Distortions of C$_{60}^{4-}$ studied by infrared spectroscopy

G. Klupp, F. Borondics, G. Oszlányi and K. Kamarás

Research Institute for Solid State Physics and Optics, Hungarian Academy of Sciences, P. O. Box 49, H-1525 Budapest, Hungary

Abstract. The Jahn-Teller effect plays a crucial role in the explanation of the insulating character of A_4C_{60} (A = K, Rb, Cs). To detect possible phase transitions arising from the interplay between the molecular Jahn-Teller distortion and the distorting potential field of the counterions, we measured the mid-IR spectra of A_4C_{60} compounds in the temperature range 90 - 300 K and found significant spectral changes with temperature in all three compounds. We also compare these spectra to that of Na_4C_{60} in its room-temperature polymeric phase, where the distortion is more pronounced and evident from the structure.

INTRODUCTION

The A_4C_{60} (A = K, Rb, Cs) fullerides are insulating, despite the predictions of band structure calculations. As an explanation, the concept of the Mott-Jahn-Teller insulator has been proposed [1]. In the C_{60}^{4-} molecule the coupling of the threefold degenerate t electronic state with the H_g vibrational modes will lead to a Jahn-Teller distortion that can change the molecular symmetry from I_h to either D_{5d} or D_{3d} (uniaxially distorted), or to D_{2h} (biaxially distorted) [2]. In Cs_4C_{60} there is direct evidence for the distortion: Dahlke et al. observed D_{2h} geometry at both 5 and 293 K by neutron diffraction [3].

Na_4C_{60} has a different structure at room temperature from the above three: it forms two dimensional polymer sheets [4]. In this polymer the fullerene balls are distorted to C_i geometry via the sigma bonds connecting the adjacent monomer units.

Here we present midinfrared (mid-IR) spectra of Na_4C_{60}, K_4C_{60}, Rb_4C_{60} and Cs_4C_{60} to compare the distortions and to draw conclusions concerning the Jahn-Teller effect in A_4C_{60}. We find the spectral pattern consistent with C_i in Na_4C_{60}. In the other three compounds, our results indicate much smaller distortion, varying with temperature. The changes suggest a staggered static distortion or a dynamic Jahn-Teller effect in the high-temperature state, and the dominance of the distortion caused by the potential field of the surrounding ions in the low temperature state.

EXPERIMENTAL

Fulleride salts with more than 95 % purity were prepared by reacting stoichiometric amounts of the alkali metal and C_{60} at 350 °C for K, Rb, Cs, and at 200 °C for Na_4C_{60}. Mid-IR transmittance of the fullerides were measured in KBr pellets pressed in dry box.
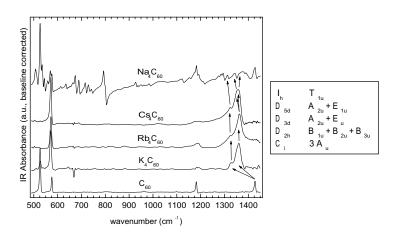
FIGURE 1. Left panel: Room temperature spectra of C_{60}, K_4C_{60}, Rb_4C_{60}, Cs_4C_{60} and Na_4C_{60} with the splitting of the highest frequency T_{1u} mode shown with arrows. Right panel: splitting of T_{1u} modes in different pointgroups.

The IR measurements were performed in dynamic vacuum in a liquid nitrogen cooled flow-through cryostat with a Bruker IFS28 FT-IR spectrometer using 2 cm^{-1} resolution.

RESULTS

The room temperature spectra of the four measured compounds compared to that of C_{60} are shown in Fig.1. In K_4C_{60} and Rb_4C_{60} the two higher-frequency T_{1u} modes of C_{60} show a twofold splitting according to fits with Lorentzians (Fig.2). Assuming a JT distortion twofold splitting occurs when the distortion is D_{3d} or D_{5d} (see right panel of Fig. 1). In Cs_4C_{60} the splitting is threefold (see fits in Fig.2), indicating D_{2h} geometry, which is in accordance with the result of neutron diffraction [3]. In Na_4C_{60} the T_{1u} modes also show a threefold splitting in accordance with the expected C_i geometry [4].

There are numerous spectral features associated with the chemical intermolecular bonds in Na_4C_{60} and the strongly distorted molecular geometry they cause. In contrast to the other A_4C_{60} fullerides, where splitting of the two lower frequency T_{1u} modes is not observed clearly with the present resolution, in Na_4C_{60} all of the T_{1u} modes are split. In addition, many strong new modes appear in the spectrum, while even Cs_4C_{60} – the A_4C_{60} compound having the lowest symmetry fulleride ion – exhibits only few weak new modes. We regard the strong feature around 800 cm^{-1} as direct evidence for the
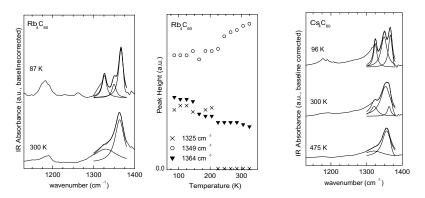
FIGURE 2. Temperature dependence of the spectra of Rb_4C_{60} and Cs_4C_{60}. First panel: the two highest frequency T_{1u} modes of Rb_4C_{60} at 87 K and at 300 K (bold line) with fitted Lorentzian curves (thin line). Second panel: change of peak height of the components of the highest frequency T_{1u} peak in Rb_4C_{60}, indicating a transition between 200 - 220 K. Third panel: the two highest frequency T_{1u} modes of Cs_4C_{60} at 96 K, at 300 K and at 475 K (bold line) with fitted Lorentzian curves (thin line).

single covalent bond, similar to those found in sigma-bonded dimers [5, 6].

