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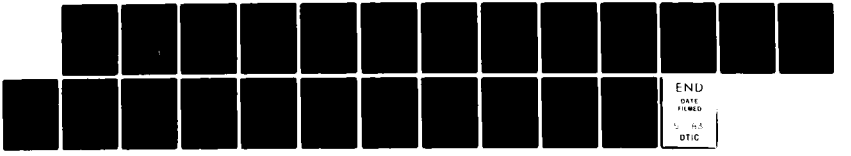

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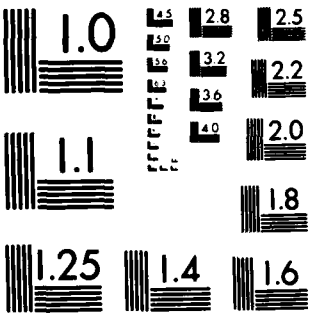


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# DIELECTRIC DISPERSION IN OPTICAL ELECTRON TRANSFER IN SOLUTION

by

Paul Delahay

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Department of Chemistry
New York, NY

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# DIELECTRIC DISPERSION IN OPTICAL ELECTRON TRANSFER IN SOLUTION

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Dielectric dispersion causes the outer-sphere reorganization free energy to vary with photon energy in optical electron transfer. The resulting distortion of the spectral response for photoelectron emission may yield misleading evidence about the emission yield vs. photon energy relationship. Dispersion is taken into account in the calculation of emission threshold energies and the correlation between optical and thermal electron transfer. Results are given for $V^{2+}$, $Cr^{2+}$, $Mn^{2+}$, $Fe^{2+}$, $Co^{2+}$, $Fe(CN)_6^{4-}$.

## 1. INTRODUCTION

Optical electron transfer in solution can be interpreted [1] on the basis of ideas transposed from theories of thermal electron transfer [1-3]. Thus, optical electron transfer is considered to be fast in comparison with subsequent reorganization of nuclear positions. The free energy of reorganization R is equated to the sum of inner- and outer-sphere contributions, $R_{in}$ and $R_{out}$. These are treated microscopically ($R_{in}$, sec. 4) and as non-equilibrium polarization of a continuous medium (sec. 2), respectively. The resulting expression for $R_{out}$ [1-4] contains the optical dielectric constant $\epsilon_{op}$ of the solvent. This quantity varies with the photon energy E at which optical electron transfer occurs because of dielectric dispersion of the solvent. The free energy $R_{out}$ therefore is a function of E in contrast to the thermal case in which $\epsilon_{op}$ is a constant, e.g., $\epsilon_{op} = 1.77$ for water at 25°C. The dependence of $R_{out}$ on E has significant implications which are examined in the present paper for the case of photoelectron emission by aqueous solutions in the 5 to 11.5 eV range [5].

## 2. FREE ENERGY OF OUTER-SPHERE REORGANIZATION WITH DIELECTRIC DISPERSION

The real and imaginary parts of the dielectric constant of a non-ideally transparent liquid are $\epsilon_1 = n^2 - k^2$ and $\epsilon_2 = 2nk$, respectively. There, $n$ is the refractive index and $k$ the absorption coefficient of the medium. The displacement current in such a dielectric is proportional to the real part $\epsilon_1$, and consequently the electronic polarization of the medium depends on $\epsilon_1$ at the appropriate frequency in the optical range. The value of $n^2 - k^2$ must be taken at the photon energy E at which electron transfer occurs. Thus, electron transfer is caused by photon absorption, and the electronic polarization of the medium therefore responds to the change of ionic valence of the photoionized species in the same scale of time as photon absorption. The quantity $n^2 - k^2$ therefore must be substituted for the optical dielectric constant in the expression for $R_{out}$. Thus,

$$R_{out}(E) = [(n^2 - k^2)^{-1} - \epsilon_s^{-1}]e^2/2a, \qquad (1)$$

where $\epsilon_s$ is the static dielectric constant of the solvent, e the electronic charge, and a the radius of the assumed spherical boundary between inner- and outer-sphere regions. The reduced and oxidized species (denoted respectively by the the subscripts r and o) have somewhat different cavity radii, and one sets $a = 2a_r a_o/(a_r + a_o)$ as is done for thermal electron transfer [6].

