PHYSICAL REVIEW B **68**, 094203 (2003)

Ab initio study of the polymer molecules $(\mathrm{TeO_2})_n$ as model systems for the local structure in $\mathrm{TeO_2}$ glass

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(Received 21 February 2003; revised manuscript received 5 June 2003; published 17 September 2003)

The equilibrium geometry and energy of formation of the polymer molecules $(\mathrm{TeO_2})_n$ with $n=2-6$ were studied within the *ab initio* B3LYP method. For each n greater than 2, several stable conformers were found. They are classified into four homologue series: the cyclic molecules built up of corner-sharing $\mathrm{TeO_3}$ pyramids, chain molecules built up of edge-sharing $\mathrm{TeO_4}$ units, cyclic molecules built up of edge-sharing $\mathrm{TeO_4}$ units, and three-dimensional framework structures built up predominantly of corner-sharing $\mathrm{TeO_4}$ units. The latter structures were shown to possess the lowest energy of formation whose limit at $n\rightarrow\infty$ was found to agree well with the experimental value of the cohesive energy in paratellurite. These molecules could be representative of the local structures in $\mathrm{TeO_2}$ glass.

DOI: 10.1103/PhysRevB.68.094203 PACS number(s): 61.43.Fs, 61.43.Bn

I. INTRODUCTION

Solid tellurium dioxide can exist in crystalline and glassy forms. Presently, three modifications of crystalline $\mathrm{TeO_2}$ are well documented. Of those, the ground state, paratellurite α-$\mathrm{TeO_2}$, has attracted the most attention by virtue of its remarkable dielectric, piezoelectric, optic, and opto-acoustic characteristics.[1,2] Another modification of crystalline $\mathrm{TeO_2}$, tellurite β-$\mathrm{TeO_2}$, has been studied by structural x-ray diffraction methods,[3] but it appears that its fundamental physical properties remain poorly known. Recently, a third crystalline modification, γ-$\mathrm{TeO_2}$, existing at ambient pressure, was found and studied using x-ray diffraction and Raman spectroscopy techniques.[4,5]

At present, special interest is paid to $\mathrm{TeO_2}$ glass which has a number of interesting properties[1] including exceptionally high hyperpolarizabilty which makes this material very promising for nonlinear optical designs. The microscopic nature of those properties remains challenging for fundamental science and its understanding demands knowledge of the peculiarities inherent in the structure of $\mathrm{TeO_2}$ glass.

Considering that the short-order atomic arrangement of glassy and crystalline solids is governed by the same basic principles as chemistry, it is generally believed that the glass and crystalline phases of any compound can be framed in similar manner, and the glassy phase is frequently regarded as a disordered form of the parent crystalline structure. Traditionally, the short-range organization of $\mathrm{TeO_2}$ glass has been discussed in terms of the structural units of the α-$\mathrm{TeO_2}$ crystalline lattice.[1,6] However, recent experimental measurements and theoretical modeling of $\mathrm{TeO_2}$ glass cast doubt on the traditional view of its structure as a distorted lattice of paratellurite α-$\mathrm{TeO_2}$.

The finding of the γ-$\mathrm{TeO_2}$ phase aggravates the skepticism. Actually, this phase appears as the first crystalline structure during the temperature-induced crystallization of $\mathrm{TeO_2}$ glass which evolves finally to α-$\mathrm{TeO_2}$. In contrast to a frameworklike constitution of α-$\mathrm{TeO_2}$, the γ lattice is framed from infinite polymerized $\mathrm{TeO_2}$ chains (similar to those in crystalline $\mathrm{SeO_2}$) which involve two particular fragments: namely, rather symmetric Te-O-Te bridges and short terminal Te-O bonds. The characteristic vibrations of those fragments dominate the the Raman spectrum of γ-$\mathrm{TeO_2}$, forming two intense bands near 426 cm^{-1} and 680 cm^{-1}, respectively.[5] Such peculiarities correspond to the main features of the Raman spectrum of $\mathrm{TeO_2}$ glass, whereas this is not the case for α-$\mathrm{TeO_2}$: its spectrum has no intense bands between 300 and 600 cm^{-1}.[1] So the spectrochemical evidence allows us to think that $\mathrm{TeO_2}$ glass would contain $(\mathrm{TeO_2})_n$ polymerized entities (precursors of the $\mathrm{TeO_2}$ chains in the γ lattice) built up from the above-mentioned structural fragments.

The existence of such entities for $n=2$ and 3 in the gaseous phase is well known,[7,8] and it can be thought that the higher-order polymers can be present in the condensed glassy state. At present, this hypothesis has no experimental evidence. Therefore, a quantum-mechanical study, capable of confirming or refusing it, seems to be an important and a topical step in understanding the nature of glassy $\mathrm{TeO_2}$. This is the subject of this paper in which the main questions are the following.

(1) Does the quantum theory predict the stability of the polymer $(\mathrm{TeO_2})_n$ molecules?

(2) Which polymer configurations are possible and which of them are the most stable?

(3) How does the polymerization energy change along with the polymerization order n?

Ab initio calculations were used in the modeling of the molecularlike clusters including the $\mathrm{TeO_4}$ groups as the basic structural units.[6,9,10] However, the objects of those studies were taken *a priori* as hypothetical molecules of complex $\mathrm{H}_x\mathrm{Te}_n\mathrm{O}_m$ acids with anions constructed analogously to the fragments existing in the crystalline polymorphs of $\mathrm{TeO_2}$, basically in α-$\mathrm{TeO_2}$. In doing so, a variety of alternative molecular complexes, which can exist in abundance in glassy state, were kept away from consideration. A doubtful feature of these studies was the use of hydrogen atoms as pseudoa-

TABLE I. Molecular structures and properties: bond lengths (Å), angles (°), ΔE (kJ/mol), and frequencies (cm^{-1}).

Molecule	Symmetry	Quantity	*Ab intio*, this work	Experiment	Reference
TeO	C_∞	ΔE	-42.6	-13.4	7
		Te-O	1.8876	1.828	13
		ω	795	798	
TeO_2	C_{2v}	ΔE	-341.7	-150.6	7
		Te-O	1.8435	1.84	14
		O-Te-O	112.9	112	
		$\omega(B_1,A_1,A_1)$	921,883,250	849,810,294	15
$(TeO)_2$	D_{2h}	ΔE	-450.0	-283.3	
		Te-O	2.046	-	
		O-Te-O, Te-O-Te	80.8, 93.6	100, -	7
		$\omega(A_g,B_{3u},B_{2u},A_{1g},A_{1g},B_{1u})$	610,604,553, 530,249,152	633,627,543, 520,137,57	
$(TeO_2)_2$	C_{2h}	ΔE	-1004.7	-581.6	
		Te-O^b, Te-O^t	2.035, 1.8183	-	7
		O^tTeO^b, TeO^bTe	104, 101	-	

toms terminating broken Te-O bonds, which is commonly used in modeling an infinite structure by finite clusters.

