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Charge transfer and curve crossings in the $[BeH_2O]^{2+}$ system

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Summary. Diabatic and adiabatic potential energy curves have been determined for the complexation of beryllium cation with a water molecule, by means of multi-reference perturbation CI. The quasi-diabatic states correspond to $Be^{2+}H_2O$ and to nine charge transfer states ($Be^+H_2O^+$): at short beryllium-water distances the ground state is essentially $Be^{2+}H_2O$, but at large distances several charge transfer states have lower energies. The nature of the curve crossings of the ground and lowest excited states in the $[BeH_2O]^{2+}$ system is clarified. The changes brought about by the presence of a second water molecule are investigated.

Key words: Charge transfer – Beryllium ion – Beryllium water complex – Diabatic states

1. Introduction

The determination of interaction potentials between metal ions and ligands is of considerable interest, mainly as a first step in understanding the structure and dynamics of ionic solutions (see for instance [1]). Pair potentials are normally used in Monte Carlo or Molecular Dynamics simulations, but in some cases sizeable contributions from higher order terms are found. The non-additivity of the potential is more important, both in absolute value and in percentage, for doubly or triply charged cations [2]. The interaction energy of such cations with electron donors contains a large charge transfer (CT) contribution, which is certainly non additive [3, 4]. In fact, all the most common metal cations with oxidation number $n > 1$, have an electron affinity (n-th ionisation potential, IP) larger than the first IP of water (12.615 eV [5]); the only exceptions are Ca^{2+}, Sr^{2+}, Ba^{2+}. As a result, for many $M^{n+}H_2O$ systems, the most stable state at large metal-water distances is a charge transfer state, $M^{(n-1)+}H_2O^+$. Because of the electrostatic repulsion, the potential curve of the CT state goes up in energy as the metal-water distance decreases, thus crossing those of other states.

An investigation of the crossings and avoided crossings involving the ground and lowest excited states of water-metal cation systems would help to clarify the nature of the interaction potentials to be adopted in the simulations. The potential curves and related nonadiabatic couplings would determine the charge transfer probabilities for metal-water collisions in vacuo, or unimolecular decompositions of charged complexes. The metal to water CT may also play a role in mediating the metal to metal CT (redox reactions) in solution.

To begin with, we decided to investigate one of the simplest systems where such a situation occurs, the $[BeH_2O]^{2+}$ complex. The beryllium-water complexes have been the object of previous ab initio studies [3, 6–12] and of Molecular Dynamics simulations [7, 9]. Special attention has been paid to the non-additivity problem [8–11], because a simulation based on two-body potentials gave a hydration number of six, in sharp contrast with the experimentally determined value of four [7]: the inclusion of a three-body term (water-beryllium-water) was effective in eliminating the discrepancy [9]. Although at least five charge transfer singlet states lie below the Be^{2+}–H_2O asymptote, only one has been theoretically studied [6]; no proper treatment of the avoided crossings between states of the same symmetry has been produced.

In this paper, we present an ab initio SCF and CI determination of 10 singlet states of the $[BeH_2O]^{2+}$ complex, from $R(\text{Be–O}) = 2.1$ a.u. to dissociation. In order to unravel the relationships between electronic states dissociating to different asymptotes, we determined quasi-diabatic states, by means of a technique already devised and tested in our group [13, 14]. A comparison with the situation encountered when more than one water molecule interact with the beryllium cation concludes this work.

2. Computational method

SCF-CI calculations have been run for the $[BeH_2O]^{2+}$ system, at 14 different Be–O distances. No attempt was made to optimise the geometry of the approaching water molecule: previous works have shown that the OH bond lengths and $\widehat{HOH}$ bond angle are not dramatically altered in the ground state of the complex [3, 8, 10]. The deformation energy of water was evaluated to 1.2% of the total interaction energy, in a 6-31G* SCF treatment [3]. The experimental geometry of neutral water, ground state, was adopted throughout, with $R(\text{OH}) = 1.8094$ a.u. and $\widehat{HOH} = 104.51°$ [15]. However, a second set of calculations were run, with $\widehat{HOH} = 180°$, because it is known that the second ionised state of H_2O ($H_2O^+ \tilde{A}^2A_1$) is linear: the energy lowering, in going from the bent to the linear water geometry, is about 1 eV, as deduced from the difference between the vertical and the adiabatic (minimum to minimum) IP [5]. We only explored C_{2v} geometries, with Be on the C_2 axis of the water molecule: the approach along this direction yields the lowest energies in the ground state, when compared with other coplanar and non coplanar approaches [6].

The basis set here adopted is the 6-311G** [16], of triple-zeta quality in the valence shells, including the *p* shell of Be; polarisation functions are provided, *d* on O and Be with exponents 1.292 and 0.25 respectively, *p* on H, with exponent 0.75.

