

Pressure-Induced Donor–Acceptor Charge Transfer in a Fullerene Molecular Complex with Ferrocene

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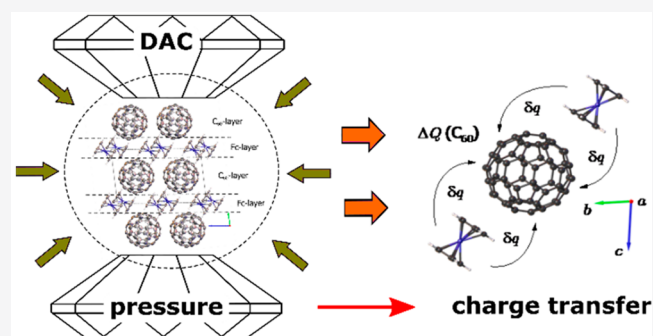
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ABSTRACT: The pressure-induced charge transfer in a molecular complex of fullerene with ferrocene, $C_{60} \cdot \{Fe^{2+}(\eta^5-C_5H_5)_2\}_2$, was studied by ab initio calculations, single-crystal X-ray diffraction analysis, and Raman spectroscopy at pressures up to 5.3 GPa. The calculations based on high-pressure crystal structure data, performed by the fragment molecular orbital method and hybrid density functional level chemistry, show a pressure-dependent partial ionization of the C_{60} and $Fe^{2+}(\eta^5-C_5H_5)_2$ molecules. At pressures up to 2 GPa, the calculated charges of the two molecules nearest to the C_{60} ferrocenes grow equally, while at $P > 2$ GPa, the transferred charges are clearly different. The unequal charge transfer is due to the different orientations of the two neighboring ferrocene molecules with respect to a fullerene molecule cage. The Raman spectra of the complex show a peculiarity near 2 GPa in the pressure dependence of the frequency and bandwidth of the ferrocene intramolecular breathing mode associated with unequal charge transfer.



INTRODUCTION

Since the discovery of C_{60} buckminsterfullerene in 1985, studies of fullerene and its derivatives have been attracting researchers' interest.¹ The family of fullerene-based compounds has been continuously growing with the synthesis of new materials, and their novel properties are attracting the interest of physicists, chemists, and material scientists. The parent molecule, C_{60} , with its unique structure, in which 60 carbon atoms are located on the near-spherical shape of a truncated icosahedron, offers a large free volume inside it as well as large interstitial free space in the condensed state. These characteristics result in a variety of chemical properties, like the intercalation with alkali metals. Fullerene derivatives with stoichiometry M_3C_{60} , where M is the alkali metal atom, are conductors and demonstrate superconductivity at relatively high temperatures.^{2,3} Another important property of a fullerene is its ability to polymerize due to a large number of unsaturated double C=C bonds in the molecular cage. Treatment of a fullerene at high pressure and high temperature leads to the formation of one-, two-, and three-dimensional C_{60} polymeric networks via a [2 + 2] cycloaddition mechanism.^{4–8}

The fullerene derivatives are of continuing interest because of their application possibilities. In particular, fullerene molecular complexes, in which close-packed molecules in the fullerene layers alternate with the layers of a molecular donor, have been attracting a lot of attention over recent years. The shortening of the intermolecular distances at high pressure increases the overlap between the highest occupied molecular

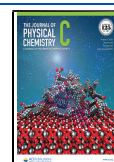
orbitals (HOMO) of the molecular donor and the lowest unoccupied molecular orbital (LUMO) of the fullerene acceptor that stimulates the charge transfer. On the other hand, numerous Raman studies of fullerene molecular complexes show that the C_{60} molecules in the fullerene layers can undergo polymerization at high pressure.^{9–11}

Another interesting feature is charge transfer-induced reversible polymerization—a mechanism that is proposed for some C_{60} and C_{70} fullerene molecular complexes.¹² As an electron acceptor, C_{60} fullerene can interact with the donor molecules to form partially charged fullerene($\delta q^\bullet$) and donor(δq^+) molecules. The value of δq of a transferred charge within the donor–acceptor pairs depends on the relative energies of the frontier molecular orbitals of the acceptor and donor and their overlapping integrals.^{13–15} The latter is determined mainly by the distance between the donor and the acceptor and their positions in the crystal structure. Since the relative position of the molecules changes during compression, it is possible to tune the charge transfer by applying an external pressure. The small negative charge of C_{60} can have a beneficial

