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H. Baessler [a], N. Riehl [a] & G. Vaubel [a]
[a] Physics Department, Technische Hoschschule, München, Germany

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Photoemission of Electrons from Alkali and Alkaline Earth Metals into Anthracene Crystals

H. BAESSLER, N. RIEHL and G. VAUBEL

Physics Department
Technische Hochschule München,
Germany

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Abstract—We have found that photoemission of electrons from cesium, sodium, calcium, and magnesium into anthracene crystals can be observed. This implies that the interfacial complex layers are thin enough not to modify the energy distribution of photoexcited electrons passing from the metal to the crystal. The main interfacial property is related to surface states which are able to trap electrons if the energy separation of the Fermi level of the metal from the edge of the lowest conduction band of anthracene is lower than the trapping energy. A maximum trap depth of 1.30 ± 0.2 eV is estimated. The occupation of the surface states therefore depends on the work function of the metal contact. These surface charges modify the threshold energies for photoemission from the metal to the crystal. They can be released optically thus giving rise to a component of the photoinjection current displaying a spectral response curve which is identical with the optical absorption of anthracene mononegative ion. The spectral response curve for injection of photoexcited metal electrons to the anthracene crystal is interpreted as a sum of two contributions: (i) injection into the narrow first conduction band and (ii) injection into a broad second band located 0.55 ± 0.05 eV above the first one.

Introduction

During the last few years a good deal of work has been done concerning the electronic conduction properties of anthracene single crystals. It has been established that the energy gap between the valence and conduction bands is in the range of 3.65 to 4.0 eV.[1,2] From the low mobility values, which are of the order of 0.5 $cm^2/Vsec$[3] and from the rate constant for bimolecular charge carrier recombination[4] it has been concluded that the mean free path of electrons and holes is of the order of the lattice parameter which leads to a band-

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width of only some 10^{-2} eV. Theoretical calculations by Le Blanc[5] and Glaeser and Berry[6] confirm these results. However, Pope *et al.*,[7] Kearns[8] and Lyons[9] have suggested that an upper and much broader conduction band should exist in anthracene which is separated by an energy gap of about 0.5 eV from the lowest conduction band. But as the transition of an electron from this upper band to the lowest band is expected to be a very rapid process (with a rate constant of $10^{12}\,\mathrm{sec}^{-1}$ or higher) it should not be possible to observe electrons moving in the upper band over appreciable distances. In order to get information about the existence of this band one has therefore to look at the generation process of charge carriers. One way to do this is to study intrinsic charge carrier formation by the action of light. These measurements have been performed by Geacintov and Pope,[10] Castro and Hornig[11] and Chaiken and Kearns.[12]

The result was that the threshold photon energy for bulk photoconduction is about 4.0 eV and that a peak of the spectral response curve appears at 4.4 eV. The fact that a second photocurrent peak is observed at 5.4 eV[10] indicates the possibility that electron excitation into higher conducting states might happen. But since Geacintov and Pope[13] have shown that autoionization of bound molecular states is the dominating process in intrinsic charge carrier formation rather than direct band-to-band transitions there is some discrepancy in the interpretation of these results. If autoionization takes place the threshold energies need not be identical to the band gap because charge-transfer-like intermediates can be involved which can be generated at lower photon energies than totaly separated charges. Furthermore, the dissociation probability of such intermediates should be a function of the band width.[4,14] Therefore it is doubtful whether autoionization can take place at all at a measureable quantum yield if the photon energy is not high enough to involve an upper conduction band. Thus no clear correlation between the peaks of intrinsic photoconduction and the energetic position of the conduction levels of the crystals has been achieved so far.

We have used the photoemission technique to inject excess electrons from metal electrodes evaporated onto an anthracene crystal. Any modification of the energy levels of the crystal due to positive holes at nearby lattice sites can be excluded in this case. The spectral resonse curve yields information about the barrier height for electron