The closed shell SCF procedure should give, at large Be–O distances, the $Be^{2+}(^1S)H_2O(X^1A_1)$ state, but it suffers from serious convergence problems for $R(\text{Be–O}) > 8$ a.u., because the last occupied orbital is localised on H_2O or on Be in turn, for successive iterations. In order to avoid such difficulties, and to obtain a set of MOs less biased towards a particular electronic state, we adopted Nesbet's SCF procedure [17], with the following occupation numbers:

$$n_1 = n_2 = n_3 = n_4 = 2, \qquad n_5 = n_6 = 5/3, \qquad n_7 = 2/3.$$

At large distances, the 5-th MO correlates with the a_1 lone pair of oxygen, the 6-th with the $b_1 p$ orbital of oxygen, and the 7-th with $2s$ of beryllium. Therefore, the above occupation numbers correspond to an average of three electronic configurations of interest in our work. In particular, it ensures proper degeneracy of the π_u orbitals of linear H_2O^+.

A Configuration Interaction follows, based on the multi-reference perturbation algorithm CIPSI [18–20]. The present application of CIPSI involved the following features. Three steps of selection of progressively enlarged variational subspaces were run, with thresholds $\eta = 0.05$, 0.03 and 0.004. A final step, run with the diagrammatic version of the program [19], involved a three class partition of the CI space: the variational space (S) and the determinants (G) from which single and double excitations (P) are generated in the perturbation; G is a subspace of S, selected with the threshold $\eta_G = 0.01$. The 4 states of A_1 symmetry required about 3500 to 5500 determinants in S, and 640 to 930 in G; less states and determinants were involved for other symmetrics. The diagrammatic version of the program employs the Møller–Plesset barycentric partition of the CI hamiltonian. The square norm of the first order correction of the wavefunction did not exceed 0.018, for any state and geometry, indicating a good degree of convergence of the iterative selection/perturbation procedure.

Quasi-diabatic zeroth-order states $|\eta_i^{(0)}\rangle$ were defined by a unitary transformation $\boldsymbol{T}^{(0)}$ of the CI eigenfunctions $\psi_k^{(0)}$ in the S subspace [13, 14]:

$$|\boldsymbol{\eta}^{(0)}\rangle = |\boldsymbol{\psi}^{(0)}\rangle \boldsymbol{T}^{(0)\dagger} \tag{1}$$

The $\boldsymbol{T}^{(0)}$ matrix is chosen so as to maximise the superposition of the $\eta_i^{(0)}$ functions with a set of reference functions R_i:

$$\sum_i |\langle \eta_i^{(0)} \mid R_i \rangle|^2 = \max \tag{2}$$

The R_i functions are, by construction, very simple diabatic functions, normally amenable to valence-bond structures, and not necessarily orthogonal to each other. Their quality, and in particular their adequacy to represent the electron correlation, is irrelevant to the accuracy of the calculation; in fact, the gist of the method is to find a set of functions, the $\eta_i^{(0)}$, which resemble as much as possible the diabatic references, and in the same time are well correlated, in so far as they span the same subspace as the adiabatic functions $\psi_k^{(0)}$. The zeroth-order electronic hamiltonian in the diabatic basis, $H_{ij}^{(0)} = \langle \eta_i^{(0)} | \mathscr{H}_{el} | \eta_j^{(0)} \rangle$, is corrected to the second order according to the Quasi Degenerate Perturbation Theory, QDPT [14]:

$$\boldsymbol{H} = \boldsymbol{H}^{(0)} + \boldsymbol{H}^{(2)} \tag{3}$$

and diagonalised to get the final adiabatic energies U_k:

$$\boldsymbol{H}\boldsymbol{T}_k = U_k \boldsymbol{T}_k \tag{4}$$

The columns $\boldsymbol{T}_k$ of the matrix $\boldsymbol{T}$, usually not very different from $\boldsymbol{T}^{(0)}$, contain the expansion coefficients of the electronic eigenstates in a quasi-diabatic basis; as such, they convey qualitative information on the composition of the adiabatic states, bearing on chemical intuition, but firmly based on accurate calculations.

In the present work, we chose to study 10 singlet states of the $[BeH_2O]^{2+}$ system, dissociating as $Be^{2+}(^1S, 1s^2)$ and $H_2O(X^1A_1)$, or $Be^+(^2S, 2s)$, $Be^+(^2P, 2p)$ and $H_2O^+(\tilde{X}^2B_1)$, $H_2O^+(\tilde{A}^2A_1)$, $H_2O^+(\tilde{B}^2B_2)$. Accordingly, the reference functions R_i were built as antisymmetrised products of subsystem wavefunctions, as

