

VIBRATIONAL SPECTRA OF C₆₀ HYDROFULLERITE PREPARED UNDER HIGH HYDROGEN PRESSURE

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C₆₀ hydrofullerite prepared at a hydrogen pressure of 6 kbar, T = 620 K over 24 hours and quenched to 80 K, has a bcc lattice of C₆₀H_x molecules, x = 24, where the interstitial H₂ molecules are dissolved in the ratio 1.4 mol.H₂/mol.C₆₀H_x. Interstitial hydrogen leaves the sample on annealing at 300 K. Vibrational spectra measured at 85 K in quenched and annealed hydrofullerite show a marked change in the intramolecular modes compared to pure C₆₀. Interstitial hydrogen contributes to the rotational modes of the H₂ molecule.

INTRODUCTION

A set of C₆₀H_x compounds, 2 ≤ x ≤ 36, was prepared using various chemical reactions.¹ The direct treatment of C₆₀ in a pure hydrogen gas atmosphere at P_{H₂} = 140 atm and T > 300 K resulted in an unstable low-concentration solid solution,² but a compound complex, C₆₀H_x with 2 ≤ x ≤ 18, was produced when pressure and temperature were increased to 50 ≤ P_{H₂} ≤ 850 atm. and T > 600 K.³ The properties of hydrofullerite properties were subjected to a brief study.¹

In this paper, we report on a C₆₀ hydrofullerite which was prepared and quenched to 80 K under a hydrogen pressure of 6 kbar, and its properties studied using several techniques, including inelastic neutron scattering (INS).

SYNTHESIS AND CHARACTERIZATION OF HYDROFULLERITE

Powder C_{60} of 99.99 wt. % purity was prepared as usual,⁴ sublimated in a vacuum and compacted to pellets. The pellets were encapsulated in copper ampoules together with AlH_3 pellets (a source of hydrogen on heating), and then treated at $T = (620 \pm 10)$ K and $P = (6 \pm 1)$ kbar for 24 h in a toroid-type high-pressure device. By the end of treatment, the device was cooled to 80 K, the sample had recovered to $P = 0$ and was stored in liquid N_2 until measurements were made. The latter procedure is further referred to as quenching under pressure.⁵

Hydrofullerite was studied as prepared (quenched) and after annealing at 300 K. A portion of the quenched samples was heated to 300 K in an evacuated calibrated volume. We found that H_2 evolution at 300 K terminated in 45 min, and the hydrogen thus evolved amounted to a molar ratio H_2/C_{60} of 1.4 ± 0.1 .

The hydrogen content of the annealed $C_{60}H_x$ sample was determined using the elastic recoil detection (ERD) method, using an electrostatic accelerator EG-5 at JINR.⁶ The $^4He^+$ ion beam of 2429 KeV energy was incident on the sample surface at an angle of 15° . The proton emission spectrum was registered at an angle of 30° with respect to the $^4He^+$ beam. The $^4He^+$ ions scattered by the carbon atoms were suppressed with an Al filter. The energy of the emitted protons depends on the depth of the H atoms within the sample, being maximum for the surface protons. The proton output is proportional to the hydrogen content.

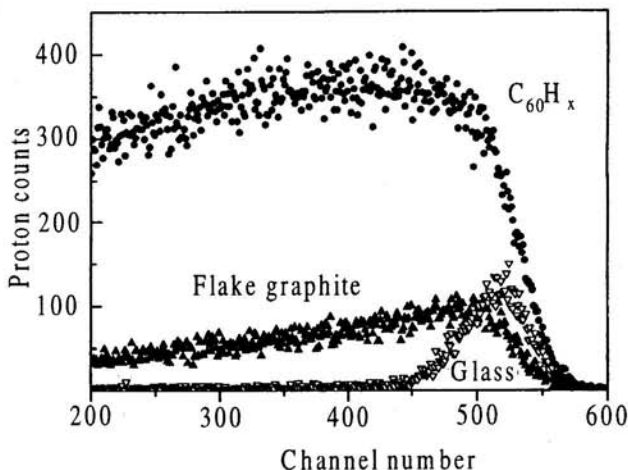


Figure 1 Proton ERD spectra for glass, flake graphite and annealed $C_{60}H_x$.

