

Local-field effects and forbidden transitions in C_{60} solid thin films

Dongmei Li, Steven Velasquez, and S. E. Schnatterly

Jesse Beams Laboratory of Physics, University of Virginia, Charlottesville, Virginia 22901

(Received 14 June 1993)

We have measured the momentum-dependent inelastic-electron-scattering spectra of C_{60} solid thin films. These data allow the oscillator strength of dipole-forbidden transitions and the dispersion coefficient of the volume plasmon to be evaluated. In addition, we evaluate the complex molecular polarizability from the dielectric function using a point-dipole model for the local-field effects. The results are consistent with the presence and calculated energies of both dipolar and quadrupolar collective molecular excitations in molecular C_{60} .

Since the discovery of C_{60} , its unique molecular structure and unusual electronic properties have provoked considerable interest both experimentally and theoretically. In this study, we report inelastic-electron-scattering (IES) measurements on C_{60} thin films. These results give information about both optically allowed and forbidden transitions over a wide energy range. In addition, we use a model of local-field effects to explain the surprisingly large shift in the energy of the molecular collective resonance between the isolated molecule and the solid.

Measurements were made using the University of Virginia's IES spectrometer, which has been described in Ref. 1. The primary beam energy was 285 keV with a resolution of 130 meV. Momentum transfers of 0.1–1.0 \AA^{-1} were covered with a resolution of 0.04–0.1 \AA^{-1} .

The IES scattering cross section can be expressed as

$$\frac{d^2\sigma}{d\omega d\Omega} \approx \frac{1}{q^2} \text{Im} \left[\frac{1}{\epsilon(q, \omega)} \right], \quad (1)$$

where ϵ is the complex dielectric function, $\hbar q$ is the momentum transfer, and $\hbar\omega$ is the energy loss. Measured spectra were corrected for multiple scattering, and absolute values of the real and imaginary parts of the dielectric functions were then obtained through a Kramers-Kronig analysis.²

C_{60} solid film samples with a thickness of about 500 \AA were prepared by evaporating C_{60} powder onto Victawet coated microscope slides. Free-standing films were later floated off on water and picked up onto electron-microscope grids.

Figure 1 shows the imaginary part of the dielectric function ϵ_2 from 1 to 9 eV for momentum transfers between 0.1 and 1 \AA^{-1} . These results agree well with earlier low- q measurements,^{3,4} and with the momentum-dependent data published by Sohmen, Fink, and Kratschmer.⁵ Most features are quite localized in that they do not disperse with q . The strongest peak at around 4.5 eV, however, shows a slight downward shift of 0.16 eV with momentum transfer from 0.1 to 1.0 \AA^{-1} . Two forbidden transitions are observed. A feature at 7.35 eV is entirely dipole forbidden while the threshold near 2 eV appears to be partially allowed appearing as a shoulder at low-momentum transfer, and growing into a peak at high q .

This peak was also observed in isolated molecules.⁶ Both theoretical⁷ and experimental⁸ work strongly suggests that the 2-eV region consists of dipole-forbidden transitions which are made partially allowed by odd-parity atomic vibrations. The operator causing transitions in IES is $\sum e^{iq\cdot r_i}$ where r_i is summed over the positions of the electrons. For localized transitions such as these the exponential operator can be expanded: $e^{iq\cdot r} = 1 + (iq\cdot r) + (iq\cdot r)^2 + \dots$. The term linear in q causes dipole-allowed transitions while the term quadratic in q causes monopole and quadrupole transitions. The inelastic-scattering cross section then involves the square of the matrix element of this operator. Thus we expect monopole and quadrupole features in the spectrum to in-

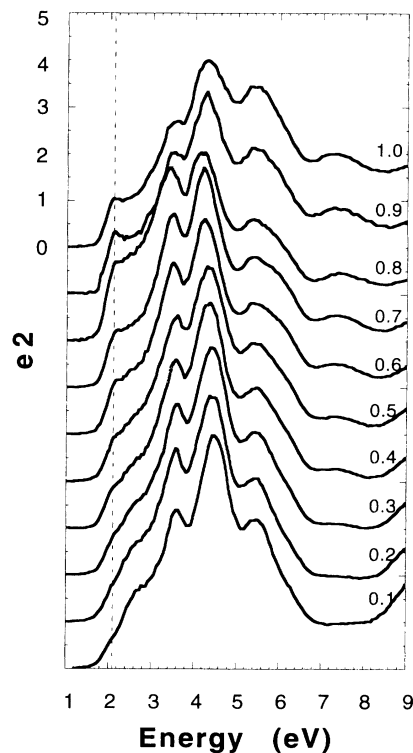


FIG. 1. The imaginary part of the dielectric function of solid C_{60} film for a variety of momentum transfers. Momentum transfers in \AA^{-1} are indicated above the curves.

