# Interaction of SF$_6$ molecules with a powerful infrared laser pulse and the separation of sulfur isotopes

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The interaction of SF$_6$ molecules with powerful CO$_2$-laser pulses has been investigated. The number of CO$_2$-laser photons absorbed per SF$_6$ molecule was examined as a function of gas pressure and radiation intensity. Sulfur isotopes were separated with enrichment factors exceeding 1000. The enrichment factors were examined as functions of the initial SF$_6$ pressure, the laser-radiation intensity, and the irradiation time.

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## 1. INTRODUCTION

One of the most important trends in the problem of controlling chemical reactions by means of laser radiation is the stimulation of reactions through the excitation of vibrational levels of the molecule by infrared (IR) laser radiation. That such radiation is photochemically active was shown by Hall and Pimental[1] back in 1963, but intensive development in this direction began only after powerful IR gas lasers became available (see the review article by Basov et al.[2]). Isotopically selective (I-S) reactions under the stimulus of IR radiation are of special interest. For most molecules, however, there are substantial limitations on the selectivity achievable with such reactions owing to the rapid vibrational-vibrational (V-V) exchange of excitation in mixtures and the rapid vibrational-translational (V-T) relaxation of the excitation.

The method of fast collisionless dissociation of molecules in a strong IR field as a result of multiphoton absorption has proved to be a more effective method for realizing I-S reactions. The I-S dissociation of molecules in a strong IR field was discovered[3] in experiments with the BCl$_3$ molecule in the field of a CO$_2$ laser. These experiments are discussed in detail in[4]. We discovered[5] the exceptionally high selectivity of the dissociation under the action of CO$_2$-laser pulses of SF$_6$ molecules having a selected sulfur isotope: the enrichment factor for the $^{34}$S isotope under the action of a series of CO$_2$-laser pulses on a cell containing gaseous SF$_6$ of the natural isotopic composition reached ~3000.

These results make the method of selective dissociation of molecules in a strong IR field unusually valuable for the separation of isotopes and require both the isotope-enrichment process itself and the characteristics of the multiphoton absorption of IR radiation by the molecule, which leads to its excitation and dissociation, to be studied in more detail. We note that the study of the multiphoton excitation of vibrational levels is of independent interest in connection with the unsolved problem of the interaction of a multilevel quantum system with a strong laser-radiation field.

In the present work we undertook an experimental study of this entire group of problems. As the material for study we chose the SF$_6$ molecule as before[5]. The choice of this material was dictated by the following considerations: first, complete data on the IR spectrum of SF$_6$ molecules of various isotopic compositions are

available; second, the time constants for the V-V and V-T processes in SF$_6$ are well known; third, the chemical binding of the fluorine atoms liberated by the dissociation of the molecules does not cause any difficulties; and finally, it is possible to produce sufficiently powerful frequency-adjustable IR radiation to assure the excitation and dissociation of SF$_6$ molecules containing any of the sulfur isotopes.

## 2. NECESSARY SPECTROSCOPIC DATA ON SF$_6$

The IR spectrum of SF$_6$ of the natural isotopic composition has been repeatedly investigated[6-8] and the fundamental vibrational frequencies of the molecule have been determined. Table I gives the data from[9,10] on the isotopic shifts for the fundamental frequencies $\nu_3$ and $\nu_4$. The V-T and V-V relaxation times of the SF$_6$ molecule have been measured by various methods in a number of studies[11-14]. Table II gives the lifetimes for the energy transfer processes in SF$_6$. The linear absorption coefficients of the SF$_6$ molecule for the P(12)—P(20) lines of the 10.6 $\mu$m band of the CO$_2$ laser range between 0.4 and 1.3 cm$^{-1}$ Torr$^{-1}$, the maximum value being reached for the P(16) line[15].

## 3. EXPERIMENTAL EQUIPMENT AND MEASURING TECHNIQUE

A pulsed CO$_2$ laser at atmospheric pressure with transverse discharge, similar to the one described by Denes[16], was used as the source of IR radiation. The electrodes of the laser (shaped to the Bruce profile) were 64 cm long, 4 cm wide, and 2 cm apart. Preliminary photoionization was effected by spark discharges between points on both sides of the electrodes. The laser resonator consisted of a dense spherical mirror of deposited gold with a curvature radius of 5 m and an echelette diffraction grating ruled on the AMTs alloy

TABLE I. Isotopic shifts for the fundamental frequencies $\nu_3$ and $\nu_4$ of Gaseous SF$_6$ and the Natural Abundances of the sulfur isotopes

| Sulfur isotope | Natural abundance, % | $\nu_3$, cm$^{-1}$ | | $\nu_4$, cm$^{-1}$ | |
|---|---|---|---|---|---|
| | | [9] | [10] | [9] | [10] |
| $^{32}$S | 95 | 947.9 | 947 | 614.5 | 615 |
| $^{33}$S | 0.75 | | 939 | | 613 |
| $^{34}$S | 4.2 | 930.5 | 930 | 611.2 | 612 |
| $^{36}$S | 0.017 | | 914 | | (608) |

