

Raman study of the conformational instability of a ferrocene molecule at high pressure: Influence of a crystal field

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Abstract

The Raman spectra of ferrocene crystals were measured at pressures up to 20 GPa, and an abnormally large bandwidth of intermolecular phonons at ambient pressure was found. With an increase in the pressure, the bandwidth increased to a maximum at ~ 2 GPa and then decreased to a minimum at ~ 4 GPa, which was equal to the pressure-independent bandwidth of intramolecular phonons. The unusual behavior of the bandwidth was related to the instability of a ferrocene molecule caused by jumps between its D_{5d} and D_{5h} conformations. A decrease in the time of jumps between the conformations to the period of crystal lattice vibrations led to a loss of coherence and broadening of intermolecular phonon bands. The energy barrier between the conformations was determined to be ~ 17.6 meV/molecule under ambient conditions and 80 meV/molecule at 4.9 GPa. An increase in the barrier with pressure was due to the enhancement of the crystal field, which resulted in the inhibition of the jumps and the stabilization of the molecule in the D_{5d} conformation.

KEYWORDS

conformational instability, high pressure, metallocenes, phonon lifetime, Raman scattering

1 | INTRODUCTION

Ferrocene $\text{FeC}_{10}\text{H}_{10}$ is the best-known member of the class of metallocenes, which are organometallic molecules consisting of two stacked cyclopentadienyl rings with a metal atom between them.¹ Cyclopentadienyl rings C_5H_5 can change their orientation relative to the fifth-order axis of the molecule, forming two stable conformations. These are an eclipsed conformation with a D_{5h} symmetry, when the upper ring is located directly above the lower one, and a staggered conformation with a D_{5d} symmetry, when it is rotated 36° relative to the lower one.^{2,3} The D_{5h} conformation has lower energy and is preferable for a free ferrocene molecule, while both conformations of the molecule are present in crystals under ambient conditions.

Five crystal modifications of ferrocene are known: disordered monoclinic phase under ambient conditions, high-pressure/room temperature ordered monoclinic phase, low-temperature triclinic phase LT1, low-temperature orthorhombic phase LT2, and low temperature phase with the incommensurate modulation. Under ambient conditions, fast jumps between the D_{5h} and D_{5d} conformations occur in the monoclinic phase, and complete conformational disorder is observed. The transition of the ambient-pressure monoclinic phase to the ambient pressure triclinic phase LT1 occurs at 163.9 K. This transition was discovered by calorimetry and the structure of the phase was studied later.^{4,5} The ordering of C_5H_5 rings in the high-pressure monoclinic phase occurs at room temperature and a pressure of 3.4–4.0 GPa when all molecules take the D_{5d} conformation.^{6,7} Between 172.8 and

163.5 K, the conformational disorder of ferrocene molecules transforms into the incommensurate modulation.⁸

According to numerical calculations, the energy of the D_{5h} conformation decreases with an increase in the pressure due to the increasing contribution of a crystal field during compression of the crystal.⁶ The energy barrier between the D_{5h} and D_{5d} conformations decreases and passes through zero at about 2 GPa, then changes its sign, and increases as the energy of the D_{5d} conformation decreases. At ~ 4 GPa, the barrier increases appreciably, the molecules are ordered predominately in the D_{5d} conformation, and a transition to the high-pressure monoclinic phase occurs.^{6,7,9}

The energy difference ΔE between the D_{5h} and D_{5d} conformations in the monoclinic crystal phase under ambient conditions was first determined in early nuclear magnetic resonance (NMR) experiments to be $\Delta E = (7.5 \pm 0.8)$ kJ/mol or $\Delta E = (78.1 \pm 8.7)$ meV/molecule.¹⁰ For a free molecule, the barrier between two conformations was determined by electron diffraction in the gas phase,² and the obtained value $\Delta E = (39 \pm 13)$ meV/molecule turned out to be half of that in the monoclinic phase.¹⁰ Later, in experiments on quasi-elastic neutron scattering, the barrier in the monoclinic and triclinic crystal phases was determined to be (45.6 ± 5.2) and (86.5 ± 6) meV/molecule, respectively.¹¹ In other NMR experiments, the barrier ΔE in the monoclinic and triclinic phases was determined to be (59.9 ± 5.2) and (106.7 ± 5.2) meV/molecule, respectively.¹² Relatively recent experiments on quasi-elastic neutron scattering in the monoclinic and triclinic phases showed that ΔE was 47.7 and 131.6 meV/molecule, respectively.¹³ Finally, theoretical studies of the electronic structure of ferrocene using the DFT method in various approximations gave the values of ΔE from 30.4 to 49 meV/molecule.³ Therefore, the results of numerous experiments and numerical calculations are rather controversial since the obtained values of ΔE are in a range of 30.4–78.1 meV/molecule for the monoclinic phase and in a range of 85.6–131.6 meV/molecule for the low-temperature triclinic phase LT1. Despite a significant difference in the results obtained, note that the lowest value of ΔE was obtained for the gas phase, and the results for the triclinic phase are always greater than for the monoclinic phase.