crease with q as q^2 relative to dipole features. This is clearly happening near 2 and 7.35 eV. We have evaluated the oscillator strength of these two features as a function of q and fit them to the form $f(q) = f_0 + \beta q^2$. For the 2-eV region $\beta = 0.25 \pm 0.1 \text{ \AA}^2$, and at 7.35 eV $\beta = 3.0 \pm 1.0 \text{ \AA}^2$.

The IES cross section has a strong peak at 26 eV which is generally considered to be a valence electron volume-plasma excitation.³ The energy of the peak shifts upward with momentum transfer about 2 eV over a 1-\AA^{-1} change in momentum transfer. The dispersion coefficient of a volume plasmon can be defined by $\alpha = \alpha^* \hbar^2 / m$ where α^* is the upward slope of peak energy versus momentum transfer squared. The dispersion coefficient of this plasmon equals 0.26 ± 0.05 . Within the free-electron approximation $\alpha = (\frac{2}{3})(E_f / \hbar \omega_p)$. For an electron density of $0.345 \times 10^{24} \text{ cm}^{-3}$, which corresponds to 240 valence electrons per C_{60} molecule, this value is 0.29, in good agreement with our measured value.

The excitation spectra of C_{60} in the 10–30-eV range present an interesting puzzle. The spectrum of isolated molecules, observed by photon ionization,⁹ and by IES,⁶ is dominated by a broad peak centered around 18 eV. Theoretical calculations attribute this feature to a collective oscillation of the valence electrons of the C_{60} molecule.^{10,11}

In Fig. 2 we show $\epsilon_2(\omega)$ as a solid line for small q for C_{60} solid films. Besides the intense valence spectra centered around 5 eV, there is an asymmetric peak at 12 eV. This differs greatly in appearance from the measurements on isolated molecules. Yet C_{60} forms Van der Waals solid in which the individual molecules hardly interact with each other at all. It is surprising to find such a large difference in spectral shape between the isolated molecules and the solid under these circumstances.

One possible explanation for this difference is that it is due to local-field enhancement. We can estimate the effects of such enhancement in the following way. Within the point-dipole approximation the complex dielectric function can be written as

$$\epsilon = 1 + \frac{4\pi n \alpha}{1 - B(q)n\alpha}, \quad (2)$$

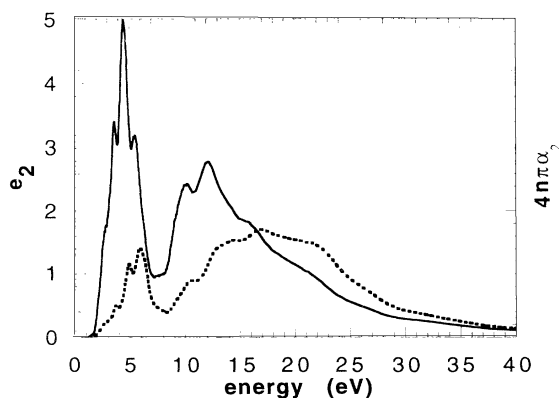


FIG. 2. The solid line is the imaginary part of the dielectric function. The dashed line is $4\pi n \alpha_2$, with α_2 as the imaginary part of the molecular polarizability. Both lines are for momentum transfer of 0.1 \AA^{-1} .

