

Photoelectron Emission Spectroscopy of Aqueous Solutions

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Irradiation of the surface of a liquid or a solution with photons of sufficient energy causes the emission of electrons into the gas phase above the liquid. Electrons can be collected by means of an electrode located in the vapor phase above the liquid, and an emission spectrum can be determined by varying the photon energy. Irradiation in the vacuum ultraviolet range at wavelengths as short as 115 nm is necessary with many aqueous solutions.

Emission of photoelectrons by a solution entails the oxidation of the emitting species, e.g., the oxidation of Fe^{2+} to Fe^{3+} in the emission by an aqueous solution of Fe^{2+} ions. Photoionization is a vertical process (Franck-Condon principle), and therefore the Fe^{3+} ion produced by photoionization of a Fe^{2+} ion initially retains the solvation nuclear configuration of the Fe^{2+} ion. Conversely, the solvation electronic configuration adjusts much more rapidly than the nuclear configuration to the change of ionic charge from +2 to +3. Thus, relaxation of the nuclear configuration of solvent molecules is slow on the scale of time considered here whereas relaxation of the electronic configuration is fast. It follows that the determination of emission spectra of solutions might provide an *experimental* way of separating the fast and slow relaxation processes in the energetics of solvation. This inference is indeed borne out.

Separation of fast and slow relaxation processes by experiment is of interest because dielectric saturation of the solvent poses a major problem in the quantitative theoretical treatment of ionic solvation. The electric field near ions such as Fe^{2+} in aqueous solution is so high that orientation of water dipoles about the ions is only disturbed in a minor way by thermal motion. Further increase in the field, e.g., from Fe^{2+} to Fe^{3+} , only marginally enhances dipole about the ions. The solvation nuclear configurations about Fe^{2+} and Fe^{3+} therefore differ much less than one would expect in the absence of dielectric saturation. Detailed model calculations of such an effect are very difficult, and recourse to experiment is advisable. Photoelectron emission spectroscopy provides a solution to this problem, as will be shown in this Account.

Significant problems besides the study of ionic solvation have been investigated by means of photoelectron emission spectroscopy of solutions. Thus, the energetics of photoelectron emission by solutions can be correlated to the thermodynamics of the oxidation process corresponding to the loss of an electron by the

emitting species in solution. This fundamental correlation is essential in the interpretation of a variety of photoionization processes, for instance, for weak acids and bases and their ions. Several examples of this simple and powerful approach will be examined.

Our basic experimental procedure¹ is easy to understand. The continuously renewed liquid film on the flange of a rotating quartz disk (Figure 1) is irradiated through a lithium fluoride window. The disk assembly is contained in an evacuated enclosure. The solution is cooled (to ca. 2 °C) to lower the vapor pressure and minimize attenuation of the photon flux by water vapor in the gap between the lithium fluoride window and the rotating disk. The photon flux is monitored by means of a sodium salicylate crystal, C (vacuum ultraviolet to visible conversion), and a photomultiplier detector located behind the glass window G. Both the photomultiplier current and the current collected by the electrode (gold grid mesh, 80% transparency) in the vapor phase are measured as a function of the photon energy E . The *emission yield* Y is computed and expressed as the number of collected electrons per incident photon at a given E . Results are displayed as an *emission spectrum* consisting of a plot of Y against E (Figure 2).

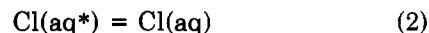
Free Energy of Emission

The energetics of photoelectron emission by a solution is fundamental for the interpretation of experimental results. In this section we illustrate the energetics for an aqueous solution of chloride ions although the treatment is readily generalized to other anions, electrically neutral species, and cations.

Photoelectron emission is represented by



where the notations (aq) and (g) denote species in solution and the gas phase, respectively. The transient configuration of the solvent molecules about the chlorine atom produced by photoionization is denoted by (aq*) in eq 1. The solvation nuclear configuration about $\text{Cl}(\text{aq}^*)$ relaxes according to



and a solvated chlorine atom is obtained. This atom may undergo further reaction, but such subsequent processes need not concern us at this stage. Relaxation from vibrationally excited states must also be considered in addition to relaxation of solvent orientation when diatomic or polyatomic molecules or ions are photoionized.

Process 1 bears some resemblance to photoelectron emission by a metal. The latter is characterized by the work function of the metal, that is, the work done in

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(1) I. Watanabe, J. B. Flanagan, and P. Delahay, *J. chem. Phys.*, **73**, 2057 (1980).

