Effects of Doping on the Vibrational Properties of C\textsubscript{60} from First Principles: K\textsubscript{6}C\textsubscript{60}

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\textit{Ab initio} calculations of the phonon spectrum of K\textsubscript{6}C\textsubscript{60} are presented, based on the local-density approximation of density-functional theory and on linear response theory. The effects of doping on frequencies and infrared intensities are identified and their physical origin discussed in detail for optically allowed modes. Whereas structural relaxation is primarily responsible for the frequency changes, and especially for the softening of tangential modes, the change in infrared relative intensities is a direct consequence of the electron transfer. The potassium vibrations are found to lie within 60–100 cm\textsuperscript{-1} and are well decoupled from C\textsubscript{60} intramolecular modes. [S0031-9007(96)00397-3]

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Vital to progress in material science is the ability to control the changes induced in the electronic and mechanical properties of a reference material by doping it with foreign atoms. Raman and infrared (IR) spectra are the basic experimental tools adopted to inspect how doping modifies the structural and dynamical properties of the pristine material. A clear understanding of the physical origin of such changes is a prerequisite for making these spectra fingerprints, necessary to the design of new compounds.

Recently, solid C\textsubscript{60} has become one of the most widely used reference materials. It is a \textsiml 1 eV gap semiconductor, which can be relatively easily tuned by metal intercalation, giving rise to a family of compounds called metal fullerides [1,2]. These are either semiconductors with different characteristics from C\textsubscript{60} or metals or superconductors, depending on the concentration and the specific nature of the intercalating metal atoms. Well-resolved Raman and IR spectra are now available for a number of these compounds (see, e.g., [3–6]). They exhibit a highly mode-selective dependence both of the frequency shifts and the intensity variations, which suggests a complex electron-phonon interaction [7,8]. Basic questions are still open. For instance, in the case of the simplest intercalation, that with heavy alkali metals, the chemical picture is almost trivial, being electrons “fully” transferred to the molecular units. However, the modifications of the C\textsubscript{60} phonon spectra is not trivial at all, and especially so their interpretation. One would like to at least be able to disentangle the mere effect of electron donation from that of the (consequent) structural relaxation of the molecule.

So far, trends with varying dopant concentration have been discussed mainly in terms of the charged phonon model [9]. This broadly associates the softening and enhancing of peaks with charge transfer and predicts a simple linear dependence of frequency shifts and a quadratic one of the IR intensities on the amount of charge transfer. The observed behavior is, however, much richer.

Going beyond this level of theory requires \textit{ab initio} calculations of the phonon structure, which consistently treat electronic and structural variables. The attempts so far are a quantum-chemical calculation of the C\textsubscript{60}\textsuperscript{5-} icosahedral \textit{Ih} molecule [10], aimed at simulating (K, Rb)\textsubscript{6}C\textsubscript{60} and a frozen-phonon calculation for K\textsubscript{3}C\textsubscript{60} [11] based on density functional theory in the local density approximation (DFT-LDA). The latter uses a minimal basis set and assumes a C\textsubscript{60}. The results of \emph{Ih} are only in fair agreement with experiment, and do not provide much insight into the microscopic mechanisms responsible for differences between the undoped and the doped materials. To this aim, we have performed an \textit{ab initio} calculation of the phonon spectra of K\textsubscript{6}C\textsubscript{60} based on DFT-LDA and on the linear-response approach [12], and analyzed the results with a novel and convenient procedure.

The choice of K\textsubscript{6}C\textsubscript{60} [13] was motivated by three considerations: (i) Highly resolved single-crystal Raman and IR spectra have recently become available [4,5] that show a clear mode-selectivity of the doping-induced effects. (ii) The anomalies in its IR spectrum have been considered with special attention and recognized [7] as the signature of strong electron-phonon coupling. (iii) Our recent calculations of the structural and electronic properties of this system [14] are in good agreement with experiment.

Our results reproduce the experimentally observed changes in intensities and frequencies, and explain the different behavior of the various modes by isolating the various effects of the metal intercalation: the direct result of the electron transfer, and that of the changes in the molecular structure, as well as those due to intermolecular interaction in the solid. We also determine the vibrations of the cations, which lie at much lower frequencies and do not couple with the C\textsubscript{60} intramolecular ones.

