Structure and Binding Energies of Monohydrated Cd and Cd^{2+}

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High-level ab initio calculations have been performed on the neutral $Cd{\cdot}H_2O$ complex, and the dication, $Cd^{2+}{\cdot}H_2O$. Effective core potentials (ECPs) are employed for cadmium, augmented with a large, flexible polarization space, which also includes diffuse functions. The calculated double ionization energy for Cd is within 0.03 eV of the experimental value, suggesting that the basis set is able to describe both Cd and Cd^{2+} well. For both complexes, three main structures were considered: C_{2v} with the cadmium atom interacting with the oxygen atom of H_2O; C_{2v} with the cadmium atom interacting with both hydrogens of H_2O; and planar C_s where the cadmium interacts with only one of the hydrogen atoms of H_2O. The global minimum for $Cd{\cdot}H_2O$ is found to be the trans C_s structure, whereas for $Cd^{2+}{\cdot}H_2O$, the charge−dipole interaction leads to the C_{2v} geometry, with the cadmium interacting with the oxygen atom of H_2O being the lowest in energy. Our best values for the binding energies, D_e, are: $Cd{\cdot}H_2O$, 134 cm^{-1} (0.4 kcal mol^{-1}); $Cd^{2+}{\cdot}H_2O$, 78 kcal mol^{-1}, employing the CCSD(T) method. We conclude that the $Cd^{2+}{\cdot}H_2O$ complex is stable with respect to charge transfer and should be observable; after correction for zero-point vibrational energy, the stability of $Cd{\cdot}H_2O$ is less certain from the results of the calculations.

I. Introduction

Cadmium is an element in Group 12 (group IIB), and hence Cd^{2+} is expected to be the most stable ion in solution, with the two 5s electrons being lost, leaving the closed-shell $\cdots 4d^{10}$ core. Thus, together with the other Group 12 elements, cadmium is often not considered as a transition metal. Cadmium is an especially noxious substance, being one of the five most toxic metals, and having a biological half-life of 10−30 years.[1]

In solution, it is the *hexaaquo* Cd(II) complex, which is the most stable form, and has been studied by Raman spectroscopy and ab initio calculations (HF and MP2 level, with 6-31G* and 6-31+G* basis sets), but the 1:1 complex was not considered.[2] The $Cd^{2+}{\cdot}(H_2O)_n$ complexes have been studied using HF, MP2, and density functional theory (DFT) methods.[3,4,5,6] Other studies include work on $Cd^{2+}(OH)_n$ ($n = 1-6$)[7] and work on cadmium complexed to larger ligands.[8] It is the purpose of the present work to investigate the 1:1 complexes of Cd and Cd^{2+} with a water molecule, which represent the most fundamental interactions between cadmium and water.

An interesting question is whether the isolated $Cd^{2+}{\cdot}H_2O$ complex will undergo charge transfer (to become $Cd^+{\cdot}H_2O^+$) because the second ionization energy of Cd is higher than the first ionization energy of H_2O.

II. Computational Details

The large number of electrons on Cd would make any all-electron calculation rather expensive, and so we elected to use effective core potentials (ECPs). As in our previous work employing ECPs, two types are used: the Los Alamos LANL2 one,[9] and the ECP28MWB one of Dolg and co-workers.[10] In each case, the valence basis set was either modified and extended, or completely redesigned. It is important, especially when looking at molecular complexes, that the basis set "behaves well" in the molecular, as well as the atomic environment. We took "behaving well" here to mean that there was a sensible wave function for cadmium (i.e., the expansion coefficients decayed smoothly, and there were no sudden positive/negative jumps), and that the basis set superposition error (BSSE) was "reasonable" in the complex (vide infra). For H_2O, standard basis sets were used, selected so that the quality of the basis sets on Cd and H_2O were balanced.

(i) Basis Set 1. For cadmium, the standard LANL2DZ basis set was employed, and augmented with a diffuse set of sp functions ($\zeta = 0.017$) and a set of diffuse d functions ($\zeta = 0.0826$); these were obtained by extending the most diffuse sp, and d functions from the standard LANL2DZ basis. Polarization functions were also added: d ($\zeta = 0.8$) and three f ($\zeta = 1.0$, 0.3333, 0.1). For this basis set, the ECP describes all electrons except the 5s and 4d valence electrons. Overall, this basis set may be designated LANL2[3s3p4d3f].

For H_2O, the standard 6-311++G(3df, 3pd) basis set was used.

The total number of basis functions is 128.

(ii) Basis Set 2. For cadmium, the ECP28MWB effective core potential was employed, where the M generally indicates that the neutral atom is used in the derivation of the ECP

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TABLE 1: First Single and Double Ionization Energies (eV) of Cd, Calculated Using Basis Sets 1−3 (see text for details)

level of theory	$Cd \rightarrow Cd^+$	$Cd \rightarrow Cd^{2+}$
MP2/basis set 1	8.920	25.300
QCISD/basis set 1	8.853	25.138
CCSD(T)/basis set 2	8.954	25.801
CCSD(T)/basis set 3	8.982	25.866
experiment[a]	8.991	25.895

[a] From ref 17.

