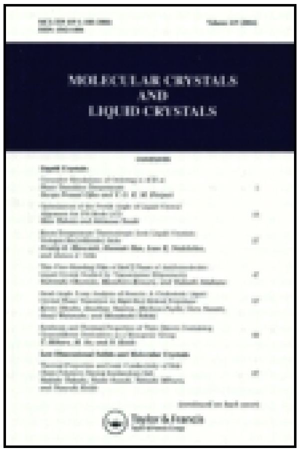


Molecular Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl15

Photoelectron Emission from Aromatic and Metallooraganic Hydrocarbons

Alfred P. Marchetti [a] [b] & David R. Kearns [a]
[a] Department of Chemistry, University of California, Riverside, Calif., 92507
[b] Research Laboratories, Eastman Kodak Company, Rochester, N.Y., 14650

Version of record first published: 21 Mar 2007.

To cite this article: Alfred P. Marchetti & David R. Kearns (1969): Photoelectron Emission from Aromatic and Metallooraganic Hydrocarbons, Molecular Crystals, 6:3-4, 299-317

To link to this article: http://dx.doi.org/10.1080/15421407008083468

Molecular Crystals and Liquid Crystals. 1970. Vol. 6, pp. 299–317

Photoelectron Emission from Aromatic and Metalloorganic Hydrocarbons‡

ALFRED P. MARCHETTI§ and DAVID R. KEARNS

Department of Chemistry,
University of California,
Riverside, Calif. 92507

Received June 25, 1969; *in revised form August* 15, 1969

Abstract—Photoelectron emission from various aromatic hydrocarbon crystals has been studied and some of the factors (space charge, sample preparation) which might influence the photoelectric threshold have been investigated. The longstanding problem of determining the "true" photoelectric threshold is re-examined, and a semi-empirical expression is derived which adequately accounts for the spectral dependence of the photoelectron emission yield, and at the same time determines the threshold. New photoelectric thresholds for a number of anthracene derivatives are also reported.

I. Introduction

The photoelectric emission threshold is a fundamental property of organic molecular crystals which is of interest in connection with various studies of the electronic properties of crystals.[1–7] For example, the difference between the crystal ionization potential, I_C, and the corresponding gas phase molecular ionization potential, I_G, is just P, the polarization energy of the crystal. The quantity $(I_G - 2P)$ is the energy of the free-electron conduction band, and $(I_G - 2P - A)$ is the energy of the lowest energy conduction band in the crystal, where A is the gas phase molecular electron affinity.[7] Because of the interrelation between I_C, A, and P and other crystal properties, and because of the difficulties of determining values for A, it would be desirable to have accurate

---

‡ This work was supported by a grant from the U.S. Army Research Office (Durham) by Grant DA-ARO-D-31-124-G804.

§ Present address: Research Laboratories, Eastman Kodak Company, Rochester, N.Y. 14650.

values of I_C for a variety of crystal systems. While the experimental measurement of photoelectric emission from organic molecular crystals is relatively straightforward, there are problems with determining accurate I_C values from the experimental data. Examination and comparison of the literature in this field indicates that some of the earlier work may have been complicated by space charge effects, impurities, and possible variations of I_C with the method of preparation of the crystals.[1-7] There is the additional, and more fundamental, difficulty that no rational procedure has been developed for deducing the true ionization threshold, I_C, from the experimental photoelectric data.[7]

In the present paper we have carried out a further examination of the influence of space charge effects and the method of sample preparation on the spectral response of the photoelectric emission from several molecular crystals. We have also developed a semi-empirical procedure for determining " true " crystal thresholds from photoelectric data, and used this to obtain I_C values for various substituted anthracenes, as well as several other aromatic compounds, ferrocene and ruthenocene.

II. Experimental

Materials: Various procedures were used to purify the compounds examined in this study. Anthracene was recrystallized from xylene, vacuum sublimed and zone refined under vacuum. 9-phenylanthracene, 9, 10-diphenylanthracene, 9-methylanthracene, and ferrocene were chromatographed on an alumina column using reagent grade benzene as a solvent. 9-bromoanthracene, 9, 10-dibromoanthracene, 9, 10-dichloroanthracene, acridine and phenazine were vacuum sublimed. Ruthenocene was obtained as a gift from Dr. T. Kuwana and had already been purified by recrystallization. Crystals of anthracene, 9-methylanthracene, 9-phenylanthracene, ferrocene, and acridine were then grown from suitable reagent grade solvents.

