Stepwise Ionization of the 2,4-Dioxybenzaldehyde and 3,4-Dimethoxypropiophenone Vapors

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Abstract—The processes of stepwise ionization of the 2,4-dioxybenzaldehyde and 3,4-dimethoxypropiophenone vapors by radiation in the range of wavelengths down to 266 nm were studied using total-current spectroscopy, mass spectrometry, and photoelectron spectroscopy. The process of two-step ionization and the resulting generation of molecular ions are dominant if the laser-radiation intensity amounts to $\approx 10^6$ W/cm^2. These molecular ions have appreciable (up to 1.8 eV) energy of vibrational excitation. As the laser-radiation intensity increases, progressively more pronounced fragmentation occurs owing to dissociation of molecular (and, possibly, fragmentation) ions as a result of absorption of at least a single additional photon. The processes leading to fragmentation of ions are suggested. It is found that the dissociation–ionization mechanism is important for the dimethoxypropiophenone. Dissociation with a breakage of the α bond in the carbonyl group with subsequent two-photon ionization of the fragments occurs when the $S_2(^1A')$ state of the $\pi\pi^*$ type is excited. © 2002 MAIK "Nauka/Interperiodica".

INTRODUCTION

We have previously studied the stepwise ionization of vapors of certain dioxy- and dimethoxy-benzene derivatives and have shown that ionization via the intermediate S_1 state occurs according to the ionization–dissociation mechanism [1, 2]. For all the studied [1, 2] molecules, the electron structure of lower levels of the cation neutral state is related to excitation (removal) of electrons. At the same time, the stepwise-ionization mechanism depends on the spectral and kinetic characteristics of intermediate states [3]; these characteristics are controlled by the electronic nature of corresponding states [4]. It is typical of aromatic aldehydes and ketones that they have closely spaced states of the $n\pi^*$ and $\pi\pi^*$ types. It was the objective of this study to investigate the effect of the low-lying $n\pi^*$-type levels of the neutral state and molecular ion on the mechanism of the energy acquisition and fragmentation in molecules when vapors are ionized by laser irradiation.

The laser ionization of vapors of some of the aromatic aldehydes and ketones has been studied [5–12]. Benzaldehyde has been studied in most detail. When the molecule is excited to the $T_1(n\pi^*)$ [12] or $S_1(n\pi^*)$ [6, 11] states, ionization occurs according to the ionization–dissociation mechanism. Processes occurring according to the dissociation–ionization mechanism have been detected on excitation to the $S_2(\pi\pi^*)$ and $S_3(\pi\pi^*)$ states [5, 7–12]. Relative contributions of the two mechanisms depend on experimental conditions.

For the simplest representatives of aromatic aldehydes and ketones (benzaldehyde and acetophenone), the sequence of lower electron states of molecular ions (M^+) has not been uniquely determined, because the ionization transitions to these states from the molecules' ground states form a single, almost structureless, band in the photoelectron spectra [13–15]. Therefore, we chose 2,4-dioxybenzaldehyde and 3,4-dimethoxypropiophenone as the compounds to study; in these compounds, the ionization transitions of the $(n)^{-1}$ type are separated in energy from at least one of the two transitions of the $(\pi)^{-1}$ type [16]. This makes it possible to attempt to study the effect of the electronic state of the ion on its decomposition.

EXPERIMENTAL

Experiments were performed using a laser photoinization spectrometer described elsewhere [1, 2, 17]. The vapor ionization under a pressure of ~10^{-4} Pa and at a temperature of about 320 K was accomplished using the focused radiation of the second harmonic of an LZhI-506 dye laser pumped by the second harmonic (532 nm) of an LTIPCh solid-state laser. We used the rhodamine 6G and B dyes, which made it possible to tune the wavelength λ in the range of 275–315 nm. The wavelength scale was calibrated using a PRK-4 mercury lamp accurate to within 0.05 nm and was checked with the use of the known reference points in the spectra of stepwise ionization of the Rb vapor. The smallest scanning step for the wavelength λ was 0.01 nm, the duration of the ultraviolet-radiation pulse was 12 ns, the energy in a pulse was 1–60 μJ, and the diameter of the focused laser beam was ~0.1 mm. The radiation of the fourth harmonic (266 nm) of the solid-state laser was also used for ionization.

In order to analyze the mass spectrum of ions and the energy spectrum of electrons, we used the time-of-flight method with the drift-region length being equal to 0.45 m. The spatially separated particle packets fall onto a chevron pair of microchannel plates, the signal from which is fed to a Pico-200-100 analog-to-digital converter that has a time resolution of 10 ns. The data acquisition, accumulation, and processing were performed using an IBM PC 486.

The field in the ionization region was 200 V/cm during the mass analysis, whereas the field gradient in the same region was no higher than 0.02 V/cm when the electron-energy spectrum was analyzed; the vapor pressure and the laser-radiation intensity were chosen so that the effect of the space charge was negligible. The resolution in the energy analysis of photoelectrons was determined from the spectra of stepwise ionization of Rb using both components of the $6^2P_{3/2, 1/2}$ state. The full width of the peaks at half-maximum was 0.04 eV at the energy of 0.56 eV, and increased to 0.15 eV at an energy of 1.70 eV.

The absorption spectrum of the organic-compound vapors in a buffer gas (3000–6000 Pa of Xe) was measured for wavelengths down to 200 nm using a laboratory spectrometer based on a KSVU commercial installation equipped with a heatable cell (of the King type) with quartz windows. The spectra were measured at a temperature of about 350 K with a resolution of 1 nm.

