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Ab initio investigation of the structures of NaOH hydrates and their Na^+ and OH^- coordination polyhedra

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ABSTRACT

Plane-wave pseudopotential density functional methods using the Perdew-Burke-Ernzerhof exchange-correlation functional were used to investigate theoretically the structures of five NaOH hydrate phases through optimization of lattice parameters and atomic coordinates. Although all the calculations were carried out with $P1$ symmetry, we find in four of the five cases that the experimentally determined space group is maintained to high accuracy. Particular focus is placed on the coordination environments of Na^+ and OH^-. The Na-O distances are, in general, overestimated; however, the sodium ion coordination polyhedra are well reproduced by the theoretical calculations, including the fivefold coordinated sodium atom in the α-$NaOH{\cdot}4H_2O$ structure. The theoretical calculations correctly predict that α-$NaOH{\cdot}4H_2O$ is lower in energy than the metastable β-$NaOH{\cdot}4H_2O$ phase; thus, the α phase is stable even in the absence of proton disorder. The octahedral coordination environment around OH^- is calculated accurately, including the distances of the weak OH^--OH_2 hydrogen bonds in which the hydroxide ion acts as the proton donor. This work provides further evidence of the reliability of the Perdew-Burke-Ernzerhof exchange-correlation functional in hydrogen bonded systems, providing a direct, unambiguous test of the elusive hydroxide-water interaction.

INTRODUCTION

Aqueous solutions of sodium salts are common in natural environments in geochemistry and biochemistry, forming electrolytes affecting phenomena such as membrane structure and function and contaminant sorption. They are also important in industrial contexts in corrosion and nuclear waste processing (Yang and Randolph 1999). Although Na^+ is often considered a "background" constituent of the electric double layer, there is increasing evidence that element-specific ion-pair formation may be more important in interfacial chemistry than previously thought (Felmy and Rustad 1998; Wesolowski et al. 2000). Thus, there is motivation to understand the preferred coordination environments of sodium and its influence on neighboring water or other molecules.

For various reasons, the sodium-water interaction is difficult to investigate experimentally (Kameda et al. 1998). The lack of suitable isotopes makes it difficult to isolate the Na-O radial distribution function using neutron diffraction, giving rise to relatively large uncertainties in the hydration number of Na^+ in water (Bruni et al. 2001). Difficulties also arise from the relative weakness of the interaction, and, hence, the diversity of coordination environments in hydrated crystals, and conformational complexity in Na^+-H_2O clusters in quantum mechanical studies. Many of these issues have been discussed by White et al. (2000) in their recent first-principles investigation of the hydration of Na^+.

Even more fundamental than the Na^+-water interaction is the hydroxide-water interaction. The OH^--water interaction has been the subject of several ab initio investigations, going back 30 years (Newton and Ehrenson 1971; Tuckerman et al. 1995; Xantheas 1995; Novoa et al. 1997; Pliego and Riveros 2000; Wei et al. 2000). Interest in solvated hydroxide ion is motivated in part by the ion's fundamental importance in proton transport in aqueous solutions (Geissler et al. 2001). Outside of these theoretical studies, little is known about the solvation of OH^- in water (Bruni et al. 2001). Investigation of the structures of hydrated hydroxide ions in crystalline phases is one area in which a much-needed connection between experimental data and theoretical calculations can be made. This connection is especially important in that the hydroxide coordination numbers in the gas-phase ab initio studies are much lower than those observed in condensed phases.

Extensive crystallographic investigations of the structures of $NaOH{\cdot}nH_2O$ (Hemily 1953, 1957; Wunderlich 1958; Beurskens and Jeffrey 1964; Seidel 1988; Jacobs and Metzner 1991; Mootz et al. 1994) provide valuable information on the sodium-water and hydroxide-water interaction in well-defined structures. In this paper, we describe computational investigations on the five major NaOH hydrates whose proton positions have been determined: $NaOH{\cdot}(1, 3.5, 4\alpha, 4\beta, 7)\ H_2O$. Because the structural uncertainties associated with the hydrated crystals are much more controlled than those for aqueous species, the structural analysis can proceed with less ambiguity. Hence, the crystalline hydrates serve as an excellent baseline in studies of aqueous solutions (Ojamae et al. 1994). The information presented here serves as a robust foundation for testing various theoretical methods that might be invoked to investigate sodium-water interactions.

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COMPUTATIONAL APPROACH

All calculations were carried out using plane-wave pseudopotential methods with the CASTEP quantum mechanics module implemented in the Cerius^2 software package from Accelrys. Milman et al. (2000) give a comprehensive review of the use of CASTEP and the plane-wave pseudopotential method in mineralogical systems.

The electronic structure is computed using density functional theory with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional (Perdew et al. 1996). This functional and its predecessor, the Perdew-Wang (Perdew et al. 1992) generalized gradient corrected functional, have been investigated more thoroughly than others in hydrogen-bonded systems (Hamann 1997; White et al. 2000; Fortes et al. 2001). Hydrogen-bonded systems have been shown to be highly sensitive to the exchange correlation energy functional (Sprik et al. 1996; Hamann 1997). Ultrasoft pseudopotentials (Vanderbilt 1990) were used with a cutoff of 370 eV. Calculations included optimization of all structural parameters, including lattice parameters. Table 1 lists for each structure the number and coordinates of the *k*-points that we used to sample the Brillouin zone.

Calculations were started from the experimental atomic positions and lattice parameters. For each structure, the *P*1 cell was generated from the X-ray diffraction data. Each structure was then subjected to a molecular dynamics run at 150 K (±50 K) for 1 ps total simulation time (time step 0.5 fs), to "shake-up" the structure before optimization. After the "shake-up," the lattice parameters and atomic positions were optimized using the BFGS technique as implemented in CASTEP, thus the reported structures are at 0 K. The optimization proceeded until the following tolerances were achieved: RMS force <0.05 eV/Å, maximum stress tensor component <0.1 GPa, RMS atom displacement <0.001 Å, change in total energy $<2 \times 10^{-5}$ eV. The self-consistent field calculation was carried out at a tolerance of 2×10^{-5} eV.

RESULTS

NaOH·H$_2$O

The arrangement of Na and O atoms in NaOH·H$_2$O was first determined by Wunderlich (1958) using single crystal X-ray diffraction. In a later study, Jacobs and Metzner (1991) used both X-ray and neutron diffraction to determine the structures of NaOH·H$_2$O and NaOD·D$_2$O, including proton/deuteron positions, at room temperature. The layered structure, shown in Figure 1, is somewhat analogous to that of brucite, but with half of the OH$^-$ ions replaced by H$_2$O molecules to balance the charge of substituting a monovalent ion for a divalent ion in the octahedral sheets. The layers are attached by weak OH-OH$_2$ hydrogen bonds (O-O distance 3.18 Å) in which the OH group is the donor and the H$_2$O molecule is the acceptor. Within the layers, infinite one-dimensional hydrogen-bonded networks of composition $H_3O_2^-$ lie parallel to the **c** axis.

The coordination environment around the sodium ion is shown in Figure 1. The short set of bonds has two hydroxide ions from different $H_3O_2^-$ chains at 2.34 Å, and one water molecule at 2.31 Å, not hydrogen-bonded to either of the OH$^-$ ions but in the same $H_3O_2^-$ chain as one of the hydroxide ions. All the bonds in the long set connect to atoms within a single $H_3O_2^-$ chain: one

TABLE 1. *k*-points used in this work for Brillouin zone sampling

Phase	Fractional Coordinates			Weight	Fourier Transform Grid
NaOH·H$_2$O	0	1/4	1/4	1/2	64 × 36 × 36
	0	1/4	–1/4	1/2	
NaOH·3.5H$_2$O	0.25	0	0	1	36 × 72 × 64
α-NaOH·4H$_2$O	0	1/3	1/4	1/3	90 × 24 × 54
	0	1/3	–1/4	1/3	
	0	0	1/4	1/3	
β-NaOH·4H$_2$O	1/4	1/4	0	1/2	36 × 36 × 75
	1/4	–1/4	0	1/2	
NaOH·7H$_2$O	1/4	0	1/4	1/2	40 × 90 × 40
	1/4	0	–1/4	1/2	

