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Fulleride ions in various crystal fields studied by infrared spectroscopy

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Abstract

We performed infrared measurements on Cs_4C_{60}, Rb_4C_{60}, K_4C_{60} and Na_2C_{60} to investigate the interplay between the molecular Jahn–Teller effect and the crystal field of the cations. We were able to tune the crystal field strength by varying the size of the cations and the temperature. Distortion patterns were derived from the observed splitting of the infrared-active C_{60} modes. We conclude that the dynamics of the distortion changes on weakening the crystal field in the following order: static distortion – constrained pseudorotation – free pseudorotation.

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1. Introduction

Jahn–Teller (JT)-type coupling of electrons and phonons plays a major role in fulleride ions, because both prerequisites for such coupling are met: multiply degenerate partially filled orbitals (due to the exceptionally high symmetry) and a large number of vibrational degrees of freedom (due to the size of the molecule). The electrons of the partially occupied t_{1u} orbital on the C_{60}^{n-} ions (where $0 < n < 6$) interact with the $8H_g$ vibrations leading to a $p^n \otimes 8H_g$ system [1]. This interaction results in the distortion of the fulleride ions from the original I_h symmetry to either D_{5d}, D_{3d} or D_{2h}. Sophisticated spectroscopic experiments in the gas phase [2] and on monolayers [3] have indeed proven the presence of such distortions. In the gas phase even the presence of pseudorotation could be shown. [2] This motion is a change in the axis of the distortion, i.e. a change of molecular shape without effective rotation of the molecule as a whole [1].

In solid fullerides the pure molecular JT effect can never be studied because of the presence of the crystal field produced by the surrounding cations. The relative weight of the crystal field (strain) can be tuned, however, by varying the temperature and the cation size. Infrared (IR) spectroscopy is ideal for detecting molecular distortions, because it is sensitive to changes in molecular symmetry. In order to follow the symmetry change with crystal field, we measured temperature-dependent IR spectra of A_4C_{60} salts (where A = K, Rb, Cs) and Na_2C_{60}. These all contain either C_{60}^{4-} or C_{60}^{2-} ions, which are related by electron-hole symmetry, and can therefore be described by the same formalism for the molecular Jahn–Teller effect [1].

Among the fullerides investigated, the crystal field is strongest in Cs_4C_{60}. The structure of this salt at room temperature and below is orthorhombic *Immm*, producing a crystal field of D_{2h} symmetry surrounding each fulleride ion. The resulting D_{2h} distortion of the C_{60}^{4-} ion in this phase was directly detected by neutron diffraction [4], constituting the only structural evidence for a distortion among the phases mentioned here.

Cs_4C_{60} undergoes a phase transition somewhere between 293 and 623 K to a tetragonal $I4/mmm$ phase

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[4]. K_4C_{60} and Rb_4C_{60} also show this structure at room temperature and below [5,6]. In these phases the average crystal field is D_{4h}. A single C_{60} molecule cannot distort into this point group as it has no C_4 axis; the molecular symmetry compatible with the crystal field would be D_{2h}. An important difference between the tetragonal and the orthorhombic phases is that in the tetragonal one the cations are located farther away from the C_{60}^{4-} ion, allowing for an occasional reorientational motion typical of fullerides. This motion leads to the appearance of a new orientation (*formally* rotated by 90° around the crystallographic *c* axis, which coincides with a C_2 axis of the molecule). The presence of the two orientations in the crystal leads to the average tetragonal structure [4]. Another consequence of the larger cation-anion distances of the tetragonal structure is a weaker crystal field.

The crystal field is even weaker in the high-temperature phase of Na_2C_{60}. Here, the rotation of the molecules is no longer hindered by the proximity of the cations. The free rotation averages out the crystal field, which is not felt by the molecule, although the cations are still present. The rotation is also the reason why the structure of this fulleride can be cubic $Fm\bar{3}m$ at high temperature. Unfortunately the low-temperature phase of Na_2C_{60} cannot be studied, as the material segregates on cooling [7].

