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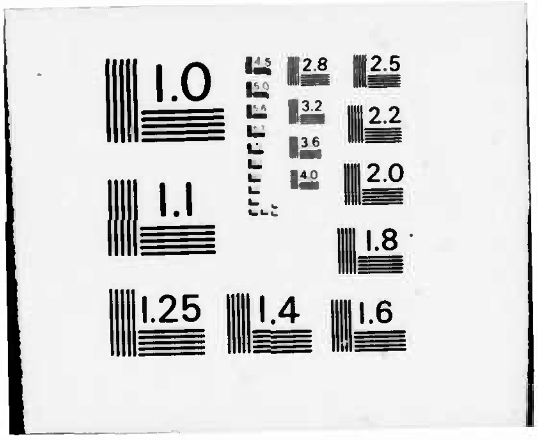
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PHOTOELECTRON SPECTROSCOPY OF LIQUIDS UP TO 21.2 eV

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PHOTOELECTRON SPECTROSCOPY OF LIQUIDS UP TO 21.2 eV

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(Received)

Photoelectron spectroscopy of liquids is investigated at variable photon energy up to 10 eV and with rare-gas resonance lines at 11.7 (ArI), 16.8 (NeI), and 21.2 (HeI) eV. Seven liquids are studied: N-methylaniline, N,N'-dimethyl-p-toluidine, formamide, hexamethyl phosphoric triamide, tetraglyme, ethylene glycol, and n-decanol. Energy distribution curves display at the higher photon energies a band structure matching the sequence of bands in the corresponding gas-phase photoelectron spectra. The bands are attributed to emission of unscattered electrons (no loss of kinetic energy to the liquid), whereas the underlying background is ascribed to scattered (in the liquid) electrons. Quantitative treatment based on this interpretation agrees with experiment. Energies characterizing either bulk or surface photoionization are determined within ±0.1 eV. The gas-liquid red shift (0.9 to 1.4 eV) and bulk-surface blue shift (0.5 to 1.3 eV) in photoionization energies are interpreted in terms of electronic polarization of the liquid medium. This is, to our knowledge, the first investigation of liquids by ultraviolet photoelectron spectroscopy above 10 eV.

I. INTRODUCTION

Photoelectron spectroscopy (PS) of liquids and solutions has been developed to the point of providing three types of basic information about photoionization (PI) in liquids and solutions[1-6]: _spectra_, _mechanisms_ and energies. Applications thus far include pure liquids[4-6] and solutions of solvated electrons,[3] inorganic ions,[4] metal complexes,[4] and organic radicals[1] in a continuous spectral range from 1 to 10 eV. These results were interpreted,[1,2] in good agreement with experiment, by assuming that all electrons underwent multiple scattering in the liquid, with loss of kinetic energy, prior to emission into vacuum. Results from solid-state PS suggest that significant emission might be observed without loss of kinetic energy to the liquid medium at photon energies above the range explored thus far. The present investigation was undertaken to test this inference and to extend the range of application of PS of liquids above the 10 eV limit of our previous work. The ArI, NeI and HeI resonance lines at[7] 11.7, 16.8 and 21.2 eV, respectively, were selected for this work. Some additional measurements were also carried out at photon energies at or below 10 eV. The liquids studied here were chosen because of their sufficiently low ($< 10^{-2}$ torr) vapor pressure upon cooling[1] and because several of them had been used as solvents in our previous work.[1,3-5]

II. EXPERIMENTAL

Instrumentation is described in some detail in a report[8] available upon request, and only some essential points are summarized here. Our previous instrument[4,5] was used with the main modifications listed below.

The monochromator and mirror system were removed (except in experiments at and below 10 eV) and replaced by a resonance lamp located in the bell jar of the instrument. This was a modified version of the lamp described by Baker and coworkers.[9,10] It operated equally well with argon, neon or helium. The photon flux ($\sim 10^{13}$ photons per sec) of the lamp was attenuated (by 10^{-2} to 10^{-3}) by means of small holes in series to avoid excessively high photocurrents ($\gtrsim$ 200 picoamp) and the attending space charge problem. The attenuated beam from the lamp was carefully aligned on the center of the rim of the rotating disk target.

The trough containing the liquid and the lower chamber of the rotating disk target were modified[8] to allow operation at temperatures as low as -50°C (versus the previous limit of -15°C). The guard plate of the rotating disk, the collector electrode and the outer grid were coated with graphite (Acheson "Aquadag") to achieve uniform contact potential.

The retarding potential was supplied by a staircase ramp in steps of 0.05 V at 0.3 or 0.6 Hz (synchronized with the 1.2 Hz for rotation of the disk target). Data on retarding potential curves were recorded in digital form for further computer processing. This was essential because of the large number of data, e.g., 400 points per curve over a 20-V interval. Analog/digital conversion was accomplished accurately by means of a Fluke 8800A autoranging digital voltmeter (5-1/2 BCD digits) interfaced to an ASR33 Teletype unit. Data were simultaneously recorded on paper tape for permanent storage and transmitted by telephone to either a Hewlett-Packard 3000 or a CDC 6600 computer. Further details are given in Ref. 8.

The energy distribution curve (EDC) corresponding to the retarding potential curve being recorded in digital form was displayed by an analog recorder for monitoring purposes. The EDC's and second derivative curves (SDC) actually used were obtained more accurately by computer differentiation of the digitalized retarding potential curve. A single-pass seven-point linear smoothing[11] was applied. All curves were computer plotted.

The retarding potential corresponding to zero kinetic energy was determined by measuring the Volta (or contact) potential between the liquid and the collector.[12] Six regularly-spaced depressions of 1 mm maximum depth were machined along the rim of the rotating disk. The capacity between the disk and the collector electrode thus exhibited six periodic and nearly sinusoidal full cycles per turn of the disk. The resulting a.c. signal at 7.2 Hz was amplified selectively, rectified, and fed into the analog/digital conversion system. The capacity current was measured as a function of retarding potential, and the resulting V-shaped curve was linearly smoothed. The average electric field between the emitting liquid surface and the collector electrode was equal to zero at the minimum of the V-plot, and the retarding potential at this point corresponded to zero kinetic energy. This minimum was determined before and after the recording of each retarding potential curve to ascertain the absence of drift due to spurious variation in contact potential. The method is simple, quite accurate (to ±0.05 eV) and applicable regardless of the vapor pressure of the liquid being studied. It is definitely superior to the method applied[13] in Ref. 6.

All liquids were purified by vacuum distillation and were rendered electrically conductive by addition of a trace ($< 10^{-3}$M) of electrolyte.[4,5]

III. DESCRIPTION OF RESULTS

Experimental EDC's are presented in Fig. 1 to 7 for liquid N-methylaniline (NMA), N,N'-dimethyl-p-toluidine (DPT), formamide (FAM), and ethylene glycol (ETG). The effect of varying the vapor pressure on the EDC is exemplified in the HeI EDC of NMA in Fig. 1. The three pressures are approximate since they were computed from the Antoine equation over an extended temperature range.[14] The effect of varying the photon energy is illustrated for NMA in Fig. 2 to 4. The HeI EDC's of liquid NMA, DPT and FAM are displayed together with their gas-phase photoelectron spectra[15,16] in Fig. 2, 5 and 6, respectively.

The following observations are made about Fig. 1 to 7:

(i) The positions and shapes of the EDC's of NMA in Fig. 1 are not significantly affected as the vapor pressure of this liquid is increased by approximately two orders of magnitude. The background below the EDC bands, however, increases with pressure.

(ii) There is a noticeable resemblance between the HeI EDC's and the gas-phase photoelectron spectra in Fig. 2, 5 and 7. Thus, the sequence of EDC maxima at 7.1, 8.6 and 9.8 eV for NMA match the 7.73, 9.03 and 10.24 eV maxima in the gas-phase spectrum in Fig. 2. Furthermore, the humps and the broad maximum in the EDC in Fig. 2 have their counterparts in the two high-energy bands in the gas-phase spectrum. Similar correlations hold between the HeI EDC's of DPT (Fig. 5) and FAM (Fig. 6) and the corresponding gas-phase spectra.

(iii) There is a red shift in the value of 21.2 - T_{max} (T_{max}, kinetic energy at the maximum of the band) in going from gas to liquid in Fig. 2, 5 and 6.

(iv) The EDC maxima for NMA disappear progressively with decreasing photon energy (Fig. 2-4) and ultimately only two humps are displayed in the 10 eV EDC. Similar observations were made for all the other liquids studied in this work. Ethylene glycol (Fig. 7) is an extreme case with no maximum and only humps in the HeI EDC.

(v) The major fraction of electrons emitted into vacuum (proportional to the area under the EDC) consists of electrons having kinetic energies below ~ 3 eV in vacuum for all HeI EDC's.

