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# Electronic transitions in some phthalocyanine and NH-rhodanine-merocyanine films studied by inelastic-electron-tunneling spectroscopy

H. Lüth, U. Roll, and S. Ewert

*2. Physikalisches Institut der Rheinisch-Westfälischen Technischen Hochschule Aachen, 5100 Aachen, Federal Republic of Germany*

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Inelastic-electron-tunneling spectroscopy on Al-$Al_2O_3$-Pb tunneling junctions at 4.2 K has been used to study electronic transitions in the energy regime between 0.5 and 2.5 eV. $\pi \rightarrow \pi^*$ singlet-triplet ($S \rightarrow T$) transitions are found and spectral structures between 0.5 and 1.0 eV for the Fe-, Co-, and Zn-phthalocyanines are attributed to transitions involving metal-ligand orbitals. Good agreement with other experimental data and theoretical calculations is given. Unexpected spectral features between 1.5 and 2.5 eV are observed which shift irreversibly in energy from one run to the next one. This effect is interpreted in terms of internal-field emission processes whose onset is shifted due to charge trapping in the dye layers.

## I. INTRODUCTION

Phthalocyanine—or tetrazatetrabenzporphin—molecules are macrocyclic aromatic compounds which contain a ring of four isoindole units linked by aza-nitrogen atoms [Fig. 1(a)]. The two central hydrogen atoms of the metal-free acid compound $H_2$-phthalocyanine can be substituted by many metals. The molecular structure of the phthalocyanine molecules is very similar to that of the naturally occuring porphyrins. Compared with these the four benzo rings give rise to a high-temperature stability and a chemical stability of the phthalocyanine molecules thus making them extremely useful as model substances for the investigation of general properties of porphyrinlike molecules under conditions like elevated temperatures or ultrahigh vacuum.

Porphyrins[1-3] and porphyrinlike molecules have attracted considerable attention for a long time for the following reasons: In biology, porphyrins (chlorophyll, hemoglobin, etc.) are of central importance in photosynthesis, oxygen transport, and a number of reduction and oxidation reactions. Phthalocyanine compounds in particular are used in heterogeneous catalysis[4] and because of their dye properties for sensitization of semiconductors.[5] Beside their catalytic activity, phthalocyanine films and single crystals exhibit interesting semiconducting properties which have not been well understood until now.[6]

The electronic structure of the molecules for smaller ionization potentials is mainly determined by the properties of the macrocyclic $\pi$ electron system which was first successfully described in terms of a ringlike "free"-electron gas.[7] Other approaches used molecular-orbital theory[8] and extended-Hückel calculations.[2,9] The main optical absorption near 2-eV photon energy is explained for all phthalocyanine compounds in terms of $\pi \rightarrow \pi^*$ singlet-singlet ($S \rightarrow S$) transitions.[10] The corresponding singlet-triplet ($S \rightarrow T$) transitions between 1 and 1.5 eV are optically forbidden and were studied by luminescence experiments until recently.[1] Additional electronic levels within the energy gap between the $\pi$ and $\pi^*$ orbitals are expected to be due to the metal-ligands (preferentially $d$-like[2,9]). $\pi^*$ singlet, triplet, metal-ligand, and/or impurity levels might form conduction-band states in a crystal or a film and might be responsible for the activated behavior of the electrical conductivity.[4,6] A detailed knowledge of all these electronic levels and transitions between them is therefore of great interest. One purpose of the present work is to make some contribution to the knowledge of metal-ligand derived electronic levels from the experimental side. Not many experimental data have been available about these levels up to now, even though extended-Hückel calculations for a variety of porphyrins[9] and phthalocyanine compounds[2] yield some theoretical insight into their molecular electronic structure.

For comparison also a linear $\pi$-bonded polymethine dye: NH-rhodanine-merocyanine [Fig. 1(b)] is studied. Except for their optically allowed singlet $\pi \rightarrow \pi^*$ transitions near 2.5 eV not much is known about the electronic structure of this compound. Detailed studies, however, have been performed by Bauer and Heiland[11] about its sensitization properties on ZnO surfaces.

In the present work inelastic-electron-tunneling spectroscopy (IETS)[12] is used to study electronic transitions of the described organic compounds because in this type of measurement selection rules for electronic excitations are not as strict as for optical excitations. de Cheveigné *et al.*[13] could show that optically allowed singlet-singlet ($S \rightarrow S$) as well as optically forbidden singlet-triplet ($S \rightarrow T$) transitions can be observed. The tunnel junctions used in IETS consist of a metal-insul-

