

Found: C, 26.34; H, 3.99; F, 24.38; N, 9.21.

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**Registry No.** I, 15684-01-2;  $\text{Cr}_2(\text{tfa})_4[(\text{EtO})_3\text{PO}]_2$ , 113274-02-5;  $\text{Cr}_2(\text{tfa})_4(\text{HMPA})$ , 113274-03-6;  $\text{Cr}_2(\text{tfa})_4(\text{DMTF})(\text{Et}_2\text{O})$ , 113274-04-7;  $\text{Cr}_2(\text{tfa})_4(\text{DMCA})(\text{Et}_2\text{O})$ , 113274-05-8;  $\text{Cr}_2(\text{tfa})_4(\text{DMF})(\text{Et}_2\text{O})$ , 113274-06-9;  $\text{Cr}_2(\text{tfa})_4[(\text{MeO})_3\text{P}](\text{Et}_2\text{O})$ , 113274-07-0;  $\text{Cr}_2(\text{tfa})_4[(\text{EtO})_3\text{PO}](\text{Et}_2\text{O})$ , 113274-08-1;  $\text{Cr}_2(\text{tfa})_4(\text{DMA})(\text{Et}_2\text{O})$ , 113274-09-2;  $\text{Cr}_2(\text{tfa})_4(\text{DMSO})(\text{Et}_2\text{O})$ , 113274-10-5;  $\text{Cr}_2(\text{tfa})_4(\text{Me}_3\text{PO})(\text{Et}_2\text{O})$ ,

113274-11-6;  $\text{Cr}_2(\text{tfa})_4(\text{HMPA})(\text{Et}_2\text{O})$ , 113274-12-7;  $\text{Cr}_2(\text{tfa})_4(\text{DMTF})_2$ , 113274-13-8;  $\text{Cr}_2(\text{tfa})_4(\text{DMCA})_2$ , 113274-14-9;  $\text{Cr}_2(\text{tfa})_4(\text{DMF})_2$ , 113274-15-0;  $\text{Cr}_2(\text{tfa})_4[(\text{MeO})_3\text{P}]_2$ , 113301-74-9;  $\text{Cr}_2(\text{tfa})_4(\text{Me}_4\text{Urea})_2$ , 113274-16-1;  $\text{Cr}_2(\text{tfa})_4(\text{DMA})_2$ , 113274-17-2;  $\text{Cr}_2(\text{tfa})_4(\text{DMSO})_2$ , 113274-18-3;  $\text{Cr}_2(\text{tfa})_4(\text{Me}_3\text{PO})_2$ , 113274-19-4.

**Supplementary Material Available:** Tables of molar magnetic susceptibility corrected for diamagnetism with Pascal's constants and raw calorimetry data (15 pages). Ordering information is given on any current masthead page.

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## Effect of d-Orbital Occupation on the Coordination Geometry of Metal Hydrates: Full-Gradient *ab Initio* Calculations on Metal Ion Monohydrates

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Hartree-Fock-Roothaan self-consistent-field calculations were performed on monohydrates of the metal ions  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Sc}^{3+}$ ,  $\text{Ti}^{2+}$ ,  $\text{Cr}^{2+}$ ,  $\text{Co}^+$ , and  $\text{Ni}^{2+}$  and the neutral  $\text{Fe}^0$ . Optimal geometries were calculated with the requirement that  $C_s$  symmetry be maintained. From these calculations the effect of the electronic interaction on the metal-water coordination geometry was isolated from bulk effects and its strength estimated. Potential energy curves were calculated for the metal ion versus the angle  $\theta_w$  (the "wag angle"). The potential energy curve for this wagging motion was found to be shallow, and in all cases except  $\text{Fe}^0$  the planar,  $C_{2v}$ , geometry ( $\theta_w = 0^\circ$ ) was found to have the lowest energy. The potential curve depended strongly on the charge of the ion and weakly on the d-orbital occupation of the transition metals.

### Introduction

Metal ion hydration, especially hydration of biologically important alkali metals, has been thoroughly studied and reviewed.<sup>1-3</sup> Clementi and co-workers performed extensive *ab initio* calculations on alkali-metal ions, including construction of potential energy surfaces for a water molecule in the field of  $\text{Li}^+$ ,  $\text{Na}^+$ , or  $\text{K}^+$  ions.<sup>4,5</sup> They obtained the lowest energy when the metal lies along the water dipole, as in Figure 1 with  $\theta_w = 0^\circ$ . Dacre did a more detailed study of the  $\text{Na}^+-\text{OH}_2$  complex and obtained results similar to those of Clementi.<sup>6</sup> The potential energy surface calculated by Clementi for the  $\text{H}_2\text{O}-\text{Li}^+$  complex was subsequently used by Impey et al. in a Monte Carlo simulation.<sup>7</sup> Bounds has used an analytical gradient technique to provide the potential terms for Monte Carlo simulations of dilute aqueous  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Ni}^{2+}$  solutions.<sup>8</sup> This is an efficient method of calculating a potential energy surface, and earlier Bounds found that a gradient calculation produced a potential surface for  $\text{Na}^+$ ,  $\text{Li}^+$ , and  $\text{K}^+$  in good agreement with that of Clementi.<sup>9</sup>

