

Raman study of the polymerized state of RbC_{60} and CsC_{60}

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We report a room-temperature Raman investigation of C_{60} and orthorhombic AC_{60} phase ($o\text{-}AC_{60}$). The $o\text{-}AC_{60}$ phase is present when the sample is slowly cooled from the AC_{60} fcc disordered phase ($T > T_c$ of about 370 K) to room temperature. In the $o\text{-}AC_{60}$ phases large changes in the intensity of intramolecular modes not active in C_{60} as well as splitting of some modes of C_{60} are observed. In addition, new modes at 342, 632, and 967 cm^{-1} are evidenced. Nevertheless, from these data the length and the geometry of the oligomers phase cannot be unambiguously defined. Only the significant differences between the $o\text{-}AC_{60}$ Raman spectrum and the Raman spectrum of photopolymerized C_{60} and pressure-induced polymerized phases of C_{60} indicate some differences in the structural organization of C_{60} monomers in the $o\text{-}AC_{60}$ phase with respect to these systems. In both $o\text{-RbC}_{60}$ and $o\text{-CsC}_{60}$ phases the low-frequency Raman spectrum as excited at 776 nm exhibits a well-defined peak at around 31 cm^{-1} . The assignment of this mode is discussed and we propose to attribute it to the interball stretching mode in the relatively long oligomer (longer than dimer). This assignment supports the mechanism of polymerization via a (2+2) cycloaddition reaction between C_{60} molecules in the $o\text{-}AC_{60}$ phase. [S0163-1829(96)01043-0]

I. INTRODUCTION

C_{60} continues to attract considerable attention due to the elegant molecular structure and the intriguing structural, dynamic, and electronic properties of the solid phases of the fullerenes. Recent experiments provide convincing evidence that the ultraviolet and visible light cause the C_{60} molecules to polymerize.¹⁻³ The Raman spectrum of phototransformed C_{60} shows significant shifts and splittings and different modes appear in the spectra.¹⁻³ In particular, the high-energy pentagonal pitch mode shifts by about 10 cm^{-1} from 1469 cm^{-1} in C_{60} to 1459 cm^{-1} in the phototransformed structure. More recently we have stated that this phototransformed state was stable in air following a peculiar thermal treatment.⁴

Recently, it was also demonstrated that the phase with AC_{60} (A =alkali metal) stoichiometry presents, when the sample is slowly cooled from $T > 410\text{ K}$ (orientationally disordered phase) to 300 K , a stable orthorhombic ($o\text{-}AC_{60}$) polymer phase consisting of linear chains of C_{60} molecules.^{5,6} This phase exhibits some rather unusual properties including an extremely short interball distance along one direction and magnetic properties which have been interpreted in terms of a 1-d metal with a transition to a magnetic state below 50 K .⁷ This low-temperature magnetic state was interpreted as due to the formation of a spin-density wave,⁸ antiferromagnet⁹ or more disordered magnetic structure like random spin freezing.¹⁰

In the present study, we report a room-temperature

Raman-scattering investigation of solid C_{60} and $o\text{-}AC_{60}$ (A =Rb, Cs) phases. The first part of this paper is devoted to a report of our experimental results in both lattice modes and intramolecular modes regions. In a second part, these results will be discussed in the framework of the existence or not of oligomers (dimer, trimer, polymer) involving covalent bonding between neighboring C_{60} ions in the $o\text{-}AC_{60}$ (A =Rb, Cs) phase.

II. EXPERIMENTS

The saturated alkali-doped C_{60} sample, CsC_{60} , was synthesized by a vapor transport method similar to that described in the literature.¹¹ An excess amount of the metal and a quantity of desolved pure C_{60} powder were put in a Pyrex tube and separated from each other by a frit. The tube was put under vacuum in a furnace and heated at $250\text{ }^\circ\text{C}$ for several days. A temperature gradient of about $10\text{ }^\circ\text{C}$ was maintained along the tube with the alkali at the cold end to prevent the metal from condensing onto the C_{60} powder. To prepare the CsC_{60} compound, we used the dilution method by direct reaction of the saturated sample with an additional stoichiometric amount of desolved C_{60} . Then the sample was heated at $250\text{ }^\circ\text{C}$ for two weeks before cooling it down below the fcc to the polymer phase-transition temperature ($100\text{ }^\circ\text{C}$) and starting a very slow temperature decrease ($5\text{ }^\circ\text{C}$ per day) to room temperature. The sample was then transferred under vacuum in through a breakseal to a Raman cell and x-ray Lindeman capillary. The x-ray-powder-diffraction data for the sample are consistent with the re-

ported data on the polymer phase.¹² For the Raman experiment the sample has been used in air. The RbC_{60} sample was prepared using the method described in Refs. 7 and 12.

