

The present work offers the scenarios of the bonding between a superoxide anion and 2D and 3D most stable clusters of a water hexamer such as a ring (chair), prism, and cage. The hydrogen bonding patterns formed in these superoxide—water hexamer complexes are analyzed along with their IR spectra in the region of the O—H stretching.

1. Introduction

The reactions that involve superoxide radical O_2^- continue to be discussed in chemistry, biophysics, biochemistry, medicine, and environmental sciences (see [2-6] and references therein). O_2^- is a major anionic charge carrier which is clustered in the atmosphere with abundant atmospheric species such as water and carbon dioxide [4]. Its interaction with water and the formation of hydrated superoxide clusters $O_2^-(H_2O)_{1\leq n\leq 4}$ [7-10, 1] have attracted a considerable interest during the last decade.

Almost all chemical reactions involving O_2^{-} are running in solutions, mainly in water, that drastically changes the properties of superoxide. These changes depend on a combination of various effects and are primarily determined by the many-body interactions between a superoxide molecule and, for example, a hydrogen-bonded water network. A typical way to grasp, which interactions in this particular case are predominant, is to model a water solvent by an appropriate water cluster(s) large enough to preserve the key features of liquid water. The early studies of the superoxide-water interactions [7-10, 1] have been mostly focused on the energetics and spectroscopy of the sequential solvation of superoxide up to four molecules of water and partly aimed at the study of the first hydration shell around superoxide. Much less has been known [10c, 10f] of how O_2^{-} actually interacts with larger water clusters, say, a water hexamer. Even much less has been known about

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whether and to what extent the hydrogen-bonded water network is disrupted while interacting with a superoxide anion or, more specifically, whether the water network remains unbroken implying the socalled "surface solvation" or water molecules assemble themselves on the same side of superoxide ("internal solvation")? These questions are addressed in the present work.

2. Model and Scenario of Bonding

A standard procedure to study the interaction between superoxide and water is to "dress" O_2^- sequentially by water molecules [7–10,1]. Another one which has not been exploited so far and which in fact models the typical processes occurring, in particular, in the atmosphere, at least at the first stage of the formation of superoxide radicals, is to directly examine its interaction with some water cluster. The latter approach constitutes the goal of the present work.

Since the hydrated superoxide $O_2^-(H_2O)_{1 \le n \le 4}$ have been already extensively studied on both experimental and theoretical sides, it is reasonable to treat larger clusters of water $(H_2O)_{n>5}$. The present work focuses on the interaction between superoxide and a water hexamer, since the latter is the smallest cluster of water molecules which exhibits a fascinating structural morphology of the co-existence of two and three dimensionalities on the almost equal energetical footing [11-14]. The most stable conformers of a water hexamer range from a 2D cyclic ring, boat, and open book to 3D cages and prisms [11-14]. These conformers are different to the great extent not only because of their dimensionality, rather they are sharply distinct in the properties such as, for example, hydrogen bond patterns, spectroscopical features, and the range of oxygen-oxygen separations.



Fig. 1. Two lower-energy conformers of superoxide with a ring (chair) water hexamer. Bond lengths are given in Å, bond angles in degrees. The O $-H \cdots O$ hydrogen bonds in a chair water hexamer are characterized by R(O-H) = 0.986 Å and $r(H \cdots O) = 1.730$ Å. The O-H bond length of "free" O-H bonds is equal to 0.961 Å

In we have studied the sequential |1|,hydration of superoxide, primarily focusing on the interplay of ionic hydrogen bonds formed between superoxide and water molecules, and the waterwater ones, partly ionic and partly moderate, and their spectroscopic appearance. This is, in fact, a manifestation of how superoxide interacts with water molecules. Another question is how it, as being formed, interacts with water clusters? What scenarios of bonding are possible? Evidently, the key features of such an interaction can be deduced from the structural analysis of the complexes $O_2^-(H_2O)_{1 \le n \le 4}$. In the present work, water clusters are modeled by lower-energy conformers of a water hexamer such as a prism, cage, book, boat, and chair (see, e.g., Fig. 1 in [14c]).

