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Review of current work on photoelectron emission spectroscopy of aqueous solutions. Theoretical background covers: free energy of emission, threshold energy for emission, reorganization free energy. Applications include: water and hydroxide ion, anions, cations, weak acids and bases and their ions.

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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 most aqueous solutions. New and significant results were recently obtained by this method: experimental separation of fast (electronic) and slow (nuclear) relaxation in ionic solvation, production and characterization of unusually high oxidation states of metals generated by photoionization in aqueous solution, information about the protonation of radicals produced by photoionization of weak acids and bases and their ions in aqueous solution. These and other results are discussed in the present Account.

A few comments may be helpful to show how experiments are performed. Details are given in reference 1. 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 (ca. $2^{\circ}C$) 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 will be discussed first, and the fundamental equation for the interpretation of experimental results will be obtained. This will be done for a concrete example, namely an aqueous solution of chloride ions (e.g., potassium chloride), but the treatment is readily transposed to anions in general, electrically neutral species and cations.

Photoelectron emission is represented by the equation,

$$Cl^-(aq) = Cl(aq_*) + e^-(g), \tag{1}$$

where the notations (aq) and (g) denote species in solution and the gas phase, respectively. Photoionization is a "vertical" process (Franck-Condon principle), and therefore the chlorine atom initially retains the solvation nuclear configuration of the chloride ion. Conversely, the chlorine atom produced by reaction 1 has the solvation electronic configuration of an electrically neutral substance. Thus, changes in nuclear configuration of solvent molecules are slow on the scale of time considered here whereas changes of electronic configuration are fast. The transient configuration of the solvent molecules is denoted by (aq_*) in eq 1. The solvation nuclear configuration about $Cl(aq_*)$ relaxes according to

$$Cl^-(aq_*) = Cl(aq), \tag{2}$$

and a solvated chlorine atom is obtained by photoionization. This atom may undergo further reaction, but such subsequent process 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 transferring an electron from the electrically uncharged metal to infinity in vacuum. The counterpart of the work function for process 1 is the free energy of emission ΔG_e. This quantity is positive and pertains to a vertical process. Conversely, process 2 involves a negative change of free energy designated as the free energy of reorganization. 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 $\Delta G_r < 0$, 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 following two reactions,

$$Cl^-(aq) + H^+(aq) = Cl(aq) + 1/2H_2(g) \tag{3}$$

$$1/2H_2(g) = H^+(aq) + e^-(g), \tag{4}$$
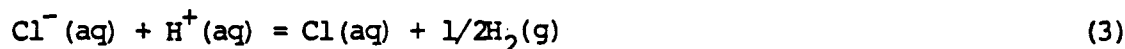
involving the changes of free energy ΔG and ΔG_H, respectively. The value of ΔG can readily be calculated from thermodynamic data in the particular case of reaction 3. This, however, is not possible in most cases because the relevant data are not available, e.g., for the oxidation of SO_4^{2-} (aq) to SO_4^- (aq) (with emission of a photoelectron).

The free energy ΔG for reaction 3 is expressed according to the usual convention of assigning zero free energies of formation to $1/2H_2(g)$ and

H^+(aq) under standard conditions. Electrons are emitted into the gas phase in our case, and the free energy of formation of the electron e^-(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, ΔG_H = 4.50 eV, was calculated by Noyes,[2] and consequently the standard free energy of formation of e^-(g) is 4.50 eV. The preceding 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 (± 0.1 V for water[3]) 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,

$$\Delta G_e = \Delta G_H + \Delta G - \Delta G_r. \tag{5}$$

This general equation is of fundamental importance in photoelectron emission spectroscopy, as will be evident from the present Account. Equation 5 is implicitly contained in the work of Henglein and coworkers.[4,5] Ballard[6] reported an equation similar to eq 5. The ΔG_r term was not included but was briefly discussed, and the value ΔG_H = 4.39 eV was obtained from consideration of two consecutive reactions equivalent to 4. Equation 5 was applied extensively in recent papers from this laboratory.[7-9]

Equation 5 clearly shows the relationship between photochemical and electrochemical oxidation.[4-9] The change of free energy ΔG pertains to reaction 3 written as an oxidation, and consequently the reduction potential for the Cl(aq)/Cl$^-$(aq) couple is E = $\Delta G/|e|$ (no minus sign!), where e is the electronic charge and E is expressed with reference to the normal hydrogen electrode. The term ΔG_H in eq 5 can be regarded as a change of "reference

electrode." The positive quantity $-\Delta G_r$ ($\Delta G_r < 0$) appears in eq 5 because $\Delta G_H + \Delta G$ pertains to an adiabatic process whereas photoelectron emission is a vertical process.

