Neutron spectroscopy of $C_{60}H_x$ quenched under hydrogen pressure

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Abstract

Inelastic neutron scattering spectra were measured at 85 K for a hydrofullerite quenched to this temperature after a synthesis at 620 K under a hydrogen pressure of 0.6 GPa, and for the same sample annealed at 300 K. The quenched sample consisted of $C_{60}H_{24}$ molecules and of interstitial molecular hydrogen (1.4 H_2 molecules per unit C_{60}). The interstitial H_2 left the sample during the annealing at 300 K. The intramolecular and intermolecular $C_{60}H_{24}$ vibrations and H_2 rotations are discussed based on the measured spectra.

Keywords: Hydrogen; Fullerenes; Vibrational spectroscopy

To prepare the hydrofullerite, C_{60} of 99.99% purity was exposed to a hydrogen pressure of 0.6 GPa at 620 K for 24 h. Then the sample was cooled to 80 K, decompressed and stored in liquid nitrogen. Part of this sample was used to determine the crystal structure (X-ray and neutron diffraction at 85 K) and the H content (hot extraction and Rutherford back-scattering of He ions) of the as-prepared hydrofullerite and of that annealed at 300 K for 35 h (referred to as the "quenched" and "annealed" samples hereafter). At 300 K the quenched $C_{60}H_x$ released hydrogen. This amounted to $\Delta x = 2.8$, leaving the H content of the sample reduced from $x \approx 27$ to $x = 24$. The $C_{60}H_x$ units of

both the quenched and the annealed hydrofullerites had a BCC lattice with $a = 12.00$ and 11.72 Å, respectively. The latter value is close to the earlier X-ray data for $C_{60}H_{36}$ [1].

The INS measurements were carried out at 85 K using the time-of-flight spectrometer KDSOG-M at the IBR-2 pulsed reactor in Dubna [2]. Aftersubtraction of the background, the data were transformed to the generalized vibrational density of states $G(\omega)$. Fig. 1 shows the $G(\omega)$ spectra of the 0.62 g sample of hydrofullerite in the quenched and annealed state together with the spectrum of a 3.2 g sample of pure C_{60} measured recently at 77 K with the same spectrometer [3].

The spectra of the annealed sample and pure C_{60} are very similar in the range 0–8 meV of intermolecular vibrations. This indicates that H atoms in the annealed $C_{60}H_x$ sample are chemically bound to the C_{60} cages. An estimation from the areas under the $G(\omega)$ curves for the annealed $C_{60}H_x$

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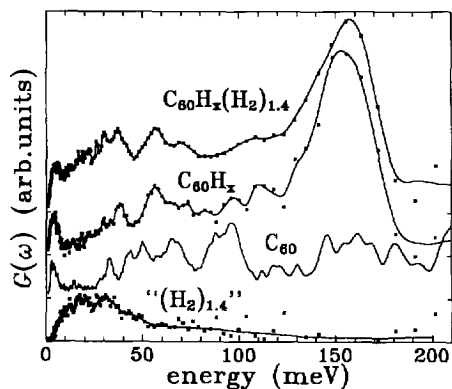
Fig. 1. Generalized vibrational density of states for the quenched $C_{60}H_{24}(H_2)_{1.4}$ and annealed $C_{60}H_{24}$ samples measured at 85 K. The difference of these spectra, "$(H_2)_{1.4}$", represents vibrations of interstitial H_2 molecules in the quenched hydrofullerite. Also shown is the spectrum of pure C_{60} at 77 K [3].
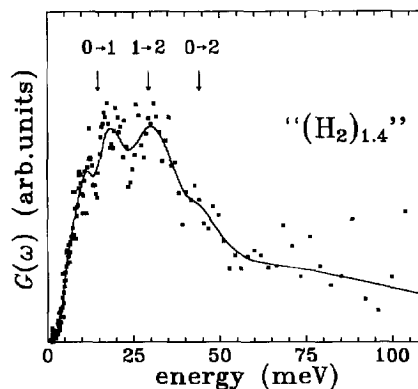
Fig. 2. The difference spectrum "$(H_2)_{1.4}$" scaled up from Fig 1. The arrows show the transition energies between the rotational states of a free H_2 molecule with the indicated rotational quantum numbers.

and pure C_{60} in the region below 8 meV gave a correct value of $x = 24$.

In the range 25–110 meV of radial intramolecular modes in pure C_{60}, the spectra of the hydrofullerites exhibit peaks at 30, 38, 56 and 70 meV. Compared to pure C_{60}, the peaks are drastically shifted in energy and have different relative intensities. This means that hydrogen strongly affects the intramolecular C–C interaction. At $\omega > 110$ meV, one large broad peak centred at $\omega \approx 55$ meV is observed in the spectra of both $C_{60}H_x$ samples. Following the spectrum interpretation for hydrogenated amorphous carbon [4], we attribute this peak to C–H bending modes.

The difference between the spectra of the quenched and annealed hydrofullerites (Fig. 1, bottom, and Fig. 2) is quite unlike the other three spectra. The difference spectrum is evidently due to the "excess" 2.8 H atoms per C_{60} in the quenched sample. The observed dissimilarity together with the lattice contraction on annealing suggest that these H atoms are not chemically bound to the C_{60} cages and occupy interstitial positions in the BCC $C_{60}H_{24}$ lattice.

As seen from Fig. 2, the peaks in the difference spectrum at 12, 18, 30 and 45 meV can be reasonably well explained within the rotator model of

molecular hydrogen [5]. The model-energy states are given by $E(J) = BJ(J + 1)$, where $B = 7.35$ meV and J is the rotational quantum number. The peaks at 30 and 45 meV agree with the $(1 \rightarrow 2)$ and $(0 \rightarrow 2)$ transitions. The latter has low intensity because it corresponds to the transition between two rotational states in parahydrogen molecules which are coherent neutron scatterers [5]. The two peaks at 12 and 18 meV are assumed to result from splitting of the $(0 \rightarrow 1)$ peak at 14.7 meV due to interaction between H_2 and nearby $C_{60}H_{24}$ molecules. A similar splitting of the $(0 \rightarrow 1)$ peak to a pair of peaks at 12.5 and 16 meV was observed earlier in the INS spectrum of molecular H_2 trapped in amorphous carbon [4].

Acknowledgements

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