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Vacuum Ultraviolet Photoelectron Emission Spectroscopy
of Water and Aqueous Solutions

Iwao Watanabe, James B. Flanagan and Paul Delahay

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8.740.1 eV for the threshold energy for amorphous ice. Threshold energies for halide and hydroxyl ions are obtained by application of the Brodsky-Tsarevsky theory of photoelectron emission by solutions: 8.7, 7.9, 7.2, 8.4 eV, respectively, for Cl^- , Br^- , I^- , OH^- ions. The emission spectrum for Br^- is deconvoluted for spin-orbit coupling. The threshold energies of these ions are higher by 1.6 to 1.8 eV than the energies at the maxima of the corresponding charge-transfer-to-solvent absorption spectra. The difference of 1.6 to 1.8 eV agrees with a theoretical prediction. Preliminary results are reported on the effect of ionic charge on the emission of phosphoric acid and phosphate ions.

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VACUUM ULTRAVIOLET PHOTOELECTRON EMISSION SPECTROSCOPY OF WATER AND
AQUEOUS SOLUTIONS

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Experimental methods are developed for the photoelectron emission spectroscopy of water and aqueous solutions (halides, hydroxyl ion, phosphoric acid and phosphates) up to 10.5 eV. The yield for emission of photoelectrons by the liquid into water vapor is measured as a function of photon energy. Threshold energies are determined by extrapolation from emission spectra. Photoelectron emission by liquid water obeys Urbach's rule and has a threshold energy of 9.3 ± 0.3 eV. This threshold is compared with the literature value of 8.7 ± 0.1 eV for the threshold energy for amorphous ice. Threshold energies for halide and hydroxyl ions are obtained by application of the Brodsky-Tsarevsky theory of photoelectron emission by solutions: 8.7, 7.9, 7.2, 8.4 eV, respectively, for Cl^- , Br^- , I^- , OH^- ions. The emission spectrum for Br^- is deconvoluted for spin-orbit coupling. The threshold energies of these ions are higher by 1.6 to 1.8 eV than the energies at the maxima of the corresponding charge-transfer-to-solvent absorption spectra. The difference of 1.6 to 1.8 eV agrees with a theoretical prediction. Preliminary results are reported on the effect of ionic charge on the emission of phosphoric acid and phosphate ions.

I. INTRODUCTION

Photoelectron emission spectroscopy of water and aqueous solutions has been studied only to a very limited extent and only in the UV range. Only two investigations on cyanometalate complexes^{1,2} and two papers on water^{3,4} have been published, to our knowledge, since earlier work was reviewed.⁵ Further work was deemed desirable for several reasons:

(i) Extension to the vacuum UV range (up to 10.5 eV) would greatly enhance the scope of such studies. (ii) The methodology of the vacuum UV photoelectron spectroscopy of liquids was developed^{6,7} in recent years, and adaptation to water and aqueous solutions seemed quite feasible. (iii) Water should be a very useful solvent because of its expected high photoionization energy in liquid phase (cf. 12.6 eV for the first band in the gas phase). (iv) Emission spectra could be correlated with absorption spectra.¹

II. EXPERIMENTAL

A. Instrumentation

A detailed report is available⁸ on instrumentation, and only essential points will be noted here. The instrument consists of the following components:

(i) The filament-type Hinteregger hydrogen lamp already used in earlier work.⁶

(ii) A vacuum-tight compartment with shutter, interchangeable filters (glass, Suprasil, sapphire, no filter) and a chopper (12 Hz). The monochromator side of this compartment was closed by an easily interchangeable lithium fluoride window which protected other optical components from degradation by the plasma and high energy photons generated in the hydrogen lamp. This compartment was connected to a differential pumping system to

avoid contamination of the hydrogen lamp by air leaking through the joint of the shaft of the chopper.

(iii) A GCA/McPherson 0.5-meter vacuum UV monochromator, model 235, with pumping system, model 815. Fixed entrance (1 mm) and exit (1 mm) slits were used. The entrance slit was closed with a vacuum-tight lithium fluoride window.

(iv) A vacuum-tight compartment (Fig. 1) with sodium salicylate converter A and photomultiplier B for monitoring of the photon flux. This compartment was closed by a lithium fluoride window C covered with a gold grid mesh D (80% transparency) serving as electron collector electrode (10 to 250 V applied voltage) for photoelectrons emitted by the liquid or solution under study. The window holder was kept at about 45°C by means of an electric heater to avoid condensation of water on the window.

(v) The vacuum-tight cell compartment (Fig. 1) with rotating quartz disk E (52 mm diameter, 2 mm thick) partially immersed in the reservoir F containing the liquid being studied. The liquid film on the face of the disk was irradiated. The gap (ca. 1 mm) between the disk and gold grid was adjusted to keep the capacitance between the liquid film and the collector electrode constant. The actual gap did vary somewhat with the speed of rotation of the disk (variable meniscus), and this is why the gap was monitored by means of capacitance measurements. The speed of rotation was adjustable (30 to 240 rpm) to ascertain the absence of contamination (Sec. II.B). The liquid in the reservoir was cooled by a glass tube G in which externally cooled nitrogen gas flowed. The temperature of the liquid was monitored with thermistor H and kept constant at 1.5°C by controlling the cooled gas flow automatically. The entire cell compartment therefore was filled with water vapor at the equilibrium pressure

(corresponding to 1.5°C of the liquid) after the compartment was evacuated and sealed off.

(vi) Electronics for processing the signal from photomultiplier B and the photoelectron emission current. A platinum wire I dipped into the cell served as electrode and was connected to a high-impedance current-voltage converter (Burr-Brown BB3430, feedback resistance of 10^9 ohms). Phase-sensitive detectors (Princeton Applied Research, model 121, and Keithley, model 822) with ancillary equipment (operational amplifier, bandpass filter) were used in both channels.

(vii) A Digital Equipment Corp. computer, model PDP 11/34, for data acquisition, processing and display (graphic terminal VT55 with hard copy unit).

Operational procedures are discussed in Ref. 8.

