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Ab Initio Studies of Donor–Acceptor Complexes between Water and Various Atoms[1]

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Abstract: Single-determinant ab initio molecular-orbital calculations have been carried out on the series of donor–acceptor complexes A–OH_2 [A = Li, Be, B, C, Na, Mg, Al] in their ground and certain excited states. Equilibrium A–O distances, dissociation energies, dipole moments, and some vibrational frequencies have been determined. Dissociation energies are shown to correlate with electrostatic interaction energies, and A–O distances correlate with suitably defined atomic radii. A model is developed that uses these correlations to predict potential-energy surfaces for members of this class of complexes. The model works best for complexes between alkali atoms and first-row Lewis bases, although it has qualitative value for other systems studied as well.

A number of experimental[2-5] and theoretical[6-11] studies have established the existence of electron donor–acceptor complexes between nucleophilic molecules and electropositive atoms. The atom–molecule bond in these systems is principally electrostatic in origin,[12] and ought to be subject to description by electrostatic models. I have previously proposed such a model[11] to predict the potential surfaces of members of this class of complex. However, the model was incomplete in that it required independent information on the structure and energy of a related complex in order to establish the distance and energy scales for the complex under study. Since this type of complex is frequently observed in rare gas matrices[2-5] (where it seems to be a precursor to various insertion reactions), represents a limiting case for interactions between gas molecules and metal surfaces,[13] and is involved in the Penning ionization of nucleophilic molecules,[11,14] it seems worthwhile to refine the theoretical model so that it can predict the equilibrium properties and potential surface for a complex without prior experimental determination or ab initio calculation.

In this paper I examine the structures, energies, and some other properties of a number of complexes A–OH_2 [A is Li(^{2}S or ^{2}P), Be(^{1}S or ^{3}P), B(^{2}P), C(^{3}P), Na(^{2}S or ^{2}P), Mg(^{1}S), or Al(^{2}P)]. I seek to establish the systematic features of this series, especially as regards the dissociation energies and equilibrium bond lengths. Several of the complexes dealt with here have been the subjects of previous calculations by other workers. However, the orbital basis sets employed have been so diverse as to obscure the trends in the results. The present calculations have been carried out with basis sets of uniform quality. In addition, I have noted and compensated for some shortcomings of the present basis sets by applying the function counterpoise correction[15] to the results.

Computational Methods

All calculations have been done in the single-determinant restricted (unrestricted) Hartree–Fock–Roothaan approximation for closed-(open-)shell systems.[16] For water, the standard molecular 6-31G** basis set of Pople et al.[17] was used, giving a total energy of −76.02235 hartrees and a dipole moment of 2.182 D at a bond length of 0.957 Å and a bond angle of 104.54°. For Li, Be, B, and C, 6-31G* basis sets[17] with atomic scale factors were used. For Na, Mg, and Al, 5s3p basis sets of McLean and Chandler[18] were used. Since the chief concern of this paper is the A–O interaction, the water geometry in all calculations was fixed at the values mentioned above, and only C_{2v} structures for the complexes were considered. (A more extensive study of the geometry of $LiOH_2$ will be presented elsewhere.[19])

The function counterpoise correction[15] consists of evaluating the interaction potential from the difference

$$\Delta E_c = E(AB;AB) - E(A;AB) - E(B;AB) \qquad (1a)$$

instead of

$$\Delta E = E(AB;AB) - E(A;A) - E(B;B) \qquad (1b)$$

The notation $E(X;Y)$ indicates that the energy is computed for system X with use of the basis set of system Y. This correction compensates for the so-called ghost orbital effect,[20] in which basis functions on system B are "borrowed" by system A (and vice versa) to repair some deficiency in the basis set of system A. Actually there is some overcompensation involved, so that the true potential energy (for a particular basis set) lies between ΔE and ΔE_c, but probably closer to the latter.[21] This point will be important later.

Results

Table I contains equilibrium A–O distances, dissociation energies, and other properties of the AOH_2 complexes, determined

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Table I. Structures, Energies, and Properties of AOH_2 Complexes[a]

A	symmetry	R_{AO}/Å	D_e/kcal mol^{-1}	$\Delta\mu$/D	g_A/e	$(d\mu/dR)_{R_e}$/D Å^{-1}	k_R/mdyne Å^{-1}
Li	$^2A_1$	1.926	13.27	3.854	−0.0611	0.320	0.706
		1.937	11.36	3.719	−0.0185	0.295	0.773
Li	$^2B_2$	1.895	22.48	1.245	−0.0895	−0.606	0.825
		1.904	21.17	1.084	−0.0636	−0.543	0.806
Be	$^1A_1$	3.521	0.56	0.755	−0.0135	−0.715	0.0102
		4.50	0.05	0.300	0.0	−0.178	$\sim 3 \times 10^{-4}$
Be	$^3B_2$	1.690	21.73	3.860	−0.2163	−2.399	1.283
		1.697	18.62	3.759	−0.1748	−2.425	1.220
B	$^2B_2$	2.617	2.70	1.017	−0.0329	−1.406	0.0548
		2.704	1.75	0.804	−0.0077	−1.168	0.0467
B	$^2B_1$	2.878	1.79	0.713	−0.0215	−0.889	0.0414
		2.981	0.99	0.533	−0.0031	−0.697	0.0379
C	$^3A_2$	2.429	3.58	0.760	−0.0282	−1.234	0.130
		2.439	2.87	0.730	−0.0224	−1.221	0.099
Na	$^2A_1$	2.318	7.95	3.391	−0.0427	0.105	0.346
		2.341	6.11	3.249	−0.0075	0.064	0.304
Na	$^2B_2$	2.235	18.46	0.795	−0.0521	−0.237	0.575
		2.248	16.60	0.660	−0.0081	−0.224	0.546
Mg	$^1A_1$	3.192	0.82	1.760	−0.0234	−1.495	0.0028
		4.65	0.06	0.539	−0.0001	−0.363	0.0010
Al	$^2B_2$	2.423	5.76	2.543	−0.0561	−3.074	0.161
		2.520	4.05	2.147	−0.0141	−2.777	0.092
Al	$^2B_1$	2.754	3.32	1.674	−0.0364	−2.038	0.0581
		2.899	2.05	1.298	−0.0049	−1.620	0.0402