The quantum-chemical calculations of excited states were performed on the basis of the ZINDO/S CI method using the ground-state geometry optimized according to the MINDO3 method.

RESULTS AND DISCUSSION

In Fig. 1, we show the absorption spectra and the spectral dependences of the total ionization current for the 2,4-dioxybenzaldehyde (DOB) and 3,4-dimethoxypropiophenone (DMP) vapors; the latter dependences were normalized to the squared luminous flux. Two absorption bands peaked at 311 and 269 nm for DOB and at 305 and 259 nm for DMP fall within the spectral range of our experiments. These bands are structureless. The peaks of the first absorption bands are appreciably shifted in reference to the long-wavelength cutoffs, which indicates that the equilibrium configurations of molecules are changed markedly as a result of excitation. The same is also true for the second DMP band. The corresponding band in the DOB spectrum features a much steeper falloff from the peak to longer wavelengths; this means that the equilibrium configurations of the ground and excited states are close to each other for DOB.

Quantum-chemical calculations made it possible to attribute the bands in the DOB spectrum to the $S_2(^1A') \longleftarrow S_0(^1A')$ and $S_3(^1A') \longleftarrow S_0(^1A')$ transitions of the ππ* type. According to the calculations, the lowest singlet excited electron state $S_1(^1A'')$ of the nπ* type is

located below the S_2 state by 1 eV; however, the $S_2(ππ*) \longleftarrow S_0$ state does not manifest itself in the absorption spectra we measured, because, according to the available data for benzaldehyde, the absorption coefficient for transition to the nπ* state is smaller than that for the ππ* transition by a factor of 60–70. In addition, the calculations indicate that no less than four triplet states terms are located in the energy region below $S_2(ππ*)$, with the lowest of these terms being represented by a level of the ππ* type. The inference about the ππ* type of the T_1 state in the oxy- and methoxybenzaldehyde derivatives had been made [18] on the basis of measurements of the phosphorescence in frozen solutions. At the same time, taking into account differences in the exactness of calculations of the singlet and triplet states, we may assert that the $T_1(ππ*)$ and $T_2(nπ*)$ states of oxybenzaldehydes are nearly degenerate (see, for example, [19]).

Arrows in Fig. 1 indicate the threshold wavelengths that correspond to the values of $0.5I_i$ ($i = 1, 2$), where I_i are the adiabatic energies of ionization accompanied with the generation of molecular ions in the ith electronic state. These energies were estimated to within ±0.1 eV using the HeI photoelectron spectra [16]. For DOB, the halved value (≈4.3 eV) of the first adiabatic ionization energy exceeds the energy of the peak of the first absorption band; thus, the ionization threshold is controlled by the adiabatic ionization energy. However, a sharp increase in the current in the vicinity of 282 nm coincides with the onset of the second absorption band. For DMP, the long-wavelength absorption cutoff coincides with $0.5I_1$; as a result, a peak corresponding to the $S_2 \longleftarrow S_0$ transition appears in the total-current spectral dependence. The shift of this peak in reference to the peak in the absorption spectrum may be explained by an increase in the cross sections for ionization of vibronic states as λ decreases; these states become occupied when the first photon is absorbed. A subsequent increase in the current in the vicinity of 285 nm sets in at a somewhat smaller wavelength than the onset of the second absorption band in DMP, which is caused by an increase in the ionization cross section due to the generation of M$^+$ ions in their first excited electronic state. The aforementioned special features of the total-current spectral dependences indicate that the laser-induced ionization is initiated by photon absorption in the $S_2 \longleftarrow S_0$ and $S_3 \longleftarrow S_0$ transitions.

