizas y dolomías que aparecen por encima de los depósitos glaciares proterozoicos (Makganyene ~ 2220 M.a., Sturtian ~700 M.a. o Marinoan 635 M.a.). Tienen características especiales en relación a carbonatos de otras épocas: cementos de aragonito bien desarrollados, ondulaciones gigantes, barita diagenética, relación isotópica deficitaria en ^{13}C etc

Los carbonatos del Arcaico (más de 2400 m.a.) no son frecuentes en la Tierra. Tienen características peculiares:

- Asociaciones de caliza y ortocuarcitas (sedimentarias o volcánicas)
- Carbonatos asociados a esquistos o cherts
- Carbonatos en asociaciones volcánicas
- Sedimentos clásticos-carbonatados

Arcaico-atmósfera más densa. Hasta 200 bares de presión.

Carbonatos Proterozoicos. *Cap carbonates*

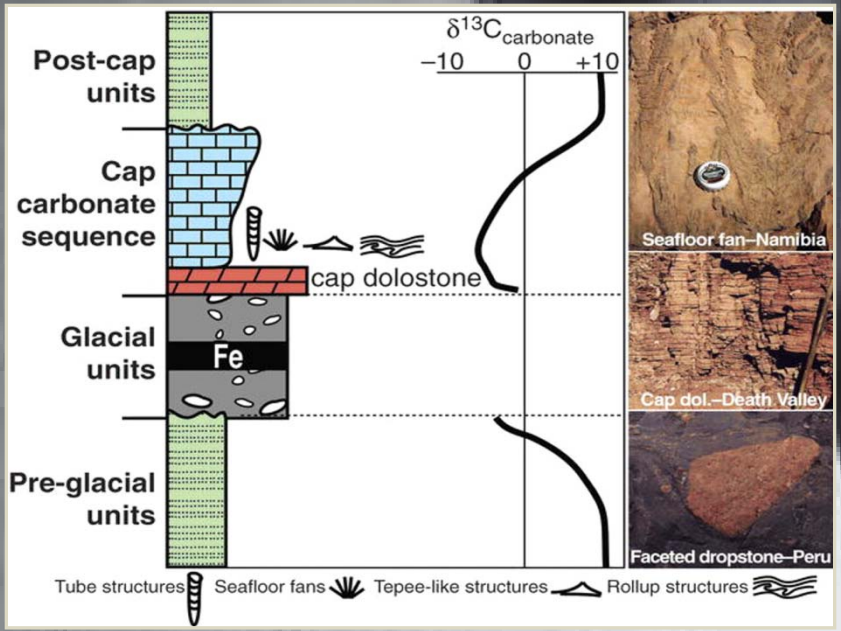
Carbonatos que están en contacto limpio con facies periglaciares. Son dolomías microcristalinas que aparecen por todo el globo, con calizas post-glaciares por encima

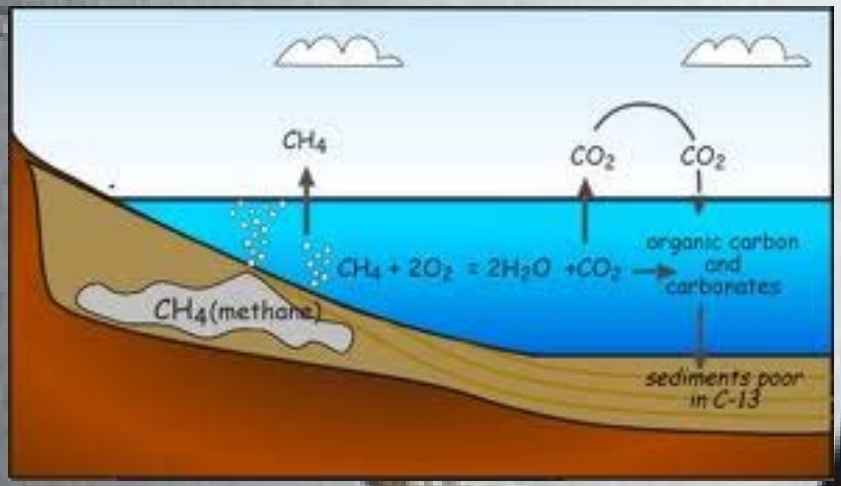
Se han propuesto 3 modelos que relacionan una deglaciación abrupta y el evento de precipitación de carbonatos (alcalinidad extrema)

- **cambio brusco de los océanos** anóxicos profundos, desgasificación de CO_2, subsecuente liberación de la alcalinidad en nuevas cuencas subsumergidas y precipitación de $CaCO_3$

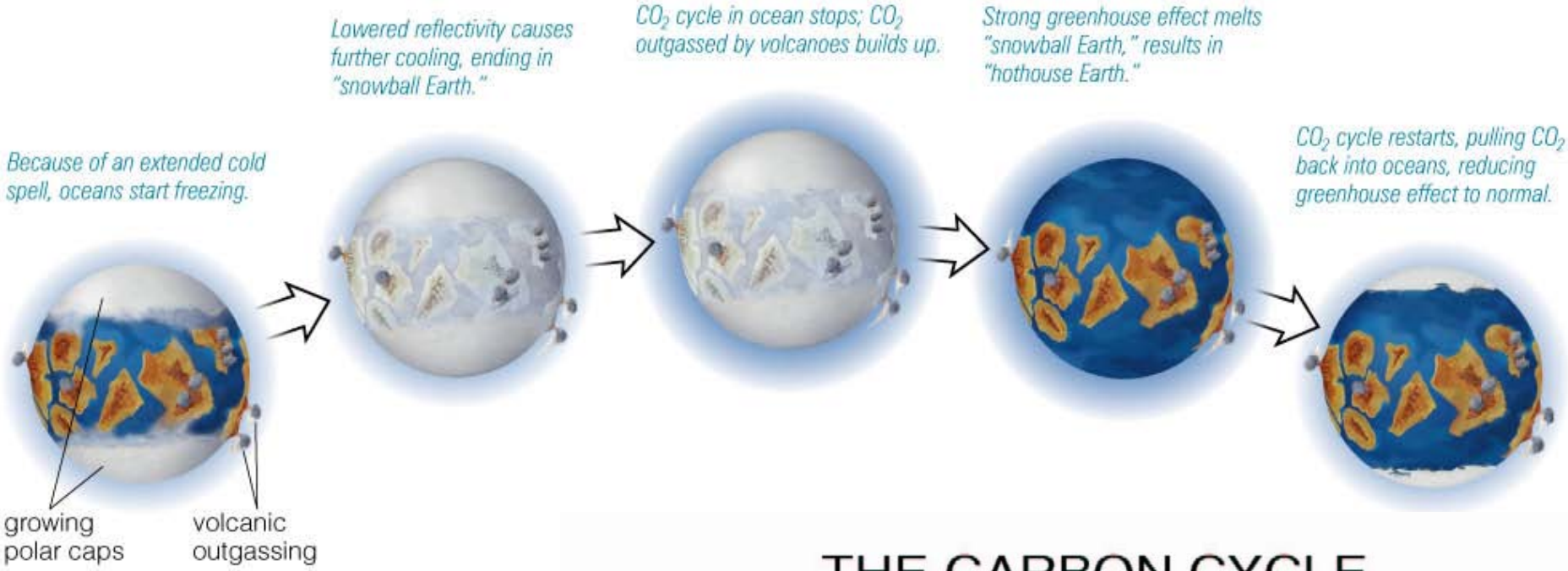
- **Snow Ball Earth**: alto grado de alteración química debido a condiciones de un super efecto invernadero y de una glaciación global. Deglaciación catastrófica cuando el nivel de pCO2 fue crítico (0.12 bares)

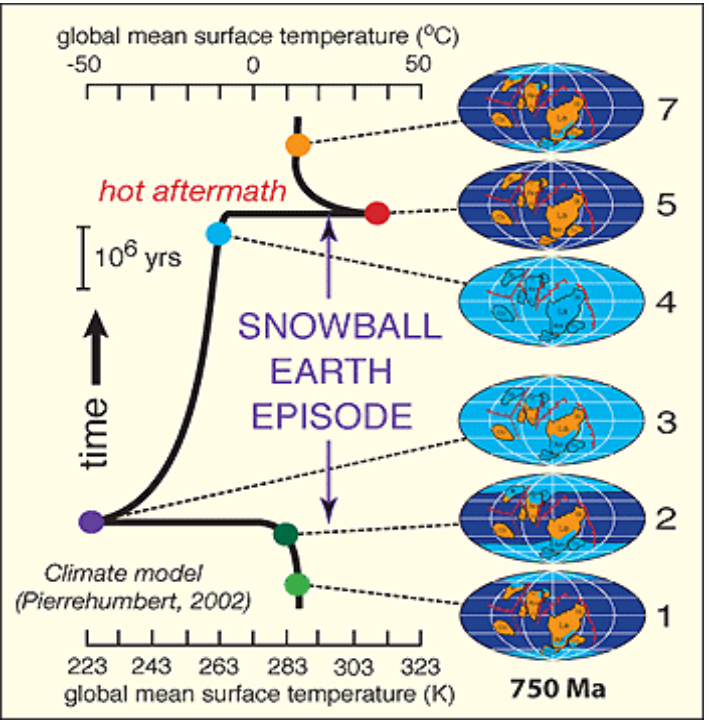
- liberación masiva de la alcalinidad por desestabilización **de clatratos de metano,** debido a la oxidación anaeróbica por sulfato-reducción

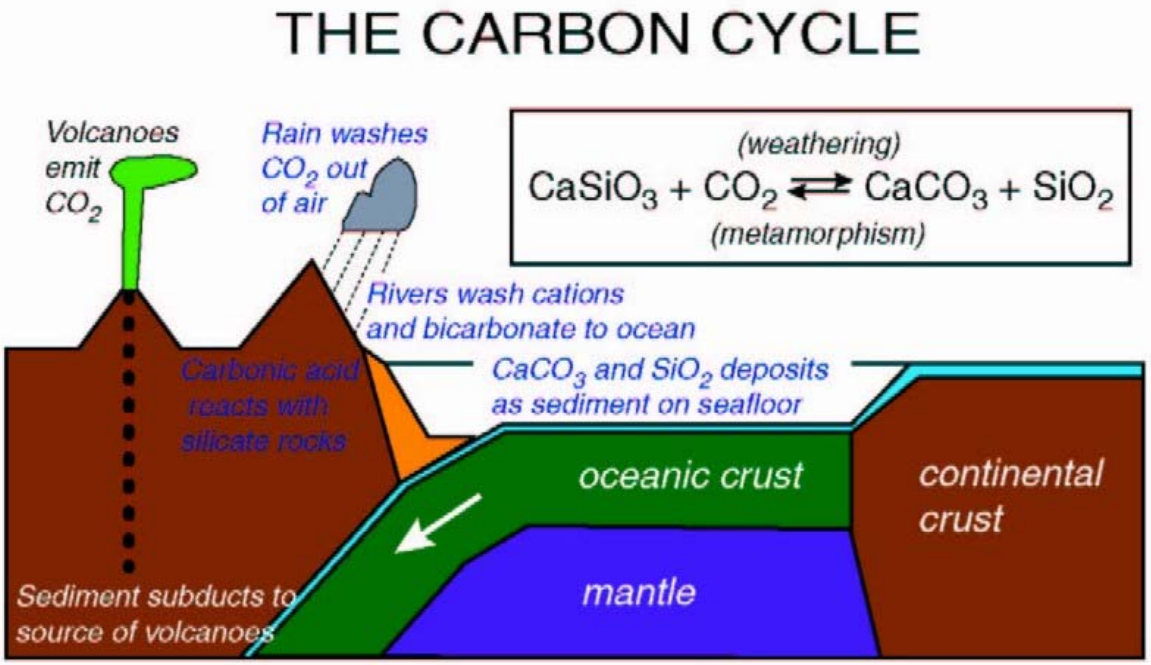




Experimentos para la posible comprobación de las hipótesis de SBE y los clatratos (baja temperatura, despresurización, precipitación de dolomita???)







[Processes lettered in blue are absent in a snowball Earth]

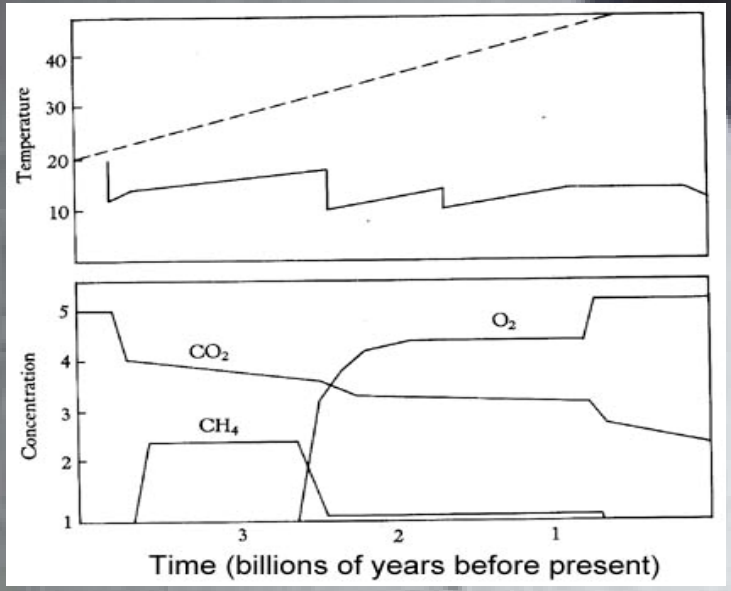
Carbonatos Arcaicos

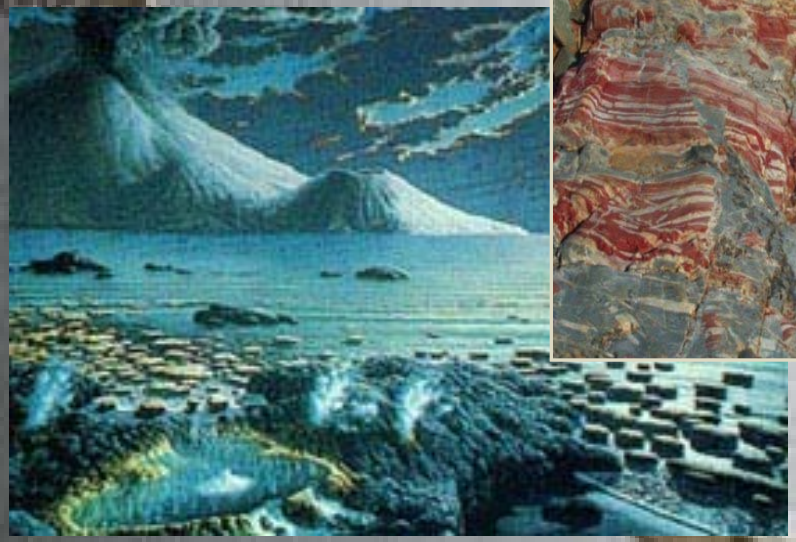
La atmósfera del Arcaico fue muy rica en CO_2. Esto pudo acidificar los océanos. Condiciones no favorables.

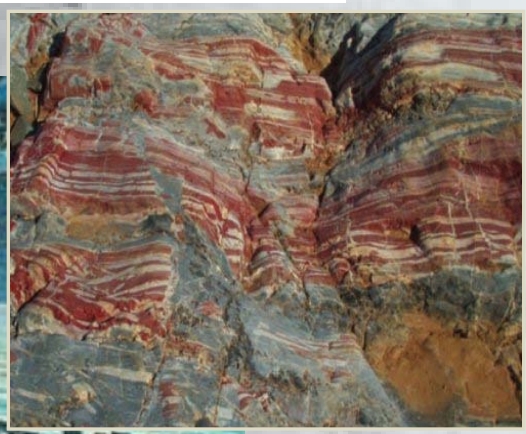
Los datos muestran que la alteración de las rocas ígneas liberó Ca^{2+} a los océanos

La corteza era delgada e inestable, con pocos lugares aptos para la precipitación masiva de carbonatos. Solo en partes profundas con favorable contenido en CO_2 (fáciles de destruir posteriormente por tectónica)

¿Cómo precipitaron los carbonatos del Arcaico teniendo en cuenta las características de la atmósfera y del océano? Desde pCO2 alta y T medias





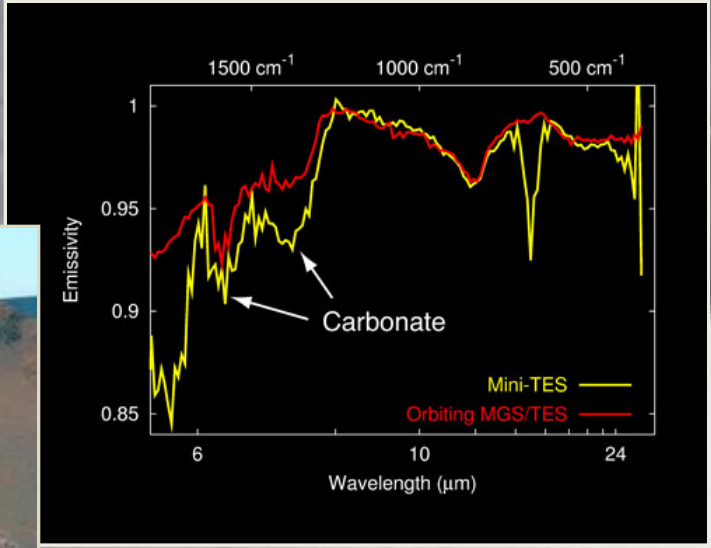


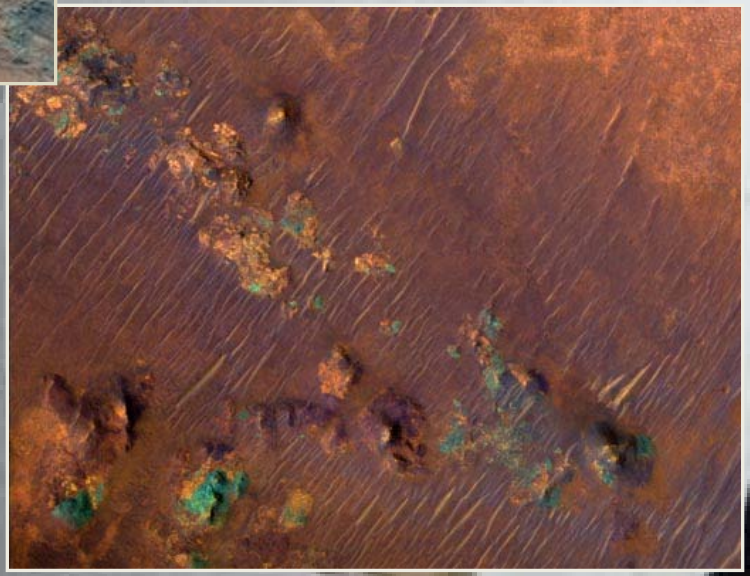
Marte primitivo-carbonatos vs. Alta P

Si Marte tuvo agua y una atmósfera mas densa podría haber formado carbonatos

El rover Spirit ha identificado carbonatos Mg-Fe (16 - 34 peso%) en Columbia Hills del cráter Gusev. Podrían haber precipitado de soluciones carbonatadas en condiciones hidrotermales a pH casi neutro en asociación con la actividad volcánica del periodo Noico

¿Son hidrotermales los carbonatos marcianos?





CO_2 EN DISOLUCIONES ACUOSAS PLANETARIAS

www.malta-consolider.com

CONSOLIDER MALTA

Matter at High Pressure

PROGRAMA INGENIO 2010

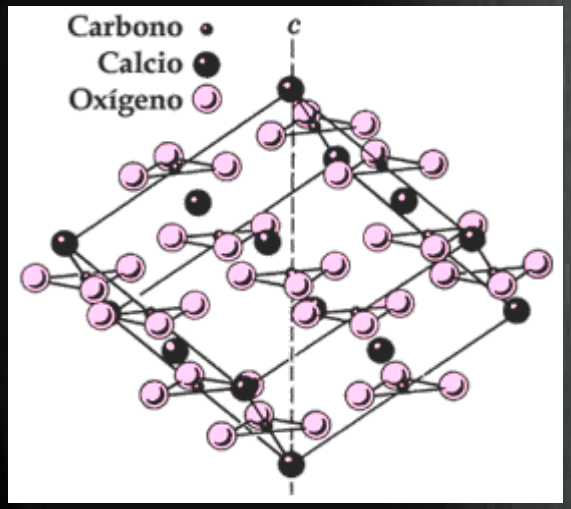
CAB

ASOCIADO AL NASA ASTROBIOLOGY INSTITUTE

CARBONATOS Y SU CLASIFICACIÓN

CALCITA

Calcita	$CaCO_3$
Magnesita	$MgCO_3$
Siderita	$FeCO_3$
Rodocrosita	$MnCO_3$
Smithsonita	$ZnCO_3$



Romboédrico

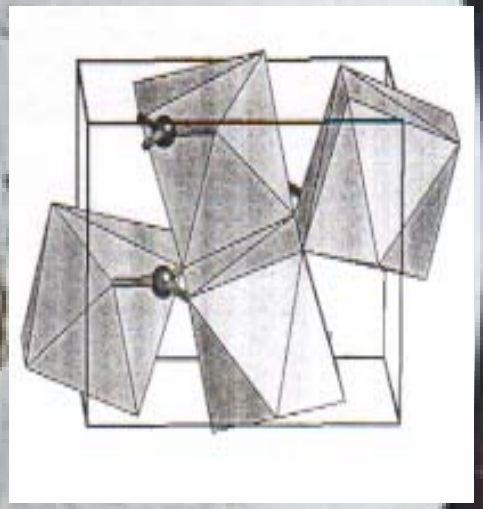
DOLOMITA

Dolomita	$MgCa(CO_3)_2$
Ankerita	$FeCa(CO_3)_2$
Kutnahorita	$MnCa(CO_3)_2$

Romboédrico

ARAGONITO

Aragonito	$CaCO_3$
Witherita	$BaCO_3$
Estroncianita	$SrCO_3$
Cerusita	$PbCO_3$



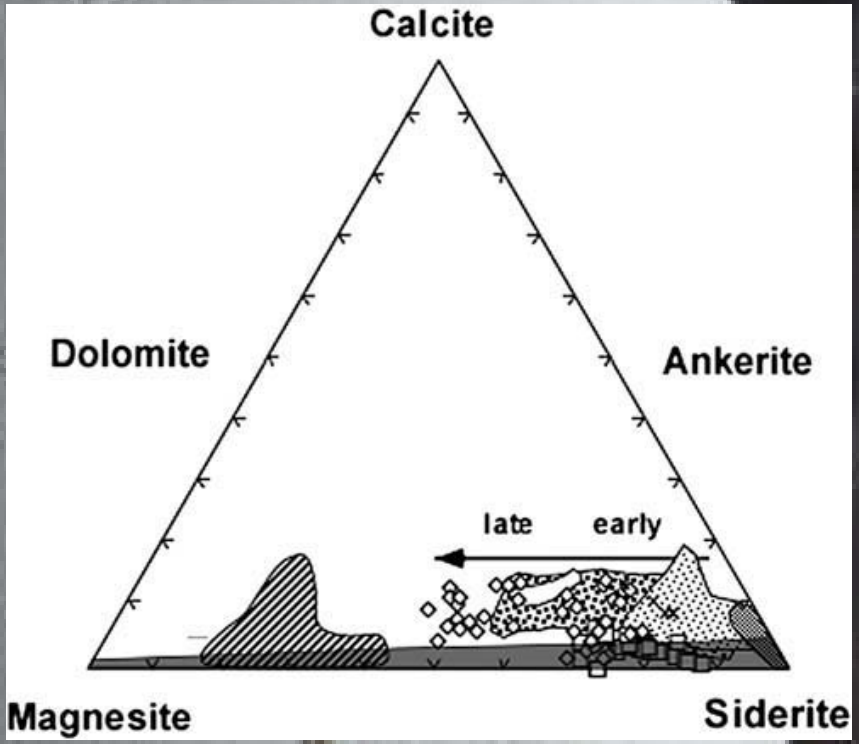
Rómbico

CARBONATOS SÍNTETICOS Y ANÁLISIS

✓Síntesis de carbonatos en C.N.

✓Comportamiento de carbonatos A distinta P y T una vez formados

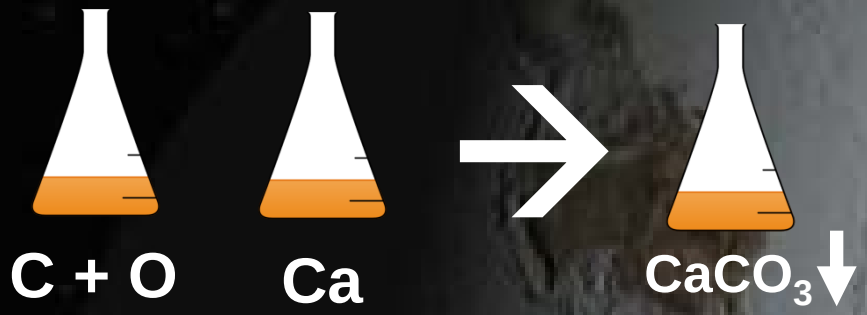
✓Síntesis a 25ºC y 1 bar

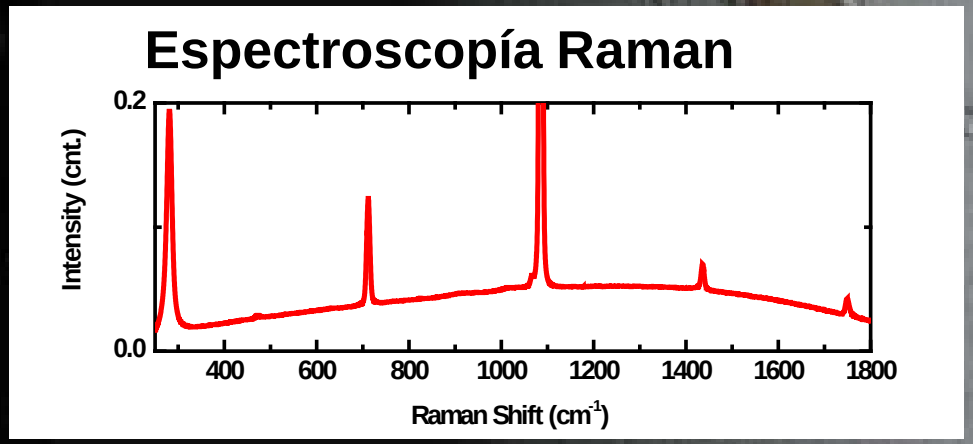


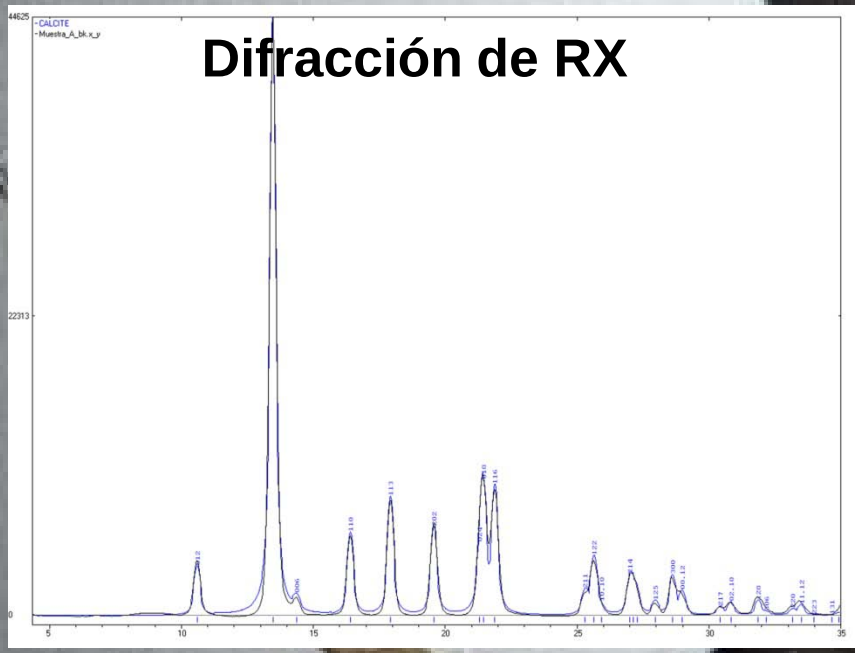
✓Difracción de RX
✓Espectroscopía Raman
✓SEM y TEM
✓Modelización geoquímica de disoluciones
✓ICP-Masas de disolución y sólidos
✓Isótopos estables (C,O)

SÍNTESIS Y ANÁLISIS DE CALCITA en C.N

✓Síntesis a 25ºC y 1 bar







CARBONATOS SÍNTETICOS:

OBJETIVOS

1º Síntesis en condiciones del Proterozoico (↑P, ↓T)

2do Síntesis en condiciones del Arcaico (↑P, ↓↑T)

- ✓Análisis " in situ" de las reacciones
- ✓Análisis " ex situ" de los minerales

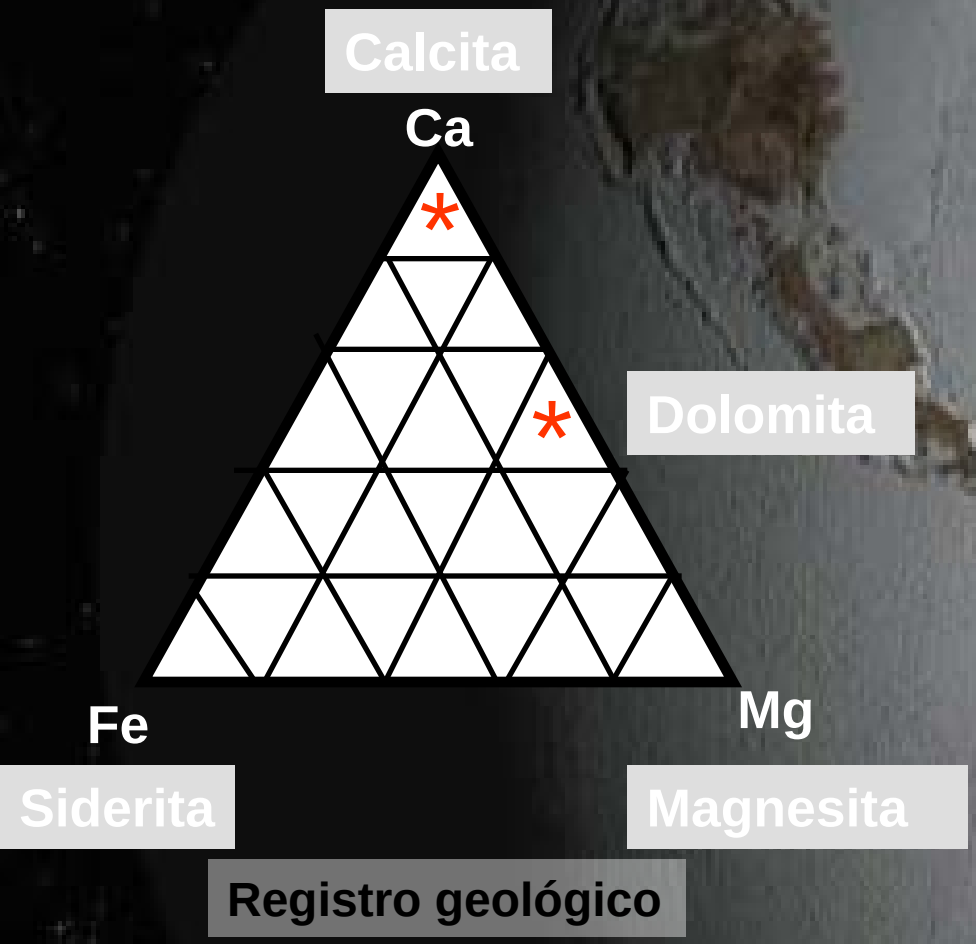
CARBONATOS SÍNTETICOS

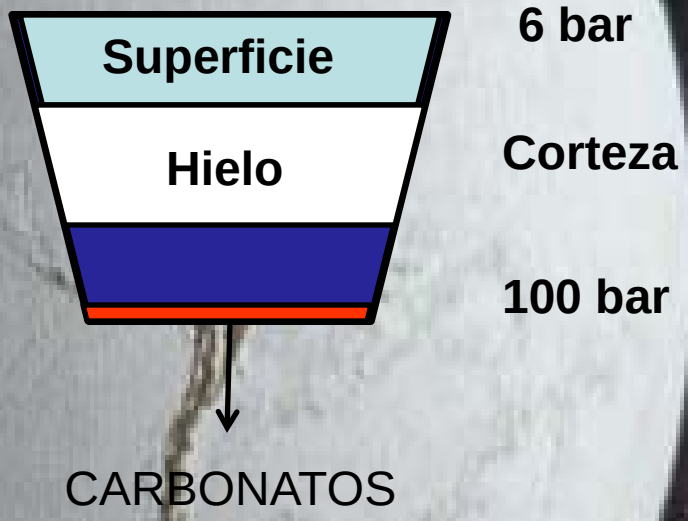
✓**Síntesis en condiciones del <u>Proterozoico</u>:**

1. A partir de HCO_3^- y H_2CO_3

2. Bajas temperaturas (0ºC y -5ºC)

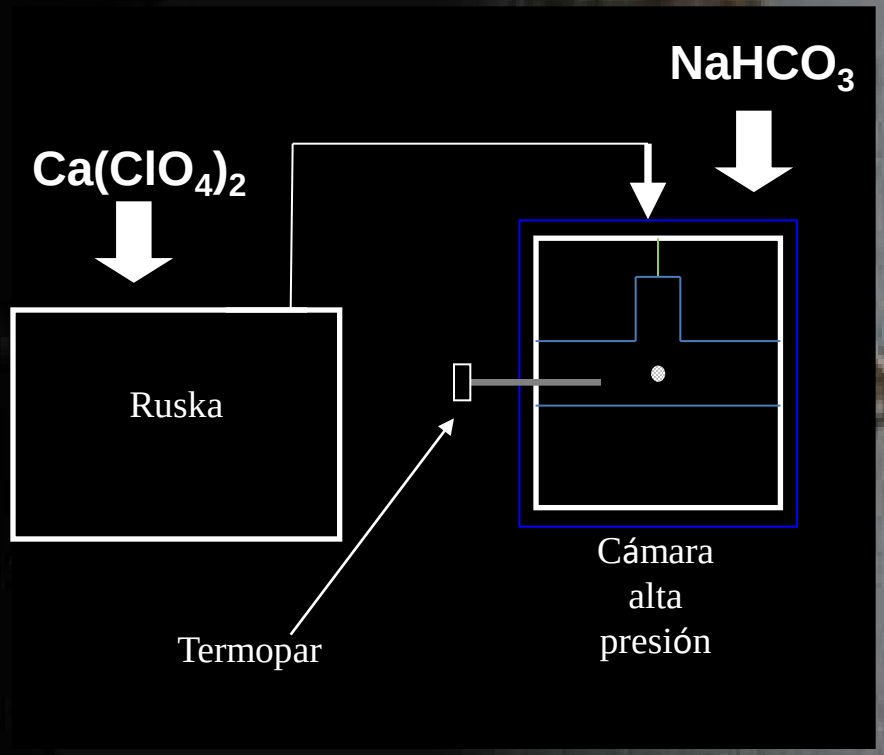
3. Presiones desde 6-100 bar

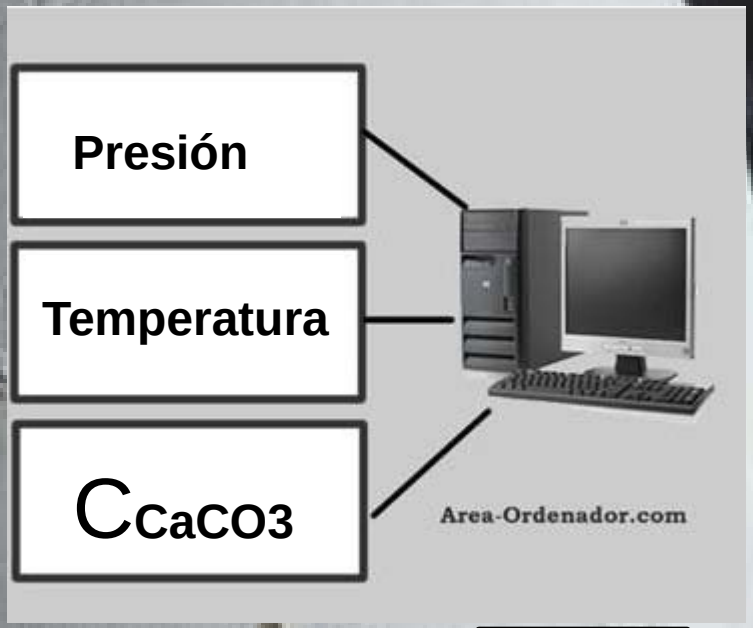


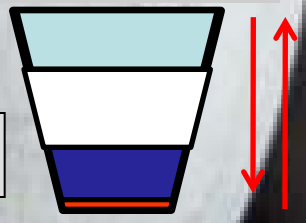


METODOLOGÍA: Síntesis de $CaCO_3$ (Proterozoico)

$$2\ NaHCO_3 + Ca(ClO_4)_2 \rightarrow CaCO_3 \downarrow + CO_2\,(g) + 2\ NaClO_4 + H_2O$$







Experimentos de compresión y descompresión a bajas T

METODOLOGÍA: Ejemplo, Síntesis de $CaCO_3$ (Proterozoico)

$$2\ NaHCO_3\ (ac) + Ca(ClO_4)_2\ (ac) \rightarrow CaCO_3 \downarrow + CO_2\ (g) + 2\ NaClO_4 + H_2O$$

$$H_2O + CO_2 \leftarrow H_2CO3 \leftarrow NaHCO_3 \rightarrow CO_3^{2-}$$

✓**Síntesis a 25ºC y 1 bar (estudio previo)**

Desplazamiento de la reacción (función del pH y concentración), Cinética rápida Rendimiento al 100%

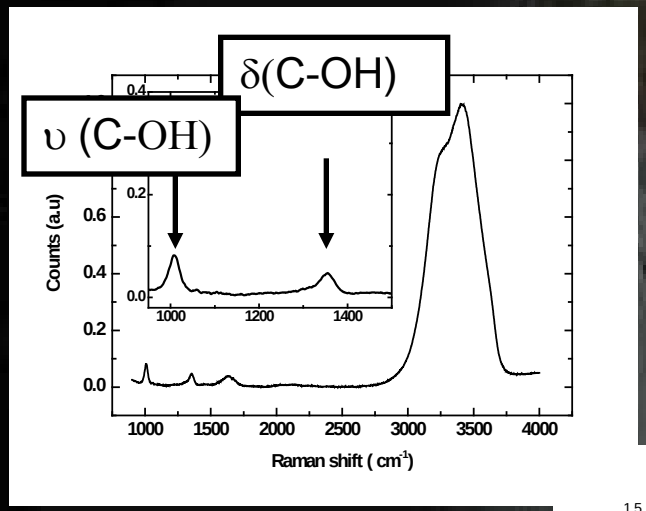
✓**Síntesis <u>Proterozoico</u>: a bajas T y altas P**

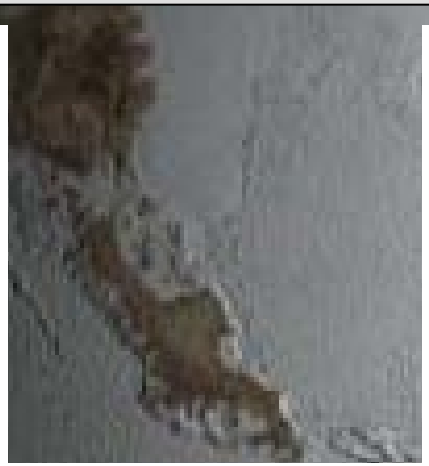
Desplazamiento de la reacción (función del CO_2), Cinética lenta Rendimiento %< 100%, restos de HCO_3^-

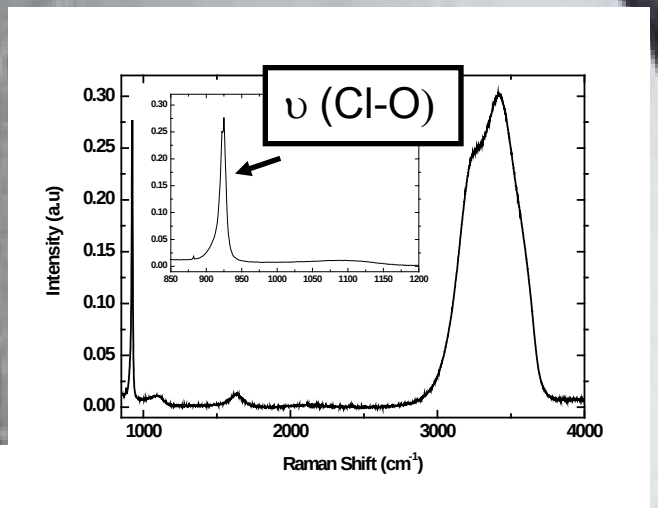
ANALALISIS “in situ”

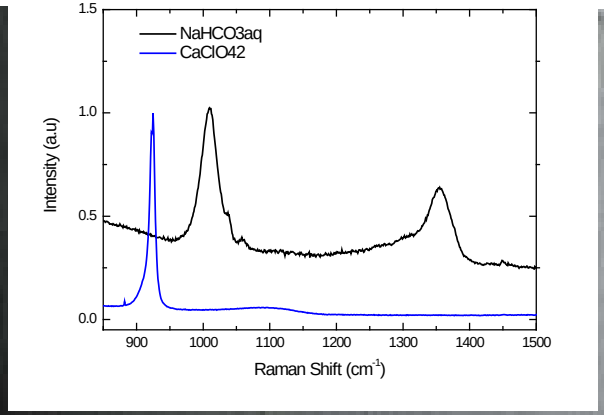
seguimiento mediante espectroscopía Raman de la disminución de la concentración de HCO_3^-

$$2\ NaHCO_3 + Ca(ClO_4)_2 \rightarrow CaCO_3 \downarrow + CO_2\,(g) + 2\ NaClO_4 + H_2O$$





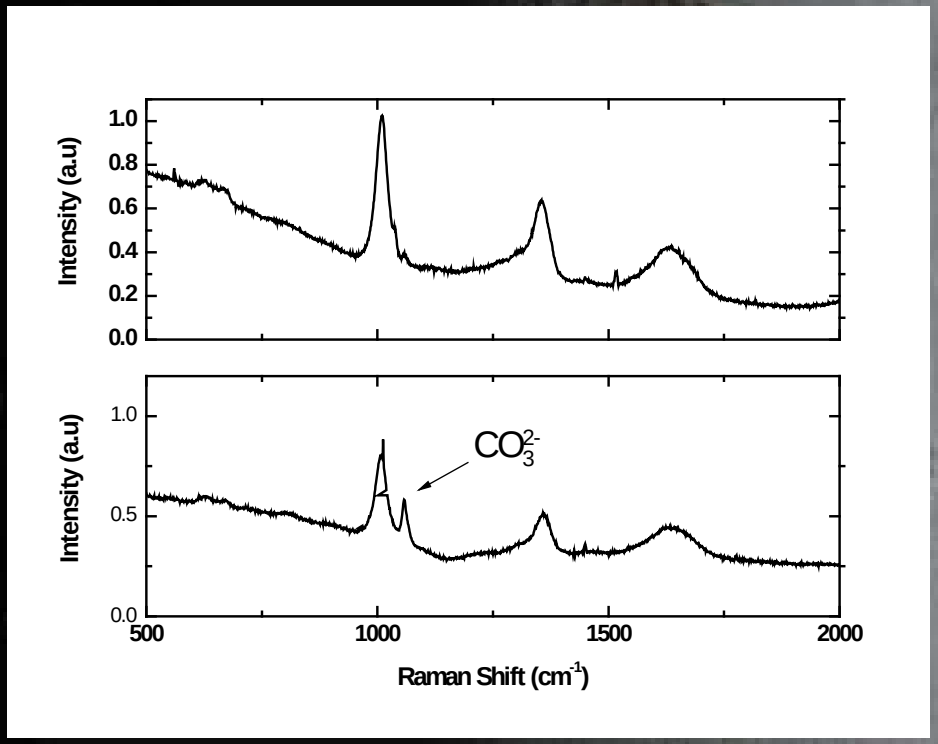


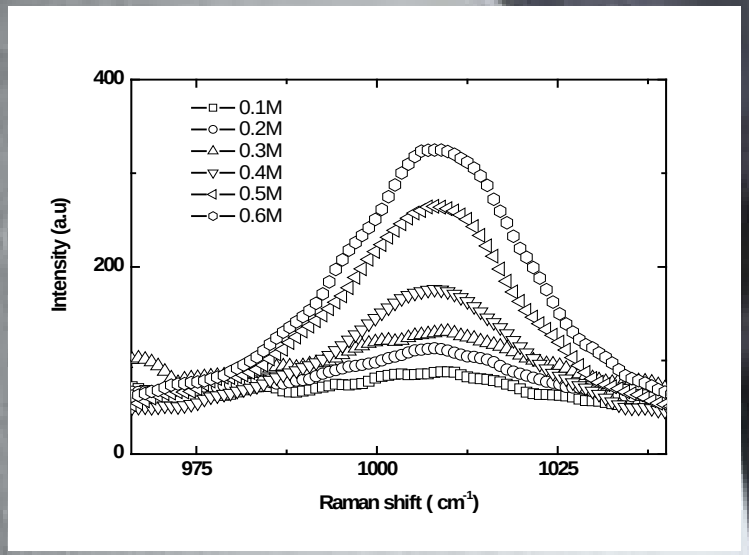


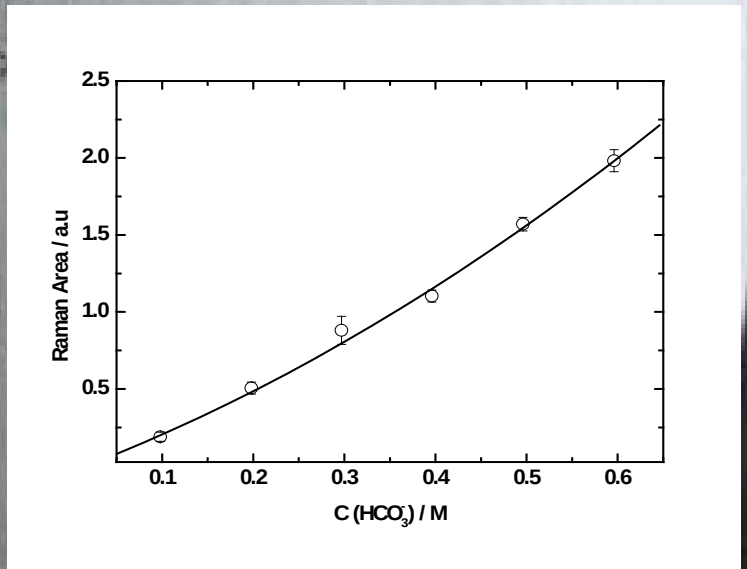
Estudio del HCO_3^-

$H_2O + CO_2\ (g) \leftarrow H_2CO3 \leftarrow HCO_3^- \rightarrow CO_3^{2-}$

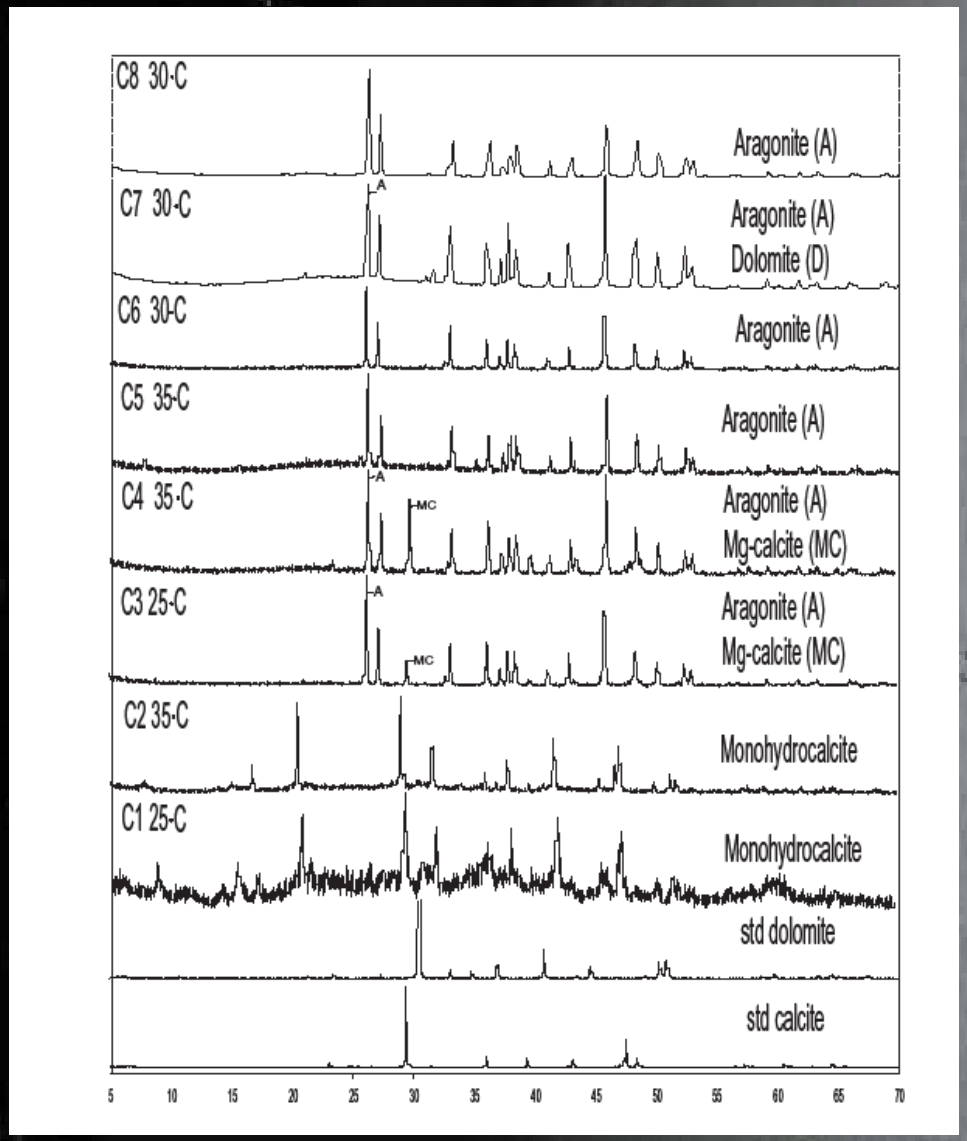
pH





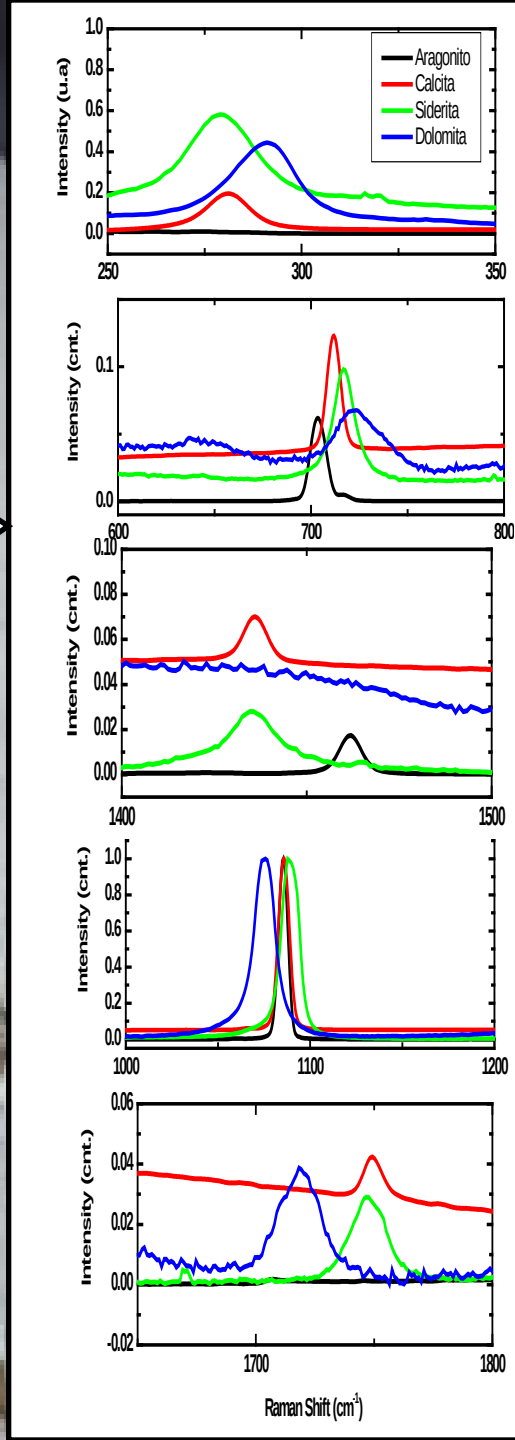


ANALALISIS “ex situ”

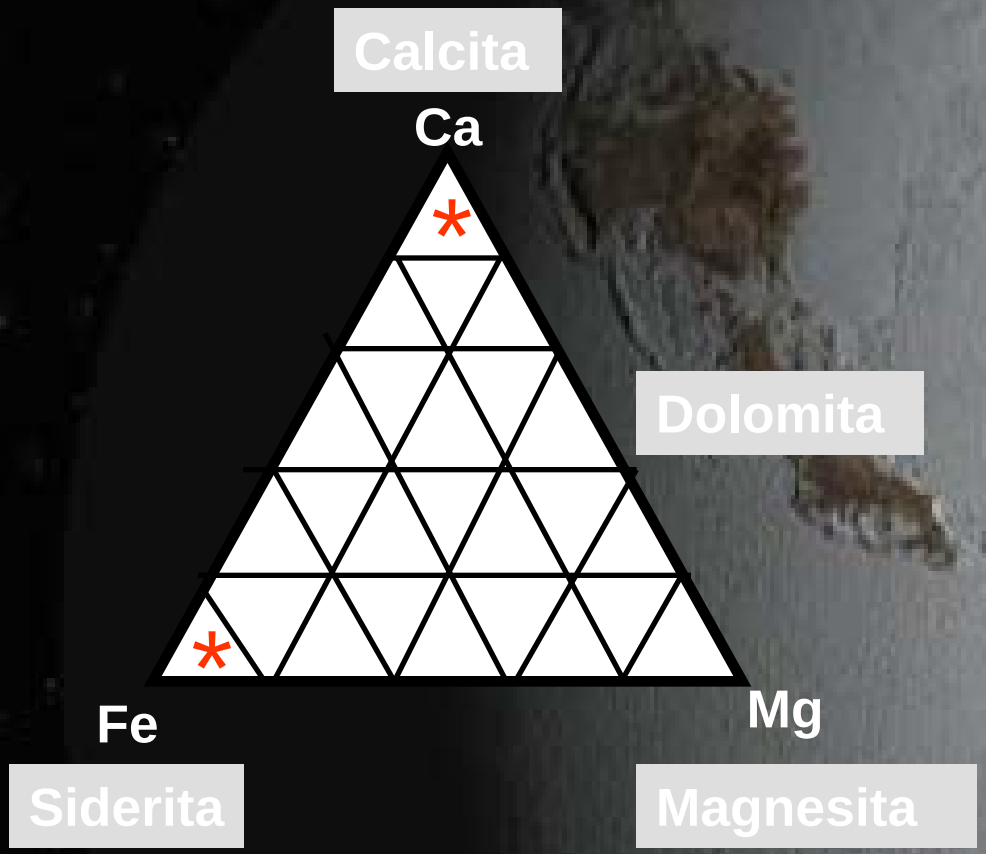


RAMAN

RX



CARBONATOS SÍNTETICOS



Registro geológico

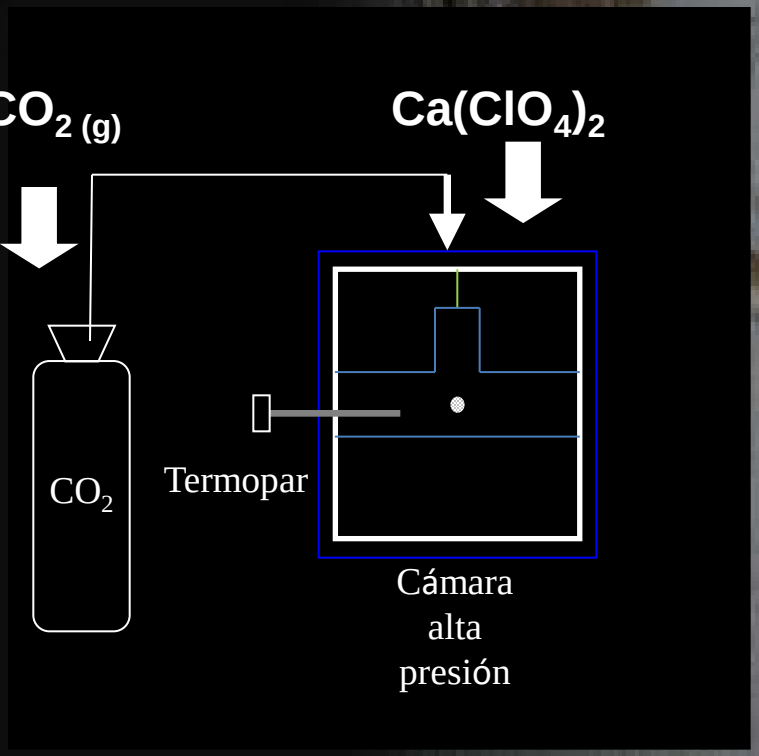
✓**Síntesis en condiciones del <u>Arcaico</u>:**

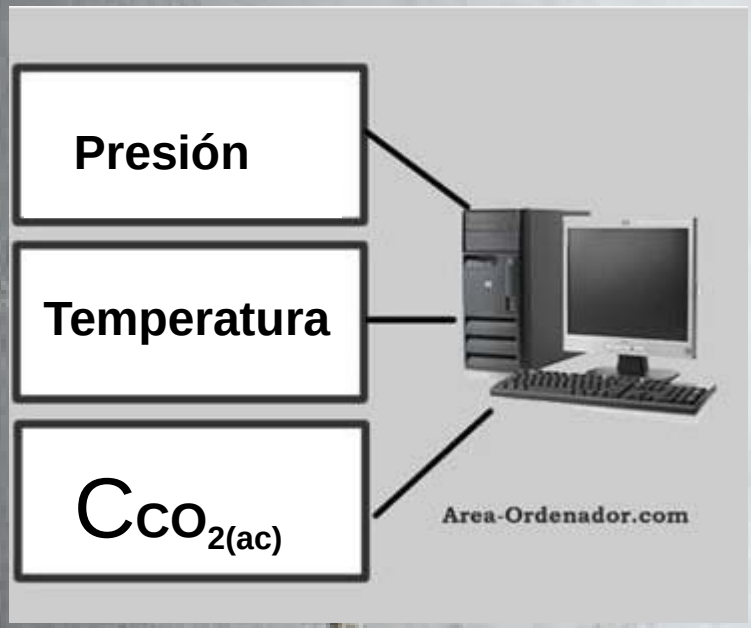
1. **A partir CO_2**
2. **Temperaturas medias (20ºC)**
3. **Presiones hasta 200 bar**

METODOLOGÍA: Síntesis de $CaCO_3$ (Aracaico)

$$CO_2\ (g) + H_2O \rightarrow CO_2\ (ac) + H_2O \rightarrow H_2CO_3$$

$$H_2CO_3 + Ca(ClO_4)_2 \rightarrow CaCO_3\downarrow + H_2ClO_4$$

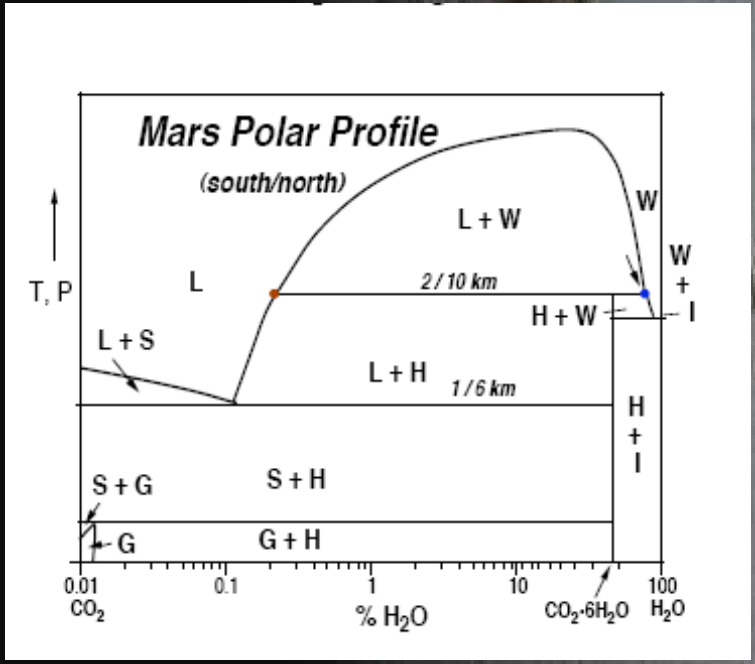




Estudio de la solubilidad del CO_2 en función de la p, T y presencia de sales

1. Carbonatos en la tierra primitiva

2. Clatratos: $CO_2 + H_2O$



Estudios cuantitativos mediante Espectroscopía Raman

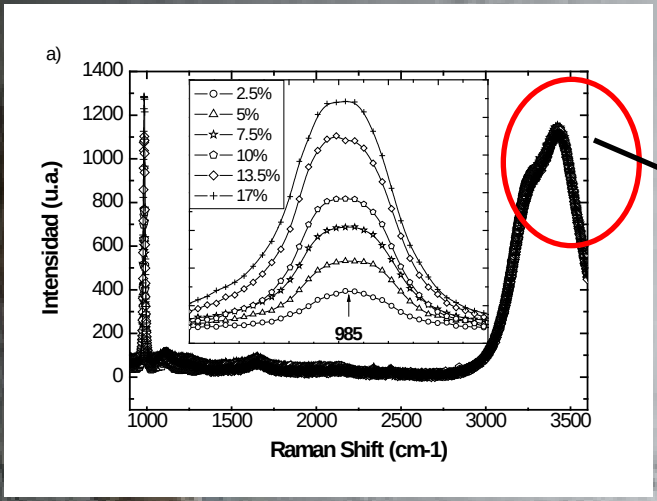
Metodología

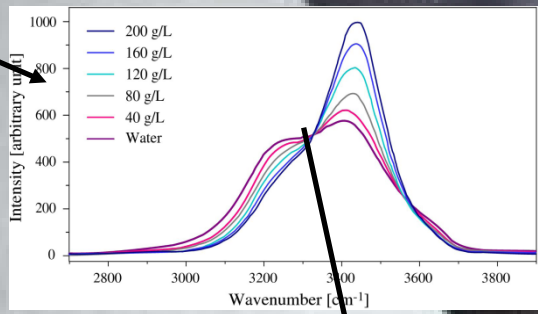
Ej: $MgSO_4$ en H_2O

Estudios cuantitativos mediante espectroscopía Raman:

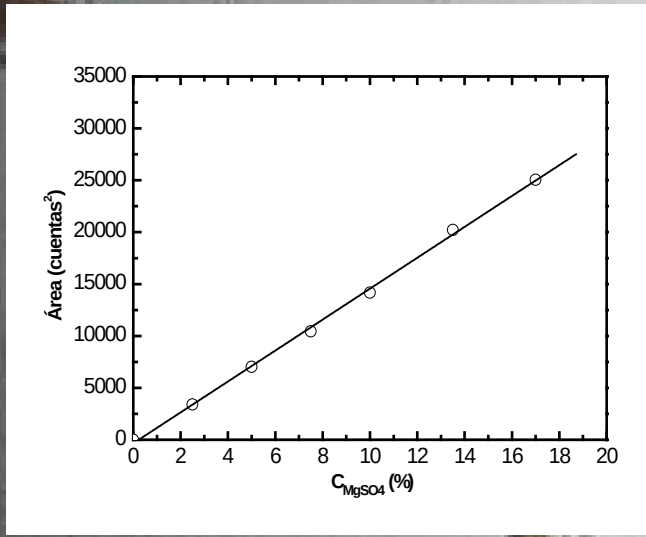
$$I = N_i \sigma(\nu_{ex}) \nu_{ex}^{\ 4} E_0 e^{-E_i / kT}$$

Intensidades o
Áreas relativas
Varía en función de:
1. P
2. T
3 concentración de sales





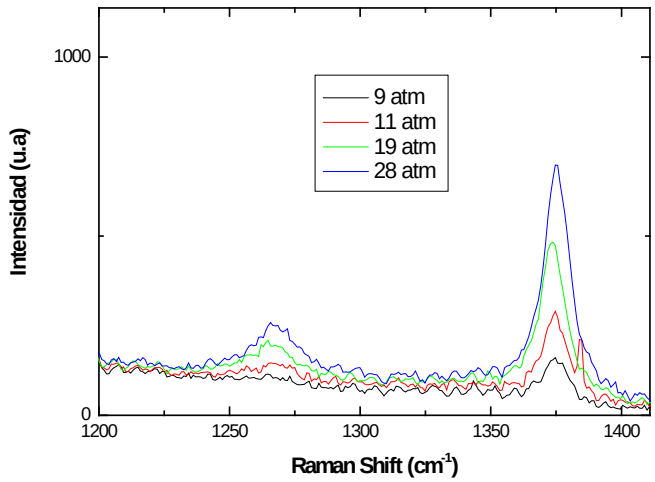
3325 cm^{-1}

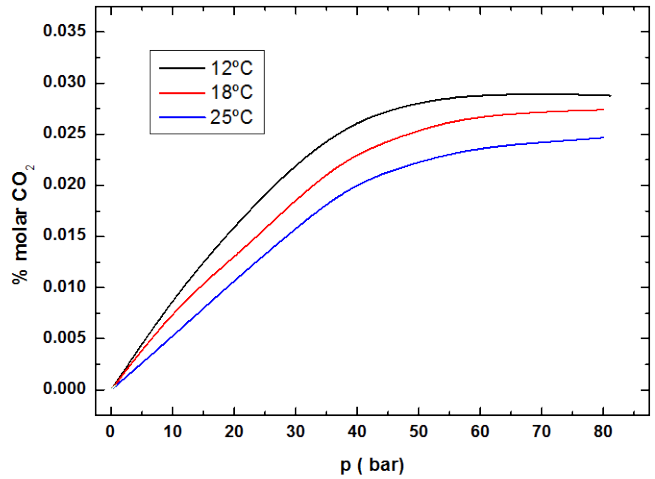


Calibrado

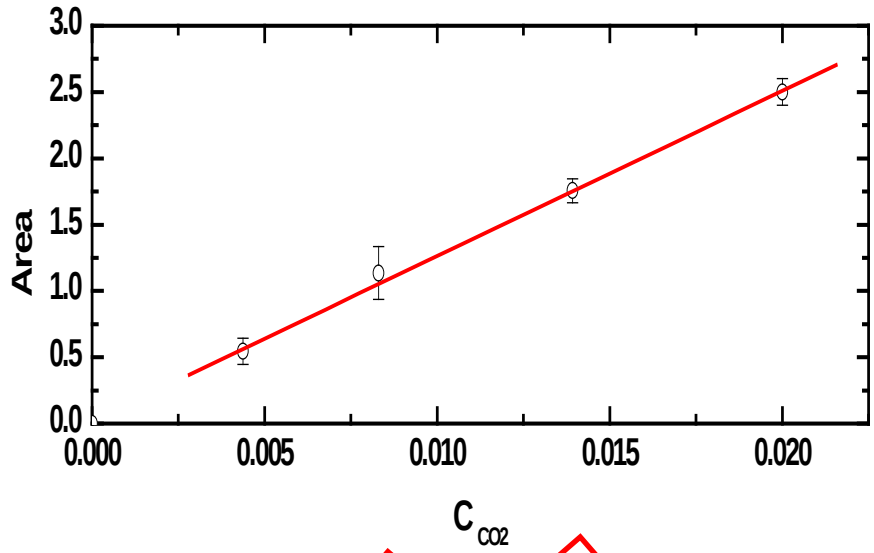
Calibración para CO_2

- $CO_2(g) \rightarrow CO_2(ac)$ vs. P, T en H_2O





Solubilidad del $CO_2(g)$ en disoluciones



Carbonatos en tierra primitiva

Clatratos

GRACIAS POR SU ATENCIÓN

www.malta-consolider.com

CONSOLIDER MALTA

Matter at High Pressure

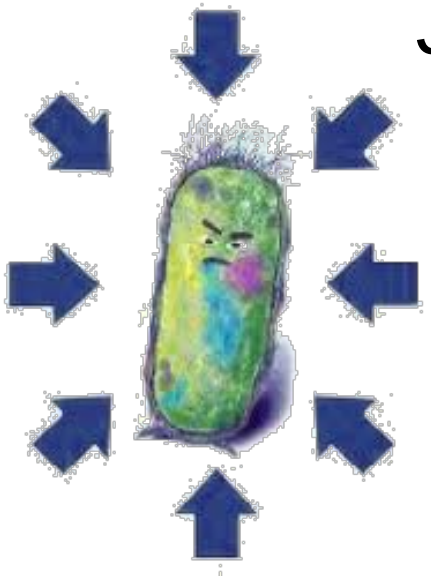
PROGRAMA INGENIO 2010

CAB

ASOCIADO AL NASA ASTROBIOLOGY INSTITUTE

Muerte y daño subletal causados por alta presión

Jordi Saldo Periago



CERPTA-UAB

ww.cerpta.com

Planta de Tecnologia dels Aliments UAB

Universitat Autònoma de Barcelona

TECNIO Be tech. Be competitive

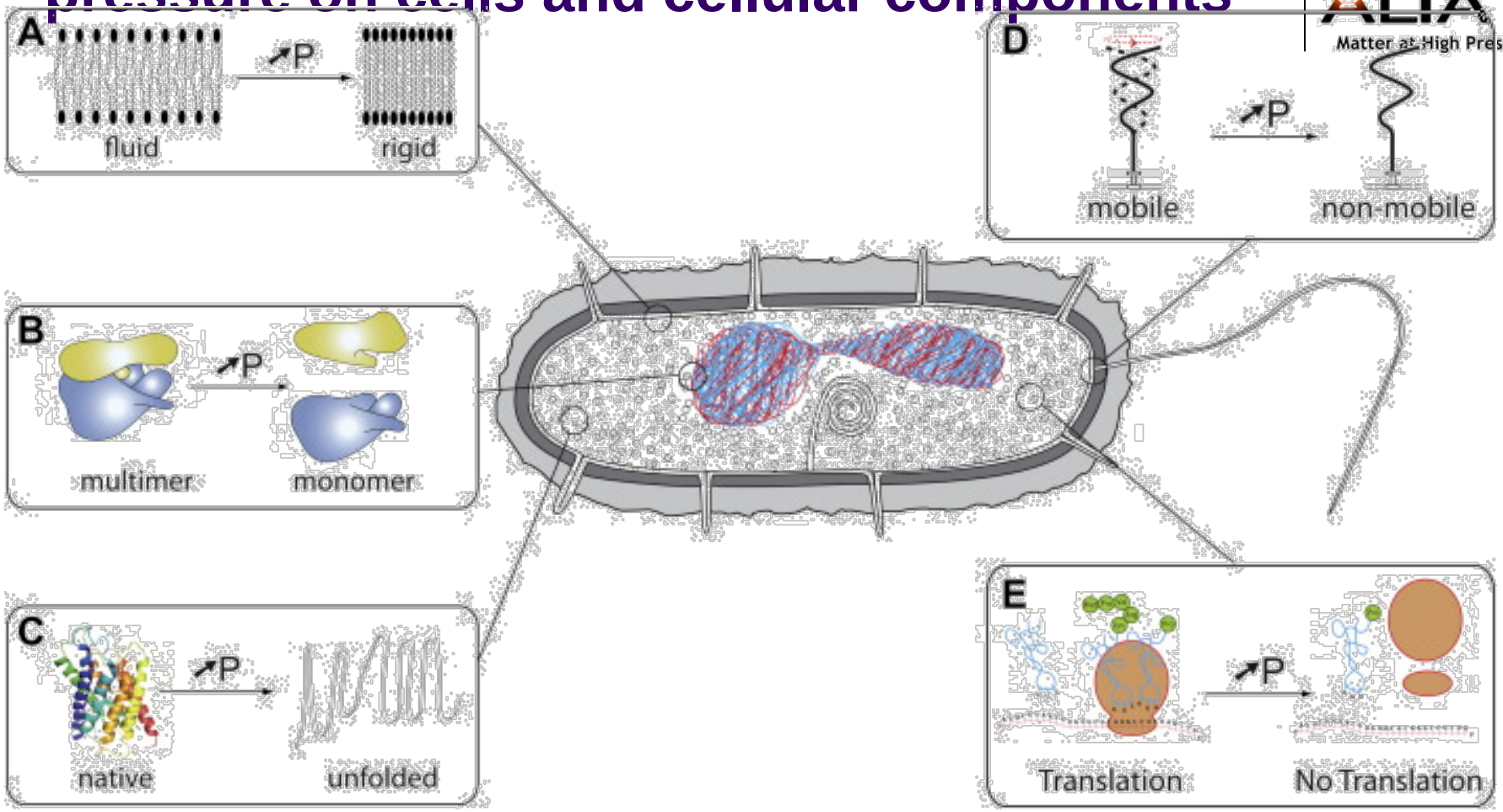
XaRTA Xarxa de Referència en Tecnologia dels Aliments de la Generalitat de Catalunya

MIRAFLORES 2011

Effects of high pressure on macromolecules

- Most of pressure effects on macromolecules are transient
  - Changes on quaternary and tertiary protein conformation
  - Depolymerisation
  - Lipid crystallisation

Examples of the effects of high hydrostatic pressure on cells and cellular components

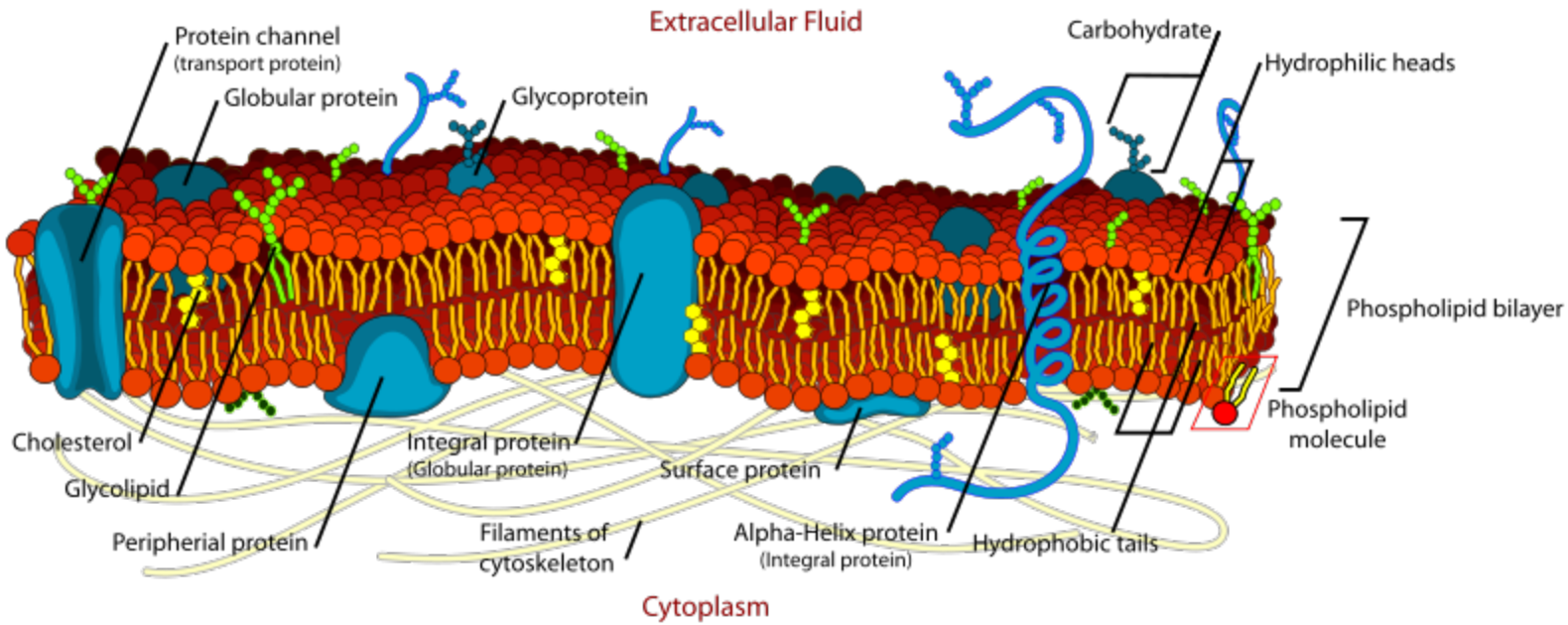


A: lipids in membranes
C: protein

B: multimeric protein assemblages
E: protein translation by ribosomes

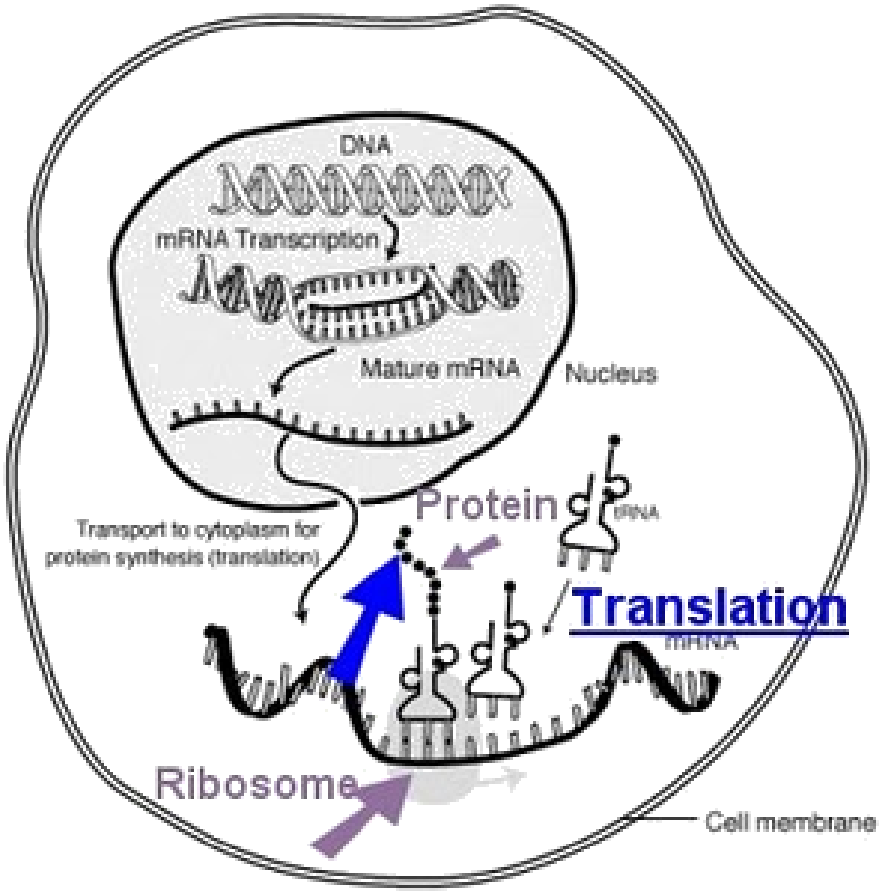
Oger & Jebba (2010) Research in Microbiology. doi:10.1016/j.resmic.2010.09.017

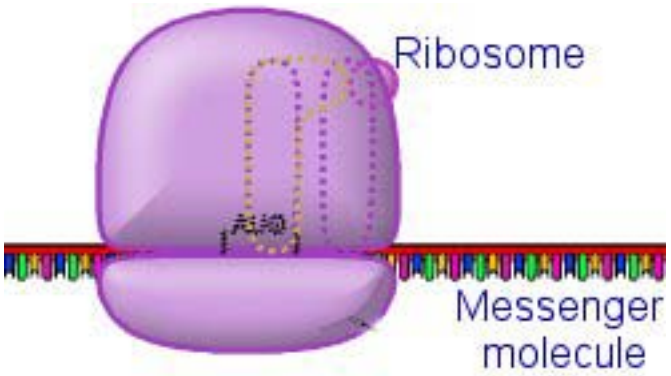
Membrane



http://en.wikipedia.org/wiki/Image:Cell_membrane_detailed_diagram.svg

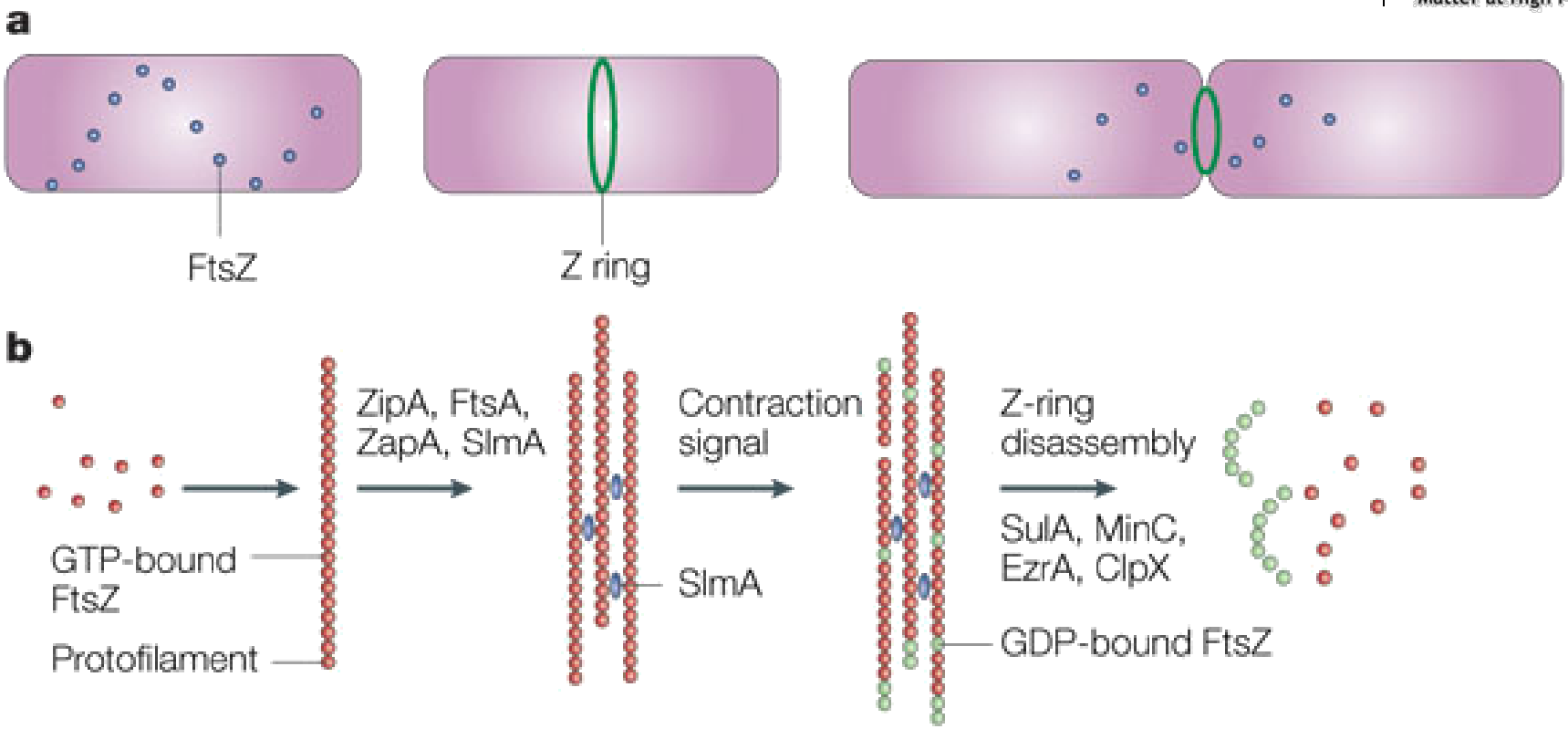
Protein synthesis system





Andrew Rowler http://idintheuk.blogspot.com/2007_01_01_archive.html

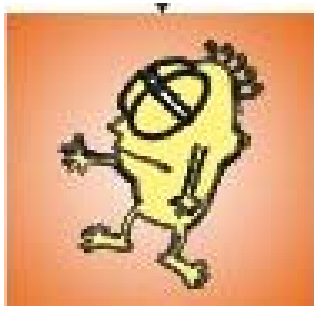
Cell division



Nature Reviews | Molecular Cell Biology

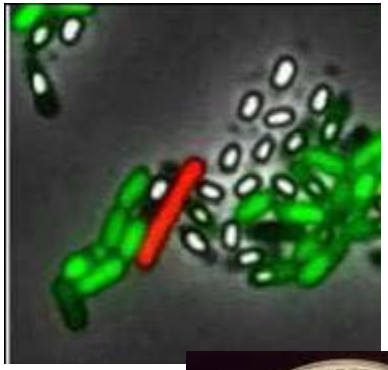
Microbial sub-populations after pressure treatment

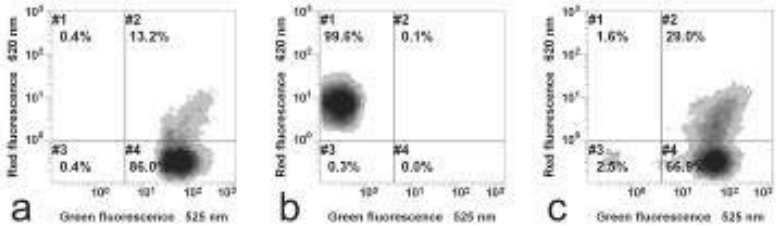
- Healthy
- Stressed
- Injured
- Dead



Techniques to distinguish between states

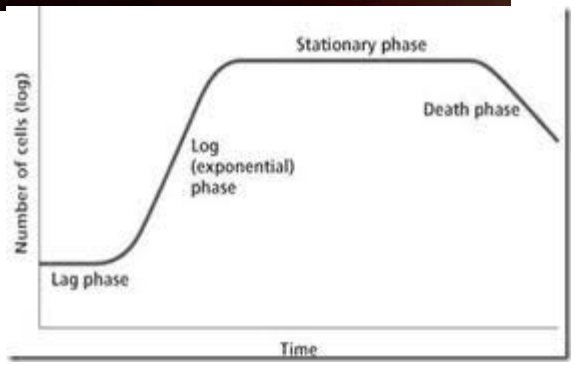
- Dyes
  - Flow cytometry



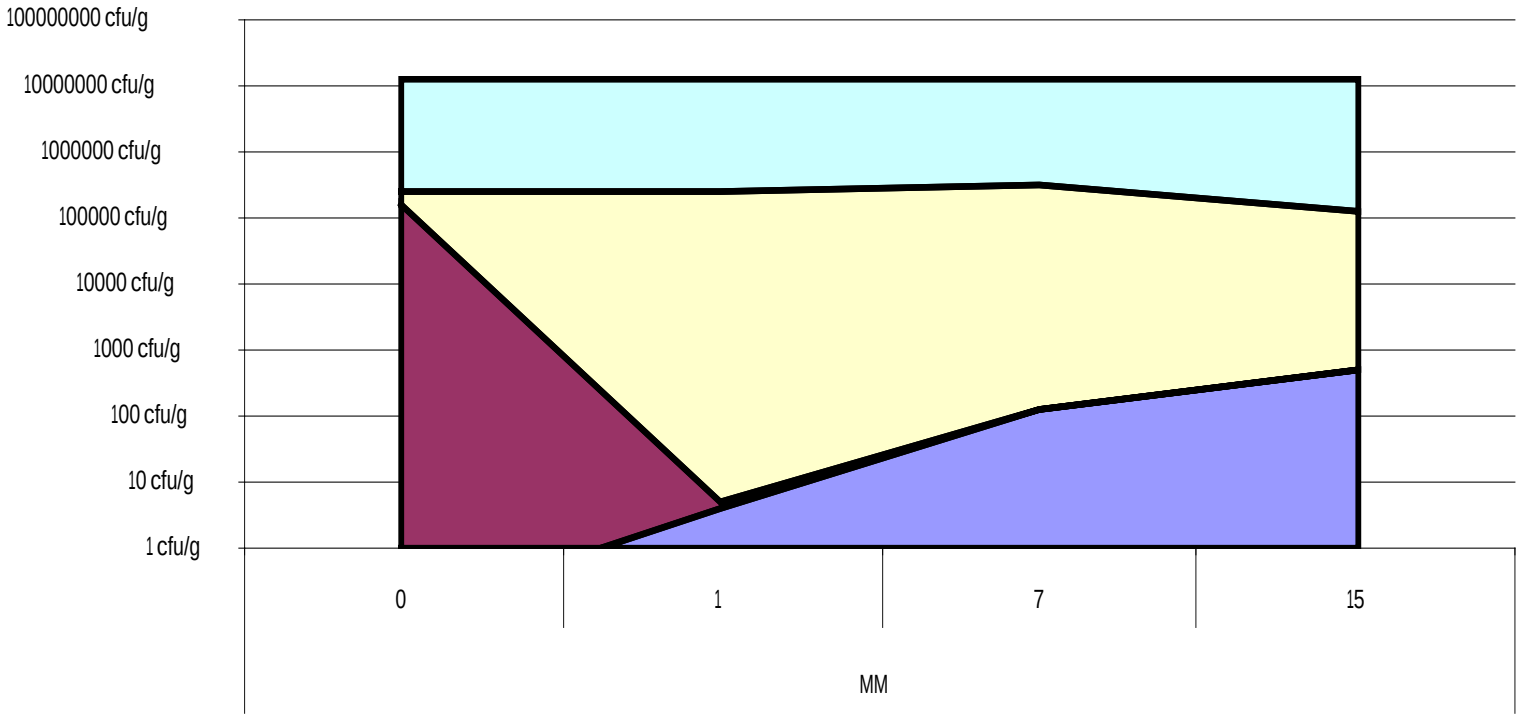


- Differential growth

- Lag phase



Matrix | Tris Buffer

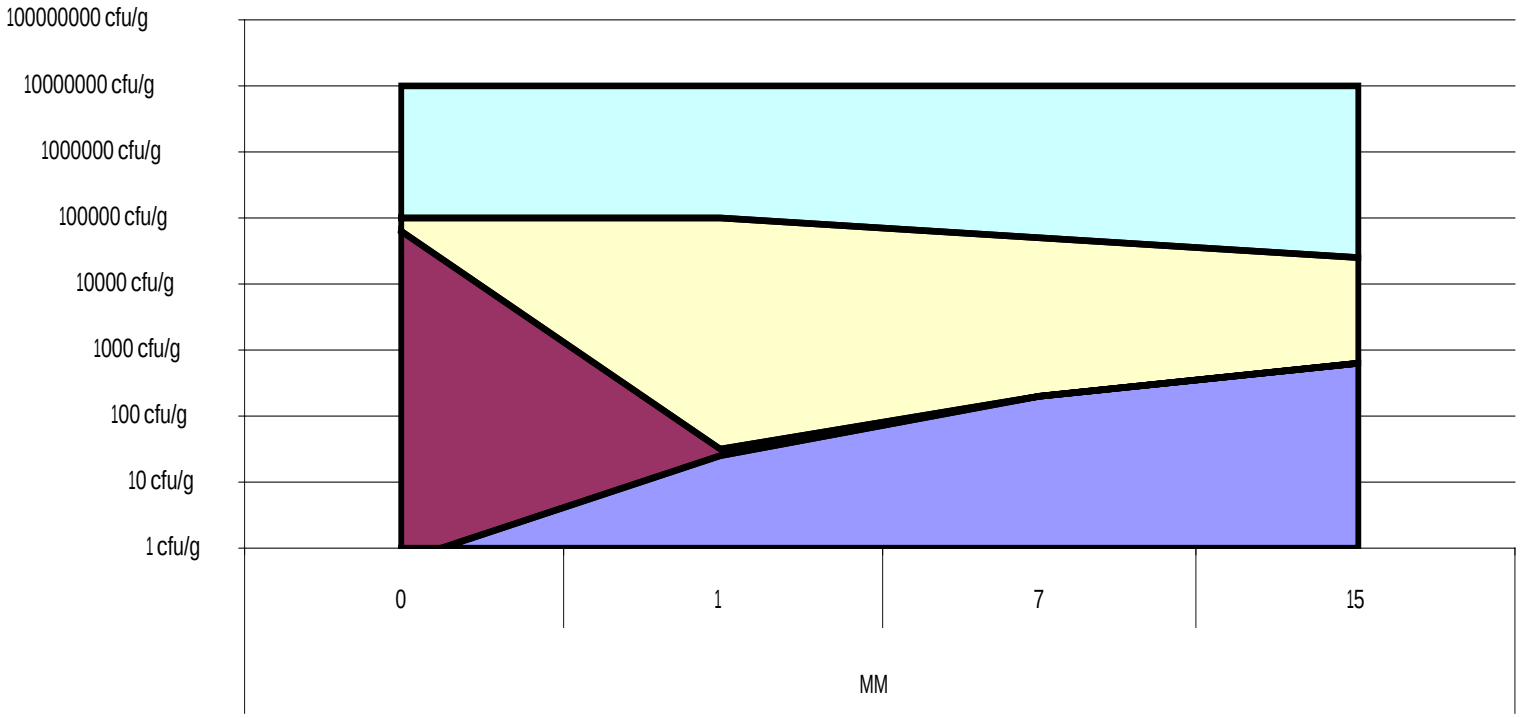


Dades

- Dead cells
- Injured cells
- Stressed cells
- Healthy cells

Code | Storage Days

Matrix | Skim Milk

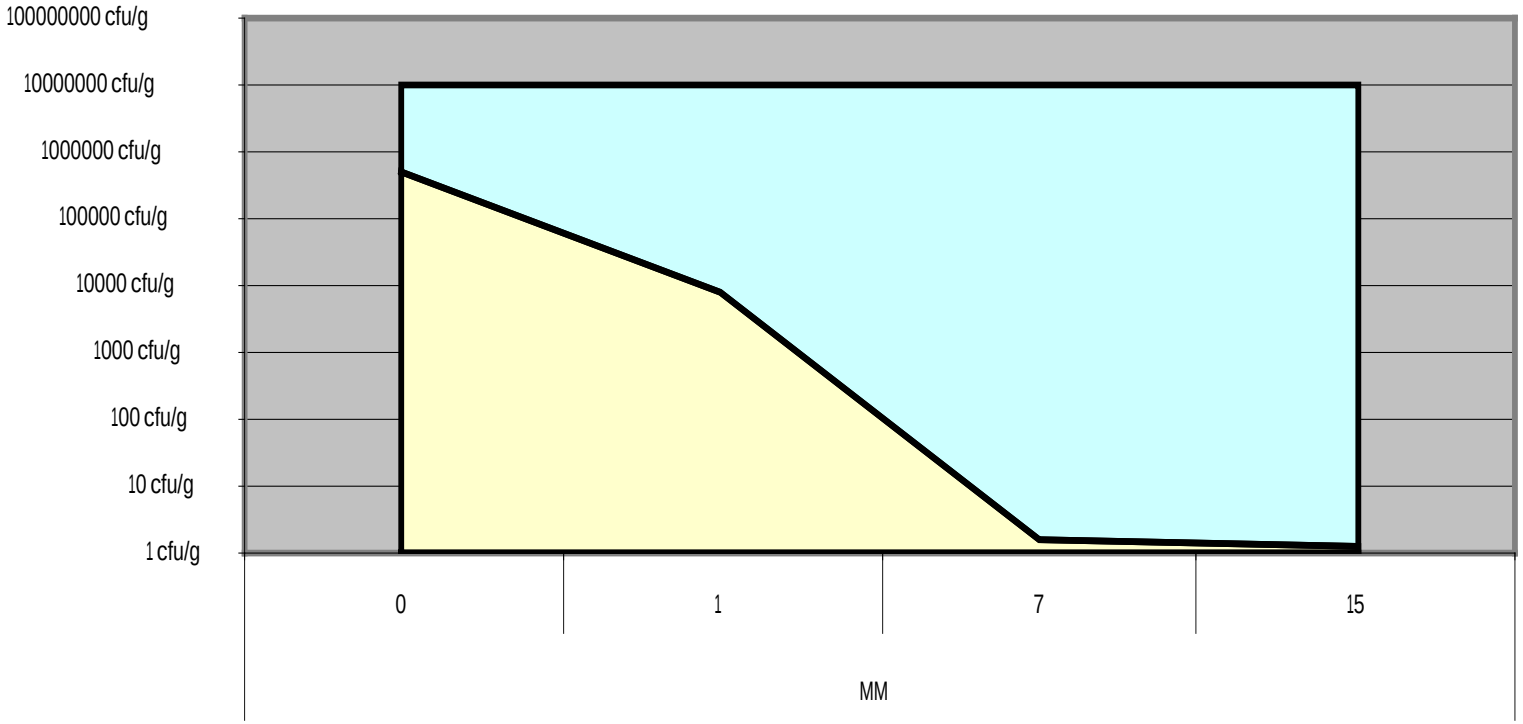


Dades

- Dead cells
- Injured cells
- Stressed cells
- Healthy cells

Code | Storage Days

Matrix | Orange Juice



Dades

- Dead cells
- Injured cells
- Stressed cells
- Healthy cells

Code | Storage Days

SISTEMAS ACUOSOS II. DISOLUCIONES

Pedro D. Sanz

Lab. Alta Presión Hidrostática en Alimentos
Departamento de Procesos
Instituto de Ciencia y Tecnología de los Alimentos y Nutrición (ICTAN)
Consejo Superior de Investigaciones Científicas
C/ José Antonio Nováis, 10
Ciudad Universitaria
E-28040 Madrid

www.malta-consolider.com
CONSOLIDER MALTA
Matter at High Pressure
INGENIO 2010

MINISTERIO DE CIENCIA E INNOVACIÓN

CSIC
CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS
INSTITUTO DEL FRIO

Miraflores de la Sierra, 24 de Enero de 2010

Materias primas

ALTA
SEGURIDAD MICROBIOLÓGICA

Productos elaborados

PROCESADO DE ALIMENTOS

MÍNIMA ALTERACIÓN
CARACTERÍSTICAS
ORGANOLÉPTICAS Y NUTRICIONALES

PROLONGACIÓN
VIDA ÚTIL

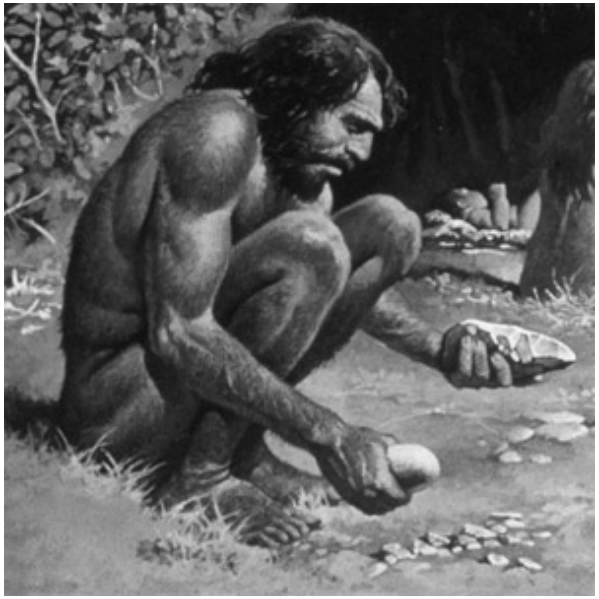
Secado Cocción

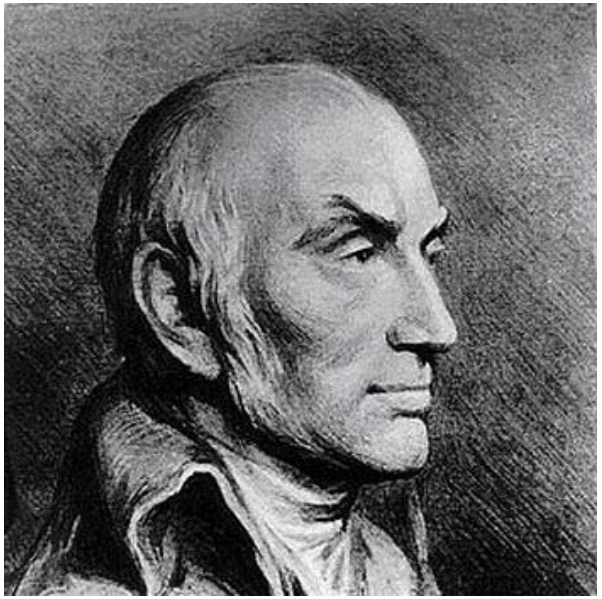
Congelación

Esterilización

Pasterización

Pascalización





Homo Sapiens

- 25 000

Appert

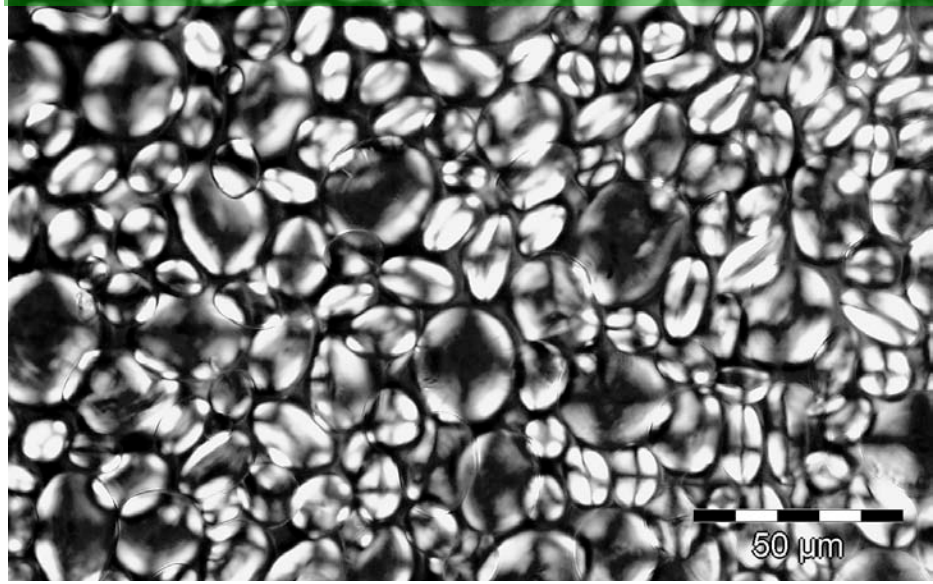
1800

Bridgman

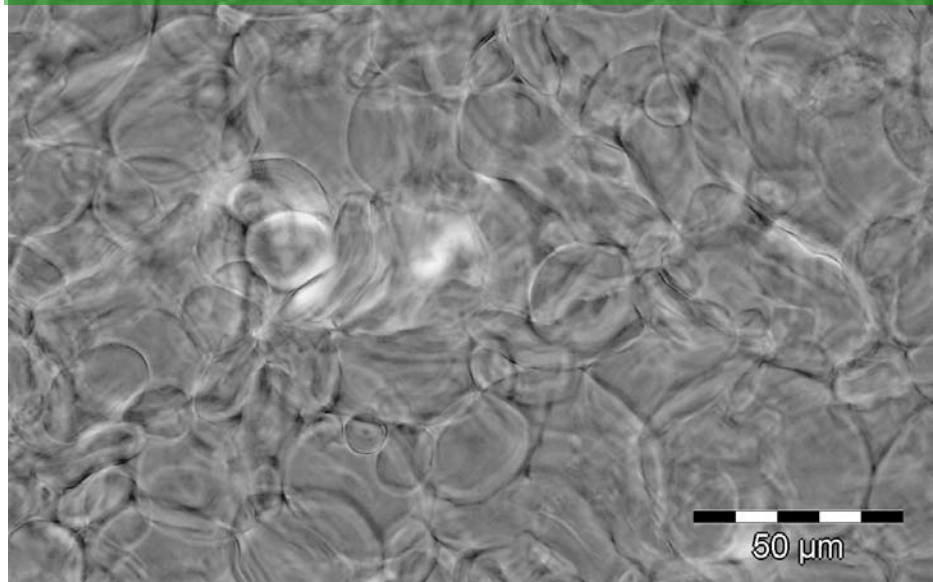
1930

Evolución de las tecnologías de conservación de alimentos

0.1MPa, 40ºC, 20min

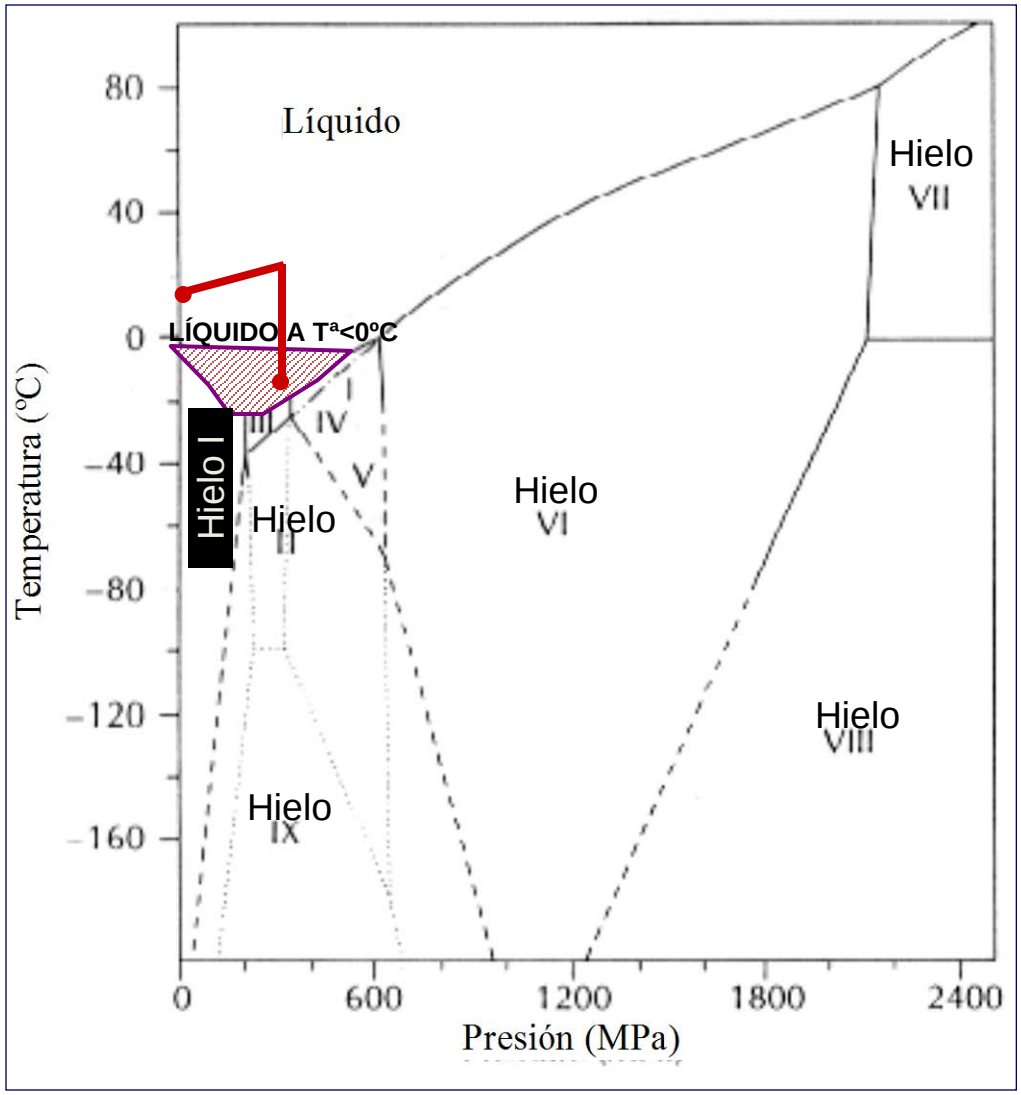


400MPa, 40ºC, 20min



Almidón
de trigo

TIPOS DE PROCESOS



- ***Conservación en estado no congelado*** a temperaturas menores de 0ºC
- ***Congelación*** con alta presión
- ***Descongelación*** con alta presión

ALTA PRESIÓN HIDROSTÁTICA:

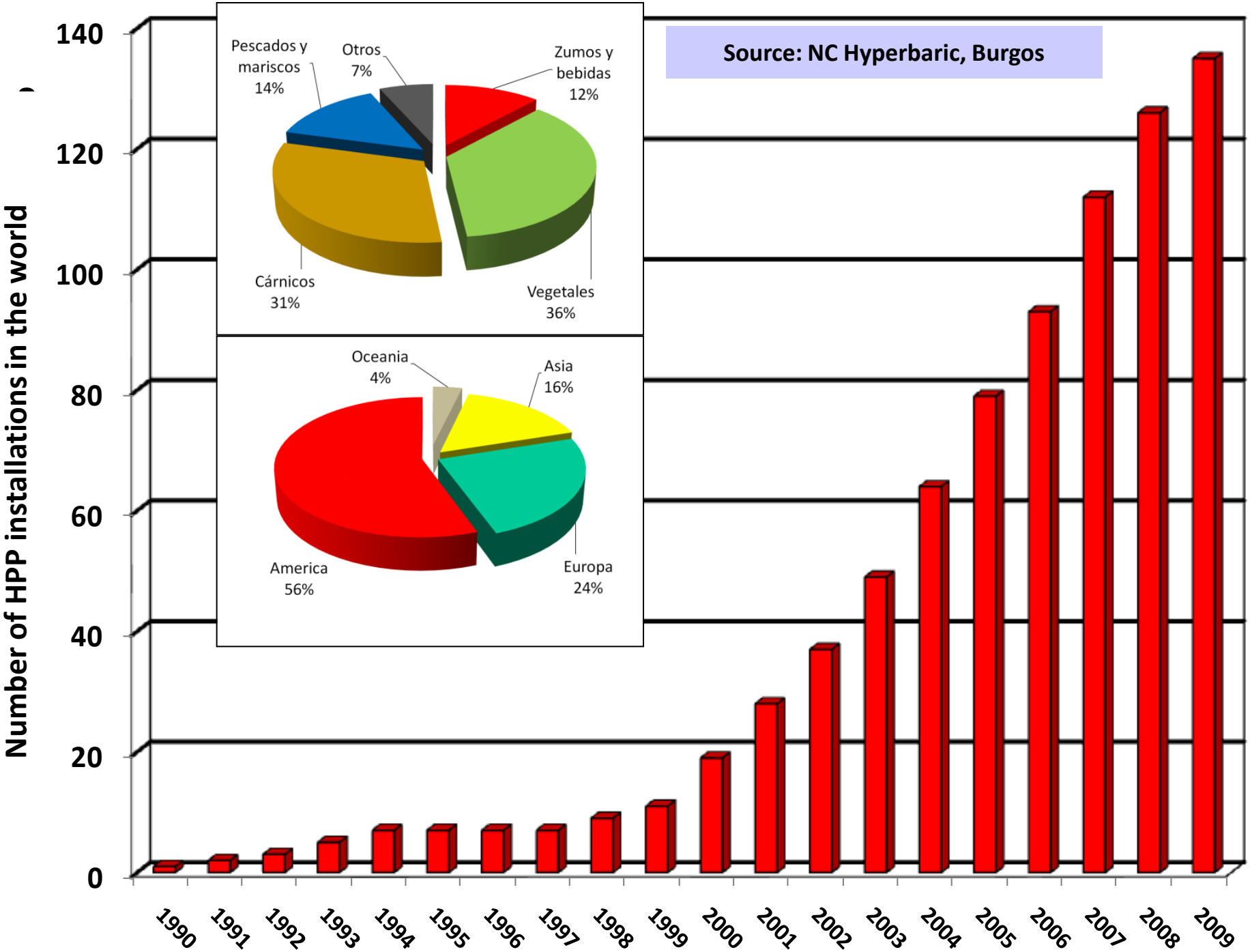
Tecnología **emergente**

Prolongación vida útil de los alimentos

Inactivación microbiana y/o enzimática

Bajo consumo energético

Respeto al **medio ambiente**


Source: NC Hyperbaric, Burgos
Number of HPP installations in the world
140
120
100
80
60
40
20
0
1990
1991
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
2005
2006
2007
2008
2009
Pescados y mariscos 14%
Otros 7%
Zumos y bebidas 12%
Cárnicos 31%
Vegetales 36%
Oceania 4%
Asia 16%
America 56%
Europa 24%

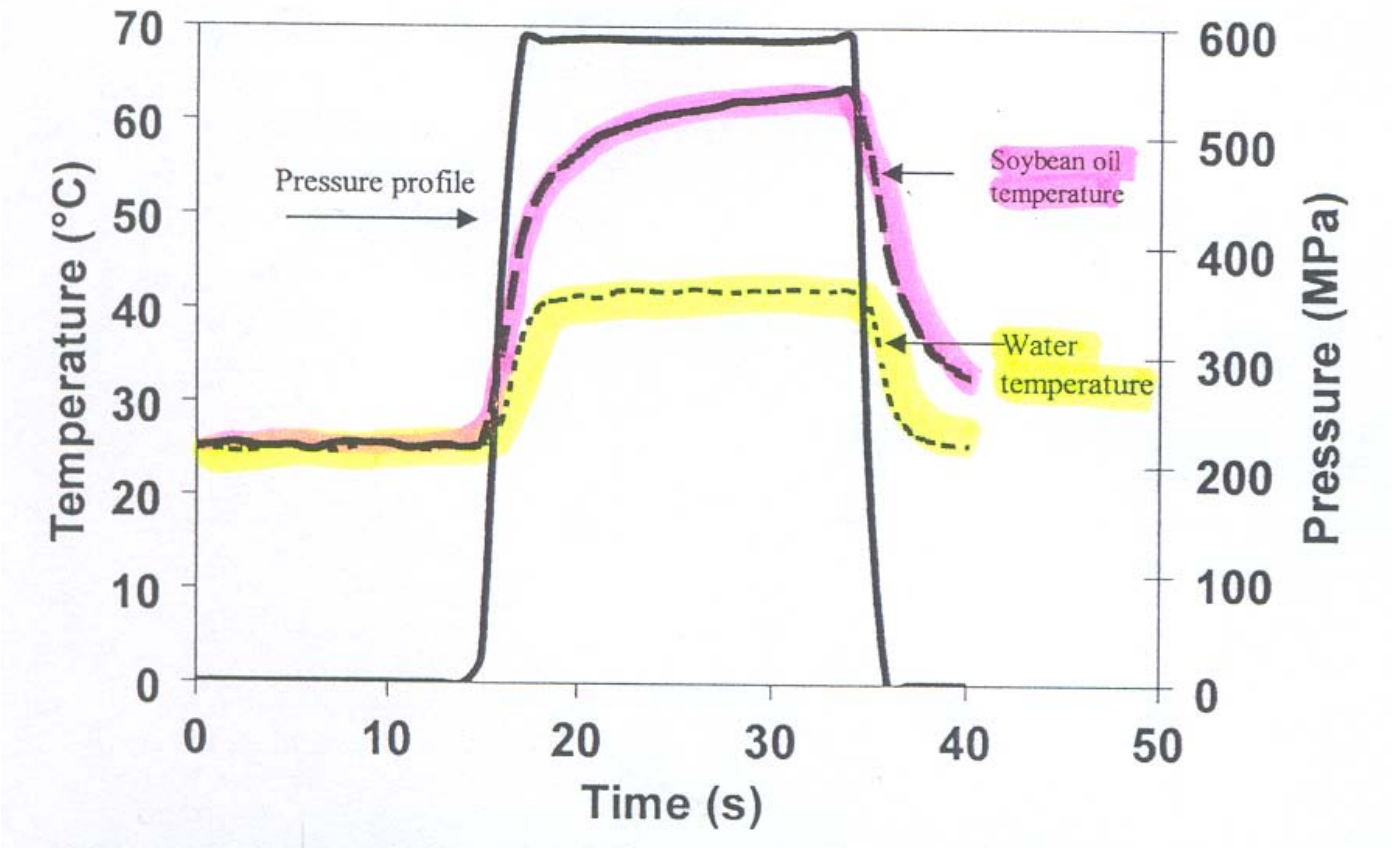
SISTEMAS ACUOSOS II. DISOLUCIONES

I. WATER AND LIFE-RELATED SYSTEMS

b. High pressure effects on aqueous solutions: salts, supramolecular aggregates and proteins

ALTAS PRESIONES

[Rasanayagam y col., 2003]

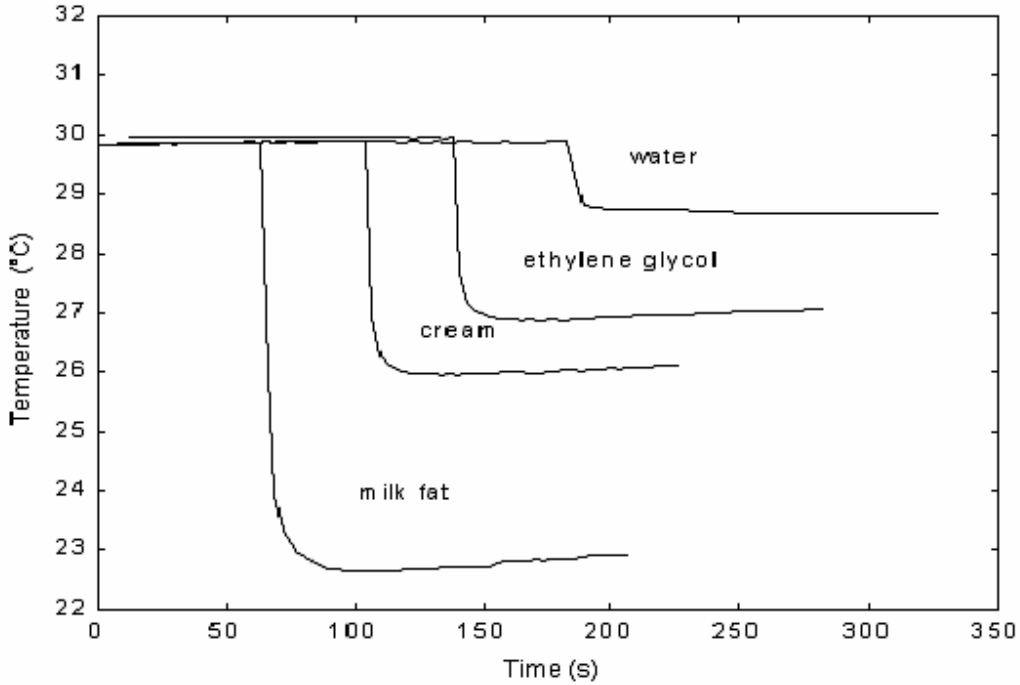


Aumento de temperatura durante la compresión

Pascal's Law Instantaneous

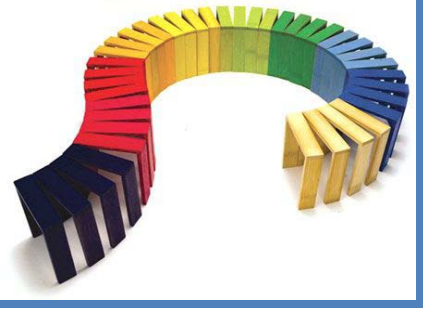
$$\frac{dT}{dP} = \frac{\alpha \cdot T_k \cdot V}{C_p}$$

slow



Otero, L.; Molina-García, A. D. & Sanz, P. D. "Thermal effect in foods during quasi-adiabatic pressure treatments" Innovative Food Science & Emerging Technologies, 1 (2), 119-126. 2000

