Two-Dimensional H₂O−Cl₂ and H₂O−Br₂ Potential Surfaces: An Ab Initio Study of Ground and Valence Excited Electronic States

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Received: September 3, 2007; In Final Form: October 12, 2007

All electron ab initio calculations for the interaction of H₂O with Cl₂ and Br₂ are reported for the ground state and the lowest triplet and singlet Π excited states as a function of both the X−X and O−X bond lengths (X = Cl or Br). For the ground state and lowest triplet state, the calculations are performed with the coupled cluster singles, doubles, and perturbative triple excitation level of correlation using an augmented triple-ζ basis set. For the $^1\Pi$ state the multireference average quadratic coupled cluster technique was employed. For several points on the potential, the calculations were repeated with the augmented quadruple-ζ basis set. The ground-state well depths were found to be 917 and 1183 cm⁻¹ for Cl₂ and Br₂, respectively, with the triple-ζ basis set, and they increased to 982 and 1273 cm⁻¹ for the quadruple-ζ basis set. At the geometry of the ground-state minimum, the lowest energy state corresponding to the unperturbed $^1\Pi$ states of the halogens increases in energy by 637 and 733 cm⁻¹, respectively, relative to the ground-state dissociation limit of the H₂O−X₂ complex. Adding the attractive ground-state interaction energy to that of the repulsive excited state predicts a blue-shift, relative to that of the free halogen molecules, of ≈1600 cm⁻¹ for H₂O−Cl₂ and ≈2000 cm⁻¹ for H₂O−Br₂. These vertical blue-shifts for the dimers are greater than the shift of the band maximum upon solvation of either halogen in liquid water.

I. Introduction

In 1976, the first high-resolution spectroscopy was performed on the dimer formed by combining hydrogen fluoride and chlorine fluoride.[1] It was found that the two monomers are not connected by a hydrogen bond, as expected, but by a bond between the fluorine atom of HF and the chlorine atom of ClF. The Cl−F−H bond angle suggested electron-pair donation from the hybridized lone pair electrons on HF into the σ^* acceptor orbital on the end of the ClF.[2] Subsequently, Legon and colleagues have studied a wide variety of dimers in which electron pairs are donated to the σ^* acceptor orbital of a dihalogen molecule.[3,4] They have proposed that such bonds be referred to as "halogen bonds"[5,6] to denote that, like hydrogen bonds, they are significantly stronger than typical van der Waals and electrostatic bonds. The relevance of such bonding has also been discussed in terms of the supramolecular structures of halocarbons in the solid phase.[7] Recently, there has been a surge in interest in the interaction between halogens and water due to the importance of heterogeneous chemistry in the atmosphere.[8] Also, new spectroscopic information has become available regarding both the perturbation of halogen excited states by water[9−11] and the ultrafast dynamics of bromine molecules in contact with water.[12] To date, the difficulty of performing accurate ab initio calculations for H₂O and Cl₂,[4]
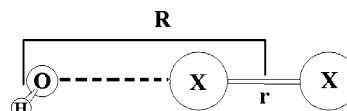

Figure 1. Coordinates used for defining the potential energy surfaces.

and for H₂O and Br₂,[3,13,14] has limited the accuracy and detail of the theory available for interpretation of the experimental results. Schofield and Jordan recently performed accurate calculations, including excited states, for chlorine molecules in hydrate cages,[15] but a limited range of geometries was investigated. This paper reports a two-dimensional study of the H₂O−Cl₂ and the H₂O−Br₂ interactions, including valence excited states, for the purpose of interpreting the spectroscopic studies.

Along with the surprisingly strong H₂O−X₂ ground-state bond energy, the band shifts for excitation to the valence band electronic transitions are extremely large. For Cl₂,[11] Br₂,[9] and I₂,[10] the peak of the UV−vis absorption band is blue-shifted by 550, 1730, and 3000 cm⁻¹, respectively, in going from the gas phase to aqueous solution. Interestingly, the shifts are significantly smaller in clathrate hydrate cages. Kerenskaya et al. have attributed the large aqueous blue-shift to the strong stabilization of the ground state and destabilization of the excited state by the nearest-neighbor interaction with water.[9] Valence electronic excitation of halogen molecules promotes an electron from the π^* orbital, perpendicular to the halogen bond, to the

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TABLE 1: Ab Initio and Experimental Geometries of the Cl$_2$−H$_2$O Complex and the Br$_2$−H$_2$O Complex[a]

Ab Initio and Experimental Geometries of the Cl$_2$−H$_2$O Complex

| | theory | | |
	MP2/AVDZ	MP2/AVTZ	experiment[b]
r_1	0.966	0.962	
r_2	2.762	2.771	2.8479
r_3		2.008	
θ	180.0	180.0	
∠H−O−H	104.1	104.4	
α	47.7	49.0	43.4

Ab Initio and Experimental Geometries of the Br$_2$−H$_2$O Complex

| | theory | | | |
	MP2/ 6-311+G(d, p) [c]	MP2/AVDZ [d]	(MP2/AVTZ)	experiment[b]
r_1		0.967	0.963	
r_2	2.826	2.791	2.797	2.8506
r_3	2.318		2.301	
θ	179.7	179.2	179.5	
∠H−O−H	103.9	105.0	104.5	
α		45.8	49.0	46.8

[a] Distances are in angstroms and angles are in degrees. [b] Reference 4. [c] Reference 13. [d] Reference 3.

