Water clathrates: model systems to study hydrogen in the confinement

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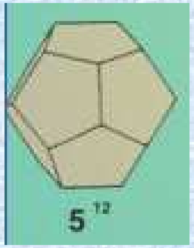
Clathrate hydrates

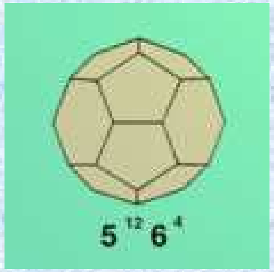
-Clathrate hydrates are inclusion compounds, formed by a network of hydrogen-bonded water molecules that is stabilized by the presence of foreign (generally hydrophobic) molecules, hosted in cages of different form present in the structure.
-Guest gases can be H_2, N_2, Ar, CH_4 and etc;
-Cheap and environmentally friendly media for gas storage;
-Several types of structures are known, only sII-type will be considered in this talk.



Unit cell of sII structure consists of:

1. 16 small cavities in the shape of pentagonal dodecahedron (5^{12})

Average diameter ~ 5.02 Å



2. 8 large cavities in the shape of hexakaidecahedron ($5^{12}6^{4}$)

Average diameter ~ 6.67 Å

Clathrates filled with H_2

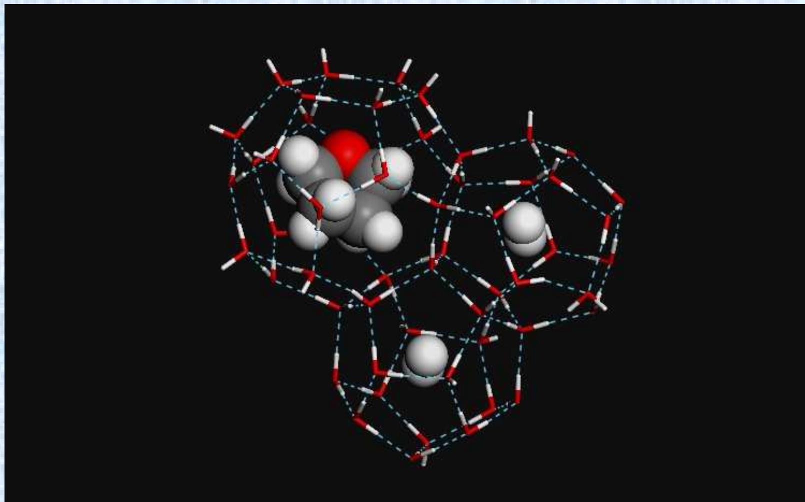
-Fully hydrogenated clathrates (H_2 in large and small cages) require high pressure (**up to 2 kbar**) and are stable up to 160K (*W.Mao, Science* 297 (2002) p. 2247),

-Filling large cavities with large molecules, such as tetrahydrofuran (THF) allows occupation of only small cages by H_2 and reduces the loading pressure to **300 bar** and increase stability temperature range of clathrates up to 280K (H. Lee et al, Nature **434**, 743 (2005))

Cavity dimensions have an impact on macroscopic properties

Occupation of cavities by hydrogen:

Small	1-2 H_2
Large	2-4 H_2



Research objectives

- Understanding of guest-host interactions on the microscopic level, in particular the role of the confinement dimensions;

Our approach:

-experimental characterization of host- guest interactions trough microscopic dynamics measured by inelastic neutron scattering;

-use THF- and fully hydrogenated clathrates to establish the response in small and large cavities respectively;

Ice framework:

