Water-Exchange Reaction of the Hexaaqua Ions of Vanadium(II), Manganese(II), and Iron(II) Revisited: A Discussion of Models with the Solvent Treated as a Dielectric Continuum

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The H_2O-exchange reaction on $V(OH_2)_6^{2+}$, $Mn(OH_2)_6^{2+}$, and $Fe(OH_2)_6^{2+}$ has been reinvestigated with *ab initio* quantum-chemical calculations that include electron correlation and hydration, whereby the second coordination sphere and the bulk solvent were treated as a dielectric continuum. In such models, activation entropies ($\Delta S^{\neq}$) and also activation free energies ($\Delta G^{\neq}$) are not available, since the second coordination sphere is not treated quantum chemically. Furthermore, no transition states for the dissociative interchange (I_d) mechanism can be obtained, most likely also because of this approximation, and this limitation applies to the hexaaqua ions, but not, for example, to the pentaamines. Therefore, in cases where this model predicts that the dissociative (D) mechanism is the most favorable one, the question remains open as to whether the D or the I_d mechanism operates. For the H_2O adducts of the reactants, $M(OH_2)_6 \cdot OH_2^{n+}$, two isomers were considered: in the first (A), the H_2O molecule in the second coordination sphere forms a single H-bond to one aqua ligand, and in the other (B), it is bound to two aqua ligands in a bridging mode. For each hexaaqua ion, associative (I_a or A) and dissociative mechanisms (D) were investigated. On the basis of reactant B, activation energies agreeing with experiment were obtained for the water exchange on the aqua ions of V^{II}, Mn^{II}, and Fe^{II}. For the water exchange on $V(OH_2)_6^{2+}$ and $Fe(OH_2)_6^{2+}$, experimental and computational data suggest an *a* and a *d* activation, respectively, whereas for $Mn(OH_2)_6^{2+}$, the activation energies, calculated for the *a* and *d* activations, are equal and, therefore, the mechanism can be attributed only *via* the comparison of the change of the sum of all $Mn^{II}-O$ bond lengths during the activation process, $\Delta\Sigma d(Mn^{II}-O)$, with the activation volume. The limitations in the attribution of substitution mechanisms on the basis of experimental activation volumes and activation energies computed with the present model are analyzed. The electronic structure of the heptacoordinated species, the transition state $[V(OH_2)_5 \cdots (OH_2)_2^{2+}]^{\neq}$ and the intermediate $Mn(OH_2)_7^{2+}$, are discussed.

Introduction. – In the previous investigations [1][2] of the H_2O-exchange reaction on first-row transition-metal hexaaqua ions (*Eqn. 1*) by quantum-chemical methods, a rather simple gas-phase model, in which the metal ion and six or seven H_2O molecules were treated quantum chemically, has been used. The activation energies for the dissociative (D), associative (A), and interchange (I_a, I, I_d) mechanisms (*Scheme*) were computed on the basis of *Eqns. 2–4*, whereby the D and the A mechanisms involve the penta- and heptacoordinated intermediates $M(OH_2)_5 \cdot OH_2^{n+}$ and $M(OH_2)_7^{n+}$.

$$\mathrm{M(OH_2)_6^{n+} + \mathbf{H_2O} \rightarrow M(OH_2)_5(\mathbf{OH_2})^{n+} + H_2O} \tag{1}$$

$$\mathrm{M(OH_2)_6^{n+} \rightarrow [M(OH_2)_5 \cdots OH_2^{n+}]^{\neq} \rightarrow M(OH_2)_5 \cdot OH_2^{n+}}\ (D \text{ mechanism}) \tag{2}$$

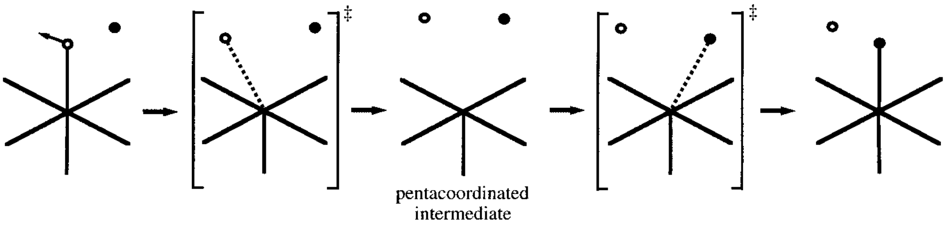
$$\mathrm{M(OH_2)_6 \cdot OH_2^{n+} \rightarrow [M(OH_2)_6 \cdots OH_2^{n+}]^{\neq} \rightarrow M(OH_2)_7^{n+}}\ (A \text{ mechanism}) \tag{3}$$

$$\mathrm{M(OH_2)_6 \cdot OH_2^{n+} \rightarrow [M(OH_2)_5 \cdots (OH_2)_2^{n+}]^{\neq}}\ (I_a, I, \text{ and } I_d \text{ mechanisms}) \tag{4}$$

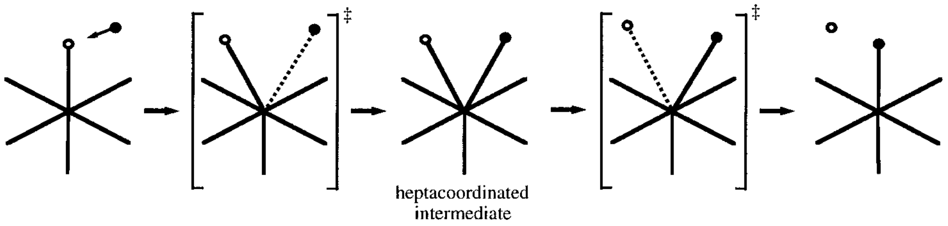
On the basis of the structures and imaginary modes of the transition states, these computations [1][2] allowed the attribution of the A, I_a, or D mechanisms to *Reaction 1*

Scheme

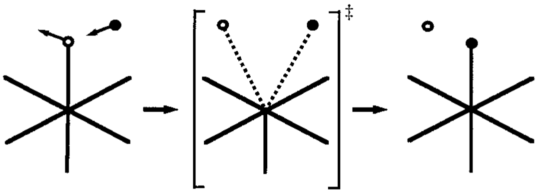
D mechanism:



A mechanism:



I_a, I, or I_d mechanism:



($M = Sc^{III}$, Ti^{III}, V^{III}, V^{II}, Cr^{III}, Cr^{II}, Mn^{III}, Mn^{II}, Fe^{III}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II}). The activation mode of interchange mechanisms can be determined *via* the sign of the change of the sum of all M–O bond lengths ($\Delta\Sigma d$(M–O); *Eqn. 5*) for the activation process. The $\Delta\Sigma d$(M–O) parameter is expected to be related to the intrinsic component of the activation volume ($\Delta V^{\neq}$).

$$\Delta\Sigma d(\mathrm{M{-}O}) = \Sigma d(\mathrm{M{-}O})_{\text{transition state}} - \Sigma d(\mathrm{M{-}O})_{\text{reactant}} \qquad (5)$$

The computed activation energies [1][2], obtained with this simple gas-phase model, agree with experimental [3] $\Delta H^{\neq}$ (or $\Delta G^{\neq}$) values, and, in cases like those of $V(OH_2)_6^{2+}$ and $Mn(OH_2)_6^{2+}$ in which equal activation energies were calculated for an associative and a dissociative activation, the mechanism was attributed by the comparison of the sign of $\Delta\Sigma d$(M–O) with that of the experimental $\Delta V^{\neq}$.

Computationally, this model is not demanding, since the number of atoms treated quantum chemically is modest. The H_2O-exchange reaction on the $Ru(NH_3)_5OH_2^{3+}$ ion has been investigated [4] recently with an improved version of this model in which dynamic and static electron correlation were included in the computation of the energies, and the second coordination sphere together with the bulk solvent were treated as a dielectric continuum in the calculation of the geometries and energies. The roles of hydration and electron correlation were discussed.

For all thus-far-investigated [1] [2] [5–8] hexaaqua ions, no transition state for the I_d mechanism has been found, most likely because, due to the omission of the second coordination sphere, H-bonding of the exchanging H_2O ligands with equatorial aqua ligands is favored over the weak $M-OH_2$ bonds. If these H-bonds are formed by H_2O molecules of the second coordination sphere, structures with weak $M-H_2O$ bonds might be obtained. At the present time, no such large calculations, which would involve at least 17 H_2O molecules, have been reported. For this reason, on the basis of the gas-phase model as well as the present one in which the second and further coordination spheres are represented by a dielectric continuum, only structures of stationary points for the *D* pathway could be obtained, when computations were performed for a dissociative activation. This result should not be taken as evidence against the existence of the I_d mechanism.

The H-bonds between H_2O (in the second coordination sphere) and coordinated amine ligands are weaker than those of aqua ligands. This might explain why, for the aquation of $Co(NH_3)_5Cl^{2+}$, $Co(NH_3)_5SCN^{2+}$, and $Co(NH_3)_5NCS^{2+}$, or the corresponding anations of $Co(NH_3)_5OH_2^{3+}$, transition states for the I_d mechanism were found [9] [10].

Substitution mechanisms are usually attributed on the basis of $\Delta V^{\neq}$, whereby values close to zero suggest the *I* mechanism, and negative or positive values indicate an *a* or a *d* activation, respectively. The experimental distinction of the *A* from the I_a mechanism, or, alternatively, the *D* from the I_d one, is very difficult, since the advancement of a proof for the existence or absence of a penta- or heptacoordinated intermediate is by no means an easy task. The magnitude of $\Delta V^{\neq}$ is not related to the mechanism in a straightforward manner, since the molar volume of the transition state (which is the measured quantity) is smaller than that of the corresponding pentacoordinated intermediate or larger than that of the heptacoordinated one [1] [2]. For both types of intermediates, *Swaddle* [11] has reported limiting values for $\Delta V^{\neq}$. Thus, in general, the experimental $\Delta V^{\neq}$ values allow only the attribution of the *activation mode* (*a*, *d*, or *I*) of a substitution reaction. The very negative $\Delta V^{\neq}$ for the H_2O exchange on $Ti(OH_2)_6^{3+}$ [12], which is close to the limiting $\Delta V^{\neq}$ (-13.5 cm^3/mol) [11] predicted for the formation of the heptacoordinated intermediate, is an exception and was taken as strong evidence for the *A* mechanism.

It is important to note that, in most cases, the experimental activation parameters, in particular the $\Delta V^{\neq}$, do not allow the distinction of the stepwise (*A* or *D*) from the concerted (I_a or I_d) mechanisms. Therefore, not all mechanisms, proposed in the literature, can be considered definitive.

In the present study, the improved model [4] was applied to the H_2O-exchange reaction on $V(OH_2)_6^{2+}$, $Mn(OH_2)_6^{2+}$, and $Fe(OH_2)_6^{2+}$ to check (for V^{II} and Mn^{II}) or to verify (for Fe^{II}), whether the thus-calculated activation energies ($\Delta E^{\neq}$) allow the distinction of the *A* from the *D* mechanism.

The previous calculations [1] on the aqua ion of V^{II} have yielded equal $\Delta E^{\ddagger}$ values for the I_a and D mechanisms, and the I_a mechanism was attributed on the basis of the negative $\Delta\Sigma d(M-O)$ parameter, since the experimental $\Delta V^{\ddagger}$ [13] is negative.

Analogous calculations [2] on Mn^{II} have given almost equal $\Delta E^{\ddagger}$ values for the A and D mechanisms, and, furthermore, because of the small energy difference (2.1 kJ/mol) between the heptacoordinated intermediate and the transition state for the A mechanism, the possibility was left open that, instead of the A, the I_a mechanism could operate. It could not be excluded [2] that the hydration energy of the transition state (for the A mechanism) is larger than that of the heptacoordinated intermediate. The comparison of the sign of experimental $\Delta V^{\ddagger}$ [14] with that of $\Delta\Sigma d(M-O)$ allowed the attribution of the A or perhaps I_a mechanism for this reaction.

The H_2O-exchange reaction on the hexaaqua ion of Fe^{II} has been suggested [14] to proceed *via* the I_d mechanism on the basis of its moderately positive activation volume. It should be remembered that this experiment neither excludes the D mechanism nor proves the I_d one. According to the gas-phase calculations, [2] and in agreement with experiment, a D mechanism was predicted to be preferred over the I_a one (by 7.5 kJ/mol), whereby it should be noted that this model cannot yield transition states for the I_d mechanism. As a test of the present computational method, this system was also reinvestigated.