The measurements of the Raman spectra of ferrocene crystals under ambient conditions showed that jumps between the conformations resulted in a significant broadening of intermolecular phonon bands compared to narrow intramolecular phonon bands.⁹ Jumps reduce the lifetime of the molecule in a specific conformation up to the period of lattice vibrations, leading to a loss of coherence of intermolecular phonons and broadening of bands. At the same time, the parameters of intramolecular

vibrations depending on interatomic distances inside the molecule do not depend on the conformation of the molecule. A change in the conformation does not affect the lifetime and bandwidth of intramolecular phonons except for C–H stretching vibrations. Similar to intermolecular phonons, the width of these bands depends on pressure: the bands broaden to a maximum at ~ 2 GPa and then narrow to a minimum at ~ 4.0 GPa.^{6,9}

This paper presents the results of measurements of the Raman spectra of ferrocene single crystals at pressures up to 20 GPa and room temperature. With an increase in the pressure, the phonon frequency increases, and the pressure shift coefficients range from 0.6 to $1.35 \text{ cm}^{-1}/\text{GPa}$ for various intermolecular and intramolecular phonon bands. Under ambient conditions, a very broad band is observed in the spectrum of intermolecular phonons, which is five times broader than intramolecular phonon bands. With an increase in the pressure, this band shifts and broadens to a maximum at ~ 2.0 GPa and then narrows to the bandwidth of intramolecular phonons at ~ 4.0 GPa, splitting into individual bands. The width of the latter bands is equal to bandwidth of intramolecular breathing and bending modes of a cyclopentadienyl ring and C–C stretching vibrations inside the ring. The bandwidth of intramolecular modes is almost independent of pressure except for intramolecular C–H stretching vibrations. The width of these bands increases with increasing pressure to a maximum at 2.0 GPa and then decreases to a minimum at 4.0 GPa similar to intermolecular phonons.

The Raman spectra of the ferrocene crystals were obtained in four series of measurements in a temperature range of 98–370 K at ambient pressure and higher pressures of 2.5, 3.5, and 4.9 GPa. The temperature dependence of the bandwidth of an intermolecular phonon has a thermal activation character and is well described by the Arrhenius equation at all pressure values. The activation energy E_A of jumps between the D_{5h} and D_{5d} conformations at ambient pressure is (17.6 ± 6.5) meV for the monoclinic phase and (23.8 ± 1.8) meV for the triclinic phase LT1. With an increase in the pressure, it increases in the monoclinic phase and reaches (23.6 ± 2.3) meV at 2.5 GPa, (63.8 ± 5.6) meV at 3.5 GPa, and (80 ± 15.4) meV at 4.9 GPa. The barrier ΔE between the D_{5h} and D_{5d} conformations increases with a decrease in the specific molecular volume at high pressure, causing crystal field enhancement.

2 | EXPERIMENTAL METHODS

The Raman spectra were measured on single crystals grown from a hexane solution of ferrocene by

evaporation for several weeks at room temperature. Samples with a size of ~ 50 to ~ 500 μm with a well-developed surface were selected for the measurements. The Raman spectra were measured in the back-scattering geometry using a set-up that consisted of an Acton SpectraPro-2500i spectrograph equipped with a Pixis2K CCD cooled down to -70°C and an Olympus BX51 microscope. A single-mode diode-pumped laser with $\lambda = 532$ nm was used for Raman excitation. The laser beam was focused on the sample using an Olympus $50\times$ objective in a ~ 1.3 μm spot. The laser radiation line in a scattered beam was suppressed using an edge filter with $\lambda = 532$ nm, the optical density OD = 6, and a transmission band from 60 cm^{-1} , and the beam intensity before the diamond anvils was ~ 2.1 mW. The measurements of the Raman spectra at high pressures and room temperature were carried out using a Mao–Bell-type diamond anvil cell. For measurements at high pressure in a temperature range of 98 – 370 K, a compact Merrill–Bassett-type high-pressure cell was used, which was compatible with a homemade nitrogen cryostat. The cryostat with a temperature controller and a resistive heater maintained the temperature in a range of 95 – 370 K with an accuracy of ± 0.4 K similar to how it was described earlier.¹⁴ The homemade diamond anvil cell with an operating pressure up to ~ 15 GPa had the form of a cylinder with both diameter and height of ~ 39 mm and fitted tightly into a cylindrical cavity inside the heat exchanger. The design ensured reliable thermal contact with the heat exchanger; the pressure was preset at room temperature and then controlled when the required measurement temperature

was reached. A methanol–ethanol 4:1 mixture was used as a pressure-transmitting medium, and pressure was calibrated according to the spectral position of the R_1 luminescence line of ruby microcrystals.¹⁵

3 | RESULTS AND DISCUSSION

Figure 1 shows the Raman spectra of the ferrocene single crystals in a wavenumber range of 75 – 550 cm^{-1} at room temperature and pressure up to 20.0 GPa. The low-wavenumber region up to ~ 270 cm^{-1} corresponds to intermolecular phonons; their intensity is magnified fivefold in the figure. In a wavenumber range of 300 – 550 cm^{-1} , there are bands of intramolecular breathing (309 and 314 cm^{-1}) and bending (389 and 393 cm^{-1}) vibration modes of the cyclopentadienyl rings relative to the molecule axis. In a region of 1100 and 3100 cm^{-1} , there are intramolecular phonon bands that correspond to the C–C and C–H stretching vibrations of the cyclopentadienyl ring, respectively (not shown in the figure). With an increase in the pressure, the frequency of all phonons increases and the bands shift towards higher energies. The shift of intermolecular phonon bands is greater than that of intramolecular phonon bands, which is typical for molecular crystals with a van der Waals bond. The exception is C–H stretching vibrations; their shift is similar to that of intermolecular phonons, which was also observed in the molecular naphthalene crystal.¹⁶

