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# Optical study of Te<sub>8</sub> ring clusters: comparison with density functional theory and a step towards materials design using nanoporous zeolite space

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The  $Te_8$  ring molecule (cluster) is poorly investigated due to the lack of experimental data. Here, we report an experimental and theoretical study of a regular array of oriented  $Te_8$  rings formed in the  $\sim$ 1.14 nm diameter cavities of zeolite LTA, which are arranged in a cubic lattice with a spacing of  $\sim$ 1.2 nm. Single crystals of LTA with encapsulated tellurium (LTA-Te) were studied using Raman spectroscopy (RS) and optical absorption spectroscopy (OAS). The experimental LTA-Te spectra were found to be in agreement with those calculated using density functional theory (PBE0 hybrid functional and def2-TZVP basis sets) for the crown-shaped  $Te_8$  ring molecule with  $D_{4d}$  symmetry. Using polarization—orientation RS, we show that the  $Te_8$  rings are oriented by their major axes along the 4-fold axes of cubic LTA. We also show that the site symmetry of  $Te_8$  in LTA-Te is lower than  $D_{4d}$ .  $Te_8$  bond-bending modes are well described in the harmonic approximation, while bond-stretching modes are mixed due to the reduced ring symmetry and, probably, anharmonicity. Importantly, OAS data of LTA-Te display dependence on the  $Te_8$  concentration, implying the interaction of the rings from neighbouring LTA cavities with the generation of the valence and conduction electron bands of such a cluster crystal.

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#### Introduction

Tellurium (Te) belongs to the same group of the periodic table as oxygen (O), sulphur (S) and selenium (Se). Since its discovery at the end of the 18<sup>th</sup> century, Te was widely used in metal alloys. Nowadays, Te and its compounds have become a real frontier of science and technology. They have found important applications in electronics, optoelectronics, photonics, phase-change materials, topological insulators, Li–Te batteries, thermoelectrics and solar cells. <sup>1-6</sup> However, elemental Te is mainly known in its chain form analogous to crystalline trigonal tellurium (t-Te) while it is nearly unknown in the ring form.

Zeolites provide a unique opportunity to form and accommodate uniform guest species in their cavities/channels where the species are oriented due to the crystalline nature of zeolites. The example, only zeolites allowed obtaining polarized Raman spectra (RS) and optical absorption spectra (OAS) of isolated Te chains and rings. Moreover, fabrication of such regular high-density Te species arrays can be considered as an important direction in the development of new functional materials, so-called cluster crystals. 14-16

Here, we study Te<sub>8</sub> rings regularly arranged in the large cavities of zeolite LTA. Importantly, we are using the polarization-orientation RS examination of zeolite single crystals. On one hand, this method can be considered as an alternative to X-ray diffraction (XRD) for the structural study of zeolite-confined clusters. On the other hand, it provides very useful information about the cluster properties and their interaction with zeolites. We also study the OAS spectra of Te<sub>8</sub> and demonstrate the effect of the interaction between Te<sub>8</sub> rings in neighboring cavities, which is important for the fabrication of real cluster crystals.

The idea of  $Te_8$  ring formation in LTA cavities was proposed in ref. 17 where the only observed RS feature at  $\sim 168~\rm cm^{-1}$  was assigned to the ring with an argument that its frequency is different from the dominant trigonal tellurium (t-Te) band frequency at  $\sim 120.5~\rm cm^{-1}.^{18,19}$  However, this observation was not confirmed later. In ref. 20, the RS of LTA-Te microcrystalline powder was re-examined. A strong band at  $\sim 182~\rm cm^{-1}$  and a weaker one at  $\sim 45~\rm cm^{-1}$  were observed and attributed rather to  $Te_{12}$  than to  $Te_8$  since  $Te_8$  requires a relatively strong symmetric bond-bending mode band at around 60 cm<sup>-1</sup>, which was not clearly detected due to laser-induced band broadening, as was found later. The LTA-Te band at  $\sim 62~\rm cm^{-1}$  accompanied by  $\sim 182~\rm cm^{-1}$  and  $\sim 45~\rm cm^{-1}$  bands was observed in ref. 21. This was a rather strong argument in favor of  $Te_8$  ring formation in LTA cavities. The observed bands at  $\sim 45$ ,

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 $\sim$ 62 and  $\sim$ 182 cm<sup>-1</sup> look similar to the bending E<sub>2</sub> and A<sub>1</sub> mode bands and stretching  $A_1$  mode bands of  $S_8$  (~153, ~222, ~480 cm<sup>-1</sup>) and Se<sub>8</sub> (~76, 111, 267 cm<sup>-1</sup>) rings.<sup>21</sup> The RS of another zeolite AFI with encapsulated tellurium (AFI-Te) showed similar bands at 41-47 cm<sup>-1</sup>, 65 cm<sup>-1</sup> and 184 cm<sup>-1</sup>. The bands were attributed to the Te<sub>8</sub> ring. However, no polarized RS study of LTA-Te single crystals has been performed yet, which could provide crucial evidence for Te<sub>8</sub> ring formation. Here, we present this evidence. Importantly, no other species but Te<sub>8</sub> was found in LTA-Te. This is beneficial for realizing the idea of cluster crystal formation.

