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Stepwise Photoionization of 1,2-Dimethoxybenzene Vapor

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Abstract—Processes of stepwise ionization of 1,2-dimethoxybenzene vapor by radiation in the range 295–275 nm were studied by the techniques of total current spectroscopy, mass spectrometry, electronic absorption spectroscopy, and threshold electron spectroscopy. A two-step ionization process via the first electronically excited state of the molecule yielding the molecular ion was found to prevail at an average laser radiation intensity less than 10^6 W/cm^2. Molecular ions possess a considerable (up to 1 eV) vibrational excitation energy. As the radiation intensity increases, the progressively stronger and deeper degradation takes place via dissociation of molecular and, probably, fragment ions due to absorption of at least one additional photon.

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 designing theoretical models for interaction of laser radiation with molecules but also for developing analytical methods of superlative sensitivity and selectivity and applying laser photoionization spectroscopy to investigation of intramolecular energy redistribution processes [1].

We have launched studies on the processes of laser-induced ionization of oxygenated benzene derivatives in the vapor phase. In the previous paper [2], we reported the results of ionization of vaporized hydroquinone (1,2-dihydroxybenzene) via the transient S_1 state. The electronic structure of 1,2-dimethoxybenzene o-$(CH_3O)_2C_6H_4$ is close to that of hydroquinone, although the presence of methyl groups as substituents results in a higher density of vibrational states in that electronic state which is intermediate in ionization and can thus alter the photophysical characteristics of its molecule and the energy accumulation mechanism.

Breen *et al.* [3] used two-step ionization of 1,2-dimethoxybenzene to resolve the structure of the S_0–S_1 transition 0–0 band due to excitation of torsional vibrations of CH_3O groups. They obtained only the spectral dependence of molecular-ion current in the two-step ionization of a supersonic beam in a narrow spectral range near the 0–0 transition of the first absorption band.

EXPERIMENTAL

The laser photoionization spectrometer and the experimental procedure used in this work are described elsewhere [2, 4]. 1,2-Dimethoxybenzene vapor at a pressure of about 10^{-4} Pa and a temperature of 300 K was ionized by a focused radiation 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 laser energy per pulse was varied from 2 to 50 μJ. The experimental setup allowed spectral dependences for total ionization current and threshold electron (with the kinetic energy close to zero) current, mass spectra, and photoelectron spectra to be obtained.

The absorption spectrum of 1,2-dimethoxybenzene vapor in a bath gas (3000–6000 Pa Xe) was obtained on a laboratory spectrometer based on a commercial complex KSVU with a King oven-type heated cell having quartz windows. The resolution for recording spectra was 1 nm, and a temperature was about 350 K.

Quantum-chemical calculations were performed by the ZINDO/S CI method using the ground state geometry determined by the analysis of HeI photoelectron spectra [6].

The enthalpies of formation of charged and neutral species used in thermochemical calculations were borrowed from Takhistov [6] unless otherwise stated, and the enthalpy of formation of 1,2-dimethoxybenzene was taken as 215.9 kJ/mol [7].

RESULTS AND DISCUSSION

Figure 1 shows the absorption spectrum and spectral dependence of the total ionization current and the threshold electron current normalized to the light flux. The contribution of resonance processes to the total current does not exceed 1% over the entire spectral region. The quantum-chemical calculations allowed the absorption in the examined spectral region to be assigned to the $S_1(^1A_1) \leftarrow S_0(^1A_1)$ $\pi\pi^*$ transition. The absorption spectrum was obtained at a higher temperature as compared to the ionization spectra. A larger contribution of hot transitions from thermally populated S_0 levels is responsible for enhanced relative intensity of the long-wavelength part of absorption spectrum.