In this study are analyzed critically the performance and shortcomings of models like the present one in which a quantum-chemically described first coordination sphere is submitted to the influence of the surrounding solvent represented as a dielectric continuum. Since such models do not require the computation of large systems, they might be widely applied.

Results. – *Model and Approximations.* The structures and energies of all reactants or products (which are identical for these exchange reactions), transition states and intermediates involved in the H_2O-exchange reaction (*Eqn. 1*) on $V(OH_2)_6^{2+}$, $Mn(OH_2)_6^{2+}$, and $Fe(OH_2)_6^{2+}$ have been calculated by *ab initio* quantum-chemical methods. The geometries were optimized with the self-consistent reaction-field model (SCRF) [15–17] by neglecting electron correlation, and the energies were calculated on the basis of the polarizable continuum model (PCM) [18–20] as described in earlier work [4]. Electron correlation within the complexes was computed on the basis of the 'multiconfigurational self-consistent-field second-order quasidegenerate perturbation' method (MCQDPT2) [21] [22] as reported in [4]. All MCQDPT2 calculations involved a single reference wave function, since there is no static electron correlation in these compounds.

Dispersion (correlation between electrons of the solute and the solvent) was neglected as well as the harmonic zero-point energy (ZPE). It has been shown [10] for the $S \rightarrow N$ isomerization and the aquation of $Co(NH_3)_5SCN^{2+}$ that the ZPEs vary within less than 4 kJ/mol for a given activation process, and that their consideration would be meaningful only when the specific solute-solvent interactions (H-bonds) are treated quantum chemically.

For the prediction of the most favorable exchange mechanism, the computation of $\Delta G^{\ddagger}$ is required. The present $\Delta E^{\ddagger}$ correspond to $\Delta H^{\ddagger}$ at 0 K without ZPE. Activation entropies at 25° were available, since the harmonic vibrational frequencies have been computed, but they cannot and do not agree with experiment because of the significant changes of the H-bonds between the first and the second coordination spheres during the activation process. It should be noted that this model is not suitable for the evaluation of $\Delta S^{\ddagger}$.

The I_a and A mechanisms are mutually exclusive, since the heptacoordinated transition state has an imaginary mode that either describes the concerted entry and leaving of the two exchanging ligands (*Fig. 1,a*) or only the motion of the entering (or leaving) ligand, whereby the others rearrange (*Fig. 1,b*). In the first case, the mechanism is I_a, and the computation of the intrinsic reaction coordinate leads to reactants and products that are identical or the mirror images of each other. The second case is an example of the A mechanism. The calculation of the intrinsic reaction coordinate yields the reactant (or product) and the heptacoordinated intermediate. If the energy difference between the transition state and the intermediate is large, the A mechanism can be attributed with confidence, whereas if it is small, one might prefer to attribute the I_a mechanism.

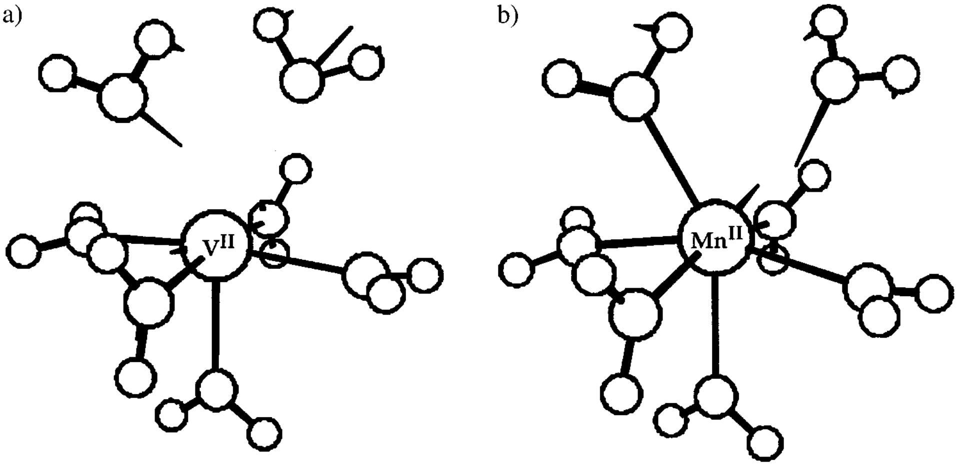


Fig. 1. *Structure and imaginary mode of transition states:* a) $[V(OH_2)_5\cdots(OH_2)_2^{2+}]^{\ddagger}$ *with* C_2 *symmetry*; b) $[Mn(OH_2)_6\cdots OH_2^{2+}]^{\ddagger}$ *with* C_1 *symmetry*

The I_d and D mechanisms are not mutually exclusive. The former has not yet been found for the H_2O exchange on metal hexaaqua ions, presumably because of the reasons mentioned in the *Introduction*. It remains to be seen whether such transition states can be obtained on the basis of larger models that include a quantum-chemically described second coordination sphere. Structures of transition states for both the I_d and the D mechanisms, have been obtained in the H_2O-exchange reactions on the aqua pentakis(methylamine) complexes of Cr^{III}, Rh^{III}, and Co^{III}, and the (aqua)(pentaammine)cobalt(III) ion as well [23–25].

It is important to note that the present model is not applicable to reactions involving spin changes, especially ones that arise from promotion of one or more electrons from a nonbonding into an antibonding orbital. The VIS spectra of hexaaqua transition-metal ions are red-shifted by a substantial amount of energy (> 30 kJ/mol) when they are calculated on the basis of the present model [25]. This indicates that the crystal-field-splitting parameter (Δ) is too small, and so are also the energy separations between the low-spin and the high-spin electronic states. In spite of the inaccuracy of Δ, the calculated activation energies for all thus-far-investigated substitution reactions of pseudo-octahedral transition-metal complexes agree with experiment, since, in all these cases [1][2][4–10][23][24], no spin change takes place in the course of the substitution process.

