

Optical spectroscopy on Monomeric and Polymeric 1:1 Fulleride Salts

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We compare infrared spectra of the C_{60}^- monoanion in different solid-state structures with each other as well with that of the neutral molecule. We relate the shift and splitting of the T_u infrared modes to the strength and anisotropy of electron-phonon coupling in those environments.

KEY WORDS: Fullerenes; optical properties; polymers

1. INTRODUCTION

C_{60} , the prime example of the recently discovered fullerenes, tends to form ionic salts by attracting up to 6 electrons. Of these, the trianions are the most extensively studied due to the A_3C_{60} superconducting compounds, where A is an alkali atom. However, intriguing solid-state effects can be found in other phases as well. The most recent examples are the alkali salts with 1:1 composition. These materials undergo several phase transitions depending on thermal history. There is growing evidence for an orthogon phase (ortho-I) consisting of covalently bound polymers [1,2] and another one (ortho-II) of dimers [3]. Vibrational spectroscopy has been used to identify the valence state of anions in C_{60} salts [4,5] and it was shown early on that electron-phonon interactions play a significant role in the infrared properties of the salts [6]. In this study, we compare the infrared spectra of different phases of RbC_{60} to $(Ph_4)_2C_{60}I$, a charge transfer salt containing C_{60}^- monoanions.

2. EXPERIMENTAL

$(Ph_4)_2C_{60}I$ crystals were grown electrochemically [7]. The process results in a composition which ensures -1 charge on the fullerene ball. RbC_{60} powder was prepared by reacting C_{60} and Rb at high temperature. Infrared spectra of the tetraphenylphosphonium salt crystals were taken under an infrared microscope in reflectance mode at room temperature; the rubidium compound was ground into KCl pellets and the transmission measured against a pure KCl reference at each temperature. The room-temperature stable phase of RbC_{60} is the ortho-I structure; it transforms to fcc above 400 K and from there can be quenched into the ortho-II form which is metastable but has a long relaxation time when kept under 250 K.

Unlike the superconducting salts or the ferromagnetic TDAE- C_{60} , both our materials are stable in air thus requiring no special precautions during measurements; a slight decomposition into C_{60} is observed when heating RbC_{60} but this does not affect our main conclusions.

3. RESULTS AND DISCUSSION

Fig. 1. shows the section of the infrared spectrum containing the two high-frequency infrared-active vibrations of C_{60} . (To facilitate the comparison, we present the data as absorption, calculated by Kramers-Kronig analysis of the reflectance and as

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$A = -\log T$ from transmission.) The two modes in question are found at 1183 and 1429 cm^{-1} , respectively, in pure C_{60} .

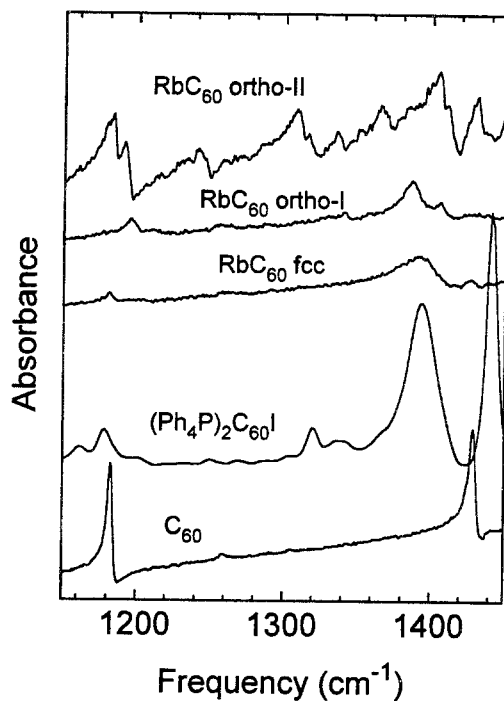


Fig. 1. Infrared spectra of C_{60} , $(\text{Ph}_4\text{P})_2\text{C}_{60}\text{I}$ and the fcc, ortho-I and ortho-II phases of RbC_{60} .

The somewhat complicated frequency shifts of the two T_u modes can be understood taking into account two solid-state effects: the change in lattice constant and the electron-phonon interaction. If the distance between fulleride ions gets shorter, the modes should harden in absence of other perturbations; electron-phonon interaction, on the other hand, causes softening whose magnitude depends on the strength of the coupling. As shown both experimentally [4,5] and theoretically [6], the highest-frequency mode has a much larger electron-phonon coupling constant than the 1183 cm^{-1} mode. Therefore, the former is indicative of the coupling, while the latter reflects the changes in lattice constant.

In $(\text{Ph}_4\text{P})_2\text{C}_{60}\text{I}$ the C_{60} ions are separated from each other by the bulky organic cations. Thus this compound can be regarded as a prototype of an isolated monoanion in a crystalline environment. The shift in the $T_u(4)$ mode from 1429 to 1394 cm^{-1} results from the on-ball electron-vibrational interaction. (Note that there are several modes of the counterion present, however, the fullerene modes can be clearly identified.) This mode does not shift appreciably

on going to the fcc phase, indicating that the fcc phase can also be regarded as an ensemble of C_{60}^- ions, interacting with the electron on the ball but not with each other. The ortho-I phase shows increased softening to 1385 cm^{-1} , along with a splitting into three components, at 1340, 1385 and 1406 cm^{-1} [5]. The softening can be related to an increased interaction with the collective electronic system and the splitting to the one-dimensional character of the polymeric chains, leading to the lifting of the three-fold degeneracy of the T_u modes. Finally, the ortho-II phase has a definite reduction in symmetry, with many more modes showing, but the vibration in question shifting up in frequency, indicative of the lattice contraction being more important than the electron-phonon coupling.

In contrast, the position of the $T_u(3)$ mode at 1183 cm^{-1} is determined by structural effects. In the fcc phase this peak is at the same position as in neutral C_{60} . The slight downshift in the phosphonium salt reflects the increased distance between fullerenes in that lattice. The significant contraction in the orthorhombic phases leads to a hardening in both ortho-I and ortho-II RbC_{60} . As expected, the hardening is more pronounced in the ortho-I phase, which shows a stronger compression along the [110] direction.

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