### Experimental and theoretical methods

Synthetic zeolite LTA with the composition Na<sub>12</sub>Al<sub>12</sub>Si<sub>12</sub>O<sub>48</sub> was used in this work. The crystal growth procedure for LTA is described in ref. 22. The sizes of the cubic LTA crystals were ~20 µm along the edge of the cube. LTA has nearly sphericalshaped large cavities with a diameter of ~1.14 nm, which are connected through narrow windows of ~0.42 nm diameter (Fig. 1). The LTA cavities are arranged in a simple cubic lattice. The zeolite structures are accessible at the International Zeolite Association website <a href="https://www.iza-structure.org/">https://www.iza-structure.org/</a> IZA-SC/ftc\_table.php.

Dehydration of zeolites in a vacuum was performed in Pyrex ampoules for several hours at  $t \sim 550$  °C. The design of the ampoules made it possible to add crystalline Te powder to the zeolite after dehydration without exposing the dehydrated samples to air. The subsequent adsorption of the Te vapour was carried out at  $t \sim 550$  °C for a few days until the brownish colour of the sample was saturated.

RS spectra of the LTA-Te single crystals were studied using a Renishaw micro-Raman spectrometer equipped with Semrock edge-filters and an Olympus micro-objective lens allowing an ~1 µm focused laser probe size. A 633 nm wavelength line of the He-Ne laser and a 785 nm line of the light-emitting diode

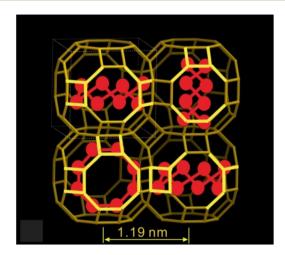


Fig. 1 Schematic view of the LTA framework with Te<sub>8</sub> rings in large

laser were used for RS excitation. Weak absorption of Te<sub>8</sub> at these wavelengths is beneficial for Te<sub>8</sub> compared to the nonabsorbing LTA matrix for obtaining the cluster Raman signal with nearly no contribution of LTA. An additional measurement with 561 nm laser diode line excitation was performed using a Nanofinder-30 Raman/AFM system (Tokyo Instruments Inc.) specially designed for the maximal RS detection sensitivity around this wavelength, which allowed LTA-Te Raman measurement at relatively high Te<sub>8</sub> absorption and very low laser excitation power in order not to strongly heat or destroy the clusters. Moreover, a Nanofinder-30 (Tokyo Instruments Inc.) was equipped with a set of three volume Bragg grating notch filters (OptiGrate Co), allowing the detection of the Raman signal with frequencies down to  $\sim 6$  cm<sup>-1</sup>. UV-visible OAS was performed using a Carl Zeiss micro-optical spectrometer with a light probe size of ~5 µm. The samples were intentionally broken to minimize their optical density in the ultraviolet (UV) spectral range and placed in glycerol between two cover glasses to minimize surface light scattering.

The Te<sub>8</sub> RS, infrared (IR) spectra and OAS were simulated using density functional theory (DFT). 23-26 The structure and vibrational frequencies of Te<sub>8</sub> were computed using the hybrid PBE0 exchange-correlation functional<sup>26</sup> and the resolution-ofidentity approximation for the Coulomb part (RI-J).<sup>27</sup> The def2-TZVP basis sets<sup>28</sup> together with the corresponding auxiliary basis sets<sup>29</sup> and small-core effective core potentials (ECPs)<sup>30</sup> were employed for Te. RS intensities were obtained in the double harmonic approximation using analytical derivatives of static electronic polarizabilities<sup>31</sup> and analytical energy Hessians. 32,33 Calculations of static polarizability derivatives used the PBE0 functional and augmented def2-TZVPD basis sets.34 IR spectra were computed in the double harmonic approximation from the analytical dipole and energy Hessians. 32,33 The vibrational frequencies were not scaled in this work. OAS was performed with time-dependent DFT (TDDFT)35 using the PBE0 functional with the RI-J approximation<sup>36</sup> and def2-TZVPD basis sets. All calculations were performed with the Turbomole program package, version 7.5. 23,37

# Structure and Raman and absorption spectra of single Te<sub>8</sub> rings via DFT calculations

The calculated  $Te_8$  ( $D_{4d}$  point group symmetry) ring structure is shown in Fig. 2(a). The bond length of  $Te_8$  is r = 0.271 nm and the second neighbour distance is R = 0.432 nm, while its bond and dihedral angles are 105.8° and 101.2°, respectively. The obtained structure parameters are in agreement with previous DFT calculations.  $^{38-42}$  The ring Z axis is directed along its 4-fold axis, while the X and Y axes lie in the molecule plane normal to the Z axis (Fig. 2(a)).

Theoretical point group analysis for the vibration modes of Te<sub>8</sub> is similar to that made for the S<sub>8</sub> molecule with a similar crown shape. 43 The Te<sub>8</sub> vibration irreducible representations

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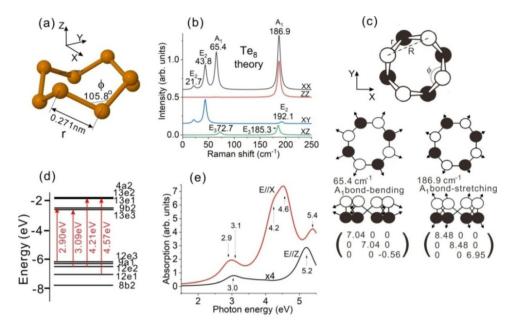


Fig. 2 Te<sub>8</sub> ring with the bond length r and angle  $\phi$  (a); calculated Raman spectra of a single free-standing Te<sub>8</sub> ring for XX, ZZ, XY and XZ polarization configurations (b); Te<sub>8</sub> atomic displacements for A<sub>1</sub> bond-bending and A<sub>1</sub> bond-stretching modes with corresponding Raman tensors (c); Te<sub>8</sub> MO diagram with dominant MO contributions to the strongest optical transitions shown in red, all for E/X (d); and calculated Te<sub>8</sub> OAS including transitions with photon energies of <5.5 eV (e).

