Potential Moderator Materials for Very Cold Neutron Sources

Rolando Granada

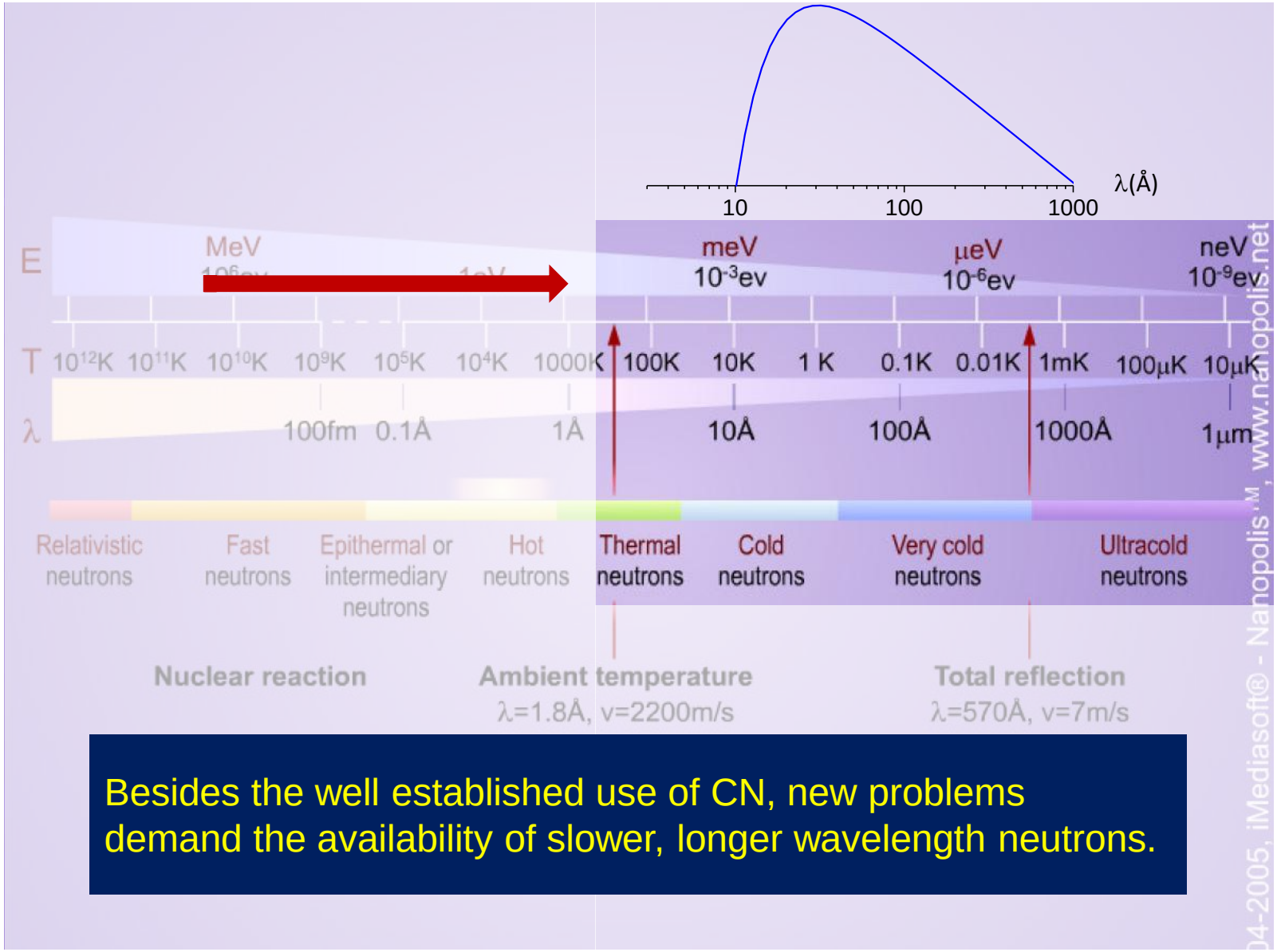
Centro Atómico Bariloche, CNEA, ARGENTINA

Comisión Nacional de Energía Atómica

Journal of Neutron Research, May 2024
DOI: 10.3233/JNR-240013

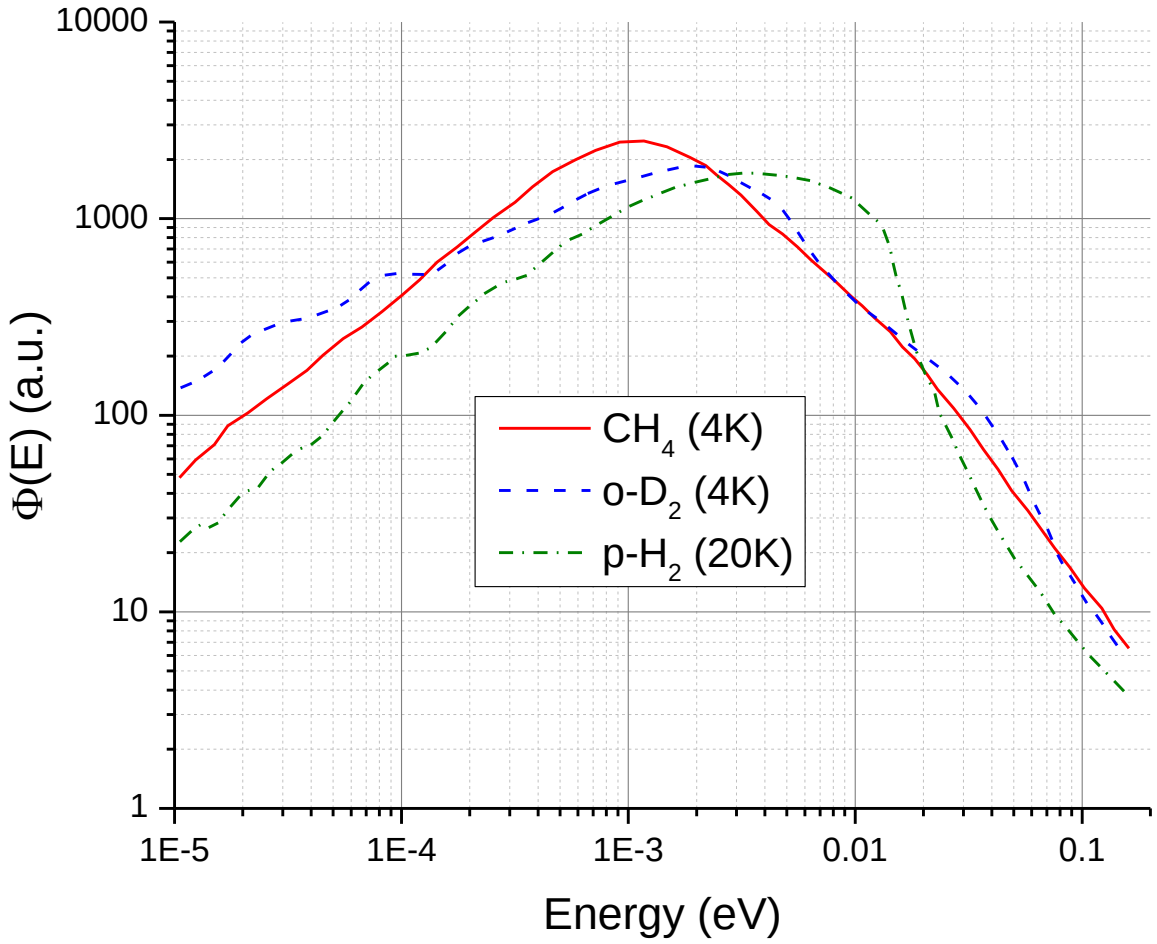
MOTIVATIONS

- ✓ The increasing demand for **long wavelength neutrons** is being motivated by the need to study larger objects and slower motions.
- ✓ Many modern neutron scattering techniques will benefit from **more intense VCN fluxes** if they could be realized.
- ✓ Results of a preliminary study aimed at identifying materials that look promising as **potential moderators for VCN** sources.
- ✓ Explore systems that present significant contributions of low-energy modes in their generalized frequency spectrum, and that implied searching for systems with **very low rotational transitions**.



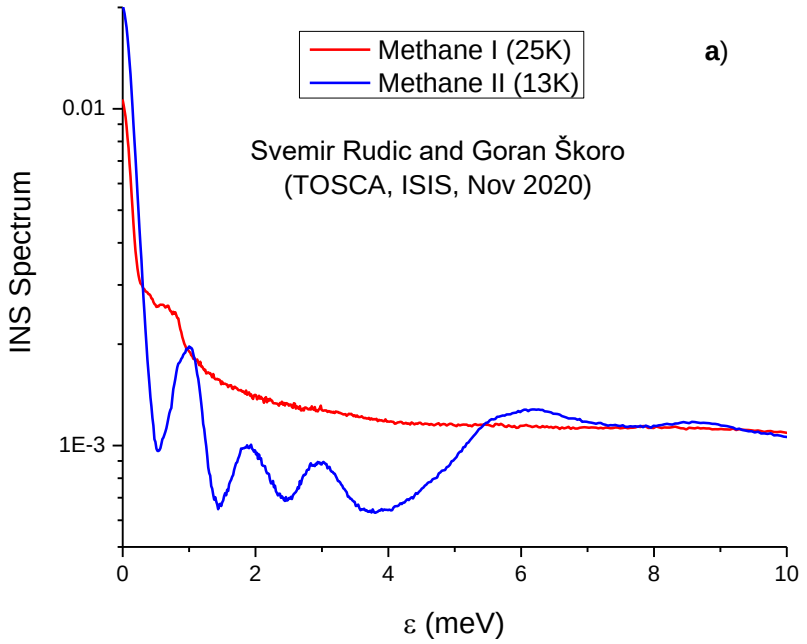
Besides the well established use of CN, new problems demand the availability of slower, longer wavelength neutrons.

