Neutron spectroscopy of C_{60} fullerite hydrogenated under high pressure; evidence for interstitial molecular hydrogen

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Abstract. Inelastic neutron scattering spectra of a hydrofullerite quenched after synthesis at 620 K under a hydrogen pressure of 0.6 GPa, and of the same sample after annealing at 300 K for 35 h, which reduced the hydrogen content by 1.4 H_2 molecules per C_{60} unit, were measured at 85 K. The quenched sample is shown to consist of $C_{60}H_x$ molecules with $x \approx 24$ and of interstitial molecular hydrogen. The interstitial molecular hydrogen left the sample during annealing at room temperature, whereas the $C_{60}H_x$ molecules were stable at this temperature. The intramolecular and intermolecular vibrations of $C_{60}H_x$ and H_2 in the fullerite are discussed in view of the measured spectra.

1. Introduction

Various chemical reaction paths have been worked out for synthesizing $C_{60}H_x$ compounds with x between 2 and 36. The methods were based either on hydrogen-atom transfer to C_{60} from other reagents in solutions [1–4] or on catalytic hydrogen absorption from the hydrogen gas phase using iodoethane as the hydrogen radical promoter [5]. A thorough discussion of the methods of chemical hydrogenation and of their products was given by Hirsch [6].

Exposure of C_{60} to molecular hydrogen at a pressure of $P_{H_2} = 0.014$ GPa and 300 K [7] yielded solid solutions with low hydrogen concentrations only, whereas syntheses at pressures P_{H_2} between 0.05 and 0.085 GPa and $T \simeq 600$ K resulted in $C_{60}H_x$ compounds with x between 2 and 18 [8]. The hydrogenated fullerites were characterized by means of electron, x-ray and neutron diffraction, nuclear magnetic resonance, infrared spectroscopy and laser desorption mass spectrometry [5–10].

This paper presents the results of an inelastic neutron scattering (INS) study of C_{60} hydrofullerites synthesized under a hydrogen pressure of 0.6 GPa.

2. Experimental details

The starting material, C_{60} of 99.99 wt% purity, was prepared as described previously [11, 12], sublimated in a vacuum better than 10^{-5} Torr at 870 K, and compacted into pellets

of 12 mm diameter and 1 mm thickness. Each pellet was placed into a copper capsule, covered with a disc of 0.01 mm thick Pd foil, and then annealed in vacuum at 620 K for 2 h to eliminate contamination with ambient gases, which could have dissolved during compacting. Then the space remaining in the capsule was filled with AlH_3 and the capsule was tightly plugged with a copper lid using gallium as a solder. Since both Cu and Ga are largely impermeable to hydrogen, the encapsulation described effectively prevents hydrogen losses during the subsequent treatment.

The assembled capsules were pressurized to 0.6 ± 0.1 GPa in a toroid-type high-pressure chamber and maintained at 620 ± 10 K for 24 h. The AlH_3 decomposes above 400 K [13], and the evolved hydrogen reacted with the fullerite after permeating through the Pd foil which isolated the fullerite from the chemically active Al. The amount of hydrogen gas inside the capsule corresponded to a ratio of $H/C_{60} \simeq 90$ and therefore hydrogen was always in excess during the experiments. The pressure of 0.6 GPa was chosen to avoid polymerization of the C_{60}, which is known to take place above 0.7 GPa [11]. At the end of the hydrogenation, the high-pressure chamber was cooled to about 80 K and disassembled under liquid nitrogen. Cooling from 620 K to 300 K took about 2 min, and further cooling from 300 K to 80 K about 1 h. The hydrofullerite produced in this way was stored in liquid N_2 until the measurements were performed.

The hydrofullerite was studied as prepared and after annealing at 300 K for 35 h. These two forms will henceforth be designated as 'quenched' and 'annealed', respectively. One pellet of the quenched sample was warmed to room temperature in an evacuated calibrated volume in order to estimate the thermal stability of the hydrofullerite and the effect of annealing on its hydrogen content. Hydrogen evolution at 300 K terminated after about 45 min. The evolved hydrogen amounted to a molar ratio of H_2 to C_{60} of 1.4 ± 0.1. The quenched sample was a light-brown solid. The hydrogen loss during annealing did not change the colour of the sample.

