AD-A157 479 NONEQUILIBRIUM ELECTRONIC POLARIZATION OF THE SOLVENT IN PHOTOIONIZATION(U) NEW YORK UNIV NY DEPT OF CHEMISTRY P DELAHAY ET AL. JUL 85 1/1

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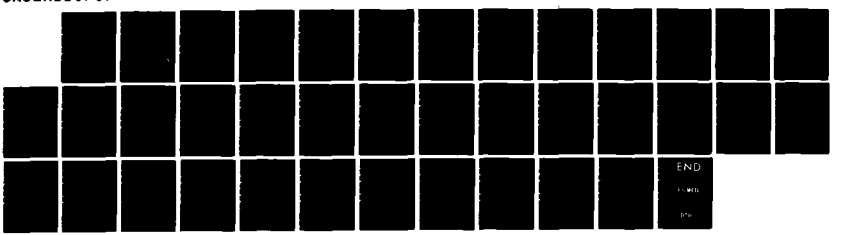

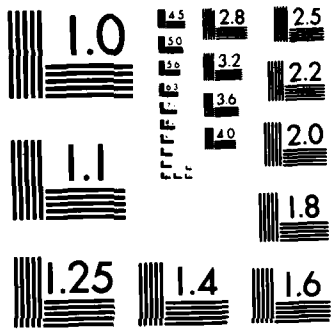

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OFFICE OF NAVAL RESEARCH

Contract N00014-K-0113

Task No. NR 359-258

TECHNICAL REPORT NO. NYU/DC/TR-8-NEW-SERIES-2

NONEQUILIBRIUM ELECTRONIC POLARIZATION OF THE SOLVENT IN PHOTOIONIZATION

by

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Submitted for publication in

Journal of Chemical Physics

New York University
Department of Chemistry
New York, NY

July 1985

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER NYU/DC/TR-8-NEW SERIES-2	2. GOVT ACCESSION NO. AD-A157479	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) NONEQUILIBRIUM ELECTRONIC POLARIZATION OF THE SOLVENT IN PHOTOIONIZATION		5. TYPE OF REPORT & PERIOD COVERED Technical Report 6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Paul Delahay and Andrew Dziedzic		8. CONTRACT OR GRANT NUMBER(s) N00014-82-K-0113
9. PERFORMING ORGANIZATION NAME AND ADDRESS New York University New York, NY 10003		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 359-258
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Arlington, VA 22217		12. REPORT DATE July 1985 13. NUMBER OF PAGES 31
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

This document has been approved for public release and sale; its distribution is unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

Submitted for publication in Journal of Chemical Physics

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Anions/cations
Dielectric dispersion
Nonequilibrium polarization
Solvation
VUV photoelectron emission

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

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S/N 0102-LF-014-6601

Unclassified

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Nonequilibrium electronic polarization of the solvent in photoionization

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(Received)

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I. INTRODUCTION

Dielectric dispersion of the solvent was shown recently[1] to affect the energetics of photoionization of ions and molecules in solution. This effect was interpreted[1,2] by assuming that the energetics of solvation of the species being photoionized is determined by the solvent polarizability α and optical dielectric constant ϵ_{op} at the photon energy E at which photoionization occurs rather than by the limiting value α^o and ϵ_{op}^o. Alternatively, one may assume that the change of ionic valence of the substance being photoionized occurs on a time scale determined by the frequency of the incident radiation. The response of the medium to the rapidly varying intense ionic field is determined under these conditions by α and ϵ_{op} at the photon energy E and not by the limiting values α^o and ϵ_{op}^o. The dispersion effect according to this model results from nonequilibrium processes involving electronic polarization of the solvent, London dispersion and Born repulsion. Energy losses resulting from the rapid variations of the ionic field must also be considered for absorbing solvents. This model is treated quantitatively and tested experimentally in the present paper. Differences in the solvent configuration around anions and cations are taken into account following a comment by Hush[3] on the earlier treatment.

The selection of the proper dielectric constant of the solvent in the present treatment follows from the three-step model[4] used in the interpretation of photoelectron emission by liquids[5,6]: (i) photoionization, (ii) transfer of quasifree electrons to the liquid-gas interface, and (iii) interfacial barrier problem. Dispersion affects only photoionization, and the dielectric constant ϵ_{op} is selected accordingly, as noted above. The proper dielectric constant (or range of dielectric constants) in the ion-electron separation of the above step (ii) is determined by the kinetic energy of the quasifree electrons generated by photoionization. The present paper is not concerned with this problem since ion-electron separation and transfer are embodied in the emission law accounted, for instance, by the theory of Refs. 5 and 6.

II. NONEQUILIBRIUM PROCESSES: TRANSPARENT SOLVENTS

A. Theoretical model

The fairly standard treatment of ionic solvation[7,8] will be adapted to the present problem with the additional consideration of the different solvent configurations around inorganic anions and cations. Electrically neutral species can be treated in terms of the continuous medium model of Sec. IIC without any particular difficulty. The volume around the ion being photoionized is divided into two regions. (i) The inner-sphere solvation shell consists of N solvent molecules coordinated to the ion. The solvent molecules are treated as point dipoles at a distance $r_o = r_c + r_w$ from the ionic charge, where r_c and r_w are the crystallographic radii of the ion and solvent, respectively. (ii) The outer-sphere region outside the sphere of radius $a = r_c + 2r_w$ is treated as a continuous medium.

The nonequilibrium contribution from electronic polarization in the present treatment is determined by the change $\Delta z = 1$ in the ionic valence and thus is independent of the value of z as in the case of nuclear reorganization of the outer-sphere region (Marcus,[9] Hush[10]). A multipole expansion[11] of the potential of the ion will be used as in the calculation of energies of ionic solvation. The polarizability of the solvent is assumed to be isotropic. This is nearly the case for water considered below in the application of the theory. Calculated energies differ by only ca. 1 percent if anisotropy is taken into account on the basis of the polarizability data of Ref. 12. The induced dipole vector is collinear with the electric field vector in the central field of the ionic charge if one assumes isotropic polarizability of the solvent. Nonlinear effects are not considered.

B. Inner-sphere solvation shell

Only the terms depending on α and ε_{op} of the solvent and the terms for London dispersion and Born repulsion are retained in the expression for the free energy of ionic solvation.[7,8] We calculate first the change of energy ΔP_{in} for the inner-sphere solvation shell for $\Delta z = 1$ and the change of polarizability from α to α^0. One has

$$\Delta P_{in} = \Delta U_{IND} + \Delta U(p_\alpha e) + \Delta U(p_\alpha p) + \Delta U(p_\alpha p_\alpha) + \Delta U(p_\alpha q) + \Delta U_L(S,s) + \Delta U_L(s,s) + \Delta U_{REP}, \quad (1)$$

where U_{IND} represents the work required for the formation of induced dipoles p_α in the inner-sphere solvation shell; the next four terms are the energies of interaction of induced dipoles with the ionic charge ($p_\alpha e$), dipoles ($p_\alpha p$), induced dipoles ($p_\alpha p_\alpha$), quadrupoles ($p_\alpha q$); $U_L(S,s)$ and $U_L(s,s)$ are the energies for solute-solvent and solvent-solvent London dispersion, respectively; U_{REP} corresponds to solute-solvent and solvent-solvent Born repulsion.