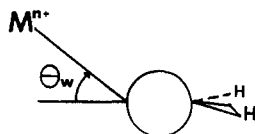
Although the potential energy surfaces used in the Monte Carlo calculations give minima for  $\theta_w$  of  $0^\circ$ , the Monte Carlo calculations of Bounds show the tendency of the water to coordinate the metal with  $\theta_w$  greater than zero, generally  $25-45^\circ$ .<sup>8</sup> This result

is in agreement with both crystal structures of metal hydrates<sup>10</sup> and the inelastic neutron scattering experiments of Enderby and co-workers.<sup>11,12</sup> It is postulated that the water-water interactions, especially hydrogen bonding, contribute to  $\theta_w$  being closer to the tetrahedral value ( $31.5^\circ$ ) than the planar.

There are still unanswered questions concerning the interaction of water molecules coordinated to metal ions. Calculations on  $\text{H}_3\text{O}^+$  give a nonplanar geometry for the gas-phase ion. What is the difference between  $\text{Li}^+$  and  $\text{H}^+$ , which makes the former planar and the latter pyramidal? The predominant interaction at a long M-O distance is certainly the ion-dipole interaction, which will favor the planar geometry. At shorter M-O distances, however, one might expect orbital interactions to induce a nonplanar geometry.<sup>13</sup> Enderby's study included the transition-metal ion  $\text{Ni}^{2+}$ , which has an unfilled d shell. One might therefore ask whether certain d-orbital occupations favor a nonplanar geometry apart from bulk interactions. The transition-metal hydrates have not been studied as extensively as those of the alkali metals, although their hydration geometries are important for understanding reactions such as the electron transfer between  $\text{Fe}^{\text{II}}(\text{H}_2\text{O})_6$  and  $\text{Fe}^{\text{III}}(\text{H}_2\text{O})_6$ .<sup>14</sup> We have attempted to answer these questions by calculating optimal geometries of the hydrates of the spherical ions  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Sc}^{3+}$ , of the ions  $\text{Ti}^{2+}$  and  $\text{Cr}^{2+}$ , with two and four d electrons, and of the ions  $\text{Fe}^0$ ,  $\text{Co}^+$ , and  $\text{Ni}^{2+}$ , with eight d electrons. In this study, rather than trying to understand all the interactions in a cluster, we will focus on the effect of the electronic interactions on the coordination geometry of a single

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**Figure 1.** General structure of the metal monohydrates.  $\theta_w$  is the angle between the metal ion and the  $\text{H}_2\text{O}$  plane, with the metal ion lying in the plane of symmetry.

**Table I.** Lowest Energy Geometries

metal ion	$r(\text{M}-\text{O})$ , Å	$r(\text{O}-\text{H})$ , Å	HOH angle, deg	energy, hartree
A. Spherical Ions				
$\text{Li}^+$	1.849	0.9537	106.3	-83.190977
$\text{Na}^+$	2.217	0.9516	105.5	-235.790848
$\text{K}^+$	2.659	0.9505	105.0	-669.440990
$\text{Ca}^{2+}$	2.340	0.9595	103.8	-746.031452
$\text{Sc}^{3+}$	1.994	0.9947	103.5	-827.564018
B. Ions with Partially Filled d Shells				
$\text{Ti}^{2+} (d_{x^2-y^2})^2$	2.074	0.9677	105.6	-916.195313
$\text{Ti}^{2+} (d_{xy})^2$	2.073	0.9667	105.6	-916.195312
$\text{Ti}^{2+} (d_{yz})^2$	2.093	0.9639	105.9	-916.182792
$\text{Ti}^{2+} (d_{xz})^2$	2.176	0.9625	105.4	-916.171528
$\text{Cr}^{2+} (d_{x^2-y^2})^2(d_{yz})^2$	1.862	0.9716	106.4	-1108.784304
$\text{Cr}^{2+} (d_{x^2-y^2})^2(d_{xz})^2$	1.966	0.9689	106.1	-1108.769994
$\text{Ni}^{2+} (d_{z^2})^a$	1.850	0.9713	108.5	-1569.419938
$\text{Ni}^{2+} (d_{xz})^a$	1.924	0.9703	106.6	-1569.394529
$\text{Ni}^{2+} (d_{yz})^a$	1.989	0.9688	106.2	-1569.384860
$\text{Ni}^{2+} (d_{xy})^a$	1.989	0.9664	106.4	-1569.376757
$\text{Co}^{+b}$	2.010	0.9528	108.0	-1445.406129
$\text{Fe}^{0c}$	2.142	0.9533	107.5	-1327.498433

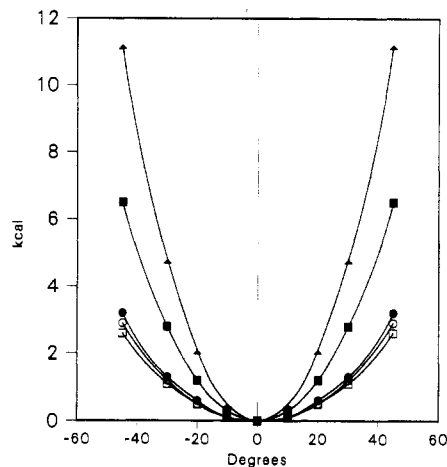
<sup>a</sup>Indicates the single unoccupied d orbital. <sup>b</sup> $\text{Co}^+$  occupation is  $(d_{x^2-y^2})^2(d_{xy})^2(d_{xz})^2(d_{yz})^2$ . <sup>c</sup> $\text{Fe}^0$  occupation is  $(4s)^2(d_{xy})^2(d_{xz})^2(d_{yz})^2$ .

water molecule bound to a metal ion.