For the excitation of the Raman spectra, an argon-ion laser at 514.5 nm and a pumped Ti-sapphire laser at 776-nm excitation were used. Interference filters and monochromators served to clean the excitation beam from plasma lines.

The Raman spectra measured at 514.5 nm were taken with a "Jobin-Yvon T64000." A Notch filter has been used as an entrance monochromator in a single spectrograph step. With this configuration, only the intramolecular modes region ($200\text{--}1700\text{ cm}^{-1}$) could be studied. The resolution was 6 cm^{-1} . For the 776-nm excitation, the Raman spectra were recorded with a Dilor XY triple spectrometer, the resolution was 3 cm^{-1} . Both external modes and intramolecular modes regions have been analyzed. In the two experiments, the signal was analyzed in a backscattering geometry and detected by a nitrogen-cooled charge coupled device detector. The laser line was focused on the sample with a limited spot size of about 15 (Jobin-Yvon T64000) and $50\text{ }\mu\text{m}$ (Dilor XY), the laser intensities were limited to approximately 5 W/cm^2 .

III. RESULTS

Experimental results of Raman spectra from C_{60} , RbC_{60} , and CsC_{60} are presented at room temperature. Figure 1 displays the spectra measured at 514.5 nm on the three systems. These spectra cover the whole frequency range of the intramolecular modes ($200\text{--}1600\text{ cm}^{-1}$). The Raman spectrum of C_{60} is dominated by the pinch mode ($\text{Ag}(2)$) at 1469 cm^{-1} . Clearly this line is softened to about 1460 cm^{-1} in RbC_{60} and CsC_{60} . On the other hand, a significant increase of the relative intensity of the Ag and Hg low-frequency modes and Hg high-frequency modes as compared to the intensity of the $\text{Ag}(2)$ mode is observed in the two AC_{60} compounds. Table I compiles the frequencies of all the lines measured in these compounds at room temperature. These results are in complete agreement with the previous data of Winter and Kuzmany.¹³

Details of the most important regions of the spectrum which show splitting and the existence of new modes are shown in Figs. 2(a)–2(c). First, it is important to underline the strong similarity of the spectra measured on RbC_{60} and CsC_{60} respectively. Indeed, as the two samples have been synthesized by two groups using different procedures, the agreement between these results emphasizes the intrinsic character of these Raman spectra.

(i) In the $230\text{--}570\text{ cm}^{-1}$ range, three behaviors may be underlined: (i) the splitting of the $\text{Hg}(1)$ mode (at around 270 cm^{-1}) and $\text{Hg}(2)$ mode (at around 430 cm^{-1}) in several components (Table I), (ii) the relatively strong intensity of the lightly shifted $\text{Ag}(1)$ mode at 492 cm^{-1} , (iii) the appearance of a new Raman line at 344 cm^{-1} . As previously observed,¹³ we have shown that this latter disappeared in the high-temperature phase of the AC_{60} compounds and did not exist in the Raman spectrum of the phototransformed phase of C_{60} .⁴ Thus, this line can be seen as the Raman signature of the AC_{60} room-temperature phase.

(ii) In the $1300\text{--}1700\text{ cm}^{-1}$ range, the same profile of the RbC_{60} and CsC_{60} Raman spectrum is observed. The most

