Neutron Measurements of Intramolecular Vibrational Modes in C_{60}

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Neutron-inelastic-scattering measurements have been made on a sample of highly purified solid C_{60}. New features in the spectrum of intramolecular modes not obtainable by optical spectroscopy have been identified. Available theoretical calculations show trends in accord with the experimental results but disagree in important details, and improved calculations are desirable.

We report measurements of the internal vibrational spectrum of the C_{60}-fullerene molecule in the solid state. Because neutron scattering is not subject to the selection rules of infrared (ir) and Raman spectroscopy, we are able to measure the distribution of *all* the vibrational modes of this unique molecule. Taken together with existing data on the electronic states,[1] the new results place stringent constraints on the theoretical description of fullerene. Theories developed for the intramolecular vibrational energies of isolated C_{60} molecules[2-6] apply to the solid because of weak intermolecular binding. The shape of the molecule is a truncated icosahedron,[7] with all the atoms equivalent and sited on the surface of a perfect sphere. This structure permits[8] 46 distinct vibrational frequencies for the 174 intramolecular modes, of which only 4 are ir active and 10 are Raman active. All such Raman and ir modes have been previously observed.[9] The combination of neutron, Raman, and ir data offers a comprehensive picture of the vibrational spectrum of C_{60} fullerene.

Our measurements have been made possible by recently developed methods[10] of producing large amounts of polycrystalline solid C_{60} (fullerite). The sample was produced as follows. A mixture of approximately 85% C_{60} and 15% C_{70} was obtained by deposition from a contact arc between two graphite rods in a He atmosphere[11] followed by Soxhlet extraction with boiling toluene and solvent removal under vacuum. In order to separate the C_{60} from this mixture, 50–75-mg batches of the extract were dissolved in a minimal amount of toluene and chromatographed on a slurry-packed 45-cm × 5-cm column of neutral alumina with 2% toluene in hexane. This gave a purple band of pure C_{60}, a mixed band of C_{60} and C_{70}, and an orange band of pure C_{70}. The mixed band from each batch was recycled through the column several times.

Since neutron-scattering experiments are sensitive to the presence of hydrogenous material, special efforts were made to reduce such contamination to a very low level. To remove these impurities the sample was placed in pentane, in which it is essentially insoluble, in a sealed flask. The mixture was frozen and rapidly thawed 3 times and the pentane was then decanted. This procedure was repeated twice after which the sample was dried at 200 °C under high vacuum. Subsequent ir measurements revealed a very clean four-line spectrum characteristic of C_{60}. Proton NMR measurements indicated about 1-at.%-H impurities in the 640-mg sample. The H content was independently determined by neutron-absorption prompt-gamma-emission spectroscopy[12] at the Cold Neutron Research Facility at the National Institute of Standards and Technology[13] (NIST) to be 0.9 ± 0.2 at. %. A neutron-diffraction measurement gave a pattern in agreement with recent x-ray results,[14,15] showing that the sample was fcc crystalline C_{60}.

Neutron-inelastic-scattering measurements were performed using a modified three-axis spectrometer at the NIST research reactor.[13] The incident neutron energy was step scanned using a crystal monochromator, and neutrons scattered by the sample to final energies less than a cutoff energy E_c were admitted to a bank of detectors at fixed scattering angle (approximately 90°) through a liquid-nitrogen-cooled low-pass neutron filter. In most of the measurements a copper (220) monochromator was used, but a pyrolytic graphite (PG) (002) monochromator was used at the lowest energies. The higher-energy-transfer measurements were made with a polycrystalline beryllium filter for which $E_c \simeq 5$ meV, and the lower-energy-transfer measurements were made using a combination Be/graphite/Be filter ($E_c \simeq 1.8$ meV), which gives higher resolution at the expense of

considerably lower count rates. Using 60' and 40' Soller collimators, respectively, before and after the monochromator crystal, the approximate FWHM energy resolution of the instrument ranged from 5 to 18 meV for the measurements with the Be filter and from 2 to 3.5 meV with the combination filter. The sample was held at 10 K within a helium-filled aluminum can using a closed-cycle He refrigerator. The complete experiment took about 6 days of beam time.