Our approach involves the study of the $(TeO_2)_n$ molecules. Such molecules with $n=1$–4 have been observed in vapors over solid and liquid TeO_2 in Refs. 7 and 8. We believe that they, as well as polymer molecules with higher n, can be closely related to the local structure of glassy TeO_2. In this study, the structure and energy of formation of $(TeO_2)_n$ molecules with $n=2$–6 were investigated. Our calculations included two stages. The first stage was predominantly of methodological character—it was aimed at choosing a proper computational method and testing its accuracy in tellurium oxide molecule calculations. This involved simulation of the structure and properties of the molecules TeO and TeO_2 and their dimers $(TeO)_2$ and $(TeO_2)_2$. Their energy of formation, structural parameter, and vibrational frequencies have been determined experimentally.[7,8] So comparison of the theoretical and experimental results provides a good test of the accuracy of the chosen computational routine.

The second and main stage of this study involved simulation of $(TeO_2)_n$ molecules with $n=3$-6. Molecular geometry optimization revealed several stable conformers for each n. Being supplemented by a polymerization energy analysis, these results allowed us to answer all of the above questions.

II. METHOD

As a computational *ab initio* routine, the density functional theory realized in Beck's three-parameter hybrid method using the Lee-Yang-Parr correlation functional (B3LYP) (Ref. 11) was chosen. This technique, being run within the 3-21G** basis set by the GAUSSIAN program,[12] was found to be capable of reproducing satisfactorily the energy, geometry, and vibrational spectrum of many-electron systems containing tellurium atoms. This method has been applied to studies of tellurium oxide molecules.[6,9,10]

In order to compare the calculated electronic energy with the experimental enthalpy of formation, we transformed the calculated electronic energy into the energy of formation ΔE, defining this quantity as the energy lowering in the reaction

$$\frac{n}{2}\mathrm{Te}_2+\frac{m}{2}\mathrm{O}_2\rightarrow\mathrm{Te}_n\mathrm{O}_m\,.$$

Thus, the energy of formation of a Te_nO_m molecule is drawn from the calculated electronic energy as follows:

$$\Delta E(\mathrm{Te}_n\mathrm{O}_m)=E(\mathrm{Te}_n\mathrm{O}_m)-\frac{n}{2}E(\mathrm{Te}_2)-\frac{m}{2}E(\mathrm{O}_2). \qquad (1)$$

All of the discussed molecular properties, including the energy of the O_2 and Te_2 molecules, were calculated by using an optimized geometry. The calculated structural parameters, energy of formation, and vibrational frequencies of the TeO, $(TeO)_2$, TeO_2, and $(TeO_2)_2$ molecules are presented in Table I together with the known experimental data.

The theory predicts a cyclic structure of the polymer $(TeO)_2$ and $(TeO_2)_2$ molecules, thus supporting the hypothesis proposed in Ref. 7. The chosen method ensures good correspondence in the geometry parameters of the TeO_2 molecule. The overestimation of the calculated vibrational frequencies in the high-frequency part of the spectra does not exceed 10% (see Table I). The vibrational frequency, computed at a moderate level of *ab initio* theory, contains known systematic errors, resulting in overestimates of about 10%–12%.[12] So the calculated frequencies presented in Table I, being multiplied by the standard scaling factor 0.89,[6] correspond well to the experimental values.

Despite a considerable overestimation of the absolute energy of formation values, the calculations reproduce well their relative variation, in particular the energy of polymerization. In fact, the experimental data[7] provide the heat of the reaction

$$2\mathrm{TeO}\rightarrow(\mathrm{TeO})_2$$

as 255 kJ/mol, whereas the corresponding theoretical value, estimated from the data of Table I, is 364.8 kJ/mol. The heat of the reaction

$$2\mathrm{TeO}_2\rightarrow(\mathrm{TeO}_2)_2$$

is 238.5 kJ/mol, according to experimental data,[7] whereas this quantity, derived from the *ab initio* calculations presented in Table I, is equal to 321.3 kJ/mol.

The results presented in Table I show that the B3LYP calculations reproduces quite reliably the structures, polymerization energy, and vibrational frequencies of the TeO, TeO_2, $(\mathrm{TeO})_2$, and $(\mathrm{TeO}_2)_2$ molecules. This allows us to anticipate that the modeling of the higher-order polymers, for which experimental information is lacking, would give trustworthy results which would provide the basis for theoretical speculations and could serve as predictive information for experimentalists.

III. RESULTS

The main subjects of our study are the $(\mathrm{TeO}_2)_n$ polymer molecules with $n=3$–6. The $(\mathrm{TeO}_2)_3$ and $(\mathrm{TeO}_2)_4$ molecules have been detected in the mass-spectroscopic experiments,[7,8] and the formation enthalpy of the $(\mathrm{TeO}_2)_3$ molecule has been estimated.[8] However, no suggestions about their structures were proposed. Our calculations revealed several stable conformers for all considered molecules. Their description and comparative analysis are presented below.

A. Single-bridge cyclic molecules

As was supposed in Ref. 7, the structure of the $(\mathrm{TeO}_2)_2$ molecule involves the plane cycle $\mathrm{Te}\langle{}^{\mathrm{O}}_{\mathrm{O}}\rangle\mathrm{Te}$ and two terminal Te-O bonds. The cyclic structure of this molecule admits of a suggestion that the larger molecules, built up of a cyclic repetition of the $_{-\mathrm{O}}{>}\mathrm{Te}{=}\mathrm{O}$ links, could appear at further polymerization. *Ab initio* calculations partly confirmed this: such cyclic configurations were found to be stable (but not the lowest energy) for $n=3{,}6$ (see Fig. 1) and unstable for $n=4{,}5$. In the stable molecules, the tellurium atoms form two bridging bonds and one terminal bond. Because of the threefold coordination of Te atoms, one can describe the structure of these cyclic molecules as a ring chain built up of TeO_3 pyramids connected by common corners.

The positions of the nonshared corners (those belonging to terminal Te-O bonds) are not fixed by the cyclic configuration. So the pyramids can rotate, thus giving rise to several molecular conformers. Geometry optimization provides the two stable configurations of the cyclic $(\mathrm{TeO}_2)_3$ molecule. In one of them [having C_{3v} symmetry and shown in Fig. 1(a)], all terminal bonds tilt out of the ring plane in the same direction. The second configuration [see Fig. 1(b)] manifests an altering terminal bond orientation without having any symmetry. According to the calculations, the energy of the nonsymmetric configuration is 13.6 kJ/mol lower than that of the C_{3v} configuration. Note that such a configuration corresponds to the maximal separation of tellurium atom lone pairs which are directed along the pyramid's axes. It can be thought that this factor determines the most stable configuration of all cyclic $(\mathrm{TeO}_2)_n$ polymers.