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injection at the contact and hence about the relative energetic position of the conduction states. Recently Williams and Dresner[15] have used this method to study hole emission into anthracene crystals. The principles of the method are the following: Photons of energy $h\nu$ are absorbed within the metal cathode after having passed through the crystal and a transparent counterelectrode. They produce hot electrons uniformly distributed in energy and isotropic in momentum space. Part of these electrons move towards the interface between metal and crystal but only those are able to enter the conduction band of the crystal which have a momentum component normal to the interface in the range $(2m\chi)^{1/2} \leqslant Pz < [2m(\chi + \delta)]^{1/2}$. Here χ denotes the barrier height for electron injection which is given by $\chi = \phi - (I - E_B) = \phi - A_C$, ($\phi$ = work function of the metal, I = ionization energy of the crystal = 5.65 eV in the case of anthracene,[16] E_B = band gap, A_C = electron affinity of the crystal) and δ denotes the band width. It has been shown[17] that the spectral response curve of the resulting photoinjection current can be described by the relation $j^{1/2} \sim h\nu - \chi$ for $\chi \leqslant h\nu \leqslant \chi + \delta$, i.e. a plot of the square root of the quantum yield versus photon energy gives a straight line with an intercept equal to the barrier height. This is the so called Fowler plot. For $h\nu > \chi + \delta$ j approaches a saturation value.[15] As in anthracene the lowest conduction band is very narrow the photoemission current into this band should saturate at photon energies slightly exceeding the threshold energy χ_1. (Some modifications are likely to occur because of vibronic splitting of this band.[18] But if a second and broader conduction band exist within the crystal it should give rise to an additional photoemission current starting at a threshold energy $\chi_2 = \chi_1 + \Delta$, where Δ denotes the energy gap between the first and the second conduction band. Preliminary measurements by Baessler and Vaubel have shown[19] that this additional current is actually observed.

Experimental

As the light has to pass through the crystal before being absorbed by the metal cathode the wavelength must be beyond the singlet absorption edge of the crystal, i.e. $h\nu < 2.9$ eV. This condition requires use of metals with low work functions as injecting contacts. Therefore we have chosen cesium, sodium, calcium, and magnesium.

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As water is known not to inject holes at an appreciable extent carefully purified and deionized water was used as anodic contact material. Chemical reaction between metal and water was prevented by an experimental arrangement which has been published elsewhere.[20] The crystals used were obtained from the Harshaw Chemical Company and had a thickness of 2 mm. Evaporation of the metal to the *ab* plane of the crystal occurred in high vacuum which ensured clean crystal surfaces due to sublimation of anthracene.

A continuous *Xe*-arc (1600 W) was focussed to the probe. The spectral response curve was taken by means of a Beckmann grating monochromator ($\lambda < 7000$ Å) or of calibrated interference filters. Special care was taken in order to prevent light of higher orders from reaching the crystal. Infrared light below 0.8 eV was removed by a water filter. The photon intensity reaching the crystal was measured by a thermopile.

Results and Discussion

The dark current at a field of 10^4 V/cm was of the order of 10^{-11} amps cm^{-2}. With Na and Cs contacts a photocurrent which was of the order of the dark current or higher was obtained if the illuminated metal was at negative polarity. At reverse polarity a photocurrent could be detected only if the wavelength of the exciting light was within the singlet absorption range of the crystal. In this case hole injection from the water anode caused by singlet excitons diffusing to the surface takes place. This does not hold for Ca and Mg because for these metals the barrier energy for hole injection ($\chi_+ = I - \phi$) is lower than the energy of the first excited singlet state. Hence photoemission of holes can also be observed.[15]

In Figs. 1 and 2 typical spectral response curves for photoinjection of electrons from Cs, Na, Ca and Mg into anthracene crystals are shown. They display the following common features:

(i) the photocurrents (j_1) start at a low photon energy threshold χ_1 and level off at higher photon energies. As a limited number of interference filters had to be used in this spectral region it was not possible to achieve a better resolution. Therefore it is not possible to draw conclusions concerning band width or any vibrational splitting of the band involved except in the case of Mg. But as the general shape of the spectral response curve is in accordance with what is expected