TABLE II. Lifetimes for energy transfer processes in SF$_6$

| $p\tau$, sec · Torr | |
|---|---|
| $V-V$ | $V-T$ |
| 1.51 [14] | 158 [14] |
| 0.72 [11] | 122 [12] |
| | 137 [13] |

(100 lines/mm) working in the autocollimation mode and having a reflection coefficient of 70% in the first order. The laser radiation was taken out from the zeroth order of the grating. Such a dispersion resonator made it possible to achieve stable selection of any of the $CO_2$-laser vibrational-rotational transitions. The width of the laser line as measured with an IR Fabry-Perot interferometer was 0.03 cm$^{-1}$. The gaseous mixture, used in the proportions $CO_2 : N_2 : He = 3 : 1 : 12$, made it possible to obtain laser pulses 90 nsec long at half height with energies per pulse up to 3 J. The energy was measured with a TPI-1 calorimeter.

The shape and length of the pulses were measured with a photon-drag detector using the dragging of the carriers in an uncooled $Ge : Au$ crystal and having a time resolution of 5 nsec or better, and with an S8-2 oscillograph having a 7 MHz pass band, which also determined the time resolution of the recording system.

To measure the absorption of the $SF_6$ as a function of various parameters of the laser radiation and of the $SF_6$ and buffer gas pressures we used glass cells 2.6 cm in diameter and 20, 50, and 100 cm long provided with NaCl and $BaF_2$ windows. In the experiments on the separation of the sulfur isotopes we used a glass cell 50 cm long and 1.2 cm in diameter having $BaF_2$ windows. In the measurements with a focused beam, the focus was formed at the center of the cell. The energies of the laser radiation at the entrance and exit windows of the cell were measured with radiation thermocouples calibrated with the TPI-1 calorimeter. Previously calibrated $CaF_2$, Ge, KRS-5, and $BaF_2$ plates were used to attenuate the laser radiation. Before admitting the gaseous mixture to the cell, the latter was pumped down to a pressure below $10^{-2}$ Torr.

The $SF_6$ used in the experiments had the natural isotopic composition and was of "pure" grade. Before the gas was admitted to the cell it was further purified by recondensation in order to remove water vapor and other impurities.

The apparatus described above was used to investigate the vibrational excitation of $SF_6$ molecules and the separation of the sulfur isotopes.

## 4. EXCITATION OF VIBRATIONAL LEVELS OF $SF_6$

The excitation of the vibrational levels was investigated as follows. A carefully collimated beam of $CO_2$-laser radiation, uniform in cross section, was directed onto the cell containing $SF_6$. At each laser pulse we simultaneously measured the energy incident on and passing through the cell. The length of the cell and the pressure within it were selected so that the gas would absorb about 10% of the incident energy; this simplified the measurements since we could assume that the intensity of the IR field was the same along the entire length of the cell.

To obtain experimental data at high power densities, the radiation was focused in the cell with a long-focus lens and the average power density in the illuminated volume of the cell was calculated. Special attention was given to the matching of the absorption data obtained with parallel and focused beams at equal average powers. As will be seen from the data presented below, the energy absorbed per molecule was practically the same in these two cases.
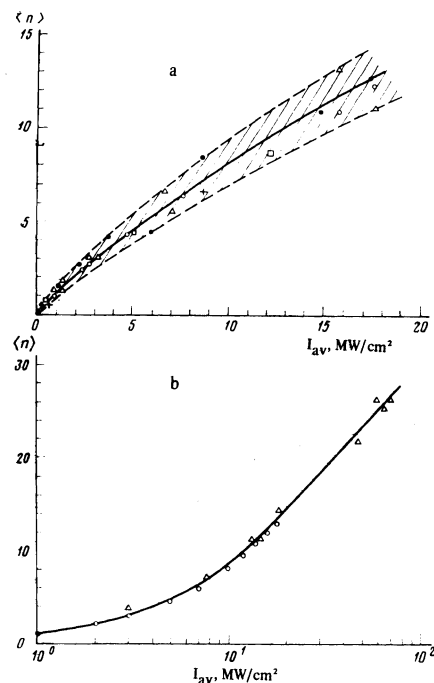


FIG. 1. Average number $\langle n \rangle$ of $CO_2$-laser radiation photons absorbed per $SF_6$ molecule vs intensity I of the incident radiation. a) Measurements made in a 100-cm long cell with an unfocused beam at the following pressures (Torr): 0.1 (squares), 0.2 (crosses), 0.4 (triangles), 0.8 (black circles), 1.2 (open circles). b) Measurements made at an $SF_6$ pressure of 0.5 Torr in a 100-cm long cell with an unfocused beam (circles) and in a 50-cm long cell with a focused beam (triangles). The average power density $I_{av}$ was defined as PL/V, where P is the incident power, V is the illuminated volume of the cell, and L is the length of the cell.

Figure 1a shows the average number $\langle n \rangle$ of photons absorbed per molecule as a function of the incident power at different $SF_6$ pressures as determined with a parallel beam at relatively low intensities (up to 15—20 MW/cm$^2$). The quantity $\langle n \rangle$ was calculated as the ratio of the number of photons of $CO_2$-laser radiation absorbed in the cell to the total number of molecules in the illuminated volume of the cell. As is evident from the figure, the average number of photons absorbed per molecule during the life of the pulse is (within the measurement errors) independent of the pressure over the range 0.1—1.2 Torr. This means that no relaxation processes take place while the pulse lasts.

