

Asymmetry of Tunnel Spectrum Intensities of Impurity Organic Molecules

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Submitted July 22, 1971

Zh. Eksp. Teor. Fiz. 62, 1023-1030 (March, 1972)

Asymmetry of the intensities of the deformation and valence oscillations of the C—H bond is experimentally observed in tunnel junctions containing organic impurities. For explanation of the characteristics observed, both the static effect, which takes into account asymmetry of the barrier transparency in inelastic tunneling of a single electron, and the dynamic effect due to "heating up" of the molecules by a beam of tunneling electrons are evoked.

A study of the tunnel spectra of organic impurity molecules has revealed that the integral intensity of the absorption lines of these molecules depend significantly on the sign of the voltage V applied to the junction^[1] (the sign + or - in Fig. 1 and throughout the text corresponds to the sign of the voltage applied to the lower film, which was oxidized). Organic molecules fall into the tunnel junction during the course of oxidation of the lower metallic film by atmospheric air, or are specially deposited on the oxide layer. To explain the influence of the polarity of the applied voltage on the intensity of the spectral bands, it does not matter which molecules have been introduced into the junction. It is only required that the impurities be sufficiently well localized on the interface between the metal and the dielectric. In the case of special vacuum evaporation of a small amount of organic matter onto the surface of the oxide layer, this requirement is definitely satisfied. On the other hand, if the organic substance is deposited during the course of oxidation of the lower film in atmospheric air containing vapors of organic substances, then it can be assumed that the impurity molecules will also be disposed in the barrier in asymmetrical fashion. Such an assumption is quite natural if it is recognized that the oxide grows towards the interior of the metal film and the organic molecules adsorbed on its surface remain at all times on the surface of the oxide.

The purpose of the present study was to investigate in detail the integral intensities of the lines corresponding to the valence and deformation oscillations of C—H bonds. It turned out that for all junctions (Al—Pb, Sn—Sn, and Sn—Pb) the integral intensities of these lines are always larger for a negative voltage V (Figs. 1-4). It is important to emphasize that the integral intensity of the lines corresponding to the optical phonons of the oxide ($V \approx 0.12$ V for Al_2O_3 and $V \approx 80$ mV for SnO_2) is always symmetrical with respect to reversal of the sign of the applied voltage.

We used in the experiments Al— Al_2O_3 —Pb, Sn— SnO_2 —Sn, and Sn— SnO_2 —Pb tunnel junctions containing organic-molecule impurities in the barrier layer. We measured the current-voltage characteristics $I(V)$ as well as their first and second derivatives dV/dI and d^2I/dV^2 as functions of V . Strictly speaking, we usually recorded automatically in the experiment the dependence of the amplitude of the second harmonic of the modulating signal V_2 on the dc voltage V across the

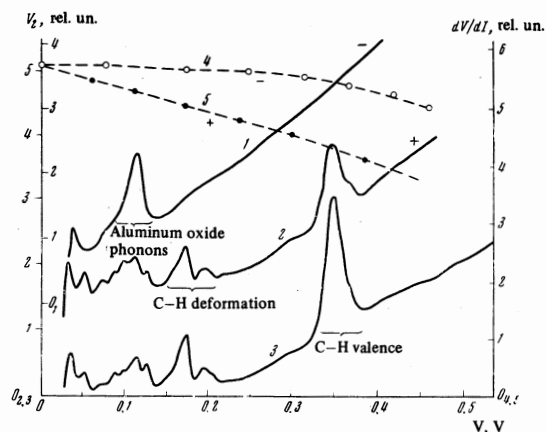


FIG. 1. Tunnel spectra of organic impurities in Al—P6 junctions. 1—“pure” spectrum corresponding to the absence of impurities in the junction, $V_1 \approx 3$ mV; 2, 3—tunnel spectrum of impurity molecules at different polarities of the applied voltage $V_1 = \text{const} = 2$ mV; 4, 5—dependence of dV/dI on V for the same junction. $T = 4.2$ K.

sample. This $V_2(V)$ dependence is connected with the second derivative of the current-voltage characteristic by the following relation:

$$V_2 = \frac{1}{4} \frac{dV}{dI} \frac{d^2I}{dV^2} V_1^2. \quad (1)$$

Consequently, to construct the sought characteristic $d^2I/dV^2 = f(V)$ it is necessary to know the change of the differential resistance of the junction $dV/dI = I/\sigma(V)$ and of the modulating voltage $V_1(V)$ following a change in the dc voltage V across the junction. These characteristics were also registered in the experiment.