Apparatus: The two types of photoemission cells which we used in our study are shown in Figs. 1A and 1B. Crystalline samples

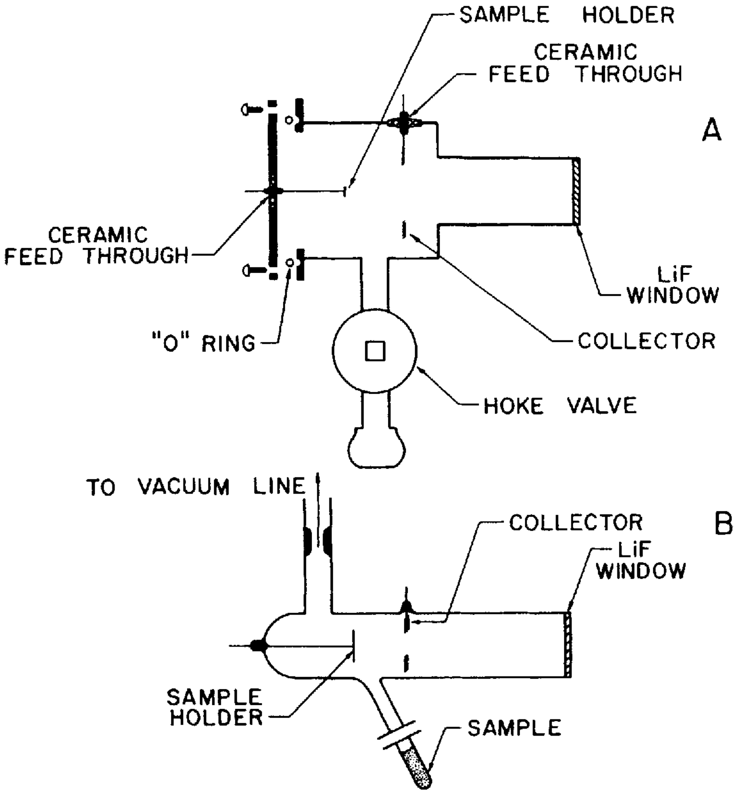


Figure 1. Schematic diagram of the cells used for the photoelectric experiments: A. Cell used for crystalline samples; B. Cell used to prepare and examine sublimed films.

were attached to the electrode with aquadag (colloidal graphite) and the cell (1A) evacuated to a pressure of 10^{-5} torr or less (for samples with a low vapor pressure). The sublimed samples were studied using the cell shown in Fig. 1B. Initially a small amount of the purified compound was placed in the side arm and the cell evacuated to a pressure of 10^{-5} torr or less. The compound was then sublimed onto the sample holder which also functioned as an electrode, and the side arm containing unsublimed material was sealed off from the vacuum system.

The spectral response of the photoelectric emission was obtained using a 0.3 meter McPherson evacuable monochromator in conjunction with appropriate light sources. The grating was blazed for 2000 Å, MgF_2 overcoated and had a linear dispersion of 26.5 Å/mm in this monochromator. All spectra were obtained using one millimeter slits. For work in the vacuum ultra violet region the monochromator was evacuated and the pressure in the monochromator chamber was maintained at less than 10^{-3} torr. The cells and lamp were attached to the monochromator with conventional " O " ring seals.

Two types of light sources were used for this investigation. A conventional 150 watt Allen type deuterium (D_2) discharge lamp was used in the ~ 1850 Å to 2400 Å region. A low pressure xenon lamp[8] (15 mm of xenon and 45 mm of krypton) was used to cover the region in the vacuum ultra violet between 1500 Å and 2100 Å. This lamp was powered by a QK-62 magnetron operating at 2.4 kilomegacycles. The magnetron was connected to a cylindrical cavity (which enclosed the lamp) designed to operate in the TM_{010} mode through a coaxial tuner.[9]

The relative photon output of the lamps was determined by replacing the sample cell with a sodium salicylate screen and a photomultiplier.[10] All spectra shown are corrected for the relative photon distribution.

The photoelectron currents were measured with a Cary model 32 vibrating reed electrometer and the output from the electrometer was recorded with a Leeds and Northrup model H strip chart recorder. The voltage used to collect the photoemitted electrons was obtained from a 90 volt dry cell.

III. Results

Experimental photoelectric emission curves for various anthracene derivatives, ferrocene, and ruthenocene are presented in Figs. 2–6. Before discussing the procedure which we have used to obtain threshold values for the photoelectric emission, we first consider two experimental factors which we find influence the spectral response curves, namely space charge and nature of the sample.

Space Charge Effects: With thin (< 0.1 mm) samples or with sublimed films the photoelectric emission currents rapidly (seconds)‡ reached a steady state value when they were illuminated and remained constant as long as the illumination conditions were not altered. With thick crystals and/or high light intensities, however, there was evidence of space charge effects (overshoot, steady state reached only after a minute or so).

An example of the build-up of space charge was found for repeated scans as shown on a thick ($\sim$ 1-2 mm) crystal of 9-phenylanthracene, as shown in Fig. 2. Each scan was completed in less than five minutes and was run from low to high energies. The initial scan produced a photoemission spectrum which was fairly structured, but subsequent runs gave spectra which showed increasing loss of structure and a significant decrease in photoemission yield in the region above the threshold. When the sample was grounded and allowed to sit for twelve hours, most of the structure returned. When the sample was grounded for only 15 minutes (not shown) there was a significant return of structure. Space charge effects appear then to shift the apparent photoelectric threshold to higher energies by perhaps 0.1 eV.

Comparison of Crystalline and Sublime Samples: The photoemission spectra of crystalline and sublimed anthracene are compared in Fig. 3. Although absolute quantum yields were not determined, current values may be compared because the sample areas were much larger than the light beam and the lamp was always maintained at the same input power. The two types of anthracene samples give similar currents at high energies, but there are significant differences in the region above threshold where the sublimed sample shows a loss of structure and a lower emission yield. At energies close to threshold, the currents are again similar and the extrapolated threshold values are very similar. A similar loss of structure is observed in going from a crystalline to a sublimed sample of 9-phenylanthracene (compare Figs. 2 and 4).

