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Inelastic neutron scattering of a quantum translator-rotator encapsulated in a closed fullerene cage: Isotope effects and translation-rotation coupling in $H_2@C_{60}$ and $HD@C_{60}$

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We report an inelastic neutron-scattering (INS) investigation of coupled quantum translation and rotation of hydrogen molecules trapped inside the closed isotropic cages of C_{60}. The low-lying states that characterize the translation-rotation manifold of the hydrogen molecules are accurately determined in our study of the INS peak energies. A comparison between the spectra of H_2 and HD isotopomers provides quantitative insight into the coupling between rotational and translational angular momentum with HD exhibiting the strongest effects due to mixing of the rotational eigenstates.

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In recent years remarkable complexes have been synthesized in which a hydrogen molecule is permanently encapsulated within the cage formed by a fullerene molecule producing a highly quantum system. The techniques used in the synthesis of such "endofullerenes" have become known as "molecular surgery" since the procedure involves opening an orifice in a fullerene cage by chemical means, the physical insertion of the hydrogen molecule through the orifice, followed finally by resealing the orifice using a series of proscribed chemical reactions.[1,2] This is a physical entrapment of the H_2 molecule and the confining potential is determined by nonbonding interactions between the hydrogen molecule and the atoms forming the cage.

In providing a practical example of an entrapped quantum particle, the system goes to the heart of quantum mechanics and is invaluable as a model system as well as for its intrinsic interest. The dynamics of the H_2 molecules are of particular interest to the present study. NMR,[3,4] infrared (IR),[5] inelastic neutron scattering (INS),[6] and specific heat[7] investigations have recently been reported with the different spectroscopies providing complementary energy windows. In the first INS investigation of a hydrogen endofullerene,[6] the technique was shown to very effectively elucidate the low-lying eigenstates of the system. This was conducted on the open-cage endofullerene $H_2@ATOCF$ where the INS spectra revealed the quantization associated with both rotational and translational degrees of freedom. The low symmetry of the cage potential meant that the orbital angular momentum was quenched and all translational and rotational degeneracies of the H_2 eigenstates were lifted. A particular advantage of the INS technique lies in its ability to mediate transitions involving changes in nuclear-spin state.[8–13] This is important for entrapped H_2 since distinct INS peaks are observed involving transitions between the nuclear-spin-isomers orthohydrogen (o-H_2) and parahydrogen (p-H_2).

$H_2@C_{60}$ defines the fundamental member of the hydrogen endofullerene family, Fig. 1. Here the intramolecular confining potential has icosahedral (I_h) symmetry, which is sufficiently high that the translational and rotational eigenstates of the H_2 molecule individually retain their full degeneracy. For an entrapped quantum rotor in an isotropic cage the translational eigenstates are classified by the principle quantum number n and the orbital angular momentum quantum number l, where $l=n,n-2,\ldots,1$ for odd n and $l=n,n-2,\ldots,0$ for even n. Furthermore, for p-H_2 the rotational quantum number J is even and the total nuclear-spin quantum number $I=0$ while o-H_2 has odd J and $I=1$. The low-lying energy levels are shown in Fig. 1.

With its high symmetry, $H_2@C_{60}$ is of special interest; possessing both rotational and orbital angular momentum there is considerable interest in investigating the coupling of translational and rotational angular momentum (TR coupling). In theoretical and computational analyses incorporating TR coupling, Xu *et al.*[14–16] have characterized the H_2 eigenstates by the total angular momentum of the system defined by quantum number $\lambda=l+J,l+J-1,\ldots,|l-J|$. This raises some degeneracies so that any observed splittings will characterize the strength and nature of this TR interaction which is mediated by interactions of the rotor with the cage potential.