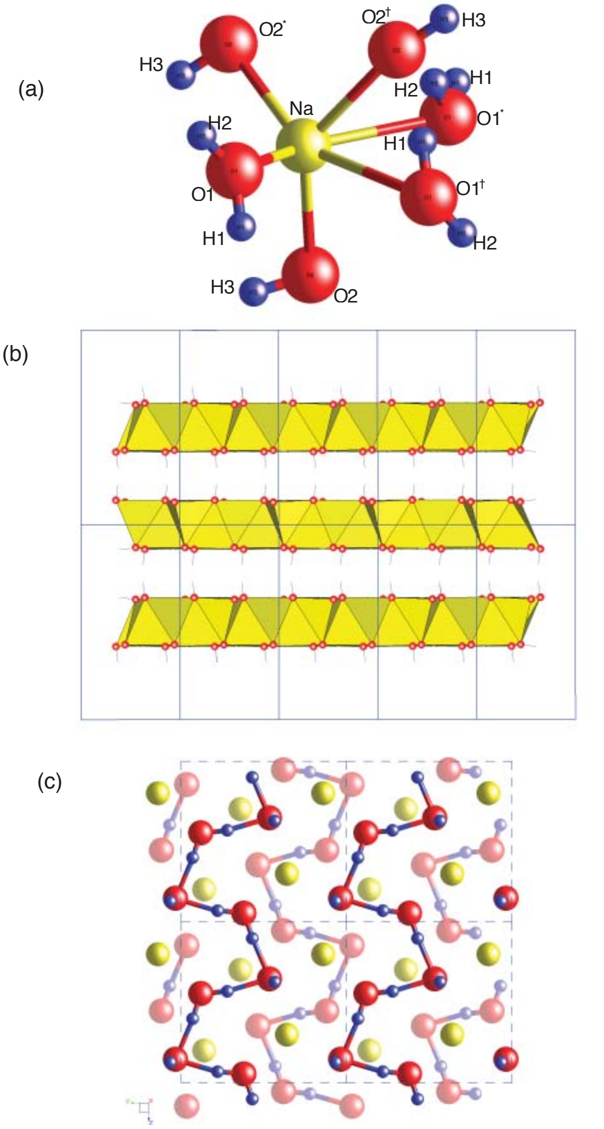

FIGURE 1. Structural characteristics of NaOH·H$_2$O. (**a**) Na(OH)$_3$(H$_2$O)$_3$ coordination polyhedron. (**b**) Polyhedral model (showing Na-centered octahedra) as viewed down the **c** axis; O atoms are red spheres, H atoms are denoted with sticks. (**c**) Intra-sheet hydrogen-bonding pattern viewed down the **a** axis. The one-dimensional networks occur in a zig-zag pattern parallel to **c**. Lower networks are depth-faded.

hydroxide ion at 2.45 Å and two water molecules, each donating a hydrogen bond to the hydroxide ion, at 2.68 Å and 2.88 Å.

The topology of this structure remained intact during the molecular dynamics simulation and quenching procedure, and the *Pbca* space group was maintained to better than 0.1%. The crystallographic parameters of the optimized configuration are shown in Table 2, and bond lengths and angles are listed in Table 3. Lattice constants are within 1% of experimental values. The coordination environment around the sodium ion is in fairly good agreement with experiment. The major discrepancy is in the longest Na-OH_2 bond (2.88 Å experimental compared to 2.98 Å calculated). The calculated O-O distances in the hydrogen bonds are in excellent agreement with the experimental distances, with differences of less than 0.02 Å including the OH^--OH_2 hydroxide-donor, water acceptor, which is exactly the same as the experimental value of 3.18 Å. As expected, the predicted O-H bond lengths far exceed the experimental ones, both for hydroxide ions and for water molecules. This arises from the free wagging motion of the H atom about the O atom in the OH bond. The calculation of hydrogen positions has been discussed recently by Milman and Winkler (2001).

TABLE 2. Crystallographic information for $NaOH{\cdot}H_2O$ (experimental data in parentheses)

Crystal System	orthorhombic	
Space Group	*Pbca*	
Temperature	0 K	(298.15)
a (Å)	11.960	(11.825)
b (Å)	6.221	(6.213)
c (Å)	6.134	(6.069)
V (Å^3)	456.41	(445.88)
Density (g/cm^3)	1.688	(1.728)

48 atoms in P_1 cell

Atomic Fractional Coordinates

Atom	*x*	*y*	*z*
Na	0.0562	0.1402	0.2012
O1	0.3832	0.1192	0.9456
O2	0.1256	0.0344	0.8538
H1	0.1270	0.5698	0.1018
H2	0.3692	0.2793	0.9309
H3	0.2053	0.4341	0.3728

TABLE 3. Structural information for NaOH· H_2O

	Experiment	Calculated	Exp – calc.
	Na-O bond lengths (Å)		
Na-O1	2.310	2.308	0.002
Na-O2*	2.340	2.359	–0.019
Na-O2	2.340	2.376	–0.036
Na-O2†	2.450	2.453	–0.003
Na-O1*	2.680	2.705	–0.025
Na-O1†	2.880	2.982	–0.102
	O-Na-O bond angles (°)		
			I Exp – calc I
O1†-Na-O2†	59.9	57.5	2.4
O1*-Na-O2†	62.0	61.4	0.6
O2-Na- O2†	139.1	137.7	1.4
O2*-Na-O2†	92.3	93.8	1.5
O1-Na-O2†	92.7	93.2	0.5
O2-Na-O1†	88.8	90.0	1.2
O2-Na-O1*	86.3	85.6	0.7
O2*-Na-O2	116.4	117.6	1.2
O2-Na-O1	104.1	103.6	0.5
O1-Na-O1†	74.4	74.1	0.3
O1-Na-O1*	147.7	147.0	0.7
O1-Na-O2*	107.8	105.6	2.2
O2*-Na-O1†	152.2	150.9	1.3
O2*-Na-O1*	93.9	97.4	3.5
O1*-Na-O1†	75.3	74.3	1.0
	O-O bond lengths in hydrogen bonds (Å)		
			Exp. – calc.
O1*-O2†	2.655	2.644	0.011
O1†-O2†	2.688	2.657	0.031
O2-O1	3.177	3.175	0.002

*, † Denote different placements of symmetrically equivalent atoms in the P1 cell.

$NaOH{\cdot}3.5H_2O$

Hemily (1953) and Wunderlich (1958) determined the arrangement of Na and O atoms in $NaOH{\cdot}3.5H_2O$. The structure was redetermined by Mootz et al. (1994). The latter study was conducted at 173 K and included the proton positions obtained by difference Fourier synthesis of the electron density. As in $NaOH{\cdot}H_2O$, the sodium ions are octahedrally coordinated. The polyhedral representation of this structure is shown in Figure 2. It consists of $Na(H_2O)_6$ octahedral chains running parallel to the **c** axis. These chains are composed of alternating edge- and face-shared octahedra. The OH^- ions are also surrounded by octahedral $(H_2O)_6$ coordination polyhedra. These coordination polyhedra are attached in edge-shared O1-O1 and O2-O2 dimers. The dimers are corner-linked to form the sheets shown in Figure 2. The hydroxide ions lie entirely outside the coordination spheres of the Na^+ ions. The mutual exclusion of the

TABLE 4. Crystallographic information for $NaOH{\cdot}3.5H_2O$ (experimental data in parentheses)

Crystal System	Monoclinic	
Space Group	$P2_1/c$	
Temperature	0 K	(173 K)
a (Å)	6.567	(6.481)
b (Å)	12.514	(12.460)
c (Å)	11.829	(11.681)
β (°)	104.14	(104.12)
V (Å^3)	942.66	(914.8)
Density (g/cm^3)	1.45	(1.50)

108 atoms in *P*1 cell

Atomic Fractional Coordinates

Atom	*x*	*y*	*z*
Na1	0.5801	0.3164	0.0997
Na2	0.4098	0.2913	0.3340
O1	0.2509	0.0323	0.0730
O2	0.0829	0.5513	0.1777
O3	0.3681	0.3795	0.9172
O4	0.4817	0.4776	0.2175
O5	0.2426	0.2415	0.1441
O6	0.9047	0.3808	0.0543
O7	0.5882	0.1365	0.0225
O8	0.7451	0.2603	0.2924
O9	0.0968	0.3932	0.3611
H1	0.1366	-0.0064	0.0946
H2	0.0153	0.5865	0.2325
H31	0.4264	0.4353	0.8733
H32	0.2217	0.4009	0.9104
H41	0.5715	0.5007	0.2951
H42	0.3370	0.5076	0.2100
H51	0.2256	0.1658	0.1168
H52	0.1143	0.2821	0.1062
H61	0.9657	0.4453	0.1018
H62	0.9029	0.3987	0.9726
H71	0.4776	0.0994	0.0505
H72	0.6622	0.0774	0.9913
H81	0.7947	0.1853	0.3042
H82	0.8702	0.3058	0.3231
H91	0.1035	0.4473	0.3011
H92	0.1567	0.4251	0.4421