‡ This was approximately the time constant of the instrument.

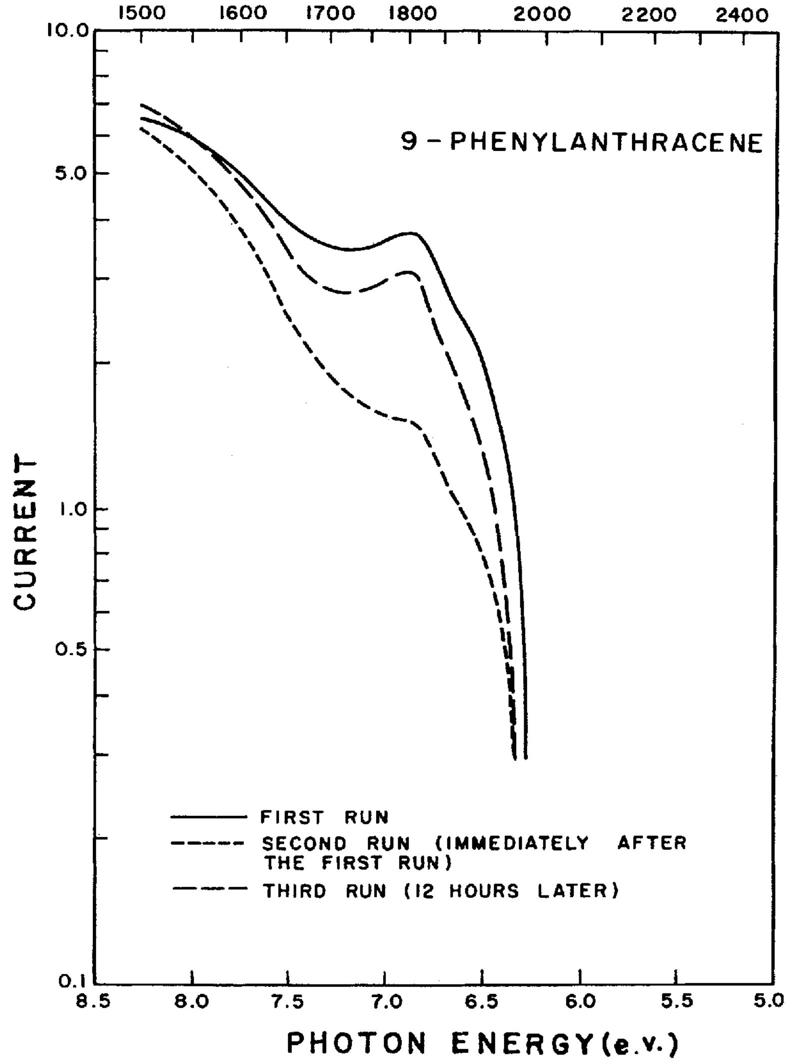


Figure 2. Photoelectric emission spectrum of a 1–2 mm thick crystal of 9-phenylanthracene illustrating the effect of spacecharge on the spectral response.

