Optical transitions of C_{60} films in the visible and ultraviolet from spectroscopic ellipsometry

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Optical spectra for C_{60} films, obtained by ellipsometry, are reported for the energy range from 1.9 to 9.5 eV. Our results are compared with related results from other optical techniques as well as photoemission results. Strong similarity to absorption measurements of dissolved C_{60} results from the strong molecular character of the solid films. We fit our spectra with Lorentzian line shapes to determine energy positions and shapes of the transitions. We observe the onset of optical absorption near 1.9 eV. We also report initial results from alkali-metal doping and a useful method for incorporating K into the bulk of film samples.

I. INTRODUCTION

The ability to produce the C_{60} molecule in large quantities has resulted in an interesting form of solid carbon.[1] Reminiscent of condensed organic molecule solids, the solid is apparently formed by weak van der Waals bonding between the molecules which are largely undisturbed. Unlike most other molecular solids, the sphere-like molecules form a three-dimensional isotropic crystal, which is fcc at room temperature with large rotational disorder of the molecules at these lattice sites. Solid specimens have been formed by crystal growth from solution and by thin-film deposition.

The optical properties of the molecules have been of initial interest with respect to their possible effect on interstellar absorption.[2] Molecular absorption spectra have been obtained for the material dissolved in nonpolar solvents such as benzene, toluene and hexane.[3,4] These results suggest that the molecule in its neutral form is probably not the cause of a cosmic absorption line. In the solid form the optical properties have been studied by transmission through thin films,[1,5] by electron energy loss,[6-10] and by ellipsometric measurement.[11] Comparison of the bulk to molecular spectra can help reveal the effects of condensation on the electronic structure. This is particularly feasible in this case due to the high symmetry of the molecules. In cases of aromatic molecules such as anthracene, the planar form complicates comparison of disordered gas or liquid phase spectra with oriented crystal properties.[12]

The optical measurements have shown an absorption onset near 1.8 eV (Ref. 13) and a series of stronger absorptions up to 6 eV. Theoretical analyses of the molecular structure indicate that this energy range is dominated by $\pi \rightarrow \pi^*$-like excitations as in aromatic organic molecules and graphite.[14-17] In order to compare strength and energy of optical transitions to band positions obtained from calculations, or density-of-states type measurements such as photoemission, the most conve-

nient optical function to use is the dielectric function ϵ. For other investigations, such as transmission properties in films, the index of refraction is of interest. Since these quantities are only indirectly obtained from absorption measurements through Kramers-Kronig transformation, it is useful to obtain them directly, as is possible with ellipsometric measurement.

Here we present the results of such measurements on thin-film samples, identifying the energy position and strength of several transitions in the visible and ultraviolet energy range. The agreement with other such measurements made on pure C_{60} films is good.[11] Some differences at low energies will be discussed below. Our spectra with more data points and over a somewhat larger energy range permit a more detailed study of the line shapes. The absorption spectrum calculated from the experimentally determined dielectric function compares well with previous transmission measurements,[1,5] but is less susceptible to difficulties from inhomogeneous film thickness, thus providing complementary confirmation of the values. The results for the films also show very strong similarity to the molecular absorption spectra, when compared using an effective medium model, emphasizing the weakness of the interaction between molecules within the solid.[3,4] We compare our transition energies to those derived from electron spectroscopy of occupied and unoccupied states[17,18] as well as from electronic structure calculations[16,19] and make tentative assignments of the bands involved in the transitions. Finally, we note that such measurements show distinct features due to transitions from unoccupied levels which become filled by doping techniques used to induce metallic properties in these solids.