B. Determination of Emission Spectra

Contamination by a spurious film of insoluble material on the surface of the liquid posed a very serious problem with water and aqueous solutions. This problem did not arise with organic solvents in earlier work,^{6,7} presumably because contaminants were soluble in the liquids being studied and their contribution to photoelectron emission was negligible. Contaminants in this work undoubtedly were surface-active, high-molecular-weight substances, namely, vacuum pump oil, impurities on glass surfaces and in water and chemicals.

Decontamination was achieved by continuously running the instrument for at least three weeks prior to the determination of emission spectra considered reliable. The water sample was renewed several times daily to wash away impurities. Distilled water was adequate in this work. Further

purification of the water by treatment with ion exchange resin and/or additional distillation did not result in any detectable change in emission spectra. Progress of decontamination was monitored by measuring the emission spectrum of water. This spectrum progressively displayed lower emission currents as contaminants were removed. Emission currents measured with contaminated water were dependent on the speed of the rotating disk. The current typically decreased by one order of magnitude when the speed was varied from 12 to 60 rpm. The current leveled off above 90 rpm. The absence of such a dependence on speed of rotation provided a reliable criterion for satisfactory decontamination. All measurements in this work were performed at 200 rpm.

Emission spectra obtained after three weeks of continuous operation were reproducible within the noise level. Moreover, water samples left for several hours in the cell did not show any detectable increase in emission current. Discrepancy between emission spectra taken the same day after decontamination was less than 5%. Similar reproducibility was achieved between measurements on consecutive days except that occasionally the discrepancy reached ca. 20%. The shape of the emission spectral curve, however, was not affected significantly after normalization. Most of the discrepancy resulted from variations in the level of scattered light as a result of color center formation in the lithium fluoride window separating the hydrogen lamp from the monochromator compartment.

Chemicals were baked at 500°C whenever feasible since contamination levels were lowered by this treatment. The glassware and rotating quartz disk were cleaned with 30% sodium hydroxide solution each time a solution was changed in the cell. The apparatus was then thoroughly washed with distilled water.

The emission spectrum of iodide displayed a small, nearly constant background which was ascribed to traces of I_3^- and/or traces of surface active impurities in crystalline potassium iodide used for preparation of the solutions. Potassium iodide was not baked at 500°C as were the other alkaline halides. The species I_3^- is easily formed by oxidation by air, especially upon irradiation, and, moreover, addition of iodine did increase the background.

Emission spectra were not corrected for attenuation of the photon flux by water vapor in the gap between the lithium fluoride window C (Fig. 1) and the rotating disk. No correction was made either for absorption by window C. These two corrections were estimated from available absorption coefficients^{9,10} and found negligible when water or aqueous solutions were near 1.5°C and the gap between window C and the rotating disk did not exceed 1 mm.

Emission currents were not corrected for backscattering of electrons emitted into the gas phase. The shape of emission spectra was not affected when the voltage applied between the collector electrode and the emitting liquid was varied from 10 to 250 V. The ratio of collected current to emitted current (not much smaller than unity¹) thus was independent of photon energy, and the complication of a backscattering correction was avoided.

C. Quantum Yield Calibration

The ratio of the collected current for photoelectron emission by the liquid to the photomultiplier output (B, Fig. 1) was obtained in the computer output as a function of photon energy. This ratio expresses the quantum yield in arbitrary units. The quantum yield scale was calibrated by determining the emission spectrum of 1,2-ethanediol (Sec. V) since the

absolute quantum yield for photoelectron emission by this substance is available.⁶ Backscattering of electrons in the gas phase is negligible because of the low vapor pressure of 1,2-ethanediol at sufficiently low temperature.⁶ Actual quantum yields for water and aqueous solutions would be somewhat higher because backscattering decreases the efficiency of electron collection.¹ Absolute calibration of photon fluxes in the vacuum UV range⁶ is difficult, and the error on absolute quantum yields is easily $\pm 25\%$ and probably somewhat higher.

A typical current of 25 picoamp for a yield of 5×10^{-3} collected electron per incident photon corresponds to a photon flux of ca 5×10^{10} photons sec^{-1} . The photon flux varied considerably with photon energy because of the many-line spectrum of the hydrogen lamp output. Moreover, the photon flux decreased by as much as one order of magnitude (especially in the upper photon energy range) as a result of the progressive degradation of the lithium fluoride window adjacent to the hydrogen lamp.

III. EQUATIONS FOR EMISSION SPECTRA AND EXTRAPOLATION TO THRESHOLD ENERGY

Equations for obtaining threshold energies from emission spectra will be listed and briefly commented upon. The emission spectra of various materials for different processes in the threshold region can be represented by the general equation^{11,12}

$$Y = A(E - E_0)^a E^b \quad (1)$$

where Y is the emission current (quantum yield), A a proportionality factor, E the photon energy, E_0 the threshold energy, and a and b parameters in the ranges $1 \leq a \leq 5/2$ and $0 \leq b \leq 3/2$. A particular form of Eq. (1), namely, $Y = A(E - E_0)^2$ was found to represent the emission spectra of benzene or rare gases in a rare-gas matrix.¹³

Photoelectron emission by solutions was treated theoretically in detail by Brodsky and Tsarevsky.¹⁴ Their theory predicts that the emission current in the threshold region can be represented by the functions $(E - E_0)^2$ or $(E - E_0)^{5/2}$ in the two limiting cases of a more general functional dependence (also given in Ref. 14). The theory by these authors was verified for the emission spectra (published by this laboratory) of ferrocyanide in water and solvated electrons in hexamethyl phosphoric triamide and liquid ammonia.

