[1] Atomic units are used in this paper.

[2] To obtain the dependence of the amplitudes on the scattering angle, it is necessary to change over to a coordinate system in which the polar axis is directed along the incident beam (see, e.g., Ref. 12).

[3] The dipole moment of OH equals 0.65 a.u. $> D_{cr}$, therefore the cross section that follows from (14) is finite at the threshold.

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Photoionization of molecules from the ground and selectively-excited states by radiation from a vacuum-ultraviolet H_2 laser

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Photoionization laser spectroscopy based on the use of vacuum ultraviolet lasers is reviewed. Descriptions are given of the design and parameters of a hydrogen VUV laser. Experiments are described on the single-photon ionization of dimethylaniline and methylaniline molecules in the region of 1600 Å, and the ionization of NO molecules by radiation in the region of 1200 Å. The two-step photoionization technique has been used to investigate the kinetics of predissociation of H_2CO molecules excited to the $^1A_2$ electronic state by a pulse from a nitrogen laser. Two-step photoionization of NO_2 molecules with radiation transformation on the first step has been investigated in the range 4470–4570 Å. The feasibility of a highly sensitive and highly selective method of detecting polyatomic molecules is examined.

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1. INTRODUCTION

Substantial success has recently been achieved in the development of lasers operating in the vacuum-ultraviolet part of the spectrum (VUV). The short-wave limit of laser radiation is at present at about 400 Å, and the spectral range $1000 \lesssim \lambda \lesssim 2000$ Å has now become accessible to the practical application of laser methods.[1,2] The high energy of the laser photon in this range opens up new possibilities for physics experiments.

One of the most promising areas for the application of short-wave lasers is photoionization laser spectroscopy of molecules.[3] The method of two-step selective photoionization of molecules, used in conjunction with the VUV laser, opens up new possibilities for the detection of infrared absorption events with probability close to unity. This relies on measurements of the ionization current. There is particular interest in the possibility of using a laser detector of complex molecules, based on the two-step photoionization of molecules followed by the mass spectrometry of the resulting ions. The practical realization of this possibility would essentially result in a laser detector of trace amounts of complex molecules, and the solution of one of the more difficult problems in physics.[4]

There is, therefore, considerable interest in the study of one- and two-step ionization of molecules. Since the ionization energy of most molecules lies in the range 8–12 eV, the VUV laser must be used, even in the two-step scheme, after excitation of the intermediate electronic state of the molecule. Experiments in this area were impeded by the absence of suitable lasers in the VUV band. Laser radiation has so far been used mainly for the step photoionization of atoms with relatively low ionization thresholds[5] and for multiphoton ionization of atoms.[6]

Two-step photoionization of molecules involving an intermediate electronic state can be used to investigate the relaxation of excited molecular states. The VUV laser pulse is then the probing pulse, and the photocurrent depends directly on the concentration of excited molecules. By delaying the probing pulse relative to the exciting pulse, it is possible to use the fall in the photoionization current to examine the decay of excited states. By varying the wavelength of the exciting radiation, it is possible to record the absorption spectrum of molecules due to an electronic transition by measuring the current associated with two-step ionization.

In this paper, we report the results of experiments on one- and two-step photoionization of molecules in a gas by laser radiation. The radiation source was the VUV H_2 laser which we have developed.[7,8] It was operated in the fast repetition regime, using transitions in the region of 1200 and 1600 Å. Preliminary results of our experiments were reported in previous papers.[9,10]

2. THE HYDROGEN LASER FOR THE VACUUM-ULTRAVIOLET

The H_2 laser employed in our experiments is shown in Fig. 1. The transverse discharge was excited in a cell with a narrow channel of $0.03\times(1 \text{ to } 2)$ cm and a length of 30 cm, using a double shaping strip line. Generation was observed for minimum line discharge voltages up to 6 kV and, for discharge voltages of 40 kV, generation was observed at gas pressures between a few Torr and 2 atm. We used cells with different discharge-channel profiles. The electrodes were placed at a certain distance from the narrow part of the working channel. We used both cells with an additional "preionizing" electrode (Fig. 1c) and electrodes with overlapping configuration (Fig. 1d). This enables us to produce a sufficiently uniform sparkless discharge, which was particularly important because spark discharges damaged the inner surface of the cell after a few hundred firings.

To produce a traveling excitation wave, the strip line was placed at the angle $\theta = \arcsin\varepsilon^{-1/2}$ to the cell (ε is the permittivity of the line insulation). The line charging voltage was usually 30 kV. The line was switched with the aid of a gas-discharge gap operated in nitrogen at 25 atm. The pulse repetition frequency was up to 300 Hz.

