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# Structure and Vibrational Spectra of Ti(IV) Hydroxides and Their Clusters with Expanded Titanium Coordination. DFT Study

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Equilibrium structures of  $H_{4-n}Ti(OH)_n$  ( $n = 2-4$ ) molecules and the  $Ti(OH)_4$  dimer and trimers were optimized at the B3LYP level of theory. Theoretical vibrational frequencies of TiO stretching modes obtained with several basis sets were compared with the existing experimental frequencies of these vibrations, and the 6-31+G(d) set was chosen for cluster calculations. Only one energy minimum was found for the  $[Ti(OH)_4]_2$  dimer, but two isomers without symmetry elements stabilized by internal hydrogen bonds and two isomers, belonging to  $C_s$  and  $C_i$  point groups, with free OH groups were found as minima at the  $[Ti(OH)_4]_3$  potential energy surface. The structure with the linear arrangement of hexacoordinated titanium atoms in the  $Ti_3O_{12}$  skeleton may be proposed for trimeric species observed in liquid titanium alkoxides as the only structure satisfying experimental spectroscopic evidence about the presence of center of inversion in these species. Frequency changes of  $TiO_4$  modes which accompany the oligomer formation are predicted and discussed.

## Introduction

Alkoxides represented by the general formula  $M(OR)_4$  are well-known precursors for obtaining inorganic oxide materials by sol–gel processes.<sup>1–3</sup> The first stage of these processes is the hydrolysis of alkoxides that leads to formation of hydroxides. For the most widely used processes based on organosilicon compounds  $Si(OR)_4$  these reactions have been thoroughly studied,<sup>1,4</sup> and in our previous works we predicted structural and spectroscopic changes on the way from silicon methoxides to hydroxides.<sup>5–7</sup>

Titanium alkoxides are also commonly used for the formation of different modifications of  $TiO_2$  (including nanocrystalline species) which have a wide range of applications from wide band gap semiconductors for solar energy conversion and photocatalytic activity to optical films, pigments, and fillers. However, the structure–vibrational spectra correlation which may be used for monitoring the first stages of these sol–gel processes are less studied. The more complicated mechanism of these reactions in the case of titanium is due to the fact that in contrast to silicon, which retains its coordination number 4, titanium atom formally tetracoordinated in initial alkoxides increases its coordination up to 6 in the final products. Nevertheless, there is strong evidence that even in precursors its coordination number is increased due to the formation of clusters. X-ray diffraction studies reveal that titanium alkoxide molecules in the solid state form a tetrameric structure in which the titanium atom achieves the octahedral coordination of oxygens inherent to titanium.<sup>8,9</sup> In the liquid state trimeric structure was revealed by cryoscopic,<sup>10,11</sup> NMR,<sup>12</sup> anisotropic Rayleigh scattering,<sup>13</sup> and X-ray absorption studies.<sup>14</sup> Although these works cannot provide any precise information about the

structure of these trimers, Russo and Nelson<sup>13</sup> proposed a linear trimer with the 6-fold-coordinated central Ti atom and 5-fold-coordinated terminal atoms, while Babonneau et al.<sup>14</sup> were in favor of a cyclic structure in which all titanium atoms have a 5-fold coordination.

Thus, the structure of the titanium–oxygen skeleton of titanium alkoxide trimers observed in solution is not known. Quantum chemistry may give an answer to the question about the possible structures of trimeric forms and their relative stabilities. In this work we analyze this problem using the simpler model of titanium hydroxide trimers. From our previous experience with silicon hydroxides,<sup>5–7</sup> we may conclude that the heavy atom skeleton of  $R_{4-n}M(OR)_n$  ( $n = 1-4$ ) monomers and oligomers has a similar structure not depending on whether R is a hydrogen atom or an alkyl group. On the other hand, the theoretical study of titanium hydroxide structure is of interest by itself, since titanium hydroxides, i.e., hydrolysis products of the first stage of sol–gel reactions, are intermediates, which determine to a great extent the structural and surface properties of the final products. However, full vibrational spectra of hydroxide monomers and oligomers may hardly be obtained due to their instability toward condensation. Therefore, theoretical predictions of their spectra may give useful information for monitoring sol–gel reactions.

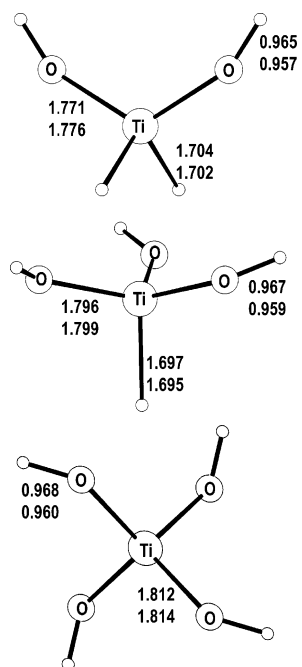
## Theoretical Calculations

The geometries of all of the stationary points have been fully optimized and characterized as energy minima by the B3LYP<sup>15,16</sup> hybrid density functional method. The existing experimental vibrational frequencies of TiO stretching vibrations for  $TiH(OH)_3$ ,  $TiH_2(OH)_2$ ,<sup>17</sup> and  $Ti(OH)_4$ <sup>18</sup> were used to assess the accuracy of different basis sets in the reproduction of these frequencies. The LANL2DZ<sup>19</sup> and the Stuttgart–Dresden<sup>20</sup> effective core potentials, Ahlrichs SVP and TZVP sets,<sup>21</sup> and standard 6-31G and 6-311G basis sets were used as they are implemented in the Gaussian 03 program.<sup>22</sup>

