

Laser-Stimulated Field Desorption of Molecular Ions from a Tungsten Emitter

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Abstract. We report here on an experimental observation of photon-stimulated field emission of molecular anthracene ions from the surface of a layer adsorbed on a tungsten field-emitter tip. When the tip is irradiated with laser pulses 249, 308, and 400 nm in wavelength falling within the absorption bands of anthracene, the stimulated ion signal is proportional to the pulse fluence. The efficiency of the process decreases with the increasing laser wavelength. Photon stimulation is believed to be due to the resonance excitation of the anthracene molecules, followed by the field ionization of the excited molecules.

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Electrostatic fields with strength as high as 10^7 V/cm are observed to give rise to field desorption of ions of molecules adsorbed on metal surfaces. The process can be stimulated if the field emitter is irradiated with light. The stimulation of field desorption is, in most cases, due to the radiation heating of the surface [1, 2]. That the quantum stimulation of the process is possible was indicated by the results of [3] in which the flux of molecular ions from a silver surface was observed to increase under the effect of a nonresonant laser radiation, the increase being proportional to the photon flux in the laser pulse. In the works reported in [4, 5], subject to investigation for the first time was the possibility of stimulating field desorption by resonant photoexcitation and ionization of the adspecies. They observed experimentally two-photon stimulation of the field desorption of molecular tetracene ions by KrF laser radiation.

This paper reports on the observation of laser stimulation of the field desorption of molecular anthracene ions from the surface of a molecular layer adsorbed on a tungsten tip under the effect of one-photon excitation, and analyzes the possible mechanisms responsible for this phenomenon. It appears to hold much promise for laser field-ion biomolecular microscopy.

1. Experimental

The experimental setup (Fig. 1) is a field-ion microscope equipped with quartz windows to let laser radiation in and out. The electric fields 10^7 to 10^8 V/cm in strength necessary to observe field desorption were produced on the apex of a tungsten tip with a radius from a few hundred to a few thousand Å. The tips used in our experiments were prepared by the standard electrochemical polishing technique, and cleaned from surface impurities prior to the experiment through controlled field evaporation of the tip material at field strength around 6 V/Å. The surface morphology was monitored on an atomic-scale resolution by helium field-ion imaging at a pressure of 10^{-5} Torr. The absolute field strength at the tip surface and the tip radius were found accurate to within 15%–20% from the best image voltage (BIV). Measured to the same degree of accuracy best image field for tungsten $E_{\text{BIV He}} = 4.5$ V/Å and $E_{\text{BIV Ar}} = 2.2$ V/Å [6].

The residual gas pressure in the chamber did not exceed 10^{-8} Torr. Anthracene molecules were adsorbed on the tungsten tip surface from the gas phase at a partial vapor pressure of 10^{-7} Torr. At field strengths below 0.7 V/Å used to observe the field desorption of anthracene, the field-desorption signal was easy to

