

Article

Sulfur, Selenium and Tellurium Ring Clusters: Experimental and Density-Functional Theoretical Study of Polarized Optical Absorption and Raman Spectra, Light-Induced Effects and Conical Intersections

Vladimir V. Poborchii ^{1,*} and Dmitrij Rappoport ^{2,3} ¹ National Institute of Advanced Industrial Science and Technology, Tsukuba 305-8565, Japan² Department of Chemistry, 1102 Natural Sciences 2, University of California, Irvine, CA 92697, USA; dmitrij@rappoport.org³ Dayhoff Labs Inc., 1 Mifflin Place, Suite 419, Cambridge, MA 02138, USA

* Correspondence: vladimir.poborchii@gmail.com

Abstract

We studied experimentally and computationally the structures and optical properties of sulfur (S), selenium (Se) and tellurium (Te) ring clusters. We encapsulated S, Se and Te into AFI, MOR, CHA and LTA zeolites via vapor adsorption or high-pressure injection from melt and studied Raman and optical absorption spectra (RS and OAS, respectively) of zeolite single crystals with incorporated S, Se and Te ring clusters. Importantly, strict orientation of the rings in zeolite crystals allowed us to study the polarization/orientation dependency of ring RS and OAS. The obtained experimental spectra are found to be in agreement with density functional theory results (DFT using the PBE0 functional and def2-TZVP basis sets) for S₈, Se₆, Se₈, Se₁₂, Te₆ and Te₈ ring molecules. The agreement is especially good for Te rings, while for S and Se rings harmonic frequency scaling factors are required. The S and Se rings display light-induced effects, which we attribute to the presence of conical intersections between their ground and excited electronic states, resulting in isomerization and subsequent fragmentation. We consider this effect using the Se₆ ring example. This phenomenon is important for understanding photostructural changes not only in chalcogen clusters but also in bulk materials such as amorphous selenium.

Keywords: chalcogen rings; Raman spectroscopy; optical absorption spectroscopy; density-functional theoretical analysis



Academic Editor: Marcello Locatelli

Received: 29 January 2026

Revised: 24 March 2026

Accepted: 8 April 2026

Published: 20 April 2026

Copyright: © 2026 by the authors.

Licensee MDPI, Basel, Switzerland.

This article is an open access article distributed under the terms and conditions of the [Creative Commons Attribution \(CC BY\)](https://creativecommons.org/licenses/by/4.0/) license.

1. Introduction

Doubly coordinated atoms of sulfur (S), selenium (Se) and tellurium (Te) form ring or chain structures. The allotropes of elemental sulfur are well characterized and consist predominantly of ring structures. In contrast, elemental tellurium primarily exists in the form of helical chains. In this sense, elemental selenium is a borderline material in the chalcogen group since it can form both rings and chains in the solid state. Selenium has attracted considerable attention since the 19th century when its photoconductivity [1] and photovoltaic [2] effects were discovered. Scientific interest in Se peaked in the mid-20th century, driven by its applications in xerography. Nowadays, S, Se, Te and their compounds are undergoing a research renaissance due to their importance for solar cells [3], topological insulators [4], phase-change materials [5], photodetectors [6], lithium batteries [7], etc. A

few years ago, Se nanoparticles were explored as potential antimicrobial agents, anticancer drugs, antioxidants and tunable light-emitting bio-markers [8]. The structure and properties of bulk Se also occupy a borderline position between molecular crystals and traditional semiconductors. Its most intriguing form is amorphous selenium (a-Se), which consists of a variety of Se species including chains and rings. This phase displays photo-induced structural changes [9], including low-temperature photomelting (photofluidity) [10].

Here, we analyze the optical properties of zeolite-confined S, Se and Te ring molecules based on polarized optical absorption and Raman spectra (OAS and RS) of zeolite single crystals containing chalcogen rings, which are examined in this and previous works. The analysis is performed by comparing experimental spectra with density functional theory results obtained using the Turbomole software package, version 7.8.1 [11]. We demonstrate good agreement between experiment and theory. Our results suggest certain structural distortions of the rings in their ground state and conical intersections of their excited states with those of related isomeric molecules. They are important for understanding photoinduced effects in a-Se and chalcogenide glasses.

2. Materials and Methods

We used four different zeolites: LTA, MOR, CHA and AFI for encapsulation of S, Se and Te into their regular pores. Zeolite structures containing ring molecules are schematically shown in Figure 1. The encapsulation was carried out using vapor adsorption with a controlled chalcogen loading density or by high-pressure injection from the melt to achieve maximum loading density. Details of the encapsulation techniques are given in Refs. [12–17]. Synthetic LTA ($\text{Na}_{12}\text{Al}_{12}\text{Si}_{12}\text{O}_{48}$), AFI ($\text{Al}_{12}\text{P}_{12}\text{O}_{48}$) as well as natural CHA ($\text{Ca}_{1.6}\text{Na}_{0.4}\text{Al}_{3.6}\text{Si}_{8.5}\text{O}_{21.6}$) and MOR ($\text{Ca}_2\text{Na}_4\text{Si}_{40}\text{Al}_8\text{O}_{96}$) zeolites were used in this work.

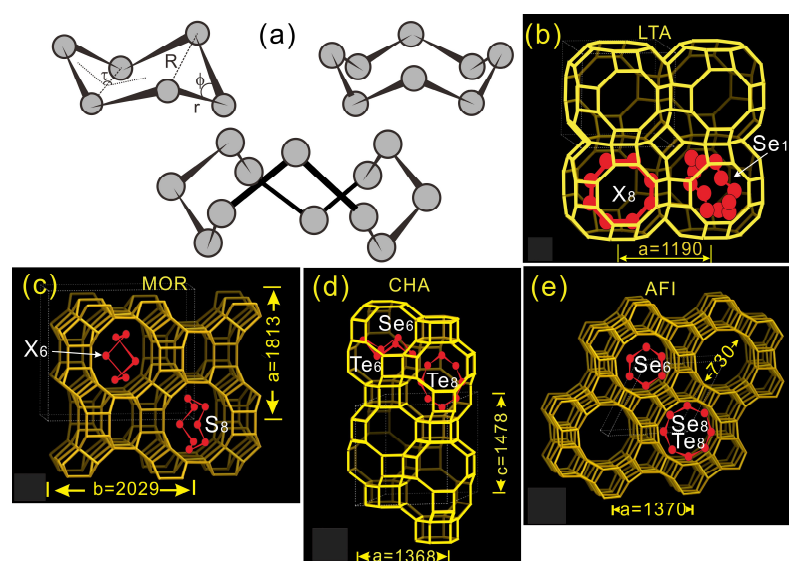


Figure 1. (a) Structures of X_6 , X_8 and X_{12} rings with $X = \text{S}, \text{Se}, \text{Te}$, r , R , ϕ and τ indicating nearest atom distance, next nearest atom distance, bond angle and dihedral angle, respectively; (b) X_8 and Se_{12} rings in LTA; (c) S_8 , Se_6 and Te_6 rings in MOR; (d) Se_6 , Te_6 and Te_8 rings in CHA; (e) Se_6 , Se_8 and Te_8 rings in AFI. Sizes are shown in pm units.

RS of zeolite single crystals with ring molecules were studied using Raman microscopes manufactured by Renishaw Co. (Wotton-under-Edge, UK), JASCO Co. (Tokyo, Japan) and Tokyo Instruments Inc. (Tokyo, Japan). The 633 nm line of the He-Ne laser as well as the 514.5 nm and 364 nm lines of the Ar^+ ion laser were used for the RS excitation. Additional RS experiments were done with the 785 nm diode laser. Micro-objective lenses with $10\times$ – $100\times$ magnifications and a numerical aperture of 0.2–0.95 were used for the RS

excitation and collection in a back-scattering geometry. RS signals of the zeolite-confined chalcogen species were significantly stronger than those of the zeolite transparent host matrices due to resonant Raman enhancement.

OAS in the visible and near-UV spectral ranges were studied using micro-spectrophotometers with a light probe size of 2–10 μm manufactured by Carl Zeiss Co. (Jena, Germany) and CRAIC Co. (San Dimas, CA, USA). To avoid light scattering from zeolite surfaces and improve transmittance, samples were immersed into glycerol and kept between two quartz cover glasses. In most of cases, single-crystal zeolite samples were intentionally broken to pieces with few-micron or submicron thickness. This enabled reliable spectral measurements up to ~ 5.15 eV for samples with relatively large planar size and optical densities up to ~ 2.5 .

RS and OAS were simulated using density functional theory (DFT) [18–20]. The structure and vibrational frequencies of the ring molecules were computed using the hybrid PBE0 exchange-correlation functional [20] and the resolution-of-identity approximation for the Coulomb part (RI-J) [21]. The def2-TZVP basis sets [22] together with the corresponding auxiliary basis sets [23] were employed for S, Se and Te, and small-core effective core potentials (ECPs) were used for Te [24]. RS intensities were obtained in the double harmonic approximation using analytical derivatives of static electronic polarizabilities [25] and analytical energy Hessians [26,27]. Calculations of static polarizability derivatives used the PBE0 functional and augmented def2-TZVPD basis sets [28]. Additionally, infrared (IR) spectra were computed in the double harmonic approximation using analytical dipole moment derivatives and energy Hessians [26,27]. OAS were simulated by time-dependent DFT (TDDFT) [29] using the PBE0 functional with the RI-J approximation [30] and def2-TZVPD basis sets. All calculations were performed with the Turbomole program package, version 7.8.1 [11,18]. Computed RS and OAS are presented as sums of Lorentz curves with full width at half-maximum (FWHM) of ~ 6 cm^{-1} and ~ 0.35 eV, respectively.

The computed structural parameters (bond lengths r , bond angles ϕ and dihedral angles τ) of the chalcogen rings are shown in Supplementary Materials Table S1. Stable ring structures correspond to the energy minima whereas normal-mode-distorted structures do not. Therefore, the structural parameters of these distorted rings should be interpreted qualitatively rather than quantitatively.

3. Results and Discussion

3.1. S_8 and S_6 Rings

S_8 rings were previously obtained in the LTA large cavities [12,17,31–33] and in the MOR channels [34]. RS of LTA-S and MOR-S showed good agreement with the known RS of S_8 molecules in solution [35]. Here we present RS and OAS of LTA-S and MOR-S obtained using higher-quality equipment (Figure 2). DFT-computed polarized RS of a single S_8 ring is shown in Figure 2a. The resulting frequencies, IR intensities and Raman activities of the S_8 ring with D_{4d} symmetry are listed in Supplementary Materials Table S2.

The experimental RS of LTA-S are displayed in Figure 2b. Assuming orientation of S_8 by its four-fold axis along the LTA four-fold axis as in Figure 1b, we simulated LTA-S RS by summing the computed RS of S_8 in three possible orientations (Figure 2c). The experiment (Figure 2b) and theory (Figure 2c) are in very good agreement. In particular, the polarization dependencies of RS intensities are nearly perfectly reproduced, which confirms the assumed orientation of S_8 in LTA. The agreement between the experimental (75, 153–155, 221 cm^{-1}) and theoretical (73.4, 150, 223 cm^{-1}) bending/torsion mode frequencies is also good. However, it is not the case for the stretching modes. The DFT-computed A_1 stretching mode frequency of 499 cm^{-1} is higher than the experimental value of 479 cm^{-1} . Scaling

the computed frequency using the recommended global scaling factor of 0.9591 [36] gives 479 cm^{-1} in excellent agreement with the experiment. Scaling vibrational frequencies by a global factor accounts for the vibrational mode anharmonicities and basis set incompleteness. The scaling factor depends on the exchange-correlation functional and the basis sets and is transferable across different chemical systems, as evidenced by the good agreement between experimental and scaled computed vibrational frequencies. Importantly, the S_8 ring symmetry in LTA is slightly distorted from the perfect D_{4d} , with the E_2 modes split off and the previously forbidden B_1 and E_1 modes observed (Figure 2b).

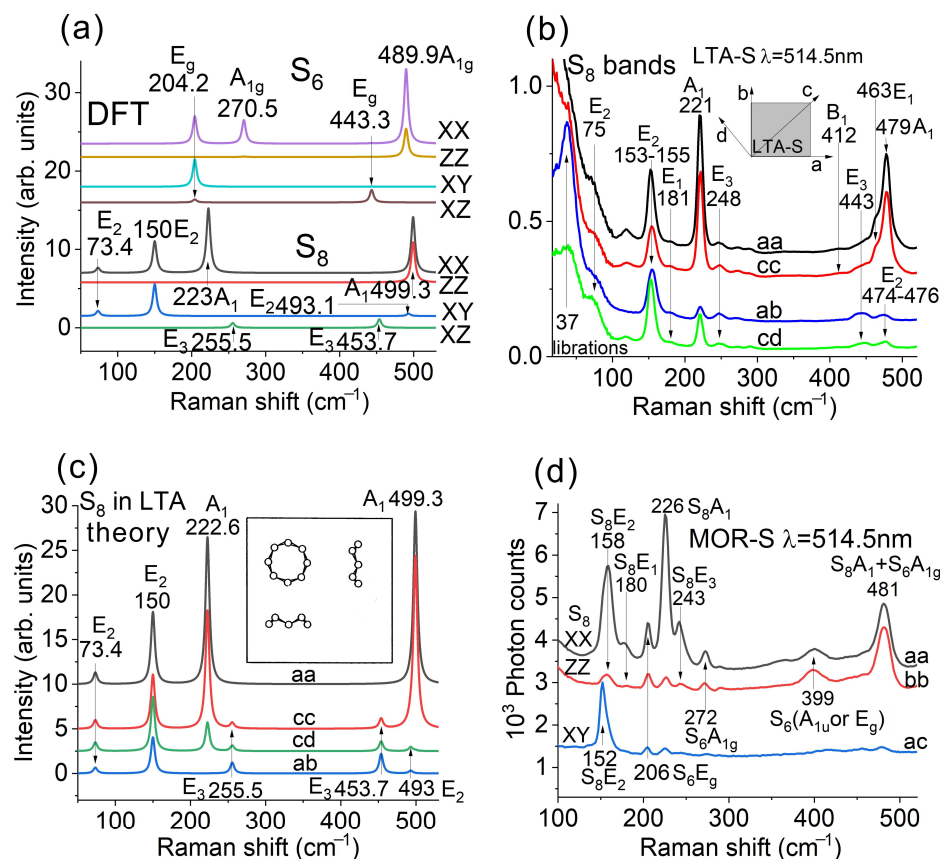


Figure 2. Raman spectra: (a) DFT calculation for S_8 and in inset for S_6 ; (b) experiment for S_8 in LTA-S; (c) calculation for S_8 in LTA; (d) experiment for S_8 and S_6 in MOR-S. The axes X, Y, Z correspond to S_8 , while the axes a, b, c correspond to the zeolites. Mode frequencies and symmetries are indicated.