$\sigma*$ orbital that acts as an electron acceptor for formation of the H$_2$O−X$_2$ bond. To analyze this hypothesis, we have calculated the interaction energy between H$_2$O and Cl$_2$ and H$_2$O and Br$_2$ as a function of both the halogen bond length and the H$_2$O−X$_2$ distance. Not only are the well depths significantly greater than would be expected for simple van der Waals and electrostatic bonding, but also the interaction energy is a strong function of the interhalogen bond length. The implications of these results for the UV−vis absorption spectra of halogen molecules interacting with water are discussed.
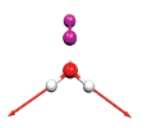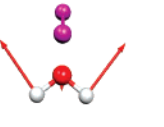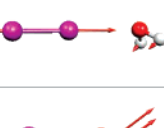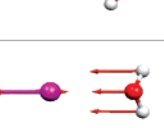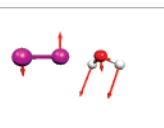
II. Methodology

Our aim is to provide a set of potential energy surfaces (PES) for H$_2$O−Cl$_2$ and H$_2$O−Br$_2$ to serve as a basis for analyzing the halogen electronic spectra when they are perturbed by water. Since bonding to water molecules induces significant charge polarization within the halogen molecules, it is important to study the halogen states as a function of the water−halogen distan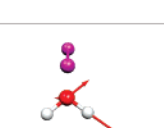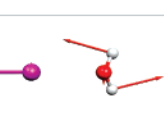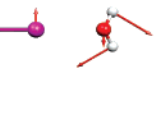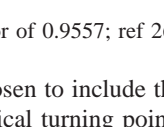ce as well as the effect on the dipole transition surfaces. The two strongest transitions in UV−vis spectra of the halogens are the B$^3\Pi_{0u}$ ← X$^1\Sigma^+_g$ and the C$^1\Pi_{1u}$ ← X$^1\Sigma_g$ transitions connecting the ground state to two of the spin orbit states that correspond to exciting an electron from the $\pi*$ orbital perpendicular to the halogen bond to the $\sigma*$ orbital along the molecular axis. In this preliminary study, spin−orbit effects are neglected, and the valence excited states were obtained as the lowest-energy triplet and $^1\Pi$ states, respectively.

First, we performed full geometry optimization and harmonic frequency analysis of the ground state at the MP2 (Møller-Plesset second-order perturbation theory) level of theory together with the AVTZ (augmented correlation consistent polarized valence triple-ζ) basis set. As previously reported,[3−5] both dimers have a nearly linear X−X−O arrangement, with the hydrogen atoms of the water molecule symmetrically bent off the X−X−O axis, as shown in Figure 1. The overall symmetry of the complexes is C_s. Next, we constructed two-dimensional surfaces (2D-PES) by varying the halogen molecule internuclear distance and the center-of-mass distance between the monomers while fixing all other geometrical parameters at their equilibrium values. The potential energy surfaces were calculated at the CCSD(T)[16] (coupled cluster singles and doubles with perturbation evaluation of triples) level of theory in order to achieve high accuracy. Test calculations with the AVQZ (augmented correlation consistent polarized valence quadruple-ζ) basis were also performed. For the $^3\Pi_u$ state, leading to ^{3}A′ and ^{3}A″ states in the complex, the RCCSD(T)[17] could be employed since both are the lowest-energy triplet states of their symmetry type. For the $^1\Pi_u$ state, leading to ^{1}A′ and ^{1}A″ states in the complex, we switch to the MR-AQCC (multireference average quadratic coupled cluster) method.[18] The main reasons for adopting the change of method are now briefly mentioned. In the present work we are mainly concerned with the properties of the A′ states although, as pointed out below, some preliminary calculations on the A″ states have also been performed. The ^{1}A′ state of the complex correlating with the $^1\Pi_u$ state of the dihalogen corresponds to an excited state of this symmetry; therefore, a change to multireference methodology is required. Also, we are interested in calculating transition dipole moments from the ground to the first excited ^{1}A′ states and these require again excited-state methodology. Each of the surfaces was calculated at the same 175 point grid of geometrical parameters, consistent with a Franck-Condon view of the transitions. For the halogen

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TABLE 2: Harmonic Vibrational Frequencies (cm^{-1}) and IR Intensities for the Cl$_2$−H$_2$O and the Br$_2$−H$_2$O Complexes

symmetry	normal modes of vibration	Cl$_2$-H$_2$O calculated[a] (relative intensities)	expt.[b]	Br$_2$-H$_2$O calculated[a] (relative intensities)	expt.[c]
A′	ν_1	3641 (9)	3637	3636 (12)	3631
	ν_2	1554 (33)	1587	1553 (31)	1586
	ν_3	530 (3)	543[c]	310 (3)	309
	ν_4	163 (100)		190 (100)	
	ν_5	105 (0)		107 (0)	
	ν_6	71 (0)		56 (0)	
A″	ν_7	3760 (40)	3723.6 3739.7	3756 (40)	3719
	ν_8	200 (7)		233 (5)	
	ν_9	60 (0)		52 (0)	

