

Theoretical Investigation of Na and Mg Atom Complexes with H₂O

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The structures, energetics, and vibrational frequencies of the Na...OH₂ and Mg...OH₂ complexes have been examined by ab initio molecular orbital methods including the effects of electron correlation by Møller-Plesset perturbation theory. The Na...OH₂ complex is predicted to be nonplanar with a Na...O distance of 2.343 Å and an energy of dissociation into Na and H₂O of 7.37 kcal/mol. The Mg...OH₂ complex is predicted to be nonplanar with a Mg...O distance of 2.321 Å and a dissociation energy of 3.82 kcal/mol. Correlation effects are found to be necessary to obtain significant binding between Mg and H₂O. The chemical bonding is analyzed in terms of one-electron densities. Considerable charge polarization of the electron density on the metal atom is found.

I. Introduction

Complexes formed between water molecules and groups IA (alkali) and IIA (alkaline earth) (groups 1 and 2)³² metal atoms have recently been studied both experimentally¹⁻⁴ and theoretically.⁵⁻¹³ These complexes are of potential interest in understanding the reaction mechanisms involving water molecules interacting with metal surfaces. Hauge and co-workers¹⁻³ have reported infrared spectroscopic studies of group IA (group 1) (Li, Na, K, and Cs) and group IIA (group 2) (Mg, Ca, Sr, and Ba) atoms codeposited with water in low-temperature argon matrices. They observed downward shifts of up to 34 cm⁻¹ in water bending frequencies, which they attributed to M...OH₂ complexes. Later studies⁴ on Li...OH₂ showed downward shifts of ≈100 cm⁻¹ in the OH stretching frequencies.

Theoretically, the Li and Be interactions with water have been the most thoroughly studied. At the correlation energy level, both are found to form significant metal-oxygen bonds [Li...OH₂: $R(\text{LiO}) = 1.900 \text{ \AA}$ and $D_e = 13.77 \text{ kcal/mol}$; Be...OH₂: $R(\text{BeO}) = 1.736 \text{ \AA}$ and $D_e = 5.53 \text{ kcal/mol}$].¹³ Without inclusion of correlation effects Be forms only a weak van der Waals complex with H₂O, whereas Li is strongly bound to H₂O even at the Hartree-Fock level. Inclusion of correlation significantly affects the predicted vibrational frequency shifts of both complexes, and reasonable agreement between the experimental and theoretical shifts of H₂O in Li...OH₂ is obtained only when correlation effects are included.¹³ In addition, there is no correlation between the magnitude of the shifts in the H₂O frequencies and the dissociation energies; i.e., the shifts are larger in the Be...OH₂ complex than in the more strongly bound Li...OH₂ complex.

The Na and Mg complexes with water have been less well studied. At the Hartree-Fock level with a very large basis set, Bentley⁹ found Mg...OH₂ to have an Mg...O distance of 3.97 Å and a binding energy of only 0.17 kcal/mol. However, a study by Kochanski and Priset¹² using second-order perturbation theory and a small basis set to determine the dispersion energy indicated that Mg...OH₂ was bound by 10.0 kcal/mol with a bond length of 2.06 Å. The Na...OH₂ complex was studied at the Hartree-Fock level by Trenary, Schaefer, and Kollman⁵ using a double ζ basis set. They found it to have a dissociation energy of 5.2 kcal/mol and a bond distance of 2.38 Å. A subsequent study by Bentley using the 6-31G** basis found a dissociation energy of 7.95 kcal/mol and a bond distance of 2.32 Å. In an experimental study, Hauge et al.³ have reported a H₂O bending frequency shift of -15 cm⁻¹ for Mg...OH₂ and -7 cm⁻¹ for Na...OH₂. Hence, these theoretical and experimental results for Mg...OH₂ and Na...OH₂

indicate a correlation between the magnitude of the shifts and the dissociation energies in contrast to the aforementioned lack of correlation for Be...OH₂ and Li...OH₂.

The question of the nature of the metal atom-molecule bond is intriguing but difficult. Several papers have considered this question. Bentley⁹ studied this in detail for a large series of metal atom-water complexes. He found that dissociation energies of alkali atom complexes correlate well with interaction energies calculated from an electrostatic model, but that contributions from other sources such as charge transfer, exchange repulsion, and dispersive effects are also important. In their study of Li and Na complexes with NH₃, H₂O, and HF Trenary, Schaefer, and Kollman^{5,6} suggested that the complexes can be described in terms of a Lewis acid-base type interaction with the strength depending on the base strength of the molecule. In their study of the Li...OH₂ and Be...OH₂ complexes Curtiss and Pople¹³ concluded that a combination of electrostatic, charge transfer, repulsive, and dispersive forces all play a part in determining whether these metal atom-water complexes will be stable.