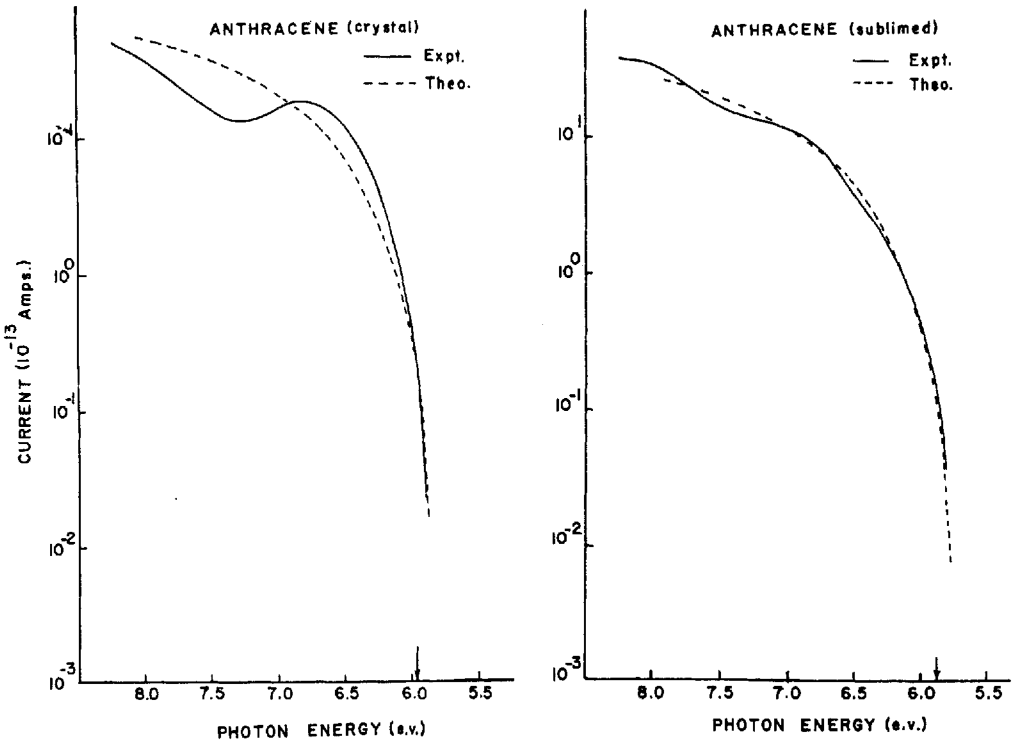
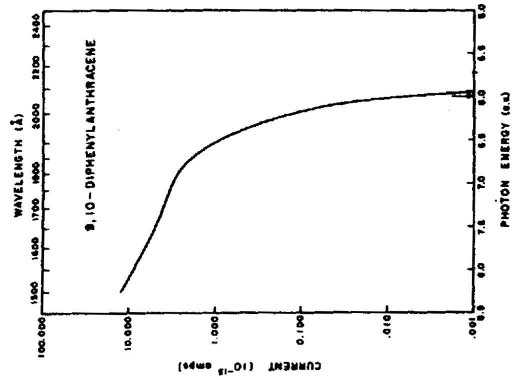
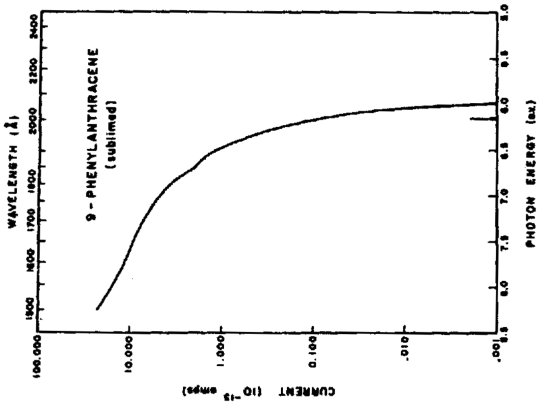
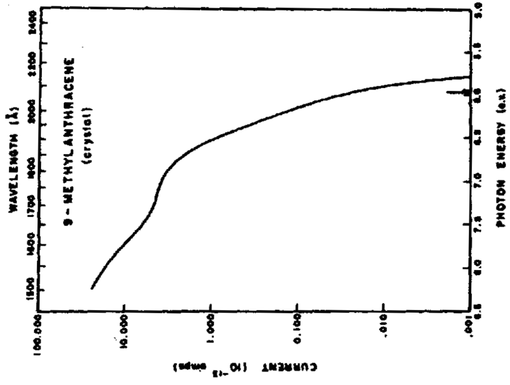


Figure 3. Comparison of the photoelectric emission from a single crystal and a sublimed film of anthracene (solid curves). The dashed curves are theoretical curves calculated using equations 7 and 9 with $P = 1.5$ eV.


WAVELENGTH (Å)
1500
1600
1700
1800
2000
2200
2400
9,10-DIPHENYLANTHRACENE
CURRENT (10^-13 amps)
100.000
10.000
1.000
0.100
.010
.001
PHOTON ENERGY (e.v.)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0


WAVELENGTH (Å)
1500
1600
1700
1800
2000
2200
2400
9-PHENYLANTHRACENE
(sublimed)
CURRENT (10^-13 amps)
100.000
10.000
1.000
0.100
.010
.001
PHOTON ENERGY (e.v.)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0


WAVELENGTH (Å)
1500
1600
1700
1800
2000
2200
2400
9-METHYLANTHRACENE
(crystal)
CURRENT (10^-13 amps)
100.000
10.000
1.000
0.100
.010
.001
PHOTON ENERGY (e.v.)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0

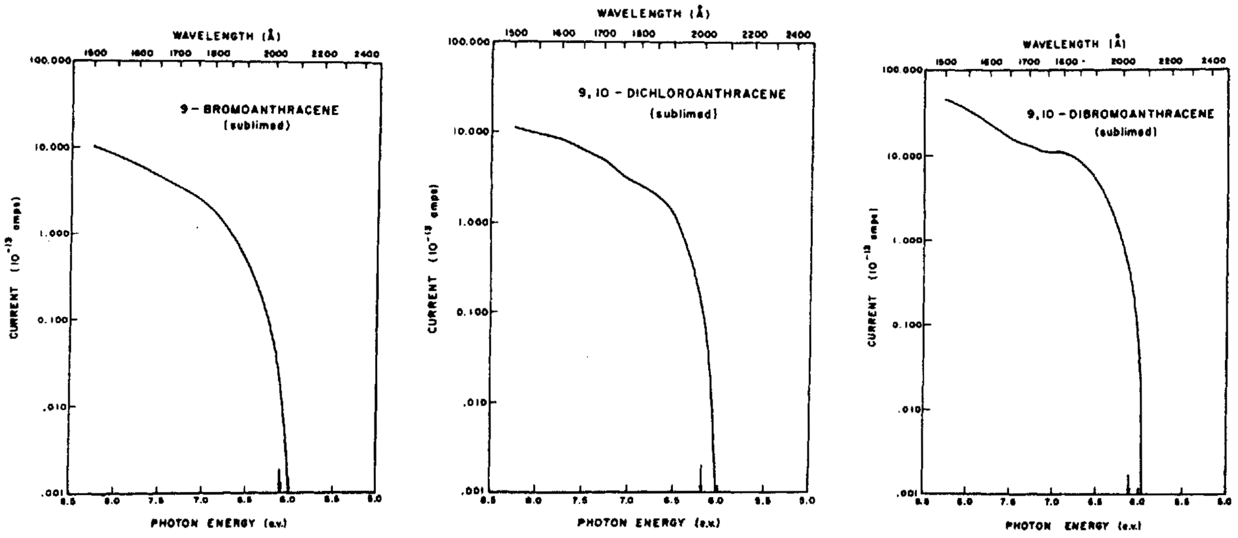


Figure 4. Photoelectric emission spectra of six substituted anthracenes.