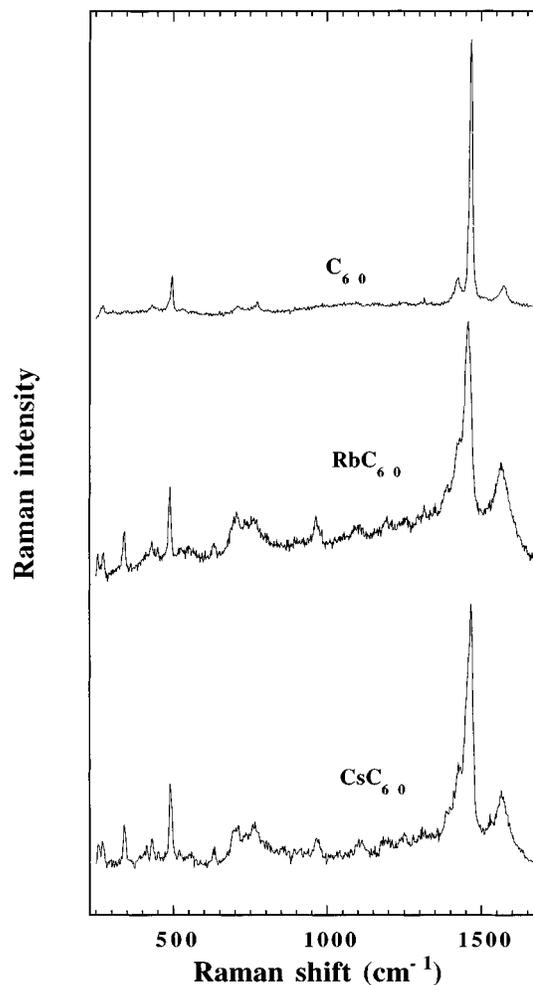


FIG. 1. Room-temperature Raman spectra as excited with 514.5 nm for C_{60} , $o\text{-RbC}_{60}$, and $o\text{-CsC}_{60}$.

intense Raman line ($\text{Ag}(2)$ mode) is shifted from 1469 cm^{-1} in C_{60} at around 1460 cm^{-1} in AC_{60} . On the other hand, the large width of this line (Γ of about 30 cm^{-1} against $\Gamma=6\text{ cm}^{-1}$ in C_{60}) suggests an overlap of several components, this result will be confirmed in the following. The $\text{Hg}(8)$ mode softens and broadens in AC_{60} . Shoulders at 1430 and 1392 cm^{-1} are also clearly evidenced.

In order to complete our information about the vibrational properties of AC_{60} room-temperature phase, a series of experiments have been performed by changing the laser energy used for the excitation. High-resolution Raman spectra of AC_{60} ($A=\text{Rb}, \text{Cs}$) have been recorded using a 776-nm excitation. A dramatic sensitivity of the AC_{60} Raman spectra intensity on the energy of the laser used for excitation has been previously shown.¹³ The aim of this study was to analyze this behavior on an homogeneous AC_{60} sample and, more interesting, to measure the low-frequency Raman spectrum. Indeed, due to the large penetration depth of the 776-nm excitation, the scattering volume is significantly bigger than the one probed with the 514.5-nm excitation and the increase of the scattering volume can allow the observation of nonresonant lattice modes.

Figures 3(a)–3(c) report the 776-nm Raman spectra in the intramolecular modes region [compared with the results dis-

TABLE I. Frequencies of the Raman intramolecular modes of C_{60} , o -Rb C_{60} , and o -Cs C_{60} as excited with 514.5 and 776 nm. The vibrational modes are assigned with respect to the Raman-active irreducible representations of C_{60} , the symbol + indicates new modes appearing in o -AC $_{60}$ with respect to this assignment.

| | C_{60} | o -AC $_{60}$ |
|-------|----------|-----------------|
| Ag(1) | 495 | 490 |
| Ag(2) | 1469 | 1462 |
| | | 1452 |
| Hg(1) | 266 | 250 |
| | 271 | 259 |
| | | 275 |
| + | | 343 |
| Hg(2) | 430 | 405 |
| | | 431 |
| | | 452 |
| + | | 632 |
| | | 695 |
| Hg(3) | 710 | 708 |
| Hg(4) | 770 | 735 |
| | | 765 |
| + | | 967 |
| | | 1085 |
| Hg(5) | 1100 | 1110 |
| Hg(6) | 1246 | 1200 |
| | | 1251 |
| Hg(7) | 1426 | 1392 |
| | | 1427 |
| Hg(8) | 1575 | 1567 |

played in Figs. 2(a)–2(c)]. If the Raman response decreases with decreasing laser energy, the profile of the spectra are close to those measured at 514.5-nm excitation. In addition, the better resolution of the 776-nm experiments clearly showed evidence of the splitting of several modes.

(i) In the 1400–1500- cm^{-1} range, as suggested from the 514.5-nm results, the Ag(2) mode clearly displays a double-peak structure; the two components are peaked at 1452 (± 2) cm^{-1} and 1462 (± 2) cm^{-1} in Rb C_{60} and Cs C_{60} [Fig. 3(c)].