Explicit forms are:

$$\Delta U_{IND} = (N/2)[(p_\alpha^o)^2/\alpha^o - p_\alpha^2/\alpha] \quad (2)$$

$$\Delta U(p_\alpha e) = -(Ne/r_o^2)(p_\alpha^o - p_\alpha) \quad (3)$$

$$\Delta U(p_\alpha p) = 2A(p/r_o^3)(p_\alpha^o - p_\alpha)\cos\beta \quad (4)$$

$$\Delta U(p_\alpha p_\alpha) = (A/r_o^3)[(p_\alpha^o)^2 - p_\alpha^2] \quad (5)$$

$$\Delta U(p_\alpha q) = -B(\Theta/r_o^4)(p_\alpha^o - p_\alpha) \quad (6)$$

$$\Delta U_L(S,s) = -(3N/2r_o^6)[I_s I/(I_s + I)]\alpha_s(\alpha^o - \alpha) \quad (7)$$

$$\Delta U_L(s,s) = -(CI/r_o^6)[(\alpha^o)^2 - \alpha^2] \quad (8)$$

$$\Delta U_{REP} = -(1/x)\{2\Delta U(p_\alpha e) + 3[\Delta U(p_\alpha p) + \Delta U(p_\alpha p_\alpha)] + 4\Delta U(p_\alpha q) + 6[\Delta U_L(S,s) + \Delta U_L(s,s)]\} \quad (9)$$

where N is the number of solvent molecules coordinated to the species being photoionized; e, the absolute value of the electronic charge; p, the permanent dipole moment of the solvent; Θ, the quadrupole moment of the solvent (Appendix); β, the angle between the induced and permanent dipoles of the solvent in the inner-sphere solvation shell; I_s and I, the gas-phase ionization energies of the solute and solvent, respectively; α_s, the polarizability of the solute taken to be independent of photon energy in the absence of dispersion data. The coefficients A, B and C were calculated by Buckingham[7] by considering solvent pairwise interactions: A = 2.296 and 7.114; B = 1.722 and 5.336; C = 0.2373 and 1.160 for tetrahedral and octahedral coordination, respectively. The Born repulsion energy U_{REP} is obtained according to Morf and Simon[8] by minimizing with respect to r_o the total contribution from the inner-sphere shell to the solvation energy. The exponent x will be taken to be 12 and 8, respectively, for inorganic anions[13] and cations.[8]

The induced dipole moment p_α^0 is obtained according to Morf and Simon[8] by minimizing with respect to p_α^0 the total energy depending on p_α^0. Thus,

$$p_\alpha^0 = \alpha^0(Ner_0^2 - 2Apr_0\cos\beta + B\Theta)/r_0(Nr_0^3 + 2A\alpha^0) \tag{10}$$

The same equation with α instead of α^0 is applied to p_α. Equation (10) reduces to the familiar equation $p_\alpha^0 = \alpha^0 F$, where $F = e/r_0^2$ is the field, if the pairwise interactions are neglected.[14] The sum of the energies in Eqs. (2) and (3) in that case is one-half of the value on the r.h.s. of Eq. (3).

The evaluation of the angle β in Eq. (4) and Θ (Appendix A) requires information about the structure of the solvent in the inner-sphere shell. Only inorganic anions and cations in aqueous solution will be considered here. The anion, hydrogen and oxygen are collinear in the simplest case[15-17] and the water dipole vector makes an angle $\beta = 52.23^\circ$ with the electric field vector of the ionic charge. The water molecules are assumed to rotate freely about the anion-hydrogen-oxygen axis.[13] Conversely, the cation and water molecule are assumed to be in the same plane in the simplest case with the cation-oxygen axis coinciding with the electric field vector of the ionic charge[15-17] ($\beta = 0$). The water molecule is assumed to rotate freely about the cation-oxygen axis.[7] Tilting of the plane of the water molecule with respect to the cation-oxygen axis, which was reported[15-17] for high electrolyte concentrations (> 1.5 M), will not be considered here but could easily be introduced in the treatment. To summarize, the limiting values $\beta = 52.23^\circ$ and $\beta = 0$ will be used for anions and cations, respectively, in the application of the theory to aqueous solutions.

C. Screening by the ionic atmosphere

The change in the free energy for electronic polarization of the outer-sphere region is treated for a continuous-medium model. One has

$$\Delta P_{out} = (e^2/2a)[(\epsilon_{op}^o)^{-1} - \epsilon_{op}^{-1}] \quad (11)$$

in the absence of screening of the ions by the ionic atmosphere. A correction must be made for the screening. The free energy contribution ΔG_{atm} from the ionic atmosphere to the free energy of electronic polarization of the outer-sphere region is,

$$\Delta G_{atm} = - (e^2/2\epsilon_{op})\kappa/(1 + \kappa a), \quad (12)$$

to the approximation of the Debye-Hückel theory. There ϵ_{op} is the optical dielectric constant, a is the radius of the inner-sphere taken to be equal to $r_c + r_w$ (Sec. IIA), and κ is the Debye-Hückel reciprocal length measured from a. The quantity κ is calculated for the static dielectric constant ϵ_s of the solvent because the ionic atmosphere is "frozen" during the rapid variations of the ionic field resulting from photoionization. Equation (12) is taken directly from the Debye-Hückel theory[18] except that ϵ_{op} is written in the denominator instead of ϵ_s. A correction identical to Eq. (12) applies to nuclear reorganization[19] in optical electron transfer except that ϵ_s appears in the denominator instead of ϵ_{op}.

It is seen from Eq. (12) that the correction for the ionic atmosphere is obtained by writing $(e^2/2R)(1/\epsilon_{op})$ with a radius $R = a + 1/\kappa$ instead of $R = a$. The energy $S\Delta P_{out}$ therefore is obtained instead of ΔP_{out} of Eq. (11), the screening factor being,

$$S = [a^{-1} - (a + 1/\kappa)^{-1}]/a^{-1}$$

$$= 1/(1 + \kappa a). \quad (13)$$

Thus, the value S = 1 corresponds to the limiting case of no screening approximated for very dilute solutions. Conversely, the value S = 0 pertains

to total screening of the outer-sphere response. One has, for instance, for a 0.1 M aqueous solution of a 1-1 electrolyte, $\kappa^{-1} \sim 6.9$ Å denoting the thickness of the ionic atmosphere outside the inner-sphere of radius a = 4.76 Å; consequently, $S \simeq 0.6$. Thus, the effect of screening by the ionic atmosphere in aqueous solutions can be very significant for electronic polarization whereas it is minor for nuclear reorganization in optical electron transfer (a few hundredths of electronvolt at most for a concentrated solution).

Expressions for the ionic screening of the discrete inner-sphere are complicated but may be closely approximated by a simple extension of the continuum outer-sphere treatment. For solutions of high ionic strength, counterions may penetrate the inner-sphere; thus, the Debye-Hückel length κ^{-1}, measured from the radius a, is negative denoting this penetration. The screening factor S is then negative allowing for the partial cancellation of the inner-sphere response by that calculated for the screened outer-sphere (see Sec. IV). For example, in a 2 M aqueous solution of a 2-1 electrolyte, the mean separation of ionic centers is ~ 6.5 Å. Given an effective common ionic radius[18] $r_c \simeq 2$ Å, the distance from one of the ions to the center of the other is 4.5 Å. Thus, the inner-sphere is penetrated to a depth of 4.76 - 4.50 = 0.26 Å. κ^{-1} as defined above is then $\simeq -0.3$ Å and consequently S is ca. -0.1.

Formula (13) is intended as a guide in the interpretation of screening rather than a quantitative equation. Application of the Debye-Hückel theory outside the range of sufficiently dilute solutions is tentative, but the original model can be improved (e.g., the recent treatment in Ref. 20). It is noted, in this respect, that departure from the theory does not arise because κ^{-1} in concentrated solutions is shorter than ionic radii since the ionic

atmosphere is always outside the sphere of of closest approach for the ions the radius of which is approximately the sum of the anionic and cationic radii.

III. NONEQUILIBRIUM PROCESSES: ABSORBING SOLVENTS

A. Real part of energies for inner- and outer-sphere regions

The dielectric constant of the solvent in the range of absorption is a complex quantity $\epsilon_1 - i\epsilon_2$. The energy density within the dielectric is $\epsilon_1 F^2/8\pi$, where $F = (e/r^2)(\epsilon_1^2 + \epsilon_2^2)^{-1/2}$ is the magnitude of the ionic field. Integrating the energy density for the volume element $dV = 4\pi r^2 dr$ between $r = a$ and $r = \infty$, one obtains the outer-sphere contribution

$$\Delta P_{out} = (e^2/2a)[(\epsilon_{op}^o)^{-1} - \epsilon_1/(\epsilon_1^2 + \epsilon_2^2)]. \tag{14}$$

Thus, Eq. (14) is simply the real part of ΔP_{out} of Eq. (11) written for a complex dielectric constant.

