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Kinetics of infrared absorption spectra of SF₆ molecules vibrationally excited by a high-power CO₂ laser pulse

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The infrared linear absorption spectra of the SF_6 molecule is studied experimentally with time resolution after multiphoton excitation in the strong field of a CO_2 laser. A comparison is made with SF_6 spectra in equilibrium heating and the existence is shown of two ensembles of molecules—cold molecules which do not interact with the field and hot, vibrationally excited molecules. Measurements are made of the fraction of molecules interacting with the field q, the average level of excitation $\langle n_q \rangle$, and the time of establishment of vibrational equilibrium as a function of the level of excitation.

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1. INTRODUCTION

In recent years a large number of studies have been devoted to the multiphoton excitation and istotopically selective dissociation of polyatomic molecules in strong infrared laser fields (see the review by Ambartzmian and Letokhov[1]). The molecule most studied in this area is SF_6, for which detailed investigations have been made of the characteristics of multiphoton absorption, dissociation, and laser isotope separation and for which a real possibility has been shown of isotope separation in large quantities.[2] An important refinement of the process is the use of the two-frequency method,[3] in which the first field excites a significant fraction of the molecules and the second, with some delay in time and detuning in frequency, dissociates the vibrationally excited molecules.

At the same time there remain unanswered many questions relating both to the excitation of the lower and higher vibrational levels and to the dissociation process.

The interpretation is particularly difficult in the case of two-frequency excitation. While the absorption spectrum and distribution of molecules in vibrational levels are known for single-frequency excitation, in two-frequency excitation the second field interacts already with a substantially nonequilibrium system, for which neither the absorption spectrum nor the vibrational distribution function $N(E_{v_i})$ are known.

Of exceptional importance is the question of the fraction of molecules q which interact with the field and of the average level of excitation of the molecules $\langle n_q \rangle$, and also the dependence of these quantities on the conditions of excitation. In experiments on measurement of absorption in a strong field[4,5] one usually determines $\langle n \rangle$—the average number of absorbed photons for all molecules in the region of the strong field, i.e., the quantity

$$\langle n \rangle = \langle n_q \rangle q.$$

However, obtaining information individually on q and $\langle n_q \rangle$ from experiments on dissociation of molecules is extremely difficult as a consequence of possible processes of successive excitation of dissociation products, and also possible recombination of dissociation products with formation of the initial molecules.

Another important question is the lifetime of molecules excited in a strong field to high vibrational states, i.e., the time of their de-excitation in collisions with unexcited molecules.

The present work is devoted to investigation with time resolution of the linear absorption spectra of SF_6 molecules after their multiphoton excitation in the strong infrared field of a CO_2 laser. This permits determination of important characteristics both of the multiphoton excitation process itself, and of the molecules excited to high vibrational states.
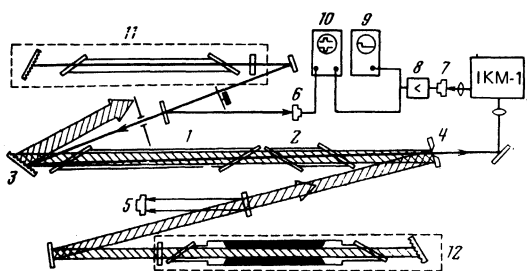
FIG. 1. Diagram of experimental apparatus: 1, 2—cuvettes with investigated gas; 3—diffraction grating; 4—mirror with opening; 5, 6—infrared detectors; 7—high-speed infrared detector; 8—wide-band amplifier; 9, 10—oscillographs; 11—continuous CO_2 laser; 12—pulsed CO_2 laser.

2. EXPERIMENTAL ARRANGEMENT AND METHOD

Figure 1 shows a diagram of the experimental apparatus for study with time resolution of linear absorption spectra of vibrationally excited SF_6 molecules. The molecules were excited by means of a pulsed CO_2 laser at atmospheric pressure with selection of vibrational-rotational lines. The energy of the radiation pulse was up to 2 J, and the length at half-height 80 nsec. The frequency of the exciting field was constant and corresponded to the Q branch of the transition $v = 0 \rightarrow v = 1$ of the ν_3 band of SF_6. The exciting radiation passed through cuvettes 1 and 2 with SF_6. The radiation of the continuous CO_2 laser with which the linear absorption in SF_6 was measured was oppositely directed. The power density of the continuous CO_2 laser in the cuvettes was 10^{-3} W/cm^2, which was significantly below the saturation level in SF_6. The radiation of the continuous CO_2 laser was extracted through a small opening in mirror 4 and after passing through the monochromator IKM-1 was directed onto a sensitive infrared photodetector 7 with a time resolution ~100 nsec. The electrical signal from the photodetector 7 was amplified by a wide-band amplifier 8 and fed to a storage oscilloscope S8-2. The output energy of the pulsed CO_2 laser was monitored by a calorimeter 5. Measurement of the initial linear absorption in SF_6 was accomplished by means of infrared detectors 6 and 7 and a two-beam oscilloscope 10. The pressure of SF_6 in the cuvettes was constant and amounted to 0.18 Torr. Two cuvettes of length 15 and 100 cm were used for the reason that the absorption of SF_6 differs greatly in different regions of the spectrum and it was necessary to provide simultaneously an optically thin layer and high sensitivity over the entire spectral region of measurement and at constant pressure. In order to avoid the action of the radiation of the high-power exciting CO_2 laser on the continuous CO_2 laser, optical coupling by means of the diffraction grating 3 was employed.