We suggest the following scenario of bonding between superoxide and the lower-energy conformers of water hexamers. The excess electron of a superoxide molecule in its doubly degenerate $X^2 \Pi_g$ ground state occupies the antibonding π^* singly-occupied molecular orbital (SOMO). The latter is characterized by two lobes lying perpendicularly to the O–O axis on each side of O_2^- . While interacting with a given water cluster, the SOMO of superoxide overlaps with the σ MOs of the neighboring O–H bonds of water molecules composing the water cluster. It causes the excess electron of O_2^- to be partially delocalized over these O-H bonds or, in other words, to be shared between two oxygens of superoxide and the proton donor O-H groups. This results in the formation of $O_2^- \cdots O$ —H ionic hydrogen bonds. We have already noticed such a trend in [1] (see also [7-10]). Namely, under the formation of the hydrated superoxides $O_2^-(H_2O)_{1-4}$, the O-O bond is sequentially shortened from 1.346 Å in O_2^- to 1.341 $(O_2^-(H_2O))$, 1.338 $(O_2^-(H_2O)_2)$, 1.334 $(O_2^-(H_2O)_3)$, and finally to 1.331 Å in the $O_2^-(H_2O)_4$ complex. Another effect is related to the neighboring water molecules. In a case of two water molecules, due to the topology of the SOMO, the superoxide molecule is keen to form two ionic hydrogen bonds which are preferentially placed in the same plane.

A rearrangement of the excess electron and its further partial localization over the O—H bonds bonded to superoxide originate a strong repulsive Coulomb potential. The latter may even break the hydrogen bond between these two water molecules. Therefore, we suggest that two different O—H groups of a water cluster may be involved in the formation of ionic hydrogen bonds with superoxide. These are either two so-called "free" O—H groups or one O— H group that forms an intramolecular hydrogen bond within a water cluster and a neghboring "free" O— H group. Which of these two groups is favorable mainly depends on how superoxide and the water cluster approach each other. This will be demonstrated

3. Computational Framework

methodology.

All computations reported in the present work were performed within the Kohn-Sham self-consistent field formalism with the hybrid density functional B3LYP potential in conjunction with the split-valence 6-311 ++G(d,p) basis set using GAUSSIAN 03 suit of packages [15].

below after a short outline of the computational

The tight convergence criterion was employed in all optimizations with lifting any geometric constraints. Harmonic vibrational frequencies were kept unscaled. The zero-point vibrational energies (ZPVE) and thermodynamic quantities were also calculated at T=298.15 K. Throughout the present work, the binding energies are ZPVE-corrected. The expectation value $\langle \mathbf{S}^2 \rangle$ was calculated to be equal to 0.750.

In the doublet electronic ground state $X^2 \Pi_g$ of O_2^- , the bond length r(O-O) = 1.3461 Å for the B3LYP/6-311++G(d,p) computational level, which agrees with the experimental value of 1.347 Å [16a]; B3LYP/6-31+G(d,p) r(O-O) = 1.351 Å [16b], MP2/6-311++G(3d,3p)+diffs(2s2p,s) r(O-O) = 1.357Å [9e], QCISD/aug-cc-pVTZ r(O-O) = 1.3418 Å [16c], CCSD(T)/aug-cc-pVTZ r(O-O) = 1.3563 Å, and QCISD(T)/aug-cc-pVTZ r(O-O) = 1.3574 Å [16c]. Its stretching vibrational mode is predicted at $1165 \text{ cm}^{-1} (\text{UB3LYP}/6-311++G(d,p)) (cf. 1090 \text{ cm}^{-1})$ [16b] and 1170.6 $\rm cm^{-1}$ (QCISD/aug-cc-pVTZ [16c]), $1103.5 \text{ cm}^{-1} (\text{CCSD}(\text{T})/\text{aug-cc-pVTZ} [16c]), 1107.8$ $\rm cm^{-1}$ (QCISD(T)/aug-cc-pVTZ [16c])). The electronic energy amounts to -150.39171 Hartree and ZPVE to 1.67 kcal/mol.

4. Low-Energy Complexes $O_2^-(H_2O)_6$

4.1. O_2^- - chair water hexamer

The interaction of superoxide with a chair (ring) water hexamer leads to two low-energy structures, O_2^- chair₁ and O_2^- —chair₂, displayed in Fig. 1. They are structurally different, and their bonding scenarios are different as well. The former arises, when O_2^- approaches a chair hexamer approximately within the hexamer plane. Then O_2^- breaks one of the chair intramolecular hydrogen bonds, namely, the bond $O_3-H_3\cdots O_8$, as shown in Fig. 1. This breakage is accompanied by the rotation of the O₈-H₈ group and the formation of two hydrogen bonds, O_3 - H_3 ··· O_1 and O_8 - H_8 ··· O_1 , where the oxygen atom O_1 of superoxide acts as a double proton acceptor. The former hydrogen bond is considerably stronger than the latter, which is indicated by two factors. First, the H-bond $r(H_3 \cdots O_1)$ in O_3 - $H_3 \cdots O_1$ comprises 1.613 Å, whereas $r(H_8 \cdots O_1) =$ 1.870 Å in O_8 -H₈···O₁. Secondly, the O_3 -H₃ bond elongates to 1.011 Å, whereas the O_8-H_8 does only to 0.980 Å. Obviously, the hydrogen bond $O_3-H_3\cdots O_1$ belongs to a proton-shared or ionic hydrogen bond. By contrast, the O_8 -H₈···O₁ bond is even slightly weaker as compared to those in a chair hexamer (see Fig. 1).