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 (1888) to the early work on the photoelectric effect (historical background in reference 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 developed[1] 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 some detail. Transport of electrons in the gas phase does not pose any serious problem, and instrumentation was briefly discussed after the introductory remarks.

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 mobile (quasifree) electrons by photoionization of a species (solute, solvent) in the liquid phase; (ii) random walk of mobile electrons with loss of kinetic energy to the liquid medium; (iii) crossing of the liquid-vapor interfacial barrier by the mobile 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 ca 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 Nemec[13] proved valuable in the analysis of energy distribution curves [14] (not reviewed here) but was not useful for the analysis of emission spectra. The quantum theory of Brodsky and Tsarevsky[15] was very successful in this respect. The transport of electrons in this theory is treated as the propagation of a wave, and the interaction with the medium is accounted for by an exponential attenuation factor. Both transmission through the interfacial barrier and reflection by this barrier are considered. The theory was criticized, not without reason, for its treatment of image forces[16] and its neglect of fluctuations.[17] Yet, the extrapolation method based on the Brodsky-Tsarevsky 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 linear plots with n = 0.4 and n = 0.5 correspond to two limiting cases of a more general equation given in reference 15. The choice of n depends on the range of kinetic energy of electrons, but the theoretical criteria are too stringent. 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 even if some aspects of the underlying theory can be argued.

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 ΔG (2.51, 1.98, 1.32 eV, respectively) and 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, $\Delta G_e (Cl^-) = 8.75$ eV, $\Delta G_e (Br^-) = 8.05$ eV, $\Delta G_e (I^-) = 7.18$ eV versus $E_t (Cl^-) = 8.81$ eV, $E_t (Br^-) = 8.05$ eV, $E_t (I^-) = 7.19$ 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 qualitatively in terms of the Gurney-Gerischer formalism developed by Henglein[4,5] for electron transfer in solution, but this analysis is beyond 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 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, ΔG_e will be equated to E_t, and ΔG_r will be calculated from eq 5 for systems for which ΔG is known. This will be done[8] for photoionization of the five

cations M^{2+} of Figure 3. The threshold energy in that case varies almost linearly with ΔG, and the calculated values of 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 E_t against 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 (ca 6 to 7 eV) threshold energy. Conversely, a high value of E_t (ca 8 eV) is obtained for the reduced form of a strongly oxidizing redox couple ($\Delta G > 1$ to 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 ion[19] yields $E_t = 5.39$ eV and $\Delta G_r = -0.32$ 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 ago[10] (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 reference 19).

The reorganization free energy will be interpreted and correlated with ionic solvation.[8] The latter is characterized by the _real free energy of solvation_ ΔG_s defined as[3] "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 from 2+ to 3+. The contribution from nuclear relaxation, $\Delta G_r = -2.11$ eV for Fe^{2+} (Figure 3), is only a small fraction of the difference of real free 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 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 real 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 available[20] but are not needed for our purpose. Consider photoelectron emission by species A^{z+} ($z \gtrless 0$) in solution, and assume that the radii of the A^{z+} and $A^{(z+1)+}$ ions are equal to simplify matters. One deduces from the Born equation,

$$R = \Delta G_r/(\Delta G_s^{z+1} - \Delta G_s^z)$$
$$= (\epsilon_o^{-1} - \epsilon_s^{-1})/(1 - \epsilon_s^{-1}), \tag{6}$$

where ϵ_o and ϵ_s are, respectively, the optical and static dielectric

constants of the solvent. One has $\epsilon_o = 1.777$ and $\epsilon_s = 78.36$ for water at $25^\circ C$, and R = 0.56 in that case. This is roughly the value of R for emission by singly charged anions[9]: R = 0.50, 0.49, 0.48, respectively, for Cl^-, Br^-, I^-; R = 0.44 to 0.51 for OH^- depending on the estimate of $\Delta G_s(OH^-)$. 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 energy for orientation polarization ΔG_r in these cases corresponds approximately to one-half of the difference between the real free energies of solvation in eq 6. In contrast with the preceding cases (z = -1 or 0), the ratio R is much smaller than 0.56 for cations (z = 1, 2, ...) and anions with multiple ionic charge (z = -2, -3, ...). The change of free energy for orientation polarization ΔG_r in those cases is only approximately one-tenth of the difference between the real free energies of eq 6. This is indeed a drastic departure from the Born model.