IV. SCATTERED AND UNSCATTERED ELECTRONS

We first rule out gas-phase PI as an explanation for the EDC maxima for the following reasons: (i) The band shapes in Fig. 1 are not significantly changed from 10^{-4} to 10^{-2} torr. (ii) The EDC maxima are significantly red-shifted with respect to the gas-phase PI energies. (iii) The pressure-dependent background in Fig. 1, indicating a contribution from gas-phase PI (especially at ~ 10^{-2} torr), was quite negligible at the pressures prevailing in the EDC determinations in this work.

The results of this work will be interpreted by assuming simultaneous emission of scattered and unscattered electrons into vacuum. By "scattered" electrons we designate electrons having undergone multiple scattering in the liquid with loss of kinetic energy prior to emission into vacuum. Conversely, "unscattered" electrons are emitted into vacuum without loss of kinetic energy to the liquid medium. The experimental EDC represents the sum of the contributions to total emission by scattered and unscattered electrons.

The EDC for scattered electrons for a substance undergoing multiple PI, such as NMA, exhibits a series of humps but no maximum[2] (except the always present maximum at low kinetic energies). Each PI process appears in the EDC as a hump, provided, of course, that the PI bands are well-resolved. Conversely, the EDC for unscattered electrons exhibits a series of Gaussian-like bands corresponding to each of the PI processes. These bands reflect the distribution of quasifree electrons upon generation by PI in the liquid. The relative contributions of the two types of EDC's depend on photon energy, and the contribution from unscattered electrons is enhanced with increasing photon energy (Fig. 2 to 4) in the range covered in this work. Band enhancement varies considerably from one substance to another, even in the same range of kinetic energies (Fig. 2 to 7). Ethylene glycol (Fig. 7) represents an extreme case with no band and only humps [just as does n-decanol (EDC not shown)]. In conclusion, at a given photon energy, the bands for unscattered electrons are superimposed on a background for scattered electrons, which increases with decreasing kinetic energy.

To a first approximation, the relative contribution of scattered electrons to total emission in a given interval of kinetic energy is proportional to the range of quasifree electrons in the liquid.[2,17] We define the range here as the average net linear displacement of quasifree electrons in the liquid for a loss of kinetic energy from one given value to another. The range thus depends on the rate of transfer of kinetic energy to the liquid medium. This rate, according to results from radiation chemistry[18] and reflectance spectroscopy,[19-21] increases rapidly with kinetic energy (in the interval covered here) above kinetic energies of the order of the lowest electronic transition of the liquid. Therefore, the range for a loss of kinetic energy from 15 to 5 eV, for instance, is much shorter than the range for a loss from 5 eV to thermalization. In fact, it appears from evidence in Sec. V-C that emission of unscattered electrons is limited, at most, to a layer a few molecules thick adjacent to the liquid-vacuum interface. Emission of unscattered electrons tends to be primarily a surface process, whereas emission is essentially a bulk process for scattered electrons. Separation of the two contributions is treated quantitatively in Sec. VI after the prerequisite determination and discussion of PI energies in Sec. V.

V. PHOTOIONIZATION ENERGIES

A. Determination from EDC's and SDC's

PI energies[22] can be determined, in principle, from EDC's of either scattered or unscattered electrons. Such determinations are feasible, for all practical purposes, only when one type of emission (scattered or unscattered electrons) is predominant to the extent that the other type does not affect significantly the PI energies thus obtained. This requirement for determinations of PI energies is met, as favorably as feasible (Sec. IV), at low (~ 10 eV) and high (21.2 eV) photon energies for scattered and unscattered electrons, respectively, at least in the range of photon energies covered in this work. In all cases, the photon energy should exceed the PI energy being measured by at least 2 to 3 eV to avoid EDC distortion in the kinetic energy interval of interest by the threshold function for transmission through the liquid-vacuum interface.

The determination of PI energies from EDC's for unscattered electrons is the more direct of the two foregoing methods, and it will be discussed first. The EDC then reflects the distribution of quasifree electrons upon generation, and consequently the procedure followed in gas-phase PS[23] can be transposed directly. Thus,

$$I(\mathrm{EDC}) = E - T_{max}(\mathrm{EDC}) \qquad (1)$$

where I(EDC) and E are the PI and photon energies, respectively, and T_{max}(EDC) is the kinetic energy at the maximum of the EDC band. Values of I(EDC) listed[24] in Table I were obtained from Eq. (1) at 16.8 and

21.2 eV to ascertain the lack of significant influence from the background of scattered electrons. The difference between the two determinations was within experimental error (±0.1 eV).

We now turn to the method for obtaining PI energies from EDC's for scattered electrons. The characteristic point of the EDC is now the point of inflection.[2] This point can be determined most conveniently by differentiating the EDC with respect to kinetic energy, that is, by obtaining the second derivative curve (SDC) of the photocurrent with respect to retarding potential. One then has[6] (see, also, Appendix)

$$I(\mathrm{SDC}) = E - T_{\mathrm{max}}(\mathrm{SDC}) - 0.52w(\mathrm{SDC}) \qquad (2)$$

where $T_{\mathrm{max}}(\mathrm{SDC})$ is the kinetic energy at the SDC maximum and w(SDC) is the halfwidth of the SDC as measured on the high kinetic energy side. The value of w(SDC) ($\sim$ 0.5 eV) was read directly on the experimental SDC's. Equation (2) was derived[6] from the theory of Ref. 2 and rests on two main assumptions: a Gaussian distribution of quasifree electrons upon generation and superposition of experimental EDC's by the procedure of Ref. 1. The first assumption is not rigorous but reasonable, and the second one was verified experimentally. It follows from Eq. (2) that SDC's should exhibit maxima independent of E when plotted against E - T, where T is the kinetic energy. This is indeed the case (Fig. 3) except when E is too low (e.g., 7.65 eV) to preclude distortion by the threshold function.[25] The random shift of ±0.1 eV in the position of the maxima was caused by the relative inadequacy of the light source and possibly minor shifts in the point of zero kinetic energy.

Values of I(SDC) listed in Table I were obtained at 10 and 11.7 eV, except for FAM and HMPA, to verify the lack of significant interference by unscattered electrons. The agreement is within the experimental error (±0.1 eV). The values of I(SDC) in Table I will be compared with gas-phase PI energies and values of I(EDC) from unscattered electrons in the next two subsections.

B. Gas-Liquid Red Shift

Values of I(SDC) in Table I are lower than the corresponding gas-phase PI energies, I_g, by 0.9 to 1.4 eV. The major part of the gas-liquid red shift, $\Delta I_{gl} = I_g - I(SDC)$, can be attributed[6] to the stabilization of the positively-charged ion (produced by PI) by electronic polarization, P_e, of the medium. The orientation polarization need not be considered for vertical processes. The barrier at the liquid-vacuum interface and molecular terms[26-28] also contribute to ΔI_{gl}. The electronic polarization energy, P_e, is readily computed by assuming that the ion produced by PI is a pointlike charge, e, at the center of a spherical cavity of radius a in the bulk of a continuous medium of optical dielectric constant ε_o. Thus,[6]

$$P_e = -(e^2/2a)[1 - (1/\varepsilon_o)] \tag{3}$$

$$a = [(3/4\pi)(M/\delta N_A)]^{1/3} \tag{4}$$

where M is the gram molecular weight, δ the density of the liquid, and N_A Avogadro's number. Values of P_e thus obtained vary from 1.0 to 1.5 eV for the liquids of Table I. The model for the calculation of P_e is quite crude but does show that ΔI_{gl} and P_e are of the same magnitude.

C. Bulk-Surface Blue Shift

Values of I(EDC) for unscattered electrons in Table I are higher than the corresponding energies I(SDC) by 0.5 to 1.3 eV. This blue shift, ΔI_{bs}, is attributed to the difference between the PI energies of a molecule in the bulk of the liquid and in the liquid-vacuum interfacial region. A significant contribution to the bulk-surface shift, ΔI_{bs}, is due to asymmetric electronic polarization of the liquid by the ions generated by PI in the interfacial layers. The electrical field of these interfacial ions (produced by PI) is, to a first approximation, half in the dielectric and half in vacuum. The stabilization energy resulting from electronic polarization of the medium therefore is roughly one-half of the electronic polarization, P_e, calculated in Sec. V-B. The PI energy is raised accordingly by $\sim P_e/2$, that is, by 0.5 to 0.8 eV for the liquids of Table I. The asymmetry of the electrical field becomes quite minor at depths beyond a few molecular dimensions and therefore is quite characteristic of surface states.

