

# A Quantum translator-rotator: Inelastic neutron scattering of dihydrogen molecules trapped inside anisotropic fullerene cages

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***A Quantum translator-rotator: Inelastic neutron scattering of dihydrogen molecules trapped inside anisotropic fullerene cages***

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**Abstract**

We report an inelastic neutron scattering investigation of the quantum dynamics of hydrogen molecules trapped inside anisotropic fullerene cages. Transitions among the manifold of quantised rotational and translational states are directly observed. The spectra recorded as a function of energy and momentum transfer are interpreted in terms of the rotational potential and the cage dimensions. The thermodynamics of *ortho*- and *para*-hydrogen are investigated through temperature dependence measurements.

In recent years some remarkable complexes have been synthesised in which a hydrogen molecule is permanently trapped inside a fullerene cage [1-3]. These endohedral H<sub>2</sub>-fullerene complexes are superb model systems for understanding quantum molecular dynamics. Because of its low mass and close confinement the H<sub>2</sub> molecule exhibits quantisation associated with all of its degrees of freedom. The Pauli Exclusion Principle also plays an explicit and fundamental role in determining the dynamical behaviour, notably through the existence of the nuclear spin-isomers, *ortho*- and *para*-hydrogen.

There has been much interest in the dynamics of H<sub>2</sub> in a variety of porous media, particularly in the context of hydrogen storage. [4,5,6] The dynamics of several endohedral H<sub>2</sub>-fullerenes have been studied by NMR [7,8] and the data have been interpreted alongside models that incorporate quantised rotational and translational states of H<sub>2</sub>. However, the energy level separations are very much larger than the characteristic energy scale associated with the magnetic interactions so that NMR is only able to probe the translation-rotation manifold indirectly. Infra-red spectra [9] have been recorded on endohedral H<sub>2</sub>@C60. Here the vibrational states are probed and the translational and rotational splittings may be inferred from the fine-structure. However, a fundamental property of quantum translator-rotators is the nuclear spin-symmetry and photons are unable to induce the necessary transitions in nuclear spin to probe the translation-rotation manifold directly.

To investigate the quantum motion, inelastic neutron scattering (INS) has a characteristic energy scale that is well-matched to the rotational constant and the expected translational splittings. The technique exhibits high sensitivity to incoherent scattering from hydrogen nuclei but importantly the neutron scattering interactions are able to induce changes in nuclear spin state; significantly this facilitates transitions between the nuclear spin isomers *ortho*- and *para*-hydrogen. In this first INS investigation of the quantum dynamics of an

endohedral H<sub>2</sub>-fullerene complex, a cage has been selected that has no symmetry so that the potential energy surface (PES) characterising the motion is fully anisotropic.

Aza-thia-open-cage-fullerene (ATOCF) contains a 13-membered opening through which H<sub>2</sub> has been introduced resulting in the endohedral 1:1 complex, H<sub>2</sub>@ATOCF shown in Fig.1. INS experiments on this complex have been conducted on the IN4 time-of-flight spectrometer at the Institut Laue-Langevin in Grenoble [10]. This instrument has high neutron flux, facilitating measurements on samples that are only available in relatively small quantities. As well as the H<sub>2</sub> inside, the side groups at the cage orifice contain hydrogen nuclei which scatter neutrons. Therefore to measure the spectrum of the entrapped H<sub>2</sub> alone it was expedient to record INS spectra from both H<sub>2</sub>-filled and empty cage samples under identical conditions and to determine the difference spectrum. Samples with high purity were prepared using published synthetic procedures [1,2] The H<sub>2</sub>@ATOCF sample mass was 492mg, equivalent to 0.46mmol H<sub>2</sub>.

Fig.1 shows the INS difference spectrum of H<sub>2</sub> molecules trapped in the ATOCF cages. This was recorded with an incident neutron wavelength of 1.8Å at a temperature of 2.5K. Time-focussing was optimised for the +15meV energy transfer region where the instrument resolution is approximately 0.35meV (Half-Width at Half-Maximum: HWHM). However, the resolution varies systematically with energy so, for example, the HWHM is approximately 0.8meV at -15meV; all transitions appear with peaks that are resolution limited. A single transition at -13.25meV appears in neutron energy gain whereas in neutron energy loss a triplet of lines, +13.25, +14.75 and +16.10meV, is observed, all with similar amplitude. A more intense band is observed in the region 17-18meV.