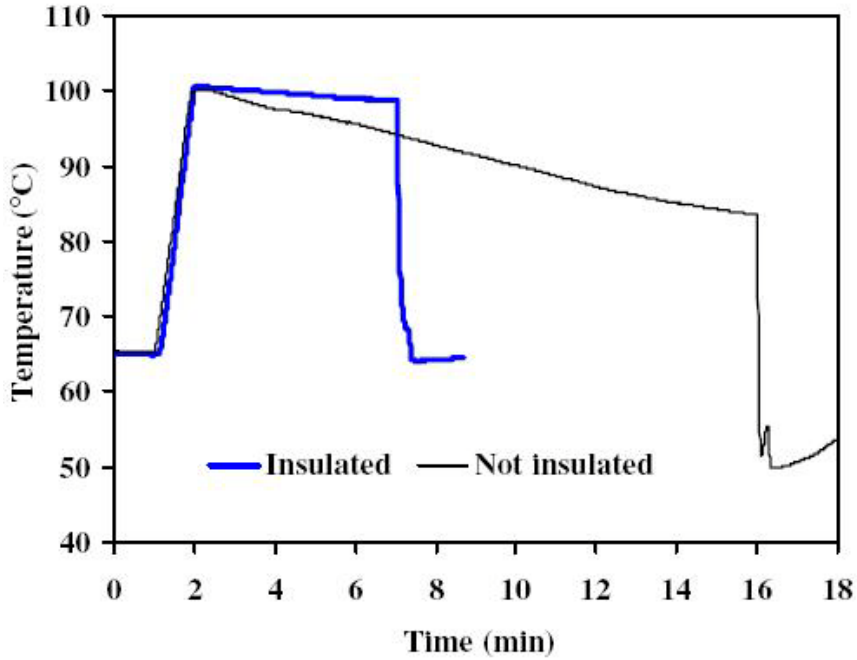
Expansion of 50 MPa at initial conditions of 30°C and 50

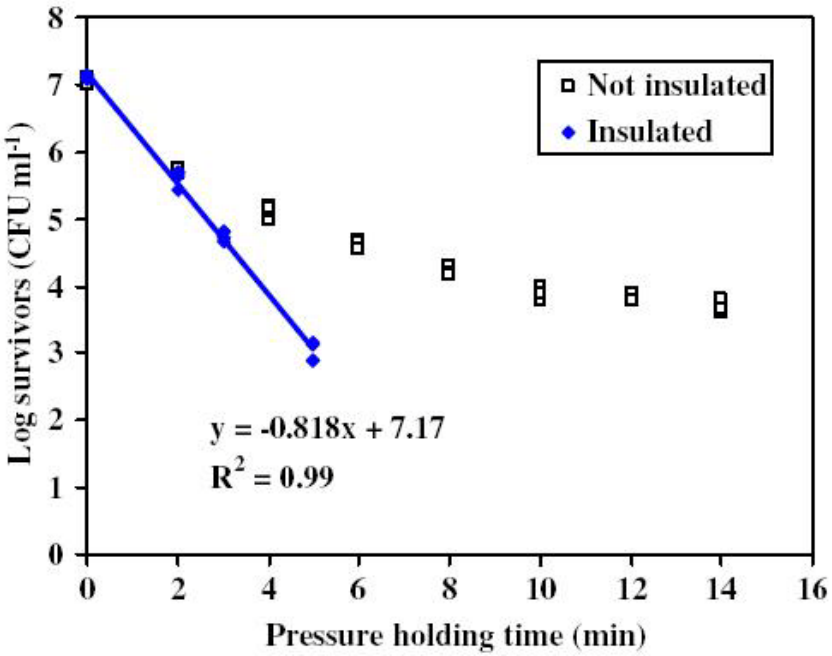


Tecnologías combinadas

PROCESADO TÉRMICO ASISTIDO POR PRESIÓN

Uniformidad térmica ESENCIAL

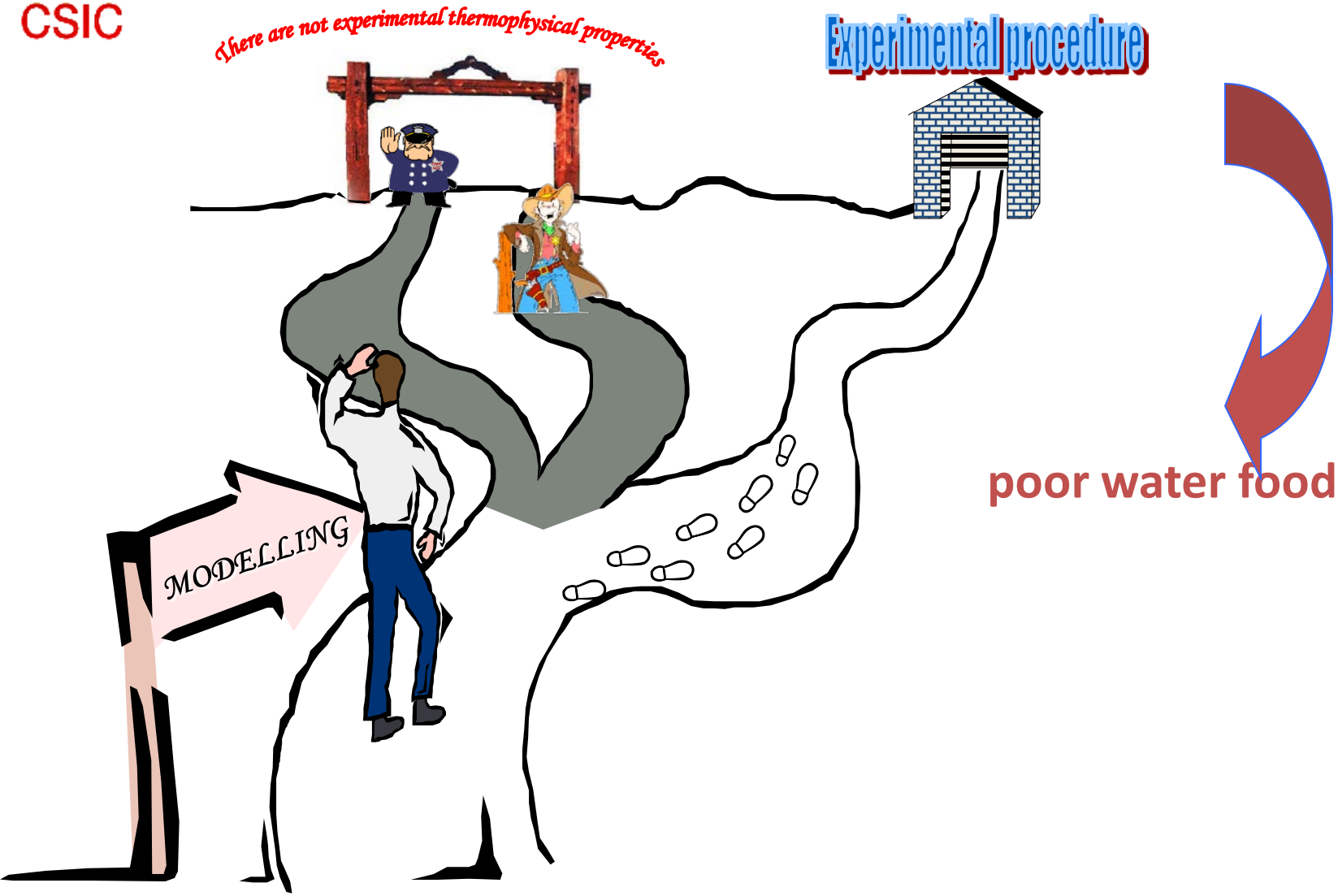




Inactivación de esporas de *Clostridium sporogenes* (PA 3679) en leche tratada a 900 MPa/ 100ºC

[Shao y col., 2004]

Colaboración con UCM-Momat



Objetivos conseguidos

SOLID SAMPLE

$$\rho C_p \frac{\partial T}{\partial t} - \nabla \cdot (k \nabla T) = Q_p$$

$$\frac{dT}{dP} = \frac{\alpha \cdot T_k \cdot V}{C_p}$$

PRESSURIZATION FLUID

$$\rho \frac{\partial \mathbf{u}}{\partial t} - \nabla \cdot \eta (\nabla \mathbf{u} + (\nabla \mathbf{u})^T) + \rho (\mathbf{u} \cdot \nabla) \mathbf{u} + \nabla P = \mathbf{g} \rho$$

$$\nabla \cdot (\rho \mathbf{u}) = 0$$

$$\rho C_p \frac{\partial T}{\partial t} + \nabla \cdot (-k \nabla T + \rho C_p \mathbf{u} T) = Q_p$$

Control

150 MPa

200 MPa

250 MPa

300 MPa

350 MPa

400 MPa

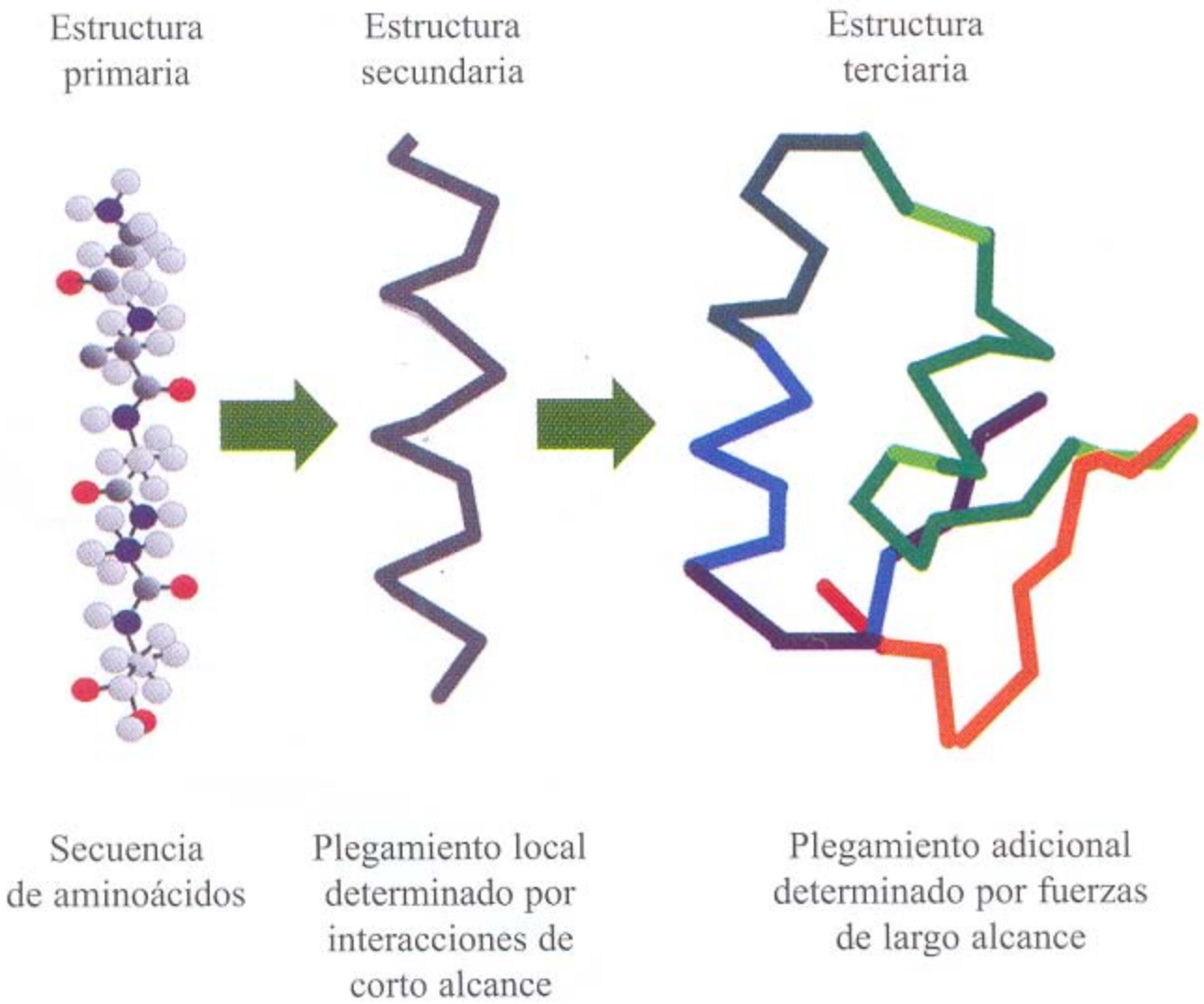
450 MPa

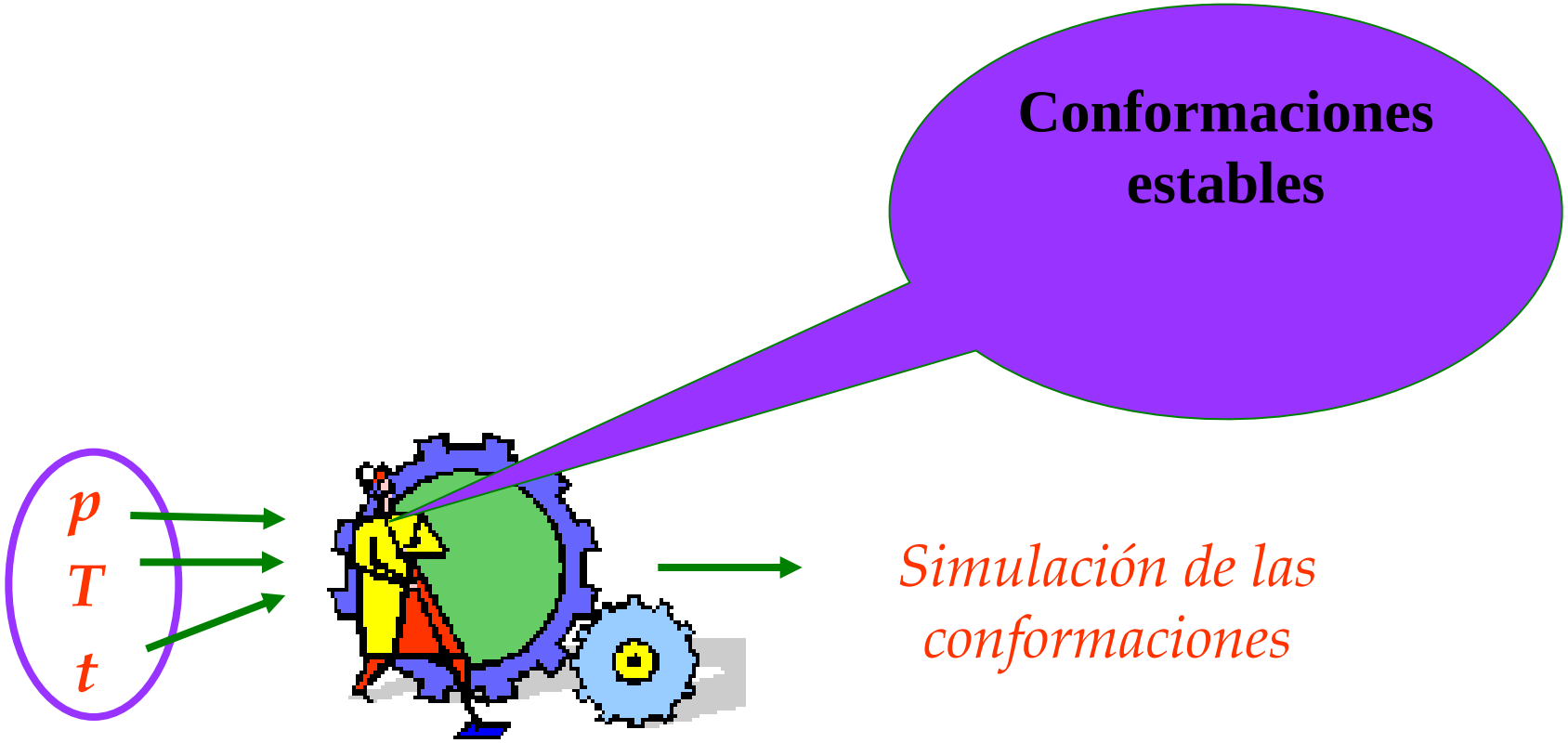
500 MPa

550 MPa

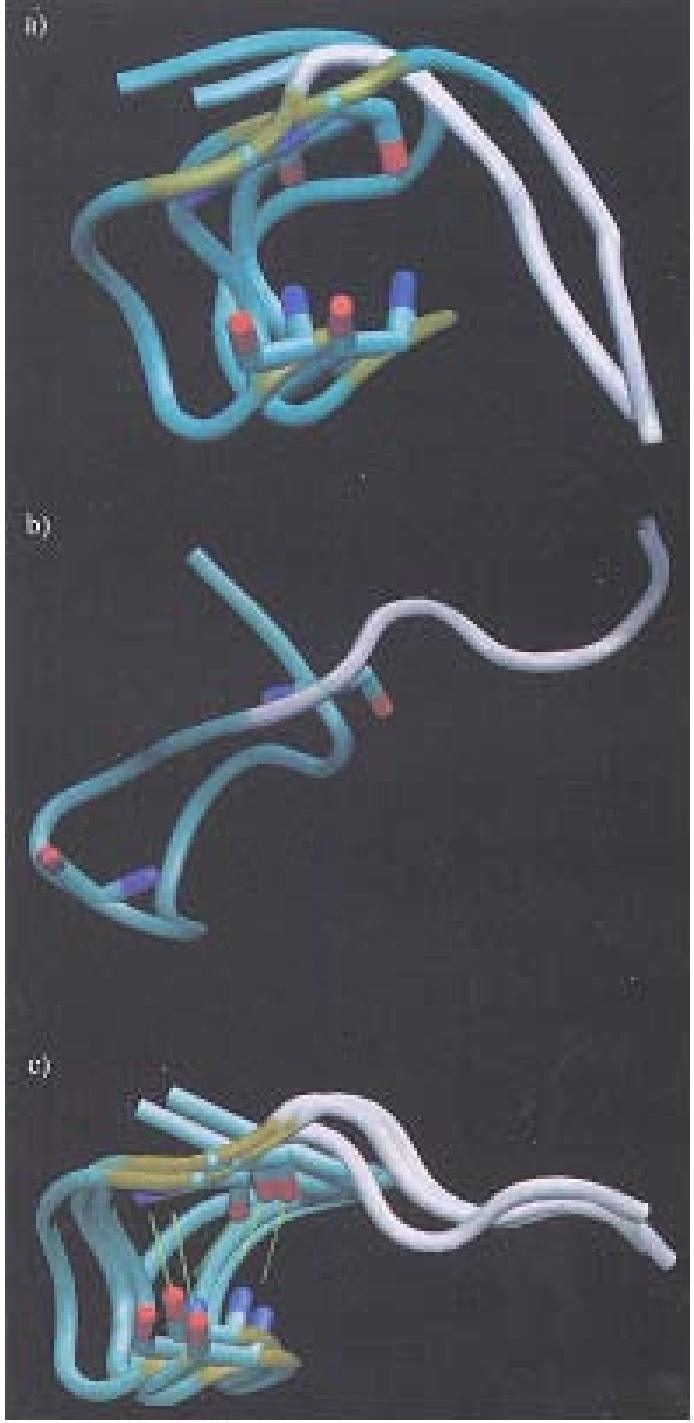
600 MPa

Control


Estructura primaria
Estructura secundaria
Estructura terciaria
Secuencia de aminoácidos
Plegamiento local determinado por interacciones de corto alcance
Plegamiento adicional determinado por fuerzas de largo alcance


Conformaciones estables
p
T
t
Simulación de las conformaciones

Un polipéctido con tres conformaciones de distinto tiempo de vida



Colaboración con UCM-SIMPOL

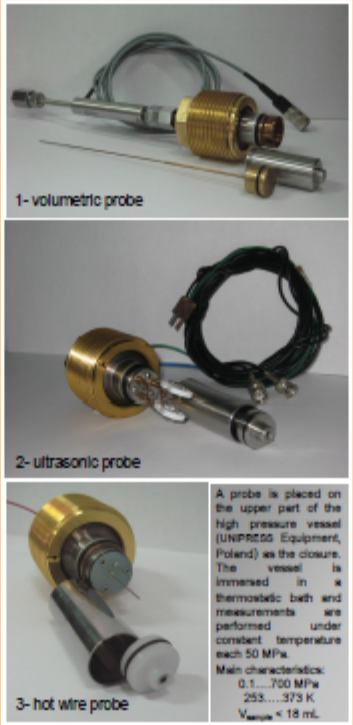
Colaboración con UCM

b. High pressure effects on aqueous solutions of supramolecular aggregates and proteins

Data on the physical properties of food and food components are still scarce at high pressure. These data are needed to develop and improve food high pressure processes.

Pressure dependence of density, isothermal compressibility, thermal expansivity, specific heat and thermal conductivity are required for numerical simulation of heat and mass transfers and of the coupled microorganism inactivation during high pressure treatment. In this way, treatment uniformity can be determined.

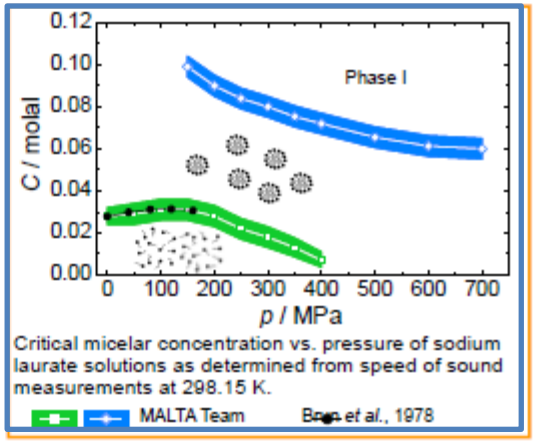
Pressure effects on protein conformation and on aggregation phenomena can be assessed by volumetric and ultrasounds techniques in situ. The apparent properties of food components in aqueous solution provide information about their behaviour with pressure in foods. Speed of sound also allows for the determination of critical micelar concentration under pressure.



High Pressure Measuring Probes

Specific volume and isothermal compressibility were determined for a wide variety of liquid foods and pressure transmitting fluids: pure water, tomato paste, orange juice, whole and skim milk, sodium caseinate aqueous solutions, vegetable oils, silicone oil, castor oil, propylene glycol, ethylene glycol and ethanol.

Ultrasonic measurements were performed in tomato paste and sodium laurate aqueous solutions.



Critical micelar concentration vs. pressure of sodium laurate solutions as determined from speed of sound measurements at 298.15 K.

References

Otero *et al.* 2010. Modelling thermophysical properties of food under high pressure. *Crit. Rev. Food Sci.*, 50(4), 344-368.

Guignon *et al.* 2010. Volumetric properties of pressure-transmitting fluids up to 350 MPa: water, ethanol, ethylene glycol, propylene glycol, castor oil, silicone oil and some of their binary mixture. *J. Chem. Eng. Data*, 55, 3017-3023.

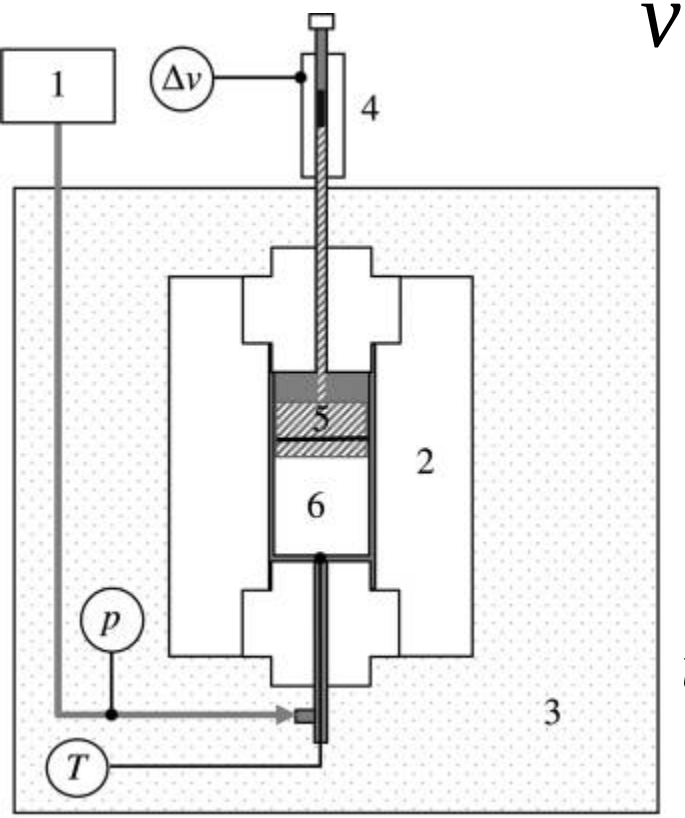
Guignon *et al.* 2010. Specific volume of liquid water from (253.15 to 323.15) K and pressures up to 350 MPa by volumetric measurements. *J. Chem. Eng. Data*, 55, 3338-3345.

Aparicio *et al.* 2011. Thermal expansion coefficient and heat capacity from sound velocity measurements in tomato paste from 0.1 MPa up to 350 MPa as a function of temperature. *J. Food Eng.*, *submitted*.

Colaboración con el Centro de Astrobiología (CSIC-INTA)

Evaluación de incertidumbres

$$v(p) = v_{ref} + \Delta v(p)$$



$$u_c(T) = \sqrt{u^2(T_s) + u^2(T_{cal}) + u^2(T_{rep})}$$

$$u_c(p) = \sqrt{u^2(p_s) + u^2(p_{cal}) + u^2(p_{rep})}$$

$$u_c(v) = \sqrt{u^2(v_{ref}) + u_c^2(\Delta v) + u^2(v_{uT}) + u^2(v_{up})}$$

Figure 1. Volumetric device: 1, high pressure hydraulic pump; 2, high pressure vessel;
3, thermostatic bath; 4, LVDT; 5, solid piston;
6, sample.

$$u_c(\Delta v) = \sqrt{\left(\frac{\partial(\Delta v)}{\partial k}\right)^2 \cdot u^2(k) + \left(\frac{\partial(\Delta v)}{\partial U_0}\right)^2 \cdot u^2(U_0) + \left(\frac{\partial(\Delta v)}{\partial U(p)}\right)^2 \cdot u^2(U(p)) + \left(\frac{\partial(\Delta v)}{\partial r}\right)^2 \cdot u^2(r) + \left(\frac{\partial(\Delta v)}{\partial m}\right)^2 \cdot u^2(m)}$$

Guignon, Bérengère; Aparicio, Cristina; Sanz, Pedro D.
“ Specific Volume of Liquid Water from (253 to 323) K and Pressures up to 350 MPa by Volumetric Measurements”.
Journal of Chemical & Engineering Data, 55, 3338–3345. 2010


High Pressure in Food Lab
ICTAN-CSIC

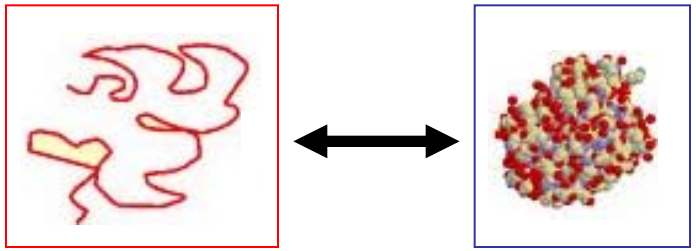
Influencia de la presión en la simulación del plegamiento de proteínas

Ramiro Perezzan Rodriguez

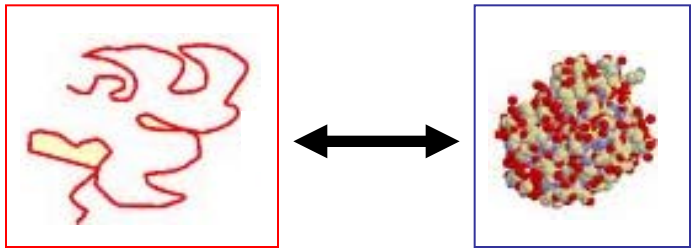
Comunidad de Madrid

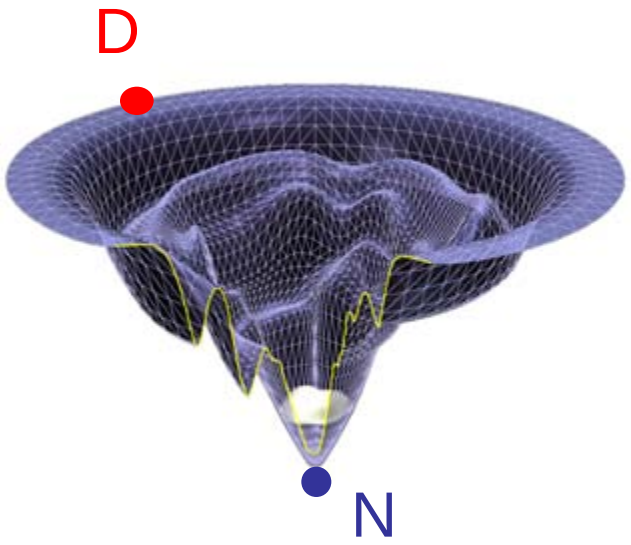
La Suma de Todos

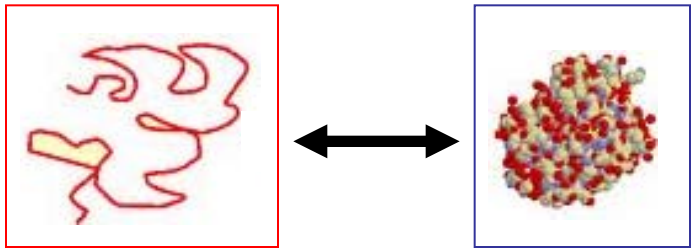
QUIMAPRES



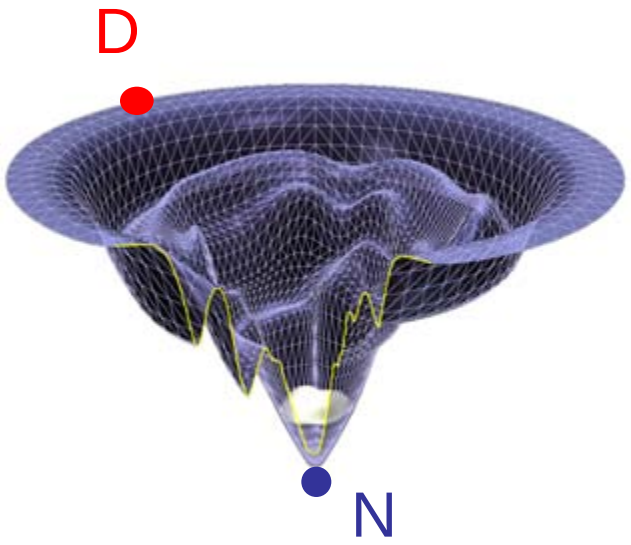
D N

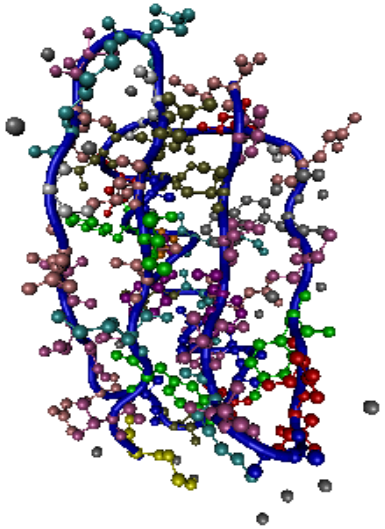

D
N


D
N

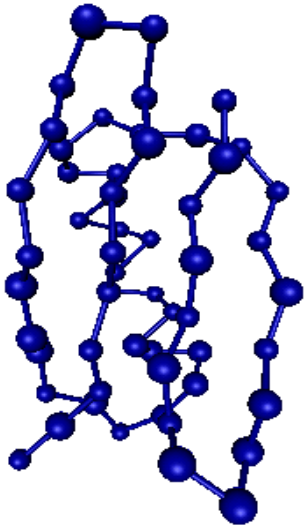


D N



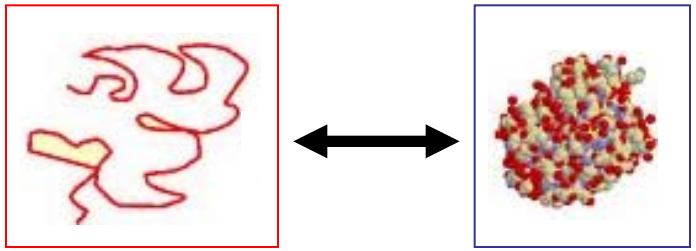


ESTRUCTURA PDB

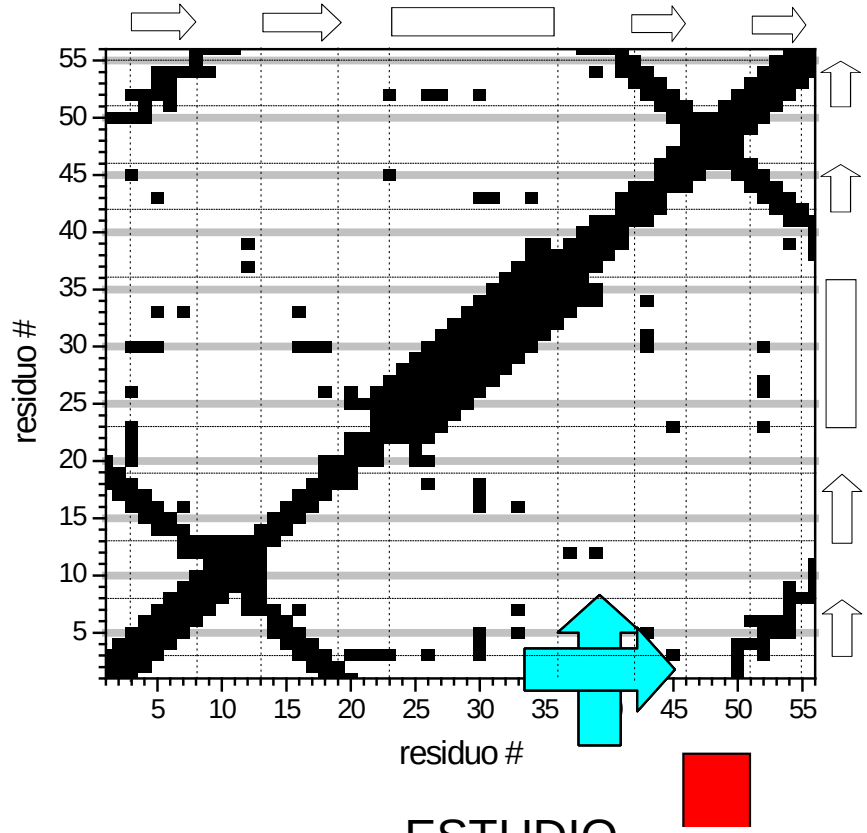


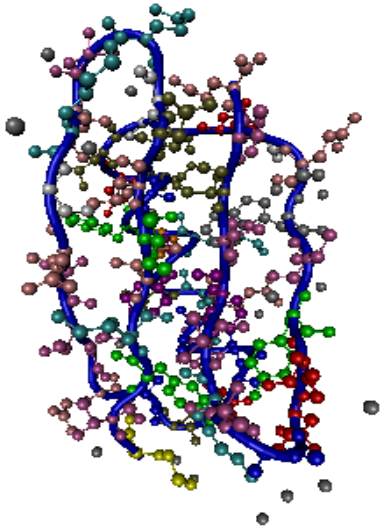
ESTRUCTURA C_α

ESTUDIO TERMODINAMICO DEL PROCESO DE PLEGAMIENTO MEDIANTE SIMULACION POR EL METODO DE MONTECARLO

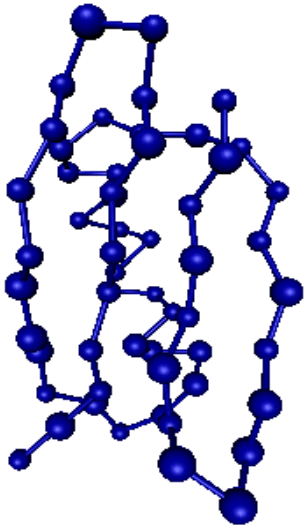


D N



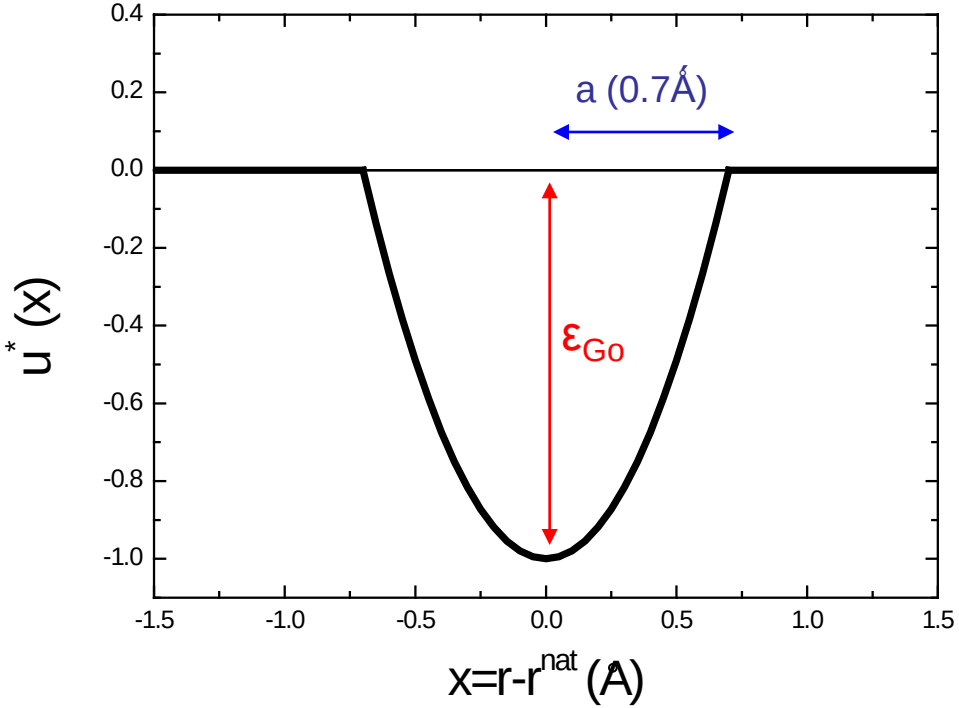


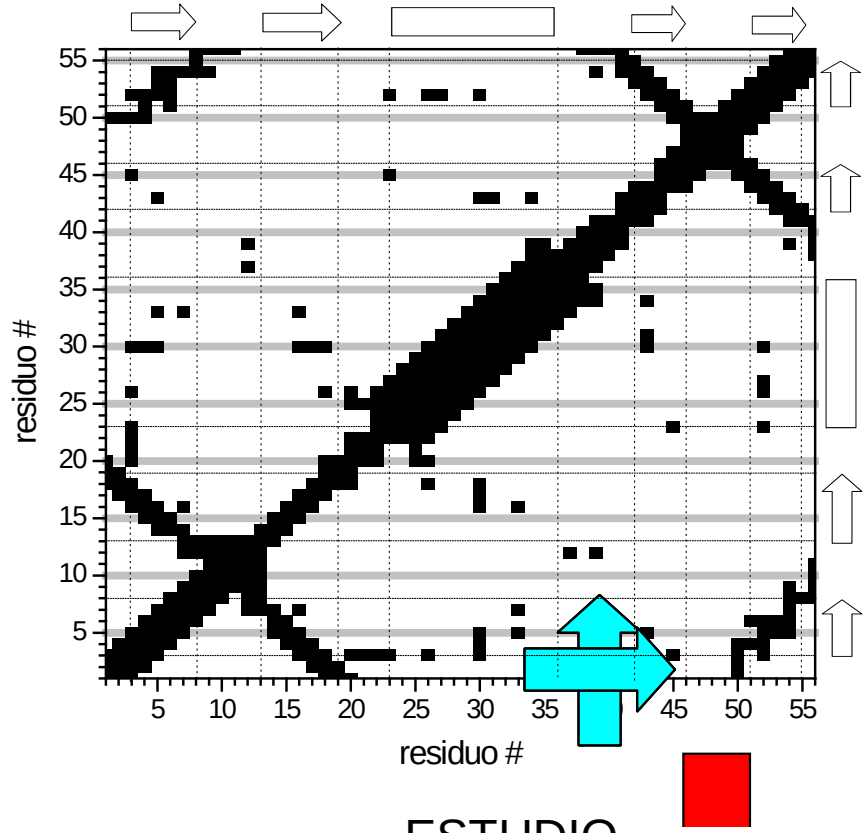
ESTRUCTURA PDB

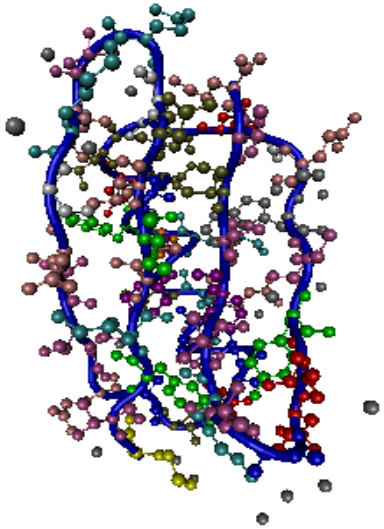


ESTRUCTURA C_α

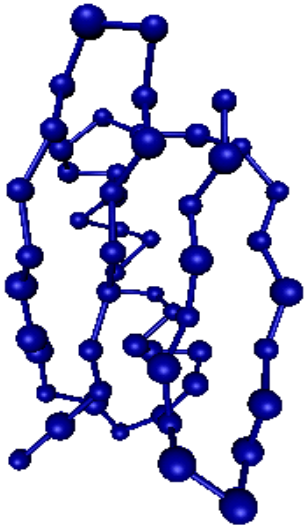
ESTUDIO TERMODINAMICO DEL PROCESO DE PLEGAMIENTO MEDIANTE SIMULACION POR EL METODO DE MONTECARLO







ESTRUCTURA PDB

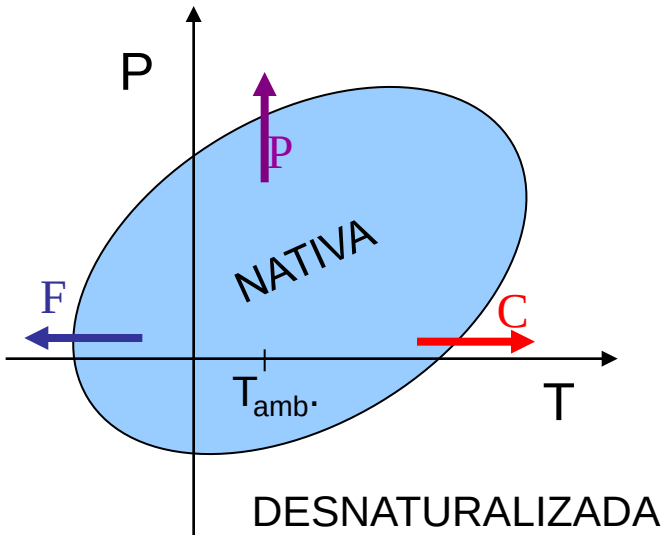


ESTRUCTURA C_α

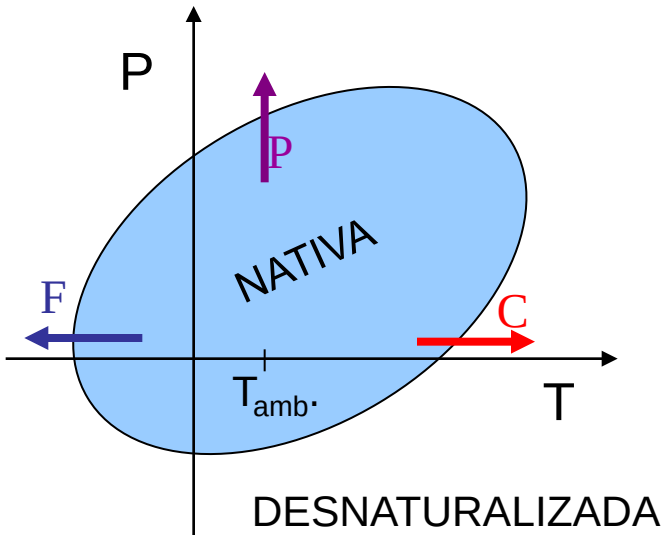
ESTUDIO TERMODINAMICO DEL PROCESO DE PLEGAMIENTO MEDIANTE SIMULACION POR EL METODO DE MONTECARLO

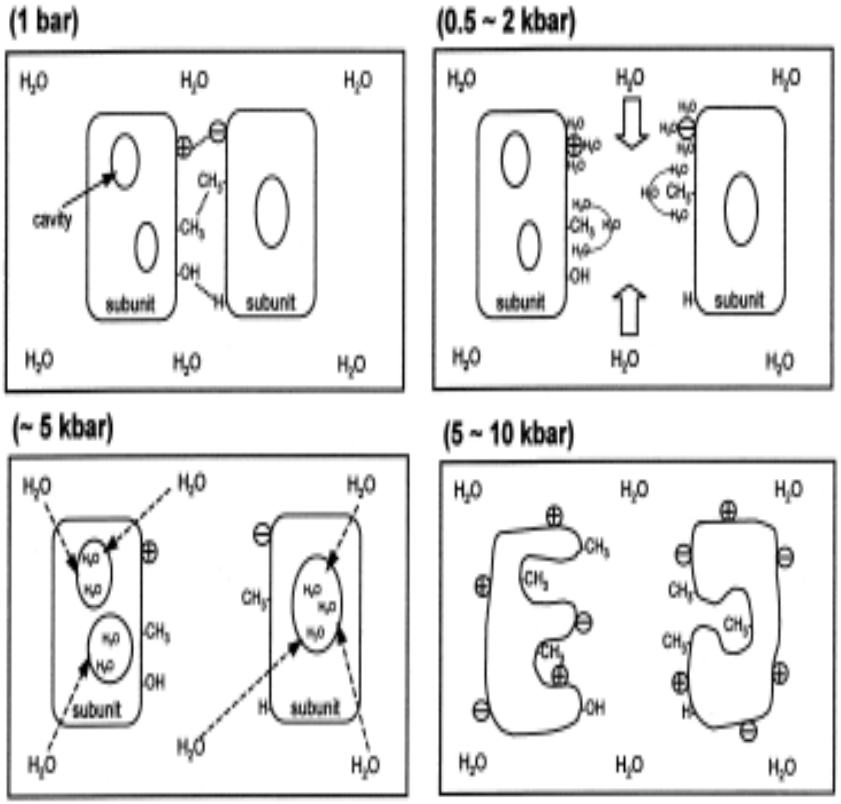
¿Cómo afecta la presión al plegamiento de proteínas?

¿Cómo afecta la presión al plegamiento de proteínas?



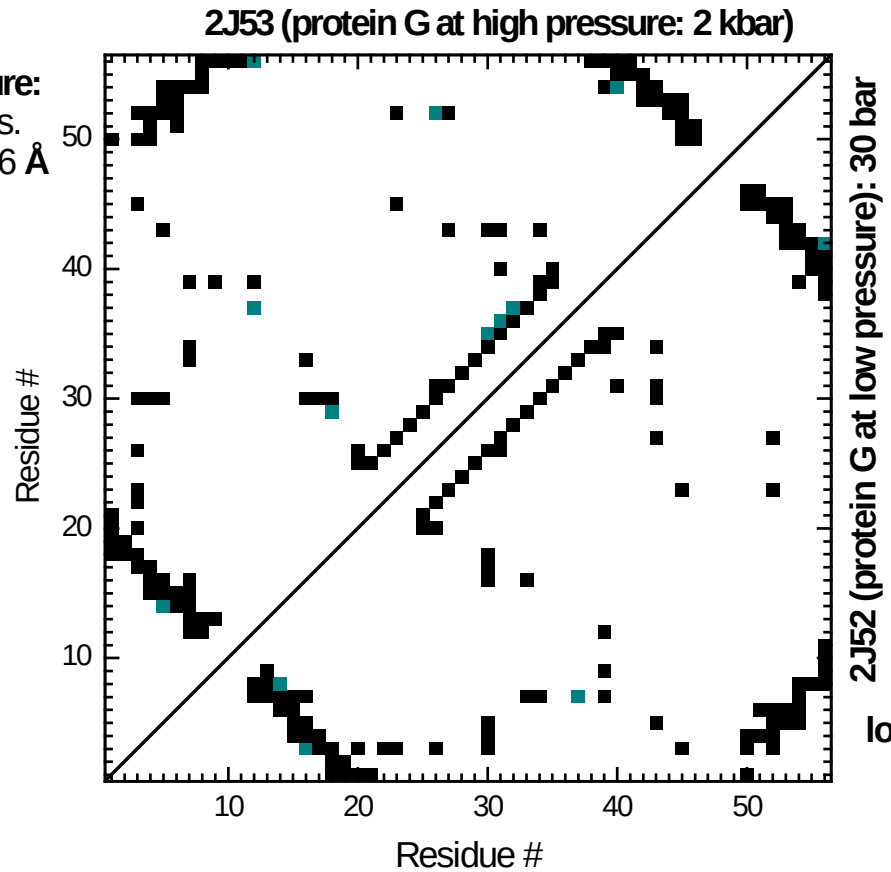
¿Cómo afecta la presión al plegamiento de proteínas?



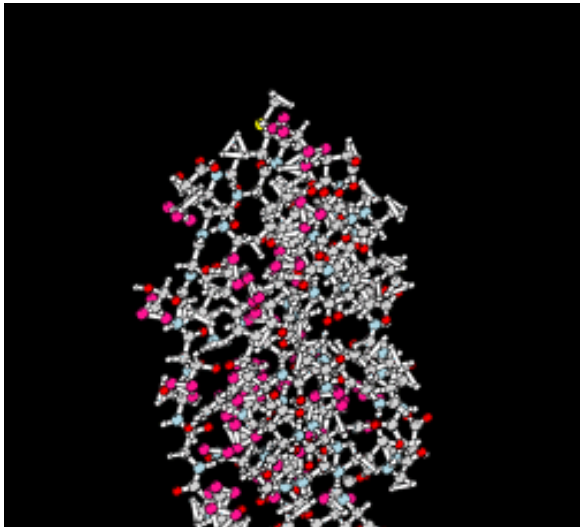


Boonchai B. Boonyaratanakornkit, Chan Beum PArk, Douglas S.Clark *Biochimica et Biophysica Acta* 1595 (2002) 235-249

high pressure:
118 l.r. cts.
R_g = 10.16 **Å**



low pressure:
113 l.r. cts.
R_g = 10.19 **Å**

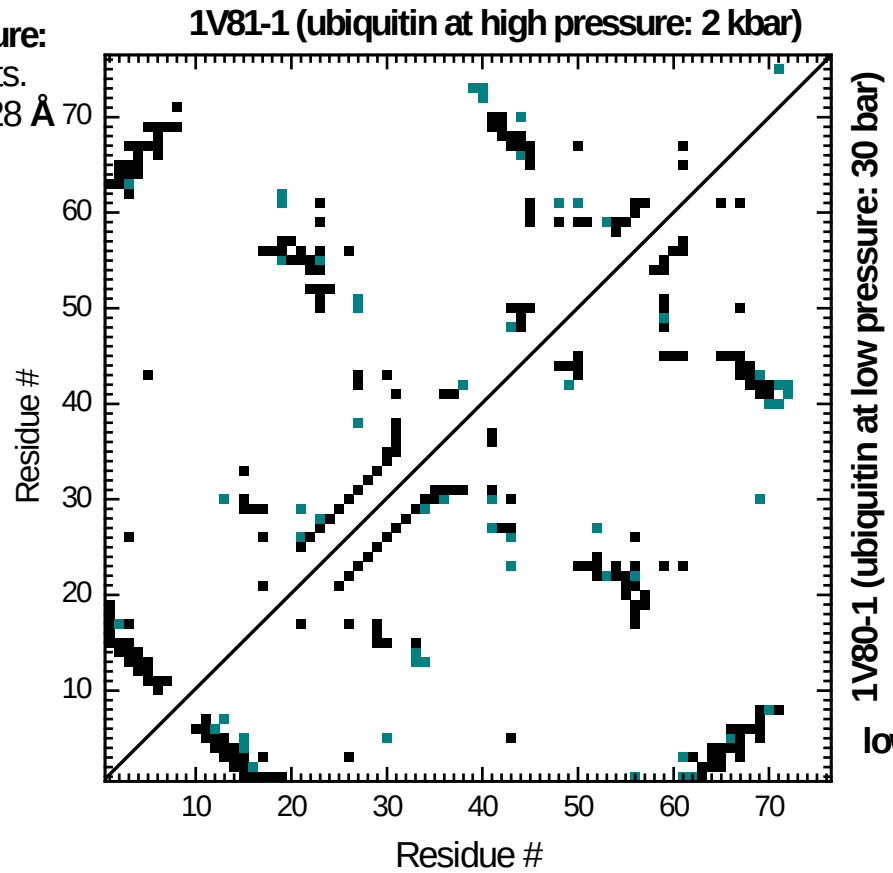


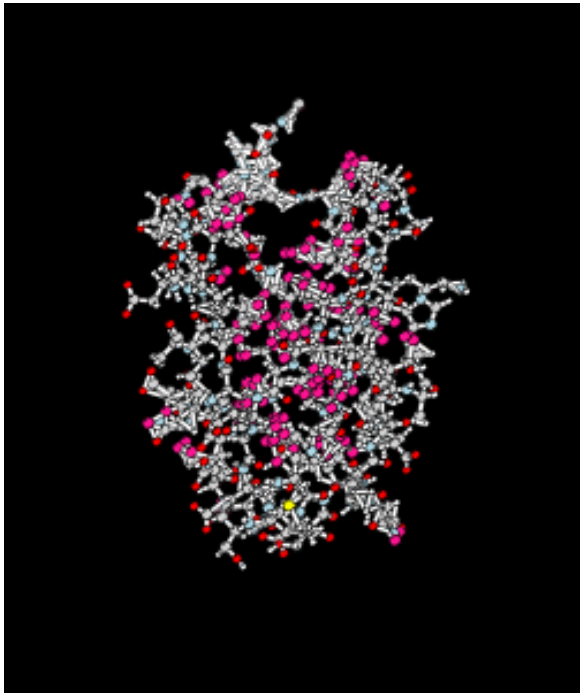
MovieMaker: a web server for rapid rendering of protein motions and interactions

Rajarshi Maiti[1,2], Gary H. Van Domselaar[1,2] and David S. Wishart[1,2,*]

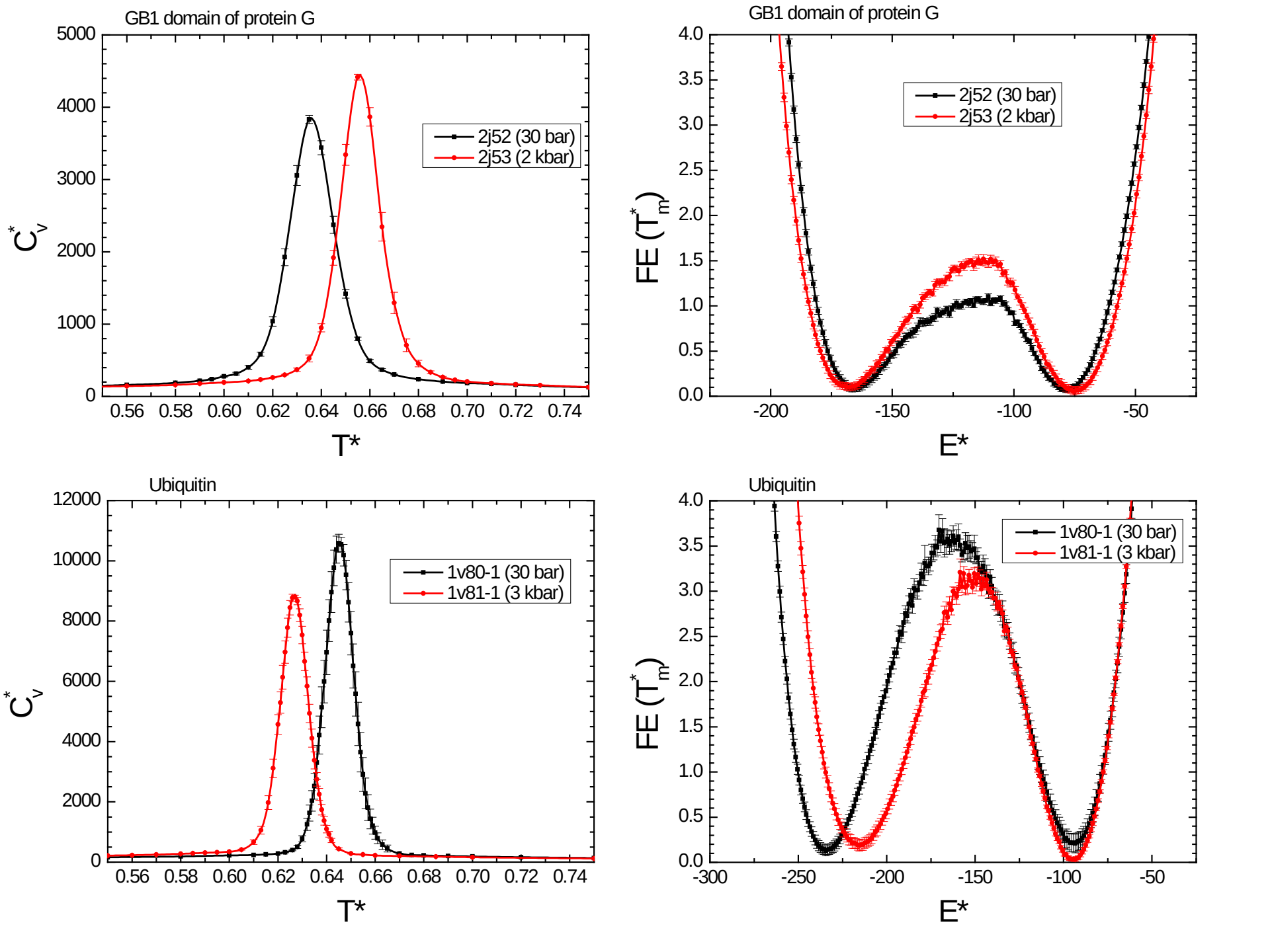
[1]Department of Computing Science and [2]Department of Biological Sciences, University of Alberta, Edmonton, AB, Canada T6G 2E8

high pressure:
147 l.r. cts.
R_g = 11.28 **Å**

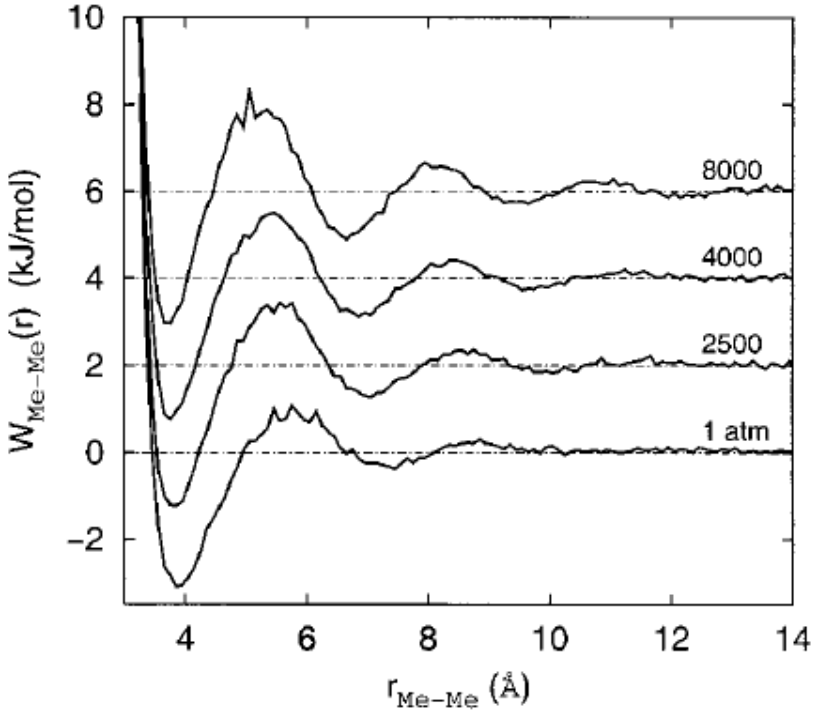




low pressure:
156 l.r. cts.
R_g = 11.34 **Å**


GB1 domain of protein G
2j52 (30 bar)
2j53 (2 kbar)
C_v^*
T*
GB1 domain of protein G
2j52 (30 bar)
2j53 (2 kbar)
FE (T_m^*)
E*
Ubiquitin
1v80-1 (30 bar)
1v81-1 (3 kbar)
C_v^*
T*
Ubiquitin
1v80-1 (30 bar)
1v81-1 (3 kbar)
FE (T_m^*)
E*

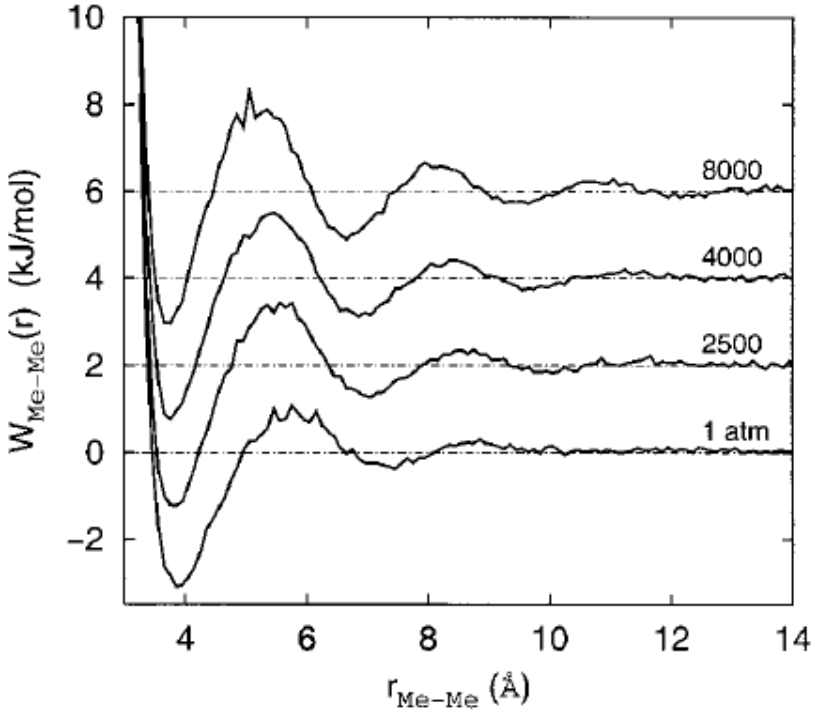
POTENCIALES DE CAMPO MEDIO PARA INTERACCIÓN DE RESIDUOS HIDROFÓBICOS BAJO PRESIÓN

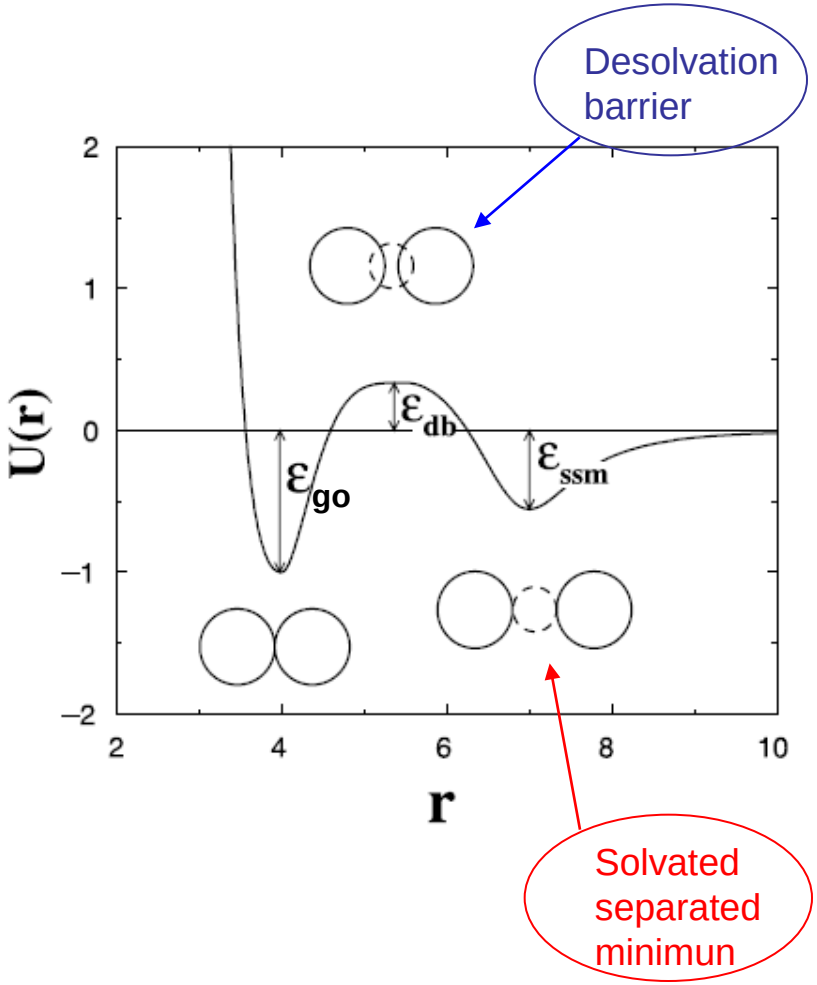


Tuhin Ghosh, Angel E. García and Shekhard Garde

J. Am .Chem Soc. **2001**, 123, 10997-11003

POTENCIALES DE CAMPO MEDIO PARA INTERACCIÓN DE RESIDUOS HIDROFÓBICOS BAJO PRESIÓN





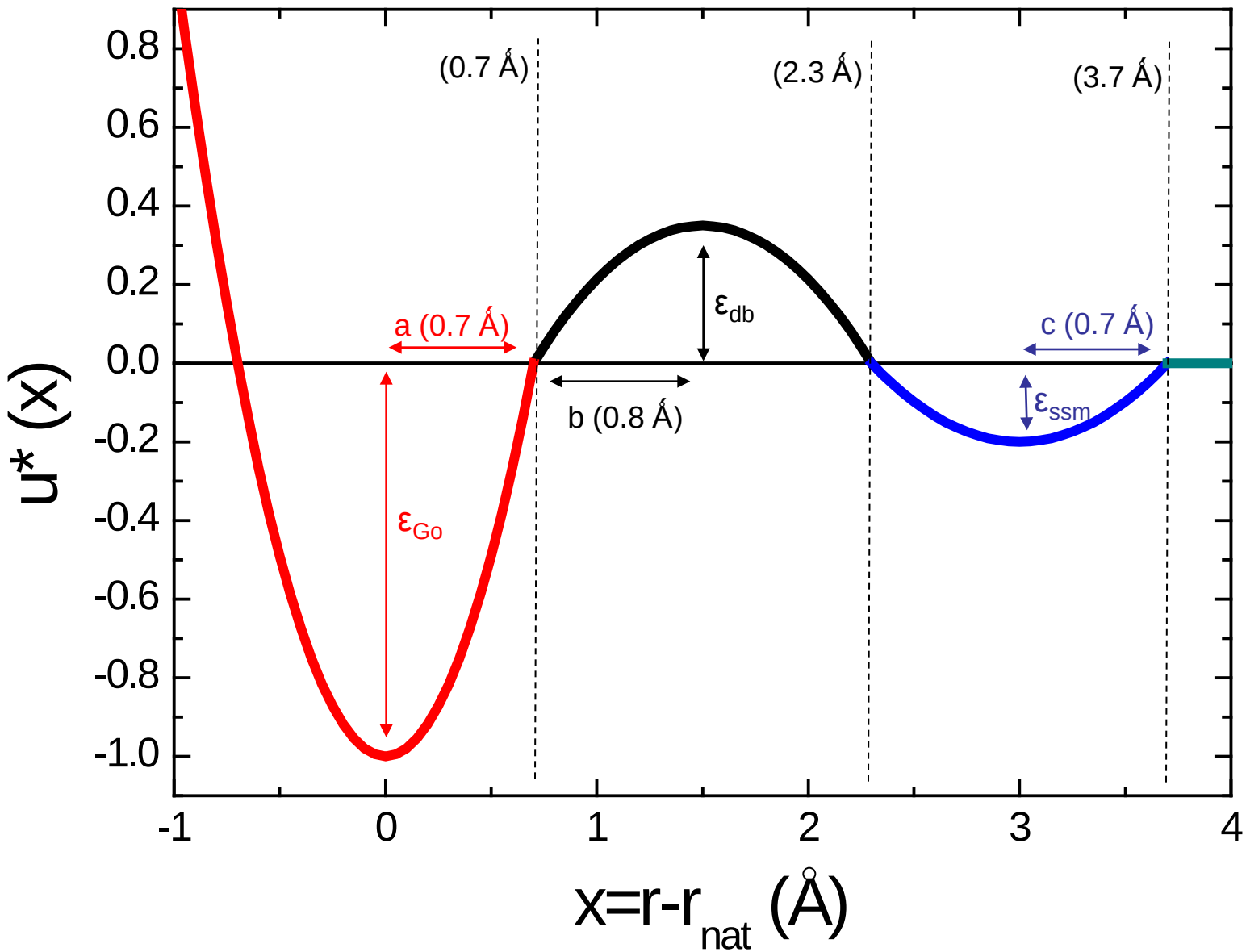
Tuhin Ghosh, Angel E. García and Shekhard Garde

J. Am .Chem Soc. **2001**, 123, 10997-11003

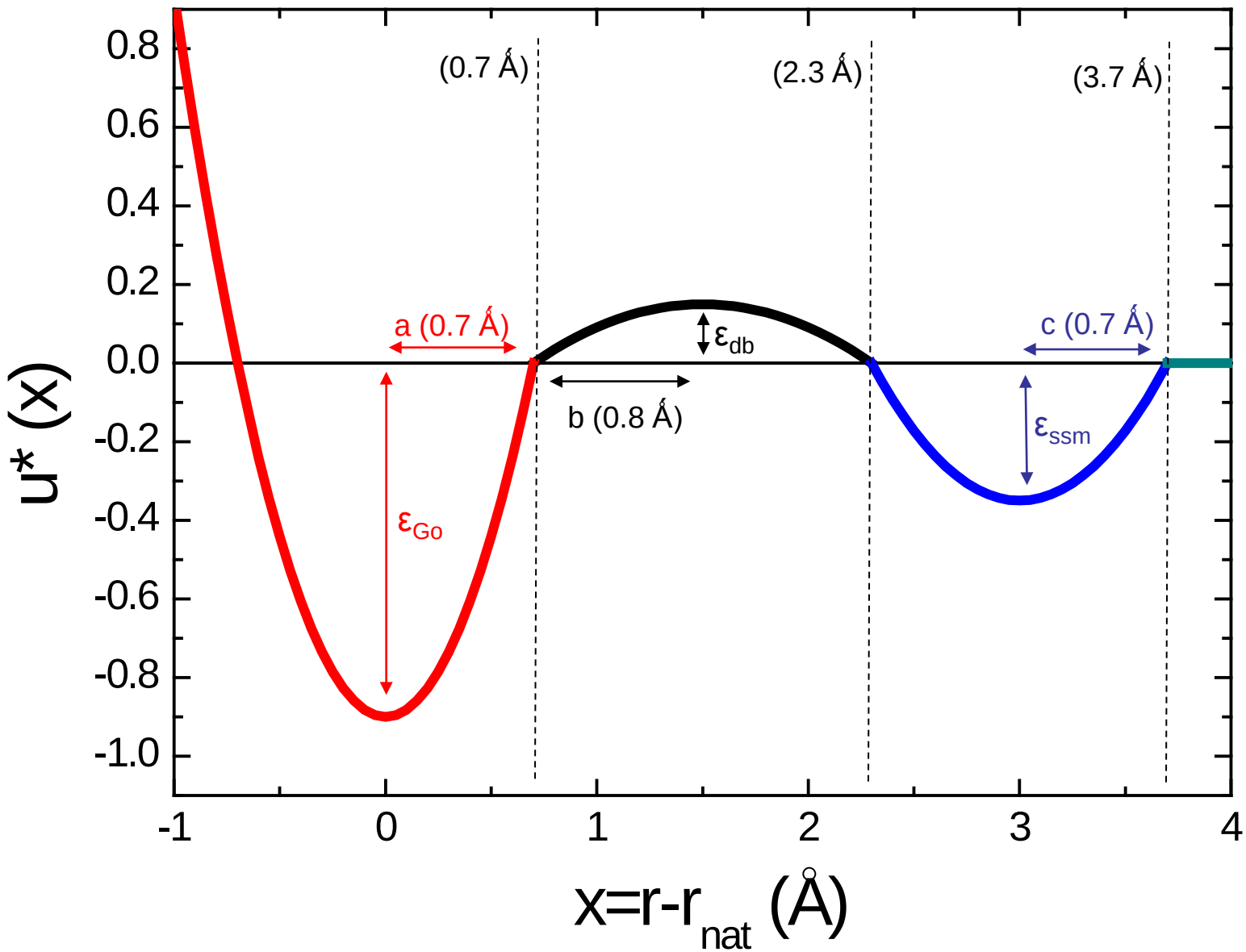
Zhirong Liu and Hue Sun Chan

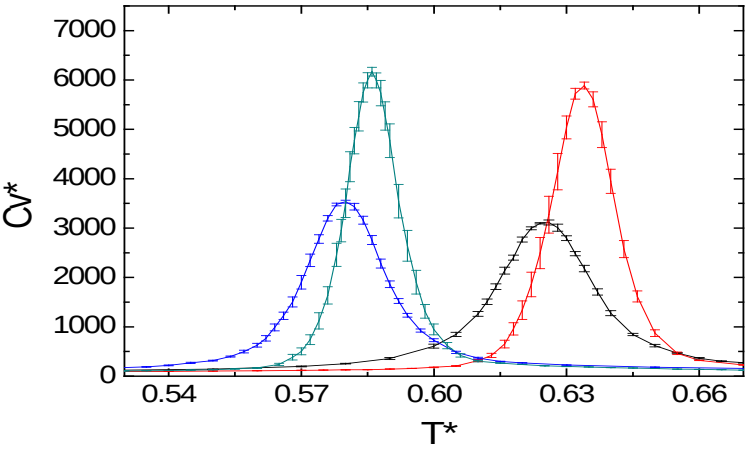
J. Mol. Bio. **2005**, 349, 872-889

ε_{go}-1.0; ε_{db}0.35; ε_{ssm}-0.20;



ε_{go}-0.9; ε_{db}0.15; ε_{ssm}-0.35;



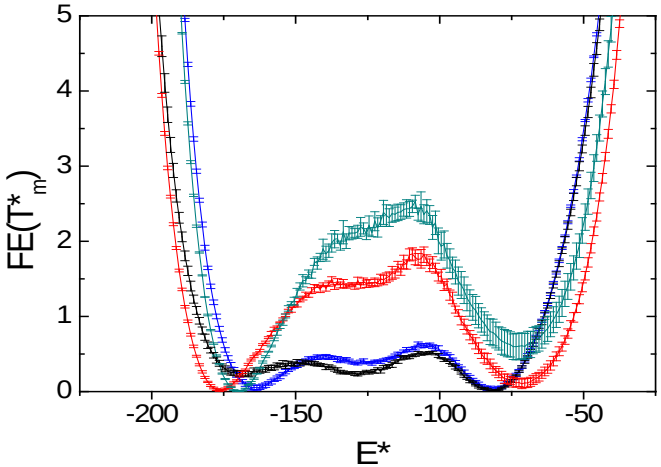


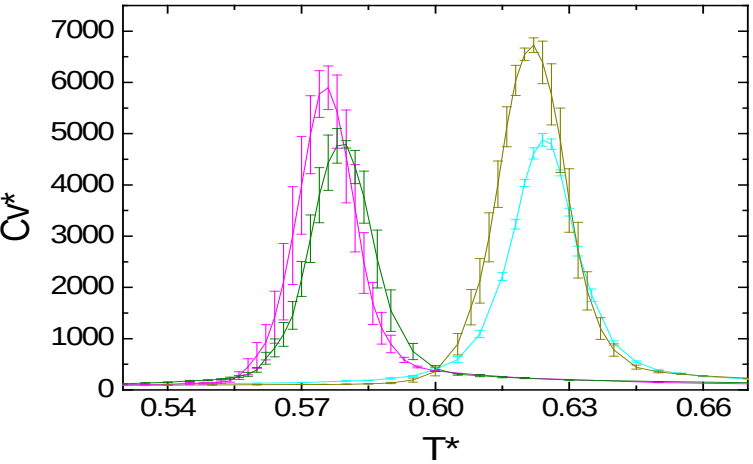
ε_{go}-1.0; ε_{db}0.0; ε_{ssm}-0.35

ε_{go}-1.0; ε_{db}0.5; ε_{ssm}-0.35

ε_{go}-0.9; ε_{db}0.0; ε_{ssm}-0.35

ε_{go}-0.9; ε_{db}0.5; ε_{ssm}-0.35



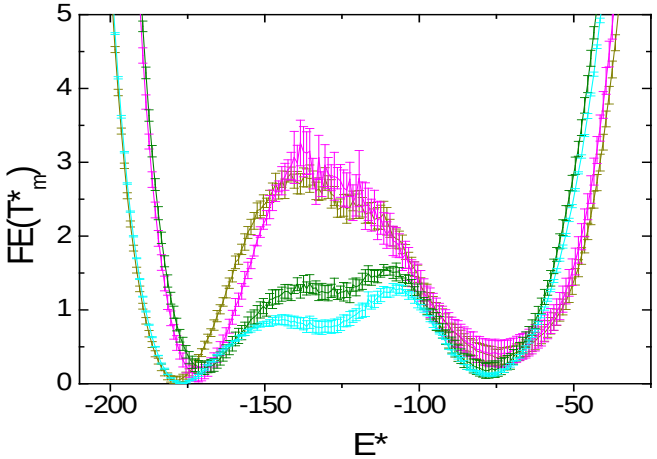


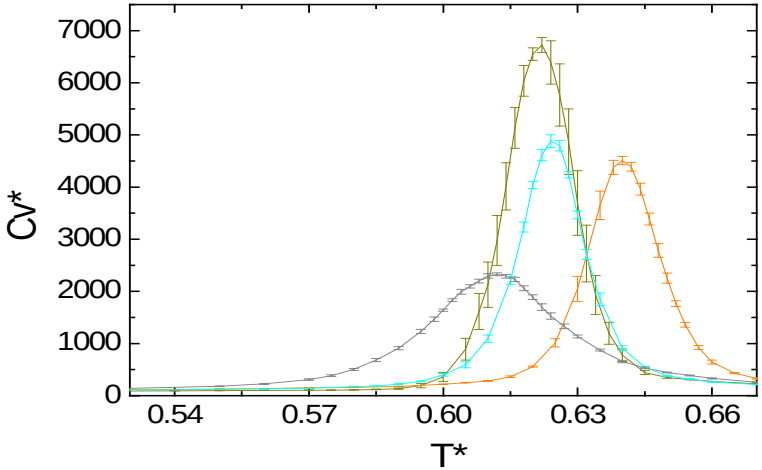
ε_{go}-1.0; ε_{db}0.5; ε_{ssm}0.0

ε_{go}-1.0; ε_{db}0.5; ε_{ssm}-0.5

ε_{go}-0.9; ε_{db}0.5; ε_{ssm}0.0

ε_{go}-0.9; ε_{db}0.5; ε_{ssm}-0.5



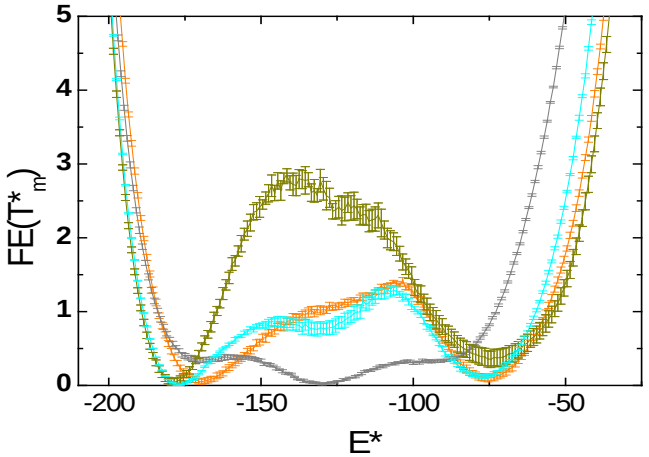


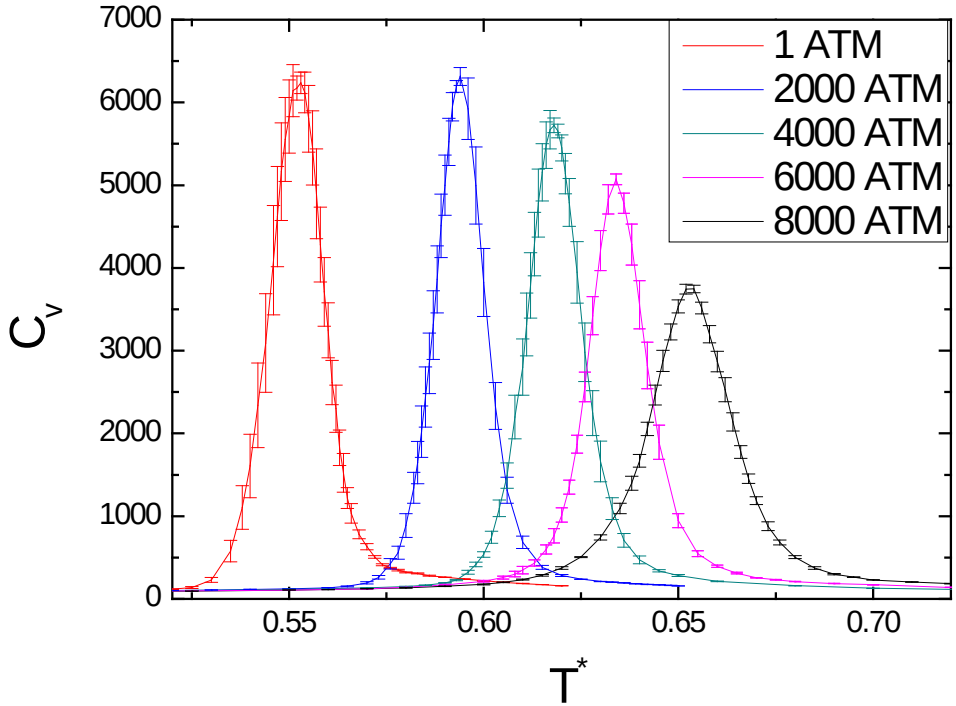
ε_{go}-1.0; ε_{db}0.0; ε_{ssm}0.0

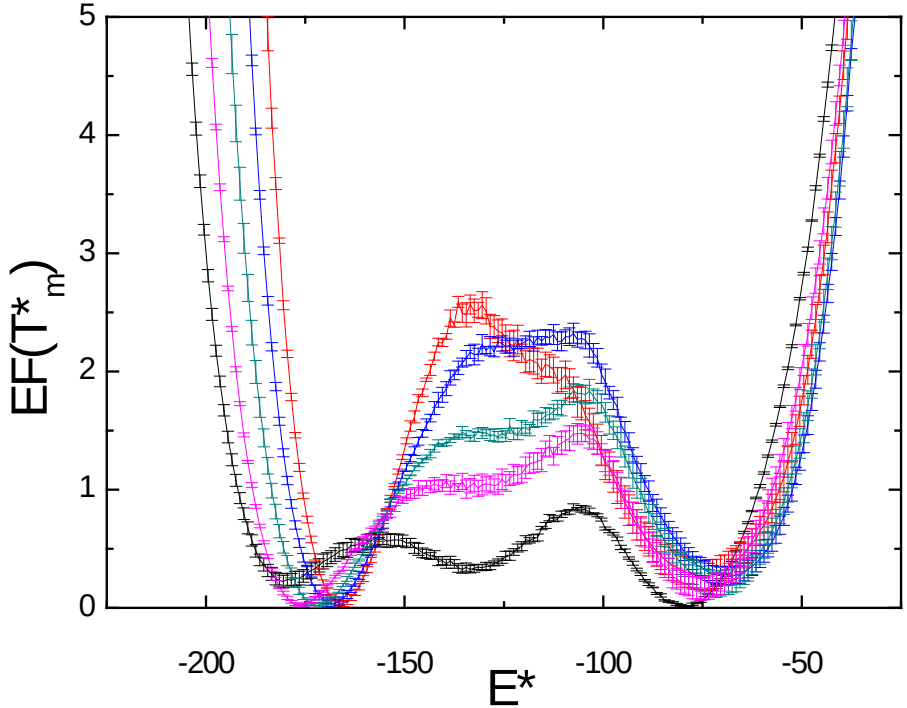
ε_{go}-1.0; ε_{db}0.5; ε_{ssm}0.0

ε_{go}-1.0; ε_{db}0.0; ε_{ssm-}0.5

ε_{go}-1.0; ε_{db}0.5; ε_{ssm}-0.5







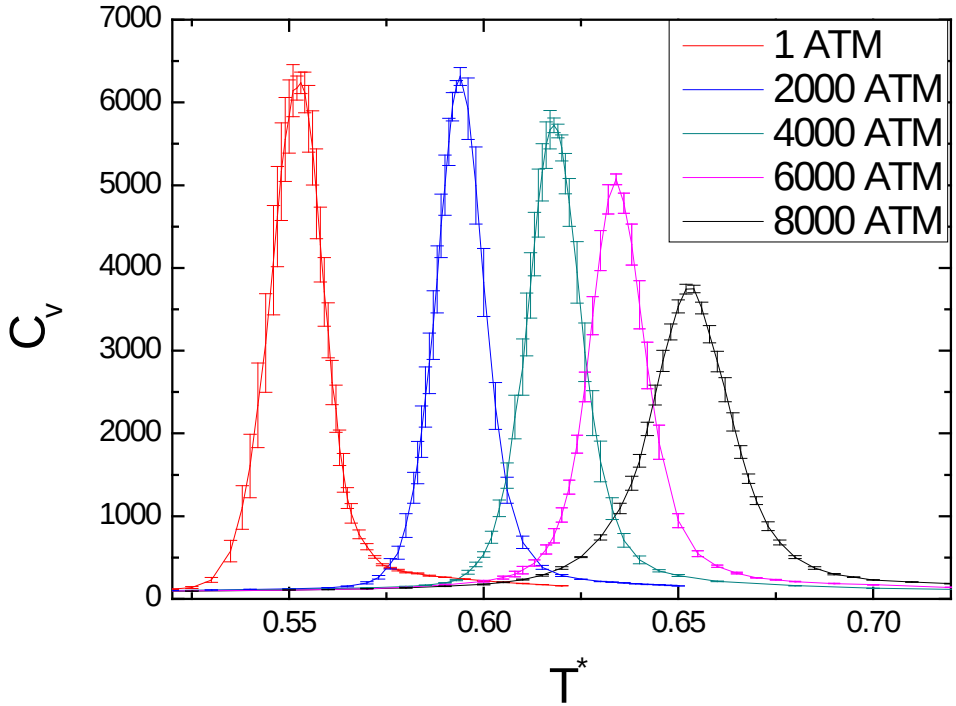
ε_{go}-0.84; ε_{db}0.35; ε_{ssm}-0.03

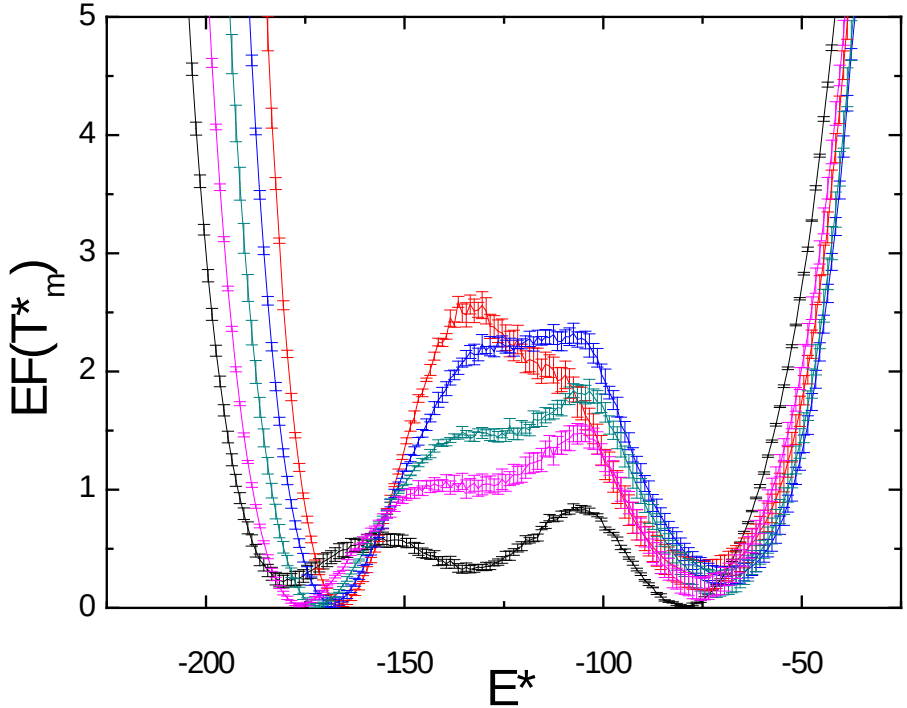
ε_{go}-0.90; ε_{db}0.35; ε_{ssm}-0.15

ε_{go}-0.96; ε_{db}0.35; ε_{ssm}-0.26

ε_{go}-1.01; ε_{db}0.35; ε_{ssm}-0.37

ε_{go}-1.07; ε_{db}0.35; ε_{ssm}-0.50





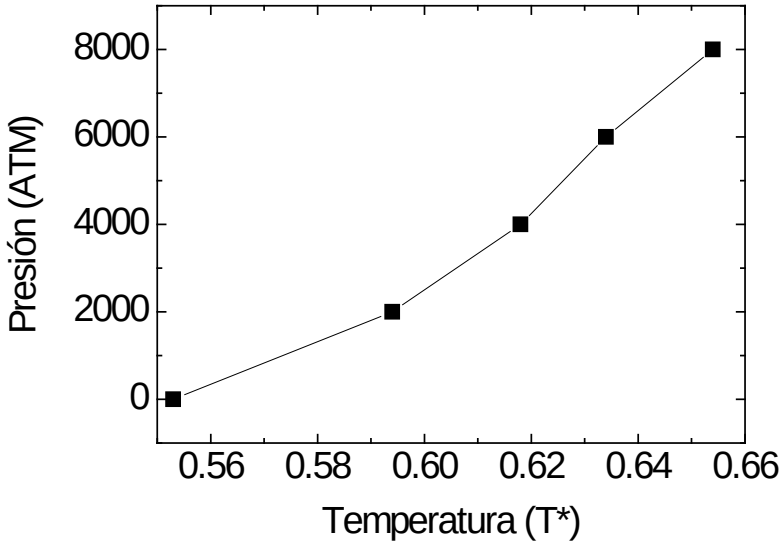
ε_{go}-0.84; ε_{db}0.35; ε_{ssm}-0.03

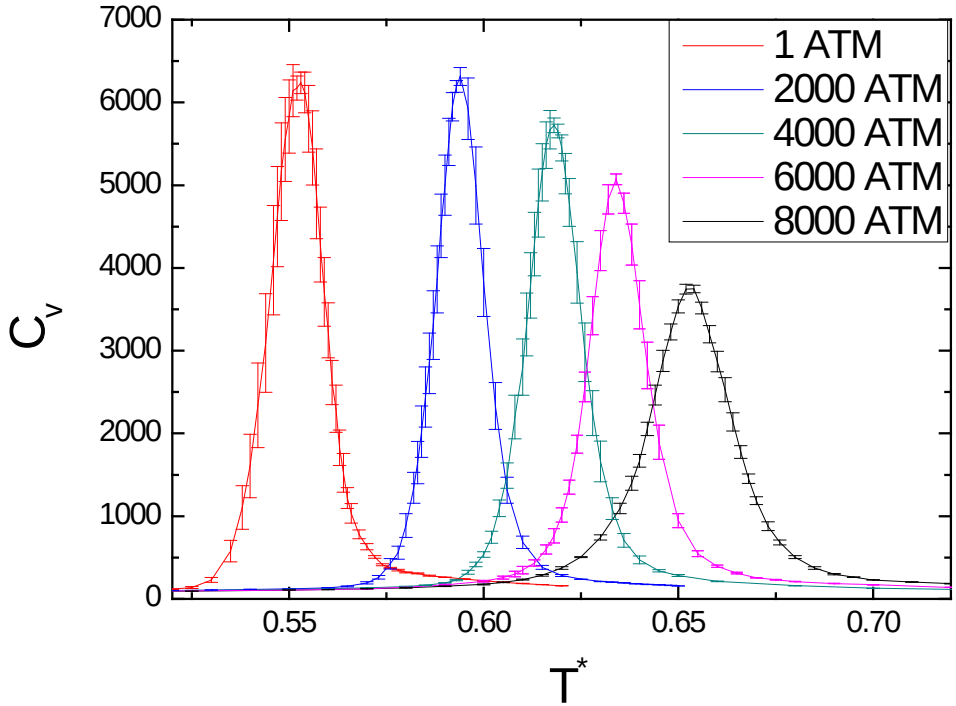
ε_{go}-0.90; ε_{db}0.35; ε_{ssm}-0.15

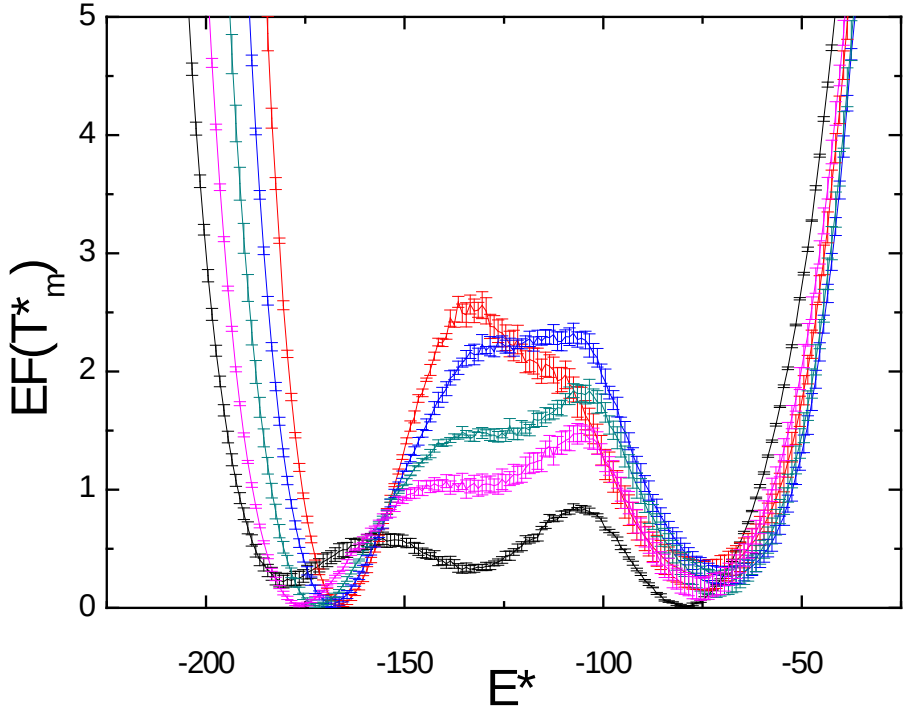
ε_{go}-0.96; ε_{db}0.35; ε_{ssm}-0.26

ε_{go}-1.01; ε_{db}0.35; ε_{ssm}-0.37

ε_{go}-1.07; ε_{db}0.35; ε_{ssm}-0.50







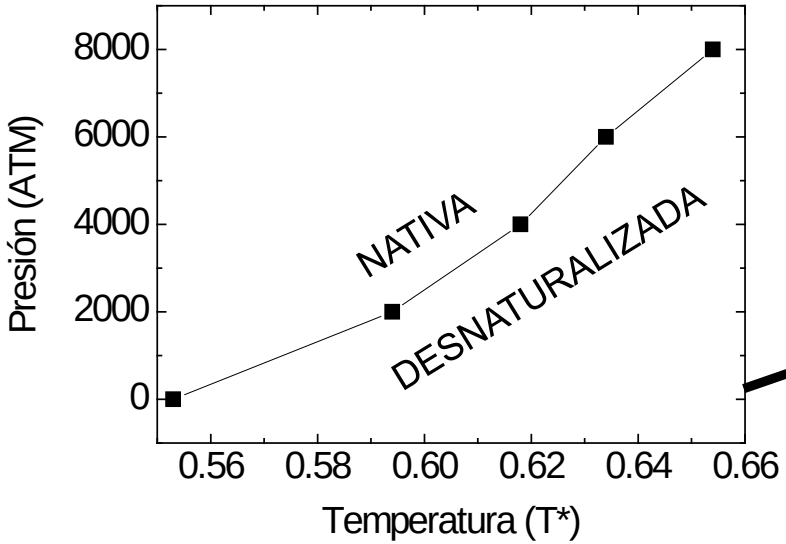
ε_{go}-0.84; ε_{db}0.35; ε_{ssm}-0.03

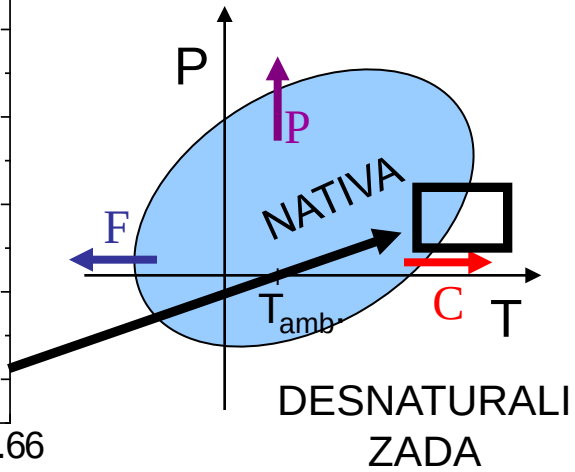
ε_{go}-0.90; ε_{db}0.35; ε_{ssm}-0.15

ε_{go}-0.96; ε_{db}0.35; ε_{ssm}-0.26

ε_{go}-1.01; ε_{db}0.35; ε_{ssm}-0.37

ε_{go}-1.07; ε_{db}0.35; ε_{ssm}-0.50





GRUPO UCM-SIMPOL

Prof. Antonio Rey Gayo

Prof. Ana María Rubio Caparrós

Dra. María Larriva Hormigos

Lcda. Marta Enciso Carrasco

Lcdo. Ramiro Perezzan Rodríguez

Comunidad de Madrid

La Suma de Todos

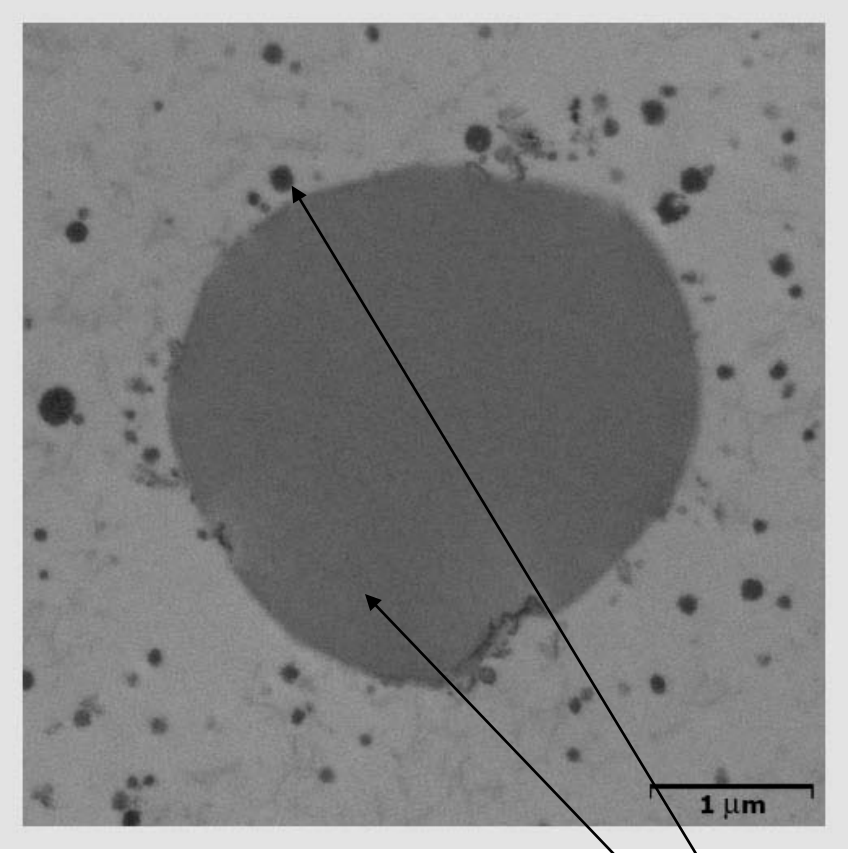
QUIMAPRES

Nanoencapsulación por Ultra Alta Presión Homogenización (UHPH)

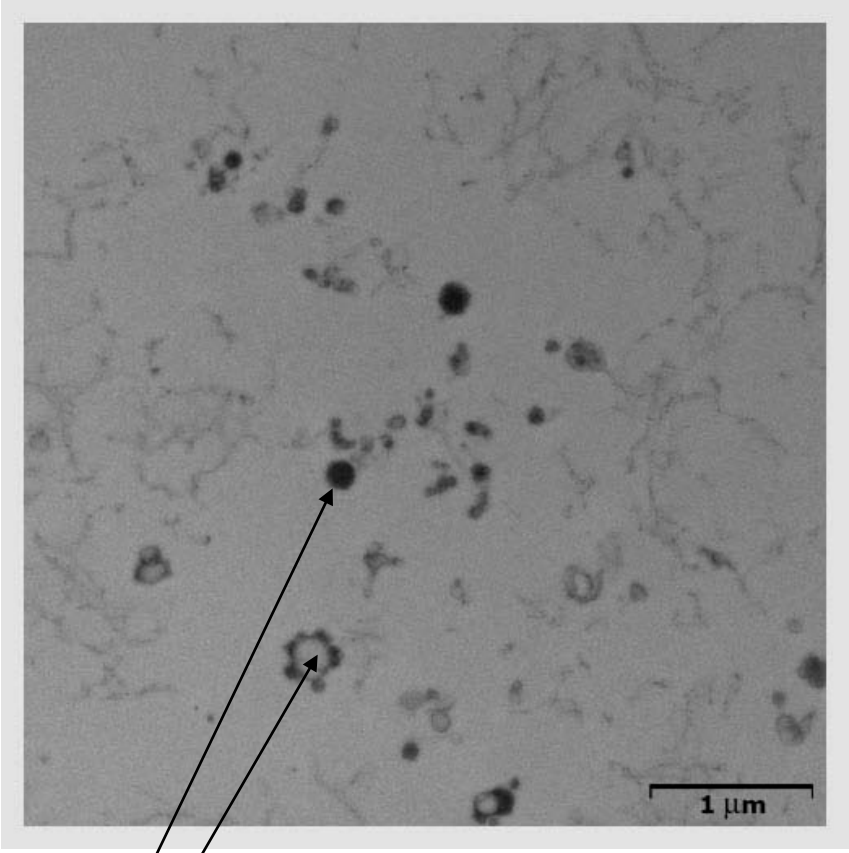
Roger Escriu Justo

Formación “natural” nanoestructuras

Leche cruda



300 MPa (30ºC)



Micelas caseina

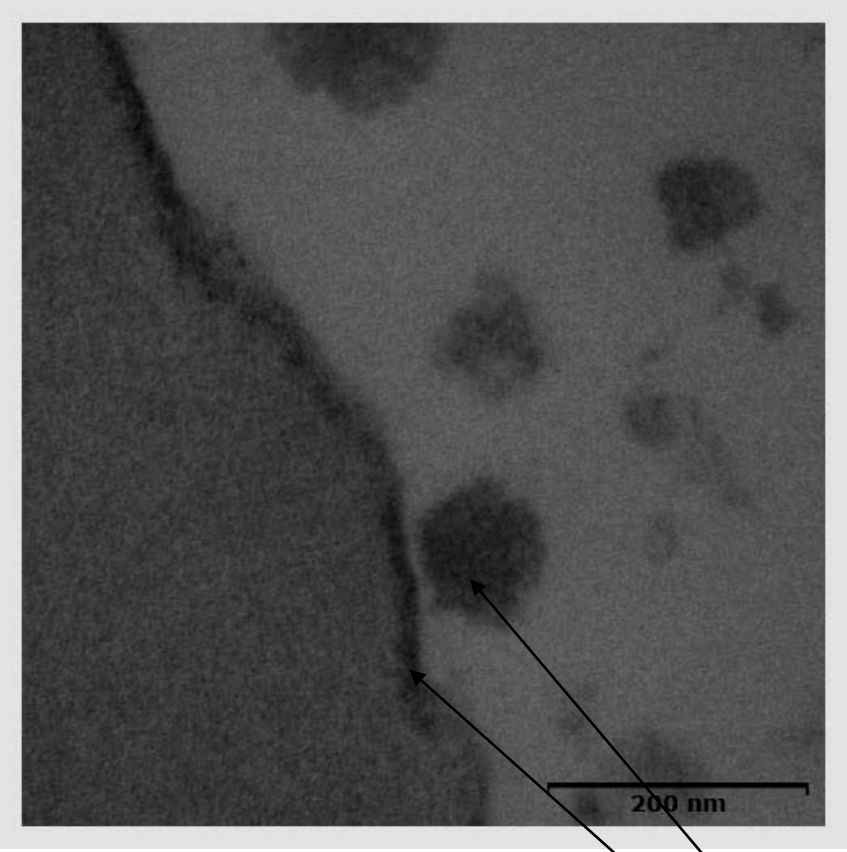
Globulos grasos

TECNIO
Be tech. Be competitive

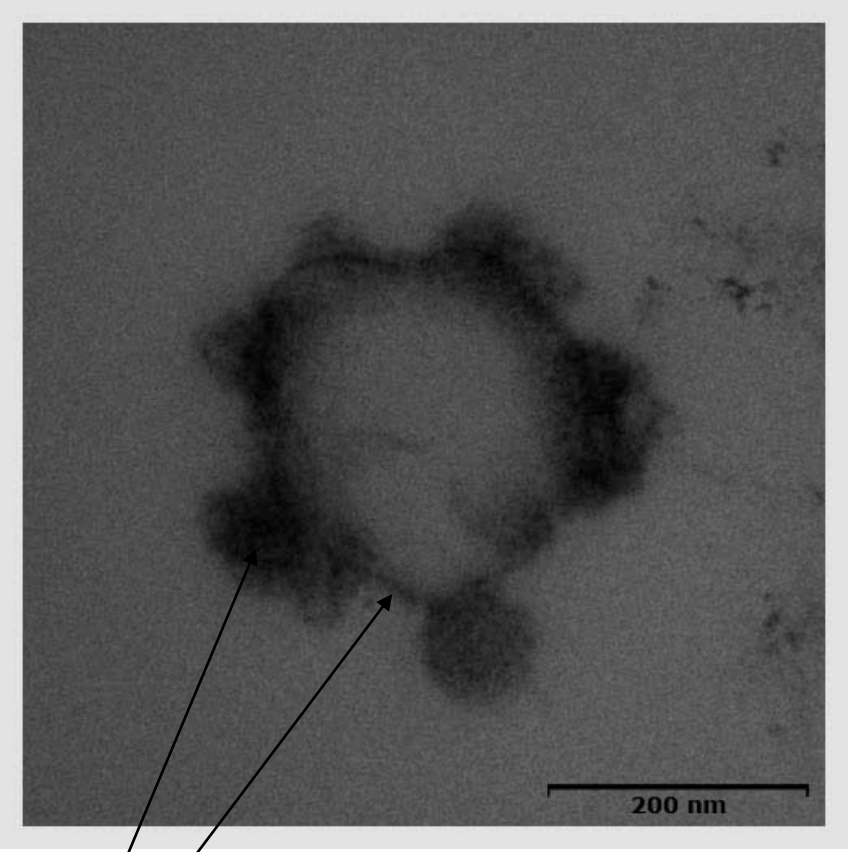
Planta de Tecnologia dels Aliments
UAB

Formación “natural” nanoestructuras

Leche cruda



300 MPa (30ºC)



Micelas caseina

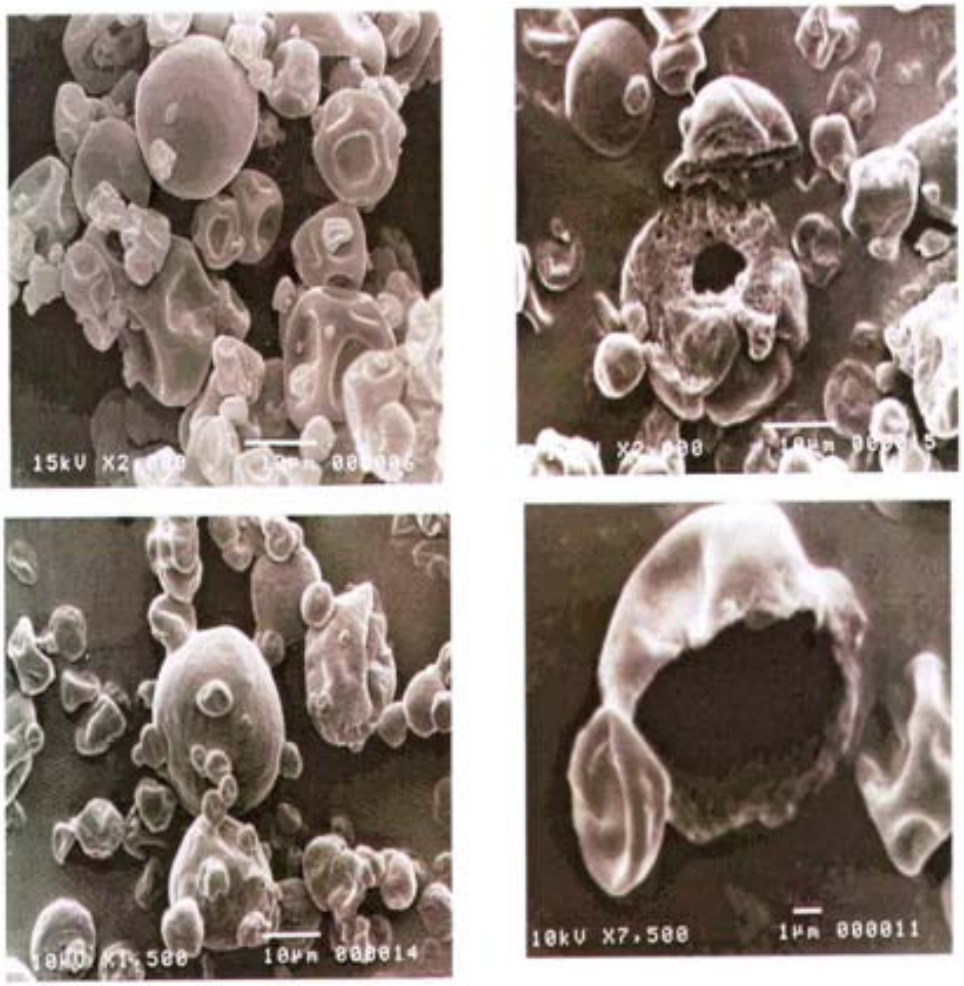
Globulos grasos

TECNIO
Be tech. Be competitive

CONSOLIDER MALTA

Planta de Tecnologia dels Aliments UAB

¿Qué es nanotecnología?



TECNIO
Be tech. Be competitive

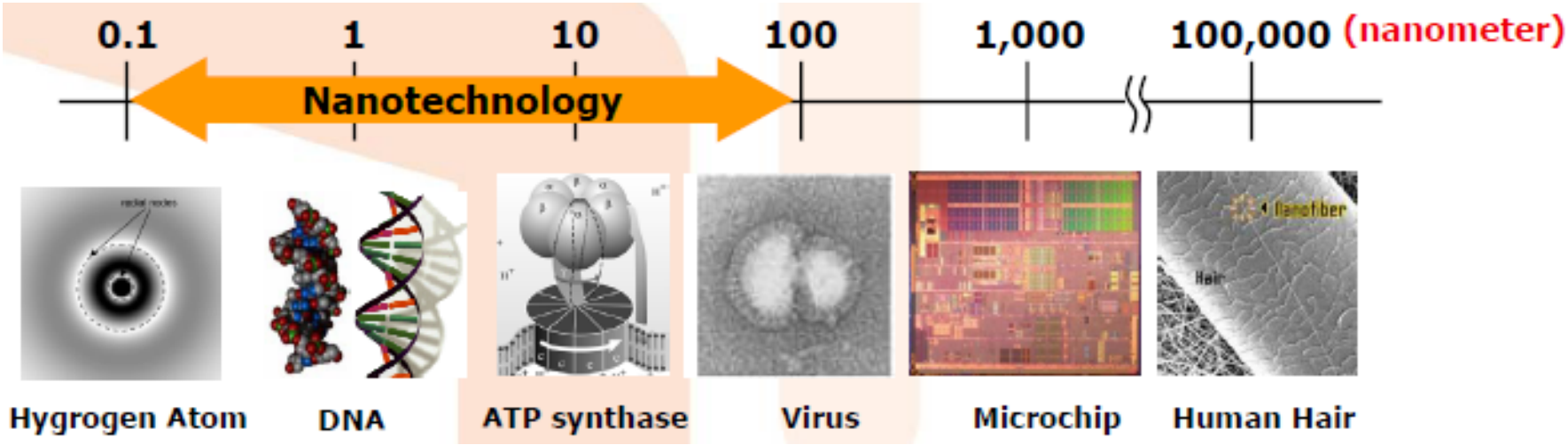
CONSOLIDER MALTA

Planta de Tecnologia dels Aliments UAB

Es un conjunto de técnicas que se utilizan para manipular la materia a la escala de **<u>átomos y moléculas</u>**.

Del griego νᾶνος (enano), τέχνη (técnica) y λόγος (ciencia)

A **escala tan pequeña**, la materia se **comporta** de modo **diferente**.



TECNIO Be tech. Be competitive

CONSOLIDER ALTA

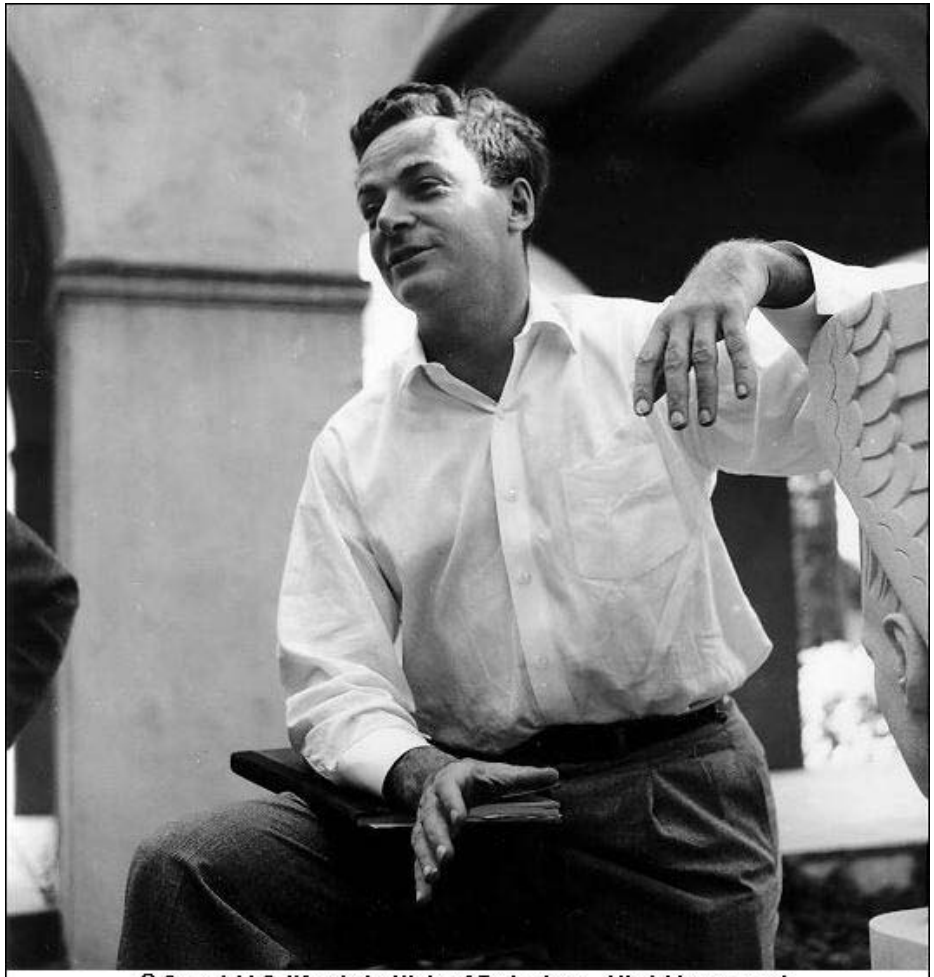
Planta de Tecnologia dels Aliments UAB

Richard P. Feynman

(precursor de la nanotecnología):

"¿Qué pasaría si nosotros pudiéramos arreglar los átomos uno por uno de la manera en que nosotros los queremos?"

