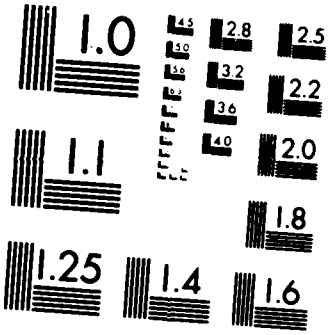
AD-A173 340 TRANSITION DIPOLE-SOLVENT INTERACTION IN OPTICAL ELECTRON TRANSFER(U) NEW YORK UNIV NY DEPT OF CHEMISTRY P DELAHAY ET AL. 30 SEP 86 NYU/DC/TR-12-NEW SERIES-2 1/1

UNCLASSIFIED N00014-82-K-0113 F/G 7/4 NL

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OFFICE OF NAVAL RESEARCH

Contract N00014-82-K-0113

Task No. NR 359-258

TECHNICAL REPORT NO. NYU/DC/TR-12-NEW SERIES-2

# TRANSITION DIPOLE-SOLVENT INTERACTION IN OPTICAL ELECTRON TRANSFER

by

Paul Delahay and Andrew Dziedzic

Prepared for publication in
Accounts of Chemical Research

New York University
Department of Chemistry
New York, NY

September 1986

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Unclassified
SECURITY CLASSIFICATION OF THIS PAGE

ADA173340

# REPORT DOCUMENTATION PAGE

| | |
|---|---|
| 1a. REPORT SECURITY CLASSIFICATION<br>NA | 1b. RESTRICTIVE MARKINGS<br>NA |
| 2a. SECURITY CLASSIFICATION AUTHORITY<br>NA | 3. DISTRIBUTION / AVAILABILITY OF REPORT<br>This document has been approved for public release and sale; its distribution is unlimited. |
| 2b. DECLASSIFICATION / DOWNGRADING SCHEDULE<br>NA | |
| 4. PERFORMING ORGANIZATION REPORT NUMBER(S)<br>NYU/DC/TR-12-NEW SERIES-2 | 5. MONITORING ORGANIZATION REPORT NUMBER(S)<br>NA |
| 6a. NAME OF PERFORMING ORGANIZATION<br>Department of Chemistry<br>New York University<br>6b. OFFICE SYMBOL (If applicable)<br>NA | 7a. NAME OF MONITORING ORGANIZATION<br>ONR |
| 6c. ADDRESS (City, State, and ZIP Code)<br>New York, NY 10003 | 7b. ADDRESS (City, State, and ZIP Code)<br>800 N. Quincy Street<br>Arlington, VA 22217 |
| 8a. NAME OF FUNDING / SPONSORING ORGANIZATION<br>8b. OFFICE SYMBOL (If applicable)<br>NA | 9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER<br>Contract N00014-82-K-0113 |
| 8c. ADDRESS (City, State, and ZIP Code) | 10. SOURCE OF FUNDING NUMBERS<br>PROGRAM ELEMENT NO. / PROJECT NO. / TASK NO. / WORK UNIT ACCESSION NO |

11. TITLE (Include Security Classification)
Transition Dipole-Solvent Interaction in Optical Electron Transfer

12. PERSONAL AUTHOR(S)
Paul Delahay and Andrew Dziedzic

| 13a. TYPE OF REPORT | 13b. TIME COVERED | 14. DATE OF REPORT (Year, Month, Day) | 15. PAGE COUNT |
|---|---|---|---|
| Technical | FROM _____ TO _____ | 9/30/86 | 30 |

16. SUPPLEMENTARY NOTATION
Prepared for publication in Accounts of Chemical Research

| 17. COSATI CODES | | | 18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) | |
|---|---|---|---|---|
| FIELD | GROUP | SUB-GROUP | Dielectric dispersion | Solutions |
| | | | Dispersion spectra | Transition dipole |
| | | | Photoemission | VUV spectroscopy |

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

A new and fundamental feature of photoionization from solutions is presented. The oscillating transition dipole for electronic transitions from bound states in solution to the continuum interacts with the surrounding molecules of the solvent. This interaction is similar to solvation. The transition dipole, oscillating at the frequency of the incident radiation, induces electronic polarization in the solvent. Thus, the minimum energy required for photoionization and the kinetic energy of quasifree electrons generated in solution vary with photon energy. This variation or shift results from dielectric dispersion of the solvent and is displayed in dispersion spectra. Such dispersion shifts are fundamental to all photoionization processes in condensed matter and thus a nonequilibrium electronic contribution to the photoionization energy is required. Before this work, only the contribution from nuclear reorganization was recognized. This phenomenon may have significant effects on photoionization rates and emission laws because of the rich structure of the dispersion spectra. The effect of ionic atmosphere screening on the dispersion shift is also investigated. Keywords:

| | |
|---|---|
| 20. DISTRIBUTION / AVAILABILITY OF ABSTRACT<br>☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS | 21. ABSTRACT SECURITY CLASSIFICATION<br>Unclassified |
| 22a. NAME OF RESPONSIBLE INDIVIDUAL<br>Paul Delahay | 22b. TELEPHONE (Include Area Code)<br>212-598-2811<br>22c. OFFICE SYMBOL |

DD FORM 1473, 84 MAR — 83 APR edition may be used until exhausted. All other editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE
Unclassified

Transition Dipole-Solvent Interaction in Optical Electron Transfer

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Received

Spectrographic transitions from one bound state to another involve a transition dipole moment. The 1s and 2p states of the hydrogen atom, for instance, have no permanent dipole moment, but the combination of these two states, which is involved in the 1s-2p transition, has a dipole moment. This dipole moment oscillates at or near the frequency of the incident radiation according to the time-dependent perturbation theory of quantum mechanics.[1] Such an oscillating transition dipole is also involved in transitions to the continuum[2] (photoionization), but in that case there is, of course, ultimate separation of the emitted electron from its parent atomic or molecular system.