The lower left part of Figure 1 depicts the Raman spectrum of intermolecular phonons at an initial pressure

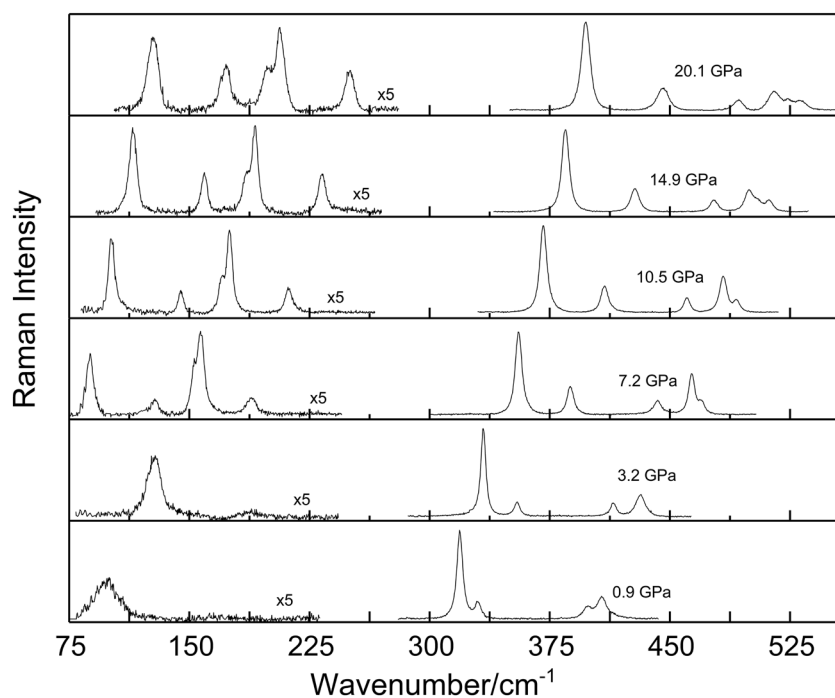


FIGURE 1 Raman spectra of ferrocene crystals in a wavenumber range of 75 – 530 cm^{-1} at room temperature and pressure up to 20 GPa.

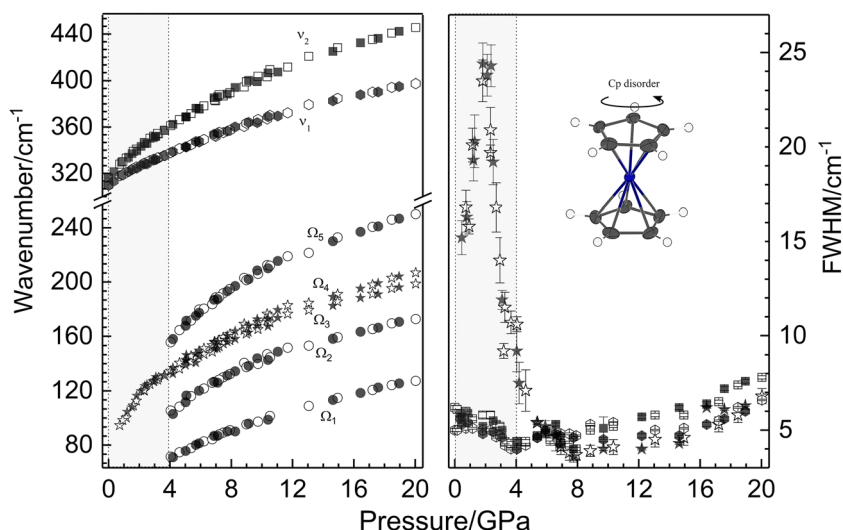


FIGURE 2 Pressure dependence of the frequency of the intermolecular modes Ω_1 – Ω_5 and intramolecular modes ν_1 and ν_2 (left panel). Pressure dependence of the width of the phonon modes Ω_1 – Ω_5 and ν_1 and ν_2 (right panel). Open and solid symbols mean increase and decrease of pressure, respectively. The region of conformational instability of the molecule at room temperature is shaded.

