Tunnel spectra of organic solvents

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A new method is developed for artificially introducing organic impurity molecules into a tunnel junction. The impurities are introduced from the solution into the cooled lower metal film, followed by lyophilic drying in vacuum. This method is suitable for the investigation of many organic molecules (particularly biopolymers), since it ensures continuity of the chemical bonds and prevents formation of agglomerates on the surface of the lower metallic film. This method was used to produce and investigate the tunnel spectra of organic spectrum in one of the DNA bases, namely adenine.

1. PROCEDURE FOR PREPARATION OF SAMPLES WITH ARTIFICIALLY INTRODUCED IMPURITIES

All the investigated tunnel samples were prepared with a lead film as a base. It was shown earlier [1] that tunnel junctions with a lead-film base, unlike junctions with aluminum or tin bases [1,2], do not exhibit the spectra of the impurity organic molecules adsorbed on the surface of the Al_2O_3 and SnO_2 films as they become oxidized in atmospheric air; the absence of the spectra was attributed to the poor adsorptivity of the lead oxide. This was precisely the reason why lead was chosen as the base film in our investigations. Observation of the tunnel spectra of artificially introduced impurities on Pb-PbO-impurity-Pb junctions has confirmed this assumption.

The main experimental difficulties in the development of a procedure for artificially introducing impurities inside the barrier are the following. First, the organic impurities must be introduced from a solution, which at room temperature is a liquid, inasmuch as other methods of introducing the organic molecules into the barrier, for example, deposition of a small amount of matter by vaporization in vacuum, frequently lead to a change in its structure, to decomposition, etc. Second, it is necessary to introduce a very small amount of the investigated substance (on the order of a monatomic layer) in order not to increase the barrier thickness greatly—meaning by more than 10–20 Å—since the tunnel current decreases exponentially with increasing barrier thickness. Thus, the materials suitable for the research are either substances with high volatility (for example, organic solvents), or low-concentration solutions (1–10 μg/ml) of the investigated substances in volatile organic solvents.

The lower and upper films of the metal (Pb) were evaporated as is customary in the preparation of tunnel junctions [3], and the lower film was oxidized 15–30 minutes in air. The prior oxidation of the lower lead film (prior to the introduction of the impurity) served to produce a solid dielectric layer, since the impurities are capable of forming a friable discontinuous layer on the surface of the metal. A drop of solution is then placed on this film, which is cooled to 180–250°K (the substrate is cooled to slow down the diffusion of the atoms over the lower film, and in many cases to prevent chemical interaction between the investigated impurity and the metallic film). To prevent moisture from settling, the impurity is introduced in an atmosphere of nitrogen gas. The solution (which usually solidifies on the substrate at the deposition temperature), is then dried at the same temperature in a vacuum ~10^{-6} Torr for 1–2 hours. The oxidized lower film with the small amount of investigated substance remaining on it is now covered with the upper metal film to form a sandwich whose filling is the oxide and the molecules of the investigated substance. It should be noted that each substance requires its own procedure of introduction into the tunnel barrier (especially, the substrate temperature and the drying time in the vacuum), and interacts in its own fashion with the lead oxide.

No tunnel junction could be produced by introducing water, heavy water, or chloroform ($CHCl_3$) into the tunnel barrier, and the samples were short-circuited over their entire area. The following solvents could be introduced into the junction and their tunnel spectra investigated: ethyl alcohol C_2H_5OH, benzene C_6H_6, carbon tetrachloride CCl_4, and acetone $(CH_3)_2CO$. It is interesting to note that Jaklevic and Lambe [2] were unable to obtain the tunnel spectra of C_6H_6 and $(CH_3)_2CO$. Obviously, these molecules are not adsorbed by the lower metallic aluminum film at room temperature. On the other hand, the tunnel spectra of C_2H_5OH obtained in [2] appear to have been strongly distorted by organic contaminants which are always present in Al-Al_1O_3-Pb samples. Of all the nucleic-acid bases introduced into the tunnel junction from solution in ethyl alcohol (adenine, guanine, thymine, uracil, and cytosine), we were able to obtain only the tunnel spectrum of adenine.

It should be noted that the method we used to introduce the impurities leads in some cases (benzene, adenine) to a definite orientation of the impurity molecules relative to the substrate. To determine the orientation of the plane of the benzene molecule relative to the metal-dielectric boundary in the tunnel junction, electron diffraction patterns were obtained of thin benzene films prepared by the method described above, but using an amorphous graphite film as the substrate instead of an oxidized metal film. It turned out that the benzene films are polycrystalline (it is interesting that benzene deposited on a cold substrate remains in the crystalline state when heated to room temperature, without melting). The dimensions of the crystallites were ~10^{-8} cm^2, and on large areas the films had a clearly pronounced texture. On 85% of the total film area and on 100% of the area of its thin spots the predominant texture corresponds to parallel orientation of the (101) plane to the surface of the lower film. Two-thirds of the total number of molecules are then parallel to the plane of the lower film, and only one-third are perpendicular.