If the substance being photoionized is in solution, the oscillating transition dipole interacts with the surrounding solvent molecules in a process which is similar to solvation. Only electronic motion is involved in this interaction to the exclusion of nuclear motion. This process is described microscopically in terms of dipole-dipole interaction and more generally as a multipole-multipole interaction. The oscillating electric field of the oscillating transition dipole in the macroscopic treatment induces electronic polarization of the solvent which is treated as a continuous medium. The transition dipole-solvent interaction causes the minimum energies required for photoionization of substances in solution to vary with the photon energy at which photoionization is observed. Thus, the kinetic energy of quasifree electrons emitted into the liquid upon generation by the photoionization process does not depend on a constant photoionization

energy, as in the gas phase, but on a photoionization energy varying with photon energy. The varying shift in the photoionization energy results from dielectric dispersion, as will be shown in the present account. This dispersion shift ($\lesssim$ 0.2 eV) was recently discovered by the authors[3] and interpreted[4,5] quantitatively. The dispersion shift affects all photoionization processes in solution and more generally in condensed matter. The dispersion shift is negligible in gas-phase photoionization because the prevailing distances between adjacent molecules are too great to allow significant transition dipole-molecule interaction.

Let us first examine the dispersion shift in terms of a continuous medium model of the solvent. A microscopic description will be given in the theoretical section. The transition dipole oscillates at or near the frequency of the incident radiation, as pointed out above, and consequently the response of the solvent is determined by its dielectric properties at the frequency of the oscillating dipole. The optical dielectric constant of gases, liquids and solids varies with the frequency of the applied electric field on account of dielectric dispersion. Thus, the optical dielectric constant $\epsilon_{op}$ of the solvent increases progressively with frequency in the vicinity of an absorption band of the solvent (normal dispersion). This increase of $\epsilon_{op}$ for water easily reaches 40 percent of its limiting value of $\epsilon_{op}^{o}$ in the near-infrared region. The oscillating transition dipole therefore interacts with the solvent at the prevailing value $\epsilon_{op}$ rather than the limiting value $\epsilon_{op}^{o}$. This effect of dispersion results in a nonequilibrium electronic contribution to the photoionization energy, as will be shown presently.

If dielectric dispersion is negligible, the free energy of photoionization of a substance in solution consists of two contributions[6]:

(i) The difference between the free energies of the initial and final states which can be calculated from thermodynamic data. For example, the initial state in the photoionization of $Fe^{2+}$ ions in aqueous solution is the hydrated $Fe^{2+}$ ion, and the final state consists of the hydrated $Fe^{3+}$ ion and a quasifree electron in water.

(ii) The free energy of reorganization of the nuclear coordinates of the solute and solvent molecules near the solute. Nuclear reorganization occurs after removal of the emitted electron from the solute because the solvent initially retains the nuclear configuration it had prior to photoionization. For instance, the nuclear configuration of the solvent around a $Fe^{2+}$ ion in aqueous solution is initially unchanged after photoionization to a $Fe^{3+}$ ion. The solvent around the $Fe^{3+}$ ion subsequently reorganizes to the final nuclear configuration of a solvated $Fe^{3+}$ ion. The free energy R thus corresponds to a <u>nonequilibrium nuclear</u> contribution to the free energy of photoionization.

The energy of transition dipole-solvent interaction under conditions of negligible dielectric dispersion of the solvent is included in the difference between the free energies of the initial and final states. It does not matter in that case how the transition occurs from the point of view of energetics. There is, of course, a transition dipole-solvent interaction in the absence of dispersion, but this interaction prevails under conditions in which the solvent has the optical dielectric constant $\epsilon^{o}_{op}$, and no explicit consideration of transition dipole-solvent interaction is necessary. If dielectric dispersion is not negligible at the prevailing photon energy, the transition dipole interacts with a solvent characterized by the optical dielectric constant $\epsilon_{op}$ rather than its limiting value $\epsilon^{o}_{op}$. The difference W between the energies for transition dipole-solvent interaction at

$\epsilon_{op}$ and $\epsilon^{o}_{op}$ therefore must be added to the two previously considered contributions to the photoionization energy. This energy consequently consists of three contributions: (i) the thermodynamic c ribution determined by the initial and final states; (ii) the nonequilibrium nuclear contribution R; and (iii) the nonequilibrium electronic contribution W.

The foregoing considerations are fundamental to the understanding of photoionization in solutions. Their validity is amply documented as far as the thermodynamic and nuclear reorganization contributions are concerned.[6] Experimental evidence for the third contribution, the dispersion shift W, is presented in the next section.

## Experimental Evidence of the Dispersion Shift

The observation of how the dispersion shift W varies with photon energy requires a precise determination of the rate of photoionization in solution as a function of photon energy. This experimental requirement is satisfied in the study of photoelectron emission by liquids and solutions.[6,7] The basic experiment is as follows:

The surface of the liquid or solution is irradiated at normal incidence with photons of sufficient energy to cause emission of electrons into the vapor phase above the liquid. Electrons emitted into the gas phase are collected by a grid electrode parallel to the surface of the liquid, and the emission current is measured. The emission yield, Y at the photon energy E, is defined as the number of electrons collected per incident photon. An emission spectrum is obtained by plotting Y as a function of E. Quantum theory[8,9] of the emission process predicts and experiment confirms[6,7] that emission follows a quadratic law,

$$Y = K(E - E_t)^2. \qquad (1)$$

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The quantity K is independent of E and its explicit form is unimportant for our purpose. The quantity $E_t$ is the threshold energy for photoelectron emission by the liquid or solution into the gas phase. Equation 1 holds for photon energies E higher than $E_t$ by at least a few tenths of an electronvolt. The exponent is greater than 2 near the threshold, but only the range of energies over which the quadratic law applies concerns us.

The threshold energy $E_t$ can be identified to a good approximation (to within 0.1 eV) with the photoionization free energy.[6,7] Thus,

$$E_t = \Delta G_{th} + R + W, \tag{2}$$

where $\Delta G_{th}$ is the difference between the free energies of the initial and final states of the photoemission process, R is the free energy of nuclear reorganization, and W is the dispersion shift. For instance, the hydrated $Fe^{2+}$ ion is the initial state in photoelectron emission from aqueous solutions of $Fe^{2+}$ ions, and the final state consists of the hydrated $Fe^{3+}$ ion and an electron in the gas phase. The terms $\Delta G_{th}$ and R do not depend on E, as noted in the introductory remarks, and consequently the dependence of $E_t$ on E is determined solely by the variations of W with photon energy. If W is nearly independent of E, one deduces from eq 2 that Y exhibits a parabolic dependence on E. Indeed, this is very nearly the case for photoelectron emission by liquid water[6,7] ($E_t$ = 10.06 eV) in agreement with predictions from the dielectric properties of liquid water near 10 eV. In general, fine structure is observed in the emission spectra, that is, in the plots of Y against E (Figure 1). This is the case for emission by aqueous[3] and nonaqueous[5] solutions of all substances examined thus far (anions, cations, molecules). This fine structure and its quantitative interpretation constitute the evidence for the dispersion shift W.