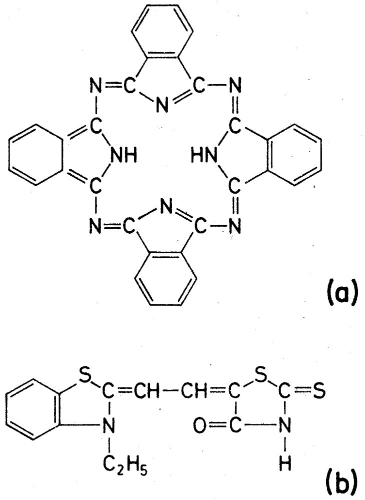

FIG. 1. Molecular structure of: (a) metal-free (acid) $H_2$-phthalocyanine, in the metal complexes the two central H atoms are substituted by a metal atom. (b) NH-rhodanine-merocyanine.

ator-metal (usually Al-$Al_2O_3$-Pb) sandwich. The molecular species under study is usually deposited onto the $Al_2O_3$ barrier before completing the junction with the Pb reference electrode. When a potential is applied across the junction, electrons can tunnel elastically from filled states in one electrode through the insulating barrier (plus dye layer) into empty electronic states in the opposite electrode. As the applied potential is increased above the electronic (or vibronic) transition energy of the molecular species in or near the barrier, a new inelastic channel for tunneling is opened thus giving rise to a slight enhancement of the tunneling current. This increase appears as a peak-like structure in the second derivative $d^2U/di^2$ of the tunnel characteristic. An extensive discussion of the method itself has been given, e.g., by Hansma.[14]

## II. EXPERIMENTAL

All experiments of the present work were performed with Al-$Al_2O_3$-Pb tunneling junctions which were prepared by *in situ* evaporation and oxidation in a vacuum cryostat which has been described elsewhere.[15] The stainless-steel cryostat is pumped by ion pumps and the working pressure is in the $10^{-7}$-Pa range. As substrate for the tunneling junctions, a quartz platelet was used and the thickness of the evaporated metal strips of Al and Pb varied between 100 and 1000 nm (not critical). Measurements of the vibrational spectra of the $Al_2O_3$ barrier (without any dye interlayer) show that these tunnels are not "clean." The typical CH and OH vibration modes near 357 and 452 meV are always found. Tunneling junctions without dye layers exhibit a typical resistance in the 100-Ω range and the $Al_2O_3$ layer has a typical thickness of about 5 nm.

The organic dye films have also been prepared by *in situ* sublimation of the dye powder from an aluminum oxide crucible onto the $Al_2O_3$ layer prior to completing the tunnel by evaporation of the Pb electrode. The tunnel itself, i.e., the $Al_2O_3$ substrate, was at room temperature during sublimation. The dye layer thickness can be estimated from its optical absorption to be in the 1–10-nm range and the tunnel resistance typically increases by factors of 10–100 due to the organic film. Measurements were done at liquid-helium temperature or in some cases at temperatures as low as 1.1 K. Structures which are attributed to inelastic excitation of electronic transitions were not affected by lowering the temperature.

The second derivative $d^2U/di^2$ of the voltage-current characteristic of the tunnel junction was measured by means of a standard ac-modulation technique with typically 1-kHz frequency. The modulation voltage was varied between 5 and 20 mV peak to peak. The current through the tunnel junction was limited by a high ohmic resistance in series.

## III. RESULTS

The commonly used measurement of $d^2U/di^2$ has the disadvantage of decreasing sensitivity for high-bias tunneling.[13] The overall shape of the spectra shown in Figs. 2–5 is characteristic for the $d^2U/di^2$ derivative at high voltages. Part of the spectra shown exhibits tails of pronounced sharp structure for voltages lower than 0.5 V which is due to inelastic excitation of vibrational modes in the dye in-

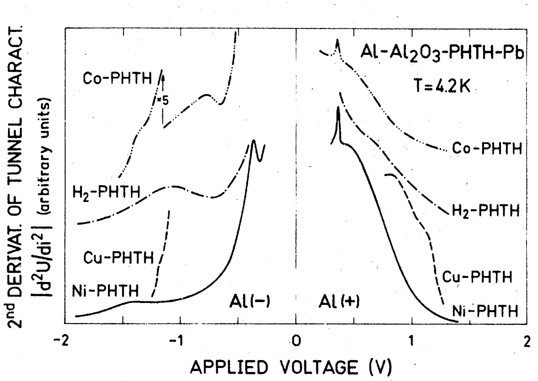

FIG. 2. Tunnel spectra measured on tunneling junctions with different phthalocyanine (PHTH) interlayers. The zero line is different for each spectrum and chosen arbitrarily. For direct comparison the absolute amount $|d^2U/di^2|$ is given without respect to the different sign for both bias directions.

