Raman Scattering Study of Ba-doped $C_{60}$ with $t_{1g}$ States

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Abstract

Raman spectra are reported for Ba doped fullerides, $Ba_xC_{60}$ (x=3, 4, and 6). The lowest frequency $H_g$ modes split into five components for $Ba_4C_{60}$ and $Ba_6C_{60}$ even at room temperature, allowing us a quantitative analysis based on the electron-phonon coupling theory. For the superconducting $Ba_4C_{60}$, the density of states at the Fermi energy was derived as $7 \, eV^{-1}$, while the total value of electron-phonon coupling $\lambda$ was found to be 1.0, which is comparable to that of $K_3C_{60}$. The tangential $A_g(2)$ mode, which is known as a sensitive probe for the degree of charge transfer on $C_{60}$ molecule, shows a remarkable shift depending on the Ba concentration, being roughly consistent with the full charge transfer from Ba to $C_{60}$. An effect of hybridization between Ba and $C_{60}$ $\pi$ orbitals is also discussed.

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I. INTRODUCTION

Since the discovery of superconductivity in alkali-metal doped $C_{60}$, extensive research on $C_{60}$ and other fullerenes has been carried out worldwide, aiming at understanding the mechanism for superconductivity and other related issues in fullerenes.\textsuperscript{1–8} Most of the theoretical models assumed that electron-phonon interaction is important for superconductivity.\textsuperscript{1–4} Based on the analysis of the linewidths in vibronic spectra excited either by light (Raman scattering) or by neutrons, the electron-phonon coupling constant $\lambda$ for $A_3C_{60}$ ($A=$ alkali metal) has been estimated. Recently, Winter and Kuzmany observed that the low frequency $H_g(1)$ and $H_g(2)$ modes lose all degeneracy and split into five components, each of which couples differently to the $t_{1u}$ electrons for single crystal of $K_3C_{60}$ at 80 K.\textsuperscript{9} These results revealed that in the superconducting state, the pairing is mediated by phonons with weak or intermediate coupling.\textsuperscript{10–12} The lowest two unoccupied molecular orbitals of $C_{60}$ are both triply degenerated, having $t_{1u}$ and $t_{1g}$ symmetry. Filling of $t_{1u}$ and $t_{1g}$ bands with electrons is achieved by intercalation of alkali metals and alkaline earth metals to $C_{60}$ solids, respectively. Nevertheless, understanding of the "$t_{1g}$ superconductors" is extremely poor in comparison with the well known $t_{1u}$ superconductors. Comparison of physical property in between the $t_{1u}$ and $t_{1g}$ superconductors is of particular interest from the view point of mechanism of superconductivity. From the $t_{1u}$ symmetry of the electrons in the conduction band a coupling is only possible to the total symmetric $A_g$ modes and to the five-fold degenerate $H_g$ modes. While the coupling to the $A_g$ mode is expected to be weak due to an efficient screening effect, the $H_g$ modes may have a significantly strong coupling constant since they allow a Jahn-Teller mechanism. A similar coupling should take place in the case of the electrons with $t_{1g}$ symmetry.

Superconductivity of Ba-doped $C_{60}$ was first discovered by Kortan et al.\textsuperscript{13} who claimed that the superconducting phase is bcc $Ba_6C_{60}$. Recently, Baenitz et al.\textsuperscript{14} on the other hand, reported that the superconducting phase is not $Ba_6C_{60}$ but $Ba_4C_{60}$. Very recently, we succeeded to synthesize single phase $Ba_4C_{60}$, and unambiguously confirmed that the
Ba$_4$C$_{60}$ is the superconducting phase. In this work, we present results of a Raman scattering study of single phase Ba$_x$C$_{60}$ ($x=3$, 4 and 6) with $t_{1g}$ states. The results indicate that the electron-phonon interaction is also important for the $t_{1g}$ superconductor, particularly in superconducting Ba$_4$C$_{60}$. In addition, some amazing results were observed, particularly for the low frequency $H_g$ modes. (1) Raman shift of the tangential $A_g$ mode for Ba$_6$C$_{60}$ is much larger than the simple extrapolation relationship between Raman shift and charge transfer in alkali metal doped C$_{60}$; while the radial $A_g$ mode nearly remains unchanged with increasing charge transfer. (2) The Raman scattering behavior is quite different among the three phases of Ba$_3$C$_{60}$, Ba$_4$C$_{60}$ and Ba$_6$C$_{60}$, especially for the low frequency $H_g$ modes. The low frequency $H_g$ modes lose all degeneracy and split into five (or four) peaks at room temperature for the Ba$_4$C$_{60}$ and Ba$_6$C$_{60}$ samples, each of which couples differently to electrons with $t_{1g}$ symmetry. The splitting of low frequency $H_g$ modes into five components even at room temperature is similar to that observed in single crystal of K$_3$C$_{60}$ at low temperature of 80 K. This is significant to understand the splitting and to evaluate the electron-phonon coupling constants for all directly coupling mode, estimating Tc in Ba-doped C$_{60}$.

