# Laser resonance photoionization spectroscopy of molecules

V. S. Antonov, V. S. Letokhov, and A. N. Shibanov

*Institute of Spectroscopy, Academy of Sciences of the USSR, Troitsk (Moscow Province)*

This review concerns the important problem of resonance interaction of laser radiation with polyatomic molecules via intermediate electronic excited states. The relation between the photoionization yield and photofragmentation of molecules and the spectroscopic and physicochemical properties of molecules in excited electronic states is discussed. The application of resonance laser photoionization to ultrasensitive (down to single molecules) detection of polyatomic molecules is examined.

## CONTENTS

## 1. INTRODUCTION

Frequency-tunable laser radiation can be used to excite selectively any quantum states of atoms and molecules of a given type. By means of multi-step excitation, it is possible to introduce selectively a considerable amount of energy into a particular type of atom or molecule, causing its selective photoionization, photodissociation, and other phototransformations. Such applications of lasers are sometimes called selective laser photophysics and photochemistry. The interest in this area is due not only to the completely new possibility of systematic study of previously inaccessible quantum states of atoms and molecules, but also important applications in science and technology. It is sufficient to mention such solved problems as laser separation of isotopes, laser detection of single atoms and molecules, laser IR photochemistry, etc. Special reviews and monographs have been devoted to this interesting area of application of lasers.[1-3]

Laser detection of single atoms and molecules based on the method of resonance multistep photoionization by frequency-tunable laser pulses was proposed about ten years ago.[4-7] The new possibilities of laser spectroscopy, opened up along this path, with very high sensitivity were discussed in 1974–1976.[8-10] Before long, in 1977, photoionization detection of single atoms in a buffer gas[11] and in a vacuum[12] was demonstrated experimentally. This path of laser spectroscopy is rapidly developing, and special reviews devoted to it have already been published.[13-15] It is entirely natural to

extend this method to detection of molecules.[1] In particular, the possibility of developing a selective laser detector of molecules based on a combination of selective photoionization of molecules by laser radiation and mass-spectrometrical detection of the photoions obtained was examined in Refs. 4 and 8. The situation with molecules is, however, more complicated. In spite of the fact that selective laser photoionization of atoms has been extensively developed, the method of laser photoionization spectroscopy of atoms cannot be directly transferred to molecules for a number of reasons.

1) The excited states of multiatomic molecules are of a much more complicated nature, and molecular absorption spectra often have little structure. This makes it much more difficult to realize photoionization of polyatomic molecules with high selectivity.

2) In contrast to atoms, molecules in intermediate excited states can undergo different photophysical and photochemical transformations, for example photodissociation, which can compete with photoabsorption and photoionization of processes.

3) The products of photoionization of polyatomic molecules, especially with the use of intense laser radiation, can be very diverse, and this essentially requires the use of the mass-spectrometric technique of analysis and detection of photoions.

4) Molecular photoabsorption cross sections, as a rule, are several orders of magnitude smaller than the atomic photoionization cross sections, which makes it necessary to use more powerful sources of radiation. At the same time, the molecular absorption and photoionization spectra usually

---

[1] We note that two-step photoionization of molecules was proposed for laser separation of isotopes in Ref. 16, but this method has not been developed.
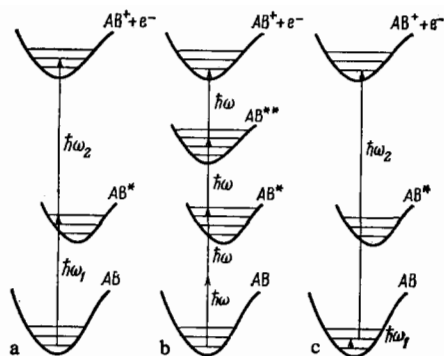
FIG. 1. Scheme of resonance laser photoionization of molecules. a) Via an intermediate electronically excited state; b) via an intermediate two-photon resonance; c) via a vibrationally excited state.

lie in the UV and VUV regions, which are relatively inaccessible to laser sources of radiation.

Nevertheless, in recent years, considerable progress has been made in the development of photoionization laser spectroscopy of molecules.[17] This is explained, first of all, by progress in laser technology, especially the development of lasers in the UV and VUV regions. Second, the combination of the method of resonance photoionization of molecules with mass-spectrometric identification of the photoions formed in the form of the so-called "two-dimensional mass-optical spectrometer," proposed previously in Refs. 4, 7, and 8, has turned out to be very effective. In a recent work,[18] this method was used to realize for the first time laser detection of single molecules in a volume irradiated by a single laser pulse.

Several basic schemes of multistep excitation, shown in a simplified manner in Fig. 1, can be used for resonance photoionization of molecules. Two-step photoionization via intermediate excited electronic-vibrational states (Fig. 1a) is the simplest type of selective stepwise photionization of molecules. Since with excitation of electronic states the energy required to ionize molecules decreases by several eV, it is possible to photoionize only excited molecules by appropriately selecting the quantum energy of the ionizing radiation ($\hbar\omega_2$, see Fig. 1a). The selectivity of the ionization in this case is determined by the selectivity of photoionization of molecules in the intermediate state. The first experiments in this direction[19,20] were performed using independent laser pulses in the first and second steps. This made it possible not only to optimize photoabsorption and photoionization of excited molecules but also to investigate the kinetics of the electronically excited states.

Since for most molecules the bands of intense electronic excitation are situated in the ultraviolet region of the spectrum $\lambda < 300$ nm, which is not easily accessible by tunable lasers, the methods of multiphoton ionization of molecules have been extensively developed. The method is based[21,22] on the use of a frequency-tunable dye laser with sharp focusing of the radiation down to the diffraction limit. In this case, a radiation intensity exceeding $10^{10}$ W/cm$^2$, with which the multiphoton absorption and ionization processes of molecules proceed efficiently, is achieved at the focal point. As the wavelength of the radiation is tuned, resonances arise at the doubled or tripled frequency of the laser with subsequent

single- or two-photon ionization of the molecule. The presence of intermediate resonances greatly increases the yield of ions and, as a result, a multiphoton ionization spectrum forms. This method turned out to be very effective for investigating the spectra of excited electronic states of molecules, especially those that are forbidden for single-photon transitions.

Vibrational spectra are most characteristic of polyatomic molecules, so that the scheme of two-step photoionization via intermediate vibrationally excited states (Fig. 1c) must in principle have higher selectivity than the scheme via the electronic states. In this scheme, however, due to the small change in the ionization energy of excited molecules (0.1–0.3 eV), ionizaton of unexcited molecules occurs as well, which greatly complicates the experimental realization of this scheme. For this reason, only a small number of experiments have been performed along this line.[23,24]

Several characteristic regimes of photoionization of molecules can be singled out depending on the intensity of the laser radiation in the UV or visible region of the spectrum.

1. Resonance two (or more)-step photoionization in weak fields (the saturation parameter of optical transitions $G \ll 1$[25,26]). In this case, we have a pure $n$-step process, which terminates when the molecule reaches the ionization limit. The power-law dependence of the yield of photoions on the radiation itensity is determined by the number of absorbed photons, and the yield of ions itself greatly depends on the properties of the intermediate electronically excited states.

2. Resonance stepwise photoionization in strong fields (saturation parameter $G \approx 1$). This case is of greatest interest for detection of molecules since the efficiency of photoionization of a molecule approaches 100%. However, on reaching the first ionization potential, the molecules as a rule continue to absorb energy, and this leads to their subsequent fragmentation. Fragmentation of molecules under the action of intense laser radiation, first observed in experiments on multiphoton ionization,[27] became the object of a large number of investigations both from the point of view of studying the physics of the processes that occur and finding the optimum conditions for photoionization detection of molecules.

3. Multiphoton ionization. The intensity of the radiation is high enough for ionization of molecules via intermediate multiphoton resonances. Subsequent resonant optical transitions fall in the region of strong saturation ($G > 1$). Strong fragmentation of molecules, up to their atomization, occurs.

Laser photoionization of molecules is presently a rapidly developing area of research. In 1978, only a few isolated papers on this subject appeared, but in the last two to three years, the number of papers has exceeded 100 (see, for example, the short review in Ref. 17). In the present review, we emphasize the main directions and methods of investigations, as well as the most important results from the point of view of developing new experimental possibilities for detecting polyatomic molecules. Here we systematically examine laser photoionization of free polyatomic molecules via intermediate real and multiphoton resonances. Photoionization

of molecules adsorbed on surfaces is then examined separately. The appearance of molecular ions in this case is explained by photoionization of desorbed neutral molecules. The review concludes with an examination of the application of the method of resonance multistep photoionization of molecules in combination with mass-spectroscopy for detection of trace quantities down to single molecules.

## 2. RESONANCE STEPWISE PHOTOIONIZATION OF MOLECULES

In multistep photoionization, the quantum transition of a molecule at each step is a resonant single-photon transition. For example, in the case of two-step photoionization, the energy of the first photon corresponds to the transition of the molecule into a real excited state. Since a transition into the ionization continuum occurs at the second step, the condition for a resonance is automatically satisfied. Due to the complicated quasidegenerate structure of the levels of polyatomic molecules in an intermediate electronic state, as well as due to the presence of different intramolecular relaxation mechanisms, the phase memory of the system in the intermediate state is lost very rapidly. This permits examining the two-step process noncoherently and describing it by simple equations for the occupancy of the levels (see, for example, Ref. 26). With respect to selectivity of ionization, this method has the important advantage of permitting independent selection of the wavelength of the exciting and ionizing radiation using two time-synchronized lasers. Variation of the delay time of the ionizing pulse relative to the exciting pulse gives the additional possibility of investigating the kinetics of photophysical processes in excited intermediate states of the molecule.

The investigation of stepwise photoionization in a mass spectrometer, when fragment ions are observed together with molecular ions, is of special value. In this case, we are dealing with a new method, in which it is not simply the occupancy of the excited state of the molecule that is being probed, but the capability of the molecule to give rise to different fragments in a two-step process is investigated. The appearance of fragment ions accompanying photoionization from an electronically excited state can depend on such factors as the presence of excitation in particular types of vibrations, equilibrium nuclear configuration of the molecule in the excited state, etc.

In strong laser fields, when the saturation parameter $G \approx 1$, the nature of the interaction of the molecule with the laser radiation becomes more complicated: molecular ions formed by two-step photoionization as well as neutral fragments formed in competing photodissociation processes can absorb additional photons, and this in general leads to the appearance of a large number of fragment ions. For this reason, a problem that is important for the detection of single molecules is finding the conditions under which the efficiency of stepwise photoionization is close to unity without loss of information on the starting molecules due to disappearance from the mass spectra of peaks of molecular and other characteristic ions. On the other hand, the investigation of the mechanisms of interaction of polyatomic molecules with intense laser radiation is of interest in itself and permits obtaining new information on the excited states of a molecule and its neutral and ionized fragments.

### a) Experimental procedure

An important factor in all experiments on resonance photoionization of molecules is the use of intense laser radiation, which permits attaining quite high ionization efficiency in multistep or multiphoton process. For example, in the case of two-step photoionization via an intermediate electronically excited state, in order to achieve saturation of the optical transition in the first step the energy density of the first radiation pulse $\Phi_1(\omega_1)$ must satisfy the condition

$$\Phi_1(\omega_1) \geqslant \Phi_{\text{sat}}^{(1)} = \frac{\hbar\omega_1}{2\sigma_{\text{exc}}}, \qquad (2.1)$$

where $\sigma_{\text{exc}}$ is the cross section for resonant excitation. This relation is valid in the optimum case, when the duration of the exciting pulse is shorter than the relaxation time of the excited state. Appreciable depletion of the excited electronic state due to stimulated transitions into the ionized state is achieved with an energy density $\Phi_2$ in the laser pulse with frequency $\omega_2$

$$\Phi(\omega_2) \geqslant \Phi_{\text{sat}}^{(2)} = \frac{\hbar\omega_2}{\sigma_i}, \qquad (2.2)$$

where $\sigma_i$ is the cross section for the transition from the excited state into the ionization continuum. For characteristic cross sections of excitation and ionization of molecules $10^{-17}$–$10^{-18}$ cm$^2$ and lifetimes of intermediate excited states $\tau_{\text{exc}} \approx 10^{-8}$–$10^{-10}$ s, the energy densities and intensities of saturation of optical transitions constitute, respectively, 0.1–1 J/cm$^2$ and $10^7$–$10^9$ W/cm$^2$. In the case of multiphoton ionization, the characteristic cross sections of two- and three-photon transitions constitute, respectively, $10^{-30}$–$10^{-36}$ cm$^4$/W and $10^{-43}$–$10^{-49}$ cm$^6$/W$^2$, so that in order to achieve an acceptable ionization efficiency it is necessary to use radiation intensities $I > 10^{10}$–$10^{11}$ W/cm$^2$.

Other important requirements imposed on laser radiation sources in experiments on multistep photoionization are related to the spectral characteristics of the molecules. The electronic absorption bands of most molecules are situated in the ultraviolet region of the spectrum, so that photon energies $\hbar\omega \gtrsim 3$–5 eV are required in order to excite electronic singlet states. The ionization potentials of polyatomic molecules usually lie in the range 8–12 eV, so that efficient photoionization of molecules out of electronically excited states in a single step requires photons with energies $\hbar\omega = 4$–8 eV.

Considerable progress in quantum electronics in the development of UV and VUV lasers has led to the fact that experimentalists now have at their disposal, in addition to the harmonics of solid state ruby and neodymium lasers, a number of powerful laser radiation sources based on excimer molecules XeCl ($\hbar\omega = 4$ eV), KrF ($\hbar\omega = 5$ eV), and ArF ($\hbar\omega = 6.4$ eV),[28] as well as a VUV laser based on the $F_2$ molecules ($\hbar\omega = 8$ eV).[29] In experiments with tunable radiation, the first and second harmonics of dye lasers ($\lambda = 260$–460 nm) pumped by nitrogen or Nd:YAG lasers are used.

Radiation pulses from gas-discharge lasers are usually synchronized with the help of hydrogen thyratrons, which

serve to commutate the discharge circuits of lasers[30] with nanosecond triggering precisions.[33]

To record photoions without separation by mass, a simple ionization chamber in the form of a cylindrical or flat capacitor is used.[32,33] To analyze photoions by mass in the presence of fragmentation, a mass spectrometer of any type recording ions with the help of a secondary electronic multiplier, which provides a detection efficiency of 30–100%, can be used. However, a time-of-flight mass-spectrometer, which permits recording the entire mass spectrum of photoions for a single laser pulse, is the most suitable.[56] Definite measures must be adopted to eliminate possible nonselective photoionization of molecules in the ion source by photoelectrons and desorption of ions from electrode surfaces under the action of scattered light. The presence of traces of oil and lubricants in the vacuum system can result in a large background due to ionization of impurities by intense UV radiation. The vapor pressure of the specimen in the ion source of the mass-spectrometer usually does not exceed $10^{-5}$ torr, which guarantees that the molecular photofragmentation processes will be collisionless.

### b) Two-step photoionization spectra of molecules

The method of stepwise laser photoionization permits recording molecular absorption spectra at very low concentrations, because the act of absorption of a photon by a molecule is recorded by the appearance of an ion with maximum sensitivity. We note that in contrast to the fluorescence method,[35] in this case it is not necessary for the excited state to emit.

The spectrum of stepwise photoionization of molecules via intermediate electronically excited states is determined by the dependence of the photoionization yield on the frequency of the laser radiation at each step. Far from saturation, the yield of ions from two-step photoionization in the absence of relaxation of the intermediate state is determined by the simple expression:

$$N_i = N_{exc} \, \sigma_{ion} \, (\omega_2) \, \Phi_2 = N_0 q \sigma_{exc} \, (\omega_1) \, \Phi_1 \sigma_{ion} \, (\omega_2) \, \Phi_2, \quad (2.3)$$

where $N_i$ is the number of ions formed per pulse, $N_{exc}$ is the number of excited molecules, $N_0$ is the number of molecules in the irradiated volume, $\sigma_{exc}$ is the cross section for excitation of molecules, $q$ is the fraction of molecules interacting with the exciting radiation at frequency $\omega_1$, $\sigma_{ion}$ is the cross section of photoionization of molecules from the excited state, and $\Phi_1$ and $\Phi_2$ are the energy densities of the radiation pulses at the first and second steps in photons/cm$^2$. The function $\sigma_{exc}(\omega_1)$ determines the excitation spectrum of the molecules. The cross section for ionization of excited molecules $\sigma_{ion}(\omega_2)$ depends on both the specific excited electronic-vibrational level and the excess energy of two photons $\hbar(\omega_1 + \omega_2)$ above the ionization limit of the molecule.

For ordinary single-photon ionization in the case of direct ionization, the molecule goes from the ground state into the ground state of the ion, and the dependence of the photoionization cross section on the radiation wavelength is approximated by a step function, which reflects the Franck-Condon factors for the transitions to the vibrational levels of

the ion.[36] Due to the superposition of transitions from different vibrational sublevels of the ground electronic state of polyatomic molecules, under ordinary conditions the stepwise nature of the dependence is smoothed out and the ionization efficiency reaches a peak smoothly in the region of vertical Franck-Condon transitions.[36] This also remains in force for two-step photoionization. However, in this case, the transition of the molecule into the state of the ion occurs from the excited electronic-vibrational levels and must therefore be included in the Franck-Condon factor between the two states.