The intensity of an inelastic tunnel process, compared with the intensity of elastic tunneling, is characterized by a relative jump of the conductivity $\Delta\sigma/\sigma$ at a voltage V satisfying the equation $eV = \hbar\omega$, where $\hbar\omega$ is the quantum of vibrational energy of the impurity molecule. It is easy to show that the quantity $\Delta\sigma/\sigma$ is connected with the observed characteristics by the following relation:

$$\frac{\Delta\sigma}{\sigma} \approx V \int_{V'}^{V''} \frac{1}{I} \frac{d^2I}{dV^2} dV, \quad (2)$$

where the voltages V' and V'' correspond to the start and end of the vibrational band ($V'' - V' \ll V$), and the integration pertains only to that part of the characteristic which is obtained by subtracting the smooth

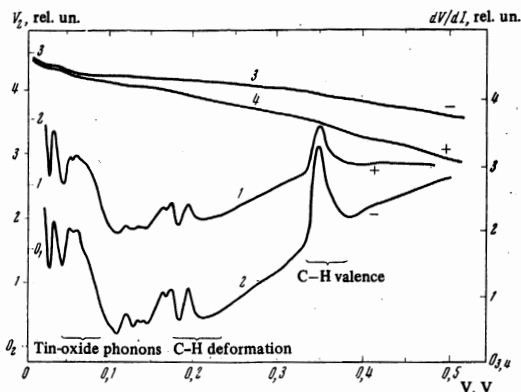


FIG. 2. Tunnel spectra of organic impurities in Sn-Pb junctions (Sn-SnO₂-organic substance-Pb): 1, 2—dependence of $V_2(V)$, $V_1 \approx 3$ mV; 3, 4—dependence of dV/dI on V for the same junction. $T = 4.2$ K.

elastic-tunneling curve $d^2I/dV^2 = f(V)$ from the observed curve. We assume also that V and I are approximately constant within the limits of each vibrational band, and can therefore be taken outside the integral sign. This is all the more correct since we shall be interested in the future only in the ratio of the intensities of the spectral bands at negative and positive polarity of the voltage. The voltages V of the corresponding lines are identical, and the currents I differ quite insignificantly.

Figure 1 shows the tunnel spectra of the impurity molecules in Al-Al₂O₃-Pb junctions (curves 2 and 3), corresponding to different polarities of the voltage V across the junction. The impurity was a small amount of uracil (C₄N₂H₄O₂) placed by vacuum evaporation between the oxide layer and the upper lead electrode. Compared with the tunnel spectrum of pure junctions (curve 1 on Fig. 1) containing no organic impurities, the tunnel spectra of junctions containing impurities reveal new bands, of which the most intense are at $V \approx 0.16-0.2$ V and $V \approx 0.35$ V and correspond to the deformation and valence vibrations of different C-H groups^[1]. The same figure shows the plots of dV/dI against V for both polarities (curves 4 and 5). These are needed to calculate d^2I/dV^2 in accordance with formula (1). The ordinate scale is graduated in relative units, since we are interested in all cases in the ratios of the corresponding quantities for different polarities, and not in their absolute values. It is clear that the graduation of the ordinate scale is the same for curves of the same type but obtained with opposite polarities. It is seen from the plots of dV/dI against V that the transparency of the barrier is larger for positive polarity. Consequently, the barrier itself has a definite asymmetry, which is opposite to the asymmetry of the intensity of the spectral lines and therefore cannot be responsible for the latter.