II. EXPERIMENT

Samples of Ba$_x$C$_{60}$ ($x=3$, 4 and 6) were synthesized by reacting stoichiometric amount of powers of Ba and C$_{60}$. A quartz tube with mixed powder inside was sealed under high vacuum of about $2 \times 10^{-6}$ torr. The samples of Ba$_3$C$_{60}$ and Ba$_6$C$_{60}$ were calcined at 600 °C for 216 hours with intermediate grindings of two times. In order to obtain high quality Ba$_4$C$_{60}$ sample, thermal annealing was carried out at 600 °C for 1080 hours with five intermediate grindings. X-ray diffraction showed that all samples were single phase, which is also confirmed by the single peak feature of the pentagonal pinch $A_g$(2) mode in the Raman spectra.

Raman scattering experiments were carried out using the 632.8 nm line of a He-Ne laser in the Brewster angle backscattering geometry. The scattering light was detected with a
Dilor xy multichannel spectrometer using a spectral resolution of 3 cm⁻¹. Decomposition of the spectra into individual lines was made with a peak-fitting routine after a careful subtraction of the background originating from the laser. In order to obtain good Raman spectra, the samples were ground and pressed into pellets with pressure of about 20 kg/cm², which were sealed in Pyrex tubes under a high vacuum of 10⁻⁶ torr.

III. RESULTS AND DISCUSSION

Figure 1 shows room temperature Raman spectra for the polycrystalline samples of \( \text{Ba}_3\text{C}_6\text{O} \), \( \text{Ba}_4\text{C}_6\text{O} \), and \( \text{Ba}_6\text{C}_6\text{O} \). For the three samples, only one peak of the pentagonal pinch \( A_g(2) \) mode is observed, providing an evidence that each sample is in a single phase. These agree fairly well with the x-ray diffraction patterns. Interestingly, the three spectra have different strongest lines; they are \( H_g(2) \), \( A_g(1) \), and \( A_g(2) \) modes for \( \text{Ba}_3\text{C}_6\text{O} \), \( \text{Ba}_4\text{C}_6\text{O} \), and \( \text{Ba}_6\text{C}_6\text{O} \), respectively. Another thing to be noted is that the half-width of all corresponding peaks of \( \text{Ba}_4\text{C}_6\text{O} \) is largest among \( \text{Ba}_x\text{C}_6\text{O} \) (\( x=3, 4 \) and 6 ) samples except for the \( A_g(1) \) mode. This result is indicative of an importance of electron-phonon coupling in Raman spectrum of \( \text{Ba}_4\text{C}_6\text{O} \). Detailed discussion is given in the following. Also, it is to be pointed out that the Raman spectrum of \( \text{Ba}_3\text{C}_6\text{O} \) sample is amazingly similar to that of \( \text{K}_6\text{C}_6\text{O} \) suggesting that the electronic states of \( \text{Ba}_3\text{C}_6\text{O} \) is similar to that of \( \text{K}_6\text{C}_6\text{O} \). This is in a fair agreement with a simple expectation that \( \text{C}_6\text{O} \) in both compounds is hexavalent.