^{a} After reduction with a scaling factor of 0.9557; ref 26. ^{b} Reference 24. ^{c} Reference 25.

coordinate, the grid points were chosen to include the equilibrium distance and to span the classical turning points for $v = 0, 1,$ and 2. For the H$_2$O−X$_2$ distance, 25 points were spread from the repulsive wall out to 16 Å to obtain a smooth representation of the interaction potential. The counterpoise method[19] has been applied throughout to correct the basis set superposition error.[20] All calculations were performed with Molpro2002.3.[21] Additionally we calculated the transition dipole moment surface for the dipole allowed transition between ground and singlet excited state.

For the MR-AQCC calculations a few comments are in order. The active space and electrons are defined by including all the valence orbitals and electrons of the constituent atoms. Since the degeneracy of the $^1\Pi_u$ electronic state is broken upon complexation leading to ^{1}A′ and ^{1}A″ electronic states, we performed a state-average procedure for these states during the orbital optimization. Since we are using different levels of theory for the calculation of ground and singlet excited states, it is necessary to scale the results so that the total energies are comparable. To achieve this, we calculated the ground-state grid with the MR-AQCC method to obtain a consistent excitation energy for all grid points: $T(r,R)^{AQCC} = E_C(r,R)^{AQCC} - E_X(r,R)^{AQCC}$. We then used these T values to adjust the C state

surface relative to the CCSD(T) ground-state surface: $E_C(r,R) = E_X^{CCSD(T)} + T(r,R)^{AQCC}$.

III. Results and Discussion

In Table 1, we present the main geometrical parameters for the optimized structures of the chlorine and bromine complexes, respectively. The new results are compared to previous calculations using smaller basis sets[4] and to experimental results from microwave spectroscopy.[3,4] The main effects of using a larger basis set in the present calculations, triple-ζ versus double-ζ, are a slightly longer O–X distance and a larger tilting angle of the water C_{2v} axis with respect to the line of centers O–X–X. Considering that experimental values represent vibrational averages, the agreement between experiment and theory is good. A more sensitive test of the adequacy of basis set and level of correlation is given by the dimer binding energies. Preliminary calculations indicated the need for using augmented correlation consistent valence basis sets, so we computed the binding energies using the AVDZ, AVTZ, and AVQZ series with both MP2 and CCSD(T) treatments of correlation. We found that MP2 overestimates the binding energies by roughly 5%, and the effect of increasing the basis is a monotonous increase of the binding energy. The corresponding H_2O–Cl_2 well-depth values at the CCSD(T) level using AVDZ, AVTZ, and AVQZ basis sets are: 865, 917, and 982 cm^{-1}. The H_2O–Br_2 well-depth values are 1149, 1182, and 1273 cm^{-1}. For H_2O–Br_2, Ramondo et al.[13] obtained a well depth of 1421 cm^{-1} (20% overestimate) using density functional theory with a B3LYP/6-311+G(d,p) functional and Pathak et al.[14] obtained a value of 2046 cm^{-1} (78% overestimate) using a BHHLYP/6-31++G-(d,p) functional. This strong dependence on the functional and the basis set suggests that further calculations are required to test the adequacy of density functional methods for these systems. Interestingly, the MP2 results using moderate-size basis sets provide a reasonable description. In particular, for the study of larger aggregates the combination of AVDZ and MP2 level of correlation may be sufficient.

In any case, the well depths are considerably larger than for corresponding van der Waals dimers. For instance, well depth for linear Ar–I_2 is 250 cm^{-1}.[22] The H_2O–X_2 well depths are somewhat less than those of typical hydrogen bonds. For instance, the H_2O dimer well depth is 1756 cm^{-1}.[23] Table 2 gives the calculated harmonic frequencies of both complexes and compares them to the available experimental data.[24,25] The theoretical values have been scaled to compensate for anharmonicity and limitations on the ab initio methodology, following the suggestions given in ref 26. For the covalent bond motions the agreement with experimental data is good. However, note that the experimental values are for matrix isolated molecules, not for isolated dimers. Unfortunately there is no direct experimental information on the van der Waals modes even though several of them have large intensities. Legon et al. reported the harmonic intermolecular stretching force constants obtained via an analysis of centrifugal distortion constants.[3] Transforming Legon's reported force constants to wavenumbers (assuming a pseudo-diatomic to calculate the reduced mass) lead to the values 97 and 102 cm^{-1} for H_2O–Cl_2 and H_2O–Br_2, respectively, which compare well with our estimates of 105 and 107 cm^{-1} as given in Table 2.

