

## LASER CHEMISTRY

# Stepwise Ionization of Hydroquinone Vapor by Monochromatic Radiation

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**Abstract**—Processes of stepwise ionization of hydroquinone vapor by radiation in the range 315–275 nm were studied using photoionization spectroscopy techniques. The two-step ionization process yielding molecular ions was found to prevail at a laser power density up to  $\sim 10^7$  W/cm<sup>2</sup>. As the radiation intensity increases, the progressively stronger and deeper degradation takes place via dissociation of the molecular and, probably, fragment ions due to absorption of at least one additional photon. The slow process of the formation of C<sub>5</sub>H<sub>6</sub>O<sup>+</sup> ions at an effective rate constant of the order of 10<sup>6</sup> s<sup>-1</sup> was observed.

Investigation of the processes of multiphoton ionization of gases and vapors is a promising line of research in laser chemistry. Such studies are necessary not only for deriving the models of interaction of laser radiation with molecules but also for the development of analytical methods of extreme sensitivity and selectivity and the application of laser photoionization spectroscopy in studying intramolecular energy redistribution processes [1].

The 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 subjected to ionization. Therefore, in order to reveal the detailed mechanism of energy accumulation by a molecule and the processes responsible for the formation of different ions, it is frequently necessary to use a few experimental methods that allow information on different characteristics of this phenomenon to be obtained [2].

In this paper, we report the results of the study of multiphoton ionization of vaporized hydroquinone by tunable laser radiation in the region 315–275 nm using the techniques of total ion current spectroscopy, mass spectrometry, photoelectron spectroscopy, and threshold electron spectroscopy. The two-step ionization of hydroquinone was previously used to resolve the structure of the absorption spectrum in the region of S<sub>0</sub>–S<sub>1</sub> transition, which was due to the existence of isomers [3–6]. In the cited works, only the spectral dependence of the molecular-ion current upon two-step ionization of a supersonic beam at the first transition band was reported.

## EXPERIMENTAL

Experiments were performed on the modified laser photoionization spectrometer described briefly in the

earlier paper [2]. Hydroquinone vapor at a pressure of about 10<sup>-4</sup> Pa was ionized by the second-harmonic radiation from an LZhi-506 dye laser pumped with the second harmonic (532 nm) of an LTI-PCh solid state laser. The Rhodamine 6G and Rhodamine C dyes were used, thus providing wavelength ( $\lambda$ ) tuning in the range 315–275 nm. The wavelength scale was calibrated accurate to 0.05 nm with a PRK-4 mercury lamp. The minimum  $\lambda$  scanning step was 0.01 nm, the UV pulse duration was 12 ns, the laser energy was 1–60  $\mu$ J, and the beam waist  $\lambda$  of focused radiation was  $\sim 0.1$  mm. In order to create the necessary concentration of molecules, a hydroquinone sample, the leak system, and the vacuum chamber were maintained at a temperature of about 310–320 K.

The ion mass and electron energy analyses were based on the time-of-flight principle at the drift length of 0.45 m. Space-resolved trains of particles arrived to a chevron pair of multichannel plates, from which a signal passed to a Pico-200-100 analog-to-digital converter (United Kingdom) having a time resolution of 10 ns. In order to detect threshold electrons with a kinetic energy close to zero, we employed their capture by space charge in the ionization region. The space charge was removed by a pulsed electric field with a field strength of 4–5 V/cm 160–170 ns after a laser pulse, and the total current of released electrons was measured with an ATsP14 CAMAC analog-to-digital converter. Data collection, acquisition, and processing was performed system by an IBM PC 486 computer.

The field strength in the ionization region was 200 V/cm for the mass spectrometric analysis, whereas the field gradient in the ionization region in the electron energy analysis did not exceed 0.02 V/cm and the vapor pressure and the intensity of laser radiation was selected in such a manner so that to make the influence of the space charge negligible.