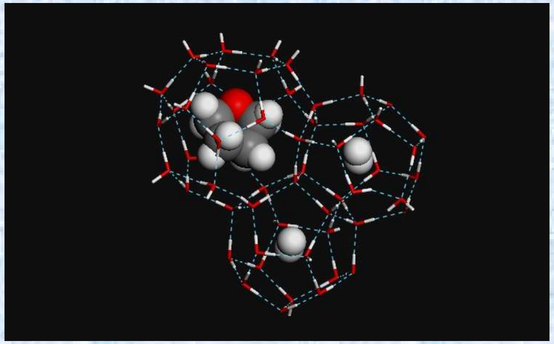
-S(Q, ω) = > VDOS

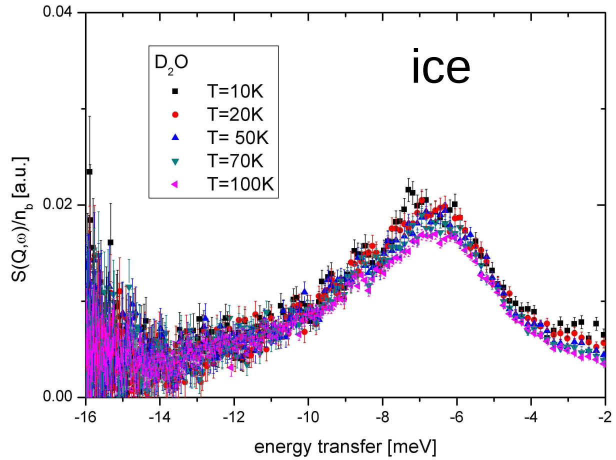
Guest molecules /H_2:

-Isolated molecules = > quantum description has to be employed, discrete energy levels for rotation and vibration / translation;

-Rotational energy levels E_b = BJ (J+1), where B=7.35meV is the rotational constant of gaseous H_2;

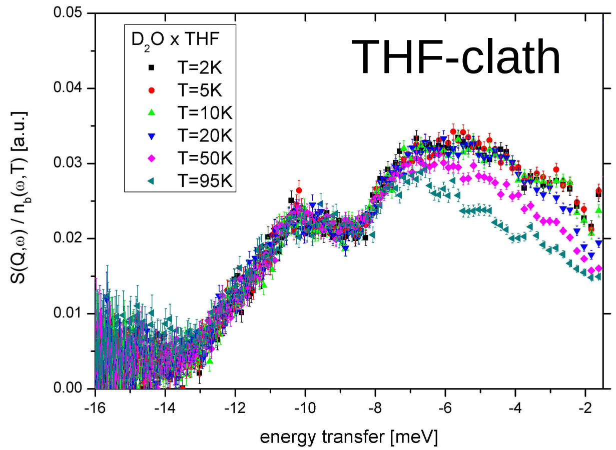
-At the energy range studied only first rotational transition J=1 -> J=0 at 14.7 meV (ortho-para transition) has been accessible;





Rigid structure of deuterated THF x D_2O at T<20K

Temperature behavior of the THF-framework show **negative anharmonicity for T>20K**: shifting of the spectra to the higher frequencies with temperature increase caused by increase of the kinetic energy of the guest molecules and softening of the clathrates structure



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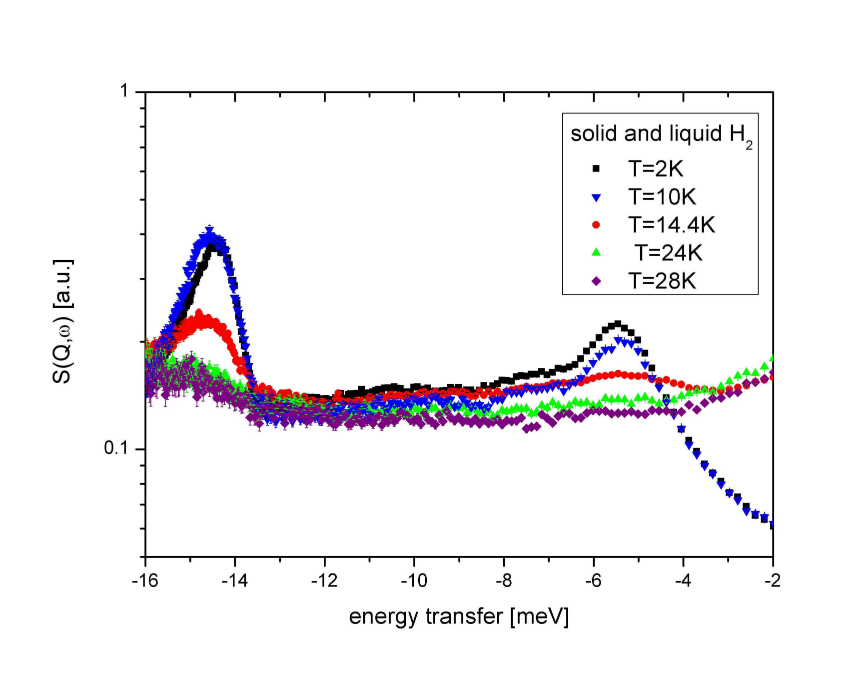
Dynamics of solid and liquid bulk hydrogen



a) Para-to-ortho peak at 14.6±0.2 meV in solid phase

b) Phonon peak at 5 meV, slight shoulders at ~ 7meV and 11 meV, disappear in liquid and gas states;

