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# Giant vibrational resonances in $A_6C_{60}$ compounds

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Formation of alkali-$C_{60}$ compounds $A_nC_{60}$ ($A$ = K, Rb) induces very large enhancements in the optical strength of two *intra*-$C_{60}$ vibrational resonances and the emergence of a strong electronic transition centered at 1.2 eV. The vibrational spectra are particularly well defined for the $A_6C_{60}$ semiconductor compounds, and it is proposed that the ca. ninetyfold enhancement of the 1428-cm$^{-1}$ mode and its large shift (to 1342 cm$^{-1}$) are generated by coupling to electronic excitations located on the molecule, consistent with recent theoretical descriptions of $C_{60}{}^{6-}$ and the ionic solid bcc-$A^+{}_6C_{60}{}^{6-}$.

Solid-state properties of $C_{60}$,[1-4] and its anionic compounds, the fullerides,[5-8] have recently attracted considerable attention. $C_{60}$ is a hollow, cagelike molecule of truncated-icosahedral morphology ($I_h$), with all carbon atoms equivalent.[9] Novel electronic properties are conferred by its 60 radial $p\pi$ electrons that fill a quasispherical *intra*-molecular band,[10] so that in some respects it can be regarded as a "superatom" with a 4.3 Å (5.0 Å) covalent (van der Waals) radius. Its basic bonding character is only weakly altered by compound formation.[11] Its chemistry is characteristic of high electronegativity, as it takes on up to six or even twelve electrons. These properties have acquired new significance with the finding of superconductivity at relatively high temperatures in $K_3C_{60}$ ($T_C$ = 20 K) and $Rb_3C_{60}$ (30 K) fulleride compounds.[12-14]

The elementary picture of alkali fullerides, as supported by theoretical calculations, is the following: The molecular solid $C_{60}$ is an insulator, corresponding to the molecule's electronic configuration $h_u^{10}t_{1u}^0t_{1g}^0$ (see Fig. 1), with a sizable gap, 1.8 eV.[3,15] It forms an fcc lattice,[2] $a$ = 14.15 Å (10.0 Å inter-$C_{60}$ distance) of 1.5-eV cohesive energy.[4] Reaction with alkali metal generates alkali-fulleride compounds, described theoretically as ionic,[16-19] namely, $A^+{}_nC_{60}{}^{n-}$ $h_u^{10}t_{1u}^n t_{2u}^0 s_A^0$, where $n$ = 0–6 seems to be achievable, consistent with filling of the $p\pi$-$t_{1u}$ band.[20] The empty $s$ band of the alkali ($A$) lies considerably higher. Identified compounds include (i) $n$ = 3, the fcc-cryolite structure[21] conductors with $a$ = 14.24 (14.43) for $A$ = K (Rb) slightly expanded from $C_{60}$ solid; (ii) $n$ = 6, the filled-band bcc semiconductor ($\rho$ = 0.05 Ω cm at 298 K);[22] (iii) an $n$ = 4 bct compound closely related to bcc-$A_6C_{60}$,[23] and (iv) indications of "expanded" fcc-like phases in the $n$ = 1–2 range.[24] It seems clear that only the $A_3C_{60}$ compounds are metallic.

Based on this progress, questions of excitations can be addressed. In particular, the nature of the vibrational and electronic excitations of these compounds remains essentially unknown, although the Raman spectra[25,26] of $A_nC_{60}$ films were recently interpreted as showing that symmetric and quadrupolar intramolecular vibrations may remain largely unchanged from that of molecular $C_{60}$. We report here some findings on the optical properties of $C_{60}$ and $A_nC_{60}$ films by photoabsorption spectroscopic methods. In the experiments, films of pure $C_{60}$, prepared as previously described,[27] grown on various optical substrates[28] are reacted with alkali vapor, and are monitored *in situ* and otherwise by electrical conductivity[6] and by optical absorption spectroscopy (infrared from 0.05–0.5 eV, near infrared 0.5–1.8 eV, each with fourier-transform instruments, and ultraviolet visible 1.5–6 eV). We have also compared the quantitative results obtained on films to the spectra of the $A_6C_{60}$ compounds formed as fine powders and characterized crystallographically, following established procedures.[14]

