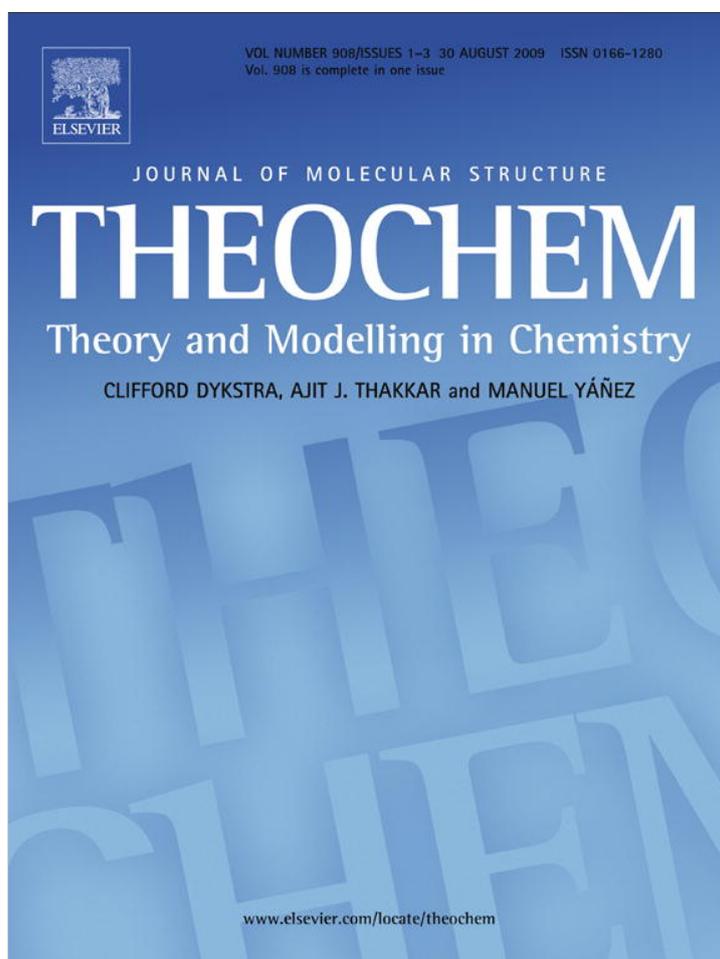


Provided for non-commercial research and education use.
Not for reproduction, distribution or commercial use.



This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

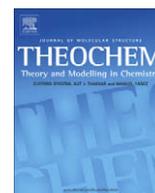
In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

<http://www.elsevier.com/copyright>



Contents lists available at ScienceDirect

Journal of Molecular Structure: THEOCHEM

journal homepage: www.elsevier.com/locate/theochem

H₂O₂ adsorption on the ice *Ih* surface. Theoretical study with systematic assessment of the orientation isomerism of the hydrogen bond network

Stanislav K. Ignatov^{a,b,*}, Alexey G. Razuvaev^b, Petr G. Sennikov^{a,c}, Otto Schrems^a^a Alfred Wegener Institute for Polar and Marine Research, Postfach 120161, D-27515 Bremerhaven, Germany^b N.I. Lobachevsky State University of Nizhny Novgorod, 23 Gagarin Avenue, Nizhny Novgorod 603950, Russia^c Institute of Chemistry of High Purity Substances of RAS, 49 Tropinin Str., Nizhny Novgorod 603600, Russia

ARTICLE INFO

Article history:

Received 6 December 2008

Received in revised form 2 April 2009

Accepted 1 May 2009

Available online 13 May 2009

Keywords:

Ice surface

Hydrogen peroxide

Ice-adsorbate interaction

Atmospheric chemistry

ABSTRACT

Semiempirical (PM3) and DFT (B3LYP/6-31++G(d,p)) calculations of the structure and energies of the variety of water clusters modeling 4680 fragments of the ice surface with different topology of the hydrogen bond network have been performed in order to analyze the contributions of various orientational isomers into the energy distributions of clusters and their impact onto the adsorption ability relatively to the H₂O₂ molecule. It was found that, in the framework of the considered model, only several kinds of surface patterns among all the possible structures have significant thermodynamic weights and, thus, have the maximum contributions into the adsorption energy. Structural and energetic properties of the adsorption complexes formed by H₂O₂ molecule with the most favourable fragments of the ice surface are analyzed on the basis of B3LYP/6-311++G(2d,2p) calculations.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

The small particles of the water ice in the atmosphere of the Earth and other planets have a remarkable effect on the atmospheric chemistry because the reactions on their surface frequently occur with significantly higher rate than it takes place in the gas phase [1]. The well-known examples of such reactions are the formation of chlorine compounds which are involved in the processes of ozone destruction [2], photolytic decomposition of mesospheric ice particles resulting in the OH radical formation [3], and the reactions of oxidants accumulated on the ice and snow particles [4]. The study of these and related processes is tightly connected to the investigation of the reactions occurring on the surface of water ice. The experimental part of this research is usually combined with theoretical modeling that is frequently performed within the cluster approach. This approach has serious restrictions when dealing with the collective properties of the surface e.g. the surface ordering/reconstruction or the thermal molecular disorder resulting to the quasi-liquid layer formation. Studies of such phenomena propose the use of the extensive surface models and sophisticated approaches like molecular dynamics, Monte-Carlo or Car-Parinello calculations (see, e.g. [5–9] and references therein). However, in many cases (adsorption energy estimates at low coverage and low temperature, the vibrational frequency shifts due to the

adsorption, etc.), the practical tasks are not so demanding and the important information can be obtained with relatively simple approaches utilizing the cluster models with the DFT optimization and frequency calculations. Moreover, because the cluster model is simpler, it allows the higher levels of quantum chemistry theories to be applied.