Analogous curves for the Sn-SnO₂-Pb junction with organic impurities entering the barrier layer during oxidation in unpurified air are shown in Fig. 2. In addition to the fact that the lower electrode and the barrier layer are made from other materials, the difference from Fig. 1 lies in the fact that in this case the modulating voltage was not constant and varied in accordance with the change of the differential resist-

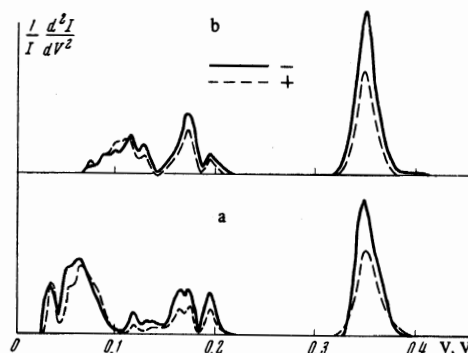


FIG. 3. Plots of $I^{-1}d^2I/dV^2$ against V for inelastic processes calculated from the experimentally obtained relations $V_2(V)$, $I(V)$ and $dV/dI = f(V)$: a—for Sn-Pb junction, $R = 19 \Omega\text{-mm}^2$, $T = 1.5$ K, $V_1 \approx 5$ mV; b—for Al-Pb junction, $R = 30 \Omega\text{-mm}^2$, $T = 4.2$ K, $V_1 = 2$ mV.

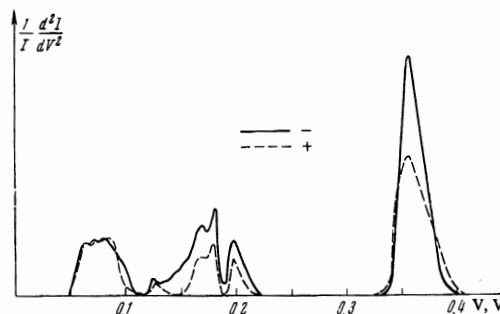


FIG. 4. Anomalous asymmetry of the intensities of the spectral lines for an Sn-Sn junction: $R = 5 \Omega\text{-mm}^2$, $T = 4.2$ K. The ratio $(A^-/A^+)_{\text{val}}$ is smaller than the ratio $(A^-/A^+)_{\text{def}}$ (see the table, sample No. 6).

ance of the sample (curves 3 and 4). Such curves could also be reduced in accordance with formula (1) in order to obtain the sought dependence of d^2I/dV^2 on V .

Figures 3 and 4 show the calculated dependences of the second derivative of the inelastic tunnel current on the voltage across the contact V , multiplied by the coefficient $1/I(V)$. These curves were obtained for experimental plots similar to those shown in Figs. 1 and 2, in accordance with formula (1) and with allowance for the current-voltage characteristic $I(V)$. The background signal due to the smooth part of the plot of d^2I/dV^2 against V was subtracted. In addition, suitable corrections were introduced for the small changes of V_1 and dV/dI in the investigated voltage interval. By the integral intensity of the band A we mean the area bounded by the corresponding line on the $I^{-1}d^2I/dV^2 = f(\pm V)$ curve. In accordance with formula (2), this quantity is proportional to the relative increment $\Delta\sigma/\sigma$ of the tunnel conductivity as a result of the inelastic processes. The latter is proportional to the transparency D of the inelastic tunneling channel, which can be different for different polarities of the applied voltage, as follows from the model described below. Thus, the intensity ratio A^-/A^+ (where A^- is the integral intensity of the lines for the negative voltage V and A^+ is the same for the positive voltage) is equal to the transparency ratio D^-/D^+ , where the sign corresponds, as usual, to the polarity of the lower oxidized film. It is seen from Figs. 3 and 4 and from

N ₀	Sample	T, °K	R, Ω-mm ²	(A ⁻ /A ⁺) _{def}	(A ⁻ /A ⁺) _{val}
1	Sn — Pb	4.2	88	1.1	1.6
2	Al — Pb	4.2	30	1.3	1.7
3	Sn — Pb	1.6	22	1.9	2.0
4	Sn — Pb	1.6	19	1.6	1.7
5	Sn — Sn	1.5	10	1.9	1.4
6	Sn — Sn	4.2	5	2.0	1.5

*Note. The error in the determination of the ratio A⁻/A⁺ is 15%.

