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LETTERS

Inelastic Neutron-Scattering Study of the Intramolecular Vibrations of the C_{70} Fullerene

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The vibrational spectrum of C_{70} has been measured by inelastic neutron scattering at 20 K. It closely resembles the spectrum of C_{60} extending smoothly from 26 to 195 meV and reflecting the close bonding similarities between the two hollow carbon cages. Satisfactory agreement with a QCFF/PI model of the C_{70} vibrations is found.

Following the recent isolation and separation of fullerenes,[1] research on their novel properties is currently progressing very fast, with a considerable body of experimental and theoretical data rapidly accumulating. Of particular interest has been the experimental information obtained by infrared, Raman,[2] and neutron[3] spectroscopic techniques on the intramolecular vibrational modes of C_{60}. Such information has not only proven invaluable in advancing our knowledge of the vibrational dynamics of these spherical carbon clusters[4] but also contributed enormously to our understanding of the mechanism responsible for superconductivity in alkali fullerides with stoichiometry A_3C_{60}.[5,6] Thus, good evidence has been amassed for phonon mediation of the pairing interaction with an electron–phonon coupling strength distributed over a wide range of phonon energies (33–195 meV).

Such a comprehensive picture of the intramolecular vibrational spectrum does not as yet exist for any of the higher fullerenes. In particular, the IR and Raman spectra have been reported for the ellipsoidal (D_{5h}) C_{70} fullerene.[2] The 204 intramolecular modes are expected to give rise to 122 singly and doubly degenerate fundamentals. From these, 31 are infrared active ($\Gamma_{IR} = 10\,A_2'' + 21\,E_1'$) and 53 are Raman active ($\Gamma_R = 12\,A_1' + 22\,E_2' + 19\,E_1''$), leaving 38 optically-inactive ($\Gamma_{silent} = 9\,A_2' + 9\,A_1'' + 20\,E_2''$) modes. No detailed comparison with existing fullerene vibrational theories has yet been undertaken. In this paper, we report for the first time inelastic neutron scattering (INS) measurements of the intramolecular vibrational spectrum of solid C_{70} at 20 K. Such measurements are not restricted by the usual optical selection rules, and, consequently, the measured spectrum is the full vibrational spectrum of C_{70}, containing information on all 122 normal modes of vibration. These data will be valuable in developing accurate global vibrational dynamic models of the fullerenes and deriving the electron–phonon coupling strengths of the vibrational modes.

The C_{70} sample (∼98.5% average purity, ∼500 mg) was prepared as described previously.[2c,7] Sublimation at 650 °C, followed by extended annealing at 250 °C (≥2 days), led to highly crystalline material with no traces of trapped solvent and a face-centered-cubic structure at room temperature. The sample was characterized by powder X-ray and high-resolution neutron diffraction and ^{13}C NMR spectroscopy. The hydrogen content was determined by prompt γ-ray neutron activation[8] analysis to be 0.046(7) % by weight.[9] INS measurements were performed using the time-focused crystal analyzer (TFXA) spectrometer at the ISIS Facility, Rutherford Appleton Laboratory, UK. TFXA is an inverted geometry white beam spectrometer employing a low final neutron energy ($E_F = 4$ meV) and achieving a resolution of the order of $\Delta\omega/(\omega \sim 2\%)$. The C_{70} sample was kept in an aluminum sachet inside a closed-cycle He refrigerator at 20 K, and data were collected over a total incident current of ∼14.7 mA (at a rate of ∼150–160 μA/h). A background correction was performed by running the empty sachet also at 20 K.

The scattering law $S(Q,\omega)$ of solid C_{70} measured in down-scattering mode between 25 and 200 meV (1 meV ≡ 8.066 cm^{-1})

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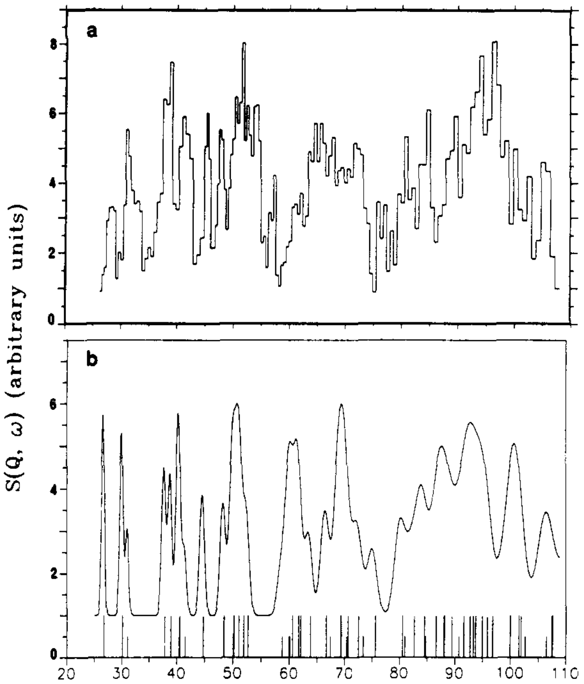

Figure 1. (a) Inelastic neutron scattering spectrum $S(Q,\omega)$ of solid C_{70} at 20 K between 25 and 110 meV. (b) Simulated spectrum using the vibrational eigenfrequencies and eigenvectors of a QCFF/PI model of C_{70} and taking into account the instrumental resolution. The bars mark the energies of the modes, their height being proportional to their degeneracy.