Figure 1 shows the effect of dielectric dispersion on $R_{out}(E)$ of eq. (1). Results are displayed as the variation of the ratio F of $R_{out}(E)$ at E to the value of $R_{out}(1.77)$ for $n^2 = 1.77$ and $k^2 = 0$ (water at 25°C). Values of n and k were taken from [7]. The shape of the curve in fig. 1 is accounted for by the effect of normal and anomalous dispersion (absorption bands at 8.2 and 10.0 eV). It is seen that $R_{out}(E)$ can be as low as 65 per cent of $R_{out}(1.77)$ and that $R_{out}(E)$ changes quite rapidly in rather narrow intervals of E. Figure 1 applies to pure water, and variations of F may be somewhat different for concentrated electrolytes, especially in the range of absorption bands of the

anion (charge transfer to the solvent). The variations of $\epsilon_s$ in (1) with electrolyte concentration are not significant since $\epsilon_s^{-1}$ for aqueous solutions is small in comparison with $(n^2 - k^2)^{-1}$.

## 3. DETERMINATION OF THRESHOLD ENERGIES BY EXTRAPOLATION

Photoelectron emission by solutions is studied [5] by determining the number of electrons collected (on an electrode above the solution) per incident photon as a function of the photon energy E. The emission yield Y thus measured is proportional to the emission current density of theory [8] to a good measure under actual experimental conditions. It was shown [8] that Y is proportional to $(E - E_t)^p$, where $E_t$ is the threshold energy of the species being photoionized and p = 2 or 5/2. This relationship follows from a more general equation for Y under suitable simplifying conditions. The exponent p = 2 corresponds to the normal case in which image forces are taken into account at the solution-vacuum interface. The value p = 5/2 holds if one assumes that the image forces are negligible.

The threshold energy $E_t$ is determined from a plot of $Y^{1/p}$ against E. This procedure was applied to water [9], inorganic anions [10] and cations [11], and weak acids and bases [12] in aqueous solution. It was found that the exponent p = 5/2 gave better fits to linear plots than p = 2 for species with $E_t < 8$ eV. Conversely, the exponent p = 2 was preferable to 5/2 for $E_t \gtrsim 8$ eV. The statistical evidence for these values of p was fairly unambiguous in most cases, but the underlying reasons for the choice of p = 5/2 were mystifying. The absence of image forces is difficult to account for, and anyhow the magnitude of image forces would conceivably depend on the kinetic energy of mobile electrons in the liquid and not on the absolute value of the photon energy. These puzzling results are accounted for by the effect of dispersion on $R_{out}(E)$ as will now be shown.

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The threshold energy is the sum of several contributions one of which is the free energy of outer-sphere reorganization $R_{out}$ (sec. 4). Call $E_t^0$ the threshold energy at $Y = 0$ in the linear extrapolation plot of $Y^{1/p}$ against E. One has $R_{out} = R_{out}^0$ at $E = E_t^0$, and a different $R_{out}(E)$ at $E > E_t^0$. The value of $E_t$ in $(E - E_t)^p$ therefore is not the constant $E_t^0$ but the quantity,

$$E_t = E_t^0 - [R_{out}^0 - R_{out}(E)], \qquad (2)$$

depending on E. Since $R_{out}(E)$ may differ from $R_{out}^0$ by several tenths of electronvolt, plots of $Y^{1/p}$ against E are distorted.