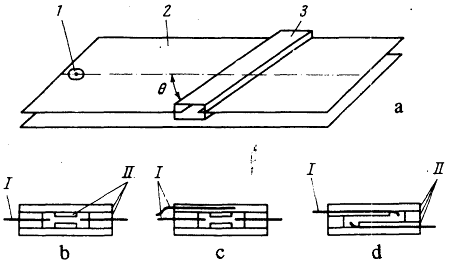

FIG. 1. Diagram illustrating the H_2 laser for the VUV band. a) Overall appearance of the laser: 1—discharge gap; 2—shaping line; 3—laser cell; b–d) types of cell (cross sections): I—electrodes; II—glass.

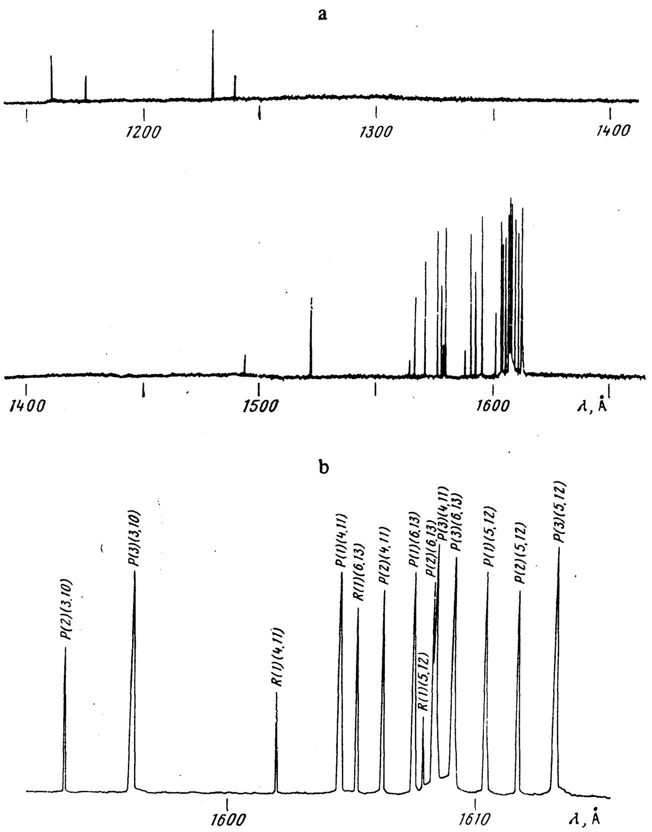

FIG. 2. VUV generation spectrum of the H_2 laser: a—overall appearance of the spectrum; b—lines in the region of 1610 Å.

The mean generated power was measured with the aid of a thermopile calibrated for pulsed, and continuous operation, and the repetition frequency was measured with a pulse counter. The exit windows of the laser were placed well away from the electrodes because their transparency tended to decrease under the influence of the gas discharge and the VUV radiation. Electrical breakdown in the direction of the windows was particularly damaging in this respect. Such breakdown was prevented by buffer volumes filled with hydrogen or nitrogen at atmospheric pressure. MgF_2 windows were found to be more stable in relation to the effect of the gas discharge and the VUV than LiF windows. The best material from this point of view for laser transitions in the region of 1600 Å was quartz.

The generation spectrum was investigated with the unique high-resolution VUV spectrograph at the Institute of Spectroscopy of the Academy of Sciences of the USSR, which included a concave diffraction grating with a radius of curvature of 6.5 m. The resolving power of the instrument was sufficient to produce complete resolution of the line spectrum of the spontaneous emission of hydrogen, and to identify the laser generation spectrum. The generation spectrum was recorded with the aid of a differentially-pumped system without intermediate windows. Figure 2a shows the general appearance of the generation spectrum of the H_2 laser in the VUV. The

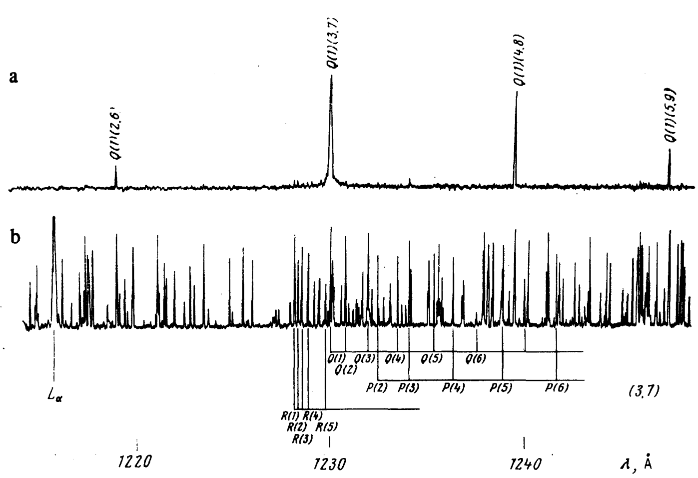

FIG. 3. Comparison of the laser (a) and spontaneous (b) emission spectra near 1200 Å; L_α is the atomic hydrogen line at 1215.670 Å.

spectrum consists of several tens of lines. Fourteen of the strongest lines lie in the region of 1600 Å within a 20 Å interval (Fig. 2b), and four lines of comparable intensity occupy a band of 80 Å in the region of 1200 Å. For comparison, Fig. 3 shows the laser and spontaneous-emission spectra of H_2 in the region of the L_α line of atomic hydrogen (1215.670 Å). The spontaneous-emission spectrum was obtained with the aid of a capillary gas discharge lamp. The laser spectrum was characterized by a low-spontaneous-emission background, the intensity of which was at least two or three orders of magnitude smaller than the intensity of the laser radiation.

