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Investigation of the Jahn–Teller effect in the C_{60}^- monoanion under high pressure

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1 Introduction C_{60} -fullerene, the highly symmetric system in nature has kindled interest among the scientific community, to investigate its intriguing properties. The neutral C_{60} molecule crystallizes in face-centered cubic (fcc) structure at room temperature and has large enough interstitial space for doping with alkali metals. Several fullerene-related compounds were synthesized and have been investigated. With appropriate doping, the properties of C_{60} can be tuned from insulating to superconducting state or even magnetic. Doping C_{60} with electrons induces interesting properties in the corresponding compounds: metallic superconducting phases A_3C_{60} (where A stands for alkali metal), semiconducting A_4C_{60} or ferromagnetic TDAE- C_{60} which are governed by various physical phenomena [1, 2].

$(Ph_4P)_2IC_{60}$ (C_{60} -tetraphenylphosphoniumiodide) is one of the charge transfer salts, synthesized by electrochemical method [3]. This fully ionic $(Ph_4P)_2IC_{60}$ is air stable. $(Ph_4P)_2IC_{60}$ is tetragonal with space group $I_{4/m}$. The $I_{4/m}$ space group sustains two geometrically equivalent orientations of the C_{60}^- ball at 90° relative to each other, resulting in a local orientational disorder that is either static or dynamic in nature, depending on temperature. The counterions are large and therefore provide an ideal framework separating the fulleride ions. Thus, we can study the isolated C_{60}^- in a crystalline environment [4].

Due to the extra electron on the fullerene ball, electron-phonon coupling plays an important role. The coupling of the

degenerate electronic states with certain vibrational modes of the molecule leads to a lowering of the total energy because of a spontaneous molecular distortion, the Jahn–Teller (JT) effect. In the C_{60}^- monoanion, the JT effect produces an ellipsoidal distortion. According to symmetry analysis [5], the H_g vibrational modes couple to the highest occupied molecular orbital (t_{1u}) of the C_{60}^- ($H_g \cdot t_{1u}$). In C_{60}^- the unpaired electron resides in one of the t_{1u} lowest unoccupied molecular orbitals of neutral C_{60} . However, the JT distortion of the C_{60}^- splits the triply degenerate t_{1u} orbital into an a_{2u} orbital and an energetically higher-lying, doubly degenerate e_{1u} orbital. Near infrared-visible spectroscopic experiments on $(Ph_4P)_2IC_{60}$ show that the electronic and vibrational properties of the C_{60}^- anion are hardly perturbed by the counterion environment [6]. Detailed temperature-dependent studies of $(Ph_4P)_2IC_{60}$ have been carried out by electron paramagnetic resonance (EPR) [4, 7, 8], Raman scattering [9], and infrared spectroscopy [10, 11], which demonstrate the dynamic JT effect at room temperature. During cooling down $(Ph_4P)_2IC_{60}$ undergoes a transition to a static JT distorted state in the temperature range 120–140 K.

Even without JT coupling, various fullerene-based compounds undergo an orientational ordering transition with decreasing temperature or increasing pressure. For example, in pristine C_{60} the orientational ordering transition causes a change in the crystal structure from fcc to simple cubic. Orientational ordering transitions were observed for

various fullerene-based materials, including alkali fullerenes [12] and C_{60} - C_8H_8 [13]. The important difference between orientational phase transitions and JT distortions is that the former involves the rotation of the fullerene ball as a whole, and the latter the movement of the individual atoms on the molecule. In $(Ph_4P)_2IC_{60}$ the fullerene anions are not rotating even at room temperature, therefore the observed changes must have a different explanation.

An interesting issue is the similarity of the effects induced either by temperature lowering or by pressure increase, as demonstrated on pristine C_{60} [1] and fullerene derivatives [14, 15]. To the best of our knowledge no pressure studies exist for $(Ph_4P)_2IC_{60}$. Vibrational spectroscopy with a good knowledge of group theory is a well suited technique to study molecular symmetry. In a pursuit to understand the fundamental properties of the C_{60} monoanion under pressure, we investigate the C_{60}^- vibrational modes of $(Ph_4P)_2IC_{60}$ and look for possible pressure-induced phase transitions.