Figure 1 shows the ERD spectra for annealed $C_{60}H_x$ and for reference samples measured in the same experiment. The reference samples were glass and flake graphite. A small peak in the spectrum of the glass is indicative of a surface hydrogen-containing

film which is usual for samples in a vacuum of 10^{-6} Torr, and the portion of the spectrum to the left of the peak shows the background. The annealed $C_{60}H_x$ sample had a uniform composition, $x = 23.5 \pm 2.5$, through the depth of 900 nm accessible to ERD. The flake graphite contained about 3 at. % H. To control the content of carbon and heavier atoms, we also measured the spectrum of the $^4\text{He}^+$ ions scattered at an angle of 135° and found about 1 at. % oxygen atoms in $C_{60}H_x$ and graphite. The oxygen could be derived from H_2O absorption from the ambient atmosphere during sample preparation for the ERD measurements; this error is taken into account in the above x value. The amount of hydrogen evolved at 300 K is added; the hydrogen content in the quenched sample is $x = 26.3 \pm 2.5$.

A structural study at 85 K demonstrated that $C_{60}H_x$ molecules formed a *bcc* lattice for both hydrofullerite states, with lattice parameters of 12.00 Å and 11.72 Å for the quenched and annealed states, respectively.

VIBRATIONAL SPECTRA OF HYDROFULLERITE

INS spectra were measured at 85 K using a spectrometer, KDSOG-M, installed at the IBR-2 pulsed reactor (JINR). The first experiment spectrum was on the quenched state, the other was after annealing at 300 K for 35 h, the background spectrum was also measured. The INS data were transformed to the generalized vibrational density of states, $G(\omega)$, shown in Figure 2.

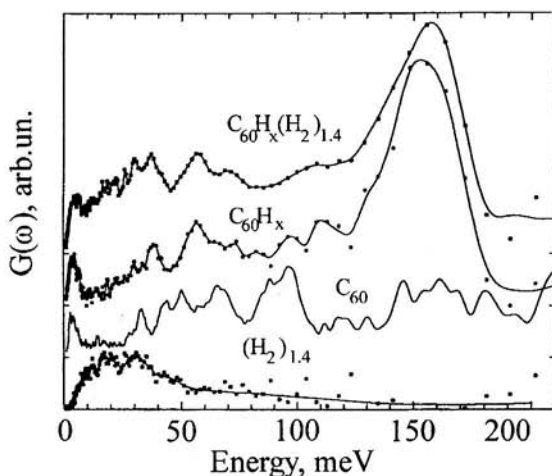


Figure 2 Vibrational spectra $G(\omega)$ of quenched $C_{60}H_x(H_2)_{1.4}$, annealed $C_{60}H_x$, and their difference $(H_2)_{1.4}$ at $T = 85$ K ($x \approx 24$). The spectrum of pure C_{60} at $T = 77$ K is also shown.⁴

Three energy intervals characteristic of different vibrational modes are usually marked in the INS spectrum of pure C_{60} : the intermolecular vibrations in the range (0–8) meV, the radial and tangential intramolecular modes, respectively, at 25 meV to 110 meV and 110 meV to 220 meV.^{4,7,8} It is clear from Figure 2 that intramolecular vibrations were drastically affected by hydrogenation. Spectra of both hydrofullerite states exhibit peaks at 30 meV, 38 meV, 56 meV and 70 meV and a more diffuse feature around 105 meV. The range of tangential intramolecular modes is covered, with an intense peak centred at $\omega \approx 155$ meV, its full width at half maximum being 35 meV. For comparison, strong peaks in the INS spectra of hydrogenated amorphous carbon have been found previously at around 150 meV and 370 meV and assigned to the C-H bending and stretching modes, respectively.^{9,10} By analogy, we attribute the peak at 155 meV to C-H bending modes. Thus, the chemical bonding of the hydrogen atoms in the $C_{60}H_x$ molecules can be derived from study of the complete modification of the intramolecular vibrational spectrum.

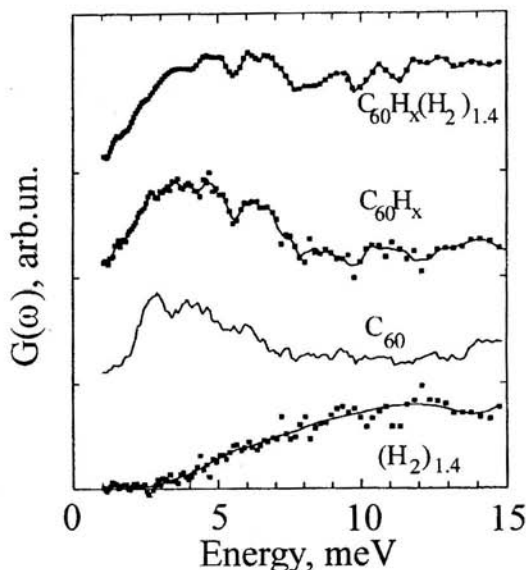


Figure 3 The same as in Figure 2 but in the energy range to 15 meV.

