1000. *Photo- and Semi-conductance in Organic Crystals. Part VIII.** *Photo-emission of Electrons from Crystals of Aromatic Hydrocarbons.*

By L. E. Lyons and G. C. Morris.

Photo-emission of electrons from single crystals has been studied and thresholds have been found for naphthacene (5·26 ev), anthracene (5·65), chrysene (5·73), naphthalene (6·76), phenanthrene (6·45), pyrene (5·81), 1,2-benzanthracene (5·68), and 1,2:5,6-dibenzanthracene (5·69). The behaviour is similar in all cases to that expected for semi-conductors. The photoemission yield is *ca.* 6 × 10^{-3} electrons/quantum in all cases. Thresholds were found at slightly lower energies than predicted previously, occurring at an energy lower by 1—2 ev than the gaseous ionization potential, a decrease attributed to polarization of the crystal by the remaining positive centre. Various properties of the currents are reported and discussed.

Photoelectric emission from aromatic hydrocarbons was apparently first recorded by Pochettino [1] who studied anthracene and observed behaviour roughly similar to that in metals. The threshold of photoemission was studied by various authors [2] in the following six years. The only aromatic hydrocarbons studied before the present work are anthracene, naphthalene, and phenanthrene. With the exception of one paper [3] on anthracene and phenanthrene, no work has been reported for over forty years. Interest in the semi- and photo-conductance of these substances recently has been considerable, and as a preliminary to extending the photo-conductance studies into the spectral region above 50,000 cm.$^{-1}$ it was necessary to understand the photo-emission phenomena in order to avoid confusing the two effects. Studies on single crystals had not been made before, and the present work even on anthracene is novel in this respect. There has been proposed [4] a semi-empirical theory to predict the photo-emission threshold.

---

* Part VII, preceding paper.

[1] Pochettino, *Atti reale Accad. Lincei*, 1906, No. 1, 355; No. 2, 17.

[2] See refs. in Hughes and DuBridge, " Photoelectric Phenomena," 1st edn., McGraw-Hill Inc., New York, 1932.

[3] Carswell and Iredale, *Australian J. Appl. Sci.*, 1953, **4**, 329.

[4] Part V, Lyons, *J.*, 1957, 5001.

EXPERIMENTAL

Two cells were employed: (*a*) A brass cylinder with a fluorite window. The collector was either the cylinder itself or a brass plate whose surface was shielded from the incident light by glass. The emitter was attached to a silica disc by " Aquadag " which formed the electrical contact. (*b*) A glass sphere about 8 cm. in diameter with an aperture for the incident light. The emitter was approximately in the centre of this sphere and was attached by " Aquadag " to a metal rod. The collector was an " Aquadag " coat on the inside of the sphere. No significant potential gradient existed in the collector. The photoelectric behaviour of Aquadag is well known and its work function remains fairly constant at 4·75 ± 0·10 ev. Aquadag is a poor electron reflector, and so distortions of the current voltage curves are decreased. Cell (*a*) could be evacuated to less than 10^{-5} mm. Hg, but cell (*b*) depended for its vacuum upon that in the spectrograph, usually about 10^{-4} mm. Hg. Cell (*a*) was used when it was unnecessary to deal with the true energy distribution of the emitted electrons, and when largest currents were wanted, for it was possible to orientate several single crystals to give a larger emitting area. Cell (*b*) was used generally, and always when undistorted current–voltage relations were wanted. However, the current–light intensity, current–time, and current–incident photon relations did not depend significantly on the type of cell.