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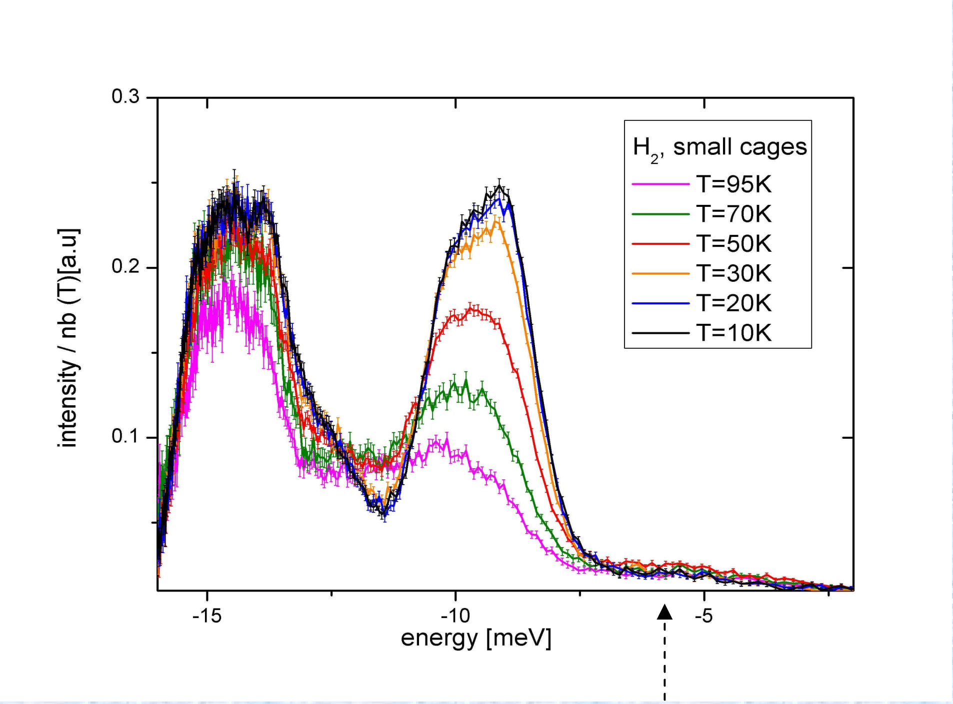
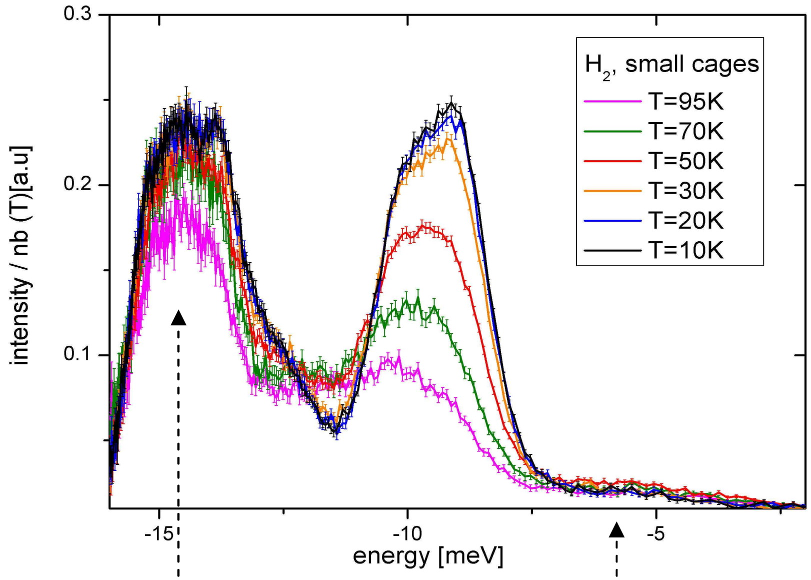
Dynamics of hydrogen confined into small cavities (1 molecules /cage)