The Raman bands of the S_8 ring are also observed in the RS of MOR-S (Figure 2d). The polarization dependence of the A_1 and E_2 bending mode band intensities clearly shows that the rings are oriented with their four-fold axes aligned along the **b**-axis of MOR [Figure 1c]. This indicates that the S_8 rings in the MOR channels are compressed along the **a**-axis, whereas they remain uncompressed along the **c**-axis of MOR. Therefore, the E_2 bending mode splitting in MOR-S ($152\text{--}158\text{ cm}^{-1}$) is even larger than that in LTA-S ($153\text{--}155\text{ cm}^{-1}$). Interestingly, a few relatively weak bands of the S_6 rings are also observed in the RS of MOR-S. The experimental bands at $\sim 206\text{ cm}^{-1}$ and $\sim 272\text{ cm}^{-1}$ can be assigned to the theoretical 204 cm^{-1} E_g and 270.5 cm^{-1} A_{1g} bond-bending modes of the S_6 ring, respectively [(Figure 2a), see also Supplementary Materials Table S3]. The polarization dependence of these band intensities is weaker than that of the S_8 ring, indicating a less strict orientation of the S_6 rings within the MOR channel.

DFT-computed OAS of single S_8 and S_6 rings are presented in Figure 3a,b, respectively [see also Supplementary Materials Tables S4 and S5]. The insets in these figures show the ring structures in the XZ plane. An additional inset in Figure 3a illustrates the p-orbital

splitting in S, Se and Te rings. The low-energy OAS in all these cases correspond to electronic transitions from the lone-pair (LP) orbitals to anti-bonding σ^* states.

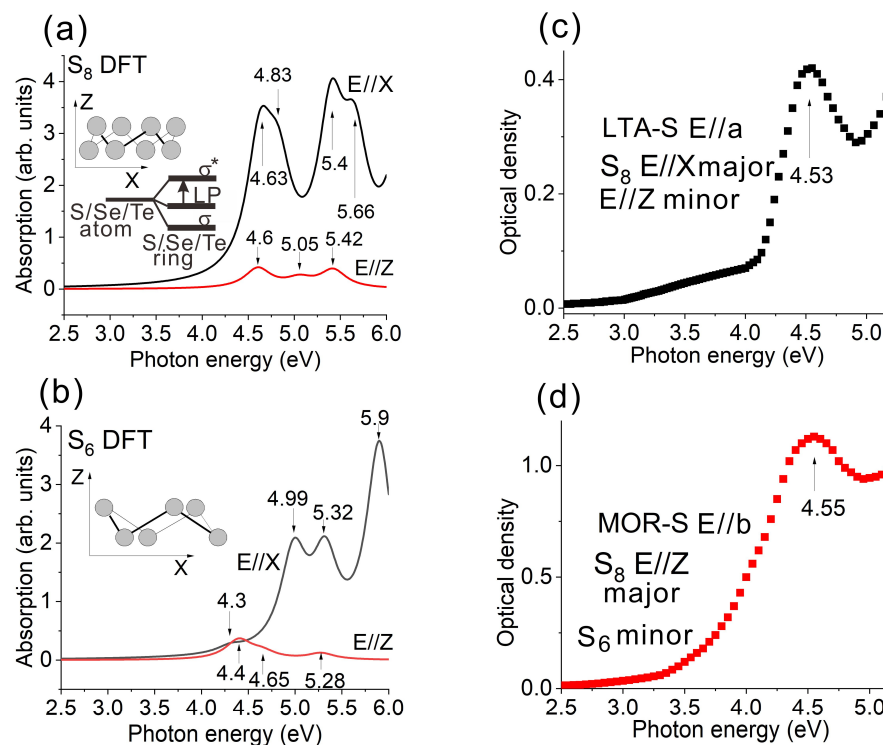


Figure 3. Optical absorption spectra: DFT calculation (a) for S_8 with insets showing the S_8 ring structure in the XZ plane and electronic structure with the atomic p-orbital splitting to the bonding σ , anti-bonding σ^* and nearly non-disturbed lone-pair (LP) orbital states; (b) for S_6 with inset showing the S_6 structure in the XZ plane; experiment for (c) S_8 in LTA-S ($E//a$); and (d) for MOR-S ($E//b$) corresponding mainly to S_8 ($E//Z$) with a minor contribution of S_6 .

For both S_8 and S_6 rings, in-plane polarized absorption ($E//X$) is stronger than the out-of-plane absorption ($E//Z$). Taking into account the orientations of the S_8 rings in LTA and MOR, we can conclude that OAS of LTA-S mainly corresponds to $E//X$ absorption with a minor contribution from $E//Z$ absorption of S_8 . In contrast, OAS of MOR-S for $E//b$ mainly corresponds to $E//Z$ absorption of S_8 with a minor contribution from S_6 absorption. Both experimental spectra show a single absorption peak at ~ 4.53 eV for LTA-S (Figure 3c) and ~ 4.55 eV for MOR-S ($E//b$) (Figure 3d), respectively. These values are in reasonable agreement with the theoretical peak energies of 4.63 eV for $E//X$ and 4.6 eV for $E//Z$ (Figure 3a).

We should note that in the previously reported LTA-S OAS a peak position at 4.35–4.4 eV [17] was observed for samples with a higher sulfur loading density, corresponding to the significant contribution of two interacting S_8 rings per LTA large cavity. In contrast, in this work, we report the OAS of LTA-S with a low sulfur loading density, corresponding to one or zero S_8 molecule per cavity. It is likely that intermolecular interactions are responsible for the downshift of the absorption peak from 4.53 eV to 4.35–4.4 eV in the case of two S_8 rings per cavity [17].

Experimentally, S_8 ring OAS were also studied in solution [37,38]. The reported absorption band energies, 4.49 eV and 4.7 eV [37], and 4.48 eV, 4.66 eV and 5.28 eV [38], are in reasonable agreement with our DFT calculations, which yielded 4.63 eV, 4.83 eV and 5.4 eV for S_8 ($E//X$). Similar to S_8 in zeolites, the absorption peaks of S_8 in solution are observed at slightly lower photon energies than predicted by DFT. This discrepancy may be explained by solvent effects or by the overestimation of the electronic transition energies

in DFT calculations. Furthermore, experimental OAS measurements were conducted at room temperature contrary to the DFT calculations implying $T = 0$ K, the S_8 ring energy gap being larger with a decrease in temperature. Another similarity of S_8 OAS in solutions with those in zeolites (Figure 3c,d) is the presence of a low-energy absorption tail extending down to ~ 3 eV. We attribute this S_8 absorption tail to triplet excitations in the 3.66–4.07 eV range [Supplementary Materials Table S4a].

To summarize this section, we conclude that our DFT calculations showed nearly perfect agreement with experimental Raman intensities and bending mode frequencies while they overestimated stretching mode frequencies. Applying harmonic frequency scale factors [36] to stretching mode frequencies improved the agreement. The DFT energies and oscillator strengths of the S_8 electronic transitions reasonably reproduced the experimental results. Our DFT-computed $r = 205.6$ pm, $\phi = 102.7^\circ$ for S_6 and $r = 204.7$ pm, $\phi = 108.1^\circ$ for S_8 [Supplementary Materials Table S1] show shorter r and nearly same ϕ compared to corresponding DFT-computed 212 pm, 103.1° and 211 pm, 109.5° [39] or 212 pm, 102.5° and 210.8 pm, 108.3° [40].

3.2. Se_6 Rings

RS and OAS of Se_6 incorporated in the pores of three different zeolites CHA, MOR and AFI (low density—LD), were experimentally studied in Ref. [41]. In some earlier works, Se_6 rings were identified in zeolites as well [34,42,43]. Se_6 ring molecules are slightly compressed in the CHA cavities possessing a nearly prolate spheroid shape with a length of ~ 1 nm and a cross-section of 0.67 nm $\times$ 0.67 nm. The rings are less compressed in the AFI channel with a cross-section of 0.73 nm $\times$ 0.73 nm. The D_{3d} symmetry of the Se_6 ring is maintained in both cases and the ring three-fold axis Z is directed along the crystal three-fold axis c . In contrast, the Se_6 ring is asymmetrically compressed in the MOR channel with a cross-section of 0.67 nm $\times$ 0.7 nm, whereas the ring three-fold axis Z is directed along the MOR b axis. The ring orientations are schematically shown in Figure 1 and the insets of Figure 4. Here, we present a more detailed optical study of Se_6 together with corresponding DFT calculations.

Figure 4 shows the theoretical and experimental RS of Se_6 [see also Supplementary Materials Table S6]. The agreement between DFT results and the experiment is very good for the bond-bending mode frequencies and intensities. However, the discrepancy between the experiment and theory is significant for the bond-stretching mode frequencies. The experimental frequency of 273 – 274 cm^{-1} of the A_{1g} bond-stretching mode is 12 – 13 cm^{-1} lower than the computed value of 285.7 cm^{-1} , which can again be attributed to the neglect of anharmonic effects in simulations, as the scaled frequency is 274 cm^{-1} , in line with experimental data. The discrepancy between the DFT-computed stretching E_g mode frequency of 271.7 and experimentally observed band frequencies 220 – 221 cm^{-1} attributed earlier to E_g [41,44] is very large. Applying the scaling factor yields 260.6 cm^{-1} , which does not fully account for the difference. Therefore, we consider the possibility to assign the observed band to the forbidden A_{1u} mode. This mode can be converted to the active A_1 mode under a ring distortion, which reduces its symmetry from D_{3d} to D_3 [see Supplementary Materials Table S1 for the structural parameters of the distortion]. The DFT-computed XX -spectrum of such a distorted ring is shown in Supplementary Materials Figure S2a and features a strong 228.8 cm^{-1} A_1 mode band. Assuming that $\sim 10\%$ of Se_6 rings are distorted, we obtain the theoretical XX -spectrum shown in Supplementary Materials Figure S2b, which is in good agreement with the experimental RS.

The polarization dependencies of the intensities of both A_{1g} and E_g bending modes show good agreement between the experiment and DFT calculations. Both modes are highly active in the XX polarization configuration and less active in the ZZ configuration,

where the E_g mode is formally forbidden by selection rules. The relatively high activity of these modes in the AFI-Se(LD) ZZ spectrum is likely associated with large amplitudes of (1) vibrations along the AFI channels and (2) librations of nearly free Se_6 molecules. Due to the ring symmetry distortion in MOR-Se, the E_g mode splits to two components at $\sim 102\text{ cm}^{-1}$ and $\sim 108\text{ cm}^{-1}$. Figure 4d suggests a C_{2h} symmetry for the Se_6 ring in MOR-Se. Therefore, the E_g bending mode splits to A_g and B_g modes with frequencies of 108 cm^{-1} and 102 cm^{-1} , respectively. This splitting, with the higher A_g mode frequency and a lower B_g mode frequency, corresponds to the Se_6 ring orientation shown in Figure 4d. The actual symmetry of Se_6 in MOR-Se may be even lower, specifically, C_s , since the A_{1g} mode at $\sim 134\text{ cm}^{-1}$ mixes with the originally inactive A_{2u} mode at $\sim 141\text{ cm}^{-1}$, with both modes being converted to the A' modes of the C_s point group.

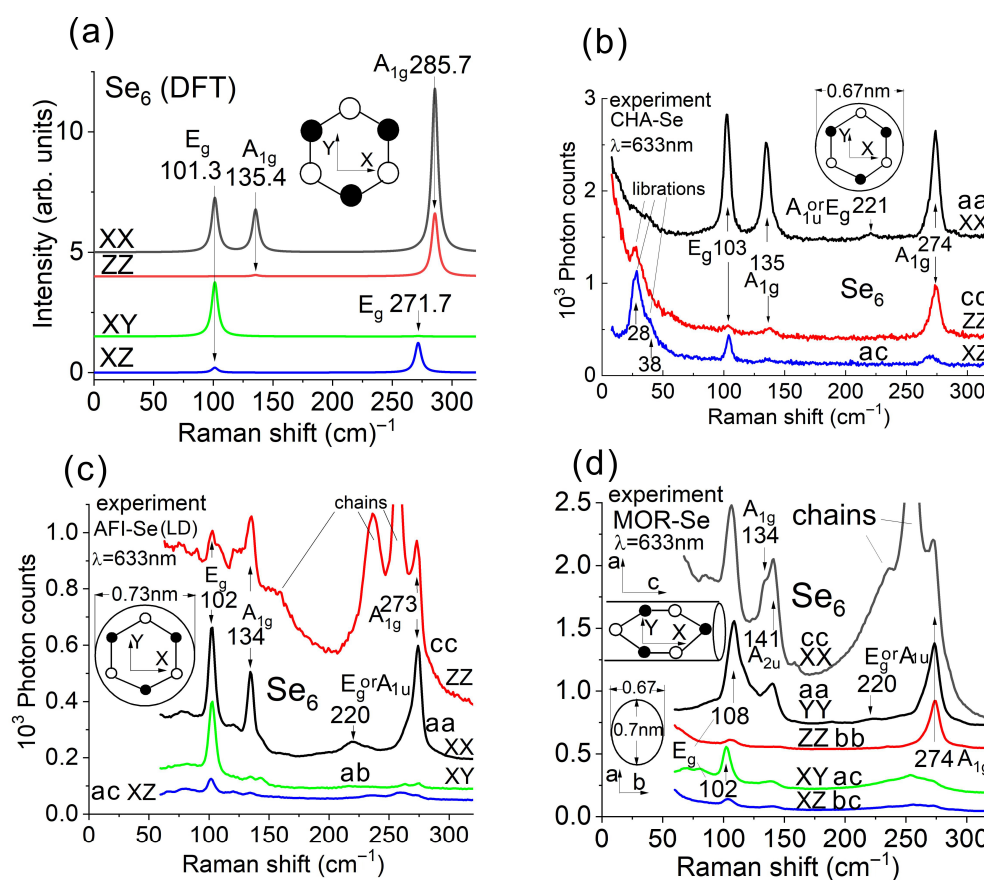


Figure 4. Polarized RS of Se_6 : (a) DFT calculation; experimental RS at the 632.8 nm wavelength (1.96 eV) excitation: (b) CHA-Se, (c) AFI-Se(LD) and (d) MOR-Se. Insets schematically show Se_6 ring in the corresponding cavities and channels, white and black circles representing to upper and lower Se atoms, respectively. The axes X, Y, Z correspond to Se_6 , while the axes a, b, c correspond to the zeolites.

The theoretical and experimental OAS of Se_6 are shown in Figure 5 [see also Supplementary Materials Table S7]. DFT-computed OAS (Figure 5a) shows three relatively weak bands at 3.67 eV, 4.06 eV and 4.22 eV and two strong bands at 4.6 eV and 5.1 eV polarized in the molecular plane ($E//X$). These absorption bands correspond to the transitions of E_u symmetry in the D_{3d} point group of Se_6 . For the $E//Z$ polarization, three relatively weak absorption bands of A_{2u} symmetry are observed. As in the case of sulfur rings, only dipole-allowed singlet electron transitions are included in the calculations.