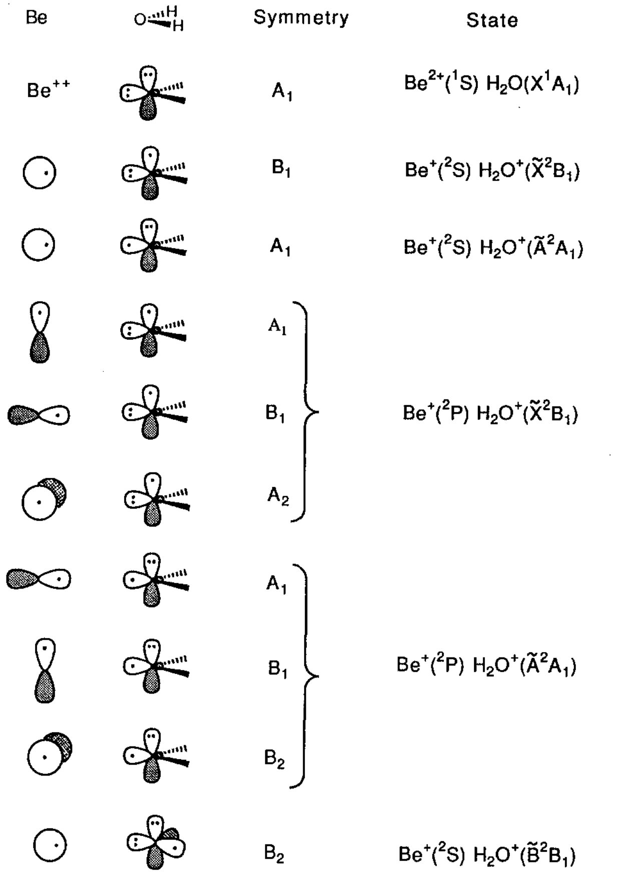

Fig. 1. Diabatic or reference states for the $[BeH_2O]^{2+}$ system. The 2*s* and 2*p* orbitals of Be are shown, when occupied; for the water molecule, the $p(b_1)$ orbital of oxygen and the $n(a_1)$ lone pair are always shown; only in the bottom line the b_2 combination of OH σ bonding orbitals is also shown (here singly occupied, doubly occupied for all other states). One or two dots indicate single or double occupancy

indicated in Fig. 1. A Gram–Schmidt orthogonalisation among the R_i functions preceded their use in the maximum overlap algorithm. The molecular orbitals defining the reference functions were obtained from SCF calculations for the isolated water molecule and beryllium cation. The values of the $\langle \eta^{(0)} | R_i \rangle$ overlaps are indicators of the adequacy of the reference functions: if they are close to 1, each R_i identifies without ambiguity the corresponding diabatic function. In the present case, the norms of the $\langle \eta_i^{(0)} | R_i \rangle$ overlaps have high values (0.8 to 0.95) for most states and geometries; only one of the A_1 references, $Be^+(^2P)H_2O^+(\tilde{A}^2A_1)$, fails at short distances (R(Be–O) = 3.5 a.u.), because the fourth state undergoes an avoided crossing, quite evident also in Figs. 2 and 3. The intruder state, $Be^+(^2P)H_2O^+(\tilde{B}^2B_2)$, might have been included in the reference set, by an *ad hoc* modification [13] of the diabatisation method; however, this was not done, because the large overlaps of the other states made the identification of the diabatic functions quite unambiguous anyway.

3. Results and discussion

In Table 1 we show the vertical charge transfer energies resulting from our perturbation CI treatment for R(Be–O) = ∞, along with experimental values.

Table 1. Energies of the $[BeH_2O]^{2+}$ system, at infinite separation, starting from the $Be^{2+}H_2O$ asymptote (−89.896862 a.u.)

State	Symmetry	Energy (eV)	Experimental[b]
		This work[a]	
$Be^{2+}(^1S)H_2O(X^1A_1)$	A_1	0.	0.
$Be^+(^2S)H_2O^+(\tilde{X}^2B_1)$	B_1	−6.06	-5.5 ± 0.1
$Be^+(^2S)H_2O^+(\tilde{A}^2A_1)$	A_1	−3.80	-3.4 ± 0.1
$Be^+(^2P)H_2O^+(\tilde{X}^2B_1)$	A_1, A_2, B_1	−2.06	-1.6 ± 0.1
$Be^+(^2P)H_2O^+(\tilde{A}^2A_1)$	A_1, B_1, B_2	+0.19	$+0.5 \pm 0.1$
$Be^+(^2S)H_2O^+(\tilde{B}^2B_2)$	B_2	+0.48	$+0.5 \pm 0.2$

[a] Fixed water geometry, from Ref. [15]

[b] Second IP of beryllium (18.211 eV) and $Be^+(^2P \leftarrow {}^2S)$ excitation energy (3.959 eV) from Ref. [23]; vertical IPs of water, with experimental uncertainties, from Ref. [5]

The total CIPSI energy for the $Be^{2+}H_2O$ state is −89.89686 a.u., hereafter assumed as the zero of the energy scale. Closed shell SCF yields −89.65639 a.u., to be compared with the estimated HF limit of -89.6788 ± 0.0010 a.u. [21, 22]. The comparison of asymptotic energy values is the only way to assess the accuracy of our calculations, in the absence of experimental measurements concerning the interaction potentials. The one previous determination of the CT energy difference, $Be^{2+} + H_2O \rightarrow Be^+(^2S) + H_2O(\tilde{A}^2A_1)$, based on a MRDCI treatment [6], gave $\Delta E = -2.1$ eV (cfr. third row of Table 1).