Under comparable experimental conditions (similar pressures and luminous fluxes), the currents observed in DOB and DMP subjected to laser-induced ionization are much lower than those recorded previously for the dioxy- and dimethoxy-benzene derivatives [1, 2]. The same relation between the currents in the case of 266-nm laser ionization of benzaldehyde and 4-oxybenzaldehyde compared to that of phenol has been reported [7]. A decrease in the efficiency of stepwise ionization is caused by the redistribution of energy in the intermediate state with formation of the products
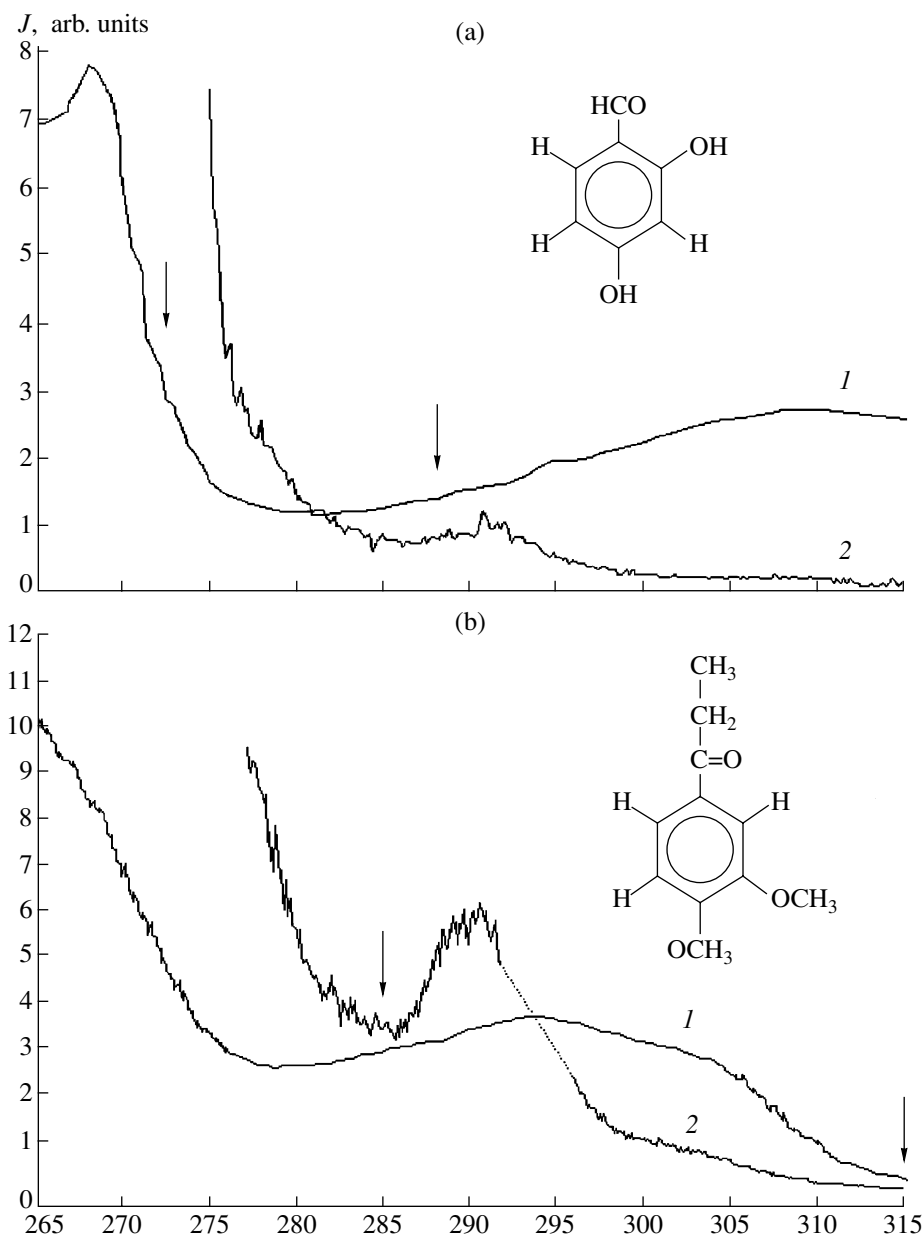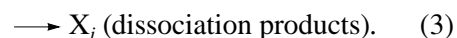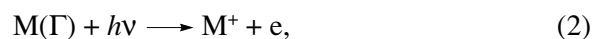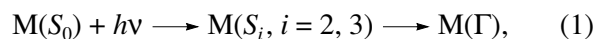
Fig. 1. The (*1*) absorption and (*2*) total current spectra of (a) 2,4-dioxybenzaldehyde and (b) 3,4-dimethoxypropiophenone.

whose ionization is impaired under experimental conditions. In particular, this redistribution may be related to the dissociation processes. Since the highest photon energy in our experiments is 4.66 eV and the fragment-ionization energy exceeds this value, the fragments can be ionized only as a result of absorption of two photons. This is unlikely, at least in the lower part of the luminous-flux range. Indeed, by reducing the laser-radiation intensity, we managed to attain complete (to within the background-signal amplitude) absence of the fragmentation ions in the mass spectra of DOB and DMP. Thus, for low luminous fluxes, the scheme of processes

occurring during laser excitation of the DOB and DMP vapors can be represented as

$$M(S_0) + h\nu \longrightarrow M(S_i, i = 2, 3) \longrightarrow M(\Gamma), \quad (1)$$

$$M(\Gamma) + h\nu \longrightarrow M^+ + e, \quad (2)$$

$$\longrightarrow X_i \text{ (dissociation products).} \quad (3)$$

In this scheme, we take into account the fact that the state Γ (initial for ionization and dissociation) may differ from the state which is optically populated owing to intramolecula energy redistribution. Process (3) does
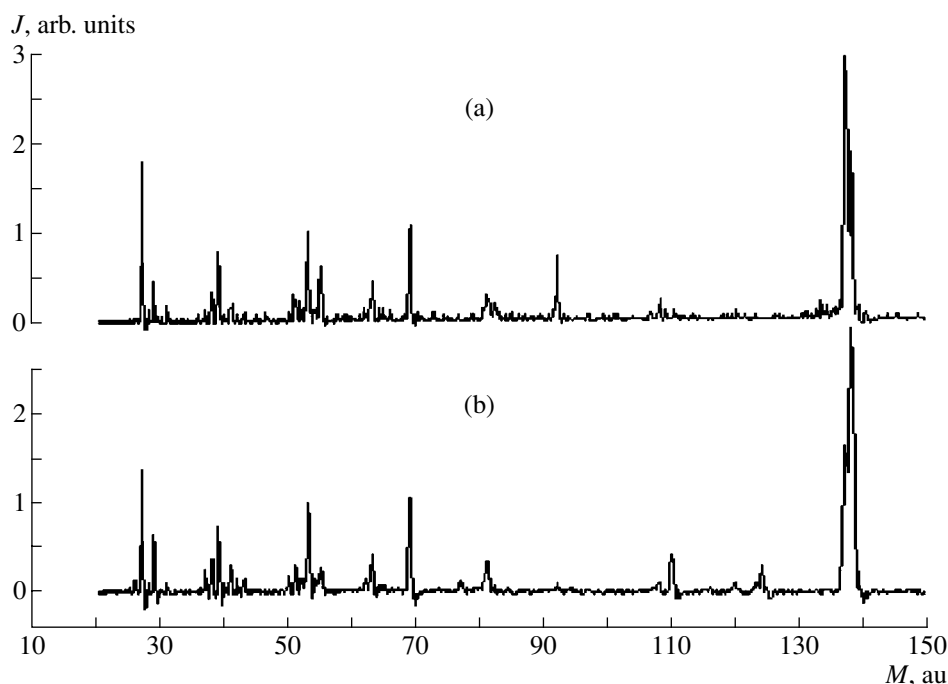
Fig. 2. The mass spectra of stepwise ionization of 2,4-dioxybenzaldehyde for ionization via the (a) S_2 and (b) S_3 intermediate states for the luminous flux amounting to $\sim 7 \times 10^6$ W/cm^2.