The frequency of the pentagonal pinch mode \( A_g(2) \) decreases with increasing Ba concentration, similarly to the case of alkali-metal doped \( \text{C}_6\text{O} \). The Raman shift of the \( A_g(2) \) mode is discussed in the following. By contrast, the frequency of the radial \( A_g(1) \) mode remains almost unchanged with Ba concentration, being different from the case of \( \text{K}_x\text{C}_6\text{O} \), where a slight up-shift of the radial \( A_g(1) \) mode was observed. The low frequency \( H_g \) modes show dramatic changes depending on the Ba concentration. In particular, clear splittings are observed for the lowest frequency \( H_g \) modes of \( \text{Ba}_4\text{C}_6\text{O} \) and \( \text{Ba}_6\text{C}_6\text{O} \). The positions \( (\omega) \) and halfwidths \( (\gamma) \) of the Raman modes observed are listed in Table I. For comparison, the
lines for pure $C_{60}$ are included in Table I. In the following, we show detailed analysis of $H_g$ modes first, and then, discuss on the $A_g$ modes.

In Fig.2 we show the results of a line-shape analysis of the Raman spectra of the $H_g(1)$ modes for $Ba_3C_{60}$, $Ba_4C_{60}$, and $Ba_6C_{60}$ samples. All modes were fit to a Lorentzian line shape. For $Ba_3C_{60}$ and $Ba_6C_{60}$, a doublet with Lorentzian components is observed, which has been observed in $K_6C_{60}$. However, the $H_g(1)$ mode has to be fit with four components for $Ba_4C_{60}$. This splitting may be attributed to the symmetry lowering due to the orthorhombic structure of this material. A similar behavior has been observed in single crystal $K_3C_{60}$ at 80 K, in which the $H_g(1)$ mode is split into five components. Position of the $H_g(1)$ components for $Ba_4C_{60}$ sample is nearly the same as that observed in $K_3C_{60}$.

Figure 3 shows the higher resolution Raman spectra in the vicinity of 400 \( cm^{-1} \) for $Ba_3C_{60}$, $Ba_4C_{60}$, and $Ba_6C_{60}$. While the cubic $Ba_3C_{60}$ shows a single peak at 432 \( cm^{-1} \), $H_g(2)$ mode is apparently split into five components in $Ba_6C_{60}$. This splitting of $H_g(2)$ mode in $Ba_6C_{60}$ is unexpected since the group theoretical consideration predicts a splitting into two in the space group $I_{m\overline{3}}$ (\( T_h^5 \)). The splitting of the $H_g(2)$ mode might suggest a symmetry lowering which is not detected in the x-ray diffraction. This type of disagreement between microscopic spectroscopy and structural analysis was observed in $Rb_3C_{60}$, and still remains an open question. A characteristic feature of the $H_g(2)$ mode of $Ba_6C_{60}$ is that the widths $\gamma$ of the components are almost the same except for the 428 \( cm^{-1} \) component. By contrast, the $H_g(2)$ mode of $Ba_4C_{60}$ shows a strong peak at the high frequency edge associated with a long tailing structure towards lower frequencies. Linewidth and lineshift for the components are clearly related. A theoretical calculation shows the electron-phonon coupling constants are very sensitive to the change in the normal coordinates, the different components of the mode correspond to the different coupling constants. It suggests that the fivefold degeneracy of the mode is lifted and each component couples with a different strength to the $t_{1g}$ carriers in $Ba_4C_{60}$.

Results of a line-shape analysis of the Raman spectra of the $H_g(3)$ modes are shown in Fig.4. A doublet of $H_g(3)$ is observed for $Ba_3C_{60}$, which is ascribed to symmetry-lowering
relative to $C_{60}$ molecules. The $H_g(3)$ mode also displays a splitting into four both in $Ba_4C_{60}$ and $Ba_6C_{60}$. The splitting of the $H_g(3)$ mode in $Ba_6C_{60}$ also contradicts with the group theoretical consideration. It is to be pointed out that this anomalous splitting of $Ba_6C_{60}$ $H_g$ modes is observed only in $H_g(2)$ and $H_g(3)$ modes. The other $H_g$ modes are singlet or doublet, being consistent with the group theoretical consideration.