[a] For each complex the first entry is without and the second entry with the counterpoise correction.

Table II. Approximate Vibrational Frequencies and Integrated Absorption Coefficients for A-O Stretching Vibrations

	$\tilde{\nu}$/cm^{-1}	A/km mol^{-1}
$LiOH_2$ ($^2A_1$)	510	0.73
$LiOH_2$ ($^2B_2$)	521	2.46
$BeOH_2$ ($^1A_1$)	9	0.22
$BeOH_2$ ($^3B_2$)	587	41.37
BOH_2 ($^2B_2$)	108	28.82
BOH_2 ($^2B_1$)	97	10.26
COH_2 ($^3A_2$)	153	8.74
$NaOH_2$ ($^2A_1$)	226	0.017
$NaOH_2$ ($^2B_2$)	303	0.21
$MgOH_2$ ($^1A_1$)	13	0.54
$AlOH_2$ ($^2B_2$)	120	30.17
$AlOH_2$ ($^2B_1$)	79	10.27

with and without the counterpoise correction. Consider first the uncorrected results. The alkalis and excited-state atoms are relatively strongly bound, the alkaline earths are weakly bound, and the others are intermediate. It appears that the dissociation energy, the dipole moment enhancement, and the charge transferred to A (as determined by Mulliken population) are all generally decreasing functions of the equilibrium A–O distance. The transferred charge and dipole-moment enhancement are consistent with the picture previously given[7,11] of these complexes: H_2O serves as an electron donor through its $3a_1$ orbital, and the interaction is stabilized by polarization of electron density on A away from the oxygen.

With the counterpoise correction, the trends noted above persist, but the details are changed. All of the dissociation energies are decreased by amounts between 1 and 3 kcal mol^{-1}. R_{AO} increases, in some cases by more than 0.1 Å. Counterpoise-corrected values of $\Delta\mu$ and q_A have been calculated by expressions analogous to eq 1a. The corrected $\Delta\mu$ are somewhat smaller than the uncorrected values, and the corrected q_A are considerably smaller, although the magnitude of the correction may be overestimated. These patterns arise because roughly 90% of the basis superposition error involves the functions on A. Small amounts of electron density from water are placed in diffuse orbitals of the acceptor atom, producing a spurious charge transfer and dipole-moment enhancement as well as an energy lowering.

The major qualitative change produced by the counterpoise correction involves the group 2A metals Be and Mg. Their complex binding energies are decreased by an order of magnitude, and their bond lengths increased by about an angström. The possibility of overcompensation by the counterpoise correction[21] prevents a conclusion about the nature of the bond (if any) in $BeOH_2$ and $MgOH_2$. The question must be resolved by more sophisticated calculations or by experiment (vide infra).

Table I also contains the harmonic force constants and dipole-moment derivatives for the A–O stretch, treating A–OH_2 as a pseudodiatomic molecule; no other degrees of freedom were examined. From these quantities the frequencies and integrated intensities of the A–O stretching vibrations can be estimated. These results appear in Table II. Note that the alkali ground-state complexes are qualitatively different from the others: they are the only complexes with positive $\partial\mu/\partial R$. At long range, $\partial\mu/\partial R$ may be expected to be negative, as the extent of electron donation from water to the metal (and thus the dipole moment) increases with decreasing R_{AO}. At short range, electron-repulsion forces arising from the Pauli exclusion principle dominate, and the electrons on H_2O are polarized away from the metal, resulting in a decrease in the dipole moment. Apparently lithium and sodium are the only atoms considered here that penetrate close enough to the water molecule to produce significant repulsive electron density shifts at their equilibrium distances. Thus, although $LiOH_2$ and $NaOH_2$ have two of the largest dipole-moment enhancements observed in this study, they have quite small predicted intensities for the AO stretch.

Comparison with Other Calculations and with Experiment. $LiOH_2$. Trenary, Schaefer, and Kollman[7,8] have calculated energies and structures for $LiOH_2$ ($^2A_1$), using a basis set somewhat larger than that used here, and obtained a dissociation energy D_e = 12.2 kcal mol^{-1}, R_{LiO} = 1.928 Å, and $\Delta\mu$ = 6.38D, in substantial agreement with the present work. They determined that improvements in the basis set decrease D_e by 1.8 kcal mol^{-1}, whereas inclusion of electron correlation increases it by 1.3 kcal mol^{-1}, the effects largely canceling.