(although ionized states were also used in the derivation of this potential) and WB implies the use of the quasirelativistic approach described by Wood and Boring,[11] which was used in ref 10 in order to derive the ECP. This ECP was developed by Dolg and co-workers,[10] with 28 electrons described by the potential (thus, the 4s, 4p, 4d and 5s electrons are treated as valence). The standard [6s5p3d] valence basis set, obtained from a [3,1,1,1,1,1/2,2,1,1,1/4,1,1] contraction was used, but augmented with the following:

one s function ($\zeta = 0.006\,333\,0$) − a ratio of 3.0 from the most diffuse s of the standard valence space;

one set of p functions ($\zeta = 0.01264$) − a ratio of 2.9 from the most diffuse p of the standard valence space;

four sets of d functions ($\zeta = 2.5, 1.0, 0.4, 0.025$);

four sets of f functions ($\zeta = 1.5, 0.5, 0.166\,667, 0.055\,56$);

three sets of g functions ($\zeta = 1.2, 0.4, 0.1333$).

Overall, this may be designated an ECP28MWB[7s6p7d4f3g] basis set. The basis set for H_2O was the standard aug-cc-pVQZ one, giving a total number of basis functions of 287.

(iii) Basis Set 3. Again, the ECP28MWB effective core potential was employed, but this time the basis set was completely redesigned (see below for rationale). The valence set added to the bare ECP was as follows:

one contracted *s* function to describe each of the 4s and 5s orbitals, these were derived from 15 even-tempered primitives, with a ratio of 2.0, ranging from $\zeta = 64.0 - 0.0039$;

one set of contracted p functions to describe the 4p orbital, this set was derived from 13 even-tempered primitives with a ratio of 2.0, ranging from $\zeta = 32.0 - 0.007\,812$;

one set of contracted d functions to describe the 4d orbital, this set was derived from 11 even-tempered primitives with a ratio of 1.8, ranging from 11.337 208 to 0.031 753.

The contraction coefficients for the above were obtained from a restricted Hartree−Fock calculation on the neutral cadmium atom, employing the (15s13p11d) basis set.

To these contracted functions were added the following:

nine even-tempered s functions with a ratio of 2.6 and $\zeta = 9.139\,52 - 0.004\,376\,59$;

nine even-tempered p functions with a ratio of 2.5 and $\zeta = 7.8125 - 0.005\,12$;

seven even-tempered d functions with a ratio of 2.65 and $\zeta = 2.791\,443\,8 - 0.008\,060\,34$;

five even-tempered f functions with a ratio of 3.0 and $\zeta = 2.7 - 0.033\,333\,3$; and

four even-tempered g functions with a ratio of 3.5 and $\zeta = 2.5 - 0.058\,309$

Overall, this basis set may be designated ECPMWB-[11s10p8d5f4g]. Together with the standard aug-cc-pVQZ basis set for H_2O, this gives a total number of basis functions of 324.

All geometry optimizations and harmonic vibrational frequency calculations were performed using Gaussian98.[12] The CCSD(T) calculations were carried out with MOLPRO2000.[13] (With the LANL2 ECP the $4d^{10}5s^2$ electrons are valence and are correlated for Cd, clearly for Cd^{2+} only the $4d^{10}$ were correlated; with the ECP28MWB ECP the $4s^24p^64d^{10}5s^2$ are valence and are correlated; in all cases, for H_2O only the O 1s electrons are frozen.) Basis set superposition error (BSSE) was accounted for by the full counterpoise correction of Boys and Bernardi,[14] fixing the geometry of water to that in the optimized complex. (The effect of geometry relaxation owing to BSSE has been investigated by a number of authors, see for example, refs 15 and 16, and is generally small.)

III. Results and Discussion

(i) Calculated Ionization Energies. One simple way to confirm that the basis set used for cadmium is performing well for Cd and Cd^{2+} is to calculate the ionization energy for the process

$$Cd \rightarrow Cd^{2+} + 2e^- \qquad (1)$$

for completeness, we also calculated the ionization energy for the process

$$Cd \rightarrow Cd^{+} + e^- \qquad (2)$$

The results are given in Table 1 and compared to the experimental values from Moore.[17] As may be seen, the agreement is very good, with that for the best calculation, CCSD(T)/Basis Set 3, being particularly encouraging. Energy changes, such as ionization energies, are notoriously difficult to calculate accurately owing to the large relaxation and correlation energy changes, and agreement to within 0.03 eV for a double ionization energy is notably satisfactory. Consequently, we were confident that our basis sets can describe both moieties well.

(ii) $Cd^{2+}\cdot H_2O$. *(a) Optimized Geometry.* For $Cd^{2+}\cdot H_2O$, optimizations were commenced at the three geometries: C_{2v} (Cd···OH_2); C_{2v} (Cd···H_2O); and C_s (Cd···H−OH). The latter two geometries optimized back to the first at the MP2/Basis Set 1 level of theory. In the case of the C_{2v} geometry with Cd^{2+} interacting with both hydrogens, the water molecule inverted, passing through a linear geometry to get back to the C_{2v} geometry with Cd^{2+} interacting with the O atom. The optimized geometries and harmonic vibrational frequencies for $Cd^{2+}\cdot OH_2$ are given in Table 2. As may be seen, the Cd−O bond length increases slightly on going from the MP2 to the QCISD level, as expected, because more electron correlation energy will allow the repulsion to be described better. The Cd−O bond length is notably short, which is not entirely unexpected for a charge−dipole interaction, especially when the charge is +2. The parameters for the water molecule are relatively unchanged. Harmonic vibrational frequencies were only calculated at the B3LYP and MP2 levels. As may be seen, the intermolecular ones are quite large indicating that the interaction energy is probably quite significant. Of note is that the MP2 total energies are lower than the QCISD total energies. In fact, for the two complexes considered in this work, it was observed that the MP*n* ($n = 2-4$) series is quite oscillatory (but converging), with the MP2 energy being lower than the MP3 one, and the MP4 energy being lower than the MP3 one, but not as low as that at the MP2 level.