Similarly, calculation of ΔP_{in} requires the value of the real part α_1 of the complex polarizability $\alpha_1 - i\alpha_2$. The values of α_1 and α_2 are obtained, at least approximately, from the Lorenz-Lorentz equation for an absorbing solvent[21]

$$(\epsilon_1 - 1 - i\epsilon_2)/(\epsilon_1 + 2 - i\epsilon_2) = \zeta(\alpha_1 - i\alpha_2), \tag{15}$$

where $\zeta = 4\pi N_A \delta/3M$, N_A being the Avogadro number, δ the density and M the molecular weight of the solvent. Equation (15) yields

$$[(\epsilon_1 - 1)(\epsilon_1 + 2) + \epsilon_2^2]/[(\epsilon_1 + 2)^2 + \epsilon_2^2] = \zeta\alpha_1 \tag{16}$$

$$\epsilon_2/[(\epsilon_1 + 2)^2 + \epsilon_2^2] = (\zeta/3)\alpha_2 \tag{17}$$

The energy ΔP_{in} is computed from Eqs. (1) to (9) by using α_1 from Eq. (16) instead of α. Equations (2) to (6) are written in complex form in terms of $\alpha_1 - i\alpha_2$ and $p_{\alpha_1} - ip_{\alpha_2}$ (Sec. IIIB). The sum of these complex energies is minimized with respect to $p_{\alpha_1} - ip_{\alpha_2}$, and the real and

imaginary parts of induced dipole are obtained accordingly. Thus,

$$p_{\alpha_1} = [K_1K_3(\alpha_1^2 + \alpha_2^2) + K_1K_2\alpha_1]/(K_2 + K_3\alpha_1)^2 + (K_3\alpha_2)^2] \quad (18)$$

$$p_{\alpha_2} = \alpha_2K_1K_2/[(K_2 + K_3\alpha_1)^2 + (K_3\alpha_2)^2] \quad (19)$$

where

$$K_1 = Ner_o^2 = 2Apr_o \cos\beta + B \quad (20)$$

$$K_2 = Nr_o^4 \quad (21)$$

$$K_3 = 2Ar_o \quad (22)$$

Use of the corrected Lorenz-Lorentz equation[21] yielded values of α_1 and α_2 slightly higher than those given by Eqs. (16) and (17) (cf. also Sec. V).

B. Imaginary part of energies for inner- and outer-sphere regions

The imaginary part ϵ_2 of the complex dielectric constant can be interpreted classically in terms of the optical conductivity $\sigma = \omega\epsilon_2/4\pi$ at the photon energy $\hbar\omega$. This interpretation holds even if the dielectric does not exhibit any conductivity from free charges, and the imaginary part ϵ_2 arises solely from bound-bound transitions. (The contribution from ionic conductivity for the systems studied in the present work is negligible.) The energy loss corresponding to absorption will be calculated for the outer- and inner-sphere regions. The loss for the outer-sphere region will be calculated first since a continuous medium treatment is directly applicable.

The conduction current density for the field F is σF. The corresponding energy loss in the dielectric is determined by the variation of F during the time interval for which the loss is calculated. This time interval is taken to be equal to the time uncertainty ω^{-1} corresponding to the photon energy $E = \hbar\omega$ at which photoionization occurs. (See formulation of the time-energy uncertainty in Ref. 22.) The ionic valence cannot be specified during the

interval ω^{-1} and consequently the loss is calculated by equating F to the change in ionic field from an ionic charge z to z + 1 as a result of photoionization. The loss per unit of time and unit volume therefore is σF^2. This result differs from the classical value[21] $\sigma F^2/2$ obtained from $\int_0^F \sigma E dE$. The experimental results on the effect of ionic atmosphere in Sec. VI strongly support the use of σF^2 instead of $\sigma F^2/2$.

The energy loss per unit volume in the time ω^{-1} is $\omega^{-1}\sigma F^2$ or $(\epsilon_2/4\pi)F^2$. The ionic field in the absence of screening by the ionic atmosphere is $(e/r^2)(\epsilon_1^2 + \epsilon_2^2)^{-1/2}$, and the volume element dV is $4\pi r^2 dr$. The energy loss in the outer-sphere region is

$$L_{out} = \epsilon_2 \int_a^\infty F^2 r^2 dr$$

$$= (e^2/a)\epsilon_2/(\epsilon_1^2 + \epsilon_2^2). \qquad (23)$$

Equation (23) is identical, except for the factor 1/2, to the negative imaginary part of the complex polarization which is associated with the real part of the polarization given by Eq. (14). The correction for the ionic atmosphere is obtained just as in Sec. IIC by introducing the radius $a + 1/\kappa$ instead of a in Eq. (23). The screening factor S of Eq. (13) therefore is also applicable to L_{out}.

The loss in the inner-sphere L_{in} is calculated analogously to L_{out} by summing the negative imaginary parts of the complex components of ΔP_{in}. This is justified by noting that the conduction current density per molecule within a time ω^{-1} is the displacement of charge out-of-phase with the real part of the ionic field due to optical conductivity. This out-of-phase charge displacement is alternatively given by the formally defined dipole p_{α_2}. The dipole p_{α_2} defined in this way interacts with the permanent and induced moments of the multipole expansion to give inner-sphere energy

losses. In this way, the inner-sphere interaction energies are damped by the optical conduction of the medium. Thus,

$$L_{in} = L(\sigma_{IND}) + L(e\sigma) + L(p\sigma) + L(p_\alpha\sigma) + L(q\sigma) + L_{REP} \tag{24}$$

where $L(\sigma_{IND})$ represents the damping of the induction energy over the interval ω^{-1} arising from the optical conductivity of the solvent. Likewise, $L(e\sigma)$, $L(p\sigma)$, $L(p_\alpha\sigma)$, $L(q,\sigma)$ represent the decrease of the interaction energies (or losses) for the charge, dipole, induced dipole and quadrupole terms of Eqs. (2) to (6), respectively. The quantity $L(\sigma_{IND})$ is the imaginary contribution from the Born repulsion. This term is included because the minimization of the interaction energies with respect to nuclear coordinates, which leads to Eq. (9), minimizes conductive losses as well. London dispersion is not applicable to the loss calculation, however. One has (cf. Sec. IIB),

$$L(\sigma_{IND}) = (N/2)[\alpha_2(p_{\alpha_1}^2 - p_{\alpha_2}^2) - 2\alpha_1 p_{\alpha_1} p_{\alpha_2}]/(\alpha_1^2 + \alpha_2)^2 \tag{25}$$

$$L(e\sigma) = (N/2)(e/r_0^2)p_{\alpha_2} \tag{26}$$

$$L(p\sigma) = -2A(pp_{\alpha_2}/r_0^3)\cos\beta \tag{27}$$

$$L(p_\alpha\sigma) = -2Ap_{\alpha_1}p_{\alpha_2}/r_0^3 \tag{28}$$

$$L(q\sigma) = B\Theta p_{\alpha_2}/r_0^4 \tag{29}$$

$$L_{REP} = (1/x)\{2L(e\sigma) + 3[L(p\sigma) + L(p_\alpha\sigma)] + 4L(q\sigma)\} \tag{30}$$

where p_{α_2} and the quantities A, B, p, Θ, x are defined in Sec. IIB.

IV. TOTAL ENERGY FOR NONEQUILIBRIUM PROCESSES

The total contribution W from nonequilibrium processes to the exclusion of nuclear reorganization will be obtained. The real and imaginary components of W are

$$P = \Delta P_{in} + \Delta P_{out} \tag{31}$$

$$L = L_{in} + L_{out}. \tag{32}$$

Thus,

$$W = (P^2 + L^2)^{1/2} \tag{33}$$

The variations of ΔP_{in}, ΔP_{out}, L_{in}, L_{out} and W with photon energy for S = 1 are displayed in Fig. 1 for liquid water for octahedral coordination of the solvent around an anion. The shapes of the curves of Fig. 1 are determined by dielectric dispersion and the absorption bands of liquid water at ca. 8.2 and 10.0 eV. This point is amplified in Sec. V and VI. Results for tetrahedral coordination around an anion are the same except that ΔP_{in} makes a contribution to W which is ca. 18 percent lower than in Fig. 1. Results for cations are similar to those for anions for the same coordination.