of 0.9 GPa. They are represented by one broad band with a wavenumber of $\sim 98 \text{ cm}^{-1}$ and a width of $\sim 19 \text{ cm}^{-1}$, which significantly exceeds the width of the breathing and bending vibration modes. The bandwidth of intramolecular phonons is $\sim 5 \text{ cm}^{-1}$ at a spectral width of the spectrograph slit of $\sim 4 \text{ cm}^{-1}$. With an increase in the pressure to ~ 2.0 GPa, the width of the intermolecular phonon band increases to $\sim 24 \text{ cm}^{-1}$, while it decreases with a further increase in the pressure. At ~ 4.0 GPa, its bandwidth decreases to $\sim 10 \text{ cm}^{-1}$ at a wavenumber $\sim 135 \text{ cm}^{-1}$, and two weak intermolecular phonons with a wavenumber of 105 and $\sim 156 \text{ cm}^{-1}$ emerge in the spectrum. This is associated probably with an increase in the peak intensity of the bands with a simultaneous decrease in the bandwidth, which facilitates their separation from the background signal. With an increase in the phonon energy at ~ 4.5 GPa, another narrow intense band with a wavenumber of $\sim 70 \text{ cm}^{-1}$ crosses the edge filter cutoff. The wavenumber of the initial broad band of intermolecular phonons reaches $\sim 140 \text{ cm}^{-1}$ at ~ 4.6 GPa; it narrows and splits into two bands, and the total number of intermolecular phonon bands reaches five. All bands in the Raman spectrum remain narrow until mechanical stresses arise during the solidification of the pressure-transmitting medium at 10 GPa. With a further increase in the pressure under nonhydrostatic compression, the stresses increase and lead to inhomogeneous broadening of the bands.¹⁷

Hence, in the Raman spectrum of ferrocene crystals under ambient conditions, the intermolecular phonon band has an abnormally large width. The width of this band increases with an increase in the pressure and reaches a maximum of $\sim 24 \text{ cm}^{-1}$ at ~ 2.0 GPa, while it decreases to a minimum at ~ 4.0 GPa with a further increase in the pressure (Figure 2, right part, stars). At the same time, the width of the intramolecular breathing vibration bands ν_1 and ν_2 changes only slightly in this

pressure range (squares and hexagons). The inset on the right side of the figure illustrates the structure of the ferrocene molecule and a change in the molecule conformation from eclipsed D_{5h} to staggered D_{5d} when the upper cyclopentadienyl ring is rotated 36° relative to the lower one. The left side of Figure 2 shows the pressure dependence of the frequency of intermolecular phonons (circles and stars) and split bands ν_1 and ν_2 of the intramolecular breathing vibration of the molecule (squares and hexagons). Open and solid symbols denote the increasing and decreasing pressure runs, respectively. All data were obtained in two independent series of measurements, the results of which are repeatable and reversible in pressure. At $P > 4$ GPa, the initially broad intermolecular phonon band splits into five narrow bands Ω_1 – Ω_5 . Note that in the Raman spectrum of molecular crystals with a monoclinic lattice and two molecules in the lattice cell, six intermolecular phonon modes are active: three modes with an A_g symmetry and three modes with a B_g symmetry. However, not all of these modes are manifested in the spectrum, as, for example, in molecular naphthalene and anthracene crystals with similar structural characteristics.^{16,18,19}

The bandwidth of all intramolecular phonons changes quite a bit in the range of hydrostatic pressures up to 10 GPa except for C–H stretching vibrations, which behave similarly to intermolecular phonons.^{6,9} The bands of the C–H vibrations in the initial pressure range are greatly broadened and overlap, and at a pressure above ~ 4 GPa they narrow and split into five components.⁶ At higher pressure five narrow bands are clearly manifested in the spectrum, possibly indicating a slight difference in the bond lengths of five C–H vibrations of the cyclopentadienyl ring.

In the Raman spectrum of ferrocene crystals, the abnormally large bandwidth of intermolecular phonons

under ambient conditions and its unusual dependence on pressure are of the greatest interest. This anomaly is related to rapid jumps between the D_{5d} and D_{5h} conformations of the molecule.^{6,9} If the frequency of jumps is comparable to that of intermolecular phonons, the coherence of lattice vibrations is disrupted, and the lifetime of phonons decreases, while the bands broaden. Jumps between the conformations have a thermal activation character: in the isobaric regime, they accelerate with increasing temperature and give rise to additional broadening of intramolecular phonon bands.²⁰ The change in the bandwidth with pressure in the isothermal regime is related most likely to a change in the energy barrier between the conformations. This is due to the enhancement of the crystal field during crystal compression; its effect on the energy of two conformations of the ferrocene molecule was studied in numerical calculations.⁶ According to these calculations, the barrier between the D_{5d} and D_{5h} conformations decreases to zero at ~ 2 GPa, then changes its sign, and increases in absolute value with a further increase in the pressure. Under ambient conditions, the energy of the D_{5h} conformation is lower than that of the D_{5d} conformation; at $P \geq 2$ GPa, their ratio changes, and the D_{5d} conformation has lower energy.

Hence, the basic contribution to the decrease in the lifetime of intermolecular phonons and the broadening of bands in the Raman spectrum is made by jumps between the conformations of the molecule, which have a thermal activation character. The magnitude of the barrier between the conformations can be determined from the isobaric temperature dependence of the bandwidth of intermolecular phonons. The bandwidth of phonon modes in Raman spectra consists of a homogeneous width resulting from the anharmonic decay of phonons and an inhomogeneous width associated with the scattering of phonons on crystal lattice defects or impurities.²¹ Note that the homogeneous width of the bands is small at low temperatures and is significantly less than the spectral width of the spectrograph slit. The inhomogeneous width in perfect crystals is also small; however, it increases with increasing imperfection. In the case of ferrocene crystals, the overwhelming contribution to the bandwidth of intermolecular phonon modes is made by a decrease in the lifetime of crystal lattice vibrations due to the loss of vibration coherence resulting from the conformational instability of the molecule. The temperature dependence of the bandwidth of intermolecular phonons related to jumps between the conformations can be represented as