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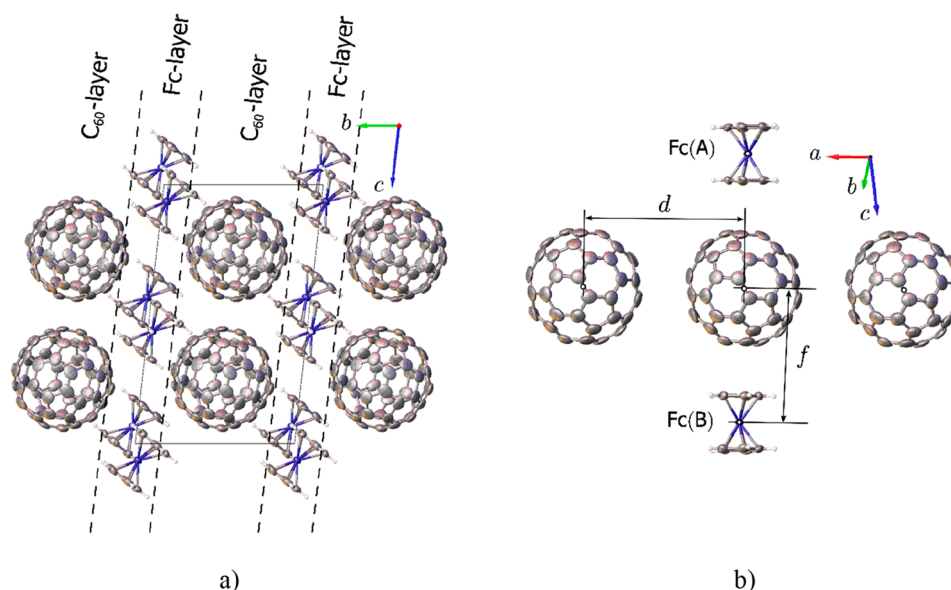


Figure 1. Crystal structure of the $C_{60}\cdot Fc_2$ complex: alternation of ferrocene and fullerene layers, view along the *a* axis (a); fullerene nearest neighbors (b)

impact on the polymerization process because the fullerene binding energy decreases and stabilizes C_{120} dimers.¹⁶ It is well known that the $C_{60}^{\bullet-}$ monoanion can form double-bonded π -dimers $(C_{60}^{\bullet-})_2$ (bond length is 1.575 Å) as well as single-bonded σ -dimers $C_{120}^{\bullet-}$ (bond length is 1.597 Å) in the triplet state.^{17,18}

In this paper, we report the results of ab initio calculations of the pressure-tuned donor–acceptor charge transfer in the fullerene complex with ferrocene, $C_{60}\cdot\{Fe^{2+}(\eta^5-C_5H_5)_2\}_2$ ($C_{60}\cdot Fc_2$), along with the Raman measurements of the phonon spectra and X-ray diffraction studies at pressures up to 5.3 GPa. The calculations based on the high-pressure structure parameters show that at up to 2 GPa the charges of the two nearest molecules to C_{60} ferrocenes grow equally, while at $P > 2$ GPa the transferred charges are clearly different. The pressure dependence of the frequency and bandwidth of the ferrocene intramolecular breathing mode of the complex show a peculiarity near 2 GPa associated with a somewhat different ionization of the neighboring ferrocene molecules.

EXPERIMENTAL SECTION

Single crystals of pristine ferrocene and the $C_{60}\cdot Fc_2$ complex were synthesized by slow evaporation of solvents from a saturated solution as previously described.¹⁹ A hexane solution of a commercial ferrocene powder and a mixture of the benzene solution of fullerene and ferrocene powders in a 2:1 = $C_6H_4Cl_2$:*x* volume ratio were used in each case. The in situ high-pressure X-ray diffraction study of the grown single crystals was performed by means of a Rigaku Oxford Diffraction Gemini R diffractometer by ω -scan rotation using Mo K α radiation $\lambda = 0.7107$ Å and by means of a Boehler-Almax design type Ia diamond anvil cell (DAC) with an available aperture of 42°. Silicon oil was used as a pressure-transmitting medium. A complete X-ray diffraction (XRD) structure analysis was done for pressures up to 5.3 GPa. The Raman spectra were recorded in the backscattering geometry using an Acton SpectraPro-2500i spectrograph equipped with an Olympus BX51 micro-Raman setup and a Peltier-cooled CCD. The 532 nm laser line was used for Raman scattering

measurements with laser powers up to ~ 180 μ W before the DAC. The high-pressure Raman measurements were carried out using a Mao-Bell type DAC. A 4:1 methanol–ethanol mixture was used as a pressure-transmitting medium, while the ruby fluorescence technique was used as a pressure calibration tool.

