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Photoemisssion from Metal Contacts into Anthracene Crystals: A Critical Review†

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Abstract—Photocurrents in anthracene crystals which have metallic contacts are discussed and it is shown that in some cases these currents can be interpreted as arising from photoemission from the metallic contact into the anthracene crystal. The experimental evidence is reviewed to ascertain which measurements can be interpreted in this way. The conclusions that can be drawn from these measurements concerning the nature of metallic contacts on anthracene crystals and the nature of the conduction states in the anthracene is examined.

1. Introduction

Anthracene has served as a model system for attempts to understand molecular crystals. In many experiments such as electro-luminescence and studies of conduction processes, contacts play a critical role, determining in many cases whether the experiment can be performed. For this reason as well as the intrinsic interest of the subject, contacts on anthracene crystals have been studied extensively.

The critical property of a contact for most purposes is the number and type of carriers the contact is capable of injecting into the crystal under the experimental conditions. And the most important factor in determining this is the relation between the chemical potential in the contact and the conducting states in the crystal. (For metallic contacts the chemical potential is just the fermi level.)

In the case of semiconductors three methods are commonly used to determine the energy difference between the fermi level of a metal

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in intimate contact with the semiconductor and the conduction or valence band of that semiconductor: differential capacitance measurements, current-voltage measurements, and photoemission measurements. In the case of insulators, such as anthracene, the first method fails because the ionized donor/acceptor density is so small that the depletion region is too wide to dominate the capacitance, while the second method fails because insulators usually contain enough deep traps that trapped space charge dominates the current-voltage characteristics. However, photoemission has been used frequently to determine the energy difference between the fermi level in a metal deposited on an insulator and the conducting states in the latter.(1,2)

Several authors have recently attempted to use photoemission from various metals into crystalline anthracene to determine the nature of the metal-anthracene interface as well as to gain information concerning the nature of the conducting states in the anthracene itself. In the case of hole injection the dependence of the photocurrent upon the energy of the incident photons for various metal contacts was generally found to be roughly the same if the photon energy scales were shifted by about the difference in work functions of the metals employed.(3) In the case of electron injection the behavior of the photocurrent is more complicated, but can be divided into three components.(4–6) As can be seen in Fig. 1, there is a low energy current component and a higher energy component, both of which have spectral response which are similar, but shifted in energy for various metals. One can also see from Fig. 1 that in the case of the higher energy current component, the quantum yield, n (photocurrent expressed in terms of number of collected electrons per incident photon) varies as $(h\nu - \Phi_B)^2$ for energies in excess of Φ_B, where Φ_B is the zero current intercept of this component. While it is not clear from Fig. 1, this is also true of the lower energy current component for a small range of energy slightly in excess of its zero current intercept. For any given metal one can find a difference between the zero current intercepts of these two components. This difference is roughly independent of the metal. Furthermore, both zero current intercepts vary roughly linearly with the work function of the metal. A third component is seen to appear as a peak in the plot of quantum yield vs photon energy at 1.8 eV, independent of the metal used. The quantum efficiency of this component relative

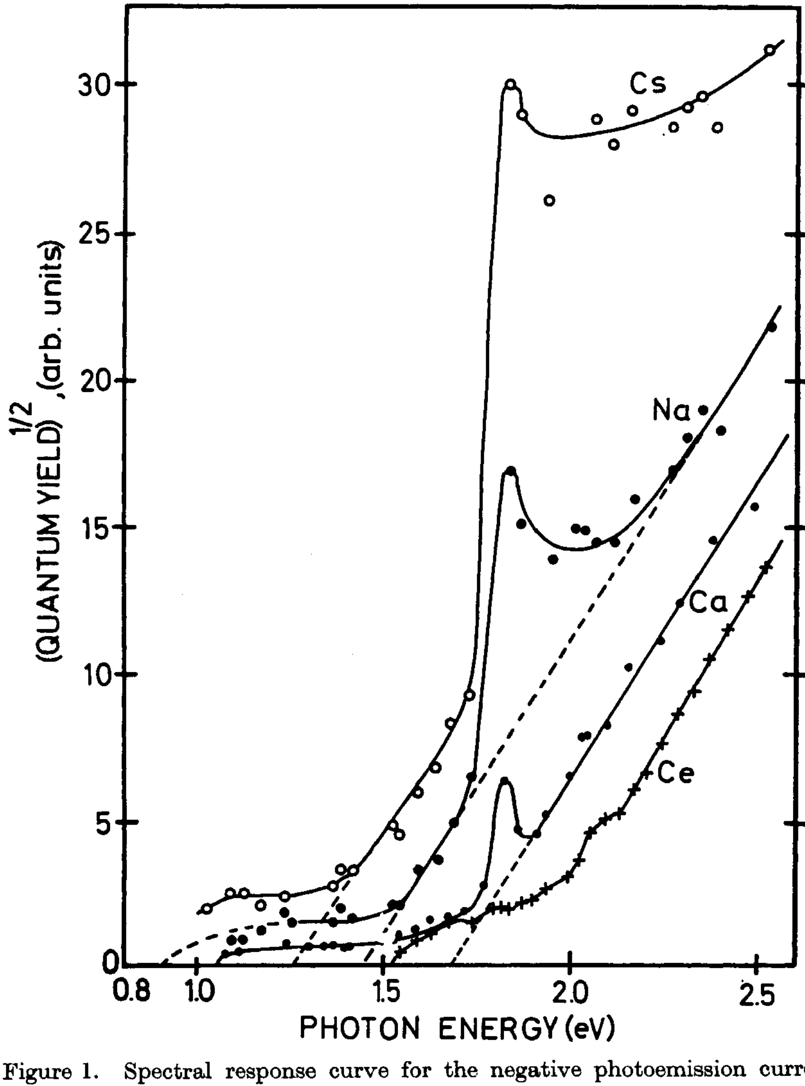

Figure 1. Spectral response curve for the negative photoemission current for various contact metals. Crystal thickness 2 mm, field strength 5000 v/cm. (taken from Ref. 8).

to that of the other two components varies with the work function of the metal.

