

Jahn-Teller distortion in Cs_4C_{60} studied by vibrational spectroscopy

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Abstract. We have measured the infrared spectra of Cs_4C_{60} in the temperature range 220 - 450 K. Two anomalies in the low-frequency modes at 270 K and 400 K point to changes in molecular or crystal structure. The most probable explanation is a rotator phase above 400 K and a fully ordered phase below 220 K; the intermediate structure is one where molecular Jahn-Teller distortions compete with crystal field effects.

INTRODUCTION

The fulleride salts A_4C_{60} (A being an alkali atom, K, Rb or Cs) are unique in the family of fullerides as they exhibit insulating behavior contrary to band structure expectations. Fabrizio and Tosatti [1] explained the discrepancy by introducing the concept of the "Mott-Jahn-Teller nonmagnetic insulator". Relatively little experimental work was performed, however, on these systems, partly because of the difficulties with single-phase preparation.

We have successfully prepared almost phase-pure Cs_4C_{60} via a solid-state reaction and followed its infrared spectrum as a function of temperature. The changes can be explained by lowering the symmetry of the molecule as the temperature decreases.

EXPERIMENTAL

Cs_4C_{60} was prepared in inert atmosphere by reacting stoichiometric amounts of Cs and ground C_{60} in a steel capsule at 350° C for five days, regrounding the mixture and subsequently repeating the heat treatment. The X-ray diffraction pattern of the crystalline part (> 90% of the resulting material) and the Raman spectrum of the sample were identical to that prepared by Dahlke et al. [2] by a liquid ammonia route. Vibrational spectroscopy is very sensitive to the presence of other fullerene phases; we did not detect any such impurity. The powder was ground with KBr and pressed into pellets, then transferred to a cryostat in inert atmosphere. Infrared spectra were taken by a Bruker IFS 28 Fourier-transform infrared spectrometer with 1 cm^{-1} resolution under dynamical vacuum.

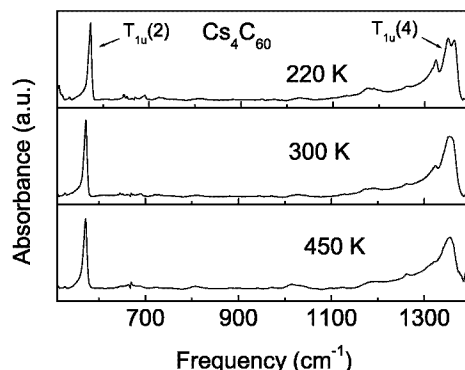


FIGURE 1. Infrared absorption of Cs_4C_{60} at three typical temperatures: ordered phase (220 K), intermediate phase (300 K) and rotator phase (450 K).

RESULTS AND DISCUSSION

Figure 1 shows the spectra in three typical temperature ranges, distinguishable by the behavior of the highest frequency $T_{1u}(4)$ IR mode, the most sensitive one to charge and symmetry-breaking effects. At low temperature this line is split into a triplet, developing into a doublet at about 270 K and further collapsing into a single line above room temperature. The situation is similar to that in K_4C_{60} , described in a previous publication [3]. We discuss here the temperature dependence of the less complicated low-frequency modes, depicted in Fig. 2. The most intense $T_{1u}(2)$ mode at 572 cm^{-1} shows two discrepancies in both linewidth and peak intensity, at 270 and 400 K, respectively. The smaller lines, not present in pure icosahedral C_{60} , disappear at the higher transition temperature; their low-temperature behavior is less clear due to their small intensity and consequent larger errors in peak height.

As to the physical picture of both the structures and their dynamics, we can only speculate at the moment. A strong structural transition is not likely, since differential scanning calorimetry failed to detect any thermal effect between 210 and 600 K. However, since infrared spectra in a molecular crystal reflect mainly internal molecular dynamics, slight changes in the shape of the fullerene balls can cause infrared signatures. From NMR relaxation rates, Zimmer et al. suggested two types of motion in K_4C_{60} [4] and Rb_4C_{60} [5]: a rapid uniaxial rotation and a reorientation, which they interpret as the flipping of the rotation axis.