II. EXPERIMENT

Our samples were made from C_{60} produced by the contact arc technique and separated by toluene solvation.[1] The dried material was then evaporated onto synthetic

quartz (Suprasil) flats in vacuum. It is important to note that the soluble carbon material includes about one part in ten of the related molecule C_{70}. While it is desirable to obtain spectra on the separated components, as has been done in some of the referenced work,[3,4,7,11] the current level of purity is sufficient for our conclusions, as confirmed by comparison with the measurements of pure C_{60}, and should not greatly affect the usefulness of the spectra for comparisons and other studies requiring optical properties as input parameters. The C_{60} purity was also improved through the evaporation process by taking advantage of the higher relative vapor pressure of C_{60}.[5]

Measurements were made at room temperature, in air and also after growth within the vacuum chamber, using standard techniques of rotating analyzer ellipsometry.[20] Measurements have been made on samples of varying thickness and age to confirm repeatability and stability. The lower energy limit of the spectra was at 1.9 eV, below which transparency allows interference from reflections at the back of the film-substrate interface. At the high-frequency end, we have somewhat extended the range of our ellipsometer beyond the typical 6 eV with improved optics, primarily a double pass monochromator with grating blazed for the ultraviolet that allows measurement to approximately 6.5 eV in air, with no observable effect from stray light. Measurements in vacuum have also been extended to 9.5 eV using a synchrotron radiation ellipsometer.[21]

In this high-energy range we have also obtained results for films doped with K, which has been shown to produce metallic character that becomes superconducting at low temperature.[22,23] For this purpose, the films were exposed to K vapor from a commercial alkali-metal source (SAES Getters, Corp.) operated at 6.0 A and at a distance of about 8 cm. Although doping in the surface region has been obtained for photoemission experiments in this manner,[24,25] we found that such exposure at room temperature produced very weak effects in the optical spectra which probe a thicker region of the sample. Successful doping was obtained by K exposure to a substrate held at liquid-nitrogen temperature for times of the order of 100 min, which produced a condensed film of K. Annealing the sample to room temperature then resulted in removal of this film, as expected due to the high vapor pressure of K at room temperature,[26] with incorporation of bulk quantities of K in the film as indicated by strong changes in the optical spectra. This indicates high mobility of K in C_{60}, even at low temperatures.

Ellipsometric measurements produce values for the complex reflectance ratio between p- and s-polarized light. The dielectic function can then be calculated based on a model of the reflection process. In this case we use the simplest model of a sharp interface between sample and air ambient. We make the reasonable assumption that the sample is isotropic (it is probably polycrystalline). Minor differences could result from surface roughness, but we anticipate that this is also small.

III. RESULTS

The calculated dielectric function $\epsilon = \epsilon_1 + i\epsilon_2$ is shown in Fig. 1 for two different samples of thickness roughly
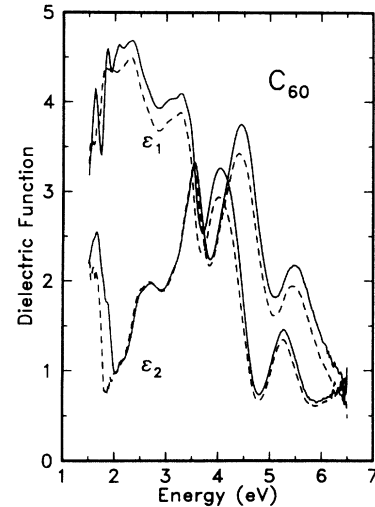

FIG. 1. Measured dielectric function for 1.5 μm (solid) and 5.5 μm (dashed) C_{60} films on quartz substrates. The first is measured after growth in vacuum and the second after several weeks in air. Sharp structure below 2 eV is spurious and results from back surface reflection interference in this transparent regime.

1.5 μm and 5.5 μm. The spectrum for the 1.5 μm sample was obtained in vacuum shortly after growth and the second spectrum is from a sample that was several weeks in air. The main differences between the two are typical of aging effects and may represent some decomposition or possibly absorption of moisture or other molecules. Other smaller differences could be due to differences in surface topography, film density or [C_{60}]/[C_{70}] ratio. In order to facilitate comparison with other measurements and provide data helpful to other studies we also show in Fig. 2 the complex index of refraction $\tilde{n} = n + ik$, the reflectance R, and the loss function $-\text{Im}(1/\epsilon)$. Also
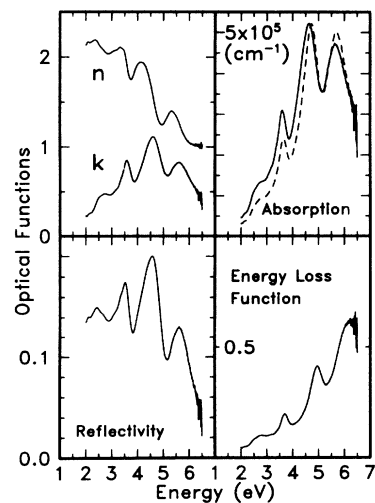