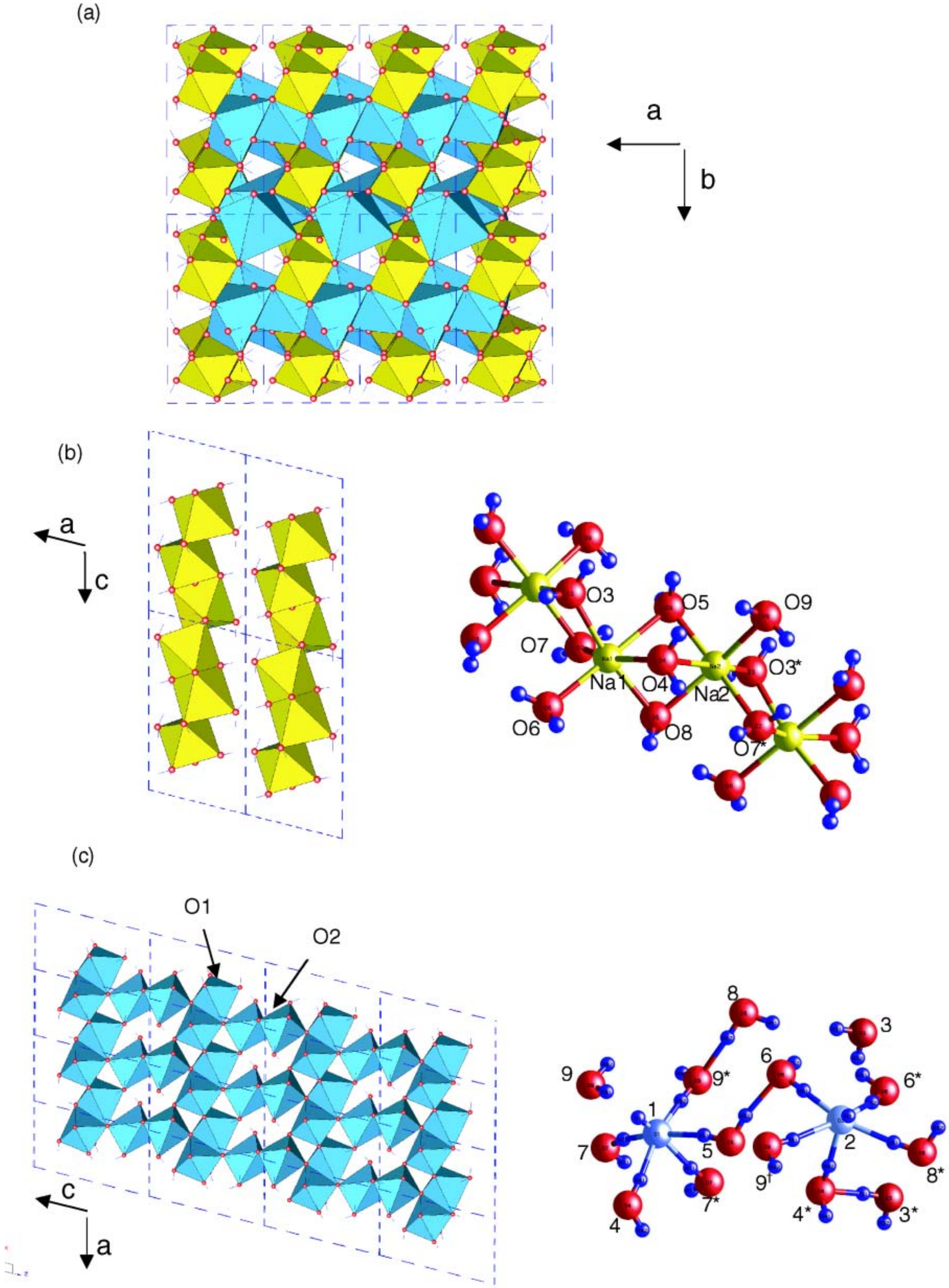

FIGURE 2. Polyhedral representation of $NaOH·3.5H_2O$. (**a**) View down **c** axis, yellow octahedra are centered on Na^+, blue octahedra centered on OH^-. (**b**) Isolated view of Na polyhedra (left), ball and stick model showing atomic arrangements (right). Yellow atoms are Na, red atoms are O, and blue atoms are protons. (**c**) Isolated view of OH-polyhedra (left), ball and stick model (right). Atoms same is in (**b**), but large cyan atoms are O from the hydroxide ion.

TABLE 5. Structural information for Na polyhedral elements in $NaOH·3.5 H_2O$

	Exp.	Calc.	Exp. – calc.		Exp.	Calc.	Exp. – calc.
Na-O bond lengths (Å)							
Na2-O8	2.346	2.402	–0.056	Na1-O7	2.403	2.457	–0.054
Na2-O4	2.673	2.806	–0.133	Na1-O5	2.503	2.575	–0.072
Na2-O5	2.322	2.332	–0.010	Na1-O4	2.518	2.621	–0.103
Na2-O9	2.388	2.505	–0.117	Na1-O6	2.403	2.435	–0.032
Na2-O3*	2.391	2.397	–0.006	Na1-O8	2.372	2.379	–0.007
Na2-O7*	2.418	2.426	–0.008	Na1-O3	2.353	2.399	–0.046
O-Na1-O angles (°)							
	Exp.	Calc.	| Exp. – calc. |		Exp.	Calc.	| Exp. – calc. |
O6-Na1-O8	95.1	96.4	1.3	O5-Na1-O7	80.7	80.3	0.4
O6-Na1-O4	101.7	102.6	0.9	O7-Na1-O8	92.3	92.0	0.3
O6-Na1-O5	177.7	176.7	1.0	O7-Na1-O4	160.4	159.6	0.8
O6-Na1-O3	92.2	91.1	1.1	O7-Na1-O3	91.6	91.6	0.0
O6-Na1-O7	97.0	96.8	0.2	O3-Na1-O8	171.2	171.2	0.0
O5-Na1-O8	84.9	85.5	0.6	O3-Na1-O4	93.5	94.3	0.8
O5-Na1-O4	80.5	80.5	0.0	O4-Na1-O8	80.3	79.6	0.7
O5-Na1-O3	87.9	87.5	0.4				
O-Na2-O angles (°)							
	Exp.	Calc.	| Exp. – calc. |		Exp.	Calc.	| Exp. – calc. |
O8-Na2-O3	98.2	97.6	0.6	O9-Na2-O5	92.9	93.8	0.9
O8-Na2-O7	89.3	87.8	1.5	O5-Na2-O3	94.8	95.3	0.5
O8-Na2-O9	158.5	158.6	0.1	O5-Na2-O7	173.4	174.1	0.7
O8-Na2-O4	76.2	76.8	0.6	O5-Na2-O4	81.1	80.6	0.5
O8-Na2-O5	90.0	90.1	0.1	O4-Na2-O3	179.2	173.0	6.2
O9-Na2-O3	102.3	103.0	0.7	O4-Na2-O7	92.3	93.6	1.3
O9-Na2-O7	85.4	86.2	0.8	O3-Na2-O7	91.9	90.4	1.5
O9-Na2-O4	83.2	83.0	0.2				

TABLE 6. Structural information for OH polyhedral elements in $NaOH·3.5 H_2O$

	Exp.	Calc.	Exp. – calc.		Exp.	Calc.	Exp. – calc.
O-OH bond lengths (Å)							
O9-O1	3.138	3.117	0.021	O4-O2	2.760	2.707	0.053
O7-O1	2.740	2.728	0.012	O6*-O2	2.910	2.892	0.018
O9*-O1	2.662	2.634	0.028	O8-O2	2.795	2.837	–0.042
O7*-O1	2.782	2.758	0.024	O3-O2	2.936	3.026	–0.090
O5-O1	2.724	2.755	–0.031	O9-O2	2.893	2.921	–0.028
O4-O1	2.725	2.752	–0.027	O6-O2	2.710	2.687	0.023
O-O(1)H-O angles (°)							
	Exp.	Calc.	| Exp. – calc. |		Exp.	Calc.	| Exp. – calc. |
O9-O1-O7	92.7	93.0	0.3	O7*-O1-O4	86.8	86.7	0.1
O9-O1-O9*	109.4	107.5	1.9	O4-O1-O7	85.7	87.3	1.6
O9-O1-O7*	174.5	173.6	0.9	O4-O1-O9*	160.5	163.3	2.8
O9-O1-O5	114.1	112.6	1.5	O4-O1-O5	94.2	91.0	3.2
O9-O1-O4	89.3	88.9	0.4	O5-O1-O7	153.2	154.3	1.1
O7*-O1-O7	83.1	82.2	0.9	O5-O1-O9	83.7	85.6	1.9
O7*-O1-O9*	74.1	76.6	2.5	O7-O1-O9	87.5	88.7	1.2
O-O(2)H-O angles (°)							
	Exp.	Calc.	| Exp. – calc. |		Exp.	Calc.	| Exp. – calc. |
O4-O2-O6*	88.3	90.9	2.6	O3-O2-O6	75.8	76.6	0.8
O4-O2-O8	88.8	87.3	1.5	O6-O2-O6*	78.8	80.0	1.2
O4-O2-O3	164.7	168.4	3.7	O6-O2-O8	152.7	155.1	2.4
O4-O2-O9	72.9	77.7	4.8	O6-O2-O9	77.0	78.2	1.2
O4-O2-O6	92.1	95.7	3.6	O9-O2-O6*	148.6	154.2	5.6
O3-O2-O6*	80.2	79.4	0.8	O9-O2-O8	128.9	126.3	2.6
O3-O2-O8	97.5	96.1	1.4	O8-O2-O6*	73.9	75.2	1.3
O3-O2-O9	112.5	108.7	3.8				

*, † Denote different placements of symmetrically equivalent atoms in the P1 cell.