2 Experimental methods

2.1 Synthesis of $(Ph_4P)_2IC_{60}$ crystals Small crystals of $(Ph_4P)_2IC_{60}$ were grown by electrocrystallization on a platinum cathode with a constant current of 30 μA . Electrolysis was carried out with the solution of C_{60} and Ph_4PI dissolved in 1:1 mixture of toluene and dichloromethane [3] at ambient conditions. Shiny black crystals of 100–300 μm size (see Fig. 1) were collected from the Pt electrode after 5 days.

2.2 High-pressure infrared measurements We carried out infrared transmission measurements with a Bruker 66v/S Fourier transform infrared spectrometer. A highly focused infrared beam was obtained by coupling an infrared microscope Bruker IR scope II with 15 \times magnification to the spectrometer. High pressure was generated by a Syassen-Holzapfel diamond anvil cell (DAC). The ruby luminescence method was used for pressure determination [16]. The transmission was measured for pressures up to 5 GPa over the frequency range 100–600 cm^{-1} with a



Figure 1 (online colour at: www.pss-b.com) Photo of $(Ph_4P)_2IC_{60}$ single crystals; one square is 1 mm wide.

resolution of 2 cm^{-1} . All measurements were carried out at room temperature. As quasi-hydrostatic pressure transmitting medium we used CsI. A microscopic view of the DAC filled with the sample, the pressure transmitting medium, and the ruby ball is shown in Fig. 2.

In order to determine the transmittance of $(Ph_4P)_2IC_{60}$ under pressure, the intensity $I_s(\omega)$ of the radiation transmitted by the mixture of the powder sample and the pressure transmitting medium was measured, as illustrated in Fig. 2. As reference, the intensity $I_r(\omega)$ transmitted by the pressure transmitting medium inside the DAC was used. The transmittance was then calculated according to $T(\omega) = I_s(\omega)/I_r(\omega)$ and the absorbance is given by $A = \log_{10}(1/T)$.

3 Results and discussion In pristine C_{60} there are four infrared active T_{1u} modes, at 526, 576, 1183, and 1428 cm^{-1} [17]. Doping C_{60} with electrons causes a symmetry lowering, induces new electronic transitions, shifts some of the fundamental T_{1u} modes, and activates some new modes in the vibrational spectra. Figure 3 shows the absorbance spectra of $(Ph_4P)_2IC_{60}$ with increasing pressure between 380 and 600 cm^{-1} at room temperature. We focus in this paper on two prominent C_{60}^- vibrational modes, namely $T_{1u}(1)$ and $T_{1u}(2)$.

C_{60}^- has incompletely filled degenerate molecular orbitals in the ground and the excited electronic states, and is thus prone to symmetry lowering by static and dynamic distortions according to the JT theorem. The JT distortion of the ground $^2T_{1u}$ and excited $^2T_{1g}$ states of C_{60}^- leads to D_{5d} or D_{3d} symmetry. The lower symmetry in turn gives rise to a rich vibrational structure in the infrared spectrum [17]. In case of $(Ph_4P)_2IC_{60}$ there are counterion (namely Ph_4P^+) modes, in addition to the C_{60}^- modes. The two T_{1u} vibrational modes of C_{60}^- are observed at about 528 and 576 cm^{-1} , respectively, at the lowest pressure (see Fig. 3). These modes do not show any significant shift compared to neutral C_{60} , despite the additional charge, but exhibit a splitting. The counterion-mode strongly overlaps with the $T_{1u}(1)$ vibrational mode, and this mode also undergoes a significant change with pressure making the analysis complicated. The $G_u(1)$ mode, which is an activated silent mode of C_{60} , is

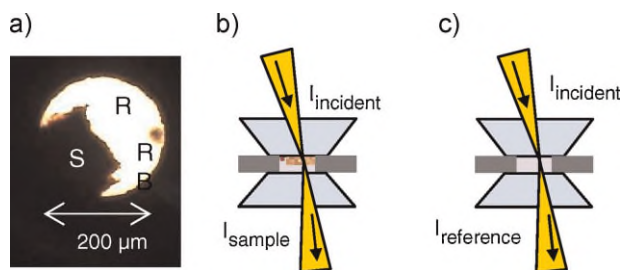


Figure 2 (online colour at: www.pss-b.com) (a) Microscopic view of the DAC with sample (S), pressure medium (R) and ruby ball (RB). Schematic diagram of transmission measurement geometry: (b) transmission through the sample and (c) transmission through the pressure transmitting medium only, used as reference.