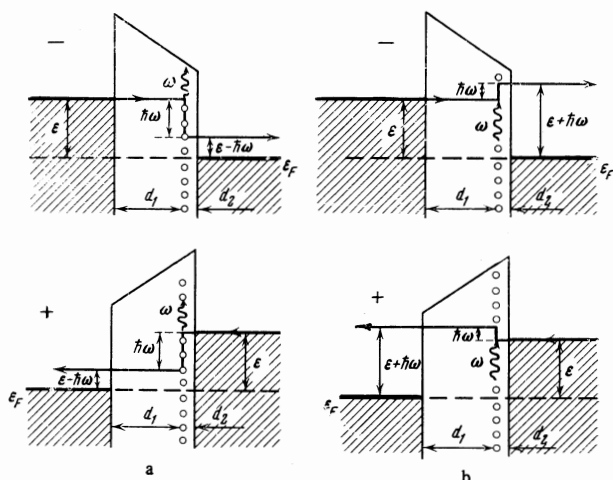


FIG. 5. Energy scheme of elastic tunneling of electrons for different positions of the impurity inside the barrier and for different polarities of the applied voltage.

the table that the asymmetry of the intensities can vary with the resistance of the junction.

Let us examine a simple model explaining qualitatively the observed effect^[2] illustrated in Fig. 5. In the case of inelastic tunneling, the electron gives up its energy to the molecular excitation after interacting with the molecule (Fig. 5a). The electron energy is thus lowered by an amount on the order of several tenths of an electron volt, i.e., several tenths of the height of the barrier, and it is natural that the probability that the electron will traverse the remaining part of the barrier depends strongly on the width of the latter. Thus, if the electron collides with a molecule at the end of its path, then the probability of observing it on the other side of the barrier will be much larger than in the case of collision with a molecule at the beginning of the path. Consequently, the tunnel processes shown on the upper part of Fig. 5a will have preference over the processes shown on the lower figure, and the intensities of the tunnel spectra will be larger at negative polarity of the lower oxidized film. The higher the excitation frequency ω (and the junction voltage $V = \hbar\omega/e$ corresponding to it) the larger should be the asymmetry, as is indeed observed qualitatively for high-resistance junctions (see Fig. 3 and the table). Quantitatively, however, the growth of the asymmetry of the intensity with increasing frequency ω should be much larger. If we assume that the impurities are located strictly on the boundary between the oxide and the upper film, then a simple calculation yields for the ratio A⁻/A⁺.

$$\frac{A^-}{A^+} = \exp \left[\frac{2}{\hbar} \sqrt{2md} \left(\sqrt{U_0 + \frac{\hbar\omega}{2}} - \sqrt{U_0 - \frac{\hbar\omega}{2}} \right) \right], \quad (3)$$

where $\hbar\omega$ is the excitation energy, U_0 is the height of the barrier, and d is its width. Substituting the corresponding values for an SnO₂ barrier^[3], namely $U_0 = 1.75$ eV, $d = 13$ Å, $\hbar\omega_{\text{def}} = 0.17$ for deformation vibrations of the C—H bond and $\hbar\omega_{\text{val}} = 0.36$ for the valence vibrations, we obtain $(A^-/A^+)_{\text{def}} = 2.4$ and $(A^-/A^+)_{\text{val}} = 6.4$. The smaller value of the asymmetry observed in the experiment can be attributed to the fact that the impurities produce a layer of finite thickness inside the barrier.

We call attention also to the fact that with further decrease of the sample resistance the asymmetry of the intensities for ω_{def} becomes larger than for ω_{val} (Fig. 4 and the table). The point is that the explanation presented above for the asymmetry of the integral intensities of the spectral lines is correct only if the average number of excitations of the molecule, N , is equal to zero and only processes with production of excitations inside the barrier are possible. On the other hand, if $N \neq 0$, then inelastic tunnel processes wherein the electron absorbs the energy of the molecular excitation become possible (Fig. 5b). It is seen from this figure that the probability of such inelastic processes will be larger for electrons that acquire additional energy at the start of their path inside the barrier. Recognizing that the inverse inelastic tunnel current is negligibly small even when N differs from zero, we obtain

$$D_{\text{abs}}^- = QN \exp \{ d_2 \omega \sqrt{2m} / (U_0 - \omega) \}, \quad (4)$$