2. Experimental

The fullerides were prepared by the reaction of stoichiometric amounts of alkali metal and C_{60} [6,7]. From the obtained fulleride powders KBr pellets were pressed in a dry box, and placed in a flow-through cryostat. During the infrared measurements the samples were held in dynamic vacuum, and the temperature was varied in the 80–500 K temperature range. The spectra were measured using a Bruker IFS 28 spectrometer with a resolution of 1 or 2 cm^{-1}.

3. Results

The measured infrared spectra are summarized in Figs. 1 and 2. The icosahedral C_{60} molecule has four IR active modes, all of which belong to the T_{1u} representation. In all spectra we see a splitting of the highest frequency mode, and observe some new modes in the 600–750 cm^{-1} region. These effects are signatures of molecular distortion, the point group of which can be deduced from the splitting pattern of the T_{1u} mode. In the D_{2h} distortion the splitting is $T_{1u} \rightarrow B_{1u} + B_{2u} + B_{3u}$, as seen in the low-temperature A_4C_{60} phases (Fig. 1). On the other hand, D_{5d} and D_{3d} distortions cause splittings into $A_{2u} + E_u$ and $A_{2u} + E_{1u}$ modes, respectively. This twofold splitting is observed at high temperature in all four fullerides (Fig. 2).

4. Discussion

By applying the cluster model to the isolated C_{60}^{4-} and C_{60}^{2-} ions it was shown that they distort into oblate and prolate shape, respectively [1]. The axis of the distortion will be determined by the position of the minima of the adiabatic potential energy surface (APES). The $p^n \otimes 8H_g$ systems have a warped APES [2] with either D_{3d} minima and D_{5d} maxima, or vice versa [8]. There are ten C_3 axes and six C_5 axes of the C_{60} molecule, so either ten D_{3d} minima or six D_{5d} minima will be realized. The saddle points between the minima are of D_{2h} symmetry [8]. This means that the D_{2h} distortion must be mainly caused by the crystal field, while in the D_{3d}/D_{5d} distortion the molecular Jahn–Teller effect dominates. The A_4C_{60} fullerides show a transition from the former to the latter distortion on heating. In both K_4C_{60} and Rb_4C_{60} this transition occurs within the tetragonal phase, proving the importance of molecular degrees of freedom over that of the environment.

In the low temperature phase of Cs_4C_{60}, where the crystal field is the strongest, we found a D_{2h} distortion, in agreement with previous neutron diffraction studies [4].

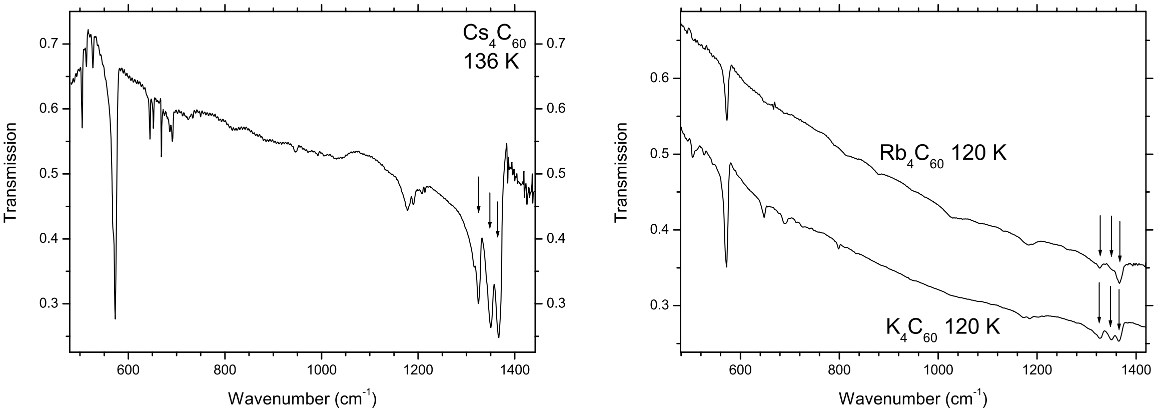

Fig. 1. Infrared spectra of C_{60}^{4-} in strong crystal field. Left panel: spectrum of Cs_4C_{60} at 136 K, i.e. in the low temperature orthorhombic phase. Right panel: spectra of Rb_4C_{60} and K_4C_{60} at 120 K. The arrows indicate the components of the split highest frequency T_{1u} mode.