Raman scattering in C_{60} and alkali-metal-doped C_{60} films

Kai-An Wang and Ying Wang

Department of Physics and Astronomy, University of Kentucky, Lexington, Kentucky 40506

Ping Zhou

Center for Applied Energy Research, University of Kentucky, Lexington, Kentucky 40511

J. M. Holden and Song-lin Ren

Department of Physics and Astronomy, University of Kentucky, Lexington, Kentucky 40506

G. T. Hager and H. F. Ni

Center for Applied Energy Research, University of Kentucky, Lexington, Kentucky 40511

P. C. Eklund

Department of Physics and Astronomy and Center for Applied Energy Research, University of Kentucky, Lexington, Kentucky 40506

G. Dresselhaus

Francis Bitter National Magnet Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

M. S. Dresselhaus

Department of Electrical Engineering and Computer Science and Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

(Received 14 October 1991)

The Raman-active modes of solid films of C_{60} and M_xC_{60} ($x \sim 6$; $M = K$, Rb, Cs) have been studied experimentally. The mode activity is dominated by intraball interactions, and the effect of the M^+ ions on the C_{60} spectrum is observed to be almost insensitive to the radius or mass of the alkali metal. The tangential modes of solid C_{60} are observed to soften in M_6C_{60} by ~ 60 cm^{-1}, which can be attributed to a charge-transfer-induced elongation of the intraball bond lengths, similar to that observed in graphite intercalation compounds. Conversely, the radial modes are found to upshift slightly, indicating that a competing mechanism counteracts the effect of the bond elongation.

In this paper we present results of Raman-scattering studies on thin solid films of C_{60} and alkali-metal-saturated C_{60}, M_xC_{60} ($M = K$, Rb, Cs). Weight-uptake measurements and elemental analysis of K-saturated C_{60} powders reported $6.7 < x < 7.3$,[1] and previous structural studies of the K- and Cs-saturated C_{60} reported $x = 6$.[1] Hereafter, we refer to the M-saturated C_{60} compound as M_6C_{60}. The Raman-active modes of solid M_6C_{60} presented here are surprisingly independent of the mass or radius of the alkali-metal ions. A doping-induced downshift in three of the high-frequency tangential C_{60} modes is found in reasonable agreement with similar studies on the intralayer modes in graphite intercalation compounds (GIC's),[2,3] where the downshift has been shown to follow the elongation of the intralayer C-C bond length.[4] The main result from this study is the simplicity of the observed Raman spectra, which stems from weak ball-ball and ball-M interactions. The Raman spectra of K-, Rb-, and Cs-doped C_{60} are essentially identical. These results, taken together, suggest that a model for superconductivity in the related M_3C_{60} compounds should be consistent with weakly coupled C_{60} molecular anions whose electronic and vibrational properties have been modified by charge transfer.

Solid C_{60} is a van der Waals–bonded insulator[5-7] with an empty sixfold-degenerate conduction band.[8] Since each carbon atom in a C_{60} ball bonds to three neighbors, as in graphite, there is a close connection between the nonplanar bonding of carbon atoms in a C_{60} molecule and the planar sp^2 trigonal bonding that occurs in graphite. Thus a certain subset of the normal modes of C_{60} associated with primarily tangential and radial displacement of the C atoms are intimately connected with the intralayer and interlayer modes of graphite, respectively. The metallic character of the M_3C_{60} compounds may be viewed as stemming from a transfer of electrons from the alkali-metal atoms to create a half-filled (t_{1u} symmetry[8]) conduction band. At saturation doping, i.e., M_6C_{60}, the t_{1u} band is full in a rigid band scheme, and the solid should be insulating as observed.[9] Recently, superconductivity has been observed in binary and ternary alkali-metal-doped C_{60} by several groups.[10-14] The relatively high T_c values [e.g., 30 K in Cs-doped C_{60} (Ref. 13) and 33 K in $Cs_xRb_yC_{60}$ (Ref. 14)] underscore the importance of understanding the nature of the vibrational modes and electron-phonon interaction in M_xC_{60}.