Data on ϵ_1 and ϵ_2 used in Fig. 1 were those recently recalculated by Painter[23] from earlier results[24-26] on reflectance spectroscopy of liquid water except for ϵ_2. The earlier[24] values of ϵ_2 in the 6.8 to 8.8 eV interval were used because the cut-off $\epsilon_2 = 0$ below 7.6 eV in Refs. 25 and 26 does not agree with the data from other workers summarized in Ref. 27. The difference is really minor in the calculation of L but not in that of the derivative dL/dE needed for comparison with experiment. The quadrupole moment components used in the preparation of Fig. 1 were taken from Ref. 28.

The effect of screening by the ionic atmosphere on the variations of the energy W of Eq. (33) with the photon energy E is shown in Fig. 2 for S = 0.3 to S = -0.1. The shape of the W against E curve hardly changes between S = 1 and 0.3, but W at a given E decreases with increasing screening. Figure 2, in fact, shows that screening can drastically reduce the magnitude of W. Whereas the outer-sphere contributions ΔP_{out} and L_{out} become dominant for $S \gtrsim 0.2$, one has only $W = (\Delta P_{in}^2 + L_{in}^2)^{1/2}$ for the case of S = 0. Negative S values even further reduce W since the inner-sphere response is decreased by counterion penetration (Sec. IIC).

V. CALCULATED DISPERSION SPECTRA

The present theory was tested experimentally by using data[1,2] on photoelectron emission by aqueous solutions of inorganic anions and cations in the 7 to 10.4 eV range of photon energy. Verification of the theory requires plots of $-dW/dE$ against the photon energy E. This will be shown first. The emission yield Y in emission experiments is defined as the number of collected photoelectrons per incident photon. One has $Y = K(E - E_t)^p$, where E is the photon energy, E_t the threshold energy, K a quantity independent of E and p = 2, 5/2 or 3 depending[6] on the range of E. A quadratic dependence was found suitable[1,2] and, in any event, conclusions to be drawn below are essentially unaffected by the choice of exponent.[1] One has in view of the form of the emission law for Y,

$$dY^{1/2}/dE = K(1 - dE_t/dE) \tag{34}$$

The threshold energy E_t is given by[29,30]

$$E_t = \Delta G_{cycle} + R + W, \tag{35}$$

where ΔG_{cycle} can be written in explicit form for a thermodynamic cycle involving the initial and final states of the emission process (including the surface potential contribution), and R is the free energy for nuclear reorganization. The quantities ΔG_{cycle} and R are not affected by dielectric dispersion and are independent of E. One obtains from Eqs. (34) and (35)

$$dY^{1/2}/dE = K[1 - dW/dE]. \tag{36}$$

It follows from Eq. (36) that the derivatives $dY^{1/2}/dE$ and $-dW/dE$ should have the same functional dependence on photon energy. The curves representing the variations of $dY^{1/2}/dE$ and $-dW/dE$ with E will be referred to, respectively, as the experimental and theoretical dispersion spectra.

From Eq. (33)

$$dW/dE = [P/(P^2 + L^2)^{1/2}]dP/dE + [L/(P^2 + L^2)^{1/2}]dL/dE. \tag{37}$$

The two terms on the r.h.s. of Eq. (37) were computed as functions of photon energy by using binomial smoothing filters[31] to obtain the derivatives dP/dE and dL/dE. This method is preferable to the use of the Savitsky-Golay convolutes previously used[1,32] to calculate the derivatives. It should be noted in this respect that the data on ϵ_1 and ϵ_2 of liquid water from Ref. 23 used in the preparation of Fig. 1 were available at 0.2 eV intervals and were interpolated by means of quadratic and quartic polynomials. Interpolation was of no consequence in the calculation of the curves of Fig. 1 but resulted in the elimination or at least damping of any fine structure the derivative curves might actually have in the 0.2 eV intervals. Figure 3 shows that the terms in dP/dE and dL/dE in Eq. (37) make comparable contributions to -dW/dE but that their extrema occur at different photon energies.

The use of the corrected Lorenz-Lorentz equation[21] increases the magnitude of $|-dW/dt|$ by ca. 10 percent but does not change the functional dependence of -dW/dt on photon energy.

The difference in the orientation of the water molecules in the inner-sphere shell around anions and cations (Sec. IIB) was investigated. Calculated dispersion spectra for cations exhibit practically the same functional dependence on photon energy as anions but the amplitude is increased, e.g., by ca. 50 percent in comparison with Fig. 3 for the following data: $N = 6$, $r_c = 0.88$ Å, $\beta = 0$, $\alpha = 1.3 \times 10^{-24}$ cm^3, $I_s = 26.4$ eV, $x = 8$ (data corresponding to the nonhydrated V^{2+} in Ref. 8).

The effect of screening by the ionic atmosphere is displayed in Fig. 4. The shape of the dispersion spectrum curve is not sensitive to screening between $S = 1$ and $S = 0.2$, but a major change in shape occurs at $S \lesssim 0.2$. This is the case because the curves corresponding to dP/dE and dL/dE peak at different photon energies (Fig. 3). The curve for $S = 0$ corresponds to the

case in which the dispersion spectrum is solely determined by the inner-sphere contributions. Conversely, the contributions from the outer-sphere region are dominant for S = 1. The photon energies at the extrema of the dispersion spectra calculated for S = 1 and S = 0 are listed in Table I. The ranges of E < 7.75 eV and 7.75 < E < 8.70 eV correspond respectively to normal and anomalous dispersion for the first absorption band of liquid water (with maximum at ca. 8.2 eV). A maximum between the two minima is displayed in the normal range, and conversely a minimum between two maxima is observed in the anomalous range. This pattern of extrema, which will be referred to as inner-outer sphere splitting, is repeated in the normal and anomalous ranges at higher photon energies for the second absorption band of liquid water (ca. 10.0 eV).

VI. COMPARISON OF EXPERIMENTAL AND CALCULATED DISPERSION SPECTRA

Experimental and calculated dispersion spectra are compared in Figs. 5 and 6 for 1-1 (NaSCN) and 1-2 ($Na_2S_2O_3$) electrolytes. The ordinate of experimental dispersion spectra is obtained in arbitrary units, and consequently the curves of Figs. 5 and 6 were normalized at the maximum (8.2 to 8.6 eV) and minimum (ca. 9.1 eV) of the experimental curves. The calculated curves were prepared for S = 0.3 and 0.15 (Fig. 5) and S = 0.0 and -0.1 (Fig. 6) for the 0.25 and 2 M solutions, respectively. These values of S are significantly different at high ionic strengths from the ones computed from Eq. (13) with κ^{-1} measured from a: 0.41 (0.25 M) and -0.14 (2 M) for a 1-1 electrolyte; 0.14 (0.25 M) and -0.40 (2 M) for a 1-2 electrolyte. This is not surprising since an accurate calculation of κ^{-1} from the Debye-Hŭckel theory in its original form, as applied in Eq. (13), is not possible at the concentrations of Figs. 5 and 6.

The experimental curves for the 2 M solution of Figs. 5 and 6 have slightly different widths than the calculated dispersion spectra. Three possible reasons at least can be advanced for this discrepancy: the uncertainty about ϵ_1 and ϵ_2 inherent to the application of the Kramers-Kronig transformation in reflectance spectroscopy[33]; the uncertainty about ϵ_2 below ca. 8.8 eV (Sec. IV); the approximation of the theoretical model in which spherical symmetry of the field is assumed around the ion undergoing photoionization.

