In-Situ Infrared Transmission Study of Rb- and K-Doped Fullerenes

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We have measured the four IR active $C_{60}$ molecular vibrations in $M_xC_{60}$ ($M = K, Rb$) as a function of doping $x$. We observe discontinuous changes in the vibrational spectra showing four distinct phases (presumably $x = 0, 3, 4, 6$). 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 new 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.

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The discovery of superconductivity in alkali doped $C_{60}$ 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 $M_xC_{60}$ as a function of alkali metal doping, for ($M = K$ and $Rb$). We show, for the first time, 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 $C_{60}$.

The truncated icosahedral structure of $C_{60}$ fullerenes belongs to the icosahedral point group, $I_h$, and has four infrared active intramolecular vibrational modes with $F_{1u}$ symmetry. These modes, with center frequencies $v_1 = 527, v_2 = 576, v_3 = 1182$, and $v_4 = 1427$ 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 $M_xC_{60}$ compounds, the alkali atoms give up one electron each to the lowest unoccupied molecular orbital (LUMO) of a $C_{60}$ molecule. As long as the on site Coulomb repulsion is not too large the triply degenerate $t_{1u}$ LUMO can hold six electrons. Therefore the $t_{1u}$ orbital is half filled by three electrons, and the material is metallic and superconducts at low temperatures. Completely filling the $t_{1u}$ orbital with six electrons makes the $C_{60}$ 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 $C_{60}$ 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 $\sim 1 \times 10^{-6}$ Torr to vapor deposit $C_{60}$ inside the sample cell. Film thickness was monitored by counting visible light interference fringes as the $C_{60}$ was deposited. Typical sample thickness was about 1.2 $\mu m$.

Our miniature sample cells are constructed of glass with two silicon windows, one of which serves as a substrate for the $C_{60}$. A small appendage contains the alkali metal and the entire sample chamber is sealed under high vacuum. The transmission spectra were obtained with a Bomem MB − 155 FTIR spectrometer at 2 cm$^{-1}$ resolution covering a 400 − 6000 cm$^{-1}$ frequency range as the sample was doped. Four-probe resistivity of the film was measured simultaneously. By carefully warming the alkali metal to increase the vapor pressure and by heating the $C_{60}$ 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 Figures 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 $M_xC_{60}$ phase. Upon further doping, the resistivity reaches a maximum, corresponding to the insulating $M_xC_{60}$ phase, after which the resistivity drops, but the features in the spectra change little, indicating that we are now just coating the sample with alkali metal and the $C_{60}$ 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, $\omega_0$, strength, $S$, and width, $\Gamma$, 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 $M_xC_{60}$ grow followed by similar layers of $M_xC_{60}$ and $M_yC_{60}$. We observe that the $v_1$ mode at 526 cm$^{-1}$ gets weaker as the
sample looses 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 is most clearly visible for the \( Rb \) doping where we see it shifts from 576 to 573 to 567 to 565 cm\(^{-1}\). Using the x-ray results \([3,4,5]\) 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 \( \nu_3 \) 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 \( K_xC_{60} \) sample where, as it is known that \( K \) diffuses more rapidly into \( C_{60} \) than \( Rb \) \([1]\). 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 our \( x = 6 \) data are in excellent agreement with previous IR measurements on \( M_xC_{60} \) published by Fu et. al. \([2]\). The phase separation seen in our data is also in agreement with previous Raman spectroscopy results \([1,4]\) 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 \( Rb_2C_{60} \) and \( K_2C_{60} \) 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 \( Rb_2C_{60} \) (1477, 1431, 1322, 1235, 1121, 1091, 689, and 655 cm\(^{-1}\)) \([1,4,5]\). 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 of the single molecule, but they have been observed in Raman spectra of crystalline \( C_{60} \) \([4,14,19]\). It should be noted that the changes in the vibrational modes due to photoexcitation of carriers \([6]\) are different from the changes reported here for chemical doping.