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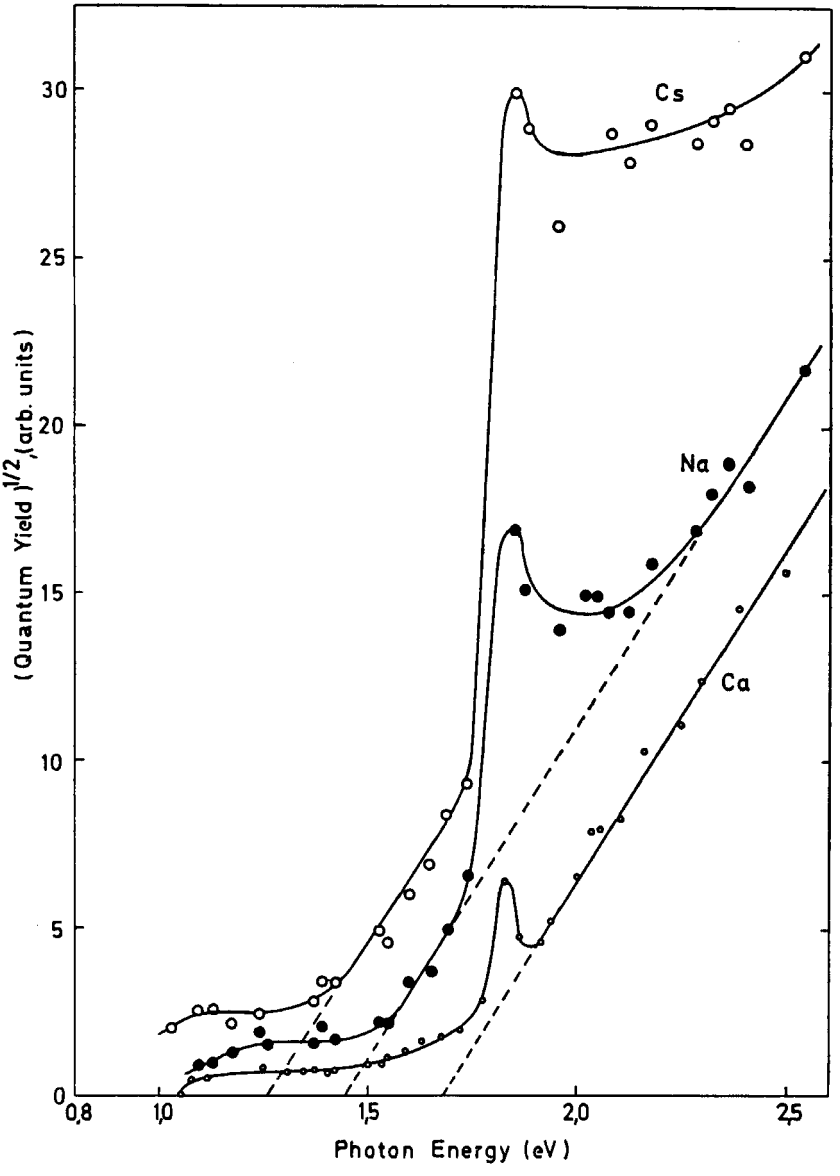

Figure 1. Square root of the photoelectric quantum yield for electron injection by Cs (—O—), Na (—●—) and Ca (—o—) electrodes versus photon energy. All points are taken with interference filters.

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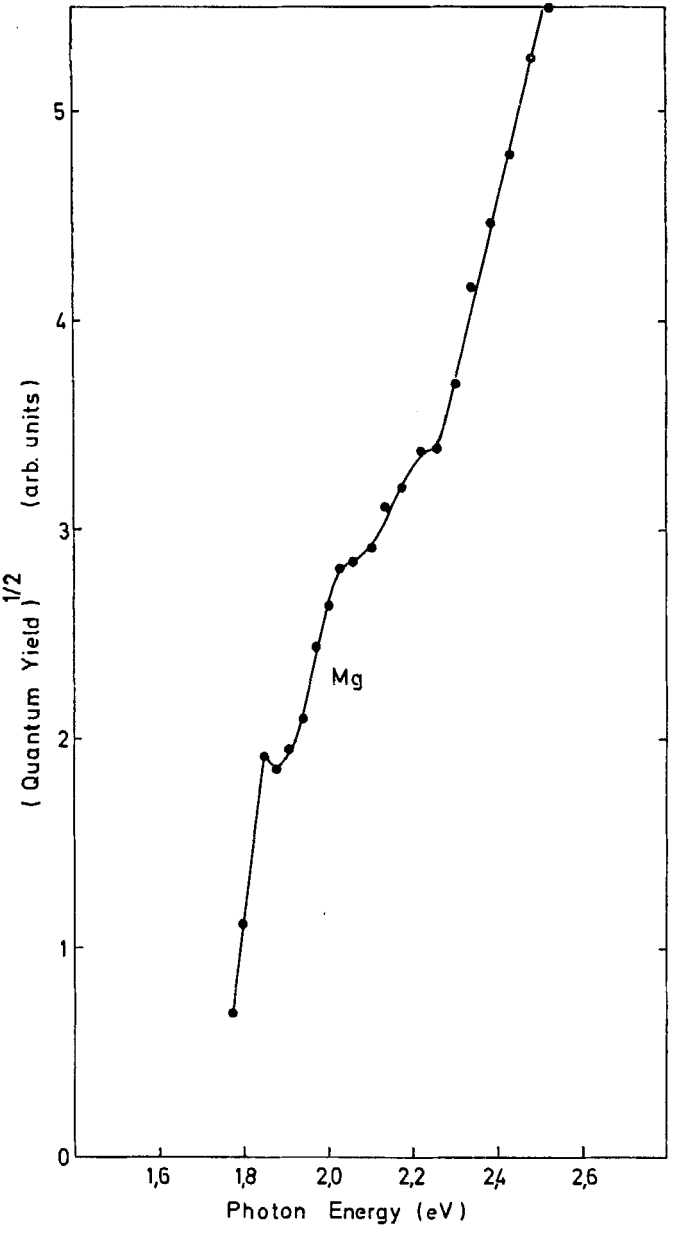