The first experimental investigations of molecular two-step photoionization spectra were performed for the nitrogen dioxide molecule.[19] The molecule $NO_2$ is a convenient object for such experiments, because it absorbs in the visible region of the spectrum. The two-step photoionization spectrum of this molecule was investigated in the region of dye-laser wavelengths 447–457 nm. The ionization potential of the molecule is $I = 9.78$ eV,[37] so that with the use of a hydrogen laser with photon energy $\hbar\omega_2 = 7.7$ eV at the second step,[38] the excess of energy of two photons above the ionization potential constituted $I - \hbar(\omega_1 + \omega_2) = 0.8$ eV. Figure 2 shows the dependence of the yield of two-step photoionization of nitrogen dioxide on the radiation wavelength $\lambda_1$ at the first step. The maximum magnitude of the photosignal corresponds to the formation of $3 \cdot 10^4$ ions/pulse. The same figure shows the measured usual spectrum of electronic absorption of the molecule. It follows from Fig. 2 that the two-step photoionization spectrum reproduces, to within the measurement error, the absorption spectrum of the molecule. This indicates that transitions into the ionization continuum far from the ionization limit from different electronic-vibrational states have a much weaker spectral dependence. This characteristic was confirmed in a number of experiments with other molecules.[39,40]

A characteristic of the two-step photoionization of nitrogen dioxide under the conditions indicated was the unexpectedly low magnitude of the cross section for photoionization from the excited state $\sigma_{ion} = 10^{-21}$–$10^{-22}$ cm$^2$.[41] At the same time, for a number of molecules, the measured cross section of photoionization out of excited electronic states falls in the range $10^{-17}$–$10^{-19}$ cm$^2$.[42] This can be explained
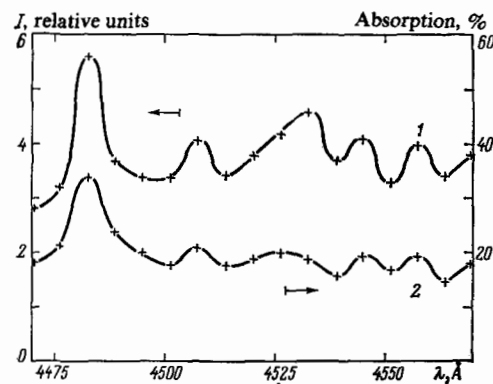
FIG. 2. Two-photon photoionization spectrum[19] (curve 1) and electronic absorption spectrum (curve 2) of nitrogen dioxide molecules.
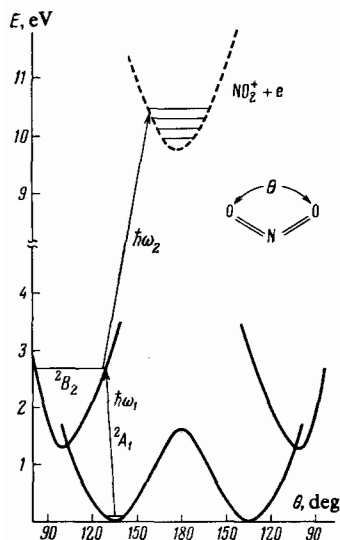
FIG. 3. Potential energy curves for the ground and electronically excited states of the $NO_2$ molecule and ion.[41]



FIG. 4. Photoionization spectrum of benzene near the ionization threshold. The laser radiation frequency at the first step is tuned to the $\sigma^1$ vibration in the $S_1$ state ($38608$ cm$^{-1}$).[45] The upper curve was measured with higher resolution.

by the considerable change in the configuration of the molecule accompanying a transition into the ionization state.[41] Indeed (Fig. 3), in the ground state the molecule is bent, forming an angle $\theta_A = 134°$, while the ion has a linear configuration. This leads to the fact that with single-photon ionization the yield of photoions near threshold is quite low due to the small Franck-Condon factors.[43] The situation is even less favorable for two-step photoionization. Absorption by the molecule in the first step for radiation wavelength in the range 440–460 nm is due primarily to the transition into the electronically excited state $^2B_2$,[44] in which the molecule is even more strongly bent than in the ground state: $\theta_B = 111°$ (see Fig. 3). For this reason, the Franck-Condon factors for the transition from the $B_2$ state into the groundstate of the ion must be very small.

A more complicated picture of two-step photoionization can be observed in the case when the energy of the two photons is near the ionization limit of the molecule. As for single-photon ionization, in the two-step process discrete states of the neutral molecule can be excited above the ionization limit. These states can then decay via nonradiative processes into the ionization continuum (autoionization). Single-photon ionization states are well known for many molecules, but in two-step photoionization, other states can be excited. The relation between direct ionization and autoionization processes in two-step photoionization of polyatomic molecules was studied in Ref. 45. In the experiments, the wavelength of the radiation at the first step was fixed and the spectrum of the photocurrent was recorded by tuning the wavelength of the ionizing radiation. The use of supersonic cooled molecular beams permitted removing the hot vibrational bands and Doppler broadening from the optical transitions of the molecules. In the case of naphthalene molecules, a stepwise dependence of the ion yield on the wavelength of ionizing radiation was observed, which indicates the direct ionization mechanism for this molecule. The spectral dependence of the yield of benzene photoions near
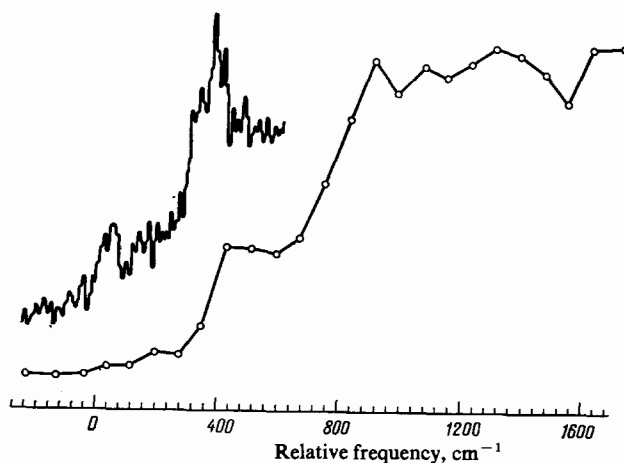
the ionization threshold exhibited a complicated structure (Fig. 4), which is explained by the superposition of direct ionization and autoionization of Rydberg states. The characteristic width of the peaks (about 100 cm$^{-1}$) gives a total decay rate of states relative to all processes (dissociation, autoionization) equal to $2 \cdot 10^{13}$ s$^{-1}$. The observation of these ionization peaks indicates that the fraction of the decay into the ionization continuum is quite high.

## c) Kinetics of excited states of polyatomic molecules

The method of stepwise laser photoionization of molecules is very convenient for studying excited molecular states, which it is difficult or impossible to observe by other methods. For example, gas-phase absorption spectroscopy requires a high concentration of excited molecules or a long absorbing medium, which greatly complicates extension of this method to the case of noninteracting molecules ("isolated molecules") at low pressure. The method of laser-induced luminescence has high sensitivity and can be used for such investigations. However, the region of its applicability is limited to those cases when the excited molecular states have a sufficiently high rate of radiation and, therefore, an acceptable quantum yield of luminescence.

Limitations related to the emissivity of the excited state are completely absent in the method of two-step photoionization, and the potentially high sensitivity is determined by the fact that the absorption of a photon by an excited molecule leads to the formation of an ion, which can then be recorded with a probability close to unity. Using time delay of the ionizing laser pulse relative to the exciting pulse, the kinetics of electronically excited states can be investigated by observing the change in the photoion yield. The efficiency of this technique was confirmed in Ref. 20 for the formaldehyde molecule. This method was later used to investigate the evolution of the $T_1$ triplet state of the toluene molecule.

The investigation of the decay kinetics of the excited $S_1$ state of the formaldehyde molecule is of great interest for the study of nonradiative intramolecular transitions.[46] The
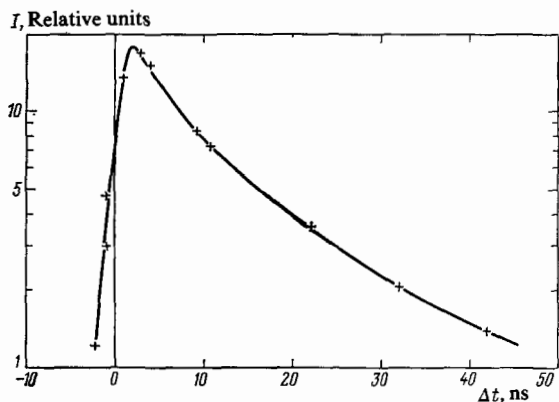
FIG. 5. Dependence of the ion yield with two-step photoionization of formaldehyde on the delay time between the exciting and ionizing laser pulses.[20]



FIG. 6. Scheme of two-step photoionization of the toluene molecule.[49] $S_0^{\#}$ indicates the high-lying vibrational levels of the ground electronic state $S_0$; $S_1$ is the first excited singlet state; $T^+$ indicates the excited vibrational levels of the triplet electronic state T; IP and IP† indicate the vertical ionization potentials from the singlet and triplet states.

characteristic magnitude of the molar extinction for the transitions $S_1 \leftarrow S_0$ is quite small ($\varepsilon = 10$), since the purely electronic dipole transition is symmetry forbidden and can be allowed only in vibrations. This results in the fact that the radiative lifetime of the molecule in the $S_1$ state is about 5 $\mu$s,[46] while the duration of the fluorescence of the molecule in this state lies in the nanosecond range and is due to nonradiative deactivation of the excited state. For this reason, the quantum yield of fluorescence is quite low, making it difficult to perform an accurate measurement of the lifetime of this state using fluorencence.[47,48] The decay of the $S_1$ state of formaldehyde was investigated by two-step photoionization[20] with the use of synchronized pulses from nitrogen and hydrogen lasers ($\hbar\omega_1 + \hbar\omega_2 = 3.7\,\text{eV} + 7.7\,\text{eV} = 11.4\,\text{eV}$).

Figure 5 shows the measured dependence of the yield of two-step photoionization of formaldehyde on the delay between the exciting and ionizing laser pulses. The growth of the signal near zero delay is due to the finite duration of the laser pulses. The drop in the signal with increasing delay is characteristically not exponential. For a different order of laser pulses, i.e., when the nitrogen laser pulse followed the hydrogen pulse, the two-step photoionization signal was not observed.

It is well known that with excitation into the $S_1$ electronic state, the formaldehyde molecule dissociates with a quantum yield close to unity, and in addition the products of dissociation accompanying absorption of radiation by the molecule in the region of 337 nm are CO and $H_2$ molecules.[46] The ionization potentials of the $H_2$ (15.4 eV) and CO (14 eV) molecules are higher than the energies of the two laser quanta, so that the only source of ions is ionization of molecules from the excited state. In this case, the drop in the output of the two-step photoionization signal accompanying the increase in the delay $\Delta t$ between the laser pulses (see Fig. 5) is entirely related to the decay of the excited state of the molecule. Comparison of the average decay time, obtained from this dependence ($\tau_{av} = 14$ ns) with results of measurements in Refs. 47 and 48, equal to 27 ns and 18 ns, respectively, shows that the latter quantity is close to the value obtained in the experiment for the lifetime of the molecule.
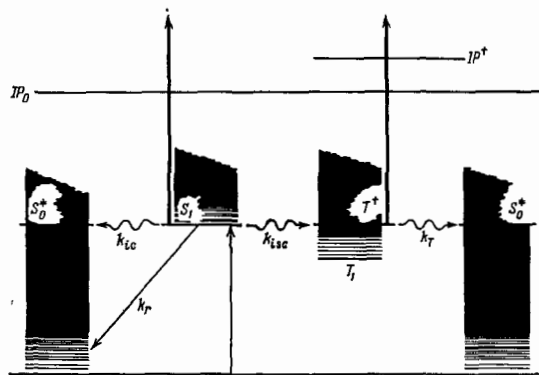
A more complicated situation occurs in the case of excitation of the toluene molecule into the first singlet state $S_1$.[49] It is known that the excited molecule can then undergo different radiative and nonradiative relaxation processes. These include: a) the radiative transition $S_1 \rightarrow S_0$; b) nonradiative conversion into the ground electronic state $S_1 \rightarrow S_0$; c) conversion into the triplet state $S_1 \rightarrow T_1$; d) the conversion $T_1 \rightarrow S_0$. As far as relaxation of excited singlet states of aromatic molecules is concerned, here a great deal of data obtained from fluorescence measurements has been accumulated. Data on the lifetime of nonradiative triplet states in the case of "isolated molecules," however, is practically nonexistent due to the absence of adequate methods for performing measurements.[49] It is therefore of great interest to apply the method of stepwise photoionization to such investigations.

The scheme of the levels and transitions in the toluene molecule in Fig 6 illustrates the idea of the experiment. Toluene molecules are excited into the $S_1$ state by a laser radiation pulse and are then probed by a sounding laser pulse at different times. Molecules excited first into the $S_1$ state can either decay into the ground electronic state or make a transition into isoenergetic levels $T_1^*$ of the triplet state $T_1$. The molecules in the $S_1$ state ionize with absorption of a second photon. The $T_1^*$ states likewise can ionize efficiently, because the energy of the second photon exceeds the vertical ionization potential from the triplet state IP* (see Fig. 6).

Figure 7 shows the typical dependence of the photoionization signal on the delay time between the exciting and ionizing laser pulses. The double exponential decay is a result of the successive decay of $S_1$ and $T_1^*$ states:

$$\frac{d\,(S_1)}{dt} = -(k_r + k_{ic} + k_{isc})\,(S_1) = -k_S\,(S_1), \tag{2.4}$$

$$\frac{d\,(T_1^*)}{dt} = k_{isc}\,(S_1) - k_T\,(T_1^*), \tag{2.5}$$

where $k_r$, $k_{ic}$, $k_{isc}$ and $k_T$ are the rate constants for radiative decay, conversion into $S_0$, conversion into $T_1^*$ and the rate constant for decay of $T_1^*$ into $S_0$.

An important problem that cannot be solved starting from the kinetic data is the ratio of the cross sections of
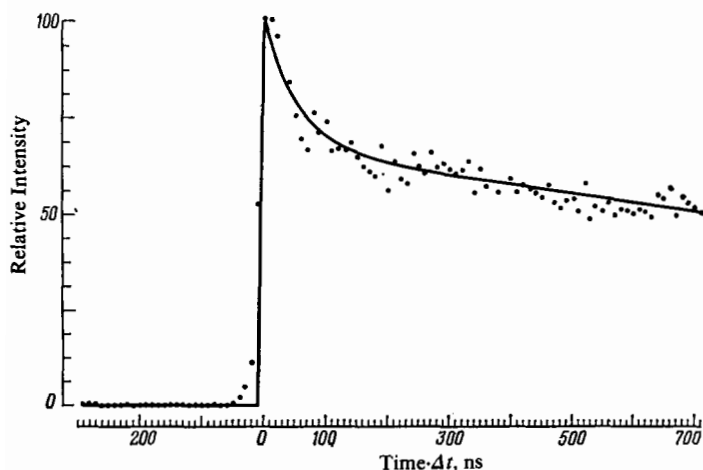
FIG. 7. Photoionization signal in toluene as a function of the delay time between the laser pulses. The fast component corresponds to decay of the $S_1$ state, and the slow component corresponds to decay of the $T_1$ state.[49]

photoionization out of the $S_1$ and $T_1^*$ states. A knowledge of this quantity permits calculating immediately the rates of all relaxation processes from the experimental dependence. In the work discussed,[49] the radiation of the short-wavelength ArF laser with photon energy 6.4 eV was especially chosen for photoionization from the excited states. For photoionization from $S_1$ and $T_1^*$ states, the excesses above the vertical ionization potentials were quite large: 2.3 eV and 1.1 eV, respectively (see Fig. 6). Taking into account the weak dependence of the efficiency of photoionization of polyatomic molecules far from the ionization limit, this gives a basis for assuming that under experimental conditions the cross sections of photoionization of $S_1$ and $T_1^*$ are approximately identical. The experimental dependence (see Fig. 7) is then described by the expression

$$(S_1 + T_1^*) = \frac{S_1\,(t=0)}{k_S - k_T} \left[ (k_S - k_{isc} - k_T)\, e^{-k_S t} + k_{isc} e^{-k_T t} \right]$$

$$(2.6)$$

with constants $k_S = 1.38 \cdot 10^7$ s$^{-1}$, $k_{isc} = 8.5 \cdot 10^6$ s$^{-1}$, and $k_T = 3.45 \cdot 10^9$ s$^{-1}$. The rate of decay of the triplet state $k_T$ turned out to be unexpectedly high, exceeding by more than two orders of magnitude the estimate made in Ref. 50.

### d) Fragmentation of molecules in the case of stepwise photoionization

The formation of fragment ions with single-photon ionization from the ground electronic state with thermal excitation has been studied in detail for many molecules.[51] The primary process is usually detachment of the electron and then, in the presence of sufficiently high vibrational or electronic excitation of the ion, cascade fragmentation of the ion occurs. The existing theory of the formation of mass-spectra of polyatomic molecules is based on the assumption that the vibrational energy of the excited ion is distributed equally over the degrees of freedom (statistical approximation).[52] Within the framework of this model it makes no difference how the molecular ion with a given store of vibrational energy was formed.

In contrast to single-photon ionization, the method of two-step photoionization permits investigating the formation of fragment ions with transitions from high-lying vibrational levels of the intermediate electronic state. In addition,

absorption of two photons by the molecule can lead to excitation of other states of the ion, which can also change the picture of fragmentation of the ion.

