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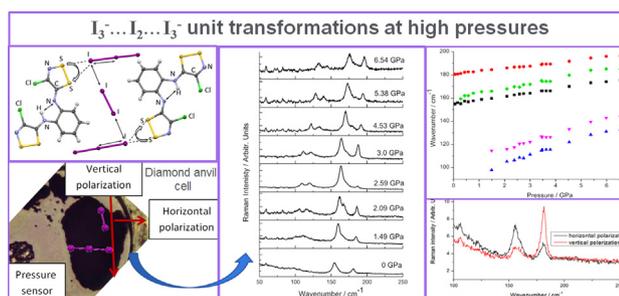
High-pressure transformation of dithiazolyldiene-dithiazolium polyiodide with N-H...N hydrogen bond: A Raman Spectroscopy study

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HIGHLIGHTS

- Dithiazolium zigzag polyiodide $I_3^- \dots I_2 \dots I_3^-$ undergoes phase transition above 1.5 GPa.
- High pressure transformations are due to the increased association within I_8^{2-} anion.
- The emergence of the band at 159 cm^{-1} is the effect of N-H...N vibrations.

GRAPHICAL ABSTRACT



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ABSTRACT

The insight into the behavior of polyiodides under non-ambient conditions can enrich the practical applications due to obtaining materials with adjustable and tunable conducting properties. In this work Raman spectroscopy study in the range 0 – 6.5 GPa has been performed for dithiazolyldiene-dithiazolium zigzag polyiodide with N-H...N hydrogen bond. Variations of band positions in the low-wavenumber region of Raman spectra have been attributed to the changes in the anionic part of the unit cell. The association of different interacting polyiodide subunits at pressure above 1.5 GPa leads to the emergence of the bands at 98 and 115 cm^{-1} due to consistent vibrations in the I_8^{2-} zigzag. The emergence of the band at 159 cm^{-1} above 0.28 GPa can be assigned to N-H...N hydrogen bond vibration. The obtained results depict undergoing structure transformations: the stronger are cation...cation and anion...anion interactions the more likely is the observation of conducting properties due to the formation of polyiodide zigzag and strongly-bound hydrogen-bonded fragment.

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1. Introduction

From a structural point of view polyiodides with organic cations [1] attract constant attention due to their enormous structural diversity, variety of 3D anionic motives based on multiple types of noncovalent interactions with iodine participation [2]. Their practical importance is reflected in a unique spectrum of properties, making them applicable as components of solar cells [3,4].

photovoltaic [5,6] and luminescent [7] materials, nonlinear optical materials [8] and iodine sorbents [9]. The Raman spectroscopy technique is the most sensitive to tiny changes in noncovalent interactions within and between polyiodide subunits [10]. Previously the effect of high pressure on the spectral properties of polyiodide units was reviewed on the level of polyiodide films [11], iodine captured inside carbon nanotubes [12] or MOFs [13], but not in the form of single crystal salt with organic cation. A recent analysis of tetraalkylammonium polyiodide transformations and corresponding changes of its conductance at high pressure

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opens a perspective horizon of non-ambient spectral studies of polyiodide single crystals [14]. Thus, the high-pressure spectral characterization of various polyiodide compositions is the next expected and desired step to understanding the structure–property relationship in polyiodide row [15]. Moreover, the extended view on different polyiodide structural organizations [16,17] singles out I_3^- zigzag as the most prominent candidate for studying the behavior of different I-I/I...I at non-ambient conditions. Thus, in this work we focus on the changes in the dynamics of anionic polyiodide motives as well as on the behavior of the bridge hydrogen atom as a function of pressure.

2. Experimental details

Dark with metal glow single crystal of (Z)-4-chloro-5-((2-((4-chloro-5H-1,2,3-dithiazol-5-ylidene)amino)phenyl)amino)-1,2,3-dithiazol-1-ium polyiodide (CDAPD) with I_3^- anion (CSD refcode SEJQAC [18]) (Fig. 1a) was obtained according to experimental procedure described previously and structurally characterized using X-Ray diffraction method.

