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Charge Transfer in C_{60}*TMTSF*2(CS_2) Complex at High Pressure: A Raman Spectroscopic Study

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The Raman spectra of the neutral state complex C_{60}*$C_{10}H_{12}Se_4$ *2(CS_2) [$C_{10}H_{12}Se_4$, tetramethyl-tetra-selenafulvalene (TMTSF)] were measured as a function of pressure at room temperature. The pressure dependence of almost all intramolecular phonon modes exhibits irreversible changes at 5.0 ± 0.5 GPa, the more characteristic of them being the irreversible softening by 9 cm^{-1} of the $A_g(2)$ pentagon-pinch (PP) mode, observed upon total pressure release. This softening is analogous to that observed in the case of KC_{60}. These observations may be attributed to an irreversible phase transition involving the transfer of one electron from TMTSF donor to C_{60} acceptor molecule.
[fullerene complexes, charge transfer, high pressure, Raman spectra]

1. Introduction and experiments

The synthesis of new chemical compounds of fullerenes and the studies of their structures, optical properties and energy spectrum is a fast growing area in the last years [1- 3]. C_{60}, having high electron affinity, can form a variety of neutral and anion state charge transfer complexes, which are interesting for their electronic properties. Of particular interest, in this family of compounds, is the study of the influence of the donor-acceptor interaction potential to the phonon and electron energy spectra of fullerene and of the effect of high pressure on this potential. In this work we present a Raman spectroscopic study of the pressure behavior of the phonon modes of the neutral state molecular complex of fullerene C_{60}*TMTSF*2(CS_2). Our motivation is to investigate the pressure-induced enhancement of the charge transfer from the donor TMTSF to the acceptor C_{60} molecule and the consequent changes in the phonon spectra.

Single crystals of C_{60}*TMTSF*2(CS_2) were grown by co-crystallization, under controlled temperature increase, of 30 ml of solution containing 7 mg of C_{60} (obtained by the Krätschmer method, purity better than 99.9%) and 18 mg TMTSF (Aldrich, purity better than 99%) in CS_2. Typical size of the crystals was of 3x3x2 mm^3. Their structure, determined by X-ray diffration, is monoclinic with lattice parameters: a = 1.5407, b = 1.2934, c = 1.2026 nm, β = 108.39^0, V = 2.2741 nm^3, space group C_m, Z = 2, ρ_{calc} = 1.929 g/cm^3, R = 0.047 [4]. The conformation of the C_{60} molecule and the distances between them are not changed significantly in comparison to the pristine C_{60} crystals. The conformation of TMTSF molecule is significantly altered and becomes non-planar [4].

High pressure was generated using the gasketed diamond anvil cell (DAC) of Mao-Bell type [5]. The 4 : 1 methanol-ethanol mixture was used as pressure transmitting medium and the ruby fluorescence technique was used for pressure calibration. Raman spectra were recorded using a triple monochromator (DILOR XY-500) equipped with a CCD cryogenic detector system. The spectral width of the system was ~5 cm^{-1}. The 514.5 nm line of Ar^+ laser was used for excitation and the power, measured directly before the cell, was kept lower than 1.5 mW. The spectra were recorded in the back scattering geometry and results from three different runs were recorded for both increasing and releasing pressure.

2. Results and Discussion

The Raman spectra of the C_{60}*TMTSF*2(CS_2) complex, shown in Fig. 1 for various pressures at room temperature, contain all the intramolecular Raman active modes observed in crystalline C_{60}. Minor differences including a small increase in the phonon frequencies, up to 5 cm^{-1}, in some modes and new

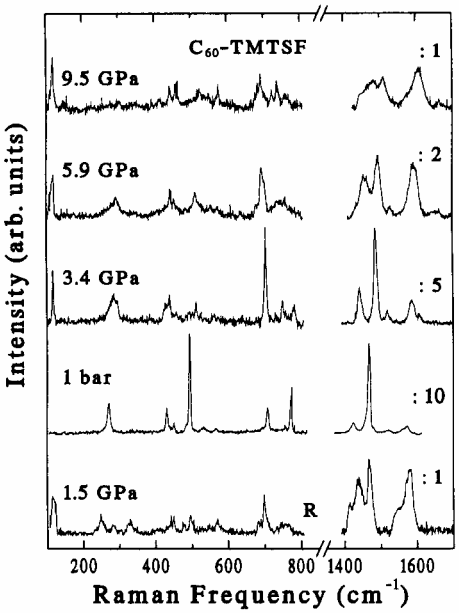

Fig. 1. Raman spectra of the C_{60}*TMTSF*2(CS_2) molecular complex at room temperature and for pressures up to 9.5 GPa. The spectrum at the bottom, marked by an R, is recorded upon pressure releasing cycle.

