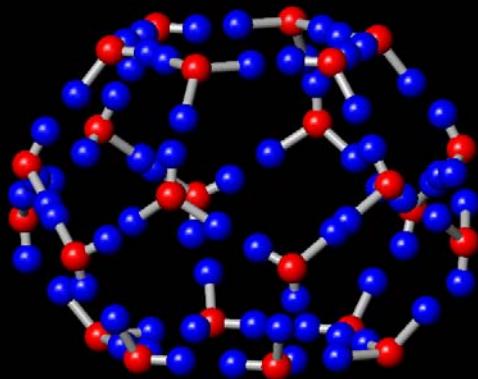
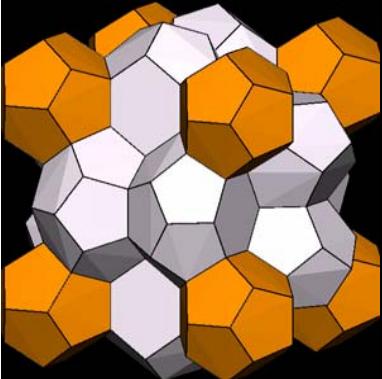


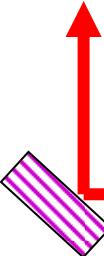
Practical Limitations of Gas Hydrate Structural Studies by Neutron and X-ray Diffraction