The concerted rotation of the water molecule in $O_8H_8H'_8$ and the intrusion of another oxygen atom O_2 of superoxide into a chair hexamer restructure the latter by breaking the intramolecular hydrogen bond between the water molecules $O_7H_7H'_7$ and $O_8H_8H'_8$ and by forming a weak water-superoxide hydrogen bond $O_7-H'_7\cdots O_2$. In addition, two other weak hydrogen bonds are also formed, viz., $O_5-H'_5\cdots O_2$ and $O_6-H'_6\cdots O_8$. They are characterized by $R(O_5-H'_5) = 0.975$ Å and $R(O_6-H'_6) = 0.972$ Å, and, respectively, by $r(H'_5\cdots O_2) = 1.933$ Å and $r(H'_6\cdots O_8) = 2.078$ Å.

A bonding scenario of the O_2^- -chair₂ coupling is suggested to be the following. Superoxide approaches a chair hexamer from above (or below) and becomes "capped" by its four "free" OH-bonds, which results in the formation of four water-superoxide hydrogen bonds (see Fig. 1). Their H-bond lengths are equal to 1.767, 1.793, 1.855, and 1.964 Å. The first one pertains to the $O_1-H'_1\cdots O_8$ which is the strongest hydrogen bond among those four. Its $O_1-H'_1$ bond lengthens to 0.991 Å. It is however less stronger than the hydrogen bond $O_3-H_3\cdots O_1$ in the complex O_2^- -chair₂ and therefore can be treated as the moderate one.

Energetically, O_2^- —chair₁ is more stable, by 2.4 kcal/mol, as compared to O_2^- -chair₂ (see Table). The ZPVE-corrected binding energy of O_2^- -chair₁ amounts to 41.7 kcal/mol. These two complexes are characterized by four newly formed hydrogen bonds between superoxide and a chair hexamer originating from the donation of water protons to superoxide. In total, they both have ten hydrogen bonds which can be classified as follows. Six water-water hydrogen bonds in O_2^- -chair₁ are weak since, for all of them, $R(O_i)$ - H_i \in (0.972 Å, 0.977 Å) and $r(H_i \cdots O_i) \in$ (1.914 \check{A} , 2.078 \check{A}) (except i = 4 and j = 3). They are thus even weaker compared to those existing in a chair hexamer. Therefore, regarding the complex O_2^- -chair₁, the superoxide-water interaction weakens, in general, the water-water intramolecular hydrogen bonds. The water molecule $O_4H_4H'_4$ bonded to another one, $O_3H_3H'_3$, that forms the ionic hydrogen bond with superoxide, is a unique exception of this observation. Its bond length $R(O_4-H_4) = 0.987$ Å is slightly larger as compared to that in a chair hexamer as though, on the contrary, its H-bond length $r(H_4 \cdots O_3)$ equal to 1.761 Å > 1.730 Å prevents the analogous charge transfer that occurs in a chair hexamer under the H-bond formation.

The hydrogen-bond pattern is quite different in O_2^- chair₂. Water molecules remoted from $O_1H_1H'_1$, that forms the moderate hydrogen bond with superoxide, are characterized by $R(O_i-H_i) \in (0.973 \text{ Å}, 0.976 \text{ Å})$ and by $r(H_i \cdots O_j) \in (1.983 \text{ Å}, 2.060 \text{ Å}), i = 3, 4, 5$. Therefore, all their water-water hydrogen bonds are weaker as compared to a chair hexamer. In contrast, two molecules of water which embrace $O_1H_1H'_1$ have stronger waterwater hydrogen bonds: $R(O_2-H_2) = R(O_6-H_6) = 0.992 \text{ Å}$ and $r(H_2 \cdots O_3) = 1.721 \text{ Å}$, although $r(H_6 \cdots O_1) = 1.745 \text{ Å}$. Notice that $R(O_2-H_2)$ and $R(O_6-H_6)$ are even slightly longer than $R(O_1-H'_1)$, the length of the watersuperoxide hydrogen bond. A strengthening of the water-

Energies (in Hartree), ZPVEs (in kcal/mol), enthalpies (in Hartree), and entropies (in cal/(mol·K)) of the studied O_2^- – water hexamer species