The non-polarized Raman spectra (Fig. 1b) were recorded on a Horiba Jobin Yvon T64000 spectrometer equipped with a liquid nitrogen-cooled charge-coupled device detection system in subtractive dispersion mode. Ar ion laser Spectra-Physics Stabilite 2017 with $\lambda = 514.5$ nm was used as an excitation light source. The effect of the different orientation of polarization vectors of the incident and scattered light is demonstrated for 0.28 GPa pressure (Fig. 1c,d). Polarization-dependent spectra were performed in

“vertical” and “horizontal” orientation with respect to the crystal position. The registration of the polarized spectra was performed at the same point of the crystal surface one after another with the change of the position of the polaroid. Although, we do not know exactly the details of crystal morphology, still as the polyiodide zigzag forms a helix-like structure and its orientation does not coincide with any crystallographic direction. Thus its diagonal location creates the possibility to register the polarized component of all characteristic vibration bands in any direction. The maximum attention should be paid to the relative intensity of the most characteristic bands of asymmetric triiodide and bound iodine. The high-pressure experiments were carried out using an incident laser beam which was focused on the sample by a 50x Olympus LMPlanFl objective lens with a numerical aperture N.A. = 0.35. The scattered light was collected in the backscattering geometry and analyzed through a polarizer and λ -plate. The membrane diamond anvil cell (DAC) device of Diacell μ Scope DAC HT(G) type (EasyLab, UK) with diamond IIa was used for Raman studies. A gasket made from stainless steel with an initial thickness of 0.25 mm was used in this DAC. Holes with a diameter of about 200–220 μ m were drilled in the gaskets pre-indented to a thickness of about 84 μ m for measuring at pressures up to 14 GPa. The pressure was monitored by shifting the 5D_0 – 7F_0 fluorescence band of Sm^{2+} ion in a small $SrB_4O_7:Sm^{2+}$ crystal placed in the vicinity of the sample within the experimental error of about 0.05 GPa (fig. S1). Silicon oil was used as a hydrostatic pressure transmission media as both classical polar mixtures, like methanol-ethanol alcohols or nonpolar hydrocarbons tend to dissolve iodine from the surface of polyiodide crystal and thus were not applicable for measurements.

