High-Resolution Electron-Energy-Loss Spectroscopy of Thin Films of C_{60} on Si(100)

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We report on the first measurements by high-resolution electron-energy-loss spectroscopy of the elementary excitations of C_{60} thin films deposited on Si(100). By varying the primary electron energy, the spectrum extending from the far ir to the far vuv has been investigated. Many spectral features are comparable to earlier observations by photon, photoelectron, and neutron spectroscopies. New molecular excitations are revealed including the lowest electronic excitation at 1.5 eV and collective excitations at 6.3 and 28 eV.

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Since the discovery of the spherical, hollow C_{60} carbon cluster [1] and of a method [2] for its bulk synthesis, many spectroscopic techniques have already been brought to bear on the elucidation of the vibrational, electronic, and other properties of this molecule in its gaseous and condensed states.

Here we report on new spectroscopic results on C_{60} obtained by high-resolution electron-energy-loss spectroscopy (HREELS) in the specular reflection geometry. We have measured the frequencies of 11 of the 46 distinct vibrational modes of the molecule and 19 bound-bound and bound-free electronic resonances from 1.5 to 30 eV. In particular, we have observed the lowest electronic excitation of C_{60} at 1.55 eV. We further argue that a single molecule can support collective resonances, similar to those of graphite, whose quanta occur at 6.3 eV for the π electrons (π plasmons) and around 28 eV for the complete valence shell (σ plasmons). We conclude by a simple evaluation of the van der Waals cohesive energy of C_{60} fullerite, a large part of which arises from the interaction between the latter σ plasmons of $l=1$ symmetry on neighboring molecules.

The experiments were conducted, in a UHV system, with a high-resolution electron spectrometer consisting of two 180° hemispherical electrostatic selectors set at 45° incidence and reflection angles and 1.5° acceptance aperture. The energy of the electron beam E_p can be varied from 0 up to 150 eV. The energy resolution is about 10 meV for the ir region and 0.06 eV for the visible and uv regions.

The fullerene powder was produced as described in [2] and sublimed onto a clean surface of Si(100) held at room temperature. The thickness of the film was estimated with a quartz oscillator to be about 60 Å. In discussing the spectra we have ascertained that one can ignore the weak contribution of the minority film constituent C_{70} ($<10\%$).

Figure 1 shows the ir spectrum below 450 meV. There are 11 distinct peaks below 200 meV at frequencies listed in Fig. 2(a) where they are compared with infrared absorption spectroscopy (IRAS) [3], Raman [3], and neutron [4] results. The most intense HREELS band at 66 meV (532 cm^{-1}) falls near the two strongest (unresolved) IRAS lines at 527 and 577 cm^{-1}. From the dielectric theory of EELS [5,6] one expects that the strongly dipole-active modes should indeed make a large contribution to the loss spectrum. However, some strength in the low-energy side of the 66-meV band is likely to be due to the Raman-active, radial-breathing mode at 496 cm^{-1}. This mode can be efficiently electron excited in a Raman-like process, i.e., via the modulation imparted by the breathing motion to the multipolar polarizability of C_{60} and hence to the interaction energy with the slow electron impinging on the molecule.

The other three intense HREELS bands at 94, 156, and 194 meV in Fig. 1 correlate better with dipole-

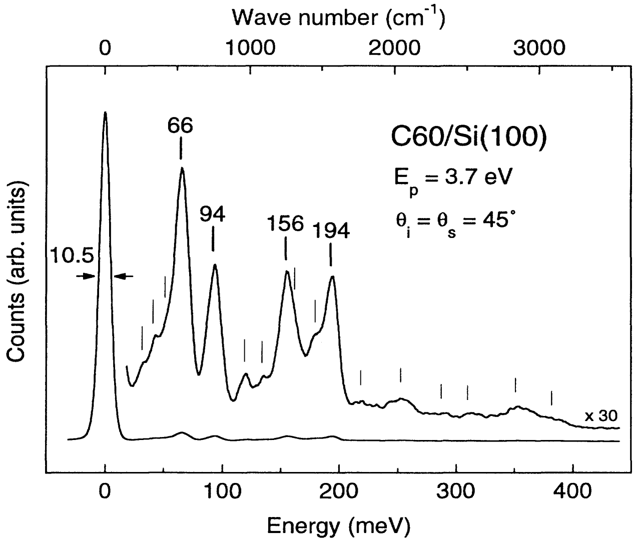

FIG. 1. HREEL spectrum of C_{60} film/Si(100) in the infrared. Peak positions are indicated by bars.