The change in the shape of dispersion spectra upon increase of the ionic strength is strikingly apparent in Figs. 5 and 6. Thus, the maximum with dominant outer-sphere contribution near 8.6 eV is prominent for the 0.25 M sodium thiocyanate solution whereas the maximum with dominant inner-sphere contribution near 8.2 eV is considerably enhanced for 2 M thiosulfate. Inner-outer sphere splitting (cf. Table I) in the 8.0 to 8.8 eV and 9.0 to 9.7 eV ranges is indeed observed. Figures 5 and 6 also show that the weak maximum at 9.38 eV in the calculated curves is greatly enhanced in the experimental curves. Inner-outer sphere splitting in the 9.0 to 9.7 eV range therefore can be strongly influenced by the nature of the anion. This <u>specific</u> effect is displayed by the 17 anions studied in Ref. 1. Thus, the height of the 9.37 eV peak is nearly independent of concentration (0.25 to 2 M) for some anions (e.g., OH^-, CO_3^{2-}, SCN^-) whereas it is strongly concentration-dependent for others (e.g., Br^-, I^-, ClO_4^-). The 9.63 eV minimum is also sensitive to the nature of the anions as is evident from Figs. 5 and 6. Particularly pronounced minima were observed in Ref. 1 with bromide at 9.62 eV and iodide at 9.59 eV. Greatly enhanced inner-outer sphere splitting was recently observed for phosphorus hexafluoride ion (0.2 M KPF_6, $E_t \sim 9.3$ eV) with the normal sequence of two maxima (10.02 and 10.35 eV) and a minimum

(10.18 eV). This enhancement from PF_6^- ion completely masked the dispersion spectrum of liquid water (E_t = 10.06 eV).

The photon energies at the extrema of the experimental dispersion spectra of the 17 anions studied in Ref. 1 in Table I compare very well with the calculated values for $-0.2 \lesssim S \lesssim 1$. It is concluded from this agreement and the interpretation in Sec. V and VI that the theory accounts remarkably well for the experimental dispersion spectra and the pronounced effect of ionic strength on their shape.

The present theory is supported also by the observed shift in threshold energy with concentration of ionic emitter for NaSCN, NaN_3, $Na_2S_2O_3$ and $Na_2S_2O_8$ over the 0.25 to 2.0 M range. Further work on this aspect will be the subject of a future publication.

VII. CONCLUSIONS

Photoionization provides a way of changing the intense ionic field in a time interval corresponding to the frequency of the incident radiation. These rapid variations of the ionic field can be used to probe the response of liquids and solutions. Experimental evidence was obtained in this way for nonequilibrium electronic processes resulting from dielectric dispersion of the solvent in photoionization. Theory predicts and experiment confirms that ionic screening can alter profoundly the balance between the contributions from inner- and outer-sphere regions to the energetics of the nonequilibrium electronic processes (inner-outer sphere splitting).

ACKNOWLEDGMENTS

This work was supported by the Office of Naval Research and the National Science Foundation. We thank Professor N. S. Hush (Theoretical Chemistry, Sydney) for pointing out to us the need to consider the difference in solvent configuration around inorganic anions and cations. Professor L. R. Painter

(Physics, University of Tennessee) kindly communicated her unpublished recalculated data on the reflectance spectroscopy of liquid water.

APPENDIX

A. Quadrupole moment

The quadrupole moment of Eq. (6) for $\beta = 0$ is[9]

$$\Theta = \Theta_a + \Theta_b \tag{A1}$$

where

$$\Theta_a + \Theta_b = 2\Theta_{zz} - \Theta_{xx} - \Theta_{yy}, \tag{A2}$$

the z-axis being in the ion-oxygen direction. For $\beta = 52.23^\circ$, one has

$$\Theta_a + \Theta_b = 2\Theta_{zz}\sec\beta - \Theta_{xx}\sec\beta - \Theta_{yy}. \tag{A3}$$

Equation (A3) was obtained by noting that the water molecule rotates about the H-O axis for $\beta = 52.23^\circ$. The quantities Θ_a and Θ_b therefore were transformed with respect to the new axis of rotation.

B. Attenuation of the field

The electric field in a conducting, isotropic medium is attenuated[34] by the factor $\exp(-\omega kr/c)$, where k is the absorption coefficient, r the depth of penetration and c the velocity of light in vacuum. The absorption coefficient k can be computed from $\epsilon_1 = n^2 - k^2$ and $\epsilon_2 = 2nk$, where n is the index of refraction. The field in the present case is proportional to r^{-2} without attenuation. The energy without attenuation is obtained by integrating $r^{-4}dV$ from a to ∞, where $dV = 4\pi r^2 dr$. With attenuation, one integrates $4\pi r^{-2}\exp(-2\omega kr/c)dr$ between a and ∞. This is done in the calculation of ΔP_{out} using the real part of $(\epsilon_1 - i\epsilon_2)^{-1}$ as noted in Sec. III. There is no attenuation of the field for the limiting value ϵ^o_{op}. One obtains

$$\Delta P_{out} = (e^2/2a)(\epsilon^o_{op})^{-1} - (e^2/2)\epsilon_1(\epsilon_1^2 + \epsilon_2^2)^{-1}[a^{-1}\exp(-\xi a) + \xi \ln \xi a - \xi^2 a + \xi^3/2.2! \ldots], \tag{A4}$$

where $\xi = 2\omega k/c$. The series in (A4) converges rapidly in the present case and

only the first term between brackets is significant. Equation (A4) reduces to Eq. (11) for $\xi = 0$. One has[23] for liquid water at 8.2 eV, $k = 0.19$, $\xi = 7.5 \times 10^{-3}$ cm^{-1} and $\exp(-\xi a) = 0.992$. Attenuation of the field thus changes the second term on the r.h.s. of Eq. (A4) by only ≈ 1 percent.

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TABLE I. Photon energies at the extrema of experimental and calculated dispersion spectra (S = 0 and 1)

Dispersion	Extremum	Dominant Contribution	Calculated[a] Photon Energy (eV)	Experimental[b] 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 8.70 eV)	min	mixed	8.58	8.42±0.06
	max	outer	8.68	8.65±0.03
normal	min	inner	9.18	9.11±0.03
(8.70 to 9.70 eV)	max	mixed	9.38	9.37±0.06
	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

[a] See Fig. 4 for $7 \leqslant E \leqslant 10$ eV.

[b] 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. 2. Average values with standard deviation ($8.16 \leqslant E \leqslant 10$ eV) for 1 M solutions of 17 inorganic anions from Ref. 1. Extrema at 10.18 and 10.35 eV obtained with 0.2 M KPF_6.

Captions to Figures

Fig. 1 Variation of energies with photon energy for liquid water and the solvent configuration around a typical inorganic anion: ΔP_{in}, L_{in} and ΔP_{out}, L_{out} for the inner- and outer-sphere regions, respectively, W the total energy from Eq. (25). Data: N = 6, r_c = 2 Å, r_w = 1.38 Å, β = 52.23°, p = 1.855 debye, $\alpha^o = 1.444 \times 10^{-24}$ cm^3, $\alpha_s = 4 \times 10^{-24}$ cm^3, I_s = 3 eV, I = 12.61 eV, x = 12. Values of ε_1 and ε_2 from Ref. 23 (see text). No screening by the ionic atmosphere (S = 1).

Fig. 2. Variations of the total energy W with photon energy for different values of the screening factor S (S = 0 for complete outer-sphere screening, S = -0.1 for partial screening of the inner-sphere). Same data as in Fig. 1.

Fig. 3. Variations of the quantities in Eq. (29) with photon energy for the data of Fig. 1.

Fig. 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, S = -0.1 for partial screening of the inner-sphere). Same data as in Fig. 1. Ordinates at the minimum at 7.42 eV from S = -0.1 to S = 1.0: -0.164, -0.196, -0.229, -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).

Fig. 5. Comparison of experimental dispersion spectra for 0.25 M (bottom) and 2 M sodium thiocyanate with dispersion spectra calculated for the data of Fig. 1 and a screening factor S = 0.3 (bottom) and 0.15 (top).

Fig. 6. Same comparison as in Fig. 5 but for 0.25 M (bottom) and 2 M sodium thiosulfate and S = 0.0 (bottom) and -0.1 (top).

