

HYDROGEN IN THE VIBRATIONAL SPECTRA OF HIGH-PRESSURE HYDROFULLERITE

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New hydrofullerite was synthesized from C_{60} fullerite treated in hydrogen atmosphere at 30 Kbar and 620 K during 24 hours. The inelastic neutron scattering (INS) spectra of the quenched as-prepared and annealed samples showed that the as-prepared hydrofullerite consisted of $C_{60}H_n$ ($n \approx 32$) molecules with molecular hydrogen dissolved onto interstitial sites. The INS and optic spectra of annealed hydrofullerite show features which are characteristic of polymeric fullerites or of endohedrally trapped H_2 molecules. The low-energy behavior of the INS spectra gives a hint that some part of hydrogen can be trapped in the atomic form.

1. INTRODUCTION

There are several works [1-4] which dealt with the properties of the C_{60} fullerite hydrogenated under high hydrogen pressure. In the first study [1-3], C_{60} was treated at 620 K under a hydrogen gas pressure of $P_{H_2} = 6$ Kbar for 24 h, then quenched to liquid nitrogen and recovered to normal pressure. The quenched product consisted of $C_{60}H_x$ molecules, $x \approx 24$, and H_2 molecules dissolved on the interstitial sites of the $C_{60}H_x$ sublattice in a molar ratio of $H_2/C_{60} \approx 1.4$. The $C_{60}H_x$ molecules were stable under normal conditions whereas interstitial hydrogen left the sample upon annealing at 300 K. Interstitial hydrogen contributed to the

inelastic neutron scattering (INS) spectrum of the quenched product several peaks close to the energies of the rotational transitions of a free H₂ molecule.

For a further study, a C₆₀ hydrofullerite was prepared and quenched under a hydrogen pressure of 30 Kbar. The first view of the INS spectra was presented in Ref. 4. This work deals mainly with the spectral features contributed from hydrogen chemically unbound to C₆₀. Some conclusions from the INS data analysis are supported by the optic measurements.

2. EXPERIMENTAL

Two hydrofullerite samples were used in this work. Sample I was synthesized at $P_{\text{H}_2} = 30$ Kbar and $T = 620$ K during 24 h, quenched to 80 K and recovered to $P = 1$ atm. The INS spectra were measured at 24 K in the range of the energy transfer 2 to 500 meV using spectrometer TFXA at ISIS (RAL, UK). The sample was studied first in the as-prepared (quenched) state, then in the state after annealing for 3 hours at 300 K in vacuum. Later, the annealed sample was studied at the eVS spectrometer at ISIS, and a value of $x = \text{H}/\text{C}_{60} = 31.6 \pm 1.0$ was obtained for its chemical composition. Sample II was prepared in a similar way, but it was recovered to $P = 1$ atm after cooling to 300 K. The elemental analysis on a part of sample II showed $x \approx 37.5$. The optic spectrum was measured on a finely ground and compacted C₆₀H_x : KBr mixture using FTIR spectrometer.

3. RESULTS AND DISCUSSION

The INS spectra from both states of sample I (curves 1 and 2 in Figure 1) are very similar at high energies. A large peak at 156 meV (split to four lines at 147.5, 154.0, 160.0 and 166.5 meV) and another marked peak at 357.5 meV were attributed, respectively, to bending and stretching C-H modes [4]. The peak at 312 meV is twice in energy of the C-H bending mode therefore it was assigned to its first overtone.

The difference between these two spectra (curve 3 in Figure 1) shares none of the features in the original curves therefore it was assumed to represent the INS spectrum from molecular hydrogen interstitially dissolved in quenched hydrofullerite [1]. The present difference spectrum shows several features at energies below 50 meV (scaled in the inset in Figure 1) which differ from those observed on hydrofullerite after the

6-Kbar synthesis. Two peaks observed at about 15.3 and 29.7 meV (marked with arrows in Figure 1) are close to energies of the first transitions between the 3-D rotational states of a free hydrogen molecule, $E_{0 \rightarrow 1} = 14.7$ and $E_{1 \rightarrow 2} = 29.4$ meV [5]. The nature of the peak at 8.9 meV is not so evident. The energy of the peak is rather close to the energy of the first transition between the 2-D rotational states of molecular hydrogen, $E_{0 \rightarrow 1} = 7.35$ meV [5]. On the other hand, this peak can also be due to splitting of the $0 \rightarrow 1$ transition between the 3-D rotational states affected by the crystal environment of the $C_{60}H_{-32}$ molecules. This indicates that a part of the H_2 molecules occupy interstitial sites in the $C_{60}H_{-32}$ crystal lattice which strongly affects the rotational behavior of hydrogen.