In this paper we report a theoretical study of the Na...OH₂ and Mg...OH₂ complexes at the correlation energy level. The purpose of this study was to investigate the effects of correlation on the dissociation energies, structures, and vibrational frequencies of these complexes. In particular, we wanted to (1) determine the strength of the Mg-O bond in Mg...OH₂ since an accurate determination of it at the correlation level has not been reported, (2) investigate these complexes at a uniform level of calculation

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TABLE I: Optimized Structures and Energies for Na···OH₂ and Mg···OH₂^{a,b}

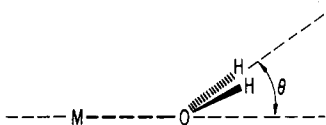
	method/basis	R(MO) ^c	∠HOH	R(OH)	θ	E	D _e ^d
Na···OH ₂	HF/6-31G**	2.330	107.3	0.945	0.0	-237.876 77	7.35
	MP2/6-31G**	2.343	105.0	0.965	46.2	-238.081 82	9.87
Mg···OH ₂	HF/6-31G**	3.166	106.5	0.944	26.2	-275.620 88	1.04
	MP2/6-31G**	2.321	105.6	0.968	46.0	-275.854 53	5.02

^a All electrons included in MP2 calculation; bond lengths in angstroms, bond angles in degrees, total energies (*E*) in hartrees, dissociation energies (*D_e*) in kilocalories/mole. ^b Optimized H₂O geometries and corresponding energies: HF/6-31G**: *R*(OH) = 0.943 Å, ∠HOH = 105.9°, *E* = -76.023 62 hartrees; MP2/6-31G**: *R*(OH) = 0.961 Å, ∠HOH = 103.9°, *E* = -76.222 45 hartrees. Energies of Na: HF/6-31G**, *E* = -161.841 44 hartrees; MP2/6-31G**, *E* = -161.843 64 hartrees. Energies of Mg: HF/6-31G**, *E* = -199.595 61 hartrees; MP2/6-31G**, *E* = -199.624 07 hartrees. ^c Distance from metal atom to oxygen. ^d Dissociation energy for M···OH₂ → M + OH₂.

TABLE II: Energies at the MP4 Level

species	total energies ^a					D _e ^c
	6-31G**	6-31+G**	6-31G**(2d)	6-31G**(f)	combined ^b	
H ₂ O	-76.231 24	-76.244 54	-76.261 13	-76.251 57	-76.294 76	
Na	-161.841 44	-161.841 44	-161.841 88	-161.841 44	-161.841 88	
Mg	-199.627 38	-199.627 46	-199.627 16	-199.627 40	-199.627 26	
Na···OH ₂	-238.087 78	-238.096 02	-238.118 82	-238.109 11	-238.148 39	7.37
Mg···OH ₂	-275.865 95	-275.874 98	-275.897 03	-275.887 97	-275.928 08	3.80

^a MP4 energies (in hartrees) at the MP2/6-31G* equilibrium geometry. Calculated using a frozen core. ^b Combined MP4 energy. ^c Dissociation energy (in kcal/mol).

Figure 1. Structure for M···OH₂.

to determine whether the trends in binding energies and vibrational frequency shifts are indeed as suggested by the previous studies (i.e., different in the second-row complexes than in the first-row complexes), and (3) to compare calculated shifts in the H₂O bending frequencies with observed values and predict the shifts in the H₂O stretching frequencies for use in assigning these bands in future spectroscopic studies. In this paper we also consider the nature of the metal–water bond in terms of the properties of the one-electron density distribution $\rho(r)$ of the Mg···OH₂ and Na···OH₂ complexes as well as the previously studied Be···OH₂ and Li···OH₂ complexes.

II. Theoretical Methods

Equilibrium geometries of Na···OH₂ and Mg···OH₂ complexes were obtained under the constraint of C_s symmetry as shown in Figure 1. All optimizations were carried out by analytic gradient techniques with second-order Møller–Plesset perturbation theory (MP2), including correlation of all electrons.^{14,15} The 6-31G** basis¹⁶ was used.