## RESULTS AND DISCUSSION

Figure 1 shows the spectral dependence of the total current and the threshold-electron current for hydroquinone after normalization with respect to the light flux. The arrow marks the position of the 0-0 band of  $S_1 \leftarrow S_0$  transition for the most stable *trans*-isomer of hydroquinone as given in Humphrey and Pratt [7] ( $33\,500.054\text{ cm}^{-1}$ ). The diffuse structure of the spectra is in satisfactory agreement with the one expected from the reported high-resolution absorption spectrum of the vapor [8] and the spectrum of (1 + 1) multiphoton ionization of hydroquinone in a supersonic beam [3, 6]. Thus, the ionization in the spectral region of interest is associated with the absorption of the first photon in the  $S_1 \leftarrow S_0$  transition. The contribution of resonance processes to the total current at  $\lambda = 281.3\text{ nm}$  does not exceed 1%. We fail to measure the spectra of threshold electrons upon ionization of higher Rydberg states by an electric field pulse. The negative result of these experiments suggests that the laser excitation of hydro-

quinone vapor does not lead to the population of the higher Rydberg states having a lifetime longer than 170 ns (the minimal time delay between a laser radiation pulse and a Rydberg state-ionizing electric field pulse).

Figure 2 depicts representative mass spectra. The abundance pattern of the mass spectra depends both on photon energy and, especially strongly, on laser energy. At an energy that does not exceed  $\sim 10\text{ }\mu\text{J}$  per pulse, the molecular ion  $M^+$  prevails in the mass spectrum. Since the adiabatic ionization energy of the more stable *trans*-isomer of hydroquinone is 7.932 eV [5], the absorption of two photons at the wavelength no greater than 312.6 nm would be sufficient for generating molecular ions. As the energy per pulse increases, the abundance of ion  $M^+$  increases reaching a plateau, which may be associated with both saturation effect and photodissociation of  $M^+$  (see below). At  $\lambda = 298.1\text{ nm}$  and an energy per pulse of  $3.5\text{ }\mu\text{J}$ , the contribution of fragment ions with masses of 81, 55, 53, and 39 (in order of increasing

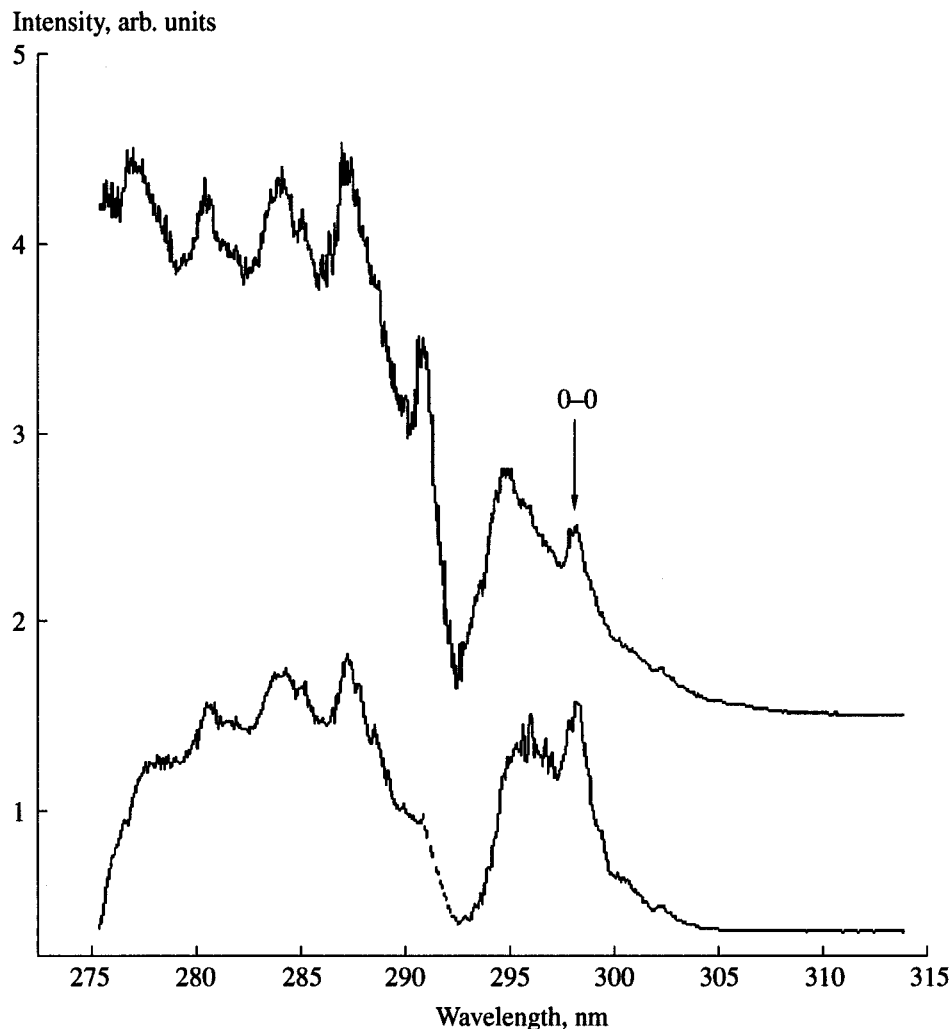


Fig. 1. Spectral dependence of the total current (upper curve) and the threshold electron current (lower curve) upon laser ionization of hydroquinone vapor.