The Urbach rule¹⁵ is also relevant to the present work. According to this rule, the absorption cross section near the absorption edge varies exponentially with photon energy. This relationship is observed for many amorphous semiconductors,¹⁵ and it also was found to be valid for water.¹⁶

IV. EMISSION SPECTRUM AND PHOTOIONIZATION OF LIQUID WATER

A. Emission Spectrum

The emission spectrum of water is displayed in Fig. 2 for the run with the least contamination, that is, with the lowest emission current. This spectrum differs considerably from the spectrum reported by Nason and Fletcher³ since their spectrum is shifted to lower photon energies by ca. 3 eV with respect to ours. The comparison is approximate since emission currents and not yields are given in Ref. 3. Difference in photon flux,¹⁷ however, cannot account for the very large shift. We suggest that the results in Ref. 3 were affected by contamination by surface-active impurities. We applied the technique outlined¹⁸ in Ref. 3 to our instrument and indeed observed emission below 7 eV. The emission current in fact increased with time and depended on the degree of contamination of the instrument. Moreover, our results are compatible with a study of photoelectron emission by ice by other investigators (Sec. IV.C).

The functional dependence of $Y^{1/a}$ vs. E did not fit the emission spectrum of Fig. 2. Urbach's rule is obeyed and the plot of $\log Y$ against E is linear (Fig. 2). Water exhibits strong hydrogen bonding and has a high dipole moment. These two features should result in a broad range of polarization states of water molecules in the liquid phase. The corresponding density of states thus accounts for the applicability of Urbach's rule. One would expect a somewhat different situation for an ionic emitter because the strong polarization of the medium by the charge on the emitter is then dominant versus dipole-dipole interactions and hydrogen bonding. This is indeed the case (Sec. V).

B. Photoionization of Liquid Water

The exponential dependence of the yield on photon energy precludes the determination of a threshold energy from the data of Fig. 2. The operational threshold for the exponential tail of the emission spectrum in Fig. 2 is judged to be 9.3 ± 0.3 eV. The photoionization energy I of liquid water about 0°C for the most probable configuration should be somewhat higher than the threshold of 9.3 eV. The energy I is at least 9.5 eV and more likely about 10 eV with an uncertainty of approximately ± 0.5 eV. The lower limit of 9.5 eV for the energy I is 0.5 eV higher than the energy of 9 eV predicted by Henglein and coworkers¹⁹ from thermodynamic cycles and a reorganization energy of 1 eV in a vertical transition.

The operational threshold energy of 9.3 ± 0.3 eV may be compared with the value ≤ 6.5 eV claimed for water²⁰ for "internal photoionization" by flash photolysis. The evidence for internal photoionization in Ref. 20 was the detection of the solvated electrons produced by flash photolysis. The difference $9.3 - 6.5 = 2.8$ eV is hardly accountable, and clearly the production of solvated electron by flash photolysis involves a process

different from photoionization of water as occurring in photoelectron emission into the gas phase. The discrepancy is smaller if one compares the energy of ≤ 6.5 eV of Ref. 20 with the threshold energy of 8.4 eV for OH^- ions in solution (Sec. V).

The photoionization energy of water in the gas phase is 12.6 eV, and therefore one estimates 2.6 ± 0.5 eV for the algebraic sum of the following energies: the energy for electronic polarization of the medium by the positive ion produced by photoionization; the energy of the quasifree electron in water with respect to the vacuum level; the surface potential at the water-water vapor interface. The value of 2.6 ± 0.5 eV is significantly lower than the electronic polarization energy of 4.4 eV calculated by Grand et al.²¹

C. Comparison with Photoelectron Emission by Amorphous Ice

The threshold of 9.3 ± 0.3 eV for liquid water is higher than the threshold energy of 8.7 ± 0.1 eV reported by Baron, Hoover and Williams²² for amorphous ice at 13 and 80 K. Other data than those of Ref. 22 obtained by photoelectron spectroscopy (UPS, XPS) of water or ice films on various substrates²³⁻²⁸ cannot be used for comparison with our result because of the uncertainty on the energy reference level (surface potential correction). The shift of 0.6 ± 0.4 eV toward higher photon energies from ice to water may be accounted for by perturbation of the electronic states of water upon condensation²⁹ and by the difference in temperature of the two sets of experiments (cf. temperature dependence of Urbach plots¹⁵). The shift of 0.6 ± 0.4 eV agrees quite well with the shift of ca. 0.5 eV one calculates from the following data: the absolute quantum yield of ca. 1.2×10^{-3} electron per incident photon at 10 eV in Ref. 22; the absolute yields of ca. 3×10^{-5} collected electron per incident photon

in Fig. 2; and the slope of 1.88 per eV for the logarithmic plot in Fig. 2. The calculation is approximate because the slopes of the Urbach plots are not exactly the same for water and ice.

V. EMISSION SPECTRA AND THRESHOLD ENERGIES OF HALIDE AND HYDROXYL IONS

The emission spectra of the halides (except F^-) and hydroxyl ions in aqueous solution are displayed in Fig. 3. The emission spectrum of water is also shown for comparison, and the spectrum of 1,2-ethanediol is given for calibration of yields (Sec. II.C). The emission spectrum of a saturated sodium fluoride solution (≈ 1 M) was identical to that of water, and therefore the photoionization energy of F^- ion in aqueous solution is too high to allow experimental study. No cation effect was observed for lithium, sodium and potassium salts. The proportionality between yield and concentration was verified for the halides in the 0.1 to 2 M range. Incidentally, this proportionality relationship is not obeyed when the instrument is not properly decontaminated.

Yields raised to the power 0.4 and 0.5 according to the Brodsky-Tsarevsky theory¹⁴ are plotted in Fig. 4 over a range of ca. 0.7 to 1 eV. The small constant background in the iodide emission spectrum (Sec. II.B) was subtracted before the plotting of Fig. 4. These plots involve the implicit assumption that the photoionization cross section of the halides in solution is a step function of photon energy. This assumption is quite correct for photodetachment in the gas phase,³⁰⁻³³ but some broadening is to be expected in solution. The $Y^{0.4}$ -plot for iodide in Fig. 4 is indeed linear and yields a threshold energy of 7.2 eV. The less satisfactory $Y^{0.5}$ -plot for this ion yields 7.3 eV, the difference of 0.1 eV between the $Y^{0.4}$ - and $Y^{0.5}$ -plots being typical of the uncertainty from the

extrapolation method. If the range of photon energies is extended above ca. 1 eV, the $\gamma^{0.5}$ -plot for iodide is quite linear whereas the $\gamma^{0.4}$ -plot becomes less linear.