The difference between ionization and absorption spectra is also observed on the short wavelength side of
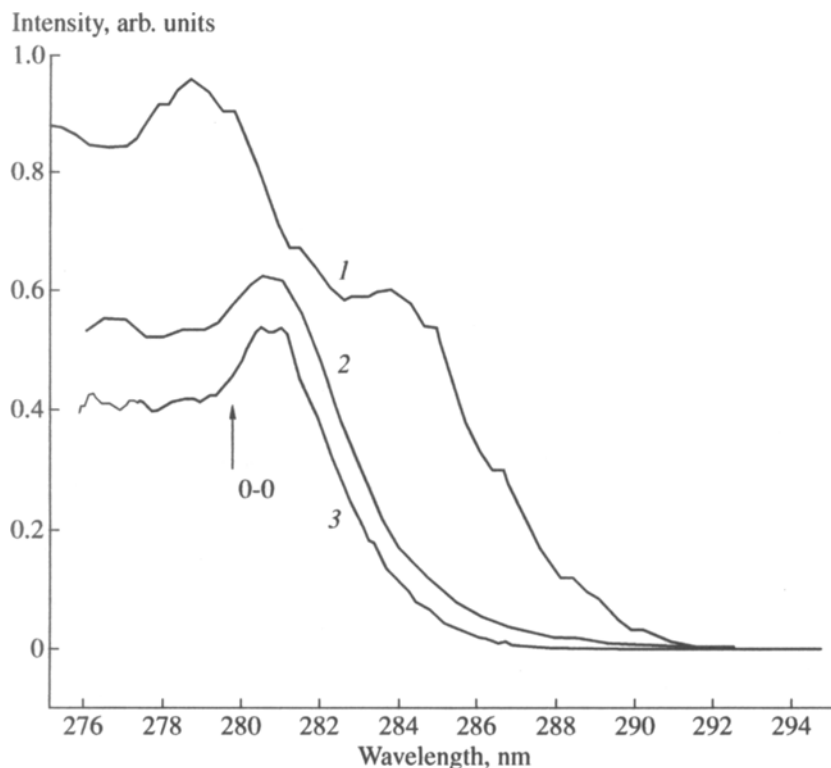
Intensity, arb. units

Fig. 1. (*1*) Absorption spectrum and spectral dependence of (*2*) the total ionization current and (*3*) the threshold electron current of 1,2-dimethoxybenzene vapor.

the 0–0 transition band. The absorption maximum at 278.7 nm is shifted with respect to the 0–0 band of the $S_1 \leftarrow S_0$ transition (279.81 nm) toward shorter wavelengths, and the ionization spectra show a small red shift of the maximum. The difference is not surprising since the spectral dependences of ionization currents are determined not only by the absorption spectrum but also by a variation in distribution of molecules over vibrational levels in the preionization state S_1 and in the probability of ionization transitions from these levels, depending on laser radiation frequency.

The adiabatic ionization energy (I_1) of 1,2-dimethoxybenzene is 7.61 eV [7]; so, the absorption of two photons at an energy higher than 3.8 eV will be sufficient for generating the molecular ion. As we can see in Fig. 1, the observed ionization threshold corresponds to a higher energy (~4.2 eV) and is determined by the probability for absorption of first photon in the $S_1 \leftarrow S_0$ transition by thermally excited molecules.

The absence of electrons with a kinetic energy (ε) greater that $2E - I_1$ (where E is the photon energy) from photoelectron spectra over the entire range of light intensity (Fig. 2) suggests that molecular ions M^+ are indeed produced only via two-photon ionization of the molecule M:

$$M + 2h\nu \longrightarrow M^+ + e(\varepsilon).$$
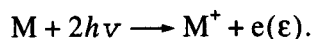
Therefore, the ladder climbing mechanism of generation of M^+ upon absorption of three or more photons can be ruled out.

In Fig. 2, the photoelectron spectra obtained at an identical wavelength but different laser radiation intensities are compared. Molecular ions are predominantly produced at a low power density of exciting radiation, whereas the contributions of molecular and fragment ions become comparable at a high density (Fig. 3). Within the limits of precision, the spectra are indistinguishable. This allows us to conclude that, as in the case of laser ionization of hydroquinone, the major pathway of formation of fragment ions is photodissociation of molecular and, probably, heavy fragment ions.