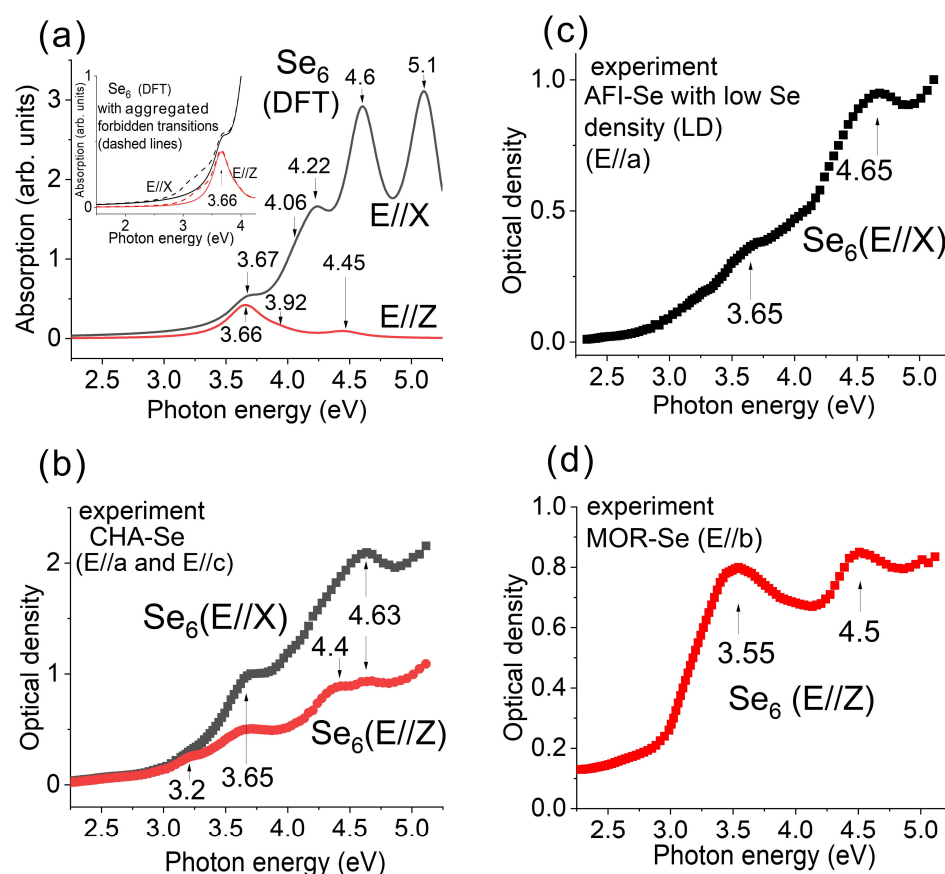


Figure 5. Polarized optical absorption spectra of Se₆: (a) DFT calculation with inset showing OAS with forbidden transitions, (b) CHA-Se, (c) AFI-Se(LD) and (d) MOR-Se. The axes X, Y, Z correspond to Se₆, while the axes a, b, c correspond to the zeolites.

Experimentally, OAS with both $E//X$ and $E//Z$ polarizations are observed in CHA-Se (Figure 5b). They show rather good agreement with the DFT results. Indeed, the experimental band energies at ~3.65 eV, ~4.4 eV and ~4.63 eV nearly coincide with the computed values. The instrumental limit of ~5.15 eV does not allow the observation of the strong band expected at ~5.1 eV. Interestingly, the experimental CHA-Se OAS clearly shows a band at ~3.2 eV, which is absent in the DFT-computed OAS. We assign the experimental ~3.2 eV band to the DFT-computed forbidden Se₆ electronic transitions of E_g (3.13 eV and 3.36 eV), A_{2g} (3.28 eV) and A_{1g} (3.43 eV) symmetry, which are activated due to the inversion symmetry breaking by the antisymmetric vibrational A_{1u} , A_{2u} or E_u modes [Supplementary Materials Table S7b–g]. As a result, weak absorption bands appear in the 3.1–3.4 eV range of the Se₆ absorption spectrum. The inset in Figure 5a shows computed Se₆ OAS with (dashed lines) and without (solid lines) the contribution of activated forbidden electronic transitions. Agreement with the experiment is improved in the former case.

The anisotropy of CHA-Se OAS appears weaker than that predicted by DFT. However, it is necessary to take into account the sample-surface scattering, which increases with photon energy. OAS measurements of Se₆ in AFI-Se(LD) and MOR-Se is available only for one polarization, namely, for $E//X$ in AFI-Se(LD) and for $E//Z$ in MOR-Se. This limitation is associated with the existence of Se chains that strongly absorb light polarized along the AFI and MOR channels. OAS measurements for MOR-Se are not feasible for $E//a//Y$ due to the crystal shape.

The AFI-Se(LD) OAS (Figure 5c) demonstrates good agreement with the DFT $E//X$ spectrum. Indeed, a weak experimental band at ~3.65 eV is in good agreement with the

theoretical band at ~ 3.67 eV, whereas a strong experimental band at ~ 4.65 eV is close to the ~ 4.6 eV theoretical value. MOR-Se OAS (Figure 5d) agrees well with the computed $E//Z$ spectrum of Se_6 (Figure 5a). Stronger and weaker experimental bands at ~ 3.55 eV and ~ 4.5 eV can be assigned to the theoretical electronic transitions at ~ 3.66 eV and ~ 4.45 eV [Figure 5a]. The ~ 3.2 eV band, which is clearly observed in the CHA-Se spectrum, is likely obscured in the low-energy shoulder of the ~ 3.55 eV band.

To summarize this section, we state that the DFT calculations demonstrate very good agreement with the experimental Raman intensities and bending mode frequencies while they have a tendency to overestimate stretching mode frequencies. Scaling factors [36] improve the agreement. The computed energies and oscillator strengths of the electronic transitions are in satisfactory agreement with the experimental ones. We hypothesize that Se_6 undergoes antisymmetric mode distortion, which leads to better agreement of computed OAS with experiment and suggests that the experimental $220\text{--}221\text{ cm}^{-1}$ Raman band corresponds to the inactive A_{1u} mode of the undistorted $\text{Se}_6(D_{3d})$, which becomes active for distorted $\text{Se}_6(D_3)$. Our DFT-computed $r = 233.6$ pm, $\phi = 101.4^\circ$ for Se_6 are in agreement with other DFT results: $r = 234$ pm, $\phi = 101^\circ$ [45] and $r = 233$ pm, $\phi = 99.4^\circ$ [46] and rather close to $r = 232$ pm [47].

3.3. Se_8 and Se_{12} Rings

There are several zeolites suitable for accommodating Se_8 rings in their cavities, namely, LTA, AFI, CaY, SrY, RbY [15,16,32,33,48–51] and some others. However, the Se_8 rings are typically accompanied by other Se species, in particular, by Se_{12} rings in LTA and by Se chains in AFI at high Se loading densities (AFI-Se(HD)). Using polarized RS of LTA-Se single crystals, we showed that single and double Se_8 rings can be formed in the large LTA cavities with their four-fold axes oriented along the LTA four-fold axes. Simultaneously, Se_{12} rings can be formed in other large cavities of the same LTA crystal with their three-fold axes oriented along the LTA three-fold axes. The Se_{12} rings were clearly identified in the RS of LTA-Se [15,16,32,33], thereby correcting earlier interpretations [52,53].

Here, we present DFT-computed RS and OAS of Se_8 and Se_{12} rings, provide additional details on the experimental RS of LTA-Se, demonstrate the OAS of LTA-Se over a wide spectral region and extract the corresponding Se_{12} OAS. We also present AFI-Se(HD) RS and wide-spectral-range OAS dominated by Se_8 rings ($E//X$). DFT-computed RS of the Se_8 ring with D_{4d} symmetry are shown in Figure 6a [see also Supplementary Materials Table S8]. They are very similar to those of S_8 (Figure 2a). Both A_1 modes bond-stretching at 279.3 cm^{-1} and bond-bending at 110 cm^{-1} are highly active in the XX polarization configuration while only the former is active in the ZZ configuration. All E_2 modes exhibit only XX and XY Raman activity due to the selection rules of the D_{4d} point group. Figure 6b demonstrates calculated RS of LTA-Se with Se_8 in three possible orientations with their four-fold axes along the LTA four-fold axes in accordance with our previous observations [15,16,32]. Importantly, the nearly purely XX -active 110 cm^{-1} A_1 bond-bending mode appears to be strongly suppressed in the ab polarization configuration.

DFT-computed RS of the Se_{12} ring with D_{3d} symmetry are shown in Figure 6c [see also Supplementary Materials Table S9]. Similar to the Se_8 ring, the symmetric bond-stretching mode (272.7 cm^{-1} A_{1g} in this case) is active in both XX and ZZ polarization configurations. In contrast to Se_8 , Se_{12} displays two symmetric bond-bending modes: the 52.9 cm^{-1} mode is XX -active while the 147.8 cm^{-1} mode is ZZ -active. Figure 6d demonstrates calculated RS of LTA-Se with Se_{12} in four possible orientations, with their three-fold axes along the LTA three-fold axes. The XX -active 52.9 cm^{-1} A_{1g} bond-bending mode is suppressed in the cd polarization configuration. The computed optical energy gap for the dipole-allowed electron transitions of Se_8 ring $E_G(\text{Se}_8) \sim 3.67$ eV [(Figure 6e),

see also Supplementary Materials Table S10] coincides with that for the dipole-allowed electron transitions of Se_6 [Figure 5a]. In contrast, the computed $E_G(\text{Se}_{12}) \sim 3.25$ eV is noticeably reduced [(Figure 6f), see also Supplementary Materials Table S11].

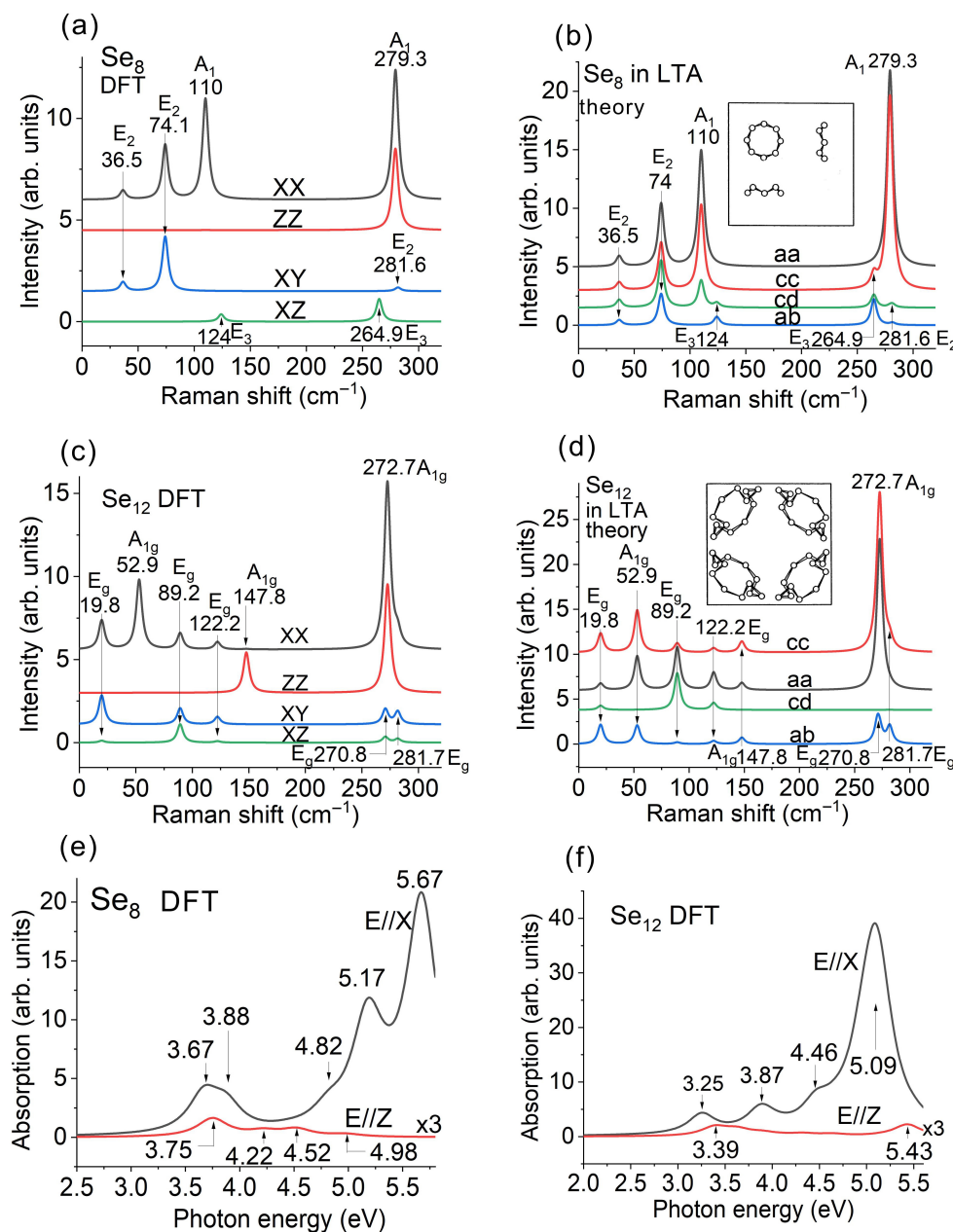


Figure 6. Raman spectra: (a) DFT calculation for Se_8 ; (b) calculation for Se_8 in LTA with the inset showing possible ring orientations in LTA; (c) DFT calculation for Se_{12} ; (d) calculation for Se_{12} in LTA with the inset showing possible ring orientations in LTA. Optical absorption spectra: (e) DFT calculation for Se_8 ; (f) DFT calculation for Se_{12} . The axes X, Y, Z correspond to Se_8 and Se_{12} , while the axes a, b, c correspond to the zeolite.

