Ordered low-temperature structure in K$_4$C$_{60}$ detected by infrared spectroscopy

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Infrared spectra of a K$_4$C$_{60}$ single-phase thin film have been measured between room temperature and 20 K. At low temperatures, the two high-frequency T$_{1u}$ modes appear as triplets, indicating a static D$_{2d}$ crystal-field stabilized Jahn-Teller distortion of the C$_{60}^{}$ anions. The T$_{1u}$ mode changes into the known doublet above 250 K, a pattern which could have three origins: a dynamic Jahn-Teller effect, static disorder between “staggered” anions, or a phase transition from an orientationally-ordered phase to one where molecular motion is significant.

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The electronic structure of fulleride salts has been a topic of intense interest since their discovery. Three recent reviews summarize the situation: Reed and Bolskar focus on isolated ions; Forgó and Mihály treat fulleride solids; and Gunnarsson concentrates on the theory of superconductivity and on band structure calculations, including the important concepts of the Jahn-Teller (JT) effect. Fulleride anions with charge other than 0 or 6 are susceptible to Jahn-Teller coupling between the electrons occupying partially-filled t$_{1u}$ orbitals and H$_g$ phonons. Because of the high degeneracy of the phonons involved, the coupled electronic Hamiltonian acquires SO(3) symmetry, higher than the original icosahedral configuration. Thus the electronic structure of the outer shell can be discussed in complete analogy with p-electrons on an atom. In any uniaxial crystal field, one expects a twofold orbital splitting to 2e$_{2u}$ and a$_u$, whereas in a biaxial system the degeneracy is completely lifted, resulting in three distinct electronic levels. (It follows from the SO(3) symmetry that the principal axes of the distortions can be taken as the axes of the crystallographic unit cell, regardless of the position of the molecule within the crystal.)

In solids the orbital splitting is small compared to the bandwidth; thus, electron correlation has to be taken into account. The most comprehensive theoretical treatment of this interplay was given by Tosatti and co-workers, who introduced the concept of the “Mott-Jahn-Teller insulator” (M-JT). The model of p-like electrons on a spherical or ellipsoidal surface was indeed successful in the interpretation of NMR, photoelectron spectroscopy, resonance Raman and magnetic data. The situation becomes different, however, once we try to measure properties that reflect the internal degrees of freedom within the C$_{60}$ ball itself. Typical examples are magnetic resonance measurements and vibrational spectroscopy. When atomic motion has to be taken into account, the symmetry can no longer be regarded as spherical. Instead, the actual shape of the molecule is determined by the combined internal (JT) and external (crystal field) distorting forces. If these result in a potential surface with several shallow wells, then the balls will assume different shapes and positions with respect to the lattice. The result will be either static disorder or random fluctuations between the minima, called the dynamic Jahn-Teller effect.

A special frustration results if the principal axis of the crystal system does not coincide with a similar molecular axis. The case of A$_4$C$_{60}$ salts is such an example. These show peculiarities in both their crystal structure and vibrational spectra. At room temperature, K$_4$C$_{60}$ and Rb$_4$C$_{60}$ form a bct crystal, with merohedral disorder similar to that in A$_2$C$_{60}$(4) in the bct cell of K$_4$C$_{60}$ there is only a C$_2$ molecular axis in the c direction, and the overall tetragonal structure is realized by the anions occupying two standard orientations with equal probability. In Cs$_4$C$_{60}$ an orthorhombic distortion was found at room temperature, resulting in a lattice compatible with D$_{2d}$, one of the subgroups of the icosahedral group yielding complete ordering of the C$_{60}$ balls.

Infrared measurements on K$_4$C$_{60}$ and Rb$_4$C$_{60}$ at room temperature by Iwasa and Kaneyasu found the T$_{1u}$ infrared active mode to be split into a doublet, a phenomenon not seen in any other alkali salt so far (excluding polymeric forms, which show a variety of splitting patterns.) They invoked a static JT distortion to explain these results. X-ray diffraction puts an upper limit of 0.04 Å for the difference between the polar and equatorial radii of C$_{60}$ (the polar direction supposed to lie in the crystallographic c-direction). To our knowledge, neither
structural nor vibrational properties of the $A_4C_{60}$ salts have been reported at low temperatures.

Details concerning the temperature dependence of the molecular dynamics in $A_4C_{60}$ salts were provided by nuclear magnetic resonance studies. Goze et al. observed four $^{13}C$ NMR lines in $Cs_3C_{60}$ collapse into a single line above 350 K, the latter spectrum being similar to $K_4C_{60}$ at room temperature. Lacking structural data, they could not draw unambiguous conclusions, but they invoked the possibility of a phase transition between an ordered and a rotationally disordered phase and even suggested that a similar transition may take place in other tetravalent alkali salts at lower temperatures. Comparing the NMR results with high-quality room-temperature x-ray diffraction data obtained in the meantime on $K_4C_{60}$ and $Rb_4C_{60}$ (which are isostructural) it seems highly possible that a phase transition occurs in all three salts, above room temperature in $Cs_4C_{60}$ and below in the other two. Due to its sensitivity to local symmetry, infrared vibrational spectroscopy should be a good indicator for such a transition. Therefore, we undertook infrared spectroscopic measurements between 20 and 300 K in $K_4C_{60}$.