The rotational energy of H<sub>2</sub> is quantised so that  $E_J = BJ(J+1)$  where  $J$  is the rotational quantum number. Rotational states have degeneracy  $2J+1$  with each

sub-state labelled by a second quantum number  $m_J = J, J-1, \dots, -(J-1), -J$ . In free  $H_2$  with a bond length  $d_{HH} = 0.74 \text{ \AA}$ , the rotational constant is  $B = 7.37 \text{ meV}$  so that the splitting of the  $J = 0$  to  $J = 1$  rotational transition for isolated  $H_2$  is  $14.74 \text{ meV}$ . This coincides with the centre line of the observed triplet in neutron energy loss. It is well-established that, arising from the exclusion principle, *ortho*-hydrogen ( $J = 1$ ) is a nuclear spin triplet with total spin  $I = 1$  while *para*-hydrogen ( $J = 0$ ) is a nuclear spin singlet  $I = 0$ . Therefore *ortho-para* hydrogen conversion is spin-restricted so, unless time-dependent interactions combining space and spin variables are available, the meta-stable *ortho*-state becomes trapped when the sample is cooled from high temperature.

The existence of a  $-13.25 \text{ meV}$  neutron energy gain peak at a temperature of  $2.5 \text{ K}$  proves that the sample is not in full thermal equilibrium. This peak is attributed to trapped *ortho*- $H_2$  molecules making transitions to the *para*- $H_2$  ground state, while transferring their excess energy to the neutrons.

The neutron energy loss and energy gain spectra are strongly asymmetric at  $2.5 \text{ K}$ . To investigate further, the temperature dependence of the neutron energy gain region was studied using incident neutron wavelength  $3.6 \text{ \AA}$  to optimise the energy resolution ( $0.6 \text{ meV}$  HWHM); the spectra are shown in Fig. 2. At  $2.5 \text{ K}$  the neutron energy gain spectrum comprises simply the  $-13.25 \text{ meV}$  peak but with increase in temperature to  $10 \text{ K}$  and above, amplitude is systematically transferred to two peaks at higher energy. The peak positions of this triplet coincide with those observed on the neutron energy loss side. Above  $80 \text{ K}$  the  $17\text{-}18 \text{ meV}$  band also begins to appear in neutron energy gain. The normalised neutron energy gain peak amplitudes are shown in Fig. 3; these were determined by fitting to the spectra in Fig. 2. It is clear that the triplet is associated with the rotational manifold so that in energy gain the neutrons are scattering from *ortho*-hydrogen,  $J = 1$  to  $J = 0$ , while in energy loss the reverse transition from *para*-

hydrogen is observed. We assign the triplet to the three states  $m_J = 0, \pm 1$  where the degeneracy of the  $J = 1$  rotational state has been lifted by the anisotropy of the potential. The solid lines in Fig. 3 are derived from the Boltzmann populations assuming internal equilibration amongst the triplet with the observed energy splittings 1.50 and 1.35 meV. There is good correspondence with the data so it is evident that the three members of the triplet of *ortho*-hydrogen come to internal equilibrium while the species as a whole remains thermally isolated from the lattice.