In reference 9, Winter and Kuzmanay gave several possible explanations for the splitting of the low frequency $H_g$ modes. (1) The splitting of the modes is understood from the merohedral disorder for the alkali derived metallic fullerides. This disorder is of low enough symmetry to allow only one dimensional representations for all modes. (2) The splitting originates from a Jahn-Teller type interaction. This interaction can give rise to a new vibrational system with rather large number of components, even more than five. Also, a contribution to the splitting from an internal strain between the doped part of the crystal and the undoped part of the crystal. In our experiments, the low frequency $H_g$ modes almost lose all degeneracy for $Ba_4C_{60}$ and $Ba_6C_{60}$, and is different from that of $Ba_3C_{60}$ which is similar to that of $K_6C_{60}$ at room temperature. In the case of $Ba_4C_{60}$, the splitting can be understood since the crystal structure is orthorhombic. However, the splitting of $Ba_6C_{60}$ is not explained from the crystal structure. Particularly, when one considers that $Ba_6C_{60}$ is isostructural to $K_6C_{60}$, the splitting of $H_g(2)$ and $H_g(3)$ modes are considerably anomalous. This result might suggest that there exists a symmetry lowering which cannot be detected by x-ray diffraction. Similar symmetry lowering is observed in the NMR spectra of $Rb_3C_{60}$. The next thing to be pointed out is that the splitting is observed even in polycrystalline samples and at room temperature, in contrast to the case of $K_3C_{60}$. In alkaline-earth-metal doped $C_{60}$, the local-density approximation calculations show a strong hybridization between the alkaline-earth-atom states and the $C_{60}$ $\pi$ states. This hybridization, which is absent in the alkali-metal doped $C_{60}$, may play an essential role for the splitting of low frequency $H_g$ modes at room temperature.

For the components of low frequency $H_g$ modes, a clear relation between line shift and line broadening is observed in $Ba_4C_{60}$, which is similar to that of single crystal $K_3C_{60}$. Winter
and Kuzmanov have pointed out that the electron-phonon interaction plays an important role in the broadening and the shift of the lines, and they deduced electron-phonon coupling constants. The phonon linewidth broadening $\gamma_i$ due to the electron-phonon interaction in a metal can be related to a dimensionless electron phonon coupling constant $\lambda_i$ given by

$$\gamma_i = \frac{1}{g_i} N(0) \lambda_i \omega_{bi}^2$$

where $N(0)$ the density of states at the Fermi level per spin and molecule, and $g_i$ and $\omega_{bi}$ the mode degeneracy and the frequency before any coupling to the electrons, respectively. The Allen’s formula given above will be used to derive the coupling constants for the eight $H_g$ modes. Frequencies of pure $C_{60}$ were used as the bare phonon frequencies.

In the framework of Allen’s theory there should be a linear relation of the form

$$\gamma = -\frac{\pi}{2} N(0) \omega_b \Delta \omega$$

between $\gamma$ the linewidth and $\Delta \omega$ the difference between the bare phonon frequency and the observed frequency. According to the experimental values of the three lowest frequency $H_g$ modes in Table I, the relations between linewidth and frequency shift is plotted in Fig.5 for $Ba_4C_{60}$ and $Ba_6C_{60}$. The $\gamma$ and $\Delta \omega$ relation for $Ba_4C_{60}$ is linear and consistent with that expected from Eq.(2). $N(0)$ can be deduced from the slope. The density of states obtained from the three $H_g$ modes are 7 eV$^{-1}$, 4 eV$^{-1}$ and 3.2 eV$^{-1}$, respectively. The discrepancy may arise from the fact that we could not use the real bare phonon frequencies for the evaluation. Geometry effects may also contribute to the shift and may be different for the modes. For $Ba_6C_{60}$, there exists no relation between the linewidth and lineshift in Fig.5b. $N(0)$ is much less than 1 eV$^{-1}$ if it were deduced basing on the relation between linewidth and lineshift in Fig.5b. It suggests $Ba_6C_{60}$ could not follow electron-phonon coupling theory. It further supports that $Ba_4C_{60}$ is superconducting phase, rather than $Ba_6C_{60}$. For the evaluation of the coupling constants as discussed below a value of 7 eV$^{-1}$ is used for $N(0)$. To our knowledge, no $N(0)$ for $Ba_4C_{60}$ is available. The calculated $N(0)$ is 4.3 states per eV$^{-1}$ and an experimental value of 5.6 eV$^{-1}$ was reported for $Ba_6C_{60}$. The averaged linewidths and
the overall coupling constants for each mode and for all \( H_g \) modes for \( Ba_4C_{60} \) are listed in Table II, together with the frequencies for the pure \( C_{60} \). The averaged linewidths are directly evaluated from the linewidths listed in Table I. The values for \( \lambda_i \) are evaluated using Eq. (1).