Variations of $(E - E_t)^2$ with $E - E_t^0$ are shown in Fig. 2 for $E_t^0 = 6$ and 8 eV, respectively. Values of $E - E_t$ were calculated from fig. 1 and the values of $R_{out}^0 = 1.02$ and 0.81 eV at $E_t^0 = 6$ and 8 eV, respectively. These values of $R_{out}^0$ correspond to the typical case of $R_{out}(1.77) = 1.15$ eV for the cations of sec. 4. The curve $(E - E_t)^2$ vs. $(E - E_t^0)$ for $E_t^0 = 6$ eV in Fig. 2 is quite close to the points representing $(E - E_t^0)^{5/2}$. This result follows directly from Fig. 1. The ratio F decreases quite rapidly with increasing E in the 6 to 7.6 eV range, and consequently $(E - E_t)^2$ increases more rapidly than $(E - E_t^0)^2$. Conversely, the curve $(E - E_t)^2$ vs. $E - E_t^0$ for $E_t^0 = 8$ eV in Fig. 2 is fairly close to the quadratic dependence $(E - E_t^0)^2$ because the decrease of F between $E = 8.6$ and 9.4 eV is less pronounced than the variations of F for $E_t^0 = 6$ eV. Apparent variation of p from 5/2 to 2 for the results of Fig. 2 are solely due to the change of $R_{out}(E)$ with E as a result of dispersion. The statistical evidence in [10-12] upon which the choice of $p = 5/2$ was based therefore is misleading and does not provide any proof that the $(E - E_t)^{5/2}$ relationship is in fact observed. A more elaborate analysis must be developed on the basis of the quadratic dependence regardless of photon energy and with consideration of the variations of $R_{out}(E)$ with photon energy.

## 4. CALCULATED FREE ENERGIES OF EMISSION VERSUS EXPERIMENTAL THRESHOLD ENERGIES

The free energy $\Delta G_m$ for photoelectron emission by an aqueous solution of a donor D(aq) is [5,11]

$$\Delta G_m = \Delta G_H + \Delta G + R + |e|\Delta\chi \ . \qquad (3)$$

There, $\Delta G_H$ and $\Delta G$ are the changes of free energy for the reactions,

$$D(aq) + H^+(aq) = D^+(aq) + 1/2H_2(g)$$

$$1/2H_2(g) = H^+(aq) + e^-(g),$$

respectively; R is the reorganization free energy taken as a positive quantity for convenience; and $\Delta\chi$ is the difference between the surface potentials $\chi[D(aq)]$ of the solution of D(aq) and $\chi(H_2O)$ of water.

One has [13] $\Delta G_H = 4.48\pm0.05$ eV on the basis of a current determination [14] of the real free energy of hydration (-11.25 eV) of the proton. This value of $\Delta G_H$ includes the contribution of the surface potential $\chi(H_2O)$ of water. The latter cannot be measured but can be estimated (0.08±0.06 eV [15]). The surface potential $\chi[D(aq)]$ is generally different from that of water, and the experimentally measurable [15] difference $\Delta\chi$ therefore appears in (3). Since the surface potential pertains to the change of potential from the liquid to vacuum, a positive value of $\Delta\chi$ corresponds to a higher barrier to emission than for $\Delta\chi = 0$. Hence, the quantity $|e|\Delta\chi$ in (3) is preceded by a positive sign. The correction is quite minor anyhow since $|e|\Delta\chi$ is in general smaller than 0.05 to 0.1 eV in absolute value [15].

The reorganization free energy is $R = R_{out}(E) + R_{in}$, where $R_{in}$ is computed from the bond-stretching model used for thermal electron transfer [1]. Thus,

$$R_{in} = (N/2)f(\Delta q_0)^2, \qquad (4)$$

where N is the number of ligands of the donor D(aq); $\Delta q_0$ is the change of equilibrium positions for vibration from the reduced species D(aq) to $D^+(aq)$; and f is the reduced force constant [6],

$$f = 2f_r f_o/(f_r + f_o). \qquad (5)$$

Equation (4) gives an energy and not a free energy [1,6], but the resulting error can be neglected since the model upon which eq. (4) is based is somewhat simplified for hexaquo ions, for instance.