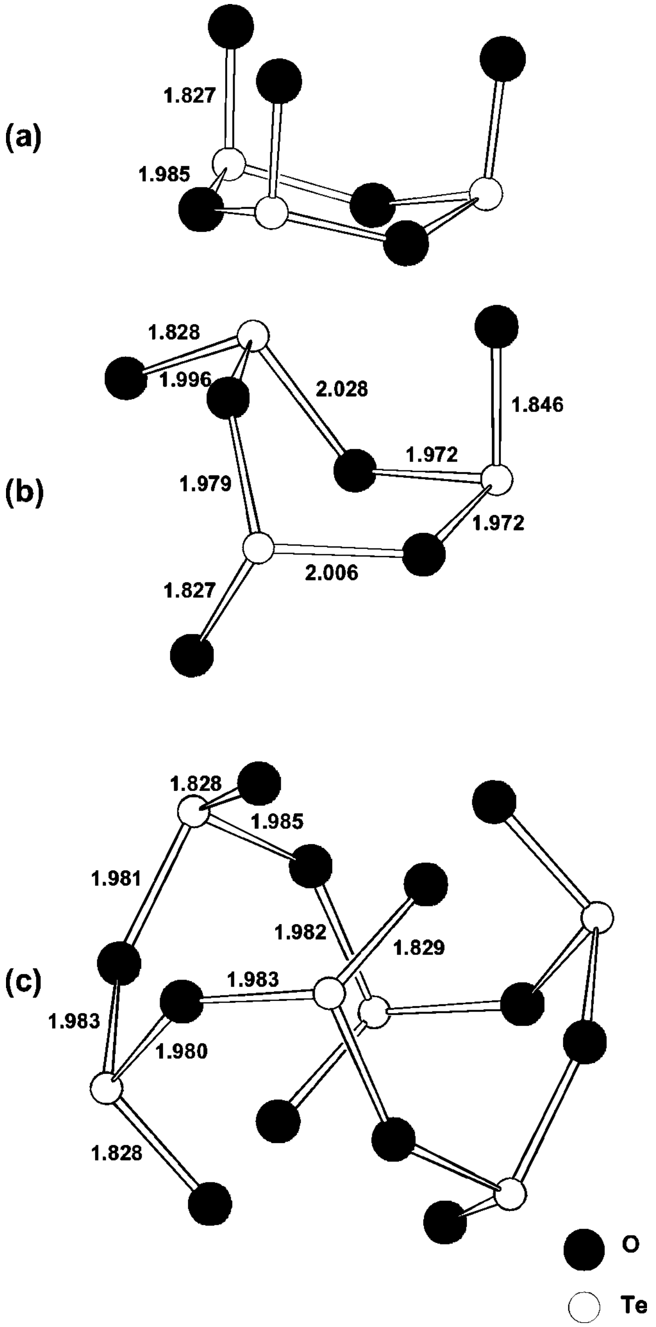

FIG. 1. Structure of the single-bridge cyclic molecules: the C_{3v} configuration of $(\mathrm{TeO}_2)_3$ (a), the nonsymmetric configuration of $(\mathrm{TeO}_2)_3$ (b), and the C_i configuration of $(\mathrm{TeO}_2)_6$ (c).

Lone-pair repulsion causes a marked ring plane distortion involving pyramid rotations around the axis lying in the ring plane. As a result, the oxygen atoms of terminal bonds approach the Te atoms of other cycle links, thus forming additional Te-O bonds. The formation of such additional bonds increases the coordination number of Te atoms and thus diminishes the total electronic energy. Distortion of the cyclic configuration of the $(\mathrm{TeO_2})_\mathrm{n}$ molecules is affected by the pyramid rotation around the axes lying in the ring plane and perpendicular to the ring circle. Sometimes, this leads to the formation of additional bonds between neighboring cycle links, thus transforming the single-bridge Te-O-Te linkage into a double-bridge $\mathrm{Te}\langle{}^{\mathrm{O}}_{\mathrm{O}}\rangle\mathrm{Te}$ one. For example, the plane configuration of the $(\mathrm{TeO_2})_4$ molecule, which corresponds to a local energy minimum within the D_{2d} symmetry constraint, was found unstable with respect to the distortion involving the pyramid rotations [see Fig. 2(a)]. No energy minimum for this molecule was found at the staggered configuration [Fig. 2(b)]. Finaly, a stable energy minimum appeared in the ring configuration built up of double-bridge linkages [Fig. 2(c)]. This type of polymer is considered below.

The cyclic configuration of the $(\mathrm{TeO_2})_5$ molecule is also unstable. In this case, the cycle distortion is more complicated: the cycle links (e.g., $\mathrm{TeO_3}$ pyramids) rotate not only around axes perpendicular to the ring circle but also around axes tangential to the ring circle. The final configuration involves one double-bridge linkage and two additional bonds between opposite cycle links, which result in a self-crossing of the cycle ring which is hiding in a framework structure which will be considered in more detail below. So cycle ring distortions give rise to the formation of additional Te-O bonds and result in other types of $(\mathrm{TeO_2})_n$ polymers with more close atomic packing.

In all the $(\mathrm{TeO_2})_n$ cyclic molecules the lengths of the terminal and bridging Te-O bonds differ markedly. The former are about 1.826 Å, and the latter vary in the range 1.97–2.00 Å, thus indicating an essentially different electron population in the terminal and bridging bonds. In fact, electron distribution analysis of the cyclic $(\mathrm{TeO_2})_3$ molecule, being carried out within the atom-in-molecule routine,[16] predicted bond orders of 1.74 and 0.88 and ionicity of 42% and 79% for terminal and bridging bonds, respectively. Hence, it is more adequate to represent terminal bonds as $\mathrm{Te{=}O}$ double bonds, but not as ionic $\mathrm{Te\text{-}O^-}$ single bonds. The Te-O-Te bridges were found almost symmetric in the cyclic molecules: the difference in bond lengths does not exceed 0.05 Å. At $n\rightarrow\infty$ the cyclic molecule is identical to an infinite $(\mathrm{TeO_2})_\infty$ linear chain which is inherent to the crystal structure of γ-$\mathrm{TeO_2}$.[4]

B. Double-bridge chain molecules

The $(\mathrm{TeO_2})_2$ molecule can be considered as the simplest representative of cyclic polymers. However, it differs from other members of this family because it contains the $\mathrm{Te}\langle{}^{\mathrm{O}}_{\mathrm{O}}\rangle\mathrm{Te}$ double bridge. Such bridges are present in some crystal structures of tellurites and β-$\mathrm{TeO_2}$.[3] One can suppose that this type of linkage gives rise to another family of $(\mathrm{TeO_2})_n$ chain polymers which can be schematically displayed as follows:

$$\mathrm{O{=}Te}\langle{}^{\mathrm{O}}_{\mathrm{O}}\rangle\mathrm{Te}\langle\cdots\rangle\mathrm{Te}\langle{}^{\mathrm{O}}_{\mathrm{O}}\rangle\mathrm{Te{=}O}. \qquad (2)$$