Additional to changes in neutron energy, the neutron momentum transfer spectrum,  $S(Q)$ , is also available. This can provide information on the physical dimension of the scattering object and on its spatial confinement. The momentum transfer,  $\hbar Q$ , is defined by the wave-vectors,  $k$ , of the incident and scattered neutrons,  $Q = k_i - k_f$ . The double differential neutron scattering cross-section for a  $J = 1$  to  $J = 0$  rotational transition in neutron energy gain converting *ortho*- into *para*-hydrogen is given by; [11,12]

$$\left. \frac{\partial^2 \sigma}{\partial \Omega \partial E} \right|_{1 \rightarrow 0} \propto x \frac{k_f}{k_i} S_{1 \rightarrow 0}(Q) \delta(E - E_f + E_i) \quad (1)$$

where  $x$  is the population of the *ortho*-hydrogen species. Applying Refs. [11,12] it may be shown that,

$$S_{1 \rightarrow 0}(Q) \propto \exp\left(-\frac{2}{3} Q^2 \langle u^2 \rangle\right) \sigma_{inc} \left[ j_1(Qd_{HH}/2) \right]^2 \quad (2)$$

where  $\frac{1}{3} Q^2 \langle u^2 \rangle$  is the Debye-Waller factor,  $\sigma_{inc}$  is the incoherent neutron scattering cross-section and  $j_n(Qd_{HH}/2)$  is the n'th-order spherical Bessel function. In Fig. 4 the  $Q$ -dependence of the amplitude of the -13.25meV neutron energy gain peak is shown for  $T = 2.5$  K, recorded with incident neutron wavelengths 1.1Å and 1.24Å. Eqn. (2) has been fitted to the experimental data.

Apart from an amplitude scaling factor, the only adjustable parameter is  $\langle u^2 \rangle$ , the mean-square displacement of the hydrogen molecule. The best fit with  $\langle u^2 \rangle_{\text{expt}} = 0.068 \pm 0.001 \text{ \AA}^2$  is shown; solid line, Fig. 4. Very good correspondence with the data is obtained. This provides independent confirmation of the assignment of the triplet to the manifold of rotational lines.

It is clear from Figs. 2 and 3 that the 17-18meV band belongs to a different manifold. The temperature dependence of the band amplitude is characteristic of a Boltzmann factor with energy  $\approx 17.5 \text{ meV}$ ; dashed line Fig. 3. The dimension of the fullerene cage has been estimated previously from the molecular structure [7] and to a first approximation the  $\text{H}_2$  molecule occupies a sphere with root mean square radius (rms),  $r_s = 0.78 \text{ \AA}$ . Using this value we are able to estimate the translational splitting. Assuming a spherical cage with infinite walls, the translational eigenfunctions are spherical Bessel functions,  $\psi_{\text{trans}}^{(n,l)}$  where  $n$  and  $l$  are quantum numbers. Applying the normal boundary conditions the eigenfunction solutions can be found numerically. Thus the ground ( $n, l = 1, 0$ ) to first excited ( $n, l = 1, 1$ ) translational splitting is,  $\Delta_{\text{trans}}^{1,0-1,1} = 10.32 \frac{\hbar^2}{2\mu r_s^2}$ , [7] where  $\mu$

is the mass of the hydrogen molecule. With  $r_s = 0.78 \text{ \AA}$ , we calculate

$\Delta_{\text{trans}}^{1,0-1,1} = 17.68 \text{ meV}$  in very satisfactory agreement with the centre of the observed band.

Additional support for the assignment of this band to  $\text{H}_2$  translation is provided by  $\langle u^2 \rangle$  determined from the  $Q$ -dependence of the rotational line. The mean square displacement of the hydrogen molecule in its ground state may be calculated from the ground state eigenfunction  $\psi_{\text{trans}}^{(1,0)}$  leading to  $\langle u^2 \rangle_{\text{sph}} = 0.068 \text{ \AA}^2$ . This is in very good agreement with the experimental value determined from Fig. 4.

Therefore, although in this provisional analysis the cage has been approximated with spherical shape, a very consistent picture has emerged, confirming the assignments to the rotational and translation manifolds. In fact the translational band has structure and is best fitted as a doublet with energies 17.10 and 17.90meV. This splitting represents, in part at least, the lifting of the three-fold degeneracy.