Configuration	Energy	ZPVE	Enthalpy	Entropy
O_2^- -chair ₁	-609.294798	97.718	-609.121882	134.310
O_2^- -chair ₂	-609.290785	97.644	-609.118070	133.901
O_2^- -prism ₁	-609.283625	97.601	-609.111274	132.162
O_2^- -prism ₂	-609.282964	96.738	-609.111923	132.466
O_2^- -cage ₁	-609.286906	96.322	-609.115955	139.389
O_2^- -cage ₂	-609.286014	96.604	-609.114820	137.256
O_2^- -cage ₃	-609.285921	96.702	-609.114631	136.256
O_2^- -cage ₄	-609.284091	96.744	-609.112725	136.495
O_2^- -cage ₅	-609.282137	96.284	-609.110876	143.139

water hydrogen bonds, $O_2-H_2\cdots O_3$ and $O_6-H_6\cdots O_1$, in comparison with a chair hexamer can be explained by the fact that their corresponding proton acceptors also act as the double proton donors to superoxide and to the neighboring water molecule (notice that this is not the case in O_2^- -chair₁). The double proton donation, especially that to superoxide, enhances a lone-pair character of O_1 and O_3 and thus "catalyzes" their proton acceptor abilities.

There is indeed a remarkable feature in the hydrogenbonded pattern of O_2^- —chair₁ and O_2^- —chair₂ that, on the one hand, sharply distinguishes them from each other and on the other hand, predetermines a slight preference of the former. This is actually the ionic hydrogen bond O_3 —H₃···O₁ that only exists in the complex O_2^- —chair₁. Notice that, among all complexes O_2^- (H₂O)_{1 $\leq n \leq 4$} studied in [1], only three complexes, II₂, IV₂, and III₃, possess more elongated O—H bonds with superoxide, whereas the complex VI₄ has the O—H bond of precisely the same length.

How are these peculiarities in the hydrogen-bond patterns of the complexes O_2^- -chair₁ and O_2^- -chair₂ manifested spectroscopically? Do their IR spectra actually reflect the distinctive features between them? In Fig. 2, we display the computed IR spectra of O_2^- chair₁ and O_2^- -chair₂ and also juxtapose them with that of a chair water hexamer. We recall that, in the region of $\approx 3000 - 4000 \text{ cm}^{-1}$, the latter has two bands: one is rather broad and IR-intensive and ranges from 3315 (corresponding to the nearly in-phase stretch with negligible IR intensity) to 3472 cm^{-1} , whereas the other is narrow, much less IR active, and peaked at 3885 - 3887 cm⁻¹. The former band is ascribed to the stretching vibrational modes of those O-H groups which participate in the intramolecular hydrogen bonds. Two mainly asymmetric O–H stretches at ≈ 3393 $\rm cm^{-1}$ (2870 and 2866 km/mol) are dominant. The latter correspond to typical "free" O-H bonds.

The IR spectrum of the complex O_2^- —chair₁ within the same interval of wavenumbers drastically differs from that of a chair water hexamer since superoxide breaks its symmetry. This spectrum comprises therein of five bands. The strongest one (1913 km/mol) centered at 2932 cm⁻¹ is associated with the stretch of the O_3 — H_3 bond that originates the strongest ionic hydrogen bond with superoxide. Its comparison with the lowest O—H stretch of a chair hexamer yields a red shift of \approx 383 cm⁻¹. The second band located at ca. 3389 cm⁻¹ corresponds to the stretch $\nu(O_4$ —H₄) (733 km/mol) of the water-water hydrogen bond O_4 —H₄… O_3 that neighbors the water-superoxide ionic one.

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The third band at ca. 3563 cm⁻¹ (748 km/mol) is mainly composed of the stretches $\nu(O_5-H'_5)$, $\nu(O_7-H'_7)$, and $\nu(O_8-H_8)$ corresponding to the weak superoxidewater hydrogen bonds. The fourth one peaked at ca. 3680 cm⁻¹ consists of four subbands at 3661 cm⁻¹ (weak water-water hydrogen bonds; 529 km/mol), 3670 cm⁻¹ (weak water-water and superoxide-water hydrogen bonds; 239 km/mol), 3690 cm⁻¹ (weak water-water hydrogen bonds, $\nu(O_6-H_6)$, $\nu(O_7-H_7)$; 475 km/mol), and 3702 cm⁻¹ (weak water-water hydrogen bonds, $\nu(O_6-H'_6)$, $\nu(O_7-H_7)$, and $\nu(O_8-H'_8)$; 268 km/mol). The fifth band at \approx 3882 - 3886 cm⁻¹ describes "free" O-H groups in O₂⁻-chair_1.

The O-H stretching IR spectrum of the complex O_2^- -chair₂ also possesses five bands which are however resulted in a quite different pattern. The first two bands are composed of the coupled O-H stretches of three strongest hydrogen bonds, $O_1-H'_1\cdots O_8$ (superoxide-water H-bond), $O_2-H_2\cdots O_3$, and $O_6 H_6 \cdots O_1$ (water-water H-bonds). More specifically, the first band consists of two subbands centered at 3253 cm^{-1} (628 km/mol) and 3278 cm^{-1} (887 km/mol), whereas the second and most intense one is at 3349 $\rm cm^{-1}$ (1232 km/mol). The O–H stretches of the weak superoxide-water hydrogen bonds also contribute to this band (see the shoulder at 3388 cm^{-1} with an IR activity of 486 km/mol in Fig. 2), as well as to the lower-intensity band at 3482 cm^{-1} (383 km/mol). The fourth band consists of the O-H stretches of both weak water-water and superoxide-water hydrogen bonds. The last one is a typical "free" O-H group band falling within the same range as in the IR spectrum of O_2^- -chair₁.