The f-values from [16] previously used [4] were computed from a Urey-Bradley potential in [17]. This gives f-values which are definitely too low, as was pointed out [18] to the writer, and experimental force constants must be used. One has [6],

$$f_r = 4\pi^2 \nu_r^2 c^2 \mu, \qquad (6)$$

where $\nu_r$ is the stretching frequency (in $cm^{-1}$) and $\mu$ the reduced mass. A similar equation applies to $f_o$. Two limiting cases have been considered for $\mu$ in the case of hexaquo ions discussed below: (i) $\mu$ is set equal to the mass of a single water molecule $m_{H_2O}$ [6,19]; (ii) $\mu = m_{H_2O} m_M / (m_{H_2O} + m_M)$, where $m_M$ is the atomic mass of $M^{2+/3+}$ [20]. Method (i) slightly overestimates $\mu$. Method (ii) certainly underestimates $\mu$ (by $\approx$ 20 to 25 per cent for the cations considered here) since it presupposes vibration between a "dry" cation $M^{2+/3+}$ and a water molecule. The first method was applied here. In the case of $Fe(CN)_6^{4-/3-}$, $\mu$ was set equal to the CN mass.

The $\Delta q_o$'s in (4) computed from crystallographic metal-ligand distances from X-ray diffraction [6,19,20] generally agree with the $\Delta q_o$'s recently determined by EXAFS for solutions [19]. The $\Delta q_o$ for $Fe(CN)_6^{4-/3-}$ is particularly low: 0.026 Å (crystallographic) vs. 0.01 Å (EXAFS, solutions) [19]. The calculation of $R_{in}$ is sensitive to $\Delta q_o$, and an error of $\pm$0.01 Å on this quantity affects $R_{in}$ by $\approx \pm 0.1$ to $\pm 0.15$ eV for the cations discussed below.

Values of $\Delta G_m$ computed from eq. (3) are listed in Table 1 with the corresponding $E_t$'s. Agreement can be considered to be good except for $Fe^{2+}$ for an a priori (no data from emission) calculation of $\Delta G_m$ in view of the uncertainties on calculated $R_{in}$'s and extrapolated $E_t$'s. The agreement for $Fe(CN)_6^{4-}$ shows that the threshold energy (5.7 eV) can be assigned to a direct bound-continuum transition. The threshold was attributed to autoionization of a bound state in [23] on the basis of the low value of $E_t$ = 5.5 eV (obtained by extrapolation with p = 5/2) and a higher $R_{in}$ value from

[16]. Assignment of emission autoionization bands [23], in general, will have to be reexamined in the light of the present work. The discrepancy for $Fe^{2+}$ is ascribed mostly to the high $E_t$'s (for p = 5/2 and p = 2) in Table 1 rather than the calculated $R_{in}$. The latter indeed agrees well with the value $R_{in}$ = 0.69 eV computed from experimental data on thermal electron transfer in sec. 5. Such a calculation from kinetic data is reliable for $Fe^{2+/3+}$ [6].

## 5. CORRELATION BETWEEN OPTICAL AND THERMAL ELECTRON TRANSFER

Optical and thermal electron transfer were correlated in [4] without consideration of dielectric dispersion. It was shown that the outer-sphere reorganization free energy $R^x_{out}$ for electron exchange (e.g., between $Fe^{2+}$ and $Fe^{3+}$) is practically the same as $R_{out}$ for photoelectron emission. The inner-sphere term $R^x_{in}$ for exchange is twice $R_{in}$ for emission since two ions are involved in exchange and only one in emission. Thus, $R^x_{out} = R_{out}$ and $R^x_{in} = 2R_{in}$, and the reorganization free energy for exchange is $R^x = R + R_{in}$. The effect of dielectric dispersion will now be considered.