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Generally speaking, the tunneling proceeds through such thin regions that one can no longer speak of a benzene-crystal lattice, inasmuch as benzene crystallizes in an orthorhombic pseudo-face-centered lattice with rather large cell parameters (a = 7.46 Å, b = 9.67 Å, c = 7.63 Å [4]), and an increase of the thickness of the potential barrier by only 5–10 Å increases the resistance by a factor 10^3–10^6. Thus, no more than one or two monolayers of benzene molecules lie in the path of the tunneling electron. The distance between the planes of the benzene molecules parallel to the substrate plane in the [101] direction is approximately 2.6 Å, while the dimensions of the molecule in the plane are equal to 5 Å. Thus, the tunnel current always flows predominantly through those spots in which the plane of the C_6H_6 molecule is parallel to the plane of the lower film, i.e., to the metal-dielectric boundary.

Electron microscopy of thin films of adenine has shown that the film has a fine-grained structure, with average grain dimensions from 50 to 700 Å. In addition, the film is single-crystal on an area 10^{-8} cm^2, although on the whole it is polycrystalline and, unlike the benzene film, has no definite texture.

2. EXPERIMENTAL RESULTS

As usual, we investigated the tunnel spectra in the experiment, i.e., the dependences of the second derivative d^2J/dV^2 of the tunnel current with respect to the voltage on the voltage V, and also the first derivatives dJ/dV and the current-voltage characteristics J(V) [5]. It should be noted that the tunnel behavior of the investigated samples with the impurities, the resistivity of which reached 100 kΩ/mm^2 in some cases, was verified most carefully. First, the quality criterion was the presence of a superconducting gap $2\Delta = 2.65$ meV and of the known spectra of the optical phonons [6,7] of lead oxide. Second, the subsequent behavior of the current-voltage characteristic should satisfy the relation [6]

$$J=\alpha(V+\gamma V^3) \tag{1}$$

at voltages $\varphi/e \gg V > 2\Delta/e$ on the sample, and third, at $V > \varphi/e$ the current-voltage characteristic should satisfy the Fowler-Nordheim law [8]:

$$\ln(J/V^2)=A+B\varphi d/eV, \tag{2}$$

where V is the voltage applied to the junction, J is the tunnel current, e is the electron charge, d is the width of the energy barrier, φ is its height, and α, γ, A, and B are constants. We investigated samples for which either all three conditions or the first two conditions were satisfied (for those samples that did not withstand high voltages).

Figure 1 shows the tunnel spectrum of ethyl alcohol, obtained by us with the Pb–PbO–C_2H_5OH–Pb sample; for comparison it also shows the spectra of Pb–PbO–Pb, and also the spectra of Al–Al_2O_3-adsorbed C_2H_5OH–Pb and Al–Al_2O_3–Pb from [2].

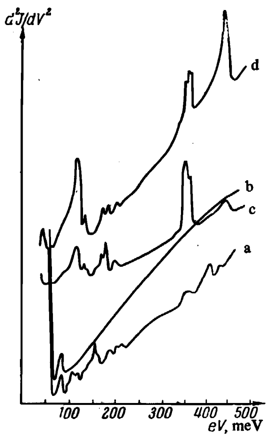

FIG. 1

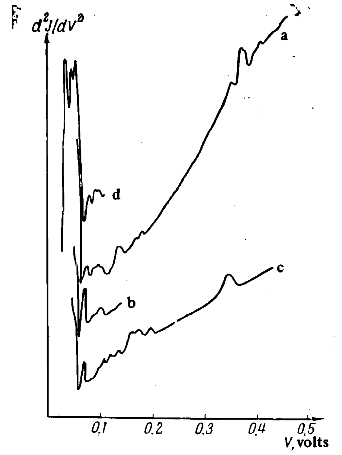

FIG. 2

FIG. 1. Tunnel spectra of ethyl alcohol: a–tunnel spectrum of C_2H_5OH in a Pb – PbO – C_2H_5OH – Pb, sample, V_1 = 5 mV; b–tunnel spectrum of Pb–PbO–Pb sample (the PbO was obtained by oxidation in atmospheric air), V_1 = 5 mV; c–tunnel spectrum of Al–Al_2O_3–Pb (the Al_2O_3 was obtained by oxidation in atmospheric air) [2]; d–tunnel spectrum of C_2H_5OH adsorbed on an Al_2O_3 film (sample Al–Al_2O_3–C_2H_5OH–Pb).