(ii) In the 230–570- cm^{-1} range [Figs. 3(a), 3(b)], splitting of the Hg(1), Hg(2), Ag(1) modes of C_{60} in several peaks is observed. At this incident wavelength, the more striking result is certainly the vanishing of the 344- cm^{-1} mode [Fig. 3(a)]. This latter result could be attributed to a peculiar resonant character of this mode in relation with the structure of fullerene molecules in the room-temperature AC $_{60}$ phase. This latter remark emphasizes the importance of this mode assignment. As discussed below, this assignment is still an open question.

The more striking results have been obtained in the low-frequency range, 10–200 cm^{-1} . In Fig. 4 are given for comparison the low-frequency Raman spectra measured in C_{60} , Rb C_{60} , and Cs C_{60} , respectively. In these spectra, the modes at around 270 cm^{-1} have been displayed to be in use as the internal reference of intensity. As expected in the fcc disordered phase of C_{60} , no lattice modes are observed. In contrast with this latter behavior, an intense and well-defined peak at around 30 cm^{-1} is evidenced in the low-frequency Raman spectrum of Rb C_{60} and Cs C_{60} . To our knowledge, it is the first time that this low-frequency mode is observed in

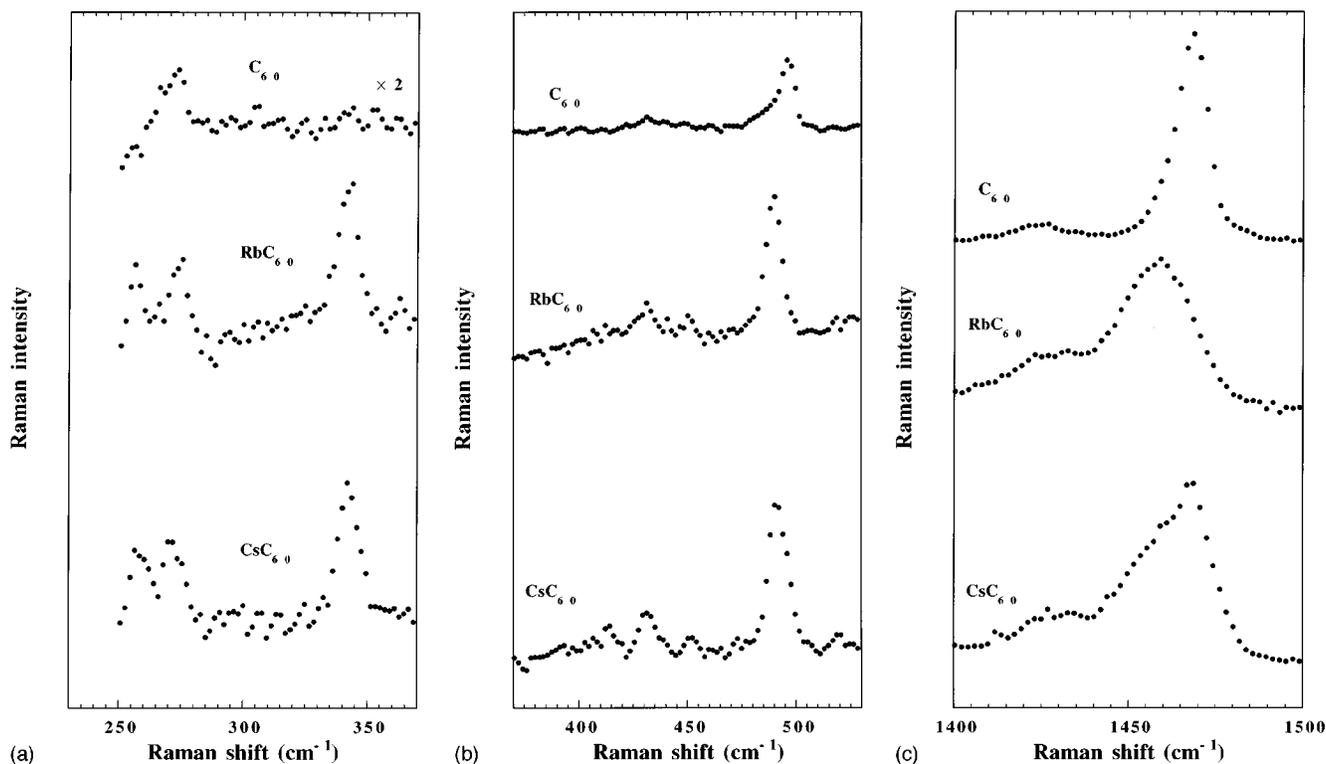


FIG. 2. Raman lines of C_{60} , o -Rb C_{60} , and o -Cs C_{60} for three characteristic regions of the spectrum as excited with 514.5 nm. (a) Spectral range of the Hg(1) mode. (b) Spectral range of Hg(2) and Ag(1) modes. (c) Spectral range of the Ag(2) mode.