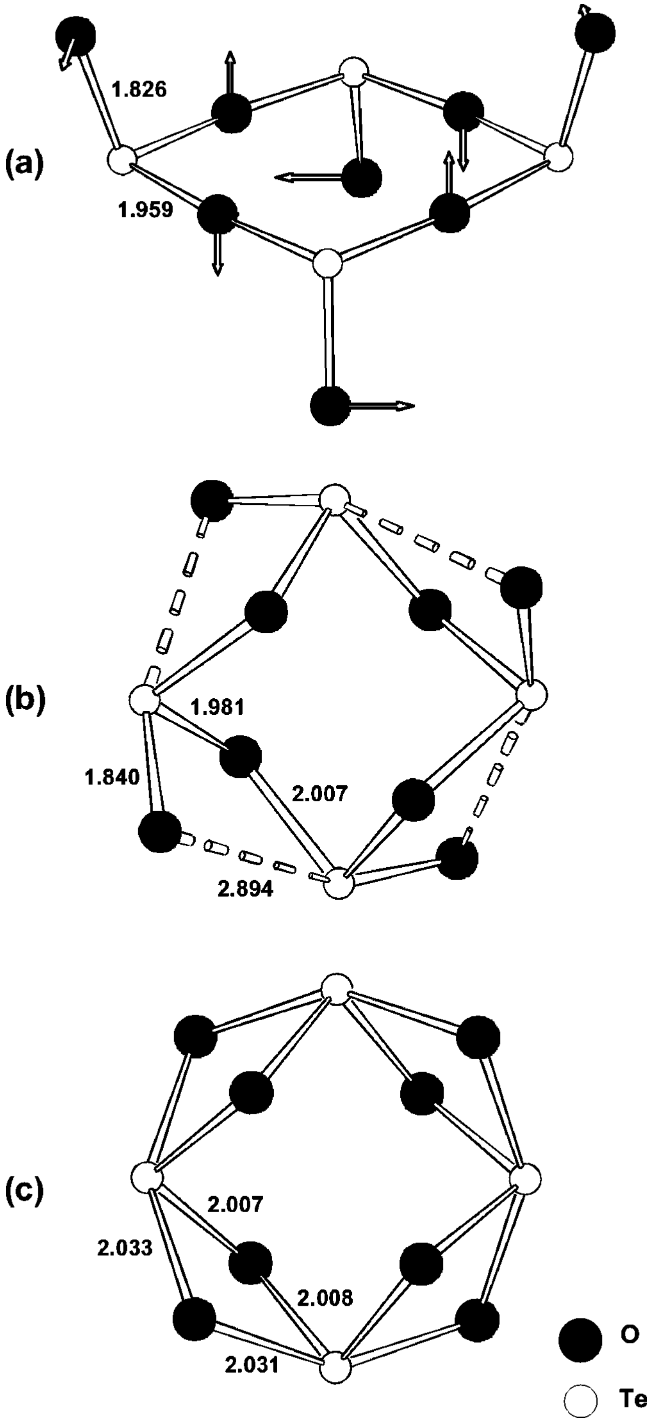

FIG. 2. Transformation of the $(\mathrm{TeO_2})_4$ cyclic molecule: eigenvector of the unstable mode in the D_{2d} single-bridge cycle configuration (a), a staggered configuration produced by the pyramid rotation (b), and the energy minimum configuration with the double-bridge cycle configuration (c).

The calculations confirmed this, and geometry optimization revealed stable configurations similar to Eq. (2) for $n=3$–6 (see Fig. 3). In these molecules, the coordination of internal tellurium atoms differs from that in cyclic polymers. The four Te-O bonds are not equivalent. The angle between the two longer bonds (~2.08 Å) is equal to 157°, and the

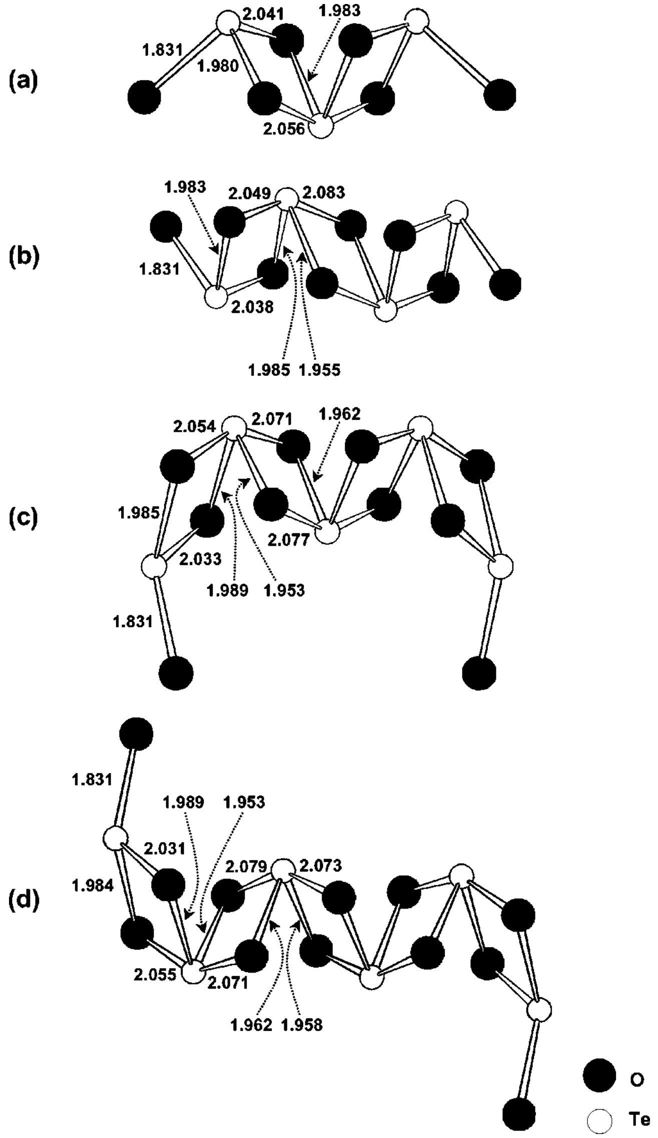

FIG. 3. Structure of the $(\mathrm{TeO}_2)_n$ double-bridge chain molecules: C_2 configuration for $n=3$ (a), C_i configuration for $n=4$ (b), C_2 configuration for $n=5$ (c), and C_i configuration for $n=6$ (d).

angle between two the shorter bonds (~1.96 Å) is about 100°. The plane of the longer bonds is almost perpendicular to that of the shorter bonds. Such a fourfold coordination of Te atoms is inherent to many tellurites anions. It is a basis structural unit of α-TeO_2. Together with the lone pair, the two short bonds form a threefold star lying in the equatorial plane, and the two long bonds are called the axial ones. Such coordination is referred to as a trigonal bipyramid (TBP). The calculated energy of these chain polymers was found to be lower than that of the corresponding cyclic isomers: the energy difference is of 24.9 and 346.0 kJ/mol for $n=3$ and $n=6$, respectively. The reason for this is quite obvious: the number of Te-O bonds is $4n-2$ in a chain molecule and only $3n$ in a cyclic $(\mathrm{TeO}_2)_n$ molecule. Hence, the relative stability of the double-bond chain polymers should increase at increasing n.