The hydrogen content of the annealed $C_{60}H_x$ sample was estimated from Rutherford backscattering of He ions [14]. The measurement showed that the hydrogen distribution over the 0.9 μm thick near-surface layer was uniform, the hydrogen content being $x = 23.5\pm2.5$. Adding the amount of hydrogen evolved at 300 K yields $x = 26.3\pm2.5$ for the composition of the quenched sample. This result is consistent with the x-values between 2 and 18 obtained previously for $C_{60}H_x$ synthesized at a lower hydrogen pressure of $P = 0.065$ GPa at $T = 623$ K [8].

The pure C_{60} fullerite has a simple cubic lattice at ambient pressure and temperatures below 255 K [15]. The lattice structure was found to change upon hydrogenation: according to neutron and x-ray diffraction data [16], at 85 K the $C_{60}H_x$ units of both the quenched and the annealed hydrofullerites form a bcc lattice with the lattice parameters of 12.00 and 11.72 Å, respectively. The colour, crystal structure and lattice parameter of the annealed sample agree with the previous data for $C_{60}H_{36}$ prepared by a chemical procedure [9]. The lattice contraction observed upon annealing at 300 K indicates that the released hydrogen stems from sites within the lattice rather than from voids.

The sample studied by INS consisted of several pellets and weighed 0.62 g. The INS measurements were carried out at 85 K using the inverted-geometry time-of-flight spectrometer KDSOG-M installed at the IBR-2 pulsed reactor in Dubna, Russia [17]. The KDSOG-M spectrometer has a high neutron flux at the sample position and provides a medium resolution $\Delta\omega/\omega = 4$–6% in the range of energy transfer from 1 to 60 meV and $\Delta\omega/\omega = 6$–10% at higher energies from 60 to 200 meV. The quenched sample was first measured as prepared, then annealed at 300 K for 35 h and measured again. The background was determined in a separate empty-can measurement and subtracted from the
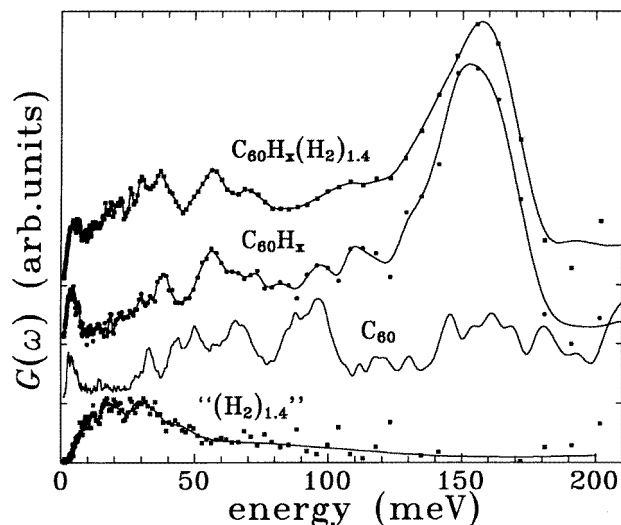
Figure 1. The generalized vibrational density of states of the quenched C$_{60}$H$_x$(H$_2$)$_{1.4}$ and annealed C$_{60}$H$_x$ samples with $x \approx 24$ measured at 85 K. The difference '(H$_2$)$_{1.4}$' between these two spectra represents the vibrations of interstitial molecular hydrogen in the quenched hydrofullerite. The spectrum of pure C$_{60}$ measured at 77 K [18] is also shown.

data obtained for the fullerites. The INS data were transformed to the generalized vibrational density of states $G(\omega)$ (figure 1), which is the standard data representation at the KDSOG-M spectrometer.

3. Vibrational spectra of hydrofullerites

The two upper curves in figure 1 represent the $G(\omega)$ spectra of the 0.62 g sample of hydrogenated C$_{60}$ in the quenched and annealed state measured at 85 K. The curve labelled 'C$_{60}$' shows the spectrum of a 3.2 g sample of pure C$_{60}$ measured recently at 77 K with the same spectrometer [18]. All three spectra are normalized to the same total incident neutron flux.

In the INS spectrum of pure C$_{60}$, three energy intervals characteristic of different vibrational modes may be distinguished: 0 to 8 meV for the intermolecular vibrations, 25 to 110 meV for the radial intramolecular modes, and 110 to 220 meV for the tangential intramolecular modes [18–25]. The energy regions of the intermolecular and radial intramolecular vibrations in the hydrofullerites studied appear to be largely the same as in pure C$_{60}$.