$$\Gamma_{\text{reorient}} = B_{\times} \exp(-E_A/K_B T) \quad (1)$$

where Γ_{reorient} is the bandwidth related to jumps between the conformations, B is the pre-exponential coefficient with energy dimensionality, E_A is the barrier between the conformations, K_B is the Boltzmann constant, and T is the temperature. This approach was previously used to describe the broadening of phonon bands in the Raman spectra of NH_4ClO_4 crystals resulting from the libration of NH_4^+ ions in the crystal lattice.²⁰ The total bandwidth of intermolecular phonons in the Raman spectra consists of Γ_{reorient} and combined contribution of homogeneous and inhomogeneous broadening of the bands. The last contribution is almost the same for intermolecular and intramolecular phonons, varies slightly with temperature, and does not depend on pressure during hydrostatic compression. Therefore, the bandwidth Γ_{reorient} can be determined with sufficient accuracy from the difference between an experimental bandwidth of the intermolecular phonons and an average bandwidth of the intramolecular phonons. The lifetime of intermolecular phonons can be estimated from the bandwidth Γ_{reorient} using the uncertainty relation in quantum mechanics $\Delta E \times \Delta t = \hbar$.²² Previously, this method was used to estimate the lifetime of phonons in aluminum, indium, and gallium nitride crystals.^{21,23,24} Based on this, the lifetime of phonons can be determined by the formula:

$$\tau = \hbar/\Gamma_{\text{reorient}} \quad (2)$$

where τ is the lifetime of phonons, Γ_{reorient} is the bandwidth of phonons, and \hbar is the Planck constant.²² The lifetime of intermolecular phonons at a pressure of ~ 2.2 GPa and the bandwidth $\Gamma_{\text{reorient}} = 19 \text{ cm}^{-1}$ is ~ 0.3 ps. This time is obviously due to the time of switching of molecule conformation: it is an order of magnitude less than the lifetime of phonons in InN and GaN crystals, which ranges from units to tens of picoseconds for different modes.^{23,24}

Since the lifetime of phonons is $\tau = \hbar/\Gamma_{\text{reorient}}$, formula (1) can be written as

$$\tau = A_{\times} \exp(E_A/K_B T) \quad (3)$$

where τ is the lifetime of phonons, $A = \hbar/B$ is the pre-exponential coefficient with time dimensionality, E_A is the barrier between the conformations, K_B is the Boltzmann constant, and T is the temperature. Figure 3 shows the Raman spectra of a ferrocene crystal at ambient pressure and four temperature values of 213, 193, 158, and 113 K in a wavenumber range of 50–340 cm^{-1} . The left side of the figure illustrates the intermolecular phonon band Ω_3/Ω_4 , while the right side depicts the split bands of the intramolecular breathing vibration ν_1 and ν_2 . The upper right inset shows the temperature dependence of the bandwidth of

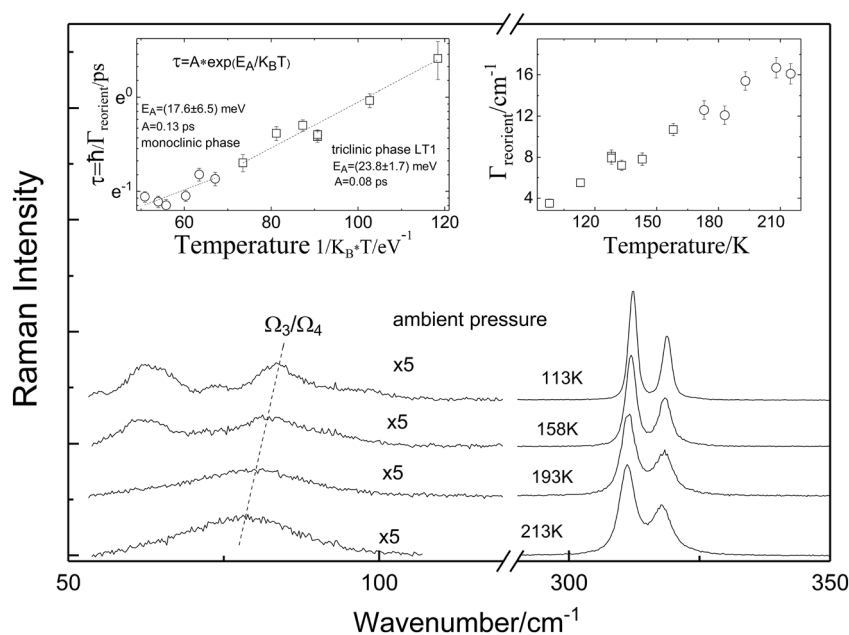


FIGURE 3 Raman spectra of a ferrocene crystal at ambient pressure and $T = 213$, 193, 158, and 113 K in a wavenumber range of $50\text{--}340\text{ cm}^{-1}$. Left: intermolecular modes Ω_3/Ω_4 ; right: intramolecular breathing vibration ν_1 and ν_2 . Right inset: temperature dependence of the bandwidth of the intermolecular phonons Γ_{reorient} . Left inset: dependence of the lifetime of phonons τ on the temperature $1/K_B T$ in a logarithmic scale. Circles: monoclinic phase; squares: triclinic phase LT1; dashed line: the Arrhenius dependence.

