

Probing the electronic structure of redox species and direct determination of intrinsic reorganization energies of electron transfer reactions

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An experimental technique capable of directly determining the intrinsic reorganization energies of bimolecular electron transfer reactions is described. Appropriate solution phase redox species are prepared in the gas phase using electrospray ionization and probed using photodetachment spectroscopy. Five metal complex anions involved in the $\text{Fe}^{2+}-\text{Fe}^{3+}$ redox couple are investigated and the intramolecular reorganization energies are measured directly from spectral features due to removing the most loosely bound $3d$ electron from the Fe(II) -complexes. The photodetachment spectra also yield electronic structure information about the $\text{Fe}^{2+}-\text{Fe}^{3+}$ redox couple and provide a common electronic structure origin for the reducing capability of the Fe(II) -complexes, the most common redox reagents. © 2000 American Institute of Physics. [S0021-9606(00)01216-2]

Electron transfer (ET) is among the most fundamental chemical processes, and is ubiquitous in biological systems. Extensive studies of this class of chemical reactions have led to a quantitative understanding of key factors influencing ET reaction kinetics,¹⁻⁴ primarily by Marcus. The Marcus theory,^{1,2} developed for outer-sphere ET with weak electronic coupling, predicts that the ET rate constant $k_{\text{ET}} = A \exp(-(\Delta G^0 + \lambda)^2/4\lambda k_B T)$, where k_B is the Boltzmann constant, A is a prefactor that includes the electronic coupling and depends on the distance between the reactants, ΔG^0 is the free energy difference between the products and reactants, and λ is the total reorganization energy [see Fig. 1(a)]. The total reorganization energy includes components from that due to geometry changes of the redox species or inner-sphere complexes (intramolecular or inner-sphere reorganization energy, λ_i) and that due to polarization changes in the dielectric solvent medium (outer-sphere or solvent reorganization energy, λ_{out}). The solvent reorganization energy is modeled in the Marcus theory using a dielectric continuum and linear response theory for polar solvents. One of the key elements in any quantitative description of ET reaction kinetics is an accurate estimate of the intrinsic reorganization energy λ_i , which is the sum of contributions from the coupled vibrations and depends on the force constants (f_i) and changes in equilibrium displacements (Δq_i) ($\lambda_i = \sum_i (1/2)f_i(\Delta q_i)^2$).¹⁻⁴ There are several experimental approaches to obtain λ_i . Conceptually, the most straightforward one is to determine geometry changes from x-ray or EXAFS structural studies of ET reactants and products and then obtain force constants by vibrational spectroscopy.^{5,6} For intramolecular ET involving mixed-valence compounds, the reorganization energy can be estimated by measuring absorption bandwidths of intervalent charge transfer transitions.⁷ Another elegant technique is resonant-enhanced

Raman scattering with a reinterpretation of Raman cross sections in terms of time-dependent models.^{8,9} Each of these approaches is experimentally rather challenging and has its limitations; and there is no generic experimental technique that allows λ_i to be easily obtained. Therefore, the majority of λ_i still rely on theoretical calculations with knowledge of the normal coordinates and harmonic approximations.^{10,11}

In this report, we demonstrate an experimental technique that allows λ_i to be obtained for bimolecular ET reactions involving transition metal complex anions using photodetachment spectroscopy in the gas phase. As shown in Fig. 1(a), the reorganization energy (λ) can be viewed as the total free energy of the ET products at the geometry (coordinates) of the reactants.¹ The intramolecular reorganization energy (λ_i) is then the total potential energy of the ET products at the geometry of the reactants. For a bimolecular ET reaction involving a reductant (red) and an oxidant (oxd), λ_i would be the sum of two terms, λ_{red} and λ_{oxd} , where λ_{red} is the intramolecular reorganization energy of the reductant (the potential energy of the reductant at the geometry of its oxidized form) and λ_{oxd} is the intramolecular reorganization energy of the oxidant (the potential energy of the oxidant at the geometry of its reduced form). As shown in Fig. 1(b), photodetachment is an oxidation process, which is analogous to a half ET reaction (because there is no electron acceptor). The photoelectron spectrum reflects the Franck-Condon factors between the ground vibrational level of the Fe(II) -complex and the vibrational levels of the Fe(III) -complex and depends on the geometry changes between the two species. Thus, the difference between the vertical (VDE) and adiabatic (ADE) detachment energies is equivalent to λ_{oxd} . As indicated by the dashed arrow in Fig. 1(b), λ_{red} , which involves the potential-energy curve of the reductant, can be determined from electron attachment experiments, which are difficult to perform. If the curvatures of the two potential-energy curves of the ET reactants and products are similar (a usual assumption in treating ET kinetics, although they are generally