The abnormally low values of the ratio R were interpreted[8] as the consequence of strong dielectric saturation. The static dielectric constant ϵ_s decreases as a result of saturation and approaches the optical constant ϵ_o. In the limit, one has R $\rightarrow$ 0 for $\epsilon_s \rightarrow \epsilon_o$ for the Born model. For instance, one calculates (eq 6) $\epsilon_s = 1.91$ from the value R = 0.084 for emission by Fe^{2+} on the simplifying assumption that the radii of Fe^{2+} and Fe^{3+} are the same. The Born model undoubtedly breaks down, but the foregoing conclusion about a <u>drastic effect of dielectric saturation</u> seems inescapable. The same conclusion was reached by Noyes[2] in his work on the real free energies of solvation of inorganic cations and anions. His conclusion based on a formal application of the Born equation is fully confirmed in our work[8,21] by evidence free of model considerations (cf. the case of Fe^{2+} above).

Dielectric saturation causes the threshold energies of cations and multiply charged anions to be much lower than the values to be expected ($E_t > 10$ eV in general) without saturation. Moreover, emission with formation of unusual oxidation states such as Cu(III) and Fe(IV) in aqueous solution (Table I) would hardly be possible without strong dielectric saturation.

Water and Hydroxide Ion

The threshold energies of liquid water[9] and hydroxide ion[7,9] in aqueous solution are 10.06 and 8.45 eV, respectively. The difference between these threshold energies will be interpreted[9] on the basis of the free energy diagram of Figure 4. The free energies of formation of liquid water and OH^-(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

$$H_2O(aq) + H^+(aq) = H_2O^+(aq) + 1/2H_2(g) \qquad (7)$$
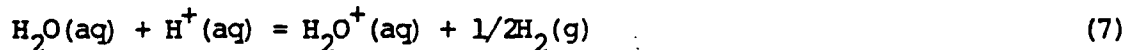
was estimated at 3.3 ± 0.3 eV on the basis of the emission results. The value of $\Delta G = 1.97$ eV for the reaction

$$OH^-(aq) + H^+(aq) = OH(aq) + 1/2H_2(g) \qquad (8)$$
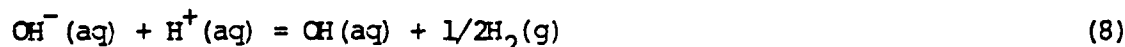
is known from thermodynamic data. One concludes from the preceding data that the change of free energy for the reaction

$$H_2O^+(aq) = H^+(aq) + OH(aq) \qquad (9)$$

is -0.5 ± 0.3 eV. Thus, the ion H_2O^+(aq) is thermodynamically unstable, and the hydroxyl radical OH(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 OH^-(aq) follows directly from Figure 4 and eq 5 (with $\Delta G_e \approx E_t$), namely

$$\begin{aligned}
E_t(H_2O) - E_t(OH^-) &= [\Delta G(OH^-) - \Delta G(H_2O)] \\
&\quad + [\Delta G(H_2O^+) - \Delta G(OH)] + [\Delta G_r(OH) - \Delta G_r(H_2O^+)] \\
&= 0.83 + 0.50 + 0.28 \\
&= 1.61 \text{ eV} \qquad (10)
\end{aligned}$$

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 H_2O^+(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 to 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

$$A^-(aq) = A^-(g) \tag{11}$$

$$A^-(g) = A(g) + e^-(g) \tag{12}$$

$$A(g) = A(aq), \tag{13}$$

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 change of free energy $\Delta G_e + \Delta G_r$ (cf. eq 1 and 2). Hence, one has

$$\Delta G_e = -\Delta G_a + \Delta G_n - \Delta G_s - \Delta G_r. \tag{14}$$

Equation 14 will be simplified. The term ΔG_n ($\lesssim 0.1$ eV in absolute value) and the contribution from vibrational relaxation to ΔG_r (a few tenths of electronvolt) can be neglected to a first approximation. The equation $\Delta G_r \approx \Delta G_s/2$ holds for A^-(aq) ions. The electron affinity EA of A(g) is the negative enthalpy of electron attachment, and one has EA $= -\Delta H_a \approx -\Delta G_a$. Equation 14 becomes with these simplifications, $\Delta G_e \approx$ EA $- (3/2)\Delta G_s$ (within ca ± 0.5 eV).

Since one has EA > 0 and $\Delta G_s < 0$, ΔG_e is the sum of two positive quantities. Extreme values[22] 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 free energies of solvation. The halides Cl^-, Br^-, I^- represent intermediate cases in which the contributions from EA (3.61, 3.36, 3.06 eV) and $-\Delta G_s$ (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, $E_t \approx E_{max} + 1.7$ (in eV), predicted[11] from a model for this type of charge transfer spectra.