(1960)



TECNIO
Be tech. Be competitive

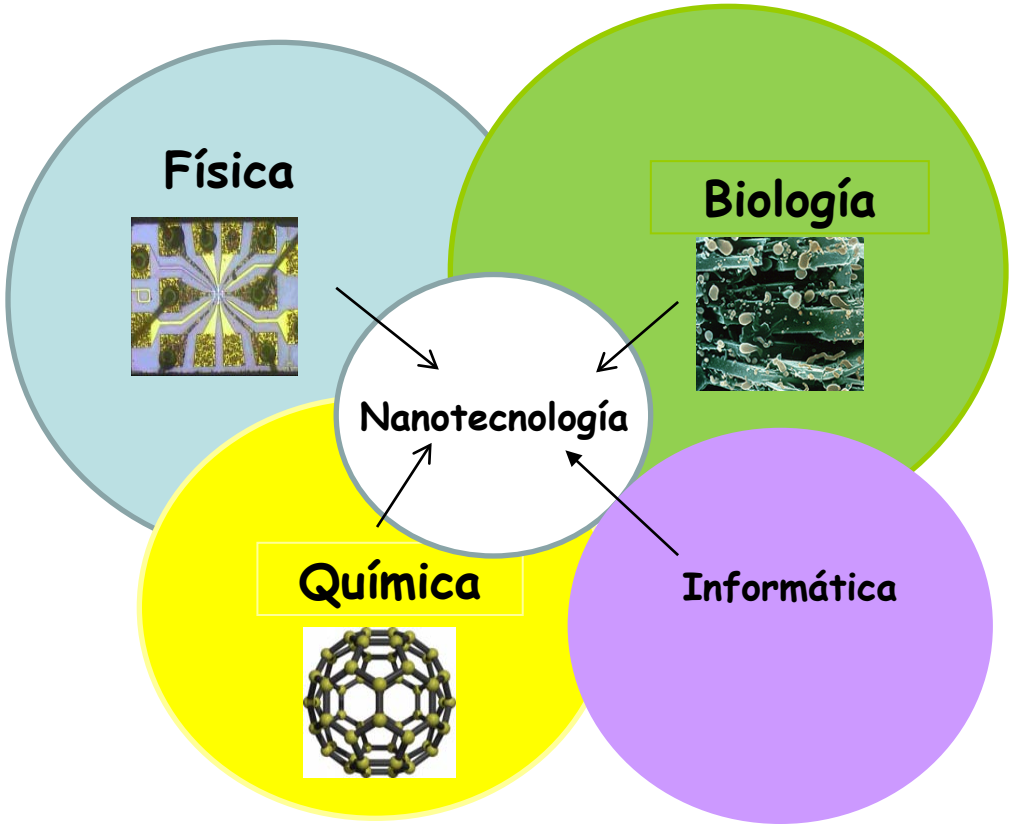
CONSOLIDER MALTA

Planta de Tecnologia dels Aliments UAB

La **NANOTECNOLOGÍA** constituye un ensamblaje interdisciplinar de **varios** campos de las ciencias naturales que están altamente especializados.

FÍSICA: En la construcción de los microscopios usados para investigar tales fenómenos y por su conocimiento de las leyes de la mecánica cuántica.

QUÍMICA: Conocimiento de la estructura del material deseado y las configuraciones de ciertos átomos



TECNIO
Be tech. Be competitive

CONSOLIDER ALTA

Planta de Tecnologia dels Aliments UAB

Ultra Alta Presión de Homogeneización (UHPH)

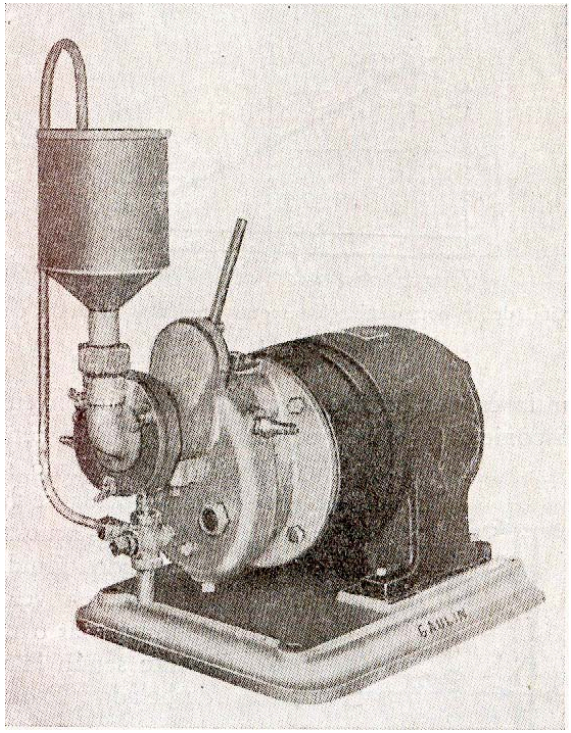
TECNIO
Be tech. Be competitive

CONSOLIDER MALTA

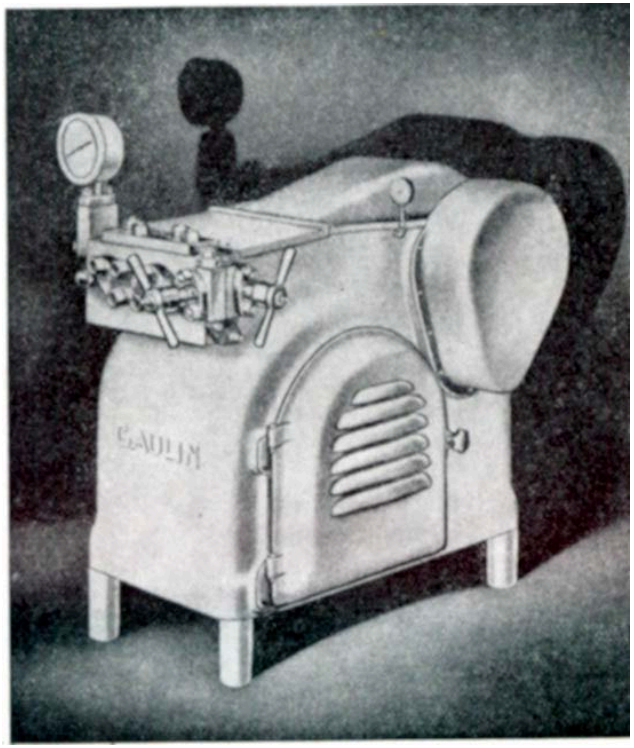
Planta de Tecnologia dels Aliments
UAB

Primeros Homogeneizadores

1900



1902. Gaulin



TECNIO
Be tech. Be competitive

CONSOLIDER ALTA

Planta de Tecnologia dels Aliments UAB

Objetivos homogeneizadores convencionales

- Estabilización de emulsiones
- Mejora del sabor
- Mejora de la textura
- Leche, nata y helados
- Presiones hasta 50 MPa

1980 nace la alta presión homogeneización (HPH)

- Presiones hasta 150 MPa
- Producir emulsiones más estables
- Mejorar la textura de los yogures
- Reducir algo la carga microbiana

Alta Presión Homogeneización (HPH)

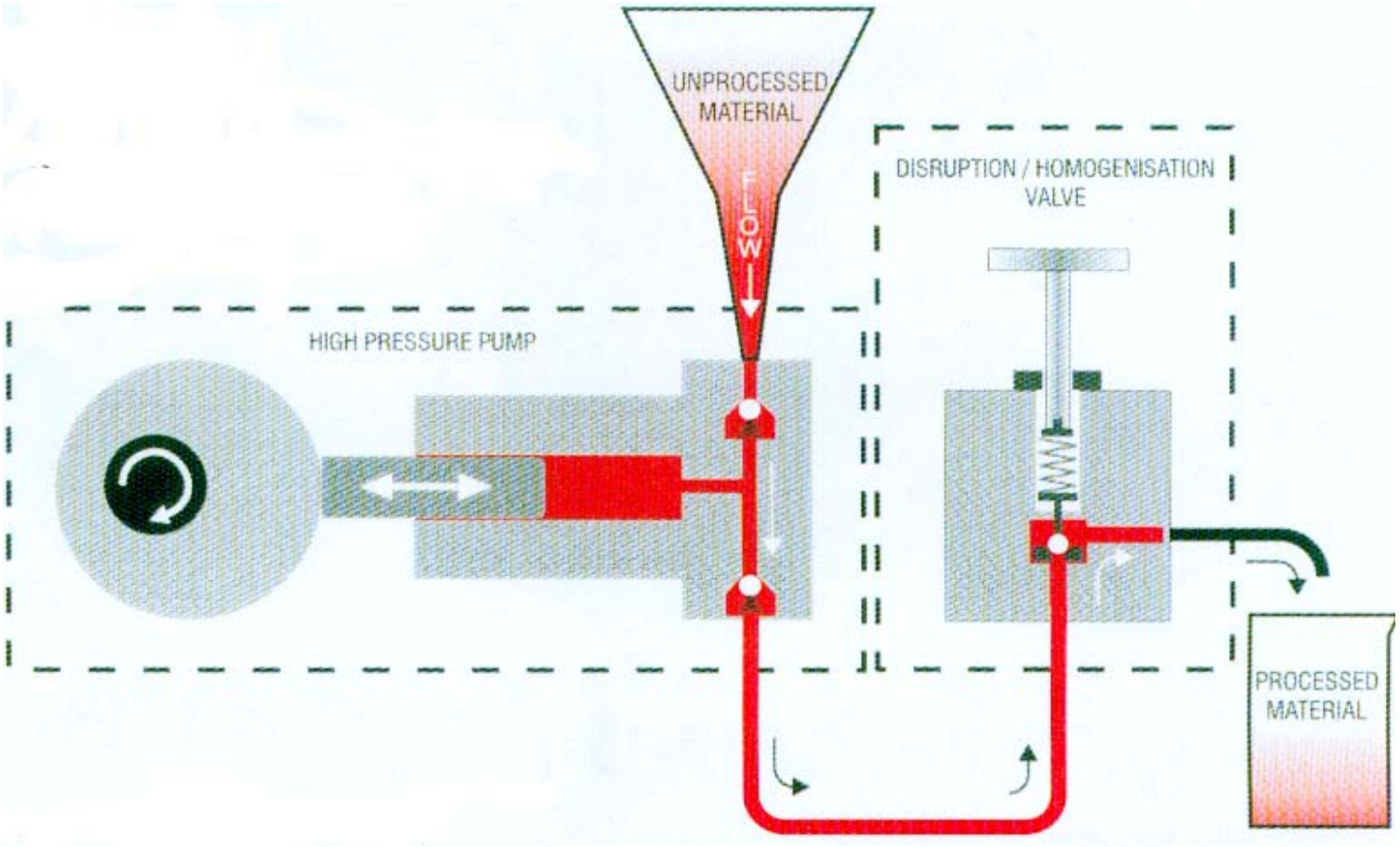
Hasta 1500 bares
(150 MPa)

TECNIO
Be tech. Be competitive

CONSOLIDER ALTA

Planta de Tecnologia dels Aliments UAB

1990. Primeros prototipos de ultra alta presión homogenización (UHPH)

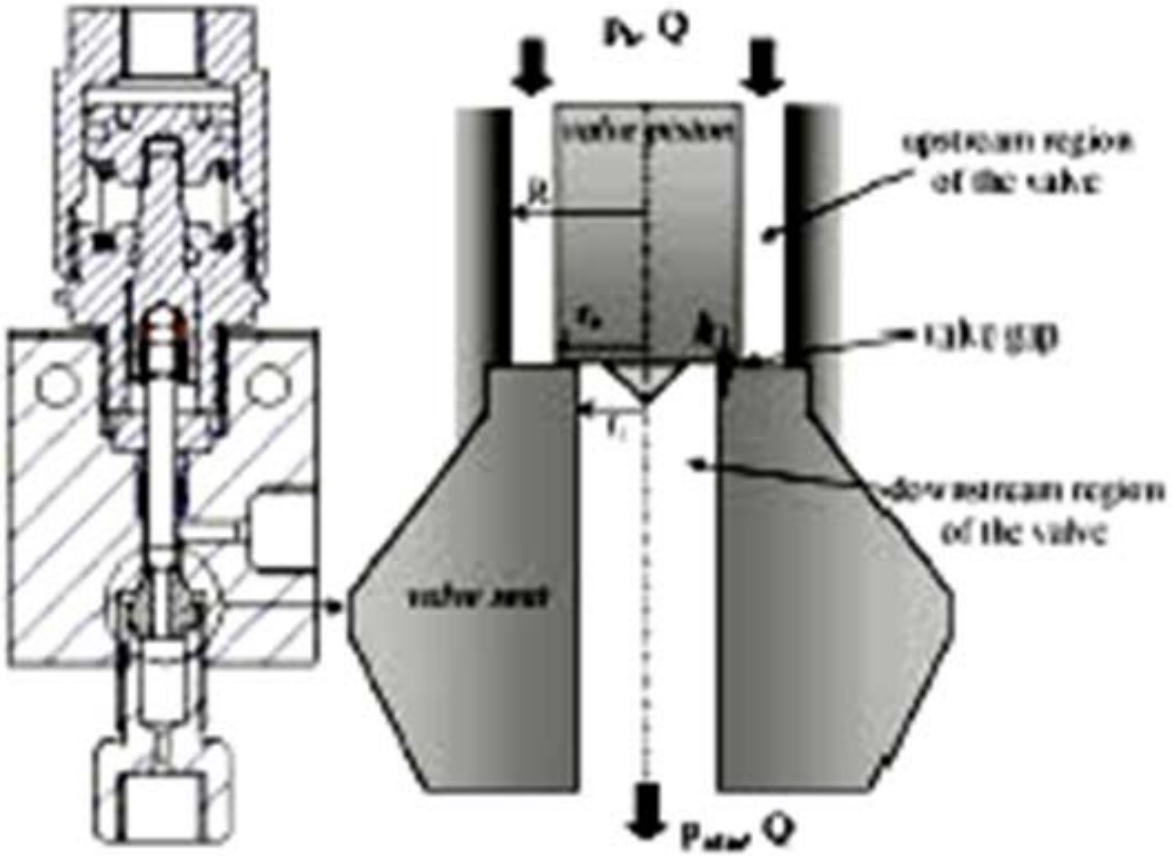


TECNIO
Be tech. Be competitive

CONSOLIDER ALTA

Planta de Tecnologia dels Aliments UAB

2003. Primeras válvulas y prototipos de UHPH con doble intensificador capaces de soportar 400 MPa

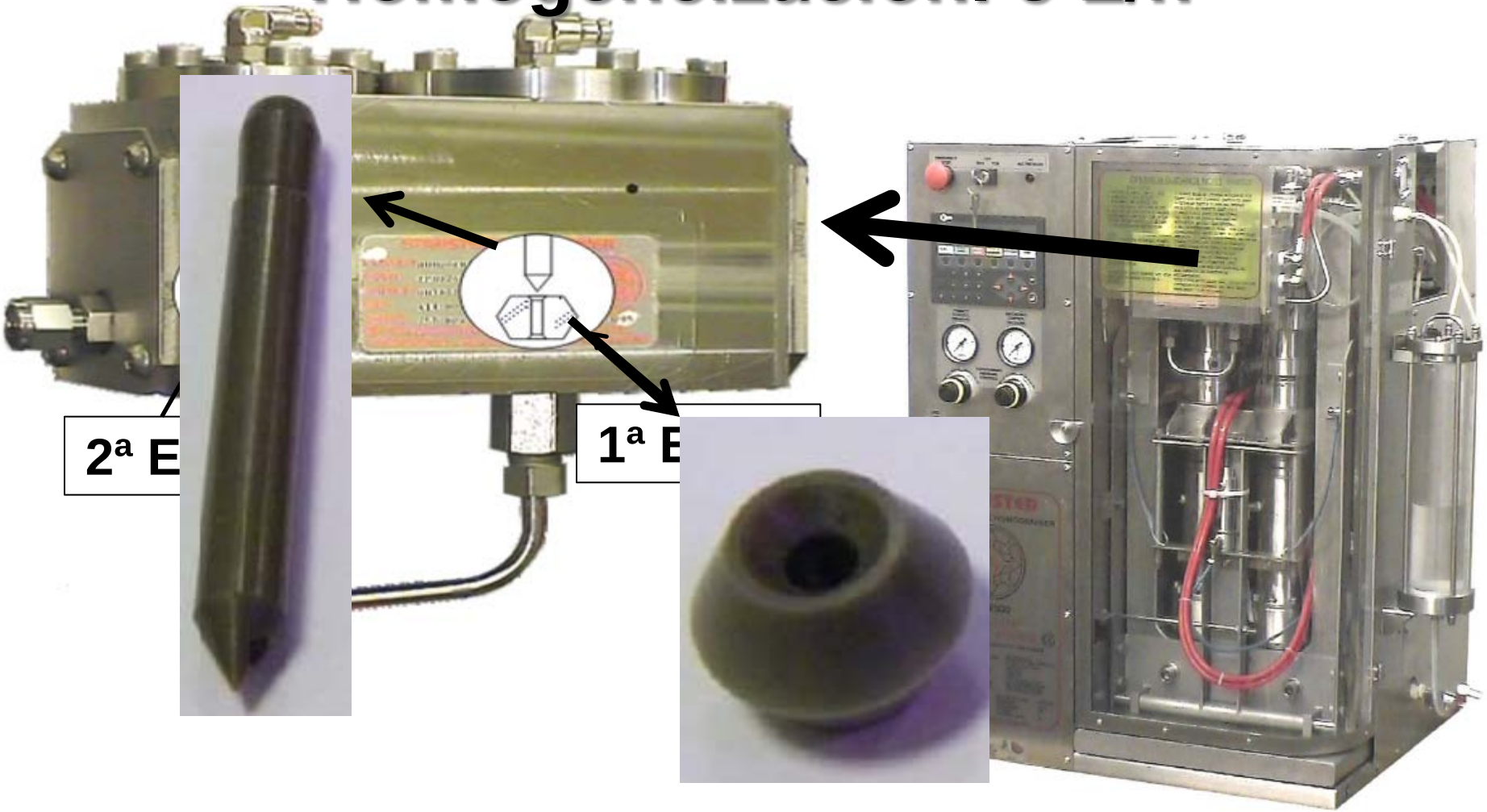


TECNIO
Be tech. Be competitive

CONSOLIDER ALTA

Planta de Tecnologia dels Aliments UAB

Equipo Ultra Alta Presión Homogeneización. 8 L/h

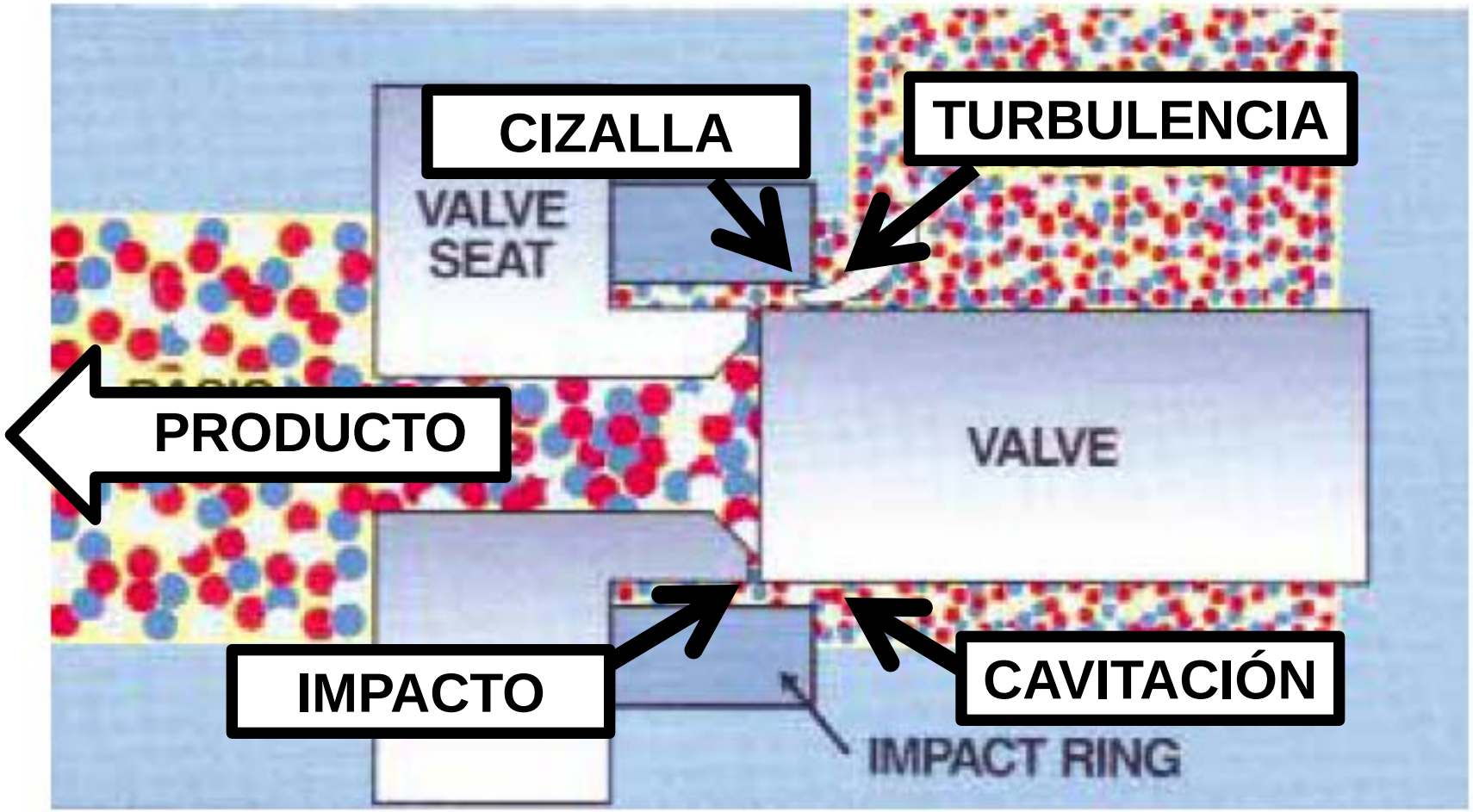


TECNIO
Be tech. Be competitive

CONSOLIDER ALTA

Planta de Tecnologia dels Aliments UAB

Válvula Homogeneización



TECNIO
Be tech. Be competitive

CONSOLIDER ALTA

Planta de Tecnologia dels Aliments UAB

Incremento de temperatura:

El incremento lineal de temperatura se produce al incrementar la presión de homogenización

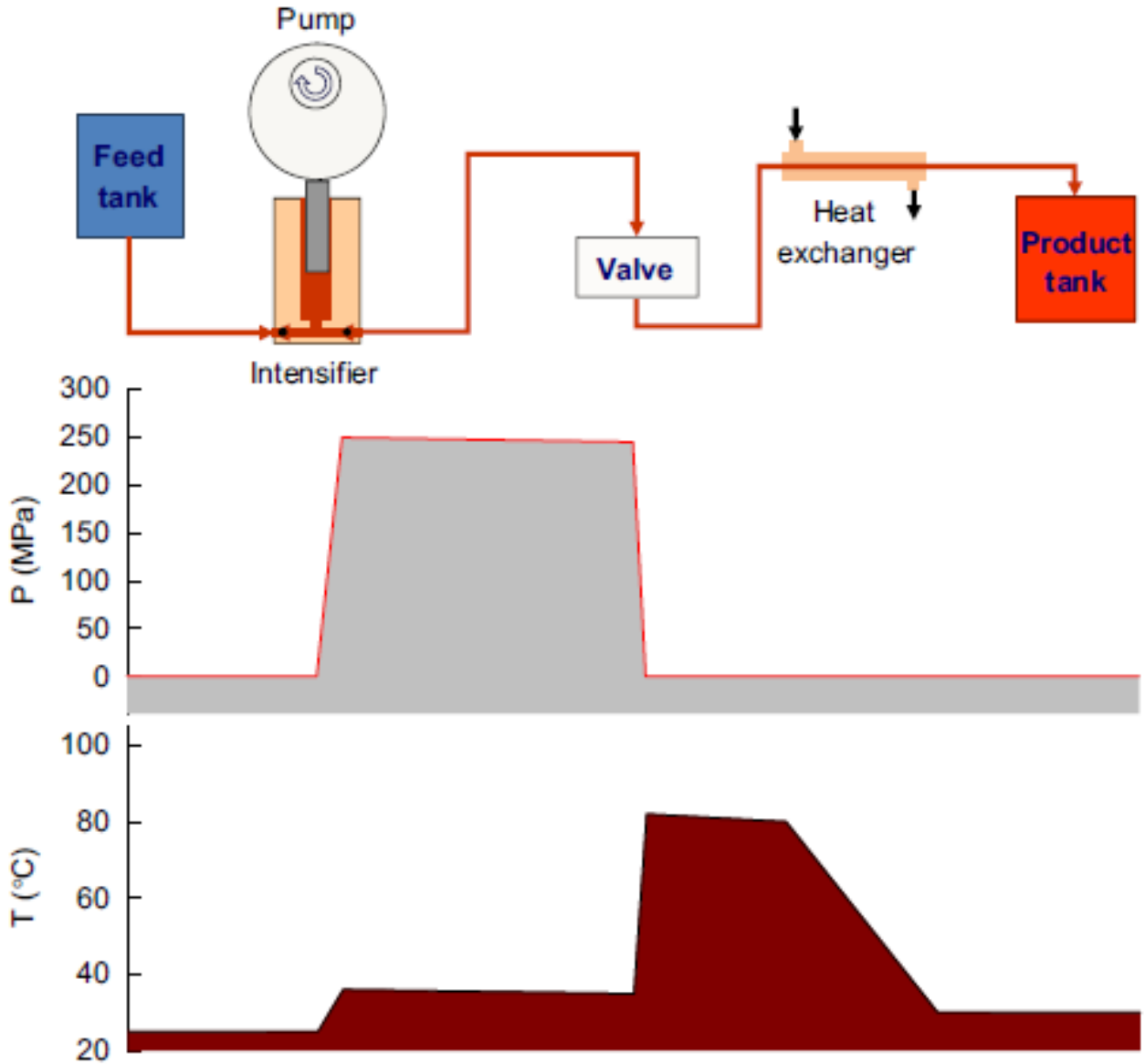
–Calentamiento adiabático debido al incremento en la presión

–Alta velocidad, turbulencia y fuerzas de corte al pasar y salir de la válvula

19.5 ± 3 ºC por 100 MPa

(*Pereda et. al, 2006; Thiebaud et al., 2003; Hayes et al., 2003; Floury et al., 2000*)

Ligero efecto térmico: Tiempo de residencia 10^{-4} s *(Floury et al., 2002)*



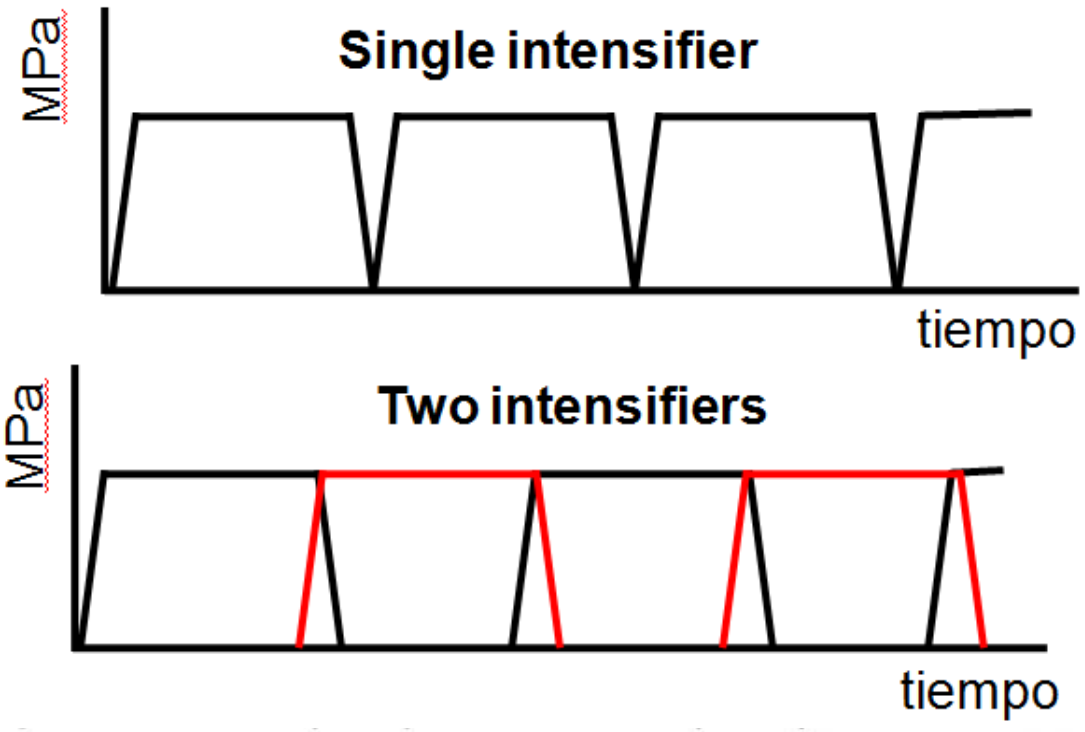
F. Donsi et al. / Chemical Engineering Science 64 (2009) 520–532

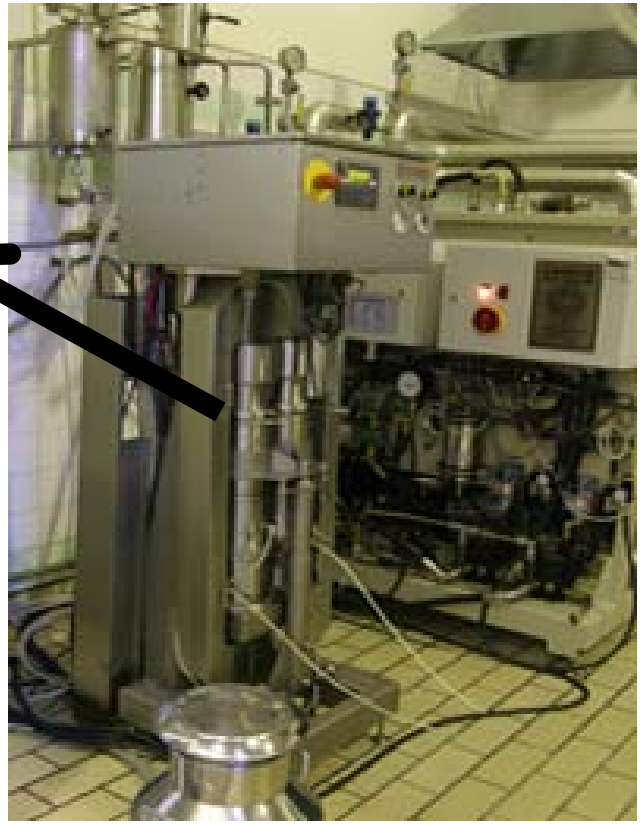
TECNIO
Be tech. Be competitive

CONSOLIDER ALTA

Planta de Tecnologia dels Aliments UAB

Equipo Ultra Alta Presión Homogeneización. 120 L/h





TECNIO
Be tech. Be competitive

CONSOLIDER ALTA

Planta de Tecnologia dels Aliments UAB

Aplicaciones en Alimentos

- Pasteurización y esterilización de alimentos fluidos
- Control de modificaciones sobre las proteínas
- Mejores texturas e incremento de la calidad
- Desarrollo de nuevos productos

- Ventajas:
  - Sistema continuo. Posibilidad de envasado aséptico
  - Economía de energía
  - Sistema higiénico de fácil limpieza y desinfección

1. Presiones de trabajo entre 100 hasta 400 MPa.
   - Gracias a nuevos desarrollos en la ciencia de los materiales
   - Diversas empresas constructoras y nuevos equipos: Microfluidizer®, Emulsiflex®, Stansted Fluid Power

2. Cavitación, turbulencia y fuerzas de cizalla.

3. Aplicaciones actuales:
   - Elaboración de nanodispersiones y nanocápsulas
   - Extracción de enzimas de las células microbianas

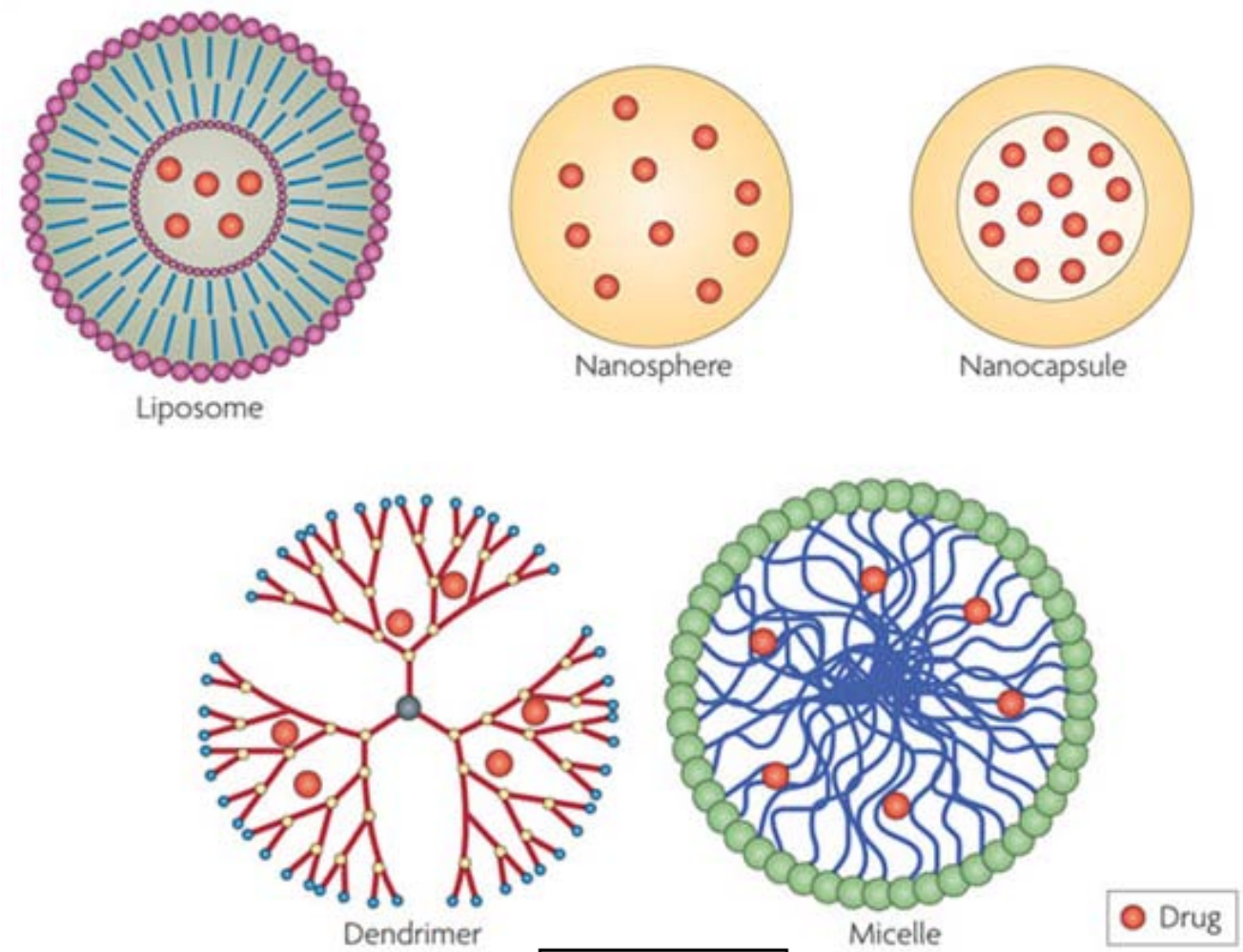
4. Potenciales aplicaciones:
   - Tratamiento de alimentos líquidos para incrementar su seguridad y sus propiedades funcionales.

TECNIO Be tech. Be competitive

CONSOLIDER ALTA

Planta de Tecnologia dels Aliments UAB

Estructura esquemática de los diferentes “nanoportadores”

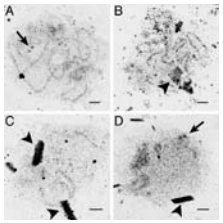


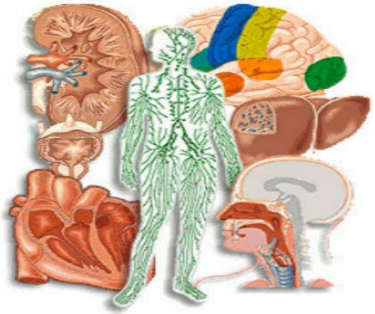
TECNIO
Be tech. Be competitive

CONSOLIDER ALTA

Planta de Tecnologia dels Aliments UAB

[redacted]





Componentes Bioactivos en Alimentos

- Inflamación
- División celular y crecimiento
- Apoptosis
- Reparación DNA
- Regulación Hormonal
- Metabolismo
- Balances energéticos

- Vitaminas
- Minerales
- Lípidos funcionales
- Bacterias Probióticas
- Amino acidos
- Proteinas
- ...

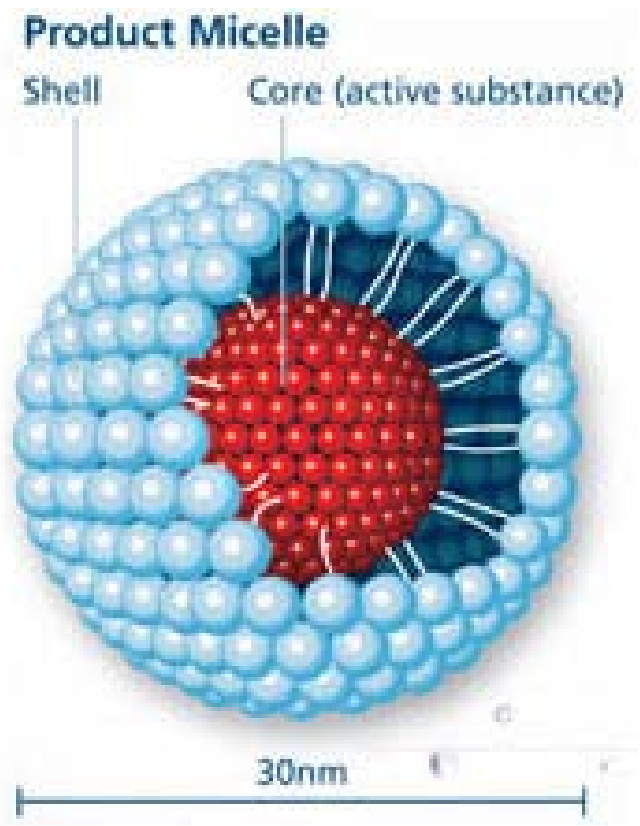
La encapsulación protege ingredientes alimentarios sensibles al calor, humedad y pH.

TECNIO
Be tech. Be competitive

CONSOLIDER MALTA

Planta de Tecnologia dels Aliments UAB

¿Cómo se hacen las nanocápsulas?



Cápsula

Componente Bioactivo

↓

Solución

↓

Pre-Homogeneización

↓

Tratamiento Ultra Alta Presión de Homogeneización

TECNIO
Be tech. Be competitive

CONSOLIDER ALTA

Planta de Tecnologia dels Aliments UAB

Nanotecnología y alimentación

NANOPARTÍCULAS comestibles para:

Crear bebidas inteligentes (con sabores y colores específicos).

“Mejorar" ciertos alimentos (nanoencapsulando antioxidantes para aumentar la absorción de alimentos específicos).

Hacer fármacos más efectivos.

TECNIO Be tech. Be competitive

CONSOLIDER ALTA

Planta de Tecnologia dels Aliments UAB

“Tip-Top Up” – Pan con Omega 3

- Nanocápsulas con Omega 3

- Nanocápsulas que se rompen únicamente en el estómago

Tip-Top bakery - Australia

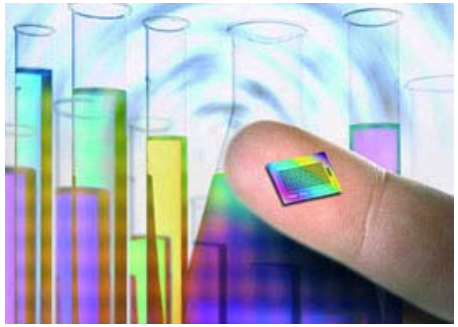
TECNIO
Be tech. Be competitive

CONSOLIDER ALTA

Planta de Tecnologia dels Aliments UAB

Otras aplicaciones de la Nanotecnología…

Pinturas protectoras contra la corrosión



Raquetas de tenis más fuertes y ligeras

Tejidos resistentes a las manchas

Pelotas de tenis de largo duración

Protectores solares y cosméticos

TECNIO
Be tech. Be competitive

CONSOLIDER MALTA

Planta de Tecnologia dels Aliments UAB

Muchas gracias!!

TECNIO
Be tech. Be competitive

CONSOLIDER MALTA

Planta de Tecnologia dels Aliments UAB

Efectos inducidos por la presión sobre agregados en medio acuoso:

Aplicación de Técnicas Volumétricas al Estudio de la Asociación de Caseínas

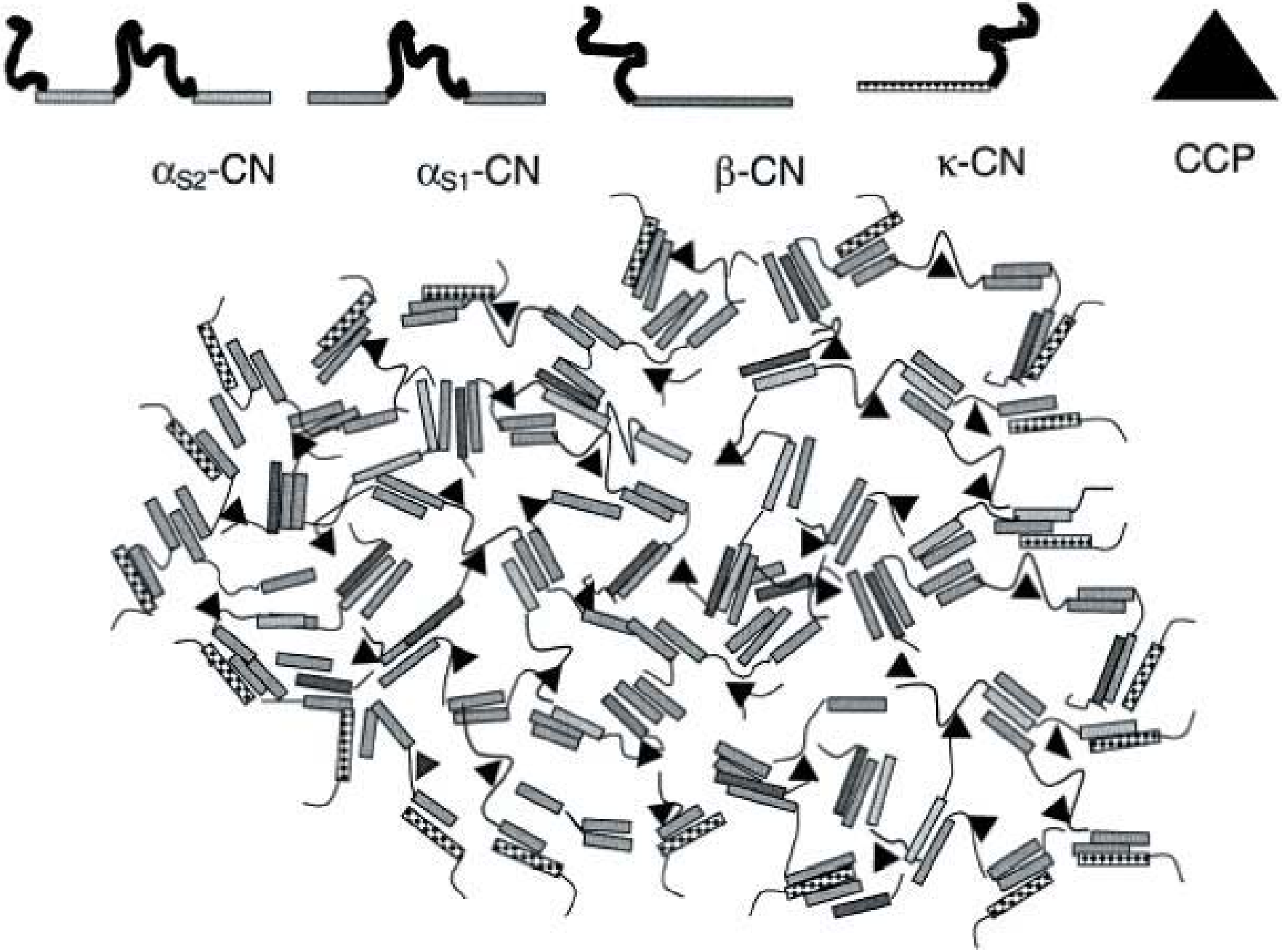
Bérengère Guignon

Instituto de Ciencia y Tecnología de los Alimentos y Nutrición

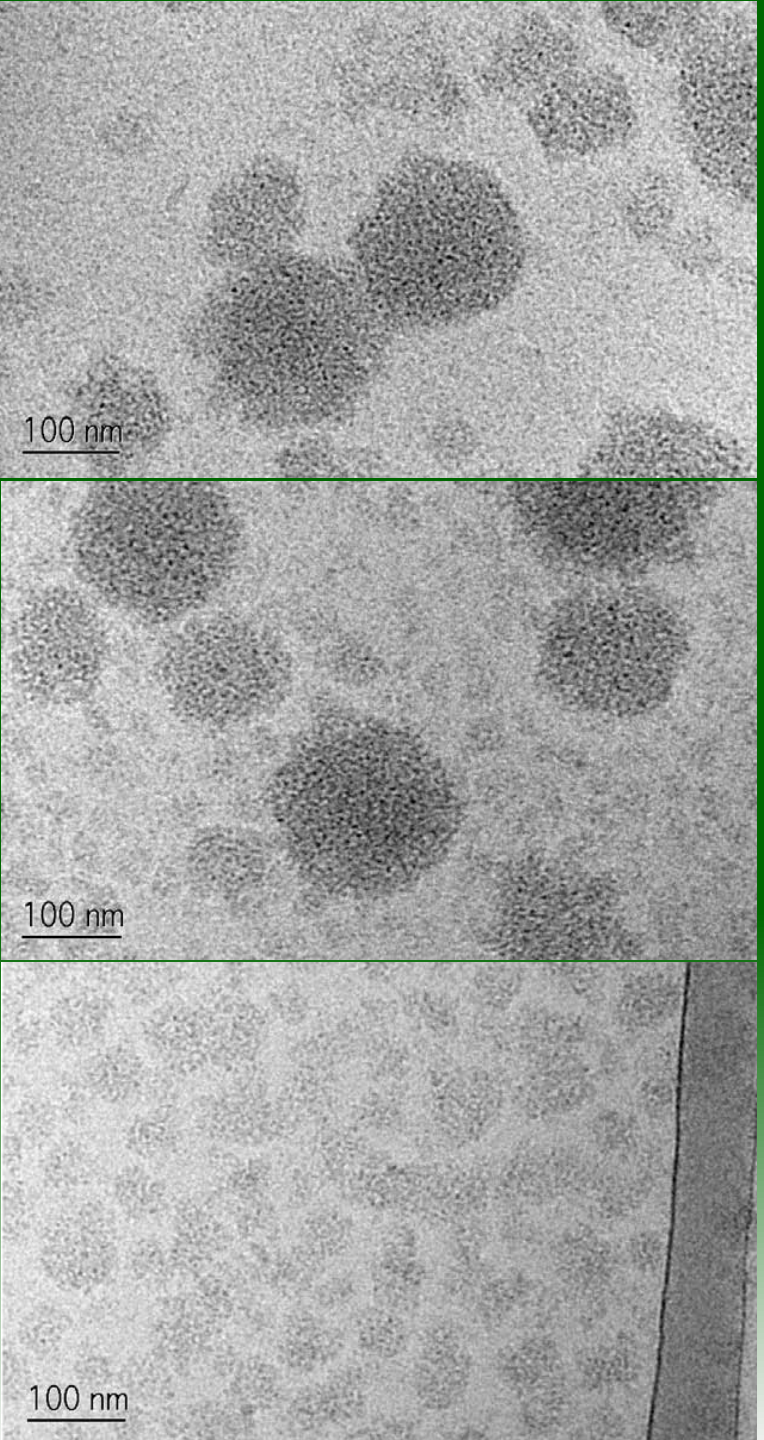
I Simposio MALTA Consolider

Miraflores de la Sierra, 23-27 enero 2011

Las caseínas


αs2-CN
αs1-CN
β-CN
κ-CN
CCP

Las altas presiones permiten modificar las propiedades tecnológicas de las caseínas



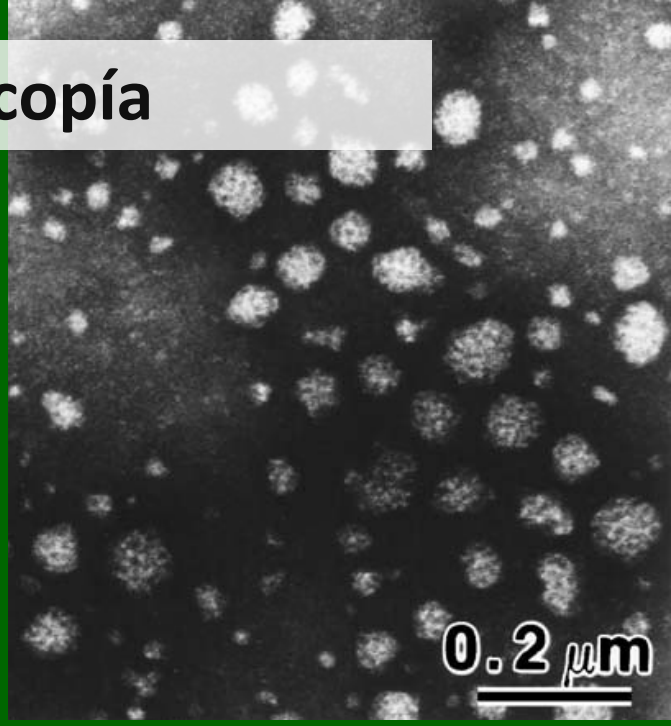
0,1 MPa

200 MPa

400 MPa

Dispersión de luz

Microscopía



Objetivo:

evaluar la aplicación de **técnicas volumétricas** para obtener información sobre el estado de agregación de las caseínas

Caracterización de propiedades volumétricas a Patm

Estrategia

Medidas macro

$v_\phi \quad k_{s\phi}$

Medidas micro

Datos publicados

Caracterización a alta presión

Medidas volumétricas

Patm	Alta Presión

$$1/\rho = v$$

Densidad ρ $\leftrightarrow$ Volumen específico $\boldsymbol{v}$

+ Velocidad del sonido u_s

$$v/u_s^2 = k_s$$

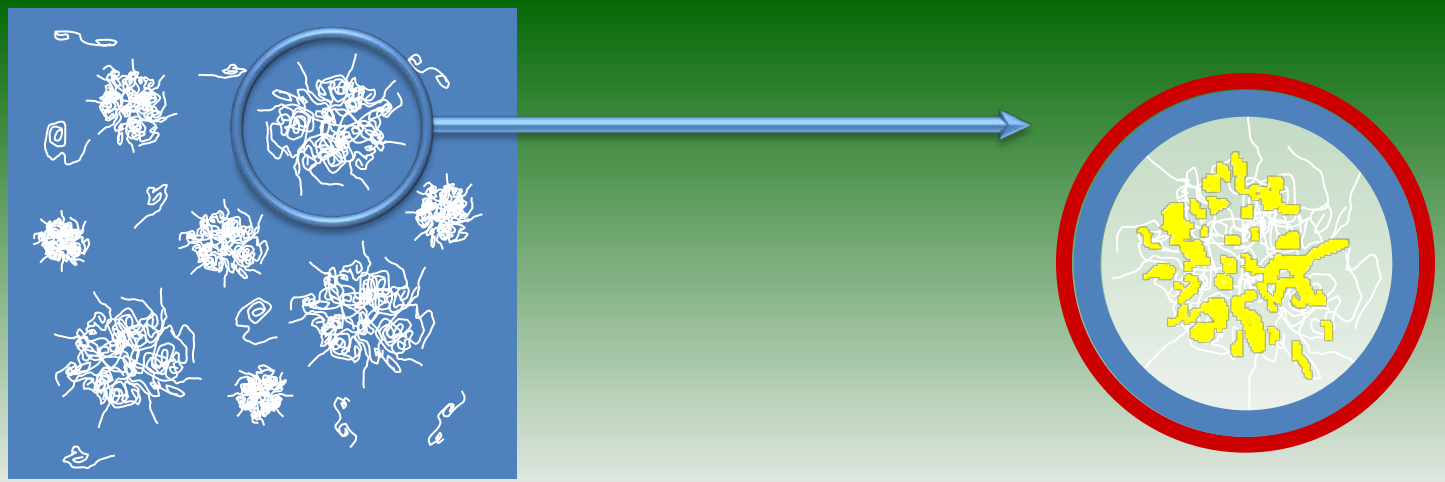
$\longrightarrow$ Compresibilidad adiabática $\boldsymbol{k_s}$

Volumen específico aparente

$$v_\phi = \frac{1}{w}\left(v - v_0\right) + v_0$$

Disolución de caseínas agua

$$v_\phi = v_{átomos} + v_{cavidad} + v_{hidratación} + v_{térmico} + v_{ideal}$$



Compresibilidad adiabática aparente

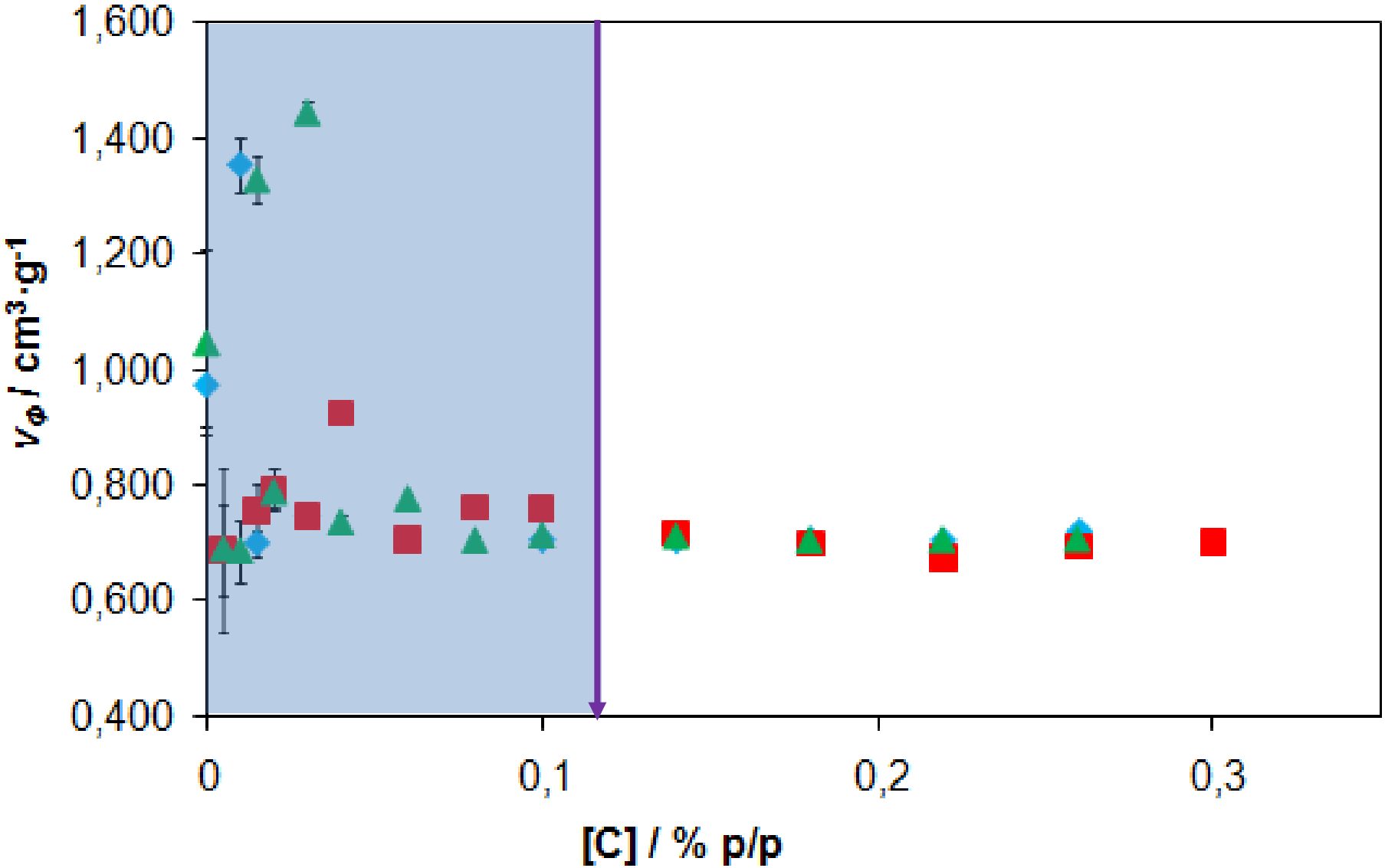
$$k_{s\phi} = \frac{1}{w}\left(\frac{v^2}{u_s^2} - \frac{v_0^2}{u_{s0}^2}\right) + \frac{v_0^2}{u_{s0}^2}$$

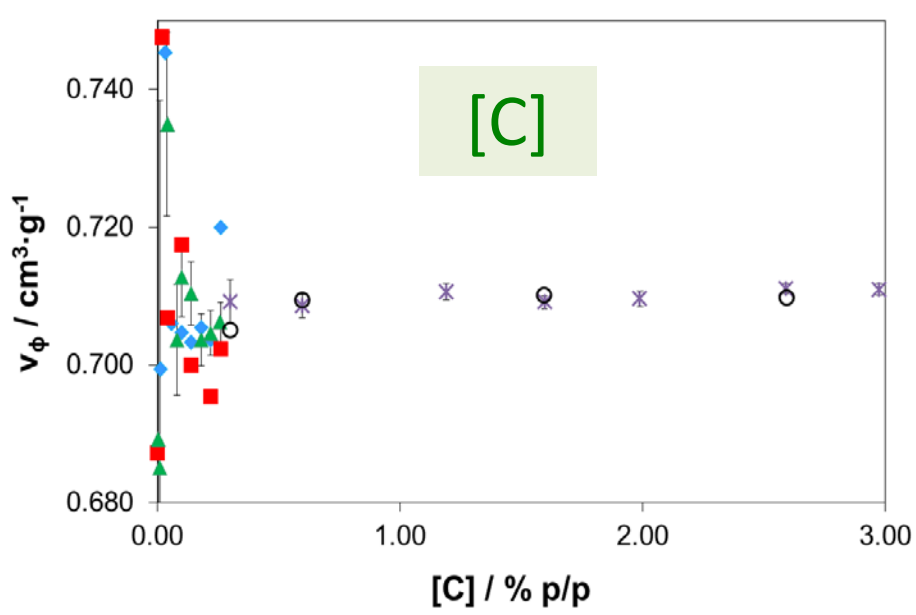
Disolución de caseínas agua

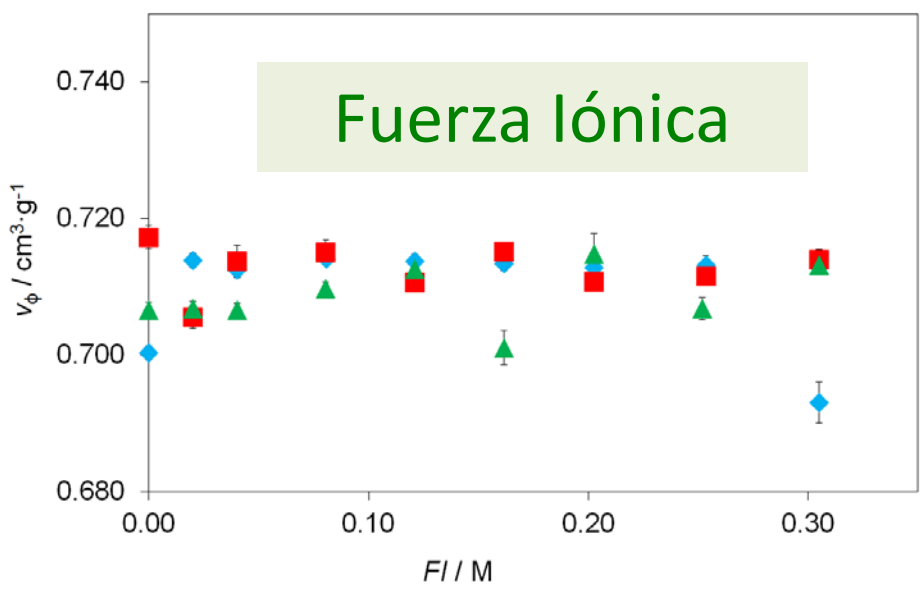
$$k_{s\phi} = k_{s\ cavidad} + k_{s\ hidratación} + k_{s\ térmico}$$

Resultados

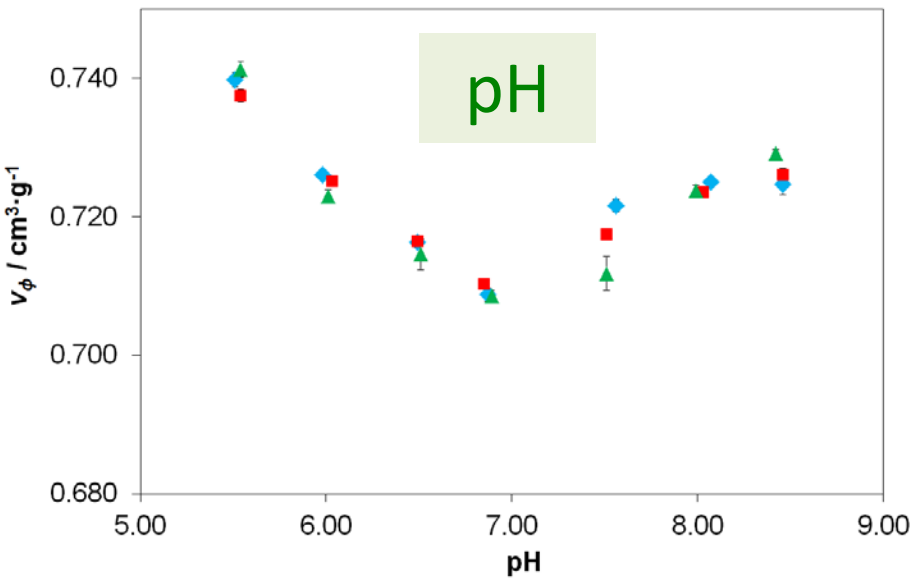
A Presión Atmosférica

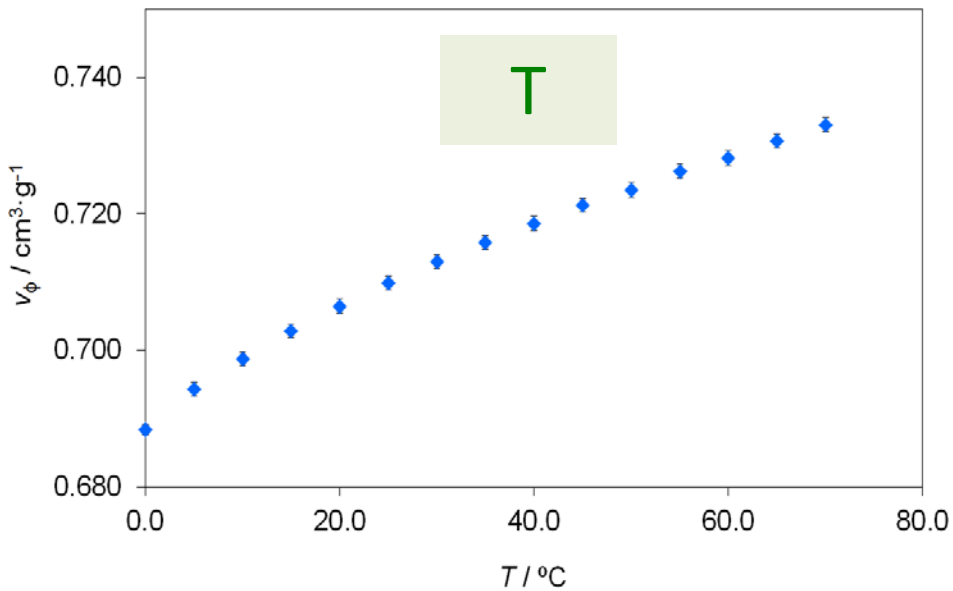




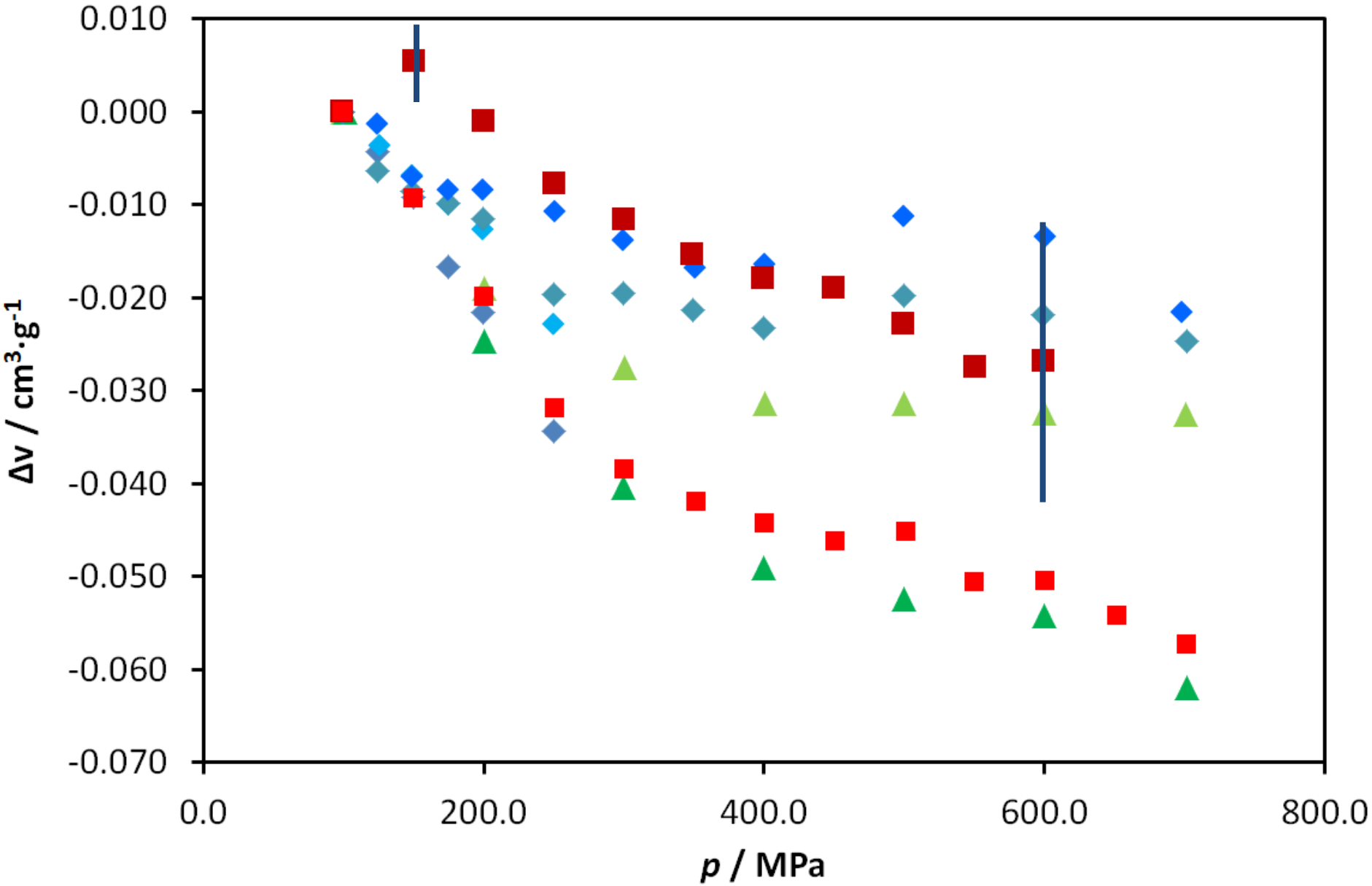


v_Φ a presión atmosférica





Δv_{Φ} a alta presión



Conclusión

A presión atmosférica:

- el proceso de asociación de las caseínas no es cooperativo
- las técnicas volumétricas son válidas para el estudio del estado de agregación de las caseínas.

A alta presión, se han identificado las siguientes dificultades para el desarrollo del método volumétrico:

- repetibilidad de p y T de un ensayo a otro (solvente, velocidad del sonido)
- incertidumbre de la presión

Efectos inducidos por la presión sobre agregados en medio acuoso. Estudio del dodecanoato de sodio mediante medidas de velocidad del sonido

Eduardo Hidalgo Baltasar

Miraflores de la Sierra 23-27 enero 2011

Introducción

Procesado de alimentos a alta presión

Sabor, olor, color

Textura

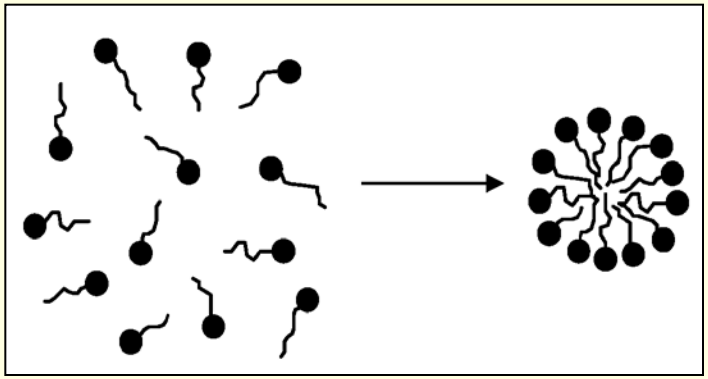
Microbiología

Economía

Medio Ambiente

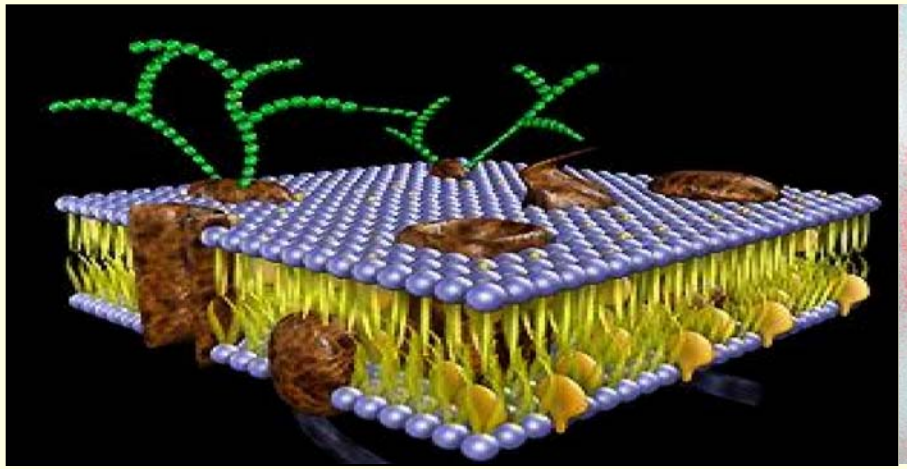
Introducción

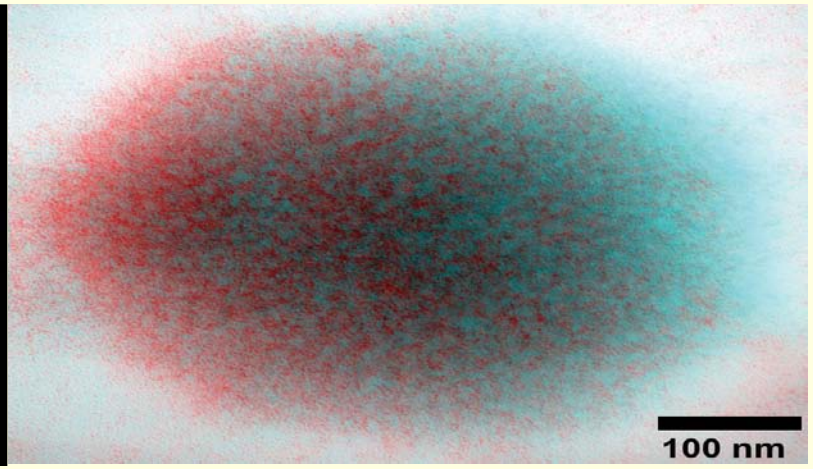
Monómeros anfifílicos



Micelas

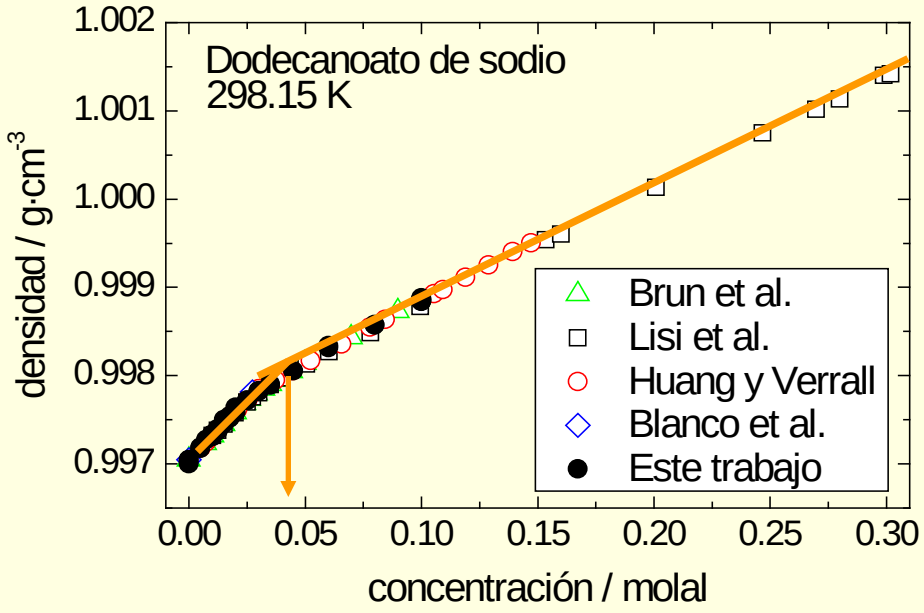
Las micelas como modelos de sistemas biológicos





Introducción

Concentración Micelar Crítica (cmc)

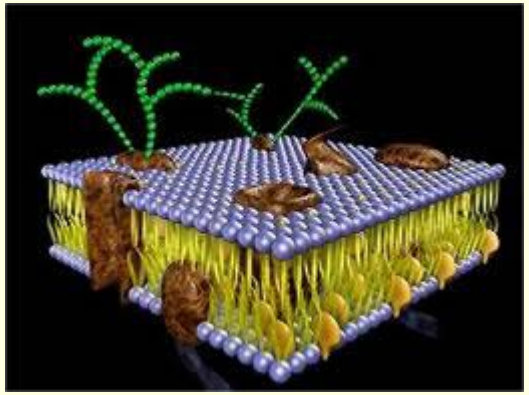


Cambio de Pendiente

cmc

Introducción

- ¿Por qué las membranas celulares se vuelven permeables?
- ¿Qué ley rige el efecto de la presión sobre las interacciones débiles?
- ¿Por qué las micelas de caseína se disocian a 150-250 MPa?



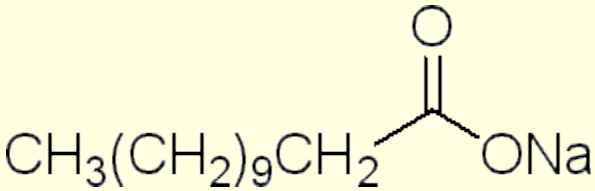
Introducción

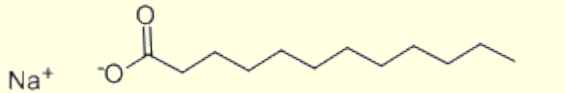
- UCM
  - Dpto. Química Física I
  - Espectroscopía Raman
  - Altas presiones: hasta 5 GPa
- CSIC-ICTAN
  - Dpto. de Procesos
  - Propiedades volumétricas y acústicas bajo presión
  - 45 mL - 700 MPa

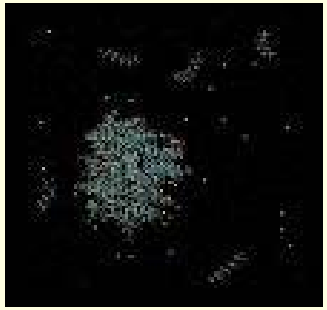
Efecto de la presión en sistemas micelares

Objetivos

- Efecto de la presión en diversas propiedades físico-químicas del sistema micelar agua-dodecanoato de sodio





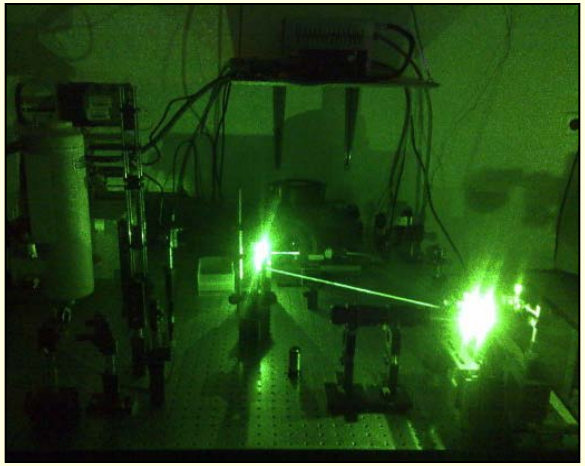


Experimentos

Densidad

Ultrasonidos

Espectroscopía Raman



Experimentos

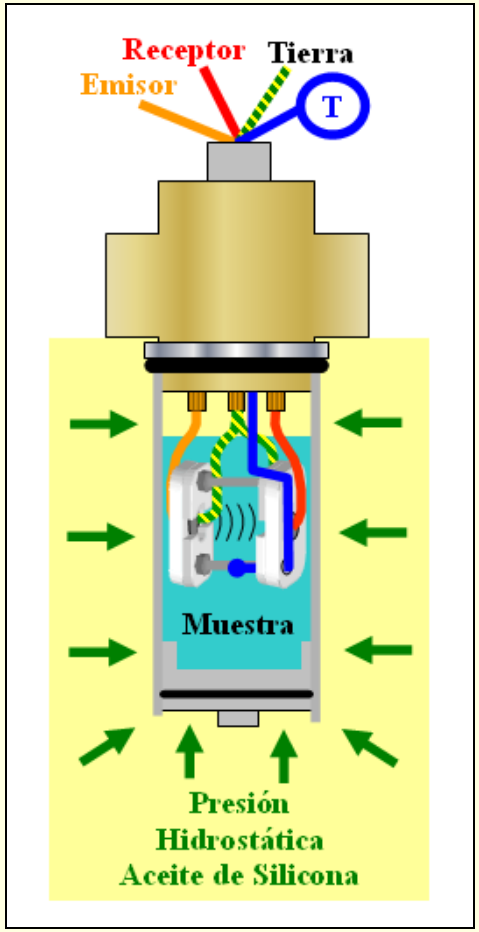
Ultrasonidos

A Presión atmosférica

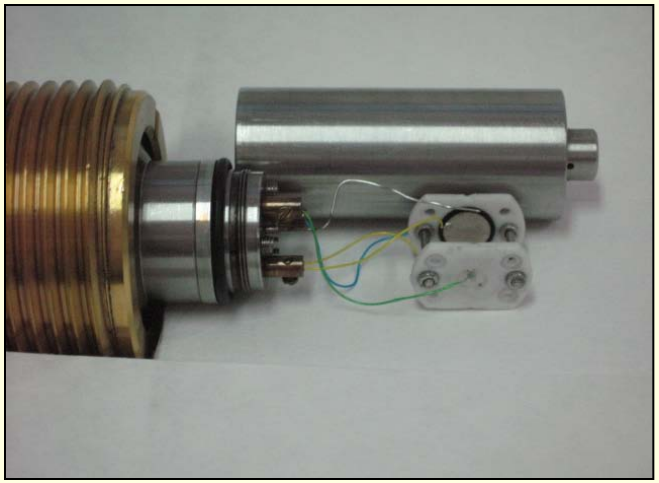
Alta Presión hasta 700 MPa

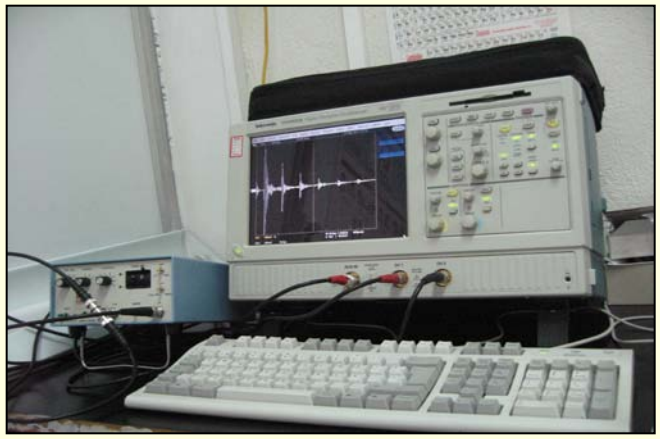
Dispositivos experimentales

- Transmisión con piezoeléctricos de 2 MHz

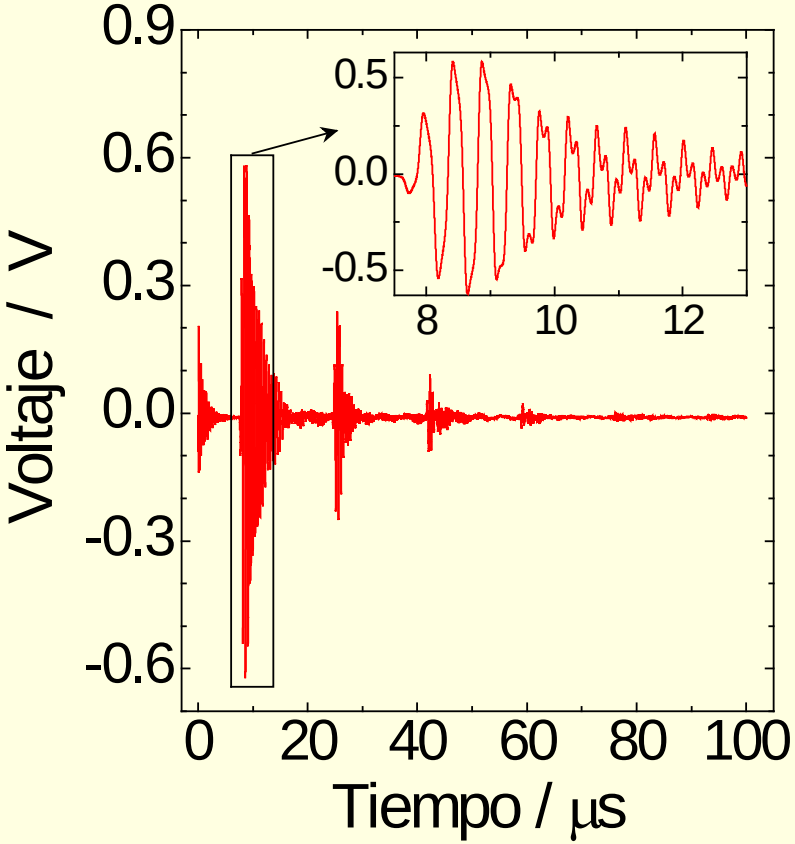


$$u_s = \frac{2d}{\Delta t}$$

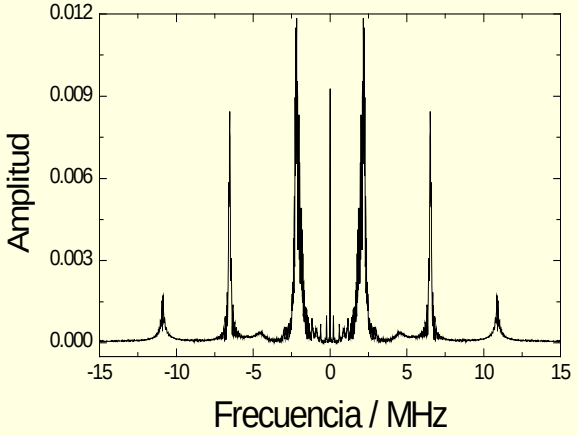


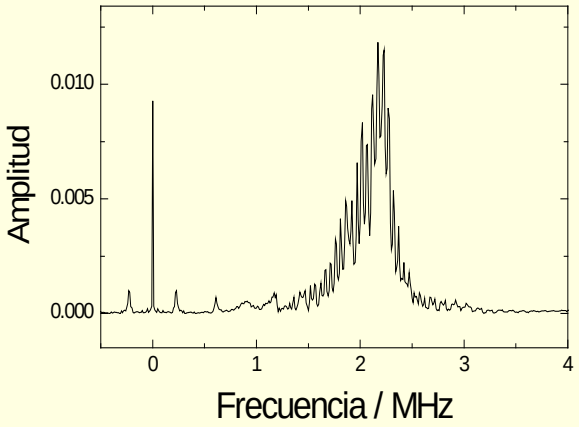


Tratamiento de la señal

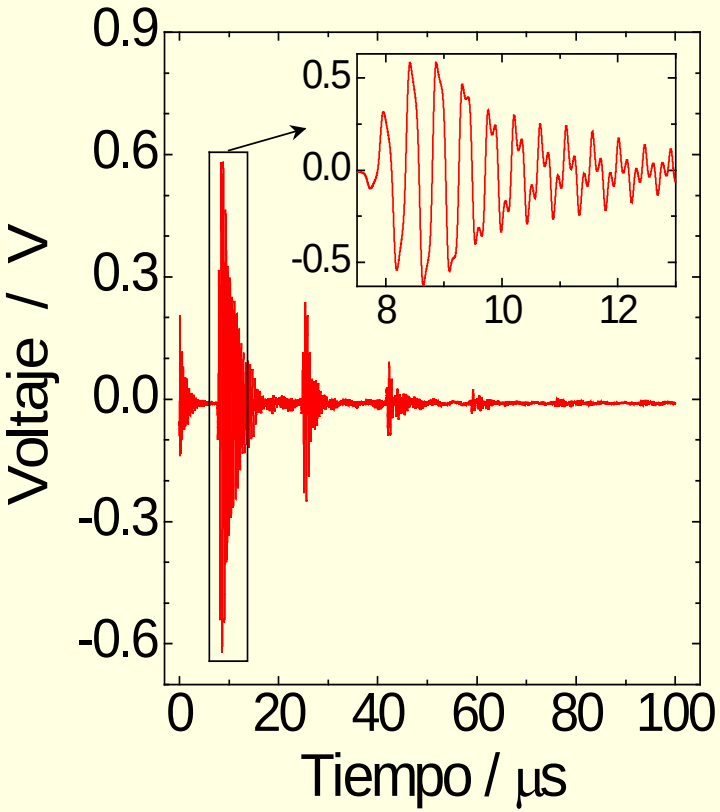


Transformada de Fourier

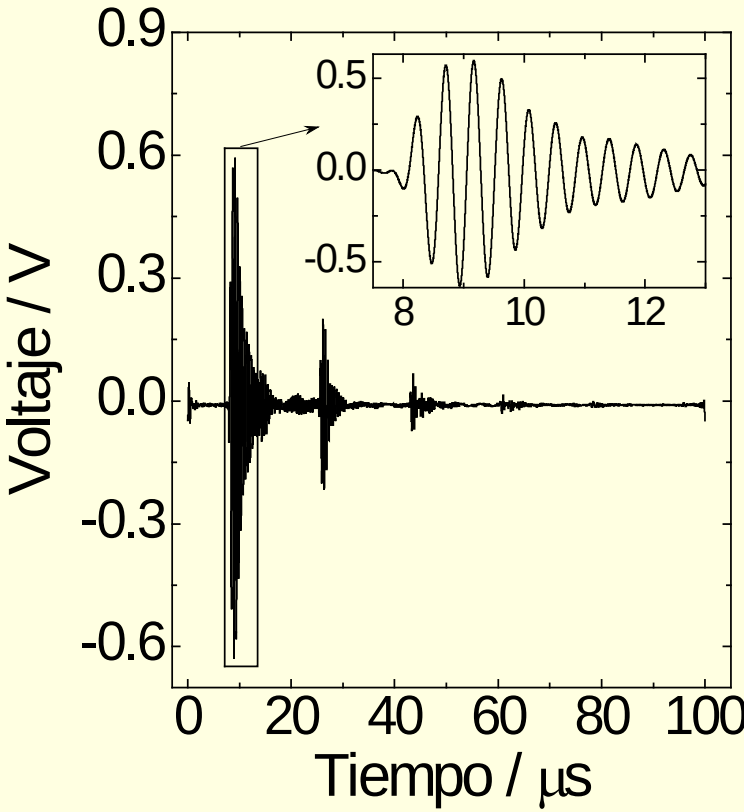




Tratamiento de la señal

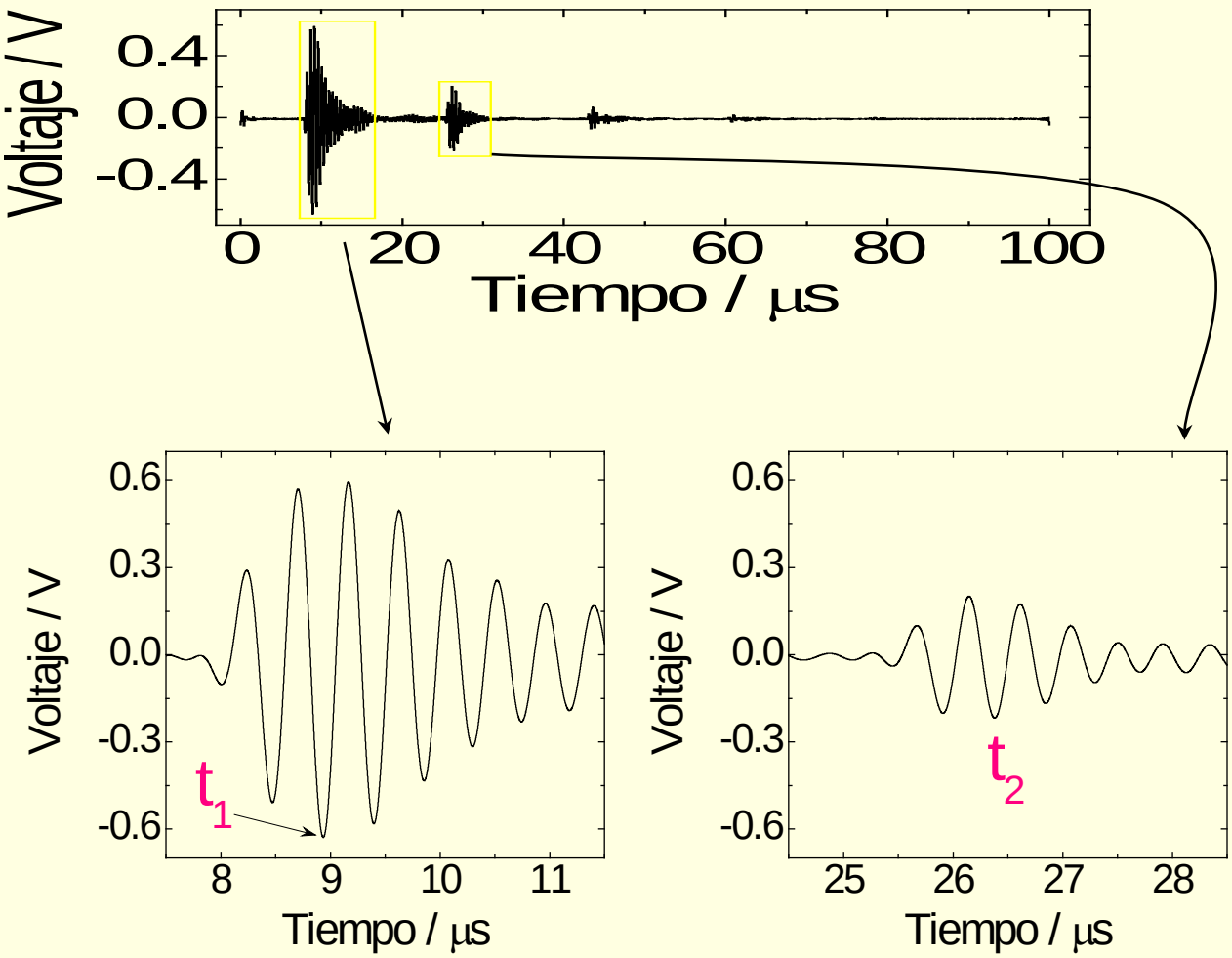


Transformada de Fourier



Leer tiempos con precisión

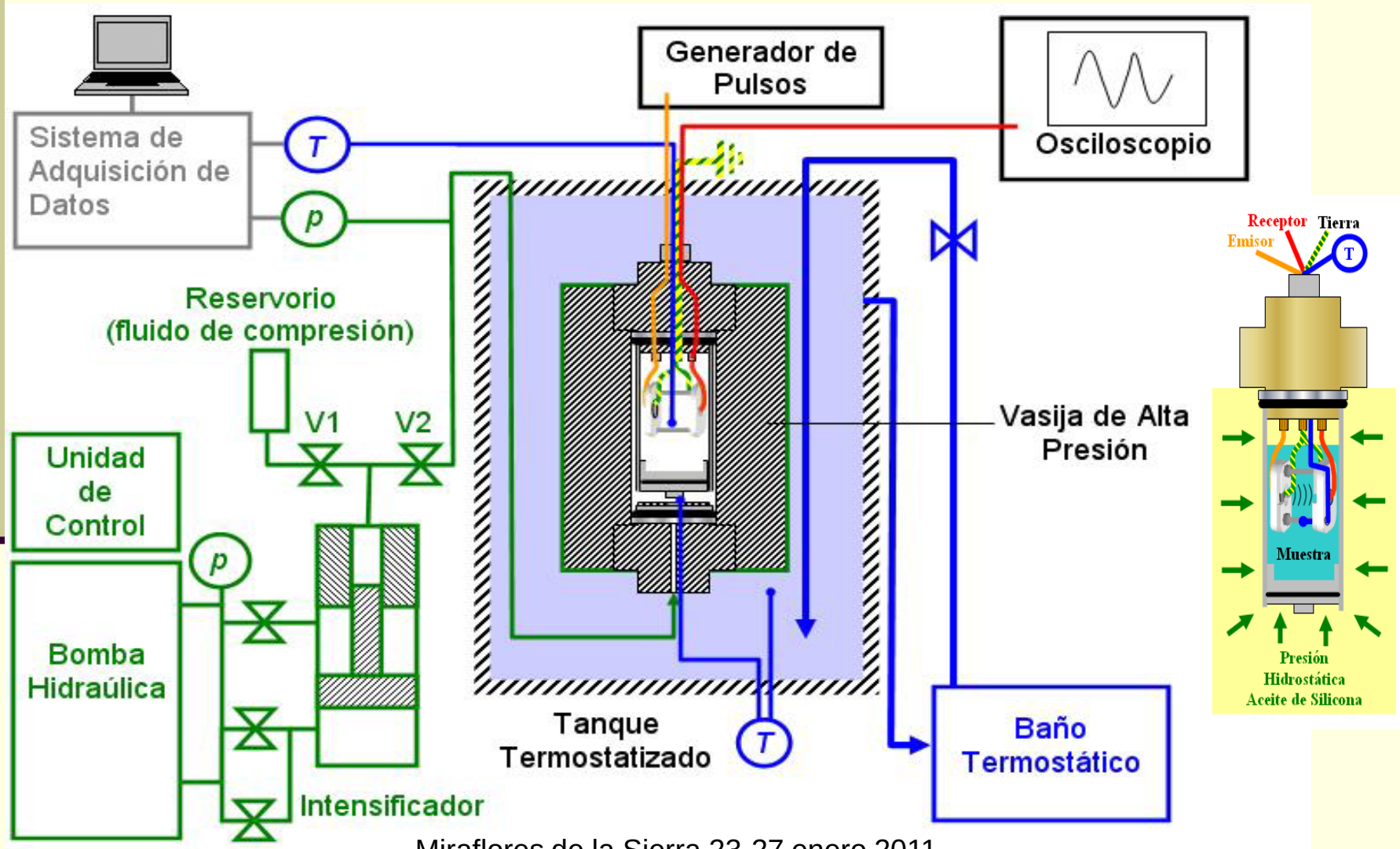
Determinación del tiempo de vuelo



$$\Delta t = t_2 - t_1$$

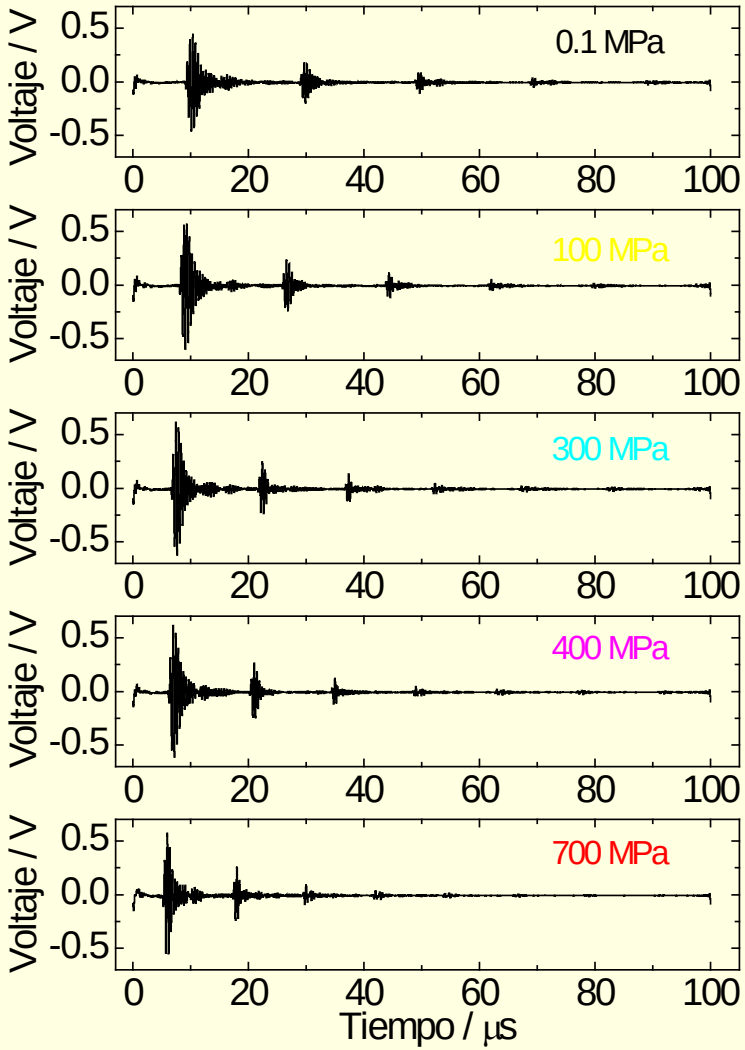
$$u_s = \frac{2d}{\Delta t}$$

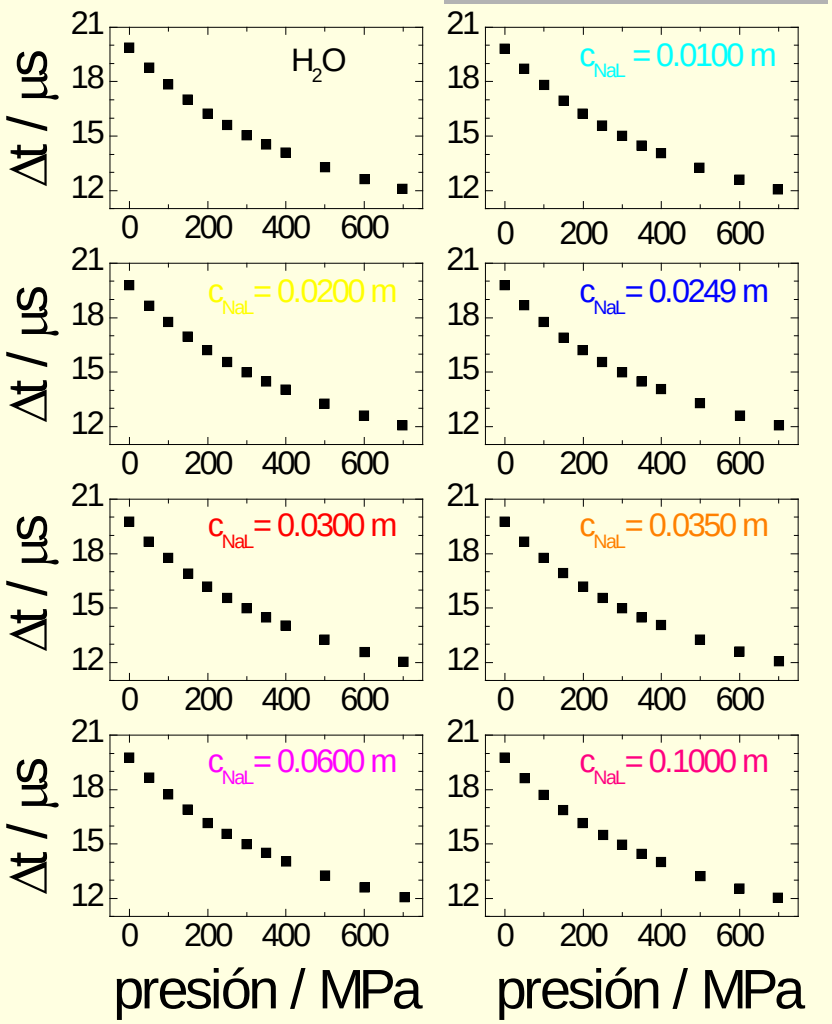
Equipo de Alta Presión



Resultados experimentales:

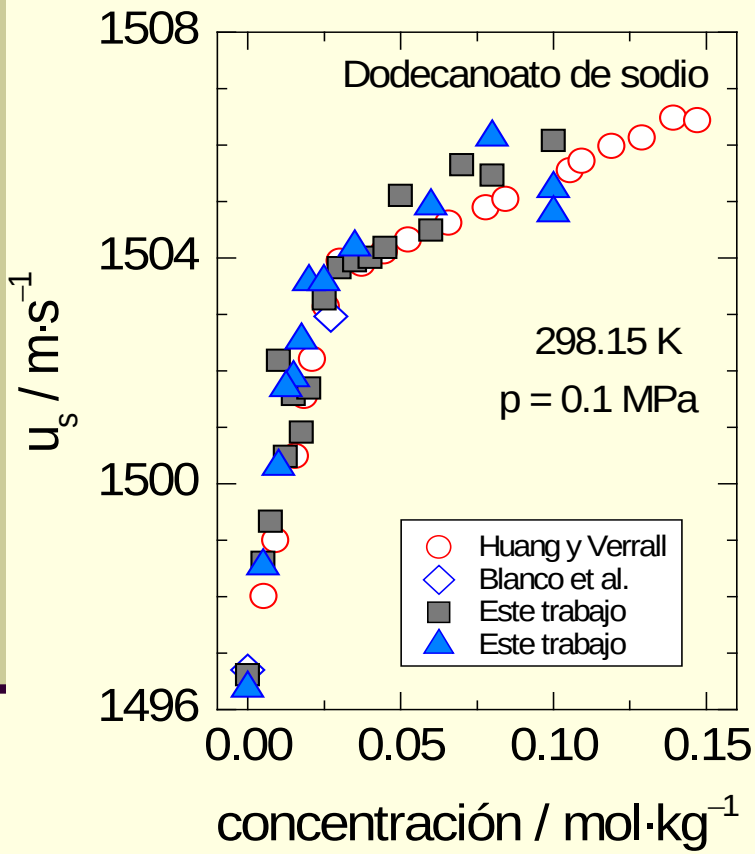
Tiempo de vuelo

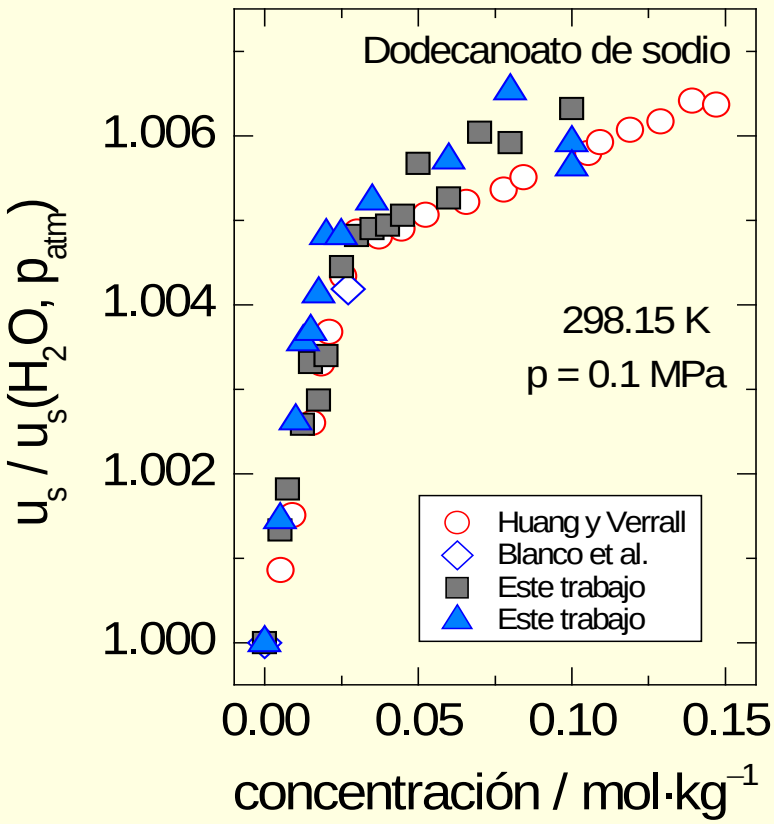




Resultados experimentales:

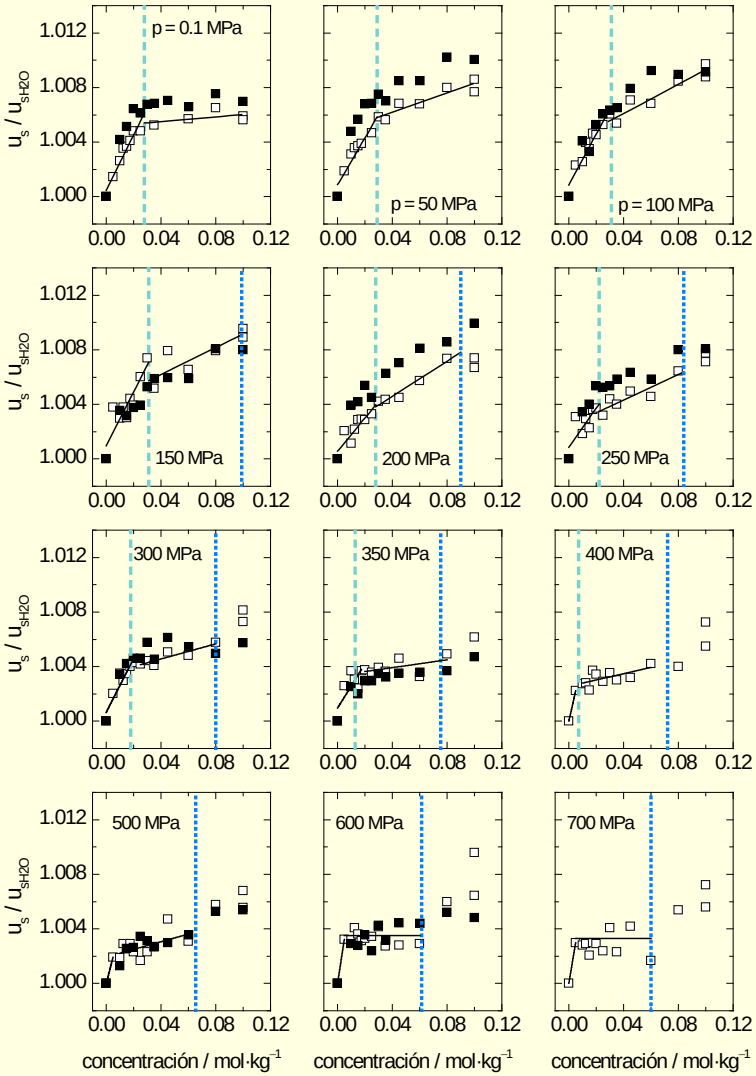
Velocidad del sonido a presión atmosférica

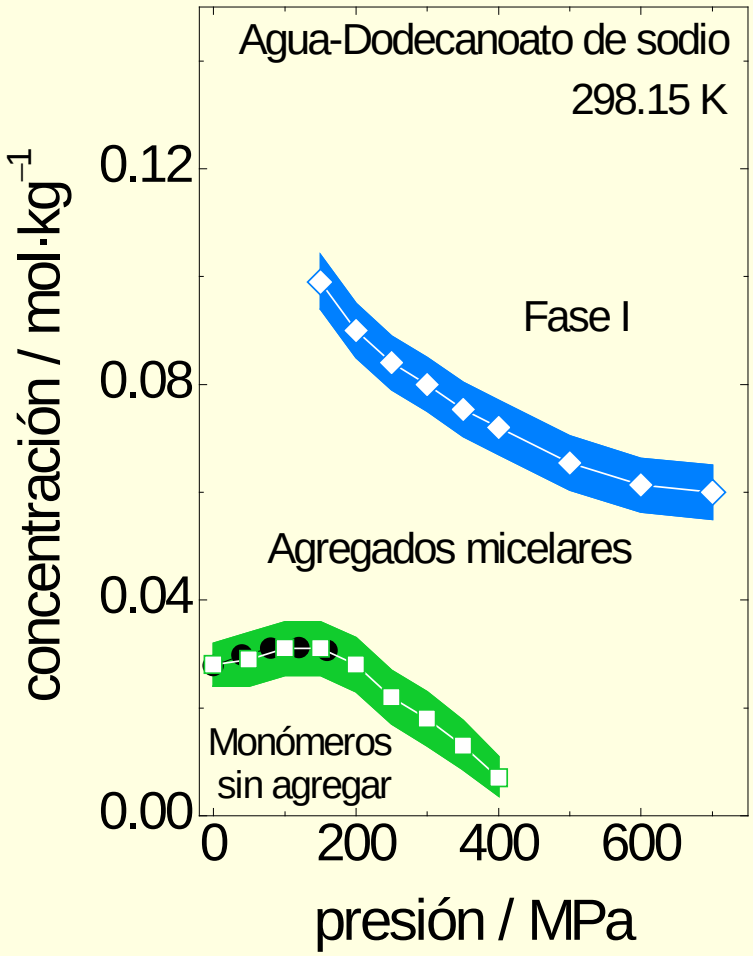




$$u_s = \frac{2d}{\Delta t}$$

Resultados experimentales:
Velocidad del sonido a altas presiones





Conclusiones

- Presión atmosférica y alta presión

Validez de la técnica de ultrasonidos

- Presión atmosférica

Densidad

Volumen molar aparente

Densidad + Ultrasonidos

Compresibilidad Adiabática

Gracias por la atención

www.malta-consolider.com

CONSOLIDER MALTA

Matter at High Pressure

PROGRAMA INGENIO 2010

CSIC

MALTA Reunión, Miraflores, España

El enlace químico en moléculas heterodiatómicas bajo la perspectiva de la teoría de Átomos Cuánticos Interaccionantes (IQA)

Aurora Costales, M. A. Blanco, E. Francisco y A. Martín Pendás

Universidad de Oviedo
Dpto. Química Física y Analítica

Organización de la charla

1. Partición energética QTAIM
2. La teoría IQA
3. Energía de enlace en moléculas heterodiatómicas
4. Conclusiones

Organización de la charla

1. Partición energética QTAIM
2. La teoría IQA
3. Energía de enlace en moléculas heterodiatómicas
4. Conclusiones

Organización de la charla

1. Partición energética QTAIM
2. La teoría IQA
3. Energía de enlace en moléculas heterodiatómicas
4. Conclusiones

Organización de la charla

1. Partición energética QTAIM
2. La teoría IQA
3. Energía de enlace en moléculas heterodiatómicas
4. Conclusiones

Partición energética QTAIM

- Partición del espacio en cuencas atómicas:

$$R^3 \rightarrow \bigcup_A \Omega_A \quad \Rightarrow \quad 1 = \sum_A \omega_A, \quad \omega_A(\vec{r}) = \begin{cases} 1 & \vec{r} \in \Omega_A \\ 0 & \vec{r} \notin \Omega_A \end{cases}$$

Partición energética QTAIM

- Partición del espacio en cuencas atómicas:
  $R^3 \rightarrow \bigcup_A \Omega_A \;\; \Rightarrow \;\; 1 = \sum_A \omega_A, \quad \omega_A(\vec{r}) = \begin{cases} 1 & \vec{r} \in \Omega_A \\ 0 & \vec{r} \notin \Omega_A \end{cases}$
- Partición de las matrices densidad:
  $\rho(\vec{r}) = \sum_A \rho_A(\vec{r})$ con $\rho_A(\vec{r}) = \rho(\vec{r})\omega_A(\vec{r})$.
  Particiones similares para $\rho_1(1;1')$ y $\rho_2(1,2)$.
  Se puede extender: Cuencas ELF, átomos difusos, ...