Let us consider, for example, the case in which the pressure is 0.1 Torr. At this pressure the time between $SF_6$-$SF_6$ collisions is 900 nsec[17], which is much longer than the base length of the laser pulse (180 nsec), so that no collisions that might lead to rotational relaxation and V-V exchange can take place during the life of the pulse (see Table II). Moreover, the duration of the exciting pulse is even shorter than the time for loss of coherence, which at a pressure of 0.1 Torr is 240 nsec[18]. The absence of rotational relaxation of the molecules during the life of the pulse means that the radiation interacts only with the small fraction q of the molecules in the illuminated region that happen to lie on one of a small number of rotational levels. This fraction may be estimated as the ratio of the width of the laser spectrum (0.03 cm$^{-1}$) to the width of the Q branch of the $SF_6$ molecular transition being excited ($\sim$2 cm$^{-1}$). It is difficult to give a more accurate estimate of q, but it may be assumed to lie in the interval 0.1—0.01. This, in turn, means that the molecules that actually absorb

the exciting radiation accumulate at least ten times more energy per molecule than the average energy per molecule given in Fig. 1a. For example, according to Fig. 1a the average number of photons absorbed per molecule at an excitation power density of 10 MW/cm² is ~8—9. In fact, the molecules that actually interact with the field each accumulates an energy of $\langle n \rangle \hbar \omega / q$ = $(80-90)\hbar\omega \approx$ 6—7 eV. All this is valid, of course, only if there is no unknown energy scattering mechanism that is highly effective at the moderate radiation powers (~10 MW/cm²) under consideration.

The absorption of radiation by the molecules at high power densities was investigated with a focused beam. In Fig. 1b we plot the average number $\langle n \rangle$ of photons absorbed per molecule for both focused and unfocused beams on the same graph, the abscissae being the intensity I of the incident radiation. We note that the results for focused and unfocused beams agree well in the region I = 3—20 MW/cm² in which both types of measurements are possible. It will be seen that $\langle n \rangle$ increases roughly logarithmically with increasing I in the region I > 10 MW/cm². It must be noted that the data shown on Fig. 1b were obtained at an SF₆ pressure of 0.5 Torr, at which no relaxation due to collisions could increase the absorbed power.

In order to clarify the relationship between rotational relaxation and the fraction of the molecules capable of absorbing the IR radiation, and consequently, between the rotational relaxation and the energy absorbed per molecule in the illuminated volume of the cell, we measured $\langle n \rangle$ as a function of the pressure of the buffer gas (H₂) at a fixed low SF₆ pressure. The results of these measurements are shown in Fig. 2. It will be seen that $\langle n \rangle$ increases comparatively sharply with increasing H₂ pressure at H₂ pressures up to 100 Torr. This increase in $\langle n \rangle$ can be interpreted as an increase in the number of molecules interacting with the field. The number of molecules interacting with the field increases by a factor of 2 when the rotational relaxation time becomes roughly equal to the pulse length. From this we can estimate the rotational relaxation time of SF₆ due to collisions with H₂ molecules as of the order of 2—3 nsec per 1 atm H₂. When the H₂ pressure increases considerably in the region above 100 Torr, the rate of increase of $\langle n \rangle$ falls off, although $\langle n \rangle$ continues to increase. This is most likely due to the coming into play of some energy transfer mechanism associated with the close resonance of the vibrational levels $\nu_2$, $\nu_4$, and $\nu_5$ of the SF₆ molecule with the rotational quantum of the H₂ molecule (586 cm⁻¹). The decrease in the number of photons absorbed per SF₆ molecule when the pressure of the SF₆ itself in the cell is increased is associated
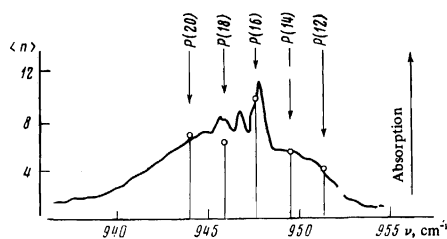


FIG. 3. Average number ⟨n⟩ of photons absorbed per SF₆ molecule (circles) vs excitation frequency; the 10.6 μm ³²SF₆ absorption band [9] is also shown for clarity.

with the decrease in the radiation intensity along the beam due to the stronger absorption at the higher pressures.

We also investigated the excitation of vibrational levels of the SF₆ molecule at various frequencies of the CO₂-laser radiation, and specifically, at the lines P(12)—P(20), the intensity of the radiation being held constant at 12 MW/cm² for these measurements. It was found that $\langle n \rangle$ does depend on the exciting frequency. Figure 3 shows the results of these measurements. For clarity, the 10.6 μm linear absorption band of SF₆, recorded with high-resolution spectrophotometers[9], is also shown on the figure. Figure 3 shows good correlation between $\langle n \rangle$ and the shape of the SF₆ absorption band, the result of the measurements at the P(18) line being an exception. Almost complete correlation was also observed between the frequency dependence of the absorption coefficients and the results of Shimitsu[15], who measured the linear absorption coefficients for the lines P(12)—P(20). However, at an intensity of ~12 MW/cm², the nonlinear absorption coefficients are about 300 times smaller than the linear absorption coefficients at the investigated frequencies.