not contribute to the recorded currents but affects the ionization efficiency.

In the upper part of the luminous-flux range, neutral fragments X_i can be ionized as a result of two-photon absorption; i.e.,

$$X_i + 2h\nu \longrightarrow X_i^+ + e. \qquad (4)$$
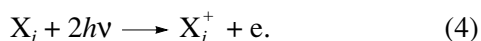
As the radiation intensity increases, the rate of process (4) becomes higher; however, dissociation yield $k/(k + \sigma_i\Phi)$ (where k is the rate constant of dissociation for all available channels, σ_i is the cross section of the intermediate-state ionization, and Φ is the photon-flux density) becomes lower compared to the channel of intermediate-state ionization (2). We can state that the relative contribution of two ionization mechanisms varies with increasing radiation intensity only after an analysis of the kinetics for processes (1)–(4). However, the information needed for such analysis is lacking. Notably, the M^+-ion signal is most intense in the mass spectra obtained under the luminous flux that is available in our experiments. Therefore, the ionization–dissociation mechanism is effective in the entire intensity range.

As far as we know, photodissociation of the DOB and DMP vapors has not been studied. If benzaldehyde is excited to the S_2 and S_3 states, the CO group becomes split off with a high quantum yield [20]; the photochemistry of acetophenone is related to the breakage of the $C_6H_5C(O)$–CH_3 bond [21]. Dissociation occurs from the triplet state (states) with the rate constants that

are no larger than 5×10^7 s^{-1} [9, 20, 21]. The 110^+ and 165^+ ions are observed in the mass spectra of the laser-induced ionization of DOB and DMP, respectively; the emergence of these ions may be attributed to ionization of fragments produced by dissociation from the intermediate state via the channels that are similar to those mentioned above (Figs. 2, 3). However, these ions can also be generated owing to photodissociation of M^+ groups. It is noteworthy that a contribution of dissociation from the intermediate state to the charged-particle current may be significant only under the condition that $k \geq \sigma_i\Phi$.