In-phase translational motion caused by framework modes

.- Shoulder around 6 meV resembles the density of states of the cages at this energy range => in-phase translational motion of H_2 molecules

Dynamics of hydrogen confined into small cavities



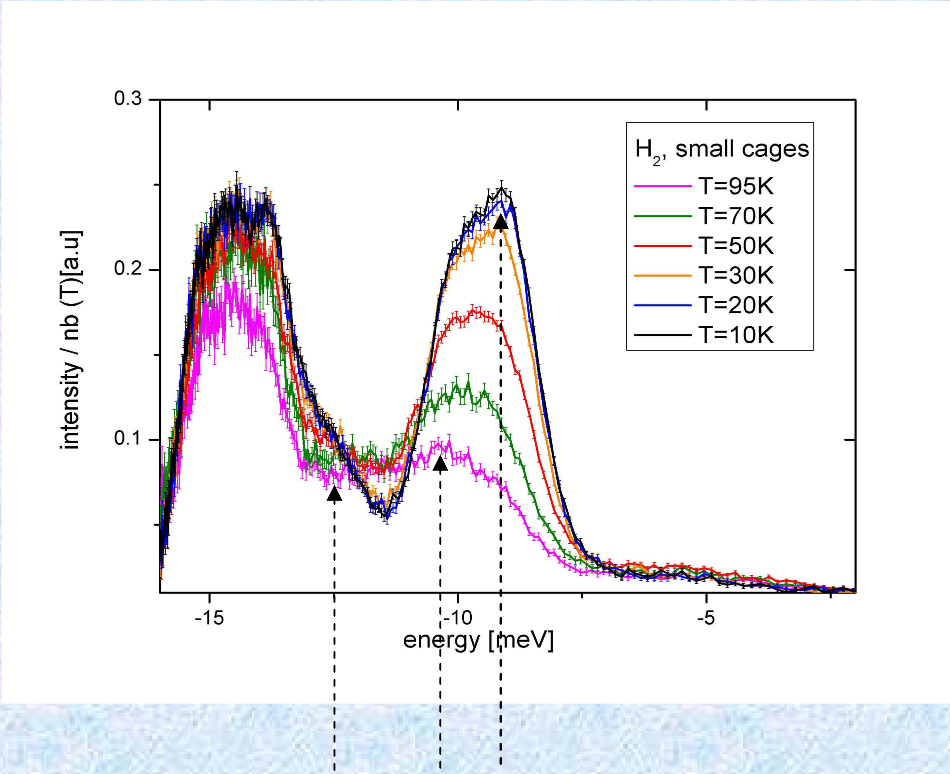
Transition from the ground rotational level to the first excited level: para-ortho transition

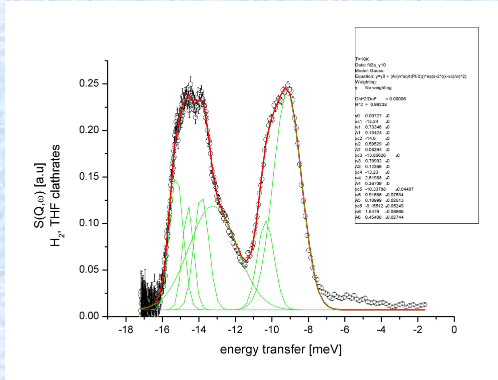
In-phase translational motion caused by framework modes

-Fine structure of para-ortho transition indicates the lifting of J=1 degeneracy, i.e. influence of the cage anisotropic environment

-Peaks position is close to the ortho-para position of the bulk hydrogen = > indicates rather weak interactions between H_2 and clathrate cage;

- para and ortho levels stay populated well above 20 K;