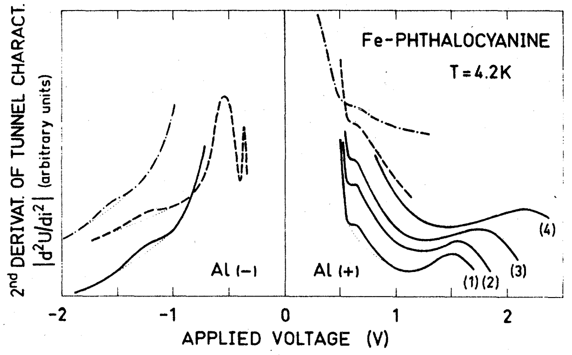

FIG. 3. Tunnel spectra measured on Al-$Al_2O_3$-(Fe-phthalocyanine)-Pb tunneling junctions. Curves plotted in different lines belong to measurements on junctions prepared in different experiments. (1), (2), (3), and (4) indicate results from subsequent runs on the same tunneling junction. Zero lines are chosen arbitrarily.

terlayers. The vibrational spectra obtained at bias below ~0.5 eV are published elsewhere.[16,17]

The present work is concerned with spectral features for applied voltages higher than 0.5 V which occur as relatively broad bumps in the $d^2U/di^2$ curves (Figs. 2–5). The tunnel spectra obtained on $H_2$-, Cu-, Co-, and Ni-phthalocyanines (Fig. 2) exhibit such structures at voltages slightly higher than 1 V and partially between 0.5 and 1 V. The energetic position of these structures listed in Table I is reproducible from run to run and also for all different tunneling junctions prepared with the same dye. The absolute signal height, on the other hand, varies from tunnel to tunnel and was not controlled in the present work. Sometimes the same structure could be observed for both bias polarities (Al positive and negative) like is seen for the case of Cu-phthalocyanine in Fig. 2. But mostly the structures were only observed for one or the other bias direction.

Results for Fe-phthalocyanine are shown in Fig. 3.

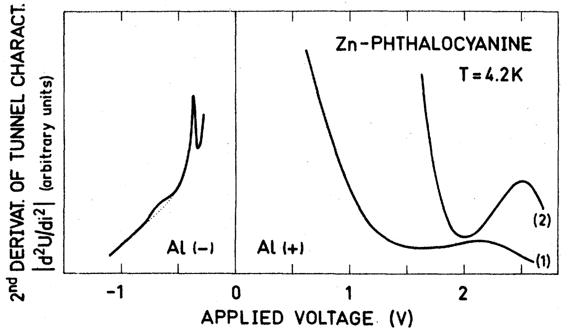

FIG. 4. Tunnel spectra measured on an Al-$Al_2O_3$-(Zn-phthalocyanine)-Pb tunneling junction. (1) and (2) indicate results of two subsequent runs on the same junction. Zero lines are chosen arbitrarily.

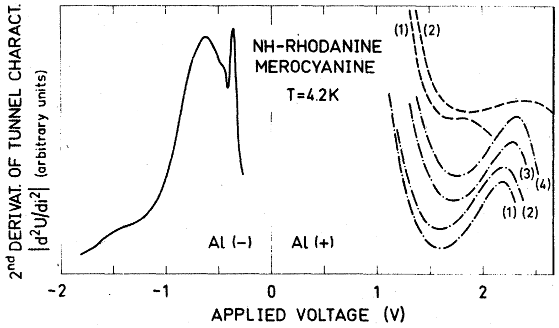

FIG. 5. Tunnel spectra measured on Al-$Al_2O_3$-(NH-rhodanine-merocyanine)-Pb tunneling junction. Curves plotted in different lines belong to measurements on junctions prepared in different experiments. (1), (2), (3), and (4) indicate results from subsequent runs on the same tunneling junction. Zero lines are chosen arbitrarily.

Reproducible structures at fixed energies were observed near 0.65 eV (mostly for positive bias at the Al electrode) and with varying intensity from tunnel to tunnel peaks near 1.2 and 1.6 eV. In cases like this where structures occured with strongly varying intensity in different experiments, a number of tunneling junctions had to be prepared to identify a particular structure.

A new interesting effect is found only when the tunneling junctions were biased with the Al-electrode positive. For Fe-phthalocyanine (Fig. 3) a strong peak occurs near 1.5 eV in the first run(1) of this experiment and is gradually shifted in the next runs (2)–(4) to finally 2.15 eV before the tunnel broke due to the high electric field. A similar effect is observed for tunneling junctions with Zn-pthalocyanine (Fig. 4). The strong structure near 2.1 eV for Al biased positive [run (1)] occurs shifted to 2.5 eV in the next run (2). In contrast with this behavior the peak near 0.65 eV (Al negative) always appears at the same energy.