The theoretical consideration in the cluster model, however, has an important feature which is frequently omitted during the modeling. This feature is the internal isomerism of the hydrogen bond network which makes representation of the ice surface non-uniform. The water ice in its most abundant atmospheric modification (ice *Ih*) has a hexagonal lattice with the oxygen atoms of the water molecules located in the nodes of the graphite-like crystalline structure with four tetrahedral O···O links. Hydrogen atoms are disordered in this crystalline modification and obey the “ice rules” [10,11]: each water molecule forms four tetrahedral hydrogen bonds with the neighbouring molecules and each H-bond is occupied by only one hydrogen, either of the same molecule or of their neighbours. Such crystal organization results in incredible large numbers of possible isomeric structures distinguished by the orientations of the H-bonds. In the real ice crystal the isomers are considered as distributed with equal (or almost equal) probabilities and the properties of ice are considered as average values of all the possible isomers. During the computational studies of ice or ice surfaces, the cluster models (see for example [12–17] and numerous references therein) propose that only one or several possible orientational isomers of the cluster have to be considered. Most frequently, the random choice of the

* Corresponding author. Address: N.I. Lobachevsky State University of Nizhny Novgorod, 23 Gagarin Avenue, Nizhny Novgorod 603950, Russia.

E-mail address: ignatov@ichem.unn.ru (S.K. Ignatov).

hydrogen bond network is used. Another frequently used way of modeling is a construction of clusters with the low dipole moment because the macroscopic ice body has no electrical moments. It should be noted, that the periodic calculations are also not free of that problem and the correct choice of the hydrogen bond topology is also a question in these studies [18–20].

Thus, independent of the theory level, the question arises how the different orientational isomers of the ice clusters contribute to the adsorption properties of the ice surface and to the properties registered in the experiment, e.g. to the infrared spectra of the ice.

In an earlier study we performed a combined FTIR and DFT investigation of the adsorption of species formed during the ozone photolysis deposited in ice and on the ice surface at 80 K [21]. It was demonstrated that the main product of this photolysis is hydrogen peroxide (H_2O_2) forming multiple hydrogen bonds on the ice surface, incorporated into the sub-surface layers and probably undergoing further isomerization and destruction in the ice network. It was also found that the FTIR spectra of the photolysis products induce a new absorption band in the region of 2860 cm^{-1} (Fig. 1). The assignment of this band is somewhat disputable. Usually, it is assigned to the $\nu_2 + \nu_6$ combination band of two deformation fundamentals of H_2O_2 . However, there is also a point of view [22] that it can be a OH valence band of the H_2O_2 molecule placed in the unusual surface environment. From this point of view, it is interesting to study how the different organization of the ice surface can influence the results obtained in our earlier study. Namely, are there any preferable structures of the hydrogen bond network of the ice surface contributing to the adsorption energy and the adsorption complex structure?

Several theoretical studies addressed to similar problems have already been performed in the past [12,23–28]. Frequently, however, only the most energetically favourable structure of the infinite ideal ice crystal unit cell was sought on the basis of DFT and model potential calculations [25] or specially developed approaches (graph invariant theory) [26–28]. For example, in the related study [12], the most favourable unit cell of the 2D ice slab was sought in order to elaborate the adequate model for the HCl adsorption on the ice surface.

In the study presented here we analyzed the adsorption energy distribution over the possible H-bond isomers and their impact onto the adsorption energy regarding to the H_2O_2 molecule. We have considered a relatively small model – a cluster of 11 water

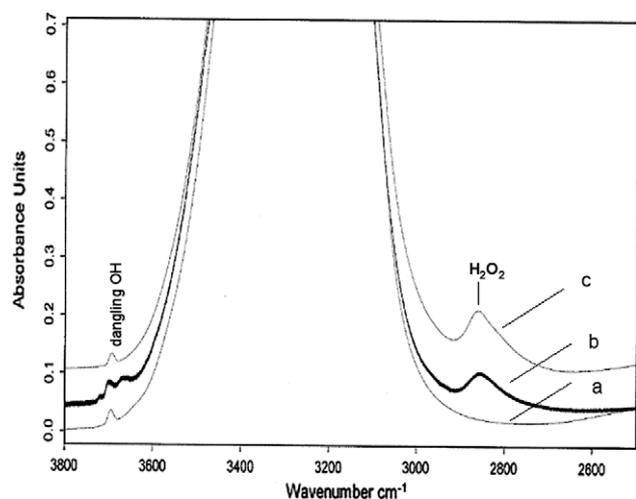


Fig. 1. FTIR spectra of ices in the OH stretching region at 80 K. (a) Spectrum of pure water ice; (b) spectrum after deposition of aqueous H_2O_2 solution; (c) spectrum of water ice originally doped with ozone after UV photolysis.

molecules without symmetry conditions – trying to elaborate the common approach suitable to answer the above questions.

