

¹²This sample was prepared from ⁵⁷Fe₂O₃ which was first reduced to metal and then converted to FeF₂ by heating in flowing HF gas. The desired composition

was obtained by melting together proper amounts of MnF₂ and ⁵⁷FeF₂. The composition of the resulting material was verified by x-ray fluorescence analysis.

PHOTOEMISSION OF ELECTRONS FROM ALKALI AND ALKALINE-EARTH METAL CONTACTS INTO ANTHRACENE*

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The spectral yield for photoemission reveals the presence in the conduction band of anthracene of a broad (~0.65 eV) continuum of allowed states followed by four narrow ($\lesssim 0.1$ eV) bands approximately 0.2 eV apart. The Fermi level in the alkali or alkaline-earth metal is fixed relative to the energy bands of anthracene by a large density of surface states. The mean free path for energetic electrons in anthracene is estimated as 40 Å.

Recently Williams and Dresner¹ have observed hole photoemission from several metal contacts into anthracene. The spectral response of the photoemission yield showed weak structure, suggesting that photoemission takes place into a system of narrow bands attributed to the interaction of molecular vibrations with a narrow electronic band. In this communication we report on electron photoemission from alkali and alkaline-earth metals into anthracene. The structure observed in the yield curves is much more pronounced in this case and provides some new information on the extensively studied structure of the conduction band of anthracene.

The specimens used were thin (30-90 μ) vapor-grown plates enclosed in sandwich-type cells. One face of the anthracene plate touches a transparent electrode, the other is in intimate contact with either a Na-K alloy or a mercury amalgam of the alkali or alkaline-earth metal. The metal is illuminated through the transparent electrode and the crystal, which are both transparent throughout the spectral range studied (1.5-0.44 μ). With a dc voltage applied (metal negative), appreciable photocurrents are observed. That these arise from photoemission from the active metal is established by the observation that the photocurrents for a pure mercury contact are at least one to two orders of magnitude lower.

Typical results for the spectral response of the quantum yield Y from three metal contacts into anthracene are shown in Fig. 1(a). Similar curves were obtained with Li and Ca amalgams. A striking feature of the data is the similarity in shape of all curves: The energy position of the threshold for photoemission ($E_T \approx 0.9$ eV) and of the various peaks are the same to within ± 0.03

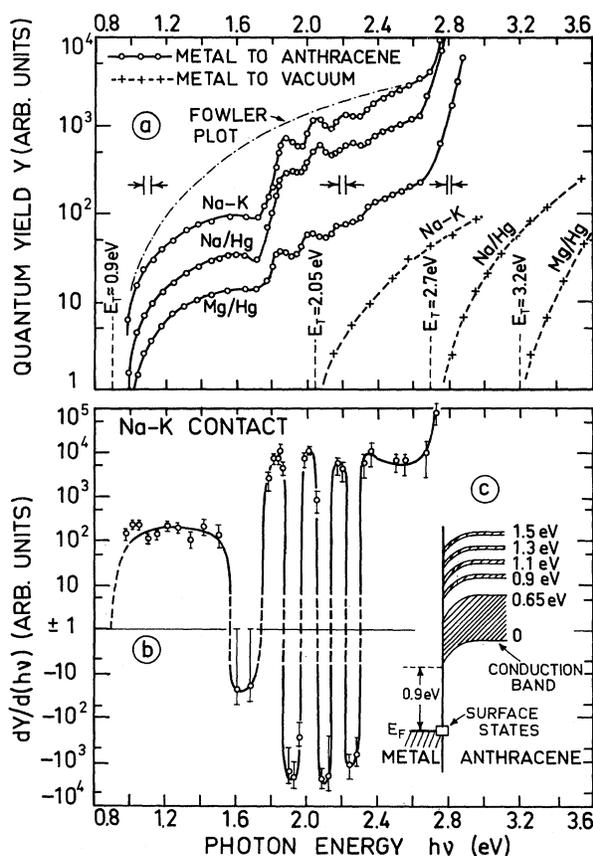


FIG. 1. (a) Quantum yield Y (electrons per incident photon) versus photon energy $h\nu$ for photoemission from Na-K alloy and from Na and Mg mercury amalgams into anthracene (solid curves) and into vacuum (dashed). (The two sets of curves are plotted on different yield scales.) Accuracy of data better than indicated by size of experimental points. (b) $dY/d(h\nu)$ vs $h\nu$ for the Na-K contact. Margin of error marked off for each point. (c) Energy band diagram at interface between alkali (or alkaline-earth) metal and anthracene.

eV, being independent of the metal work function. This immediately indicates that the Fermi level in the metal is fixed relative to the energy bands of anthracene by a large density of surface states.² The charged surface states probably consist of anthracene negative ions formed at the interface by the alkali or alkaline-earth metal.³ An estimate for their density can be obtained by comparing the work functions of the different metals. These are given by the thresholds of the dashed curves in Fig. 1(a) which represent the measured spectral yields for photoemission into vacuum. Clearly the difference in work function between the Na-K and Mg/Hg electrodes exceeds 1 eV. This means that in the case of the Na-K contact the voltage drop across the metal/anthracene spacing is at least 1 V, which provides² a lower limit of about 10^{13} cm⁻² for the density of negatively charged surface states. Because of this large density, the energy position of the surface states should be very close to the Fermi level.