We shall describe INS investigations that have been conducted on a $H_2@C_{60}$ sample containing a mixture of entrapped hydrogen isotopomers; H_2 and HD. As we shall show, this is of particular interest because, with the mass of the quantum particle available as a variable to the experiment, isotopomer studies elucidate in more depth the effects on the quantum dynamics of TR coupling and the cage potential. Furthermore, arising from the Pauli exclusion principle (PEP), the statistical thermodynamic properties of H_2 and HD are significantly different, providing both insight into the quantum nature of the system as well as facilitating spectral line assignments from the temperature dependence.

A 190 mg powdered sample containing a mixture of entrapped isotopomers $H_2@C_{60}$, $HD@C_{60}$, and $D_2@C_{60}$ was produced using published procedures, Fig. 1.[1,2] The final solvent used in the preparation was CS_2 and occluded solvent

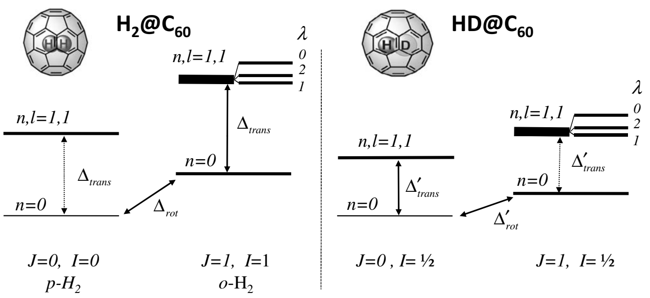

FIG. 1. The energy levels of the quantum rotator translators, $H_2@C_{60}$ and $HD@C_{60}$. The quantum numbers n, l, J, I, and λ are defined in the text.

was removed by heating under vacuum for an extended period. The ratio of the three isotopomers $H_2:HD:D_2$ was approximately 1:1:0.2. The INS spectra were recorded on the IN4C time-of-flight neutron-scattering spectrometer at the Institut Laue-Langevin, Grenoble. Since the incoherent neutron-scattering cross section of ^1H nuclei is much larger than that of ^2H and ^{12}C, the INS spectra are dominated by scattering from ^1H in the H_2 and HD molecular species. In Fig. 2, the INS spectra recorded at $T=1.8$ K with incident neutron wavelengths of $\lambda_n=1.65$ Å and $\lambda_n=1.8$ Å are presented. Neutron kinematics in the IN4C spectrometer means these two spectra embrace a different energy-transfer range with different energy resolutions; the latter is also a function of neutron energy transfer. The peak at 14.6 meV in neutron energy (NE) loss is the $J=0$ to $J=1$ rotational transition of H_2 which interconverts the ground states of p-H_2 and o-H_2. This peak energy coincides closely with the rotational transition in free H_2. The reverse transition appears at the same energy transfer in NE gain. As was observed in the INS spectrum of the anisotropic cage material,[6] the appearance of the NE gain peak demonstrates that o-H_2 and p-H_2 are not in thermal equilibrium since at 1.8 K p-H_2 would be the only species present in an equilibrium. The two spin isomers are unable naturally to interconvert[17] and when the sample is cooled the metastable o-H_2 species retains its abundance characterized by some earlier high-temperature epoch.

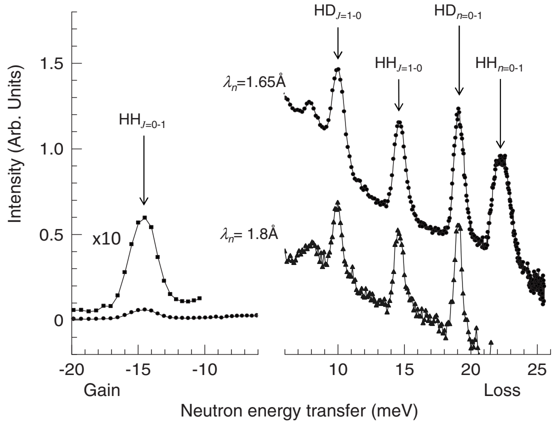

FIG. 2. The INS spectrum of $H_2@C_{60}:HD@C_{60}$ recorded at 1.8 K on the IN4C time-of-flight spectrometer. The $\lambda_n=1.8$ Å spectrum is offset.