2. Theoretical approach

The ice cluster consisting of 11 water molecules was constructed in a manner to describe the basal (0 0 0 1) plane of the ice Ih crystal. Initially, the oxygen atoms were placed into the crystalline positions of an ideal hexagonal lattice with the O–O distance 2.77 \AA [29], see Fig. 2. The cluster allows all the possible orientations of four water molecules of the surface layer in the ice crystal to be represented. The remaining molecules stand for the border conditions of the crystalline environment.

Based on the configuration of the oxygen atoms, the special computer code generated all possible orientations of the water molecules in a cluster leaving the oxygen positions intact and selected the structures obeying the ice rules. Among the generated configurations ($6^{11} = 362797056$ in total), there are 354294 of the “ice-rule” structures. From these configurations only the clusters were selected with the single O–H bonds of the border water molecules oriented downwards (the second O–H bonds of border molecules could take any directions). It is believed that this selection does not abuse seriously the generality of the model. At the same time it reduces the number of possible configurations dramatically and only 4680 cluster structures remain.

Among the resulting 4680 configurations, some structures are mutually isomorphic (i.e. identical with each other due to the symmetry of the cluster). Using the special algorithm [30], only the unique (non-isomorphic) configurations were selected and their “weights” in a whole set were determined. In terms of mathematical group theory, this task is a problem for the determination of the group orbits and counting of elements in each orbit. This classification results in 789 orbits (unique structures which are non-isomorphic to each other): 18 orbits with three elements (isomorphic structures) and 771 orbits with six elements.

The unique structures can be distinguished by the hydrogen bond network in the cluster and subsequently have different energies. To determine the energy distributions in the selected cluster set, quantum chemical calculations were performed for all the 789 non-isomorphic structures using the semi-empirical PM3 method. The calculations comprised the partial geometry optimization of the cluster structure. In a course of optimization, the geometries of four water molecules of the surface layer in the cluster were completely free whereas the remaining molecules (border molecules of the clusters) were fixed (the positions of oxygen atoms corresponded to their ideal crystalline positions, hydrogen atoms were located at the O–O links and the O–H distances were taken equal to 0.958 \AA). The optimized cluster energies were then used to obtain the energy distributions of the cluster structures.

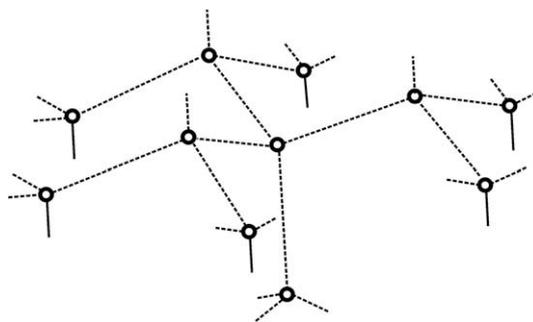


Fig. 2. Structure of oxygen atoms network in the clusters describing the ice surface. Possible directions of hydrogen bonds are shown with dashed lines, fixed OH moieties are shown with solid lines.

During the analysis special attention was paid to the differences between the clusters describing the different surface regions, e.g. the clusters with different numbers of dangling hydrogen or oxygen atoms.

3. Results

The clusters under investigation have three unfixed oxygen atoms on their top. Thus, there can be 0, 1, 2 or 3 dangling OH-bonds at the top of cluster. Hereafter, we will refer to these structures as 0, I, II, or III types of clusters, correspondingly (0 – dangling oxygen and I – dangling OH group on any top oxygen atom, II – two dangling OH groups on any two top oxygens, III – three OH groups occupying all the top oxygens). Among the 789 unique clusters, there are 196 structures of type 0, 362 – of type I, 199 – of type II, and 32 – of type III. The corresponding numbers of all the “ice-rule” structures (including the mutually isomorphous ones) are 196, 2160, 1180, and 180 (4680 in total). In Fig. 3 the energy distributions among all the clusters which were constructed using the energy bins of 0.1 kJ mol^{-1} each are shown.

It is evident from Fig. 3 that the different surface types (0, I, II, III) typically have different energies. The type III clusters have only small contributions due to the low number of the structures feasible. The energies of type 0 structures are typically higher than the energies of type I and II. The most favourable structures are the structures of type II and (close to them) type I. It is interesting that three most energetically favourable structures are separated by a rather remarkable energy gap from all the remaining structures and the energy differences between the low-energy structures are rather significant.