In Table 3, the monomer harmonic vibrational frequencies are compared to those of the analogous modes in the complexes. As expected, the halogen bond is weakened due to donation of oxygen lone-pair electron density into the halogen σ^* orbital, resulting in a decrease of its vibrational frequency. For the water

TABLE 3: Dihalogen Bond (X–X) and H_2O Intramolecular Harmonic Frequencies (cm^{-1}) in the Isolated Monomers and the Dimers, and Shifts $\Delta = (\nu_{monomer} - \nu_{complex})$

		isolated monomer	Cl_2–H_2O[d]	Δ	Br_2–H_2O[e]	Δ
			Experimental			
Cl_2		559[a]	543[e]	16		
Br_2		325[b]			309	16
H_2O	ν_1	3657[c]	3637	20	3631	26
	ν_2	1595[c]	1587	7	1586	8
	ν_3	3756[c]	3723	32	3719	36
			Calculated[f]			
Cl_2		545	530	15		
Br_2		319			310	9
H_2O	ν_1	3652	3641	11	3636	16
	ν_2	1556	1554	2	1553	3
	ν_3	3772	3760	12	3756	16

[a] Reference 33. [b] NIST Chemistry Webbook (http://webbook.nist-.gov/chemistry) http://srdata.nist.gov/ cccbdb/expvibs2.asp. [c] References 34 and 35. [d] Reference 24. [e] Reference 25. [f] After reduction with a scaling factor of 0.9557; ref 26.

moiety also, each of the normal-mode frequencies decreases upon complex formation with the halogen. In each case, the calculations reproduce the experimental trend but underestimate the experimentally observed shifts. Again, we note that the experimental results are for matrix isolated species. Upon complexation, the halogen internuclear distance increases by roughly 0.01 Å, the O–H distances increase by a few thousandths of an angstrom, and the bending angle in water increases by a few tenths of a degree, consistent with the relatively weak nature of the interaction. Just as the well depth is larger for H_2O–Br_2 than for H_2O–Cl_2, so are perturbations to the structures of the isolated monomers. A Mulliken analysis of the MP2 charge distribution in the complexes shows a polarization of the halogen molecule with the atom closer to oxygen acquiring a slightly positive charge (Cl ≈ 0.05, Br ≈ 0.06) and the other halogen atom acquiring a similar but negative charge. For bromine the charge transfer is larger than for chlorine, but it is still much smaller than the polarization for both. This result is in agreement with the analysis of Legon et al.[3,4] based on nuclear quadrupole coupling constants, which predicts a negligible intermolecular electron transfer but a small intramolecular electron transfer which increases as a function of the polarizability of the dihalogen. It seems then that there is a general agreement that the charge transfer for these systems is small (≤ -0.01 au), regardless of the methodology used to estimate it.[27–29]

The properties discussed so far all belong to the ground electronic states. Both the $^3\Pi_u$ and $^1\Pi_u$ excited electronic states of the halogen are formally obtained by a π_g-to-σ_u single-electron excitation from the ground electronic state. In Table 4, we present some of the spectroscopic properties of the isolated diatomic excited states as a test for the adequacy of the methodology used. Since we do not include spin–orbit effects in order to compare with experiment we have used the average of the A and B state excitation energies to compare with the calculated $^3\Pi_u$ state, whereas for the $^1\Pi_u$ state we use the C state properties. There is an overall good agreement between theory and experiment for both dihalogens. The largest differences are observed for the T_e values of the $^3\Pi_u$ state; the calculations underestimate the experimental value. In the case of T_{vert}, it is observed that for Cl_2 the agreement is better than for Br_2, reflecting the importance of spin–orbit coupling for the latter. However, there is also considerable uncertainty in the experimental values of T_{vert} since they are obtained by fitting the repulsive part of the curve to continuous spectra.[30] Besides the

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TABLE 4: Spectroscopic Constants of Cl$_2$ and Br$_2$[j]

	Cl$_2$						Br$_2$					
	r_e(Å)		T_{vert} (cm^{-1})		T_e (cm^{-1})		r_e (Å)		T_{vert} (cm^{-1})		T_e (cm^{-1})	
	calcd	exptl	calcd	exptl	calcd	exptl	calcd	exptl	calcd	exptl	calcd	exptl
X	2.02	1.99[a]	0	0	0	0	2.32	2.28[a]	0	0	0	0
$^3\Pi_u$	2.43	2.43[b]	24028 (25088)	24766[i]	16802 (17589)	17630[e]	2.69	2.68[f]	18822 (19897)	21302[g]	14170 (14835)	14852[h]
$^1\Pi_u$			30244 (31443)	30562[c] 30726[d] 30780[i]					23190 (24353)	24353[g]		

[a] Reference 36. [b] Reference 37. [c] Reference 38. [d] Reference 39. [e] Average value of results coming from refs 36 and 40. [f] Reference 41. [g] References 42 and 43. [h] Average value of results coming from ref 36. [i] Reference 30. [j] Experimental T_e values for the triplet state correspond to averages of the spin−orbit A and B states; values in parentheses refer to the AVQZ basis set. See text for details of calculations.