Fragmentation of the benzaldehyde molecule accompanying two-step photoionization ($\hbar\omega_1 + \hbar\omega_2 = 3.7$ eV + 7.7 eV = 11.4 eV) was investigated in Refs. 41, 53, and 54. The energy of the two photons exceeded not only the ionization potential of the molecule $I = 9.5$ eV but also the appearance potential of the fragment ion with detachment of the hydrogen atom,[55] so that a peak corresponding to the fragment ions $C_6H_5CO^+$ was observed in the mass spectrum of the photoions (Fig. 8). An interesting feature is the much larger, compared with single-photon ionization at the same energy, yield of fragment ions (see Fig. 8). This could be due primarily to the fact that the form of the distribution of the vibrational energy of ions over different modes can differ considerably for single- and two-step photoionization.[46] Absorption of a photon with energy 3.7 eV by a benzaldehyde molecule corresponds to an electronic transition of the type n→$\pi^*$, i.e., a transition of an electron from a nonbinding atomic orbital of oxygen into an antibonding molecular $\pi^*$ orbital. The restructuring of the electronic configuration occurs primarily in the aldehyde group CHO. Since the antibonding orbital of the molecule is occupied, the parameters of the bonds in the aldehyde group, especially the C–O bond, change considerably. This leads to the fact that in an electronic transition, vibrations are excited primarily in the region of the aldehyde group. After absorption of light with
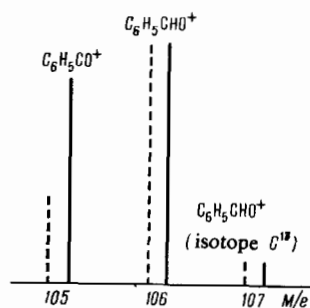


FIG. 8. Photoionization mass-spectrum of the benzaldehyde molecule with two-step (continuous lines) and single-step (dashed lines) ionization with a photon energy of 11.4 eV.[54]

$\hbar\omega_1 = 3.7$ eV, the vibrational degrees of freedom of the molecule, after conversion into the triplet state, contain 0.6 eV of energy. After absorption of the second photon, ionization occurs from the molecular state with a large store of vibrational energy, localized in the aldehyde group, which increases the probability of formation of the fragment ion with detachment of the aldehyde hydrogen atom.

Another factor that leads to a large yield of fragment ions in two-step photoionization is that in the case of single-photon ionization, the nuclear configuration of the neutral molecule and of the ion differ little from one another due to the fact that the $n$-electron of the oxygen, which does not participate in the formation of the molecular bond, is removed. For this reason, in spite of the fact that the photon energy of 11.4 eV exceeds the ionization threshold by the quite large amount of 1.9 eV, according to the Franck-Condon principle, ions with small vibrational excitation will be formed with highest probability (Fig. 9). The excess energy of the photon above the ionization limit will be carried off by the electron. In two-step photoionization, the intermediate electronic state has a considerably changed nuclear configuration in the region of the chromophore, which can lead to a displacement of the peak in the vibrational energy distribution function of the ions formed (see Fig. 9). This must likewise facilitate an increase in the fraction of fragment ions.

A different picture of fragmentation is observed in photoionization of polyatomic molecules in a strong laser field, capable of saturating the optical transitions of the molecules. In this case a molecule can acquire an energy greatly exceeding the ionization potential, which gives rise to strong fragmentation of the molecule.

We shall briefly examine the results obtained for the benzene molecule, which is a very convenient object for investigation of photoionization and photofragmentation pro-
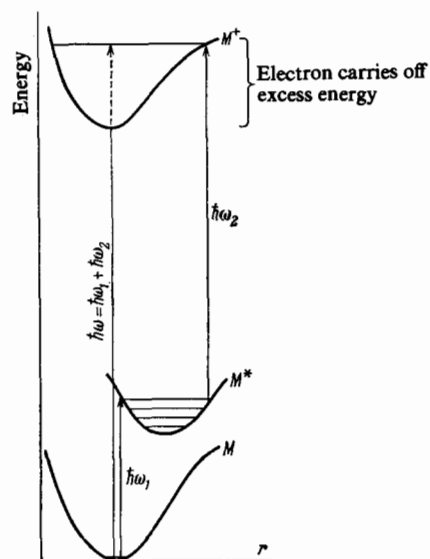


FIG. 10. Mass-spectra of the benzene molecule. a) Photoionization mass-spectrum with radiation intensity $I = 10^5$ W/cm$^2$ ($\lambda = 249$ nm, $\tau = 20$ ns); b) with $I = 2\cdot10^6$ W/cm$^2$ [56]; c) with $I = 3\cdot10^8$ W/cm$^2$ [59]; d) mass spectrum with electron impact, $E_{el} = 70$ eV for comparison.



FIG. 9. Franck-Condon transitions with single- and two-step photoionization.[41] The energy excess above the ionization potential of the molecule with single-photon ionization is carried away by the electron; with two-step photoionization, it is transformed into the vibrational energy of the ion.
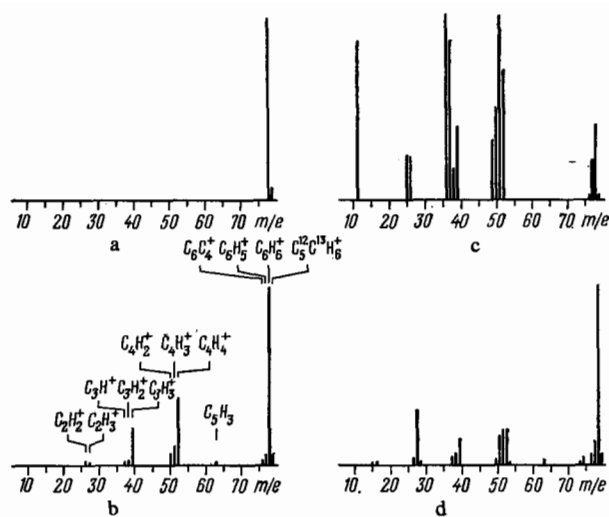
cesses in polyatomic molecules,[56–60] because the amount of available thermochemical and spectroscopic data is largest for this molecule. The energy of the first excited electronic state $S_1$ of the benzene molecule is greater than one-half the ionization potential ($I = 9.25$ eV), and this permits photoionizing excited molecules by a second photon in a single-frequency laser field ($2\hbar\omega > I$).

Figure 10 shows the mass spectra of photoions of benzene, formed under the action of the radiation of an excimer KrF laser with $\hbar\omega = 5$ eV. For low fluxes of radiation energy $\Phi < 10^{-4}$ J/cm$^2$, only molecular ions formed with two-step photoionization (Fig. 10a) are observed in the mass spectrum. As the energy of the laser pulses increases, increasingly lighter fragment ions appear in the mass spectrum (Fig. 10b). For radiation energy fluxes $\Phi > 5$ J/cm$^2$, fragmentation becomes very intense (Fig. 10c) and exceeds fragmentation under electron bombardment with electron energies of 70 eV (Fig. 10d). Under these conditions, one of the strongest peaks in the mass spectrum is the ionic component $C^+$ (see Fig. 10c). The appearance potential of atomic carbon ions is about 27 eV,[20] and, therefore, in order for this ion to form, the molecule (or its fragments) had to absorb not less than six photons. The total yield of ions is very large and approaches 10% with a radiation energy flux of about 10 J/cm$^2$.[60] Aside from the high efficiency, photoionization of benzene by excimer laser radiation is selective. For example, even with maximum radiation intensities, such atmospheric components as $H_2$, $H_2O$, etc. are practically completely absent in the mass spectra of the photoions.

The lifetime of the benzene molecule in the intermediate electronically excited state is higher than the duration of the laser pulse.[60] This leads to high efficiency of formation of molecular ions with absorption of two UV photons. Further formation of fragment ions will occur during the laser pulse in the process of successive photodissociation of ions, beginning with the molecular ions. The appearance of fragment
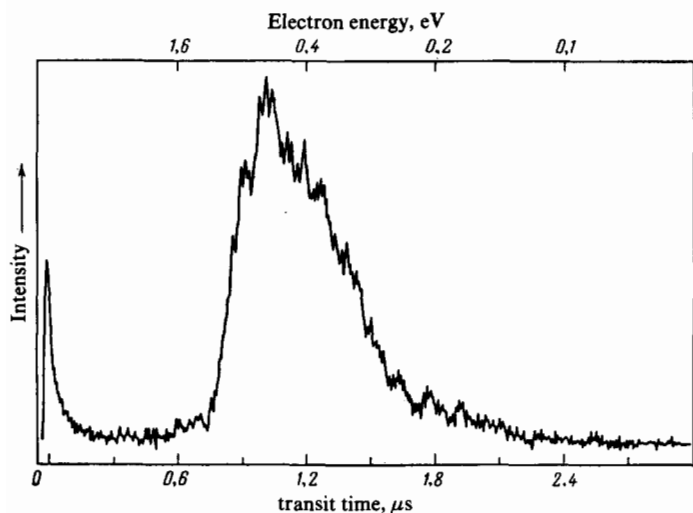
FIG. 11. Energy distribution of photoelectrons with photoionization of benzene by KrF laser radiation.[62]

ions with intensities of $10^7$–$10^9$ W/cm$^2$ (see Fig. 10) cannot be explained by absorption of photons by the neutral molecule with a transition into highly excited autoionized states,[27,61] because the rate of decay of autoionized states, as a rule, exceeds $10^{12}$–$10^{13}$ s$^{-1}$, i.e., it greatly exceeds the rate of laser induced transitions above the ionization limit.

Direct confirmation of the mechanism of ionic photodissociation was obtained by measurements of the kinetic energy of photoelectrons.[62] Such measurements permit estimating the energy stored in the molecule at the time the electron is detached. Figure 11 shows the energy distribution of photoelectrons with step photoionization of benzene molecules by KrF laser radiation. The maximum energies of the photoelectrons (see Fig. 11) do not exceed the difference in the energies of the two photons (10 eV) and the ionization potential of the molecule (9.25 eV). This indicates that the neutral molecule does not have time to acquire a large amount of energy, by absorbing three or more laser photons before it was ionized.

To understand the processes involved in the accumulation of energy and fragmentation in the ionic subsystem, it is of great interest to investigate the spectral dependence of the yield of different fragment ions.

Figure 12 shows the dependence of the yield of molecular and fragment ions of anthracene on the frequency of laser radiation ("two-dimensional" mass-optical spectrum) with an energy density of $6 \cdot 10^{-1}$ J/cm$^2$. In spite of the fact that all isotopic and fragment ions were actually resolved in the mass spectrum, for simplicity, for each group of ions with a constant number of carbon atoms $C_n$, the total magnitude of all peaks with different number of hydrogen atoms is plotted in the figure. For the molecular ions $C_{14}^+$, the peaks in the photoionization spectrum correspond precisely to the vibrational structure of the electronic transition in the first step.[40] Among the fragment ions, ions of the type $C_{12}^+$ have the highest yield (see Fig. 12). The spectrum of the yield of these ions is on the whole similar to the spectrum of the molecular ions $C_{14}^+$. However, the relative magnitude of the signal of fragment ions $C_{14}^+$ increases more rapidly with increasing photon energy. In addition, an appreciable increase

in the yield of $C_{12}^+$ ions is observed at a laser radiation frequency of $29.4 \cdot 10^3$ cm$^{-1}$. For the lighter fragment ions $C_{10}^+$ and $C_{11}^+$, the dependence of their yield on the radiation frequency is even stronger. A yield of these ions, sufficient for reliable recording, was observed only in the shortest wavelength region of the spectrum. The increase in the yield of fragment ions with a decrease of the wavelength of the laser radiation is qualitatively explained by the fact that with a constant number of absorbed quanta, the degree of excitation of the photoions formed increases. Thus, within the spectral interval in which the mass-optical spectrum of anthracene was measured, the energy of a single photon varied by 0.37 eV. With three-step photoionization, the energy absorbed by the molecule increases with decreasing wavelength already by $3 \cdot 0.37$ eV $= 1.1$ eV, and this leads to more efficient fragmentation of the molecule.

Thus, on the whole, the spectral dependence of the yield of fragment ions is analogous to the dependence for molecular ions, while the increase of the fraction of fragment ions with a decrease in the radiation wavelength is related to the increase in the absorbed energy.
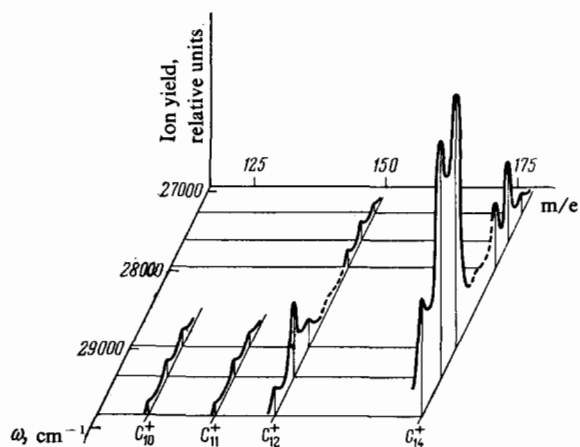


FIG. 12. Mass-optical spectrum of the anthracine molecule with laser pulse energy density of $6 \cdot 10^{-2}$ J/cm$^2$.[40]
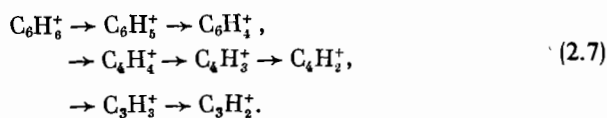
### e. Statistical model of fragmentation of molecules

Comparison of the picture of fragmentation with laser photoionization in a strong resonant field and by electron bombardment (see Fig. 10) shows that in both cases the qualitative composition of photoproducts is practically identical, but the degree of fragmentation in the first case can be much higher. With ionization by electron bombardment, the molecule immediately acquires an energy of about 20 eV, exceeding the ionization potential, after which ionization of the molecule occurs with subsequent cascade decay of the overexcited ion into fragments. In spite of the fact that the energy of the ionizing electrons is quite high (usually 70–100 eV), due to the Franck-Condon principle, in a vertical transition only a small fraction of this energy in the form of vibrational and electronic excitation is transferred to the ion. With repeated absorption of photons under the action of quite intense UV radiation, this restriction is absent and the energy absorbed per molecule can greatly exceed 30 eV. This is facilitated by the fact that the electronic structure of the ions formed is, as a rule, similar to that of radicals, and for this reason, ions absorb radiation resonantly in the visible and UV region of the spectrum.

The relative yield of different fragment ions in laser photoionization corresponds qualitatively to their appearance potentials: peaks of fragment ions with low appearance potentials have the highest intensity in the mass spectrum.[46]

All this indicates that, at least for benzene, the direction of fragmentation of the molecule is determined primarily by the energetics of the molecular bonds with any method of ionization, and the difference of the fragmentation pattern with ionization by intense laser radiation is related only to the high magnitude of the absorbed energy.

In this connection, an attempt was made in Refs. 63 and 64 to calculate the fragmentation of molecular ions of benzene in the field of intense UV laser radiation based on the statistical theory of unimolecular reactions. For the case of benzene, it is well known that the basic channels of fragmentation of the initial $C_6H_5^+$ ion with excitation energies of 5–10 eV are the reactions[63]

$$\begin{aligned}
C_6H_6^+ &\rightarrow C_6H_5^+ \rightarrow C_6H_4^+, \\
&\rightarrow C_4H_4^+ \rightarrow C_4H_3^+ \rightarrow C_4H_2^+, \\
&\rightarrow C_3H_3^+ \rightarrow C_3H_2^+.
\end{aligned} \qquad (2.7)$$

The threshold of formation of the primary fragments $C_6H_5^+$, $C_4H_4^+$, and $C_3H_3^+$ lies near 4 eV. Taking (2.7) as the first step of fragmentation, all decays of the following type are also included in the analysis:

$$C_mH_n^+ \rightarrow C_hH_l^+ + C_{m-h}H_{n-l}. \qquad (2.8)$$
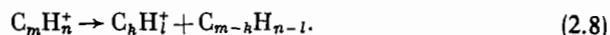
Here it is assumed that the molecular ions of benzene, formed with the absorption of two UV photons by the molecule, continue to absorb radiation, and it is also assumed that all the absorbed energy is uniformly distributed by means of rapid nonradiative relaxation of electronic states over vibrational degrees of freedom of the ion. Then, by examining the probability of decay and the energy content of all fragments statistically (according to the RRKM theory[65]), the total pattern of fragmentation can be calculated.

Figure 13a shows the results of such a calculation of fragmentation of benzene by KrF laser radiation. The cross section for absorption of radiation by $C_6H_6^+$ ions, was chosen to be equal to $2 \cdot 10^{-18}$ cm$^2$. Comparison of the results of measurements (Fig. 13b) shows satisfactory qualitative agreement between the model calculation and experiment.

Further refinement of the theoretical model of fragmentation of molecules in an intense UV laser radiation field must include a more realistic examination of the process of absorption of radiation energy by the ionic system. Actually, already with an excitation energy of molecular benzene ions of 7–8 eV, the rate of their dissociation, calculated according to RRKM, is about $10^{10}$ s$^{-1}$.[66] For this reason, during a nanosecond pulse different fragments are formed, which in their turn can likewise absorb radiation and, thus, form parallel fragmentation channels. Figure 14 shows a diagram of the basic channels of formation of benzene fragments under the action of radiation with photon energy of 4.78 eV. A calculation using this more complete scheme[66] leads to better agreement with experiment and permits explaining a number of peculiarities in the intensity ratios of ionic components in the mass spectrum within groups with the same number of carbon atoms $C_n$.