H: 50x52x88 mm^3
D: 140x140x200 mm^3



Adapted from F. X. Gallmeier et al 2018 J. Phys.: Conf. Ser. 1021 012083

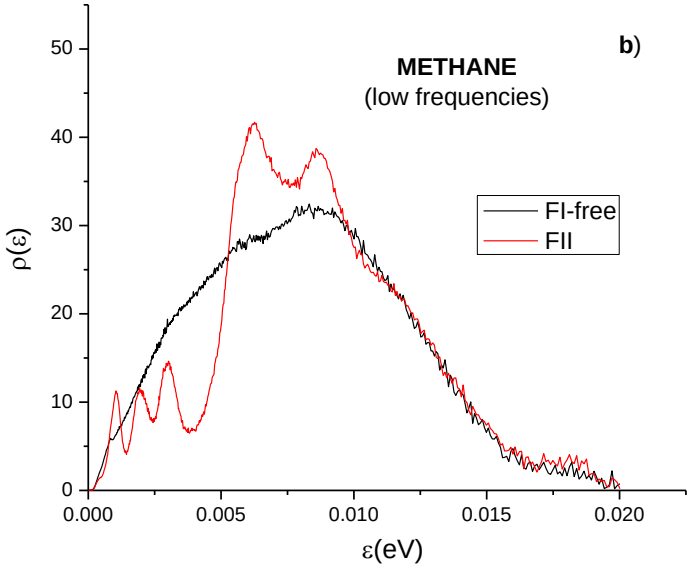
METHANE II

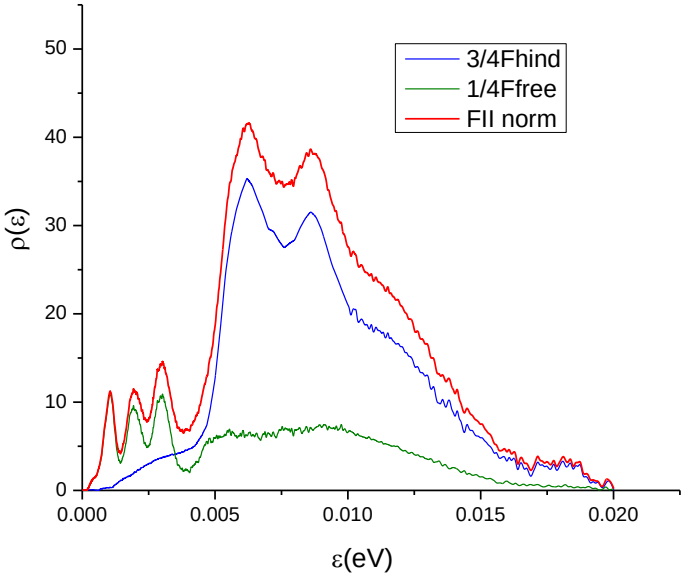


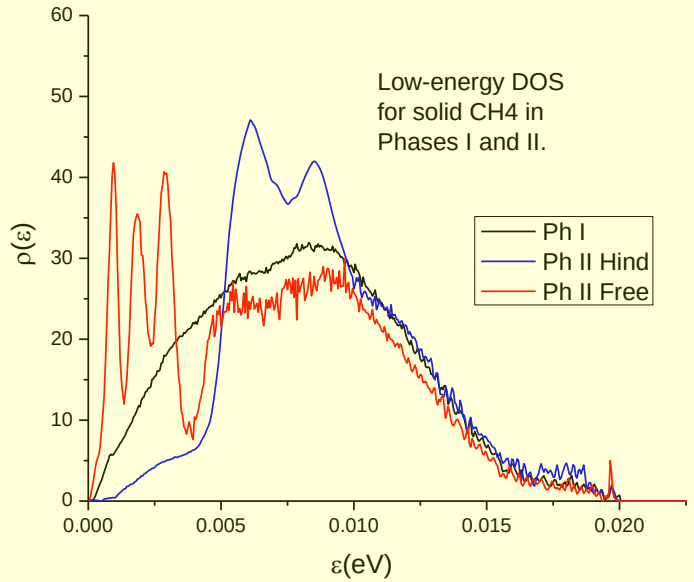
The measured INS spectra of solid Methane I (25K) and II (13K) are shown over a small energy transfer range.

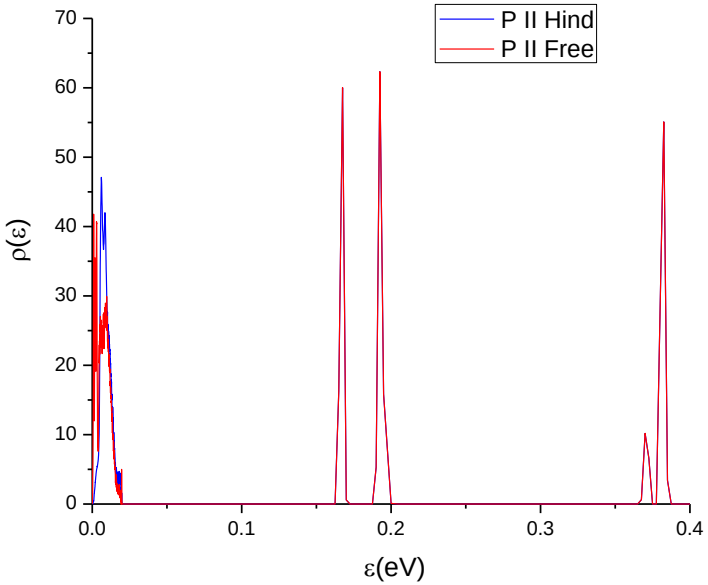
$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{inc+1ph} = N\,\frac{\sigma_{inc}}{4\pi}\,\frac{k}{k_0}\,\frac{Q^2}{4M}\exp(-2W)\,\frac{\boldsymbol{Z(\omega)}}{\omega}\,[n(\omega)+1]$$