If the whole cluster set is considered as thermally equilibrated (the assumption which will be discussed in the next section), it can be described by the Boltzmann distribution at the given temperature. Fig. 4 shows the energy distribution at $T = 250 \text{ K}$ for the whole set of structures weighed with the Boltzmann factor $w(E)$:

$$w(E_i) = Z^{-1} \exp(-(E_i - E_0)/RT)$$

$$Z = \sum_i \exp(-(E_i - E_0)/RT)$$

Here, i is the index enumerating the structures; E_i is the energy of the given cluster; E_0 is the minimum energy among all the clusters

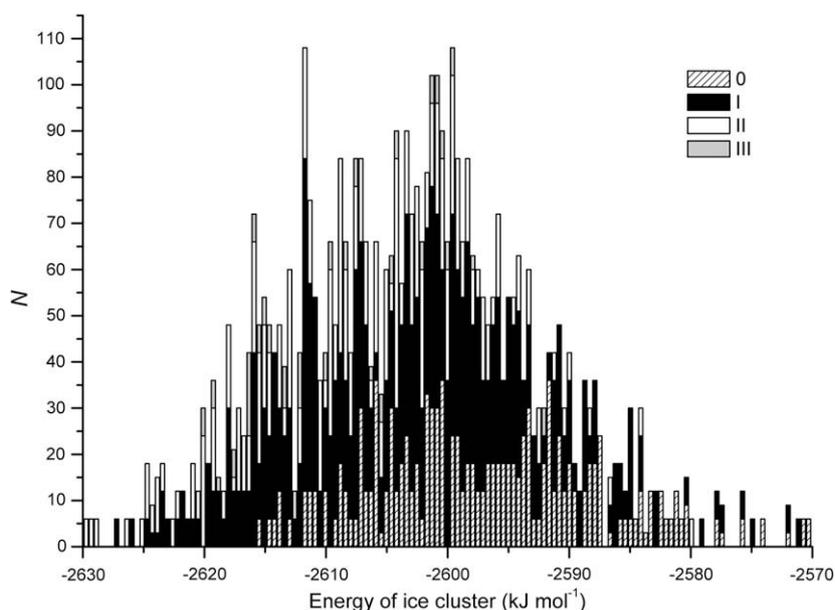


Fig. 3. Number of the cluster structures (N) obeying the ice rules (4680 in total) as a function of the energy of clusters.

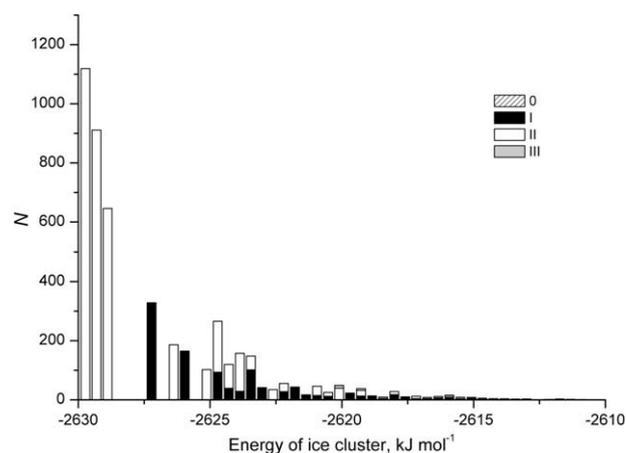


Fig. 4. Thermal distribution of the structures obeying the ice rules based on the Boltzmann energy distribution at $T = 250 \text{ K}$.

in a set; R is the universal gas constant and T is the absolute temperature.

The most important conclusion from Fig. 4 is that only a small part of possible structures in the given model contributes in a large extent to the distribution of structures at the ice surface. In fact, only 25 most favourable unique structures provide almost 90% of the graph square in Fig. 4. Thus, as a first approximation, we consider only 25 most favourable structures composing the ice surface.

Because this conclusion was obtained by using the semi-empirical quantum chemical method, some doubts remain, however, concerning the accuracy of the energies calculated. To improve the accuracy, we repeated the geometry optimizations for the 25 most favourable structures using the density functional theory at the B3LYP/6-31++G(d,p) level. The PC GAMESS program was used for the calculation [31,32] with the B3LYP1 version of the functional implemented therein. The geometry restrictions in the partial optimization were the same as in the previous PM3 optimization for all the clusters and the starting points for the optimizations were the same as in the PM3 calculations. The results of the optimization are shown in Table 1. Fig. 5 illustrates the comparison

Table 1
Energies and energy distribution parameters of ice clusters calculated at the B3LYP/6-31++G(d,p) level.