The absolute measurement was made by using a calibrated Schwarz linear thermopile (sensitivity 7·7 μv/μw in a vacuum). A Perkin–Elmer amplifier model 107 or a Pye microvoltmeter and amplifier amplified the output. Relative intensities were obtained by using fixed entrance and exit slits and measuring the fluorescence intensity from a sodium salicylate coating on glass by a 1P28 photomultiplier.[5]

The spectrograph was a Hilger 3-metre normal-incidence, concave-grating, vacuum-spectrograph used in the first order (dispersion 5·78 Å/mm.). The rough wavelength scale was replaced by a scale calibrated with mercury and hydrogen emission lines to read to 0·5 Å. In the photomultiplier post, directly behind the slit, the cells were aligned, electrical connections being made through a " Perspex " plate Rotation of the wavelength handle simultaneously rotated the grating and camera to maintain focus, but did not significantly alter the position of the light beam incident on the crystal.

Crystals of naphthalene, anthracene, phenanthrene, naphthacene, pyrene, chrysene, 1,2-benzanthracene, and 1,2:5,6-dibenzanthracene were used as photoemitters. Single crystals formed by sublimation in an inert atmosphere were used in preference to films formed by vacuum-sublimation which are often microcrystalline deposits. It was possible to grow naphthalene and anthracene crystals 10 mm. × 10 mm. of varying thickness. The other substances gave crystals up to 5 mm. × 5 mm. with varying thickness. The face developed was the (001) plane except for the benzanthracenes which gave the (010) plane as the well-developed face. For pyrene and phenanthrene, the developed (001) face would twin along the (010) face unless the cooling conditions after sublimation were carefully controlled. Anthracene and naphthacene were the most thoroughly examined, because their absorption spectra and photoconduction properties were also being investigated.

The purification of the substances has been described.[7] Unclean surfaces affect the emission properties of many substances.[2] Any attempt to follow the rigorous outgassing and cleaning techniques [5] usually employed for metals and semiconductors was not feasible and was probably unnecessary to a large extent. The relatively high vapour pressure of these hydrocarbons, ranging from *ca.* 10^{-7} mm. Hg for naphthacene to *ca.* 10^{-1} mm. Hg for naphthalene at 300° K, meant that in most cases the surface was cleaned by sublimation from the crystal into the liquid-air traps employed when pumping. For naphthalene this evaporation was too rapid to permit measurements on the crystals used (about 2 microns thick) for more than 30 min. Anthracene crystals under similar conditions lasted for some hours. Naphthacene lasted several days, and in this case the evaporation may not have been sufficient to clean the surface thoroughly. The emission properties did not alter significantly after evacuation for several days.

[5] Apker and Taft, *Phys. Rev.*, 1950, **79**, 964; 1951, **81**, 698, 814, 1496; Apker, Taft, and Dickey, *ibid.*, 1948, **74**, 1462.

[6] Dejardin and Schwegler, *Rev. Opt.*, 1934, **13**, 313, 353; Johnson, Watanabe, and Tousey, *J. Opt. Soc. Amer.*, 1951, **41**, 702; Watanabe and Inn, *ibid.*, 1953, **43**, 32.

[7] Part III, Lyons and Morris, *J.*, 1957, 3648; Morris, M.Sc. Thesis, Sydney, 1957.

The possibility remains that the evacuation produced surface irregularities in that evaporation may have been faster at some parts of the crystal surface than at others. Photo-oxides [8] on the surface of the crystals were also possibly present. Care in the preparation of the crystal would ensure that little photo-oxide occurred at this stage, but since the crystal mounting was conducted in both air and light, some would be formed; however, no effect of this was noted.

An Allen-type hydrogen lamp was used with a band pass of about 5 Å. The lamp output was determined both in absolute units and also in relative units at frequent intervals. The cell was placed behind the exit slit.

The collector bias could be altered by a variable d.c. battery power supply. The photon intensity could be altered by the entrance slit, or by one of the four pre-adjusted exit slits put in position by moving the plate-racking device. The emission current was amplified by a vibrating-reed electrometer (Electronic Industries Inc., Model 33C) and recorded by a Varian Associates recorder model G10. The collected current was also measured but it was preferred to record the emission current. Stability of the amplifier utilizing a 10 in. diam. potential drop resistor was better than 10^{-15} A and the time constant was about 3 sec.