VI. QUANTITATIVE TREATMENT OF EDC'S AND SDC'S

A. Theory

The EDC's and SDC's with simultaneous emission of unscattered and scattered electrons will now be accounted for quantitatively. The EDC theory[2] based on a random walk model with loss of kinetic energy to the liquid medium will be applied for the two simplifying conditions stated before in Sec. V-A. The two parameters of the EDC for scattered electrons are the bulk PI energy, I(SDC), and the width, w_b, of the Gaussian distribution of quasifree electrons upon generation by PI in the bulk of the liquid. The two parameters of the EDC for unscattered electrons are the surface PI energy, I(EDC), and the width, w_s, of the distribution upon generation supposed to be Gaussian. The widths w_b and w_s are not assumed to be necessarily equal. The energies I(SDC) and I(EDC) are determined directly from experiment (Sec. V-A). The width w_b is related[6] to the halfwidth w(SDC) of Eq. (2) by $w(SDC) = 1.242(w_b/2)$ and is therefore readily obtained from experiment. The width w_s is read on the EDC band for unscattered electrons and, if necessary, is corrected as mentioned below.

The four parameters I(SDC), I(EDC), w_b, and w_s represent first approximations because experimental SDC's are somewhat distorted by a contribution from unscattered electrons, and, vice versa, experimental EDC bands for unscattered electrons are superimposed on a background for scattered electrons. Thus, the SDC and EDC maxima are somewhat shifted from the energies to be expected in the absence of distortion, and the widths w_b and w_s are also slightly off for the same reason. A correction for w_s was made by a single iteration in the application of Sec. VI-B.

We introduce the dimensionless parameters

$$z = (1.665/w_b)\{T - [E - I(SDC)]\} \qquad (5)$$

$$z_o = (1.665/w_b)[I(SDC) - I(EDC)] \qquad (6)$$

and write the EDC equation

$$dN/dz = F(z)/F(z_o) + k \exp\{-[(z - z_o)(w_s/w_b)]^2\} \qquad (7)$$

where F(z) is the contribution from scattered electrons according to Ref. 2, Eq. A(8), k is an adjustable parameter characterizing the contribution from unscattered electrons, and N is a dimensionless quantity proportional to the photocurrent. One has $dN/dz = 1 + k$ at $z = z_o$, where 1 and k represent the contributions from scattered and unscattered electrons, respectively. The meaning of k thus is immediate. The SDC equation is obtained[29] by differentiation of Eq. (7) according to the treatment of parabolic cylinder functions in Ref. 30.

The extent of SDC distortion for a varying contribution from unscattered electrons can be judged from Fig. 9. The values $z_o = -2$ of Fig. 9 corresponds to the order of magnitude of the bulk-surface shifts in Table I and experimental widths. The EDC for $k = 0.3$ would exhibit a maximum since d^2N/dz^2 changes sign. Figure 9 also shows the progressive shift of the SDC maximum as k increases, i.e., a shift of ca. 0.5 unit of z in absolute value (~ 0.2 eV for $w_b \sim 0.6$ eV) from $k = 0$ to 0.3.

B. Application

The theory was applied to the lowest PI of NMA at I(SDC) = 6.4 eV (Table I) and the resulting calculated SDC's and EDC's are compared with the experimental curves in Fig. 10 and 11, respectively. The width w_s of the band for unscattered electrons at I(EDC) = 7.1 eV (Table I) could not be read directly because of a non-negligible background of scattered electrons. The resulting EDC widening was estimated at 20% by application of Eq. (7), and the width w_s after this correction was $1.2w_b$. The greater distribution width for unscattered electrons than for scattered electrons arises apparently from the dependence of the asymmetric electronic polarization (Sec. V-C) on the depth from the liquid-vacuum iterface.

The agreement between experimental and calculated SDC's and EDC's in Fig. 10 and 11 is good, especially if one considers that the analysis involves only a single adjustable parameter (k) and that the other parameters are experimental.[31] Departure from calculated curves at the lower kinetic energies is caused (except for k = 0 in Fig. 10) by overlapping of the next PI transition and not by failure of the theory. This point was ascertained by calculating the extent of overlapping from theory.

The contribution from unscattered electrons increases with photon energy from k = 0.08 at 10 eV to k = 2.8 at 21.2 eV. In fact, the SDC calculated for k = 0 agrees quite well with the experimental SDC in Fig. 10, except at the lower kinetic energies. The unscattered electron contribution is already quite important at 11.7 eV (k = 0.5) and the ArI EDC indeed exhibits a maximum. The maxima of the 10 eV and ArI SDC's correspond to I(SDC) = 6.4 and 6.3 eV (Table I), respectively, whereas one would have expected from Fig. 9 a shift of ~ 0.2 eV in the opposite direction. This disagreement with theory is nearly at the limit of experimental errors of ±0.1 eV.

VII. CONCLUSION

Three conclusions are reached: (i) Photoelectron spectroscopy of liquids, explored here up to 21.2 eV, is experimentally feasible and yields reliable data. (ii) Results can be interpreted quantitatively by assuming simultaneous emission of unscattered and scattered electrons (in the sense discussed in the paper). (iii) Energies characterizing either bulk or surface photoionization can be determined and interpreted. This is, to our knowledge, the first investigation of liquids[32] by ultraviolet photoelectron spectroscopy above 10 eV.

ACKNOWLEDGMENT

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APPENDIX: QUALITATIVE INTERPRETATION OF SDC'S

We present here a qualitative discussion of EDC's and SDC's which supplements the fairly elaborate quantitative theory of Ref. 2. The emission process is divided into the following three consecutive steps: (i) generation of quasifree electrons by PI in the liquid; (ii) transport of quasifree electrons in the liquid; (iii) transmission through the liquid-vacuum interface. Consider step (i) in a slab of thickness δx at a depth x from the interface. Assume that the energy distribution of quasifree electrons generated in this slab travels toward the interface without distortion but with a loss of kinetic energy increasing in a monotonic fashion with the depth x. The energy distribution for emission from the liquid into vacuum is obtained by summation of the contributions from all the slabs of thickness δx from $x = 0$ (the slab at the interface) to the maximum depth from which emitted electrons can originate. This maximum depth is determined by the maximum kinetic energy available for transfer to the liquid medium. This summation process yields, in this qualitative interpretation, the experimental EDC. The distribution therefore can be reclaimed by differentiation of the EDC with respect to kinetic energy, that is, by obtaining the SDC.

The drastic simplification made here about the traveling undistorted distribution is, of course, not introduced in the quantitative treatment of Ref. 2. The problem is treated instead as a random walk with energy transfer to the liquid medium.

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[22] More accurately, we should refer[6] to external PI energies since electrons are collected in vacuum in PS of liquids. Conversely, internal PI energies pertain to experiments, such as photoconductivity measurements, in which electrons are collected in the liquid. Moreover, PI energies to be discussed characterize a vertical transition from the most probable ground state configuration in the liquid.

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[24] I(SDC) for ethylene glycol are not listed because they varied with photon energy by more than ±0.1 eV. I(SDC) $\approx$ 9.5 eV for n-decanol is tentative.

[25] Figure 8 supersedes a similar figure in Ref. 6 which was prepared with a less accurate point of zero kinetic energy than the present Fig. 8.

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TABLE I. Photoionization Energies, Shifts, and Electronic Polarization

Substance[a]	E (eV)	I^b(EDC) (eV)	I^b(SDC) (eV)	$I_g{}^c$ (eV)	$\Delta I_{g1}{}^d$ (eV)	$\Delta I_{bs}{}^e$ (eV)	$P_e{}^f$ (eV)
NMA	10.0		6.4	7.73	1.3		1.2
			7.9	9.03	1.1		
	11.7		6.3	7.73	1.4		
			7.9	9.03	1.1		
			9.3	10.24	0.9		
	16.8	7.1				0.7	
		8.8				0.9	
	21.2	7.1				0.7	
		8.6				0.7	
		9.8				0.5	
DPT	10.0		6.1	7.48	1.4		1.0
	11.7		6.1		1.4		
	16.8	6.9				0.8	
	21.2	6.8				0.7	
FAM	11.7		8.9	10.33	1.4		1.4
	16.8	10.0				1.1	
	21.2	9.8				0.9	
HMPA	11.7		7.0				1.5
			9.1				
	16.8	8.3				1.3	
		9.8				0.7	
	21.2	8.3				1.3	
		10.0				0.9	

TGL	10.0		8.3		1.0
	11.7		8.4		
	16.8	9.4		1.1	
	21.2	9.3		1.0	

---

[a] NMA, N-methylaniline; DPT, N,N'-dimethyl-p-toluidine; FAM, formamide; HMPA, hexamethyl phosphoric triamide; TGL, bis-2(2'-methoxy-ethoxy)-ethyl ether (tetraglyme).

[b] Within ±0.1 eV.

[c] See Fig. 2, 5 and 6, respectively.

[d] Gas-liquid red shift in absolute value.

[e] Bulk-surface blue shift in absolute value

[f] At 25°C.