FIG. 2. Tunnel spectra of benzene, carbon tetrachloride, acetone, and adenine: a–benzene, V_1 = 3 mV; b–carbon tetrachloride, V_1 = 1.5 mV; c–acetone, V_1 = 3 mV; d–adenine, V_1 = 2.5 mV.

The tunnel spectra of benzene, carbon tetrachloride, and acetone, obtained for the first time in this study, are shown in Fig. 2. The spectra of C_2H_5OH were obtained for six samples of Pb–PbO–C_2H_5OH–Pb, those for C_6H_6 were obtained for three samples of Pb–PbO–C_6H_6–Pb, those for CCl_4 were obtained for one sample of Pb–PbO–CCl_4–Pb and those for $(CH_3)_2CO$ were obtained for three samples of Pb–PbO–$(CH_3)_2CO$–Pb. It should be noted that it is very difficult to obtain tunnel samples of sufficiently high resistivity with CCl_4, since it appears that the CCl_4 molecule is very easily evaporated from the PbO surface. It is seen from the figure that the presence of absorption bands of impurity molecules on Pb–PbO–impurity–Pb junctions can be reliably determined only at energies eV > 60 meV, inasmuch as this region contains only one optical-phonon absorption peak of lead oxide at eV = 70 meV, and it is of very low intensity [9]. It should also be noted that PbO has a relatively low effective-barrier height, $\bar{\varphi} = 1.3$–1.4 eV [7] as compared with the oxides of other metals, such as SnO_2 ($\bar{\varphi} \approx 1.8$–$2.0$ eV) [7], InO ($\bar{\varphi} \approx 1.9$ eV) [7], and Al_2O_3 ($\bar{\varphi} = 1.95$ eV) [6], and therefore in the voltage region up to 500 mV the current-voltage characteristics of the Pb–PbO–Pb junctions already have considerable nonlinearity, and consequently a relatively large background (smooth part) in the plot of d^2J/dV^2 vs. V. In many cases this limits the modulation amplitude V_1 and makes it impossible to investigate the intensities of the absorption lines in detail. All that can be determined are the positions of these lines; in some cases it is necessary for this purpose to subtract the background.

3. DISCUSSION OF EXPERIMENTAL RESULTS

As is well known [2], inelastic tunneling with different interaction mechanisms between the tunneling electrons and impurity molecules is described by the same matrix elements as infrared (IR) absorption and Raman scattering (RS) of light. The obtained tunnel spectra must therefore be compared with the IR and RS spectra of the same substances. It should be noted, however, that all the tunnel spectra were obtained at helium temperatures 1.5–4.2°K, whereas the IR and RS spectra used for the comparison are usually obtained at room temperature (we found in the literature only the IR spectrum of benzene at 170°K) [10]. The influence of the temperature on the spectrum is appreciable: when the temperature is lowered, some lines shift towards lower energies, and others vanish completely or are split into several lines; all this leads to certain difficulties when the tunnel, IR, and RS spectra are compared.

A comparison of the tunnel spectra of the organic solvents with the IR and RS spectra of the same substances [10-16] is shown in Fig. 3 together with the previously obtained [2] spectrum of ethyl alcohol (the height of the line in the RS spectrum corresponds, as usual, to the line intensity, while the thickness corresponds to its width). As seen from the figure, the agreement of the tunnel spectrum obtained with Pb–PbO–C_2H_5OH–Pb samples with the IR and RS spectra of C_2H_5OH is much better than for the Al–Al_2O_3–adsorbed C_2H_5OH–Pb sample [2]. In addition, generally speaking, the spectrum of the ethyl alcohol adsorbed on the Al_2O_3 surface [2] differs little from the spectrum of the air adsorbed from the room on the Al_2O_3 (Fig. 1, curves c and d), and nothing can be said concerning this spectrum in the region of the strong intrinsic absorption bands, which are always present in Al–Al_2O_3–Pb samples at energies 60 meV < eV < 150 meV and 410 meV < eV < 460 meV. It is possible that the strong absorption lines of ethyl alcohol, which are located near eV values 110, 135, 215, and 415 meV, are not observed in the Al–Al_2O_3–C_2H_5OH–Pb samples because of the presence of strong intrinsic absorption bands, and possibly also because reactions can occur on the Al_2O_3 surface, which serves as a catalyst, and the spectrum observed by Jaklevic and Lambe [2] may be the product of such a reaction.