In contrast, the marked similarity of the hydrofullerite to the pure C_{60} spectra is observed in the range of intermolecular vibrations (Figure 3). A strong peak around 2.8 meV, a split peak around 4.3 meV, and one at 6.0 meV in the pure C_{60} spectrum, have been assigned earlier as librational and translational phonon modes.^{4,7} It can be assumed, by analogy, that peaks observed in the hydrofullerite spectra at 2.6 meV and 3.5 meV are due to librational modes, that at 6.5 meV is due to translational modes, and modes of both kinds contribute to the peak at 4.8 meV. Regarding low-energy modes with

$\omega < 8$ meV, chemically bound hydrogen and carbon atoms in $C_{60}H_x$ molecules of the annealed sample are considered to perform common motion. Then the hydrogen content in the annealed $C_{60}H_x$ can be estimated from comparison of the areas under the $G(\omega)$ curves for $C_{60}H_x$ and pure C_{60} at $\omega < 8$ meV, provided that the spectra are normalized to the incident neutron flux, the sample weight, the molecular mass, the momentum of inertia and the neutron scattering cross-section. The estimated value, $x \approx 24$, agrees with the ERD data.

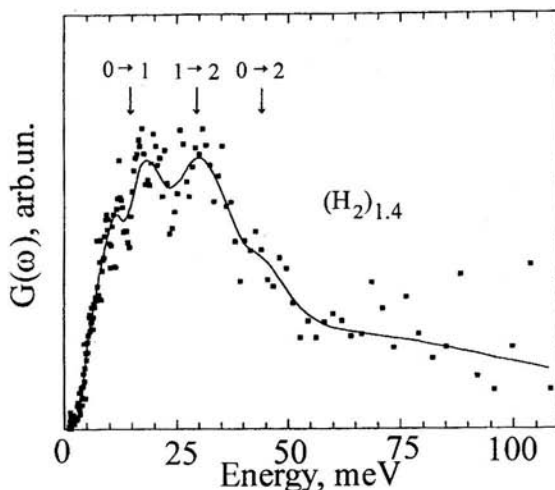


Figure 4 Difference spectrum $(H_2)_{1.4}$ from Figure 2, at a larger scale. Arrows show the rotational transition energies of a free H_2 molecule with the indicated quantum numbers.

A comparison of the INS spectra from the quenched and annealed hydrofullerite states is also worth noting. The difference between the two spectra is shown on a large scale in Figure 4. The difference is evidently due to excess hydrogen atoms which left the quenched sample on annealing at 300 K. The difference spectrum has no features characteristic of fullerites, hence, this fraction of the hydrogen was not chemically bound to the $C_{60}H_x$ molecules. Other data indicate that excess hydrogen was dissolved on the interstitial sites of the $C_{60}H_x$ lattice as H_2 molecules. Firstly, the volume reduction on heating, 42 \AA^3 per H_2 molecule evolved, is close to the molecular volume of solid hydrogen, 38 \AA^3 . Furthermore, the spectrum in Figure 4 shows peaks near 12 meV, 18 meV, 30 meV and 45 meV. The nature of these peaks is well explained by the rotator model of molecular hydrogen¹¹ which gives the molecular rotational levels with the equation $E = BK(K + 1)$, where $B = 7.35$ meV and K is the rotational quantum number. The arrows in Figure 4 mark the transition energies between the states of the H_2 molecule, with $K = 0, 1$ and 2 . A correspondence between the $1 \rightarrow 2$ and $0 \rightarrow 2$ transition energies and the spectral features is obvious. Two peaks at 12 meV and 18 meV are observed in the spectrum, instead of the $0 \rightarrow 1$ transition with

$\Delta E = 14.7$ meV. This splitting seems to result from the interaction between H_2 and nearby $C_{60}H_x$ molecules. A similar splitting of the $0 \rightarrow 1$ transition peak was found earlier in the INS spectrum of molecular H_2 trapped in amorphous carbon.^{9,10}

CONCLUSION

The reaction of hydrogen with solid C_{60} at $P_{H_2} = 6$ kbar and $T = 620$ K yields a compound where part of the hydrogen (~ 24 at.H/mol. C_{60}) is chemically bound and the rest (~ 1.4 mol. H_2 /mol. C_{60}) is dissolved in the bcc $C_{60}H_x$ lattice as interstitial H_2 molecules. Interstitial H_2 leaves hydrofullerite at 300 K. The effect of hydrogen on the intermolecular vibrational spectra is small, but drastic changes occur in the range of intramolecular vibrations. In particular, a strong peak of the C-H bending modes occurs at 155 meV. The interstitial H_2 molecule contributes to the spectra of molecular rotational modes modified by the $C_{60}H_x$ environment.

Acknowledgments

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