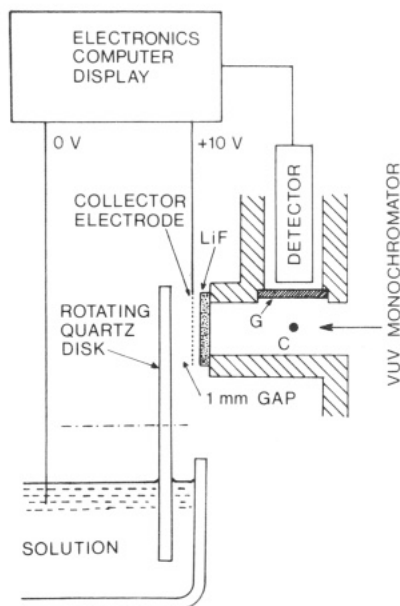


Figure 1. Schematic diagram of instrument for the determination of emission spectra.¹

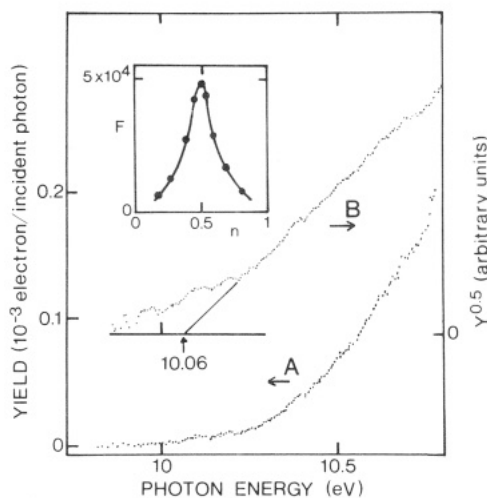
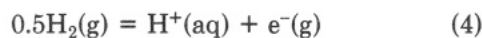
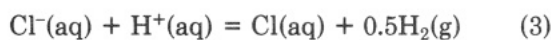


Figure 2. Photoelectron emission spectrum of liquid water at 1.5 °C (curve A) and plot of $Y^{0.5}$ against E (line B). The statistical F test of exponent of the yield is in inset.⁹ $F = R^2(N - 2)/(1 - R^2)$, where R is the correlation coefficient for least-square fitting and N is the number of points.

transferring an electron from the electrically uncharged metal to infinity under vacuum. The counterpart of the work function is the change of free energy for process 1 with all species in their standard states. This quantity, which is positive and pertains to a vertical process, will be referred to as the *free energy of emission* ΔG_e . Conversely, process 2 involves a negative change of free energy, designated as the *free energy of reorganization*, ΔG_r . The quantity ΔG_r includes a contribution from vibrational relaxation for diatomic or polyatomic species.

The sum $\Delta G_e + \Delta G_r$, which is smaller than ΔG_e since ΔG_r is negative, is the change of free energy for the adiabatic process (in the spectroscopic sense) represented by the sum of reactions 1 and 2. This adiabatic process can also be regarded as the sum of the reactions



involving the changes of free energy ΔG and ΔG_H , respectively. The free energy ΔG for reaction 3 is expressed according to the usual convention of assigning zero free energies of formation to $0.5\text{H}_2(\text{g})$ and $\text{H}^+(\text{aq})$ under standard conditions. The value of ΔG can readily be calculated from thermodynamic data in the particular case of reaction 3. This, however, is not possible in most cases because the relevant data are not available, e.g., for the oxidation of $\text{SO}_4^{2-}(\text{aq})$ to $\text{SO}_4^-(\text{aq})$ (with emission of a photoelectron). Electrons are emitted into the gas phase in our case, and the free energy of formation of the electron $\text{e}^-(\text{g})$ must be expressed in a way consistent with eq 3. This is done by introducing reaction 4. The change of free energy for this reaction, $\Delta G_H = 4.50 \text{ eV}$, was calculated by Noyes.² This value of ΔG_H does not include the contribution from the surface potential at the solution–water vapor interface. The surface potential will be neglected here since it is small ($\pm 0.1 \text{ V}$ for water³) and nearly cancels out when differences of free energies of emission are considered.

The processes represented by reactions 1 plus 2 and reactions 3 plus 4 are equivalent, and the corresponding changes of free energy $\Delta G_e + \Delta G_r$ and $\Delta G + \Delta G_H$ must be equal. Hence

$$\Delta G_e = \Delta G_H + \Delta G - \Delta G_r \quad (5)$$

This general equation is of *fundamental importance* in photoelectron emission spectroscopy because it correlates the thermodynamics of oxidation in solution with the energetics of photochemical oxidation. Equation 5 is implicitly contained in the work of Henglein and co-workers.^{4,5} Ballard⁶ reported an equation similar to eq 5. The ΔG_r term was not included but was briefly discussed, and the value $\Delta G_H = 4.39 \text{ eV}$ was obtained from consideration of two consecutive reactions equivalent to eq 4. Equation 5 was applied extensively in recent papers from this laboratory.⁷⁻⁹

The sum $\Delta G_H + \Delta G$ in eq 5 represents the change of free energy for the sum of reactions 3 and 4, that is, with the standard state of the electron taken as the vacuum level at infinity outside an electrically uncharged solution. The sum $\Delta G_H + \Delta G$ pertains to an adiabatic process (in the spectroscopic sense) whereas the free energy of emission ΔG_e is defined for a vertical process. The adiabatic and vertical processes are correlated by eq 5 via the free energy of reorganization ΔG_r for relaxation of the solvation nuclear configuration (eq 2). The quantity ΔG_r therefore can be calculated from eq 5, as will be shown below, provided ΔG_e and ΔG are known.