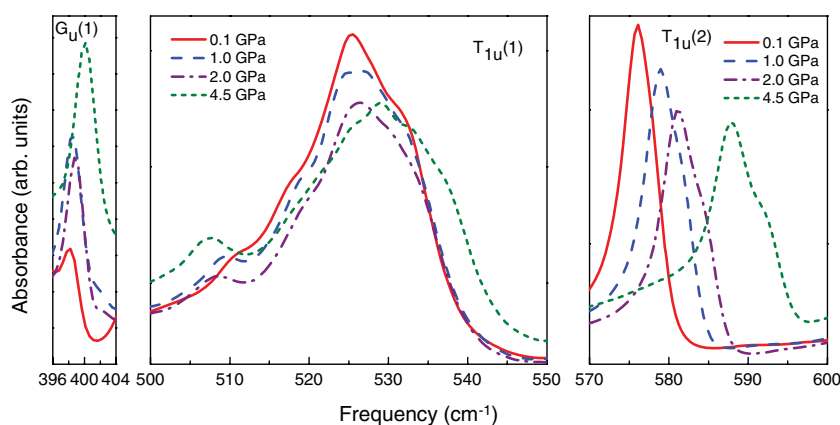


Figure 3 (online colour at: www.pss-b.com) Infrared absorbance spectra of $(\text{Ph}_4\text{P})_2\text{IC}_{60}$ in the region $380\text{--}600\text{ cm}^{-1}$ showing the C_{60}^- vibrational modes.

observed at 398 cm^{-1} , as shown in Fig. 3. The activation of a silent mode [10] is due to the symmetry lowering from I_h to D_{3d}/D_{5d} , which is a consequence of the JT effect. The counterion modes and their pressure dependence are not discussed in this paper. In order to find possible evidence of any change in the JT distortion, the frequency of each vibrational mode was extracted by fitting the absorbance spectra with Lorentzian functions. The frequency of the modes as a function of pressure is plotted in Fig. 4.

3.1 Ambient conditions It is evident from Fig. 4 that the $T_{1u}(1)$ and $T_{1u}(2)$ modes show a two-fold splitting already at ambient conditions ($\sim 0.1\text{ GPa}$). These splittings signal a small distortion of the C_{60}^- with a symmetry reduction from I_h . The changes in symmetry are reflected by the type of the splitting of the vibrational modes. IR measurement frequencies are of the order of 10^{13} s^{-1} which is faster than the JT tunneling frequency. Therefore, it averages out the individual features of the D_{3d} or D_{5d} distortions. According to EPR studies the distortion is dynamic in nature [4]: there are several D_{3d} or D_{5d} distorted states along various axes of the molecule, separated by shallow energy minima. These states

are connected through a movement called pseudorotation, which causes the disorder in the dynamic system. In agreement with our data, the room-temperature dynamic JT effect has been reported by FIR temperature-dependent studies [10, 11]. The other significant mode observed in our measurements is the $G_u(1)$ mode, which shows no splitting at ambient conditions.

3.2 High pressure The two-fold split $T_{1u}(1)$ and $T_{1u}(2)$ modes harden with increase in pressure, as presented in Fig. 4. Previous studies on C_{60} and related compounds have revealed the signature of an ordering transition induced by pressure and temperature [14, 15, 18]. The nature of this transition has been found more complicated than simple orientational ordering [18]. In contrast, no anomalies could be resolved for the $T_{1u}(1)$ and $T_{1u}(2)$ modes in $(\text{Ph}_4\text{P})_2\text{IC}_{60}$ for the whole pressure range studied (see Fig. 3). Table 1 summarizes the vibrational modes of C_{60}^- , their assignment, strength, and pressure dependence.