<i>i</i>	Structure ID	Calculated energy E_{tot} , a.u.	Relative energy ΔE , kJ mol ⁻¹	Statistical weight g_i	Boltzman factor w_i	Fraction of structures $w_i N$	Pattern type
1	101	-840.886789	0.0	6	0.4861	2275.0	A
2	180	-840.88605	1.9	6	0.1909	893.5	B
3	99	-840.885791	2.6	6	0.1377	644.3	A
4	100	-840.885436	3.6	6	0.0880	411.9	A
5	209	-840.884879	5.0	3	0.0218	101.8	B
6	179	-840.884392	6.3	6	0.0235	110.1	B
7	178	-840.883845	7.7	6	0.0118	55.2	B
8	95	-840.883677	8.2	6	0.0095	44.6	A
9	113	-840.883346	9.0	6	0.0063	29.4	A
10	49	-840.883262	9.3	6	0.0056	26.4	A
11	208	-840.883065	9.8	6	0.0044	20.6	B
12	94	-840.882742	10.6	6	0.0029	13.7	A
13	93	-840.882531	11.2	6	0.0022	10.5	A
14	473	-840.882364	11.6	6	0.0018	8.5	C
15	163	-840.882053	12.4	6	0.0012	5.7	B
16	182	-840.881941	12.7	3	0.0005	2.5	B
17	47	-840.881794	13.1	6	0.0009	4.1	A
18	477	-840.881791	13.1	6	0.0009	4.1	C
19	111	-840.881777	13.2	6	0.0009	4.0	A
20	320	-840.881759	13.2	6	0.0008	4.0	D
21	112	-840.881568	13.7	6	0.0007	3.1	A
22	475	-840.881473	14.0	6	0.0006	2.8	C
23	48	-840.881341	14.3	6	0.0005	2.3	A
24	495	-840.880912	15.4	6	0.0003	1.4	D
25	181	-840.879888	18.1	6	0.0001	0.4	B
			Sum	144	1.0000	4680	

between the relative energies of clusters calculated at the PM3 and DFT levels. The correlation between the calculated values is about 0.85 and shows that the agreement between the two methods is not perfect. However, it is evident from Table 1 that the main conclusions made on the basis of PM3 calculations remain valid also for the DFT calculations: 25 structures chosen as the most favourable ones on the basis of PM3 calculations provide almost 99% of the structures occupied at 250 K. The most favourable structures are the same unique clusters (Nos. 99–101 and 180 in the set of non-isomorphous structures) as in the case of the PM3 calculations.

The structures presented in Table 1 can be classified by the hydrogen bond “pattern” distinguished by the orientations of four H₂O molecules at the top of the clusters. It is interesting that all 25 structures in Table 1 can be classified by only four pattern types shown in Fig. 6. It should also be noted that most of the structures presented here are of type A and B patterns with only five clusters of C and D types. Moreover, all the most energetically favourable

clusters have the A and B pattern. Among the 4680 structures feasible in the given cluster set the thermally weighted number of structures are 3469.5 of A type, 1190.8 of B type, 15.4 of C type and 5.3 of D type. This allows the conclusion that we can approximately describe the equilibrium surface of water ice in the given model as a mixture of only two types of structures: pattern A and pattern B taken in an approximate amount of 3:1 (based on the rounded ratio 3469.5 to 1190.8). Fig. 7 shows the optimized geometry parameters of the two most stable structures (1 and 2) belonging to the A and B patterns. The geometry optimizations performed at the B3LYP/6-31++G(d,p) and B3LYP/6-311++G(2d,2p) levels results in the similar geometries. Therefore, only B3LYP/6-311++G(2d,2p) geometry parameters are shown in Fig. 7.

In order to study the adsorption energies of the H₂O₂ molecule coordinated with a variety of clusters of different H-bond orienta-

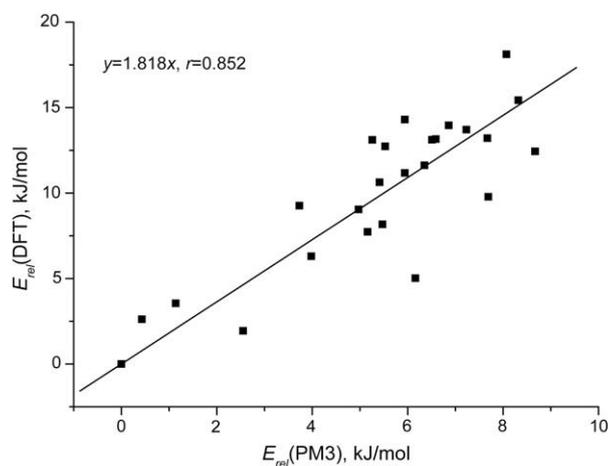


Fig. 5. Comparison between the relative cluster energies (relatively to the minimum cluster energy) calculated by the PM3 and DFT methods for 25 structures from Table 1.

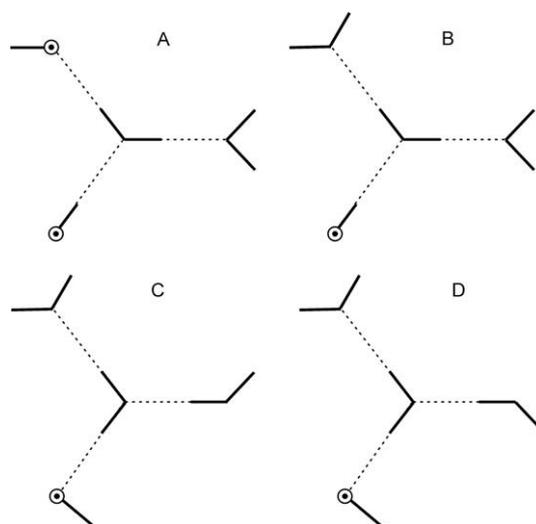


Fig. 6. Orientation patterns of four top water molecules in the clusters from Table 1. Points in circles designate the OH-bonds directed upward.