Experimental RS of LTA-Se single crystals with the maximum possible Se loading density are shown in Figure 7a–d. The polarization configurations aa, ab, cc and cd are the same as those for LTA-S RS [Figure 2b]. Importantly, the RS of LTA-Se varies with the excitation wavelength. Due to the smaller energy gap of Se_{12} compared to Se_8 , the Se_{12} Raman bands are resonantly enhanced at $\lambda = 514.5$ nm. Therefore, both Se_8 and Se_{12} roughly equally contribute to the LTA-Se RS at $\lambda = 785$ nm (Figure 7a–d, black curves) well below the energy gap while resonantly enhanced Se_{12} bands dominate at $\lambda = 514.5$ nm

124 cm^{-1} (E_3) and 279.3 cm^{-1} (A_1). The suppression of the **XX**-active A_1 bond-bending mode band at $\sim 113 \text{ cm}^{-1}$ in the **ab**-polarization configuration is a clear indication of the Se_8 ring orientation with its four-fold axis along the LTA four-fold axis similar to the S_8 ring. Se_8 bands are also observed in the RS of AFI-Se(HD) (Figure 7e), which refers to AFI-Se with a high Se loading density. The bands at $\sim 42 \text{ cm}^{-1}$, $\sim 75 \text{ cm}^{-1}$, $\sim 114 \text{ cm}^{-1}$ and $\sim 269 \text{ cm}^{-1}$ are similar to the DFT-computed bands of Se_8 at 36.4 cm^{-1} (E_2), 74.1 cm^{-1} (E_2), 110 cm^{-1} (A_1) and 279.3 cm^{-1} (A_1). High activity of the **XX**-active modes in the **aa**-polarization configuration and their low-activity in the **cc**-configuration suggest the orientation of the four-fold axis of Se_8 along the **c**-axis of AFI.

Figure 7f shows the experimental OAS of LTA-Se and AFI-Se(HD). LTA-Se(1) and LTA-Se(8) correspond to Se loading densities of $\sim$ one Se atom and eight Se atoms per LTA large cavity, respectively. As we showed earlier [15], LTA-Se(8) displays a much higher $\text{Se}_{12}/\text{Se}_8$ concentration ratio than LTA-Se(1). Therefore, Se_{12} OAS can be extracted using the procedure described in Ref. [15]. Here, we extend this analysis to a wider spectral range up to $\sim 5.15 \text{ eV}$. DFT predicts relatively strong absorption for $E//X$ and weaker absorption for $E//Z$ for both Se_8 and Se_{12} (Figure 6e,f).

Theoretical bands of Se_8 at 3.67–3.88 eV and 4.82 eV can be associated with the experimental bands of LTA-Se(1) at $\sim 3.85 \text{ eV}$ and $\sim 4.85 \text{ eV}$ (black) and with those of AFI-Se(HD) at $\sim 3.75 \text{ eV}$ and $\sim 4.75 \text{ eV}$ (green). Theoretical bands of Se_{12} at 3.25 eV, 3.87 eV, 4.46 eV and 5.09 eV can be associated with the corresponding experimental bands at 3.0–3.3 eV, $\sim 3.7 \text{ eV}$, $\sim 4.5 \text{ eV}$ and $\sim 5.1 \text{ eV}$ (blue). The doublet at 3.0–3.3 eV can result from the splitting of the 3.25 eV E_u -symmetry transition.

To summarize this section, Se_8 and Se_{12} rings form in the LTA large cavities. The Se_8 rings are oriented with their four-fold axes along the LTA four-fold axes. The Se_{12} rings are oriented with their three-fold axes along the LTA three-fold axes. Experimental Raman frequencies and intensities agree well with DFT-computed values for bond-bending modes of both Se_8 and Se_{12} rings. DFT overestimates bond-stretching mode frequencies are due to neglecting anharmonic effects. Applying harmonic scaling factors [36] improves the agreement, yielding 268 cm^{-1} for the $\text{Se}_8 A_1$ mode in line with experiment and 261.5 cm^{-1} for the $\text{Se}_{12} A_{1g}$ mode close to experimental 258 cm^{-1} . Experimental OAS of Se_8 and Se_{12} are in reasonable agreement with the DFT-computed spectra, and the energy gap of Se_{12} is smaller than that of Se_8 . Our DFT-computed structural parameters of Se_8 $r = 233.6 \text{ pm}$, $\phi = 101.4^\circ$ are close to $r = 233 \text{ pm}$, $\phi = 100^\circ$ [46] but differ from $r = 236 \text{ pm}$, $\phi = 108.65^\circ$ [54]. Our parameters of Se_{12} $r = 232.9 \text{ pm}$, $\phi = 105.5; 106.1^\circ$ differ from the reported DFT results $r = 236 \text{ pm}$, $\phi = 107.17\text{--}108.74^\circ$ [54] and $r = 237.7 \text{ pm}$ [55]. For both Se_8 and Se_{12} $r = 231 \text{ pm}$ was reported in Ref. [47].

3.4. Te_8 and Te_6 Rings

In contrast to sulfur and selenium, which form rather stable ring molecules, tellurium rings are very exotic clusters requiring specific conditions for their stabilization. Bulk crystalline Te and amorphous Te consist of chains. However, as we recently showed, space restriction in the LTA cavities makes the formation of Te_8 rings realistic. LTA-Te was found to be an example of a uniform regular array of Te_8 rings [56]. Te_8 rings were also found in AFI-Te with a high Te loading density [14]. Te_6 rings exhibited their signatures in the RS of MOR-Te [14,34]. In both cases, Te rings coexist with Te chains in the zeolite channels.

DFT-computed RS of Te_6 and Te_8 rings are shown in Figure 8a,b [see also Supplementary Materials Tables S12 and S13]. They are rather similar to those of S_6/Se_6 and S_8/Se_8 , respectively. Symmetric bond-bending modes at 80 cm^{-1} ($\text{Te}_6 A_{1g}$) and 65.4 cm^{-1} ($\text{Te}_8 A_1$) show high Raman activity in the **XX** polarization configuration and low activity in the **ZZ** configuration. In contrast, symmetric bond-stretching modes at 192.7 cm^{-1}

(Te₆ A_{1g}) and 186.9 cm^{−1} (Te₈ A₁) show comparable Raman activities in the **XX** and **ZZ** configurations. DFT-computed OAS of Te₆ and Te₈ [Figure 8c,d], see also Supplementary Materials Tables S14 and S15] show smaller optical energy gaps compared to S₆/Se₆ and S₈/Se₈. Rather strong absorption bands are observed in the violet spectral range of Te₆ and Te₈ at energies around 3 eV. The *E*//*X* absorption dominates over the *E*//*Z* absorption for both rings.

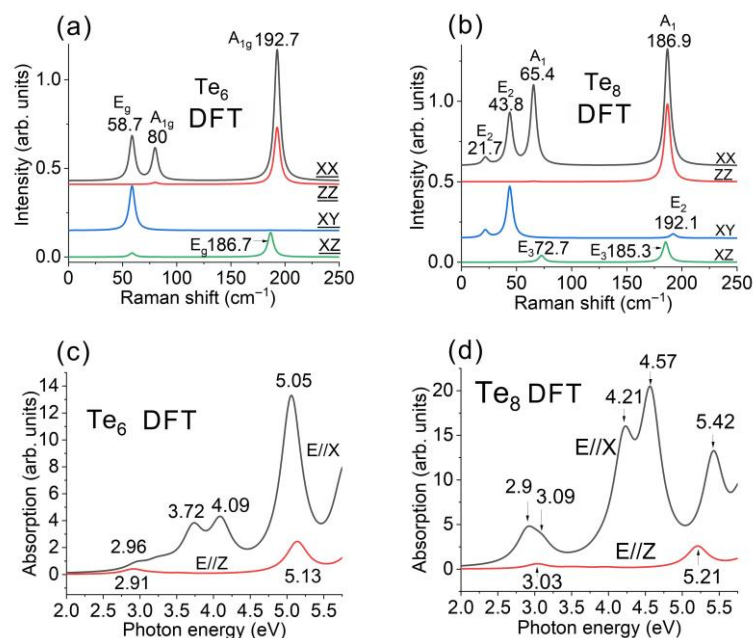


Figure 8. DFT-computed RS of Te₆ (a) and Te₈ (b); DFT-computed OAS of Te₆ (c) and Te₈ (d).

Theoretical RS of Te₈ in LTA for the **aa**, **cc**, **ab** and **cd** polarization configurations were obtained by summing of the Raman responses of three Te₈ rings in their three possible orientations in the LTA crystal (Figure 9a). They are qualitatively similar to the theoretical RS of S₈ in LTA (Figure 2c) and Se₈ in LTA (Figure 6b). Corresponding experimental polarization dependencies of the LTA-Te bands in the Te₈ bond-bending mode region (Figure 9b) appear to be in good agreement with the theoretical ones (Figure 9a). The experimental frequency of 64 cm^{−1} is very close to the calculated frequency 65.4 cm^{−1} of the Te₈ A₁ bond-bending mode. The experimental 64 cm^{−1} band is rather strong in the **aa** and **cc** polarization configurations and it is still not weak in the **cd** configuration while the band completely disappears in the **ab** configuration. This is a consequence of the two-dimensional character of the Raman tensor of this mode [Supplementary Materials Table S13] with only two strong diagonal tensor components. In contrast, the Raman tensor of the Te₈ A₁ bond-stretching mode is rather three-dimensional [Supplementary Materials Table S13]. The observed polarization dependence of the Te₈ A₁ bond-bending mode intensity is a clear indication of the orientation of the Te₈ fourfold axis along the fourfold axis of LTA.

The calculated Te₈ E₂ bond-bending mode frequency of 43.8 cm^{−1} is in good agreement with the observed 46–50 cm^{−1} band frequencies of LTA-Te. The splitting of the degenerate E₂ mode indicates a structural distortion of Te₈ in LTA and, therefore a reduced symmetry compared to the initial D_{4d} symmetry of the ring. Interestingly, the splitting of the Te₈ E₂ mode by 8.3% in LTA is very strong, in contrast to the weaker splitting by ~1.3% for the corresponding E₂ mode at 153–155 cm^{−1} of S₈ and 78–79 cm^{−1} of Se₈.

Interestingly, in contrast to S₈ and Se₈, the experimental symmetric bond-stretching mode frequency of Te₈ (182–183 cm^{−1}) lies between the unscaled computed frequency of 186.7 cm^{−1} and the scaled frequency of 179 cm^{−1}. This result may reflect the more accurate DFT prediction of bond lengths in case of Te₈. Moreover, effective core potentials (ECPs)

are used to describe the inner shells of Te, which alters the basis set incompleteness and may reduce the need for frequency scaling.

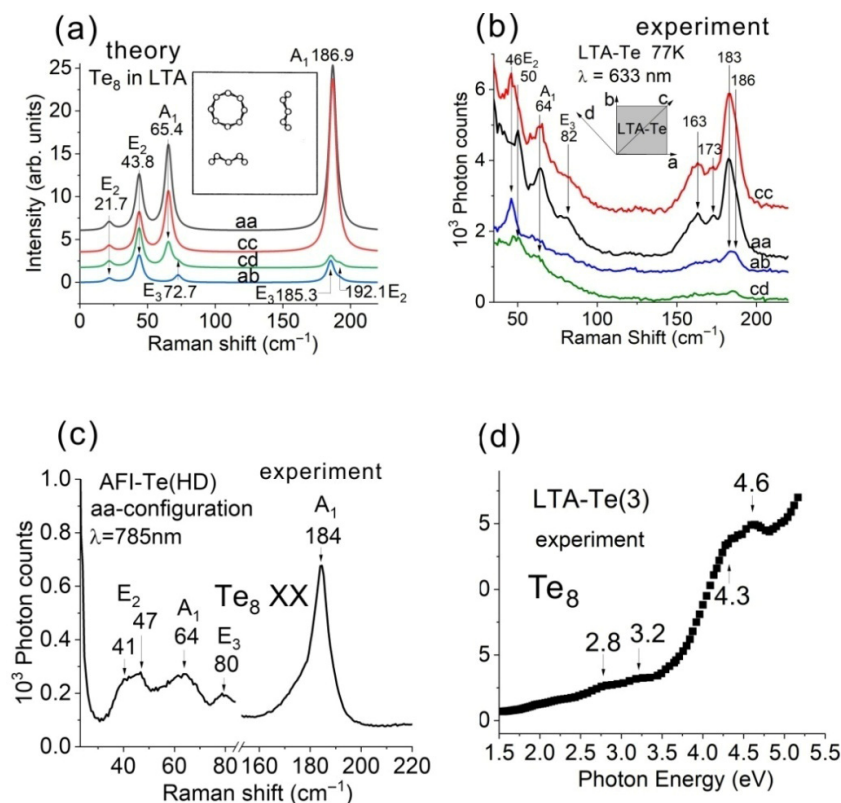


Figure 9. Theoretical RS of Te_8 in LTA for different polarization configurations (a); experimental RS of LTA-Te at $T \sim 77$ K and $\lambda = 633$ nm (b); experimental RS of AFI-Te with high Te loading density for aa-configuration at $T \sim 300$ K and $\lambda = 785$ nm (c); experimental OAS of LTA-Te with $\sim$ three Te atoms per cavity (d).

Bond-stretching-mode bands of Te_8 are rather broad and overlap with each other. For band sharpening, we took the RS measurement of LTA-Te at a temperature $T \sim 77$ K [Figure 9b]. Assuming structural distortion in Te_8 , we can conclude that the Raman bands in the Te_8 bond-stretching-mode region at $162\text{--}163\text{ cm}^{-1}$ and $171\text{--}173\text{ cm}^{-1}$ likely originate from the E_3 mode and the formerly inactive B_1 mode, respectively, while the $182\text{--}183\text{ cm}^{-1}$ and 186 cm^{-1} bands correspond to the A_1 and E_2 modes of Te_8 . The originally inactive E_1 bond-stretching mode may also contribute to the observed Raman bands.

Another example of Te_8 formation in zeolites is AFI-Te. As shown in Ref. [14], Te_8 bands can be observed in the AFI-Te RS recorded in the aa polarization configuration. We show such a spectrum in greater detail in Figure 9c. The dominant band at $\sim 184\text{ cm}^{-1}$ is attributed to the A_1 bond-stretching mode of Te_8 . The bands at $\sim 64\text{ cm}^{-1}$ and $\sim 80\text{ cm}^{-1}$ are assigned to the A_1 and E_3 bond-bending modes, respectively. The doublet at $41\text{--}47\text{ cm}^{-1}$ is attributed to the E_2 bond-bending mode.

Importantly, the experimental LTA-Te(3) OAS (Figure 9d) shows nearly perfect agreement with the computed OAS of Te_8 (Figure 8d). Similarly to the bond-stretching mode frequencies, this result may reflect the more accurate DFT prediction of bond lengths in Te_8 .