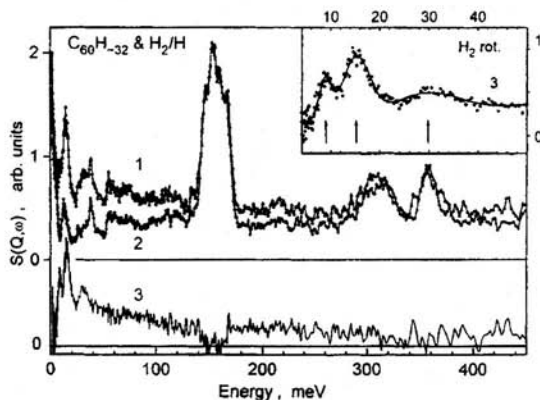


FIGURE 1 The INS spectra of hydrofullerite synthesized at 30 Kbar and quenched to 80 K (curve 1), then annealed at 300 K (curve 2), both at 24 K. The difference between the two spectra (curve 3) represents the vibrations of interstitial H_2 molecules in the quenched hydrofullerite (shown in the inset on a larger scale). The solid curve in the inset is a three-Gaussian fit.

The INS spectrum from annealed $C_{60}H_{-32}$ is compared in Figure 2 to that earlier measured on polymeric C_{60} [6] (curves 2 and 3, respectively). This comparison highlights a remarkable peak observed on $C_{60}H_{-32}$ around 13 meV. It has no analogy in the spectrum of the 6-Kbar hydrofullerite [1-3]. Proximity of the energy of the peak to that of the polymeric vibrational band justifies an assumption of polymerization of the 30-Kbar hydrofullerites. Alternatively, we note that another peak can be marked in curve 2 at an energy of 25.5 meV (arrows in Figure 2), which is approximately twice of 13 meV. This correspondence is very similar to that discussed above for the energies of the 3-D rotational transitions in

interstitial hydrogen. As interstitial hydrogen rapidly leaves the sample at 300 K, an alternative explanation of these features is molecular hydrogen trapped endohedrally in the $C_{60}H_{-32}$ molecules. The optic spectrum of sample II (Figure 3) was measured in order to test the latter hypothesis. Numerous spectral features below 1600 cm^{-1} (200 meV) as well as a prominent split band at 2800 to 2900 cm^{-1} due to stretching C-H modes are not discussed here in detail. But there was a small peak at 4728 cm^{-1} (586 meV, see the inset in Figure 3) whose energy can be compared to the vibrational energy of a free H_2 molecule, 540 meV [5]. Occurrence of the H_2 vibrational peak is consistent with the peaks of the H_2 rotational transitions, interaction with the wall of the C_{60} cage being responsible for the IR activity of the vibrational mode and for the energy shift.

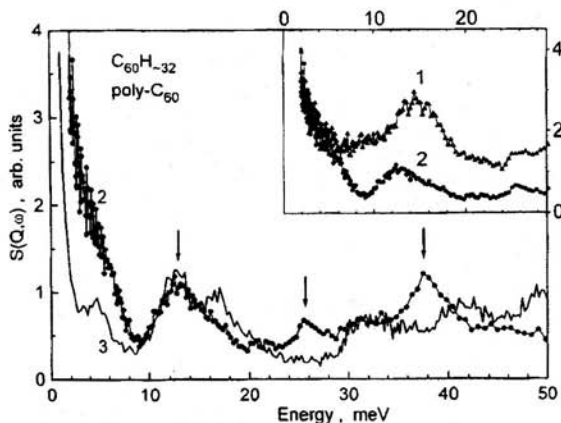


FIGURE 2 The INS spectra of quenched hydrofullerite (curve 1), annealed hydrofullerite (curve 2), and polymeric C_{60} [6] (curve 3).