Glass shields removed unwanted light. A piece of glass replacing the crystal gave no current. The crystals used were thick enough (2—10 microns usually) to absorb all the incident radiation. Sufficient voltage, *ca.* 10 v, was used on the collector for a saturation current to be registered. Current–time relations were always obtained to ensure that a steady state was reached. Stray light was measured by various means. Photon energies above 9·2 ev were excluded by the light's passing through a fluorite window. Scattered light below 5500 cm.$^{-1}$ was checked by using as a filter a layer of air 1 cm. thick in a piece of fused silica, whilst a photomultiplier was set to measure light energies above 55,000 cm.$^{-1}$. Filters of glass, fused quartz, air, and synthetic sapphire were used A measure of the photoemission from the crystal in the region of zero light transmission showed that, up to 66,000 cm.$^{-1}$, stray light produced less than a 10% error in the current. Above 66,000 cm.$^{-1}$ the signal-to-stray light ratio became so small that measurements were made to 70,000 cm.$^{-1}$ only. The stray-light intensity here produced about a 30% error in the current.

RESULTS

Current–Time Relation.—Time effects greater than 5 sec. were registered reliably. With sublimation flakes a current steady with time for an hour or so was usual. With rather thick emitters (*ca.* 2 mm.) the current slowly decayed during several seconds but finally reached a steady value. When the crystal evaporated readily, *e.g.*, with naphthalene, the current gradually decayed to zero. Evidently, as the crystal became thinner by evaporation, the incident light was not fully absorbed, and so the photoemission yield decreased.

A change in the photon energy did not affect the results noticeably. Energies near the threshold value could not be completely investigated because of the small yield in this region. No noticeable effect was found for an alteration in the light intensity from about 10^9 to 10^{12} quanta per sec. (Q/sec.). In this latter case, polychromatic light was used.

Current–Light Intensity Relation.—The light intensity was varied 50-fold by calibrated neutral filters. A representative set of results for three substances at one photon energy is given in Fig. 1. Other substances behaved similarly. A change in the photon energy did not affect the linearity of the relation.

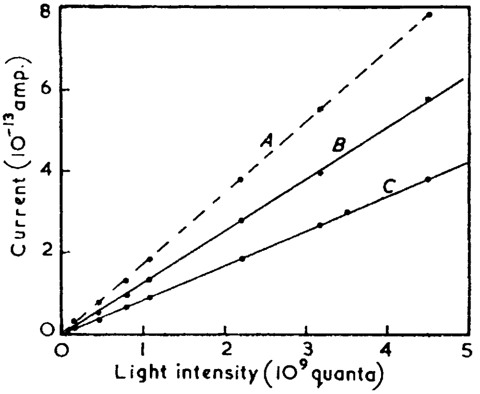
Current–Field Strength Relation.—Results were obtained by using monochromatic light. Before any voltage was applied, the value of the emission at zero volts was taken to enable the difference from the zero reading to be recorded. Figs. 2 and 3 show the relation for anthracene and naphthacene crystals, different photon energies being used. (The ordinate has been scaled so that the saturation currents at different wavelengths coincide, thus making allowance for alterations in both yield and light intensity.) Other hydrocarbons gave similar curves. The I_e–E relation did not depend on the light intensity over the ten-fold range used. It was, however, different for thick crystals (2—3 mm.). A reverse current was produced at voltages more negative than 1·2 v, a fact attributable to the presence of stray fields. Further, in thick crystals, the value at which the curve plunged into the abscissa altered with both the thickness of crystal and the time of illumination. Because of these effects, observations were confined to thin crystals.