Schultz, McLean, Pedersen, and Jarnagin[13] have computed minimal basis set wave functions for $LiOH_2$ as part of a study of H_2O adsorption on Li clusters and surfaces. They reported R_{LiO} = 1.735 Å, D_e = 39.8 kcal mol^{-1}, and q_{Li} = −0.21 e. As expected, the small basis set exaggerates the strength of the interaction. The interesting feature is that $LiOH_2$ is very similar to $Li_{10}OH_2$ for interaction of OH_2 with a surface-layer atom.

$LiOH_2$ has been observed in argon matrices by Meier, Hauge, and Margrave, who have reported hyperfine coupling constants for lithium[2] and vibrational frequency shifts for the H_2O bending mode.[3] Calculations of these quantities will be presented elsewhere.[19]

Trenary et al.[8] have reported equilibrium energies and distances for the lowest excited states of $LiOH_2$ in a double ζ basis set. These states are formed by promoting a lithium 2s electron to one of the 2p orbitals. The resulting states are $^2A_1$, $^2B_1$, and $^2B_2$; the occupied 2p orbitals are respectively along the C_{2v} axis, perpendicular to this axis and to the plane of the water molecule, and perpendicular to the C_{2v} axis but in the molecular plane. the $^2A_1$ state is repulsive, due to the overlap of the Li(2p) orbital and $3a_1$ on H_2O. The chief difference between $^2B_1$ and $^2B_2$, which are both attractive, is that the quadrupole moment–quadrupole moment interaction stabilizes $^2B_2$ and destabilizes $^2B_1$. This pattern of states is repeated in all systems studied here which have a $...2p^1$ or $...3p^1$ electron configuration on the atom A. Trenary's results for $LiOH_2$ are D_e = 26.8 (22.5) kcal mol^{-1} and R_{LiO} = 1.86 (1.85) Å for $^2B_2$ ($^2B_1$). As expected, lack of d orbitals on O makes the attractive interaction seem stronger in their calculation than in Table I.

$BeOH_2$. Trenary et al.[8] reported that they determined $BeOH_2$ to have a repulsive interaction but did not specify their basis set. More recently, Curtiss and Frurip[10] calculated equilibrium geometries, energies, and H_2O bending vibration frequency shifts for $BeOH_2$ and $MgOH_2$ (vide infra). Their largest basis set for $BeOH_2$ differs from the present one only in having no p orbitals on H. They report R_{BeO} = 3.662 Å and D_e = 0.62 kcal mol^{-1}, with the minimum energy occurring at an angle of 72.9° between the BeO bond and the C_{2v} axis. They state that moving Be to the C_{2v} axis while keeping R_{BeO} fixed raises D_e by about 0.1 kcal mol^{-1}, so their results basically agree with the present ones. Curtiss and Frurip's basis set has the same deficiencies as the present one and does not help to resolve the question of whether or not $BeOH_2$ is bound. The results of Trenary et al.,[8] if carried out in the same size basis set used for $LiOH_2$, suggest that $BeOH_2$ is not bound except perhaps by dispersion forces.

The excited states of $BeOH_2$ have not previously been studied. The transition $2s^2 \rightarrow 2s^12p^1$ makes the beryllium atom much more electropositive in directions perpendicular to the occupied 2p orbital, hence the large dissociation energy. A similar effect has been observed by Swope and Schaefer[22] in calculations on the $Be^*-C_2H_4$ and $Be^*-C_2H_2$ complexes.

BOH_2, COH_2. The present calculations on BOH_2 have been carried out for the $^2B_1$ and $^2B_2$ states arising from $B(1s^22s^22p^1\ ^2P)$. COH_2 has been studied in the $^3A_2$ state arising from $C(1s^22s^22p_x{}^12p_y{}^1\ ^3P)$. The only other states of COH_2 likely to be bound are $^1A_1$ arising from $C(1s^22s^22p_x{}^2$ or $2p_y{}^2\ ^1D)$.

I am not aware of any previous theoretical or experimental studies of these species. In view of the fact that COH_2 is definitely not (and BOH_2 probably not) the minimum-energy isomer, it would be interesting, though beyond the scope of this paper, to determine whether barriers to rearrangement exist for these systems.

$NaOH_2$. A calculation by Trenary et al.,[7] using a larger basis set than employed in the present work, obtained D_e = 5.2 kcal mol^{-1}, R_{NaO} = 2.38Å, q_{Na} = –0.024 e, and $\Delta\mu$ = 3.28 D. These results are in fair agreement with the uncorrected results of Table I and in better agreement with the corrected results. The excited states of $NaOH_2$ have not been previously studied.

$MgOH_2$. A previous calculation by Curtiss and Frurip[10] used the standard 6-31G* basis for H_2O and a basis of 12s, 10p, and 4d functions, contracted to 4s2p1d, for Mg.[23] They obtained D_e = 2.34 kcal mol^{-1} at R_{MgO} = 2.44 Å, a considerably stronger interaction than reported in Table I. However, their Mg basis set was smaller than that used here and may have provided some ghost orbital stabilization.

The question of stability of $MgOH_2$ has apparently been resolved by experiment: Hauge, Gransden, Kauffman, and Margrave[4] have identified it in argon matrix by the shift induced in the H_2O bending frequency. They suggested a linear correlation between dissociation energy and frequency shift. This would imply that $MgOH_2$ is twice as strongly bound as $NaOH_2$, a far cry from the results of Table I.