Investigation of the dissociation energies of the complexes was done using complete fourth order Møller–Plesset perturbation theory (MP4)¹⁷ with a frozen-core approximation at the MP2/6-31G** optimized geometries. The 6-31G** basis set and three extensions of it were used: (1) addition of s and p diffuse functions¹⁸ to the non-hydrogen atoms (6-31+G**), (2) doubling of the d-polarization functions on the non-hydrogen atoms (6-31G**(2d)), and (3) addition of f functions to the non-hydrogen atoms (6-31G**(f)). Standard exponents¹⁹ for these additional functions were used. Final total energies were obtained assuming

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additivity of the effects of these three basis extensions. This method is similar to that used previously in a study of the Li···OH₂ and Be···OH₂ complexes.¹³

Shifts in the harmonic vibrational frequencies of H₂O in Na···OH₂ and Mg···OH₂ were determined at the MP2/6-31G** level from the ratio of the H₂O diagonal force constants (symmetric stretch, asymmetric stretch, and bend) in the complex to the corresponding values in free H₂O. The diagonal force constants for this latter method were evaluated by quadratic fitting to points on the potential energy surface.²⁰ This approximate method of calculating the shifts was tested¹³ by comparison with a full-frequency calculation for Be···OH₂ and found to be accurate to within 4%. Calculations of the structures, dissociation energies, and vibrational frequencies at the HF/6-31G* level were also carried out for comparison with the MP2/6-31G** results.

III. Results and Discussion

A. Structures and Dissociation Energies. The optimized structural parameters of Na···OH₂ and Mg···OH₂ at the HF/6-31G** and MP2/6-31G** levels are given in Table I. For Na···OH₂ the MP2/6-31G** equilibrium structure is nonplanar ($\theta = 46.2^\circ$) with an Na···O distance of 2.343 Å. A structure constrained to be planar (C_{2v}) was also optimized and is only 0.24 kcal/mol less stable than the nonplanar one. Comparing with free H₂O (MP2/6-31G** level), the HOH angle opens up by 1.1° and the OH bond distance increases by 0.004 Å. For Mg···OH₂ the MP2/6-31G** structure is also nonplanar (0.29 kcal/mol more stable than the planar configuration) with a Mg···O distance of 2.321 Å. Interaction with Mg causes the HOH bond angle to open up by 1.7° and the OH bond distance to increase by 0.007 Å. The HF/6-31G** results in Table I indicate that when correlation effects are included at the 6-31G** basis set level the Mg–O bond distance is shortened by 0.84 Å (3.166 Å to 2.321 Å).

The MP4 total energies of Na···OH₂ and Mg···OH₂ at the 6-31G**, 6-31+G**, 6-31G**(d), and 6-31G**(f) levels are given in Table II. Also given in the table are the dissociation energies at the combined MP4 energy level (derived from the four basis sets). For Na···OH₂, *D_e* is 7.37 kcal/mol. The correlation energy contribution to this *D_e* is 3.06 kcal/mol. (This quantity was derived from the combined Hartree–Fock (HF) energies at the MP2/6-31G** geometry.) For Mg···OH₂, *D_e* is 5.02 kcal/mol with a correlation contribution of 5.1 kcal/mol.

The results reported here for Na···OH₂ are in general agreement (bond distance and dissociation energy) with the findings of the

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TABLE III: H₂O Vibrational Frequency Shifts^{a,b} and M–O Frequencies (in cm⁻¹)^{a,b}

method/basis	bend	shifts		M–O freq
		stretch		
		sym	asym	
Na...OH ₂ ^c	HF/6-31G**	-10	-24 -25	230
Na...OH ₂	MP2/6-31G**	-19 [-7.4] ^c	-58 -63	242
Mg...OH ₂	HF/6-31G**	-9	-10 -7	84
Mg...OH ₂	MP2/6-31G**	-32 [-15.7] ^c	-93 -96	203

^aHF/6-31G** results are from full frequency calculations. The frequencies for H₂O monomer are 1770, 4147, and 4264 cm⁻¹. ^bThe MP2/6-31G** shifts are calculated from the ratio of the force constant in H₂O to the corresponding one in the complex. The frequencies of H₂O are 1684, 3895, and 4033 cm⁻¹. The MP2/6-31G** M–O frequencies are calculated from the M–O stretching force constant assuming a pseudodiatomic model. ^cExperimental results from ref 3.

previous studies at the HF level.^{5,9} The previous calculations were done on planar geometries with rigid H₂O structures. For the Mg...OH₂ complex our final value for *D_e* of 5.02 kcal/mol is significantly smaller than the value of 10.0 kcal/mol previously reported by Kochanski and Prissette¹² at the correlation level. This is due to the larger basis sets and higher order of perturbation theory used in this study. Our Mg...O distance (2.32 Å) is also significantly longer than the 2.06 Å which they report.