C. Double-bridge cyclic molecules

In the above discussion of the distortions in the single-bridge cyclic molecules, we noted that TeO_3 pyramid rotations could result in the formation of additional bonds between neighboring cycle links, thus transforming Te-O-Te single bridges into $\mathrm{Te}\langle{}^{\mathrm{O}}_{\mathrm{O}}\rangle\mathrm{Te}$ double bridges. If such a transformation takes place throughout the cycle, a cyclic molecule built up of double-bridge linkage appears. These configurations were found stable for $n=4,5,6$ (see Fig. 4). Alternatively, these molecular structures can be considered as appearing from linear double-bridge chain molecules in the course of closing the chain ends. All Te atoms in these molecules have TBP coordination. Throughout the series, the average angle between axial bonds (mean length of 2.02 Å) is equal to 150°, whereas the average angle between equatorial bonds (mean length of 2.00 Å) is equal to 103°.

As was mentioned above, the $\mathrm{Te}\langle{}^{\mathrm{O}}_{\mathrm{O}}\rangle\mathrm{Te}$ double bridge subunit has been observed in different tellurite crystal structures. However, such type of linkage is less frequent than the simple Te-O-Te bridge. For example, only the single-bridge linkage occurs in the crystal structure of paratellurite. One can suppose that the preference of the single bridges is caused by a more longer Te-Te separation inherent to such bridges. It can be thought that there should be another type of polymer structure in which the TBP coordination of Te atoms would coexist with a predominantly single-bridge linkage.

D. Framework molecules

These polymer molecules are built up of corner- and edge-sharing pyramids and TBP's, thus making a three-dimensional framework structure. We believe that they are the most representative for the local structure in glassy TeO_2. Such molecules have been found by energy minimization for all n greater than 3. Searching for these molecular species, we have performed geometry optimization for several TeO_2 clusters borrowed from the paratellurite lattice. Two such structures with $n=4$ and $n=5$ are shown in Figs. 5(a) and 5(b). Their structures have some resemblence to the initial configuration. In these molecules, one can distinguish one TBP surrounded by three and four pyramids, respectively. The molecule shown in Fig. 5(c) appeared in the course of relaxation of the tilted $(\mathrm{TeO}_2)_5$ cyclic polymer. This molecular structure is built up of the three TBPs and two pyramids. The highly symmetric $(\mathrm{TeO}_2)_6$ molecule [see Fig. 5(d)] is the simplest finite cluster containing the corner-connected TBP's only. These polymers can be considered as molecular analogs of α-TeO_2.

One can describe the structure of all these molecules as a three-dimensional (3D) network framed from corner-sharing (single bridge) or edge-sharing (double bridge) TeO_4 TBP's and TeO_3 pyramids. It can be seen that in these molecules, TBP's are more frequent than pyramids, single bridges dominate over double bridges, and terminal $\mathrm{Te{=}O}$ bonds are rare.

E. Energy of formation

In order to characterize quantitatively the relative stability of different polymers, one should compare their energy of

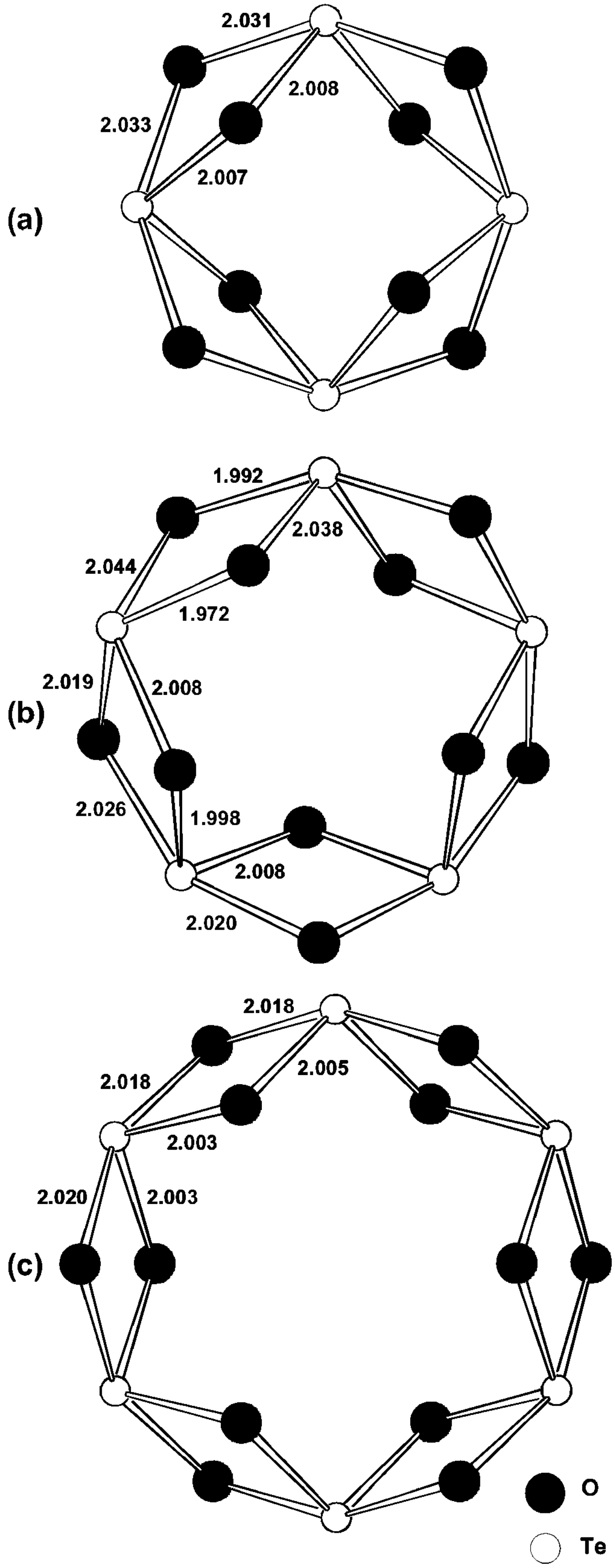

FIG. 4. Structure of the $(TeO_2)_n$ double-bridge cyclic molecules: S_4 configuration for $n=4$ (a), C_s configuration for $n=5$ (b), and C_{2h} configuration for $n=6$ (c).