At each point of a scan, neutrons were counted until a predetermined number of neutrons had been detected in a low-efficiency fission monitor located in the incident beam. Normalized backgrounds, determined from 10-K empty-container runs, were subtracted from each of the sample runs. No further data reduction was performed. Within the one-phonon incoherent approximation the resulting data are essentially proportional[16] to the amplitude-weighted vibrational density of states of C_{60}. Corrections for multiphonon scattering and for departures from the incoherent approximation are unlikely to materially shift any of the observed peaks or features in the spectrum.
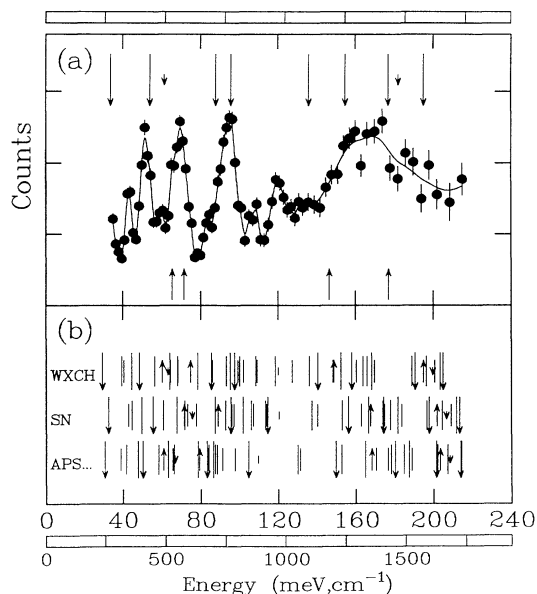
Figure 1(a) shows low-resolution data which span almost the entire range of vibrational energies; note that $(1 \text{ meV}) \simeq (8.066 \text{ cm}^{-1})$. The same data up to 80 meV are shown in Fig. 2(a) together with higher-resolution data taken using the combination filter (open symbols). In Figs. 1(a) and 2(b), ir and Raman lines from Ref. 9 are shown for comparison by up and down arrows, respectively. The lengths of the arrows are proportional to the degeneracies of the lines; note that the four ir lines are triply degenerate, two Raman lines are singly degenerate, and the remaining Raman lines are fivefold degenerate. The higher-resolution neutron peaks at 34 (274), 54 (436), and 61 meV (492 cm^{-1}) correspond very well with peaks in the optical data. The lower-resolution neutron spectrum above 80 meV, which includes many modes in addition to those that are Raman active or ir active, cannot be uniquely matched to the optical data.

In general, the distribution of vibrational frequencies in C_{60} closely resembles the vibrational density of states (VDOS) of graphite in that it shows a three-peaked structure between 40 and 120 meV together with a broad feature between 140 and 200 meV.[16,17] In contrast the