The departure from the quadratic law resulting from the dispersion shift can be displayed conveniently by direct application of eq 1. It follows from this equation that a plot of $Y^{1/2}$ against E is linear if $E_t$ is independent of E. This linear relationship is obeyed in the range of validity of the quadratic emission law, that is, for E higher than $E_t$ by a least a few tenths of an electronvolt. One deduces from eq 1,

$$dY^{1/2}/dE = K(1 - dE_t/dE) \tag{3}$$

or in view of the equality $dE_t/dE = dW/dE$ (see above),

$$dY^{1/2}/dE = K(1 - dW/dE) \tag{4}$$

Variations of $E_t$ with E therefore are detected readily from a plot (Figure 2) of $dY^{1/2}/dE$ against E. Such plots are termed <u>dispersion spectra</u>.

Dispersion spectra such as those of Figure 2 are <u>determined essentially by the solvent</u> and in a minor way by the nature and concentration of the substance being photoionized. This conclusion is valid for figure 2 in which the four dispersion spectra of very different inorganic anions are strikingly similar. This essential property of dispersion spectra was established in a series of experiments covering the photoelectron emission by aqueous solution of 17 inorganic anions,[3] inorganic cations[10] and various molecules.[10] The evidence also includes a study of photoelectron emission by various organic liquids.[5] It was also shown that dispersion spectra do not result from experimental artifacts having their origin in the source of vacuum ultraviolet radiation or the monochromator and optical system.[5] Attenuation of the photon flux by absorption by the solvent was also ruled out as a possible cause of the results displayed in dispersion spectra.[3,4] Finally, it should be noted that dispersion spectra are not very sensitive to the choice of exponent in the emission law of eq 1. If one assumes, for instance, that the yield Y is proportional to $(E - E_t)^{5/2}$, the resulting dispersion

spectrum, $dY^{2/5}/dE$ against E, is quite similar to the plot of $dY^{1/2}/dE$ against E for the same substance, and both dispersion spectra exhibit the same characteristic features (e.g., extrema) at nearly the same photon energies.

## Theory of the Dispersion Shift

A theory of the dispersion shift must account for the rather rich structure of experimental dispersion spectra (Figure 2). Furthermore, this structure must be accounted for primarily on the basis of the dielectric properties of the solvent in the prevailing range of photon energies. These requirements follow directly from the observation that dispersion spectra are determined primarily by the nature of the solvent.

Two limiting cases may be considered in the calculation of the transition dipole-solvent interaction energy:

(i) One assumes that the photoelectron produced by photoionization is "ejected" so far from its parent (ion or molecule) that the electrostatic interaction between the parent species and the ejected electron is negligible. Thus, one assumes complete separation of the ejected electron from its parent. The energy for the interaction between the oscillating transition dipole and the solvent is then calculated by considering only the change in the parent field from initial to final state. No attempt is made to follow the time evolution of the transition dipole-solvent interaction. Indeed, the matrix element for absorption refers only to the initial and final states, and photon absorption is interpreted in terms of an annihilation operator acting in occupation space.[11]

(ii) One assumes that the transition dipole is represented by a point dipole whose magnitude oscillates at or near the frequency of radiation. Energy for interaction with the solvent is then calculated for a given, plausible magnitude of the point dipole.

The first approach is akin to the treatment of ionic solvation with the restriction that only electronic motion is taken into account to the exclusion of nuclear motion in the solvent. The second approach is related directly to the calculation of the free energy of solvation of a dipole with the same restriction about nuclear motion as for the first approach. The dielectric properties of the solvent in both approaches are taken at the frequency of the incident radiation (cf. introductory remarks). Detailed theoretical calculations of the enthalpy of ionic solvation have been made,[12-14] and a fairly standard model is available[13] for such calculations for inorganic cations. The different orientations of solvent molecules around inorganic anions and cations in aqueous solution[15] can readily be taken into account.[4] This model yields solvation enthalpies within a few percent of the enthalpies deduced from experimental data for inorganic ions in aqueous solution. In contrast, the solvation of a point dipole is treated[15] for a cruder model (continuous medium) than ionic solvation. It turns out that the ionic and dipole solvation models yield essentially the same functional dependence on photon energy for dispersion spectra of aqueous solutions in the 7 to 10 eV range of photon energies.[5] The dispersion shifts calculated from the ionic solvation model are too high by a factor of 2 or 3 whereas the values of W from the dipole solvation model are too low by at least an order of magnitude. This is to be expected from models corresponding to limiting cases. Only the dependence of W on photon energy, as reflected in plots of $-dW/dE$ against E (eq 4), will be discussed in the present account. The ionic solvation model, which is fully satisfactory for this purpose, is retained solely here.

In the case of ions, the volume around the ion being photoionized is divided into two regions. (i) The <u>inner-sphere shell</u> consists of N solvent

molecules around the photoionized ion. The solvent molecules are treated as point dipoles at a distance of $r_c + r_w$ from the ionic charge, $r_c$ and $r_w$ being the crystallographic radii of the central ion and water, respectively. (ii) The outer-sphere region outside the sphere of radius $a = r_c + 2r_w$ is treated as a continuous medium. The continuous medium model is used exclusively for the photoionization of electrically neutral species. The inner-sphere shell is treated microscopically in terms of the polarizability $\alpha$ of the solvent whereas the outer-sphere region is given a macroscopic treatment based on the optical dielectric constant $\epsilon_{op}$ of the solvent. The quantities $\alpha$ and $\epsilon_{op}$ are related by the Lorenz-Lorentz equation.[17] The polarizability $\alpha$ and dielectric constant $\epsilon_{op}$ are real quantities for transparent solvents and are complex for absorbing solvents. The case of transparent solvents is treated first.

The electric field of the solute induces a dipole in each of the N solvent molecules in the inner-sphere shell. The induced moment is proportional to the solvent polarizability. These induced dipoles experience different interactions which can be calculated by using a multipole expansion of the central field: charge-induced dipole, dipole-induced dipole, induced dipole-induced dipole and quadrupole-induced dipole interactions. Solute-solvent and solvent-solvent London dispersion and Born repulsion must also be taken into account. All these energies of interaction depend directly or indirectly on the solvent polarizability.