Figure 2. Square root of the photoelectric quantum yield for electron injection by a Mg electrode versus photon energy. Points are taken with a grating monochromator.

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for photoemission of electrons from a metal into a narrow conduction band we conclude that for photon energies $\chi_1 \leqslant h\nu < \chi_1 + 0.55$ eV injection into the lowest and narrow conduction band of anthracene is the dominating process. The quantum yields at photon energies at which saturation is observed are of the order of 10^{-7} in the case of Cs and Na and somewhat lower in the case of Ca.

(ii) at photon energies $\chi_2 = \chi_1 + \Delta$, where $\Delta = 0.55 \pm 0.05$ eV, further marked increase of the injection current occurs. This additional current j' can be regarded as a sum of two current components $j' = j_2 + j_{\text{int}}$, where j_2 stands for injection of photoexcited metal electrons into a second conduction band of the anthracene crystal and j_{int} for photoinjection from an interfacial layer between metal and crystal. This interpretation is supported by the following arguments.

The Injection current j_{int}

The spectral response curve of the injection current j_{int} is obtained by subtracting j_1 and j_2 from the total current. In the spectral region where j_{int} dominates, j_2 is determined by extrapolation according to the relation $j_2 \sim h\nu - \chi_2$. Figure 3 shows that j_{int} starts at a photon energy of about 1.75 eV, peaks at 1.85 eV and decays at higher energies. As the absolute magnitude of j_{int} decreases more rapidly with increasing work function of the contact metal (see Fig. 1) than j_2 it is not possible to detect j_{int} for $h\nu > 1.9$ eV in the case of Ca.

The shape of the spectral response curve of j_{int} indicates that this injection current is connected with a discrete optical transition. As the position of the peak roughly coincides with the O—O band of the forbidden singlet triplet absorption of crystalline anthracene, which lies at 14749 cm^{-1},[21] one might suppose that j_{int} is due to charge injection by triplet excitons diffusing to the electrodes. But this process can be ruled out by a numerical estimation: it is well established that the singlet triplet absorption coefficient is of the order of $10^{-4}\,\text{cm}^{-1}$. As the diffusion length l of triplet excitons is about 20 μ,[22,23] the number of excitons reaching one of the electrodes is given by $\dot{n} = 1/2I\alpha l = 10^{-7}I$, where I denotes the incident photon flux, i.e. the maximum quantum yield should be 10^{-7} provided that every exciton hitting the electrode is able to inject one charge

