

Selectivity of dissociation of polyatomic molecules in a two-frequency IR laser field

R. V. Ambartsumyan, Yu. A. Gorokhov, V. S. Letokhov,
G. N. Makarov, A. A. Puretskiĭ, and N. P. Furzikov

Spectroscopy Institute, USSR Academy of Sciences

(Submitted January 21, 1976)

Pis'ma Zh. Eksp. Teor. Fiz. **23**, No. 4, 217–220 (20 February 1976)

A method is proposed for the dissociation of polyatomic molecules in a two-frequency IR laser field. In this method, a weak resonant field excites the molecules selectively, and a strong nonresonant subsequent field produces excitation into the quasicontinuum and dissociation. An appreciable increase of the dissociation selectivity is obtained.

PACS numbers: 32.20.Qd

1. The discovery and investigation of isotopically selective dissociation of polyatomic molecules in a strong IR laser field^[1,2] has raised the question of the development of a method of increasing the selectivity of the dissociation process. In the present communication, we propose to use a two-frequency IR laser field for the dissociation of polyatomic molecules. In this method, the field of frequency ν_1 is weak and is tuned to resonance with the absorption band of the molecule. This field excites selectively the first few vibrational levels of the molecule to the limit of the vibrational "quasicontinuum." The second strong nonresonant field of frequency ν_2 is used for subsequent dissociation of the molecules (Fig. 1a). The method is based on a mechanism proposed in^[3] for the dissociation of polyatomic molecules in a strong IR field of a laser.

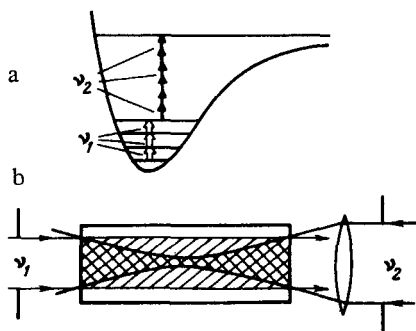


FIG. 1. a) Dissociation of molecules by a two-frequency IR laser field: ν_1 —frequency of weak selecting radiation, ν_2 —frequency of strong nonresonant radiation b) Geometry of experiment.

In the two-frequency dissociation method, in contrast to the one-frequency action by a strong field, the laser radiation power at the first, selecting stage ν_1 is low and hardly broadens the vibrational-rotational absorption lines of the molecules; this makes it possible to increase greatly the selectivity of the dissociation processes.

2. The experiments were performed on gaseous sulfur hexafluoride. A stainless steel cell 120 mm long and 10 mm in diameter was filled with SF₆ at 0.12 Torr. The SF₆ cell could be cooled to $T = 193 \pm 5$ °K. The irradiation was with two transverse-discharge atmospheric-pressure CO₂ lasers with dispersion resonators. The first laser (ν_1) emitted pulses of 0.5 J energy and 250 nsec duration, while the second (ν_2) delivered 2 J at 90 nsec. The synchronization was such that the pulses from the high-power laser of frequency ν_2 were delayed relative to the low-power laser of frequency ν_1 by 1.5 ± 0.5 μ sec. The radiation at frequency ν_1 was applied to the cell in the form of an unfocused beam ($I \sim 1-5$ MW/cm²), while the radiation at frequency ν_2 was focused with a lens of focal length $f = 100$ mm (Fig. 1b).

We investigated experimentally the dependence of the dissociation rate of the SF₆ molecule on the frequency ν_1 at a fixed frequency of the high-power laser $\nu_2 = 1084.6$ cm⁻¹ (R(30) line). We note that the SF₆ dissociated only when the cell was simultaneously exposed to the two lasers. The rate of SF₆ dissociation was defined as $w = (1/n) \ln(N_0/N)$ (N_0 is the number of molecules in the cell prior to the irradiation, N after the irradiation, and n is the number of irradiation pulses) and determined from the IR absorption spectra of the SF₆.

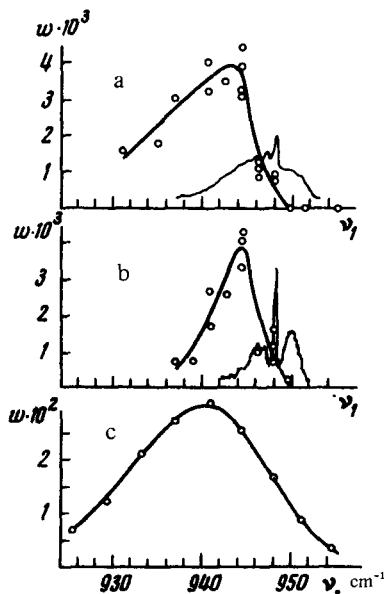


FIG. 2. Resonance characteristics of dissociation of SF₆ in IR laser field: a—two-frequency regime: $I_{\nu_1} = 4$ mW/cm², $I_{\nu_2, av} = 58$ MW/cm², $\nu_2 = 1084.6$ cm⁻¹, $T = 300$ °K. On the right is shown the absorption spectrum of the SF₆ molecule at $T = 300$ °K^[4]; b—the same, at $T = 193$ °K. On the right is shown the absorption spectrum of SF₆ at $T = 153$ °K^[5]; c—single-frequency regime, $I_{av} = 31$ MW/cm², $T = 300$ °K.^[3]