The interplay of experimental and theoretical data on $MgOH_2$ was so unsatisfactory as to prompt me to carry out additional calculations with a larger basis set. Using McLean and Chandler's $12s9p \rightarrow 6s5p$ contraction for Mg[18] and Dunning's double-ζ plus polarization basis set[24] for H_2O, I obtained an SCF (counterpoise corrected) dissociation energy of 0.17 (0.11) kcal mol^{-1} at a distance of 3.972 Å (4.160 Å). It seems unlikely that additional basis functions will produce a substantially stronger bond.

After the calculations of the previous paragraph had been completed, a paper appeared by Kochanski and Prissette[25] in which $MgOH_2$ was reported to have a well depth of 10.03 kcal mol^{-1} at R_{MgO} = 2.06 Å, with the binding *entirely due to dispersion.* Kochanski and Prissette calculated an SCF potential curve and added to it a dispersion contribution obtained by second-order perturbation theory. Since the present basis set is somewhat larger than theirs, an improved total potential for $MgOH_2$ can be obtained by adding my SCF potential and their dispersion contribution, yielding D_e = 7.09 kcal mol^{-1} and R_e = 2.12 Å. The $MgOH_2$ dissociation energy is thus comparable to or slightly greater than that of $NaOH_2$, in qualitative accord with the expectation of Hauge et al. mentioned above.

$AlOH_2$. Trenary et al.,[8] using a basis set somewhat larger than the present one, determined D_e = 4.4 kcal mol^{-1} at R_{AlO} = 2.55 Å for the $^2B_2$ state, in fair agreement with the present results. Kurtz and Jordan[9] used an effective core potential plus valence-orbital description of Al and a double-ζ basis set for H_2O and obtained D_e = 12.3 kcal mol^{-1} at R_{AlO} = 2.12 Å. D_e dropped to 8.5 kcal mol^{-1} at R_{AlO} = 2.25 Å when they replaced the core potential with an all-electron description. The large differences between Kurtz and Jordan's results and the others are probably due to the lack of d functions on oxygen.

Hauge, Kauffman, and Margrave[5] have codeposited Al and H_2O in argon matrices and have detected reaction products, but have not observed the shifted H_2O bending frequency that seems characteristic of AOH_2 complexes. It might be that $AlOH_2$ is not a local minimum on the Al + H_2O potential surface. The calculations of Kurtz and Jordan[9] indicated no barrier to insertion of Al into an OH bond.

Electrostatic Models of the Interaction Potential. A previous study[11] of the $Ne^*(^3P) + H_2O$ interaction, which is analogous to that between Na and H_2O, revealed that the potential surface was very similar *in shape* to the surface of the electrostatic potential around the water molecule. This suggested that an appropriate model for the intermolecular potential could be obtained simply by rescaling the electrostatic potential to reproduce the energy and distance of the minimum in the intermolecular potential. That is,

$$V_{AD}(R,\theta,\phi) = a\phi_D(bR,\theta,\phi), \qquad (2)$$

in which V_{AD} is the intermolecular potential of the donor–acceptor complex, ϕ_D is the electrostatic potential of the donor, $a = V_{AD}(\mathbf{R}_{min})/\phi_D(\mathbf{R}'_{min})$, and $b = R'_{min}/R_{min}$. $\mathbf{R}_{min}$ ($\mathbf{R}'_{min}$) is the location of the minimum on the surface of $V_{AD}(\phi_D)$. For eq 2 to be appropriate, $\mathbf{R}_{min}$ and $\mathbf{R}'_{min}$ should have very similar θ and ϕ components. Equation (2) was tested on Ne* + H_2O, and gave satisfactory agreement, especially for the attractive parts of the potential.

This model is strictly applicable only for spherically symmetric acceptor atoms, since atoms with partially filled p shells have more complicated multipolar interactions with polar molecules. It is satisfactory for rare gas metastables since the open p shell is part of the atomic core, and its influence is not strongly felt until quite small intermolecular distances are reached. The model has some pertinence to quadrupolar atoms along the molecular symmetry axis, as seen by the following example. Equation 2 predicts a definite relationship for A–O stretching force constants, namely, that the dimensionless quantity $kD_e{}^{-1}R_e{}^2$ should be constant. For

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the molecules of Table I (excluding $BeOH_2$ and $MgOH_2$), this quantity is 29.8 ± 7.1, which is good constancy considering that D_e spans an order of magnitude and R_e a range of 1.4 Å.

To apply this model to other systems, one needs a representation of $\phi_D(\mathbf{R})$ and estimates of the two quantities R_{min} and $V_{AD}(\mathbf{R}_{min}) = D_e$. Numerous examples of electrostatic potential surfaces appear in the work of Scrocco, Tomasi, and co-workers.[26] Analytical representations of molecular electrostatic potentials can be obtained, for example, from the point-charge models of Kollman[27] or Bentley's atomic multipole expansions.[28] [The analytical models are long-range approximations and lack the penetration component of the electrostatic potential. They need to be supplemented by a penetration term such as eq 23 of Politzer and Parr.[29]] The difficulty lies in the determination of R_{min} and $V_{AD}(\mathbf{R}_{min})$. I shall use the data of Table I to establish some rules for estimating these quantities.