DOS of solid CH_4

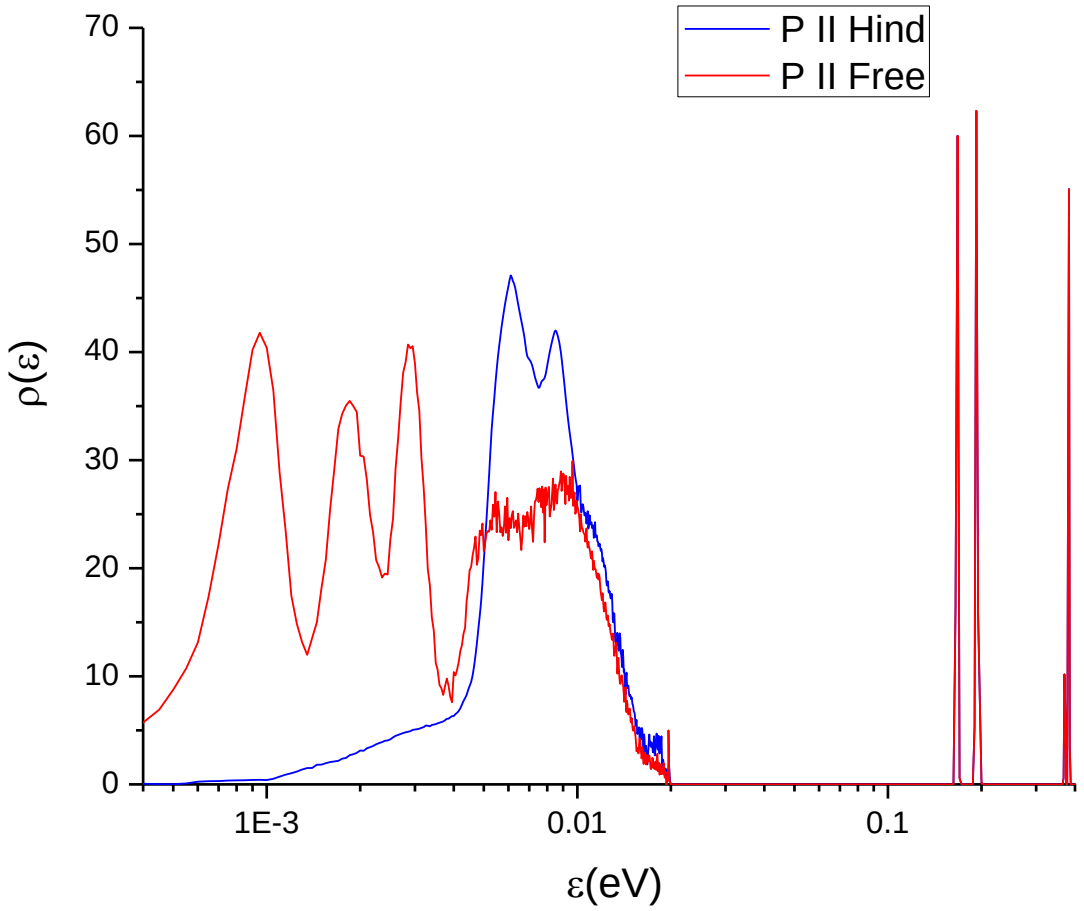


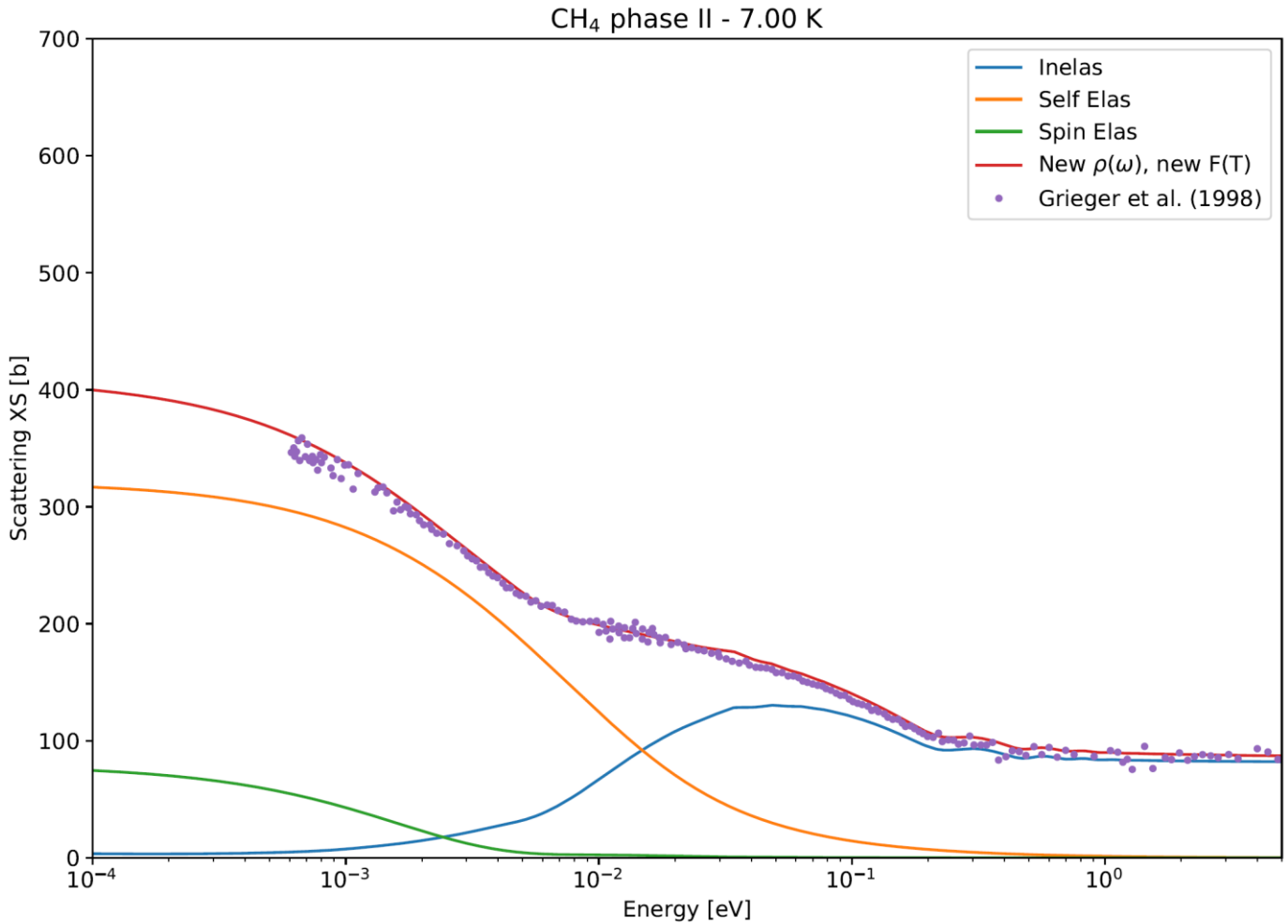


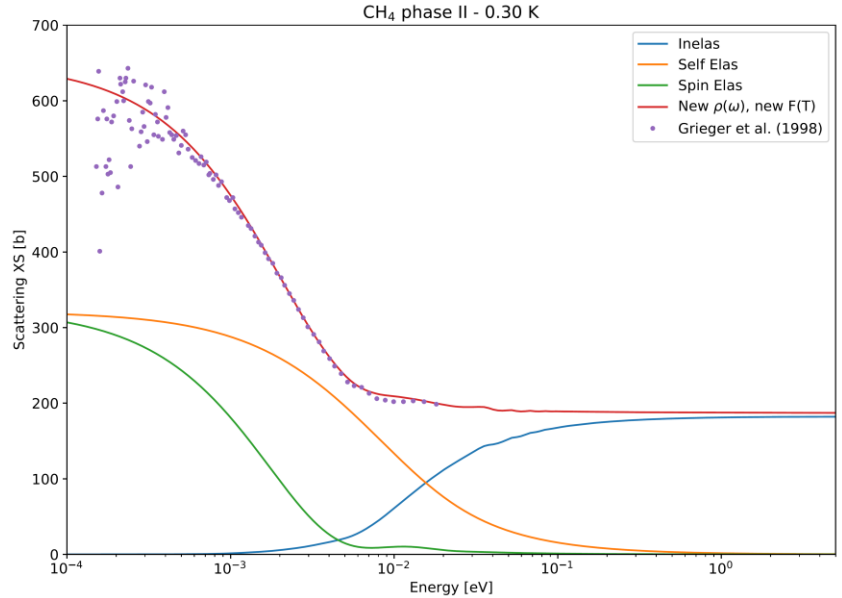


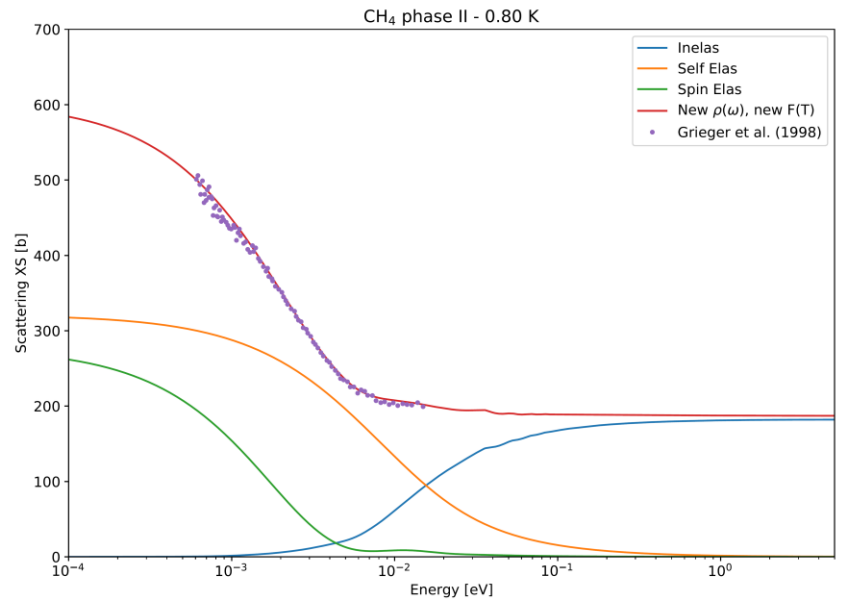


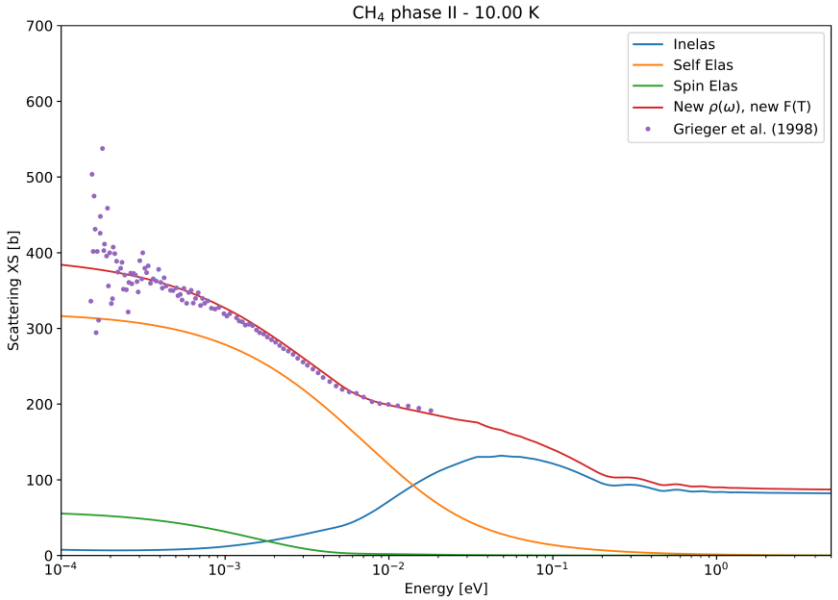
DOS of solid CH_4 (II)

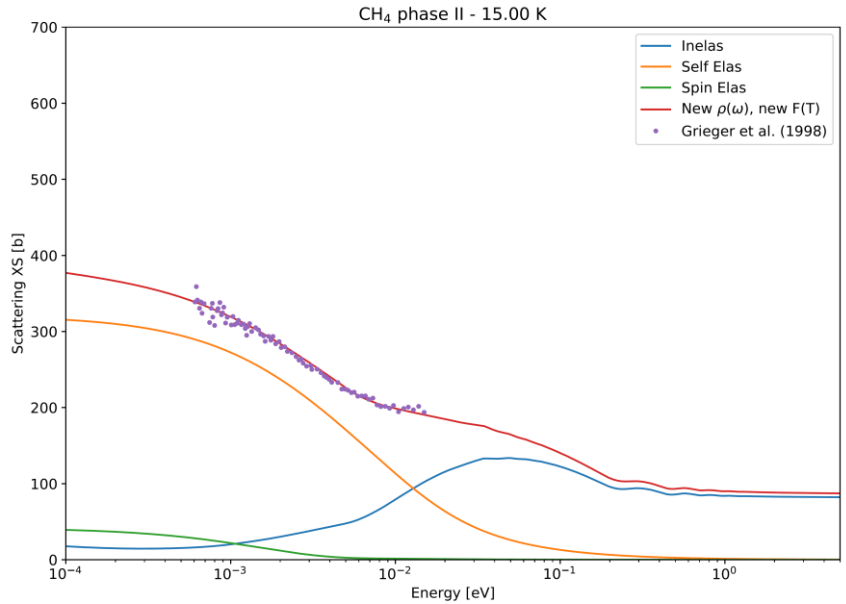



CH4 phase II - 7.00 K
Inelas
Self Elas
Spin Elas
New ρ(ω), new F(T)
Grieger et al. (1998)
Scattering XS [b]
Energy [eV]
0
100
200
300
400
500
600
700
10−4
10−3
10−2
10−1
100

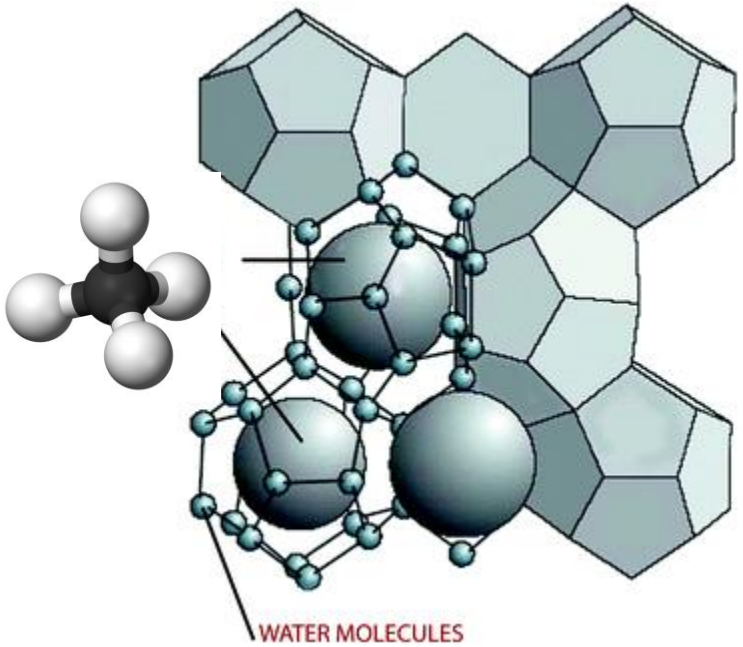

CH4 phase II - 0.30 K
Inelas
Self Elas
Spin Elas
New ρ(ω), new F(T)
Grieger et al. (1998)
Scattering XS [b]
Energy [eV]


