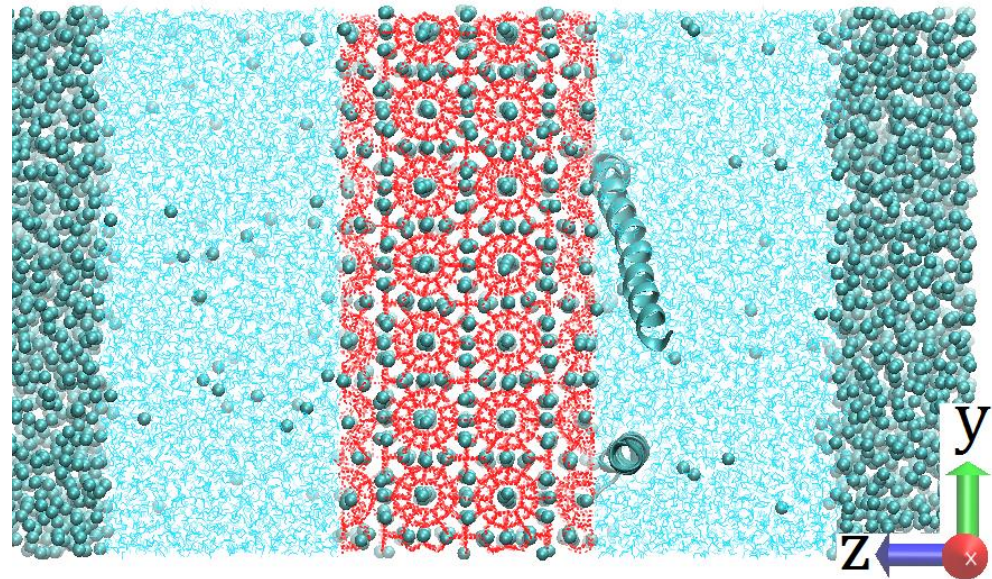
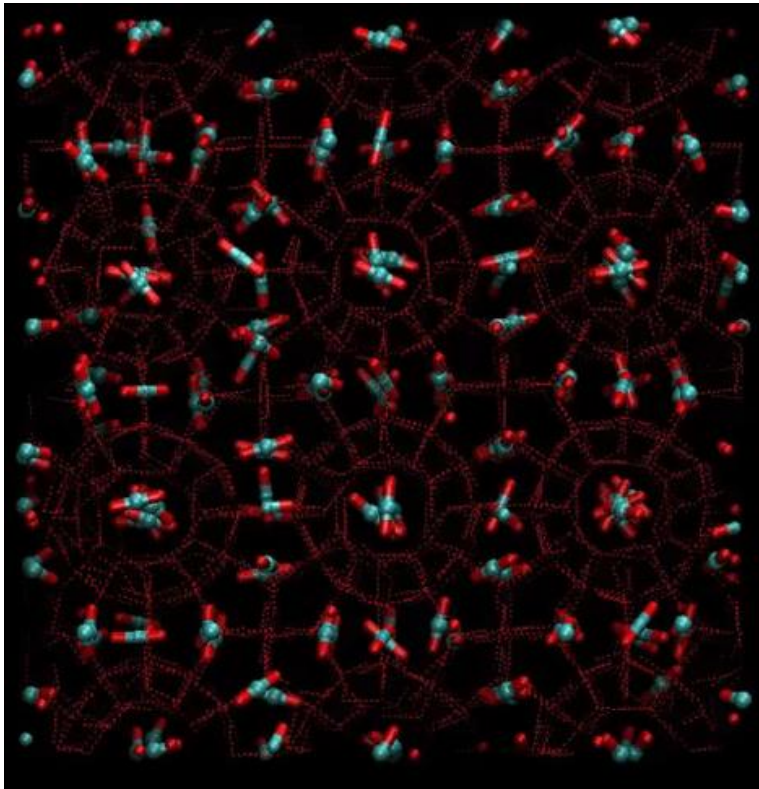


# Molecular Dynamics Simulations of Clathrate Hydrates



Saman Alavi

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University of Ottawa

February 23, 2021 (salavish@uottawa.ca)

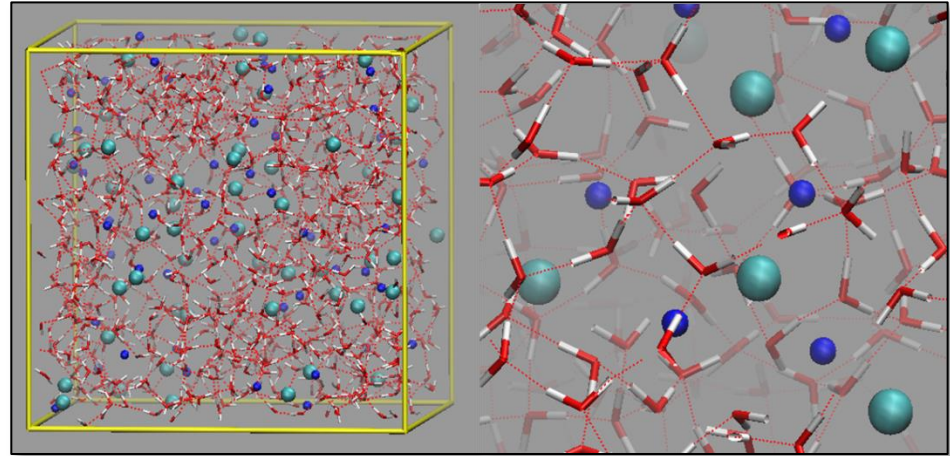
## Outline

- Short description of classical molecular dynamics (MD) simulations
- Clathrate hydrates: Formation and structure
- Clathrate hydrate thermodynamic inhibitors: Methanol
- Clathrate hydrate kinetic inhibitors: Antifreeze proteins
- Dynamics of guests in clathrate hydrates: NMR lineshapes of CO<sub>2</sub> in structure I clathrate hydrate

# Classical molecular dynamics

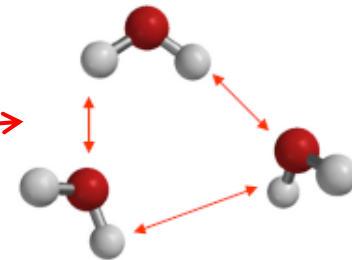
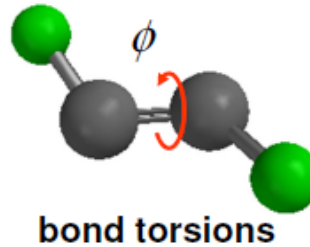
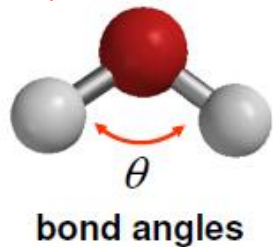
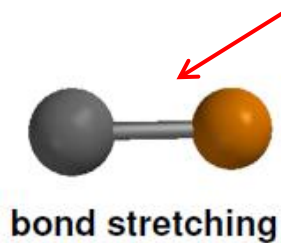
The position and velocity of every atom,  $i$ , are determined by solving Newton's equations:

$$\begin{cases} m_i \frac{d^2 x_i}{dt^2} = F_{x,i}(\{\mathbf{r}\}) \\ m_i \frac{d^2 y_i}{dt^2} = F_{y,i}(\{\mathbf{r}\}) \\ m_i \frac{d^2 z_i}{dt^2} = F_{z,i}(\{\mathbf{r}\}) \end{cases}$$



- The coupled equations for the motion of all molecules are solved numerically using the finite difference method;
- We get  $\{\mathbf{r}_i(t), \mathbf{v}_i(t)\}$  for all atoms  $i$ , and all time  $t$ .

Force on atom  $i$  from all other atoms in the system



non-bonded potentials

- van der Waals
- electrostatic
- hydrogen bonding

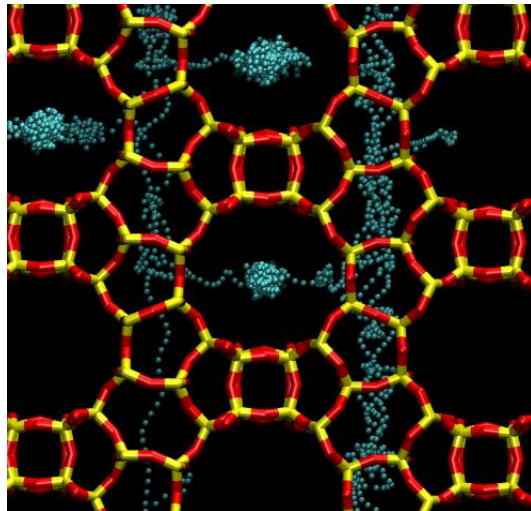
# Motions of atoms in a MD simulation are coupled to the external “environment”

The distribution of microscopic (*mechanical*) variables  $\mathbf{r}_i$  and  $\mathbf{v}_i$  for each atom / molecule must be consistent with chosen external macroscopic (*thermodynamic*) constraints and the relations of statistical mechanics.

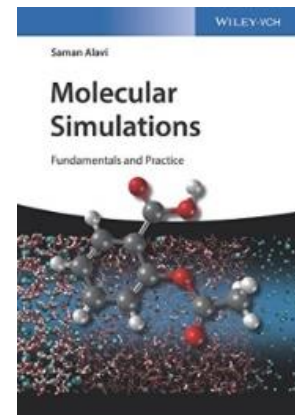
For example:

- Velocities of molecules follow the Maxwell-Boltzmann distribution;
- Temperature / pressure or volume of system are kept fixed;
- Other quantities obey the canonical ensemble (NVT) / isothermal-isobaric ensemble (NPT) / ... statistical mechanical distributions.

## Motion of gas molecules in a zeolite



## For further reading:



# Clathrate hydrates: Ice-like inclusion compounds

## PHILOSOPHICAL TRANSACTIONS.

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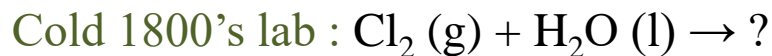
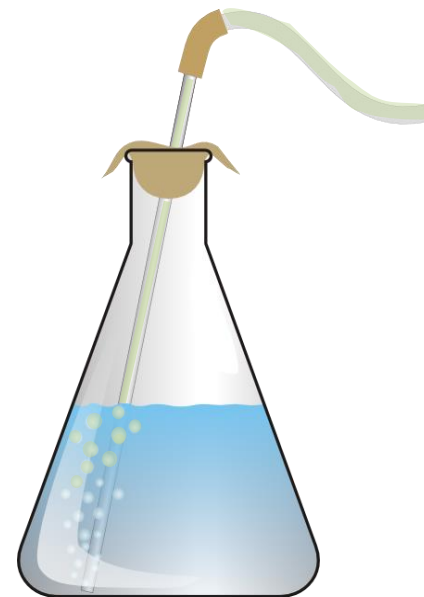
I. *The Bakerian Lecture. On some of the Combinations of Oxymuriatic Gas and Oxygene, and on the chemical Relations of these Principles, to inflammable Bodies.* By Humphry Davy, Esq. LL. D. Sec. R. S. F. R. S. E. M. R. I. A. and M. R. I.

Read November 15, 1810.



Sir Humphry Davy

What happens when  $\text{Cl}_2$  gas is bubbled through water?



# Clathrate hydrates: Ice-like inclusion compounds

## PHILOSOPHICAL TRANSACTIONS.

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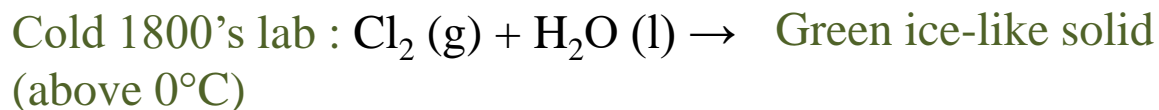
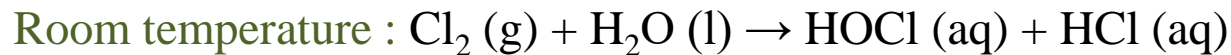
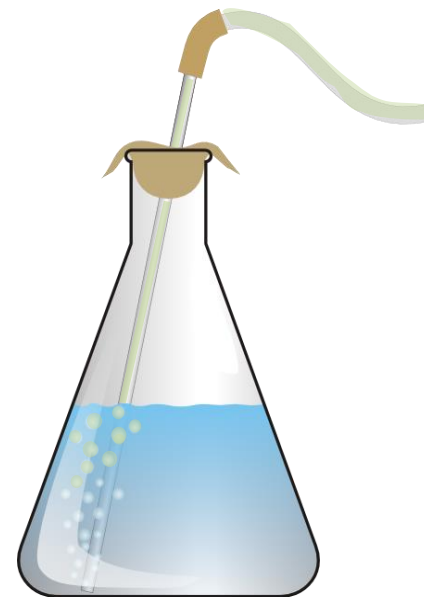
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# Clathrate hydrates: Ice-like inclusion compounds

## PHILOSOPHICAL TRANSACTIONS.

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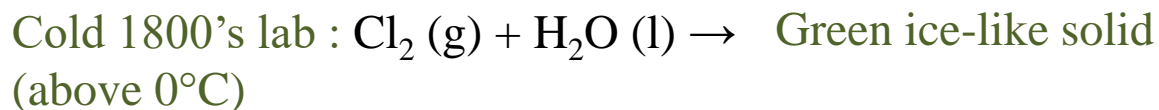
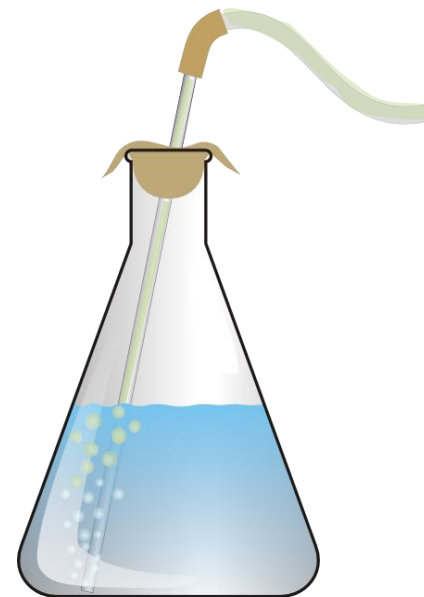
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Read November 15, 1810.



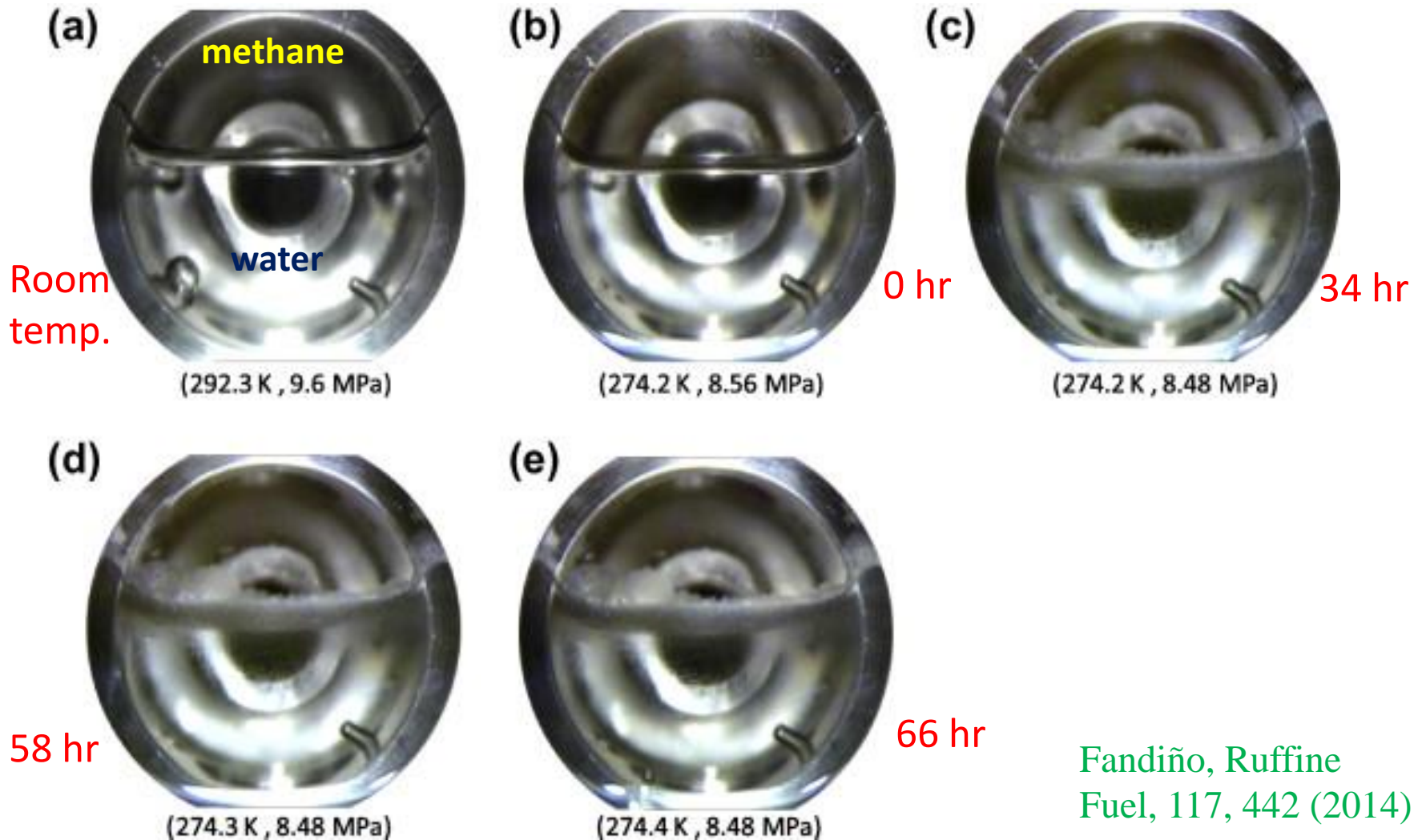
Sir Humphry Davy

What happens when  $\text{Cl}_2$  gas is bubbled through water?



