

LASER  
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## Stepwise Photoionization of 1,2-Dihydroxybenzene Vapor

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**Abstract**—The stepwise ionization processes of 1,2-dihydroxybenzene vapor at 315–275 and 266 nm were studied by the techniques of mass spectrometry, total ionization current spectroscopy, and zero electron kinetic energy spectroscopy. A two-step ionization process yielding the molecular ion prevails at a laser intensity up to  $\sim 10^7$  W/cm<sup>2</sup>. As the radiation intensity increases, fragmentation takes place via the dissociation of molecular and fragment ions due to absorption of one additional photon. The formation pathways of principal fragment ions are discussed.

In continuation of the study on the mechanism of laser ionization of oxygenated benzene derivatives in the vapor phase [1, 2], we examined the stepwise ionization of 1,2-dihydroxybenzene (catechol). The electronic structure of catechol is close to that of the previously studied hydroquinone (1,4-dihydroxybenzene). Both molecules are characterized by  $\pi\pi^*$  transitions that almost coincide in absorption spectra and close values of the first ionization potential. However, the second ionization energy of catechol is 0.4 eV lower than that of hydroquinone [3]; therefore, the absorption of two photons in the spectral range of our studies can lead to the formation of catechol cations in an electronically excited state. In addition, there is weak intramolecular hydrogen bonding in catechol [4, 5]. It was interesting whether these specific properties of catechol would affect the mechanism of laser ionization.

The two-step ionization of catechol was previously employed to resolve the structure of the absorption spectrum in the region of the  $S_0$ – $S_1$  transition due to the existence of rotamers and excitation of torsional vibrations of the  $S_1$  state [4–7]. In the cited works, only the spectral dependences of the current of molecular ions  $M^+$  were obtained upon ionization of a supersonic jet in a narrow ( $<1200$  cm<sup>-1</sup>) region near the 0–0 transition of the first absorption band.

### EXPERIMENTAL

The spectrometer and the experimental procedure used in this work are described elsewhere [1, 2, 8]. Catechol vapor at a pressure that did not exceed  $10^{-3}$  Pa and a temperature of 340 K was ionized with a focused beam from a dye laser having a short-wavelength tuning limit of 275 nm or by the 266-nm fourth-harmonic radiation from a solid state laser. The fluence rate was varied within  $2 \times 10^6$ – $2 \times 10^7$  W/cm<sup>2</sup> (2–20  $\mu$ J/pulse).

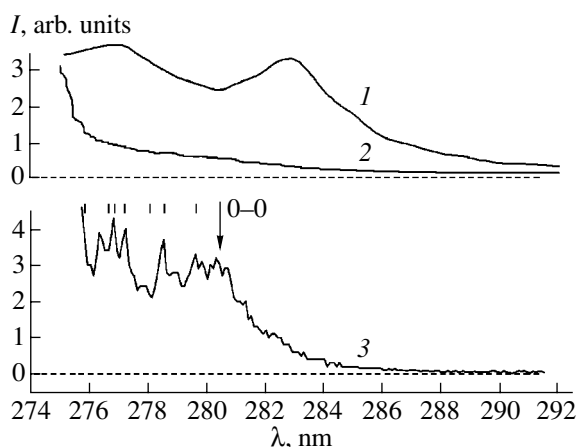
In thermochemical calculations, the formation enthalpies were used as given in Takhistov [9] unless otherwise stated. The enthalpy of formation of the cat-

echol molecular ion  $M^+$  was calculated from the formation enthalpy of catechol ( $-274.8$  kJ/mol [10]) and the adiabatic ionization energy  $I_1 = 8.168$  eV [7].

### RESULTS AND DISCUSSION

Figure 1 shows the spectral dependences of the total ionization current and the current due to electrons produced by pulsed-field ionization of high Rydberg states (ZEKE-PFI spectrum) normalized by the square radiation intensity, in comparison with the absorption spectrum of catechol, where the arrow marks the position of the 0–0 band of the  $S_1 \leftarrow S_0$  transition (280.5 nm [7]). The signals at longer wavelengths are due to transitions in thermally excited molecules.