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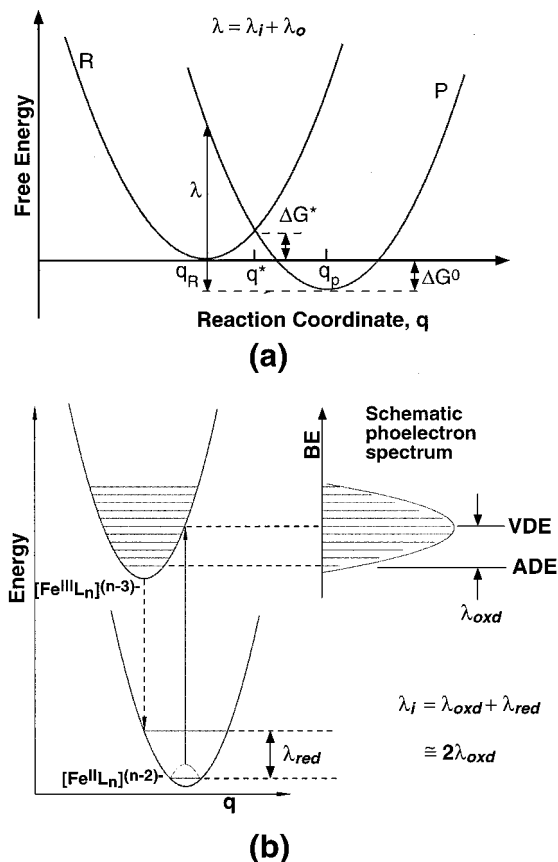


FIG. 1. (a) The Marcus diabatic free energy curves for unsymmetrical electron transfer reactions. λ —reorganization energy (equal to the sum of the intramolecular reorganization energy, λ_i , and the outer-sphere reorganization energy, λ_o); ΔG^* —activation barrier; ΔG^0 —free energy difference between reactants and products. (b) Schematic potential curves showing photodetachment of an Fe(II)-complex and the hypothetical photoelectron spectrum. The difference between the vertical (VDE) and adiabatic (ADE) binding energies represent the potential energy of the Fe(III)-complex at the geometry of the Fe(II)-complex and is called the oxidant intramolecular reorganization energy, λ_{oxd} . For a full bimolecular electron transfer reaction, $\lambda_i = \lambda_{oxd} + \lambda_{red}$, where λ_{red} is the reductant intramolecular reorganization energy. For self-exchange reactions ($\Delta G^0 = 0$) and assuming that the curvatures of the oxidant and reductant are similar, $\lambda_i \approx 2\lambda_{oxd}$.

different),^{5,12} $\lambda_{red} \approx \lambda_{oxd}$ for a self-exchange reaction ($\Delta G^0 = 0$). For unsymmetrical ET reactions ($\Delta G^0 \neq 0$), one can estimate the whole λ_i by measuring the photodetachment spectra of the reduced forms of the two reactants. We have developed an experimental technique that couples an electro-spray ion source with photodetachment photoelectron spectroscopy (PES), which has the potential to allow many anionic redox species involving in ET reactions to be investigated.¹³ We have studied a series of $[ML_6]^{2-}$ species ($M = \text{Re, Os, Ir, Pt; L} = \text{Cl, Br}$) and found a remarkable correlation between the electron binding energies measured in the gas phase and their redox potentials in solution.¹⁴ Here we report PES experiments and measurements of λ_i for several metal complexes involving the $\text{Fe}^{2+} - \text{Fe}^{3+}$ redox couple. We will show that the PES experiments not only yield information about λ_i , but also provide important electronic structure and energetic information of ET reactants.