Faraday (1823) determined the formula to be:  $\text{Cl}_2 \cdot 10\text{H}_2\text{O}(\text{s})$  7

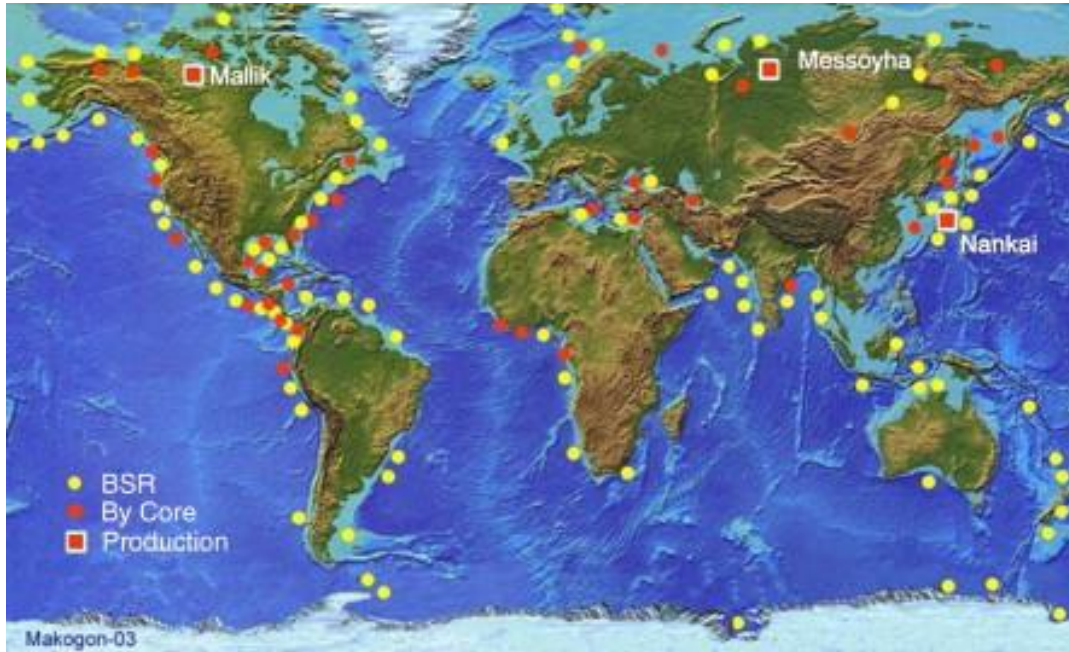
Clathrate hydrates are ice-like inclusion compounds that form when compressing many gases with water



- Solid clathrate hydrates can form above the freezing point of water
- Methane is concentrated over 5000 times in the hydrate over the solubility in water

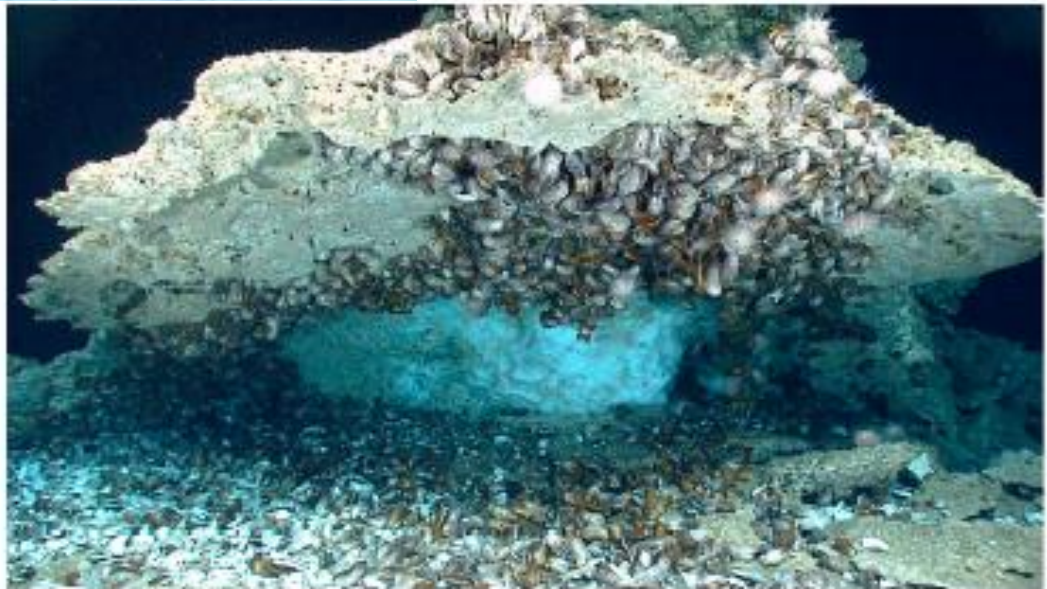


Natural deposits of methane clathrate hydrates are found in the ocean floor and under permafrost layers (Yuri F. Makogon, 1965)



Methane hydrate deposits

Methane hydrate sample  
in deep ocean  
(note stability  
temperature is above  
freezing point of water)

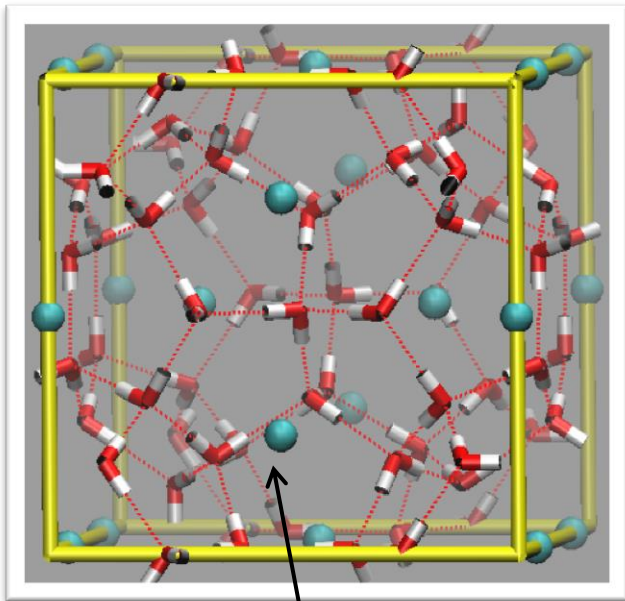


# Crystal structure of clathrate hydrates (1949 – 1965)

Water forms an open framework that encapsulates the “guest” molecules  
The specific water framework and cages formed depend on the size of the guest.

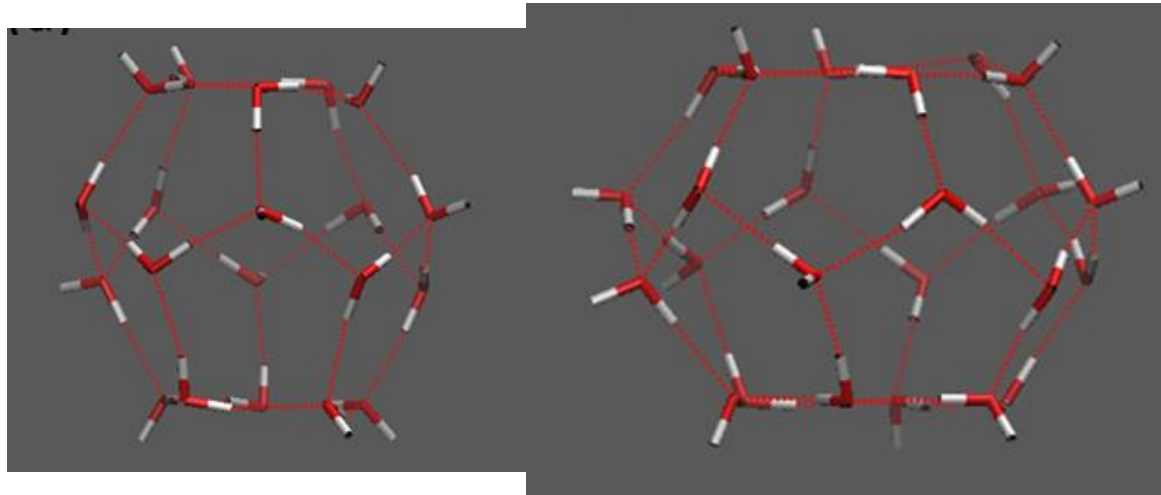
## Structure I (small guest molecules)

Cubic unit cell



Methane  
encapsulated in  
the water cage

Cages making up the unit cell structure



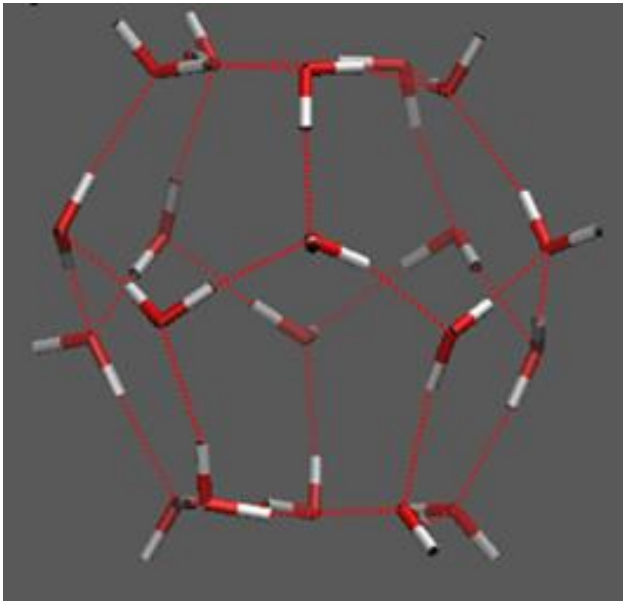
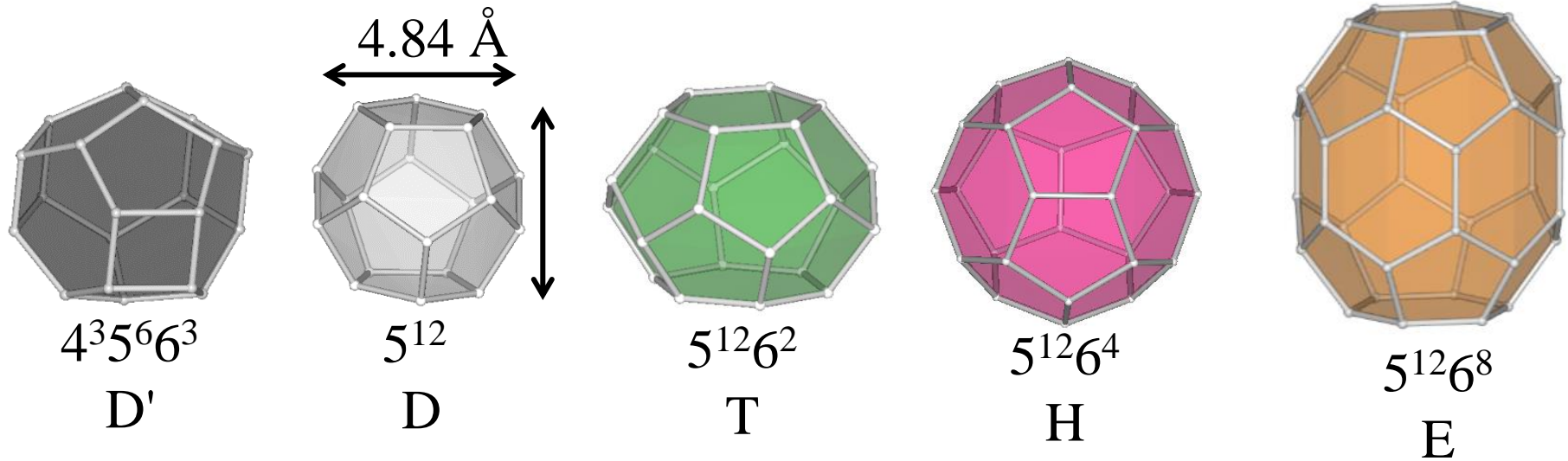
$5^{12}$

D: dodecahedral  
(small)

$5^{12}6^2$

T: tetrakaidecahedral  
(large)

# Water cage structures in common clathrate hydrate structures

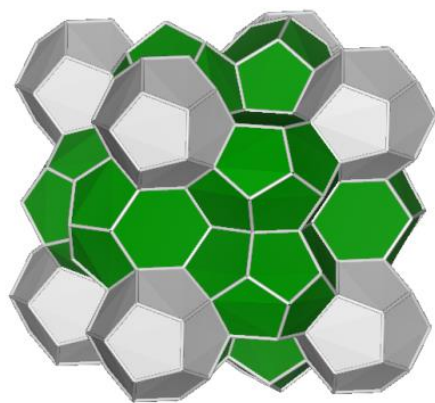


Cages are made of hydrogen bonded water molecules:

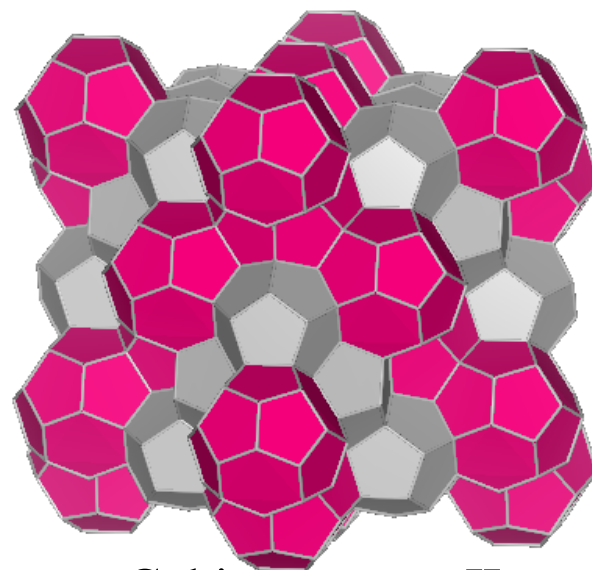
- Hydrogen bonds obey the ice rules
- Hydrogen orientations are disordered in the unit cell
- O-H...O hydrogen bond angles are  $\sim 108^\circ$ ,  $\sim 120^\circ$ ,  $\sim 90^\circ$

# Structures of canonical clathrate hydrates with neutral guest molecules

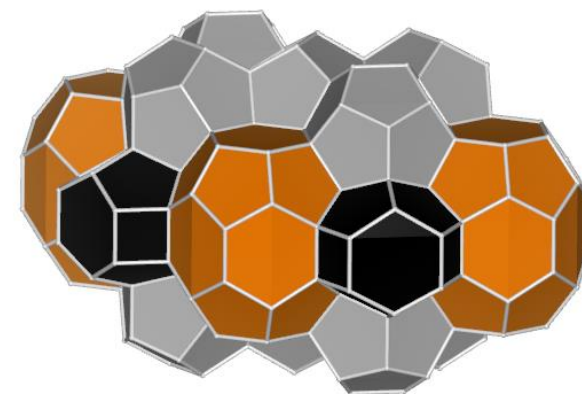
Structure Type	Unit cell content Space group	Typical unit cell parameters	Cages
CS-I Structure I	2D·6T·46H <sub>2</sub> O $Pm\bar{3}n$	$a = 11.9 \text{ \AA}$	5 <sup>12</sup> (D) 5 <sup>12</sup> 6 <sup>2</sup> (T)
CS-II Structure II	16D·8H·136H <sub>2</sub> O $Fd\bar{3}m$	$a = 17.0 \text{ \AA}$	5 <sup>12</sup> (D) 5 <sup>12</sup> 6 <sup>4</sup> (H)
HS-III Structure H	3D·2D'·E·34H <sub>2</sub> O $P6/mmm$	$a = 12.2 \text{ \AA}$ $c = 10.0 \text{ \AA}$	5 <sup>12</sup> (D) 4 <sup>3</sup> 5 <sup>6</sup> 6 <sup>3</sup> (D') 5 <sup>12</sup> 6 <sup>8</sup> (E)



Cubic structure I  
CS-I (sI)

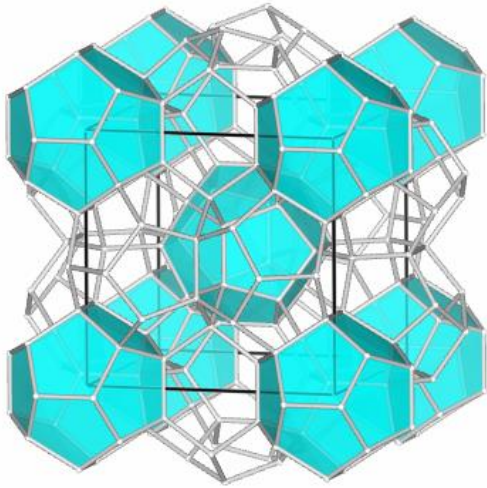


Cubic structure II  
CS-II (sII)

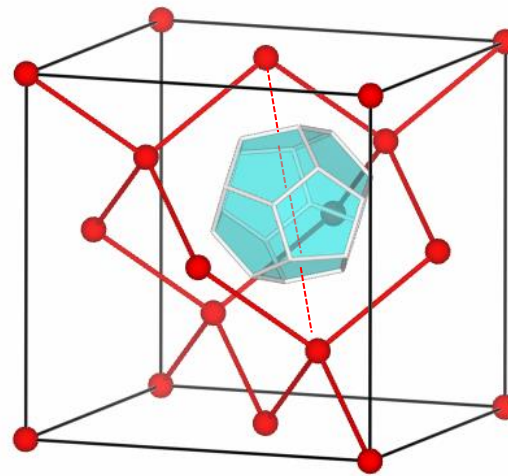


Hexagonal structure II  
HS-III (sH) 12

# sI and sII clathrates unit cells are related to cubic structures in alloys



sI clathrate:  
Body centered cubic with respect to  $5^{12}$  cages



sII clathrate:  
Diamond lattice with respect to  $5^{12}6^4$  cages

Structure determination was performed by  
- von Stackelberg - Claussen - Pauling and Marsh

*Acta Cryst.* (1958). **11**, 184

**Complex Alloy Structures Regarded as Sphere Packings.  
I. Definitions and Basic Principles**

BY F. C. FRANK

*H. H. Wills Physics Laboratory, University of Bristol, England*

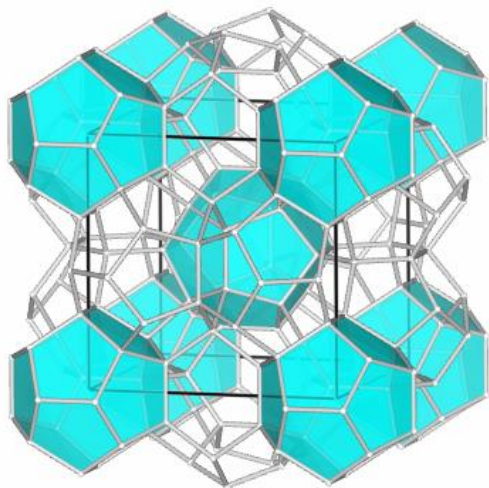
AND J. S. KASPER

*Research Laboratory, General Electric Company, Schenectady, N.Y., U.S.A.*

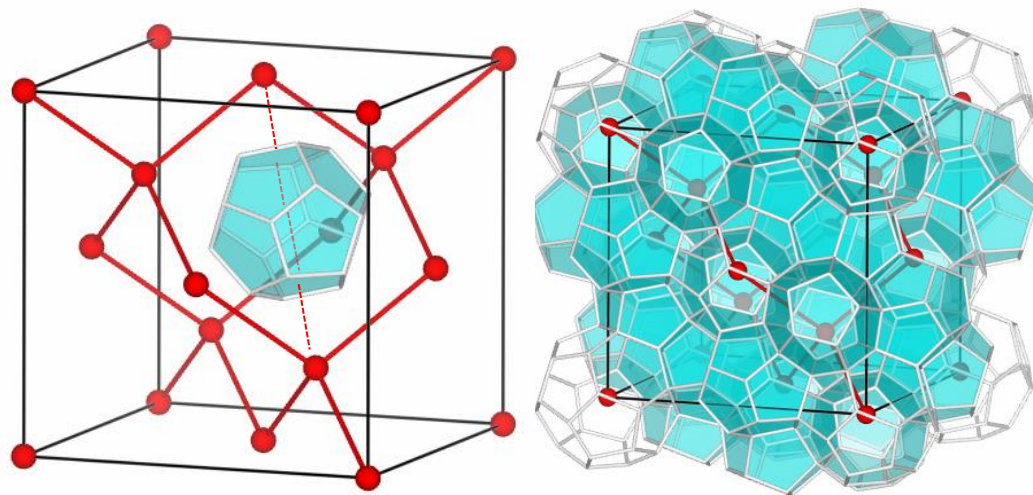
(Received 12 August 1957)

Hydrate structures are related to the Frank-Kasper structures in alloys

# sI and sII clathrates unit cells are related to cubic structures in alloys

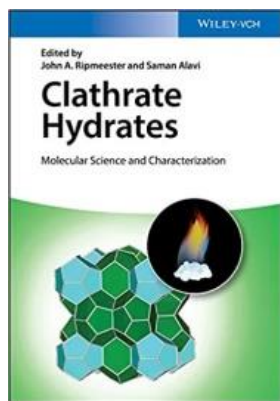


sI clathrate:  
Body centered cubic with respect to  
 $5^{12}$  cages



sII clathrate:  
Diamond lattice with respect to  $5^{12}6^4$   
cages

Please see our book (to be published this year) for further reading



Edited by J. A. Ripmeester & S. Alavi  
(13 Chapters)

# Clathrate hydrate thermodynamic inhibitors: Methanol

In oil and natural gas pipelines, moisture and C1 to C3 gases can lead to the formation of gas hydrates at temperatures above 0°C.