Also on tunneling junctions with NH-rhodanine-merocyanine interlayers (Fig. 5) two types of structures are found. For Al biased negative a small band near 1.5 eV is found reproducible in its energetic position. With Al positive a strong structure occurs near 1.85 eV [run (1), dashed curve] and is shifted to about 2.4 eV in the next run (2). This shift is gradual as is clearly demonstrated in Fig. 5 (dashed-dotted curves) by a series of different runs (1)–(4) taken one after each other on the same tunnel. This band could be shifted finally to a maximum energy of 2.6 eV before the tunnel broke. Control experiments in which the reproducibility with respect to phase adjustment was checked, support that these "run-dependent" structures are not caused by phase

TABLE I. Comparison of electronic transition energies found in IETS (present work) with values known from other experimental work. The $\pi \rightarrow \pi^*(S \rightarrow T)$ energies are taken from Ref. 1: ($A$) means from absorption measurements and ($L$) from luminescence studies, respectively. The $\pi \rightarrow \pi^*(S \rightarrow S)$ energies have been determined in the present work by means of optical-absorption measurements on sublimated films. The underlined values belong to the main absorption maximum.

| | Transition energies (eV) from present work | | | Trans. energy (eV) of $\pi \rightarrow \pi^*$ $(S \rightarrow T)$ | Trans. energy (eV) of $\pi \rightarrow \pi^*$ $(S \rightarrow S)$ | | |
|---|---|---|---|---|---|---|---|
| $H_2$-phthalocyanine | 0.68 | 1.07 | | | 1.79 | $\underline{1.95}$ | |
| Fe-phthalocyanine | 0.63 | 1.2 | 1.6 | | 1.72 | $\underline{1.86}$ | 2.03 |
| Co-phthalocyanine | 0.75 | 1.35 | | 1.23 ($A$) | 1.8 | $\underline{2.0}$ | |
| Ni-phthalocyanine | | 1.4 | | 1.33 ($L$) | 1.81 | $\underline{2.0}$ | |
| Cu-phthalocyanine | | 1.15 | | 1.16 ($L$) | 1.77 | $\underline{1.99}$ | |
| Zn-phthalocyanine | 0.65 | | | 1.13 ($L$) | 1.77 | $\underline{2.0}$ | |
| NH-rhodanine-merocyanine | | 1.5 | | | 2.25 | $\underline{2.48}$ | 2.87 |

changes between reference and measurement channel.

For comparison also the optical-absorption spectra of dye layers have been measured. The dye layers were prepared by sublimation of the phthalocyanine and NH-rhodanine-merocyanine dyes onto transparent quartz substrates. Since the optical absorption of these $\pi \rightarrow \pi^*(S \rightarrow S)$ transitions is well known in literature,[18] only the energetic positions of the main absorption peaks observed in the present work are given in Table I. For all dye films prepared in that way the optical absorption consists of a broad band whose main maximum is underlined in Table I.

## IV. INTERPRETATION AND DISCUSSION

### A. Electronic transitions

IETS measurements in the high bias regime (0.5–2.5 eV) on Cu-phthalocyanine and other organic compounds [xenocyanine, tetracyanine, *bis*-(4-dimethylaminothiobenzil)-nickel, pentacence, $\beta$-carotene] have already been performed by other authors.[13,19] The spectral features attributed in that work to electronic transitions are similar in intensity and half-width with the structures seen as little bumps in the $d^2U/di^2$ characteristic in Figs. 2–5.

Our interpretation that the peak at 1.15 eV on Cu-phthalocyanine (Fig. 2, Table I) is mainly due to $\pi \rightarrow \pi^*$ $(S \rightarrow T)$ transitions, is in agreement with conclusions from previous IETS studies of Léger *et al.*[13,19] as well as with results from luminescence investigations.[1] From a comparison with these luminescence ($L$) or absorption ($A$) measurements (Table I), the spectral structures found near 1.35 eV for Co-phthalocyanine and near 1.4 eV for Ni-phthalocyanine in the present IETS curves are suggested to be mainly caused by $\pi \rightarrow \pi^*(S \rightarrow T)$ transitions. By analogy the transitions observed in the present work at 1.07 eV for $H_2$-phthalocyanine and at 1.2 eV for Fe-phthalocyanine are most probably also due to $\pi \rightarrow \pi^*$ $(S \rightarrow T)$ transitions. For $H_2$- and Fe-phthalocyanines $S \rightarrow T$ transitions have not been observed in luminescence to our knowledge up to now. There is no obvious explanation why the $S \rightarrow T$ transition found in luminescence[1] at 1.13 eV on Zn-phthalocyanine could not be observed in IETS.

For NH-rhodanine-merocyanine up to now only the optically allowed $\pi \rightarrow \pi^*$ $(S \rightarrow S)$ transitions are known and have carefully been studied.[20] In absorption, a broad structure (width ~0.5 eV) centered around 2.5 eV is found. Taking the ratio between $S \rightarrow S$ and $S \rightarrow T$ transition energies as a first hint, it seems reasonable to interpret the structure found at 1.5 eV on the NH-rhodanine-merocyanine layer in terms of $\pi \rightarrow \pi^*(S \rightarrow T)$ transitions.