Two isomers have been reported [5] for the H_2O adducts of the reactants, $M(OH_2)_6 \cdot OH_2^{n+}$. In the first (A), which has been used in the calculations [1][2] on the first-row transition-metal hexaaqua ions on the basis of the gas-phase model, the H_2O molecule in the second coordination sphere is H-bonded to one H_2O ligand of the first coordination sphere (*Fig. 2,a*). This isomer is a substructure of the hydrated $Cr(OH_2)_6^{3+}$ ion [26]. In the other isomer (B), the H_2O molecule in the second coordination sphere is H-bonded in a bridging mode to two H_2O ligands of the first coordination sphere (*Fig. 2,b*). This structure [5] was obtained by computations of the intrinsic reaction coordinate starting from transition states for the I_a or A mechanism. It should be noted that this isomer is not a substructure of the hydrated $Cr(OH_2)_6^{3+}$ ion. The activation energies were calculated on the basis of both isomers of the reactants.

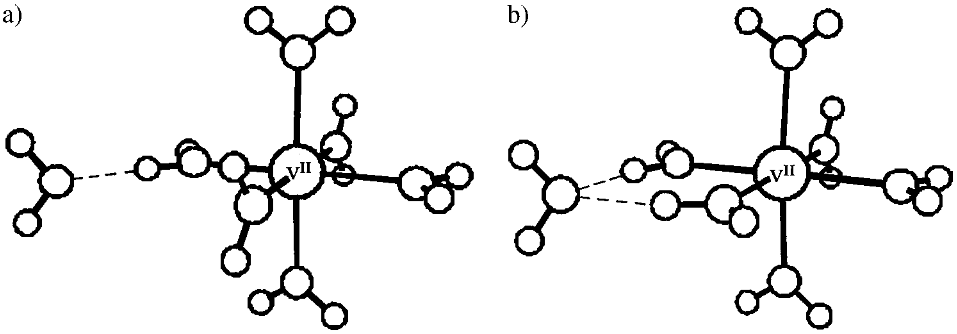


Fig. 2. *Structure of the H_2O adduct of the reactant $V(OH_2)_6 \cdot OH_2^{2+}$:* a) *isomer A*; b) *isomer B*

Activation Energies. The geometries, optimized at the SCRF [15–17] level, are insignificantly different from those obtained [1][2] previously for the free ions in the gas phase. This has already been observed for all species involved in the H_2O exchange on $Ru(NH_3)_5OH_2^{3+}$ [4].

The total energies of the hydrated ions, calculated on the basis of the PCM [18–20] with and without electron correlation are given in *Table 1*. The experimental $\Delta H^{\ddagger}$ values [13][14] for the H_2O exchange on the hexaaqua ions of V^{II}, Mn^{II}, and Fe^{II}, and the corresponding computed $\Delta E^{\ddagger}$ values are reported in *Table 2*. An associative, either I_a or A, and the D pathways have been investigated for each metal ion, whereas it should be remembered that, for the H_2O-exchange reactions on hexaaqua ions, this model fails to yield transition states for I_d mechanism. The $\Delta E^{\ddagger}$ values computed [1][2] for the free ions in the gas phase are also included for comparison.

Table 1. *Total Energies of the Hydrated Species* (with and without Electron Correlation)a)

Species	Symmetry	Mechanism	E(PCM)b)	E(PCM + MP2)c)
$V(OH_2)_6^{2+}$	T_h	*D*	– 526.841674	– 528.036245
$[V(OH_2)_5\cdots OH_2^{2+}]^{\ddagger}$	C_s	*D*	– 526.815905	– 528.008913
$V(OH_2)_5\cdot OH_2^{2+}$	C_s	*D*	– 526.816037	– 528.008660
$V(OH_2)_6\cdot OH_2^{2+}$ (A)d)	C_s	I_a	– 602.870399	– 604.259319
$V(OH_2)_6\cdot OH_2^{2+}$ (B)e)	C_s	I_a	– 602.873520	– 604.264218
$[V(OH_2)_5\cdots (OH_2)_2^{2+}]^{\ddagger}$	C_2	I_a	– 602.851727	– 604.239285
$Mn(OH_2)_6^{2+}$	T_h	*D*	– 559.261994	– 560.480853
$[Mn(OH_2)_5\cdots OH_2^{2+}]^{\ddagger}$	C_{2v}f)	*D*	– 559.248436	– 560.468468
$Mn(OH_2)_5\cdot OH_2^{2+}$	C_2	*D*	– 559.249207	– 560.470540
$Mn(OH_2)_6\cdot OH_2^{2+}$ (A)d)	C_s	*A*	– 635.290492	– 636.703538
$Mn(OH_2)_6\cdot OH_2^{2+}$ (B)e)	C_s	*A*	– 635.294403	– 636.709268
$[Mn(OH_2)_6\cdots OH_2^{2+}]^{\ddagger}$	C_1	*A*	– 635.283489	– 636.696709
$Mn(OH_2)_7^{2+}$	C_2	*A*	– 635.284998	– 636.698305
$Fe(OH_2)_6^{2+}$	S_6	*D*	– 578.594140	– 579.845217
$[Fe(OH_2)_5\cdots OH_2^{2+}]^{\ddagger}$	C_sg)	*D*	– 578.577996	– 579.829653
$Fe(OH_2)_5\cdot OH_2^{2+}$	C_s	*D*	– 578.580219	– 579.833256
$Fe(OH_2)_6\cdot OH_2^{2+}$ (A)d)	C_s	I_a	– 654.622290	– 656.067580
$Fe(OH_2)_6\cdot OH_2^{2+}$ (B)e)	C_s	I_a	– 654.626765	– 656.074452
$[Fe(OH_2)_5\cdots (OH_2)_2^{2+}]^{\ddagger}$	C_2	I_a	– 654.611560	– 656.056747

a) Units: hartrees. b) Electron correlation is neglected. c) Electron correlation is included. d) Isomer A in which the H_2O in the second coordination sphere is H-bonded to one H_2O ligand (*Fig. 2,a*). e) Isomer B in which the H_2O in the second coordination sphere is H-bonded to two adjacent H_2O ligands in a bridging mode (*Fig. 2,b*). f) Computation in C_2 symmetry. g) Computation in C_1 symmetry.