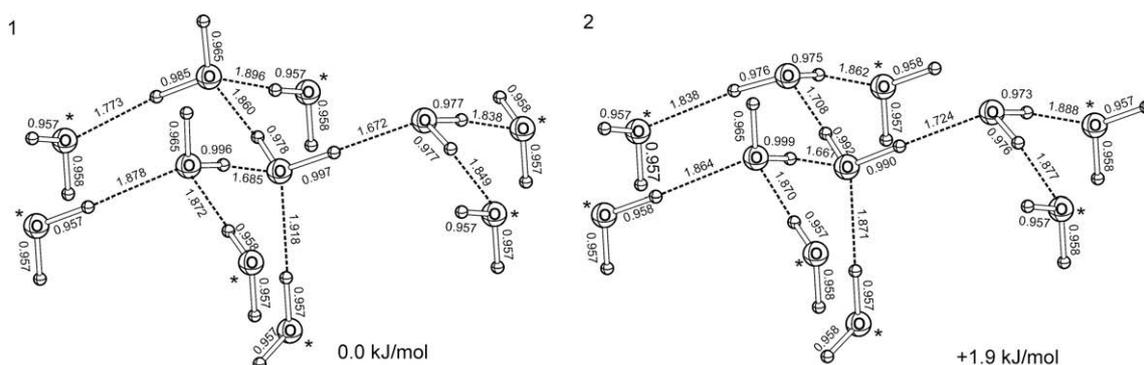


Fig. 7. Optimized geometries of the two most favourable water clusters (structures 1 and 2) from Table 1. The molecules which are fixed during the optimization are marked with asterisks.

tions, we performed the PM3 calculation of the coordination energy of the H_2O_2 molecule at all 789 unique cluster structures. The calculations were started from different initial points. To set up the starting point, the initially optimized H_2O_2 molecule was placed at approximately 3 Å over the top of a cluster and rotated by a sequence of Euler angles chosen in such a manner that all possible spatial orientations of the H_2O_2 molecule are covered. In total, 32 orientations of the H_2O_2 molecules were tested as starting points for the geometry optimization of the adsorption complex for each of the 789 unique cluster structures. For every starting point, the partial geometry optimization was repeated until standard stopping criteria were fulfilled. The structure with the minimum absolute energy was chosen among all resulting structures (structures corresponding to the different starting points distinguished by the Euler angles of the initial H_2O_2 position). The geometry parameters and the adsorption energy of the most favourable adsorption complexes were then analyzed.

Fig. 8 presents the adsorption energy distribution among all cluster structures obeying the ice rules. As it is evident from Fig. 8, the adsorption energy distribution has four maxima. Maximum adsorption energy corresponds to several structures of type

I. The second (highest) peak corresponds mostly to structures of type II. The adsorption energies of structures III are typically distributed in a broad range whereas structures 0 typically contribute to the medium-value energies.

Fig. 9 shows the adsorption energy as a function of the cluster energy. One can conclude that the maximum absolute adsorption energies (excluding several single peaks on the right) correspond to the clusters of lowest energy. They are typically by 4–5 kJ mol^{-1} higher than the energies of the remaining group of clusters. This fact can be significant if the clusters with random orientation of hydrogen bonds are used for the adsorption energy estimation. From this point of view the only clusters with large impact to the Boltzmann distribution should be used for the adsorption energy distribution.

As it becomes evident from Table 1, the two most favourable clusters are the unique structures 101 (type A pattern) and 180 (type B pattern). It should also be stressed that these structures are typical for all the clusters from the group of most favourable structures (from the 25 clusters present in Table 1). Thus, the coordination of the H_2O_2 molecule to these structures results in the most significant contribution to the adsorption energy.

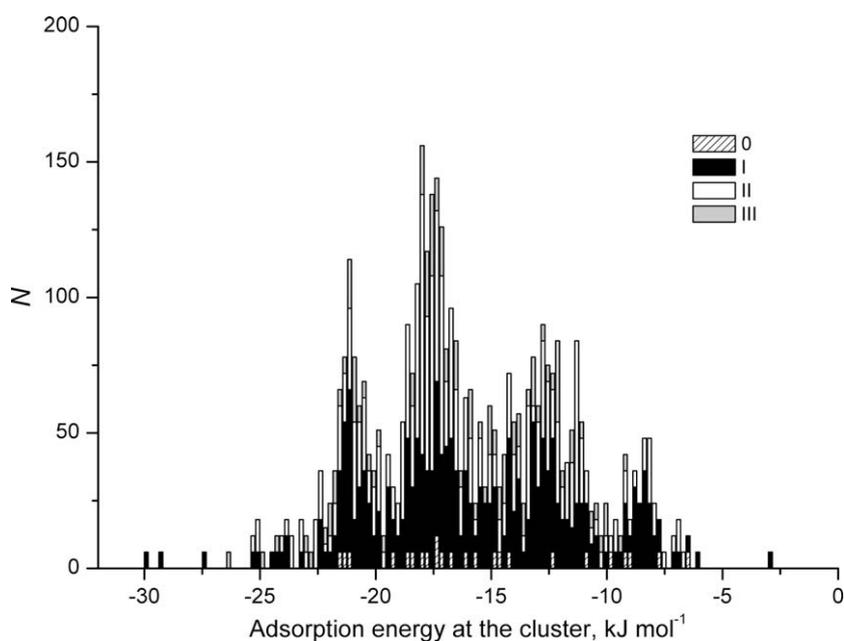


Fig. 8. Adsorption energy distributions for the 4680 clusters obeying the ice rules.