Unlike the case of hydroquinone [1], the total current spectrum of catechol is structureless and does not correlate with the absorption spectrum. The rise in the total current in the region in which the absorption cross section is weakly dependent on the wavelength  $\lambda$  is associated with an increase, with decreasing  $\lambda$ , in the ionization cross sections of vibronic states populated by absorption of the first photon. This assumption is consistent with the results of quantum-chemical calculations showing a substantial difference in the geometry of equilibrium configurations of the ground-state  $M^+$  and the  $S_0$  and  $S_1$  state [7] and with the shape of the first band of the HeI photoelectron spectrum [3]. The calculations suggest planar equilibrium configurations in the ground state of the neutral and the cation and a nonplanar configuration in the  $S_1$  state, which is confirmed by the appearance of intense overtones and combination bands associated with torsional vibrations of OH in the resonance-enhanced multiphoton ionization (REMPI) spectrum of a supersonic molecular beam of catechol [4, 5]. This structure is absent from the REMPI spectrum of hydroquinone [11] because its molecule remains planar in the  $S_1$  state as well [12]. The excitation of low-frequency torsional vibrations in the  $S_1 \leftarrow S_0$  and ionization transitions also explains the more dif-



**Fig. 1.** (1) Absorption spectrum and (2) total ionization current and (3) and ZEKE-PFI electron current spectra of catechol vapor.

fuse character of the spectral dependences shown in Fig. 1 as compared with hydroquinone.

In the measurements of ZEKE-PFI spectra, electrons with zero kinetic energy are detected; i.e., the condition of optical double resonance between the initial, intermediate, and ionic states is fulfilled. This significantly reduces the set of transitions contributing to the detected signal. Therefore, ZEKE-PFI spectra display the structure which can be attributed to both the cation energy spectrum [8] and the spectrum of vibrational levels in the intermediate state. The vertical bars in Fig. 1 mark the position of intense  $S_1 \leftarrow S_0$  transition bands in the REMPI spectrum of supersonic catechol molecular beam [5]. It is seen that the structure is associated with the spectrum of the intermediate  $S_1$  state.

The effective lifetimes of Rydberg states was determined by measuring a decrease in the intensity of ZEKE-PFI electron signals with increasing the delay of a Rydberg state-ionizing field pulse after a laser pulse. For all  $\lambda \leq 283$  nm, the obtained values fall in the range  $150 \pm 15$  ns.

Figure 2 depicts the laser ionization photoelectron spectra of catechol obtained at  $\lambda = 283$  and 266 nm. The abscissa is graduated in the excitation energy of  $M^+$  ions generated by two-photon ionization,  $E_e = 2E - I_1 - \epsilon$ , where  $E$  is the photon energy and  $\epsilon$  is the photoelectron energy. For the spectrum at  $\lambda = 283$  nm corresponding to the region of hot transitions, a correction for thermal energy in the  $S_0$  state is introduced. It is seen that the most abundant molecular ions are  $M^+$  with an excitation energy of about 0.3 eV at  $\lambda = 283$  nm or 0.9 eV at  $\lambda = 266$  nm. Moreover, a portion of  $M^+$  ions has the maximum excitation energy attainable at a fixed photon energy—from 0.6 eV at  $\lambda = 293$  nm to 1.1 eV at  $\lambda = 266$  nm.

Within the measurement error, the spectra are not changed by varying the radiation intensity over the entire accessible range, including the region of strong fragmentation. This finding in combination with the detection of  $M^+$  ions in mass spectra suggest that, as in the case of previously studied hydroquinone and veratrole, the principal pathway of formation of fragment ions is the photodissociation of molecular and fragment ions. Alternative schemes, the ionization of neutral fragments produced via dissociation of the molecule from an intermediate state or the autoionization of the molecule after absorption at least three quanta, suggest that the spectra should depend on the radiation intensity.

The absorption of a 283-nm photon primarily leads to the population of the  $S_1(0^0)$  state. If ionization results from the absorption of the second photon by the molecule in this state, close vibration energy distributions of  $M^+$  produced by single-photon ionization transitions from the  $S_1$  and  $S_0$  states should be expected because of a small difference in the equilibrium interatomic distances, except for the torsional coordinates (see above) of the  $S_1$  and  $S_0$  states [7]. The most probable transition to the ground state of the cation  $D_0$  in the HeI photoelectron spectrum [3] is shifted by approximately 0.4 eV relative to the 0–0 ionization transition. The spectrum shown in Fig. 2 is qualitatively consistent with the one predicted in terms of the above considerations.