The geometry of the $Cd^{2+}\cdot H_2O$ complex is very similar to that of the $Zn^{2+}\cdot H_2O$ complex, which has been studied by a number of workers (see, for example, refs 18 and 19). In ref 18, MP2 calculations were performed using a double-ζ valence basis set with a p polarization function: the $Zn^{2+}\cdots O$ bond length was calculated to be 1.90 Å, with a charge of +1.74 on the Zn atom, −0.89 on the O atom, and +0.57 on the H atoms. In ref 19, B3LYP calculations were employed with a double-ζ

TABLE 2: Optimized Geometry and Harmonic Vibrational Frequencies for $Cd^{2+}·H_2O$ employing Basis Set 1 (b_2 Vibrations Are In-plane)

level of theory	E_{tot}/E_h	R_{Cd-O}/Å	R_{O-H}/Å	$\angle_{HOH/°}$	frequencies/ cm^{-1}
B3LYP	−123.741 148	2.117	0.976	107.9	284(b_1), 432(a_1), 675(b_2), 1642(a_1), 3627(a_1), 3688(b_2)
MP2	−122.441 551	1.946	0.973	107.4	535(b_1), 547(b_2), 634(a_1), 1650(a_1), 3673(a_1), 3732(b_2)
QCISD	−122.429 412	1.967	0.970	107.2	

TABLE 3: Computed Total Energies, E_{Tot}, and Interaction Energies, ΔE, for the Complex Formation of $Cd^{2+}(OH_2)$ at the CCSD(T)//QCISD/Basis Set 1 Geometries

	basis set 2		basis set 3	
	CCSD	CCSD(T)	CCSD	CCSD(T)
E_{tot}/E_h	−242.981 528	−243.004 381	−243.187 400	−243.214 691
ΔE(CP)/kcal mol^{-1} [a]	−76.3	−77.3	−76.6	−77.8

[a] Full counterpoise correction employed − see text.

basis set, and very similar results were obtained to those of ref 18. In both cases, the binding energy was calculated giving values of 95 and 102 kcal mol^{-1}, respectively. Comparing the results for $Cd^{2+}·H_2O$ in Table 2, it may be seen that the B3LYP and QCISD results are in reasonable agreement as far as the geometry is concerned, suggesting that the B3LYP method is reasonably reliable for optimized geometries, which is in disagreement with the conclusions of ref 20 where it was concluded hybrid functionals yielded M^{2+}·ligand bond lengths that were too short. The calculated Mulliken charges at the QCISD/Basis Set 1 level of theory were +1.64(Cd), −0.80-(O), and +0.58(H), which are very similar to those obtained by other workers for $Zn^{2+}·H_2O$.

It is interesting to compare the geometry of isolated water at the QCISD/Basis Set 1 level of theory, with that of the water in the complex. The geometry of water at this level of theory is $R_{OH} = 0.957$ Å, and $\angle_{HOH} = 104.3°$. Thus, in the $Cd^{2+}·H_2O$ complex, the water bond angle has opened out, suggesting that charge transfer has occurred, leading to a lowering of the lone-pair/OH-bond repulsion, and so an opening out of the HOH bond. This is confirmed by the calculated Mulliken populations, which, in isolated water, indicate charges of −0.94(O) and +0.47(H). Such effects have also been seen in larger $M^{2+}·(H_2O)_n$ complexes.[18]

(b) Binding Energies. Single-point energies were calculated at the CCSD and CCSD(T) levels of theory employing the QCISD/Basis Set 1 geometry, with the results given in Table 3. It is immediately apparent that the binding energies are significant at ca. 3.5 eV, again reflecting the significant charge density of the Cd^{2+}. The calculation with Basis Set 2 led to a substantial total BSSE (∼5.5 kcal mol^{-1}), which was almost entirely located on the Cd^{2+}. This also turned out to be the case for $Cd·H_2O$ and so the cadmium basis set was redesigned to give Basis Set 3, (description given in the Computational Details above). The BSSE was reduced to less than 1 kcal mol^{-1}, which is just over 1% of the interaction energy for $Cd^{2+}·H_2O$. It is apparent with both basis sets that the effect of triples is minimal here, with the CCSD and CCSD(T) values being very similar. The interaction energy after correction for BSSE (Table 3) may be seen to be very similar using both basis sets, indicating that for this complex, the valence basis set is close to saturation, and allows us to cite a value of 78 kcal mol^{-1} for the binding energy of $Cd^{2+}·OH_2$. Note that there may be some residual core-valence correlation energy effects which will alter this value; however, because the core electrons here are quite deep in energy, this effect on the final binding energy is likely to be small. This value may be compared to previous values of 74 kcal mol^{-1} (HF level)[4] and 73.8 kcal mol^{-1} (MP2 level).[5,6]

(c) Stability. The calculated binding energy of $Cd^{2+}·H_2O$, 78 kcal mol^{-1}, is significantly less than that of $Zn^{2+}·H_2O$ (ca. 100 kcal mol^{-1}, 4.3 eV). This is the general trend that one would expect, with the effective nuclear charge as experienced outside an atom or ion being reduced with the heaviness of the nucleus, owing to the shielding effect of the additional electrons. This in turn leads to more covalency in the bonding, which is also manifested in the slightly smaller Mulliken charge on the Cd dication compared to that of the Zn dication (although a direct comparison is not strictly possible since different basis sets have been employed in the different studies). The binding energy of $Cd^{2+}·H_2O$ is still significant at over 3.4 eV.