The challenge for this experimental approach is how to prepare the appropriate redox species in their reduced forms

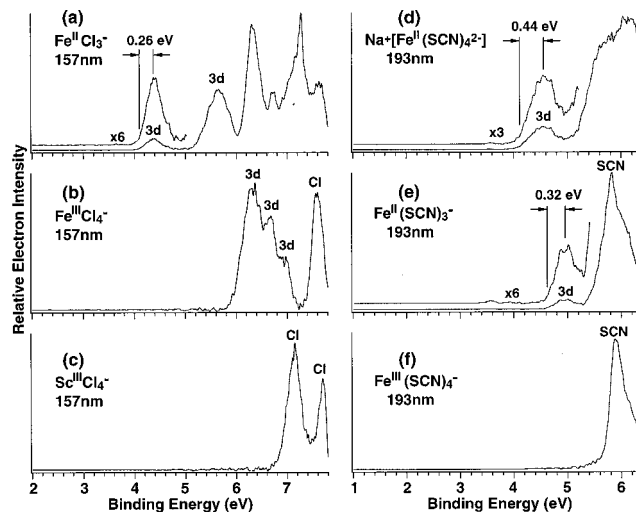


FIG. 2. Photoelectron spectra of (a) $\text{Fe}^{\text{II}}\text{Cl}_3^-$; (b) $\text{Fe}^{\text{III}}\text{Cl}_4^-$, and (c) $\text{Sc}^{\text{III}}\text{Cl}_4^-$ at 157 nm (7.866 eV), and (d) $\text{Na}^+[\text{Fe}^{\text{II}}(\text{SCN})_4]^{2-}$, (e) $\text{Fe}^{\text{II}}(\text{SCN})_3^-$, and (f) $\text{Fe}^{\text{III}}(\text{SCN})_4^-$ at 193 nm (6.424 eV). The difference between the VDE and ADE for the first weak feature in the Fe(II)-complexes are indicated (see also Table I). The labels indicate the nature of the detachment features. The electro-spray solutions used in the first three cases were a 10^{-3} M solution of FeCl_2 , FeCl_3 , and ScCl_3 , respectively, dissolved in a water-methanol (10/90 volume ratio) mixed solvent. The $\text{Fe}^{\text{II}}(\text{SCN})_4^-$, $\text{Fe}^{\text{II}}(\text{SCN})_3^-$ and $\text{Na}^+[\text{Fe}^{\text{II}}(\text{SCN})_4]^{2-}$ anions were prepared from spraying a 10^{-3} M solution of $\text{FeCl}_2 - \text{NaSCN}$ (1/4 molar ratio) dissolved in a water-methanol (10/90 volume ratio) solvent, where some of Fe(II) species were oxidized in situ Fe(III) probably by residual O_2 in the solution.