The change in the ionic valence of the solute resulting from photoionization causes a change in the energies of the interactions in the inner-sphere shell. If dielectric dispersion is negligible, the net change of interaction energies in the inner-sphere shell is included in the difference of energies between the initial and final states of the photoionization

process. Actually, the solvent polarizability $\alpha$ at the radiation frequency prevails in photoionization instead of the value $\alpha^o$ in the absence of radiation (cf. introductory remarks). The contribution $\Delta P_{in}$ for the inner-sphere shell to the dispersion shift W therefore is equal to the difference between the net interaction energies calculated for the polarizabilities $\alpha$ and $\alpha^o$. The detailed calculation is given in ref. 4.

The contribution $\Delta P_{out}$ from the outer-sphere region to the dispersion shift W is equal to the difference between the free energies of electronic polarization of the medium for the dielectric constants $\epsilon_{op}$ at the radiation frequency and $\epsilon^o_{op}$ without radiation. The free energy difference $\Delta P_{out}$ is calculated from the Born model of ionic solution. Thus,

$$\Delta P_{out} = (e^2/2a)[(\epsilon^o_{op})^{-1} - \epsilon^{-1}_{op}], \tag{5}$$

where e is the electronic charge, and the radii a was defined above.

The optical dielectric constant at photon energies at which the solvent absorbs radiation is a complex quantity[17] $\epsilon_1 - i\epsilon_2$ in which the real part $\epsilon_1$ pertains to polarization of the medium and the imaginary part $\epsilon_2$ corresponds to the dissipation of energy in the medium. The polarizability $\alpha$ is also a complex quantity.[17] The dispersion shift W consists now of a real part $P = \Delta P_{in} + \Delta P_{out}$ for polarization of the solvent and an imaginary part L for losses or dissipation of energy in the medium. The real P of W is calculated for the same model of inner- and outer-sphere regions as for transparent solvents by generalization of the equations applied to the latter case.[4] For instance, the result,

$$\Delta P_{out} = (e^2/2a)[(\epsilon^o_{op})^{-1} - \epsilon_1/(\epsilon_1^2 + \epsilon_2^2)], \tag{6}$$

for an absorbing solvent reduces to eq 5 for $\epsilon_2 = 0$ (transparent medium).

The calculation of the imaginary part L of W poses a problem which is not encountered in ionic solvation. The latter deals with a static problem of

polarization which is treated by considering the initial and final states of the solvation process. The calculation of L pertains to a dynamic problem dealing with the energy dissipated as heat in the medium between the initial and final states of the photoionization process. The problem is related to the treatment of the dissipation of energy in a dielectric having a significant ionic and/or electronic conductivity. The calculation for absorbing solvents is attacked classically by introducing the concept of an optical conductivity $\omega\varepsilon_2/4\pi$ at the photon energy $h\omega$. This interpretation holds even if the dielectric (solvent) does not exhibit any conductivity from free charges,[18] and the imaginary part $\varepsilon_2$ of the optical dielectric constant arises solely from bound-bound transitions of the solvent. The loss of energy is calculated in ref. 4 for the inner-sphere shell ($L_{in}$) and the outer-sphere region ($L_{out}$). The quantity $L_{out}$, for instance, is obtained from the conduction current and the corresponding ohmic loss which results from the optical conductivity and the change of the field around the photoionized species from the initial to the final state. One obtains[4]

$$L_{out} = (e^2/a)\varepsilon_2/(\varepsilon_1^2 + \varepsilon_2^2). \tag{7}$$

The loss $L_{in}$ is calculated much in the same way as $\Delta P_{in}$ for transparent solvents by summing the negative imaginary parts of the complex components of $\Delta P_{in}$. Details are given in ref. 4.

The dispersion shift is

$$W = (P^2 + L^2)^{1/2}, \tag{8}$$

where $P = \Delta P_{in} + \Delta P_{out}$ and $L = L_{in} + L_{out}$ are the real and imaginary parts of W, respectively, as noted above. Comparison with experimental dispersion spectra by application of eq 4 requires the derivative dW/dE, namely

$$dW/dE = [P/(P^2 + L^2)^{1/2}]dP/dE + [L/(P^2 + L^2)^{1/2}]dL/dE. \tag{9}$$

Variations of $-dW/dE$ and its two components (eq 9) with photon energy are displayed in Figure 3 for liquid water.[4] These curves were computed by using the literature values of $\epsilon_1$ and $\epsilon_2$ obtained by reflectance spectroscopy of liquid water. The latter exhibits (up to 10 eV) two absorption bands[19] having their maxima at ca. 8.2 and 10.0 eV, respectively. Figure 3 shows that the term in the derivative $dL/dE$ (eq 9) pertaining to the energy loss in the solvent approaches zero at or near the photon energies of the absorption maxima. Conversely, the term in the derivative of $dP/dE$ (eq 9) corresponding to polarization of the solvent reaches a maximum at or near the photon energy of the absorption maximum. The relative importance of these two contributions to $dW/dE$ determines the effect of the ionic strength of the solution on the shape of dispersion spectra. This point is discussed in the next section.

## Inner-outer Sphere Splitting from Screening by the Ionic Atmosphere

The curve representing the variations of $-dW/dE$ with photon energy in Figure 3 resembles the dispersion spectra of Figure 2, but a more detailed comparison of experiment and theory requires the consideration of electrostatic screening by the ionic atmosphere. This screening was not taken into account in the previous calculation. One may assume to a first approximation that the ionic atmosphere around the ion being photoionized lowers the amplitude of the electric field in the outer-sphere region but not in the inner-sphere shell. Screening in the inner-sphere is introduced later. Thus, $\Delta P_{out}$ and $L_{out}$ decrease with increasing ionic strength whereas $\Delta P_{in}$ and $L_{in}$ are not affected, at least to a first approximation. The relative importance of the contributions from the inner-sphere and outer-sphere regions therefore varies with ionic strengths, and the shape of the dispersion spectrum changes accordingly. This change is shown in Figure 4

in which screening is characterized by the factor S. One has s = 1 in the absence of screening and S = 0 for complete screening of the outer-sphere regions ($\Delta P_{out} = 0$, $L_{out} = 0$). A calculation of S based on the Debye-Hückel theory is given in ref. 4. The factor S = -0.1 in Figure 4 is empirical and is introduced to account for partial screening of the inner-sphere shell as well as possible counterion penetration of the first hydration sphere for high ionic strength solutions.

The change in the shape of the dispersion spectra of Figure 4 becomes quite pronounced for $S \lesssim 0.2$. There is a change in shape because the terms in dP/dE and dL/dE of eq 9 peak at different photon energies (Figure 3). The photon energies at the extrema of the dispersion spectra for S = 1 and S = 0 are listed in Table I. A maximum in dispersion spectra is observed between two minima in the range of normal dispersion, and conversely a minimum between two maxima appears in the range of anomalous dispersion. This pattern of extrema was referred to as <u>inner-outer sphere splitting</u> in ref. 4.