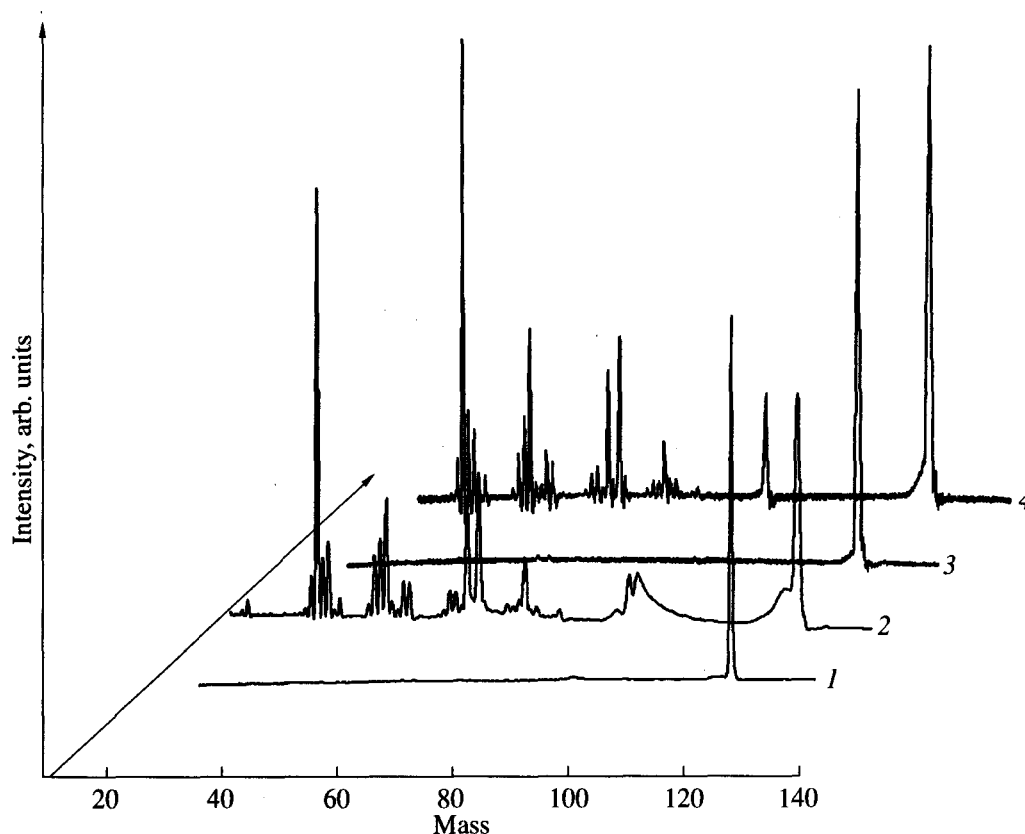


Fig. 2. Mass spectra of hydroquinone ionized in the vapor phase by laser radiation at (1, 2) 281.3 and (3, 4) 298.1 nm and an energy of (1, 3) 4 and (2, 4) 40  $\mu\text{J}/\text{pulse}$ .

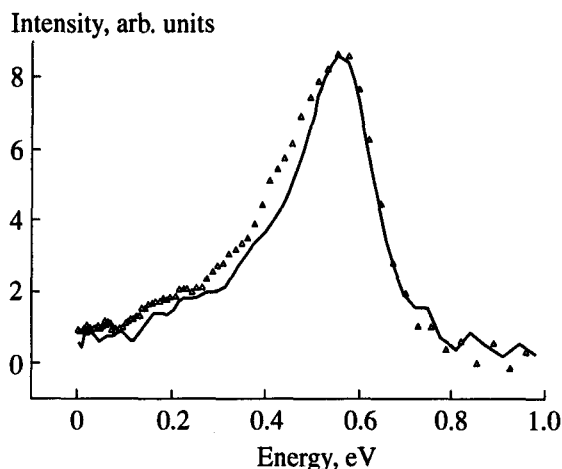
ion current) to the total current is about 5%, and the current of molecular ions does not exceed 15% of the total current at the energy per pulse of 65  $\mu\text{J}$ . As the laser radiation intensity increases, the contribution of lighter ions increases. The peak at the mass to charge ratio of 82 (spectrum 2 in Fig. 2) displays in the region of high masses a long tail due to degradation of  $\text{M}^+$  yielding this fragment during the flight from the ionization region to the detector (metastable decomposition). The effective rate constant of the process was evaluated from the tail length as  $(2-3) \times 10^6 \text{ s}^{-1}$ .

