4584 *Inorg. Chem.* **1998,** *37,* 4584−4588

Vertical Ionization Energies and Electron Affinities of Ions in Solution from Outer-Sphere Charge Transfer Transition Energies

S. I. Gorelsky, V. Yu. Kotov, and A. B. P. Lever*

Department of Chemistry, York University, Toronto, Ontario, Canada M3J 1P3

Received February 27, 1998

Outer-sphere charge transfer (OSCT) transitions are shown to correlate with previously published photoelectron emission threshold energies. From these data it is possible to generate a set of parameters, I_D and I_A, which define these OSCT energies, where I_D is identified as the solution phase vertical ionization potential, and I_A is the solution phase vertical electron affinity. An easy procedure for deriving these data for a wide variety of cations and anions is presented. The application of these data leads to a powerful procedure for extracting reorganization and solvation energies of value in a variety of applications.

Introduction

Ionization potential (IE) and electron affinity (EA) data are useful for applications where the energies of frontier orbitals are required. Gas phase adiabatic ionization energies (IE_g^A) are available from various techniques including ion cyclotron resonance and high-pressure gas phase mass spectrometry. Photoelectron techniques provide values for gas phase vertical ionization energies (IE_g^V). The difference between the vertical and adiabatic gas phase numbers relates to the reorganization energies following loss or gain of an electron.

In the solution phase, the adiabatic ionization energies (IE_s^A) are simply the redox potentials. Aqueous phase vertical ionization energy data (IE_s^V) are available for a small range of simple anions in water using photoelectron emission threshold energies.[1,2] Aside from these simple anions, solution phase vertical ionization energy data are not available.

Gas phase electron affinity data are available, and adiabatic electron affinities in solution phase are, of course, redox potentials. No experimental data exist for solution phase vertical electron affinities[3] where, in particular, such data for cations would be useful.

The availability of solution phase vertical ionization energies and electron affinities would be very valuable not only to address the energies of frontier orbitals but also as a new means to extract reorganization and solvation energies for kinetic and photochemical applications.

Pearson[4] addressed, in 1986, the problem of deriving solution phase IE_s and EA_s data with estimates of such data from other thermodynamic information, but the results were rather crude. A means to obtain such data from outer-sphere charge transfer (OSCT) spectra is discussed in this contribution. Aqueous phase vertical IE_s^V data for a wide range of anions are displayed in Table 1, and aqueous phase vertical electron affinity (EA_s^V) values are displayed in Table 2. The procedure is not limited to water, and data for other solvents is potentially extractable.

Table 1. $I_D(IE_s^V)$, Charge Transfer to Solvent Energies (CTTS), Redox Potentials, and Reorganization Energies in Aqueous Solutions (298 K)

donor	N^a	$I_D(IE_s^V)$, eV	Δ,[b] eV	E(CTTS),[c] eV	$E°(D^+/D)$,[d] V vs NHE	χ^D, eV[e]
$[W(CN)_8]^{4-}$	3	5.64	0.01	4.7	0.456	0.69
$[Fe(CN)_6]^{4-}$	19	5.69	0.06	4.8	0.358	0.78[f]
$[Mo(CN)_8]^{4-}$	6	5.86	0.05		0.84	0.52
$[Mn(CN)_5(NO)]^{3-}$	1	6.02			0.6	0.92
$[Os(CN)_6]^{4-}$	10	6.18	0.03		0.63	0.74[f]
$[Ru(CN)_6]^{4-}$	18	6.30	0.04	5.1	0.9	0.78[f]
$[Pt(CN)_4]^{2-}$	1	6.86				
NO_2^- [g]	2	6.97	0.04	5.9	1.04	1.43
N_3^- [g]	4	7.02	0.05	6.1	1.33	1.19
$SeCN^-$	4	7.05	0.03	5.3	1.27	1.28
$S_2O_3^{2-}$ [g]	6	7.07	0.06	5.8	1.35	1.22
I^- [g]	9	7.21	0.07	5.4	1.33	1.38
SO_3^{2-} [g]	2	7.21	0.01	5.5	0.63	2.08
SCN^- [g]	9	7.35	0.06	5.6	1.63	1.22
$C_2O_4^{2-}$	6	7.60	0.04			
OCN^-	2	7.62	0.11		2.66	0.46
CH_3COO^-	1	7.71				
Br^- [g]	5	7.81	0.16	6.4	1.92	1.39
SO_4^{2-}	1	8.19		7.1	2.43	1.26
Cl^- [g]	5	8.33	0.1	7.1	2.41	1.42