3.1. Intermolecular vibrations

Renker *et al* [19–21] have shown that the intermolecular librational modes in the low-temperature simple cubic phase of pure C$_{60}$ give rise to a strong peak at around 2.6 meV and to two peaks at 3.5 and 5.0 meV, which overlap with peaks at 4 and 6 meV arising from the transverse and longitudinal translational phonon modes. The low-energy part of the $G(\omega)$ spectrum of C$_{60}$ [18] shown in figure 2 exhibits a strong peak at 2.8 meV, a split peak centred at around 4.3 meV and another peak at 6.0 meV, in agreement with [19–21].
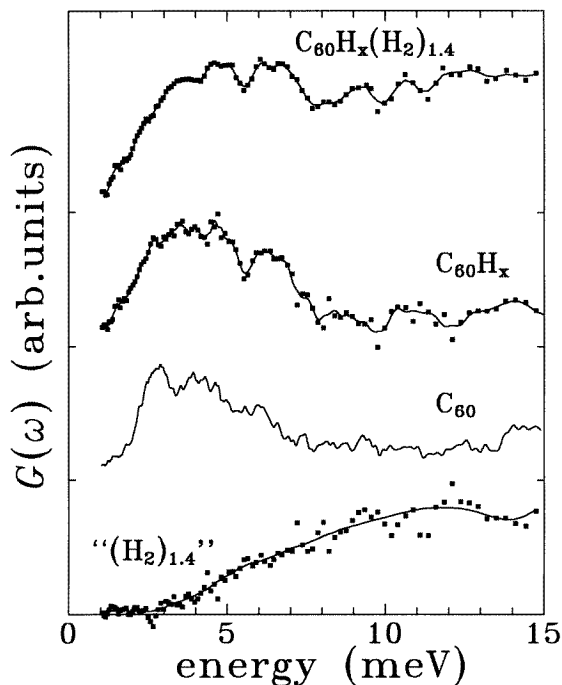
Figure 2. The same as figure 1, but showing only the energy range up to 15 meV.

The spectra of both hydrogenated C_{60} samples (figure 2) exhibit peaks at 2.6, 3.5 and about 4.8 and 6.5 meV. Those at 2.6 meV and 6.5 meV are close to the librational and translational peaks of C_{60}. This suggests that they are also due to singularities of the librational and translational phonon dispersion curves. By analogy with the C_{60} spectrum, one can also assume that the peak at 3.5 meV is librational, whereas the one at 4.8 meV arises from both librational and translational vibrations.

It has been shown [6] that hydrogen uptake distorts the C_{60} cages; it also changes the electronic configuration and transforms the simple cubic crystal lattice to a bcc one, which brings about a decrease in the nearest-neighbour coordination number from 12 to 8. The observed similarity of the peak positions in the intermolecular part of the C_{60} and $C_{60}H_x$ spectra must therefore be considered as the result of these various effects nearly compensating each other.

The distribution of the scattering intensity over the 0 to 8 meV range is very similar for pure C_{60} and for the annealed $C_{60}H_x$ sample, but different for the quenched sample, especially above about 5 meV. As a consequence of the large total neutron scattering cross-section of hydrogen compared to that of carbon ($\sigma_{total}^{H} = 82.02$ b, $\sigma_{total}^{C} = 5.551$ b [26]), the INS spectra of the hydrofullerites mainly represent scattering on hydrogen atoms. In the rigid-body approximation, the partial atomic generalized vibrational densities of states for carbon and bound hydrogen atoms, $G_C(\omega)$ and $G_H(\omega)$, are proportional to each other for the translational modes because the corresponding phonon eigenvectors for the C and H atoms are the same. For the librational modes, however, the shapes of $G_C(\omega)$ and $G_H(\omega)$ may differ. In particular, the contribution of the librational modes to $G_H(\omega)$ may be higher than that to $G_C(\omega)$ because of the larger librational amplitude of H atoms, which are further

away from the centre of the molecule than the corresponding C atoms.

