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Ionization of Toluene Vapor by 266-nm Radiation

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Abstract—Photoelectron spectra of stepwise ionization of toluene vapor by 266-nm radiation were obtained. The kinetic energy range of produced photoelectrons unambiguously indicates the formation of $C_7H_7^+$ ions by the ionization–dissociation mechanism.

Mechanisms of processes of multiphoton ionization of gases and vapors are quite various and depend on both characteristics of laser radiation and spectral-kinetic properties of molecules that are subject to ionization. Therefore, understanding the detailed mechanism of energy accumulation by molecules and processes responsible for the formation of different ions in a particular system presents a complicated problem. Meanwhile, solving this problem is necessary for developing and verifying theoretical models of interaction of laser radiation with molecules, elaborating analytical techniques of extreme sensitivity and selectivity, and using the laser photoionization spectroscopy methods in studying intermolecular energy redistribution processes.

In studies of multiphoton ionization processes, a mass spectrometric technique is most frequently used, as it gives direct information on the mass of produced ions. However, some ions can emerge in a different sequence of elementary events, and mass spectrometry cannot unequivocally reveal this sequence. A direct technique of studying the mechanism of energy buildup in a molecule is the energy analysis of photoelectrons.

The stepwise ionization of toluene by the fourth-harmonic radiation of a Nd-YAG laser (266 nm) was studied by the mass spectrometric technique [1, 2]. The abundance of ions in the mass spectra was affected by the laser radiation flux density, although the molecular ion $C_7H_8^+$ and the fragment ions $C_7H_7^+$ was found to prevail at a low flux density. Matyuk *et al.* [1] analyzed the kinetics of formation of the ions $C_7H_7^+$ by the ionization–dissociation scheme
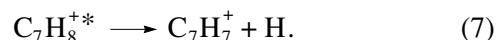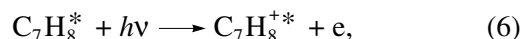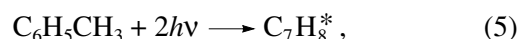
$$C_6H_5CH_3 + 2h\nu \longrightarrow C_7H_8^+ + e, \qquad (1)$$

$$C_7H_8^+ + h\nu \longrightarrow C_7H_7^+ + H \qquad (2)$$
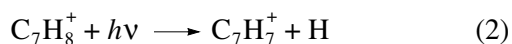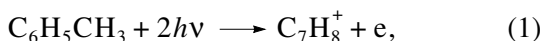
and obtained the photodissociation cross sections for ions $C_7H_8^+$, in agreement with independent measurements [3].

The approximate character of the analysis of the ion formation kinetics in [1] and the difference in excitation energy distribution of dissociating ions in [1, 3] require experimental evidence to rule out alternative mechanisms of formation of $C_7H_7^+$. One of these is the dissociation–ionization mechanism

$$C_6H_5CH_3 + h\nu \longrightarrow C_7H_7 + H, \qquad (3)$$

$$C_7H_7 + 2h\nu \longrightarrow C_7H_7^+ + e. \qquad (4)$$
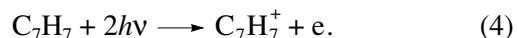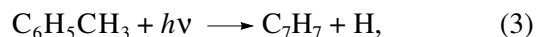
There is also a plausible mechanism involving the over-threshold energy buildup by virtue of absorption of the third photon by the parent molecule in the super-excited state [4]

$$C_6H_5CH_3 + 2h\nu \longrightarrow C_7H_8^*, \qquad (5)$$

$$C_7H_8^* + h\nu \longrightarrow C_7H_8^{+*} + e, \qquad (6)$$

$$C_7H_8^{+*} \longrightarrow C_7H_7^+ + H. \qquad (7)$$

Note that all three mechanisms are three-photon processes and do not contradict the experimental dependences of the abundance of $C_7H_7^+$ ions on laser photon fluence. The most probable mechanism can be determined by analyzing the energy of electrons produced by multiphoton ionization [5].

We obtained a photoelectron spectrum for stepwise ionization of toluene by 266-nm radiation. The spectrum permits us to rule out all the mechanisms of formation of $C_7H_7^+$ except the ionization–dissociation scheme.

In this work, we used a laser photoionization spectrometer that allowed not only mass spectra and photoelectron spectra of stepwise ionization to be measured. Toluene vapor at a pressure ~10^{-3} Pa was ionized by a focused fourth-harmonic radiation from an LTI-PCh laser with a pulse duration of 10 ns. Both mass spectral and photoelectron energy analysis were performed in the time of flight mode at a drift area length of 0.4 m.

$P(\varepsilon)$, arb. units
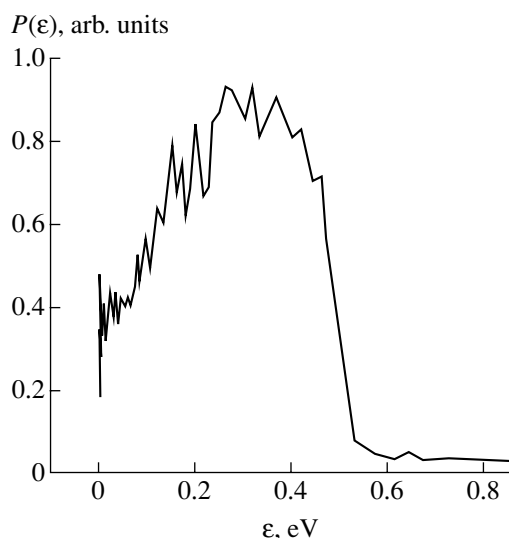
Photoelectron spectrum of toluene vapor ionized by 266-nm radiation.