For free H<sub>2</sub> the  $J = 1$  rotational state is threefold degenerate, however, the ATOCF cage is ellipsoidal and so presents an anisotropic potential energy surface to the entrapped H<sub>2</sub>. We identify three mutually perpendicular axes  $XYZ$  representing the orientation of the H<sub>2</sub> molecule and we shall assume that the potential energy about these axes is dominated by cosine terms with two-fold symmetry, reflecting that of the H<sub>2</sub> molecule. If the respective direction cosines of the H-H vector are  $\cos_x$ ,  $\cos_y$  and  $\cos_z$  we may write the anisotropic rotational potential as,

$$V = V_x (1 - \cos_x^2) + V_y (1 - \cos_y^2) + V_z (1 - \cos_z^2) \quad (3)$$

where  $V_x$ ,  $V_y$  and  $V_z$  represent the amplitudes of the respective barriers to rotation. Numerical solutions of the rotational Hamiltonian  $\hat{H}_R = -\frac{\hbar^2}{2\mu} \nabla^2 + V$  have been found in the basis of free-rotor functions; the latter are spherical harmonics. The effect of the anisotropic potential is to lift the rotational degeneracy as observed experimentally. With  $V_x = 3.58$ ,  $V_y = -3.46$ ,  $V_z = -0.12$  meV the calculated  $J = 0 \leftrightarrow 1$  energy transfers are 13.38, 14.86, 16.20meV, in good agreement with the observed rotational spectrum. There is one axis that is almost neutral to rotation; the remaining two have barrier heights that are less than one-half the rotational constant. Therefore, any tunnelling effects are minimal and the system is in the free-rotor limit. The eigenfunctions of  $J = 1$  are akin to

the p-orbitals in atomic structure, with  $m_j = \pm 1$  mixing equally such that the states with energy 16.26meV and 13.38meV are the real and imaginary combinations. The thermal equilibration among the three rotational sub-states plays an important role in the NMR spectroscopy and relaxation of the endohedral H<sub>2</sub>-fullerenes and the energy levels and splittings determined by INS are in good qualitative agreement with NMR models [7].

An energy level scheme appropriate to H<sub>2</sub>@ATOCF is sketched in Fig. 5. In spherical symmetry the first excited translational state is three-fold degenerate but in the presence of an anisotropic cage this degeneracy is fully lifted. In this case the translational states are described by three quantum numbers  $n_x, n_y, n_z = 1, 2, \dots$ . In INS it may be shown that the translational excitations of *ortho*-hydrogen dominate over those of *para*-hydrogen [11]; the scattering is from a compound entity, the H<sub>2</sub> molecule, and pure translational transitions in *para*-hydrogen with  $I = 0$  are governed by the coherent scattering cross-section,  $\sigma_{coh} = 1.8$  barns, which is much smaller than  $\sigma_{inc} = 80.3$  barns that governs the translational transitions in *ortho*-hydrogen with  $I = 1$ . This is another manifestation of the nuclear spin-symmetry of H<sub>2</sub> so the observed translational peaks arise predominantly from *ortho*-hydrogen.

In the spectrum of Fig. 1 two translational transitions are resolved. No rotational fine structure is observed so these features involve no change in  $m_j$ . It appears that the third translational transition is absent from the energy window of Fig. 1. One axis of the ATOCF cage is significantly narrower than the other two with an effective radius estimated to be 0.60Å compared with a rms radius of 0.78Å for the cage as a whole [7]. Scaling the observed translations at  $\approx 17.5$ meV by the factor  $0.78^2/0.60^2$  we therefore estimate the energy of the third translational peak to be approximately 29-30meV. INS spectra have been recorded out to these energies: no INS peaks are observed in the range 20-29meV but a band of

overlapping peaks is observed in the range 29-40meV. However, this is the region where higher order rotational transitions are also expected along with overtones of the 17-18meV translational band. Therefore further studies are underway to formally identify the third translational splitting.

In this first INS investigation of a H<sub>2</sub> molecule inside a fullerene cage the quantisation of rotational and translational degrees of freedom has been directly observed. The anisotropy of the PES leads to the degeneracies being fully raised and the rotational potential characterising the interactions with the cage wall has been determined from the rotational spectrum. The system is a model for quantum dynamics and further investigations are proceeding into the coupling of translational and rotational modes. We are now in the process of combining data from INS, NMR and infrared spectroscopy to build up a complete picture of the energy level structure for the confined quantum rotor.