OH^- and Na^+ ions from each others' coordination environment is found in every hydrate beyond the monohydrate phase.

Again, the overall structure and $P2_1/c$ space group is maintained during the optimization procedure. The lattice parameters and fractional coordinates are given in Table 4, and the Na-O bond lengths and O-Na-O angles are given in Table 5. A "ball and stick" representation of part of one of the $Na(H_2O)_6$ chains is shown in Figure 2. The notation and atom numbering scheme is the same as that used by Mootz et al. (1994). As in the case of $NaOH·H_2O$, the long Na-O bonds appeared to be overestimated by about 0.1 Å (0.13 Å for the Na2-O4 bond). As in the experimental structure, the Na1-O4 and Na2-O4 bonds are the longest. The Na-O9 bond also is significantly overestimated (2.388 Å experimental vs. 2.505 Å calculated).

There are two different OH^- ions in the structure. The hydrogen-bonding relationships are illustrated in Figure 2 and listed in Table 6. The O1 hydroxide ion has octahedral coordination with five hydrogen-bond donating and one hydrogen-bond-accepting water molecules. The O2 hydroxide ion also has an octahedral coordination environment, but one that is highly distorted and consists of six hydrogen-bond-donating water molecules. In contrast to the O1 hydroxide ion, the O2 hydroxide ion donates no hydrogen bonds. For the most part, the O-O distances for hydrogen-bonded O atoms are in good

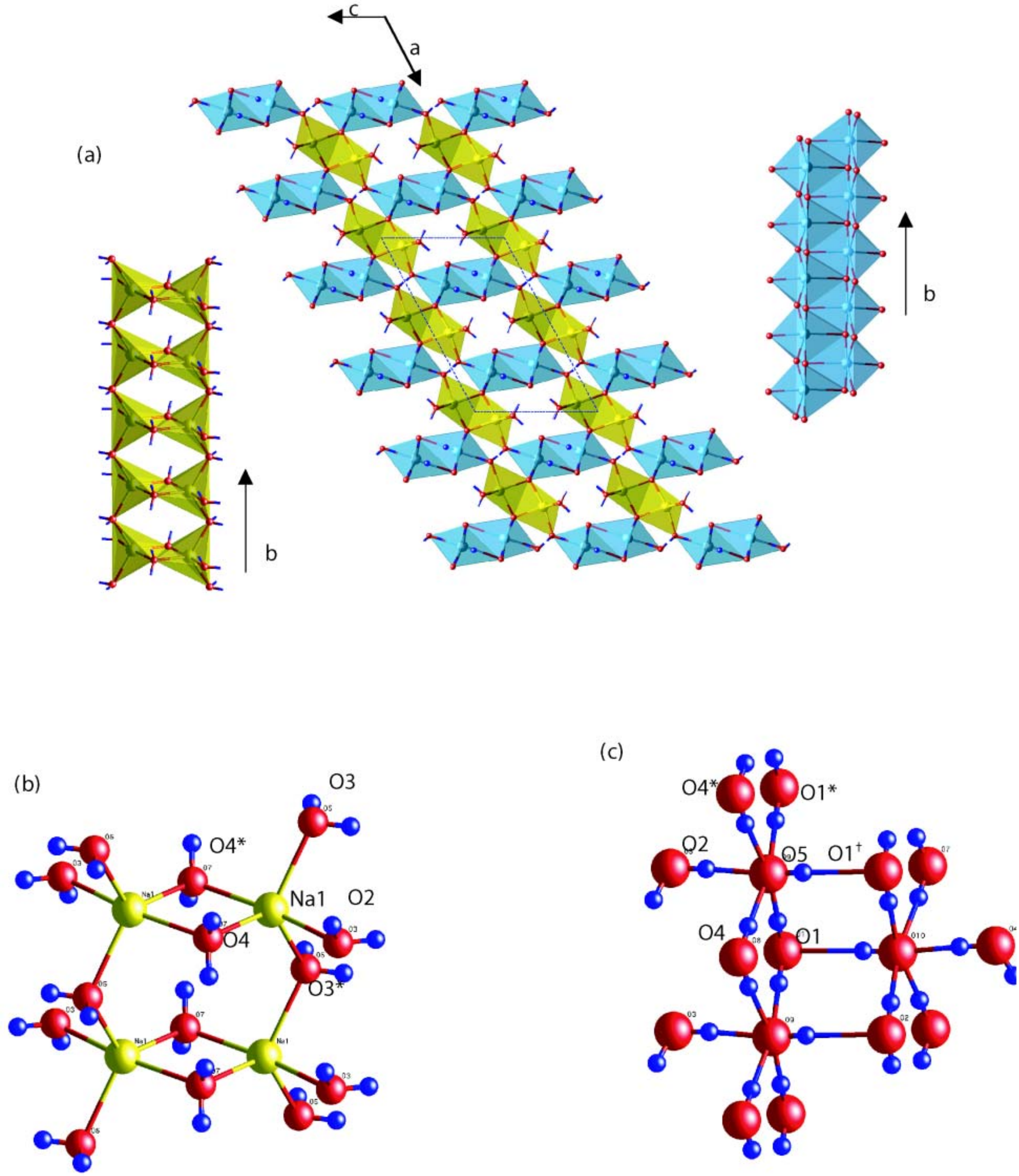

FIGURE 3. Polyhedral model of α-$NaOH{\cdot}4H_2O$. (**a**) Center: view down **b** axis, yellow polyhedra are centered on Na^+, blue octahedra are centered on OH^-. Right: connectivity of OH^- octahedra along the **b** axis shown normal to the **c**-**b** plane, Left: connectivity of Na^+ polyhedra (trigonal bipyramids) along the **b** axis. (**b**) Ball-and-stick representation of the Na^+ trigonal bipyramids (yellow = Na, red = O, dark blue = H). (**c**) Ball-and-stick detail of OH^- octahedra (same color scheme as in [**b**]).

agreement with the experiment. The worst disagreement is for the O3-(H32)-O2 and O3-(H31)-O4 bonds, perhaps because the model has difficulty representing the unusual six hydrogen-bond-acceptor coordination environment around O2 [the O3-(H31)-O4 bond is not listed in Table 6, but is 2.839 Å experimental vs. 2.734 Å calculated].

α-$NaOH{\cdot}4H_2O$

The Na and O positions in α-$NaOH{\cdot}4H_2O$ were first determined by Hemily (1957). A later study by Beurskens and Jeffrey (1964) confirmed Hemily's analysis. Seidel (1988) determined the structure a third time, using the difference-Fourier-synthesis method to locate hydrogen atom positions at a temperature of 243 K. The structure is shown in Figure 3, and the crystallographic data are given in Table 7. As pointed out by Beurskens and Jeffrey (1964) and Seidel (1988), the structure can be visualized in terms of two polyhedral elements, one defined by the coordination of the Na^+ ions and the other defined by the coordination of the OH^- ions. The sodium-centered polyhedra are unusual in that the Na^+ ion is fivefold coordinated by water molecules. The trigonal bipyramidal coordination polyhedra form dimeric chains parallel to the **b** axis. The dimeric units are defined by two edge-sharing coordination polyhedra. The shared edge connects an axial O atom with an equatorial O atom. The dimeric units are connected to other dimeric units by corner-sharing equatorial O atoms. Another polyhedral element in the structure is defined by distorted octahedral coordination polyhedra around the hydroxide ion $OH(H_2O)_6$. These octahedra form edge-sharing dimeric chains aligned parallel to the chains of Na^+ coordination polyhedra. The relevant structural relationships are illustrated in Figure 3.