B. Vibrational Frequencies. Vibrational frequency shifts and M...O frequencies for Na...OH₂ and Mg...OH₂ are given in Table III. For Na...OH₂ the three H₂O frequencies are predicted at the MP2/6-31G** level to shift downward in the complex. For the Mg...OH₂ complex, despite the smaller *D_e*, the H₂O vibrational frequencies in the Mg...OH₂ complex shift downward by larger magnitudes than in Na...OH₂. Hence, similar to the first-row complexes (Be...OH₂ and Li...OH₂), the shifts in the H₂O frequencies of the second-row complexes (Na...OH₂ and Mg...OH₂) do not correlate with the binding energies. However, the M...O stretching frequencies in Table III do correlate with the binding energies; i.e., the Na...OH₂ complex has a higher M–O frequency than Mg...OH₂.

The results in Table III indicate that the MP2/6-31G** shifts in the bending mode of H₂O in Na...OH₂ and Mg...OH₂ (-19 and -32 cm⁻¹, respectively) are in the same direction as the observed shifts (-7.4 and -15.7 cm⁻¹, respectively), but about twice the size. Similarly, for the Li...OH₂ complex the MP2/6-31G** shift in the H₂O bending mode is too large (-28 vs. the observed value of -17.5). No experimental results have been reported for Be...OH₂ where the predicted shift is the largest (-83 cm⁻¹). The HF/6-31G** frequencies in Table III indicate that the shifts are quite sensitive to the level of theory used. The MP2/6-31G* shifts in Table III should provide qualitative predictions of the shifts in the stretching frequencies of H₂O in the complexes. For the Li...OH₂ complex, MP2/6-31G** shifts in the water stretching frequencies were within about 20% of the observed shifts.^{4,13}

C. Analysis of Metal Atom–Water Bond. We have investigated the bond that is formed between the metal atom (M) and water by analyzing the one-electron densities of the complexes. For comparison purposes we have included the two previously studied complexes, Li...OH₂ and Be...OH₂,¹³ in this analysis. The results presented are based on HF/6-31G** densities at the MP2/6-31G** geometries of the complexes (MP2/6-31G** for the Li and Be complexes).

An investigation of the electron density distribution $\rho(r)$ of the complex M...OH₂, in particular the changes in $\rho(r)$ upon an approach of H₂O and M, provides useful information about the forces acting in the complex. Changes in $\rho(r)$ are revealed by plotting the difference density

$$\Delta\rho(r) = \rho(r)_{\text{complex}} - \rho(r)_{\text{procomplex}}$$

The density distribution of the procomplex is given by the superposition of the density distribution of M and H₂O where both fragments are kept in the positions which they have in the complex. In Figure 2, contour line diagrams of the calculated difference density distribution, $\Delta\rho(r)$, of Be...OH₂ are shown. Positive

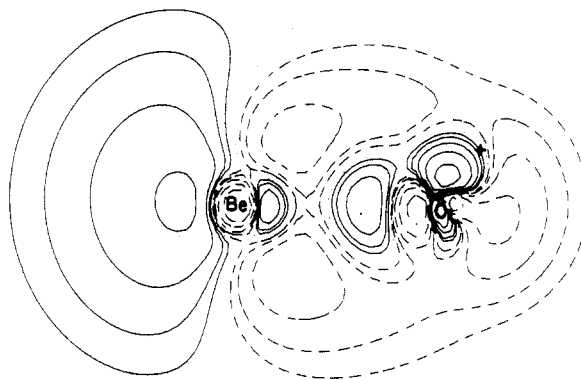


Figure 2. Calculated difference electron density distribution $\Delta\rho(r)$ (e/Å³) for the Be...OH₂ complex (MP2/6-311G** *C_s* structure from ref 13) in the plane corresponding to the *C_s* plane in Figure 1. The positions of the H's (out of the plane) are denoted by +.