B.C. Chakoumakos

Center for Neutron Scattering

Oak Ridge National Laboratory, Oak Ridge, Tennessee



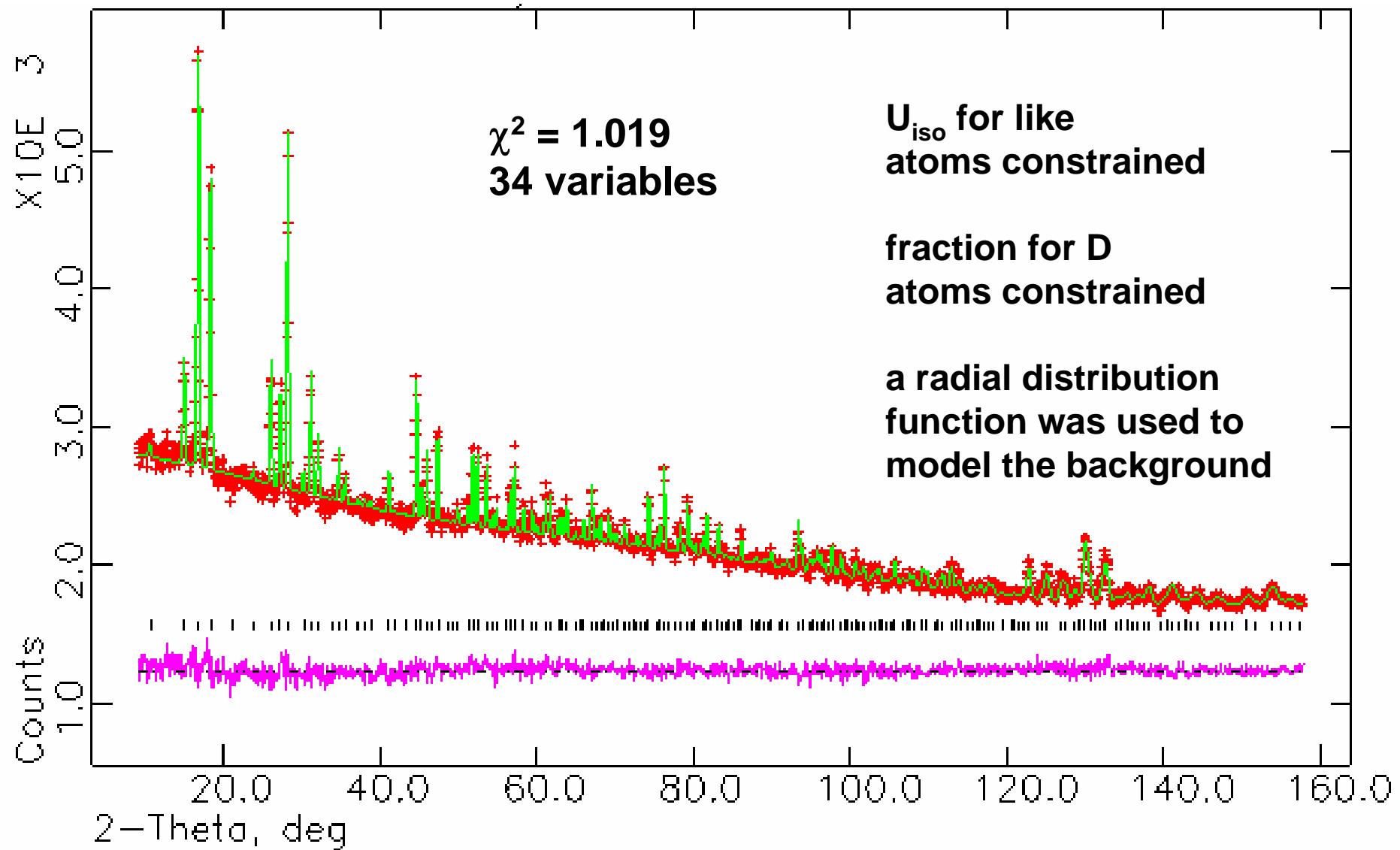


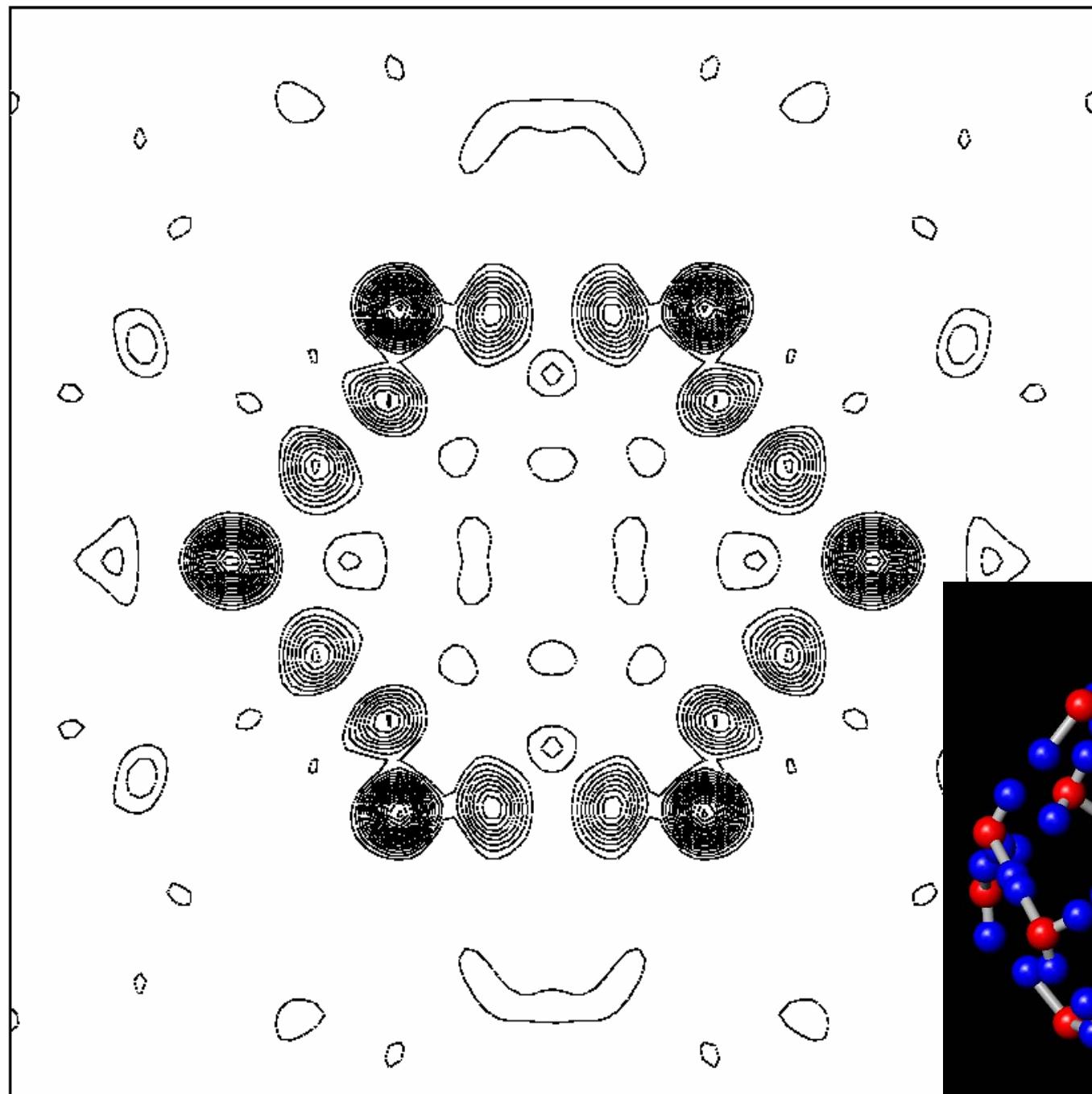
Rietveld structure refinement method using neutron powder diffraction data

- lattice dimensions
- atom positions
- site occupancies
- atomic displacement parameters
- magnetic structures
- quantitative analysis of multi-phase samples
- texture analysis
- residual stress analysis

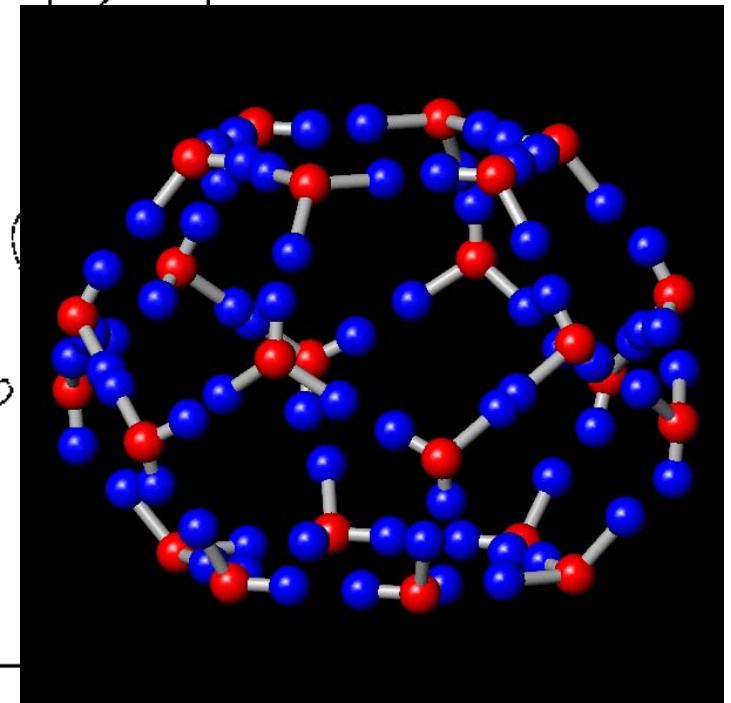
as a function of:
composition,
temperature,
pressure,
magnetic field,
Electric field,
chemical potential.