[a] Number of points. $I_D(IE_s^V)$ values are referenced to the experimental vertical ionization potential of the $[Fe(CN)_6]^{4-}$ ion; see text. [b] Average deviation $|h\nu_{calcd} - h\nu_{exptl}|$ for ion associates with this ion. [c] Charge transfer to solvent (water) transition energy.[12−17] [d] Standard redox potential.[5−11] [e] Reorganization energies calculated from eq 13. These should be treated with caution since the electrochemical data are collected over a wide variety of conditions and will not always be entirely appropriate for the conditions under which the OSCT transition is recorded; also see text. [f] After application of spin−orbit correction (see text). [g] Average values for threshold emission evaluation of IE_s^V are as follows (eV): NO_2^-, 7.57; N_3^-, 7.45; $S_2O_3^{2-}$, 7.28; I^-, 7.13; SO_3^{2-}, 7.11; SCN^-, 7.2; Br^-, 7.93; Cl^-, 8.8.

OSCT Energies

The formation of ion pairs [D][A] (and higher associates) (D = donor, usually carrying negative charge, and A = acceptor, usually carrying positive charge) in solutions can cause the appearance of one or several new broad absorption bands in the electronic spectrum.[25] These new absorption bands are charge transfer electronic transitions from a reductant ion to the associated oxidant ion. They are known either as outer-sphere charge transfer (OSCT) or ion-pair charge transfer (IPCT) transitions. The OSCT bands also appear in the spectra of the

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(3) IE^A of M(−1) is related to $-EA^A$ of M(0).

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Table 2. $I_A(EA_s^V)$, Redox Potentials, and Reorganization Energies in Aqueous Solutions (298 K)

acceptor	EC[a]	N	$I_A(EA_s^V)$, eV	Δ, eV	$E°(A/A^-)$, V vs NHE	χ^A, eV
$[Ru(en)_3]^{3+}$	d^5	2	4.48	0.02	0.21	0.23
$[Ru(NH_3)_5(py)]^{3+}$	d^5	10	4.32	0.07	0.3	0.48
$[Ru(NH_3)_5(CH_3CN)]^{3+}$	d^5	2	4.26	0.16		
$[Fe(CN)_6]^{3-}$	d^5	4	4.16	0.02	0.358	0.7
$[Ru(NH_3)_5(im)]^{3+}$	d^5	1	4.11		0.1	0.49
$[Ru(NH_3)_6]^{3+}$	d^5	10	4.02	0.03	0.1	0.58
$[Ru(NH_3)_5(H_2O)]^{3+}$	d^5	2	3.98	0.01	0.2	0.72
$[Ru(NH_3)_5(Cl)]^{2+}$	d^5	3	3.8	0.05	−0.04	0.66
$[Co(phen)_3]^{3+}$	d^6	2	3.78	0.14	0.39	1.11
$[Cu(phen)_2]^{2+}$	d^9	1	3.65		0.174	1.02
$[Eu@2.2.1]^{3+}$	f^6	3	3.41	0.04	−0.18	0.91
$[Fe(CN)_5(NO)]^{2-}$	d^6	2	3.31	0.06	−0.075	1.12
$[Os(NH_3)_5(H_2O)]^{3+}$	d^5	2	3.1	0.03		
$[Co(NH_3)_4(pzCO_2)]^{2+}$	d^6	1	3.09			
$[Rh(bpy)_3]^{3+}$	d^6	3	3.08	0.03	−0.5	0.92
$[Co(tacn)_2]^{3+}$	d^6	11	3.06	0.08	−0.41	1.03
$[Co(NH_3)_5(N\text{-}Mebpy)]^{2+}$	d^6	1	3.04			
$[Co(sep)]^{3+}$	d^6	11	3.04	0.07	−0.30	1.16
$[Co(edta)]^-$	d^6	2	2.99	0.09	0.37	1.88
$[Os(NH_3)_5(Cl)]^{2+}$	d^5	3	2.94	0.05	−0.85	0.71
$[Co(NH_3)_5(py)]^{3+}$	d^6	1	2.9			
$[Co(chn)_3]^{3+}$	d^6	1	2.8		−0.28	1.42
$[Co(pn)_6]^{3+}$	d^6	1	2.76		−0.26	1.48
$[Co(en)_3]^{3+}$	d^6	13	2.74	0.03	−0.21	1.55
$[Co(NH_3)_6]^{3+}$	d^6	11	2.67	0.09	0.108	1.94
$[Pt(NH_3)_5(Cl)]^{3+}$	d^6	4	2.66	0.04		
$[Cu(en)_2]^{2+}$	d^9	1	2.42		−0.38	1.7
$[Cr(en)_3]^{3+}$	d^3	3	2.06	0.02	−0.66	1.78
$[Cr(NH_3)_6]^{3+}$	d^3	1	1.88			
bulk H_2O	CS	13	1.3	0.3		