TABLE IV: Polarizabilities (α) for Metal Atoms Li, Na, Be, Mg; Comparison of Geometries and Interaction Energies for M...OH₂

species	α , ^a Å ³	MP2 geometry ^b		interaction energy, kcal/mol	
		<i>R</i> (M–O), Å	θ , deg	D-ID ^c	MP4 ^d
Li	24.3	1.90	40.1	-12.7	-13.8
Na	23.6	2.34	46.2	-3.5	-7.4
Be	5.6	1.74	54.8	-5.0	-5.5
Mg	10.6	2.32	46.0	-1.7	-3.8

^aCRC Handbook of Chemistry and Physics, 67th ed; CRC: Boca Raton, FL, 1986–1987. The value for H₂O is 1.45 Å³. ^bTheoretical results at the MP2 level from this work and ref 13. ^cDipole-induced dipole interaction energy calculated from $E(R) = \mu^2_{\text{H}_2\text{O}}\alpha_M(1 + 3\cos^2\theta)/2R^6$ (from Hirschfelder, J. O.; Curtiss, C. F.; Bird, R. B. *Molecular Theory of Gases and Liquids*; Wiley: New York, 1954; p 984). For H₂O $\mu = 1.85$ D used; *R*(M–O) values from the MP2 geometry used. ^dMP4 interaction energies from this work and ref 13.

TABLE V: Analysis of the Local Maxima *l*₁ and *l*₂ of $-\nabla^2\rho(r)$ Corresponding to the Oxygen Lone Pairs^a

		$-\nabla^2\rho(r)$	
		<i>l</i> ₁	<i>l</i> ₂
Li...OH ₂	<i>l</i> ₁	149.992	0.337
	<i>l</i> ₂	159.172	0.334
Na...OH ₂	<i>l</i> ₁	150.488	0.337
	<i>l</i> ₂	158.053	0.334
Be...OH ₂	<i>l</i> ₁	147.773	0.338
	<i>l</i> ₂	161.135	0.334
Mg...OH ₂	<i>l</i> ₁	154.007	0.336
	<i>l</i> ₂	161.307	0.334
H ₂ O	<i>l</i> ₁ = <i>l</i> ₂	161.796	0.334

^aDistances in angstroms; $\nabla^2\rho(r)$ values in e/Å⁵. ^bValence sphere radius of the lone pairs of H₂O.

(negative) contour lines indicate that $\rho(r)$ increases (decreases) upon interaction of M with H₂O. Negative charge is pushed from the front to the back of the Be atom by the incoming H₂O molecule which means that the spherical density distribution of Be is polarized by H₂O. At the same time the density in the regions of the lone pair electrons of H₂O is pulled in the direction of Be. This leads to a difference density pattern that seems to be typical of molecular complexes stabilized partially or predominantly by electrostatic forces.²¹ The qualitative changes in $\rho(r)$ for the other complexes are similar to these described for the Be...OH₂ complex.

An estimate of the magnitude of the electrostatic forces (dipole-dipole induced interaction) can be made from the polarizabilities (α) in Table IV. According to the values of α in Table IV, the interactions should be 2–4 times larger in the group IA (group 1) complexes than in the group IIA (group 2) complexes.

(21) This type of analysis has recently been carried out for the interaction of H⁺ with AH_{*n*} in AH_{*n*+1}⁻ compounds which have an ion-dipole interaction; Cremer, D.; Kraka, E. *J. Phys. Chem.* **1986**, *90*, 33.

This is in line with the MP4 dissociation energies of these complexes (see Table IV). However, if one compares Li...OH₂ with Na...OH₂ and Be...OH₂ with Mg...OH₂, the interaction energies are not parallel to the α values. Some, but not all, of the difference can be accounted for by the fact that the H₂O can approach Li (Be) much closer than Na (Mg) before repulsive forces become dominant. Obviously, there are other forces contributing to the stabilities of the M...OH₂ complexes.²² They may arise from charge transfer or bonding overlap.