Current–photon energy curves. These are given for such substances in Figs. 4—6 for a

---

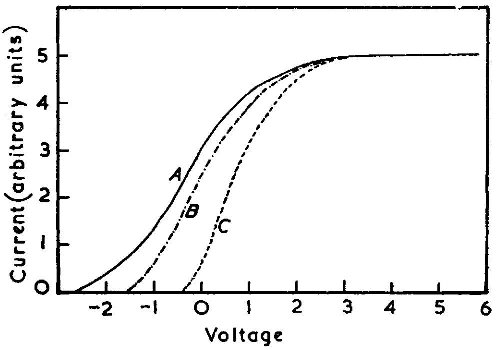
[8] Bree and Lyons, *J. Chem. Phys.*, 1956, **25**, 384, 1284.

Fig. 1. *Photo-emission current–light intensity relation.*



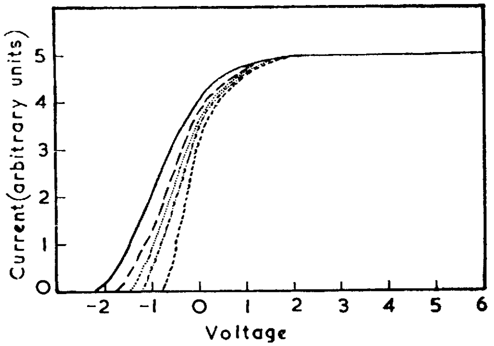
A, Anthracene; B, chrysene; C, pyrene.

Fig. 2. *Normalized photo-emission current–voltage relation for anthracene.*



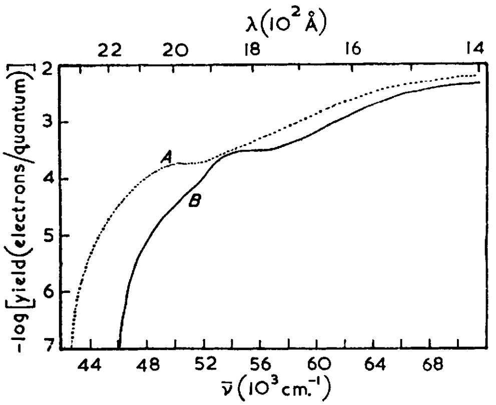
hν: (*A*) 6·69, (*B*), 7·82, (*C*) 8·86 ev.

Fig. 3. *Normalized photo-emission current–voltage relation for naphthacene.*



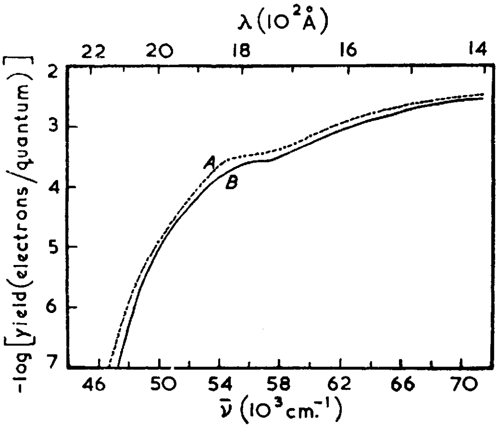
hν: (- - -) 6·88, (— · —) 7·30, (. . .) 7·51, (— —) 7·76, (——) 8·24 ev.

Fig. 4. *Spectral distribution of the photo-emission yield.*



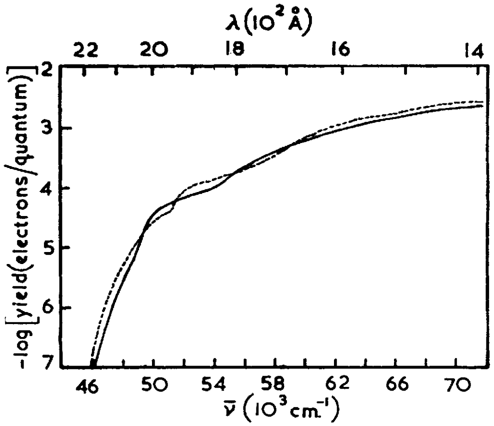
A, Naphthacene; B, anthracene.

Fig. 5. *Spectral distribution of the photo-emission yield.*



A, Chrysene; B, pyrene.