Seidel (1988) refined the structure in space group *C*2/*m*. This introduces disorder into the structure, resulting in half-occupancy for the proton on the axial O2 water molecules. Seidel (1988) obtained poor convergence and no improvement in *R*-factors in the attempted refinement within the *C*2 space group, which eliminates the disorder associated with the half-occupancy. For our purposes, the disorder was removed by arranging the two O2 networks in the unit cell into right- and left-handed hydrogen-bonding arrangements. This breaks the symmetry; therefore, we cannot use the same notation to describe the structure as used by Seidel (1988). The structure converged to space group $P2_1/c$.

TABLE 7. Crystallographic information for α-$NaOH{\cdot}4H_2O$ (experimental data in parentheses)

Crystal System	monoclinic	
Space Group	$P2_1/c$	($C2/m$)
Temperature	0 K	(243 K)
a (Å)	15.666	(15.561)
b (Å)	4.284	(4.123)
c (Å)	9.731	(9.491)
β (°)	118.32	(117.37)
V (Å)	575.27	(540.7)
Density (g/cm³)	1.29	(1.37)

60 atoms in P1 cell

Atomic Fractional Coordinates

Atom	*x*	*y*	*z*
H1	0.80746	0.69988	0.38937
H2	0.30485	0.17958	0.38768
H3	0.73258	0.48720	0.82823
H4	0.25822	0.32793	0.02200
H5	0.57137	0.98577	0.66665
H6	0.45916	0.98411	0.61156
H7	0.85009	0.82475	0.79828
H8	0.35184	0.30056	0.80254
H9	0.79670	0.51030	0.61153
O1	0.65088	0.00786	0.56898
O2	0.71245	0.48135	0.91056
O3	0.52369	0.98017	0.70663
O4	0.60837	0.51180	0.14385
O5	0.77259	0.51950	0.68768
Na1	0.54617	0.48335	0.85652

The bond lengths and angles are listed in Tables 8 and 9. Of course, the structural parameters cannot strictly be compared with the disordered experimental structure. It can be stated that the Na-O bond lengths are generally longer than in the ordered structure. The experimental O4-OH distance, 2.75 Å, is close to the average of the bond lengths in the lower-symmetry equivalents (2.697 Å and 2.829 Å, average 2.763 Å). The H_2O-OH-OH_2 angles also are consistent with experimental results,

TABLE 8. Structural information for Na polyhedral elements in α-$NaOH{\cdot}4H_2O$

	Calc.	Exp. ($C2/m$ space group)
	Na-O bond lengths (Å)	
Na1-O3	2.400	2.3570
Na1-O7	2.490	2.3900
Na1-O5	2.510	2.4130
Na1-O7*	2.415	2.3650
Na1-O5*	2.531	2.4130
	O-Na-O angles (°)	
O4-Na2-O6	88.1	
O4-Na2-O8*	169.0	
O4-Na2-O8	87.0	
O4-Na2-O6*	88.0	
O8*-Na2-O6	97.2	
O8*-Na2-O8	82.0	
O8*-Na2-O6*	98.2	
O6-Na2-O8	119.1	
O6-Na2-O6*	116.4	
O8-Na2-O6*	123.8	

*, † Denote different placements of symmetrically equivalent atoms in the P1 cell.

TABLE 9. Structural information for OH polyhedral elements in α-$NaOH{\cdot}4H_2O$

O-OH bond lengths (Å)	
O9-O8	2.7760
O9-O1	2.6960
O9-O3	2.7480
O9-O8*	2.8290
O9-O1*	2.7720
O9-O2	3.2480
O-OH-O angles (°)	
O3-O9-O8*	83.000
O3-O9-O1*	81.800
O3-O9-O2	175.60
O3-O9-O1	87.000
O3-O9-O8	88.100
O2-O9-O8*	92.900
O2-O9-O1*	95.700
O2-O9-O1	97.100
O2-O9-O8	94.200
O8*-O9-O1*	76.600
O8*-O9-O1	169.90
O8*-O9-O8	99.700
O1*-O9-O1	103.20
O1*-O9-O8	169.60
O1-O9-O8	78.700

*, † Denote different placements of symmetrically equivalent atoms in the P1 cell.

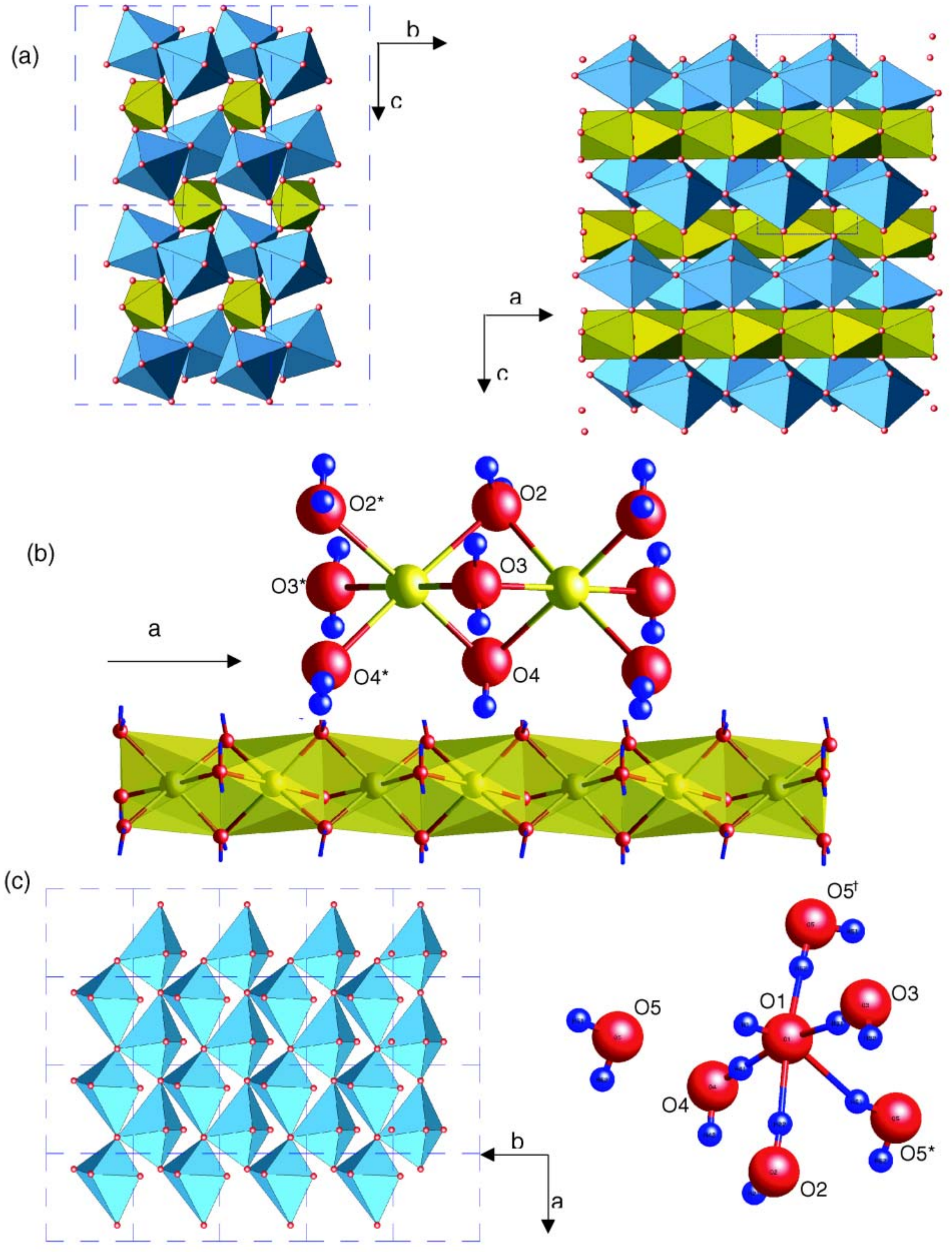

FIGURE 4. Polyhedral model of β-$NaOH \cdot 4H_2O$. (**a**) Left: view down **a** axis, yellow polyhedra are centered on Na^+, blue octahedra are centered on OH^-. Right: view down **b** axis. (**b**) Ball-and-stick representation of the Na^+ trigonal bipyramids (yellow = Na, red = O, dark blue = H). (**c**) Ball-and-stick detail of OH^- octahedra [same color scheme as in (**b**)].

in the sense that the hydroxide ion tends to pop outward from the center of the octahedron in the direction of the OH-OH$_2$ hydrogen bond donated by the hydroxide ion.