In Fig. 3, the photoelectron spectra obtained at the same wavelength (281.3 nm) but differing (approximately by an order of magnitude) laser energies are collated. The spectra have been corrected for the analyzer transmittance function. The solid-line spectrum refers to the radiation intensity at which  $\text{M}^+$  ions dominate in the mass spectrum, and the second spectrum has been measured under conditions when the contributions of the molecular and the fragment ion to the total current were comparable. The spectra coincide within the experimental error ( $\sim 10\%$ ). This similarity suggests that the major pathway of formation of fragment ions (with a branching ratio of at least 0.9) is photodissociation of molecular and, probably, heavy fragment ions. Alternative mechanisms, the ionization of neutral fragments produced by dissociation of the molecule from a transient state or the autoionization of the molecule

after absorption of at least three photons, suggest the dependence of photoelectron spectra on radiation intensity.

The analysis of the obtained photoelectron spectra is out of the scope of the present work. Let us only highlight the points significant for further discussion. Comparison of the spectra with the HeI photoelectron spectrum of hydroquinone reported in Palmer *et al.* [9] shows that, under our conditions, the molecular ions are formed only in the ground electronic state  $X^2B_g$ . However, a part of molecular ions has the vibrational excitation energy close to the maximum attainable value at a given photon energy, which ranges from 0.19 at  $\lambda = 295.0 \text{ nm}$  to 1.08 eV at 275.2 nm. This circumstance should be taken into account in the analysis of possible formation pathways for fragment ions. Note that molecular ions with the limiting vibrational excitation are formed in the resonance processes of vibrationally induced autoionization or ionization of higher Rydberg states by dissipated electric fields. The HeI photoelectron spectrum also enables us to identify electronic transitions in the ion  $\text{M}^+$  that result in its fragmentation, these are the energy-overlapped transitions  $^2A_u \leftarrow X^2B_g$  ( $\pi^*\pi$  type) and  $^2B_u \leftarrow X^2B_g$  ( $\sigma^*\pi$  type).

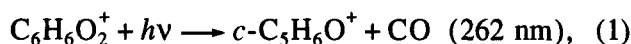
Let us try to identify the formation processes for some fragment ions on the basis of the model of preferred degradation of ions by less endothermic chan-



**Fig. 3.** Photoelectron spectrum of hydroquinone vapor ionized by 281.3-nm radiation at a laser energy of (solid line) 4 and (triangles) 40  $\mu\text{J}/\text{pulse}$ .

nels, which is widely used in mass spectrometry [10]. Steric hindrances will be taken into account by excluding the O atom from migration to atoms that occur far from it. The heats of reactions were determined with the use of the formation enthalpy of the hydroquinone molecular ion, 27.9 kJ/mol, obtained from the values of the aforementioned ionization energy and the heat of formation as given in [11]. The heats of formation for fragments were borrowed from the book [10].

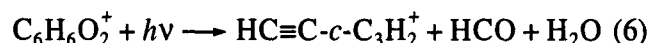
It is the molecular ion alone which can be the precursor of the fragment ions appearing at low laser radiation intensities. Based on the above estimates, we propose that these ions may be formed as follows:



Given in the parentheses are the threshold wavelength values for photodissociation of unexcited molecular ions. The energy estimations show that the internal energy of the ion  $\text{M}^+$  generated by absorbing two photons by a molecule is insufficient for degradation, which agrees with the finding that only molecular ions are produced at low light fluxes. The absorption of one photon by  $\text{M}^+$  in the spectral region relevant to this work opens degradation channels (2)–(4). Allowance for the vibrational excitation energy in  $\text{M}^+$  (see above) results in lowering of the  $\lambda$  threshold of process (1) upon absorption of one photon below 295 nm. From the mass spectra recorded with a step size of 0.5 nm in this spectral region, we determined the threshold wavelength as  $294 \pm 1$  nm. The CO and HCO elimination

processes were observed earlier upon laser ionization of phenol [12] and cresols [13], respectively.