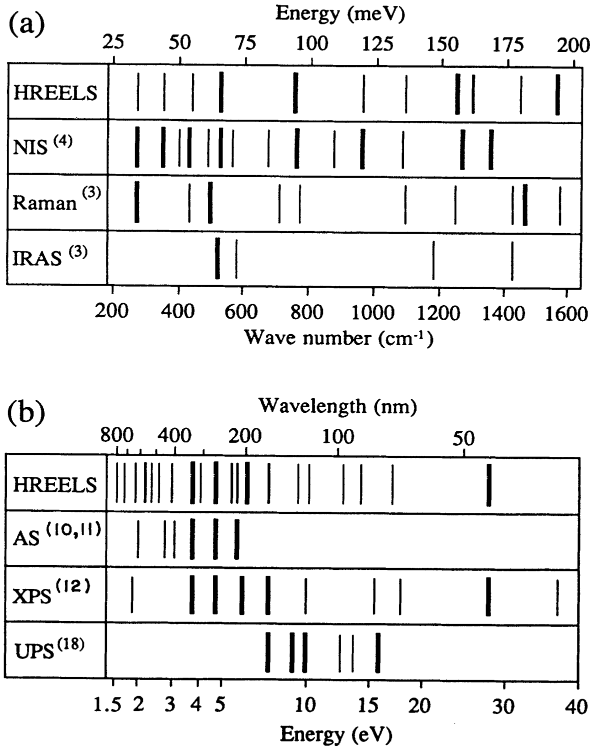

FIG. 2. Peak positions of excitation bands of C_{60} as measured by several techniques. (a) ir range. (b) Visible-vuv range. The strong features in each spectroscopy are indicated by a thick line. Note the nonlinear energy scale in (b).

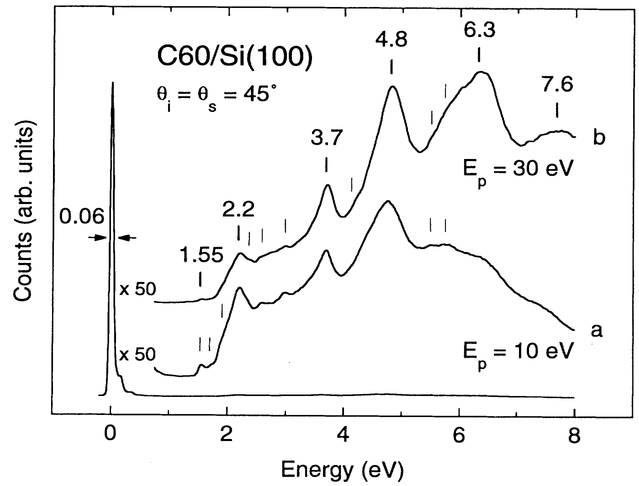

FIG. 3. The visible and uv HREEL spectrum of C_{60}/Si(100) for two primary electron energies: curve *a*, 10 eV and curve *b*, 30 eV. Peak positions are indicated by bars.

inactive, Raman, or neutron lines than with the other two weak IRAS lines at 1183 and 1428 cm^{-1}. A qualitative indication as to the nature of the carbon frame motions giving rise to the strong HREELS bands can be gained from the phonon dispersion relations on a basal surface of crystalline graphite observed by the same HREELS technique [7]. In graphite, there are large density of vibrational states around 55, 90-100, 155, and 180-200 meV. These four frequency domains closely correspond to our four C_{60} strongest bands, as if dense concentrations of vibrational frequencies of a graphitic sheet persisted when warping the sheet into the C_{60} spherical geometry.

The weak bands above 200 meV in the HREEL spectrum (Fig. 1) are combination bands with energies higher than 200 meV obtainable from our four strongest HREELS peaks. The 360-meV band can include a contribution from the CH stretch of a minor hydrocarbon contamination.