### f) Role of neutral fragments

Experiments performed with a large number of molecules[57,60,68,69] have shown that in many cases the picture of the interaction of molecules with the intense radiation can differ considerably from the one examined above. The degree of ion fragmentation can be much higher, and the relative yield of molecular ions can be very low even with low laser radiation intensities. This is related to the dissociation of molecules accompanying excitation into intermediate electronic states. In this case, the main ionization channel could be photoionization of neutral molecular fragments. Thus, in one of the first works,[68] in the photoionization of acetaldehyde the energy of two UV photons was much lower
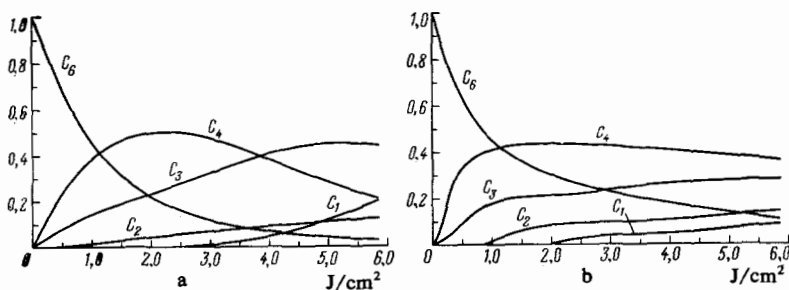


FIG. 13. Dependence of the relative intensities of different $C_n^+$ ion groups for benzene on the energy flux density of laser radiation: a) theoretical calculation[63]; b) experiment.[59]
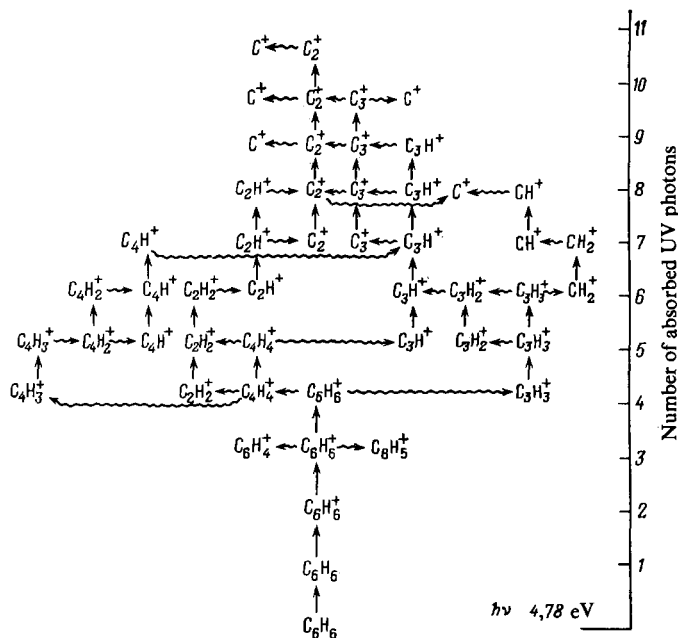
Number of absorbed UV photons

$h\nu$  4,78 eV

than the ionization potential of the molecule, which led to complete disappearance of the molecular ion due to the high rate of the competing process of dissociation from the highly excited state. Dissociation also plays a large role in photoionization of the benzene molecule by ArF laser radiation ($\lambda = 193$ nm) via the intermediate electronically excited state $^1B_{1u}$.[59] Analysis of data on the photoion yield in this case permitted estimating, with some assumptions about the cross section of photoionization out of the excited state, the lifetime of this state, which turned out to be of the order of $10^{-11}$ s.[59]

In the experiments examined, the dissociation time of the molecules investigated in the intermediate excited states was much shorter than the duration of the laser pulse, which results in a high quantum yield of dissociation and, as a result, effective suppression of direct stepwise photoionization of molecules. The neutral molecular fragments formed, which absorb at the frequency of the laser radiation, can then ionize during the laser pulse. However, ionization of neutral molecular fragments can play a large role in the formation of the photoionization mass spectrum of polyatomic molecules, even in the presence of stable intermediate states. The transition of a molecule into a state above the ionization limit from the electronically excited state with a large reserve of vibrational energy or with the nuclear configuration of this

state differing considerably from the configuration of the ion, can result in a sharp increase in the fraction of dissociating molecules and, correspondingly, a drop in the yield of molecular ions.[60] For this reason, in order to achieve maximum efficiency of stepwise photoionization of molecules with a minimum degree of fragmentation, the energy of the ionizing photon must exceed the vertical ionization potential of the molecule from the excited state.[60] As was established in Ref. 70, this condition is apparently satisfied in photoionization of benzene by radiation at the fourth harmonic of the Nd:YAG laser.

## 3. MULTIPHOTON IONIZATION OF MOLECULES

Multiphoton ionization represents the case of ionization of molecules in an extremely intense laser field, $I > 10^{10}$ W/cm$^2$. Multiphoton processes are usually described by the first nonvanishing term in the nonstationary perturbation series expansion. The general expression for the probability of $n$-photon ionization has the form $W^{(n)} = \sigma_n I^{(n)}$, where $I$ is the radiation intensity and $\sigma_n$ is the cross section of the multiphonon process. The expression for $\sigma_n$ contains a summation over all molecular states, including the continuum. For example, for the case $n = 4$, which is typical for multiphoton ionization of ions, the expression for $\sigma_4$ has the form

$$\sigma_4(\omega_l) \sim \left| \sum_1 \sum_2 \sum_3 \frac{\langle f \mid V \mid 3\rangle \langle 3 \mid V \mid 2\rangle \langle 2 \mid V \mid 1\rangle \langle 1 \mid V \mid i\rangle}{(E_3 - E_i - 3\hbar\omega_l)(E_2 - E_i - 2\hbar\omega_l)(E_1 - E_i - \hbar\omega_l)} \right|^2 .$$

(3.1)

In this expression i and f correspond to the initial bound state and the final state in the ionization continuum; the indices 1, 2, and 3 indicate the intermediate first, second, and third quantum states, respectively; $\omega_l$ is the frequency of the laser radiation; and $V$ is the molecule-field interaction Hamilton-

ian. The numbers in the matrix elements indicate virtual states accompanying absorption of one, two, or three photons. When the radiation frequency $\omega_l$ is tuned, depending on the position of the intermediate molecular levels, resonances can arise at the fundamental, doubled, and tripled fre-

quencies. The ionization yield in this case increases considerably if the selection rules for multiphoton transitions are satisfied and, thus, the multiphoton ionization spectrum forms. Since the electronic absorption bands of most molecules begin in the UV region of the spectrum, when using radiation from tunable dye lasers, two- and three-photon resonances are typically recorded. The characteristic cross sections for the two- and three-photon transitions constitute, respectively $10^{-48}$–$10^{-54}$ cm$^4 \cdot$s and $10^{-80}$–$10^{-86}$ cm$^6 \cdot$s$^2$ [71] with the radiation intensity $I$ expressed in photons/cm$^2 \cdot$s.

The multiphoton ionization method is now widely used for spectroscopy of excited states of polyatomic molecules, especially states forbidden to single-photon transitions (see reviews in Refs. 17, 72, 73). An important advantage of the method is the possibility of investigating Rydberg states lying in the VUV region of the spectrum, as well as ionizing practically any molecules with the help of tunable lasers in the visible region. The presence of two- or three-photon absorption from the ground state in the first step fundamentally requires high radiation intensities, and for this reason, the mass spectrum of the photoproducts is very complicated. Fragmentation of molecules accompanying multiphoton ionization, as a rule, exceeds fragmentation under electron impact.

## a) Spectra of multiphoton resonances

Information on multiphoton ionization is obtained primarily in the form of spectra. It is significant that the selection rules in multiphoton transitions differ from the single-photon rules. For example, a transition between levels with identical parity is forbidden for single-photon transitions, but is allowed for two-photon transitions. Thus spectroscopic data obtained with multiphoton ionization supplement the usual single-photon spectroscopy. In many cases, it is possible to investigate electronic states of molecules which previously were not observed at all.

Figure 15 shows the spectrum of multiphoton ionization of the benzene molecule with wavelength tuning of the laser radiation over the range 365–400 nm.[67] The first question that arises in the analysis of the spectra is the identification of resonances in the observed multiphoton ionization spectrum. As indicated by the arrow in Fig. 15, the three-photon ionization potential of benzene corresponds to a wavelength of 402 nm, so that the signal at shorter wavelengths corresponds to three-photon ionization and to four-photon ionization in the 400–450 nm region. The observed structure of the spectrum in the 365–400 nm region can in principle arise as a result both of resonances with the bound molecular states at the doubled frequency of the radiation and of autoionization states above the ionization limit in the case of a three-photon transition. However, from an analysis of the vibrational structure and its comparison with the well-known single-photon spectrum in the region of the autoionization states, it follows that the observed structure arises due to two-photon resonances. The only state, known up to the present time, in this region is the $^1B_{iu}$ state. The two-photon transition into this state can be vibrationally allowed
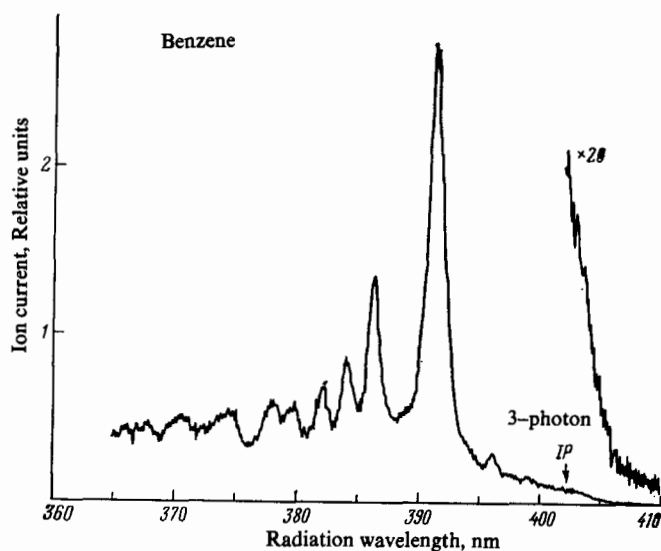


FIG. 15. Photoionization spectrum of two-photon resonances ($^1E_{1g} \leftarrow {}^1A_{1g}$) of benzene.

and can give rise to the multiphoton ionization spectrum. However, the position of the maximum peak in the spectrum, as well as the observed shift accompanying deuteration, contradict this proposition. Four different types of states are allowed in the two-photon transition from the ground state into a state with $D_{6h}$ symmetry. These are: $^1A_{1g}$, $^1E_{1g}$, $^1E_{2g}$, and $^1A_{2g}$. The transition into the $^1A_{2g}$ state is forbidden if the two photons are identical. The presence of $E_{2g}$ vibrations in the transition indicate a Jahn–Teller effect in the excited state, which indicates either a $^1E_{1g}$ or $^1E_{2g}$ state. The symmetry of the $^1E_{1g}$ state was established from measurements of the ionization yield using linear and circular polarization. A new $^1E_{ig}$ electronic state, previously predicted theoretically, has thus been observed and identified based on multiphoton ionization spectra.

The spectrum of three-photon resonances in benzene in the 400–500 nm region corresponds practically completely to transitions into Rydberg states and, in addition, the three-photon Rydberg structure is practically identical to the single-photon absorption spectrum, with the exception of the difference in the intensities, indicating the strong effect of the $^1A_{1g}$ components in the two-photon virtual state.

The multiphoton ionization spectra of a large number of polyatomic molecules have been investigated in an analogous manner (see the reviews in Refs. 17, 72, 73). In spite of the fact that the method of multiphoton ionization of molecules appeared comparatively recently, it is now already the standard method and is widely used to investigate the electronic spectra of molecules.

## b) Fragmentation accompanying multiphoton ionization

Historically, the fact that photoionization of polyatomic molecules by powerful laser radiation is usually accompanied by intense fragmentation was first discovered precisely in experiments on multiphoton ionization.[27] It was previously assumed that the number of photons absorbed by

a molecule corresponds to the minimum number required by the energetics to attain the lowest ionization potential. The formation of fragments with high appearance potentials was neglected. However, fragmentation of the molecule down to atomic ions $C^+$ was recorded already in the first experiments on multiphoton ionization of benzene.[27] It follows from the appearance potentials of the fragment ions that at least nine photons each with an energy of 3.17 eV is required for formation of $C^+$ ions.[27] The dependence of the yield of light fragments on the radiation intensity in this case was stronger than for heavy ions, but nevertheless, the exponent does not exceed 3.5 even for $C^+$ ions, which indicates the strong saturation of multiphoton absorption. The exponential dependence is actually determined by the first step of the two- or three-photon absorption: further transitions, leading to ionization and fragmentation of molecules, are usually resonant transitions and are close to being saturated.

In addition to the mechanisms discussed in Sec. 2 for the formation of photoionization mass spectra of molecules, such as photodissociation of molecular ions and photoionization of neutral fragments in strong fields, which are typical for experiments on multiphoton ionization with $I > 10^9$–$10^{10}$ $W/cm^2$, other mechanisms of interaction of molecules with radiation can also play an important role. These primarily include the process of accumulation of energy by molecules in a laser field. A model of multiphoton excitation according to which polyatomic molecules, having absorbed an energy exceeding the ionization potential, do not have time to lose an electron and continue to be excited along the network of high-lying autoionization levels with subsequent autoionization accompanied by fragmentation of molecules, was proposed in Refs. 27 and 66. In the case of the benzene molecule, this possibility was investigated experimentally using synchronized UV and visible laser pulses with wavelengths of 241 nm and 483 nm, respectively.[76] With an intensity of 3 $MW/cm^2$, the action of a single UV radiation pulse led to the formation of only a molecular ion. On the other hand, the intensity of the visible radiation equalled 0.4 $BW/cm^2$, which is sufficient for multiphoton ionization of benzene if the two-photon transition from the ground state is allowed by the selection rules. When the doubled frequency of the visible radiation was tuned to the vibrational sublevel of the $S_1$ state, forbidden for the two-photon transition, no ionization signal was observed. Under these conditions, the combined action of UV and visible radiation led to intense fragmentation in the mass spectrum, typical for multiphoton ionization.[27] In this case, however, it remains unclear whether the molecule is excited by the visible radiation along the network of autoionization states or the visible radiation gives rise to fragmentation of the ions. To clarify this, the visible radiation was delayed relative to the UV radiation by 17 ns by an amount sufficient for autoionization of the intermediate state. In this case, the photoionization mass spectrum turned out to be completely analogous to the preceding case. This leads to the conclusion that the process of excitation of neutral molecules along the network of autoionization levels cannot compete with autoionization even with intense radiation $10^9$ $W/cm^2$ and, therefore, the main input of energy to the medium with multiphoton ionization occurs
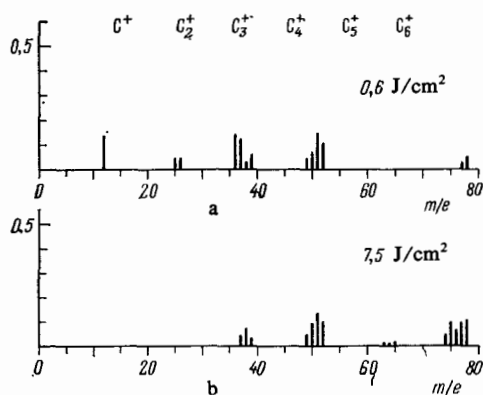


FIG. 16. Photoionization mass spectra of benzene with different intensities and durations of laser radiation. a) $I = 3 \cdot 10^8$ $W/cm^2$ (0.6 $J/cm^2$), $\tau = 20$ ns[59]; b) $I = 3.7 \cdot 10^{11}$ $W/cm^2$ (7.5 $J/cm^2$), $\tau = 20$ ps.[77]

in the ionic subsystem.

A difference occurs, however, in the fragmentation of ions by high-intensity radiation. Figure 16 shows the photoionization mass spectra of benzene, measured with radiation intensities of $3 \cdot 10^8$ $W/cm^2$ and $2.7 \cdot 10^{11}$ $W/cm^2$.[7] Comparison of these mass spectra shows that under the action of a picosecond pulse (Fig. 16b) whose intensity is three orders of magnitude greater than in the case of the nanosecond pulse (Fig. 16a), fragmentation in the mass spectrum is considerably lower even with an energy flux in the radiation pulses an order of magnitude greater than in the first case (see Fig. 16a). This difference in the action of nanosecond and picosecond laser pulses on a benzene molecule is related to the fact that in the weaker field ions fragment in successive processes of absorption of photons and dissociation of ions, beginning with the molecular ion (see Sec. 2), while in an extremely strong laser field ($I \geqslant 3 \cdot 10^{11}$ $W/cm^2$), the rate of radiation-induced transitions is so high that the ions have time to acquire a large amount of energy before they dissociate. Deactivation of reexcited molecular benzene ions apparently occurs predominantly with detachment of hydrogen atoms (see Fig. 16b).

### c) "Entropy" model of fragmentation

A detailed theoretical calculation of fragmentation of polyatomic molecules in an intense laser radiation field is an exceedingly difficult problem and requires knowledge of an enormous amount of spectroscopic and photochemical data for all intermediate photoproducts. For this reason, in many investigations,[63,64,78,79] a great deal of attention was devoted to developing approximate computational methods. As already discussed above, fragmentation of polyatomic molecules with multiphoton ionization depends strongly both on the intensity and on the wavelength of the laser radiation. Under identical conditions photoionization mass spectra of isomers likewise differ considerably.[61] While such a dependence of fragmentation on the radiation parameters and the molecular structure is of great interest for different applications, the degree to which this dependence reflects the specific (dynamic) properties of the processes of photoexcitation and photofragmentation of individual molecules in a strong

laser field remains an important question. To investigate this question, a method of calculating the statistically most favorable pattern of fragmentation of molecules with multiphoton ionization was developed in Refs. 78 and 79. According to Refs. 78 and 79, the statistically most favored fragmentation pattern is one in which the maximum entropy of the medium consisting of noninteracting particles—the initial molecules and their neutral and ionized fragments—is attained: The only parameter determining fragmentation here is the average magnitude of the absorbed energy per initial molecule.