in the gas phase from solution samples. The electro-spray ionization technique developed by Fenn *et al.*¹⁵ has been shown to be a powerful soft ionization method to transport ionic species from a solution sample to the gas phase and has been widely used in biological mass spectrometry.¹⁶ Recently, we have developed an experimental technique coupling electro-spray with PES to investigate multiply charged anions.^{13,17-20} This technique is also ideally suited for obtaining molecular information about solvent-free redox species.¹⁴ Here we report some of our initial results for five Fe(II)-complexes, as shown in Figs. 2(a), 2(d), 2(e), 3(a), and 3(c), for $\text{Fe}^{\text{II}}\text{Cl}_3^-$, $\text{Na}^+[\text{Fe}^{\text{II}}(\text{SCN})_4]^{2-}$, $\text{Fe}^{\text{II}}(\text{SCN})_3^-$, $\text{Fe}^{\text{II}}(\text{SCH}_3)_3^-$, and $\text{Na}^+[\text{Fe}^{\text{II}}(\text{S}_2\text{-o-xy})_2]^{2-}$, respectively, where $\text{S}_2\text{-o-xy}$ represents *o*-xylyl- α , α' -dithiolate and $[\text{Fe}^{\text{II}}(\text{S}_2\text{-o-xy})_2]^{2-}$ is known as the Holm-Ibers analogue for the ET reaction center in rubredoxin.²¹⁻²³ The ionic species were mass analyzed by time-of-flight mass spectrometry¹³ and identified firmly by their characteristic natural isotope patterns. The most striking feature in all these PES spectra is the weak lowest binding energy band in each case, regardless of the ligand type or number. The relatively weak intensity and the observed energy gap between this feature and the next higher binding energy feature in all the spectra suggest that it probably has the same origin in all the five species. If this band corresponds to removal of the most loosely bound Fe 3d electron, the detachment process would represent an oxidation of $\text{Fe}(\text{II}) \rightarrow \text{Fe}(\text{III})$. Consequently, the difference between the VDE and ADE, as shown in Figs. 2 and 3 and in Table I, would correspond to the potential energy of the Fe(III)-complex at the geometry of the Fe(II)-complex, i.e., λ_{oxd} , according to Fig. 1(b).

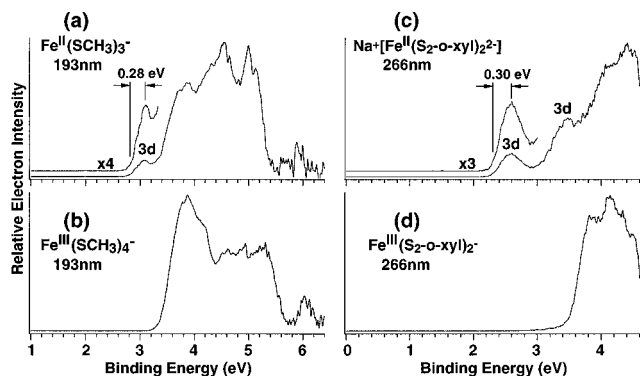


FIG. 3. Photoelectron spectra of (a) $\text{Fe}^{\text{II}}(\text{SCH}_3)_3^-$ and (b) $\text{Fe}^{\text{III}}(\text{SCH}_3)_4^-$ at 193 nm (6.424 eV), and (c) $\text{Na}^+[\text{Fe}^{\text{II}}(\text{S}_2\text{-o-xy})_2]^{2-}$ and (d) $\text{Fe}^{\text{III}}(\text{S}_2\text{-o-xy})_2^-$ at 266 nm (4.661 eV). $\text{Fe}^{\text{II}}(\text{SCH}_3)_3^-$ and $\text{Fe}^{\text{III}}(\text{SCH}_3)_4^-$ were prepared by spraying a 10^{-3} M solution of $[(\text{CH}_3)_4\text{N}^+]_2\text{FeCl}_4-\text{NaSCH}_3$ (1/4 molar ratio) in a pure methanol solvent. The Fe(III) species were generated again by *in situ* oxidation due to residual O_2 in the solution. The Holm–Ibers analogs in both oxidation states were synthesized according to Ref. 23 and a 10^{-3} M solution was used in a pure ethanol solvent in each case.