(symmetries) with calculated frequencies and IR/Raman activities are shown in Table 1. The  $E_1$  symmetry corresponds to the IR activity for the light polarized in the ring plane ( $E/\!\!/X$  or  $E/\!\!/Y$ ), while the  $B_2$  symmetry corresponds to the  $E/\!\!/Z$  IR activity. Calculated  $Te_8$  Raman intensities for different polarization configurations are equal to their squared Raman tensor components (XX, ZZ, XY, XZ) for each mode, which are determined by the corresponding atomic displacements and related molecular polarizability derivatives. The corresponding values in Table 1 are given in atomic units of  $10^{-2}e^2a_0/E_h$ , where e,  $a_0$  and  $E_h$  are the electron charge, Bohr radius and Hartree energy, respectively.

The calculated RS spectra of  $Te_8$  for different polarization configurations, corresponding to the Raman tensor components from Table 1, are shown in Fig. 2(b). Raman bands are represented as Lorentz curves with the amplitudes corresponding to the calculated Raman activities and half-widths of 5 cm<sup>-1</sup> for all bands.

The dominant band in the calculated RS spectra of  $Te_8$ , displaying comparable XX and ZZ activities, corresponds to the  $A_1$  symmetric bond-stretching mode at a frequency of  $186.9~{\rm cm}^{-1}$ . In contrast, the  $A_1$  bond-bending mode at  $65.4~{\rm cm}^{-1}$  displays high XX activity and nearly negligible ZZ activity. Fig. 2(c) shows atomic displacements and Raman tensors of these two

Table 1 Te<sub>8</sub> normal vibrations: symmetries, computed frequencies, IR intensities and Raman activities

Symmetry	Frequency (cm <sup>-1</sup> )	IR intensity (km mol <sup>-1</sup> )	Raman activity XX	Raman activity ZZ	Raman activity XY	Raman activity XZ
$\overline{\mathrm{E}_2}$	21.7	0	-0.49	0	-2.08	0
_	21.7	0	-2.08	0	0.49	0
$\mathbf{E}_2$	43.8	0	-4.38	0	-3.36	0
_	43.8	0	3.36	0	-4.38	0
$\mathbf{E_1}$	56.9	0.524	0	0	0	0
_	56.9	0.524	0	0	0	0
$A_1$	65.4	0	-7.04	0.56	0	0
$B_2$	68.6	0.128	0	0	0	0
$E_3$	72.7	0	0	0	0	-1.86
o .	72.7	0	0	0	0	-0.86
$B_1$	179.9	0	0	0	0	0
$E_3$	185.3	0	0	0	0	-3.54
5	185.3	0	0	0	0	-0.17
$A_1$	186.9	0	-8.48	-6.95	0	0
E <sub>1</sub>	188.1	1.29	0	0	0	0
•	188.1	1.29	0	0	0	0
$E_2$	192.1	0	1.21	0	-1.05	0
=	192.1	0	-1.05	0	-1.21	0

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 $A_1$  modes, which explain the difference in their ZZ activities. One can consider the A<sub>1</sub> bond-stretching as a breathing mode since both in-plane and off-plane Te<sub>8</sub> dimensions expand and contract the in-phase, while the A<sub>1</sub> bond bending mode is an important instrument for Te<sub>8</sub> ring orientation determination.

The E<sub>2</sub> bond-bending mode at 43.8 cm<sup>-1</sup> is rather active in the XX and XY configurations, while inactive in the ZZ configuration. Similar but weaker activity is displayed by the E2 torsion and stretching modes at 21.7 cm<sup>-1</sup> and 192.1 cm<sup>-1</sup>, respectively. The E<sub>3</sub> bond-bending mode at 72.7 cm<sup>-1</sup> and the bond-stretching mode at 185.3 cm<sup>-1</sup> dominate in the XZ configuration spectrum.

In addition to the Te<sub>8</sub> Raman-active modes, there are several inactive modes: E<sub>1</sub> bond-bending at 56.9 cm<sup>-1</sup>, B<sub>2</sub> bond-bending at 68.6 cm<sup>-1</sup>, B<sub>1</sub> bond stretching at 179.9 cm<sup>-1</sup> and E<sub>1</sub> bond stretching at 188.1 cm<sup>-1</sup>, which can become active when the ring  $D_{4d}$  symmetry is reduced. As we mentioned above, the E1 and B2 modes are IR-active.

The calculated partial molecular orbital (MO) diagram of Te<sub>8</sub> including the highest occupied MOs and the lowest unoccupied MOs is presented in Fig. 2(d). These MOs consist of combinations of Te 5p orbitals, as determined by Mulliken population analysis. The occupied orbitals correspond to Te lone pairs, while the unoccupied orbitals have antibonding character with respect to Te-Te bonds. The largest MO contributions to the allowed electronic transitions with photon energies <4 eV and the largest oscillator strengths are shown in red. It should be noted that the electron transition energies take into account excitonic effects. Therefore, the transition energies are less than the orbital energy differences of the dominant MO contributions. All these four transitions have E<sub>1</sub> symmetry, implying the polarization of light  $E/\!/X$ .