Threshold Energy for Emission

The central problem is to determine some characteristic energy from emission spectra and to find the relationship between this energy and ΔG_e of eq 5. This problem was solved only recently, although the idea of studying photoelectron emission by solutions dates back

- (2) R. M. Noyes, *J. Am. Chem. Soc.*, **84**, 513 (1962); **86**, 971 (1964).
- (3) B. Case and R. Parsons, *Trans. Faraday Soc.*, **63**, 1224 (1967).
- (4) A. Henglein, *Ber. Bunsenges. Phys. Chem.*, **78**, 1078 (1974); **79**, 129 (1975).
- (5) A. J. Frank, M. Gratzel, and A. Henglein, *Ber. Bunsenges. Phys. Chem.*, **80**, 593 (1976).
- (6) R. E. Ballard, *Chem. Phys. Lett.*, **42**, 97 (1976).
- (7) K. von Burg and P. Delahay, *Chem. Phys. Lett.*, **78**, 287 (1981).
- (8) P. Delahay, K. von Burg, and A. Dziedzic, *Chem. Phys. Lett.*, **79**, 157 (1981).
- (9) P. Delahay and K. von Burg, *Chem. Phys. Lett.*, **83**, 250 (1981).

(1888) to the early work on the photoelectric effect (historical background in ref 10). Three conditions had to be fulfilled: (i) A theory became available for the analysis of emission spectra. (ii) Transport of electrons in the gas phase was understood.¹¹ (iii) Instrumentation was developed¹ for the determination of emission spectra of aqueous solutions in the vacuum ultraviolet range. Only the first of these three problems will be discussed in detail. Transport of electrons in the gas phase does not pose any serious problem, and the instrumentation has already been discussed.¹

The theory of photoelectron emission by liquids and solutions was developed in several stages. A three-step model for emission, which was inspired from solid-state physics, was proposed initially by the author.¹² Emission was considered as a sequence of the following three consecutive steps: (i) generation of delocalized (quasi-free) electrons by photoionization of a species (solute, solvent) in the liquid phase; (ii) random walk of delocalized electrons with loss of kinetic energy to the liquid medium; (iii) crossing of the liquid-vapor interfacial barrier by the delocalized electrons reaching it. A phenomenological equation for the emission current derived from this model provided a qualitative understanding of emission spectra.¹² An essential feature of the experimental method also follows from this model. Thus, electrons are emitted into the gas phase from a layer of solution having a thickness of the order of the thermalization length of low-energy (a few electronvolts at most) electrons in aqueous solution. This length is ~ 2 to 4 nm, and consequently there is hardly any attenuation of the photon flux as a result of absorption by water in the layer from which emitted electrons originate. Conditions of a *thin-layer technique* are achieved.

The three-step model was developed further by treating electrons generated by photoionization either as classical particles or according to quantum mechanics. The classical approach developed by Nemeč¹³ proved valuable in the analysis of energy distribution curves¹⁴ (not reviewed here) but was not useful for the analysis of emission spectra. The quantum theory of Brodsky and Tsarevsky¹⁵ was very successful in this respect. The transport of electrons in this theory is treated as the propagation of a spherical wave, and the interaction with the medium is accounted for by an exponential attenuation factor. The barrier problem is treated in the threshold approximation, that is, details of the barrier at the solution-gas interface can be ignored provided that the thickness of the interfacial layer is small in comparison with the de Broglie wavelength of electrons emitted into the gas phase. Both transmission through the interfacial barrier and reflection by this barrier are considered. The Brodsky-Tsarevsky theory was criticized,^{16,17} but the extrapola-

Table I
Threshold Energies of Aqueous Solutions^{a,b}

OH ⁻ (8.45), H ₂ O (10.06)
Cl ⁻ (8.81), Br ⁻ (8.05), I ⁻ (7.19)
ClO ₃ ⁻ (8.21), BrO ₃ ⁻ (7.88), IO ₃ ⁻ (7.44), ClO ₄ ⁻ (8.45)
SO ₃ ²⁻ (7.17), S ₂ O ₃ ²⁻ (7.27), SO ₄ ²⁻ (8.65), S ₂ O ₈ ²⁻ (7.33)
NO ₂ ⁻ (7.57), NO ₃ ⁻ (7.46), N ₃ ⁻ (7.46), N ₃ ⁻ (7.35)
H ₃ PO ₄ (9.45), H ₂ PO ₄ ⁻ (9.23), HPO ₄ ²⁻ (8.79), PO ₄ ³⁻ (7.44)
H ₃ AsO ₄ (9.44), H ₂ AsO ₄ ⁻ (9.09), HAsO ₄ ²⁻ (8.50), AsO ₄ ³⁻ (8.30)
HCO ₃ ⁻ (9.07), CO ₃ ²⁻ (7.40), CNS ⁻ (7.20)
Sn ²⁺ (7.42), Pb ²⁺ (7.23), In ³⁺ (7.15), Tl ⁺ (7.40)
Cu ²⁺ (7.83), Ag ⁺ (7.60)
Ni ²⁺ (8.35), Co ²⁺ (8.60)
Fe ²⁺ (7.38), Fe ³⁺ (7.03)
Mn ²⁺ (8.08), Cr ²⁺ (6.14), Cr ³⁺ (7.33)
V ²⁺ (6.38), V ³⁺ (7.06), Ti ³⁺ (6.90)
weak acids and anions: formic (10.0, 7.55), acetic (9.00, 7.82), propionic (9.08, 8.42), <i>n</i> -butyric (8.99, 8.23), oxalic (8.26, 7.50, 7.32), tartaric (8.55, 7.72, 7.37), citric (8.66, 8.52, 8.39, 7.48)
weak bases and cations: triethylamine (6.73, 7.57), aniline (7.39, 8.44), ethylenediamine (7.20, 7.47, 8.13)