The quantity $R^x_{out}$ for exchange is generally computed for $\epsilon_{op} = 1.77$ for dilute aqueous solutions at 25°C, that is, $R^x_{out} = R_{out}(1.77)$. Hence,

$$R^x = R + R_{in} + \Delta R_{out}, \tag{7}$$

where the correction for dispersion is $\Delta R_{out} = R_{out}(1.77) - R_{out}(E)$, $R_{out}(E)$ being computed at $E = E_t$. The free energy of activation $\Delta G^{\neq}$ for electron exchange without net change of free energy is [1-3], $\Delta G^{\neq} = w + R^x/4$, where w is the work required to bring from infinity in solution the two reactants together in the activated complex.

Values of $\Delta G^{\neq}$ from (7) are listed in Table 2 with experimental values taken from [1]. This comparison, it must be stressed, is only tentative because calculated values of $\Delta G^{\neq}$ should be compared with the activation free energy for electron transfer within the precursor complex [6]. Data are included only for couples for which $\Delta G^{\neq}$ can be computed reasonably well from $\Delta G^{\neq} = R^x/4 + w$ [1-3]. Thus, exchange for $Co^{2+/3+}$ is known to be anomalously slow [19]. The

"experimental" value $\Delta G^{\neq} = 0.75$ eV for $Mn^{2+/3+}$ obtained in [1] from the Marcus cross relationship differs markedly from the value $\Delta G^{\neq} = 1.06$ eV computed from $R^x$. Experimental (0.47 eV [1]) and calculated (0.31 eV) $\Delta G^{\neq}$'s for $Fe(CN)_6^{4-/3-}$ also disagree.

Discrepancies in Table 2 can be interpreted on the basis of values of $R_{in}$ computed from $\Delta G^{\neq} = R^x/4 + w$ [1-3] by using the experimental $\Delta G^{\neq}$'s in Table 2 and calculated values of $R^x_{out}$ ($= R_{out}(1.77)$). Errors on $\Delta G^{\neq}$ and $R^x_{out}$ affect the value of $R_{in}$, and application of the equation for $\Delta G^{\neq}$ is assumed to be justified. Values of $R_{in}$ thus obtained obviously must be viewed with caution. One has $R_{in} = 1.09$, 1.39, 0.69 eV for $V^{2+}$, $Cr^{2+}$, $Fe^{2+}$, respectively, vs. 1.41, 1.27, 0.73 eV in Table 1. One concludes that the main source of discrepancy between calculated and experimental $\Delta G^{\neq}$'s in Table 2 is mostly the high $R_{in}$ of Table 1 for $V^{2+/3+}$ and the high $E_t$ (and consequently high R) for $Fe^{2+/3+}$. Agreement for $Cr^{2+/3+}$ is reasonable.

In conclusion, consideration of dispersion is essential in future determinations of experimental threshold energies. Free energies of emission computed from data independent of emission generally agree with available threshold energies within extrapolation error. Correlation between optical and thermal electron transfer provides, whenever feasible, further verification of the self-consistency of all data.

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Table 1

Calculated free energies of emission vs. experimental threshold energies.

| | $\Delta G$ (eV) | $R_{out}$ [a] (eV) | $R_{in}$ [b] (eV) | $\Delta G_m$ (eV) | $E_t$ [c] (eV) |
|---|---|---|---|---|---|
| $V^{2+}$ | -0.25 | 0.99 | 1.41 | 6.63 | 6.38 (p=5/2) |
| | | | | | 6.74 (p=2) |
| $Cr^{2+}$ | -0.41 | 1.01 | 1.27 | 6.35 | 6.14 (p=5/2) |
| | | | | | 6.51 (p=2) |
| $Mn^{2+}$ | 1.56 | 0.95 | 1.51 | 8.50 | 8.08 (p=2) |
| $Fe^{2+}$ | 0.77 | 0.93 | 0.73 | 6.91 | 7.35 (p=5/2) |
| | | | | | 7.47 (p=2) |
| $Co^{2+}$ | 1.84 | 0.95 | 1.63 | 8.90 | 8.60 (p=2) |
| $Fe(CN)_6^{4-}$ | 0.36 | 0.77 | 0.06 | 5.67 | 5.5 (p=5/2) |
| | | | | | 5.7 (p=2) |

