Reorganization criteria and their effects on inner-sphere barriers for transition metal redox pairs $M(H_2O)_6^{2+/3+}$ ($M = V$, Cr, Mn, Fe and Co)

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The models and formalisms for the inner-shell energy barrier of transition metal complexes are considered according to three reorganization criteria. The inner-shell reorganization energies and activation energies of several hexahydrate redox pairs of the first transition row elements, $M(H_2O)_6^{2+/3+}$ ($M = V$, Cr, Mn, Fe and Co), are calculated by different formalisms. The extent of the anharmonicities in the vibrations of the metal ion and the ligands in the reorganization process of these complexes is determined. The inner-shell barriers of these redox pairs are dependent on the reorganization model used. The contributions of the individual reactants to the inner-shell barrier are sensitive to the model used.

1 Introduction

The calculation of vertical reorganization and activation energies of reactants in electron-transfer processes is an essential part in the theory of electron transfer reactions.[1–4] The energy indices adopted are frequently divided into two parts: the inner-sphere contribution of the primary bond system and the outer-sphere or solution-sphere contribution. The inner-sphere reorganization of reactants corresponds to the primary bond-stretching and -bending vibrations of molecules. In the process reactants reorganize to the transition state, which has a suitable nuclear configuration to electron transfer. The inner-sphere reorganization barriers are generally calculated from a bond-stretching model based on the harmonic oscillator force field approximation for central ions having well-defined coordination numbers,[5] for example, for electron transfer between $Co(H_2O)_6^{2+}$ and $Co(H_2O)_6^{3+}$. The outer-sphere barriers are generally derived from the classical theory of nonequilibrium polarization of a continuous medium.[6–9] A detailed description of electron transfer process has been derived by Marcus.[10,11] In his electron transfer theory, the many-dimensional potential energy surfaces for the reactants and products were reduced to harmonic free energy curves that are a function of a single reaction coordinate, provided a hypothetical change in charge on the reactants produces a proportional change in the dielectric polarization of the surrounding medium. Marcus further assumed that the free energy curves describing the distortions of the reactants and products from their equilibrium states are also harmonic.[12] It should be noted that although the reorganization process of the reactants in electron transfer reactions might have an entropy contribution, this entropy contribution is assumed to be negligible in the classic model. If this is true, the reorganization free energy and the reorganization energy can be used interchangeably.

The energy of the reactants including the surrounding medium E_R and the energy of the products E_P as a function of the reaction coordinate are plotted in Fig. 1. Here, the reorganization parameter λ is the vertical difference between the energies of the non-interacting reactants and products for a self-exchange electron transfer reaction at the equilibrium configuration of the reactants. For electron transfer reactions of transition metal complexes of the type $ML_6^{2+/3+}$ (L denotes the ligand), the change of the nuclear configuration of the reacting system between the reactant state and the product state is generally assumed to be exclusively due to a change of the inner-shell radius of the complex.[3] Thus, the reaction coordinate can be identified with the distance r between the central ion and ligands. The energy of the inner-shell part of the reacting system can be represented as a function of the reaction coordinate, r, $E_{in} = E_{in}(r)$.

In contrast, the activation energy ΔE^* is the difference between the energies of the reactants at their transition state configuration and their equilibrium configuration. If, as shown in Fig. 1, the relevant potential energy curves are parabolic, then $\lambda = 4\Delta E^*$ for a self-exchange reaction. Within the Marcus framework the activation energy is obtained by locating the common minimum on the potential energy surfaces of the

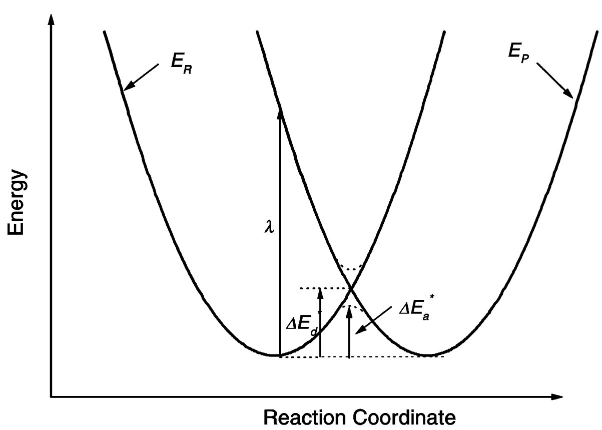

Fig. 1 Plot of the energy curves of the reactants (E_R) and products (E_P) *vs.* the reaction coordinate for a self-exchange reaction. λ denotes the vertical reorganization energy. $\Delta E_d^\ddagger$ denotes the diabatic activation energy and ΔE_a^* denotes the adiabatic activation energy.