The Mulliken populations²³ of Mg...OH₂ and Na...OH₂ indicate a significant amount of charge transfer from H₂O to the metal atom, although not as large as the Li and Be complexes. At the MP2/6-31G** geometries, the HF/6-31G** charge transfer is 0.062e for Na...OH₂ and 0.082e for Mg...OH₂. For Li...OH₂ and Be...OH₂, the values are 0.079e and 0.169e, respectively. Preliminary calculations of the virial charge of Be in Be...OH₂ supports the Mulliken analysis result that there is a charge transfer from H₂O to Be.²⁴

We now present an analysis of the electron density distribution $\rho(r)$ and the Laplacian concentration $\nabla^2\rho(r)$ of the four complexes. It has been found that the bonding interactions between two atoms lead to a path of maximum electron density (MED) linking the atoms in question. A MED path can be considered as a necessary condition for chemical bonding. However, a MED path is also found in van der Waals complexes. Therefore, Cremer and Kraka²⁵ have suggested adding a sufficient condition for chemical bonding based on energetic aspects. The energy density $H(r)$ is given by $H(r) = G(r) + V(r)$, where $G(r)$ and $V(r)$ correspond to a local kinetic energy density and a local potential energy density, respectively.²⁶ Analysis of a variety of different bonds²⁵ suggests that covalent bonding is characterized by a predominance of the local potential energy density $V(r)$ at r_b and, hence, $H(r_b) < 0$. In contrast, weak inter- or intramolecular interactions as experienced in ionic, hydrogen bonding or in van der Waals systems lead to a positive value of $H(r_b)$. Small positive values of $H(r_b)$ of about 0.1 hartrees/Å³ are calculated for the M...OH₂ complexes considered here. This suggests that there exists only a weak interaction between M and O in the complexes. The electron density at the saddle point r_b , which can be used as a measure of bond order,²⁷ is less than 50% that of a "normal" MO bond (such as LiOH, NaOH, BeO, NaO). These results correlate with the lengthening of the MO distance (20–35%) in the M...OH₂ complexes compared to the "normal" MO bond.

The dipole-induced dipole interaction due to the polarizability of the metal atoms can be analyzed in terms of the Laplace field $\nabla^2\rho(r)$ which is indicative of concentration and depletion of charge.²⁸ In an isolated M atom there exist spherical surfaces where $\nabla^2\rho(r)$ attains maximum or minimum values corresponding to local concentration or depletion of electronic charge.²⁹ The uniform spheres of $-\nabla^2\rho(r)$, in particular the "valence sphere" of

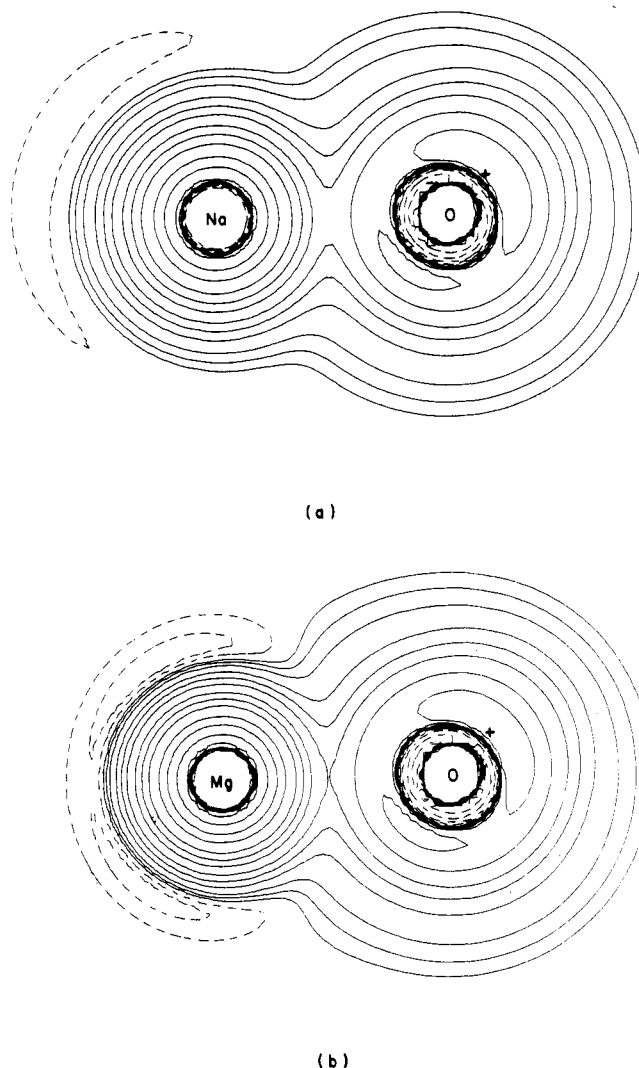


Figure 3. $\nabla^2\rho(r)$ plots for Na...OH₂ (a) and Mg...OH₂ (b) complexes (MP2/6-31G** C_s structures in Table I) in the plane corresponding to the C_s plane in Figure 1. The positions of the hydrogens, both of which are out of the plane, are denoted by +. (Inner shell parts with $\nabla^2\rho(r) < 0$ are not shown.)