CH4 phase II - 0.80 K
Inelas
Self Elas
Spin Elas
New ρ(ω), new F(T)
Grieger et al. (1998)
Scattering XS [b]
Energy [eV]

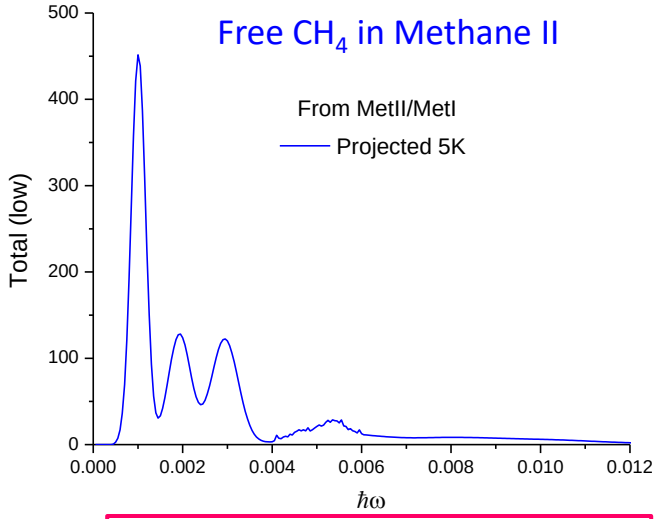

CH4 phase II - 10.00 K
Inelas
Self Elas
Spin Elas
New ρ(ω), new F(T)
Grieger et al. (1998)
Scattering XS [b]
Energy [eV]


CH4 phase II - 15.00 K
Inelas
Self Elas
Spin Elas
New ρ(ω), new F(T)
Grieger et al. (1998)
Scattering XS [b]
Energy [eV]

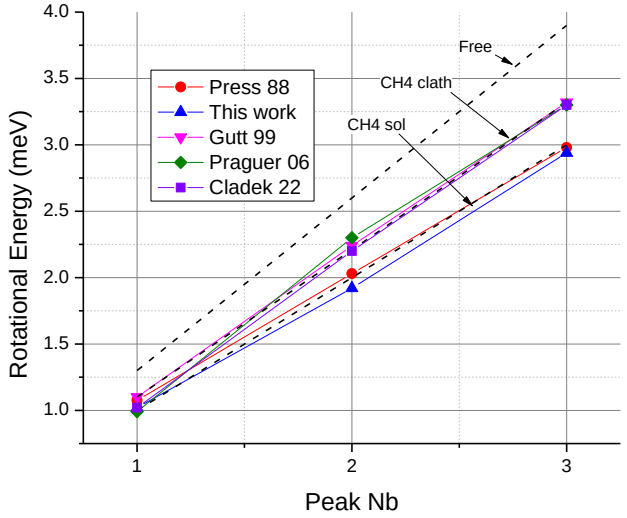
METHANE d-CLATHRATE



DOS of CH_4 in d-Clathrate



$\hbar\omega$: 1.02 meV, 1.92 meV, 2.94 meV

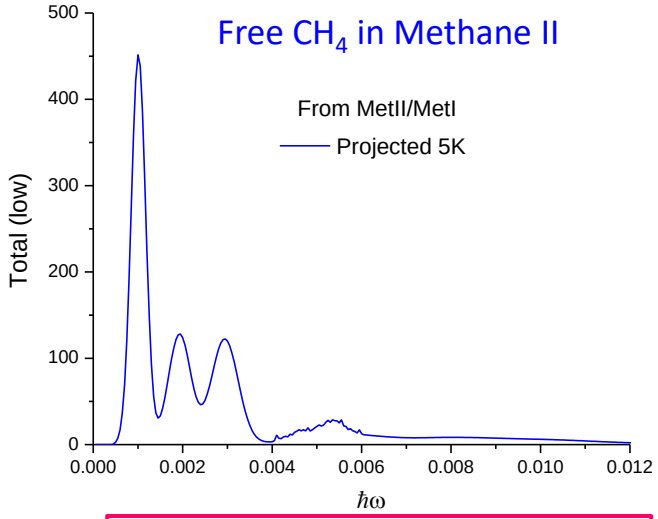


The eigenvalues of the Hamiltonian for *free* rotating CH_4 molecules are

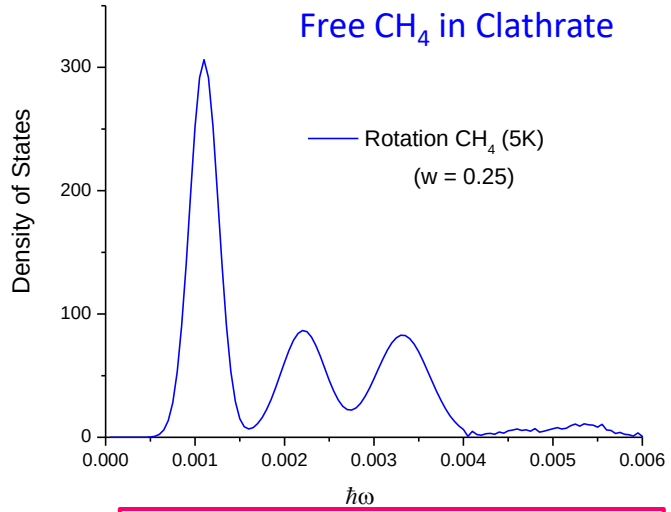
$$E_j = \hbar^2\, j(j+1)\, /(2I_0)$$

with the value of the rotational constant $\hbar^2 /(2I_0) = 0.655$ meV.

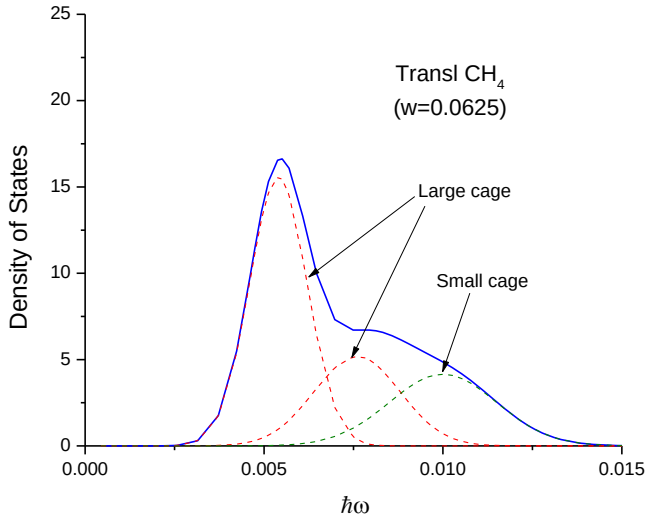
DOS of CH_4 in d-Clathrate



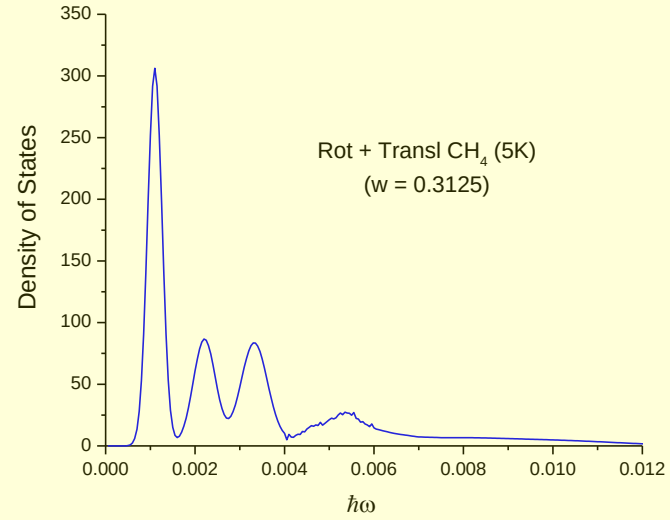
$\hbar\omega$: 1.02 meV, 1.92 meV, 2.94 meV



$\hbar\omega$: 1.1 meV, 2.21 meV, 3.32 meV



J.R. Granada, from measured data [J. Baumert, Thesis, 2003]
(5.4 meV, 7.6 meV, 10 meV)



Fuel 327 (2022) 125197

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

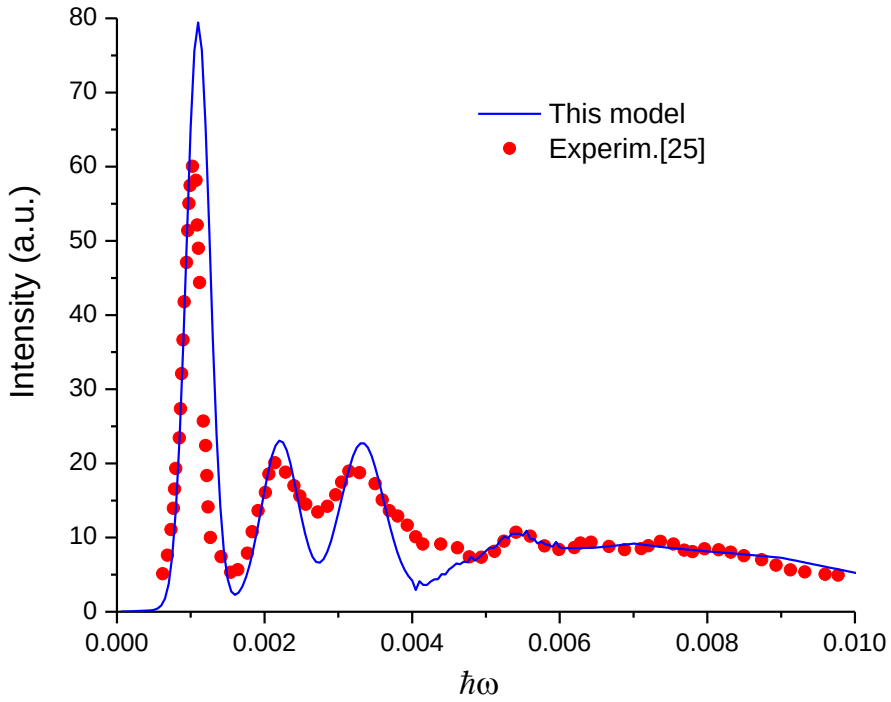
Full Length Article

In situ inelastic neutron scattering of mixed CH_4–CO_2 hydrates

Bernadette R. Cladek [a,b], A.J. Ramirez-Cuesta [b], S. Michelle Everett [b], Marshall T. McDonnell [c], Luke Daemen [b], Yongqiang Cheng [b], Paulo H.B. Brant Carvalho [d], Christopher Tulk [b], Matthew G. Tucker [b], David J. Keffer [a], Claudia J. Rawn [a,*]