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**Figure 1.** Equilibrium geometries of titanium hydroxides  $H_{4-n}Ti(OH)_n$  ( $n = 2-4$ ) and bond lengths in Å obtained at the B3LYP/6-31+G(d) (upper figures) and B3LYP/6-311++G(3df,p) levels of theory.

## Results and Discussion

Optimized geometries of isolated titanium hydroxide molecules in the gas phase are depicted in Figure 1. Structural differences between titanium and silicon (silanediol) hydroxides may be exemplified by the comparison of the  $H_2X(OH)_2$  equilibrium structures for  $X = Si$  and  $Ti$ . In silanediols the interaction of lone pairs or negative hyperconjugation due to  $n(O)-\sigma^*(SiO)$  orbital interaction<sup>23</sup> results in the  $C_2$  structure with the  $HOSiO$  dihedral angle close to  $60^\circ$ . Smaller overlap of these orbitals (due to larger  $TiO$  interatomic distances) diminishes this effect in  $H_2Ti(OH)_2$ , and the only energy minimum found at the potential energy surface (PES) of this molecule belongs to the  $C_{2v}$  point group for this molecule with  $HOTiO$  dihedral angle ( $\tau$ ) equal to zero, while a similar structure in the case of silicon is a transition state. However, the  $C_{3v}$  structure with  $\tau = 0$  for  $HTi(OH)_3$  appears to have an imaginary vibrational frequency and the energy minimum belongs to a  $C_3$  structure, although the dihedral  $\tau$  angle is rather small (ca.  $10^\circ$ ). For  $Ti(OH)_4$  the stationary point of  $D_{2d}$  symmetry (with  $\tau = 0$ ) is also a transition state and an energy minimum corresponds to an  $S_4$  structure with a substantially larger  $\tau$  dihedral angle of ca.  $45^\circ$ .

Several molecules containing  $TiO$  bonds were identified in the matrix IR spectroscopic investigations of  $Ti$  atoms codeposited with  $H_2O$  in excess argon.<sup>17,18</sup> Zhou et al.<sup>17</sup> have ascribed two bands in the  $TiO$  stretching frequency range, namely at  $806$  and  $776\text{ cm}^{-1}$ , to  $H_2Ti(OH)_2$  species, while a band at  $844\text{ cm}^{-1}$  was assigned to  $HTi(OH)_3$  stretching vibration. Wang and Andrews<sup>18</sup> attributed the  $766\text{ cm}^{-1}$  band to  $Ti(OH)_4$ .

Thus, we obtained vibrational data to assess the description of  $TiO$  stretching frequencies by different basis sets. Predicted frequencies are compared with experiment in Table 1.

First, note that the assignments of Zhou et al.<sup>17</sup> for  $H_2Ti(OH)_2$  and  $HTi(OH)_3$  do not coincide with our results. For  $Ti(OH)_4$ , the assignment of ref 18 is used in Table 1. The frequency of the degenerate  $TiO_3$  stretching mode obviously converges to the experimental  $806\text{ cm}^{-1}$  value, while this band was assigned to  $H_2Ti(OH)_2$ . In addition, there is a clear

**TABLE 1: Equilibrium Geometry Parameters (Bond Lengths in Å, Bond Angles in deg) and Frequencies of  $TiO$  Stretching Vibrations of  $TiH_2(OH)_2$ ,  $TiH(OH)_3$ , and  $Ti(OH)_4$  Molecules, Obtained at the B3LYP level of Theory<sup>a</sup>**

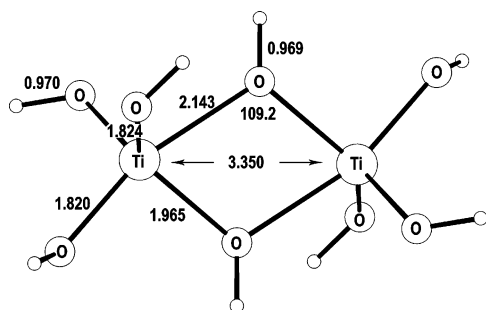
	A	B	C	D	E	F	G	H	exptl
<b><math>Ti(OH)_4</math></b>									
$r(TiO)$	1.780	1.786	1.805	1.806	1.812	1.818	1.808	1.814	
$\alpha(TiOH)$	180.0	162.4	129.3	124.1	129.0	132.0	137.1	130.1	
$\nu(TiO_4(E))$	836	811	801	792	769	775	775	767	766 <sup>c</sup>
<b><math>TiH(OH)_3</math></b>									
$r(TiO)$	1.771	1.772 <sup>b</sup>	1.788	1.787	1.796	1.802	1.792	1.799	
$\alpha(TiOH)$	179.3	176.7	136.6	105.3	103.9	103.9	103.4	137.1	
$\nu(TiO_3(E))$	880	856	841	832	806	812	813	803	806 <sup>d</sup>
<b><math>TiH_2(OH)_2</math></b>									
$r(TiO)$	1.762	1.762	1.762	1.757	1.771	1.779	1.773	1.776	
$\alpha(TiOH)$	172.6	170.6	156.6	153.9	155.2	159.5	161.7	154.8	
$\nu_{as}(TiO_2)$	919	884	888	887	851	858	855	848	844 <sup>d</sup>
$\nu_s(TiO_2)$	808	809	813	816	782	782	780	779	776 <sup>d</sup>