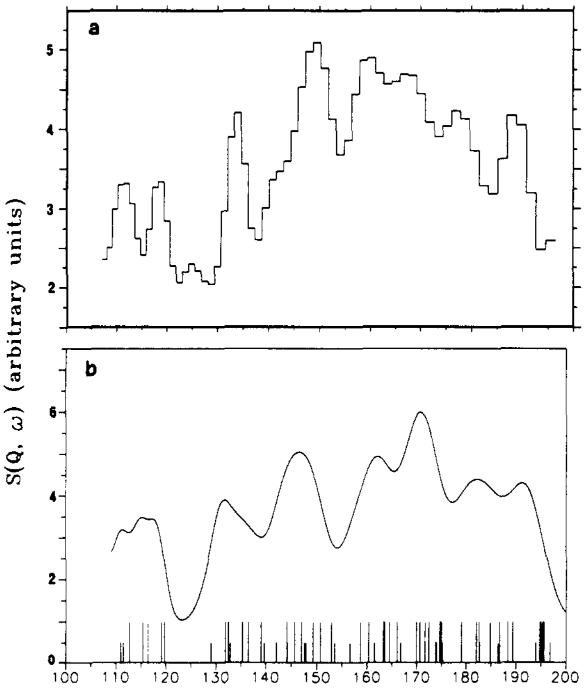

Figure 2. (a) Smoothed inelastic neutron scattering spectrum $S(Q,\omega)$ of solid C_{70} at 20 K between 110 and 200 meV. (b) Simulated spectrum as described in the caption of Figure 1b. The principally stretching-in-character modes with energy > 135 meV were softened (see text).

is shown in Figures 1a and 2a as a function of energy transfer, ω. In contrast to C_{60}, which has many highly degenerate modes, the vibrational modes of C_{70} are at most doubly degenerate and hence are expected to give rise to weaker features in the INS spectrum. However, the long counting times and the purity of the present sample allowed us to record a highly resolved spectrum of the principally radial modes up to 110 meV (Figure 1a). On the other hand, the plethora of principally tangential modes at energies >110 meV, together with the instrumental characteristics that lead to large Debye–Waller factors and wash out some of the vibrations, did not allow us to record a similar quality spectrum in the high-energy region. In order to extract the essential vibrational features in this range, the spectrum was smoothed using a Fourier filtering technique, and the result is shown in Figure 2a. The vibrational spectrum extends smoothly from 26 to 195 meV with the lowest E_2' intramolecular mode (vide infra) found at 28.4(2) meV (cf. 33.1(1) meV in C_{60}). It is very similar to the C_{60} spectrum,[3] in agreement with their close bonding similarities. All the distinct peaks identified in the spectrum are collected together in Table I.

TABLE I: Experimental Frequencies of the Vibrational Modes[a] of C_{70} and Preliminary Assignments

assignment (point group D_{5h})	neutron spectrum	infrared[2a] and Raman[2c] spectra
E_2'	28.4(2)	28.0 (R)
E_1''	31.3(2)	31.2 (R)
A_1'	33.0(3)	32.1 (R)
E_2'	37.8(2)	
E_2''	38.5(2)	
E_1', A_2'', A_1''	41.6(2)	
E_1'	45.4(1)	
E_2''	47.9(2)	
A_1', E_1', E_2'', E_1'', E_2'	49.9(6), 51.8(1.0), 54.3(2), 57.1(2)	48.8 (R), 50.8 (R), 51.7 (R), 53.3 (R), 56.5 (R), 56.8 (IR)
	61.3(9), 64.4(5), 67.4(2.2), 72.1(5)	60.6 (R), 64.5 (R), 66.2 (R), 66.4 (IR), 67.8 (R), 70.1 (IR), 70.2 (R), 71.7 (IR)
E_2''	76.6(8)	
	80.9(5)	79.6 (IR)
	84.6(5)	83.6 (IR)
	89.3(7), 93.1(6), 96.4(5)	86.8 (R), 91.2 (R), 98.6 (IR)
	101.5(8)	
	105.4(2)	
	111.5(1)	
	118.5(1)	
	133.9(2)	131.5 (R), 134.8 (IR), 140.5 (IR)
	149.0(1)	146.3 (R), 151.4 (R), 152.0 (R)
	159.4(5)	160.4 (R)
	168.0(5)	164.8 (R), 167.1 (R), 169.2 (R)
	177.7(3)	175.3 (IR), 176.4 (R), 177.4 (IR), 181.1 (IR), 181.6 (R)
	188.2(3)	187.1 (R), 193.7 (R)

[a] In meV, 1 meV ≡ 8.066 cm^{-1}.