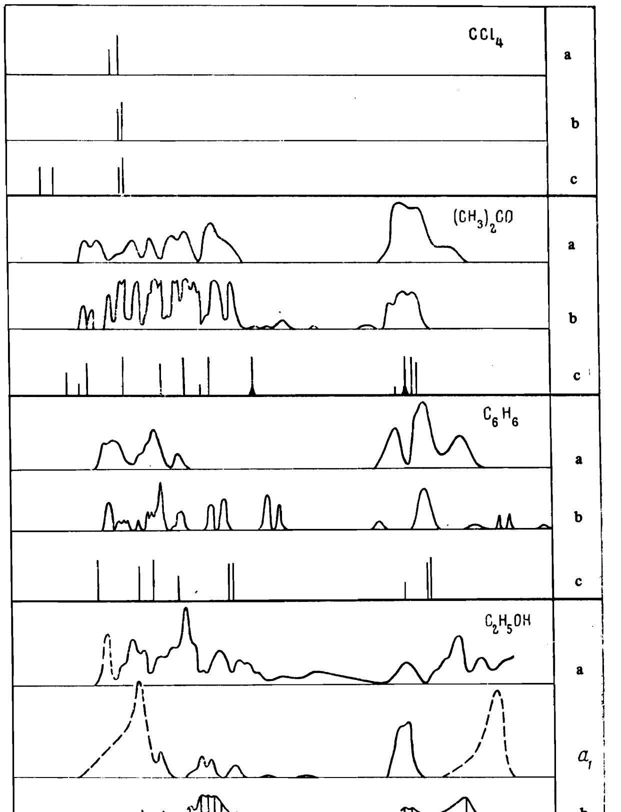

FIG. 3. Comparison of tunnel spectra of organic solvents with the infrared absorption spectra and with Raman-scattering spectra: a–tunnel spectra, b–IR absorption spectra; c–RS spectra; a_1–tunnel spectrum of ethyl alcohol as obtained in [2].

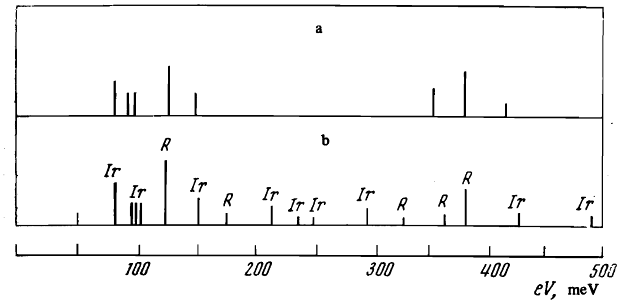

FIG. 4. Comparison of theoretically expected absorption bands in the tunnel spectrum [17] (a) for the benzene-molecule planes oriented parallel to the metal-dielectric boundary, with the experimentally observed tunnel spectrum (b). Each frequency in Fig. b is marked by the spectrum in which it is active, IR (IR) or RS (R).

It also follows from Fig. 3 that the tunnel spectra of all the investigated organic solvents agree satisfactorily with their IR and RS spectra. Only in the case of benzene is there an appreciable discrepancy: the strong absorption lines in the energy region eV = 180–200 meV, which are present in the IR spectra, are almost entirely missing from the tunnel spectrum. It appears that we were able to observe for the first time the difference between the selection rules of IR, RS, and tunnel spectroscopy, with the benzene molecule oriented in a definite fashion inside the tunnel barrier (see [11]) and having a high degree of symmetry (sixfold axis) as an example.

The tunnel-spectroscopy selection rules for highly symmetrical molecules of benzene, carbon tetrachloride, and acetone oriented in a barrier were considered by one of the authors [17]. Figure 4 shows a comparison of the calculated active frequencies of C_6H_6 for parallel orientation of the C_6H_6 planes and of the barrier with the experimentally observed tunnel spectrum; the agreement is satisfactory (the low-intensity bands of the tunnel spectrum in the energy region 200 meV < eV < 300 meV are not shown in Fig. 4a). On the other hand, the acetone and carbon tetrachloride molecules are arbitrarily oriented in the interior of the barrier, and their tunnel spectrum contains frequencies that are active both in the IR and in the RS spectra.

Of all the nucleic-acid bases–adenine, guanine, thymine, cytosine, and uracil–introduced into a tunnel junction from a solution in ethyl alcohol (the solution concentration was 1–10 μg/ml), only the samples with adenine yielded a tunnel spectrum (Fig. 2), and then only in the energy range 60 meV < eV < 120 meV. In all other cases, in spite of the good quality of the tunnel samples, oscillations analogous to those observed earlier [18] were observed in the $d^2J(V)/dV^2$ plots, and their nature has not yet been explained.

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