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reactants and products. Another way of describing the reorganization process is through the use of separate energy curves for individual reactants and products. For a self-exchange reaction, only a single pair of energy curves is needed. The individual curves are shown in Fig. 2.

In the study of the inner-sphere energy barrier in electron transfer reactions, different reorganization criteria, such as reorganizing reactants to the transition state, to the midpoint of the reaction coordinate or to the intersection of the individual reactant parabolas, are sometimes used. In the present work, we give the calculation formalisms of the inner-sphere energy barrier to different degrees of sophistication against three organization criteria. We have studied in detail several self-exchange reactions of hexahydrate complexes $M(H_2O)_6{}^{2+/3+}$ ($M = V$, Cr, Mn, Fe and Co), expressed as:

$$M(H_2O)_6{}^{2+} + M(H_2O)_6{}^{3+} \rightarrow M(H_2O)_6{}^{3+} + M(H_2O)_6{}^{2+} \quad (1)$$

The inner-sphere reorganization energy of these hexahydrate redox pairs were earlier reported, using the semi-empirical quantum chemical INDO method,[13] the classical locked dipole orientation model (LDO) model[14,15] and the improved average dipole orientation (IADO) model.[14,15] In these systems, however, the electron correlation is expected to play an important role. Its neglect would lead to large errors in determining the energies as well as electronic configuration of reacting systems. In the present study, the structures and energies of hexahydrate complexes were determined by the unrestrained Moller–Plesset second-order perturbation theory. Based on the results of our theoretical calculations, we discuss the dependence of the inner-shell barrier on the reorganization model used. Furthermore, we show that the contributions of the individual reactants to the inner-shell barrier is a sensitive function of the model used.

This paper is organized as follows. We first present the inner-sphere reorganization and activation models of the self-exchange reaction expressed in eqn. (1). Various formalisms to derive λ_{in} and ΔE^*_{in} are given in section 2. The details of the computational method adopted are given in section 3. Results and discussions are shown in section 4. The conclusions of this study are summarized in section 5.

2 Theoretical models: various formalisms for the vertical reorganization energy and activation energy

2.1 Inner-sphere reorganization model and inner-sphere reorganization energy

As shown in Fig. 1, the reorganization parameter λ is the vertical difference between the energies of the non-interacting reactants and products at the reactants' equilibrium configuration for an electron-transfer reaction with zero energy change. Since identical force constants for reactant and product curves were proposed, this energy difference is also equal to the difference between the reactant and product energies at the equilibrium configuration of the products, (see Fig. 1).

Assuming that vertical electron transfer takes place from the reduced species to the oxidized species prior to structural reorganization of molecules, we can divide the electron transfer process of eqn. (1) into two sub-processes:

$$\begin{aligned} &M(H_2O)_6{}^{2+}(r_z) + M(H_2O)_6{}^{3+}(r_{z+1}) \\ &\quad \rightarrow M(H_2O)_6{}^{3+}(r_z) + M(H_2O)_6{}^{2+}(r_{z+1}) \end{aligned} \quad (2)$$

$$\begin{aligned} &M(H_2O)_6{}^{3+}(r_z) + M(H_2O)_6{}^{2+}(r_{z+1}) \\ &\quad \rightarrow M(H_2O)_6{}^{3+}(r_{z+1}) + M(H_2O)_6{}^{2+}(r_z) \end{aligned} \quad (3)$$

where r_z and r_{z+1} are the equilibrium nuclear configurations of the two species of a couple. Eqn. (2) denotes the electron transfer process and eqn. (3) denotes the structural reorganization process. The two sub-processes accompanying energy changes are shown in Fig. 2.

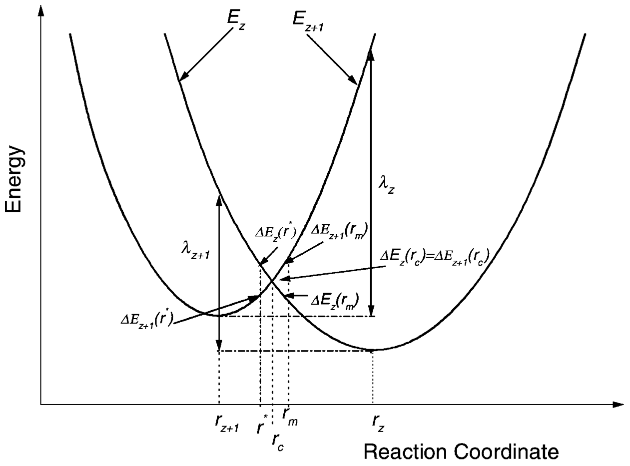

Fig. 2 Plot of the energy of the individual reactants *vs.* metal–ligand distance.