$C_{60}$ films of thickness ranging 300–2000 Å, grown by sublimation in vacuum onto a variety of optical and electrical substrates (KBr, quartz, and AgCl), are visually

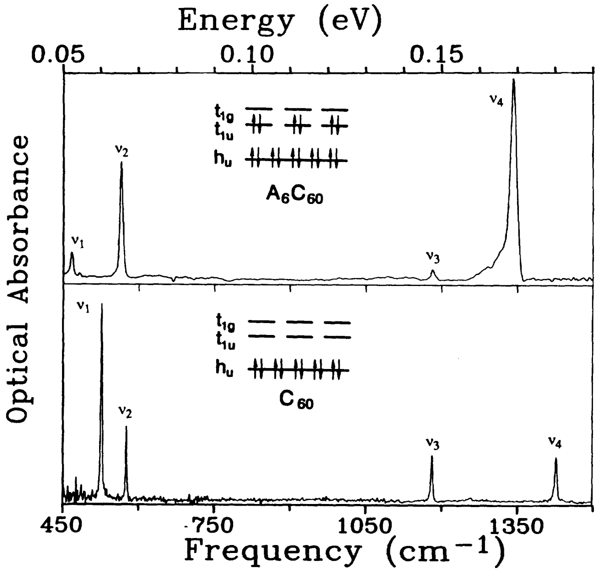

FIG. 1. Optical absorption spectrum in the midinfrared region for films of $C_{60}$ (lower panel) and $K_6C_{60}$ (upper panel), recorded at 1 and 4 cm$^{-1}$ resolution, respectively. The insets show the orbital energy levels of the two compounds (cf. Ref. 10).

TABLE I. Vibrational resonances in $C_{60}$ and $A_6C_{60}$. $\omega$ (width) is the resonance frequency, $\alpha_{\max}$ is the absorption coefficient at peak maximum; shift in resonance peak from $C_{60}$ to $A_6C_{60}$ (same Rb and K); enhancement factor in the integrated intensity of the resonance.

| Mode | $\omega(C_{60})$ ($cm^{-1}$) | $\alpha_{\max}$ ($10^4$/cm) | $\omega(A_6C_{60})$ | $\alpha_{\max}$ | Shift ($cm^{-1}$) | Enhancement |
|---|---|---|---|---|---|---|
| $\nu_1$ | 526(3) | 4.6 | 467(6) | 3.6 | −59 | 2 |
| $\nu_2$ | 576(3) | 1.8 | 565(7) | 17 | −11 | 33 |
| $\nu_3$ | 1182(4) | 1.0 | 1182(9) | 1.7 | 0 | 3 |
| $\nu_4$ | 1429(5) | 1.0 | 1342(16) | 31 | −87 | 88 |

uniform, yellow, or yellow-brown in appearance, and have optical spectra (not shown) in excellent agreement with those reported earlier. The film thickness is calculated from the optical absorbance at the ultraviolet band maxima, using in particular the published extinction coefficients[27,29] and density[1] to obtain $\alpha = 7\times10^5$/cm at 0.27 $\mu$m. A typical optical absorption spectrum in the midinfrared region (0.05–0.2 eV) is shown in Fig. 1 for a 600-Å-thick film. The four bands agree well in position and intensity with those of Ref. 1, and represent the only electric-dipole-allowed modes ($t_{1u}$) of the $C_{60}$ molecule,[30] which are only weakly perturbed in the ambient solid. They are denoted here by $\nu_1$, $\nu_2$, $\nu_3$, $\nu_4$, in order of increasing frequency.