[a] From $FR_{out}(1.77)$ with F at $E = \Delta G_m$ (Fig. 1). Values of $R_{out}(1.77)$ computed, respectively, for a = 3.48, 3.48, 3.56, 3.51, 3.48 Å from $a_r$ and $a_o$ in [21] and a = 4.65 Å from [16].

[b] Calculated for N = 6; f = 1.7 x $10^5$ dyne $cm^{-1}$ for $Cr^{2+}$ [19]; f from $\nu_r$ = 389 $cm^{-1}$ and $\nu_o$ = 490 $cm^{-1}$ for all other cations except $\nu_r$ = 395 $cm^{-1}$ for $Mn^{2+}$ [20,22]; f = 4.5 x $10^5$ dyne $cm^{-1}$ for $Fe(CN)_6^{4-}$ from $\nu_r$ = 585 $cm^{-1}$ and $\nu_o$ = 511 $cm^{-1}$ from [20,22]; $\Delta q_0$ = 0.20 ($Cr^{2+}$), 0.14 ($Fe^{2+}$), 0.21 ($Co^{2+}$), 0.026 ($Fe(CN)_6^{4-}$) Å from [19] and 0.195 ($V^{2+}$), 0.2 ($Mn^{2+}$) Å from [20].

[c] First $E_t$ for p = 5/2 for $V^{2+}$, $Cr^{2+}$, $Fe^{2+}$, $Fe(CN)_6^{4-}$. Second $E_t$ from emission spectra used in [11] for all cations and [23] for $Fe(CN)_6^{4-}$, but for extrapolation with p = 2. Only extrapolation for p = 2 for $Mn^{2+}$ and $Co^{2+}$ [11].

Table 2

Calculated and experimental free energies of activation for electron exchange

| | $R$ [a] (eV) | $\Delta R_{out}$ [b] (eV) | $w$ [c] (eV) | $\Delta G^{\neq}$ [d] (calculated) (eV) | $\Delta G^{\neq}$ [e] (experimental) (eV) |
|---|---|---|---|---|---|
| $V^{2+/3+}$ | 2.15 (p=5/2) | 0.15 | 0.04 | 0.97 (p=5/2) | 0.87 |
| | 2.51 (p=2) | | | 1.06 (p=2) | |
| $Cr^{2+/3+}$ | 2.07 (p=5/2) | 0.13 | 0.05 | 0.92 (p=5/2) | 1.03 |
| | 2.44 (p=2) | | | 1.01 (p=2) | |
| $Fe^{2+/3+}$ | 2.10 (p=5/2) | 0.18 | 0.06 | 0.81 (p=5/2) | 0.69 |
| | 2.22 (p=2) | | | 0.84 (p=2) | |

[a] From eq. (3) and data in Table 1.

[b] From $R_{out}$ in Table 1 and the corresponding $R_{out}(1.77)$.

[c] From [4].

[d] For $R_{in}$ in Table 1.

[e] From [1].

## Captions to Figures

Fig. 1. Plot of the ratio F of the outer-sphere reorganization free energy $R_{out}(E)$ at the photon energy E to $R_{out}(1.77)$ computed for $n^2 = 1.77$ and $k^2 = 0$.

Fig. 2. Spectral response for emission $(E - E_t)^2$ with consideration of dispersion compared with the responses $(E - E_t^0)^2$ and $(E - E_t^0)^{5/2}$ without dispersion.