Following Kollman,[30] we can estimate the electrostatic contribution to the interaction energy for these systems as follows:

$$E_{es} = \int \rho_D(\mathrm{r}_D)\phi_A(\mathrm{r}_A)\,\mathrm{dr}$$

where ρ_D is the charge density of the donor molecule and ϕ_A is the electrostatic potential due to the charge density of the acceptor atom. Approximate water by a finite dipole:

$$\rho_D(\mathrm{r}) = q[\delta(\mathrm{r} - \mathbf{R}_C - \mathbf{d}) - \delta(\mathrm{r} - \mathbf{R}_D + \mathbf{d})]$$

where $\mathbf{R}_D$ is the location of the oxygen nucleus, $\delta(\mathbf{x})$ is the Dirac delta function, and $\mu_D = 2qd$ is the dipole moment of water. Then

$$E_{es} = q[\phi_A(\mathbf{R}_D + \mathbf{d}) - \phi_A(\mathbf{R}_D - \mathbf{d})] \qquad (3)$$

The electrostatic potentials of the spherically symmetric acceptor atoms are well described by exponential functions[31] over the range of internuclear distances of interest:

$$\phi_A(r) = Ce^{-\beta r} \qquad (4a)$$

For quadrupolar acceptor atoms, the appropriate expression is

$$\phi_A(r) = Q_{A0}r^{-3} \qquad (4b)$$

Substituting eq 4 into eq 3 and taking the limit $d \rightarrow 0$, we obtain

$$E_{es} = \beta R^2\phi_A(R)\phi_D(R) \qquad (5a)$$

and

$$E_{es} = 3R\phi_A(R)\phi_D(R) + Q_{A2}Q_{D2}/R^5 \qquad (5b)$$

respectively. $\phi_D(R)$ is the potential of the donor molecule at the acceptor nucleus. Q_{xm} is the *m*th component of the quadrupole moment of system x. The last term in eq 5b arises from an electrostatic interaction that makes no contribution to the electrostatic potential along the A–O internuclear axis.

Figure 1 shows the correlation between E_{es} and D_e. A least-squares fit gives

$$D_e = 1.17 - 0.428E_{es} \qquad (r^2 = 0.948) \qquad (6)$$

if all energy terms are expressed in kcal mol^{-1}. The total interaction energy consists of electrostatic, induction charge-transfer, exchange, overlap-repulsion, and dispersion contributions, so it is not surprising that E_{es} does not tell the whole story. The significance of eq 6 is twofold: It supports Kollman's assertion[30] that the electrostatic potential frequently correlates with the dissociation energy of intermolecular complexes, and it permits the estimation of dissociation energies for this class of complex from a simple model.

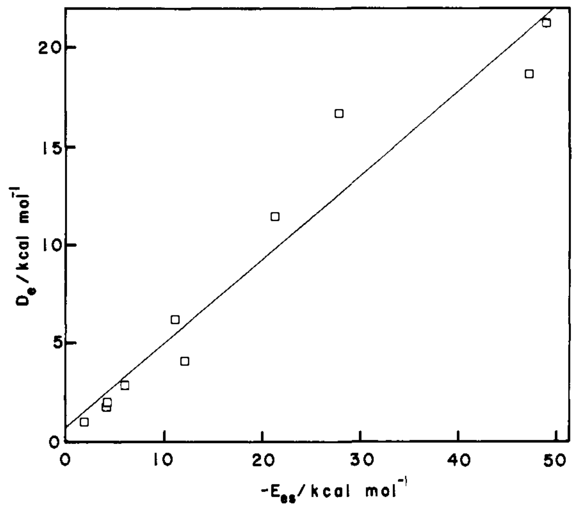

Figure 1. Ab initio dissociation energies vs. calculated electrostatic interaction energies for AOH_2 complexes. The line is from eq 6.

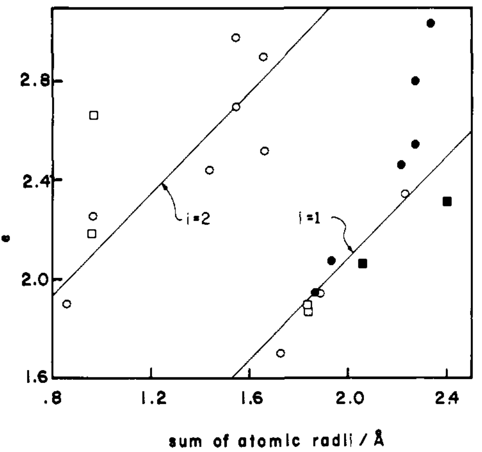

Figure 2. Ab initio equilibrium intermolecular distance vs. sum of atomic radii for various complexes. Open circles, AOH_2 data, this paper; solid circles, data from Trenary et al., ref 7; open squares, complexes involving C_2H_2 and C_2H_4 from ref 8 and 22; solid squares, $MgOH_2$ and $CaOH_2$ data from Kochanski and Prissette, ref 25. The lines are from eq 7.