There are also  $E/\!\!/Z$ -allowed transitions of  $B_2$  symmetry. However, their oscillator strengths appeared to be much lower than those of the strongest  $E/\!\!/X$  transitions (Table 2). The calculated OAS spectra of  $Te_8$  for polarizations of light  $E/\!\!/X$  and  $E/\!\!/Z$  are shown in Fig. 2(e). Allowed electronic transitions (E<sub>1</sub>

Table 2 Computed dipole-allowed electron transitions of Te<sub>8</sub>

Symmetry	Photon energy (eV)	Oscillator strength	
E <sub>1</sub>	2.90	0.104	
$B_2$	3.03	0.016	
$E_1$	3.09	0.053	
$B_2$	3.45	0.003	
$E_1$	3.53	0.001	
$B_2$	3.61	0.003	
$E_1$	3.89	0.012	
$B_2$	3.96	0.004	
$E_1$	4.11	0.006	
E <sub>1</sub>	4.21	0.357	
E <sub>1</sub>	4.35	0.002	
$E_1$	4.57	0.525	
$B_2$	5.21	0.071	
$E_1$	5.42	0.333	
$B_2$	5.77	0.008	
E <sub>1</sub>	5.82	0.229	
$\mathbf{B}_{2}$	5.94	0.002	

for  $E/\!\!/X$  and  $B_2$  for  $E/\!\!/Z$ ) with photon energies of up to 5.5 eV were computed. Due to the difference in the oscillator strengths, the  $E/\!/X$  absorption is stronger than the  $E/\!/Z$  one. The E//X absorption is mainly represented by transitions at photon energies of ~2.9, ~3.1, ~4.2, ~4.6 and ~5.4 eV, while the  $E/\!\!/Z$  one is determined by transitions at photon energies of  $\sim$ 3,  $\sim$ 3.6,  $\sim$ 4 and  $\sim$ 5.2 eV. The corresponding absorption bands are approximated by the Lorentz curves with half-widths of  $\sim 0.6$  eV.

### Experimental polarized Raman spectra of LTA-Te single crystals

Using Te vapor adsorption, we obtained LTA-Te samples with Te loading densities of ~3 and ~8 atoms per cavity (at. per cav.). Unlike the RS of LTA-Se with different loading densities showing changes in the Se<sub>8</sub>/Se<sub>12</sub> intensity ratio, 44 LTA-Te RS spectra did not show any qualitative dependence on the Te loading density except an increase in the Raman signal of the same bands with an increase in the Te density. This is a strong argument in favour of the formation of only one stable Te cluster in the LTA cavities.

RS spectra of LTA-Te with a loading density of ~8 at. per cav. at an excitation wavelength of 785 nm are shown in Fig. 3(a). We performed measurements in four different polarization configurations: aa, cc, ab and cd (see the inset in Fig. 3(a)) similar to the polarization-orientation Raman study of LTA with sulphur LTA-S<sup>12</sup> and LTA with selenium LTA-Se. 12,44,45 Experimentally, we rotated the LTA-Te crystals in the ab plane with incident and scattered light polarizations (1) parallel and (2) perpendicular to each other. The procedure was described in detail earlier.12 Theoretical RS spectra of LTA-Te for the aa, cc, ab and cd polarization configurations were obtained via summation of the Raman responses of three Te<sub>8</sub> rings in their three possible orientations in LTA crystals [Fig. 3(b)].

The experimental LTA-Te RS spectra display rather good correspondence with the calculated ones. Indeed, the bands at 162 cm<sup>-1</sup> and 183 cm<sup>-1</sup> can be assigned to the Te<sub>8</sub> E<sub>3</sub> and A<sub>1</sub> bond-stretching modes similar to the 442 cm<sup>-1</sup> and 480 cm<sup>-1</sup> bands of S<sub>8</sub> in LTA-S [Fig. 3(c)]. The correspondence between the experiment and theory looks especially good for the A<sub>1</sub> mode frequency (experimental: ~183 cm<sup>-1</sup> vs. theoretical: 186.9 cm<sup>-1</sup>) and intensity (the strongest band in the spectrum). At first glance, the polarization dependence of its intensity also looks reasonable: the band is strong in aa and cc polarization configurations, while it is weak in ab and cd configurations as expected for the A<sub>1</sub> modes. Actually, as we have shown below, the situation is more complicated for the bond stretching modes due to a possible mode mixing effect but, in a rough approximation, the assignment of the 183 cm<sup>-1</sup> band to the A<sub>1</sub> bond-stretching mode looks reasonable.

Polarization dependencies of the LTA-Te bands in the Te<sub>8</sub> bond-bending mode region appear to be qualitatively similar to those of the bond-bending modes of  $S_8^{\ 12}$  [Fig. 3(c)] and

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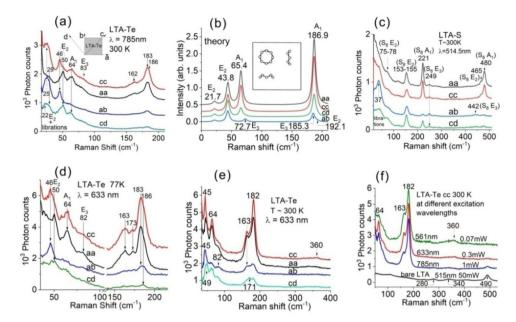


Fig. 3 LTA-Te Raman spectra of aa, cc, ab and cd polarization configurations at room temperature and 785 nm wavelength excitation with the inset schematically showing LTA-Te cubic crystals and the a, b, c and d axes (a); summation of the calculated Raman spectra of three Te<sub>8</sub> orientations in LTA (see the inset) for aa, cc, ab and cd polarization configurations (b); LTA-S Raman spectra of aa, cc, ab and cd polarization configurations at  $T \sim 77$  K and 633 nm wavelength excitation (d); LTA-Te Raman spectra of aa, cc, ab and cd polarization configurations at room temperature and 633 nm wavelength excitation (e); and LTA-Te Raman spectra of the cc polarization configuration at different excitation wavelengths with the unpolarized spectrum of bare LTA (black curve) (f).