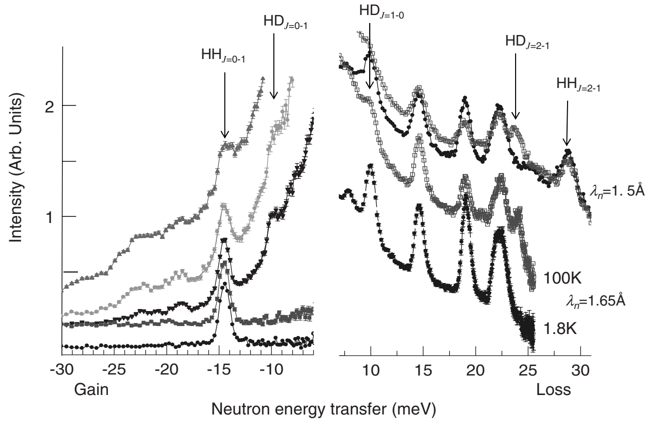

FIG. 3. The temperature dependence of the INS spectrum. NE gain $\lambda_n=3$ Å: $T=1.8$, 20, 80, 120 200 K ascending (all ×5). NE loss $\lambda_n=1.65$ and 1.5 Å: $T=1.8$ K (closed symbols) and 100 K (open symbols). Spectra offset for clarity.

Further assignments of the spectrum are facilitated by studying the temperature dependence, Fig. 3. Due to the lack of conversion, the concentrations of o-H_2 and p-H_2 are independent of temperature so any temperature dependence in the INS spectrum of H_2 is due to the Debye-Waller factor alone.[9] By contrast, the HD isotopomer is not subject to the PEP, there are no nuclear-spin isomers, both $J=0$ and $J=1$ species have $I=\frac{1}{2}$ and the eigenstates of HD attain thermal equilibrium. Therefore, at the lowest temperature only the $J=0$ state of HD is populated, however with an increase in temperature this readily converts to $J=1$. Consequently, the amplitudes of INS peaks associated with HD exhibit a much stronger dependence on sample temperature than those of H_2. Applying this principle to the spectra in Fig. 3 leads us to assign the peaks at 14.6 and 22.3 meV to H_2 while the peaks at 10.0 and 19.1 meV arise from HD.

The rotational spectrum of a diatomic rotor is governed by $E_J=(\hbar^2/2I_m)J(J+1)$, where I_m is the moment of inertia. Therefore, scaling by the ratio of the reduced masses, the $J=0$ to $J=1$ rotational peak for HD is expected at 11 meV; in fact this peak is observed at 10.0 meV. The discrepancy is a signature of TR coupling, to which we shall return. Unlike its compatriot in H_2 this HD rotational peak is absent in NE gain at $T=1.8$ K, emphasizing the difference in spin-symmetry properties of the two isotopomers. However, with increasing temperature ($T=100$ K) this HD peak does attain observable amplitude in NE gain as the $J=1$ state becomes thermally populated, simultaneously leading to a significant reduction in amplitude of the NE loss peak. The normalized amplitudes of the $J=0\leftrightarrow1$ peaks for HD in NE loss and gain are plotted in Fig. 4. The solid lines depict the amplitudes assuming Boltzmann populations showing good agreement with the experimental data.