The plots of Fig. 4 for bromide ion deviate significantly from linearity. However, the emission spectrum of this ion consists of two overlapping spectra because of the 0.5 eV spin-orbit coupling observed in the gas phase.³⁰ Linearity for the $\gamma^{0.5}$ -plot was restored after deconvolution. The experimental yield curve A (Fig. 5) was fitted with curve B accounting for the dependence of the yield on $(E - E_1)^2$, where E is the photon energy and E_1 the lower threshold energy. Curve B was then subtracted from the experimental curve A. The resulting curve corresponds to the contribution from photoionization with threshold energy E_2 . The $\gamma^{0.5}$ -plot of this curve (line C in Fig. 5) is indeed linear, and the difference between the threshold energies, $E_1 = 7.9$ eV and $E_2 \approx 8.5$ eV, thus obtained is equal to the splitting energy of 0.5 eV. This analysis, however, leads to the conclusion that the cross section for transition to the $^2P_{3/2}$ state is less than one-fifth of the cross section for the $^2P_{1/2}$ state, and this seems unreasonable.

The plots of Fig. 4 for chloride ion are not satisfactory, and the emission spectrum is best represented by an exponential dependence on photon energy in the threshold region. We tentatively selected 8.7 eV as the threshold energy of this ion in aqueous solution. Conversely, the plots for hydroxyl ion in Fig. 4 are quite linear, and the corresponding threshold energy for this ion is 8.4 eV.

Threshold energies thus obtained are listed in Table I with the corresponding energies at the maxima of the charge-transfer-to-solvent (CTTS) spectra.³⁴ The threshold energies are higher than the CTTS

energies by 1.7 ± 0.1 eV in agreement with the predicted value¹ of this difference. Threshold energies were available only for ferrocyanide ion in aqueous solution at the time of the work in Ref. 1, and verification of the 1.7-eV relationship was tentative because of uncertainty in the assignment of bands in the absorption spectrum of ferrocyanide. This relationship now rests on firmer experimental evidence. It should be pointed out, however, that the difference between threshold energy and the energy at the maximum of the CTTS spectrum may differ from 1.7 eV. The CTTS state is considered³⁴ as rather localized near the central electron-emitting molecule or ion whereas the energy level for the CTTS state referred to the vacuum level may vary from one system to another.

VI. EMISSION SPECTRA OF PHOSPHORIC ACID AND PHOSPHATE IONS

A preliminary study was made of phosphoric acid and phosphate ions to find out the effect of ionic charge on photoionization. The emission spectra are shown in Fig. 6. Yields increase from H_3PO_4 to PO_4^{-3} . The emission for H_3PO_4 is somewhat higher than for water, and the emission of PO_4^{-3} is comparable to that of Br^- but somewhat weaker. The contribution from OH^- ions to emission should be quite negligible for PO_4^{-3} .

Two effects must be considered: (i) the change in solvation energy from H_3PO_4 to PO_4^{-3} ; (ii) the Coulombic interaction between the species produced by photoionization and the quasifree electron being generated by this process. Increase in the solvation energy from one species to another should decrease the corresponding yield at a given photon energy. The Coulombic interaction changes from attraction for photoionization of H_3PO_4 to strong repulsion for PO_4^{-3} . The yields should increase accordingly since geminate recombination is favored for H_3PO_4 and strongly hindered for PO_4^{-3} . The static dielectric constant of liquid water is applicable to solvation

processes to the crude approximation of the Born equation.³⁵ Conversely, the optical dielectric constant of water must be used, to a first approximation,³⁶ in calculating the Coulombic interaction between charged parent species and the free electron being generated. Moreover, the solvation energy is proportional to the square of the ionic valence according to the Born equation whereas the Coulombic interaction with quasifree electrons should depend on the ionic valence. One therefore expects that solvation be dominant with respect to the effect of Coulombic interaction, and one would predict a decrease of yield from H_3PO_4 to PO_4^{-3} . The opposite trend is in fact observed, and the difference in threshold energy of the species H_3PO_4 to PO_4^{-3} in the gas phase offsets the effect of solvation and Coulombic interaction in geminate recombination. A trend similar to that from phosphate ions to phosphoric acid is observed for hydroxyl ion (8.4 eV, Sec. V) to water (9.3±0.3 eV, Sec. IV.B).

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- ³⁶Relaxation must be considered, and the problem is quite involved. See A Mozumder in Electron-Solvent and Anion-Solvent Interactions, L. Kevan and B. C. Webster, eds. (Elsevier, Amsterdam, 1976), pp. 139-173.

TABLE I. Threshold and CTTS-spectrum energies.

| Ion | Threshold energy (eV) | CTTS-spectrum energy ³⁴ (eV) | Energy difference (eV) |
|-----------------|-----------------------|---|------------------------|
| Cl ⁻ | 8.7 | 6.98 | 1.7 |
| Br ⁻ | 7.9 | 6.27 | 1.6 |
| I ⁻ | 7.2 | 5.43 | 1.8 |
| OH ⁻ | 8.4 | 6.63 | 1.8 |

CAPTIONS TO FIGURES

FIG. 1. Schematic diagram of rotating disk target and photomultiplier compartment. A, wire covered with sodium salicylate; B, photomultiplier; C, lithium fluoride window; D, gold grid mesh; E, rotating quartz disk; F, reservoir containing liquid or solution; G, glass tube for cooled gas; H, thermistor; I, platinum wire electrode.

FIG. 2. Yield vs. photon energy for water at 1.5°C (curve A) and Urbach plot (line B).

FIG. 3. Yield vs. photon energy for 2 M solutions of KI (A), KBr (B), KCl (C), KOH (D), and for water (E) and 1,2-ethanediol (F) at 1.5°C.