The individual contributions to the coupling constant from each \( H_g \) mode are listed in Table II. The three lowest frequency \( H_g \) modes dominate the contribution to \( \lambda \), yielding over 70% of the total value. Large coupling constants of the low \( H_g \) modes were also observed in \( K_3C_{60} \).[\text{footnote}]\footnote{Within the BCS framework, the superconducting transition temperature \( T_c \) can be evaluated basing on the experimental values for \( \lambda \) by the McMillan equation

\[
T_c = \frac{\hbar \omega_{ln}}{1.2k_B} \exp\left[\frac{-1.04(1 + \lambda)}{\lambda - \mu^* - 0.62\lambda\mu^*}\right]
\]

where \( \omega_{ln} \) is the logarithmic averaged phonon frequency, \( k_B \) is the Boltzmann constant, and \( \mu^* \) is Coulomb repulsion between conduction electrons. According to the observed frequencies and the evaluated coupling constants, the \( \omega_{ln} \) was determined as 490 cm\(^{-1}\). With this value and \( \lambda \), the superconducting transition temperature of 7 K can be evaluated, assuming the \( \mu^* \) value as 0.3, however, which is anomalously large. The value for \( \mu^* \) is much larger than 0.18 in \( K_3C_{60} \) in the same way for evaluation of \( T_c \). It might suggest a difference between \( t_{1u} \) and \( t_{1g} \) superconductors. To evaluate \( T_c \), on the other hand, the logarithmic averaged phonon frequency of 150 cm\(^{-1}\) is obtained if the \( \mu^* \) is set as a reasonable value 0.2. In this case, the phonon frequency is significantly smaller than the intramolecular vibration range. Interestingly, the small phonon energy associated with superconductivity is also suggested by analysis of another \( t_{1g} \) superconductor \( A_3Ba_3C_{60} \).[\text{footnote}]\footnote{Let us switch to the arguments on the totally symmetric \( A_g \) modes. Figure 6 shows the Raman shift of the \( A_g(2) \) pentagonal pinch mode as a function of nominal charge transfer simply derived from the chemical formula for \( Ba_xC_{60} \). In this figure, we plotted the present results of \( Ba_xC_{60} \), as well as that of \( K_xC_{60} \) reported by Duclos et al.[\text{footnote}]\footnote{and the theoretical results of Jishi and Dresselhaus[\text{footnote}]\footnote{for comparison. Since the plots of \( Ba_xC_{60} \) approximately fall on an extrapolation of \( K_xC_{60} \) or theoretical line, the charge transfer value from Ba to}
C_{60} is almost complete. The molecular valences of Ba_{x}C_{60} (x=3, 4, 6) are regarded as -6, -8, and -12, respectively. However, the situation is more complicated than the case of alkali doped materials. Several band calculations and experiments\textsuperscript{21,22,26} suggest a strong effect of hybridization of Ba and C_{60} orbitals. If this is the case, the net charge transfer to C_{60} is expected to be incomplete. In the present result, however, the charge transfer is approximately complete. Moreover, the slope of Ba_{x}C_{60} is steeper than that of K_{x}C_{60} or theory. These results indicate that the phonon mode should be reconsidered in the presence of metal-fullerene hybridization. Especially, there is a difference of 10 cm\(^{-1}\) between the experimental and theoretical values for Ba_{6}C_{60}. The theory of Jishi and Dresselhaus focuses on the mode softening of the tangential vibrational A\(_{g}\) mode for the alkali-metal derived fullerides, the hybridization between intercalants and C_{60} was not considered.