The peaks at 19.1 and 22.3 meV have energy transfers in the ratio 1:1.17 coinciding closely with the ratio of the reduced masses of H_2 and HD, 1:1.15. This behavior is characteristic of translational modes associated with a harmonic cage potential. Therefore, the peak at 22.3 meV is assigned to the $n=0\rightarrow1$ translational transition of o-H_2 ($J=1$). This falls in an energy range consistent with modes observed in

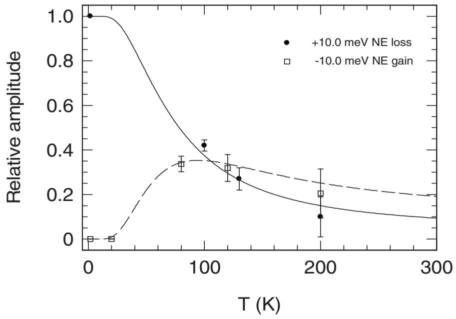

FIG. 4. The temperature dependence of the $J=0 \leftrightarrow 1$ INS peaks in NE gain and loss for HD@C_{60}: the amplitudes are plotted relative to the amplitude at 1.8 K with Debye-Waller correction factors applied, determined from the temperature dependence of the +14.6 meV peak. Solid lines: INS amplitude assuming Boltzmann populations within the manifold of translation-rotation lines of HD.

the open-cage fullerene H_2@ATOCF,[6] IR of the excited vibrational state,[5] heat-capacity measurements,[7] and estimates of the effective internal cage dimensions.[3] In the INS spectrum, p-H_2 ($J=0$) does not contribute with significant amplitude to this translational transition. This is another manifestation of the quantum nature of the system where the two hydrogen nuclei with total spin $I=0$ present a compound scattering entity to the arriving neutrons. As a result, the contribution of p-H_2 to this purely translational peak is governed by the coherent scattering cross section which is only 2% of the ^{1}H incoherent scattering cross section.

Given the reduced mass ratio, the peak at 19.1 meV is assigned to the $n=0 \rightarrow 1$ translational transition in HD. Since $I=\frac{1}{2}$ for HD, both $J=0$ and $J=1$ species can contribute to the amplitude of this peak, in contrast to H_2. However, at 1.8 K it will be dominated by the $J=0$ species.

In the range 28–29.0 meV a peak is observed in spectra recorded with neutron wavelength $\lambda=1.5$ Å. This appears to be an asymmetric pair with its largest component centered at 29.0 meV. This peak has only weak temperature dependence, suggesting it originates from H_2. Given it is centered at an energy transfer close to twice the $J=0 \rightarrow 1$ rotational peak, we assign this to the $J=1$ to $J=2$ rotational transition. At 100 K a "hot-band" is observed at 23.8 meV. Applying the principle that only the spectrum of the HD species is strongly affected by temperature, this peak is assigned to that species. Since its temperature dependence seems to mirror the appearance of the HD rotational peak in NE gain this peak probably originates in $J=1$. A strong candidate is the $J=1$ to $J=2$ rotational transition. Unlike its compatriot in H_2, this energy splitting is significantly more than twice that of the $J=0$ to $J=1$ rotational peak for HD. This absence of simple scaling is a signature of TR coupling.

For the low-lying states of H_2 observed in this INS investigation, the effects of TR coupling are evidently fairly subtle; as predicted by Xue *et al.* the main rotational peaks appear as singlets at the resolution observed and the $J=0 \rightarrow 1$ and $J=1 \rightarrow 2$ rotational peak energies scale simply in the ratio 1:2. However, there is excess width in the translational peak of o-H_2 at 22.3 meV observed at both 1.8 and 100 K. According to the energy level scheme in Fig. 1 this may represent a splitting of the total angular momentum states $\lambda=0,1,2$ of $(n,l,J)=(1,1,1)$. The model calculations of Xu *et al.*,[16] based on a cage potential characterized by an optimized Lennard-Jones C-H interaction, predict a triplet of states with energies $22.1|_{\lambda=1}$, $22.9|_{\lambda=2}$, and $24.2|_{\lambda=0}$ meV above the o-H_2 ground state. The model splitting between the $\lambda=1$ and $\lambda=2$ components corresponds well with an estimate of the splitting of the INS line under the assumption it is a doublet (0.7 meV). However, a splitting as large as that predicted for the $\lambda=0$ component does not seem to be supported by the observed spectrum. The calculation of Xu *et al.* was conducted on the first excited vibrational state of the molecule so while qualitative comparisons with the width of the INS peak may be made, it may not yet be appropriate to make a detailed quantitative comparison with the calculated splitting of the triplet.