FIG. 4. Yield to the power 0.4 (top of each plot) and 0.5 (bottom) vs. photon energy for 2 M KI (A), 2 M KBr (B), 2 M KCl (C) and 2 M KOH (D). The scales for the $Y^{0.4}$ and $Y^{0.5}$ plots are different. Data from Fig. 3.

FIG. 5. Yield vs. photon energy for 2 M KBr (curve A). Calculated yield (see text) vs. photon energy in threshold region (curve B). Yield to the power 0.5 vs. photon energy for the curve obtained by subtraction of curve B from curve A (line C).

FIG. 6. Yield vs. photon energy for 1 M solutions of K_3PO_4 (A), K_2HPO_4 (B), KH_2PO_4 (C), H_3PO_4 (D).

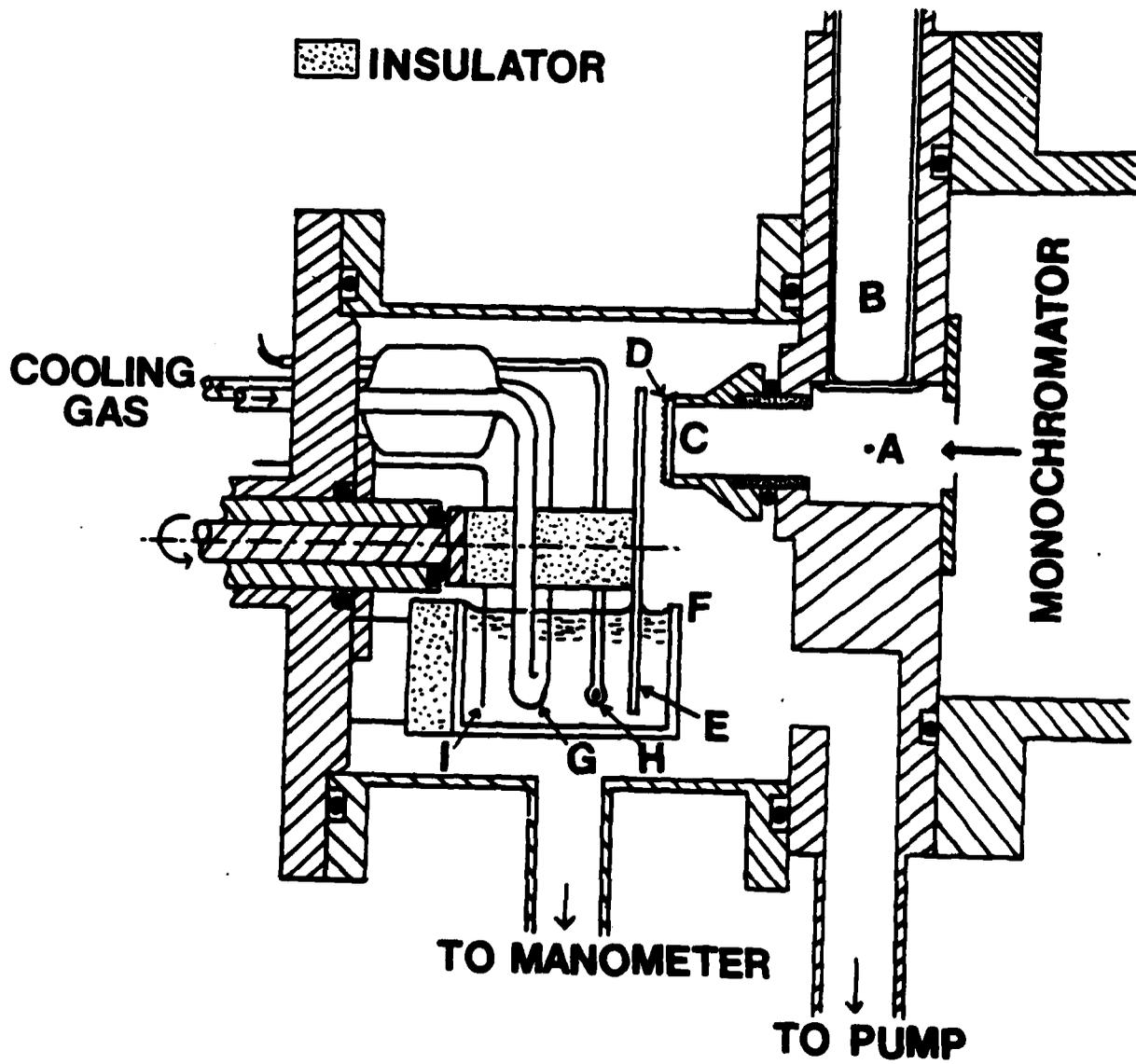


FIG. 1

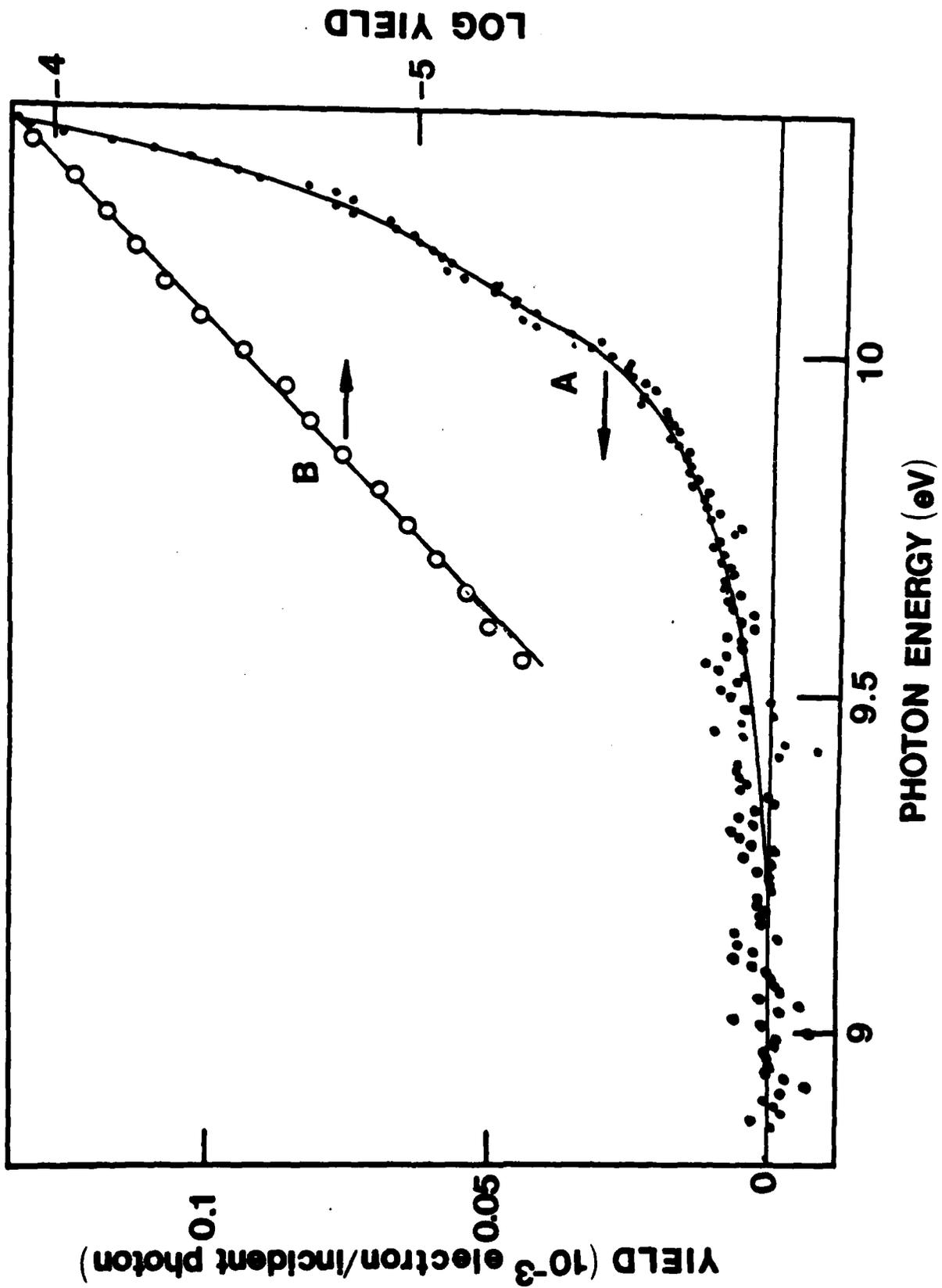


FIG. 2

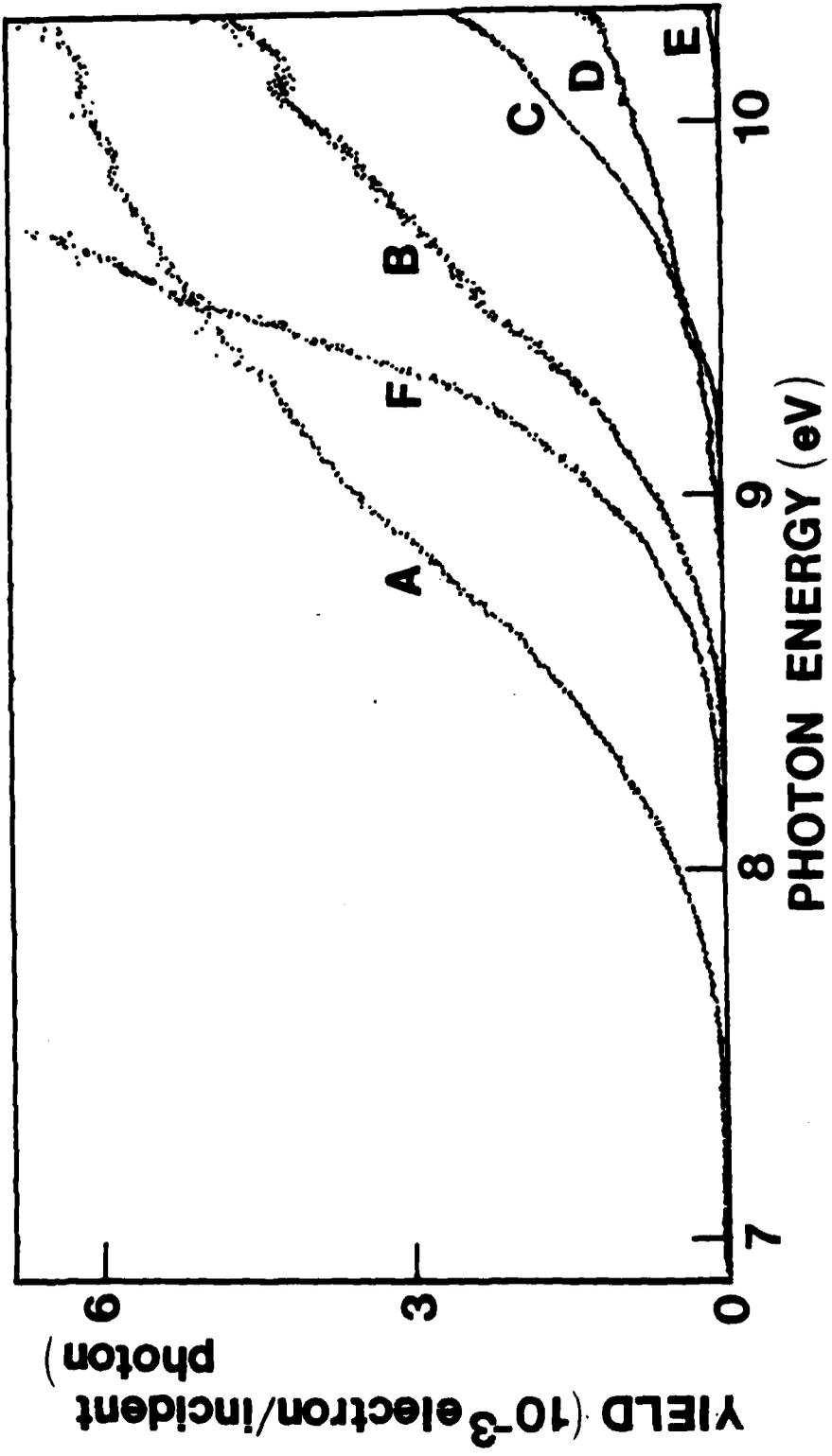