TABLE 5: Equilibrium Distance for X−O and Binding Energies (D_e) for the Ground, First Excited Triplet, and Singlet States of the X$_2$−H$_2$O Complexes[a]

	Cl$_2$−H$_2$O		Br$_2$−H$_2$O	
state	R_{Cl-O} (Å)	D_e (cm^{-1})	R_{Br-O} (Å)	D_e (cm^{-1})
X	2.82	917	2.87	1182
B	3.60	95	3.67	139
C	3.67	67	3.77	107

[a] See text for calculation details.

neglect of spin−orbit coupling (and other relativistic effects in the case of bromine) the difference might be due to the inherent difficulty in the ab initio calculation of dihalogen systems, as has been emphasized in previous theoretical studies.[31,32] We performed larger calculations with the AVQZ basis, and indeed there is a noticeable improvement (the corresponding values are given in parentheses in Table 4).

The change in the electronic charge distribution on the halogen molecules when going from the ground state to the excited states should have a significant effect in the intermolecular interactions between the halogen and the water molecule. In Table 5, we present the H$_2$O−X$_2$ binding energies and O−X equilibrium intermolecular distance for the ground and excited electronic states for X−X distances fixed at the ground-state values. As discussed above, the ground electronic state is characterized by a moderate binding energy—significantly stronger than a typical van der Waals interaction but somewhat weaker than a typical hydrogen bond. For both excited electronic states there is a large increase in the intermolecular distance and a corresponding large decrease in binding energy. The effect can be easily explained on the basis of an increased Pauli repulsion in the excited states due to the half-occupancy of the σ_u orbital. In effect, the excited-state bond lengths and well depths are what might have been expected for simple van der Waals bonding. Given that the $^1\Pi_u$ excited singlet state was calculated with MRAQCC whereas the $^3\Pi_u$ was calculated with the more reliable RCCSD(T), the differences in binding energy between the two states might be smaller than those predicted here. The information presented for the excited states corresponds to the A′ spatial symmetry complexes. For the chlorine complex we also calculated the ^{3}A″ surface to estimate how large the differences between them would be. The ^{3}A″ complex shows an O−Cl internuclear distance 0.075 Å longer and a binding energy 23 cm^{-1} smaller than the more stable ^{3}A′ state. These are subtle effects that can be measured via spectroscopy. A more detailed study including the A″ states and spin−orbit coupling effects is underway.

We now present information regarding the dependence of the intermolecular potential on the halogen internuclear separation. In Figure 2a−c, we show cuts of the interaction potential surfaces for five values of the dihalogen internuclear distance

for each of the three electronic states of the chlorine complex. The dichlorine distances span the range of vibrational motion for $v = 0$, 1, and 2 in the ground electronic state. For each state there is a strong dependence of the intermolecular potential on the dihalogen vibrational coordinate. In general, the dependence has a monotonous behavior: the H$_2$O−X$_2$ attraction increases as the halogen distance increases. For the ground state, the well depth varies by 70%, comparing the largest to the smallest value over the selected distance range. For the excited states the effect is even more dramatic: a purely repulsive interaction is obtained for small X−X distances, and the maximum well-depth value is several times deeper than that at the reference geometry. The trends for the excited states are obviously complicated by the fact that the interhalogen interaction is also complicated for these states. Still it is worth pointing out that the observed behavior is consistent with a decrease of the σ^* orbital energy upon stretching the halogen bond, thus becoming a better acceptor of charge from the water lone pair.

Figure 3a−c presents the analogous results for the bromine complex. The range of well depths for the ground electronic state is less for H$_2$O−Br$_2$ than for H$_2$O−Cl$_2$, but this is partly due to the fact that the vibrational amplitudes are smaller for the heavier bromine moiety. The maximum H$_2$O−X$_2$ excited-state well depths are similar for H$_2$O−Br$_2$ and for H$_2$O−Cl$_2$. Clearly, the strong X−X dependence of the H$_2$O−X$_2$ interaction potentials will be very important for an accurate prediction of the spectra of the complexes.

Given the strong dependence of the H$_2$O−X$_2$ interaction on internuclear separation, and the polarization of the halogen by the interaction with water, it seems likely that the transition dipole surfaces are also quite interesting. These are presented for the spin-allowed excitation to the A′ component of the C state in Figure 4a−b. In the case of chlorine the transition moment decreases upon stretching the Cl−Cl bond, also corresponding to an increased H$_2$O−Cl$_2$ attraction, up to the equilibrium value. For higher values of the bond distance there is a stable zone, but with a slight decrease of the transition dipole. Thus it appears that Franck-Condon excitation may tend to be somewhat localized toward the inner turning point of the Cl−Cl stretch. With respect to the intermolecular distance, the transition dipole decreases upon approach of the monomers passing through a minimum. It is interesting to notice that, roughly speaking, the quenching of the transition dipole is correlated with an increasing attraction of the monomers.