Changes in the discharge conditions (charging voltage, gas pressure, and so on) have practically no effect on the intensity ratios of the laser lines in the region of the Lyman or Werner bands. All that happens is that the total intensity is altered. Generation on the Werner transitions in the region of 1200 Å was found to be more critical in its dependence on the experimental conditions. The strongest laser radiation corresponding to these transitions was obtained in the cell with the "preionizing" electrode (Fig. 1c). For the cell with the profile shown in Fig. 1b, the spectral brightness corresponding to Werner transitions was lower by a factor of 4–6 and, for the cell with the overlapping electrodes, by a factor of 2 or 3.

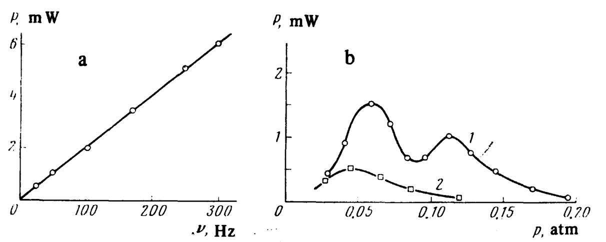

FIG. 4. Energy characteristics of the VUV H_2 laser based on the Lyman transitions (λ = 1610 Å, cell d in Fig. 1). a) Mean generated power as a function of repetition frequency (p_{H_2} = 0.06 atm, V = 40 kV). b) Mean generated power as a function of pressure for different voltages: curve 1—35 kV; curve 2—15 kV (pulse repetition frequency 100 Hz).

Figure 4 shows some characteristics of the laser based on the Lyman transitions. It was found experimentally that the average radiation power was a linear function of the repetition frequency (Fig. 4a). When the energy per pulse was 25 μJ and the repetition frequency of the generated pulses was 200 Hz, the maximum mean power of the emitted radiation was 5 mW. Prolonged operation at a repetition frequency of 300 Hz was accompanied by the heating of the laser cell, and the radiation power fell by a factor of approximately 2 or 3. The optimum gas pressure was about 40 Torr (Fig. 4b). Some of the characteristics of the laser radiation associated with the Werner transitions in the region of 1200 Å were measured by the photoionization method and are reproduced in the next section.

Experiments on the photoionization of molecules by laser radiation in the region of 1610 Å were performed with a repetition frequency of the H_2 laser pulses of 10 Hz and mean radiation power of about 0.1 mW. This corresponded to 10^{14} photons/sec, which was sufficient for photoionization experiments.

3. ONE-STEP PHOTOIONIZATION OF MOLECULES

Methylaniline and dimethylaniline molecules with the relatively low ionization potentials of 7.3 and 7.1 eV, respectively, were chosen for experiments on one-step ionization of molecules from the electronic ground state. The NO molecule (ionization potential 9.1 eV) was chosen for photoionization by laser radiation corresponding to the Werner transitions at 1200 Å.

3.1. Photoionization by Laser Radiation in the Region of 1600 Å

In the case of experiments in the region of 1600 Å, the photocurrent was recorded in an ionization chamber, 10 cm long, with plane-parallel electrodes, 0.5 cm apart. The laser radiation was directed onto two identical photoionization chambers (Fig. 5) through a system of buffer volumes with BaF_2 windows, 0.8 mm thick, designed to eliminate laser radiation in the region of 1200 Å. The buffer volumes were designed for the electrical decoupling of the chambers from the high voltage in the laser supply system. One of the chambers (4) was filled with

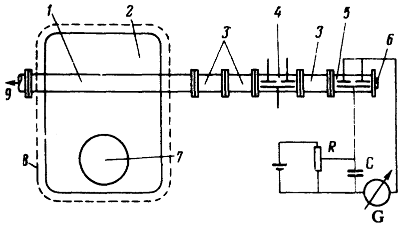

FIG. 5. Schematic diagram of experiments on one-step ionization of molecules by VUV H_2 laser radiation: 1—laser cell; 2—storage line; 3—buffer volumes; 4, 5—photoionization chamber; 6—luminescence screen; 7—discharge gap; 8—screen; 9—to VUV spectrograph.

dimethylaniline containing 1% impurities, and the other (5) with methylaniline of chemical purity, at the saturated vapor pressure (0.5 and 0.4 Torr, respectively). We used photoionization chambers with upper electrodes in the form of two identical sections. This was done in order to estimate the absorption of the laser radiation in the cell. To do this, we recorded the photocurrent ratio for each section. The mean current in the photoionization chamber circuit was measured with the F116/2 microammeter or a galvanometer. A luminescence screen was used to monitor the transmission of laser radiation through the system and to adjust the cells. Illumination of the electrode surfaces by laser radiation was prevented by introducing the necessary stops into the laser beam.