 $Se_8$  <sup>12,44,45</sup> rings in LTA. Indeed, the 46–50 cm<sup>-1</sup> band polarization-orientation dependence is similar to that of the E2 band at 74-76 cm $^{-1}$  or 77-79 cm $^{-1}$  of Se $_8$ <sup>45</sup> and the E $_2$  band at 153-155 cm<sup>-1</sup> of S<sub>8</sub> [Fig. 3(c)]. The calculated Te<sub>8</sub> E<sub>2</sub> bondbending mode frequency of 43.8 cm<sup>-1</sup> is in good agreement with the observed 46-50 cm<sup>-1</sup> band frequencies of LTA-Te. The splitting of the degenerate E2 mode indicates structural distortion of Te<sub>8</sub> in LTA and therefore a reduced symmetry compared to the initial  $D_{4d}$  symmetry of the ring. For example, a slight reduction of the  $Te_8$  symmetry from  $D_{4d}$  to  $C_{4v}$  would split the E<sub>2</sub> mode into B<sub>1</sub> and B<sub>2</sub> modes, active in XX and XY polarization configurations, respectively. This is exactly what we experimentally observed. Interestingly, the splitting of the Te<sub>8</sub>  $E_2$  mode in LTA is very strong, ~8.3%, in contrast to the weaker splitting of the corresponding  $E_2$  modes of  $S_8$ , ~ 1.3%, and  $Se_8$ , ~ 2.6%.

The LTA-Te 64 cm<sup>-1</sup> band displays polarization dependence similar to the  $A_1$  symmetric bond-bending mode band of  $S_8$  at ~221 cm<sup>-1</sup> [Fig. 3(c)] and the analogous band of  $S_8$  at ~112 cm<sup>-1</sup>.<sup>12,44,45</sup> The frequency of 64 cm<sup>-1</sup> is very close to the calculated frequency of 65.4 cm<sup>-1</sup> of the Te<sub>8</sub>  $A_1$  bond-bending mode [Fig. 2(b); 3(b)]. The experimental 64 cm<sup>-1</sup> 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 2-dimensional character of the Raman tensor of this mode with only two strong diagonal tensor components in contrast to the rather 3-dimensional tensor of the  $A_1$  bond-stretching mode [Fig. 2(c)]. Correspondingly, the single free-

standing  $Te_8$   $A_1$  bond-bending mode band is strong in the XX polarization configuration and negligibly weak in the ZZ configuration with the zero XY and XZ activities [Fig. 2(b)]. Theoretical calculation of this mode activity in the RS spectra of LTA-Te [Fig. 3(b)] is also in very good agreement with the experiment, namely high aa activity and no ab activity. This is a clear indication of the orientation of the  $Te_8$  4-fold axis along the 4-fold axis of LTA.

The experimental LTA-Te  $\sim 83~\text{cm}^{-1}$  band looks similar to the 248 cm<sup>-1</sup> E<sub>3</sub> bond-bending mode band of S<sub>8</sub> [Fig. 3(c)]. It can be attributed to the E<sub>3</sub> bond-bending mode of Te<sub>8</sub> with a calculated frequency of 72.7 cm<sup>-1</sup>. The  $\sim$ 29 cm<sup>-1</sup> band of LTA-Te can be attributed to the E<sub>2</sub> torsional mode of Te<sub>8</sub> with a calculated frequency of 21.7 cm<sup>-1</sup>. A broad  $\sim$ 25 cm<sup>-1</sup> band, probably, originates from the superposition of the second component of the E<sub>2</sub> torsional mode and the ring librations in the LTA cavity.

As we mentioned above, the bands of LTA-Te in the bond-stretching mode region require more detailed consideration. Fig. 3(d) shows LTA-Te RS in this region taken at temperature  $T \sim 77$  K and an excitation wavelength of 633 nm with better resolved bands due to their temperature-induced narrowing. Fig. 3(e) shows room temperature LTA-Te RS at the same excitation wavelength in a wider spectral range. Four bands at  $\sim 163$  cm<sup>-1</sup>,  $\sim 173$  cm<sup>-1</sup>, and  $\sim 183$  cm<sup>-1</sup> and its shoulder at  $\sim 186$  cm<sup>-1</sup> can be observed in Fig. 3(d). The shoulder is, probably, associated with the Te<sub>8</sub> E<sub>2</sub> bond-stretching mode (theoretical frequency of  $\sim 192$  cm<sup>-1</sup>). Taking into account our preliminary assignment of the 182-183 cm<sup>-1</sup> and 162-163 cm<sup>-1</sup>

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bands to the  $Te_8$   $A_1$  and  $E_3$  modes, respectively, we have to attribute the 171–173 cm<sup>-1</sup> band to the forbidden  $B_1$  (theoretical frequency of  $\sim$ 180 cm<sup>-1</sup>) mode which can be activated due to the reduced symmetry of  $Te_8$  in the LTA cavity, and we found that the bands in the bond-stretching mode region can be mixed.