The correlation between the frequency dependence of the energy absorption and the shape of the absorption band is not surprising, since the absorption coefficient at a given frequency is mainly determined by the number of molecules in rotational levels that interact with radiation at that frequency. These measurements also confirm the result that at low SF₆ pressures only a small fraction of the molecules interact with the radiation during the lifetime of a laser pulse.

## 5. SEPARATION OF SULFUR ISOTOPES

As was shown earlier[5], when the cell is irradiated with focused CO₂-laser radiation the SF₆ molecules whose isotopic composition is such that they can absorb in the frequency region to which the laser has been tuned undergo irreversible dissociation, as a result of which the residual gas mixture becomes enriched in the unexcited isotopes of the molecule owing to the "burning out" of the others. To determine the separation of the isotopes we made IR analyses (using an RKS-24 spectrophotometer) and mass analyses (using an MI-1309 mass spectrometer) of the gas before and after irradiating the cell with focused (f = 50 cm) CO₂-laser radiation.

The results of a mass analysis (based on the ionic fragment[1] SF₅⁺) of the gas remaining in the cell after irradiation are presented in Table III. The same results were also obtained in analyzing for other ionic fragments. It is evident from the results presented in the
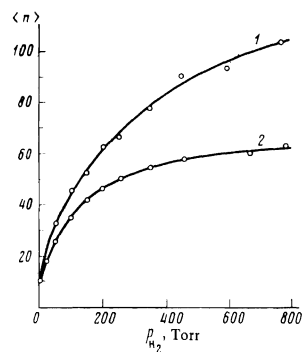


FIG. 2. Number of CO₂-laser radiation photons absorbed per SF₆ molecule vs pressure of the buffer gas (H₂) measured in a 100-cm long cell at an incident radiation intensity of 12 MW/cm² and SF₆ pressures of 0.5 Torr (curve 1) and 1.1 Torr (curve 2).

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TABLE III. Results of isotope separation experiments

| Irradiated molecule | Laser line and frequency (cm⁻¹) | Number of irradiation pulses | Irradiated gas mixture (Torr) | | | | Isotopic composition after irradiation (%) | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | SF₆ | NO | HBr | H₂ | ³²SF₆ | ³³SF₆ | ³⁴SF₆ | ³⁶SF₆ |
| Without irradiation | – | – | – | – | – | – | 95 | 0.75 | 4.2 | 0.017 |
| ³²SF₆ | P(12)–951.19 | 100 | 0.18 | – | – | – | 57 | 2.5 | 40.5 | <0.1 |
| » | » | 100 | 0.18 | 2.0 | – | – | 70 | 2.4 | 27.4 | <0.1 |
| » | » | 100 | 0.18 | – | 2.0 | – | 73.5 | 1.72 | 24.4 | <0.1 |
| » | » | 100 | 0.18 | – | – | 2.0 | 80 | 1.48 | 18.5 | <0.1 |
| » | » | 400 | 0.18 | – | – | 2.0 | 2.5 | ≈0.7 | 96 | ≈0.6 |
| » | P(16)–947.74 | 2000 | 0.18 | – | – | 2.0 | 0.8 | 1.8 | 97 | ≈0.6 |
| ³⁴SF₆ | P(40)–927.97 | 500 | 0.18 | – | – | 2.0 | >99.5 | <0.1 | ≈0.25 | <0.01 |

FIG. 4. IR absorption spectrum of the $\nu_3$ vibrations of SF₆ a) natural isotopic mixture, b) mixture enriched in the present experiments.

table that, for example, the enrichment factor for ³⁴SF₆ with respect to ³²SF₆ molecules on irradiation with 2000 laser pulses on the P(16) line is

$$K(^{34}/_{32}) = \frac{[^{34}SF_6]_*}{[^{32}SF_6]_*} \Big/ \frac{[^{34}SF_6]_0}{[^{32}SF_6]_0} = 2800, \tag{1}$$

where the square brackets indicate the molecular concentrations in the mixture and the subscripts "0" and "*" refer to the unirradiated and irradiated mixtures, respectively.

From Table III we can also find the enrichment factor of the mixture in the isotope ³⁶SF₆ with respect to ³²SF₆ resulting from irradiation of the mixture with 400 laser pulses at the P(12) line:

$$K(^{36}/_{32}) \approx 1200.$$

In addition, we can conclude from the results presented in Table III that in the present experiments the enrichment factors for the various sulfur isotopes are virtually independent of the composition of the acceptors added to the SF₆. This can be accounted for by the fact that the dissociation of the SF₆ takes place irreversibly even without acceptors. We note that in none of the experiments whose results are presented in Table III was more than 10% of the incident energy absorbed in the cell.