Let $\mathscr{X}_j$ be the number of molecules or radicals of type $j$ and let $X_{ij}$ be the fraction of these particles in the quantum state $i$. Then

$$\sum_i X_{ij} = 1, \tag{3.2}$$

$$\sum_j \mathscr{X}_j = \mathscr{X}, \tag{3.3}$$

where $\mathscr{X}$ is the total number of fragments. The entropy of the system $S$ is expressed as follows:

$$S = -R \sum_j \mathscr{X}_j \ln \mathscr{X}_j - R \sum_j \mathscr{X}_j \sum_i X_{ij} \ln X_{ij} + R\mathscr{X} \ln \mathscr{X}, \tag{3.4}$$

where $R$ is the gas constant. The problem thus reduces to finding the values of $\mathscr{X}_j$ and $X_{ij}$ that maximize expression (3.4) under the following restrictions: a) conservation of the average absorbed energy $\langle E \rangle$:

$$\langle E \rangle = \sum_j \mathscr{X}_j \sum_i \varepsilon_{ij} X_{ij}, \tag{3.5}$$

where $\varepsilon_{ij}$ is the energy of the quantum state $i$ for a particle of type $j$, and b) conservation of matter and charge.

The results of the calculation of fragmentation of the benzene molecule together with the measured mass spectra are shown in Fig. 17. The good agreement between the experimentally obtained mass spectra and the computed spectra for $\langle E \rangle = 37$ eV is evident. This indicates the considerably statistical character of the fragmentation of a molecule in multiphoton ionization ($\lambda = 504$ nm, $E_{las} = 7.5$ mJ). In the case of the triethylenediamine molecule,[79] a disagreement with experiment is observed in the intensity ratios of the ion peaks in the region $M/e = 54$–58. Of the five molecules investigated in Ref. 79, this is the largest disagreement with experiment, and it is apparently related to the nonstatistical nature of the processes involved. Nevertheless, in most cases[79,80] the "entropy" model of photofragmentation of molecules by intense laser radiation agrees well with experiment.

## 4. RESONANT PHOTOIONIZATION ACCOMPANYING IRRADIATION OF A SURFACE

All cases examined above concerned photoprocesses with formation of photoions accompanying irradiation of molecules in a low-pressure gas, when molecules can be viewed, during the course of the interaction with the laser pulse, as being isolated from collisions with one another or with the walls. Meanwhile, there is great interest in obtaining ions by irradiating molecules on the surface of a metal or dielectric. Moreover, this process is actually related to pho-
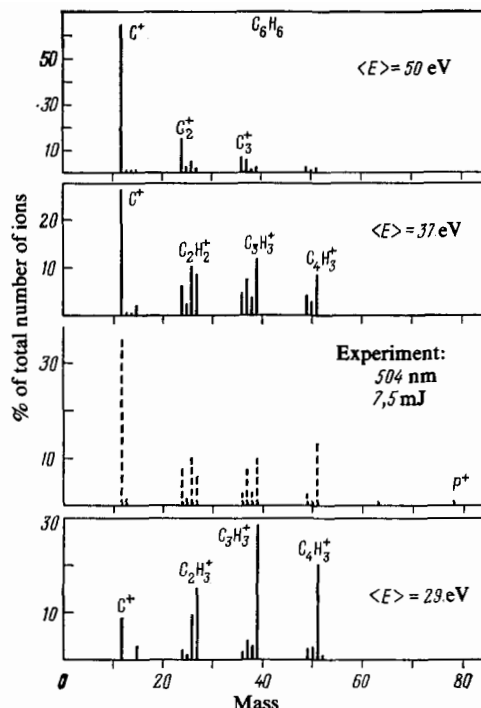


FIG. 17. Comparison of photoionization mass spectra, calculated in the statistical limit, with experimental results for the benzene molecule.[79]

toionization of molecules in the gas phase. For this reason, we have included this case amongst the problems examined in this review.

### a) Production of molecular ions upon irradiation of a surface

Processes leading to the formation of free ions accompanying the action of laser radiation on the surface of a solid have attracted a great deal of attention for a long time. In investigations conducted during the last few years in different laboratories, laser radiation with parameters varying over a very wide range was used: pulse durations varied from continuous radiation to $10^{-11}$ s, wavelengths varied from the IR to the UV region, and intensities varied from several watts to $10^{11}$ W. The action of radiation with such different parameters on a surface must give rise to very diverse processes, leading to the formation of ions. The investigation of these processes is of great practical interest. For example, laser-stimulated formation of ions is already used now in mass spectrometric analysis of a wide class of materials ranging from refractory materials to biological molecules.

The mechanism of ionization accompanying the action of intense laser radiation on a surface with intensity $I = 10^9$–$10^{11}$ W/cm$^2$, leading to strong heating ($T > 1000$ °C) of the surface of the solid, intense vaporization of the material, and formation of a plasma has been studied in greatest detail.[81] In this case, the ionization process has a thermal character and is described by the Langmuir-Saha equation. This method for obtaining ions is used in mass spectrometry of inorganic specimens.[82] This method is of little use in analyzing specimens containing complicated organic molecules be-

cause it leads to complete decomposition of these molecules due to the strong heating of the material.

Since 1968 a number of laboratories have begun intense investigations of the mechanisms of laser-stimulated formation of ions of organic molecules on the surface of solid specimens.[83–87] Both pulsed radiation with intensity $10^4$–$10^9$ W/cm$^2$ [83,86] and continuous $CO_2$ laser radiation[85] were used in the investigations. One of the mechanisms of formation of ions of organic molecules consists of the following: the pulse of laser radiation heats the surface, intense vaporization of the material leads to the formation of a quite dense cloud of the vapor in which chemical reactions occur (proton transfer, addition of the cation of an alkali metal, etc.), leading to the formation of ions.[88,89] Both positive and negative ions $(M + H)^+$, $(M - H)^-$, $(M + alkali)$ and fragment ions are observed in the mass spectrum. To explain the results obtained on the LAMMA (laser microprobe mass analyzer) apparatus, it was proposed in Ref. 90 that "collective, non-equilibrium processes in the condensed phase" are responsible for the formation of ions.

It was reported in Refs. 86, 91, and 92 that molecular ions form upon irradiation of crystalline specimens of the bases of nuclei acids and anthracene with UV laser pulses with moderate intensity $(I + 10^4$–$10^6$ W/cm$^2)$. An important feature of the observed process is the absence of fragment ions. Only molecular ions $M^+$ were observed in the mass spectra. It was observed that the ion yield increases with the photon energy. For the case of adenine, estimates showed that with the minimum recorded ionic signal, the heating of the surface did not exceed 100 °C, which is much lower than the melting temperature of adenine $(T_m = 360$ °C) and cannot lead to intense vaporization of the specimen. These facts indicate that the process observed in Refs. 86, 91, and 92 differs considerably from the processes described previously. A number of hypotheses was proposed in Refs. 91 and 92 concerning the mechanism of formation of such ions, but the following simple model was proposed only recently in Ref. 93 as a result of special experiments: the laser radiation pulse slightly heats the surface, thereby increasing the probability of desorption of molecules from the surface during the laser pulse. Molecules leaving the surface are resonantly ionized by the same radiation, as described in Sec. 2. Estimates performed within the framework of the proposed model agree well with the experimental results.

### b) Experimental procedure

In experiments with a surface, the specimen is usually placed directly into the ion source of the mass spectrometer.[86,91] This permits analyzing the masses of the ions forming under the action of the laser radiation on the surface. When a time-of-flight mass spectrometer is used, the electrical pulse can be applied to the ion gun with different delay relative to the laser pulse, and this facilitates bunching of ions with different masses with respect to initial velocities.[95] The regime in which the ion pulse is recorded with velocity bunching permits working with maximum mass resolution. In the absence of such bunching $(\tau_d = 0)$, it is possible to

measure the distribution function of ions over the initial velocity $f(v_0)$.

Different types of specimens were used in the experiments in Ref. 93: fine-crystalline adenine powder; single-crystalline anthracine films; polycrystalline rhodamine 6G films, obtained with rapid vacuum evaporation of a solution of rhodamine 6G in alcohol; fine crystalline peptide powder.

The electrode on which the specimen was placed could be cooled to $T = 200$ K.

### c) Formation of ions of molecules constituting crystals

The characteristic mass spectra of ions, formed upon irradiation of crystalline powders of adenine and anthracene, are shown in Figs. 18a and b. The mass spectrum of adenine obtained on the LAMMA apparatus is presented for comparison (Fig. 18c).[96] As is evident from the figure, the first two mass spectra consist only of molecular ions, in contrast to the third mass spectrum (see Fig. 18c), where the protonated molecular ion $(M + H)^+$ dominates, and there is a number of fragment ions.

The ion yield depends sharply on the energy flux $\Phi$ of laser pulses. For the case of adenine crystals, this dependence is approximated by $N_i \propto \Phi^7$.

A comparison of the yield of molecular ions obtained upon irradiation of adenine by nanosecond $(\tau = 20$ ns, $\lambda = 249$ nm) and picosecond $(\tau = 30$ ps, $\lambda = 266$ nm) pulses[92] shows that the formation of ions is determined by the density of the absorbed energy $\Phi \varkappa$, where $\varkappa$ is the coefficient of absorption of the crystal per unit length, and not by
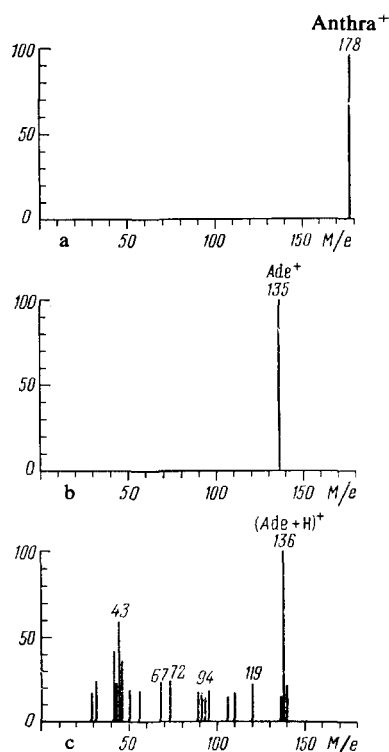


FIG. 18. Characteristic mass spectra of ions forming upon irradiation of crystalline powders of anthracene (a) and adenine (b) by KrF laser radiation.[86,91] The mass spectrum of adenine obtained on the LAMMA apparatus[56] (c) is presented for comparison.

the radiation intensity. If it is assumed that the energy absorbed in the crystal is completely thermalized, then, neglecting the thermal conductivity, the maximum possible heating of the surface with a characteristic energy flux $\Phi = 4$ mJ/cm$^2$ constitutes $\Delta T = \Phi x / c\rho = 200$ °C; here $c$ and $\rho$ are the specific heat capacity and specific weight of adenine. Under such heating, the rate of desorption of molecules from the surface can be expected to increase considerably.

It was observed in Ref. 92 that together with the formation of molecular ions, upon irradiation of adenine neutral molecules also fly off from the surface. The surface of the specimen was irradiated with picosecond pulses, and the neutral molecules were recorded with the help of a photoionizing KrF laser pulse, which irradiated a small region above the surface of the specimen. This observation suggested the following elementary mechanism of ion formation: the pulsed heating of the surface of the specimen with irradiation → desorption of neutral molecules → photoionization of free molecules above the surface.

This hypothesis was checked as follows.[93] The probability of desorption of a molecule per unit time $W_{des}$ or the inverse lifetime of an adsorbed molecule on the surface are determined by the Arrhenius formula:

$$W_{des} = \tau_{ads}^{-1} = \omega \exp\left(-\frac{E_{ads}}{kT}\right), \qquad (4.1)$$

where $\omega = 10^{12}$–$10^{14}$ s$^{-1}$ is the rate factor and $E_{ads}$ is the energy of adsorption of a molecule on the surface with temperature $T$. For example, for adenine the probability of desorption decreases by a factor of ten due to cooling of the surface heated by the laser pulse approximately $\tau_{cool} = 80$ ns after termination of the laser pulse ($\tau_p \approx 15$ ns). Therefore, a much larger number of neutral molecules accumulates in the space above the surface after termination of the laser pulse than during it. The number of molecules desorbed after the laser pulse can be measured by irradiating the surface with a second pulse of laser radiation after a time $\tau_{12}(\tau_f > \tau_{12} > \tau_{cool})$, where $\tau_f$ is the time for molecules to fly away from the irradiated region. The flux of energy in the second laser pulse $\Phi_2$, of course, must be less than the energy flux $\Phi_{th}$, producing the appearance of an ionic signal upon irradiation of the surface by a single laser pulse.

To check this model, an experiment was performed[93] with two KrF laser pulses ($\lambda = 248$ nm).

The pulse of the probing KrF laser with a delay of $\tau_{12} = 2$ $\mu$s was oriented along the surface of the specimen, touching it so that all molecules leaving the surface after the first KrF laser pulse entered the region of ionization of the probing pulse. Measurements were performed with an energy flux $\Phi_1 = 4$ mJ/cm$^2$ in the first pulse and $\Phi_2 = 2.3$ mJ/cm$^2$ in the second. The ionic signal was absent when the specimen was illuminated only by the second pulse. The measurements showed that the number of ions formed from neutral molecules under the action of the second pulse is 11 times greater than the number of ions forming under the action of the first pulse on the adenine surface. If the fact that the ion yield for the second pulse depends on $u_2 \propto \Phi_2^2$ (two-step ionization) is taken into account, then for equal fluxes of

energy the ratio of the number of ions will equal $(u_2/u_1)(\Phi_1/\Phi_2)^2 = 36$.

The experimental results[93] thus suggest that ions forming under the action of the first pulse appear as a result of photoionization of molecules which flew off from the surface during the laser pulse. Desorption of neutral molecules, which are subsequently ionized by the second laser pulse in the gas phase, continues for a longer period of time after termination of the first pulse.

Inasmuch as ion formation is preceded by thermal evaporation of molecules from the surface, the ionic signal $N_i$ is proportional to the product of the desorption probability $P_{des}$ and the multiphoton ionization yield $\eta_{ion}(\lambda)$:

$$N_i \sim N_0 P_{des}(\Phi, \lambda)\, \eta_{ion}(\lambda), \qquad (4.2)$$

where $N_0$ is the number of irradiated molecules on the surface.

The probability of desorption of a molecule $P_{des}$ during the laser pulse $\tau$ evidently equals

$$P_{des} = 1 - \exp\left[-\int_0^\tau W_{des}(t)\, dt\right], \qquad (4.3)$$

where $W_{des}$ is the rate of desorption (4.1).

The magnitude of the heating $\Delta T$ has a maximum in the region of maximum absorption $x(\lambda)$. Thus the desorption probability $P_{des}$ depends sharply on the density of the energy absorbed in the specimen $\Phi x(\lambda)$ and together with the spectral dependence of photoionization $\eta_{ion}(\lambda)$ determines the resonant character of the ion yield. This explains the results obtained with irradiation of adenine by pulses with $\lambda = 249$, 308, and 337 nm (Fig. 19). The yield of adenine ions is maximum for radiation with $\lambda = 249$ nm, which falls in the elec-
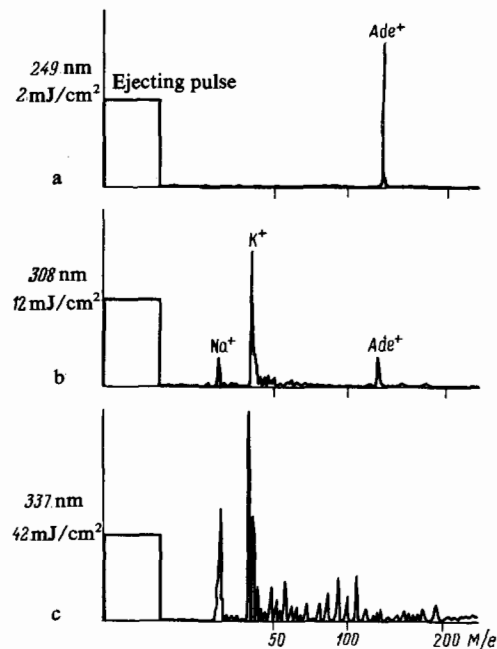


FIG. 19. Mass spectra obtained upon irradiation of adenine by laser pulses with wavelengths $\lambda = 249$ nm (a), 308 nm (b), and 337 nm (c), gradually leaving the electronic absorption band of adenine.[91]

tronic absorption band of adenine. Radiation with $\lambda = 308$ nm falls on the edge of the absorption band, when $\varkappa(\lambda)$ and $\eta_{ion}(\lambda)$ decrease. For this reason, ions are observed with a considerably higher energy density of the laser radiation. Finally, radiation with $\lambda = 337$ nm lies outside the resonant absorption band of adenine, which sharply decreases $\varkappa(\lambda)$ and $\eta_{ion}(\lambda)$. To observe the mass spectrum it is necessary in this case to use radiation with much higher intensity, when strong heating of the material and formation of plasma due to nonresonant absorption are possible. In this case, strong fragmentation of molecules occurs and the molecular ion $(M)^{+}$ is not observed.

### d) Formation of ions of molecules adsorbed on a surface

With the thermal mechanism of desorption of molecules form the surface and their subsequent photoionization in the gas, it is in principle possible to observe ions of any molecules adsorbed on the surface, if they are susceptible to multiphoton ionization. Such effects have been observed in experiments with adenine crystals, if anthracene vapor was present in the volume of the mass spectrometer. When an adenine crystal is irradiated by UV pulses, the mass spectrum contains both adenine and anthracene ions. When the volume above the surface was irradiated, only anthracene molecules were observed, but the signal with $\Phi = 6$ mJ/cm$^{2}$ was two to three times weaker. Cooling of the ion gun containing the specimen to $T = 200$ K greatly decreased the signal of anthracene ions from the gas phase and increased the signal from the surface. This leads to the conclusion that anthracene ions are formed as a result of photoionzation of anthracene molecules adsorbed on the adenine surface. This suggests that ions of both the molecules constituting the crystals and of adsorbed molecules are formed by the same mechanism.