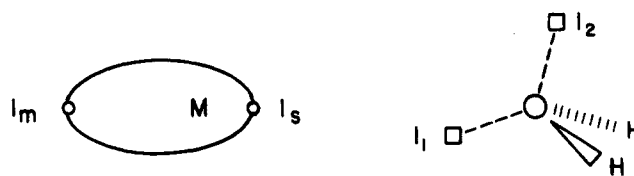


Figure 4. Illustration of the points (l_1, l_2, l_3, l_m) at which $-\nabla^2\rho(r)$ has been evaluated.

$-\nabla^2\rho(r)$, are distorted upon bond formation with other atoms, or, as in this particular case, upon dipole-induced dipole interaction with a water molecule. The $\nabla^2\rho(r)$ plots for Na...OH₂ and Mg...OH₂ are given in Figure 3. They show that the interaction between M and OH₂ occurs at the lone pair side of the water molecule. According to the model of avoidance of charge concentration recently developed by Cremer and Kraka³⁰ the lone pair l_1 pushes charge at M from the front to the backside. The lone pair l_1 itself is drawn toward M.

This finding can be discussed quantitatively in terms of the two local maxima l_1 and l_2 , illustrated in Figure 4, of $-\nabla^2\rho(r)$ in the valence sphere of the O atom. The $-\nabla^2\rho(r)$ values at the local maximum are given in Table V. In general, local valence sphere

(22) Evidence for this also comes from calculations on He and Ne atom interactions with H₂O at the distances in the metal atom complexes. Since the polarizabilities of He and Ne are 10–100 times smaller than that of the metal atoms, they can provide a rough idea of the repulsive energies of the metal atom complexes. They are nearly as large or larger than the interaction energies calculated from the simple dipole-induced dipole model in Table IV. At the HF/6-31G* level the interaction of He with H₂O in the equilibrium structure of Be...OH₂ and Li...OH₂ is repulsive by +21.5 and +11.1 kcal/mol, respectively. The interaction of Ne with H₂O in the equilibrium structures of Na...OH₂ and Mg...OH₂ is repulsive by +4.3 and +3.9 kcal/mol, respectively.

(23) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833.

(24) Kraka, E.; Cremer, D., work in progress.

(25) Cremer, D.; Kraka, E. *Croat. Chem. Acta* **1984**, *57*, 1265.

(26) $G(r) = 1/2 \nabla \nabla \Gamma^1(r, r')$; $V(r) = \text{tr } \sigma(r)$; $\sigma = 1/4 (\nabla \nabla + \nabla' \nabla') - (\nabla \nabla' + \nabla' \nabla) \Gamma^1(r, r')$, where $\Gamma^1(r, r')$ defines the first-order density matrix.

(27) Bader, R. F. W.; Slee, T. S.; Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* **1983**, *105*, 5061.

(28) This becomes obvious when considering the definition of the second derivative of ρ in the one-dimensional case: $\lim(\Delta x \rightarrow 0) \{ \rho(x) - 1/2 [\rho(x - \Delta x) + \rho(x + \Delta x)] \} = 1/2 \lim(\Delta x \rightarrow 0) \{ [\rho(x + \Delta x) - \rho(x)] - [\rho(x) - \rho(x - \Delta x)] \} = -1/2 (d^2\rho/dx^2) \Delta x^2$. If the second derivative is negative, $\rho(x)$ is larger than the average value of ρ at all neighboring points; Morse, P. M.; Feshbach, H. *Methods of Theoretical Physics*; McGraw-Hill: New York, 1953; Vol. 1, p 6.

(29) Bader, R. F. W.; Essen, H. *J. Chem. Phys.* **1984**, *80*, 1943.

(30) Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* **1985**, *107*, 3811.