The pronounced structure in the yield curves, especially around the narrow peaks, cannot arise from variations with wavelength of the optical constants of the metals, since such variations would be expected to be slower and would certainly not occur at the same energies for all five metals studied. Rather, the undulations in the yield curves should reflect the structure of the conduction band of anthracene. This structure is seen best by taking¹ the derivative of Y with respect to $h\nu$, as plotted in Fig. 1(b). The plot reveals a broad positive plateau above threshold which drops abruptly to a negative value (or possibly zero). This is followed by three pairs of narrow, positive-negative peaks and a fourth positive peak which merges into a smoothly rising curve at higher photon energies. The plateau corresponds to photoemission into a broad continuum of states about 0.65 eV wide. Some structure is apparent in the plateau, but the accuracy is not sufficient to resolve it. The four peaks at higher energies correspond to photoemission into narrow bands, about 0.1 eV wide and approximately 0.2 eV apart. Figure 1(c) is a schematic energy band diagram of the metal/anthracene interface constructed on the basis of Fig. 1(b). The diagram depicts the relation between the Fermi level E_F in the metal and the conduction band of anthracene. The bands are bent downwards because of the proximity of the low-work-function metal. The bending is essentially the same for all five metals due to the strong clamp-

ing action of the surface states. The threshold of 0.9 eV represents the energy distance between E_F and the lowest observable conducting state of the crystal at the interface.

The occurrence of negative values of $dY/d(h\nu)$ indicates that surface states contribute to the photoemission yield. Photoemission from a metal (which is characterized by a nearly uniform electron distribution in energy below E_F) is expected¹ to result in $dY/d(h\nu) \geq 0$. The only way in which the derivative can change sign rapidly is by excitation from a sharply peaked distribution in energy of electrons at the interface. From the dips in Y following the three narrow peaks in Fig. 1(a) one concludes that the contribution of surface states to the photoemission process amounts to 20-30% of the total yield. That the metal is the chief contributor to photoemission is indicated also by the shape of the yield curves [see Fig. 1(a)]. Smoothed out, these curves resemble a Fowler plot (dot-dashed curve), which is characteristic of photoemission from a metal contact.⁴ Photoemission originating from a discrete set of surface states should result in a considerably slower rise of Y with $h\nu$.

At any given voltage, Y is directly proportional to the light intensity. In the higher field range [$(1-5) \times 10^4$ V/cm], it increases steeply with field F and can be fitted to a relation of the type $Y \propto \exp(-CF^{-1/2})$, where C is a constant.⁵ This relation can be accounted for in terms of the image-force potential. The mean free path for energetic electrons in anthracene derived on this basis is about 40 Å, which is not an unreasonable value.⁶

The yield measured for a Na/Hg contact in the range 1.9-2.4 eV is about 10^{-6} electron/incident photon. If the exponential function is extrapolated to $F = \infty$, Y would reach 10^{-4} . The actual extrapolated value should be considerably larger because the sodium concentration in the amalgam is only 1%.

The photoemission data add some important information to the existing knowledge of the conduction-band structure of anthracene. Intrinsic-photoconductivity^{7,8} and external-photoemission⁹ measurements establish the presence of a broad, free-electron conducting state in anthracene, starting at 4.0 eV above the valence band. Theoretical calculations and the small measured electron mobility indicate that electron transport occurs in a narrow (0.01-0.1 eV), tight-binding conductivity band.^{10,11} Its precise position is not known—it must be lower than 4.0 eV and is probably⁹ above 3.45 eV. Very likely the broad con-

tinuum revealed by photoemission comprises both the tight-binding and free-electron bands. With the presently available resolution, the separation between the two cannot be reliably inferred from the data, although the small undulations around the plateau of Fig. 1(b) might well be meaningful. An argument in favor of identifying the bottom of the photoemission continuum with the tight-binding band is provided by the data for the magnesium contact. The lowest measured work function of Mg/Hg (obtained when the amalgam is freshly exposed in vacuum) is 3.0 eV. This means that the crystal affinity must be larger than¹² 2.1 eV (=3.0-0.9). External photoemission measurements^{9,13} indicate that the valence band is 5.65 eV below the vacuum level. Hence the energy gap must be smaller than about 3.55 eV, which is reasonable. Were the tight-binding band assumed to lie below the observed threshold, one would have derived a larger value for the affinity and a correspondingly lower upper limit for the gap.

The free-electron band is terminated sharply at ~0.65 eV above the lowest conducting state. After a forbidden zone of 0.2-0.3 eV there is a series of four narrow bands about 0.2 eV apart. These probably arise from the interaction of molecular vibrations with a narrow electronic band, molecular vibrations in anthracene typically having energies¹¹ of approximately 0.2 eV. This situation is unusual. Intuitively, one would have expected the free-electron band to overlap with other, higher bands to form a continuum of states extending up to the vacuum level.

Molecular crystals are excellent media for band-structure studies by photoemission measurements because of the expected rapid varia-

tions in density of states. The use of alkali and alkaline-earth contacts may be most advantageous since emission from surface states enhances the degree of structure in the yield curves, enabling a more precise determination of band parameters.

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