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Molecular electronic transitions observed by inelastic tunneling spectroscopy

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The method of inelastic tunneling spectroscopy has been extended to the observation of *electronic* transitions of organic molecules. The aim of this work was to study the selection rules and to analyze the shape and strength of the observed transitions. We find that both singlet-singlet and singlet-triplet transitions can be observed with roughly the same intensity, but the peaks are found to be rather wide. The first point is explained by the interaction mechanism between the tunneling electrons and the molecules, the second by the interactions of the molecules with their environment.

I. INTRODUCTION

Inelastic tunneling spectroscopy has been used extensively to study the vibrational spectra of various molecules,[1-5] and has found several useful applications.[2,3,6-10] The method has been extended to the observation of electronic transitions of organic molecules. These were first observed on copper phthalocyanine (PcCu) by Léger *et al.*,[11] then in rare-earth oxides by Adane *et al.*[12]

PcCu has an optically forbidden singlet-triplet (S_0-T_1) transition at 1.15 eV and an optically allowed singlet-singlet (S_0-S_1) transition at 1.8 eV. Surprisingly, only the former was observed. This brought up the problem of the electron-molecule interaction mechanism, and led us to make a more systematic study of high-bias tunneling spectroscopy.

II. EXPERIMENTAL TECHNIQUES

Since the tunnel junctions we used (Al-Al_2O_3-Pb or Mg-MgO-Pb with an insulating layer of 20 to 30 Å) break down beyond 2 to 2.5 V, it was necessary to select molecules with particularly low electronic levels. We also wished to observe both singlet-singlet (S-S) and singlet-triplet (S-T) transitions. On these two criteria we selected the following molecules:

Molecules with S-S transitions: xenocyanine: S_0-S_1 at 1.3 eV; tetracyanine: S_0-S_1 at 1.3 eV; and bis (4-dimethylaminodithiobenzil) nickel: S_0-S_1 at 1.25 eV. The first two are laser dyes and the third is used as a Q-switch for neodynium-glass lasers.

Molecules with S-T transitions: cooper phthalocyanine: S_0-T_1 at 1.15 eV and S_0-S_1 at 1.8 eV; carotene: S_0-T_1 not yet observed optically, as far as we know, but believed to be below 1.5 eV (Ref. 13); and pentacene: S_0-T_1 at 0.8 eV and S_0-S_1 between 1.9 and 2.1 eV.

We used Al-Al_2O_3-Pb or Mg-MgO-Pb junctions. As the molecules studied are complex and rather easily dissociated, the doping of the junctions requires care. Two methods were used: evaporation of the molecule, or doping in solution.[3] The first method has the advantage of producing junctions free of impurities since they are oxidized in a controlled oxygen plasma, but it could only be used for the more stable molecules (PcCu and pentacene). The second method is better adapted to use with unstable molecules. It has the disadvantage of introducing impurities, since the oxidation takes place in room air. Luckily, their electronic transitions are at too high energy to appear in our experiments. (On the other hand, the vibrational spectrum become very complex. If necessary, this can be avoided by working in a controlled atmosphere.)

The apparatus used to obtain first, second, and third derivatives of the characteristic curves $I(V)$ of the junctions is described in Ref. 14. It is shown that the second derivative $(1/\sigma)(d\sigma/dV)$ (where $\sigma = dI/dV$) is better adapted to high-bias tunneling than the more classic d^2V/dI^2.

To deduce the noise in the characteristic curves, we used a multichannel analyzer. We show, in Ref. 15, that it can practically eliminate the $1/f$-type noise present *in the measured function*, whereas a lock-in detector is incapable of doing this. As tunnel junctions are particularly unstable at high bias, the multichannel analyzer is quite essential.

III. EXPERIMENTAL RESULTS

We were able to observe transitions in each of the molecules studied.

A. Singlet-singlet transitions

Figure 1 shows the spectra obtained for tetracyanine. The transition can be seen in both polari-

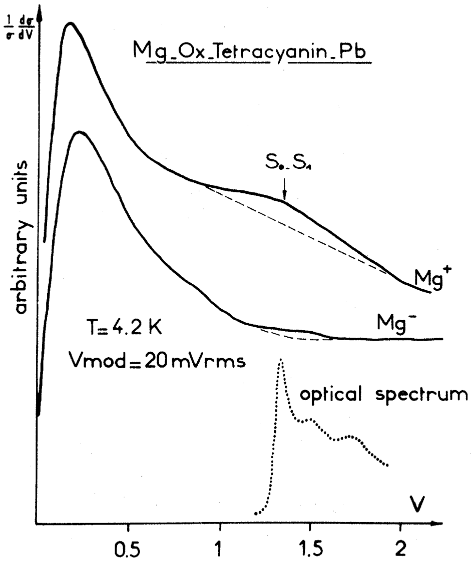

FIG. 1. Tunnel and optical spectra of tetracyanine.

ties. It is more apparent in the polarity Mg^+, but the relative conductance variation $\Delta\sigma/\sigma$ is of a few percent in both polarities. The optical spectrum of the molecule in solution is shown for comparison. The peak on the tunneling curve is seen to be correctly situated, but much widened.