A priori estimation of the equilibrium internuclear distance R_{AD} is more difficult. Figure 2 shows R_{AD} plotted against the sum of donor and acceptor atomic radii as defined by Pauling.[32] Because R_{AD} is less sensitive to basis set size than is D_e, I have included data for complexes studied by Trenary et al.[7] The data resolve themselves into two groups, distinguished by the presence or absence of occupied valence-shell p orbitals. I have fit the data with the function

$$R_{AD} = 1.031\sum r_p + (1.089\ \text{Å})\delta_{i,2} + 0.022\ \text{Å} \qquad (7)$$

the three coefficients having been determined by least squares. The average error is 0.12 Å overall and 0.08 Å for molecules with $i = 1$. $\delta_{i,2}$ is the Kronecker delta function with $i = 1$ for spherically symmetric atoms and 2 for quadrupolar atoms, except as noted below. The form of eq 7 was not motivated by anything except convenience. Equation 7 does not differentiate between B_1 and B_2 states of molecules like $AlOH_2$. Figure 2 has some other

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(26) Scrocco, E.; Tomasi, J. *Top. Curr. Chem.* **1973**, *42*, 95–170 and references therein.

(27) Kollman, P. A. *J. Am. Chem. Soc.* **1978**, *100*, 2974–2984.

(28) Bentley, J. In "Chemical Applications of Atomic and Molecular Electrostatic Potentials", Politzer, P., Truhlar, D. G., Eds.; Plenum: New York, 1981; pp 63–84.

(29) Politzer, P.; Parr, R. G. *J. Chem. Phys.* **1974**, *61*, 4258–4262.

(30) Kollman, P. A. In "Chemical Applications of Atomic and Molecular Electrostatic Potentials", Politzer, P., Truhlar, D. G., Eds.; Plenum: New York, 1981; pp 243–255.

(31) Atomic electrostatic potentials and quadrupole moments were calculated from the wave functions given by Clementi and Roetti [Clementi, E.; Roetti, C. *Atom. Data Nuc. Data Tables* **1974**, *14*, 177–478].

(32) Pauling, L. In "The Nature of the Chemical Bond"; Cornell University Press: Ithaca, 1960; pp 224 and 246. For cases in which the molecule encounters an atomic s orbital rather than the nominally outermost p orbital, I have used a corrected radius based on the orbital radii of Waber and Cromer [Waber, J. T.; Cromer, D. T. *J. Chem. Phys.* **1965**, *42*, 4116–4123]. For instance, for Al I used $r'_p = r_p - (r_{wc}[3p] - r_{wc}[3s])$, where r_p is the Pauling atomic radius and r_{wc} the Waber-Cromer orbital radius. For a case like Li(^{2}P), I used $r_{wc}[1s]$ directly.

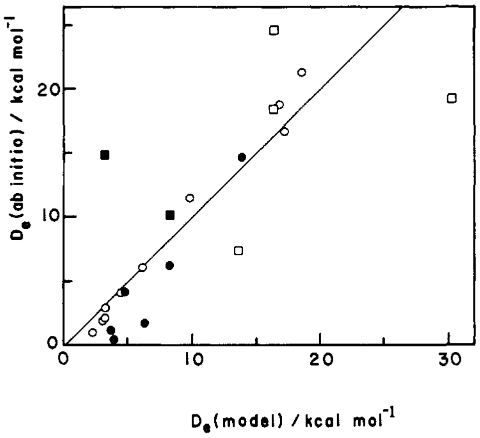

Figure 3. Ab initio dissociation energies vs. dissociation energies calculated from eq 5–7. Symbols as in Figure 2. The line indicates the position of exact agreement between model and ab initio calculation.

interesting features. Kochanski and Prissette's data[25] for $MgOH_2$ and $CaOH_2$ have been included in the figure (although not in the fit) and are seen to fall near the line for $i = 1$, even though they are dominated by dispersion interactions at R_e. The data for $LiPH_3$ and $LiSH_2$ are not well described by eq 7. Since these are the only examples with second-row Lewis bases, it is difficult to draw any conclusions about them. $BeOH_2$ ($^3B_2$) lies near $i = 1$ instead of $i = 2$. I have no explanation for this. Data from Schaefer and co-workers on complexes such as LiC_2H_4 ($^2B_2$,$^2B_1$),[8] BeC_2H_4 ($^3B_2$), and BeC_2H_2 ($^3B_2$)[22] have also been included in the figure (although not in the fit). The lithium results lie near $i = 2$ and the beryllium results near $i = 1$, so its seems to be characteristic of Be($1s^22s^12p^1$) to be described by eq 7 with $i = 1$.

The regularities of Figure 2 and the form of eq 3 require some discussion. Radii for the Lewis bases were single-bond covalent radii. For the metal atoms, tetrahedral covalent radii were used where available. These are obtained from internuclear distances in XY crystals, where X is in the nth periodic group and Y is in the $(8 - n)$th group. For the alkali atoms, single-bond metallic radii have been used, which are obtained from metallic internuclear distances. The implication of eq 7 with $i = 1$ is that the A–O bond length is consistent with a covalent single bond. This is an interesting result. The LiO bond in $LiOH_2$ is practically nonpolar compared to that in LiOH. The latter's bond length is 0.3 Å shorter, due to the ionic interaction. For quadrupolar acceptor atoms ($i = 2$), eq 7 indicates that the A–O bond is about 1.1 Å longer than would be expected for a covalent bond. Since the rule of thumb is that van der Waals contact distances are ~1.6 Å greater than covalent bonds,[33] eq 7 thus implies a weak interaction for these species. The quadrupolar atoms considered here tend to form covalent bonds via hybridized atomic orbitals, whereas in AOH_2 complexes they are well described by unhybridized orbitals. Covalent atomic radii may thus be inappropriate for them, resulting in (or at least contributing to) the factor of 1.089 Å in eq 7.

