Appreciable increase of the dissociation rate of polyatomic molecules in the red shift of the nonresonant frequency under conditions of two-frequency laser action

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We report experimental observations of an appreciable increase in the rate of dissociation of the molecules SiF_4 and SF_6 by radiation of two pulsed CO_2 lasers in the case when the emission frequency of one of them is strongly shifted towards longer wavelengths relative to the frequency of the principal vibrational transition. The observed effect is attributed to singularities of the dispersion curve of the band structure of the quasi-continuum in the spectrum of the high vibrational states of the molecule.

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When vibrational levels of molecules are resonantly excited by IR laser emission, collisionless dissociation of the molecules is observed if the laser radiation is intense enough.[1,2] An important role is played in this process by the stage of passage through the lower vibrational levels and by the subsequent acquisition of the energy of the upper vibrational states in the quasi-continuum.[3] Separation, corresponding to these stages, of the functions of the lasers that effect the resonant excitation and the passage through the quasi-continuum was first realized experimentally with two-frequency IR laser action.[4]

We report here experimental observation of an appreciable increase in the dissociation rates of the molecules SiF_4 and SF_6 in the case of a strong red shift, relative to the principal vibrational transition, of the emission frequency of the laser that effects the passage through the quasi-continuum.

The experiment was performed with the setup illustrated in Fig. 1. Two pulsed atmospheric-pressure CO_2 lasers, tunable to the emission lines of CO_2,
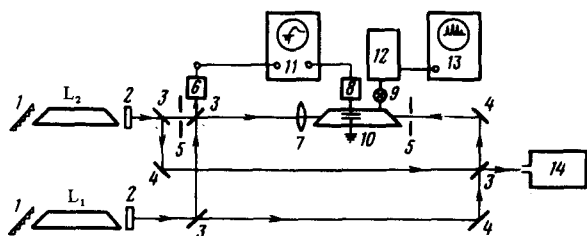
FIG. 1. Experimental setup: L_1, L_2—CO_2 lasers, 1—diffraction gratings, 150 lines/mm, 2—germanium exit mirrors, 3—BaF_2 beam splitters, 4—pivoted mirrors, 5—diaphragms, 6—photon-drag detector, 7—BaF_2 lens, 8—ion-current signal amplifier, 9—leak valve, 10—cell with capacitor, 11—S8-2 oscilloscope, 12—mass-spectrometer pickup, 13—mass spectrometer, 14—monochromator.

were used. To increase the tuning range of laser L_2, we used a mixture of the molecules ^{12}C, $^{16}O_2$, and $^{13}C^{16}O_2$ in approximately equal amounts. The energy of the radiation pulses was 1—2 J, the duration was ~100 nsec, and the tail parts of the pulses were reduced to a minimum by using working mixtures with small nitrogen contents. The instants of generation of lasers L_1 and L_2 were synchronized.

Figure 2 shows the dependence of the SiF_4 molecule dissociation ion current on the frequency of laser L_2 at a fixed frequency of laser L_1 (1029.4 cm^{-1}, P38 line of the 001—020 band), which coincides with the maximum absorption of the ν_3 vibration of the SiF_4 molecule. The emission power of laser L_2 was maintained constant at 2.0 MW in the course of the frequency tuning. This emission was focused into a cell with SiF_4 by a lens having $F = 13$ cm (intensity at the focus ~200 MW/cm^2). The radiation of the resonant laser was not focused, and its intensity in the cell was 5 MW/cm^2. The SiF_4 pressure in the cell was 1 Torr. It is seen that the derivation of the frequency of laser L_2 from resonance, towards lower frequencies, by an amount 80 cm^{-1} leads to a twenty-
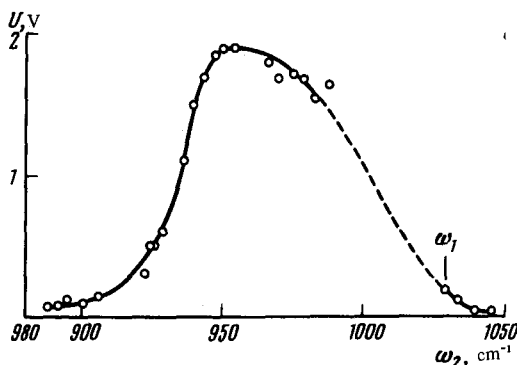