The photoelectron spectrum at  $\lambda = 266$  nm is characterized by a low probability of transitions to the  $M^+$  states in the region of the equilibrium configuration and by a shift of the most probable transitions toward higher  $E_e(M^+)$  energies. When a 266-nm photon is absorbed, the vibronic  $S_1$  states with the total energy of vibrational excitation of 0.25–0.5 eV including the contribution of hot transitions are populated. At the qualitative level, the change in the shape of the photoelectron spectrum can be explained as follows. As the energy of vibrational excitation increases, the Franck–Condon region of ionization transitions is extended for the starting ionization state. In addition, rapid intramolecular redistribution of vibrational energy over isoenergetic states leads to the situation that some excitation energy is localized in Franck–Condon inactive modes and is transferred to  $E_e(M^+)$  without change (the  $\Delta v_i = 0$  rule [13]).

Assuming that the ionization were preceded by the intersystem crossing to a triplet  $T$  state or internal conversion to the  $S_0$  state, the vibrational excitation energy in the state prior to ionization would be increased by the difference in the electronic energy between the  $S_1$  and  $T$  or between  $S_1$  and  $S_0$  states. Then, the 283-nm spectrum would resemble the spectrum obtained at  $\lambda = 266$  nm. Therefore, we believe that the molecular ions under the conditions of our experiments are produced by two-step ionization via the  $S_1$  state.

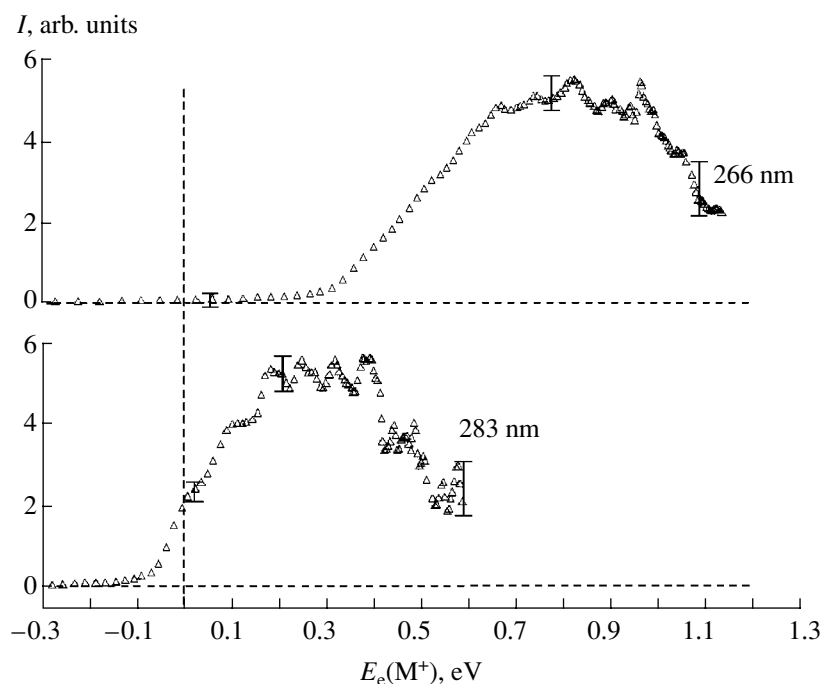


Fig. 2. Photoelectron spectra of catechol.

Let us consider a possible contribution of ionization transitions to the first electronically excited state of the cation  $D_1$  with the vertical ionization energy of 9.25 eV [3]. As the transition into the  $D_0$  state, they correspond to the removal of  $\pi$  electrons and the intensity distributions in the first two bands of the HeI photoelectron spectrum are close [3]. This resemblance allows the adiabatic ionization energy yielding the  $D_1$  state to be estimated at 8.8 eV. However, the probability of the  $0-0$   $D_1 \leftarrow S_1$  transitions is very low and becomes comparable to that of the  $D_0 \leftarrow S_1$  transitions in the overlapping  $E_e$  region when the threshold is exceeded by 0.3–0.4 eV. Therefore, a small contribution of the transitions to the  $D_1$  state may be expected only at  $\lambda = 266$  nm.