For clarity and to demonstrate the physical separation of the isotopes, the residual gas after irradiation was frozen out of the irradiated cell and placed in a small cell suitable for measuring IR spectra. The initial cell had been so irradiated as to bring the concentration of the ³²SF₆ molecules down to the concentration of the ³⁴SF₆ molecules. Figure 4a shows the IR spectrum of the natural SF₆ mixture before irradiation in a cell 6 cm long and 25 cm³ in volume at a pressure of 1 Torr. Figure 4b shows the IR spectrum obtained after condensation into the same cell of the residual SF₆ mixture resulting from irradiating natural SF₆ at a pressure of 0.5 Torr in a cell 100 cm long and 500 cm³ in volume. The increase in the relative concentrations of the ³⁴SF₆ and ³⁶SF₆ molecules due to burning out of the ³²SF₆ molecules is very clearly evident.

The results of our study of the enrichment factor K(34/32) as a function of the intensity of the laser radiation are presented in Fig. 5. In these experiments the pressure in the cell was 0.32 Torr and the number of irradiation pulses was held constant at 450. The results show that the selectivity of the enrichment process is extremely critical to changes in the intensity of the laser radiation, rising much more rapidly with increasing intensity than the number of absorbed photons (Fig. 1).

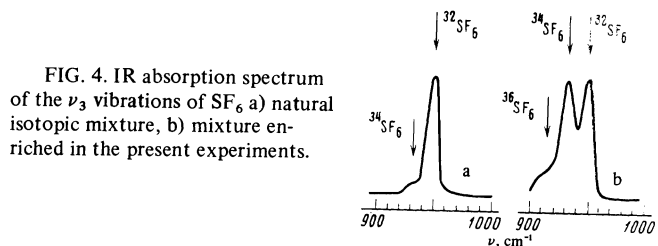The measured dependence of the enrichment factor K(34/32) of the residual mixture on the initial SF₆ pres-
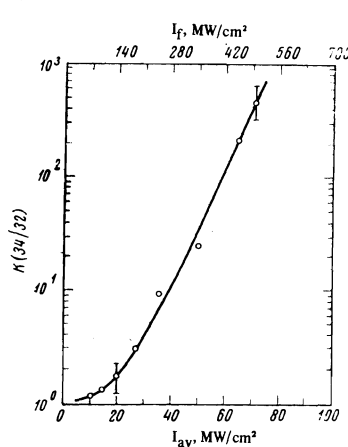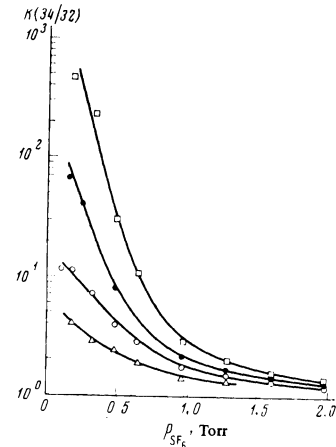
FIG. 5

FIG. 6

FIG. 5. Enrichment factor vs radiation intensity for SF₆ at 0.32 Torr irradiated with 450 pulses. $I_{av}$ is the average intensity and $I_f$ is the intensity at the focus of the lens.

FIG. 6. Enrichment factor vs SF₆ pressure for irradiation with the following numbers of pulses: 50 (triangles), 100 (open circles), 200 (black circles), 400 (squares).

sure p in the cell is shown in Fig. 6 for various numbers of irradiation pulses. It will be seen that the enrichment factor falls sharply (as $e^{1/p}$) with increasing pressure p and reaches its largest values at SF₆ pressures below 0.5 Torr. As the SF₆ pressure rises, K tends to unity, i.e., enrichment ceases. One can also obtain the dependence of K on the number of irradiation pulses from Fig. 6. It should be emphasized, however, that this dependence does not characterize the intrinsic selectivity of the dissociation of the irradiated molecules since it depends on the number of undissociated molecules in the entire volume. The kinetics of the enrichment of the residual gas and its relation to the selectivity of the molecular dissociation are discussed below in Sec. 6.

One reason for the fall in the enrichment factor with increasing SF₆ pressure in the irradiated cell may be an increase in the contribution from nonselective dissociation of SF₆ due to thermal heating of the gas as a result of vibrational relaxation of excited molecules that do not reach the dissociation point. This effect can be neglected at low pressures, since, for example, the V-T relaxation time at 0.2 Torr is 750 μsec (Table II) while the time for diffusion to the wall at this pressure is ~450 μsec, i.e., in this case the molecules are deactivated at the wall without heating the gas.

Table IV gives the frequencies of the absorption bands of the products formed in a glass cell 12 cm long initially containing SF₆ at a pressure of 1.5 Torr and irradiated for 30 min at a pulse rate of 1.5 sec⁻¹.

TABLE IV

| Absorption band center frequency, $cm^{-1}$ | Absorption band width, $cm^{-1}$ | Absorption band intensity | Absorbing molecule | Absorption band center frequency, $cm^{-1}$ | Absorption band width, $cm^{-1}$ | Absorption band intensity | Absorbing molecule |
|---|---|---|---|---|---|---|---|
| 1650 | ~30 | weak | ? | 1100 | ~160 | weak | $SOF_2$ |
| 1450 | ~30 | average | ? | 855 | ? | very weak | ? |
| 1330 } | ~30 | » | $SOF_2$ | 810 | ~40 | strong | $SOF_2$ |
| 1340 } | | | | 750 | ~50 | » | $SOF_2$ |

We have not yet been able to identify all the compounds whose absorption bands are listed in Table IV. However, the presence of $SOF_2$ molecules in the reaction products has been established[19]. A mass analysis of the products from irradiation of $SF_6$ under the conditions of our experiment revealed strongly rising peaks at mass numbers 48, 67, 86, and 105, which apparently correspond to the ion fragments $SO^+$, $SOF^+$, $SOF_2^+$, and $SOF_3^+$, so we may assume that $^{32}SOF_4$ molecules are produced.