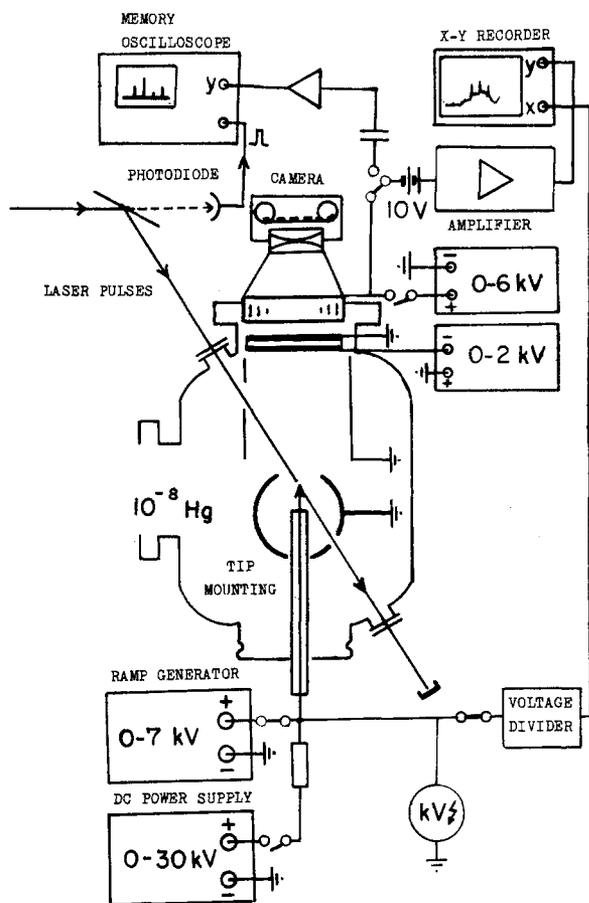


Fig. 1. Experimental setup

separate from the background noise due to field ionization and photoionization in the gas phase.

Photostimulated processes were studied using pulsed excimer and dye lasers with a fluence of 10^{-5} to 10^{-1} J/cm². Laser radiation was directed through an 1 mm (diam) aperture on to the tip at an angle of 25° to its axis via one of the quartz windows and then let out of the chamber via the other window.

The ions produced were registered by means of two microchannel plates (MCP) in a chevron arrangement and a phosphor screen. The distance between the apex of the tip and the front edge of MCP was $l = 6$ cm. The time of flight of the anthracene ions, $t = l(2Ue/m)^{-1/2}$, varied over the range of 0.5 to 2 μ s, depending on the tip voltage U , and considerably exceeded the characteristic laser pulse duration of 20 ns. This made it possible to carry out the time-of-flight mass separation of the ions. The time-of-flight was measured from the leading edge of the laser pulse. The accuracy of measurement was determined by the instrumental response function and amounted to 0.1 μ s, and so the accuracy of determining the mass of ions was $\pm 10\%$.

All the experimental results presented below were obtained at a field-emitter temperature of $T = 295 \pm 2$ K.

2. Experimental Results

When studying ordinary field desorption, the total ion current from the specimen was monitored as a function of applied voltage while raising the voltage in a linear fashion (like in [7]). Figure 2 presents ion current curves obtained using a tip with $U_{\text{BIVHe}} = 14.5$ kV and the respective apex radius $R = U_{\text{BIVHe}} / (5 \cdot E_{\text{BIVHe}}) = 644$ Å. The voltage ramp rate was equal to 50 V/s, and the respective ramp rate of the field strength on the tip apex was $dE/dt = (4.5/U_{\text{BIVHe}})(dU/dt) = 0.016$ V/(Å · s). The curve (a) was obtained after a 10-min exposure of the tip to anthracene vapor at a zero tip potential. The field strength was in this case increased to 1.25 V/Å. The curve (b) was obtained immediately after the curve (a), without any additional exposure of the tip to anthracene vapor. When anthracene was pumped out of the system, there was practically no ion signal in this range of the field strengths. It is clear from a comparison between these curves that the wide peak of the curve (a) is due to field desorption of anthracene molecules, the signal at field strengths in excess of 0.6 V/Å being related to the field ionization in the gas phase.

We revealed an important feature in the behavior of the ion signal, namely, the fact that the average ion current at a given field strength is independent of the tip-voltage scan rate (the scan rate being varied over the range 0 to 150 V/s). When the field strength was fixed at an arbitrary value, the average ion current remained unchanged during times substantially longer than the scanning time. This suggests an important role of the migration of anthracene molecules from the shank to the apex of the tip.

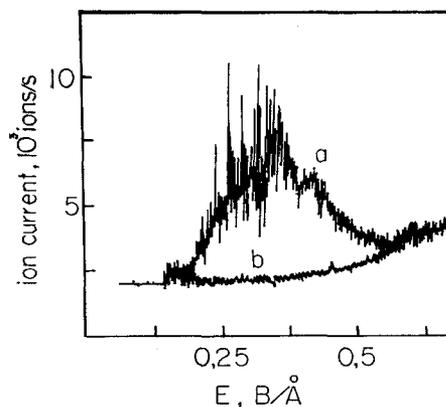


Fig. 2. Ion current as a function of the field strength at the tip, the field strength being increased in a linear fashion

In studying laser-stimulated field desorption, qualitatively similar results were obtained with tips differing in the apex radius ($R=500$ to 1000 Å) and at different field strengths at the tip. The results given below were obtained using a field-emitter tip with $U_{BIVAF}=17.6$ kV and the respective apex radius 1600 Å. The tip voltage equal to 2.9 kV corresponded to a field strength of 0.36 V/Å at the tip, which is close to the maximum ion signal in the case of ordinary field desorption.