Pristine C_{60} films were deposited onto silicon (100) substrates by sublimation in a vacuum of $\sim 10^{-6}$ Torr.

Alkali-metal doping was carried out in a sealed quartz tube containing the film (200 °C) and alkali metal (100 °C) in opposite ends. The reactions were carried out for 1 h, which produced a color change in the films and a ~ 37 cm^{-1} downshift of the strongest Raman line of pristine C$_{60}$ at 1469 cm^{-1}. The ampoules were returned to the furnace for another hour under the same conditions and no further downshift of the peak was observed. Raman spectra (300 K) were collected in the Brewster angle backscattering geometry[15] and cylindrical focusing of low ($P < 40$ mW) laser radiation (spot size: 1×0.1 mm^2) was found necessary to prevent laser-induced damage to the C$_{60}$ films. M_6C$_{60}$ films were studied in their growth ampoules; pristine films were handled in air but the spectra were collected with N$_2$ gas flowing over the surface of the film.

Figure 1 shows low-resolution (6 cm^{-1}) unpolarized Raman spectra of pristine C$_{60}$ and M_6C$_{60}$; all films were ~ 1000 Å in thickness. Weak lines are observed in the C$_{60}$ spectrum at 1099 and 1248 cm^{-1}. They are not due to a minority inclusion of C$_{70}$, as no Raman lines are observed in our spectra near strong C$_{70}$ line frequencies reported by Meijer et al.[16] The counterparts of the C$_{60}$ lines in the M_6C$_{60}$ films appear at 1094 and 1237 cm^{-1}. The weak lines seen in Fig. 1 above 1573 cm^{-1} vary in strength from that shown in Fig. 1, to even weaker intensities in other samples. The doped spectra are all remarkably similar, exhibiting very little dependence on the mass, radius, or electronic levels of the respective alkali-metal constituents. The features at 520 and 965 cm^{-1} in the C$_{60}$ spectrum (Fig. 1) are identified with the silicon substrate.[17] These features vanish in the doped films, indicating higher optical absorption near the laser wavelength (4880 Å) in M_6C$_{60}$ than in pristine C$_{60}$. Two (three) strongly polarized modes are observed for C$_{60}$ (M_6C$_{60}$), and are identified below on the basis of symmetry considerations. In contrast to the case of C$_{60}$, two of the M_6C$_{60}$ lines at ~ 271 and ~ 429 cm^{-1} are resolved as doublets at higher resolution. In Table I we collect the Raman data for C$_{60}$ and Rb$_6$C$_{60}$ films, including the depolarization ratio (I_{HV}/I_{HH}) (Ref. 18) and the peak widths [full width at half maximum (FWHM)]. Similar data are obtained for K- and Cs-doped C$_{60}$ and will be presented elsewhere.[19]