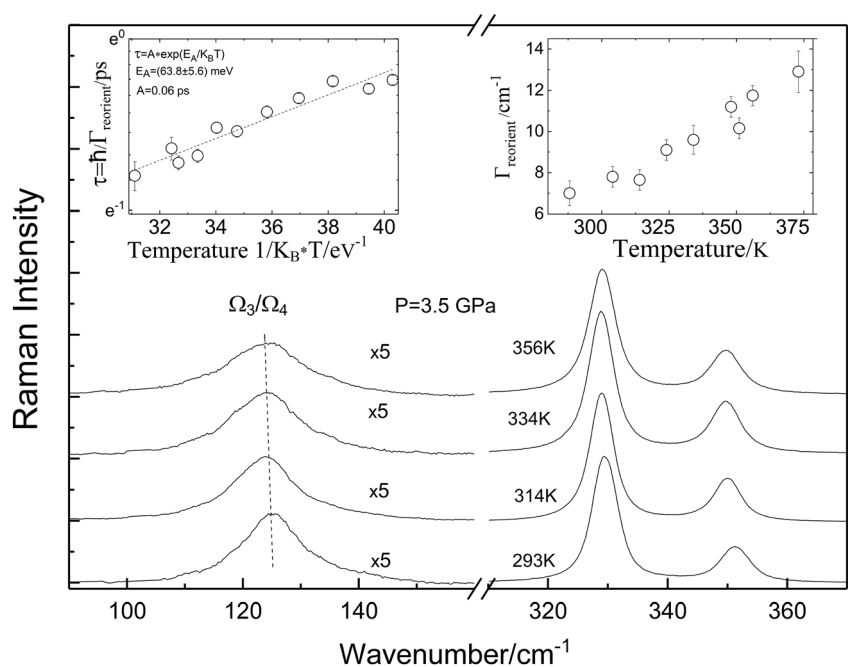


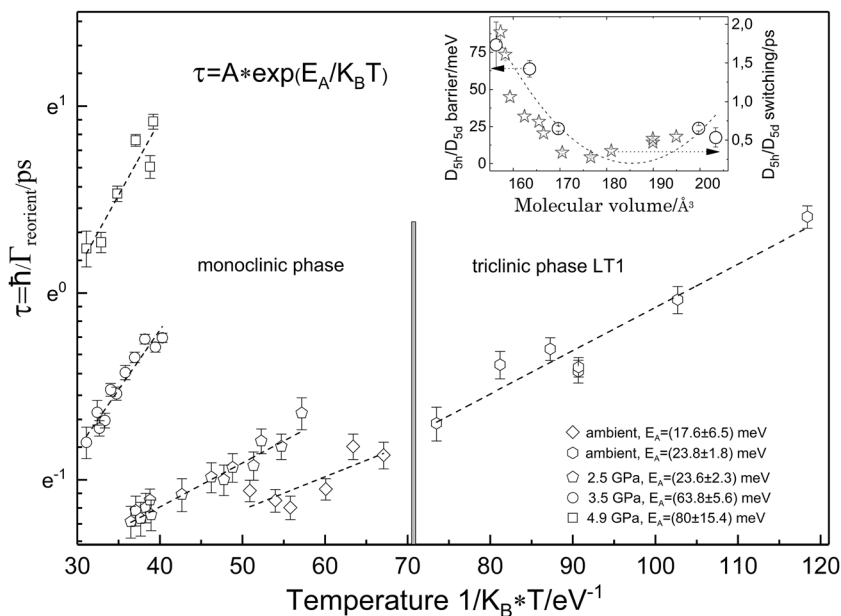
FIGURE 4 Raman spectra of a ferrocene crystal at 3.5 GPa and $T = 293$, 314, 334, and 356 K in a wavenumber range of $90\text{--}370\text{ cm}^{-1}$. Left: intermolecular modes Ω_3/Ω_4 ; right: intramolecular breathing vibration ν_1 and ν_2 . Right inset: temperature dependence of the bandwidth of the intermolecular phonons Γ_{reorient} . Left inset: dependence of the lifetime of phonons τ on the temperature $1/K_B T$ in a logarithmic scale; dashed line: the Arrhenius dependence.

the intermolecular phonons Γ_{reorient} . In the inset, circles and squares, respectively mark data for the monoclinic phase at temperatures above 163.9 K and the triclinic phase LT1 below 163.9 K. The upper left inset shows the dependence of τ on the temperature $1/K_B T$ in a logarithmic scale; here, circles and squares also mark data for the monoclinic and triclinic phases. The experimental data for both phases are well described by the Arrhenius dependence $\tau = A \times \exp(E_A/K_B T)$, which is marked with a dashed line in the figure. The approximation was carried out separately for two crystal phases, and the energy barrier between the D_{5h} and D_{5d} conformations is (17.6 ± 6.5) meV for the monoclinic phase and (23.8 ± 1.7) meV for

the triclinic phase LT1. Note that these values of the energy barrier for both phases are less than all previously obtained experimental and calculated values.^{2,3,10–13}