To confirm that indeed the first feature in the Fe(II)-complexes is due to removal of the most loosely bound Fe3*d* electron, we performed further studies on all the corresponding Fe(III)-complexes, which are compared to the corresponding Fe(II)-complexes in Figs. 2 and 3. All the Fe(III)-complexes show much higher electron binding energies and no weak low binding energy features are observed in any case. For $\text{Fe}^{\text{III}}\text{Cl}_4^-$ [Fig. 2(b)], we observe that its highest occupied molecular orbital (HOMO) is in fact still due to 3*d*-derived orbitals by comparing with the spectrum of ScCl_4^- [Fig. 2(c)], which has no occupied 3*d*MOs. For $\text{Fe}^{\text{III}}(\text{SCN})_4^-$, our data suggest that its HOMO is due to the SCN^- ligand [Fig. 2(f)]. The same seems to be also true for $\text{Fe}^{\text{III}}(\text{SCH}_3)_4^-$ [Fig. 3(b)] and $\text{Fe}^{\text{III}}(\text{S}_2\text{-o-xy})_2^-$ [Fig. 3(d)], whose HOMO appears to be due to the ligands or mixtures of the 3*d* and the ligands based on the appearance of the spectra. In addition, we have measured the PES spectra of $\text{Fe}^{\text{II}}\text{Br}_3^-$ and $\text{Fe}^{\text{II}}\text{I}_3^-$ (not shown). The first two features of the $\text{Fe}^{\text{II}}\text{Br}_3^-$ and $\text{Fe}^{\text{II}}\text{I}_3^-$ spectra are almost identical to that of the $\text{Fe}^{\text{II}}\text{Cl}_3^-$ spectrum, whereas the higher binding energy features, which are due to the ligands, differ in the PES spectra of the three species. These results unequivocally demonstrate that the first two detachment features and the HOMO of $\text{Fe}^{\text{II}}\text{Cl}_3^-$ are indeed due to the Fe 3*d* orbitals.

TABLE I. Adiabatic (ADE) and vertical (VDE) binding energies, relaxation energies (λ_{oxd}), and energy gaps (ΔE) measured from photodetachment experiments for the five Fe(II)-complexes.

	ADE (eV)	VDE (eV)	λ_{oxd} (eV)	ΔE (eV) ^a
$\text{Fe}^{\text{II}}\text{Cl}_3^-$	4.10 (0.06)	4.36 (0.06)	0.26	1.3
$\text{Fe}^{\text{II}}(\text{SCN})_3^-$	4.64 (0.05)	4.96 (0.08)	0.32	0.9
$\text{Na}^+[\text{Fe}^{\text{II}}(\text{SCN})_4]^{2-}$	4.12 (0.05)	4.56 (0.08)	0.44	1.0
$\text{Fe}^{\text{II}}(\text{SCH}_3)_3^-$	2.80 (0.06)	3.08 (0.05)	0.28	0.9
$\text{Na}^+[\text{Fe}^{\text{II}}(\text{S}_2\text{-o-xy})_2]^{2-}$	2.30 (0.05)	2.60 (0.05)	0.30	0.9

^aEstimated from the VDE's of the first and second detachment features from the respective photoelectron spectra.