Table 2 reports the $[BeH_2O]^{2+}$ complexation energies, without zero point energy correction, obtained with different theoretical treatments. They all refer to the $Be^{2+} + H_2O$ asymptote, although this is not the lowest state at infinite separation. We can safely assume that our results are among the most accurate, as far as the 6-311G** basis set is more flexible than any other previously employed for beryllium-water complexes, and an exhaustive treatment of the electron correlation has been carried out. One state, single point calculations at the 3-21G* optimised geometries [10] give practically the same result; at this level, the basis set superposition error has been evaluated by means of the counterpoise method in 3.3 kcal/mol (SCF) and 3.8 kcal/mol (CIPSI). The most complete study of $[Be(H_2O)_n]^{2+}$ complexes is given in Ref. [10]; unfortunately, it employed the 3-21G and 3-21G* basis sets, which overestimate the binding energy of a single water molecule by some 15 to 25 kcal/mol; a similar trend had already been put in evidence for Li^+ and Na^+ complexes [24]. The SCF calculations, on which the Molecular Dynamics simulations were based [7–9], yield a complexation energy in better agreement with ours, although they employ a basis set somewhat less flexible than 3-21G*. In fact, the Huzinaga–Dunning *DZ* basis for Be does not contain *p* orbitals; only one set of *p*, and no *d*, functions, were introduced, with the role of polarisation functions. This feature may lead to underestimate the CT contribution (see below) and therefore the complexation energy.

In the C_{2v} point group, we treated four states belonging to the A_1 irrep, one to A_2, three to B_1 and two to B_2. The closed shell $Be^{2+}H_2O$ state belongs to A_1. Figure 2 shows the A_1 diabatic energies, H_{ii}, Eq. (3), as functions of R(Be–O), with a bent water molecule (experimental geometry). Figure 3 shows the corre-

Table 2. Complexation energies of $Be^{2+}H_2O$, D_e, from different theoretical treatments (kcal/mol). No zero point energy corrections. Be–O bond distances in a.u.

Reference	Method	Basis set	H_2O geom. relax.	R(Be–O)	D_e
This work	CIPSI	6-311G**	NO	2.839	146.4
This work[a]	SCF	6-311G**	YES	2.840	146.7
This work[a]	SCF	without CT[b]	YES	2.840	115.4
This work[a]	CIPSI	6-311G**	YES	2.840	145.3
This work[a]	CIPSI	without CT[b]	YES	2.840	110.4
[8]	SCF	STO-3G	YES	2.772	205.3
[8]	SCF	DZ[c]	YES	2.925	145.3
[7]	SCF	DZ + pol[c]	NO[d]	2.903	136.7
[8]	SCF	DZ + pol[c]	YES	2.903	135.6
[8]	SCF	TZ + pol[c]	YES	2.814	147.0
[8, 10]	SCF	3-21G	YES	2.867	169.0
[10]	MP3	3-21G	YES[e]	2.867	172.9
[10]	SCF	3-21G*	YES	2.840	161.2
[10]	MP3	3-21G*	YES[e]	2.840	168.3
[6]	SCF	with CT[f]	NO	2.90	134.5
[6]	MRDCI	with CT[f]	NO	2.90	129.1
[6]	SCF	without CT[f]	NO	3.00	111.7
[3]	SCF	4-31G	YES	2.876	156.5
[3]	SCF + CP[g]	4-31G	YES	2.891	152.2
[3]	SCF	6-31G*	YES	2.835	148.6
[3]	SCF + CP[g]	6-31G*	YES	2.837	145.6

[a] Single calculation, one state, with 3-21G* geometry [10]

[b] 6-311G** on O and H, only the two inner *s* functions on Be

[c] Double-zeta and triple-zeta Huzinaga–Dunning basis sets, originally without *p* functions on Be; +pol means that *d* functions are added on O and *p* functions on Be and H

[d] R(Be–O) and D_e deduced from the analytic potential used in MD simulations [7]

[e] SCF geometry

[f] O(4*s*, 3*p*, 1*d*), H(2*s*, 1*p*). The basis set "with CT" on Be(4*s*, 2*p*) allows to accommodate a third electron, the basis "without CT" (2*s* functions only) does not

[g] Counterpoise correction of the basis set superposition error

sponding adiabatic energies, U_k, Eq. (4). In general, all the CT diabatic states have repulsive coulombic potentials, while the $Be^{2+}H_2O$ curve is attractive, because of the beryllium charge-water dipole interaction. Therefore, the $Be^{2+}H_2O$ state undergoes two avoided crossings, one around R(Be–O) = 14 a.u., with $Be^+(^2P)H_2O^+(\tilde{X}^2B_1)$, and another one around 8 a.u., with $Be^+(^2S)H_2O^+(\tilde{A}^2A_1)$. The former has a minimum energy gap of about 0.0035 eV, the latter of 0.3 eV: the large difference between the two values is mainly due to the rapid decrease of the state-to-state interaction matrix elements H_{ij} with the Be–O distance. A Be^{2+} ion and a water molecule, freely attracted along the C_{2v} minimum energy path, would go through both avoided crossings, with Massey parameters [25] $\xi_1 = 0.005$ and $\xi_2 = 3.8$, respectively. The outer crossing is therefore classifiable as essentially "diabatic" and the inner one as "adiabatic", but in both cases sizeable transition probabilities occur: charge transfer cross sections for water-beryllium cation collisions are certainly not negligible.