As shown above, MOR channels accommodate Se helical chains and Se_6 rings. The rings are oriented with the three-fold axis along the b-axis of MOR. The actual symmetry of the Se_6 ring in the MOR channel is lower than the D_{3d} symmetry suggested by theory. Splitting of the E_g bond-bending mode as well as the mixture of the A_{1g} and A_{2u} bond-bending modes of Se_6 in MOR confirm its structural distortion. Figure 10a shows

MOR-Te RS, which has many similarities to the MOR-Se RS. Indeed, a strong **cc**-active band at $\sim 168\text{ cm}^{-1}$ undoubtedly corresponds to Te helical chains. The rest of the MOR-Te bands can be attributed to Te_6 . The 63 cm^{-1} and 68 cm^{-1} bands most likely originate from the E_g bond-bending mode of Te_6 similar to the $102\text{--}108\text{ cm}^{-1}$ bands of Se_6 in the MOR-Se RS. The $83\text{--}89\text{ cm}^{-1}$ doublet in the MOR-Te RS is similar to the $134\text{--}141\text{ cm}^{-1}$ one in the MOR-Se RS. It can be assigned to the mixed A_{1g} and A_{2u} bond-bending modes of Te_6 . The bond-bending modes of Te_6 are active in the **aa**- and **cc**-polarization configurations, while they are inactive in the **bb**-configuration, which proves the orientation of the rings with their three-fold axes along the **b**-axis of MOR. The DFT-computed frequencies of the Te_6 bond-bending modes 58.7 cm^{-1} (E_g), 80 cm^{-1} (A_{1g}) and 90.9 cm^{-1} (A_{2u}) are in good agreement with the experimental values.

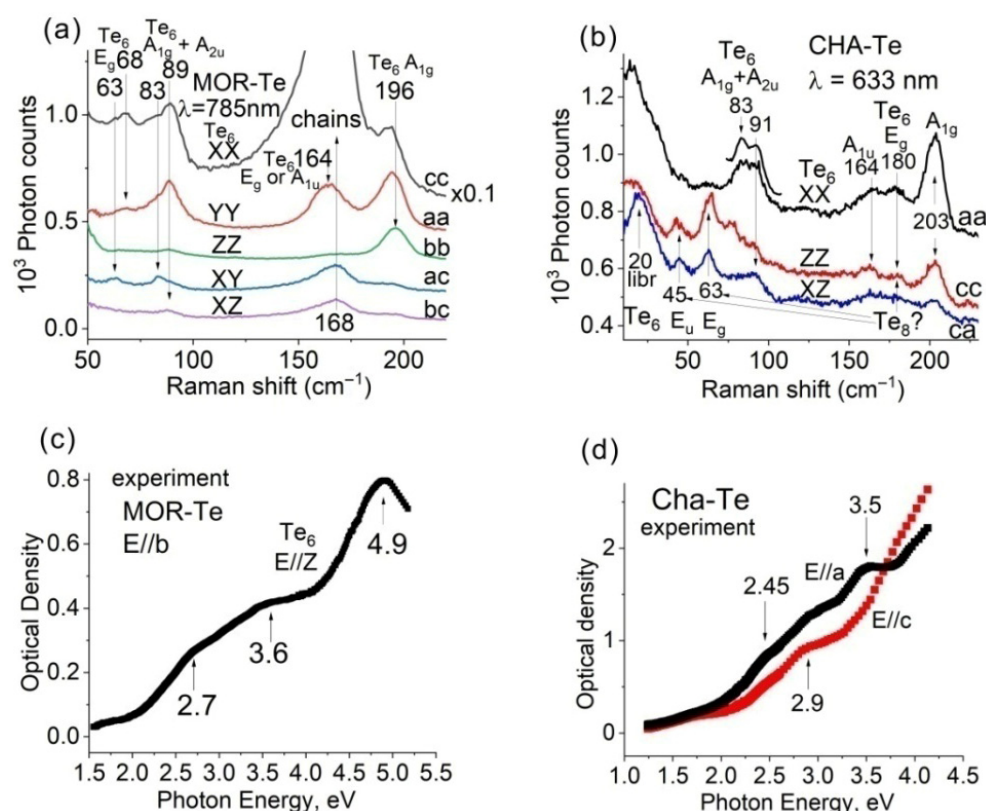


Figure 10. Experimental RS of MOR-Te (a) and CHA-Te (b) for different polarization configurations; experimental OAS of MOR-Te for E//b (c) and CHA-Te for E//a (black) and E//c (red) (d).

The A_{1g} bond-stretching mode band of Te_6 at $\sim 196\text{ cm}^{-1}$ in the MOR-Te RS is similar to the analogous band of Se_6 at $\sim 274\text{ cm}^{-1}$ in the MOR-Se RS. It is active in the **aa**-, **bb**- and **cc**-polarization configurations. The DFT-computed unscaled frequency 192.7 cm^{-1} of this mode nearly coincides with the experimental value. Another bond-stretching mode band of Te_6 at $\sim 164\text{ cm}^{-1}$ is observed in the **aa**-spectrum of MOR-Te. The band is also active in the **cc**-configuration, but it is overshadowed by the strong Te chain band at $\sim 168\text{ cm}^{-1}$. The asymmetry of the $\sim 168\text{ cm}^{-1}$ band, with a low-frequency shoulder, supports this assignment. The 164 cm^{-1} band can be attributed to the E_g or A_{1u} modes of Te_6 . The DFT-computed frequencies of the corresponding modes are 186.7 cm^{-1} and 168.5 cm^{-1} . The experimental polarization dependence of the 164 cm^{-1} band intensity is in good agreement with the theoretical E_g mode, while its frequency better matches the theoretical A_{1u} mode.

One may assume that Te_6 rings can be formed in CHA cavities similar to Se_6 rings. Indeed, we observe several bands in the RS **aa** spectrum of CHA-Te (Figure 10b), which

can be attributed to Te_6 . The $83\text{--}91\text{ cm}^{-1}$ doublet can be assigned to the mixed A_{1g} and A_{2u} bond-bending modes of Te_6 . The strong 203 cm^{-1} band most likely originates from the A_{1g} bond-stretching mode, while the 164 cm^{-1} and 180 cm^{-1} bands can be assigned to the A_{1u} and E_g bond-stretching modes, respectively. The high frequency of the 203 cm^{-1} band is associated with significant compression of the ring in the CHA cavity. In contrast to the Se_6 ring in the CHA cavity, the Te_6 ring clearly demonstrates its structural distortion with its symmetry reduction. The bond-bending-mode mixing reveals this. The corresponding $83\text{--}91\text{ cm}^{-1}$ doublet is inactive in the *cc* spectrum, indicating that the ring is oriented with its three-fold axis along the *c*-axis of CHA. The A_{1g} bond-stretching-mode band at $\sim 203\text{ cm}^{-1}$ weakens in the *cc* spectrum compared to the *aa* spectrum but remains observable. This observation is also compatible with the Te_6 ring orientation with its major axis along the *c*-axis of CHA.

Two distinct bands at $\sim 45\text{ cm}^{-1}$ and $\sim 63\text{ cm}^{-1}$ are observed in the *cc* and *ca* spectra of CHA-Te. Their frequencies suggest that the bands can be assigned to the E_u and E_g bond-bending modes of Te_6 , respectively. However, their polarization dependencies are challenging to interpret. Theoretically, the E_g mode should be active in the *aa* spectrum and inactive in the *cc* spectrum. We assume that the structural distortion is significant. Therefore, the selection rules can be strongly affected. However, we can also consider another possibility. The CHA cavity is able to accommodate a Te_8 ring with its *XY* plane in the *ac* plane of the zeolite. In this case, the $\sim 45\text{ cm}^{-1}$ and $\sim 63\text{ cm}^{-1}$ bands may originate from the E_2 and A_1 bond-bending modes of Te_8 .

OAS of MOR-Te *E//b* (Figure 10c) and CHA-Te (Figure 10d) display features of Te_6 . The MOR-Te OAS shows three bands at $\sim 2.7\text{ eV}$, $\sim 3.6\text{ eV}$ and $\sim 4.9\text{ eV}$. Theoretical calculations suggest *E//Z* allowed transitions at 2.91 eV, 3.2 eV, 3.54 eV and 5.14 eV. The 2.91 eV and 5.14 eV bands are clearly seen in the DFT-computed *E//Z* OAS of Te_6 (Figure 8c). We attribute the experimental $\sim 2.7\text{ eV}$ and $\sim 4.9\text{ eV}$ bands to the 2.91 eV and 5.14 eV transitions of Te_6 , respectively. The 3.2 eV and 3.54 eV *E//Z* allowed electron transitions have lower oscillator strengths and are not seen in the theoretical spectrum. However, they may be enhanced due to structural distortions of Te_6 . Therefore, we tentatively assign the observed $\sim 3.6\text{ eV}$ band to the enhanced 3.54 eV transition. On the other hand, the *E//X*-allowed transitions at 3.72 eV can also contribute to the observed $\sim 3.6\text{ eV}$ band of MOR-Te because the selection rules of Te_6 can be strongly disturbed.

CHA-Te OAS display features at $\sim 2.45\text{ eV}$, $\sim 2.9\text{ eV}$ and 3.5 eV , which can be attributed to Te_6 . Indeed, the $\sim 2.45\text{ eV}$ band energy is in good agreement with the lowest-energy forbidden transitions of Te_6 at 2.56 eV (E_g) and 2.62 eV (A_{2g}). These transitions can be activated by antisymmetric ring vibrations, similar to those of Se_6 considered in the previous sections. Additionally, as mentioned above, the Te_6 ring in CHA-Te is strongly compressed, which may lead to noticeable shifts of the low-energy electron transitions. Both allowed 2.96 eV *E//X* and 2.91 eV *E//Z* transitions of Te_6 can contribute to the experimentally observed feature of CHA-Te at $\sim 2.9\text{ eV}$. The third band at $\sim 3.5\text{ eV}$, clearly observed in the *E//a* spectrum of CHA-Te, can be associated with the allowed 3.72 eV *E//X* transition.

Interestingly, the *E//c* absorption of CHA-Te becomes stronger than the *E//a* absorption at energies above 3.7 eV. One possible explanation is a strong in-plane compression of Te_6 , which may enhance the *E//Z* absorption of the molecule. Indeed, a very much anisotropic 2D-like Te_6 ring can convert into more or less 3D-like cluster due to the compression. Another possibility is a contribution from Te_8 absorption. As mentioned above, if Te_8 exists in CHA-Te, the molecule is most likely oriented in the *ac* plane of CHA. Therefore, the *E//X* absorption of Te_8 , which dominates over its *E//Z* absorption, likely contributes to the *E//c* absorption of CHA-Te.

To summarize this section, Te_8 rings are formed in the LTA large cavities. The Te_8 rings are oriented such that their four-fold axes align with the LTA four-fold axes. Experimental Raman frequencies and intensities are found to be in good agreement with DFT-computed ones for both bond-bending and bond-stretching modes of Te_8 rings. The observed splitting of the Te_8 bond-bending modes suggests the reduction of the ring D_{4d} symmetry in the LTA cavity. The bond-stretching modes exhibit mixing due to the reduced symmetry of the rings and the essential anharmonicity of their vibrations. The DFT-computed OAS of Te_8 shows remarkably good agreement with the experimental OAS of LTA-Te. Te_8 rings are also formed in the AFI channels, with their four-fold axes oriented along the channel. Te_6 rings are formed in MOR channels and CHA cavities. Their experimental RS and OAS show good agreement with DFT-computed ones. CHA-Te RS and OAS suggest the existence of some amount of Te_8 rings in CHA cavities. The structural parameters obtained from our DFT calculations: Te_6 $r = 272$ pm, $\phi = 100.5^\circ$ and those of Te_8 $r = 271$ pm, $\phi = 105.8^\circ$. These values differ from previously reported DFT results: Te_6 $r = 275$ pm, $\phi = 101^\circ$ and Te_8 $r = 274$ – 275 pm, $\phi = 106.3^\circ$ [54]; Te_8 $r = 274$ – 275 pm, $\phi = 106.3^\circ$ [57].

3.5. Interaction of the Chalcogen Rings with Light and Photostructural Effects

All chalcogen ring molecules considered above display strong absorption bands in the UV. Therefore, one can expect photo-induced effects when the molecules are irradiated with UV light. A number of studies have reported the UV-light-induced conversion of S_8 rings to sulfur chains in liquid sulfur [58–60]. Pulsed laser light with a wavelength of 355 nm was used in the experiment [58] and produced photo-induced polymerization of liquid sulfur. An ab initio molecular dynamics simulation suggested rapid ring opening due to a photo-induced electronic transition [59]. A more comprehensive study using a combination of time-dependent DFT and the similarity-transformed equation-of-motion coupled cluster (STEOM-CCSD) method [60] showed the importance of triplet states in the photo-induced S_8 bond breaking.

Figure 11 demonstrates photo-induced effects in the RS of several our samples, which were recorded with continuous laser excitation at a wavelength of 364 nm. Figure 11a shows the **bb**-spectrum of MOR-S. In addition to the S_8 and S_6 bands analogous to those observed in the **bb**-spectrum excited with $\lambda = 514.5$ nm [Figure 2d], one can see the bands at ~ 582 cm^{-1} and ~ 1164 cm^{-1} . We assign the ~ 582 cm^{-1} band to the S_2^- fundamental while the ~ 1164 cm^{-1} band to its overtone. For reference, see, for example the work in [61], where S_2^- fundamentals in ultramarine were observed at 586–590 cm^{-1} at room temperature. The S_2^- bands appear in the MOR-S RS as a result of the S_8 and S_6 ring breaking under 364 nm light irradiation.

Similar bands are observed in the LTA-S RS at ~ 583 cm^{-1} and ~ 1165 cm^{-1} [Figure 11b]. Additionally, a broad S_4^{2-} band at ~ 446 cm^{-1} , similar to the 454 cm^{-1} band of S_4^{2-} [62], is observed in the LTA-S RS excited with 364 nm light. The S_8 ring-breaking mechanism is likely the same as that proposed for liquid sulfur polymerization. The difference in the final result is associated with spatial restriction and the zeolite environment, which provides extra electrons. Therefore, S_2^- and S_4^{2-} anions are formed in the zeolites.

We should note that the S_8 absorption at the 364 nm wavelength in both MOR-S and LTA-S is rather weak since the corresponding photon energy of 3.41 eV is well below the first allowed absorption band of S_8 or S_6 (Figure 3). The 364 nm absorption in fact corresponds to the absorption tails of S rings that arise from forbidden electronic transitions, in particular triplet excitations. In contrast, the Se_8 and Se_{12} rings show absorption at this wavelength due to relatively strong allowed electronic transitions. These rings also display fragmentation effects under 364 nm light irradiation. The neutral Se_2 band at ~ 382 cm^{-1} and its overtone at ~ 762 cm^{-1} are observed in the AFI-Se(HD)

aa spectrum excited with 364 nm light (Figure 11c). Similar bands at lower frequencies $\sim 377\text{ cm}^{-1}$ and $\sim 750\text{ cm}^{-1}$ are present in the RS of LTA-Se [Figure 11d]. Both $\sim 382\text{ cm}^{-1}$ and $\sim 377\text{ cm}^{-1}$ frequencies are close to the $\sim 386\text{ cm}^{-1}$ fundamental frequency of neutral Se_2 [63]. One can expect that Se_2^- anions rather than neutral Se_2 molecules, to be stabilized in the zeolites. However, with this assumption, we should expect the same effect as was observed in sodalite with selenium (SOD-Se) under 364 nm irradiation [63], where Se_2^- anions with the absorption band at $\sim 3.4\text{ eV}$ [64] were photo-ionized due to perfect resonance with 364 nm light. Thus, neutral Se_2 molecules were formed. In fact, LTA-Se with 17 Se atoms per simplified unit cell case [16] is very similar to the SOD-Se case since both samples initially contain Se_2^- anions.