<sup>a</sup> Basis sets used: A = LAN2DZ; B = SDD; C = SVP; D = 6-31G(d); E = 6-31+G(d); F = TZVP; G = 6-311+G (d); H = 6-311++G (3df,p). <sup>b</sup> The structure obtained with this basis set has no symmetry; averaged parameter is shown. <sup>c</sup> Experimental data from ref 18. <sup>d</sup> Experimental data from ref 17.

convergence of theoretical frequencies of  $H_2Ti(OH)_2$  to  $844$  and  $776\text{ cm}^{-1}$ . The band with the former frequency was assigned by Zhou et al.<sup>17</sup> to  $HTi(OH)_3$ . Another indication of the wrong assignment may be noticed in the frequencies of  $TiH$  stretching modes. In ref 17, bands at  $1688$  and  $1666\text{ cm}^{-1}$  were ascribed to  $H_2Ti(OH)_2$ , while the band at  $1634\text{ cm}^{-1}$  was ascribed to  $HTi(OH)_3$ . Although absolute values of the theoretical frequencies of these vibrations can hardly be compared with experiment due to the high anharmonicity of these modes, their relative values are usually reliable. All our calculations predict the  $\nu(TiH)$  frequency of  $HTi(OH)_3$  to be higher than those of  $H_2Ti(OH)_2$ . This correlates with equilibrium bond length order (Figure 1): in  $HTi(OH)_3$  they are noticeably shorter than in  $H_2Ti(OH)_2$ .

The comparison of theoretical and experimental frequencies in Table 1 indicates that the effective core potential methods (LAN2DZ and SDD) reproduce  $\nu(TiO)$  frequencies completely unsatisfactorily. A slightly better agreement is observed in the double- $\zeta$  quality sets without diffuse functions, such as SVP and 6-31G(d). Triple- $\zeta$  sets, especially 6-311++G(3df,p), provide excellent agreement. Error in the last set does not exceed  $3\text{ cm}^{-1}$  (Table 1). However, a substantially smaller basis set, that is, 6-31+G(d), gives comparable accuracy. Since the size of the basis sets is a crucial factor for the optimization of larger systems such as  $Ti(OH)_4$  trimers, for these calculations the 6-31+G(d) basis set will be used.

The effect of the increase of titanium coordination on structure and vibrational spectra may be traced by regarding the  $Ti(OH)_4$  dimer. Three plausible structures of a dimer were optimized, i.e., with two, three, and four bridging oxygens. The latter model is that proposed by Martin and Winter.<sup>24</sup> The optimization of all these structures converged to only one viable dimer with two bridging oxygen atoms (Figure 2), in agreement with Weingarten and van Wazer,<sup>12</sup> who argued that the structure with four bridging oxygens would be prohibitively strained and proposed the dimeric structure with two bridging oxygens for  $[CH_3(CH_2)_3O]_2TiCl_2$  and  $(CH_3CH_2O)_2TiBr_2$  in benzene solution. Dimeric structures of titanium alkoxides were also found by X-ray diffraction analysis in the adducts of  $Ti_2(OR)_8$  with two alcohol<sup>25</sup> and two amine<sup>26</sup> molecules. In these complexes titanium increases its coordination number from 5 in the dimer to 6 by bonding with these molecules.