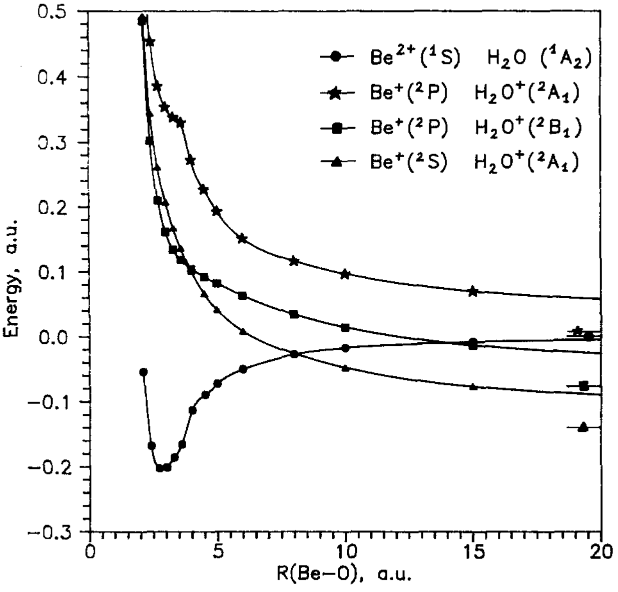

Fig. 2. Diabatic energies for the A_1 states as functions of R(Be–O). Water molecule in the experimental geometry. The zero of the energy scale corresponds to the $Be^{2+}H_2O$ asymptote

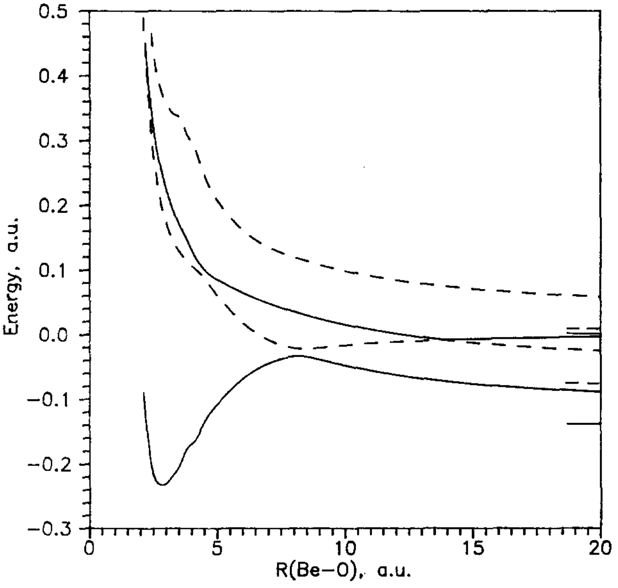

Fig. 3. Adiabatic energies for the A_1 states as functions of R(Be–O). Water molecule in the experimental geometry. The zero of the energy scale corresponds to the $Be^{2+}H_2O$ asymptote

The adiabatic dissociation of $[BeH_2O]^{2+}$ in the C_{2v} symmetry leads to $Be^+(^2S)H_2O^+(\tilde{A}^2A_1)$, with $D_e = 58.7$ kcal/mol and an activation barrier determined by the lowest avoided crossing, $\Delta E^* = 125.2$ kcal/mol. However, at large Be–O distances, the lowest state is $Be^+(^2S)H_2O^+(\tilde{X}^2B_1)$, and belongs to another irrep, B_1. If this dissociation limit is considered, D_e is further lowered to only 6.8 kcal/mol. The lowest B_1 and A_1 energy curves cross each other at R(Be–O) = 6 a.u., 92.8 kcal/mol above the A_1 minimum. The crossing is actually a conical intersection, because displacing Be out of the H_2O plane eliminates the

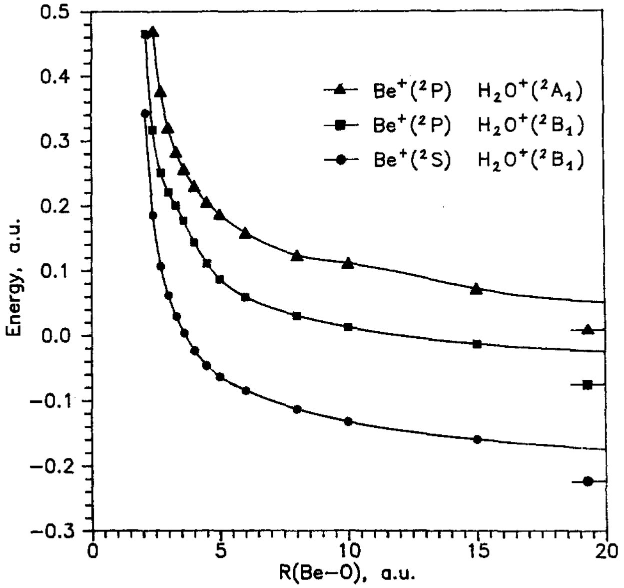

Fig. 4. Diabatic energies for the B_1 states as functions of R(Be–O). Water molecule in the experimental geometry. The zero of the energy scale corresponds to the $Be^{2+}H_2O$ asymptote