It should be noted that both the vertical reorganization energy and activation energy of the reacting system are the sum of the contributions of the individual reactants:

$$\lambda_{in}(r_z, r_{z+1}) = \lambda_z(r_z \rightarrow r_{z+1}) + \lambda_{z+1}(r_{z+1} \rightarrow r_z) \quad (4)$$

The first term on the right hand side in eqn. (4) is the energy required to change the metal–ligand distance in the reduced species from r_z to r_{z+1}, and the second term is the energy required to change the distance in the oxidized species from r_{z+1} to r_z.

From Fig. 2, we have

$$\lambda_z(r_z \rightarrow r_{z+1}) = E_{z+1}(r_z) - E_{z+1}(r_{z+1}) \quad (5)$$

$$\lambda_{z+1}(r_{z+1} \rightarrow r_z) = E_z(r_{z+1}) - E_z(r_z) \quad (6)$$

where $E_z(r_z)$ and $E_{z+1}(r_{z+1})$ are the energies of the reduced and oxidized species at the respective equilibrium configurations; $E_z(r_{z+1})$ is the energy of the reduced species at the equilibrium configuration of the oxidized species and $E_{z+1}(r_z)$ is energy of the oxidized species at the equilibrium configuration of the reduced species.

Subscripts z and $z + 1$ denote the reduced and oxidized species of a couple, respectively. r_z and r_{z+1} are the equilibrium nuclear configurations of the two species. r^*, r_m and r_c are respectively the common nuclear configurations of the two species at the transition state, the midpoint of the reaction coordinate and the intersection of the individual reactant parabolas. $\Delta E_i(r^*)$ ($i = z$ or $z + 1$) denotes the energy required to reach the transition state, $\Delta E_i(r_m)$ is the energy required to reach the midpoint of the reaction coordinate and $\Delta E_i(r_c)$ is the energy required to reach the intersection of the individual reactant parabolas.

Alternatively, provided that the metal–ligand vibrations are harmonic (at least to the intersection region), the vertical inner-sphere reorganization energy can be estimated by using the George–Griffith model,[16] which makes use of the equilibrium bond lengths and symmetrical stretching (breathing) frequencies of the reactants.[17] Denoting $(r_z - r_{z+1})$ by Δr, the vertical inner-shell reorganization energy is given by:

$$\lambda_{in}(f_z, f_{z+1}) = 6\left(\tfrac{1}{2}\left[(f_z + f_{z+1})(\Delta r)^2\right]\right) \quad (7)$$

where f_z and f_{z+1} are the equilibrium force constants of the ion–ligand bond of the reduced and oxidized species, respectively. The experimental value of the force constant of the ion–ligand bond can be obtained from measured vibrational spectra from

$$f_{i,\,\mathrm{Expt}} = 4\pi^2 m_\mathrm{L} C^2 \omega_i^2 / N \qquad (i = z \text{ or } z+1) \tag{8}$$

where m_L is the molecular weight of the ligand, C is the velocity of light, ω_i is the experimentally obtained symmetric stretching frequency of an ith ion–ligand bond, and N is the Avogadro's number.

In the absence of experimental vibrational spectroscopic data, the values of force constants f_i can be obtained theoretically from the relation:

$$f_{i,\,\mathrm{Theor}} = \left.\frac{\partial^2\{E_i(r_i)\}}{\partial^2 r}\right|_{r=r_i} \qquad i = z \text{ or } z+1 \tag{9}$$

where $E_i(r_i)$ is the total energy of the complex as a function of ion–ligand bond distance, r_i. As eqn. (7) is based on the harmonic oscillator approximation, it can be accepted that eqn. (4) to (6) are of higher accuracy.

It is evident from eqn. (7) that the contributions of the breathing modes of the individual reactants to λ_in are directly proportional to their respective force constants.