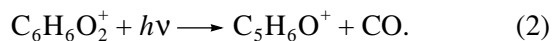
At low laser intensities, only  $M^+$  is generated. An increase in the intensity progressively enhances fragmentation (Fig. 3). The character of fragmentation upon laser-induced ionization of catechol is close to that observed for hydroquinone [1]. The most significant difference is the appearance of a mass spectral peak at the mass to charge ratio of 92 ( $92^+$ ) corresponding  $H_2O$  elimination from  $M^+$ :



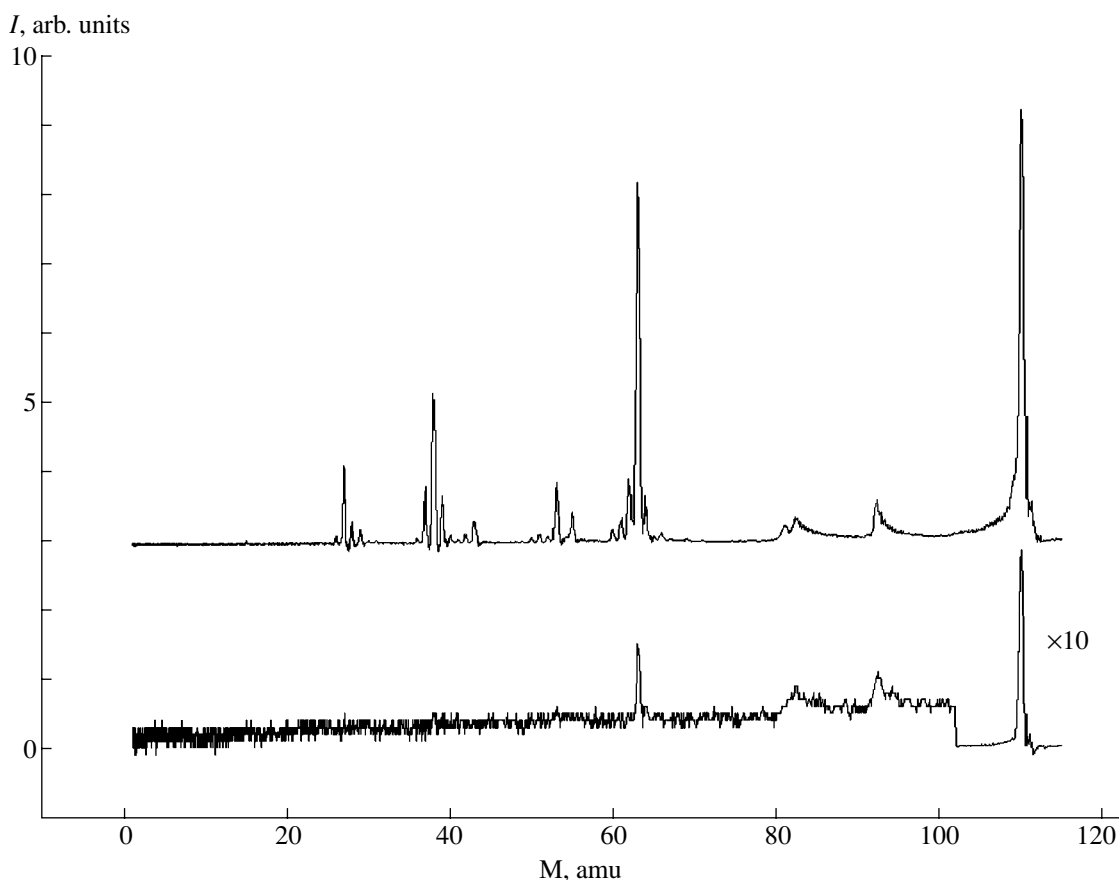
which is the most abundant fragment ion at a radiation flux density of  $\sim 3 \times 10^6$  W/cm<sup>2</sup>. The formation of this ion is due to the intramolecular H-bonding of the catechol, and can be used for analytical purposes to distinguish between the isomers. There are also other differences in the peak intensity distribution in the mass

spectra of catechol and hydroquinone. For example, the ions at  $38^+$  and  $39^+$  of the group of  $C_3H_n^+$  ions are the most abundant for catechol and hydroquinone, respectively, which can also be explained by the easier migration of the H atom to neutral fragments because of H-bonding. The shape of peaks at  $92^+$  and  $82^+$  suggests their formation in the processes of metastable degradation of  $M^+$  with the effective rate constants of  $\sim 10^6$  s<sup>-1</sup>.