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 holds[8]

$$\Delta G_e^z = \Delta G_i^z + \Delta G_s^{z+1} - \Delta G_s^z - \Delta G_r^{z+1}, \tag{15}$$

where G_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 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: $I^z = 20$, 30 to 37, 43 to 57 eV, respectively, for $z = 1$, 2, 3; $-\Delta G_s^z = 3.5$ to 5, 15.5 to 21, 42 to 45 eV, respectively, for $z = 1$, 2, 3; $-\Delta G_r^{z+} < $ ca 2.5 eV. Equation 15 therefore involves the difference of relatively large numbers in comparison with

ΔG_e^z. There is partial cancellation of the terms, and the range of E_t values 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 E_t^z and 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^2 and I_t^2 is even more striking if the threshold energies are corrected for the difference ΔE_f in the ligand field stabilization energies for the $M^{3+}_{(aq)}$ and $M^{2+}(aq)$ hexaquo ions in an octahedral field[8] (ΔE_f calculated from data in reference 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 cations[21] (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^-,

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

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 $\Delta G(A^-) - \Delta G(HA) = \Delta G_K = -0.0592 \log K$, 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 $\Delta G_r(A) - \Delta G_r(HA^+)$ should not exceed a few tenths of 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 $\Delta G(HA^+) - \Delta G(A)$ in eq 16 is the change of free energy for the protonation reaction $H^+ + A = HA^+$ 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 reference 21 to the acids H_nA (n = 2, 3) and their anions.

Equation 16 can be transposed to the difference between the threshold energies $E_t(B) - E_t(HB^+)$ of a base B and its cation BH^+. The difference between the free energies of formation $\Delta G(BH^+) - \Delta G(B) = \Delta G_K$ is negative. One has (in electronvolts) $\Delta G_K = -0.0592 \log K_p$, where K_p is the equilibrium constant for the protonation reaction $B + H^+ = BH^+$. One has, for instance, $\Delta G_K = -0.64$ eV for triethylamine (Table I). The difference between the reorganization free energies $\Delta G_r(BH^{2+}) - \Delta G_r(B^+)$ is negative and not negligible (perhaps -0.5 eV) because of the difference in ionic charge of the species involved (and despite dielectric saturation). Conversely, the quantity $E_t(B) - E_t(HB^+) - \Delta G_K$ for the bases and cations of Table I are quite small, e.g., -0.20 eV for triethylamine. One concludes from these considerations that the quantity $\Delta G(B^+) - \Delta G(BH^+)$ is positive. This quantity is the change of free energy for the dissociation $BH^{2+} = H^+ + B^+$, and consequently BH^{2+} is stable and B^+ protonates provided the pH is not too high. The case of ethylenediamine (Table I) and its cation BH_2^{2+} can be analyzed in a similar way.[21]

Conclusion

The approach in the photoelectron emission spectroscopy of aqueous solutions is simple and direct in its essence: 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.[24]

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Table I

Threshold Energies of Aqueous Solutions[a,b]

OH^- (8.45), H_2O (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), $S_2O_3^{2-}$ (7.27), SO_4^{2-} (8.65), $S_2O_8^{2-}$ (7.33)

NO_2^- (7.57), NO_3^- (7.46), N_3^- (7.35)

H_3PO_4 (9.45), $H_2PO_4^-$ (9.23), HPO_4^{2-} (8.79), PO_4^{3-} (7.44)

H_3AsO_4 (9.44), $H_2AsO_4^-$ (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), n-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.

Captions to Figures

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

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

Figure 3. Plot of threshold energy and reorganization free energy against the free energy[8] $\Delta G = |e|E^{O}$ (E^{O} standard reduction potential for the M^{3+}/M^{2+} couple).

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

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]