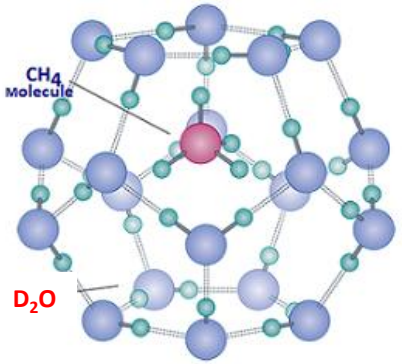
INS data compared with the *weighted DOS* of the system:

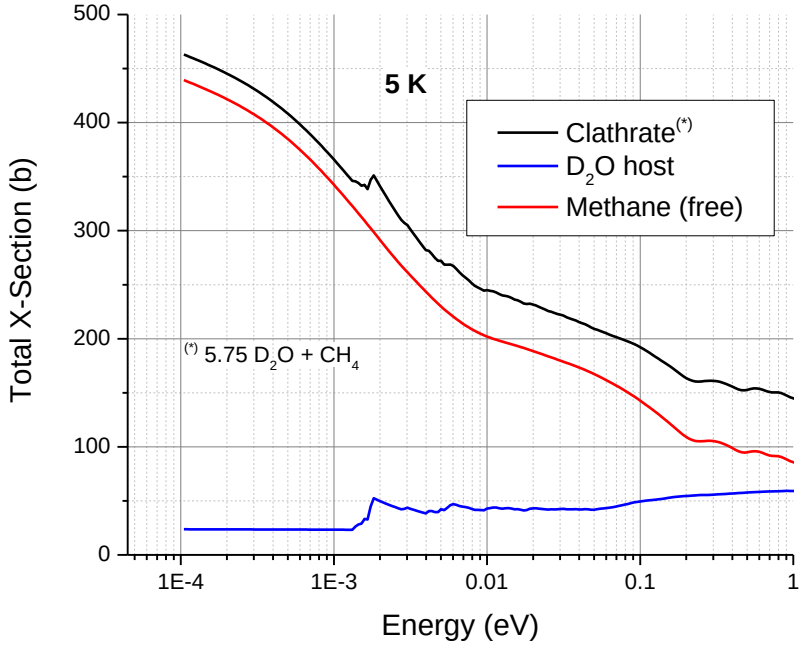
$\cong$ σ(4H) ρ(H in CH4) + 5.75 σ(2H) ρ(H in H2O ice)