^a Values of E_t in electronvolts. Standard deviation of 0.01 to 0.03 eV in general.^{7-9,21} ^b Results for cations generally obtained with chloride or perchlorate solutions.

tion method based on this theory is amazingly successful in the analysis of emission spectra of aqueous solutions. Thus, a plot of Y^n against the photon energy E (Figure 2), where $n = 0.4$ or 0.5 , is linear, and extrapolation to $Y^n = 0$ yields the *threshold energy* E_t (Table I). Departure from linearity very near E_t arises from simplifications inherent to the theory. The exponents $n = 0.4$ and 0.5 correspond, respectively, to the neglect and consideration of image forces in the treatment of the barrier problem. In practice, data are processed by computer, and the best value of the exponent, $n = 0.4$ or 0.5 , is determined by means of statistical analysis (F test;¹⁸ Figure 2). As a rule of thumb, one has $n = 0.4$ for $E_t < 8$ eV and $n = 0.5$ for $E_t > 8$ eV for aqueous solutions. Linear extrapolation plots have been obtained in this laboratory with extremely good statistics for numerous ions and molecules in aqueous solution, and the linearity of the extrapolation plots is well established, although the reason why image forces can be neglected in some cases is really not understood at this time.

Threshold energies were correlated to free energies of emission by recourse to experiment.^{7,9} The Cl⁻, Br⁻, and I⁻ ions in aqueous solution were selected for this purpose because both the free energies of oxidation ΔG (2.51, 1.98, 1.32 eV, respectively) and reorganization ΔG_r (-1.74, -1.57, -1.36 eV) of eq 5 can be calculated quite accurately from independent data. Thus, one computes from eq 5 the free energies of emission $\Delta G_e(\text{Cl}^-) = 8.75$ eV, $\Delta G_e(\text{Br}^-) = 8.05$ eV, $\Delta G_e(\text{I}^-) = 7.18$ eV vs. the threshold energies $E_t(\text{Cl}^-) = 8.81$ eV, $E_t(\text{Br}^-) = 8.05$ eV, $E_t(\text{I}^-) = 7.19$ eV. The relationship, $\Delta G_e \approx E_t$, therefore, holds for these ions, even if one allows for the uncertainty from the neglect of the surface potential (cf. discussion of eq 5). This conclusion, in the general case, can be justified qualitative in terms of the Gurney-Gerischer formalism developed by Henglein^{4,5} for electron transfer in solution, but this analysis is beyond

(17) Yu. V. Pleskov, *J. Electroanal. Chem.*, **105**, 227 (1979).

(18) P. R. Bevington, "Data Reduction and Error Analysis for the Physical Sciences", McGraw-Hill, New York, 1969, p 199.

(10) B. Baron, P. Chartier, P. Delahay, and R. Lugo, *J. Chem. Phys.*, **51**, 2562 (1969).

(11) P. Delahay, P. Chartier, and L. Nemeč, *J. Chem. Phys.*, **53**, 3126 (1970).

(12) P. Delahay, *J. Chem. Phys.*, **55**, 4188 (1971).

(13) L. Nemeč, *J. Chem. Phys.*, **59**, 6092 (1973).

(14) H. Aulich, P. Delahay, and L. Nemeč, *J. Chem. Phys.*, **59**, 2354 (1973).

(15) A. M. Brodsky and A. V. Tsarevsky, *J. Chem. Soc., Faraday Trans. 2*, **72**, 1781 (1976).

(16) Yu. Ya. Gurevich, Yu. V. Pleskov, and Z. A. Rotenberg, "Photoelectrochemistry", H. S. Wroblowa, Translator, Consultants Bureau, New York, 1980, pp 196-198.

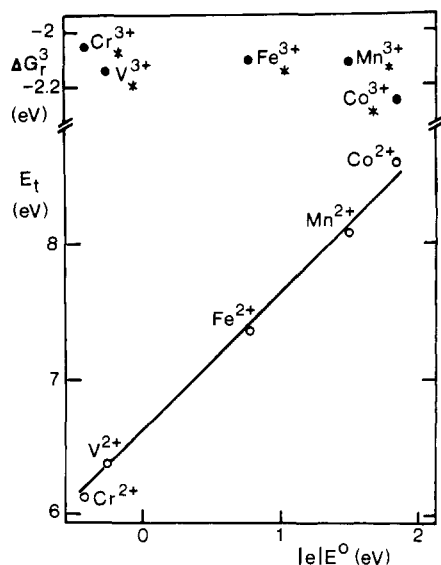


Figure 3. Plot of threshold energy and reorganization free energy against the free energy⁸ $\Delta G = |e|E^\circ$ (E° = standard reduction potential for the M^{3+}/M^{2+} couple).

the scope of this Account. In conclusion, there is no reason to doubt that the equation $\Delta G_e \approx E_t$ holds in general (within a few tenths of an electronvolt or even better).