The temperature dependence of the bandwidth of intermolecular phonons was measured in the isobaric regime at 2.5, 3.5, and 4.9 GPa. Figure 4 shows the Raman spectra of ferrocene crystals at a pressure of 3.5 GPa and temperatures of 293, 314, 334, and 356 K in a wavenumber range of $90\text{--}370\text{ cm}^{-1}$. The left side of the figure illustrates the intermolecular phonon band Ω_3/Ω_4 , while the right side depicts the split bands of the breathing mode ν_1 and ν_2 . The initial width of the intermolecular phonon band at room temperature is $\sim 12\text{ cm}^{-1}$, and

FIGURE 5 Dependence of the lifetime of phonons τ on the temperature $1/K_B T$ in a logarithmic scale in the monoclinic and triclinic phases. Rhombi and hexagons: ambient pressure, pentagons, circles, and squares at 2.5, 3.5, and 4.9 GPa, respectively; dashed lines: the Arrhenius dependence. Inset: circles – dependence of the activation energy E_A on specific molecular volume; asterisks – dependence of the switching time of the D_{5h}/D_{5d} conformations on specific molecular volume; dashed line – approximation by a parabola.



its wavenumber is 125 cm^{-1} . With an increase in the temperature to 356 K, the band broadens to $\sim 17.5 \text{ cm}^{-1}$, and phonon frequency slightly decreases due to the thermal expansion of the crystal lattice. In the right upper inset circles indicate the temperature dependence of the width of this band Γ_{reorient} . In the left inset, the same symbols depict the values of $\tau = \hbar/\Gamma_{\text{reorient}}$ depending on the temperature $1/K_B T$ in a logarithmic scale, and a dashed line shows the approximation of these data by the Arrhenius equation $\tau = A \times \exp(E_A/K_B T)$. The lifetime of intermolecular phonons at room temperature is 0.8 ps and decreases to 0.6 ps at 373 K; the experimental data are well described by the Arrhenius equation with the activation energy of jumps between two conformations $E_A = (63.8 \pm 5.6) \text{ meV}$.

Figure 5 shows summarized experimental data for the isobaric temperature dependence of phonon lifetime and their approximation by the Arrhenius dependence $\tau = A \times \exp(E_A/K_B T)$ in four series of measurements at different pressures in the monoclinic and triclinic phases. Rhombi correspond to ambient pressure, pentagons, circles, and squares correspond to pressures of 2.5, 3.5, and 4.9 GPa, respectively, and dashed lines are an approximation of the experimental results by the Arrhenius dependence. On the right side of the figure, hexagons indicate the same dependence at ambient pressure for the low-temperature triclinic phase LT1. The activation energy E_A for jumps of the molecule between the D_{5h} and D_{5d} conformations in the monoclinic phase increases with an increase in the pressure from $(17.6 \pm 6.5) \text{ meV}$ at ambient pressure to $(23.6 \pm 2.3) \text{ meV}$ at 2.5 GPa, $(63.8 \pm 5.6) \text{ meV}$ at 3.5 GPa, and $(80 \pm 15.4) \text{ meV}$ at 4.9 GPa. In the triclinic phase, the magnitude of the barrier E_A at ambient pressure is slightly greater than that in the monoclinic phase and is

$(23.8 \pm 1.8) \text{ meV}$. In the inset of Figure 5, circles show the experimental values of the activation energy E_A as a function of volume per molecule. The specific molecular volume at different pressures was calculated using structural data and parameters of the Murnaghan equation of state obtained earlier.⁹ With an increase in the pressure, the parameters of the lattice cell and the specific molecular volume decrease, while the crystal field increases. The specific molecular volume also decreases under the transition from the monoclinic to the triclinic phase LT1 since the number of molecules in the unit cell doubles while its volume increases disproportionately.⁹ A dashed line in the inset shows an approximation of the experimental data by a parabola that passes through zero at a minimum at a molecular volume of 185 \AA^3 corresponding to a pressure of $\sim 1.1 \text{ GPa}$. The data obtained generally confirm the numerical calculations,⁶ although the zero value of the barrier ΔE corresponds to a slightly lower pressure. The stars in the inset show the experimental dependence of the lifetime of intermolecular phonons on the specific molecular volume at room temperature. In fact, the lifetime of phonons under these conditions coincides with the time of switching between the D_{5h} and D_{5d} conformations. This dependence also has the form of a parabola with a minimum value of 0.3 ps at a molecular volume of 177 \AA^3 corresponding to a pressure of $\sim 1.8 \text{ GPa}$. Despite some differences in the minima of these curves, a correlation between the two dependencies reflects the relationship between the conformations switching time and the magnitude of the barrier between them. Note that some differences between the experimental and calculated data are most likely associated with the accuracy of the experimental and calculation methods used.

4 | CONCLUSIONS

In the Raman spectra of ferrocene crystals under ambient conditions, the bandwidth of the intermolecular phonons significantly exceeds that of intramolecular phonon bands. With an increase in the pressure, the bandwidth increases further to a maximum at ~ 2 GPa and then decreases to the bandwidth of intramolecular phonons at ~ 4 GPa. The broadening of the intermolecular phonon band is due to the conformational instability of the molecule and results from thermally activated jumps between the D_{5d} and D_{5h} conformations. The residence time of the molecule in each conformation decreases to the period of intermolecular phonons, which leads to a loss of coherence of the vibrations and broadening of the bands. Intramolecular vibrations retain coherence since they do not depend on changes in the molecule conformation, and the corresponding bands do not broaden.