The photon energies at the extrema of experimental dispersion spectra from rather extensive data are compared in Table I with the corresponding theoretical values. The excellent agreement between experiment and theory give strong support to the present interpretation of the dispersion shift and its calculation. The shapes of calculated and experimental curves representing dispersion spectra also agree quite well (Figure 5) for dilute (0.25 M NaCNS) and concentrated (2 M $Na_2S_2O_3$) solutions. A divalent anion was selected for the concentrated solution to achieve high ionic strength and insure extensive screening by the ionic atmosphere. The experimental results of Figure 5 and the change in the shape of dispersion spectra upon increase of the ionic strength confirm the theoretical predictions of Figure 4.

## Conclusion

A fundamental and novel feature of photoionization in solution is discussed in the present account. Thus, dielectric dispersion of the solvent and interaction between transition dipoles and the solvent result in a nonequilibrium electronic contribution (dispersion shift) to the photoionization energy of substances in solution. Only the nonequilibrium contribution from nuclear reorganization to the photoionization energy had been recognized and studied prior to the work discussed here. The dispersion shift should affect all photoionization processes in solution and, more generally, in condensed matter. The effect of this shift is readily observed under conditions of significant dielectric dispersion. Photoionization rates and emission laws therefore can be affected significantly because of the rather rich structure of dispersion spectra. Screening by the ionic atmosphere can also be investigated in a novel way on the basis of dispersion spectra.

The present account was prepared with support from the Office of Naval Research.

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Table I

Photon Energies at the Extrema of Calculated and Experimental Dispersion Spectra of Aqueous Solutions[4]

| Dispersion | Extremum | Dominant contribution | Calculated photon energy, eV | Experimental photon energy, eV |
|---|---|---|---|---|
| normal | min | inner | 7.24 | no datum |
| (< 7.75 eV) | max | mixed | 7.30 | 7.30 |
| | min | outer | 7.42 | 7.41 |
| anomalous | max | inner | 8.24 | 8.16±0.06 |
| (7.75 to | min | mixed | 8.58 | 8.42±0.06 |
| 8.70 eV) | max | outer | 8.68 | 8.65±0.03 |
| normal | min | inner | 9.18 | 9.11±0.03 |
| (8.70 to | max | mixed | 9.38 | 9.37±0.06 |
| 9.70 eV) | min | outer | 9.63 | 9.63±0.12 |
| anomalous | max | inner | 9.96 | 9.86±0.04 |
| (> 9.7 eV) | min | mixed | 10.11 | 10.18 |
| | max | outer | 10.32 | 10.35 |

Data for 0.5 M $VCl_2$ and 1 M $CrCl_2$ (7.30 and 7.41 eV) and 0.05 M $K_4Fe(CN)_6$ (7.41 eV) from ref 10. Average values with standard deviation ($8.16 \leqslant E \leqslant 10$ eV) for 1 M solutions of 17 inorganic anions from ref 3. Extrema at 10.18 and 10.35 eV obtained in ref 4 with 0.2 M $KPF_6$.

List of Captions

Figure 1. Variations of the yield with photon energy for photoelectron emission by 1 M aqueous solutions of different anions. Sodium salts except for potassium carbonate. The yield is defined as the number of collected electrons per incident photon. Relative scales of ordinates A to E: 3.0, 5.8, 2.2, 1.5, 1.0 (weakest signal).[3]

Figure 2. Dispersion spectra of 1 M aqueous solutions of different anions. Sodium salts except for potassium carbonate. Relative scale of ordinates from A to E: 1.9, 1.4, 1.1, 1.0 (weakest signal).[3]

Figure 3. Variations of -dW/dE with photon energy (top) and dependence of the two contributions of -dW/dE (eq 9) on photon energy (bottom).[4]

Figure 4. Variations of -dW/dE with photon energy for different values of the screening factor S (S = 0 for complete screening of the outer-sphere region, S = -0.1 for partial screening of the inner-sphere shell). Complete data for the calculations in ref 4. Ordinates at the minimum at 7.42 eV from S = -0.1 to S = 1.0: -0.164, -0.196, -0.299, -0.263, -0.297, -0.541. Ordinates at the maximum (photon energy between parentheses) from S = -0.1 to S = 1.0: 0.151 (8.20 eV), 0.151, (8.24 eV), 0.162 (8.35 eV), 0.181 (8.41 eV), 0.216 (8.68 eV), 0.509 (8.68 eV).

Figure 5. Comparison of the experimental dispersion spectra ($dY^{1/2}/dE$ against E) of 0.25 M NaCNS (bottom) and 2 M $Na_2S_2O_3$ (top). Calculated dispersion spectra (-dW/dE against E) for the same data as Figure 4 and a screening factor S = 0.3 (bottom) and -0.1 (top). The dispersion spectra for 2 M NaCNS and 0.25 M $Na_2S_2O_3$ (not shown) are intermediate between the curves shown here.