Partición energética QTAIM

- Partición del espacio en cuencas atómicas:
  $R^3 \to \bigcup_A \Omega_A \;\; \Rightarrow \;\; 1 = \sum_A \omega_A, \quad \omega_A(\vec{r}) = \begin{cases} 1 & \vec{r} \in \Omega_A \\ 0 & \vec{r} \notin \Omega_A \end{cases}$
- Partición de las matrices densidad:
  $\rho(\vec{r}) = \sum_A \rho_A(\vec{r})$ con $\rho_A(\vec{r}) = \rho(\vec{r})\omega_A(\vec{r})$.
  Particiones similares para $\rho_1(1;1')$ y $\rho_2(1,2)$.
  Se puede extender: Cuencas ELF, átomos difusos, ...
- Así se induce una partición de la energía total
  $E = E_1 + E_2 + \frac{1}{2}\sum_{A,B\neq A} V_{nn}^{AB}$ con
  $E_1 = \sum_A T^A + \sum_{A,B} V_{en}^{AB}$
  $E_2 = \sum_A V_{ee}^{AA} + \frac{1}{2}\sum_{A,B\neq A} V_{ee}^{AB}$

Teoría IQA: términos de 1 & 2-átomos

Términos energéticos: T^A, V_{nn}^{AB}, $V_{en}^{AB} = V_{ne}^{BA}$, V_{ee}^{AB}

$A = B$ (1 átomo), $A \neq B$ (2 átomos)

Teoría IQA: términos de 1 & 2-átomos

Términos energéticos: T^A, V_{nn}^{AB}, $V_{en}^{AB} = V_{ne}^{BA}$, V_{ee}^{AB}

$A = B$ (1 átomo), $A \neq B$ (2 átomos)

- $E_{\text{net}}^A = T^A + V_{en}^{AA} + V_{ee}^{AA}$,
  equivalente a las energías de los átomos libres

Teoría IQA: términos de 1 & 2-átomos

Términos energéticos: T^A, V_{nn}^{AB}, $V_{en}^{AB} = V_{ne}^{BA}$, V_{ee}^{AB}

$A = B$ (1 átomo), $A \neq B$ (2 átomos)

- $E_{\text{net}}^{A} = T^A + V_{en}^{AA} + V_{ee}^{AA}$,
  equivalente a las energías de los átomos libres
- $E_{\text{int}}^{AB} = V_{nn}^{AB} + V_{en}^{AB} + V_{ne}^{AB} + V_{ee}^{AB}$,
  incluye todas las interacciones interatómicas interpartículas

Teoría IQA: términos de 1 & 2-átomos

Términos energéticos: T^A, V_{nn}^{AB}, $V_{en}^{AB} = V_{ne}^{BA}$, V_{ee}^{AB}

$A = B$ (1 átomo), $A \neq B$ (2 átomos)

- $E_{\text{net}}^{A} = T^A + V_{en}^{AA} + V_{ee}^{AA}$,
  equivalente a las energías de los átomos libres
- $E_{\text{int}}^{AB} = V_{nn}^{AB} + V_{en}^{AB} + V_{ne}^{AB} + V_{ee}^{AB}$,
  incluye todas las interacciones interatómicas interpartículas
- $E = \sum_A E_{\text{net}}^{A} + \frac{1}{2} \sum_{A,B \neq A} E_{\text{int}}^{AB}$,
  incluye las energías de los átomos cuánticos más una suma de sus interacciones de pareja

Energías de enlace y de deformación

- E_{bind} se define respecto a una referencia
  $E_{\mathrm{bind}} = E - \sum_A E^A_{\mathrm{vac}}$

Energías de enlace y de deformación

- E_{bind} se define respecto a una referencia
  $E_{\mathrm{bind}} = E - \sum_A E^A_{\mathrm{vac}} = \sum_A E^A_{\mathrm{def}} + \frac{1}{2}\sum_{A,B\neq A} E^{AB}_{\mathrm{int}}$
- Definimos la E_{def} como la diferencia entre las energías atómicas en la molécula y en el vacío
  $E^A_{\mathrm{def}} = E^A_{\mathrm{net}} - E^A_{\mathrm{vac}}$

Energías de enlace y de deformación

- $E_{\rm bind}$ se define respecto a una referencia
  $E_{\rm bind} = E - \sum_A E^A_{\rm vac} = \sum_A E^A_{\rm def} + \frac{1}{2}\sum_{A,B\neq A} E^{AB}_{\rm int}$
- Definimos la $E_{\rm def}$ como la diferencia entre las energías atómicas en la molécula y en el vacío
  $E^A_{\rm def} = E^A_{\rm net} - E^A_{\rm vac} \equiv E^A_{\rm def}({\rm CT}) + E^A_{\rm def}({\rm CR})$
  - Transferencia de carga, $E^A_{\rm def}({\rm CT}) > 0$ para $Q^A > 0$ (catión), negativa para el anión
  - Redistribución de carga: $E^A_{\rm def}({\rm CR}) > 0$
- En general, $E^A_{\rm def} > 0 \Rightarrow \sum E^A_{\rm def} > 0 \Rightarrow \sum E^{AB}_{\rm int} < 0$ y para que exista enlace: compensación entre deformaciones pequeñas e interacciones estabilizantes grandes

Interacciones: Coulomb & exch-corr

- Definiendo $\rho_2^{\mathrm{C}}(1,2) = \rho(1)\rho(2)$ y $\rho_2^{xc} = \rho_2 - \rho_2^{\mathrm{C}}$:

$$V_{ee}^{AB} = V_{\mathrm{C}}^{AB} + V_{xc}^{AB}$$

- Definiendo $V_{\mathrm{cl}}^{AB} = V_{\mathrm{C}}^{AB} + V_{en}^{AB} + V_{ne}^{AB} + V_{nn}^{AB}$:

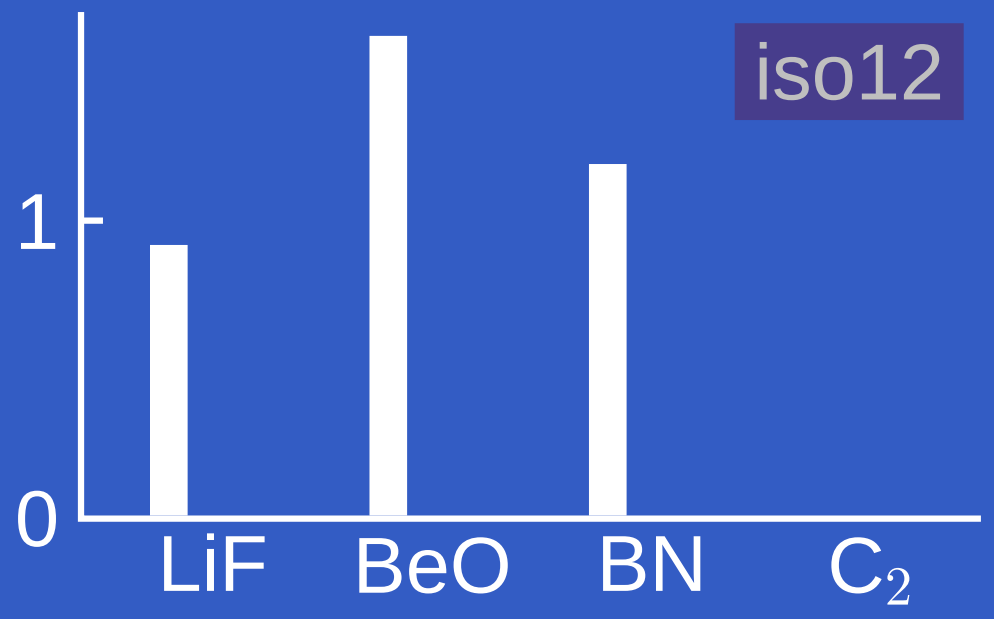
$$E_{\mathrm{int}}^{AB} = V_{\mathrm{cl}}^{AB} + V_{xc}^{AB}$$

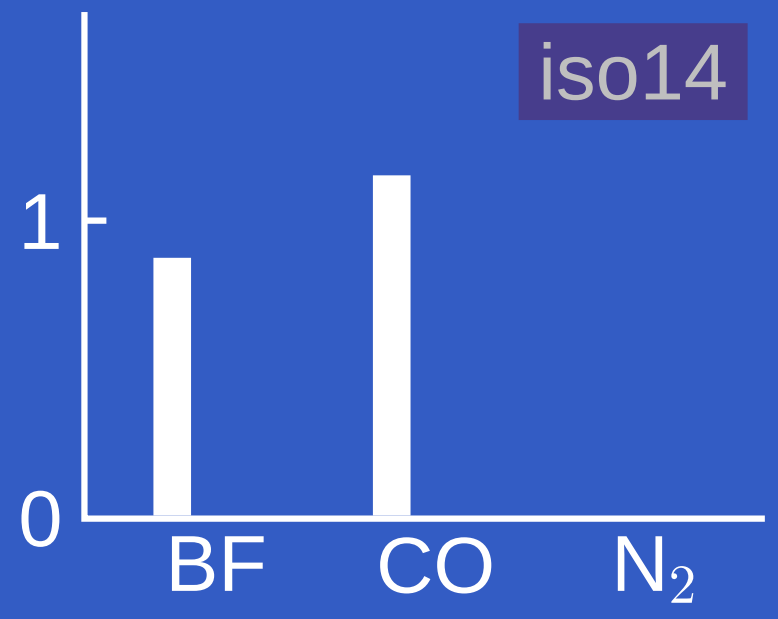
- Para densidades bien-separadas, $V_{\mathrm{cl}}^{AB} \simeq$ multipolar, $E_Q^{AB} = Q^A Q^B / R_{AB} \Rightarrow$ ionicidad
- $V_{xc}^{AB} = \int_A \int_B \rho_2^{xc} r_{12}^{-1}$ relacionada con la covalencia. El orden de enlace se mide con $\delta_{AB} = 2\left|\int_A \int_B \rho_2^{xc}\right|$, que determina el número de pares de electrones compartidos

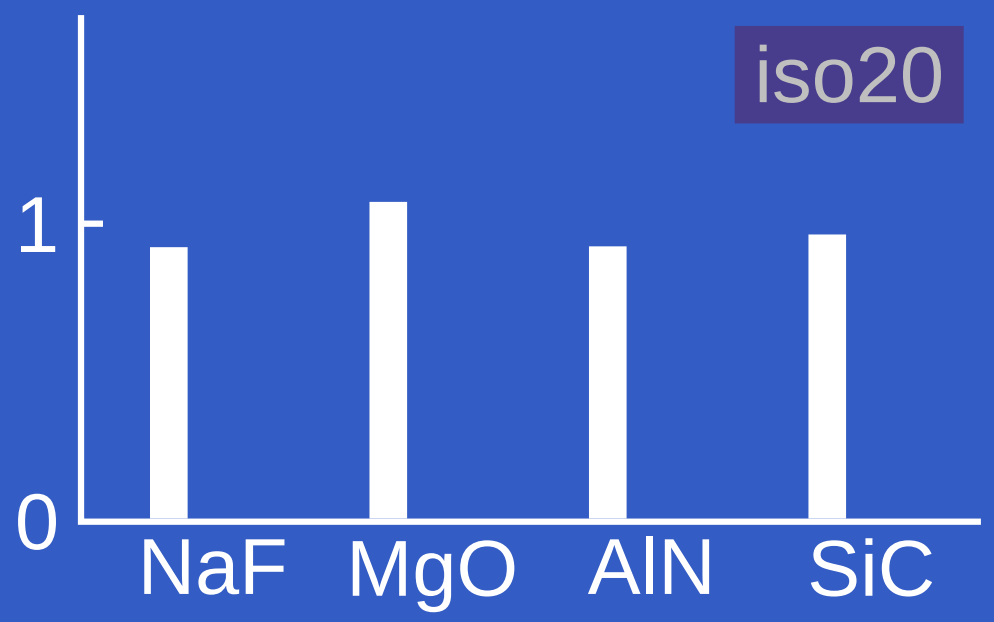
Detalles computacionales

- Heterodiatómicas: series isoelectrónicas, 12e (LiF, BeO, BN, C_2), 14e (BF, CO, N_2), y 20e (NaF, MgO, AlN, SiC)
- TZV(d) cálculos CAS: $[8, 8]$ (iso12, 20), y $[10, 10]$ (iso14)
- 1-2 % error en R_e, 5-10 % en D_e con respecto a valores experimentales
- Integraciones IQA 2-e: $600(r) \times 3890$(Lebedev) $+ \beta$-esferas
- Errores en $Q < 1$ me y 0.1 mE_h en las energías
- Unidades: Q en e, E en E_h

Ionicidad y cargas atómicas

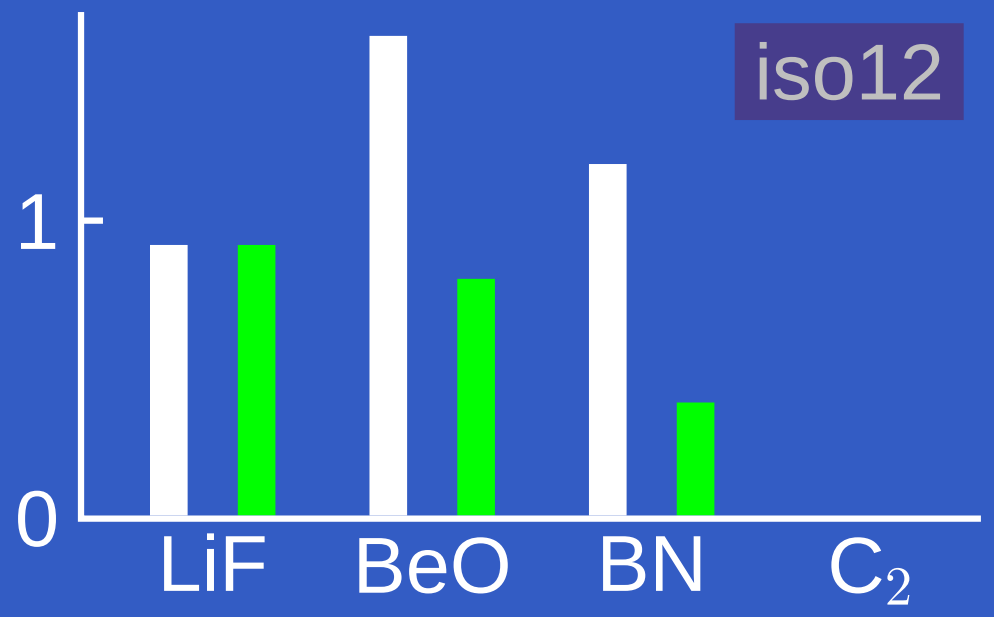


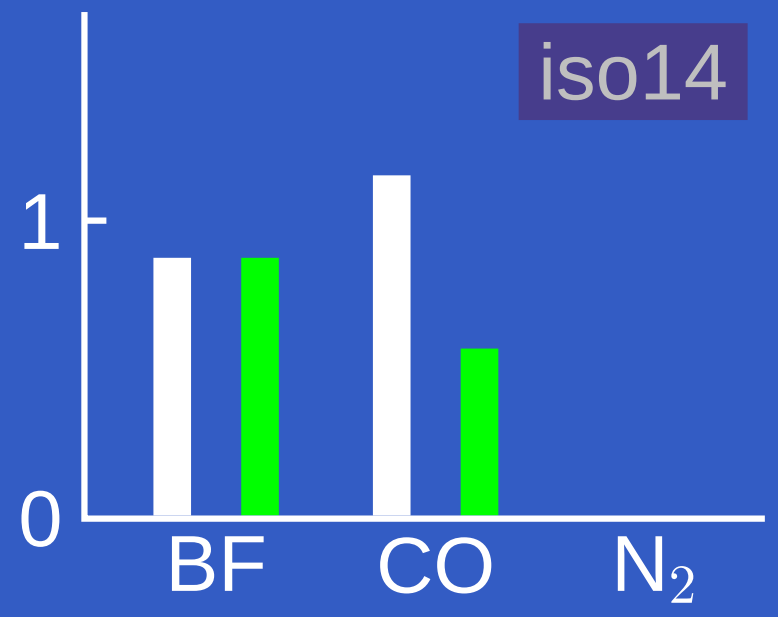


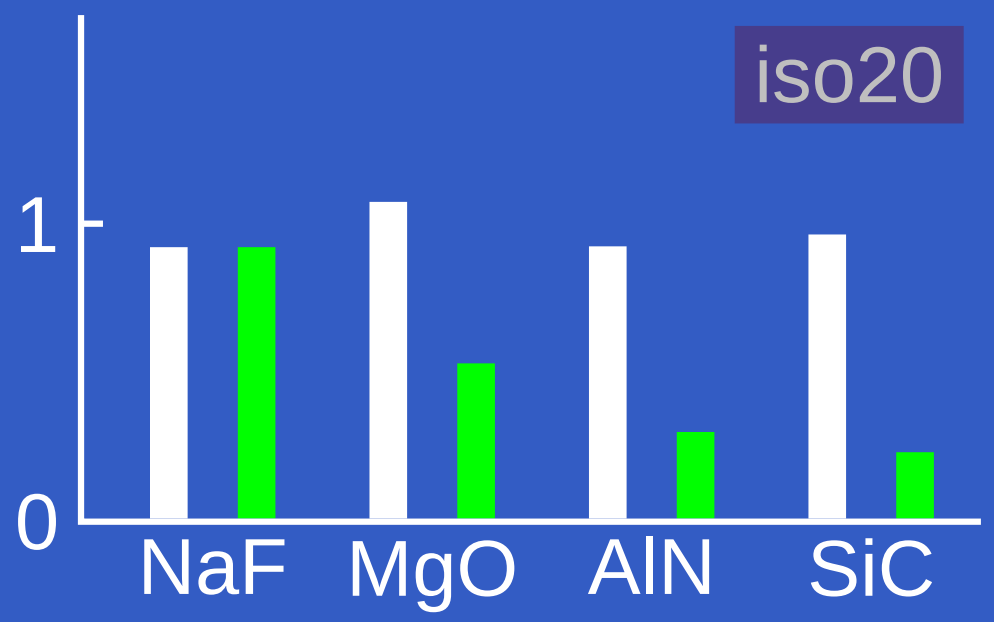


Q^A

Ionicidad y cargas atómicas



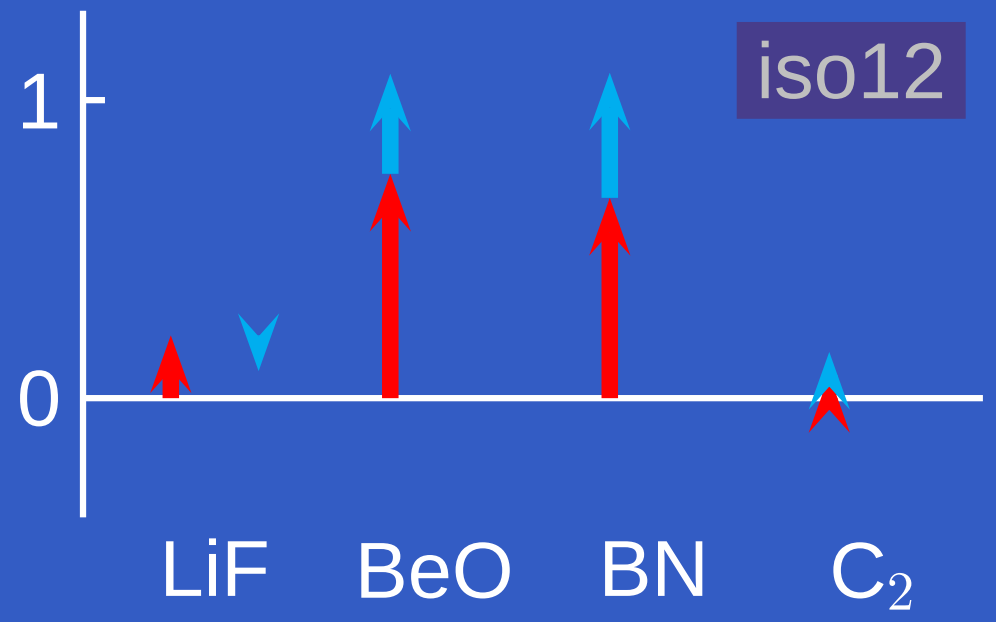


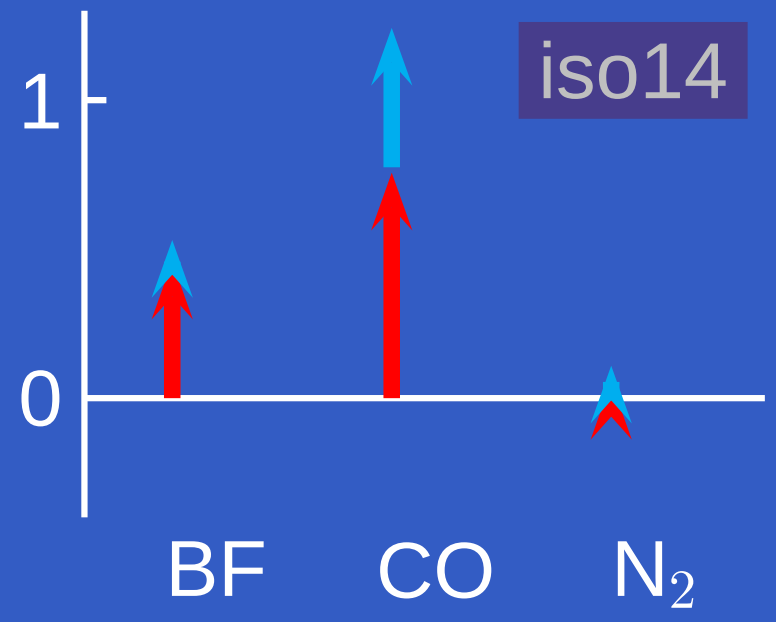


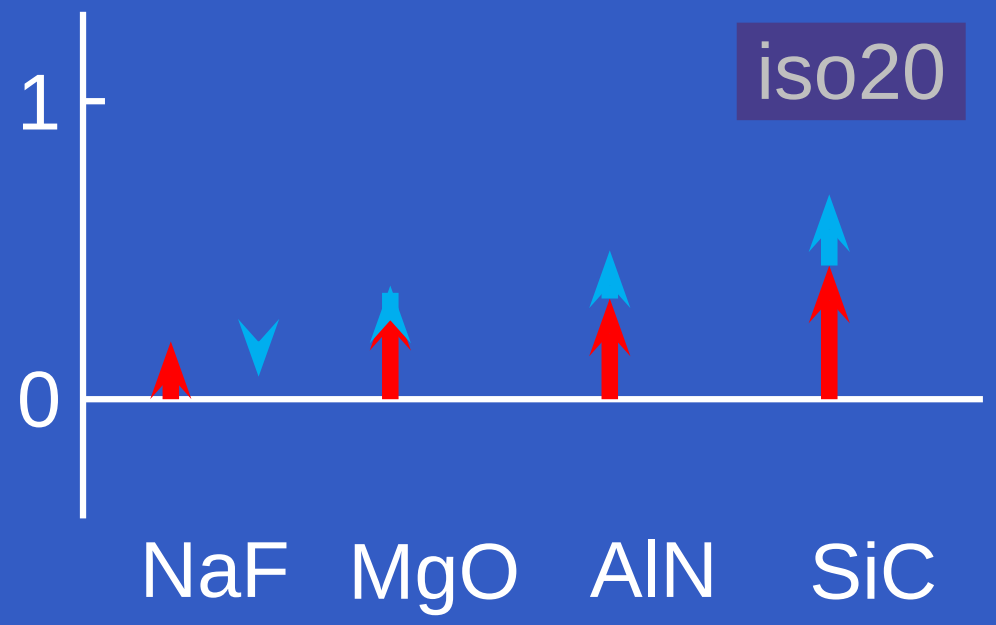
Q^A Q^A/Q^A_{nom}

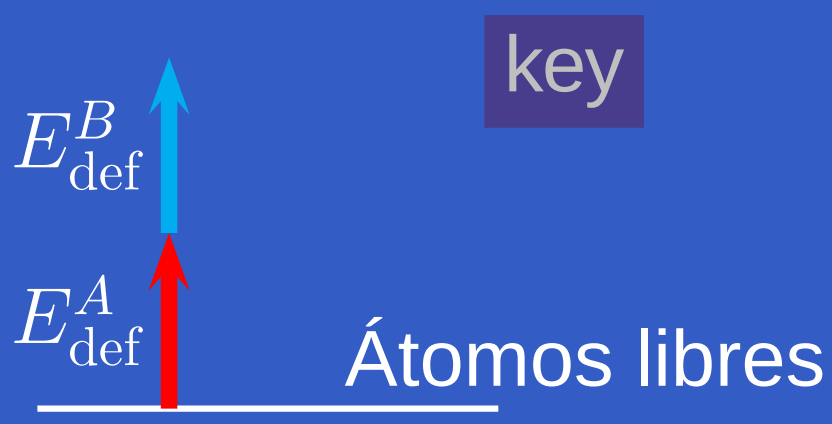
La ionicidad se define, en general, comparando con los hipotéticos iones nominales

Componentes de la Energía de enlace

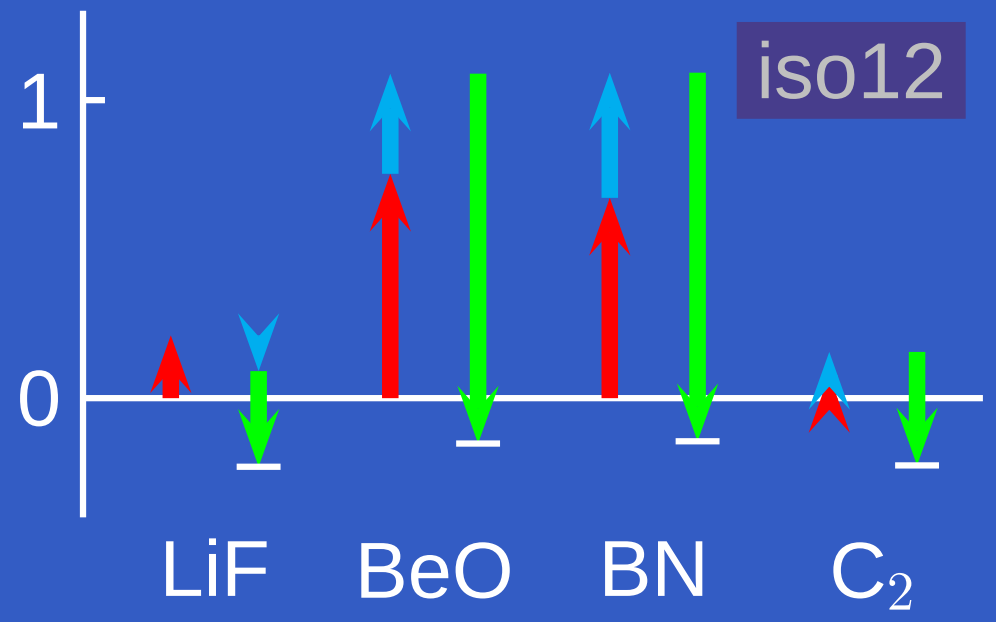


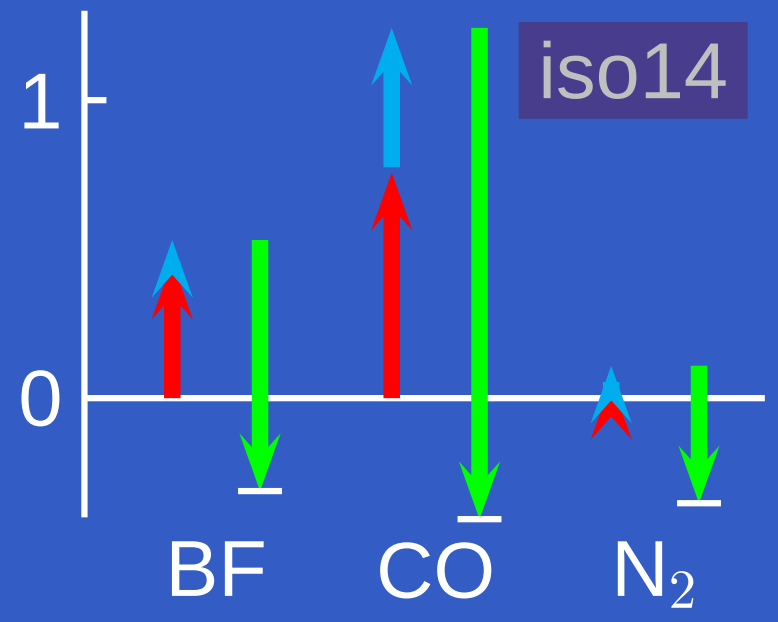


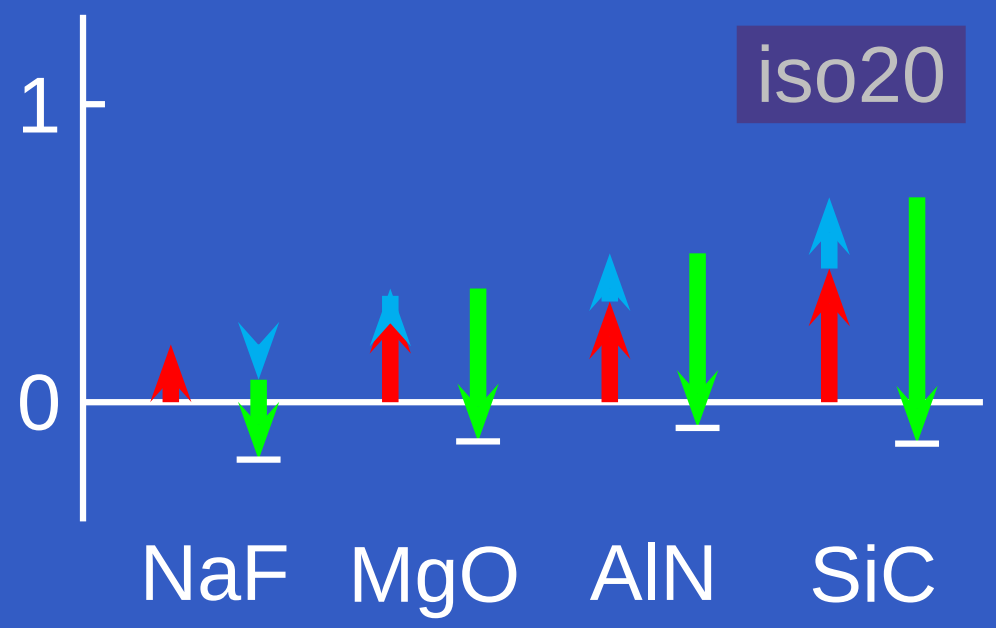


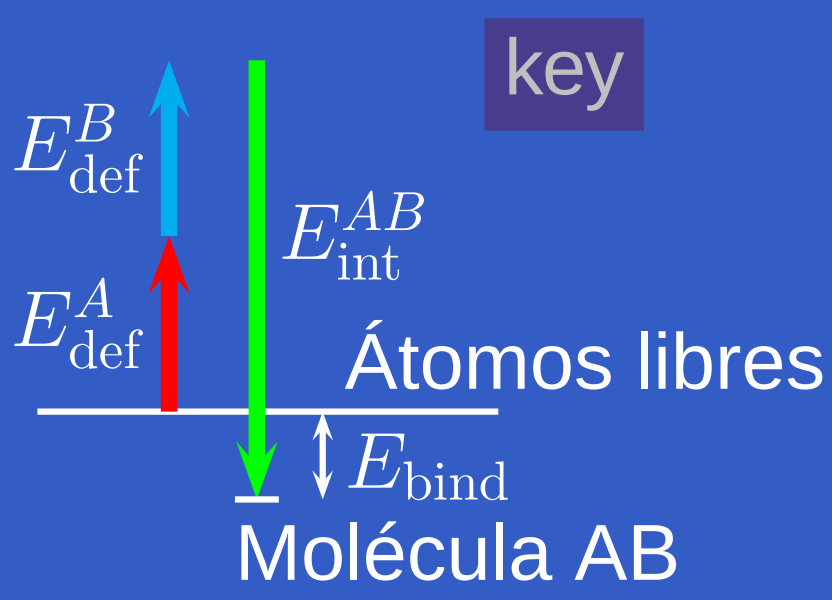


Componentes de la Energía de enlace

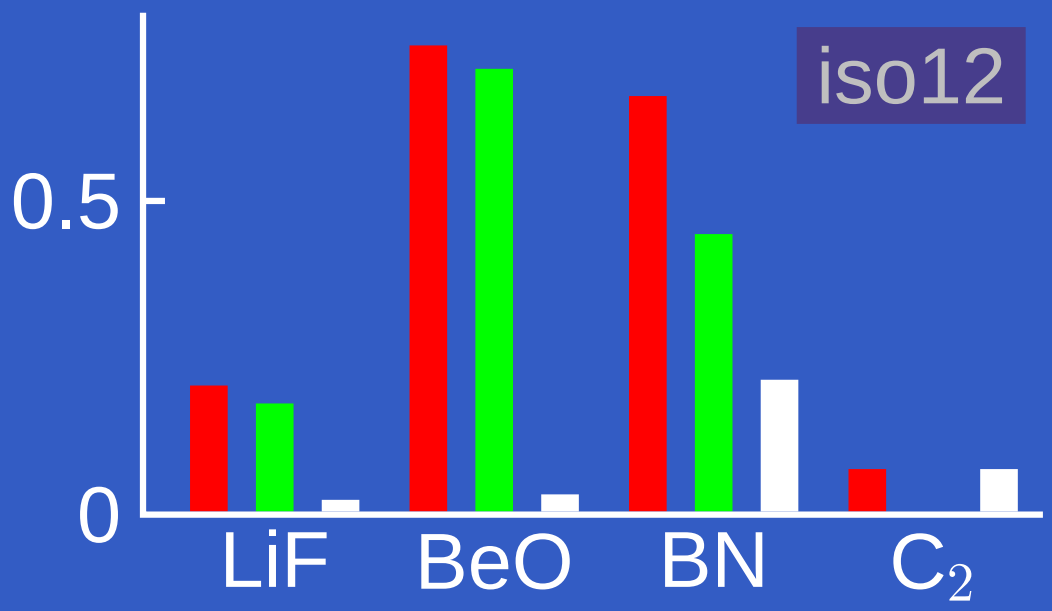


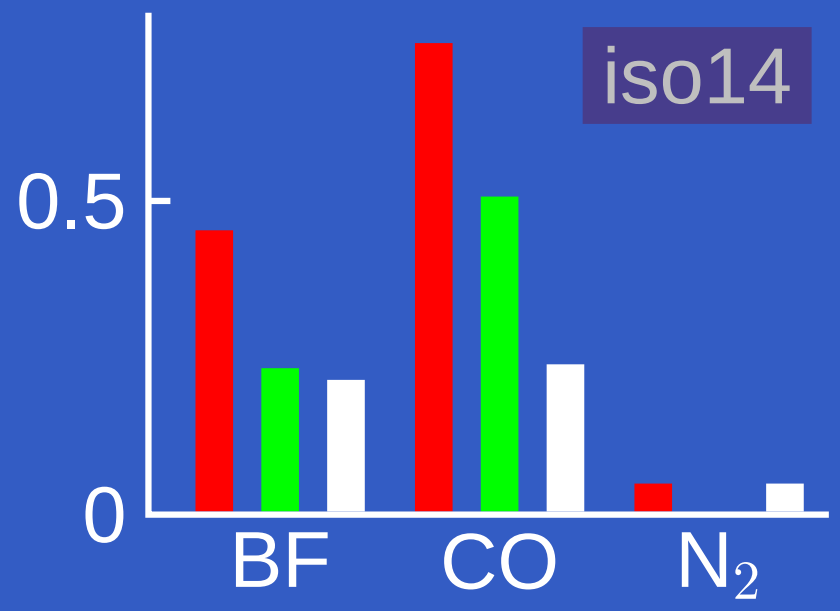


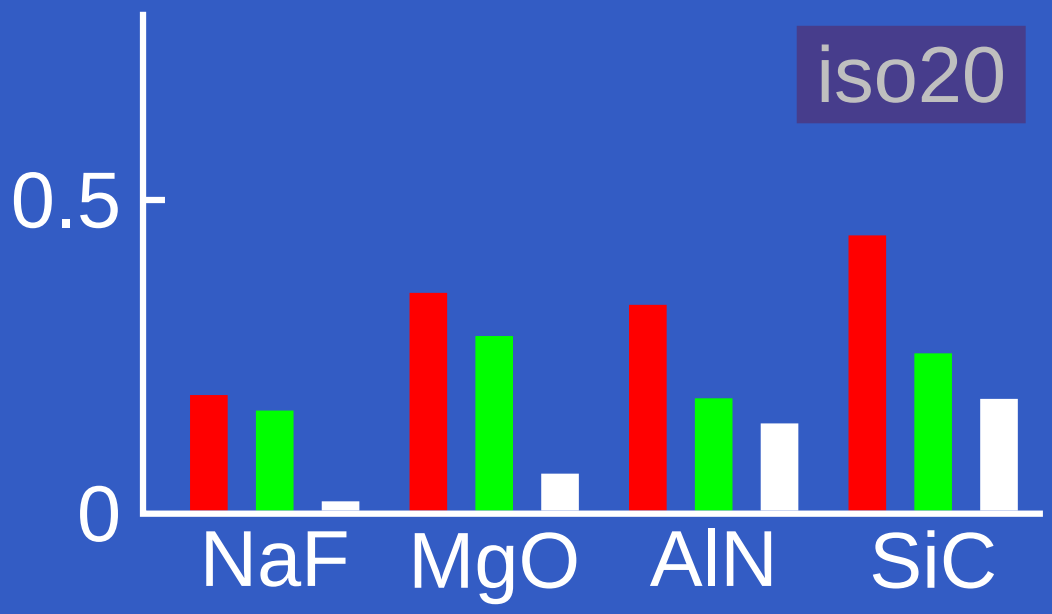




Componentes de Deformación ($Q^A > 0$)







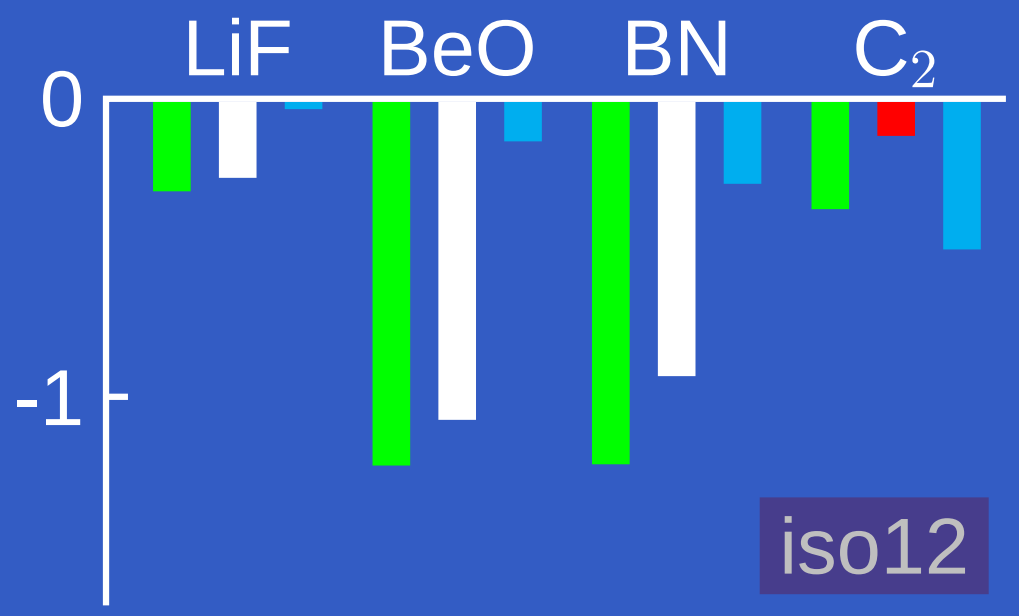
$$E^A_{\mathrm{def}} = (\mathrm{CT}) + (\mathrm{CR})$$

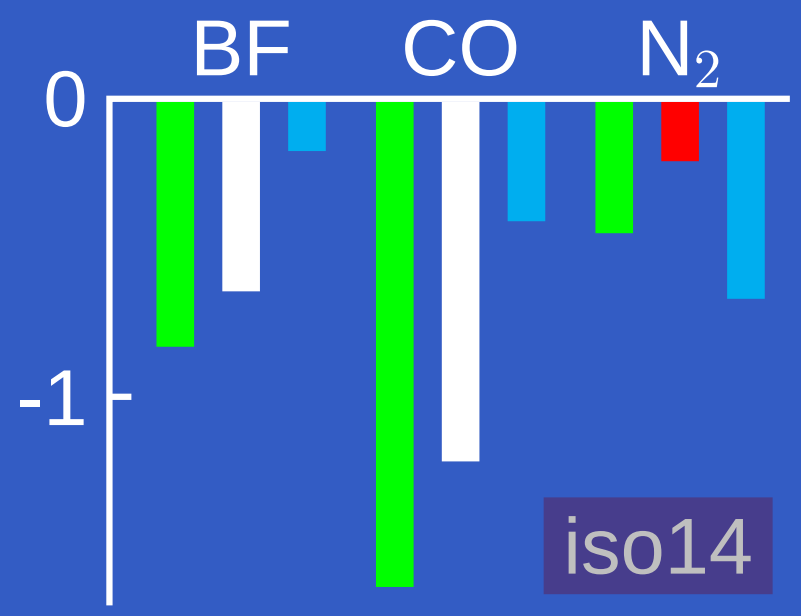
$$(\mathrm{CT}) = \sum \mathrm{IP}_i \times q_i$$

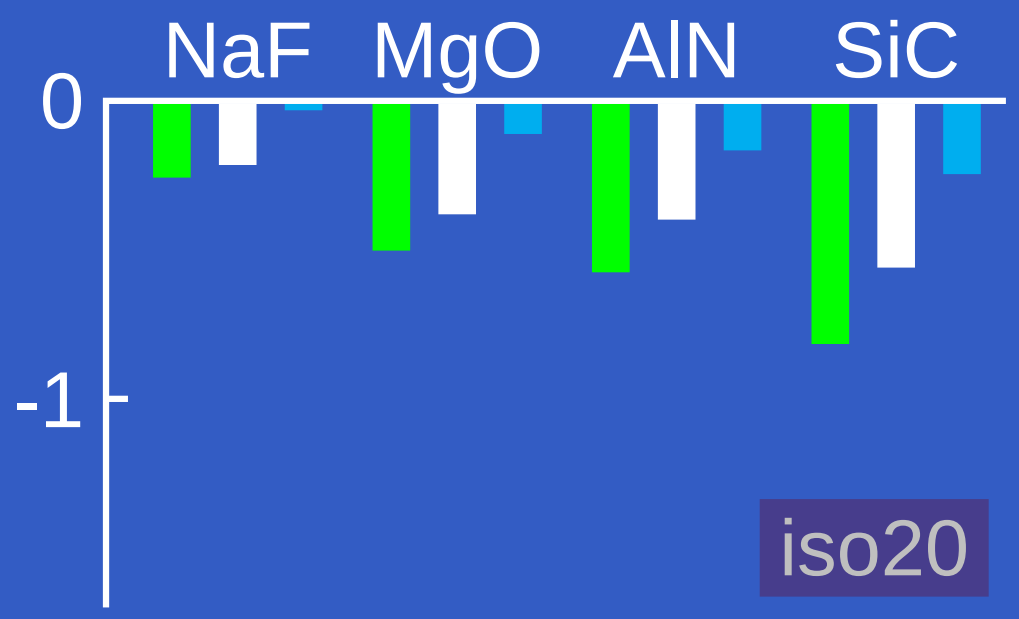
$Q^B < 0$: $(\mathrm{CT}) = \sum \mathrm{AE}_i \times q_i$

difícil calcular AE; son muy polarizables $\Longrightarrow$ CR alta

Componentes de Interacción





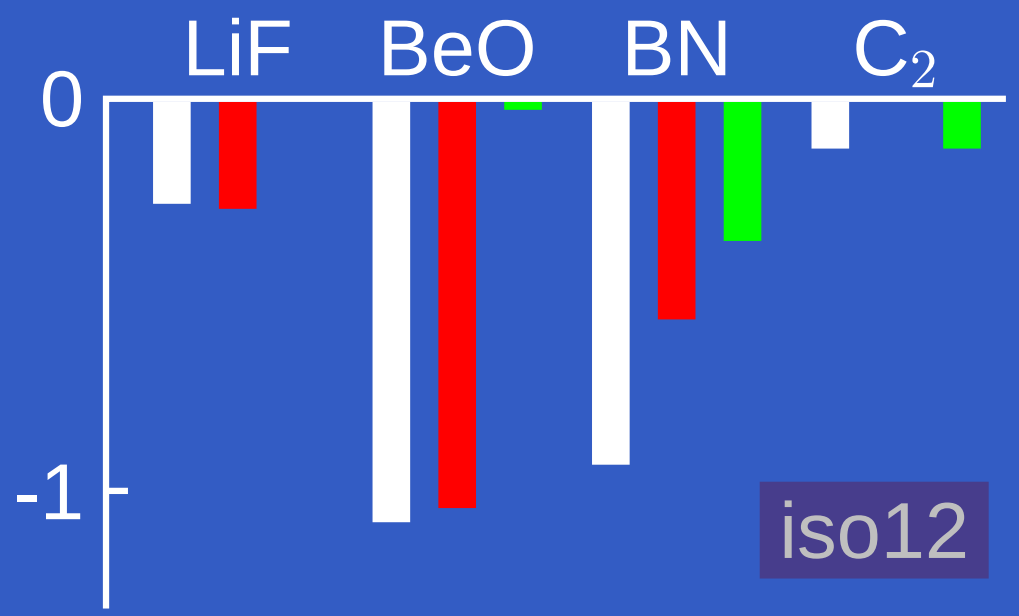


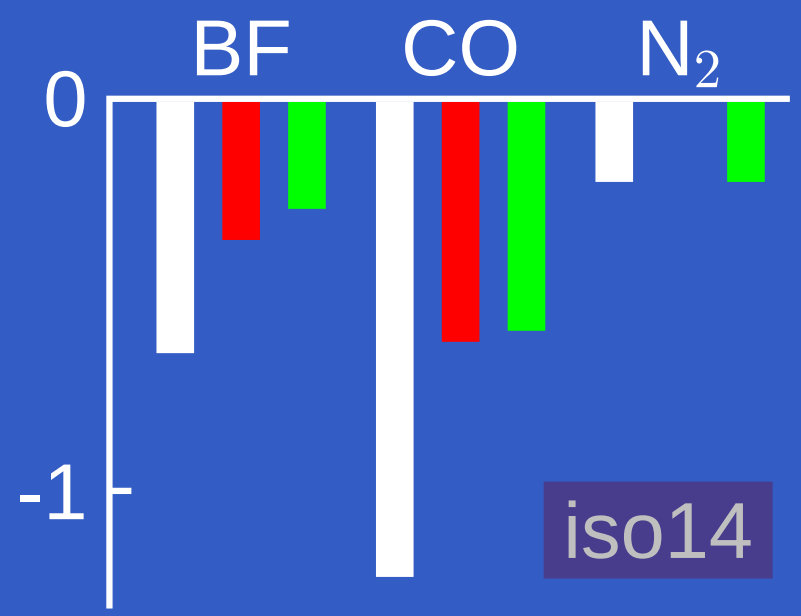
$$E_{\text{int}}^{AB} = V_{\text{cl}}^{AB} + V_{xc}^{AB}$$

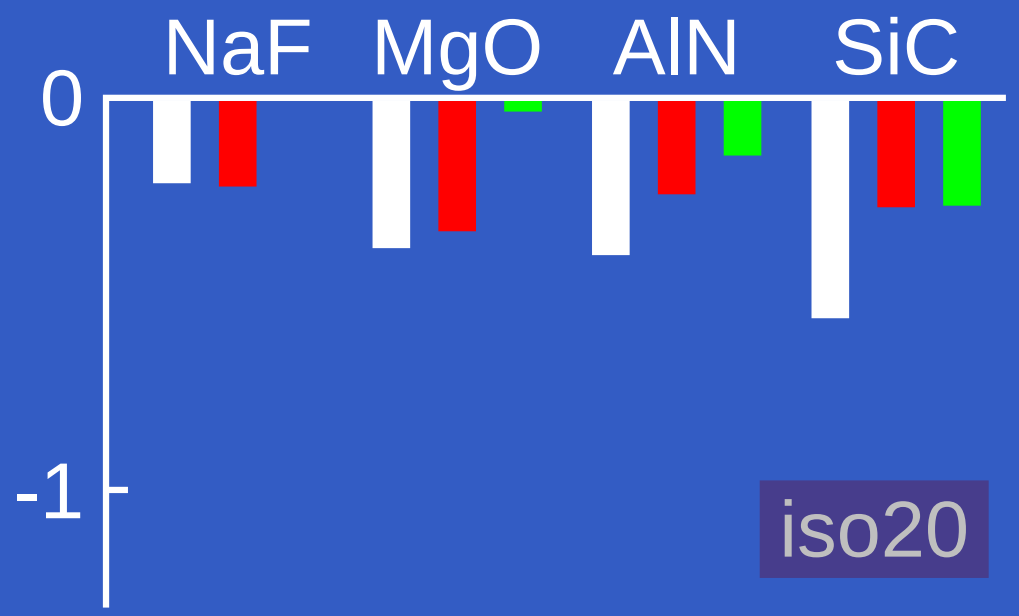
$V_{\text{cl}}^{AA} > 0$ in A_2

La covalencia está principalmente unida a V_{xc}^{AB}

Interacción Clásica





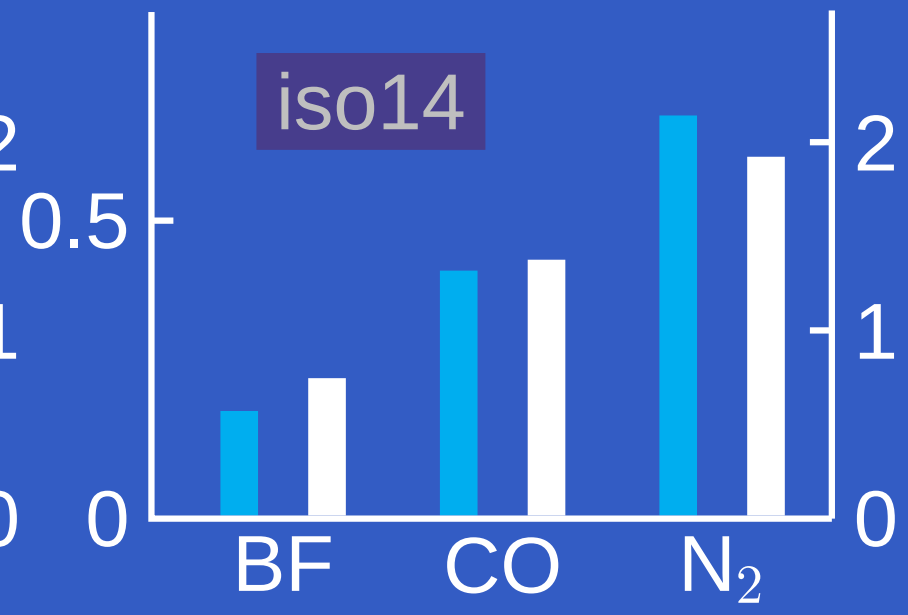


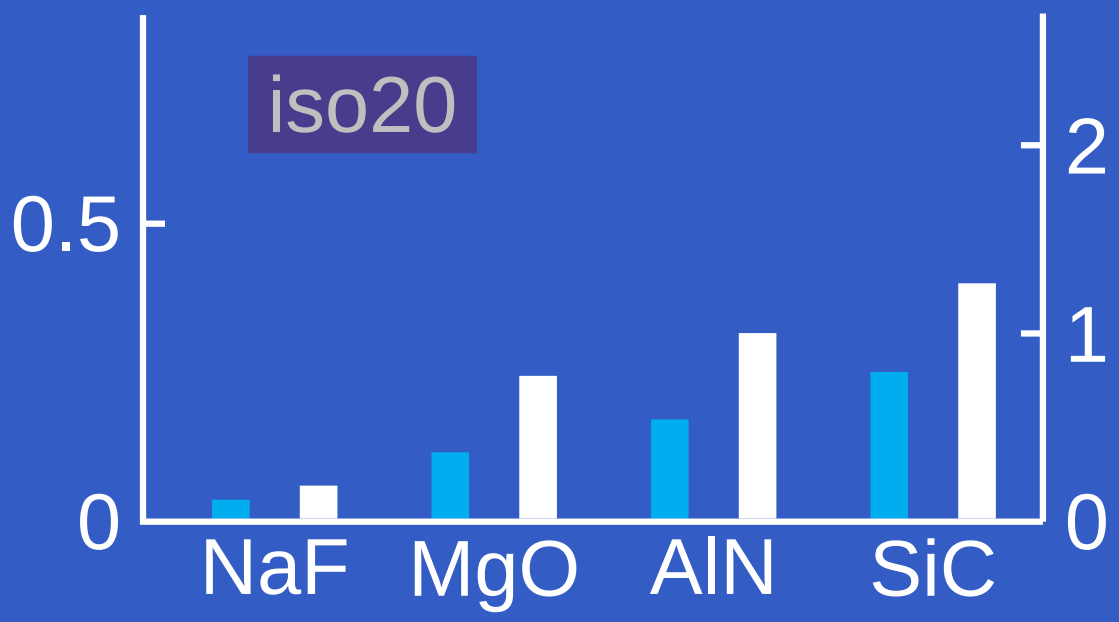
$V_{\rm cl}^{AB}$ $E_{\rm Q}^{AB}$

$V_{\rm cl}^{AB}$-$E_{\rm Q}^{AB}$ (en general < 0; LiF, NaF $\gtrsim 0$)

$E_{\rm Q}^{AB}/V_{\rm cl}^{AB}$ mide el grado de ionicidad

Energía de Cambio-correlación





-V_{xc}^{AB} ($V_{xc}^{AB} < 0$ siempre)

δ_{AB} (pares e^- compartidos)

La covalencia está principalmente unida a V_{xc}^{AB} o δ_{AB}

Conclusiones

- IQA permite una descomposición energética de E_{bind} con sentido físico
- La energía de enlace es un balance entre un valor positivo de la deformación (preparación) y uno más negativo de la energía de interacción
- Las huellas de la ionicidad: gran $E^{A}_{\mathrm{def}}(\mathrm{CT})$ y $E^{AB}_{Q}/V^{AB}_{\mathrm{cl}}$
- El orden de enlace (δ_{AB}) y V^{AB}_{xc} correlacionan con la covalencia
- Ambos caracteres pueden estar presentes en el mismo enlace en diferentes grados, pero no son complementarios! (Ej., CO)

Further equations

- $\rho_1 = \sum_A \rho_1^A, \quad \rho_2 = \sum_{A,B} \rho_2^{AB}$
- $T^A = \int_\infty \hat{T} \rho_1^A = \int_A \hat{T} \rho_1$
- $V_{en}^{AB} = V_{ne}^{BA} = \int_A -\frac{Z_B}{r_{1B}} \rho$
- $V_{nn}^{AB} = Z_A Z_B / R_{AB} \; (A \neq B)$
- $V_{ee}^{AA} = \frac{1}{2} \int_A \int_A \rho_2 r_{12}^{-1} \; (A = B)$
- $V_{ee}^{AB} = \int_A \int_B \rho_2 r_{12}^{-1} \; (A \neq B)$
- $\rho_2^{\mathrm{C}}(1,2) = \rho(1)\rho(2)$
- $\rho_2^{\mathrm{X}}(1,2) = -\rho_1(2;1)\rho_1(1;2)$
- $\rho_2 = \rho_2^{\mathrm{C}} + \rho_2^{xc} = \rho_2^{\mathrm{C}} + \rho_2^{\mathrm{X}} + \rho_2^{\mathrm{corr}}$

UNIVERSITAT JAUME·I

INCORPORANDO LA PRESIÓN HIDROSTÁTICA EN SIMULACIONES DE ESTRUCTURA Y REACTIVIDAD QUÍMICA EN SISTEMAS CONDENSADOS. MÉTODOS QM/MM+DM

José Javier Ruiz Pernía, Juan Andrés Bort.

Reunión proyecto MALTA, Miraflores, Madrid 24/Enero/2010

INTRODUCCIÓN

MÉTODOS QM/MM + DM

- La mayoría de los sistemas y reacciones químicas tienen lugar en presencia de un entorno (en fase condensada).
  - Procesos en disolución.
  - Reacciones enzimáticas, en sólidos, etc
- La fase condensada (entorno) juega un papel fundamental en la termodinámica y en la cinética química

INTERÉS

¿Cómo influye ese medio condensado en la estructura y reactividad química?

Métodos QM (Cuánticos)

- Buena precisión
- Sistemas pequeños
- Nº átomos <50

PROBLEMA

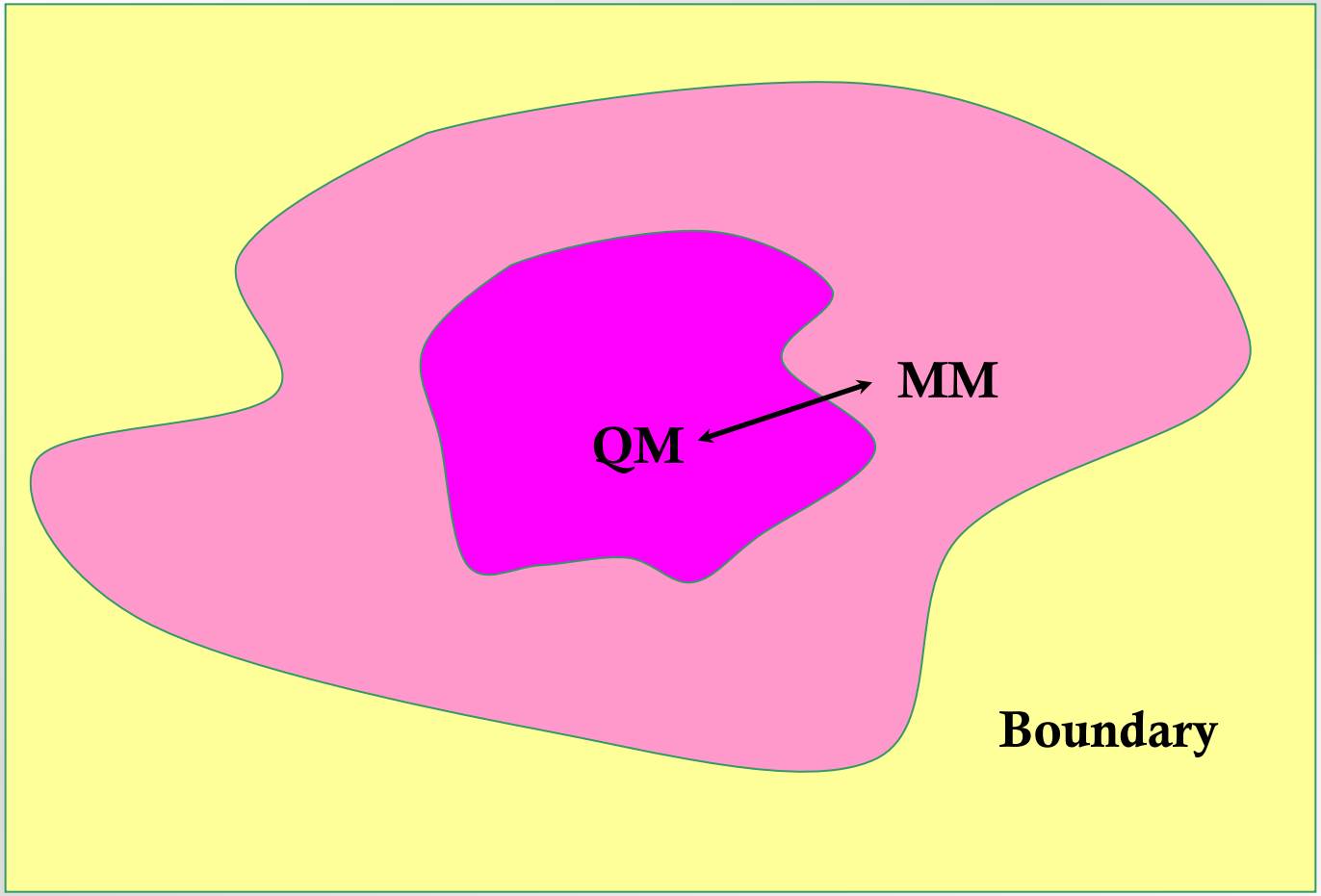
Los medios condensados se caracterizan por un gran número de átomos. Estudio complicado

Métodos MM (Clásicos)

- Campo de fuerzas
- Sistemas grandes
- Nº átomos >100000

INTRODUCCIÓN

MÉTODOS QM/MM



QM = Directamente involucrados en la ruptura y formación de enlaces químicos

$$E, \frac{\partial E}{\partial R_i}, \frac{\partial E^2}{\partial R_i^2}$$

MM = Afectan a la reacción indirectamente

$$E, \frac{\partial E}{\partial R_i}$$

$$\hat{H}_{eff} = \hat{H}_{QM} + \hat{H}_{MM} + \hat{H}_{QM/MM} + \hat{H}_{BOUND}$$

INTRODUCCIÓN

MÉTODOS QM/MM + DM

#1 Generación de la Superficie de Energía Potencial (SEP)

**** descripción híbrida cuántica/clásica:***

[CHARMM & DYNAMO]

#2 Exploración de la SEP

**** búsqueda puntos singulares con métodos flexibles:***

[GRACE / CHARMM & DYNAMO]

#3 Cálculo de la Energía Libre

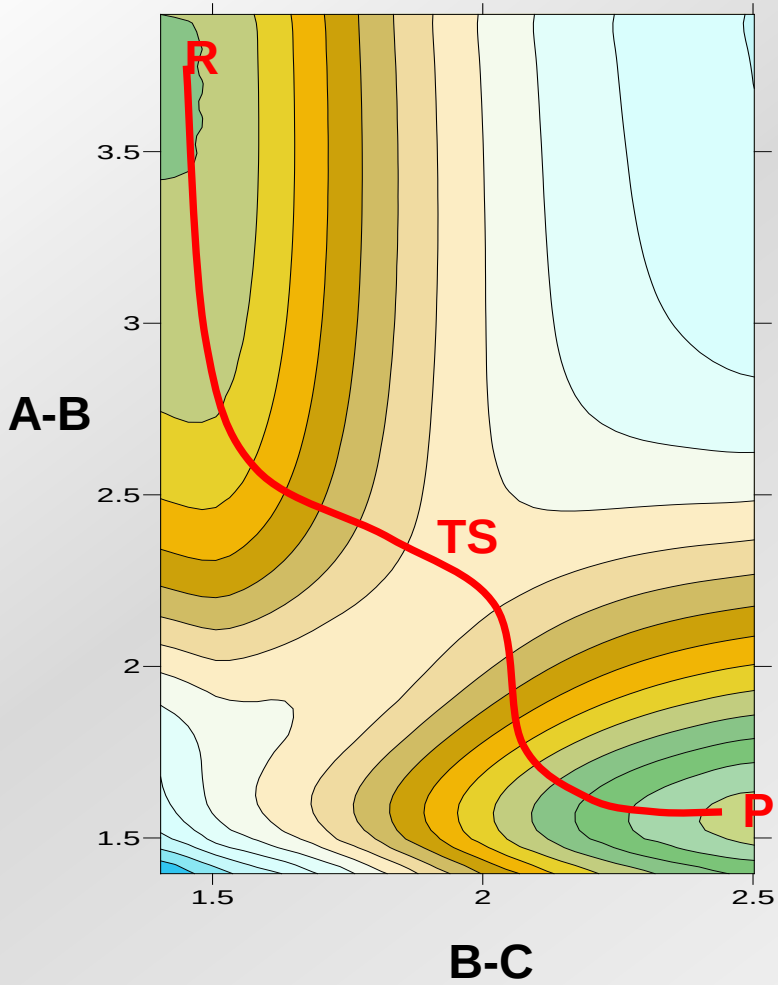
**** métodos simulación estadística:***

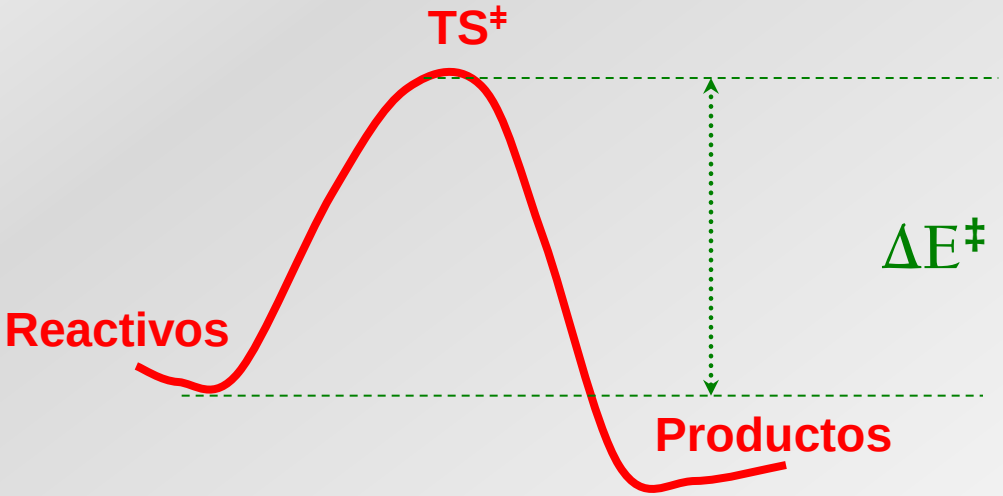
[DYNAMO]

INTRODUCCIÓN

Superficies de Energía Potencial (SEP)

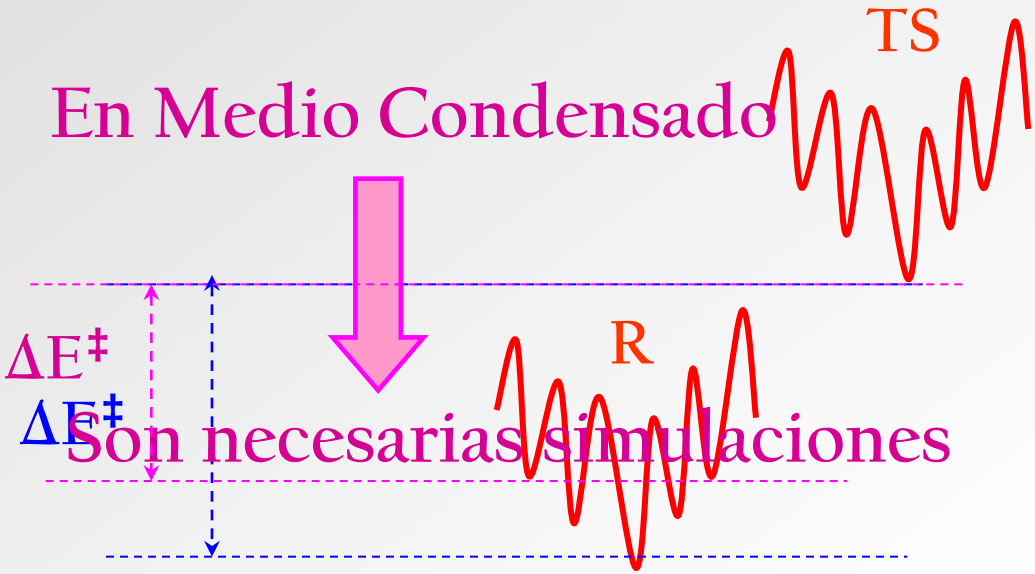
$$AB + C \longrightarrow A + BC$$





Sistemas Grandes

En Medio Condensado

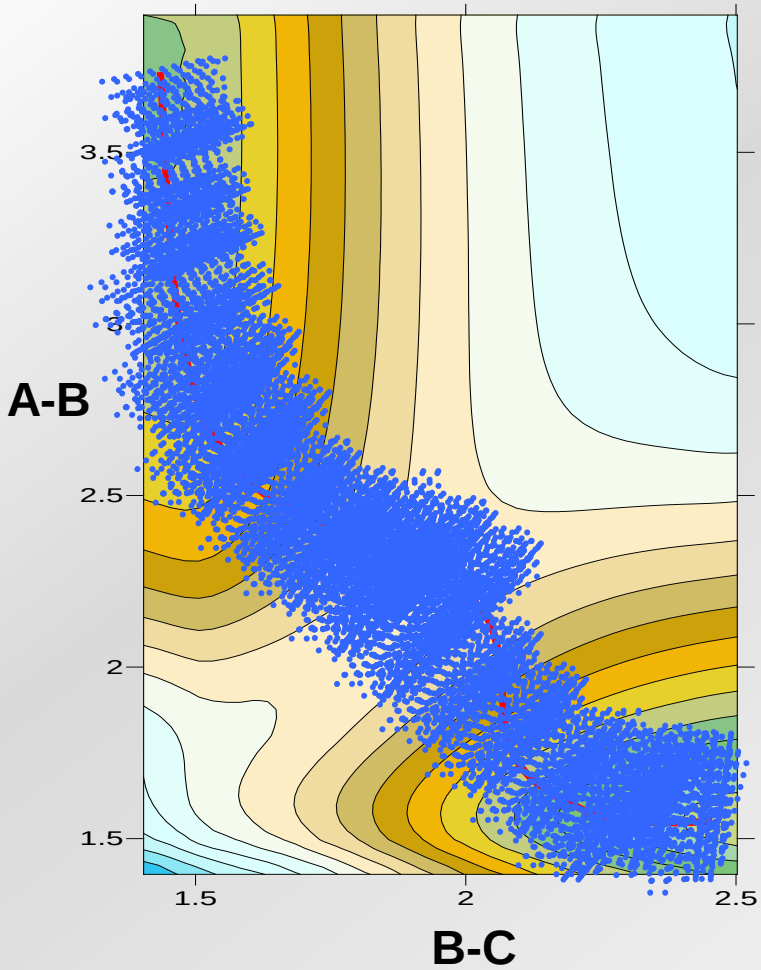


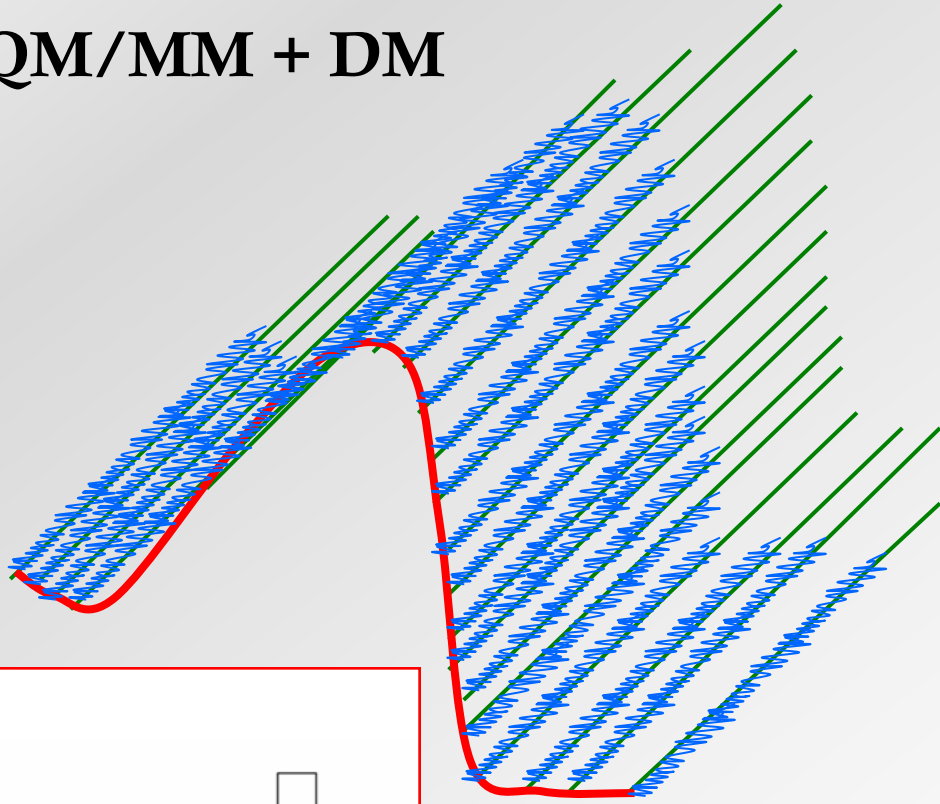
Son necesarias simulaciones

INTRODUCCIÓN

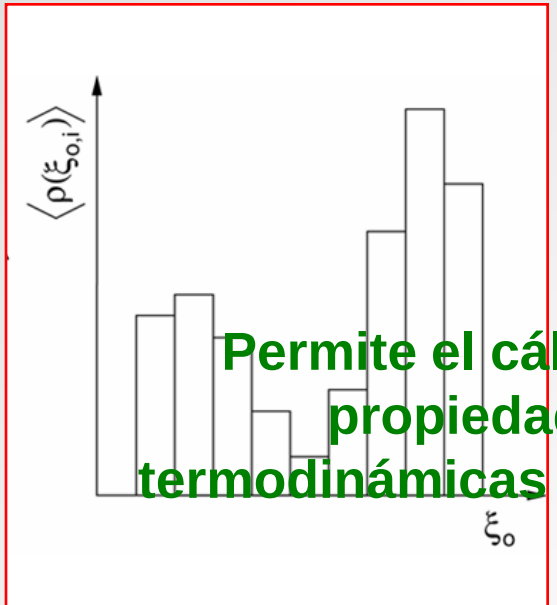
Simulaciones QM/MM + DM

AB + C ⟶ A + BC





ζ= d(A-B) – d(B-C)



Permite el cálculo de propiedades termodinámicas y cinéticas

OBJETIVOS

Simulación del Efecto de la Presión

Incorporar la presión hidrostática en simulaciones de <u>estructura y reactividad</u> química de sistemas químicos en fases condensadas (moléculas en disolución, enzimas, etc..).

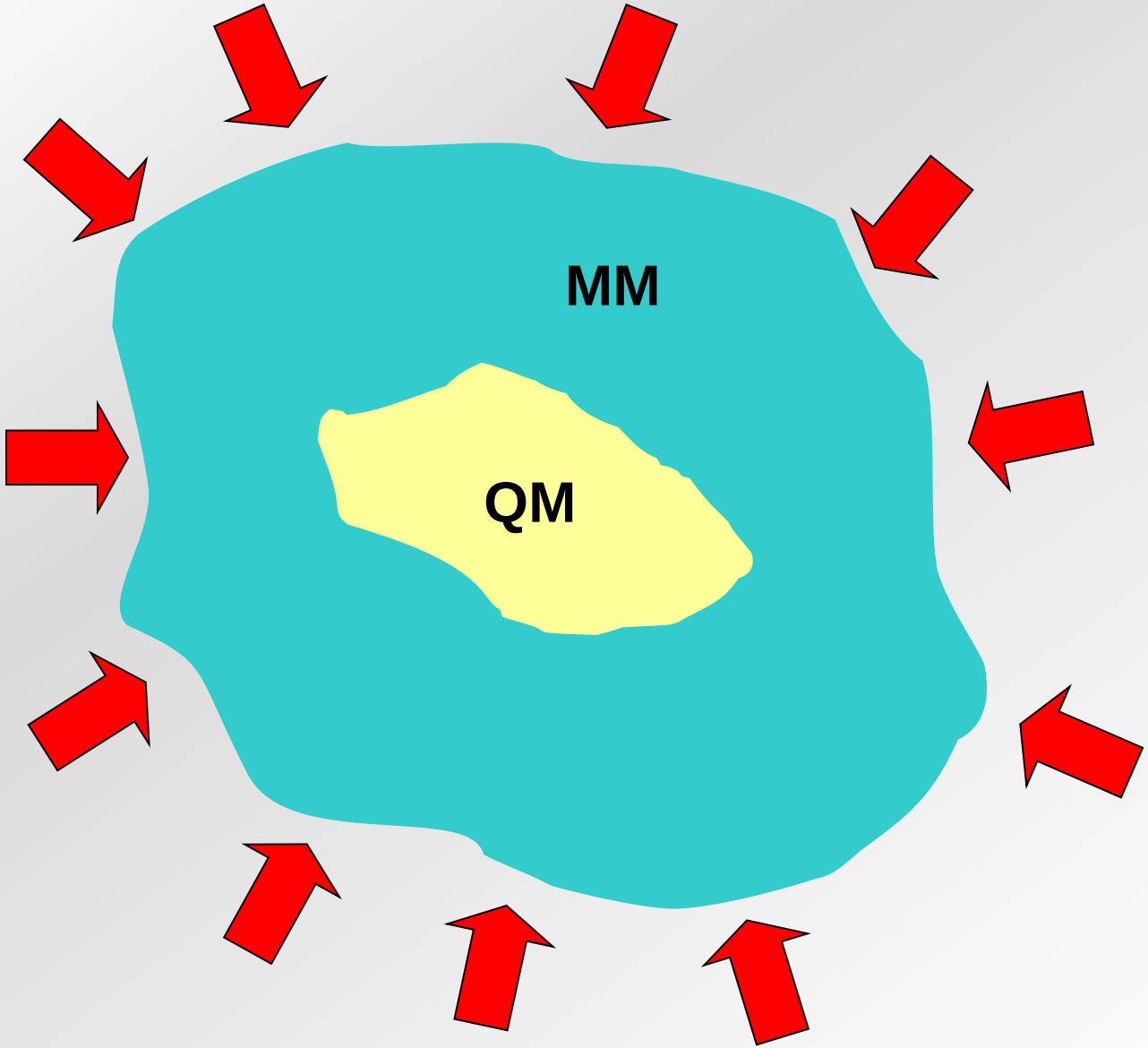
Modelización de la propiedades físicas y químicas.

Comparación con datos experimentales

Calcular la influencia de la presión sobre las propiedades termodinámicas y cinéticas (estructura y reactividad química)

METODOLOGÍA

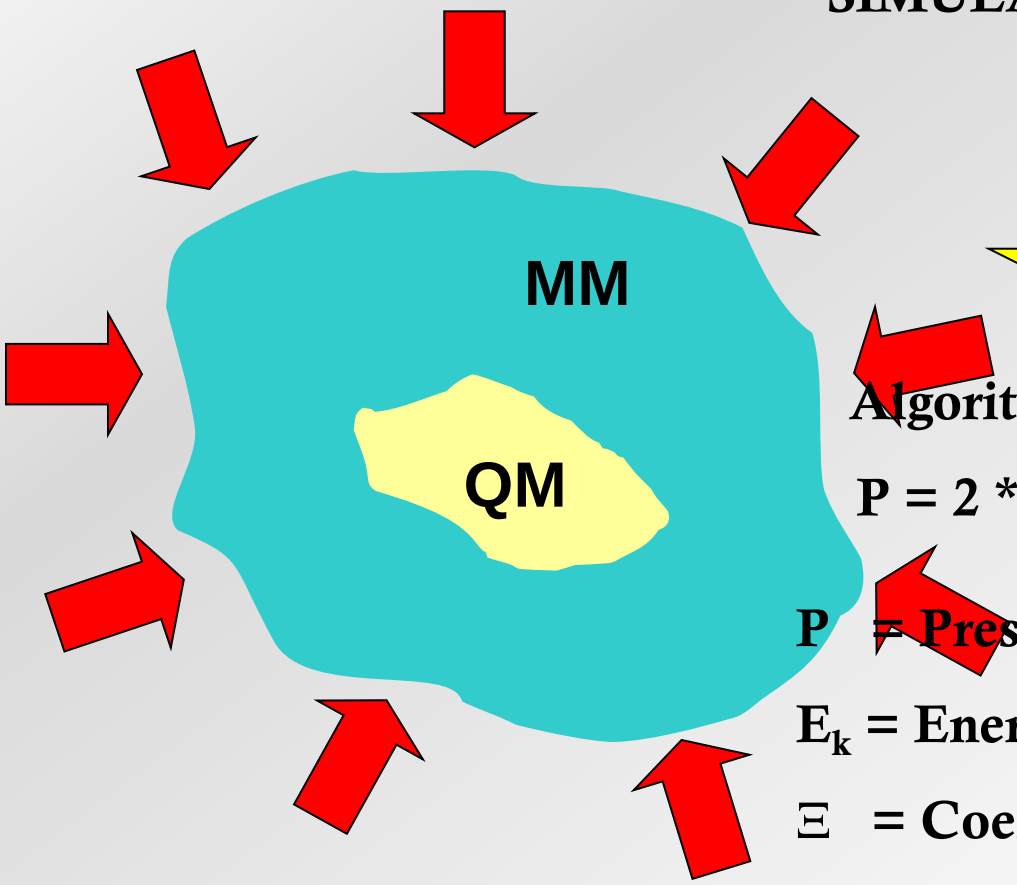
¿Presión hidrostática en simulaciones QM/MM + DM?



METODOLOGÍA

¿Presión hidrostática en simulaciones QM/MM + DM?

SIMULACIONES NPT



Algoritmo de Berendsen

$$P = 2 * (E_k - \Xi) / 3 * V$$

P = Presión instantánea

E_k = Energía cinética

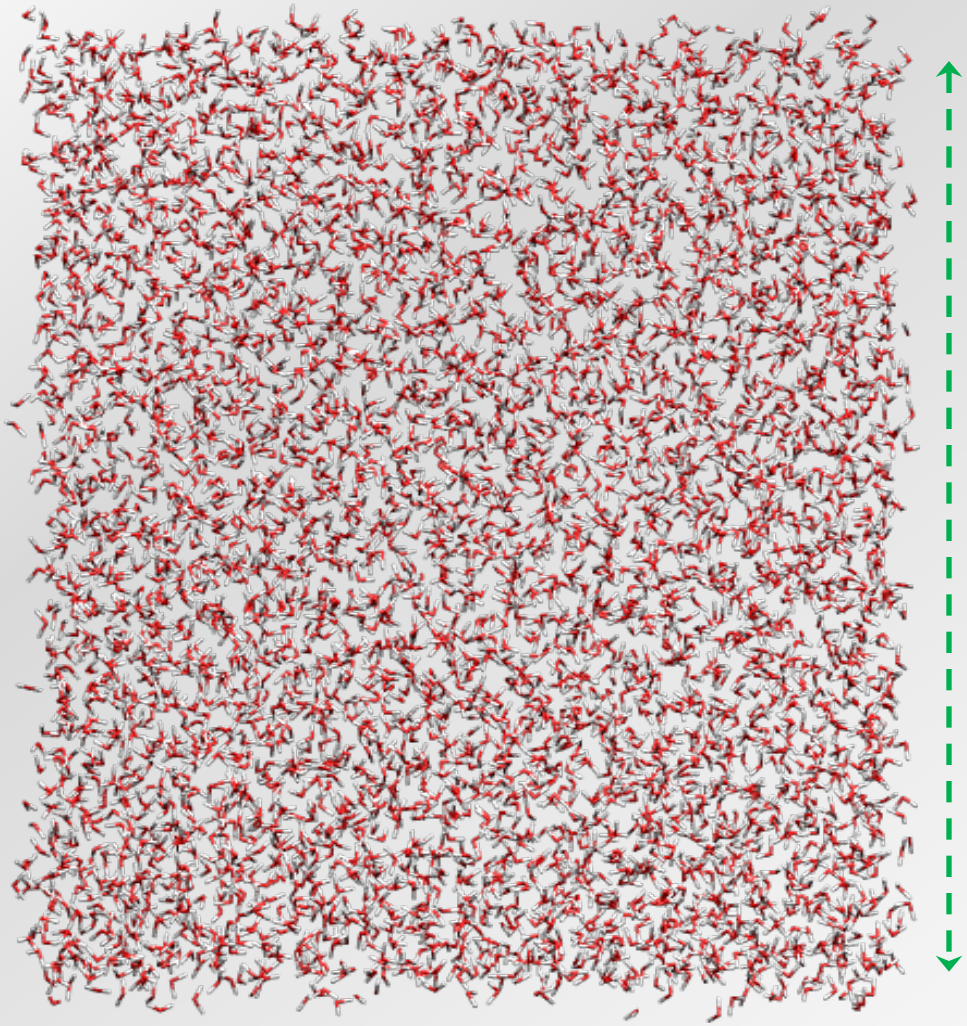
Ξ = Coeficiente del virial

V = Volumen

¿El caso más sencillo: agua?

METODOLOGÍA

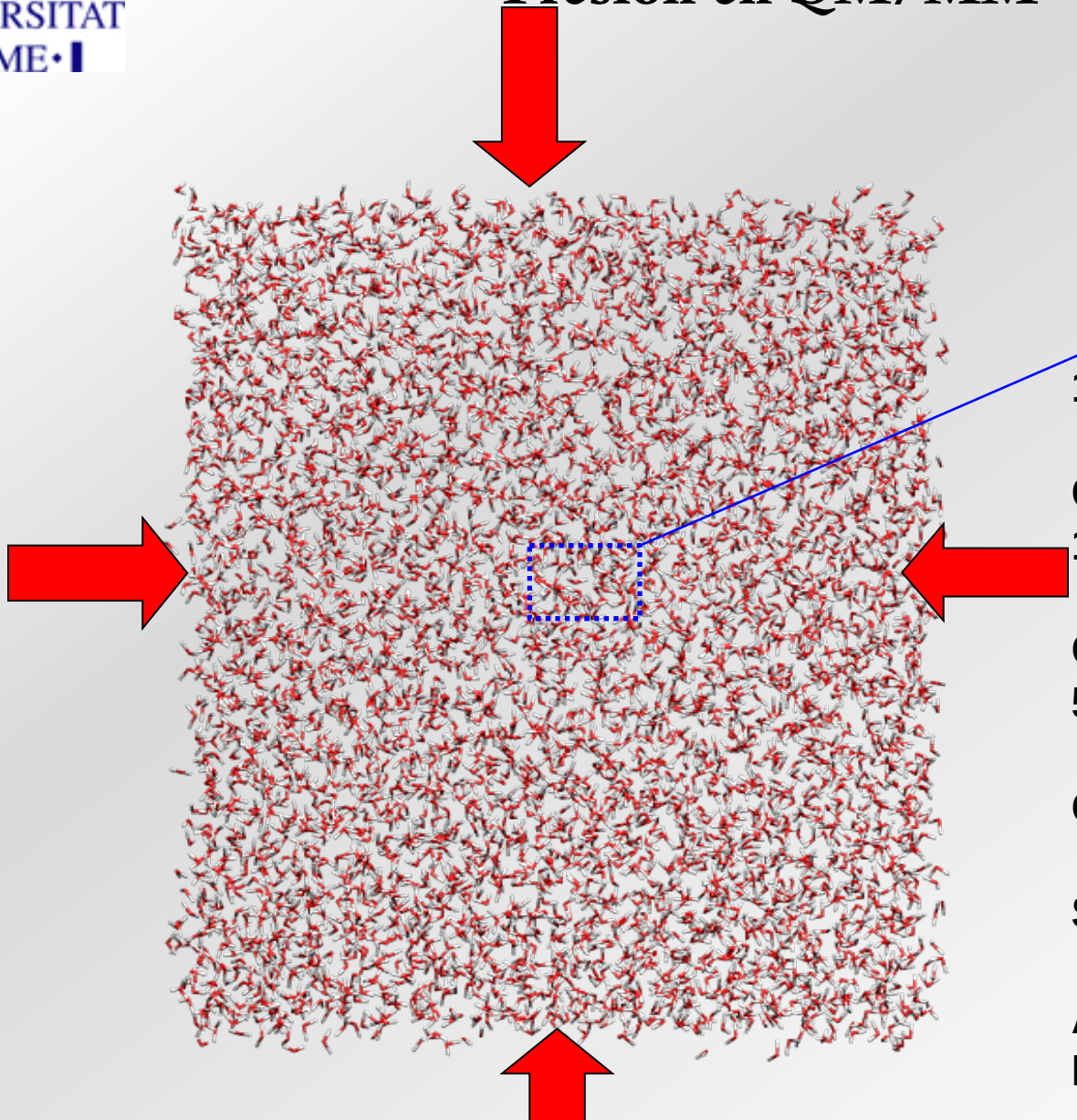
Incorporando la presión hidrostática en simulaciones QM/MM + DM

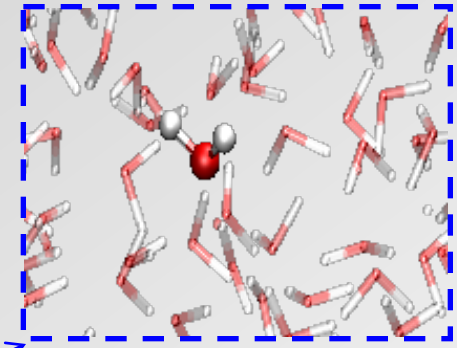


Simular y calcular la densidad del H_2O en función de la $P_{hidrostática}$

METODOLOGÍA

Presión en QM/MM





1 molécula AM1

Caja 31.4 Å de lado, 1033 moléculas TIP3P

Caja 55.4 Å de lado, 5831 moléculas TIP3P

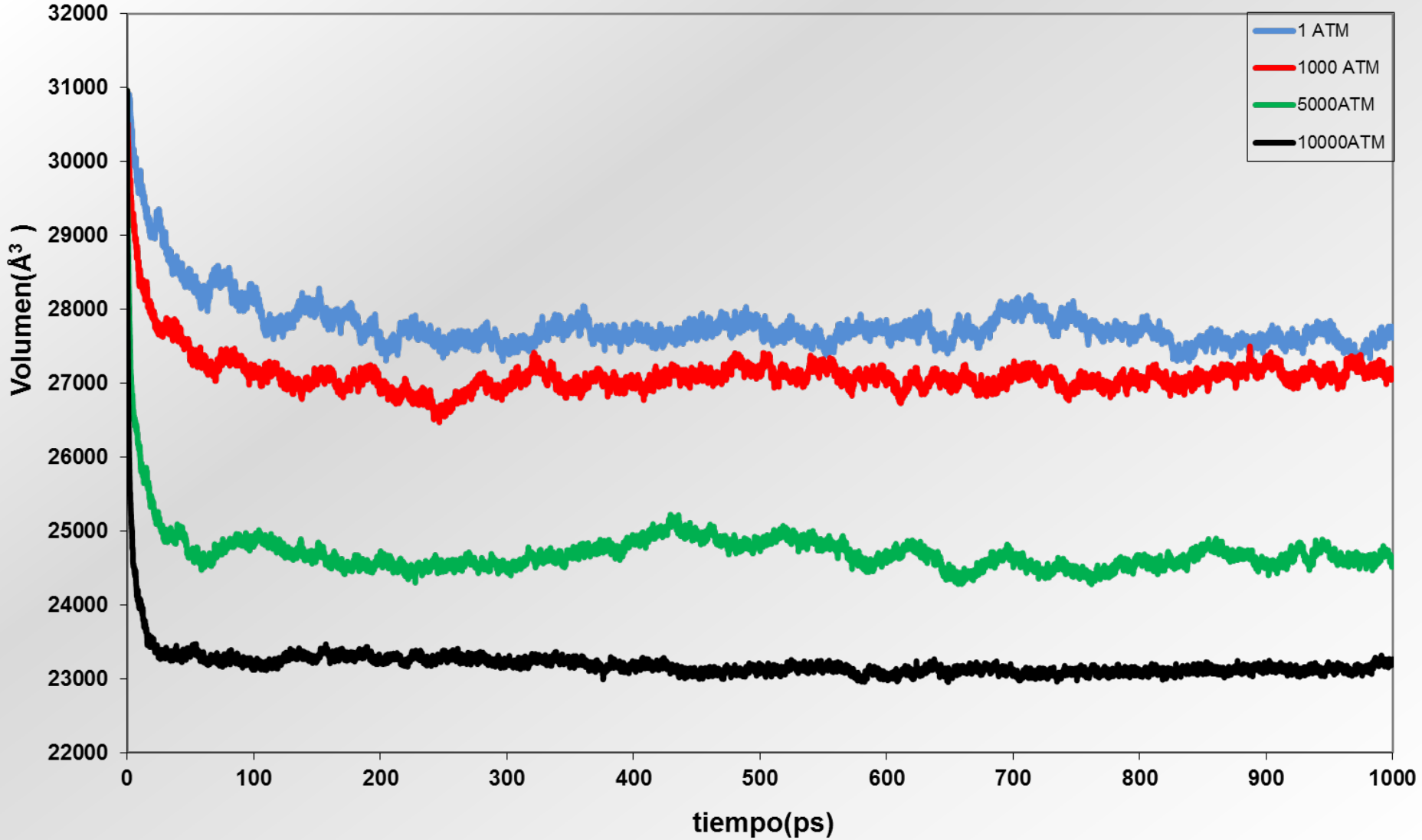
Cut-off 10.5, 11.5 y 12.5

Simulación NPT

Algoritmo de Berendsen

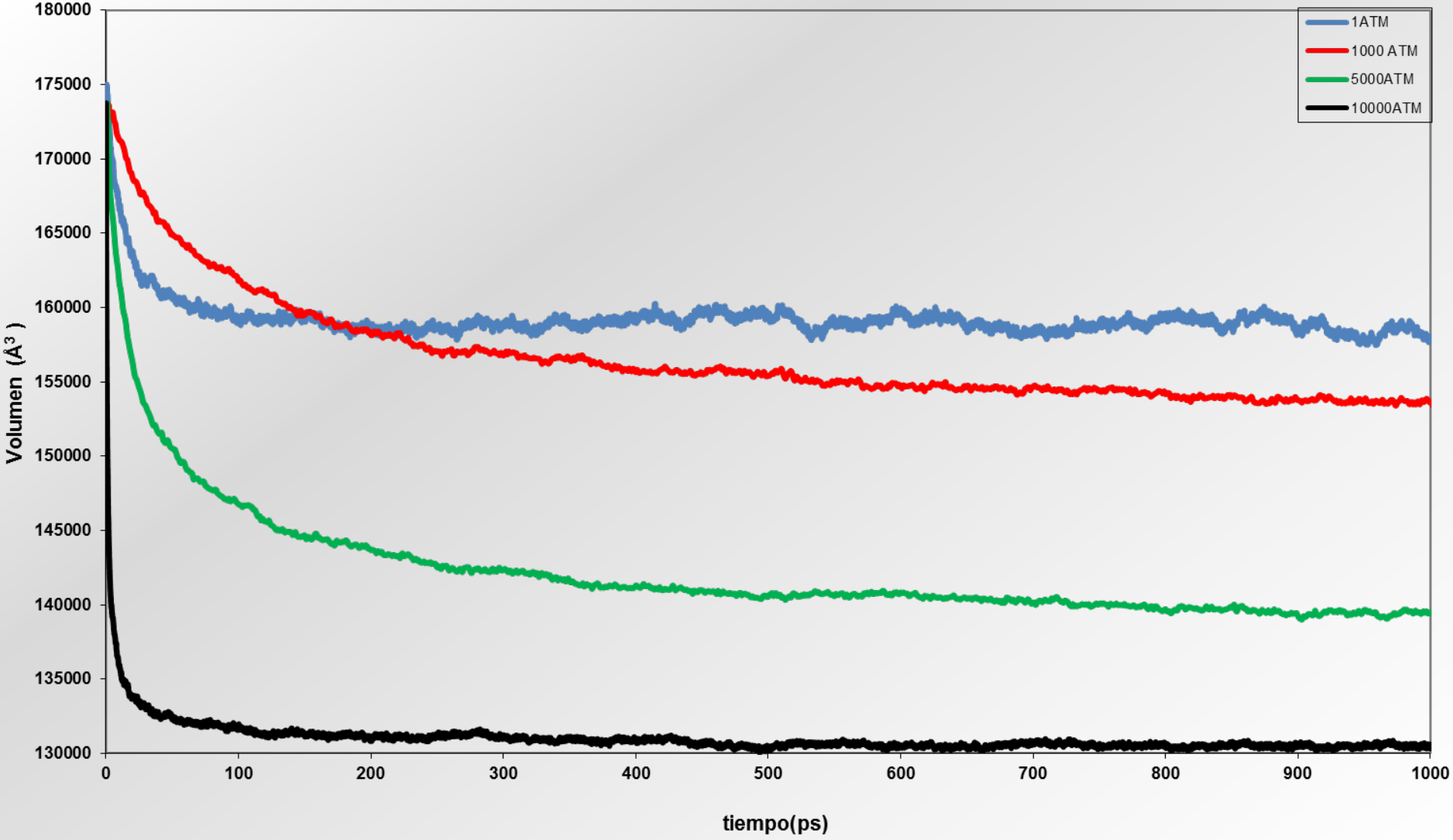
RESULTADOS

Sistema Agua AM1/TIP3P (caja 31.4 Å de lado)



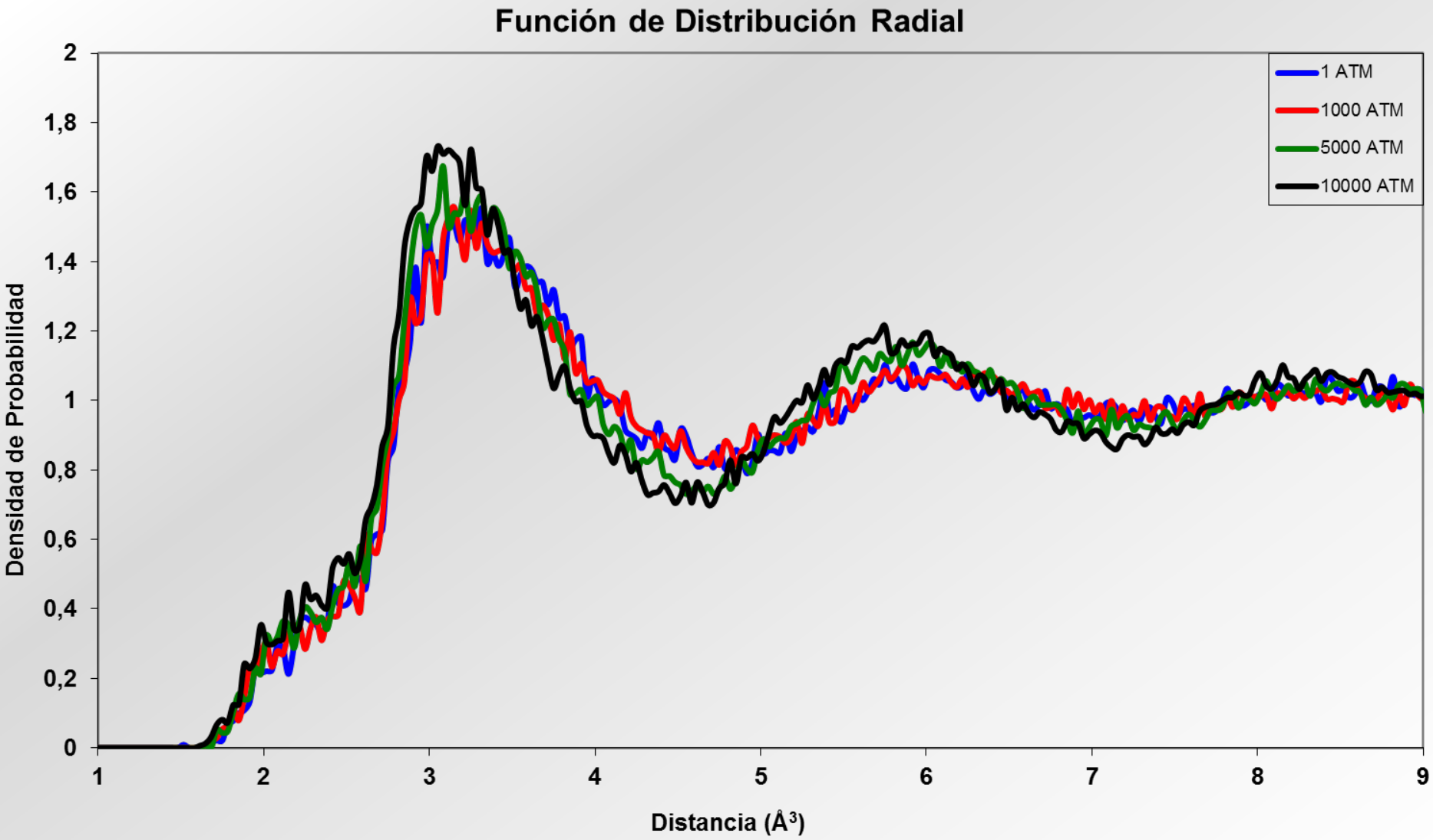
RESULTADOS

Sistema Agua AM1/TIP3P (caja 55.4 Å de lado)



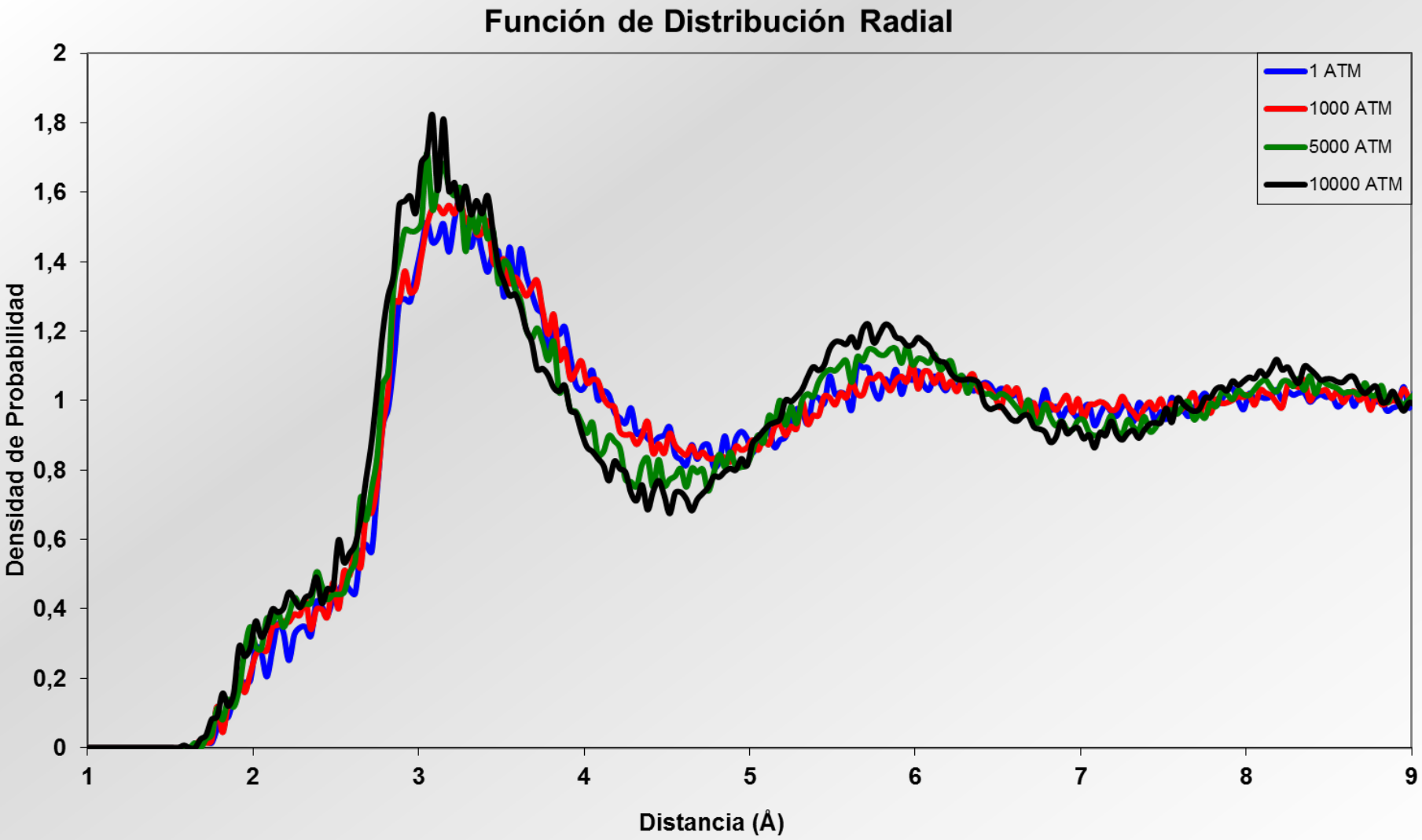
RESULTADOS

Sistema Agua AM1/TIP3P (caja 31.4 Å de lado)



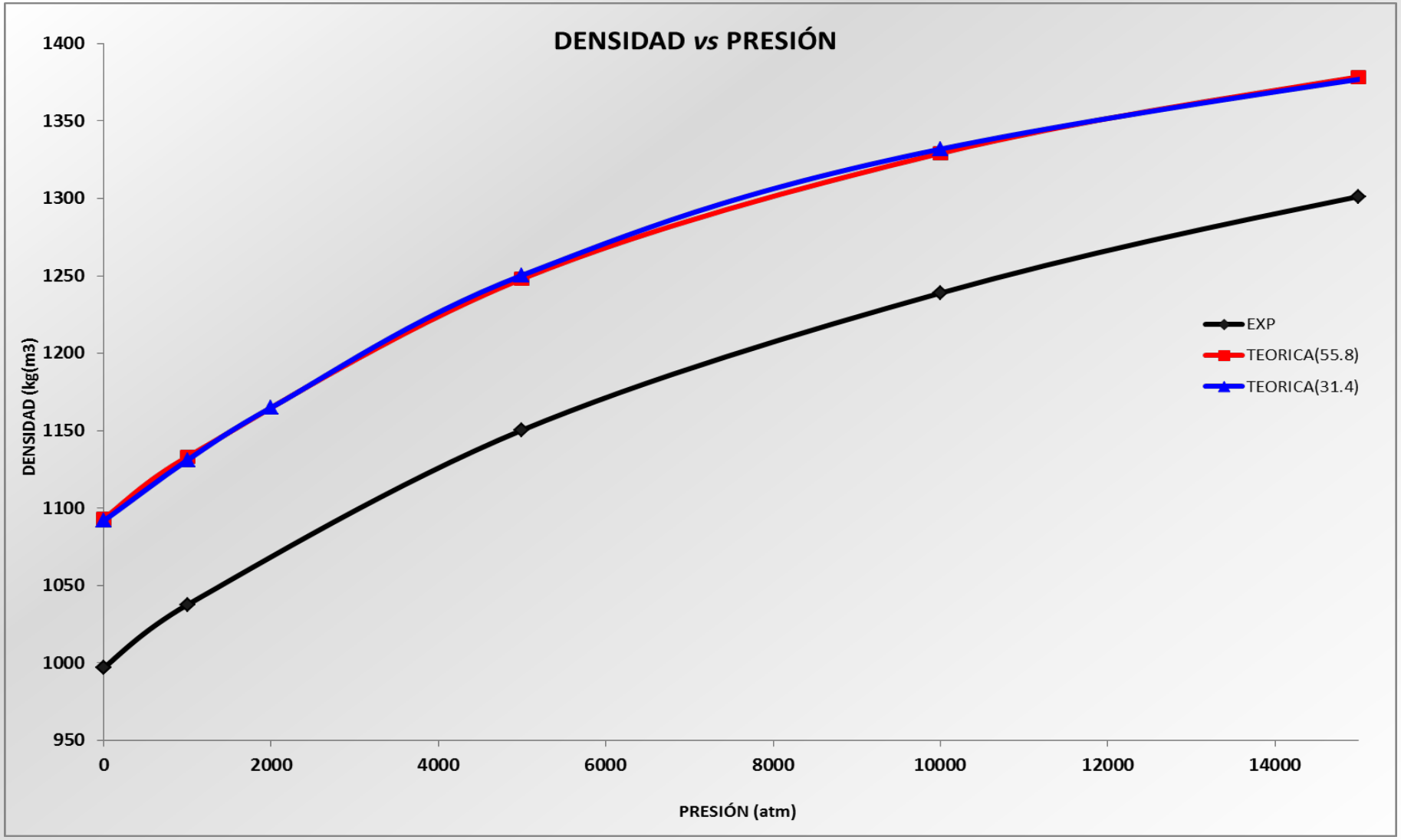
RESULTADOS

Sistema Agua AM1/TIP3P (caja 55.4 Å de lado)



RESULTADOS

Sistema Agua AM1/TIP3P



RESULTADOS

DESARROLLO METODÓGICO

¿Es posible modificar la ecuación de Berendsen para obtener un comportamiento más realista de los campos de fuerza clásicos?

$$P = 2 * (E_{ke} - \Xi) / 3 * V$$

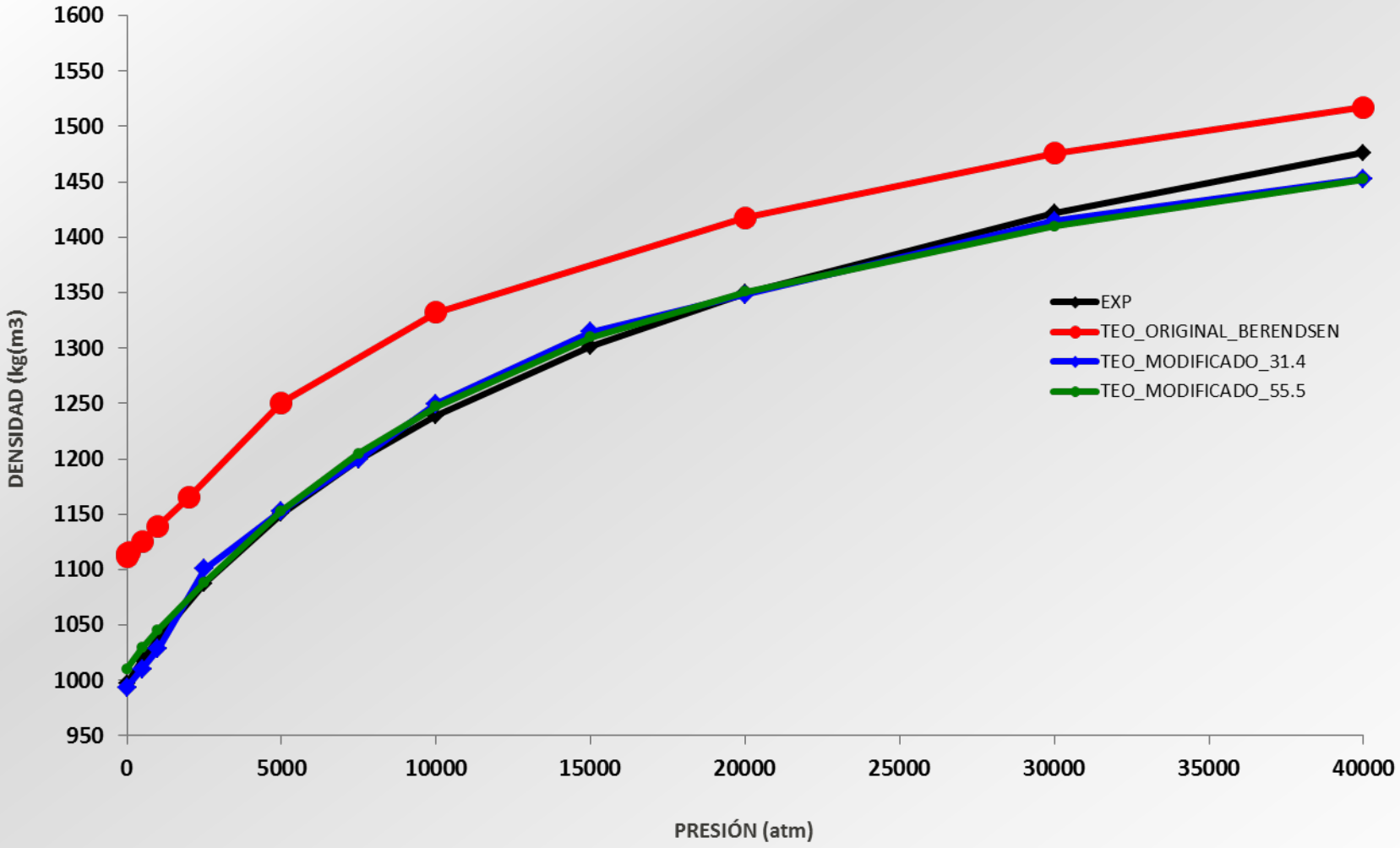
$$P = X * E_{ke} - Y * \Xi) / 3 * V$$

Factor Pre-Energía Cinética

Factor Pre-Virial

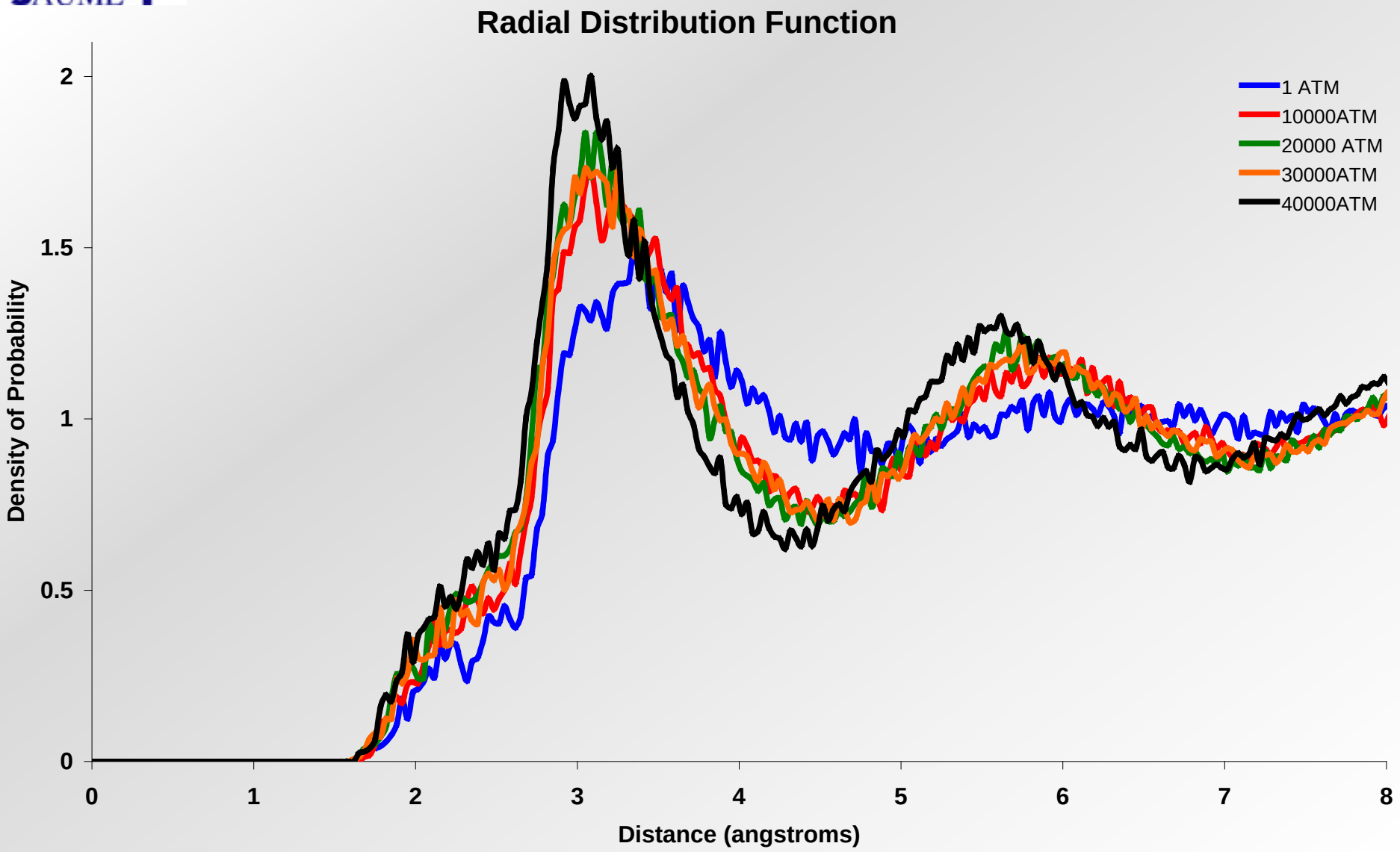
RESULTADOS

Sistema Agua AM1/TIP3P



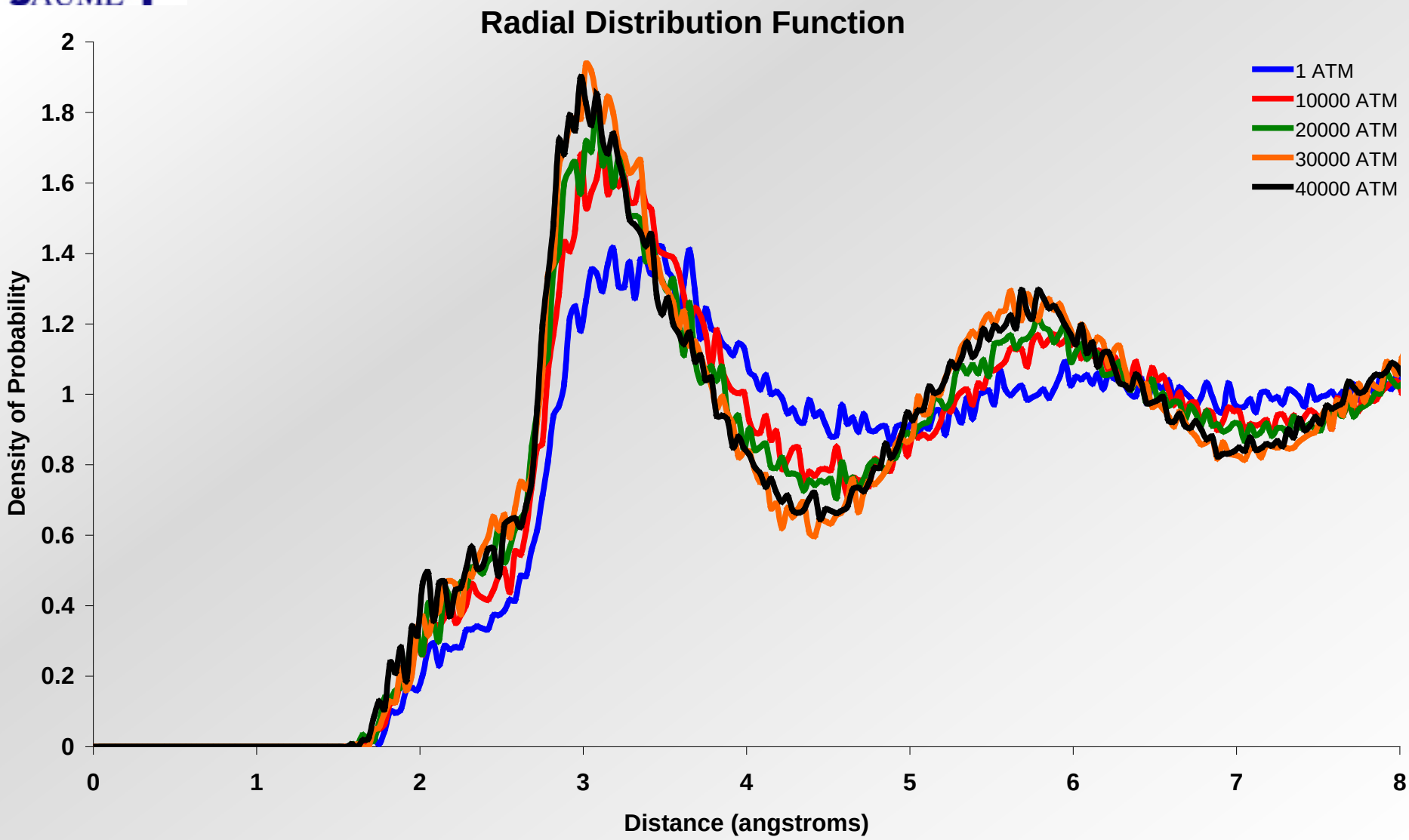
RESULTADOS

Sistema Agua AM1/TIP3P (caja 31.4 Å de lado)



RESULTADOS

Sistema Agua AM1/TIP3P (caja 55.4 Å de lado)

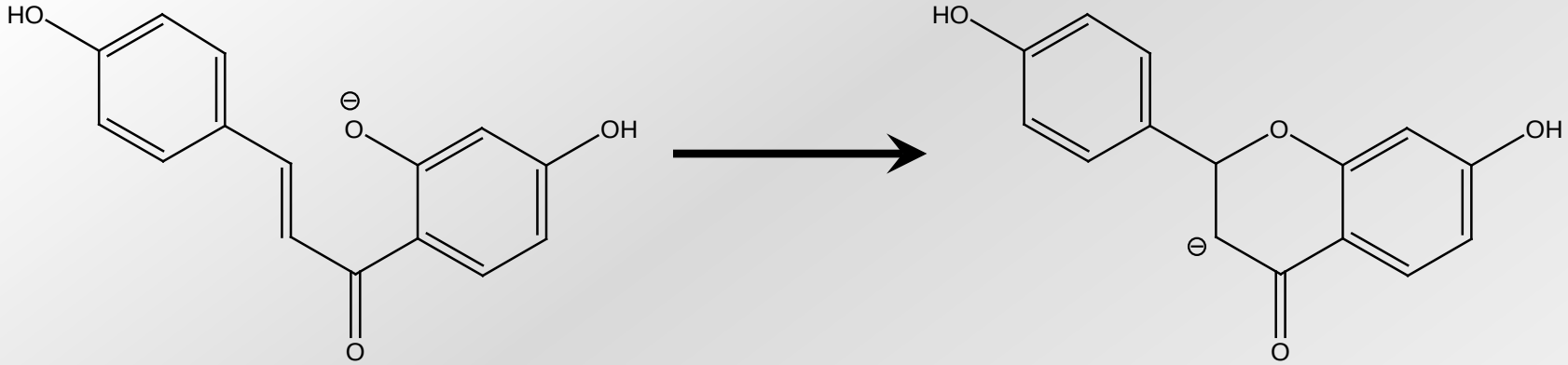


UNIVERSITAT JAUME·I

REACTIVIDAD QUIMICA

RESULTADOS

Paso de Chalcona a Isoflavona



En disolución (agua)

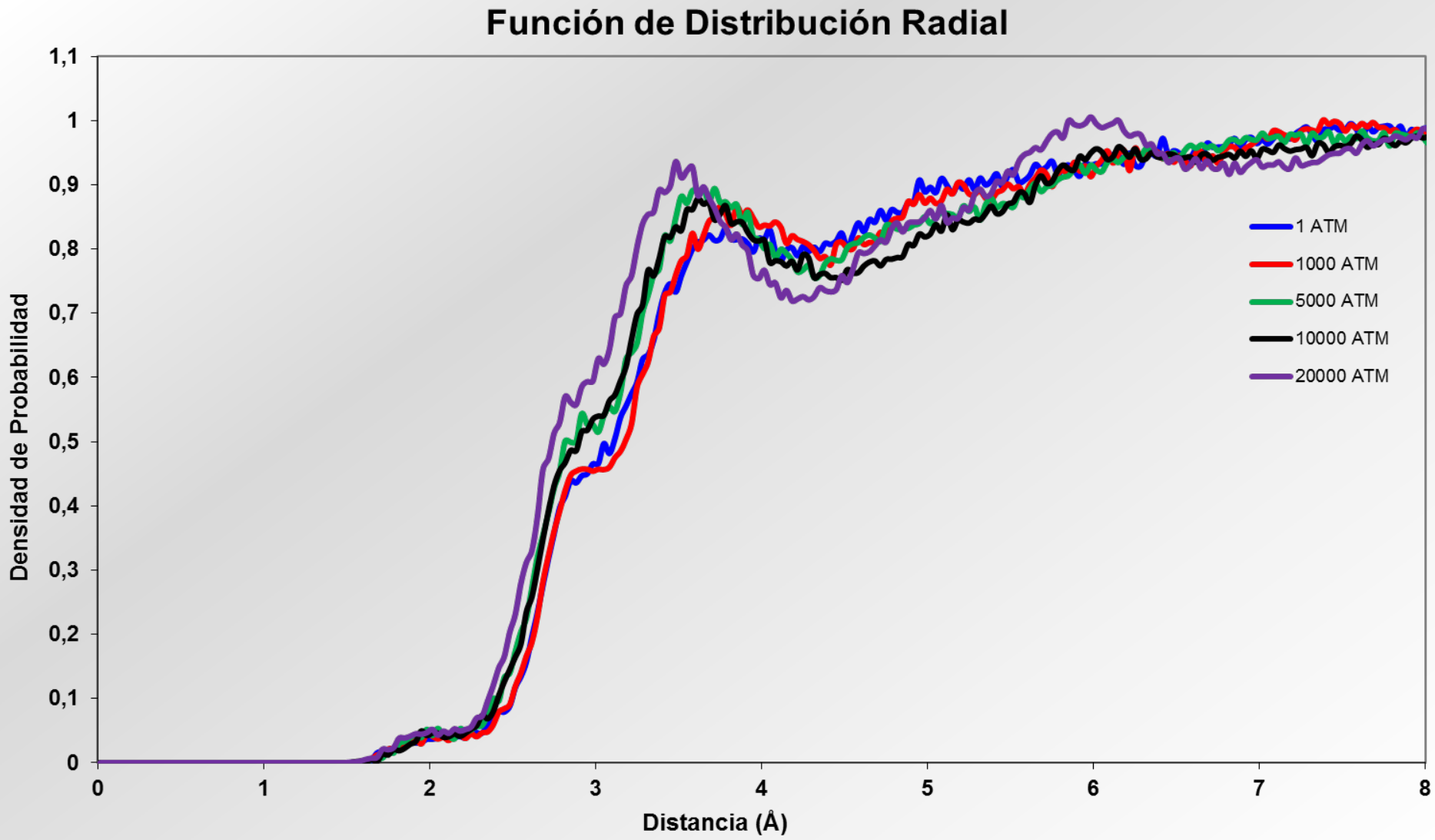
- 30 átomos QM (AM1)
- 17439 átomos TIP3P (5813 moléculas de agua de solvatación)
- Caja de 55.4 Å de lado

En medio enzimático

- 30 átomos QM (AM1)
- 3231 átomos OPLS-AA (enzima)
- 47745 átomos TIP3P (15915 moléculas de agua de solvatación)
- Caja de 79.8 Å de lado

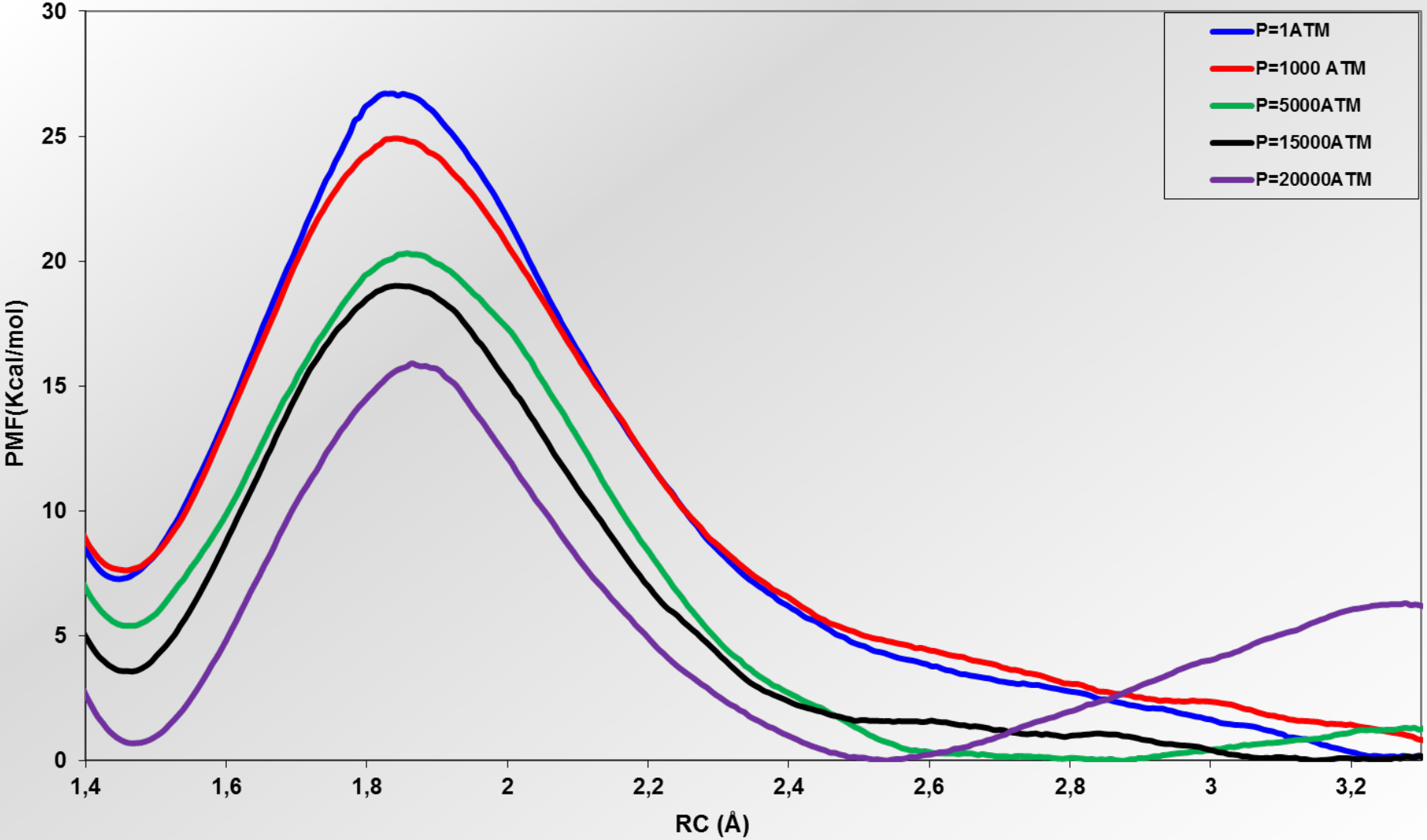
RESULTADOS

Reacción Chalcona-Isoflavona en agua (caja 55.4 Å)



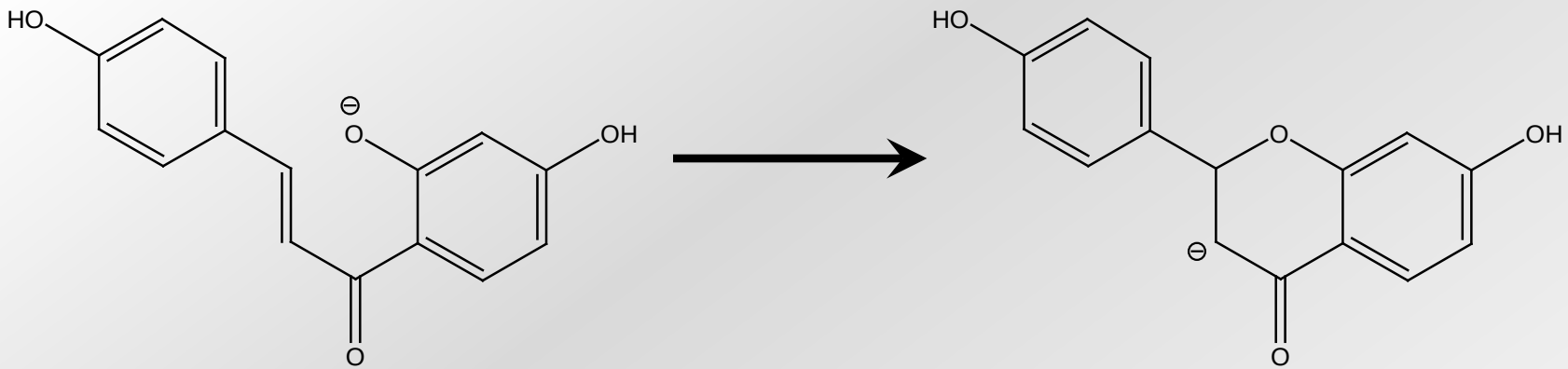
RESULTADOS

Perfiles Energía Libre AM1/MM. Reacción en agua



RESULTADOS

Potenciales de Fuerza Media AM1/MM. Reacción en agua



Presión(atm)	RC‡ (Å)	ΔPMF‡ (Kcal/mol)
1	1.837	26.7
1000	1.839	24.9
5000	1.857	20.3
15000	1.840	19.0
20000	1.863	15.9

CONCLUSIONES

- Se ha desarrollado, implementado y aplicado una metodología QM/MM+DM novedosa para la simular la estructura y reactividad química en fases condensadas, incluyendo la presión hidrostática.