In the energy range between 0.5 eV and 1 eV, Jaklevic *et al.* have detected structures which they attributed to band-structure effects (quantum size effect) in the Pb electrode.[21] These structures, however, are dips with a sign opposite to that of inelastic excitation bands and they occur only for negative bias at Al. Since the present bands below 1 eV do not show this characteristic behavior, they are interpreted in terms of true inelastic excitations of electronic transitions. In the energy regime below 1 eV, transitions are expected between the $\pi$-electron system of the macrocyclic ring and some metal-ligand orbitals. Not much experimental data about the energetic positions of these levels are available up to now. On the other hand, extended-Hückel calculations have been performed by Zerner and Gouterman[9] for porphyrins and by Schaffer *et al.*[2] for phthalocyanine molecules. The main results of these calculations (only single electron states) for some

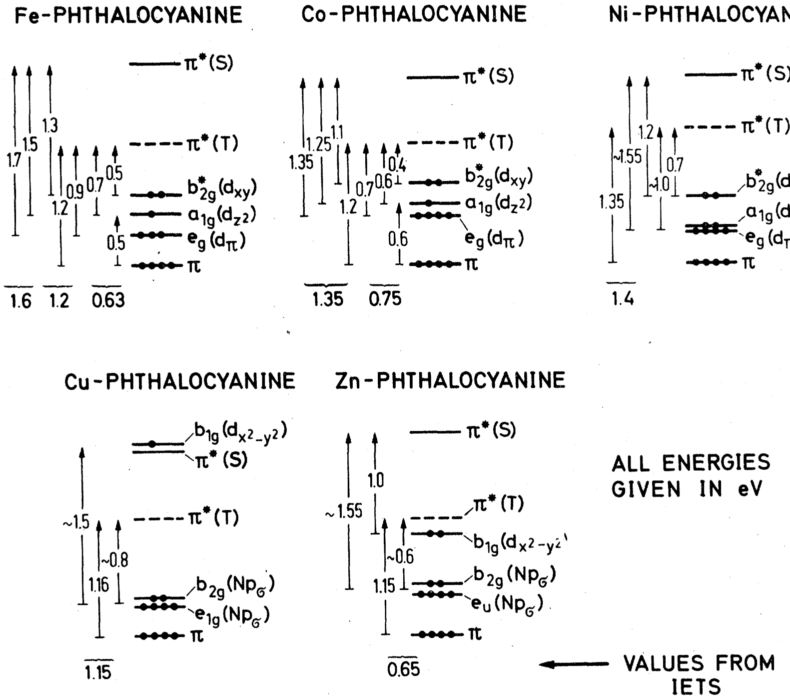

FIG. 6. Calculated level schemes for phthalocyanine molecules after Schaffer *et al.* (Ref. 2). Energy differences are marked by arrows. Nomenclature and occupation of the metal ligand derived levels are taken from Ref. 2. Splitting of the $\pi$ level (Ref. 2) is not taken into account and the position of the $\pi^*(T)$ level is taken from optical experiments (Ref. 1) or estimated by analogy. Transition energies observed in the present IETS study are given below each level scheme.

phthalocyanines in the energy range of the $\pi$, $\pi^*$ orbitals are shown in Fig. 6. The triplet $\pi^*(T)$ levels are taken from optical experiments[1] or are estimated by analogy.

The nomenclature from Ref. 2 is used except for the $\pi$ and $\pi^*$ levels. Since fine structure is not relevant for interpreting the broad IETS spectral bands, $\pi$ and $\pi^*$ orbitals are given as single levels without taking notice e.g., of the splitting of the $\pi$ orbital into $a_{1u}(\pi)$ and $a_{2u}(\pi)$ levels.[2] Furthermore, orbitals that are nearly degenerate with the $\pi$ levels, like, e.g., the nitrogen-derived state $a_{1g}(Np_\sigma)$ in Cu-phthalocyanine, are not plotted. Also the occupation of the different levels (Mulliken population analysis) is taken from the work of Schaffer *et al.*[2] even though levels near midgap between $\pi^*(S)$ and $\pi$ might be differently occupied when the molecules form a $p$-type semiconducting film like that expected in the present experiment (Fermi level probably in the lower half of the forbidden band). Since optical selection rules do not seem to be important for inelastic processes in IETS, all possible transitions shown in Fig. 6 by arrows might be taken into account for the interpretation of the measured transition energies.

There is fairly good agreement between the present experimental results and the calculated level schemes as is now discussed in more detail. Because of the spectral width of the observed structures theoretical transitions being separated from each other by less than about 0.3 eV should show up as one band in IETS.