The charged-phonon theory by M. J. Rice and Han-Yong Choi \([13]\) predicts many of the features we observe, in particular, the enhancement of the strength and the softening of the 1428 cm\(^{-1}\) mode upon doping. In Figure 3 we illustrate how the addition of electrons to a complex molecule can enhance the strength of a "silent" IR active phonon. Figure 3(a) depicts an eigenmode of the molecule, characterized by two pairs of atoms oscillating in opposite phase. This mode is "IR active" in the sense that it has odd symmetry. However, as long as only symmetric electronic states are allowed, the mode is "silent" since there is no net dipole moment in the direction of the electric field. In Figure 3(b) we allow for asymmetric states, i.e. electron transfer between the two pairs of atoms. The electron transfer naturally couples to the atomic displacements via the rearrangement of electronic states, and it also generates an electric dipole moment. Rice and Choi \([17]\) argue that in \( C_{60} \), electrons excited between the between the \( t_{1u} \) and the next higher energy \( t_{1g} \) molecular orbitals create a coupling to the infrared active vibrational modes, and simultaneously soften the vibration frequency (Figure 3). In view of the agreement between the experiment and theory for the \( \nu_4 \) mode, it is all the more surprising that the \( \nu_1 \) mode does not follow the same behavior. We argue that this mostly radial mode is more sensitive to the inter-molecular forces, and its frequency is influenced by the FCC to BCC phase transition.

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 focussed on the Raman active \( A_g \) and \( H_g \) modes \([18]\). 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, \( \sum \Gamma_i / \omega_0^2 = (\pi/2)N(E_F)\lambda \) \([19]\), 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) \([15]\). 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 works and describe how our data could relate to a superconducting pairing mechanism in these materials.

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[1] A.F. Hebard et. al., Nature 350, 600 (1991); K. Holczer
FIG. 1. \(Rb_xC_{60}\) infrared transmission spectra as a function of \(x\). (a) shows the lower two vibrational modes (\(\nu_1\) and \(\nu_2\)) and (b) shows the upper two modes (\(\nu_3\) and \(\nu_4\)). The curves are offset for clarity. Undoped \(C_{60}\) is the top curve and the sample is further doped going down in the figure. The bottom curve is for fully doped \(Rb_xC_{60}\). The minimum in the resistivity of the sample corresponds to the curve labeled ‘min’. Vertical lines are guides to indicate the assignments of vibration frequencies, as obtained from numerical fits.

FIG. 2. The same as Figure 1 now for \(K_xC_{60}\).

FIG. 3. Schematic illustration of charge-transfer induced infrared activity. The arrowed circles represent atoms moving within a single “molecule”; the symmetry of the oscillation is odd. In (a) only even electronic states are allowed and therefore the strength of the IR active vibration is small. In (b), the electron transfer couples the mode to the external field by introducing a dipole moment.

FIG. 4. The frequency of the \(\nu_4\) IR mode vs. the inferred composition for \(Rb\) doped \(C_{60}\). Circles refer to the calculation of Rice and Choi (Ref. [15]).

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.

| \(C_{60}\) | \(M_3C_{60}\) | \(M_4C_{60}\) | \(M_6C_{60}\) |
|---|---|---|---|
| \(\nu_1\) | \(\omega_0(\text{cm}^{-1})\) | 526 | 472 | 467 |
| | \(S\) | .02 | .008 | .03 |
| | \(\Gamma(\text{cm}^{-1})\) | 2.5 | 1.5 | 3 |
| \(\nu_2\) | \(\omega_0(\text{cm}^{-1})\) | 576 | 573 | 570 | 565 |
| | \(S\) | .008 | .019 | .022 | .17 |
| | \(\Gamma(\text{cm}^{-1})\) | 2.7 | 3 | 3.7 | 2.8 |
| \(\nu_3\) | \(\omega_0(\text{cm}^{-1})\) | 1182 | 1182 | 1182 |
| | \(S\) | .0018 | .003 |
| | \(\Gamma(\text{cm}^{-1})\) | 4.2 | 5.8 |
| \(\nu_4\) | \(\omega_0(\text{cm}^{-1})\) | 1428 | 1393 | 1363* | 1340 |
| | \(S\) | .001 | .012 | .016 | .08 |
| | \(\Gamma(\text{cm}^{-1})\) | 4.5 | 20.8 | 23 | 7.2 |

*Values in table are for \(Rb_xC_{60}\). \(K_xC_{60}\) differs for \(\nu_4\): \(\omega_0 = 1369\text{cm}^{-1}\), \(S = .028\), and \(\Gamma = 21\text{cm}^{-1}\).