Reorganization Free Energy

The reorganization free energy ΔG_r will be interpreted by following the opposite approach to the one at the end of the preceding section. Thus, the free energy of emission ΔG_e will be equated to the threshold energy E_t , and ΔG_r will be calculated from eq 5 for systems for which the free energy of oxidation ΔG is known. This will be done⁸ for photoionization of the five cations M^{2+} of Figure 3. The threshold energy in that case varies almost linearly with the free energy of oxidation ΔG and the calculated values of the free energy of reorganization ΔG_r are nearly the same (-2.05 to -2.25 eV). In general, however, ΔG_r varies significantly from one species to another even for a series of chemically similar substances (e.g., for the halides discussed in the preceding section). Plots of the threshold energy E_t against the free energy of oxidation ΔG for such a series are not linear in general, and even if they appear linear, they do not have a unit slope. The general rule holds nevertheless that the reduced form of a strongly reducing redox couple ($\Delta G < 0$) has a low (~6 to 7 eV) threshold energy. Conversely, a high value of E_t (~8 eV) is obtained for the reduced form of a strongly oxidizing redox couple ($\Delta G > 1$ -2 eV). These limits are, of course, approximate.

Reorganization free energies cover the range $-2.3 < \Delta G_r < -0.3$ eV for the substances studied thus far in aqueous solution. The limit of ca. -2.3 eV corresponds, for instance, to ions such as M^{2+} in Figure 3. The lowest absolute value of 0.3 eV pertains to bulky ions with multiple charge such as $W(CN)_8^{4-}$. Analysis of the emission spectrum of this ion¹⁹ yields a threshold energy $E_t = 5.39$ eV and a free energy of reorganization $\Delta G_r = -0.32$ eV ($\Delta G = 0.57$ eV). The cyanometalate complexes generally have rather small reorganization free energies (ca. -0.3 to -0.7 eV) and low threshold energies

(<6 eV), and irradiation in the ultraviolet range is sufficient to cause photoelectron emission. Thus, the ion $Fe(CN)_4^{4-}$, for instance, was found long ago¹⁰ (1923) to display emission: $E_t = 5.53$ eV, $\Delta G = 0.36$ eV, $\Delta G_r = -0.67$ eV (from the analysis of the emission spectrum in ref 19).

The reorganization free energy will be interpreted and correlated with ionic solvation.⁸ The latter is characterized by the *real energy of solvation* ΔG_s , defined as³ "the free energy change in the process where an ion in field-free space is inserted into a large quantity of solution which carries no net electrical charge". Values of ΔG_s can be calculated from thermodynamic data^{2,3} with additional considerations outside the realm of thermodynamics. One has,² for instance, $\Delta G_s(Fe^{2+}) = -19.63$ eV and $\Delta G_s(Fe^{3+}) = -44.87$ eV for aqueous solutions. Solvation involves changes in both the electronic and nuclear configurations of solvent molecules. Conversely, the reorganization process in the photoelectron emission by Fe^{2+} ions, for instance, involves only the relaxation of the nuclear configuration of solvent molecules following the change of ionic charge of ionic charge from 2+ to 3+. The free energy of reorganization for nuclear relaxation, $\Delta G_r = -2.11$ eV for Fe^{2+} (Figure 3), is only a small fraction of the difference of real energies of solvation, $\Delta G_s(Fe^{3+}) - \Delta G_s(Fe^{2+}) = -44.87 + 19.63 = -25.24$ eV, namely $(-2.11)/(-25.24) = 0.084$. The Franck-Condon principle was applied in reaching this conclusion, but no model of the solvation process was introduced. Determination of the free energy of reorganization ΔG_r by means of photoelectron emission spectroscopy thus provides an *experimental* method of separating fast (electronic) and slow(nuclear) relaxation in ionic solvation. This is a significant result.

The preceding results will be reformulated by treating the solvent as a continuous medium undergoing electronic and orientation polarization as a result of ionic solvation. The free energy of solvation is then given by the Born equation. The approach is quite crude but straightforward. Better models and methods of calculation are available²⁰ but are not needed for our purpose. Consider photoelectron emission by species A^{z+} ($z < 0$) in solution, and assume that the radii of the A^{z+} and $A^{(z+1)+}$ ions are equal to simplify matters. One has

$$R = \frac{|(z+1)^2 - z^2| \Delta G_r / (\Delta G_s^{z+1} - \Delta G_s^z)}{(\epsilon_0^{-1} - \epsilon_s^{-1}) / (1 - \epsilon_s^{-1})} \quad (6)$$

where ϵ_0 and ϵ_s are, respectively, the optical and static dielectric constants of the solvent. The factor $|(z+1)^2 - z^2|$ appears in eq 6 because the solvation free energy is proportional to the square of the ionic charge whereas the reorganization free energy is independent of z (cf. theories of electron transfer and nonequilibrium polarization).