Therefore, the VDE and ADE difference from the first detachment feature in each of the five Fe(II)-complexes can be used to evaluate the geometrical relaxation energy upon oxidation [Fig. 1(b)], i.e., λ_{oxd} , which is given in Figs. 2 and 3 and also in Table I. It is interesting to note that the relaxation energy depends on both the ligand type and numbers. The most ionic species, $\text{Fe}^{\text{II}}\text{Cl}_3^-$, among the five complexes gives a relatively small relaxation energy of 0.26 eV. By comparing the data of $\text{Na}^+[\text{Fe}^{\text{II}}(\text{SCN})_4]^{2-}$ and $\text{Fe}^{\text{II}}(\text{SCN})_3^-$, we see that the four-ligand species gives a larger relaxation energy, which is expected because of the larger numbers of vibrational modes for the larger system. The tetrahedral $\text{Fe}^{\text{II}}(\text{SCN})_4^{2-}$ dianion is not stable as a gaseous species and requires a Na^+ ion to be stabilized. We could not make significant amounts of the corresponding ion-pair complexes for $\text{Fe}^{\text{II}}\text{Cl}_4^{2-}$ and $\text{Fe}^{\text{II}}(\text{SCH}_3)_4^{2-}$, which are also unstable in the gas phase. Based on the results of the $\text{Na}^+[\text{Fe}^{\text{II}}(\text{SNC})_4]^{2-}$ and $\text{Fe}^{\text{II}}(\text{SCN})_3^-$ species, we expect that the relaxation energies for the Fe(II) tetrahedral complexes should be larger by about 0.12 eV than the corresponding three-ligand $\text{Fe}^{\text{II}}\text{L}_3^-$ complexes. This suggests that the relaxation energy for $\text{Fe}^{\text{II}}(\text{SCH}_3)_4^{2-}$ would be about 0.4 eV, which is still smaller than the 0.57 eV value obtained from a recent theoretical investigation by Koerner and Ichiye,²⁴ who used $\text{Fe}^{\text{II}}(\text{SCH}_3)_4^{2-}$ to model the electronic structure of the active site of rubredoxin. Furthermore, the Holm–Ibers analogue, $\text{Fe}^{\text{II}}(\text{S}_2\text{-o-xy})_2^{2-}$, which we were able to stabilize by a Na^+ ion pair [Fig. 3(c)], yielded an even smaller relaxation energy (0.30 eV), probably due to the relative rigidity of the o-xylyl- α,α' -dithiolate ligands.

The PES spectra of the Fe(II)-complexes also contain important and explicit electronic structure information about these redox species. The substantial energy gap observed in each Fe(II)-complex (also see Table I) indicates the stability of the high spin d^5 electron configuration in Fe(III) and provide direct electronic structural basis for the fact that Fe(II) can be easily oxidized to Fe(III), while the latter is much more difficult to be oxidized further. The much higher electron binding energies of all the Fe(III)-complexes and their complicated electronic structures as revealed by the PES data also provide evidence for the electronic origin for the $\text{Fe}^{2+}-\text{Fe}^{3+}$ redox couple, probably the most common redox pair. In fact the energy gap observed in the PES spectra of the Fe(II)-complexes is quite unique, in that, we have not observed such a large energy gap in several other redox couples, such as $\text{Cu}^+-\text{Cu}^{2+}$, or other 3*d* metal complexes, whereas we have observed similar energy gaps in all the Fe(II)-complexes that we have measured, including a few that are not shown (FeBr_3^- , FeI_3^- , and FeCN_4^{2-}). This indicates the special nature of the d^6/d^5 or $\text{Fe}^{2+}-\text{Fe}^{3+}$ redox couple and may explain the ubiquity of the $\text{Fe}^{2+}-\text{Fe}^{3+}$ redox couple, particularly in biological systems.

A central issue in studying ET reaction dynamics is to obtain a detailed understanding of how the dynamics (rate constants and barriers) are determined by molecular and electronic structures of the reactants, the nature of the interaction between them, how the initial states are prepared, and the overall energetics.⁴ We demonstrate here that by preparing the appropriate redox complexes in the gas-phase photo-

detachment experiments are a powerful technique to gaining molecular electronic structure and energetic information for ET reactants. The intramolecular reorganization energy can be straightforwardly obtained from photodetachment experiments of the appropriate reduced forms of the reactants by assuming that the curvatures of the potential-energy curves of the redox species are similar. More importantly, real biological electron transfer reagents can be prepared using the electrospray technique¹⁶ and their intrinsic reorganization energies should be easily obtained, similar to those shown here with the simpler redox species. It should be pointed out that the reorganization energies obtained here are for gaseous species and they may differ from those in solutions due to changes of structures and binding of the gaseous species from those in solutions. However, this effect may be investigated by examining redox species with controlled solvent numbers in the gas phase. Furthermore, the solvated redox species also offer an exciting possibility to directly obtain the reorganization energies due to the solvent polarization and thus obtain both parts and the whole of λ for ET reactions.

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