Interband dielectric function of C_{60} and M_6C_{60} (M = K,Rb,Cs)

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We report the room-temperature optical properties of C_{60} and M_6C_{60} determined from the near-normal-incidence reflection and transmission experiments. The observed peak positions in $\epsilon_2(\omega)$ for C_{60} and M_6C_{60} compare well with recent band-structure calculations and suggest that the M_6C_{60} compounds exhibit a weak hybridization between the C_{60} and M states, consistent with the Raman-scattering studies of M_6C_{60}. The onset of absorption across the energy gap between the highest occupied molecular orbital (MO) and the lowest unoccupied MO in C_{60} is measured to be 1.7 eV.

X-ray-diffraction studies have shown recently that three distinct compositions of alkali-metal (M) -doped C_{60} fullerite compounds can be prepared: M_3C_{60}, M_4C_{60}, and M_6C_{60}.[1] The first two phases are metallic, and the third is insulating, as would be expected from the progressive filling of the C_{60}-derived t_{1u} band due to charge transfer from the alkali-metal atoms to the C_{60} clusters. Of particular interest in the M_xC_{60} compounds is the observed superconductivity in the M_3C_{60} phase: K_3C_{60} (T_c=18 K),[2] Rb_3C_{60} (T_c=30 K),[3] $CsRb_2C_{60}$ (T_c=31 K),[4] and Cs_2RbC_{60} (T_c=33 K).[4] Furthermore, transition temperatures T_c as high as 43–47 K have been reported for $Rb_xTl_yC_{60}$.[5] In this paper, we report results of optical studies to determine the dielectric function $\epsilon(\omega)$ of C_{60} and M_6C_{60} (M=K,Rb,Cs) over the photon energy range 0.5–6.0 eV. We find essentially the same experimental $\epsilon(\omega)$ for K_6C_{60}, Rb_6C_{60}, and Cs_6C_{60}, and therefore conclude that these compounds are principally ionic, exhibiting weak hybridization between C_{60} and M states. These results suggest that the same behavior should occur in the M_3C_{60} compounds as well.

The C_{60} and M_6C_{60} films studied in this work were prepared as described previously.[6] Alkali-metal doping was accomplished by sealing excess alkali metal (150 °C) and the C_{60} film (200 °C) in opposite ends of a quartz tube maintained at the indicated temperatures for several hours. Room-temperature optical reflectance (R) and transmission (T) spectra were taken at near normal incidence. C_{60} films were handled briefly in air, but the data were taken with a gentle flow of N_2 gas passing over the sample surface. M_6C_{60} films were studied in their quartz growth ampoules and their spectra were corrected for the transmission loss due to the ampoule walls. Raman scattering was used to characterize the C_{60} and M_6C_{60} films which exhibited, respectively, strong polarized Raman lines at $\sim$1469 and $\sim$1432 cm^{-1}, respectively.[6,7] This mode has been identified with the A_g symmetry, "pentagonal pinch" mode of a C_{60} cluster. The downshift of this mode frequency with M doping has been attributed to a charge-transfer-induced softening of the intramolecular C-C bonds.[6–9]

In Fig. 1 we show the reflectance (R) and transmittance (T) of C_{60} and M_6C_{60} films on Suprasil substrates. The (R,T) data are represented by the dashed curves, and the solid curves are calculated using standard expressions[10] for a thin film on a substrate of known refractive index including contributions from multiple internal reflection inside the film. The analysis requires that a parametric form for the dielectric function $\epsilon(\omega)$ be inserted into the expressions for R and T. We use the form given by a sum of Lorentz oscillators[11]

$$\epsilon(\omega)=\epsilon_1+i\epsilon_2=\epsilon_{\text{core}}-\sum_{j=1}^{n}\frac{\omega_{Pj}^2}{\omega^2-\omega_{Rj}^2+i\omega\Gamma_j}\ , \qquad (1)$$

where ω_{Rj}, ω_{Pj}^2, and Γ_j are, respectively, the center frequency, strength, and full width of the jth oscillator, and ϵ_{core} is the core dielectric constant used to approximate interband absorption well beyond the range of the data. The calculated curves in Fig. 1 are determined by adjusting the oscillator and film thickness parameters to fit the R and T data *simultaneously*. As can be seen, the data are reasonably well fit by this procedure. In Table I we collect the $\epsilon(\omega)$ parameters obtained by this analysis for C_{60} and M_6C_{60}.