weak Raman peaks have been observed. The fact that the main Raman frequencies of the intramolecular phonon modes of the C_{60} molecule, within the C_{60}*TMTSF*2(CS_2) complex, practi-

cally coincide with those of the pristine C_{60} crystal, indicates that there are no significant changes of the conformation of the C_{60} molecule in the C_{60}*TMTSF*2(CS_2) complex with respect to the pristine C_{60} crystal. On the contrary, this is an indication that the distances between the C_{60} molecules within the complex are close to those in the pristine C_{60} crystal. These qualitative estimations are in accordance with the results of the X-ray study of the crystal structure of the C_{60}*TMTSF*2(CS_2) [4]. A number of relatively weak Raman peaks observed in the spectrum, are similar to those observed in the Raman spectrum of pristine C_{60} crystal. These modes may be associated with second order two-phonon scattering. There is no clear indication that some of those weak Raman peaks may have their origin to intramolecular phonon modes of the TMTSF molecule. This may be understood, in our opinion, from the fact that the cross-section for Raman scattering of the C_{60} molecule may be larger than that of the TMTSF molecule.

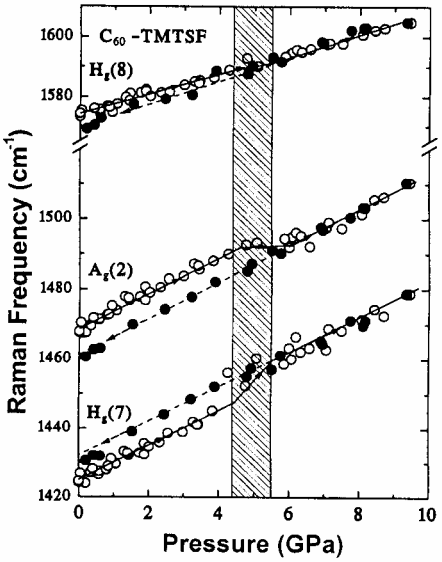

Fig. 2. Pressure dependence of $H_g(7)$, $A_g(2)$ and $H_g(8)$ intramolecular phonon frequencies. Open (solid) symbols correspond to data taken at three pressure runs for increasing (decreasing) pressure. Solid lines (dashed lines) are guides to the eye for increasing (decreasing) pressure. The shaded area shows the pressure region of the phase transition.

The pressure dependence of the phonon frequencies in the high and low frequency region of the spectrum of C_{60}*TMTSF*2(CS_2) complex, are shown in figures 2 and 3. The pressure behavior of the three strongest modes $H_g(7)$, $A_g(2)$ and $H_g(8)$, shown in Fig. 2, is quite different from that of the C_{60} crystals [6]. The phonon frequencies of the C_{60}*TMTSF*2(CS_2) were monotonicaly increased in the pressure region 0 to ~5.0 GPa. No indications of phase transitions, similar to the two-stage orientational ordering phase transition in the C_{60} crystals [6], were seen in this pressure region. The slopes of the pressure dependencies of the $H_g(7)$, $A_g(2)$, and $H_g(8)$ modes, listed in Table 1, are somehow changed at

Table 1. Pressure dependence coefficients for some phonon mode frequencies of C_{60}*TMTSF*2(CS_2) obtained from least-square fits to the experimental data.

Symmetry	ω_i(P=0) (cm^{-1})	$\partial\omega_i/\partial P$ (cm^{-1}/GPa)	ω_i(P=0) (cm^{-1})	$\partial\omega_i/\partial P$ (cm^{-1}/GPa)
	(P < 5 GPa)		(P > 5 GPa)	
Increasing pressure				
$H_g(7)$	1424	5.2	1439	4.1
$A_g(2)$	1468	5.3	1459	5.3
$H_g(8)$	1574	3.3	1568	4.1
Decreasing pressure				
$A_g(2)$	1455	5.5	—	—
$H_g(8)$	1563	4.7	—	—

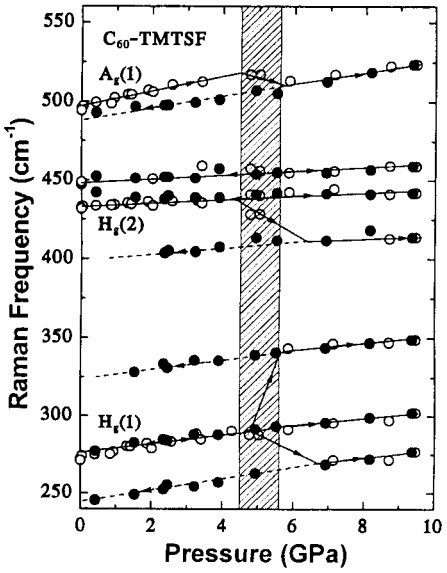

Fig. 3. Pressure dependence of $H_g(1)$, $H_g(2)$ and $A_g(1)$ intramolecular phonon frequencies. Open (solid) symbols correspond to data taken at three pressure runs for increasing (decreasing) pressure. Solid lines (dashed lines) are guides to the eye for increasing (decreasing) pressure. The shaded area shows the pressure region of the phase transition.

pressures higher than 5.0 GPa. At the same time a jump-like softening of about 9 cm^{-1} in the $A_g(2)$ mode, accompanied by a similar hardening of the $H_g(7)$ mode, were observed near 5 GPa. The pressure dependence in the low frequency region (Fig. 3) reveals similar changes in the intramolecular modes of this region at ~5.0 GPa. $H_g(1)$ and $H_g(2)$ are split while $A_g(1)$ is softened and these changes are irreversible too.