**Figure 2.** B3LYP/6-31+G(d) equilibrium geometry of the  $\text{Ti}(\text{OH})_4$  dimer. Bond lengths in Å.

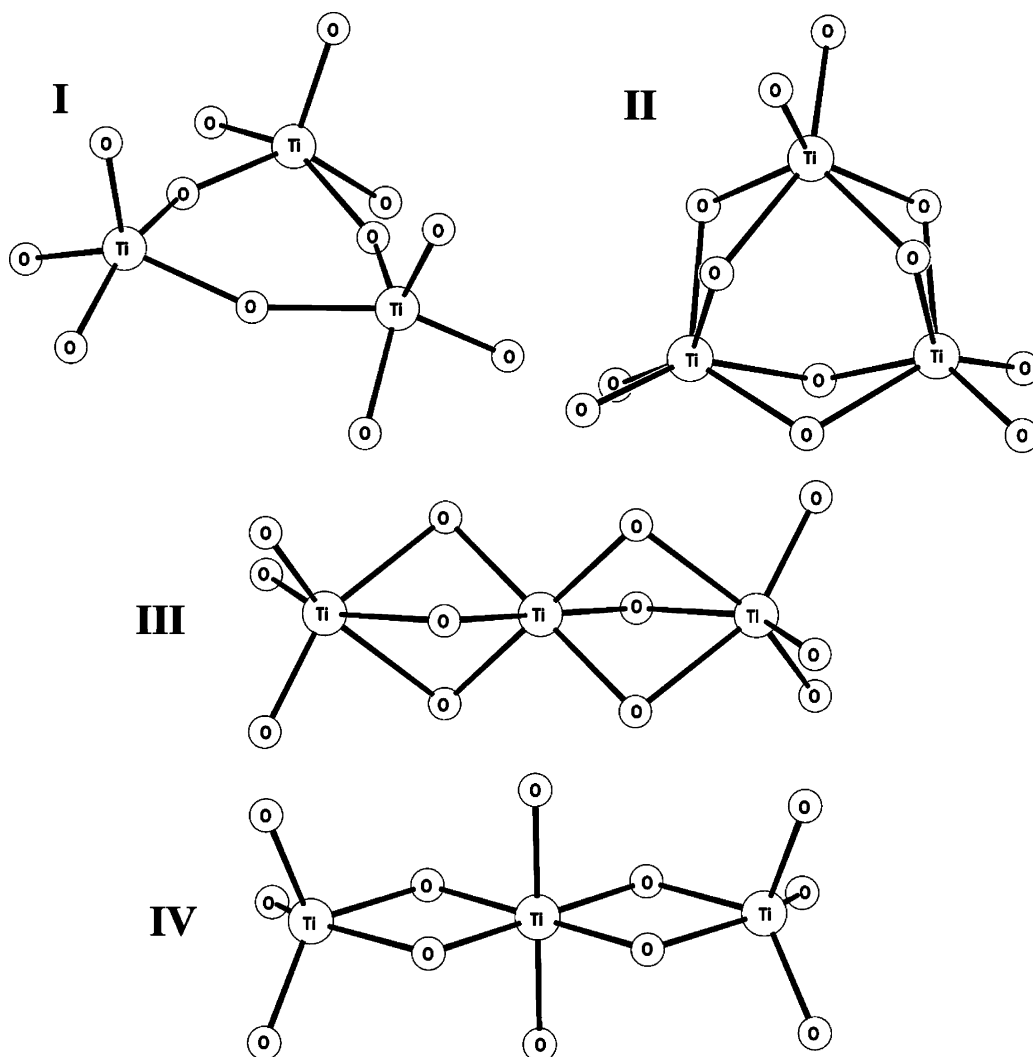
In the predicted dimeric structure both titanium atoms have 5-fold coordination (Figure 2). There exist two types of bridging Ti–O bond: TiO bonds of the  $\text{Ti}(\text{OH})_4$  tetrahedra are shorter than those connecting two tetrahedra. Terminal TiO bonds are substantially shorter than bridging and only slightly longer than TiO bonds in a monomer (Figure 1).

In the experimental studies of the liquid phase of titanium alkoxides, the existence of trimers composed of  $\text{TiO}_4$  tetrahedra, which form TiOTi bridges and thus expand titanium coordination, was detected.<sup>10–14</sup> Four plausible structures for the  $\text{Ti}_3\text{O}_{12}$  skeleton were proposed in these works (Figure 3): the cyclic structure (I), the spherical structure built from the  $\text{Ti}_2\text{O}_8$  dimer