The case of bromine is illustrated in Figure 4b. Regarding the vibrational dependence, it is qualitatively similar to the case of chlorine but the effects are stronger. Also in this case there is a monotonous decrease of the transition dipole upon stretching the bromine molecule. The intermolecular distance dependence is similar to the case of chlorine. again showing a correlation
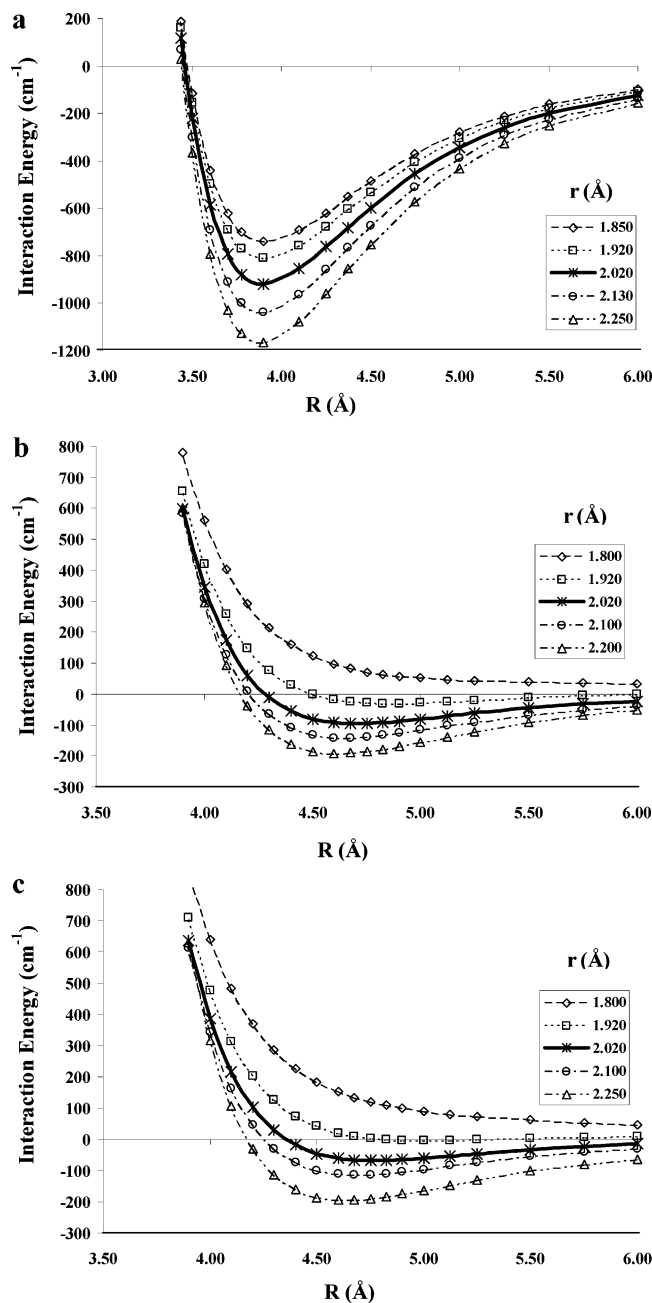
Figure 2. (a) Interaction energies as a function of intra- and intermolecular degrees of freedom for the ground state of the Cl_2-H_2O complex at CCSD(T)/AVTZ level of theory. (b) Interaction energies as a function of intra- and intermolecular degrees of freedom for the lowest triplet state of the Cl_2-H_2O complex ($^3A'$) at the RCCSD-(T)/AVTZ level of theory. (c) Interaction energies as a function of intra- and intermolecular degrees of freedom for the lowest singlet excited state of the Cl_2-H_2O complex ($^1A'$) at the MRAQCC/AVTZ level of theory.

Figure 3. (a) Interaction energies as a function of intra- and intermolecular degrees of freedom for the ground state of the Br_2-H_2O complex at the CCSD(T)/AVTZ level of theory. (b) Interaction energies as a function of intra- and intermolecular degrees of freedom for the lowest triplet state of the Br_2-H_2O complex ($^3A'$) at the RCCSD-(T)/AVTZ level of theory. (c) Interaction energies as a function of intra- and intermolecular degrees of freedom for the lowest singlet excited state of the Br_2-H_2O complex ($^1A'$) at the MRAQCC/AVTZ level of theory.

between quenching and increasing intermolecular attraction. We will further analyze the geometrical effects of the transition moment on the observed spectra in a future publication. It will be necessary to include spin−orbit coupling in the calculations to obtain nonzero values for the B ← X transition moments.