The similarity in the intermolecular part of the vibrational spectra of the annealed C$_{60}$H$_x$ sample and of pure C$_{60}$ thus indicates that most hydrogen atoms in the annealed sample are tightly, i.e., chemically, bound to C$_{60}$ molecules. A rough estimate of the hydrogen content of the annealed C$_{60}$H$_x$ sample can be obtained by comparing the areas under the $G(\omega)$ curves in the region below 8 meV for C$_{60}$H$_x$ and pure C$_{60}$, provided that the spectra are normalized to the incident neutron flux, the sample weight, the molecular mass, the moment of inertia, and the neutron scattering cross-section. Under the assumption of exohedral hydrogen addition [6], this comparison yields a value of $x \approx 24$ for the annealed sample, which agrees with the Rutherford backscattering data. This corroborates the suggested interpretation of its spectrum.

The quenched sample contains about 12% more hydrogen than the annealed one, which results in a noticeable increase and redistribution of the scattering intensity. The latter suggests that the additional hydrogen in the quenched sample interacts much less strongly with the C$_{60}$H$_x$ units than the hydrogen still present in the annealed specimen. This observation will be discussed in section 3.3 in more detail.

3.2. Intramolecular vibrations

In the range of radial intramolecular modes in pure C$_{60}$, i.e., between 25 and 110 meV, the spectra of the hydrofullerites exhibit four peaks at 30, 38, 56 and 70 meV, as well as some features at around 105 meV (figure 1). Compared to those for pure C$_{60}$, the positions and relative intensities of the peaks are quite different. Nevertheless, the peaks observed for the hydrofullerites should also arise from radial intramolecular modes, since no other vibrations of C$_{60}$H$_x$ molecules can be expected in this energy range.

The difference between the spectra of the radial modes in pure fullerite and in hydrofullerites shows that the intramolecular C–C interaction is strongly changed by the hydrogenation. Together with the only slight variation of the intermolecular vibrations, this suggests that the hydrogen atoms are tightly bound in the C$_{60}$H$_x$ molecules, thereby significantly affecting the C–C bonds.

For $\omega > 110$ meV, the INS spectra of both hydrofullerites show a large, broad peak centred at $\omega \approx 155$ meV, with a shoulder on the lower-energy side and a full width at half-maximum of 35 meV. Previously [27, 28], pronounced peaks at around 150 and 370 meV have been found in the INS spectra of hydrogenated amorphous carbon and have been assigned to the C–H bending and stretching modes, respectively. Similar modes should also occur in hydrofullerites. We therefore attribute the peak at 155 meV to C–H bending modes. The tangential intramolecular modes characteristic of pure C$_{60}$ for $\omega > 110$ meV (figure 1) are presumably hidden in hydrofullerites under the broad peak of the C–H bending modes. The peak of the C–H stretching modes expected at energies of the order of 370 meV could not be studied in the present work due to the insufficient statistics of the spectrum in this energy region.

3.3. Vibrations of interstitial hydrogen

The difference between the INS spectra of the quenched and annealed hydrofullerites is shown at the bottom of figures 1 and 2, and on a larger scale in figure 3. This difference spectrum is attributed to neutron scattering on the 'excess' hydrogen atoms in the quenched sample, i.e., on the hydrogen that could be removed by annealing at room temperature. The shapes of the difference spectrum and of the spectra of the fullerites themselves are quite
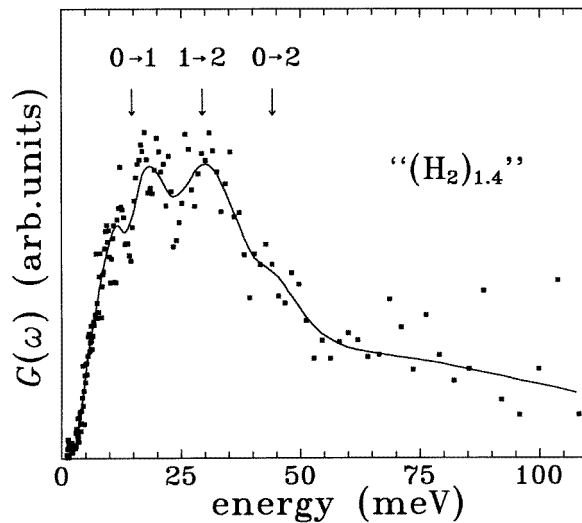
Figure 3. The difference spectrum '$(H_2)_{1.4}$' from figure 1 presented on a larger scale. The arrows indicate the energies of the transitions between the rotational states of a free hydrogen molecule with the given rotational quantum numbers.

unlike. In particular, the difference spectrum exhibits a very low intensity in the range of the intermolecular vibrations for $\omega < 4$ meV (figure 2) and in the range of the C–H bending modes at around 155 meV (figure 1). This means that the 'excess' hydrogen is not chemically bound to the $C_{60}H_x$ molecules and therefore must occupy interstitial positions in the bcc hydrofullerite lattice.