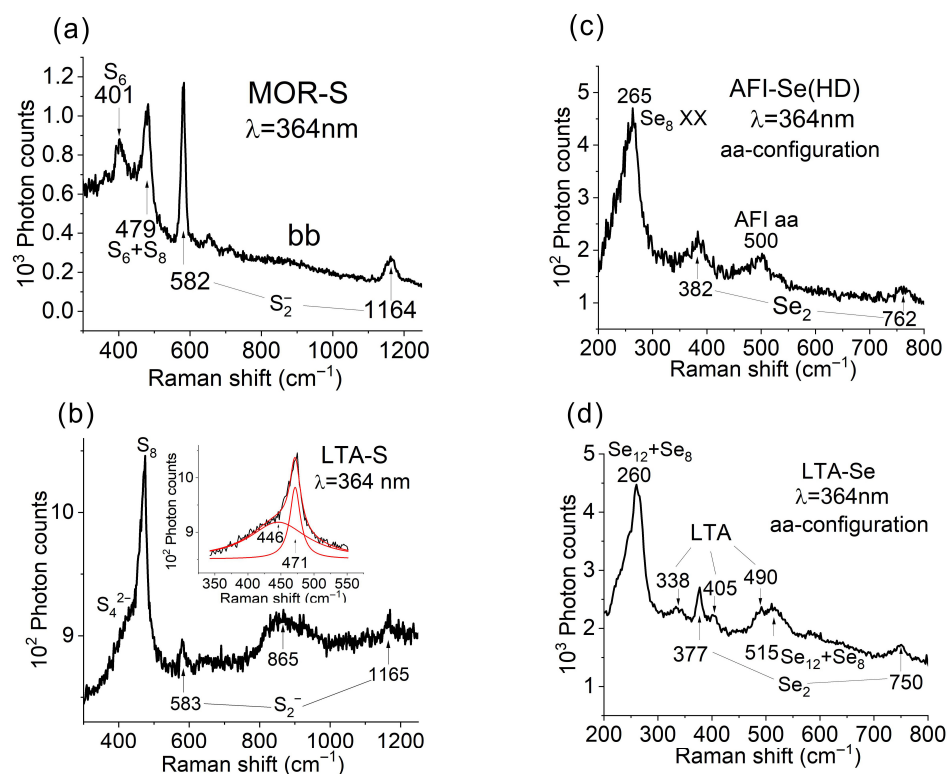


Figure 11. Experimental RS obtained with the 364 nm wavelength excitation of MOR-S (a), LTA-S (b), AFI-Se(HD) (c) and LTA-Se (d).

Let us consider photoinduced effects on chalcogen rings under visible light irradiation. Importantly, Se_6 interacts strongly with light at photon energies much lower than its formal electronic energy gap of $\sim 3.2\text{ eV}$ since the absorption bands are rather broad and triplet excitations [Supplementary Materials Table S7a] may contribute.

Figure 12a clearly demonstrates a laser-induced heating effect on Se_6 in CHA-Se at the laser excitation wavelength of 514.5 nm, corresponding to a photon energy of $\sim 2.41\text{ eV}$. Indeed, the A_{1g} bond-stretching mode frequency decreases from $\sim 272.5\text{ cm}^{-1}$ to $\sim 268.5\text{ cm}^{-1}$ as the excitation laser power (P) increases from $\sim 0.25\text{ mW}$ to $\sim 1.5\text{ mW}$. The heating effect causes even stronger frequency decrease of the E_g (or maybe A_{1u}) bond-stretching mode from $\sim 219.5\text{ cm}^{-1}$ to $\sim 211.5\text{ cm}^{-1}$ over the same increase in laser power (Figure 12b). The laser-induced heating depends on the light polarization. The heating is stronger for the $E//X$ than for $E//Z$ polarization (Figure 12a, black and violet curves).

Surprisingly, the bond-bending mode frequencies slightly increase as the laser power increases up to $\sim 0.5\text{ mW}$, then slowly decrease with a further increase in power (Figure 12b). The effect may be associated with the Se_6 ring confinement in the CHA cavity, which causes bond angle contraction and an increase of the corresponding frequencies with a

slight heating, when the bond lengths become larger. A similar effect is observed upon decreasing the temperature to $T \sim 77$ K [Figure 12c]. The bond-bending mode frequencies of ~ 103 cm^{-1} and ~ 136 cm^{-1} at $T \sim 77$ K are lower than those of ~ 105 cm^{-1} and ~ 137 cm^{-1} at an ambient temperature of ~ 300 K. (In this case, the ring temperature is slightly higher due to laser-induced heating). We also observe a non-thermal photoinduced effect in the low-temperature RS of CHA-Se, namely, the band at ~ 309 cm^{-1} and its overtone at ~ 617 cm^{-1} appear in the CHA-Se spectrum at $T \sim 77$ K. Most likely, the bands belong to Se_2^- anions. This may be associated with photoinduced fragmentation of Se_6 to three Se_2 molecules trapped in chabazite in the form of Se_2^- anions.

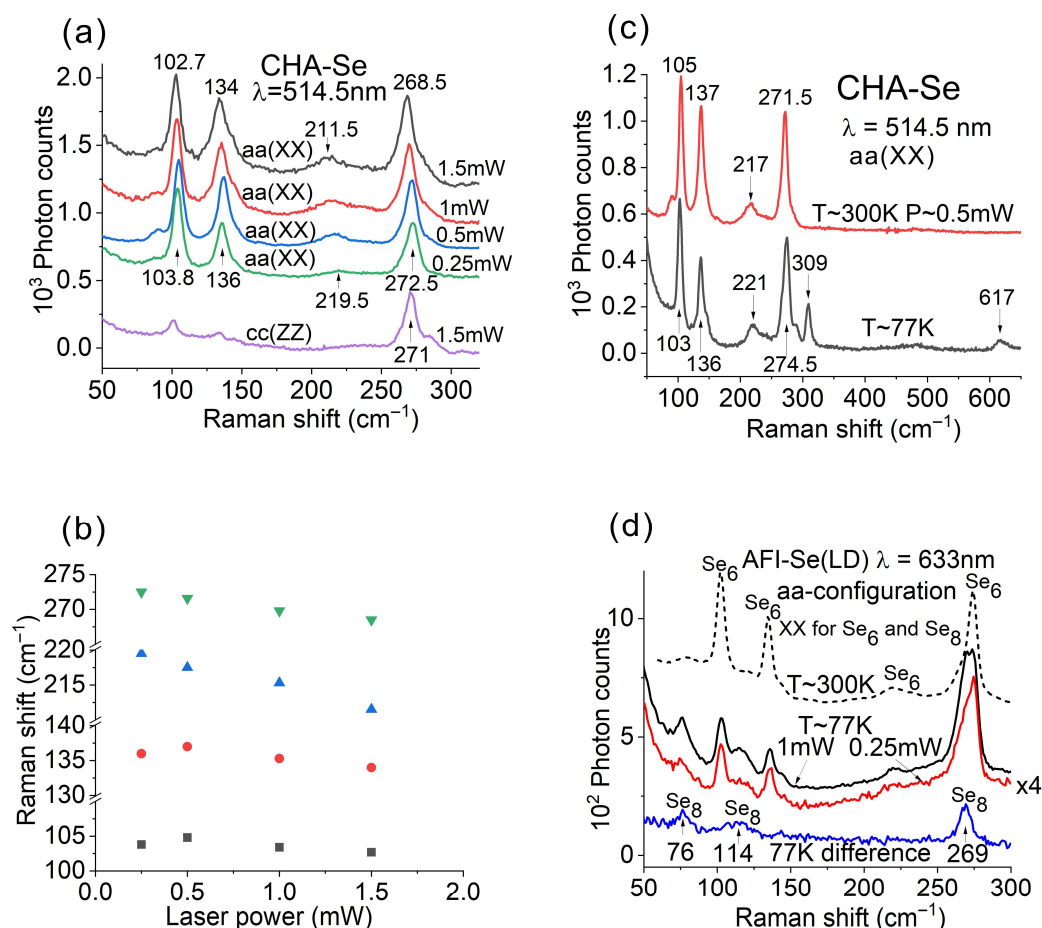


Figure 12. (a) RS of CHA-Se at $\lambda = 514.5$ nm at different excitation powers (P) for aa -configuration (black, red, blue and green curves) and for cc -configuration at $P \sim 1.5$ mW (violet curve); (b) A_{1g} bond-stretching-mode Raman band position dependency on P ; (c) CHA-Se RS at $T \sim 77$ K (black curve) and at $T \sim 300$ K at $P \sim 0.5$ mW (red curve); (d) RS of AFI-Se(LD) in the aa -configuration at $\lambda = 633$ nm at $T \sim 77$ K with $P \sim 1$ mW (black curve), $P \sim 0.25$ mW (red curve) and their difference (blue curve), dashed line showing corresponding $T \sim 300$ K spectrum for reference.

Figure 12d demonstrates a photoinduced effect with an even lower photon energy of ~ 1.96 eV corresponding to a 633 nm laser line. AFI-Se(LD) Raman aa -spectra were recorded at $T \sim 77$ K with excitation laser powers of ~ 0.25 mW (red curve) and ~ 1 mW (black curve). Both spectra display additional bands compared to the room-temperature spectrum, which contains nearly exclusively Se_6 bands [dashed curve, see also Figure 4c]. The additional bands are more pronounced in the spectrum recorded with the ~ 1 mW laser power. The differential spectrum between the normalized ~ 1 mW and ~ 0.25 mW spectra is shown as a blue curve in Figure 12d. Three characteristic bands of the Se_8 ring at frequencies of ~ 76 , ~ 114 and ~ 269 cm^{-1} are clearly recognized. Thus, in the relatively large space of the AFI

channels, more stable Se_8 rings are formed at the expense of the less stable Se_6 rings due to photoinduced fragmentation of Se_6 . We should note that prolonged illumination of AFI-Se(LD) with ~ 0.25 mW 633 nm light causes the same effect as the increase in the laser power.

Interestingly, we do not observe any photostructural effects for Se_8 and Se_{12} in LTA-Se at the low-power excitations $P \leq 1$ mW with the laser wavelengths of 514.5 nm or 633 nm, either at $T \sim 300$ K or $T \sim 77$ K. (We do not consider here the thermal destruction of Se_{12} due to photoinduced heating at higher 514.5 nm laser powers [33]). One reason for this is the higher absorption of Se_6 compared to Se_8 and Se_{12} within the 1.96–2.41 eV photon energy range. This is confirmed by the DFT-computed energy gaps of Se_6 , Se_8 and Se_{12} [Figure 13a] taking into account allowed and forbidden singlet excitations [Supplementary Materials Tables S7, S10 and S11] as well as triplet excitations [Supplementary Materials Tables S7a, S10a and S11a]. We observe that the Se_6 energy gap is smaller than those of Se_8 and Se_{12} . The computed energy gap of ~ 2.67 eV for Se_6 triplet excitations is rather close to the 1.96–2.41 eV photon energy range, where the photostructural effects for Se_6 are observed. Another contributing factor is the low stability of Se_6 in the excited state.

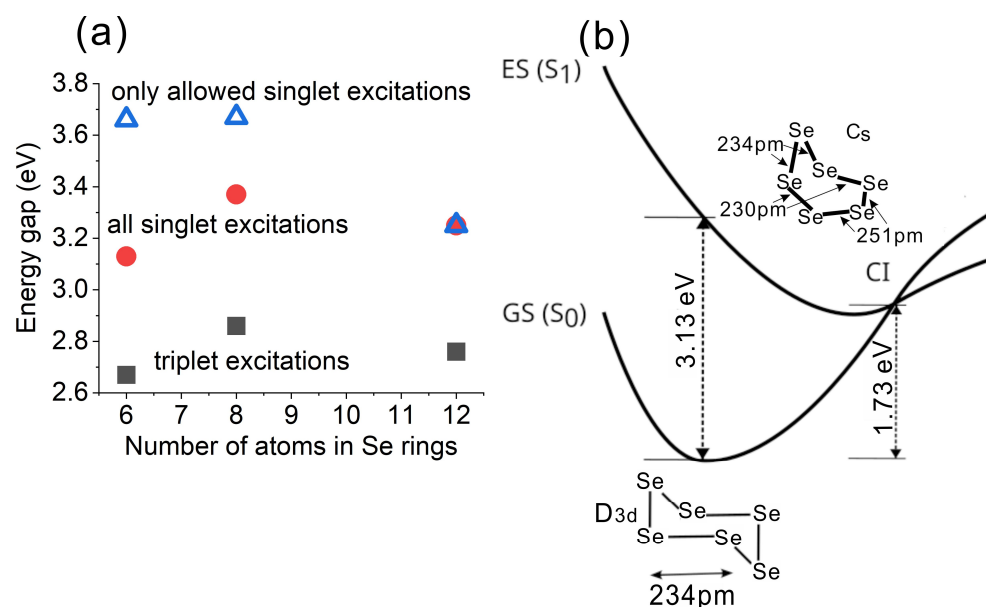


Figure 13. (a) DFT-computed energy gaps of Se rings vs. the number of Se atoms in the ring for triplet excitations (black squares), for all singlet excitations (red circles) and only allowed singlet excitations (blue triangles); (b) schematic representation of potential energy surfaces of the ground state (GS, S_0) and the lowest singlet excited state (ES, S_1) of the Se_6 ring from DFT calculations. The approximate conical intersection (CI, S_0/S_1) lies about 1.73 eV above the S_0 minimum. The horizontal axis denotes schematically the configuration coordinate for CI- S_0 relaxation. The S_0 minimum energy structure (D_{3d}) and the approximate CI (C_s) are annotated with their bond lengths.

Let us consider possible structural effects for Se_6 in its excited state. While our methods do not allow the calculation of relativistic effects required for accurate simulation of the intensities of triplet excitations, such as the ~ 2.67 eV excitation, we consider the lowest forbidden singlet transition at ~ 3.13 eV (Figure 13b), which can be activated via electron-vibration coupling. The important point is that the excited states of the $\text{Se}_6(D_{3d})$ are energetically very close to those of some other, less-stable forms of Se_6 .

Figure 13b demonstrates a conical intersection (CI) between the potential energy surfaces of the ground state (GS, S_0) and the lowest singlet excited state (ES, S_1) of the Se_6 molecule. The DFT calculations were performed using the PBE0 functional [20] and the

def2-TZVP basis set [22]. The approximate conical intersection (CI, S_0/S_1) was obtained by minimizing the S_0 – S_1 energy gap. The computed energy differences do not include zero-point vibrational corrections. Se_6 with the C_s structure, corresponding to CI, is shown in Figure 13b inset.