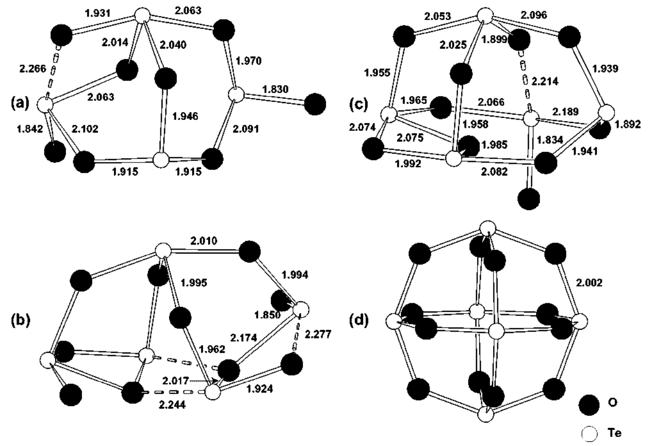

FIG. 5. Structure of the $(TeO_2)_n$ framework molecules: one TBP and three pyramids for $n=4$ (a), one TBP and four pyramids for $n=5$ (b), three TBP's and two pyramids for $n=5$ (c), and the O_h configuration with six TBP's for $n=6$ (d). Additional bonds longer than 2.2 Å are shown by dotted lines.

formation per one formula unit. This quantity (which is referred below as a specific energy of formation) is defined as

$$\delta E = \frac{1}{n}\Delta E, \tag{3}$$

with ΔE defined in Eq. (1). Another important characteristic of the chemical bounding is the average coordination number, which can be defined as the number of valence bonds per one Te atom. The calculated specific energy of formation for all considered molecules is presented in Fig. 6 against the average coordination number. It is evident from definition (2) that the right-hand side of Eq. (3) is negative. Its magnitude (positive value) is shown in Fig. 6. The dependences in Fig. 6 allow us to conclude that this quantity increases with in-

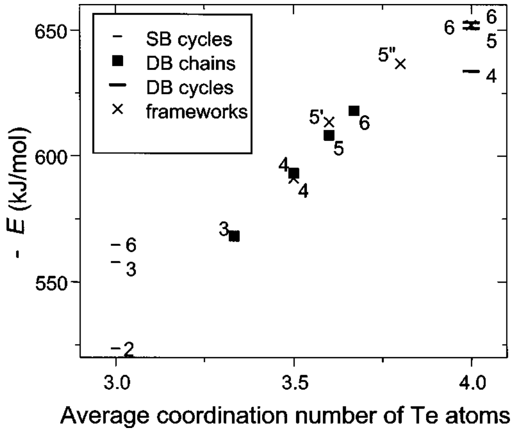

FIG. 6. Specific energy of formation of the $(TeO_2)_n$ polymer molecules vs the average coordination number of tellurium atoms. Values of n are shown to each symbol. The abbreviations SB (single bridge) and DB (double bridge) are used in the series notation. The energy values of the two framework structures with $n=5$ shown in Figs. 5(b) and 5(c) are marked as 5′ and 5′, respectively.

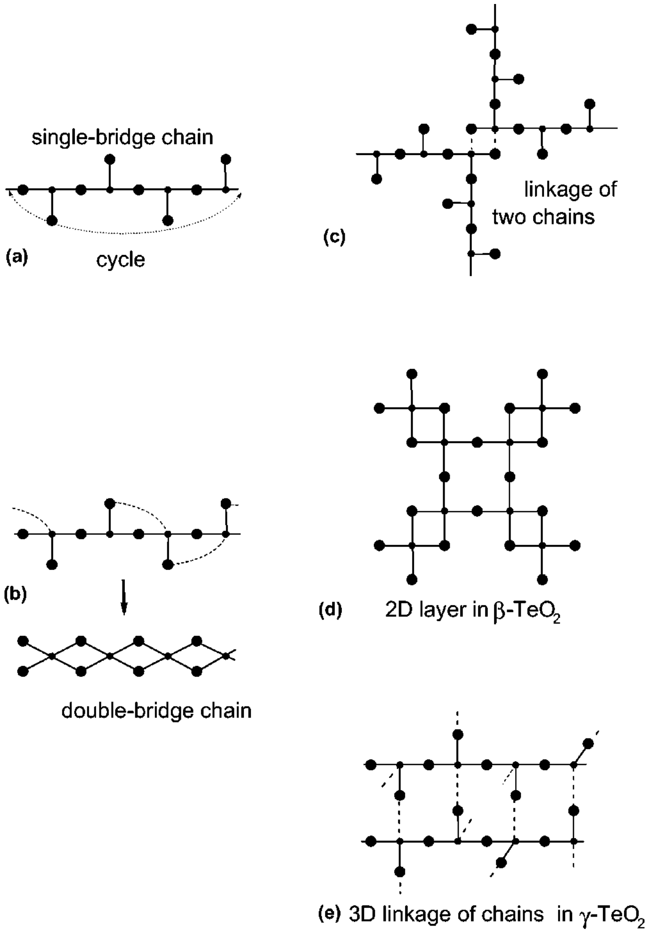

FIG. 7. Possible structural subunits of the $(\mathrm{TeO_2})_n$ polymers: linear chain of the corner-linked $\mathrm{TeO_3}$ pyramids (a), evolution of terminal Te-O bonds into the complementory Te-O-Te bridges leading to the formation of a double-bridge chain composed of the edge-sharing $\mathrm{TeO_4}$ TBPs (b), intersection of two single-bridge chains via the double-bridge linkage (c), combination of the double-bridge and single-bridge linkages (d), and interconnection of single-bridge chains leading to the formation of a framework structure (e).

creasing n in all series. In general, the magnitude of the formation energy is proportional to the average coordination number.

The data presented in Fig. 6 enable us to estimate the limit value of δE at $n\to\infty$ as -650 kJ/mol. This value would correspond to an infinite polymer structure. The lowest specific energy of formation was found in double-bridge cyclic polymers and framework molecules.