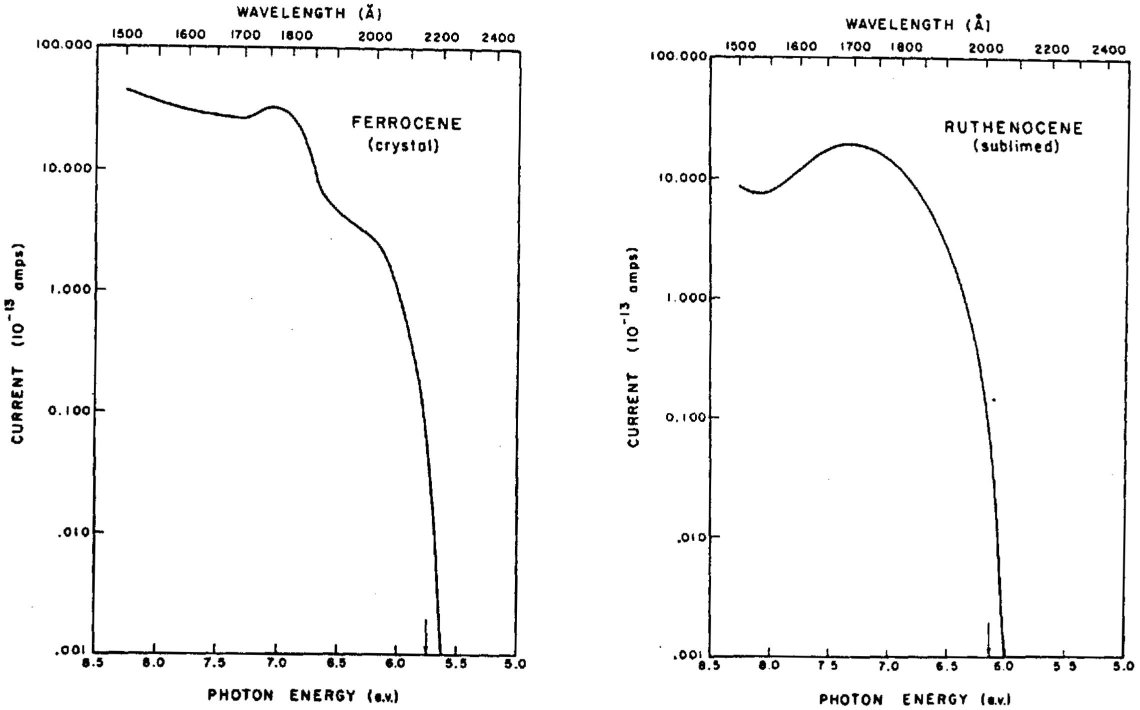


Figure 5. Photoelectric emission spectra of ferrocene and ruthenocene.