Table 2. *Experimental and Calculated Activation Energies for* Reaction 1a)

M^{II}	Mechanism (isomer)	$\Delta H^{\ddagger}$b)	$\Delta E^{\ddagger}$(PCM)	$\Delta E^{\ddagger}$(PCM + MP2)	$\Delta E^{\ddagger}$(free ion)c)
V	*D*		67.7 (67.3)d)	71.8 (72.4)d)	58.0 (56.7)d)
V	I_a (A)	61.8	49.0	52.6	57.9
V	I_a (B)	61.8	57.2	65.5	65.8e)
Mn	*D*		35.6 (33.6)d)	32.5 (27.1)d)	32.4 (25.9)d)
Mn	*A* (A)	32.9	18.4 (14.4)f)	17.9 (13.7)f)	30.9 (28.8)f)
Mn	*A* (B)	32.9	28.7 (24.7)f)	33.0 (28.8)f)	39.9e) (37.8)e)f)
Fe	*D*	41.4	42.4 (36.5)d)	40.9 (31.4)d)	34.8 (23.1)d)
Fe	I_a (A)		28.2	28.4	42.3
Fe	I_a (B)		39.9	46.5	52.9e)

a) Units: kJ/mol. b) Experimental values [13][14]. c) Previous calculations [1][2] on the free ions in the gas phase. d) ΔE for the pentacoordinated intermediate. e) This work. f) ΔE for the heptacoordiuated intermediate.

Hexaaquavanadium(II) Ion. As already mentioned, the $\Delta E^{\ddagger}$ values calculated originally [1] on the basis of reactant A (*Fig. 2,a*) for the free aqua complexes in the gas phase are equal for the I_a and *D* mechanisms and similar to the experimental $\Delta H^{\ddagger}$ value (*Table 2*). If isomer B (*Fig. 2,b*) is taken as a reactant, the I_a mechanism would require a higher activation energy than the *D* mechanism (at the *in vacuo* level). The inclusion of hydration without electron correlation lowers the activation energy, $\Delta E^{\ddagger}$(PCM), for the I_a mechanism and raises that for *D*. When electron correlation is included, the mechanism favored remains I_a over D, and the activation energy, $\Delta E^{\neq}$(PCM + MP2) calculated on the basis of reactant B is close to the experimental value, whereas with reactant A a value too-low was obtained. It should be noted that, in this case, the most reliable calculations (which include hydration and electron correlation) predict that the I_a mechanism has the lowest activation energy independent of the chosen isomer for the reactant.

Hexaaquamanganese(II) Ion. According to the original calculations [2] on the free ions and reactant A, the $\Delta E^{\neq}$ values for the A and D mechanisms, are almost equal (*Table 2*). With isomer B as a reactant, the a activation would be unfavorable with respect to the D pathway as for V^{II} (at the *in vacuo* level). When hydration without electron correlation is included, the A mechanism is more advantageous than the D pathway. The most reliable computations that take into account hydration and electron correlation predict that the A mechanism with isomer A as a reactant is the preferred one. Its calculated $\Delta E^{\neq}$(PCM + MP2) is, however, too low by 15 kJ/mol compared with experiment, whereas, with reactant B, $\Delta E^{\neq}$(PCM + MP2) is equal to the experimental $\Delta H^{\neq}$ value for the D and A pathways, and the attribution of the exchange mechanism is still impossible on the basis of $\Delta E^{\neq}$ as in the previous [2] study. The too-low activation energy, calculated for reactant A, would predict correctly that the A pathway is most favorable, but, because of its large deviation from the experimental value, it should not be considered.

In the original [2] gas-phase calculations, the heptacoordinated intermediate had an energy only slightly lower than that of the corresponding transition state. Since this energy difference of 2.1 kJ/mol increased to 4.2 kJ/mol upon inclusion of hydration (*Table 2*), it might be preferable to attribute the A rather than the I_a mechanism for the H_2O exchange on $Mn(OH_2)_6^{2+}$.

Hexaaquairon(II) Ion. Its exchange reactions were reinvestigated because, according to the calculations on the free ions, the D mechanism was favored over I_a by a relatively small energy difference of 7.5 kJ/mol (*Table 2*). This reaction can, therefore, be considered a stringent test for the improved model. As for V^{II} and Mn^{II}, $\Delta E^{\neq}$(PCM) for the I_a pathway with reactant A is too low. The $\Delta E^{\neq}$(PCM) for the D and the I_a pathways with isomer B as a reactant are almost equal and agree with experiment, but did not allow distinction of the two mechanisms. When electron correlation was included, the I_a pathway was predicted to be more favorable on the basis of reactant A, but $\Delta E^{\neq}$(PCM + MP2) does not agree with $\Delta H^{\neq}$. Since for the other two metal ions as well, reactant A yielded $\Delta E^{\neq}$(PCM + MP2) values that are too low, this isomer is not appropriate for this computational model. The D mechanism requires a $\Delta E^{\neq}$ lower than that for I_a when isomer B is used as a reactant, and $\Delta E^{\neq}$(PCM + MP2) for the D pathway agrees with experiment.

It should be remembered that transition states for the I_d mechanism are not available on the basis of this model, and, therefore, the calculations leave open the question of whether the D or the I_d mechanism operates.

Discussion. – *Computations on the Free Ions in the Gas Phase*. In the previous studies [1][2], the calculations have been performed with reactant A (*Fig. 2,a*) only, because it was likely to be a substructure of 'genuine' hexaaqua ions in aqueous solution. The agreement of calculated and observed activation energies is surprisingly good. Since isomer B (*Fig. 2,b*) yielded accurate results for the improved computational model (in which electron correlation and hydration effects are included), calculations on the free ions with isomer B have also been performed for comparison (*Table 2*). The thus-obtained activation energies are higher by 8–10 kJ/mol than those based on reactant A. The deviations from $\Delta H^{\neq}$ are, however, smaller than 10 kJ/mol for V^{II} and Mn^{II} for which the I_a and A mechanisms apply. It is important to note that, on the basis of reactants B, the D (or I_d) mechanism would have been predicted incorrectly to be the most favorable for all three reinvestigated transition-metal hexaaqua ions. The success of the original studies is due to the (lucky) choice of the reactant structure. The role of the structure of the reactant will be discussed below.