## 6. KINETICS OF THE ENRICHMENT PROCESS

In our experiments the isotope separation was monitored by examining the isotopic composition of the residual gaseous $SF_6$ under continuous irradiation by a sequence of $CO_2$-laser pulses. It is obvious that at the beginning of the irradiation when only a small fraction of the $SF_6$ molecules have dissociated the enrichment of the residual gas will also be small, although the enrichment of the molecules produced as a result of dissociation of $^aSF_6$ molecules (the raised prefix a labels the irradiated isotope) may be considerable. The enrichment of the produced molecules in the isotope $^aS$ is determined by the selectivity of the dissociation of the $^aSF_6$ molecules as compared with the molecules of other isotopic compositions. On the other hand, when the irradiation has been continued so long that virtually all the $^aSF_6$ molecules have dissociated while the dissociation of $SF_6$ molecules of other isotopic compositions continues, although at a lower rate, the enrichment of the produced molecules in the $^aS$ isotope ceases. At the same time, the enrichment of the remaining very small fraction of the $SF_6$ molecules may continue and reach very large values.

For a quantitative analysis let us consider the simplest model of the dissociation of a two-component mixture of molecules with the initial concentrations $N_{a0}$ and $N_{b0}$ by pulses of radiation in resonance with the molecules containing the isotope a. Let the dissociation rates of molecules a and b be $d_a$ and $d_b$, respectively. The quantity $d_a$ ($d_b$) is defined as the average over the volume of the cell of the probability for the irreversible dissociation of a single molecule a (b) under the action of a single pulse multiplied by the number of pulses per unit time. Since the molecules a are in the better resonance with the field, we have $d_a > d_b$, and the selectivity of the dissociation of molecules a is defined as the ratio $s = d_a/d_b$ (high selectivity means large values of s: s ≫ 1).

The concentrations of molecules a and b decrease exponentially with time (or with the number of pulses):

$$N_a = N_{a0} \exp(-d_a t), \quad N_b = N_{b0} \exp(-d_b t). \quad (2)$$

Here it is assumed that the dissociation rates remain unchanged as the initial molecules are burned out and the chemical composition and pressure of the gaseous mixture change. This is an entirely acceptable first approximation for the method under consideration at low

gas pressures since the dissociation process is determined mainly by the IR field. Then, by definition (1), the enrichment factor of the residual gas in the isotope b will be given by

$$K_{res}\left(\frac{b}{a}\right) = \frac{N_b}{N_a} / \frac{N_{b0}}{N_{a0}} = \exp\{(d_a - d_b)t\} = \exp\left(\frac{s-1}{s}d_a t\right). \quad (3)$$

The total pressure of the residual gas $N = N_a + N_b$ varies as follows:

$$N/N_0 = \delta_a \exp(-d_a t) + \delta_b \exp(-d_b t), \quad (4)$$

where $N_0 = N_{a0} + N_{b0}$, and $\delta_a = N_{a0}/N_0$ and $\delta_b = N_{b0}/N_0$ are the relative concentrations of the isotopes in the initial mixture.

The enrichment factor for the produced molecules in the isotope a is given by

$$K_{prod}\left(\frac{a}{b}\right) = \frac{N_{a0} - N_a}{N_{b0} - N_b} / \frac{N_{a0}}{N_{b0}} = \frac{1 - \exp(-d_a t)}{1 - \exp(-d_b t)}. \quad (5)$$

When the degree of separation of the initial mixture is low ($d_a t$, $d_b t \ll 1$) we have

$$K_{prod}(a/b) = d_a/d_b = s, \quad (6)$$

i.e., the enrichment of the produced molecules is determined by the selectivity s of the dissociation of molecules a.

It is evident from Eqs. (3)—(5) that with exponentially deep "burn out" of the initial molecules a and b, arbitrarily high enrichment of the relatively few remaining molecules in the isotope b becomes possible. Figure 7 shows the variation with time (or with number of pulses) of the enrichment factors of the residual and produced molecules for three different values of the selectivity s (s = 1.1, low selectivity; s = 2, moderate selectivity; and s = 10, high selectivity).

In our experiments the enrichment factors K(34/32) and K(36/32) reached values exceeding 1000 when the $SF_6$ molecules were sufficiently burned out (the residual $SF_6$ pressure reached values below 1% of the initial pressure). When the molecules are largely burned out, the enrichment factor of the residual gas is of course no longer equal to the selectivity s of the dissociation, and to determine s one must use Eqs. (3) and (4), i.e., one must simultaneously measure the enrichment factor $K_{res}(b/a)$ and the change in the pressure of the residual gas.