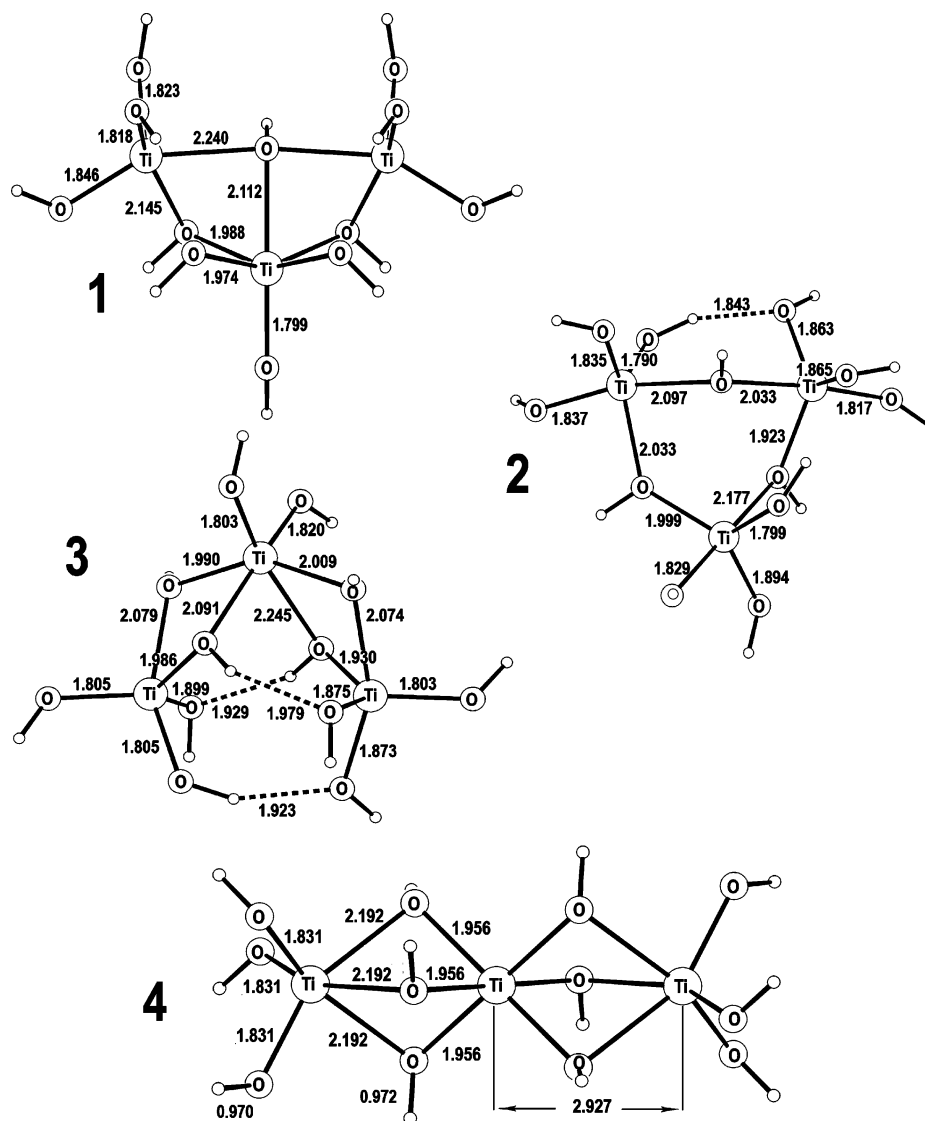
connected by the third  $\text{TiO}_4$  tetrahedron (II), and structures with the linear arrangement of three titanium atoms (III, IV). The designation of the trimeric structures is taken from the paper of Babonneau et al.<sup>14</sup>

Structures III and IV differ in that in III there are three TiOTi bridges between each pair of Ti and all three titanium atoms are hexacoordinated, while in IV there are two bridges between titaniums and only a central Ti atom has a 6-fold coordination. However, the opinion about the preference of these structures is controversial: Weingarten and van Wazer<sup>12</sup> and Babonneau et al.<sup>14</sup> consider that structure I provides the best fit to their experimental data, while Russo and Nelson<sup>13</sup> argue that light-scattering data indicate rather definitely that the structure in solution is the one designated IV.

In order to check which way of merging  $\text{TiO}_4$  tetrahedra to form trimers leads to stable forms and which isomer is energetically most favorable, we carried out the optimization of the  $\text{Ti}(\text{OH})_4$  trimers starting from the structures depicted in Figure 3. At the first step of optimization, symmetry elements were imposed in order to keep the topology of the TiO skeleton pertaining to those four structures. From these, only structure III was found to be an energy minimum. For the remaining three structures, which appeared to be saddle points, the symmetry restrictions were relaxed and optimization was continued. Although such an approach does not guarantee the absence of other plausible energy minima, it is highly probable that all low-



**Figure 3.** Plausible structures of the trimer formed by  $\text{TiO}_4$  tetrahedra as proposed in experimental studies of titanium alkoxides.<sup>10–14</sup>



**Figure 4.** Structures corresponding to energy minima at the  $\text{Ti}_3(\text{OH})_{12}$  potential energy surface optimized at the B3LYP/6-31+G(d) theory level. Bond lengths in Å.

**TABLE 2: Total Energies ( $E_e$ ; in au) of Minima Found at the Potential Energy Surfaces of  $[\text{Ti}(\text{OH})_4]_3$  and Their Relative Energies (in kcal/mol) [B3LYP/6-31+G(d)]**

structure	symmetry	$E_e$	$\Delta E_e$	$\Delta E_0$	$\Delta E_{298}$
1	$C_s$	-3458.905 93	14.9	13.7	14.2
2	$C_1$	-3458.918 53	7.0	5.5	6.3
3	$C_1$	-3458.929 66	0.0	0.0	0.0
4	$C_i$	-3458.912 96	10.5	9.5	9.8

energy isomers in the vicinity of the structures proposed by experimentalists were found. The search for an energy minimum starting from the cyclic structure (I in Figure 3) resulted in two isomers. The first crablike structure of  $C_s$  symmetry contains a significantly distorted  $\text{Ti}_3\text{O}_3$  cycle in which a titanium atom forms a bond with the opposite oxygen (1 in Figure 4). The second form, although being also substantially distorted, does not have a short TiO interatomic distance inside the cycle, but possesses a strong intramolecular hydrogen bond between terminal hydroxide groups (2 in Figure 4). This bonding sufficiently stabilizes the latter structure, and it lies 8 kcal/mol lower in energy than structure 1 (Table 2).