- Se ha obtenido un adecuada representación del campo de fuerzas MM, para reproducir el comportamiento del agua. i.e, la representación de la densidad en función de la presión, utilizando la ecuación de Berendsen modificada.

- Se ha estudiado la reacción de chalcona a isoflavona en agua, obtiéndose los perfiles de energía libre y las estructuras de transición, reactivos y productos en función de la presión hidrostática. En curso, la reacción en medio enzimático.

PERSPECTIVAS DE FUTURO

- Estudiar la influencia de la presión hidrostática en el mecanismo molecular de reacciones orgánicas (S_N2, S_N1, E2, Diels-Alder, etc..) en agua

- Desarrollar potenciales, MM, para simular la estructura y reactividad química en otros disolventes.

- Extender la metodología a reacciones químicas en sistemas biológicos (enzimas).

- Aumentar el nivel cuántico de representación de la parte QM (DFT, *ab-initio*, híbrido, etc).

- Estudiar la posible influencia de la presión como coordenada colectiva sobre la coordenada distinguida.

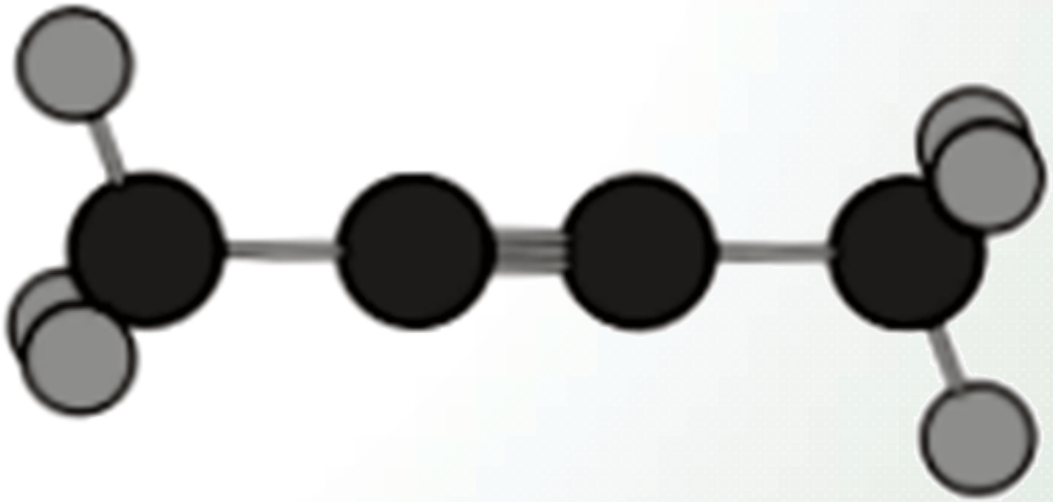
UNIVERSITAT JAUME·I

AGRADECIMIENTOS

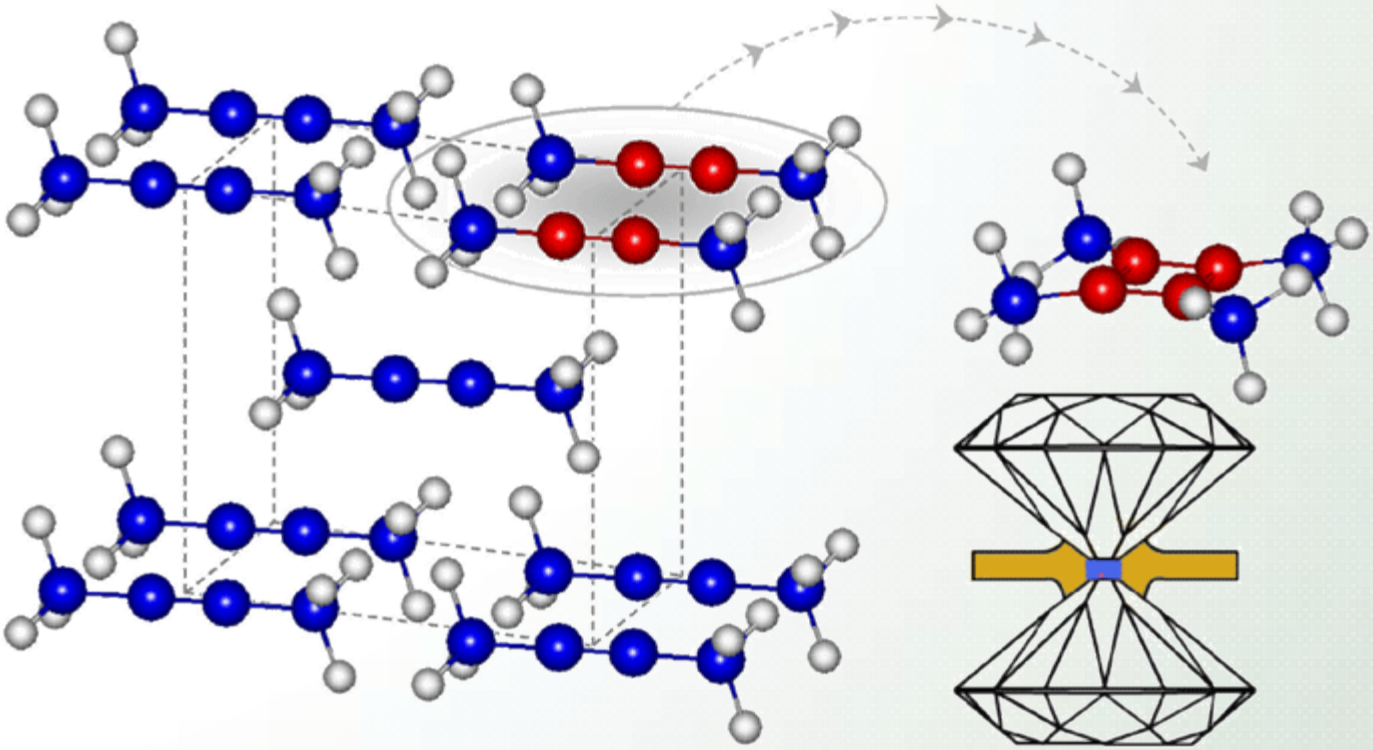
Juan Andrés Bort,
Armando Beltrán,
Lourdes Gracia Edo
y
Sergio Martí

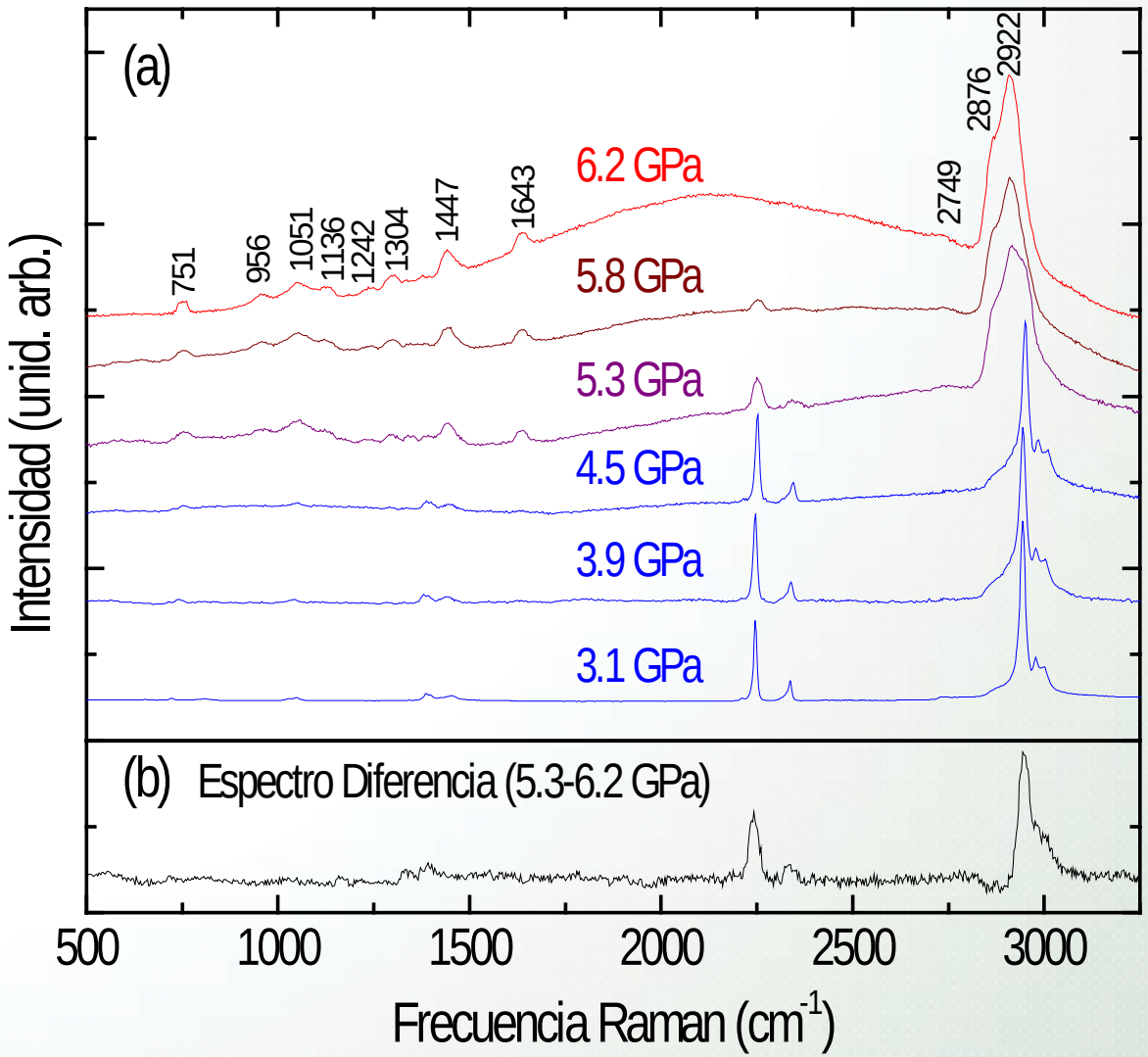
Modelización de la alta presión con métodos de función de onda

Reactividad a alta presión del dimetilacetileno



Dimetilacetileno (DMA)




(a)
751
956
1051
1136
1242
1304
1447
1643
2749
2876
2922
6.2 GPa
5.8 GPa
5.3 GPa
4.5 GPa
3.9 GPa
3.1 GPa
(b) Espectro Diferencia (5.3-6.2 GPa)
Intensidad (unid. arb.)
500
1000
1500
2000
2500
3000
Frecuencia Raman (cm-1)

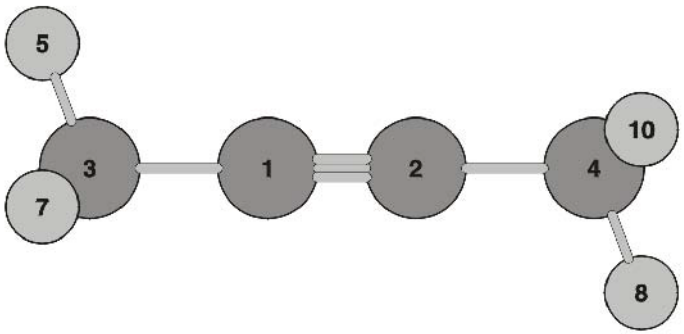
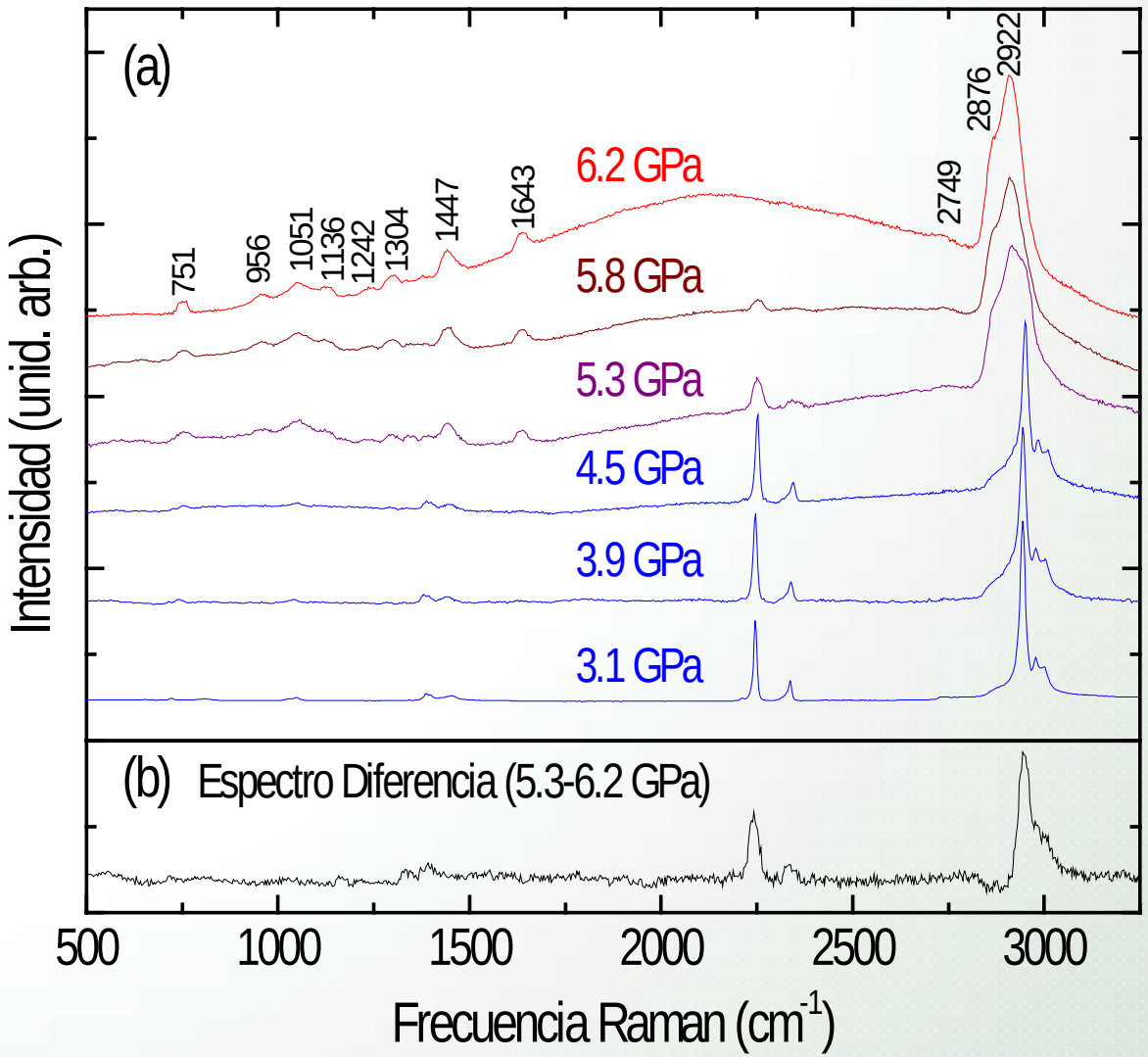


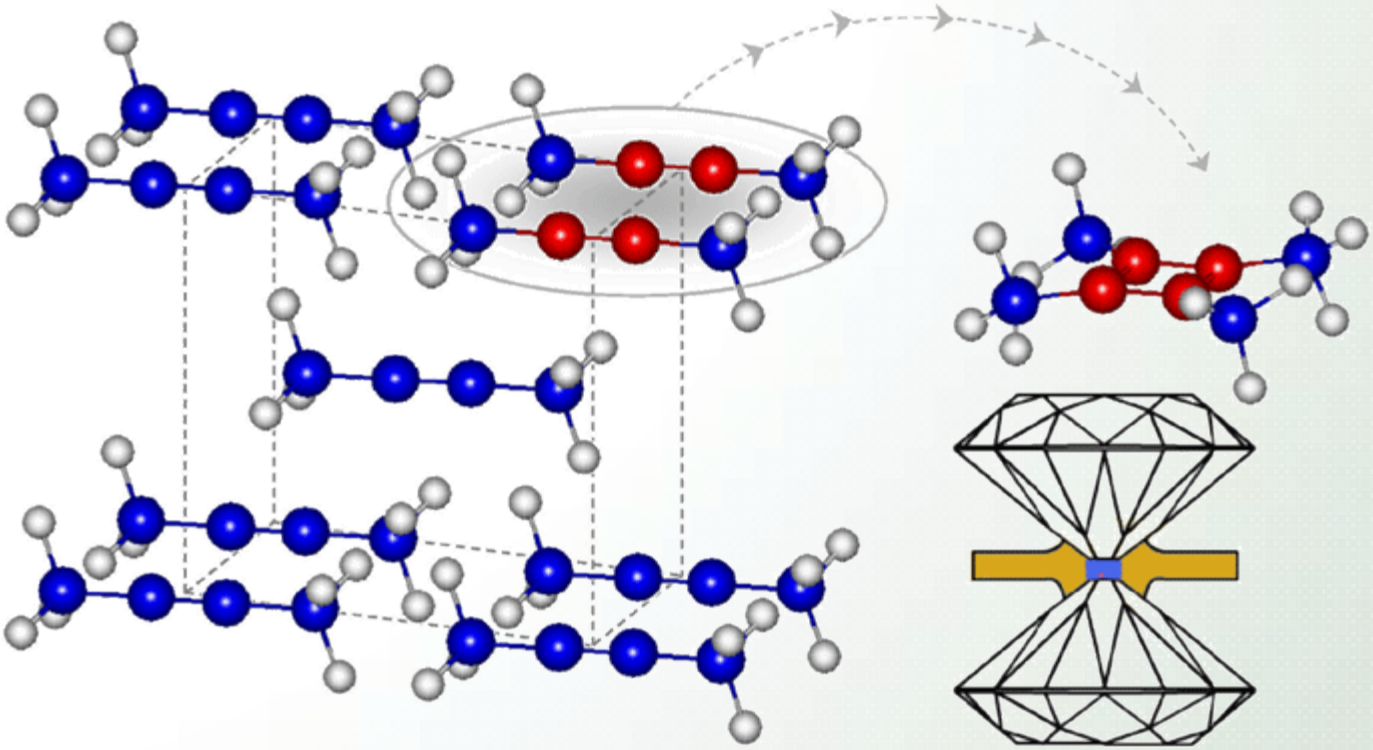
Tabla 4.1: Parámetros geométricos calculados y experimentales [85] del DMA. Las distancias se expresan en Å y los ángulos en grados. Base: 6-31++G(d,p) para B3LYP, MP2, CASSCF y MRMP2 y ondas planas para CASTEP.

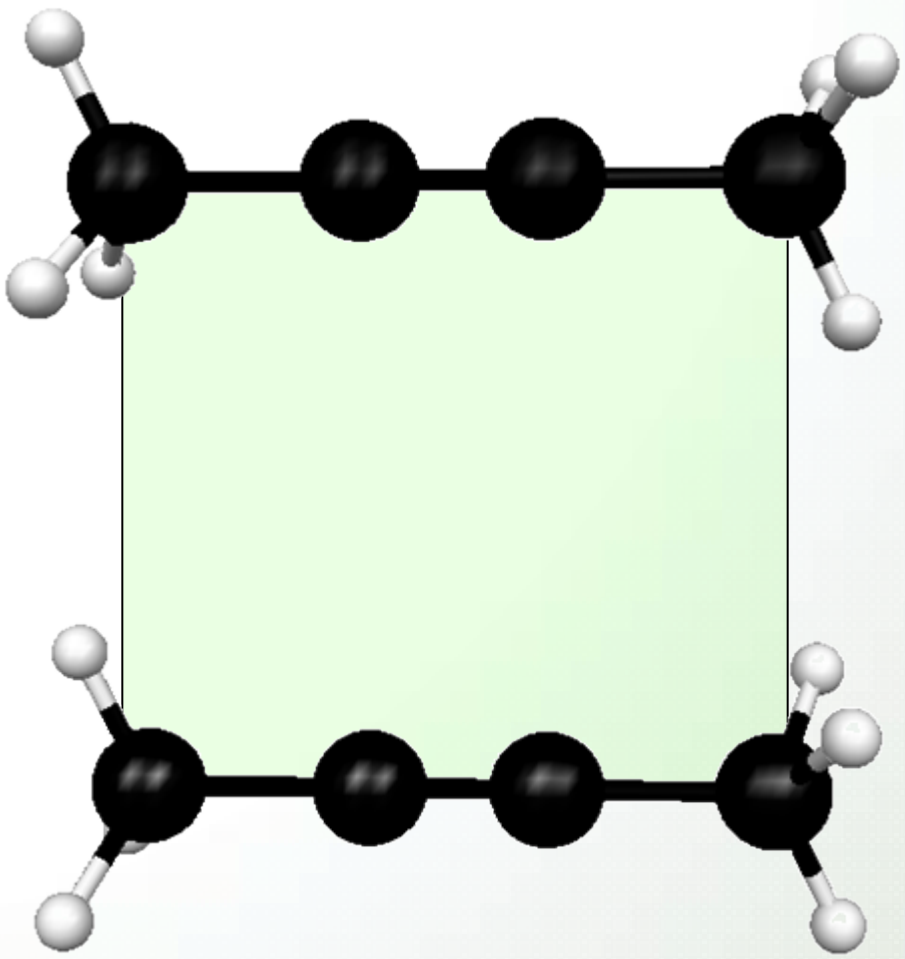
Método	$r_{C_1C_3}$	$r_{C_1C_2}$	$r_{C_3H_5}$	$a_{C_3C_1C_2}$	$a_{H_5C_3C_1}$
B3LYP	1.463	1.212	1.096	179.2	111.2
MP2	1.464	1.224	1.090	179.6	110.8
CASSCF(4,4)	1.472	1.200	1.084	179.5	110.7
MRMP2(4,4)	1.471	1.199	1.084	179.3	110.7
Castep	1.434	1.194	1.091	179.8	118.2
Experimental, fase II	1.468	1.201	1.091	178.5	111.4

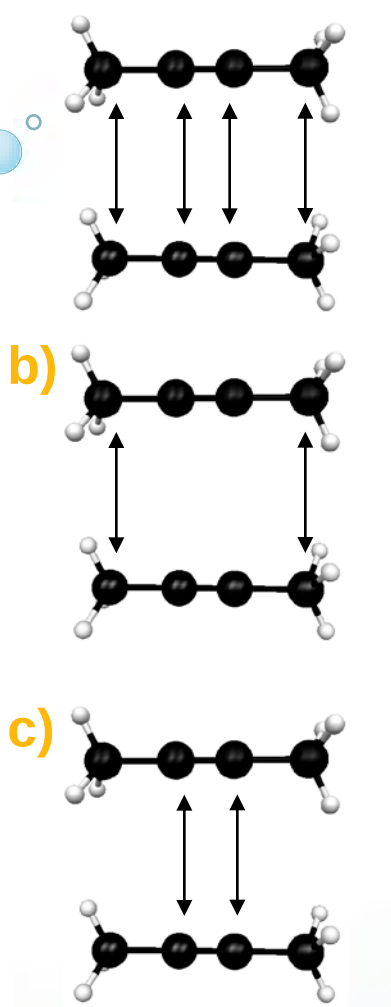
Tabla 4.2: Frecuencias calculadas y experimentales [26] del DMA (en cm^{-1}). La bases usadas han sido la 6-31++G(d,p) para B3LYP, MP2 y CASSCF y ondas planas para CASTEP/PBE.

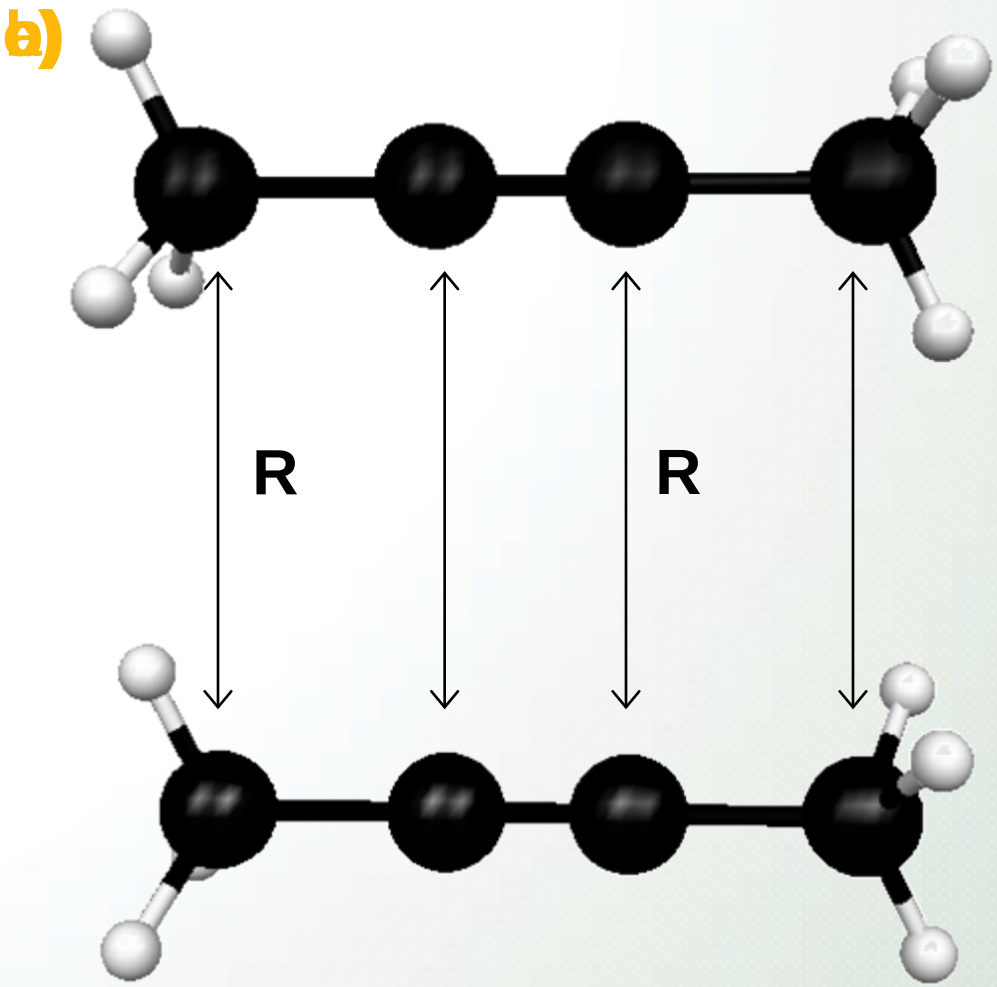
Descripción	Modo	Experimental	Castep	B3LYP	MP2	CAS(4,4)
$\equiv C - C$ flexión	ν_{16}	390	409	378	206	440
$C - CH_3$ tensión	ν_4	723	724	725	730	747
CH_3 rocking	ν_{15}	1048	1046	1055	1062	1103
CH_3 deformación	ν_3	1399	1391	1423	1459	1546
	ν_{14}	1455	1450	1484	1526	1587
$C \equiv C$ tensión	ν_2	2290[1]	2281	2358	2298	2476
CH_3 tensión	ν_1	2946	2954	3031	3117	3193
	ν_{13}	2979	3018	3093	3207	3259

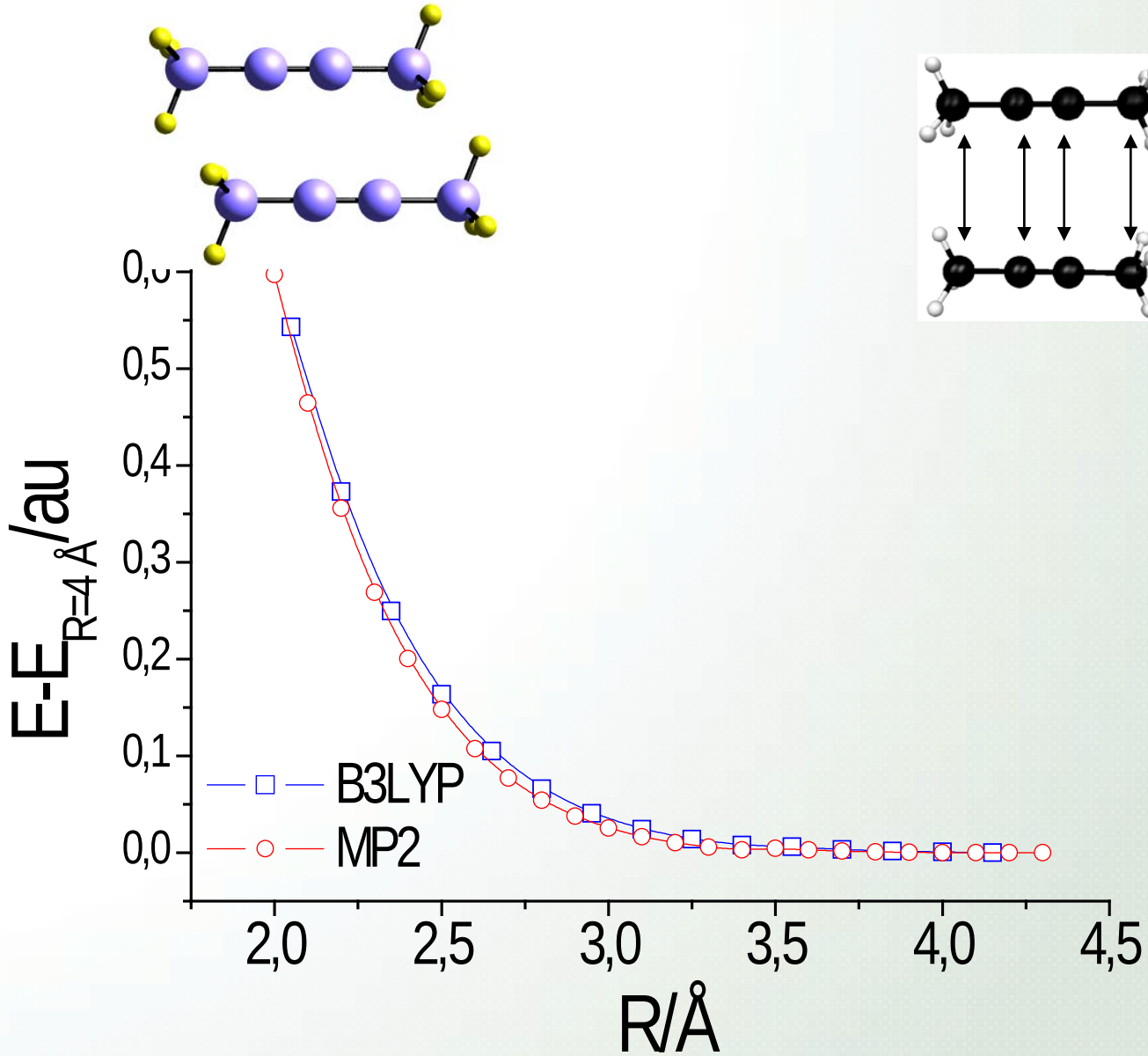

(a)
751
956
1051
1136
1242
1304
1447
1643
2749
2876
2922
6.2 GPa
5.8 GPa
5.3 GPa
4.5 GPa
3.9 GPa
3.1 GPa
(b) Espectro Diferencia (5.3-6.2 GPa)
Intensidad (unid. arb.)
500
1000
1500
2000
2500
3000
Frecuencia Raman (cm-1)

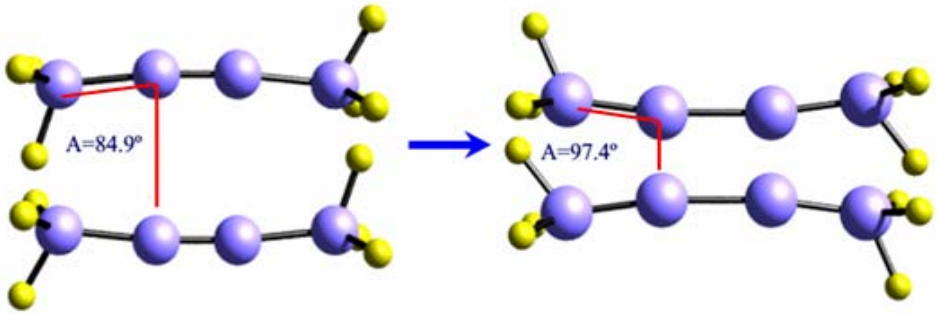


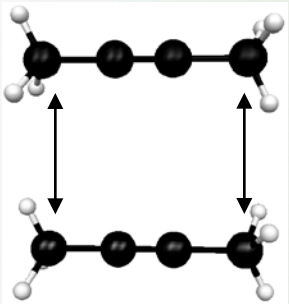


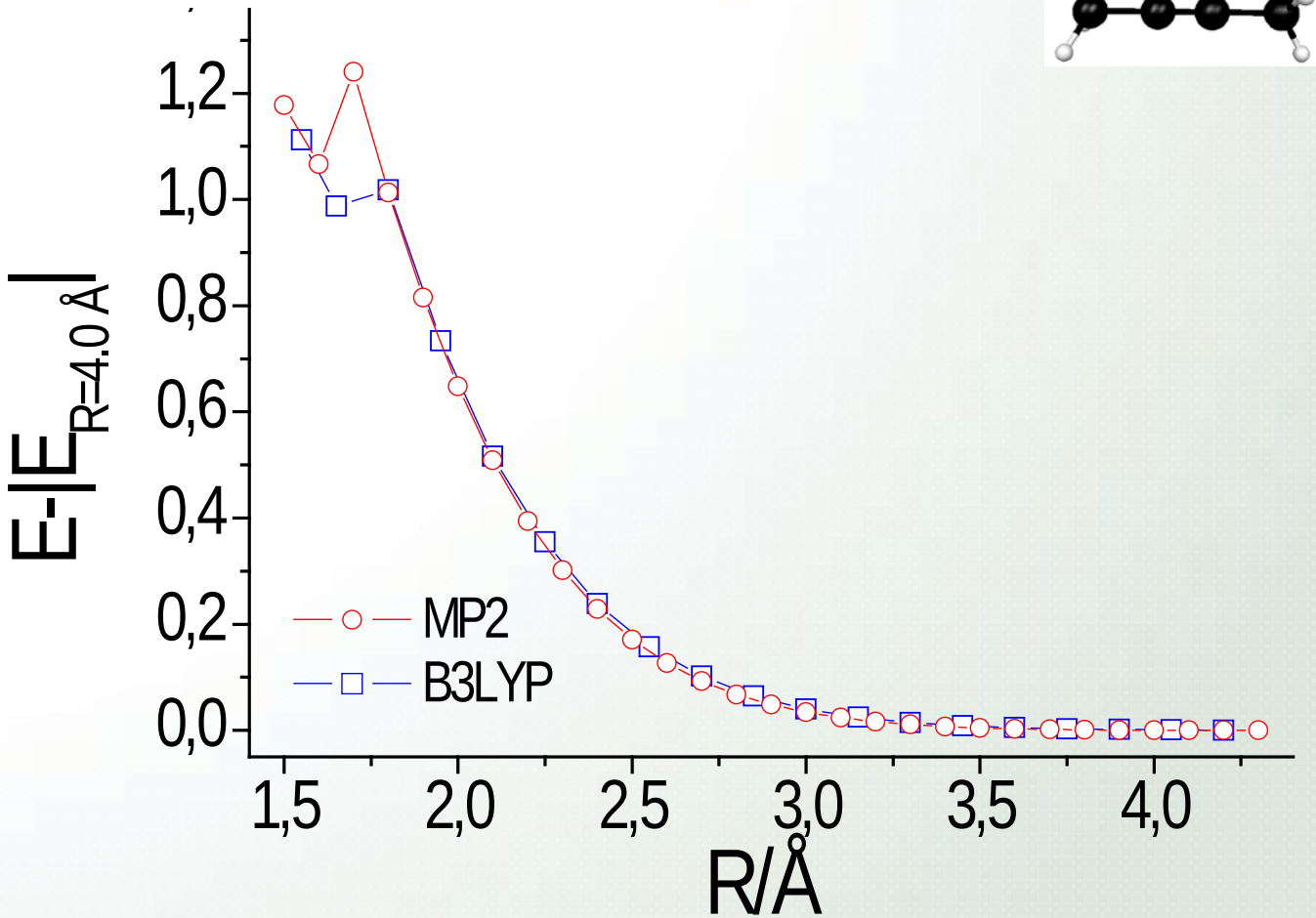

b)
c)

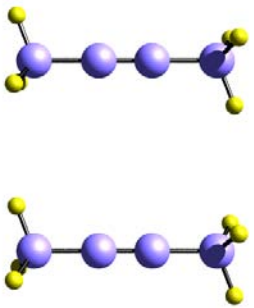

a)
R
R

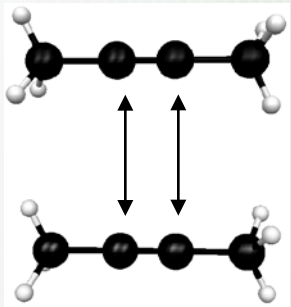

0,6
0,5
0,4
0,3
0,2
0,1
0,0
E-E$_{R=4\,Å}$/au
B3LYP
MP2
2,0
2,5
3,0
3,5
4,0
4,5
R/Å

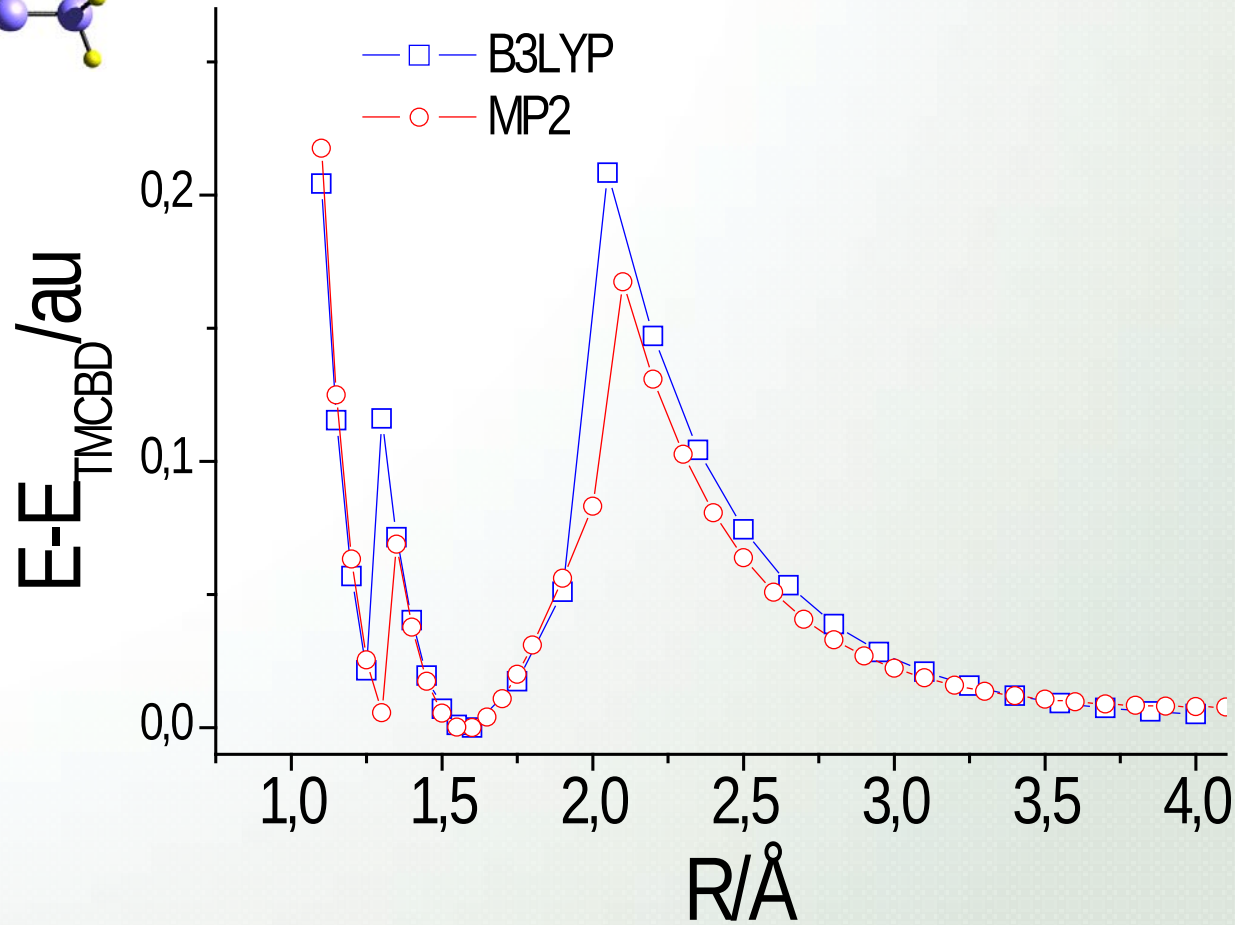

A=84.9º
A=97.4º

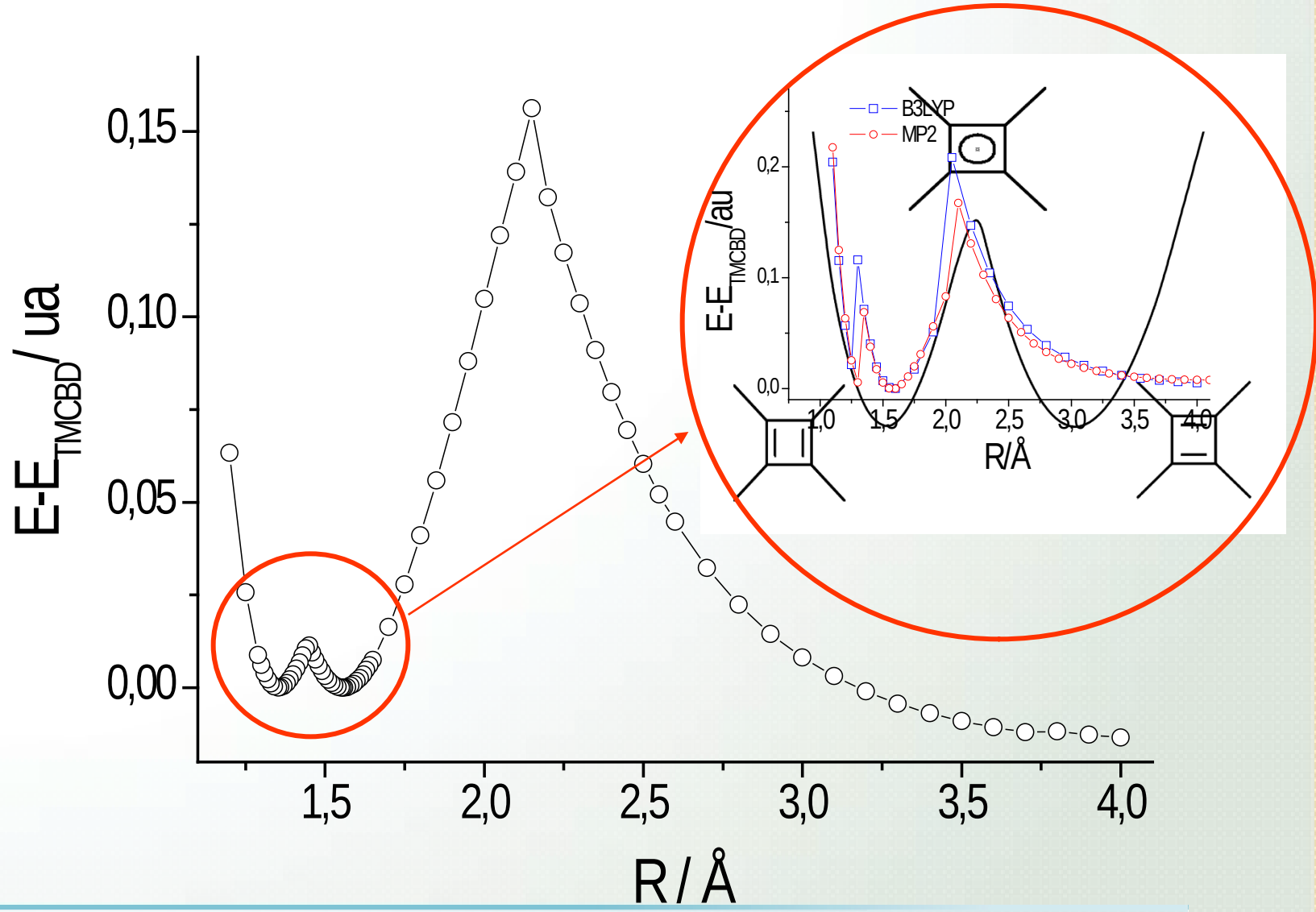


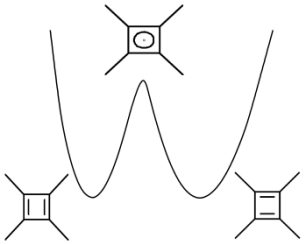

E-|E_R=4.0Å|
1,2
1,0
0,8
0,6
0,4
0,2
0,0
MP2
B3LYP
1,5
2,0
2,5
3,0
3,5
4,0
R/Å

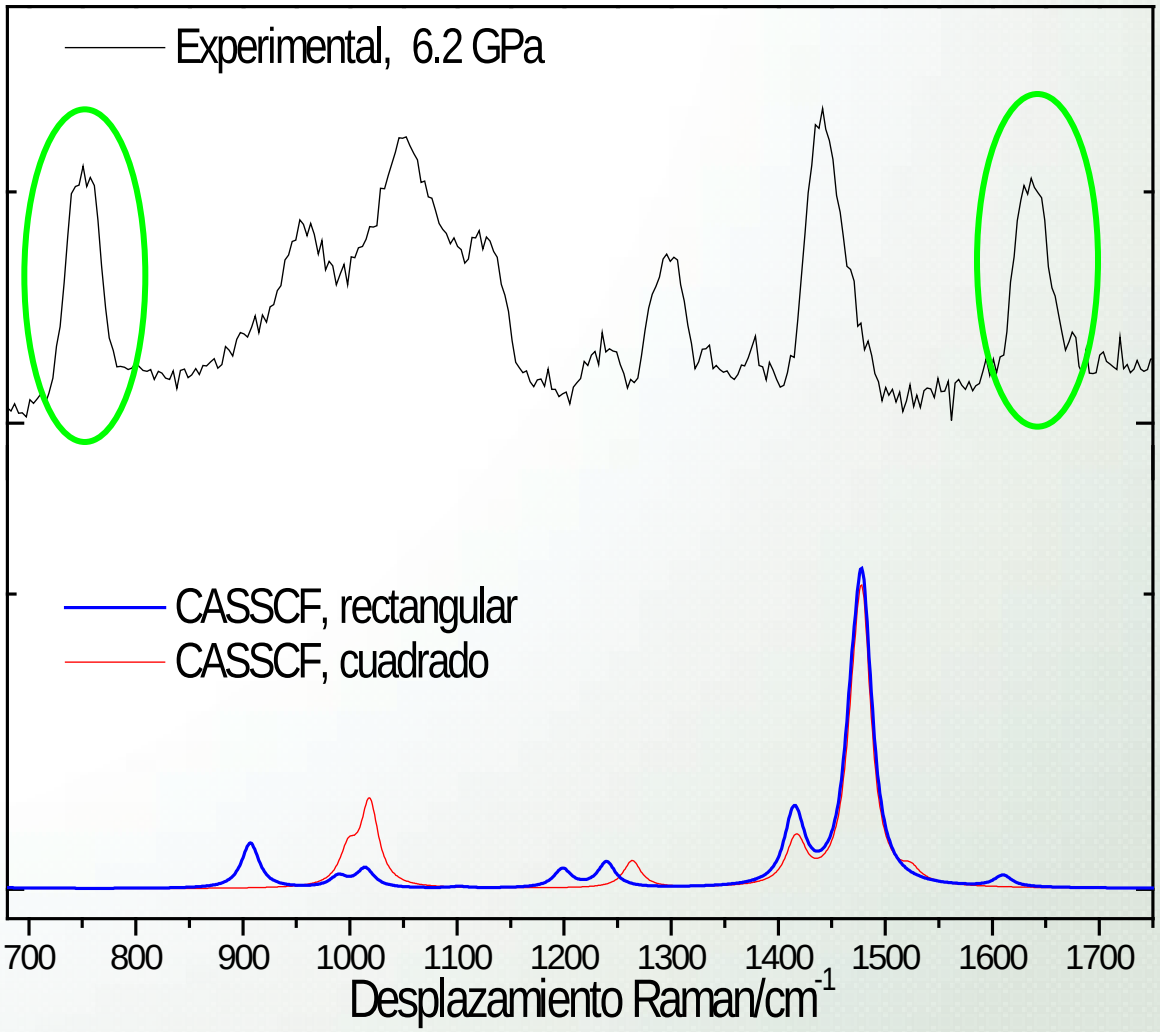


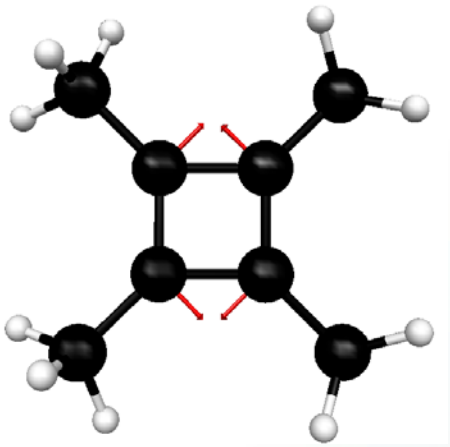



B3LYP
MP2
0,2
0,1
0,0
E-E_TMCBD/au
1,0
1,5
2,0
2,5
3,0
3,5
4,0
R/Å


0,15
0,10
0,05
0,00
E-E$_{TMCBD}$ / ua
1,5
2,0
2,5
3,0
3,5
4,0
R / Å
B3LYP
MP2
0,2
0,1
0,0
E-E$_{TMCBD}$/au
1,0
1,5
2,0
2,5
3,0
3,5
4,0
R/Å

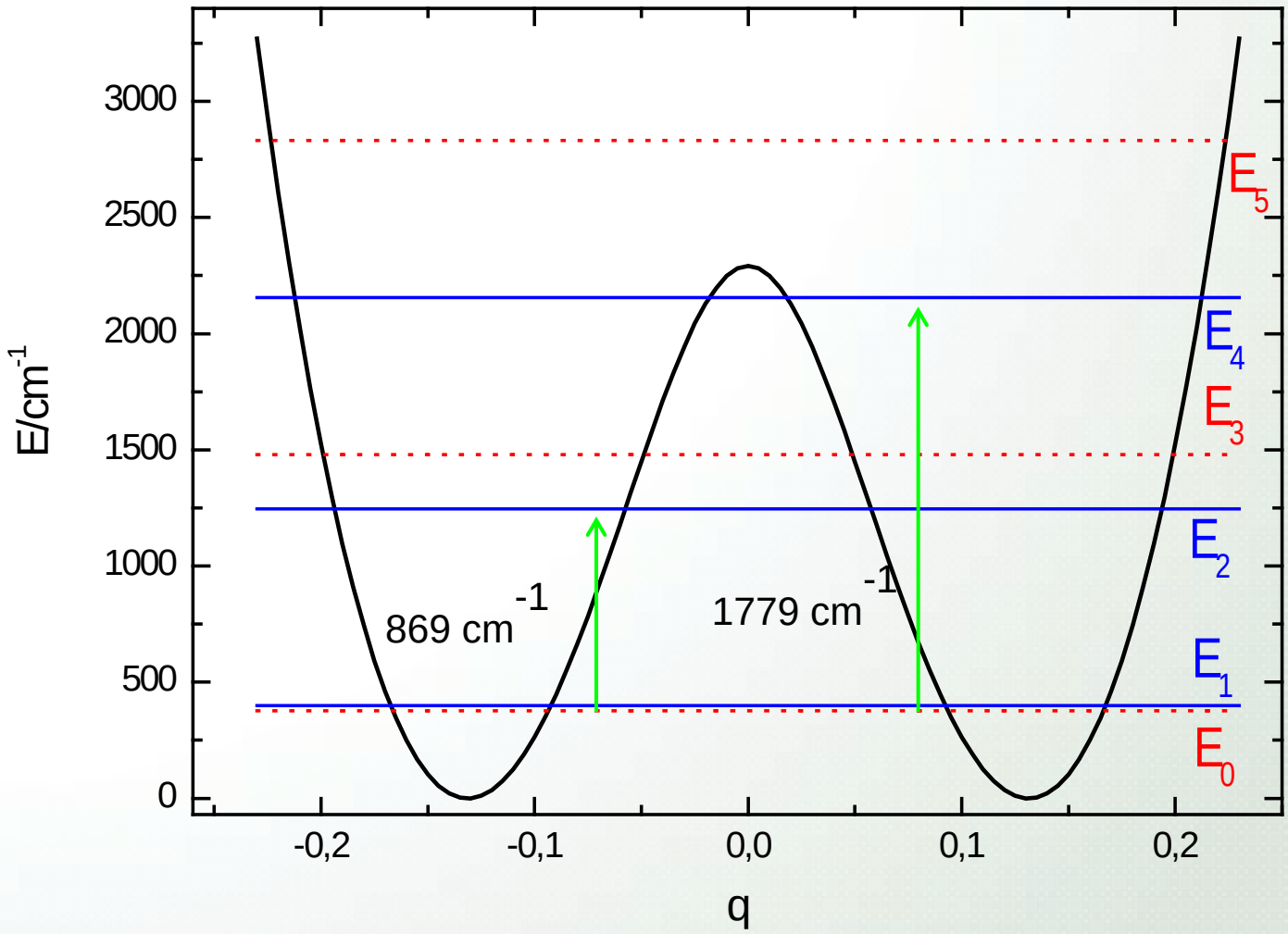


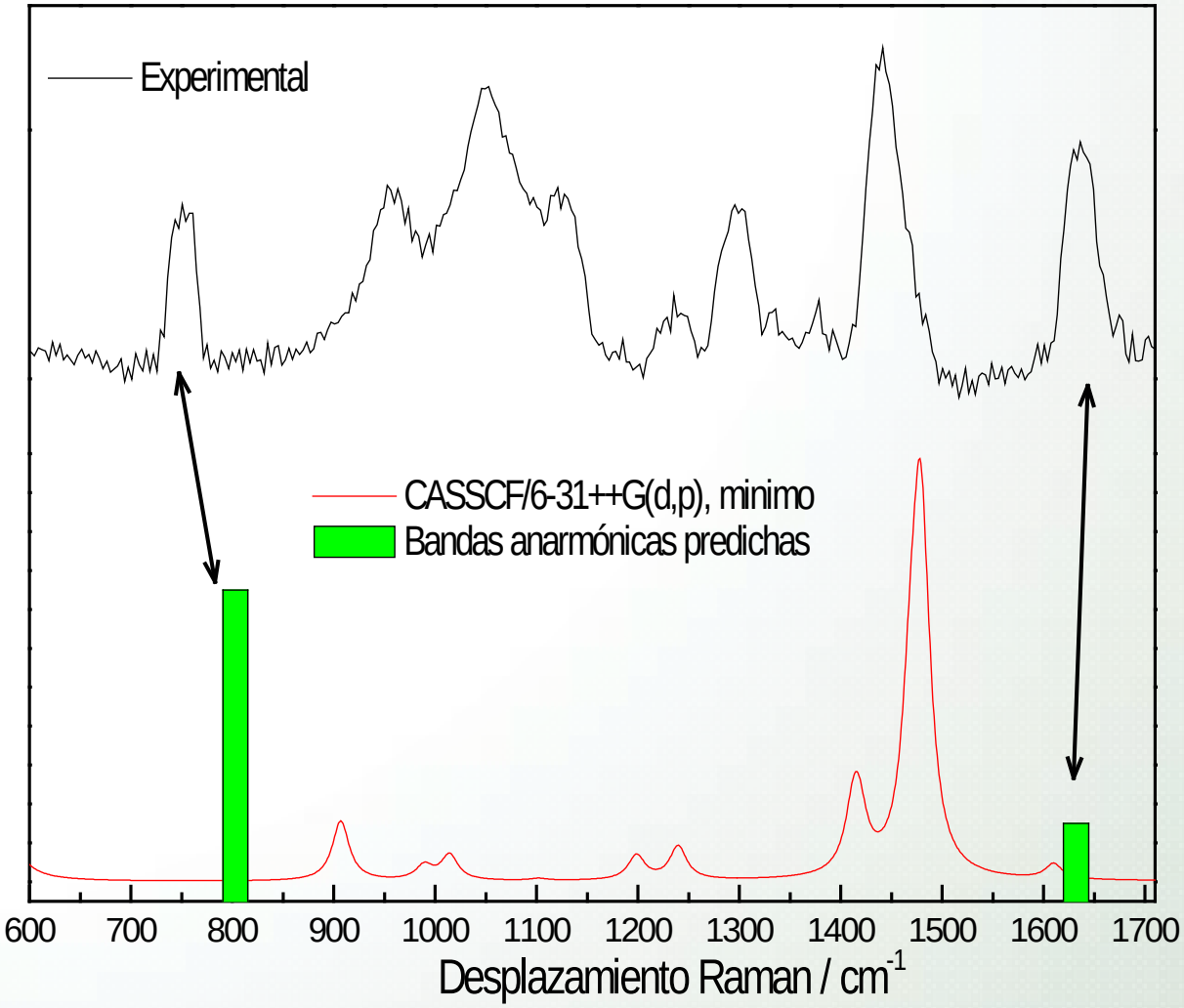

Experimental, 6.2 GPa
CASSCF, rectangular
CASSCF, cuadrado
700
800
900
1000
1100
1200
1300
1400
1500
1600
1700
Desplazamiento Raman/cm-1

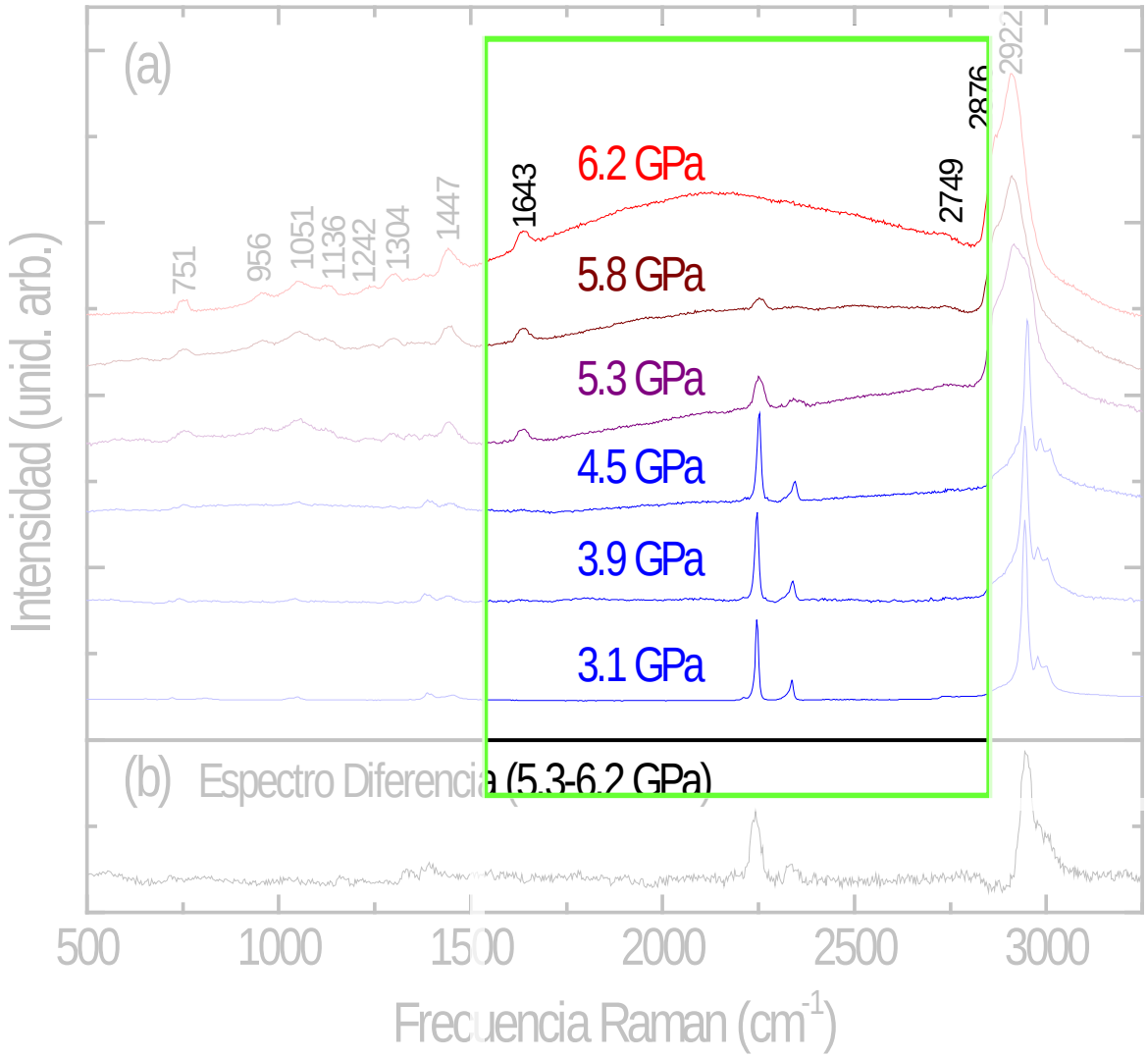


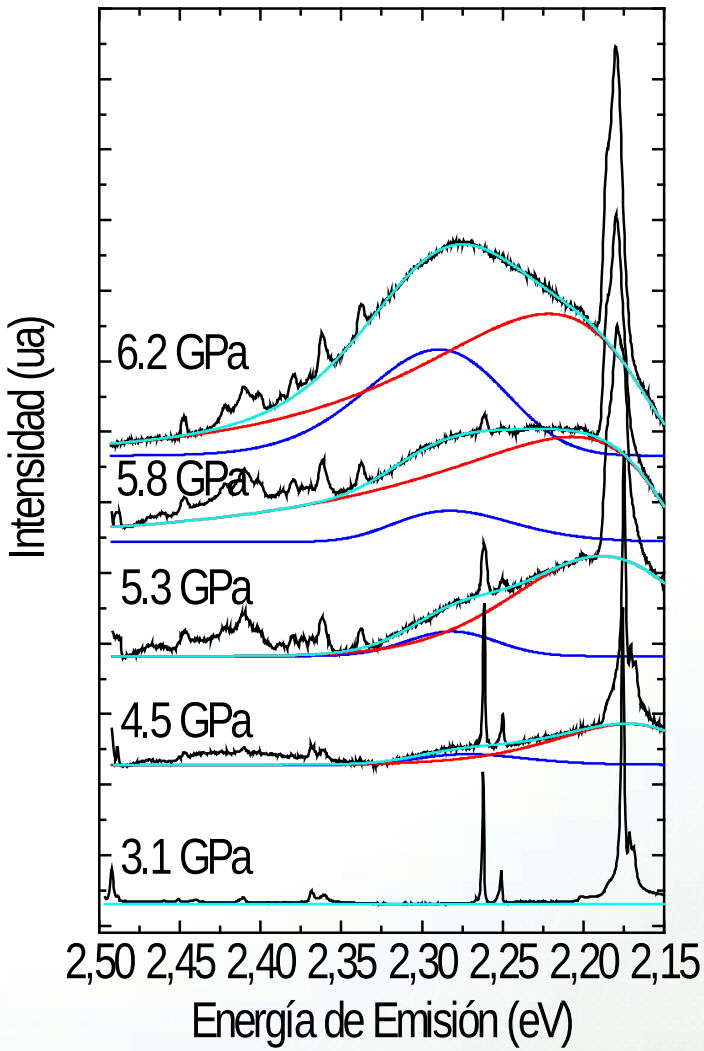
Modo imaginario a 1554 cm^{-1}
relacionado con la automerización

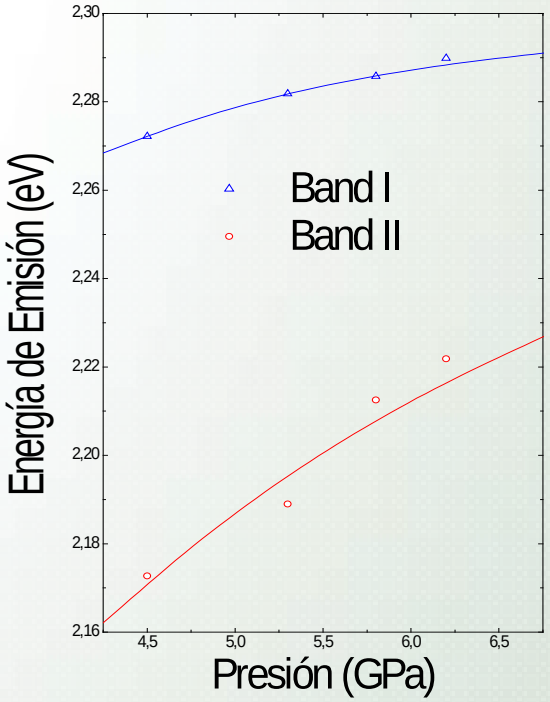
$$H(q) = -\frac{1}{2\mu}\frac{d^2}{dq^2} + aq^2 + bq^4 + c\exp(-dq^2)$$

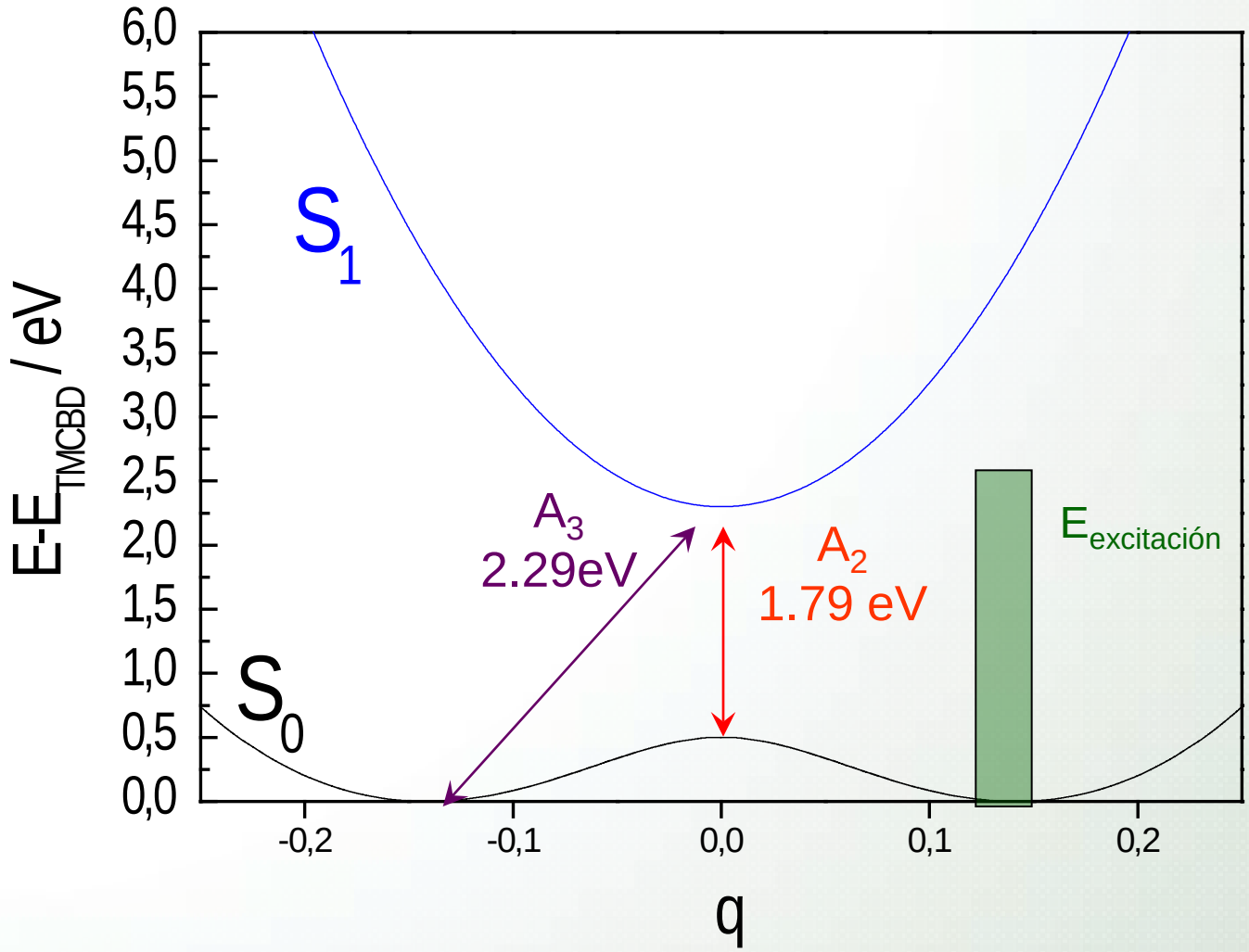



Experimental
CASSCF/6-31++G(d,p), minimo
Bandas anarmónicas predichas
600
700
800
900
1000
1100
1200
1300
1400
1500
1600
1700
Desplazamiento Raman / cm-1

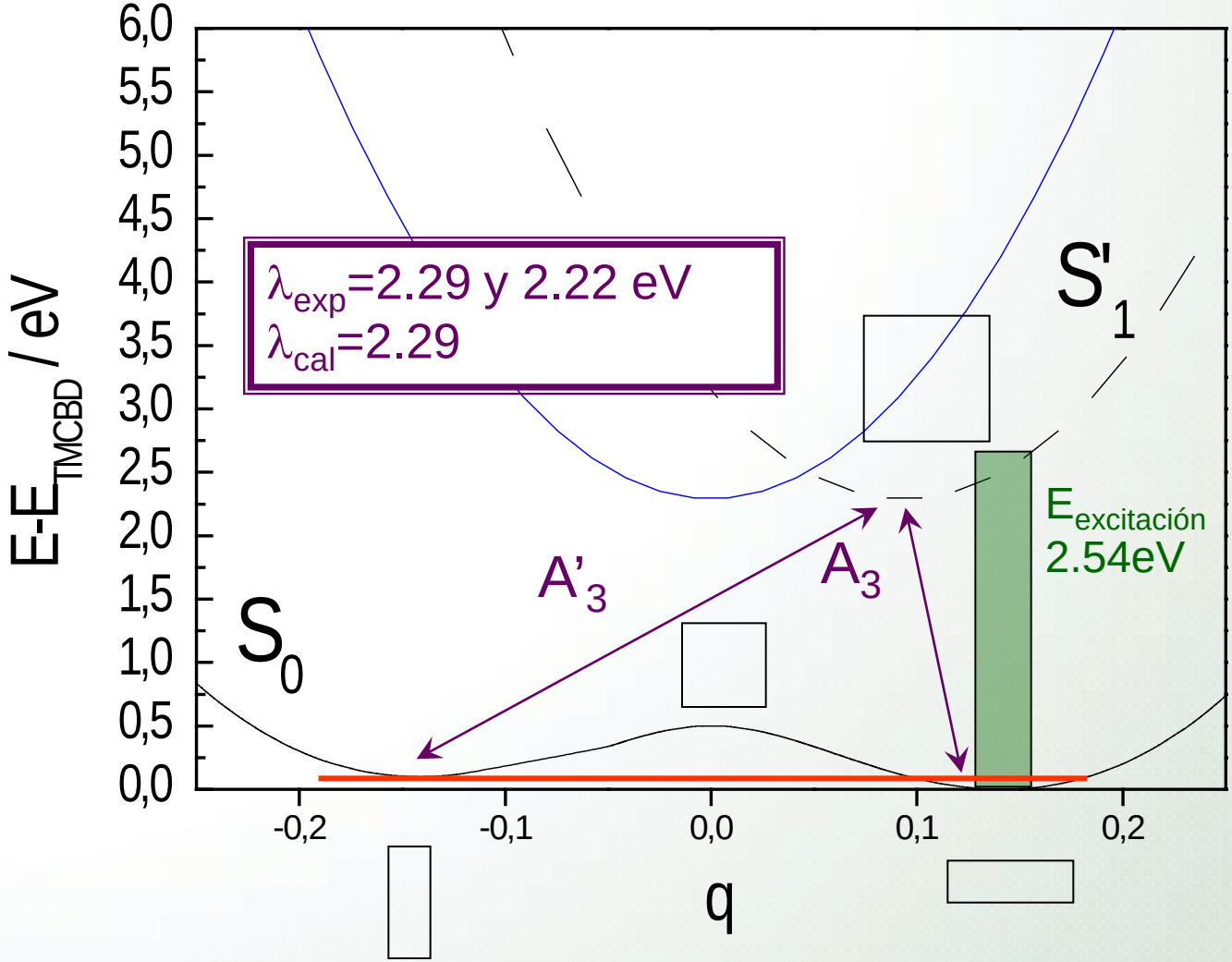

(a)
751
956
1051
1136
1242
1304
1447
1643
2749
2876
2922
6.2 GPa
5.8 GPa
5.3 GPa
4.5 GPa
3.9 GPa
3.1 GPa
(b) Espectro Diferencia (5.3-6.2 GPa)
Intensidad (unid. arb.)
500
1000
1500
2000
2500
3000
Frecuencia Raman (cm-1)


6.2 GPa
5.8 GPa
5.3 GPa
4.5 GPa
3.1 GPa
Intensidad (ua)
2,50 2,45 2,40 2,35 2,30 2,25 2,20 2,15
Energía de Emisión (eV)


Band I
Band II
Energía de Emisión (eV)
2,30
2,28
2,26
2,24
2,22
2,20
2,18
2,16
4,5 5,0 5,5 6,0 6,5
Presión (GPa)

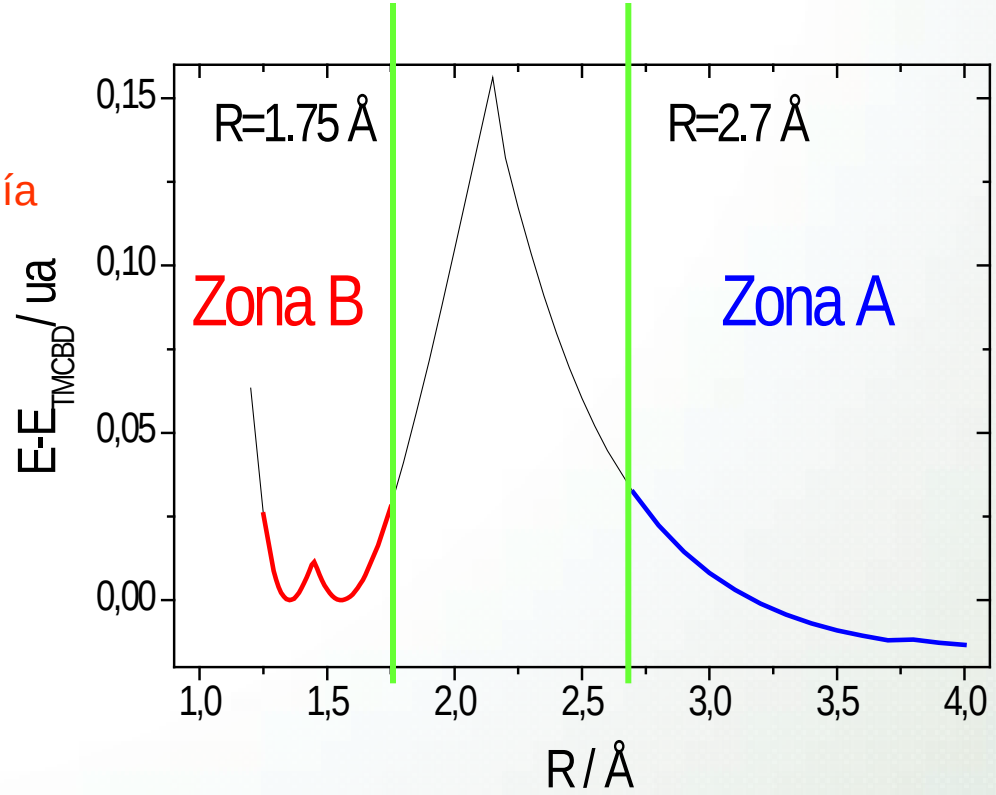

6,0
5,5
5,0
4,5
4,0
3,5
3,0
2,5
2,0
1,5
1,0
0,5
0,0
E-E_TMCBD / eV
S1
S0
A3
2.29eV
A2
1.79 eV
Eexcitación
-0,2
-0,1
0,0
0,1
0,2
q

Modelo de Drickamer



1. Metodología MCSCF

2. Cambios químicos



1. Metodología monodeterminantal

2. Cambios Físicos

- Correlación P-R

Gracias por su atención

Duke UNIVERSITY

Joint Use of the Catastrophe Theory and the Analysis of the Electon Density (QTAIM, ELF and NCI) in reactivity

J. Andrés[1], S. Berski[2], and J. Contreras-García[3]

[1]Departamento de Química Física y Analítica, Universitat Jaume I
[2]Faculty of Chemistry, University of Wroclaw
[3]Department of Chemistry, Duke University

SUMMARY

- Non-covalent interactions have a unique signature and their presence can be revealed solely from the electron density.

- This approach provides a rapid and rich representation of van der Waals interactions, hydrogen-bonds, and steric repulsion.

- It only requires the atomic coordinates as input

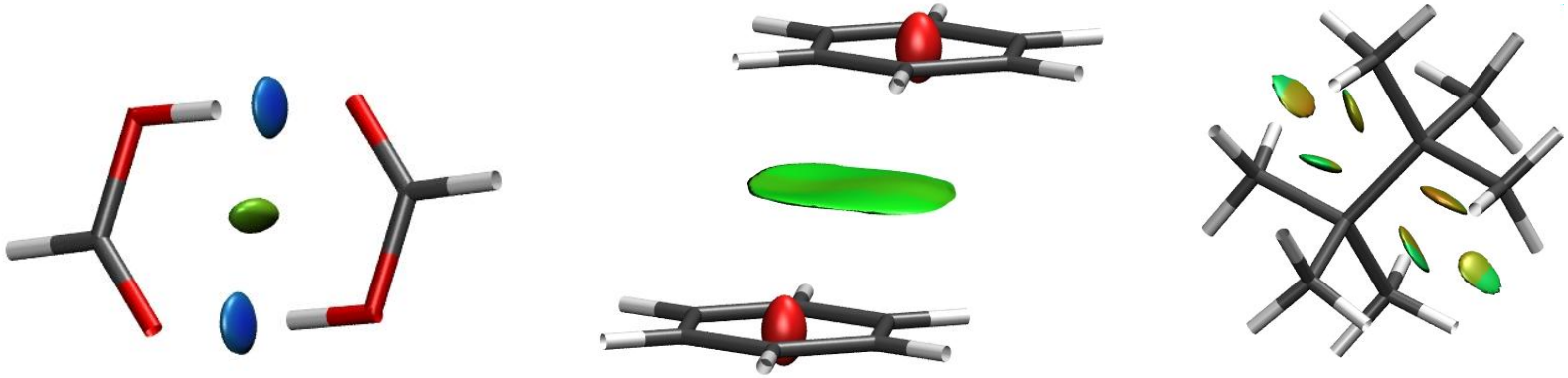
- It is applicable to a wide range of systems: small/large, organic/inorganic, solids, etc.

- This tool offers exciting possibilities in design and generation of leads.

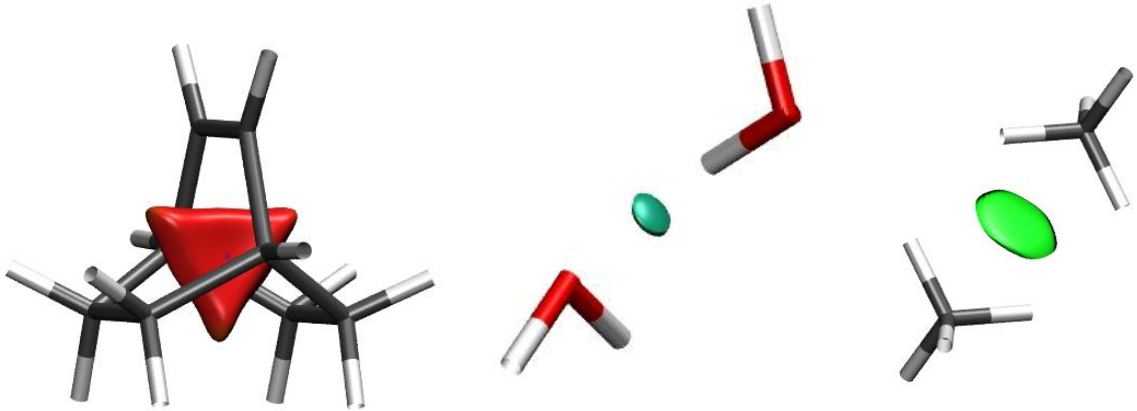
Reference: J. Am. Chem. Soc. 132, 6498 (2010).

SMALL MOLECULES

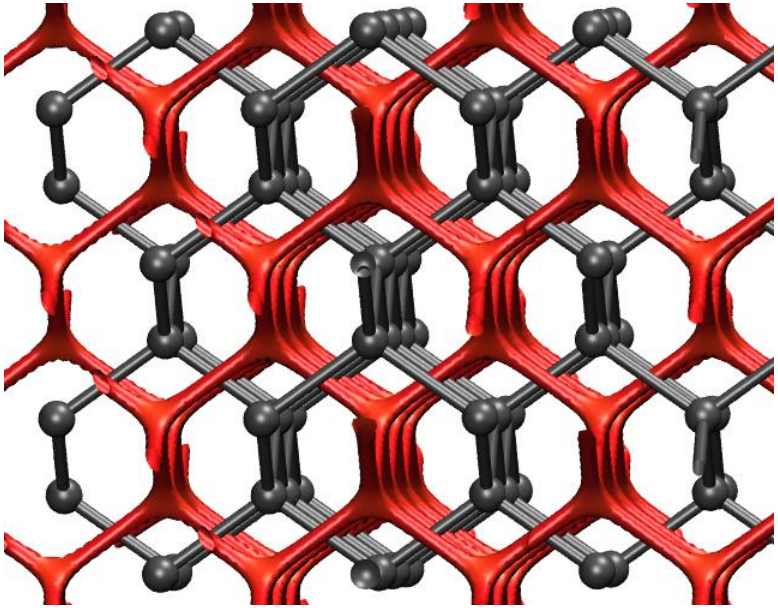
We have recently developed an index for visualizing non covalent interactions



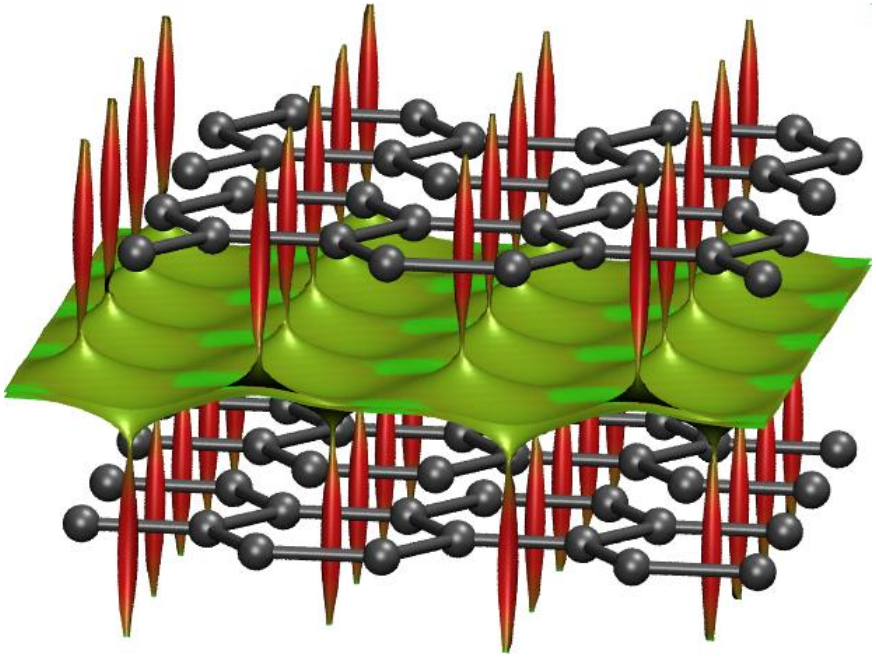
Strong and attractive $\rho > 0 \quad \lambda_H > 0$
Weak $\rho \approx 0 \quad \lambda_H \approx 0$
Strong and repulsive $\rho > 0 \quad \lambda_H > 0$



SOLIDS



Diamond



Graphite

BIOMOLECULES

•One of the major areas of application of weak interactions are biomolecules

•HOWEVER, SCF calculations are extremely slow

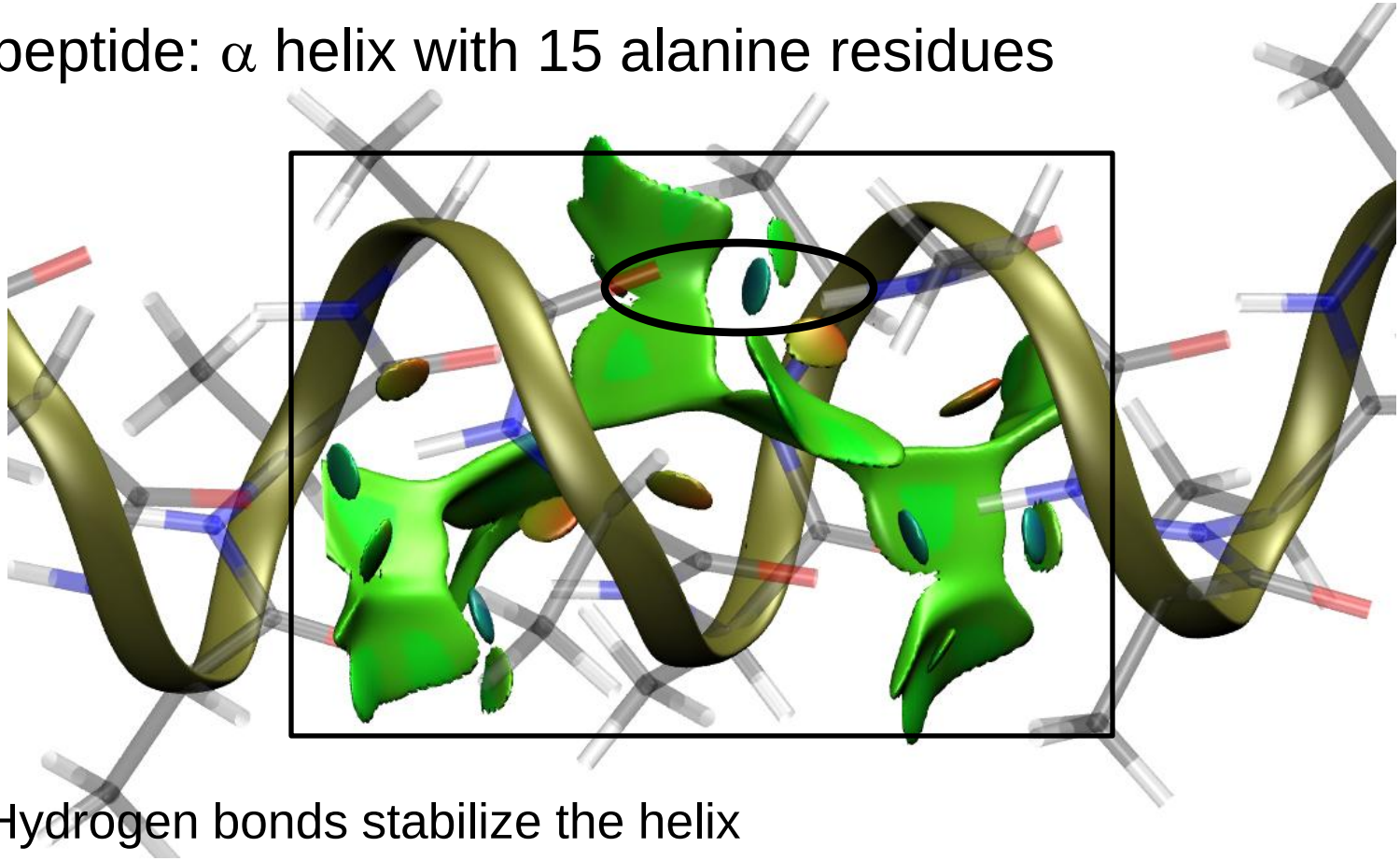
•Reduced density gradient characteristics are preserved from promolecular to SCF density

•only require input atomic coordinates,

• very fast calculation; applicable to large systems

BIOMOLECULES

Polipeptide: α helix with 15 alanine residues

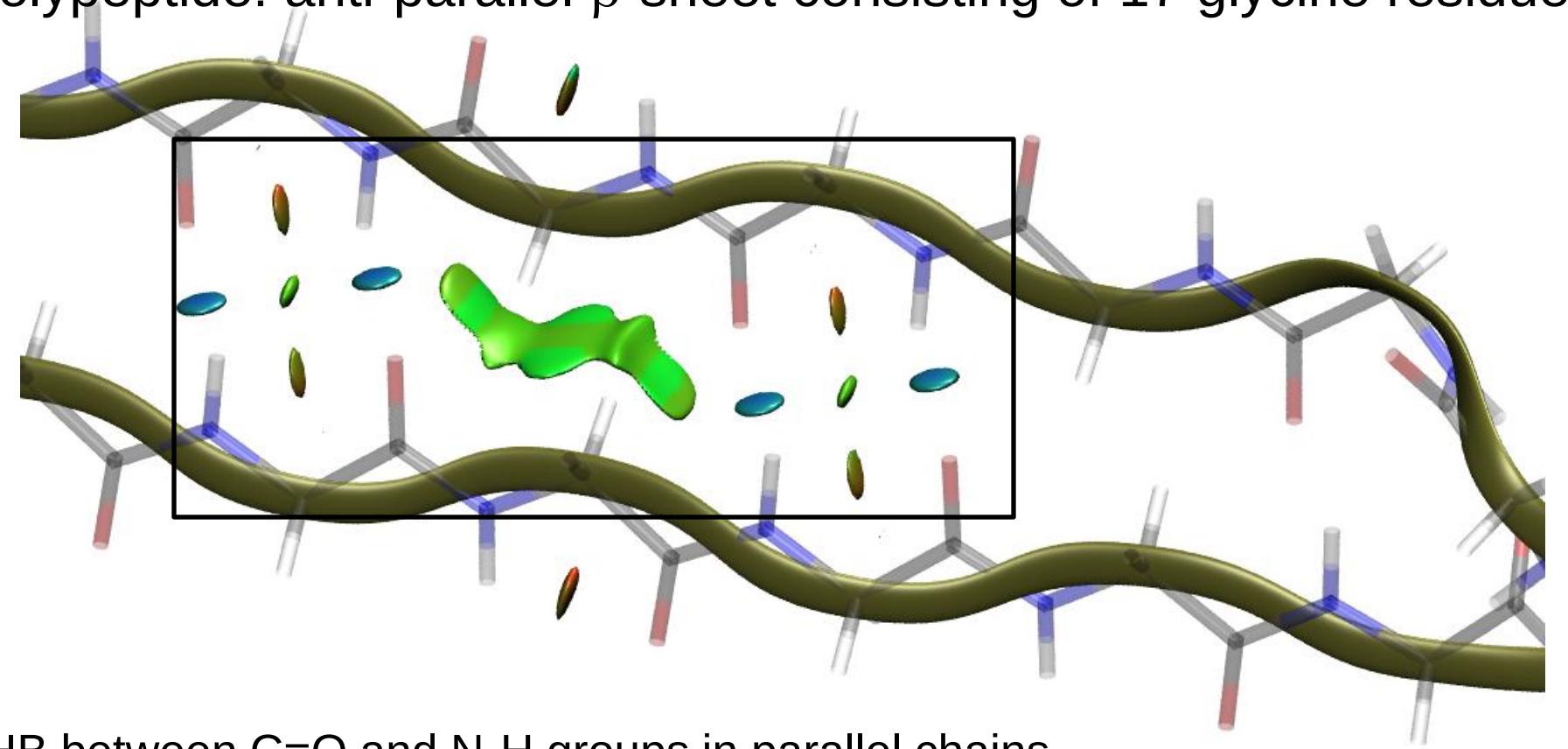


•Hydrogen bonds stabilize the helix

•Big region of van der Waals interaction inside the helix and between methyle lateral chains one step away

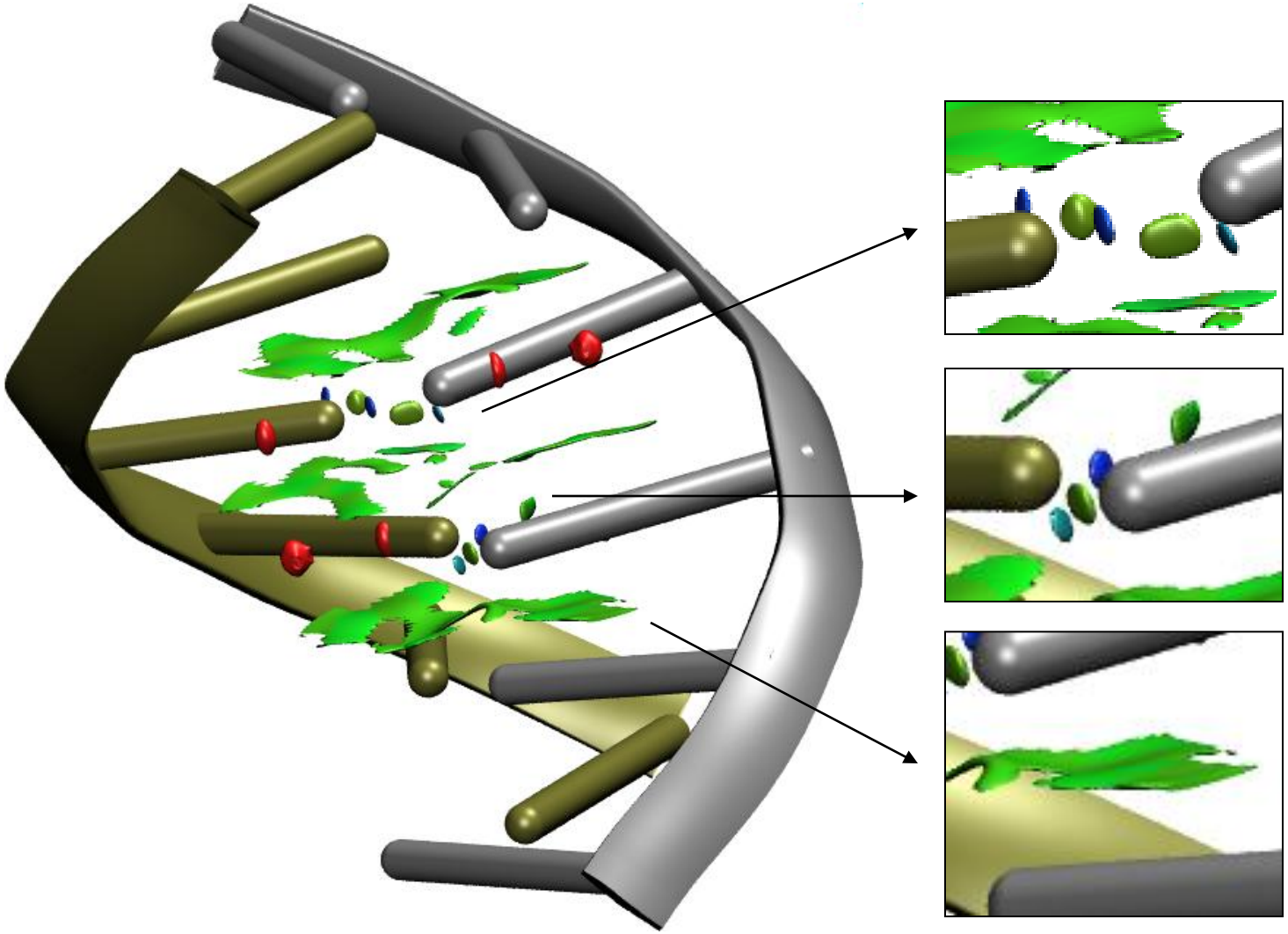
BIOMOLECULES

polypeptide: anti-parallel β-sheet consisting of 17 glycine residues



- HB between C=O and N-H groups in parallel chains
- Van der Waals interactions between CH_2 groups

BIOMOLECULES



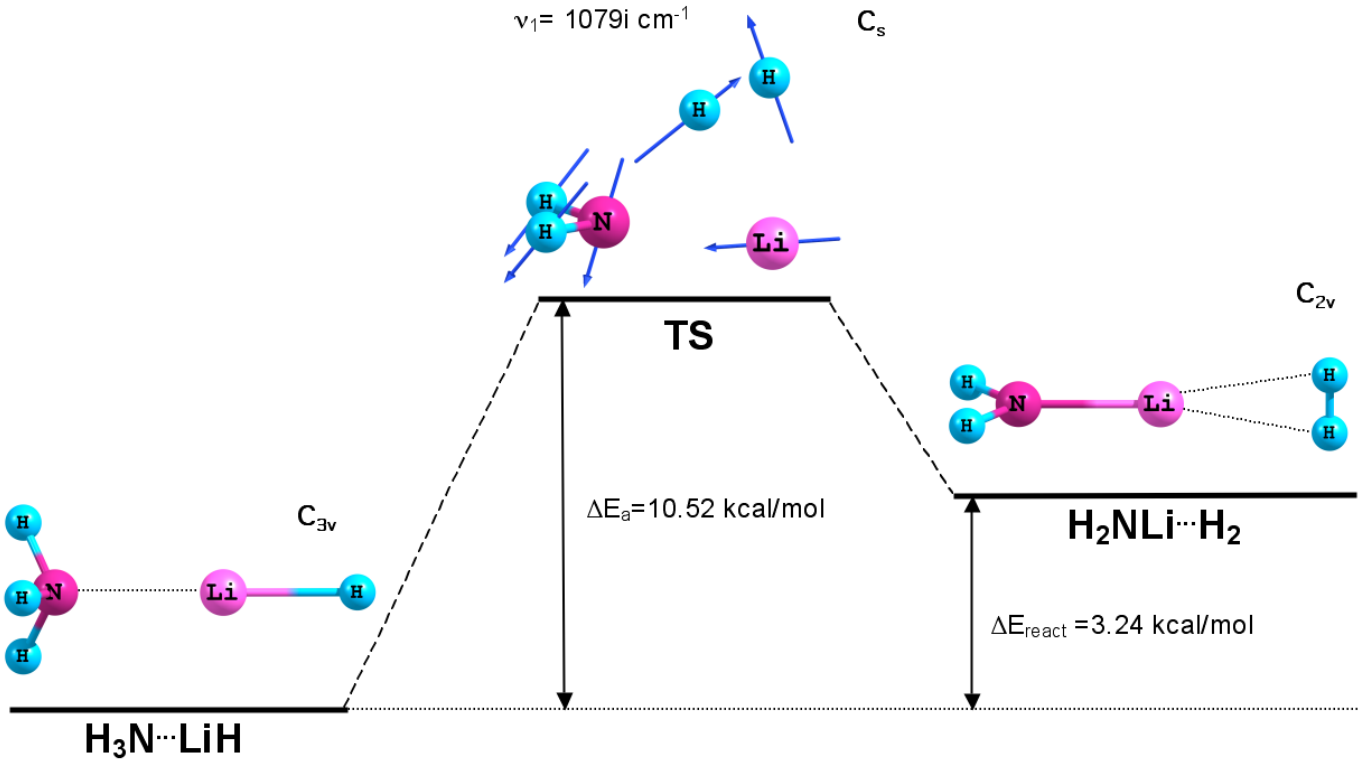
H-bonds between bases

π-stacking

REACTIVITY

Non covalent interactions are also crucial for reactivity

REACTIVITY

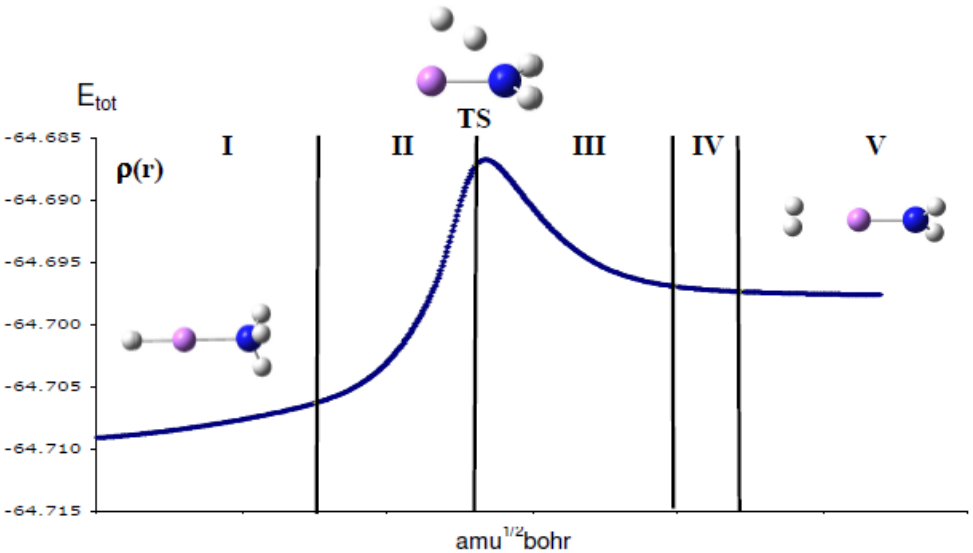


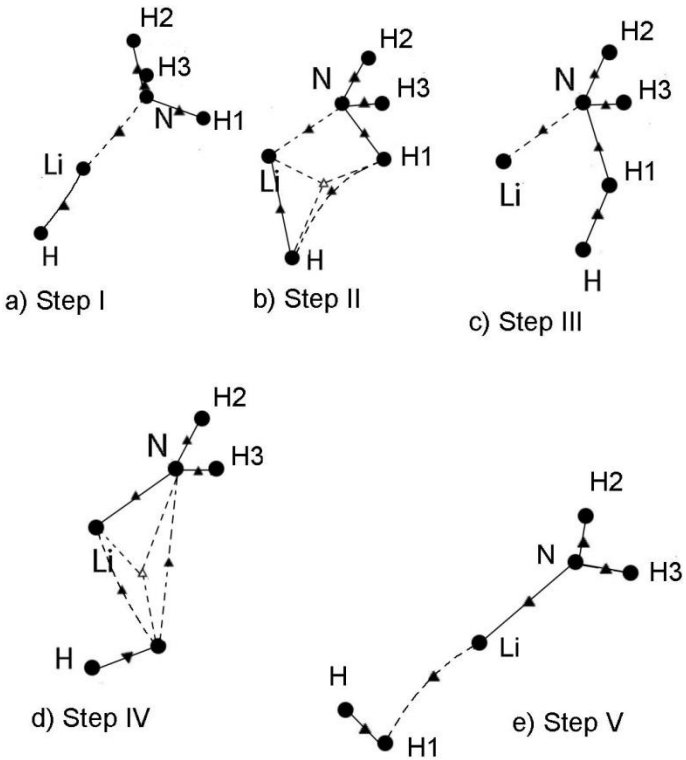
•This reaction is a well known method for the utilization of hydrogen-based energy. This is a first step in a simple
way for fast ammonia utilization or production of hydrogen storage materials.
•The pathway associated with the intrinsic reaction coordinate has been calculated at the B3LYP/aug-cc-pVTZ level.

REACTIVITY

The mechanism has been thoroughly analyzed using topological analysis of:

•The electron density (Five steps)

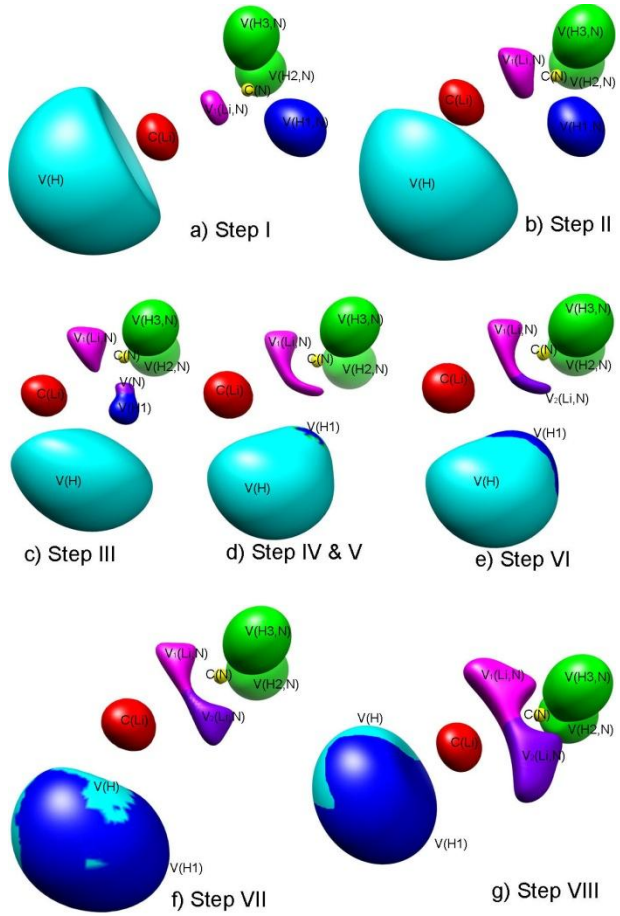


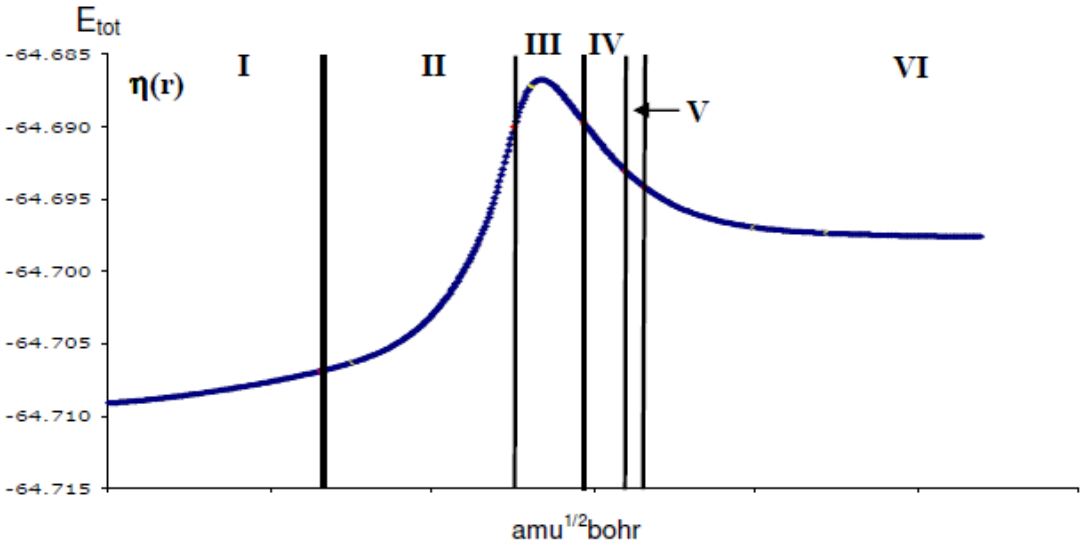


REACTIVITY

The mechanism has been thoroughly analyzed using topological analysis of:

•Electron Localization Function (Eight steps)

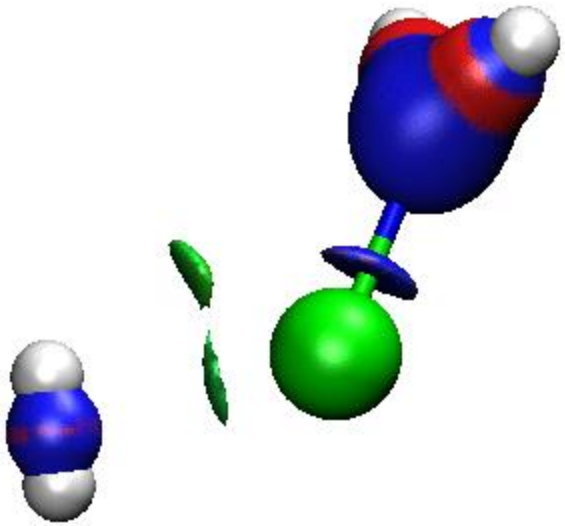




REACTIVITY

What about non covalent interactions?