3. The measurement results are shown in Fig. 2. On the top (a) is shown the frequency dependence obtained at room temperature. The figure shows also the SF₆ absorption line spectrum at $T = 300$ °K.^[4] In the lower part (b) is shown the same dependence, but obtained at $T = 193$ °K: the line absorption spectrum of the SF₆ molecule at $T = 153$ °K was taken from^[5]. In the lower part (c), for comparison, is shown the dependence of w on the frequency of the laser radiation in the case of SF₆ dissociation in a single-frequency strong field, as obtained by us earlier.^[3]

It is seen from the figure that in the case of the two-frequency method of dissociation the width of the resonance curve greatly decreases ($\sim 5 \text{ cm}^{-1}$ at $T = 193^\circ\text{K}$ and $\sim 12 \text{ cm}^{-1}$ at $T = 300^\circ\text{K}$) in comparison with the single-frequency dissociation regime ($\sim 20 \text{ cm}^{-1}$ at $T = 300^\circ\text{K}$). It is clearly seen that the high-frequency edge of the resonance curve is greatly shifted and becomes steeper. This indicates that no dissociation takes place upon excitation of the R branch of the $\nu = 0 \rightarrow \nu = 1$ transition. This fact confirms the conclusion drawn in^[3], that for rotational compensation of the anharmonicity, the transitions to the first vibrational level should take place in the P branch. The observed dissociation in the region of the R branch of the $\nu = 0 \rightarrow \nu = 1$ transition in the case of single-particle excitation (Fig. 2c) is attributed to the influence of the strong resonant field needed for the dissociation of the molecules. The appreciable decrease of the low-frequency edge of the resonance curve with decreasing temperature (Fig. 2b) is connected with the "freezing-out" of the hot absorption band.

Measurements of w as functions of the intensity of the weak field of frequency ν_1 have shown that the dissociation rate increases approximately in proportion to the square root of the intensity in the range from 50 kW/cm^2 to 2 MW/cm^2 , as does also the number of quanta absorbed by one molecule at the same values of the intensity.^[2]

Measurements were made of the dissociation rate as a function of the frequency ν_2 of the strong field at a fixed frequency $\nu_1 = 942.4 \text{ cm}^{-1}$ (line $P(22)$)—the dispersion characteristics of the vibrational quasicontinuum; these measurements have shown that dissociation is observed also when the detuning of the frequency ν_2 from the absorption band of SF_6 is $\Delta\nu_2 > 100 \text{ cm}^{-1}$. At $\Delta\nu_2 \approx 50 \text{ cm}^{-1}$ the dissociation rate coincides with the value obtained in the case of single-frequency excitation at the same strong-field intensity. Measurements of the enrichment coefficient in the dissociation product SOF_2 have shown that the selectivity of the dissociation process in the two-frequency field decreases exponentially with increasing delay time (from 0 to $7 \mu\text{sec}$) of the laser pulses of frequency ν_2 relative to the pulses of the laser of frequency ν_1 .

The results demonstrate an appreciable increase of the selectivity of the excitation and dissociation in comparison with the single-frequency field, a result important for the separation of the isotopes of heavy elements with small isotopic shifts. This method increases greatly the range of molecules suitable for isotope separation, since the required intensity of the resonant field is smaller by a factor of approximately 10^3 than in the case when a single-frequency field is used, thereby facilitating the choice of the laser for the selection stage ν_1 . In addition, the proposed method uncovers great possibilities for the investigation of the properties and behavior of polyatomic molecules in a "quasicontinuum" of vibrational states.

¹R. V. Ambartsumyan, V. S. Letokhov, E. A. Ryabov, and N. V. Chekalin, *Pis'ma Zh. Eksp. Teor. Fiz.* **20**, 597 (1974) [*JETP Lett.* **20**, 273 (1974)]; *Zh. Eksp. Teor. Fiz.* **69**, 72 (1975) [*Sov. Phys.-JETP* **42**, 36 (1975)].

²R. V. Ambartsumyan, Yu. A. Gorokhov, V. S. Letokhov, and G. N. Makarov, *Pis'ma Zh. Eksp. Teor. Fiz.* **21**, 375 (1975) [*JETP Lett.* **21**, 171 (1975)]; *Zh. Eksp. Teor. Fiz.* **69**, 1956 (1975) [*Sov. Phys.-JETP* **42**, No. 2 (1975)].

³R. V. Ambartsyryan, Yu. A. Gorokhov, V. S. Letokhov, G. N. Makarov, and A. A. Puretskii, *Pis'ma Zh. Eksp. Teor. Fiz.* **23**, 26 (1976) [*JETP Lett.* **23**, 22 (1976)].

⁴H. Brunet and M. Perez, *J. Mol. Spectrosc.* **29**, 472 (1969).

⁵P. I. Hauston and J. I. Steinfeld, *J. Mol. Spectrosc.* **54**, 335 (1975).