β-NaOH·4H$_2$O

Mraw and Giaque (1974) showed that β-NaOH·4H$_2$O is metastable with respect to the α phase. The structure was first determined by Seidel (1988) and was reported in the general literature by Mootz and Seidel (1990). These studies included determination of proton positions and were conducted at 118 K. The structure was interpreted in terms of two conceptual elements, shown in Figure 4. The first element consists of infinite chains of face-sharing Na$^+$(H$_2$O)$_6$ octahedra. These chains run parallel to the **a** direction. The second element consists of weakly undulating layers of OH(H$_2$O)$_6$ polyhedra. These layers are oriented parallel to the Na$^+$(H$_2$O)$_6$ octahedral chains. Unlike the α-tetrahydrate phase, these octahedra are highly distorted and are arranged in corrugated sheets of loosely packed, corner-sharing polyhedra. This unfavorable arrangement probably contributes to the metastability of the β phase relative to the α phase.

In the molecular dynamics simulation and optimization, space group $P2_12_12_1$ was maintained to better than 0.1 percent. Crystallographic data are given in Table 10. Relevant bond lengths and angles are given in Tables 11 and 12. Na-O bond lengths, as in the other structures, are overestimated. The overestimation is not uniform, ranging from 0.15 Å (Na-O4 and Na-O2*) to 0.04 Å (Na-O3*). The longest (Na-O2*) and shortest (Na-O3*) Na-O bonds are consistent between the experimental and theoretical structures. The calculated hydrogen-bonding relationships, both in terms of the O-O distances and H-O—H angles, are in reasonable accord with experiment.

The total energy calculated for the α phase is indeed about 0.16 eV/formula unit below that of the β phase. This comparison is hardly conclusive, as we are leaving out the question of zero-point energies, but does indicate that the presence of five-fold coordinated Na$^+$ atoms is not necessarily accompanied by a large energy penalty, when weighed against the much better-established anion coordination polyhedral arrangement in the α phase. The comparison also indicates that proton disorder is not the only cause of the lowering of the free energy of the α phase relative to the β phase.

TABLE 10. Crystallographic information for β-NaOH·4H$_2$O (experimental data in parentheses)

Crystal system		monoclinic
Space Group	$P2_12_12_1$	
Temperature	0 K	(118 K)
a (Å)	6.621	(6.237)
b (Å)	6.506	(6.288)
c (Å)	13.231	(13.121)
V (Å)	570.02	(514.6)
Density (g/cm^3)	1.31	(1.44)

60 atoms in $P1$ cell

Atomic Fractional Coordinates

Atom	x	y	z
Na1	0.4998	0.7431	0.5010
O1	0.2567	0.3192	0.7009
O2	0.2625	0.9137	0.6203
O3	0.2377	0.4851	0.5134
O4	0.2385	0.8848	0.3776
O5	0.3189	0.3221	0.2977
H1	0.4039	0.3248	0.7042
H21	0.2377	0.8354	0.6831
H22	0.2645	0.0603	0.6419
H31	0.2393	0.4072	0.5795
H32	0.2540	0.3910	0.4564
H41	0.2397	0.8082	0.3110
H42	0.2555	0.0300	0.3600
H51	0.4665	0.3068	0.2998
H52	0.2903	0.4600	0.2633

TABLE 11. Structural information for Na polyhedra in β-NaOH·4H$_2$O

	Exp.	Calc.	Exp. – calc.
Na-O bond lengths (Å)			
Na-O2	2.3920	2.4890	–0.097
Na-O3	2.3730	2.4200	–0.047
Na-O4	2.4050	2.5510	–0.146
Na-O2*	2.4380	2.5770	–0.139
Na-O3*	2.3360	2.3760	–0.040
Na-O4*	2.3860	2.4020	–0.016
O-Na-O angles (°)			
	Exp.	Calc.	Exp. – calc.
O2-Na-O3	80.5	79.2	1.3
O2-Na-O4	82.3	79.4	2.9
O2-Na-O2*	176.3	176.1	0.2
O2-Na-O3*	96.1	97.9	1.8
O2-Na-O4*	97.7	98.4	0.7
O3-Na-O4	82.8	78.9	3.9
O3-Na-O2*	103.2	104.6	1.4
O3-Na-O3*	175.0	175.6	0.6
O3-Na-O4*	100.0	100.7	0.7
O4-Na-O2*	98.1	101.7	3.6
O4-Na-O3*	93.2	97.4	4.2
O4-Na-O4*	177.2	177.8	0.6
O2-Na-O3*	80.3	78.3	2.0
O2-Na-O4*	81.7	80.5	1.2
O3-Na-O4*	84.0	82.8	1.2

*, † Denote different placements of symmetrically equivalent atoms in the P1 cell.

TABLE 12. Bond lengths and angles for OH coordination polyhedron in β-NaOH·4H$_2$O

	Exp.	Calc.	Exp. – calc.
O-OH bond lengths (Å)			
O1-O5	3.541	3.834	–0.293
O1-O3	2.698	2.708	–0.010
O1-O2	2.774	2.846	–0.072
O1-O5*	2.933	3.041	–0.108
O1-O4	2.662	2.689	–0.027
O1-O5†	2.705	2.709	–0.004
O-OH-O angles (°)			
	Exp.	Calc.	| Exp. – calc. |
O5-O1-O3	100.2	98.3	1.9
O5-O1-O2	79.0	76.5	2.5
O5-O1-O5*	148.7	148.5	0.2
O5-O1-O4	87.7	82.3	5.4
O5-O1-O5†	116.1	112.6	3.5
O5*-O1-O3	90.8	94.7	3.9
O5*-O1-O2	72.0	74.6	2.6
O5*-O1-O4	78.2	81.8	3.6
O5*-O1-O5†	91.3	94.7	3.4
O5†-O1-O3	96.2	94.7	1.5
O5†-O1-O2	162.6	168.1	5.5
O5†-O1-O4	87.8	90.9	3.1
O4-O1-O3	168.4	173.6	5.2
O4-O1-O2	84.1	82.4	1.7
O2-O1-O3	89.0	91.5	2.5

*, † Denote different placements of symmetrically equivalent atoms in the P1 cell.