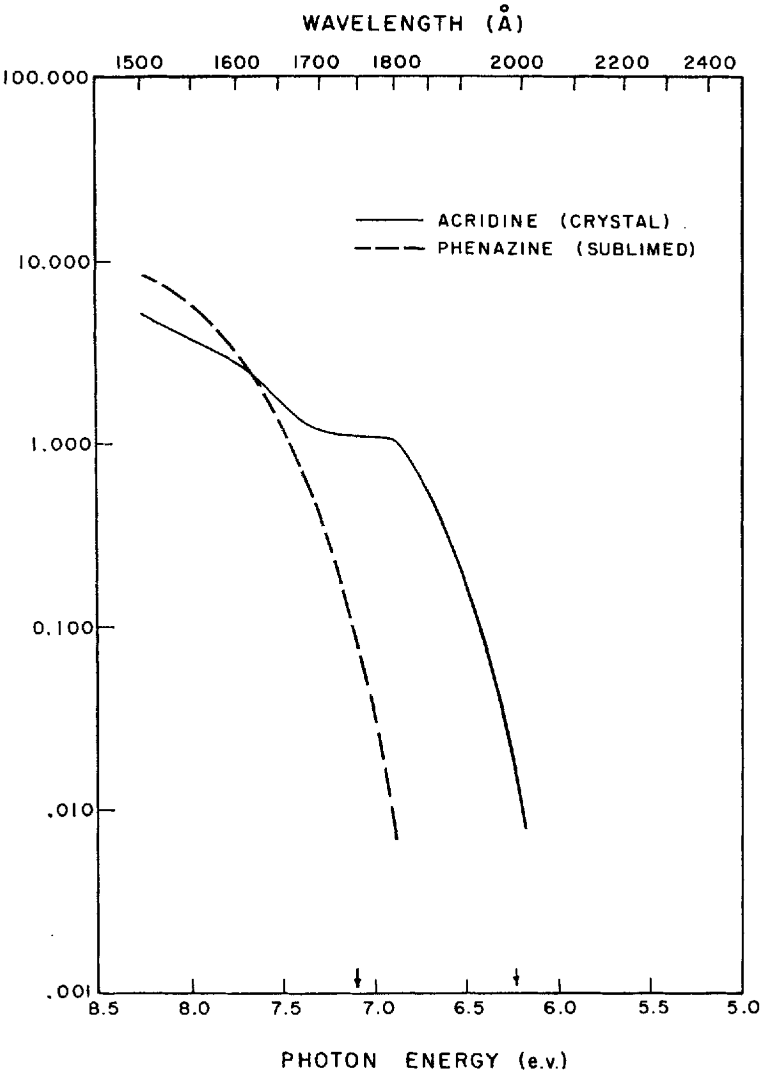


Figure 6. Photoelectric emission spectra of acridine and phenazine.

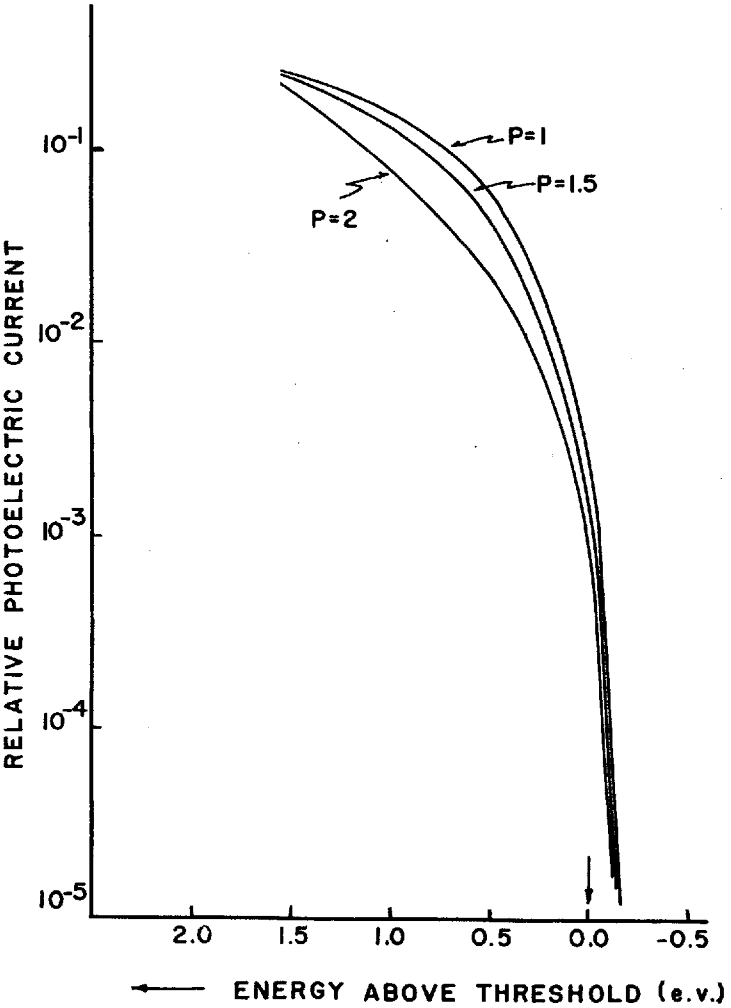


Figure 7. Theoretical photoelectric emission curves calculated with equations 7 and 9.

The most probable cause of these differences is space charge. Although the crystalline anthracene samples are poor conductors, they were very thin (less than 100 microns thick) and apparently made good electrical contact with the sample holder. The sublimed samples of anthracene, on the other hand, are probably composed of small crystallites which make poor electrical contact with one another and, as the data for 9-phenylanthracene demonstrate, the build-up of charge produces a definite loss of structure in the photo spectrum.

By way of comparison we find that Lyons' photoemission curves for anthracene are similar to ours in the high and low energy regions, but in the region above the threshold, Lyons' curve appears to be intermediate between the two extremes shown in Fig. 3.[4]

Analysis of the Photoelectric Emission Curves: In order for the experimental photoelectric yield curves to be useful, we must have a suitable procedure for calculating the true threshold, I_C, from the spectral response curve. The procedure which we have used for this purpose is based on the following model. The photoelectric emission process is treated in essentially the same manner as if it were a gas phase ionization, with certain important modifications. Conceptually, the ionization process will involve the following factors:

(i) The relative probability that absorption of a photon of energy $h\nu$ by a molecule in the crystal will lead to ejection of an electron into the crystal with kinetic energy in the range E to $E+dE$ will be determined by a cross section function $n(E,h\nu)$ which depends upon both E and $h\nu$. If we assume that the initial ionization can be treated as a molecular process, then, from an examination of gas phase photoionization curves in the literature, we conclude $n(E,h\nu)$ must have the following properties:[6] $n(E,h\nu)$ obviously goes to zero when $E > (h\nu - I_C+P)$, because $(h\nu - I_C+P)$ is the maximum amount of energy which can appear as kinetic energy of the ejected electron while it is still in the crystal. The experimental gas phase ionization curves indicate that above the threshold, the total number of electrons generated varies only slowly with the photon energy, and that the relative number of electrons which are emitted with kinetic energy between 0 and the maximum possible value is remarkably constant for a given photon energy.[6] These considerations suggest the following simple expression for $n(E, h\nu)$

$$n(E, h\nu)dE = \left(\frac{K}{h\nu - I_C + P}\right) dE \tag{1}$$

where K is some constant and the factor $(h\nu - I_C + P)$ simply keeps the total number of photoelectrons emitted constant regardless of $h\nu$. To conserve energy this expression is only applicable for kinetic energies, E, up to $(h\nu - I_C + P)$ in the crystal.