[a] Electronic configuration of ion. [b] Number of points. [c] Average deviation $|h\nu_{calcd} - h\nu_{exptl}|$ for ion associates with this ion. [d] Standard redox potential.[6,10,18−24] Also see Table 1 footnotes. [d] For ligand notations refer to the references in the Supporting Information. Especially see cautionary comments concerning the reorganization energy estimations.

corresponding crystals.[18,26] A relatively large amount of experimental data has been collected for these ion associates in aqueous solutions (Supporting Information).

Further, it is well established that the energies of these OSCT bands for closed-shell species can be written[27]

$$h\nu(\mathrm{OSCT}) = \mathrm{IE_s}^V - \mathrm{EA_s}^V + C - W \tag{1}$$

where $\mathrm{IE_s}^V$ is the vertical ionization energy of the donor and $\mathrm{EA_s}^V$ is the vertical electron affinity of the acceptor, in solution, both regarded as positive quantities, C is an electron repulsion term, and W is a small work term.[28]

The free energy of formation of ion pairs in water tends to be very small, e.g., equilibrium constants lie in the range 10^2−10^3.[28] This would introduce a work term of the order of 0.1−0.2 V. In fact we are concerned with the difference between two work terms, that associated with the ground state ion pair and that associated with the Franck−Condon excited state ion pair. Moreover, recent studies with species of the type $[D]$-$[A]_n$, associates with an increasing number, n, of acceptors surrounding a donor,[29] reveal that the OSCT bands in such species have an intensity increasing with n, but an energy essentially independent of n. Thus within the accuracy of this analysis, the work term contributions (W) can be disregarded.

To evaluate the repulsion term C, note that the excitation energy for transfer of an electron from a donor orbital of energy ϵ_D to an acceptor orbital of energy ϵ_A in the ground and excited states ${}^1\Psi_g$ and ${}^1\Psi_e$, respectively, can be written[30]

$$h\nu({}^1\Psi_e \leftarrow {}^1\Psi_g) = \epsilon_A - \epsilon_D - J_{AD} + 2K_{AD} + E_{corr} + E_{relax} \tag{2}$$

where J_{AD} and K_{AD} are the familiar two-center[30] Coulombic and exchange electron interaction terms connecting orbitals on donor D and acceptor A, E_{corr} is a change in correlation energy going from the ground state to an excited state, and E_{relax} is the electronic relaxation energy.[30] We may formally connect these orbital energies to vertical ionization energies and electron affinities through the Rayleigh−Schroedinger approximation as developed in[31]

$$\epsilon_A - \epsilon_D + E_{corr} + E_{relax} = \mathrm{IE_s}^V - \mathrm{EA_s}^V \tag{3}$$

It follows then that

$$C = -J_{AD} + 2K_{AD} \tag{4}$$

A similar equation can be written for open-shell acceptors with one unpaired electron, such as low-spin d^5 Ru(III) and Fe(III) species and d^9 Cu(II) species, namely,[32]

$$h\nu({}^2\Psi_e \leftarrow {}^2\Psi_g) = \mathrm{IE_s}^V - \mathrm{EA_s}^V - J_{AD} + 0.5K_{AD} - W \tag{5}$$

where it is assumed that the OSCT electron transition occurs from a doubly occupied orbital into the SOMO.