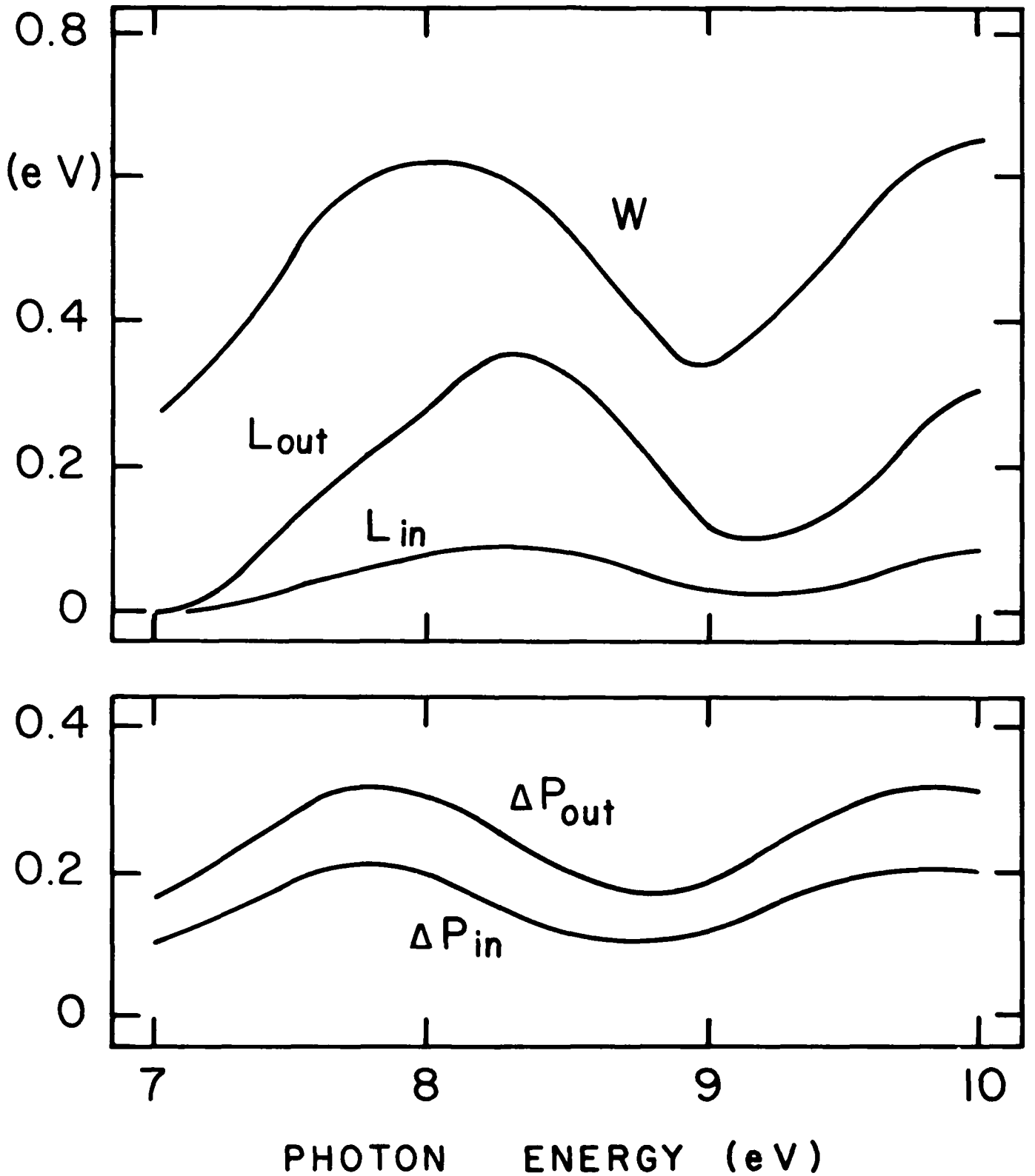
0.8
(e V)
0.4
0.2
0
W
Lout
Lin
0.4
0.2
0
ΔPout
ΔPin
7
8
9
10
PHOTON ENERGY (eV)