Figure 6 shows the photoionization saturation current curves for dimethylaniline (1) and methylaniline (2). The mean photocurrent in dimethylaniline was 0.05 μA. Control experiments were carried out with nitrogen laser radiation (3.7 eV), and by filling the chamber with helium or oxygen and using the H_2 laser radiation. There was no photocurrent in the photoionization chamber circuit in these experiments. The ratio of the photocurrents in the sections of the chambers for dimethylaniline and for methylaniline was roughly the same and equal to 0.9 ± 0.05.

We must now estimate approximately the photoionization current in our experiments. The laser radiation absorption coefficient at a pressure of 0.5 Torr was measured by determining the photocurrent ratio for the identical sections of the cells and was found to be $K = 0.02\ \mathrm{cm}^{-1}$, i.e., there was very little absorption in the cell of length $L = 10$ cm. The photoionization current could therefore be represented by the simple expression

$$I = e\gamma K L P_{av}/\hbar\omega, \qquad (1)$$

where γ is the photoionization yield and P_{av} is the average laser radiation power in the cell. If we take into account the radiation losses at the three windows separating the laser from the photoionization chamber (about 60%) and the beam stops (50%), we find that $P_{av} \approx 0.03$ mW. The photoionization yield of dimethylaniline for $\lambda = 1600$ Å is, to within an order of magnitude, $\gamma = 0.1$.[11] Equation (1) then gives a photoionization current of $I \approx 0.1$ μA for dimethylaniline, which is in satisfactory agreement with the experimental values if we bear in mind the approximate nature of the original data. The relatively low current in the cell containing methylaniline can be explained by additional losses of laser radiation at the two intermediate windows, the absorption of radiation in the cell filled with dimethylaniline, and the stopping down of the laser beam. The photoionization yield for methylaniline is also probably reduced because of the higher ionization potential.

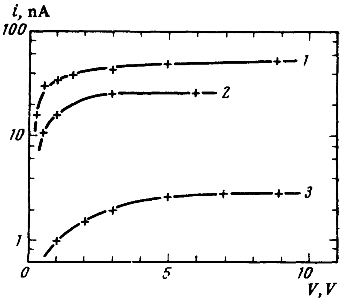

FIG. 6. One-step photocurrent due to the ionization of molecules as a function of voltage across the photoionization chamber. Curve 1, 2—dimethylaniline and methylaniline, ionization by 1610 Å laser radiation at repetition frequency of 10 Hz and mean generated power of 0.1 mW, 3—NO, ionization by 1200 Å radiation.

3.2. Photoionization of NO in the Region of 1200 Å

In the experiments on laser photoionization in the region of 1200 Å, the signal due to the photoelectric effect produced by scattered VUV was reduced by making the cathode of the photoionization chamber in the form of a thread and the anode in the form of a plane. The cell was 6 cm long and the windows were cleaved lithium fluoride crystals with a transmission of about 50% at 1200 Å. With this particular illumination geometry, about 25% of the laser radiation entered the cell. The NO was purified by repeated freezing in liquid nitrogen. Figure 6 shows the photocurrent saturation curve at NO pressure of 0.2 Torr (curve 3).

The threshold photoionization wavelength for NO is 1350 Å.[12] In the region of 1160 Å, which contains the strongest laser line, the total absorption cross section of the molecule is 2×10^{-18} cm for a photoionization quantum yield of 80%.[12] This enables us to perform an independent determination of the laser generation power near 1200 Å. Figure 7 shows the mean laser power calculated from the photocurrent as a function of the voltage and pressure of hydrogen in the laser cell. The radiation power plotted as a function of voltage has a maximum near 20 kV, which is probably due to a change in the geometry of the discharge in the cell. Under optimum conditions in the laser cell employed, the average power generated by the H_2 laser in the region of 1200 Å is up to 1 μW at a repetition frequency of 10 Hz.

The above results demonstrate the value of the hydrogen laser operating in the VUV as a means of producing photoionization of molecules and, in turn, as a method of using photoionization for absolute measurements of the VUV power produced by the H_2 laser.