LIST OF FIGURES

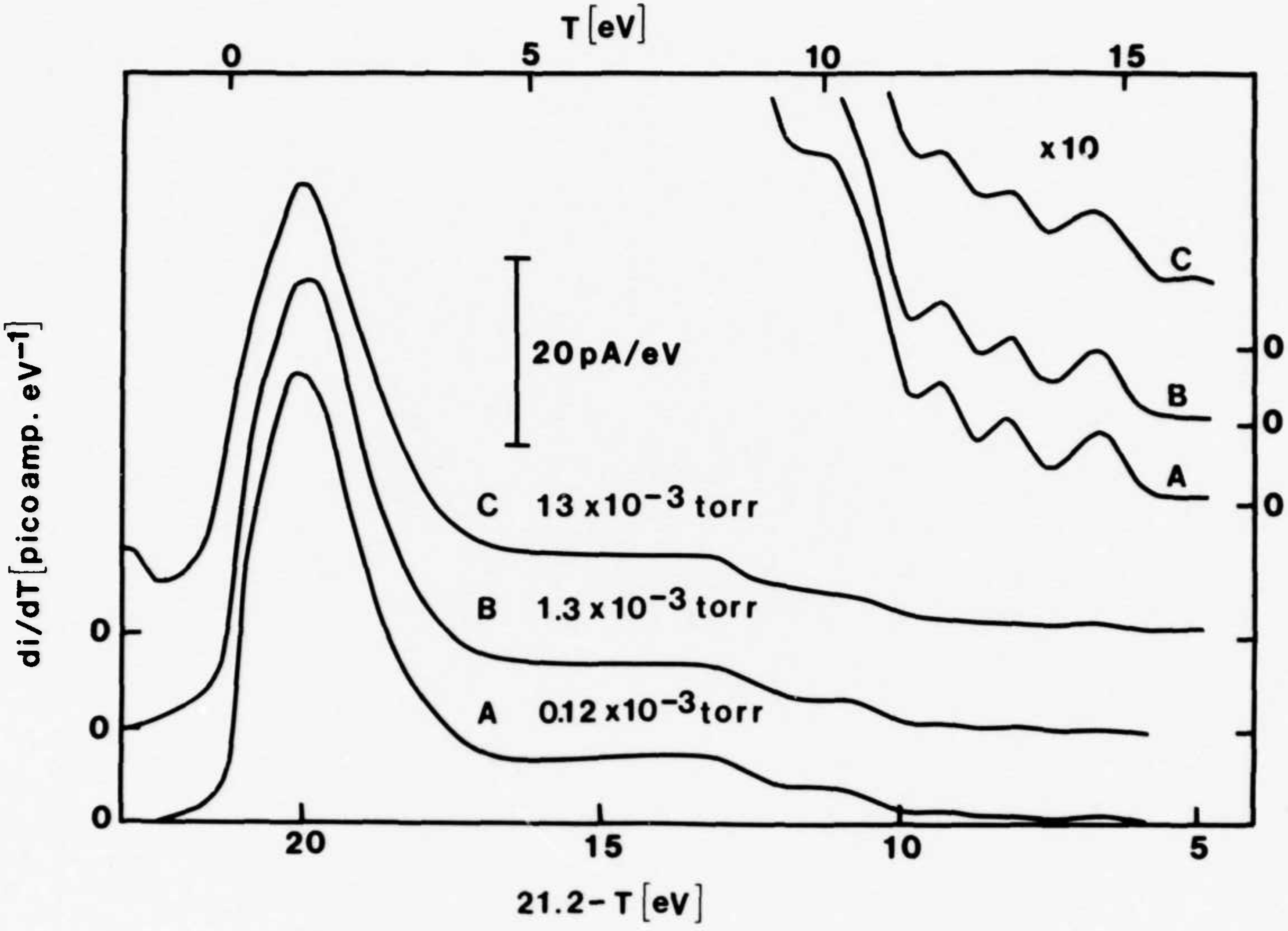
T [eV]
0
5
10
15
x10
C
B
A
0
0
0
20pA/eV
C 13 x10^-3 torr
B 1.3 x10^-3 torr
A 0.12 x10^-3 torr
di/dT [picoamp. eV^-1]
0
0
0
20
15
10
5
21.2-T [eV]

FIG. 1

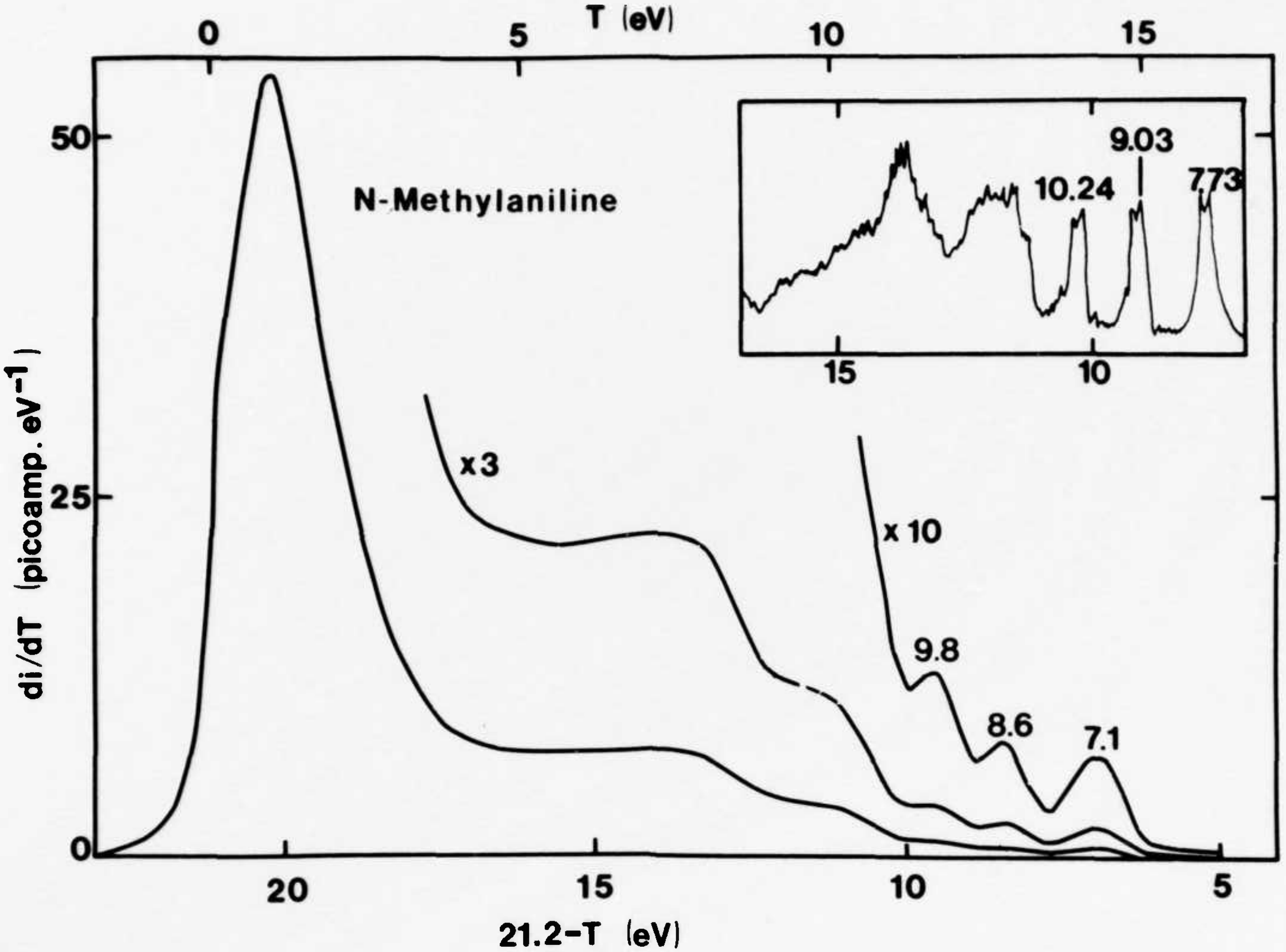
T (eV)
0
5
10
15
50
25
0
di/dT (picoamp. eV⁻¹)
N-Methylaniline
x3
x 10
9.8
8.6
7.1
10.24
9.03
7.73
15
10
20
15
10
5
21.2−T (eV)