FIG. 1. (a) The neutron-scattering spectrum of C_{60}, measured with the Cu(220) monochromator and Be filter. The ordinate is proportional to the number of counts normalized to the monitor detector (see text). The line through the points is a guide to the eye. The upward- and downward-pointing arrows represent ir-active and Raman-active modes, respectively, as measured by Bethune et al. (Ref. 9); the lengths of the arrows are proportional to the degeneracies of the lines. (b) Calculated vibrational frequencies for C_{60}, according to Wang et al. (WXCH) (Ref. 4), Stanton and Newton (SN) (Ref. 2), and Adams et al. (APS...) (Ref. 5). Upward- and downward-pointing arrows again represent ir-active and Raman-active modes, respectively. The length of each line or arrow is proportional to the degeneracy of the frequency.
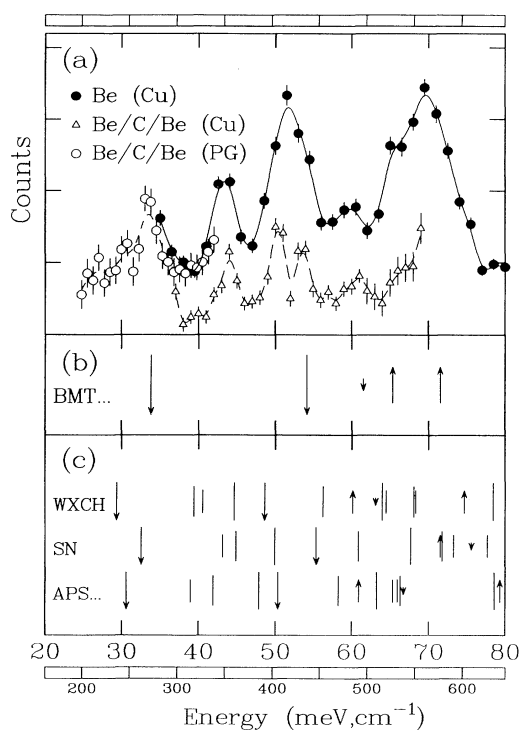

FIG. 2. In the neutron-scattering spectra of (a) different symbols represent measurements with the indicated filter (monochromator) combinations. The ordinate is described in the caption to Fig. 1; the normalizations of the three sets of data are arbitrary. Lines through points are guides to the eye. The upward- and downward-pointing arrows at (b) represent ir-active and Raman-active modes, respectively, measured by Bethune et al. (BMT...) (Ref. 9). The calculated lines in (c) are described in the caption of Fig. 1(b).

VDOS of diamond has a broad band between 70 and 110 meV and a prominent peak between 140 and 180 meV with a clear cutoff beyond this latter energy.[18]

Various quantum-mechanical model calculations of the vibrational energies for C_{60} are shown in Fig. 1(b). Again, up arrows identify ir-active modes and down arrows Raman-active modes. There is a rich structure between ~ 30 and ~ 120 meV, a sparsely populated region between ~ 120 and ~ 150 meV, and two dense bands between ~ 160 and ~ 220 meV. The calculations differ significantly in the relative placement of various lines, notably the ir-active modes and the singly degenerate Raman-active modes, and in overall scale. None of the theories agrees in detail with all of the data. The work of Wang et al.[4] (WXCH) shows somewhat better overall agreement in scale than that of Stanton and Newton[2] (SN) or Adams et al.[5] (APS...), and comes considerably closer in correctly placing the ir lines. It also has several lines around 120 meV where there are neutron peaks. WXCH derive the vibrational frequencies from a tight-binding model of the electronic band structure, while SN use the modified neglect of differential overlap method and APS... use the quantum molecular-dynamics method. We have chosen not to show phenomenological mass and spring calculations both because the results of Ref. 8 differ markedly from the observed data and because our own such calculations suggest that the data cannot be satisfactorily described in this way using a small number of parameters.

We now turn to the high-resolution data between 20 and 80 meV. Figure 2(c) shows the calculated lines; the lengths of the lines are again proportional to their degeneracies. Each of the theories shown in Fig. 2(c) presents some discrepancies with the neutron and optical data shown in Figs. 2(a) and 2(b). Looking at the placement of the ir-active modes and the singly-degenerate A_g Raman mode, we see that the work of WXCH is closest. Whereas there are differences in the energies of the calculated lines, there is a persistent pattern among the various theories. The lowest energy line at 34 meV (274 cm^{-1}), which is the Raman-active H_g "squashing" mode, is well separated from the others. The symmetry of the next five lines has been identified by theory. Using the pattern emerging from these calculations we tentatively assign the low-energy neutron peaks as follows: the peak at 44 meV (355 cm^{-1}) to a combination of a F_{2u} (or T_{3u}) and a G_u mode; the peak at 50 meV (403 cm^{-1}) to a H_u mode; the peak at 54 meV (436 cm^{-1}) to a Raman-active H_g mode; and the peak at 61 meV (492 cm^{-1}) to a G_g mode. The optical experiment also shows a singly degenerate A_g mode at 61 meV, and the theories differ widely in the placement of this mode. Beyond these six lines each calculation presents a distinct pattern, and the neutron spectrum is insufficiently resolved to distinguish among them.