Mehl, however, has argued that these currents cannot be interpreted as arising from electron emission from the contact metals into anthracene crystals because alkali metals form injecting contacts to anthracene.(7) To support this assertion he shows a plot of dark current vs voltage for electron injection from a molten *Cs* contact into an anthracene crystal which was about 40 μm thick. This plot shows a rapid rise of current with increasing voltage, followed by a region in which $I \propto V^2$, followed by a saturation current of about 10^{-2} amp/cm^2 for voltages in excess of about 100 volts. Mehl suggested that since his work showed alkali contacts were injecting, the observed photocurrent could arise from (1) photoexcitation of trapped carriers for the region of low photon energy (0.8 eV – 1.8 eV), (2) production of carriers at the contact by triplet excitons generated in the bulk of the anthracene for photon energies greater than 1.8 eV, and (3) production of carriers at the contact by singlet excitons generated in the bulk for photon energies greater than 2.9 eV.

This paper drew vigorous rebuttals from the authors of " photoinjection " papers.(8–12) These papers refined and extended the measurements described earlier and generally confirmed the results outlined earlier. But since these authors are not in complete agreement among themselves as to the proper interpretation of these data, we shall treat the various current components separately. We shall discuss first the currents whose region of sensitivity shifts with metal work function and then the current component whose spectral response is independent of metallic work function. But first of all we must discuss Mehl's assertion that photoemission is not what is observed.

2. Space-Charge-Limited Current?

Mehl is certainly correct in saying that if a sample is operating in a space-charge-limited (scl) mode, one cannot observe photoemission because scl means that the contact is supplying carriers at a rate in excess of the current carrying capacity of the crystal and increasing the excess will not increase the current (in first order). Moreover, although Mehl was specifically referring to alkali metal contacts to anthracene, the question he raised is of more general applicability. One expects Richardson-Schottky emission from any contact and if there is a high ratio of trapped charge to free charge, a small Richardson-Schottky current may lead to scl conditions. Since a high ratio of trapped charge to free charge is frequently encountered in insulators, one may ask if photoemission from a metal to an insulator can ever be observed.

Richardson-Schottky (RS) emission from metals into insulating solids has often been observed.(13) Perhaps the observations which are most germane to the present discussion are those of Dresner on anthracene.(14) In this case the cathode consisted of a charge transfer complex formed by reacting alkali metals with the anthracene crystal. When the injecting contact is a metal one expects a current described by the RS equation[15]

$$J = \frac{4\pi e m (kT)^2}{h^3} \exp(-\Phi_B/kT)\exp(\beta_{RS}E_0^{1/2}) \qquad (1)$$

where $\beta_{RS} = (e/kT)(e/4\pi\epsilon_0\kappa)^{1/2}$, ϵ_0 is the permittivity of free space, κ is the high-frequency dielectric constant[16], E_0 is the field at the cathode-crystal interface, and other symbols have their conventional meanings. If a localized charge is left behind after emission, the above equation should be modified by substituting $\beta_{PF} = 2\beta_{RS}$ for β_{RS} and the equation becomes known as the Poole-Frenkel equation. Evaluating κ using the index of refraction (n_γ at 546 nm) to obtain the high frequency dielectric constant,(17) one finds $2\,kT\beta_{PF} = 1.09 \times 10^{-23}\ \mathrm{coul}\cdot\mathrm{m}^{1/2}\cdot V^{1/2}$, which is in excellent agreement with the value $1.1 \times 10^{-23}\ \mathrm{coul}\cdot\mathrm{m}^{1/2}\cdot V^{1/2}$ measured by Dresner. (Dresner calculated a value of β_{PF} equal to about $\frac{1}{2}$ of the value we have found. It seems likely that he used the low frequency rather than the high frequency dielectric constant).

Although one can calculate a barrier height of about 0.7 eV from the value of the saturation current in Mehl's data if one assumes Poole–Frenkel (PF) emission (in fair agreement with values reported from photoemission), this doesn't diminish the force of his argument. For even when one admits that a barrier exists, one must also admit that something limits the current to values orders of magnitude below the PF limit and if this limiting factor is space charge, it is hard to make a case for observation of photoemission. Simmons has considered emission from a metal into an insulator in the presence of moderate to high fields.(18) He argues that because of the high scattering rate present in insulators one must modify the usual RS (or PF) description. Simmons' program was carried out in detail by Emtage and O'Dwyer who solved the continuity equation for charge, utilizing a potential that included image effects (which leads to RS lowering), but which excluded space charge effects.(19) Their results may be written in the form

$$J = e\mu N E_0 \exp(- \Phi_B/kT) \tag{2}$$

for low fields and in the form

$$J = e\mu N \left(\frac{kT}{e\pi}\right)^{1/2} \left(\frac{16\pi\epsilon_0\kappa E_0^3}{e}\right)^{1/4} \exp(- \Phi_B/kT + \beta_{RS}E_0^{1/2}) \tag{3}$$

for high fields (in Mks units) where N is the insulator density of states at the band edge, μ is the mobility and other symbols are as in Eq. (1).(20) For anthracene Helfrich and Mark have deduced that $N = 3 \times 10^{21}/\mathrm{cm}^2$.(21)

These equations are plotted as the solid line in Fig. 2 for a barrier of 0.8 eV (a typical value for an alkali metal on anthracene (4,12), at 290°K. It should be emphasized that these equations do not include the effect of space charge, and should thus be an upper limit on the current in these circumstances. Child's law is shown as the dashed line in the same figure for a crystal 1 mm thick which is devoid of traps. It might seem from this curve that space charge is never important at practical voltages. This is, however, misleading since traps can considerably modify this picture.(22) The dotted line in this figure shows the data for electron current while the dot-dash line shows the data for hole current for a typical anthracene crystal 0.62 mm thick which had injecting contacts.(23) Since trap densities vary widely, one may find in practice cases quite different from this, which is given only by way of illustration. (Similar comments hold for the emission limited curve since small charges in Φ_B or T (0.05 eV or 20°C) will change this current by an order of magnitude).

