In situ infrared transmission study of Rb- and K-doped fullerenes

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We have measured the four IR-active C60 molecular vibrations in MxC60 (M =K, Rb) as a function of doping x. We observe discontinuous changes in the vibrational spectra showing four distinct phases (presumably x = 0, 3, 4, and 6). The 1427-cm⁻¹ and 576-cm⁻¹ modes show the largest changes shifting downward in frequency in four steps as the doping increases. Several very weak modes are visible in the x = 6 phase and are possibly Raman modes becoming weakly optically active. We present quantitative fits of the data and calculate the electron-phonon coupling of the 1427 cm⁻¹ IR mode.

The discovery of superconductivity in alkali-metal-doped C60 (Ref. 1) has prompted a great deal of excitement and a large body of research. Since electron-phonon coupling proved to be responsible for superconductivity in many materials, the relation between the charge carriers and the lattice vibrations is important. Here we present a study of the infrared-active molecular vibrations of MxC60 as a function of alkali-metal doping x for (M = K and Rb). We show the shift of some IR modes to lower frequencies in discrete steps, corresponding to the four known stable phases, x = 0, 3, 4, 6. We also perform an analysis of how the change in the vibrational modes is related to the introduction of carriers into the lowest unoccupied molecular orbital band of C60.

The truncated icosahedral structure of C60 fullerenes belongs to the icosahedral point group Ih and has four infrared-active intramolecular vibrational modes with F1u symmetry. These modes, with center frequencies ν1 = 527, ν2 = 576, ν3 = 1182, and ν4 = 1427 cm⁻¹, have been experimentally observed. The 527- and 576-cm⁻¹ modes are associated with primarily radial motion of the carbon atoms, while the 1182- and 1427-cm⁻¹ modes are primarily tangential motion.

In the MxC60 compounds, the alkali atoms give up one electron each to the lowest unoccupied molecular orbital (LUMO) of a C60 molecule. As long as the on-site Coulomb repulsion is not too large the triply degenerate t1u LUMO can hold six electrons. Therefore the t1u orbital is half filled by three electrons, the material is metallic, and it superconducts at low temperatures. Completely filling the t1u orbital with six electrons makes the C60 a band insulator and the structure becomes body-centered cubic. An insulating phase at x = 4 has also been observed with a body-centered-tetragonal structure.

The C60 for this study was prepared using the well-known technique of Kratschmer et al. The resultant fullerene powder was loaded into a tantalum boat and heated to about 500 °C in a vacuum of ~ 1 x 10⁻⁶ Torr to vapor deposit C60 inside the sample cell. Film thickness was monitored by counting visible light interference fringes as the C60 was deposited. Typical sample thickness was about 1.2 μm.

Our miniature sample cells are constructed of glass with two silicon windows, one of which serves as a substrate for the C60. A small appendage contains the alkali metal, and the entire sample chamber is sealed under high vacuum. The transmission spectra were obtained as the sample was doped with a Bomem MB-155 Fourier-transform infrared (FTIR) spectrometer at 2 cm⁻¹ resolution covering a 400-6000 cm⁻¹ frequency range. Four-probe resistivity of the film was measured simultaneously. By carefully warming the alkali metal to increase the vapor pressure and by heating the C60 film to increase the diffusion rate of the metal into the film, a slow, continuous doping was achieved. During potassium doping, the substrate was maintained at 120 °C and the metal at 100 °C. For Rb, the corresponding temperatures were 85 °C and 70 °C, respectively. The infrared spectra were obtained with the film samples at their substrate temperatures.

The results of the infrared spectroscopy in situ with alkali-metal doping are displayed in Figs. 1 and 2. Since at low frequencies the transmitted intensity is roughly proportional to the square of the resistivity, the IR measurement by itself is a good indicator of the doping process. Indeed, both the dc resistivity and the transmission exhibit a minimum as the doping proceeds. Kochanski et al. associate this minimum with the metallic M3C60 phase. Upon further doping, the resistivity reaches a maximum, corresponding to the insulating M6C60 phase, after which the resistivity drops, but the features in the spectra change little, indicating that the sample begins to coat with alkali metal and the C60 is fully doped (x = 6). At this stage, closer visual inspection reveals metallic films on the window surfaces.

We have performed quantitative fits to both sets of doping data. The vibrational spectra are accurately fit using a dielectric function composed of Lorentzian oscillators and a dc conductivity to mimic the changing conductivity observed as doping progresses. This yields the center frequency ω0, strength S, and width Γ of each mode. We present the results and our assignments of corresponding phases in Table I. We interpret the data as follows: As the doping proceeds, layers of M3C60 grow followed by similar layers of M4C60 and M6C60. We ob-
serve that the \( \nu_1 \) mode at 526 cm\(^{-1} \) gets weaker as the sample loses all \( x = 0 \) phase and reappears at 468 cm\(^{-1} \) in the \( x = 6 \) phase. The \( \nu_2 \) mode shifts in discrete steps and grows in strength during the doping process. This effect is most clearly visible for the Rb doping where it shifts from 576 to 570 to 565 cm\(^{-1} \). Using the x-ray results,\(^9,10,7,6 \) which indicate that only the \( x = 0, 3, 4, \) and 6 phases are stable at this temperature, we associate these modes with the \( x = 0, 3, 4, \) and 6 phases, respectively. The \( \nu_2 \) mode at 1182 cm\(^{-1} \) is enhanced by a factor of almost 2 in the \( x = 6 \) phase. Looking at the \( \nu_4 \) mode, we can again see distinct phases. This mode is enhanced by a factor of 80 in the \( x = 6 \) phase.

