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Optically detected librons and phonons in crystalline C_{60}

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Well-defined intermolecular modes of crystalline C_{60} were studied by means of Fourier-transform Raman and far-infrared spectroscopy. The librational modes are seen to gradually soften and broaden in energy as the temperature is raised from 10 to ~260 K at which point the libron intensity abruptly vanishes, consistent with the order-disorder phase transition. The librational modes, which are in general agreement with the less well-resolved neutron-scattering results, are found to be remarkably sharp at low temperature.

The recent feasibility of producing relatively large quantities of C_{60} (Ref. 1) has led to a flurry of structural studies of this remarkable material. It has been shown that at room temperature the C_{60} molecules undergo rapid isotropic rotation[2] while their centers of mass are positioned on a fcc lattice.[3] Below ~260 K, the crystal undergoes a first-order orientational phase transition to a simple cubic (sc) structure with a four-atom basis.[4] Since in this phase there exists long-range orientational order in addition to translational order, there will be collective orientational excitations, librons, in addition to the translational excitations, phonons.

A host of researchers have reported on the intramolecular vibrational modes of C_{60} as free molecules and in the fcc and sc crystalline states, a complete review of which is beyond the scope of this paper. Determination of the *intramolecular* or external modes has been much less successful in comparison. The translational modes are all of ungerade symmetry while the librational modes are all of gerade symmetry.[5] The translational modes should then, in principle, be infrared (IR) active while the librational modes should be Raman active. These lattice modes, however, are expected to be low in energy due to the mass of the molecules and the nature of the bonding in the crystalline state (predominantly van der Waals), thus making detection difficult. The first report of translational modes measured via far-infrared (FIR) absorption showed two strong features at 26 and 58 cm^{-1} (Ref. 6) but these were later shown to be extrinsic lines, possibly related to water absorption, not features intrinsic to the C_{60} crystal.[7] In determining the librational mode energies, Raman spectroscopy has been inconclusive to date. Several groups have reported weak features at various energies and tentatively assigned them to librational excitations, although the structure was not reproducible in all samples.[8–10] Inelastic neutron scattering (INS) has proven to be a powerful technique in measuring both the translational and the librational modes of the solid.[11,12] INS is not restricted by the selection rules of IR and Raman spectroscopy, but it does suffer from relatively poor resolution and signal to noise.

In this paper we present a conclusive Raman measurement of the zone-center librational modes of crystalline C_{60}. A laser rejection technique was employed which allowed for measurement of Raman shifts as low as ±10 cm^{-1} while retaining the superior sensitivity and resolution of Fourier-transform Raman (FT Raman) spectroscopy. The librational modes were found to be much sharper than revealed by INS, having a full width at half maximum (FWHM) of only 1.2 cm^{-1} at low temperature, and displaying interesting fine structure. The librons were seen to gradually soften and broaden as the temperature was raised toward the order-disorder transition. At the order-disorder transition the libron intensity vanished quite abruptly and was replaced by a strong Lorentzian background, indicative of scattering due to the isotropic rotation of the C_{60} molecules. The two zone-center translational modes of T_u symmetry have also been measured via FIR absorption on the same crystalline samples and were found to be considerably sharper than previously reported[7] for powder samples.

The samples were prepared from C_{60} powder (Texas Fullerenes) which had a C_{60} purity (in terms of fullerenes) of 99.9%. Single crystals of volumes from 0.1 to >1 mm^3 were grown by sublimation in a temperature gradient under vacuum in quartz tubes, after outgassing the powder at 250 °C.[13] The crystals were transferred directly from the growth tube into a varitemp Dewar which was immediately evacuated and backfilled with He gas. For the FIR absorption measurements the crystals were outgassed under vacuum in the Dewar at 100 °C before cooling in He. The crystals were relatively free of molecular oxygen as determined by its characteristic luminescence spectrum.[14] All of the spectroscopy was done using a Bomem DA8.01 Fourier-transform interferometer.

The FT Raman spectra were collected using 780.25-, 794.98-, 852.36-, and 894.60-nm excitation from a Ti:sapphire laser and a silicon avalanche photodiode detector. The laser rejection was provided by the resonance absorption of atomic cesium and rubidium vapor. Alkali-metal vapors have been previously shown to provide an extremely narrow notch filter for dispersive Raman spectroscopy (Ref. 15 and references therein), but to our knowledge these filters have not been previously applied to FT Raman measurements. A quartz cell containing an excess of the alkali metal and some N_2 gas as a

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quenching agent is placed either between the sample and the interferometer or the interferometer and the detector. The excitation source is tuned onto one of the resonance absorption lines of the atomic vapor which then provides almost total rejection of scattered laser light at moderate cell temperatures, while being entirely transparent at only $\sim \pm 10$ cm^{-1} from the laser line. We will report further details of this method elsewhere. Most of the measurements presented here were done at the 894.60-nm transition of Cs, for which a cell temperature of 210 °C gave good rejection of the relatively broad laser line (no etalon was used) while having a notch full width of only 6 cm^{-1} at the 50% transmission points.