One has $\epsilon_0 = 1.777$ and $\epsilon_s = 78.36$ for water at 25 °C, and $R = 0.56$ in that case. This is roughly the value of R for emission by singly charged anions:^{9,21} $R = 0.50, 0.49, 0.48$, respectively, for Cl^-, Br^-, I^- ; $R = 0.44$ - 0.51 for OH^- depending on the estimate of the free energy of solvation $\Delta G_s(OH^-)$. The value $R \approx 0.50$ also holds for emission by liquid water,⁹ that is, for emission by an electrically neutral species. The change of free en-

(19) L. Nemeč and P. Delahay, *J. Chem. Phys.*, **57**, 2135 (1972).

(20) B. Case in "Reactions of Molecules and Electrodes", N. S. Hush, Ed., Wiley-Interscience, New York, 1971, pp 45-134.

(21) K. von Burg and P. Delahay, *Chem. Phys. Lett.*, in press.

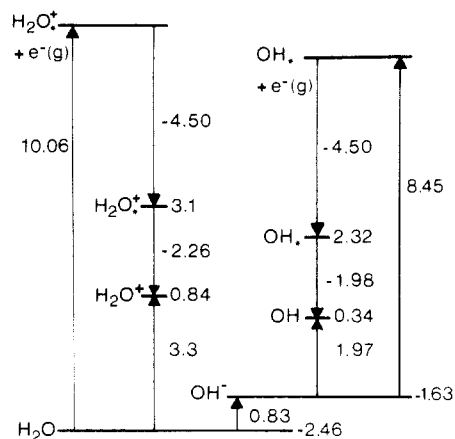
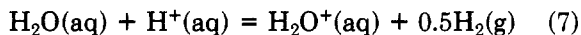


Figure 4. Free energies of formation and free energy changes (in electronvolts) for photoelectron emission by water and hydroxide ion.⁹

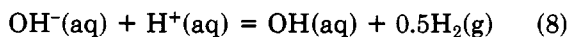
ergy for orientation polarization ΔG_r , in these cases corresponds approximately to one-half of the difference between the free energies of solvation in eq 6. The ratio R is somewhat lower in the case of Fe^{2+} already considered above. Thus, $\Delta G_r = -2.11$ eV, $\Delta G_s^3 - \Delta G_s^2 = -25.24$ eV, and one computes $R = (3^2 - 2^2) \times 2.11/25.24 = 0.42$. This value of R can be interpreted as the result of dielectric saturation.² Solving eq 6 for ϵ_s with $R = 0.42$, one obtains $\epsilon_s \approx 4.1$ vs. 78.36 in the absence of dielectric saturation. The foregoing analysis does not require the introduction of an ionic radius. This is a distinct advantage since the assignment of radii is tentative in applications of continuous medium models to solvation. Dielectric saturation about other cations is examined in ref 8, but the factor $|(z+1)^2 - z^2|$ of eq 6 was mistakenly omitted. The conclusions thus reached nevertheless agree qualitatively with the preceding result for Fe^{2+} . These results show that there is undoubtedly some dielectric saturation in solvation processes, but the limitations of continuous medium models should be kept in mind in evaluating numerical results.

Water and Hydroxide Ion

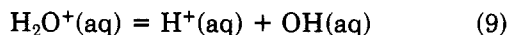
The threshold energies of liquid water⁹ and hydroxide ion^{7,9} in aqueous solution are 10.06 and 8.45 eV, respectively. The difference between these threshold energies will be interpreted⁹ on the basis of the free energy diagram of Figure 4. The free energies of formation of liquid water and $\text{OH}^-(\text{aq})$ ions differ by $0.0592 \log 10^{-14} = 0.83$ eV on account of the dissociation of water. The free energy change ΔG for the reaction



was estimated at 3.3 ± 0.3 eV on the basis of the emission results. The value of $\Delta G = 1.97$ eV for the reaction



is known from thermodynamic data. One concludes from the preceding data that the change of free energy for the reaction



is -0.5 ± 0.3 eV. Thus, the ion $\text{H}_2\text{O}^+(\text{aq})$ is thermodynamically unstable, and the hydroxyl radical $\text{OH}(\text{aq})$ does not protonate to any extent. These conclusions

are consistent with experimental kinetic data.⁹

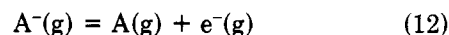
The difference in threshold energy for H_2O and $\text{OH}^-(\text{aq})$ follows directly from Figure 4 and eq 5 (with $\Delta G_e \approx E_t$), namely

$$E_t(\text{H}_2\text{O}) - E_t(\text{OH}^-) = [\Delta G(\text{OH}^-) - \Delta G(\text{H}_2\text{O})] + [\Delta G(\text{H}_2\text{O}^+) - \Delta G(\text{OH})] + [\Delta G_r(\text{OH}) - \Delta G_r(\text{H}_2\text{O}^+)] = 0.83 + 0.50 + 0.28 = 1.61 \text{ eV} \quad (10)$$

The notation $\Delta G(X)$ in eq 10 denotes the free energy of formation of species X. The three contributions in eq 10 arise because water is only slightly dissociated (0.83 eV), the ion $\text{H}_2\text{O}^+(\text{aq})$ is unstable (0.5 eV), and the reorganization free energies of OH and H_2O^+ ions are different (0.28 eV).