One may say in summary that it is possible to have dark currents which are contact limited to rather small values so that photoemission can be observed. In cases where trapping raises the space charge to such a level as to make observation of photoemission

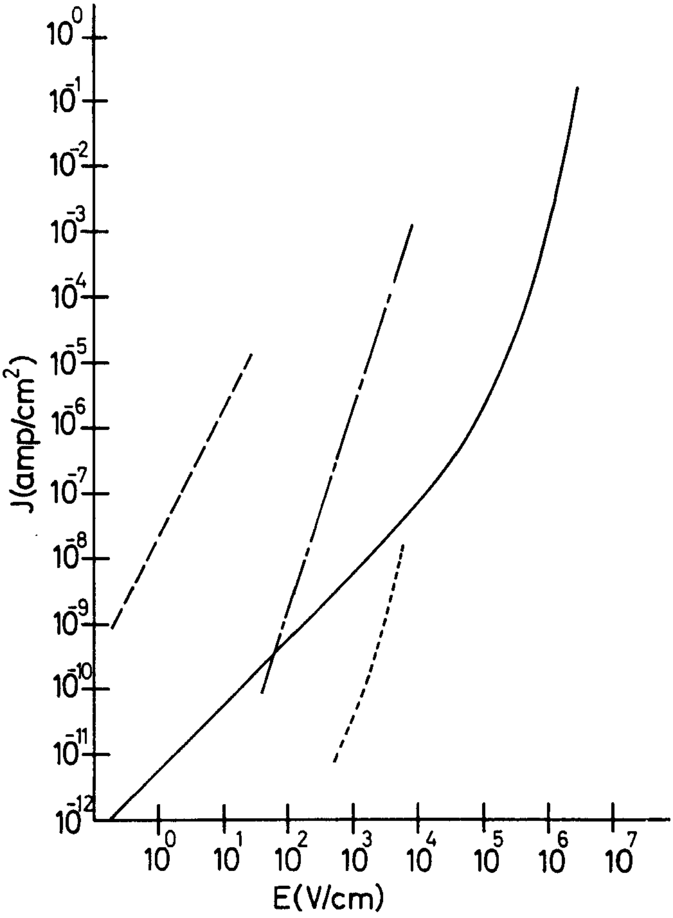

Figure 2. Dark currents in anthracene under various conditions. Solid line, emission limited current after Eq. 3 of text; dashed line, calculated scl current in 1 mm thick crystal devoid of traps; dot-dash line, experimental scl hole current in 0.6 mm thick crystals with traps; dotted line, experimental scl electron current in 0.6 mm thick crystal with traps.

impossible an experimental remedy may exist. One can illuminate the crystal with light of energy appropriate for emptying the traps which is modulated at one frequency (say d.c.) while illuminating the contact with light which is modulated at a second frequency. One may then be able to observe the current at the second frequency which is emitted into a crystal freed of space charge effects.

3. Ambulatory Photocurrents

Having concluded that it is possible to observe photoemission from metals into anthracene, we turn to the questions of whether photoemission has been, in fact, observed, and if so, what interpretations can be made of these observations. Recall that we have earlier differentiated between photocurrents whose spectral response remains generally unchanged in shape but is shifted in wavelength as the work function of the metal is varied and those whose spectral response is not shifted in wavelength as the work function of the metal is varied. For the sake of whimsy, we call the former ambulatory and the latter sedentary.

In Fig. 3 is shown diagramatically the simplest thing that can happen when a metal is brought into intimate contact with an

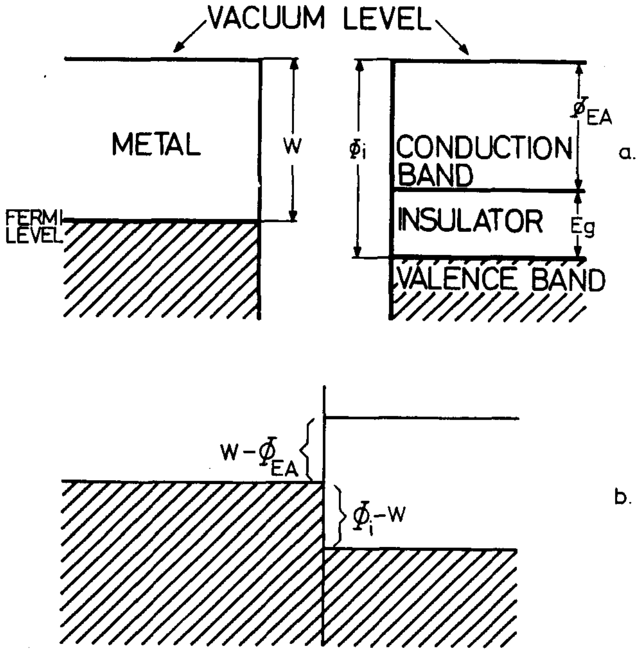

Figure 3. Schematic representation of bring together of metal and ideal insulator devoid of surface states. W is metal work function; Φi and Φ_{EA} are ionization potential and electron affinity, respectively, of insulator; E_g is energy gap.

insulator, nothing. In this case the barrier to hole injection, from, the metal into the insulator, Φ_B^+, is just the ionization energy, Φ_i, minus the metal work function, W; the barrier to electron injection, Φ_B^-, is simply W minus the electron affinity, Φ_{EA}, and the sum of these two barriers, $(\Phi_i - \Phi_{EA})$, is the energy gap, E_g. In this simple model the barrier should vary linearly with the metal work function.

When a photon of energy, $h\nu$, strikes the metal in Fig. 3, it can excite an electron to any energy between the fermi level, E_F, and $E_F + h\nu$. (Although this discussion is restricted to electrons, the complementary discussion for holes is obvious.) One assumes that the excited electrons are distributed uniformly in energy and isotropically in momentum space. Then if $h\nu > \Phi_B^-$, the number of electrons in an incremental energy range around $h\nu$ which have momentum directed toward the barrier great enough to surmount the potential difference is proportional to $(h\nu - \Phi_B^-)$. The photocurrent I_{ph} (the integral over all particles with enough momentum toward the barrier to surmount the barrier) is related to photon energy by $I_{ph} \propto (h\nu - \Phi_B^-)^2$. Thus a plot of $\sqrt{I_{ph}}$ vs $\cdot\, h\nu$ yields a straight line with a zero current intercept equal to Φ_B^-. This relation has been shown to be generally valid.⁽¹⁾ (We should perhaps remark at this point that whenever we say photocurrent it should be understood to mean photocurrent normalized to some standard photon flux).