We follow the linear-response method, as previously applied to the vibrational and dielectric properties of the C\textsubscript{60} molecule [15]. The technical details are the same as in [15]. We use norm-conserving LDA pseudopotentials to represent the electron-ion interaction, and a plane-wave basis set. For potassium we use a one-electron pseudopotential (1e-nlcc) [14], which incorporates the nonlinear core correction of the exchange and correlation functionals, needed to account for the effects of the core-valence
TABLE I. Calculated vibrational frequencies of C\textsubscript{60}-like modes in K\textsubscript{3}C\textsubscript{60}. Bold: Optically active modes. Units are cm\textsuperscript{-1}.

<table>
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<tr>
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<tbody>
<tr>
<td>(A\textsubscript{g}(1))</td>
<td>707</td>
<td>507</td>
<td>507</td>
<td>501</td>
<td>12</td>
<td>9, 6</td>
</tr>
<tr>
<td>(A\textsubscript{g}(2))</td>
<td>1469</td>
<td>1432</td>
<td>1431</td>
<td>135</td>
<td>-35</td>
<td>-36, -36</td>
</tr>
<tr>
<td>(H\textsubscript{g}(1))</td>
<td>274, 266</td>
<td>281, 269</td>
<td>280, 268</td>
<td>11</td>
<td>6, 5</td>
<td></td>
</tr>
<tr>
<td>(H\textsubscript{g}(2))</td>
<td>412, 419</td>
<td>419, 427</td>
<td>419, 427</td>
<td>12</td>
<td>-8, -9</td>
<td></td>
</tr>
<tr>
<td>(H\textsubscript{g}(3))</td>
<td>660, 660</td>
<td>656, 676</td>
<td>656, 676</td>
<td>-51</td>
<td>-44, -47</td>
<td></td>
</tr>
<tr>
<td>(H\textsubscript{g}(4))</td>
<td>770, 769</td>
<td>761</td>
<td>760, 728</td>
<td>13</td>
<td>-11, -25</td>
<td></td>
</tr>
<tr>
<td>(H\textsubscript{g}(5))</td>
<td>1107, 1109</td>
<td>1094, 1120</td>
<td>1093, 1122</td>
<td>12</td>
<td>5, 6</td>
<td></td>
</tr>
<tr>
<td>(H\textsubscript{g}(6))</td>
<td>1264, 1268</td>
<td>1237</td>
<td>1232, 1237</td>
<td>15</td>
<td>-11, -14</td>
<td></td>
</tr>
<tr>
<td>(H\textsubscript{g}(7))</td>
<td>1423, 1414</td>
<td>1383</td>
<td>1384</td>
<td>113</td>
<td>-43, -38</td>
<td></td>
</tr>
<tr>
<td>(H\textsubscript{g}(8))</td>
<td>1508, 1498</td>
<td>1476</td>
<td>1481, 1474</td>
<td>-74</td>
<td>-97, -95</td>
<td></td>
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TABLE II. K\textsubscript{3}C\textsubscript{60}: Theoretical and experimental frequencies \(\omega\) of the optically C\textsubscript{60}-like active modes and shifts \(\Delta\omega\) with respect to C\textsubscript{60}. We use the labeling of the \(I\textsubscript{h}\) group. The \(H\textsubscript{g}\) modes split into a triplet \(T\textsubscript{g}\) (left) and a doublet \(E\textsubscript{g}\) (right). The experimental values are ascribed according to the calculated ordering. Their shifts refer to the centers of gravity. Units are cm\textsuperscript{-1}.

<table>
<thead>
<tr>
<th>Mode</th>
<th>Theory</th>
<th>Exp.</th>
<th>Exp.</th>
<th>Theory</th>
<th>(\Delta\omega)</th>
<th>Exp.</th>
<th>Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(T\textsubscript{1u}(1))</td>
<td>466</td>
<td>467</td>
<td>467</td>
<td>1</td>
<td>-61</td>
<td>-61, -60</td>
<td></td>
</tr>
<tr>
<td>(T\textsubscript{1u}(2))</td>
<td>571</td>
<td>565</td>
<td>564</td>
<td>-15</td>
<td>-12, -12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(T\textsubscript{1u}(3))</td>
<td>1215</td>
<td>1182</td>
<td>1183</td>
<td>-3</td>
<td>0, 0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(T\textsubscript{1u}(4))</td>
<td>1395</td>
<td>1340</td>
<td>1341</td>
<td>-67</td>
<td>-86, -88</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
the Raman active $H_x(7)$, and $H_y(8)$. The picture is not as simple, however. There are cases, such as the $H_y(2)$ and $T_{1u}(3)$ for which structural changes tend to harden slightly. Also, for $H_y(3)$, the redshift is large ($\Delta \omega = -50 \text{ cm}^{-1}$) but is exclusively due to the electron transfer.