The band at 182-183 cm<sup>-1</sup> shows slightly stronger activity in the cc polarization configuration than that in the aa configuration, which is clearly seen in the room temperature RS of LTA-Te obtained by excitation with 633 nm light, as shown in Fig. 3(e). This can be associated with the mode mixing due to the reduced symmetry of the Te<sub>8</sub> rings. Interestingly, the 2<sup>nd</sup> order Raman band of Te<sub>8</sub> can be recognized in the cc configuration spectrum at  $\sim 360 \text{ cm}^{-1}$  [Fig. 3(e)]. An even stronger 2<sup>nd</sup> order Raman band can be clearly seen at an excitation wavelength of 561 nm [Fig. 3(f), green curve] due to the resonant Raman enhancement. The band is very broad covering the spectral range from ~300 cm<sup>-1</sup> to ~375 cm<sup>-1</sup>. Importantly, LTA bands do not contribute to the 2<sup>nd</sup> order Raman band of Te<sub>8</sub> since even the strongest LTA band at ~490 cm<sup>-1</sup> [Fig. 3(f), black curve] does not contribute to LTA-Te RS obtained by excitation with 561 nm light.

Summarizing this section, the polarization dependence of the  $A_1$  bond-bending mode Raman band of  $Te_8$  indicates the orientation of the ring by its 4-fold axis along the LTA 4-fold axis, while that of the  $E_2$  bond-bending mode suggests a noticeable symmetry reduction of the ring from the ideal  $D_{4d}$  point group symmetry.  $Te_8$  bond-stretching modes are mixed due to the ring symmetry reduction. The Raman bands at  $162-163~{\rm cm}^{-1}$  and  $171-173~{\rm cm}^{-1}$ , probably, originate from the  $E_3$  mode and formerly inactive  $B_1$  mode while the Raman bands at  $182-183~{\rm cm}^{-1}$  and  $186~{\rm cm}^{-1}$  originate from 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.

# Optical absorption spectra of LTA-Te single crystals

Fig. 4(a and b) show the OAS of LTA-Te with the loading densities of  $\sim$ 3 atoms per cavity [LTA-Te(3)] and  $\sim$ 8 atoms per cavity [LTA-Te(8)]. Absorption bands at  $\sim$ 2.8 eV, 3.2 eV, 4.3 eV and 4.6 eV are observed in the OAS of LTA-Te(3), while absorption bands at  $\sim$ 2.6 eV, 3.2 eV and 4.4 eV are observed in the OAS of LTA-Te(8). The spectra indicate that the energy band gap decreases when the Te loading density increases. Moreover, LTA-Te(8) bands look slightly broader than those of LTA-Te(3). In particular, the absorption band doublet at  $\sim$ 4.3 eV and 4.6 eV, resolved in LTA-Te(3), looks like a single band at  $\sim$ 4.4 eV.

First, the observed experimental OAS spectra of LTA-Te [Fig. 4(a and b)] appeared to be in nearly perfect agreement with the theoretical OAS spectra of  $Te_8$  [Fig. 2(e)]. The agreement with theoretical OAS for a single  $Te_8$  ring is especially good for LTA-Te(3) with approximately two rings per five cavities. We have to note that surface light scattering, which

increases with the photon energy, contributes to the experimental spectra. In contrast, theoretical spectra do not include this effect and do not include high-energy transitions (>5.5 eV in Fig. 2(e)). This may produce an impression that the experimental and theoretical spectra are different. However, actually, they are very similar.

Secondly, differences between the OAS of LTA-Te(3) and LTA-Te(8) indicate a noticeable interaction between the Te<sub>8</sub> rings in neighbouring LTA cavities, in particular, for LTA-Te(8) with one ring per cavity. In Fig. 4(b), we show the spectral positions of the Raman excitation laser lines, clearly indicating rather strong absorption of LTA-Te(8) at a wavelength of 561 nm corresponding to the resonant Raman effect [Fig. 3(f)]. To avoid laser-induced heating/destruction of Te<sub>8</sub>, we used a very low 561 nm laser power of  $\sim$ 0.07 mW. At weaker LTA-Te absorption corresponding to wavelengths of 785 nm and 633 nm [Fig. 4(b)], we were able to use higher laser powers of  $\sim$ 1 mW and  $\sim$ 0.3 mW, respectively [Fig. 3(f)].

In order to examine a possible effect of the ring interaction on the OAS spectrum of LTA-Te, we theoretically considered three possible Te<sub>8</sub> ring dimers with a separation of ~1.2 nm between the ring centres [Fig. 4(c)]. The corresponding calculated dimer OAS spectra are shown in Fig. 4(d). The effect of the ring interaction is indicated by the absorption enhancement with an increase in the ring interaction, which is the weakest in the "face-to-face" configuration and the strongest in the "side-to-side" configuration. Due to the inter-ring interaction, the unoccupied MOs of the Te<sub>8</sub> rings organize conduction bands of the LTA-Te cluster crystals, while the highest occupied MOs organize its valence band. The conduction and valence bands should be rather narrow. Therefore, a variety of non-linear electric conductance effects predicted for narrow semiconductor superlattice mini-bands<sup>46</sup> can be expected in the LTA-Te electric properties. A negative differential electric resistance of LTA-Te observed in ref. 47 confirms this.