Turning to the visible range, Fig. 3, curve *a*, shows a spectrum with primary electrons of 10 eV (resolution, 60 meV). There is a very clear peak at 1.55 eV. We believe we are observing here, at high resolution, the accurate value of the first one-electron excitation in C_{60}. This transition may, but because of possible excitonic effects, need not coincide with the highest-occupied molecular orbital–lowest-unoccupied molecular orbital level separation such as theoretically predicted at 1.7 eV [8] or with the C_{60} fullerite band gap calculated at 1.5 eV [9]. The HREEL visible spectrum comprises seven further peaks up to 4 eV. They are listed in Fig. 2(b) along with data from other spectroscopies. Two peaks are outstanding at 2.2 and 3.7 eV. The latter corresponds to the sharp 329-nm peak observed in the absorption spectrum (AS) of thick C_{60} samples [10,11] as well as in x-ray photoemission spectroscopy (XPS) [12]. The former is absent from both AS and XPS. The other six visible peaks are weaker structures occurring at 1.72, 1.92, 2.36, 2.58, 3.0, and 4.1 eV.

Above 4 eV, see Fig. 3, curve *a*, there is a large HREELS peak at 4.8 eV which definitely correlates with the familiar strong AS band at 260 nm and with the strong XPS peak at the same energy. This peak and the two intense HREELS peaks at 2.2 and 3.7 eV discussed previously have intensities which remain nearly independent of the primary electron energy E_p in a wide range from 10 to 50 eV, as shown in the two sample spectra of Fig. 3, curves *a* and *b*. This is in sharp contrast to the behavior of the next group of intense peaks around 6 eV. This group is in fact made of three peaks: two peaks of nearly constant intensity at 5.5 (225 nm) and 5.8 eV (214 nm) and a third, initially smaller, one at 6.3 eV (197 nm), whose intensity grows continuously when E_p increases above 10 eV. For E_p at or above 30 eV, the 6.3-eV peak intensity saturates (Fig. 3, curve *b*) and dominates the 5.8-eV one which persists as a shoulder. Together with the 4.8-eV peak, the 6.3-eV shouldered band forms the familiar "camelback" structure so characteristic of the AS spectrum of C_{60} [10].

It is instructive to compare the present HREEL spectra in the 6-eV region to the corresponding spectrum of a graphite basal surface [13,14]. In crystalline graphite, there is the so-called π-plasmon peak at 6.3 eV in the loss function $\mathrm{Im}\varepsilon^{-1}$ for small momentum transfer measured by EELS [13-15] or reflectance spectroscopy [16]. It has been interpreted [16] as arising from collective oscillations of the π-electron system. Such oscillations derive from the existence of a group of one-electron π-to-π^* transitions around 4.5 eV in the band structure of graphite. We suggest that the presently observed HREELS peaks of fixed intensity from 2.2 to 5.8 eV represent one-electron π-to-π^* transitions of the C_{60} molecule, whereas the variable intensity peak at 6.3 eV would be the collective excitation in the molecular π-electron system deriving mainly from the 4.8-eV transition. It can be shown that a transport of the graphite dielectric function to a model of the C_{60} molecule consisting of a spherical dielectric shell of finite thickness (warped graphitic layer) produces a dipolar excitation around 6 eV which is the energy quantum $\hbar\omega_\pi$ for tangential, $l=1$ density fluctuations of the π electrons. These π plasmons have a strong dipole moment along a diameter of the molecule and hence can be easily excited by inelastic electron scattering (or by light absorption of the Mie type). The variability of the corresponding peak intensity with primary electron energy E_p is a consequence of the *long-range* nature of dipole scattering which causes the forward peaking of the inelastic cross section along the specular direction. On increasing E_p, the dipole scattering angular lobe shrinks towards the narrow spectrometer aperture, which increases the count rate. A similar effect has been clearly observed in the infrared regime, e.g., for CO molecules adsorbed on Cu(100) [17]. By contrast, the one-electron transitions have a strength which remains nearly independent of E_p (see Fig. 3, curves *a* and *b*) since they cause nearly isotropic scattering in virtue of the impact or *short-range* nature of their coupling to the electrons.

Moving to the vuv region, two spectra taken with primary electron energies E_p at 70 and 150 eV are shown in Fig. 4. The observed peaks are compared to the data of photon spectroscopies in Fig. 2(b). There are six HREELS peaks which remain nearly constant in relative intensity for increasing E_p. The first peak at 7.6 eV is the strongest and correlates very well with the lowest ionization energy of the C_{60} molecule as determined by Lichtenberger *et al.* [18] by ultraviolet photoemission spectroscopy (UPS). The next five peaks occur at positions close to but not exactly coincident with UPS lines [12,18]. Figure 4 further illustrates the emergence of a broad band around 28 eV when E_p increases. We interpret this feature as due to the excitation of embryonic "σ plasmons," i.e., collective motions (principally the $l=1$ modes) of the entire 240 electrons of the valence shell. The intensity of this peak, relative to the 6-eV camelback which remains fairly unchanged throughout, has been observed to grow continuously with increasing primary energy. We argue that this is due to the same long-range dipole coupling effect as we proposed for the emergence of the π plasmon at 6.3 eV. The present interpretation of the 28-eV peak which makes it a purely molecular property is consistent with the fact that the fullerites are van der Waals solids in which the intermolecular interactions per molecule are of the order of 1 or 2 eV at most, i.e., small as compared to the σ plasmon quantum.