AÑADIR AQUÍ LA PELI

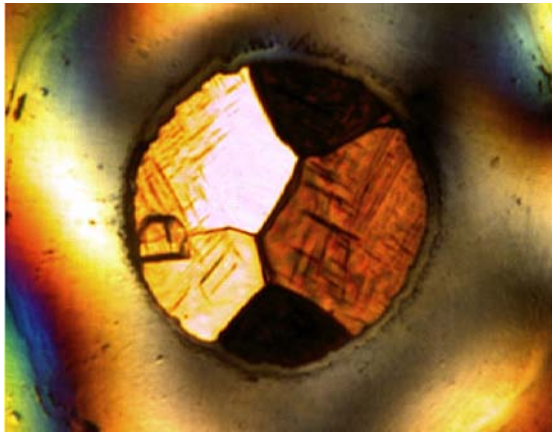


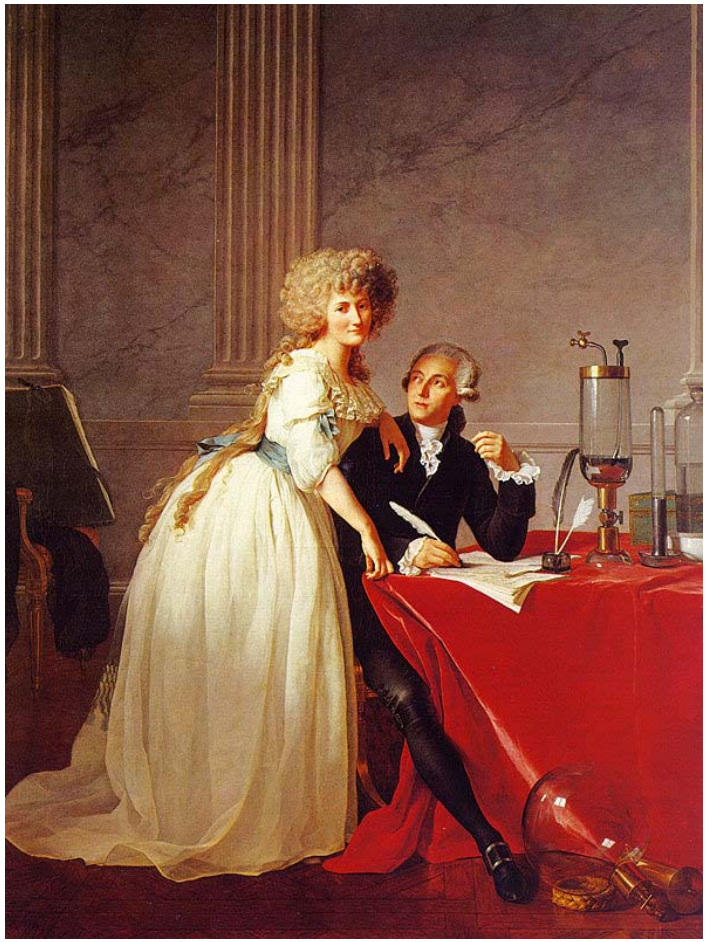
Magnetism in solid oxygen under pressure

Stefan Klotz

IMPMC

Université P&M Curie, Paris



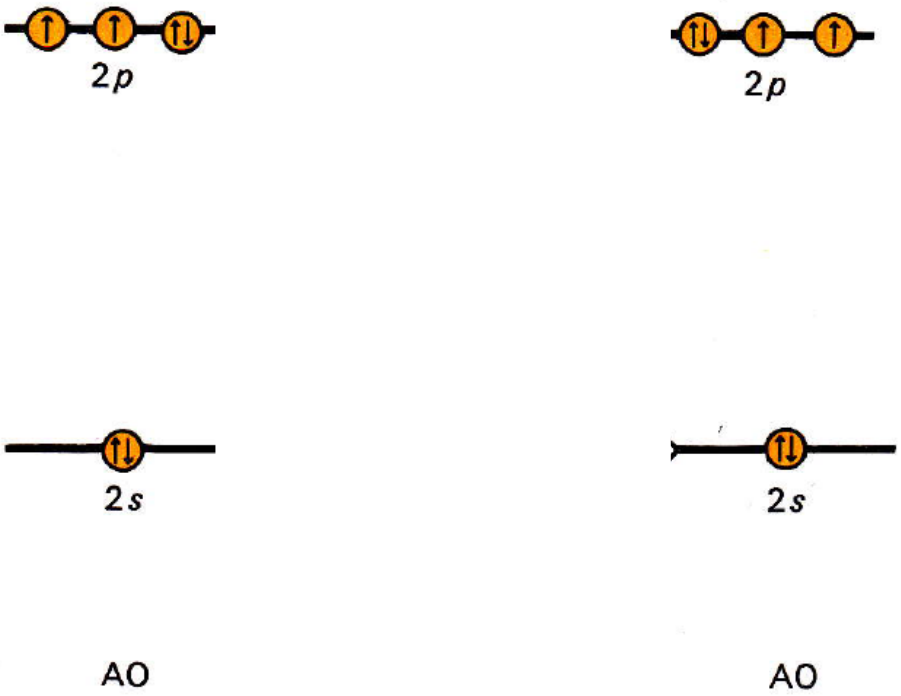


A.L. Lavoisier
(1743-1794)

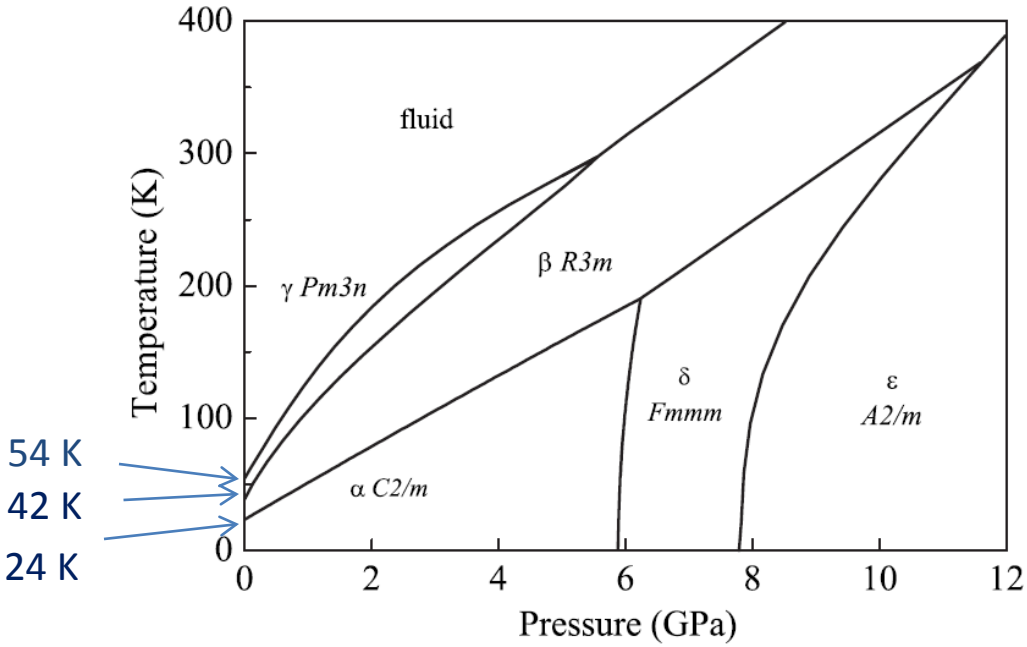
ὀξύς (oxys) -γενής (-genēs)

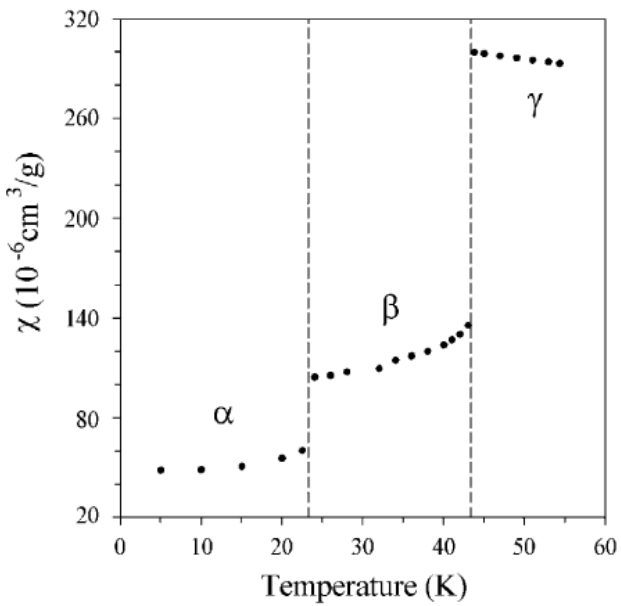
« acid former »

Oxygen

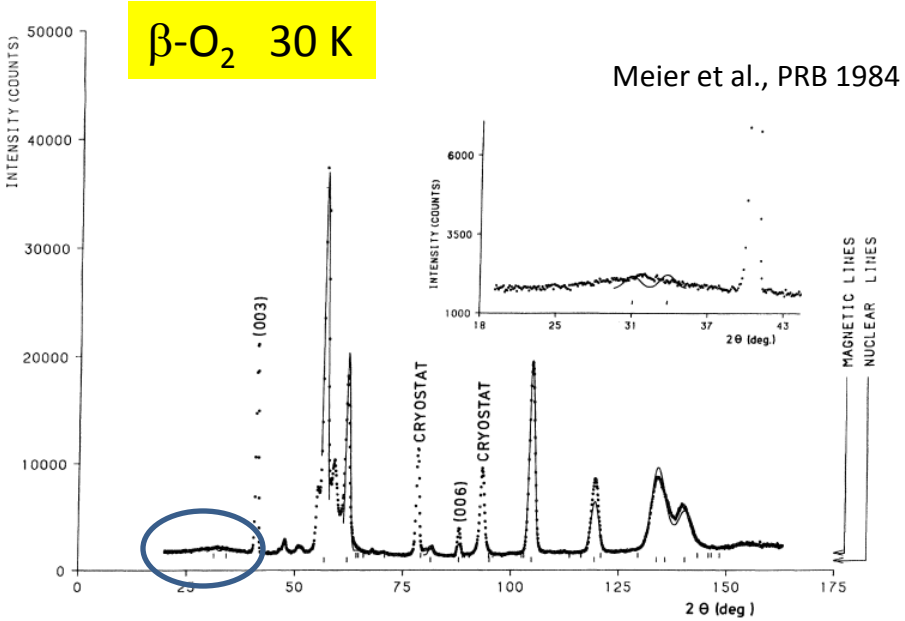


1848:	Faraday:	Paramagnetic nature of O_2
1910:	Kamerlingh Onnes:	Magn. suscept. of liquid and solid O_2
1963:	Alikhanov:	Magn. structure of solid O_2 (neutrons, 1 bar)
2004:	Goncharenko:	Mag. struct. of δ-O_2 under pressure (neutrons, 6 GPa)

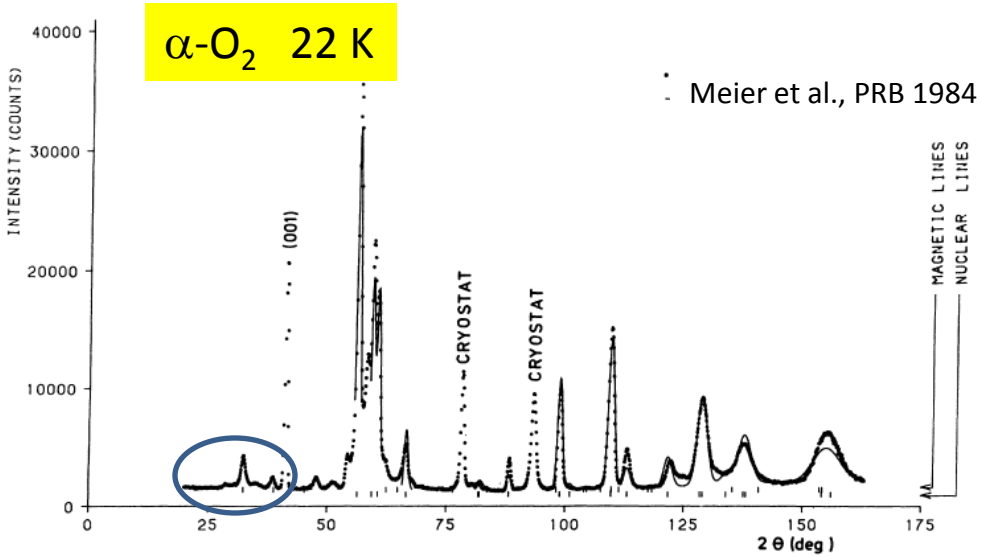

400
300
200
100
0
Temperature (K)
fluid
γ Pm3n
β R3m
δ
Fmmm
ε
A2/m
α C2/m
54 K
42 K
24 K
0
2
4
6
8
10
12
Pressure (GPa)


320
260
200
140
80
20
χ (10 -6cm 3/g)
α
β
γ
0
10
20
30
40
50
60
Temperature (K)

O_2 at 1 bar

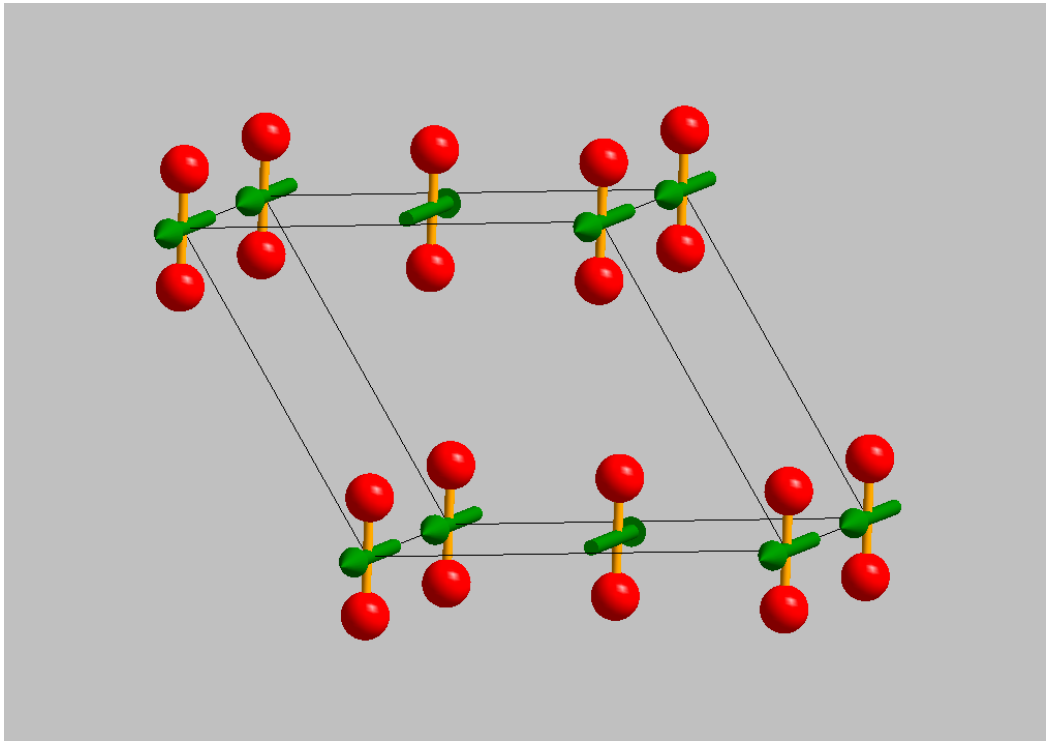


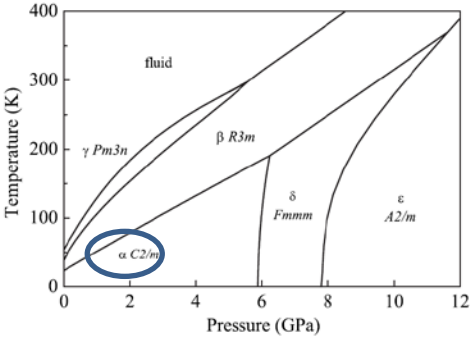
β: short-range ordered



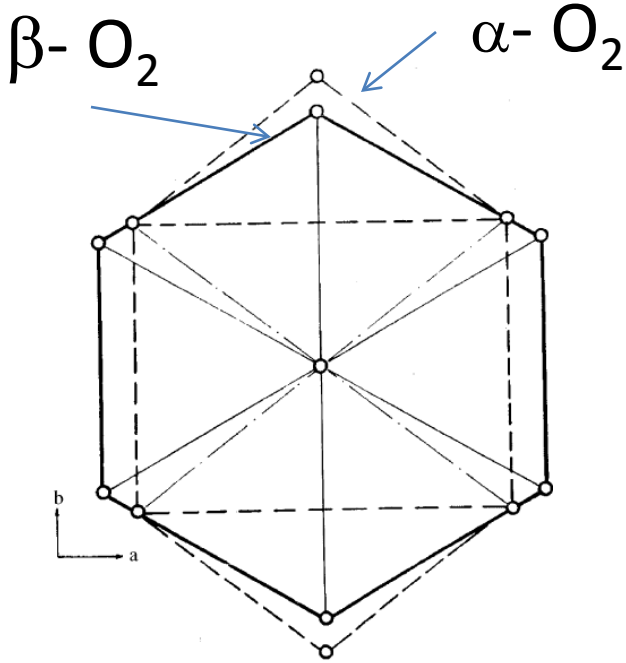
α: antiferromagnetic

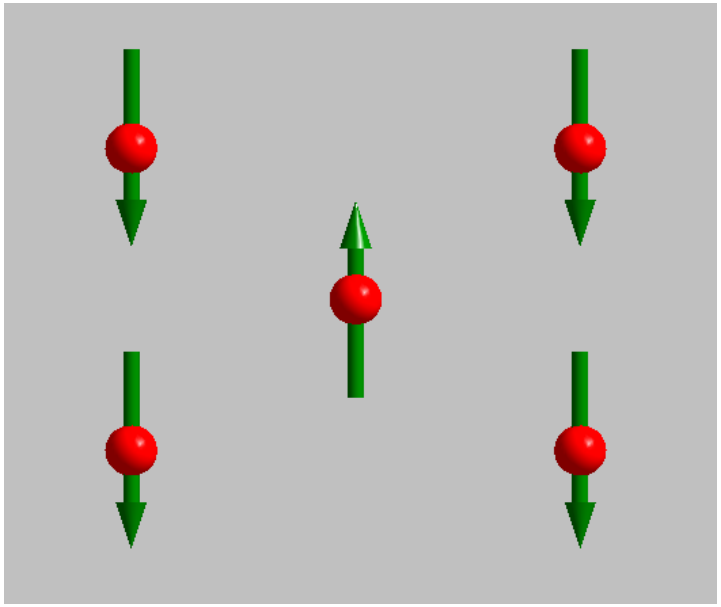
α- oxygen



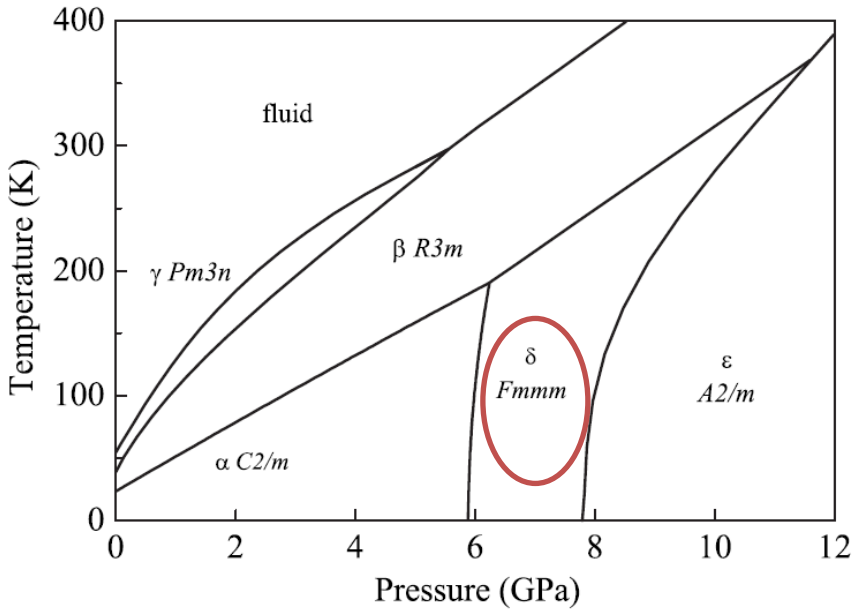


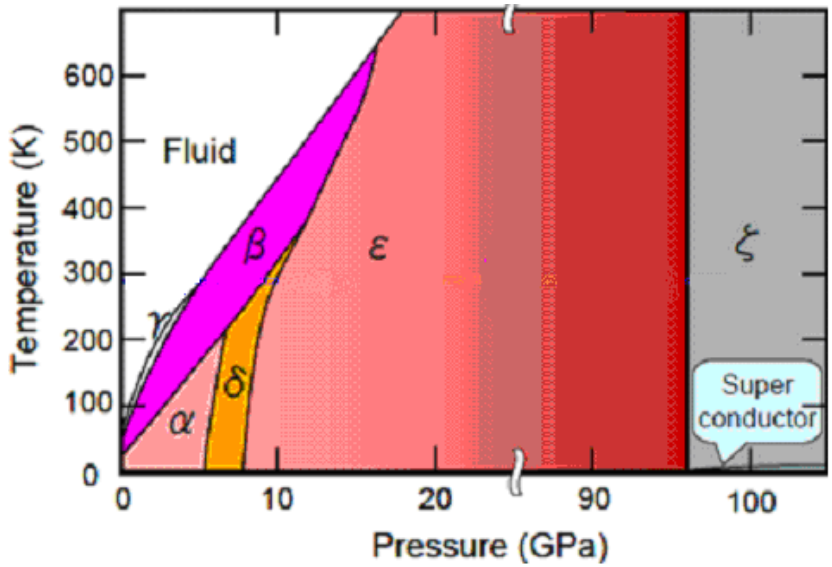
$b/a = 0.79 \neq 3^{1/2}/2$


β- O_2
α- O_2
b
a

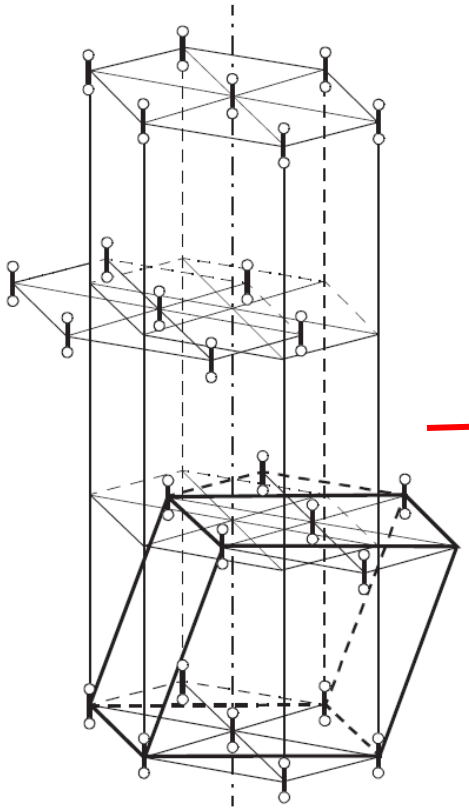


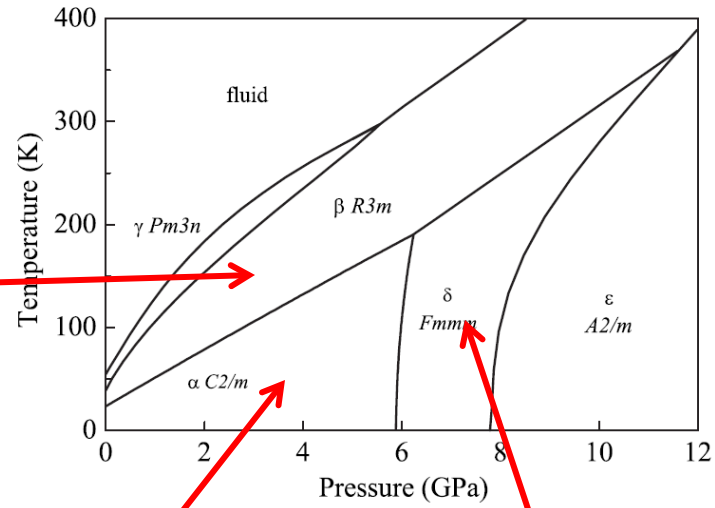
δ- oxygen

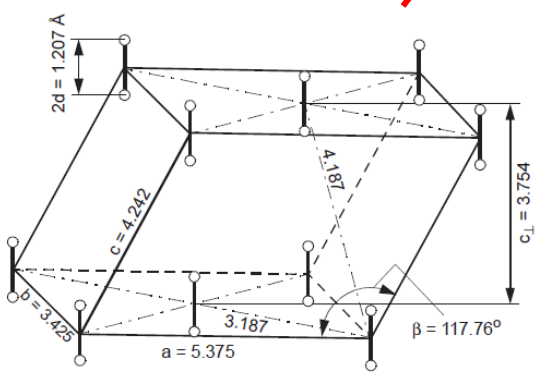

400
300
200
100
0
Temperature (K)
fluid
γ Pm3n
β R3m
α C2/m
δ
Fmmm
ε
A2/m
0
2
4
6
8
10
12
Pressure (GPa)

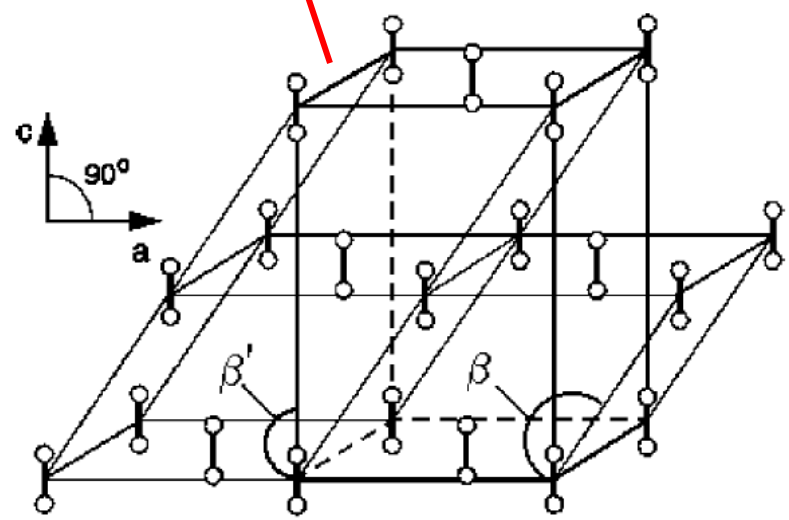

600
500
400
300
200
100
0
Temperature (K)
Fluid
β
ε
ζ
γ
δ
α
Super conductor
0
10
20
90
100
Pressure (GPa)

Nuclear Structures

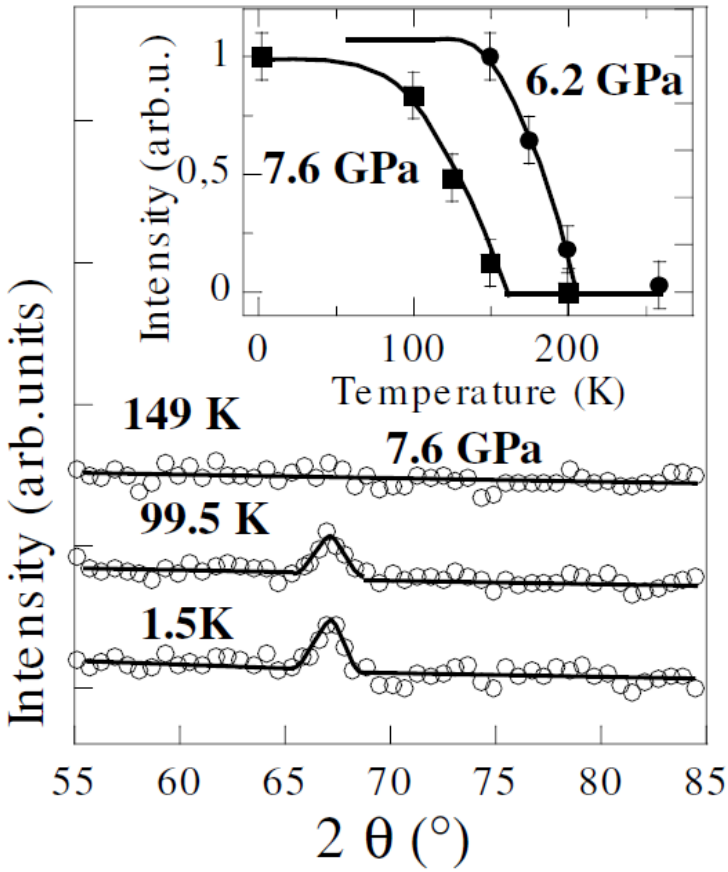






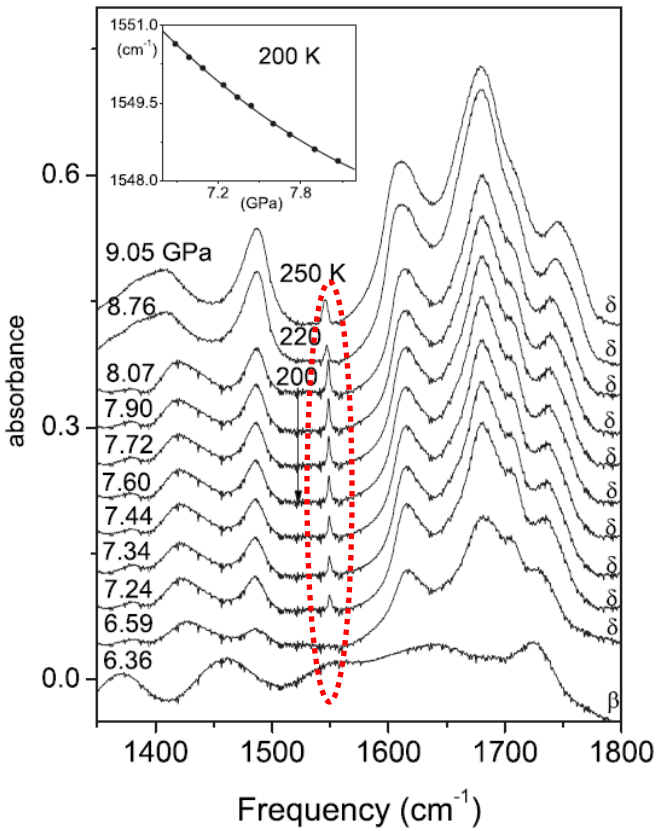


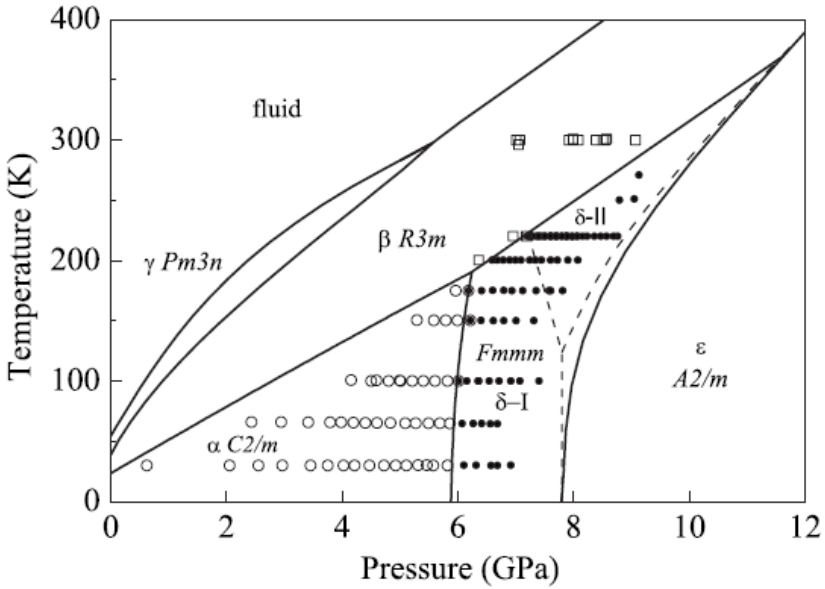
Previous high P neutron experiments



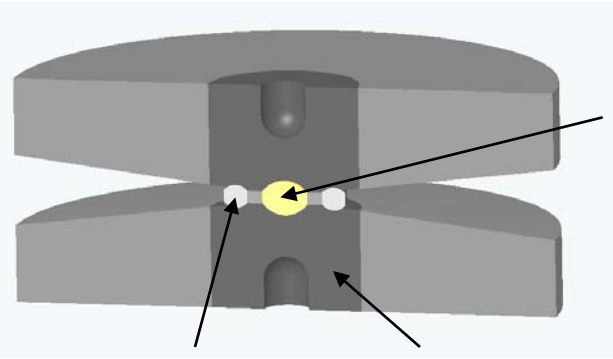
Goncharenko, PRL 2004

Infrared absorption
(diamond anvil cell)





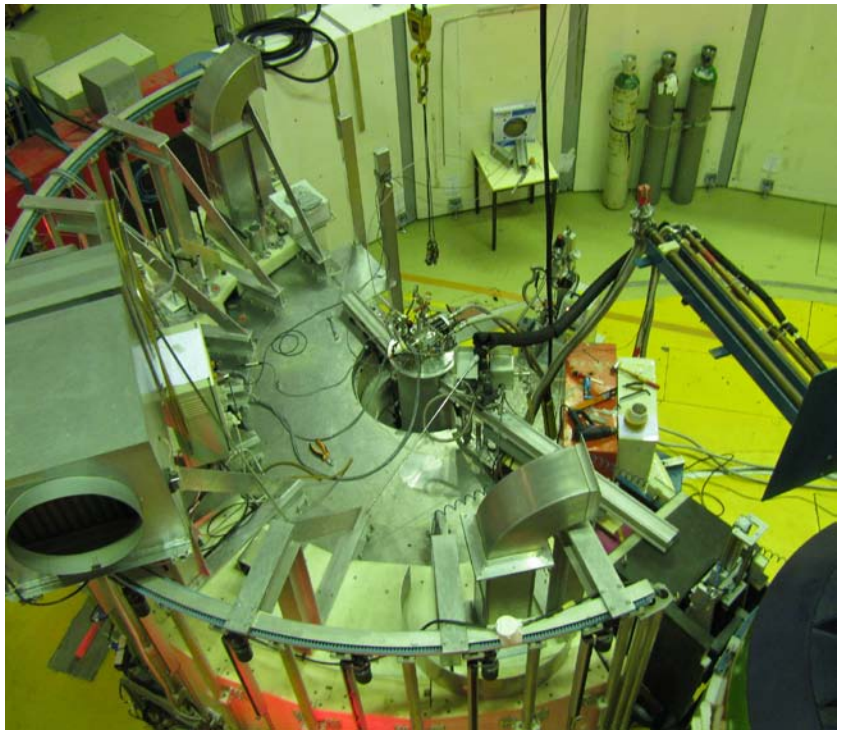
Gorelli et al., PRB 2008



~ 10 GPa for V =100 mm^3
~ 30 GPa for V = 10 mm^3

3.5-320 K

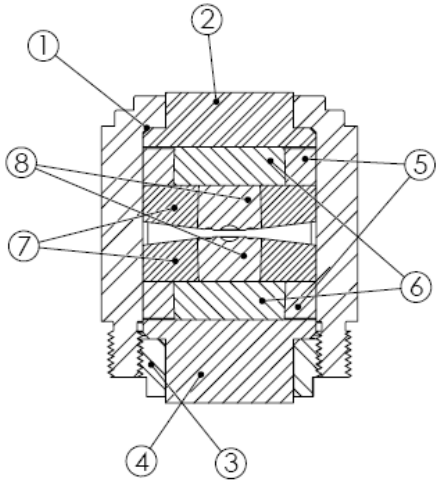
see also talk Domingo Martinez
martes 17:40

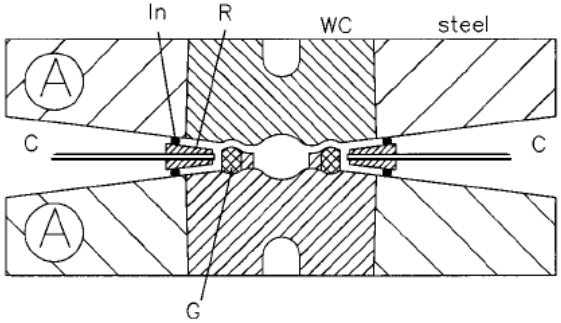


D20 high intensity diffractometer
ILL, Grenoble, France

Future:
XTREMED: dedicated high P diffractometer at ILL
(Javier Campo Ruiz miércoles 10:45)

Sample loading





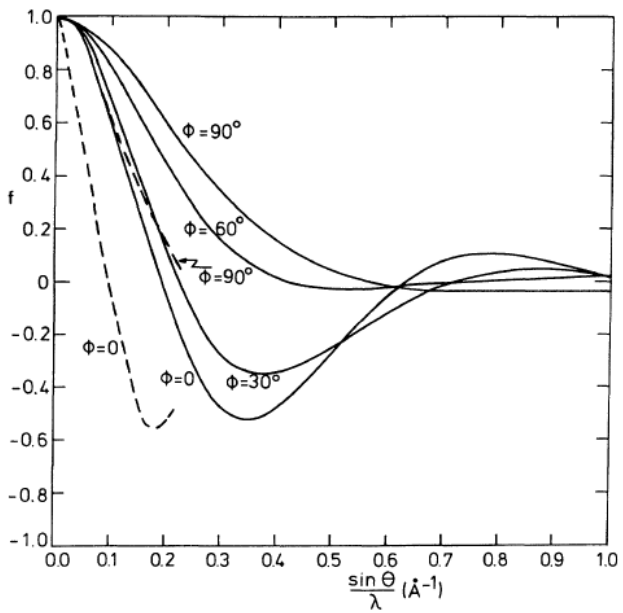
Condensation at 77 K

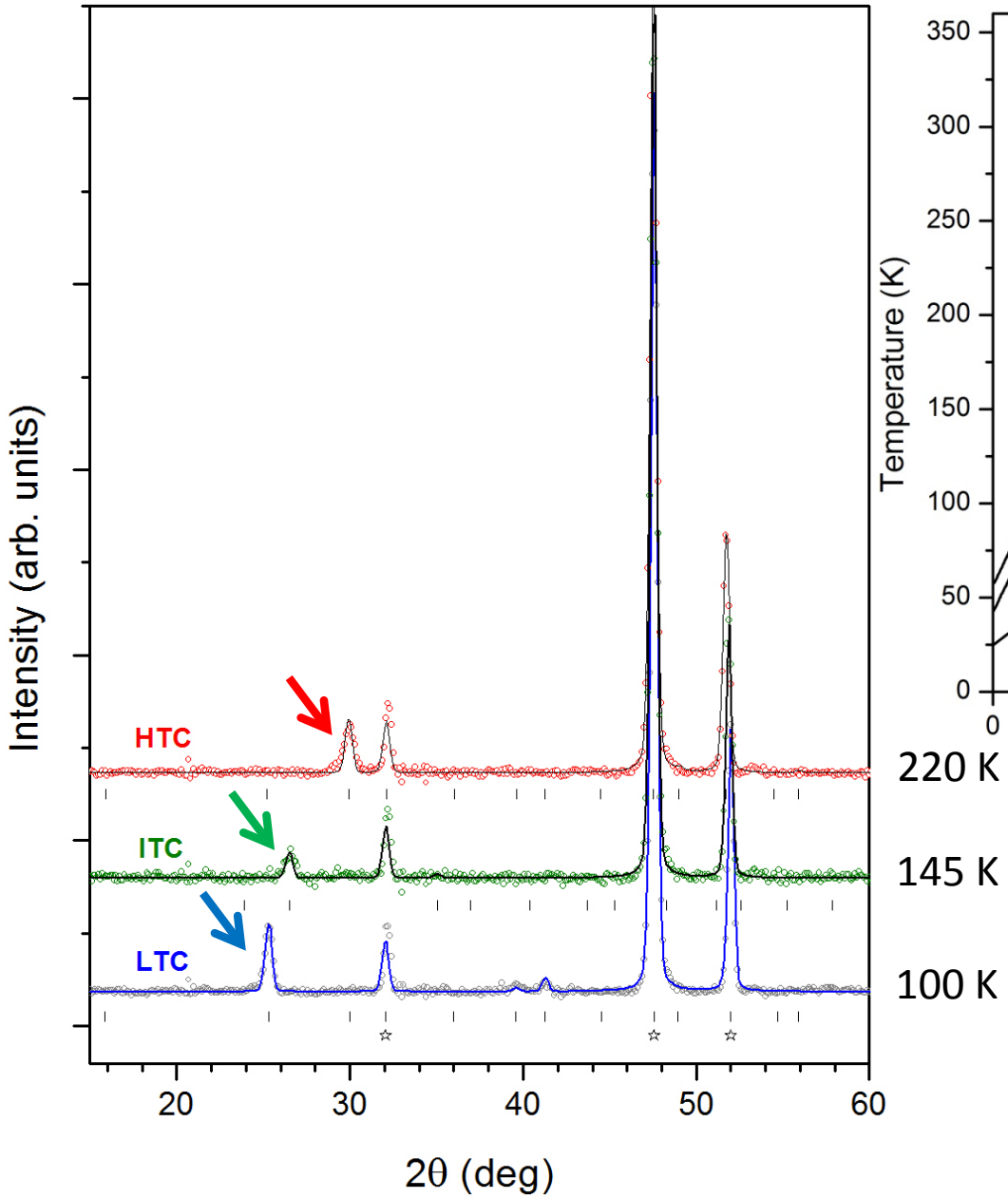
Gas loader

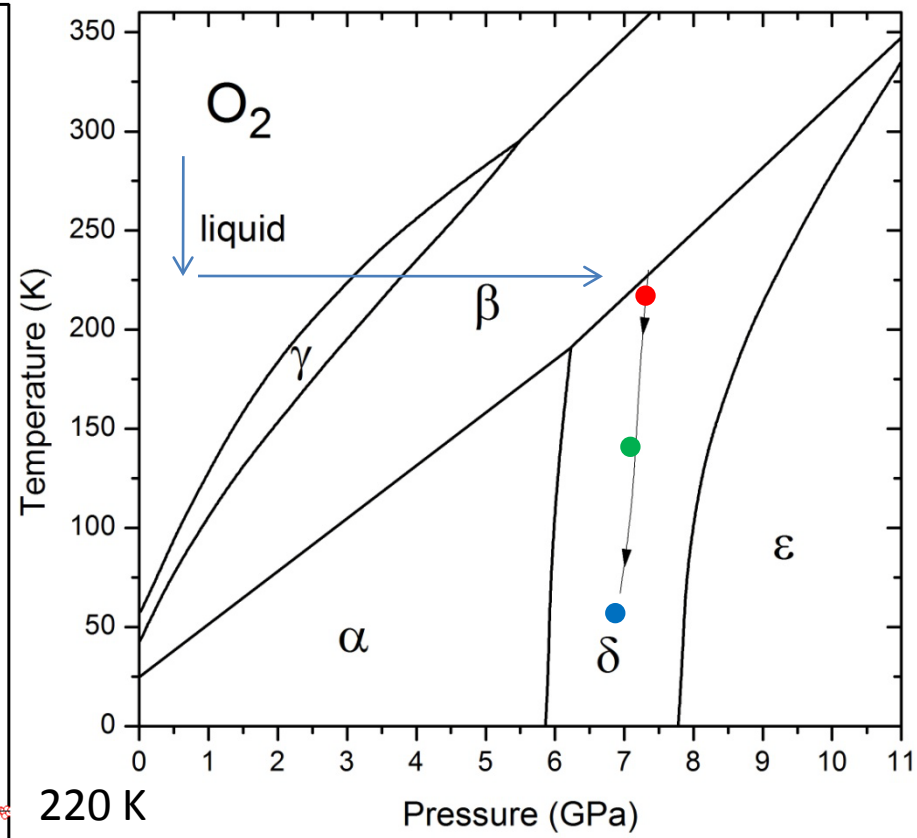
P_{max}=2000 bar
Compatible with hydrogen

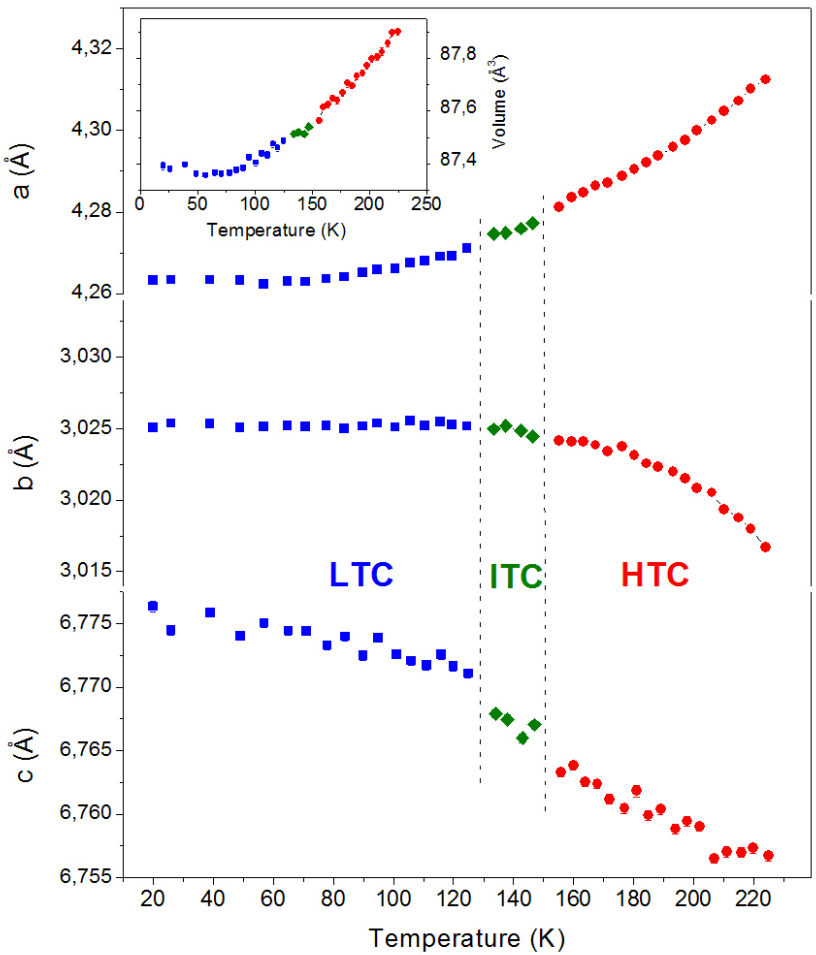
Difficulties

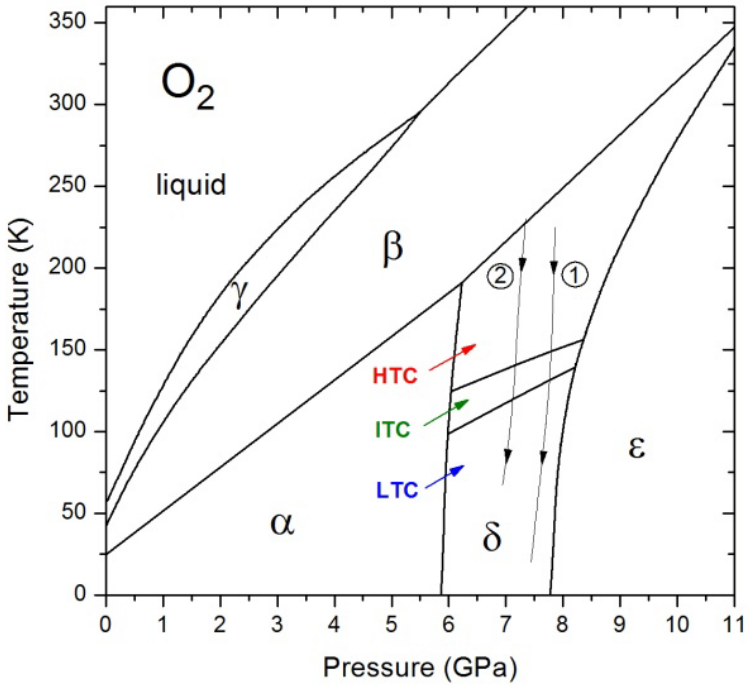
- Texture (imperfect powder) due to the formation of single crystals
- Strong compressibility: ~ 50% from 1-8 GPa
- Uncontrollable download
- Analysis: anisotropic magnetic form factor




Intensity (arb. units)
HTC
ITC
LTC
220 K
145 K
100 K
20
30
40
50
60
2θ (deg)

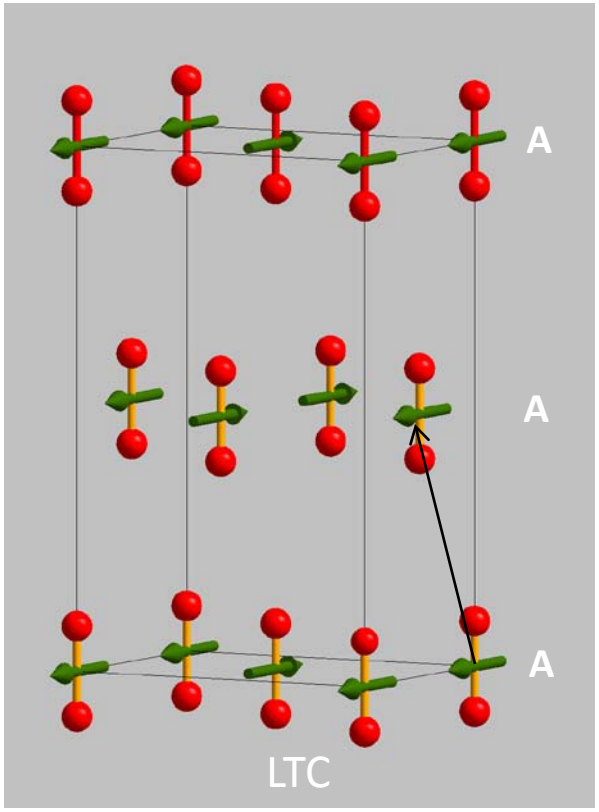

O2
liquid
β
γ
α
δ
ε
Temperature (K)
Pressure (GPa)
0
50
100
150
200
250
300
350
0
1
2
3
4
5
6
7
8
9
10
11

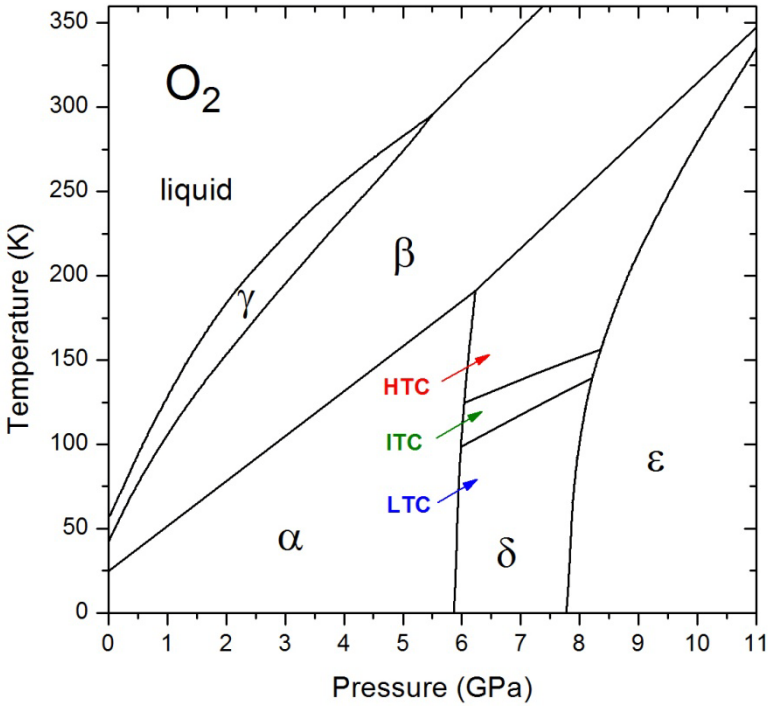

a (Å)
b (Å)
c (Å)
Temperature (K)
Volume (Å³)
LTC
ITC
HTC


O2
liquid
β
γ
α
δ
ε
HTC
ITC
LTC
Temperature (K)
Pressure (GPa)

LTC Structure

(Low Temperature Commensurate)

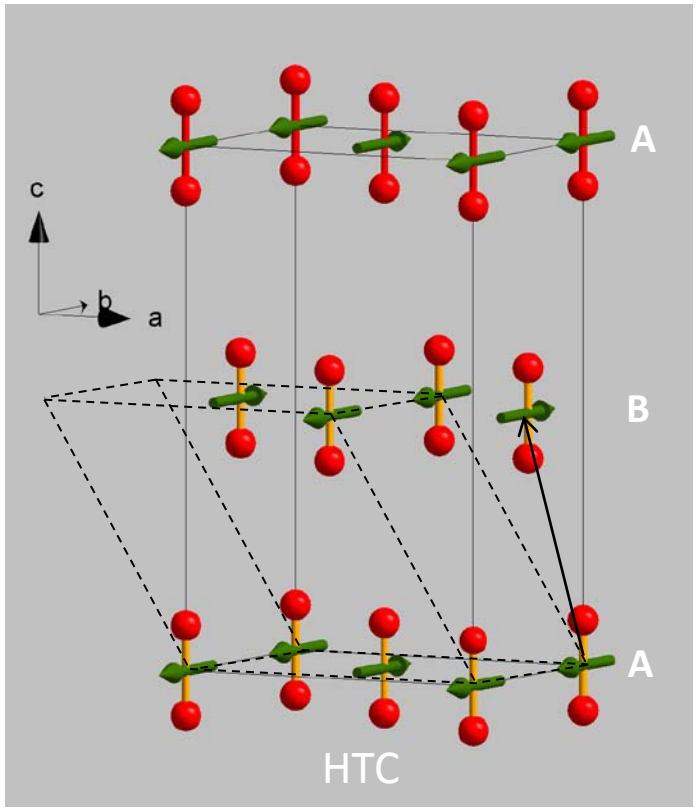


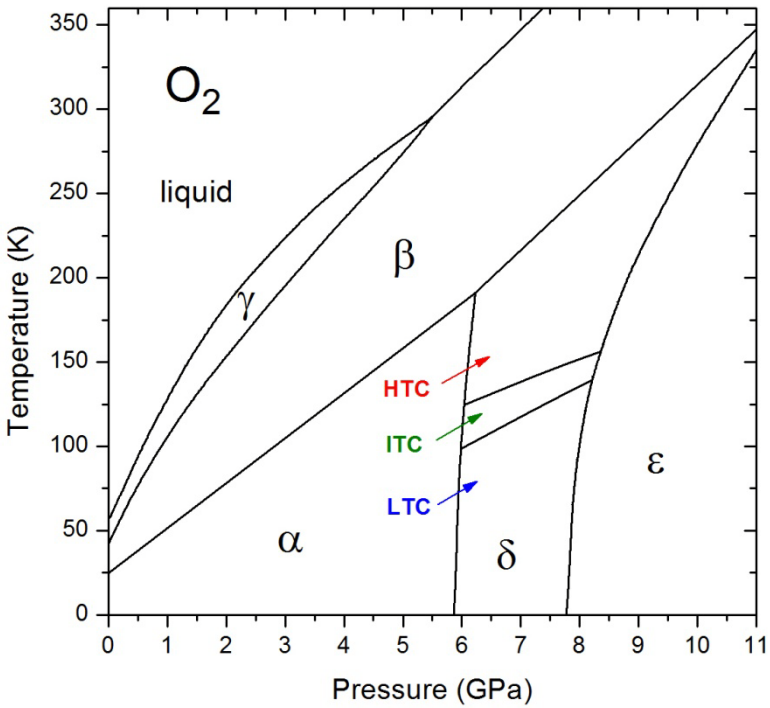


Ferromagnetic coupling between layers

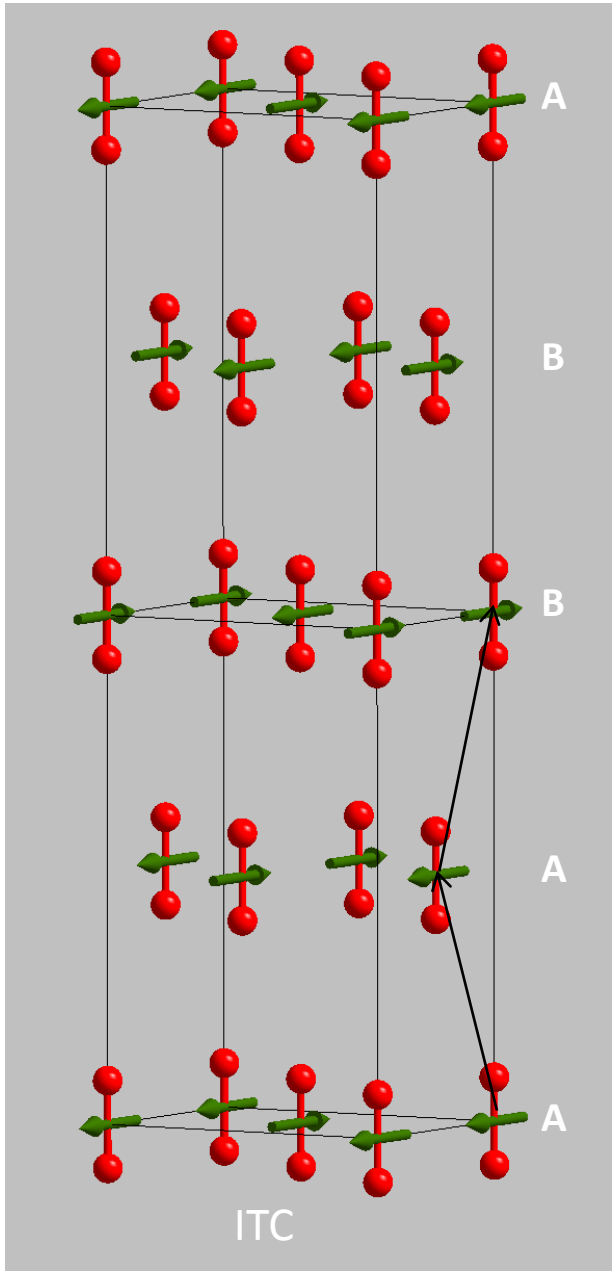
HTC Structure

(High Temperature Commensurate)



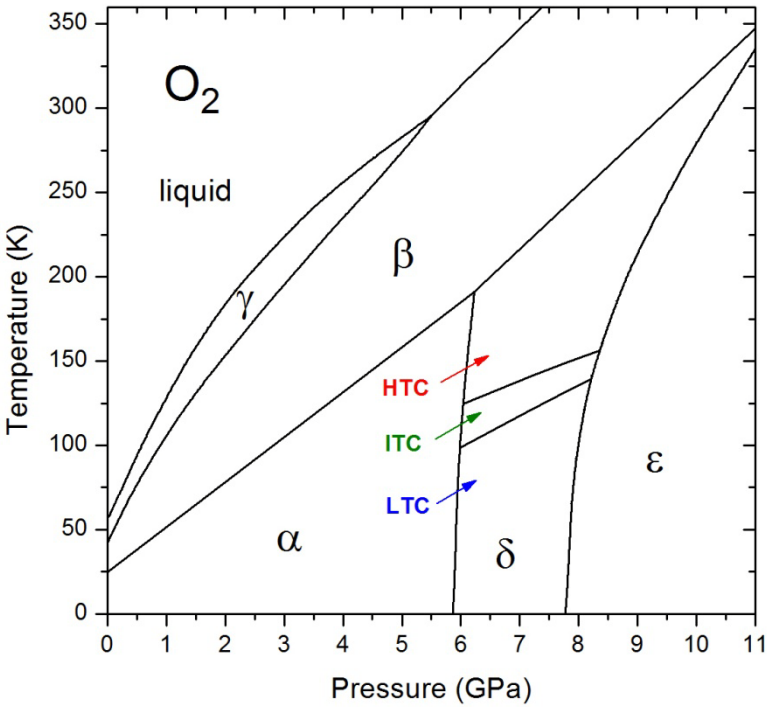


Anti-ferromagnetic coupling between layers



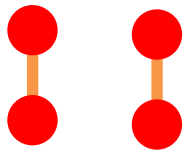
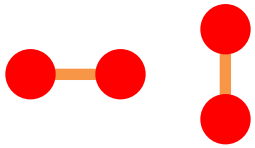
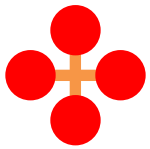
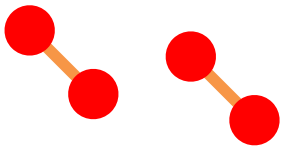
ITC Phase

(Intermediate Temperature Commensurate)



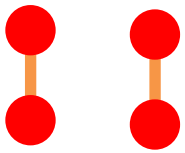
$$H = -J\, S_1 \cdot S_2$$

Hemert et al., PRL 51 (1983)

		J	alignment	
parallel		-	↓↑	AF
linear		-	↓↑	AF
T		-	↓↑	AF
X		+	↑↑	F
S		+	↑↑	F

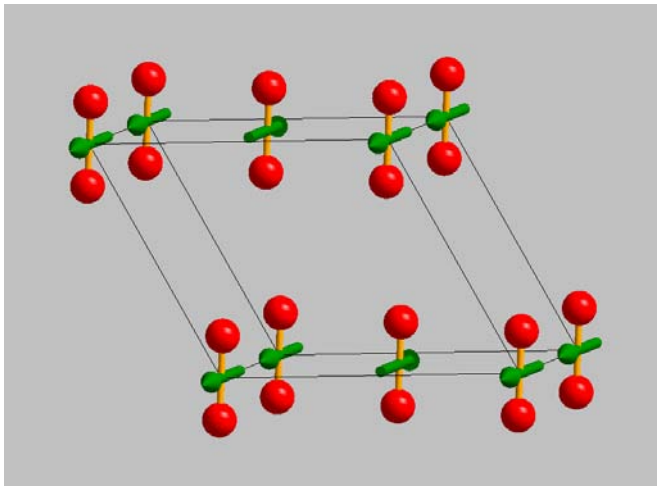
spin alignment: in-plane

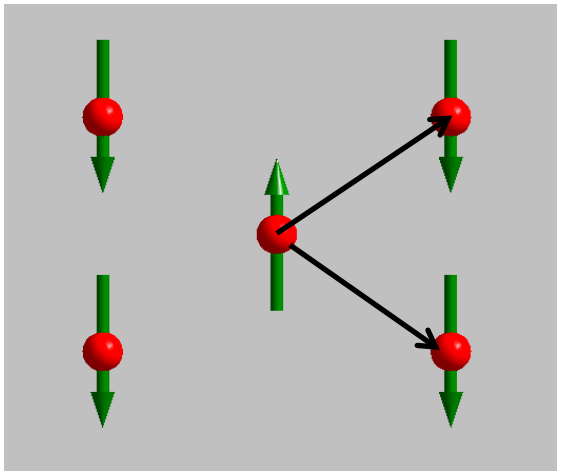
« parallel »



J<0

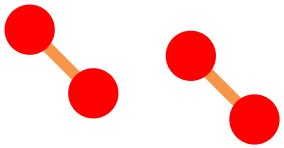
(Hemert et al., PRL 51 (1983) and others)





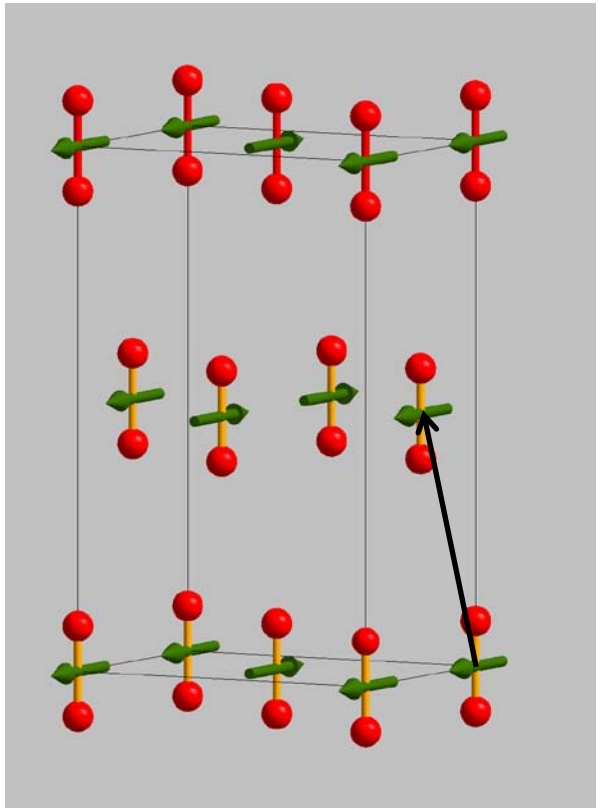
spin alignment: inter-plane

« shifted parallel »

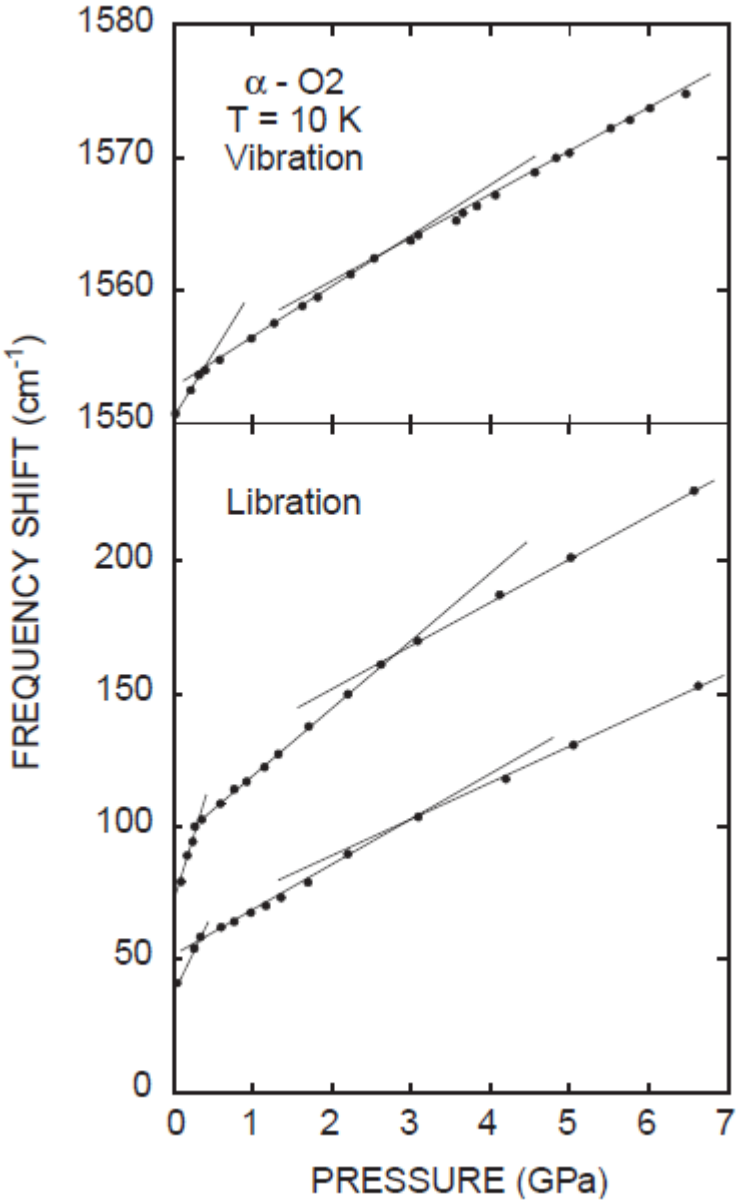


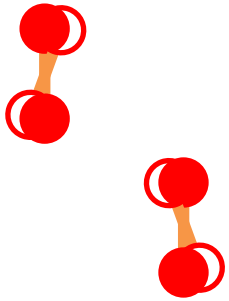
J ≥0

(Hemert et al., PRL 51 (1983) and others)



LTC phase

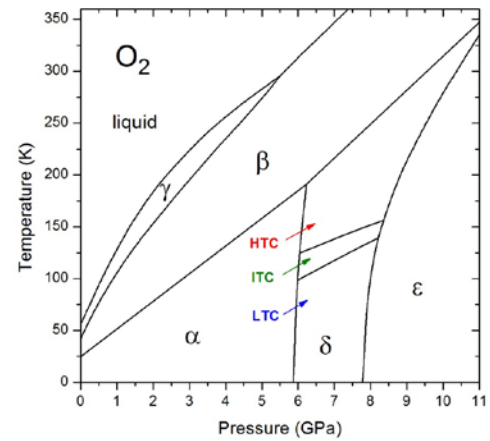




140 K

Jodl et al., PRB 1985

$$(\partial T/\partial P)_{\langle u^2\rangle} = -\frac{(\partial \ln\langle u^2\rangle/\partial P)_T}{(\partial \ln\langle u^2\rangle/\partial T)_P}$$



$$\left.\begin{aligned}(\partial \ln\langle u^2\rangle/\partial T)_P &= 5\times 10^{-3}\ \mathrm{K}^{-1}\\ (\partial \ln\langle u^2\rangle/\partial P)_T &= -8\times 10^{-2}\ \mathrm{GPa}^{-1}\end{aligned}\right\}\quad (\partial T/\partial P)_{\langle u^2\rangle} = 16\ \mathrm{K/GPa}$$

measured: $\approx 15\ \mathrm{K/GPa}$

Conclusions

Solid O_2 at 8 GPa is antiferrimagnetically ordered at room temperature

There are three different AF structures in the δ-phase

Transitions seem to be governed by the librational motion of the O_2 molecules

Is an effect of the strong dependence of exchange interaction on the mutual orientation of neighboring molecules.

Muchas gracias por la atención!

Simposio

MALTA-Consolider

23-27 Enero 2011, Miraflores de la Sierra

www.malta-consolider.com

Moderador Mercedes Taravillo Corralo UCM

Ponencias Sistemas Moleculares I	*Caracterización de yunques de zafiro y moissanita a alta presión*	Elena del Corro García UCM
	Presión interna de disoluciones acuosas	Nubia Judith Mendoza Lugo UCM
	Síntesis de Resinas Fósiles a alta presión. Resina, copal y ámbar	Óscar Rodríguez Montoro UCM

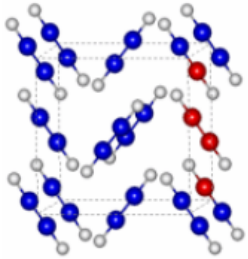
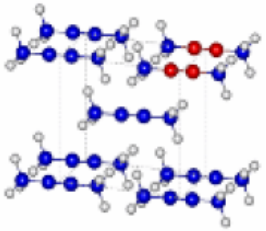
Sistemas Moleculares I – Materiales NOCH

- Los sistemas materiales objeto de estudio específico en el desarrollo de la actividad investigadora que se propone contienen nitrógeno, oxígeno, carbono o hidrógeno (materiales **NOCH**).

- Esta familia de materiales es extremadamente importante para nuestros propósitos por dos razones: 1) están relacionados con nuestros proyectos actuales de investigación individuales, y 2) intervienen en problemas de interés general en ciencias de la vida, de la Tierra y de los materiales.

Pressure as a probe on unsaturated NOCH systems

Sistemas Moleculares I – Materiales NOCH

Work Plan II. a.	SCIENTIFIC SCOPE	
Field Coordinator M. Taravillo	**Scientific Questions** - Pressure-induced polymorphism in **NOCH** systems - Pressure induced conformational changes in flexible molecules. Packing effects in the solid state - Non-covalent interactions and its response to pressure in the solid state - Effect of pressure on hydrogen-bonded **NOCH** solids. Glassy phases	
Leading Groups UCM - UJI		
Supporting Groups All	**Specific Goals** - Polymorphism in sort *n*-alkanes, *n*-alkohols and benzene derivatives - Polymorphism in rigid molecules R – C≡C – R' and R – C≡N derivatives - Amorphous phases in alcohols and amines	
Related Fields Water related Reactivity NOCH and minerals		

physico-chemical phenomena involving NOCH molecular systems

Principales efectos de la presión en cristales moleculares

Cambios en las distancias interatómicas

- intramolecular
- intermolecular

Longitudes de enlace

Ángulos de enlace

Ángulos de torsión

Ángulos dihedros

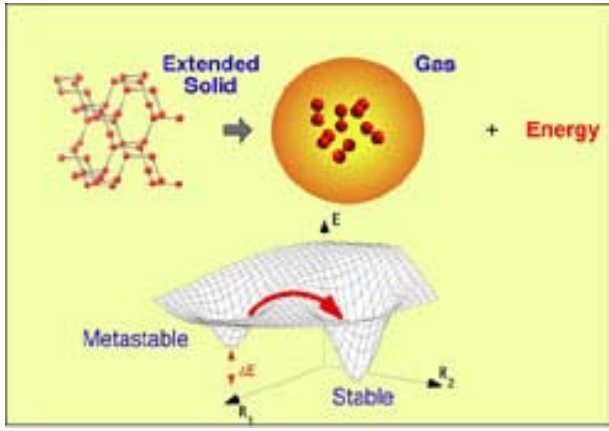
Redistribución de la densidad electrónica

- Transferencia de carga
- tautomerización
- ionización
- disociación → dimerización
- Apertura de ciclos → polimerización

Interés de estos estudios

Materiales sintetizados a altas p y T recuperados con propiedades tecnológicas importantes

- Propiedades ópticas
- Propiedades mecánicas
- Superconductividad a alta temperatura

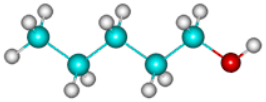


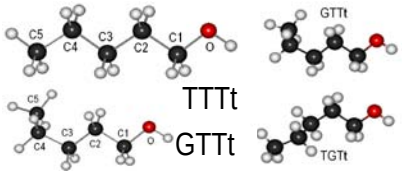
Sistemas Moleculares I – Materiales NOCH

BACKGROUND EN EL GRUPO UCM EN SISTEMAS MOLECULARES

1. Equilibrio conformacional a alta presión

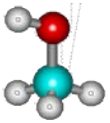
1-Pentanol

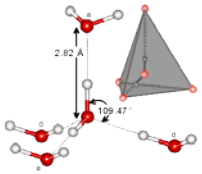


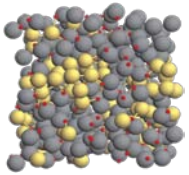


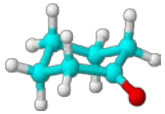
2. Fenómenos de agregación a alta presión

Metanol
Agua
Agua-Metanol
Ciclohexanona



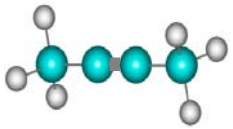


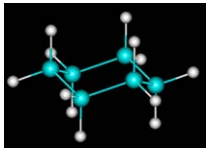


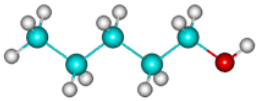


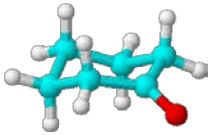
3. Transiciones de fase/polimorfismo a alta presión

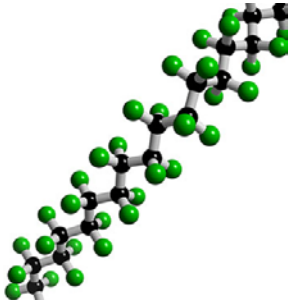
Dimetilacetileno (2-butino)
Pentanol, 2-metil-2-butanol
Ciclohexano, Ciclohexanona
Teflón® (politetrafluoroetileno)





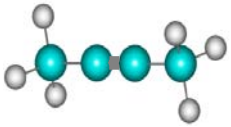


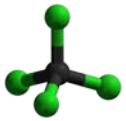




4. Reactividad Química en Fase Condensada

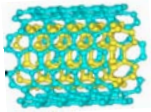
Monóxido de Carbono (CO)
Dimetilacetileno (2-butino)
Tetracloruro de Carbono



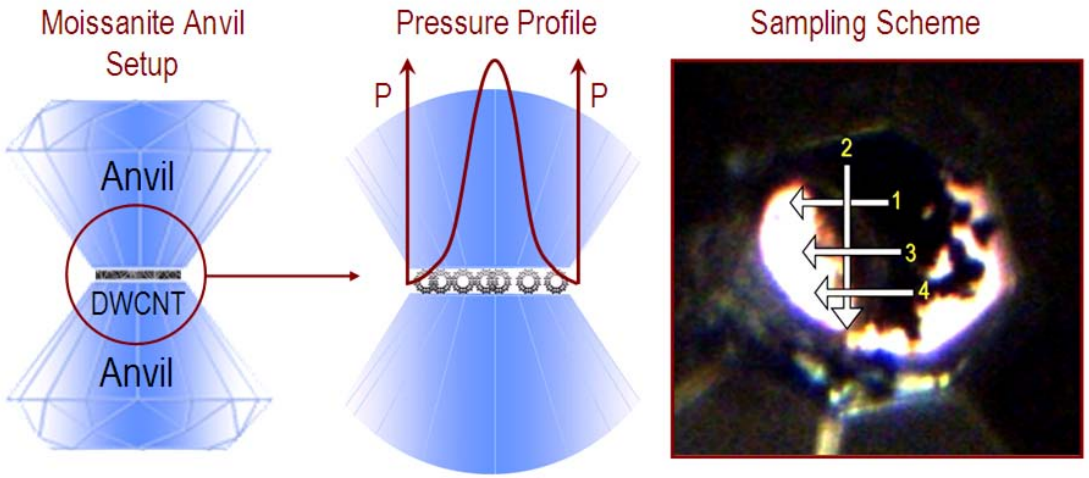


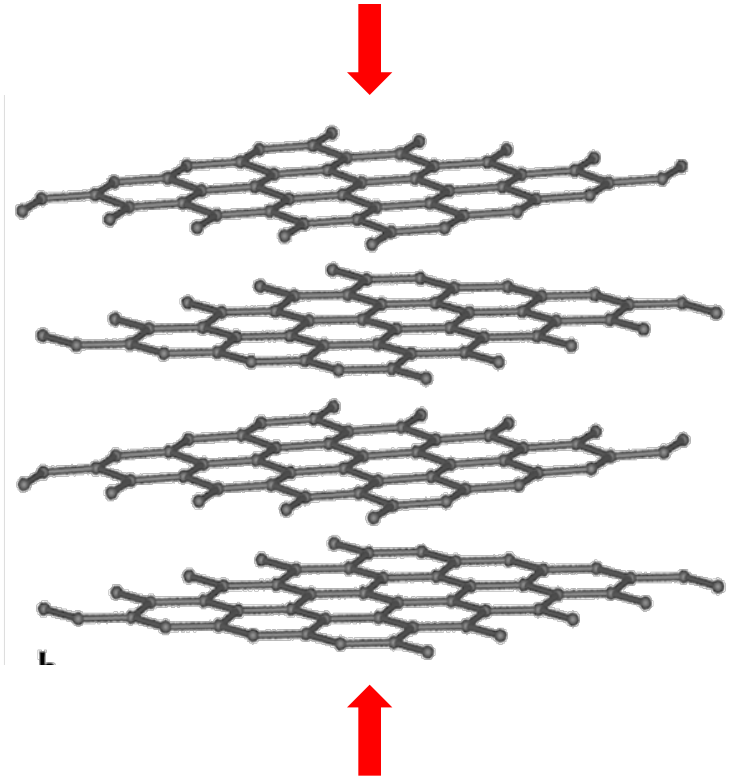
5. Nanomateriales bajo presión

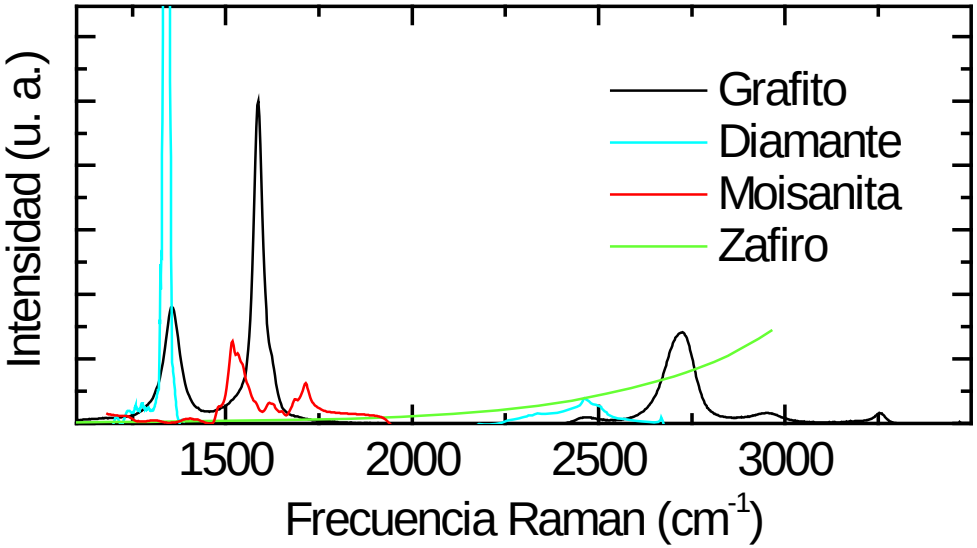
Nanotubos de Carbono de Doble Pared



GENERACIÓN DE CONDICIONES NO-HIDROSTÁTICAS

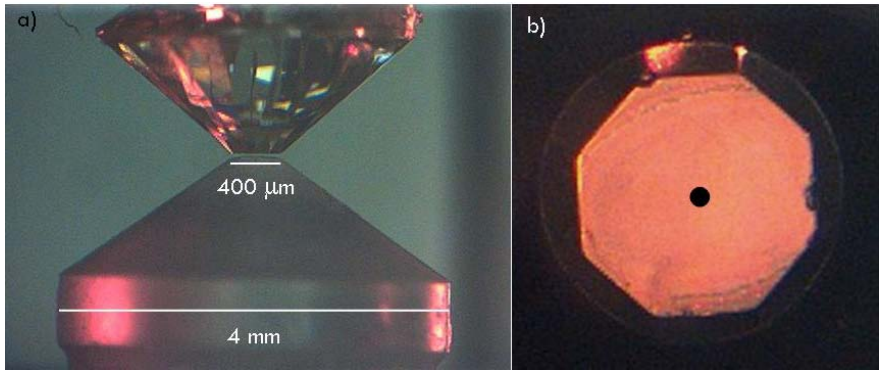


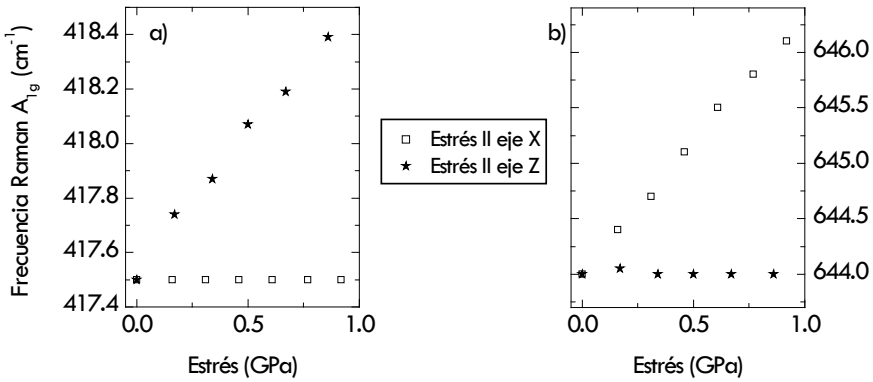


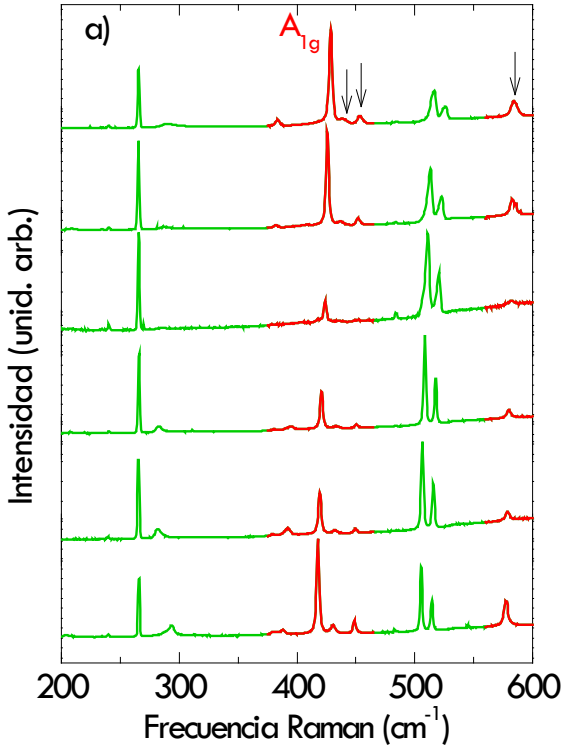


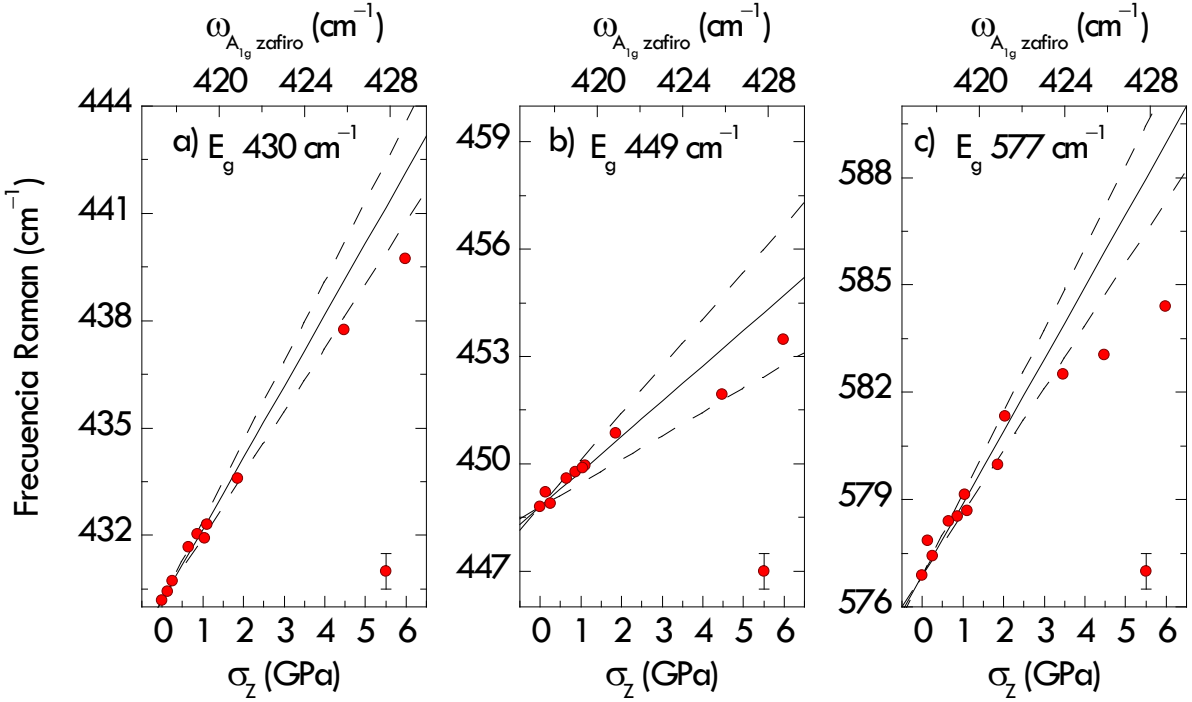
- Uso de yunques de moissanita (CSi) y de zafiro que permiten analizar una parte del espectro Raman de compuestos derivados del carbono que es enmascarada por el diamante.

GENERACIÓN DE CONDICIONES NO-HIDROSTÁTICAS



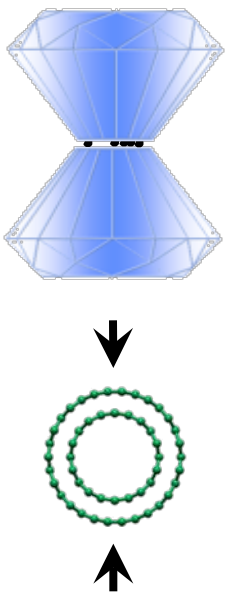


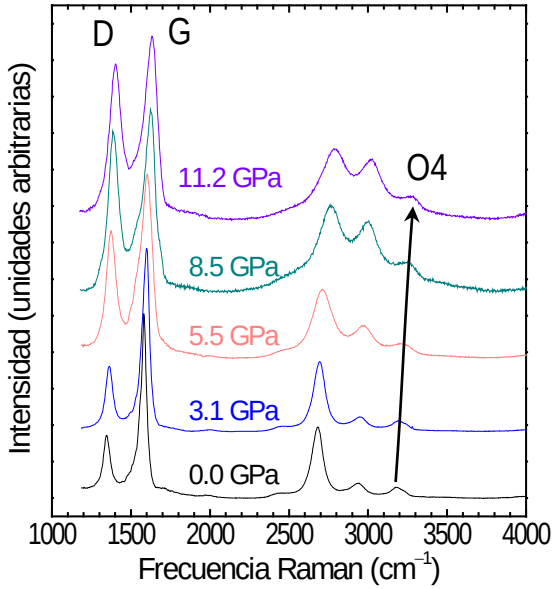


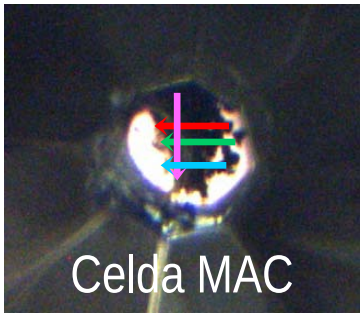


GENERACIÓN DE CONDICIONES NO-HIDROSTÁTICAS

DWCNT



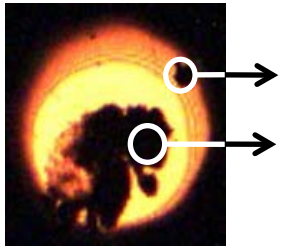


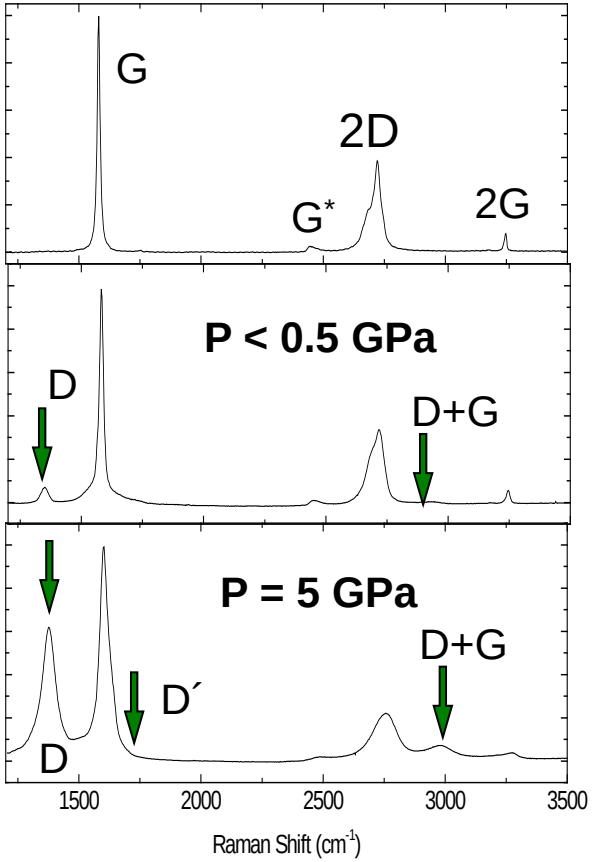


GRAFITO

Desorden incucido por la presión

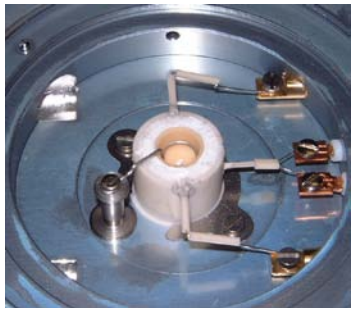
HOPG dentro de la celda

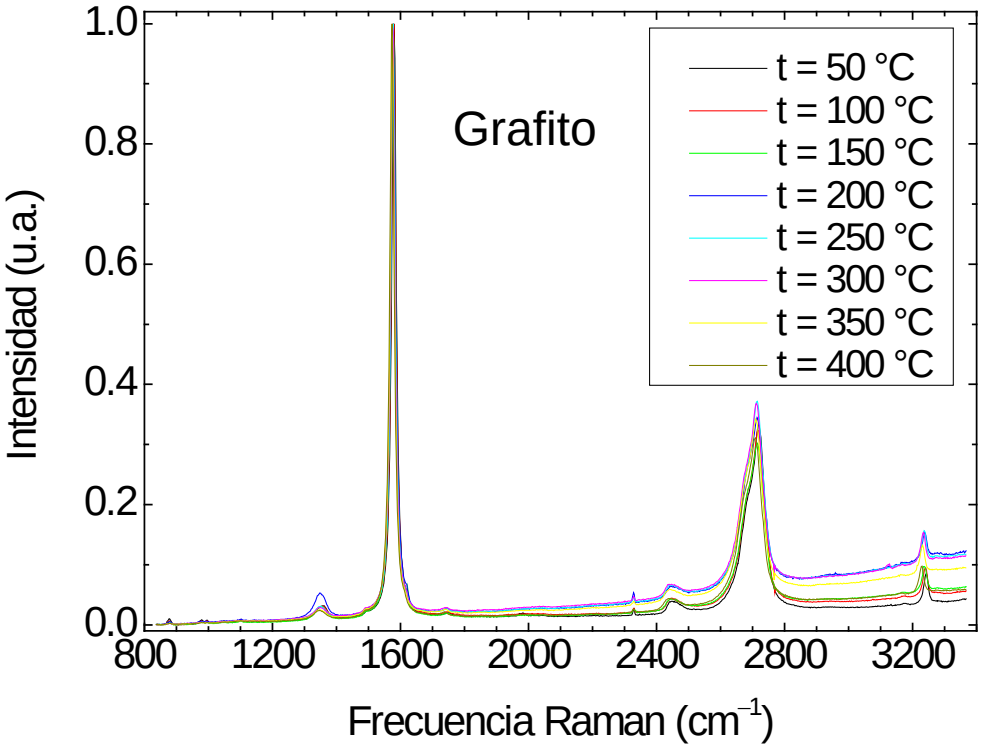


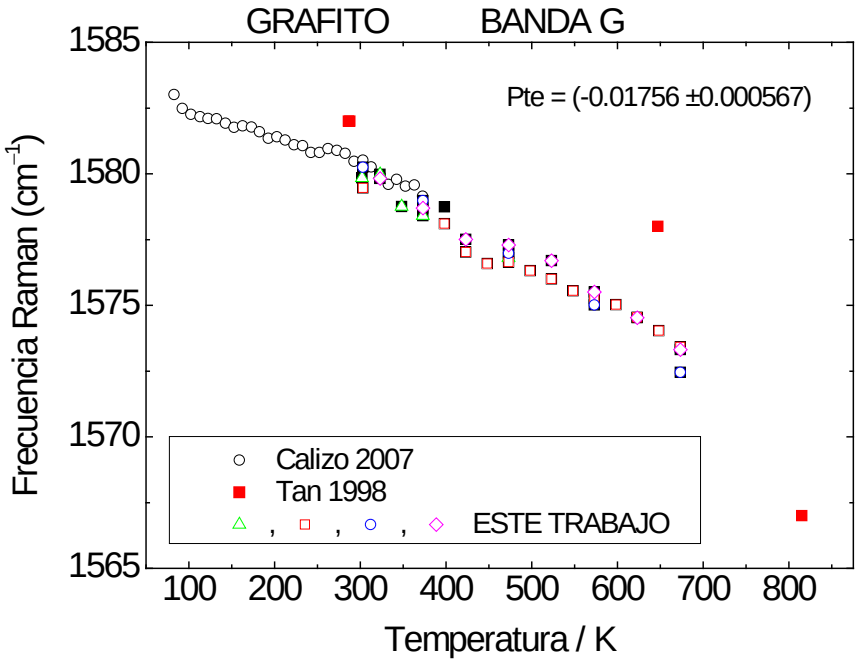


OTROS RESULTADOS

- High temperature microscope stage (Linkam TS1500)
  - Medidas hasta 1800 K a presión ambiente
  - Melting
  - Fonones
  - Ecuación de estado







REACTIVIDAD INDUCIDA POR LA PRESIÓN

Percy Williams Bridgman
Harvard University, USA
1882-1961
Nobel de Física 1946

Transiciones Irreversibles destacadas

-Fósforo

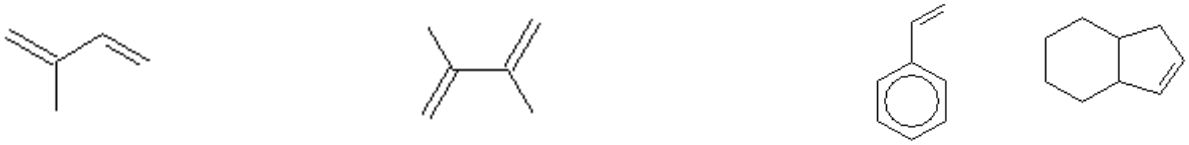
-CS_2

Transformaciones irreversibles de compuestos orgánicos bajo altas presiones. P. W. Bridgman y J. B. Conant, Proc. Nat. Acad. Sci. U.S. 15, 680-683 (1929).

Observaciones

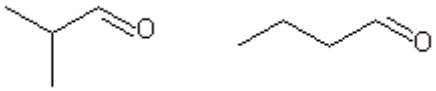
- Compuestos parcialmente polimerizados al someterlos a una presión de 0.9 GPa durante 24 horas

Isopreno, 2,3-dimetil-1,3-butadieno, estireno, indeno



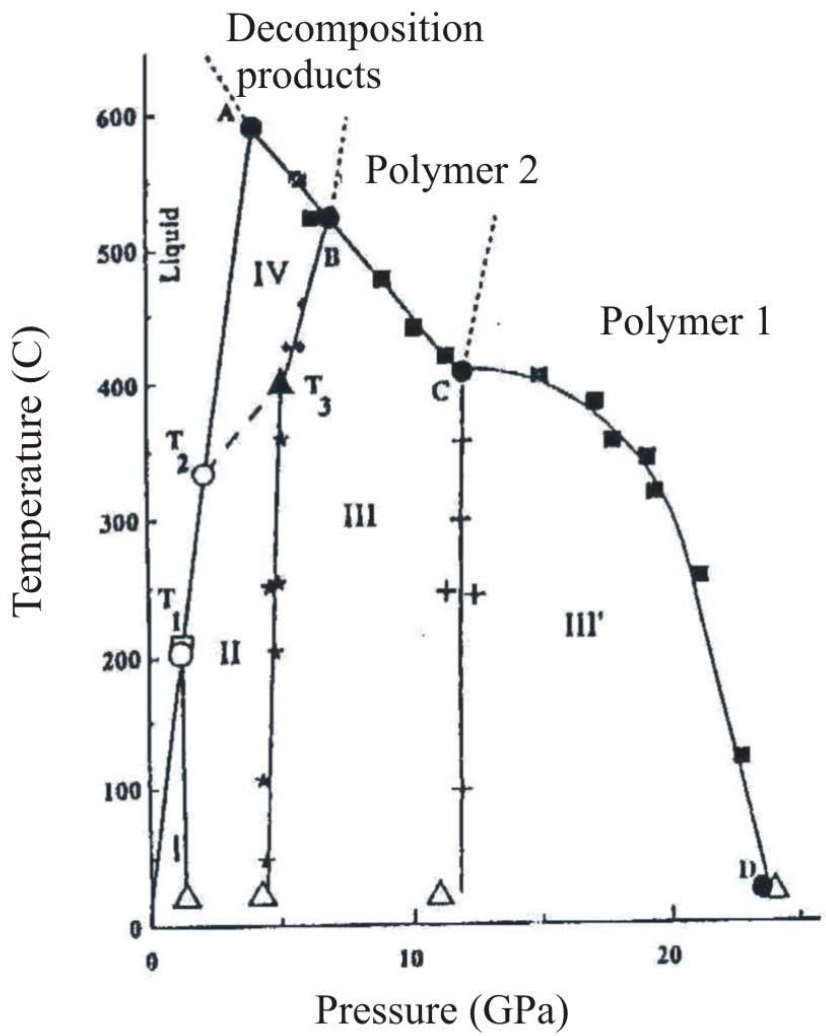
- Compuestos transformados al someterlos a una presión de 1.2 GPa durante 40 horas

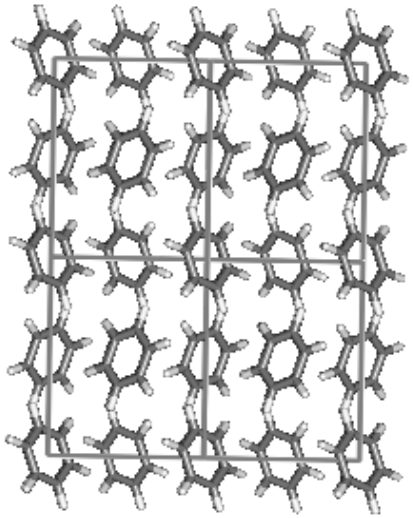
Isobutanal, n-butanal



Ejemplo: Benceno

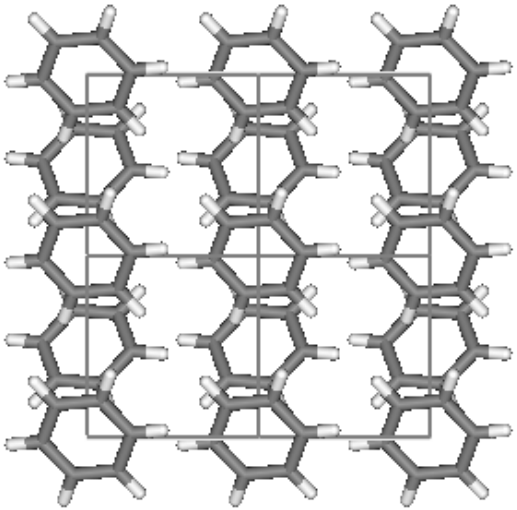
Diagrama de fases





Fase a baja temperatura y presión ambiental
Pbca

Ángulo entre los anilos de benceno: 90° 22"



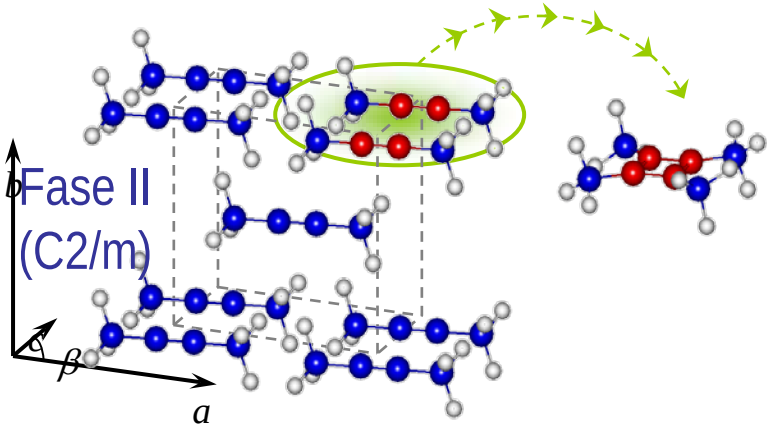
Fase a alta presión (>1.2 GPa)
$P2_1/c$

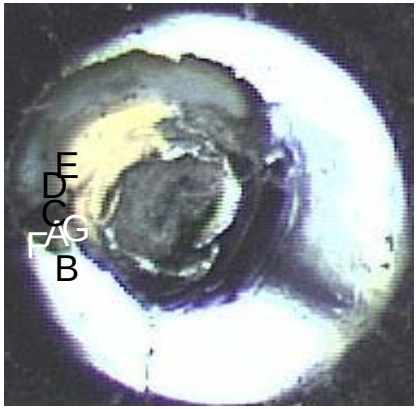
Ángulo: 120°

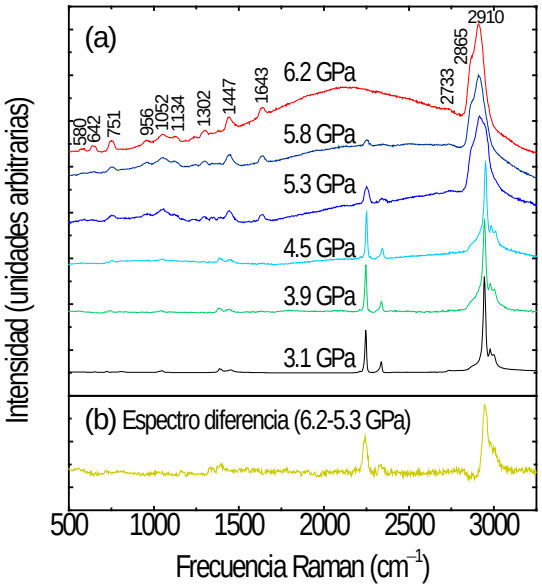
REACTIVIDAD INDUCIDA POR LA PRESIÓN DEL DIMETILACETILENO

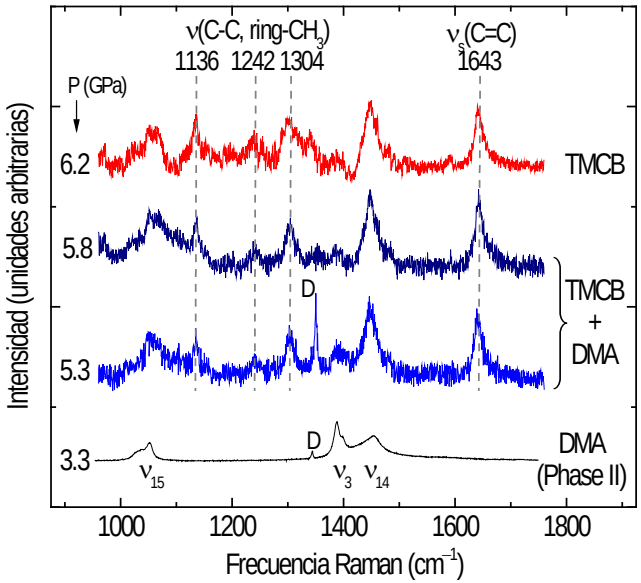
Alta presión:
Formación de Moléculas Inestables a presión ambiente: anillos de tetrametilciclobutadieno

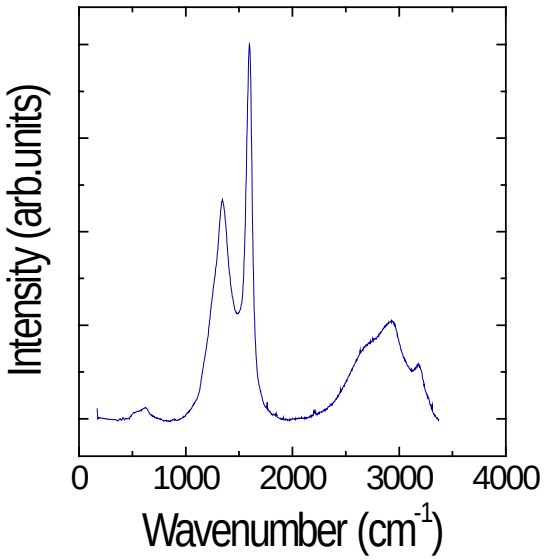
Descompresión:
Residuo: Material nanografítico







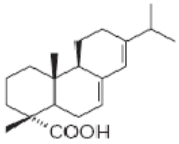




COMPUESTOS DE INTERÉS PARA POLIMERIZAR A ALTA PRESIÓN

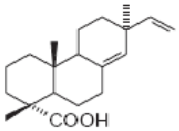
DITERPENOS

Abietane Type



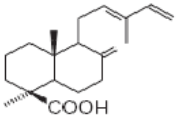
Abietic acid

Pimarane Type

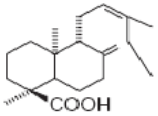


Pimaric acid

Labdane Type

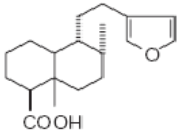


Communic acid



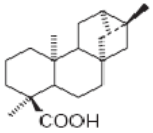
Ozoic acid

Clerodane Type



Hardwickiic acid

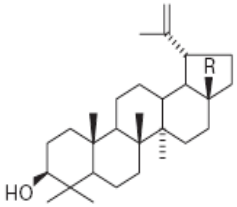
Kaurane Type



Trachylobanic acid

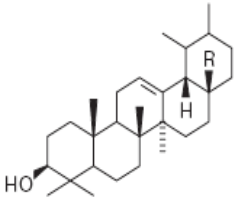
TRITERPENOS

Lupane Type



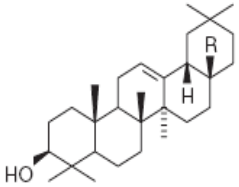
R = CH_3 Lupeol
R = CH_2OH Betulin
R = COOH Betulinic acid

Ursane Type



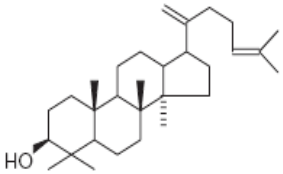
R = CH_3 α-Amyrin
R = COOH Ursolic acid

Oleanane Type



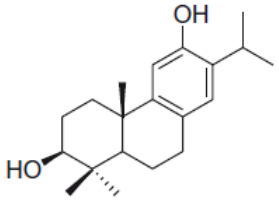
R = CH_3 β-Amyrin
R = COOH Oleanolic acid

Dammarane Type

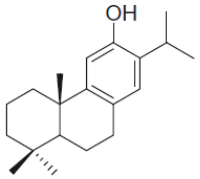


Dammaradienol

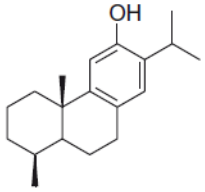
TERPENOS FENÓLICOS



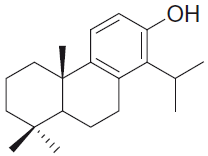
XII. Hinokiol



Ferruginol



XIV. 18-Norferruginol

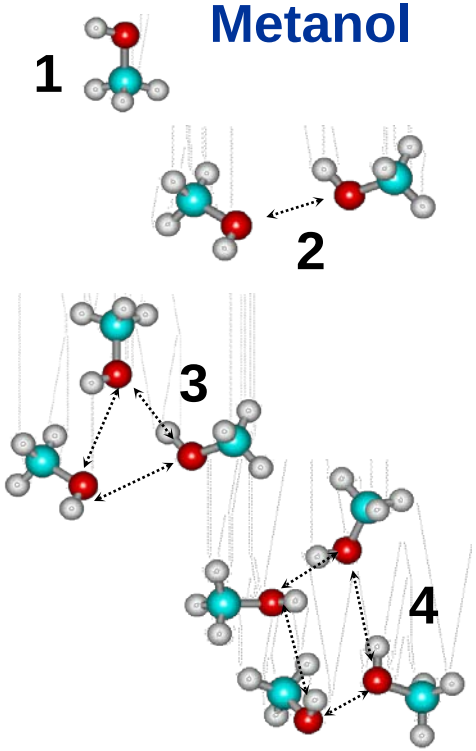


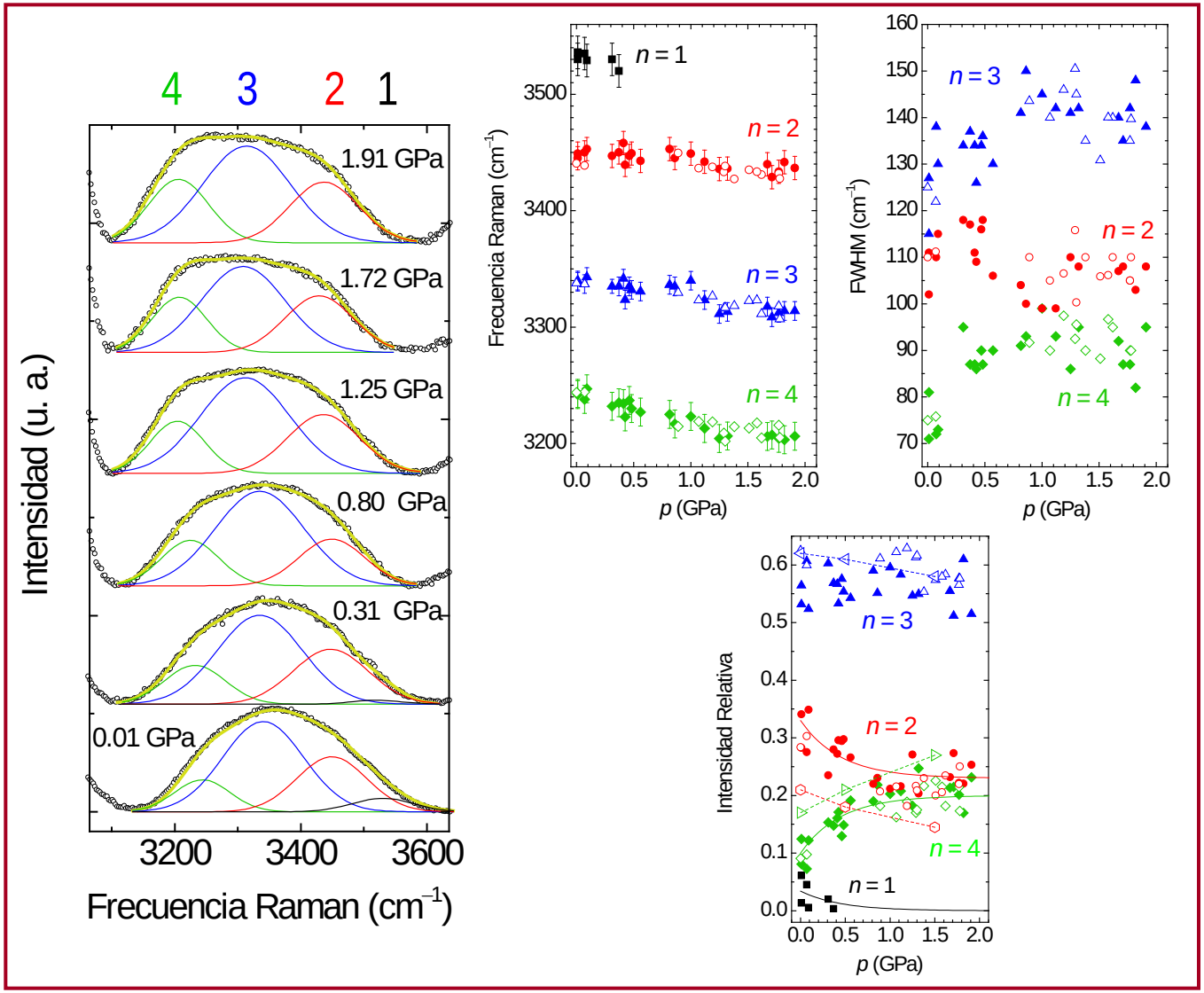
Totarol

FENÓMENOS DE AGREGACIÓN A ALTA PRESIÓN

Efecto de la Presión en el Enlace de Hidrógeno del Metanol Líquido

Agregados Metanol

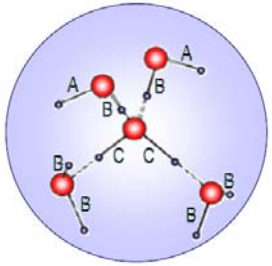


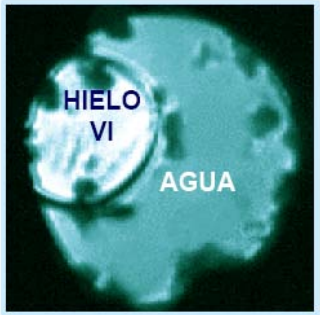


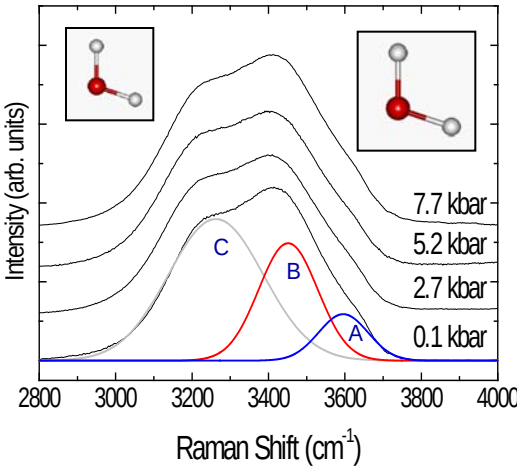
EFECTO DE LA PRESIÓN EN EL ENLACE DE HIDRÓGENO

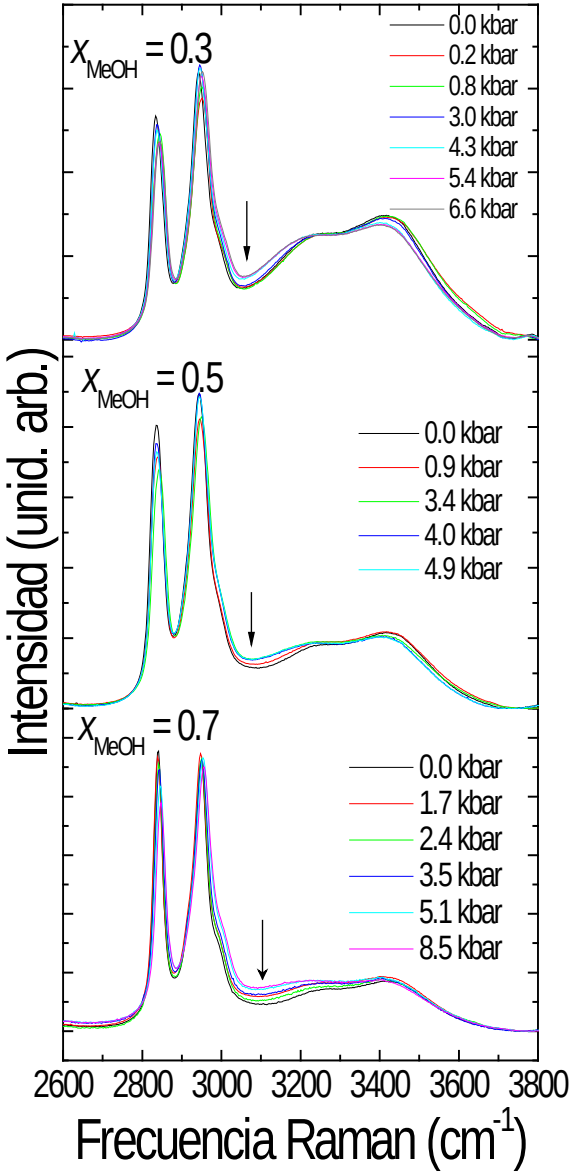
FENÓMENOS DE AGREGACIÓN A ALTA PRESIÓN

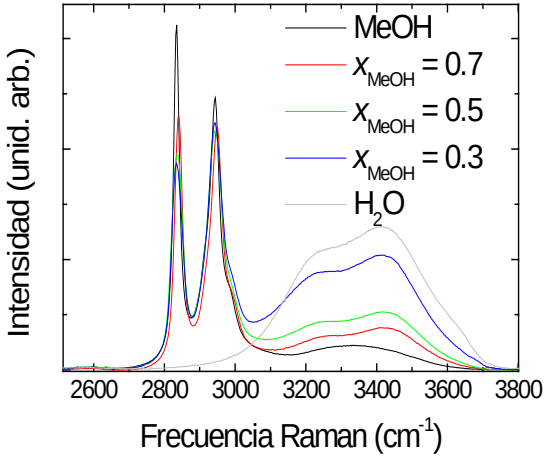
Agua



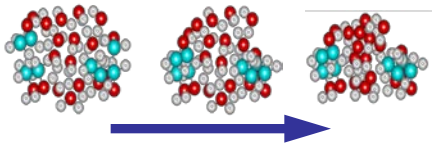








- La presencia de agua provoca la compresión de las moléculas de metanol.
- Las variaciones con la composición se dan independientemente en agregados de agua y metanol.
- Un aumento de la presión no provoca cambios en la estructura del agua hasta que no se alcanza una composición constante de agregados de metanol.



FENÓMENOS DE AGREGACIÓN A ALTA PRESIÓN

- Al mezclar agua y metanol el aumento de entropía que se observa es mucho más pequeño que el que se esperaría para una disolución ideal.