The former are not representative as possible local structures of the glassy state because approaching each other the double-bridge chains show a high ability of intersecting as is shown in Fig. 7(d). This leads to the formation of 2D infinte polymers similar to those found in β-$\mathrm{TeO_2}$. In contrast, agglomeration of the framework molecules at $n\to\infty$ can be imagined as an infinite 3D network built up of corner-connected TBP's. Being ordered, such a structure would correspond to α-$\mathrm{TeO_2}$. So one can compare the theoretical limit value of δE with the experimental cohesive energy in that crystal estimated as the energy of sublimation

$$\mathrm{TeO_2(solid)\to TeO_2(gas)},$$

which was estimated experimentally in Refs. 7 and 8 as 288.7 and 272.0 kJ/mol, respectively. Our calculations provide a quite comparable estimation:

$$\delta E(\mathrm{TeO_2 molecule}) - \delta E(n\to\infty)$$

$$= -342 + 650 = 308 \ \ \mathrm{kJ/mol}.$$

Ab initio calculations show that the magnitude of the specific formation energy increases at increasing n in all series, and its limit value agrees well with the experimental estimation of the cohesive energy of paratellurite. This answers the first and third of the questions asked in the Introduction.

IV. DISCUSSION

Consider first the polymerization energy defined as the energy reduced in the reaction

$$n\mathrm{TeO_2}\to(\mathrm{TeO_2})_n$$

divided by n. This quantity, determined for dimer $(\mathrm{TeO_2})_2$ from the experimental data presented in Table I, takes the value -140.2 kJ/mol. The polymerization energy of $(\mathrm{TeO_2})_3$ derived from the study in Ref. 8 is equal to -147.8 kJ/mol. Thus, experimental measurements showed that the polymerization energy of $(\mathrm{TeO_2})_n(n>1)$ is of the same order as the formation energy of an isolated $\mathrm{TeO_2}$ molecule (see Table I). *Ab initio* calculations reproduce this fact satisfactorily well and offer its explanation: the new bonds appearing in the course of polymerization are of the same length and same electron occupancy and have the same magnitude of force constants as the bonds in the $\mathrm{TeO_2}$ molecule. Strictly speaking, it is impossible to classify the bonds in these polymers as intramolecular and intermolecular ones. So consolidation of $\mathrm{TeO_2}$ molecules differs from that in a molecular crystal like $\mathrm{SO_2}$. In $(\mathrm{TeO_2})_n$ molecules, this solidification process is similar to full-scale polymerization in organic molecules such as polyethylene, for example.

Answering the second of the questions asked in the Introduction, the four main types of possible $(\mathrm{TeO_2})_n$ polymers have been found. They are described in Sec. III. The corner-sharing linkage of the $\mathrm{TeO_3}$ pyramids results in the formation of single-bridge cycle polymer molecules, where the basic subunit is the $\genfrac{}{}{0pt}{}{-\mathrm{O}}{-\mathrm{O}}\rangle\mathrm{Te{=}O}$ group. A similar Te atom environment is found experimentally in the structure of some tellurite anions such as $(\mathrm{Te_3O_7})^{2-}$ or $(\mathrm{Te_4O_{11}})^{2-}$, for example. The same subunits form infinite $(\mathrm{TeO_2})_\infty$ chains in the crystal structure of γ-$\mathrm{TeO_2}$. Formally, these chains can be considered as a limit of the cycle configuration at $n\to\infty$. The edge-sharing linkage of the $\mathrm{TeO_4}$ TBP's gives rise to another type of polymer with the Te atoms linked by the $\mathrm{Te}\langle\genfrac{}{}{0pt}{}{\mathrm{O}}{\mathrm{O}}\rangle\mathrm{Te}$ double bridges. These are the double-bridge chain polymer molecules. On closing the ends of such chains, they transform into double-bridge cycle polymer molecules. Energetically, these configurations are more stable than the single-bridge cycles owing to a greater number of Te-O bonds. These double-bridge subunits were found in tellurite anions and in the crystal structure of β-TeO_2. However, they are less abundant than single Te-O-Te bridges. It may be related to a rather short Te-Te distance inherent to the double-bridge linkage. In the crystal structures, the TBP's and TeO_3 pyramids are linked more often by single bridges—i.e., via corner sharing. The corner-connected TBP's are the basic subunits in paratellurite—the ground-state structure of TeO_2. Such a type of linkage results in the formation of $(TeO_2)_n$ framework polymer molecules. *Ab initio* calculations show that this type of polymerization provides the highest energy gain at increasing n, and the limit value of this energy agrees well with the experimental estimation of the cohesive energy of paratellurite.

A linear chain of corner-linked TeO_3 pyramids, which involves the single Te-O-Te bridges, is schematically displayed in Fig. 7(a). An alternative structure, a linear chain of the edge-sharing TBP's, which consists of the double bridge $\mathrm{Te}\langle{}^{\mathrm{O}}_{\mathrm{O}}\rangle\mathrm{Te}$, is shown in Fig. 7(b). The formation of such a double-bridge chain can be considered as resulting from the evolution of the terminal Te-O bonds of a single-bridge chain into complementory Te-O-Te bridges as is shown in Fig. 7(b). The same mechanism can provoke terminal Te-O bonds to form interchain bridges as is shown in Fig. 7(e), thus resulting in the creation of framework structures. This takes place in γ-TeO_2, where the O atoms of terminal bonds (1.86 Å) form interchain bonds (2.20 Å) which are somewhat longer than the intrachain bridge bonds (1.95–2.02 Å).[4]

Various combinations of the four types of polymerization cause a great variety of possible $(TeO_2)_n$ structures. For example, it is possible to imagine the intersection of two single-bridge chains (or two cyclic polymers) via double-bridge linkage [see Fig. 7(c)] as well as the intersection of two double-bridge chains via single-bridge linkages [see Fig. 7(d)]. By the way, the structure shown in Fig. 7(d), being periodically repeated in two dimensions, forms the layer structure of β-TeO_2.[3]

The high polymerization ability of TeO_2 molecules is caused by the flexibility of the Te atom valence electron distribution, owing to which the coordination number of Te atom can vary from 2 to 4. This, as well as the presence of a lone pair, distinguishes TeO_2 from other glass-forming oxides. In the molecules under study, the two basic coordination polyhedra of Te atoms are the TeO_4 TBP and TeO_3 pyramid. The four Te-O bonds in TBP coordination are the single bonds. The corresponding electron configuration is shown in Figs. 8(a) and 8(b). The valence state of the Te atom in TBP coordination can be characterized as a "valence saturation." If all Te atoms are in this state, no more valence bonds can be formed. Such a situation takes place in α-TeO_2—the ground-state structure of TeO_2. In the molecular structures considered in this study, a similar situation was found only in the frameworklike $(TeO_2)_6$ polymer shown in Fig. 5(d). This explains its low specific formation energy. Thus, our formation energy analysis allows the conclusion that the cohesive energy of the TeO_2 polymorphs increases in the series γ, β, α, successively.