4.2. O_2^- – prism water hexamer

Even a first glance at Fig. 3 displaying two most stable complexes between superoxide and a prism water hexamer convinces that a prism largerly preserves its shape while interacting with superoxide. It is worth mentioning in this regard that a prism water hexamer consists of two water triangles. Say, the upper one has one water molecule, $O_3H_3H'_3$, acting as a double proton donor (only within this triangle), another one, $O_4H_4H'_4$, as a donor-acceptor, and the third, $O_5H_5H'_5$, as a double proton acceptor. Two "free" O-H groups, O₄-H₄ and O_5 —H₅, on the latter two molecules cast as possible interactive sites to bind the superoxide anion. The lower water triangle with a similar donor-acceptor pattern (viz., within this triangle, $O_6H_6H'_6$ as a double proton donor, $O_7H_7H_7'$ as a donor-acceptor, and $O_8H_8H_8'$ as a double proton acceptor) has, in contrast, a single "free"

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Fig. 2. Computed IR spectra of the complexes O_2^- —chair₁ (*a*) and O_2^- —chair₂ (*b*) and a chair water hexamer (*c*). The Lorentzian line half-width is equal to 20 cm⁻¹

O-H group O_8 -H₈. Therefore, interacting with the lower triangle, superoxide has to break one of its hydrogen bond, by analogy with the bonding scenario for the complex O_2^- -chair₁. This might be the hydrogen bond O_6 -H'₆ $\cdots O_8$ as the weakest and mostly strained one $(R (O_6-H'_6) = 0.971 \text{ Å}, r(H'_6 \cdots O_8) = 2.101 \text{ Å}, and$



Fig. 3. Two low-energy conformers of superoxide with a prism water hexamer. Bond lengths are given in Å, bond angles in degrees.

 $\angle O_6H'_6O_8 = 140.2^\circ)$. These interaction sites for binding superoxide in the upper and lower triangles of the prism water hexamer define two bonding scenarios that are realized in the complexes O_2^- -prism₁ and O_2^- -prism₂, respectively.

Energetically, the complex O_2^- —prism₁ is characterized by a binding energy of 37.8 kcal/mol with respect to the infinitely separated superoxide and a water prism and slightly less stable (by 0.4 kcal/mol) than O_2^- —prism₁ (see Table). It is also weaker by 6.9 kcal/mol as compared to the complex O_2^- —chair₁. However, the direct binding of superoxide with a water prism appears to be stronger as compared to that with a water chair, which is manifested, in its turn, by strong ionic hydrogen bonds: O_4 —H₄… O_2 and O_5 —H₅… O_1 in O_2^- —prism₁ and O_6 —H'₆… O_1 and O_8 —H₈… O_2 in O_2^- —prism₂. The indication of a stronger character of these ionic hydrogen bonds is threefold. First, each complex O_2^- —prism_i (i = 1, 2) possesses two ionic bonds, instead of a single one in O_2^- —chair₁ and a moderate one in O_2^- —chair₂. Secondly, they are rather strong in geometric terms for the following two reasons:

(i) their O–H bond lengths obey the double inequality 1.002 Å $\leq R(O-H) \leq 1.030$ Å (precisely, in O₂⁻-prism₂ and 1.020 Å in O₂⁻-prism₁) and the rhs bound exceeds 1.011 Å, the O–H bond length of the ionic bond of O₂⁻-chair₁. Moreover, these two upper bounds, 1.020 and 1.030 Å, are larger as compared to the O–H bond lengths of any ionic hydrogen bonds reported for the complexes O₂⁻(H₂O)_{1\leq n\leq 4} [1];

(ii) since their H-bonds are equal to 1.546 and 1.697 Å for O_2^- —prism₁ and 1.609 and 1.678 Å for O_2^- —prism₂, the shorter one of each complex is stronger than the ionic H-bond of O_2^- —chair₁ characterized by the H-bond equal to 1.613 Å.

Thirdly, let us compare, to argue, the IR spectra of the superoxide—chair complexes and those of the superoxide—prism displayed in Fig. 4 in the region of the O—H stretching vibrations. The lowest bands in the IR spectra of both superoxide—prism complexes centered, correspondingly, at 2750 and 2406 cm⁻¹ are shifted downward by 182 and 526 cm⁻¹ as compared to that in the IR spectrum of O_2^- —chair₁.