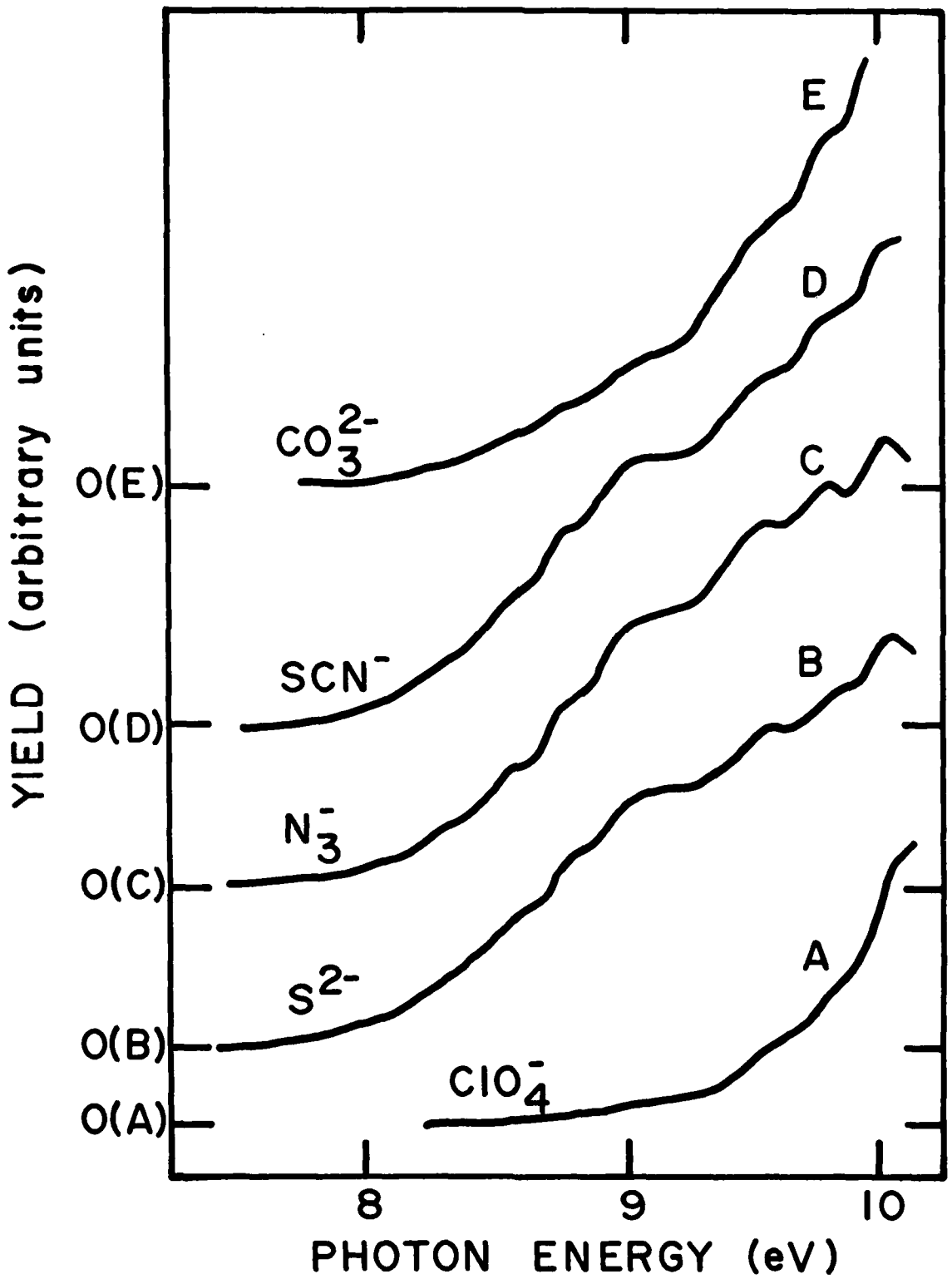
YIELD (arbitrary units)
O(E)
O(D)
O(C)
O(B)
O(A)
$CO_3^{2-}$
$SCN^-$
$N_3^-$
$S^{2-}$
$ClO_4^-$
E
D
C
B
A
8
9
10
PHOTON ENERGY (eV)

FIG. 1

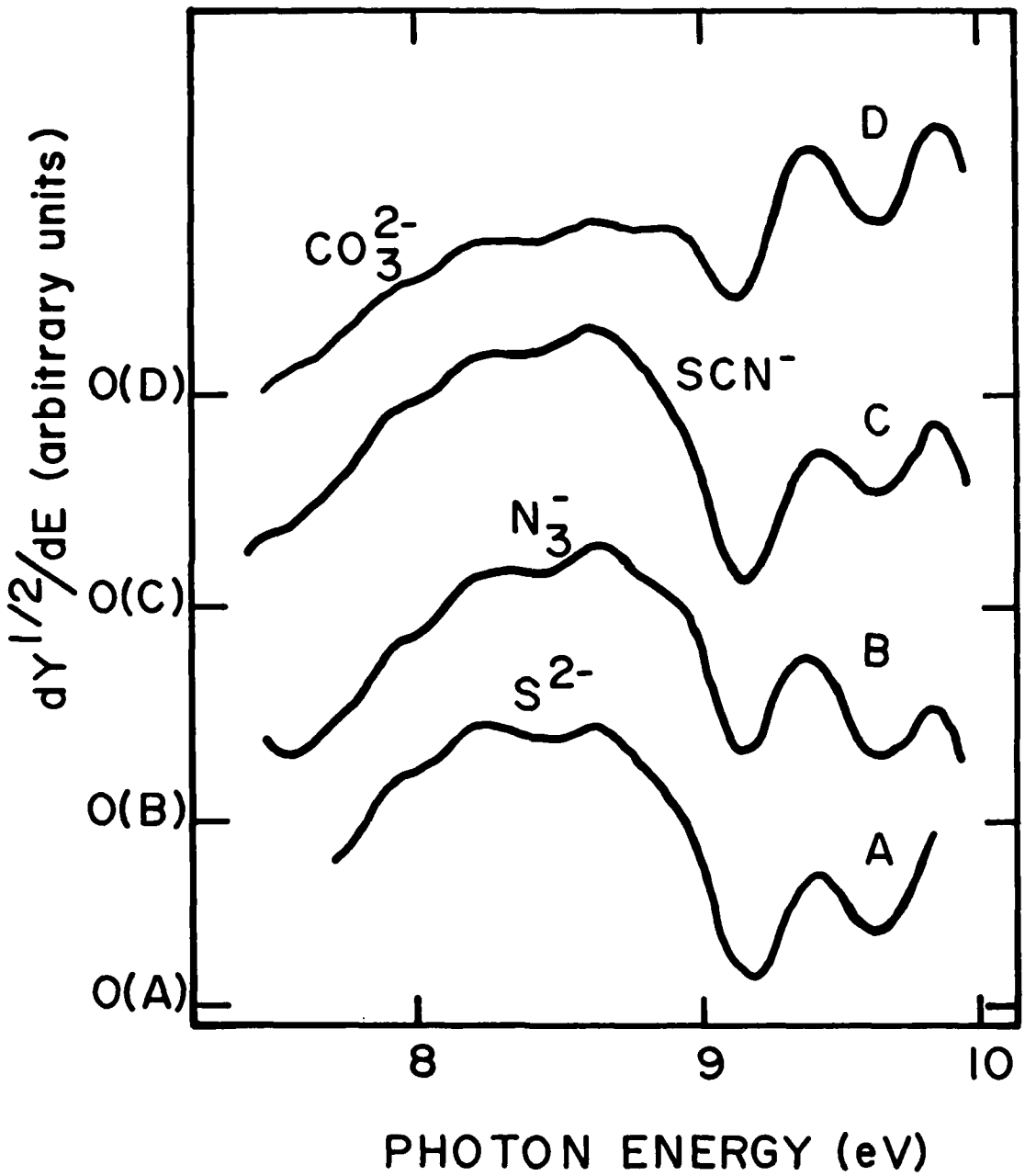
dY^1/2/dE (arbitrary units)
O(D)
O(C)
O(B)
O(A)
CO3 2-
SCN-
N3-
S2-
D
C
B
A
8
9
10
PHOTON ENERGY (eV)

