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Measurement of Contact Potential Difference for Organic Crystals. Work Function of Violanthrene

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A vibrating-reed type cell for measuring contact potential difference was constructed and successfully applied for organic crystals. From the observed contact potential difference for violanthrene against graphite, the work function has been estimated as 4.50 ± 0.1 eV. In association with the activation energy for electrical conductivity, 0.8—0.9 eV, the electronic energy diagram for violanthrene has been illustrated, which revealed the extrinsic nature of semiconduction and the energy gap, 2.3—2.5 eV, being comparable with the first excited singlet state of violanthrene molecule.

The electrical properties of organic compounds in crystalline state, made of conjugated π-electron systems, have been extensively investigated and their semiconductive characters are now widely accepted.[1] Such a molecular crystal may be approximated to be an assembly of neutral molecules, the interactions between them being relatively weak. In contrast to covalent semiconductors such as silicon or germanium, there are no dangling bonds on the surface of molecular crystals which may give rise to unfilled energy levels in the forbidden gap. The electrical properties of molecular crystals may thus be expected to be relatively simple with respect to surface conditions. However, a number of cases have been reported where the electrical properties of such crystals are influenced by the surface conditions. In spite of its potential significance relatively few studies have been made on the surface properties of molecular crystals. This may be attributed partly to the lack of appropriate methods for investigation. Conductivity measurements are sometimes unsatisfactory with respect to reproducibility and the effect of impurity doping has not been well understood for this calss

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[1] F. Gutmann and L. E. Lyons, "Organic Semiconductors," John Wiley & Sons, New York, N. Y. (1967).

of crystals.

Measurements of work function can be used as an efficient means for surface studies. The work function is a quantity which depends on the surface as well as on the bulk properties. When data are obtained for clean surfaces they can be used in discussing how surface and bulk properties are related to each other. Further, gas adsorption experiments may yield information about interactions between the adsorbed molecules and the crystal surface.

Measurements of contact potential differences of organic crystals were reported by several authors. However, numerical data published on work function are still very scarce. From the experiments on photoemission the threshold energy can be obtained. This quantity corresponds to the energy of the filled band, whereas the work function gives the location of the Fermi level. Nelson has reported measurements of contact potential differences[2] using the electron beam retardation technique. His data are mainly on organic dyes deposited on inorganic semiconductors such as cadmium sulfide. The same technique was applied to the measurements of the contact potential differences of several organic compounds.[3] The vibrating condensor method was applied to the photovoltage measurements.[4] Irradiation with light produced change in contact potential difference. This was attributed to the difference of diffusion of mobile electrons and holes, *i. e.*, the Dember photovoltage. Analogous information was obtained by Putzeiko[5] using a related technique, Bergmann's condensor method. The surface under test and a transparent conducting plate, a mica plate made half transparent by vacuum evaporation of platinum, constituted the capacitor. The surface was irradiated an by intermittent light through the transparent electrode. This gave rise to an alternating photovoltage. Harada *et al.*[6] have published the results of several experiments on photoemission. They include contact potential differences obtained from current-voltage characteristics for several aromatic compounds, from which the work functions for the organic crystals can be evaluated.

The present paper describes the determination of the work function for organic crystals through measurements of contact potential differences using the vibrating condensor method. Compared to other methods such as thermionic or photoelectric emission which are employed in surface studies, this method is advantageous in that it allows measurements without introducing distubances on the surface; it requires a sample to be neither heated nor irradiated. Further, it does not require vacuum; it allows measurements in various gases at wide range of pressure. The electronic structure of crystalline violanthrene will be discussed on the basis of the work function observed.

Experiment

A vibrating-reed type cell, made of Pyrex glass, was constructed for measuring contact potential differences (Fig. 1). A copper disc (1) with an area of about 1.5 cm$^{2)}$ coated with gold by vacuum evaporation served as a substrate. It was set over an oven (3) where the sample was sublimed onto the surface. The disc covered with a layer of the sample was then transferred to the centre of the cell by an iron wire pulled by turning a ground joint (4). It constituted a parallel plate capacitor coupled with a reference electrode (2). The two electrodes were about 1 mm apart. The reference electrode was a film of colloidal graphite (Aquadag) which was painted on a thin Pyrex plate and treated in air at 500°C for an hour. The reference electrode was held by a glass rod. A piece of iron was attached to the glass rod which brought the reference electrode into resonant vibration by means of an electromagnet, which was driven by an audio range oscillator coupled with a power amplifier. The frequency of vibrations ranged from 50 to 70 Hz. The glass rod was covered with conductive silver paint and served as a lead.

The inner wall of the spherical part of the cell was coated with gold by vacuum evaporation and grounded in order to avoid disturbances due to charging. The coating served also as a shielding against electric fields outside.