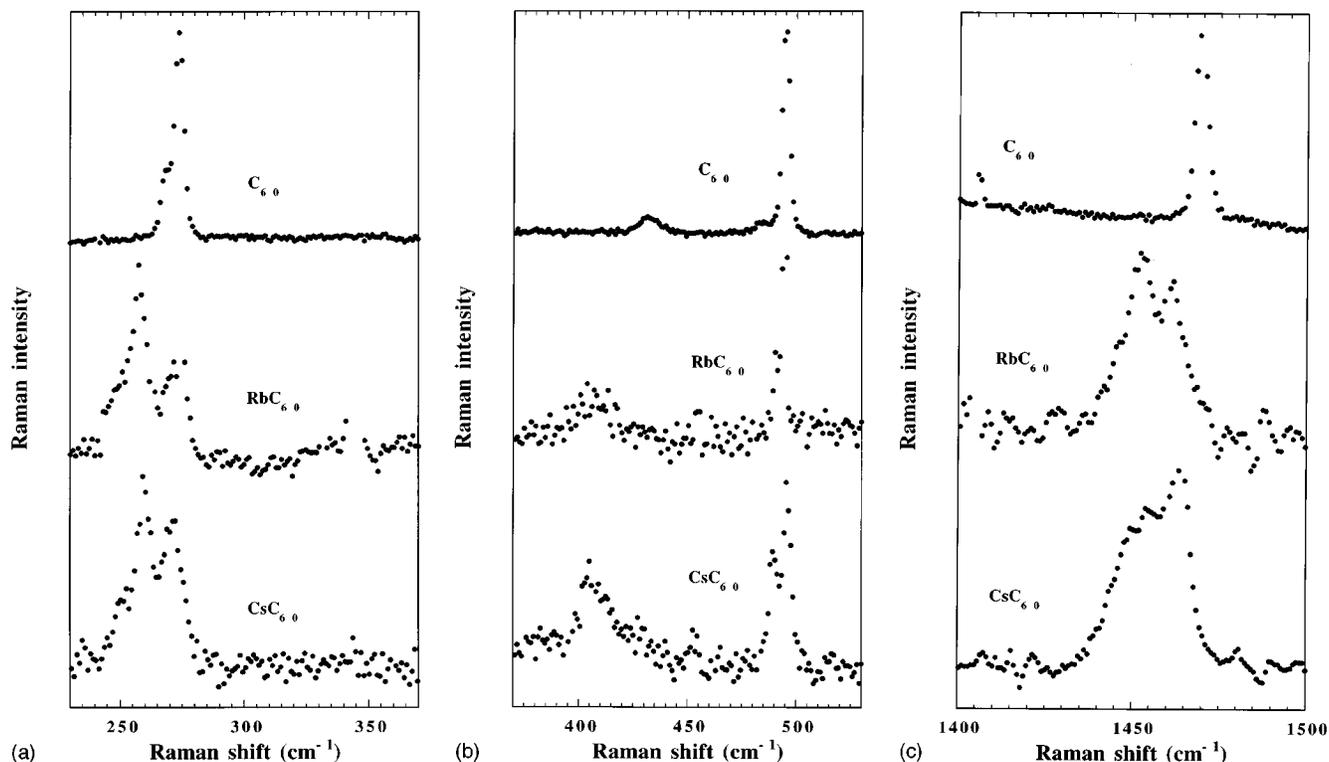


FIG. 3. Raman lines of C_{60} , o - RbC_{60} , and o - CsC_{60} for three characteristic regions of the spectrum as excited with 776 nm. (a) Spectral range of the Hg(1) mode. (b) Spectral range of Hg(2) and Ag(1) modes. (c) Spectral range of the Ag(2) mode.

the room-temperature phase of AC_{60} compounds. The similarity between the Raman spectrum measured on RbC_{60} and CsC_{60} gives the evidence of the intrinsic character of this low-frequency Raman spectrum. It is important to emphasize that no 30-cm^{-1} mode has been observed in the Raman spectrum of the phototransformed C_{60} . In phototransformed C_{60} , only a weak line at around 118 cm^{-1} is evidenced for a 776-nm excitation.¹⁴ A 118-cm^{-1} line with a relative strong intensity has been previously observed for a 488 nm (Ref. 15) and a 514.5-nm excitation.¹⁶

The temperature dependence of the o - AC_{60} low-frequency Raman spectrum has been also analyzed in the temperature range 100–300 K. The low-frequency mode is observed at near the same frequency (30 cm^{-1}) in this entire temperature range.