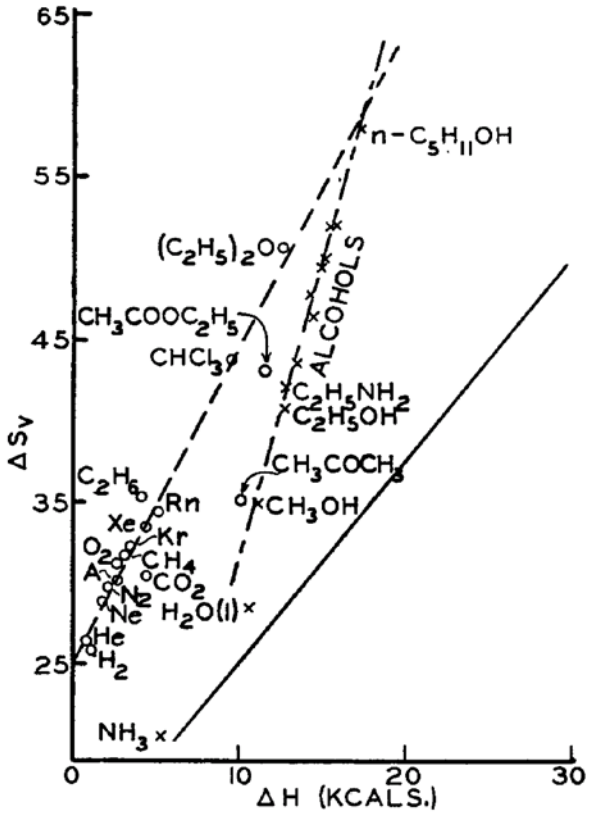


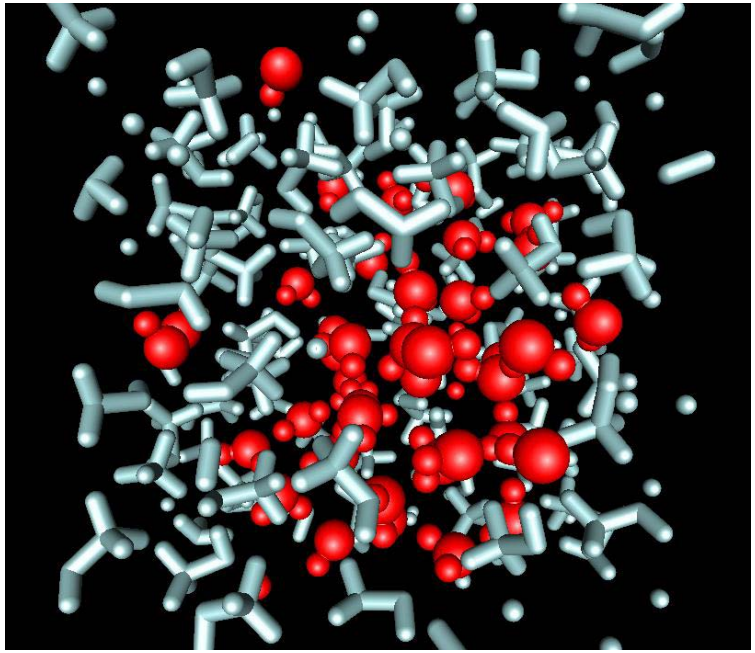
FIG. 3. ΔS_2 for non-ionic solutes in water at 25°C. Data are from Table IV.

letters to nature
NATURE | VOL 416 | 25 APRIL 2002 |

Molecular segregation observed in a concentrated alcohol–water solution

S. Dixit*, J. Crain*, W. C. K. Poon*, J. L. Finney† & A. K. Soper‡

- Experimentos de difracción de neutrones.
- Mezcla concentrada metanol-agua 7:3.
- Se concluye que las anomalías termodinámicas se deben a una mezcla incompleta a nivel molecular de las moléculas de metanol y agua.
- La estructura del agua en la mezcla es cercana a la del agua pura.

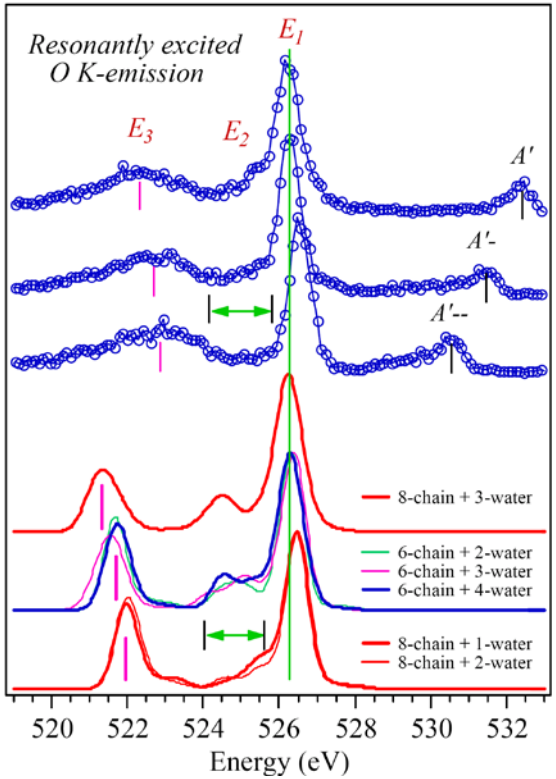


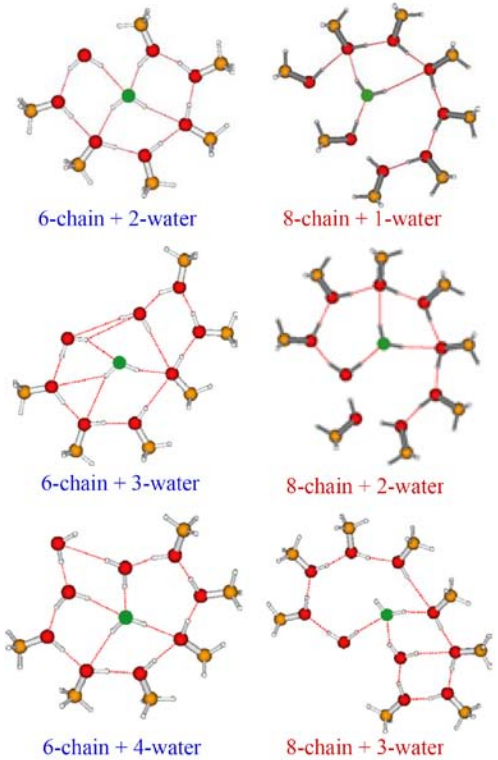
FENÓMENOS DE AGREGACIÓN A ALTA PRESIÓN

VOLUME 91, NUMBER 15 PHYSICAL REVIEW LETTERS week ending 10 OCTOBER 2003

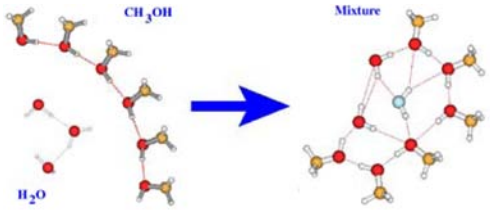
Molecular Structure of Alcohol-Water Mixtures

J.-H. Guo,[1,*] Y. Luo,[2,†] A. Augustsson,[1,3] S. Kashtanov,[2] J.-E. Rubensson,[3] D. K. Shuh,[4] H. Ågren,[2] and J. Nordgren[3]





- Espectroscopía de emisión de rayos-X.
  - Para una mezcla equimolar agua-metanol, las moléculas de ambos compuestos se mezclan de forma incompleta a nivel molecular.
  - Existe un nuevo mecanismo para aumentar el orden en la disolución, las moléculas de agua unen cadenas de metanol para formar anillos con 6 y 8 moléculas de metanol.



CONSOLIDER MALTA

www.malta-consolider.com

Simposio

MALTA-Consolider

23-27 Enero 2011, Miraflores de la Sierra

Presión interna de disoluciones acuosas

Nubia Judith Mendoza Lugo
Departamento Química-Física
Universidad Complutense Madrid
MALTA CONSOLIDER

Contenido

1. Introducción
2. Sistemas OH
   - Agua+Metanol
   - Agua+Etanol
   - Etanol+Metanol
3. Características de la Experimentación
4. Resultados
5. Perspectivas

1. Introducción

Los resultados que presentaré en este trabajo forman parte de mi proyecto de tesis doctoral.

Los sistemas que estamos estudiando son: agua-metanol, agua-etanol y etanol-metanol, en función de la concentración y la presión, mediante Espectroscopía Raman.

El objetivo final de nuestro estudio es confirmar que el efecto de mezcla es similar al que ejerce la presión sobre las moléculas en estado líquido. Para ello llevaremos a cabo estudios de alta presión para los componentes puros y trataremos de correlacionar las variaciones de frecuencia, intensidad, etc. de las bandas en función de la concentración.

2. Sistemas OH

Hemos empezado nuestros experimentos con la mezcla agua-metanol, eligiendo el metanol por ser una de las más simples moléculas anfifílicas y porque poseemos resultados Raman a alta presión en ambos sistemas.

Éste estudio, junto con el del agua-etanol, sirven de referencia para acometer estudios más complejos tales como la formación de micelas, bicapas, etc en diferentes disolventes.

La mezcla etanol-metanol completa nuestro trabajo y tiene especial interés en el campo de las altas presiones.

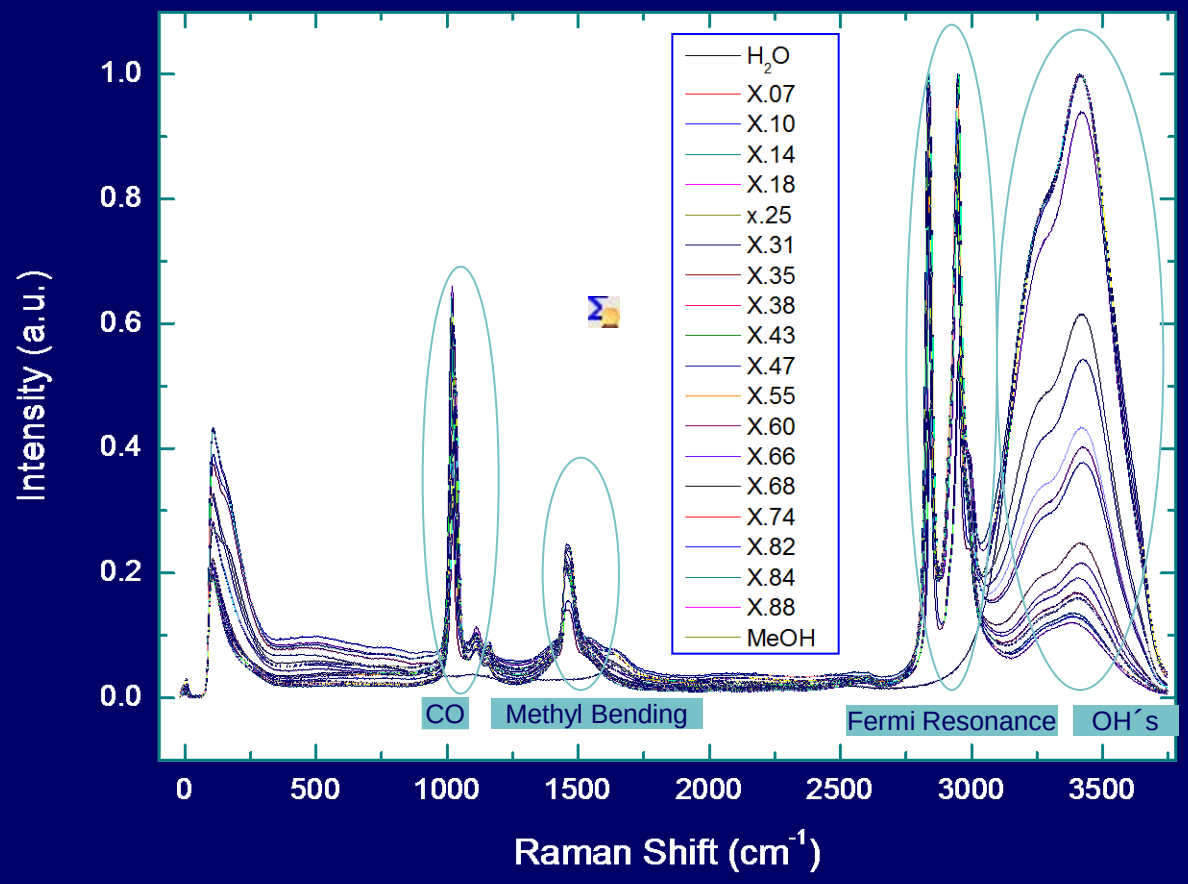
3. Características de la Experimentación

Espectrómetro Raman BWTEK

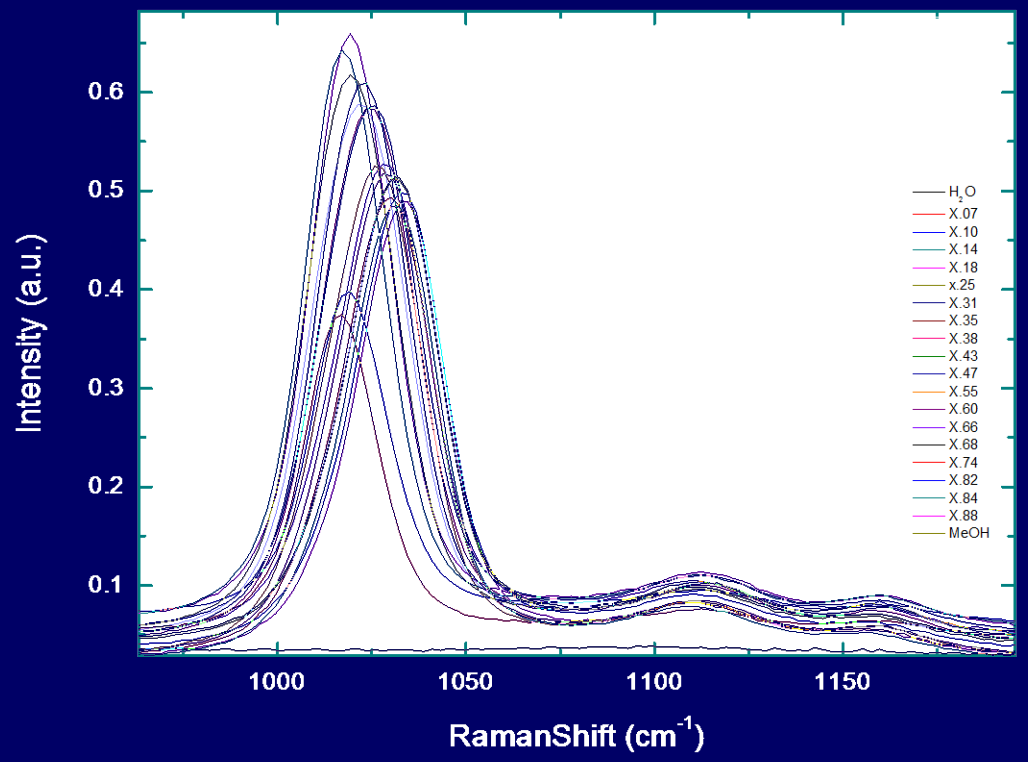
- ✓ Excitación Láser 532nm
- ✓ Resolución $\pm 2\ cm^{-1}$
- ✓ Objetivo10x
- ✓ Tiempo de adquisición 600-1200ms
- ✓ Acumulaciones: 30

H_2O+MeOH

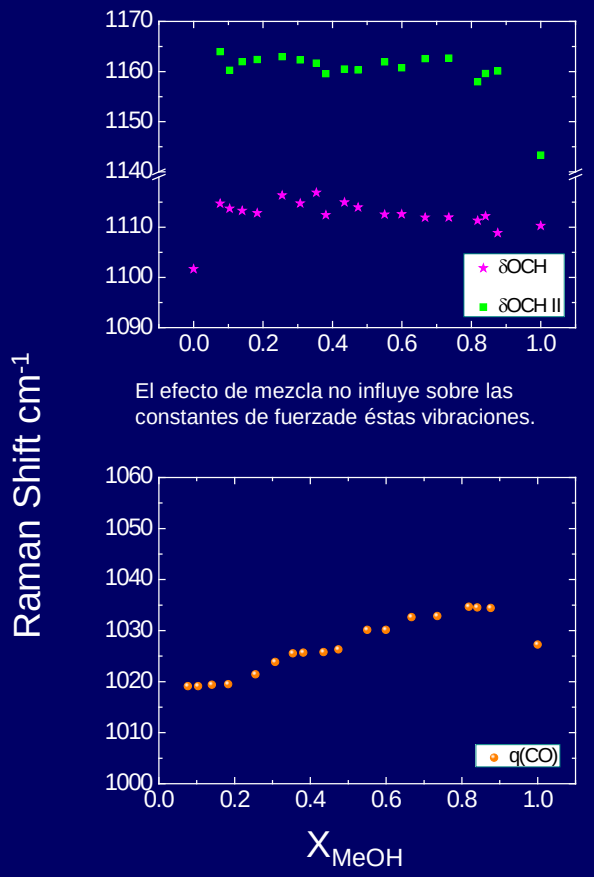
Análisis de cuatro zonas de los espectros H_2O + MeOH



Zona de C-O



Representación de la variación con la fracción molar del MeOH

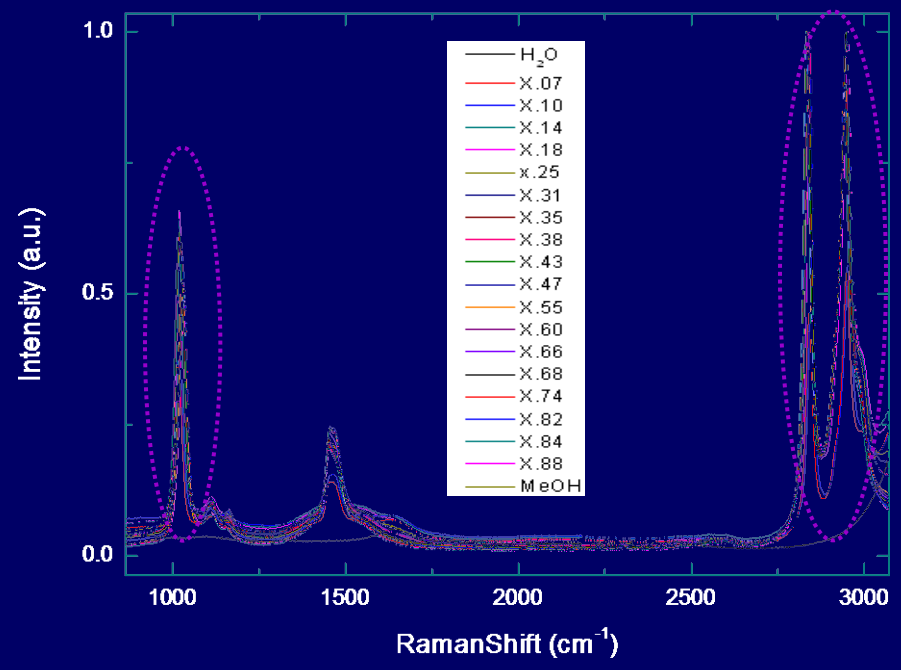


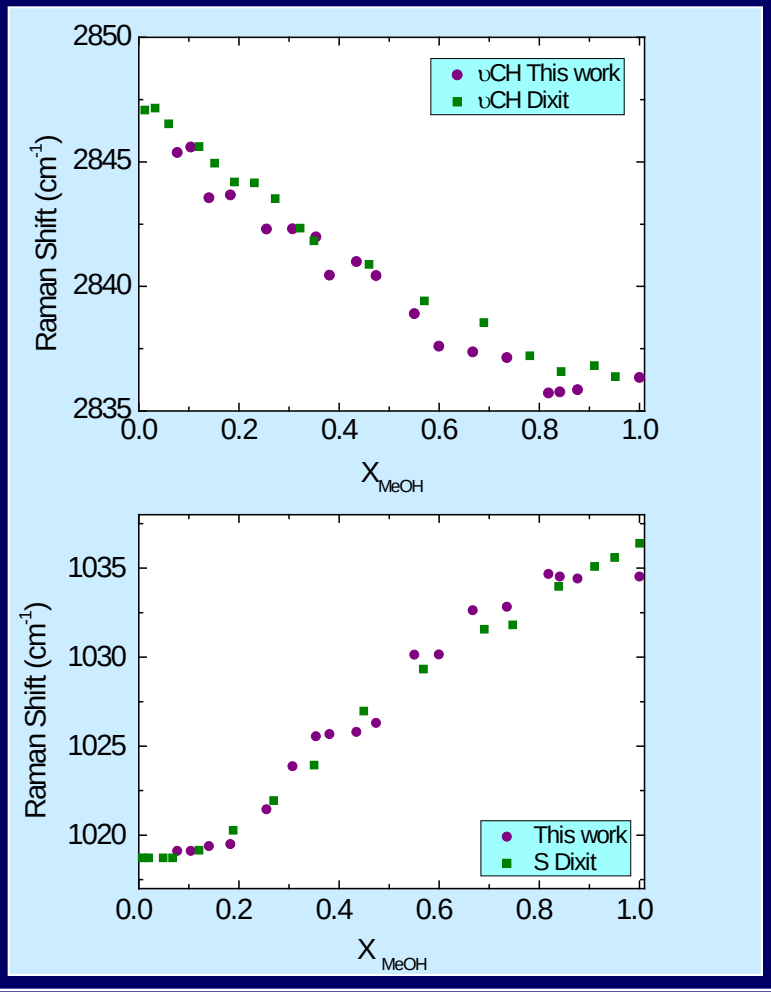
El efecto de mezcla no influye sobre las constantes de fuerzade éstas vibraciones.

T. Sim. Del CO la dependencia con la concentación se puede separar en 3zonas. Esta banda nos permitirá establecer una relación entre los efectos de solvatación y presió

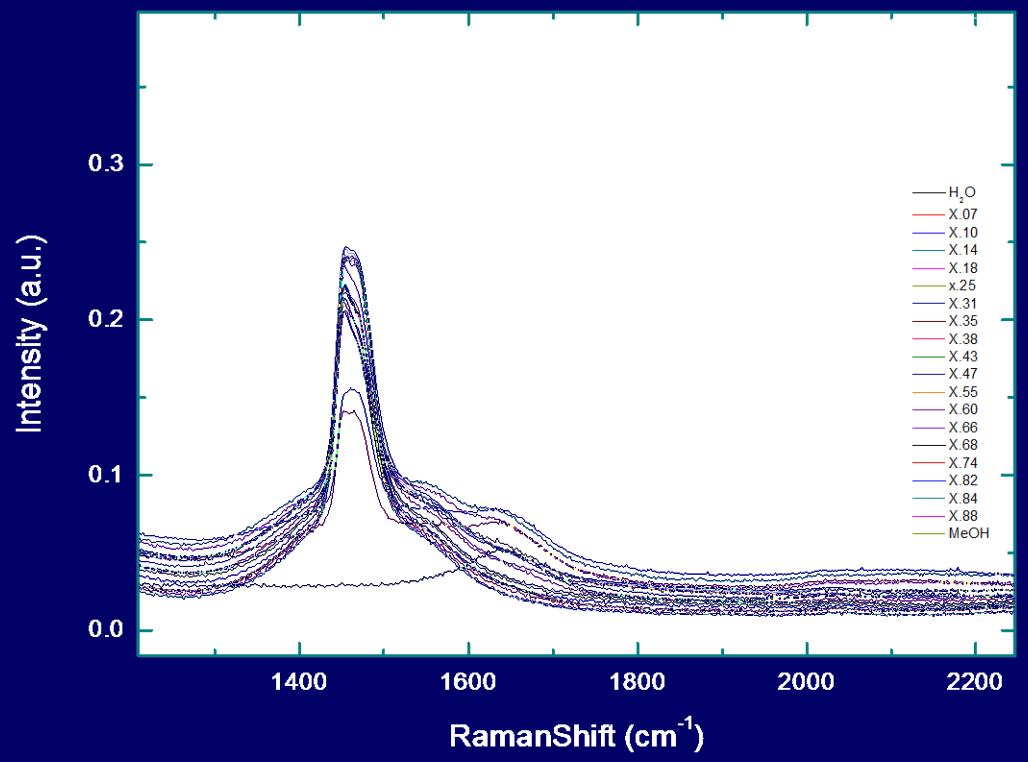
Comparación de resultados

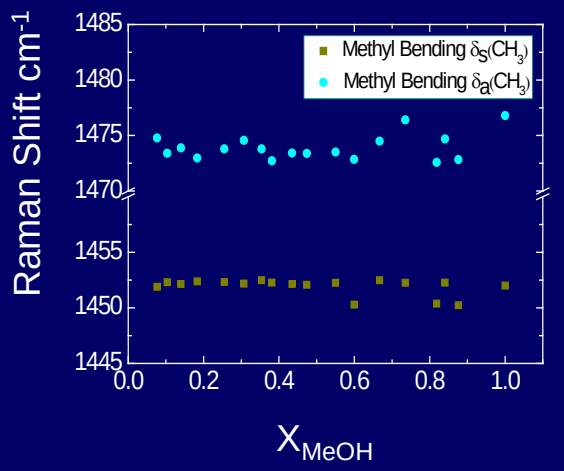
Se podría decir que cuando el H2O hidrata una molécula anfifílica, solvata primero la mitad POLAR y después la mitad NO POLAR (CH3).





Bending del Metilo

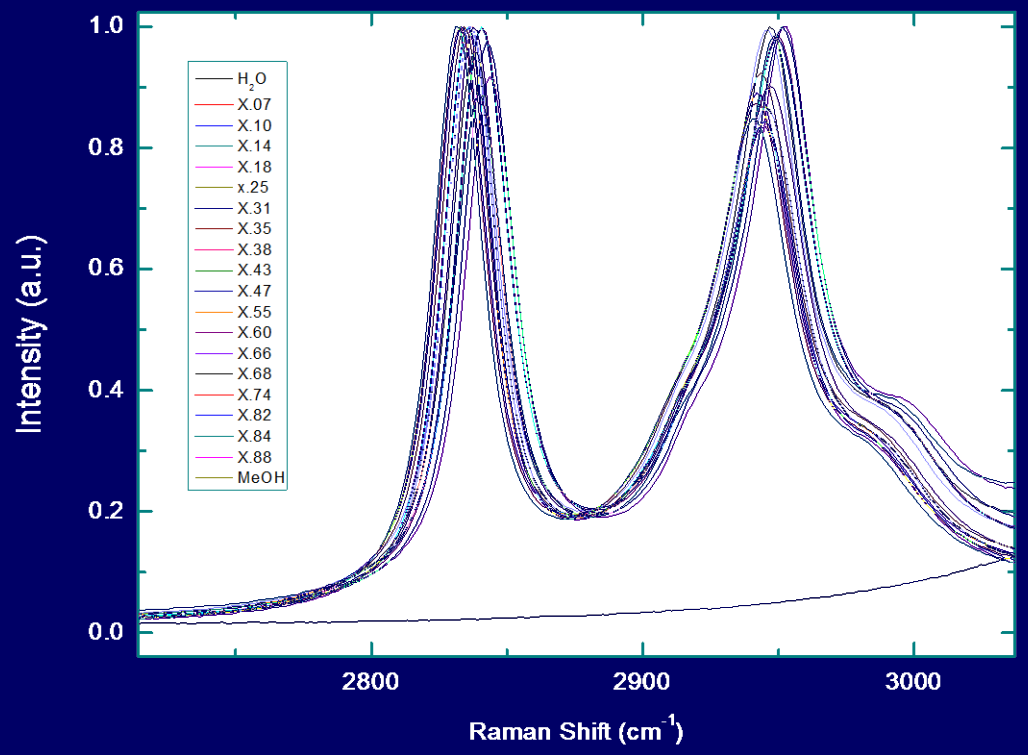


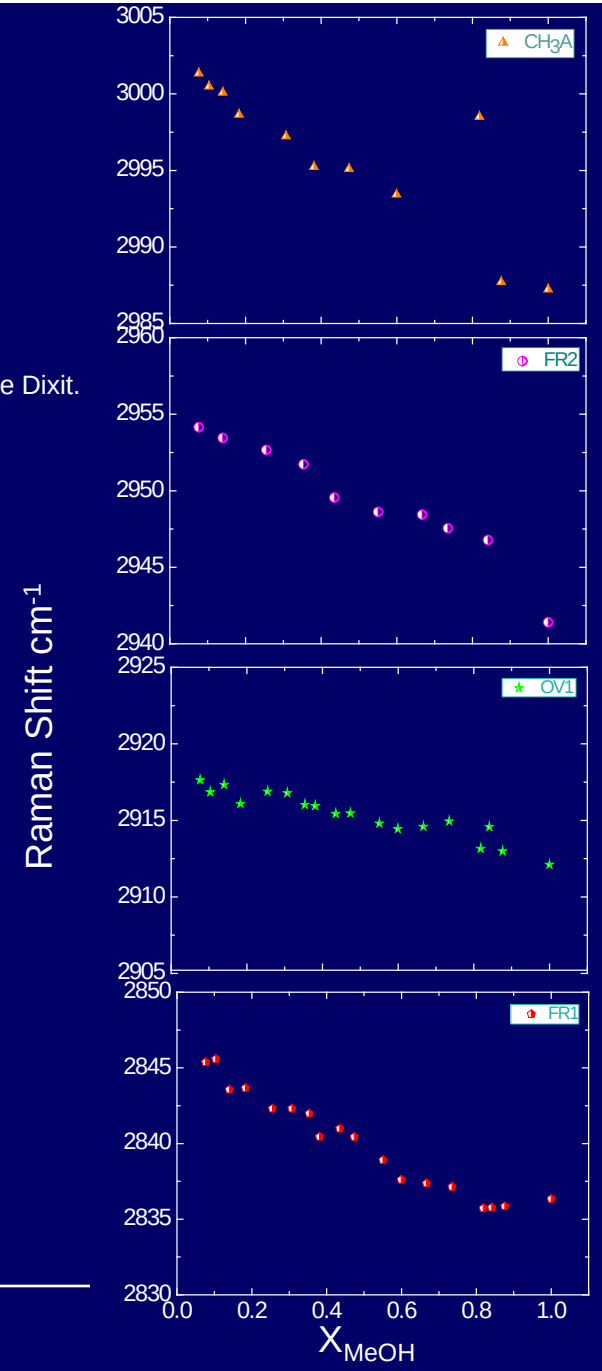


Observamos cómo, en este caso igual que en el bending del OCH no existe dependencia con la concentración de la frecuencia para ésta vibración.

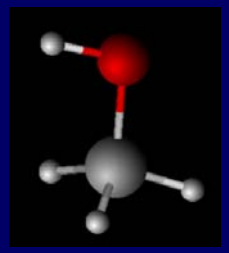
Resonancia de Fermi

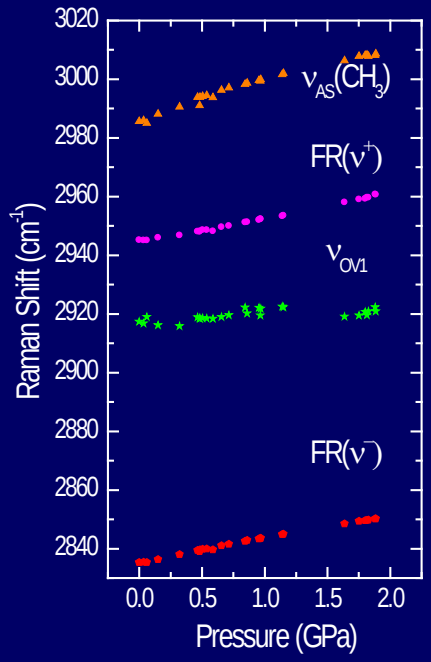
Las bandas centadas en 2845 y 2950 cm-1 son las que nos van a permitir correlacionar los efectos de presión y solvatación para el gpo.CH3.
Hemos comparado nuestros resultados para la banda de menor fcia con los de Dixit.

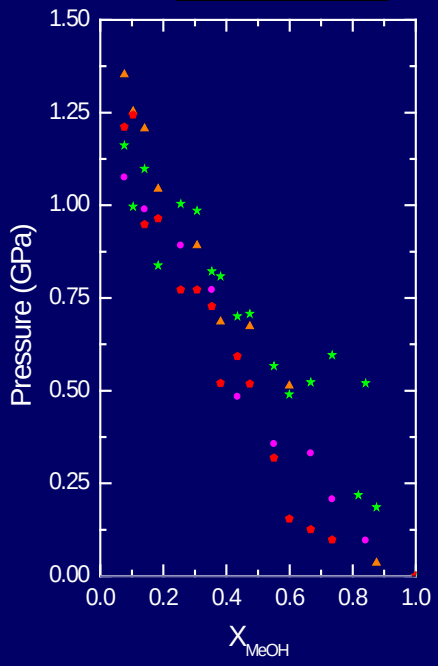




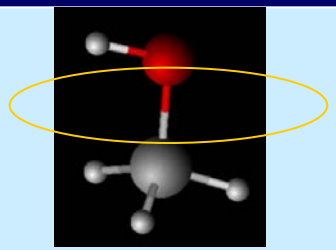
El efecto de mezcla se traduce en una ligera compresión del grupo CH_3 al aumentar la proporción de agua

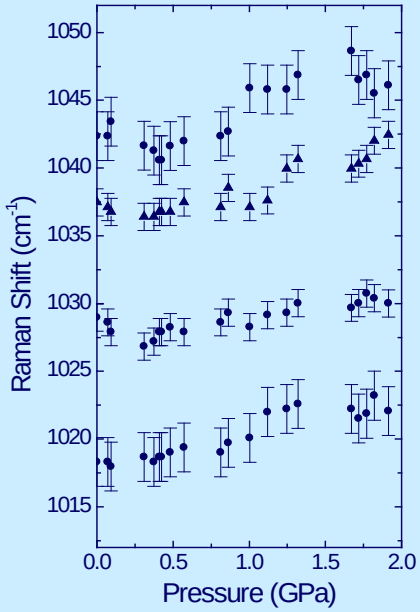


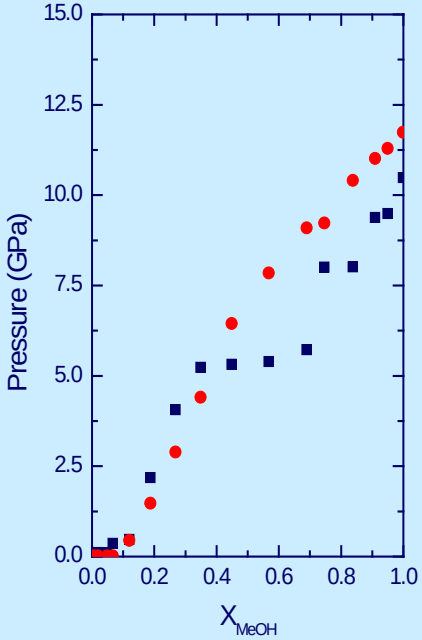




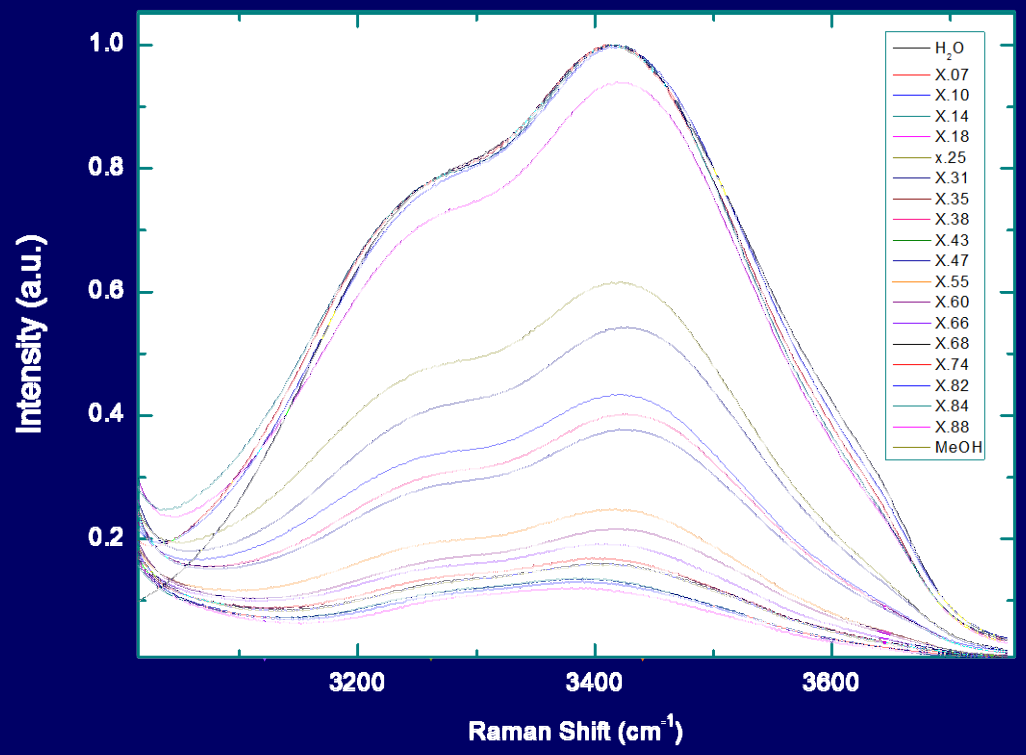
El efecto de mezcla es un orden de magnitud mayor y de signo contrario en el enlace CO.

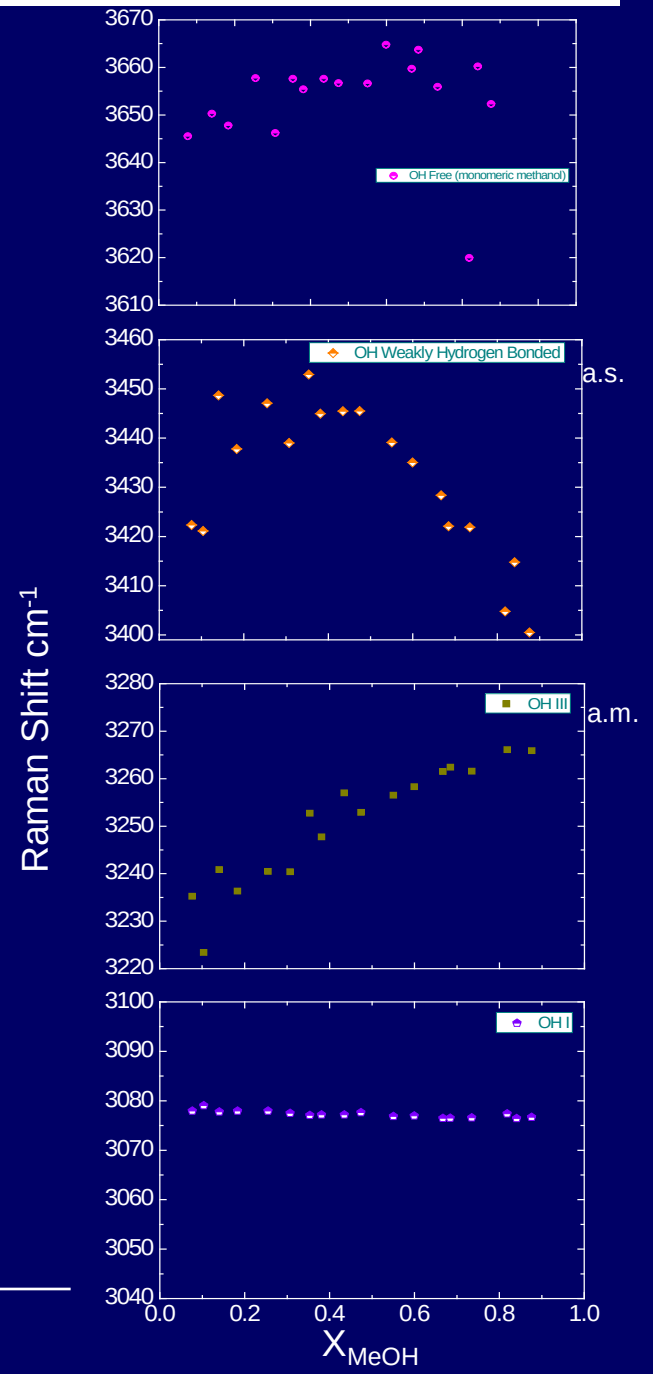






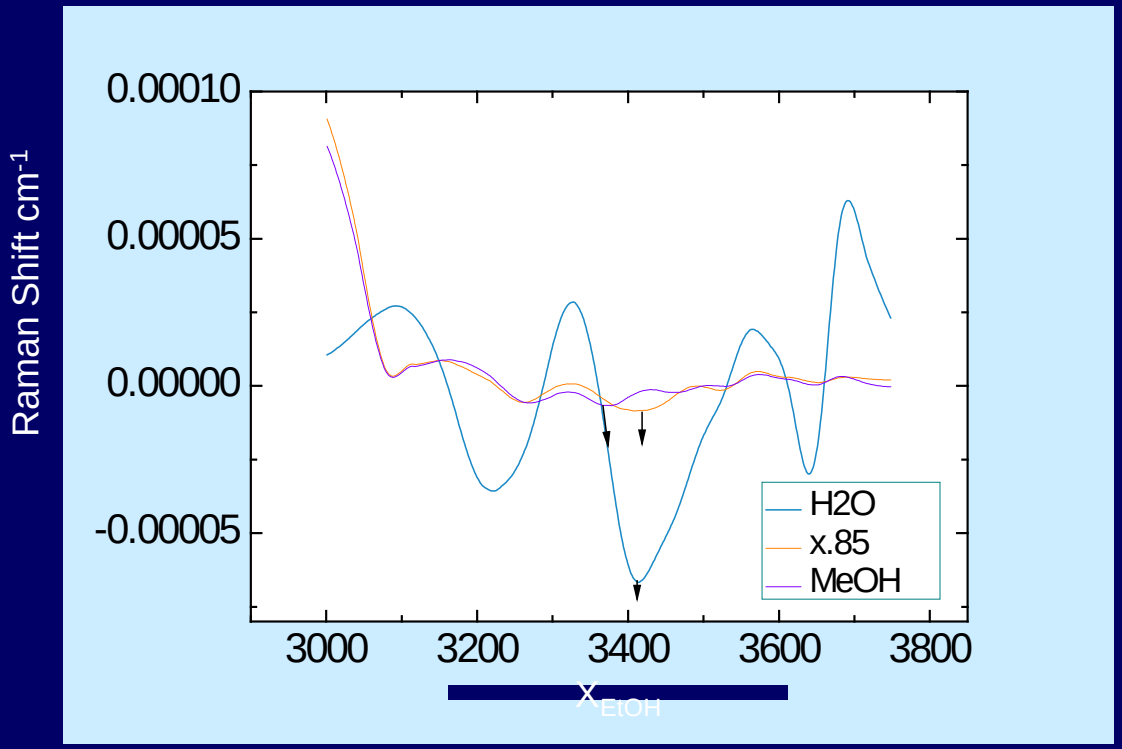
Zona de los OH´s





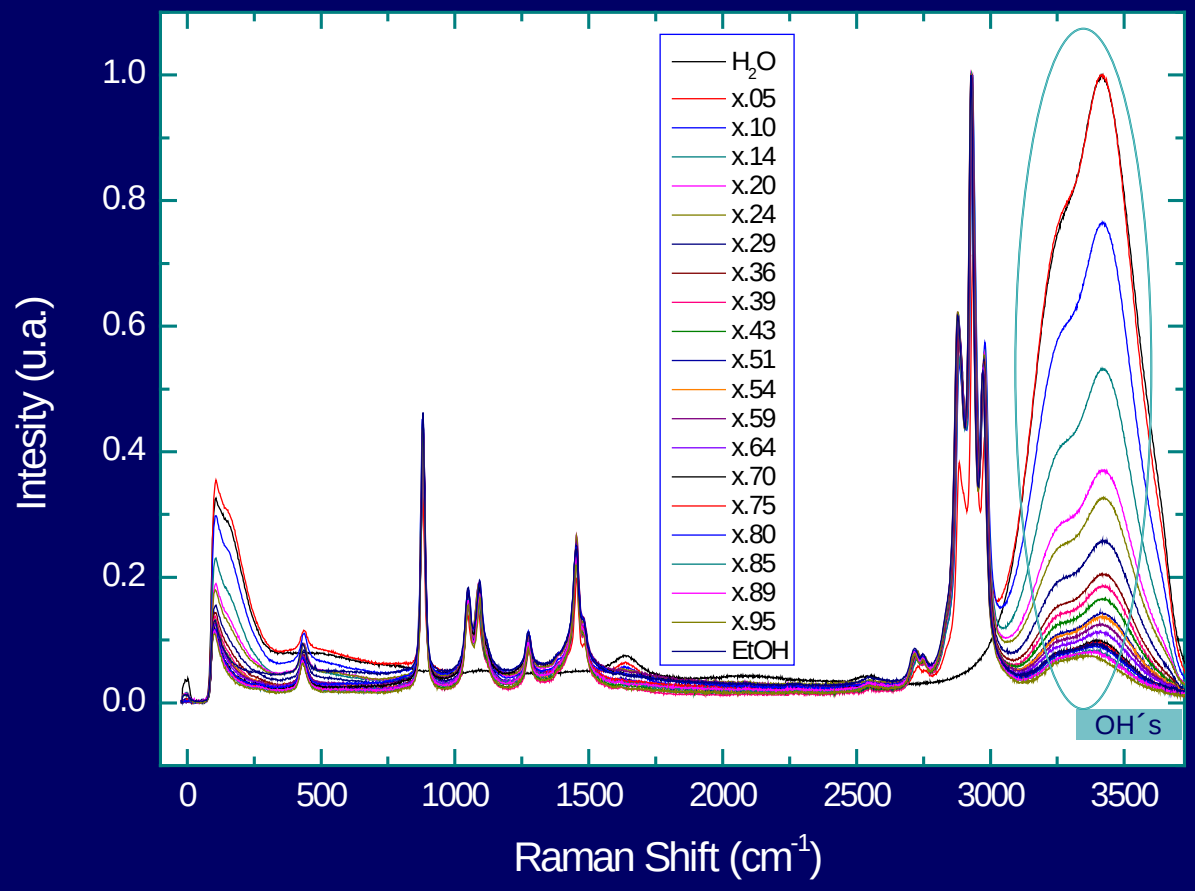
Análisis de la 2da derivada de la zona de los OH´s

En la posiciones de las bandas podemos ver cómo cuando pasamos de MeOH puro a fracción molar .85, la posición del mínimo se desplaza prácticamente hasta la posición de mínimo del agua pura. Indicando que pequeñas cantidades de agua alteran mucho la estructura del MeOH.

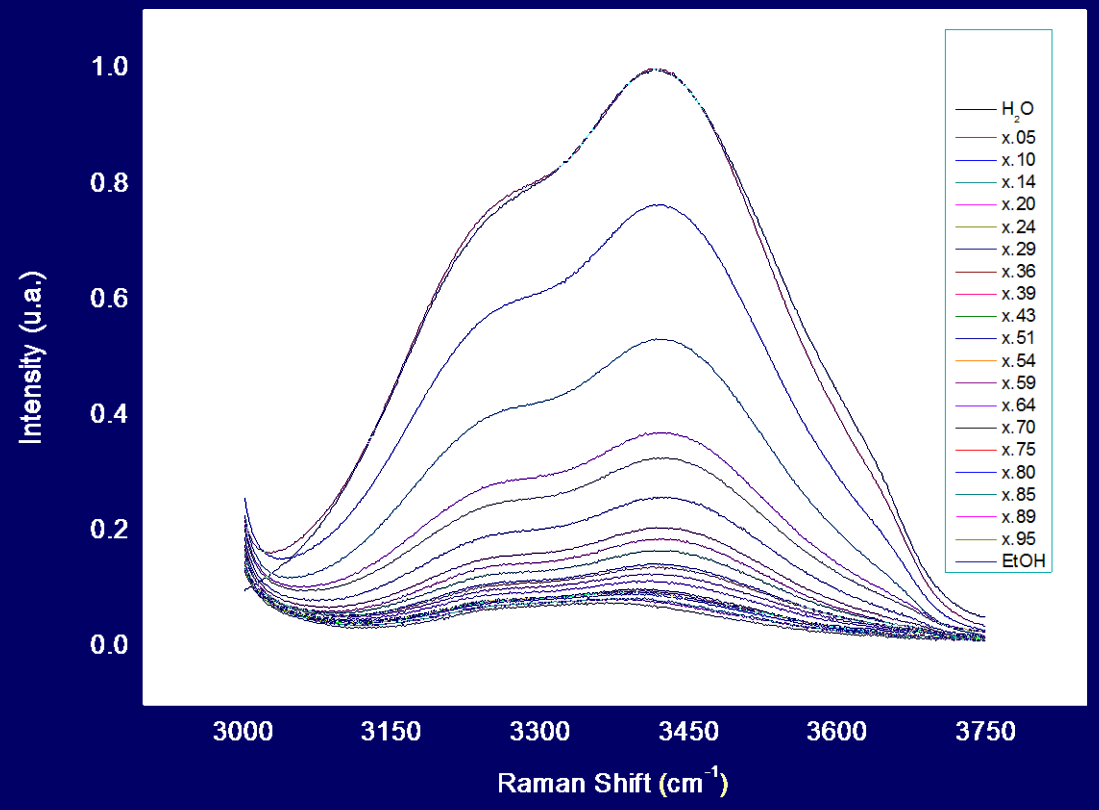


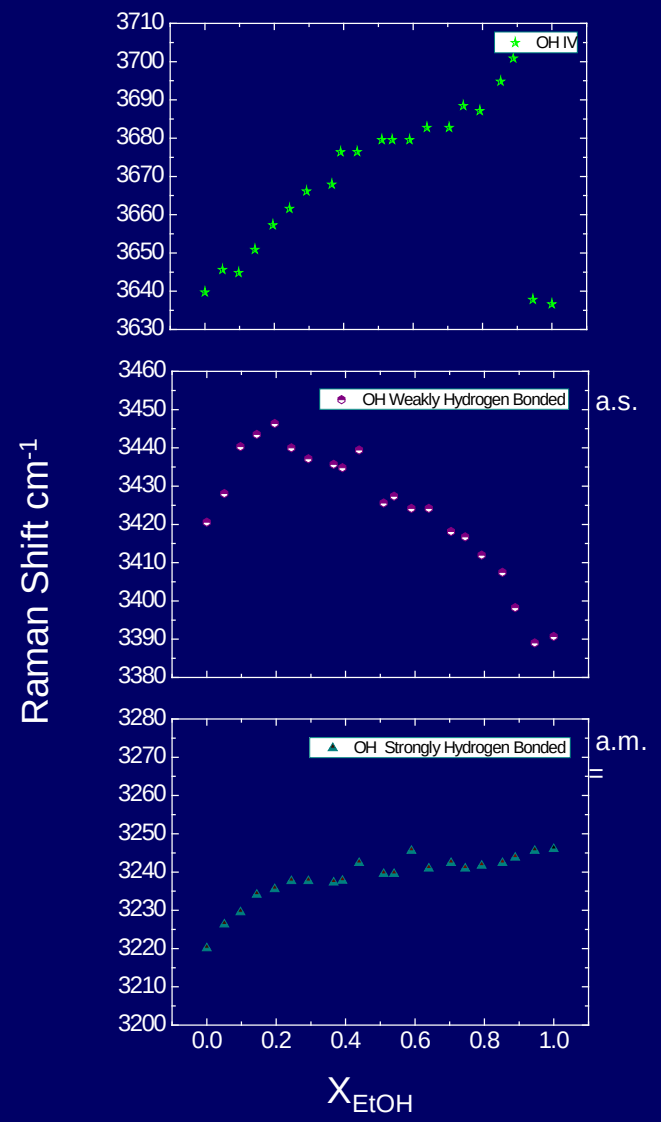
H_2O+EtOH

Análisis de zona de los OH´s de los espectros H2O + EtOH.



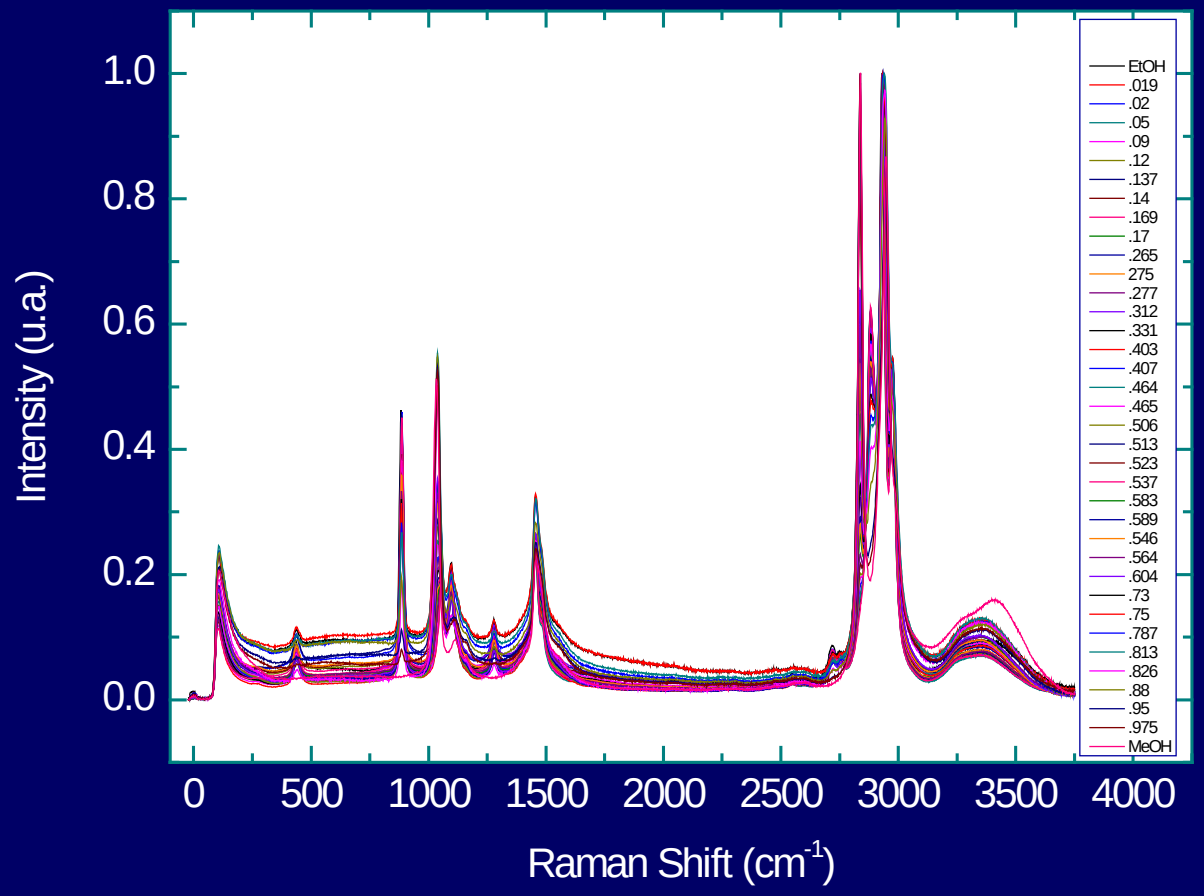
Zona de los OH´s



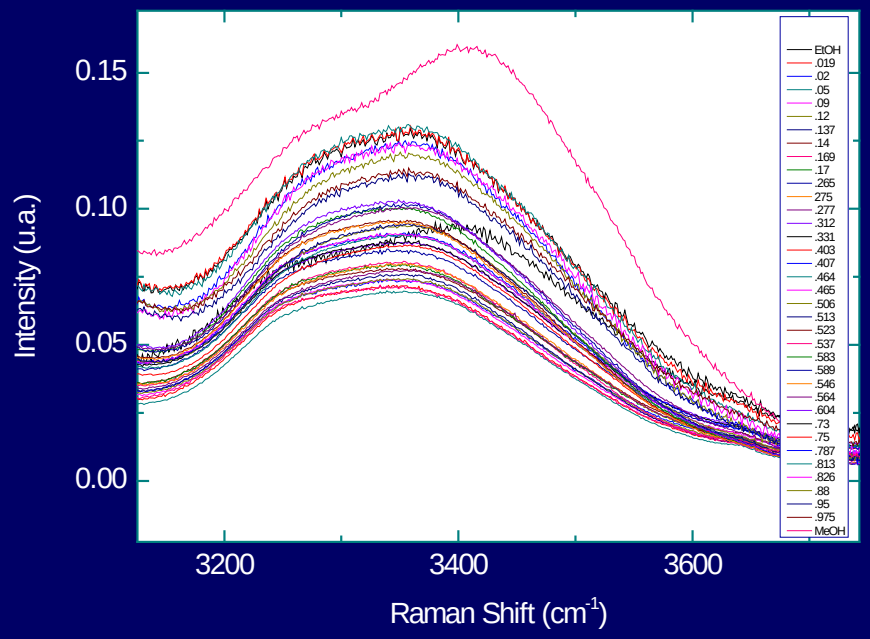


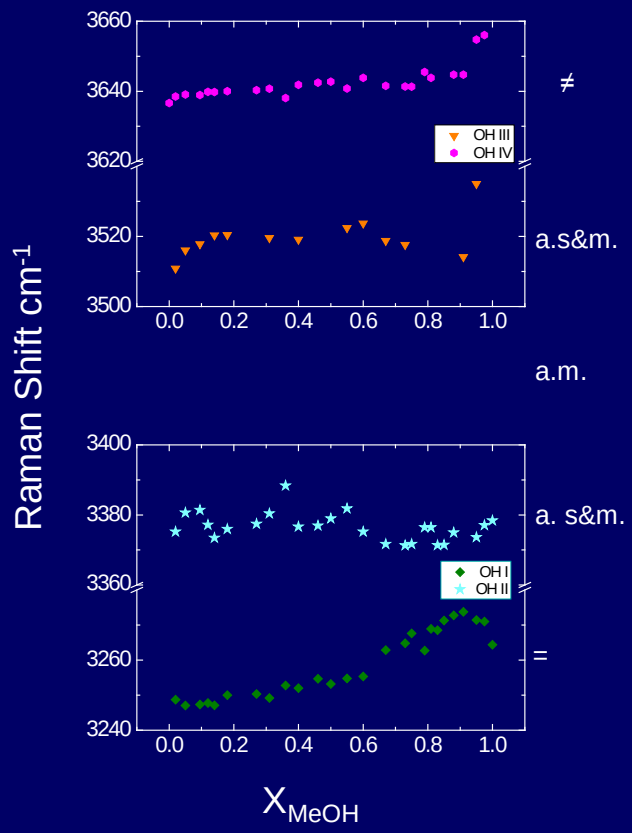
H_2O+MeOH

Análisis de zona de los OH´s de los espectros de EtOH+MeOH.



Zona de los OH´s





5. Perspectivas

- Medir el espectro Raman de Etanol puro en función de la presión.
- Completar el análisis de nuestros datos experimentales para las mezclas agua-etanol y etanol-metanol.
- Hacer una interpretación de los resultados obtenidos correlacionando los efectos de presión y de hidratación de forma análoga a lo que hemos hecho con la mezcla Agua-Metanol.
- Utilizar los resultados de la mezcla etanol-metanol para aplicaciones tanto en el campo de las altas presiones como en el estudio de sistemas biológicos.

Gracias por su atención…

"Síntesis de Resinas Fósiles a alta presión"

Reunión MALTA-CONSOLIDER. Enero 2011

Óscar Rodríguez Montoro
UNIVERSIDAD COMPLUTENSE DE MADRID
Departamento de Química-Física I. Universidad Complutense de Madrid

QUIMAPRES

CONSOLIDER MALTA Matter at High Pressure

PROGRAMA INGENIO 2010

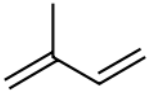
Dirigido por: Valentín García Baonza y Mercedes Taravillo Corralo

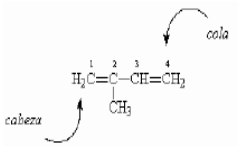
OBJETIVOS

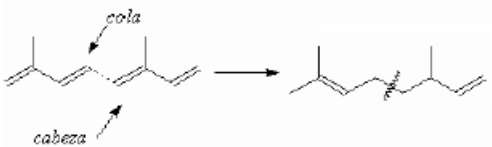
- ✓ **Estudio de la influencia de la presión en la formación de resinas fósiles.**
- ✓ **Estudio del comportamiento de los terpenos a alta presión por métodos espectroscópicos.**
- ✓ **Síntesis por polimerización a alta presión de resinas fósiles. Ámbar, Copal y Resinas.**
- ✓ **Imitación de los procesos de fosilización por alta presión (ausencia o presencia H_3O^+).**
- ✓ **Establecimiento de una escala de tiempo geológica, Presión vs. Tiempo.**
- ✓ **¿Búsqueda de Carbones no grafíticos (combustibles fósiles)?**

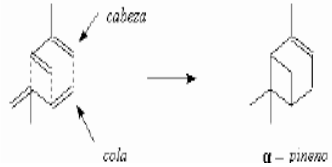
TERPENOS

ISOPRENO

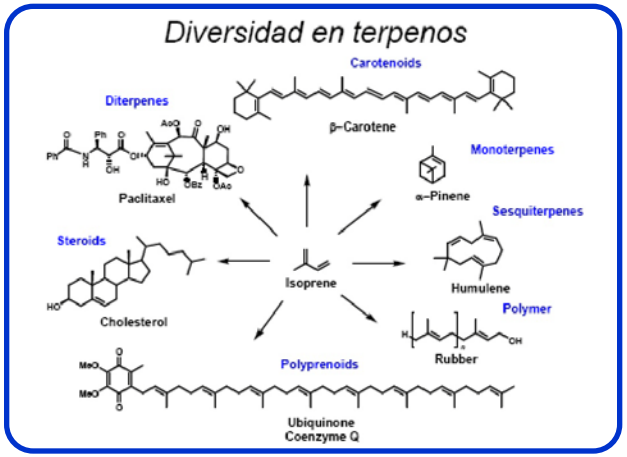






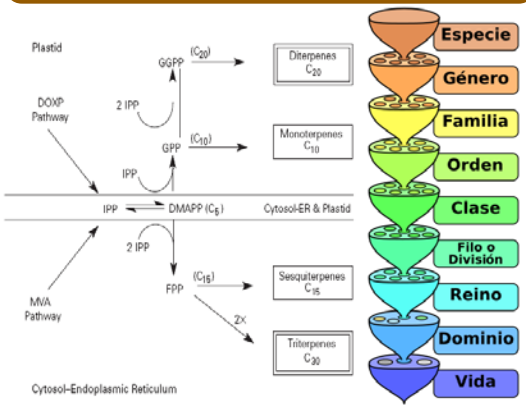


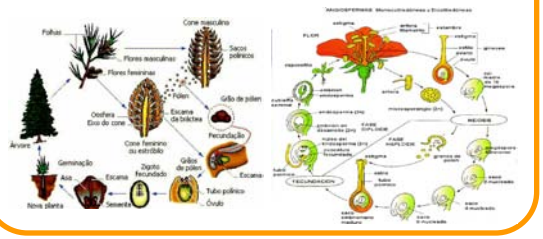
DIVERSIDAD Y CLASIFICACIÓN



Unidades 5 C	Nombre	Total carbonos
2	Monoterpenos	10
3	Sesquiterpenos	15
4	Diterpenos	20
6	Triterpenos	30
8	Tetraterpenos	40
>20	Politerpenos	>100

NATURALEZA

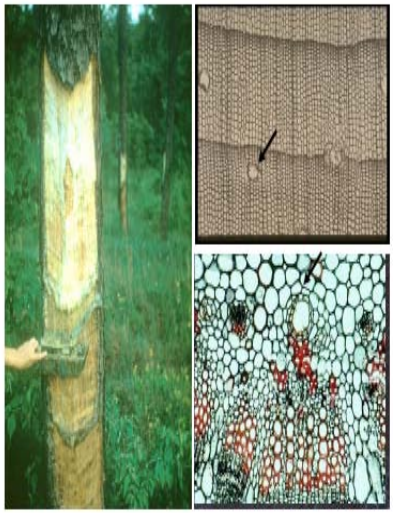




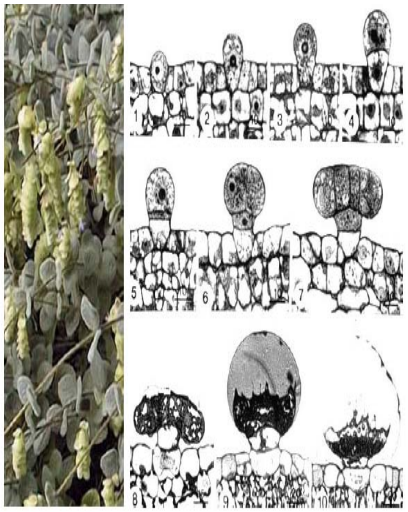
CLASES Y TIPOS DE RESINAS

SECRECIONES RESINOSAS

CANALES DE RESINA



PELOS GRANULARES



TIPOS DE ÁRBOLES RESINOSOS - CONÍFERAS

Pinaceae (Pino)

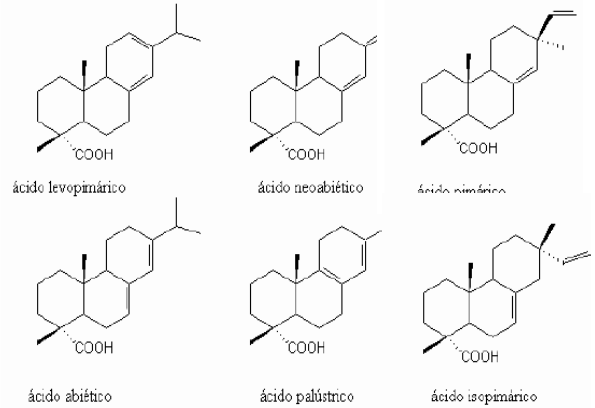
Cupressaceae (ciprés y cedro)

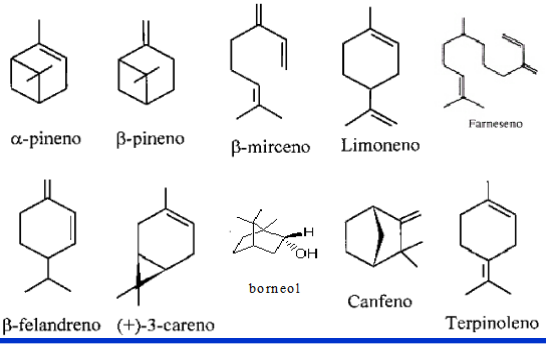
Aracariaceae

Agathis Robusta

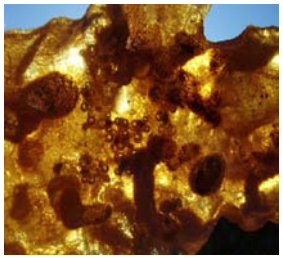
TERPENOS RESINOSOS- Ej. Resina Alpina

De la oleorresina se pueden separar, su **componente sólido** (**colofonía o pez rubia**) **y líquido** (**aguarrás o esencia de trementina**), que tienen diferentes usos en la industria.





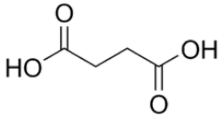
FORMACIÓN DE RESINAS FÓSILES



RESINA → COPAL → ÁMBAR

Tiempo (millones de años)

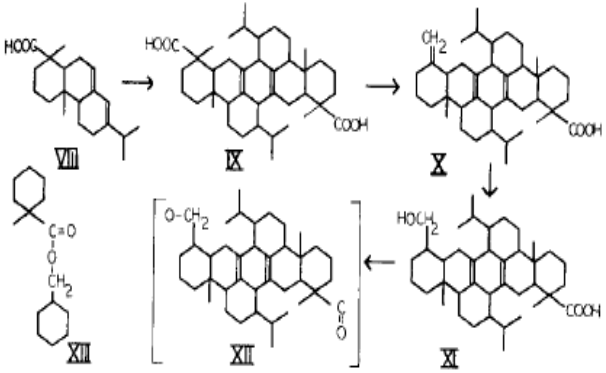
- La **Resina** sufre un proceso de polimerización y se transforma en **Copal**, reacciones posteriores entre las cadenas de moléculas producen el **Ámbar**.
- El **Copal** es una resina del mismo origen que el Ámbar pero que va de semifósil (Pleistoceno, Mioceno) a las resinas actuales.
- El Copal tarda decenas de millones de años para cambiar a **Ámbar**. De todos los ámbares, el del Báltico es el más importante, con una presencia de ácido succínico en proporción del 3 al 8 por ciento, ha dado lugar a diferentes opiniones sobre si el auténtico ámbar debería ser sólo aquel que contuviera ácido succínico o no.

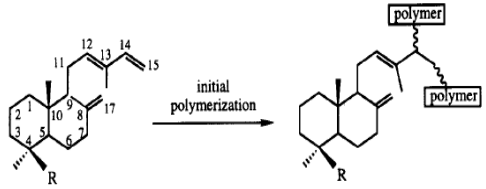


- Actualmente se tiende a dividir las resinas fósiles en **succinitas**, con ácido succínico, y **retinitas** sin ácido succínico, y a todas ellas si son fósiles se les considera ámbar.
- Es frecuente que algunos ámbares lleven sulfuros (pirita) o calcita.

- 1º pérdida de la fracción más volátil.

- Se piensa que durante la formación del ámbar, dos procesos químicos están presentes: reacciones de **condensación** alquílicas (Dields-Alder) y **polimerizaciones tipo vinílicas**.



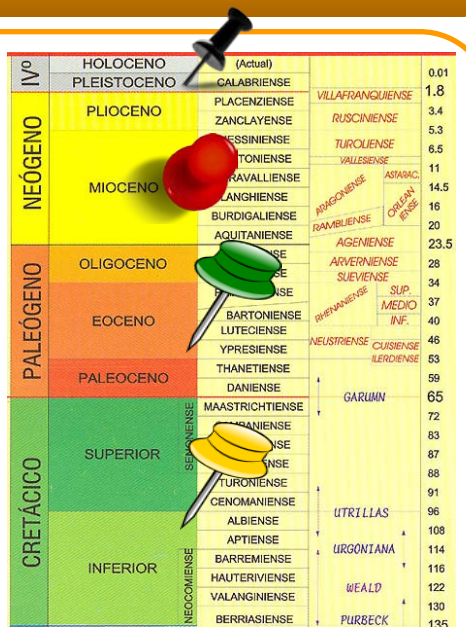


(1a) Communic acid (R = CO_2H)
(1b) Communol (R = CH_2OH)
(1c) Biformene (R = CH_3)

(1d) 14,15-polylabdatriene

Fig. 1. Polymerization of the labdatrienes communic acid (a), communol (b), and biformene (c) yielding a 14,15-polylabdatriene polymer (d).

YACIMIENTOS DE ÁMBAR (Origen geográfico)



- El ***Ámbar de Canadá*** (Chemawinita o Cedarita) es de color marrón. Es muy antiguo, se cree procede de coníferas del Cretáceo (60 a 130 millones de años). Es también retinita.
- El ***Ámbar de España*** puede ser de yacimientos del Cretácico en Álava, Teruel y Cantabria, este último (cerca de la cueva de El Soplao) descubierto en 2007, de alrededor de hace 100 millones de años y de gran interés por la cantidad de insectos y artrópodos (arañas) incluidos. Los **otros yacimientos** de Ámbar del Cretácico tanto en España como en el resto de los países donde se han encontrado (Líbano, Israel, Jordania, oeste de Francia, sur de Gran Bretaña, Noreste de España) no tienen tantos insectos. Se ha encontrado también un raro Ámbar azul de este período, las mejores piezas son las que se formaron de forma subaérea (en cavidades dentro del tronco).
- El ***Ámbar del Báltico o Succino***, de los primeros yacimientos conocidos y de los más importantes. Procede de las costas de Dinamarca, Suecia, norte de Alemania, Polonia y parte de Rusia. La mayor parte se recoge del mar, flotando o en el fondo y en menor proporción en excavaciones o minas. Suele ser de color amarillo miel a pardo, a veces con tonos rojizos anaranjados y hasta casi blancos, transparentes o nebulosos. Procede de coníferas del Eoceno (40 a 60 millones de años). Es el de mayor proporción de ácido succínico, del 3 al 8 por ciento, por tanto es succinita. Su uso y comercio se remonta hasta la prehistoria.
- El ***Ámbar de Myanmar (antigua Birmania)***, llamado Burmita, es de colores fuertes, principalmente marrón oscuro y algo turbios. Es succinita por llevar un 2 por ciento de ácido succínico. Muy fluorescente. Lleva frecuentemente calcita en el interior de las fisuras y le da una apariencia moteada característica. Procede de burseráceas del Eoceno (40 a 60 millones de años).
- El ***Copal de Rumanía (Rumanita)*** es muy rico en colores: pardo amarillento a marrón profundo, granate, verdoso y casi negro. Lleva gran cantidad de sulfuros que le proporcionan el color característico. La proporción de ácido succínico es del 1 al 5 por ciento, es succinita. Se originó en el Mioceno a partir de leguminosas (10 a 25 millones de años).
- El ***Copal de Sicilia (Simetita,*** nombre derivado de su lugar de origen, el río Simeto), es uno de los más bellos. De color rojo oscuro, azulado, verdoso, y raramente amarillo. Suele ser transparente. No lleva ácido succínico, es retinita; pero tiene gran cantidad de sulfuros. Procede de burseráceas del Mioceno (10 a 25 millones de años).
- El ***Copal de México***, se presenta en el Distrito de Chiapas. Tonos de rojo, amarillo y casi negro. Es una retinita procedente de leguminosas (Hymenaea) del Mioceno.
- El ***Copal de la República Dominicana*** es de color amarillo pálido a marrón, raramente rojo, a veces azul, que es el más apreciado. Muy fluorescente a la luz UV. Procede de leguminosas tipo algarrobo, del Mioceno (10 a 25 millones de años). No tiene ácido succínico, es retinita.
- ***Otros yacimientos más jovenes*** se encuentran también en EE.UU., Japón, Tanzania (Copal joven procedente del Pleistoceno, 1 a 10 millones de años), y en Nueva Zelanda (Ambrita).

ESTUDIOS PREVIOS DE TERPENOS A ALTA PRESIÓN

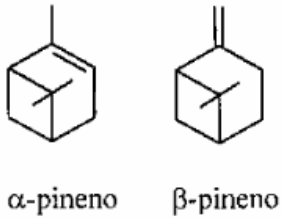
(…) Isoprene is polymerized to rubber (…)

Conant, J. B., Tongberg, C. O. Polymerization reactions under high pressure. I. Some experiments with isoprene and butyraldehyde. J. Am. Chem. Soc. 52, 1659 (1930).

> 1,2 GPa

Studies in the Terpene Series. XVIL. The Thermal Isomerization of Pinane at High Pressure

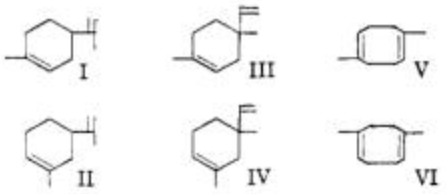
Ipatieff et al. Studies in the Terpene Series. XVIL. The Thermal Isomerization of Pinane at High Pressure. J. Am. Chem. Soc. (1953)



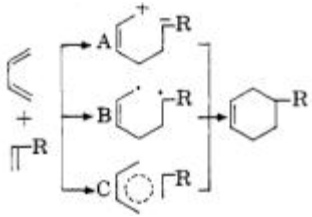
400 ºC; 80 MPa

Organic Reactions Under High Pressure. IV. The Dimerization of Isoprene

C. Walling and J. Peisach. Organic Reactions Under High Pressure. IV. The Dimerization of Isoprene. J. Am. Chem. Soc. (1958)

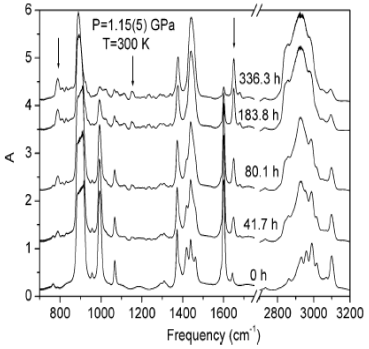


> 1,2 GPa



Dimerization and Polymerization of Isoprene at High Pressures

Citroni, M; Ceppatelli, M; Bini, R, et al. Dimerization and Polymerization of Isoprene at High Pressures. J. Phys. Chem. B 2007, 111, 3910-3917



< 2,6 GPa

Figure 1. IR spectra recorded during the room temperature reaction of isoprene at 1.15 GPa. The first spectrum (0 h) of the kinetics is entirely due to the monomer and is measured just after the pressure of the experiment has been set. The arrows indicate the absorption bands of the product that do not overlap with monomer peaks.

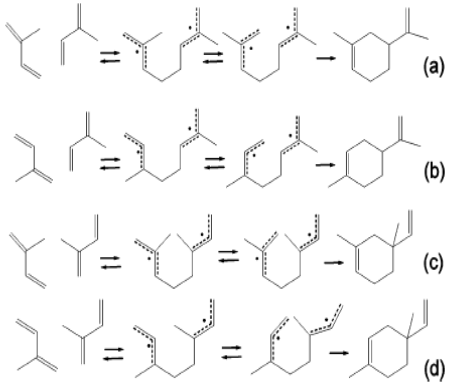


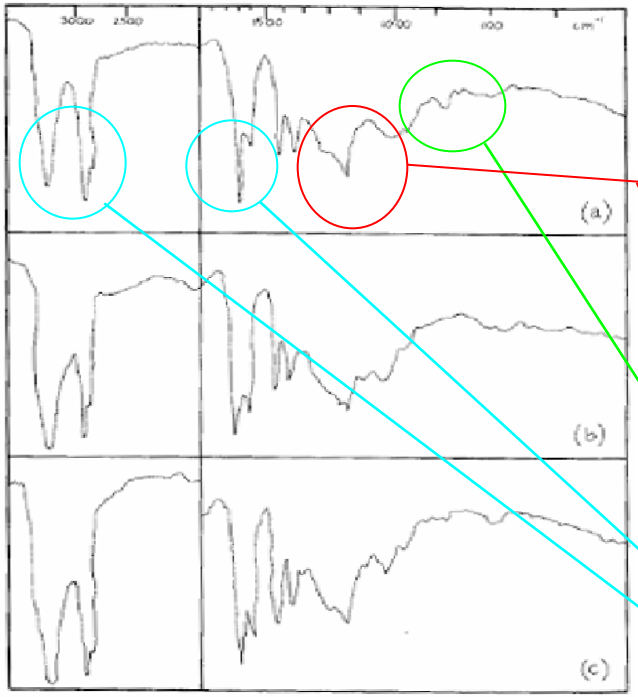
Figure 12. Possible dimerization paths leading, from top to bottom, to sylvestrene (a), limonene (b), 4-ethenyl-2,4-dimethylcyclohexene (c), and 4-ethenyl-1,4-dimethylcyclohexene (d).

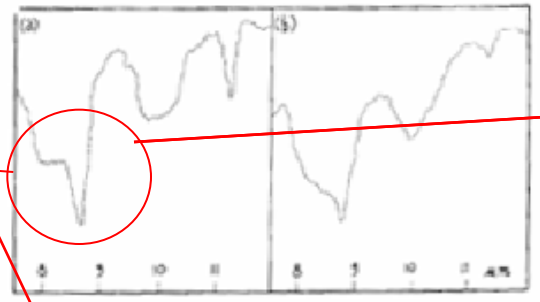
ESPECTROSCOPIA DEL ÁMBAR (I)

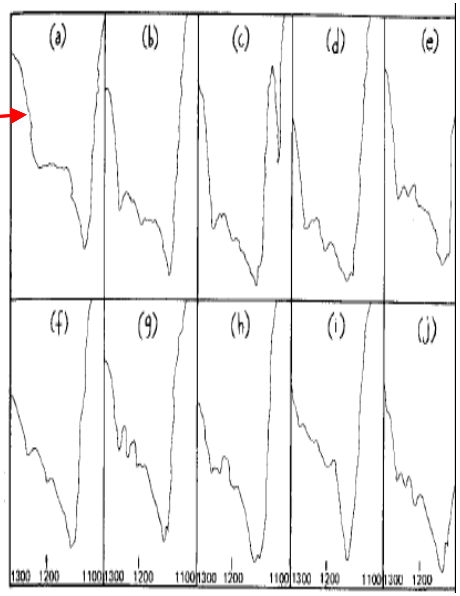
TRANSFORMACIONES MOLECULARES COMUNES DEPENDIENTES DEL TIEMPO ACAECIDAS EN LAS RESINAS FÓSILES

(1) Pérdida progresiva de dobles enlaces olefínicos (especialmente los enlaces exocíclicos).
(2) Desaparición de grupos funcionales (oxidación extrema).
(3) Incremento proporcional de componentes aromatizados, pero muy lejos en proporción con los porcentajes encontrados en maderas fosilizadas o incluso en bancos de carbón.

"Spectroscopic Investigations of Amber". C. W. Beck. Applied Spectroscopy Reviews, 1520-569X, Volume 22, Issue 1, 1986, Pages 57–110





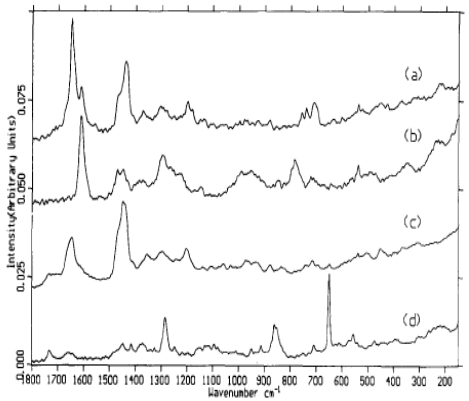


- 1150 cm^{-1}, deformación del enlace simple C-O, precedido por un hombro ancho entre 1250-1175 cm^{-1}.

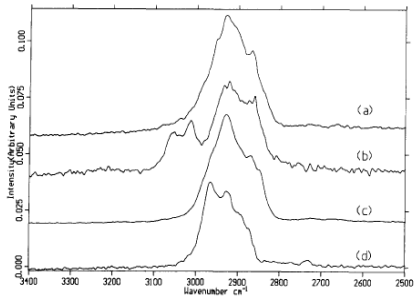
- 890 cm^{-1} deformaciones fuera del plano de dialquiletilenos asimétricos, $CR_2=CH_2$ (dobles enlaces exocíclicos); 1650 cm^{-1}, bandas de tensión C=C no conjugados; 3095 cm^{-1} bandas de tensión C-H.

ESPECTROSCOPIA DEL ÁMBAR (II)

"Fourier transform-Raman spectroscopy of amber". H. G. M. Edwards, D. W. Farwell. Spectrochimica Acta Part A 52 (1996) 1119-1125



Se comparan ámbares de diferentes tipos, que aunque tienen un espectro Raman similar en la región de 2000-3000 cm^{-1}, al compararlos con los de resina de pino contemporánea, se observa a 3020 cm^{-1} las bandas de alargamiento *v(CH,* stretching), debidas al enlace del grupo C=CH- que está ausente en las muestras de resinas fosilizadas.



Asignaciones vibracionales del ámbar

Table 1
Wavenumbers/cm^{-1} and vibrational assignments for amber

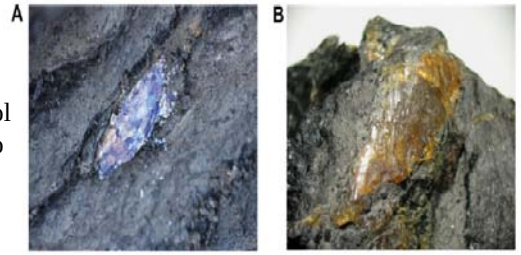
$\tilde{\nu}$/cm^{-1}	Approximate assignment of vibrational mode
2965 m, sh	$\nu(CH_3)$ stretching
2930 s	$\nu(CH_2)$ stretching
2892 m, sh	$\nu(CH_2)$ stretching
2871 ms	$\nu(CH_3)$ stretching
2850 m, sh	$\nu(CH_3)$ stretching
2728 w	$\nu(CH_1-CH_2)$ terminal
1734 mw	ν(C–O) stetching ester
1646 ms	ν(C=C) stetching
1610 m, w, sh	ν(C=C) stetching
1450 s	$\delta(CH_2)$ deformation
1420 w	
1356 m	$\delta(CH_3)$ deformation
1298 m	$\delta(CH_2)$ twisting
1245 w	
1205 m	
1143 w	
1108 w	ν(C–C)
1060 w	ν(C–C); ν(C–O)
1034 w	ν(C–O)
1014 vw	ν(C–O)
976 m, br	$\rho(CH_2)$
938 mw, br	$\rho(CH_3)$
881 mw	ν(COC)
838 mw, br	
742 w	
718 m	
696 w	
651 mw	ν(C–S) stretching
540 w	ν(COC) in-plane deformation
504 m, br	ν(S–S) stretching; ν(COC)
454 m, br	δ(CCO)
375 w	δ(CCC)
310 w	τ(CCO)

ÁMBAR DE LA CUEVA DEL SOPLAO-Patrimonio

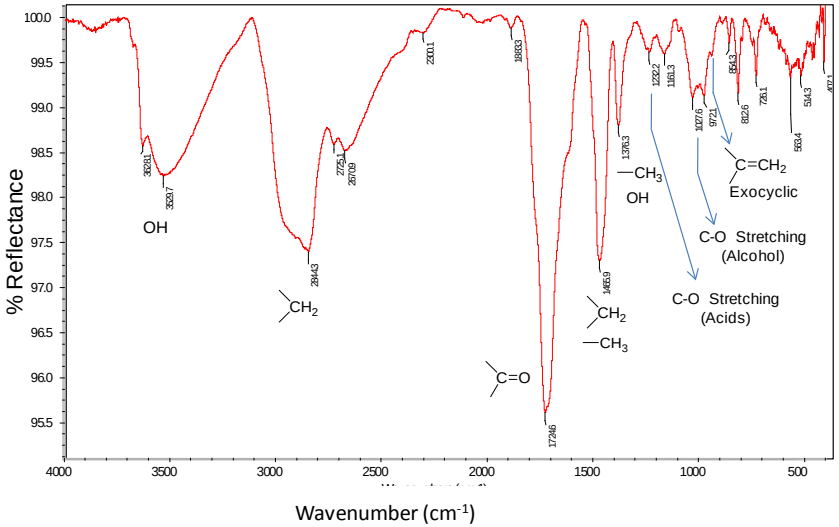
"Terpenoids in extracts of Lower Cretaceous ambers from the Basque-Cantabrian Basin (El Soplao, Cantabria, Spain): Paleochemotaxonomic aspects". C. Menor-Salván, M.Najarro, F. Velasco, I.Rosales, F. Tornos, Bernd R. T. Simoneit. Organic Geochemistry xxx (2010) xxx–xxx. In Press.

2 tipos de ámbar de diferente origen biológico

Terpenoides fenólicos:
- Ferruginol, Totarol y Hinokiol
- Ácidos pimárico e isopimárico
- Azulenos



- Ácidos pimárico e isopimárico
- Ausencia de terpenos fenólicos

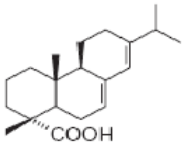


El FTIR de ambos tipos de ámbar encontrados tiene espectros similares.

COMPUESTOS DE INTERÉS PARA POLIMERIZAR A A. P.

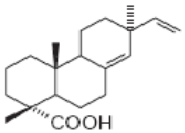
DITERPENOS

Abietane Type



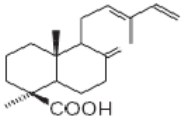
Abietic acid

Pimarane Type

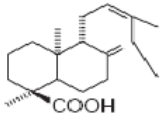


Pimaric acid

Labdane Type

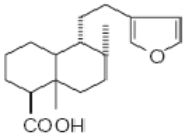


Communic acid



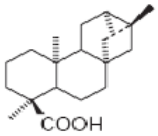
Ozoic acid

Clerodane Type



Hardwickiic acid

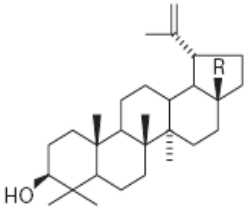
Kaurane Type



Trachylobanic acid

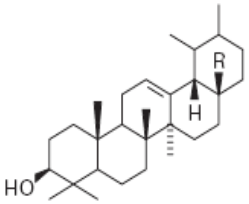
TRITERPENOS

Lupane Type



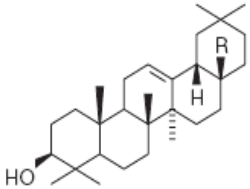
R = CH_3 Lupeol
R = CH_2OH Betulin
R = COOH Betulinic acid

Ursane Type



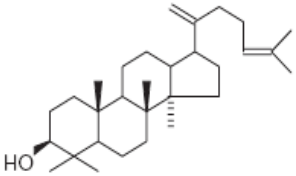
R = CH_3 α-Amyrin
R = COOH Ursolic acid

Oleanane Type



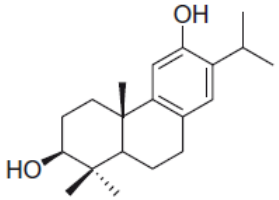
R = CH_3 β-Amyrin
R = COOH Oleanolic acid

Dammarane Type

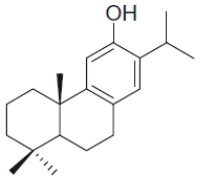


Dammaradienol

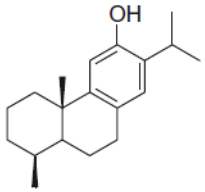
TERPENOS FENÓLICOS



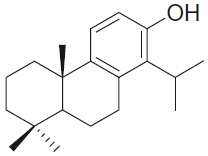
XII. Hinokiol



Ferruginol



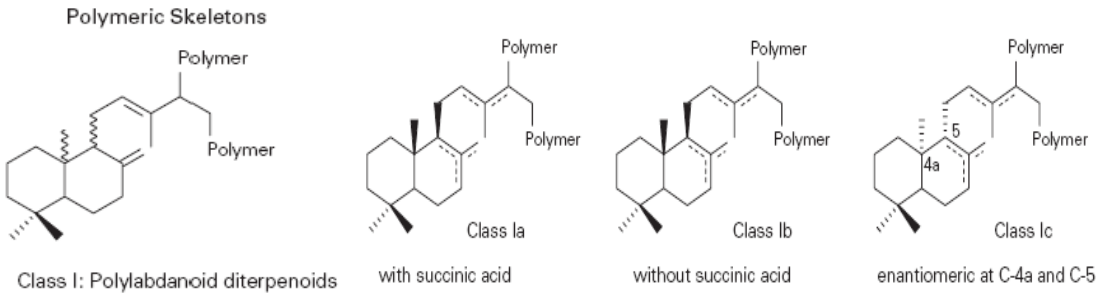
XIV. 18-Norferruginol

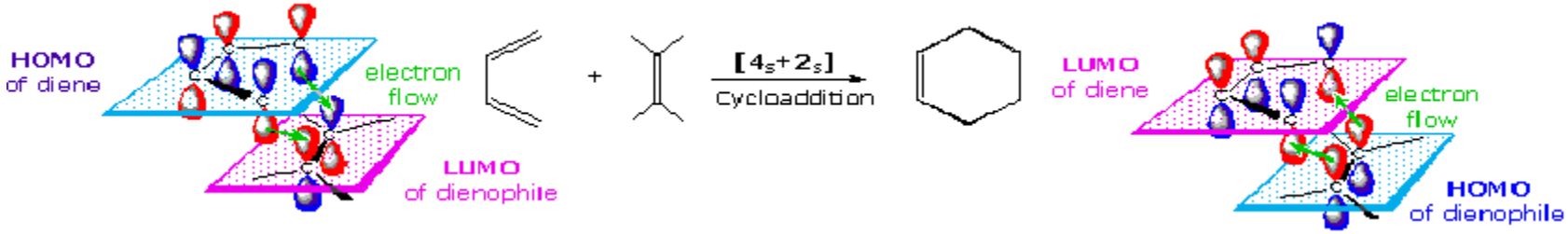


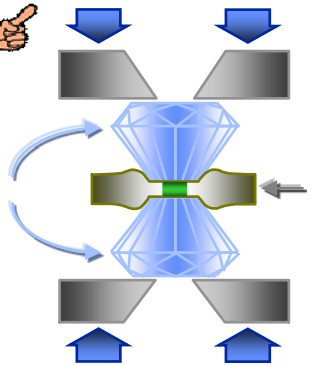
Totarol

ESTRATEGIAS PARA LOS EXPERIMENTOS

REACCIONES DIELDS-ALDER Y VINÍLICAS







- ¿Qué λ del láser usar?
- ¿Hasta qué presiones llegar?
- ¿Qué tipo de yunques usar?
- ¿Evitar la luminiscencia o realizar medidas de ellas?
- ¿Cómo utilizar el ámbar sin ir en contra del Código Penal?

"gracias por la atención"

QUIMAPRES

CONSOLIDER MALTA

Matter at High Pressure

PROGRAMA ingenio 2010

Óscar Rodríguez Montoro
UNIVERSIDAD COMPLUTENSE DE MADRID
Departamento de Química-Física I. Universidad Complutense de Madrid

Funciones de Distribución del Número de Electrones (EDF): Conexión con los orbitales del hueco de Fermi promediado en un dominio del espacio real (DAFH)

The Journal of Chemical Physics **131**,124125 (2009)

E. Francisco, A. Martín Pendás y M. A. Blanco
Universidad de Oviedo

Contenido

1. Introducción
2. Metodología
3. Resultados y discusión
4. Resumen y conclusiones

I. Introducción

- La obtención de información química relevante a partir de Ψ
  PROBLEMA NO TRIVIAL. La dificultad $\uparrow$ al $\uparrow$ la complejidad de Ψ.
- De entre los muchos métodos desarrollados ...
  - Funciones de Distribución del Número de Electrones (EDF)
    Si $\Omega_1 + \Omega_2 + \ldots \Omega_m = \mathcal{R}^3, \quad \Omega_k \cap \Omega_{l \neq k} = \emptyset, \quad n_1 + n_2 + \cdots + n_m = N$
    EDF $= \{P(n_1, n_2, \ldots, n_m\} = \{P(S)\}$ donde
    $P(S) =$ Probabilidad de hallar n_1 e^- en Ω_1, n_2 en Ω_2,..., n_m en Ω_m.
    Las EDFs son útiles para ...
    - ⋆ Aditividad aproximada de las propiedades de grupos funcionales.
    - ⋆ Particiones energéticas.
    - ⋆ Definir nuevos conceptos (e.g. Est. resonantes en el espacio real, RSRS).
    - ⋆ Clasificación de enlaces químicos
    - ⋆ Caminos de enlace $\equiv$ canales privilegiados de intercambio mecano-cuántico.
  - Domain Averaged Fermi Hole (DAFH) analysis (Robert Ponec)
    $\rho^{\text{hole}}(\boldsymbol{r}|\boldsymbol{r}_1) \longrightarrow \langle \boldsymbol{r}_1 \rangle_\Omega \longrightarrow G^\Omega(\boldsymbol{r}) \Rightarrow$
    Muy útil para entender/interpretar differentes aspectos de la naturaleza del enlace químico, e.g.
    - ⋆ Moléculas hipervalentes y/o ricas en electrones.
    - ⋆ Moléculas recién sintetizadas.
    - ⋆ Estructura de MOX_4 (M=Os,Ru; X=F,Cl,Br,I).
    - ⋆ Enlace metal-metal en $Re_2Cl_8^{2-}$ ...

I. Introducción

Objetivos de este trabajo:

- Establecer la conexión entre EDF & DAFH.
- Análisis del enlace en ejemplos sencillos.

Condiciones:

- $\Psi(1,N) = \det\left[\varphi_1(1)\varphi_2(2)\ldots\varphi_N(N)\right]$.
- $\mathcal{R}^3 = \Omega + \Omega'$ (QTAIM)

II. Metodología: A. DAFH

- $\rho^{\text{hole}}(\boldsymbol{r}_2|\boldsymbol{r}_1) = \rho(\boldsymbol{r}_2) - \frac{\rho_2(\boldsymbol{r}_1,\boldsymbol{r}_2)}{\rho(\boldsymbol{r}_1)} \Rightarrow \rho^{\text{hole}}_{\Omega}(\boldsymbol{r}_2) = \rho(\boldsymbol{r}_2) - \frac{\int_\Omega \rho_2(\boldsymbol{r}_1,\boldsymbol{r}_2)d\boldsymbol{r}_1}{\int_\Omega \rho(\boldsymbol{r}_1)d\boldsymbol{r}_1}$

  DAFH $\equiv G^{\Omega}(\boldsymbol{r}) = N_\Omega \rho^{\text{hole}}_{\Omega}(\boldsymbol{r}) = \int_\Omega \rho_2^{\text{xc}}(\boldsymbol{r}_1,\boldsymbol{r})d\boldsymbol{r}_1 = \sum_{i,j}^{N} \varphi_i(\boldsymbol{r})\langle\varphi_i|\varphi_j\rangle_\Omega \varphi_j^\star(\boldsymbol{r})$.
- $G^{\Omega}(\boldsymbol{r}) = \sum_{i,j}^{N} \varphi_i(\boldsymbol{r})\mathbf{S}_{ij}\varphi_j^\star(\boldsymbol{r}) = \boldsymbol{\varphi}\mathbf{S}\boldsymbol{\varphi}^\dagger$, donde $\mathbf{S} \equiv \langle\boldsymbol{\varphi}|\boldsymbol{\varphi}\rangle_\Omega$.
- $G^{\Omega}(\boldsymbol{r})$ tiene muchas propiedades importantes.
- Diag $\mathbf{S} \Rightarrow \mathbf{U}$ y $\mathbf{n}$. $\Rightarrow$ DAFH MOs $\boldsymbol{\phi} = \boldsymbol{\varphi}\mathbf{U}$ & $G^{\Omega}(\boldsymbol{r}) = \sum_{i=1}^{N} n_i|\phi_i(\boldsymbol{r})|^2$.
- $\langle\phi_i|\phi_j\rangle_{\mathcal{R}^3} = \delta_{ij} \quad \langle\phi_i|\phi_j\rangle_\Omega = \delta_{ij}\, n_i \quad (\star) \quad \langle\phi_i|\phi_j\rangle_{\Omega'} = \delta_{ij}\,(1-n_i)$.
- $\Psi(1,N)$ es invariante frente a $\mathbf{U}\Rightarrow$
  $\Psi(1,N) = \det\left[\varphi_1(1)\varphi_2(2)\ldots\varphi_N(N)\right] = \det\left[\phi_1(1)\phi_2(2)\ldots\phi_N(N)\right]$.
- $\rho(\boldsymbol{r}) = \sum_i^N |\phi_i(\boldsymbol{r})|^2$, ¡¡Cada ϕ_i contribuye con un e$^-$ a ρ!!
- A partir de $(\star) \Rightarrow n_i =$ Probabilidad de hallar el e$^-$ descrito con ϕ_i en Ω
  $=$Fracción del e$^-$ descrito con ϕ_i contenido en Ω

II. Metodología: B. EDF

- La probabilidad de que exactamente n electrones estén en Ω y $N-n$ en Ω' es:

$$\begin{aligned} p^{\Omega}(n) &= \frac{N!}{n!(N-n)!}\int_{\Omega} d\boldsymbol{r}_1\cdots d\boldsymbol{r}_n \int_{\Omega'} d\boldsymbol{r}_{n+1}\cdots d\boldsymbol{r}_N\,|\Psi|^2 \qquad (1)\\ &= \frac{1}{n!(N-n)!}\sum_{\boldsymbol{q}\in \mathrm{perm}(1,\cdots,N)} \det[\tilde{\mathbf{S}}_{ij}(q_j)], \end{aligned}$$

donde $\tilde{\mathbf{S}}_{ij}(q_j) = \begin{cases} \langle\phi_i|\phi_j\rangle_{\Omega} = \delta_{ij}n_i & 1\le q_j\le n \\ \langle\phi_i|\phi_j\rangle_{\Omega'} = \delta_{ij}(1-n_i) & n+1\le q_j\le N \end{cases}$

- ¡¡ $\tilde{\mathbf{S}}$ es diagonal en la base DAFH !!
- Si $\boldsymbol{p}_1^i = (n_i, 1-n_i) \Rightarrow \{p^{\Omega}(n), n=0,1,\ldots,N\} \equiv \boldsymbol{p}_N = \otimes_{i=1}^{N}\boldsymbol{p}_1^i$.

CONCLUSIÓN: Si Ψ = Det(Slater) $\Rightarrow$Los electrones son estadísticamente independientes cuando son descritos con los MO's que diagonalizan el Hueco de Fermi.

II. Metodología

EJEMPLO ($N = 3 \Rightarrow$ 4 posibilidades)

$\otimes_{i=1}^{3} \boldsymbol{p}_1^i = (n_1, 1-n_1) \otimes (n_2, 1-n_2) \otimes (n_3, 1-n_3) = (p^\Omega(3), p^\Omega(2), p^\Omega(1), p^\Omega(0))$:

$$
\begin{aligned}
p^\Omega(3) &= n_1 n_2 n_3 \\
p^\Omega(2) &= n_1 n_2 (1-n_3) + n_1 (1-n_2) n_3 + (1-n_1) n_2 n_3 \\
p^\Omega(1) &= n_1 (1-n_2)(1-n_3) + (1-n_1) n_2 (1-n_3) + (1-n_1)(1-n_2) n_3 \\
p^\Omega(0) &= (1-n_1)(1-n_2)(1-n_3)
\end{aligned}
$$

- $p^\Omega(3) =$ Producto de 3 eventos independientes.
- $p^\Omega(2) =$ Suma de 3 productos de 3 eventos independientes.
- $p^\Omega(1) =$ Suma de 3 productos de 3 eventos independientes.
- $p^\Omega(0) =$ Probabilidad de 3 eventos independientes.

Obviamente: Cada $p^\Omega(n)$ es invariante frente al intercambio de 2 electrones cualuesquiera.

II. Metodología: Indicadores químicos del enlace

- Índice de deslocalizacion (DI) Ω y Ω' $\sim$ Orden de enlace Ω y Ω'

$$\delta^{\Omega,\Omega'} = \sum_{i=1}^{N} 2n_i(1-n_i) = \sum_{i=1}^{N} \delta_i^{\Omega,\Omega'}$$

  - Los electrones contribuyen de manera independiente al enlace.
  - ϕ_i muy localizado en $\Omega(n_i \simeq 1)$ u Ω' $(n_i \simeq 0) \Rightarrow \delta_i \simeq 0$ (CORE).
  - Deslocalizacion apreciable en Ω y Ω' $(0 < n_i < 1) \Rightarrow \delta_i \neq 0$ (VALENCIA).
  - Igual deslocalizacion de ϕ_i en Ω y $\Omega'(n_i \simeq 0.5) \Rightarrow \delta_i^{\max} \simeq 0.5$.
- En capas cerradas cada ϕ_i está duplicado $\Rightarrow$

$$\delta^{\Omega,\Omega'} = \sum_{i=1}^{N/2} 4n_i(1-n_i) = \sum_{i=1}^{N/2} \delta_i^{\Omega,\Omega'}$$

El máximo valor posible de cada $\delta_i^{\Omega,\Omega'}$ es entonces 1.0.

III. Resultados y discusión

CASOS SENCILLOS

- Bien descritos con Ψ's monodeterminantales.
- Diagramas de orbitales moleculares LCAO conocidos.

SISTEMAS

- Moléculas diatómicas: H_2,He_2, Li_2, Be_2, (B_2,$^3\Sigma_u^+$), C_2, N_2, (O_2,$^3\Sigma_g^-$) y F_2.
- Hidruros: AH_n (A=Li,Be,B,C,N,O,F)

III. Resultados y discusión

molécula H_2

- $\boldsymbol{S}^{\alpha} = \boldsymbol{S}^{\beta} = \langle \sigma_g | \sigma_g \rangle_{\Omega} = 0.5$
- $(\phi_1^{\alpha} = \phi_1^{\beta} = \sigma_g)$ y $(n_1^{\alpha} = n_1^{\beta} = 0.5)$
- $(\delta_i^{\alpha} = \delta_i^{\beta} = 0.5)$

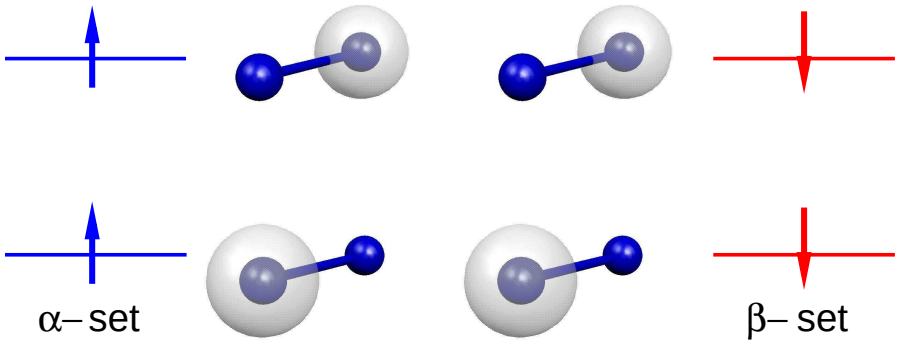
- El e$^-$ α no siente al β y *viceversa*
- En general, $\Psi =$ Det de Slater $\Rightarrow$ Bloques α y β son indep.

molécula He_2

- En este caso $\Rightarrow \boldsymbol{S}^{\alpha} = \boldsymbol{S}^{\beta} =$

$$\begin{pmatrix} \langle \sigma_g | \sigma_g \rangle_{\Omega} & \langle \sigma_g | \sigma_u \rangle_{\Omega} \\ \langle \sigma_u | \sigma_g \rangle_{\Omega} & \langle \sigma_u | \sigma_u \rangle_{\Omega} \end{pmatrix}$$

- con $\langle \sigma_g | \sigma_g \rangle_{\Omega} = \langle \sigma_u | \sigma_u \rangle_{\Omega} = 0.5$ y $\langle \sigma_g | \sigma_u \rangle_{\Omega} = \langle \sigma_u | \sigma_g \rangle_{\Omega} \approx 0.5$.
- $n_1 \approx 0.0$, $n_2 \approx 1.0$
  $\Rightarrow \phi_1 = 1\sigma_g + 1\sigma_u = 1s_A$
  $\Rightarrow \phi_2 = 1\sigma_g - 1\sigma_u = 1s_B$,
  $\delta_1 = \delta_2 \approx 0.0$



III. Resultados y discusión

molécula Li_2

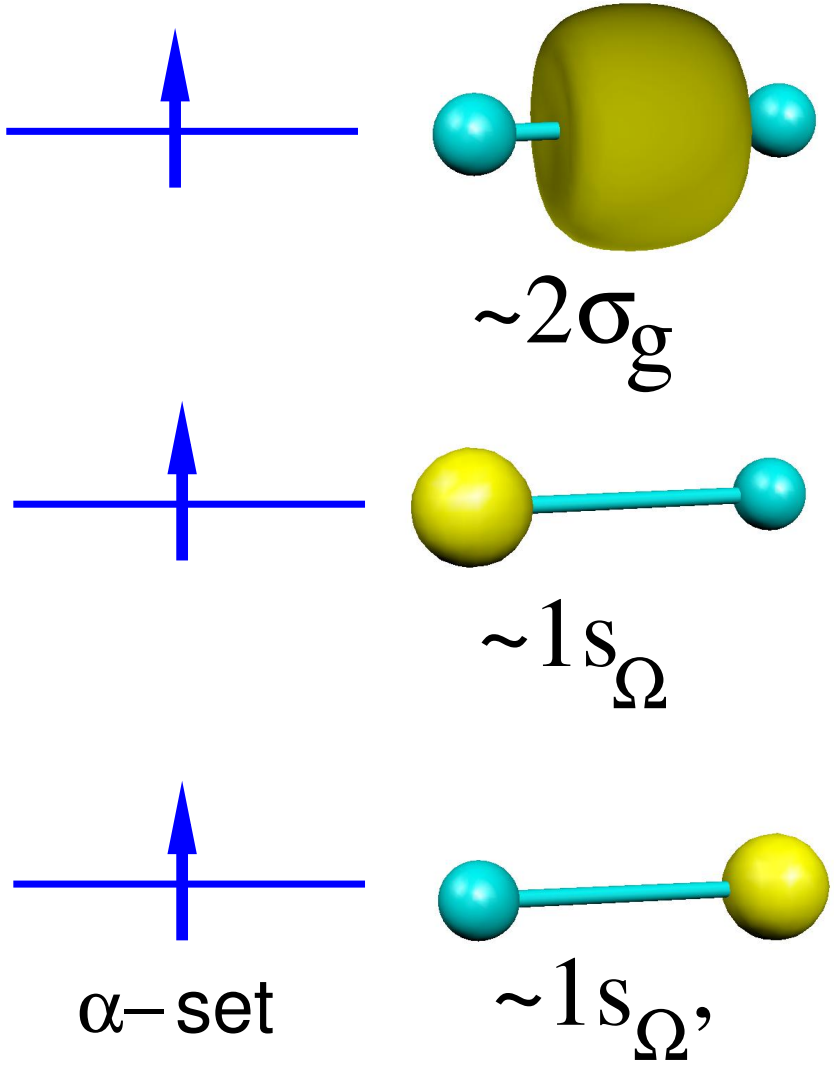
- $(3 \times 3)\boldsymbol{S}^{\alpha} = \boldsymbol{S}^{\beta}$, $1\sigma_g$,$1\sigma_u$,$2\sigma_g$.

$$\mathbf{S}^{\alpha} = \left(\begin{array}{cc|c} 0.5 & 0.5 & 0.0 \\ 0.5 & 0.5 & \simeq 0.0 \\ \hline 0.0 & \simeq 0.0 & 0.5 \end{array}\right)$$

-

	1	2	3
n_i	1.000	0.000	0.500
ϕ_i	$\approx 1s_A$	$\approx 1s_B$	$\approx 2\sigma_g$
δ_i	0.000	0.000	0.500

- 2 MO's son simétricos y casi completamente localizados en ambos núcleos de Li, y 1 MO deslocalizado por igual en ambos núcleos, $\delta \approx 1.0$.



III. Resultados y discusión

- molécula Be_2:Cualitativamente muy similar a He_2
  - ($\mathbf{S}^\alpha = \mathbf{S}^\beta = 4 \times 4$): $(1\sigma_g, 1\sigma_u) \rightarrow (1s_\Omega, 1s_{\Omega'})$ y $(2\sigma_g, 2\sigma_u) \rightarrow (2s_\Omega, 2s_{\Omega'})$.
- DAFH HF:H_2,Li_2 = Enlace sencillo, He_2,Be_2 = Enlace residual.
- molécula B_2: Capa abierta: ($\mathbf{S}^\alpha = 6 \times 6$, $\mathbf{S}^\beta = 4 \times 4$).
  - Bloques α y β diferentes
  -

	$n_1(\delta_1)$	$n_2(\delta_2)$	$n_3(\delta_3)$	$n_4(\delta_4)$	$n_5(\delta_5)$	$n_6(\delta_6)$
α	0.0 (0.0)	1.0 (0.0)	0.16 (0.26)	0.84 (0.26)	0.5 (0.5)	0.5 (0.5)
β	0.0 (0.0)	1.0 (0.0)	0.16 (0.26)	0.84 (0.26)		

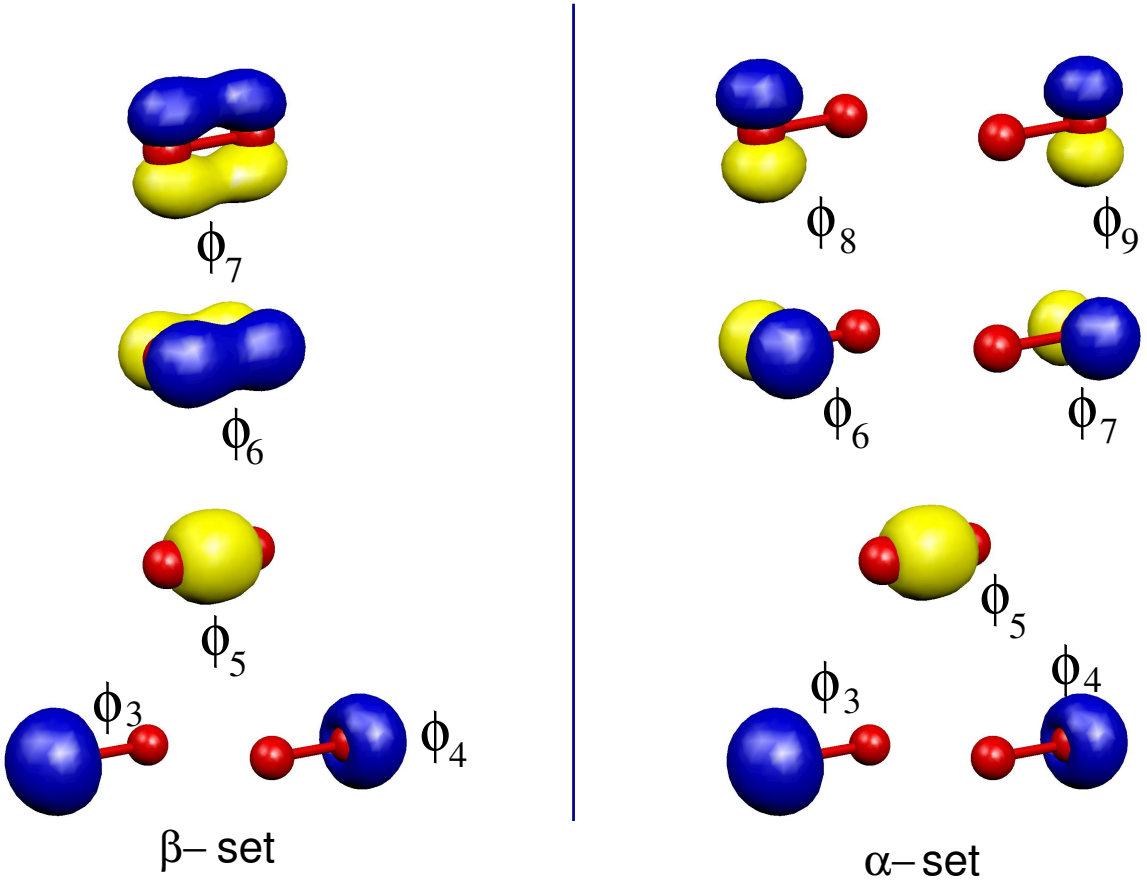
  - $\phi_{1,2} \simeq 1\sigma_g \pm 1\sigma_u \simeq (1s_\Omega, 1s_{\Omega'})$ $\quad \phi_{3,4} \simeq 2\sigma_g \pm 2\sigma_u + \epsilon(1\sigma_g \pm 1\sigma_u)$ $\quad$ (α y β).
  - $(\phi_5,\phi_6) = (1\pi_{ux}, 1\pi_{uy})$ Orbitales canónicos de HF
- molécula C_2 ($\mathbf{S}^\alpha = \mathbf{S}^\beta = 6 \times 6$)
  - Similar a B_2 añadiendo 2 e^- $\beta \Rightarrow (\phi_5,\phi_6) = (1\pi_{ux}, 1\pi_{uy}) \Rightarrow \delta \uparrow$ respecto a B_2.
- molécula N_2 ($\mathbf{S}^\alpha = \mathbf{S}^\beta = 7 \times 7$)
  -

$n_1(\delta_1)$	$n_2(\delta_2)$	$n_3(\delta_3)$	$n_4(\delta_4)$	$n_5(\delta_5)$	$n_6 = n_7$
0.0 (0.0)	1.0 (0.0)	0.01 (0.01)	0.99 (0.01)	0.5 (0.5)	0.5

  - $\phi_5 \simeq c_1 2\sigma_g + c_2 3\sigma_g$ $\quad (\phi_6,\phi_7) = (1\pi_{ux}, 1\pi_{uy})$ orbitales canónicos de HF, $\delta = 3.0$

III. Resultados y discusión

molécula O_2 (capa abierta) ($\mathbf{S}^{\alpha} = 9 \times 9$, $\mathbf{S}^{\beta} = 7 \times 7$).

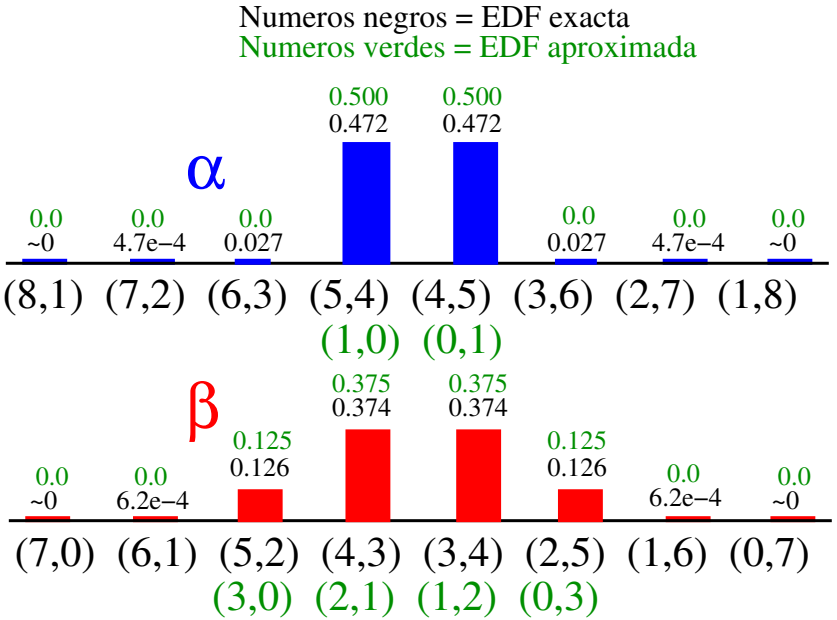


- $\beta \simeq N_2 \Rightarrow 3\ e^-$ (uno σ y 2 π) con máxima desloc. ($n_i = 0.5$).
- α: $\pi^1_{ux}\ \pi^1_{gx}\ \pi^1_{uy}\ \pi^1_{gy}$ Rep. Pauli entre (π_{ux},π_{gx}) y (π_{uy},π_{gy}) $\Rightarrow$ Localización.

III. Resultados y discusión

¿Cómo recuperar la EDF a partir de los n_i?