Anions

The threshold energies of the anions studied thus far^{7,21} are in the 7.2–9.2-eV range (Table I). These energies will be correlated to gas-phase electron affinities in the case of univalent anions. Consider the reactions



involving the change of free energy $-\Delta G_s$, $-\Delta G_a$, and ΔG_n , respectively. The sequence of reactions 11 to 13 is equivalent to the adiabatic process involving the sum of the free energies of emission and reorganization, $\Delta G_e + \Delta G_r$ (cf. eq 1 and 2). Hence, one has for the free energy of emission

$$\Delta G_e = -\Delta G_a + \Delta G_n - \Delta G_s - \Delta G_r \quad (14)$$

Equation 14 will be simplified. The free energy of solvation ΔG_n (≤ 0.1 eV in absolute value) and the contribution from vibrational relaxation to ΔG_r (a few tenths of an electronvolt) can be neglected to a first approximation. The equation $\Delta G_r \approx \Delta G_s/2$ holds for $\text{A}^-(\text{aq})$ ions, as was shown in the section on the free energy of reorganization. The electron affinity EA of $\text{A}(\text{g})$ is the negative enthalpy of electron attachment, and one has $\text{EA} = -\Delta H_a \approx -\Delta G_a$. Equation 14 becomes with these simplifications $\Delta G_e \approx \text{EA} - (3/2)\Delta G_s$ (within ca. +0.5 eV).

Since one has $\text{EA} > 0$ and $\Delta G_s < 0$, the free energy of emission ΔG_e is the sum of two positive quantities. Extreme values²² of EA for the anions studied thus far are 1.83 eV for OH and 5.82 eV for ClO_4^- . The ions OH^- and ClO_4^- nevertheless have by coincidence the same threshold energy (8.45 eV) because the difference of electron affinity is compensated by the difference between the real energies of solvation. The halides Cl^- , Br^- , I^- represent intermediate cases in which the contributions from the electron affinity EA (3.61, 3.36, 3.06 eV) and the real energy of solvation $-\Delta G_s$ (3.46, 3.18, 2.81 eV) are similar for each of these three anions.

Threshold energies have also been correlated to the energy E_{max} at the maximum of the absorption bands of anions exhibiting charge transfer to the solvent.⁷ The correlation between E_t and E_{max} is approximately linear, in agreement with the relationship $E_t \approx E_{\text{max}} + 1.7$ (in eV), predicted¹¹ from a model for this type of charge-transfer spectra.

(22) L. G. Christophorou, "Atomic and Molecular Radiation Physics", Wiley-Interscience, New York, 1971, p 546–551, 565–571.

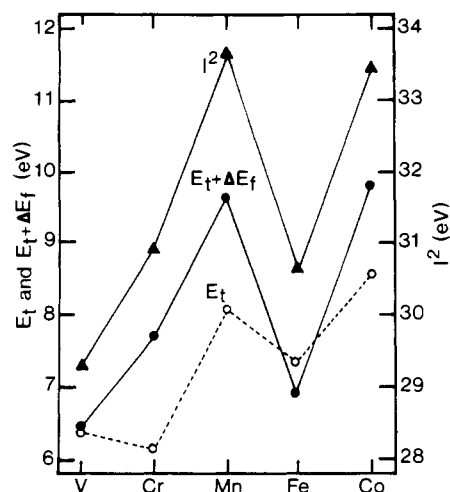


Figure 5. Correlation between ionization potential and threshold energy corrected for the difference ΔE_f between the ligand field stabilization energies for M^{3+} and M^{2+} in an octahedral field.⁸ Threshold energies from Table I and values of ΔE_f from ref 23.

Cations

Threshold energies of cations M^{z+} (Table I) will be correlated to the gas-phase ionization potentials I^z of the M^{z+} ions just as values of E_t for anions were correlated to gas-phase electron affinities. The following relationship holds⁸ for the free energy of emission:

$$\Delta G_e^z = \Delta G_i^z + \Delta G_s^{z+1} - \Delta G_s^z - \Delta G_r^{z+1} \quad (15)$$

where ΔG_i^z is the free energy for the gas-phase ionization of M^{z+} and the superscript represents the ionic charge. Equation 15 is similar to eq 14. The right hand side of eq 15, except for $-\Delta G_r^{z+1}$, is equal (cf. eq 5) to $\Delta G_H + \Delta G^z$, where ΔG^z is the free energy change for the oxidation of M^{z+} to $M^{(z+1)+}$ in a reaction similar to eq 3. The free energy of ionization ΔG_i^z can be calculated from ΔG^z , ΔG_s^z , ΔG_s^{z+1} , but the necessary data are generally not available, and one simply equates ΔG_i^z to the ionization potential I^z (enthalpy).