Note that M^+ ions generated by laser ionization have a broad vibrational energy distribution $E_v = 2E - I_1 - \varepsilon$ in the ground electronic state. At a wavelength $\lambda = 280.9$ nm ($E = 4.41$ eV), there is the maximum probability of formation of M^+ with $E_v = 0.61$ eV, and at $\lambda = 266.1$ nm ($E = 4.66$ eV), the most abundant ions have $E_v = 1.04$ eV. The half-widths of the distributions also somewhat increase (from 0.4 to 0.5 eV) with increasing the photon energy (from λ of 280.9 to 266.1 nm, respectively). The distributions are narrower than those in the HeI photoelectron spectra [5]. This indicates that the equilibrium configuration in the S_1 state is interme-
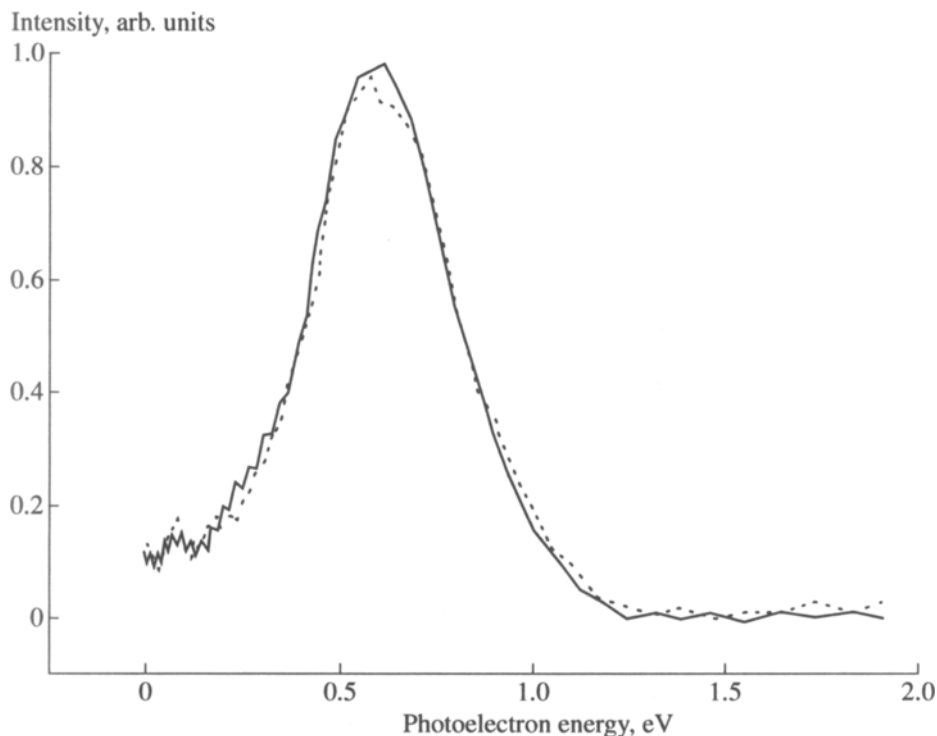
Fig. 2. Photoelectron spectra of 1,2-dimethoxybenzene vapor ionized by 280.9-nm radiation at a laser energy of (dashed line) 3 and (solid line) 13 µJ/pulse.

diate between equilibrium configurations of the ground states of M and M$^+$.

Figure 3 shows representative mass spectra of ions generated by 280.9-nm laser radiation in the 0–0 band of the $S_1 \leftarrow S_0$ transition. The pattern of change in mass spectra remains qualitatively the same for other photon energies. As in the case of hydroquinone studied previously [2], the severity of fragmentation of M$^+$ is strongly enhanced by increasing the power density of laser radiation.

At the lower fluence limit, the most abundant fragment ion is the one having a mass number of 123 corresponding to detachment of CH$_3$ group from M$^+$. The appearance energy of this ion is equal to 9.03 eV, as determined by the one-photon photoionization mass spectrometry [7], which corresponds to a two-photon ionization threshold wavelength of 274.6 nm. However, the ion (M–CH$_3$)$^+$ is also observed in mass spectra at $\lambda > 274.6$ nm, and the extrapolation of the 123$^+$/M$^+$ ionic current intensity ratio to zero fluence by five sets of measurements at different wavelengths gives the value 0.02 ± 0.02. Therefore, we believe that the contribution of the two-quantum ionization process yielding the ions at 123$^+$ is insignificant under the given experimental conditions and the observed peaks at mass number 123 in the mass spectra are due to photodissociation of M$^+$:

$$M^+ + h\nu \longrightarrow C_7H_7O_2^+ + CH_3 \quad (1.42 \text{ eV}). \quad (1)$$
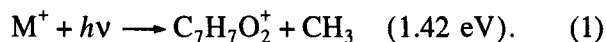
Given in the parentheses is the threshold energy for photodissociation of unexcited M$^+$, as calculated from thermochemical data. This threshold value suggests that it is sufficient to absorb one photon by the molecular ion to open up channel (1). The process of detachment of radicals R, such as H, CH$_3$, and C$_2$H$_5$, was also observed upon laser ionization of RO-monosubstituted benzenes [8–11]. In agreement with our results, its was assumed in all cases that ionization follows the two-photon ionization–M$^+$ photodissociation mechanism.