A simplified formalism to calculate λ_in can be obtained by defining a common, reduced force constant f_in for the two species of a redox pair:

$$f_\mathrm{in} = \frac{2 f_z f_{z+1}}{f_z + f_{z+1}} \tag{10}$$

Replacing f_z and f_{z+1} in eqn. (7) by f_in, we have:

$$\lambda_\mathrm{in}(f_\mathrm{in}) = 6 f_\mathrm{in}(\Delta r)^2 \tag{7b}$$

Substitution of eqn. (10) into eqn. (7b) gives:

$$\lambda_\mathrm{in}(f_\mathrm{in}) = 12 \frac{f_z f_{z+1}}{f_z + f_{z+1}} (\Delta r)^2 \tag{7b$'$}$$

2.2 Inner-sphere activation energy

In the theoretical study of the inner-sphere activation energy in self-exchange reactions, different reorganization criteria are sometimes used.[18] In this section we consider three reorganization models, which give different formalisms of the activation energy.

2.2.1 Reactants reorganize to the transition state in Marcus framework. Considering the activation process within the framework of Marcus theory, the activation energy ΔE^* is the difference between the energies of the reactants in their transition state configuration and their equilibrium configuration. In the electron transfer processes of transition metal complexes of type $\mathrm{M(H_2O)_6}^{2+/3+}$, energy conservation requires that the metal–ligand distances in the two reactants adjust to a common value (transition state configuration) where $E_\mathrm{R} = E_\mathrm{P}$ prior to the electron transfer. We denote this common distance by r^*; the activation energy is given by:

$$\Delta E^*_\mathrm{in}(r^*) = \{E_z(r^*) - E_z(r_z)\} + \{E_{z+1}(r^*) - E_{z+1}(r_{z+1})\} \tag{11}$$

If a harmonic vibration for the ion–ligand bonds of the individual reactants is assumed, the energy required to reorganize the two reactants to the transition state configuration is given by:

$$\Delta E^*_\mathrm{in}(r^*) = 6\left[\frac{1}{2} f_z (r_z - r^*)^2 + \frac{1}{2} f_{z+1} (r^* - r_{z+1})^2\right] \tag{12}$$

Minimizing the activation energy yields:

$$r^* = \frac{f_z r_z + f_{z+1} r_{z+1}}{f_z + f_{z+1}} \tag{13}$$

Substitution of eqn. (13) into eqn. (12) gives:

$$\Delta E^*_\mathrm{in}(r^*) = \frac{3 f_z f_{z+1}}{f_z + f_{z+1}} (\Delta r)^2 \tag{12b}$$

It should be noted that in order to reorganize reactants to the transition-state the contributions of the individual reactants to the activation energies are not equal, because the breathing force constants of the two species of a couple differ. f_{z+1} is larger than f_z. This implies that the reduced species reorganizes more than the oxidized species. Substituting r^* into eqn. (12), we find that the ratio of the contributions of the individual reactants is inversely proportional to their force constants. This differs from the contributions of force constants to λ_in.

Comparing eqn. (7) with eqn. (12b), it now can be rewritten as:

$$\lambda_\mathrm{in}(r^*) = \Delta E^*_\mathrm{in}(r^*)\left(4 + \frac{f_{z+1} - f_z}{f_z f_{z+1}}\right) \tag{7c}$$

It is apparent from eqn. (7c) that the inner-sphere activation energy is slightly less than one-quarter of the inner-sphere reorganization energy. The reason for the breakdown of the often-used $\Delta E^*_\mathrm{in}(r^*) = \frac{1}{4}\lambda_\mathrm{in}(r^*)$ relation is the deviation from parabolic behavior of the potential energy surface considered.

When replacing f_z and f_{z+1} in eqn. (12) and (13) by f_in, we obtain:

$$\Delta E^*_\mathrm{in}(f_\mathrm{in}) = \Delta E^*_\mathrm{in}(f_z, f_{z+1}) = \frac{3 f_z f_{z+1}}{f_z + f_{z+1}} (\Delta r)^2 \tag{12c}$$

$$r^*(f_\mathrm{in}) = \frac{1}{2}(r_z + r_{z+1}) \tag{13b}$$

Note that the adoption of the reduced force constant does not change the value of ΔE^*_in. Thus, the two reactants reorganize to the same extent with $\Delta E^*_\mathrm{in}(f_\mathrm{in})$ now equal to $\frac{1}{4}\lambda_\mathrm{in}(f_\mathrm{in})$.