One has for the cations of Table I: the ionization potentials $I^z = 20, 30-37, 43-57$ eV, respectively, for $z = 1, 2, 3$; the negative real energies of solvation $-\Delta G_s^z = 3.5-5, 15.5-21, 42-45$ eV, respectively, for $z = 1, 2, 3$; $-\Delta G_r^{z+} < \text{ca. } 2.5$ eV. Equation 15 therefore involves the difference of relatively large numbers in comparison with the free energy of emission ΔG_e^z . There is partial cancellation of the terms, and the range of threshold energies E_t in Table I is only ca. 2.5 eV. Data for emission by Fe^{2+} are typical: $\Delta G_e^2 \approx E_t^2 = 7.38$ eV (Table I), $\Delta G_i^2 = 30.51$ eV (calculated from $\Delta G^2 = 0.77$ eV; compare with $I^2 = 30.64$ eV), $\Delta G_s^2 = -19.63$ eV, $\Delta G_s^3 = -44.87$ eV, and $\Delta G_r^3 = -2.11$ eV (from eq 15).

Equation 15 suggests a simple correlation between the threshold energy E_t^z and the ionization potential I^z in a series of cations provided the algebraic sum of other terms in this equation is nearly constant. This is the case for the cations of the five metals of Figure 5. The correlation between E_t^z and I^z is even more striking if the threshold energies are corrected for the difference ΔE_f in the ligand field stabilization energies for the $M^{3+}(\text{aq})$ and $M^{2+}(\text{aq})$ hexaquo ions in an octahedral

field⁸ (ΔE_f calculated from data in ref 23).

Weak Acids and Bases and Their Ions

Weak acids in most cases have higher threshold energies than their anions, and conversely weak bases have lower threshold energies than their cations²¹ (Table I). These observations can be accounted for by the method of analysis used for water and hydroxide ion. One has for the acid HA and its anion A^-

$$E_t(\text{HA}) - E_t(A^-) = [\Delta G(A^-) - \Delta G(\text{HA})] + [\Delta G(\text{HA}^+) - \Delta G(A)] + [\Delta G_r(A) - \Delta G_r(\text{HA}^+)] \quad (16)$$

where $\Delta G(X)$ represents the free energy of formation of species X. Equation 16 is similar to eq 10 for water and hydroxide ion. Each of the three terms on the right-hand side of eq 16 will be examined.

One has $\Delta G(A^-) - \Delta G(\text{HA}) = \Delta G_K = -0.0592 \log K$, where ΔG_K is expressed in electronvolts and K is the dissociation constant of HA. Since $K > 10^{-5}$ for the acids of Table I, one has $\Delta G_K < 0.3$ eV. The term $\Delta G_r(A) - \Delta G_r(\text{HA}^+)$ should not exceed a few tenths of an electronvolt at most because the ions HA^+ and A^- have the same charge in absolute value and have comparable sizes. Moreover, the contributions from vibrational relaxation should nearly cancel out. The difference of reorganization free energies therefore can be neglected in eq 16 to the approximation of a few tenths of electronvolt. The term $\Delta G(\text{HA}^+) - \Delta G(A)$ in eq 16 is the change of free energy for the protonation reaction $\text{H}^+ + A = \text{HA}^+$ involving the products of the photoionization of A^- and HA. Inspection of the values of E_t in Table I shows (with $\Delta G_K < 0.3$ eV) that this change of free energy is positive. Thus, the ion HA^+ is unstable and the radical A does not protonate to any significant extent in aqueous solution. This analysis is extended in ref 21 to the acids H_nA ($n = 2, 3$) and their anions and to the weak bases of Table I and their cations.

Conclusion

The approach in the photoelectron emission spectroscopy of aqueous solutions is simple and direct in its essence:²⁴ determine threshold energies and interpret (eq 5) the results in terms of free energies for adiabatic oxidation (ΔG) and reorganization (ΔG_r). Conditions for aqueous solutions are particularly favorable because of the high threshold energy (10.06 eV) of water, but application to other solvents and a variety of solutes should be feasible and interesting.²⁵

Our work on photoelectron emission spectroscopy was supported by the Office of Naval Research and the National Science Foundation.

(23) T. M. Dunn, D. S. McClure, and R. G. Pearson, "Crystal Field Theory", Harper and Row, New York, 1965, p 82.

(24) Other significant work on photoelectron emission by solutions, not reviewed here, includes recently observed photon-induced electron-transfer processes. Cf. K. von Burg and P. Delahay, *Chem. Phys. Lett.*, **83**, 199 (1981).

(25) Nonaqueous solvents of low vapor pressure were in fact used in earlier work²⁶ (not reviewed here) on energy distribution curves. Such solvents were not used thus far in the determination of threshold energies, although some of the earlier emission spectra could be analyzed for that purpose.

(26) L. Nemeč, L. Chia, and P. Delahay, *J. Phys. Chem.*, **79**, 2935 (1975).