Theoretical analysis of the electronic structure, vibration spectra, and charge transfer was performed using the FIREFLY²⁰ and GAMESS US²¹ programs. All calculations were based on density functional level theory (DFT), actually UHF/B3LYP//cc-pVTZ(C,H)+LANL2DZ(Fe), with mixed basis sets for light and heavy atoms. An effective core potential for the LANL2DZ basis was used to replace the core electrons of the iron atoms. The calculation of the charge transfer was performed using the fragment molecular orbital method (FMO)^{22,23} incorporated into GAMESS US. During the FMO calculation, all molecules had a fixed geometry, which was taken from the experimentally obtained structures and did not undergo any relaxation. In the case of the vibration spectra calculations of the neutral and charged ferrocene, their molecular geometries were additionally optimized with the same level of theory.

RESULTS AND DISCUSSION

The crystal structure of the $C_{60}\cdot Fc_2$ complex under ambient conditions was studied for the first time by Crane and co-authors in 1996.¹⁹ In general, it has a layered structure with alternating fullerene and ferrocene layers (see Figure 1a). Under ambient conditions, each C_{60} molecule is surrounded by six neighbors in the fullerene layers with the shortest distances between the molecule centers $d = 10.060$ Å (two neighbors) and 11.015 Å (four neighbors). The closely located C_{60} molecules within the fullerene layer are separated by the distance $f = 8.320$ Å from the Fc molecules in the upper and lower neighboring ferrocene layers (see Figure 1b). The angle between the center-to-center direction of the neighboring fullerene and the ferrocene molecules and the molecular axis of the ferrocene is about 6.5°. Since the Fc molecule axes are almost perpendicular to the fullerene cage, the π -conjugated

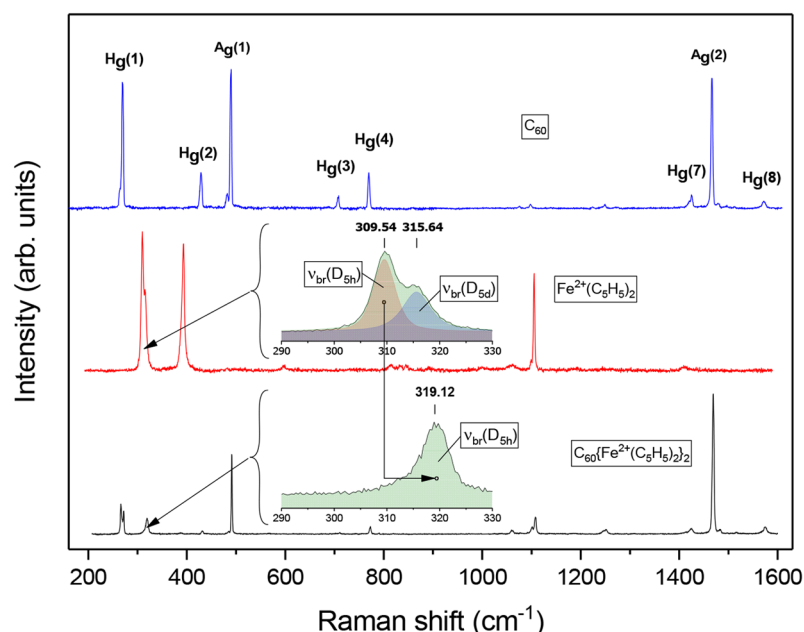


Figure 2. Raman spectra of pristine ferrocene, crystalline C_{60} , and $C_{60}\cdot Fc_2$ complex at ambient pressure and room temperature.

