

Intermolecular Interaction in TeO<sub>2</sub> Crystal

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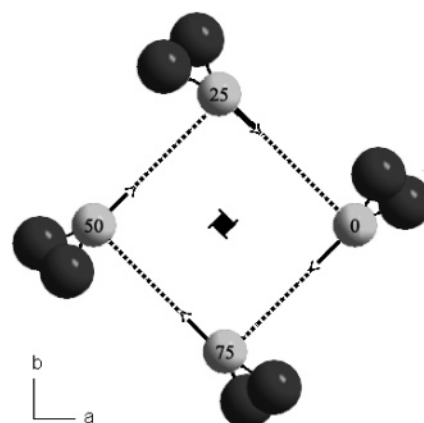
It is shown that the abnormal long-range Te–Te intermolecular interaction in TeO<sub>2</sub> crystals may be related to the tunneling of electrons from the 5s<sup>2</sup> active lone pairs of Te<sup>4+</sup> ions and their partial delocalization on neighboring Te<sup>4+</sup>.

Dioxides of p-elements TeO<sub>2</sub> and SeO<sub>2</sub> are characterized by abnormally high melting temperatures for molecular crystals ( $T_m = 1005$  K and  $T_m = 613$  K). These properties have much in common with ionic crystals such as TiO<sub>2</sub> ( $T_m = 2143$  K) and SnO<sub>2</sub> ( $T_m = 1900$  K). However, a lattice of the paratellurite  $\alpha$ -TeO<sub>2</sub> (space group  $P4_12_12$ ;  $a = 4.812$  Å;  $c = 7.615$  Å;  $Z = 4^{1,2}$ ) is constructed from isolated corner molecules of TeO<sub>2</sub> ( $D(\text{Te–O}) = 1.903$  Å and  $\angle(\text{O}_1\text{–Te–O}_1) = 102.0^\circ$ ), and in this respect,  $\alpha$ -TeO<sub>2</sub> exhibits features of the molecular crystal. According to the <sup>125</sup>Te NMR data, the Te atoms of the nearest-neighbor molecules are connected by unusual intermolecular interactions (“bonds”) Te–Te ( $D(\text{Te–Te}) = 4.07$  Å, Figure 1<sup>3</sup>). It was noted that these bonds may be responsible for the high melting temperatures and for the abnormally big anisotropy of acoustic properties of the paratellurite. In particular, the speeds of the shift elastic waves decrease by up to 0.6 km/s in directions [110] and  $[\bar{1}\bar{1}0]$  (the directions closest to the orientation of Te–Te bonds), whereas these speeds achieve values of 4.2 and 2.1 km/s in the [100] and [001] directions, respectively.<sup>4</sup>

The distorted structure of TeO<sub>2</sub> molecules is attributable to vibronic coupling, in parallel with pyramidal structures of AX<sub>3</sub> molecules (A = P, As, Bi; X = F, Cl, Br, I) which were investigated by the density functional theory (DFT) method.<sup>5,6</sup> However, these structural arrangements are obtainable from geometry molecular optimization by the second-order local Möller–Plesset method (LMP2).<sup>7</sup>

In the present work, we investigate the structure of TeO<sub>2</sub> molecules by the ab initio restricted Hartree–Fock (RHF) and LMP2 methods.<sup>8–10</sup> The optimization of molecular geometry was carried out for the molecule TeO<sub>2</sub> and also, for comparison, for the isoelectronic three-nuclear molecules SeO<sub>2</sub>, and SO<sub>2</sub> and O<sub>3</sub> (with melting temperatures of 197.5 and 81 K, respectively). The starting geometry was chosen as linear for all of the molecules. All calculations were carried out by the program Jaguar 5.5.<sup>11</sup> The atomic basis 6-31G(p,d) was used for O and S,<sup>12</sup> and the quasi-relativistic basis Lavcp,<sup>13</sup> for the heavy atoms Te and Se.

The result from RHF and RHF+LMP2 calculations is the detection of the instability of the linear configuration of MO<sub>2</sub> molecules (Table 1). Accounting for electron correlations leads to substantial changes in the geometry of all molecules. The



**Figure 1.** Arrangement of the TeO<sub>2</sub> molecules and the Te–Te bonds in the (001) plane of  $\alpha$ -TeO<sub>2</sub> crystal. The vertical coordinates of Te atoms are indicated in percents of  $c_0$  period. The arrows mirror the orientations of lobes of  $\Psi_{\text{LP}}(\text{Te})$  functions.

**TABLE 1: Calculated Energies ( $\Delta$ ) and Geometry Parameters of MO<sub>2</sub> (M = O, S, Se, Te) Molecules (Bond Lengths ( $D$ ) Are in Å, and Bond Angles ( $\angle$ ) Are in Degrees)**