Transition from one mode to another was accomplished by changing the polarity and magnitude of the voltage applied to the units of ion optics. The optics calculated for this purpose allowed us to localize the ionization region fairly well in space even for gaseous targets and to withdraw a considerable portion (up to 100% for ion detection and up to 6% for photoelectron energy analysis) of ionization-induced charged particles for mass and energy analysis. The spatially separated trains of particles arrived to a chevron pair of multichannel plates, from which a signal was read out with a stroboscopic voltmeter. The data acquisition and processing system was based on the CAMAC crate and IBM PC computer units.

The transform of time-of-flight photoelectron distribution $P(t)$ into kinetic energy distributions $P(\varepsilon)$ was performed according to the conventional ratio $P(\varepsilon)\Delta\varepsilon = P(t = k/\varepsilon^{0.5})\Delta t$. The electron energy scale was calibrated in terms of shifts of time-of-flight distributions by additional acceleration of electrons prior to arrival to the drift area with known increments in kinetic energy.

A photoelectron spectrum of toluene at a laser pulse energy of ~1 µJ is shown in the figure. The line intensities in the spectrum are directly proportional to toluene vapor pressure. The photon fluence dependence is close to the square-law function. Note that the Nd-YAG fourth-harmonic frequency (37 576.78 cm^{-1} [6]) corresponds to the dip in the toluene absorption spectrum [7], for which the absorption cross section is an order of magnitude smaller that the maximum value for the 0–0 band of the $S_0 \longrightarrow S_1$ transition. This implies that there is a considerable sensitivity margin for recording photoelectron spectra.

Meek *et al.* [8] reported photoelectron spectra obtained by two-step ionization of toluene via some vibronic states of S_1 with a tunable dye laser using the effusion beam technique. These spectra exhibit vibrational structure. In our experiments, the structure was not resolved because of superimposition of the spectra from thermally excited S_0-state molecules with different excitation energies, poorer resolution of the energy analysis and detuning of the excitation radiation from the resonance frequency. However, the intensity distribution in our spectrum is in agreement with the envelope of the spectrum of molecular-beam cooled toluene ionized by 37 477 cm^{-1} radiation corresponding to that of the 0–0 band of $S_0 \longrightarrow S_1$ transition: the maximums in both spectra occur at the maximum kinetic energies of electrons allowed by the conservation law, and the spectrum length is identical. It should be pointed out that no fast electrons with a kinetic energy above ~0.5 eV were observed.

The threshold energy of the formation of $C_7H_7^+$ from toluene is 10.71 ± 0.03 eV [9]. If three photons are indeed absorbed, reaction scheme (5)–(7) suggests that produced electrons must have a kinetic energy up to 3.3 eV, which is not the case. Consequently, this mechanism is unrealistic.

Let us make a similar evaluation of dissociation–ionization mechanism (3) and (4). The flash photolysis of toluene with a wide-band light source afforded benzyl radicals [10]. The threshold energy of dissociation (3) to unexcited benzyl radicals is 3.6 ± 0.1 eV, as calculated from the enthalpies of formation of toluene (73.18 kJ/mol [11]), benzyl radical (200.0 ± 6.3 kJ/mol [12]), and H atom (217.6 kJ/mol [13]). Upon dissociation of complex molecules, an excess photon energy is basically transformed into the energy of vibrational excitation of a molecular fragment. Since the adiabatic ionization energy of the benzyl radical is 7.2487 eV [14], the maximum kinetic energy of electrons produced by (4) must be as high as 3.18 eV. A study on the ionization processes involving vibrationally excited molecules indicates that ionization transitions with the conservation of gained vibrational energy are preferred ($\Delta v = 0$ rule) [8]. If this is also true for the photoionization of the benzyl radical possessing 1.1 eV of vibrational energy, the ionization transition that generates photoelectrons with $\varepsilon = 2.08$ is most probable.

Similar consideration of other dissociation–ionization schemes involving the formation of neutral or charged cyclic fragments with known thermochemical characteristics at different stages gives even greater values of the photoelectron kinetic energy. Burton and Noyes [15] obtained a value of 1 ± 0.1 for the total luminescence and intersystem crossing quantum yield, which also suggests that the contribution of the dissociation–ionization mechanism is insignificant for an excitation energy that falls in the region of the 0–0 band of $S_0 \longrightarrow S_1$ transition.

In summary, the photoelectron energy analysis unequivocally suggests that, of the three discussed

schemes for the formation of $C_7H_7^+$ ions by stepwise ionization of toluene, the mechanism proposed in [1] is operative.

ACKNOWLEDGMENTS

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