TABLE VI: Analysis of the Saddle Point l_s and the Local Maximum l_m of $-\nabla^2\rho(r)$ in the Valence Sphere of the M Atom^a

	Li		Na		Be		Mg	
$-\nabla^2\rho(r_p)^b$	0.041		0.0002		0.613		0.032	
p^c	1.328		1.862		0.883		1.386	
	Li...OH ₂		Na...OH ₂		Be...OH ₂		Mg...OH ₂	
	l_m	l_s	l_m	l_s	l_m	l_s	l_m	l_s
$-\nabla^2\rho(r_i)^b$	0.082	-4.319	0.018	-2.362	1.026	-3.845	0.081	-1.893
p^c	1.358	0.821	1.797	1.141	0.839	0.729	1.360	1.092

^aDistances in angstroms; $-\nabla^2\rho(r)$ values in $e/\text{\AA}^5$. ^b r_p , point on the valence sphere of the M atom. ^cValence sphere radius.

maxima can be assigned to bonding and nonbonding electrons on the basis of simple models.³¹ There is a decrease in the charge concentration at l_1 of about 7–10%, while the charge concentration at the lone pair l_2 not pointed toward the metal atom remains about the same as in the free water molecule. The valence sphere radii for the two lone pairs of H₂O, $p(l_1)$ and $p(l_2)$, in the complex are given in Table V. They represent the distance from a point on the valence sphere to the atomic nucleus. The results indicate a slightly increased valence sphere radius for l_1 , the lone pair directed toward the metal atom, in comparison to the lone pairs of the water molecule, while the lone pair l_2 behaves like a "normal" water lone pair.

Indicative of the polarization of charge on the metal atom is the deformation of the valence sphere of the M-atom, see Figures 3 and 4. For the isolated M atoms one finds a valence sphere with uniform $-\nabla^2\rho(r)$ values given in Table VI. In the complex, charge is depleted on the frontside of the M atom in a direction toward the l_1 lone pair of the O atoms and is concentrated at the backside as a result of the interaction with the water molecule. This is reflected quantitatively by the negative values of $-\nabla^2\rho(r)$ at the saddle point l_s in the direction toward the O atom and the local maxima l_m on the opposite side, which are slightly greater than the corresponding $-\nabla^2\rho(r)$ values of the free atoms. The distortion

of the M atom in IA complexes is greater than that in the IIA complexes as reflected by the stationary points l_m and l_s of the valence sphere concentration (see Table VI). It is interesting to note that this goes in line with the finding that the dissociation energy of the MO bond is greater in IA complexes than that in the IIA complexes.

IV. Conclusions

The following conclusions can be drawn from the results on the Na...OH₂ and Mg...OH₂ complexes presented here.

1. Correlation effects are very important in the Mg...OH₂ complex as a tight complex is found only when correlation is included. The shifts in the H₂O frequencies in both complexes are sensitive to inclusion of correlation energy. Shifts in the H₂O stretching frequencies are predicted to be on the order of 50–100 cm^{-1} .

2. Similar to results for Be...OH₂ and Li...OH₂, the shifts in the H₂O vibrational frequencies in the complex cannot in general be used as a measure of the dissociation energies. In both the first and second row no correspondence is found between the magnitude of the dissociation energy and the magnitude of the frequency shift.

3. Analyses of the one-electron densities of Na...OH₂ and Mg...OH₂ as well as Li...OH₂ and Be...OH₂ clearly show the importance of charge polarization on the metal atom in these complexes. Other forces, arising from charge transfer or bonding overlap, must also contribute to the stabilities of these complexes.

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Registry No. Na, 7440-23-5; Mg, 7439-95-4.

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(32) In this paper the periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

The Dipositive Dimeric Ion Hg₂²⁺: A Theoretical Study

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Various properties of Hg₂²⁺(g) are calculated from relativistic quantum mechanics. For comparison, calculations are also made on a nonrelativistic basis. The relativistic values of R_e and ω_e agree well with observed values in those crystals or solutions where the effects of surroundings are expected to be small. The relativistic effect reduces R_e by 0.28 Å, raises ω_e by 67 cm^{-1} , and increases D_e by 24 $\text{kcal}\cdot\text{mol}^{-1}$. A modified Born-type calculation is carried out for the hydration energy which recognizes the quadrupole moment and the nonspherical shape. Good agreement is obtained with experimental thermodynamic data for aqueous Hg₂²⁺.

The ion Hg₂²⁺ is unique as a dipositive dimeric aqueous species with a broad range of stability. Other polymeric dipositive species have been detected recently, but only under very limited and specially selected conditions. In contrast, the mercurous ion was identified as a dimeric species by simple chemical methods over 80 years ago^{1,2} and plays a major role in the chemistry of mercury.

Thus, a study of Hg₂²⁺(g) by quantum and statistical thermodynamic theoretical methods is of interest as a reference related

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