The isobaric temperature dependence of the bandwidth of intermolecular phonons in a range of 98 — 370 K at ambient and high pressures of 2.5, 3.5, and 4.9 GPa is well described by the Arrhenius equation. The activation energy E_A for jumps between the D_{5h} and D_{5d} conformations at ambient pressure is (17.6 ± 6.5) and (23.8 ± 1.8) meV for the monoclinic and triclinic phases, respectively. This is less than any data previously obtained in experiments on inelastic neutron scattering and NMR, which, in addition, differ significantly from each other.^{2,3,10–13} The magnitude of the barrier in the monoclinic phase increases with pressure and reaches (23.6 ± 2.3) meV at 2.5 GPa, (63.8 ± 5.6) meV at 3.5 GPa, and (80 ± 15.4) meV at 4.9 GPa. An increase in the barrier between the D_{5h} and D_{5d} conformations is caused by a decrease in the specific molecular volume followed by an enhancement of the crystal field during compression of the crystal. The dependence of the barrier magnitude on the specific molecular volume is described by a parabola with zero at 185 \AA^3 corresponding to a pressure of ~ 1.1 GPa. The residence time of the molecule in each conformation is also described by a parabolic function of molecular volume with a minimum value of 0.3 ps at 177 \AA^3 corresponding to a pressure of ~ 1.8 GPa. The correlation between these dependencies reflects the relationship between the barrier magnitude and the residence time of the molecule in each conformation. The data obtained are in rather good agreement with the results of numerical calculations of the contribution of the crystal field to the barrier.⁶

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CONFLICT OF INTEREST STATEMENT

The author declares no potential conflict of interests.

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REFERENCES

- [1] T. J. Kealy, P. L. Pauson, *Nature* **1951**, *168*, 1039.
- [2] A. Haaland, J. E. Nilsson, *Acta Chem. Scand.* **1968**, *22*, 2653.
- [3] X. Zhen-Feng, Y. Xie, H. F. Wen-Lin Feng, I. I. I. Shaefer, *J. Phys. Chem. A* **2003**, *107*, 2716.
- [4] J. W. Edwards, G. L. Kington, R. Mason, R. Trans, *Faraday Soc.* **1960**, *56*, 660.
- [5] P. Seiler, J. D. Dunitz, *Acta Crystallogr. Sect. B: Struct. Crystallogr. Cryst. Chem.* **2020**, *1979*, B35.
- [6] D. Paliwoda, K. Kowalska, M. Hanfland, A. Katrusiak, *J. Phys. Chem. Lett.* **2013**, *4*, 4032.
- [7] D. Paliwoda, M. Hanfland, A. Katrusiak, *J. Phys. Chem. C* **2019**, *123*, 25719.
- [8] A. Katrusiak, M. Rusek, M. Dušek, V. Petříček, M. Szafranski, *J. Phys. Chem. Lett.* **2023**, *14*, 3111.
- [9] A. V. Kuzmin, K. P. Meletov, M. A. Faraonov, *J. Phys. Chem. C* **2022**, *126*, 3688.
- [10] C. H. Hohn, J. A. Ibers, *J. Chem. Phys.* **1959**, *30*, 885.
- [11] A. B. Gardner, J. Howard, T. C. Waddington, R. M. Richardson, J. Tomkinson, *Chem. Phys.* **1981**, *57*, 453.
- [12] A. Kubo, R. Ikeda, D. Nakamura, *Chem. Lett.* **1981**, *10*, 1497.
- [13] M. Appel, B. Frick, T. L. Spehr, B. Stühn, *J. Chem. Phys.* **2015**, *142*, 114503.
- [14] K. Meletov, *Instruments and Experimental Techniques*, **2020**, *63*, 291.
- [15] J. D. Barnett, S. Block, G. J. Piennarini, *Rev. Sci. Instrum.* **1973**, *44*, 1.
- [16] K. Meletov, *Phys. Solid State* **2013**, *55*, 581.
- [17] A. Jayaraman, *Rev. Sci. Instrum.* **1986**, *57*, 1013.
- [18] D. A. Dows, L. Hsu, S. S. Mitra, O. Brafman, M. Hayek, W. B. Daniels, R. K. Crawford, *Chem. Phys. Lett.* **1973**, *22*, 595.
- [19] M. Nicol, M. Vernon, J. T. Woo, *J. Chem. Phys.* **1992**, *1975*, 63.
- [20] T. Chakraborty, S. S. Khatri, A. L. Verma, *J. Chem. Phys.* **1986**, *84*, 7018.
- [21] J. W. Pomeroy, M. Kuball, H. Lu, W. J. Shaff, X. Wong, A. Yoshikava, *Appl. Phys. Lett.* **2005**, *86*, 223501.
- [22] L. D. Landau, E. M. Lifshitz, *Quantum mechanics: non-relativistic theory*, Third ed., Pergamon, New York **1977**.
- [23] M. Kuball, J. M. Hayes, Y. Shi, J. H. Edgar, *Appl. Phys. Lett.* **1958**, *2000*, 77.
- [24] T. Beechem, S. Graham, *Appl. Phys. Lett.* **2008**, *103*, 093507.

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