## Theory

Calculations were done by using the Hartree-Fock-Roothaan method<sup>15</sup> and the generalized valence bond (GVB) method of Goddard.<sup>16</sup> The geometry optimizations in all cases were done by using full-gradient techniques. The basis functions used in this study were obtained by a least-squares fit of linear combinations of Gaussian functions to near-Hartree-Fock-limit-quality Slater type functions.<sup>17</sup> The metal core functions were fit by three Gaussians, which were then contracted to a single function. The 3d orbitals on Ti, Cr, Fe, Co, and Ni were fit by four Gaussian functions, which were then split into a contraction of three functions and a single diffuse function. The basis set on the hydrogen and oxygen was Pople's 4-31G<sup>18</sup> plus a single d-orbital function with an exponent of 0.85 added to the oxygen. The calculations of optimal geometry for  $\text{Li}^+$  and  $\text{Na}^+$  hydrates were repeated by using Pople's 3-21G basis<sup>19</sup> for  $\text{Li}^+$  and  $\text{Na}^+$ , with no change in the results.

In this study use was made of level shifting. The Hartree-Fock-Roothaan procedure will usually converge to the lowest energy state of closed-shell molecules, i.e., the global minimum. The computational technique of level shifting can be used, however, to obtain convergence to excited closed-shell states, which are local minima for the closed-shell energy surface. This is accomplished by swapping orbitals between the occupied and virtual sets and then minimizing the mixing of the occupied and virtual sets. If, however, an occupied orbital is swapped with a virtual orbital of the same symmetry, then level shifting cannot prevent convergence to the original state, because mixing between orbitals of the same symmetry is too facile. All calculations were done by using the GAMESS program<sup>20</sup> and were run on the Texas A&M Amdahl 5860 computer or at the Cornell Theory Center Production Supercomputer



**Figure 2.** Energy versus  $\theta_w$  for the ions  $\text{Li}^+$  (●),  $\text{Na}^+$  (○),  $\text{K}^+$  (□),  $\text{Ca}^{2+}$  (■), and  $\text{Sc}^{3+}$  (▲). The curve is fit by cubic spline.

**Table II.** O-H Bond s/p Ratios<sup>a</sup>

$\theta_w$ , deg	$\text{Li}^+$	$\text{Ca}^{2+}$	$\text{Cr}^{2+}$	$\text{H}_3\text{O}^+$
0	0.4988	0.4948	0.5502	0.6972
10	0.4983	0.4942	0.5463	0.6350
20	0.4962	0.4926	0.5344	0.6043
30	0.4934	0.4895	0.5233	0.5782
44 <sup>b</sup>				0.5478

<sup>a</sup>The amount of s and p character was determined by taking the square root of the sum of the squares of contracted and diffuse s and p orbitals in the localized (Boys) O-H orbital. The value for the water O-H bond in our basis set is 0.4401. <sup>b</sup>Optimal angle for  $\text{H}_3\text{O}^+$  in our basis set.

Facility with FPS264 Array Processors attached to an IBM 3090-400 computer.

## Results and Discussion

The calculated bond lengths and angles and total energies are shown for the lowest energy geometries in Table I. All geometries shown in Table I are at  $\theta_w = 0^\circ$  except for that of  $\text{Fe}^0$ , which is at  $\theta_w = 45^\circ$ . A table of all calculated geometries is available as supplementary material. The geometry optimizations were begun with a  $\theta_w$  value of  $20^\circ$ , and in each case (except  $\text{Fe}^0$ ) the optimization procedure brought the metal back into the water plane. To calculate a potential curve for bending,  $\theta_w$  was fixed at 10, 20, 30, and  $45^\circ$  and all other bond lengths and the HOH angle were optimized. The results of the calculations on the spherical ions are shown in Figure 2.