Unfortunately, a number of complications arise which alter this simple picture. Before the metal is joined to an insulating (or semiconducting) crystal, the fermi level in this crystal has the same position relative to valence and conduction bands throughout the crystal (i.e. thermal equilibrium exists). When the metal and crystal are brought together, their fermi levels will not, in general, coincide. To reach a new quasi-equilibrium, states near the contact empty or fill. The resulting dipole layer gives rise to field of sufficient magnitude that far from the contact the fermi level is not perturbed from its initial relationship to the bands. Thus, since the relation between fermi level and bands changes and since the fermi level is constant, the bands bend. The distance over which states fill or empty, and thus over which the band-bending occurs, is proportional to the square root of the difference in fermi levels of the unperturbed metal and crystal, and is inversely proportional to the square root of the net density of states available for filling or emptying. This distance, the depletion layer thickness, varies from less than 1Å in metals, to 10–100Å in relatively highly doped semi-conductors, to tenths of mm in good insulators. Although this phenomenon has important device applications (e.g. variactor diode), it concerns us here only in so far as it affects collection of photoinjected charge. Band bending *hinders charge collection* if a photoinjected carrier must go over a potential maximum in passing from the injecting to the collecting contact, as might well be the case for hole injection in an n-type semiconductor. Fortunately, in wide gap semiconductors and insulators the density of ionized states is usually so small that the resulting field can be overcome with relatively small bias fields and the band bending presents no essential difficulty. (Similar remarks hold for band bending arising from the trapped charge that may exist in a contact limited structure).(24)

A matter of somewhat more concern is the possibility that an interfacial layer exists between metal and crystal. It has been shown in some instances that such an interfacial layer can effect the measured magnitude of the surface barrier.(2,25) This problem has been studied in some detail by Crowell and coworkers.(26) As long as the contact metal doesn't react with the crystal, interfacial layers can be avoided by cleaning the crystal surface prior to deposition of the contact. However, even in the case that interfacial layers exist, the relative relationship between various states in the crystal are preserved so that cases may exist in which interfacial layers prevent measurement of the potential difference between the fermi level of the metal and the conducting states of the crystal and yet the measurements yield valuable information concerning the relationships of the various conducting states in the crystal. In this respect interfacial layers are similar to surface states, which we shall have occasion to discuss in more detail later.

3.1. Holes

Williams and Dresner wished to study the barriers to hole injection from a number of metals into anthracene. For a gold contact on anthracene they found a dark current which varied linearly with applied voltage and which was about 5×10^{-13} amp/cm^2 at a voltage corresponding to about 10^3 V/cm.(3,27) From Eq. 3 one calculates a current of about 5×10^{-14} amp/cm^2 for these conditions. It seems that one must search for other explanations of this current (e.g. surface leakage, emission from the edge of the contact when the field is high, bulk impurity ionization, etc.). The important point being that this current is certainly emission limited and the photocurrents can be safely interpreted as photoemission from the metal into the anthracene crystal.

In Fig. 4 is presented a curve taken from (3) showing that the

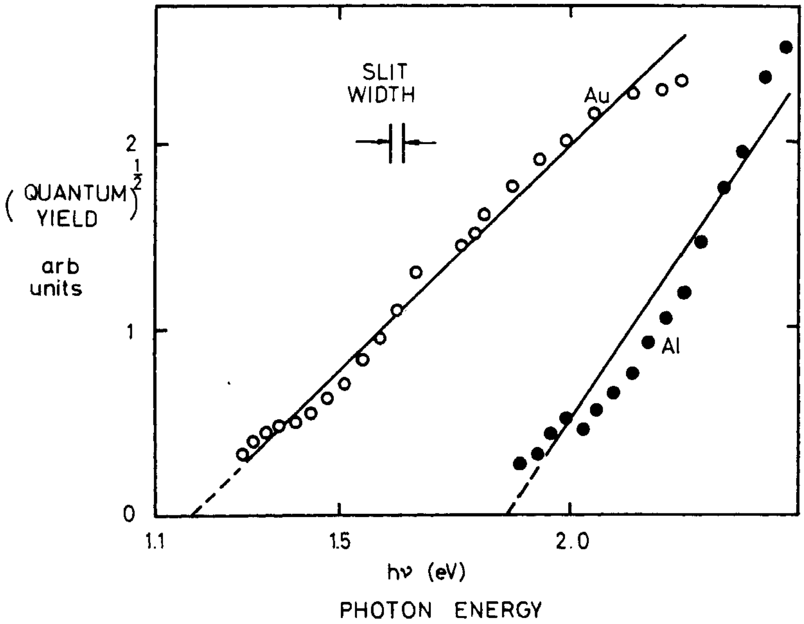

Figure 4. Square root of the quantum yield for photoemission vs photon energy for photoemission of holes into anthracene from aluminum and gold. (Taken from Ref. 3).

quantum yield follows approximately the expected relation. From such plots Williams and Dresner determined the barrier to hole injection into anthracene from Au, Ag, Pb, and Mg. These results are shown as the open circles in the plot of barrier height vs work function shown in Fig. 5.

William and Dresner argue that the simple model we have presented must be modified in the case of crystals with very narrow

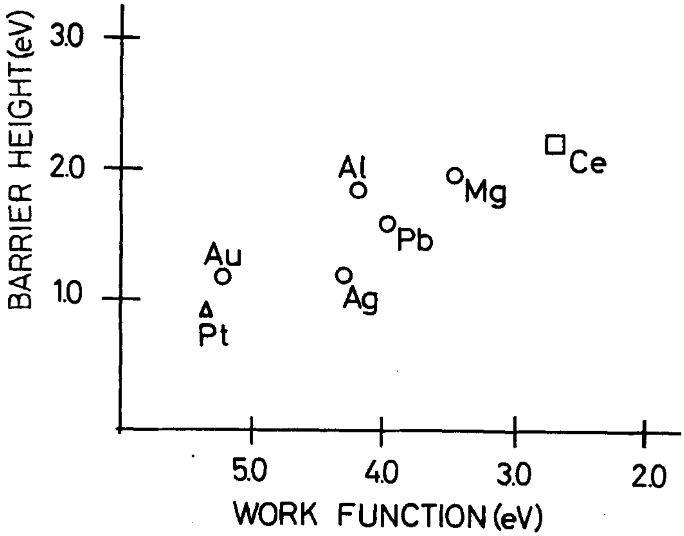

Figure 5. Barriers to emission of holes from various metals into anthracene. For the circles, the barrier heights were measured by Williams and Dresner (Ref. 3) and work functions were taken from Ref. 38. For the square, the barrier height was measured by Vaubel and Baessler (Ref. 9) and the work function was taken from Ref. 49.

bands. In this case, they assert, the narrow band can be considered a delta function which samples the uniform energy distribution of excited electrons and results in a photocurrent having the form of a step function. In the case of a molecular crystal one expects the electronic levels to be vibrationally split into a number of roughly equally spaced levels as shown in Fig. 6a.(28) Each level gives rise to a step function of current beginning at Φ_{B0}^{+}, Φ_{B1}^{+}, ... These step functions combine to give the staircase quantum yield, n, shown schematically in Fig. 6b. The derivative at the quantum yield, $\mathrm{d}n/\mathrm{d}\nu$, yields the splitting in a much clearer manner as is shown in 6c.