A gold film was used also as an auxiliary standard electrode, which was formed by vacuum evaporation onto a Pyrex plate. The contact potential difference between the freshly evaporated gold film and a standard graphite surface showed a large drift immediately after

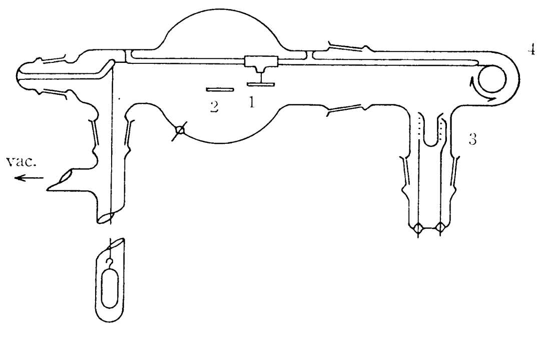

Fig. 1. The cell.
1. Sample, 2. Reference electrode, 3. Oven, 4. Ground joint. The signal is fed from the sample electrode. The reference electrode is connected with the potentiometer.

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[2] R. C. Nelson, *J. Opt. Soc. Am.*, **46**, 1016 (1956).

[3] Ref. 1, p. 796.

[4] I. A. Akimov, *Doklady Akad. Nauk SSSR*, **128**, 691 (1959).

[5] E. K. Putzeiko, *ibid.*, **129**, 303 (1959).

[6] Y. Harada and H. Inokuchi, This Bulletin, **39**, 1443 (1966); M. Kochi, Y. Harada and H. Inokuchi, *ibid.*, **40**, 531 (1967).

evaporation, but after several hours of exposure to the air it attained a stationary value which was found to be fairly reproducible. The work function of this "aged" surface was determined to be 5.1 eV from the contact potential difference against the graphite surface.

A potentiometer made of a mercury battery and a Helipot, a precision variohm, supplied potential for the reference electrode. The signal from the sample electrode was amplified with a preamplifier with imput resistance of 10^{12} ohm and was put into an oscilloscope. The cell and the preamplifier were placed in a shielding cage. The null indication procedure was employed in which the potentiometer was adjusted to give a minimum magnitude of the signal. In order to minimize the hum noize of commercial frequency (50 Hz), the lead connecting the sample and the preamplifier should be as short as possible. The cell was not quite satisfactory as the lead was designed to serve also as a cable to carry the sample electrode. To maintain steady vibrations of the reference electrode and to avoid vibrations in other parts of the cell, care must be taken to prevent mechanical disturbances.

The sensitivity of the apparatus was ±1 mV for a uniform metal surface. When the surface was covered by an organic film, it exhibited a higher noise level and gave a lower sensitivity. The sensitivity of measurements for organic films was generally 20 to 30 mV. The reproducibility of the surface is a factor which must be considered. It was the principal factor for the experimental error in the case of violanthrene.

Measurements were carried out in a vacuum of 10^{-5} Torr, but the cell was designed for measurements in various ambient gases. Sublimation of organic compounds was performed in the cell in order to measure uncontaminated films. Ground joints and grease were used.

Conductivity measurements were made with a vibrating reed electrometer. A surface type arrangement was employed, with Aquadag electrodes.

Violanthrene was prepared from violanthrone, a commercial product, by reduction with powdered zinc metal. After it was treated by usual chemical methods, the final purification was made by successive sublimation in vacuum.

Results and Discussion

The work function of an electrical conductor can be evaluated by the relation

$$\Phi = \Phi_0 - \Delta$$

where Φ denotes the work function of the sample, Φ_0 that of the references material and Δ the contact potential difference. For this relation to be valid the thermal equilibrium of electrons between the sample and the reference material must be attained. If the equilibrium is not attained, the observed contact potential difference depends not only on the sample but also on the substrate materials employed. The preliminary experiments were made for violanthrene film deposited on several kinds of metals. The results are summarized in Table 1. For Φ_0, the value of 4.74±0.1 eV for graphite was adopted after Apker *et al.*[7] In evaluating from the observed contact potential differences, it is essential that the work function of the reference surface be constant throughout the measurements. We did not measure the work fuction of the graphite films used. However, the contact potential difference measurements revealed that the constancy of the work function of the graphite film made by the procedure described above was kept within the range of ±0.05 eV. The work function of the sample thus evaluated shows a good constancy within the experimental error irrespective of the substrate metal and indicates that the above relation is valid.

TABLE 1. THE EFFECT OF THE SUBSTRATE MATERIAL ON THE OBSERVED WORK FUNCTION OF VIOLANTHRENE

Substrate	Reference	Φ (eV)
Pt	Aquadag	4.5
Cu	Aquadag	4.4
Brass	Aquadag	4.5
Au	Aquadag	4.5
Au	Au	4.5
Ni	Au	4.5

Having thus verified that the observed contact potential difference does not depend on the choice of the substrate metal, we employed gold as the substrate. As an auxiliary standard a gold film evaported on a Pyrex plate was also used. Its work function was determined to be 5.1 eV using graphite as the primary standard, Table 2 shows the results of the measurements. For both reference materials the same value of 4.50±0.1 eV was obtained for the work function of violanthrene.