Figure 2 may explain this widening. We show the tunnel spectrum obtained for xenocyanine, in the polarity where it is most apparent. Below it are the optical spectra obtained in solution (a), and in a thin film (b). We see that the thin-film spectrum is much wider than the one for the solution. The widening observed in tunnel spectra seems therefore to be due to the environment of the molecules and not to the tunneling mechanism itself. We shall discuss this point in Sec. V.

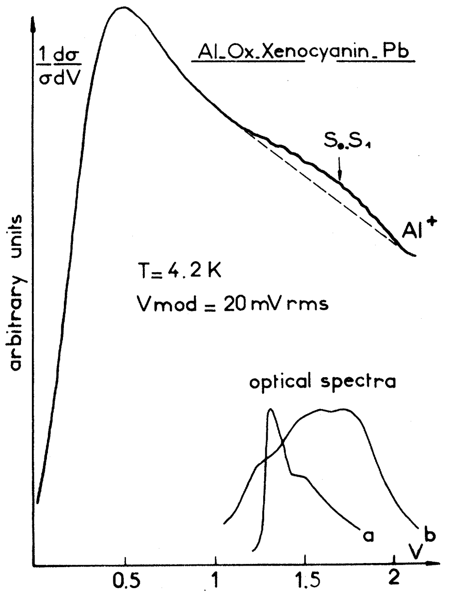

FIG. 2. Tunnel and optical spectra of xenocyanine; (a) optical spectrum in solution; (b) optical spectrum of a thin film.

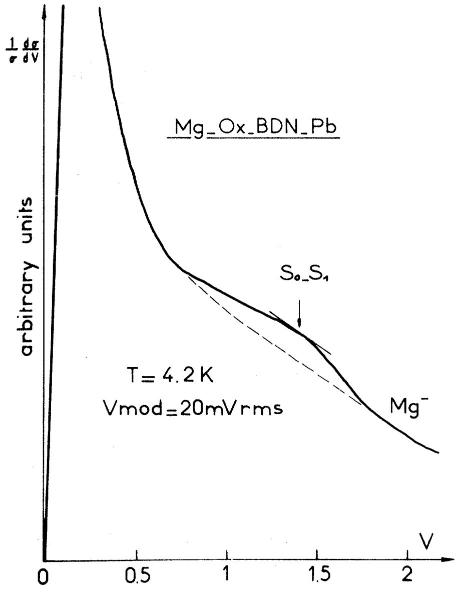

FIG. 3. Tunnel spectrum of bis (4-dimethylaminodithiobenzil) nickel.

Figure 3 shows the spectra obtained with bis (4-dimethylaminodithiobenzil) nickel. The *S-S* transition is wide, and centered at about 1.3 eV, as expected. The relative conductance variation $\Delta\sigma/\sigma$ is of a few percent.

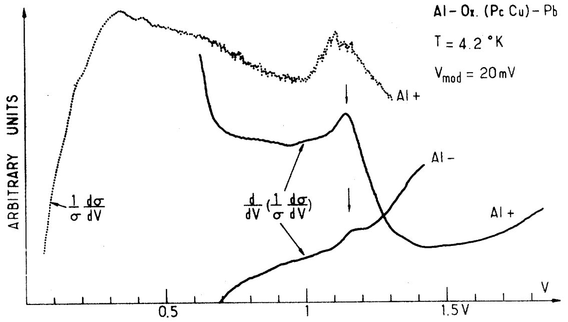

FIG. 4. Tunnel spectra of copper phthalocyanine. A third derivative enables the S_0-T_1 transition to be seen in both polarities.

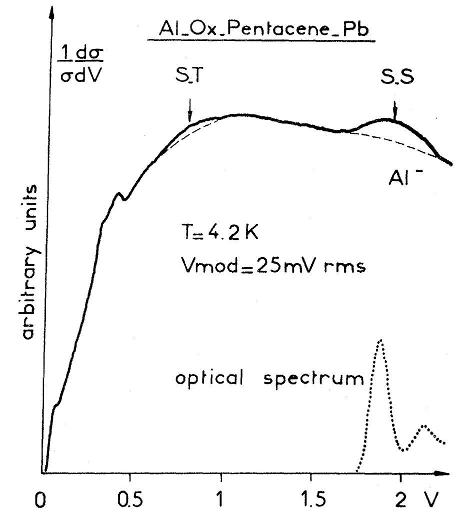

FIG. 5. Tunnel and optical spectra of pentacene.