In Figs. 2(a) (C_{60}) and 2(b) (M_6C_{60}) we display the experimental values of $\epsilon_2(\omega)$ calculated according to Eq. (1)

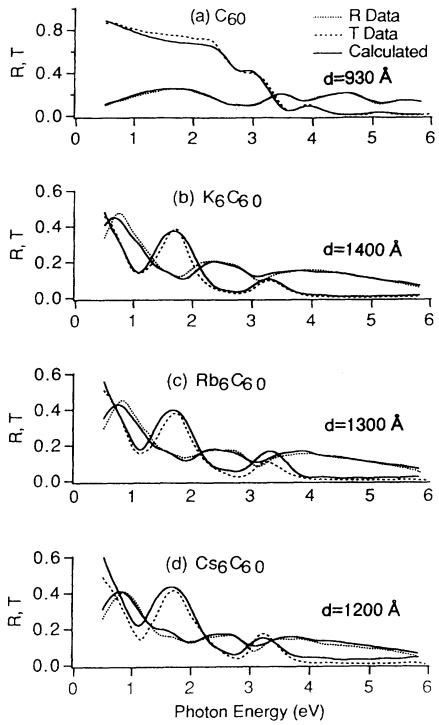

FIG. 1. Reflectance (R) and transmittance (T) of C_{60} and M_6C_{60} films on Suprasil substrates as a function of photon energy. The values given for the film thickness d were determined from the standard (R,T) expressions (Ref. 10) for a thin film with multiple reflections inside the film.

using parameter values found in Table I. The thin solid curves in Figs. 2(a) and 2(b) represent theoretical results for $\epsilon_2(\omega)$ calculated recently by Xu, Huang, and Ching[12] which include the $\mathbf{A}\cdot\mathbf{p}$ matrix elements. For comparison, the $\epsilon_2(\omega)$ data for C_{60} obtained previously by ellipsometry[13] are also shown as (+++++). In agreement with theoretical calculations,[12] the data in the figures

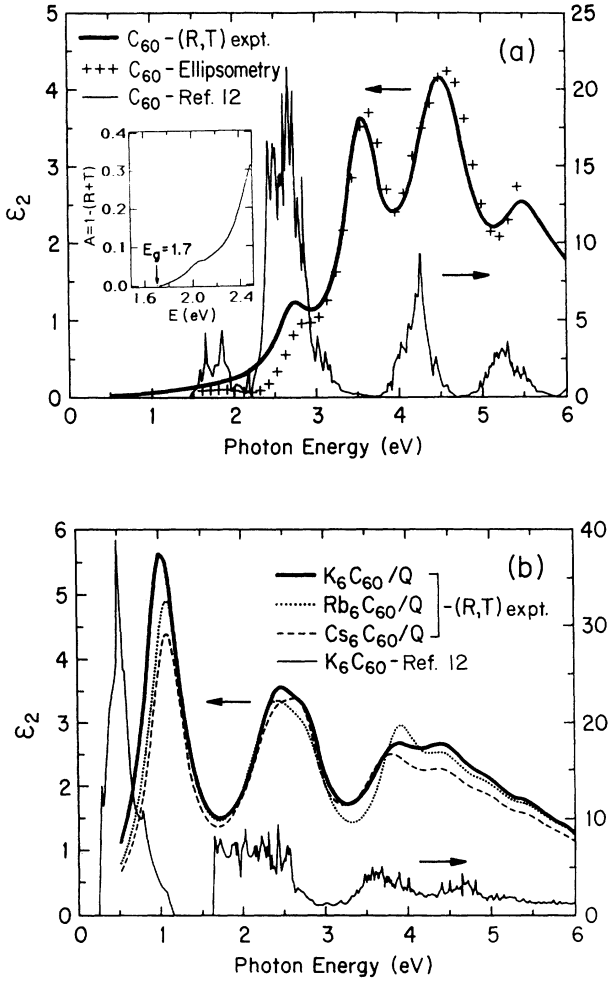

FIG. 2. Comparison of the experimental $\epsilon_2(\omega)$ data for C_{60} and M_6C_{60} with theory (Ref. 15). The inset in panel (a) shows the gap between the highest occupied molecular orbital (MO) and the lowest unoccupied MO (E_g) of 1.7 eV for C_{60}.

TABLE I. Interband optical parameters (in eV) for C_{60} and M_6C_{60}. For the (R,T) data analysis, ϵ_{core} of 2.4 and 3.0 were used for C_{60} and M_6C_{60}, respectively.

			V_1-C_1	V_1-C_2, V_2-C_1	V_2-C_2				
C_{60}	Ellipsometry	ω_R		2.73	3.56	4.56	5.56		
		(ω_P,Γ)		(0.64,0.34)	(2.25,0.46)	(3.87,0.75)	(2.49,0.63)		
	R,T	ω_R		2.73	3.56	4.52	5.50	6.00	
		(ω_P,Γ)		(1.0,0.5)	(2.3,0.52)	(3.8,0.87)	(2.3,0.7)	(2.5,1.0)	
	Ref. 15	$\bar{\omega}_{\text{int}}$	1.9	28,29	3.9				
	Ref. 12	$\bar{\omega}_{\text{int}}$	1.8	2.6,2.9	3.7				
Rb_6C_{60}	R,T	ω_R	1.10	2.40,2.80	3.90	4.47	5.0	5.5	6.0
		(ω_P,Γ)	(1.62,0.52)	(2.2,0.8)(1.5,0.6)	(2.1,0.6)	(2.5,0.92)	(1.8,0.8)	(1.8,0.8)	(1.8,0.8)
Cs_6C_{60}	R,T	ω_R	1.10	2.42,2.75	3.80	4.47	5.00	5.5	6.0
		(ω_P,Γ)	(1.5,0.5)	(2.2,0.85)(1.4,0.5)	(2.4,0.9)	(2.25,0.92)	(1.7,0.8)	(1.7,0.8)	(1.7,0.8)
K_6C_{60}	R,T	ω_R	1.05	2.45,2.80	3.85	4.47	5.00	5.5	6.0
		(ω_P,Γ)	(1.75,0.55)	(2.3,0.8)(1.3,0.5)	(2.4,0.9)	(2.5,0.92)	(1.8,0.8)	(1.8,0.8)	(1.8,0.8)
	Ref. 14	$\bar{\omega}_{\text{int}}$	1.0	1.9,2.7	3.7				
	Ref. 12	$\bar{\omega}_{\text{int}}$	0.8	2.4,2.4	4.1				