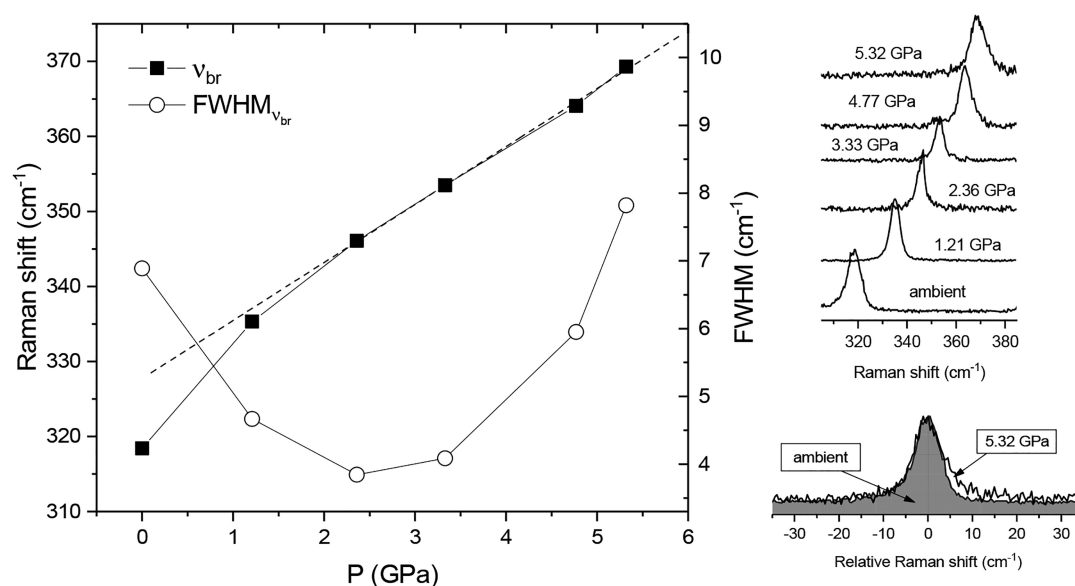


Figure 3. Ferrocene breathing mode in the Raman spectra of the $C_{60}\cdot Fc_2$ complex at various pressures (right). Pressure dependence of the frequency and bandwidth of the breathing mode (left).

electronic systems of the two molecules may effectively interact due to a rather close location. It is expected that this interaction forms slightly charged $(C_{60})^{\delta q^-}$ and $(Fc)^{\delta q^+}$ ions because of the redistribution of molecular charges which grows with a decrease in the intermolecular distances at high pressure.

Typically, formation of ions from highly symmetric molecules gives rise to small distortions of a molecular cage and results in symmetry lowering. The distortions affect intramolecular vibration spectra due to the elongation/shortening of molecular bonds. The latter can be detected by XRD structure analysis when their magnitude is sufficiently high. In our case, a progressive charge transfer from ferrocene to fullerene molecules at high pressure leads to gradual elongation of the ferrocene molecule as shown in a recent

study of the crystal structure of the $C_{60}\cdot Fc_2$ complex at pressures up to 5 GPa.²⁴ The study of this issue from various points of view, including X-ray structure analysis, ab initio calculations, and Raman spectroscopy at high pressure, in order to find the signs of charge transfer is of great interest.

Generally, the cyclopentadienyl rings in a ferrocene molecule are highly flexible and exhibit jumping rotations around its 5-fold axis under ambient conditions which can be suppressed under low temperature or high pressure. Furthermore, theoretical studies of the ferrocene molecular structure in the gas phase at various levels of complexity (DFT, second-order Møller–Plesset perturbations theory, and etc.) predict two close in energy conformations which can coexist in crystals: eclipsed with D_{5h} symmetry (equilibrium state) and staggered with D_{5d} symmetry (saddlepoint).^{25,26} The cyclopentadienyl

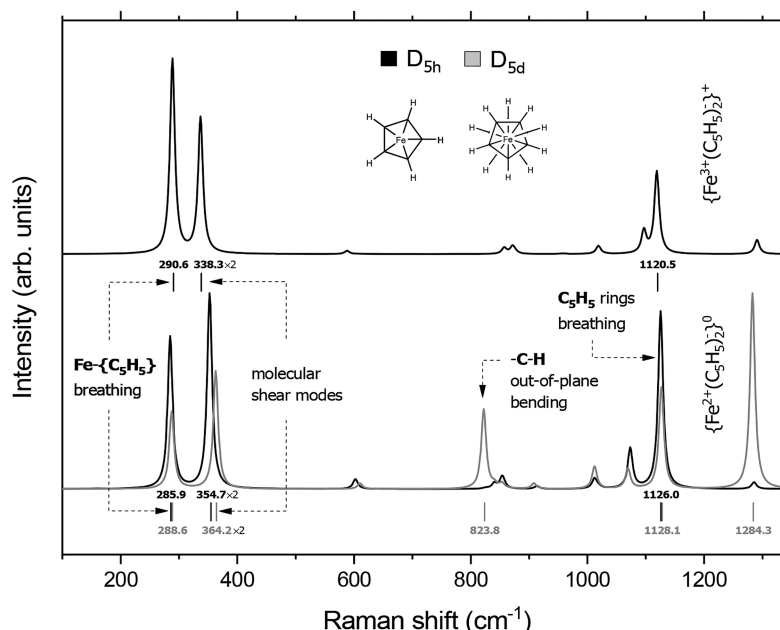


Figure 4. Calculated Raman spectra of Fc and Fc⁺ molecules (unscaled frequencies).