To illustrate this procedure we did experiments in which the enrichment and the change in the pressure of the residual gas were simultaneously recorded. The results of one of these experiments at an $SF_6$ pressure of 1.6 Torr, at which the relative enrichment is low (see Fig. 6), are presented in Fig. 8. In this experiment we used a cell 10 cm long and 3 cm in diameter irradiated by 3-J $CO_2$-laser pulses at the P(16) line, the radiation being focused within the cell by a 6-cm focal length lens at the entrance window of the cell. The increase in $K_{res}(34/32)$ and the beginning of the decrease in $K_{prod}(32/34)$ on reaching conditions of substantial burn-out of the molecules are clearly evident. The value of $K_{res}(32/34)$ at the beginning of the irradiation immediately gives the selectivity s of the dissociation of the $^{32}SF_6$ molecules: s ≈ 3.5 at an $SF_6$ pressure of 1.6 Torr. On reducing the pressure to 0.2 Torr, s increases sharply, reaching values much greater than 10. This follows from a mass-spectrometer analysis of the produced molecules.
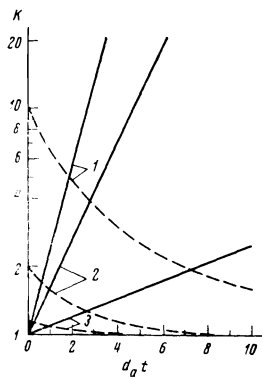
FIG. 7



FIG. 8

FIG. 7. Enrichment factors for the residual gas and the produced molecules vs time (or number of irradiation pulses) in the selective dissociation of molecules a in a two-component mixture, calculated for various values of the dissociation selectivity s: 1—s = 10, 2—s = 2, 3— s = 1.1. The full lines represent $K_{res}(b/a)$, and the dashed curves, $K_{prod}$ (a/b).
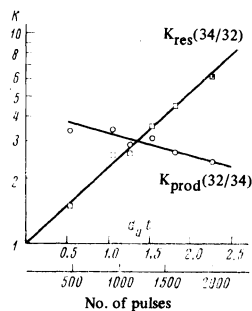
FIG. 8. Experimental values of the enrichment factors $K_{res}(34/32)$ for the residual gas (squares) and $K_{prod}(32/34)$ for the produced molecules (circles) vs number of irradiation pulses in the dissociation of $^{32}SF_6$ molecules in the natural isotopic mixture at an initial pressure of 1.6 Torr.

## 7. DISCUSSION

Isotopic selectivity. The main problem of practical interest is that of the maximum isotopic selectivity achievable in the dissociation of the molecules. Figure 3 shows that the frequency dependence of the average number $\langle n \rangle$ of photons absorbed per molecule correlates with the absorption coefficient of the $\nu_3$ band of the $SF_6$ molecule. This frequency dependence essentially describes the number of $SF_6$ molecules coming into resonance with the laser radiation.

It is clear that the limit of achievable selectivity is set by the extent to which the absorption bands of the molecules of different isotopic compositions (normalized to the same molecular concentration) overlap at the exciting frequency, and therefore depends on the isotopic shift and shape of the absorption bands. This is also clearly evident from Fig. 9, on which we have plotted the experimental values of the enrichment factors K(33/32) and K(34/32). The enrichment factor increases exponentially with increasing isotopic shift (see Table I) of the vibrations excited by the laser. Under conditions in which the molecules have been largely burned out and the relation between the enrichment factor $K_{res}$ and the dissociation selectivity s is given by Eq. (3), this corresponds to an at least linear increase of s with increase of the isotopic shift between the centers of the molecular absorption bands.

From all this it follows that in order to obtain the maximum enrichment for an isotopic mixture one should cool the irradiated gas since cooling greatly narrows the absorption bands[20] and thus reduces their overlap. In some cases when the gas condenses at low temperatures it is useful to employ the cooling effect of flow through a nozzle, which makes it possible to achieve considerable cooling without appreciable condensation[21].

The multiphoton absorption mechanism. Now that the high selectivity of collisionless dissociation of molecules in a strong IR field and the effectiveness of its use to separate isotopes in a comparatively simple and practical manner have been demonstrated, it is of great interest to understand the specific mechanism of the multiphoton absorption of IR radiation by the molecule.

A characteristic feature of the observed multiphoton absorption of IR radiation is the very great energy absorbed by the molecule. As was mentioned in Sec. 4, at a power level of 10 $MW/cm^2$, which is still insufficient for strong dissociation, the molecule accumulates an energy $E_{abs}$ of $\langle n \rangle q^{-1} \hbar \omega \approx 6$—7 eV (at q = 0.1), and at the 80 $MW/cm^2$ power level, $E_{abs}$ exceeds 30 eV.

We note that the phenomenon of multiphoton dissociation of molecules under the action of radiation whose frequency $\omega$ is much higher than the frequency $\omega_{vib}$ of the molecular vibrations $(\omega \gg \omega_{vib})$ is well known. The first calculations of such a process were published by Askar'yan[22] and by Bunkin et al.[23]. These authors also discussed the buildup of molecular vibrations by the action of radiation at the frequency $\omega \approx \omega_{vib}$ and at multiples of that frequency. Dissociation of the molecules (according to the Morse-oscillator model) begins at radiation intensities of the order of $10^{12}$ $W/cm^2$. The dissociation under the action of IR radiation that we investigated has nothing to do with the problem discussed in[22,23] since it takes place in resonant radiation fields with $\omega \approx \omega_{vib}$ at intensities some 3—5 orders of magnitude lower than are required for the multiphoton dissociation discussed in those papers.

