Electronic structure of C\textsubscript{60} films

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A complete set of fundamental optical functions of fullerite (C\textsubscript{60}) films in the range 1.5–7 eV is calculated from the known spectra of the imaginary and real parts of the dielectric permittivity. The total permittivity spectrum is expanded into elementary components. Three main parameters are determined for each component (the energy of the band maximum, the band half-width, and the oscillator strength). An interpretation of these components of the permittivity is proposed on the basis of published theoretical band calculations for fullerite.

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In recent years there have been many publications on the third (after diamond and graphite) modification of carbon — the giant C\textsubscript{60} molecule — in the form of a free molecule (fullerene), in solutions, and in the solid state (fullerite) as thin films and small single crystals.\textsuperscript{1–5} The absorption spectra of free C\textsubscript{60} molecules and C\textsubscript{60} molecules in various solvents as well as the absorption and reflection spectra of fullerite have confirmed that the individuality of the electronic structure of the C\textsubscript{60} molecule is retained, for the most part, in the crystal.\textsuperscript{5–8}

Fullerite C\textsubscript{60} is the lowest representative of the fullerite C\textsubscript{n} group. The properties of fullerites can be modified considerably, including elevation of the superconducting transition temperature to 30 K, by the intercalation of various impurity atoms. It is therefore of fundamental importance to investigate the electronic structure of fullerite over a wide range of intrinsic absorption energies.

The objective of this report is to remedy deficiencies in Refs. 7 and 8, to derive a complete set of optical functions of fullerite in the energy range 1.5–7 eV, and to determine the most complete spectrum of optical transitions and their parameters.

The most accurate spectra of the imaginary part (\(\varepsilon_2\)) and the real part (\(\varepsilon_1\)) of the dielectric constant of C\textsubscript{60} films in the range 1.5–7 eV have been obtained in Ref. 7 from the room-temperature reflection and transmission spectra. The films were deposited on fluoride and fused quartz substrates at a substrate temperature of 393 K. The air-exposed surface of the film changes with time. The spectra of the reflection coefficient \(R(E)\) from the films through the substrate (Figs. 1 and 2) were therefore used for the calculations of \(\varepsilon_2\) and \(\varepsilon_1\). We calculate all the remaining optical functions on the basis of the spectra in Ref. 7, using standard equations\textsuperscript{9,10} (Fig. 1). The experimental \(\varepsilon_2\) spectrum contains maxima at 2.75 eV, 3.55 eV, 4.50 eV, and 5.50 eV, along with a weak band at \(\sim 2.05\) eV and a step at 2.5 eV. The calculated absorption functions \(\mu\) (absorption coefficient), \(k\) (extinction coefficient), and \(E^2\varepsilon_2\) have a similar structure except that the maxima are shifted approximately 0.05 eV toward higher energies, and the absorption coefficient \(\mu\) is a maximum in the two shortest-wavelength bands. The maxima of the real part of the dielectric constant \(\varepsilon_1\) are situated at 2.4 eV, 3.18 eV, 4.1 eV, and 5.3 eV, i.e., they are shifted approximately 0.3–0.4 eV toward higher energies from the \(\varepsilon_2\) maxima. The spectra of the reflection coefficient \(R\) and the refractive index \(n\) also contain four principal bands; the maxima of \(n\) and \(\varepsilon_1\) are very close to each other, while the reflection bands are shifted quite far toward higher energies, with the \(R\) maxima near the \(\varepsilon_2\) maxima. The curve representing the number \(n_{\text{eff}}\) of valence electrons involved in transitions up to a given energy \(E\) closely resembles the \(\varepsilon_2\) spectrum, where \(n_{\text{eff}}\approx 0.25\) and 1.5 in the first two long-wavelength transitions (\(E<4\) eV) and \(\sim 6\) in the next two, strongest transitions (\(E=4.5\) and 5.5 eV). The maxima of the bulk and surface electron loss characteristics \(-\text{Im} \varepsilon^{-1}\) and \(-\text{Im} (1+\varepsilon)^{-1}\), situated at \(\sim 6.5\) eV and 6 eV, are associated with the excitation of \(\pi\)-plasmons; the remaining maxima at 2.8 eV, 3.7 eV, and 4.9 eV and the structures at \(\sim 6.1\) eV are shifted approximately 0.05–0.5 eV from the \(\varepsilon_2\) maxima and are attributable to transitions similar in nature to those identified with the \(\varepsilon_2\) maxima.

This complete set of fundamental optical functions of a fullerite C\textsubscript{60} single crystal in the energy range 1.5–7 eV affords the first graphic evidence of the relationship of their structures and gives them absolute numerical values. It can be used to analyze the spectrum of possible transitions in greater detail and for theoretical calculations of the electronic structure.

Chiu et al.\textsuperscript{11} have measured the transmission spectrum of a thick (thickness \(d=0.3\) cm) C\textsubscript{60} single crystal. According to the calculations, allowed direct transitions begin at an energy \(E\approx 1.7\) eV (300 K). The experimental data on the absorption spectra of C\textsubscript{60} thin films in the range 1–6 eV (Ref. 12) are in good agreement with our calculated data on the positions of the maxima of the bands and the values of the absorption coefficient. The spectrum of characteristic electron losses of C\textsubscript{60} films, obtained with use of high-resolution instrumentation, contains peaks at 2.8 eV, 3.7 eV, and 4.8 eV (Refs. 13 and 14), in good agreement with our calculations. The good agreement between the cited experimental
data\textsuperscript{11–14} and our calculated data for the absorption and characteristic electron loss spectra attest to the reliability of the $e_2$ and $e_1$ measurements in Ref. 7 and our calculations of the complete set of optical functions for C$_{60}$ films in the range 1.5–7 eV.

We have obtained the following conceptually new information by expanding the total $e_2$ curve into components. For this purpose we have relied on the method of Argand diagrams used many times in previous work.\textsuperscript{15,10} The spectrum of the total curve is often reconstructed by a set of $N$ symmetric Lorentz oscillators with parameters $E_i$ (energy), $H_i$ (half-width), and $f_i$ (oscillator strength) by fitting $3N$ parameters, despite the obvious ambiguity and excessive number of fitting parameters (e.g., as in Ref. 8, the number of such parameters for ten bands attains 30!). The method of Argand diagrams avoids fitting parameters altogether. Its basic scheme is to treat the spectra of two functions simultaneously: not only the imaginary part of the permittivity, but

FIG. 1. (a) Experimental $e_1$ spectrum (1) from Ref. 7 and calculated spectra of $R$ (2) and $n$ (3). (b) Experimental $e_2$ spectrum (1) from Ref. 7 and calculated spectra of $k$ (2), $\mu$ (3), and $E^2 e_2$ (4). (c) Calculated spectra of $n_{\text{eff}}$ (1), $-\text{Im } e^{-1}$ (2), and $-\text{Im}(1 + e)^{-1}$ (3).