The question then arises as to whether it is possible to use OSCT energies to extract aqueous phase vertical ionization energies and electron affinities. The problem is that eqs 1 and

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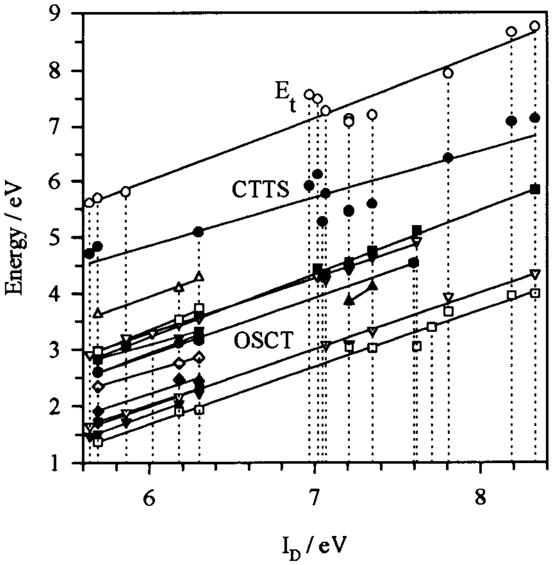

Figure 1. OSCT, CTTS (refs 12−17), and experimental vertical ionization energies (E_t) (refs 1 and 2) of reductant ions in aqueous solutions vs I_D. To construct this diagram using eq 6, an I_D value of 5.69 eV was assumed for the $[Fe(CN)_6]^{4-}$ ion. This then permits one to derive I_A values for each acceptor bound to the $[Fe(CN)_6]^{4-}$ ion. These I_A values can then be used to derive I_D values of other donors. Each parallel line in the figure is derived from a single acceptor bound to the range of donors defined by the I_D values, with a different acceptor for each line.

5 contain differences so that to obtain individual values at least one value has to be accurately known or defined as an arbitrary reference.

Suppose eq 1 is rewritten in the form

$$h\nu(\mathrm{OSCT}) = I_D - I_A \tag{6}$$

where the Coulombic and exchange terms (and work terms) may be subsumed into one or both parameters. One may now generate a set of relative I_D and I_A values based upon an arbitrary predefined reference I'_D. Plotting the observed OSCT energy for constant A and varying D against I_D generates a series of essentially parallel lines for each different acceptor A as shown in Figure 1. From such a relative set of donor and acceptor values, the agreement between OSCT energies calculated via eq 6 and the experimental data (Supporting Information) is exceptionably good (Figure 2) ($R = 0.993$ for 99 points, with an average deviation of 0.06 eV). This is an excellent fit considering the large bandwidths of OSCT bands ($\Delta_{1/2} = 0.5-1.2$ eV) and possible errors in OSCT energies because difference spectra are often used to find OSCT band maxima. The existence of the parallel lines and the excellent statistics validate eq 6. The ability to predict OSCT energies for any combination of donors and acceptors from a set of parameters based upon an arbitrary reference has been demonstrated previously by Hennig and Billing.[25,33]

The key to extracting vertical ionization energies and electron affinities lies in the observation that, if the photoelectron threshold emission energies of some common ions are also plotted, using the same arbitrary reference, against I_D for the donor ion, one discovers a linear relationship *with essentially the same slope as in the aforementioned OSCT plot* (Figure 1). It is therefore possible, rather than using an arbitrary reference, to map the I_D scale directly against these photoelectron emission energies.