In summary, concerning the room-temperature Raman spectrum of o - AC_{60} phase some results can be emphasized:

- (i) The large increase in scattering from modes not Raman active for isolated C_{60} molecules.
- (ii) The general splitting of C_{60} modes.
- (iii) The double peak structure for the Ag(2) mode: $1452(\pm 2)\text{ cm}^{-1}$ and $1462(\pm 2)\text{ cm}^{-1}$.
- (iv) The peculiar resonant character of the new mode at 344 cm^{-1} : intense and well defined for a 514.5-nm excitation, not appearing for a 776-nm excitation.
- (v) The observation of a well-defined peak at around 30 cm^{-1} .

In the following we shall discuss all these results in comparison with assignments and behaviors predicted from others experimental works^{13–16} and theoretical models.^{17–19}

IV. DISCUSSION

Concerning the high-frequency range ($200\text{--}1600\text{ cm}^{-1}$) Raman spectrum, our data are in perfect agreement with those of Winter and Kuzmany,¹³ the differences observed between our spectra as excited with 776 nm and those of the previous authors as excited at 754 nm are only due to a better homogeneity of our powder samples with respect to the expected inhomogeneity in the depth of their doped single crystal of C_{60} . From the general agreement between all these data, the intrinsic behaviors of the o - AC_{60} Raman spectrum displayed in Figs. 1–4 are confirmed.

The fundamental problem to solve now is as follows: What is the molecular units (nonbonded C_{60} , oligomer, polymer chain) which are present in the o - AC_{60} phase? To answer this question we begin the discussion with information which can be derived from the Raman investigation of the intramolecular dynamics:

(a) In the usual framework of the formation of a dimer or polymer state the molecular symmetry of C_{60} is lowered from I_h to D_{2h} , consequently the irreducible representations of the D_{2h} group being all one dimensional a splitting of all the Hg modes of C_{60} is expected in the polymer phase. This effect is clearly observed in Figs. 1–4. However, splitting is also expected in nonbonded C_{60} ions in an ordered $Pm\bar{3}n$ lattice.

(b) New modes appear in the Raman spectrum of the o - AC_{60} phase. Several have been assigned to odd-parity (ungerade) vibrations,²⁰ especially the Raman signature of the polymer phase pointed at 344 cm^{-1} [a mode at 343 cm^{-1} was observed in the infrared spectrum of C_{60} (Ref. 21)]. For

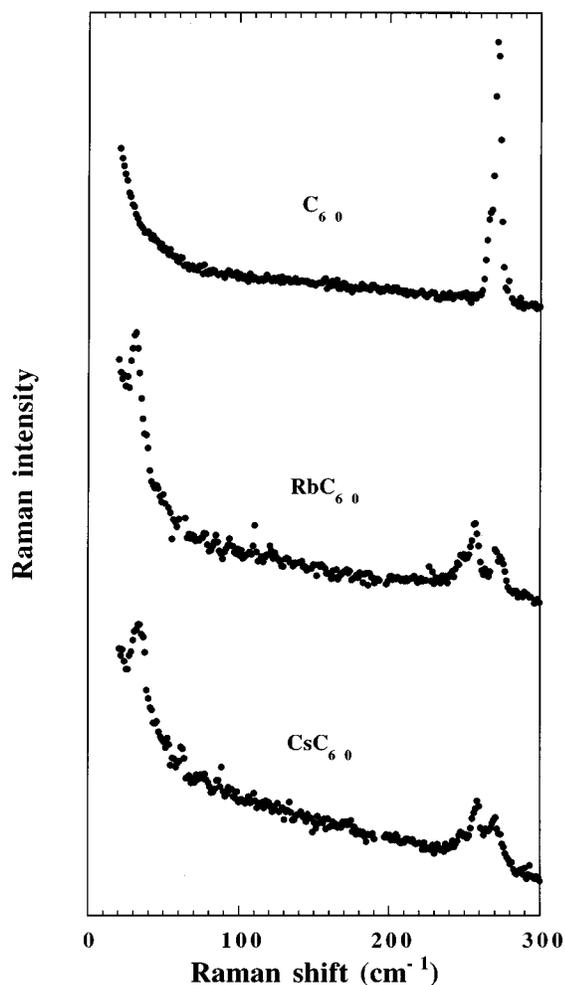


FIG. 4. Low-frequency room-temperature Raman spectra of C_{60} , o - RbC_{60} , and o - CsC_{60} as excited with 776 nm.

