

Infrared study on pressure-induced charge delocalization in Cs₂TCNQ₃

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Pressure dependence of several molecular vibration modes in Cs₂TCNQ₃ has been observed through the infrared absorption measurements. The behavior of the C-CN and C-H stretching modes suggests that phase transition takes place at around 3.6 GPa. The π^* electrons, which are localized on TCNQ⁻ molecules in the low-pressure phase, are delocalized significantly in the high-pressure phase. However, the radical-like and neutral-like molecules still coexist at high-pressure phase indicating that the electrons are not completely delocalized. The electron-molecular-vibration (emv) coupled mode disappears at high-pressure phase in coincident with the disappearance of the inter-radical charge transfer band S₁, proving the strong coupling between them.

Keywords: TCNQ compound, semiconductor-to-metal transition, molecular vibration.

1. Introduction

Cs₂TCNQ₃ crystallizes into a columnar structure consisting of a periodic stack of TCNQ⁰/TCNQ⁻/TCNQ⁻ [1], resulting in a semiconductor with the lowest optical energy gap of 0.3 eV [2]. The radicals TCNQ⁻ are dimerized, so that the uppermost valence band is formed by the π^* orbit of spin singlet. Since the on-site repulsion energy $U \approx 1.2$ eV [3] of the π^* electrons is higher than the optical energy gap, Cs₂TCNQ₃ may be regarded as a charge-transfer semiconductor of the 1/3-filled Hubbard system [4].

The high-pressure electric resistivity measurement has shown that this material undergoes the phase transition to a metallic state at around 3 GPa [5]. However, the optical energy gap remains unclosed [2] throughout the phase transition indicating that the metallic state in this material should be considered different from the ordinary metals. The results from the high-pressure Raman scattering experiment suggest that the electrons are completely delocalized from TCNQ-

radical molecules at high pressure resulting in a homogeneous distribution of charge along the TCNQ molecular stack [6].

The purpose of this work is to study the electronic mechanism underlying the above mentioned phase transition in Cs₂TCNQ₃. We measure the pressure dependence of infrared absorption due to molecular vibration. The infrared spectroscopy gives the complementary information on the charge distribution along the TCNQ stack to the Raman spectroscopy. In particular, the infrared spectroscopy allows us to observe the e-mv coupled modes, which are unobservable by the Raman spectroscopy.

2. Experimental

The Cs₂TCNQ₃ salt is synthesized from the reaction of TCNQ with an excess of CsI, and the single crystals of this material were obtained by recrystallization of the salt from acetonitrile-ether solution. The as grown single crystals of Cs₂TCNQ₃, about 10 μm thick, are used as

the samples. The pressure is generated using DAC. The daphne oil and flourinert (FC-40) are used as the pressure-transmitting medium for the measurement in the C-CN and C-H stretching region, respectively. The unpolarized infrared absorption is measured using a spectrometer system (Jasco FT/IR-410) equipped with a microscope. The ruby fluorescence method is used for calibrating the pressure.

3. Results

Figure 1 shows the absorption spectra in the C-CN stretching region at several pressures. The features at 1205 and 1211 cm^{-1} at the ambient pressure arise from neutral and radical molecules, respectively. These features show a blue-shift with increasing pressure, while increasing their energy spacing. At around 3.6 GPa they abruptly displace toward each other about half the way of the energy spacing. It is noteworthy that in the high-pressure phase radical-like and neutral-like molecules still coexist.

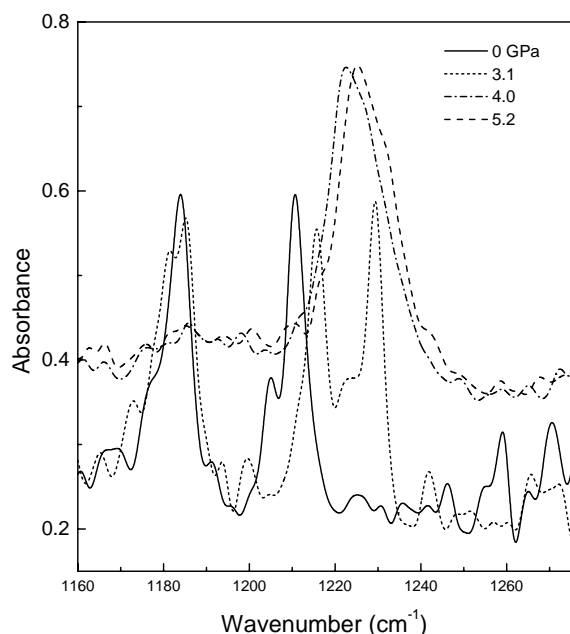


Fig. 1. Absorption spectra in the C-CN stretching region at several pressures.

The feature at 1183 cm^{-1} is the symmetric a_g mode. The a_g modes are originally infrared inactive in an isolated TCNQ molecule. They become infrared active as the result of the interaction of the molecular vibration with charge transfer, which is known as the electron molecular vibration (e-mv) coupling [7]. The frequency of the e-mv mode remains almost unchanged at low pressures. The e-mv mode disappears above 3.6 GPa, in coincidence with the disappearance of the electronic band S_1 , which is the counterpart of the e-mv mode [1,8]. Pressure dependencies of those modes are shown in Fig. 2.