$$D_{\text{rad}}^- = Q(N+1) \exp \{ -d_2 \omega \sqrt{2m} / (U_0 - \omega) \},$$

$$D_{\text{abs}}^+ = QN \exp \{ d_1 \omega \sqrt{2m} / (U_0 - \omega) \},$$

$$D_{\text{rad}}^+ = Q(N+1) \exp \{ -d_1 \omega \sqrt{2m} / (U_0 - \omega) \},$$

$$\omega / (U_0 - e) \ll 1.$$

Here $Q = D_0 m U_1^2 / 4U_0$, D_0 corresponds to the transparency of the barrier for the elastic tunneling channel, d_1 is the distance from the lower film to the molecular inclusions, d_2 is the distance from the upper film to the molecules, $d = d_1 + d_2$, m is the electron mass, U_1 is the energy of the interaction between the tunneling electron and the molecule, and ϵ is the electron energy reckoned from the Fermi level. The sought intensity ratio A⁻/A⁺ is equal to

$$A^-/A^+ = D^-/D^+ = (D_{\text{abs}}^- + D_{\text{rad}}^-) / (D_{\text{abs}}^+ + D_{\text{rad}}^+).$$

At temperatures $T = 1.5-4.2^\circ\text{K}$ ($kT = 0.1-0.4$ mV) the equilibrium number N of the molecular excitations differs from zero only if the relaxation processes are slowed down, namely, if the average lifetime τ of the molecular excitation is larger than or equal to the mean time τ_{em} between the successive inelastic collisions of two electrons with the molecule. On the other hand, if $\tau \ll \tau_{\text{em}}$, then $N = 0$ and the value of the ratio D^-/D^+ is determined entirely by processes in which molecular excitations are produced.

The case $\tau \gtrsim \tau_{\text{em}}$ is much more complicated. It is necessary to take into account here the dynamics of the creation and annihilation of the excitations in the barrier, and there always exists a certain distribution of N about its equilibrium value. It should also be noted that τ and τ_{em} depend strongly on the frequency of the

molecular excitation ω (τ and τ_{em} decrease with increasing ω), on the current flowing through the sample at a given fixed voltage corresponding to a definite molecular excitation (and consequently also on the resistance R of the sample), and on the temperature T . According to our estimates, and according to estimates by others^[4], the lifetimes of the vibrational, vibrational-rotational, and rotational molecule energy levels excited by the electrons can be quite large, up to several seconds. This is due to the fact that the frequencies corresponding to these levels are low, and the probability of photon emission is $\sim \omega^2/c^3$, i.e., $\tau \sim c^3/\omega^3$. In our case the energy difference between neighboring vibrational levels (as well as between vibrational-rotational levels) amounts to $\hbar\omega \approx 100$ – 300 MeV, and for rotational levels $\hbar\omega \approx 1$ – 10 meV. Therefore $\tau = 10^{-3}$ – 1 sec for vibrational and vibrational-rotational levels. The probability of transition of the molecule into the unexcited state by emission of phonons is also small, since this process should be of the multiphonon type for vibrational and vibrational-rotational levels, and is forbidden for rotational levels, since the phonons have zero angular momentum.

Let us estimate τ_{em} for our samples. The resistance R ranges from 5 to 100 Ω/mm^2 (see the table). At $V = 100$ – 500 mV applied to the sample, the tunnel current through the sample is $I = 100$ – 1 mA/ $\text{mm}^2 = 10^{16}$ – 10^{18} electrons/ mm^2 . Out of these electrons, only 1% are effective, i.e., only 10^{14} – 10^{16} electrons collide inelastically with the molecule. If the density of the C–H groups is of the order of 10^{13} groups/ mm^2 ,

then $\tau_{em} = 10^{-1}$ – 10^{-3} sec. We see thus that the case when $\tau \sim \tau_{em}$ is quite probable. From a comparison of the results of the theoretical estimates and the experimental data for low-resistance contacts, listed in the table, it follows that $N = 1$ for at least the valence vibrations of the C–H bond.

In conclusion, we note that it would be quite interesting to perform an experiment in which the position of the impurity inside the barrier would vary in a specified manner; such an experiment would, however, be quite difficult. It is more realistic to investigate junctions with different relative thicknesses of the layers d_1 and d_2 . Part of the barrier would consist of an oxide of thickness d_1 , and the other part would be a layer of impurity molecules of thickness d_2 . The conclusions of the present paper are applicable to such a structure, too.

We are deeply grateful to I. O. Kulik for useful discussions of certain theoretical questions.

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