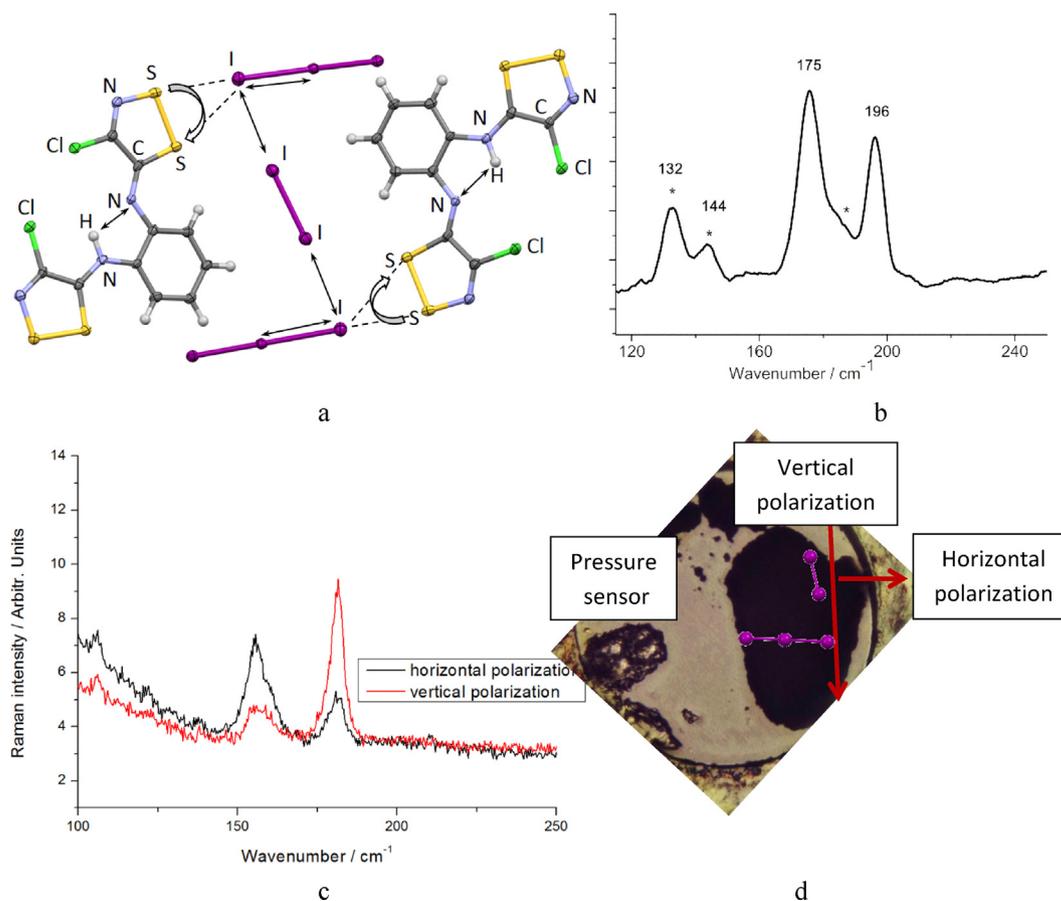


Fig. 1. a) Fragment of the crystal structure of 2CDAPD I_3^- ; straight and curved arrows depict the directions of atomic displacements for newly emerged stretching and bent vibrations, correspondently according to *ab initio* calculations; b) experimental Raman spectrum at 6.53 GPa, newly emerged bands with the increase of pressure are marked with an asterisk; c) polarized Raman spectra at 0.28 GPa; d) schematic representation of the sample in DAC and the directions of polarization vectors of the incident and scattered light with respect to polyiodide subunits.

3. Results and discussion

Crystal structure of CDAPD contains centrosymmetric zigzag [I...I]...I...I...[I...I] with two types of bound diiodine molecules interacting via the strong halogen bond with I⁻ anion. Such polyiodide organizations are relatively frequent crystal packing motives in the row of heterocyclic polyiodide salts [19,20]. These two I₂ molecules have unequal bond lengths according to X-ray diffraction data and differ from each other from a spectral point of view (Fig. 1b). Polarized Raman spectra (Fig. 1c, d) reveal that vertical orientation of polarization vector better corresponds to bound I₂ (band at 180 cm⁻¹) while the horizontal one better matches with I₂ inside asymmetric I₃ (band at 160 cm⁻¹). This observation matches with the structural features of I₈²⁻ anion, where asymmetric triiodide and bound I₂ are located almost perpendicular to each other within one plane (Fig. 1a). This fact is also consistent with the previous study of polarized spectra of oriented single crystal polyiodides of different compositions and crystal morphology [21]. Below 1.5 GPa, the sample demonstrates significant luminescent in the low-frequency region below 120 cm⁻¹, and this effect complicates observation of bands in this region (Fig. 2a, b). Above 1.5 GPa the luminescence vanishes and allows to estimate the shift of two bands at 98 and 115 cm⁻¹, which presumably can be attributed to vibrations of I₈²⁻ zigzag according to the comparison with corresponding stretching bands of inner I atoms at 76 and 113 cm⁻¹ for pentaiodide I₅ anion according to Ref [1]. They have relatively high intensity even at high pressures unlike libration modes, which tend to vanish with the increase of pressure. Thus they might reflect the effect of compression on I₈²⁻ zigzag bringing it closer to two overlapping I₅ motives in the limit case. The change of luminescence level may be due to the changes in band gap and/or λ_{ex} so that the laser excitation energy becomes not sufficient for induction of optical transitions in crystal.

The behavior of bands of bound I₂ (157 and 179 cm⁻¹ at ambient conditions) with pressure is almost linear, demonstrating no significant changes in anionic zigzags except for the different speed of band shift: 2.4 cm⁻¹/GPa for stronger bounded with shorter

bond length and 3.1 cm⁻¹/GPa for I₂ with longer bond length as a part of asymmetric triiodide I₃. At low pressures above 0.28 GPa, a new band appears near the band of asymmetric I₃ at 159 cm⁻¹. Due to its position, it may be seemingly attributed to the region of typical bound I₂ vibrations. However, careful analysis of crystal structure does not reveal possibilities to form such a unit without any observable changes in positions of two other bound I₂ vibrations (see fig. S2 for the possible scheme of zigzag transformation). Moreover, its shifting speed is higher (4.1 cm⁻¹) than it should be expected as if it corresponds to I-I vibration. Thus this band more likely corresponds to N-H...N hydrogen bond band similarly to the previously observed example in the structure of diiodobutenyl-bis-thioquinolinium triiodide (IVOVOG [22]) with a similar N-H⁺...N motif. Theoretic calculation of Raman spectrum (Crystal17 [23], DFT/B3LYP, TZVP (other elements)/DZVP (I) basis sets [24] reveals the existence of weak intensity modes at 153 and 168 cm⁻¹, which are affected by the deformation of dithiazolium ring and include displacements of atomic positions of S atoms involved in chalcogen bonding as well as of N(3) atom involved in N-H...N hydrogen bond.