The $\text{Se}_6(C_s)$ structure is unstable. It can disintegrate, for example, into $\text{Se}_4 + \text{Se}_2$. The appearance of Se_2^- in CHA-Se after 514.5 nm light irradiation and an increase in amount of Se_8 in AFI-Se(LD) due to 633 nm light exposure confirm this. Importantly, we observe these effects at $T \sim 77$ K and do not observe them at $T \sim 300$ K. Most likely, relaxation of the photo-excited $\text{Se}_6(D_{3d})$ to its ground state at $T \sim 300$ K occurs via vibrations without conversion to unstable forms of Se_6 . However, at $T \sim 77$ K, vibrational relaxation is not sufficiently effective. Conversion of $\text{Se}_6(D_{3d})$ into unstable forms, such as $\text{Se}_6(C_s)$, followed by disintegration, becomes much more likely. This is why we observe formation of Se_2^- in irradiated CHA-Se and increase of amount of Se_8 in irradiated AFI-Se(LD) at $T \sim 77$ K.

To summarize this section, we observe a rather strong interaction of the zeolite-confined chalcogen rings with light. The interaction is very strong in case of the UV light exposure. Under the 364 nm wavelength light irradiation, S_8 and $\text{Se}_8/\text{Se}_{12}$ rings disintegrate producing mainly diatomic molecules, S_4^{2-} also being identified in case of LTA-S. Under normal conditions, at room temperature and with low-power visible light excitation, all chalcogen rings exhibit ordinary heating depending on their absorbance. A peculiarity of heating a molecule in the restricted space of a zeolite cavity is that the molecule bond lengths increase while bond angles decrease. Correspondingly, the molecule bond-stretching mode frequencies decrease while the bond-bending mode frequencies increase. Se_6 rings in CHA-Se clearly demonstrate this. At $T \sim 77$ K with no heating effect, the Se_6 rings disintegrate under rather low photon energy (~ 1.96 eV and ~ 2.41 eV) light irradiation. This is associated with (1) their non-zero absorption of Se_6 in this spectral range due to their triplet excitations, and (2) conversion of the stable form of $\text{Se}_6(D_{3d})$ in the excited state to unstable ones. An example of conical intersection producing $\text{Se}_6(C_s)$ is also presented.

4. Conclusions

S, Se and Te ring clusters were examined experimentally using RS and OAS as well as theoretically using DFT. Incorporation of the rings into free spaces of zeolite single crystals (LTA, MOR, AFI, CHA) allowed us to study the polarized RS and OAS of oriented rings and compare them with the corresponding spectra computed using DFT. Firstly, we determined structural parameters of the rings [Supplementary Materials Table S1], which appeared to be close to the known experimental values for S_8 (our $r = 204.7$ pm, $\phi = 108.4^\circ$ vs. $r = 204.6$ pm, $\phi = 108.2^\circ$ [65]), Se_6 [our $r = 233.6$ pm, $\phi = 101.4^\circ$ vs. $r = 238$ pm, $\phi = 101.1^\circ$ [44] (the experimental value of 238 pm in rhombohedral crystal is slightly larger than that of individual Se_6)] and Se_8 (our $r = 232.7$ pm, $\phi = 106.9^\circ$ vs. $r = 233.4$ pm, $\phi = 105.8^\circ$ [66]). Regarding RS and OAS, we have found a very reasonable agreement between the experimental and theoretical spectra of S_8 , Se_6 , Se_8 , Se_{12} , Te_6 and Te_8 rings. The agreement is nearly perfect for the bond-bending mode Raman frequencies and intensities. However, the computed bond-stretching mode frequencies of S and Se rings are overestimated compared with the experimental values because of the absence of anharmonic effects. Scaling factors [36] improve the agreement. No significant discrepancy occurs for Te rings. DFT-computed OAS of the S_8 , Se_6 , Se_8 , Se_{12} , Te_6 and Te_8 rings generally show good agreement with experimental results. However, experimental OAS show some features with photon energies lower than those of the computed allowed singlet electron transitions. We demonstrate activation of the low-energy forbidden singlet electron transitions of Se_6 at 3.1–3.4 eV due to interaction of electrons with antisymmetric vibrational modes, the energy of the first allowed singlet transition being ~ 3.66 eV. Even a lower energy of ~ 2.67 eV is suggested by the DFT-computed

triplet electron excitation of Se₆. Experimentally, no distinct Se₆ absorption band was observed; only a tail appeared in this spectral range. Photostructural effects due to the exposure of Se₆ to ~1.96 eV and ~2.41 eV light at *T* ~77 K are observed. Conversion of the stable form of Se₆(D_{3d}) in the excited state to unstable ones likely follows a complex mechanism. An example of a conical intersection producing Se₆(C_s) is considered. Importantly, at the same conditions, no such effect is observed for Se₈, which possesses a larger triplet and singlet energy gap than Se₆. Since Se₈ is a building block of α-Se [67], we can conclude that the photostructural effects in this material, induced by the 1.96–2.41 eV light, are not related to individual Se₈ rings, although rings interacting with neighboring rings or chains, and thus exhibiting a reduced energy gap, may be responsible for these effects. In contrast, individual Se₈ and S₈ rings display fragmentation due to exposure to 364 nm (3.41 eV) UV light at room temperature. This photon energy corresponds to the Se₈ singlet excitations and S₈ triplet excitations below the singlet electron transition energies. Conical intersections can be responsible for the effects.

Taking into account recent publications on intramolecular dispersion forces in large chalcogen rings [68], infrared spectra of sulfur allotropes, their fragmentation and presence in the interstellar space and atmosphere of planets [69], lone-pair-enabled polymorphism and photostructural changes in chalcogenide glasses [70], structural and optical properties of chalcogen chains and nanowires [71–77], etc., we consider our work as an important contribution to this rapidly developing field of science. Applications in medicine hold particular promise for novel materials like MXenes [78] and Se nanoparticles [79] due to their antibacterial properties.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/analytica7020032/s1>.

Author Contributions: Conceptualization, V.V.P. and D.R.; methodology, V.V.P. and D.R.; software, D.R.; validation, V.V.P. and D.R.; formal analysis, V.V.P. and D.R. investigation, V.V.P. and D.R.; resources, V.V.P.; data curation, V.V.P.; writing—original draft preparation, V.V.P.; writing—review and editing, V.V.P. and D.R.; visualization, V.V.P. and D.R.; supervision, V.V.P.; project administration, V.V.P. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: The data are available on request.

Acknowledgments: We thank V.P. Petranovskii, S.G. Romanov, S.V. Kholodkevich, V.V. Zhuravlev, Y.A. Barnakov and A.V. Fokin for sample preparation.

Conflicts of Interest: D.R. is an employee of Dayhoff Labs Inc., 1 Mifflin Place, Suite 419, Cambridge, MA 02138, USA.

Abbreviations

The following abbreviations are used in this manuscript:

RS	Raman spectra
OAS	Optical absorption spectra
LTA	Linde type zeolite A
MOR	Mordenite
CHA	Chabazite
AFI	AlPO ₄ -5
DFT	Density functional theory
CI	Conical intersection

References

- Smith, W. Effect of light on selenium during the passage of electric current. *Nature* **1873**, *7*, 303. [\[CrossRef\]](#)
- Adams, W.G.; Day, R.E. The action of light on selenium. *Proc. R. Soc.* **1876**, *25*, 113. [\[CrossRef\]](#)
- Hadar, I.; Song, T.-B.; Ke, W.; Kanatzidis, M.G. Modern Processing and Insights on Selenium Solar Cells: The World's First Photovoltaic Device. *Adv. Energy Mater.* **2019**, *9*, 1802766. [\[CrossRef\]](#)
- Zhang, H.; Liu, C.-X.; Qi, X.-L.; Dai, X.; Fang, Z.; Zhang, S.-C. Topological insulators in Bi₂Se₃, Bi₂Te₃ and Sb₂Te₃ with a single Dirac cone on the surface. *Nat. Phys.* **2009**, *5*, 438–442. [\[CrossRef\]](#)
- Cao, T.; Wang, R.; Simpson, R.E.; Li, G. Photonic Ge-Sb-Te phase change metamaterials and their applications. *Prog. Quantum Electron.* **2020**, *74*, 100299. [\[CrossRef\]](#)
- Reznik, A.; Baranovskii, S.D.; Rubel, O.; Juska, G.; Kasap, S.O.; Ohkawa, Y.; Tanioka, K.; Rowlands, J.A. Avalanche multiplication phenomenon in amorphous semiconductors: Amorphous selenium versus hydrogenated amorphous silicon. *J. Appl. Phys.* **2007**, *102*, 053711. [\[CrossRef\]](#)
- Mendes, T.C.; Nguyen, C.; Barlow, A.J.; Cherepanov, P.; Forsyth, M.; Howlett, P.C.; MacFarlane, D.R. A safe Li-Se battery in an ionic liquid-based electrolyte operating at 25–70 °C by using a N,S,O tri-doped mesoporous carbon host material. *Sustain. Energy Fuels* **2020**, *4*, 2322–2332. [\[CrossRef\]](#)
- Mal, J.; Veneman, W.J.; Nancharaiyah, Y.V.; van Hullebusch, E.D.; Peijnenburg, W.J.G.M.; Vijver, M.G.; Lens, P.N.L. A comparison of fate and toxicity of selenite, biogenically and chemically synthesized selenium nanoparticles to zebrafish (*Danio rerio*) embryogenesis. *Nanotoxicology* **2017**, *11*, 87–97. [\[CrossRef\]](#) [\[PubMed\]](#)
- Elliott, S.R. A unified model for reversible photostructural effects in chalcogenide glasses. *J. Non-Cryst. Sol.* **1986**, *81*, 71–98. [\[CrossRef\]](#)
- Poborchii, V.V.; Kolobov, A.V.; Tanaka, K. Photomelting of selenium at low temperature. *Appl. Phys. Lett.* **1999**, *74*, 215–217. [\[CrossRef\]](#)
- Franzke, Y.J.; Holzer, C.; Andersen, J.H.; Begušić, T.; Bruder, F.; Coriani, S.; Sala, F.D.; Fabiano, E.; Fedotov, D.A.; Fürst, S.; et al. TURBOMOLE: Today and Tomorrow. *J. Chem. Theory Comput.* **2023**, *19*, 6859–6890. [\[CrossRef\]](#) [\[PubMed\]](#)
- Seff, K. The Crystal Structure of a Sulfur Sorption Complex of Zeolite 4A. *J. Phys. Chem.* **1972**, *76*, 2601–2605. [\[CrossRef\]](#)
- Bogomolov, V.N. Liquids in ultrathin channels (Filament and cluster crystals). *Usp. Fiz. Nauk.* **1978**, *124*, 171–182. [\[CrossRef\]](#)
- Poborchii, V.V.; Fokin, A.V.; Shklyayev, A.A. Optical properties of extreme tellurium nanowires formed in subnanometer-diameter channels. *Nanoscale Adv.* **2023**, *5*, 220–227. [\[CrossRef\]](#)
- Poborchii, V.V.; Fokin, A.V. Raman and optical absorption spectra of oriented Se₈ and Se₁₂ rings formed in zeolites: Dependence on the Se loading density. *Microporous Mesoporous Mater.* **2022**, *338*, 111954. [\[CrossRef\]](#)
- Poborchii, V.V.; Petranovskii, V.P.; Glukhov, I.A.; Fotiadi, A.A. Optical study of oriented double-Se₈-ring clusters and luminescent Se₂[−] anions in LTA at extremely high selenium loading density. *Microporous Mesoporous Mater.* **2023**, *348*, 112395. [\[CrossRef\]](#)
- Poborchii, V.V.; Petranovskii, V.; Glukhov, I.A.; Fotiadi, A.A. Single crystal polarization-orientation Raman spectroscopy of zeolite LTA with confined S₃[−] anions—High dielectric constant nanoporous material. *Mater. Chem. Phys.* **2024**, *316*, 129103. [\[CrossRef\]](#)
- Balasubramani, S.G.; Chen, G.P.; Coriani, S.; Diedenhofen, M.; Frank, M.S.; Franzke, Y.J.; Furche, F.; Grotjahn, R.; Harding, M.E.; Hättig, C.; et al. TURBOMOLE: Modular program suite for ab initio quantum-chemical and condensed matter simulations. *J. Chem. Phys.* **2020**, *152*, 184107. [\[CrossRef\]](#)
- Perdew, J.P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868. [\[CrossRef\]](#)
- Perdew, J.P.; Ernzerhof, M.; Burke, K. Rationale for mixing exact exchange with density functional approximations. *J. Chem. Phys.* **1996**, *105*, 9982–9985. [\[CrossRef\]](#)
- Eichkorn, K.; Treutler, O.; Öhm, H.; Häser, M.; Ahlrichs, R. Auxiliary Basis Sets to Approximate Coulomb Potentials. *Chem. Phys. Lett.* **1995**, *240*, 283–290, Erratum in *Chem. Phys. Lett.* **1995**, *242*, 652–660. [\[CrossRef\]](#)
- Weigend, F.; Ahlrichs, R. Balanced Basis Sets of Split Valence, Triple Zeta Valence and Quadruple Zeta Valence Quality for H to Rn: Design and Assessment of Accuracy. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305. [\[CrossRef\]](#)
- Weigend, F. Accurate Coulomb-fitting basis sets for H to Rn. *Phys. Chem. Chem. Phys.* **2006**, *8*, 1057–1065. [\[CrossRef\]](#)
- Peterson, K.A.; Figgen, D.; Goll, E.; Stoll, H.; Dolg, M. Systematically Convergent Basis Sets with Relativistic Pseudopotentials, II. Small-Core Pseudopotentials and Correlation Consistent Basis Sets for the Post- d Group 16–18 Elements. *J. Chem. Phys.* **2003**, *119*, 11113–11123. [\[CrossRef\]](#)
- Rappoport, D.; Furche, F. Lagrangian Approach to Molecular Vibrational Raman Intensities Using Time-Dependent Hybrid Density Functional Theory. *J. Chem. Phys.* **2007**, *126*, 201104. [\[CrossRef\]](#)
- Deglmann, P.; Furche, F.; Ahlrichs, R. An Efficient Implementation of Second Analytical Derivatives for Density Functional Methods. *Chem. Phys. Lett.* **2002**, *362*, 511–518. [\[CrossRef\]](#)
- Deglmann, P.; May, K.; Furche, F.; Ahlrichs, R. Nuclear Second Analytical Derivative Calculations Using Auxiliary Basis Set Expansions. *Chem. Phys. Lett.* **2004**, *384*, 103–107. [\[CrossRef\]](#)