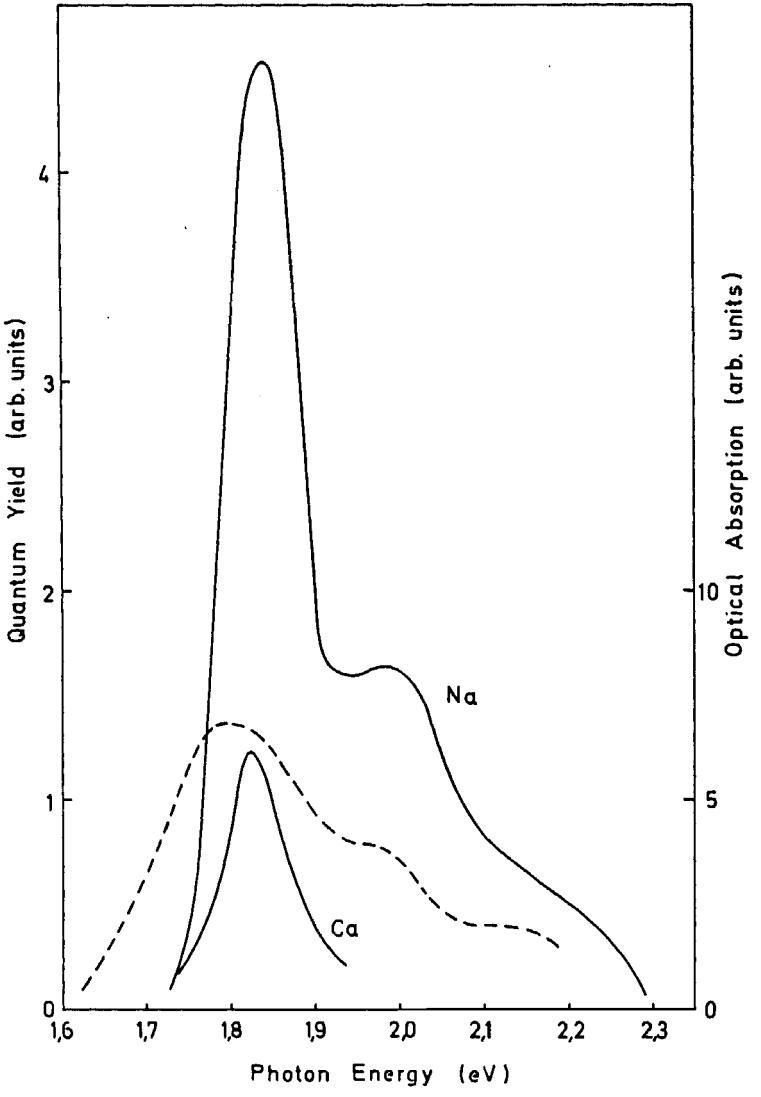

Figure 3. Spectral response curves for the " interfacial " electron injection current j_{int}. The curves are obtained by subtracting the current components j_1 and j_2 which are due to photoemission into the first and second conduction band from the total current j. The broken line is the absorption spectrum of the anthracene mononegative ion associated with Na^+ (after Buschow, Dieleman and Hoijtink[31]).

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carrier. Yet this condition can be fulfilled only at very high external fields (e.g. 10^6 V/cm). In contrast to this the measured quantum yield at a moderate field (10^4 V/cm) is about 10^{-5} using a cesium cathode. Furthermore the magnitude of j_{int} depends on what metal contact is applied. Hence injection cannot happen at the water anode. At reverse polarity no photocurrent is detectable. This fact proves that j_{int} is an electron current, too, and argues against any injection caused by excitons, because in general the quantum efficiency for exciton induced hole injection is at least one order of magnitude higher than for electron injection.

There are two remaining possibilities to explain the injection current j_{int}. The first one has been proposed by Vaubel and Baessler[20] and is based on the idea that charge transfer complex formation between metal atoms and anthracene molecules takes place at the interface. The blue colour of the interface seems to support this assumption. Generally the CT absorption band of alkali anthracene complexes in solution is located near 2 eV. Several authors[24,25] have shown, for example, that the injection rates of electrolytic contacts containing certain dyestuffs are greatly enhanced if the dyestuff molecules are optically excited. The energy condition to be fulfilled for that kind of sensitized electron injection to occur is that the binding energy of an electron in the first excited singlet level of the dyestuff is lower than the electron affinity of the crystal: $I_{ds} - E_1 < I_C - E_B^{(1)}$ (I_{ds} = ionization energy of the dyestuff, E_1 = lowest excitation energy, I_c = ionization energy of the crystal). As the ionization energy of Na anthracene complexes is about 3 eV[26] one might suppose that they can also act as a source for sensitized electron injection. With $E_B^{(1)} = 3.7$ eV the energy condition is $E_1 \leqslant 1.25$ eV which indeed is fulfilled.