It is interesting to consider the following question: is $Cd^{2+}·H_2O$ observable? Initially, with such a large binding energy, one would conclude “yes”; however, the possibilities of charge transfer and intracluster reactions need to be considered. It is well-known that it is difficult to form isolated 1:1 $M^{2+}·H_2O$ complexes in the gas-phase because charge-transfer between M^{2+} and H_2O is expected to occur, leading to the formation of M^+ and H_2O^+, followed by rapid Coulomb repulsion. However, if M^{2+} is collided with H_2O slowly in the presence of a third body then formation of the $M^{2+}·H_2O$ complex is possible. Direct photoionization is also possible; however, as will be shown below, the minimum energy geometry of $Cd·H_2O$ is very different to that of $Cd^{2+}·H_2O$ and so the Franck−Condon factors are expected to be very small. It is also possible that reaction in small $M^{2+}·(H_2O)_n$ complexes can occur, and there are detailed studies of such processes by Kebarle[21] and Stace[22] and their co-workers on $Mg^{2+}·(H_2O)_n$. Such reactions are likely to have an activation energy barrier, and so have increased likelihood if there is energy present within the cluster.

Whether the $Cd^{2+}·H_2O$ complex is inherently stable or not depends on the position of the $Cd^+·H_2O^+$ curves and indeed it would be very interesting to examine the charge-transfer process. This process commences on a potential energy curve that correlates to two singlet dissociation products [$Cd^{2+}(^1S)$ and $H_2O(\tilde{X}^1A_1)$], but the charge transfer state ($^1B_1$) correlates with two doublet states [Cd^+ (^2S) and H_2O^+ ($\tilde{X}^2B_1$)], hence a curve crossing occurs between these two singlet surfaces. There will also be a $^3B_1$ $Cd^+·H_2O^+$ surface expected to be lying to lower energy than the corresponding singlet one (by Hund’s rules). An investigation of the position and nature of the singlet crossing point would be very interesting, but challenging theoretically—our initial attempts to look at this open-shell singlet led to convergence to the $Cd^{2+}·H_2O$ curve: this result directly indicates that the $Cd^{2+}·H_2O$ minimum lies lower in energy than the $Cd^+·H_2O^+$ curve. It is noteworthy that the $Cu^{2+}·Ar$, $Ag^{2+}·Ar$, and $Au^{2+}·Ar$ complexes have recently been observed in a mass spectrometer by Stace and co-workers,[23] and calculations presented in that work indicate that the minimum of the $M^{2+}·Ar$ potential lies below that of the charge-transfer minimum, even though at the dissociation limit charge transfer is

TABLE 4: Optimized Geometries and Harmonic Vibrational Frequencies for the Three Orientations of $Cd{\cdot}H_2O$ Employing Basis Set 1 (b_2 Vibrations are In-plane)

level	E_{tot}/E_h	intermolecular bond length/Å	R_{O-H}/Å	angles/°	frequencies/cm^{-1}
			trans-planar $Cd\cdots H-OH$ C_s		
B3LYP	−124.546 067	$R_{Cd-H} = 3.291$	$R_{O-H1} = 0.963$ $R_{O-H2} = 0.961$	$\angle_{HOH} = 105.0$ $\angle_{CdHO} = 179.0$	36(a′), 95(a′), 148(a″), 1625(a′), 3794(a′), 3896(a′)
MP2	−123.239 270	$R_{Cd-H} = 2.730$	$R_{O-H1} = 0.961$ $R_{O-H2} = 0.959$	$\angle_{HOH} = 104.0$ $\angle_{CdHO} = 168.6$	108(a′), 205(a′), 290(a″), 1626(a′), 3837(a′), 3962(a′)
QCISD	−123.224 991	$R_{Cd-H} = 2.788$	$R_{O-H1} = 0.959$ $R_{O-H2} = 0.957$	$\angle_{HOH} = 104.3$ $\angle_{CdHO} = 168.6$	
			$Cd\cdots OH_{2\ C2v}$		
MP2	−123.237 637	$R_{Cd-O} = 2.915$	$R_{O-H} = 0.961$	$\angle_{HOH} = 104.4$ $\angle_{CdOH} = 127.8$	85(b_2), 108(a_1), 190(b_1), 1621(a_1), 3834(a_1), 3958(b_2)
QCISD	−123.223 854	$R_{Cd-O} = 2.994$	$R_{O-H} = 0.958$	$\angle_{HOH} = 104.5$ $\angle_{CdOH} = 127.7$	
			$Cd\cdots H_2O$ C_{2v}		
MP2	−123.238 161	$R_{Cd-H} = 2.870$	$R_{O-H} = 0.961$	$\angle_{HOH} = 102.6$ $\angle_{CdHO} = 113.6$	138(a_1), 161(b_2), 263(b_1), 1639(a_1), 3844(a_1), 3950(b_2)
QCISD	−123.223 495	$R_{Cd-H} = 2.952$	$R_{O-H} = 0.958$	$\angle_{HOH} = 103.3$ $\angle_{CdHO} = 113.6$	