The cyclic ion  $\text{C}_3\text{H}_3^+$  represents the most stable isomer, and process (5) seems to be the least endothermic. Thus, the formation of the  $c\text{-C}_3\text{H}_3^+$  ion requires the absorption of two photons by the molecular ion. This requirement is consistent with the stronger fluence dependence for the current of ions with a mass number of 39 than for the current of ions produced in processes (1)–(4). The absorption of at least four photons seems to be required for the generation of ions with  $m/z$  63. The formation of the most stable ethynylcyclopropenyl ion [10] in the process



requires at least 6.15 eV. With absorption of two photons, reaction (6) can proceed via a consecutive mechanism involving the formation of the  $c\text{-C}_5\text{H}_5\text{O}^+$  ion (process (2)) which dissociates upon absorption of the second photon. The successive degradation route is supported by the observed invariability of the current intensity ratio of the ions at  $m/z$  63 and 81 with varying the light flux over a wide (more than by an order of magnitude) range,  $0.50 \pm 0.02$  at  $\lambda = 298.1$  nm and  $0.45 \pm 0.05$  at  $\lambda = 305$  nm.

At laser energies exceeding 50 or 15  $\mu\text{J}/\text{pulse}$  in the long- or the short-wavelength region, respectively, the processes of formation of light ions having a mass of 27 ( $\text{C}_2\text{H}_3^+$ ), 28 ( $\text{C}_2\text{H}_4^+$ ,  $\text{CO}^+$ ), 29 ( $\text{HCO}^+$ ), and 26 ( $\text{C}_2\text{H}_2^+$ ) prevail. Their formation requires the absorption of at least four photons; however, the available data are insufficient for deciding which of the plausible processes are favorable.

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#### REFERENCES

1. Letokhov, V.S., *Lazernaya fotoionizatsionnaya spektroskopiya* (Laser Photoionization Spectroscopy), Moscow: Nauka, 1987.
2. Kleimenov, V.I., Feofilov, A.G., Akopyan, M.E., Aleksandrov, M.S., Ivanov, V.S., and Medynskii, G.S., *Khim. Vys. Energ.*, 1998, vol. 32, no. 4, p. 291 [*High Energy Chem.* (Engl. transl.), 1998, vol. 32, no. 4, p. 257].
3. Tembreull, R., Dunn, T.M., and Lubman, D.M., *Spectrochim. Acta, Part A*, 1986, vol. 42, no. 8, p. 899.
4. Dunn, T.M., *Chem. Phys. Lett.*, 1985, vol. 121, nos. 4–5, p. 453.
5. Oikawa, A., Abe, H., Mikami, N., and Ito, M., *Chem. Phys. Lett.*, 1985, vol. 116, no. 1, p. 50.

6. Tzeng, W.B., Narayanan, K., Hsieh, C.Y., and Tung, C.C., *Spectrochim. Acta, Part A*, 1997, vol. 53, no. 14, p. 2595.
7. Humphrey, S.J. and Pratt, D.W., *J. Chem. Phys.*, 1993, vol. 99, no. 7, p. 5078.
8. Beck, C.A., *J. Chem. Phys.*, 1950, vol. 18, no. 9, p. 1135.
9. Palmer, M.H., Moyes, W., Speirs, M., and Ridyard, J.N.A., *J. Mol. Struct.*, 1979, vol. 52, no. 2, p. 293.
10. Takhistov, V.V., *Organicheskaya mass-spektrometriya* (Organic Mass Spectrometry), Leningrad: Nauka, 1990.
11. Zhigiang Wang Day, P.N. and Pachter, R., *Chem. Phys. Lett.*, 1995, vol. 237, nos. 1-2, p. 45.
12. Matyuk, V.M., Polevoi, A.V., Potapov, V.K., and Prokhoda, A.L., *Khim. Vys. Energ.*, 1982, vol. 16, no. 2, p. 99.
13. Ta-Chau Chang and Johnston, M.V., *J. Phys. Chem.*, 1987, vol. 91, no. 4, p. 884.
14. Hopkinson, A.C. and Lien, N.H., *J. Am. Chem. Soc.*, 1986, vol. 108, no. 11, p. 2843.