A similar structure with a different pattern of intramolecular hydrogen bonding was also found as an energy minimum, but it is not reported here since it lies higher in energy. We cannot

exclude that there exist different isomers of 2 and 3 of higher energy, which differ by the number of hydrogen bonded OH groups, but they have no interest to our study, which is concentrated on the structure of the  $\text{TiO}$  skeleton.

The optimization of the spherical structure II (Figure 3) with the imposed symmetry plane leads to a stationary point retaining this structure. However, this point is not an energy minimum, but rather is a saddle point of the second order (two imaginary vibrational frequencies). Removing the symmetry requirements allows the strains obviously inherent to this spherical structure to relax and results in structure 3 (Figure 4) in which the connection of the two dimers by the third is broken and replaced by intramolecular hydrogen bonds. The structure gains its stability through formation of rather short hydrogen bonds (3 in Figure 4). It is the global energy minimum of the  $[\text{Ti}(\text{OH})_4]_3$  system.

Optimization of both linear structures III and IV (in Figure 3) results in only one structure (4 in Figure 4) which corresponds to that of III in the designation of Figure 3. In this structure all three titanium atoms are in a 6-fold coordination. The  $\text{TiO}$  skeleton of this structure is close to  $D_{3d}$  symmetry and there is only one type of TiO terminal bond. Bridging TiO bond lengths differ: those of central distorted octahedra are shorter than those



**TABLE 3: Theoretical Frequencies ( $\text{cm}^{-1}$ ) of TiO Stretching and TiOH Bending Vibrations for the  $\text{Ti}(\text{OH})_4$  Monomer,  $[\text{Ti}(\text{OH})_4]_2$  Dimer, and the Linear Centrosymmetric Form of the  $[\text{Ti}(\text{OH})_4]_3$  Trimer**

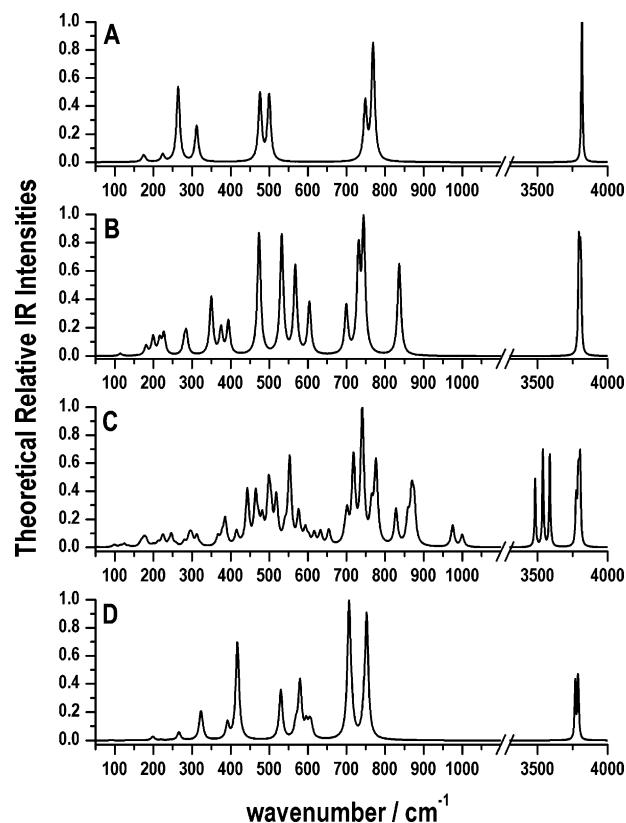
monomer	dimer		trimer (4)		assignment
	Ag	Au	Ag	Au	
	837	837			$\delta(\text{TiOH}_{\text{bridge}})$
			768		
			757		
			756		
				752	
				746	
				745	
		744	713		$\nu(\text{TiO}_{\text{terminal}})$
769 E	736		707		
749 B		731	706		
697 A	726		699		
		699	672		
	682		671		
		604	641		$\nu(\text{TiO}_{\text{bridge}}) + \delta(\text{TiOH}_{\text{terminal}})$
	593		632		
	590		628		
500 B		567	627		
491 A	552		608		
476 E		532	604		
	482		600		
		473	597		
			581		
			578		

belonging to terminal octahedra (4 in Figure 4). The other linear structure IV (Figure 3), in which the central titanium atom is hexacoordinated and two terminal atoms are pentacoordinated, does not correspond to an energy minimum.