Let us thoroughly study the IR spectra of both superoxide—prism complexes. The former one of O_2^{-} —prism₁ is marked by two highly intense bands at 2750 cm⁻¹ (1206 km/mol) and 3061 cm⁻¹ (2083 km/mol), both assigned to the aforementioned ionic hydrogen bonds O_4 —H₄… O_2 and O_5 —H₅… O_1 . The next band featuring at 3267 cm⁻¹ and characterized by an IR activity of 836 km/mol describes the O—H stretch of a single and rather peculiar hydrogen bond O_8 —H'₈… O_3 that links two water triangles. Due to the values $R(O_8$ —H'₈) = 0.993 Å and $r(H'_8 \cdots O_3) = 1.723$ Å, it is treated as a moderate hydrogen bond. The remaining bands are assigned to water-water H-bonded and "free" O—H groups.

A spectroscopic hallmark of O_2^- —prism₂ is indeed, as already noticed, its lowest IR band in the region of O—H stretching vibrations that is centered at 2406 cm⁻¹ and characterized by a significant IR activity equal to 3026 km/mol (see Fig. 4). In contrast to the mostly red-shifted ones that we observe in the spectra of the complexes O_2^- —chair₁, O_2^- —chair₂, and O_2^- —prism₁, this band is assigned to the symmetric stretch of the superoxide-water hydrogen bond O_6^- — $H'_6 \cdots O_1$ coupled to the water-water one, O_5 — $H_5 \cdots O_6$. By ionicity, the latter is somewhat superior to the

former due to its bond lengths: $R(O_5-H_5) = 1.038$ Å and $r(H_5 \cdots O_6) = 1.501$ Å. Structurally, this strongly ionic bond O_5 — H_5 ··· O_6 establishes the H-bonding link between the water triangles in the complex O_2^- -prism₂ and resembles that in a prism water hexamer, where this hydrogen bond is characterized by the longest O-H bond of 0.998 Å and an H-bond length of 1.682 Å. The specificity of this hydrogen bond consists in that it is the only one in the upper water triangle that donates a proton to the lower triangle of the water prism, precisely, to the water molecule ${\rm O}_6{\rm H}_6{\rm H}_6'$ which is a double H-bond acceptor in the lower triangle. Since the latter water molecule, while interacting with superoxide, restructuralizes one of its water-water Hbond to be the superoxide-water one, it strengthens its proton acceptor ability by forming a stronger hydrogen bonding interaction with the water molecule linker $O_5H_5H'_5$ that acts within the upper water triangle solely as a double H-bond donor. The neighboring O-H stretch band predicted at 2667 cm^{-1} (1108 km/mol) describes the asymmetric stretch of the superoxidewater hydrogen bond $O_6-H'_6\cdots O_1$ and the water-water one, O_5 — H_5 ··· O_6 . The next band at 3110 cm⁻¹ (1626 km/mol) is mostly attributed to the O-H stretch of another and less ionic superoxide-water hydrogen bond $O_8-H_8\cdots O_2$. The rest of the IR bands are typical of the O-H stretches of the interior H-bonds of a prism water hexamer which are rather weakly perturbed by the bonding with superoxide.

4.3. O_2^- - cage water hexamer

Five different scenarios of bonding between cage water hexamer and superoxide are identified in the present study (see Fig. 5). Only one of them mostly preserves a cage shape, while a cage water hexamer interacts with superoxide, and actually leads to the most stable complex O_2^- -cage₁ among all studied cage-superoxide structures. Its binding energy, taken with respect to the infinitely separated cage water hexamer and superoxide, amounts to 40.8 kcal/mol. It is however less stable by 3.6 kcal/mol than $O_2^-{\rm -chair_1},$ albeit more stable by 3.3 kcal/mol than $O_2^-{\rm -prism_1}$ (see Table). The energetically closer scenarios result in the complexes O_2^- -cage₂ and O_2^- -cage₃, less stable than O_2^- -cage₁ by only 0.8 and 1.0 kcal/mol, respectively. As follows from Fig. 5, they both structurally resemble a ladder rather than a cage. In fact, they are two limited protontransfer structures linked to each other via the concerted proton transfer within the fourfold water ring. The latter is governed by the transition-state linker O_2^- -cage^{ts}_{2 $\Leftrightarrow 3$},



2000

1000



Fig. 4. Computed IR spectra of the complexes O_2^- -prism₁ (*a*) and O_2^- -prism₂ (*b*) and a prism water hexamer (*c*). The Lorentzian lineshape half-width is equal to 20 cm⁻¹

3000

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а

4000

b



Fig. 5. Most stable conformer O_2^- -cage₁ of superoxide with a cage water hexamer. Bond lengths are given in Å, bond angles in degrees.