FIG. 2. Dependence of the amplitude of the ion current in SiF_4 on the frequency of laser L_2 at a fixed frequency 1029 cm^{-1} of laser L_1.
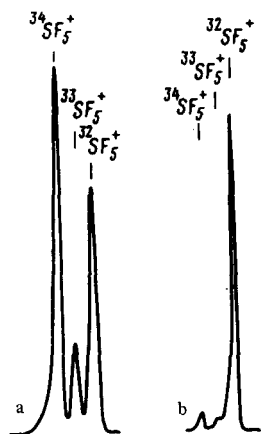
FIG. 3. Mass spectrum of the residual SF_6 gas after irradiation by 200 synchronized pulses of the lasers L_1 and L_2, tuned to the following frequencies: a) $\omega_1 = 944.2$ cm^{-1}, $\omega_2 = 894$ cm^{-1}, b) $\omega_1 = \omega_2 = 944.2$ cm^{-1}; the radiation is not focused, the intensity of each laser is 3 MW/cm^2.

fold increase of the dissociation ion current. The character of the dependence of the visible luminescence accompanying the dissociation on the laser emission frequency is similar to that shown in Fig. 2.

Observation of the dissociation ion current[5] is a convenient means of direct experimental study of the considered processes. At the same time, experiment has shown that dissociation of the SF_6 molecules is not accompanied by an ion current or by visible luminescence. Therefore the effect of the red shift in the dissociation of SF_6 molecules was investigated by using a dynamic mass spectrometer whose pickup was directly coupled to the irradiated cell, and the isotopic composition of the residual SF_6 gas was analyzed.

A cell 20 cm long, 1.4 cm in diameter, and with initial SF_6 pressure 0.2 Torr was irradiated by 100 pulses of lasers L_1 and L_2. The emission of the resonant laser L_1, tuned to the frequency 944.2 cm^{-1} (the P20 line of the transition 001—100) was not focused, and its intensity in the cell was 3.5 MW/cm^2. The emission of laser L_2, of intensity 6 MW, was focused into the cell by a lens with $F = 13$ cm. When the frequency of this laser was changed from 944.2 to 894 cm^{-1} (the P22 line of the 001—100 transition of the $^{13}C^{16}O_2$ molecule), the isotopic-enrichment coefficient was increased by seven times.

A red shift of the frequency of laser L_2 decreases greatly the threshold of isotopically selective dissociation of the SF_6 molecules. Figure 3 shows mass spectra of the residual SF_6 gas (the SF_5^+ splinter ion) when the cell is irradiated by unfocused beams of lasers L_1 and L_2 of equal intensity 3.5 MW/cm^2 (0.5 J/cm^2) for the cases when the laser L_2 is tuned to 944.2 and 894 cm^{-1}. In the former case there is no isotopic enrichment and in the latter cases the ^{34}S enrichment reaches a factor of 28.

The results of the experiments can be explained within the framework of the notions concerning the band structure of the quasi-continuum in the spectrum of the high vibrational states of molecules. [6] The frequency dependence shown in Fig. 2 is in essence the dispersion curve of the band structure. Since the centers of the bands shifted towards lower energies relative to the energy

level of the harmonic oscillator, the observed red shift of the maximum of the dispersion curve can be a certain average measure of anharmonicity of the band structure.

In addition, when a molecule lands on lower levels of the bands, the dissociation can be facilitated because of the lower dissociation limit for the lower levels, which are more strongly coupled to the dispersal states.

The emission of a laser that contributes to the acquisition of energy by the molecule in the quasi-continuum can also stimulate dissociation of the molecule.[6] It appears that it is useful to perform experiments on the dissociation of polyatomic molecules by using three lasers, corresponding to the three principal stages of this process—the passage through the lower levels, the acquisition of the energy in the quasi-continuum of the upper levels, and the dissociation of the molecules.

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