FIG. 2. Optical functions calculated from the dielectric function data of the 1.5 μm C_{60} film. The dashed line represents absorption for an effective medium representing a dilute solution, as described in the text, and has been arbitrarily scaled to fit the plot.

shown are absorption coefficient $\alpha = \omega \epsilon_2 / nc$, as well as the absorption calculated for a Maxwell-Garnett effective medium model[27] of bulklike C$_{60}$ particles dissolved in a host with the dielectric constant of hexane, which in a first-order approximation for a dilute solution is proportional to $\omega \epsilon_2 / ([\epsilon_1 + 2\epsilon_h]^2 + \epsilon_2^2)$.

In general it can be seen that the measured ϵ_2 spectra are composed of optical absorption bands at 2.6, 3.5, 4.4, and 5.5 eV, which are sharp features suggesting that they have molecular character. Near 1.9 eV, the sample becomes transparent enough for interference effects from the back of the film. This interference results in the spurious structure below 2 eV in Fig. 1. We show this structure as indication of probable gap position.

In Fig. 3, high-energy results from the synchrotron radiation measurements are given for a 1 μm film, both undoped and after reaction with K. We were unable to independently determine K composition, but even higher levels appear to be possible. At higher levels, our measurements have been less consistent possibly due to inhomogeneity. By comparison with electron-energy-loss spectroscopy (EELS) measurements,[8] we believe the composition is near K$_3$C$_{60}$. Results below about 5 eV are distorted due to second-order light being passed by the MgF$_2$ polarizer prism. Measurement at liquid nitrogen temperature gave nearly identical results in this energy range.

In the pure film we see that after the sharp features from the near ultraviolet and a shoulder near 6 eV, comes a region of lower absorption followed by broader features near 7.5 and 8.9 eV as well as apparently at higher energy. The dramatic difference in feature sharpness below and above 6 eV suggests that this is the boundary between $\pi \rightarrow \pi^*$ transitions and transitions with σ-like orbitals. Note that the ionization potential for the solid is reported to be near 7.3 eV.[18] The low values of ϵ_1 and ϵ_2 near 6.5 eV correspond to the electron-energy-loss peak described as the π plasmon.[9] The K doping manifests itself in a shifting to lower energy and merging of the features below 6.5 eV, as well as a reduction in magnitude. The minima in the ϵ values near 6 eV again correspond to the shifted peak position observed with EELS.[8] At higher energies there is a change in ϵ_2 as if the absorption edge near 8.5 eV is also shifted to lower energy.

IV. DISCUSSION

We first compare our results to other optical measurements. Transmission measurements in this energy range were performed on film samples with a similar purity level.[1,5,11] These results look very similar to our calculated absorption. The energy positions of the peaks are the same although our magnitudes are about 25% lower, which could be due to differences in film density or perhaps to difficulties with film thickness determination. The results of another ellipsometric investigation[11] are also in good agreement with our results although they show lower absorption at lower energy and indicated a higher value of the optical gap. The difference may be due to the presence of residual C$_{70}$ in our samples, but is probably due to difficulties with interference in the thinner samples of the other experiment. We note that our low energy cutoff corresponds well to absorption measurements of the absorption onset[13] as well as to the EELS measurements,[7] and conclude that the excitation gap between occupied and unoccupied bands is not higher than 1.9 eV. The fact that we obtain back surface reflection interference at nearly the same energy for both our sample thicknesses is a measurement of the abruptness at this threshold.