Figure 20 presents the dependences of the ionic signals on the energy flux of laser radiaton $\Phi$ for anthracene adsorbed on the surface of adenine or rhodamine 6G. For anthracene adsorbed on adenine (Fig. 20a) at $T = 200$ K, the dependence is approximated by $u \propto \Phi^{8}$, and at $T = 300$ K it is close to the dependence of the ionization yield $\eta_{ion}(\Phi)$ of anthracene vapor on the energy flux. These facts can be explained as follows. At low temperature of the specimen the number of ions is determined by the number of molecules desorbed during the pulse and by their ionization yield. The rate of desorption depends very sharply on the temperature of the surface and, therefore, on the energy flux of the laser pulse. At $T = 300$ K all molecules are desorbed at the beginning of the laser pulse, so that the ionization yield is determined primarily by the ionization efficiency in the gas phase.

For anthracene on rhodamine 6G (Fig. 20b), the exponent in the dependence $u \propto \Phi^{n}$ varies from $n = 9$ at $T = 200$ K to $n = 4.5$ at $T = 300$ K. At $T = 200$ K and $\Phi = 16$ mJ/cm$^{2}$ the signal due to anthracene ions, when the rhodamine 6G surface is irradiated, is a factor of $10^{3}$ greater than with irradiation of the volume above the surface. Therefore, the method of adsorption of molecules on a surface can greatly increase the sensitivity of detection of molecules in the photoionization mass spectrometer.
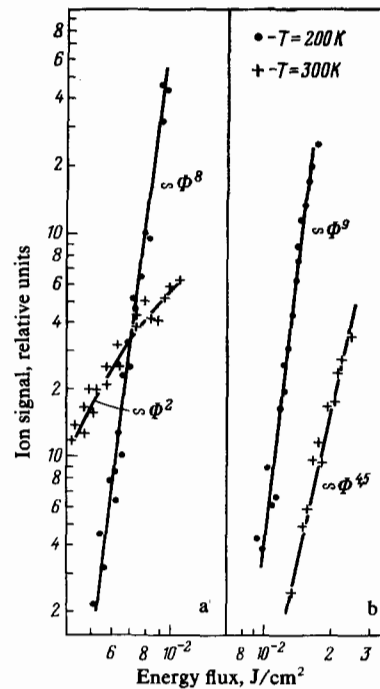


FIG. 20. Dependence of the ion signal on the energy flux of the laser pulse $\Phi$ upon irradiation of anthracene adsorbed on the surface of adenine (a) and rhodamine 6G (b) at two different temperatures.[93]

Comparison of the amplitudes of the ionic signals corresponding to irradiation of a surface and of the volume above the surface permits estimating the lifetime of the adsorbed molecule on the surface $\tau_{ads}$ and the energy of adsorption $E_{ads}$. Indeed, for a "gas-surface" equilibrium the concentration of molecules adsorbed on the surface $n_s$ and in the gas phase $n_g$ are related by the expression

$$n_s = \frac{1}{4} n_g v_0 \tau_{ads}, \tag{4.4}$$

where $v_0$ is the average velocity of molecules in the gas. Assume that all molecules on the surface are desorbed by the first laser pulse ($P_{des} = 1$). Then the number of ions forming under the action of the second laser pulse equals $N_i^s = n_s S \eta_{ion}$, where $S$ is the irradiated surface area from which desorption occurs. When the volume $V$ above the surface is irradiated, the number of ions formed equals $N_i^g = n_g V \eta_{ion}$. Therefore, the ratio of the integrated ionic signals corresponding to irradiation of the surface and of the volume equals

$$\frac{N_i^s}{N_i^g} = \frac{1}{4} \tau_{ads} v_0 \frac{S}{V}. \tag{4.5}$$

The experimental ratio $N_i^s/N_i^g$ in the case of naphthalene molecules adsorbed on rhodamine 6G is $2 \cdot 10^3$ at $T = 200$ K. From here it is possible to determine the lifetime of the molecule on the surface $\tau_{ads} = 0.18$ s and to estimate, from (4.1), the energy of adsorption of naphthalene on rhodamine 6G: $E_{ads} \approx 0.6$ eV.

### e) Nonequilibrium processes accompanying picosecond irradiation of a large molecule on a surface

In experiments with nanosecond and even 30-picosecond pulses, the electronic excitation energy relaxed to ther-

mal energy and gave rise to nonselective thermal desorption and subsequent photoionization of molecules. The search for nonequilibrium processes of detachment of the molecular ion of an excitable chromophore of a large molecule on a surface is of great interest. This is important, in particular, for realizing a laser photoionic projector of molecules.[98-100] Of course, nonequilibrium, selective with respect to the chromophore, detachment of a molecular ion can probably be observed only with irradiation of a large molecule by a subpicosecond laser pulse. Proceeding along this path, we performed experiments[101,102] with radiation pulses whose duration varied from 20 ns to 5 ps.

The experiments were performed with fine crystalline powder of peptide, whose molecule is a chain consisting of three amino acids (tryptophane, alanine, and glycine) with protective acetate and ester groups at the ends. One of the amino acids entering into the peptide—tryptophane—contains a chromophoric group—an indole ring, whose system of conjugate bonds determines the absorption of the peptide in the near UV region.

The experiment consisted of irradiating a peptide specimen with pulses of different duration: 10 ns, 30 ps (Nd:YAG laser, fourth harmonic) and 5 ps (Nd:phosphate glass laser, fourth harmonic).

The mass spectra of the positive ions formed upon irradiation are shown in Fig. 21. The typical mass spectrum consists of several intense peaks, which correspond to different fragments of the peptide molecule. Each fragment contains a chromophoric group and forms as a result of fragmentation of the molecule primarily along the peptide bonds. One of



FIG. 21. Mass spectra forming upon irradiation of peptide powder by laser pulses of different durations: 20 ns (a), 30 ps (b), and 5 ps (c).[101]

the lightest fragment ions corresponds to the ion of the chromophore (it is circled in Fig. 21a).

The mass spectra obtained are not normalized to the sensitivity of the apparatus for ions of different masses. For this reason, the relationship between the ion peaks within a single mass spectrum is only of a qualitative character. However, this does not interfere with the comparison of different mass spectra with one another.

The dependence of the total ion yield on the energy flux of the laser pulses is very sharp, as in the case of simpler molecules. At the same time, the ratio between the different peaks in the mass spectrum remains practically constant in the range of energy fluxes investigated from the threshold of appearance ($\Phi_{th} = (2-4)\cdot 10^{-3}$ J/cm$^2$) to the maximum recorded magnitude ($10^4$ ions/pulse, $\Phi = 10^{-2}$ J/cm$^2$) with fixed pulse duration.

Comparison of mass spectra obtained with different radiation pulse durations shows the following: 1) a decrease in the pulse duration leads to a significant increase in the fraction of chromophore ions and with $\tau_p = 5$ ps the magnitude of the corresponding peak in the mass spectrum becomes maximum; 2) in this case, new fragment ions do not appear in the mass spectrum, and this indicates the absence of additional fragmentation of molecules.

The sharp dependence of the ion yield on the energy flux of the laser radiation and simultaneously the constancy of the pattern of the mass spectrum with fixed pulse duration suggests that in this case the recorded ions are formed as a result of ionization and fragmentation, above the surface of the specimen, of neutral molecules evaporating during the course of the pulse.

The growth of the chromophore ion fraction in the case of picosecond pulses is probably related to the fact that the chromophoric group can absorb two and more photons and can become detached before total randomization of the absorbed energy in the molecule.

For picosecond pulse durations, together with intramolecular nonequilibrium processes, the surface can play an important role in the formation of the mass spectrum, because over the time of the pulse molecules have time to fly away from the surface to distances comparable to the dimensions of the molecules themselves. For example, for $\tau_p = 5$ ps, the displacement of molecules over the time of the pulse is only 7–10 Å. In the case of subpicosecond pulses, detachment of the molecular ion of a chromophore molecule, which has not yet moved away from the surface, can be observed. In other words, with the use of subpicosecond laser pulses it is possible to go from photoionization spectroscopy of free molecules, which is the subject of the present review, to photoionization spectroscopy of molecules on a surface.

## 5. APPLICATION OF RESONANT LASER PHOTOIONIZATION TO DETECTION OF POLYATOMIC MOLECULES

Analysis of substances by the mass spectrometric method consists of transforming the molecules of the specimen into ions followed by separation and analysis of the ions according to the mass-to-charge ratio. Mass-spectrometrists have always made great efforts to create sources of ions with
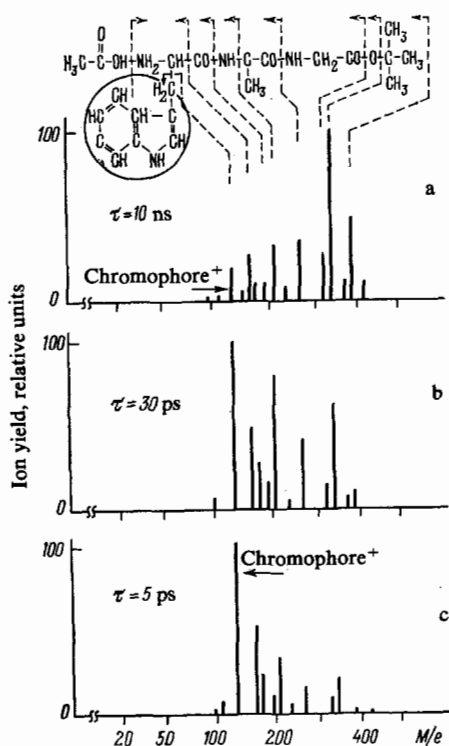
high ionization efficiency with moderate fragmentation of molecules. Successes achieved in this direction make the mass-spectrometric method of analysis one of the most sensitive methods. Under favorable conditions, it is possible to analyze an amount of matter as small as $2.5 \cdot 10^{-14}$ g.[103] The characteristic efficiency of transformation into ions, followed by detection of the ions, in modern mass spectrometers constitutes $10^{-5}$ of the number of molecules[103] and, therefore, is still far from the limit. The situation with selectivity is much worse. Mass spectra of molecules, as a rule, consist of a set of fragment ions, and molecular ions often are completely absent. In spite of the fact that analysis of fragments gives valuable information on the structure of molecules, it is very difficult to analyze a multicomponent mixture. Due to the superposition of mass spectra, analysis of a molecular component with a low fractional content is especially difficult. This is overcome to a large extent by preliminary separation of components of the mixture in a chromatograph,[103] which, however, does not solve the problem completely.

A fundamentally new approach to the problem of analysis of trace quantitites of complex molecules was first proposed and developed in the works cited above.[4,7] The essence of the method consists of selective multistep laser photoionization of molecules followed by mass-spectrometric analysis of the products of ionization. In this method, the selectivity of ionization is determined by the selectivity of excitation of molecules into vibrational and electronic states and can be very high. With wavelength tuning of the exciting laser radiation, the mass spectrum of photons is modulated by the optical absorption spectrum and, in this manner, information on molecules is obtained in the form of highly selective two-dimensional mass-optical spectra. In addition, the efficiency of laser photoionization can be very high. Progress achieved in recent years in this direction makes laser photoionization one of the most sensitive methods of detection of polyatomic molecules.

### a) Detection of single molecules

When molecules are photoionized by intense UV laser radiation, there is a difficulty related to the possiblity of absorption by the molecule (or its fragments) in the intense laser radiation field of a much larger number of photons than necessary for simple photoionization. As a result, a strongly fragmented mass spectrum is obtained, and information on the initial molecules can be lost. Investigation of the mechanism of formation of the photoionization mass spectrum of molecules under the action of intense UV laser radiation (see Sec. 2) showed that the limiting efficiencies of ionization with moderate fragmentation of molecules are achieved under conditions when the intermediate electronically excited state is stable over the duration of the laser pulse and the energy of the laser quantum at the second stage exceeds the vertical ionization potential of the molecule out of the excited state. The last condition corresponds to a small probability of dissociation of the molecule after absorption of the second photon compared with ionization.
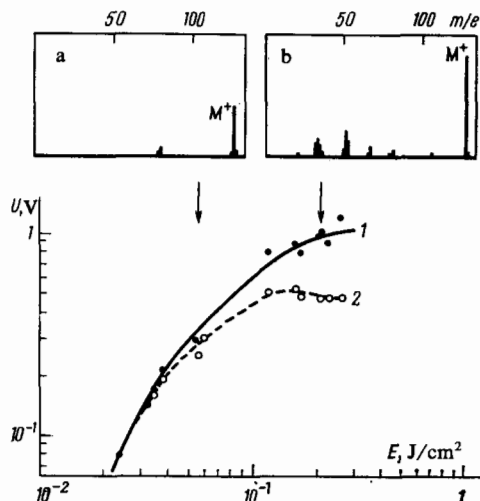


FIG. 22. Dependence of the integrated photoionic signal (curve 1) and the signal from molecular ion of naphthalene (curve 2) on the energy density of the laser radiation pulses ($\lambda = 249$ nm) and mass spectrum of the photoions formed.[18]

An experiment on detection of single molecules of naphthalene[18] was performed precisely in the indicated optimum, regime. The molecules were excited into the first electronic singlet state and the excited molecules were ionized by excimer KrF laser radiation with $\lambda = 249$ nm. The lifetime of the intermediate electronic singlet state was comparable to the duration of the laser pulse of 20 ns, and the energy of the two laser photons exceeded by almost 2 eV the ionization potential of the molecule, which is equal to 8.12 eV. The photoions were recorded with the help of a time-of-flight mass spectrometer. A mixture of naphthalene vapor and air at a pressure of $10^{-5}$ torr was irradiated.

Figure 22 shows the dependences of the ionic signal, summed over all masses (curve 1) and separately for the molecular ion (curve 2), on the energy density of the laser radiation pulses, and the mass spectra of the photoions formed. For relatively low radiation pulse energies, the ionization yield of naphthalene is a quadratic function of energy and practically only the molecular ion is observed in the mass spectra (oscillogram $a$ in Fig. 22). For laser energies exceeding 0.05 J/cm², both the molecular and integrated ionic signal of naphthalene saturate. In the region 0.15–0.20 J/cm² the dependence of the total signal reaches a plateau, which is accompanied by some increase in the fraction of fragments in the mass spectrum. The small drop in the yield of molecular ions occurs due to their dissociation in the laser radiation field.

The quadratic nature of the yield of photoions in the low-energy range is explained by the two-step process of photoionization of the molecule, inasmuch as the ionization potential of naphthalene $I = 8.12$ eV is less than the energy of two laser quanta $2\hbar\omega = 10$ eV. Saturation of ionization of naphthalene in the region 0.05–0.10 J/cm² agrees qualitatively with the saturation of absorption of photons on the first step, calculated according to the well-known cross section of absorption in the gas phase. Attainment of the plateau in the total ionic signal at pulse energies of 0.15–0.20 J/cm² indicates that the absorption of photons at the second

step also saturates. Since the energy of two laser photons greatly exceeds the ionization potential of molecules and a nonlocalized $\pi$-electron is detached with photoionization, the competition between dissociation of molecules and ionization acompanying absorption of the second photon can be neglected. Therefore, the efficiency of photoionization at such laser radiation energies is close to 100%. Under the given conditions the sensitivity of detection of naphthalene molecules in the experiment over the course of a single laser pulse equalled four molecules in the photoionization volume.[18] This magnitude corresponds to a naphthalene partial pressure of $10^{-14}$ torr and a relative concentration in air of $10^{-9}$.

The results obtained are practically limiting with respect to the efficiency of detection of molecules in the photoionization volume and correspond to detection of single molecules over the course of a single pulse. We note that achievement of high sensitivity of detection of naphthalene molecules contributed greatly to the selectivity of laser stepwise photoionization. The basic components of air were completely absent from the mass spectrum of the photoions because simple molecules do not absorb in the 250-nm range. Even such selectivity of ionization with respect to classes of molecules greatly increases the analytic possibilities of mass spectrometry. In standard magnetic mass spectrometers, for example, there is a constant background at all masses due to scattered ions, which restricts the detectable relative concentrations to the level $10^{-6}$–$10^{-9}$.[104]

We note that naphthalene molecules are not unique from the point of view of the possibilities of their detection via photoionization. Table 1 presents experimental data on the efficiencies of two-step photoionization of a number of molecules in a single-frequency laser field with intensity $10^7$ W/cm$^2$.[35] It is significant that fragmentation of molecules was practically absent at this radiation intensity. It is evident from the table that when the laser radiation intensity is close to the saturation intensity, the efficiency of photoionization of molecules is very high and is close to 100%.

An important advantage of laser photoionization is the possibility of detecting molecules with an efficiency close to unity within very short time intervals $\tau = 10^{-8}$–$10^{-11}$ s. This opens up new possibilities for mass-spectrometrical investigations of rapid processes. Thus, in Ref. 92, precisely this method was used to record desorption of neutral molecules from the surface of molecular crystals stimulated by picosecond laser pulses (see Sec. 4) and in addition the number of molecules leaving the surface within a single laser pulse was of the order of 10–100 molecules/pulse.

The main disadvantage of the method of selective laser stepwise photoionization, as also of electron impact, is that it is suitable only for molecules which can be put into the gas phase. In this respect, the experiments described in Sec. 3 on combined formation of molecular ions under irradiation of a surface by pulsed UV laser radiation whose wavelength falls in the absorption band of the material are of great interest:

moderate pulsed heating of the surface with $\rightarrow$ resonant absorption

thermal desorption of neutral $\rightarrow$ molecules.

multiphoton resonance photoionization

This process is of interest for photoionization mass-spectrometry of molecules on the surface of a material. Moreover, experiments with molecules adsorbed on the surface of a specimen,[93,94] prove that the sensitivity of photoionization detection of molecules can be radically increased (by a factor of $10^3$). The increase of sensitivity is achieved by accumulating molecules on the surface while their density in the gas phase is extremely low. Thus an alternative approach is possible to the development of a laser photoionization detector of molecules based on the following sequence of processes:

accumulation of molecules on the surface of the $\rightarrow$ adsorbent

pulsed thermal desorption of accumulated $\rightarrow$ molecules

multiphoton resonance photoionization of desorbed free molecules.