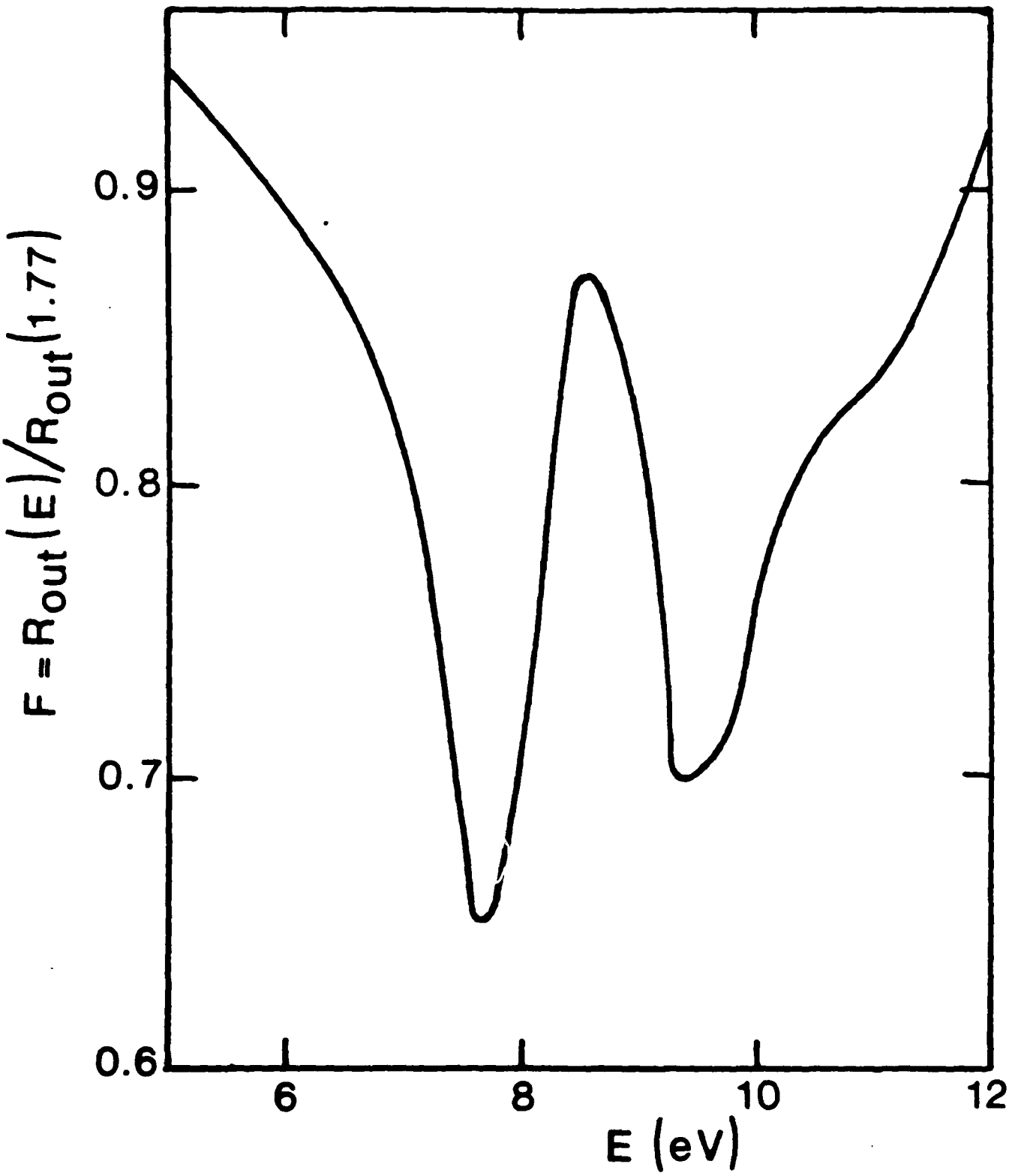


FIG. 1

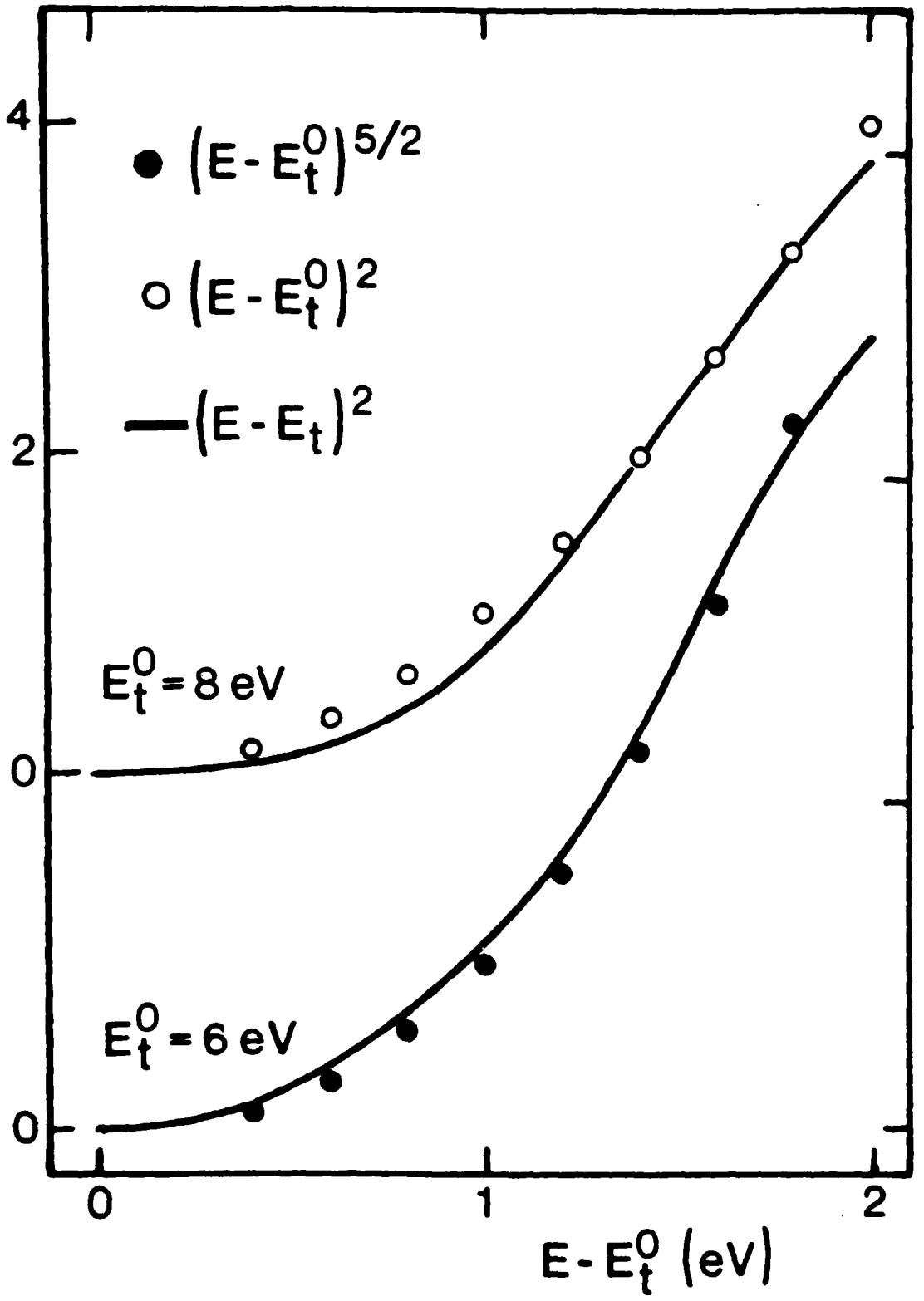


FIG. 2

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