	O <sub>3</sub>	SO <sub>2</sub>	SeO <sub>2</sub>	TeO <sub>2</sub>
$D_{\text{start}}(\text{M–O})$	1.1	1.2	1.4	1.8
$\angle(\text{O–M–O})_{\text{start}}^\circ$	180	180	180	180
$D_{\text{RHF}}(\text{M–O})$	1.204	1.414	1.570	1.718
$D_{\text{RHF+LMP2}}(\text{M–O})$	1.305	1.481	1.656	1.801
$D_{\text{exp}}(\text{M–O})^{14}$	1.278	1.43	1.607 <sup>a</sup>	1.90
$\angle(\text{O–M–O})_{\text{RHF}}$	118.9	118.9	114.5	112.8
$\angle(\text{O–M–O})_{\text{RHF+LMP2}}$	118.4	119.5	116.2	114.0
$\angle(\text{O–M–O})_{\text{exp}}^{14}$	116.8	119.5	114 <sup>a</sup>	102.0
$\Delta_{\text{RHF}}, \text{hr}^b$	−0.289	−0.466	−0.321	−0.316
$\Delta_{\text{RHF+LMP2}}, \text{hr}^b$	−0.223	−0.653	−0.555	−0.471

<sup>a</sup> In the vapor phase.<sup>15</sup> <sup>b</sup>  $\Delta = E + \text{ZPE} - \Sigma$ , where  $E$  is the total energy of the MO<sub>2</sub> molecules, ZPE is the zero-point energy of the MO<sub>2</sub> molecules, and  $\Sigma$  is the sum of the total energies of the M<sup>0</sup> and 2O<sup>0</sup> atoms.

linear molecules MO<sub>2</sub> transform into  $C_1$  (averaged  $C_{2v}$ ) configurations with geometrical parameters close to the experimental data in both the crystal and gas phases. It is important that the distortions of the molecules MO<sub>2</sub> are accompanied by the transition of the lone pairs  $ns^2$  of the central ions M<sup>4+</sup> into mixed s–p states. We had studied the electronic structure of MO<sub>2</sub> molecules using NBO analysis.<sup>16</sup> It was found that

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substantial changes take place in the state of  $ns^2$  lone pairs of  $M^{4+}$  ions in the distorted molecules  $MO_2$ :

$$\Psi_{LP}(Te[5s^2]) = 0.8798 \psi(5s) - 0.4744 \psi(5p_x) + \dots;$$

$$\Psi_{LP}(Se[4s^2]) = 0.8627 \psi(4s) - 0.5047 \psi(4p_x) + \dots;$$

$$\Psi_{LP}(S[3s^2]) = 0.8301 \psi(3s) - 0.5524 \psi(3p_x) + \dots;$$

$$\Psi_{LP}(O[2s^2]) = 0.7292 \psi(2s) - 0.6834 \psi(2p_x) + \dots;$$

where  $\Psi_{LP}$  is the mixed state wave function of the  $ns^2$  lone pair and  $\psi(ns)$  and  $\psi(np)$  are atomic wave functions. The  $x$  axis is oriented along the  $C_2$  symmetry axis of the  $MO_2$  molecule; dots mean omitted inputs of other excited states  $\psi[(n+1)s]$ ,  $\psi[(n+1)p]$ , etc.

Thus, the empirical data discussed earlier<sup>16,17</sup> about the spatial distribution of the electron density of stereoactive lone pairs of molecules receive a quantitative confirmation. However, the physical nature of the long-range Te—Te intermolecular interaction, stabilizing the “loose” structure (Figure 1), is not clear.

One possible explanation of that phenomenon may be related to the finite probability of tunneling of electrons through the potential barrier providing the localization of lone pairs of  $M^{4+}$  ions. A similar explanation was offered for the occurrence of abnormal electronic transitions,  $2_{3/2} \rightarrow 6s_{1/2}$ , in the fine structure of X-ray absorption edge (XANES) in  $\alpha$ -PbO,  $\beta$ -PbO, and  $Bi_2O_3$ .<sup>18</sup> These transitions should not be observed for completely filled states with wave function  $\Psi_{LP}$ . In crystalline  $TeO_2$ , similar transitions ( $2_{3/2} \rightarrow 5s_{1/2}$ ) in the fine structure of X-ray absorption edge were found.<sup>19</sup> It is worth mentioning that electrostatic forces from electronic pairs and  $O^{2-}$  ions in  $MO_2$  molecules reduce the height of this barrier and increase the probability of tunneling of lone pair electrons along the bisector of the  $MO_2$  molecule. The calculated effective charges on atoms of oxygen in  $MO_2$  molecules are  $-1.07e$  in  $TeO_2$ ,  $-0.94e$  in  $SeO_2$ ,  $-0.89e$  in  $SO_2$ , and  $-0.16e$  on terminal atoms in  $O_3$  (results of the NBO analysis). Thus, one can expect that tunneling-related partial delocalization of the lone pairs of  $M^{4+}$  ions on the central atoms of neighboring  $MO_2$  molecules is highest for  $TeO_2$ .

The influence of tunneling of lone pairs on intermolecular interaction can be estimated as follows. Because of the finite transparency of the potential barrier providing localization of lone pairs, tunnel splitting of the energy state corresponding to a mixed wave function,  $\Psi_{LP}$ , takes place. The value of the splitting ( $\Delta E$ ) may qualitatively characterize the energy of the resulting intermolecular interaction, and its order is determined from the ratio  $\Delta E \sim k(h^2/mD^2)$ , where  $k$  is the factor of relative transparency of the barrier,  $h$  is Planck's constant, and  $m$  is the electron mass.<sup>20</sup> Using  $k \approx 0.1$ , estimated from NMR data for  $TeO_2$ ,<sup>3</sup> one finds  $\Delta E \sim 1.5$  eV, which exceeds the typical energy of van der Waals interactions but is less than the energy of covalent interactions.

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