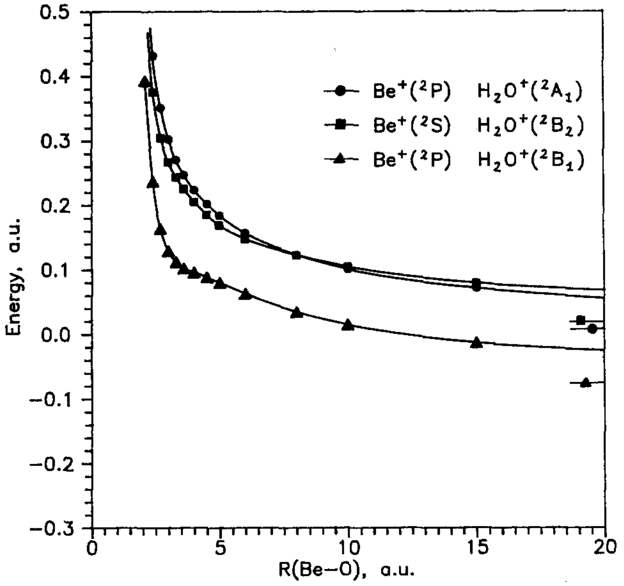

Fig. 5. Diabatic energies for the A_2 and B_2 states as functions of R(Be–O). Water molecule in the experimental geometry. The zero of the energy scale corresponds to the $Be^{2+}H_2O$ asymptote

separation between the A_1 and B_1 manifolds. In collisions or half-collisions, another channel is open, leading to charge-transfer with low-energy products.

Figures 4 and 5 show the diabatic energies of B_1, A_2 and B_2 states. They are all dominated by coulomb repulsion, as already seen for the CT A_1 states. However, these curves, with two exceptions, are less repulsive at short distances (R(Be–O) = 3 to 4 a.u.), than implied by the $1/R$ law. The stabilisation can be mainly attributed to dative bonding, involving the n orbital on oxygen and $2s$ or $2p_z$ on beryllium. The two overlapping orbitals on different centers contain one, two, or three electrons, depending on the electronic state (see Fig. 1): the A_1 and A_2 combinations of $Be^+(^2P)$ and $H_2O^+(\tilde{X}^2B_1)$ are the most stabilised (less repulsive) states, and both have two electrons in the dative bond. The only two states which do not benefiit from σ bonding are $Be^+(^2S)H_2O^+(\tilde{A}^2A_1)$ and $Be^+(^2P)H_2O^+(\tilde{A}^2A_1)$, both in the A_1 irrep, although they also have two electrons in the same orbitals. To understand this, notice that the distinction between the two states under consideration and $Be^{2+}(^1S)H_2O(X^1A_1)$ is not sharp, as far as the overlap between the n orbital on oxygen and $2s$ or $2p_z$ on beryllium is not negligible: in fact, at short Be–O distances, the reference functions representing these states partially overlap, while all others do not, having a different symmetry or at least a different occupation of the b_1 orbitals. Dative bonding stabilises the $Be^{2+}(^1S)H_2O(X^1A_1)$ state, but the orthogonality constraint prevents the two other states to lower their energy by covalent interactions involving the same orbitals. As a result of different extents of stabilisation, the repulsive diabatic curves are not parallel, and several crossings occur; the adiabatic curves for B_1, A_2 and B_2 states are very close to the diabatic ones, except that the crossing of the B_2 states at R(Be–O) $\simeq 8$ a.u. is "avoided".

The above discussion also shows that important physical effects such as charge transfer and polarisation of the water molecule cannot be perfectly separated: in fact, an increase of the electron density in the n orbital of oxygen (polarisation), at short distances, partially implies a larger degree of charge transfer, because of the overlap of O and Be orbitals.

The $\tilde{X}^2B_1$ and $\tilde{A}^2A_1$ states of H_2O^+ become degenerate ($^2\Pi_u$) in the linear geometries: the energy of the former increases by about 1 eV with respect to vertical ionisation, while that of the latter decreases by the same amount [5]. As a result, the potential energy curves for A_1 states with linear water, shown in Fig. 6, are rather different from those of Fig. 3. In particular, the linear water geometry is preferred to the bent one for R(Be–O) > 6 a.u., in the lowest A_1 state: the dissociation limit is lowered to 26.3 kcal/mol (from 58.7).