28. Rappoport, D.; Furche, F. Property-Optimized Gaussian Basis Sets for Molecular Response Calculations. *J. Chem. Phys.* **2010**, *133*, 134105. [\[CrossRef\]](#)
29. Bauernschmitt, R.; Ahlrichs, R. Treatment of Electronic Excitations within the Adiabatic Approximation of Time Dependent Density Functional Theory. *Chem. Phys. Lett.* **1996**, *256*, 454–464. [\[CrossRef\]](#)
30. Bauernschmitt, R.; Häser, M.; Treutler, O.; Ahlrichs, R. Calculation of Excitation Energies within Time-Dependent Density Functional Theory Using Auxiliary Basis Set Expansions. *Chem. Phys. Lett.* **1997**, *264*, 573–578. [\[CrossRef\]](#)
31. Bogomolov, V.N.; Petranovskii, V.P.; Poborchii, V.V.; Kholodkevich, S.V. Absorption, Raman and ESR spectra and the dielectric permittivity of NaA-S cluster crystals. *Sov. Phys. Solid State* **1983**, *25*, 1415–1417; *Fiz. Tverd. Tela*, **1983**, *25*, 2466–2470.
32. Poborchii, V.V. Raman microprobe polarization measurements as a tool for studying the structure and orientation of molecules and clusters incorporated into cubic zeolites: S₈ and Se₁₂ rings in zeolite A. *J. Chem. Phys.* **2001**, *114*, 2707–2717. [\[CrossRef\]](#)
33. Poborchii, V.V. Raman spectra of sulfur, selenium or tellurium clusters confined in nano-cavities of zeolite A. *Solid State Commun.* **1998**, *107*, 513–518. [\[CrossRef\]](#)
34. Poborchii, V.V. Polarized Raman and optical absorption spectra of the mordenite single crystals containing sulphur, selenium or tellurium confined in the one-dimensional nanochannels. *Chem. Phys. Lett.* **1996**, *251*, 230–234. [\[CrossRef\]](#)
35. Scott, D.W.; McCollough, J.P.; Kruse, F.H. Vibrational Assignment and Force Constants of S₈ from a Normal-Coordinate Treatment. *J. Mol. Spec.* **1964**, *13*, 313–320. [\[CrossRef\]](#)
36. Tikhonov, D.S.; Gordiy, I.; Iakovlev, D.A.; Gorislav, A.A.; Kalinin, M.A.; Nikolenko, S.A.; Malaskeevich, K.M.; Yureva, K.; Matsokin, N.A.; Schnell, M. Harmonic scale factors of fundamental transitions for dispersion-corrected quantum chemical methods. *Chem. Phys. Chem.* **2024**, *25*, e202400547. [\[CrossRef\]](#)
37. Steudel, R.; Jensen, D.; Gobel, P. Optical Absorption Spectra of the Homocyclic Sulfur Molecules S_n (n = 6, 7, 8, 9, 10, 12, 15, 20) in Solution. *Ber. Bunsenges. Phys. Chem.* **1988**, *92*, 118–122. [\[CrossRef\]](#)
38. Datta, A. ACNDO/2 calculation of the electronic states of S₈, Se₄S₄ and Se₈. *J. Mol. Struct.* **1983**, *92*, 93–102. [\[CrossRef\]](#)
39. Jones, R.O.; Ballone, P. Density functional and Monte Carlo studies of sulfur. I. Structure and bonding in S_n rings and chains (n = 2–18). *J. Chem. Phys.* **2003**, *118*, 9257–9265. [\[CrossRef\]](#)
40. Millefiore, S.; Alparone, A. Ab initio study of the structure and polarizability of sulfur clusters, S_n (n = 2–12). *J. Phys. Chem. A* **2001**, *105*, 9489–9497. [\[CrossRef\]](#)
41. Poborchii, V.V. Oriented Se₆ ring clusters in zeolite single crystals: Polarized Raman microscopy, optical absorption spectra and photo-induced effects. *Microporous Mesoporous Mater.* **2020**, *308*, 110559. [\[CrossRef\]](#)
42. Poborchii, V.V.; Kolobov, A.V.; Oyanagi, H.; Romanov, S.G.; Tanaka, K. Structure of selenium incorporated into nanochannels of mordenite: Dependence on ion exchange and method of incorporation. *Chem. Phys. Lett.* **1997**, *280*, 10–16. [\[CrossRef\]](#)
43. Wirnsberger, G.; Fritzer, H.P.; Zink, R.; Popitsch, A.; Pillep, B.; Behrens, P. Isolated Se₆ Rings in the Voids of a Weakly Interacting, Electroneutral, and Crystalline SiO₂ Matrix: Combined Experimental and Theoretical Study. *J. Phys. Chem. B* **1999**, *103*, 5797–5801. [\[CrossRef\]](#)
44. Nagata, K.; Ishibashi, K.; Miyamoto, Y. Raman and infrared spectra of rhombohedral selenium. *Jap. J. Appl. Phys.* **1981**, *20*, 463–469. [\[CrossRef\]](#)
45. Hohl, D.; Jones, R.O.; Car, R.; Parrinello, M. The structure of selenium clusters—Se₃ to Se₈. *Chem. Phys. Lett.* **1987**, *139*, 540–545. [\[CrossRef\]](#)
46. Oligschleger, C.; Jones, R.O.; Reimann, S.M.; Schober, H.R. Model interatomic potential for simulations in selenium. *Phys. Rev. B* **1996**, *53*, 6165–6173. [\[CrossRef\]](#)
47. Demkov, A.A.; Sankey, O.F. Theory of zeolite supralattices: Se in zeolite Linde type A. *J. Phys. Condens. Matter* **2001**, *13*, 10433–10457. [\[CrossRef\]](#)
48. Goldbach, A.; Sabounji, M.-L. Selenium/zeolite Y nanocomposites. *Acc. Chem. Res.* **2005**, *38*, 705–712. [\[CrossRef\]](#) [\[PubMed\]](#)
49. Goldbach, A.; Iton, L.; Sabounji, M.-L. On the formation of isolated Se₈ rings in zeolites. *Chem. Phys. Lett.* **1997**, *281*, 69–73. [\[CrossRef\]](#)
50. Poborchii, V.V.; Kolobov, A.V.; Caro, J.; Zhuravlev, V.V.; Tanaka, K. Polarized Raman spectra of selenium species confined in nanochannels of AlPO₄-5 single crystals. *Chem. Phys. Lett.* **1997**, *280*, 17–23. [\[CrossRef\]](#)
51. Poborchii, V.V.; Kolobov, A.V.; Caro, J.; Zhuravlev, V.V.; Tanaka, K. Dynamics of Single Selenium Chains Confined in One-Dimensional Nanochannels of AlPO₄-5: Temperature Dependencies of the First- and Second-Order Raman Spectra. *Phys. Rev. Lett.* **1999**, *82*, 1955–1958. [\[CrossRef\]](#)
52. Bogomolov, V.N.; Poborchii, V.V.; Kholodkevich, S.V.; Shagin, S.I. Electronic and vibrational spectra of 10-Å selenium clusters; cluster model of amorphous selenium. *JETP Lett.* **1983**, *38*, 532–535; *Pis'ma Zh. Eksp. Teor. Fiz.* **1983**, *38*, 439–441.
53. Bogomolov, V.N.; Poborchii, V.V.; Kholodkevich, S.V. Size effects in the vibrational spectrum of 10-Å selenium particles. *JETP Lett.* **1985**, *42*, 517–520; *Pis'ma Zh. Eksp. Teor. Fiz.* **1985**, *42*, 419–421.
54. Sharma, T.; Sharma, R.; Tamboli, R.A.; Kanhere, D.G. Ab initio investigation of structural and electronic properties of selenium and tellurium clusters. *Eur. Phys. J. B* **2019**, *92*, 51. [\[CrossRef\]](#)

55. Alparone, A. Structural, energetic and response electric properties of cyclic selenium clusters: An ab initio and density functional theory study. *Theor. Chem. Acc.* **2012**, *131*, 1239–1252. [\[CrossRef\]](#)
56. Poborchii, V.V.; Rappoport, D. Optical study of Te₈ ring clusters: Comparison with density functional theory and a step towards materials design using nanoporous zeolite space. *Nanoscale* **2024**, *16*, 9436. [\[CrossRef\]](#) [\[PubMed\]](#)
57. Akola, J.; Jones, R.O. Structure and dynamics in amorphous tellurium and Te_n clusters: A density functional study. *Phys. Rev. B* **2012**, *85*, 134103. [\[CrossRef\]](#)
58. Sakaguchi, Y.; Tamura, K. Photoinduced polymerization and relaxation in liquid sulphur. *J. Phys. Condens. Matter* **1995**, *7*, 4787–4801. [\[CrossRef\]](#)
59. Shimojo, F.; Hoshino, K.; Zempo, Y. Photo-induced bond breaking in the S₈ ring: An ab initio molecular-dynamics simulation. *J. Phys. Condens. Matter* **1998**, *10*, L177–L182. [\[CrossRef\]](#)
60. Cho, E.; Pratik, S.M.; Pyun, J.; Coropceanu, V.; Bredas, J.-L. Ring-to-Chain Structural Relaxation of Elemental Sulfur upon Photoexcitation. *ACS Mater. Lett.* **2022**, *4*, 2362–2367. [\[CrossRef\]](#)
61. Clark, R.J.H.; Cobbold, D.G. Characterization of sulfur radical anions in solutions of alkali polysulfides in dimethylformamide and hexamethylphosphoramide and in the solid state in ultramarine blue, green, and red. *Inorg. Chem.* **1978**, *17*, 3169–3174. [\[CrossRef\]](#)
62. Ward, A.T. Raman spectrum and force constants of S₄^{2−}. *Mater. Res. Bull.* **1969**, *4*, 581–590. [\[CrossRef\]](#)
63. Schlaich, H.; Lindner, G.-G.; Feldmann, J.; Golbel, E.O.; Reinen, D. Optical Properties of Se₂[−] and Se₂ Color Centers in the Red Selenium Ultramarine with the Sodalite Structure. *Inorg. Chem.* **2000**, *39*, 2740–2746. [\[CrossRef\]](#) [\[PubMed\]](#)
64. Poborchii, V.V.; Lindner, G.-G.; Sato, M. Selenium dimers and linear chains in one-dimensional cancrinite nanochannels: Structure, dynamics, and optical properties. *J. Chem. Phys.* **2002**, *116*, 2609–2617. [\[CrossRef\]](#)
65. Rettig, S.J.; Trotter, J. Refinement of the structure of orthorhombic sulfur, α-S₈. *Acta Cryst.* **1987**, *C43*, 2260–2262. [\[CrossRef\]](#)
66. Foss, O.; Janickis, V. Crystal structure of γ-monoclinic selenium. *J. Chem. Soc. Dalton Trans.* **1980**, *4*, 624–627. [\[CrossRef\]](#)
67. Lu, W.; Li, Z.; Feng, M.; Zheng, L.; Liu, S.; Yan, B.; Hu, J.-S.; Xue, D.-J. Structure of amorphous selenium: Small ring big controversy. *J. Am. Chem. Soc.* **2024**, *146*, 6345–6351. [\[CrossRef\]](#) [\[PubMed\]](#)
68. Gleiter, R.; Haberhauer, G.; Rominger, F. A new look on larger sulfur and selenium rings—Dispersion forces and shapes of larger cycles. *Eur. J. Inorg. Chem.* **2019**, *34*, 3846–3853. [\[CrossRef\]](#)
69. Ferrari, P.; Berden, G.; Redlich, B.; Waters, L.B.F.M.; Bakker, J.M. Laboratory infrared spectra and fragmentation chemistry of sulfur allotropes. *Nat. Commun.* **2024**, *15*, 5928. [\[CrossRef\]](#)
70. Kolobov, A.V.; Kuznetsov, V.G.; Krbal, M.; Zabotnov, V. Lone-pair-enabled polymorphism and photostructural changes in chalcogenide glasses. *Materials* **2023**, *16*, 6602. [\[CrossRef\]](#)
71. Tanaka, K.; Saitoh, A. Photoluminescence in sulfur and selenium chains: Polaronic exciton dynamics. *Comput. Mater. Sci.* **2026**, *263*, 114403. [\[CrossRef\]](#)
72. Kirczenow, G. Novel low-energy geometries of single double and triple tellurium atomic helices. *J. Phys. Condens. Matter* **2025**, *37*, 135302. [\[CrossRef\]](#) [\[PubMed\]](#)
73. Evarestov, R.A.; Porsev, V.V.; Kuruch, D.D.; Cherezova, P.Y. Torsion and axial deformations of chalcogen helical chains (S, Se, Te): First principles calculations using line symmetry groups. *Nanomaterials* **2025**, *15*, 505. [\[CrossRef\]](#) [\[PubMed\]](#)
74. Cull, W.J.; Ramasse, Q.M.; Biskupek, J.; Rance, G.A.; Cardillo-Zallo, I.; Weare, B.L.; Fay, M.W.; Whitney, R.R.; Scammell, L.R.; Fernandes, J.A.; et al. Flexible selenium nanowires with tunable electronic bandgaps. *Adv. Mater.* **2025**, *37*, 2501821. [\[CrossRef\]](#)
75. Qin, J.K.; Liao, P.Y.; Si, M.; Gao, S.; Qiu, G.; Jian, J.; Wang, Q.; Zhang, S.Q.; Huang, S.; Charnas, A.; et al. Raman Response and Transport Properties of Tellurium Atomic Chains Encapsulated in Nanotubes. *Nat. Electron.* **2020**, *3*, 141–147. [\[CrossRef\]](#)
76. Poborchii, V.V.; Sachkov, V.A.; Shklyaev, A.A.; Fokin, A.V.; Geshev, P.I. Photonic and phononic properties of oriented 5 nm diameter tellurium nanowires. *J. Phys. Chem. Sol.* **2024**, *185*, 111806. [\[CrossRef\]](#)
77. Poborchii, V.V.; Sachkov, V.A.; Shklyaev, A.A.; Geshev, P.I. Nano-channel anisotropic optical material containing ~5 nm diameter aligned Se nanowires with enhanced photo-structural effects and unique photonic, electronic, phononic and thermal properties. *Opt. Mater.* **2026**, *169*, 117712. [\[CrossRef\]](#)
78. Ajmal, Z.; Qadeer, A.; Singh, K.; Al Mahmud, A.; Lakhan, M.N.; Prodeep, H.; Hussain, B.; Ullah, A.; Khan, H.R.; Ibrahim, E.H.; et al. A comprehensive review on MXenes for various applications. *Appl. Energy* **2025**, *397*, 126136. [\[CrossRef\]](#)
79. Salah, M.; Elkabbany, N.A.S.; Partila, A.M. Evaluation of the cytotoxicity and antibacterial activity of nano-selenium prepared via gamma irradiation against cancer cell lines and bacterial species. *Sci. Rep.* **2024**, *14*, 20523. [\[CrossRef\]](#)

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.