IV. Comparison with Spectroscopic Data

As stated in the introduction, the motivation for these calculations is twofold. First, since the nature of the interaction between water and halogen molecules is not well-known, it is useful to analyze the bonding in greater detail and with increased
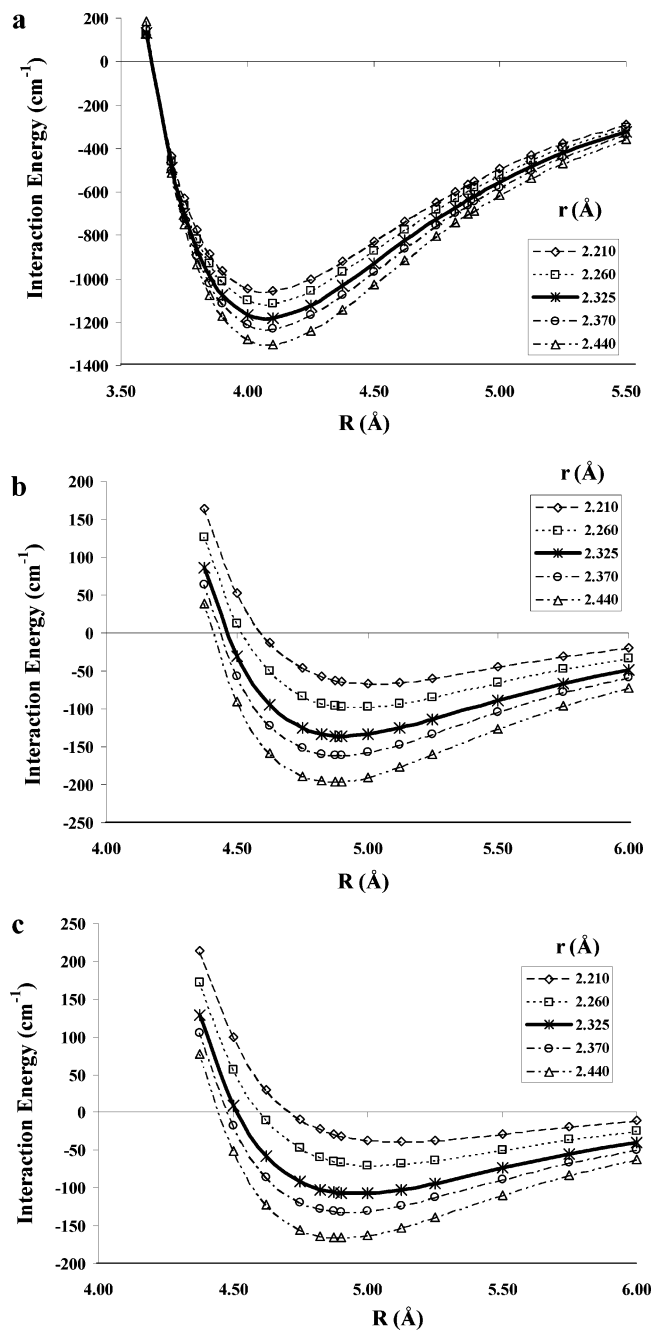
accuracy. To do this, we have calculated two-dimensional potentials for the ground state that yield the current best estimates for the well depths and also show that the water−halogen interaction is very sensitive to the interhalogen distance. The second motivation for these calculations is that new experimental results have become available for the spectroscopy of halogens in aqueous solution, amorphous ice, and clathrate hydrate cages.[9−11] Thus, we have presented the first ab initio results for the electronic excited states of the H_2O-Cl_2 and the H_2O-Br_2 dimers. Aiming for an eventual simulation of experimental spectra, we also reported two-dimensional poten-

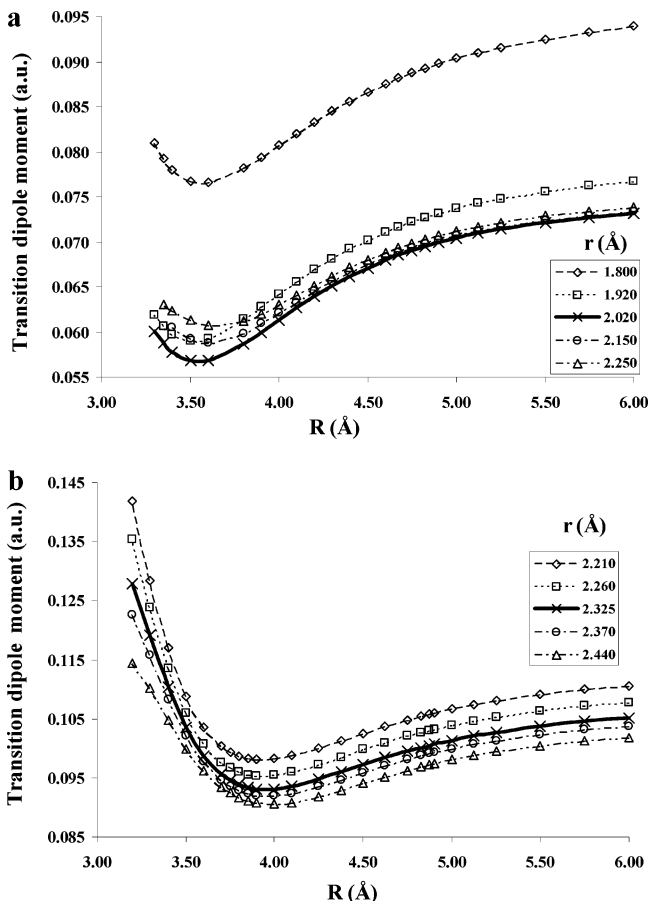2-D H₂O−Cl₂ and H₂O−Br₂ Potential Surfaces

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Figure 4. (a) Transition dipole moment from the ground to lowest singlet excited state of the Cl_2–H_2O complex as a function of intra- and intermolecular degrees of freedom at the MRAQCC/AVTZ level of theory. (b) Transition dipole moment from the ground to lowest singlet excited state of the Br_2–H_2O complex as a function of intra- and intermolecular degrees of freedom at the MRAQCC/AVTZ level of theory.

tials for the $^3\Pi$ and $^1\Pi$ excited states, and two-dimensional transition moments for the formally allowed $C^1\Pi_{1u} \leftarrow X^1\Sigma_g$ transition.