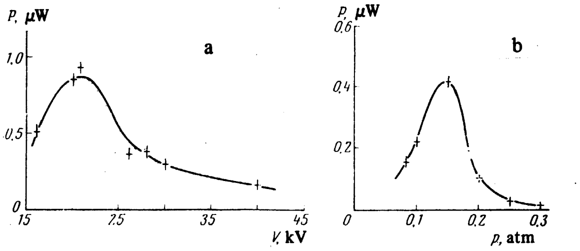

FIG. 7. Some characteristics of the H_2 laser using the Werner transitions (1200 Å), measured with a photoionization chamber containing NO: a—mean generated power as a function of the laser supply voltage. Hydrogen pressure in the laser chamber 0.12 atm, repetition frequency 10 Hz; b—mean generated power as a function of hydrogen pressure in the laser cell. Line charging voltage 40 kV, repetition frequency 10 Hz.

4. TWO-STEP PHOTOIONIZATION OF MOLECULES

The two-step photoionization experiments were performed with H_2CO and NO_2 molecules using intermediate excited electronic states. We measured the lifetime of the H_2CO molecules in the intermediate electronic state and recorded the electronic absorption spectrum of NO_2 by the two-step photoionization method.

4.1. Photoionization of H_2CO

The photoionization of the H_2CO molecules was performed by the combined application of a nitrogen laser pulse ($\lambda = 3371$ Å), which excited the ${}^1A_2$ electronic state, and the hydrogen laser radiation (in the region of 1600 Å) producing ionization of the excited molecules. The ionization potential of the formaldehyde molecule is 10.87 eV and the combined energy of the two-laser photons is $\hbar_1 + \hbar_2 = 3.7 + 7.7$ eV $= 11.4$ eV, which is sufficient for the photoionization of this molecule.

The experimental setup is shown in Fig. 8. The nitrogen (7) and hydrogen (1) laser pulses were sent in opposite directions into the ionization chamber 9 filled with formaldehyde. The nitrogen laser radiation was focused by the quartz lens 8 with a focal length of 10 cm. The nitrogen laser pulse energy was 0.3 mJ and that of the hydrogen laser 1 μJ. The N_2 laser pulse length was measured with the FEK-15 coaxial photocell and the I2-7 oscillograph. It was found to be 2 nsec. The windows were made from quartz with a transmission at 1600 Å of 80%. The length of the ionization chamber was 10 cm and its diameter was 5 cm. The cathode was a platinum wire, 0.1 mm in diameter. The ion-current pulse was amplified by an amplifier with an input capacitance of 8 pF and an input resistance of 1 GΩ. The result was recorded on the S8-2 oscillograph. The noise in the recording system corresponded to the noise charge of 1000 ions. The voltage across the ionization chamber was varied within 1–80 V. The formaldehyde was prepared from paraform and was purified by the method described by Spence and Wild.[13] The gas pressure was varied in the range 0.001–2 Torr and was measured with the VT-3 thermocouple gauge.

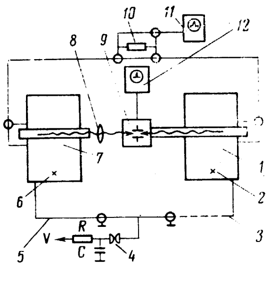

FIG. 8. Schematic illustration of experiments on two-step photoionization of formaldehyde by VUV radiation from the H_2 laser: 1, 2—storage line and H_2 laser discharge gap; 3, 5—discharge cable; 4—discharge gap in the pulsed charging circuit; 6, 7—storage line and discharge gap of N_2 laser; 8—lens; 9—photoionization chamber; 10—shunt; 11—oscillograph I2-7; 12—amplifier and S8-2 oscillograph.

The design of the hydrogen and the nitrogen lasers was the same and was similar to that employed previously.[7,8] The generation delay time of one laser relative to the other was measured by determining the time between breakdown in the laser cells. The trailing time of the voltage across the laser cell was 2 nsec. Since laser generation was produced on the front of the discharge, the uncertainty in the time shift between the generated pulses did not exceed ±1 nsec. The locking system for the laser pulses operated as follows. When the triggering discharge gap 4 (see Fig. 8) was fired, the storage capacitor C became connected across the charging cables 3 and 5. The laser shaping lines were charged in a time of about 15 nsec and the discharge gaps 2 and 6 fired when the maximum voltage was reached. To stabilize the breakdown time, the discharge gaps were illuminated by an auxiliary spark. The time of firing of the discharge gaps could be varied continuously within 5 nsec by varying the nitrogen gas pressure. The delay time was varied by varying the length of the charging cable in the hydrogen laser. The voltage across the laser cells was measured with the aid of the coaxial shunt 10. Voltage pulses from the two lasers were applied simultaneously to the shunt with different polarities, and were recorded by the I2-7 nanosecond interval meter.

