Franz-Keldysh effect in laser-stimulated field desorption of thin molecular layers

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An experimental study of laser-stimulated single-photon field desorption is reported. The desorption spectrum is described on the basis of the Franz-Keldysh effect. The corresponding shift of the photoconduction boundary in an amorphous layer of anthracene is 1.1 ± 0.1 eV at an electric field of 4×10^7 V/cm in a vacuum.

1. Tunneling processes in solids are attracting considerable interest. For applications involving molecular condensed media, the best-developed method is the tunneling-spectroscopy method based on the use of metal-insulator-metal structures.[1] A promising method for studying tunneling processes in atomic and molecular insulating layers is the method of field desorption.[2,3] The tunnel structure in this case is a thin insulating layer deposited in a vacuum on the sharp point of a metal emitter (W, Pt, Ir, etc.). This letter is the first report of a manifestation of the Franz-Keldysh effect in a single-photon laser-stimulated field desorption of thin molecular layers.

2. The experimental apparatus consists of a field-ion microscope[2] with provision for introducing a laser beam. Studies of the laser stimulation of field desorption were carried out with molecular layers of anthracene deposited on a tungsten needle at room temperature. We used the beams from pulsed excimer lasers and dye lasers.

Figure 1 shows the experimental results on the total number (N) of molecular anthracene ions desorbed from the sharp point as a result of irradiation by a pulse from an XeCl excimer laser ($\lambda = 308$ nm) versus (a) the energy fluence of the laser beam, Φ, and (b) the thickness of the adsorbed anthracene layer, Δ. The field at the sharp point in a vacuum was 4×10^7 V/cm. Similar linear results were observed over a broad range of the field at the sharp point, at various laser wavelengths.

As the wavelength of the light decreases, we observe a monotonic increase in the efficiency of the laser stimulation, γ. In the experiments we measured the stimulation efficiency with respect to that at a 308-nm wavelength ($\hbar\omega = 4$ eV): $\gamma = (N/N_{308}) \cdot (\Phi_{308}/\Phi)$. Figure 2 shows γ as a function of the energy of the laser photon for several excimer and dye lasers, measured with a field of 4×10^7 V/cm at the sharp point. The marks on the energy scale at the top show the energy of the low-lying singlet state, ϵ_{S_1}; the boundary of the conduction band, ϵ_G; the ionization potential I_c (all for crystalline anthracene[4]); and the difference between the ionization potential I_c and the work function of tungsten, ϕ.

The results found for the observed laser-stimulated field desorption can be summarized as follows: 1) a linear dependence on the energy fluence, which indicates the presence of a single-photon mechanism; 2) a linear dependence on the thickness of the adsorbed layer, which indicates that the stimulation involves a process that occurs in

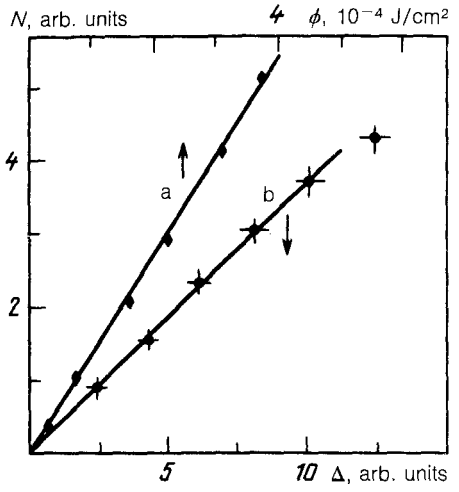

FIG. 1. The signal representing the laser-stimulated field desorption versus (a, ♦) the laser energy fluence and (b, ●) the thickness of the adsorbed anthracene layer.

the interior of the layer; 3) the occurrence of the effect below the red absorption boundary of crystalline anthracene in the absence of a field (and, especially below the conduction band); and 4) a monotonic increase in the stimulation efficiency with increasing photon energy.