2.2.2 Reactants reorganize to the midpoint of the reaction coordinate. The midpoint of the reaction coordinate is defined by

$$r_\mathrm{m} = \frac{1}{2}(r_z + r_{z+1}) \tag{14}$$

With this reorganization criterion eqns. (11) and (12) can be rewritten as:

$$\Delta E_\mathrm{in}(r_\mathrm{m}) = [E_z(r_\mathrm{m}) - E_z(r_z)] + [E_{z+1}(r_\mathrm{m}) - E_{z+1}(r_{z+1})] \tag{11b}$$

$$\Delta E_\mathrm{in}(r_\mathrm{m}) = \frac{3}{4}(f_z + f_{z+1})(\Delta r)^2 \tag{12d}$$

Note that this reorganization criterion does not change the values of λ_in. Now $\Delta E_\mathrm{in}(r_\mathrm{m})$ is also equal to $1/4\lambda_\mathrm{in}$. It can readily be seen that $\Delta E^*_\mathrm{in}(r^*) < \Delta E_\mathrm{in}(r_\mathrm{m})$ and that the contributions of the reactants to $\Delta E_\mathrm{in}(r_\mathrm{m})$ at the midpoint configuration are proportional to their force constants. This is inverse to their contributions to $\Delta E^*_\mathrm{in}(r^*)$.

2.2.3 Reactants reorganize to the intersection of the individual reactant parabolas. The energies of two species of a redox pair are the same at the intersection configuration r_c (Fig. 2), that is $E_z(r_\mathrm{c}) = E_{z+1}(r_\mathrm{c})$. r_c is defined in eqn. (15) and shown in Fig. 2:

$$r_\mathrm{c} = \frac{\sqrt{f_z}\, r_z + \sqrt{f_{z+1}}\, r_{z+1}}{\sqrt{f_z} + \sqrt{f_{z+1}}} \tag{15}$$

Substituting eqn. (15) into eqs. (11) and (12), we have:

$$\Delta E_\mathrm{in}(r_\mathrm{c}) = [E_z(r_\mathrm{c}) - E_z(r_z)] + [E_{z+1}(r_\mathrm{c}) - E_{z+1}(r_{z+1})] \tag{11c}$$

$$\Delta E_\mathrm{in}(r_\mathrm{c}) = \frac{6 f_z f_{z+1}}{\left(\sqrt{f_z} + \sqrt{f_{z+1}}\right)^2} (\Delta r)^2 \tag{12e}$$

3 Structural model and computational details

In this section, we consider several prototype systems for self-exchange electron-transfer reactions, $M(H_2O)_6^{2+/3+}$ (M = V, Cr, Mn, Fe and Co). Furthermore we give the details of the theoretical calculation adopted.

The $M(H_2O)_6^{2+/3+}$ (M = V, Cr, Mn, Fe and Co) complexes are oriented in a way that the M–O bond vectors are parallel to the Cartesian axes, that is, the M–O framework has O_h symmetry and the H_2O groups are rotated so as to yield overall T_h symmetry[19] (Fig. 3) The present calculations are carried out at the unrestrained Moller–Plesset second-order perturbation theory with Gaussian 98 programs.[20] For the metal atoms of the first transition row, we use the Wachters–Hay[21,22] all-electron basis set extended with an f polarization function and a d diffuse function, using the scaling factors of Raghavachari and Trucks.[23] For O and H, we use 6-311+G(d) basis sets. The geometry optimization of an isolated H_2O group was first performed. The O–H bond length and H–O–H angle amount to 95.96 pm and 106.63°. These values are in good agreement with the experimental values of 95.72 pm and 104.5°. Then M–O distances in $M(H_2O)_6^{z+}$ ($z = 2$ or 3) complexes are optimized while limiting the geometrical parameters of H_2O at their pre-optimized values. The results are shown in Table 1.

In order to obtain the relevant potential surfaces (curves), we performed the potential energy surface scan for $M(H_2O)_6^{z+}$ ($z = 2$ or 3) complexes *vs.* ion–ligand (M–O) distance. The energy of the complex as a function of the M–O bond distance is obtained by using a polynomial curve fitting method. For the sake of ensuring good precision of the results, a ninth power curve fitting was used:

$$E_i(r) = c_0 + c_1 r + c_2 r^2 + c_3 r^3 + \cdots + c_9 r^9 \quad (i = z \text{ or } z+1) \qquad (16)$$

where, $E_i(r)$ is the total energy of $M(H_2O)_6^{2+}$ or $M(H_2O)_6^{3+}$, r is the M–O bond distance and c_k ($k = 0, 1, 2\ldots9$) are the fitted constants. The resulting energy-distance profiles are given in Fig. 4 and 5 for $Fe(H_2O)_6^{2+}$ and $Fe(H_2O)_6^{3+}$, respectively. Similar curves have been derived for the other transition metal complexes. They are not given in the present work for simplicity.