Figure 9 shows the number of ions produced as a function of the delay time $\Delta t = t_{N_2} - t_{H_2}$ between the laser pulses at a formaldehyde pressure of 0.9 Torr. When $\Delta t > 0$, the decay of the ion current is not a simple ex-

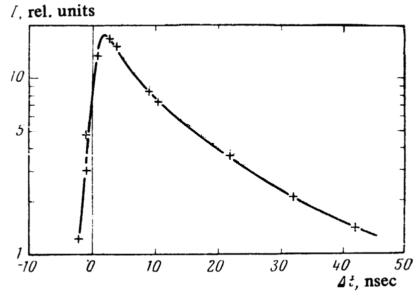

FIG. 9. Photocurrent due to two-step photoionization of formaldehyde as a function of delay time between the nitrogen and hydrogen laser pulses.

ponential. For $\Delta t < 0$, i.e., when the pulses appear in the opposite sequence, the two-step photoionization process is not observed in formaldehyde. The characteristic size of the two-step photoionization signal is 10^5 ions/pulse.

The excited state $^1A_2$ of formaldehyde predissociates with a quantum yield of about unity, and the main dissociation products resulting from the absorption of radiation in the region of 3371 Å are $(H_2 + CO)$.[14] The ionization potentials of H_2 (15.4 eV) and CO (14 eV) are higher than the VUV laser photon energy and, therefore, the only source of ions can be the ionization of formaldehyde from the excited state. The ion-current decay curve is then found to repeat the decay of the excited states. The lifetime of the $^1A_2$ state of H_2CO has been determined[15] from the decay of luminescence during the excitation of the molecule by nitrogen laser radiation, and was found to be 27 nsec. Another measurement was subsequently carried out[16] and the result was $(18 \pm 1) \times 10^{-9}$ nsec. This value was found to be independent of pressure in the formaldehyde pressure range 1–10 Torr.

The nonexponential decay of the $^1A_2$ excited state of formaldehyde has been observed by Young and Moore[17] and was ascribed to the vibrational relaxation of the excited state. Another reason for the nonexponential decay may be the simultaneous excitation of two-vibrational states of the electronic $^1A_2$ state.[17] Houston and Moore[18] have reported that the time at which the dissociation products $H_2 + CO$ appear under excitation of the $^1A_2$ state by the nitrogen laser pulse is greater by almost two orders of magnitude than the luminescence decay time, i.e., the dissociation occurs through an intermediate and relatively long-lived state. The nature of this state is at present unclear. One cannot therefore unambiguously conclude that the measured decay curve (Fig. 9) is exclusively due to the $^1A_2$ state or that the intermediate state provides an appreciable contribution to the photoionization. The answer to this question, and further information on the intermediate state, must await studies of the decay kinetics of excited states by the method of two-step ionization in a broad range of time intervals and gas pressures. We note that the method of two-step photoionization of molecules through an intermediate electronic state can be effectively used for investigating the excited states of many molecules. Its main advantage is that it can be used to investigate predissociating and nonradiating quantum states of molecules.

4.2. Photoionization of NO_2

We have investigated experimentally the two-step photoionization of the NO_2 molecule in which the intermediate electronic state was excited by a tunable dye laser working in the region of the electronic transition $^2A_1 \to {}^2B_1$ (4470–4570 Å). Ionization was produced by a VUV pulse from the H_2 laser in the region of 1600 Å. The ionization potential of NO_2 is 9.78 eV and the combined energy of the two laser photons is $2.7 + 7.7$ eV $= 10.4$ eV, so that the NO_2 molecule can be ionized only in the two-step fashion. The electronic excitation of the NO_2 molecule was achieved with a laser using the 4.7-methylumbelliferone dye with nitrogen laser pumping. The nitrogen laser pulse energy was 3 mJ at a generation length of 12 nsec. The dye laser pulse energy was 60 μJ which corresponded to a conversion coefficient of 2%. The spectral width of the radiation was about 1 Å. In the case of the hydrogen laser, the energy per pulse was 1 μJ. The laser pulse locking was achieved by charging the Blumlein line of the hydrogen laser and the storage capacitor of the nitrogen laser (Fig. 10) from the same voltage pulse generator incorporating the TGI1-1000/25 thyratron.

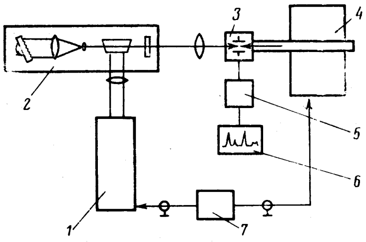

FIG. 10. Schematic arrangement of experiments on two-step photoionization of NO_2 molecules: 1—hydrogen laser; 2—dye laser; 3—ionization chamber; 4—hydrogen laser; 5—amplifier; 6—storing system and strip-chart recorder; 7—pulse generator.