The shifts in the \( \nu_2 \) and \( \nu_4 \) modes for the K-doped sample show only three clear phases. This may be due to more uniform doping of the \( K_2C_60 \) sample, as it is known that K diffuses more rapidly into \( C_60 \) than \( Rb.^{11} \) Vibrational modes are more difficult to detect in a homogeneous metallic film since the high reflectivity, due to conduction electrons, dominates the response.

The resultant values for the \( x = 6 \) data in this work are in excellent agreement with previous IR measurements on \( M_6C_60 \) published by Fu et al.\(^{12} \) The phase separation seen in our data is also in agreement with previous Raman-spectroscopy results\(^{11,13} \) where, for example, the change in the \( A_g (2) \) pinch mode originally at 1458 cm\(^{-1} \) clearly shows distinct phase separation. Note that this mode, like the \( \nu_4 \) mode in the IR spectrum, involves stretching of the C=C double bonds.

The \( Rb_6C_60 \) and \( K_6C_60 \) spectra also show some very weak modes at 1461, 1418, 1317, 1284, 1240, 1190, 1146, 943, 688, 645, and 532 cm\(^{-1} \). These are similar in frequency to several Raman-active modes for \( C_60 \) (1458, 1430, 1396, 1315, 1241, 1190, 1140, 950, and 533 cm\(^{-1} \)) and \( Rb_6C_60 \) (1477, 1431, 1322, 1235, 1121, 1091, 689, and 655 cm\(^{-1} \)).\(^{11,14,15} \) We may be observing Raman modes becoming weakly IR active in our fully doped samples. Some of these modes are not allowed by the symmetry.

FIG. 2. Same as Fig. 1 now for \( K_6C_60 \).
TABLE I. Lorentzian oscillator fits to the four IR intramolecular vibrations of $M_xC_{60}$ ($M=$Rb and K) assigned to the different stable phases ($x = 0, 3, 4, 6$). The numbers are essentially the same for both dopants except as noted. $\omega_0$ is the center frequency, $S$ is the strength ($S = \omega_0^2/\omega^2$), and $\Gamma$ is the width of each vibrational mode.

<table>
<thead>
<tr>
<th></th>
<th>$C_{60}$</th>
<th>$M_3C_{60}$</th>
<th>$M_4C_{60}$</th>
<th>$M_6C_{60}$</th>
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</thead>
<tbody>
<tr>
<td>$\omega_0$ (cm$^{-1}$)</td>
<td>526</td>
<td>472</td>
<td>467</td>
<td></td>
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<tr>
<td>$\nu_1$</td>
<td>$S$ 0.02</td>
<td>0.008</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>$\Gamma$ (cm$^{-1}$)</td>
<td>2.5</td>
<td>1.5</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>$\omega_0$ (cm$^{-1}$)</td>
<td>576</td>
<td>573</td>
<td>570</td>
<td>565</td>
</tr>
<tr>
<td>$\nu_2$</td>
<td>$S$ 0.008</td>
<td>0.019</td>
<td>0.022</td>
<td>0.17</td>
</tr>
<tr>
<td>$\Gamma$ (cm$^{-1}$)</td>
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<td>3</td>
<td>3.7</td>
<td>2.8</td>
</tr>
<tr>
<td>$\omega_0$ (cm$^{-1}$)</td>
<td>1182</td>
<td></td>
<td>1182</td>
<td></td>
</tr>
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<td>$\nu_3$</td>
<td>$S$ 0.0018</td>
<td></td>
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<td></td>
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<tr>
<td>$\Gamma$ (cm$^{-1}$)</td>
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<td></td>
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<tr>
<td>$\omega_0$ (cm$^{-1}$)</td>
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<td>1393</td>
<td>1363*</td>
<td>1340</td>
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<tr>
<td>$\nu_4$</td>
<td>$S$ 0.001</td>
<td>0.012</td>
<td>0.016</td>
<td>0.08</td>
</tr>
<tr>
<td>$\Gamma$ (cm$^{-1}$)</td>
<td>4.5</td>
<td>20.8</td>
<td>23.7</td>
<td>7.2</td>
</tr>
</tbody>
</table>

*Values in table are for $\text{Rb}_4\text{C}_{60}$. $\text{K}_4\text{C}_{60}$ differs for $\nu_4$ : $\omega_0 = 1369$ cm$^{-1}$, $S = 0.028$, and $\Gamma = 21$ cm$^{-1}$.

of the single molecule, but they have been observed in Raman spectra of crystalline $C_{60}$.