Computations on the Hydrated Ions. Although this model is better than the original gas-phase one, it is still approximate. Hydration has not been treated with the same model in the geometry optimizations and in the energy computations for reasons already discussed [4]. Also, the geometries have been optimized by neglecting dynamic electron correlation. The most serious approximation is, however, the omission of the second coordination sphere, since it is treated as a dielectric continuum, and the H-bonds between the first and the second coordination spheres are not considered in this model.

The $\Delta E^{\neq}(\mathrm{PCM}+\mathrm{MP2})$ data, calculated on the basis of reactant A, predict that the *a* activation is most favorable for all three metal ions, whereas quantitatively correct $\Delta E^{\neq}$ values were obtained with reactant B. On the basis of this reactant and model, and in agreement with experiment, the lowest $\Delta E^{\neq}$ values were obtained for the H_2O exchange *via* the I_a and D (or I_d) mechanisms on the hexaaqua ions of V^{II} and Fe^{II}, respectively. However, this model does not allow us to distinguish the A from the D (or I_d) pathway for Mn^{II}. In this case, the attribution of the (A) mechanism has, therefore, to be made on the basis of the sign of $\Delta\Sigma d(\mathrm{M-O})$ [2].

Role of the Structure of the Reactant. The $\Delta E^{\neq}$ values closest to experimental $\Delta H^{\neq}$ values were obtained in the calculations on the free ions when reactant A (*Fig. 2,a*) was used. In contrast, the improved model, which takes into account hydration and electron correlation, yielded the most accurate $\Delta E^{\neq}$ values with reactant B (*Fig. 2,b*). Why is isomer A the 'right' reactant for the free ions and isomer B the 'right' one for the hydrated ions?

First, it should be noted that none of these reactants corresponds to the 'genuine' reactant. Second, the model, represented by *Eqns. 2–4* is very simple, since only six or seven H_2O molecules are treated quantum chemically. In the following, the various factors that contribute to $\Delta E^{\neq}$ will be discussed. It will be shown how or to what extent they are taken into account by the present model.

Two kinds of processes, which occur in a concerted manner, contribute to the activation energy of the *Reaction 1:* the first involves the events in the first coordination sphere, bond making and bond weakening. For H_2O exchange on $V(OH_2)_6^{2+}$ *via* the I_a mechanism (*Eqn. 4*, *Scheme*), this would be the conversion of one $V^{II}-O$ bond of the reactant into two (weak) $V^{II}\cdots O$ bonds of the transition state and the rearrangement of the five 'spectator' $V^{II}-O$ bonds. The second type of process is the reorganization of all other H_2O molecules surrounding the complex. It may involve changes of the number of H_2O molecules in the second, third, and further coordination spheres, as well as the alteration of the strength and number of hydrogen bonds.

The models, which involve *ab initio* quantum-chemical calculations of hydrated or free ions in the gas phase on the basis of *Eqns. 2–4*, take into account both above-described processes in an *approximate* way. The events in the first coordination sphere are treated explicitly by neglecting, however, the H-bonds to the second coordination sphere. In the gas-phase model, the second kind of processes involving the rearrangement of the surrounding H_2O is represented merely by the breaking of a single H-bond, which is present in reactant A and absent in the transition state $[V(OH_2)_5 \cdots (OH_2)_2^{2+}]^{\neq}$ (*Figs. 1,a*, and *2,a*). In the improved model, which takes into account hydration and electron correlation, the second type of process is modeled by breaking two H-bonds in reactant B. The reorganization of all other H_2O molecules is taken into account by the polarizable continuum model (PCM), [18–20] but here H-bonding is also neglected.

The above-asked question could be answered tentatively as follows: with reactant A, the gas-phase model yielded accurate $\Delta E^{\neq}$ values, because the energy for both of the above-mentioned processes is reproduced well *in this combination*. Alternatively, reactant B in combination with the quantum-chemical model that takes into account hydration and electron correlation also yielded correct $\Delta E^{\neq}$ values. In both cases, there is most likely a cancellation of errors.

The question of why, with these combinations, accurate $\Delta H^{\neq}$ values can be obtained, remains open. In other words, the origin of the success of *Eqns. 2–4* in the computation of $\Delta E^{\neq}$ is unknown. It may even be surprising that such a simple model, which neglects essentially the whole environment of the aqua ion, can reproduce $\Delta H^{\neq}$ values accurately. Nevertheless, the improved model, which includes hydration and electron correlation, correctly reproduced also the $\Delta H^{\neq}$ for the H_2O exchange on $Ru(NH_3)_5OH_2^{3+}$ [4]. Furthermore, this model predicted, in agreement with experiment, that the I_a mechanism is more advantageous than the D one.

Alternative Computational Methods. Classical and *ab initio* molecular-dynamics (MD) simulations have been performed on the H_2O-exchange reaction of aqua ions with lower activation energies. These computations are discussed in the recent review article of *Helm* and *Merbach* [27]. The most promising method, the *ab initio* MD, like the *Car-Parrinello* technique [28], explicitly takes into account all solute-solvent interactions, in particular the H-bonds between the first and the second coordination spheres. In this respect, it is superior to the model discussed (*Eqns. 2–4*), but it is inferior for the computation of alternative pathways that require higher $\Delta E^{\neq}$, since these events might readily escape detection. Furthermore, reactions involving spin changes cannot be treated. The H_2O-exchange reaction on (low-spin) $Co(OH_2)_6^{3+}$ might be such an example; this reaction has been suggested [29] to proceed *via* a transition state having a high-spin electronic state.

In contrast to the *ab initio* MD simulations, the treatment of solute-solvent interactions on the basis of the present model (*Eqns. 2–4*) is approximate, and this explains why neither the activation entropy ($\Delta S^{\neq}$) nor $\Delta G^{\neq}$ is available. The $\Delta S^{\neq}$ and $\Delta G^{\neq}$ parameters could, in principle, be computed *via ab initio* MD simulations, but such methods have not yet been applied to transition-metal ions, presumably because rather long simulation times would be required. They would be in the nano- to microsecond region for Mn^{II} and Fe^{II}, and on the order of milliseconds for V^{II}.