The lifetime of the excited electronic state of NO_2 lies in the microsecond range[19] and, therefore, the delay of the hydrogen laser pulse relative to the nitrogen pulse was held constant at 10 nsec during these experiments. The repetition frequency of the laser pulses was 10 Hz. The ions were recorded by a previously described cylindrical ionization chamber. The amplifier output was received by a storage system using averaging steps of 100 pulses in order to reduce the spread in the output signal due to instabilities in the hydrogen-laser generation energy. Part of the dye-laser emission was diverted into a cell containing NO_2 at a pressure of 2 Torr. The length of this cell was 10 cm and absorption of the radiation was measured by spectrum scanning.

Figure 11 shows the current resulting from the two-step photoionization of the NO_2 molecule as a function of the wavelength of the exciting radiation. The maximum current corresponds to 30 000 ions produced in the chamber per pulse. For comparison, curve 2 in Fig. 11 shows the absorption spectrum of the same molecule obtained with the dye laser. It is clear from the figure

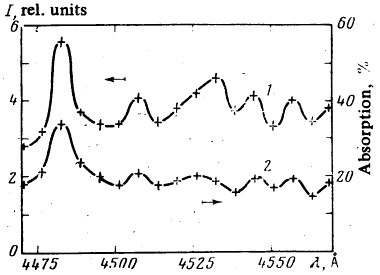

FIG. 11. Photocurrent due to two-step ionization (1) and absorption (2) as a function of the dye laser wavelength in the case of NO_2 molecules.

that the two-step photoionization signal repeats to within experimental error the absorption spectrum at the first step.

The method of recording electronic absorption spectra of molecules with the aid of two-step photoionization is distinguished by high sensitivity. It will be shown below that it can, in principle, be used to detect individual photon-absorption events in the visible and ultraviolet parts of the spectrum. This will require a sufficiently powerful VUV laser for the second step in order that the excited molecules can be ionized with probability close to unity. However, in our experiments, the two-step ionization process was found to be accompanied by one-photon photoionization by the hydrogen-laser radiation of the residual gas in the ionization chamber and the impurity in the material under investigation. In all the experiments, the background was about 10 000 ions/pulse per 1 μJ of H_2 laser energy. A consequence of this was that the signal-to-noise ratio did not improve when the VUV laser energy was increased.

5. SENSITIVITY OF SELECTIVE DETECTION OF MOLECULES BY SELECTIVE STEP PHOTOIONIZATION

We must now estimate the potentialities of the method of selective step photoionization as a means of detecting polyatomic molecules with the aid of laser radiation. We shall consider a simple model of the two-step process when laser radiation of frequency ω_1 selectively excites vibrational (or, for some molecules, electronic) states of the molecule (Fig. 12a).

Owing to excitation, the long-wave edge of the photoionization band of the molecule is shifted toward the red. In reality, the deformation of the photoionization band under vibrational (or electronic) excitation has a more complicated character which depends on the particular structure of the electronic terms of the molecule. However, for rough estimates, it is sufficient to assume that the excitation of the molecule into an intermediate state is accompanied by a change in the photoionization cross section σ_{phi} by an amount $\Delta\sigma$. Having chosen the frequency of the additional laser radiation in the region of maximum change in the photoionization cross section (Fig. 12b), we can photoionize the molecules that have been selectively excited by radiation of frequency ω_1. Since the shift of the photoionization limit under vibrational excitation is known to be less than the width of the edge of the photoionization band, one-step photoionization of the unexcited molecules will unavoidably take place. Moreover, during the absorption of the short-wave photon $\hbar\omega_2$, the photoionization process will compete with the photodissociation process with cross section $\sigma_{phd}(\omega_2)$.

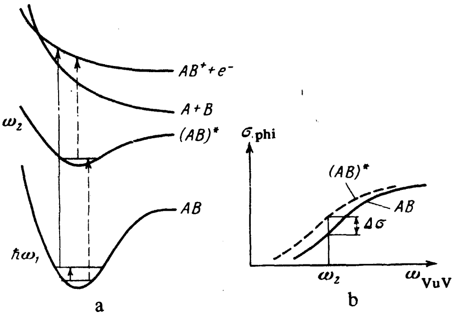

FIG. 12. Molecular levels (a) and photoionization cross sections of the molecules near the threshold (b).

The optimum situation for the detection of molecules is that where laser radiation of frequency ω_1 excites the maximum number of molecules. The energy density in the first laser pulse must then satisfy the condition

$$\mathscr{E}(\omega_1) \geqslant \mathscr{E}^{(1)}_{sat} = \hbar\omega_1/2\sigma_{exc}, \tag{2}$$

where σ_{exc} is the cross section for the excitation of the molecules into the intermediate state, and the length of the laser pulse is assumed to be less than the relaxation time of the excited states. The number of molecules taken up to the excited state under condition (2) is $N_{exc} \approx N_0 q/2$, where N_0 is the number of molecules in the ground state in the illuminated volume and q is the relative fraction of molecules in resonance with the exciting radiation. For maximum photoion yield, the laser pulse at frequency ω_2 must have the following energy density:

$$\mathscr{E}(\omega_2) \leqslant \mathscr{E}^{(2)}_{sat} = \hbar\omega_2/(\sigma_{phi}+\sigma_{phd}). \tag{3}$$

Each excited molecule will then decay with probability close to unity along the photoionization and photodissociation channels.