It is also interesting to compare our results with absorption measurements of the molecules in a transparent solvent. These measurements have been made on separated C$_{60}$ and C$_{70}$ solutions, and two separate studies gave essentially identical results.[3,4] For this purpose, we have calculated the absorption for a Maxwell-Garnett effective medium for a dilute solution as described above. As a simplification, we have used a constant dielectric function for the host solvent of 1.9, similar to hexane. This function is given by the dashed curve of Fig. 2, and represents the optical response of a hypothetical solution of particles large enough to have the properties of the solid, but small compared to the light wavelength. Differences between this curve and the absorption curve of the molecular solution can then be attributed to electronic structure changes due to condensation. Comparison of our figure with the data of Ren et al.[11] for absorption in a film and solution shows that much of the difference can be described by this effective medium model. The C$_{60}$ solution spectra are very similar to our results. The C$_{70}$ molecule shows stronger absorption in the region below 3 eV and so this may be responsible for some of the intensity of our samples in this region also. The strong absorption peaks of the effective medium calculation are shifted by only about 0.1 eV to lower energy compared to the solution spectra, and somewhat broadened, again emphasizing the largely molecular character of the solid.
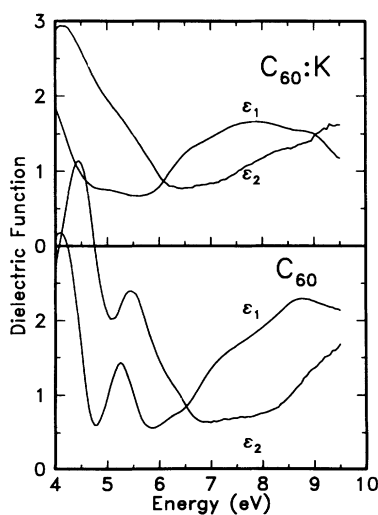

FIG. 3. Measured dielectric function data for a 1 μm film obtained in the vacuum ultraviolet with synchrotron radiation. The upper curve shows the result of K doping, which we estimate by comparison with other results to be near composition K$_3$C$_{60}$.

The relative magnitude of the 5.7 eV feature to the 4.7 eV feature is higher for our calculation than for the actual solution spectra. This could be due to an increase in the actual dielectric function of hexane at higher energy, but may also represent another result of condensing into a solid. Naturally, the solvent itself may change the spectra with respect to isolated molecules.

The similarity of the spectra for solid and solution encourages us to consider assignments of the optical transitions based on molecular orbitals. Several sets of calculations resulted in similar ordering of the orbitals identified by their representation in the icosahedral symmetry group.[14,15] Band-structure calculations indicate that this orbital character is largely retained in the solid,[16,19] with bandwidths being generally narrower than the spacing between orbital-derived bands. Photoemission and inverse photoemission measurements of films also give spectra with sharp moleculelike features, further supporting this idea.[17]

In Fig. 4 we show a possible energy-level diagram using the ordering and symmetry of orbitals reported in Ref. 15, and energy positions estimated from the photoemission and inverse photoemission results.[17] For this purpose, we used the energy spacing between peaks or critical points within the occupied or unoccupied states spectra. Estimates of the positions are thus limited in accuracy, due to our somewhat subjective determination of shoulders and to overlap with other features, to $\pm$ 0.3 eV. Band dispersion also affects these estimates. The gap between occupied and unoccupied states is not obtained from these spectra which give ionization potential and electron affinity, respectively. (For molecular crystals, the difference between these need not correspond to the energy gap for nonionizing transitions. Evidence for this distinction can be seen in the change in relative position of the conduction band as it becomes occupied due to

FIG. 5. Fits of experimental data (crosses) with Lorentzian line shapes. Model 1, dashed; model 2, solid. The second derivative of the data and model 2 are shown in the inset.
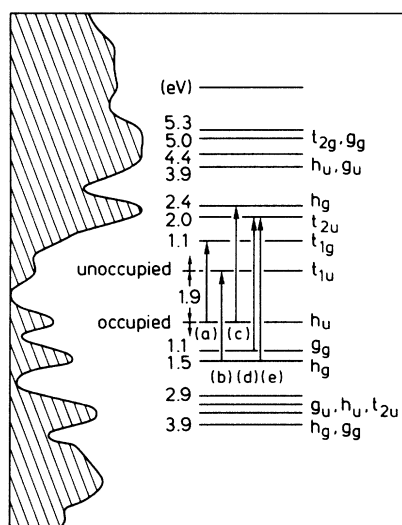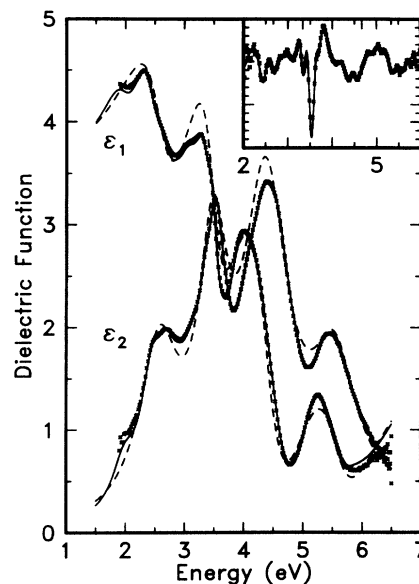