The existence of a CT complex layer could account for a second effect; as partial electron transfer from Na to anthracene takes place a dipole layer is formed which builds up a retarding potential φ for electron injection from the metal through the interface to the crystal. (For geometrical reasons it can be assumed that the dipoles are partly oriented at the interface). This is equivalent to an enhancement of the metal work function giving rise to an increased threshold energy for photoemission: $\chi = \phi_{\text{vac}} + \varphi - (I - E_B)$. The experimental values of $E_B^{(1)} + \varphi = I + \chi_1 - \phi_{\text{vac}}$ are listed in table 1;

they are decreasing with increasing ϕ_{vac}. For Mg holds $E_B^{(1)} + \varphi = E_B^{(1)}$, i.e. $\varphi = 0$.‡ This is to be expected since the tendency for complex formation decreases with increasing ionization potential of the electron donor.

But there is one discrepancy; the current peak j_{int} which should be correlated with the energy of the CT transition should be shifted to higher photon energies, too, if the workfunction of the metal increases.[27] An approximately linear relationship should hold. This is in contrast to the experimental result: replacing Cs by Ca the energy position of j_{int} is not changed. Therefore we now conclude that the main contribution to j_{int} is not due to injection by the complex but to optical release of electrons trapped at the surface of the anthracene crystal.

TABLE 1 Energy Values for χ_1, χ_2, ϕ_{vac}, $E_B^{(1)} + \varphi$ (the values in brackets are calculated from the data for injection into the second band), and φ. The last column gives the quantum yield η_{int} for the interfacial current j_{int} at $h\nu = 1.85$ eV (error at least a factor of 2).

	χ_1	χ_2	ϕ_{vac}[28]	$E_B^{(1)} + \varphi = -I + \chi_1 - \phi_{vac}$	φ	η_{int}
Cs		1.25	1.96	(4.4)	0.7	10^{-5}
Na		1.45	2.28	(4.3)	0.6	$5 \cdot 10^{-6}$
Ca	1.07	1.65	2.71	4.0	0.3	$> 5 \cdot 10^{-7}$
Mg	1.75	2.30	3.68	3.7	0	

From space-charge-limited currents it is known[29] that trapping centers in the bulk of the crystal are continuously distributed in energy. This results from the fact that they are not due to chemical impurities but to structural defects. As traps at a clean anthracene surface etched by sublimation will probably be also due to defects, it is reasonable to assume that a certain surface trap distribution $N(E_t)$ exists rather than a discrete trapping level. The binding energy E_t of an electron in a trap is taken relative to the edge of the lowest conduction band. Immediately after bringing a metal in contact with anthracene, i.e. no charge exchange has occurred yet, the energy distance between the Fermi level of the metal and the

‡ The band gap $E_B^{(1)}$ must be equal to χ_1 plus the barrier height χ_+ for photoemission of holes into the valence band. Taking $\chi_1 = 1.75$ eV and $\chi_+ = 1.97$ eV[15] (both for Mg) yields $E_B^{(1)} = 3.70 \pm 0.05$ eV.

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lowest conduction band of anthracene is equal to $\chi_{1o}=\phi_{vac} - (I - E_B^{(1)})$. If surface traps are present below the Fermi level of the metal, i.e. $E_{t_{max}} > \chi_{1o}$‡ metal electrons can fall into these traps. They form an electrostatic double layer with a potential φ which gives rise to an increase of the barrier height $\chi_1 = \phi_{vac} + \varphi - (I - E_B^{(1)}) > \chi_{1o}$. An equilibrium is established if the energy of the highest occupied traps is equal to χ_1, i.e. the Fermi level at the surface of the crystal is equal to $\phi_{vac} + \varphi$. This leads to the following dependence of the barrier height χ_1 on ϕ_{vac}; using metals with relatively high workfunctions one has $\chi_{1o} > E_{t_{max}}$.

Hence no surface traps can be filled in steady state and χ_1 which is identical with χ_{1o} in this case depends linearily on ϕ_{vac}. Surface charging starts if ϕ_{vac} is lowered so that $\phi_{vac} \leqslant E_{t_{max}} + (I - E_B^{(1)})$ resp. $\chi_{1o} \leqslant E_{t_{max}}$ is reached. At this point the slope of the curve $\chi_1(\phi_{vac})$ decreases. From Fig. 4 it can be seen that the critical value of ϕ_{vac} is 3.25 ± 0.2 eV. Hence the maximum binding energy of electrons on surface states must be $E_{t_{max}} = 1.3 \pm 0.2$ eV. Upon further reduction of ϕ_{vac} more surface states are filled leading to an increase of φ. But injection is not entirely surface controlled as it is often found with ionic inorganic materials.[30] There is still a residual dependence of χ_1 on ϕ_{vac} which is due to the fact that the number of surface states per unit energy interval is limited. Therefore the surface Fermi level moves with ϕ_{vac}. From $\frac{\delta\chi_1}{\delta\phi_{vac}}$ the number of surface states $N(E_t)\,dE$ in an energy interval dE can be estimated, but this shall be the subject of a further publication.