Methane hydrate

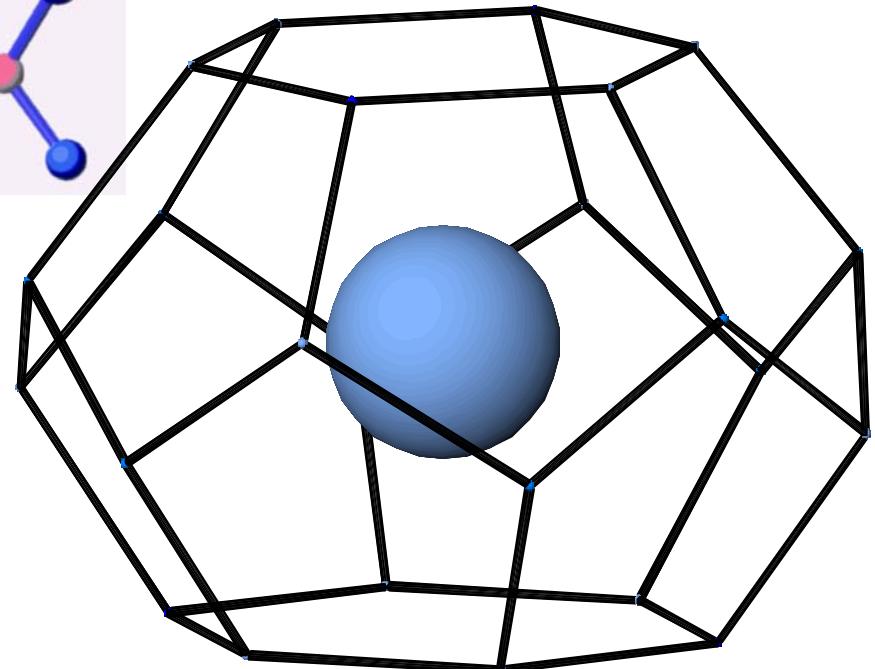
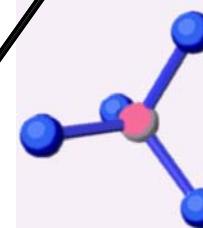
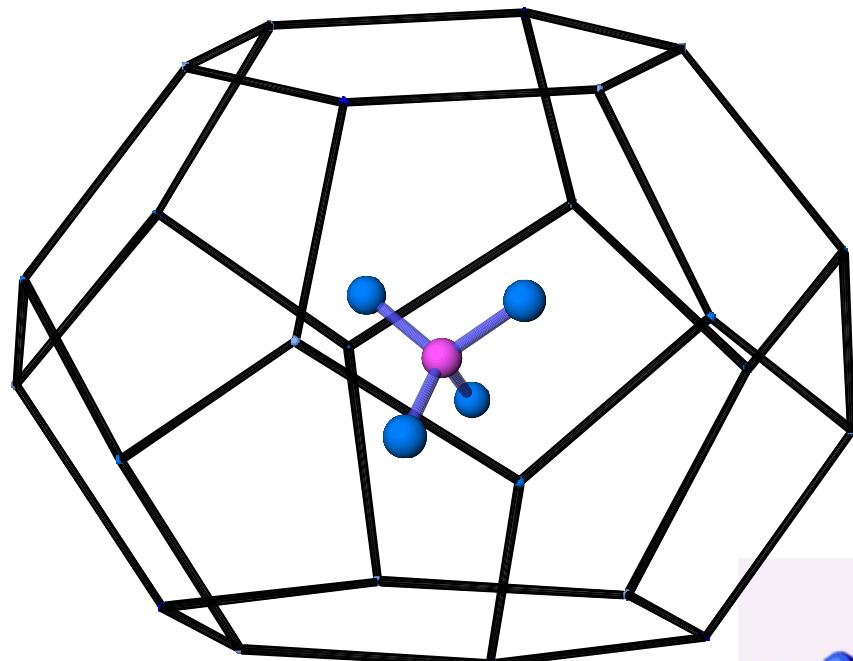