show that C_{60} and the M_6C_{60} compounds exhibit a series of distinguishable peaks in $\epsilon_2(\omega)$ on the order of ~ 1 eV in width, suggesting that the optical transitions are between narrow, well-separated bands of states identified with particular C_{60} orbitals. Since our results for $\epsilon_2(\omega)$ are almost identical for $M=$K, Rb, and Cs, we rule out the assignment of any of the features in Fig. 2(b) to charge-transfer excitations between C_{60}- and M-derived electronic energy bands, or to transitions between M states. In the case of M_6C_{60}, one is struck by the observation that the experimental $\epsilon_2(\omega)$ are insensitive to the electronic configuration or ionic radius of the respective alkali-metal atom. This indicates that M_6C_{60} is strongly ionic, and that the hybridization between the alkali metal and C_{60} states is weak. A similar conclusion was reached by Erwin and Pederson,[14] who calculated only a 4% admixture of K and C_{60} states in K_6C_{60}. Furthermore, this view is consistent with the Raman-scattering results which reveal that the Raman mode frequencies are only weakly sensitive to M.[6,7]

A comparison between energy-band theory and our data can be made. We begin with C_{60}. In agreement with Saito and Oshiyama,[15] Xu, Huang, and Ching[12] report that the band gap E_g [gap between the highest occupied molecular orbital (MO) and the lowest unoccupied MO] is direct and at the X point. Our experimental value $E_g \sim 1.7$ eV is lower than our earlier estimate of $E_g \sim 2.3$ eV from ellipsometry results.[13] The current value is obtained directly from the energy absorption spectrum $A(\omega)=1-(R+T)$ which is shown in the inset to Fig. 2(a), and can be compared to theoretical predictions of 1.5 eV (Ref. 15) and 1.4 eV.[16] The thick solid curve in Fig. 2(a) is a model fit to the experimental (R,T) data and shows a low-energy tail that smears the true absorption edge at 1.7 eV.

To assign peaks in the low-energy $\epsilon_2(\omega)$ data to particular band-to-band transitions, we adopt the following notation for the conduction (C_n) and valence (V_n) bands closest to the Fermi level. For C_{60}: $V_1=h_u$, $V_2=g_g,h_g$, $C_1=t_{1u}$, and $C_2=t_{1g}$, where we are using the molecular-orbital labels, and for M_6C_{60}: $V_1=t_u$, $V_2=h_u$, $C_1=t_{1g}$, and $C_2=t_{2u},h_g$. V_1 and C_1 lie closest to the Fermi level; the energy-band calculations suggest that the g_g- and h_g-derived bands in C_{60}, and the t_{2u}- and h_g-derived bands in M_6C_{60} are too close together in energy to give rise to separate peaks in $\epsilon_2(\omega)$ and therefore we have grouped them together. Consistent with this notation, the four lowest energy features in $\epsilon_2(\omega)$ for both C_{60} and M_6C_{60} are identified with the transitions $V_1\rightarrow C_1$, $V_1\rightarrow C_2$, $V_2\rightarrow C_1$, and $V_2\rightarrow C_2$. These labels are indicated in Table I and allow a comparison between experiment and theory. The experimental values are just ω_R [Eq. (1)] and the theoretical values $\bar{\omega}_{\rm int}$ are taken from the difference between band centers in the respective model calculations.

As seen from Table I, good agreement between the $\bar{\omega}_{\rm int}$ positions calculated by Saito and Oshiyama[15] and by Xu, Huang, and Ching[12] with our data for C_{60} is obtained, although an experimental determination of the lowest-energy (weak) peak in $\epsilon_2(\omega)$ was not made. In the case of K_6C_{60} the values we estimate for the $\epsilon_2(\omega)$ peak positions of Erwin and Pederson[14] and Xu, Huang, and Ching[12] are also found to be in reasonably good agreement with our data. It should also be noted that for M_6C_{60}, the oscillators introduced in our fits to the R,T data with resonant frequencies above 4.5 eV are not associated with any sharp spectral features and were introduced to simulate the broad structure in our data above 4 eV [Fig. 2(b)]. Hence no attempt is made to compare the theoretical and experimental peak positions in the photon energy range above 4.5 eV.

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