Magalhães Gama et al. Hydrate formation. NTNU, Trondheim 2014



<http://www.wsj.com/articles/u-s-judge-finds-bp-grossly-negligent-in-2010-deepwater-horizon-disaster-1409842182>

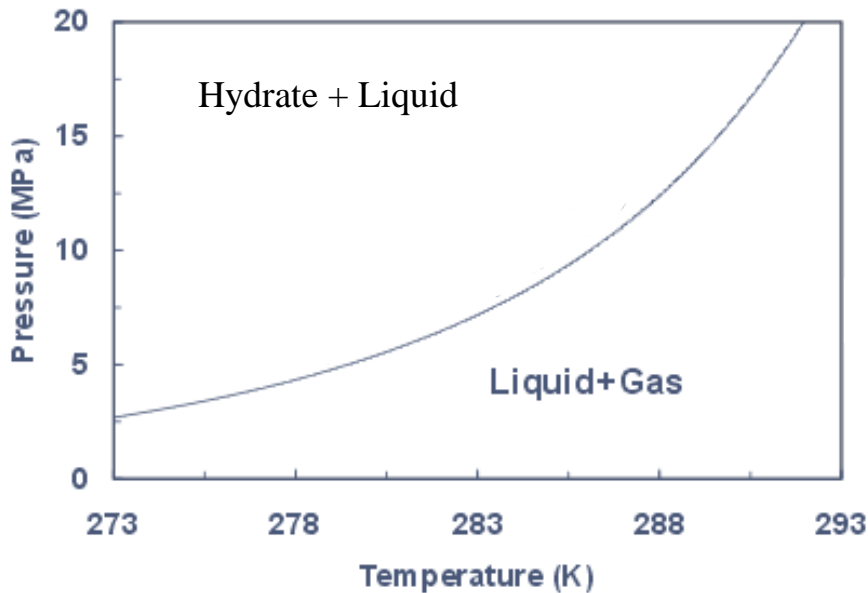
- The engineering field of **flow assurance** aims to prevent hydrate formation
- This is done primarily through the use of expensive heating systems or chemical additives in gas pipeline operations
- Between \$200 million - \$ 1 billion each year is spent in industry to prevent hydrate buildup in pipelines.

(MIT News: <http://web.mit.edu/newsoffice/2012/undersea-ice-clog-mitigation-0412.html>)

# Thermodynamic hydrate inhibitors

Condition of chemical equilibrium during hydrate formation:

$$\mu_{hydrate}(X, p, T) = \mu_{aqueous\ phase}(X, p, T) + \mu_{methane}(p, T)$$

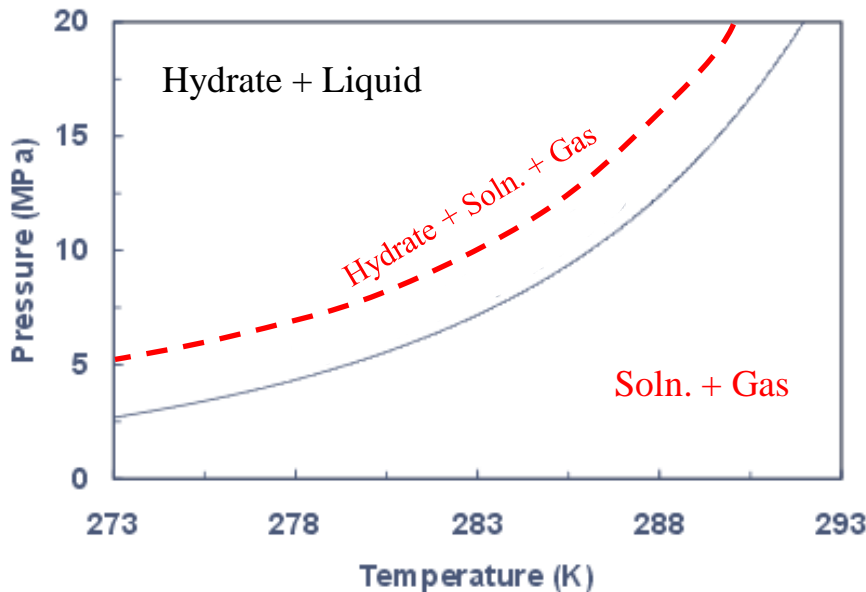




# Thermodynamic hydrate inhibitors

Condition of chemical equilibrium during hydrate formation:

$$\mu_{hydrate}(X, p, T) = \mu_{aqueous\ phase}(X, p, T) + \mu_{methane}(p, T)$$



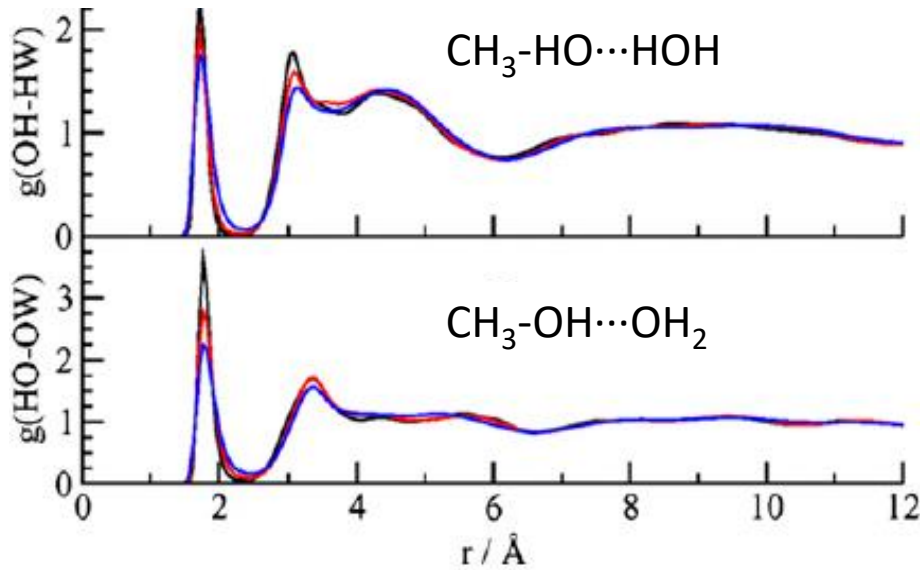
Methanol is a thermodynamic inhibitor to hydrate formation:

Through hydrogen bonding, methanol:

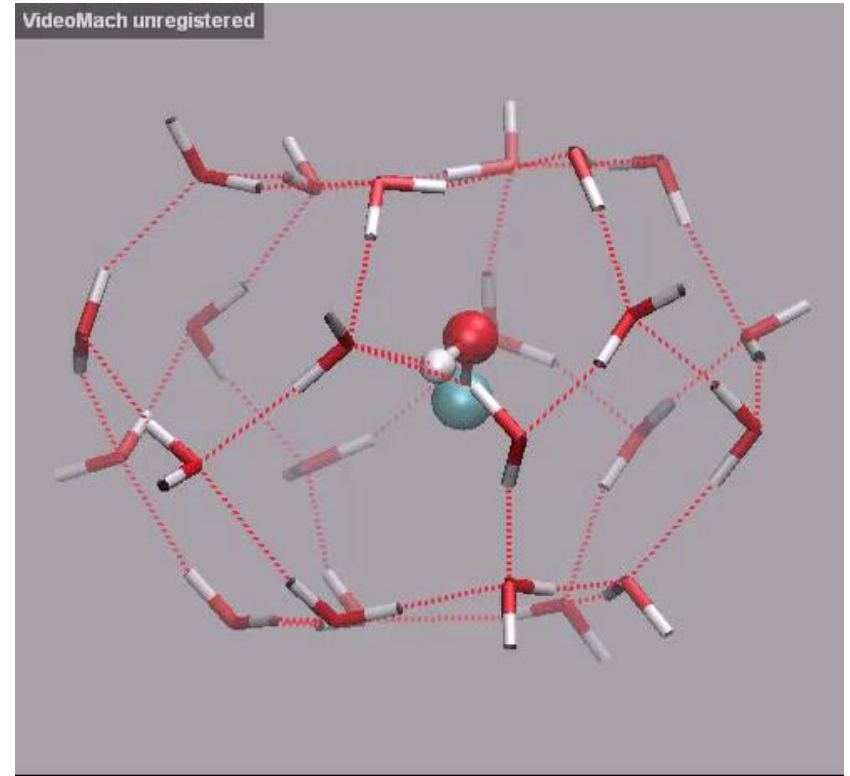
- i. Stabilizes the solution phase;
- ii. Destabilizes the solid hydrate framework.

At high temperatures, strong hydrogen bonds between methanol and water destabilizes the clathrate hydrate cages

Radial distribution function of water - methanol



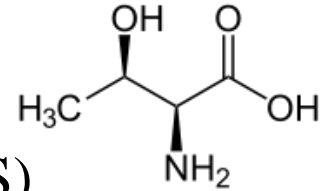
Methanol in a sI large cage at 200 K  
(extracted from a periodic simulation)



- Large amounts of methanol must be used to get sufficient hydrate inhibition (becomes expensive)
- Methanol is toxic and hazardous to work with

## Kinetic hydrate inhibitors: Antifreeze proteins?

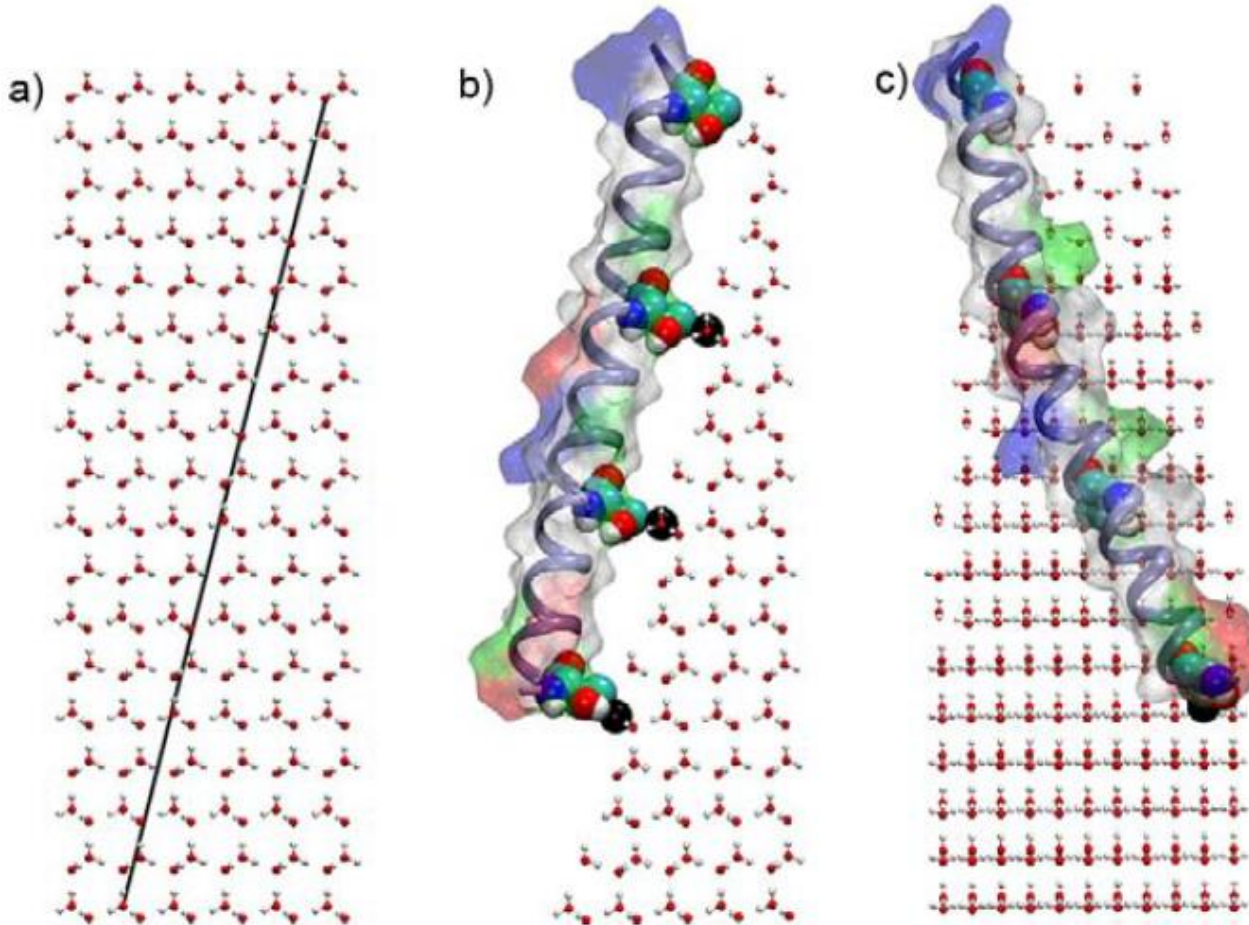
- Antifreeze proteins (AFPs) bind to ice crystals and prevent / slow down ice recrystallization
- Usually threonine rich proteins
- AFPs bind to water / ice through the ice binding surface (IBS)
- Spacing on the IBS matches specific facets of the ice surface.







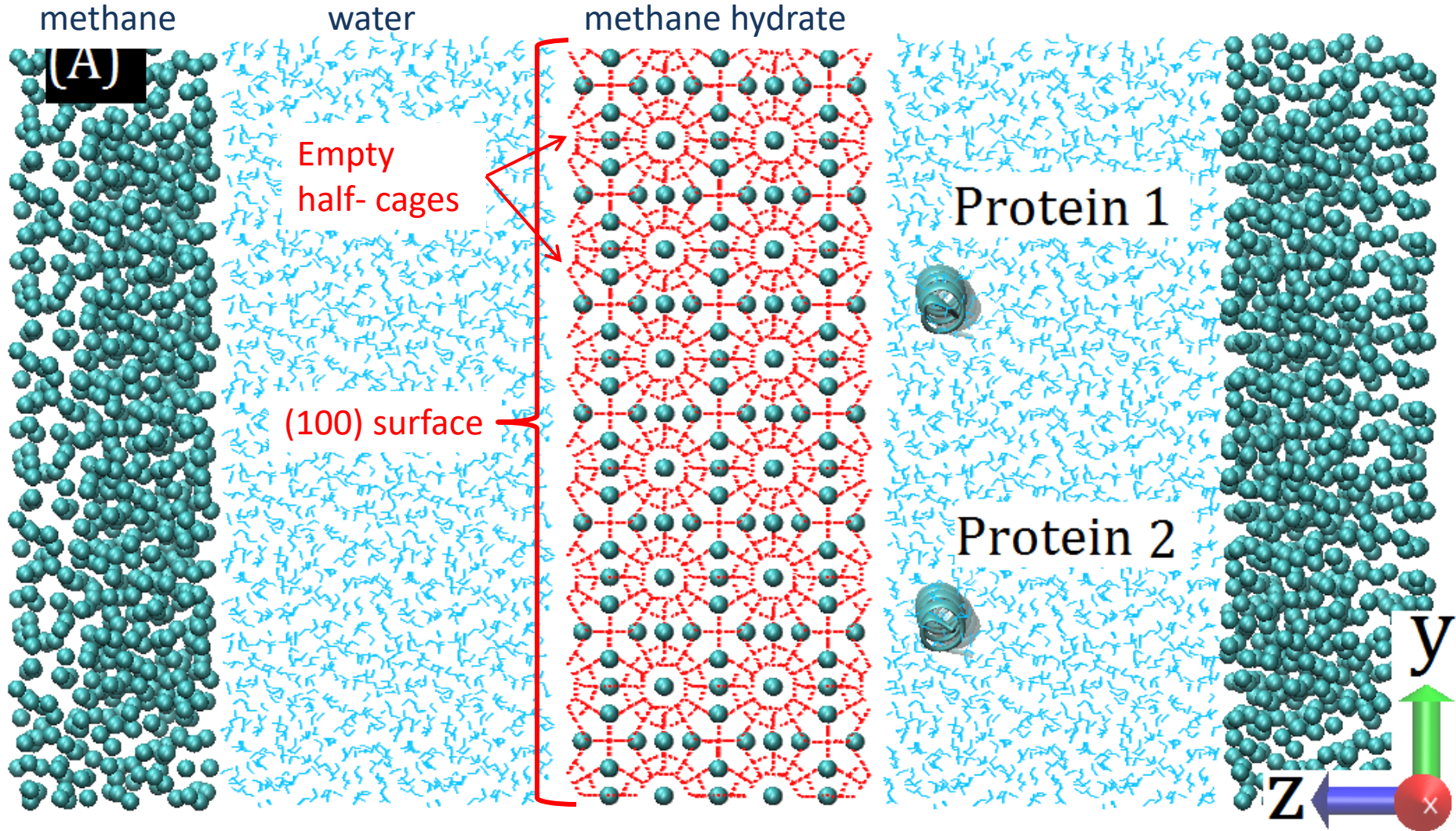
# Binding of wf-AFP occurs on the {2021} plane of hexagonal ice



- Spacing of water on the {2021} surface corresponds to the spacing of threonines in the AFP.

- AFPs show some hydrate inhibition activity, why?
- Clathrate hydrates do not have the same crystal structure as Ih

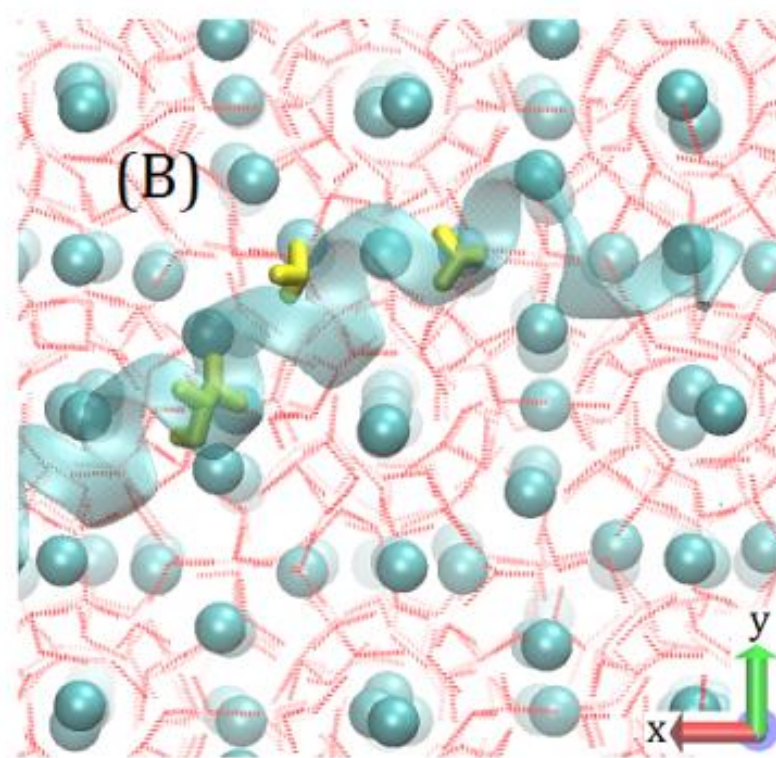
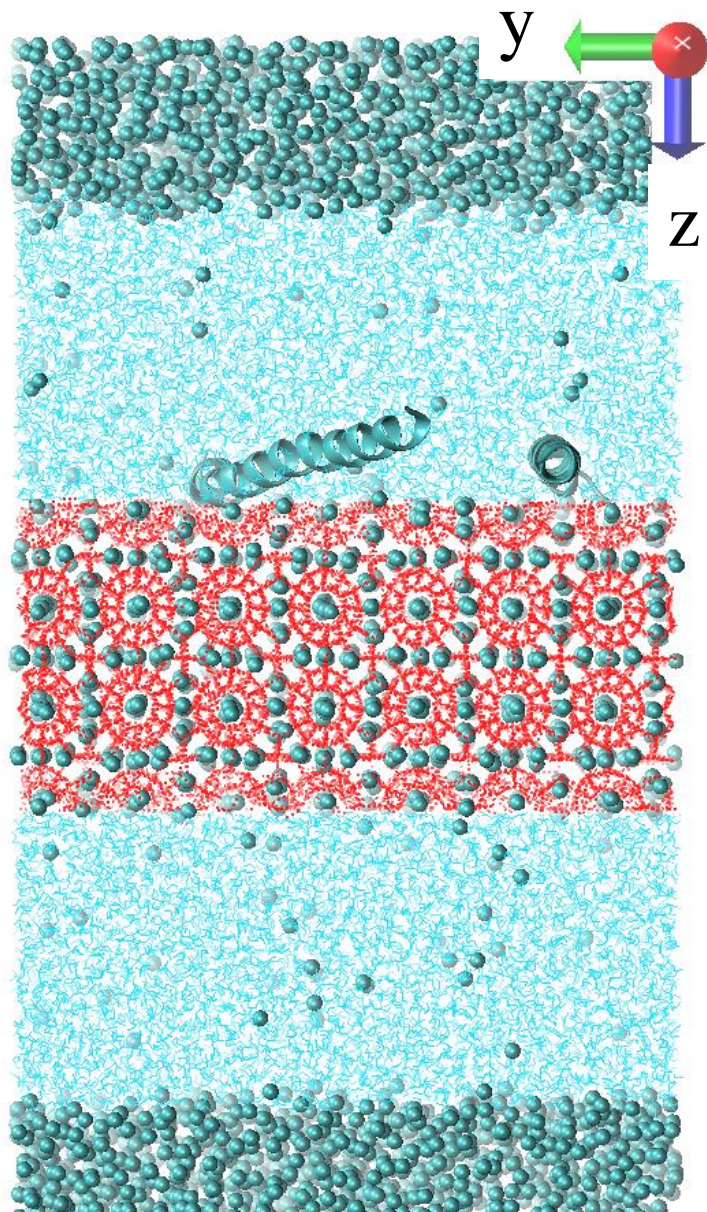
# Simulation setup for wf-AFP near methane hydrate (100) surface