4. Conclusions

High-pressure Raman spectra of I₈-zigzag polyiodide of (Z)-4-chloro-5-((2-((4-chloro-5H-1,2,3-dithiazol-5-ylidene)amino)phenyl)amino)-1,2,3-dithiazol-1-ium cation with N-H...N hydrogen bond were obtained; comparable interpretation of observed structural and spectral changes has been made. The studied crystal demonstrates the changes in the positions of the bands, corresponding to the vibrations of the anionic part of the cell and the N-H...N hydrogen bond band. The emergence of the newly observed band at 159 cm⁻¹ above 0.28 GPa is most likely due to N-H...N vibrations according to the 153 and 168 cm⁻¹ modes in theoretical Raman calculations. Increasing intensity of the bands at 98 cm⁻¹ and 115 cm⁻¹ above 1.5 GPa can be due to the growing effect of the association within I₈²⁻ anion due to the decrease of the distances between interacting units.

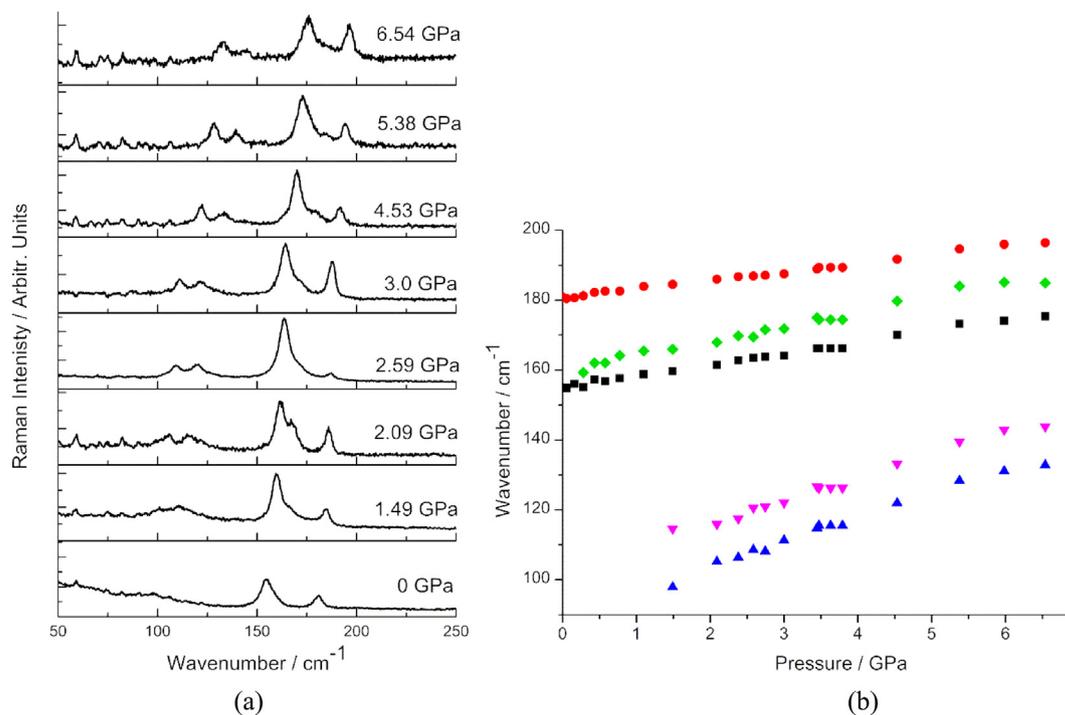


Fig. 2. a) the changes in Raman spectra from 0 to 6.53 GPa; b) dependency of band positions with pressure.

CRediT authorship contribution statement

I.D. Yushina: Data curation, Writing – original draft, Visualization, Investigation. **A.S. Krylov:** Investigation, Writing – review & editing. **O.I. Bol'shakov:** Resources. **O.A. Rikitin:** Methodology, Validation, Funding acquisition. **E.V. Bartashevich:** Conceptualization, Supervision, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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