FIG. 2

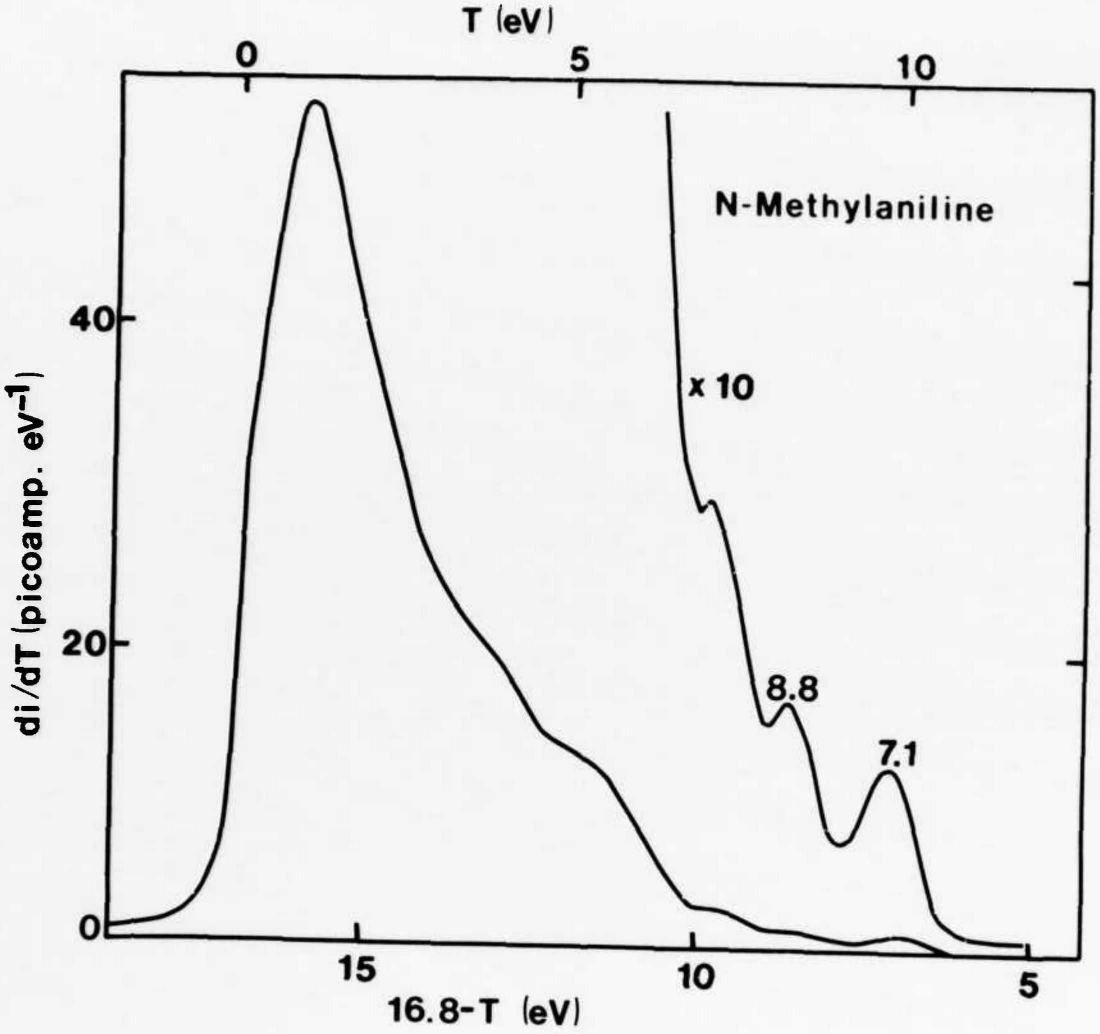
T (eV)
0
5
10
N-Methylaniline
x 10
8.8
7.1
di/dT (picoamp. eV^{-1})
40
20
0
15
10
5
16.8-T (eV)

FIG. 3

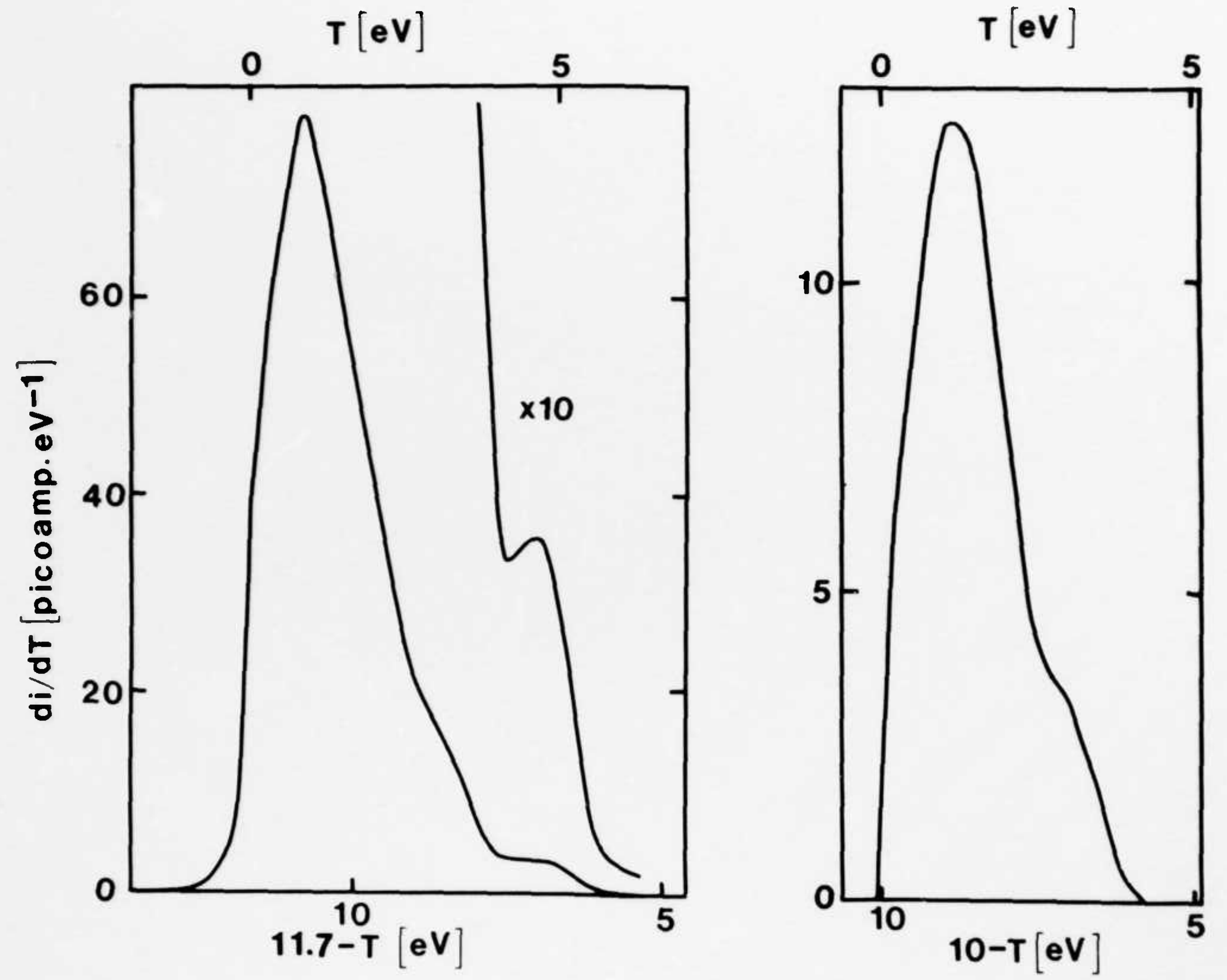
T [eV]
0
5
60
40
20
0
di/dT [picoamp.eV−1]
x10
10
5
11.7−T [eV]
T [eV]
0
5
10
5
0
10
5
10−T [eV]