B. Singlet-triplet transitions

Figure 4 gives the spectra obtained with copper phthalocyanine. The S-T transition is expected at 1.15 eV, and can be clearly seen in the polarity Al^+, on the second derivative. A third derivation was necessary to confirm its presence in the other polarity. As reported in Ref. 11, the S-S transition expected at 1.8 eV could not be seen. As we shall see, in Sec. V, this may be due to a "loss of sensitivity" of the method at very high bias.

Figure 5 shows the tunnel spectrum for pentacene. The S-T transition is seen at 0.9 eV ($\Delta\sigma/\sigma \simeq 1\%$) and the S-S transition at 1.9 eV ($\Delta\sigma/\sigma \simeq 4\%$) (the optical spectrum of the S-S transition is also shown for an amorphous film[16] of pentacene). This is the highest bias at which we have been able to observe an electronic transition.

In Fig. 6 we see the spectra obtained with β-carotene with a peak at 1.3 eV. We believe this to be the S-T transition, which, to our knowledge, has not been observed by optical methods because it is too strongly forbidden.

IV. COMMENTS

These results call for a certain number of comments. First, the S-S and S-T transitions appear with much the same intensity (in each case the change in conductance due to the apparition of the inelastic channel is of a few percent). This is contrary to what is found in optical spectroscopy where S-T transitions are "forbidden," and appear weaker by several orders of magnitude, than "allowed" S-S transitions.

Secondly, the transitions are weaker than in optical spectroscopy, when compared to the intensity of vibrational transitions. The oscillator strength of an allowed (S-S) electronic transition is about 10^4 times that of a vibrational one. There are of course several vibrating radicals per molecule ($\simeq 20$ in our cases). This leaves an intensity ratio of about 500, whereas in tunneling spectroscopy one finds a ratio of only about 10.

Finally, our peaks are much wider than those seen in optical spectra. As we showed, this may be related to the thin-film structure of the molecule layer. In Sec. V we shall try to explain these points.

V. THEORETICAL CONSIDERATIONS

The first theoretical interpretation of inelastic tunneling was made by Scalapino and Marcus[17] (extended by Lambe and Jaklevic[1]). Using a dipole model of a vibrating radical, they show the inelastic contribution to the tunneling current to be proportional to the matrix element of the dipole moment between initial and final states. Therefore, in the far infrared, tunnel spectra are expected to closely resemble optical spectra, and this is indeed what is found experimentally.[1,2] As we have seen, this resemblance no longer exists for electronic transitions. To begin with, optical selection rules do not hold.

To explain this point, it would be necessary to know the exact mechanism of the interaction between a tunneling electron and a molecule embedded in the barrier. One may gain some insight into the problem, however, by referring to another case in which optical selection rules are lifted: the ex-

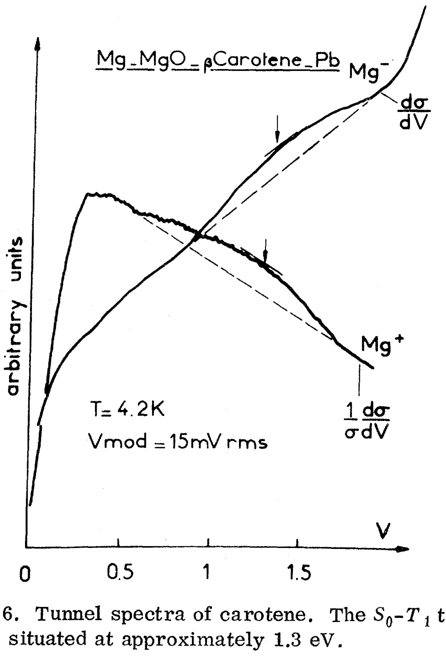

FIG. 6. Tunnel spectra of carotene. The S_0-T_1 transition is situated at approximately 1.3 eV.

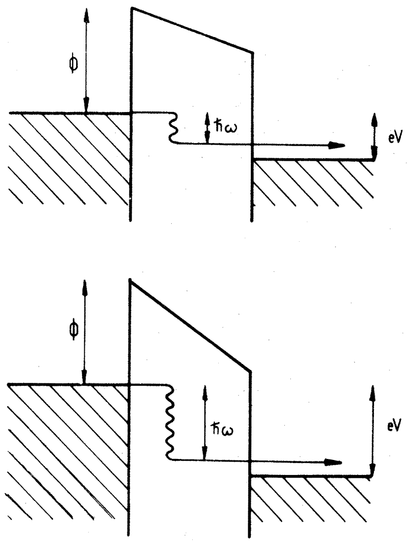

FIG. 7. Attenuation of the inelastic current due to a high-energy transition: the electron having lost more energy "sees" a higher barrier.

citation of molecular electronic transitions by low-energy electron impact. It has been shown that while direct interaction terms account for the excitation of singlet-singlet transitions, exchange interaction can allow singlet-triplet transitions to be excited.[18-20] The situation is obviously more complicated when the incident electron is tunneling, but it seems likely that the same type of interaction can take place. This could explain our seeing both singlet-singlet and singlet-triplet transitions.