The Fourier-transform infrared absorption measurements were made using a mercury lamp source and a 1.6-K bolometer detector. The crystals were mounted in a stress-free manner between a 100-cm^{-1}-long pass cold filter and a polyethylene wedge.

A typical low-temperature Raman spectrum is shown in the bottom curve of Fig. 1. The sharp peak centered at zero shift is predominantly fluorescence from the atomic vapor filter, modulated at the laser modulation period (the filter being between the interferometer and the detector), as opposed to break through of the laser light itself. The data presented have not been corrected for the absorption of the atomic vapor filter, explaining the central dips in the high-temperature spectra of Fig. 1. Clearly visible in Stokes scattering at 10 K are two features centered at 18.5 and 21.8 cm^{-1}. The FWHM of the 18.5-cm^{-1} component, after correcting for the 1.2-cm^{-1} instrumental resolution, can be estimated to be ~ 1.2 cm^{-1}. We assign these features to librational modes of the C$_{60}$ crystal based upon their temperature evolution as shown in Fig. 1. The spectra are all on the same intensity scale, simply shifted for clarity, while the region ± 3 cm^{-1} of the laser line has been omitted for all but the 10-K spectrum. As the temperature is raised, the anti-Stokes scattering grows in intensity as one expects, as does the Stokes scattering due to the thermal population factor, allowing additional weaker modes to be observed.

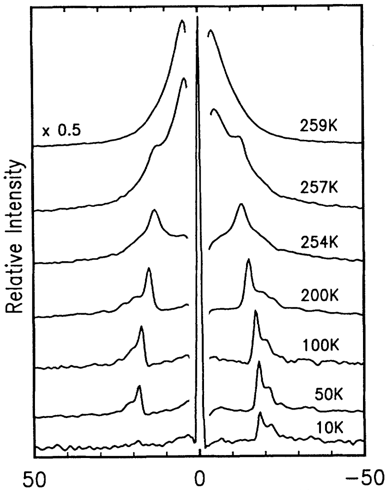

FIG. 1. Temperature evolution of the C$_{60}$ librational modes. The spectra have not been corrected for the absorption of the laser rejection filter.

If these features are librons, they must vanish at ~ 260 K, the temperature of the order-disorder transition.[4] As can be seen from Fig. 1, between 257 and 259 K, the features do indeed vanish, replaced by a strong Lorentzian background centered at the laser frequency, as expected for light scattering from freely rotating molecules.[16] There appears to be a few degrees of laser heating of the sample, since FT Raman studies of the intramolecular modes (to be reported elsewhere) on these same samples using much lower laser power have verified a sharp phase transition at 260.3 K (T increasing) and at 259.4 K (T decreasing).

The energy of the strongest libron peak softens by $\sim 30\%$ while the FWHM of the observed band more than triples from 10 to 258 K, as shown in Fig. 2. The integrated intensity of the Stokes libron band is also shown, as is the observed, uncorrected intensity of the Lorentzian background. Figure 2 shows that the librons do not soften to zero energy or broaden remarkably at the order-disorder transition. Instead, the librons abruptly decrease in intensity above 256 K, and vanish by 259 K, at the same time as the Lorentzian scattering grows rapidly in intensity. The Raman data presented were collected using 894.60-nm excitation, although identical results were obtained using 780.25- and 794.98-nm excitation. These features were reproducible and had the same intensity relative to the intramolecular modes in all the samples studied, although different samples did have different backgrounds underlying the Raman signal. At 852.36 nm, if T was < 30 K, all the samples showed a different and stronger spectrum than that reported here, which we believe is due to the resonant enhancement of an extrinsic impurity-related feature. This resonance vanished at $T > 30$ K, under which conditions the 852.36-nm Raman spectra were identical to the ones reported here.