Recent x-ray-diffraction experiments indicate that pristine C$_{60}$ exhibits a simple cubic structure below 249 K, with space group $Pa3$ (or T_h^6).[20] There are four balls per unit cell in this structure located at sites with T_h symmetry. The number of allowed Raman modes in this low-temperature structure is therefore very large: 31 $A_g(1)$ modes, 31 $E_g(2)$ modes, and 89 $T_g(3)$ modes, where the symmetry label is followed by the mode degeneracy in parentheses. At room temperature, on the other hand, the balls are spinning with a long rotational time compared to a Raman-scattering event ($\sim 10^{-14}$ sec).[21] On this time scale, the average site symmetry for each ball is even lower, and a large number of modes are therefore anticipated. What is observed here and in previous work by Meijer et al.[16] is ten Raman lines (2 $A_g + 8$ H_g) for solid C$_{60}$, the number predicted by group theory for an isolated C$_{60}$ ball with icosahedral symmetry I_h.[22-25] The A_g
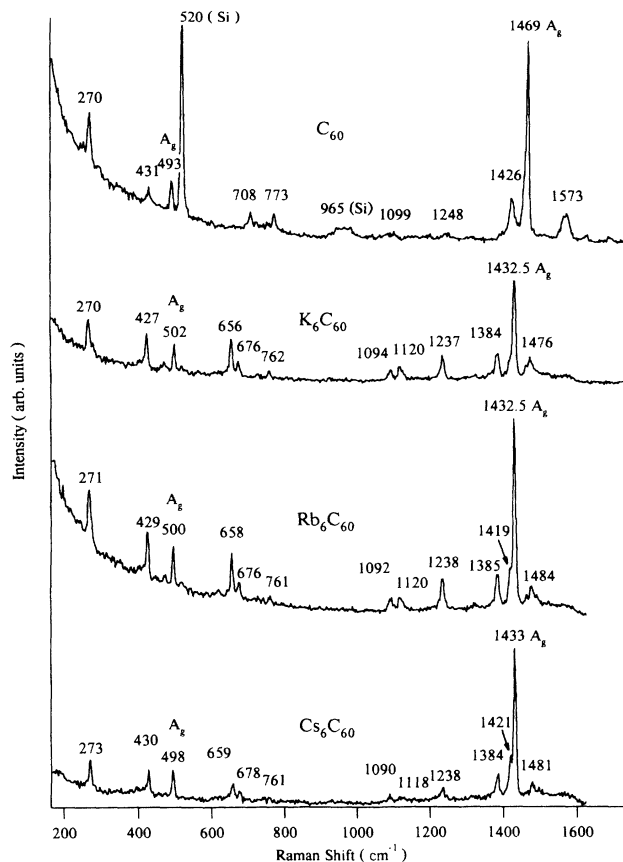

FIG. 1. Low-resolution (~ 6 cm^{-1}) Raman spectra taken at $T = 300$ K for solid films of C$_{60}$ and saturation-doped M_xC$_{60}$ ($x \sim 6$, $M =$ K, Rb, Cs). Polarization properties and FWHM's for Rb$_6$C$_{60}$ and C$_{60}$ appear in Table I.

modes are identified by their polarized character and appear at 493 cm^{-1} (radial[24]) and 1469 cm^{-1} (tangential[24]); the remaining eight lines are unpolarized, consistent with H_g symmetry. Thus we conclude that the ball-ball interactions in solid C$_{60}$ are weak and the Raman activity turned on by these interactions is insufficient to allow experimental detection.

The $T = 300$ K structure of M_6C$_{60}$ is Im(3) (or equivalently T_h^5).[1] This symmetry will give rise to approximately twice as many C$_{60}$-derived, Raman-active modes for M_6C$_{60}$ than an isolated C$_{60}$ molecule. However, only five new lines are observed; four can be identified as partners in doublets. The splitting between lines in these doublets is $\sim 10-30$ cm^{-1}, which are grouped as pairs in Table I. It is therefore reasonable to assign these pairs of lines to a splitting of the H_g symmetry modes of C$_{60}$ activated by the incorporation of M^+ ions. However, their polarization behavior indicates that a further lowering of the symmetry at 300 K must take place. The H_g modes of C$_{60}$ should split into diagonally polarized E_g and off-diagonally unpolarized T_g modes under T_h^5 symmetry. Numerous other Raman-active modes anticipated for solid M_6C$_{60}$ are therefore found to exhibit insufficient Raman activity. It should be remarked that the Raman line shape for all the modes in C$_{60}$ and M_6C$_{60}$ is observed to be

TABLE I. Experimental Raman-mode frequencies for C_{60} and Rb_xC_{60} ($x \sim 6$) at $T = 300$ K. Theoretical results for molecular C_{60} and previous experimental results on solid C_{60} are included for comparison.