(ii) Since measurements are carried out at finite temperatures where thermal excitations may help contribute to the ionization process the above expression for $n(E, h\nu)$ should be multiplied by a factor

$$\frac{\exp(-\Delta E/kT)}{kT} d\Delta E$$

where ΔE is the additional kinetic energy provided to an ejected electron by thermal excitation.

(iii) Because of the strong attenuation of the exciting light beam as it penetrates the crystal, the actual photon intensity, $I(x)$, at any depth, x, in the crystal will be given by

$$I(x) = I_0 \exp(-\gamma x). \tag{2}$$

(iv) Although the initial ionization act produces electrons which can move about in the crystal (photoconduction) in order to leave the crystal and contribute to the photoelectric effect, these electrons must be directed toward the surface of the crystal and with sufficient velocity normal to the surface so that they can escape into the vacuum. If the initial photo-ejection of electrons is isotropic, the fraction of the photoelectrons which is directed at some angle to the normal to the surface which lies between θ and $\theta + d\theta$ is just

$$f(\theta) = \sin\theta\, d\theta/2. \tag{3}$$

If the emission were anisotropic then $f(\theta)$ would have to be multiplied by the appropriate anisotrophy factor. The component of momentum normal to the surface will then be just $(2mE)^{1/2}\cos\theta$.

(v) Finally, we have to include a scattering factor to take into account that electrons initially directed toward the surface with enough kinetic energy to escape may be scattered before they reach the surface. If we assume that only one such scattering event is needed to prevent an electron from escaping, then the probability that an electron with sufficient kinetic energy will escape when it is directed at some angle θ with respect to the normal to the surface is given by

$$P(\theta) = 2\beta \exp(-\beta x/\cos\theta) \tag{4}$$

where x is the distance normal to the surface and β is some scattering parameter. This assumption should be valid near the threshold where a small loss in energy could prevent an electron from escaping.

Combining all of the above factors and integrating leads to the following expression for the variation of the photoelectric emission yield with photon energy

$$i(\nu) = \int_{E,X,\theta,\Delta E} \cdots \int \left[I_0 e^{-\gamma x}\,dx\right]\left[\frac{K\,d\,E}{(h\nu - I_C + P)}\right]\left[\frac{e^{-\Delta E/kT}\,d\Delta E}{kT}\right]$$
$$\left[\frac{\sin\theta\, d\theta}{2}\right]\left[e^{-\beta x}/\cos\theta\right]2\beta. \tag{5}$$

If E is less than P, then the additional energy $(P - E)$ needed to escape the crystal must be provided by thermal excitation, so that θ ranges from 0 up to some maximum value $\theta_{\max}$ where $\cos\theta_{\max} = (P/E_{\max})^{1/2} = [P/(E + \Delta E)]^{1/2}$. Integration of Eq. (5) over x and θ yields the following expression for the photoelectric yield

$$i(\nu) = \left(2I_o/kT\right)\iint_{E,\Delta E}\left(1 - P/(E + \Delta E)\right)\left(e^{-\Delta E/kT}\right)\frac{KdE\,d\Delta E}{(h\nu - I_C + P)}. \tag{6}$$

In order to obtain the above expression we further assumed that the mean free path of the electron in the crystal, $(1/\beta)$, is short compared with the extinction depth, $1/\gamma$. In carrying out the integration of the above expression, we want to distinguish between two experimental situations.

In the subthreshold region, the total kinetic energy provided by the exciting light is insufficient to eject electrons from the crystal and the deficiency $(P - E)$ must be made up by thermal excitation. Hence ΔE is allowed to range from a minimum value of $(P - E)$ all the way up to infinity. The integral in expression (6) can now be integrated and if we retain only the leading terms in the resulting expression, and further restrict our attention to energies very near the threshold such that $(I_C - h\nu) < P$, but large enough so that $(I_C - h\nu) > kt$ then the following expression for $i(h\nu)$ is obtained

$$i(\nu) \propto \frac{I_0 K (kT)^2}{P(h\nu - I_C + P)} e^{-(I_C - h\nu)/kT}. \tag{7}$$

For a fixed temperature we see that this expression predicts that below the threshold the photoelectric yield will vary essentially exponentially with $(I_C - h\nu)/kT$.