$T = 275$  K and  
 $P = 800$  bar

Bagherzadeh, Alavi, Ripmeester, Englezos  
[PCCP 2015, 17, 9984-9990.](#)

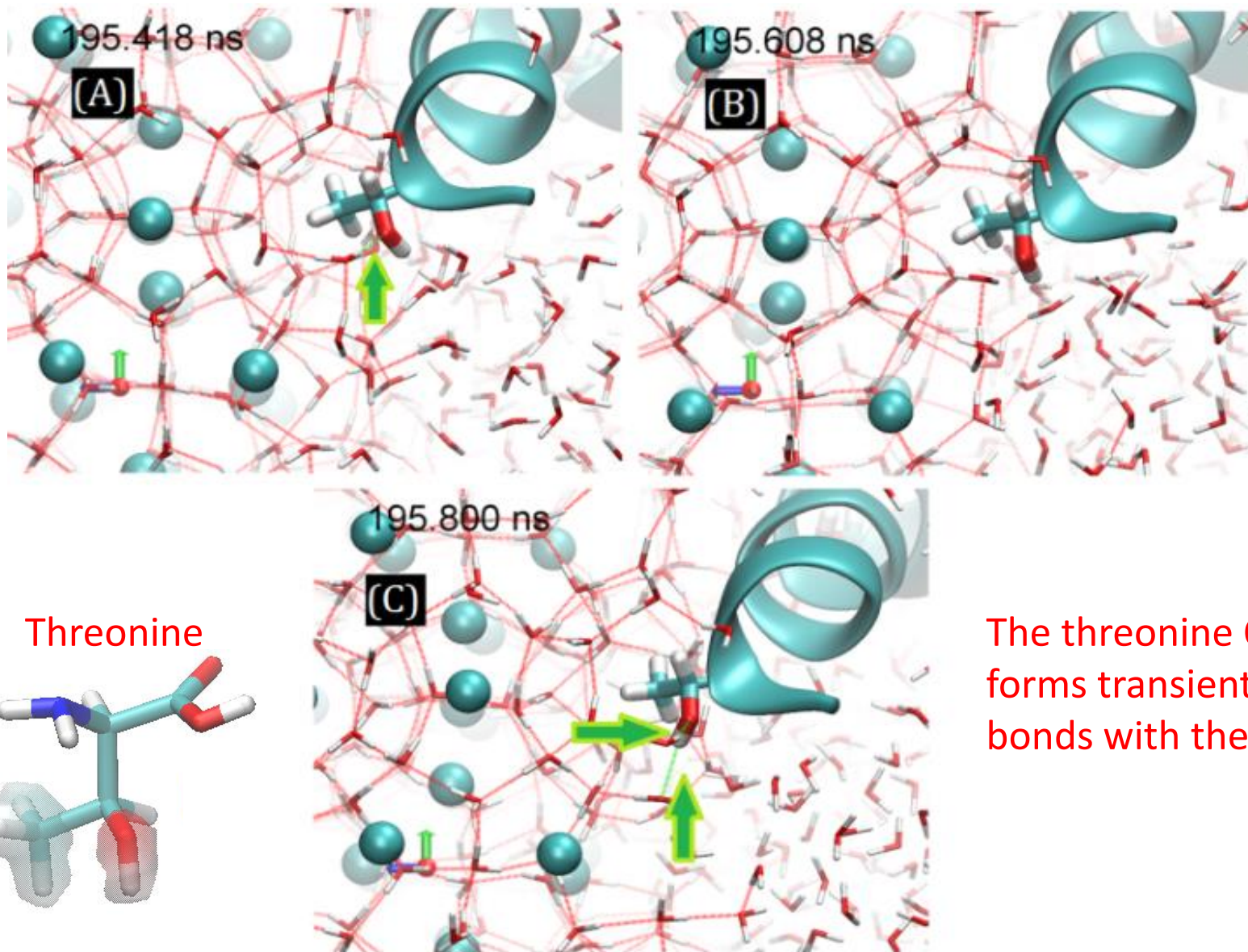
# Simulation results after 200 ns



The AFP resides on the surface with the ice binding surface interacting with the hydrate



# A threonine methyl group is anchored in a methane hydrate empty cage

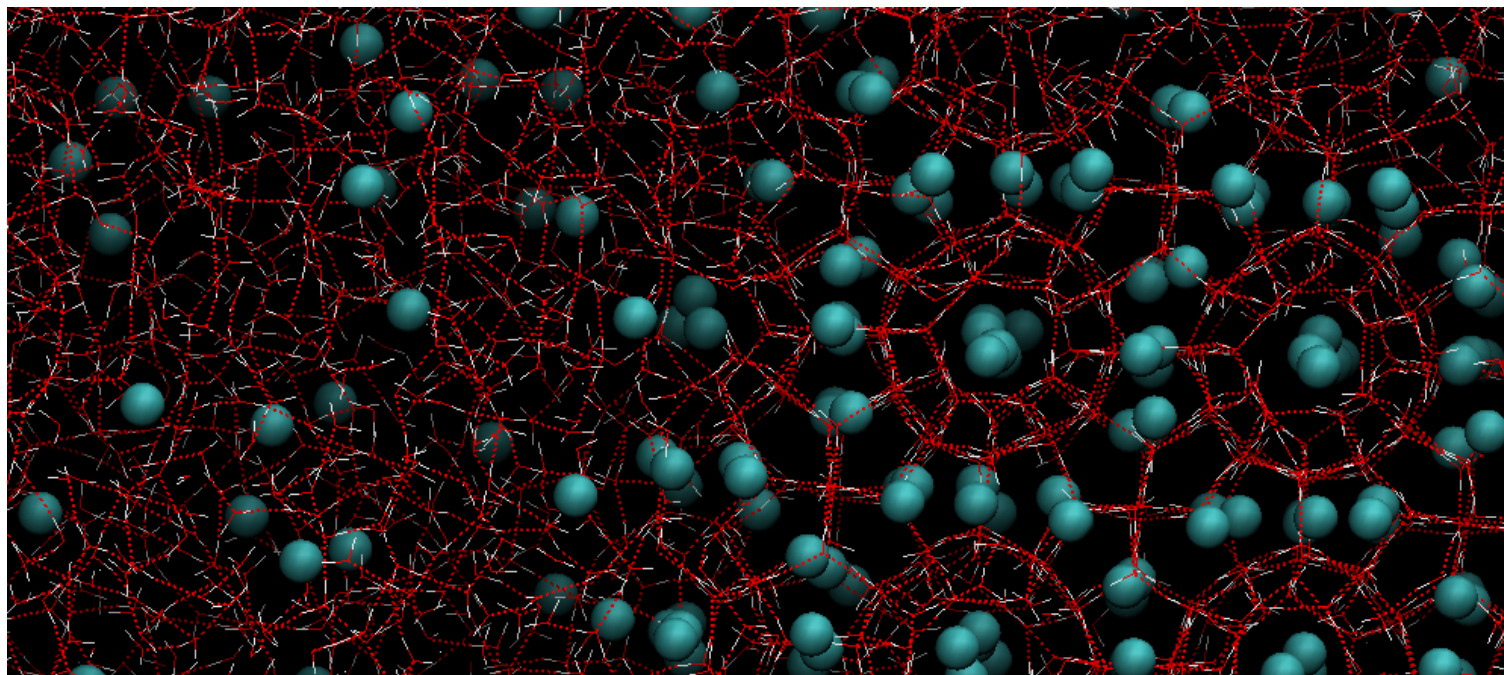
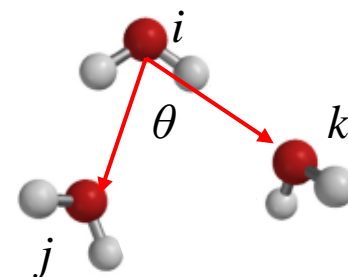


## $F_3$ order parameter to distinguish local structure in water / hydrate

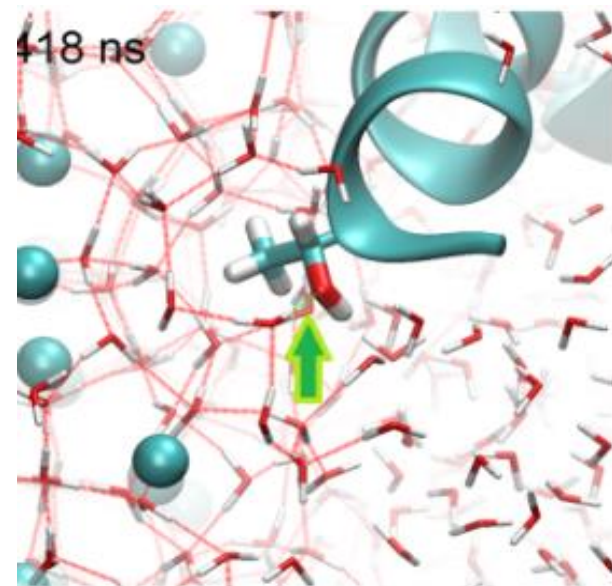
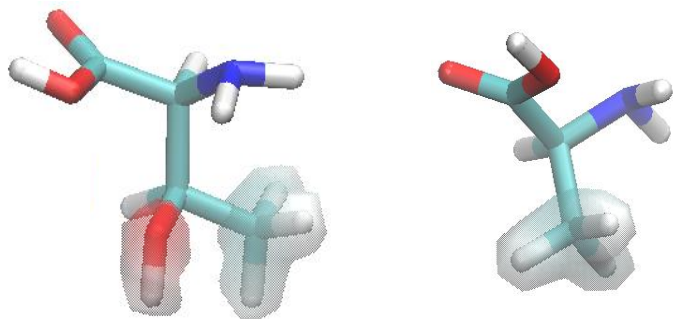
$$F_3 = \langle [|\cos\theta_{jik}| |\cos\theta_{jik}| + \cos^2 109.5^\circ] \rangle$$

$j$ ,  $i$ , and  $k$  are a triplet of water molecules within 3.5 Å of each other

$$F_3 = \begin{cases} 0.09 & \text{for liquid water} \\ 0.015 & \text{for CH}_4 \text{ hydrate} \end{cases}$$

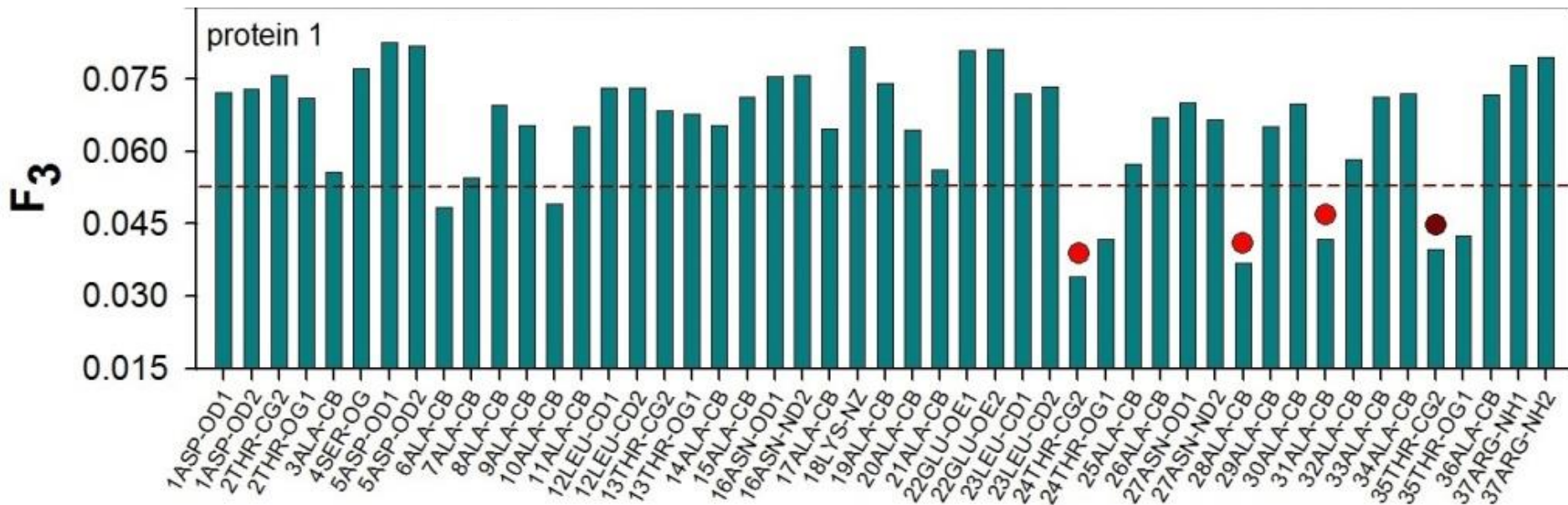


# $F_3$ order parameter for amino acid pendant groups at 200 ns

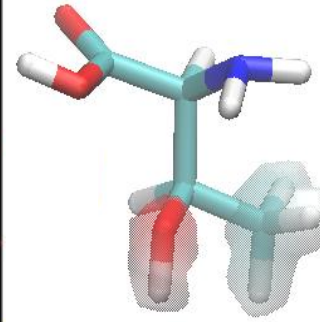
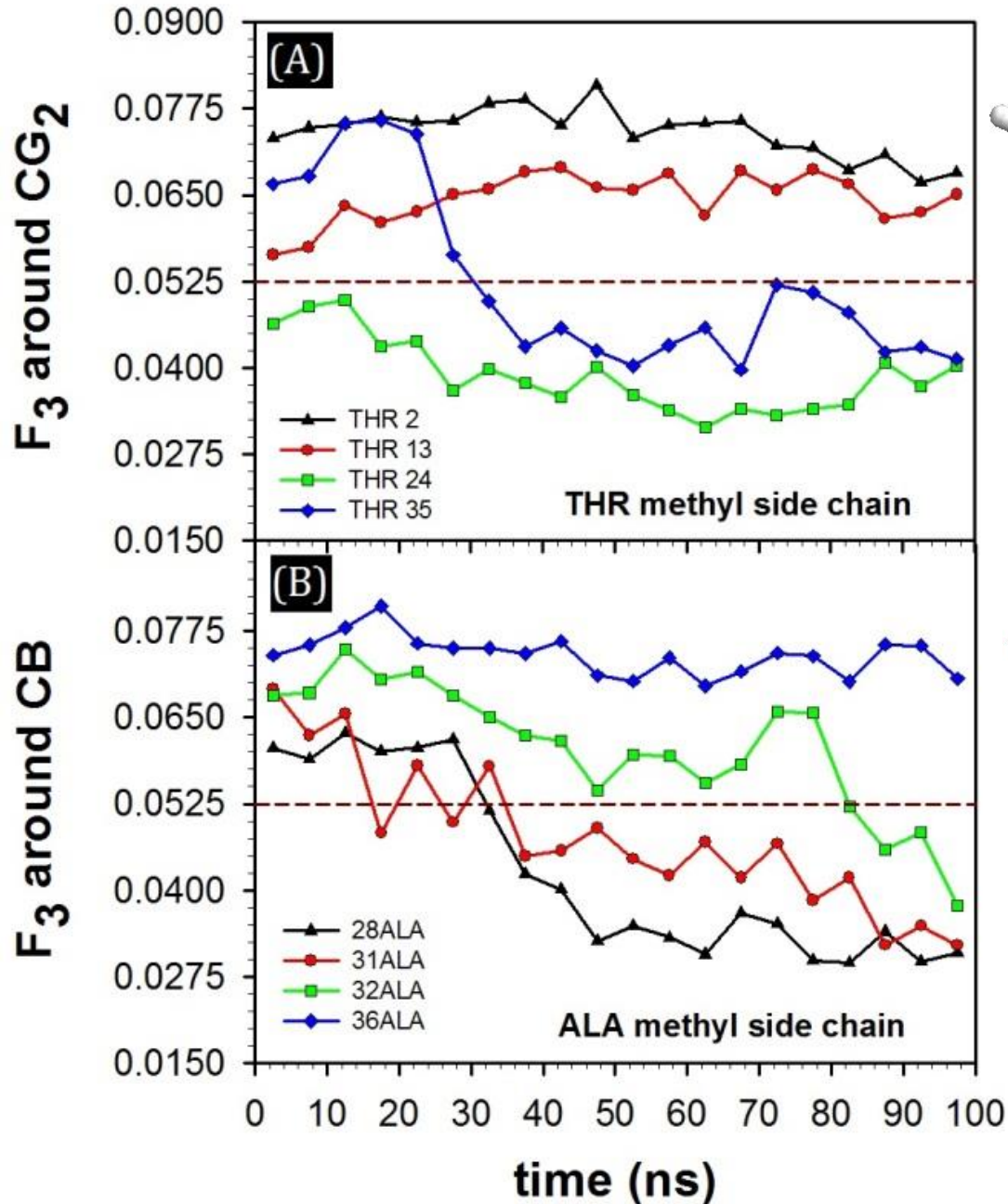


$$F_3 = \langle [|\cos\theta_{jik}| |\cos\theta_{jik}| + \cos^2 109.5^\circ] \rangle$$

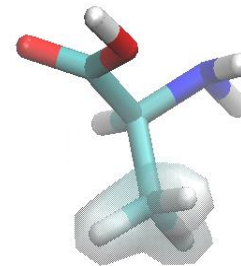
$j$ ,  $i$ , and  $k$  are a triplet of water molecules within 3.5 Å of the amino acid pendent group



# Change in water environment around pendant groups with time



-As a threonine  
-CH<sub>3</sub> group is  
incorporated into  
an empty half-cage  
on the surface,  
-CH<sub>3</sub> groups from  
near-by alanines  
start binding to the  
surface;

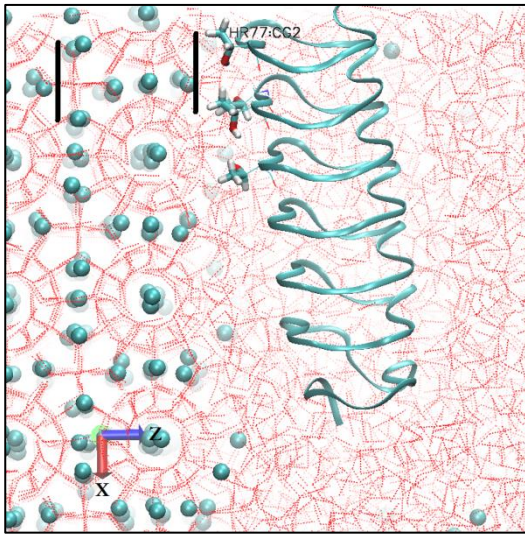


Is this a general  
mechanism?  
Can we use it to  
design hydrate  
inhibitors?

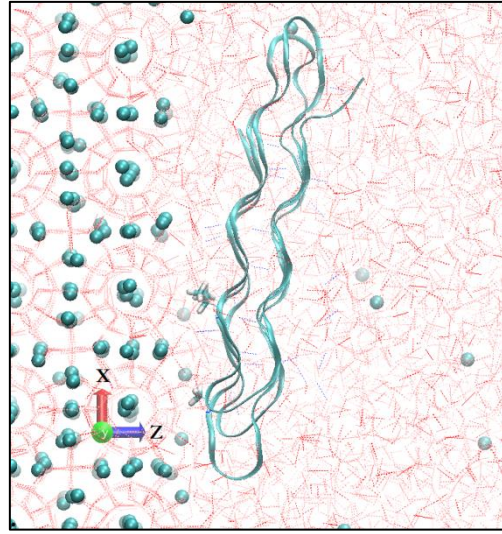
# Do other antifreeze proteins bind to hydrate surfaces in a similar way?