The experimental cell consists of two $C_{60}$ films on substrates sealed to a Pyrex tube containing alkali metal under vacuum. The cell is heated in the spectrometer cavity using heating tape and a temperature controller. Exposure of $C_{60}$ films to alkali-metal vapor introduces drastic changes in the optical absorption, culminating finally in spectra like that shown in Fig. 1 (upper panel). By correlating these changes with the time evolution in the resistivity,[31] we conclude that this spectrum is that of the terminally reacted $K_6C_{60}$ compound. This conclusion was separately confirmed by obtaining a similar spectrum (not shown) for a finely ground mull incorporating $K_6C_{60}$ from a powder sample whose x-ray diffraction pattern agrees with Zhou *et al.*[22] Several features of this spectrum are notable, as follows.

(1) An essentially identical spectrum is observed for $Rb_6C_{60}$, indicating that the properties are largely molecular, perhaps those of $C_{60}{}^{6-}$.

(2) A one-to-one correspondence exists between the $A_6C_{60}$ bands and those of $C_{60}$, despite drastically different shifts and enhancements (Table I). No new modes (i.e., of non-$t_{1u}$ symmetry) emerge, arguing against significant symmetry breaking. A similar conclusion was reached on the basis of the Raman spectra.[25,26]

(3) The absorption intensity overall, and of two modes ($\nu_2$ and $\nu_4$) in particular, are strongly enhanced. Integration of the $\nu_2$ and $\nu_4$ bands indicates enhancements near 33 and 90, respectively (Table I).

(4) The bands of the enhanced modes are significantly broadened and the $\nu_4$ resonance is unsymmetrical. Their shapes appear to be independent of preparation rate and the final temperature of the film over $T = 20–120\,°C$.

These results suggest that the vibrational dynamics are more strongly modified than indicated by earlier discussions, e.g., of Raman measurements.[25,26] A strong, non-symmetry-breaking enhancement mechanism is operating; the magnitude of the enhancement suggests that an electronic character has been acquired, since the estimated transition dipole is now too large to be accounted for by the vibrations of $C_{60}{}^{(6-)}$, nor is the mechanism obvious from recent descriptions of this material's structure or its thermally activated conductivity.

With careful control, spectra distinct from $C_{60}$ and $K_6C_{60}$ can be observed from slowly reacting samples, as indicated in Fig. 2 for the $\nu_4$ mode. Analogous to the intermediate-stage Raman spectra described recently, the bands seem to lie in an intermediate position between the two limits; they are also broader or are multipeaked, and exhibit strong intensity enhancement. From our observations of the conductance minima in identically treated films, it is reasonable to suppose that these intermediate stages with multiple peaks represent the much discussed phase separation into the conducting $K_3C_{60}$ phase, but no attempt has been made to determine directly which features correspond to it. The $\nu_1$ and $\nu_2$ resonances in the 460–580 $cm^{-1}$ region show a similar evolution, but the 1182-$cm^{-1}$ mode is remarkably unaltered in position and intensity throughout the entire process. However, the $A_6C_{60}$ spectrum (Fig. 1) is always observed with extended exposure to alkali vapor. Substantially extended exposure can finally reduce the transmission of the film so strongly

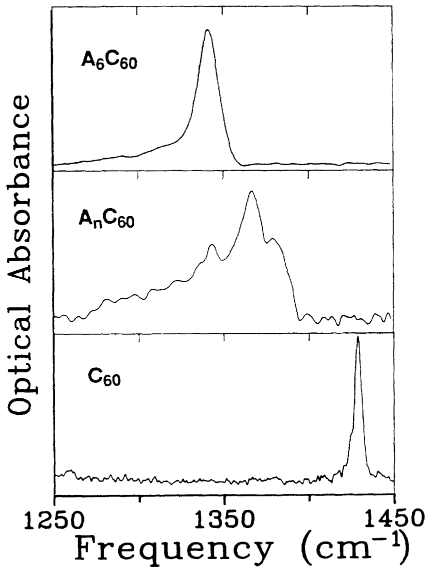

FIG. 2. Evolution of the $\nu_4$ band region.

that the spectrum cannot be observed, which we interpret as the deposition of an alkali-metal overlayer.