# Te<sub>8</sub> interaction with LTA and its librations *vs.* temperature

According to the calculated  $Te_8$  structure [Fig. 2(a)], the diameter of the ring, including the van der Waals radius of  $\sim$ 0.2 nm of the Te atom, is  $\sim$ 1 nm, which is slightly smaller than the LTA large cavity diameter. Therefore, one can expect that the  $Te_8$  ring is slightly shifted from the cavity center along the 4-fold LTA axis similar to the  $S_8$  and  $Se_8$  rings<sup>12,44,45</sup> but not as much as in the cases of  $S_8$  and  $Se_8$ . This should cause  $Te_8$  symmetry reduction from  $D_{4d}$  at least to  $C_{4v}$  [Fig. 5(a)]. We imposed the bond angle changes in order to simulate such structural distortion. The angles of type  $\phi$ 1 were enlarged while those of type  $\phi$ 2 were reduced. The second nearest neighbor distances R = 0.418 nm and 0.446 nm in Fig. 5(a) correspond to  $\Delta \phi = \phi$ 1  $- \phi$ 2 = 5° (R = 0.432 nm for undisturbed  $Te_8$ ).

The experimentally observed splitting of the  $E_2$  bond-bending mode [Fig. 3(a, d and e)] is, definitely, a sign of  $D_{4d}$ 

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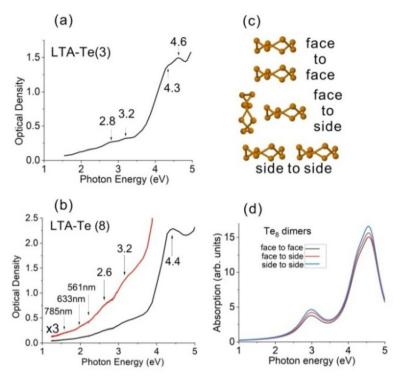


Fig. 4 Experimental absorption spectra of LTA-Te(3) (a) and LTA-Te(8) (b); three  $Te_8$  dimers considered for the calculation of the effect of ring interaction on the absorption spectrum (c); and calculated absorption spectra of the considered  $Te_8$  dimers including transitions with photon energies of <5 eV (d).

symmetry reduction. It is important to verify whether the observed E<sub>2</sub> mode splitting fits the ring structure distortion shown in Fig. 5(a) or not. Due to the Te<sub>8</sub> symmetry reduction from  $D_{4d}$  to  $C_{4v}$ , the  $E_2$  bond-bending mode splits into  $B_1$  and B<sub>2</sub> modes, displaying XX and XY Raman activities, respectively. We performed calculations of the B<sub>1</sub> and B<sub>2</sub> mode frequencies and intensities as a function of the distortion  $\Delta \phi$ . The results are shown in Fig. 5(b). The B<sub>1</sub> mode frequency increases while the  $B_2$  mode frequency decreases with  $\Delta \phi$ . This corresponds well to our experimental observation for the E<sub>2</sub> bond-bending mode with the LTA-Te aa-active component frequency higher than that of the ab-active component. Thus, we conclude that the Te<sub>8</sub> structural distortion shown in Fig. 5(a) reasonably describes the experimentally observed splitting of the E2 bondbending mode of Te<sub>8</sub>. However, even stronger symmetry reduction of Te<sub>8</sub> is possible.

As we mentioned in the Introduction, Raman polarization-orientation spectroscopy in application to the zeolite-confined cluster structure study can be considered in some sense as an alternative to XRD. Indeed, using Raman polarization-orientation spectroscopy, we can determine a type of cluster (molecule) and its orientation in a zeolite. Then we can suggest its possible location in the zeolite when we know its size. However, we can only guess what sort of interaction occurs between the Te atoms and the zeolite. For understanding this point, the XRD data would be very useful. However, a structural analysis of LTA-Te by XRD is rather difficult because Te is distributed statistically inside the cavities. The resulting scatter-

ing power of Te sites with partial occupancy is comparable to those of Na<sup>+</sup> cations and water molecules filling spaces not occupied by Te.

The  $\sim$ 20 micron size of LTA-Te is insufficient for single-crystal XRD, while powder XRD of zeolites with clusters is, definitely, not effective for the examination of the cluster structure. It shows that the zeolite filling with clusters or molecules causes just changes in the relative intensities of the XRD peaks like, for example, in ref. 48 and its ESI, where a number of different types of zeolites, including LTA, with/without sulphur clusters were examined using powder XRD. In contrast, XRD analysis of  $\sim$ 65 micron size LTA single crystals containing sulphur clearly showed double S<sub>8</sub> ring cluster formation in each large cavity, <sup>49</sup> which is in agreement with the published RS results <sup>12,50,51</sup> and this work [Fig. 3(c)].

An XRD study of  $\sim$ 60 micron size LTA-Te single crystals was performed in ref. 52. The XRD analysis suggested the interaction of Te atoms with the zeolite oxygen atoms and cations, while it showed low occupancy and high temperature factors for Te atomic sites. Therefore, the authors could not make any univocal conclusion about the Te cluster structure and they proposed several options including Te<sub>8</sub> rings.