FIG. 4. Schematic energy-level diagram using molecular orbital ordering from Ref. 15, and estimated energy positions from photoemission and inverse photoemission spectra of Ref. 17, which are represented by the curves on the left. Symmetry-allowed transitions are indicated by arrows.

doping with K.[24,25]) Instead we use a gap value of 1.9 eV which is consistent with many of the optical measurements.

The lower energy transitions allowed by the molecular symmetry are also indicated in Fig. 5. The values for the transition energies are then determined assuming a gap of 1.9 eV, which is a nonallowed transition for the molecule, and rigid band positions. The transition energies derived from the figure for the $h_u \rightarrow t_{1g}$, $h_g \rightarrow t_{1u}$, $h_u \rightarrow h_g$, $g_g \rightarrow t_{2u}$, and $h_g \rightarrow t_{2u}$ transitions are then near 3.0, 3.4, 4.3, 5.0, and 5.4 eV, respectively. By comparing these derived values with our optical spectra, we tentatively assign $h_u \rightarrow t_{1g}$ to the 2.6 eV transition region, $h_g \rightarrow t_{1u}$ to the 3.5 eV, $h_u \rightarrow h_g$ to the 4.4 eV, and $g_g, h_g \rightarrow t_{2u}$ to the 5.6 eV regions. In addition: the weaker structure near 6 eV in Fig. 3 could be associated with transitions to the lowest unoccupied orbital t_{1u} from the large density of states near 3.5 eV binding energy which include h_g symmetry states, and transitions from this region to the two strong features in the unoccupied density of states at 2.4 and 4–5 eV above t_{1u} may be responsible for the broader features at 7.7 and 8.9 eV.

These assignments are readily compared with the calculations of optical properties by Ching *et al.*[19] and in general the agreement is good, although not surprisingly the intensities are rather different. The primary difference, other than that the calculation takes more transitions into account than the simple allowed molecular transitions, is in the energy position of the $V2 \rightarrow C1$ or $h_g \rightarrow t_{1u}$ transition which we attribute to the measured feature at 3.5 eV, and in the calculation is at significantly lower energy. Since these transitions should be hindered by doping which fills the conduction band, and this seems to be the case for the 3.5 eV feature according to EELS measurements[8] and to our preliminary optical studies,

we believe our assignment correctly describes the 3.5 eV absorption.

This assignment of the optical transitions still leaves some points to be explained. It puts the centroid of the first allowed transition at 3 eV. While the film spectra show appreciable absorption in this range, the solution results show only weak structure[3,4] and it is unclear why this allowed transition should be so weak for the molecule. We note, however, that a recent calculation for the molecules indicates that this transition should be strongly screened by collective excitations, apparently corresponding to the π plasmon.[28] This effect might also bring the magnitudes from the band-structure calculation[19] into closer agreement with the data. Calculation of the transitions using a larger gap value can also solve this problem by assigning the 3.5 eV structure to $h_u \rightarrow t_{1g}$, but does not fit well the measurements at higher energies. (In this case we would expect the 4.4 eV absorption to be strongly reduced by doping.) Discrepancies between transition energies derived from ionizing and nonionizing excitation spectra may result from band dispersion or be indications of strong correlation effects beyond the one-electron band picture. This is also indicated by the nonrigid shifting of the photoemission peaks during doping experiments.[24,25]

In order to better understand the optical results, we have attempted to model the spectra as the sum of Lorentzian line shapes. The results are shown in Fig. 5 and tabulated in Table I. Two models are shown. The first is composed of only four Lorentzians for the four structures, as well as high-energy absorption to adjust the

TABLE I. Models of the spectra as the sum of Lorentzian line shapes.