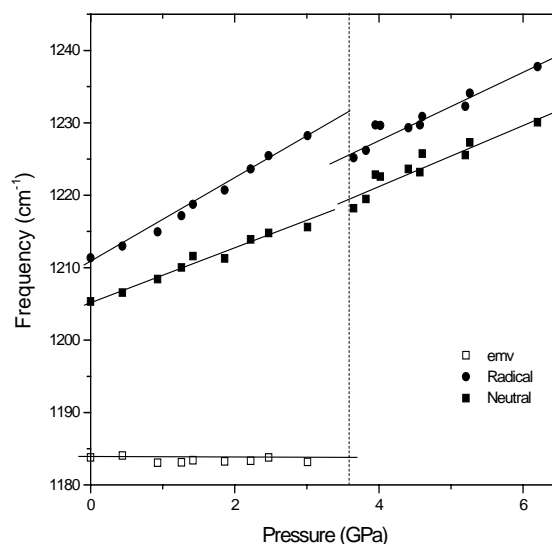


Fig. 2. Pressure dependencies of the frequency of molecular vibration modes in the C-CN stretching region

Figure 3 shows the absorption spectra in the C-H stretching region at several pressures. The $b_{2u}V_{36}$ mode belonging to radical and neutral molecules are observed at 3038 and 3054 cm^{-1} , respectively, at ambient pressure. They are blue-shifted with increasing pressure while maintaining their energy spacing. When the pressure exceeds 3 GPa, the mode belonging to the neutral molecules abruptly displaced toward low energy side so that the energy spacing abruptly decreases. At around

3.6 GPa they recover blue-shifting while maintaining their spacing. The pressure dependencies of the frequency of those modes are shown in Fig. 4.

We have intended to observe other modes such as C=C and C=N vibrations, but failed because of the strong absorption of the diamond and the pressure transmitting medium.

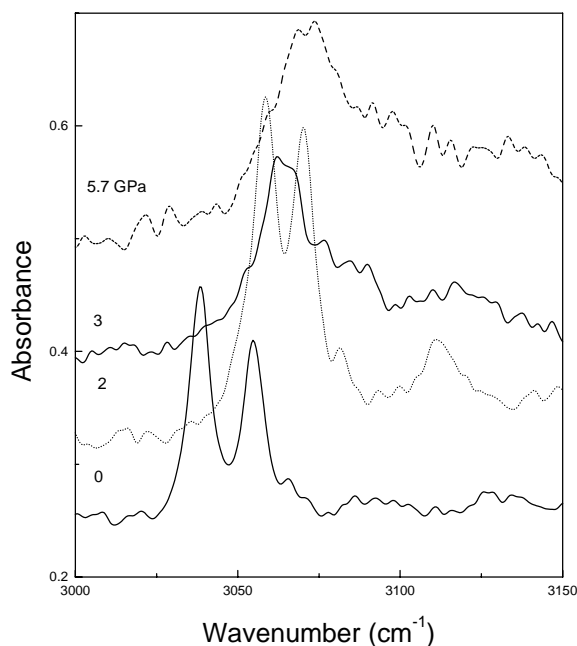


Fig. 3. The C-H stretching modes at several pressures.

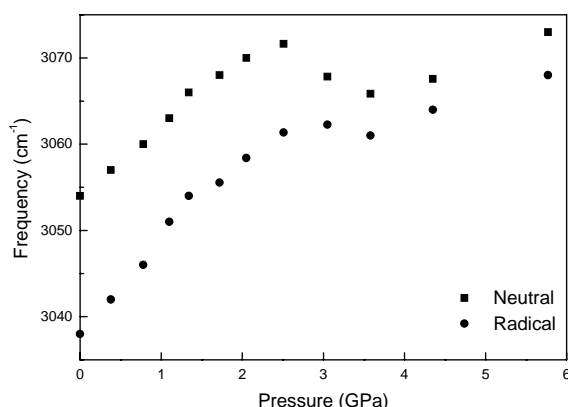


Fig. 4. The pressure dependencies of the C-H stretching modes.

4. Discussion

The results explained above clearly show that a pressure-induced electronic phase transition occurs at around 3.6 GPa. The energy spacing between the neutral and radical modes of both vibrations that abruptly decreases at high pressure indicates that the π^* electrons are significantly delocalized from radical to neutral molecules. However, in the high-pressure phase radical-like and neutral-like molecules still coexist indicating that the π^* electrons are not completely delocalized. This makes significant difference from results the Raman scattering measurement, which suggested that at high-pressure phase TCNQ molecules have a homogeneous ionicity [6].

The disappearance of the e-mv coupled mode above 3.6 GPa in coincidence the disappearance of the S_1 band are reminiscent of the results from temperature dependent optical absorption measurement in $(\text{NMe}_4)_2\text{TCNQ}_3$ [7]. The S_1 band is assigned to the electron transfer between the adjacent radical molecules. The close resemblance between the properties of S_1 and the e-mv coupled modes suggests the strong coupling between them.

5. References

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