The calculated metal-oxygen distances for the  $\text{Na}^+$ ,  $\text{Li}^+$ , and  $\text{K}^+$  hydrates agree well with those of Clementi, which were obtained by using a larger basis set. It should be pointed out, however, that the purpose of the study is not to obtain accurate absolute values for bond lengths and angles of hypothetical monohydrates; rather, our purpose is to understand the dependence of coordination geometry, especially  $\theta_w$ , upon electronic interactions. Although it is not as large as the basis set used by Clementi, our basis set is adequate for the prediction of trends in the geometry. Clementi and Corongiu showed the necessity of configuration interaction (CI) calculations to accurately describe the  $\text{H}_2\text{O}-\text{Be}^{2+}$  potential surface and indicated that the need for CI in calculating interactions between water molecules and +2 ions is general.<sup>21</sup> Configurations with  $\text{M}^+(\text{OH}_2)^+$  character are important for a proper description of the interaction potential of dications and water. Clementi and Corongiu indicated, however, that the importance of CI decreases for the series  $\text{Be}^{2+}$  to  $\text{Mg}^{2+}$  to  $\text{Ca}^{2+}$ . The influence of CI on our calculations was tested for the lowest energy closed-shell state of  $\text{Ti}^{2+}$ . The potential curve for  $\theta_w$  was recalculated by using a GVB description of the metal-water  $\sigma$  bond. The potential energy curve was slightly flatter, in the GVB calculation, but the planar geometry remained

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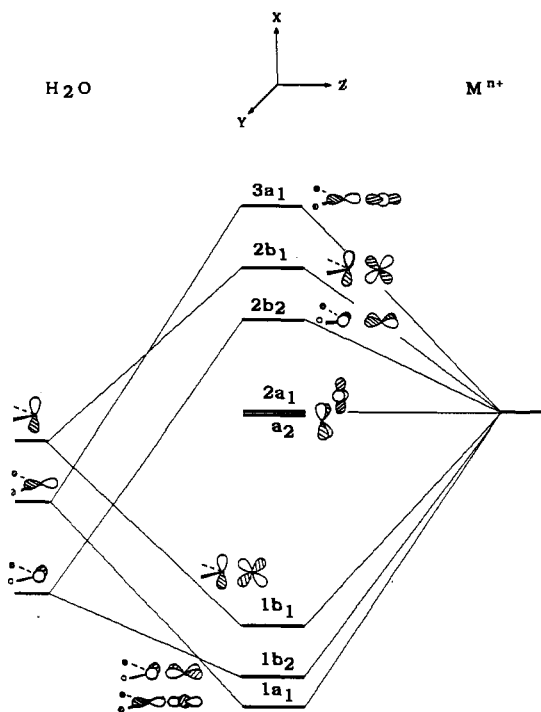


Figure 3. Interaction diagram for metal d orbitals and water valence orbitals.

the energy minimum. The Ti–O and O–H bond lengths and the HOH angle changed very little. The presence of polarization functions on the  $\text{Ca}^{2+}$  ion also had only a small effect. When d orbitals were added to the  $\text{Ca}^{2+}$  ion, the planar geometry remained the energy minimum but the Ca–O bond shortened to 2.257 Å.

It has been previously shown that  $\text{H}_3\text{O}^+$  assumes a nonplanar geometry,<sup>22</sup> and one might expect that the alkali metal ion monohydrates would also be nonplanar. The pyramidal geometry of  $\text{H}_3\text{O}^+$  is due to the proton's ability to cause rehybridization of the water orbitals. Free  $\text{H}_2\text{O}$  is hybridized in such a way that the s to p ratio in the bond is low, reflecting the tendency to keep the oxygen lone pair high in s character.<sup>23</sup> If an  $\text{H}^+$  ion approaches along the water dipole, then electrons are donated to the  $\text{H}^+$  from a  $p_z$ -2s hybrid; i.e., in planar  $\text{H}_3\text{O}^+$  the O–H bonds are  $sp^2$  hybrids and the lone pair is in a p orbital. The  $\text{H}_3\text{O}^+$  ion therefore adopts a pyramidal configuration, which allows more charge transfer from the electrons in p orbitals and leaves some s character in the lone-pair orbital. The metals investigated here, however, are not strong enough acids to force this rehybridization; the composition of the water orbitals changes very little upon interaction with the metal ion. This is shown in Table II. Binding  $\text{Li}^+$ ,  $\text{Ca}^{2+}$ , or  $\text{Cr}^{2+}$  in the plane of the water does not change the nature of the water orbitals. The oxygen lone pair remains high in s character; therefore, the complex need not adopt a nonplanar geometry to add s character to the lone pair. Since the orbital interactions do not strongly favor a bent geometry, the ion–dipole interactions set the  $\theta_w$  value at  $0^\circ$ . The maximum energy required for a bend of  $45^\circ$  due to the classical ion–dipole interaction alone (assuming the dipole calculated for free water in our basis set and no charge transfer to the metal) is between 5 and 10 kcal for  $\text{Li}^+$ ,  $\text{Na}^+$ , and  $\text{K}^+$ . This is close to our calculated value of about 3 kcal.

Complexes of transition-metal ions have the added effect of partially filled d shells. The major orbital interactions between metal d orbitals and water valence orbitals (at  $\theta_w = 0^\circ$ ) are shown in Figure 3. The calculations for  $\text{Ti}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Cr}^{2+}$  were done with various d-orbital occupancies but restricted to  $^1A_1$  ( $^1A'$  for

nonzero  $\theta_w$ ) states. With the use of virtual-orbital level shifting, however, it is possible to obtain convergence (defined as the largest change in the density matrix of less than  $10^{-5}$ ) to both the lowest lying and excited  $^1A_1$  states.