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## Figure Legends

Fig. 1 The INS difference spectrum of hydrogen in H<sub>2</sub>@ATOFC recorded at 2.5K on the IN4 time-of-flight spectrometer; incident wavelength 1.8Å.

Fig. 2 The temperature dependence of the neutron energy gain spectrum of H<sub>2</sub>@ATOFC; incident wavelength 3.6 Å. The dashed lines are the fitted components of the rotational triplet of *ortho*-hydrogen. The solid line includes the translational band at 17-18meV.

Fig. 3 The temperature dependence of the amplitudes of the rotational triplet observed in neutron energy gain (● 13.25; ■ 14.75; ▼ 16.10meV). The model assuming thermal equilibration among the rotational triplet is shown with solid lines. Open circles and dashed line; amplitude of the translational doublet.

Fig. 4 Neutron momentum transfer spectrum  $S(Q)$  for the -13.25meV rotational line in neutron energy gain:  $T=2.5K$ . The solid line is the fit with Eqn. (2).

Fig. 5 A schematic showing the low-lying rotational and translational energy levels of H<sub>2</sub>@ATOFC.

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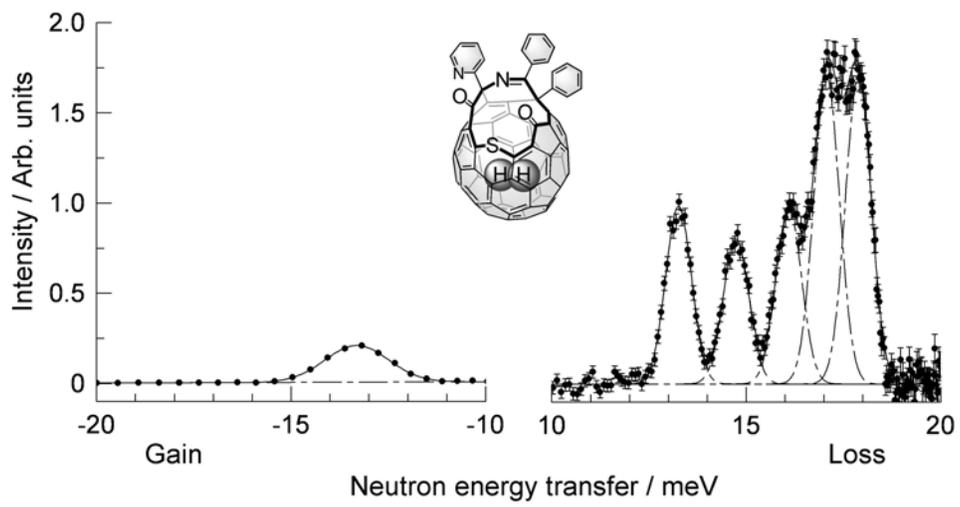