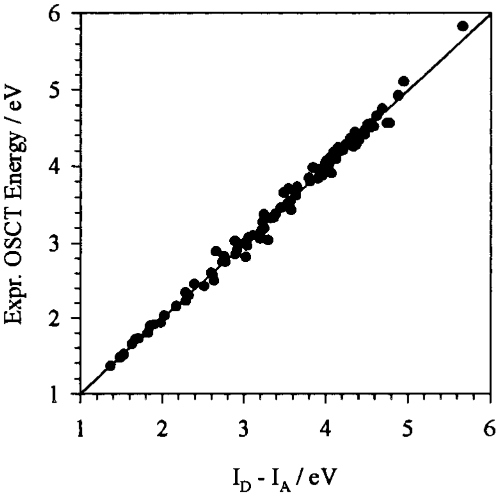

Figure 2. Experimental and calculated OSCT energies (experimental data provided as Supporting Information, 99 points). Data from Table 1 where $N = 1$ were excluded from this plot since they, *inter alia*, were used to define the line.

Rather than use a global average of all these threshold energies, we have referenced I_D to the ferrocyanide ion since its threshold emission energy has been measured accurately[1,2] and there are a large number of OSCT data points with this ion; *thus for* $[Fe(CN)_6]^{4-}$ $IE_s^V = 5.69$ *eV* $= I_D$. *Then, the extensive set of* I_D *values generated through a least squares analysis of the data and listed in Table 1 correspond directly with the aqueous phase, vertical ionization energies of these donor species*. For the other ions for which threshold emission energies are available, the agreement between measured values and their I_D values is very acceptable.

The variation in IE_s^V (I_D) is consistent with chemical intuition, with halides in the expected sequence, having among the highest IE_s^V values, while the metalloanionic species with large negative charges have the lowest values of IE_s^V (See Table 1). A useful aspect of this procedure is the ease with which hitherto unrecorded IE_s^V data can be collected simply by mixing an appropriate ion associate and recording the OSCT band energy.

It now follows that the I_A values (Table 2) reflect the electron affinities for closed-shell acceptors via

$$EA_s^V = I_A - J_{AD} + 2K_{AD} - W \tag{7}$$

and, for the acceptor ions with one unpaired electron,

$$EA_s^V = I_A - J_{AD} + 0.5K_{AD} - W \tag{8}$$

If the Coulombic and exchange terms can be estimated, then aqueous phase vertical electron affinities, unobtainable by any other method, can also be derived. The two-center coulomb integral J_{AD} has the asymptotic value R^{-1} (au) (the upper limit) as the internuclear distance, R, becomes large. At relatively close distances J_{AD} is frequently approximated by the empirical formulas of Mataga−Nishimoto[34] or Ohno:[35]

$$J_{AD}\,(\mathrm{au}) = (R\,(\mathrm{au}) + \delta)^{-1} \quad \text{or} \quad J_{AD} = (R^2 + \delta^2)^{-1/2} \tag{9}$$

where δ (au) $= 2/(J_{AA} + J_{DD})$. Typical values for J_{AA} and J_{DD} for the orbitals involved in OSCT transitions range from 6 to 10 eV. So J_{AD} (eV) ~ 14/(R (Å) + 2). However this analysis

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does not reflect the solution phase in which the ion pairs reside. The Coulombic interaction must be reduced by the factor of the dielectric constant of water (78 at 25 °C), and hence J_{AD} (eV) $\sim 0.18/(R\ (\text{Å}) + 2)$.

The internuclear distance, R, between two ion centers, $r_A + r_D$, is a variable parameter from one ion pair to another, but in most ion pairs considered here the close contact distance between the donor and acceptor centers is approximately the same (~5.5−6 Å for ion pairs with two transition metal complexes, and ~4.3−5 Å for [metal complex]X_n (X^- = halogen or pseudohalogen).[34−49]

The exchange interaction term K_{AD} falls off exponentially[30] and at the distance of an ion pair can be neglected; hence $K_{AD} = 0$ at large internuclear distances. In summary, both J_{AD} and K_{AD} can be neglected in the aqueous phase and (neglecting W)

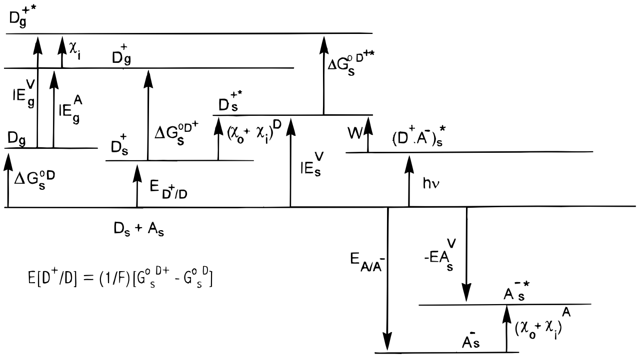
$$\mathrm{EA_s}^{\mathrm{V}} = I_A \tag{10}$$