At 1.8 K the 19.1 meV translational peak for HD appears as a singlet within the resolution of the spectrometer. This observation is in agreement with the TR model since, in contrast to H_2, at 1.8 K the INS peak in HD is dominated by the $J=0$ species and since the rotational angular momentum is zero the first excited translational level is not split by TR coupling. A splitting into a triplet is only expected for the $J=1$ state of HD which will only be populated at the higher temperatures. There is evidence in the 100 K spectrum for additional components in this region that may arise from the $J=1$ triplet of HD; for example, the center of mass of the HD translational peak moves to lower energy by 0.1 meV and there may be some additional scattering intensity above the baseline in the region 18–22 meV. However, the resolution and sensitivity is not yet sufficiently high to make a formal assignment of any temperature-dependent fine structure.

A small peak appears at 7.9 meV in NE loss at 1.8 K. The energy difference between the translational and rotational peaks of H_2 is 7.7 meV so this peak may arise from the translation-rotation splitting between $n=0$ $J=1$ of o-H_2 and $n=1$ $J=0$ of p-H_2. That no translational fine structure is expected for this transition could explain the small energy-transfer difference, Fig. 1, however, further supporting evidence is required to confirm this assignment.

Particularly revealing in this INS investigation is the comparison between the behavior of H_2 and HD. As earlier indicated, the $J=0$ to $J=1$ rotational splittings of these species do not scale with the moments of inertia. Here the symmetry of the molecule has a profound influence. For H_2 the rotational splitting closely matches the value observed for free H_2 but in this investigation the hydrogen molecule is entrapped and experiences a substantial potential with the cage wall. However, because this potential is nearly isotropic there is little effect on the rotational spectrum. Solutions of the Schrödinger equation by Xu *et al.*[16] show that the cage potential leads only to a marginal mixing of the rotational states; J remains a good quantum number for H_2 and the rotational constant is only marginally affected by the confinement. These properties are consistent with the INS spectra of H_2@C_{60}. However, Xu *et al.*[15] have also analyzed the eigenstates of HD@C_{60} based on a model cage potential. This reveals a substantial mixing of the rotational states of HD arising from its interactions with the wall; J is not a good quantum number for HD so that the calculated effective rotational constant is substantially different from that of free HD. The latter concurs well with one of the principle observations arising from this INS investigation where the $J=0 \leftrightarrow 1$ rotational transition of HD is some 10% smaller than that predicted by scaling the energy of the same transition in H_2. The strong mixing is also revealed in the ratio of the $J=0 \leftrightarrow 1$ and $J=1 \leftrightarrow 2$ peak energies for $HD@C_{60}$, which unlike its compatriot in $H_2@C_{60}$ deviates significantly from 2.

Evidently, the difference between H_2 and HD arises not only from the mass but also from the asymmetric distribution of that mass in the HD species. Because the center of mass does not coincide with the center of the HD bond, the rotational sphere for HD has a radius that is approximately 33% larger than that of H_2, influencing the potential experienced. The effects of TR coupling influence both isotopomers but these are particularly strong for $HD@C_{60}$ where there is substantial mixing of eigenstates. There is good correspondence between the INS spectra and the theoretical structure devised for TR coupling by Xu *et al.*[14–16] With mass available as an experimental variable this INS investigation on the two isotopomers has revealed both the existence and extent of TR coupling and the strong influence of the PEP in determining the statistical thermodynamics of the system. The spectral resolution of the current experiments was insufficient to resolve any additional splittings of the pure rotational line, inferred to be of order 0.1 meV from specific-heat measurements.[7] Further quantitative insight into TR coupling and any small anisotropies in the cage potential arising from crystal-field distortions associated with the order-disorder transition at 260 K will be sought from further detailed INS measurements at higher energy transfer and with higher resolution.

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