Super Threshold Region: $h\nu > I_C$. In the region above the threshold where $h\nu > I_C$, integration of Eq. (6) leads to the following expression for the photoelectric current:

$$i(\nu) \propto \frac{I_0 K}{(h\nu - I_C + P)} \left[\frac{(kT)^2}{P} + (h\nu - I_C) + kT \left(\frac{h\nu - I_C}{h\nu - I_C + P} \right) - P \ln \frac{(h\nu - I_C + P)}{P} \right]. \tag{8}$$

Since both P and $(h\nu - I_C)$ are larger than kT, we may approximate Eq. (8) with the simpler expression

$$i(\nu) \propto \frac{I_0 K}{(h\nu - I_C + P)} \left[(h\nu - I_C) - P \ln \left(\frac{h\nu - I_C + P}{P} \right) \right]. \tag{9}$$

In order to make use of the theoretical expressions we have constructed plots of the photoelectric yield predicted by Eqs. (7) and (9) for several different values of P, the polarization energy, and these are presented in Fig. 7. As may be seen by comparison of these theoretical curves with the experimental data shown in Figs. 3–6, the general shape of the experimental curves is well accounted by the theoretical curves, and as Fig. 3 demonstrates, it is possible to get quite a decent fit of the observed photoelectric curves over 4 orders of magnitude change in current. The location of the true threshold is automatically fixed once the experimental curve is fitted with one of the theoretical curves. In Table 1 we have listed the values of the photoelectric thresholds obtained by this fitting procedure.

In attempting to fit the experimental photoelectric emission data with the theoretical curves, the only adjustable parameter is P, which should be just the polarization energy. It is comforting to note that the best fit of the experimental data was generally obtained with $P = 1.5 - 2$ eV, and this is nearly identical to the value obtained from $P = I_G - I_C$. We take this agreement as at least a partial confirmation of the model which we have proposed.

In the past, threshold values have often been taken as the energy where the photoelectric yield drops to some arbitrary fraction of the maximum yield. Since our analysis shows that the behavior of the photoelectric current in the low energy region is due to a thermal tail, this procedure is certainly questionable. The fact that it results in values which are only slightly smaller than our values is simply due to the steeply descending behavior of the photoelectric current below the threshold.

It is interesting to note that all of the substituted anthracenes have solid state ionization thresholds which are larger than the parent hydrocarbon. This suggests that either the polarization energies are slightly smaller or that the gas phase ionization potentials of the substituted compounds are larger than that of anthracene, or both. Ionization potentials for a few of the substituted anthracenes have just been measured and found to be somewhat larger than the value for anthracene. The polarization energies, on the other hand, are about the same as for anthracene.

Table 1 Photoelectron Threshold Energy Values

Compound	Preparation	I_C(eV)		I_G	P
		This work	Other		$(I_G – I_C)$
Anthracene	X	5.95 eV	5.65 (a)	7.40 (d)	1.45
Anthracene	S	5.85	5.6 –6.2 (b)		1.55
9-Methylanthracene	X	5.95			
9-Bromoanthracene	S	6.10			
9, 10-Dibromoanthracene	S	6.08	4.9–5.3 (c)	7.75 (e)	1.67
9, 10-Dichloroanthracene	S	6.10			
9-Phenylanthracene	X	6.25			
9-Phenylanthracene	S	6.10			
9, 10-Diphenylanthracene	S	6.05			
Acridine	X	~ 6.2		7.78 (d)	~ 1.6
Phenazine	S	~ 7.1			
Ferrocene	X	5.75		7.05 (d)	1.30
Ruthenocene	S	6.15			

(a) Lyons, L. E. and Morris, G. C., *J. Chem. Soc.*, 5192 (1960).
(b) Hughes, A. L., *Phil. Mag.* **24**, 380 (1912).
(c) Mackie, J. C., Ph.D. Thesis, University of Sydney (1963).
(d) Reference 7.
(e) Happ, G. P. and Maier, D. P.—Private Communication.
X = Crystal
S = Sublimed

REFERENCES

1. Pochettino, A., *Atti Reale Accad. Lincei*, **1**, 355 (1906); **2**, 17 (1906).
2. See references in Hughes and DuBridge, *Photoelectric Phenomena*, 1st. edn., McGraw-Hill Inc., New York, 1932.
3. Carswell, D. J. and Iredale, T., *Aust. J. Appl. Sci.* **4**, 329 (1953).
4. Lyons, L. E. and Morris, G. C., *J. Chem. Soc.*, 5192 (1960).
5. Kearns, D. R. and Calvin, M., *J. Chem. Phys.* **34**, 2026 (1961).
6. Terenin, A. and Vilessov, F., in *Advances in Photochemistry*, Vol. 2, W. A. Noyes, G. S. Hammond and J. N. Pitts, John Wiley and Sons, New York (1967) and references cited therein.
7. Gutmann, F. and Lyons, L. E., *Organic Semiconductors*, John Wiley and Sons, New York (1967) and references cited therein.
8. Tanaka Y. and Zilihoff, M., *J. Opt. Soc. Am.* **44**, 254 (1954); Wilkinson P. G. and Tanaka, Y., *J. Opt. Soc. Am.* **45**, 344 (1955); Tanaka, Y., *J. Opt. Soc. Am.* **45**, 710 (1955).
9. Harvey, A. F., *Microwave Engineering*, Academic Press, New York (1963).
10. Allison, R., Burns, J. and Tuzzolinio, A. J., *J. Opt. Soc. Am.* **54**, 747 (1964).