- Si $n_i \simeq 1.0 \Rightarrow \phi_i \in$ CORE de Ω o si $n_i \simeq 0.0 \Rightarrow \phi_i \in$ CORE de Ω', y pueden excluirse del cálculo de la EDF
$$\Rightarrow \boldsymbol{p}_N = \otimes_{i \in \text{deslocalizado}} \boldsymbol{p}_1^i.$$
- EDF completa $=$ Producto directo de las $\boldsymbol{p}_1^i$'s de valencia.
- Ejemplo, molécula O_2



- aprox EDF $\alpha = \boldsymbol{p}_1^5 = (0.5, 0.5)$
- aprox EDF $\beta = \boldsymbol{p}_1^5 \otimes \boldsymbol{p}_1^6 \otimes \boldsymbol{p}_1^7 = (0.5, 0.5) \otimes (0.5, 0.5) \otimes (0.5, 0.5) = (0, 0, 0.125, 0.375, 0.375, 0.125, 0, 0)$

Hidruros AH_n (A=Li,Be,B,C,N,O,F) (Capa cerrada)

- Diferentes definiciones de Ω y Ω' (excepto en LiH y FH),
- Nuestra elección Ω =H y Ω' =AH_{n-1}.
- Resultado: Todos los ϕ_i excepto ϕ_1 tienen $n_i \approx 0.0$
  $\Rightarrow$ ϕ_2,ϕ_3,$\cdots$ localizados en AH_{n-1}.
- Sólo el par (α, β) asociado a ϕ_1 está deslocalizado en Ω y Ω'.
-

	LiH	BeH_2	BH_3	CH_4	NH_3	H_2O	HF
n_1	0.9490	0.9129	0.8043	0.4890	0.3057	0.1880	0.1186
δ_1	0.0967	0.1591	0.3148	0.4998	0.4245	0.3053	0.2091
δ	0.1040	0.1859	0.4003	0.5560	0.4622	0.3278	0.2227

- El grado de localización de ϕ_1 en H decrece del LiH al HF:
  $\Rightarrow$ IMAGEN DAFH de enlace covalente polarizado sencillo entre Ω y Ω'.

IV. Resumen y conclusiones

- DAFH MO's para $\Psi(1,N)$ Det Slater $\Rightarrow$ Electrones estadísticamente independientes: $\{p^{\Omega}(n)\} \equiv \boldsymbol{p}_N = \otimes_{i=1}^{N} \boldsymbol{p}_1^i$.
- $n_i \neq$ Ocupación de ϕ_i sino que es la probabilidad de que un electrón descrito con ϕ_i esté en la región Ω
- DAFH MO's con $n_i \simeq 1$ ó $n_i \simeq 0$ están muy localizados en Ω u Ω' y no contribuyen al enlace, $\delta_i \simeq 0.0$, mientras que los MO's máximamente enlazantes ($\delta_i \simeq 0.5$) son los más deslocalizados en Ω y Ω' simultáneamente, $n_i \simeq 0.5$.

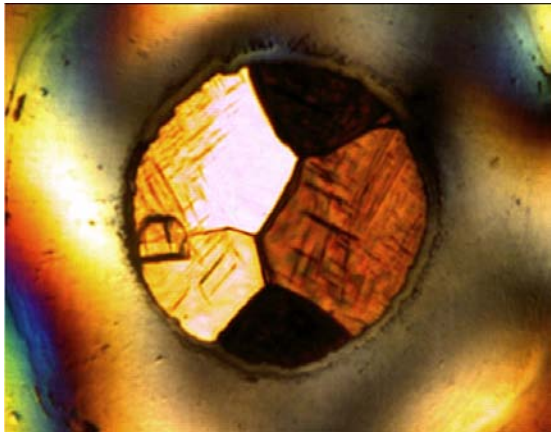
¿ Validez y posible extensión a $\Psi(1,N)$ Multi-Det ?

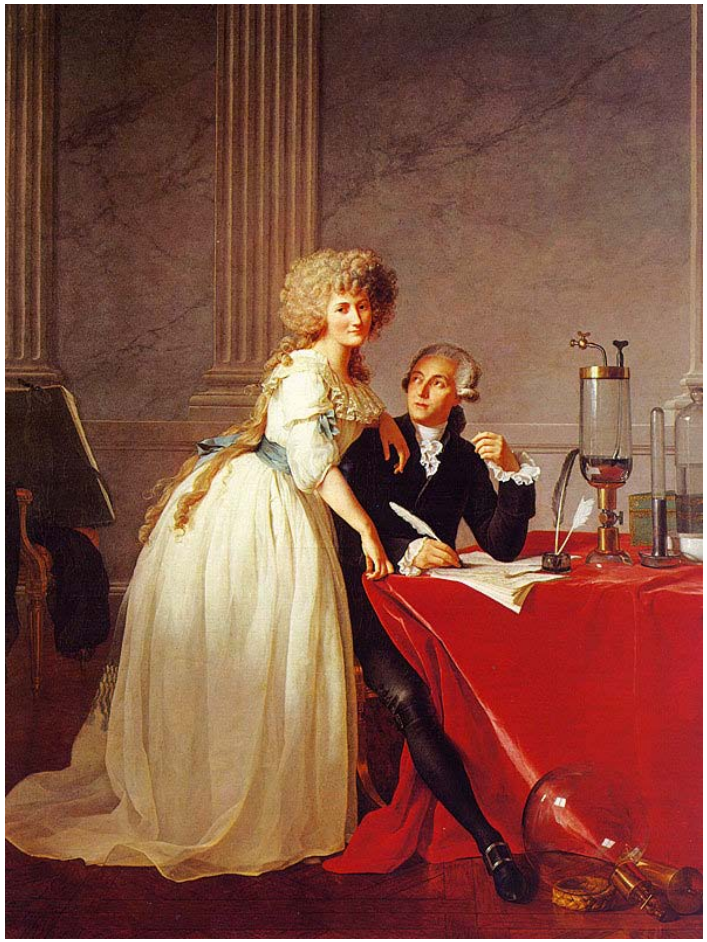
Magnetism in solid oxygen under pressure

Stefan Klotz

IMPMC

Université P&M Curie, Paris



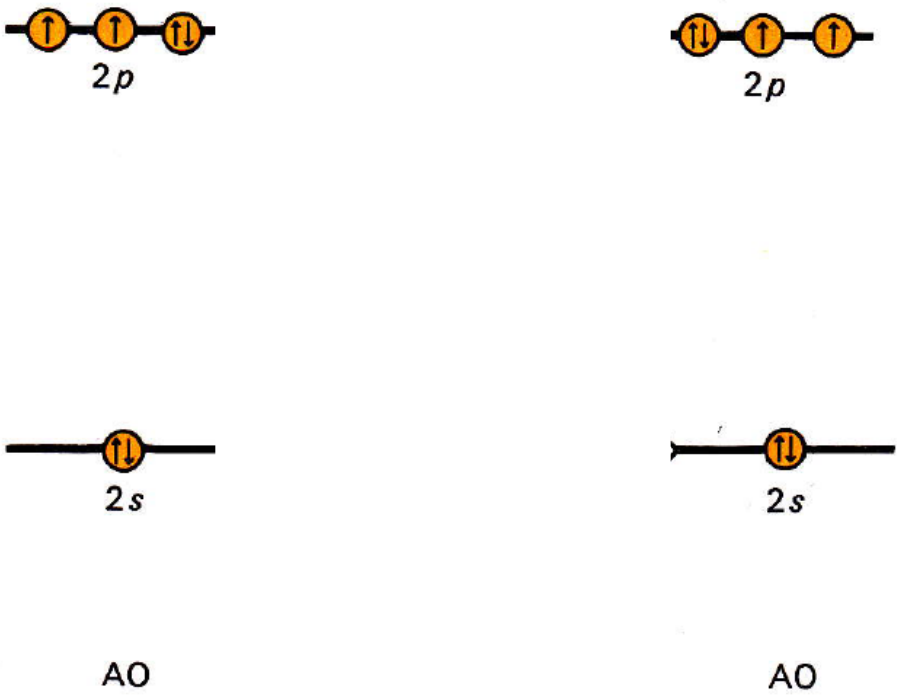


A.L. Lavoisier
(1743-1794)

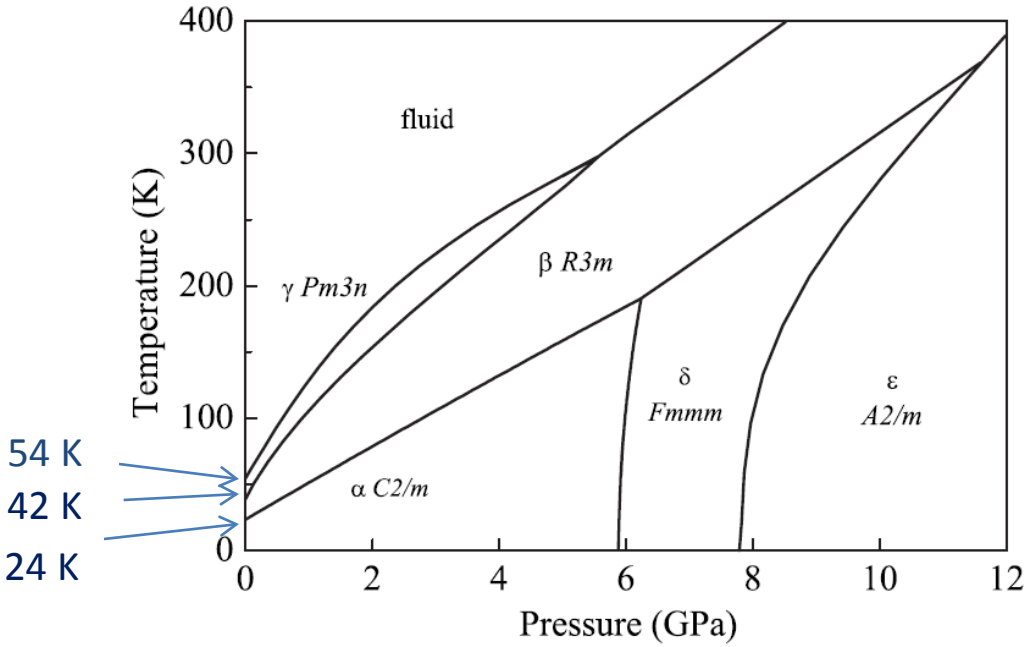
ὀξύς (oxys) -γενής (-genēs)

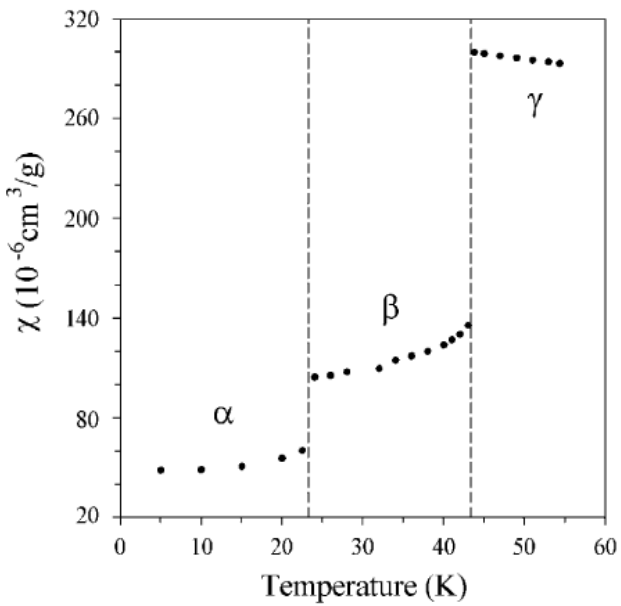
« acid former »

Oxygen

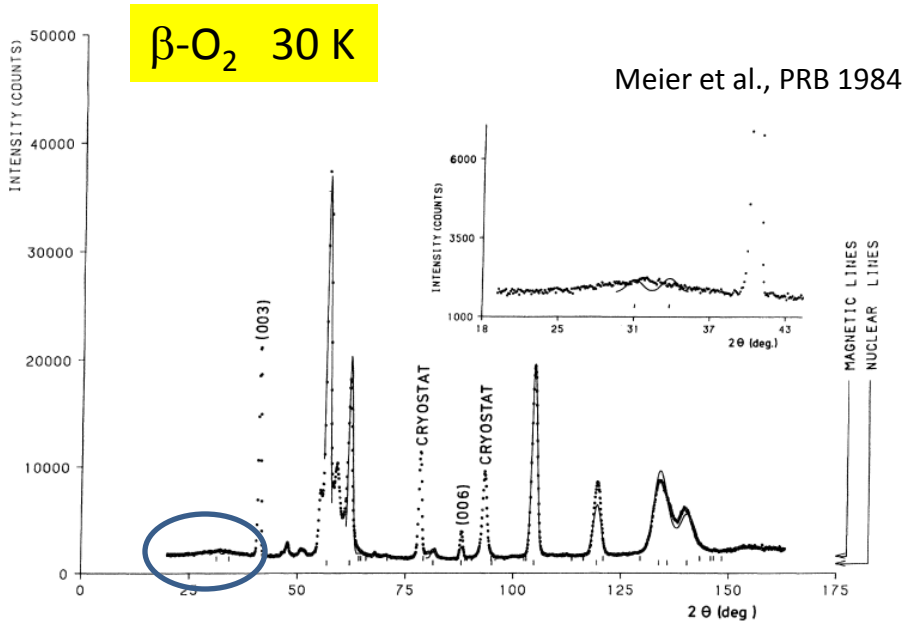


1848:	Faraday:	Paramagnetic nature of O_2
1910:	Kamerlingh Onnes:	Magn. suscept. of liquid and solid O_2
1963:	Alikhanov:	Magn. structure of solid O_2 (neutrons, 1 bar)
2004:	Goncharenko:	Mag. struct. of δ-O_2 under pressure (neutrons, 6 GPa)

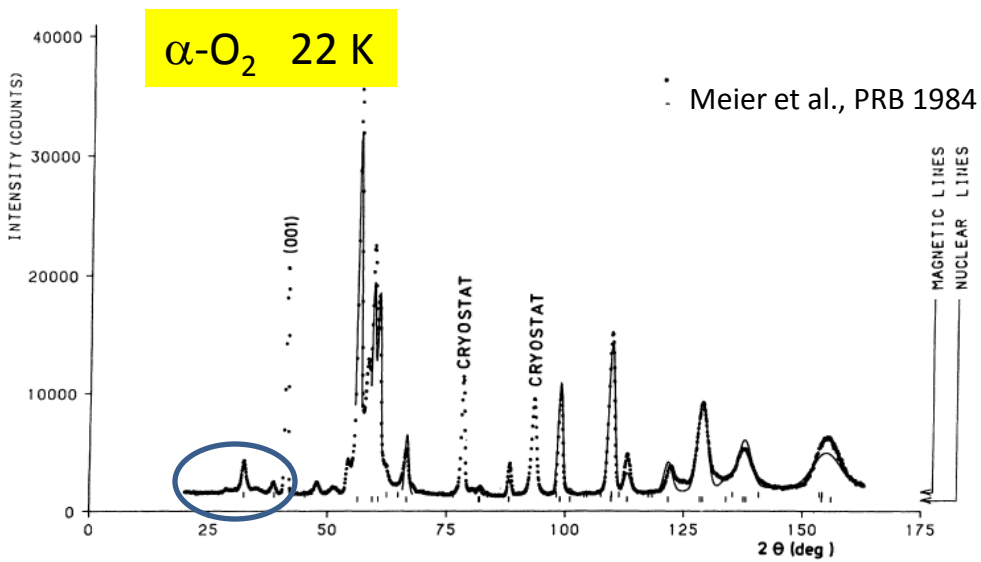

400
300
200
100
0
Temperature (K)
fluid
γ Pm3n
β R3m
δ
Fmmm
ε
A2/m
α C2/m
54 K
42 K
24 K
0
2
4
6
8
10
12
Pressure (GPa)


320
260
200
140
80
20
χ (10 -6cm 3/g)
γ
β
α
0
10
20
30
40
50
60
Temperature (K)

O_2 at 1 bar

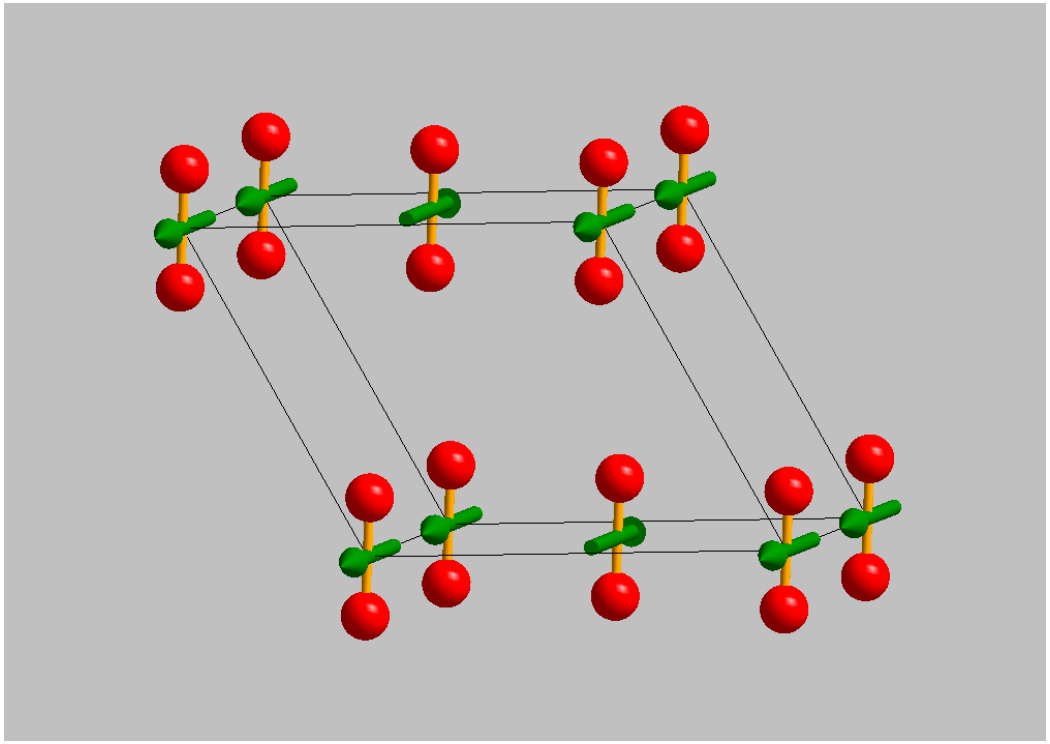


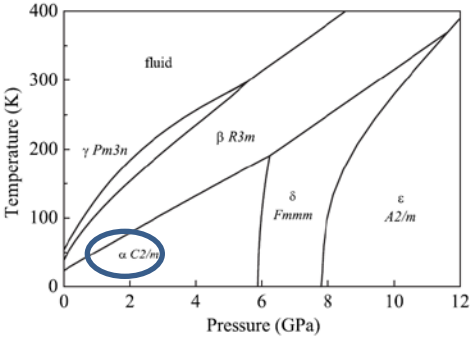
β: short-range ordered



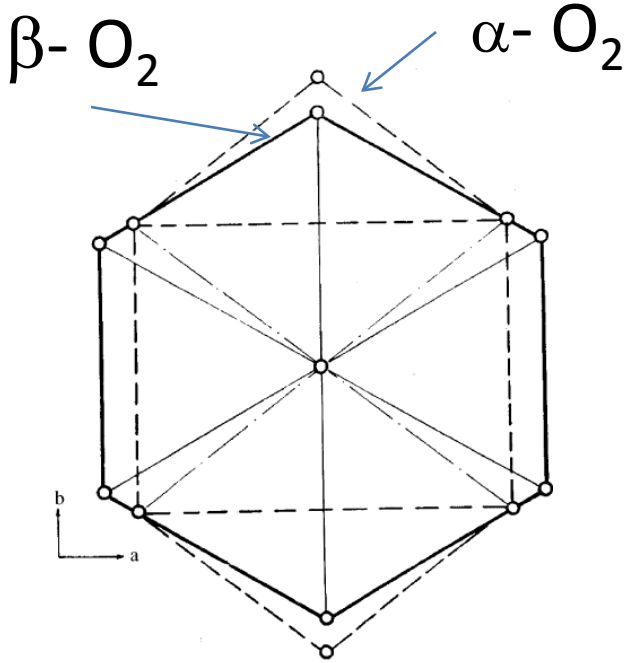
α: antiferromagnetic

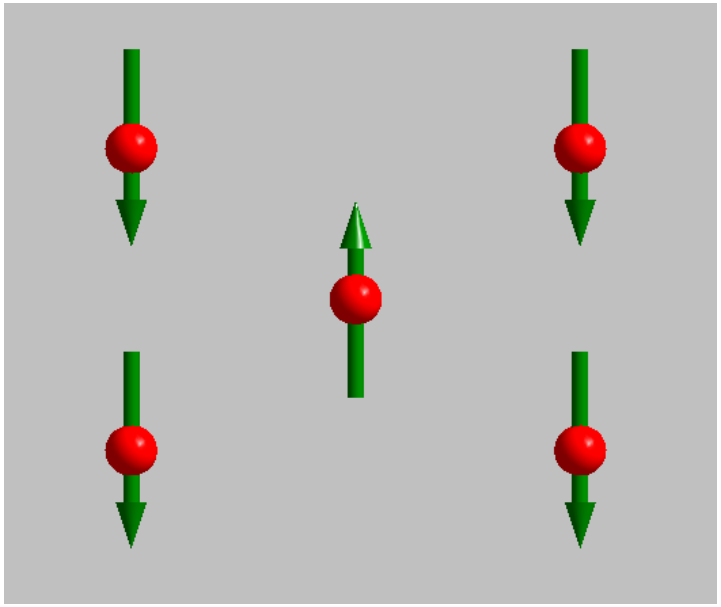
α- oxygen



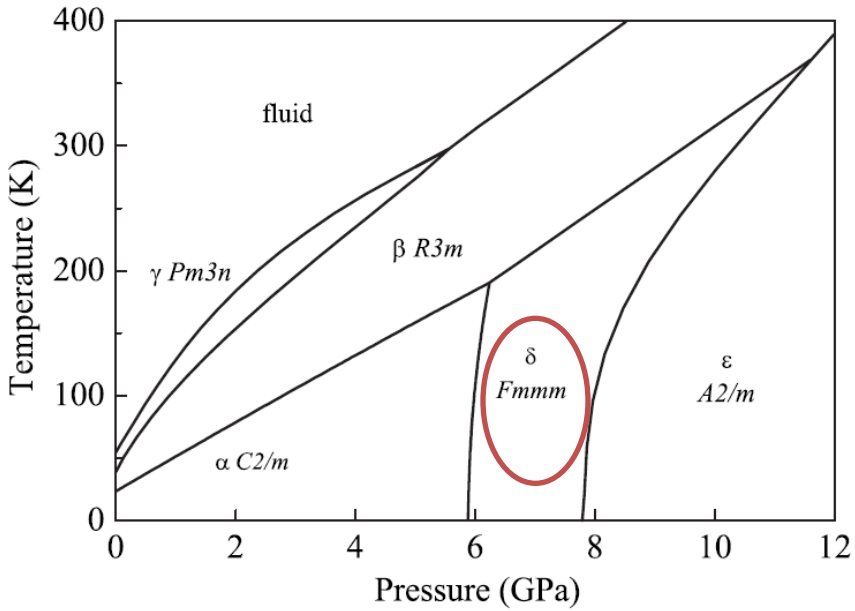


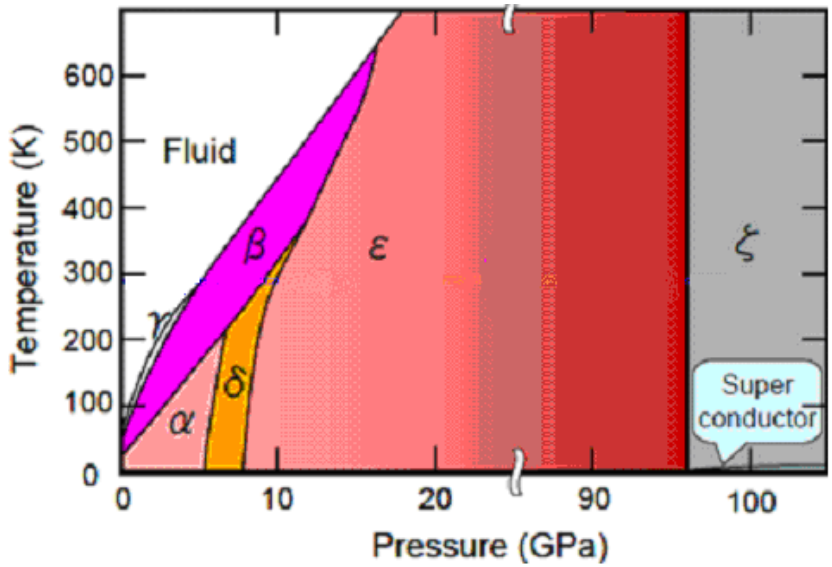
$b/a = 0.79 \neq 3^{1/2}/2$


β- O_2
α- O_2
b
a

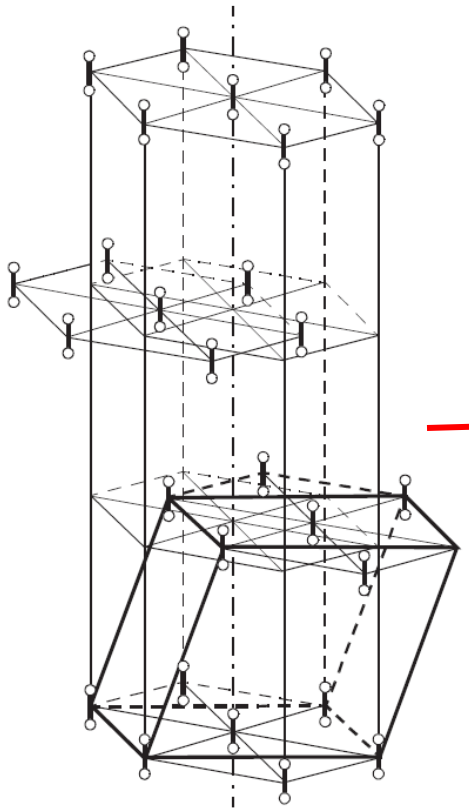


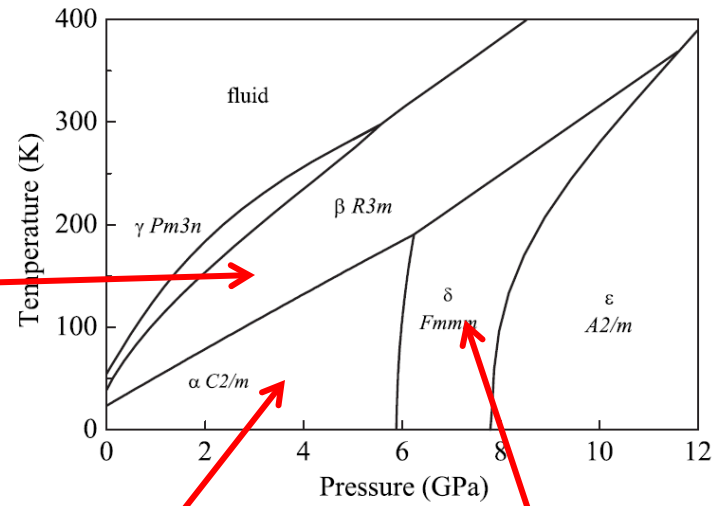
δ- oxygen

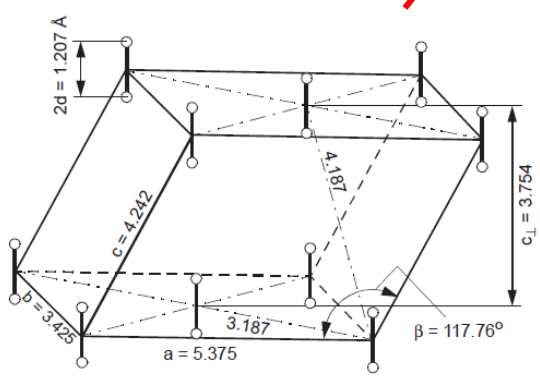

400
300
200
100
0
Temperature (K)
fluid
γ Pm3n
β R3m
α C2/m
δ
Fmmm
ε
A2/m
0
2
4
6
8
10
12
Pressure (GPa)

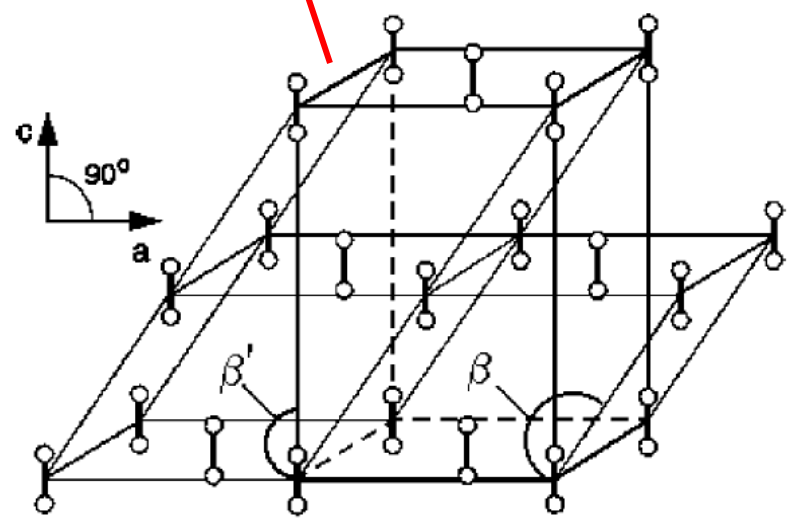

600
500
400
300
200
100
0
Temperature (K)
Fluid
β
ε
ζ
γ
δ
α
Super conductor
0
10
20
90
100
Pressure (GPa)

Nuclear Structures

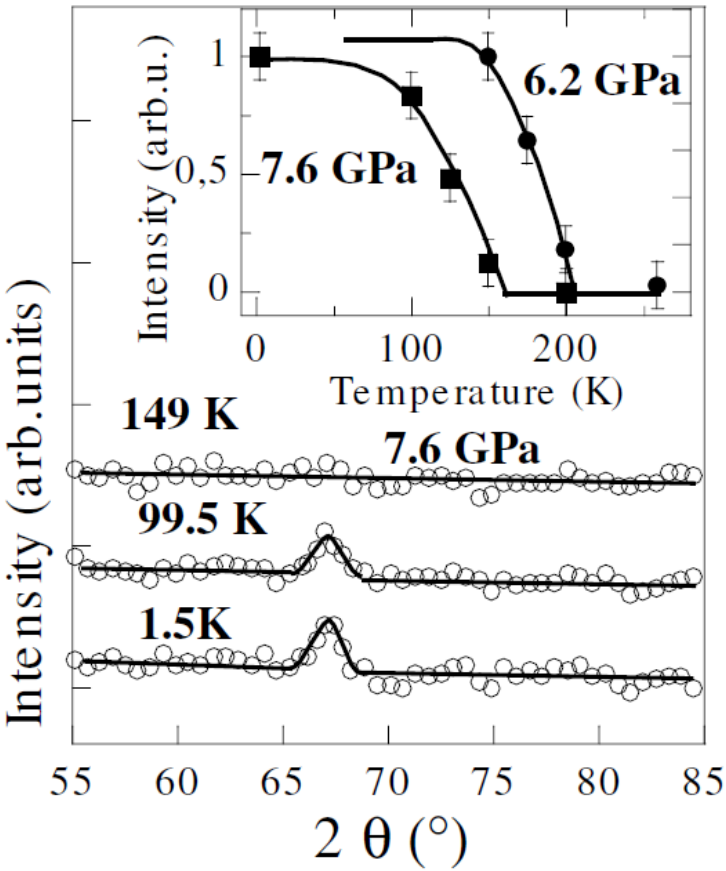






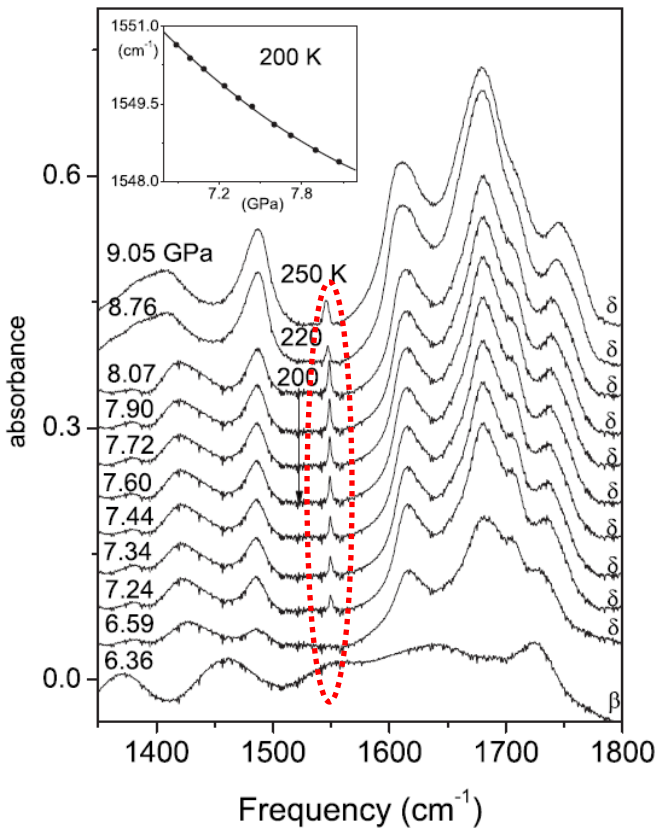


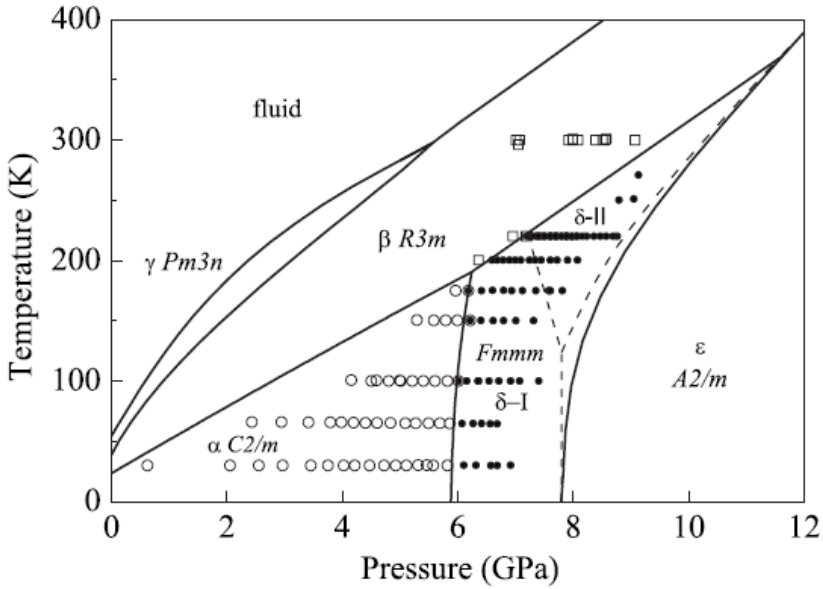
Previous high P neutron experiments



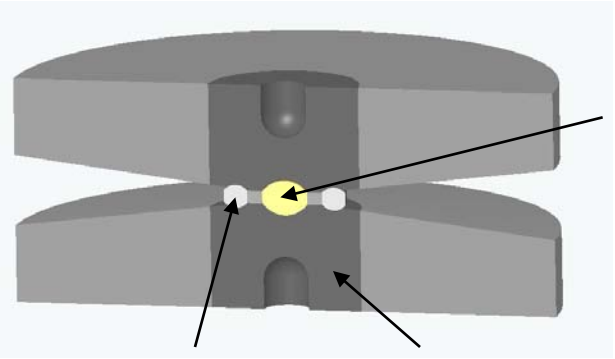
Goncharenko, PRL 2004

Infrared absorption
(diamond anvil cell)





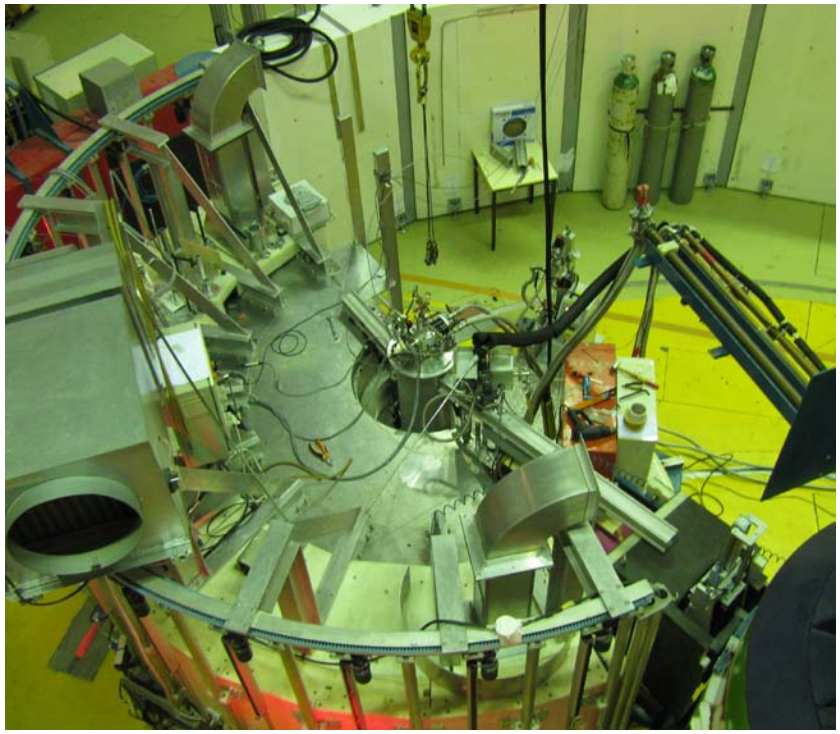
Gorelli et al., PRB 2008



~ 10 GPa for V =100 mm^3
~ 30 GPa for V = 10 mm^3

3.5-320 K

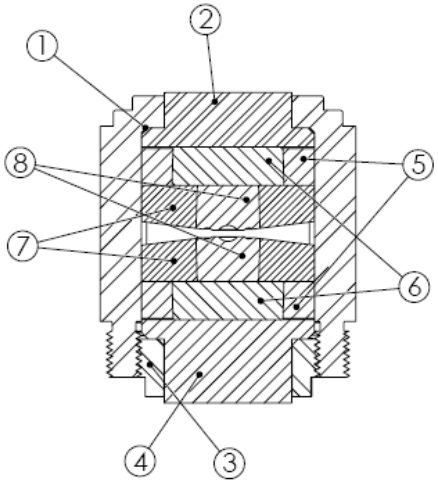
see also talk Domingo Martinez
martes 17:40

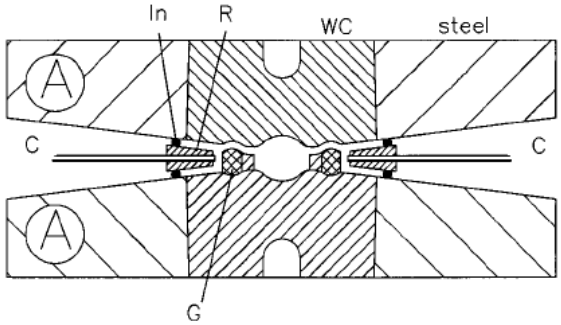


D20 high intensity diffractometer
ILL, Grenoble, France

Future:
XTREMED: dedicated high P diffractometer at ILL
(Javier Campo Ruiz miércoles 10:45)

Sample loading





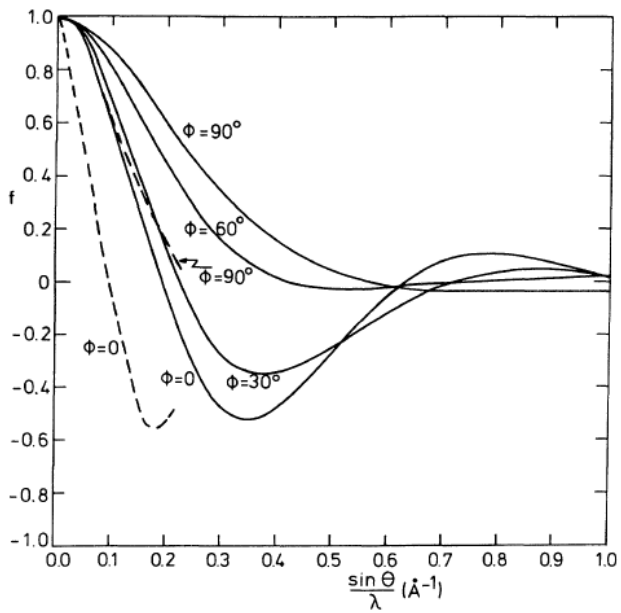
Condensation at 77 K

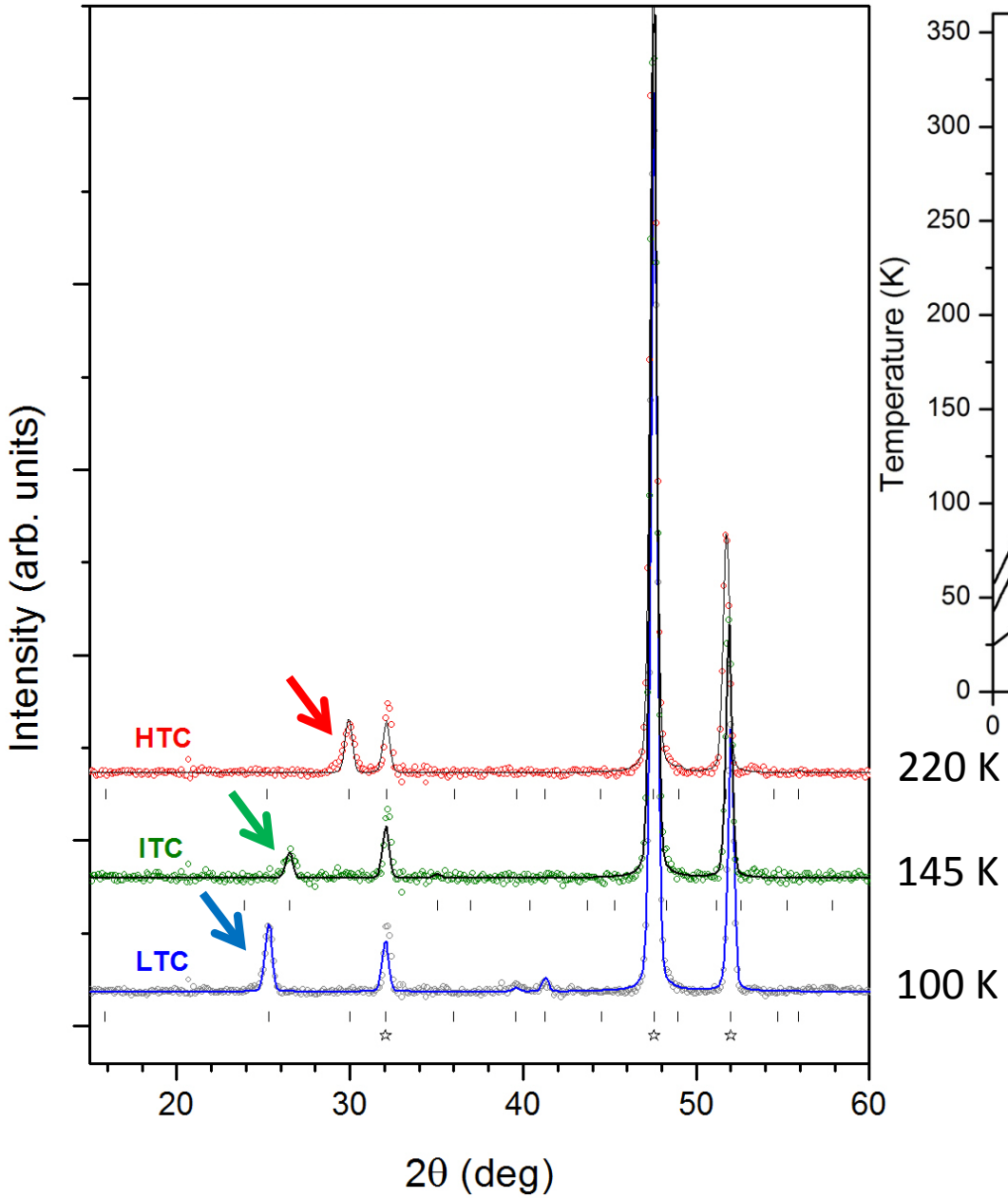
Gas loader

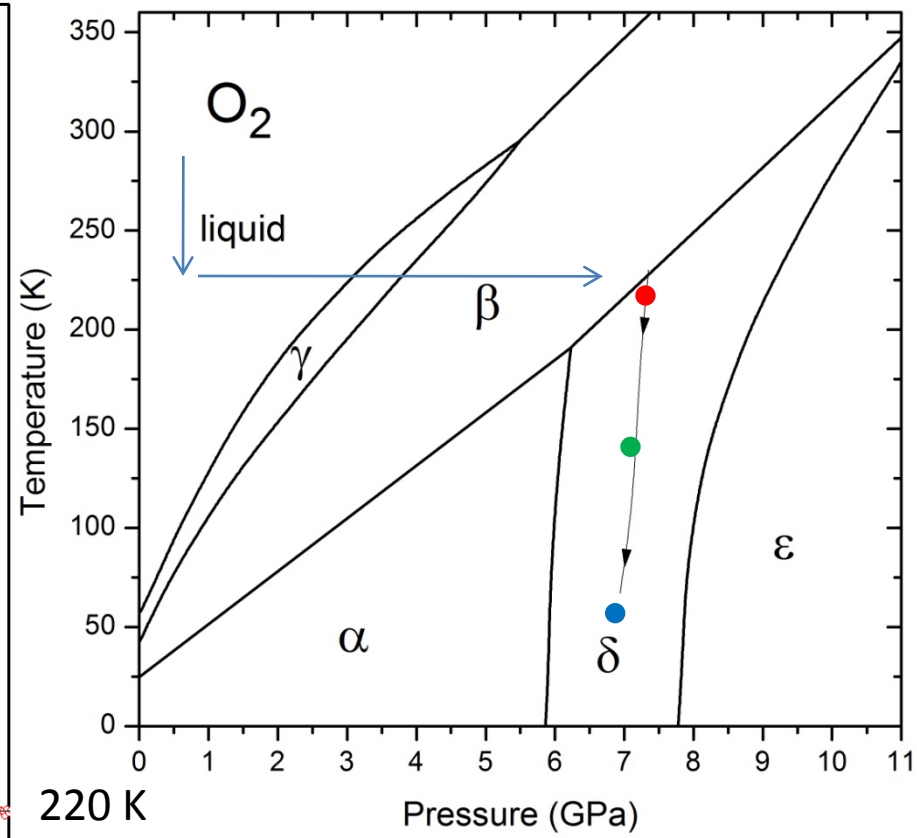
P_{max}=2000 bar
Compatible with hydrogen

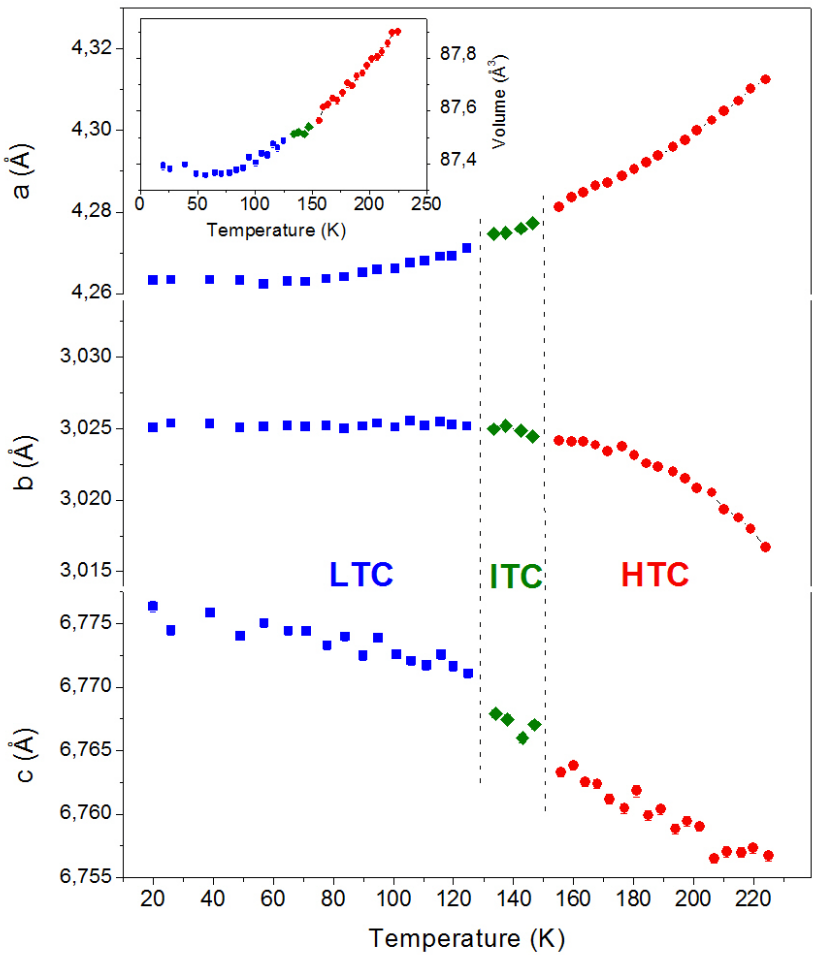
Difficulties

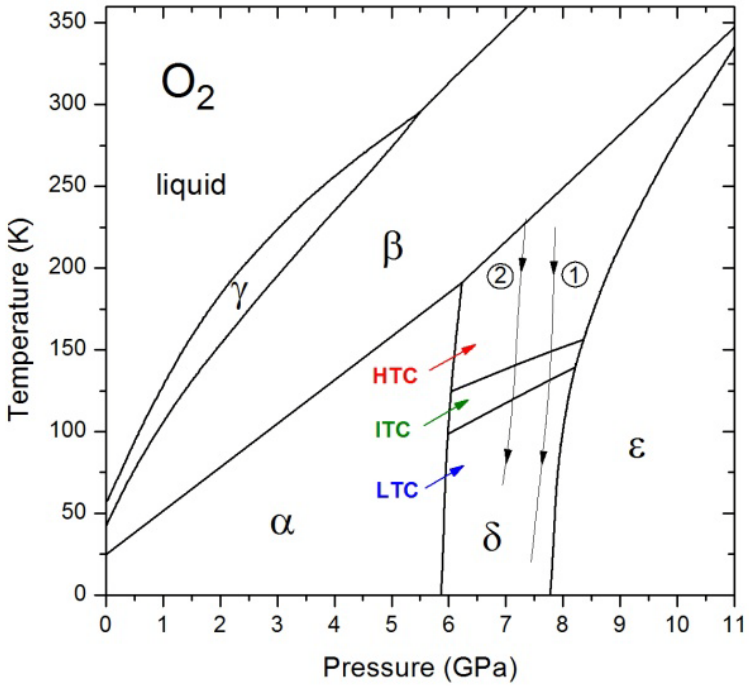
- Texture (imperfect powder) due to the formation of single crystals
- Strong compressibility: ~ 50% from 1-8 GPa
- Uncontrollable download
- Analysis: anisotropic magnetic form factor




Intensity (arb. units)
HTC
ITC
LTC
220 K
145 K
100 K
20
30
40
50
60
2θ (deg)

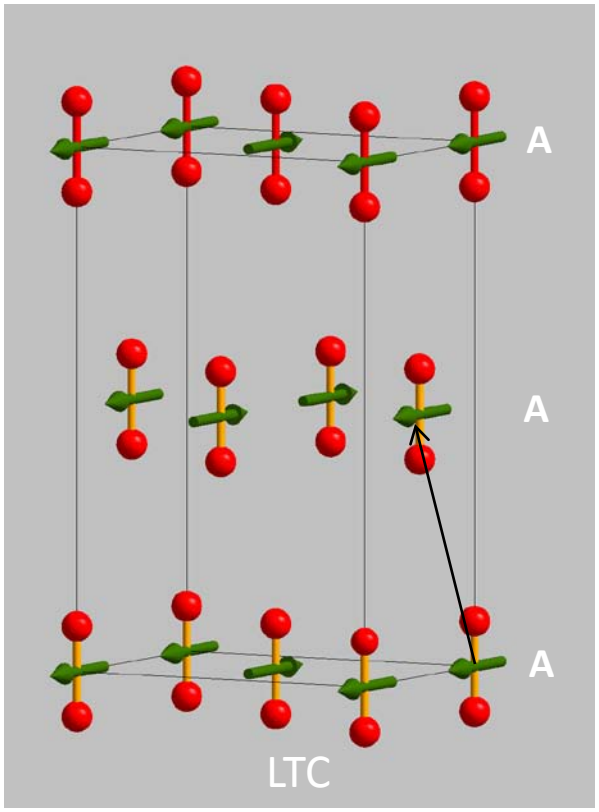

O2
liquid
β
γ
α
δ
ε
Temperature (K)
Pressure (GPa)
0
50
100
150
200
250
300
350
0
1
2
3
4
5
6
7
8
9
10
11

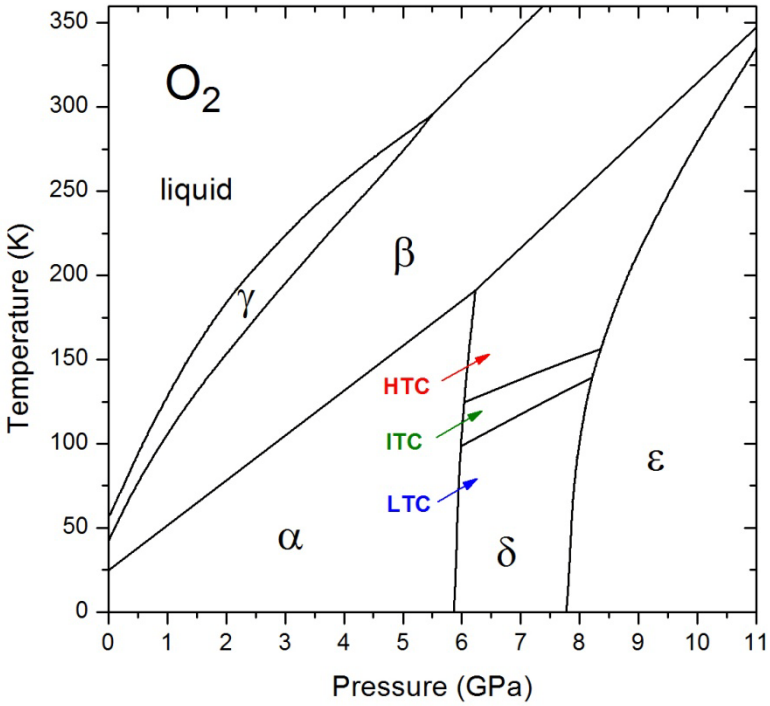

a (Å)
b (Å)
c (Å)
Temperature (K)
Volume (Å³)
LTC
ITC
HTC


O2
liquid
β
γ
α
δ
ε
HTC
ITC
LTC
Temperature (K)
Pressure (GPa)

LTC Structure

(Low Temperature Commensurate)

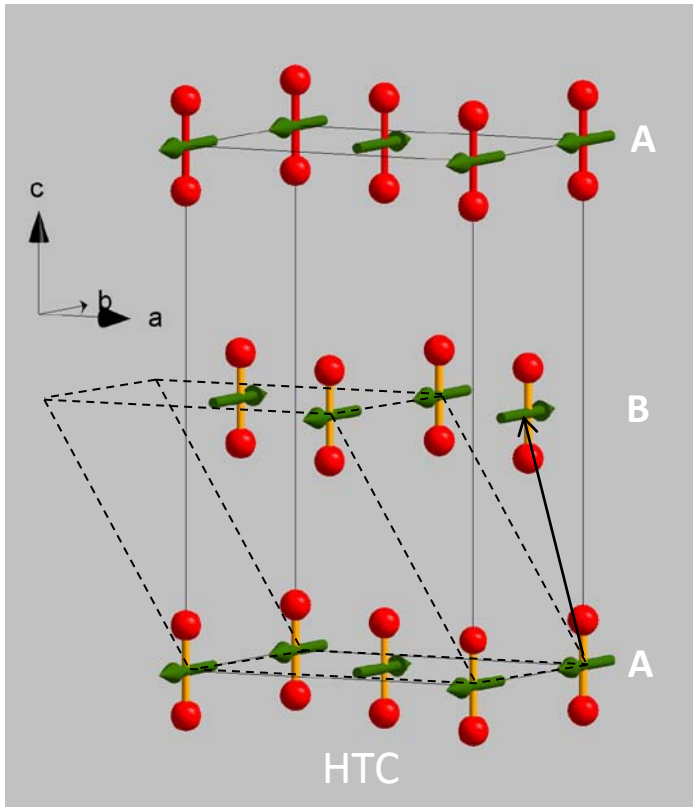


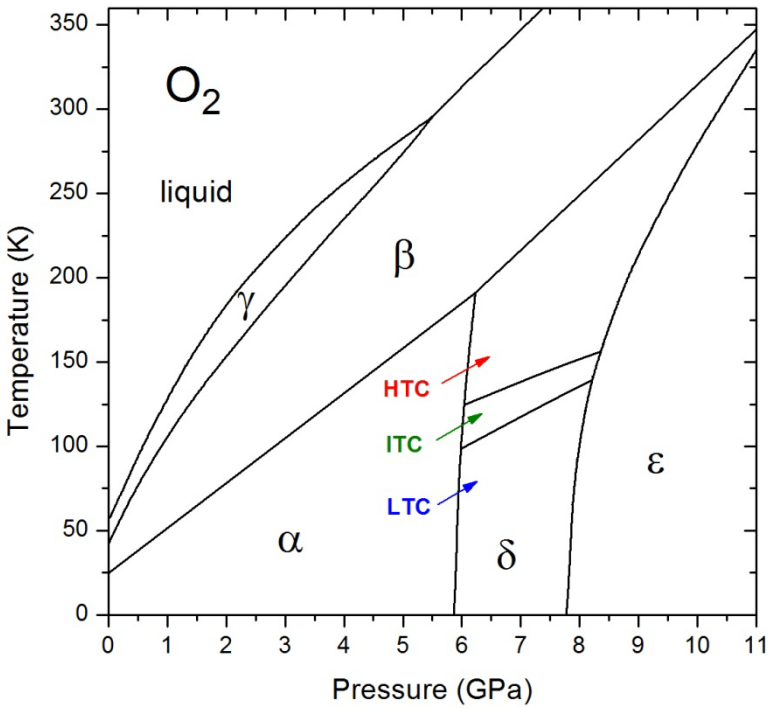


Ferromagnetic coupling between layers

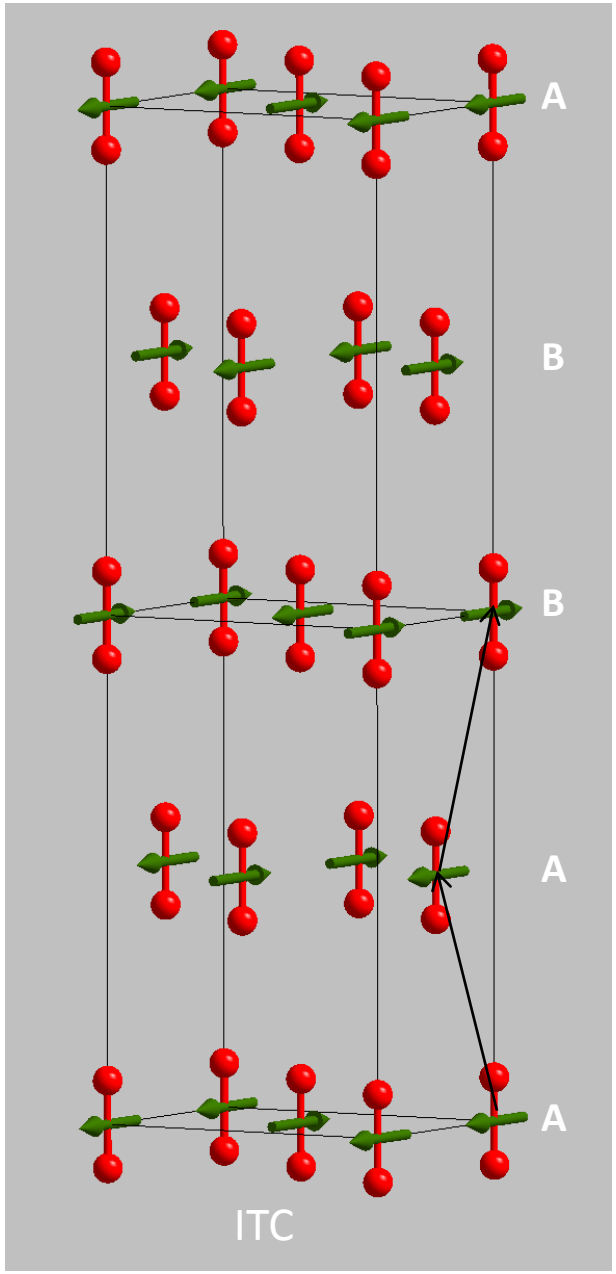
HTC Structure

(High Temperature Commensurate)



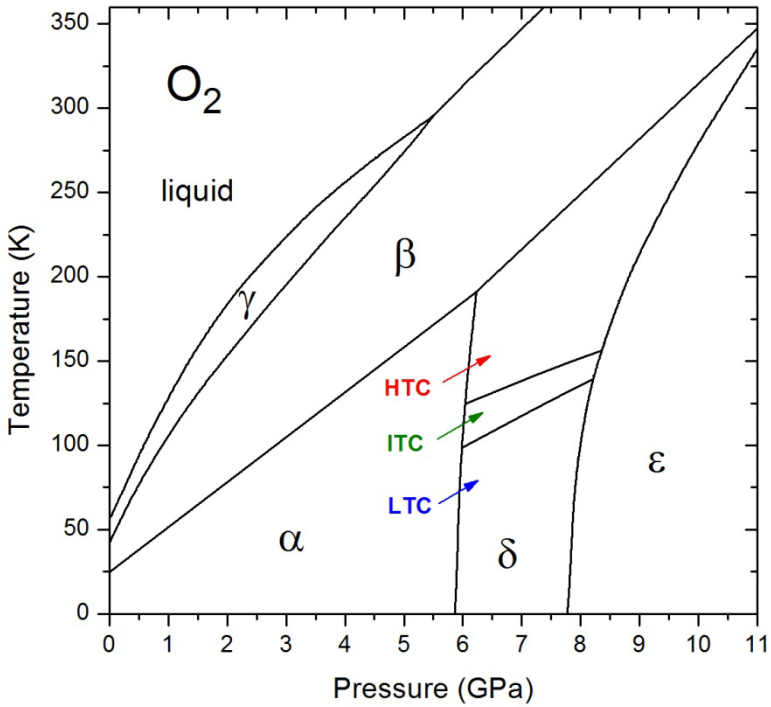


Anti-ferromagnetic coupling between layers



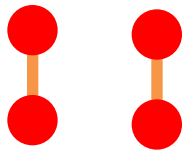
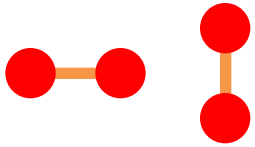
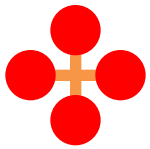
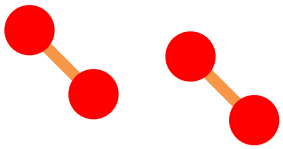
ITC Phase

(Intermediate Temperature Commensurate)



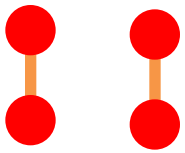
$$H = -J\, S_1 \cdot S_2$$

Hemert et al., PRL 51 (1983)

		J	alignment	
parallel		-	↓↑	AF
linear		-	↓↑	AF
T		-	↓↑	AF
X		+	↑↑	F
S		+	↑↑	F

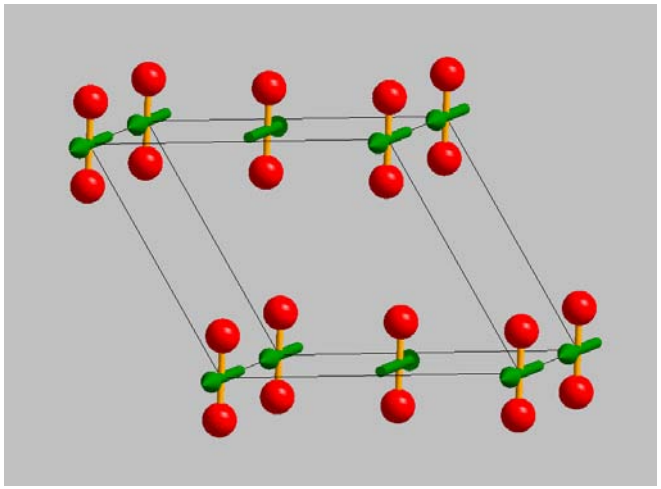
spin alignment: in-plane

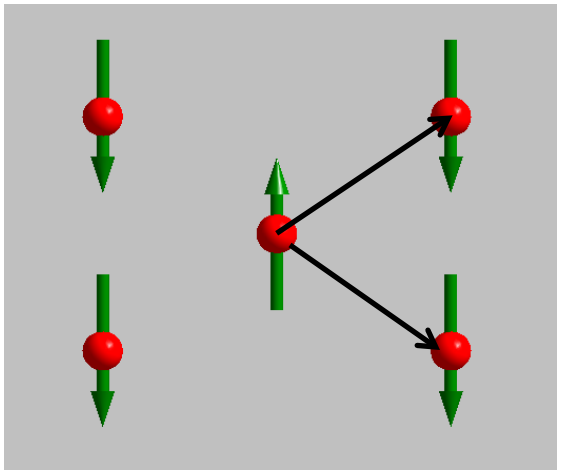
« parallel »



J<0

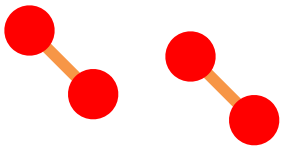
(Hemert et al., PRL 51 (1983) and others)





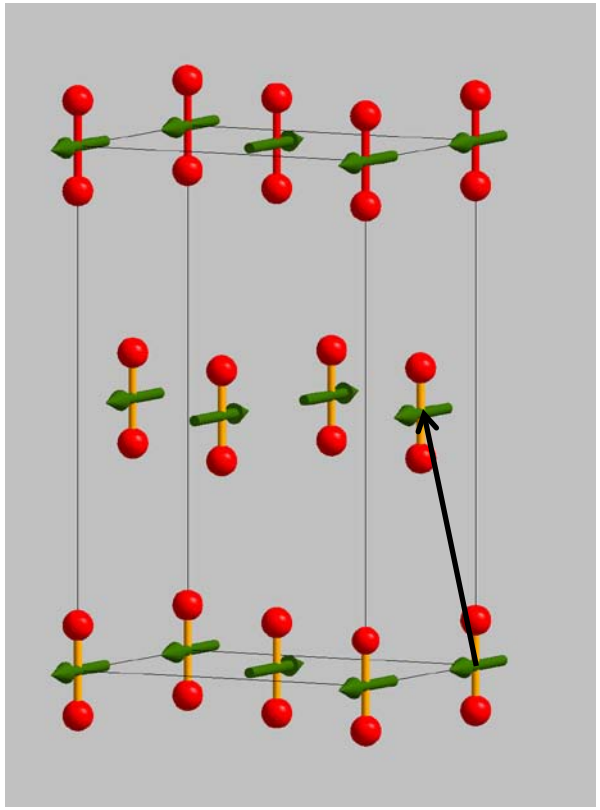
spin alignment: inter-plane

« shifted parallel »

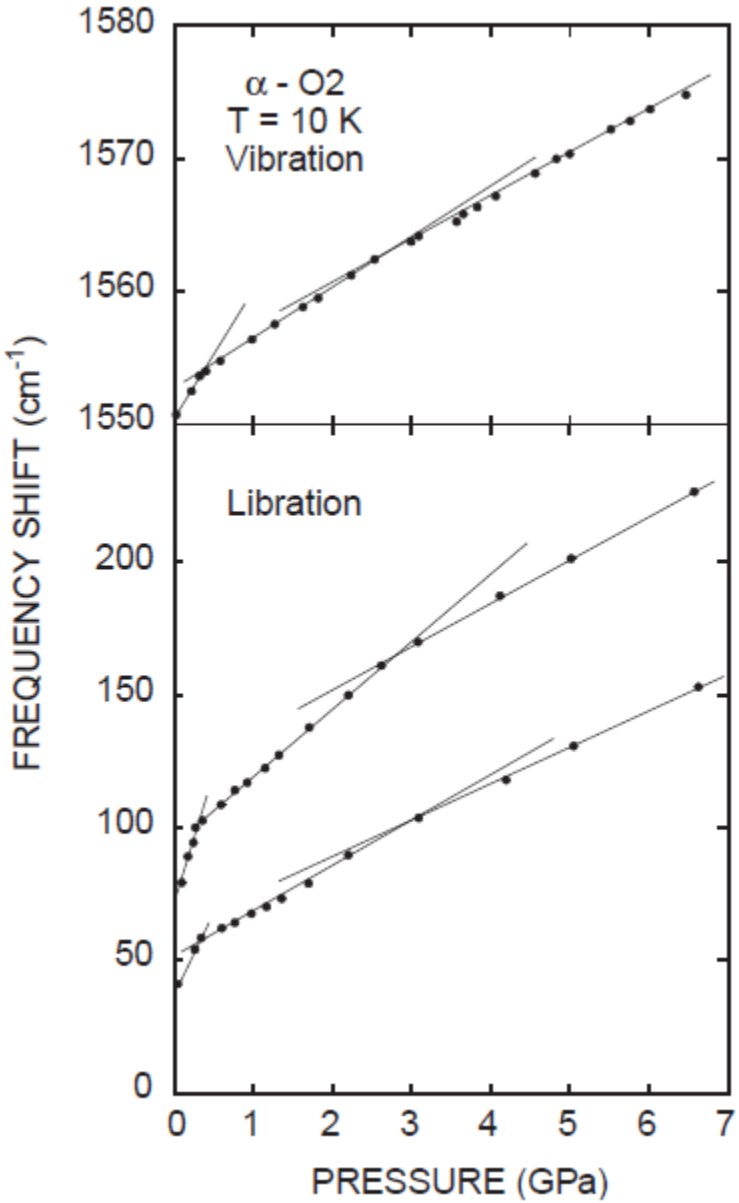


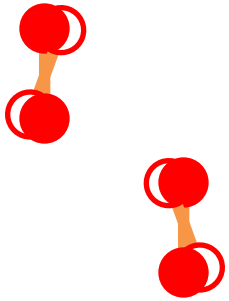
J ≥0

(Hemert et al., PRL 51 (1983) and others)



LTC phase

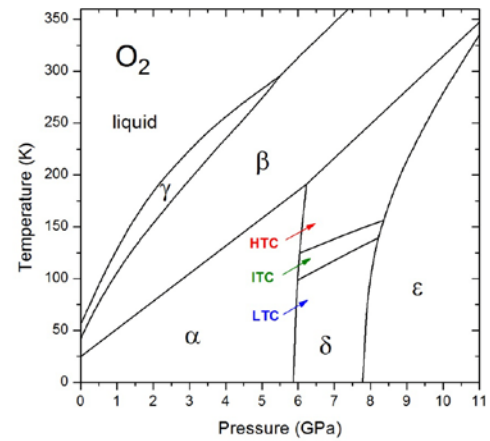




140 K

Jodl et al., PRB 1985

$$(\partial T/\partial P)_{\langle u^2\rangle} = -\frac{(\partial \ln\langle u^2\rangle/\partial P)_T}{(\partial \ln\langle u^2\rangle/\partial T)_P}$$



$$\left.\begin{aligned}(\partial \ln\langle u^2\rangle/\partial T)_P &= 5\times 10^{-3}\ \mathrm{K}^{-1}\\ (\partial \ln\langle u^2\rangle/\partial P)_T &= -8\times 10^{-2}\ \mathrm{GPa}^{-1}\end{aligned}\right\}\quad (\partial T/\partial P)_{\langle u^2\rangle} = 16\ \mathrm{K/GPa}$$

measured: $\approx 15\ \mathrm{K/GPa}$

Conclusions

Solid O_2 at 8 GPa is antiferrimagnetically ordered at room temperature

There are three different AF structures in the δ-phase

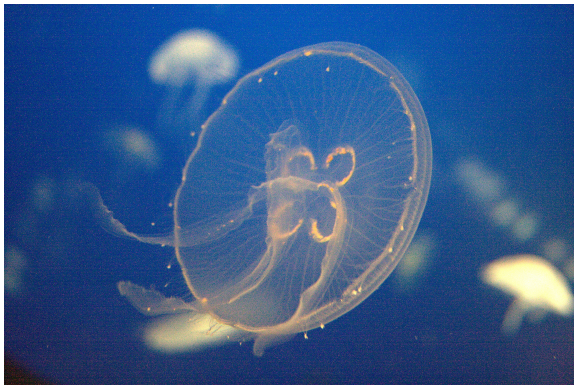
Transitions seem to be governed by the librational motion of the O_2 molecules

Is an effect of the strong dependence of exchange interaction on the mutual orientation of neighboring molecules.

Muchas gracias por la atención!

Topological partition of the elastic constants of crystals into atomic contributions

Alberto Otero-de-la-Roza and Víctor Luaña



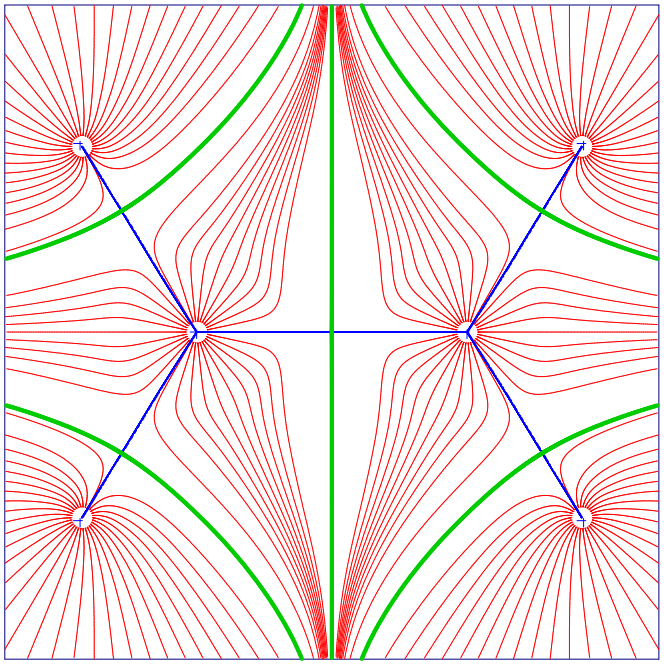
Departamento de Química Física y Analítica, Universidad de Oviedo

48 EHPRG International Conference, Uppsala, 25–29 July 2010

Content

1. Quantum Theory of Atoms in Molecules (QTAIM) partition of the space
2. Partition of the bulk modulus B and $\kappa = B^{-1}$
   - Inluences on B_Ω and κ_Ω
3. Elastic equation of state
4. How to partition the c_{ij} and s_{ij} elastic constants
   - Partitioning c_{11}
   - Partitioning c_{12}
   - Partitioning s_{11} and s_{12}
   - Partitioning c_{44} and s_{44}
   - Internal consistency of the partitioning
5. Partitioning in four families of oxide crystals
6. Conclusions
7. Acknowledgement

Quantum Theory of Atoms in Molecules (QTAIM) partition of the space

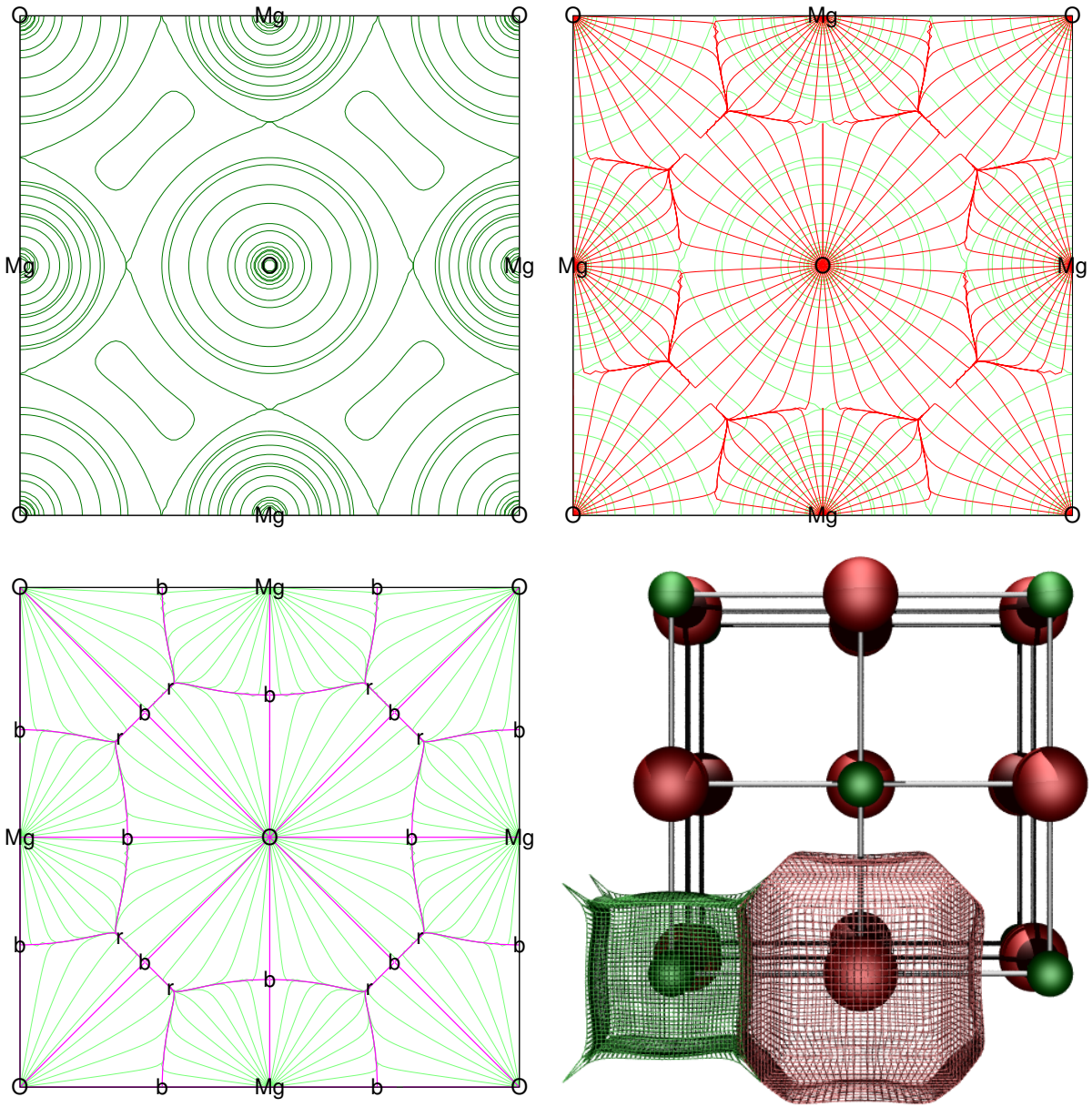


C_2H_4: ethylene

- 3D space is divided into *atomic basins* by the $\nabla\rho(\boldsymbol{r})$ gradient vector field.
- Each basin is such that $\nabla\rho(\boldsymbol{r}_S)\cdot\boldsymbol{n}(\boldsymbol{r}_S)=0$ (*zero flux condition*), i.e. gradient lines do not cross the *inter-atomic surface* (IAS) that separates two bonded basins.
- The only exception is a single *bond path*, the crest or ridge that connects two bonded nuclear peaks and crosses the IAS through the *bond critical point* or mountain pass.

- The zero flux condition guarantees that all quantum mechanical operators are locally well defined, hermitian, and can be integrated on each basin to produce the atomic contribution to the properties of the whole system: $\langle F\rangle_\Omega=\int_\Omega \hat{F}[\rho]\rho(\boldsymbol{r})d\boldsymbol{r}$.
- Basin contributions are strictly additive, $\langle F\rangle=\sum_\Omega\langle F\rangle_\Omega$, and they can be transferred from one compound to another as far as the shape of the basin do not change much.

QTAIM partition in the MgO crystal



Partition of the bulk modulus B and $\kappa = B^{-1}$

- The partition of atomic compressibility is simple:

$$\kappa = \frac{1}{B} = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right), \quad V = \sum_{\Omega} V_{\Omega}, \quad f_{\Omega} = V_{\Omega}/V,$$

$$\kappa_{\Omega} = \frac{1}{B_{\Omega}} = -\frac{1}{V_{\Omega}}\left(\frac{\partial V_{\Omega}}{\partial p}\right) \implies \boxed{\kappa = \sum_{\Omega} f_{\Omega}\kappa_{\Omega}}.$$

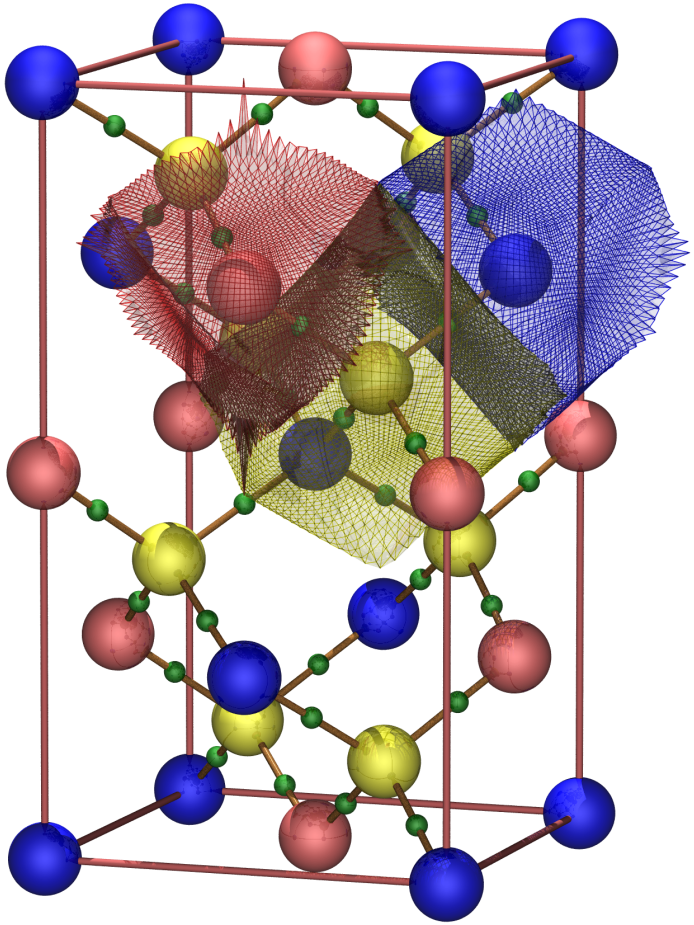
- This provides a very practical analytical tool. We can see, for instance, that the compressibility of spinels is controlled by the oxide ion (PhysRev B **62** (2000) 13970):

AB_2O_4	B (GPa)	B_A	B_B	B_{O}	f_{O}
$MgAl_2O_4$	215.2	282.1	331.9	201.6	0.8127
$MgGa_2O_4$	211.2	261.2	283.9	196.1	0.7486
$ZnAl_2O_4$	214.8	246.0	335.2	203.3	0.7690
$ZnGa_2O_4$	213.3	241.2	308.6	195.7	0.7070

- $B_{\mathrm{O}} \approx B < B_{\mathrm{Zn}} < B_{\mathrm{Mg}} < B_{\mathrm{Ga}} < B_{\mathrm{Al}}$.
- In the static approximation ($T = 0$ K, no ZPE) it *should* be possible to partition all thermodynamic observables into basin contributions.

Inluences on B_Ω and κ_Ω:

• atomic number • polarizability • charge transfer (electronegativity)
• coordination index • crystal structure • what else?



$AgGaSe_2$ (chalcopyrite phase)

	Ag	Ga	Se
$\mathcal{Q}$	$+0.28$	$+1.00$	-0.64

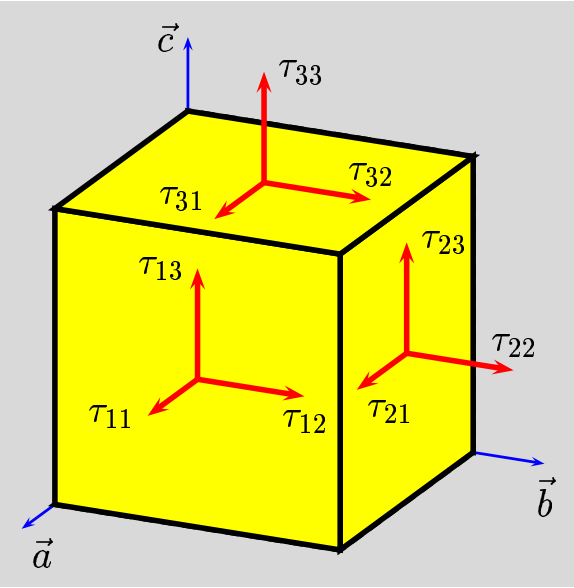
$$c = 31\%, \quad f = 2.6\%$$

Ω	f_Ω	κ_Ω (TPa^{-1})	B_Ω (GPa)
Ag	0.238	17.7	56.6
Ga	0.157	22.3	44.8
Se	0.603	19.6	51.1
	Total	19.5	51.2

$B(^{31}\mathrm{Ga}) < B(^{34}\mathrm{Se}) < B(^{47}\mathrm{Ag})$ are ordered by atomic number!

We lack a systematic study of the B_Ω's!!!

Elastic equation of state



- For small deformations of the crystal cell around an equilibrium configuration:

$$\phi = \frac{E - E_0}{V_0} = \frac{1}{2}\sum_{ij,kl} c_{ijkl}\epsilon_{ij}\epsilon_{kl} = \frac{1}{2}\sum_{ij,kl} s_{ijkl}\tau_{ij}\tau_{kl}. \qquad (1)$$

- Using symmetric deformation components:

$$\epsilon_{ij} = \frac{1}{2}\left[\frac{\partial \delta x_i}{\partial x_j} + \frac{\partial \delta x_j}{\partial x_i}\right], \quad \delta x = x - x_0, \quad x \in \{a, b, c\}. \qquad (2)$$

- Strain-stress linear relationships:

$$\tau_{ij} = \frac{\partial \phi}{\partial \epsilon_{ij}}, \quad \tau_{ij} = \sum_{kl} c_{ijkl}\epsilon_{kl}, \quad \epsilon_{ij} = \sum_{kl} s_{ijkl}\tau_{kl}. \qquad (3)$$

- Voigt notation:

τ_{11}	τ_{22}	τ_{33}	τ_{23}	τ_{31}	τ_{12}	ϵ_{11}	ϵ_{22}	ϵ_{33}	$2\epsilon_{23}$	$2\epsilon_{31}$	$2\epsilon_{12}$
τ_1	τ_2	τ_3	τ_4	τ_5	τ_6	ϵ_1	ϵ_2	ϵ_3	ϵ_4	ϵ_5	ϵ_6

- Elastic constants and compliances:

$$c_{ij} = \left(\frac{\partial \tau_i}{\partial \epsilon_j}\right)_{\boldsymbol{\epsilon}',\mathbf{0}}, \quad s_{ij} = \left(\frac{\partial \epsilon_i}{\partial \tau_j}\right)_{\boldsymbol{\tau}',\mathbf{0}}, \quad \boldsymbol{c} = \boldsymbol{s}^{-1}. \qquad (4)$$

How to partition the c_{ij} elastic constants

- The partition of the energy, $E = \sum_\Omega E^\Omega$, would provide a direct partition of c_{ij}:

$$\phi = \sum_\Omega \phi^\Omega,\ \phi^\Omega = \frac{E^\Omega - E_0^\Omega}{V_0} \Rightarrow\ c_{ij} = \sum_\Omega c_{ij}^\Omega,\ c_{ij}^\Omega = \left(\frac{\partial^2 \phi^\Omega}{\partial \epsilon_i \partial \epsilon_j}\right)_{\boldsymbol{\epsilon}',\mathbf{0}}. \tag{5}$$

However, *we still can't partition the cell energy with the required precision*.

- The indirect way uses the partition of the cell volume:

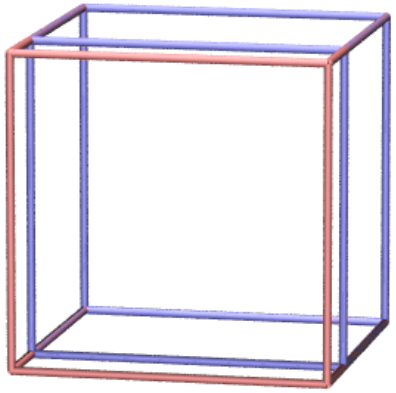
$$c_{ij} = \left(\frac{\partial \tau_i}{\partial \epsilon_j}\right)_{\boldsymbol{\epsilon}'} = \frac{\partial \tau_i}{\partial V}\frac{\partial V}{\partial \epsilon_j} = \frac{\partial \tau_i}{\partial V}\sum_\Omega \frac{\partial V^\Omega}{\partial \epsilon_j} = \sum_\Omega c_{ij}^\Omega, \qquad \boxed{c_{ij}^\Omega = \left(\frac{\partial V^\Omega}{\partial \epsilon_j}\right)\left(\frac{\partial V}{\partial \tau_i}\right)^{-1}} \tag{6}$$

- We need to calculate $(E, V, V^\Omega ...)$ for appropriate finite deformations of the unit cell: $\boldsymbol{R} \longrightarrow \boldsymbol{R}' = \boldsymbol{R}(\mathbf{1} + \boldsymbol{\epsilon})$. In the case of cubic systems:

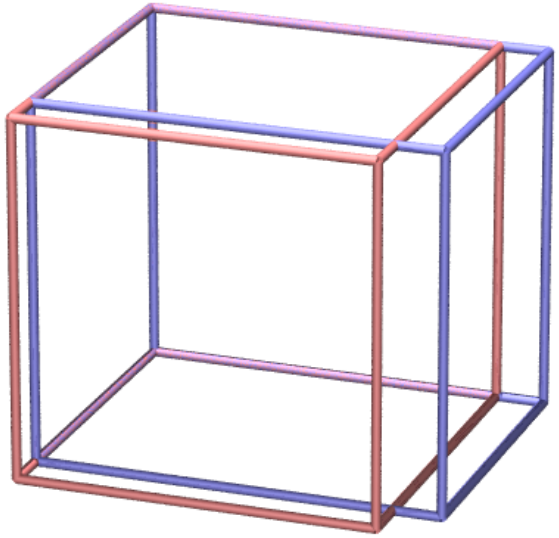
$$\boldsymbol{R}' = \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & a \end{pmatrix} \begin{pmatrix} 1+\epsilon_1 & 2\epsilon_6 & 2\epsilon_5 \\ 2\epsilon_6 & 1+\epsilon_2 & 2\epsilon_4 \\ 2\epsilon_5 & 2\epsilon_4 & 1+\epsilon_3 \end{pmatrix} \tag{7}$$

$$\begin{aligned} V = V_0\{&1 + \epsilon_1 + \epsilon_2 + \epsilon_3 + \epsilon_1\epsilon_2 + \epsilon_2\epsilon_3 + \epsilon_3\epsilon_1 + \epsilon_1\epsilon_2\epsilon_3 \\ &-4\epsilon_4^2 - 4\epsilon_5^2 - 4\epsilon_6^2 - 4\epsilon_1\epsilon_4^2 - 4\epsilon_2\epsilon_5^2 - 4\epsilon_3\epsilon_6^2 + 16\epsilon_4\epsilon_5\epsilon_6\} \end{aligned} \tag{8}$$

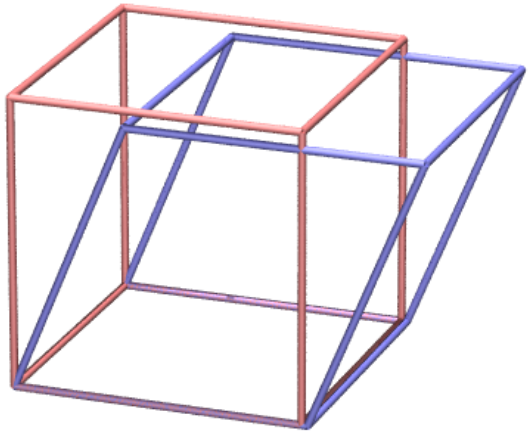
Deformations of the cubic cell



$\Phi(\epsilon_1) \Rightarrow c_{11}$



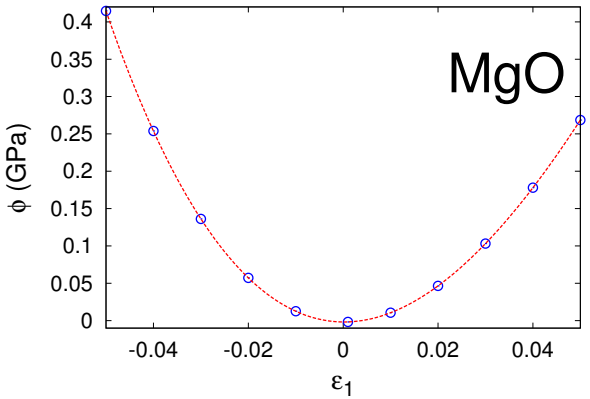
$\Phi(\epsilon_1, \epsilon_2) \Rightarrow c_{12}, c_{11}$

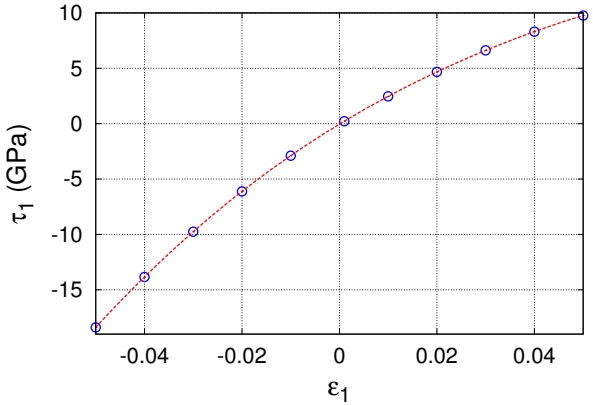


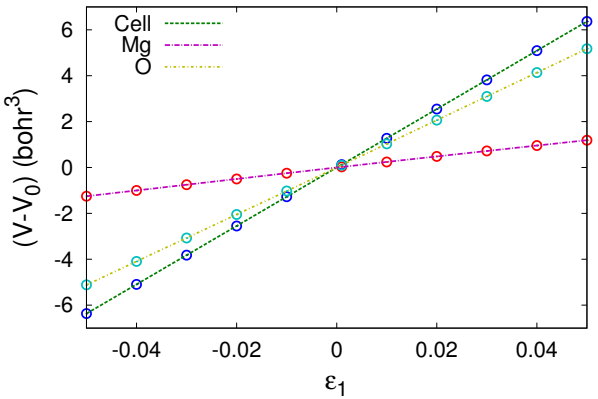
$\Phi(\epsilon_4) \Rightarrow c_{44}$

Partitioning c_{11}

$$c_{11} = \sum_{\Omega} c_{11}^{\Omega}, \qquad c_{11}^{\Omega} = \left(\frac{\partial V_{\Omega}}{\partial \epsilon_1}\right)_{\boldsymbol{\epsilon}',\mathbf{0}} \left(\frac{\partial V}{\partial \tau_1}\right)_{\boldsymbol{\epsilon}',\mathbf{0}}^{-1} \tag{9}$$





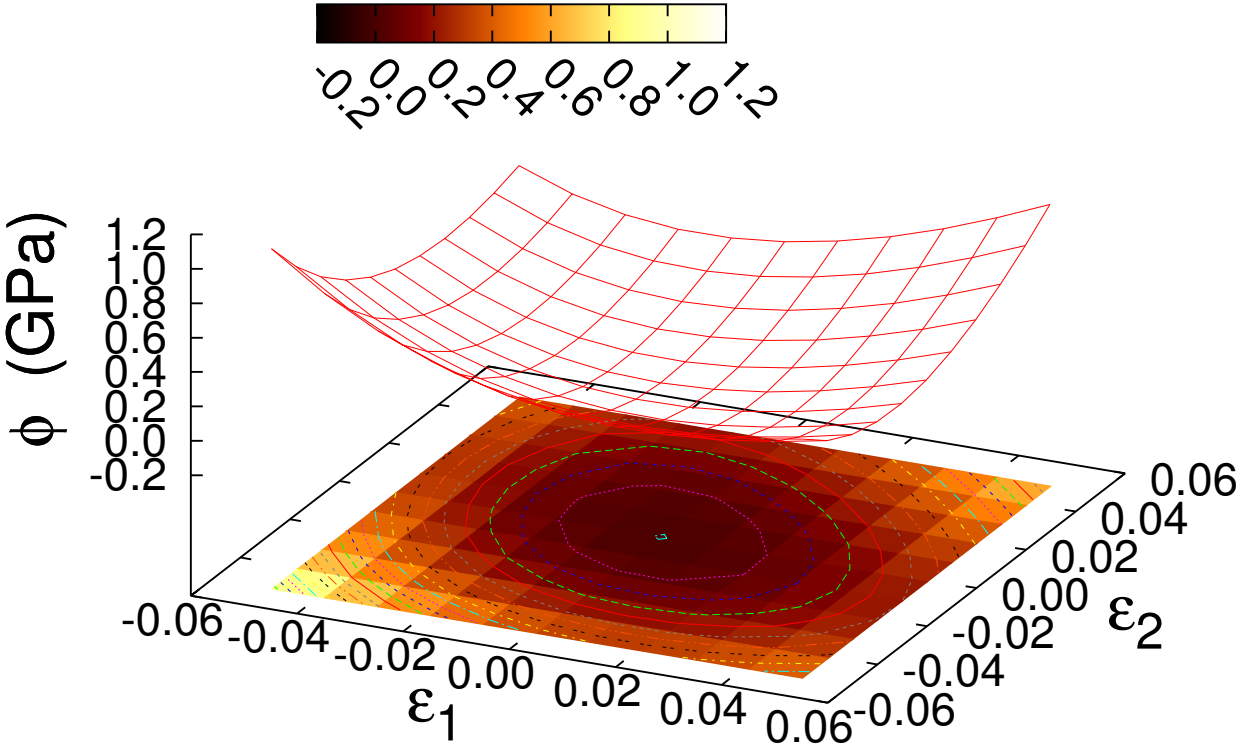


$$V(\epsilon_1, \boldsymbol{\epsilon}'=\mathbf{0}) = V_0(1+\epsilon_1) \tag{10}$$

		Mg	O	cell
$\mathcal{Q}_{\Omega}$	(e)	1,71	$-1,71$	
$\mathcal{V}_{\Omega}$	(bohr^3)	31,70	95,65	127,35
c_{11}^{Ω}	(GPa)	51,50	215,56	267,06

Partitioning c_{12}

$$c_{12}^{\Omega} = \left(\frac{\partial V_\Omega}{\partial \epsilon_2}\right)_{\boldsymbol{\epsilon}',\mathbf{0}} \left(\frac{\partial V}{\partial \tau_1}\right)^{-1}_{\boldsymbol{\epsilon}',\mathbf{0}}, \quad \tau_\xi = \left(\frac{\partial \phi}{\partial \epsilon_\xi}\right)_{\boldsymbol{\epsilon}',\mathbf{0}}, \quad c_{12}^{\Omega} = \left(\frac{\partial V_\Omega}{\partial \epsilon_1}\right)_{\boldsymbol{\epsilon}',\mathbf{0}} \left(\frac{\partial V}{\partial \tau_2}\right)^{-1}_{\boldsymbol{\epsilon}',\mathbf{0}} \tag{11}$$



Ω	c_{12}^{Ω}
Mg	16,87
O	71,13
cell	88,09

$$V(\epsilon_1, \epsilon_2, \boldsymbol{\epsilon}'=\mathbf{0}) = V_0(1 + \epsilon_1 + \epsilon_2 + \epsilon_1\epsilon_2) \tag{12}$$

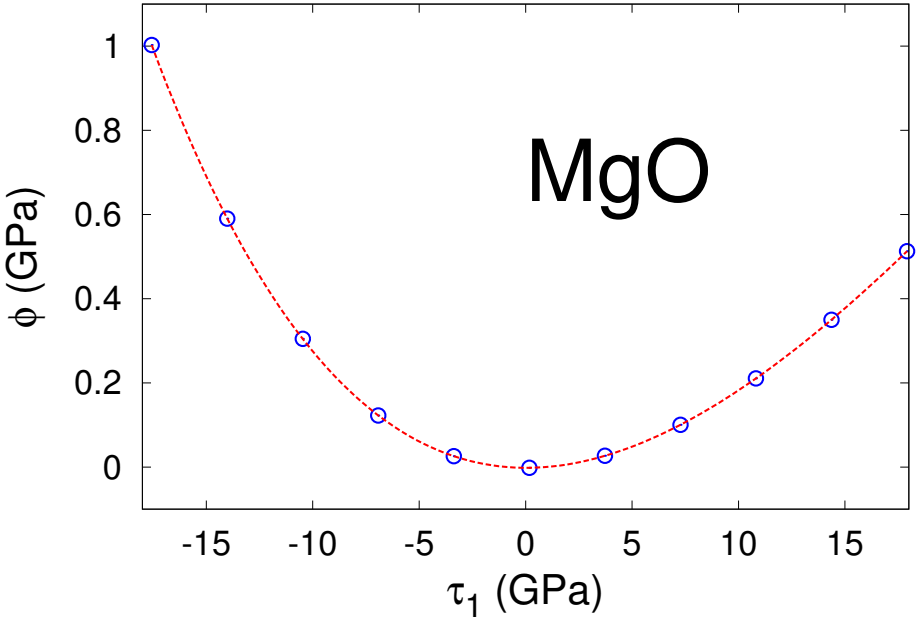
Partitioning s_{11} and s_{12}

$$s_{ij} = \left(\frac{\partial \epsilon_i}{\partial \tau_j}\right)_{\boldsymbol{\tau}',\mathbf{0}} \Rightarrow s_{ij} = \sum_{\Omega} s_{ij}^{\Omega}, s_{ij}^{\Omega} = \left(\frac{\partial V^{\Omega}}{\partial \tau_j}\right)\left(\frac{\partial V}{\partial \epsilon_i}\right)^{-1}\Bigg|_{\boldsymbol{\tau}',\mathbf{0}} \tag{13}$$

We have tested two different approaches:

- Using the capability of ABINIT for introducing constant stress conditions into the electronic structure calculations.
- Assuming linear stress-strain relationships ($\boldsymbol{\epsilon} = \boldsymbol{s}\boldsymbol{\tau} = \boldsymbol{c}^{-1}\boldsymbol{\tau}$), we determine the cell shape for a given stress condition.

The first approach do not assumes linearity, but both produce equivalent s_{ij} values and partitions.

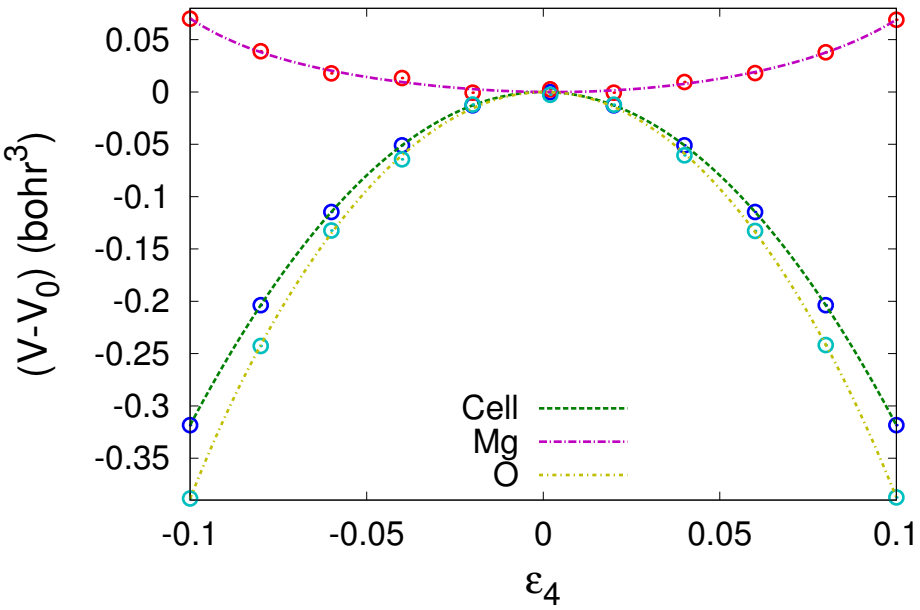


(TPa^{-1})	s_{11}^{Ω}	s_{12}^{Ω}
Mg	0,862 8	−0,213 2
O	3,616 4	−0,897 0
Cell	4,479 2	−1,110 2

Partitioning c_{44} and s_{44}

- $\tau_4 = c_{44}s_4$ and the same $\Phi(\epsilon_4, \boldsymbol{\epsilon}'=0)$ data can be used to obtain both c_{44} and s_{44}.
- $\left.\frac{\partial V}{\partial \epsilon_4}, \frac{\partial V^\Omega}{\partial \tau_4}\right|_{\boldsymbol{\tau}',\mathbf{0}}$ and $\left.\frac{\partial V}{\partial \tau_4}, \frac{\partial V^\Omega}{\partial \epsilon_4}\right|_{\boldsymbol{\epsilon}',\mathbf{0}}$ are *zero* and the formulas previously used give a $0/0$ indeterminacy ...
- ... but we can use L'Hôpital:

$$c_{44} = \sum_\Omega \frac{\partial^2 V^\Omega}{\partial \epsilon_4^2} \Big/ \left.\frac{\partial^2 V}{\partial \tau_4 \partial \epsilon_4}\right|_{\boldsymbol{\epsilon}',\mathbf{0}}, \qquad s_{44} = \sum_\Omega \frac{\partial^2 V^\Omega}{\partial \tau_4 \partial \epsilon_4} \Big/ \left.\frac{\partial^2 V}{\partial \epsilon_4^2}\right|_{\boldsymbol{\tau}',\mathbf{0}}. \tag{14}$$



	c_{44} (GPa)	s_{44} (TPa^{-1})
Mg	$-25{,}19$	$-1{,}149$
O	$172{,}79$	$+7{,}915$
Cell	$147{,}79$	$+6{,}767$

Internal consistency of the partitioning

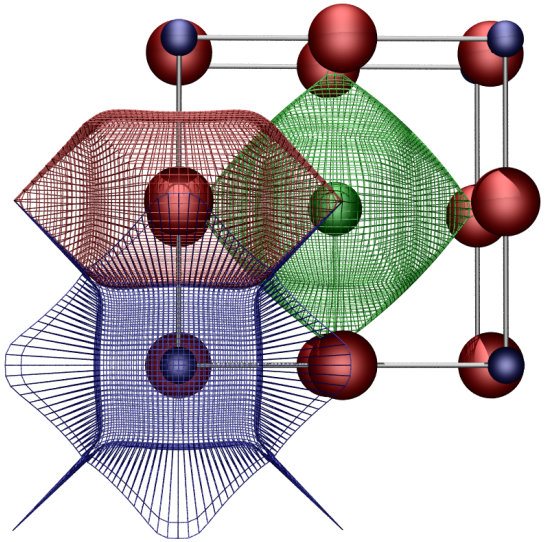
We are used to:

- $\boldsymbol{c}^{-1} = \boldsymbol{s}$ (General).
- $B = (c_{11} + 2c_{12})/3, \quad \kappa = 3(s_{11} + 2s_{12}), \quad c_{44} = 1/s_{44}$ (Cubic crystals).

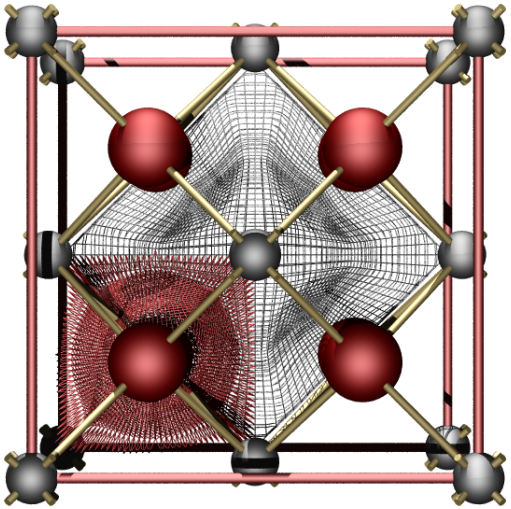
However, with the c_{ij}^{Ω} and s_{ij}^{Ω}:

- $c_{ij} = \sum_{\Omega} c_{ij}^{\Omega}$ and $s_{ij} = \sum_{\Omega} s_{ij}^{\Omega}$.
- $\kappa^{\Omega} = 3(s_{11}^{\Omega} + 2s_{12}^{\Omega})$ ...
- ... but $B^{\Omega} \neq (c_{11}^{\Omega} + 2c_{12}^{\Omega})/3$.
- $c_{44}^{\Omega} \neq 1/s_{44}^{\Omega}$.
- $\boldsymbol{c}^{\Omega} \neq \left(\boldsymbol{s}^{\Omega}\right)^{-1}$.

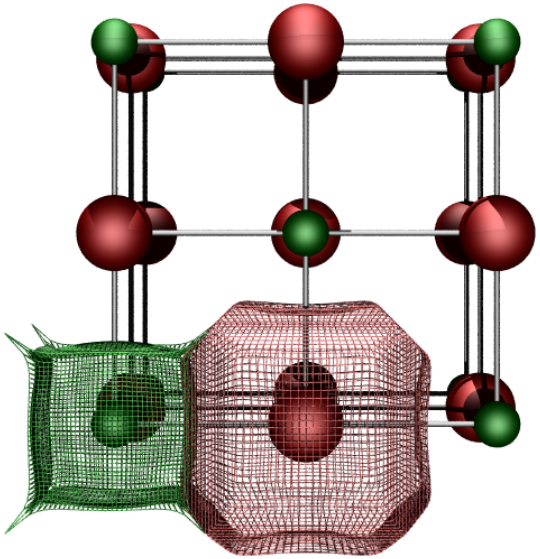
Partitioning in four families of oxide crystals



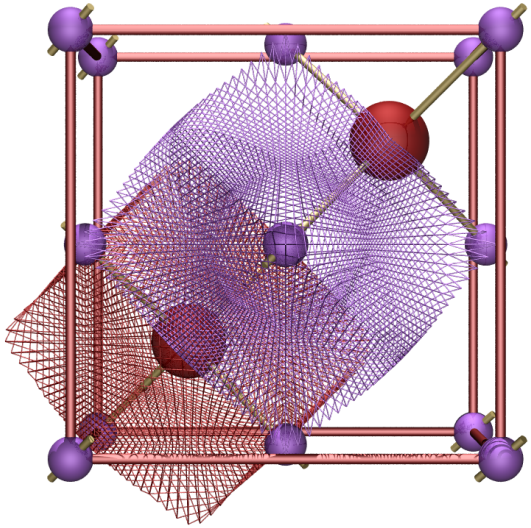
Perovskite: $CaTiO_3$



Inverse fluorite: Li_2O



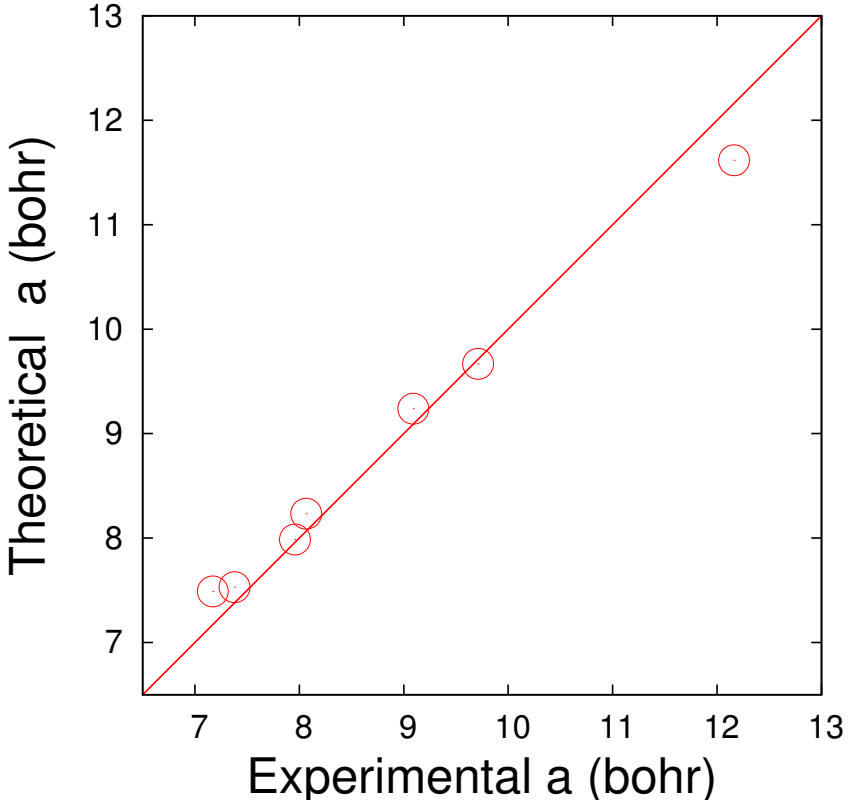
Rock salt: MgO

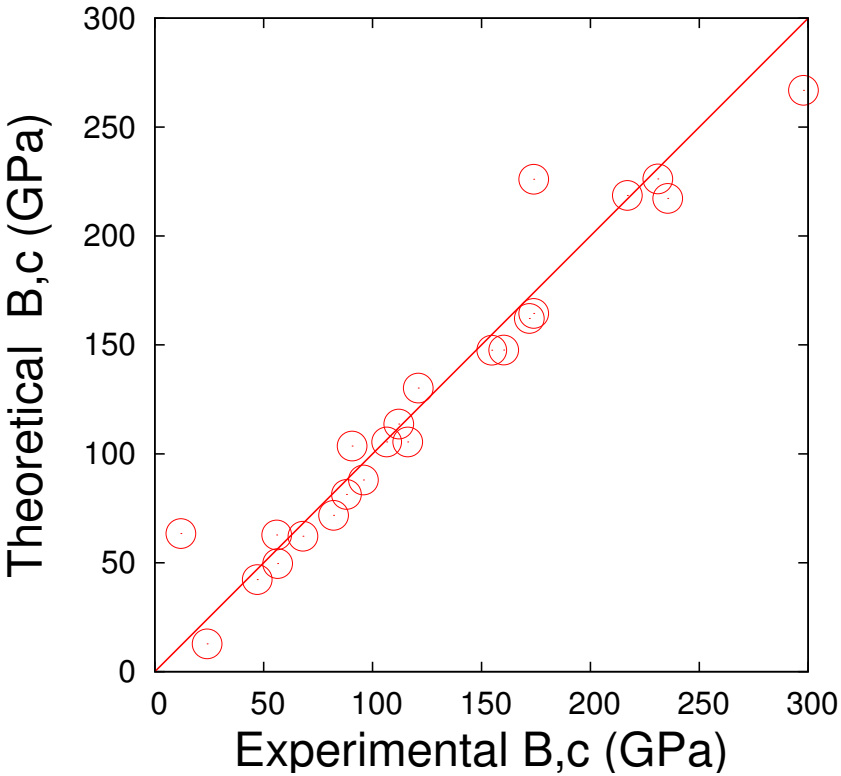


Cuprite: Cu_2O

Calculation details

- Electronic structure calculations: ABINIT.
- Relativistic norm conserving pseudopotentials (Troulier-Martins).
- The xc functional: PBE96 GGA. PW: $E_{cut} = 41\,\mathrm{hy}$. $\Delta E \approx 1 \cdot 10^{-5}\,\mathrm{hy}$.
- Topological analysis: CRITIC2 (`qtree`, lev. 8) with interpolations from a $200 \times 200 \times 200$ grid of $\rho(\boldsymbol{r})$ values.





$AM\mathbf{O}_3$ perovskites

	$CaTiO_3$			$SrTiO_3$			$MgSiO_3$		
c, f, B	65	4,5	162	65	4,9	164	85	11,7	226
Ω	Ca	Ti	$\langle O \rangle$	Sr	Ti	$\langle O \rangle$	Mg	Si	$\langle O \rangle$
V^Ω	89	50	94	111	51	88	38	18	80
$\mathcal{Q}^\Omega$	1,63	2,17	−1,27	1,60	2,17	−1,26	1,77	3,27	−1,68
f^Ω	0,21	0,12	0,67	0,26	0,12	0,62	0,13	0,06	0,81
B^Ω	209	206	147	212	208	146	284	196	221
κ^Ω	4,79	4,85	6,80	4,73	4,80	6,86	3,52	5,09	4,52
c_{11}^Ω	52	29	79	65	30	75	35	24	96
c_{12}^Ω	14	8	21	18	8	21	17	12	46
c_{44}^Ω	23	−29	47	25	−30	33	37	−65	68

Units: c, f (%); V (bohr^3); $\mathcal{Q}$ (e); B, c_{ij} (GPa); κ, s_{ij} (TPa^{-1}).

Conclusions

- *The QTAIM partitioning of the c_{ij} and s_{ij} elastic constants is possible by following the evolution of the cell energy and volume, E and V, and that of the basin volumes, V^{Ω}, under appropriate finite deformations of the unit cell.*
- *Keeping the stresses constant to get the s_{ij} compliances is possible either by using the linear strain-stress relationship ($\boldsymbol{\epsilon} = \boldsymbol{s}\boldsymbol{\tau}$) or by impossing constant stress conditions in the electronic structure calculations, like the* ABINIT *code does.*
- *A good precision on the basin volumes is required, particularly in the computation of the delicate shear moduli. This has been possible with the new techniques developed for* CRITIC2.
- *The s_{ij}^{Ω} fulfill the internal consistency rules. For instance: $\kappa_{\Omega} = 3(s_{11} + 2s_{12})$.*
- *We are still working on the rules that govern the basin partition.*
- *Are you interested in any important case?*

- *Funds have been provided by the Spanish Ministerio de Ciencia e Innovación under grant CTQ2009-08376.*
- *The research is part of the MALTA Consolider Ingenio initiative (grant no. CSD2007-00045). See* `http://www.malta-consolider.com/`.

GOBIERNO DE ESPAÑA MINISTERIO DE CIENCIA E INNOVACIÓN

www.malta-consolider.com CONSOLIDER INGENIO 2010 MALTA Matter at High Pressure

UNIVERSIDAD DE OVIEDO

GOBIERNO DE ESPAÑA MINISTERIO DE EDUCACIÓN

Dedicated to the memory of Miguel Álvarez Blanco (1969–2010), who left behind two small children and a beloved wife.