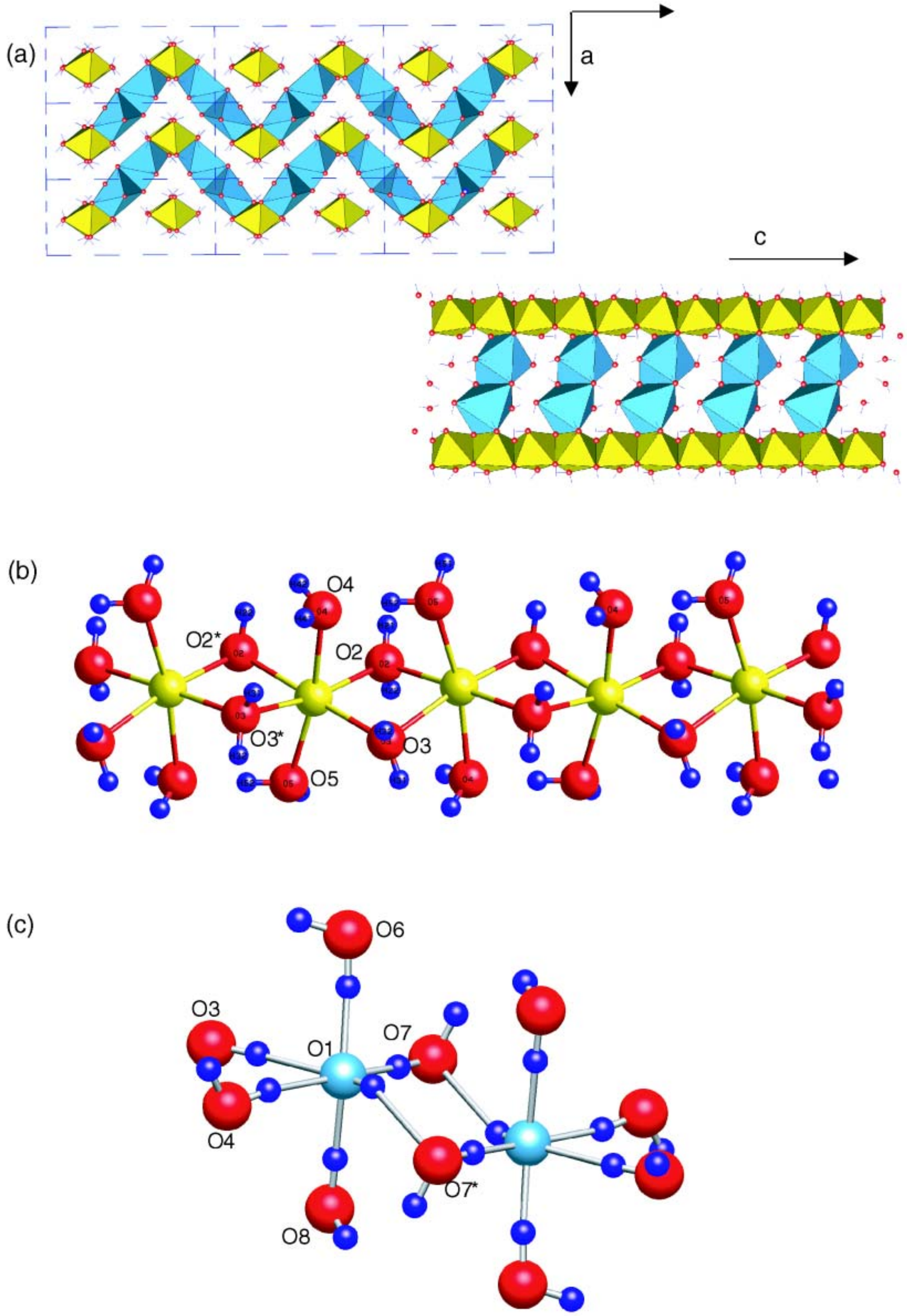

FIGURE 5. (**a**) Polyhedral model of NaOH·7H_2O. Upper: view down **c** axis, yellow polyhedra are centered on Na^+, blue octahedra are centered on OH^-. Lower: connectivity of Na^+ and OH^- polyhedra along the **c** axis, viewed approximately along <110>. (**b**) Ball-and-stick representation of Na^+ polyhedra (yellow = Na, red = O, dark blue = H). (**c**) Ball-and-stick representation of OH^- polyhedra [same color scheme as in (**b**)].

$NaOH{\cdot}7H_2O$

The structure of $NaOH{\cdot}7H_2O$ was first determined by Hemily (1953). The structure was later refined by Mootz et al. (1994) at 123 K, including determination of the proton positions. The structure, shown in Figure 5, can be viewed in terms of edge-sharing $Na(H_2O)_6$ of infinite extent parallel to the **c** axis. These polyhedra are hydrogen-bonded along the apical water molecules, with O5 as the donor and O4 as the acceptor. As shown in Figure 5, these chains are linked together by highly distorted, dimeric, edge-sharing octahedral coordination polyhedra about OH^-.

The $P2_1/c$ space group was maintained to better than 0.1 percent after the optimization procedure. Lattice parameters are compared with those obtained by Mootz et al. (1994) in Table 13, and a comparison of bond lengths and angles is given in Tables 14 and 15. Unlike the other structures, all Na-O distances are in good accord with those obtained in the X-ray studies, each being within about 2% of the experimental value (with predicted bond lengths unanimously overestimated).

TABLE 13. Crystallographic information for $NaOH{\cdot}7H_2O$ (experimental data in parentheses)

Crystal System	monoclinic	
Space Group	$P2_1/c$	
Temperature	0 K	(123 K)
a (Å)	7.425	(7.344)
b (Å)	16.433	(16.356)
c (Å)	6.920	(6.897)
b (°)	92.63	(92.91)
V (Å^3)	843.54	(827.5)
Density (g/cm^3)	1.31	(1.33)

96 atoms in *P*1 cell

Atomic Fractional Coordinates

Atom	*x*	*y*	*z*
Na1	0.4998	0.7431	0.5010
O1	0.2567	0.3192	0.7009
O2	0.2625	0.9137	0.6203
O3	0.2377	0.4851	0.5134
O4	0.2385	0.8848	0.3776
O5	0.3189	0.3221	0.2977
H1	0.4039	0.3248	0.7042
H21	0.2377	0.8354	0.6831
H22	0.2645	0.0603	0.6419
H31	0.2393	0.4072	0.5795
H32	0.2540	0.3910	0.4564
H41	0.2397	0.8082	0.3110
H42	0.2555	0.0300	0.3600
H51	0.4665	0.3068	0.2998
H52	0.2903	0.4600	0.2633

TABLE 14. Na-O bond lengths and O-Na-O angles in $NaOH{\cdot}7H_2O$

	Exp.	Calc.	Exp. – calc.
		Na-O bond lengths (Å)	
Na-O2	2.3490	2.3820	–0.033
Na-O4	2.4120	2.4600	–0.048
Na-O5	2.3650	2.4100	–0.045
Na-O3*	2.4310	2.4630	–0.032
Na-O2*	2.4040	2.4450	–0.041
		O-Na-O angles (°)	
	Exp.	Calc.	l Exp. – calc. l
O5-Na-O2*	84.4	85.9	1.5
O5-Na-O3*	92.3	91.5	0.8
O5-Na-O3	96.9	95.4	1.5
O5-Na-O2	97.8	99.3	1.5
O5-Na-O4	169.1	170.2	1.1
O4-Na-O2*	87.7	88.5	0.8
O4-Na-O3*	79.6	80.1	0.5
O4-Na-O3	90.8	90.0	0.8
O4-Na-O2	90.1	89.0	1.1
O2-Na-O2*	93.6	92.1	1.5
O2-Na-O3*	169.7	169.0	0.7
O2-Na-O3	87.2	88.6	1.4
O3-Na-O2*	178.4	178.3	0.1
O3-Na-O3*	93.5	92.8	0.7
O2*-Na-O3*	85.4	86.1	0.7

*, † Denote different placements of symmetrically equivalent atoms in the P1 cell.

DISCUSSION

To make this investigation as general as possible, the calculations were done for all known $NaOH{\cdot}nH_2O$ crystal structures where proton positions have been determined. The wide variety of structures investigated allows a much more reliable structural analysis than could be obtained using results from a single phase.

The Na-O distances are clearly overestimated in many of the structures. There is no instance, except for the shortest Na-OH_2 bond in the monohydrate phase, in which the Na-O bond length is not overestimated. However, the overestimation is far from uniform. For example, four of the Na-O bonds in $NaOH{\cdot}1H_2O$ are within 0.025 Å of the experimental values; only the longest bond is significantly in error. In the water-rich $NaOH{\cdot}7H_2O$, all the Na-O bond lengths are within 0.05 Å of the experimental values. This is exceptionally good for the relatively long Na-O bond. The overall behavior of the Na-O bonds is shown in Figure 6. The tendency toward long Na-O bonds is consistent with the ab initio investigation of the aqueous Na^+ ion by White et al. (2000). They calculated an average Na-OH_2 distance of 2.5 Å, about 0.1 Å longer than X-ray investigations of the radial distribution function.

The O-Na-O angles are remarkably well predicted; most are within one or two degrees of the experimental values. This

TABLE 15. O-OH distances and O-OH-O angles in OH coordination polyhedron in $NaOH{\cdot}H_2O$

	Exp.	Calc.	Exp. – calc.
		O-OH bond lengths (Å)	
O1-O7	2.6420	2.6280	0.014
O1-O6	2.6820	2.7340	–0.052
O1-O3	2.9360	2.9130	0.023
O1-O4	2.7510	2.8230	–0.072
O1-O7*	3.271	3.315	–0.044
O1-O8	2.7100	2.6950	0.015
		O-OH-O angles (°)	
	Exp.	Calc.	l Exp. – calc. l
O7*-O1-O6	121.8	118.2	3.6
O7*-O1-O3	152.8	152.1	0.7
O7*-O1-O4	90.1	87.1	3.0
O7*-O1-O8	76.4	77.8	1.4
O3-O1-O7	100.0	102.7	2.7
O3-O1-O6	79.0	79.6	0.6
O3-O1-O4	66.0	67.0	1.0
O3-O1-O8	88.5	89.1	0.6
O8-O1-O7	86.8	87.7	0.9
O8-O1-O6	158.0	161.9	3.9
O8-O1-O4	85.8	84.4	1.4
O4-O1-O7	164.2	167.1	2.9
O4-O1-O6	105.0	103.7	1.3
O6-O1-O7	77.8	81.2	3.4

*, † Denote different placements of symmetrically equivalent atoms in the P1 cell.