	Model 1			Model 2	
E_0	E_p	Γ	E_0	E_p	Γ
			2.0	0.65	0.5
			2.45	1.04	0.45
2.6	1.8	0.8	2.71	1.04	0.45
			2.9	0.4	0.3
			3.15	1.3	0.55
			3.355	0.7	0.25
3.5	2.2	0.6	3.535	1.48	0.33
			3.695	0.59	0.27
			4.1	1.82	0.63
4.4	3.5	0.9	4.365	1.715	0.5
			4.581	1.715	0.5
			4.8	1.3	0.6
			5.1	0.08	0.08
			5.35	1.3	0.5
5.55	2.6	0.9	5.58	1.55	0.55
			5.95	1.75	1.0
7.7	1.0	1.0	7.7	1.0	1.0
8.9	2.2	1.2	8.9	2.2	1.2
10.0	3.5	1.2	10.0	3.5	1.2
12.2	10.0	2.5	12.2	10.0	2.5

absolute value of ϵ_1. The second uses many more peaks, but achieves an extremely good fit. Also in this case, the number and position of the peaks are not arbitrary, but were indicated by the critical points revealed in a second derivative of the spectrum as shown in the inset. The precision of the parameter values for this case is clearly too high in relation to the difference between the spectra from different samples, but the values are reported to demonstrate the good fit that is possible. Either addition of the Lorentzian strengths, E_p^2, or applying the sum rule directly to our ϵ_2 data give that the equivalent of $\approx$12 electrons per molecule are participating in the absorptions up to 6.5 eV. This may be compared to the 28 electrons per molecule occupying the first three orbitals. The number is also lower than that for graphite where about 1 electron per atom participates in the Drude and $\pi \rightarrow \pi^*$ excitations.[29] This result is also in agreement with the screening of low-energy transitions by collective excitations.[28]

The success of the fits is an indication and result of the strong molecular character of the electronic structure. The peaks are, however, too numerous, compared to the number of orbitals available, if all degeneracies hold. In particular, it can be seen that three of the features can be decomposed into two doublets as well as broader features. The 3.5 eV feature appears as a sharp central peak with sharp smaller peaks on both sides. The structure of these features may well be the result of band dispersion. In particular the doublet structure may correspond to band maxima and minima. On the other hand, the strong moleculelike character suggests the possibility of nondegenerate final-state configurations for the molecules. It would be interesting to better understand the validity of single-electron models for this solid vis-à-vis the importance of configuration interactions which have been shown important for molecular transition calculations.[30]

Finally, we point out again the possibility to verify our assignments by comparison with heavily K-doped material, where transitions to the t_{1u} level will be quenched and new transitions from this level will be possible. In addition to these changes, other results due to nonrigid band movements are possible. According to our assignments, we could expect the peak at 3.5 eV to vanish and new peaks near 1.1 and 2.4 eV, corresponding to $t_{1u} \rightarrow t_{1g}$ and $t_{1u} \rightarrow h_g$, to appear. This seems to be consistent with the EELS observations of Ref. 8. In addition the transitions causing the broad 6 eV peak could be eliminated as suggested by our high-energy spectra. The strong effect on the 5.6 eV peak is more difficult to explain using only this rigid band picture.

V. CONCLUSION

Comparison of our measurements with those by other techniques, as well as theoretical structures of C_{60} have enabled a tentative assignment of optical features to molecularlike transitions. Compatibility with density-of-states spectra from ionizing excitation spectra is reasonable. However, there remain difficulties and it will

be interesting to better understand the relative influence of band dispersion and configuration-interaction effects. Our measurements support a value for the optical gap near 1.9 eV or below. Our assignments seem to be compatible with changes in the spectra resulting from alkali-metal doping. Finally, in the course of the latter measurements we have found a convenient method for achieving K doping to significant depths in thin films.

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