FIG. 4

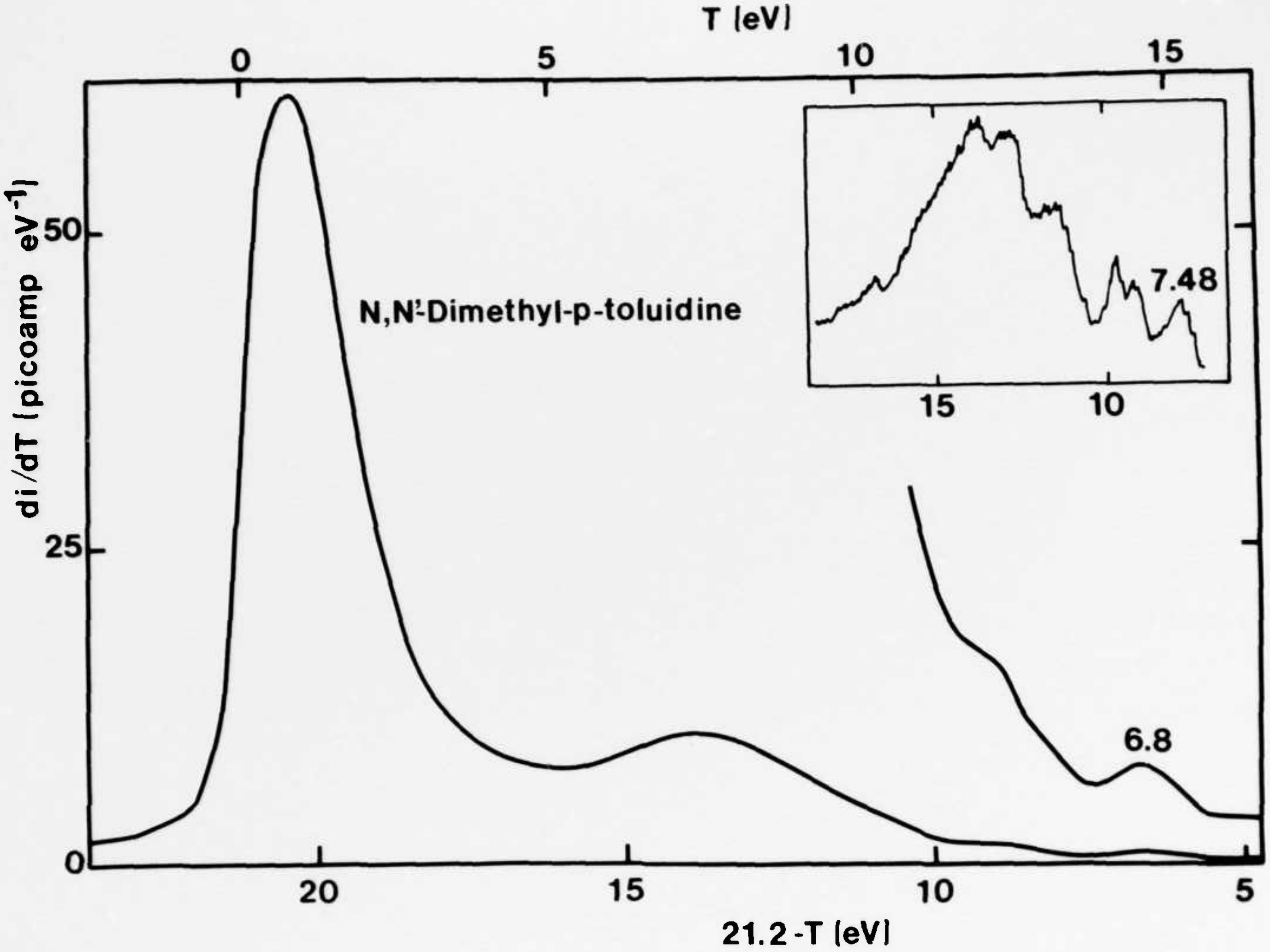
T (eV)
0
5
10
15
di/dT (picoamp eV^{-1})
50
25
0
N,N'-Dimethyl-p-toluidine
15
10
7.48
6.8
20
15
10
5
21.2 - T (eV)

FIG. 5

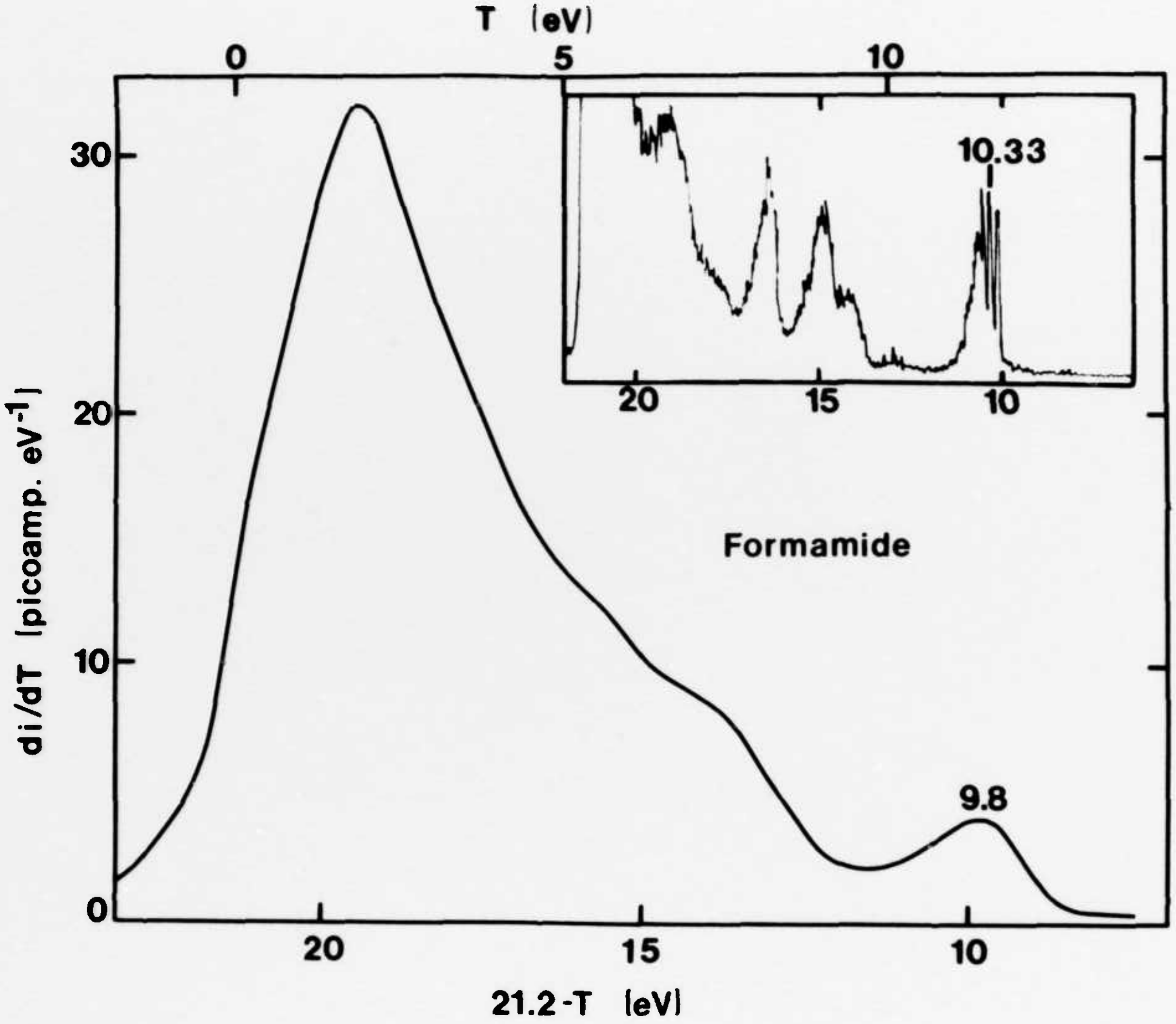
T (eV)
0
5
10
di/dT (picoamp. eV^{-1})
30
20
10
0
10.33
20
15
10
Formamide
9.8
20
15
10
21.2-T (eV)

FIG. 6

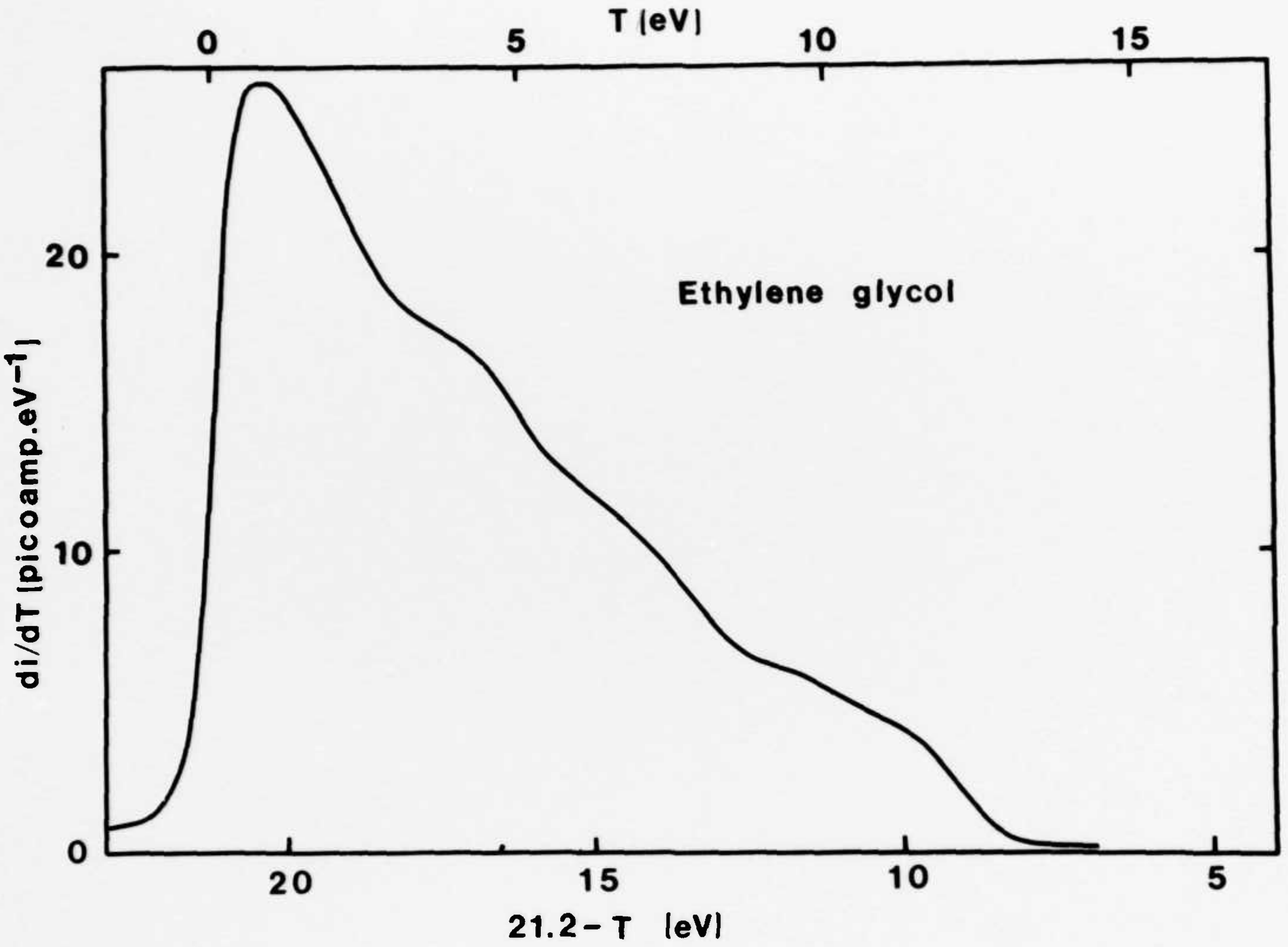
T (eV)
0
5
10
15
20
10
0
di/dT (picoamp.eV⁻¹)
Ethylene glycol
20
15
10
5
21.2 − T (eV)