The theoretical force constants for the ion–ligand bonds, $f_{i,\text{DFT}}$, can be obtained for $r = r_i$ ($i = z$ or $z + 1$), when using eqn. (9) and differentiating $E_i(r)$ of eqn. (16) with respect to r. The experimental values of the force constants, $f_{i,\text{Expt}}$, were obtained with the use of eqn. (8). Substituting the values of f_i and r_i into the formalisms mentioned above, the inner-sphere reorganization energy and activation energy of every redox pair are obtained. These results are shown in Tables 2 and 3.

4 Results and discussion

4.1 Geometry parameters

Since λ_{in} and ΔE^*_{in} depend crucially on the deviations of the nuclear configurations of the two species of a couple between the equilibrium and the transition states, we compared calculated equilibrium distances between the metal-ion and ligands with available experimental data. The data in Table 1 also

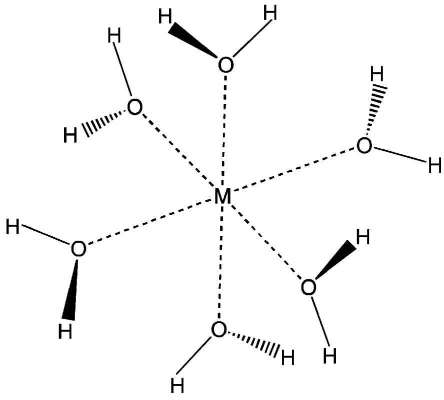

Fig. 3 Structural model of a $M(H_2O)_6^{z+}$ ($z = 2$ or 3) cluster (T_h symmetry).

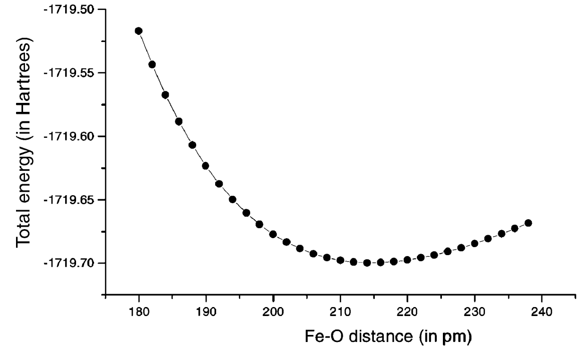

Fig. 4 Plot of energy $E(r)$ *versus* the Fe–O distance for $Fe(H_2O)_6^{2+}$.

Table 1 Equilibrium metal–ligand bond length (in pm) hexahydrate complexes

		$V(H_2O)_6^{2+/3+}$	$Cr(H_2O)_6^{2+/3+}$	$Mn(H_2O)_6^{2+/3+}$	$Fe(H_2O)_6^{2+/3+}$	$Co(H_2O)_6^{2+/3+}$
r_z[a]	This work	223.6	218.5	219.2	214.6	209.9
	INDO[b]	229	224	220	213	2.08
	Expt[e]	225.5	207[c,d] 230[c,f]	217	210	
r_{z+1}[a]	This work	206.1	200.0	201.5	203.4	188.0
	INDO[b]	216	210	204	202	1.95
	Expt[b]	207.5	204	199	197	
Δr[g]	This work	17.5	18.5	17.7	11.2	21.9
	INDO[b]	13	14	16	11	13
	Expt[e]	18	20[h]	18	13	21

[a] r_i ($i = z$ or $z + 1$) denotes the ion–ligand distance in the reduced or oxidized species at the equilibrium state. [b] Data from ref. 13. [c] Data from ref. 25. [d] Equatorial distance. [e] Experimental crystal radii from ref. 24. [f] Axial distance. [g] $\Delta r = r_z - r_{z+1}$. [h] Average values over all six Cr–O bonds taken equal to $\{[4\cdot(0.09)^2 + 2\cdot(0.32)^2]/6\}^{1/2}$.

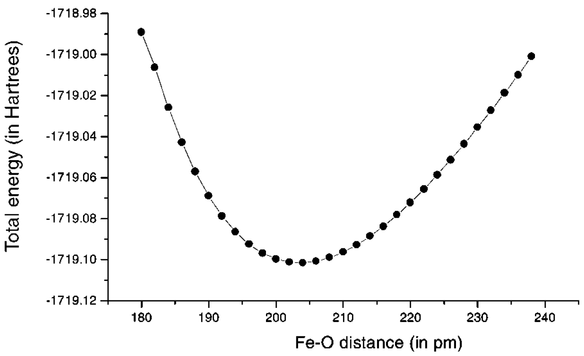

Fig. 5 Plot of energy $E(r)$ *versus* the Fe–O distance for $Fe(H_2O)_6{}^{3+}$.

included previous results of the semi-empirical quantum chemical INDO calculations.