both dimer or polymer molecules (group symmetry D_{2h}) as well as the orthorhombic lattice as $Pmnn$ with inversion symmetry the presence of ungerade modes in the Raman spectrum implies disorder. Thus, it is surprising that the 344-cm^{-1} mode was not observed in C_{60} where orientational disorder exist and was not evidenced in the phototransformed phase and in the pressure-induced polymerized phases of C_{60} where strong fullerenes interactions and disorder are expected. In addition, this mode displays a peculiar resonant Raman character that is opposite to its assignment as an infrared mode induced from disorder in the Raman spectrum.

(c) In the AC_{60} high-temperature range, a single sharp peak $Ag(2)$ is observed at 1462 cm^{-1} , in agreement with the expected shift of the pentagonal pinch mode induced from the AC_{60} charge transfer (6 cm^{-1} by electron²²). In the o - AC_{60} phase, two components at 1462 and 1452 cm^{-1} are observed. The shift of about 10 cm^{-1} for the second component with respect to the position of the mode in the high-temperature range suggests a polymerization process of C_{60}^- ions analogous to the one observed in the phototransformed phase: a (2+2) cycloaddition process.² Consequently, the 1452-cm^{-1} line would be the Raman signature of a polymerized state and the 1462-cm^{-1} line could be assigned to the rest of the nonpolymerized C_{60}^- ions in the o - AC_{60} phase. Nevertheless an analysis of the temperature

dependence of the parameters of these components seems to indicate that the lines at about 1462 cm^{-1} observed in both fcc and orthorhombic AC_{60} phases are not the same and the splitting of the pentagonal pinch mode would be an intrinsic feature of the o - AC_{60} Raman spectrum.¹³

(d) Calculated Raman spectra obtained from different methods of calculation such as generalized tight-binding molecular dynamics,¹⁷ first-principles quantum molecular dynamics,¹⁸ and a density-functional based nonorthogonal tight-binding method¹⁹ predict the vibrational features of isolated oligomers and polymers (with various geometries) of C_{60} . A comparison between the observed vibrational lines with these calculated spectra can be made. It is important to note that in all these theoretical works, the charge transfer from the alkali metal to fullerene, the interchain interactions as well as the presence of alkali metal in the lattice (A- C_{60} interaction) are not taken into account. It is also important to remark that in all of these works large discrepancies between calculated and experimental frequencies in the high-frequency range (pinch mode region) are observed. Nevertheless, for these authors, the calculated behavior (displacement and intensity) of the pinch modes as a function of the length and geometry of C_{60} oligomers can be compared with the experimental behavior measured in a Raman study. From this comparison, the length and the geometry of C_{60} oligomers present in a real sample can be derived.

From Porezag *et al.*,¹⁹ the shift of the $Ag(2)$ pentagonal pinch mode is about 10 cm^{-1} for all balls with only one square ring (like in dimer). This shift is about 20 cm^{-1} in all balls with two connections to others on the opposite side of C_{60} (for instance, the central ball in the linear trimer). This behavior is close to the one predicted by Adams *et al.*:¹⁸ a shift of 10 cm^{-1} in dimer and a shift of about 37 cm^{-1} in the infinite chain of C_{60} . In consequence, the shift of about 10 cm^{-1} experimentally observed in the C_{60} phototransformed phase leads us to propose the C_{60} dimer as the dominant oligomer in this phase.^{13,14,18}

If the effect of the charge and intermolecular interactions could be neglected, the comparison between the Raman spectrum of o - AC_{60} and the calculated spectrum of dimer and polymer could also give some indications about the geometry and the length of oligomer present in the o - AC_{60} phase. As previously indicated the pinch mode in the o - AC_{60} phase shows a double-peak structure and the low-frequency component of this structure is shifted to about 10 cm^{-1} from the high-temperature mode frequency. In the assumption of the existence of oligomers in the o - AC_{60} phase, this comparison also suggest C_{60} dimers as dominant oligomers. However, these calculations do not predict a splitting of the $Ag(2)$ model as experimentally observed.