It can be seen from Table I that the frequency of the radial A\(_{g}\) mode for Ba\(_{3}\)C\(_{60}\) is 506 cm\(^{-1}\). The upshift is as high as 13 cm\(^{-1}\) relative to pure C\(_{60}\). But, upon further doping with barium, the frequency nearly remains unchanged, being different from alkali-metal doped C\(_{60}\), which shows a continuous hardening of A\(_{g}\)(1) mode as a function of alkali metal concentration.\textsuperscript{17} The mode-stiffening effect is due to electrostatic interactions which produces sufficient stiffening to encounter the softening of the mode expected on the basis of charge-transfer effects.\textsuperscript{16,27} In the case of Ba derived fullerides, there exists a strong hybridization between the Ba atoms and the \(\pi\)-type functions of the C\(_{60}\) network. This may lead to a decrease in the electrostatic interactions, so that the frequency of the radial A\(_{g}\) mode nearly remains unchanged with increasing Ba concentration.

**IV. CONCLUSION**

Raman scattering studies of single phase Ba\(_{3}\)C\(_{60}\), Ba\(_{4}\)C\(_{60}\), and Ba\(_{6}\)C\(_{60}\) have been carried out. The lowest frequency H\(_{g}\) modes split in to five components for Ba\(_{4}\)C\(_{60}\) and Ba\(_{6}\)C\(_{60}\). A characteristic relation between lineshift and linewidth is observed in Ba\(_{4}\)C\(_{60}\), this is consistent with that expected by electron-phonon interaction. While Ba\(_{6}\)C\(_{60}\) does not exhibit
such behavior. The characteristic relation is used to evaluate the N(0), the electron-phonon coupling constants are evaluated basing on the Raman results in the framework of Allen’s theory. The radial $A_g$ mode shows a different behavior from alkali derived fullerides, the frequency remains unchanged with increasing Ba concentration; the effect of charge transfer on the softening of the tangential $A_g$ mode is larger in the alkaline-earth metal doped $C_{60}$ than in alkali derived $C_{60}$. These discrepancies may arise from the hybridization between intercalants and $C_{60}$ in alkaline-earth metal doped $C_{60}$.

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TABLE I. Positions and linewidths (in parentheses) for the Raman modes in $C_{60}$ and $Ba_xC_{60}$ $(x=3, 4$ and $6)$

| $I_h$ mode | $C_{60}$  | $Ba_3C_{60}$ | $Ba_4C_{60}$ | $Ba_6C_{60}$ |
|------------|-----------|-------------|-------------|-------------|
|            | $\omega$ ( $\gamma$ ) | $\omega$ ( $\gamma$ ) | $\omega$ ( $\gamma$ ) | $\omega$ ( $\gamma$ ) |
|            | ( cm$^{-1}$ ) | ( cm$^{-1}$ ) | ( cm$^{-1}$ ) | ( cm$^{-1}$ ) |
| $A_g(1)$   | 493       | 505.9 ( 4.2 ) | 507.2 ( 2.7 ) | 506.5 ( 5.0 ) |
| $A_g(2)$   | 1469      | 1430.8 ( 13.0 ) | 1413.4 ( 15.0 ) | 1372.5 ( 12.1 ) |
| $H_g(1)$   | 270       | 273 ( 5.3 ) | 247.4 ( 18.3 ) | 274.5 ( 5.2 ) |
|            |           | 278.7 ( 4.6 ) | 262.2 ( 1.8 ) | 281.8 ( 2.6 ) |
|            |           |           | 269.5 ( 10.2 ) |           |
|            |           |           | 279.4 ( 4.9 ) |           |
| $H_g(2)$   | 431       | 432.3 ( 5.3 ) | 340.8 ( 2.3 ) | 385.6 ( 4.4 ) |
|            |           |           | 381 ( 23.0 ) | 405.8 ( 2.2 ) |
|            |           |           | 396.6 ( 14.9 ) | 415.6 ( 2.4 ) |
|            |           |           | 413 ( 11.5 ) | 428 ( 16.8 ) |
|            |           |           | 431.9 ( 5.2 ) | 438.8 ( 2.8 ) |
| $H_g(3)$   | 709       | 648.2 ( 8.5 ) | 621 ( 37.7 ) | 585.2 ( 4.8 ) |
|            |           | 681.6 ( 7.8 ) | 651.2 ( 12.3 ) | 602.1 ( 5.2 ) |
|            |           |           | 680.7 ( 10.5 ) | 622.3 ( 3.7 ) |
|            |           |           | 694 ( 9.5 ) | 651.8 ( 12.0 ) |
| $H_g(4)$   | 773       | 760.7 ( 8.4 ) | 751.9 ( 11.0 ) | 732.5 ( 8.5 ) |
| $H_g(5)$   | 1099      | 1091.7 ( 18.5 ) | 1090.6 ( 11.8 ) | 1082 ( 6.0 ) |
|            |           | 1117.3 ( 12.8 ) | 1117 ( 12.0 ) | |
| $H_g(6)$   | 1248      | 1227.6 ( 16.1 ) | 1215.4 ( 9.4 ) | 1224 ( 26 ) |
|            |           |           | 1234.1 ( 13.8 ) | |
| $H_g(7)$   | 1426      | 1322.1 (42.6) | 1322 ( 48.6 ) | |
|            |           | 1388.1 ( 26.7 ) | 1381 ( 32.1 ) | |
| $H_g(8)$   | 1573      | 1474.4 ( 26.1 ) | 1461.7 ( 51.0 ) | 1437 ( 25.0 ) |
TABLE II. Positions, averaged linewidths and electron-phonon coupling constants normalized to the density of states at the Fermi energy for eight fivefold degenerate Hg modes for $Ba_4C_{60}$ sample.

