Optical spectroscopy on Monomeric and Polymeric 1:1 Fulleride Salts

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We compare infrared spectra of the C60 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 orthogonal 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_60I, a charge transfer salt containing C_60 monoanions.

2. EXPERIMENTAL

(Ph_4)_2C_60I 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
A = -logT from transmission.) The two modes in question are found at 1183 and 1429 cm\(^{-1}\), respectively, in pure C\(_{60}\).

In (Ph\(_4\))\(_2\)C\(_{60}\)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\(_{u}(3)\) 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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