ELECTRONICS
COMPUTER
DISPLAY

0 V

+10 V

DETECTOR

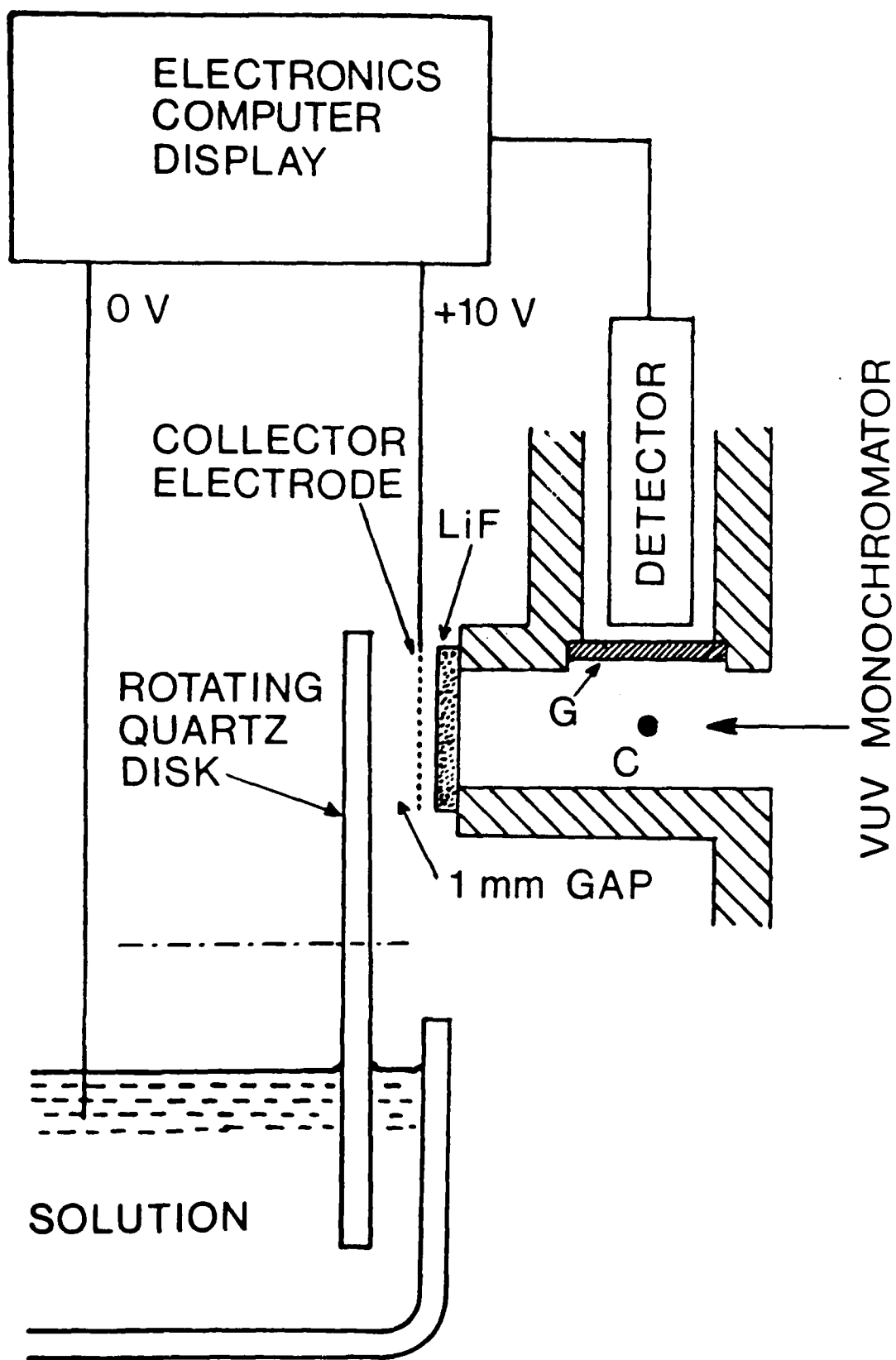VUV MONOCHROMATOR

COLLECTOR