expected to be spontaneous—this is a consequence of the large charge-induced dipole interaction. Associated with the open-shell $^1B_1$ singlet for $Cd^+{\cdot}H_2O^+$ is the corresponding $^3B_1$ triplet and we performed a single-point energy calculation at the MP2/Basis Set 1 level of theory at the corresponding optimized geometry of $Cd^{2+}{\cdot}H_2O$. The result indicated that the (repulsive) $Cd^+{\cdot}H_2O^+$ $^3B_1$ state was ~140 kcal mol^{-1} (~6 eV) higher in energy. Given that the open-shell $Cd^+{\cdot}H_2O^+$ singlet is expected at even higher energies, then the amount of mixing between the two singlet states is expected to be minimal, and the $Cd^{2+}{\cdot}H_2O$ wave function is expected to be "clean" with no appreciable mixing from the other singlet state, and of single-reference character: a result supported by the small T1 CCSD(T) diagnostic ($T1 < 0.0103$ for $Cd^{2+}{\cdot}H_2O$; $T1 < 0.017$ for Cd•H2O)—see ref 24 for details of the T1 diagnostic. In addition, even if spin−orbit coupling leads to mixing of singlet and triplet character, the large energy gap between the $^3B_1$ state and the $Cd^{2+}{\cdot}H_2O$ state suggests that such mixing will be negligible in the vicinity of the $Cd^{2+}{\cdot}H_2O$ minimum but could be important near the crossing point of the two curves (making characterization of the charge-transfer process even more challenging).

The above result gives a qualitative picture of the curves involved here, without the need for detailed calculations on all three states involved. At the dissociation limits the $Cd^{2+} + H_2O$ asymptote lies 3.8 eV above the $Cd^+ + H_2O^+$ one. The $Cd^{2+}{\cdot}H_2O$ curve then decreases in energy by 3.5 eV to the minimum. Note that this indicates that the $Cd^{2+}{\cdot}H_2O$ minimum lies close to, but slightly above the $Cd^+ + H_2O^+$ asymptote. The $Cd^+{\cdot}H_2O^+$ curve, however, is repulsive, owing to the Coulomb repulsion between the two moieties, and so quickly increases in energy with decreasing R. This leads to a barrier to charge transfer from the $Cd^{2+}{\cdot}H_2O$ minimum to the $Cd^+{\cdot}H_2O^+$ curve, indicating the stability of internally cold $Cd^{2+}{\cdot}H_2O$; it is clear, however, that internally hot $Cd^{2+}{\cdot}H_2O$ may undergo charge transfer readily.

(iii) $Cd{\cdot}H_2O$. *(a) Optimized Geometry.* For $Cd{\cdot}H_2O$, again the three orientations discussed above were considered, and the optimized geometries at the MP2/Basis Set 1 level of theory are given in Table 4. All three structures were calculated to be minima at this level of theory (all real frequencies). The lowest energy structure corresponded to the *trans*-planar C_s one, which was also the case at the QCISD/Basis Set 1 level of theory. This structure has the Cd atom attached to one of the H atoms, with the C_{2v} isomer, $Cd\cdots OH_2$, being very close in energy. As the Cd atom moves between the two H atoms, it must pass over a barrier, but interestingly, at the MP2 level, the symmetric $Cd\cdots H_2O$ geometry was a minimum, although there is no guarantee that this does not become a saddle-point at higher levels of theory. As with $Cd^{2+}{\cdot}H_2O$, the MP2 energy is lower than the QCISD energy for these complexes, and again oscillatory (but convergent) behavior in the MPn series was observed. Again, the bond lengths increase going from MP2 to QCISD, suggesting that electron repulsion is an important consideration here.

It is interesting to compare these results for those of other neutral 1:1 complexes of a metal and H_2O (work up to 1999 on the spectroscopy and bonding of neutral and singly charged Group 1, 2, and 13 metal complexes containing water has been reviewed by Fuke et al.[25]). The geometry of $Li{\cdot}H_2O$ has been optimized at the HF/6-31++G** level of theory[26] and the reported minimum was a C_{2v} geometry with the Li atom interacting with the O atom of water; similarly, $Na{\cdot}H_2O$ was optimized at the HF/6-31+G* level of theory and again a similar C_{2v} minimum was found.[27] Some time ago, Watanabe et al.[28] reported the geometry of $Al{\cdot}H_2O$, and again, Al interaction with O in a C_{2v} arrangement was reported. $Be{\cdot}H_2O$ has also been studied[29,30] at the HF/STO-3G level and was found to have a nonplanar minimum, with the Be interacting with the O of water, but a planar minimum was obtained at the HF/3-21G level. We note, however, that none of these studies appears to have considered the metal interacting in a C_s arrangement, and so it is not clear whether, for these complexes, there might also be a global minimum with the metal interacting with a hydrogen atom. Also, the levels of theory employed are rather low, and no account of correlation energy was included, thus the electrostatic effects present will naturally be emphasized, and any dispersion effects will not be capable of being described.

