

Selective dissociation produced by the action of a strong IR field on weak composite oscillations of polyatomic molecules

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We investigate dissociation and isotope separation induced by a strong IR field acting on various composite vibrations of the molecules SF_6 and CCl_4 . We show that the dissociation rate is proportional to the dipole moment of the excited radiation.

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1. The phenomenon of *selective collisionless dissociation* of molecules under the influence of strong IR radiation was discovered in.^[1,2] This discovery was preceded by investigations^[4-6] of the molecule luminescence excited by a focused CO_2 -laser pulse.^[3] This phenomenon is quite interesting from the physical point of view, since it is the result of a phenomenon that has not been investigated at all, namely multiphoton absorption of radiation by the vibration of a polyatomic molecule.

In all the cited studies, the molecule dissociation and isotope separation were effected by the action of the IR radiation on the fundamental vibrational bands of the molecules. In this article we present experimental results that point to the existence of an analogous phenomenon of isotopically-selective collisionless dissociation of molecules when IR radiation acts on composite vibrations (overtones) of a molecule (with SF_6 as an example), which are weaker by a factor 10^4 than the fundamental vibrational bands. This result, in our opinion is of interest both for the understanding of the mechanism of multiphoton absorption by vibrations of polyatomic molecules, but for the extension of the possibilities of the isotope-separation method discovered in^[1,2] to include many other molecules whose fundamental absorption bands do not coincide with the emission frequencies of the available high-power IR lasers.

2. The chosen object of the investigation was the SF_6 molecule, whose dissociation and whose energy acquisition in a strong IR field were investigated in sufficient detail.^[7] This molecule has three absorption bands in the effective operating region of the high-power CO_2 lasers listed in Table I. The presence of an isotopic

shift in the ν_3 vibration makes it also possible to compare the selectivity of the dissociation in the excitations of the vibrations ν_3 and $(\nu_2 + \nu_3 - \nu_5)$.

We investigated experimentally the dependence of the number of dissociated molecules on the number of irradiation pulses at frequencies corresponding to different oscillations, other conditions being equal. An isotopic analysis with a mass spectrometer, was also carried out of the residual SF_6 gas in the cell, for the purpose of determining the selectivity of the dissociation of the excited $^{32}SF_6$ molecules relative to the $^{34}SF_6$ molecules.

We used in the experiment a CO_2 laser with a transverse discharge at atmospheric pressure, and with a dispersion resonator. The laser produced pulses of 1.5 J energy on any line at a lasing spectrum width 0.035 cm^{-1} . The SF_6 was irradiated in a glass cell of length 55 mm and diameter 20 mm, with NaCl windows. The laser radiation was focused into the cell with an NaCl lens of focal length $f = 50 \text{ mm}$. The power density

TABLE I. Dissociation of SF_6 molecule.

Excited vibration	Transition frequency, cm^{-1}	Band half-width, cm^{-1}	Relative intensity*, s_k	Number of pulses w_k , for SF_6 to go to the level $l/e \cdot w_k$
ν_3	947	5	1	$2.1 \cdot 10^2$
$\nu_2 + \nu_6$	986	9	10^{-2}	$2.3 \cdot 10^3$
$\nu_2 + \nu_3 - \nu_5$	1056	20	$4.6 \cdot 10^{-5}$	$4.8 \cdot 10^4$

*The band intensity (the coefficient of absorption at the maximum per unit length at a fixed pressure) was normalized to the intensity of the ν_3 band.

for the possible mode locking, the presence of which could increase the radiation intensity at the focus.

3. Experimental results. When the SF₆ is irradiated with CO₂-laser pulses, the amount of the residual gas SF₆ decreases like

$$N = N_0 \exp(-wt), \quad (1)$$

where t is the irradiation duration or the total number of irradiation pulses, w is the rate of dissociation per pulse under the given experimental conditions (it depends on the ratio of the volume of the strong-field region to the total volume of the cell). The figure shows the experimental dependence of the SF₆ consumption under the action of the composite vibration ($\nu_2 + \nu_3 - \nu_5$). This dependence agrees with (1).

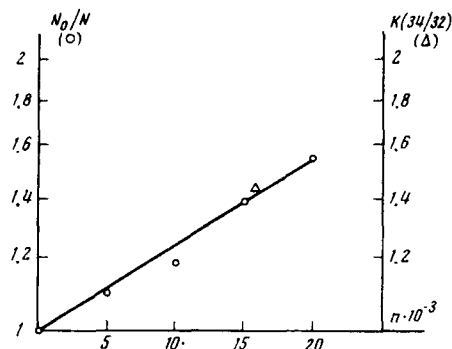
Table I lists the experimental data on the dissociation of SF₆ acted upon in three radiation bands. The dissociation rates w_k of SF₆, other conditions being equal, can be approximated for the different bands by the relation

$$\frac{w_k}{w_n} = \left(\frac{s_k}{s_n} \right)^{1/2}, \quad (2)$$

where s_k are the normalized intensities of the absorption bands (the subscripts k and n pertain to different composite molecule vibrations--see Table I).