Irradiating the tip with laser pulses at $\lambda=308$ nm (XeCl excimer laser), 249 nm (KrF excimer laser), and 394 – 412 nm (dye laser) was observed to give rise to a pulsed ion signal up to 5×10^2 ions/pulse. On an oscilloscope screen this took the form of a signal with an amplitude of a few hundred ions whose the time-of-flight corresponded to within 10% to the mass of anthracene, which appeared against a background of random single-ion signals recurring on the average at 0.1 to 1 ms intervals. In the laser fluence range 10^{-5} to 10^{-3} J/cm² (or intensity range 10^3 to 10^5 W/cm²) and at the laser wavelengths listed above, the ion signal was observed to be linear in the radiation fluence incident upon the tip. Figure 3 presents the respective plot for $\lambda=308$ nm. Each data point of this and the subsequent plots was obtained by averaging from 20 to 50 laser pulses depending on the signal level.

In the absence of the field, there was no laser-induced signal from the tip. When the laser beam was displaced from the tip, no stimulated ion signal was observed. The signal was also absent when anthracene vapor was pumped out of the system.

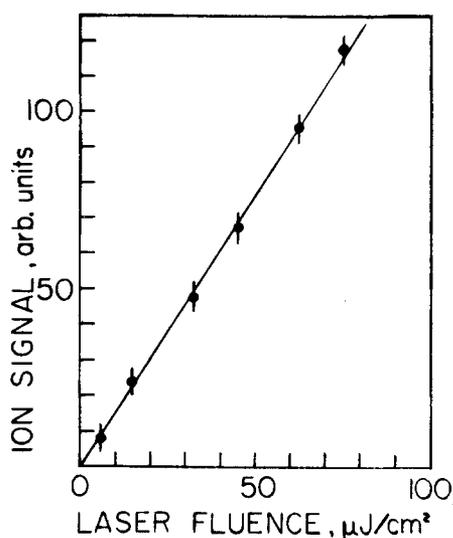


Fig. 3. Laser-stimulated ion signal as a function of the laser fluence incident upon the tip. Field strength at the tip 0.36 V/Å, radiation wavelength 308 nm

When the sample was irradiated with a dye laser at $\lambda=555$ nm, stimulation of field desorption was observed to occur at considerably higher laser fluences (about 3×10^{-2} J/cm²). The strong nonlinear dependence of the ion signal on the laser fluence at this wavelength (Fig. 4) indicates that the stimulative effect is in this case due to the radiation heating of the tip.

Figure 5 illustrates the results of investigation into the efficiency of laser stimulation of the field desorption of molecular anthracene ions at various wavelengths, see also [8]. The absolute ion signal value at a wavelength of 249 nm was around 100 ions at a fluence of 50 μJ/cm².

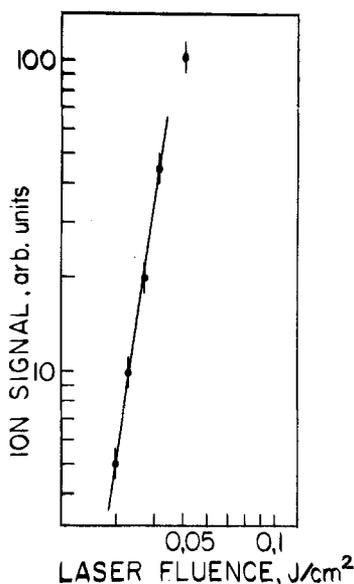


Fig. 4. Laser-stimulated ion signal as a function of the laser fluence incident on the tip. Field strength at the tip 0.36 V/Å, radiation wavelength 555 nm