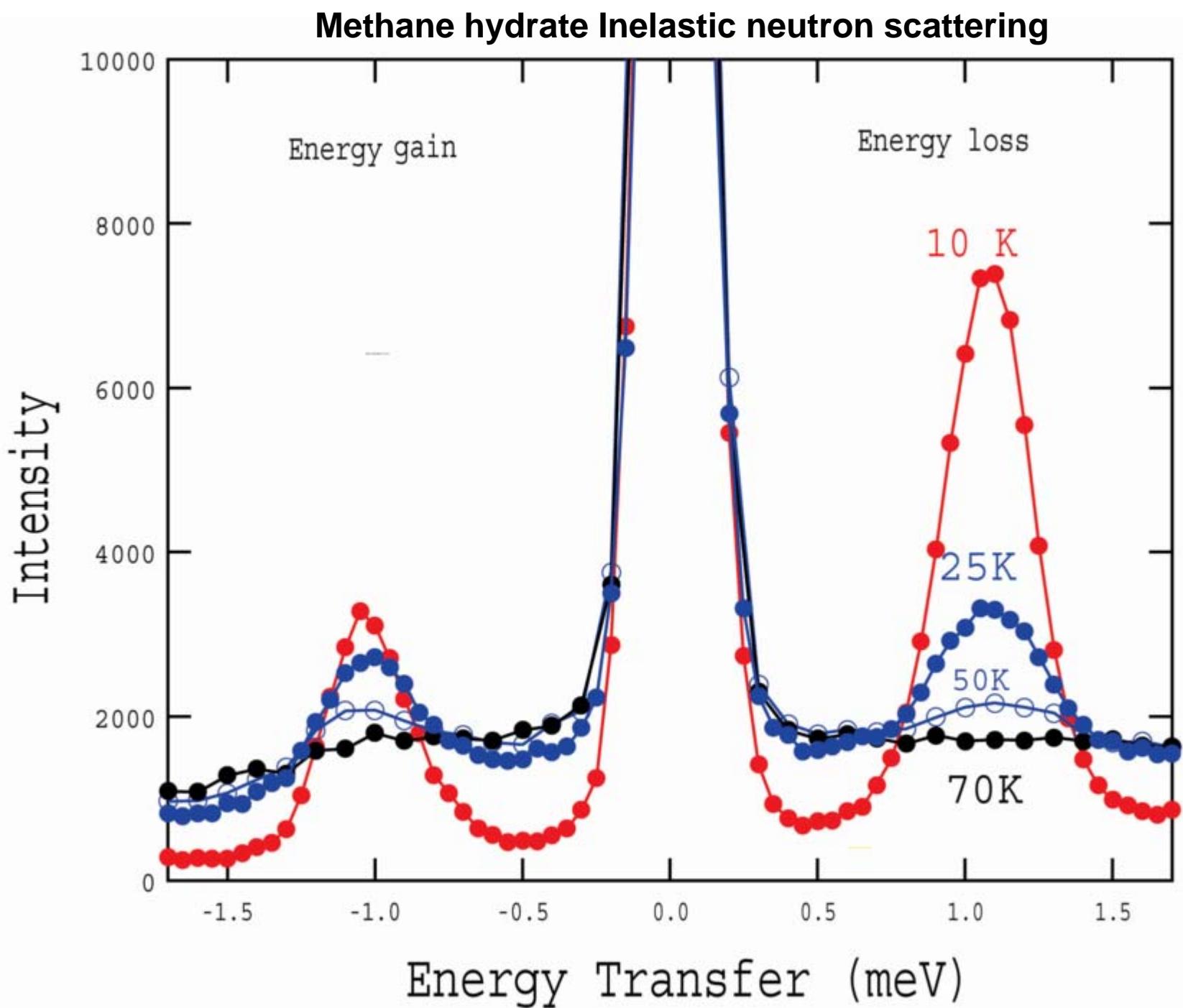


F_{obs} map
6-ring
100K
CO₂ hydrate

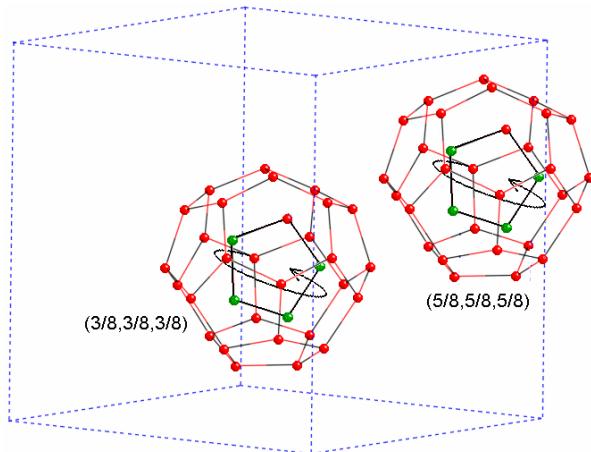


**Guest molecules are in motion
even at low temperatures**



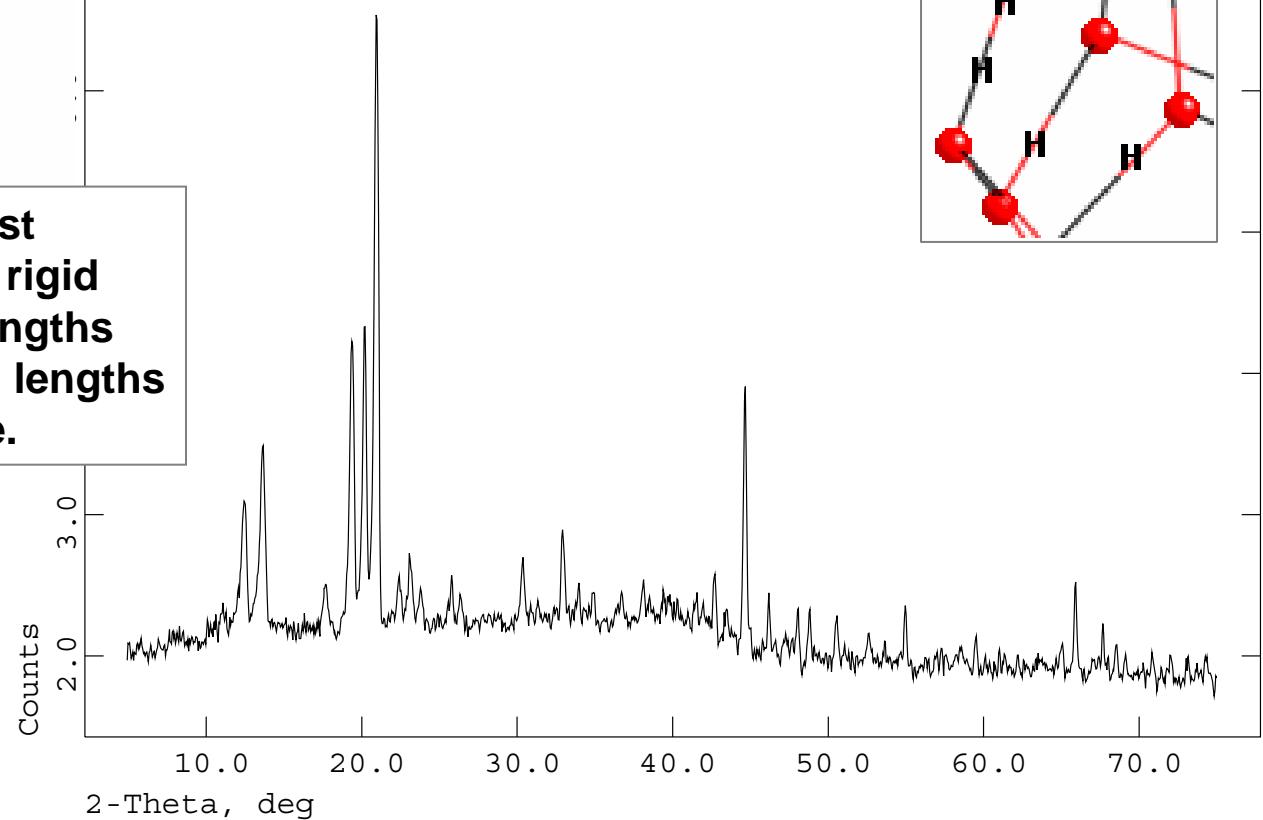
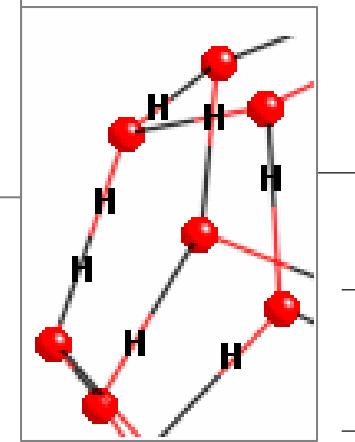