The following formation channel is proposed for the ion at  $82^+$ :



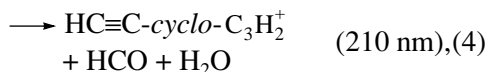
The elimination of CO from  $M^+$  was postulated in the analysis of mass spectra of two-color laser-ionization [14] and electron-ionization [15] mass spectra of phenol. The fragment ion was shown [15] to have the 1,3-cyclopentadiene structure. Thus, we should expect the appearance of an ion with the structure of 1,3-cyclopentadienol. We determined the enthalpy of formation of this ion from the formation enthalpy of the neutral ( $-51$  kJ/mol [16]) and  $I_1$  ( $8.3 \pm 0.3$  eV). The latter value was obtained from the ionization energy of 1,3-cyclopentadiene and typical values of a change in the ionization energy of cyclic compounds with the double bond upon replacement of H by OH. The calculated heat of reaction (2) corresponds to the threshold  $\lambda = 886$  nm; therefore, this channel is opened by the absorption of a single photon over the entire spectral range studied. This conclusion is consistent with the finding that the ion at  $82^+$  appears with the group of ions displayed in the mass spectrum at low radiation intensities. The



**Fig. 3.** Mass spectra of catechol ionized by 283-nm laser radiation at an intensity of  $3 \times 10^6$  (lower spectrum) and  $1.5 \times 10^7$  W/cm<sup>2</sup> (3 and 15  $\mu$ J/pulse, respectively).

alternative formation channel of the 82<sup>+</sup> ion via C<sub>2</sub>H<sub>4</sub> elimination from M<sup>+</sup> involves more complex rearrangement, and by our estimates, is more endothermic. At the same time, we did not observe a similar process upon laser-induced ionization of 1,2-(CH<sub>3</sub>O)<sub>2</sub>C<sub>6</sub>H<sub>4</sub> [2], which may be explained by the absence from this molecule of the hydroxylic H to migrate to the ring.

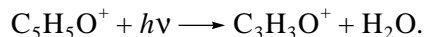
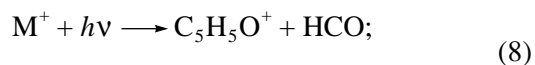
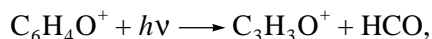
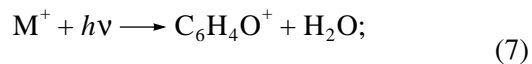
The ions at 81<sup>+</sup>, 63<sup>+</sup>, and 55<sup>+</sup> are assumed to form by the same processes as in the case of hydroquinone ionization:



and the ion at 53<sup>+</sup> which has not been considered previously [1] is presumably formed by

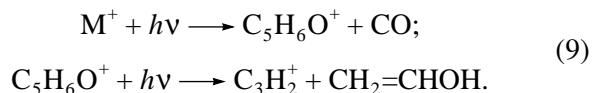


Given in the parentheses are the threshold  $\lambda$  values for the photodissociation of unexcited M<sup>+</sup>. The energy of one photon is sufficient for triggering channels (3), (5), and (6). As in the case of hydroquinone, to initiate process (4), it is necessary that at least two photons be absorbed in the spectral region relevant to this work. The absorption of another photon by M<sup>+</sup>\* with an excitation energy exceeding the threshold values for several dissociation channels is low under our experimental conditions. Therefore, we assume that the second photon is absorbed by the fragment ions at 92<sup>+</sup> or 81<sup>+</sup> having higher absorption cross sections, rather than by the M<sup>+</sup>\* ions:

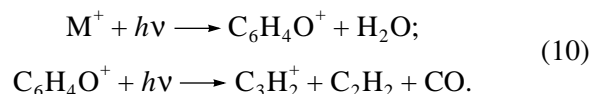


Pathway (7) is absent for hydroquinone, and the ion at 63<sup>+</sup> has a higher abundance in the catechol mass spectrum.

The absorption of two photons is also necessary for the formation of the ions at 38<sup>+</sup>. The elimination of the neutral fragments CO and CH<sub>2</sub>=CHOH is an energetically favored process having a threshold energy of 6.49 eV. To calculate it, we used the formation enthalpy of C<sub>3</sub>H<sub>2</sub><sup>+</sup> equal to 1376 kJ/mol [17]. Based on the above considerations, the process should be assumed to occur via the formation of the intermediate 82<sup>+</sup> ion:



The process involving H<sub>2</sub>O, CO, and C<sub>2</sub>H<sub>2</sub> elimination is more endothermic (threshold energy 7.65 eV), and it also occurs in two steps:



The formation of the ion at 92<sup>+</sup>, which is absent from the mass spectrum of hydroquinone, by ionization of catechol followed by its dissociation via pathway (10) explains the higher abundance of the 38<sup>+</sup> ion in the catechol mass spectrum.

Light hydrocarbon ions contributing considerably to the mass spectrum at the intensities near the upper limit of our experimental range are most probably produced by photodissociation of heavier fragment ions; more definite information on their origin does not seem obtainable at present.

#### ACKNOWLEDGMENTS

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