The $G_u(1)$ mode shifts to higher frequencies with increasing pressure up to 2 GPa (see Fig. 4). Fitting this mode with one Lorentz oscillator over the whole studied pressure range results in a considerable increase in the oscillator width above 2 GPa (see Fig. 5). This finding suggests a splitting of the $G_u(1)$ mode into at least two modes at around 2 GPa (see Fig. 4 for frequencies), consistent with temperature-dependent infrared studies on $(\text{Ph}_4\text{P})_2\text{IC}_{60}$ which revealed a doublet splitting of the $G_u(1)$ mode at 150 K [10, 11]. According to group theory, a two-fold splitting of the $G_u(1)$ mode is expected as the system settles down for D_{3d} (or lower) symmetry. The increase of the

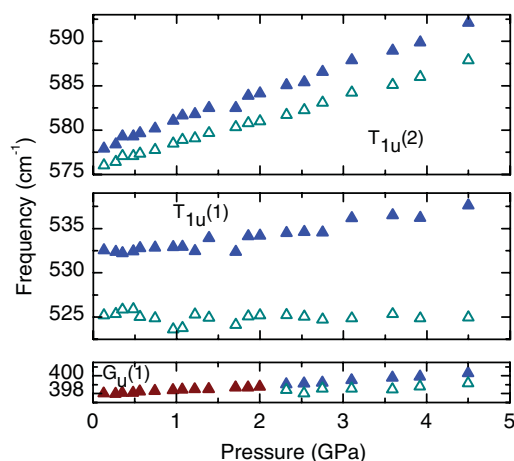


Figure 4 (online colour at: www.pss-b.com) Pressure-dependent frequency positions of the C_{60}^- vibrational modes in $(\text{Ph}_4\text{P})_2\text{IC}_{60}$.

Table 1 Pressure dependence of vibrational modes of $(\text{Ph}_4\text{P})_2\text{IC}_{60}$ and their assignments.

C_{60}^- mode	assignment	strength	pressure dependence
398	$G_u(1)$	weak	hardens, splits at higher pressure
525	$T_{1u}(1)$	strong	hardens
575	$T_{1u}(2)$	strong	hardens

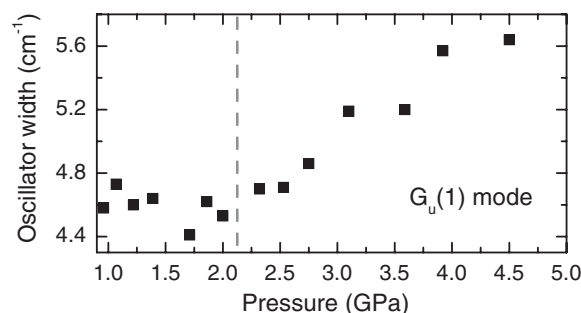


Figure 5 Pressure-dependent oscillator width of the $G_u(1)$ mode. The vertical dashed line marks the transition pressure.

barrier between energy minima with decrease in temperature results in a transition to the static JT state. The observed splitting above a certain pressure can be ascribed to the crystal lattice compression which causes steric crowding hindering the C_{60}^- pseudorotation. Similar effects were found in the A_4C_{60} systems, where the steric crowding is caused by the size of the cation when going from potassium to cesium [19]. The other factors which may influence the transitions – the dynamics of the counterion and interaction between C_{60}^- and counterion – may drive the system to an energetically favorable D_{3d} distortion.

4 Conclusions The dynamic JT effect in $(Ph_4P)_2IC_{60}$ is revealed by the low frequency T_{1u} modes of the C_{60}^- molecular ions. The dynamic nature of the JT effect is due to a competition between many nearly equivalent symmetries, possibly D_{5d} and D_{3d} in nature. At higher pressures there is steric crowding due to compression. This increases the distortion potential of the cations, thus transforming the system to an ordered state with D_{3d} or lower symmetry. The splitting of the $G_u(1)$ mode above 2 GPa signals the dynamic-to-static transition.

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