The temperature dependence of the IR spectrum of Rb_4C_{60} and Cs_4C_{60} is shown in Fig. 2. The spectra of K_4C_{60} are similar to Rb_4C_{60}, and were shown in Ref. [7]. At low temperature the two highest frequency T_{1u} modes of all three A_4C_{60} salts are split into three, corresponding to a D_{2h} distortion (Fig. 1). On heating these three lines collapse into two, corresponding to a uniaxial distortion. (The latter finding in Cs_4C_{60} is contrary to our earlier statement [8] and reflects the results of the fits shown here.) The change of the spectra with temperature can be best followed by the disappearance of peaks, shown in Fig. 2 and in Ref. [8]. The transitions found occur in the following temperature ranges: K_4C_{60}: 260 - 280 K, Rb_4C_{60}: 200 - 220 K, Cs_4C_{60}: 400 K.

DISCUSSION

In Cs_4C_{60} the low temperature crystal structure is orthorhombic (*Immm*) [3], thus the D_{2h} fulleride ions are orientationally ordered. On heating the crystal structure changes to tetragonal (*I4/mmm*) [3]. By analogy, a similar structural phase transition in K_4C_{60} and Rb_4C_{60} is also likely: NMR relaxation time measurements [9] point in this direction and this was the explanation put forward in our earlier publications [7, 8]. However, a gradual freezing of molecular motion below the IR time scale would also result in similar spectral changes. In this case, the anions could still show orientational disorder occupying two standard orientations in a tetragonal structure. The importance of time scales is also reflected in the fact that the line splitting in Cs_4C_{60} occurs at a higher temperature than in NMR measurements, where a change has been detected between

300 and 350 K [10].

As the potential energy surface of these systems has minima at either D_{5d} or D_{3d} symmetry, and saddle points at D_{2h} symmetry [2], a biaxial distortion can only be realized when the potential field of the surrounding ions lock the molecules in a D_{2h} geometry. As both the tetragonal and orthorhombic arrangements lead to such a potential field, the structure cannot be deducted from the spectra only. Further diffraction studies are needed to clarify this point.

In the high temperature A_4C_{60} phases the crystal structure is bct [11], but the spectra are only consistent with D_{3d} or D_{5d} molecular geometry. As the main axis in these point groups is neither two- nor fourfold, the distortion of the anion obviously is not determined by the crystal field of the solid alone. There are two possible scenarios for the structure of this phase: a staggered static distortion [1, 8] where the molecule's main axis does not coincide with the c axis of the crystal, or a dynamic Jahn-Teller effect where pseudorotation occurs between uniaxial geometries with a characteristic frequency lower than that of the infrared. The fact that the transition temperatures do not scale with cation size is another indication that more than one process is involved. Sorting out the contributions from molecular dynamics and crystal field is a complicated procedure, but exactly this perspective makes these materials interesting.

ACKNOWLEDGMENTS

REFERENCES

1. Fabrizio, M., and Tosatti, E., *Phys. Rev. B* **55**, 13465 (1997).
2. Chancey, C. C., and O'Brien, M. C. M., *The Jahn-Teller effect in C_{60} and Other Icosahedral Complexes* (Princeton University Press, Princeton, 1997).
3. Dahlke, P., and Rosseinsky, M. J., *Chem. Mater.* **14**, 1285 (2002).
4. Oszlányi, G., Baumgartner, G., Faigel, G., and Forró, L., *Phys. Rev. Lett.* **78**, 4438 (1997).
5. Kamarás, K., Tanner, D. B., and Forró, L., *Fullerene Sci. Tech.* **5**, 465 (1997).
6. Kürti, J., Borondics, F., and Klupp, Gy., *AIP Conference Proceedings* **591**, 25 (2001).
7. Kamarás, K., Klupp, G., Tanner, D. B., Hebard, A. F., Nemes, N. M., and Fischer, J. E., *Phys. Rev. B* **65**, 052103 (2002).
8. Kamarás, K., Klupp, G., Borondics, F., Gránásy, L., and Oszlányi, G., *AIP Conference Proceedings* **633**, 55 (2002).
9. Brouet, V., Alloul, H., Garaj, S. and Forró, L., *Phys. Rev. B* **66**, 155122 (2002).
10. Goze, C., Rachdi, F. and Mehring, M., *Phys. Rev. B* **54**, 5164 (1996).
11. Fleming, R. M., Rosseinsky, M. J., Ramirez, A. P., Murphy, D. W., Tully, J. C., Haddon, R. C., Siegrist, T., Tycko, R., Glarum, S. H., Marsh, P., Dabbagh, G., Zahurak, S. M., Makhija, A. V., and Hampton, C., *Nature* **352**, 701 (1991).