rings of the ferrocene molecule in pristine Fc crystals under ambient conditions are disordered and occupy both positions as shown earlier.²⁷ In contrast, the ferrocene molecules in the C₆₀·Fc₂ complex are completely ordered, occupying only the D_{5h} conformation.

The Raman spectra of the pristine C₆₀ crystal (top spectrum), the pristine ferrocene crystal (middle spectrum), and the fullerene complex with ferrocene, C₆₀·Fc₂ (bottom spectrum), are shown in Figure 2. The main ferrocene and fullerene peaks in the Raman spectra of the C₆₀·Fc₂ complex do not overlap; therefore, they can be clearly separated and assigned. The most intensive peaks in the Raman spectra of the complex refer to the totally symmetric A_g modes of the C₆₀ molecule, while several weaker modes refer to degenerated H_g modes. In addition, the spectrum of the complex contains some modes of ferrocene near 320 and 1100 cm⁻¹; however, their intensity is not as large as in a pristine ferrocene crystal (see the center of Figure 2). One of these modes located at 1107.9 cm⁻¹ in the spectrum of the complex corresponds to the phonon mode with a frequency of 1105.3 cm⁻¹ in pristine ferrocene. A more intense second ferrocene band at 319.1 cm⁻¹ corresponds to split peaks at 309.5 and 315.6 cm⁻¹ in the Raman spectra of pristine Fc crystals. In the charge transfer study, the latter Fc mode is of interest because its frequency is rather sensitive to the charge state of the ferrocene molecule. The pressure behavior of the Raman mode near 310 cm⁻¹ in pristine ferrocene crystals was studied by W. Cui and co-authors.⁹ At ambient pressure, it looks like a single peak with a shoulder that splits into two peaks in an initial pressure range, while the separation increases with pressure and exceeds 10 cm⁻¹ at 1 GPa. The splitting of this mode was attributed to the structural inequivalence of two ferrocene molecules,⁹ which contradicts the results of the detailed structural studies with a completely ordered one-half Fc in the asymmetric part of the unit cell.²⁸

In the Raman spectra of the C₆₀·Fc₂ complex, the 319.1 cm⁻¹ peak of the breathing mode of ferrocene looks like a single peak; however, it has an asymmetric shape that suggests

a multicomponent composition (see insert in Figure 2). In addition, the full width at a half-maximum (fwhm) of this peak varies nonmonotonically with pressure. The pressure dependence of the fwhm and the pressure shift of this peak are shown in Figure 3. These data were obtained from the experimental Raman spectra by fitting the phonon bands with the Voigt profile. The pressure dependence of the fwhm shows a minimum near ~2.5 GPa; it monotonously decreases up to 2.5 GPa and then increases with a further increase in the pressure. The superimposition of the ferrocene Raman bands at ambient and high pressure shown in the lower right panel of Figure 3 reveals the asymmetric band profile: at 5.32 GPa the band has a skew toward high wavenumbers. The pressure behavior of the ferrocene Raman band can be explained assuming that it consists of two peaks which have slightly different pressure dependence. They are getting close to each other when the pressure is increasing from ambient pressure to 2.5 GPa; the peaks coincide at this pressure, while they move apart with a further increase in the pressure. The proximity of these subpeaks prevents their reliable separation, so that they appear as a single band with variable width. The pressure dependence of the ferrocene mode frequency in the Raman spectra of the complex is depicted in the right top panel in Figure 3. The frequency linearly increases with pressure at $P \geq 2.5$ GPa in accordance with the relation $327.74 [\text{cm}^{-1}] + 7.7 [\text{cm}^{-1} \cdot \text{GPa}^{-1}] \cdot P$ but deviates from it at pressures $P \geq 2$ GPa (see the line fitting in Figure 3). The change of the slope takes place near 2.5 GPa when the band is the narrowest and has almost a Lorentzian shape.