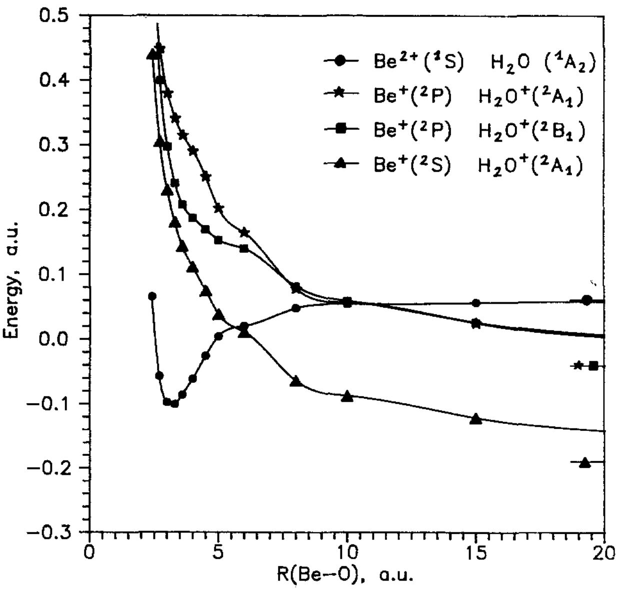

Fig. 6. Diabatic energies for the A_1 states as functions of R(Be–O). The water molecule is linear. The zero of the energy scale corresponds to the $Be^{2+}H_2O$ asymptote with water in the experimental (bent) geometry

The ground state, at bonding distances is stabilised by charge transfer, involving not only the $\sigma(a_1)$, but also the $p(b_1)$ orbitals: this is shown by the contribution of the $Be^+(^2P)H_2O^+(\tilde{X}^2B_1)$ diabatic state to the ground adiabatic wavefunction. Considering the diabatic potential, instead of the adiabatic one, amounts in a first approximation to neglecting the CT contribution to the hydration energy: in this way, we have $D_e = 128.3$ kcal/mol, 18.1 less than the adiabatic D_e. The energy decomposition scheme applied in Ref. [3] yielded a CT term of −21.6 kcal/mol (6-31G* + counterpoise calculation). We repeated the single point calculations with 3-21G* geometries [10], using the 6-311G** basis set for O and H, but only two *s* functions for Be; with such a basis set only the 1*s* orbital of Be is correctly described, so that no charge transfer can occur. The results, shown in Table 2, indicate that CT accounts for 31.3 kcal/mol of the binding energy at SCF level, or 34.9 kcal/mol at CIPSI level.

Consider now the complexation by a second water molecule; quite clearly, it cannot transfer as much electronic charge, to the beryllium ion, as the first one, and the CT stabilisation energy will be much less. Figure 7 shows the potential energy curve for the approach of a second water, while the first one is held fixed at a Be–O distance of 3 a.u. All the atoms are on the same plane, O–Be–O on the same line, with C_{2v} symmetry; CIPSI calculations for a single state have been performed. As expected, both the SCF and the CIPSI curves are much closer to the diabatic curve for the single water case, than to the adiabatic one. The second hydration energy was 122.4 kcal/mol (SCF) or 123.3 (CIPSI). The difference, with respect to the single water D_e, is 23.1 kcal/mol, including about 4 kcal/mol of water-water repulsion [10]. Again, single point calculations based on 3-21G* geometries give almost identical results: $D_e = 123.0$ kcal/mol (SCF) and 122.9 (CIPSI). With only two *s* functions on Be (no charge transfer allowed) we obtain $D_e = 104.2$ kcal/mol (SCF) and 98.7 (CIPSI). The CT contribution to the binding energy is 11–12 kcal/mol less than in the single water case. Previous determinations of one and two waters D_e gave differences in the same order of

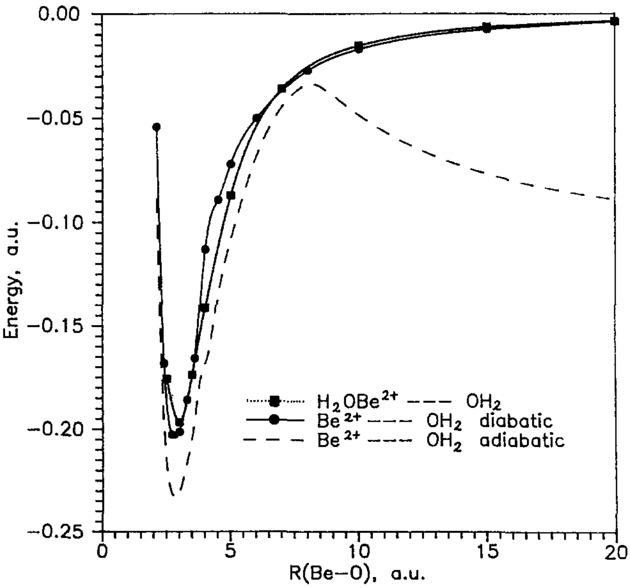

Fig. 7. Ground state adiabatic energy (CIPSI-MPB) for the $[Be(H_2O)^2]^{2+}$ system. Planar C_{2v} arrangement, water molecules in the experimental geometry. One *R*(Be–O) distance is fixed (3 a.u.), the second variable. The diabatic $(Be^{2+}H_2O)$ and adiabatic curves with only one water molecule are shown for comparison. The zero of the energy scale corresponds to the $[BeH_2O]^{2+} + H_2O$ or $Be^{2+} + H_2O$ asymptotes