In our previous study on the $Rn{\cdot}H_2O$ complex,[31] the global minimum was also with the Rn on a hydrogen atom in a C_s geometry; however, it has been reported that $He{\cdot}H_2O$ has a minimum with the He on the O atom in a C_{2v} geometry.[32] We rationalized this in terms of two competing effects: the dipole/induced-dipole interaction, which would favor the rare gas atom sitting on the oxygen atom, and the Pauli repulsion between the electron of the rare gas atom and the atoms in water. Clearly, He has less electrons than Rn, and despite being considerably less polarizable, it prefers to stay associated with the oxygen atom; Rn, however has a much larger number of electrons, and despite its higher polarizability, moves toward a hydrogen atom, where the Pauli repulsion is less, but it can still interact with the $\delta+$ charge present; such effects are clearly present here. A metal atom is naturally much more electropositive than a rare

TABLE 5: Computed Total Energies, E_{tot}, and Interaction Energies, ΔE, for Complex Formation of the Three Cd·H_2O Isomers at the CCSD(T)/Basis Set 3//QCISD/Basis Set 1 Geometries[a]

level	quantity	Cd···HO−H C_s	Cd···OH_2 C_{2v}	Cd···H_2O C_{2v}
CCSD	E_{tot}/E_h	−244.005 027	−244.004 814	−244.003 963
		[−244.005 193]	[−244.005 143]	[−244.004 436]
	ΔE_{tot}(CP)/cm^{-1}	−23.4	+58.0	+250.9
		[−20.3][b]	[−21.0][b]	[−2.8][b]
CCSD(T)	E_{tot}/E_h	−244.041 069	−244.040826	−244.040 223
		[−244.041 172]	[−244.041 088]	[−244.040 588]
	ΔE_{tot}(CP)/cm^{-1}	−102.6	−61.5	+78.8
		[−133.7][b]	[−128.7][b]	[−9.5][b]

[a] CP indicates that the full counterpoise correction has been performed—see text. [b] These results were obtained at a slightly different geometry. This geometry was obtained at the QCISD level, with Basis Set 1, where the most diffuse *f* exponent was changed from 0.1 to 0.011 11—see text.

gas atom, and one might naturally expect the metal to want to interact with the δ- O atom, but clearly there is a competition here of a number of interaction terms that are leading to the Cd atom being almost as happy interacting with H as O. With regard to other metal·H_2O complexes, it is clear that higher levels of theory are required to determine which structures are the global minima, and thus to be able to draw some conclusions on what the important trends in bonding are in these fundamental complexes.

(b) Binding Energy. The QCISD/Basis Set 1 geometries were then employed in single-point CCSD(T)/Basis Set 3 calculations, and the results are given in Table 5. This redesigned basis set leads to an acceptable BSSE, which, although still a large fraction of the interaction energy (ca. 35−40% of the uncorrected interaction energy), amounts to < 3 cm^{-1} BSSE per electron for Cd·H_2O, which we feel is reasonable. This magnitude of BSSE is almost the same size as that achieved for Rn·H_2O;[31] note that the same magnitude of BSSE was obtained for the Rn·NO^+ molecular complex,[33] but because of the larger interaction energy for the charged complex, the percentage contribution is very much smaller. It is noteworthy that triples make a very large contribution to the binding energy of all three neutral isomers.

In addition to the above, we also had (inadvertently) performed CCSD(T) calculations on geometries optimized at the QCISD level using Basis Set 1, but with the most diffuse *f* exponent being 0.011 11 rather than 0.1. This led to a geometries that were very similar to those reported in Table 4, but the bond lengths were slightly longer (for example R_{Cd-H} was 2.855 Å rather than 2.788 Å); the QCISD energies were, however, the lowest with the tighter *f* function. As it happens, the energies at the geometries with the longer intermolecular bond length were slightly lower than with using the Basis Set 1 as reported herein (see results in square brackets in Table 5); in addition, the binding energy for the C_s structure was a little lower with the more diffuse *f* function. The major differences were that for the Cd···OH_2 structure, the more diffuse *f* function led to the QCISD geometry being a saddle point, and had a very significant effect on the binding energies of both C_{2v} structures. These results indicate that at the RCCSD(T) level, the basis set requirements are more demanding than at the QCISD level, and that the optimized geometry at the RCCSD(T) level will have a longer R_{Cd-H} bond length than at the QCISD level; this is in line with our conclusions on going from MP2 to QCISD: the correlation energy is serving to describe better the repulsion energy, and hence leading to longer intermolecular bond lengths. From the above, our most accurate binding energies are those that arose as a result of CCSD(T)/Basis Set 3 calculations at the QCISD/Basis Set 1 (most diffuse *f* exponent = 0.01111) level.

(c) Stability. The Cd·H_2O complex has a very small binding energy at 134 cm^{-1} (0.4 kcal mol^{-1}). This energy will be reduced by the zero-point vibrational energy (MP2/Basis Set 1), which is 335 cm^{-1}, when summed over all of the intermolecular vibrational modes. Note that this does not necessarily imply that the complex is unbound because it is only the zero-point vibrational energy along the dissociation coordinate which will affect the dissociation energy. It is clear, however that, if stable, this is a weakly bound complex that will be undergoing large amplitude vibrational motion, and so may have an average zero-point (r_0) geometry far from the r_e one.

