Distortion and orientation of fulleride ions in A_4C_{60}

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Abstract.
A_4C_{60} compounds (A = K, Rb, Cs) are good candidates to exhibit the Mott-Jahn-Teller insulating state. We present near-IR and neutron scattering data to reflect molecular and crystal stucture changes with temperature. We show how the size of the cation affects the structural and electronic properties of these compounds.

The joint appearance of the Mott insulating state and the Jahn-Teller (JT) effect was first suggested for the A_4C_{60} (A = alkali metal) compounds [1]. In the C_{60}^{4-} molecule the Jahn-Teller distortion changes the molecular symmetry from I_h, either by a uniaxial distortion to D_{5d} or D_{3d} or by a biaxial distortion to D_{2h} [2]. From the splitting of the vibrational states found in mid-IR (MIR) experiments [3, 4] it is known that the distortion is temperature dependent: a transition from biaxial to uniaxial occurs on heating. The transition temperature depends on the cation: it is 400 K in Cs_4C_{60} and 270 K in K_4C_{60}. In this work we show that this molecular change can also be detected by transitions between the split electronic states in the near-IR (NIR) and from the splitting of high symmetry intramolecular vibrations observed in inelastic neutron scattering.

A_4C_{60} compounds were prepared by reacting stoichiometric amounts of the alkali metal and C_{60} at 350 °C in a dry box. The purity, checked by x-ray diffraction and Raman scattering was over 95% in all samples. Temperature dependent IR measurements were performed on KBr pellets in dynamic vacuum in a liquid nitrogen cooled flow-through cryostat with a Bruker IFS 66v/S spectrometer.

Temperature dependent neutron diffraction data were collected on the NCNR BT1 diffractometer using Cu(311) monochromator and a wavelength of $\lambda = 1.5403$Å. Inelastic neutron scattering spectra were collected on the NCNR BT4 beamline using the filter analyser neutron spectrometer for high energies and the triple-axis spectrometer for the librational studies. Details are given in Refs. [5, 6].

Rietveld analysis of powder diffraction data proved that in Cs_4C_{60} there is a structural transition from orthorhombic to tetragonal [7]. To look for a similar change in K_4C_{60} and Rb_4C_{60}, we have performed temperature dependent neutron diffraction measurements. We found that the structure of both K_4C_{60} and Rb_4C_{60} remains tetragonal ($I4/mmm$) between 6 K and 300 K (Figure 1).

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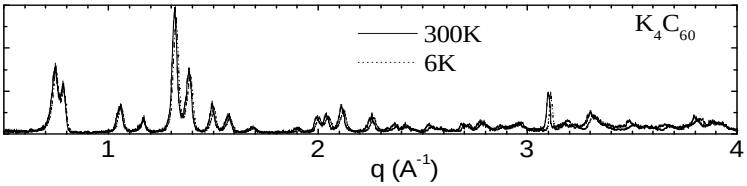

FIGURE 1. Neutron diffraction profiles of K_4C_{60} at 6 K and 300 K, showing only a small thermal contraction of the lattice but no change in symmetry or unit cell.

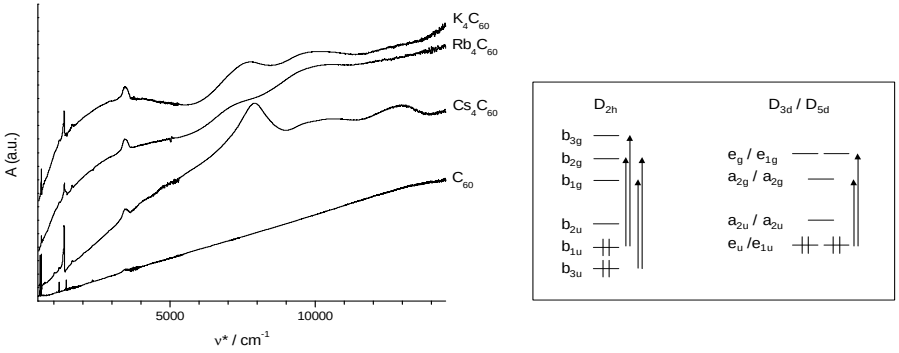

FIGURE 2. MIR and NIR spectrum of K_4C_{60}, Rb_4C_{60} and Cs_4C_{60} without background correction. Second panel shows the allowed transitions between the split molecular orbitals of the distorted fulleride ions leading to the observed peaks in the NIR. The ordering of the levels on this figure is arbitrary.

The ($I4/mmm$) structure is analogous to the high temperature Cs_4C_{60} structure: a disordered arrangement comprising two fulleride ion orientations [7, 8]. In contrast, the fulleride ions are orientationally ordered in the orthorhombic phase [9]. It was shown [7, 9] that this orientational order appears to avoid close Cs–C contacts, which would arise in the disordered structure. This frustration is released at high temperature. In K_4C_{60} and Rb_4C_{60} the orientational order does not appear on cooling, presumably because there is no frustration due to the smaller alkali–C contacts.

Intramolecular electronic transitions can provide information about changes in the molecular geometry. While C_{60} does not have an electronic transition in the 1000-14000 cm^{-1} region, fulleride ions show intramolecular $t_{1u} \rightarrow t_{1g}$ excitations due to the added electrons. The degeneracy of these states is lifted by the distortion, resulting in multiple spectral lines. In the solid, transitions between t_{1u} derived states on neighboring sites are also possible [10].