Future work:

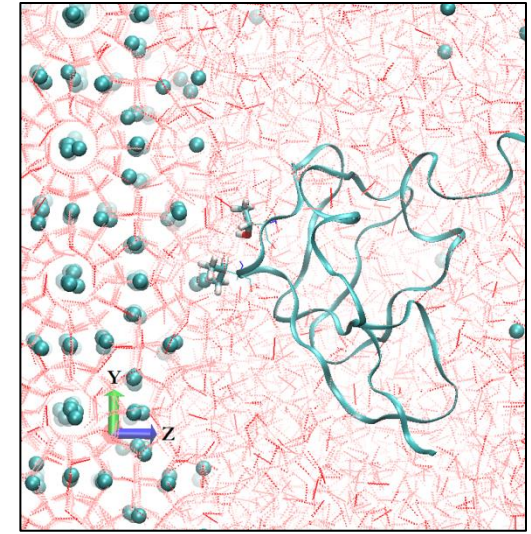
- Studying other AFPs
- Designing other kinetic hydrate inhibitors based on the same principles



Yellow-Mealworm AFP



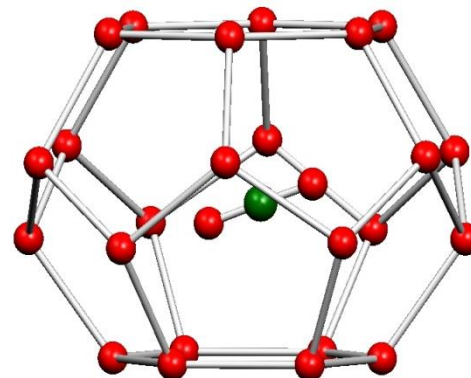
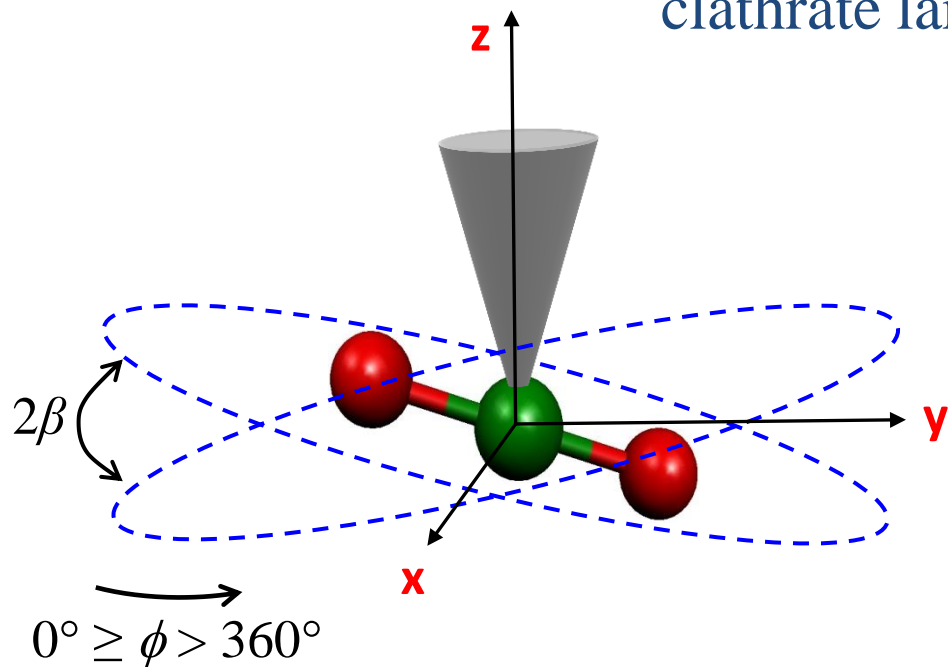
Snow flea AFP



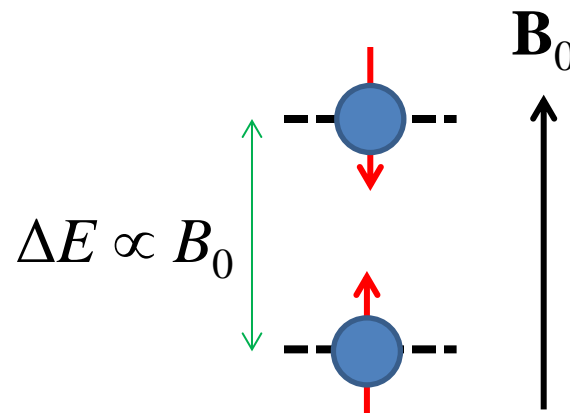
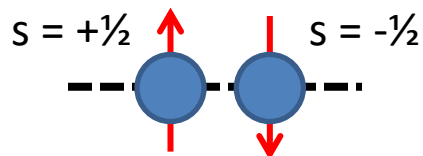
Ocean Pout AFP



# Calculation of solid-state NMR lineshapes for CO<sub>2</sub> in structure I clathrate large cages



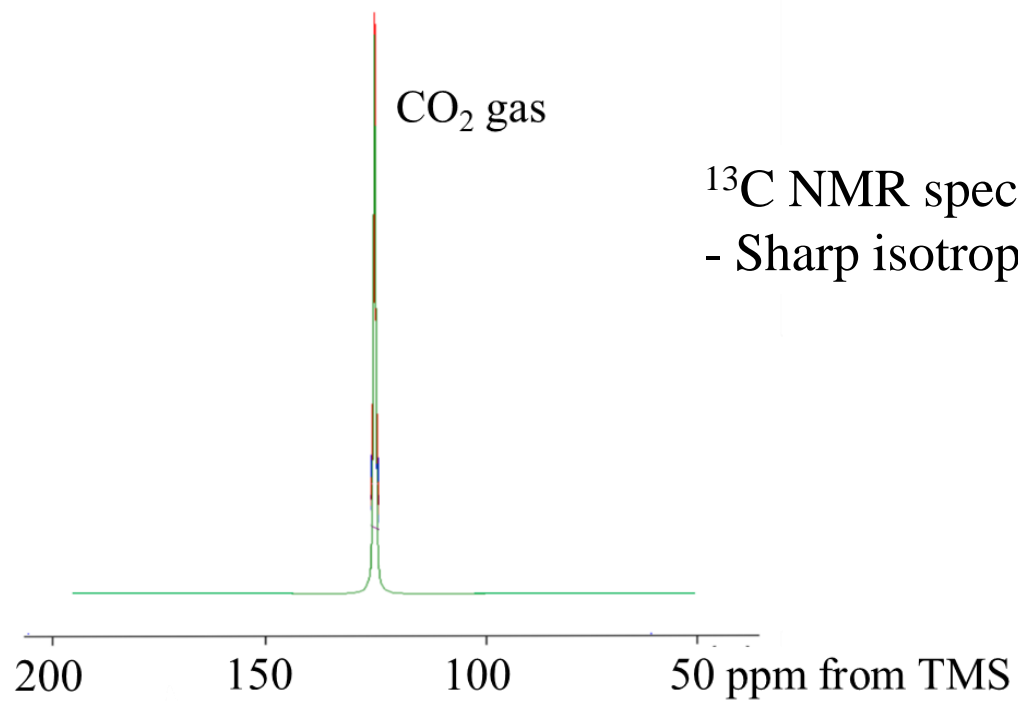
spin  $\frac{1}{2}$  nuclei are degenerate in the absence of a magnetic field



S. Alavi, P. Dornan, T. K. Woo (2008). Determination of NMR Lineshape Anisotropy of Guest Molecules within Inclusion Complexes from Molecular Dynamics Simulations. *ChemPhysChem* **9**, 911-919.

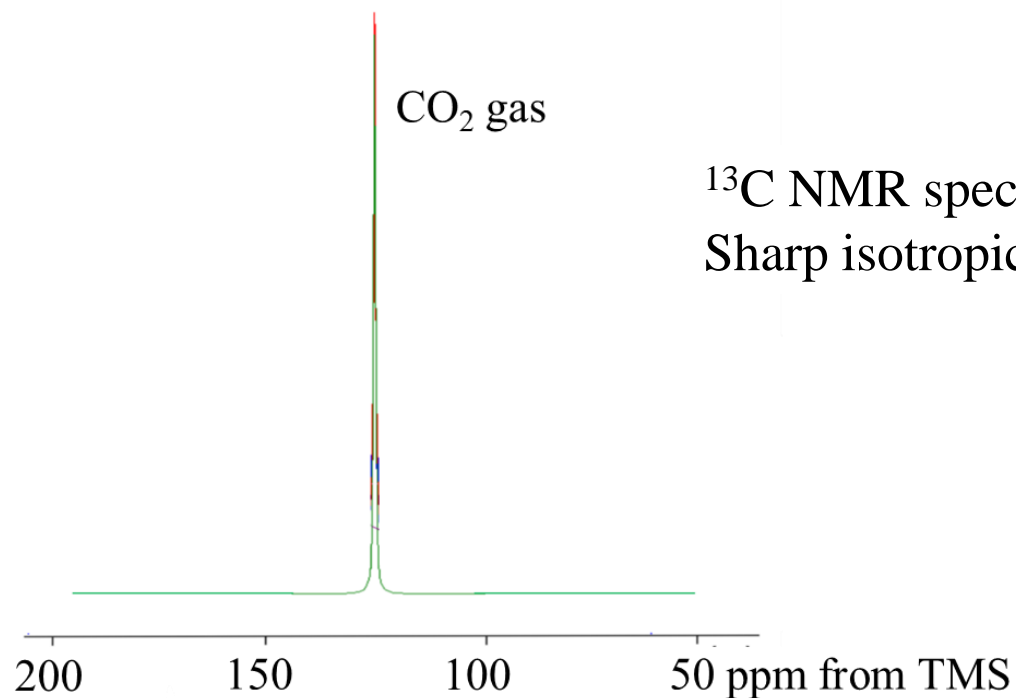
H. Mohammadimanesh, S. Alavi, T. K. Woo, B. Najafi (2011). Molecular dynamics simulation of <sup>13</sup>C NMR lineshapes of linear molecules in structure I clathrate hydrate. *Phys. Chem. Chem. Phys.* **13**, 2367-2377.

# NMR lineshape of gas phase and solid-state CO<sub>2</sub>

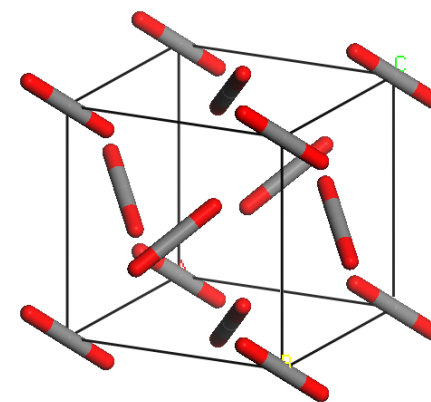
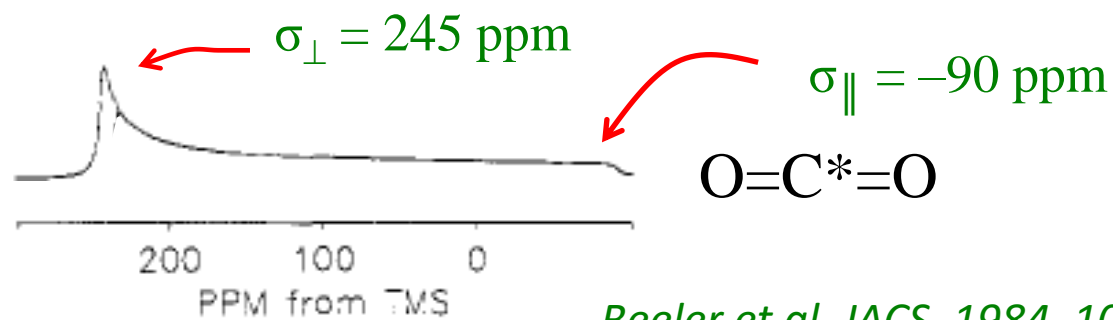


<sup>13</sup>C NMR spectrum of CO<sub>2</sub> gas  
- Sharp isotropic peak

# NMR lineshape of gas phase and solid-state CO<sub>2</sub>



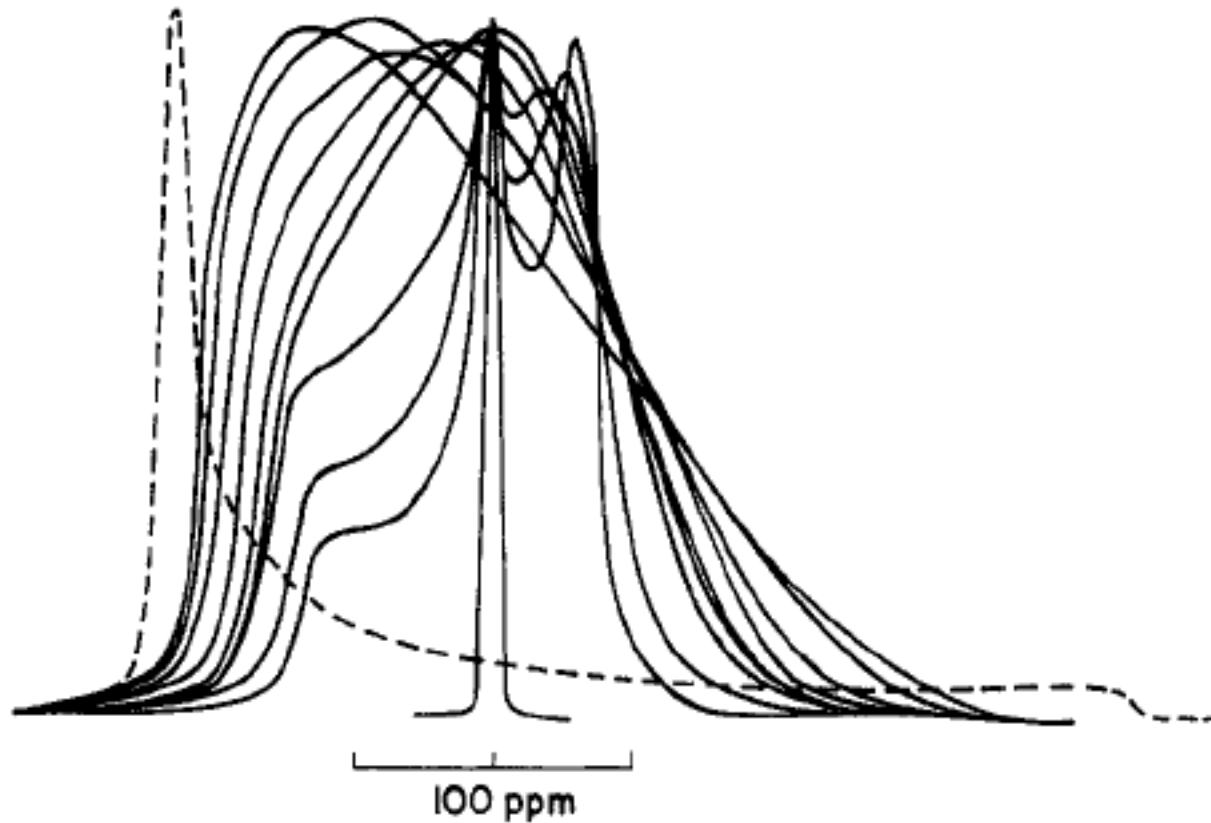
<sup>13</sup>C NMR spectrum of CO<sub>2</sub> solid is a broad non-isotropic peak