Fig. 6. *Spectral distribution of the photo-emission yield.*



(——) 1,2:5,6-*Dibenzanthracene*; (- - -) 1,2-*benzanthracene.*

constant number of quanta incident on the exit slits. The slits were kept constant when the wavelength was altered, and the results then corrected for the spectral distribution of the light source.

The results in Fig. 4 are the average of about five different crystals for both anthracene and naphthacene. The general shape of the curves did not alter significantly from crystal to crystal, although the magnitude of the photo-emission current varied over about a four-fold range at lower energies, but very little at higher energies. The results in Figs. 5 and 6 are the average of two crystals for each substance. Naphthalene and phenanthrene were also examined, but owing to their rapid rate of evaporation the results were not very reproducible. The threshold frequencies were reliably obtained, however, as several readings could be obtained before evaporation affected the results.

The use of polarized light would have been helpful in all experiments, but especially in the determination of the spectral distribution. Insufficient light intensity was available for such measurements.

Threshold frequency. This is given for each hydrocarbon studied in the Table. The threshold is taken by extrapolation to a quantum yield of 10^{-9} electron per incident quantum. Boltzmann factors do not explain the observed tailing off in the photo-emission at lower energies.

Threshold values of the photon energy required for photo-emission.

Compound	Threshold			Compound	Threshold		
	(Å)	($cm.^{-1}$)	ev		(Å)	($cm.^{-1}$)	ev
Naphthalene	1830	54,500	6·76	1,2:5,6-Dibenzanthracene	2180	45,900	5·69
Phenanthrene	1940	52,000	6·45	1,2-Benzanthracene	2180	45,800	5·68
Pyrene	2130	46,900	5·81	Anthracene	2200	45,600	5·65
Chrysene	2160	46,200	5·73	Naphthacene	2360	42,400	5·26

DISCUSSION

Space-charge might be expected to be a difficulty with hydrocarbon crystals since their D.C. resistivity is about 10^{17} ohm cm^{-1}. Definite effects were observed only with thick crystals. With very thin crystals a constant photo-emission current with time was obtained. Although this in itself does not prove the absence of space-charge it is consistent with the existence of only a small charge. Even a small voltage drop (0·2 v) across the crystal would be sufficient [9] for space-charge effects to be almost completely reduced. A negative result was obtained in an experiment in which the light causing photo-emission was supplemented by other radiation designed to neutralize any space-charge. This second radiation was of a wavelength absorbed appreciably by all layers of the crystal in its path. The lack of any increase in I_e showed that space-charge effects were unimportant.

The Magnitude of the Currents and their Spectral Dependence.—Figs. 4, 5, and 6 indicate that caution must be used when discussing current magnitudes. There is a marked increase of current with increasing incident photon energy. For currents arising from photons with energies several ev above the threshold, the quantum yield varies little from substance to substance, being about $6 \times 10^{-3} \pm 2 \times 10^{-3}$ e/Q. The quantum efficiency of photo-emission is thus not as high as that for metals [10] or for some other insulators.[11]

The photo-emission yield is greater than that for photocurrents measured by a surface-cell technique. The ratio of electrons in the external circuit to the quanta absorbed when an applied field of 1 v/cm. is operative varies from 10^{-7} for anthracene to 5×10^{-11} for naphthalene.[7] As stated in our previous work, oxygen adsorbed on the surface altered the quantum yield. Northrop and Simpson [12] measured current magnitudes on samples prepared so that oxygen is absent during illumination. They found a fairly constant quantum yield in each of the pure hydrocarbons. However, the presence of a disc on the surface opposite the electrodes and a disc on the electrode surface makes the experimental arrangement rather different from a conventional surface cell. Northrop and Simpson's

---

[9] Part VII, Lyons and Mackie, preceding paper.

[10] *E.g.*, Hinteregger and Watanabe, *J. Opt. Soc. Amer.*, 1953, **43**, 604.