FIG. 1

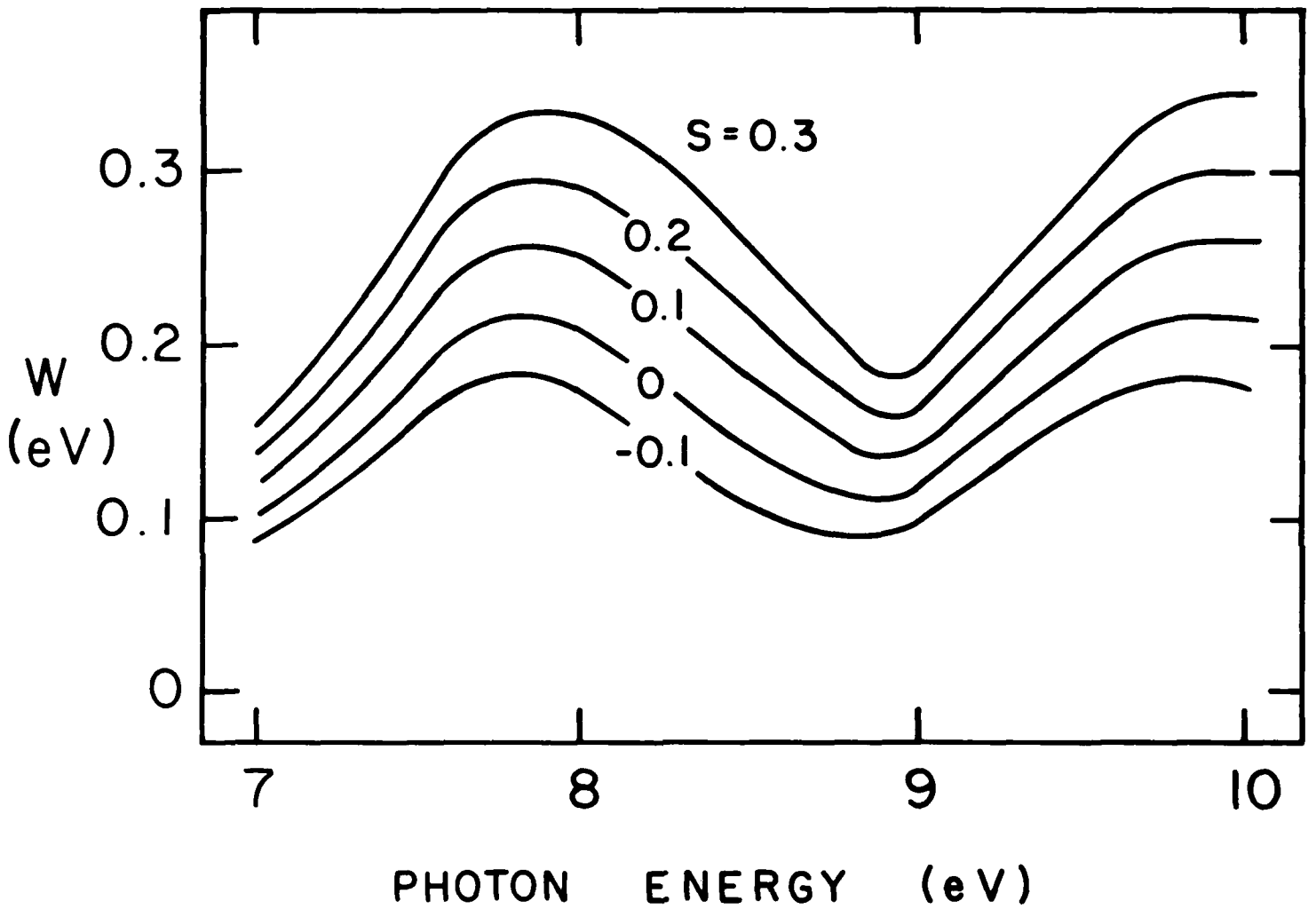

FIG. 2

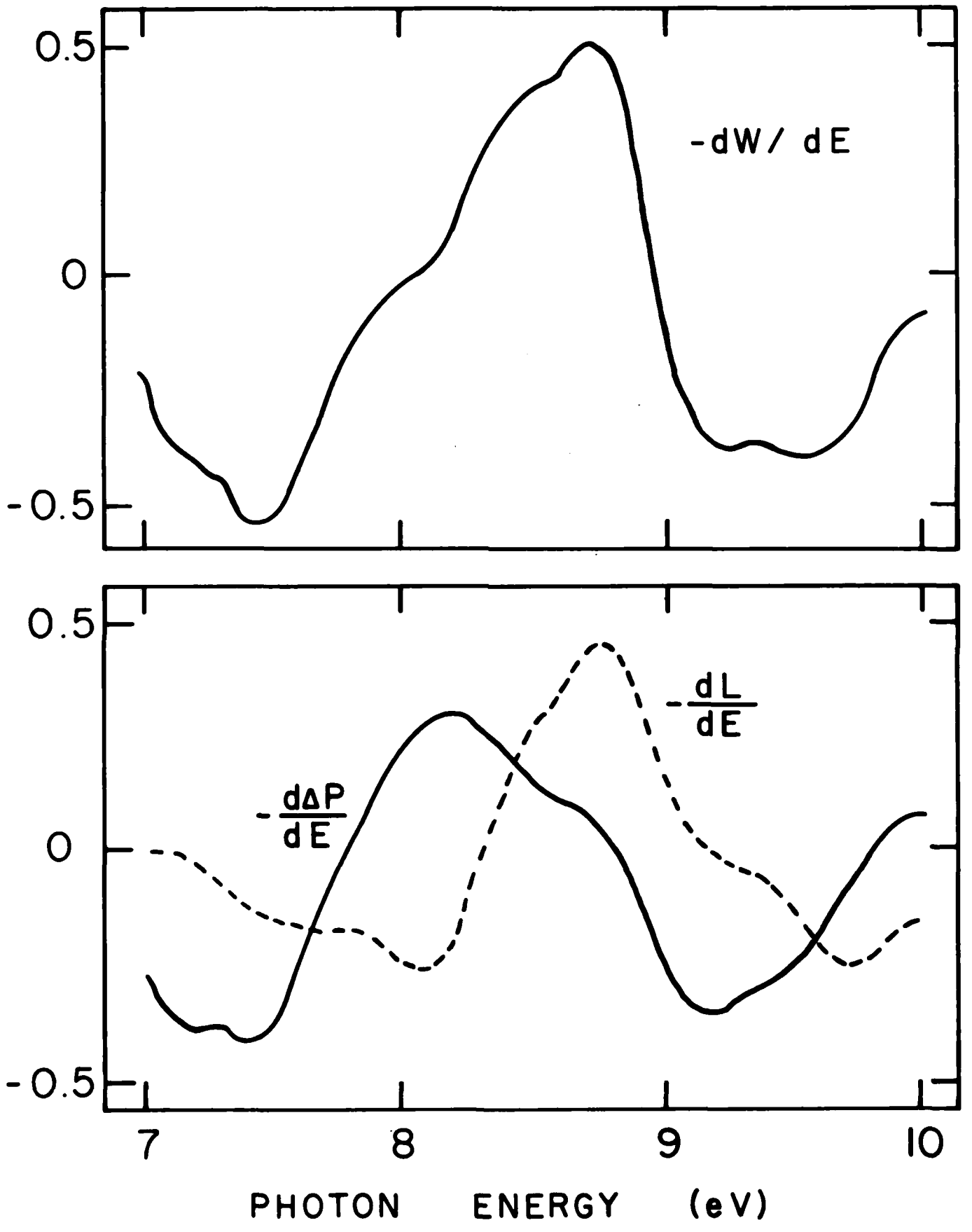

FIG. 3

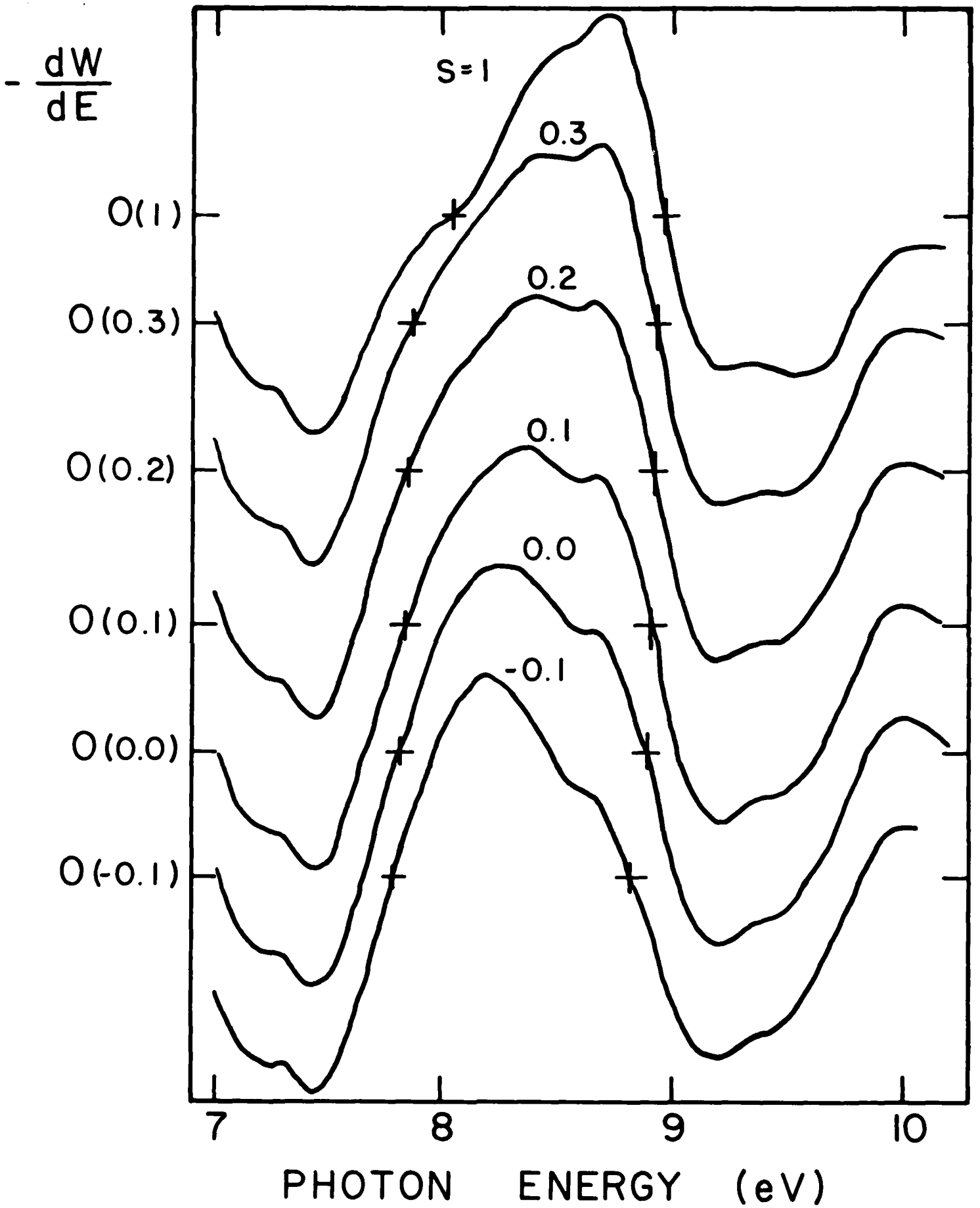
- dW/dE
S=1
0.3
0.2
0.1
0.0
-0.1
O(1)
O(0.3)
O(0.2)
O(0.1)
O(0.0)
O(-0.1)
7
8
9
10
PHOTON ENERGY (eV)