If this condition is satisfied, the photoelectron spectra of the laser-induced ionization should depend on the luminous flux because the intermediate-state and dissociation-fragment spectra do not generally coincide. A low level of electron signal with energy resolution made it possible to obtain only photoelectron spectra of a rather low quality (Figs. 4, 5). For DOB, the intensity distribution in the photoelectron spectrum at $\lambda = 266$ nm does not change more than 10% when the irradiation intensity is increased by a factor of 6. Arrows in Figs. 4 and 5 indicate the electrons' kinetic energies ε that correspond to the formation of unexcited M^+ ions from unexcited molecules as a result of two-photon absorption: $\varepsilon_m = 2h\nu - I_1(M)$. Electrons with high kinetic energies are not observed in the spectra. An appreciable fraction of electrons have a kinetic energy in the range of 0–0.5 eV, which corresponds to genera-
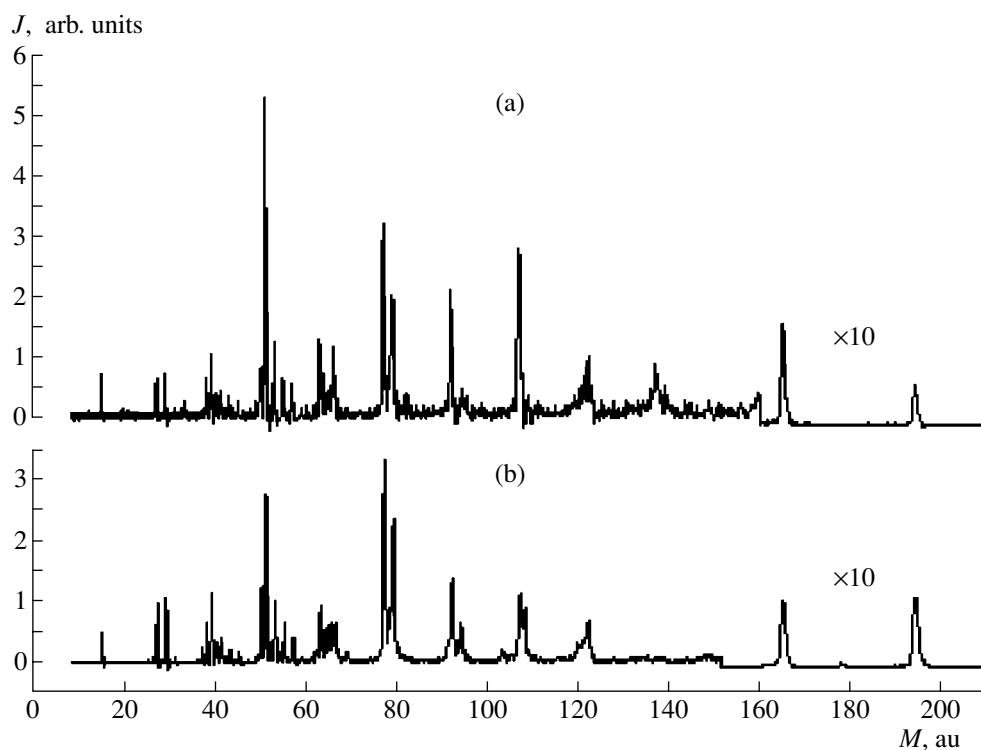
Fig. 3. The mass spectra of stepwise ionization of 3,4-dimethoxypropiophenone for ionization via the (a) S_2 and (b) S_3 intermediate states for the luminous flux amounting to $\sim 8 \times 10^6$ W/cm^2.
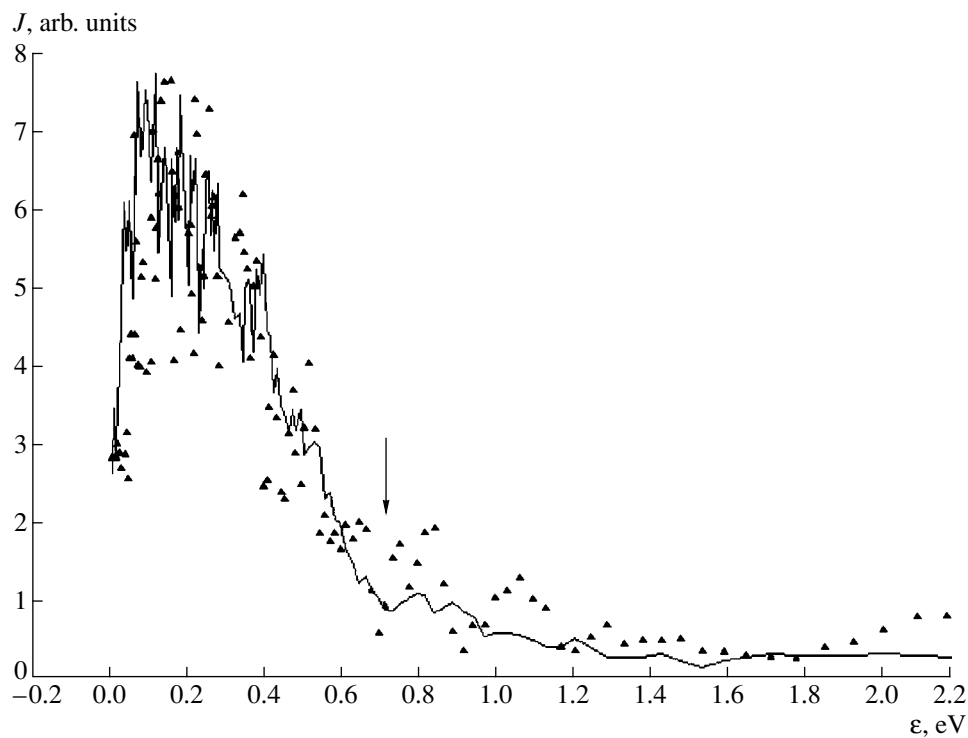

Fig. 4. The photoelectron spectra of 2,4-dioxybenzaldehyde under excitation with $\lambda = 266$ nm and for the luminous fluxes amounting to $\sim 2 \times 10^6$ W/cm^2 (triangles) and $\sim 1.2 \times 10^7$ W/cm^2 (the solid line).
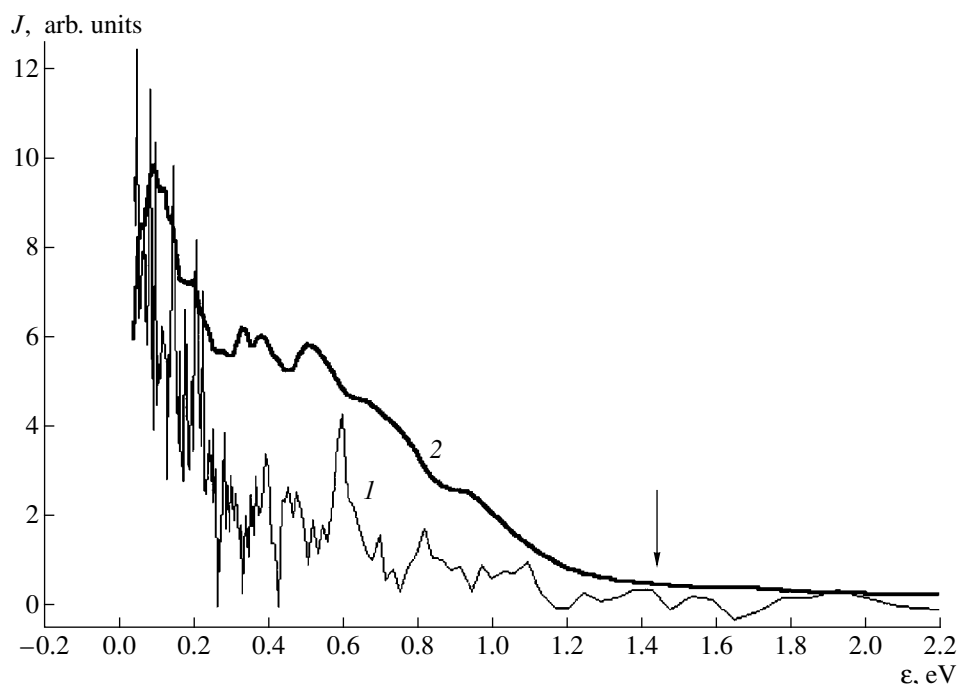
Fig. 5. The photoelectron spectra of 3,4-dimethoxypropiophenone irradiated with photons of $\lambda = 266$ nm for luminous fluxes amounting to (*1*) $\sim 2 \times 10^6$ and (*2*) $\sim 2 \times 10^7$ W/cm^2.