For Fe-, Co-, Ni-phthalocyanines all of the experimentally observed peaks can be attributed to transitions involving the $\pi$, $\pi^*$, and the metal-ligand $d$ orbitals. Even better agreement between experiment and theory is achieved if one assumes that the $b_{2g}^*(d_{xy})$ levels for these three compounds are lower in energy, maybe nearly degenerate with the $a_{1g}(d_{z^2})$ and/or $e_g(d_\pi)$ levels. Then, transition energies as low as 0.4 eV for Co-phthalocyanine or as low as 0.7 eV for Ni-phthalocyanine that are not observed in experiment would not be expected from theory. The $b_{2g}^*(d_{xy})$ orbital is the high-energy component that results from a splitting of the $d_{xy}$ metal orbital into $b_{2g}^*(d_{xy})$ and $b_{2g}(d_{xy})$ (degenerate with $\pi$) levels via interaction with the nitrogen derived $b_{2g}(Np_\sigma)$ orbital. To get better agreement with experiment, only this interaction must be assumed to be less prominent. The present results, therefore, suggest less delocalization of the metal $d$ orbitals for Fe-, Co-, Ni-phthalocyanines than is given in the theoretical model.[2]

For Cu-phthalocyanine only one electronic transition at 1.15 eV could be found experimentally in this work as well as in previous IETS studies.[19] In contrast with the theoretical level scheme depicted in Fig. 6, this implies that the nitrogen-derived levels $b_{2g}(Np_\sigma)$ and $e_{1g}(Np_\sigma)$ should be located at slightly lower energy, maybe degenerate with the $\pi$ orbitals, thus giving rise only to a broadening of the $\pi \rightarrow \pi^*$ transitions. The theoretical result of Schaffer *et al.*[2] that for Cu-phthalocyanine in contrast with the situation in Cu-porphyrin,[9] the $b_{1g}(d_{x^2-y^2})$ is nearly degenerate with the $\pi^*(S)$ level is supported by the present experiments. For a situation like it is given in Cu-porphyrin[9] one would expect additional transitions below 1 eV.

A similar degeneracy of the $b_{2g}(Np_\sigma)$ levels with the $\pi$ levels might be given in Zn-phthalocyanine. This would explain why no transitions are observed near 1.5 eV as suggested by Fig. 6. The band observed experimentally at 0.65 eV might also be explained by transitions from $\pi$ into a partially occupied $b_{1g}(d_{x^2-y^2})$ level if this would be located at slightly lower energy. Nevertheless the problem remains why the $\pi \rightarrow \pi^*$ $(S \rightarrow T)$ transition near 1.13 eV[1] could not be seen in IETS.

For $H_2$-phthalocyanine the lowest energy transition is expected to be the $\pi \rightarrow \pi^*$ $(S \rightarrow T)$ transition near 1.07 eV. The additionally observed 0.68 eV peak, therefore, is most probably due to an impurity level. It is well known that $H_2$-phthalocyanine is extremely reactive with respect to metal contaminations.

It is an open question at present why no $\pi \rightarrow \pi^*(S \rightarrow S)$ *transitions* could be observed for the phthalocyanine compounds near 1.9 eV nor for NH-rhodanine-merocyanine near 2.4 eV. Too low sensitivity of the experimental technique used might be the reason or the structures are covered by elastic processes which are discussed in Sec. IV B. Neither Léger *et al.*[19] could detect the $\pi \rightarrow \pi^*(S \rightarrow S)$ transitions in Cu-phthalocyanine.

### B. Internal-field emission and charging effects

The prominent structures seen in Figs. 3–5 for the polarity Al positive which shift to higher energies from one run to the next on the same tunneling junction cannot be explained in terms of inelastic excitation of molecular electronic transitions. It seems very unlikely that a possible reorientation of molecules within the dye layer due to the relatively high applied voltages changes electronic transition energies by more than 0.5 eV. Bands due to partially destroyed molecules (due to the action of the high fields) can be ruled out, since the vibrational spectra and the "true" electronic transitions are unaffected. Furthermore, the strong intensity of the peaks in a bias regime, where the present experimental technique yields only relatively low sensitivity, suggests a mechanism which differs from that which is responsible for the structures ascribed to inelastic processes. Even though the sublimated dye layers have an estimated thickness between 1 and 10 nm (comparable with $Al_2O_3$ layer) they increase the tunnel resistance by a factor of 10–100. A tunneling phenomenon rather than a conductance effect, therefore, seems to be responsible for the broad shifting structures in Fig. 3–5.

Structures comparable in intensity and half-width have already been described by Gundlach and Hölzl[22,23] for Al-$Al_2O_3$-Al junctions without any additional interlayer. These structures have been explained by a rapid increase of the tunneling current when the Fermi level in one electrode is lifted across the work function of the opposite electrode. From this critical bias on the electrons have to tunnel through a triangular shaped energy barrier (in the simplest case without space charge) and the effective barrier width is decreased in dependence on the external voltage. Effects of this kind might be responsible for the strong spectral structures seen near −0.5 eV in Fig. 3 for Fe phthalocyanine with Al negative and near −0.6 eV in Fig. 5 for NH-rhodanine-merocyanine with Al negative. In particular on "clean" tunnel junctions (without phthalocyanine) where similar spectral features can also be observed near energies of −0.7 and +1.2 eV this interpretation might be adequate.