Figure 3 shows a Raman spectrum taken at 77 K in which librational fine structure is clearly evident. INS studies of both powdered[11] and single crystal[12] C$_{60}$ have observed a broad (~ 8 cm^{-1} FWHM) librational peak at 2.4 meV (~ 20 cm^{-1}) in good agreement with the sharp

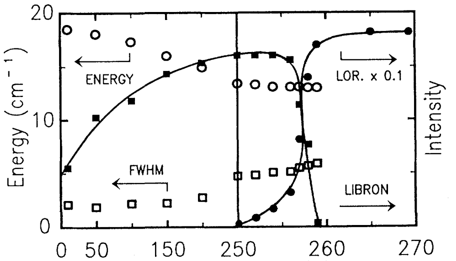

FIG. 2. Temperature dependence of the librational peak energy (○), FWHM (□), and integrated Stokes intensity (■). The uncorrected Lorentzian scattering intensity (●) has been scaled down by a factor of 10. Note that two different temperature scales are used above and below 250 K, so the apparent change of the slope of the energy and FWHM curves at 250 K is not real.

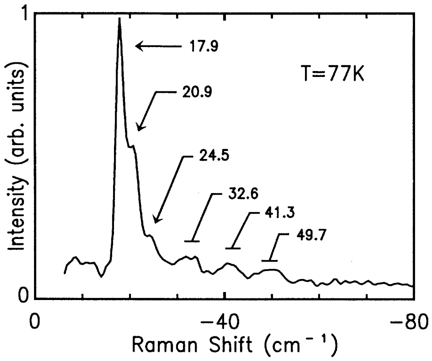

FIG. 3. Stokes scattering from crystalline C_{60} at 77 K. The instrumental resolution was 1.2 cm^{-1}. The intensity of the 17.9-cm^{-1} libron is $\sim\frac{1}{150}$ that of the 496-cm^{-1} intramolecular mode at this temperature.

librational modes appearing at 17.9, 20.9, and 24.5 cm^{-1} in Fig. 3. The INS study of single-crystal C_{60} (Ref. 12) also reported broader librational peaks at 3.6 and 4.6 meV ($\sim$29 and 37 cm^{-1}, respectively) in correspondence with some of the higher-energy structure seen in Fig. 3. In their INS study of powdered C_{60}, Neumann *et al.*[11] reported mode softening similar to that shown in Fig. 2 as the temperature was raised from 10 to 250 K, while the width of their peak broadened to over 16 cm^{-1}. Pintschovius *et al.*[12] point out that this may be misleading as an INS measurement of a powder sample measures the density of libron states rather than distinct *k*-vector librons. In an INS study of single-crystal C_{60} they observed no softening or broadening of the zone-center 2.4-meV librational peak, although as mentioned above, the poorer resolution of INS relative to FT Raman may account for the inability of INS to detect the librational mode softening we observe in single-crystal samples.

Libron and phonon dispersion curves for crystalline C_{60} have been calculated starting from a van der Waals interaction between rigid C_{60} molecules together with different intermolecular potentials accounting for the nonuniform charge distribution on the C_{60} molecule.[17–19] Zone-center librational modes calculated from these models appear in energy from 7 to 20 cm^{-1}, a range which includes our lowest experimentally observed modes. However, in contrast to these theoretical predictions, there is no indication in our Raman data of scattering lower in energy than the strongest mode, appearing at 18.5 cm^{-1} at 10 K.

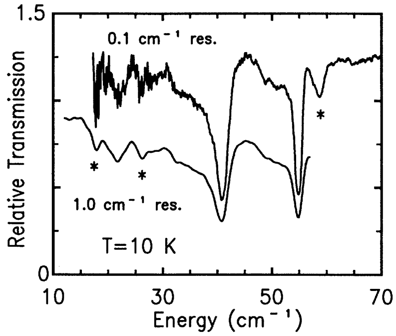

FIG. 4. Far-infrared absorption of crystalline C_{60} relative to that of crushed CaF_2. Peaks labeled with an * are extrinsic features thought to be related to water absorption on the C_{60} (Ref. 7).