tion of the M$^+$ ions with the excitation energies in the range of 0.3–0.8 eV.

Electrons with $\varepsilon < \varepsilon_m$ are also dominant in the photoelectron spectra of DMP. We emphasize that an increase in λ brings about a shift of ε_m in the photoelectron spectra; this shift is linearly proportional to the photon energy. For low luminous fluxes, an increase in the electron current in the energy range corresponding to formation of electron-excited M$^+$ ions with $I_2 \approx$ 8.7 eV is observed in the spectra obtained under excitation with $\lambda = 266$ and 275 nm for low luminous fluxes. However, in contrast to DOB, a significant increase in the fraction of electrons with energies in the range of 0.3–1.0 eV is observed in the photoelectron spectra of MDP as the luminous flux increases (Fig. 5). Such changes may be caused by both the two-photon ionization of the products of dissociation from the intermediate state and the processes of intramolecular energy redistribution in this state, which do not induce the dissociation.
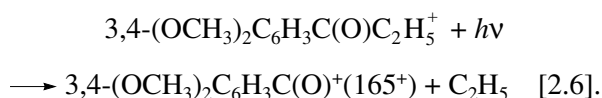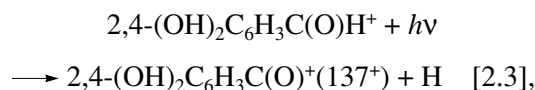
In any case, a discrepancy between the DOB and DMP photoelectron spectra should be caused by special features of nonradiative transitions after light-induced population of the states. A DOB molecule belongs to the class of bifunctional derivatives of benzene with an intramolecular H bond; for these derivatives, in contrast to other aromatic aldehydes, fluorescence with a large Stokes shift is observed if the $S_2(\pi\pi^*) \longleftarrow S_0$ transition is excited [22–26]. This fluo-

rescence is related to radiative transition from the $S_2(\pi\pi^*)$ state after a fast intramolecular proton transport. Such fluorescence was observed under excitation of the 2-oxybenzaldehyde vapors [25, 26] whose electronic structure is close to that of DOB. In this case, the rate constant for the proton transport is equal to $\sim 10^9$ s^{-1} and is controlled by the competition with the internal conversion $S_2(\pi\pi^*) \longrightarrow S_1(n\pi^*)$ [23]. An intense phosphorescence (rather than fluorescence) with characteristics typical of radiative decay of the $T_1(n\pi^*)$ state was observed in propiophenone under excitation to the $S_2(\pi\pi^*)$ and $S_3(\pi\pi^*)$ states [27]. If these special features of nonradiative transitions are retained for the molecules under investigation, we should expect that the singlet states in the state Γ initial for ionization have a larger weight in DOB than in DMP.

Although an analysis of experimental data does make it possible to completely exclude a certain contribution of the dissociation–ionization mechanism to the results of our experiments, we attempt to identify the processes of formation of the fragmentation ions in terms of the ionization–dissociation mechanism. To this end, we employ the model (used widely in mass spectrometry) that implies that dissociation of ions via the least endothermic channels is predominant (see, for example, [28]). We take into account the steric inhibitions by giving preference to the processes that are unrelated to the motion of heavy ions to large distances. When estimating the heat of reactions, we used the published values of the enthalpies of formation [28, 29].
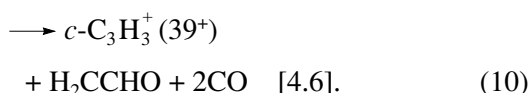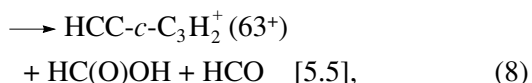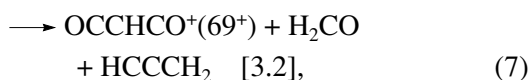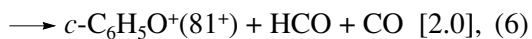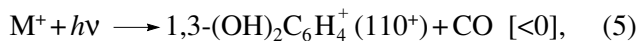
The unavailable values were estimated using the group-contribution method [28]; for ions, the HyperChem 5.0 software package for quantum-chemical calculations was used. The test calculations of ions with known enthalpies of formation showed that the calculated values were overestimated by no larger than 20–40 kJ/mol. When analyzing the formation channels for light fragmentation ions, we considered not only the M^+ ions but also the fragmentation ions whose concentration was comparable to the concentration of the M^+ ions for low luminous fluxes.