Table 2

Total energies, adsorption energies, and adsorption energies corrected by BSSE for the H₂O₂ molecule coordinated to the most energetically favourable clusters from Table 1.

	E_{tot} , a.u.	ΔE , kJ mol ⁻¹	$\Delta E + \text{BSSE}$, kJ mol ⁻¹	$\Delta E + \text{BSSE} + \text{ZPE}^a$, kJ mol ⁻¹
<i>B3LYP/6-31++G(d,p)</i>				
Structure 1 + H ₂ O ₂	-992.464299	-49.6	-43.7	-23.9
Structure 2 + H ₂ O ₂	-992.463312	-49.0	-42.5	-22.4
<i>B3LYP/6-311++G(2d,2p)</i>				
Structure 1 + H ₂ O ₂	-992.8124801	-43.6	-40.2	-32.6
Structure 2 + H ₂ O ₂	-992.8114887	-43.2	-39.5	-31.6

^a Vibrations of boundary groups are excluded.

parison with B3LYP/6-311++G(2d,2p). It is not clear, however, whether the results with the higher level are more reliable. Thus, the difference in the ZPE-corrected energy should be considered as the internal uncertainty of the quantum chemical theory. Within this uncertainty, the zero temperature enthalpy of adsorption is estimated to be in the range of 22–32 kJ mol⁻¹. These estimates are close to the ZPE-corrected energy obtained in [21] for the coordinated H₂O₂ molecule and remarkably different from the maximum adsorption energies obtained for other species considered in [21].

4. Discussion

We investigated the structure and properties of the adsorption complexes of H₂O₂ on ice surfaces using a model for the systematic study of the orientational isomerism of the hydrogen bond network in ice crystals. The model is based on several implicit assumptions: (1) structure of oxygen atoms network is close to the well-defined crystalline structure; (2) ice surface is considered to be under equilibrium conditions; (3) surface structures are distributed correspondingly to their energies and obeying the Boltzmann distribution.

The question whether the equilibrium crystalline structure can be considered as a reference configuration for the ice surface is of great importance for the above analysis. The experimental and theoretical studies demonstrate that the ice surface is not a well-defined crystalline structure at the temperatures higher than 180–190 K and significant disorder of oxygen lattice takes place (see, e.g. [5,7] and the references therein). At higher temperatures formation of a layer of water molecules takes place where the H₂O molecules undergo almost free translational and rotational movements [7]. Moreover, serious arguments were obtained recently [6] supporting the idea about existence of the so-called Fletcher phase on the ice surface – the alternating rows of dangling H and dangling O atoms. This idea was proposed by Fletcher [33] on the basis of theoretical analysis of electrostatic interaction between the surface groups and it was demonstrated [6] that it is qualitatively consistent with the experimental results of He atoms scattering and the sum frequency generation spectroscopy as well as with the classical potential calculations in the extensive periodic slab models.

The description of the phenomena like the quasi-liquid layer or Fletcher phase formation proposes the use of the complicated surface models comprising tens or hundreds of molecules and the corresponding theoretical approaches. However, the ideal structures presented here can be considered as limiting structures representing the different contributions of the disordered configurations at the partially amorphized surface or the instantaneous configurations of a quasi-liquid layer. It should be noted that even at the high degree of disorder the ideal structure conformations contribute significantly to the disordered molecular ensemble as it follows

from the distributions obtained in [7]. Moreover, the cluster approach does not contradict the existence of the Fletcher phase because its construction proposes the large contribution of the A or B patterns considered here in terms of the cluster model.

The assumption on the Boltzmann energy distribution of the cluster structures, neglects the long-range interactions between the surface groups and cannot represent the global distributions arising due to the long-range order. From this point of view, the long-range (collective) interactions of the surface groups can change the set of structures preferable for the single molecule adsorption. However, the analysis performed in [6] shows that within the same “surface phase” (i.e. within the same kind of the long-range OH ordering) the energy distribution is rather similar to that presented in Fig. 3. Moreover, the long-range ordering is probably not perfect (at least at higher temperatures) and the violation of the local Boltzmann distribution is probably not pronounced. Besides of all, this is also supported by the general applicability of cluster models in adsorption studies.

Based on the results for the model considered here one can conclude that the effect of different network organization can probably be taken into account if the simplified model of the ice surface is considered where only several most favourable surface structures are considered (e.g. patterns A and B) on the top of the cluster.