The model for background scattering from the clathrate hydrate takes into account diffuse scattering from both the host and the guest positions



Positional disorder of guest molecules represented as rigid bodies, with correlation lengths given by the internal bond lengths and cage-to-cage distance.

Positional disorder of D in D_2O host lattice, with correlation lengths given by O-H bond lengths (0.95 Å) and D-D distance (0.75 Å)



Structure I, $Pm3n$, $a = 12 \text{ \AA}$, $S_2L_6 \cdot 46\text{H}_2\text{O}$

	x	y	z	f	mult	symmetry	$(\times 100 \text{ \AA}^2)$	U_{iso}
Host Lattice								
O_k	0	0.3082(6)	0.1166(6)	1	$24k$	$m..$	2.17(7)	
O_i	0.1824(5)	0.1824(5)	0.1824(5)	1	$16i$.3.	2.17(7)	
O_c	0	1/2	1/4	1	$6c$	-4 <i>m.2</i>	2.17(7)	
D_{kc}	0.0634(9)	0.2639(9)	0.1374(8)	1/2	$48/$	1	3.25(9)	
D_{ik}	0.1181(8)	0.2286(9)	0.1643(11)	1/2	$48/$	1	3.25(9)	
D_{ki}	0	0.4326(11)	0.1996(11)	1/2	$24k$	$m..$	3.25(9)	
D_{kk}	0	0.3765(12)	0.1547(12)	1/2	$24k$	$m..$	3.25(9)	
D_{ii}	0	0.3226(13)	-0.0365(10)	1/2	$24k$	$m..$	3.25(9)	
D_{ck}	0.2316(9)	0.2316(9)	0.2316(9)	1/2	$16i$.3.	3.25(9)	
Cage positions								
large	0	1/4	1/2	1	$6c$	-4 <i>m.2</i>	6.0	
small	0	0	0	1	$2a$	$m-3.$	4.0	

25 structural parameters (isotropic, host lattice only)

Structure II, $Fd\bar{3}m$, $a = 17 \text{ \AA}$, $S_{16}L_8 \cdot 136\text{H}_2\text{O}$

	x	y	z	f	mult	symmetry	$(\times 100 \text{ \AA}^2)$	U_{iso}
Host Lattice								
O _i	0.1825(1)	0.1825(1)	0.3708(2)	1	96g	..m	1.45(3)	
O _k	0.2178(2)	0.2178(2)	0.2178(2)	1	32e	.3m	1.45(3)	
O _c	1/8	1/8	1/8	1	8a	-4m.2	1.45(3)	
D _{ii(a)}	-0.1618(3)	-0.0192(3)	0.1464(3)	1/2	192i	1	2.19(4)	
D _{ii(b)}	0.1413(2)	.01413(2)	0.3733(5)	1/2	96g	..m	2.19(4)	
D _{ik}	0.1957(3)	0.1957(3)	0.3150(5)	1/2	96g	..m	2.19(4)	
D _{ki}	0.2050(4)	0.2050(4)	0.2729(4)	1/2	96g	..m	2.19(4)	
D _{kc}	0.1847(4)	0.1847(4)	0.1847(4)	1/2	32e	.3m	2.19(4)	
D _{ck}	0.1591(3)	0.1591(3)	0.1591(3)	1/2	32e	.3m	2.19(4)	
Cage positions								
small	0	0	0	1	16c	.-3 m	4.0	
large	0	1/4	1/2	1	8b	-43m	6.0	

23 structural parameters (isotropic, host lattice only)

Approaches to model the rotationally disordered guest molecules

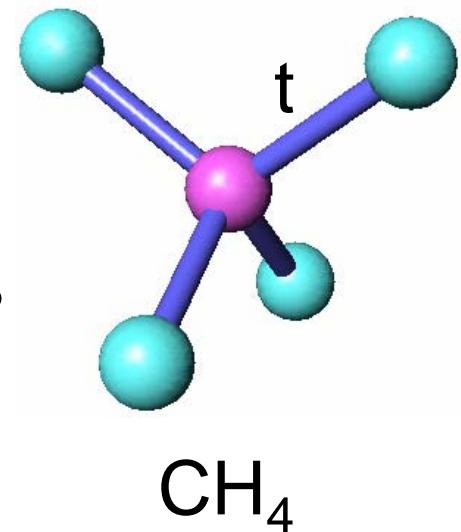
- Ignore
- Scattering from rotationally disordered molecule
 - e.g., Gutt et al. (2002) Appl. Phys. A 74, S1299
- Disordered rigid body

Rigid body constraints

For methane hydrate, two rigid bodies are used with different translation vectors for the two different sized cages

t(1) centered at 0,0,0 - two small cages

atom	x	y	z	mult	frac
C	0	0	0	2	1
H	$\sin 54.735$	0	$\cos 54.735$	48	1/24
H	$-\sin 54.735$	0	$\cos 54.735$	48	1/24
H	0	$\sin 54.735$	$-\cos 54.735$	48	1/24
H	0	$-\sin 54.735$	$-\cos 54.735$	48	1/24