A strong mode dependence of the frequency shifts was also found for the Li$_2$C$_60$ molecule [20], and the role of the double-bond lengthening in causing a significant softening of tangential modes was pointed out.

The IR spectrum of K$_4$C$_{60}$ is interesting in view not only of the doping-induced frequency shifts (see Table I), but also of the intensity changes (see Table III). These features have long been regarded as signatures of a mode-selective electron-phonon coupling [7], but a satisfactory interpretation is still lacking. Reference [12] has provided a general method for the calculation of IR oscillator strengths from linear-response DFT. In [15], this was successfully applied to C$_{60}$. The oscillator strength of the $\nu$th mode is given by

$$ f(\nu) = \sum_{\alpha} \left| \sum_{i,\beta} Z_{\alpha \beta}(i) e_\beta(i|\nu) \right|^2, \quad (1) $$

where $e_\beta(i|\nu)$ is the normalized eigenmode, $\alpha$ and $\beta$ are Cartesian polarizations, $i$ runs over the atoms in the unit cell, and $Z_{\alpha \beta}(i)$ is the effective-charge tensor [12]

$$ Z_{\alpha \beta}(i) = Z_\nu(i) \delta_{\alpha \beta} + \frac{4}{N} \sum_{k \in \text{BZ}} \sum_{\nu} \sum_{c} \left( \langle \psi_{v,k} | \delta V_{\beta}^{\text{ph,bare}}(i) | \psi_{c,k} \rangle \langle \psi_{c,k} | \delta V_{\alpha}^{E,\text{scf}} | \psi_{v,k} \rangle / \epsilon_{v,k} - \epsilon_{v,k} \right). \quad (2) $$

$Z_\nu$ is the ionic charge, BZ stands for the Brillouin zone, $\epsilon_{v,k}$ and $\epsilon_{v,k}$ denote valence and conduction bands, respectively, $\psi_{v,k}$ and $\psi_{c,k}$ the Kohn-Sham states, $\delta V_{\beta}^{\text{ph,bare}}(i)$ the linear variation of the bare electron ion potential with respect to a displacement of the $i$th atom along the $\beta$ direction, and $\delta V_{\alpha}^{E,\text{scf}}$ that of the screened potential with respect to an applied electric field.

We reduce the sum over the BZ to the $P$ point [17] as for the electron density [14]. The $k$ summation in Eq. (2) is more slowly convergent, so the calculated intensities must be considered only an estimate. Of central interest here is their change from C$_{60}$ to K$_4$C$_{60}$, rather than their absolute values. To minimize the convergence error, we consider also C$_{60}$ in a bcc solid, and evaluate the intensities for the two systems with the same atomic density (our system I) within the same approximation. The intensity ratios, Table III, are compared with the values from experiment.

In agreement with experimental observation: (i) All the IR intensities are enhanced as a result of doping—a fact readily understandable as a consequence of the decrease of the effective energy gaps $\epsilon_{v,k} - \epsilon_{c,k}$ in Eq. (2). This is reflected in the dielectric constant $\epsilon_0$, for which we calculate an increase by $\sim 3$ from bulk C$_{60}$ ($\epsilon_0 = 4.4$) to K$_4$C$_{60}$ ($\epsilon_0 = 12.2$). (ii) An important change in the relative intensities of the four $T_{1u}$ modes takes place, and $T_{1u}(2)$ and $T_{1u}(4)$ become prominent.