FIG. 7

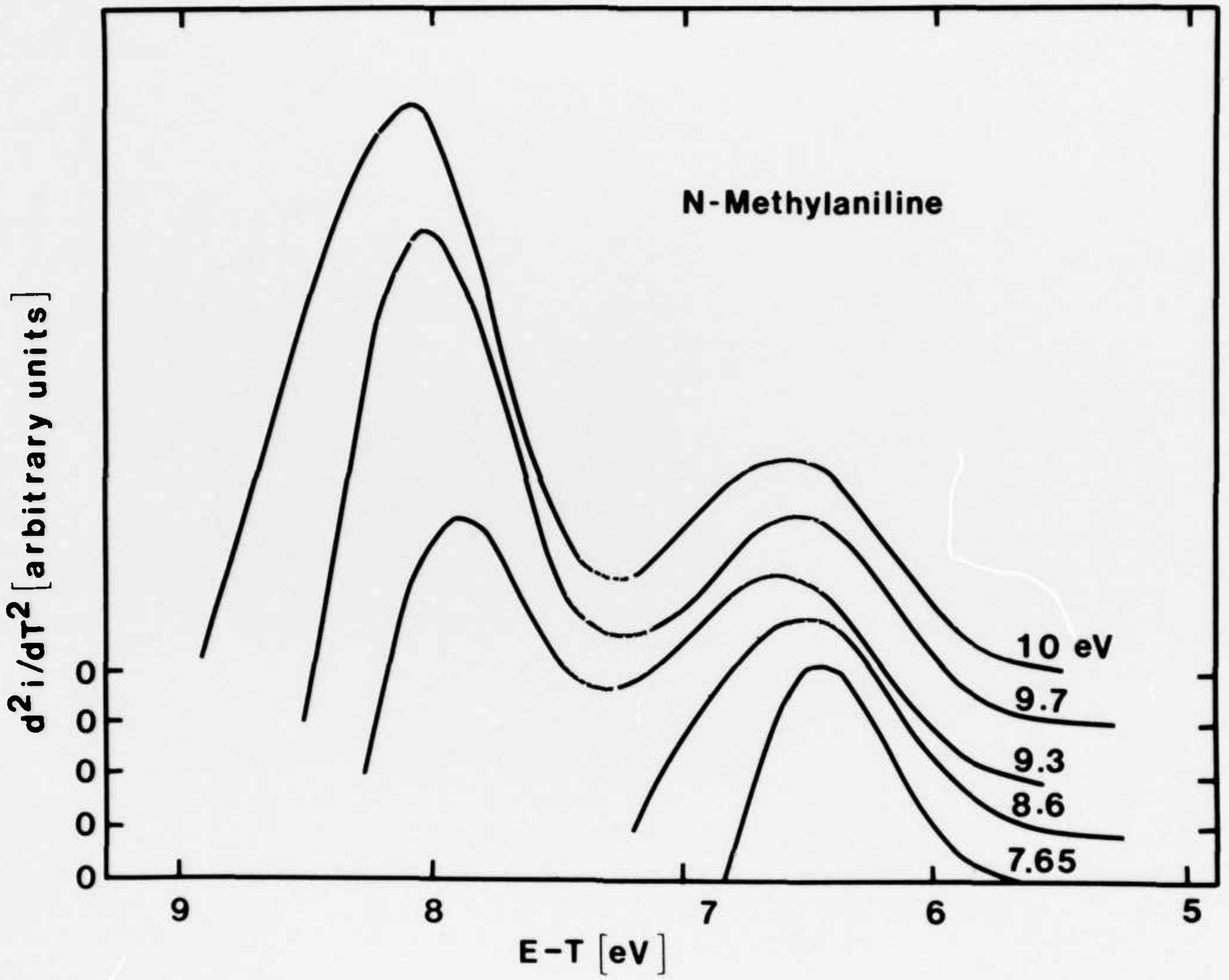
N-Methylaniline
10 eV
9.7
9.3
8.6
7.65
d^2i/dT^2 [arbitrary units]
0
0
0
0
0
9
8
7
6
5
E−T [eV]