For tunneling junctions with phthalocyanine or NH-rhodanine-merocyanine interlayers like those in Figs. 3–5 also the spectral shifts have to be explained. These shifts, which are irreversible for at least the time a particular tunnel was studied (at maximum 48 h), suggest an interpretation in terms of charging effects in the dye layer. Storage of electronic charge in merocyanine layers has been studied in detail by Broich and Heiland.[24] These authors could show that electron densities up to $10^{17}$ $cm^{-3}$ can be stored in sublimated merocyanine layers at low temperature for days and that only light irradiation can restore the initial conditions. Irreversible charge storage induced by high electric fields has also been observed by Lundström *et al.* in chlorophyll films.[25]

The following model, therefore, is suggested for the explanation of the structures which shift after application of high electric fields (Figs. 3–5). When the Fermi energy $E_F$ in the Pb electrode is lifted with respect to $E_F$ on the Al side so that electrons can elastically tunnel within the dye layer and reach empty levels within the "conduction" band $E_c$ of the organic semiconductor the tunneling current is expected to increase thus causing a peaklike structure in the second derivative of the $I$-$V$ characteristic. This tunneling process with the conduction band as final states is usually called internal field emission[26] (FE). During this process, electrons are assumed to be trapped within the dye layer, probably in deep-lying trapping levels, thus giving rise to a space charge and a

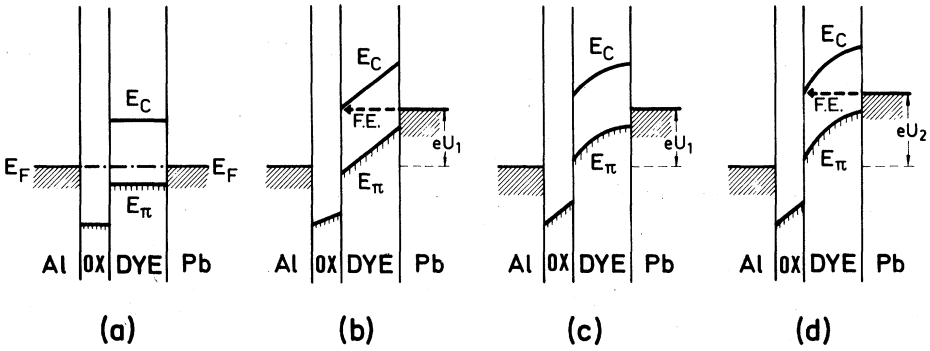

FIG. 7. Qualitative band-scheme model for an Al-$Al_2O_3$-dye-Pb tunnel (a) without and (b)–(d) with applied voltages $U_1$ and $U_2$. OX means oxide ($Al_2O_3$). $E_F$ is the Fermi energy, $E_\pi$ the valence band formed by $\pi$ orbitals, and $E_c$ the lower-conduction-band edge; FE indicates a possible internal-field-emission process.

redistribution of the electric potential between the $Al_2O_3$ and the dye layer. The onset of the internal FE process, therefore, is observed at somewhat higher voltages than in the case where no charge was trapped in the dye.

In more detail the situation is depicted schematically in Fig. 7. The electronic states in the dye layer are described in terms of a band scheme model like in semiconductors even though atomistic details of the electrical conductivity in phthalocyanine or NH-rhodanine-merocyanine layers are not well understood. The field distribution within the $Al_2O_3$ layer (OX) is qualitatively described by one single valence band level whereas for the dye layer the valence band is assumed to consist of $\pi$ molecular orbitals. The nature of the conduction-band states $E_c$ is not further specified. As is known from other work[6] in both types of dyes $p$-type conducitivity is found and in particular from uv-photoemission work of Koch and Grobman[27] one can estimate $E_F - E_\pi \approx 0.4$ eV for Mg- and Pb-phthalocyanine layers. In Figs. 7(a) and 7(b) flat bands within the phthalocyanine layer are plotted, since nothing is known about space charge layers or charge trapping at the initial conditions. When the external voltage (Pb negative) reaches the value $U_1$ [Fig. 7(b)] the internal FE process sets on and increases the tunnel conductance since due to the empty conduction-band states $E_c$ the width of the tunnel barrier is divided into two parts: phthalocyanine layer width and $Al_2O_3$ (OX) layer width. Because of the exponential dependence on barrier width this should increase the elastic tunnel current considerably. The FE process shown in Fig. 7(b) now is responsible for electron injection into the phthalocyanine layer. The resulting irreversible trapped electron space charge bends the bands in the phthalocyanine layer so that in a subsequent run the situation of Fig. 7(c) is given when the same external voltage $U_1$ is applied. At this voltage the FE process can no longer happen due to the band curvature. A higher voltage $U_2$ [Fig. 7(d)] must be applied to induce the FE process and the spectral structure being caused by this process occurs at higher energy $|eU_2|>|eU_1|$. Further electron trapping in subsequent runs causes a shift of the onset energy for the FE process to higher and higher energies as is observed in experiment. The present interpretation also explains that the spectral structures can be shifted to higher energies than the singlet $\pi \rightarrow \pi^*$ gap in the phthalocyanine (~1.8 eV) and the NH-rhodanine-merocyanine (~2.4 eV) layers. The initial onset of the FE spectral structure at energies lower than the band gap of the phthalocyanine layer might be determined by initial space charge layers (band bending), the exact location of $E_F$ with respect to $E_\pi$ and/or additional processes which have similar effects like the FE process shown in Fig. 7, e.g., Zener tunneling between valence and conduction band, impurity field ionization[26] in the phthalocyanine or NH-rhodanine-merocyanine layer. The observed asymmetry that the FE process only shows up in the spectra for Pb negative might be understood in terms of the geometrical asymmetry of the tunneling junction. Lifting the Fermi level $E_F$ on the Al side in Fig. 7 does not bring the high density of metallic states into "contact" with the dye conduction band $E_c$. The $Al_2O_3$ interlayer (OX) is intermediate.