Using eq 5–7, one can calculate the dissociation energies of the complexes considered here, as well as those considered by Schaefer and his colleagues.[7,8,22] The necessary input is given in Table III and the results in Figure 3. The only large discrepancies are for $LiPH_3$ and $LiSH_2$ [for which eq 7 is inappropriate], the various complexes involving the π-donor Lewis bases C_2H_2 and C_2H_4 [for which eq 5 and 6 may be inappropriate], and $CaOH_2$ [for which the electrostatic contribution is not paramount]. The models discussed here are qualitatively sound and quantitatively capable of producing bond lengths accurate to better than 0.2 Å and dissociation energies accurate to better than 3 kcal mol^{-1} in many cases. While they have been derived explicitly for the interaction of electropositive atoms with σ-donor Lewis bases, they suggest that similar generalizations might be found for other types of complex.

Table III. Atomic and Molecular Properties[a] for Structure and Energy Calculations

A. Spherically Symmetric Atoms

atom	radius/Å	C/e Å^{-1}	β/Å^{-1}
Li(^{2}S)	1.23	3.566	2.071
Be(^{1}S)	1.06	8.177	2.863
Na(^{2}S)	1.57	3.424	1.928
Mg(^{1}S)	1.40	9.222	2.515

B. Quadrupolar Atoms

atom	radius/Å	Q_{A0}/10^{-26} esu cm^2	Q_{A2}/10^{-26} esu cm^2
Li(^{2}P)	0.19	4.636	5.800
Be(^{3}P)	1.06	2.722	3.402
B(^{2}P)	0.88	2.580	3.225
C(^{3}P)	0.77	2.020	0
Na(^{2}P)	0.30	5.397	6.746
Al(^{2}P)	0.99	3.776	4.721

C. Lewis Base Molecules

molecule	radius/Å	μ/D	Q_{D0}/10^{-26} esu cm^2	Q_{D2}/10^{-26} esu cm^2
NH_3	0.70	2.241	−2.929	0
H_2O	0.66	2.181	−0.186	1.977
HF	0.64	2.092	2.354	0
PH_3	1.10	0.755	−2.500	0
SH_2	1.04	1.379	−3.883	0.792
C_2H_2	0.77	0.0	7.141	0
C_2H_4	0.77	0.0	2.015	2.479

[a] This table contains properties calculated from wave functions with basis sets comparable to those used in this paper. Conversion to SI units: electrostatic potential, 1 e Å^{-1} = 1.6022 × 10^{-9} C m^{-1}; quadrupole moment, 10^{-26} esu cm^2 (= 1 buckingham) = 3.3357 × 10^{-40} C m^2; dipole moment, 1 Debye = 3.3357 × 10^{-30} C m. Multipole moments are as defined by Buckingham [Buckingham, A. D. In "Physical Chemistry. An Advanced Treatise. Volume IV. Molecular Properties", Henderson, D., ed.; Academic Press: New York, 1970, pp. 349–386], except that for Q_2, the real combination $2^{-1/2}(\xi_{22} + i\xi_{2-2})$ is used.

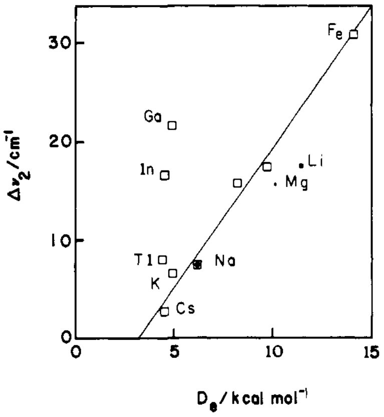

Figure 4. Experimental vibrational frequency shift $\Delta\nu_2$ vs. dissociation energy for AOH_2 complexes. Solid circles indicate ab initio results, and open squares indicate results from eq 5–7. The line is a least-squares fit to the model results for spherically symmetric atoms only and is given by $\Delta\nu_2/\text{cm}^{-1} = -9.1 + 2.87D_e/\text{kcal mol}^{-1}$.

Discussion

In this paper, a series of ab initio calculations has been used to support and parametrize some crude models for the structures and dissociation energies of a family of donor–acceptor complexes. These models may be exploited in several ways. They may be used to estimate the binding energy and atom–molecule stretching frequency of complexes observed in rare gas matrices. One may estimate the same quantities for the case of molecules absorbed

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(33) Pauling, L., ref 32, p 263. See also: Bernstein, R. B.; Muckerman, J. T. *Adv. Chem. Phys.* **1967**, *12*, 389–486.

on metal surfaces, in order to examine differences (or similarities) between atom–molecule and surface–molecule bonds. One can exploit the analogy between alkali atoms and rare gas metastables to compute approximate potential surfaces for Penning ionization processes in Lewis bases.