FIG 8

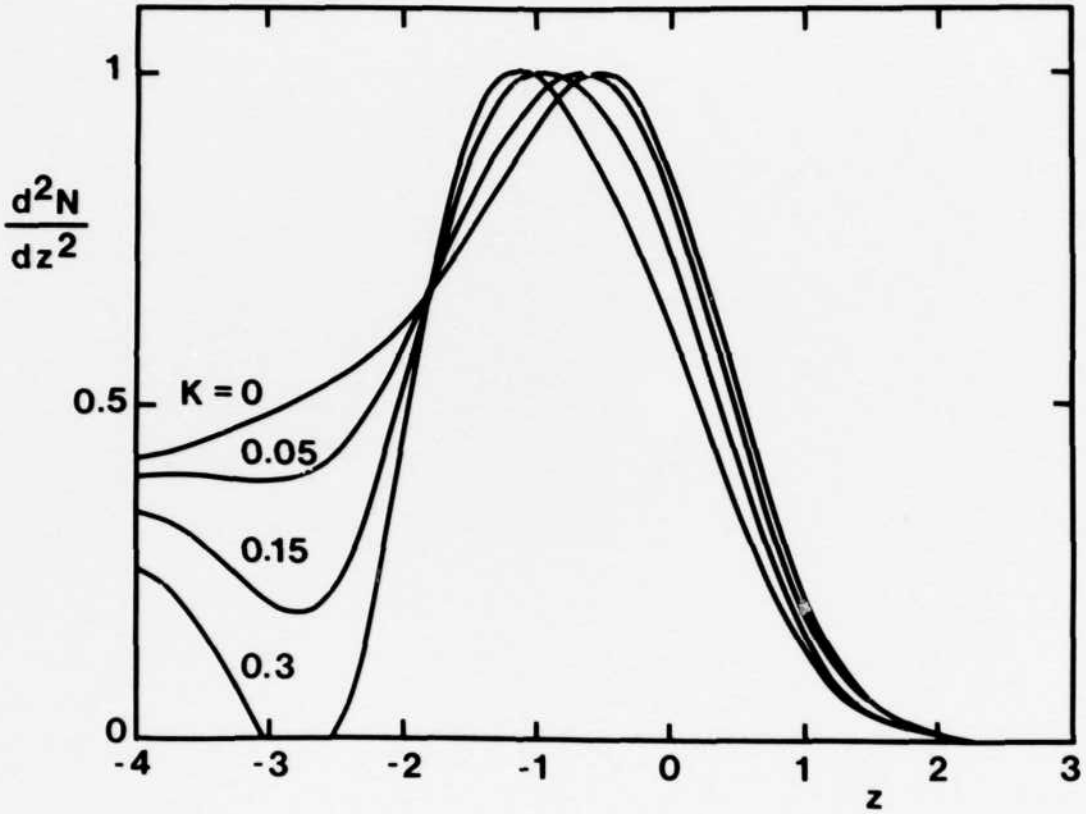

FIG. 9

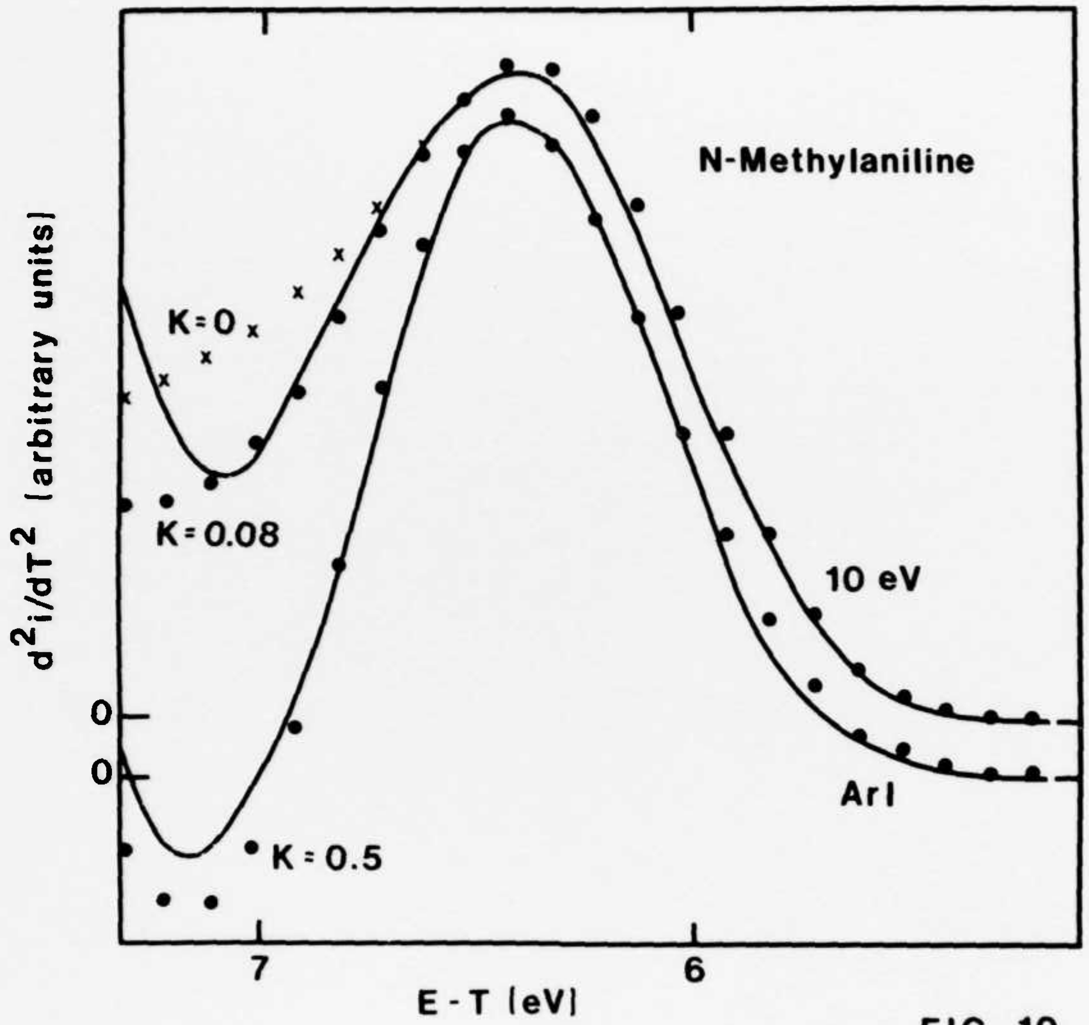
N-Methylaniline
d²i/dT² (arbitrary units)
0
0
K = 0
K = 0.08
K = 0.5
10 eV
ArI
7
6
E - T (eV)

FIG. 10

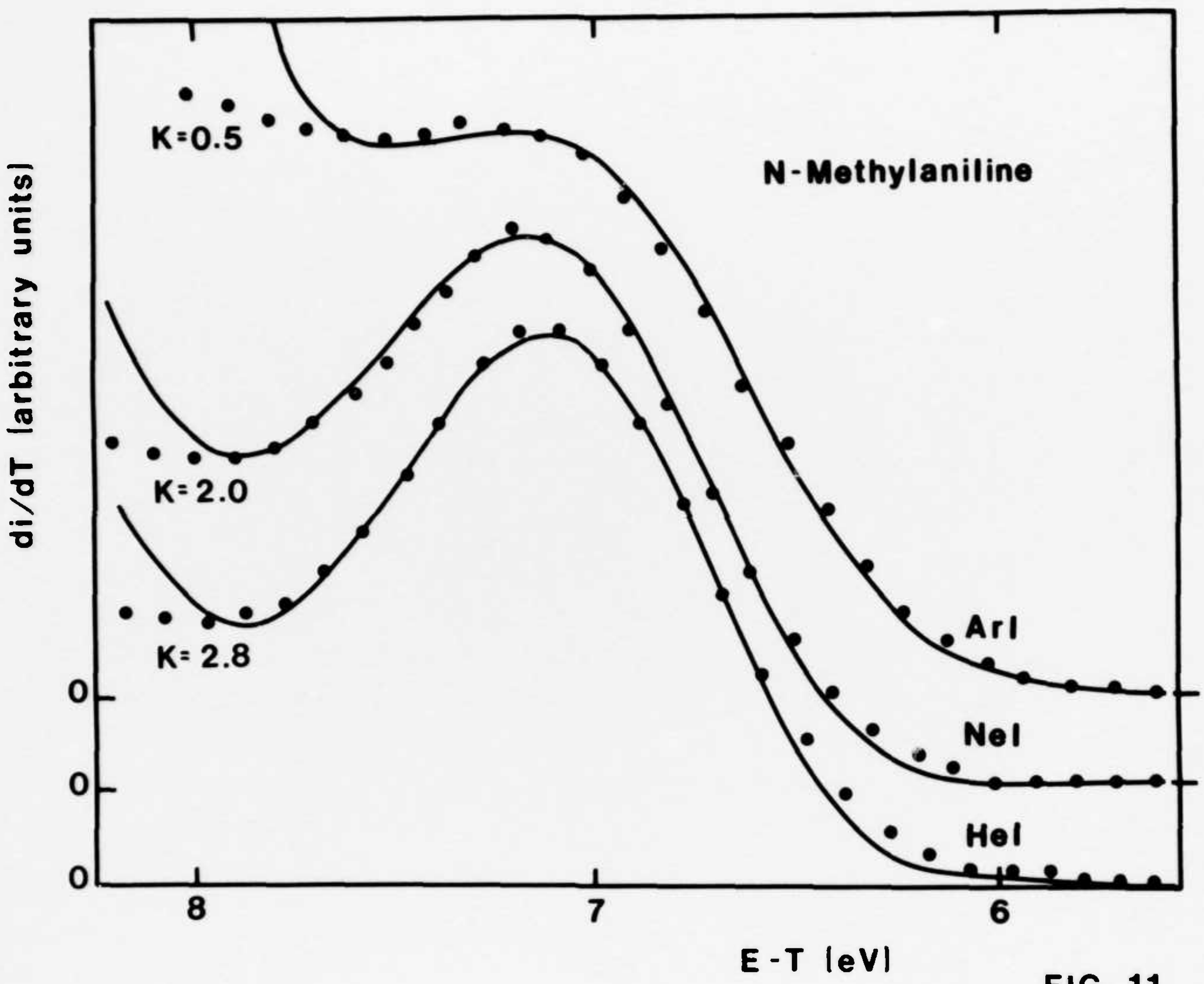
N-Methylaniline
K=0.5
K=2.0
K=2.8
ArI
NeI
HeI
di/dT (arbitrary units)
0
0
0
8
7
6
E-T (eV)

FIG. 11

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Photoelectron spectroscopy of liquids is investigated at variable photon energy up to 10 eV and with rare-gas resonance lines at 11.7 (ArI), 16.8 (NeI), and 21.2 (HeI) eV. Seven liquids are studied: N-methylaniline, N,N'-dimethyl-p-toluidine, formamide, hexamethyl phosphoric triamide, tetraglyme, ethylene glycol, and n-decanol. Energy distribution curves display at the higher photon energies a band structure matching the sequence of bands in the corresponding gas-phase photoelectron spectra. The bands are attributed to emission of unscattered electrons (no loss of kinetic energy to the liquid), whereas the underlying background is ascribed to scattered (in the liquid) electrons. Quantitative treatment based on this interpretation agrees with experiment. Energies characterizing either bulk or surface photoionization are determined within ±0.1 eV. The gas-liquid red shift (0.9 to 1.4 eV) and bulk-surface blue shift (0.5 to 1.3 eV) in photoionization energies are interpreted in terms of electronic polarization of the liquid medium. This is, to our knowledge, the first investigation of liquids by ultraviolet photoelectron spectroscopy above 10 eV.

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