ELECTRODE

LiF

ROTATING
QUARTZ
DISK
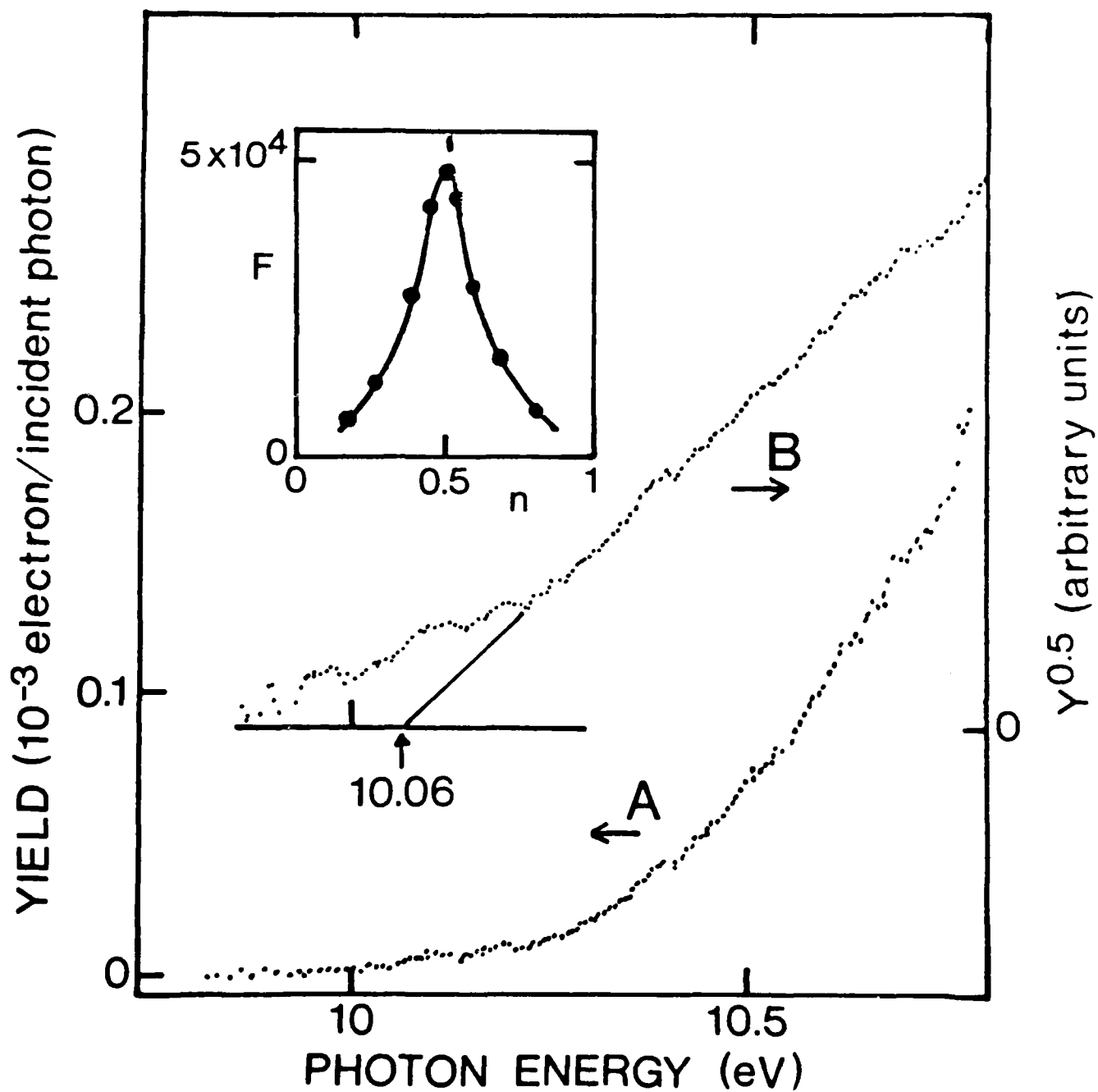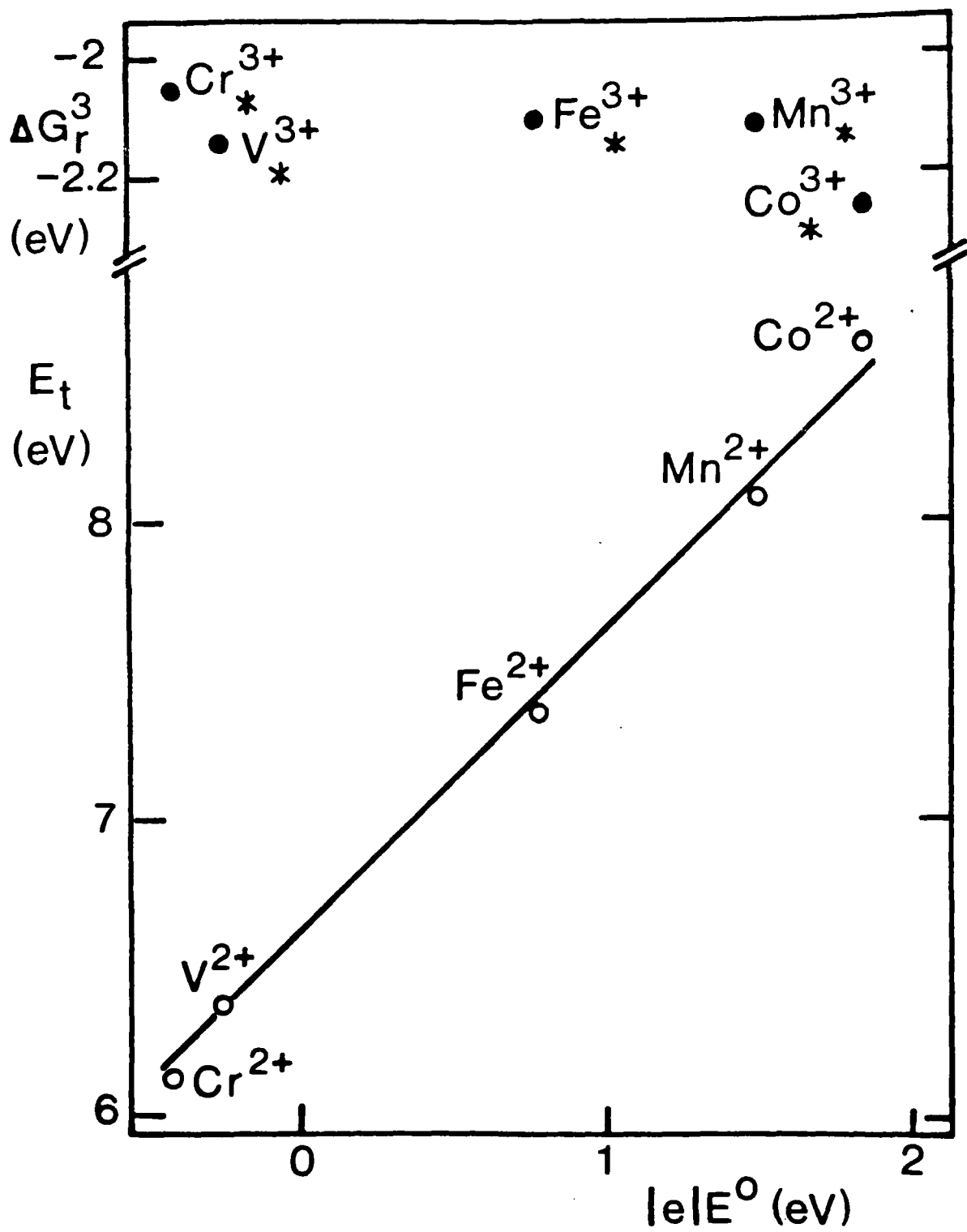
G