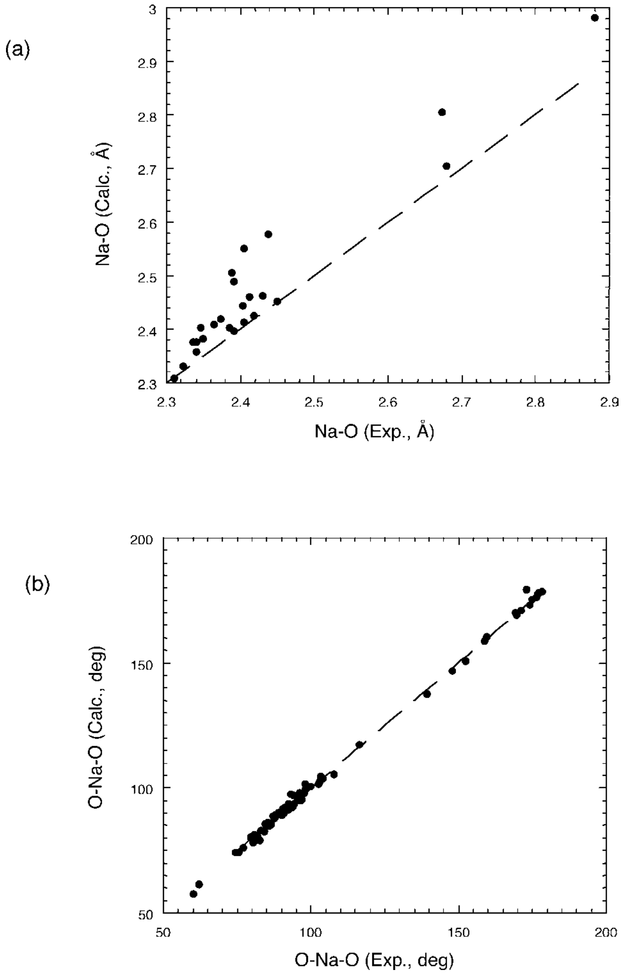

FIGURE 6. (**a**) Correlation between experimental and calculated Na-O bonds including all crystals except for α-$NaOH·4H_2O$, which has a different space group than the experimental structure. The straight line corresponds to a slope of unity (i.e., perfect agreement between calculation and experiment). (**b**) Same representation of O-Na-O angles.

is impressive because some of the angles are quite strongly distorted away from the 90–180° octahedral angles in the four structures having octahedrally coordinated sodium ions. A comprehensive comparison is shown in Figure 6.

It is also important to point out the stability of the fivefold coordinated configuration for the sodium ion. It is interesting that in the ab initio study of White et al. (2000), the average coordination number of the sodium ion was close to five (5.2). We do, in fact, find that in the case of the tetrahydrate, the fivefold-coordinated structure has the lowest energy. This is somewhat surprising, given the overestimation of the $Na-OH_2$ bond length. Apparently, this is not enough to stabilize the β phase, having sixfold configuration, over the α phase. Again, we feel that the major factor governing the stability of the α-tetrahydrate phase is the much more efficient packing of OH coordination polyhedra in the α phase.

Predicted and experimental O-O distances and O-H–O angles in hydrogen bonds are compared in Figure 7. There is some scatter in these results, but, on average, these quantities are very well predicted with the PBE exchange-correlation functional. Clearly there are no systematic errors, as observed for the Na-O polyhedra. Also note that the $HOH-OH^-$ bond lengths are as well predicted as the H_2O-HOH bond lengths. Nor does it appear that the HOH-OH hydrogen bonds are considerably shorter than the $HOH-OH_2$ bonds, as suggested by Bruni et al. (2001). Even the very weak OH^--OH_2 bonds, where the hydroxide ion is the hydrogen-bond donor, are, on the whole, quite well predicted (n = 1: 3.18 exp., 3.18 calc.; n = 3.5: 3.12 Å exp., 3.14 Å calc.; α n = 4: 3.11 Å exp., 3.24 Å calc.; β n = 4: 3.54 Å exp., 3.83 Å calc.; n = 7 3.27 Å exp., 3.31 Å calc.). The only serious error is in the β-tetrahydrate phase, where the predicted distance is nearly 0.3 Å longer than that determined from X-ray diffraction.

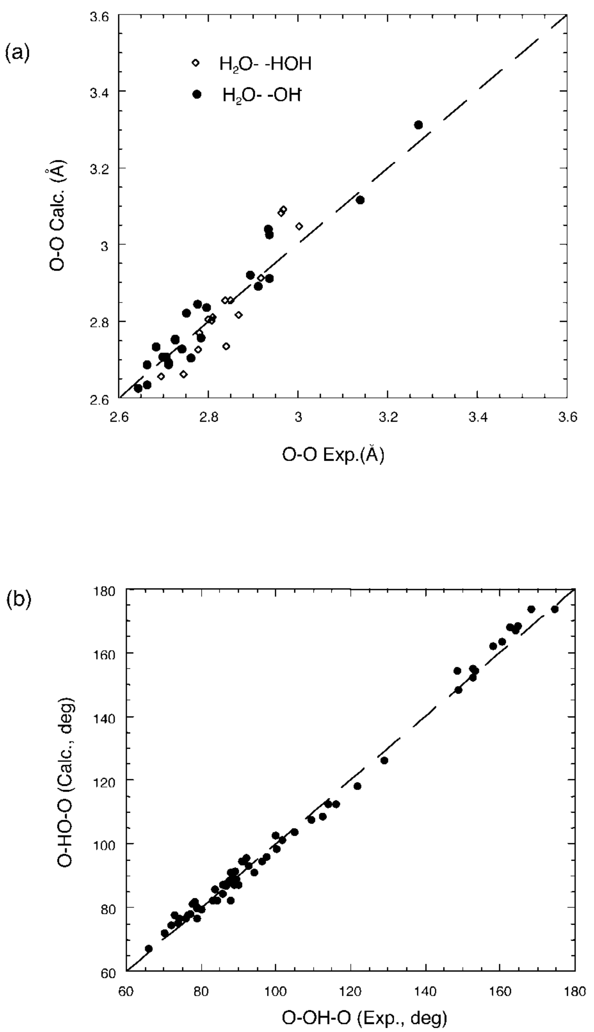

FIGURE 7. (**a**) Correlation between experimental and calculated O-OH bonds for all crystals except α-$NaOH·4H_2O$, which as a different space group than the X-ray structure. The straight line corresponds to a slope of unity (i.e., perfect agreement between calculation and experiment). Diamonds represent water-water hydrogen bonds; filled circles represent water-OH^- hydrogen bonds. (**b**) Same representation of $O-OH^--O$ angles.

It is important to point out the major limitations in our approach. First, all structures are determined at 0 K rather than dynamically at the experimental temperature. It is unlikely that the results would improve if the calculations were instead carried out using constant stress molecular dynamics simulations (Wentzcovitch et al. 1993) at the temperatures corresponding to the X-ray structure determinations. Indeed, they may get worse, as the Na-O bond lengths appear to be overestimated already. It is possible, however, that some of the long Na-O bonds would improve, as the distortion may be less in a dynamic structure than in a static structure. Another point to stress is that we ignore the quantum nature of the proton. It would be interesting to redo these calculations using path-integral molecular dynamics with delocalized protons. With our current computational resources, this type of calculation is not possible without an unjustifiably large investment of computer time. However, it may be that hydrated crystalline solids would provide an excellent forum for the investigation of the importance of quantum effects associated with proton delocalization, particularly if coupled with experimental determinations of orientational dependence of proton conductivity. Finally, as is the case with nearly every ab initio determination of a crystal structure, this work would benefit considerably from a conformer searching procedure that would be more capable of finding polymorphs other than the starting structure. We have tried to address this issue to some extent with the "shake-up" resulting from the initial 1 ps molecular dynamics simulation experiment. While this is better than nothing, it would clearly be worthwhile to attempt a more comprehensive search.

In conclusion, we emphasize that the overall performance of the DFT plane wave model is excellent. It is highly significant that this approach was able to reproduce all the known coordination environments of both the sodium ion and hydroxide ion. By contrast, we ran into considerable difficulties in attempting to account for the structural characteristics of these phases using classical models. Despite extensive efforts, we were unable to generate a Na-O potential function that, in conjunction with the H^+-OH^--H_2O potentials (Halley et al. 1993), would reproduce even the basic topology of the NaOH $3.5H_2O$ and α-NaOH·$4H_2O$ phases. Such attempts were approached both from the standpoint of fitting to gas-phase calculations, which yielded considerable success in the Fe-O-OH-H_2O system (Rustad 2001), and from a completely empirical standpoint in which the Na-O interaction was adjusted to reproduce the bulk crystals as closely as possible. This suggests that a large part of the difficulty is in the OH^--H_2O and H_2O-H_2O interactions. Despite the surprising ability of the model of Halley et al. (1993) to reproduce various aspects of the gas-phase OH^--H_2O clusters (Rustad 2001), calculation of the structure of the extended hydrogen-bond networks found in crystalline solids (and, by analogy, in aqueous solutions) seems to involve an additional degree of subtlety. We also emphasize that the optimal classical Na-O interaction did yield excellent results for the Na^+ ion in aqueous solution. It also accurately reproduced the behavior of the O-O, O-H, and H-H radial distribution functions in 10 m NaOH aqueous solutions. This finding underscores the need to incorporate, where possible, the results of studies on hydrated crystalline solids, especially when performing "extrapolative" calculations on inhomogeneous systems such as interfaces.

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