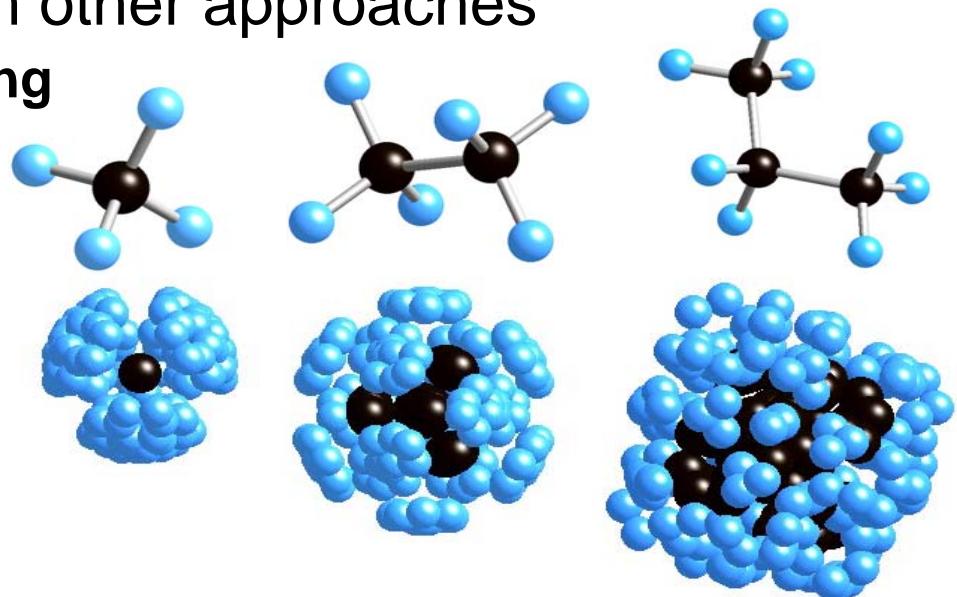


t(2) centered at 0, $\frac{1}{4}$, $\frac{1}{2}$, - six large cages

atom	x	y	z	mult	frac
C	0	1/4	1/2	6	1
H	$\sin 54.735$	0	$\cos 54.735$	48	1/8
H	$-\sin 54.735$	0	$\cos 54.735$	48	1/8
H	0	$\sin 54.735$	$-\cos 54.735$	48	1/8
H	0	$-\sin 54.735$	$-\cos 54.735$	48	1/8

Caged Molecules Modeled with Rigid Body Formalism

- Accounts for preferred positions or orientations within cages
- Yields bond length changes in the caged molecule
- Yields mean-square displacement of cage occupant
- The temperature dependence of the T tensor yields another measure of the positional disorder
- Results can be correlated with other approaches
 - **quasi-elastic neutron scattering**
 - **inelastic neutron scattering**
 - **Raman spectroscopy**
 - **NMR**