Motivated by the possibility of an electronic role for the observed enhancement and shifts, we have recorded the electronic spectra in the previously unexamined near-infrared region (0.5–1.8 eV). In contrast to the spectrum in the visible-ultraviolet region (1.8–5.5 eV), strong changes are observed, Fig. 3, concomitant with those in the midinfrared region. An extremely strong broadband emerges centered at 1.2 eV, with a much weaker shoulder at 0.7 eV. Following the assignment of $C_{60}^-$ in solution,[8] we assign this band as the allowed component, $A_g \rightarrow T_{1u}$, of the complex of terms arising from $t_{1u} \rightarrow t_{1g}$ orbital transition, which is $t_{1u}^6 \rightarrow t_{1u}^5 t_{1g}^1$ in $C_{60}^{6-}$. The band maximum is at an essentially identical location to that of $C_{60}^-$,[8] it is considerably broader, indicative of solid-state effects (conduction band), and has a peak absorption coefficient of $\alpha(1.2\ \text{eV}) = 3\times10^5/\text{cm}$, which is 4 times stronger at peak than $C_{60}^-$, $\alpha(1.2\ \text{eV}) = 7\times10^4/\text{cm}$,[8] and at least twice as wide. When properly scaled for the $\nu$ dependence of absorption, this band is as strong as the ultraviolet absorption bands up to the collective absorptions. Figure 3 also shows that the near-infrared spectrum has a weaker tail extending to low energies, or essentially to the anomalously enhanced and broadened $\nu_4$ peak near 0.2 eV.

Existing theoretical descriptions of the $A_6C_{60}$ semiconductors,[17–20] based upon its known bcc structure, offer little help in interpreting the excitations: The $C_{60}$ molecule is perturbed from its free structure toward even more ideal truncated icosahedron structure (now both kinds of bonds have about the same length); the molecule is surrounded by 24 quasiequivalent $A^+$ ions, the eight nearest-neighbor $C_{60}$ molecules at only slightly changed distances from pure $C_{60}$ solid, and it is computed to be highly charged, near $C_{60}^{6-}$, i.e., the alkali $s$ bands are unoccupied and lie much higher in energy. The band gap ($t_{1u}$-$t_{1g}$) is calculated to be in the 0.4-eV range, as compared to the derived 0.22 eV from conductivity studies,[31] but no band edge is observed optically near either energy. A more consistent picture emerges from the detailed calculations of the free anions, $C_{60}^{n-}$ ($n = 1$–6) by Negri, Orlandi, and Zerbetto,[20] who find for $C_{60}^{6-}$ that the lowest excitations are to magnetic states and are optically forbidden; the $A_g \rightarrow T_{1u}$ excitation arising discussed above lies near 1.0 eV, just as in the $C_{60}^-$ case.

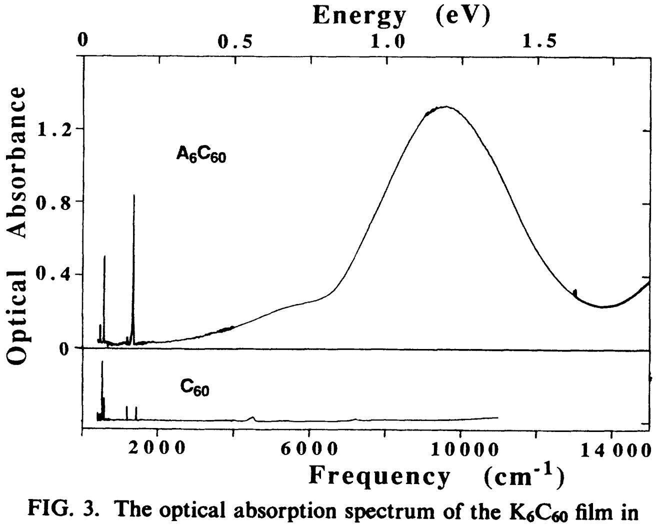

FIG. 3. The optical absorption spectrum of the $K_6C_{60}$ film in the near-infrared region (0.5–1.8 eV), revealing the emergence of a strong new band centered at 1.2 eV and shoulder at 0.7 eV. The spectrum of $C_{60}$ is shown below for comparison, multiplied by 5 relative to the upper curve. At the far left is the midinfrared spectrum placed on the same scale.