TABLE 2. THE WORK FUNCTION OF VIOLANTHRENE

Reference	CPD (eV)	Φ (eV)
Au	0.5	4.6
Au	0.63	4.47
Au	0.70	4.40
Au	0.6	4.5
Aquadag	0.2	4.5
Aquadag	0.24	4.50
	mean	4.50±0.1

The temperature dependence for the electrical conductivity of violanthrene was measured with a surface type arrangement. It is well expressed by the relation

$$j = j_0 \exp(-E/kT)$$

within the temperature range of 53 to 191°C, where

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[7] L. Apker, E. Taft and J. Dickey, *Phys. Rev.*, **74**, 1462 (1948).

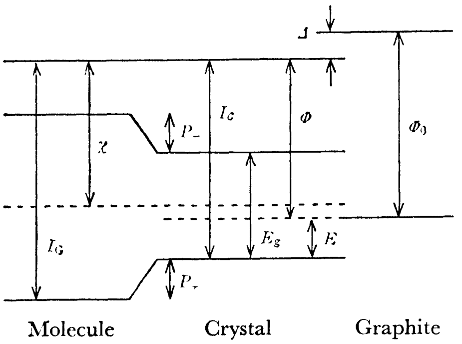

Fig. 2. The energy diagram for violanthrene in the isolated and in the crystalline state.
I_G, I_C, Ionization energy; P_+, P_-, polarization energy; Φ, work function; E_g, band gap; Δ, contact potential difference; E, activation energy for electrical conduction.

j is the observed current. The activation energy E was found to be 0.8—0.9 eV.

A tentative electronic energy diagram can be constructed, as shown in Fig. 2, using experimental and theoretical data available. Figure 2 represents energy levels of violanthrene for gaseous and crystalline states. The ionization energy of gaseous violanthrene is estimated to be 6.84 eV.[8] For alternant hydrocarbons Mulliken's electronegativity, $\chi=(I+A)/2$, can be approximated by the mean value of the energy of the highest occupied orbital and the energy of the lowest vacant orbital, where I and A denote the ionization energy and the electron affinity respectively. This quantity has been estimated from experimental data for alternant hydrocarbons to be 4.15 eV.[9]

In Fig. 2 are also shown the energy levels of graphite which stands in the electrical equilibrium with crystalline violanthrene. The contact potential difference between violanthrene and graphite was observed to be 0.24 eV.

When an electron is emitted from a neutral crystal it leaves behind a positive charge which polarizes the medium surrounding it. This stabilizes the electric charge in a dielectric atmosphere compared to the isolated charge in the vacuum. The polarization energy corresponds to the difference in ionization energies of gaseous and crystalline states. An analogous discussion leads to the conclusion that the electron affinity of a molecule must be larger for the crystalline state than for the gaseous state. The energy difference, the polarization energy due to a negative charge in a crystal, seems to be the same as that for positive charge in the crystal. As the Fermi level must be located half way between the top of the filled levels and the lowest conducting level in an intrinsic semiconductor, we conclude that the work function of crystalline alternant hydrocarbons is equal to the molecular electronegativity χ. Energy levels are illustrated in Fig. 2, in which 0.8—0.9 eV, obtained as the activation energy for dark conduction, is assigned as the energy difference between the top of the filled band and the Fermi energy. Thus the ionization energy and the band gap are evaluated to be 5.3 to 5.4 eV and 2.3 to to 2.5 eV, respectively.

The ionization energy of 5.20 eV for crystalline violanthrene was obtained form the threshold energy for photoelectric emission.[10] Kearns and Calvin have reported measurements of photoelectric emission for several crystalline compounds including violanthrene.[11] Their values for crystal ionization energy are generally lower than those obtained by other investigators by 0.5 to 0.6 eV, as in pentacene and metal-free phthalocyanine.

In conclusion, the Fermi level does not lie midway between the valence band and the conduction band. The origin of its extrinsic nature, whether it comes from the presence of some chemical or structural impurities in the bulk or from some surface conditions such as gas adsorption, remains to be explored. It is worth noteing that the band gap is comparable with the energy for the first excited singlet state of violanthrene molecule, *i.e.*, 2.5 eV.

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[8] H. Kuroda, *Nature*, **201**, 1214 (1964).

[9] R. S. Becker and E. Chen, *J. Chem. Phys.*, **45**, 2403 (1966).

[10] T. Hirooka, M. Kochi, H. Inokuchi and Y. Harada, This Bulletin, **42**, 1481 (1969).

[11] D. Kearns and M. Calvin, *J. Chem. Phys.*, **34**, 2026 (1961).