With low light fluxes, ion peaks having a lower intensity appear at mass numbers 95, 80, 65, and 41 (Fig. 3). The formation processes of these ions, at least at the lower limit of laser radiation intensity, involve one-photon dissociation of M$^+$. The ion peak at 95$^+$ is broadened on the side of higher mass (Fig. 3), which indicates that the formation takes place not only in the ionization space but also in the acceleration area upon traveling of the predecessor ion to the drift space. In contrast, the peak at 123$^+$ is broadened on the low mass side, which is explained by the metastable degradation 123$^+$ $\longrightarrow$ 95$^+$ in the region between the drift space and the detector. Observation of the metastable degradation allows the sequence of processes M$^+$ $\longrightarrow$ 123$^+$ $\longrightarrow$ 95$^+$ induced by photon absorption to be unambiguously detected. The mass number 95 corresponds to two possible empirical formulas of ions, C$_6$H$_7$O$^+$ and C$_5$H$_3$O$_2^+$. Generation processes of these ions may be as follows:
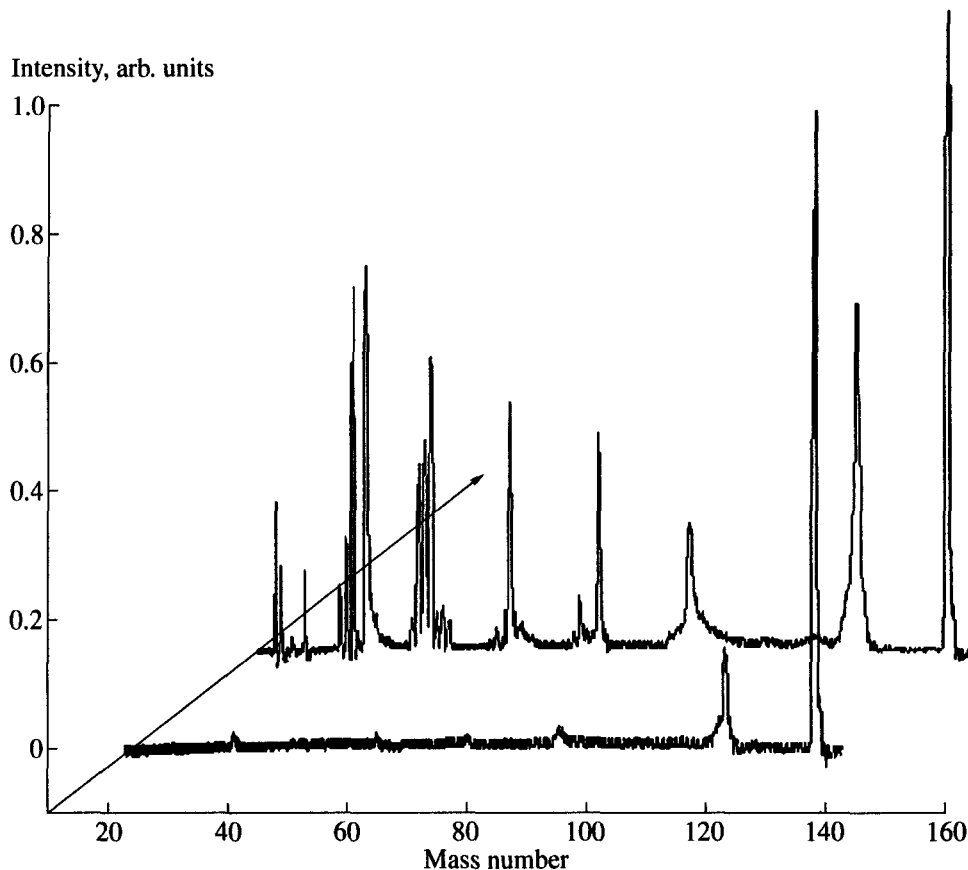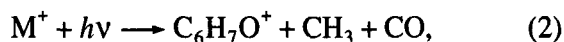
Fig. 3. Mass spectra of 1,2-dimethoxybenzene ionized in the vapor phase by 280.9-nm laser radiation at an energy of 3 (lower spectrum) and 13 μJ/pulse (upper spectrum).

$$M^+ + h\nu \longrightarrow C_6H_7O^+ + CH_3 + CO, \qquad (2)$$

$$\longrightarrow C_5H_3O_2^+ + CH_3 + C_2H_4. \qquad (3)$$

Process (3) rather than (2) includes a much more complex skeletal rearrangement of M^+. In addition, the collision-induced dissociation mass spectra of ions at 95^+ generated from 1,2-dimethoxybenzene by electron impact reportedly resemble those of protonated phenol $C_6H_5OHH^+$ [12]. Therefore, process (2) should be preferred. The threshold energy is estimated from the proton affinity (829 kJ/mol [13]) and the formation enthalpy (–96 kJ/mol [14]) of phenol at 2.59 eV; so, reaction (2) can indeed proceed as a one-photon process in the spectral region of our interest.