Within this picture, conceivable enhancement and mode-softening mechanisms that can be ruled out include: (i) the charging of the $C_{60}$ molecule, because the effect is too large and mode specific, (ii) coupling to the low-frequency ionic lattice vibrations of $K^+$ and $Rb^+$ ions, or (iii) coupling of intramolecular transitions to the charge-transfer transitions ($C_{60}$-to-metal), both of which appear unlikely in view of the similarity of $K_6C_{60}$ and $Rb_6C_{60}$. Instead, we believe that a molecular mechanism can explain the enhancement, leaving the damping to be explained by extended states (see below), in terms of a vibronic coupling in which certain vibrations promote (virtual) excitations of electrons across the $t_{1u}$-$t_{1g}$ gap. In particular, the coupling can be calculated to lowest order by treating the high-frequency $\nu_4$ mode and the $A_g \rightarrow T_{1u}$ electronic excitation from which intensity is acquired within the Herzberg-Teller (HT) coupling scheme.[32] The coupling incorporates into the $|A_g, v=1\rangle$ excitation (weak transition dipole) an admixture of the $|T_{1u}, v=0\rangle$ state (very large transition dipole), to the extent given by $a = \lambda(\omega/\omega_e)$, where $\omega$ and $\omega_e$ are the vibrational and electronic excitation frequencies (0.17 and 1.2 eV). Here the parameter $\lambda$ is the dimensionless first-order coupling constant given as usual by $(Mh\omega^3)^{-1/2}\langle A_g|(\delta U/\delta Q)_{Q=0} \times |T_{u1}\rangle$, where $U$ is the electron-nuclei interaction, and $Q$ and $M$ are the normal coordinate and reduced mass of the $\nu_4$ mode. The vibrational resonance then borrows a fraction of the electronic transition's total intensity given simply by $a^2$, multiplied by $\omega/\omega_e$ to correct for the absorption rate. With $a^2 = \lambda^2/50$, one estimates $\lambda$ near 0.7. This is an extremely large factor that should be calculable by first-principles or semiempirical vibronic theory. The same formalism may be used to calculate the mode softening, and, in the event that the HT calculation proves insufficient, a higher-order (nonadiabatic) theory incorporating the same may be adequate.

None of these considerations addresses the linewidth or damping, which is particularly large for the high-frequency $\nu_4$ mode $\Delta\omega/\omega = 0.012$. Given the coincidence of this mode with the indirect conduction-band onset, it seems possible that the decay is into these states, which are based on molecular excitations of different symmetry. This could be demonstrated by photoconductivity measurements on resonantly excited $K_6C_{60}$ at low temperatures.

In closing, we point out some superficial similarities to another class of material: The doping of polyacetylene $(CH)_x$ generates a much-discussed enhancement of two vibrational modes (also near 0.18 eV) to an intensity near $a = 10^3/\text{cm}$,[33] as compared with $10^5/\text{cm}$ here, a difference that once again points to the very strong electron-phonon interaction evidenced here. An extremely strong midgap absorption band (0.7 eV) also emerges in doped $(CH)_x$,[33] which has no analog in $A_6C_{60}$. Finally, we are aware of proposals[34] that coupling to high-frequency *intra*-molecular vibrations might account for the relatively high-$T_c$ values in $A_3C_{60}$; the vibrations discussed are those appearing in the Raman spectrum ($h_g$ symmetry modes), but the experimental evidence is indirect (damping or disappearance of these resonances).[25,26] Since the completion of this work, Rice and Choi have published an explanation of our results based on the charged phonon effect.[35]

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