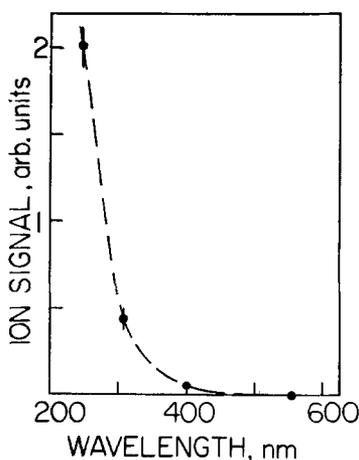


Fig. 5. Efficiency of laser stimulated desorption at various radiation wavelengths

3. Discussion

When irradiating a field-emitter, laser radiation interacts with molecules in the gas phase, the molecular layer adsorbed on the emitter surface, and the emitter material. In this case, there can occur various mechanisms leading to the formation of ions above the field-emitter tip. Below we will briefly discuss the possible elementary processes and estimate their contribution to the observed effect.

Let us first of all consider the processes associated with the excitation of anthracene molecules in the gas phase.

(a) *Laser photoionization of anthracene molecules in the gas phase* cannot explain the observed effect. The ion signal registered at time $t = l(2Ue/m)^{-1/2}$ after the laser pulse can be due only to ions produced away from the tip at distances less than the apex radius – the characteristic electric field strength drop distance. A volume of $R^3 = 10^{-15} \text{ cm}^3$ at an anthracene residual gas pressure of 10^{-7} Torr ($n = 3.5 \times 10^9 \text{ cm}^{-3}$) contains $3.5 \times 10^{-6} \ll 1$ anthracene molecules.

(b) The observed laser-stimulated ion signal cannot be related to the *excitation of molecules in the gas phase, followed by their field ionization*. At laser pulse fluences less than 1 mJ/cm^2 ($n_{ph} < 1.5 \times 10^{15}$ photons/cm²) and typical anthracene absorption cross sections $\sigma = (1 \div 5) \times 10^{-17} \text{ cm}^2$ the fraction of exited molecules $\sigma n_{ph} < 0.08$. The lifetime of anthracene molecules in the first singlet state $\tau_{S_1} = 5 \text{ ns}$ is shorter than the laser pulse duration $\tau_p = 20 \text{ ns}$. Thus, the number of excited molecules capable of reaching the apex of the tip does not exceed $(4/3)\pi \cdot (v\tau_p)^3 n \sigma n_{ph} = 0.1 \ll 10^2$ ions/pulse. The entrainment of molecules by the field, which manifests itself in a factor of $\xi = (\pi\alpha E^2/2kT)^{1/2}$ increase in the flux of molecules incident on the tip, as compared with the gas-kinetic value [9], at field strengths $E \lesssim 0.5 \text{ V/\AA}$, increases this estimate only insignificantly. Thus, for the polarizability, $\alpha = 25 \text{ \AA}^3$ (for anthracene, $\alpha_{xx} = 35.2 \text{ \AA}^3$, $\alpha_{yy} = 25.6 \text{ \AA}^3$, and $\alpha_{zz} = 15.1 \text{ \AA}^3$ [10]), and so $\xi = 5$.

When discussing the stimulation mechanisms connected with the action of laser light on the *emitter surface*, consideration should be given first of all to (c) *thermal stimulation*. Let us estimate the heating of the tungsten tip at a characteristic laser fluence of $F = 10^{-4} \text{ J/cm}^2$. During the time the laser pulse lasts, $\tau_p = 2 \times 10^{-8} \text{ s}$, heat diffuses a distance of $(2\chi\tau_p) = 10^{-4} \text{ cm}$. (For tungsten, the thermal diffusivity $\chi = 0.51 \text{ cm}^2 \cdot \text{s}^{-1}$.) Thus, the temperature distribution across the tip can be considered homogeneous, and the heat withdrawal along the tip can be disregarded. With the laser radiation being completely absorbed by the adsorbed anthracene layer and the tungsten tip, the heating $\Delta T = 2F/(\pi\rho cR) = 2 \text{ K}$. Clearly such a negli-