FIG. 2

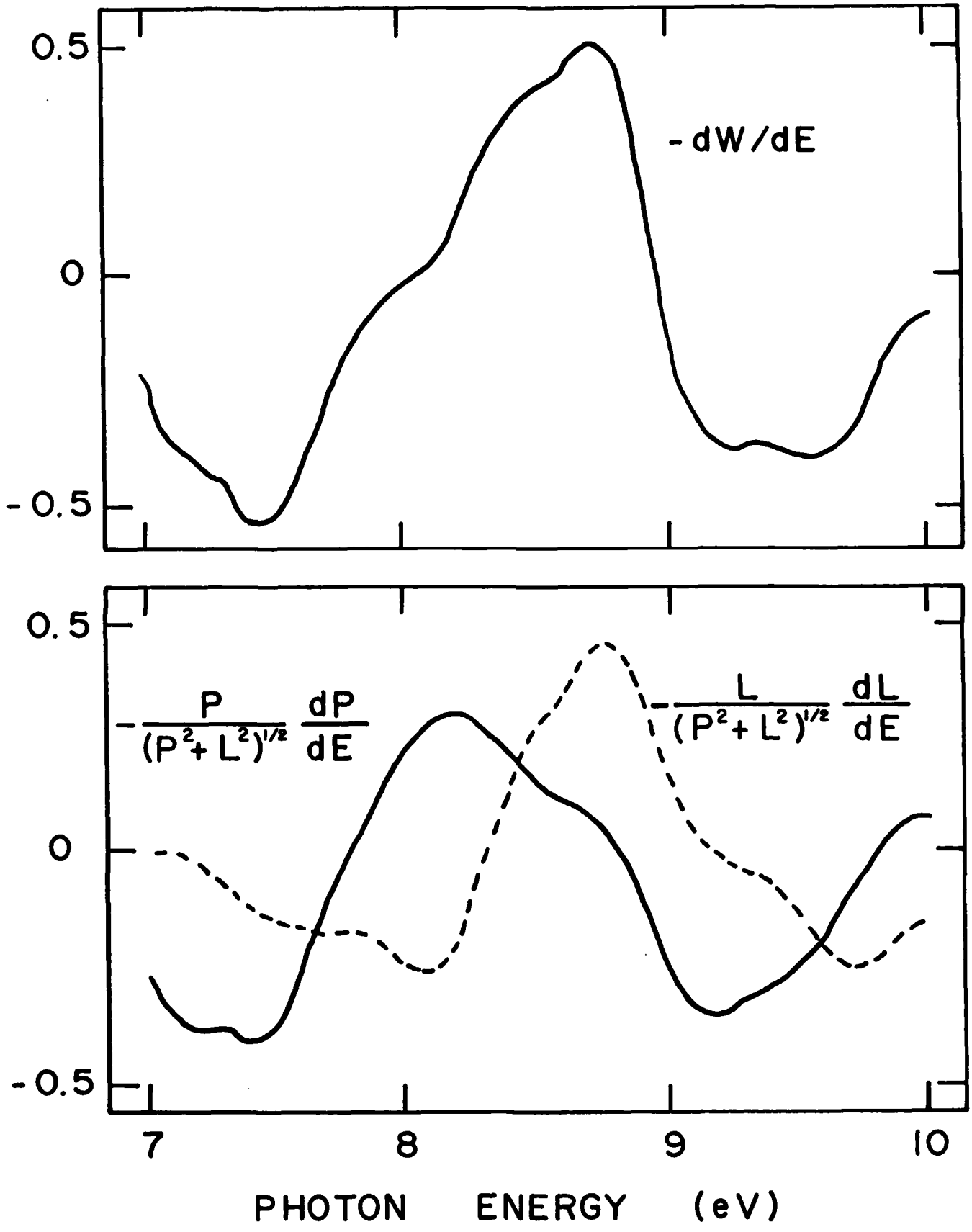
0.5
0
-0.5
-dW/dE
0.5
0
-0.5
$-\frac{P}{(P^2+L^2)^{1/2}}\frac{dP}{dE}$
$-\frac{L}{(P^2+L^2)^{1/2}}\frac{dL}{dE}$
7
8
9
10
PHOTON ENERGY (eV)