Table 2 displays a selection of $\mathrm{EA_s}^{\mathrm{V}}$ values whose values range from the weakly accepting d^3 $[Cr(NH_3)_6]^{3+}$ ion through a group of more strongly accepting d^6 species such as $[Rh(bpy)_3]^{3+}$ to even more strongly accepting d^5 species such as $[Ru(en)_3]^{3+}$.

Charge Transfer to Water

Figure 1 also contains data for the charge transfer to solvent (water) (CTTS) excitation energies.[12−17] This process is akin to the vertical ionization energy except that the electron is excited to the water local to the donor, rather than to vacuum. One may anticipate a linear relationship between $\mathrm{IE_s}^{\mathrm{V}}$ and $h\nu$(CTTS) with a slope of 1, and this was indeed reported by Delahay.[1] However, Takahashi[2] questions this result, and the data shown here in Figure 1 do suggest a slope lower than 1. This may be due, as Takahashi proposes, to variations in the free energy of the electron in the vicinity of different anions. The quality of the data is not very good, as indicated by the scatter in the plot, so that it is really not possible to deduce the slope accurately. An I_A value for water as an acceptor can be derived (1.3 eV), but it is not statistically very reliable and indeed may not be a constant and may be very dependent upon the nature of solute. Note that the energy of the backward process, a photoelectric threshold for a bulk hydrated electron, is approximately 3.2 eV.[50]

Scheme 1



Reorganization Energies

There are alternative procedures for analyzing OSCT energies. One approach involves recognizing that one may also write, for a closed-shell acceptor,

$$h\nu(\mathrm{OSCT}) = \Delta E^\circ + \chi \tag{11}$$

where ΔE° is the driving force for electron transfer from donor to acceptor in the ion pair and χ is the total reorganization free energy for thermal electron transfer.[28,51] Assuming that the required driving force is approximately equal to the difference in the observed solution phase redox potentials $E[D^+/D] - E[A/A^-]$, eq 11 can be rewritten as outlined in Scheme 1, as

$$h\nu(\mathrm{OSCT}) = E[D^+/D] - E[A/A^-] + (\chi_o + \chi_i)^D + (\chi_o + \chi_i)^A - W \tag{12}$$

where $(\chi_o + \chi_i)^D$ and $(\chi_o + \chi_i)^A$ are the sums of the inner- and outer-sphere reorganization energy contributions for the donor and acceptor, respectively. Various authors have demonstrated that for a given donor, with variation of the acceptor (or vice versa), $h\nu$(OSCT) is indeed a reasonable linear function of $E[A/A^-]$ (or $E[D^+/D]$).[25,28,33,52] The magnitude of $h\nu$(OSCT) is generally significantly larger than the difference $E[D/D^-] - E[A^+/A]$ so that, overall, the inner- and outer-sphere reorganization energy contributions are quite large (vide infra).

The $\mathrm{IE_s}^{\mathrm{V}}$ and $\mathrm{EA_s}^{\mathrm{V}}$ values can be correlated[53] with the $E[D^+/D]$ and $E[A/A^-]$ potentials using Scheme 1, as

$$E[D^+/D] = \mathrm{IE_s}^{\mathrm{V}} - 4.5 - (\chi_o + \chi_i)^D \tag{13}$$

$$E[A/A^-] = \mathrm{EA_s}^{\mathrm{V}} - 4.5 + (\chi_o + \chi_i)^A \tag{14}$$

where the −4.5 eV correction is to correct vacuum to NHE. The availability of redox data and these $\mathrm{IE_s}^{\mathrm{V}}$ and $\mathrm{EA_s}^{\mathrm{V}}$ terms allows one to test eqs 12−14 to provide an additional method to extract reorganization energy information of value in particular to kinetic and photochemical studies of electron transfer processes.