For the ion–ligand distances in $M(H_2O)_6{}^{2+}$ or $M(H_2O)_6{}^{3+}$, our results from the MP2 calculations are in good agreement with the experimental findings. We calculated the overall variations in equilibrium M–O distances from the oxidized species to the reduced species ($\Delta r = r_z - r_{z+1}$), which is the important quantity for the calculation of the organization energy and activation energy. The values of Δr for all redox pairs considered in this work are also in good agreement with the crystallographically measured distances in the ground states. Although the earlier INDO results[13] are in qualitative agreement with the experimental values, the overall variations in equilibrium M–O distances for the five redox pairs are much smaller than the observed ranges. In the present calculations of Δr values, the quantities important for the calculations of the reorganization energy and activation energy are treated more reliably than in the earlier INDO method.

Table 2 Force constants of ion–ligand bonds of hexahydrate complexes (in mdyn Å^{-1})

	$f_{i,\text{Expt}}$[a]	$f_{i,\text{LDO}}$[b]	$f_{i,\text{IADO}}$[c]	$f_{i,\text{INDO}}$[d]	$f_{i,\text{MP2}}$[e]
$V(H_2O)_6{}^{2+}$	1.60	0.92	0.85	1.16	1.35
$V(H_2O)_6{}^{3+}$	2.44	2.17	2.02	1.67	2.33
$Cr(H_2O)_6{}^{2+}$	1.60	1.01	0.93	1.54	1.25
$Cr(H_2O)_6{}^{3+}$	2.54	2.34	2.18	2.40	2.22
$Mn(H_2O)_6{}^{2+}$	1.60	1.10	1.02	1.56	1.45
$Mn(H_2O)_6{}^{3+}$	2.54	2.74	2.55	2.15	2.34
$Fe(H_2O)_6{}^{2+}$	1.60	1.22	1.12	1.72	1.29
$Fe(H_2O)_6{}^{3+}$	2.54	2.74	2.25	2.16	2.31
$Co(H_2O)_6{}^{2+}$	1.60	1.28	1.15	2.03	1.23
$Co(H_2O)_6{}^{3+}$	2.54	2.96	2.76	2.43	2.47

[a] From eqn. (8) using symmetric stretching frequencies of the ion–ligand bonds from ref. 24. and references therein. [b] Results obtained using LDO model from ref. 14 and 15. [c] Results obtained using the IADO model from ref. 14 and 15. [d] Results obtained using the INDO method from ref. 13. [e] Results of this work using MP2 method.

4.2 Force constants

In Table 2 we compare computed results for the force constants, $f_{i,\text{MP2}}$, obtained by using MP2 method for hexahydrate complexes, with those obtained from the experimentally observed spectroscopic frequency data, $f_{i,\text{Expt}}$, and with the theoretical results obtained using the INDO method, $f_{i,\text{INDO}}$, locked dipole orientation (LDO) model, $f_{i,\text{LDO}}$, and the improved average dipole orientation (IADO) model, $f_{i,\text{IADO}}$. The calculated $f_{i,\text{MP2}}$ agree well with the experimental results. They are better than the results of earlier LDO and IADO calculations, and also than those using the INDO method. We also found that the ratios of the force constant of the reduced and oxidized species for the five redox pairs are 0.6 or so. These values are close to the experimental findings.

4.3 Inner-sphere reorganization energy

The theoretical inner-sphere reorganization energies derived by the three formalisms are shown in Table 3. Obviously, the values of $\lambda_{\text{in}}(r_z, r_{z+1})$ are larger than the values of $\lambda_{\text{in}}(f_z, f_{z+1})$ and $\lambda_{\text{in}}(f_{\text{in}})$, which are the approximate results in the harmonic oscillator potential function since the terms higher than quadratic term in the potential function are neglected. In fact, the vibrations between the metal ion and the ligands are not, in general, harmonic along the reaction coordinate, so the harmonic approximation could lead to large errors. We definite the anharmonicity effect in the reorganization process as the fractional difference between the $\lambda_{\text{in}}(r_z, r_{z+1})$ and the $\lambda_{\text{in}}(f_z, f_{z+1})$ or $\lambda_{\text{in}}(f_{\text{in}})$:

$$\frac{\lambda_{\text{in}}(r_z, r_{z+1}) - \lambda_{\text{in}}(f_z, f_{z+1})}{\lambda_{\text{in}}(r_z, r_{z+1})} \quad \text{or} \quad \frac{\lambda_{\text{in}}(r_z, r_{z+1}) - \lambda_{\text{in}}(f_{\text{in}})}{\lambda_{\text{in}}(r_z, r_{z+1})}$$