C

1 mm GAP

SOLUTION

FIG. 1

FIG. 2

FIG. 3
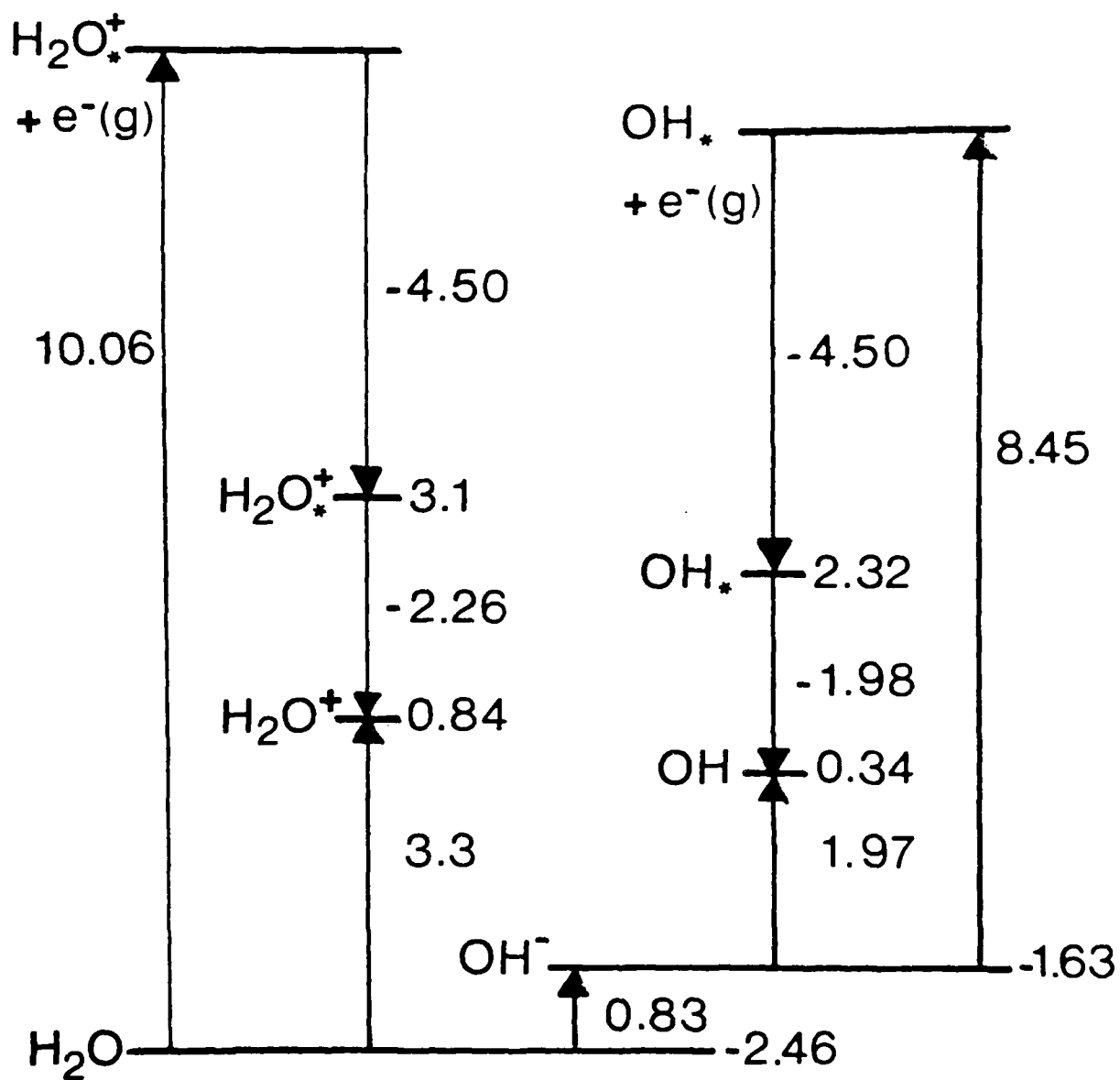
FIG. 4