*Beeler et al. JACS, 1984, 106, 7672.*

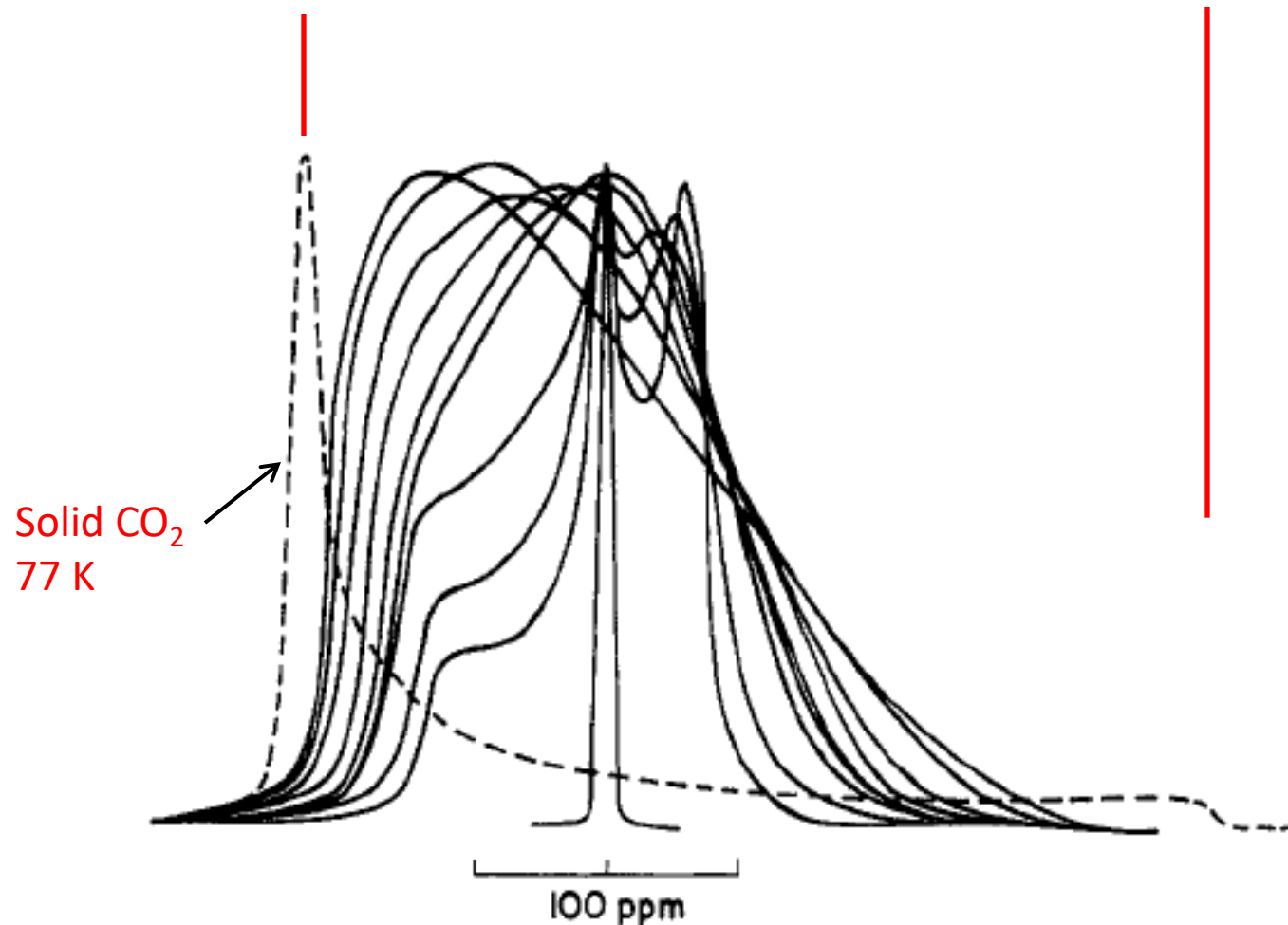


# $^{13}\text{C}$ NMR lineshapes of solid state $\text{CO}_2$ and sI $\text{CO}_2$ clathrate



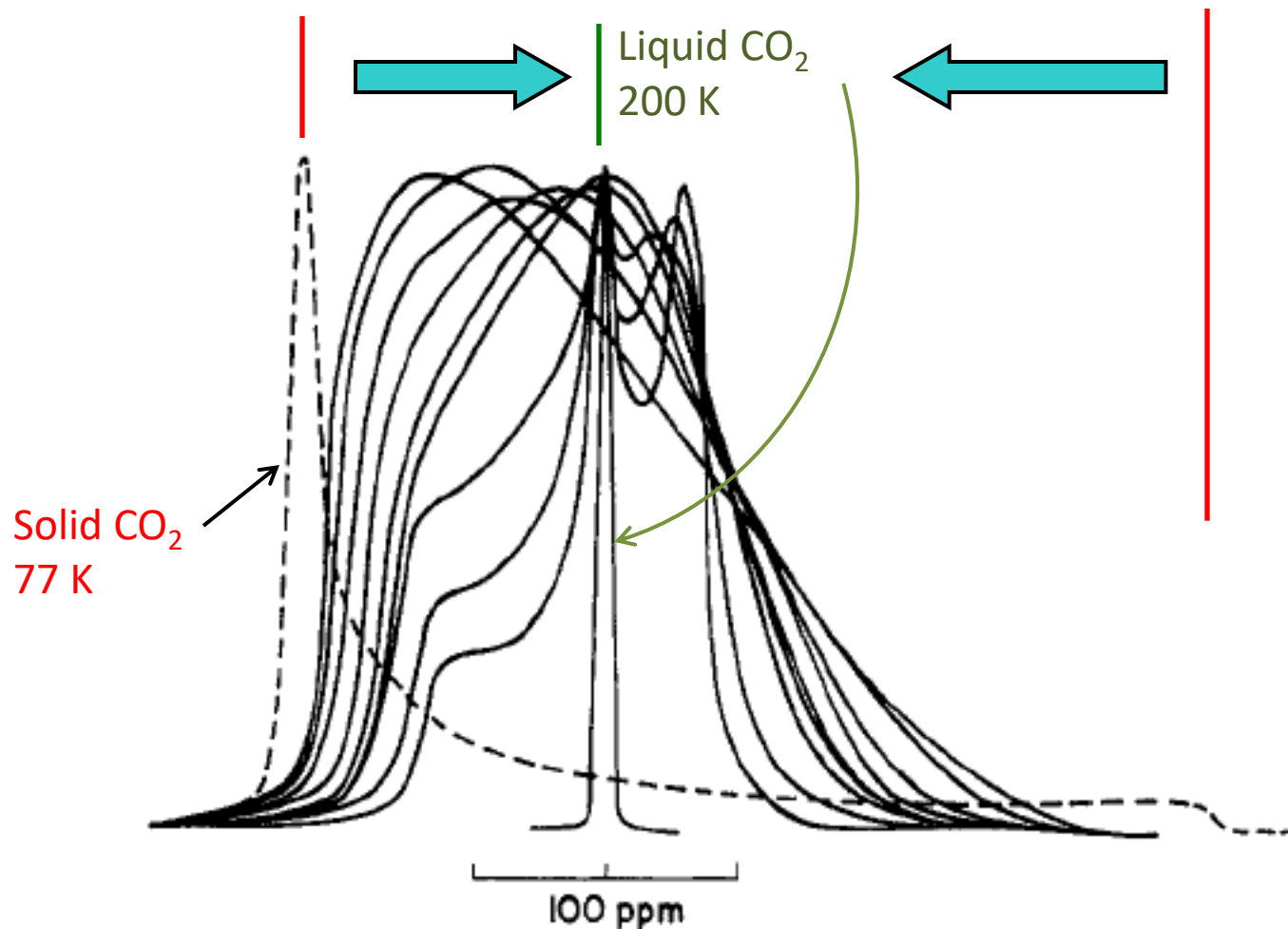
The  $^{13}\text{C}$  NMR lineshape of  $\text{CO}_2$  clathrate hydrate changes as a function of temperature

# $^{13}\text{C}$ NMR lineshapes of solid state $\text{CO}_2$ and sI $\text{CO}_2$ clathrate



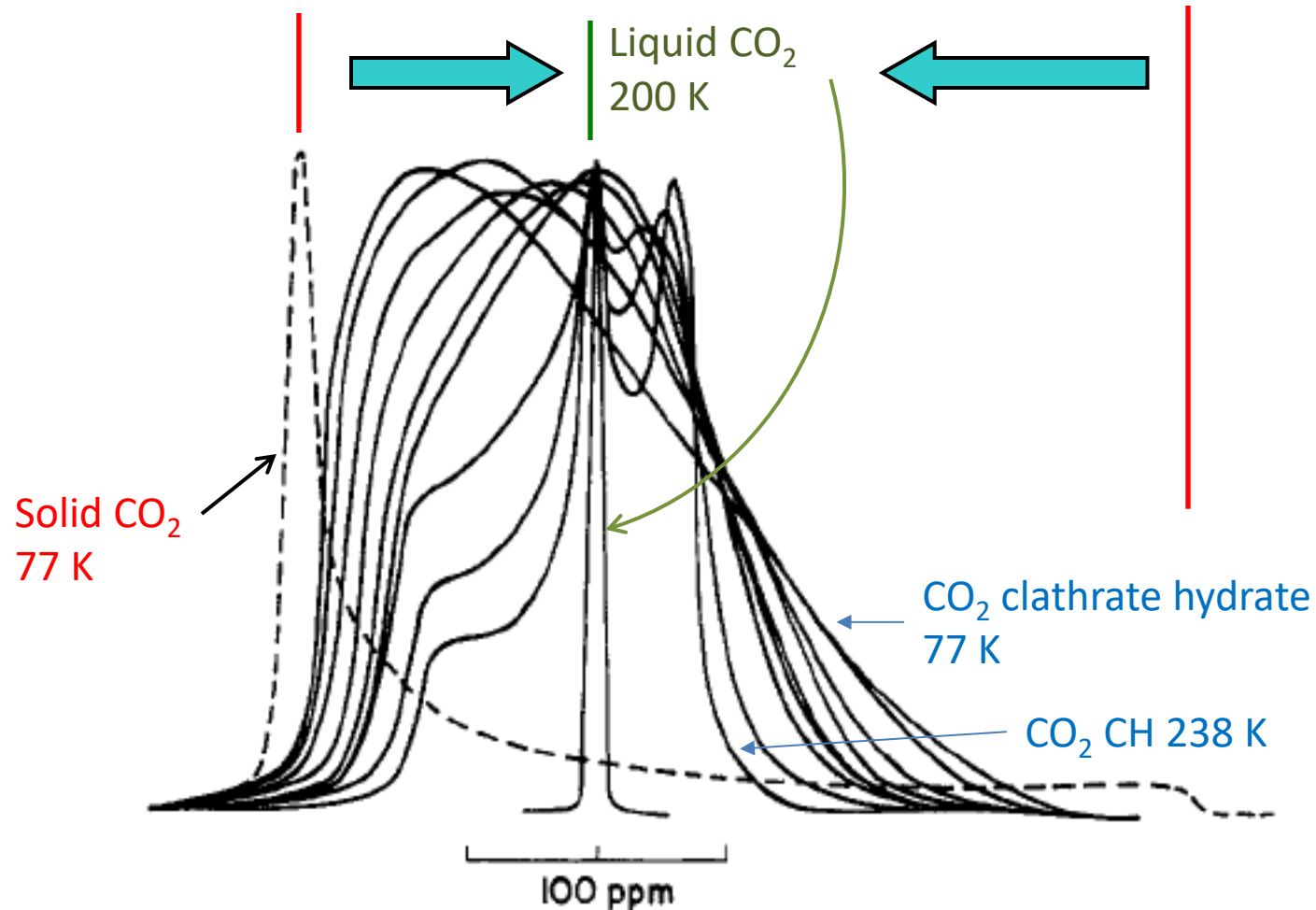
The  $^{13}\text{C}$  NMR lineshape changes as a function of temperature

# $^{13}\text{C}$ NMR lineshapes of solid state $\text{CO}_2$ and sI $\text{CO}_2$ clathrate



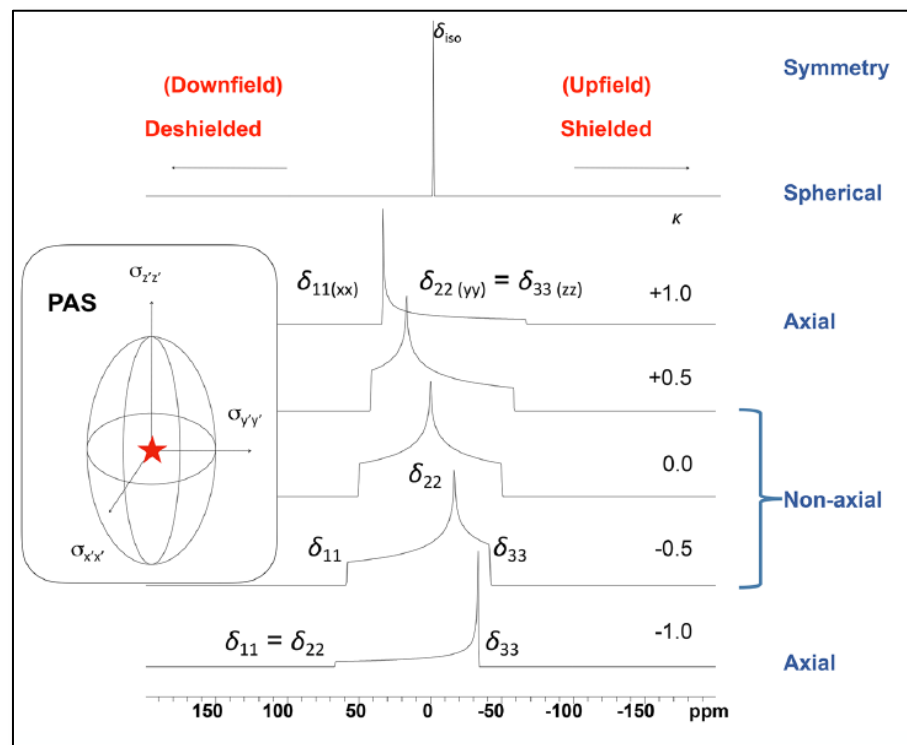
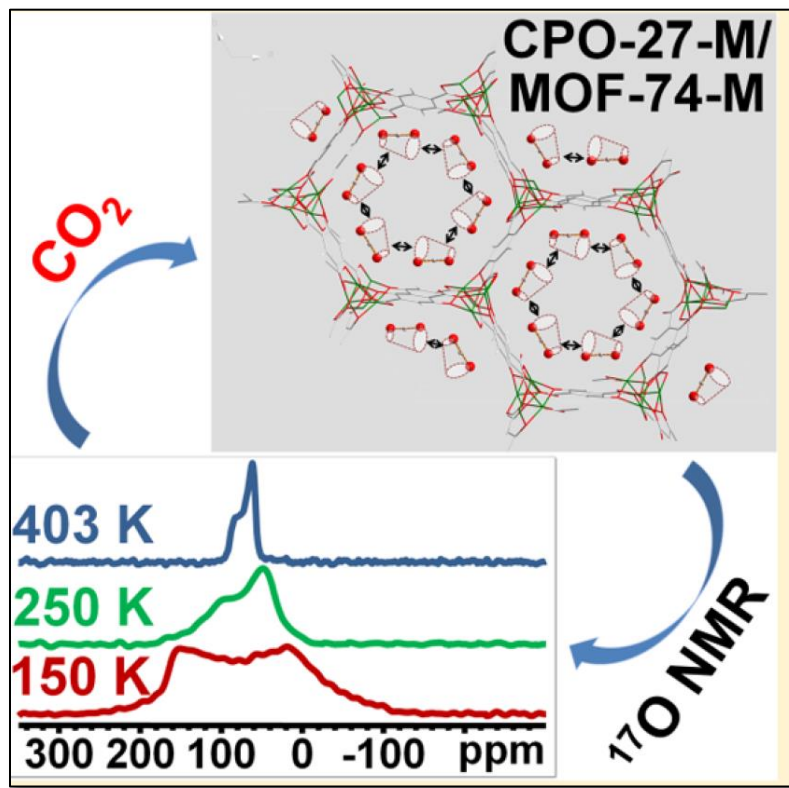
The  $^{13}\text{C}$  NMR lineshape changes as a function of temperature

# $^{13}\text{C}$ NMR lineshapes of solid state $\text{CO}_2$ and sI $\text{CO}_2$ clathrate



The  $^{13}\text{C}$  NMR lineshape changes as a function of temperature

# NMR lineshapes of adsorbed CO<sub>2</sub> in Metal-Organic Frameworks



## Wobbling and Hopping: Studying Dynamics of CO<sub>2</sub> Adsorbed in Metal–Organic Frameworks via <sup>17</sup>O Solid-State NMR

Wei David Wang,<sup>†,‡</sup> Bryan E. G. Lucier,<sup>†</sup> Victor V. Tersikh,<sup>§</sup> Wei Wang,<sup>\*‡</sup> and Yining Huang<sup>\*‡</sup>

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<sup>§</sup>Department of Chemistry, University of Ottawa, Ottawa, Ontario Canada, K1N 6N5

## Solid-State NMR Investigations of Carbon Dioxide Gas in Metal–Organic Frameworks: Insights into Molecular Motion and Adsorptive Behavior

Valencia J. Witherspoon,<sup>●</sup> Jun Xu,<sup>●</sup> and Jeffrey A. Reimer<sup>\*●</sup>

Department of Chemical and Biomolecular Engineering, University of California, Berkeley, Berkeley, California 94720, United States

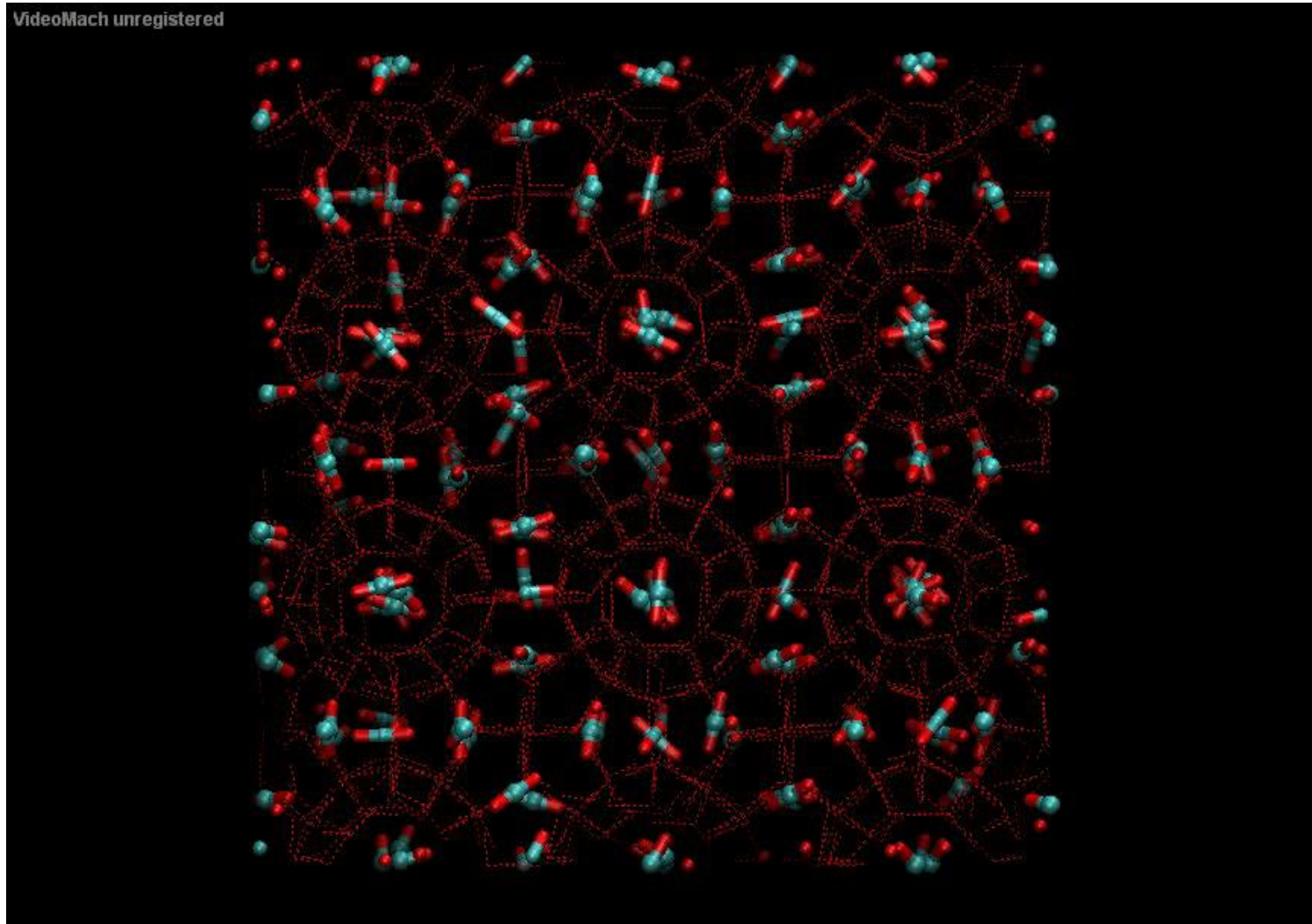
# Molecular dynamics of CO<sub>2</sub> guest motion in sI clathrate

Can MD be used to understand guest motion in cages and changes in NMR lineshape?

- 3×3×3 simulation cell of sI CO<sub>2</sub> clathrate with CO<sub>2</sub> in small and large cages
- DL\_POLY code
- SPC/E potential for water
- Harris – Yung potential for CO<sub>2</sub>
- 1 fs time step
- 100 ps total equilibration time
- Short range potential energy cutoff 15 Å

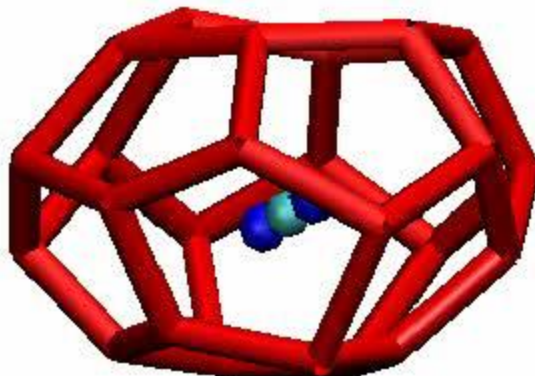
$$V(inter) = \sum_{i=1}^{N-1} \sum_{j>i}^N \left\{ 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \right\}$$

# CO<sub>2</sub> clathrate hydrate phase at 100 K



CO<sub>2</sub> guests are mobile in the sI clathrate hydrate cage

Simulated guest motion in an individual cage is complex:  
“High” temperature limit (**275 K**)



How can the motion of the CO<sub>2</sub> guest molecules be related to the lineshapes in the NMR spectra?