The mass number 80 also corresponds to two possible empirical formulas, $C_6H_8^+$ and $C_5H_4O^+$. It is more likely that the hydrocarbon ion forms, having the structure of 1,3-cyclohexadiene cation. Neutral fragments cannot be unequivocally detected; nonetheless, the least endothermic process is

$$M^+ + h\nu \longrightarrow cyclo\text{-}C_6H_8^+ + H_2CO + CO \qquad (4)$$

$$(1.73 \text{ eV}).$$
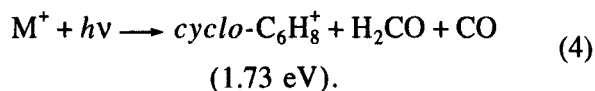
The threshold energy was calculated using the ionization energy of 9.29 eV [15] and the formation enthalpy of 108 kJ/mol [14] for 1,3-cyclohexadiene. Note that the formation of the $C_5H_4O^+$ ion having the cyclopentadienone cation structure cannot be ruled out from the thermodynamic point of view. The spontaneous or photon absorption-induced dissociation of $C_8H_8^+$ ions can yield light hydrocarbons ions prevailing in mass spectra at high laser radiation intensities.

The ion at 65^+ is certainly the hydrocarbon ion $C_5H_5^+$ having the most stable cyclic structure. In the electron ionization mass spectrum, its formation is associated with the degradation of M^+ by successive elimination of CH_3, CO, and H_2CO [16]. Our data are consistent with this mechanism.

$$M^+ + h\nu \longrightarrow cyclo\text{-}C_5H_5^+ + CH_3$$
$$+ H_2CO + CO \quad (4.86 \text{ eV}). \qquad (5)$$
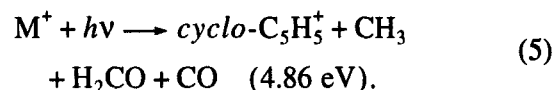
Although channel (5) is closed for unexcited M^+ in terms of energy consideration, we have shown above that the excitation energy of ions generated via two-photon ionization of M^+ is sufficient to open this chan-

nel over the entire spectral range examined. The proposed mechanism of formation of ions 65^+ agrees with the observation of low-intensity tailing toward higher masses for most of the obtained mass spectra, which may be explained by the metastable degradation $95^+ \longrightarrow 65^+ + H_2CO$ with a rate constant of the order of 10^7 s^{-1}.

The ion at 41^+ can also have two empirical formulas, $C_3H_5^+$ or OC^+CH. The formation of a hydrocarbon ion seems to be the most probable. The most stable ion is $CH_2=CHCH_2^+$ [6] and, of the neutral fragments having the empirical formula $C_5H_5O_2$, the most stable species is the radical $\cdot C(O)CH=CHCH_2C(O)H$ with the enthalpy of formation of -83.7 kJ/mol [17] The threshold energy for photodissociation of M^+ yielding the aforementioned fragments is equal to 3.52 eV, i.e., it can be initiated by absorption of one photon. However, the energetics admits that the $C_3H_5^+$ ion can form by one-photon dissociation of M^+ in combination with other neutral fragments.

At a laser radiation energy exceeding ≈ 10 μJ/pulse, peaks due to hydrocarbon ions $C_2H_4^+$, $C_2H_3^+$, $C_4H_2^+$, $C_4H_3^+$, $C_4H_4^+$, etc. have an intensity comparable to that of the mass spectral peaks considered above (Fig. 3). The formation process of these ions can involve the dissociation of both M^+ and heavier fragment ions triggered by absorption of one or more photons. Their variety and the lack of information do not allow us to speculate on the particular nature of such processes.

Despite the identical mechanism of energy accumulation (ionization–dissociation), the laser ionization mass spectra of hydroquinone [2] and 1,4-dimethoxybenzene strongly differ over the entire studied range of laser energy fluence.

ACKNOWLEDGMENTS

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