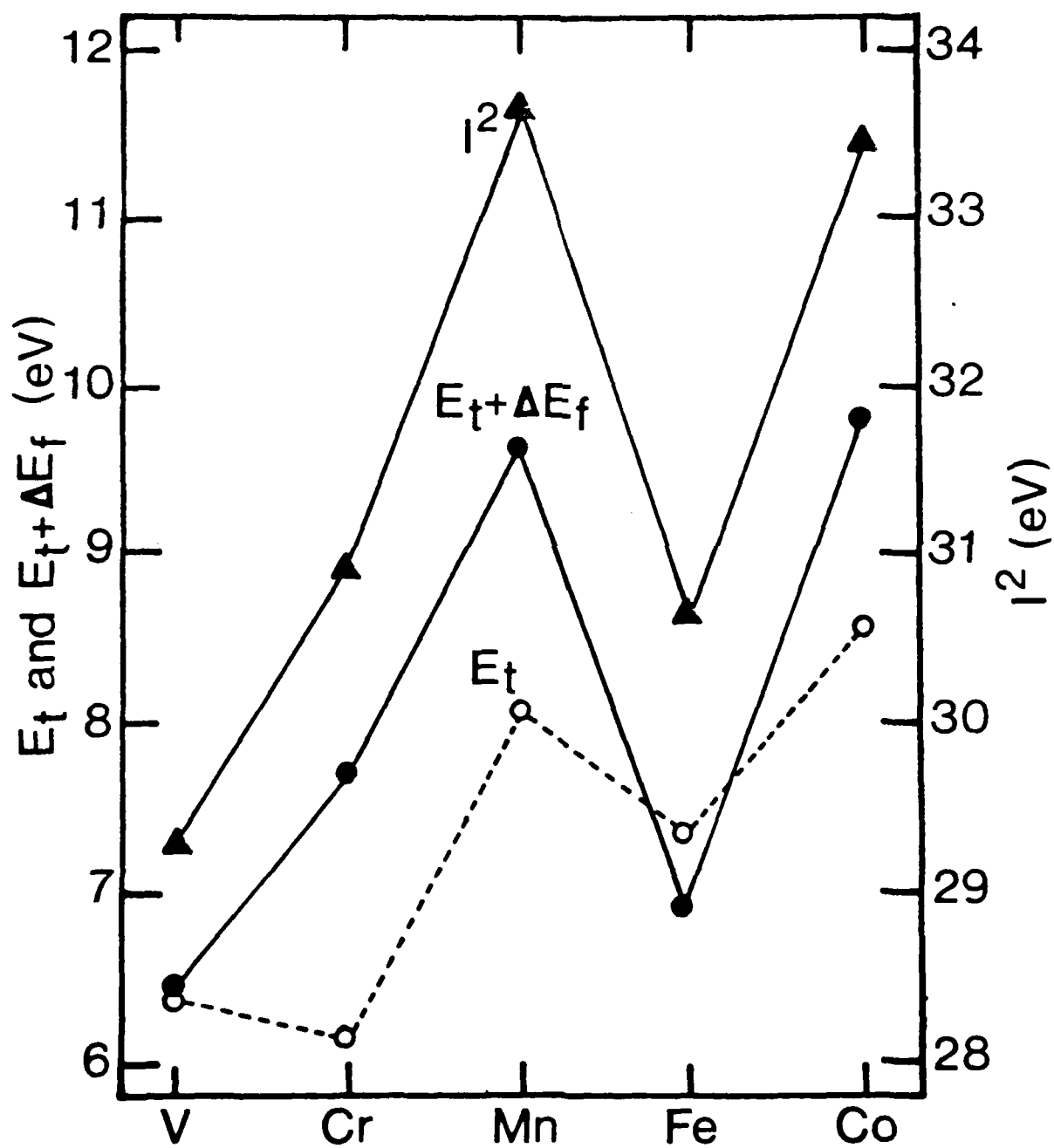
FIG. 5

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