| Modes | $\omega\ (cm^{-1})$ | $\bar{\gamma}\ (cm^{-1})$ | $\lambda/N(E_F)$ |
|-------|----------------------|----------------------------|------------------|
| $H_g(1)$ | 270 | 8.8 | 0.062 |
| $H_g(2)$ | 431 | 11.4 | 0.032 |
| $H_g(3)$ | 709 | 17.4 | 0.018 |
| $H_g(4)$ | 773 | 11.0 | 0.009 |
| $H_g(5)$ | 1099 | 11.9 | 0.005 |
| $H_g(6)$ | 1248 | 11.6 | 0.004 |
| $H_g(7)$ | 1426 | 40.0 | 0.010 |
| $H_g(8)$ | 1573 | 51.0 | 0.011 |
| $\Sigma$ | | | 0.151 |
FIGURE CAPTIONS

Figure 1:
Room temperature Raman spectra of $Ba_3C_{60}$, $Ba_4C_{60}$, and $Ba_6C_{60}$.

Figure 2:
Raman spectra of the $H_g(1)$ mode for $Ba_3C_{60}$, $Ba_4C_{60}$, and $Ba_6C_{60}$. The dash lines are computer fits for the individual components, which add up to the full line on the top of the experimental results.

Figure 3:
Raman spectra of the $H_g(2)$ mode for $Ba_3C_{60}$, $Ba_4C_{60}$, and $Ba_6C_{60}$. The dash lines and full line have the same meaning as in Fig.2

Figure 4:
Raman spectra of the $H_g(3)$ mode for $Ba_3C_{60}$, $Ba_4C_{60}$, and $Ba_6C_{60}$. The dash lines and full line have the same meaning as in Fig.2

Figure 5:
Plot of linewidth $\gamma$ versus observed frequency shift $\Delta \omega$ for the individual components of the $H_g(1)$, $H_g(2)$, and $H_g(3)$ modes, circles for the $H_g(1)$ mode; triangles for the $H_g(2)$ mode; squares for the $H_g(3)$ mode. (a) for the sample $Ba_4C_{60}$; (b) for the sample $Ba_6C_{60}$.

Figure 6:
Charge transfer-Raman shift relation for the $A_g(2)$ pinch mode. Squares represent the experimental results of $Ba_xC_{60}$, circles are from the results of $K_xC_{60}$ reported by Duclos et al. (Ref.15), and triangles refer to calculations from theory of Jishi and Dresselhaus (Ref.16).
Fig. 1
Fig. 2
Fig. 3

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Fig. 6