One may infer from the qualitative MO diagram, given in Figure 3, which orbitals will be occupied as d electrons are added to the metal. For  $\text{Ti}^{2+}$  the lowest energy is obtained when the single d-electron pair occupies either the  $d_{xy}$  ( $a_2$ ) or  $d_{x^2-y^2}$  ( $a_1$ ) orbital, both of which are nonbonding. The results shown in Table I confirm that these two  $^1A_1$  states are nearly degenerate and have very similar geometries. The next orbital above the  $a_1$ ,  $a_2$  nonbonding pair is the  $b_2$  antibonding orbital. This is the antibonding interaction between the  $b_2$  water O–H bond and the Ti  $d_{yz}$  orbital. The large energy difference between the water  $b_2$  orbital and the metal d orbitals implies that their interaction will be weak. As shown in Table I, occupying the  $d_{yz}$  orbital gives an energy 0.013 hartree higher than the energy of the nonbonded occupations. If the electron pair is forced into the antibonding  $p_x$ - $d_{xz}$  ( $b_1$ ) orbital, rather than the nonbonding orbitals, then the calculated energy increases by 0.024 hartree. The antibonding  $a_1$  orbital cannot be occupied, because the electrons move into the nonbonding  $d_{x^2-y^2}$  orbital, which is also  $a_1$  symmetry, despite the use of large level shifters.

When the d-electron pair is forced into an antibonding rather than a nonbonding orbital, a ligand to metal donation becomes a four-electron repulsive interaction. The greater the importance of a given donation, the greater will be the lengthening of the M–O bond when that d orbital is occupied. From qualitative molecular orbital theory one would expect the strongest interactions where energy differences between the orbitals are minimized and where overlap is largest. A relatively strong interaction is therefore expected for the  $b_1$  orbitals, because the  $p_z$  lone pair is the HOMO of the water molecule, and for the  $a_1$  (metal  $d_{z^2}$ ) interaction, because the  $\sigma$  overlap between the  $d_{z^2}$  and the oxygen  $p_z$  orbitals is substantial. The results in Table I show that the Ti–O bond lengthens by more than 0.10 Å when the  $d_{xz}$  orbital is occupied instead of the nonbonding  $d_{x^2-y^2}$  or  $d_{xy}$ . There is, however, little change in the Ti–O distance upon filling the Ti  $d_{yz}$  orbitals, which confirms the weakness of the  $b_2$  interaction.

Another system that allows one to evaluate the importance of donation into specific d orbitals is  $\text{Ni}^{2+}$ - $\text{OH}_2$ , which has a single unoccupied d orbital. We can force a given orbital to remain unoccupied by using level shifting. The lowest energy  $^1A_1$  state is obtained when the  $a_1$  antibonding orbital is left unoccupied, as one would expect from the MO diagram. If this orbital is empty, the  $\sigma$  donation into the metal  $d_{z^2}$  orbital is conserved, and thus the shortest Ni–O bond (1.850 Å) is also calculated for this occupation. Similarly, the first excited  $^1A_1$  state is calculated when  $b_1$  is the only antibonding orbital left empty. In this case the  $\pi$  rather than the  $\sigma$  donation is conserved, and the Ni–O bond lengthens by 0.074 Å. If both the  $a_1$  and  $b_1$  orbitals are occupied, but the  $b_2$  orbital is forced into the virtual set, the energy is higher yet and the Ni–O bond is 0.149 Å longer than the Ni–O bond of the ground  $^1A_1$  state. If the nonbonding  $d_{xy}$  ( $a_2$ ) orbital, rather than  $d_{yz}$  ( $b_2$ ), is forced into the virtual set, the energy goes up but the Ni–O bond does not lengthen. We may conclude that there is some interaction between the water  $b_2$  orbital and Ni  $d_{yz}$  but it has a negligible effect on the Ni–O bond length. The order of bonding ability  $a_1 > b_1 > b_2 > a_2 = a_1$  ( $d_{x^2-y^2}$ ) was also found by Bauschlicher for  $\text{Ni}^+$ .<sup>26</sup>

The potential energy curve for  $\theta_w$  will also depend on the d-orbital occupation. The water–d-orbital interactions that are most strongly affected by a change in  $\theta_w$  are  $a_1$  ( $d_{z^2}$ ) and  $b_1$ . (Note that in this work all results are presented in terms of the  $C_{2v}$  coordinate convention, as shown in Figure 1.) The energies of the nonbonding d orbitals and the  $b_2$  bonding and antibonding orbitals are almost unchanged. The  $d_{z^2}$ - $p_z$  bonding interaction weakens as  $\theta_w$  is increased to  $45^\circ$ . As shown in Figure 4a, the  $d_{z^2}$  and  $p_z$  orbitals point slightly away from each other at  $\theta_w = 45^\circ$ , which increases the out-of-phase interaction. The  $d_{xz}$ - $p_x$  bond,