An example of their application may prove useful. Hauge, Margrave, et al.[3-5] have reported infrared spectra arising from the codeposition of water molecules and metal atoms in an argon matrix. In particular, they observed shifts in the H_2O bending frequency that they attributed to formation of AOH_2 (A = Li, Na, K, Cs, Mg, Fe, Ga, In, Tl). They also suggested the existence of a linear relationship between this frequency shift, $\Delta\nu_2$, and the dissociation energy of the complex. These complexes can be characterized by the methods reported here.[34] The results are presented in Figure 4 as a plot of $\Delta\nu_2$ vs. D_e. It appears that the alkali metals plus Mg and Fe fall on a line, whereas the group 3 metals fall on a much steeper line. The first group of atoms is spherically symmetric (the small quadrupole moment of Fe is unimportant for the energetics) and interact with water chiefly through the $3a_1$ (lone pair) orbital. The group 3 atoms have in addition an *np* electron which can interact with the $1b_2$ (OH bonding) orbital. Thus it is plausible that the two types of complex have different effects on the H_2O bending vibration. The electronic interactions underlying the frequency shift require a detailed study of force constants with a larger basis set than the present one.

Another interesting application of this set of models would be the calculation of cross sections for Penning ionization processes, such as the Penning electron-energy distribution, since an approximate excited-state potential is available here and the ionic potential may be approximated in a straightforward manner. However, neither a facile method of calculating the three-dimensional autoionization width nor a simple treatment of the anisotropic scattering problem is at hand yet.

Registry No. $LiOH_2$ (aquo form), 63313-34-8; $LiOH_2$ (hydrate form), 81408-53-9; $BeOH_2$ (aquo form), 81423-16-7; $BeOH_2$ (hydrate form), 81408-54-0; BOH_2 (aquo form), 81423-15-6; BOH_2 (hydrate form), 81408-55-1; COH_2 (aquo form), 81434-73-3; COH_2 (hydrate form), 81423-13-4; $NaOH_2$ (aquo form), 63313-37-1; $NaOH_2$ (hydrate form), 81408-56-2; $MgOH_2$ (aquo form), 81408-83-5; $MgOH_2$ (hydrate form), 81408-57-3; $AlOH_2$ (aquo form), 67187-38-6; $AlOH_2$ (hydrate form), 81408-58-4.

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(34) The calculations are carried out by using data from Table III and ref 31 in eq 5–7, except for Cs and Tl, for which wave functions are not available. For these cases, valence-orbital exponents and quadrupole moments are obtained by extrapolating from the lower members of their respective groups in the periodic table.

Elementary Reconstitution of the Water Splitting Light Reaction in Photosynthesis. 1. Time-Resolved Fluorescence and Electron Spin Resonance Studies of Chlorophyll *a* Dihydrate Photoreaction with Water in Nonpolar Solutions

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Abstract: The path of $(\mathrm{Chl}\ a\cdot 2\mathrm{H_2O})_n$ hydrated chlorophyll *a* in its photoreaction with water is studied by means of time-resolved fluorescence and electron spin resonance techniques. It is shown that the observed ESR effects are primarily attributable to the weakly fluorescent aggregates of chlorophyll *a* dihydrate, $(\mathrm{Chl}\ a\cdot 2\mathrm{H_2O})_{n\geq 2}$. By contrast, monomeric chlorophyll *a* hydrate in nonpolar solutions containing an excess of water is photochemically inactive and instead gives rise to comparatively strong fluorescence as well as delayed fluorescence characterized by oscillatory behavior, indicative of a charge-transfer feedback mechanism. The observation of reversible, light-induced ESR signals of aggregated radical cations, $(\mathrm{Chl}\ a\cdot 2\mathrm{H_2O})_{n\geq 2}{}^{+\cdot}$, in the 10^{-1}–10-s domain, five decades in time removed from the oscillatory process of monomeric chlorophyll *a* hydrate suggests the critical dependence of Chl *a* photochemical properties on the state of molecular aggregation. Evidence is obtained for the aggregation of hydrated Chl *a* as the dimer, $(\mathrm{Chl}\ a\cdot 2\mathrm{H_2O})_2$, and multiples of the hexamer, $(\mathrm{Chl}\ a\cdot 2\mathrm{H_2O})_6$. The conversion of light into electrochemical potential is quantified by a weak coupling limit treatment of nonadiabatic electron transfer in terms of measured effects of ESR lifetime lengthening and line-width narrowing. The observed differences in the optical and photocatalytic properties of $(\mathrm{Chl}\ a\cdot \mathrm{H_2O})_2$, $(\mathrm{Chl}\ a\cdot 2\mathrm{H_2O})_{n\geq 2}$, monomeric hydrated Chl *a*, and Chl *a* not complexed with water provide the rationale for proposing different stereospecific Chl *a*–H_2O aggregates as models to account for the dramatic differences in the properties of P680, P700, and light-harvesting chlorophyll associated with P680.

The storage of solar energy as fuel for the living world results from the water splitting reaction in plant photosynthesis in which oxygen is evolved and the hydrogen from water reduces carbon dioxide to carbohydrates. The mechanisms underlying this reaction may be interpreted in terms of the structural constituency of the chlorophyll *a* (Chl *a*) molecule, a pheophytin in which the hydrogen atoms at the center of the macrocycle are replaced by a Mg atom.[1] The electrophilic Mg atom and the nucleophilic cyclopentanone ring, which contains the two carbonyl groups at C9 and C10, provide the sites for molecular aggregation involving protic solvent molecules, such as water. Interactions involving the asymmetric carbon at C10 give rise to stereospecific adducts

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(1) L. P. Vernon and G. R. Seely, eds., "The Chlorophylls", Academic Press, New York, 1966.