The most intense fragmentation-ion signals in the mass spectra in the entire studied range of luminous fluxes are those of the ions corresponding to the breakage of one of the α bonds in the M^+ carbonyl group:

$$2,4\text{-}(OH)_2C_6H_3C(O)H^+ + h\nu$$

$$\longrightarrow 2,4\text{-}(OH)_2C_6H_3C(O)^+(137^+) + H \quad [2.3],$$

$$3,4\text{-}(OCH_3)_2C_6H_3C(O)C_2H_5^+ + h\nu$$

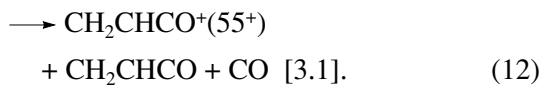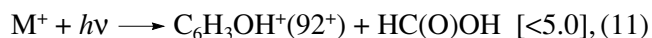$$\longrightarrow 3,4\text{-}(OCH_3)_2C_6H_3C(O)^+(165^+) + C_2H_5 \quad [2.6].$$

The values of the threshold energies for the formation of the fragmentation ions under the conditions of ionization of unexcited molecules are given in the brackets and are expressed in electronvolts. We note that these values are independent of the fragmentation mechanism. Absorption of a single photon by an M^+ group is sufficient for generation of the above ions in the entire spectral range of our studies. The 109^+ ion corresponding to the breakage of the second α bond is absent in the DOB mass spectrum. The similar 137^+ ion $(3,4\text{-}(CH_3O)_2C_6H_3^+)$ becomes distinguishable in the DMP mass spectrum only if ionization is accomplished by radiation with $\lambda > 300$ nm, which will be explained below.

The following formation processes are suggested for other characteristic fragmentation ions in the mass spectrum of the DOB laser-induced ionization at $\lambda = 266$ nm:

$$M^+ + h\nu \longrightarrow 1,3\text{-}(OH)_2C_6H_4^+ (110^+) + CO \quad [<0], \quad (5)$$

$$\longrightarrow c\text{-}C_6H_5O^+(81^+) + HCO + CO \quad [2.0], \quad (6)$$

$$\longrightarrow OCCHCO^+(69^+) + H_2CO$$
$$+ HCCCH_2 \quad [3.2], \quad (7)$$

$$\longrightarrow HCC\text{-}c\text{-}C_3H_2^+ (63^+)$$
$$+ HC(O)OH + HCO \quad [5.5], \quad (8)$$

$$\longrightarrow c\text{-}C_4H_5^+ (53^+) + 2CO + HCO \quad [3.9], (9)$$

$$\longrightarrow c\text{-}C_3H_3^+ (39^+)$$
$$+ H_2CCHO + 2CO \quad [4.6]. \quad (10)$$

Spontaneous decomposition of M^+ with the resulting formation of the resorcinol ion (the heat of reaction is ~ -15 kJ/mol) is possible; however, since the 110^+ ions are not formed at low luminous fluxes, we chose process (5). The alternative variant of 110^+-ion formation related to the splitting off of C_2H_4 is excluded because such a process is not observed in the laser-induced ionization of dioxy-derivatives of benzene [1]. At the same time, processes similar to (6)–(10) have been observed for the dioxy-derivatives of benzene. Due to the energy of vibrational excitation of M^+, the channels given by (9) and (10) are available in the spectral region under investigation, whereas process (8) requires absorption of two photons as in the case of dioxy-derivatives of benzene. This is consistent with emergence of the 63^+ peak in the mass spectrum only for luminous fluxes in the vicinity of the higher limit of the fluxes used in our experiments.

The 137^+ and 55^+ ions are represented, in addition to the aforementioned ions, with higher relative intensity (along with a peak at 92^+) in the DOB mass spectrum obtained at $\lambda = 311$ nm (the peak of the first absorption band). For this λ, the energy of two photons is insufficient for the DOB ionization; therefore, the M^+ ions are formed as a result of three-photon absorption. An excess in energy over I_1 amounts to 3.5 eV; the photoelectron spectra obtained for this value of λ are indicative of the M^+ generation with an excitation energy of up to ~ 1.8 eV. This also represents the cause of the M^+ fragmentation in the long-wavelength region of the spectrum. The 92^+ and 55^+ ions are formed in the following processes as a result of dissociation induced by one-photon absorption:

$$M^+ + h\nu \longrightarrow C_6H_3OH^+(92^+) + HC(O)OH \quad [<5.0], (11)$$

$$\longrightarrow CH_2CHCO^+(55^+)$$
$$+ CH_2CHCO + CO \quad [3.1]. \quad (12)$$

We observed a process similar to (12) in the course of laser-induced ionization of hydroquinone and catechol; process (11) is related (as in catechol) to the presence of an intramolecular hydrogen bond.

It has been noted that the 137^+ ions are observed in the DMP mass spectra obtained after ionization by long-wavelength radiation; these ions are absent in the mass spectrum if the radiation with $\lambda = 266$ nm is used (Fig. 3). Other distinctions are also observed. The ratio between the currents of the 165^+ and M^+ ions in the mass spectrum at $\lambda = 306$ nm is larger by a factor of 2–2.5 than that at $\lambda = 266$ nm.