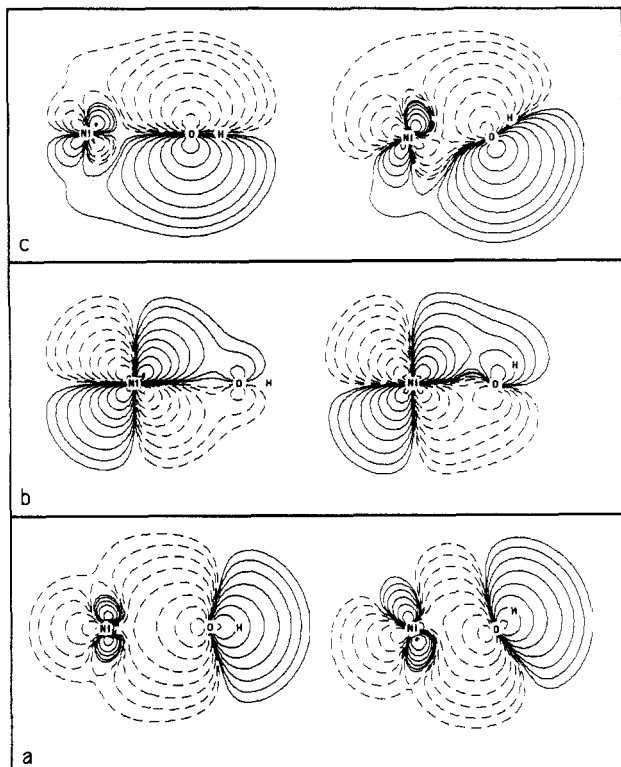
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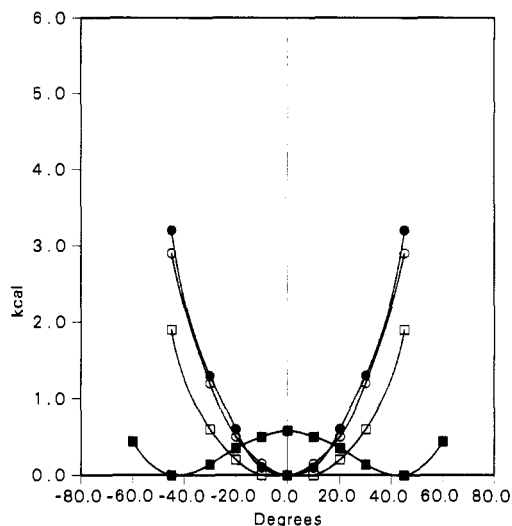


**Figure 4.** Molecular orbital plots for (a) the  $d_{xz}$ - $p_x$  bonding orbital, (b) the  $d_{xz}$ - $p_x$  bonding orbital, and (c) the  $d_{xz}$ - $p_x$  antibonding orbital of  $\text{Ni}^+\text{-H}_2\text{O}$  at  $\theta_w = 0$  and  $45^\circ$ . All plots are of the  $xz$  plane. The locations of the projections of the hydrogen atoms onto the  $xz$  plane have been given for reference.

which is shown in Figure 4b, changes very little in energy upon bending. The  $d_{xz}$ - $p_x$  antibonding orbital, however, decreases in energy because it becomes more nonbonding as the metal is rotated out of the water plane. This can be seen in Figure 4c by the constructive interference between the Ni and O atoms at  $45^\circ$ . An occupied  $d_{xz}$ - $p_x$  antibonding orbital therefore favors a bent structure. The  $a_1$  bond, as well as the classical dipole interaction, will, however, favor the planar geometry. The question is which of the competing effects is strongest in the complexes with occupied  $2b_1$  orbitals.

The  $d_{xz}$ - $p_x$  antibonding orbital must remain occupied as the metal is bent out of the plane of the water if its effect on the potential energy curve is to be analyzed. As the symmetry of the system is reduced to  $C_s$ , however, both the  $b_1$  and  $a_1$  representations become  $a'$ . For  $\text{Ti}^{2+}\text{-OH}_2$  there is only one electron pair; if it is forced to occupy the antibonding  $d_{xz}$ - $p_x$  orbital instead of the nonbonding  $d_{x^2-y^2}$  orbital, lowering the symmetry to  $C_s$  will allow the orbitals to mix in the SCF process and the nonbonding orbital will become occupied. To keep the  $d_{xz}$ - $p_x$  antibonding orbital occupied, the lower lying  $a'$  orbital must be occupied as well. The simplest system in which one can compare the energy of the planar and bent geometries, while keeping the  $d_{xz}$ - $p_x$  antibonding orbital occupied, must have two electron pairs.