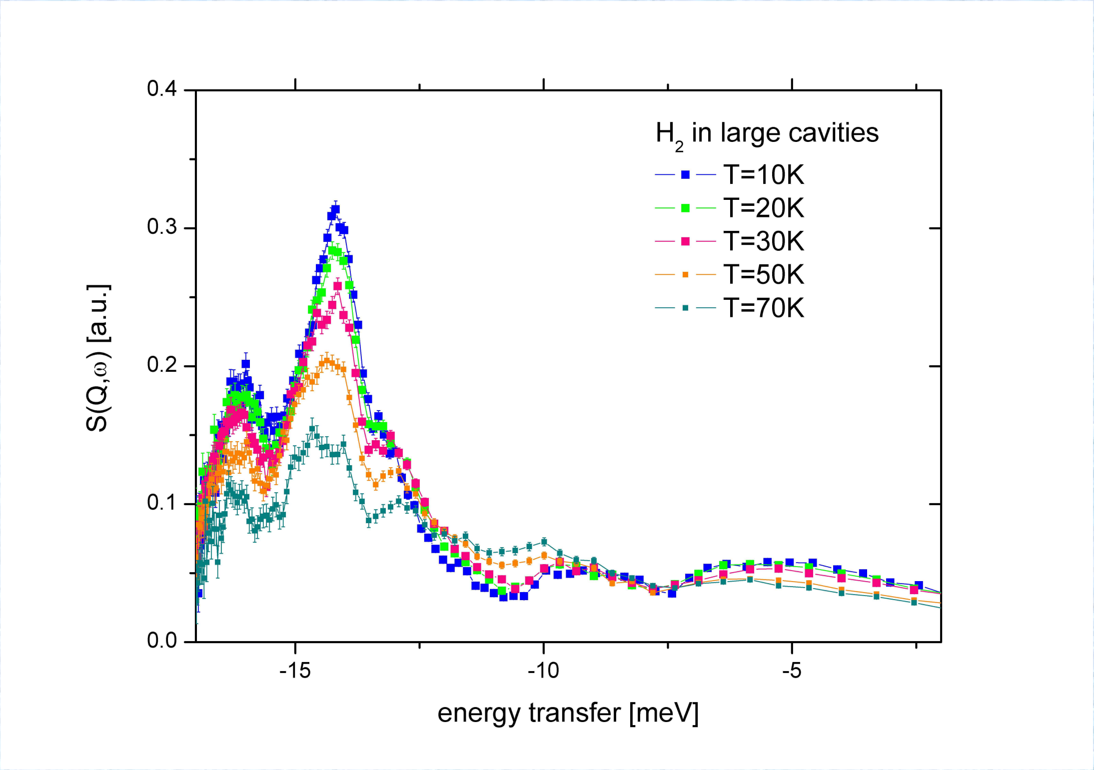




-New modes, not observable in bulk hydrogen and obviously caused by confinement;

-Temperature dependence is different for ortho-para transition and " confinement modes", while the ortho-para peaks keeping their position, positions of "confinement modes" shift towards each other;

Dynamics of hydrogen confined into large cages (2 molecules / cage)