Fig 1: Horsewill et al

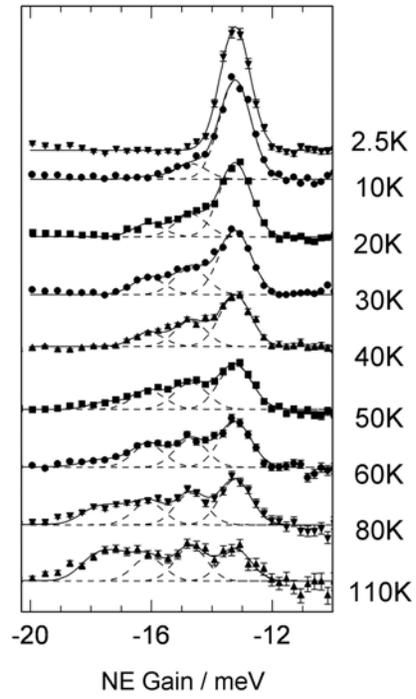


Fig 2: Horsewill et a

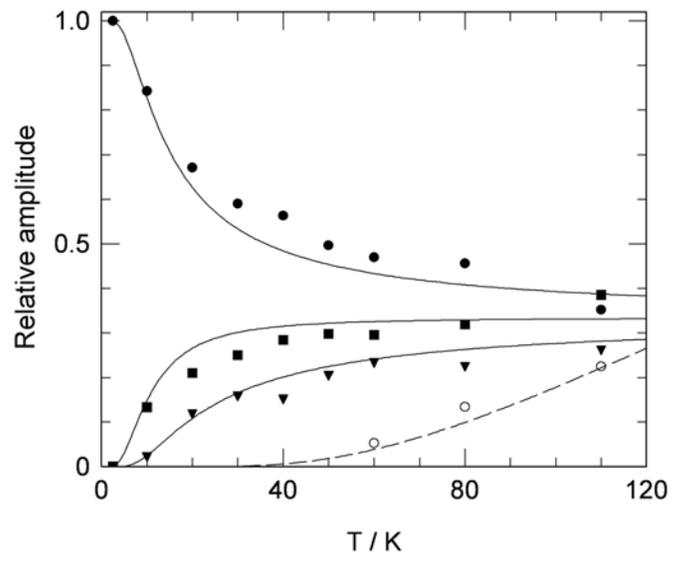


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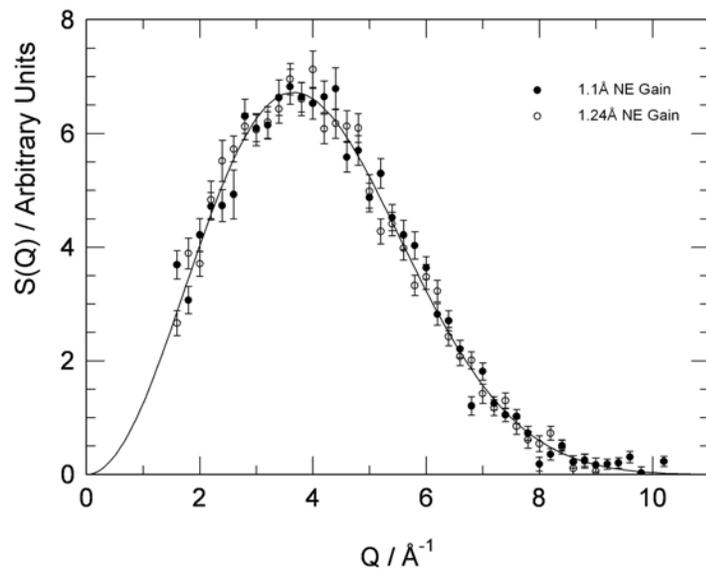


Fig 4: Horsewill et a

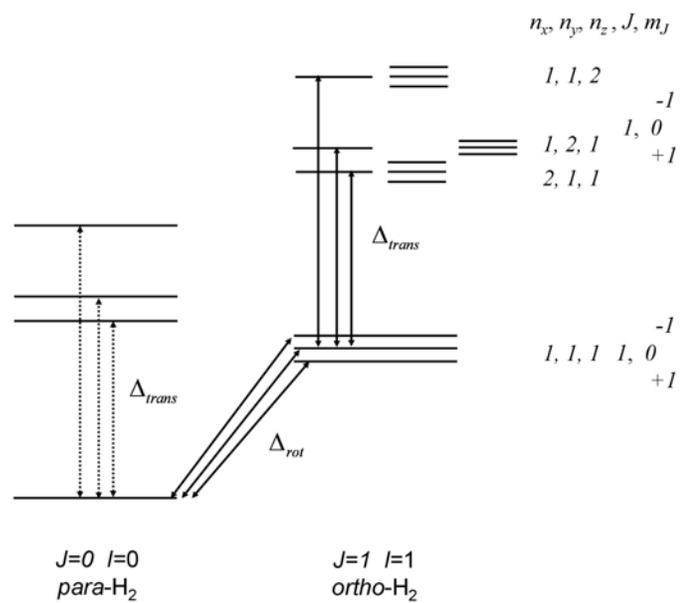


Fig 5: Horsewill et al