This requirement is met in  $\text{Cr}^{2+}\text{-OH}_2$ . The purpose of calculations on  $\text{Cr}^{2+}\text{-OH}_2$  was only to determine whether occupation of  $d_{xz}$ - $p_x$  can affect  $\theta_w$ ; therefore, we did not perform calculations on all possible occupancies of the metal d orbitals, as was done with  $\text{Ni}^{2+}$  and  $\text{Ti}^{2+}$ . Calculations were performed on the lowest energy  $^1A_1$  state and the  $^1A_1$  state in which the  $d_{xz}$ - $p_x$  antibonding orbital remains occupied upon bending the metal out of the water plane. (One might expect the lowest energy  $^1A_1$  state for this system to be  $(d_{xy})^2(d_{x^2-y^2})^2$ . This is, however, not the case due to the large electron repulsion energy for four electrons in the  $xy$  plane.) When we force the  $d_{xz}$  orbital to be occupied, the Cr-O bond length increases and the energy goes up, as is expected from the results on Ti and Ni. Despite the  $d_{xz}$ - $p_x$  antibonding interaction, however, the planar geometry remains the minimum for



**Figure 5.** Energy versus  $\theta_w$  for the ions  $\text{Ti}^{2+}$  ( $d_{x^2-y^2})^2$  ( $\bullet$ ),  $\text{Ni}^{2+}$  ( $d_{x^2-y^2})^2(d_{xz})^2(d_{xy})^2(d_{yz})^2$  ( $\circ$ ),  $\text{Cr}^{2+}$  ( $d_{x^2-y^2})^2(d_{xz})^2$  ( $\square$ ),  $\text{Co}^+$  ( $d_{x^2-y^2})^2(d_{xz})^2(d_{xy})^2(d_{yz})^2$  ( $\square$ ), and  $\text{Fe}^0$  ( $d_{xz})^2(d_{yz})^2(d_{xy})^2(4s)^2$  ( $\blacksquare$ ). Note that the values for  $\text{Cr}^{2+}$  and  $\text{Ni}^{2+}$  differ by less than 0.1 kcal.

the potential curve. The factors that favor a planar geometry, namely overlap of the water and the metal  $d_{z^2}$  orbitals and the ion-dipole interaction, outweigh the  $d_{xz}$ - $p_x$  antibonding interaction for  $\text{Cr}^{2+}\text{-OH}_2$ .

The ion-dipole interaction weakens and charge transfer to the metal decreases as the charge on the metal is reduced from  $2+$  to  $1+$  to  $0$ . Calculations were therefore done on the lowest energy closed-shell states of the  $\text{Co}^+$  and  $\text{Fe}^0$  monohydrates to determine if lowering the charge would allow the  $d_{xz}$ - $p_x$  antibonding interaction to induce a nonplanar geometry. These systems meet the requirement of keeping the antibonding  $d_{xz}$ - $p_x$  orbital occupied upon bending. The results given in Figure 5 show that the curve flattens for the  $\text{Co}^+$  ion, but only for  $\text{Fe}^0$ , in which the ion-dipole interaction is absent and donation to the metal is not as important, does the metal bend out of the plane. The  $\text{Fe}^0\text{-OH}_2$  system also has the  $4s$ , rather than the  $d_{x^2-y^2}$ , orbital occupied in the ground state. The water dipole penetrates part of the  $4s$  orbital, which weakens the induced dipole-dipole bonding.

The  $\text{Fe}^0\text{-OH}_2$  bond is weaker and perhaps more difficult to calculate accurately. An experimental study<sup>24</sup> and several theoretical studies of neutral transition-metal-water complexes have been published recently. Blomberg and co-workers<sup>25</sup> and Bauschlicher<sup>26</sup> have published detailed theoretical studies of a single water bound to neutral transition metals. Bauschlicher has also shown that CI is not critical for an accurate description of  $\text{Ni}^0\text{-OH}_2$ .<sup>27</sup> Bauschlicher<sup>26</sup> and Blomberg<sup>28</sup> show that the induced dipole-dipole interaction is a major part of the bonding, and therefore, the water basis set must be large enough to accurately reproduce the water dipole. The water dipole in our basis set is 0.864 au, compared to 0.78 au for the Hartree-Fock limit and an experimental value of 0.72 au. Our results therefore err toward the planar geometry and provide only an estimate of the energy of bending for  $\text{Fe}^0\text{-OH}_2$ .

We may conclude that the ion-dipole interaction and  $\sigma$  donation set  $\theta_w$  at  $0^\circ$  in the monohydrated metal ions. This is in agreement with Bauschlicher, who concluded that the bonding of  $\text{Ni}^+\text{-OH}_2$  was dominated by electrostatic terms.<sup>26</sup> When fully hydrated, ions such as  $\text{Ni}^{2+}$  will have a decreased net charge and the orbital interactions will begin to influence the energy of bending. The  $d_{xz}$ - $p_x$  antibonding interaction, however, favors the bent geometry only weakly. Calculations by Bauschlicher on a single water bound to a neutral 14-atom Ni cluster found  $\theta_w$  to be zero, but only 0.001 eV was required for bending.<sup>29</sup> On the basis of our  $\text{Fe}^0$  results

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the maximum energy gain by bending would be estimated at 2 kcal. Thus, hydrogen bonding, which is worth roughly 6 kcal, should dominate the wag angle of water molecules coordinated to ions both in solution and in the solid state.