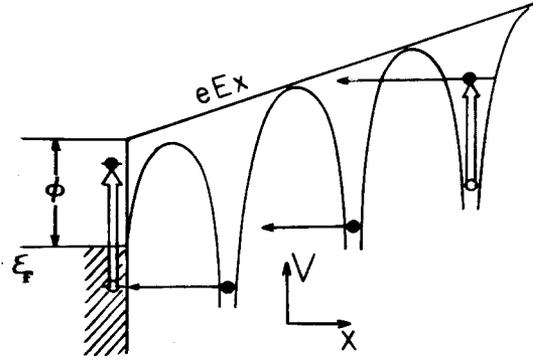


Fig. 6. Electron potential energy curves illustrating the field ionization of molecules in a layer adsorbed on a metal surface. Arrows indicate the electron tunnelling. Double-straight arrows show the possible mechanisms responsible for photostimulation of the field ionization of molecules in an adsorbed layer

gible heating cannot explain the observed photostimulation of field desorption. In contrast, with fluences in the order of 30 mJ/cm^2 at $\lambda = 555 \text{ nm}$, $\Delta T \approx 300 \text{ K}$. It is readily apparent that stimulation is in this case due to radiation heating.

The mechanism, considered earlier [11], of (d) *ionization through the generation of electron-hole pairs in the surface metal layer, followed by the injection of the holes into the adsorbed layer* (Fig. 6) seems little probable because of the short lifetime (10^{-14} to 10^{-15} s) of nonequilibrium charge carriers in the metal and, accordingly, the low efficiency of the charge transfer process. But at the present time we cannot definitely discard this mechanism.

The effect observed is most likely due to (e) *resonance single-photon absorption of laser radiation by anthracene molecules, followed by their ionization in a strong electric field* (Fig. 6). Let us analyze the experimental results from the standpoint of this mechanism. That the process is of single-photon character agrees with the linear fluence dependence of the ion signal at wavelengths of 249, 308, and 400 nm covering some absorption bands of anthracene [12] and the absence of any nonthermal signal at 555 nm where anthracene does not absorb.

An important part in this mechanism is played by a tunneling process causing its quantum efficiency to drop with increasing wavelength. In fact, the spectral dependence of the tunneling process efficiency $\eta(\omega)$ is determined by the product of the absorption spectrum $\sigma(\omega)$ and the tunneling quantum yield spectrum $\phi(\omega)$: $\eta(\omega) = \sigma(\omega)\phi(\omega)$. $\phi(\omega)$ is in turn equal to $1 - \exp(-R\tau)$, where τ is the relaxation time of the excited state. (In the general case, it is necessary to integrate over all intermediate states.) The tunneling rate R contains an exponential function of the barrier height $(U - \hbar\omega)$.

For example, for a triangular barrier [13], we have

$$R(\omega) = \nu \exp \left[- \frac{4(2m)^{1/2}}{3\hbar E e} (U - \hbar\omega)^{3/2} \right],$$

where $\nu = 10^{16} \text{ s}^{-1}$ is the characteristic electron-barrier "collision frequency". Thus, the behavior of the spectral efficiency of stimulated field desorption agrees qualitatively with the stimulated field ionization model.

4. Conclusion

We have observed laser stimulation of the field desorption of molecular anthracene ions from the surface of an adsorbed anthracene layer. With the laser radiation falling within an absorption band of anthracene, the stimulated ion signal has been experimentally found to depend linearly on the laser fluence, which suggests a one-photon character of the stimulation mechanism. In the case of resonance excitation, the efficiency of the process drops with increasing wavelength. The dependence obtained with the sample being irradiated with a nonresonance laser light of a considerably higher fluence is characteristic of thermal stimulation. The experimental results obtained with resonance laser excitation point to the following stimulation mechanism: resonance excitation of anthracene molecules on the field-emitter surface \rightarrow ionization of the excited molecules by a field \rightarrow desorption of the ions.

It should be readily apparent that based on this phenomenon, one may hope to implement the idea of laser field-ion biomolecular microscope [14] (see also [15] where they tried to realize this idea experimentally). Such a microscope would help to obtain spectral

information, with an atomic scale spatial resolution, on the electronic structure of complex molecules. However, to solve this problem requires further investigations and a search for conditions necessary for an effective charge transfer from a selectively ionized chromophore to an adspecies whose diffusion during the desorption time is insignificant.

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