| C60 | | | | Rb6C60 |
| Experiment | | Theory | | Experiment |
This work	Meijer et al. (Ref. 16)	Negri, Orlandi, and Zerbetto (Ref. 25)	Stanton and Newton (Ref. 24)	This work
270.0 [4.2,0.52] [a]	273	258	263(69.3) [b]	271.5 [0.9,0.54] 277.0 [0.7,0.85]
430.5 [5.5,0.40]	437	440	447(90.0)	421.5 [0.8,0.61] 428.5 [<1,0.65]
493.0 [2.5,0.02] [c]	496 [c]	513 [c]	610(100) [c]	500.0 [0.4,0.12] [c]
708.0 [7.5,0.40]	710	691	771(96.5)	657.5 [2.2,0.74] 676.5 [<1,0.00] [d]
772.5 [9.0,0.38]	774	801	924(30.5)	760.5 [2.0,068]
1099 [7,]	1099	1154	1261(9.6)	1092.0 [11,0.78] 1120.5 [12,0.35]
1248 [7,]	1250	1265	1407(2.1)	1238.5 [0.8,0.57]
1426.0 [7.5,0.44]	1428	1465	1596(0.8)	1385.0 [8.7,0.60] 1419.5 [11,0.14] [d]
1468.5 [1.5,0.10] [c]	1470 [c]	1442 [c]	1667(0.0) [c]	1432.5 [2.7,0.10] [c]
1573.0 [9.5,0.52]	1575	1644	1722(1.2)	1483.5 [15,0.80]

[a]Numbers in brackets are natural line width (cm^{-1}) and depolarization ratio (I_{HV}/I_{HH}), respectively.
[b]Number in parentheses is percentage of radial-mode character.
[c]A_g modes.
[d]Polarized E_g mode.

Lorentzian and not Gaussian. The latter line shape results from inhomogeneous broadening from a random distribution of defects, such as might arise from incomplete intercalation of M atoms. Lower-frequency Raman-active modes associated with interball motion are anticipated but have not been observed in this study. Collected in Table I are calculated frequencies for molecular C_{60} according to Negri, Orlandi, and Zerbetto,[25] which exhibit the best agreement with experiment, and Stanton and Newton,[24] which provide another point of comparison, as well as an estimate of the percent radial character of the vibrational eigenmodes.

The observation that the downshift of the highest-frequency tangential modes in solid C_{60} is independent of the nature of the alkali-metal dopant is interpreted as a clear indication that the charge-transfer-induced elongation of the average C-C bond length dominates the effect, and the downshift is not significantly mediated by interball or M-ball interactions. Haddon et al.[9] reported previously the x-dependent downshift of the A_g mode of C_{60} at 1469 cm^{-1} (Ref. 26) to 1445 cm^{-1} in highly conducting K_xC_{60} ($x \cong 3$) and 1430 cm^{-1} in the highly doped but insulating compound ($x \cong 6$). In agreement with our view, they also identify this softening with electron donation to the ball. In addition, we find that other high-

frequency tangential modes also soften upon doping to $x = 6$. The solid C_{60} lines at 1426 and 1469 cm^{-1} downshift by ~ 40 cm^{-1}, and the 1573-cm^{-1} line downshifts by ~ 100 cm^{-1} in solid M_6C_{60}. Previous theoretical studies by Chan, Ho, and Kamitakahara[2] of charge-transfer effects on the Raman-active intralayer modes in GIC's report a charge-transfer shift $(\Delta\omega_{ct}/q_c) = -880$ cm$^{-1}/e$, where q_C is the average charge per C atom donated to the graphene layers in units of electrons per C atom. Assuming six electrons transferred per C_{60}, and using an average mode downshift of 60 cm^{-1} for the highest three tangential modes, we arrive at $(\Delta\omega_{ct}/q_C) = -600$ cm$^{-1}/e$, or $\sim 70\%$ of the effect in GIC's.[2]

In GIC's, a universal relationship between C-C bond length and q_C was proposed first by Pietronero and Strassler[3] on the basis of empirical calculations. Later, Chan et al.[4] performed ab initio calculations of the effect and found a weaker relationship between the C-C bond length (d_{CC}) and q_C. X-ray- and neutron-diffraction studies in the alkali-metal GIC's do show a clear universal relationship between d_{CC} and q_C. A value $q_C = -0.1$ e in GIC's is associated with an elongation $\Delta d_{CC} = 0.010$ Å (Ref. 4). In contrast to the high-frequency tangential C_{60} modes, the low-frequency radial C_{60} mode at 493 cm^{-1} (A_g) increases by ~ 7 cm^{-1} upon doping to M_6C_{60}, indi-

cating that a competing effect overwhelms the effect of C-C bond elongation. This conclusion is supported by recent theoretical calculations indicating that an electrostatic interaction arising from the charged C_{60} ball is partly responsible for the upshift.[27]

[1]O. Zhou *et al.*, Nature (London) **351**, 462 (1991).