Structure and Electronic Structure of the Heptacoordinated Species: a) *Transition State* $[V(OH_2)_5 \cdots (OH)_2)_2^{2+}]^{\neq}$. Its structure and imaginary mode are depicted in

Fig. 1,a, and the corresponding qualitative orbital diagram (*Fig. 3*), which is valid for first-row transition-metals only, has already been presented [2]: in heptacoordinated species, regardless of whether they are transition states or intermediates, the five 3d orbitals are split roughly into three levels. In the first (d_α), there are two nonbonding orbitals, corresponding approximately to two of the three d_π ('t_{2g}') levels of octahedral complexes. In the second moderately antibonding level (d_β), there are also two orbitals: one arises from the destabilization of a d_π ('t_{2g}') orbital and the other one from the stabilization of a d_σ^* ('e_g^*') orbital of a pseudo-octahedral complex. The third orbital (d_γ) is strongly antibonding and corresponds approximately to the other d_σ^* ('e_g^*') level in octahedral symmetry.

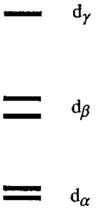


Fig. 3. *Qualitative orbital diagram* [2] *of heptacoordinated species* (transition states or intermediates)

For V^{II}, exhibiting a high-spin $3d^3$ electron configuration, the two nonbonding d_α and one moderately antibonding d_β levels are singly occupied in the transition state $[V(OH_2)_5 \cdots (OH_2)_2^{2+}]^{\neq}$ with C_2 symmetry, whereas the other d_β orbital as well as the d_γ one are empty.

Four molecular orbitals are involved in the two $V^{II} \cdots O$ bonds of the exchanging H_2O ligands: the bonding $\sigma(V^{II} \cdots O)$ orbitals, MOs 31 and 32 (*Fig. 4*), are *a* and *b* species (C_2 symmetry) and correspond to the lone pairs of the two exchanging H_2O ligands. These lone pairs lie approximately in the H–O–H plane. Upon localization by preserving the C_2 symmetry, their shape changes only slightly. These $V^{II} \cdots O$ bonds are relatively weak, because of their length of 2.67 Å. The corresponding antibonding $\sigma^*(V^{II} \cdots O)$ orbitals (*Fig. 5*) have almost pure 3d character: MO 42 with *b* symmetry (*Fig. 5,a*) would be a d_π ('t_{2g}') orbital in pseudo-octahedral symmetry. In the transition state $[V(OH_2)_5 \cdots (OH_2)_2^{2+}]^{\neq}$, it is antibonding because of its interaction with the σ orbitals of the two exchanging aqua ligands. This orbital is the lower of the two d_β levels and, therefore, singly occupied. The other moderately antibonding d_β level, MO 47 with *a* symmetry (*Fig. 5,b*), would be a d_σ^* ('e_g^*') orbital in pseudo-octahedral symmetry. Its stabilization in heptacoordinated species, with respect to pseudo-octahedral coordination, is due to the relatively long $V^{II} \cdots O$ bonds and their positions off the C_2 axis. MO 47 is energetically higher than MO 42 because of the destabilization caused by the $V^{II}-O$ bond of the aqua ligand in axial position. The d_γ level is the antibonding orbital in the equatorial plane; it looks like an e_g^* orbital of the $d_{x^2-y^2}$ type in octahedral symmetry.

b) *Heptacoordinated Intermediate* $Mn(OH_2)_7^{2+}$. In the high-spin $3d^5$ electron configuration of Mn^{II}, all orbitals of the d_α, d_β, and d_γ levels (*Fig. 3*) are singly occupied. In contrast to V^{II}, the second d_β level, MO 47 (*Fig. 5,b*), is occupied by one electron. This leads to the elongation of the axial $Mn^{II}-O$ bond, and the occupation of the