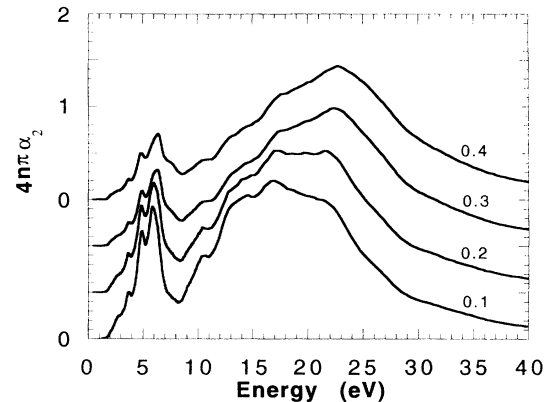


FIG. 3. Molecular polarizability for a variety of momentum transfers. Momentum transfers in \AA^{-1} are indicated above the curves.

where n is the density of molecules, α is the polarizability of an individual molecule, and $B(q)$ is the momentum-dependent local-field factor for the fcc lattice.¹² For $q = 0.1 \text{ \AA}^{-1}$ appropriate for the data of Fig. 2, we estimate B to be about 4.5 which is an average value over all directions in the fcc lattice. Knowing ϵ , we can then solve Eq. (2) for $\alpha = \alpha_1 + i\alpha_2$. Figure 2 shows as a dashed line the value of $4\pi n \alpha_2$ which, within this model, is the value of ϵ_2 without local-field contribution, plotted along with ϵ_2 for the solid. At low energies the local field enhances the magnitude of ϵ_2 by a factor of 5–6 compared with $4\pi n \alpha_2$. This factor decreases with increasing energy, becoming unity at about 16 eV, and becomes a suppression of the strength above that energy. The overall shape of $4\pi n \alpha_2$ is very close to that observed in photoionization,⁹ and agrees reasonably with the molecular electron-scattering results.⁶ Some discrepancy in shape exists between our results and those of Ref. 6. As described in that paper, however, a kinematic correction factor which was not completely worked out may explain the differences.

The spectra shown in Fig. 2 are dipole transitions since q is small. As q is increased, quadrupole modes can also be excited. Recently, Davids *et al.*¹¹ have evaluated the energies of multipole modes of C_{60} molecules. They find a dipole mode at 18 eV, just as we observe, and quadrupole modes in the 23–25-eV range. Lower-energy modes of both types are also predicted. Figure 3 shows our evaluation of $4\pi n \alpha_2(q, \omega)$ for four different q values. As the momentum transfer is raised, the strength in the 23–25-eV region increases, becoming the peak of the spectrum. This is the behavior expected if quadrupole modes occur at that energy, since qr where r is the radius of the C_{60} molecule varies from 0.35 to 1.4 for the data shown. Earlier IES measurements on gaseous C_{60} show results qualitatively similar to those presented here.⁶ In that work $qr > 1$ for both scattering angles used, so quadrupole modes should contribute to both spectra presented.

These results confirm the presence of dipole-forbidden components of optical transitions at 2 and 7.35 eV in C_{60} . They also provide support for the energy assignments of both dipolar and quadrupolar molecular collective modes in this material.

- ¹P. C. Gibbons, J. J. Ritsko, and S. E. Schnatterly, *Rev. Sci. Instrum.* **46**, 1546 (1975).
- ²S. E. Schnatterly, in *Solid State Physics: Advances in Research and Applications*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1979), Vol. 34.
- ³G. Gensterblum and J. J. Pireaux, *Phys. Rev. Lett.* **67**, 2171 (1991).
- ⁴Ryuichi Kuzuo, Masami Terauchi, and Michiyoshi Tanaka, *Jpn. J. Appl. Phys. Lett.* **30**, L1817 (1991).
- ⁵E. Sohmen, J. Fink, and W. Kratschmer, *Z. Phys. B* **86**, 87 (1992).
- ⁶John W. Keller, *Chem. Phys. Lett.* **193**, 89 (1992).
- ⁷K. Yabana and G. F. Bertsch, *Chem. Phys. Lett.* **197**, 32 (1992).
- ⁸Z. Gasyna, P. N. Schatz, J. P. Hare, H. W. Kroto, and R. Taylor, *Chem. Phys. Lett.* **177**, 394 (1991).
- ⁹I. V. Hertel *et al.*, *Phys. Rev. Lett.* **68**, 784 (1992).
- ¹⁰George F. Bertsch, Aurel Bulgac, David Tomanek, and Yang Wang, *Phys. Rev. Lett.* **67**, 2690 (1991).
- ¹¹P. S. Davids, L. Wang, A. Saxena, and A. U. Bishop (unpublished).
- ¹²S. R. Nagel and T. A. Witten, *Phys. Rev. B* **11**, 1623 (1975).