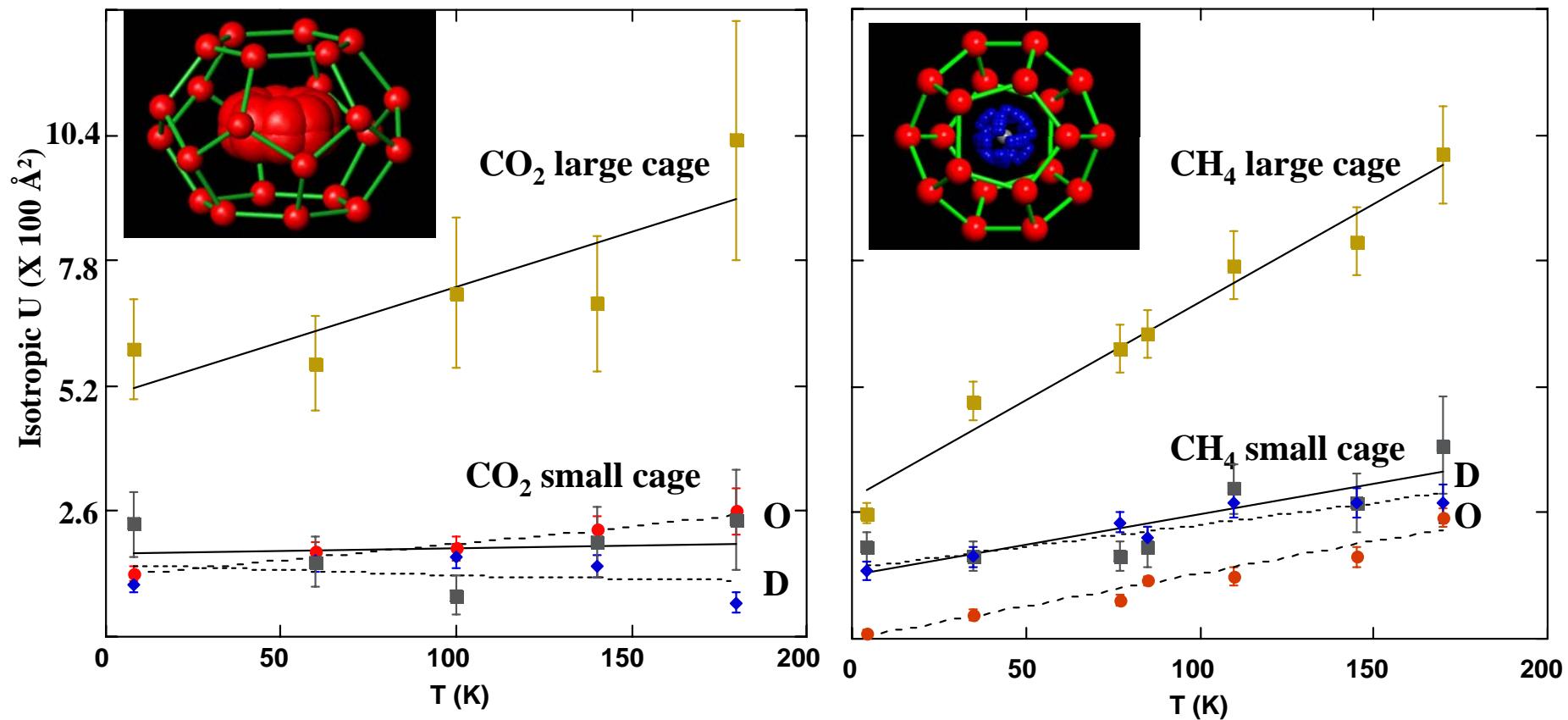


Methane

Ethane

Propane

The temperature dependence of the atomic displacement parameters compared between CO₂ hydrate and CH₄ hydrate



Collaborators

Oak Ridge National Laboratory

Claudia Rawn

Adam Rondinone

Michael Lance

Hsin Wang



U.S.G.S. (Menlo Park)