FIG. 3

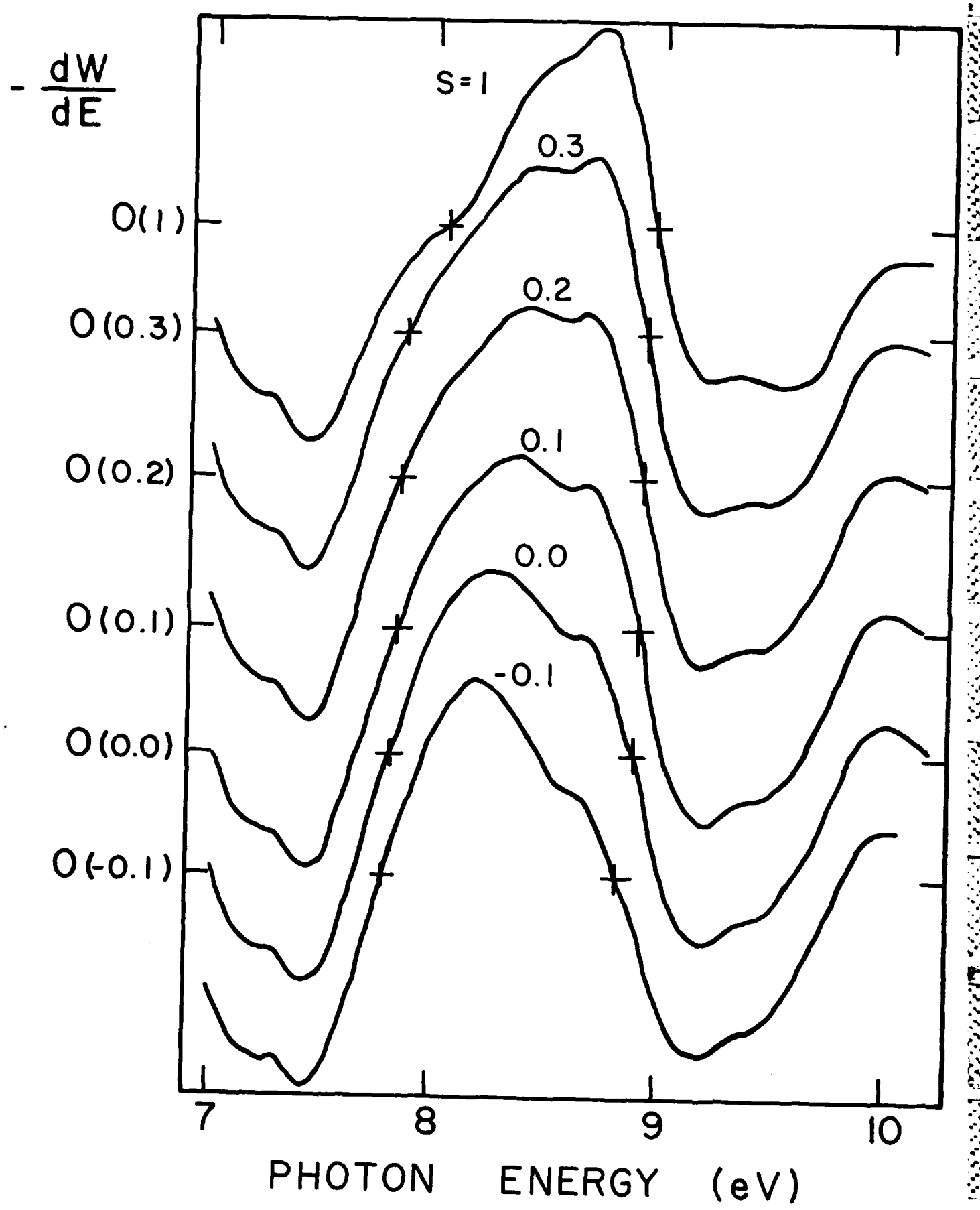
$-\frac{dW}{dE}$
S=1
0.3
0.2
0.1
0.0
-0.1
O(1)
O(0.3)
O(0.2)
O(0.1)
O(0.0)
O(-0.1)
7
8
9
10
PHOTON ENERGY (eV)

FIG 4

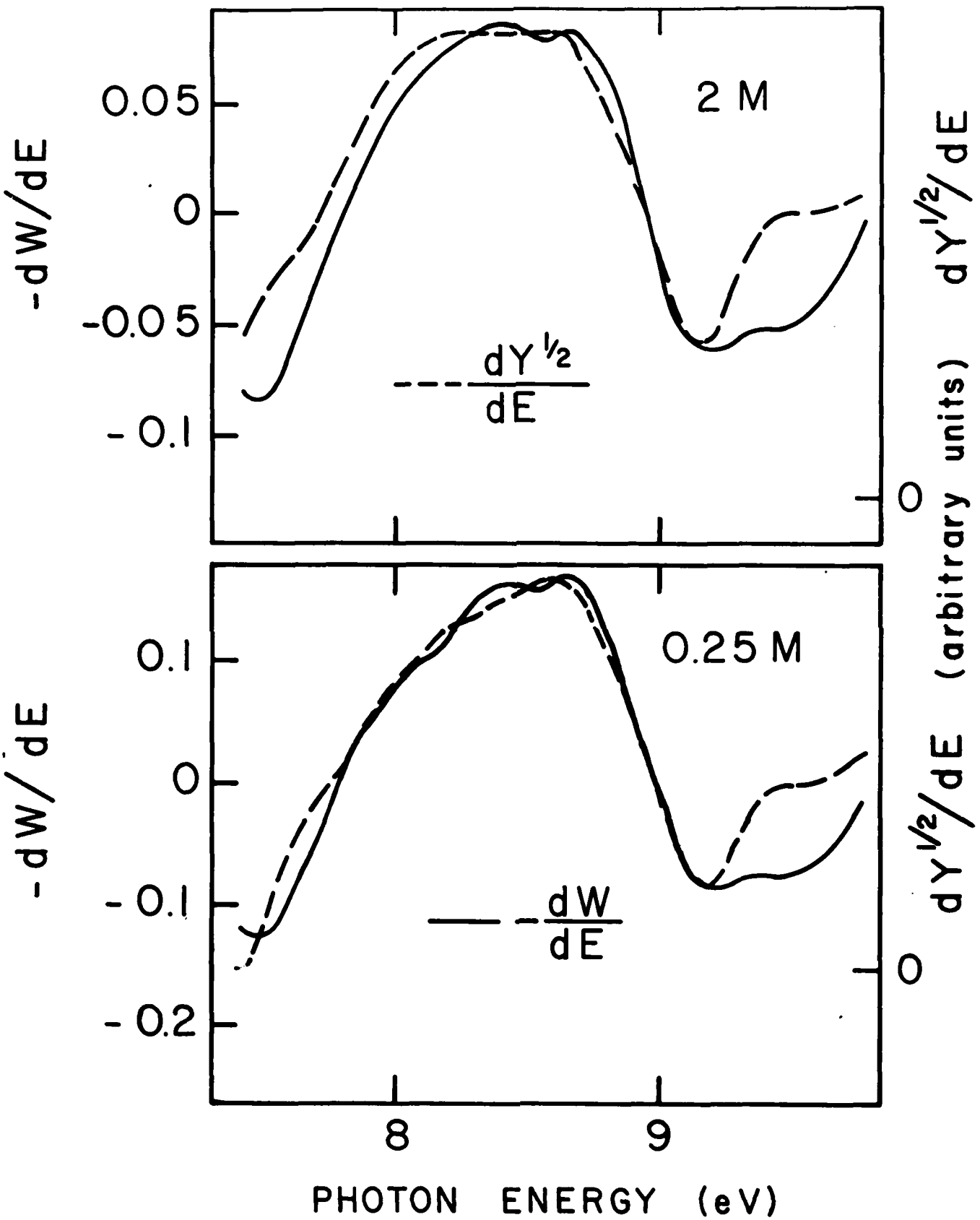
0.05
0
-0.05
-0.1
-dW/dE
2 M
dY ½/dE
0
dY½/dE (arbitrary units)
0.1
0
-0.1
-0.2
-dW/dE
0.25 M
dW/dE
0
dY½/dE
8
9
PHOTON ENERGY (eV)

FIG. 5

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