The arrangement of  $\text{TiO}_4$  tetrahedra of isomer 4 (Figure 4) may be considered as a candidate for the most stable isomer of titanium alkoxide trimer, observed in solution, since the absence of coincidence of IR and Raman bands below  $800\text{ cm}^{-1}$  assigned to trimeric species of titanium tetraethoxide<sup>27</sup> may evidence the centrosymmetric structure of the trimer. Although in the  $[\text{Ti}(\text{OH})_4]_3$  system structure 4 lies higher in energy than the hydrogen bonded isomer 3, in the  $[\text{Ti}(\text{OAlk})_4]_3$  system the similar centrosymmetric linear stable form may be the most stable isomer, since hydrogen bonding which stabilizes structure 3 is absent in these systems.

The conclusion that the arrangement of  $\text{TiO}_4$  tetrahedra appropriate to structure 4 may form a core of titanium tetralkoxide trimers observed in experiment<sup>10–14</sup> contradicts the conclusions about its structure proposed by the authors of these works. Russo and Nelson<sup>13</sup> based their assumption that this structure is a linear trimer in which the terminal Ti atoms are pentacoordinated and the central is octahedral with two non-bridging oxygens (IV in Figure 3) on two facts: the large measured optical anisotropy of trimeric species, which may be reproduced only in a model IV (i), and the absence of coincidence of IR and Raman bands below  $800\text{ cm}^{-1}$ , which indicates that the molecule in solution is centrosymmetric (ii). In our opinion these arguments cannot be decisive in favor of structure IV because model anisotropy calculations strongly depend upon the conformations of the side ethyl groups and because the center of symmetry possesses both a linear trimer with TiO skeleton structure and the titanium tetraethoxide monomer.

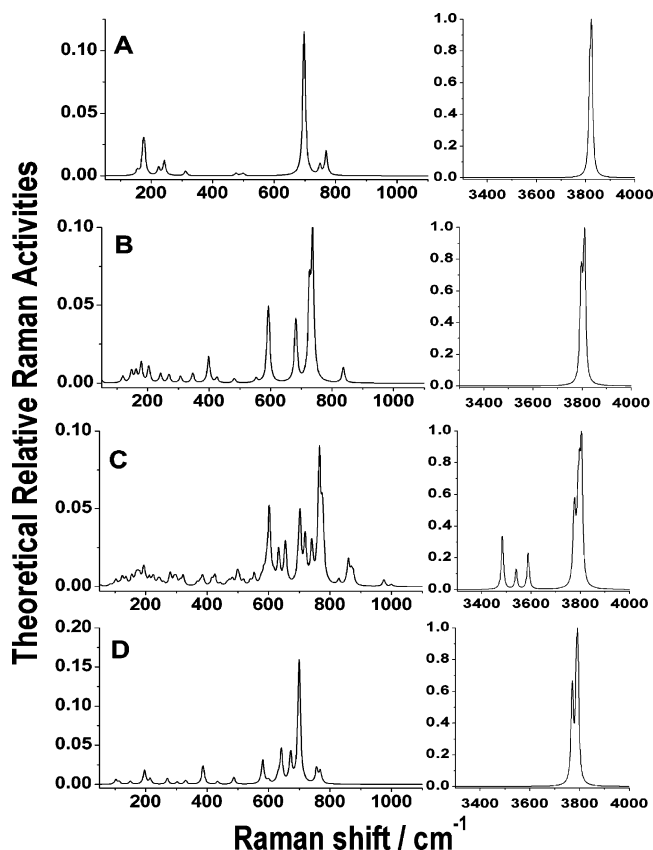
Babonneau et al.<sup>14</sup> based their arguments in favor of the cyclic structure on two experimental facts: the XANES data for titanium alkoxides do not show any evidence of a pure octahedral symmetry (i), and EXAFS results evidence that the

**Figure 5.** Predicted IR spectra of  $\text{Ti}(\text{OH})_4$  (A), its dimer (B), and two isomers 3 (C) and 4 (D) of the  $[\text{Ti}(\text{OH})_4]_3$  trimer.

ratio between short (terminal) and long (bridging) TiO distances is 3.4/1.8 (ii). As concerns argument (i), we may notice that our results show that, in all equilibrium structures found which contain 6-fold coordinated titanium, octahedra are strongly distorted and rather far from being “pure”. Also all structures contain not two, but rather three types of TiO bonds: terminal in the 1.8–1.9 Å range, short bridging in the 1.9–2.0 Å range, and long bridging bonds that lie in the 2.0–2.2 Å range. Thus, in order to sort them to two types of bonds, we should unite two types of bonds into one type. In structure 4 (Figure 4) the difference between the lengths of long and short bridging bonds is 0.236 Å, while that between short bridging and terminal bonds is almost 2 times smaller, that is, 0.125 Å. Therefore, it is natural to unite terminal and short bridging bonds into one group. In this case the ratio between these bond lengths will be 12/6, which is close to the experimental 3.4/1.8 value.

**Vibrational Spectra.** Vibrational spectroscopy may be the main tool for the characterization of oligomeric species predicted in this work. Therefore, it is useful to discuss the spectral changes upon formation of these species and to outline spectral features which may be used to identify monomers, dimers, and different forms of trimers.