FIG. 3

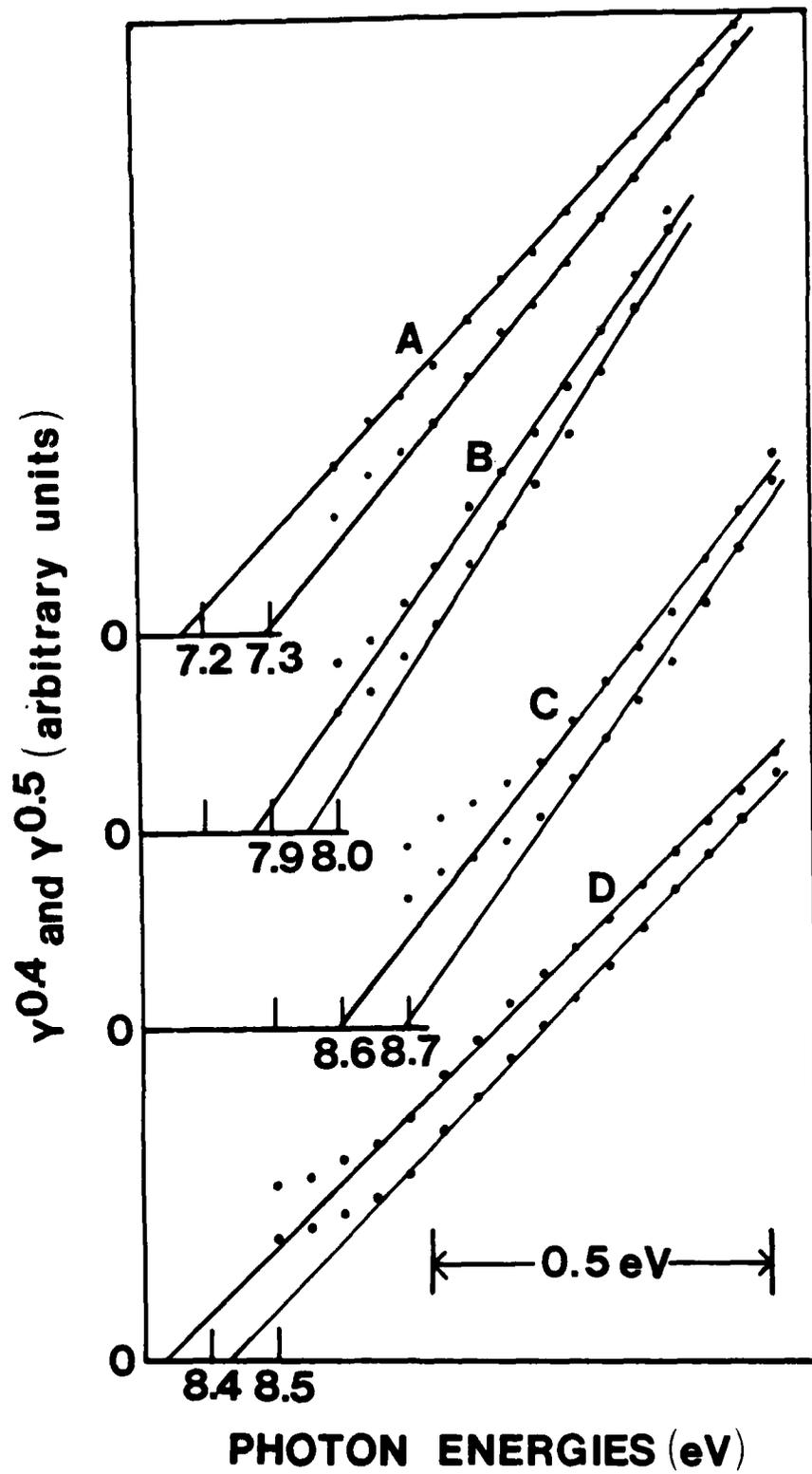


FIG. 4

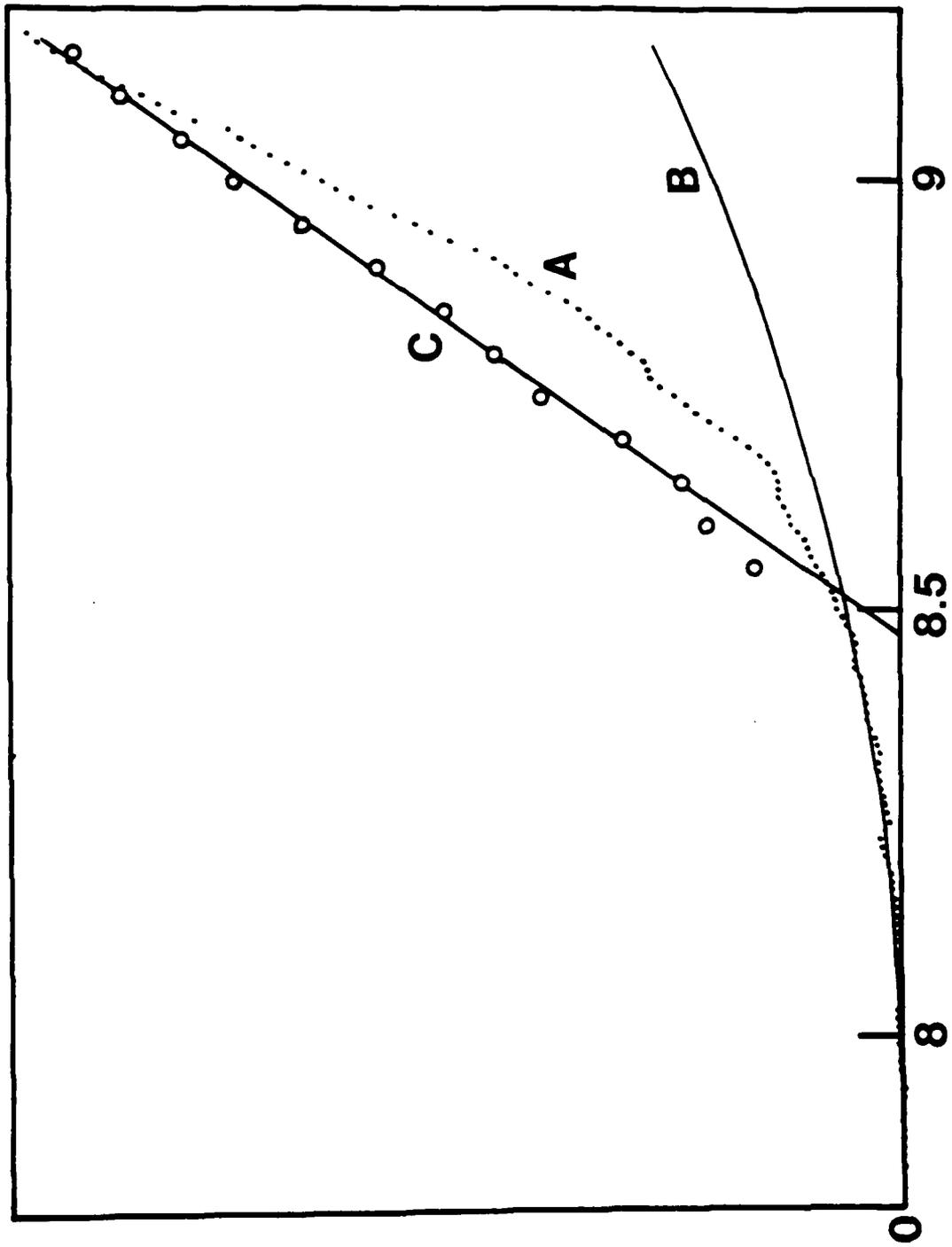


FIG. 5

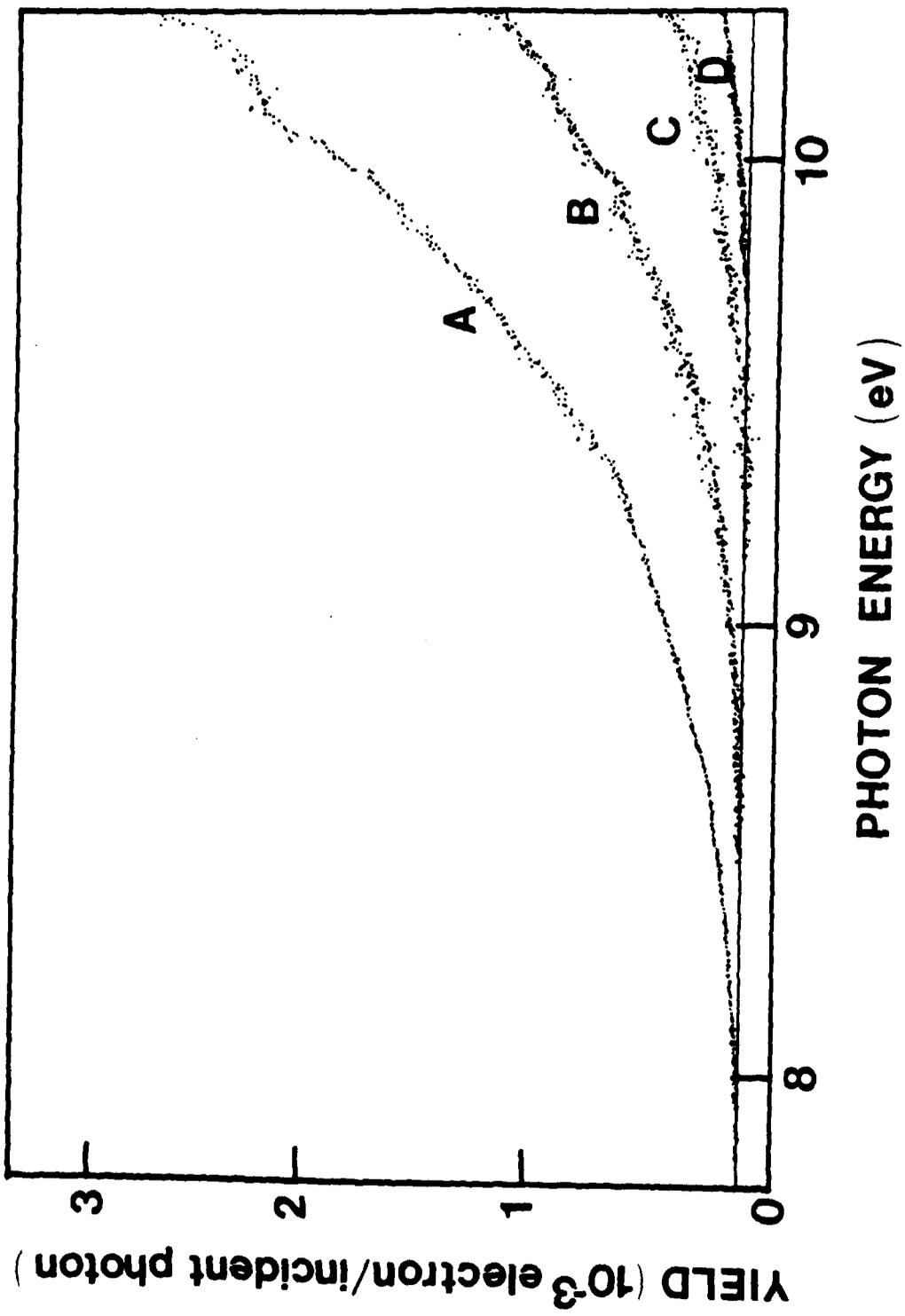


FIG. 6

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