In order to reveal the changes in the Raman spectra associated with charge transfer, we performed quantum chemical calculations of the neutral and positively charged ferrocene molecules, Fc and Fc⁺. The HOMO of both the D_{5h} and the D_{5d} conformations of the ferrocene molecule is mainly formed by the d levels of the central Fe atom. Their total contribution to the HOMO is slightly less than 90%, in compliance with the Mulliken population analysis. Thus, after the removal of one electron from ferrocene (Fc → Fc⁺

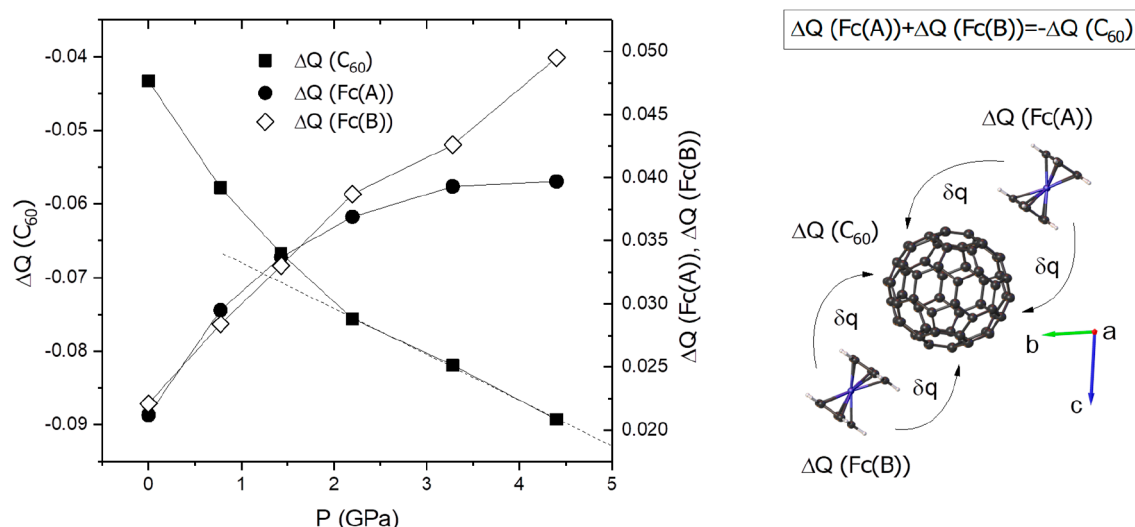


Figure 5. Interactions between the C_{60} molecule and neighboring ferrocene molecules (FMO2 method).

transition), the iron atom should change its oxidation state from $Fe^{2+} \rightarrow Fe^{3+}$. Structural analysis of ferrocene optimized by the B3LYP method reveals the elongation of the Fe–C bond from 2.077 (2.079 Å) to 2.094 Å (2.079 Å) in both molecular conformations D_{5h} (D_{5d}) when neutral ferrocene transforms to Fe^+ . The calculations of the phonon spectra were performed after the preliminary optimizations of the molecular geometry with D_{5h} (eclipsed conformation) and D_{5d} (staggered conformation) symmetries. Figure 4 shows the simulated Raman spectra after the convolution of computed intensities with the Lorentzian function.

According to the DFT calculations, only two types of Raman active vibration modes of ferrocene are found in the 200–400 cm^{-1} spectral range. The first of them is a Fe– C_5H_5 breathing vibration mode which reveals itself as a single peak at 285.9 cm^{-1} for the D_{5h} conformation and 288.6 cm^{-1} for the D_{5d} ferrocene molecule conformation. The second is a shear vibration mode with frequencies of 354.7 and 364.2 cm^{-1} for the D_{5h} and D_{5d} conformations of the ferrocene molecule, respectively. When ferrocene becomes positively charged ($Fe \rightarrow Fe^+$), the breathing and shear mode frequencies of eclipsed ferrocene shift to higher frequencies of 290.6 (D_{5h}) and 338.3 cm^{-1} (D_{5d}).