The pressure dependence of the intramolecular phonon frequencies of the C_{60}*TMTSF*2(CS_2) in the initial pressure re-

gion 0 - 3.0 GPa differs essentially from that of the pristine C_{60} crystal. In the pristine C_{60} crystal the $A_g(2)$ PP-mode, as well as other intramolecular modes, exhibit a considerable softening in the pressure region 0 - 0.4 GPa [7]. This was explained as the manifestation of the pressure-induced orientational ordering phase transition from the face centered cubic to the simple cubic crystal structure. At normal pressure this transition takes place at 250 K and the transition temperature increases with pressure [8]. The final stage of the pressure-induced orientational ordering takes place at pressure 2.4 GPa, where fullerite transforms to a phase with complete freeze out of the jumps of the C_{60} molecules between the two equilibrium orientational positions in the simple cubic structure [9]. These characteristics in the pressure dependence do not show up in the spectrum of C_{60}*TMTSF*2(CS_2). This is compatible with the X-ray scattering data, indicating that the C_{60} molecules in the C_{60}*TMTSF*2(CS_2) complex are orientationally ordered at room temperature and normal pressure.

The most interesting features of the pressure dependence of the phonon modes of C_{60}*TMTSF*2(CS_2) are the prominent changes at 5.0 ± 0.5 GPa, associated with the softening of all phonon modes and the splitting of some of them. These changes are irreversible and the residual softening, observed in the recovered material upon total release of pressure, varies from 5 up to 18 cm^{-1} for the various modes. The softening of the intramolecular phonons of pristine C_{60}, mainly of $A_g(2)$ PP-mode, observed under various degrees of illumination [10,11], is reversible under conditions of low illumination and has been associated with the creation of the triplet excited C_{60} states [10]. On the other hand, under more intense illumination this softening of the PP-mode becomes irreversible and has been associated to the photodimerization of the C_{60} molecules [11]. Similar softening of the PP-mode has been observed also in high pressure and temperature polymerized C_{60} samples [12].

The softening of the intramolecular modes of C_{60} has also been observed in the intercalated C_{60} compounds M_6C_{60}, M = K, Rb, Cs [13]. In this case the frequencies of the Raman active modes are insensitive to the M atom, and therefore to the lattice expansion caused by doping with alkali-metal atoms with larger ionic radii. This softening has been attributed to the elongation of the intramolecular bond lengths induced by charge transfer from alkali metal atoms to the C_{60} molecule and the resulting softening of the force constants [13]. The softening of the $A_g(2)$ PP-mode in this case is equal to 37.5 cm^{-1} for all studied compounds. Winter and Kuzmany [14] have studied the softening of the PP-mode for the K_xC_{60} series of compounds with x varying from 0 up to 6. The main result of their study is that the PP-mode softens almost linearly with increasing x and, consequently, the charge transfer from K to C_{60} molecule. They have found, in particular, that in the case of the KC_{60} compound the softening of PP-mode is equal to ~9 cm^{-1}.

The pressure-induced softening of phonon modes in the C_{60}*TMTSF*2(CS_2) molecular complex may be associated with the charge transfer between the TMTSF donor and C_{60} acceptor molecules. At normal pressure the van der Waals type interaction between donor and acceptor molecules is too weak and they form the neutral state molecular complex with weak charge transfer. The gradual reduction of the intermolecular donor-acceptor distances and the enhancement of the interaction between them at higher pressures, results in the charge-transfer phase transition, taking place in the region 5.0 ± 0.5 GPa. During the phase transition a transfer of one electron from TMTSF to C_{60} molecule takes place forming a new anion state C_{60}^{-1} charge-transfer complex. As a result, the transformation of the material becomes irreversible and the PP-mode exhibits a residual softening by 9 cm^{-1}, observed upon total release of pressure, in complete analogy to the case of KC_{60} [14].

In conclusion, the pressure dependence of the frequencies of the intramolecular phonon modes of the neutral state molecular complex C_{60}*TMTSF*2(CS_2) shows a softening of the majority of phonon modes and a splitting of some of them at 5.0 ± 0.5 GPa. The residual softening of the $A_g(2)$ PP-mode, upon total pressure release, is equal to ~9 cm^{-1} and is the same as in the case of potassium doped fullerene KC_{60}. These changes are associated with an irreversible pressure-induced phase transition which, in our opinion, has a charge-transfer character, resulting in the formation of the C_{60}^{-1} anion state charge-transfer molecular complex.

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