magnitude as ours: $\Delta D_e = 24.4$ kcal/mol (3-21G*, MP3 [10]), $\Delta D_e = 15.2$ kcal/mol (DZ, SCF [8]). In particular, the DZ-SCF calculations of Refs. [7–9], on which the Molecular Dynamics simulations were based, give a second hydration energy of 120.4 kcal/mol, almost identical to ours: the weakness of the basis set they used, probably causing an underestimate of CT effects, becomes a minor source of error in the two waters case.

Polarisation of the H_2O molecules also plays an important role in the non-additivity of pair potentials. We can evaluate its contribution as follows. Let us call $\mathscr{E}_{Be}$ the electric field generated by the Be^{2+} cation at the location of a water ligand, and $\mathscr{E}_{H_2O}$ the electric field generated by the other water molecule at the same location; $\mathscr{E}_{Be}$ and $\mathscr{E}_{H_2O}$ are parallel and opposite in sign, with $|\mathscr{E}_{Be}| \gg |\mathscr{E}_{H_2O}|$. The polarisation energy for one water molecule is proportional to $-\mathscr{E}^2_{Be}$, while that of two water molecules is proportional to $-2(\mathscr{E}_{Be} + \mathscr{E}_{H_2O})^2 \simeq -2\mathscr{E}^2_{Be} - 4\mathscr{E}_{Be}\mathscr{E}_{H_2O}$. Thus, the polarisation contribution to the non-additivity is a fraction $4|\mathscr{E}_{H_2O}/\mathscr{E}_{Be}|$ of the polarisation energy for the single water case, which is 81.7 kcal/mol according to the energy decomposition scheme of Ref. [3]. Given a beryllium-water distance of 3 a.u. and a water dipole of 0.736 a.u., we evaluate a contribution of 10 kcal/mol, roughly half of the total non-additivity and about the same as the CT contribution (notice that this simplified charge-dipole model is quite consistent with the computed electrostatic energy for the $[BeH_2O]^{2+}$ complex [3] and with the water-water repulsion energy [10]). Considering that charge transfer influences the electric field to a large extent, it is quite apparent that a cross effect of CT and polarisation will also be an important source of non-additivity.

The one and two waters potential energy curves differ dramatically at large Be–O distances: in fact the lowest A_1 CT state lies higher than the $Be^{2+}(H_2O)_2$ state, provided that one of the water molecules complexes the beryllium cation and stabilises its double charge. In this region, the similarity between the two waters adiabatic curve, and the single water diabatic one, is striking (see Fig. 7).

4. Conclusions

This work shows the complexity of the ground and lowest excited potential energy surfaces of one of the simplest systems constituted by a doubly charged cation and a ligand. One should consider that the number of low-lying charge transfer states is larger with transition metals, because of the crowding of many atomic terms in a range of a few eV. Triply charged cations, because of their large electron affinities (third IP), will cause the curve crossings and avoided crossings between CT and non CT states to occur at lower energies and closer metal-ligand distances than in $[BeH_2O]^{2+}$. Therefore, such featues will influence more deeply the properties of solutions and the condensed state chemistry, in particular redox reactions. The determination of quasi-diabatic states is shown to be a valuable tool to disentangle such complex situations, and to help in building up simplified models.

Charge transfer and water polarisation are key features in establishing the energetics of metal-ligand complexes, and in particular the non-additivity of interaction potentials: notice, however, that CT and polarisation effects cannot be perfectly separated and quantified. The present results show that the potential energy curves for the complexation of Be^{2+} with the first and with the second water molecule are widely different, mainly because of a shift in the relative energies of CT and non CT states; addition of more water molecules is expected to cause relatively minor changes. The true adiabatic potential for a beryllium ion + single water is dramatically inadequate to represent the reality of solutions, especially in the long-range, repulsive region. Actually, the pair potentials formerly used in simulations [7, 9], being obtained from closed shell SCF calculations, cannot reproduce the avoided crossings with CT states: they are qualitatively similar to those here shown for the two waters case. All these considerations point to the use of effective pair potentials in simulations of cation-ligand systems: this is probably the best way to overcome the non-additivity problem, without resorting to many-body terms. Effective pair potentials suited to simulate aqueous solutions should be obtained from calculations with two, or perhaps more, water ligands, as done in this work. Another way to determine an effective potential is to apply a general treatment of the solvent effect, such as the continuum dielectric model [26], to the cation-single ligand subsystem.

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