Dissociation of molecules isolated in a matrix by infrared radiation

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We report the first observation of selective action of ir laser radiation on molecules isolated in solid matrices at low temperatures.

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1. Dissociation of molecules in the gas phase under the influence of high-power resonant infrared (IR) radiation[1] is by now a process that has been sufficiently well investigated. Interest in this question was due mainly to the new possibility of separating isotopes by dissociation of molecules of one isotopic composition from a mixture.[2] The question of the interaction between molecules in the solid phase, on the one hand, and high-power IR radiation on the other, has not been investigated to this day. In this article we report the first observation of selective dissociation of molecules isolated in a low-temperature matrix by means of high-power IR laser radiation.

2. We investigated experimentally the dissociation of an SF_6 molecule placed in a low-temperature matrix. The mixture $SF_6:Ar(SF_6:CO)$ at concentrations $1:2000-1:500$ was deposited on a CsI substrate secured on the cold finger of a helium cryostate. The temperature of the substrate was varied with a gold-chromel thermocouple and amounted to 8—10 °K. We used both pulsed and continuous sputtering of the matrix.[3] The width of the ν_3 absorption band in $^{32}SF_6$ with center at 939 cm^{-1} was 4 cm^{-1} for an argon matrix and 5.5 for a CO matrix at a spectral resolution 1.5 cm^{-1}.

In the experiments, the solid matrix was irradiated by a frequency-tunable atmospheric-pressure CO_2 laser. The intensity was varied from 5 to 30 MW/cm^2, the pulse duration was 90 nsec, the generation linewidth was 0.035 cm^{-1}. The irradiation was at 942.4 or 940.5 cm^{-1}. This excited the short-wave wing of the $^{32}SF_6$ absorption line. The energy absorbed in the matrix was not more than 30% of the initial value. IR spectrophotometry was used in the experiment to register the decrease of the absorption by the $^{32}SF_6$ molecule at the frequency of the ν_3 transition under the influence of the CO_2 laser radiation.

3. *Results.* Figure 1(a) shows the section of the absorption spectrum of SF_6 of natural isotopic composition, obtained by evaporation of the $SF_6:Ar$ mixture, while the right-hand side shows the spectrum after exposure to CO_2 laser pulses. It is seen from the figure that the absorption of $^{32}SF_6$ decreases. A similar result was obtained with a CO matrix. The principal results are summarized in the table.

The decrease of the absorption of $^{32}SF_6$ under the influence of the laser pulses can be due to ordinary evaporation as a result of thermal heating of the

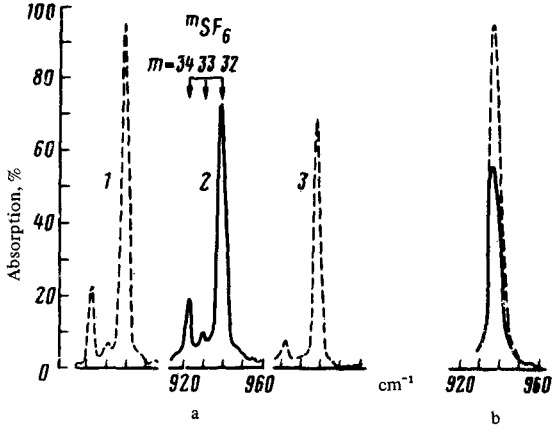

FIG. 1. a) Infrared absorption spectra of an SF_6 molecule isolated in a solid matrix: (1)—prior to irradiation; (2)—after irradiation by 110 pulses of a CO_2 laser ($\omega = 940.5$ cm^{-1}, $I = 5.4$ MW/cm^{-2}; (3)—for comparison with (2), the IR spectrum of SF_6 prior to irradiation with identical intensity of the $^{32}SF_6$ peak is shown; b) change of the form of the absorption spectrum due to the dissociation of the $^{32}SF_6$ molecule in the inhomogeneously broadened short-wave wing of the spectrum.

matrix. This possibility was specially investigated by analyzing the isotopic content of the SF_6 remaining in the matrix after the irradiation, the results of which are also given in the table. As a result of the thermal action, the $^{32}SF_6$ and $^{34}SF_6$ should have been consumed at equal rates. Experiment reveals a predominant consumption of $^{32}SF_6$ subjected to the irradiation. Thus, isotropic selective dissociation of SF_6 takes place, which is equivalent to enriching the dissociation products or of the SF_6 remaining in the matrix by the isotopes ^{32}S or ^{34}S, respectively.

It should be noted that in the case of a deep degree of dissociation of the $^{32}SF_6$, the maximum of the absorption in $^{32}SF_6$ shifted towards lower frequencies. Thus, for the CO matrix, the shift amounted to 2 cm^{-1} [Fig. 1(b)]. This fact is explained by the "burning out" of the molecules in the inhomogeneously broadened absorption contour on the short-wave side.

TABLE I.

Matrix	Concentration	Radiation frequency, cm^{-1}	Intensity, MW/cm^2	Number of pulses	Fraction of molecules dissociated per pulse, W	Coefficient of isotopic enrichment, K according to consumption	Coefficient of isotopic enrichment, K according to residue
Ar	1 : 1250	940.5	5.4	110	$1.2 \cdot 10^{-3}$	2.60	1.81
	–	942.4	25	20	$5.8 \cdot 10^{-3}$	1.70	1.35
CO	1 : 500	–	5.4	150	$3.8 \cdot 10^{-3}$	1.50	1.87

In the irradiation zone, darkening of the matrix was observed. Additional irradiation after the appearance of the darkening resulted in damage to the matrix.

Thus, the presented experimental results offer unequivocal evidence of observation of dissociation of an isolated molecule by IR radiation. Observation of isotopic selectivity in such a dissociation uncovers a possibility of both applying this process for isotope separation in condensed media, and for investigating the interaction of infrared laser radiation with molecules isolated in solid matrices.

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