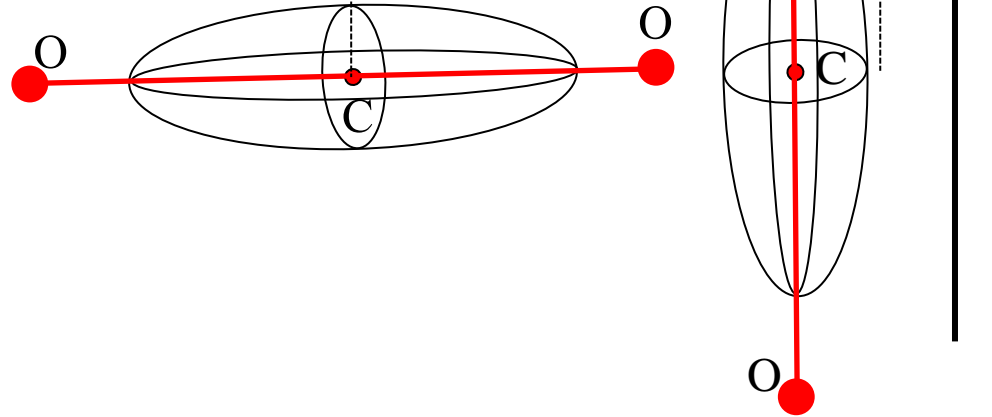
# The NMR transition: The chemical shielding (shift) tensor

$$\mathbf{B}_{local} = (\mathbf{1} - \boldsymbol{\sigma}) \cdot \mathbf{B}_0$$

Local magnet field at nucleus

Chemical shielding tensor

chemical shielding ellipsoid

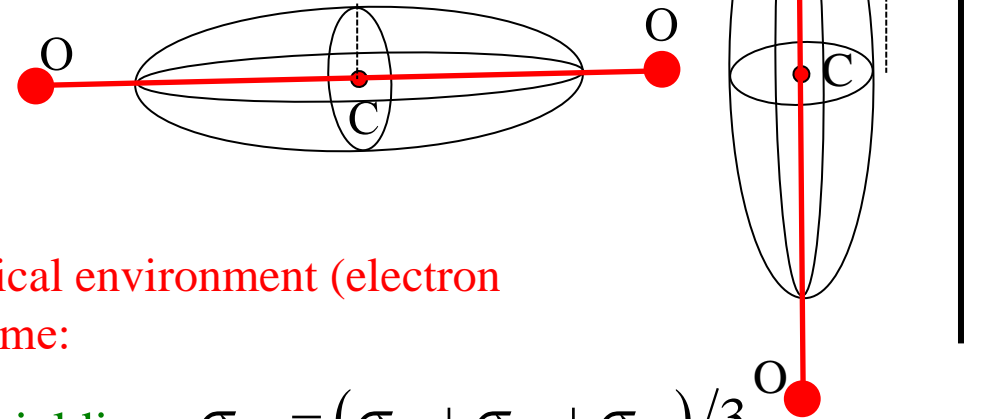


# The NMR transition: The chemical shielding (shift) tensor

$$\mathbf{B}_{local} = (\mathbf{1} - \boldsymbol{\sigma}) \cdot \mathbf{B}_0$$

Local magnet field at nucleus      Chemical shielding tensor

chemical shielding ellipsoid



Chemical shielding tensor captures the chemical environment (electron distribution). In the principle axis (“PA”) frame:

$$\boldsymbol{\sigma}_{PA} = \begin{pmatrix} \sigma_{11} & 0 & 0 \\ 0 & \sigma_{22} & 0 \\ 0 & 0 & \sigma_{33} \end{pmatrix}$$

Isotropic shielding

Span

Skew

$$\sigma_{iso} = (\sigma_{11} + \sigma_{22} + \sigma_{33})/3$$

$$\Omega = (\sigma_{11} - \sigma_{33})$$

$$K = \frac{3(\sigma_{22} - \sigma_{iso})}{\Omega}$$

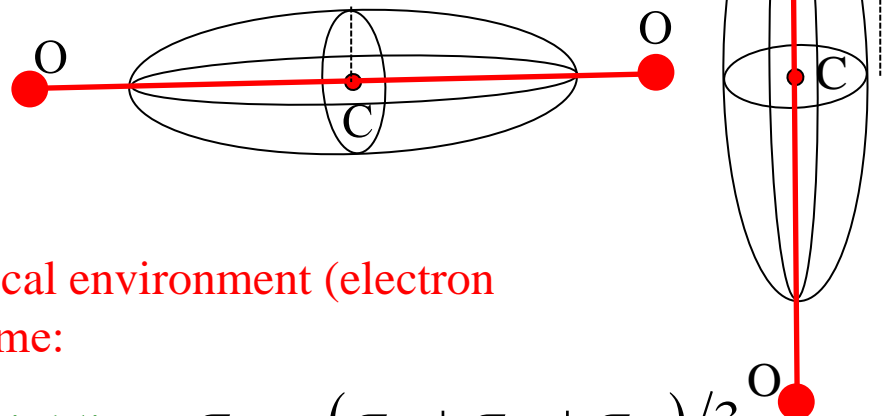
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Isotropic shielding

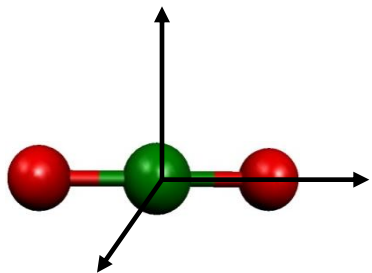
Span

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$$\Omega = (\sigma_{11} - \sigma_{33})$$

$$K = \frac{3(\sigma_{22} - \sigma_{iso})}{\Omega}$$



For linear molecules

$$\boldsymbol{\sigma}_{PA} = \begin{pmatrix} \sigma_{11} & 0 & 0 \\ 0 & \sigma_{11} & 0 \\ 0 & 0 & \sigma_{33} \end{pmatrix} = \begin{pmatrix} \sigma_{\perp} & 0 & 0 \\ 0 & \sigma_{\perp} & 0 \\ 0 & 0 & \sigma_{\parallel} \end{pmatrix}$$

## MP2 / 6-311++G(d,p) calculations of the chemical shielding tensor

$$\text{CO}_2 \quad \boldsymbol{\sigma}_{PA} = \begin{pmatrix} -39.9 & 0 & 0 \\ 0 & -39.9 & 0 \\ 0 & 0 & 285.6 \end{pmatrix} \quad \sigma_{\text{iso}} = 68.6$$

**TMS**  $\sigma_{\text{iso}} = 194.1$  Calculated shielding for tetramethylsilane standard

$$\delta_{\text{iso}}(\text{CO}_2) = \sigma_{\text{iso}}(\text{TMS}) - \sigma_{\text{iso}}(\text{CO}_2) = 125.5 \text{ ppm}$$

$$\delta_{\text{expt.}} = 124.2 \text{ ppm} \quad \text{For liquid CO}_2$$

$$\boldsymbol{\sigma}_{PA} = \sigma_{11} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -2 \end{pmatrix}$$

Without loss of generality, defining  $\sigma_{\text{iso}} = 0$

# MP2 / 6-311++G(d,p) calculations of the chemical shielding tensor

$$\text{CO}_2 \quad \boldsymbol{\sigma}_{PA} = \begin{pmatrix} -39.9 & 0 & 0 \\ 0 & -39.9 & 0 \\ 0 & 0 & 285.6 \end{pmatrix} \quad \sigma_{\text{iso}} = 68.6$$

**TMS**

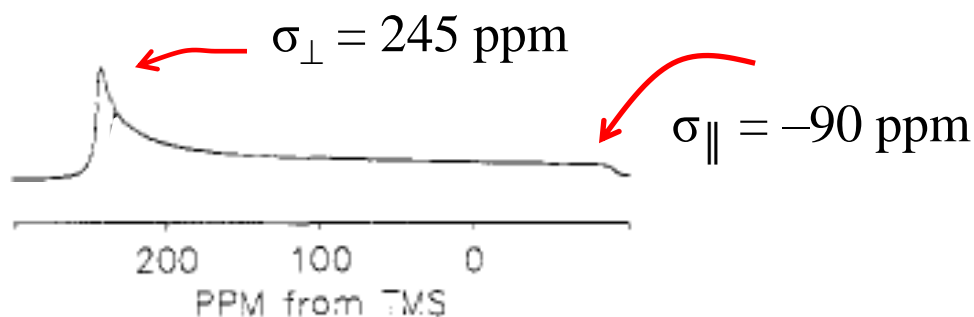
$$\sigma_{\text{iso}} = 194.1$$

Calculated shielding for  
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**For liquid CO<sub>2</sub>**



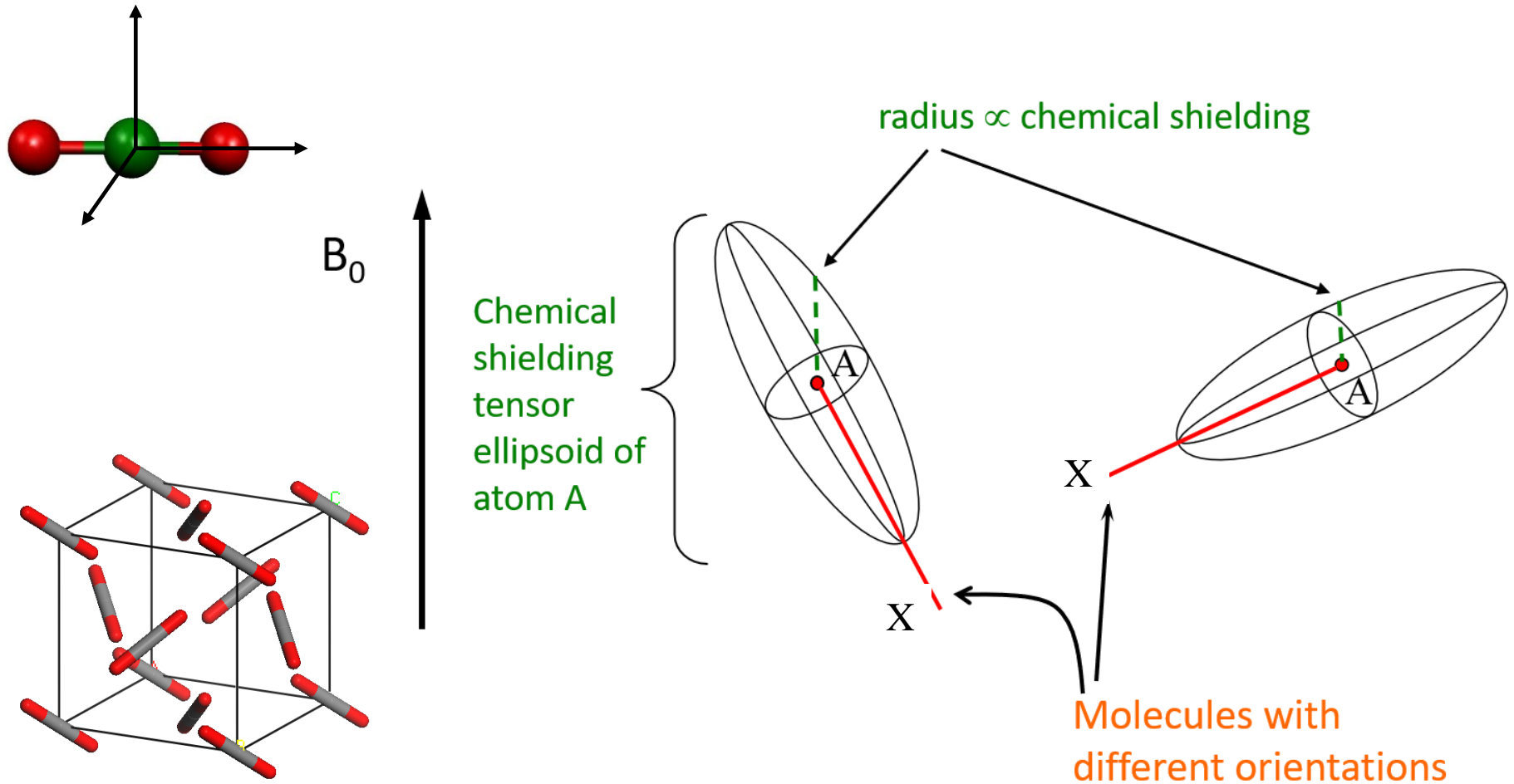
**For solid CO<sub>2</sub>**

$$\boldsymbol{\delta}_{PA} = \begin{pmatrix} 234 & 0 & 0 \\ 0 & 234 & 0 \\ 0 & 0 & -91.5 \end{pmatrix}$$

$$\boldsymbol{\sigma}_{PA} = \sigma_{11} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -2 \end{pmatrix}$$

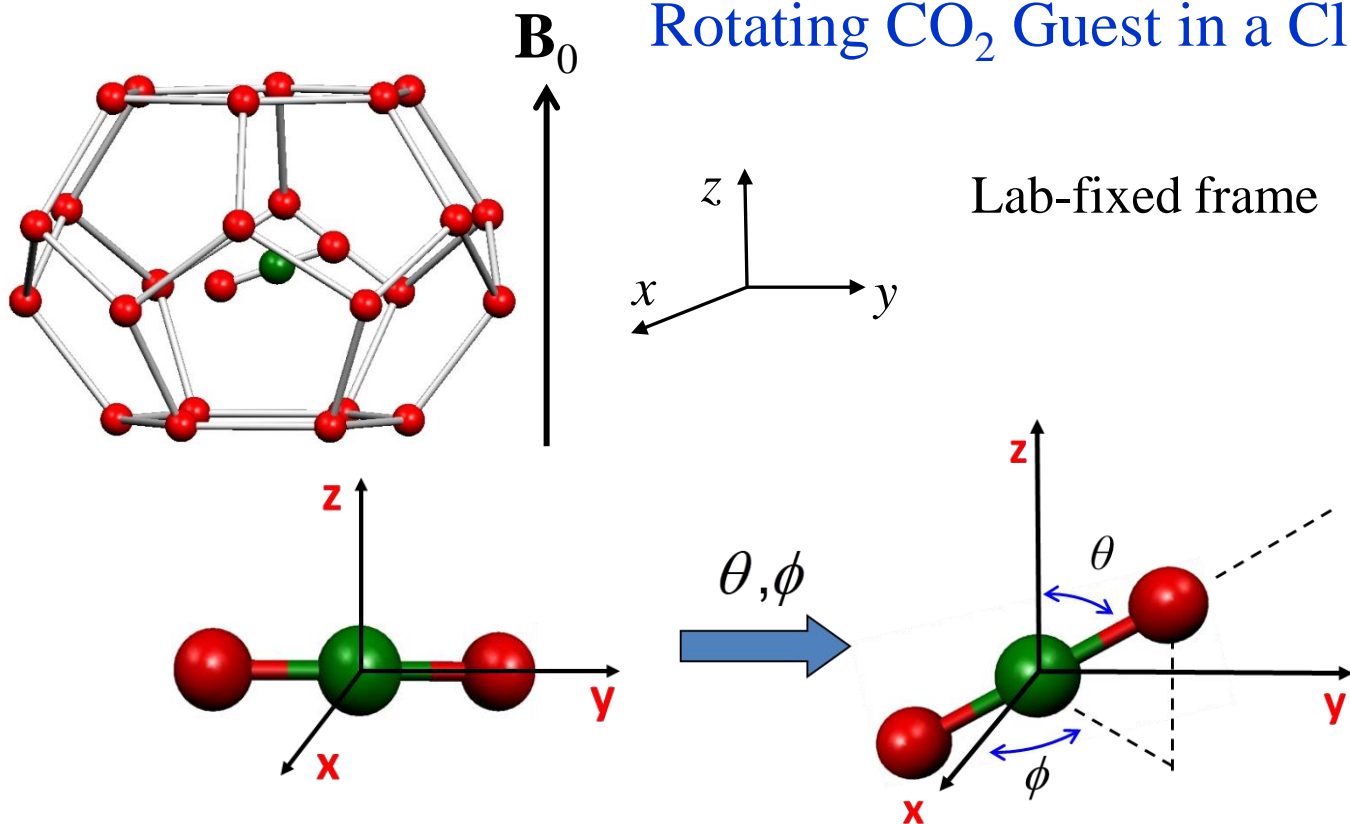
**Without loss of generality, defining  $\sigma_{\text{iso}} = 0$**

# The motion of molecules affects their orientation and NMR spectra



- Molecules in the gas rotate freely
- Molecules in the solid are arranged in fixed directions in the solid
- Molecules in the clathrate hydrate cages may have limited motion in certain directions

# Rotating CO<sub>2</sub> Guest in a Clathrate Cage



Rotation of the molecule is reflected in the rotation of the chemical shielding tensor

$$\sigma_{\text{LAB}}(\theta, \phi) = \mathbf{R}^{-1}(\theta, \phi) \sigma_{\text{PA}} \mathbf{R}(\theta, \phi) \longleftarrow \text{Rotation matrix}$$

$$\sigma_{\text{LAB}}(\theta, \phi) = \sigma_{11} \begin{pmatrix} 1 - 3 \cos^2 \phi \sin^2 \theta & 3/2 \sin 2\phi \sin^2 \theta & 3/2 \cos \phi \sin 2\theta \\ 3/2 \sin 2\phi \sin^2 \theta & 1 - 3 \sin^2 \phi \sin^2 \theta & -3/2 \sin \phi \sin 2\theta \\ 3/2 \cos \phi \sin 2\theta & -3/2 \sin \phi \sin 2\theta & 1 - 3 \cos^2 \theta \end{pmatrix} 47$$

The NMR lineshape of the rotated CO<sub>2</sub> is determined by diagonalizing the chemical shielding tensor

Diagonalizing the matrix

$$\sigma_{11} \begin{pmatrix} 1 - 3 \cos^2 \phi \sin^2 \theta & 3/2 \sin 2\phi \sin^2 \theta & 3/2 \cos \phi \sin 2\theta \\ 3/2 \sin 2\phi \sin^2 \theta & 1 - 3 \sin^2 \phi \sin^2 \theta & -3/2 \sin \phi \sin 2\theta \\ 3/2 \cos \phi \sin 2\theta & -3/2 \sin \phi \sin 2\theta & 1 - 3 \cos^2 \theta \end{pmatrix} \Rightarrow \sigma'_{11}, \sigma'_{22}, \sigma'_{33}$$

For the new orientation:  $\sigma'_{iso} = \sigma_{iso}$

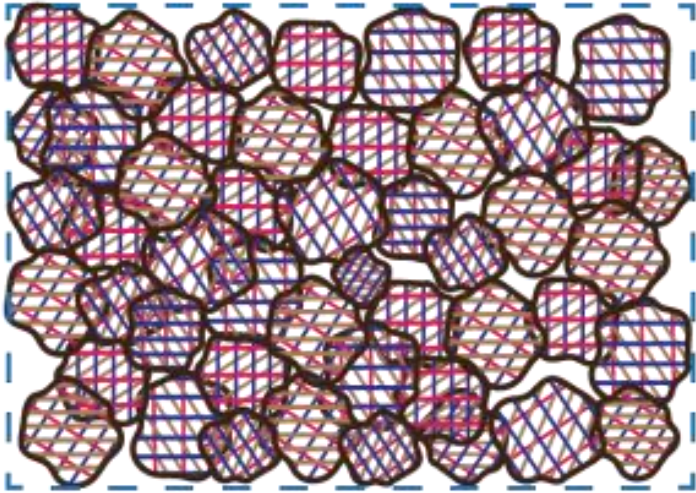
$$\Omega' \neq \Omega$$

$$\kappa' \neq \kappa$$

The lineshape changes as a result of molecule rotation!