Using the RS of LTA-Te, the interaction between the  $Te_8$  ring and the zeolite can be probed via observation of the Te ring librations vs. temperature. Taking into account the  $S_8$  libration frequency of  $\sim 37~{\rm cm}^{-1}$  [Fig. 3(c)] and assuming approximately the same van der Waals interaction force with LTA for both  $S_8$  and  $Te_8$ , we can roughly estimate the expected

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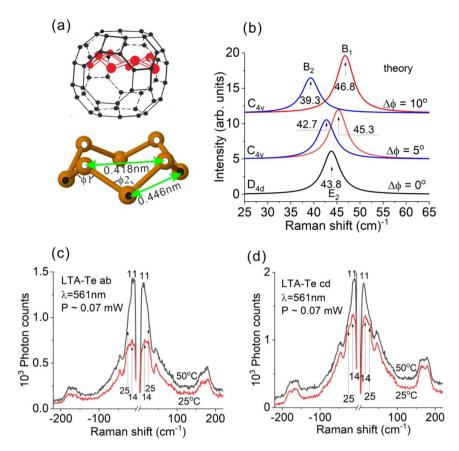


Fig. 5 Te<sub>8</sub> ring shifted up from the centre of the LTA large cavity (top) with the  $C_{4v}$  structural distortion corresponding to the bond angle difference  $\Delta\phi = \phi 1 - \phi 2 = 5^{\circ}$  (bottom), the white and black spots show Te atoms in the top and bottom layers, respectively (a); calculated RS spectra of the Te<sub>8</sub> ( $D_{4d}$ ) E<sub>2</sub> bond-bending mode (black) and Te<sub>8</sub> ( $C_{4v}$ ) B<sub>1</sub> (red) and B<sub>2</sub> (blue) bond-bending modes (b); and experimental low-frequency RS of LTA-Te at stage temperatures of ~25 °C and ~50 °C for ab (c) and cd (d) polarization configurations.

Te<sub>8</sub> room temperature libration frequency as  $\sim$ 18.5 cm<sup>-1</sup> using the square root of the Te and S mass ratio, which is  $\sim$ 2.

In the LTA-Te RS spectra obtained by excitation with 785 nm light,  $Te_8$  librations, probably, contribute to the broad  $\sim$ 22–25 cm<sup>-1</sup> band [Fig. 3(a)]. Instrumental limitations did not allow RS detection at frequencies <20 cm<sup>-1</sup> at this excitation wavelength. In contrast, such measurements were available at 561 nm light excitation. A weak point of this wavelength is that the corresponding  $Te_8$  absorption and light-induced heating are not negligible.

Fig. 5(c and d) show the Stokes and anti-Stokes low-frequency RS of LTA-Te in ab and cd polarization configurations at ~25 °C and ~50 °C temperatures of the heat-controlling table. We roughly estimated the laser-induced heating from the Stokes/anti-Stokes intensity ratio as ~20–30 °C, the value that should be added to the heating table temperature. In the RS taken at ~25 °C table temperature, one can see a ~25 cm<sup>-1</sup> band in combination with a ~14 cm<sup>-1</sup> band for both configurations. The last band, definitely, originates from the Te<sub>8</sub> librations. With the increase of the table temperature to ~50 °C, it shifts to a lower frequency of ~11 cm<sup>-1</sup> and displays significant enhancement. This corresponds to the intensification of librations and the reduction of the ring interaction with LTA.

The position of the  $\sim$ 25 cm<sup>-1</sup> feature remains unchanged, confirming its origin from the internal torsional E<sub>2</sub> mode of Te<sub>8</sub>.

Thus, the Te<sub>8</sub> libration amplitudes strongly increase with a moderate increase in the LTA temperature. This corresponds to a rather weak van der Waals interaction of Te<sub>8</sub> with LTA. At room temperature, the libration amplitudes are, probably, quite strong as well. This explains high temperature factors observed for Te sites,<sup>52</sup> which complicates the XRD analysis of LTA-Te. In contrast, this effect does not cause any trouble for polarization–orientation Raman spectroscopy, which appears to be a very fruitful method of zeolite-confined cluster study providing information on the cluster structure with distortions, orientation and interaction with zeolites.

### Conclusions

In summary, the electronic and vibrational properties of  $Te_8$  rings were studied experimentally using Raman and absorption optical spectroscopy and theoretically using density functional theory. A good agreement is obtained between (1) the theoretical optical absorption and Raman spectra of isolated  $Te_8$  and (2) those of  $Te_8$  formed in the large cavities of the

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zeolite LTA. Owing to zeolite utilization, this is a big step in the experimental study of Te<sub>8</sub>, which is limited by the fabrication of exotic compounds like  $Cs_3Te_{22}^{53}$  or cluster registration in molecular beams.<sup>54</sup> Polarization-orientation Raman spectra of LTA-Te show that the rings are oriented by their major axes along the 4-fold axes of LTA. The observed splitting of the Te<sub>8</sub> bond-bending modes suggests the reduction of the ring  $D_{4d}$ symmetry in the LTA cavity. The bond-stretching modes demonstrate mixing due to the reduced symmetry of the ring and, probably, the essential anharmonicity of the vibrations. Even moderate heating of LTA-Te causes significant intensification of Te<sub>8</sub> librations in the LTA cavities, which corresponds to a rather weak van der Waals interaction between the ring and the zeolite. Experimental optical absorption spectra of LTA-Te display dependence on the Te loading density due to the electronic interaction of Te<sub>8</sub> from neighbouring cavities, which increases with an increase in the loading density. The effect is confirmed using DFT calculations of the absorption spectra of Te<sub>8</sub> dimers. The observed Te<sub>8</sub> ring-ring interaction is beneficial for the formation of cluster crystals with narrow electron bands and predicted non-linear electric properties. On the other hand, our results can be interesting in the sense of relationships with other inorganic 8-membered ring clusters such as Pd<sub>8</sub>.55

### Conflicts of interest

There are no conflicts to declare.

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