The FIR absorption spectra of the same C_{60} crystals are shown in Fig. 4. Due to increased elastic scattering from the small particles at shorter wavelengths, a strongly sloping baseline is produced if the sample transmission spectrum is ratioed against the transmission from an empty sample holder. This sloping baseline is present in both the paper by Huant *et al.*[6] and the work by FitzGerald and Sievers.[7] The sample spectra in Fig. 4 were ratioed against the transmission of a collection of calcium fluoride crystals whose particle size distribution matched that of the crystalline C_{60} sample. This approximately compensated for the elastic scattering, and also accounts for the relative transmission being greater than 1 in one run and less than 1 in the other, the absolute scattering magnitude not being very reproducible when the crystals are exchanged. The 0.1-cm^{-1} resolution spectrum was collected with a 25-μm Mylar beam splitter, while a 50-μm beam splitter was used for the 1.0-cm^{-1} resolution spectrum. The two strong absorptions at 40.8 and 54.8 cm^{-1} with FWHM of 2.0 and 1.4 cm^{-1}, respectively, are assigned to the two IR-allowed translational modes, in concurrence with FitzGerald and Sievers,[7] although our peaks are considerably narrower, perhaps due to the higher crystallinity of our sample. The peaks labeled with an asterisk are features believed to be associated with water absorption.[7] We believe that a third peak seen at 21 cm^{-1} in our spectra may be an intrinsic feature of the C_{60} solid. The intensity of the three extrinsic peaks can be reduced by heating the sample under vacuum and then increased again by exposure to air, while no such behavior occurs for the 21-cm^{-1} peak. Also, a feature at the same energy is present in the Raman data. The calculated[17–19] energies of the zone-center translational modes of T_u symmetry are $\sim$30 and 45 cm^{-1}, in relatively poor agreement with the experimentally determined energies.

In summary, we have presented a detailed Raman study of the external modes of crystalline C_{60}. What was previously reported[11,12] as a broad peak at $\sim$2.4 meV in inelastic neutron-scattering data has been resolved into distinct librational modes of unprecedented sharpness which have been shown to gradually soften and broaden as the temperature is raised toward the order-disorder transition. At the transition temperature, the librational mode intensity vanishes abruptly and is replaced by a Lorentzian scattering background due to the free rotation of the molecules. We have verified a recent determination[7] of the zone-center optical-phonon energies by FIR absorption, and shown that these modes are much sharper in high-quality crystals than was earlier thought. Molecular-dynamics calculations using two different intermolecular potentials[17–19] do not at present accurately account for either the librational or the translational mode energies seen in experiment.

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[1] W. Krätschmer *et al.*, Nature (London) **347**, 354 (1990).

[2] R. Tycko, G. Dabbagh, R. M. Fleming, R. C. Haddon, A. V. Makhija, and S. M. Zahurak, Phys. Rev. Lett. **67**, 1886 (1991).

[3] R. M. Fleming *et al.*, in *Clusters and Cluster-Assembled Materials,* edited by Robert S. Averback, Jerzy Bernholc, and David L. Nelson, MRS Symposia Proceedings No. 206 (Materials Research Society, Pittsburgh, 1991), p. 691.

[4] P. A. Heiney *et al.*, Phys. Rev. Lett. **66**, 2911 (1991).

[5] G. Dresselhaus, M. S. Dresselhaus, and P. C. Eklund, Phys. Rev. B **45**, 6923 (1992).

[6] S. Huant, J. B. Robert, G. Chouteau, P. Bernier, C. Fabre, and A. Rassat, Phys. Rev. Lett. **69**, 2666 (1992).

[7] S. A. FitzGerald and A. J. Sievers, Phys. Rev. Lett **70**, 3175 (1993).

[8] P. H. M. van Loosdrecht, P. J. M. van Bentum, and G. Meijer, Phys. Rev. Lett. **68**, 1176 (1992).

[9] P. H. M. van Loosdrecht, P. J. M. van Bentum, M. A. Verheijen, and G. Meijer, Chem. Phys. Lett. **198**, 587 (1992).

[10] M. Matus and H. Kuzmany, Appl. Phys. A **56**, 241 (1993).

[11] D. A. Neumann *et al.*, J. Chem. Phys. **96**, 8631 (1992).

[12] L. Pintschovius *et al.*, Phys. Rev. Lett. **69**, 2662 (1992).

[13] M. A. Verheijen, H. Meeks, G. Meijer, E. Raas, and P. Bennema, Chem. Phys. Lett. **191**, 339 (1992).

[14] M. K. Nissen, S. M. Wilson, and M. L. W. Thewalt, Phys. Rev. Lett. **69**, 2423 (1992).

[15] M. J. Pelletier, Appl. Spectrosc. **47**, 69 (1993).

[16] R. Folland, D. A. Jackson, and S. Rajagopal, Mol. Phys. **30**, 1063 (1975).

[17] X. P. Li, J. P. Lu, and R. M. Martin, Phys. Rev. B **46**, 4301 (1992).

[18] M. Sprik, A. Cheng, and M. L. Klein, J. Phys. Chem. **96**, 2027 (1992).

[19] T. Yildirim and A. B. Harris, Phys. Rev. B **46**, 7878 (1992).