However, the envelope of n should vary linearly with $(h\nu - \Phi_{B0}^{+})$ rather than quadratically as found experimentally. This difficulty disappears with a minor correction to the above argument. As discussed previously, the number of particles in an increment of energy around $h\nu$ which can surmount the potential barrier is proportional to $(h\nu - \Phi_B)$. Thus, if the ith level is very narrow, the quantum yield for this level is proportional to $(h\nu - \Phi_{Bi}^{+})$. The quantum yield, n, from all the vibrationally split levels is the sum

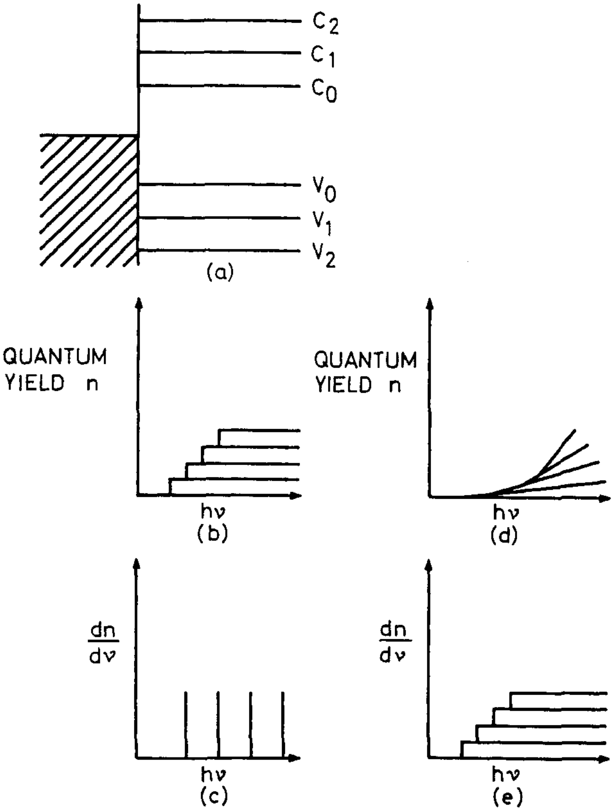

Figure 6. Schematic depiction of photoemission from metal into insulator with very narrow bands. (a) Energy diagram. (b), (c) quantum yield and its derivative when the acceptance angle is not considered. (d), (e) quantum yield and its derivative when acceptance angle is taken into account. (See text.)

of a number of linear ramps and has a quadratic envelope as is shown in Fig. 6d. Figure 6e shows $dn/d\nu$ to be a series of step functions with a linear envelope.

Williams and Dresner argue that the fluctuations seen in the curves of Fig. 4 are a manifestation of the vibrational splitting. To display this structure better they plot $dn/d\nu$ versus $h\nu$ which is shown in Fig. 7. As we anticipated, this seems to be better described as a series of step functions with linear envelope than as a series of delta functions. One should note the resolution on these measurements is only about $\frac{1}{3}$ of the splittings which are to be measured.

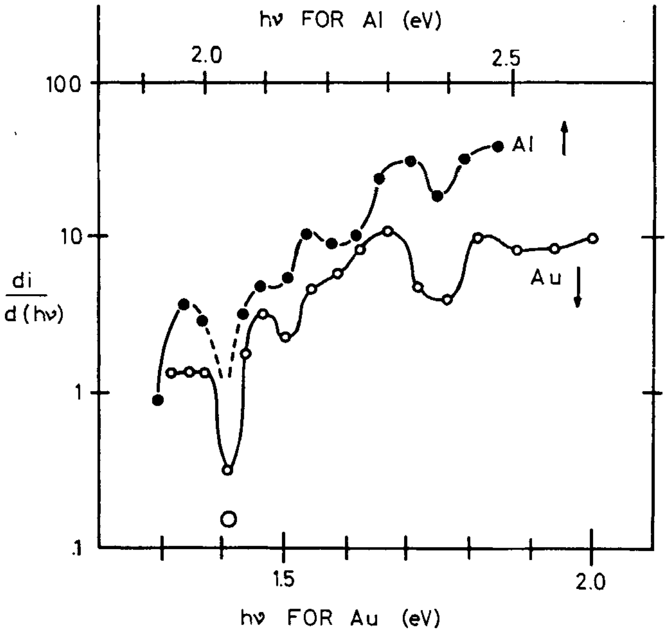

Figure 7. Derivative with respect to energy of the quantum yield for photoemission for gold and aluminum on anthracene. The point marked ○ belongs to the aluminum. It cannot actually be plotted on the logarithmic scale used here because the slope was negative at this energy. It is put on the graph to indicate that the curve for aluminum dips sharply at this point. Note that the energy scales have been shifted with respect to one another to facilitate comparison of the curves (Taken from Ref. 3).

Recent measurements by Dresner of hole emission from a colloidal platinum electrode are worth mentioning in this regard.(29) A ten-fold increase in the quantum yield of this contact relative to those employed in the above work allowed a resolution which varied from 10 meV to 20 meV over the spectral range of interest. The data shows an envelope which varies as $(h\nu - \Phi_B^+)^2$ as expected, but superimposed on this envelope are definite peaks and valleys which repeat with a period of 0.175 eV, the splitting of the principal ladder of vibrational states. These clearly defined peaks and valleys lend support to the idea that the vibrational splitting of the molecule influences the photoemission structure, but this structure cannot be explained in terms of simple transitions from a continuum to a series of discrete states. One must invoke either discrete initial and final states or a two step process involving discrete intermediate and final states to explain a structure of this type. Analysis of this phenomenon would appear to be a worthwhile theoretical problem. One caveat to observe in interpreting this data is that the photoinjected charge may also be photoassisted from traps while crossing the anthracene crystal and hence the small dips near 1.1 eV and 1.4 eV may have the same origin as those seen in the photocurrent-action spectrum at these wave lengths.(30) One must also take into account the absorption by the anthracene vibration bands at 1.1 eV and 1.4 eV which reduce the light reaching the injecting back contact (see Fig. 8) when one will analyze this data in detail.