[11] *E.g.*, Taylor and Hartmann, *Phys. Rev.*, 1959, **113**, 1421.

[12] Northrop and Simpson, *Proc. Roy. Soc.*, 1958, *A*, **244**, 377.

Table 1 and Fig. 6 do not enable one to work out quantum yields unless the electrode separation is known. Their results give a quantum efficiency of approximately 10^{-11} $e\ Q^{-1}$ cm.$^{-1}$. To approximate to our measurements of efficiency, an electrode separation of 10^{-4} cm. would be necessary. A value larger than this was most likely used, so that the efficiency is smaller than that found in our measurements. Any presence of space-charge in their experiments would have affected the numerical result. The quantum efficiency of photo-emission at high energies does not differ very much from one hydrocarbon to another, even although the fluorescence efficiency varies markedly in the same group of compounds. It seems likely, therefore, that an electron is released faster than fluorescence occurs. Values of the threshold frequency determined experimentally may shift slightly for higher light intensities. For anthracene 10^{16} incident quanta would alter the measured value by less than 1000 cm.$^{-1}$.

For metals, the question of a change in the threshold value, together with the closely connected one of the existence of a sharply defined maximum velocity of emission, has received much attention.[13] Thresholds for metals are usually obtained by Fowler's method of extrapolation to the threshold at absolute zero. Experimentally, errors may arise because the surface contamination alters the threshold frequency, occluded gases changing the threshold to either higher or lower energies depending on the gases.

For aromatic hydrocarbon crystals, as for other semi-conductors, the measured threshold could be altered by impurity centres.[14] There is no definite information from our work regarding the effect of occluded gases on the threshold however, and it would seem from the work on other insulating crystals such as the alkali halides [5] that impurity emission is the main trouble hindering the determination of a definite threshold. Further work is needed at this point.

The only previous results for thresholds of these hydrocarbons have been for films and not for single crystals. Carswell and Iredale [3] obtained a value for anthracene close to that of Hughes,[2] namely, *ca.* 46,000 cm.$^{-1}$ (2180 Å), and for phenanthrene a value of *ca.* 42,400 cm.$^{-1}$ (2360 Å). Our value for phenanthrene is lower than their results but this could well be due to three aspects of their experimental arrangement, namely, the use of a film, the lack of resolution of the light sources giving only a crude measurement of the threshold, and causing emission from the electrode due to light penetrating the film.

The values of the threshold energies can be correlated with a number of optical and electrical properties of the substances. With little variation, the order of threshold frequencies in the group of compounds correlates with the order of the energy of an electronic transition from the molecular ground state to the lowest excited singlet state (cf. Clar's *p*-band [15]) or lowest excited triplet level; [16] the ionization potential of the free molecule,[17] the electron affinity of the free molecule; [17] the radical affinity—methyl,[16] ethyl,[18] and trichloromethyl; [19] the energy of an electronic transition from the ground state to the lowest excited state of the charge transfer band formed by the molecule with an electron acceptor; [20] the maximum free valency in the molecule; [21] the minimum " atom localization " energy; [22] and the magnitude of the photocurrent from the crystals in dry air.[23]

[13] Fowler, " Statistical Mechanics," 1st edtn., Cambridge Univ. Press, Teddington, 1936; Vonsovskii, Sokolov, and Veksler, *Uspekhi Fiz. Nauk*, 1955, **50**, 477; Huguenin and Valat, *J. Phys. Radium*, 1956, **17**, 967.

[14] Spicer, *Phys. Rev.*, 1958, **112**, 114; *Radio Corporation of America Rev.*, 1958, **19**, 555.

[15] Clar, " Aromatische Kohlenwasserstoffe," 2nd edtn., Springer-Verlag, Berlin, 1952.

[16] Szwarc, *J. Chem. Phys.*, 1955, **23**, 204.

[17] Matsen, *J. Chem. Phys.*, 1956, **24**, 602.