[2]C. T. Chan, K. M. Ho, and W. A. Kamitakahara, Phys. Rev. B **36**, 3499 (1987).

[3]L. Pietronero and S. Strassler, Phys. Rev. Lett. **47**, 593 (1981).

[4]C. T. Chan, W. A. Kamitakahara, K. M. Ho, and P. C. Eklund, Phys. Rev. Lett. **58**, 1528 (1987).

[5]W. Kratschmer, L. D. Lamb, K. Fostiropoulous, and D. R. Huffman, Nature (London) **347**, 354 (1990).

[6]H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Carl, and R. E. Smalley, Nature (London) **318**, 162 (1985).

[7]R. M. Fleming *et al.*, in *Clusters and Cluster-Assembled Materials*, edited by R. S. Averback, D. L. Nelson, and J. Bernhole, MRS Symposia Proceedings No. 206 (Materials Research Society, Pittsburgh, 1991), p. 691.

[8]R. E. Curl and R. E. Smalley, Nature (London) **242**, 1017 (1988).

[9]R. C. Haddon *et al.*, Nature (London) **350**, 320 (1991).

[10]A. F. Hebard, M. J. Rosseinsky, R. C. Haddon, D. W. Murphy, S. H. Glarum, T. T. M. Palstra, A. P. Ramirez, and A. R. Korton, Nature (London) **350**, 600 (1991).

[11]M. J. Rosseinsky *et al.*, Phys. Rev. Lett. **66**, 2830 (1991).

[12]K. Holczer *et al.*, Science **252**, 1154 (1991).

[13]S. P. Kelty, C. C. Chen, and C. M. Lieber, Nature (London) **352**, 223 (1991).

[14]K. Tanigaki, T. W. Ebbesen, S. Saito, J. Mizuki, J. S. Tsai, Y. Kubo, and S. Kuroshima, Nature (London) **352**, 222 (1991).

[15]The laser radiation is incident at ~45° to the surface normal and polarized in the plane of incidence.

[16]G. Meijer *et al.*, in *Clusters and Cluster-Assembled Materi-*

als (Ref. 7), p. 619.

[17]K. Uchinokura, T. Sekine, and E. Matsuura, Solid State Commun. **11**, 47 (1972).

[18]HH is horizontally polarized incident light and scattered light. HV is horizontally polarized incident light and vertically polarized scattered light.

[19]Ping Zhou, Kai-An Wang, Ying Wang, P. C. Eklund, M. S. Dresselhaus, G. Dresselhaus, and R. A. Jishi (unpublished).

[20]P. A. Heiney, J. E. Fischer, A. R. McGhie, W. J. Romanow, A. M. Denenstein, J. P. McCauley, Jr., and A. B. Smith III, Phys. Rev. Lett. **66**, 2911 (1991). Also see A. B. Harris *et al.*, Phys. Rev. Lett. (to be published); W. I. F. David *et al.*, Nature (London) **353**, 147 (1991).

[21]C. S. Yannoni, R. D. Johnson, G. Meijer, D. S. Bethune, and J. R. Salem, J. Phys. Chem. **95**, 9 (1991).

[22]D. E. Weeks and W. G. Harter, J. Chem. Phys. **90**, 4744 (1989).

[23]Z. C. Wu, D. A. Jelski, and T. F. George, Chem. Phys. Lett. **137**, 291 (1987).

[24]R. E. Stanton and M. D. Newton, J. Phys. Chem. **92**, 2141 (1988).

[25]F. Negri, G. Orlandi, and F. Zerbetto, Chem. Phys. Lett. **144**, 31 (1988).

[26]S. J. Duclos *et al.*, Solid State Commun. (to be published). These authors reported that C_{60} films not exposed to air exhibit a strong line at 1458 cm^{-1} rather than 1469 cm^{-1} as reported in this work and Ref. 9.

[27]R. A. Jishi and M. S. Dresselhaus (unpublished).