In this approach it is possible to use lasers with low repetition frequency. It is not difficult to imagine as well a variant of such a detector in which molecules desorbed in pulses enter a pulsed supersonic jet for cooling and subsequent more selective photoionization detection in the cooled jet.

### b) Two-dimensional mass-optical detection of molecules

Photoionization detection of single molecules of naphthalene in Ref. 18 was achieved with the help of a single laser with fixed radiation frequency $v = 4 \cdot 10^4$ cm$^{-1}$. It is significant that even in such a simple scheme there is a selectivity of ionization, which permits singling out polyatomic molecules with conjugate double bonds against a background of simple molecules. However, in order to detect polyatomic molecules in complicated mixtures, a high selectivity of ioniza-

TABLE I. Experimental values of the absorption cross sections for radiation in the first and second steps and the efficiency of two-step photoionization of some polyatomic molecules in a single-frequency laser field.[42] The radiation frequency corresponded to the onset of electronic absorption of the molecules.

| | $\langle \sigma_1 \rangle$, cm$^2$ | $\langle \sigma_2 \rangle$, cm$^2$ | $I_{sat}$, W/cm$^2$ | Ionization yield, $I = 10^7$ W/cm$^2$, % |
|---|---|---|---|---|
| Benzene | $2.7 \cdot 10^{-17}$ | $3.4 \cdot 10^{-18}$ | $1.5 \cdot 10^8$ | 3.7 |
| Thiophene | $1.8 \cdot 10^{-17}$ | | | 0.01 |
| Toluene | $6.0 \cdot 10^{-18}$ | $2.0 \cdot 10^{-17}$ | $3.3 \cdot 10^7$ | 6.2 |
| Naphthalene | $4.8 \cdot 10^{-18}$ | $1.6 \cdot 10^{-19}$ | $2.8 \cdot 10^9$ | 0.05 |
| Aniline | $4.5 \cdot 10^{-17}$ | $2.0 \cdot 10^{-17}$ | $2.3 \cdot 10^7$ | 25 |

100   Sov. Phys. Usp. 27 (2), February 1984

Antonov et al.   100

tion of molecules is necessary. Thus, for example, in detecting naphthalene ions with a molecular mass equal to 128 it is, in general, necessary to distinguish these ions from molecular ions of other molecules with mass 128, such as $C_2H_2Cl_2O_2$, $C_8H_{16}O$, $C_9H_{20}$, $C_7H_{12}O_2$, $C_8HO_{12}$, and others. In addition, with inadequate selectivity of ionization the useful signal of the molecular mass can be masked by different fragment ions from heavier molecules. The required selectivity can be achieved by adding to the known mass-spectrometric methods of analyzing multicomponent mixtures[103] a channel containing spectral information on molecules with stepwise photoionization using frequency-tunable lasers. In this case, information on the initial molecules acquires a two-dimensional character: the magnitude of the signal at the output of the mass spectrometer depends simultaneously both on the mass of the ion and on the frequency of the laser radiation. Such two-dimensional mass-optical recording was demonstrated in Ref. 40 for the anthracene molecule (see Fig. 12) with a laser radiation intensity close to the intensity of saturation of optical transitions, as well as under conditions of multiphoton ionization.[27,105] In all cases, fragment ions, each of which can have its own, differing from other ions, spectral dependence of the yield, appear in the mass spectra. Thus the method of selective laser photoionization permits obtaining very characteristic two-dimensional "maps" of molecules. Based on the high information content of two-dimensional mass-optical spectra, the required selectivity can in principle be obtained in detection of different molecules whose structure and molecular weight are close.

In some cases spectral selectivity of stepwise photoionization can be sufficient for detection of polyatomic molecules in air with the help of a simple ionization chamber without separation of ions by mass.[106,107,33]

### c) Comparison of different schemes of selective laser photoionization of molecules

We shall examine different schemes of laser photoionization from the point of view of attaining maximum sensitivity and selectivity of detection of polyatomic molecules.

*1) Multiphoton ionization of molecules.* The method of multiphoton ionization of polyatomic molecules is currently widely used for systematic investigation of the spectroscopy of excited states of molecules, especially states forbidden for single-photon transitions.[72,73] An attractive aspect of the method is the relative simplicity of obtaining multiphonon spectra and the higher, compared with fluorescence measurements, sensitivity. Another advantage is the possibility of using visible and near-ultraviolet radiation to investigate electronic states lying in the vacuum ultraviolet region of the spectrum. Although multiphoton ionization in the mass spectrum gives much new information on photoionization and photofragmentation of molecules under the action of intense laser radiation, nevertheless, systematic use of multiphoton ionization of molecules for mass-spectral analysis is hardly suitable due to the high degree of fragmentation and comparatively low efficiency of ionization of molecules.

*2) Stepwise photoionization of molecules through intermediate electronic states.* In this variant, two schemes can be

distinguished: a) stepwise photoionization in a single-frequency laser field and b) independent steps of excitation and photoionization of molecules using time-synchronized laser pulses.

In the first case, for efficient photoionization of molecules the laser radiation frequency $\omega$ must satisfy the condition $2\hbar\omega > I$, where $I$ is the ionization potential of the molecule. In this case, the only restriction on the intensity of the laser radiation is the loss of mass-spectral information due to strong fragmentation of molecules. The efficiency of ionization of molecules in this scheme is very high and, in many cases, approaches 100%. However, for many molecules, with this choice of frequency of the laser radiation and high-lying electronic states, which can rapidly deexcite via dissociation and electronic conversion which compete with photoionization, are excited. The absorption spectra of polyatomic molecules in this region often have no structure.

With respect to selectivity the second scheme with independent excitation and ionization frequencies has greater possibilities. When using far-UV and VUV radiation in the step involving photoionization of molecules from an excited state, two-dimensional spectra of molecules with wavelength tuning of the exciting radiation in the long-wavelength region of electronic transitions, where the molecular spectra have greatest structure, can be obtained. An additional channel of information concerning the lifetimes of excited molecules appears in this scheme with ionization of molecules from excited states by a delayed laser pulse. It should be noted, however, that in this scheme extraneous channels of photoionization, whose suppression requires restricting the maximum intensity of radiation both at the first and second steps, can in principle exist. This decreases the efficiency of selective two-step photoionization. Indeed, in the typical case $2\hbar\omega < I < 2\hbar\omega_2$, where $\omega_1$ and $\omega_2$ are the frequencies of laser radiation at the first and second steps, respectively, two-step photoionization of molecules through the high-lying electronic states by laser radiation of the second step is possible (Fig. 23c). In addition, three-step photo-
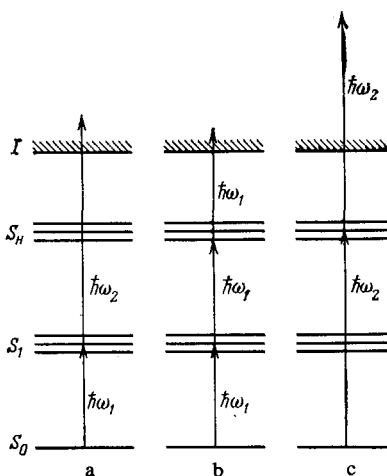


FIG. 23. Schemes of the possible photoionization channels for molecules in a two-frequency laser field. a) Selective two-step photoionization; b) three-step photoionization under the action of laser radiation in the first step; c) two-step photoionization of molecules by laser radiation in the second step.

ionization can exist with resonant absorption by the molecule of a sequence of three photons of the exciting laser with frequency $\omega_1$ (Fig. 23b).

Let us compare the relative contributions of each of the three channels of photoionization of a molecule (see Fig. 23). For an estimate, we shall assume that all cross sections of optical transitions indicated in Fig. 23 are equal and that the lifetimes of all intermediate levels exceed the laser pulse duration. We shall assume that the statistical weights of the upper levels for all transitions is much greater than for the lower levels. This permits neglecting the reverse transitions under the action of the radiation. It is clear that for an energy density of the laser radiation close to the saturation energy of the transitions $\Phi \approx \Phi_{sat} = \hbar\omega/\sigma$, all three channels make approximately the same contribution to ionization of the molecule. Under conditions that are far from saturation, the number of ions forming along these channels will be

$$N_i^{(a)} = \frac{\Phi_1}{\hbar\omega_1} \frac{\Phi_2}{\hbar\omega_2} \sigma^2 N_0, \qquad (5.1)$$

$$N_i^{(b)} = \frac{1}{6} \left( \frac{\Phi_1}{\hbar\omega_1} \right)^3 \sigma^3 N_0, \qquad (5.2)$$

$$N_i^{(c)} = \frac{1}{2} \left( \frac{\Phi_2}{\hbar\omega_2} \right)^2 \sigma^2 N_0, \qquad (5.3)$$

where $\Phi_1$ and $\Phi_2$ are the energy densities of the laser pulses at the first and second steps, and $N_0$ is the number of molecules in the photoionization volume. It is evident that the numbers of ions in channels (5.2) and (5.3) have higher-order power-law dependences on the energy density of the radiation pulses $\Phi_1$ and $\Phi_2$, so that as the energies of the laser pulses decrease, the ratio of the useful signal of two-step ionization along channel (5.1) to the background (5.2) and (5.3) will increase owing to a reduction of ionization efficiency. Choosing, for example, the ratio $N_i^{(a)}/(N_i^{(b)} + N_i^{(c)}) = 10$, we obtain from (5.1)–(5.3) an efficiency of selective two-step photoionization equal to 0.01%.

For real molecules, the situation can be more favorable. The principal difference from the model analysis lies in the fact that in the highly excited electronic states, which participate in transitions along channels (5.2) and (5.3) (see Fig. 23), the rates of nonradiative excitation relaxation processes can be so high that photoionization from these states will be strongly suppressed. Thus, for example, in experiments[19,20,54] on selective two-step photoionization with excitation of a number of molecules (formaldehyde, benzaldehyde, benzophenone, and others) into highly excited states with VUV radiation with photon energy 7.7 eV, the two-stepped ionization signal was not observed.

Under optimal conditions for absence of extraneous channels of photoionization, the selectivity of ionization is determined by the electronic absorption spectra of molecules. It is well known, however, that electronic absorption spectra of polyatomic molecules are much less characteristic in the gas phase than vibrational IR spectra. The selectivity of photoionization through electronic states can be radically increased with the use of cooled supersonic molecular beams. The possibility of using supersonic molecular beams to cool complicated molecules, such as, for example, phthalocyanine $(C_{32}N_8H_{18})$, has been recently demonstrated.[108]

The absorption spectrum of this molecule under the conditions of deep cooling of vibrational and rotational degrees of freedom consisted of lines with width $0.5–1$ cm$^{-1}$. Separate vibrational-rotational lines were completely resolved in the electronic absorption spectrum of the oxalyl fluoride $(C_2O_2F_2)$ molecule, cooled in a pulsed supersonic beam to 0.17 K.[109] In this sense, we can talk about the achievement of limiting quantum selectivity in absorption of radiation.

Let us estimate the limiting sensitivity of the method of stepwise laser photoionization through intermediate electronic states in combination with the supersonic cooled molecular beam for detection of impurities in the atmosphere. The expression for the number of selectively forming ions within a single pulse has the form

$$N_{ion} = \eta_{det} Y_{ion} \gamma n_{beam} V_p, \qquad (5.4)$$

where $\eta_{det}$ is the efficiency of detection of photoions, $Y_{ion}$ is the yield of two-step photoionization, $\gamma$ is the relative concentration of impurity molecules in air, $n_{beam}$ is the density of molecules in the beam, and $V_p$ is the photoionization volume. Assuming that the threshold of detection of molecules equals the detection of a single selectivity formed photon and substituting the values $\eta_{det} = 0.5$,[56] $Y_{ion} = 1$,[19] and $n_{beam} = 2 \cdot 10^{14}$ cm$^{-3}$, corresponding to a maximum gas pressure of $5 \cdot 10^{-3}$ torr with which collisionless extraction of ions from the beam is still possible, and $V_p = 0.1$ cm$^3$, we obtain $\gamma = 10^{-13}$, which corresponds to a detection threshold of $3 \cdot 10^6$ molecules/cm$^3$ in air.

*3) Stepwise photoionization through intermediate vibrational states of molecules.* Vibrational spectra are the most informative for polyatomic molecules and, for this reason, stepwise photoionization through intermediate vibrational states is of special interest from the point of view of selectivity of detection of trace substances. The realization of this scheme encounters certain difficulties, related to the fact that with vibrational excitation the shift in the photoionization limit is known to be less than the width of the photoionization band edge and a single-photon ionization of unexcited molecules will unavoidably occur. A much worse situation can occur with superposition of intense single-photon ionization mass spectra from molecules of another type with a lower ionization potential. In addition, with absorption of a short-wavelength radiation quantum $\hbar\omega_3$, the photoionization process competes with photodissociation, because the sum of the laser photon energies is not much greater than the ionization potential of the molecule and the Franck-Condon factors for the transition with ionization can in general be small.

The sensitivity and selectivity of this scheme can be greatly increased by using the following: a) multistep vibrational excitation, which will lead to a considerable shift in the photoionization limit from the excited state and, as a result, to an increase in the fraction of selective ions; b) a cooled molecular beam. In this case, the occupancy factor $q$ of the molecular state in resonance with the laser field can be close to one, which will radically increase both the selectivity and the sensitivity of detection. In this case, the efficiency of selective photoionization will be determined only by the com

102    Sov. Phys. Usp. **27** (2), February 1984

Antonov *et al.*    102

peting process of dissociation upon absorption of a short-wavelength photon.

*4) Successive excitation of intermediate vibrational and electronic states.* This scheme is a combination of the two preceding schemes and combines the selectivity of vibrational spectra of molecules with such advantages of the scheme involving photoionization via the electronic states, as the absence of a single-photon ionization background and the possibility of obtaining information on the lifetimes of electronically excited molecules. In addition, as in the preceding cases, an important component part of the technique is the use of supersonic pulsed molecular beams. An adequate mass-spectrometric technique must guarantee detection of the mass-spectrum of photoions within a single pulse. The first experiment along these lines was recently performed with the NO molecule, which was ionized in successive processes of vibrational excitation and multiphoton transitions under the action of dye laser radiation.[24]

Summarizing the discussion of the possible schemes of resonance stepwise photoionization of polyatomic molecules by laser radiation, we emphasize that it is entirely realistic that a highly selective laser detector of trace quantities of molecules, whose sensitivity will be several orders of magnitude higher than the sensitivity of all existing analytical methods, will be developed in the near future. Success along this path will be achieved as a result of the combination of the most diverse achievements of experimental physics: first, the technique of low-temperature molecular jets; second, the technique of multistep excitation of high-lying vibrational levels by tunable *IR* laser radiation and subsequent photoionization of vibrationaly excited molecules directly or through intermediate electronic states; third, the technique of time-of-flight mass spectrometric detection of the products of photoionization of molecules. Figure 24 shows the simplified schemes of the quantum transitions of highly selective stepwise photoionization of molecules and a possible design of such a laser detector of molecules. Realization of this idea should greatly expand the possibilities of analytical spectroscopy and chemistry and should in principle solve the long-standing problem of experimental physics: detection of "smell" by physical methods with a sensitivity which is accessible today only to the olfactory senses of living organisms.[10,110]

Of course, further investigation of resonance interaction of laser radiation with molecules will undoubtedly lead to the development of new possibilities of highly selective photoionization. For example, resonance excitation of vibrations of molecules in a biharmonic field due to Raman transitions[111] followed by photoionization of excited molecules[112] deserves attention. In this case, by selecting excitation frequencies near an electronic transition it is not only possible to increase the cross section of the Raman process[113] but also to gain additional selectivity of vibrational excitation of a definite chromophoric group.

It should be emphasized that the high selectivity of resonance photoionization of molecules via vibrational states will permit detecting not only traces of molecules of a specific type, but also single molecules containing rare isotopes.
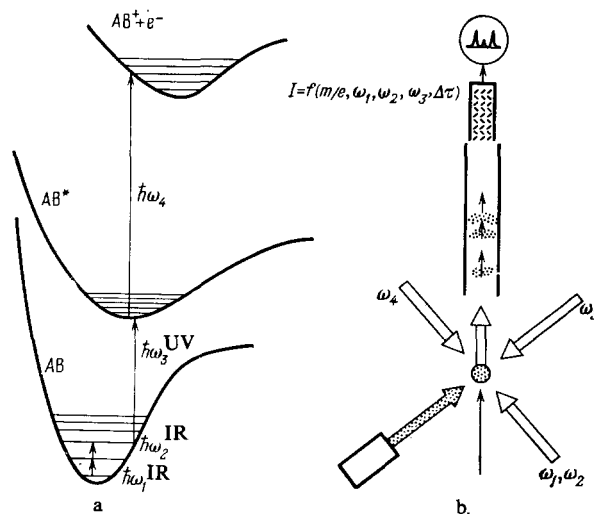


FIG. 24. Highly selective laser detector of trace quantities of molecules. a) Optimum scheme of multistep selective photoionization via intermediate vibrational and electronic states; b) possible design of a detector with a pulsed source of cooled molecules and a time-of-flight mass spectrometer.

The method of multistep resonance photoionization of atoms is already being successfully developed for this purpose.[114,94] The method of resonance photoionization of molecules also opens up, in an entirely analogous manner, new possibilities. In particular, for detection of rare molecules containing $^{14}C$.[97]

[1] V. S. Letokhov, Usp. Fiz. Nauk **125**, 57 (1978) [Sov. Phys. Usp. **21**, 405 (1978)]; In: Progress in Optics, edited by E. Wolf, North-Holland, Amsterdam, Vol. 16, p. 1 (1978)

[2] A. Ben-Shaul, Y. Haas, K. L. Kompa, and R. D. Levine, Lasers and Chemical Change, Springer-Verlag, New York (1981) (Springer Series in Chemical Physics Vol. 10).