# The solid-state NMR sample of CO<sub>2</sub> clathrate hydrate is a powder



- The powder sample is composed of many crystallites
- Crystallites are arranged in random orientations ( $\Theta, \Phi$ ) with respect to the magnetic field
- A “powder averaging” gives an estimate of the observed NMR signal

<https://cms.eas.ualberta.ca/xrd/sample-preparation/>

Observed signal for crystallite  $i$  with  $(\Theta, \Phi)$

$$\nu_i(\Theta, \Phi) = \sigma'_{i,iso} + (\Delta\sigma'_i/3)(3\cos^2\Theta - 1 + \eta'_i \sin^2\Theta \cos 2\Phi)$$

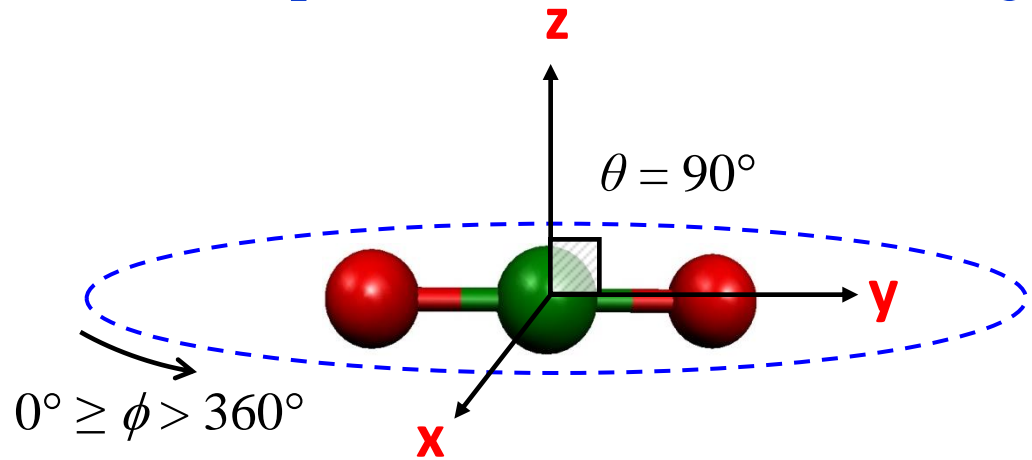
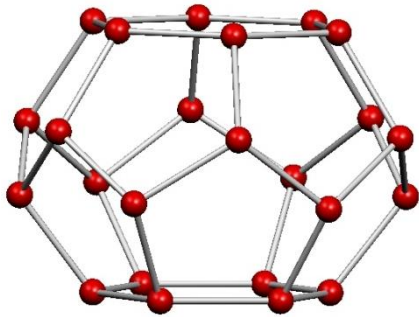
Average shielding tensor  
of crystallite  $i$

$$\Delta\sigma' = \sigma'_{33} - (\sigma'_{22} + \sigma'_{11})/2$$

$$\eta'_i = (\sigma'_{22} - \sigma'_{11})/(\sigma'_{33} - \sigma'_{iso})$$

Sample all values of  $\Theta$  and  $\Phi$  and bin the result for each chemical shift to obtain the lineshape

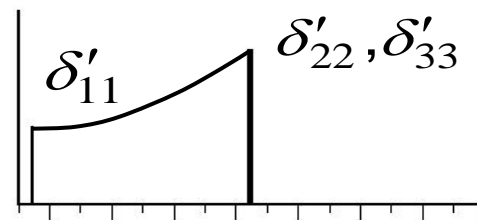
# Case 1: Modelling free rotation in a plane in the center of the cage



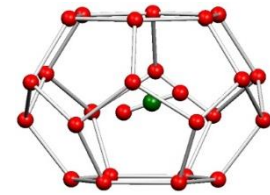
$$\sigma_{\text{LAB}}(90^\circ, \phi) = \sigma_{11} \begin{pmatrix} 1 - 3 \cos^2 \phi & 3/2 \sin 2\phi & 0 \\ 3/2 \sin 2\phi & 1 - 3 \sin^2 \phi & 0 \\ 3/2 \cos \phi & -3/2 \sin \phi & 1 \end{pmatrix}$$

Assuming uniform rotation of the guest allows averaging over  $\phi$  from 0 to  $2\pi$ :

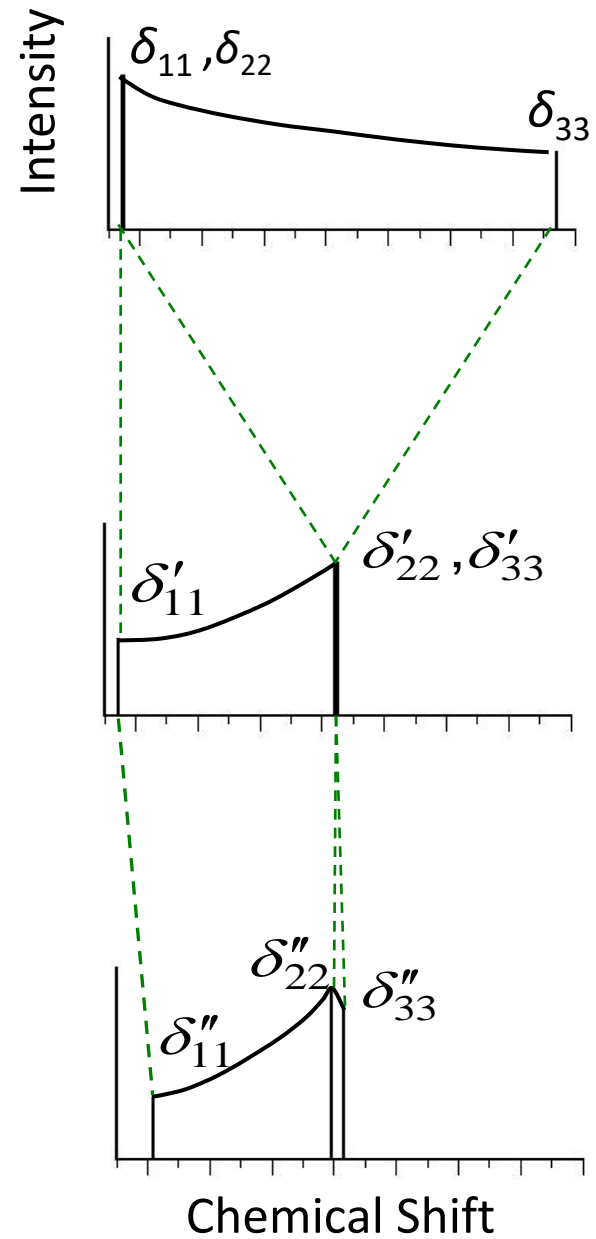
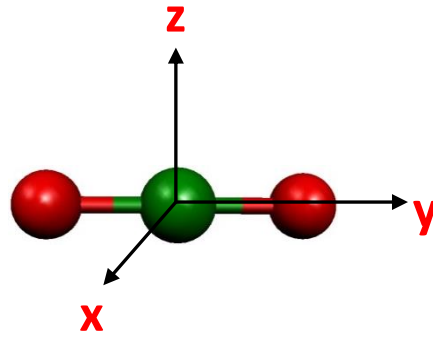
$$\bar{\sigma}_{\text{LAB}} = \sigma_{11} \begin{pmatrix} -1 & 0 & 0 \\ 0 & +1/2 & 0 \\ 0 & 0 & +1/2 \end{pmatrix}$$



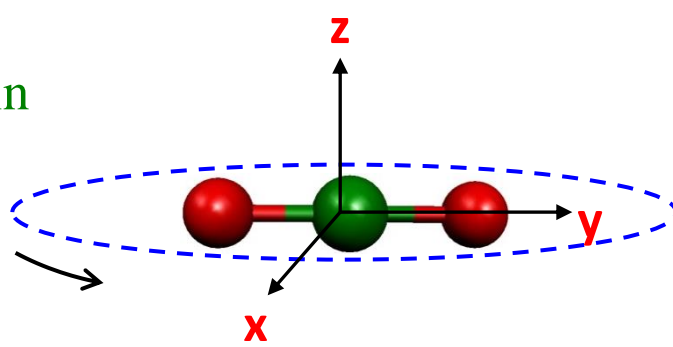
# Models for CO<sub>2</sub> guest rotation in the clathrate hydrate T cages (fit to experiment)



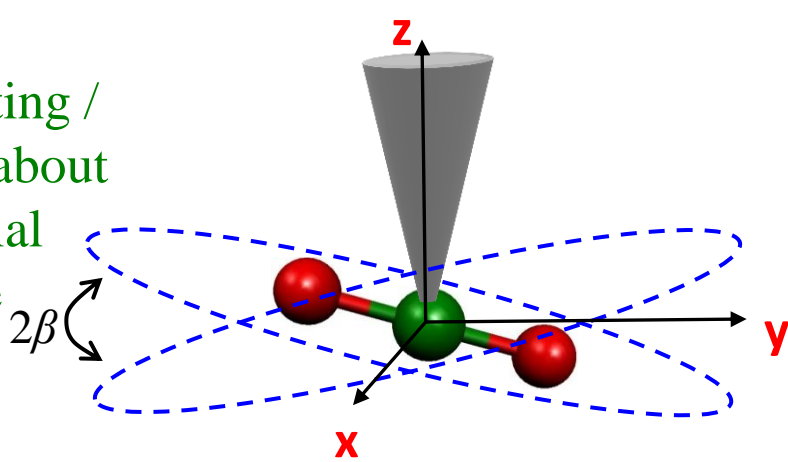
CO<sub>2</sub> is stationary in the T cages



CO<sub>2</sub> is rotating in the equatorial plane of the T cages

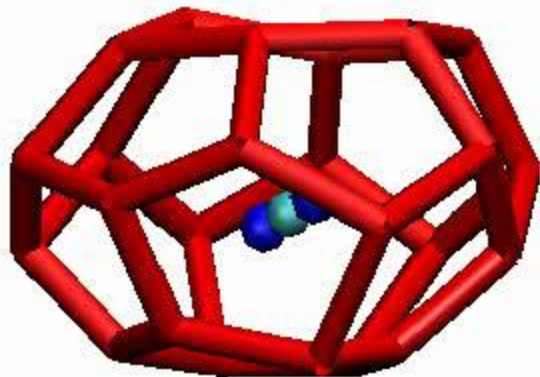


CO<sub>2</sub> is rotating / precessing about the equatorial plane of the T cages

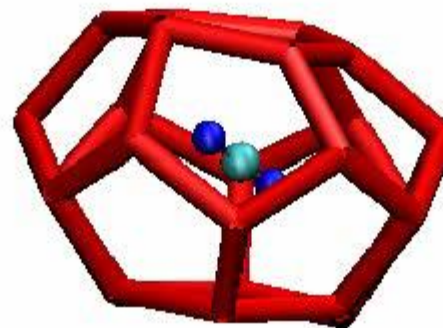


# Simulated guest motion in the cage is complex:

“High” temperature limit (**275 K**)



“Low” temperature limit (**100 K**)



hopping motion?

$$\sigma'_{ii}(T) = \frac{1}{4\pi} \int_0^{2\pi} d\varphi \int_0^\pi \sin\theta d\theta P(\theta, \varphi, T) \sigma_{\text{LAB}}(\theta, \varphi)$$

## Effect of guest rotation on observed chemical shift tensor components

$$\sigma_{\text{LAB}}(\theta, \phi; T, t) = \sigma_{11} \begin{pmatrix} 1 - 3 \cos^2 \phi \sin^2 \theta & 3/2 \sin 2\phi \sin^2 \theta & 3/2 \cos \phi \sin 2\theta \\ 3/2 \sin 2\phi \sin^2 \theta & 1 - 3 \sin^2 \phi \sin^2 \theta & -3/2 \sin \phi \sin 2\theta \\ 3/2 \cos \phi \sin 2\theta & -3/2 \sin \phi \sin 2\theta & 1 - 3 \cos^2 \theta \end{pmatrix}$$

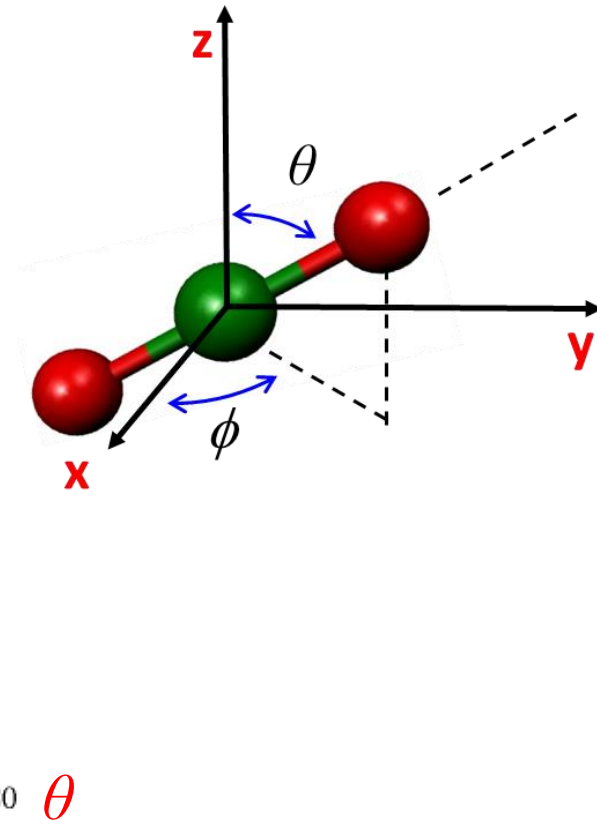
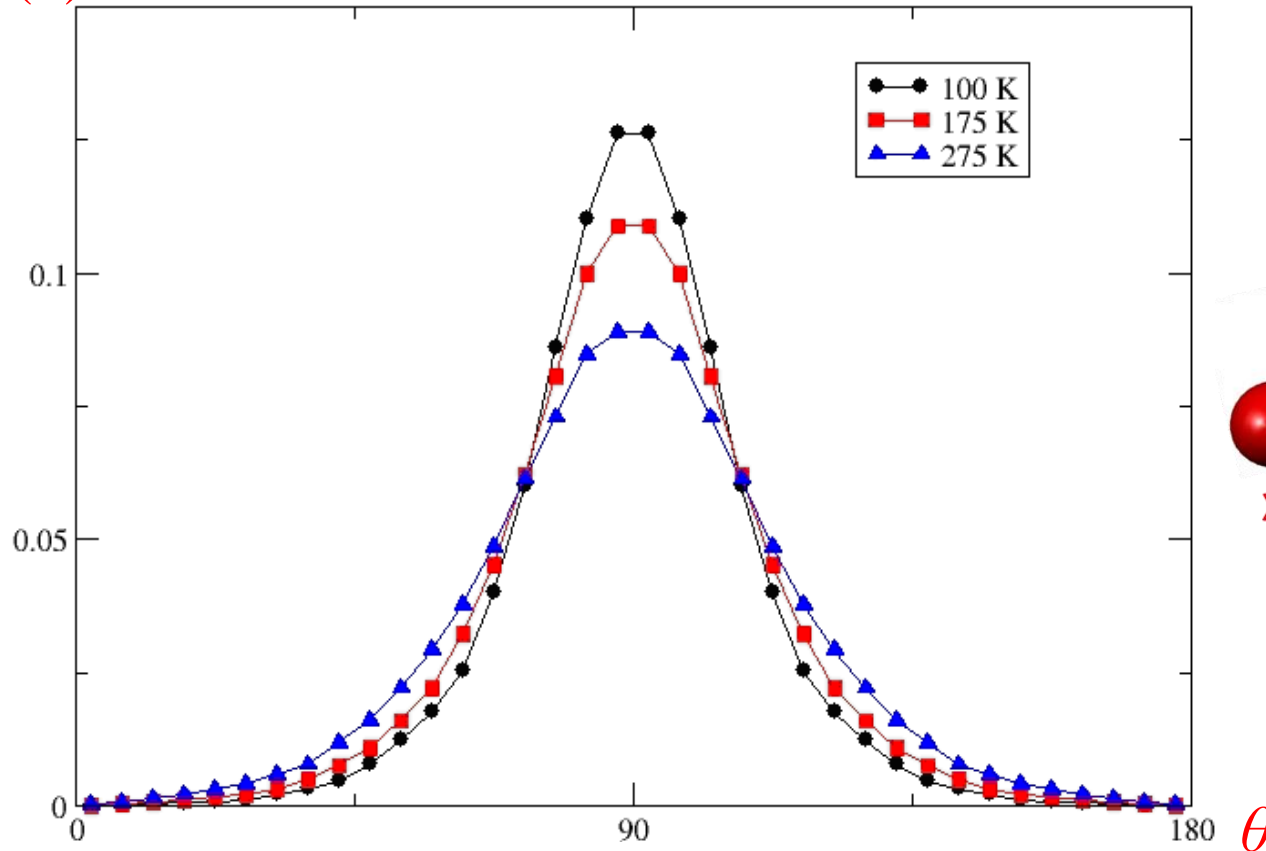
If the molecules move during the NMR experiment, a thermodynamic average of the angles of the orientation of the molecules has to be made over the simulation trajectory

$$\sigma_{\text{LAB}}(\theta, \phi; T) = \begin{pmatrix} \langle \sigma'_{11} \rangle & \langle \sigma'_{12} \rangle & \langle \sigma'_{13} \rangle \\ \langle \sigma'_{21} \rangle & \langle \sigma'_{22} \rangle & \langle \sigma'_{23} \rangle \\ \langle \sigma'_{31} \rangle & \langle \sigma'_{32} \rangle & \langle \sigma'_{33} \rangle \end{pmatrix} \quad \text{Canonical ensemble average of each chemical shielding tensor component}$$

We diagonalize the matrix to determine the eigenvalues, which are the thermodynamic averaged principle components of the shielding tensor

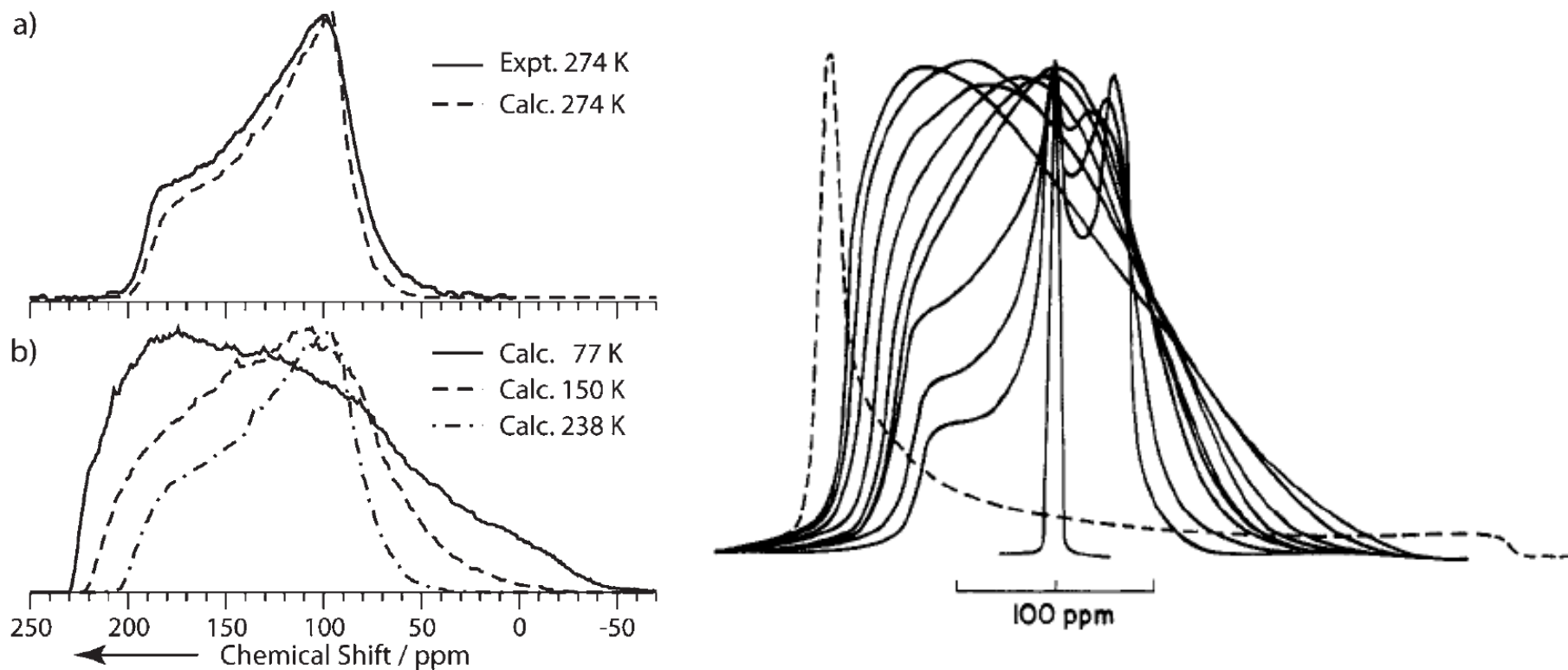
# Distribution of the $\theta$ -angle of molecular axis of CO<sub>2</sub> molecules in sI large cage from molecular dynamics simulations

$P(\theta)$



Analytical models are incomplete and the MD reveals the full range of motion

# Experimental solid state $^{13}\text{C}$ NMR spectrum of $\text{CO}_2$ in large sI cages



Agreement between computed lineshapes from MD and experimental spectra is quite good!

## Future directions:

- Study low temperature motion of guests in cages (hopping motion vs. continuous motion in cages)
- Other guests in clathrates (see Prof. Mohammadimanesh's papers)
- Guest species in zeolites
- CO<sub>2</sub> and other guests in MOFs
- Determination of other NMR parameters (relaxation times with MD)



# Acknowledgments to coworkers of last fifteen years

(Projects in this talk are shown in red)

## University of Ottawa

- Tom Woo
- Peter Dornan
- Andrew Sirjoosingh
- Peter Boyd
- Michael Nohra
- Hana Dureckova
- Parisa Naeiji

## University of British Columbia

- Peter Englezos
- Alireza Bagherzadeh

## Keio University

- Ryo Ohmura
- Masaki Hiratsuka
- Sanehiro Muromachi
- Satoshi Takeya (AIST)

## National Research Council, Ottawa

- John A. Ripmeester
- Christopher I. Ratcliffe
- Konstantin Udachin
- Robin Susilo
- Kyuchul Shin
- Alondra Torres Trueba

## Isfahan University of Technology

- Bijan Najafi
- Mohammad Hossein Kowsari
- Hossein Mohammadimanesh
- Afsaneh Maleki
- Hamid Mosaddeghi