By comparing the calculated phonon spectra of the Fc molecule and the experimental Raman spectra of a pristine ferrocene crystal, we can conclude that a double peak near 300 cm^{-1} corresponds to the breathing intramolecular mode. Taking into account the structural disorder of the cyclopentadienyl rings in pristine Fc crystals under ambient conditions,^{27–29} the reason for splitting may be related to the presence of both eclipsed and staggered molecular conformations in solid ferrocene. Thus, the left maximum should be attributed to the D_{5h} breathing mode, ν_{br} (D_{5h}), and the less intense right maximum should be attributed to the D_{5d} breathing mode, ν_{br} (D_{5d}), as shown in the inset of Figure 2. Meanwhile, in the Raman spectra of the $C_{60} \cdot Fc_2$ complex there is only one ferrocene peak in this energy region. It is assigned to the Fe– C_5H_5 breathing mode of eclipsed ferrocene because only this molecular conformation was found in the X-ray diffraction study of the complex.²⁴ Concerning the observed pressure-induced variation of the peak width, one may assume that such behavior may be related to the presence of partially

charged ferrocene molecules. The breathing mode frequency for Fe^+ is too close to the frequency of a neutral molecule ($\Delta\nu_{br} = 4.7$ cm^{-1} , see the calculated spectra in Figure 4) and has nearly the same calculated intensity; this is the reason why it is difficult to allocate and separate them from each other in the experimental spectra. Note that an intramolecular shear mode is not present in the Raman spectra of the $C_{60} \cdot Fc_2$ complex (see Figure 2), most likely due to its suppression by the crystal field of the complex.

To detect the effect of pressure on the charge transfer, we have to estimate the dependence of the transferred charge on pressure using the fragment molecular orbital calculations method. The FMO method is based on the fragmentation of the whole system with the following calculation of each part (fragment) separately in the electric field of the other fragments. We used the two-body FMO2 implementation of FMO, which means that fragments are treated as a set of individual molecules (Fc, C_{60}) and their pairs (Fc– C_{60} , Fc–Fc). According to FMO calculations, each fragment was initially set as neutral with the integer numbers of the electrons. After performing the charge transfer calculations between the fragments ΔQ , it was added as correction data from the fragment pair calculations. The plots in Figure 5 show the pressure dependence of $\Delta Q(C_{60})$ for fullerene and two neighboring ferrocene molecules, $\Delta Q(Fc(A))$ and $\Delta Q(Fc(B))$, where charge is expressed in GAMESS US atomic units. Due to the location of the ferrocene cyclopentadienyl rings and their orientation with respect to the fullerene π -electronic orbitals, the calculations predict a small amount of transferred charge $\Delta Q(Fc(A)) \approx \Delta Q(Fc(B)) \approx 0.02$ au even at ambient pressure. Concerning the pressure-induced charge transfer, it grows with pressure equally for both ferrocene molecules up to 2 GPa. For higher pressures, an additional positive charge on Fc(A) tends to saturate at 0.04 au, while the charge of the other ferrocene molecule continues to increase. This peculiarity in the pressure behavior of an additional charge on two ferrocene molecules $\Delta Q(Fc)$ results in a change in the growth of the transferred negative charge to fullerene $\Delta Q(C_{60})$; the pressure coefficient decreases from -0.016 to -0.006 GPa^{-1} at 2 GPa (see Figure 5). Thus, the pressure dependence of the transferred charge for two ferrocene molecules indicates that one of them interacts stronger with

fullerene than the other. This is related to the difference in the mutual orientation of interacting molecular pairs $\text{Fc(A)}-\text{C}_{60}$ and $\text{Fc(A)}-\text{C}_{60}$, namely, to its variation during crystal compression. Note that the calculations of pressure-induced charge transfer look underestimated because its value at 4.5 GPa is considerably smaller than that derived from the XRD data.²⁴ Finally, the asymmetric charge transfer from neighboring to fullerene ferrocene molecules may be the reason why the width of the breathing mode increases with pressure; it may be related to the different pressure shift of the two molecules due to the difference in their charge.

CONCLUSIONS

The ferrocene-to-fullerene charge transfer in the $\text{C}_{60}\cdot\text{Fc}_2$ complex was studied at pressures up to 5.3 GPa by quantum-chemical calculations, X-ray structure analysis, and Raman spectroscopy. It was shown that the partial ionization of the ferrocene molecule increases with pressure. The calculations predict two differently charged $\text{Fc}^{\delta q+}$ ions as a result of the nonequal interactions between the π -conjugated electronic systems of fullerene and the crystallographically independent ferrocene molecules. This peculiarity was observed in the pressure behavior of the width and frequency of the Fc molecule breathing mode in the Raman spectra near 2 GPa.

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Notes

The authors declare no competing financial interest.

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