TABLE 6: Computed Total Energies, E_{Tot}, and Interaction Energies, ΔE, for Complex Formation of the trans Planar C_s Isomer of Cd·H_2O, and Cd^{2+}·H_2O at the B3LYP/Basis Set 3//B3LYP/Basis Set 1 Level of Theory

species	E_{tot}/E_h	ΔE_{tot}(CP)[a]
Cd·HO−H C_s	−244.204 788	−55.8 cm^{-1}
Cd^{2+}·H_2O C_{2v}	−243.366 752	−83.5 kcal mol^{-1}

[a] Full counterpoise correction performed—see text.

(iv) Density Functional Theory (DFT) Studies. We are a little wary about the application of DFT methods to molecular complexes because the frequently used functionals have not been derived for such species. Our experience is that generally an over-estimation of the bonding occurs for singly charged species [see, for example work on Ar·NO^+ (ref 34) and NO^+·CO (ref 35)]; however, we note that the literature is full of examples where people have successfully applied DFT methods to charged metal−ligand complexes. For doubly charged metal cations, it is to be expected that DFT methods would perform well because short bond lengths and strong bonding is expected. Indeed, recently, Alcamí et al.[20] applied DFT methods to metal−ligand dications, and made a number of conclusions (when compared to QCISD results), viz.: that hybrid functionals led to metal−ligand bond lengths that were too short; that nonhybrid functionals led to better agreement as regards the metal−ligand bond length; and that generally DFT methods led to interaction energies that were too large by 2−6 kcal mol^{-1}.

We used the B3LYP hybrid functional with Basis Set 1, and optimized the geometries of Cd·H_2O (C_s isomer) and Cd^{2+}·H_2O. These results are included in Tables 2 and 4, and are commented on below. We also obtained the binding energies of these species using B3LYP/Basis Set 3, correcting for BSSE. The results are given in Table 6.

The results of the geometry optimization for Cd^{2+}·H_2O (C_{2v}) (see Table 2) indicated that the B3LYP method *underestimates* the chemical bonding, leading to an intermolecular bond length that was only ∼0.1 Å too long compared to the QCISD method, which is in very good agreement. The lowest B3LYP vibrational frequencies are too small compared to the MP2 method, which again might indicate that the B3LYP method is underestimating the bonding slightly. Note that this result is in direct contrast to that reached by Alcamí and co-workers[20] who concluded that hybrid functionals led to intermolecular bond lengths that were too short compared to QCISD calculations. It is clear that basis sets must also be playing a role in the conclusions from these studies, and caution must be made when making general conclusions in such matters; the basis sets used in ref 20 were significantly smaller than those employed herein, and so we expect our conclusions to be more reliable. For $Cd{\cdot}H_2O$ (C_s isomer), the calculated intermolecular bond length is ca. 0.6 Å too long compared to the QCISD method, and again, the lowest vibrational frequencies also indicate that an underestimation of the chemical bonding is occurring.

Regarding the binding energies, the B3LYP result (see Table 6) for $Cd^{2+}{\cdot}H_2O$ is a little too high compared to the CCSD(T) results (in agreement with the general conclusions of ref 20), but the agreement is fairly good. For $Cd{\cdot}H_2O$, on the other hand, the binding energy is much smaller at the B3LYP level, being significantly less than half the CCSD(T) value.

It is clear from these studies that where the bonding is strong, such as in $M^{2+}{\cdot}H_2O$, then the B3LYP method can perform well for metal-containing complexes; however, for neutral complexes, where the bonding is much weaker, then the B3LYP method does not perform as well.

V. Conclusions

Geometry optimizations at the QCISD level, and binding energies at the CCSD(T) level have been employed with ECP-based basis sets, augmented with a large, flexible valence spaces that contain a large number of polarization and diffuse functions. The conclusion for $Cd^{2+}{\cdot}H_2O$ is that, as for all known M^{2+} monohydrates (to the authors' knowledge), the most stable isomer is the C_{2v} one with the M^{2+} interacting with the O atom of H_2O. In contrast, for the neutral complex, there are two or three stable minima, one with the Cd interacting with the O atom (C_{2v} symmetry), one with the Cd atom interacting with the two hydrogen atoms equally (η^2), but also one with the Cd atom interacting with a hydrogen atom in a C_s geometry; the latter is the lowest in energy. The latter isomer is similar to that obtained for $Rn{\cdot}H_2O$, but does not appear to have been considered for other metal monohydrates, where only the C_{2v} structure with the metal interacting with the O atom appear to have been studied. The C_s geometry may be rationalized in terms of its having a lower Pauli repulsion than the C_{2v} structure, but it is clear that there are a number of effects that have to be balanced in these complexes.

Our best value for the binding energy of $Cd^{2+}{\cdot}H_2O$ is 78 kcal mol^{-1}, with that for $Cd{\cdot}H_2O$ being 0.4 kcal mol^{-1} (134 cm^{-1}). We conclude that the $Cd^{2+}{\cdot}H_2O$ complex is stable to charge transfer, and should be observable, but its formation will require some care. Our calculations are less conclusive as to the stability of $Cd{\cdot}H_2O$, owing to the magnitude of the binding energy calculated here, relative to the zero-point vibrational energy; however, we feel that the strong dipole of H_2O will lead to a stable complex, interacting with the induced dipole on Cd.