Some possible mechanisms for multiphoton absorption were discussed in[4] in connection with the excitation and dissociation of $BCl_3$ molecules. In particular, it was shown in[4] that multiphoton excitation of a molecule with the anharmonicity compensated the by broadening of the transitions in a strong resonance field of intensity $10^9$ $W/cm^2$ is possible only out to levels with $v \simeq 10$. Such excitation, of course, cannot explain the rapid dissociation of the molecule, which requires an energy of $\sim 5$ eV or higher, i.e., the excitation of a $v \approx 40$ vibrational level of the molecular vibrational mode being excited. The experiments described here show that excitation of the same vibrational levels and dissociation of the $SF_6$ molecule can be achieved at much lower intensities ($10^6$—$10^7$ $W/cm^2$). At such intensities the field broadening is at least an order of magnitude less than the anharmonicity and cannot even explain the excitation of the v = 2 level. Hence the effect of broadening of the molecular transitions in a resonant IR field due to the dynamic Stark effect is apparently even less important than was indicated in[4]. Thus, it remains unclear why the molecule so easily overcomes the "anharmonicity barrier" even for the first few vibrational transitions.
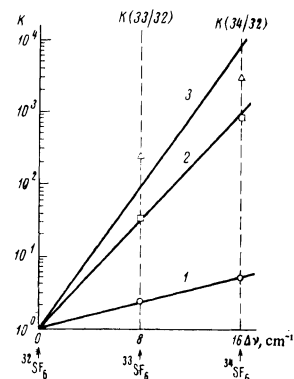
It was suggested by Isenor et al.[24], and again recently by Akulin et al.[25], that the molecule may dissociate from highly excited states, which, however, are still far from the dissociation limit, as a result of the fact that the spectrum of transitions between highly excited multiply degenerate molecular levels is almost continuous. This removes the problem of the frequency of the vibrational transitions between highly excited levels becoming different from the frequency of the field on account of anharmonicity and in principle can assure rapid excitation of the molecule to the dissociation point. When a strong field interacts with a continuum of overlapping component frequencies, a large number of normal vibrations should obviously be excited at once. This can to some extent explain how a molecule can accumulate a store of energy considerably exceeding the dissociation energy from an IR field in resonance with a molecular bond. A weak point of this model is the fact that the oscillator strength for transitions in the continuum in a field of monochromatic radiation that covers only a narrow section of the spectrum ($\Delta \omega / \omega_{vib} \ll 10^{-3}$) is small. Neither is it known at what vibrational level does the spectrum of transitions begin to become continuous. This problem deserves further theoretical and experimental study.

Now let us turn our attention to the fact that the excitation of a large number of modes as a result of transitions between highly excited vibrational levels at component frequencies can be treated in terms of fast radiationless intramolecular relaxation of vibrational excitation. Suppose that a molecule has acquired a store $E_{vib}^{(i)}$ of vibrational energy in some single degree of freedom $\nu_i$. Because the vibrations are anharmonic (the potential in which the atoms move is not a harmonic oscillator potential) the normal coordinates of the molecule interact with one another, and this makes it impossible to localize the energy in a given degree of freedom. Even if the vibrational energy is initially concentrated in a single degree of freedom, the energy will proceed to redistribute itself over all the degrees of freedom. The redistribution time depends on the strength of the interaction between the degrees of freedom, being shorter for a more complex molecule or for a higher initial store of vibrational energy[26]. Thus, we may suppose that a molecule excited by a strong IR field to a high lying state, which, however, is till far from the dissociation point, will transfer the excitation to other degrees of freedom extremely rapidly. As a result, the energy in the degree of freedom being excited will be much less than the dissociation energy, whereas the total energy in all the vibrational degrees of freedom may quickly exceed the dissociation energy and therefore lead to the dissociation of the molecule.

There are some facts that indicate that the dissociation mechanism is closely related to the complexity of the molecule and to the fact that the field interacts with a large number of molecular degrees of freedom. For example, the characteristic intensities at which $SF_6$ molecules dissociate is considerably lower than the intensity necessary to dissociate $BCl_3$. In similar experiments with the triatomic molecule $OCS$[27] no dissociation was observed at power levels of the order of $10^9$ W/cm$^2$. In addition, experiments on the dissociation in a strong IR field of a sequence of compounds containing C and $C_2$ groups ($CH_3OH$, $C_2F_3Cl$, $C_2H_5OH$, ...) have shown[28] that the molecule dissociates into individual atoms or into fragments containing the strongest bonds (of the $C_2$ type). Moreover, the composition of the dissociation products of a given molecule does not depend on the vibrational mode chosen for excitation.

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[1])Unfortunately a terminological inaccuracy crept into the caption to Fig. 1 of our previous paper [5]: the ion fragment $SF_5^+$ was erroneously called a radical.

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