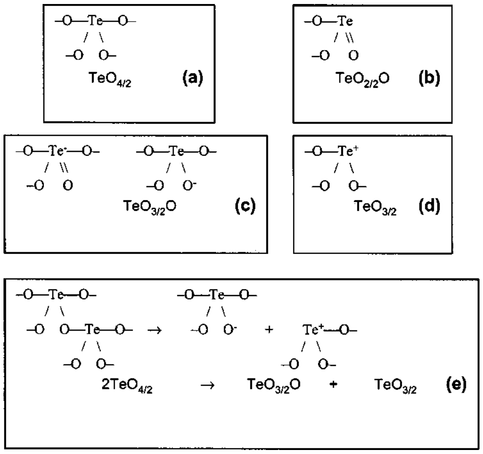

FIG. 8. Te atom configuration in the $(TeO_2)_n$ polymer molecules: TBP (a), pyramid with one terminal bond (b), TBP with one terminal bond (c), and pyramid without terminal bond (d). The hypothetical scheme of the bridge breaking as a model of the glass formation process in pure TeO_2 (e).

The pyramidlike subunits shown in Fig. 8(b) are inherent to all single-bridge cyclic polymers and to the terminal groups in the double-bridge chain polymers. In such a coordination, the valence ability of the Te atom is not saturated. This makes these subunits very active for a further polymerization. If there are two or more such groups, they could unite by transforming the terminal bonds into bridging ones. As a result, the fragments shown in Figs. 8(c) and 8(d) would appear. In the first of them, the Te atom forms three bridging bonds and one terminal bond and, in the second one, only three bridging bonds. According to notation of Ref. 17, these structural fragments are labeled as $TeO_{3/2}O$ and $TeO_{3/2}$. In our calculations, these subunits occur in the $(TeO_2)_4$ and $(TeO_2)_5$ framework molecules. In both of them, the correspondence between the number of bonds and number of valence electrons is broken. Formally, there are five binding molecular orbitals in the $TeO_{3/2}O$ unit and three binding molecular orbitals in the $TeO_{3/2}$ unit. Since the Te atom possess four valence electrons (apart from two electrons forming the lone pair), one can expect that electron transfer between these two fragments would take place in order to restore the balance between the number of valence bonds and the number of valence electrons, as is shown in Figs. 8(c) and 8(d). The electron population analysis was in line with this suggestion: the Mulliken charge of Te atom in $TeO_{3/2}$ was always higher than that in $TeO_{3/2}O$. However, the difference does not exceed $0.2e$. This indicates a considerable electron delocalization throughout the molecule.

The $TeO_{3/2}O$ fragment was found in some crystal structures of tellurite anions.[17,18] In Ref. 17, this subunit is denoted as $TeO_{3/2}O^-$. This implies that the terminal bond is a Te-O^- single bond, as is shown on the right side of Fig. 8(c). However, *ab initio* calculations do not confirm this. The calculated bond length, electron occupancy, and force constant values indicate that this bond is closer to the double-bond unit shown on the left side of Fig. 8(c). Strictly speaking, such a configuration implies seven valence electrons on the Te atom. So its formal charge is $-1e$. Calculations show that the actual electronic structure of this fragment is a resonance between the two alternatives shown in Fig. 8(c).

In our study, $TeO_{3/2}O$ and $TeO_{3/2}$ structural fragments result from agglomeration of TeO_2 molecules. They are inherent to the species intermediate between a completely disintegrated molecules and an infinite framework of completely polymerized TeO_2. And vice versa, they can appear in melting the framework structure, as is shown in Fig. 8(e). Hence, they can play an important role in the glass formation process. In Ref. 19, the subunit $TeO_{3/2}O$ was considered as an intermediate agent in the evolution of the TeO_2 network due to the addition of a modifying oxide. So far as we know, the $TeO_{3/2}$ subunit was never considered as a participant in the glass formation process. This can be explained by the fact that it was not found in the crystal structure of tellurites. And this is explicable, since in the presence of a free oxygen anion (induced by the addition of a modifier oxide), the positively charged $TeO_{3/2}$ subunit would transform into a $TeO_{3/2}O$ one. So $TeO_{3/2}$ subunits do not exist in tellurites, but they could exist in pure glassy TeO_2.

V. SUMMARY AND CONCLUSION

Despite a good stability of TeO_2 molecules, the chemical mechanism of their agglomeration differs from the formation of a molecular crystal like SO_2. It is highly likely that for tellurium dioxide the condensation process would involve the formation of polymer associates, similar to those in organic polymers. In such compunds, it is impossible to classify the bonds into intramolecular and intermolecular ones. The great variety of predicted polymer structures of $(TeO_2)_n$ is related to the high flexibility of the Te atom valence electron distribution. The Te atom can form two, three, and four valence bonds. According to our calculations, $TeO_{2/2}O$, $TeO_{4/2}$, $TeO_{3/2}$, and $TeO_{3/2}O$ fragments can be found in $(TeO_2)_n$ polymer molecules. The TBP subunits ($TeO_{4/2}$) are the most energetically preferable because they provide the maximal number of valence bonds. The linkage of TBP's through corner sharing is preferred to edge sharing because the latter involves short Te-Te distances. The most stable polymer structure at $n\rightarrow\infty$ is the 3D infinite framework of the corner-connected TeO_4 TBP's. The corresponding limit value of the calculated energy of formation well agrees with the experimental cohesive energy of α-TeO_2.

The $TeO_{3/2}O$ and $TeO_{3/2}$ structural fragments are found to be characteristic of structures intermediate between completely disintegrated molecules and the infinite framework of crystalline TeO_2. They must appear at melting the crystalline TeO_2 as a result of breaking the Te-O-Te bridges. The fusion of these two fragments gives rise to a recrystallization of glassy TeO_2. The Te-O-Te bridges in all simulated molecular structures were found to be rather symmetric. All found molecular configurations [with exception of the $(TeO_2)_6$ framework molecule] contain the terminal Te═O bonds. It is significant that the main features in the Raman spectrum of TeO_2 glass, the broad intensive band around 400-500 cm^{-1} and the peaks at 670 and 780 cm^{-1}, evidence the presence of these structural fragments: symmetric Te-O-Te bridges and terminal Te═bonds.

In the framework molecular structures found in this study, Te-O separations of about 2.2–2.3 Å are present. They are shown in Fig. 4 by dotted lines. Their appearance can be interpreted as a result of approaching of two TeO_3 pyramids. Presence of such a coordination of Te atoms (denoted as $3+1$) in tellurite glasses was detected in the NMR study.[19,20] Neutron diffraction studies of TeO_2 glass (see, for example, Ref. 10) show a peak in the radial distribution function just around 2.2 Å . This favors the hypothesis of similarity of the above-mentioned $(TeO_2)_n$ molecules to the structural subunits of glassy TeO_2, thus allowing us to consider them as model entities for simulation the local structure, vibrational spectra and dielectric properties of glassy TeO_2, as well as the objects of further experimental studies.

ACKNOWLEDGMENTS

This study was done while M.S. was an invited researcher in the SPCTS laboratory of the University of Limoges, and he would like to thank the staff for their hospitality and helpful discussions. This research was suported by the Center National de la Recherche Scientifique (France).

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