[18] Smid and Szwarc, *J. Amer. Chem. Soc.*, 1956, **78**, 3322.

[19] Kooyman and Farenhorst, *Trans. Faraday Soc.*, 1953, **49**, 58.

[20] Brieglieb and Czekalla, *Z. Elektrochem.*, 1959, **63**, 6; Foster, *Nature*, 1958, **181**, 337; 1959, **183**, 1253.

[21] Burkitt, Coulson, and Longuet-Higgins, *Trans. Faraday Soc.*, 1951, **47**, 553.

[22] Brown, *Quart. Rev.*, 1952, **6**, 63; Coulson, *J.*, 1955, 1435.

[23] Lyons and Morris, *Proc. Phys. Soc.*, 1956, *B*, **69**, 1162.

Of course, many of these properties have been shown to be connected by previous authors, and the significance of this has been discussed elsewhere.[7] That photo-emission thresholds can also be correlated illustrates that the current is dependent upon electronic properties of the substances.

The threshold frequency for anthracene was calculated[4] for anthracene as 6·2 ev. Use of a recently determined value for the ionization potential of the anthracene molecule instead of that previously estimated alters this calculated threshold to 5·9 ev, which compares reasonably with the threshold observed at 5·7 ev. For naphthalene the theory predicts 7·3 ev and the observations give 6·8 ev. The theory therefore yields values which are slightly high, although not as high as expected by Fox.[24]

Over the range of photon energies used (5·5—9·0 ev), the measurable current changed by a factor of about 10^4. This behaviour is similar to that of both metals and some other insulators. Several theories have been put forward to explain the yield curve for metals and insulators,[25] but at present there is no adequate theory to explain quantitatively the dependence of photo-emission yield on frequency of exciting radiation. Spicer[14] has given a semi-empirical model for photo-emission from semiconductors. It should be possible to adjust his expression for the yield to our curves, but the significance of the parameters needed to make this adjustment would be uncertain. The alkali antimony compounds for which the theory was put forward have an electron affinity of *ca.* 0·3 ev, the photoconductivity and absorption have similar thresholds, and the photo-emission threshold is only slightly displaced from the other thresholds. For the aromatic hydrocarbon crystals photo-emission starts at least several ev above the photoconduction threshold. The electron affinity of the crystal would then be of the order of several ev, upon the assumption that the photoconduction is intrinsic.

From Figs. 4—6, it will be seen that certain weak maxima occur in the yield at positions: naphthacene 50,000 cm.$^{-1}$; 1,2:5,6-dibenzanthracene *ca.* 52,000 cm.$^{-1}$; 1,2-benzanthracene 52,400 cm.$^{-1}$; anthracene 54,000 cm.$^{-1}$; chrysene 55,000 cm.$^{-1}$; pyrene 55,500 cm.$^{-1}$. These maxima occur at 0·8 ± 0·2 ev above the threshold. The maxima might have been expected to be associated with a rise in the absorption of light by the crystal. However, the absorption spectra of anthracene and naphthacene crystals do not show a pronounced maximum in the required region. The maximum extinction coefficient (in polarized light) occurs just before this region. Yield curves taken with polarized light may show an alteration in the positions of the maxima, but, pending such results, it seems unlikely that an increased absorption in the crystal causes these yield maxima.

Defect levels must next be considered. The crystal spectra of anthracene and naphthacene do not give evidence of the presence of defect levels, but their concentration would probably be too small for detection. Pronounced maxima in the I_e–ν curves were observed in the alkali halides by Apker and Taft,[5] who showed that they were due to F centres. An exciton propagated through the crystal lattice after light absorption ionized an F centre in a secondary process, thus freeing an electron for emission. At lower energies any photo-emission is due to direct ionization of the F centres by the incident photons. The aromatic hydrocarbons differ from the pure alkali halides in which absorption and photo-emission start at nearly the same wavelength. Direct ionization of any impurity centre should not be of great significance for the hydrocarbons, for the hydrocarbon itself absorbs the incident radiation strongly outside the region of photo-emission. None the less, defect levels could cause an increase of the photo-emission yield by enabling ionization by some secondary process. No definite decision on this point could be drawn from the present results.