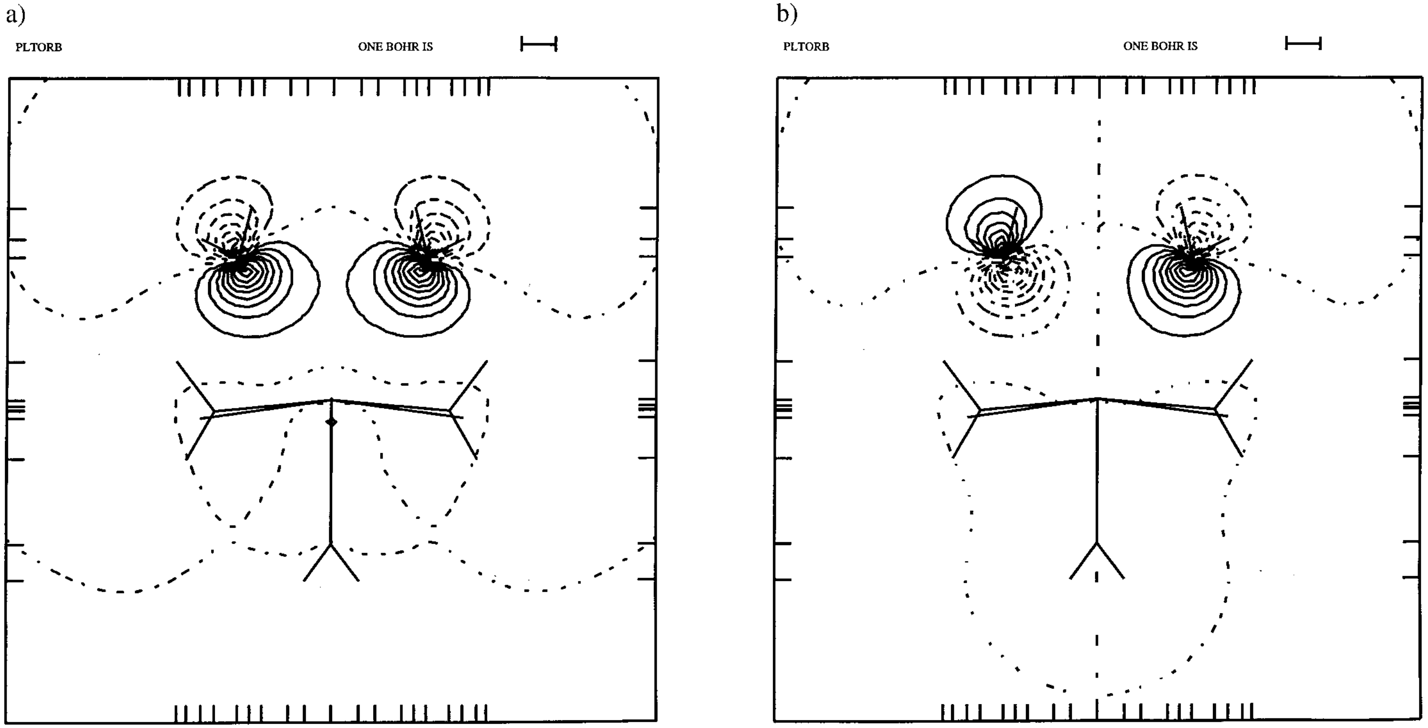


Fig. 4. *Contour plots depicting the two σ($V^{II}\cdots O$) orbitals of [$V(OH_2)_5\cdots(OH_2)_2^{2+}$]$^+$* (in the O···V···O plane): a) *MO 31* (*a* species); b) *MO 32* (*b* species)

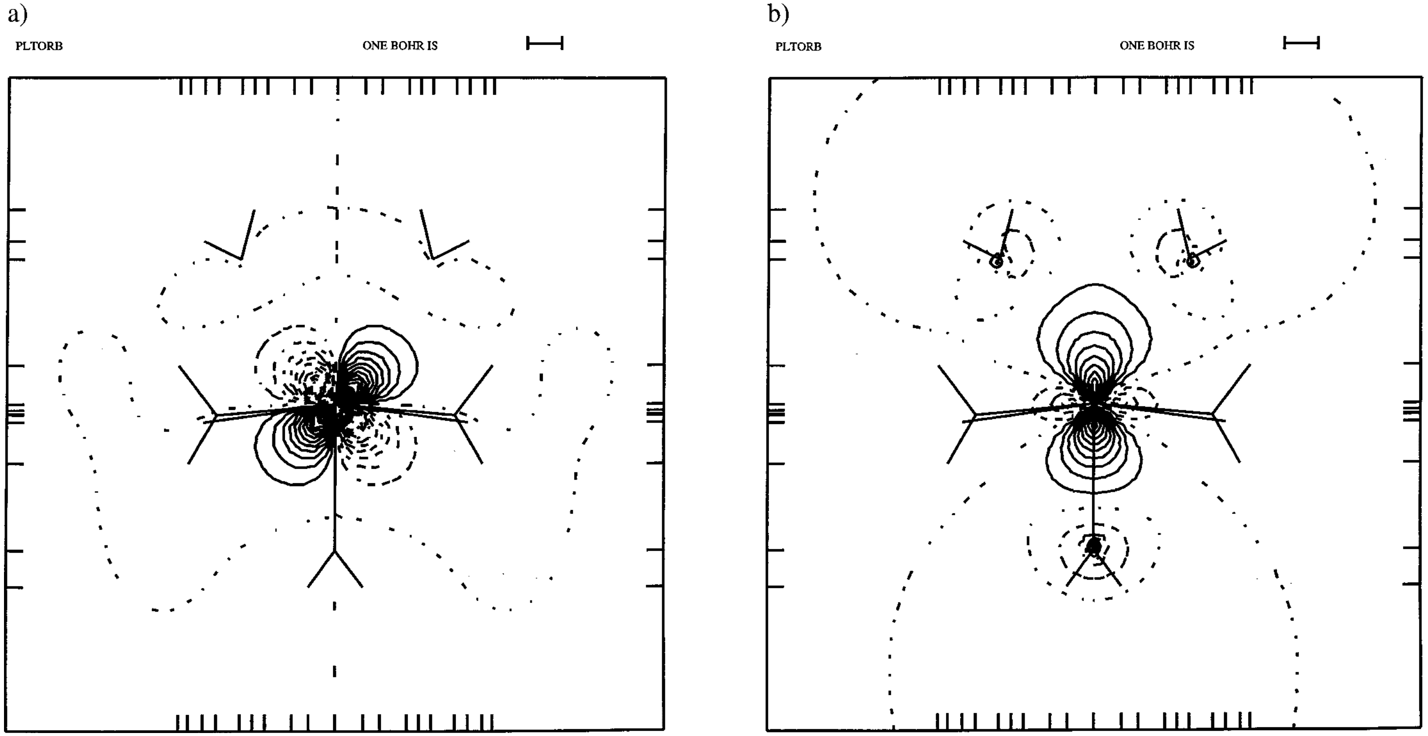


Fig. 5. *Contour plots depicting the two* $\sigma^*(V^{II}\cdots O)$ *orbitals of* $[V(OH_2)_5\cdots(OH_2)_2^{2+}]^+$ (in the O···V···O plane): a) *MO 42* (*b* species); b) *MO 47* (*a* species)

strongly antibonding d_γ level (which lies in the equatorial plane) causes an elongation of the four equatorial $Mn^{II}-O$ bonds. Thus, the occupation of the second d_β and the d_γ level leads to an elongation of the axial and equatorial $Mn^{II}-O$ bonds (in comparison with the corresponding $V^{II}-O$ bonds). Due to the occupation of all three antibonding orbitals (d_β and d_γ levels, *Fig. 3*) in the heptacoordinated intermediate $Mn(OH_2)_7^{2+}$, the seven $Mn^{II}-O$ bonds have about the same length of 2.25–2.38 Å. It should be noted that, in the transition state $[V(OH_2)_5 \cdots (OH_2)_2^{2+}]^{\ddagger}$, there are five 'normal' $V^{II}-O$ bonds with lengths of 2.210–2.225 Å, whereas the two $V^{II} \cdots O$ bonds of the exchanging H_2O ligands are considerably longer (2.67 Å).

Computational Details. All calculations were performed on a *HP 9000/C200* workstation using the *GAMESS* [30] program.

The basis sets of *Stevens et al.* [31] were used for V, Mn and Fe, where the 1s, 2s, and 2p shells are represented by relativistic effective core potentials, the 3s, 3p, 4s, and 4p shells have double-ζ quality, and the 3d shell has triple-ζ quality. For O and H, 6–31G(d) basis sets [32][33] were used ($\alpha_{3d}(O) = 1.20$ [34]).

The geometries and energies were computed as described in [4].

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