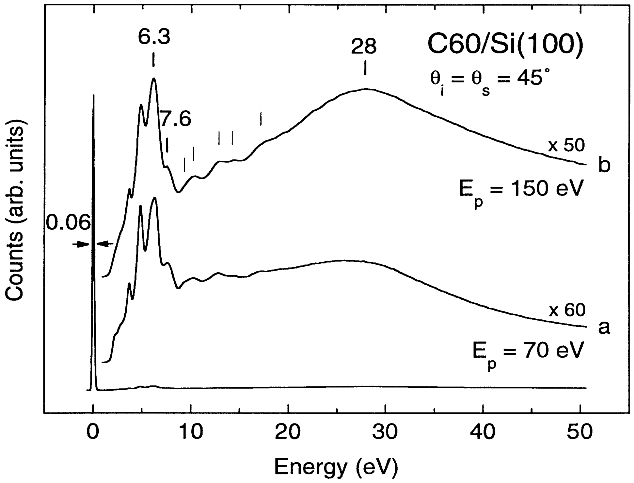

FIG. 4. The uv and vuv HREEL spectrum of C_{60}/Si(100) for two primary electron energies: curve *a*, 70 eV and curve *b*, 150 eV. Peak positions are indicated by bars.

Finally, we note that the van der Waals cohesive energy of C_{60} fullerite can be understood as originating primarily from the zero-point fluctuations of the tangential, $l=1$ σ plasmons, via the weak dipole-dipole interactions of neighboring molecules. A qualitative evaluation of this energy can be obtained as follows. Let $n=4/a^3$ be the molecule number density in the fcc lattice of parameter a and let $\alpha(\omega)=\alpha(0)/(1-\omega^2/\omega_\sigma^2)$ be a Lorentzian model for the σ-electron dynamical polarizability of the C_{60} molecule (we ignore the π plasmons of weaker dipole strength and smaller zero-point energy). Start from the Clausius-Mosotti formula which embodies the dipole-dipole interactions in cubic lattices: $\varepsilon(\omega)=(1+2z/3)/(1-z/3)$, where $z(\omega)=4\pi n\alpha(\omega)$. The zero of $\varepsilon(\omega)$ gives the frequency $\omega_L=\omega_\sigma(1+2z_0/3)^{1/2}$ of the longitudinal polarization eigenmodes of long wavelengths in the solid, whereas the pole of $\varepsilon(\omega)$ occurs at the doubly degenerate frequency $\omega_T=\omega_\sigma(1-z_0/3)^{1/2}$ of transverse modes, where $z_0=z(0)$. We neglect the dispersion of the polarization waves for finite k in the Brillouin zone. Then the van der Waals energy per molecule is given by the shift in zero-point energy of the above three modes on going from the equilibrium value of a to infinite a: $W=\frac{1}{2}\hbar(\omega_L+2\omega_T-3\omega_\sigma)$. Use $a=14$ Å and $\alpha(0)\approx 64$ Å^3 for the static polarizability of C_{60} (i.e., about 1 Å^3 per C atom, a value close to the best theoretical estimate of 65 Å^3 calculated by Fowler, Lazaretti, and Zanasi [19]).

This gives $z_0=1.17$. We choose $\hbar\omega_\sigma=25.6$ eV for which the HREELS surface loss function $-\mathrm{Im}[\varepsilon(\omega)+1]^{-1}$ peaks at the observed $\hbar\omega=\hbar\omega_\sigma(1+z_0/6)^{1/2}=28$ eV. With these parameters, one finds $W=-1.33$ eV. This constitutes a major piece of the cohesive energy evaluated at -1.6 eV by the local-density approximation [9] and at -1.9 eV by model pair potentials [20]. Neglecting the dispersion of polarization waves overestimates the van der Waals attraction [21] but multipolar contributions from π and σ plasmons of higher l's should provide additional binding.

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