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**Registry No.** Li(H<sub>2</sub>O)<sup>+</sup>, 51518-07-1; Na(H<sub>2</sub>O)<sup>+</sup>, 51518-11-7; K(H<sub>2</sub>O)<sup>+</sup>, 111681-71-1; Ca(H<sub>2</sub>O)<sup>2+</sup>, 68433-66-9; Sc(H<sub>2</sub>O)<sup>3+</sup>, 113162-13-3; Ti(H<sub>2</sub>O)<sup>2+</sup>, 113162-14-4; Cr(H<sub>2</sub>O)<sup>2+</sup>, 113162-15-5; Co(H<sub>2</sub>O)<sup>+</sup>, 113162-16-6; Ni(H<sub>2</sub>O)<sup>2+</sup>, 113162-17-7; Fe(H<sub>2</sub>O)<sup>0</sup>, 98652-47-2.

**Supplementary Material Available:** A table of all calculated geometries and energies (4 pages). Ordering information is given on any current masthead page.

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## Valence Fluctuations in the YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> Superconductor

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The electronic structures of copper oxide clusters representing the new superconducting materials YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> and La<sub>2-x</sub>M<sub>x</sub>CuO<sub>4</sub> (M = Ba, Sr) have been calculated by semiempirical molecular orbital methods. For YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> the orbital energies indicate that the Cu's located in the CuO<sub>3</sub> "chains" are primarily "trivalent", while the Cu's in the CuO<sub>2</sub> "dimpled planes" are primarily "divalent". The effects of the oxygen breathing mode on the charge distributions and orbital energies are investigated for different electronic configurations. The results indicate that the oxygen breathing modes can cause significant charge fluctuations on the Cu's in the clusters. For certain electron configurations, a double-well type potential may exist for oxygen movement between Cu's in the "chains". This may cause an instability at oxygen stoichiometries near 6.75 and result in a phase separation. A phase diagram is proposed for YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub>, which suggests that the 94 K high-temperature superconducting phase is characterized by an oxygen stoichiometry near 7.0. The phase diagram predicts that a plateau should exist for T<sub>c</sub> in the region x = 0.0-0.25 and that in this region two phases are present which are characterized by compositions having oxygen stoichiometries either in the range 6.5-6.75 or close to 7.0.

### I. Introduction

The discovery of oxide superconductors with T<sub>c</sub>'s as high as 94 K has raised questions concerning the mechanism of superconductivity in these materials. One of the remarkable features of the superconducting oxides is that the oxygen stoichiometry requires copper in both La<sub>2-x</sub>M<sub>x</sub>CuO<sub>4</sub> (M = Ba, Sr) and YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> to exist in a mixed oxidation state, leading from the outset to the recognition that valence fluctuations may be involved in the superconducting mechanism.<sup>1-3</sup>

The structure of the high-temperature YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> superconductor has been studied by X-ray diffraction<sup>4</sup> and more recently by neutron diffraction.<sup>5</sup> There are two crystallographically distinct copper atoms in the unit cell: one-third of the copper atoms are in the b-c plane consisting of CuO<sub>3</sub> "chains", while two-thirds are in "dimpled" CuO<sub>2</sub> a-b planes (see Figure 1). The two planes are separated by yttrium layers without any oxygen, thus minimizing Cu-O-Cu bond overlap between copper-containing planes.<sup>5</sup> The structure suggests that the electronic properties of the material could be highly anisotropic and furthermore raises the possibility that valence fluctuations of the type Cu<sup>2+</sup> ⇌ Cu<sup>3+</sup> may occur between copper ions. Such considerations have important consequences, both for the mechanism of superconductivity and the superconducting properties of these materials.

To discuss mixed valency in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> it must be recognized that, of the constituent oxides, only those of Cu can deviate to any appreciable extent from the stoichiometric formulas Y<sub>2</sub>O<sub>3</sub>, BaO, and CuO since Y<sub>2</sub>O<sub>3</sub> and BaO are extremely stable thermodynamically. An oxygen content greater than 6.5, therefore, requires an equivalent amount of Cu to be in the +3 oxidation state. Hence, the average oxidation state of Cu in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> is given by 2.33 - 0.66x and varies from +2 to +2.33 in going from an oxygen stoichiometry of 6.5 to one of 7.0.

Because of the unique structure of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> a question arises concerning the statistical distribution of Cu<sup>3+</sup> between the

two crystallographic sites. In particular, the very short Cu(1)-O(4) bond length of 1.843 Å suggests that Cu<sup>3+</sup> is primarily located in the "chains" rather than the "planes" by analogy with the well-authenticated Cu<sup>3+</sup> compound KCuO<sub>2</sub> where similar short Cu-O distances have been found.<sup>6</sup> It is the exact distribution of Cu<sup>3+</sup> between the a-b and b-c planes and the change in that distribution as a function of oxygen stoichiometry that become very important considerations if Cu<sup>2+</sup> ⇌ Cu<sup>3+</sup> valence fluctuations are, in fact, involved in the mechanism of superconductivity in these materials.<sup>1-3</sup>

Band structure calculations<sup>7-15</sup> of varying degrees of sophistication have been reported on the La<sub>2-x</sub>M<sub>x</sub>CuO<sub>4</sub> and YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> materials. For YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> these calculations have generally shown that the CuO<sub>3</sub> chains contain Cu<sup>3+</sup> while the

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