The stopping potential–incident photon energy curves (Fig. 7) allow a measurement

---

[24] Fox, *Phys. Chem. Solids*, 1959, **8**, 439.

[25] Mitchell, *Proc. Roy. Soc.*, 1934, *A*, **146**, 442; Makinson, *Phys. Rev.*, 1949, **75**, 1908; Huntington and Apker, *ibid.*, 1953, **89**, 352.

of ***h*/*e*** from the slope. Condon [26] pointed out that, for this, semi-conductors are more useful than metals. The stopping potential used is that potential at which no current is measured for a particular photon energy. Corrections for contact potential difference were not made as they do not affect the slope of the curve. The measured slope is 3·93 × 10^{-15} v sec. The theoretical value is 4·13 × 10^{-15} v sec. The closeness of these values indicates that space-charges and other side effects were not causing much trouble, for it would be expected that any surface and space-charge would alter with different incident photon energies and the different intensities of the incident photon beams used. The result provides some justification for neglecting side effects when discussing the spectral dependence. However, one small anomaly presents itself. In Fig. 7, the slopes for anthracene and naphthacene are separated by about 0·3 ev, but their threshold frequencies are 0·4 ev different. This could possibly be due to inaccuracies in either the current–voltage curves or the extrapolation technique for the threshold, or else to the presence of impurity levels altering the threshold.

Extrapolation of the line in Fig. 7 to the threshold energy gives the minimum stopping potential, V'_0, as —0·7 v for anthracene and —0·9 v for naphthacene. The negative sign means that the V'_0 value is of opposite sign to the stopping potentials usually measured which are regarded as positive, *i.e.*, the sign of the emitter potential relative to that of the collecter. By measuring the stopping potential for a metallic emitter, and then that for the hydrocarbon crystal, in principle it is possible to determine the energy gap from the full to the conduction band. Various attempts were made to do this by using scraped copper, nickel, and platinum emitters. The results gave either a very small gap (anthracene) or a negative gap (naphthacene). An improved technique in examining the metals is indicated. The cleaning of the metals was not as thorough as that for the more volatile hydrocarbons. Heating under a vacuum to drive out occluded gases would have been necessary.

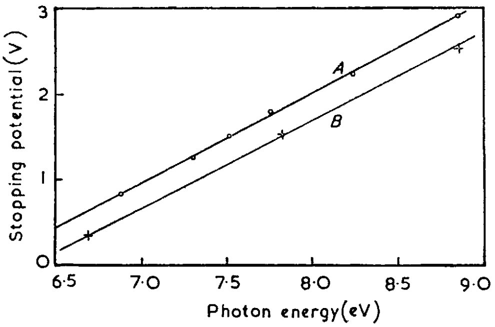


FIG. 7. *Stopping potential–photon energy relation.*
A, Naphthacene; B, anthracene.

The current–field strength curves. The true energy distribution of the electrons should be given by a differentiation of the I_e–E relation. Although the I_e–E curves were reasonably reproducible, the derivative curves of these were subject to a rather large error. Further, in order to obtain the most meaningful results, it is necessary to scale the abscissa in units of V_0–V. This was not possible, and the alternative of plotting log I_e against log V was adopted. The resultant curve approximated to a straight line for negative voltages. The slope gave the value of " m " as *ca.* 1·25 in the expression of Apker, Taft, and Dickey [5] for the energy distribution of the emitted electrons.

We thank General Motors-Holden Ltd. for the grant of a Fellowship to G. C. M.

THE UNIVERSITY OF SYDNEY, SYDNEY, N.S.W., AUSTRALIA. [*Received, April 11th,* 1960.]

[26] Condon, *Phys. Rev.*, 1938, **54**, 1089.