Indeed a relationship between $\{E[D/D^-] - E[A^+/A]\}$ and $h\nu$(OSCT) (Figure 3) is evident even though variations in the total reorganization energies from one species to another do cause scatter. Using eq 12, the total reorganization energies are seen to be in the range 1−2 eV, which is entirely

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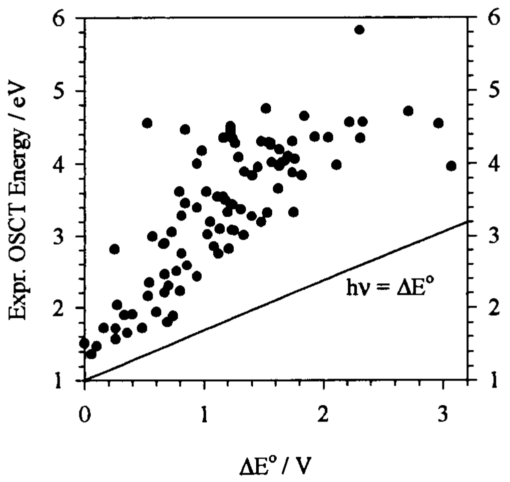

Figure 3. Plot showing the relationship between ΔE(redox) and $h\nu$-(OSCT) in electronvolts.

reasonable.[40] It is now feasible to extract values of the individual donor and acceptor reorganization energies using eqs 13 and 14. These are included in Tables 1 and 2 but are only intended to be shown as examples of the method and should be treated with caution. The necessary redox potentials were extracted from the literature, but the conditions of measurement vary widely; the redox data are not all guaranteed to be accurate and may possibly allude to processes other than those indicated such as involving protonated species.

Solvation Energies

Through Scheme 1, solvation terms may be derived through use of an appropriate cycle. For example,

$$\mathrm{IE}_s{}^{V} + \Delta G^\circ{}_s{}^{D+}* = E(D^+/D) + \Delta G^\circ{}_s{}^{D+} + \chi_i \qquad (15)$$

This information can also be used in energy cycles to obtain new information. For example, given the gas phase ionization energy of a halogen anion,[54] the hydration energy of the anion[55] and its vertical ionization energy in water,[2] then the energy to place a halogen atom into water whose local solvation shell is organized for the anion is uphill by $\Delta G^\circ{}_s{}^{D+}* = 1.82 \pm 0.13$, 1.62 ± 0.15, and 1.44 ± 0.14 eV for Cl, Br, and I, respectively (eq 15), assuming, for a halogen atom, $\chi_i = 0$. This result can probably be explained by noting that the positive ends of the water dipoles are oriented toward the chloride ion, which has now been replaced by a neutral entity resulting in appreciable repulsion energy local to the halogen atom. In addition, the thermodynamics of dissolution of a neutral species are dominated by changes in water−water interactions rather than water−solute interactions.[12]

Spin−Orbit Correction

In some cases it is necessary to apply a spin−orbit correction in situations where electronic states are significantly split by spin−orbit coupling, usually leading to a multiple OSCT transition. Examples are the OSCT bands from $[M(CN)_6]^{4-}$ species.[9] An OSCT transition occurs to two spin−orbit states shifting the overall band maximum to the higher frequencies. Here the spin−orbit correction will be 0.05 eV for Fe, 0.12 eV for Ru, and 0.31 eV for Os.

Conclusions

This OSCT analysis provides a convenient method to extract vertical solution phase ionization energies and to derive hitherto unavailable vertical solution phase electron affinities. It also provides an additional method to evaluate reorganization energies and solvation energies which play a major role in electron transfer processes. It is extendable to other solvents; however, it would be necessary to collect some photoelectron threshold emission data in the new solvent, to provide the appropriate reference.

Acknowledgment. We are indebted to the Natural Sciences and Engineering Research Council (Ottawa, Canada) for financial support. S.I.G. is indebted to the Province of Ontario, Canada, for a graduate scholarship. We also thank Prof. J. F. Endicott (Wayne State University) for useful discussion.

Supporting Information Available: A literature database of OSCT energies with literature references, used to create the data tabulated in the paper, including Figure 2 (5 pages). Ordering information is given on any current masthead page.

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