Qualitatively the whole picture is independent of the nature of the conduction-band states which are not well known in these organic semiconductors.[6] Singlet, triplet $\pi^*$ states, metal-ligand $d$ states, or impurity levels might be taken into account. A rough estimation of the charge density neccessary to shift, e.g., the NH-rhodanine-merocyanine structure in Fig. 5 from 1.8 to 2.6 eV (maximal observed value) is possible. If the electrons that are trapped after subsequent application of the external bias are assumed to form a homogeneous density distribution all over the dye layer, Poisson-equation requires a parabolic dependence of the band bending $V$ on the thickness of the dye layer $d$.

$$V = e\rho_0 d^2/2\epsilon_0\epsilon\,, \qquad (1)$$

where $\rho_0$ is the homogeneously distributed electron density which is stored in the layer. The dielectric constant $\epsilon$ of the dye layer is assumed to be one, since only the order of magnitude can be estimated. From Figs. 7(b)–7(d) it is obvious that in a rough approximation the increase $\Delta U = U_2 - U_1$ in the onset energy for the FE process is given by the change in band bending $\Delta V$ due to the trapped charge density. From Eq. (1) one derives an electron density increase of $\Delta\rho_0 \approx 10^{17}$ cm$^{-3}$, which is required approximately to explain the maximal shift by about 0.8 eV for NH-rhodanine-merocyanine. A mean value for the dye layer thickness $d$ of 10 nm has been assumed. The estimated value of the charge density trapped in the NH-rhodanine-merocyanine layer is in good agreement with results obtained from totally different experiments.[24] This might be taken as a support for the present interpretation of the observed peak shifts in terms of charge trapping.

It should be emphasized that the discussed charge trapping effect does not effect any true inelastic process so that peaks due to inelastic excitation of electronic and vibronic transitions are not shifted as is observed in the experiment. Even if charging would shift the molecular orbitals on the energy scale these shifts can not show up in the spectra (true inelastic transitions) since only the ~$10^{-5}$ part of all molecules are affected.

Structures which shift after subsequent application of high external fields have not been observed up to now even though some work has already been done on similar systems (see, e.g., Refs. 13 and 19. A reason might be that these authors used thinner dye layers with less charging. Broich and Heiland[24] could show that for NH-rhodanine-merocyanine layers the amount of charge which is trapped is proportional to the layer thickness. Also space-charge layers present in the dye film before application of external fields might affect internal FE processes. Asymmetric behavior with respect to the bias polarity and/or supression of the whole effect in some cases might be explained in that way.

## V. CONCLUSIONS

The present work clearly demonstrates the usefulness of IETS for the investigation of electronic transitions if, in particular, they are optically forbidden. The obtained results allow an experimental check of the detailed calculated energy-level schemes for phthalocyanines.[2] Nevertheless, a number of questions concerning inelastic tunneling on electronic transitions remain open. The lack of any fine structure, particularly in comparison with optical spectra, is not well understood. There are parameters, like impurity concentration, geometrical disorder and space charge in the organic dye layer which are not under control but can influence the occurence of one or the other peak for a particular bias polarity. Furthermore, there might be physical reasons that $S \rightarrow S$ transitions could not be found whether in the phthalocyanine nor in the NH-rhodanine-merocyanine compounds.

For the first time to our knowledge the present paper reports structures in IETS which shift on the energy scale from run to run. The interpretation in terms of "elastic" internal field emission processes is of general interest and the explanation of the peak shifts in terms of band bending and charge trapping is adequate but needs further experimental proof.

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