displayed in Fig. 5 and characterized by the transition frequency equal to 656 cm⁻¹ (B3LYP/6-31+G(d)). O_2^- -cage^{ts}_{2 \Leftrightarrow 3} determines the ZPVE-corrected proton-transfer barrier that amounts to 22.4 kcal/mol (B3LYP/6-31+G(d)) relative to the energy-minimum structure O_2^- -cage₂. The last two structures, O_2^- -cage₄ and O_2^- -cage₅ are placed higher than O_2^- -cage₁ by 2.2 and 3.0 kcal/mol, respectively. Structurally, they may be correspondingly referred to a bent ladder and a square $-O_2^-$ -distorted pentagon.

The complexes O_2^- -cage_{1-3,5} are characterized by a single strong ionic superoxide-water hydrogen bond of the D^1A^2 type whose R(O-H) varies from 1.027 (O_2^- - $(O_2^--Cage_3)$ and 1.047 ($O_2^--Cage_2$) and 1.047 ($O_2^--Cage_2$) and reaches 1.054 Å in O_2^- -cage₁. The exceptional complex O_2^- -cage₄ features two ionic superoxide-water hydrogen bonds with R(O-H) = 1.006 Å (D²A²) and 1.026 Å (D^1A^2) . Notice that O_2^- -cage₁ has the longest and hence the strongest ionic hydrogen bond O_3 -H₃···O₁ among all studied complexes that are formed between superoxide and water hexamers. Its H-bond length $r(\mathrm{H}_3\cdots\mathrm{O}_1)$ equal to 1.472 Å is the shortest one. That is why, we anticipate that the lowest O-H stretch band of O_2^- -cage₁ is the most downshifted one. This is seen in Fig. 6 that displays the computed IR spectra of all O_2^- -cage₁₋₅ complexes.

The stretching mode $\nu(O_3-H_3)$ of the complex O_2^- cage₁ is predicted at 2223 cm^{-1} (2496 km/mol), that is downshifted by 183 cm^{-1} as compared to that of the complex O_2^- -prism₂. It is separated by 847 cm⁻¹ from the next IR band of O_2^- -cage₁ (precisely, centered at 3070 cm^{-1} and characterized by an IR activity of 1725 km/mol, see Fig. 6) assigned to the stretch of the water-water hydrogen bond O_7 — H_7 ··· O_5 . The latter is referred to the water-water ionic hydrogen bond since its $R(O_7 - H_7) = 1.004$ Å and $r(H_7 \cdots O_5) = 1.656$ Å. We suggest that its ionicity is related to the cooperativity of the water-water hydrogen bonding interaction, because this water molecule $O_7H_7H_7'$ is a double proton acceptor and a single proton donor to the water molecule that donates its protons to both superoxide-water hydrogen bonds. In a cage water hexamer, it is partly the analog of the molecule $O_3H_3H'_3$ (Fig. 5) referred to the same donor-acceptor type. The latter is characterized by the $R(O_3-H_3) = 0.996$ Å, that can be ascribed to a moderate H-bond rather than to a weak one, and exhibits the stretch at 3222 cm^{-1} . The third lowest IR band of O_2^- -cage₁ centered at 3171 cm⁻¹ (1075 km/mol) is assigned, as anticipated according to the chain of inequalities for R(O-H) (1.054 Å > 1.004 Å > 0.998 Å), to the stretch of another superoxide-water

hydrogen bond which is certainly a moderate one. The rest of the IR bands corresponds to the stretching modes of water-water hydrogen bonds and three "free" O-H groups.

Similar IR patterns are exhibited by the complexes O_2^- -cage₂ and O_2^- -cage₃ (see Fig. 6). The lowest O-H stretch IR band is correspondingly identified at 2323 $\rm cm^{-1}$ (2314 km/mol) and 2372 $\rm cm^{-1}$ (2180 km/mol) and assigned to the strongly ionic superoxide-water hydrogen bond O_3 -H₃···O₁. The latter is slightly stronger in O_2^- -cage₂ that is indicated by a longer O–H bond (by 0.003 Å) and a shorter H-bond (by 0.011 Å). By analogy with the complex O_2^- -cage₁, the next O–H IR band of O_2^- -cage₂ (3109 cm⁻¹; 1552 km/mol) and O_2^- -cage₃ $(\overline{3082} \text{ cm}^{-1}; 2006 \text{ km/mol})$ corresponds to a single ionic water-water H-bond, either $O_6-H_6\cdots O_5$ in O_2^- -cage₂ or $O_7-H_7\cdots O_8$ in O_2^- -cage₃. The latter pertains to the D^1A^1 -type water molecule that donates, through this bond, its proton to the D^2A^1 -type water molecule which donates, in its turn, one of its protons to another $D^{2}A^{1}$ -type water molecule that forms the hydrogen bond with superoxide. These H-bonded chains from a strong water-water H-bond to a superoxide-water H-bond are different for both O_2^- -cage₂ and O_2^- -cage₃ complexes. The most striking difference between them consists in that the H-bonded chain in O_2^- -cage₂ ends at the strong superoxide-water H-bond O_3 -H₃···O₁, whereas that in O_2^- -cage₃ ends at the moderate superoxide-water H-bond O_4 -H₄...O₂. The latter that exists in both complexes gives rise to the third O–H IR band centered at 3224 $\rm cm^{-1}$ (1344 km/mol) in $\rm O_2^-\text{-}cage_2$ and at 3200 cm^{-1} (1054 km/mol) in O₂⁻-cage₃. The remaining O-H IR bands shown in Fig. 6 are attributed to water-water H-bonded and "free" O-H groups of the water hexamer subsystem.