Highly polycrystalline films of $C_{60}$ were grown on Si IR windows using a “hot-wall” technique. We estimate a thickness of 300 nm from the spacing of interference fringes in the infrared, assuming an index of refraction $n = 2$. A glass and metal doping cell was constructed incorporating a potassium source and ZrO getter (SAES Getters/USA Inc.), replicating earlier preparations from Bell Labs. The cell was thoroughly outgassed at 300 °C and sealed at a base pressure of $10^{-7}$ torr. During doping the cell was kept at 200 °C and the resistance was monitored. The minimum resistance corresponding to $K_4C_{60}$ was observed and the time required to reach $K_4C_{60}$ composition estimated. Then the sample was transferred in an Ar filled glovebox into a copper holder and epoxied in place.

Spectra were taken in the midinfrared by a Bruker IFS28 Fourier-transform infrared spectrometer with an MCT detector and in both the far and midinfrared by a Bruker IFS113v instrument using a Si bolometer and a DTGS detector, respectively. Temperature dependence was measured in a He flow cryostat while warming up, to avoid possible hysteresis effects. Although the measurements were taken in reflection mode with the silicon window facing the incident light path, our results are essentially transmittance data. This is because the experimental arrangement resulted in the light passing through the silicon window and the sample film twice, once on entering the sample and a second time after being reflected from the copper back plate. Because we were mainly interested in the change in spectral line positions, we did not undertake any correction for reflection from the silicon window, and assumed 100% reflection from the copper.

Figure 1 shows the infrared spectrum of the film at 300 K and at 20 K. The 300 K spectrum is identical to that measured by Iwasa and Kaneyasu the most pronounced feature being the asymmetric doublet at 1323 and 1353 cm$^{-1}$. The $T_{1u}(3)$ mode at 1177 cm$^{-1}$ is broader than that in other fulleride salts, but shows no explicit splitting. Neither of these peaks coincides with infrared vibrations of other fulleride ions; moreover, characteristic peaks of other fulleride ions are absent, giving evidence for the phase purity of the film. The low-frequency $T_{1u}$ mode region is obscured by multiphonon Si absorption occurring between 570 and 700 cm$^{-1}$, therefore we concentrate on the high-frequency region, where neutral isolated $C_{60}$ has two (triply degenerate) normal modes at 1183 and 1429 cm$^{-1}$. In Figure 2, this part of the spectrum is depicted at 20, 200, and 300 K. An obvious change occurs between 300 K and 200 K; at 20 K the structure becomes sharper, but otherwise the spectrum is identical to that at 200 K. At our heating rate of 2 K/min, we observed this change between 250 and 260 K. The two high-frequency $T_{1u}$ modes both evolve into a triplet below this temperature (a set at 1168, 1184 and 1206, and another at 1327, 1347 and 1364 cm$^{-1}$).

The threefold splitting in the $T_{1u}$ peaks is a clear signature of biaxial symmetry, a complete lifting of the threefold degeneracy in the vibrational levels. A straightforward explanation is the existence of an ordered crystal structure at low temperature, similar to that of $Cs_4C_{60}$. There, the site symmetry of the balls is $D_{3h}$, a direct subgroup of $I_h$. This subgroup is also special in the sense that it can describe one possible shape of a JT distorted icosahedral molecule, resulting from linear coupling between $t_{1u}$ electrons and $H_g$ phonons. The principal axis of the point group coincides with that of the crystal space group, thus all the conditions for a crystal-field stabilized static JT distortion are met. We conclude that the likely explanation for the low-temperature infrared spectrum of $K_4C_{60}$ is such a structure.
FIG. 2. Infrared spectra of K₄C₆₀ in the region of the high-frequency C₆₀ molecular vibrations, at three different temperatures.

It is not straightforward to interpret the spectrum at 300 K, where the structure is known. If we assume a static merohedral disorder with appropriate JT distortion, then molecules with different standard orientations should give the vibrational spectrum of the local symmetry, D₂h, and thus should not differ from the low-temperature spectra. Because the spectra do differ, we suggest that either the molecules are trapped in more complicated orientations (the "staggered static distortion" introduced by Fabrizio and Tosatti), or that dynamical processes are involved. The two allowed distorted point groups for t₁u-H₂g coupling besides D₂h are D₃d and D₅d. The principal axes of these two distorted symmetries go respectively through the center of the hexagonal and pentagonal faces of the C₆₀ molecule. The staggered static distortion would have neighboring anions with principal axes different from c, but symmetric around it; no experimental corroboration of this idea has been reported. It is interesting to compare the measured upper limit for the static distortion, 0.04 Å, with the only hitherto known C₆₀ distorted structure, that of C²⁺ in (PPN)$_2$C₆₀ (The JT coupling in this ion is supposed to be very similar to the tetravalent anion, because they are related by electron-hole symmetry.) There, a distortion of 0.033 Ångströms was enough to produce a split EPR signal in accordance with symmetry lowering of the anion but the point group was C₁, lower than that predicted by the JT effect alone (due to the complicated organic counterions), and involved a considerable D₅d character, pointing to a D₆d distortion stabilized by crystal field effects and locked into a configuration with even lower symmetry.