Our conclusions regarding the B3LYP method is that for strongly bound M^{2+} complexes, they perform reasonably well, as regards both geometry and binding energy; however, for the much more weakly bound neutral complexes, such calculations are less definitive.

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References and Notes

(1) Cotton, F. A.; Wilkinson, G. A. *Advanced Inorganic Chemistry*, 4th ed.; Wiley-Interscience: New York, 1980.

(2) Rudolph, W. W.; Pye, C. C. *J. Phys. Chem. B* **1998**, *102*, 3564.

(3) Antony, J.; Hansen, B.; Hemmingsen, L.; Bauer, R. *J. Phys. Chem. A* **2000**, *104*, 6047.

(4) Probst, M. M. *J. Mol. Struct. (THEOCHEM)* **1992**, *253*, 275.

(5) Gresh, N.; Garmer, D. R. *J. Computat. Chem.* **1996**, *17*, 1481.

(6) Garmer, D. R.; Gresh, N. *J. Am. Chem. Soc.* **1994**, *116*, 3556.

(7) Gresh, N.; Giessner-Prettre, C. *New J. Chem.* **1997**, *21*, 279.

(8) Hemmingsen, l.; Ryde, U. *J. Chem. Phys.* **1996**, *100*, 4803, and references therein.

(9) See Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270; 284; 299.

(10) Andrae, D.; Häussermann, Dolg, M.; Stoll, H.; Preuss, H. *Theor. Chim.* Acta **1990**, *77*, 123. Schautz, F.; Flad, H.-J.; Dolg, M. *Theor. Chem. Acc*. **1998**, *99*, 231.

(11) Wood, J. J.; Boring, A. M. *Phys. Rev. B* **1978**, *18*, 27 016.

(12) Gaussian 98, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

(13) MOLPRO is a package of ab initio programs written by H.-J. Werner, P. J. Knowles, with contributions from, J. Almlöf, R. D. Amos, A. Berning, M. J. O. Deegan, F. Eckert, S. T. Elbert, C. Hampel, R. Lindh, W. Meyer, A. Nicklass, K. Peterson, R. Pitzer, A. J. Stone, P. R. Taylor, M. E. Mura, P. Pulay, M. Schuetz, H. Stoll, T. Thorsteinsson, D. L. Cooper. With the CCSD treatment being described in: C. Hampel, K. Peterson, H. J. Werner, Chem. Phys. Lett. **1992**, 190, 1.

(14) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 533.

(15) van Duijneveldt, F, B.; van Duijneveldt-vand der Rijdt, J. G. C. M.; van Lenthe, J. H. *Chem. Rev.***1994**, *94*, 1873.

(16) Lee, E. P. F.; Dyke, J. M. *Mol. Phys.* **1991**, *73*, 375.

(17) Moore, C. E. *Atomic Energy Levels* (Natl. Bur. Stand., Circ. 467) US Department of Commerce, Washington, D. C., 1949.

(18) Bock, C. W.; Katz, A. K.; Glusker, J. P. *J. Am. Chem. Soc.* **1995**, *117*, 3754.

(19) Pavlov, M.; Siegbahn, P. E. M.; Sandström, M. *J. Phys. Chem. A* **1998**, *102*, 219.

(20) Alcamí, M.; González, A. I.; Mó, O.; Yáñez, M. *Chem. Phys. Lett.* **1999**, *307*, 244.

(21) Peschke, M.; Blades, A. T.; Kebarle, P. *Int. J. Mass Spectrosc.* **1999**, *187*, 685.

(22) Barran, P. E.; Walker, N. R.; Stace, A. J. *J. Chem. Phys.* **2000**, *112*, 6173.

(23) Walker N. R.; Wright, R. R.; Barran, P. E.; Cox, H.; Stace, A. J. *J. Chem. Phys.* **2001**, *114*, 5562.

(24) Lee, T. J.; Taylor, P. R.; *Int. J. Quantum Chem. Symp.* **1989**, *23*, 199.

(25) Fuke, K.; Hashimoto, K.; Iwata, S. *Adv. Chem. Phys.* **1999**, *110*, 431.

(26) Hashimoto, K.; Kamimoto, T. *J. Am. Chem. Soc.* **1998**, *120*, 3560.

(27) Hashimoto, K.; Morokuma, K. *J. Am. Chem. Soc.* **1994**, *116*, 11 436.

(28) Watanabe, H.; Aoki, M.; Iwata, S. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 3245.

(29) Hashimoto, K.; Yoda, N.; Iwata, S. *Chem. Phys.* **1987**, *116*, 193.

(30) Hashimoto, K.; Yoda, N.; Osamura, Y.; Iwata, S. *J. Am. Chem. Soc.* **1990**, *112*, 7189.

(31) Lee, E. P. F.; Wright, T. G. *J. Phys. Chem. A* **1999**, *103*, 7843.

(32) Tao, F.-M.; Li, Z.; Pan, Y.-K. *Chem. Phys. Lett.* **1996**, *255*, 179.

(33) Lee, E. P. F.; Gamblin, S. D.; Wright, T. G. *Chem. Phys. Lett.* **2000**, *322*, 377.

(34) Wright, T. G. *J. Chem. Phys.* **1996**, *105*, 7579.

(35) Wright, T. G.; Lee, E. P. F. *Chem. Phys. Lett.* **2001**, *340*, 179.