Even for H_2O–X_2 dimers, whose experimental electronic excitation spectra have yet to be determined, a theoretical simulation of the spectra will require a sophisticated simulation since the equilibrium geometry of the ground state lies below the repulsive regions of the excited-state potential, and since the vibrational amplitudes on the ground-state potential are significant. Also, as discussed above, the transition moment functions for these spectra are quite sensitive to geometry. Although the calculations presented here may serve as a basis for such calculations, they are beyond the scope of this paper. Here, we present a preliminary interpretation of the new spectra by analyzing the vertical excitation energies of the two dimers from the equilibrium internuclear geometry, comparing this to that of the free halogens, and finally, briefly discussing how the calculated blue- shifts relate to experimental measurements.

Adding the H_2O–X_2 well depth and the excited-state repulsion at the ground-state equilibrium geometry, and subtracting the analogous difference for the free halogen, yields a first estimate of the spectral blue-shift. The values obtained, $\approx$1600 cm^{-1} for H_2O–Cl_2 and $\approx$2000 cm^{-1} for H_2O–Br_2, are remarkably large for a single solvent molecule. (More detail is given in Table 6.) These values are even larger than the experimental blue-shifts for aqueous solution, also given in Table 6, which are obtained from the band maxima. Since the

TABLE 6: Blue-Shifts (cm⁻¹) of the Absorption Maximum for the Complexes and Condensed Phases of Water

	C−X	B−X
H_2O–Cl_2 interaction	1554	1516
aqueous solution[a]	550	
H_2O–Br_2 interaction	1916	1877
aqueous solution[b]	1730	1760
amorphous ice, $T = 120$ K[b]	1710	1640
Br_2 hydrate ($5^{12}6^2$,$5^{12}6^3$)[b]	880	890

[a] Reference 11. [b] Reference 9.

band maxima are controlled by Franck-Condon factors, the comparison we make here is appropriate. Corrections to this simple comparison will be discussed below. In the case of H_2O–Br_2 the calculated dimer blue-shift and the experimental values are about the same, within either the experimental uncertainty or the accuracy of the calculation. In the case of H_2O–Cl_2, the calculated dimer value is significantly larger than the experimental value.

That the calculated dimer blue-shifts are already equal to or larger than the entire aqueous solvent shifts is intriguing, and this suggests a variety of followup studies to this investigation. First, it would be really valuable to obtain data for the isolated H_2O–Cl_2 dimers for comparison to the calculations. Work is in progress to provide more sophisticated simulations of the spectra from the potentials and transition moment functions provided here. These include estimation of zero-point energy and vibrational motion effects by calculating ground-state vibrational wave functions, including the influence of the variation of the transition moment with geometry and including the effects of spin–orbit coupling. In the longer term, it may be possible to include more water molecules in the analysis. This will be especially challenging since mapping out a many-body potential will be quite difficult for this system, and the effects of dynamics on the spectrum will be crucial for a realistic analysis.

Summary and Conclusions

We have reported two-dimensional potential energy surfaces for the interaction between bromine and chlorine molecules with H_2O for the ground and two low-lying valence excited states. The combination of highly correlated ab initio methodology and extensive basis sets allowed us to provide the most reliable theoretical predictions on the complexes to date as well as the first reliable calculations for the excited electronic states of the dimers. The H_2O–X_2 intermolecular well depth is found to be much deeper and to occur at shorter distances for the ground state than for the excited electronic states. Also, each of the intermolecular potentials is found to depend strongly on the X−X distance, while the transition moment depends strongly on both degrees of freedom considered in the calculation. Comparison with experimental data indicates the reliability of our predictions. In particular, we stress the good agreement with results from rotational spectroscopy. In accord with previous theoretical studies and experimental modeling of nuclear quadrupole constants, our calculations predict a minor role for intermolecular charge transfer in the complexes. This is also reflected in the small geometrical changes and vibrational frequency shifts of the monomers upon complexation. There is, however, an important polarization of the X−X bond upon complexation with water.

Initial estimates for the blue-shifts in the H_2O–X_2 valence excitation spectra are made by adding the ground-state well depth and the excited-state repulsion at the equilibrium geom-

etry. In each case, the initial estimate for the dimer blue-shift is even larger than the blue-shifts observed in aqueous solution. The reasons for this overestimation are discussed, and further calculations to obtain more accurate values are in progress. While these calculations provide information to partially interpret the large solvent shifts for aqueous solutions of halogen molecules, they also make it clear that a complete modeling of the spectra will be a considerable challenge. In this respect, the inclusion of additional water molecules might be performed by taking advantage of the fact that a good description of the system can be obtained using MP2 methods.

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