Electrons trapped at surface states will probably be attached to anthracene molecules thus forming negative ions. The positive counterions will be located at the metal site of the interface. Buschow, Dielemann and Hoijtink[31] have investigated the spectra of anthracene mononegative ions associated or not associated with Na^+ions. They have found that the only effect of association is to shift the absorption spectra by not more than 0.05 eV towards higher energies. In Fig. 3 the absorption spectrum of Ac^- in the neighbourhood of Na^+ is shown. The close similarity to our spectral response curves for j_{int}—which in fact are independent on the contact

‡ χ_1 denotes the position of the Fermi level of the metal relative to the lowest conduction band of anthracene.

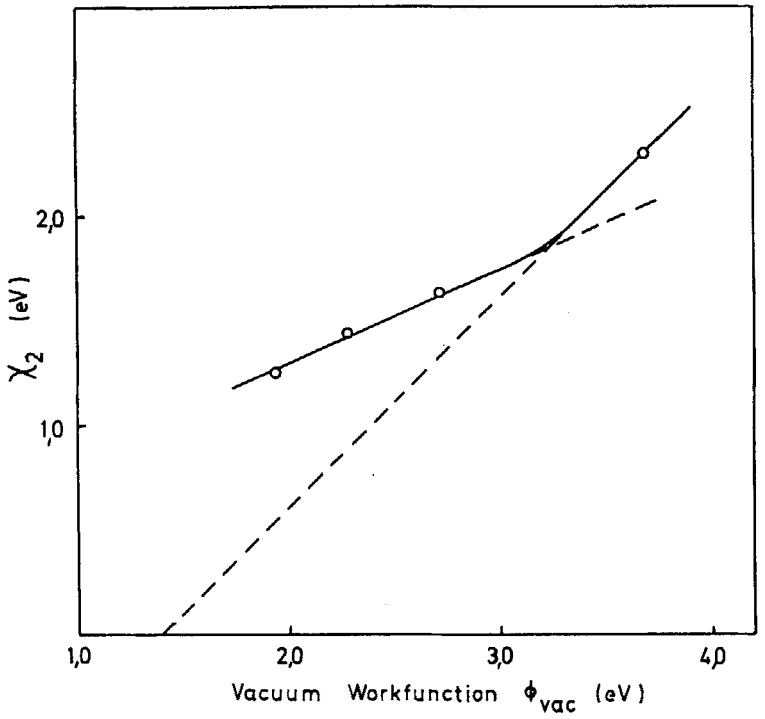

Figure 4. Dependence of χ_2 on the vacuum workfunction of the metal. The broken line is the expected behavior in the absence of surface states. The intercept is equal to the distance of the bottom of the second band from the ionization level and is given by $I_C - E_B^{(1)} + \Delta = 1.4$ eV (taking $E_B^{(1)} = 3.7$ eV).

metal within the experimental error of 0.05 eV—seems to us to be a strong indication that j_{int} is due to the release of electrons from surface traps by optical excitation of the corresponding ions to their first excited singlet states. Since trapping levels can be occupied in the energy range $1.3 > E_t > 0.7$ eV (the upper bound is due to thermal release at room temperature) below the lowest conduction band, and since the second conduction band covers the energy region 0.55 to 1.1 eV above the lowest band the first excited singlet state of Ac^- overlaps with the delocalized states of the second conduction band. Hence direct optical release can be regarded as an autoionization process just as intrinsic photocarrier production at neutral crystal sites. As the number of trapped electrons is propor-