Among the large number of semiempirical and ab initio theoretical calculations[4] of the vibrational properties of fullerenes, quantum chemical force field methods for π-electrons (QCFF/PI) have fared particularly well[3b,4b,4g,4h] in predicting the vibrational frequencies of C_{60}. We now compare our experimental results with the predictions of a QCFF/PI model calculation[4g] of C_{70}. For anisotropic oscillators in powder samples, the scattering law $S(Q,\omega)$ may be expressed as[10]

$$S(Q,\omega) \propto \sum_{\nu} \{(1/3)(Q^2 \operatorname{Tr} \mathbf{B}_\nu) \exp(-Q^2 \alpha_\nu)\} \qquad (1)$$

$$\alpha_\nu \approx (1/5)\{\operatorname{Tr} \mathbf{A} + 2(\mathbf{B}_\nu{:}\mathbf{A}/\operatorname{Tr} \mathbf{B}_\nu)\}$$

where $\mathbf{B}_\nu$ is the mean square displacement tensor of the scattering atom in internal mode ν, $\mathbf{A}$ is the total mean square displacement ($=\Sigma_\nu \mathbf{B}_\nu$), and $Q = |\mathbf{Q}|$ is the momentum transferred during scattering. The theoretical scattering law (eq 1) was calculated by employing the eigenfrequencies and eigenvectors of the QCFF/PI model. This was then convoluted with the measured resolution function of the TFXA spectrometer, and the results are shown in Figures 1b and 2b. The agreement between the experiment and the model calculations appears satisfactory.

The low-energy-transfer region of the spectrum (Figure 1a) is remarkably well resolved, given the large number of modes and their low degeneracies. The model calculations of Figure 1b are in excellent agreement with the experimental data, leading to some unambiguous assignments. The first intramolecular mode occurs at 28.4(2) meV and is assigned to an E_2' mode; its width of 1.5(6) meV is larger than expected from instrumental effects alone and should arise from dispersion effects. The next band shows a clearly resolved shoulder on its high-energy side and can be assigned to an E_1'' (31.3(2) meV) and an A_1' (33.0(3) meV) mode. Then we come across a doublet, assigned to the Raman-active E_2' (37.8(2) meV) and the optically-inactive E_2'' (38.5(2) meV) mode. The intensity of the next band at 41.6(2) meV is consistent with the presence of three modes (E_1', A_2'', and A_1''), as predicted by the model calculations. The following two bands are very sharp, with widths close to the instrumental resolution, and are assigned to an IR-active E_1' (45.4(1) meV) and an optically-inactive E_2'' (47.9(2) meV) mode. Even though individual assignment of vibrational modes becomes difficult at higher energies, the shape of the simulated spectrum follows the experimental data very closely. There is a series of three composite vibrational bands extending from 50 to 58 meV, 58 to 75 meV, and 80 to 105 meV; they are nicely matched by the calculated features in the simulated spectrum. The isolated feature at 76.6(8) meV may be tentatively assigned to an E_2'' mode.

Figure 2a shows the INS spectrum in the energy region 110–200 meV. There are two well-pronounced features at 111.5 and 118.5 meV, followed by a prominent cutoff in the vibrational density of states between 122 and 128 meV. This cutoff occurs in the QCFF/PI simulated spectrum at 124 meV. At higher energies, the appearance of the simulated DOS is similar to experiment but substantially shifted to higher energies, extending to 220 meV. This may be understood by recalling that the vibrational modes in this energy region involve predominantly C–C stretching; a common feature of quantum chemical calculations is that they lead to overestimation of the eigenfrequencies of stretching modes. In order to attempt a meaningful comparison with the experiment, we shifted the calculated spectrum rigidly to lower energies by softening the calculated frequencies, in the energy region 135–220 meV, according to the expression $\omega_{\text{scaled}} = \omega_0 + 0.9(\omega_{\text{calc}} - \omega_0)$ with $\omega_0 = 135$ meV. This leads to a fair agreement (Figure 2b) with the experimental spectrum, which shows peaks at 133.9, 149.0, 159.4, 168.0, 177.7, and 188.2 meV. It also reproduces fairly well the observed cutoffs at ~138, 155, 174, and 182 meV.

In conclusion, high-resolution INS measurements of the vibrational spectrum of the fullerene C_{70} at 20 K have been presented. Satisfactory agreement is found with a QCFF/PI model of both the frequencies and intensities of the vibrational modes. The present experimental results extend the vibrational data available on fullerenes to include C_{70} for the first time. Combined with the earlier data on C_{60}, they are expected to serve as a benchmark for the development of the accurate quantum mechanical description of the fullerenes, through detailed comparisons with the predictions of semiempirical or ab initio calculations of the vibrational dynamics of C_{60} and C_{70}.

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