The anharmonicity effects vary from 13% to 20% for five redox pairs. The results show that the harmonic potential function cannot give a good fit to the actual vibrations between the metal ion and ligands. However, it can be modified by appending a cubic term on the harmonic oscillator potential function. The cubic force constant can be obtained by differentiating $E(r)$ of eqn. (16) three times with respect to r. We found that the values of the cubic force constants of the redox couples studied in this paper are of same order of magnitude as the quadratic force constant, f's. If the contribution of the cubic term to the vertical reorganization energy is omitted, a large error in λ_{in} could be made, especially for those that undergo large changes in the nuclear configuration from the reactants to the product state. We also found that the value of λ_{in} is underestimated by about 10% when using the reduced force constant instead of the individual force constants.

Table 3 Calculated inner-sphere reorganization energy and activation energy (in kJ mol^{-1}) for the redox couples $M(H_2O)_6{}^{2+/3+}$ (M = V, Cr, Mn, Fe and Co)[a]

	$V(H_2O)_6{}^{2+/3+}$	$Cr(H_2O)_6{}^{2+/3+}$	$Mn(H_2O)_6{}^{2+/3+}$	$Fe(H_2O)_6{}^{2+/3+}$	$Co(H_2O)_6{}^{2+/3+}$
$\lambda_{\text{in}}(r_z, r_{z+1})$[a]	223	248	235	95	336
$\lambda_{\text{in}}(f_z, f_{z+1})$[b]	204	214	214	82	320
$\lambda_{\text{in}}(f_{\text{in}})$[c]	189	198	203	75	284
$\Delta E_{\text{in}}(r^*)$[d]	47	50	51	19	71
$\Delta E_{\text{in}}(r_{\text{m}})$[e]	51	54	54	21	80
$\Delta E_{\text{in}}(r_{\text{c}})$[f]	48	50	51	19	73

[a] Eqn. (4)–(6). [b] Eqn. (7). [c] Eqn. (7b). [d] Eqn. (12b). [e] Eqn. (12d). [f] Eqn. (12e).

4.4 Activation energy in the different reorganization models

In the bottom of Table 3 the activation energies in the three reorganization models are compared with each other. As shown in Fig. 2, the contributions of the individual reactants to the activation energy is dependent on the reorganization models used. From Fig. 2 we found that $\Delta E_z(r^*) > \Delta E_{z+1}(r^*)$ when the reactants reorganize to the transition state, $\Delta E_z(r_c) = \Delta E_{z+1}(r_c)$ when reactants reorganize to the intersection of the individual reactant parabolas, and that $\Delta E_z(r_m) < \Delta E_{z+1}(r_m)$ when the reactants reorganize to the midpoint of the reaction coordinate. Here ΔE_z denotes the contribution of the reduced species of a couple to the activation energy and ΔE_{z+1} is that of the oxidized species. Our calculated results show that $\Delta E_{\mathrm{in}}(r_c)$ is closer to $\Delta E_{\mathrm{in}}(r^*)$ than $\Delta E_{\mathrm{in}}(r_m)$. So reorganizing the reactants to the intersection point of the individual reactant parabolas, instead of to the actual transition state, is a reasonable approximation in the calculation of the inner-sphere reorganization energy.

5 Conclusions

Models and formalisms of the inner-shell reorganization of transition metal complexes were summarized in this paper according to three reorganization criteria. The relevant energy barriers were calculated for the five redox pairs of the first transition row employing *ab initio* quantum chemistry techniques. The following conclusions can be drawn from our present study of the self-exchange reactions. (i) The anharmonicities in vibration between the transition metal ion and ligands in the reorganization process of the reactants account for about 20% of the reorganization energy. (ii) The value of the inner-sphere reorganization energy is underestimated about 10% when using the reduced force constant. (iii) The contributions of the individual reactants to the activation energy are sensitive to the reorganization model used. (iv) It is a reasonable approximation in the calculation of the inner-sphere reorganization energy that reorganize reactants to the intersection point of the individual reactant parabolas instead to the actual transition state.

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