3. The laser stimulation of the field desorption apparently results from an ionization of a molecular layer in an electric field, accompanied by the absorption of a photon. Some possible elementary processes are (a) photoionization, (b) photogeneration of electron-hole pairs in the emitter material, followed by the tunneling of an electron from the molecular layer to a vacant level in the metal, (c) a resonant absorption of a photon in the layer, followed by a tunneling ionization of an exciton, and (d) a tunneling accompanied by the absorption of a photon (the Franz-Keldysh effect). The experimental results listed above can be clearly described at a qualitative level in terms of a Franz-Keldysh effect.

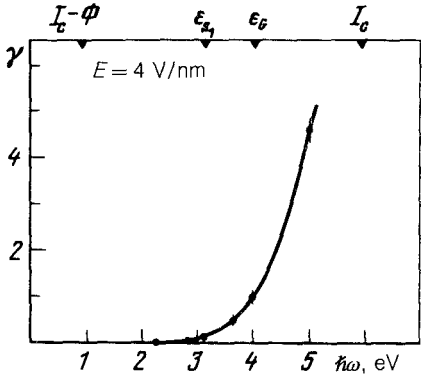

FIG. 2. Efficiency of the laser-stimulated field desorption as a function of the photon energy.

The Franz-Keldysh effect consists of a shift of the boundary of the intrinsic optical absorption in a semiconductor or insulator in the presence of an external electric field.[5,6] In the fields of 10^7–10^8 V/cm in the present experiments, significant shifts of the photoconductivity boundary should be observed.

The Franz-Keldysh effect leads to a spectrum

$$\alpha(\omega) \propto \exp\left\{-\left(\frac{\epsilon_0 - \hbar\omega}{\Delta\epsilon}\right)^{3/2}\right\}, \tag{1}$$

$$\Delta\epsilon = \left(\frac{9e^2E^2\hbar^2}{32\mu}\right)^{1/3} = 1,29\,E^{2/3}\,\mu^{-1/3}, \tag{2}$$

where ϵ_0 is the distance between the bands which are coupled by a tunneling transition with the absorption of a photon of energy $\hbar\Omega$, $\mu^{-1} = m_e^{-1} + m_h^{-1}$ is the reduced mass of the electron and hole, and E is the electric field in the insulating layer. In the last expression, $\Delta\epsilon$ is expressed in electron volts, the field E in units of 10^8 V/cm = 1 V/Å, and μ in units of the mass of a free electron. A fit of the experimental data on the spectrum of the laser-stimulation efficiency by expression (1) yields $\epsilon_0 = 5.9 \pm 0.5$ eV and $\Delta\epsilon = 1.1 \pm 0.1$ eV. A corresponding curve is shown in Fig. 2.

The value of ϵ_0 is the same as the ionization potential of the anthracene crystal, and it does not agree with the band gap $\epsilon_G = 4$ eV. These results seem quite natural: Even in an ideal anthracene crystal the bands of excited electron states, including the conduction bands, have a small width, about 0.1 eV, and the corresponding effective masses of the electrons and holes are 5–20 times the mass of a free electron.[4] A thin layer of anthracene on tungsten is apparently amorphous; correspondingly, the levels of the individual molecules are distributed at random along a width on the order of 0.1 eV, and the electrons and holes are localized. Under these conditions a tunneling accompanied by the absorption of a photon occurs effectively to states corresponding to the ionization of the anthracene layer. The ionization energy of an amorphous layer is roughly equal to the ionization energy of a crystal.

Most of the uncertainty in the estimates of $\Delta\epsilon$ stems from the absence of data on the internal electric field. There are indications that the dielectric constant K is close to unity in such fields. If we set $\mu = 1$ and $K = 1$ for estimates, we find $\Delta\epsilon = 0.7$ eV. The value found experimentally, $\Delta\epsilon = 1.1$ eV, thus seems quite reasonable.

The observation of a laser-stimulated single-photon field desorption of molecular ions raises the possibility of the development of a laser photoion microscope.[7]

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