Our analysis in terms of the I-IV systems shows that the variation of the IR intensities and of the dielectric constant is dominated by the direct effect of the electron transfer. In fact, the values obtained for our system (III) are almost identical with the final ones. The structural relaxation has only a minor influence. This is at odds with the phonon frequency changes, for which it plays the major role, and explains in particular why the softening of an IR active mode is not necessarily accompanied by an enhancement of its intensity. In fact, a modest IR intensity is observed for $T_{1u}(1)$ in spite of the measured large frequency change, and vice versa for $T_{1u}(2)$. In the case of $T_{1u}(4)$, for which both frequency and intensity change in a dramatic way, the dominant mechanisms are also different, the former being due to the structural relaxation [see Fig. 1(a)].

So far, the interpretation of the IR spectrum has relied on the charged phonon model, which neglects structural
TABLE IV. Calculated vibrational frequencies of potassium ions in K$_6$C$_{60}$. The two lines refer to two different calculations as explained in the text. Units are cm$^{-1}$.

<table>
<thead>
<tr>
<th>K-pseudo</th>
<th>$A_g$</th>
<th>$E_g$</th>
<th>$T_g$</th>
<th>$T_u$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1e-nlcc</td>
<td>68</td>
<td>102</td>
<td>83</td>
<td>123</td>
</tr>
<tr>
<td>9e</td>
<td>64</td>
<td>98</td>
<td>60</td>
<td>97</td>
</tr>
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</table>

As a consequence of the charge transfer only, it predicts the occurrence of a simultaneous softening and intensity enhancement for any mode that couples the $t_{1u}$ to the $t_{1g}$ orbitals. This could qualitatively account for the observed behavior of $T_{1u}(2)$ and $T_{1u}(4)$. However, in view of the above discussion, this picture is oversimplified. We have also analyzed the validity of a two-level ($t_{1u}$-$t_{1g}$) model for calculating the IR intensity, by extracting the contribution of the individual electronic excitations to the effective charges in Eq. (2). The situation is much more complex, and only in the case of $T_{1u}(4)$ can the $t_{1u}$-$t_{1g}$ channel be considered the dominant one [21].

In Table IV, we list the frequencies of the vibrational modes of K, which turn out to be decoupled from the rest. Raman spectra [22] exhibit a relatively intense peak at 33 cm$^{-1}$, a weak shoulder at 48 cm$^{-1}$, a broad band at $\sim$ 75 cm$^{-1}$, and a peak with resonant character at 105 cm$^{-1}$. The lowest one was ascribed to the librational mode of K$_n$, which turn out to be decoupled from the rest. The K atoms at equilibrium occupy quasitetrahedral sites $(0.25 - \delta, 0, 0.5)$ on the faces of the cube. Their Raman active modes are four: one $A_g$, which can be described as the breathing of the rhombohedral cluster, one $E_g$, and two $T_g$. Only the $E_g$ doublet could be experimentally assigned, at 105 cm$^{-1}$, on the basis of its resonance properties. Our calculations performed with the 1e-nlcc pseudopotential (first row in Table IV) yield the $E_g$ doublet at 102 cm$^{-1}$, but do not predict any Raman intensity below 68 cm$^{-1}$. To check the accuracy of these results, we have performed the entire phonon calculation again, using a 9e-pseudopotential which reduces the frozen core to the $3s$ and $3p$ electrons. The calculations with the new pseudopotential renders accurate calculations much more demanding. In Ref. [14] an energy cutoff of 35 Ryd was used for the plane wave expansion of the electron wave function. Here we use a higher cutoff (45 Ryd) to have a better description of the dynamical properties. Negligible differences ($<0.003$ Å) result in the equilibrium bond lengths.

[16] In Ref. [14] an energy cutoff of 35 Ryd was used for the plane wave expansion of the electron wave function. Here we use a higher cutoff (45 Ryd) to have a better description of the dynamical properties. Negligible differences ($<0.003$ Å) result in the equilibrium bond lengths.
[17] The absence of an energy gap, as in the case of K$_6$C$_{60}$, renders accurate calculations much more demanding.
[21] The $t_{1u}$-$t_{1g}$ channel is absent in C$_{60}$. The valence electrons states are in $h_q$ orbitals, whose first dipole-allowed coupling is to the $t_{1g}$, separated by more than 2 eV.
[23] Calculations with both pseudopotentials reproduce the experimental values for the interatomic distance of K$_2$C$_{60}$ within 1% and that of the vibrational frequency within 5%.