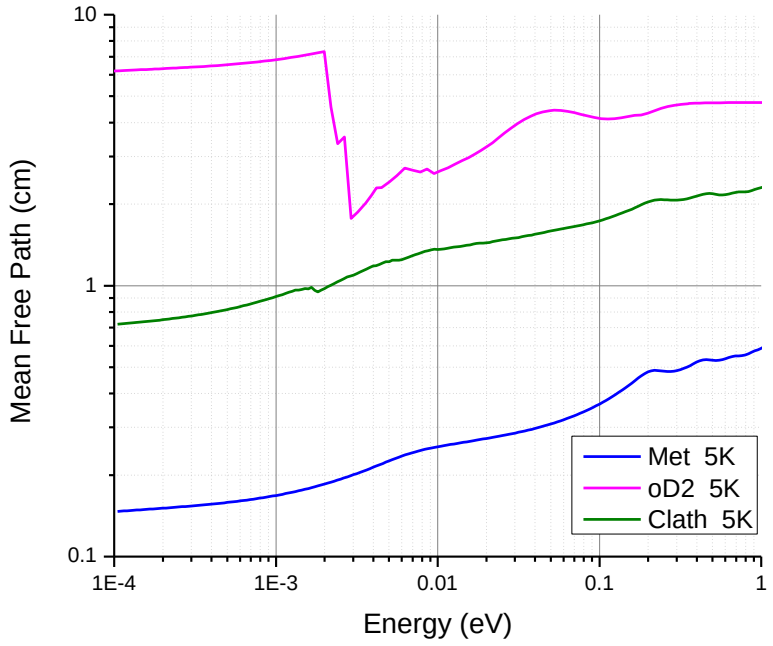


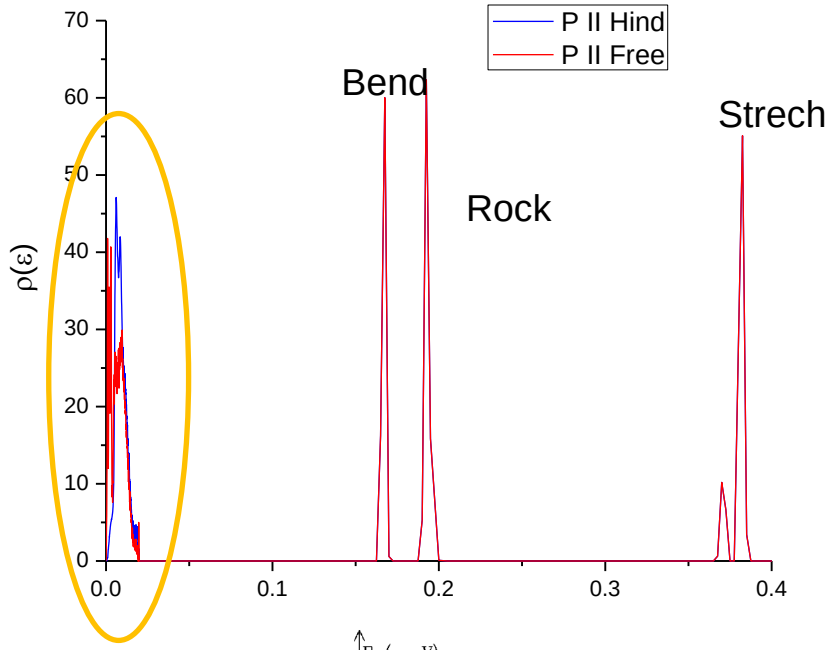
Protonated Methane Clathrate, 5K

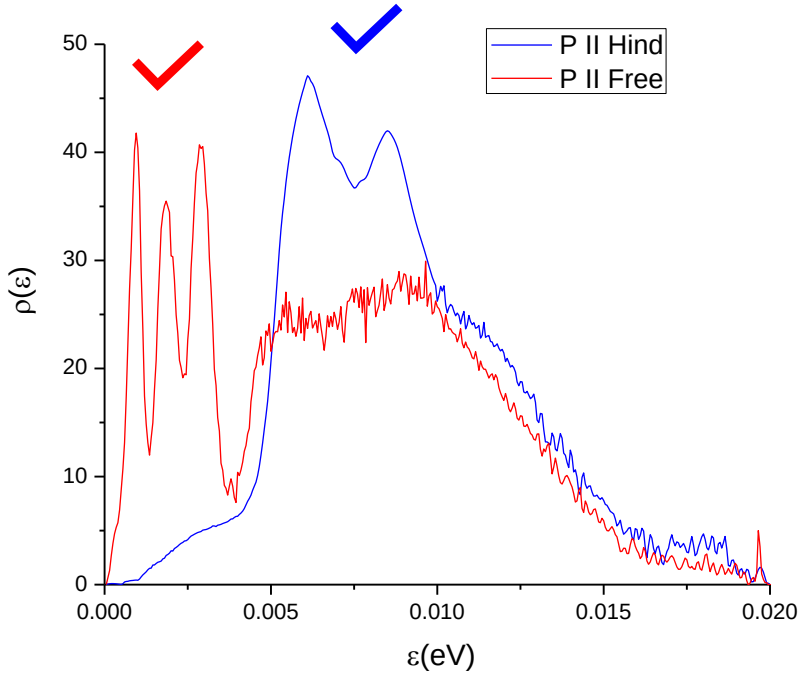
XS CH_4 *d*-CLATHRATE

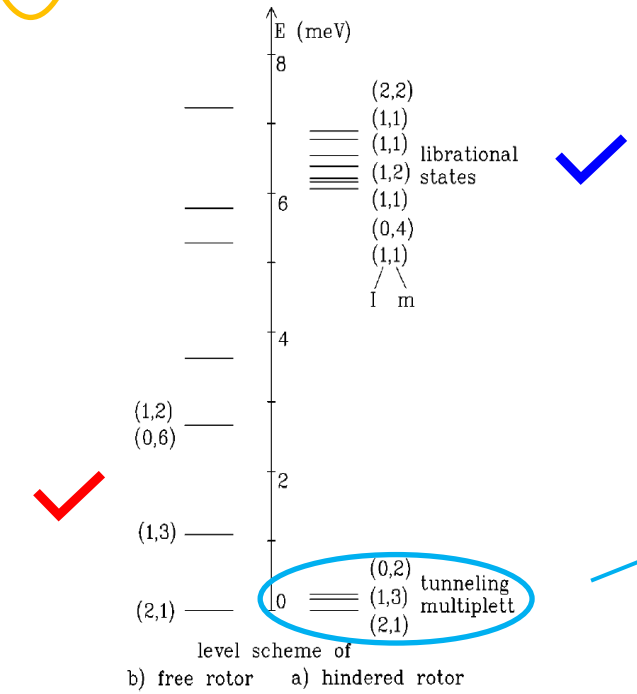


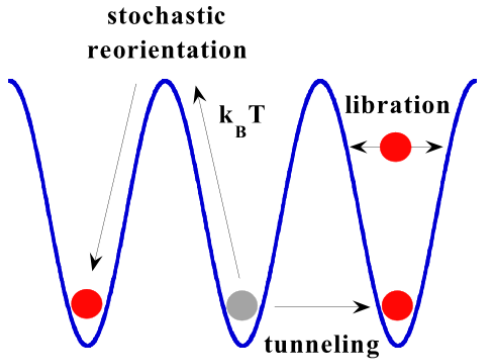


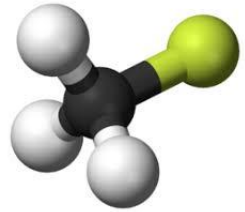






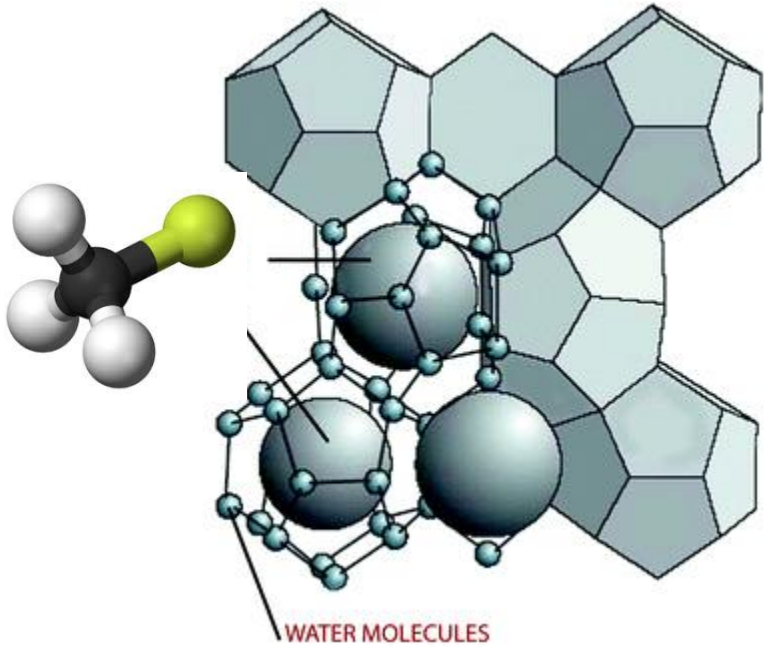


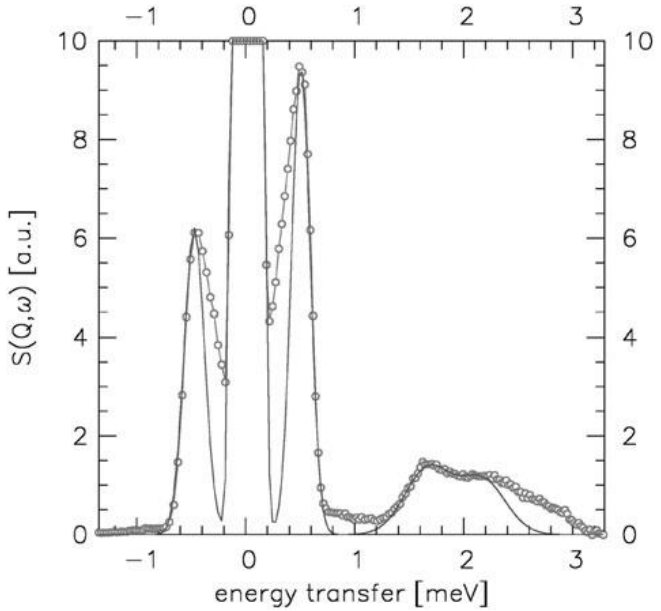




Dynamics of methyl groups in molecular solids

METHYL FLUORIDE IN CLATHRATE





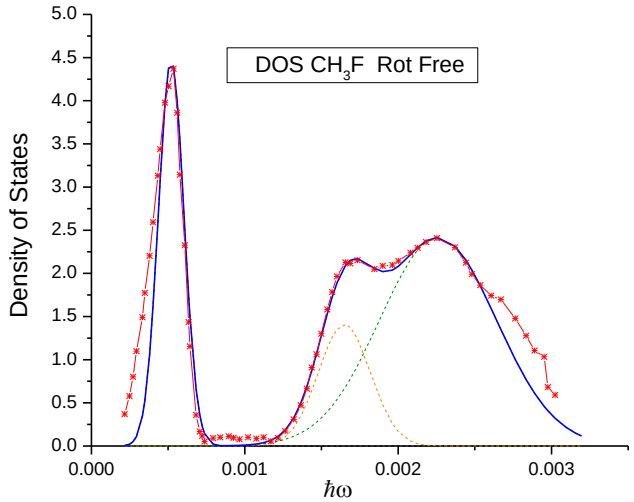
1228 | Phys. Chem. Chem. Phys., 2005, 7, 1228–1234

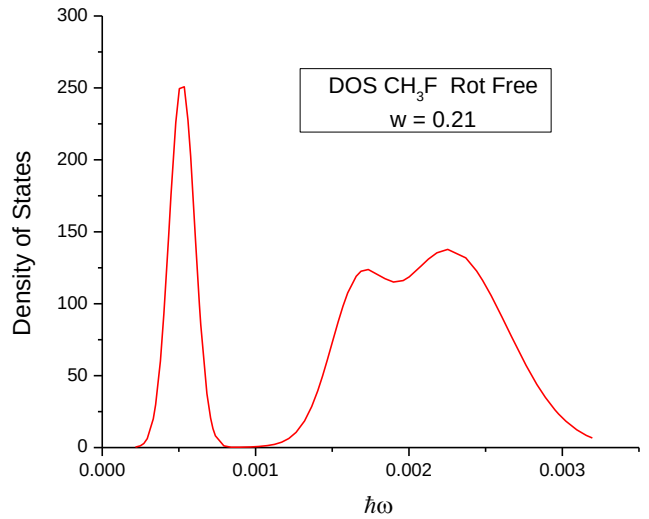
Adsorption sites and rotational tunneling of methyl groups in cubic I methyl fluoride water clathrate†

M. Prager,[a] J. Baumert,[b] W. Press,[b] M. Plazanet,[b] J. S. Tse[c] and D. D. Klug[c]

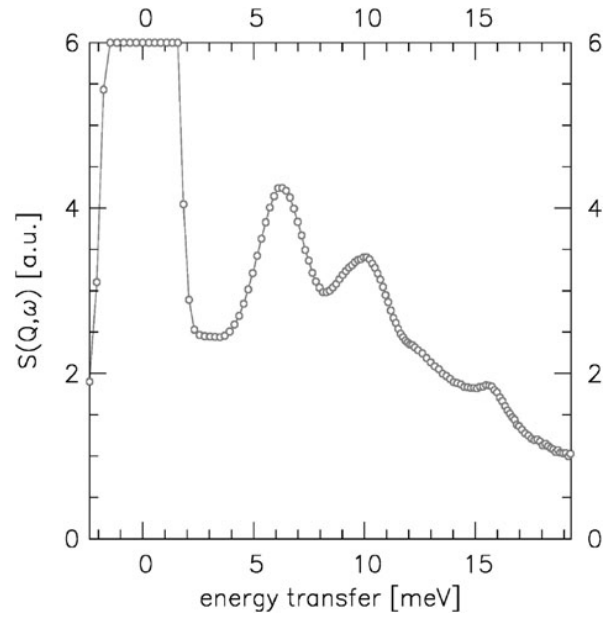
Fig. 9 Lower resolution spectrum including higher rotational levels of methyl fluoride water clathrate. Fully protonated sample. Sample temperature $T = 2.0$ K. Spectrometer: IN5 of ILL. Wavelength $\lambda = 4.5$ Å. Average momentum transfer $Q = 2.3$ Å^{-1}.

$$S(Q,\omega) = \bar{\sigma}\frac{\hbar^2 Q^2}{2\bar{m}}\exp(-2W)\frac{G(\omega)}{\hbar\omega}[n(\omega)+1]$$





$\hbar\omega$: 0.52 meV, 1.65 meV, 2.26 meV



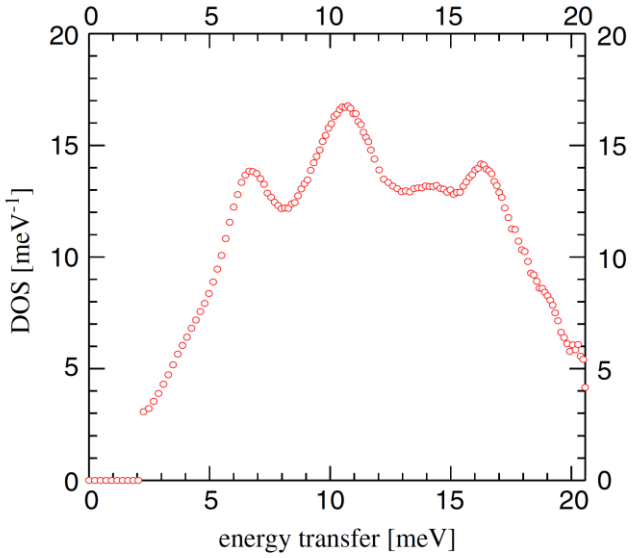


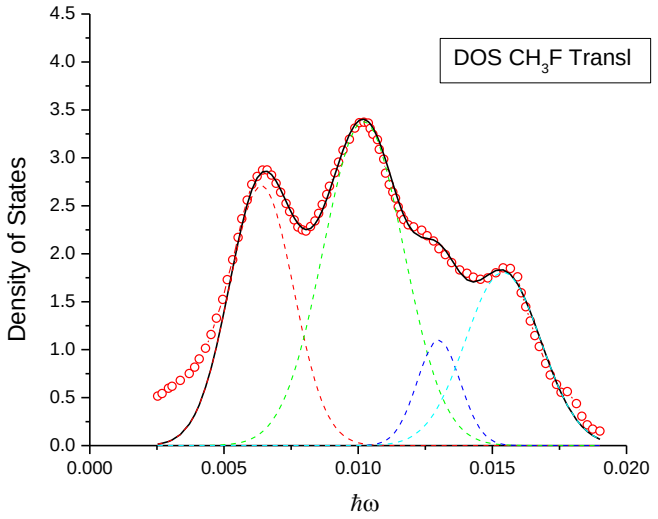
Figure 7. Generalized density of states of $CH_3I \cdot 17D_2O$ in the meV range.

Adsorption sites and rotational tunneling of methyl groups in cubic I methyl fluoride water clathrate†

M. Prager,[a] J. Baumert,[b] W. Press,[b] M. Plazanet,[b] J. S. Tse[c] and D. D. Klug[c]

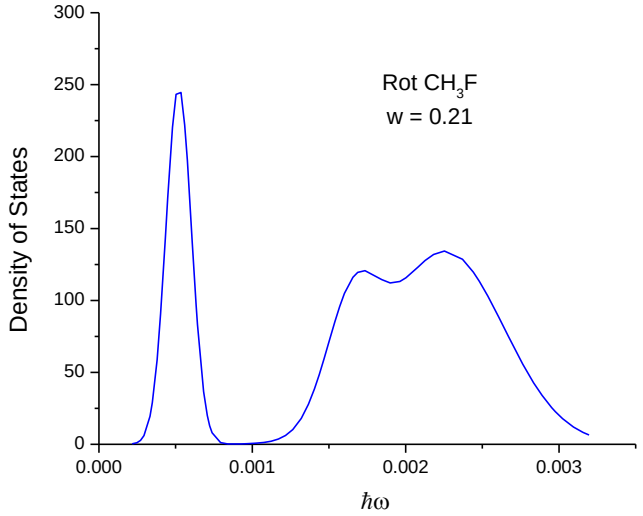
Fig. 2 Neutron scattering spectrum taken in the regime of lattice modes and summed over all scattering angles. Spectrometer: SV29 at Forschungszentrum Jülich. Wavelength $\lambda = 1.81$ Å. Sample temperature $T = 4.2$ K. Average momentum transfer $Q = 4.9$ Å^{-1}.