In the case of K₄C₆₀, however, the C₃ axes seem more special. We consider first their role in A₄C₆₀, which adopts a remarkably similar molecular arrangement in the ab plane with two standard orientations, connected formally by a 90° rotation around the c axis. In Rb₃C₆₀ and K₃C₆₀ the rearrangement between the two standard orientations can also occur through a 44.5° jump around a C₃ axis, lying in the crystallographic (111) direction, and it has been shown by neutron scattering experiments that this motion involves a considerably lower energy barrier than the jump around C₂. Subsequent NMR studies indicate that a fast uniaxial rotation takes place around a fixed axis, accompanied by a slow motion which was interpreted as the flipping of the molecule while keeping the same rotational axis. The existence of a fast and slow orientational motion has also been reported in A₄C₆₀. If one invokes the special role of the C₃ axes, then it is possible that the easy motion around this axis lowers the energy of the D₃d distortion over both D₅d and D₂h.

At this point, we turn to the description by Chancey and O’Brien of the dynamical Jahn-Teller effect in C₆₀. They introduce the concept of "pseudorotation", a succession of symmetry-allowed distortions (generally a genuine rotation should involve changes in the positions of atoms, because it takes the molecule from one standard orientation to another). This motion should go through distorted states which mainly involve axial components (D₃d and/or D₅d) and can be considered as the dynamic equivalent of the staggered state proposed by Fabrizio and Tosatti. Based on vibrational spectra, it is not possible to distinguish between the dynamic process and the staggered state, so long as biaxial (D₂h) distortions are not involved; both the spatial and time average of uniaxially distorted states would give a twofold line splitting. The transition between the low- and high-T states, however, would be different in the two cases. A staggered tetragonal phase can only evolve from an ordered structure through a structural phase transition. Such a transition could, of course, also happen between an ordered and a dynamically disordered phase, as in pristine C₆₀, but it is also possible that the disordered state develops from the ordered one by the rotational frequencies increasing above a critical value. The first case should lead to a discontinuity at the transition temperature observable by any spectroscopic method, regardless of time scale; the second scenario would give different transition temperatures depending on the time scale of the experiment relative to the autocorrelation time of the motions. From the parameters given by Zimmer et al, the autocorrelation time τ is 33 ns at 200 K and 1 ns at 300 K, which can be regarded as static on the time scale of molecu-
lar vibrations. The same calculation for the fast uniaxial rotation gives 71 ns at 200 K and 130 ps at 300 K, still too slow to cause collapsing of infrared lines. (In C\textsubscript{60}, \(\tau = 6.4\) ns at 200 K, below the structural phase transition,\textsuperscript{[12]} where infrared lines are observably split,\textsuperscript{[13]} and 12 ps at 300 K, in the rotator phase, where there is only a single infrared peak per T\textsubscript{1u} mode.) We conclude therefore that the temperature evolution of the infrared spectra cannot be explained by simple activated behavior of some molecular motion; rather, an abrupt phase transition has to occur to a state where the rotations are faster. Suggestions for a phase transition have been put forward by Goldoni et al.\textsuperscript{[14]} based on an anomaly in the C-1s photoemission linewidth below 150 K, which they correlate with the peak in the NMR spin-spin relaxation time\textsuperscript{[15]}, and attributed to the stopping of the slow reorientational motion. We find this suggestion difficult to reconcile with the results presented here, in part because our transition temperature is higher than 150 K, and in part because the splitting of IR lines should be related to the fast motion rather than the slow reorientation.

More structural and spectroscopic data are clearly needed on fulleride salts to fully understand their intriguing behavior. In addition, vibrational spectra of isolated ions could tell whether the splitting at either high or low temperature is caused by an inherent molecular JT distortion or by a crystal field effect brought about by the surrounding cations. Indirect proof of a molecular distortion comes again from studies on C\textsubscript{60}, where the same EPR structure was found in the PPN crystal and in frozen solution, indicating that the effect of crystal structure was not dominant. Therefore, we think it possible to have a D\textsubscript{2h} configuration in the low-temperature state and a combination of the two axially distorted forms, D\textsubscript{5d} and D\textsubscript{3d}, connected by a pseudorotation, in the high-temperature state.

In conclusion, we observed a change in the T\textsubscript{1u}(3) and T\textsubscript{1u}(4) infrared-active vibrations of C\textsubscript{60} in K\textsubscript{4}C\textsubscript{60} from doublet to triplet in the 200-300 K range. We propose a structural bct-to-orthorhombic transition to take place in this region.

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