The IR spectrum of the complex O_2^- -cage₄ in the O–H stretching region that is also displayed in Fig. 6 is markedly different from those of the more stable complexes between superoxide and a cage water hexamer. This difference is primarily in that the two lowest IR bands, which are computed at 2638 cm^{-1} (2182 km/mol) and 3050 cm^{-1} (2466 km/mol), describe correspondingly the O-H stretches of two ionic superoxide-water hydrogen bonds, $O_3 - H_3 \cdots O_1$ and O_4 -H₄···O₂. The third band at 3213 cm⁻¹ (1018 km/mol) is assigned to $\nu(O_5-H_5)$ of the ionic waterwater hydrogen bond. The IR spectrum of O₂⁻-cage₅ (Fig. 6) shares many similar features, though not all ones, with that of O_2^- -cage₄ and is specific in some sense. Its lowest IR band peaked at 2651 cm^{-1} (2335) km/mol) corresponds to the strongest ionic superoxide-



Fig. 6. Computed IR spectra of the complexes O_2^- -cage₁ (a), O_2^- -cage₂ (b), O_2^- -cage₃ (c), O_2^- -cage₄ (d), O_2^- -cage₅ (e), and a cage water hexamer (f). The Lorentzian lineshape half-width is equal to 20 cm⁻¹

water hydrogen bond O_3 — $H_3 \cdots O_1$. The next two bands are actually ascribed to the symmetric and asymmetric stretches of the coupled ionic superoxide-water and ionic water-water hydrogen bonds O_4 -H₄···O₁ and O_5 -H₅···O₄. Interestingly, the latter is stronger than the former, since its O_5 -H₅ bond is longer by 0.006 Å than

the O_4 — H_4 and its H-bond $H_5 \cdots O_4$ is shorter by 0.059 Å as compared to $H_4 \cdots O_1$. The slightly ionic waterwater H-bond O_8 — $H_8 \cdots O_3$ that joins the strongest superoxide-water H-bond O_3 — $H_3 \cdots O_1$ contributes to the fourth IR band of O_2^- —cage₅.

5. Conclusions

In the present work, we have proposed and elaborated a number of bonding scenarios that occur between the superoxide anion and 2D and 3D most stable structures of a water hexamer cluster such as a chair (ring), prism, and cage. The hydrogen-bonded patterns of the resulted complexes have been analyzed along with their computed IR spectra in the region of O-H stretching vibrational modes. We have demonstrated that each of the studied water hexamer structures admits either an internal or surface solvation scenario depending on the reaction route. We have also shown the existence of two limited proton-transfer structures, O_2^- -cage₂ and O_2^- -cage₃ linked to each other via the concerted proton transfer within the fourfold water ring and identified the corresponding transition-state linker O_2^- -cage^{ts}_{2 $\Leftrightarrow 3$}. However, the ZPVE-corrected proton-transfer barrier determined by O_2^- -cage^{ts}_{2 $\Leftrightarrow 3$} and amounting to 22.4 kcal/mol (B3LYP/6-31+G(d)) relative to the energyminimum structure O_2^- -cage₂, is rather high that apparently prevents its occurrence.

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ВЗАЄМОДІЯ СУПЕРОКСИДУ О $_2^-$ З КЛАСТЕРАМИ ВОДИ. 2. КОМПЛЕКСИ СУПЕРОКСИДУ І ГЕКСАМЕРУ ВОДИ

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Резюме

Запропоновано і детально розроблено ряд сценаріїв зв'язування, які здійснюються між аніоном супероксиду та дво- і тривимірними найбільш стабільними структурами кластера гексамеру води — кріслом (кільцем), призмою і кліткою. Проаналізовано структури гідрогенних зв'язків утворених комплексів разом з їхніми інфрачервоними спектрами в області розтягувальних вібраційних мод О-Н-груп.