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tional to φ and hence related to the workfunction of the metal it is clear that j_{int} must decrease upon replacing Cs and Ca. Furthermore the absolute quantum yields for j_{int} are in the right order of magnitude. According to[31] the extinction coefficient for Ac^- is about 10^{-4} 1 mole^{-1} cm^{-1}. In order to produce a potential $\varphi = 0.7$ eV one needs $n = \frac{\varphi \epsilon \epsilon_0}{ed}$ trapped electrons separated by a distance d from their image charges. Assuming $d = 6$ Å one gets $n = 4.10^{13}$ cm^{-2}. These should give rise to a relative optical absorption of 10^{-4}, which is therefore an upper limit for the photoelectric yield. The experimental value at 10^4 V/cm is $\eta_{\text{int}} = 5.10^{-6}$ (for Na). In the investigated range η_{int} is a linear function of the field. This is a familiar result reflecting the fact that the number of electrons escaping recombination with their image charges is a linear function of the applied field. Thus the existence of surface states trapping electrons can account both for magnitude and spectral response of j_{int} and for the dependence of the barrier height χ_1 on the workfunction ϕ_{vac}.

Photoemission into the Second Band of Anthracene

From Fig. 1 it can be seen that the current component j_2 varies independently from j_{int} upon variation of the cathodic material. This indicates that j_2 is neither connected with a complex layer nor with surface states. From the fact that j_2 follows closely the Fowler relation $j_2^{1/2} \sim h\nu - \chi_2$ we conclude that it is due to photoemission of electrons from the metal into the second conduction band of the anthracene crystal. The difference in the threshold energies $\Delta = \chi_2 - \chi_1$ must be equal to the energy gap between the first and this second band. The average value obtained from the measurements with Ca and Mg is $\Delta = 0.55 \pm 0.05$ eV. An improvement of the experimental sensitivity showed that the previously[19,20] reported values of χ_1 for Na and Cs cathodes were too high by about 0.1 eV leading to a value for Δ being too low by 0.1 eV. With respect to the magnitude of Δ this energy difference cannot be related to any vibrational splitting of the lowest conduction band, because the vibrational energies of anthracene are in the range 0.1 to 0.2 eV. Furthermore, j_2 does not display any significant departure from the

square root behavior which could be related to any vibronic splitting.‡ This is an indication that injection into a band is occurring whose width is larger than the vibrational energy. From the photon energy range within which Fowler's relation is fulfilled Baessler, Riehl and Vaubel[32] have estimated the width of this band to be about 0.5 eV.

One could argue that j_2 is not due to injection into a second band but to the lowest band and j_1 is due to photoemission of electrons into surface states below the first conduction band. But despite the

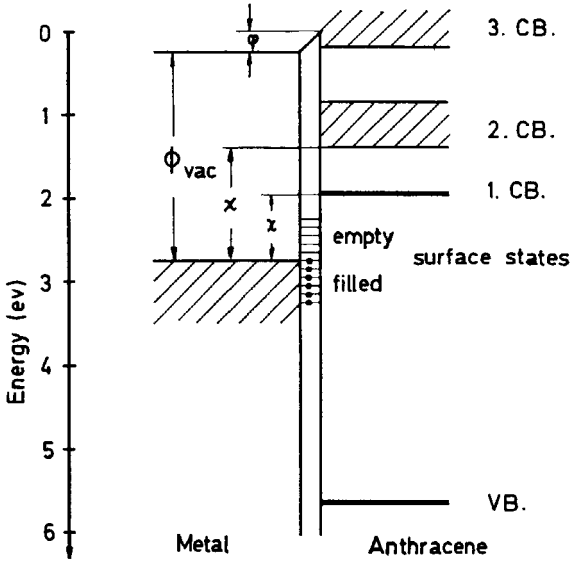

Figure 5. Energy diagram of conduction levels in crystalline anthracene.

fact that the latter effect should operate at a lower yield than the observed one (10^{-7}) this would lead to a band gap which is too high for at least the amount of Δ. Furthermore it is incompatible with the arguments presented above.

A detailed investigation of the spectral response curve for photoemission of electrons from Na to anthracene near the singlet absorption edge of the crystal has shown[20] that a third conduction level exists the edge of which is located 1.72 eV above the lowest conduction band. This edge is not identical with the ionization of the crystal

‡ The well resolved j_1-curve for Mg reveals the vibronic splitting of the lowest conduction band (see Fig. 2).

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determined by photoemission of electrons from the crystal surface into vacuum as has been supposed previously. It is lower by about 0.2 eV.

The results obtained so far are summarized in Fig. 5. The energy gap between valence and lowest conduction band is taken to be about 3.7 eV. This value is subject to an experimental reconfirmation.

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