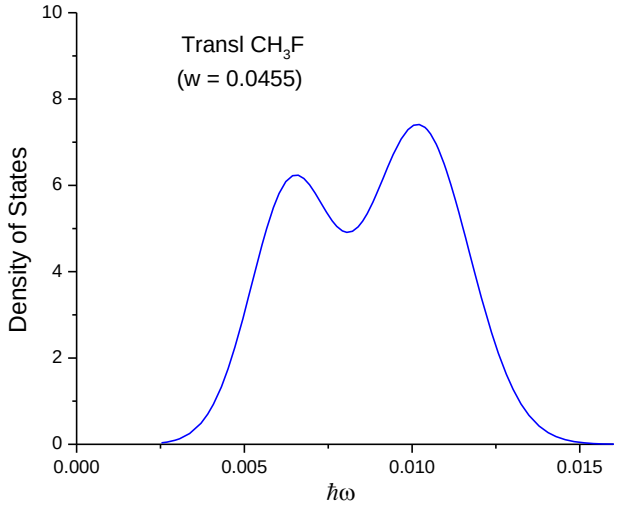
$$S(Q,\omega) = \bar{\sigma}\frac{\hbar^2 Q^2}{2\bar{m}}\exp(-2W)\frac{G(\omega)}{\hbar\omega}[n(\omega)+1]$$

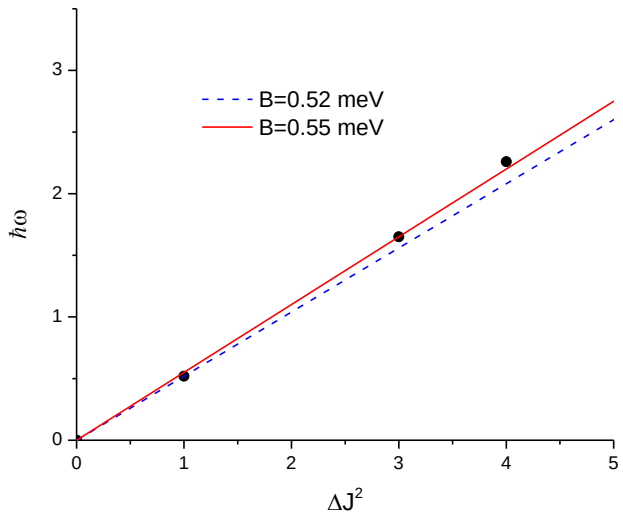


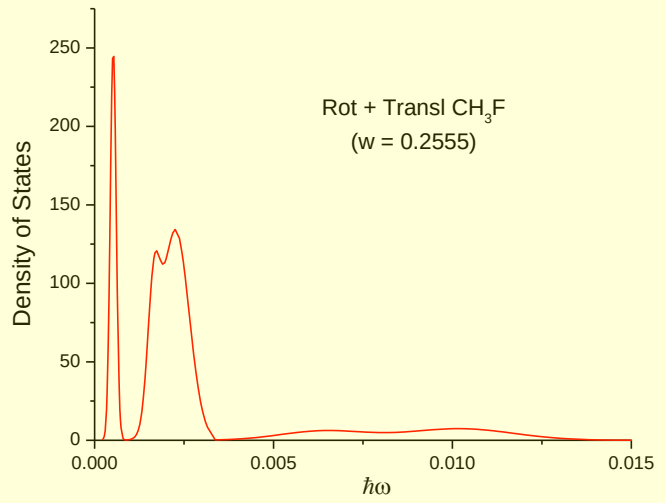
ħω: 6.39 meV, 10.2 meV, 13 meV, 15.4 meV

DOS – CH_3F in Clathrate



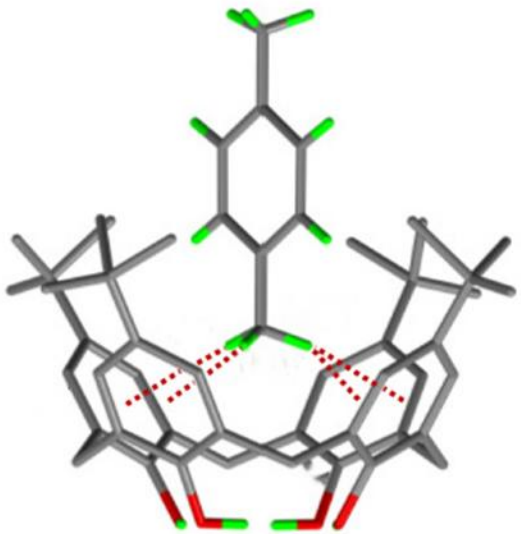




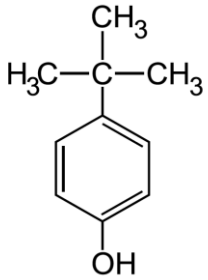


METHYL ROTATIONS in
CALIXARENE SUPRAMOLECULAR COMPLEXES

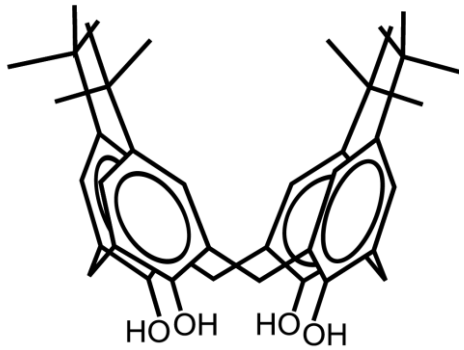
p -tert-butyl-calix[4]arene(2:1) p -xylene



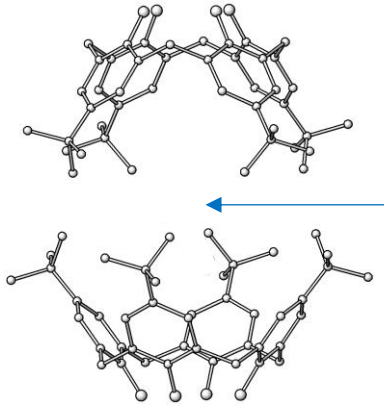
p-tert -butylphenol



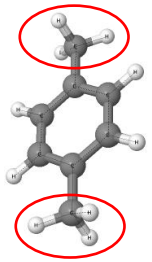
p-tert-butylcalix[4]arene



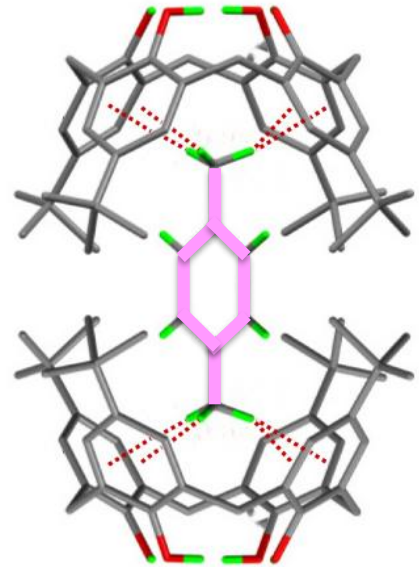
p-tert-butyl-calix[4]arene(2)



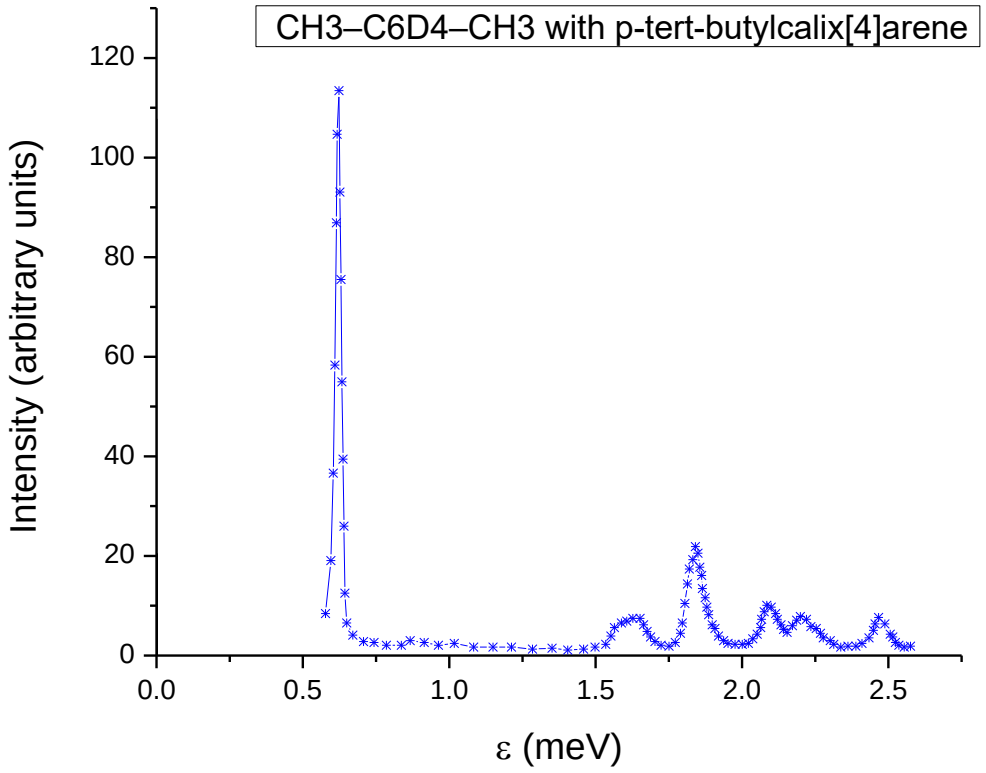
p-xylene



The molecular units, the conformation, and the actual structure of the calixarene complex.