This offers evidence that the probability of molecule dissociation in the strong field is proportional to the transition dipole moment μ , and not to its square as expected from simplest considerations. The fact that a simple relation (2) between the dissociation rate of SF₆ and the transition strength is observed for entirely different vibrations indicates that the dissociation of the SF₆ proceeds via the same channels for all types of excitation. This is possible, in particular, if the greater part of the SF₆ molecules dissociates as a result of collisions of highly-excited molecules.

4. The selectivity of the dissociation in action on weak composite vibrations was investigated by measur-



Dependence of the relative consumption of SF₆ on the number of CO₂-laser pulses when the irradiation is at the composite vibration $\nu_2 + \nu_3 - \nu_4$ (left-hand ordinate axis--circles). The enrichment coefficient $K(^{34}\text{S}/^{32}\text{S})$ is marked on the right-hand axis (triangles). The scale is logarithmic.

TABLE I. Dissociation of CCl₄ molecules.

Laser frequency, cm ⁻¹	Enriched isotope	Enrichment coefficient
979.7	¹³ C	7.30
987.6	¹³ C	1.00
971.9	³⁷ Cl	1.15
979.7	³⁵ Cl	1.05

ing the isotopic enrichment of the residual gas SF₆ by the ³⁴SF₆ isotope following the action on the $\nu_2 + \nu_3 - \nu_5$ vibration of the ³²SF₆ molecule. The enrichment coefficient was $K(^{34}\text{S}/^{32}\text{S}) = 1.4$ after 1.5×10^4 pulses. This enrichment coefficient corresponds exactly to the decrease of the total SF₆ pressure in the irradiated cell (see the figure). This means that irradiation causes only the ³²SF₆ molecule to dissociate, and consequently it is possible in principle to attain much larger enrichment coefficients $K(^{34}\text{S}/^{32}\text{S})$ in the case of a deeper consumption (dissociation) of the SF₆ in the irradiated cell.^[7]

Similar experiments were performed with the CCl₄ molecule under the influence of CO₂-laser radiation in various composite vibrations. It was observed in these experiments that certain composite vibrations (in particular, $\nu_2 + \nu_3$) do not fit a relation of the type (2). The action of an IR field on these vibrations does not cause a noticeable dissociation of the CCl₄ molecule. This indicates that there exist at least two channels of multi-quantum dissociation of this molecule. In addition, an isotopically selective dissociation of the ¹²CCl₄ molecules and of the CCl₄ molecules with the isotopes ³⁵Cl or ³⁷Cl had been reached. The isotopic enrichment was measured by determining one of the dissociation products, the molecule C₂Cl₆. The results of these experiments are given in Table II.

At certain excitation frequencies there is no enrichment. This can be attributed quite naturally to the fact that, owing to the absence of any data on the isotopic shifts in the excited band, we were unable to choose the proper laser frequency for the selective dissociation of the molecules.

¹R. V. Ambartsumyan, V. S. Letokhov, E. A. Ryabov, and N. V. Chekalin, ZhETF Pis. Red. 20, 597 (1974) [JETP Lett. 20, 273 (1974)].

²R. V. Ambartsumyan, Yu. A. Gorokhov, V. S. Letokhov, and G. N. Markarov, *ibid.* 21, 375 (1975) [21, 171 (1975)].

³N. R. Isenor and M. C. Richardson, Appl. Phys. Lett. 18, 224 (1971).

⁴V. S. Letokhov, E. A. Ryabov, and O. A. Tumanov, Zh. Eksp. Teor. Fiz. 63, 2025 (1975) [Sov. Phys.-JETP 36, 1069 (1973)]; Optics Comm. 5, 168 (1972).

⁵R. V. Ambartsumian, N. V. Chekalin, V. S. Dojikov, V. S. Letokhov, and E. A. Ryabov, Chem. Phys. Lett. 25, 1281 (1974).

⁶N. R. Isenor, V. Merchant, R. S. Hallsworth, and M. S. Richardson, Canad. J. Phys. 51, 1281 (1973).

⁷R. V. Ambartsumyan, Yu. A. Gorokhov, V. S. Letokhov, and G. N. Makarov, Zh. Eksp. Teor. Fiz. 69, 1956 (1975) [Sov. Phys.-JETP 42, No. 6 (1975)].