FIG. 4

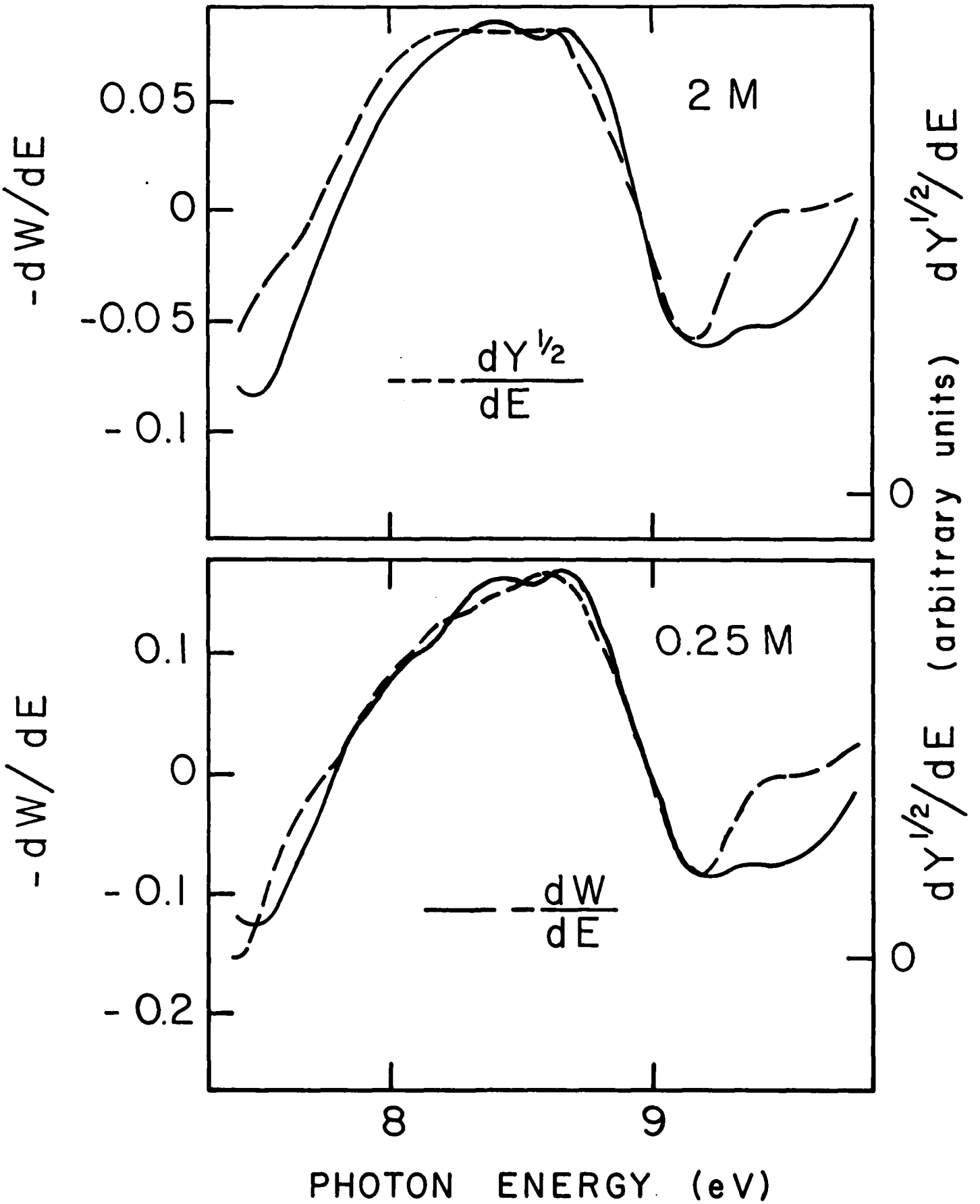
2 M
0.25 M
0.05
0
-0.05
-0.1
0.1
-0.2
-dW/dE
-dW/ dE
dY^1/2/dE
dY^1/2/dE (arbitrary units)
dY 1/2 / dE
dW / dE
8
9
PHOTON ENERGY (eV)

FIG. 5

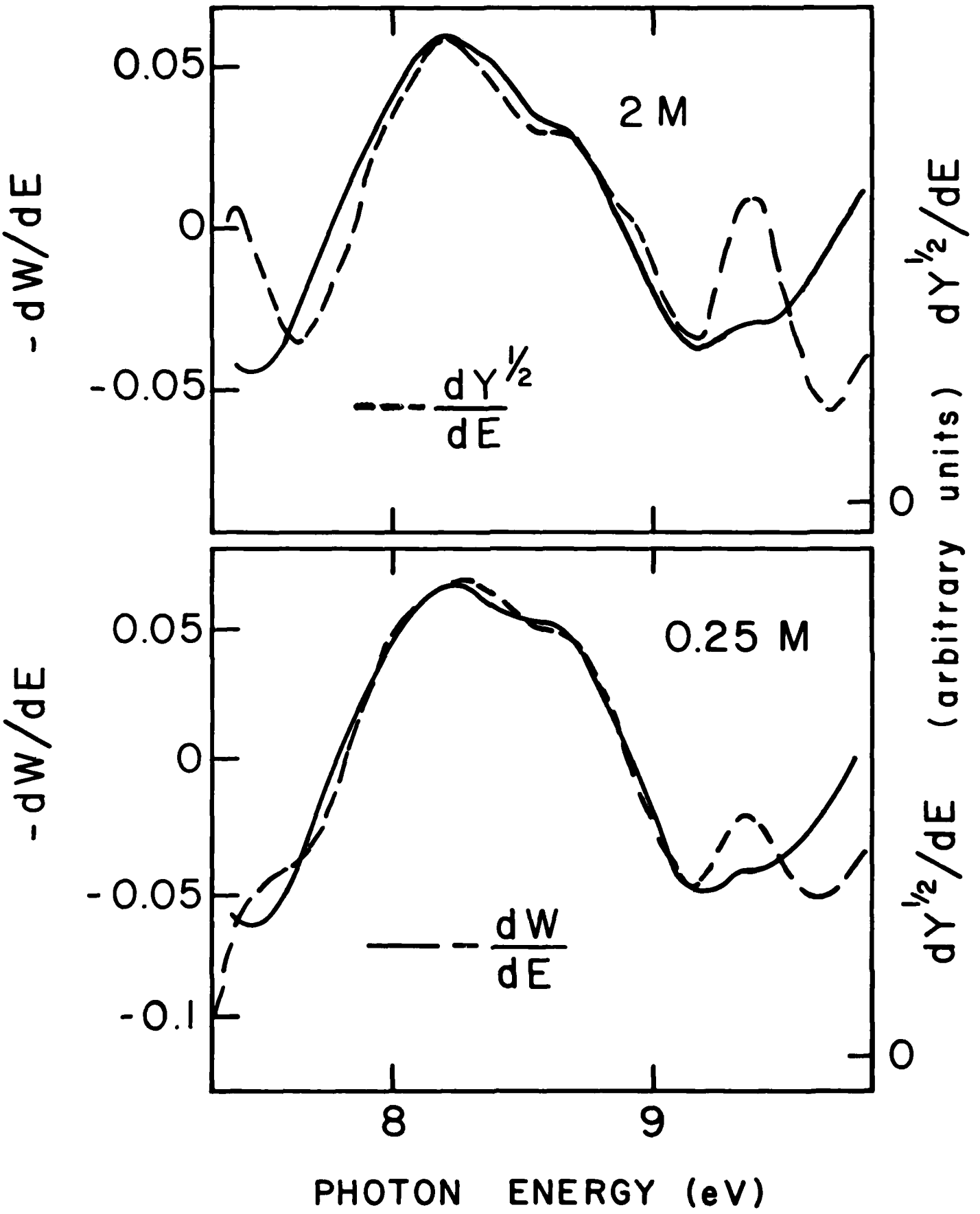
0.05
0
-0.05
2 M
$\frac{dY^{1/2}}{dE}$
-dW/dE
$dY^{1/2}/dE$ (arbitrary units)
0.05
0
-0.05
-0.1
0.25 M
$\frac{dW}{dE}$
8
9
PHOTON ENERGY (eV)

FIG. 6

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