p -tert-butyl-calix[4]arene(2:1) p -xylene



P. Schiebel *et al.*,
J. Phys.: Condens. Matter **10** (1998) 2221

Transition	Energy (meV)	Obs. intensity	Calc. intensity
$0 \rightarrow I$	0.626	100 (±3)	100
$I \rightarrow II$	1.24	2 (±1)	2
$I \rightarrow III$	1.60	11 (±3)	12
$0 \rightarrow II + I \rightarrow IV$	1.85	39 (±4)	39
$I \rightarrow V$	2.10	15 (±1)	15
$0 \rightarrow III$	2.21	19 (±2)	17
$0 \rightarrow IV$	2.48	13 (±1)	12
$0 \rightarrow V$	2.73	4 (±3)	12

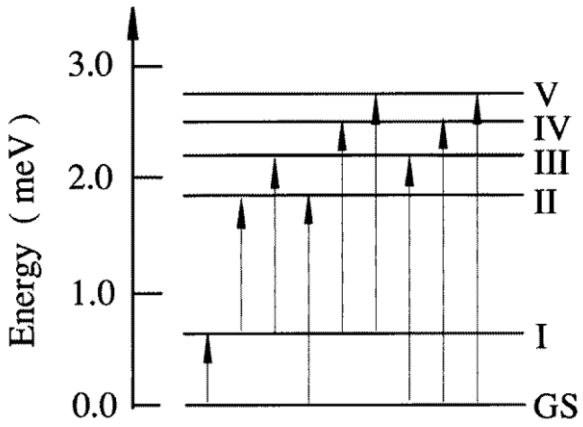
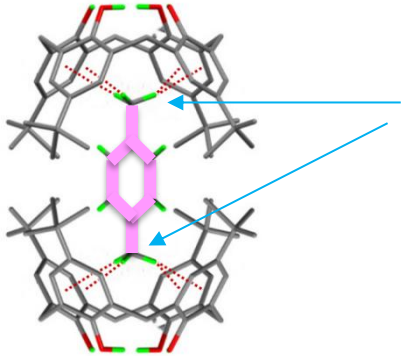
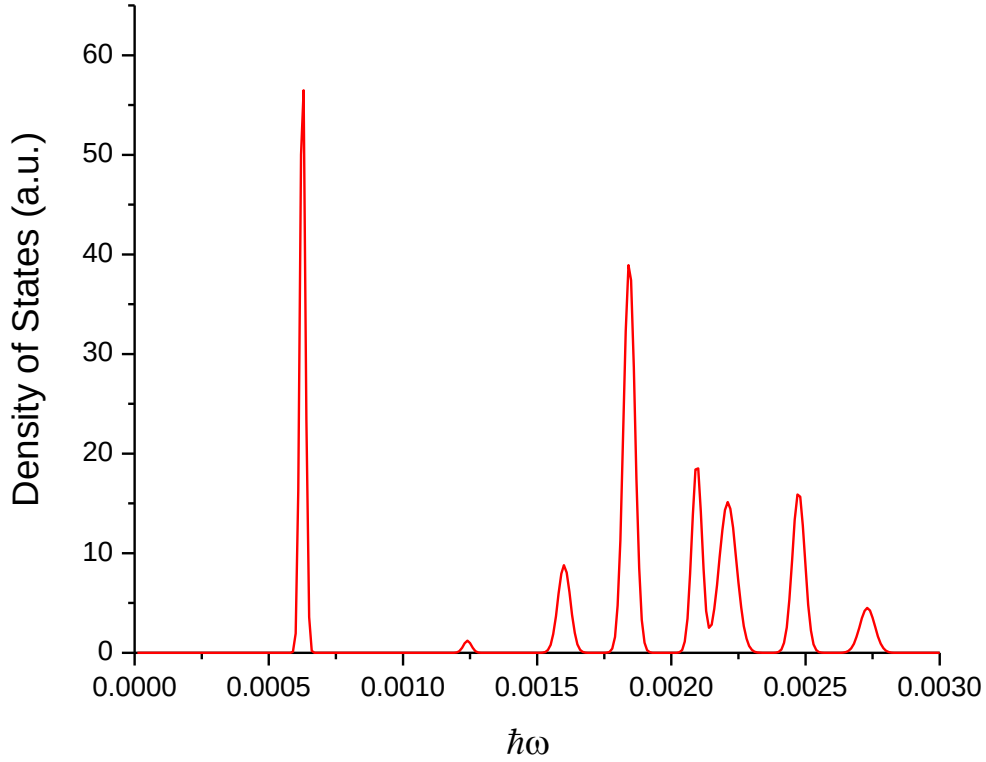


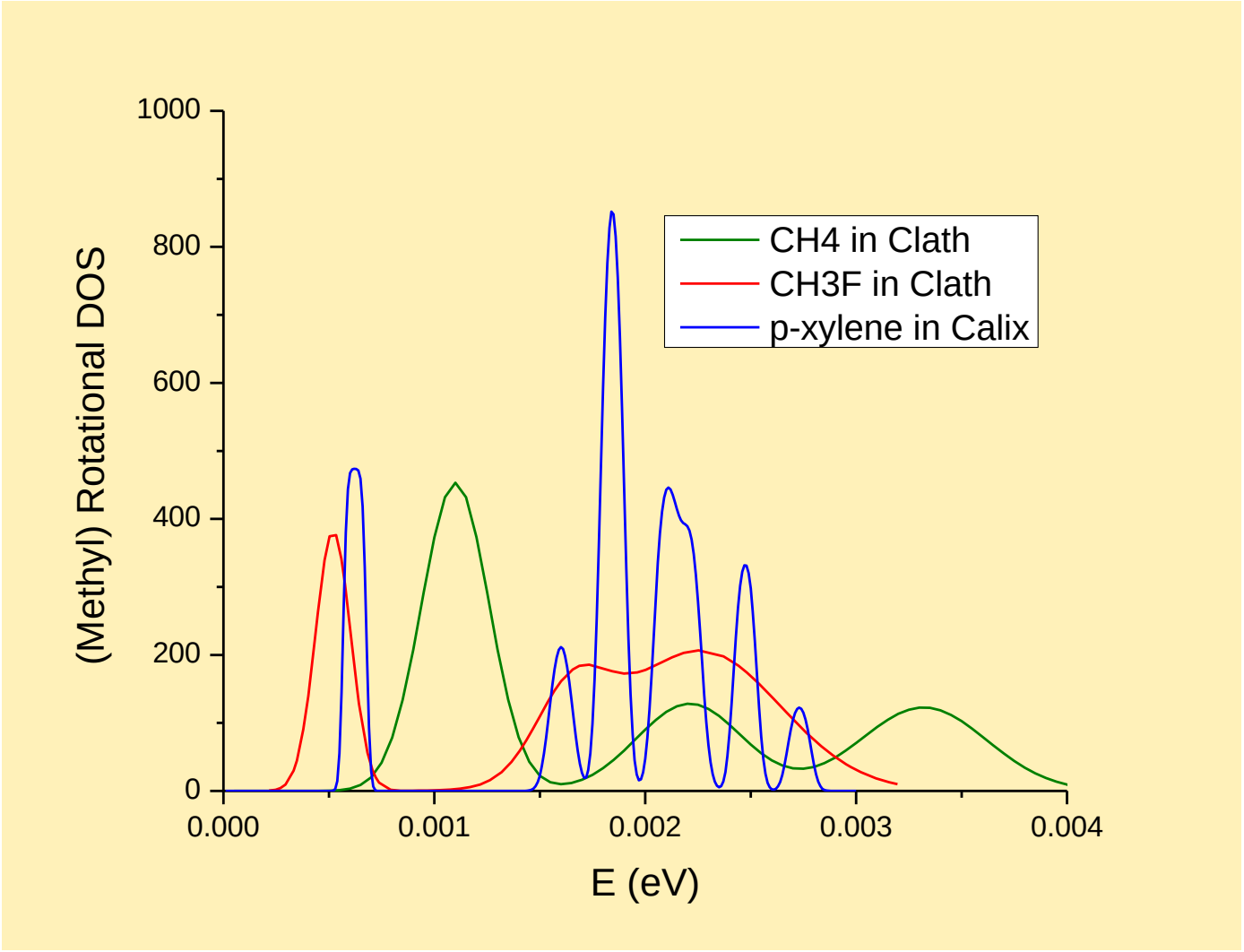
Figure 5. Energy level scheme for the rotation–translation motion of the *p*-xylene methyl groups in the calixarene complex. The arrows indicate transitions with non-zero intensity.



Methyl rotations in
p -tert-butyl-calix[4]arene(2:1) p -xylene



Derived from P. Schiebel *et al.* (1998)


1000
800
600
400
200
0
(Methyl) Rotational DOS
0.000
0.001
0.002
0.003
0.004
E (eV)
CH4 in Clath
CH3F in Clath
p-xylene in Calix

CONCLUSIONS

We have explored and proposed a few molecular systems that show dynamical features of interest to act as moderators to produce **very cold neutrons**. Their densities of states have been derived from available experimental information, which are the relevant input for the elaboration of reliable scattering kernels, using modern computer packages.

It is important to emphasize that at the few Kelvins temperature range that those VCN moderators should operate, spin correlations develop amongst the protons in the CH_3 and CH_4 units and they must properly be accounted for in the cross sections' calculations.

CONCLUSIONS

A very interesting material for producing VCN´s is the supramolecular complex *p-tert*-Butyl-Calix[4]arene(2:1)*p*-Xylene at low temperatures. The reason is the very rich low energy excitations´ spectrum associated with the dynamics of the methyl groups in the p-xylene molecule. An additional, highly important property associated with this system is its expected strong radiation resistance due to the capacity of the aromatic rings to redistribute the energy of incident photons or fast neutrons, thus avoiding the radiolytic hydrogen production within a moderator immersed in strong radiation fields.

CONCLUSIONS

Finally, I wish to emphasize that the ideas presented here are the result of an exploratory study, aimed at showing a possible road rather than defining new materials that could perform well as VCN moderators.

This kind of ideas must be investigated with extensive use of experimental information, typically inelastic and other neutronic measurements. For this purpose, besides the availability of good spectrometers in all major neutron sources, smaller, highly flexible CANS (e.g. Hokkaido LINAC, LENS) will be needed to test new materials and validate their scattering kernels and cross section libraries.

THANKS FOR YOUR ATTENTION

Proceedings of the Workshop on Applications of a Very Cold Neutron Source

ARGONNE NATIONAL LABORATORY

ANL-05/42

Proceedings of the Workshop on Applications of a Very Cold Neutron Source

August 21-24, 2005

prepared by
Intense Pulsed Neutron Source Division
Argonne National Laboratory

ANL-05/42

Argonne National Laboratory is managed by
The University of Chicago for the U.S. Department of Energy