For the INS spectra of annealed $C_{60}H_{-32}$, we calculated the contribution from the multiphonon neutron scattering and the one-phonon spectrum (Figure 4). An iterative procedure of this calculation using multiconvolution of the one-phonon spectrum was described earlier [7]. The experimental spectrum in the range to 200 meV and in an interval around the C-H stretching mode, 340 to 380 meV, was taken at the first step as a starting spectrum. In this case, the calculated multiphonon contribution was about twice as large as the experimental intensities over 200 meV. This indicated that the one-phonon part of the spectrum was overestimated. Several attempts showed that a good agreement could be

obtained when intensities at low energies, $E < 8$ meV, were approximated with a Debye law, $G(\omega) \sim \omega^2$, as shown in Figure 4.

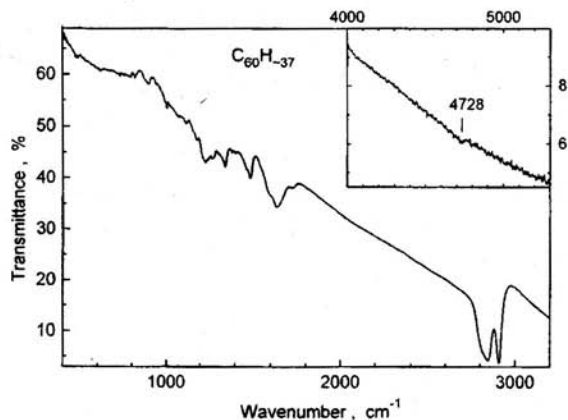


FIGURE 3 The FTIR spectrum of hydrofullerite synthesized at 30 Kbar without high-pressure quenching (sample II). The inset shows the spectral feature at 4728 cm^{-1} (586 meV).

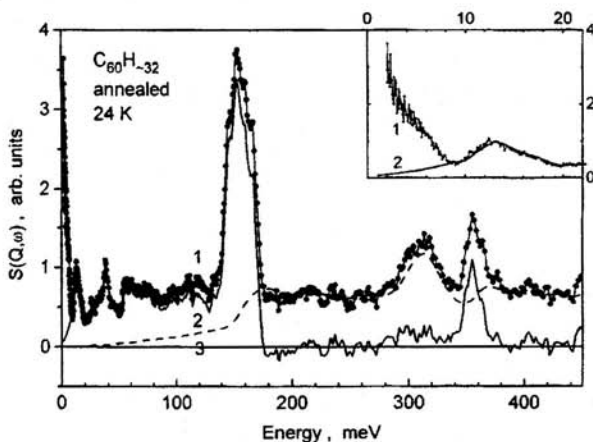


FIGURE 4 The experimental INS spectrum of the annealed hydrofullerite (curve 1), the calculated one-phonon spectrum (curve 2) and the calculated contribution from the multiphonon neutron scattering. The one-phonon spectrum was approximated with the Debye law, $G(\omega) \sim \omega^2$, in the range $E < 8$ meV.

A question arose therefore: what was the nature of the excess intensity at $E < 8$ meV? This excess could not be related to the C_{60} vibrational motion due to small scattering cross-section of carbon atoms. This could not be

due to bound hydrogen atoms because these atoms would also contribute to the multiphonon scattering. Hence, this excess should be due to hydrogen unbound to the C_{60} molecules. Molecular hydrogen has only a coherent neutron scattering cross-section at the energies less than 14.7 meV (the para – ortho transition energy in hydrogen) therefore it also cannot be responsible for the excess intensity. We conclude therefore that the excess intensity in the low-energy spectral range is an indication of atomic hydrogen trapped endohedrally in the $C_{60}H_x$ molecules. This assumption is reasonable if we assume that hydrogen molecules dissociate in the process of trapping into the C_{60} cage.

4. CONCLUSIONS

The vibrational spectra of hydrofullerites synthesized under high pressure are indicative of various phenomena inherent only for thus prepared compounds. First, this method results in $C_{60}H_x$ compounds with interstitially dissolved molecular hydrogen. Second, either polymerization or endohedral molecular hydrogen can explain some of the spectral features of high-pressure hydrofullerites. Finally, the low-energy behavior of the INS spectra is a hint that some part of hydrogen is trapped in the atomic form.

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