In conclusion, no new definitive arguments about the length and geometry of oligomers in the o - AC_{60} phase have been obtained. Nevertheless these results suggest significant differences in the organization of C_{60} monomers in the o - AC_{60} phase, phototransformed C_{60} , and pressure-induced C_{60} polymerized phases.

We are going to discuss the information about the structure of the o - AC_{60} phase which can be derived from the Raman investigation of the low-frequency modes region. The presence of a well-defined low-frequency mode at about

30 cm^{-1} is clearly stated in the *o*-AC₆₀ (*A* = Rb, Cs) Raman spectrum. On the other hand, the proximity of the frequency of this mode in the two compounds investigated 31 cm^{-1} in *o*-RbC₆₀, 33 cm^{-1} in *o*-CsC₆₀, means that any alkali atoms motions are involved in this vibration. Two assignments can be proposed for this mode.

(1) The proximity of this mode position with the position of the librational modes in the ordered C₆₀ and C₇₀ phases (in the range $10\text{--}30\text{ cm}^{-1}$)^{23,24} suggest attributing the 30 cm^{-1} mode to a lattice mode and more precisely to a libration mode of the *o*-AC₆₀ phase. Assuming the existence of covalent bonds between C₆₀ in the *o*-AC₆₀ phase implies that the librating units are oligomers of C₆₀ [(C₆₀)_{*N*}; dimer *N* = 2, trimer *N* = 3, . . .]. The oligomer mass being *N* times the C₆₀ mass, the hardening of the intermolecular force constant necessary to obtain an oligomer libration at around 30 cm^{-1} seems to be unrealistic: it is about *N* times stronger than the one in the C₆₀ ordered phase. Consequently, the assignment of the 30 cm^{-1} mode to a libration leads us to propose that the librating units in the *o*-AC₆₀ phase are C₆₀ molecules with only an enhancement of interfullerene coupling. Obviously this last explanation is opposite to the existence of covalent bonds between C₆₀ molecules.²⁰

(2) On the other hand, the dependence of the interball stretching mode in linear oligomers has been recently calculated.¹⁹ A clear softening of this mode with an increase of the length of the (C₆₀)_{*N*} linear oligomer has been established: 89 cm^{-1} in (C₆₀)₂ (dimer), 61 cm^{-1} in (C₆₀)₃ (trimer), 47 cm^{-1} in (C₆₀)₄. Consequently, another possible assignment of the low-frequency 30 cm^{-1} peak is the interball stretching mode in a relatively long (C₆₀)_{*N*} oligomers. Obviously, and opposite to the previous assumption, this attribution implies the existence of covalent bonds between

C₆₀. Recent ¹³C NMR results obtained on strictly the same *o*-CsC₆₀ sample as the one used in Raman experiments strongly support this assignment.²⁵ Indeed, from the NMR experiments, the existence of *sp*³ carbon has been unambiguously stated in both *o*-RbC₆₀ and *o*-CsC₆₀ samples.^{25,26} Nevertheless, and in order to state definitively this interpretation, Raman spectra using a 776-nm excitation may be recorded in the high-temperature phase of AC₆₀ samples (*T* > 400 K). Indeed, if our interpretation is correct, the 30 cm^{-1} low-frequency mode may vanish in the orientationally disordered high-temperature phase.

V. CONCLUSIONS

In this paper, high- and low-frequency room-temperature Raman spectra performed on the *o*-AC₆₀ phase (*A* = Rb, Cs) have been reported. The Raman spectrum measured in the intramolecular modes region shows several differences with the Raman spectrum measured in the phototransformed phase and in the pressure-induced polymerized phases of C₆₀. For instance, the splitting of the pinch mode and the line at the 344 cm^{-1} mode are nonobserved in these phases. These results suggest differences in the organization of C₆₀ monomers in the *o*-AC₆₀ phase, phototransformed C₆₀, and pressure-induced C₆₀ polymerized phases.

The Raman spectrum measured in the low-frequency range in *o*-RbC₆₀ and *o*-CsC₆₀ shows a well-defined peak at about 30 cm^{-1} . Comparison with the expected position of the interball stretching mode in linear oligomers of different lengths indicates the existence of relatively long oligomers (longer than dimer) in the *o*-AC₆₀ phase. Consequently, and in agreement with recent NMR data²⁵ the low-frequency Raman results strongly support the mechanism of the creation of interfullerene linkages via a (2+2) cycloaddition reaction in the *o*-AC₆₀ phase.¹⁹

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