If this analogy is correct, it means that tunnel results cannot be compared with optical ones, which invalidates our second comment on the relative strength of vibrational and electronic transitions. It remains interesting all the same, to see whether the fact that a transition is located at high bias causes it to be attenuated. Figure 7 shows schematically how this could happen: an electron that has lost a lot of energy "sees" a higher barrier than one that has only lost a little.

To make this point clear, we compared the inelastic current due to an interaction, located at the center of the barrier, with an energy $\hbar\omega$ of (a) 0.4 eV (roughly that of a C-H vibration) and (b) 1.4 eV (roughly that of an electronic transition).

We used Fermi's golden rule:

$$I_{\text{inel}} = \frac{4\pi e}{\hbar} \sum_{k,k'} |W_{kk'}|^2 \, \delta(E_k - E_{k'} - \hbar\omega) \times [f(E_k) - f(E_k + eV - \hbar\omega)],$$

with

$$W_{kk'} = \langle \Psi_k^{\text{left}} | h | \Psi_{k'}^{\text{right}} \rangle .$$

The interaction h was taken so that

$h = 0$ if $z \neq \frac{1}{2}d$,

$h = h_0$ if $z = \frac{1}{2}d$,

and the wave functions were calculated in a WKB approximation:

$$W_{kk'n} = \int dr_{\parallel} dz \, \frac{\langle n | h_0 | 0 \rangle}{\sqrt{L_d L_g S}} e^{i(k_{\parallel} - k'_{\parallel}) r_{\parallel}} \exp\left[- \int_0^{d/2} \left(\frac{2m^*}{\hbar^2} (\Phi + \mathcal{E}_F - eVz/d - E_z) \right)^{1/2} dz \right]$$
$$\times \exp\left[- \int_{d/2}^{d} \left(\frac{2m^*}{\hbar^2} (\Phi + \mathcal{E}_F - eVz/d - E_z) \right)^{1/2} dz \right] .$$

The integration over z is immediate. The sum over k, k' becomes an integration over the energies E and E', that we performed numerically. We took the barrier height $\Phi = 2$ eV and the Fermi energy $\mathcal{E}_F = 11.6$ eV of aluminium in Al-Al_2O_3-Pb junctions, the effective mass $m^* = m_e/z$, the barrier width $d = 20$ Å.

We also calculated the elastic current under the same conditions, and then deduced the variation of conductance $\Delta\sigma/\sigma$ due to the opening of the inelastic channel in each case. We found that this variation was about 30 times smaller when the interaction (of fixed intensity) was situated at 1.4 rather than at 0.4 eV.

This is of course a rough calculation (for example, the interaction is no doubt not localized), but it does show that high-energy transitions are attenuated because of the deformation of the barrier (this is the case of PcCu). To put this another way, the quantity $\Delta\sigma/\sigma$ is not a very good measure of the intensity of a transition at high energy, since the inelastic conductance $\Delta\sigma$ is not proportional to the matrix element of the interaction.

The final point to consider is the widening of the transitions. As we have shown in Fig. 2 the width of the peaks in the tunnel spectra is about the same as that found in the optical spectra of a thin film. It seems therefore to be related to the configuration of the molecules in a thin film, randomly oriented yet in strong interaction with each other and with their environment. For example, Kirtley and Hansma[21] have suggested an interaction of the molecules with their image dipoles reflected by the counterelectrode.

VI. CONCLUSION

We have been able to observe electronic transitions between both singlet-singlet levels and singlet-triplet levels, by tunneling spectroscopy.

The spectra have three main characteristics: (i) S-S and S-T transition are seen with roughly the same intensity. This can be understood by considering the interaction mechanism between the electron and the molecule. (ii) Transitions at high energies are somewhat attenuated in comparison to transitions at low energies, because of the deformation of the junction barrier. (iii) The peaks obtained are wide. This seems due to the interactions of the molecules with their environment.

The absence of selection rules is an advantage: it allowed us to observe the forbidden S-T transition of β-carotene. Because of this and because the method is sensitive and well adapted to the study at surface phenomena, tunneling spectroscopy seems *complementary* to optical spectroscopy.

The problem of the width of the peaks remains to be clearly understood—and, if possible, solved. We plan to focus our attention on this point in the future, as it is the key to eventual applications of tunneling spectroscopy of electronic transitions.

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