Laura Stern

Steve Kirby

Sue Circone



JAERI

Yoshi Ishii

NIST/Hamilton College

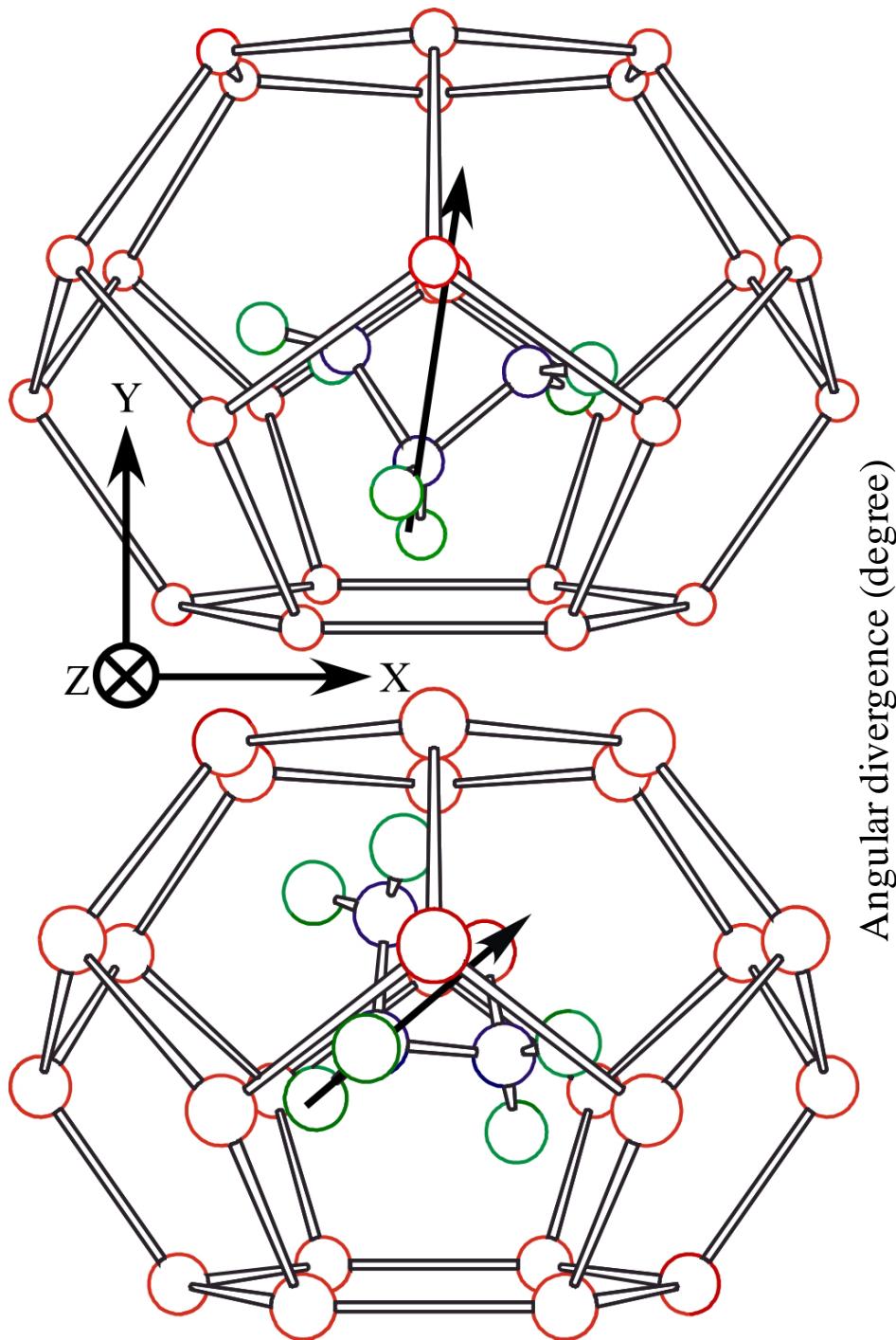
Camille Jones

Colorado School of Mines

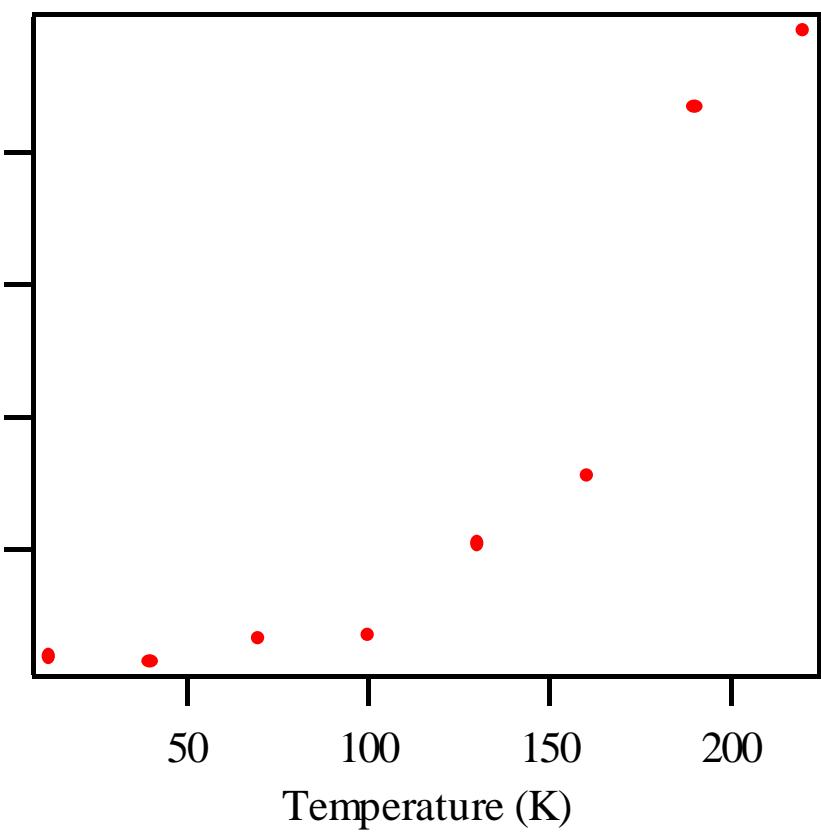
Dendy Sloan

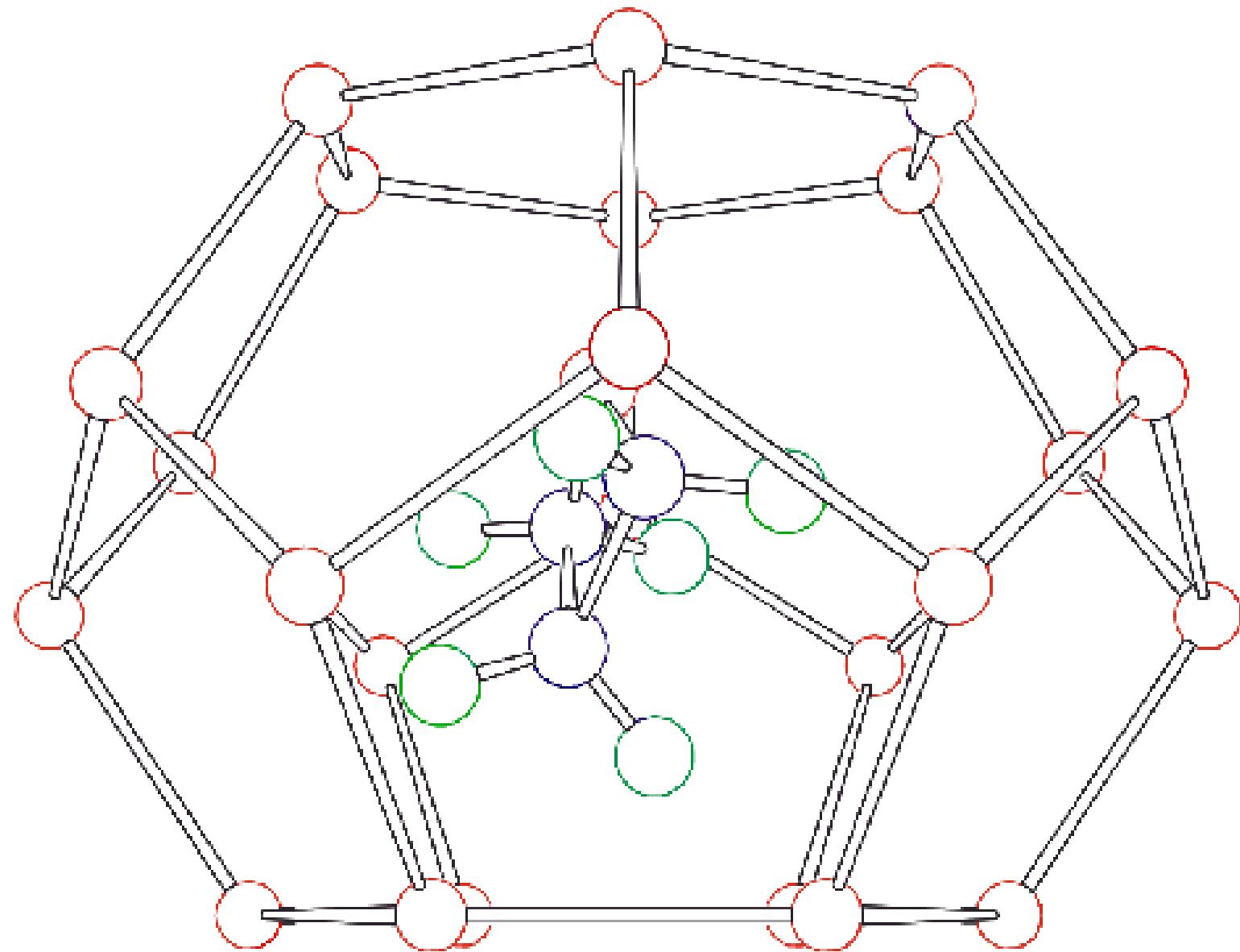
Michael Eaton

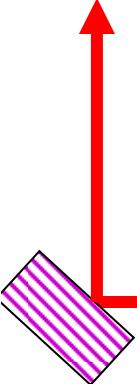




Angular divergence (degree)







Deuteriation reduces incoherent scattering for neutron diffraction