[3] V. S. Letokhov, Nelineĭnye selektivnye fotoprotsessy v atomakh i molekulakh (Nonlinear Selective Photo Processes in Atoms and Molecules), Nauka, Moscow (1983); V. S. Letokhov, Nonlinear Laser Chemistry, Springer-Verlag, New York (1982) (Springer Series in Chemical Physics, Vol. 22).

[4] R. V. Ambartzumian and V. S. Letokhov, Appl. Opt. **11**, 354 (1972).

[5] C. B. Moore, Acc. Chem. Res. **6**, 323 (1973).

[6] V. S. Letokhov, Science **190**, 344 (1975).

[7] V. S. Letokhov in: Frontiers in Laser Spectroscopy, Proc. of Les Houches School, June 30–July 26, 1975, Vol. 2, edited by R. Balina, S. Haroche, and S. Liberman, North-Holland, Amsterdam (1977), p. 771.

[8] V. S. Letokhov in: Tunable Lasers and Applications, Proc. of the Loen Conference, Norway, 1976, edited by A. Mooradian, T. Jaeger, and P. Stokseth, Springer-Verlag, New York (1976), p. 122 (Springer Series in Optical Sciences, Vol. 3).

[9] V. S. Letokhov, Laserspektroskopie, Academie-Verlag, Berlin (1977).

[10] V. S. Letokhov, Usp. Fiz. Nauk **118**, 199 (1976) [Sov. Phys. Usp. **19**, 109 (1976).

[11] G. S. Hurst, M. H. Nayfeh, and J. P. Young, Appl. Phys. Lett. **30**, 229 (1977).

[12] G. I. Bekov, V. S. Letokhov, and V. I. Mishin, Pis'ma Zh. Eksp. Teor. Fiz. **27**, 52 (1978) [JETP Lett. **27**, 47 (1978)].

[13] N. V. Karlov, B. B. Krynetskiĭ, V. A. Mishin, and A. M. Prokhorov, Usp. Fiz. Nauk **127**, 593 (1979) [Sov. Phys. Usp. **22**, 220 (1979)].

[14] G. S. Hurst, M. G. Payne, S. D. Kramer, and T. P. Young, Rev. Mod. Phys. **51**, 767 (1979).

[15] V. I. Balykin, G. I. Bekov, V. S. Letokhov, and V. I. Mishin, Usp. Fiz. Nauk **132**, 293 (1980) [Sov. Phys. Usp. **23**, 651 (1980)].

[16] J. Robieux and J. M. Anclair, French Patent No. 1391738, Appl. 10/21/63 (Publ. 1/2/65), USA Patent No. 3343087, Appl. 9/16/64 (Publ. 5/6/69).

[17] V. S. Antonov and V. S. Letokhov, Appl. Phys. **24**, 89 (1981).

103    Sov. Phys. Usp. **27** (2), February 1984

Antonov *et al.*    103

[18]V. S. Antonov, V. S. Letokhov, and A. N. Shibanov, Opt. Comm. **38**, 182 (1981).

[19]V. S. Antonov, I. N. Knyazev, V. S. Letokhov, and V. G. Movshev, Zh. Eksp. Teor. Fiz. **73**, 1325 (1977) [Sov. Phys. JETP **46**, 697 (1977)].

[20]S. V. Andreyev, V. S. Antonov, I. N. Knyazev, and V. S. Letokhov, Chem. Phys. Lett. **45**, 166 (1977).

[21]P. M. Johnson, M. R. Berman, and D. Zakhaim, J. Chem. Phys. **62**, 2500 (1975).

[22]G. Petty, C. Tai, and F. W. Dalby, Phys. Rev. Lett. **34**, 1207 (1975).

[23]A. S. Sudbo, P. A. Schulz, D. J. Krajnovich, Y. T. Lee, and Y. R. Shen, Opt. Lett. **4**, 219 (1979).

[24]P. Esherick and R. J. M. Anderson, Chem. Phys. Lett. **70**, 621 (1980).

[25]V. S. Letokhov and V. P. Chebotaev, Printysipy nelineĭnoĭ lazernoĭ spektroskopii (Principles of Nonlinear Laser Spectroscopy), Nauka, Moscow (1975) [Engl. Transl. in Ref. 26].

[26]V. S. Letokhov and V. P. Chebotayev, Nonlinear Laser Spectroscopy, Springer-Verlag, New York (1977) (Springer Series in Optical Sciences, Vol. 4).

[27]L. Zandee and R. B. Bernstein, J. Chem. Phys. **71**, 1359 (1979).

[28]K. Rhodes [Ed.]. Excimer Lasers, Springer-Verlag, New York (1979) (Topics in Applied Physics, Vol. 30).

[29]J. R. Woodworth and J. K. Rice, J. Chem. Phys. **69**, 2500 (1978).

[30]V. S. Antonov, Kvant. Elektron. **5**, 915 (1978) [Sov. J. Quantum Electron. (Moscow) **8**, 524 (1978)].

[31]M. Yu. Gel'tsel', A. D. Panfilov, S. S. Sobolev, and L. I. Yudin, Prib. Tekh. Eksp. **2**, 121 (1965).

[32]S. V. Andreyev, V. S. Antonov, I. N. Knyazev, V. S. Letokhov, and V. G. Movshev, Phys. Lett. A **54**, 91 (1975).

[33]R. Frueholz, J. Wessel, and E. Wheatley, Anal. Chem. **52**, 281 (1980).

[34]V. G. Fleĭsher, Prib. Tekh. Eksp. **2**, 115 (1962).

[35]J. D. Winefordner in: New Applications of Lasers to Chemistry, edited by G. Heiftje, Am. Chem. Soc. Symp. Ser., No. 85 (1978).

[36]M. E. Akopyan, in: Uspekhi fotoniki (Progress in Photonics), Leningrad State University, Leningrad (1977) No. 6, p. 3.

[37]V. N. Kondrat'ev [Ed.], Energii razryva khimicheskikh svyazeĭ. Potentsialy ionizatsii i srodstvo k élektronu (Energy of Rupture of Chemical Bonds. Ionization Potential and Electron Affinity), Nauka, Moscow (1974).

[38]V. S. Antonov, I. N. Knyazev, and V. G. Movshev, Kvant. Elektron. **2**, 1305 (1975) [Sov. J. Quantum Electron. (Moscow) **5**, 709 (1975)].

[39]J. H. Brophy and C. T. Rettner, Chem. Phys. Lett. **67**, 351 (1979).

[40]V. S. Antonov and A. N. Shibanov, Opt. Spektrosk. **52**, 390 (1982) [Opt. Spectrosc. **52**, 234 (1982)].

[41]V. S. Antonov, Opt. Spektrosk. **52**, 10 (1982) [Opt. Spectrosc. **52**, 5 (1982)].

[42]U. Boesl, H. J. Neusser, and E. W. Schlag, Chem. Phys. **55**, 193 (1981).

[43]T. Nakayama, M. Y. Kitamore, and K. Watanabe, J. Chem. Phys. **3**, 1180 (1959).

[44]V. M. Donnelly and F. Kaufman, J. Chem. Phys. **69**, 1456 (1978).

[45]M. A. Duncan, T. G. Dietz, and R. E. Smalley, J. Chem. Phys. **75**, 2118 (1981).

[46]E. S. Yeung and C. B. Moore, J. Chem. Phys. **58**, 3988 (1973).

[47]K. Sakurai, G. Capelle, and H. P. Broida, J. Chem. Phys. **54**, 1412 (1971).

[48]T. Aoki, T. Morikawa, and K. Sakurai, J. Chem. Phys. **59**, 1543 (1973).

[49]T. G. Kietz, M. A. Duncan, and R. E. Smalley, J. Chem. Phys. **76**, 1227 (1982).

[50]K. C. Smyth, J. A. Schiavone, and R. S. Freund, J. Chem. Phys. **61**, 1789 (1974).

[51]N. W. Reid, Intern. J. Mass Spectr. Ion Phys. **6**, 1 (1971).

[52]P. B. Terent'ev, Mass-spektrometriya v organicheskoĭ khimii (Mass Spectrometry in Organic Chemistry), Vysshaya shkola, Moscow (1979).

[53]V. S. Antonov, I. N. Knyazev, V. S. Letokhov, V. M. Matyuk, V. G. Movshev, and V. K. Potapov, Pis'ma Zh. Tekh. Fiz. **3**, 1287 (1977) [Sov. Tech. Phys. Lett. **3**, 531 (1977)].

[54]V. S. Antonov, I. N. Knyazev, V. S. Letokhov, V. M. Matiuk, and V. K. Potapov, Opt. Lett. **3**, 37 (1978).

[55]L. I. Iskakov and V. K. Potapov, Khim. Vys. Energiĭ **5**, 265 (1971).

[56]V. S. Antonov, V. S. Letokhov, and A. N. Shibanov, Appl. Phys. **22**, 293 (1980).

[57]M. Seaver, J. W. Judgens, and J. J. Decorpo, Intern. J. Mass Spectr. Ion Phys. **34**, 159 (1980).

[58]S. Rockwood, J. P. Reilly, K. Hohla, and K. L. Kompa, Opt. Comm. **28**, 175 (1979).

[59]J. P. Reilly and K. L. Kompa, J. Chem. Phys. **73**, 5468 (1980).

[60]V. S. Antonov, V. S. Letokhov, and A. N. Shibanov, Zh. Eksp. Teor. Fiz. **78**, 2222 (1980) [Sov. Phys. JETP **51**, 1113 (1980)].

[61]D. M. Lubman, R. Naaman, and R. N. Zare, J. Chem. Phys. **72**, 3034 (1980).

[62]J. T. Meek, R. K. Jones, and J. P. Reilly, J. Chem. Phys. **73**, 3503 (1980).

[63]F. Rebentrost, K. L. Kompa, and A. Ben-Shaul, Chem. Phys. Lett. **77**, 394 (1981).

[64]F. Rebentrost and A. Ben-Shaul, J. Chem. Phys. **74**, 3255 (1981).

[65]B. Andlaner and Ch. Ottinger, J. Chem. Phys. **55**, 293 (1971).

[66]W. Dietz, H. J. Neusser, V. Boesl, and E. W. Schlag, Chem. Phys. **66**, 105 (1982).

[67]R. S. Dygdala and K. Stefanski, Chem. Phys. **53**, 51 (1980).

[68]J. P. Reilly and K. L. Kompa, Adv. Mass. Spectr. **9** (1980).

[69]T. G. Dietz, M. A. Duncan, M. G. Liverman, and R. E. Smalley, J. Chem. Phys. **73**, 4816 (1980).

[70]R. S. Pandolfi, D. A. Gobeli, and M. A. El-Sayed, J. Chem. Phys. **75**, 4403 (1981).

[71]L. J. Rothberg, D. P. Gerrit, and V. Vaida, J. Chem. Phys. **75**, 4403 (1981).

[72]P. M. Johnson, Acc. Chem. Res. **13**, 20 (1980).

[73]M. B. Robin, Appl. Opt. **19**, 3941 (1980).

[74]P. M. Johnson, J. Chem. Phys. **64**, 4143 (1976).

[75]J. O. Berg, D. H. Parker, and M. A. El-Sayed, J. Chem. Phys. **68**, 5661 (1978).

[76]U. Boesl, H. J. Neusser, and E. W. Schlag, J. Chem. Phys. **72**, 4327 (1980).

[77]P. Hering, A. G. M. Maaswinkel, and K. L. Kompa, Chem. Phys. Lett. **83**, 222 (1981).

[78]J. Silberstein and R. D. Levine, Chem. Phys. Lett. **74**, 6 (1980).

[79]J. Silberstein and R. D. Levine, J. Chem. Phys. **75**, 5735 (1981).

[80]D. A. Lichtin, R. B. Berstein, and K. R. Newton, J. Chem. Phys. **75**, 5728 (1981).

[81]J. F. Ready, Effects of High-Power Laser Radiation, Academic Press, New York (1971).

[82]B. E. Knox in: Trace Analysis by Mass Spectrometry, edited by A. J. Ahearn, Academic Press, New York (1972).

[83]E. Unsold, F. Hillenkamp, and R. Nitsche, Analysis **4**, 115 (1976).

[84]M. A. Posthumus, P. G. Kistemaker, H. L. C. Meuzellar, and M. C. Ten Noever de Braw, Anal. Chem. **50**, 985 (1978).

[85]R. Stoll and F. W. Rollgen, Org. Mass Spectr. **14**, 642 (1979).

[86]V. S. Antonov, V. S. Letokhov, and A. N. Shibanov, Pis'ma Zh. Eksp. Teor. Fiz. **31**, 471 (1980) [JETP Lett. **31**, 441 (1980)].

[87]R. J. Comnzemius and J. M. Capellen, Intern. J. Mass Spectr. Ion Phys. **34**, 197 (1980).

[88]U. Schade, R. Stoll, and F. W. Rollgen, Org. Mass Spectr. **16**, 441 (1981).

[89]G. J. Q. Van der Pegl, J. Haverkamp, and P. G. Kistemaker, Org. Mass Spectr. **16**, 416 (1981).

[90]F. Hillenkamp in: Proc. of the Second Workshop on Ion Formation from Organic Solids, Springer-Verlag, New York (1982).

[91]V. S. Antonov, V. S. Letokhov, and A. N. Shibanov, Appl. Phys. **25**, 71 (1981).

[92]V. S. Antonov, V. S. Letokhov, Yu. A. Matveetz, and A. N. Shibanov, Laser Chem. **1**, 37 (1982); Poverkhnost' **1**, 54 (1982).

[93]S. E. Egorov, V. S. Letokhov, and A. N. Shibanov in: Proc. of Intern. Conference of Surface Studies with Lasers, Mauterndorf. Salzburg, Austria, March 1983, edited by F. R. Aussenegg, A. Leitner, and M. E. Lippitsch, Springer-Verlag, New York (1983), p. 156 (Springer Series in Chemical Physics Vol. 33).

[94]Yu. A. Kudriavtzev and V. S. Letokhov, Appl. Phys. B **29**, 219 (1982).

[95]W. C. Wiley and I. H. McLaren, Rev. Sci. Instrum. **26**, 1150 (1955).

[96]B. Schueler and F. R. Krueger, Org. Mass. Spectr. **15**, 295 (1980).

[97]Yu. A. Kudryavtsev, V. S. Letokhov, and E. V. Moskovets, Preprint Inst. Spektrosk. Akad. Nauk SSSR, Troitsk, Moscow Oblast' (1983).

[98]V. S. Letokhov, Kvant. Elektron. **2**, 930 (1975) [Sov. J. Quantum Electron. (Moscow) **5**, 506 (1975)].

[99]V. S. Letokhov, Comm. Atom. Mol. Phys. **11**, 1 (1981).

[100]V. S. Letokhov, V. S. Likhachev, V. G. Movshev, and S. V. Chekalin, Kvant. Elektron. **9**, 2117 (1983) [Sov. J. Quantum Electron. (Moscow) **12**, 1377 (1982)].

[101]V. S. Antonov, S. E. Egorov, V. S. Letokhov, and A. N. Shibanov, Pis'ma Zh. Eksp. Teor. Fiz. **36**, 29 (1982) [JETP Lett. **36**, 33 (1982)].

[102]V. S. Antonov, E. V. Khoroshilova, N. P. Kus'mina, V. S. Letokhov, Yu. A. Matveetz, A. N. Shibanov, and S. E. Egorov in: Picosecond Phenomena III, edited by K. N. Eisenthal, R. M. Hochstrasser, W. Kaiser, and A. Laubereau, Springer-Verlag, Berlin (1982), p. 310 (Springer Series in Chemical Physics), Vol. 230.

[103]W. V. Ligon, Science **205**, 151 (1979).

[104]A. A. Sysoev and M. S. Chupakhin, Vvedenie v mass-spektrometriyu

104    Sov. Phys. Usp. **27** (2), February 1984

Antonov *et al.*    104

(Introduction to Mass Spectrometry), Atomizdat, Moscow (1977), p. 79.

[105] D. A. Lichtin, S. Datta-Ghosh, K. R. Newton, and R. B. Bernstein, Chem. Phys. Lett. **75**, 214 (1980).

[106] C. Klimcak and J. Wessel, Appl. Phys. Lett. **37**, 138 (1980).

[107] J. H. Brophy and C. T. Rettner, Opt. Lett. **4**, 337 (1979).

[108] P. S. H. Fitch, C. A. Haynam, and D. H. Levy, J. Chem. Phys. **73**, 1064 (1980).

[109] M. G. Liverman, S. M. Beck, D. L. Louts, and R. E. Smalley, J. Chem. Phys. **70**, 192 (1979).

[110] P. L. Kapitsa, Éksperiment. Teoriya. Praktika (Experiment. Theory. Practice), Nauka, Moscow (1977), p. 325.

[111] S. A. Akhmanov and N. I. Koroteev, Metody nelineǐnoǐ optiki v spektroskopii rasseyaniya sveta (Methods of Nonlinear Optics in Light-Scattering Spectroscopy), Nauka, Moscow (1981).

[112] I. M. Beterov, N. V. Fateev, and V. P. Chebotaev, Pis'ma Zh. Eksp. Teor. Fiz. **36**, 251 (1982) [JETP Lett. **36**, 307 (1982)].

[113] P. P. Shorygin, Usp. Khim. **40**, 694 (1971).

[114] V. S. Letokhov, Comm. Atom. Molec. Phys. **1**, 257 (1981).

Translated by M. E. Alferieff