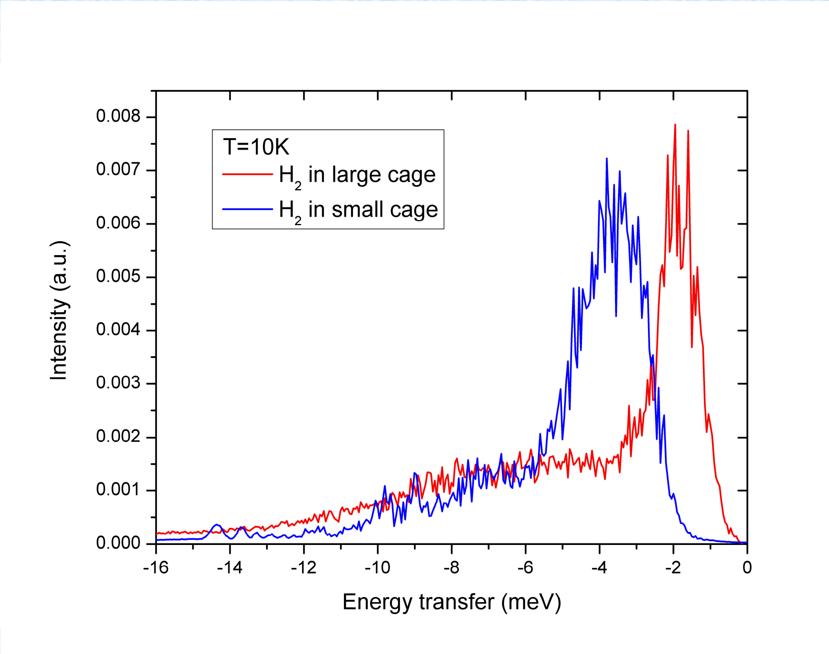


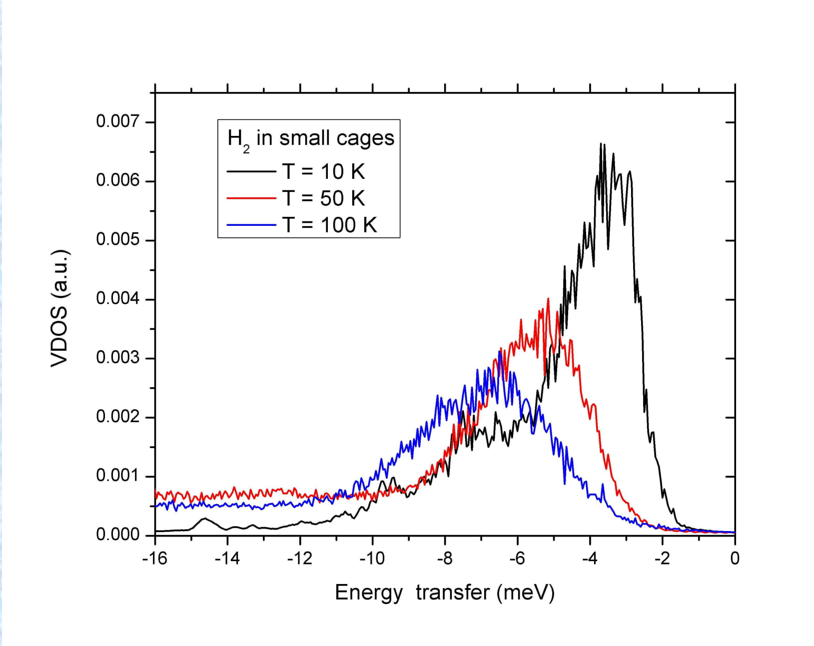
- Absence of strong " confinement modes " in large cages;

- No splitting of para-ortho transition, indicating little interaction beween H_2 and host in the large cage;

- Stronger relaxation with temperature of para-ortho transition;

Molecular dynamics calculations- information about translational motion





Temperature dependence of the DOS shows negative anharmonicity: decrease of DOS and shifting to higher frequencies with temperature increase, trend observed for H_2 in small cages around 9-12 meV, thus translational modes shall contribute to the DOS in this range;

Origin of the “ confined modes”

-Appearance of the strong signal on 9-11 meV range in the small cage;

- Absence of such signal in the large cage:

- Negatively anharmonic temperature dependence indicates relation to translational modes in the confinement;

- Stronger guest – host interactions in the small cage;

Possible explanations:

Scenario 1: rattling

Problems:.

-Neutron scattering intensity is proportional to the number of hydrogen atoms

-Amount of hydrogen is at least the same in the large and small cages

We should observe the signal of the same strength shifted to the lower frequencies in the large cages

Scenario 2: hybrid motion, caused by coupling of rotational and translational levels

- Guest-host interactions lift degeneracy of J=1 level, decreasing the gap between ortho-para states in the small cage;

- Overlap of the rotational and translational spectra = > coupling of rotational and translation degrees of freedom = > new hybrid motion

Conclusions

-The effects of the confinement of H_2 are dramatically different in cages of two different sizes, 5.02 and 6.67 Å;

-The effect of confinement is stronger in the small cages, where we observe the splitting of para-ortho transition caused by the anisotropy of the cage and an additional strong dynamical feature centered around 9 and 12 meV;

-The behavior of H_2 confined into the large cages resembles in contrast the behavior of the bulk hydrogen and show a peak corresponding to para-ortho transition at 14.2 meV and translational modes centered around 6 and 9 meV

-Though the temperature dependence of the dynamic features around 9 and 12 meV indicate the link to translational modes, those modes can not explain the intensity difference between the H_2 in large and small cages;

- The enhanced intensity at 9 -12 meV range can be explained by the emergence of intense hybrid modes at the overlap of the rotational and translational spectra in the small cages caused by the coupling of rotational and translation degrees of freedom;