Several reasons lead to the conclusion that the interstitial hydrogen in the quenched sample is present in the form of H_2 molecules.

(i) First, interstitial hydrogen in the atomic form has never been observed in molecular crystals, and hydrofullerites have no specific features suggesting an exception.

(ii) Second, the volume decrease upon annealing of the quenched sample is about 42 $\mathring{A}^3$ per H_2 molecule evolved [16]. This is close to 38.044 $\mathring{A}^3$ per H_2 molecule, the specific volume of solid hcp molecular hydrogen at 4.5 K [29].

(iii) Third, the main features of the difference spectrum can be reasonably well explained by the rotator model [30] describing the rotational spectra of gaseous, liquid and hcp solid molecular H_2.

According to the model mentioned in reason (iii), the rotational energy states are given by $E_K = BK(K + 1)$, where $B = 7.35$ meV and K is the rotational quantum number. Even values of K are possible only for a total nuclear spin $I = 0$ (para-hydrogen), and odd values of K only for $I = 1$ (ortho-hydrogen). Transitions between rotational states with the same parity of the rotational wavefunction are possible only for unchanged I (ortho–ortho and para–para transitions), and transitions between states with different parity may occur only when I changes (ortho–para and para–ortho transitions) [30]. The energies of the transitions between the states with $K = 0$, 1 and 2 are indicated by arrows in figure 3.

For $\omega < 50$ meV, the difference spectrum involves many experimental points, and various smoothing procedures reveal four peaks at the same energies of 12, 18, 30 and around

45 meV. The latter two values agree well with $\Delta E_{1\to2} = 29.4$ meV and $\Delta E_{0\to2} = 44.1$ meV for molecular hydrogen. The peak at 45 meV has low intensity because it corresponds to the transition between two rotational states in para-hydrogen molecules which are coherent neutron scatterers [30]. The average energy of the two lower peaks is 15 meV, which is close to the value $\Delta E_{0\to1} = 14.7$ meV for the para–ortho transition in free H$_2$ molecules. These two peaks at 12 and 18 meV are assumed to result from a splitting of the $(0 \to 1)$ peak due to the interaction between H$_2$ and nearby C$_{60}$H$_x$ molecules. A similar splitting of the $(0 \to 1)$ peak into 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 [27, 28].

One can expect that interstitial hydrogen in the quenched C$_{60}$H$_x$ sample was in thermal equilibrium during the INS measurement at 85 K because the sample had been rather slowly cooled under pressure from 300 to 80 K and then kept in liquid N$_2$ for about a week before the measurement. At $T = 85$ K, the equilibrium ortho/para population ratio is close to $3\exp(-\Delta E_{0\to1}/kT) \approx 0.4$, i.e., about 70% of the hydrogen molecules are in the para state and about 30% in the ortho state. The relative intensities of the peaks in the difference spectrum are consistent with a predominant occupation of the ground para state.

4. Conclusions

The reaction of hydrogen with solid C$_{60}$ at $P_{H_2} = 0.6$ GPa and $T = 620$ K yields a hydrofullerite with a H/C$_{60}$ ratio of $x \approx 27$. The major part of the hydrogen, corresponding to $x \approx 24$, is chemically bound to C$_{60}$ molecules, whereas a minor part, corresponding to $x \approx 2.8$, is dissolved interstitially as H$_2$ molecules in the bcc lattice of C$_{60}$H$_x$. The interstitial hydrogen is only weakly fixed in the lattice and escapes at 300 K in the course of hours, causing the lattice to contract.

The INS spectra of C$_{60}$ and C$_{60}$H$_x$ are very similar in the range of the intermolecular vibrations, but differ considerably in the range of the intramolecular ones. The C–H bending modes in hydrofullerites give rise to a strong, broad peak at 155 meV.

The spectral contribution of the interstitial H$_2$ molecules arises from their rotational modes, which are modified by the surrounding C$_{60}$H$_x$ units.

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