The increase in the number of ions produced by selective two-step photoionization under the optimum conditions (2) and (3) is given by the following simple expression:

$$\Delta N_i^{(2)} = N_{exc}\frac{\Delta\sigma}{\sigma_{phi}+\sigma_{phd}} = N_0\frac{q}{2}\frac{\Delta\sigma}{\sigma_{phi}+\sigma_{phd}}. \tag{4}$$

The number of ions produced as a result of nonselective one-step photoionization is

$$N_i^{(1)} = N_0\frac{\sigma_{phi}}{\sigma_{phi}+\sigma_{phd}}. \tag{5}$$

The problem in the detection of molecules is to record a small number of selectively produced ions, $\Delta N_i^{(2)}$, against the background of fluctuations $(N_i^{(1)})^{1/2}$ in the large number of nonselective ions $N_i^{(1)}$. Hence, we have immediately the following estimate for the minimum number of detectable molecules:

$$N_0^{min} = \frac{1}{\eta}\left(\frac{2}{q}\right)^2\left(\frac{\sigma_{phi}}{\Delta\sigma}\right)\left(\frac{\sigma_{phi}+\sigma_{phd}}{\Delta\sigma}\right), \tag{6}$$

where η is the efficiency with which the resulting ions are recorded.

Under the optimum conditions of maximum possible change in the photoionization cross section of the molecules after excitation ($\Delta\sigma = \sigma_{phi}$), a small contribution of photodissociation to the breakup of the molecules ($\sigma_{phd} \ll \sigma_{phi}$), and a high ion-detection efficiency ($\eta \approx 1$), the sensitivity of the method corresponds to the detection of individual molecules in quantum states interacting with the exciting laser field, i.e., the limit of sensitivity. This sensitivity can be achieved in practice in the case of selective two-step photoionization of atoms for which the above conditions can easily be satisfied.[5] These conditions are completely satisfied for molecules in the case of excitation of a suitable intermediate electronic state when it is possible to ensure a large shift of the photoionization band edge and to ensure that $\Delta\sigma \approx \sigma_{phi} \gtrsim \sigma_{phd}$.

However, for selective detection of polyatomic molecules, the maximum interest is in the excitation of molecules into vibrational states because this type of excitation is much more selective. The diffuseness of the photoionization band edge in this case ensures that the condition $\Delta\sigma \ll \sigma_{phi}$ is satisfied and, as a rule, photodissociation with $\sigma_{phd} \gg \sigma_{phi}$ competes with photoionization. This reduces the limiting sensitivity of this method of detection, but the sensitivity is still better than that of other ways of detecting polyatomic molecules.[3] A particularly fundamental point is the possibility of combining the method of selective photoionization of molecules, which provides information on the optical spectrum of the molecule, with the mass spectrometer which provides information on the mass of the detected molecule and its photoionization products.

6. CONCLUSIONS

In the vacuum ultraviolet, research efforts have until recently been concentrated on the solution of the relatively complicated problem of producing working laser systems. The above series of experiments on one- and two-step laser photoionization of molecules demonstrates the practical value of the VUV laser (in the present case, the H_2 laser) in physics experiments, and its importance in the development of new methods of investigation.

The use of the medium under investigation in the gaseous phase at relatively high pressure (about 1 Torr), and of ordinary ionization chambers, in these experiments was justified largely by simplicity. However, this type of experiment is subject to many characteristic difficulties. The main difficulty in the two-step photoionization experiments is the "background" one-photon ionization of the residual gas in the ionization chamber, or of the impurity in the medium under investigation, by the VUV laser radiation. This undesirable phenomenon is frequently eliminated by using a mass-spectrometric technique for ion detection. The accompanying reduction in the sensitivity of the method due to the substantial reduction in the pressure of the gas under investigation, is compensated by the fact that it is then possible to use secondary-electron multipliers capable of recording individual ions. From the point of view of developing a laser detector of complex molecules, there is particular interest in using molecular beams, since this is capable of producing a considerable improvement in the selectivity of the above photoionization method. The first experiments on one-step photoionization of molecules in the beam of a mass spectrometer have demonstrated the effectiveness of using VUV lasers for this purpose.[20] The next development should be to achieve two-step photoionization of molecules through an intermediate vibrational state in the beam of a mass spectrometer.

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