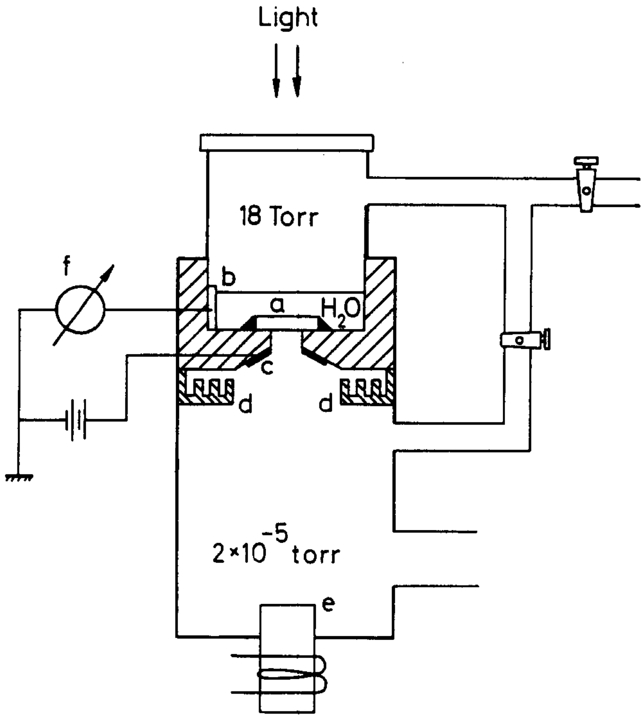

Figure 8. Vacuum conductivity cell. a crystal, b gold contact, c short circuit between the lower (Na) electrode and a contact for power supply was provided by the evaporated Na layer spreading over part of the sample holder, d guard ring system to avoid any contact between the evaporated Na layer and the metal wall of the chamber, e evaporation vessel, f Keithley $\mu\mu$-ammeter (taken from Ref. 5).

3.2. ELECTRONS

The literature concerning electron emission is less clear than that for hole emission. This may result from the greater apparent complexity of the systems encountered and the different methods which have been employed in attempting to explore the several phenomena arising from this complexity. As should be apparent from the earlier discussion, the natural choice of metals for electron emission experiments is those with low work functions, the alkali metals. Unfortunately for physics, which deals most successfully with simple systems, a consequence of low work functions is high chemical reactivity. Faced with this possibility, some workers have chosen to deliberately react the alkali metals with the anthracene and study a system composed of anthracene ions on anthracene, while others have chosen to investigate systems which were believed to be metal in contact with anthracene crystals with at worst a monolayer of ions between metal and crystal.

The chief exponents of the latter school, which we shall discuss first, are Baessler and his coworkers. Their experimental arrangement is shown in Fig. 8 to acquaint the reader with the techniques generally used in these measurements.⁽⁵⁾ The metal from which the photoemission is to be measured is evaporated into one side of the crystal and the photoresponse measurements are made without disturbing the sample or breaking the vacuum. This type of arrangement where the radiation which excites the electrons to be emitted into the crystal passes through one electrode (the front contact) and the crystal before striking the injecting electrode is often referred to as a back walled cell. Such an arrangement is essential where the emitting contact must be thick either because of the nature of its manufacture (as in the case of reacted contacts) or because of a propensity for the metal to react with the atmosphere (as in the case of alkali metal contacts). In addition to using this rather ingenious arrangement which avoids atmospheric deterioration of the alkali contact, these authors evaporated the alkali contact in about 10 sec in hopes of minimizing diffusion of the metal into the anthracene which they envision as the mechanism involved in the formation of a thick charge transfer complex layer.⁽⁴⁾ One should perhaps note that a standard technique used by Baessler *et al.* was the sublimation of several surface layers from their crystal prior to evaporation in an attempt to insure a clean surface. (Williams and Dresner employed the same technique in their hole emission studies). The success of this technique depends upon the ratio of the sublimation rate to the monolayer cover time for contaminants at the temperature and vacuum employed. Lacking information concerning these parameters, we cannot evaluate the efficacy in this instance.

The direction of their work was already determined in early studies of Cs and Na contacts from which they reported observing ambulatory photocurrents with two components, the lower energy component having a zero intercept of 0.8 eV and 1.0 eV for Cs and Na, respectively, while the higher energy component had an extrapolated zero intercept 0.45 eV above the lower energy intercept.[4,5] The lower energy component is attributed to emission into a very narrow ($\sim 10^{-2}$ eV) conduction band while the higher energy component is attributed to injection into a wider (0.6 eV) upper conduction band.(6) The dark current was reported to be less than 10^{-12} A at 10^{3} V across a crystal 2 mm thick with a contact area of 0.3 cm^2. We calculate a dark current density of 4×10^{-11} amps/cm^2 for the reported Na barrier of 1.0 eV and a dark current density of 3×10^{-8} amps/cm^2 for the reported Cs barrier of 0.8 eV at this field using Eq. (3). Although the reported dark current is a bit lower than that calculated for Na and considerably lower than that calculated for Cs (there is no indication in the paper whether this dark current is for Na, Cs, or typical of both), this does not necessarily indicate scl current. It may be that only a small portion of the contact area is actually an active contact as has been observed by Dresner in the case of gold.(14) That something of this nature may have occurred and that space charge was not the limiting factor is made plausible by the observation that the dark current varied linearly with the applied voltage.(31) From these considerations and others which will be discussed later it seems fairly certain that the observed photocurrents are a result of photoemission from the contact and not optical detrapping as suggested by Mehl. The measured zero intercept for the low energy component (and thus the splitting of the two bands) should be accepted with reservations since Dresner has pointed out that water absorbs light strongly in the vicinity of the measured zero intercepts.(12)

This early work on electron emission from alkali metals was soon followed by a series of measurements on other metals. The results are summarized in Fig. 9 where the barriers to emission into the lower, $\Phi_{\bar{B}1}$, and upper, $\Phi_{\bar{B}2}$, conduction bands (4,5,8–11) are plotted as a function of metal work function. We consider the wide and consistent variation of barrier height with work function as the best evidence that this is a surface phenomenon and not photo-assisted scl current in the bulk. Baessler and Vaubel further argue that since they observe d.c. photocurrents of 10^{-8} amps/cm^2, the observed currents cannot arise from photo-detrapping of current limiting space charge because at the observed rate, the trapped charge must soon be exhausted, an argument supported by our calculations of maximum thermally injected current based on Eq. (3). Finally one