In summary, inelastic neutron measurements on fullerite have provided information on additional modes not observed in optical studies, as well as good overlap with these studies. A comparison with theory has allowed identification of a number of new modes. While moderate agreement is observed with current theories, significant differences exist. In particular, the placement of the ir lines appears to be rather sensitive to the details of theoretical models of vibrational energies based on electronic structure, as does the overall scale of the vibrational energies. The present experimental results, taken together with recent photoemission results[1] on electronic energy spectra, provide stringent constraints on the quantum-mechanical description of fullerenes.

[1]J. H. Weaver, José Luís Martins, T. Komeda, Y. Chen, T. R. Ohno, G. H. Kroll, N. Troullier, R. E. Haufler, and R. E. Smalley, Phys. Rev. Lett. 66, 1741 (1991).

[2]R. E. Stanton and M. D. Newton, J. Phys. Chem. 92, 2141 (1988).

[3]Z. Slanina, J. M. Rudzinski, M. Togasi, and E. Osawa, J. Mol. Struct. (Theochem) 202, 169 (1989).

[4]C. Z. Wang, C. H. Xu, C. T. Chan, and K. M. Ho (private communication).

[5]G. B. Adams, J. B. Page, O. F. Sankey, K. Sinha, J. Menendez, and D. R. Huffman (private communication).

[6]For additional references to theoretical work see the review article by H. W. Kroto, A. W. Allaf, and S. P. Balm (to be published).

[7]H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, and R. E. Smalley, Nature (London) 318, 162 (1985).

[8]D. E. Weeks and W. G. Harter, J. Chem. Phys. 90, 4744 (1989).

[9]D. S. Bethune, G. Meijer, W. C. Tang, H. J. Rosen, W. G. Golden, H. Seki, C. A. Brown, and M. S. de Vries, Chem. Phys. Lett. 179 (to be published).

[10]W. Krätschmer, L. D. Lamb, K. Fostiropoulos, and D. R. Huffman, Nature (London) 347, 354 (1990).

[11]R. Taylor, J. P. Hare, K. Abdul-Sada, and H. W. Kroto, J. Chem. Soc., Chem. Commun. 20, 1423 (1990).

[12]M. P. Failey, D. L. Anderson, W. H. Zoller, G. E. Gordon, and R. M. Lindstrom, Anal. Chem. 51, 2209 (1979).

[13]H. J. Prask, Neutron News 1, 9 (1990).

[14]R. M. Fleming, T. Siegrist, P. M. March, B. Hessen, A. R. Kortan, D. W. Murphy, R. C. Haddon, R. Tycko, G. Dabbagh, A. M. Mujsce, M. L. Kaplan, and S. M. Zahurak, Mater. Res. Soc. Symp. Proc. 206 (to be published).

[15]J. E. Fischer, P. A. Heiney, A. R. McGhie, W. J. Romanow, A. M. Denenstein, J. P. McCauley, Jr., and A. B. Smith, III, Science (to be published).

[16]A. D. B. Woods, B. N. Brockhouse, M. Sakamoto, and R. N. Sinclair, in *Inelastic Scattering of Neutrons in Solids and Liquids* (IAEA, Vienna, 1961), p. 487.

[17]R. Al-Jishi and G. Dresselhaus, Phys. Rev. B **26**, 4514 (1982), presents a theoretical VDOS for graphite; unpublished experimental measurements for graphite, using neutron methods described in the text, have been carried out by R. L. Cappelletti, W. A. Kamitakahara, and J. R. D. Copley.

[18]W. Weber, Phys. Rev. B **15**, 4789 (1977).