The low- and high temperature structure is relatively simple to understand. Dahlke et al. [2] determined the room-temperature structure by Rietveld refinement; we accept their results for the low-temperature phase. This would be a cooperative Jahn-Teller distortion with a C_{60} point group symmetry D_{2h} , compatible with a body centered orthorhombic crystal structure (illustrated schematically in Fig. 3a). Above room temperature, the NMR results of Goze et al. [6] indicate rapid rotation of C_{60} balls, similar to

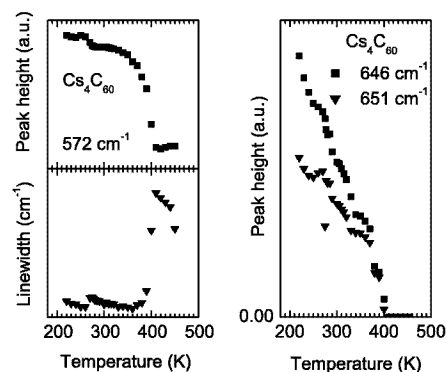


FIGURE 2. Left panel: temperature dependence of the peak height and linewidth of the $T_{1u}(2)$ infrared-active mode. Right panel: peak height of activated infrared lines vs. temperature.

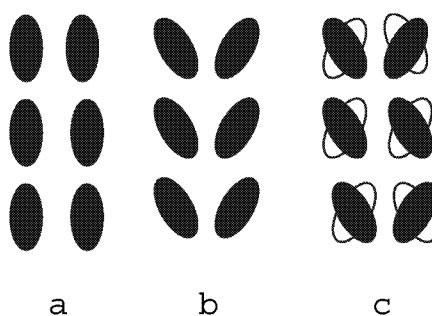


FIGURE 3. Possible arrangements of JT distorted C_{60} ions: a) ordered, b) staggered static, c) rotator. The long axis of the ellipsoids is a C_3 or C_5 molecular axis.

the fcc (rotator) phase of pure C_{60} (Fig. 3c). If the reorientation is fast enough, it smears out the splitting of the $T_{1u}(4)$ mode and increases the linewidth of the $T_{1u}(2)$ mode, while the low-intensity modes become silent. (We estimate the required time scale for this effect as a few picoseconds, from that of pristine C_{60} in its rotator phase [7]. Unfortunately, relaxation rates are only available for K_4C_{60} and Rb_4C_{60} [4, 5] and have to be considered tentative even there, because of controversies in terms of the electronic background to be subtracted [8].)

The intermediate phase, where the structure stays orthorhombic but the spectrum changes, clearly constitutes a puzzle. Given the fact that in the intermediate phase of Cs_4C_{60} the $T_{1u}(4)$ mode shows up as a doublet (compatible with a uniaxial distortion of

the C_{60} molecule, point group D_{3d} or D_{5d}), we suggest that in this phase the molecular axis differs from the principal axis of the unit cell (Fig. 3b). At the first transition ($a \rightarrow b$), thermal motion of the atoms should be enough to change the balls from biaxial to uniaxial symmetry (this distortion having the largest JT stabilization energy [9]). The motion is similar to the pseudorotation introduced by Chancey and O'Brien [10]. The orthorhombic character of the crystal would be preserved with occasional hindered rotation (slow reorientation is permitted in the structure resolved in Ref. [2]).

Recently, a theory about linewidth changes of forbidden lines has been proposed by Martin and Mihaly [11], called "motional diminishing". It is tempting to offer an explanation of the peak height of the weaker lines (Fig. 2, right panel) based on this theory, however, since the allowed 572 cm^{-1} peak is broadening rather than narrowing in this region (similarly to pristine C_{60} around the orientational phase transition [12]), we believe that all lines reflect the symmetry change and internal dynamics of the C_{60}^{4-} anions rather than that of the environment. Local symmetry lowering without long-range reorientation could also explain the lack of thermal effects around the transitions. Further structural and spectroscopic evidence is needed before the question can be finally settled; the intriguing possibility of a dynamic JT effect, however, justifies to carry out such investigations.

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