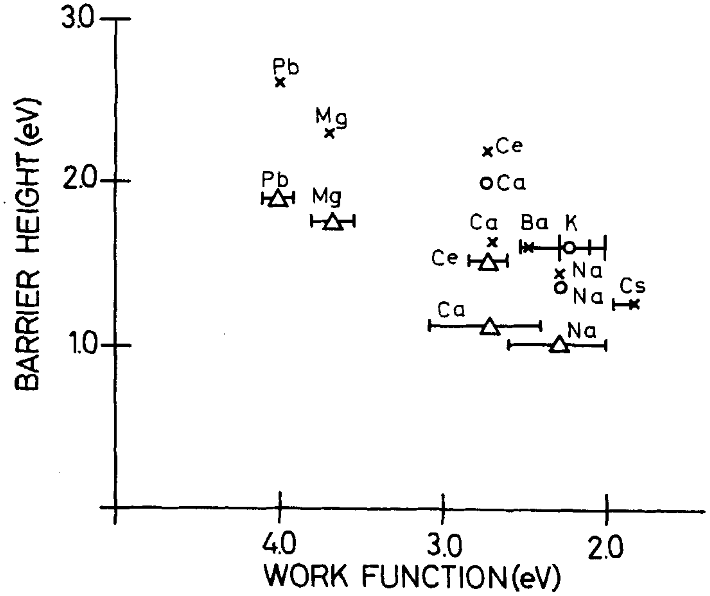

Figure 9. Barriers to emission of electrons from various metals into upper and lower conduction bands of anthracene. vs work function of metal. △ and X represent barriers to emission into lower and upper bands, respectively, as measured by Baessler and Vaubel (see Table 1 for exact references) while O represents barriers to emission into the upper band as measured by Donnini and Abetino (Ref. 30). The work functions were taken from Ref. 38, while the error bars on the work function were estimated from the scatter of the values reported in this compilation.

may note that if the observed currents arose from photo-detrapping then one should also observe photocurrent after reversing the polarity, a phenomenon which was absent from the work under discussion, but which has been observed in other cases.(32,33)

Several additional aspects of this work are worthy of discussion. In the cases of Ce and Mg, it was possible to observe photoemission into both the highest hole band and the lowest electron band. Williams' and Dresner's value 1.97 eV for Φ_B^+ for Mg was confirmed while Φ_B^+ for Ce was found to be 2.20 eV. Recall from Fig. 3 and the accompanying discussion that the sum of the two barrier heights allows an unambiguous determination of the energy gap, Eg, which was found to be 3.72 ± 0.03 eV.(11) As has been noted, this method of determining the energy gap, which has been employed with success on other materials, whose band gaps have been independently determined by optical absorption measurements,(34) is independent of any assumptions concerning presence of surface states, or interfacial layer, and of the work function of the metal employed.

One should also note that structure similar to that observed for hole emission was also observed for electron emission.(9) In the case of electron injection it was also interpreted as emission into vibrationally split bands. The resolution in these measurements is low so that one would certainly wish for confirmation of these results with higher resolution before attempting detailed analysis.

Examination of Fig. 9 or Table 1 shows that the splitting between lower and upper conduction bands is 0.58 ± 0.03. The values for Φ_{B2}^- seem to have been obtained by extrapolating the upper portions of the photocurrents to zero.(8) Although it is a minor matter, one should point out that the components of current arising from processes with lower thresholds should first be subtracted from the total current and the square root of the remaining current plotted against $h\nu$ in a manner analogous to the classic work of MacFarlane *et al.*(35) The values of Φ_{B2}^- as determined from the zero intercept would then be shifted to slightly higher energies and the splitting between the bands would increase slightly.

Some confirmation of the work on upper bands may be found in a paper by Donnini and Abetino.(36) They also found photocurrents whose spectral dependence could be described by $I(\nu) \propto (h\nu - \Phi_B^-)^2$ and whose intercept varied with the metal used. The barrier heights they determined from the zero intercepts are plotted as circles in Fig. 9 and can be seen to be in general agreement with those determined by Baessler *et al.* Because of the paucity of information concerning experimental conditions given in this paper, we cannot evaluate the reliability of the data except to remark that the barrier heights seem to have been found from plots of 4 or 5 points.

TABLE 1 Compilation of values of barriers to injection of holes into the valence band, Φ^+_B, and to injection of electrons into the first, Φ^-_{B1}, and second, Φ^-_{B2}, conduction bands. The superscripts indicate the sources. a, Ref. 3; b, Ref. 9; c, Ref. 11; d, Ref. 5; e, Ref. 50; f, Ref. 36; g, Ref. 29.

Metal	Φ^+_{B1}	Φ^-_{B1}	Φ^-_{B2}
Ag	1.20[a]		
Al	1.86[a]		
Au	1.17[a]		
Ba			1.63[e]
Ca		1.07[c]	1.65,[c] 2.0[f]
Ce	2.20[b]	1.52[b]	2.1[b]
Cs			1.25[d]
K			1.6[f]
Mg	1.97[a]	1.75[c]	2.30[c]
Na		1.0[d]	1.45,[d] 1.37[f]
Pb	1.8[a]	1.92[e]	2.60[e]
Pt	0.89[g]		

The final point from this work to be discussed is the question of the existence of surface states. It is well established that in covalent inorganic semiconductors a high density of surface states exists near the center of the bandgap. The fermi level in a metal contact is pinned at the energy level of these states due to the Coulomb potential arising from charges residing in the surface states.(37) A small change in the position of the fermi level causes a large change in the occupancy of these states and thus a large change in the Coulomb potential. Baessler and Vaubel have suggested on the basis of their data shown in Fig. 9 that the barrier heights follow two linear relationships, one valid for higher barriers where there are no surface states and a second which is valid for lower energy barriers and which reflects some surface state pinning.(10,11) In compiling Fig. 9 we have used the same compilation of work functions as Baessler and Vaubel.(38) We have estimated the errors in the work functions from the scatter in the values reported in this compilation. It may surprise the reader that metal work functions are known so poorly, but recall that this is a surface property which is very sensitive to surface contaminants and that all of these work functions were measured prior to 1954 (i.e. before the development of readily available ultrahigh vacuum systems). We would suggest that Fig. 9 can be best fit with a single straight line. Baessler and Vaubel have also suggested that surface state pinning may effect the Au and Ag hole barriers. In this case the value of 0.89 eV which Dresner recently measured for the hole barrier for platinum would argue strongly against the two line hypothesis.