The increase of titanium coordination in the dimer brings about substantial changes in vibrational spectra in the 500–850  $\text{cm}^{-1}$  region (Table 3 and Figures 5B and 6B). Stretching vibrations of terminal TiO bonds remain in the same 680–770  $\text{cm}^{-1}$  range in which  $\nu(\text{TiO})$  bands of the monomer are situated, although these bands are slightly shifted to lower frequencies. However, bridging bond stretchings lower their frequencies and become mixed with terminal  $\delta(\text{TiOH})$  and  $\delta(\text{OTiO})$  deformations in the 450–650  $\text{cm}^{-1}$  spectral region. In the IR spectrum of the dimer these changes manifest themselves in the appearance of four strong bands in this region instead of two in a monomer (Figure 5A,B). In the Raman spectrum a strong band



**Figure 6.** Predicted Raman spectra of  $\text{Ti}(\text{OH})_4$  (A), its dimer (B), and two isomers **3** (C) and **4** (D) of the  $\text{Ti}_3(\text{OH})_{12}$  trimer.

appears at  $600\text{ cm}^{-1}$ . The most interesting feature of the dimer vibrational spectrum is that the bridging  $\delta(\text{TiOH})$  modes significantly increase their frequency from  $470\text{--}500\text{ cm}^{-1}$  in a monomer to  $837\text{ cm}^{-1}$  in a dimer. This shift results in the appearance of a strong IR band above  $800\text{ cm}^{-1}$ , i.e., in the region free from monomeric bands (Figure 5B).

Strong IR bands of hydrogen bonded  $\delta(\text{TiOH})$  remain in the  $800\text{--}900\text{ cm}^{-1}$  region of the trimer **3** with intramolecular hydrogen bonds (Figure 5C), while in the isomer **4**, in which TiOH groups are not perturbed by hydrogen bonding, frequencies of bridging TiOH group deformations lie in the  $700\text{--}800\text{ cm}^{-1}$  region (Table 3 and Figures 5D and 6D). Due to the high anharmonicity of OH stretching vibrations, the absolute values of harmonic theoretical frequencies in the spectral range are usually far from experimental values, but their number and relative positions are usually reliable. The characteristic feature of oligomers in the OH stretching frequency range is the appearance of two  $\nu(\text{OH})$  bands, due to the difference in bond lengths of terminal and bridging OH groups (Figures 2 and 4). In the frequency range below  $800\text{ cm}^{-1}$  the appearance of bands both in IR and Raman spectra in the  $500\text{--}650\text{ cm}^{-1}$  region may characterize the formation of trimers (Figures 5 and 6). Note that, although the exact wavenumbers of  $\text{Ti}_3\text{O}_{12}$  normal modes in the  $500\text{--}650\text{ cm}^{-1}$  range in the predicted IR spectrum of  $[\text{Ti}(\text{OH})_4]_3$  and the experimental IR spectrum of titanium tetraethoxide may differ significantly, the presence of only two strong IR bands in this region in the theoretical spectrum of isomer **4** (Figure 5D) and in the  $\text{Ti}(\text{OEt})_4$  liquid-phase IR spectrum<sup>27</sup> may indicate the fact that in liquid  $\text{Ti}(\text{OEt})_4$  trimers have a structure similar to that of isomer **4**. The lower number of  $\text{TiO}_4$  modes in this region is explained by the high symmetry of this structure and by the presence of terminal bonds with only one bond length in structure **4**. In contrast to this,

asymmetric structures (exemplified in Figures 5C and 6C by the predicted spectra of the most stable isomer **3**) have numerous IR bands with high intensity in the  $600\text{--}500\text{ cm}^{-1}$  region.

## Conclusions

The structure of titanium hydroxides was optimized and vibrational spectra were predicted with the B3LYP method with different basis sets. The best compromise between the accuracy of the reproduction of experimental vibrational frequencies of TiO stretching modes of  $\text{TiH}_2(\text{OH})_2$ ,  $\text{TiH}(\text{OH})_3$ , and  $\text{Ti}(\text{OH})_4$  molecules and the basis set size was provided by the 6-31+G(d) set.

The assignment of experimental bands in the IR spectra of  $\text{TiH}_2(\text{OH})_2$  and  $\text{TiH}(\text{OH})_3$  species was revised on the basis of theoretical spectra.

Only one structure with pentacoordinated titanium atoms was found at the  $\text{Ti}_2(\text{OH})_2$  PES.

Four energy minima were found at the  $\text{Ti}_3(\text{OH})_{12}$  PES. Two of them correspond to structures with intramolecular hydrogen bonds between terminal OH groups and have lower energy, but do not possess any symmetry elements.

In two other structures of  $C_s$  and  $C_i$  symmetries terminal OH groups do not form intramolecular hydrogen bonds and lie higher in energy than hydrogen bonded isomers.

The structure of the titanium–oxygen skeleton of the linear isomer is close to  $D_{3d}$  symmetry and may be proposed for trimeric species detected experimentally in liquid titanium tetraethoxide and tetraisopropyl oxide, since the absence of coincidence of IR and Raman bands assigned to them may evidence the centrosymmetric structure of the trimer.

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