As long as the electron is confined to a single molecule, symmetry arguments predict that the intraband electron-phonon scattering, relevant to superconductivity, is dominated by Raman modes. Therefore, the attempts to explain superconductivity in the fullerenes focused on the Raman-active $A_g$ and $H_g$ modes. However, for extended electronic or vibrational states, the IR modes may become important too. In fact, we see evidence for damping of the vibrational modes by conduction electrons. According to the sum rule, $\sum \Gamma_1/\omega^2_0 = (\pi/2)N(E_F)\lambda$, the broadening of the vibrational mode is related to the electron-phonon coupling. The largest change, 16.3 cm$^{-1}$, in the widths was observed in the $\nu_4$ mode. This leads to a contribution of 0.055 states/eV in $N(E_F)\lambda$ for each of the three degenerate modes. Considering that there are 180 vibrational modes for the $C_{60}$ molecule,
a coupling of this magnitude is significant although the strongest electron-phonon coupling seen to date is for the $H_g(2)$ Raman mode (0.25 states/eV). It remains to be seen how important this coupling is for superconductivity.

In summary, we have measured the four infrared-active intramolecular vibrational modes of $C_{60}$ as a function of $Rb$ and $K$ doping. Quantitative presentation of our measurements and assignments of the modes to different stable phases of $M_xC_{60}$ were made. We show that our results are consistent with previous work and describe how the data could relate to a superconducting pairing mechanism in these materials.

This work was supported by NSF Grant No. DMR9202528. We would like to thank M. J. Rice, P. B. Allen, G. L. Carr, and K. Holczer for valuable discussions. Thanks to J. Marecek of the SUNY at Stony Brook chemistry department for $C_{60}$ separation and purification and to J. Kirz and S. Lindaas for the use of high-vacuum equipment.

Errata

Erratum: Importance of Coulomb interactions in anisotropic superconductors

P. J. Hirschfeld and D. Einzel

The discussion at the top of p. 8840 implies that the formalism of Klemm et al.\textsuperscript{1} yields a different result for the frequency-dependent electromagnetic response than that found in this work because of the failure to include the long-range Coulomb interaction. Klemm et al. calculate the surface impedance $Z$ of an anisotropic superconductor for normal incidence of the electromagnetic wave. In this case it may be shown that the two approaches arrive at the same result in the limit $\Omega \ll \Omega_{pl}$, where $\Omega$ is the external frequency and $\Omega_{pl}$ the plasma frequency.

The result Eq. (13) should read

$$\vec{K}_{tot} = \vec{K}^{ex} - \frac{q \vec{K}^{ex} \cdot q}{q \cdot \vec{K}^{ex} \cdot q} + \delta \vec{K},$$

where

$$\delta \vec{K} = \Omega_q^2 \left[ \frac{(\vec{K}^{ex} \lambda_{eq} - \vec{K}^{ex} \cdot \vec{q}) \cdot \vec{q} (\vec{K}^{ex} \lambda_{eq} - \vec{K}^{ex} \cdot \vec{q})}{K^{ex}_{eq} \lambda_{eq} \cdot (\Omega^2 - \Omega_q^2) + \Omega_q^2 \lambda_{eq}} \right],$$

and we have defined $\lambda_{eq} = q \lambda \cdot q$ and $K^{ex}_{eq} = q \vec{K}^{ex} \cdot q$.

The response $\delta \vec{K}$ may be thought of as the contribution of the gauge mode in the limit of strong long-range Coulomb interaction. It is therefore not generally the case that the gauge mode "cancels" from the final result for the current. It will vanish in the special case of a conventional superconductor with effective mass anisotropy [cf. Eq. (14)]. In the case of order parameter anisotropy, $\delta \vec{K}$ is nonzero at nonzero temperature and at angles $\theta$ between the $\hat{c}$ axis of the crystal and $q$ different from 0 and $\pi/2$. Since $\delta \vec{K}$ is of order $q^2$ and nonsingular at the Anderson-Bogoliubov frequency $\Omega_q$, the corrections it provides are always small in type-II materials.

The authors are grateful to Professor K. Scharnhorst for pointing out the above errors.


Erratum: In situ infrared transmission study of Rb- and K-doped fullerenes
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The preliminary assignments in this paper of the positions of the $x=3$ and $x=4$ IR lines were incorrect. Further unambiguous x-ray identification of the $x=1$ phase\textsuperscript{1} indicates that the correct assignments of the $F_{1u}(4)$ vibration are 1428 cm$^{-1}$ for $C_{60}$, 1393 cm$^{-1}$ for $M_1C_{60}$, 1363 cm$^{-1}$ for $M_3C_{60}$, and 1340 cm$^{-1}$ for $M_4C_{60}$ in agreement with recent work by Kuzmany et al.\textsuperscript{2} The middle two column titles of Table I and the middle two experimental points in Fig. 4 should be adjusted accordingly.


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