The room temperature spectra of K_4C_{60}, Rb_4C_{60} and Cs_4C_{60} are shown in Fig. 2. Above 6000 cm^{-1} intramolecular transitions between the split t_{1u} and t_{1g} states can be found [10]. This transition is fourfold split in Cs_4C_{60}, and twofold split in K_4C_{60} and Rb_4C_{60} (Fig.2). Based on group theory there are four dipole allowed transitions in the

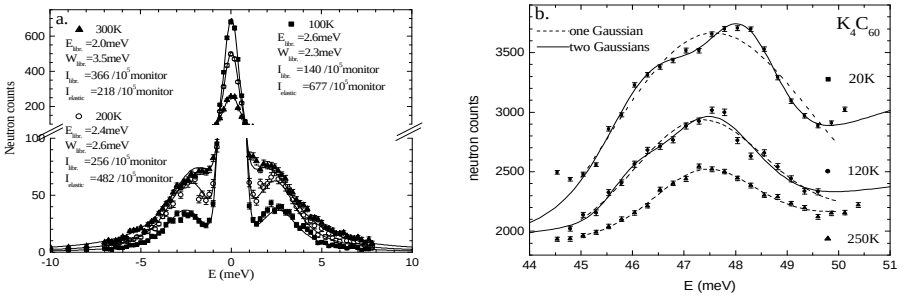

FIGURE 3. a. Low energy inelastic spectra of K_4C_{60}. Squares: 300K, circles: 200K, triangles: 100K. Lines are fits to the data. Note the change in scale in the y-axis. b. Neutron vibrational spectrum of K_4C_{60} showing the temperature dependent splitting of the $H_u(1)$ mode.

case of a biaxially distorted ion, and two in the case of an uniaxially distorted one (see inset of Fig.2). Therefore the fulleride ion is biaxially distorted in Cs_4C_{60} and uniaxially in K_4C_{60} and Rb_4C_{60}. This finding is consistent with the MIR results [3, 4].

Upon heating, the spectrum of Cs_4C_{60} also develops two peaks, indicating a transition to uniaxial distortion, in accordance with MIR results [4]. MIR experiments found this biaxial–uniaxial transition to be also present in K_4C_{60} and Rb_4C_{60}, although at different temperature.

In the latter two compounds the molecular change is present even though the neutron diffraction measurements did not reveal a structural phase transition. This confirms that the driving force behind the molecular change is an interplay between the molecular Jahn-Teller effect and the crystal potential. In both the tetragonal and the orthorhombic phase, the symmetry of the environment (the alcali cation sublatice) distorts the fulleride ion biaxially. This distortion is dominant at low temperature [3, 4]. At higher temperature the molecular JT forces are dominant, resulting in a uniaxially distorted fulleride ion [3, 4].

the cations around a fulleride ion have such a symmetry, that they distort the fulleride ion biaxially. This distortion is dominant at low temperature [3, 4]. At higher temperature the molecular JT forces are dominant, resulting in a uniaxially distorted fulleride ion [3, 4].

Below 6000 cm^{-1} intermolecular transitions between the split t_{1u} states can be seen [10]. The transitions are weaker in Cs_4C_{60}, which indicates a more difficult electron hopping, due to the larger interfullerene separation in Cs_4C_{60}.

Low energy neutron inelastic scattering is a well established technique to study the rotational potential of C_{60} in pristine and doped fullerides [5]. The excitations observed are due to C_{60} molecules librating about their equilibrium position. Figure 3a shows the librational peaks in K_4C_{60} at selected temperatures. Similar data were collected on Rb_4C_{60}.

The main features are the elastic line and the librational peak at $\approx$2 meV. The intensity of the elastic line decreases with increasing temperature due to the Debye-Waller effect,

while the width is resolution limited. The peak at ≈2 meV is a librational mode since the Q-dependence follows that expected for C_{60} with intensity maxima at $Q = 5.65$Å and $Q = 3.5$Å while the Q-dependence of the weaker features above 5 meV are flat indicating more translational character [5, 11]. The librations do not show any drastic change as a function of temperature that would indicate a change in the C_{60}^{4-} orientational potential. Following Ref. [11], we can estimate the magnitude of the orientational potential barrier. Using $E = 2.0$ meV for the measured librational energy at 300 K for K_4C_{60} we get 160 meV for hops between orientations related by 44.5° rotations and 630 meV for hops by 90° around (001). The librational energy in Rb_4C_{60} at 300 K was also found to be 2.0 meV.

In A_4C_{60} the MIR spectra show a splitting of the degenerate T_{1u} modes at 146 meV and 166 meV at low temperature [3, 4]. Neutron vibrational spectroscopy can yield similar information on all intramolecular modes without limitations from selection rules. We measured the NVS spectra for K_4C_{60} and Rb_4C_{60} between 25–150 meV in the temperature range 20 K to 300 K. Here, we focus on the peak centered at 47.5 meV at room temperature as this is the only mode that is observed to split within instrumental resolution (1.3 meV). By comparing it to pristine C_{60}, this peak can be assigned to the 5-fold degenerate $H_u(1)$ mode. Figure 3b shows the inelastic neutron spectra of K_4C_{60} at selected temperatures. We fit the spectra with either one or two Gaussians and a sloping background and found that the line is best described by a single Gaussian above 150 K while a split is revealed by the two-Gaussian fit at lower temperature. The discrepancy of the observed transition temperature between the neutron and optical work may be a result of different instrumental resolution.

In summary, the structure and rotational dynamics of K_4C_{60} and Rb_4C_{60} remain unchanged between 6 K and 300 K. Therefore the observed changes in the vibrational spectra are proof of Jahn-Teller distortion of the C_{60}^{4-} anions.

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