It is evident that the influence of the different choice of the hydrogen bond topology in the clusters with adsorbed H₂O₂ results in 10–15% changes of the adsorption energy (in comparison with similar calculations with the random H-bond topology). Thus, the effect of the various H-bond topologies on the calculated energetic parameters is not significant from the practical point of view (from the point of view of applied theoretical chemists who use the cluster models for the approximate estimates of the adsorption parameters) because the internal uncertainty of the cluster model itself and the theoretical method has a similar or even larger uncertainty value. However, to be more specific, the entire majority of clusters can be characterized as a set of only two or several most favourable structures. The performed study also demonstrates that some local structures and patterns on the ice surface are distinguished by a remarkable different energy and, consequently, some of them can significantly dominate on the ice surface due to their energetic favourability.

Acknowledgements

This work was partially supported by the Russian Foundation for Basic Research (Project No. 07-03-00390). S.I. and P.S. thank the Alfred-Wegener Institute and the German Academic Exchange Service (DAAD) for financial support during the course of the work.

References

- [1] C. Girardet, C. Toubin, Surf. Sci. Rep. 44 (2001) 159.
- [2] R.P. Wayne, Chemistry of Atmospheres, Clarendon Press, Oxford, 1991.
- [3] B.J. Murray, J.M.C. Plane, Atmos. Chem. Phys. 5 (2005) 1027.
- [4] J.P.D. Abbatt, Chem. Rev. 103 (2003) 4783.
- [5] G.-J. Kroes, Surf. Sci. 275 (1992) 365.
- [6] V. Buch, H. Groenzin, I. Li, M.J. Shultz, E. Tosatti, Proc. Natl. Acad. Sci. USA 105 (2008) 5669.
- [7] Y.A. Mantz, F.M. Geiger, L.T. Molina, M.J. Molina, B.L. Trout, J. Chem. Phys. 113 (2000) 10733.
- [8] M.T.C. Martins-Costa, M.F. Ruiz-López, Chem. Phys. 332 (2007) 341.
- [9] R. Vácha, P. Slavíček, M. Mucha, B.J. Finlayson-Pitts, P. Jungwirth, J. Phys. Chem. A 108 (2004) 11573.
- [10] D. Bernal, R.H. Fowler, J. Chem. Phys. 1 (1933) 515.
- [11] L. Pauling, J. Am. Chem. Soc. 57 (1935) 2680.
- [12] Y.A. Mantz, F.M. Geiger, L.T. Molina, M.J. Molina, B.L. Trout, J. Phys. Chem. A 105 (2001) 7037.
- [13] A. Milec, C. Struniewicz, R. Moszynski, P.E.S. Wormer, J. Chem. Phys. 115 (2001) 349.
- [14] N.T. Hashimoto, Y. Hara, M. Nagaoka, Chem. Phys. Lett. 350 (2001) 141.

- [15] S.C. Xu, J. Chem. Phys. 111 (1999) 2242.
- [16] S.C. Xu, X.S. Zhao, J. Phys. Chem. A 103 (1999) 2100.
- [17] L. Cwiklik, V. Buch, Phys. Chem. Chem. Phys. 11 (2009) 1294.
- [18] F. Borget, T. Chiavassa, A. Allouche, J.P. Aycard, J. Phys. Chem. B 105 (2001) 449.
- [19] C. Manca, A. Allouche, J. Chem. Phys. 114 (2001) 4226.
- [20] C. Manca, C. Martin, A. Allouche, P. Roubin, J. Phys. Chem. B 105 (2001) 12861.
- [21] S.K. Ignatov, P.G. Sennikov, H.-W. Jacobi, A.G. Razuvaev, O. Schrems, Phys. Chem. Chem. Phys. 5 (2003) 496.
- [22] P.G. Sennikov, S.K. Ignatov, O. Schrems, Chem. Phys. Chem. 6 (2005) 392.
- [23] V. Buch, S.P. Sandler, J. Sadlej, J. Phys. Chem. B 102 (1998) 8641.
- [24] J. Lekner, Physica B 252 (1998) 149.
- [25] T.K. Hirsch, L. Ojamäe, J. Phys. Chem. B 108 (2004) 15856.
- [26] J.-L. Kuo, J.V. Coe, S.J. Singer, Y.B. Band, L. Ojamäe, J. Chem. Phys. 114 (2001) 2527.
- [27] J.-L. Kuo, M.L. Klein, J. Phys. Chem. B 108 (2004) 19634.
- [28] J.-L. Kuo, S.J. Singer, Phys. Rev. E 67 (2003) 016114.
- [29] A.F. Wells, Structural Inorganic Chemistry, Oxford University Press, Oxford, 1986.
- [30] A.G. Razuvaev, S.K. Ignatov, O.B. Gadzhiev, O.A. Usacheva, Vestnik of Lobachevsky State Univ. Nizhny Novgorod 6 (2007) 59 (Russ. Ed.).
- [31] M.W. Schmidt, K.K. Baldrige, J.A. Boatz, S.T. Elbert, M.S. Gordon, J.H. Jensen, S. Koseki, N. Matsunaga, K.A. Nguyen, S.J. Su, T.L. Windus, M. Dupuis, J.A. Montgomery, J. Comput. Chem. 14 (1993) 1347.
- [32] A.A. Granovsky, PC GAMESS. Available from: <<http://classic.chem.msu.su/gran/games/index.html>>.
- [33] N.H. Fletcher, Phil. Mag. B 66 (1992) 109.