Simple arguments would not lead one to expect to find intrinsic surface states associated with anthracene crystals. In a simple model calculation Shockley considered the effect of the strength of interatomic interactions on the surface states and showed that for interactions weak enough that second order terms don't mix the atomic states, the surface states lie very near the band edges.(39) Shockley's argument is not dependent upon the basis states being atomic so that it can easily be extended to molecular crystals. Since the molecular basis functions are weakly interacting in the sense of Shockley, one can conclude that anthracene should not exhibit barrier pinning from intrinsic surface states.

One should note, however, the possibility that there are surface states which arise from defects introduced in the crystal either during growth, or during preparation of the crystal (cleaving, polishing, etc.) or of the contact (surface heating by the evaporated metals). This suggestion is supported by recent work of Baessler and Vaubel which indicates that surface state pinning may depend upon the manner of crystal growth.(40) The ratio of the change of barrier height to change of metal work function lies in the range 0.5–0.7 for both holes and electrons, a value consistent with a uniform distribution of surface states of density $\sim 10^{13}/\text{cm}^2\text{–eV}$. We believe the question of surface states is yet open and that further measurements would help to clarify this matter.

Photoemission from reacted metal-anthracene complexes has been reported several times in the literature.(12,32,33) In their second paper, Many *et al.* state that "the entire spectral yield curve observed originates from optical excitation out of a single discrete set of traps ".(33) Since this is not a contact effect, this work will not be considered further here. The work of Dresner is more ambiguous. He states that in his measurements the dark current increases rapidly with voltage in the range 400–600 V and increases proportional to $V^{2.9}$ for voltages in excess of 600 V.(12) This dark current-voltage characteristic is very similar to those observed with injecting electrolytic contacts where the dependence was attributed to scl current in the presence of an exponential trap distribution.(41–43) Since the " photoemission " measurements were made at a voltage of 100 V in the presence of a dark current of 10^{-10} amp/cm^2, we find it likely that the current was scl and the observed photoresponse resulted from photo-detrapping, as in the work of Many *et al.*, not photoemission from the contact. This work is, therefore, also excluded from further discussion.

4. Sedentary Photocurrents

In their earliest work on photoemission from Cs and Na contacts Baessler and his coworkers(4,5) observed a peak in the photocurrent occurring at about 1.8 eV. In later measurements this peak was also observed for Ca contacts.(8) These photocurrents are shown in Fig. 1. Since these peaks vary in amplitude with the work function of the metal contact, the observed phenomena must involve the metal-anthracene interface and since the current peaks can only be seen with the metal contact negative, the charge carriers involved must be electrons.

Three suggestions have been advanced for the origin of these currents: sensitized charge injection from a charge transfer complex, charge injection by triplet excitons striking the surface and charge transfer from the first excited singlet state of the anthracene negative ion. The first suggestion was put forth by Baessler and Vaubel in their early work,(4) but as they point out in later work, if the origin is sensitized injection from a charge transfer complex, the peak should be correlated with the *CT* transition which varies with the work function of the metal.(11,44) Thus this suggestion is eliminated. The second suggestion originates with Mehl[7] and is supported by Dresner,(12) but Baessler reports a quantum yield of 10^{-5} for Cs contacts.(11)

Since the $S_0 \rightarrow T_1$ absorption coefficient is 3.4×10^{-4} cm^{-1} at the absorption at 6200 Å and since the diffusion length for triplet excitons is about 10^{-3} cm(45), one can calculate an upper limit on the quantum yield of $\sim 3 \times 10^{-7}$ which is clearly much too small to account for the observations. The final suggestion is that there exists a band of surface states extending upwards from about 1.3 eV below the lowest conduction band.(11) These states are filled when the fermi level in the metal becomes equal in energy to a state. A filled state is an anthracene minus ion which is opposed by a positive metal ion. The absorption spectrum of an anthracene minus ion corresponds to the observed photocurrent spectrum and is only weakly dependent on the alkali ion with which the anthracene is associated (and, in fact, is insensitive to whether or not the anthracene ion is associated with a positive ion).(46) It is suggested by Baessler *et al.* that the anthracene minus ion is optically excited to its lowest singlet state from which the excited electron passes to the broad second conduction band of the anthracene crystal by a process analogous to autoionization. Since calculations of a quantum yield give a maximum value of about 10^{-4},(11) this seems to be the only proposed mechanism capable of explaining the data.

This, of course, lends support to the suggestion that there may be surface states lying below the conduction band. Indirect support for the suggestion that the sedentary electron current comes from anthracene negative ions is found in a paper of Mulder and de Jonge who have found a hole photocurrent coming from gold contacts on anthracene crystals which has the same spectrum as the absorption of anthracene plus ions.(47) This tends to support Baessler and Vaubel's suggestions that there exist surface states near the valence band. The support would be stronger if the observation of Mulder and de Jonge were confirmed and extended to other metals. If the surface state ion explanation is correct in its entirety one would also expect to find a broader valence band lying below the highest one. A broader valence band lying below a narrow upper one has, in fact, been invoked recently to explain measurements of Hall mobility in anthracene.(48)

Dresner argues that the first dip in the quantum yield curve he measures for holes from platinum is a confirmation of the existence of this structure. We would suggest that this dip is of the same magnitude as the other dips which are also associated with peaks attributed to vibration structure, and that there is, therefore, no reason to attach a special significance to the first dip.

5. Summary

The conditions under which photoemission from metal contacts into insulating crystals can be observed have been discussed. It has been concluded that both electron and hole emission have been observed from metal contacts on anthracene. From these measurements the existence of a narrow highest valence band and a narrow lowest conduction separated by 3.72 ± 0.03 eV as well as a broader second conduction band beginning 0.6 eV above the edge of the first conduction band has been inferred. Structure in the quantum yield curves has been interpreted by some authors as evidence for vibrational splitting of the high valence band and lowest valence band. Evidence suggesting the possible existence of surface states in the vicinities of the valence and conduction bands have been found. The measured potential barriers to injection of carriers from various metals into anthracene are summarized in Table 1.

In spite of the impressive results yielded by the photoemission technique as summarized above much remains to be done to clarify, confirm, and extend these results so that anthracene may serve as a model system from which this powerful technique can be extended to other organic crystals.

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