From the energy standpoint, the 137^+ ions cannot be formed as a result of one-photon dissociation of M^+ in the spectral range under consideration; in fact,

$$M^+ + h\nu$$

$$\longrightarrow 3,4\text{-}(OCH_3)_2C_6H_5^+ (137^+) + C_2H_5CO. \quad [\sim 5.0].$$
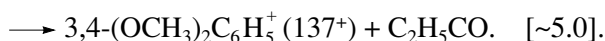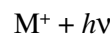
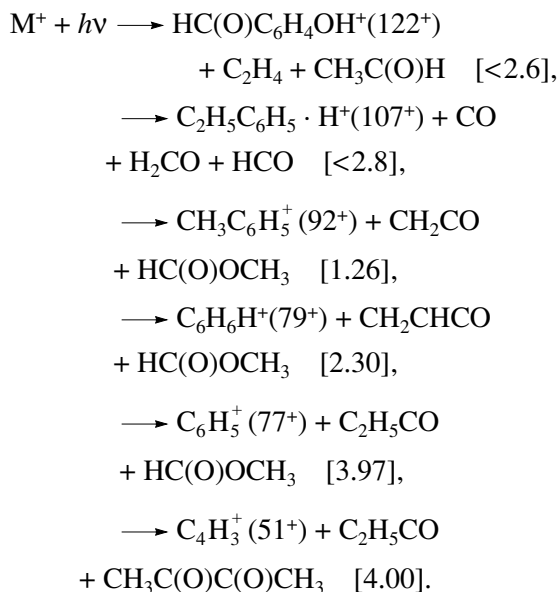Therefore, the emergence of the 137^+ ions under irradiation with $\lambda = 306$ nm is caused by the formation of the $(CH_3O)_2C_6H_3$ radicals with an estimated value of $I_1 \approx 6.7$ eV as a result of the $S_2(^1A') \longleftarrow S_0(^1A')$ transition; it is the two-photon ionization of these radicals that gives rise to the 137^+ peak in the mass spectrum. As the photon energy increases other dissociation channels, with rate constants higher than that for $(CH_3O)_2C_6H_3$ formation, become available. Ionization of the forming fragments yields the same peaks in the mass spectrum as does the dissociation of M^+ (see below).

A higher relative intensity of the peak corresponding to the 165^+ ions at $\lambda = 306$ nm may be accounted for by a greater role of the dissociation–ionization mechanism in ionization via the S_2 state. Specifically, dissociation of DMP with breakage of the $3,4\text{-}(CH_3O)_2C_6H_3C(O)\text{–}C_2H_5$ occurs with subsequent two-photon ionization of fragments; i.e., we have

$$M^+ + h\nu \longrightarrow M^*$$
$$\longrightarrow 3,4\text{-}(OCH_3)_2C_6H_3C(O) + C_2H_5 \quad [\sim 3.8],$$
$$3,4\text{-}(OCH_3)_2C_6H_3C(O) + 2h\nu$$
$$\longrightarrow 3,4\text{-}(OCH_3)_2C_6H_3C(O)^+ + e \quad [\sim 6.5].$$
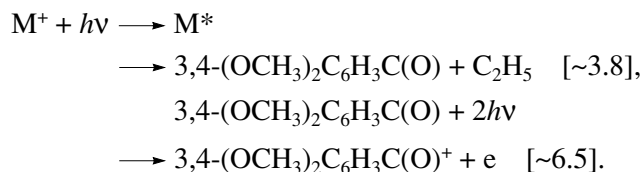
As was mentioned above, the inclusion of the dissociation–ionization mechanism makes it possible to explain the observed redistribution of intensities in the photoelectron spectra as the luminous flux increases.

We suggest the following processes of production of fragmentation ions (unconsidered above) in the course of the laser-induced ionization of DMP:

$$M^+ + h\nu \longrightarrow HC(O)C_6H_4OH^+(122^+)$$
$$+ C_2H_4 + CH_3C(O)H \quad [<2.6],$$
$$\longrightarrow C_2H_5C_6H_5 \cdot H^+(107^+) + CO$$
$$+ H_2CO + HCO \quad [<2.8],$$
$$\longrightarrow CH_3C_6H_5^+ (92^+) + CH_2CO$$
$$+ HC(O)OCH_3 \quad [1.26],$$
$$\longrightarrow C_6H_6H^+(79^+) + CH_2CHCO$$
$$+ HC(O)OCH_3 \quad [2.30],$$
$$\longrightarrow C_6H_5^+ (77^+) + C_2H_5CO$$
$$+ HC(O)OCH_3 \quad [3.97],$$
$$\longrightarrow C_4H_3^+ (51^+) + C_2H_5CO$$
$$+ CH_3C(O)C(O)CH_3 \quad [4.00].$$

The above-suggested processes of the formation of ions observed in the mass spectra of DOB and DMP do not exclude a certain contribution of other processes as well, especially in the vicinity of the upper limit of luminous fluxes, including the photodissociation of the fragmentation ions. This inference is supported by a large number of low-intensity peaks in the region of small masses. As mentioned above, ionization of the dissociation products from intermediate states and dissociation of the $3,4\text{-}(OCH_3)_2C_6H_3C(O)^+(165^+)$ can contribute to peaks in the mass spectrum of DMP.

CONCLUSION

The presence of low-lying states of the $n\pi^*$ type in the DOB and DMP molecules does not affect the mechanism of the energy acquisition and of fragmentation during laser-induced ionization of organic vapors. In the spectral region down to 266 nm and at the luminous-flux density as high as $\sim 2 \times 10^7$ W/cm^2, the laser-induced vapor ionization occurs by the ionization–dissociation mechanism. For DMP, a contribution of the dissociation–ionization mechanism was detected as well. If there is an excitation to the $S_2(^1A')$ state, dissociation with breakage of the α bond in the carbonyl group occurs with subsequent two-photon ionization of the fragments. The processes leading to production of the main fragmentation ions are suggested.

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