As the result of presence of anharmonicity of the vibrations, the absorption spectrum of highly excited molecules is displaced toward longer wavelengths. This means that on turning on the exciting field the absorption coefficient in the region of the initial absorption band decreases and the intensity of radiation transmitted through the cuvette increases. At the same time on the long-wavelength side a new absorption band appears and

the intensity of transmitted radiation decreases. By measuring the amount of change of the intensity of the probing radiation $\pm\Delta I(t, \nu)$ it is possible at any moment of time after the pulse to determine the absorption coefficient and, by changing the frequency of the probing radiation, to determine the absorption spectrum of the molecules

$$K(t, \nu) = K_0(\nu) - L^{-1} \ln[1 \pm \Delta I(t, \nu)/I(\nu)], \qquad (2)$$

where

$$K_0(\nu) = -L^{-1} \ln [I(\nu)/I_0] \qquad (3)$$

is the initial absorption coefficient, L is the length of the cuvette, and I_0 and I are the intensities of the radiation of the continuous CO_2 laser in the absence of gas and with gas.

3. EXPERIMENTAL RESULTS

In our experiments the level of excitation of the SF_6 molecules was always below the dissociation threshold, so that the total number of SF_6 molecules remained constant. In Figs. 2a and b we have shown the evolution with time of the linear absorption spectrum of SF_6 after action of an exciting pulse with energy density $\Phi = 0.16$ J/cm^2 (Fig. 2a) and $\Phi = 0.34$ J/cm^2 (Fig. 2b). (The arrow shows the excitation frequency.) The dashed line 1 corresponds[6] to the linear absorption spectrum of SF_6 at $T = 300$ K. Here one can see the Q branch of the transition $0 \rightarrow 1$ of the ν_3 mode and the Q branch of the thermal bands. The points show the linear absorption measured in the CO_2 laser lines before action of the strong infrared field. Curve 2 is the SF_6 absorption spectrum immediately after action of the CO_2 laser pulse. It is evident that a strong decrease in absorption occurs in the initial band and an increase of absorption on the long-wavelength side. An important feature is the appearance of two peaks in the absorption spectrum. At a time 2.5 μsec after the action of the pulse (curve 3) there are as before two peaks, which now are already significantly closer to each other, and after 15 μsec (curve 4) a common maximum is formed whose position and height are practically unchanged up to 100 μsec.
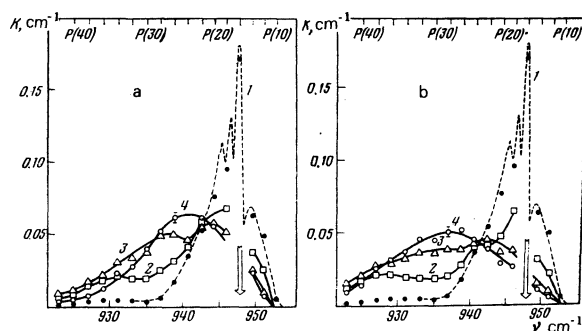

FIG. 2. Evolution of the absorption spectra of SF_6 gas after multiphoton excitation. Curve 1 is the SF_6 absorption spectrum at $T = 300$ K (Ref. 6); •—initial absorption at the generation frequencies of the CO_2 laser at $T = 300$ K. Curves 2, 3, and 4 are SF_6 absorption spectra after a time τ from the end of the CO_2 laser pulse; 2—$\tau = 0$, 3—$\tau = 2.5 \mu$sec; 4—$\tau = 15 \mu$sec; $P = 0.18$ Torr; $\Phi = 0.16$ J/cm^2 (a); $\Phi = 0.34$ J/cm^2 (b).

As will be shown later, this spectrum (for $t \geqslant 15$ μsec) corresponds to the equilibrium absorption spectrum with a common vibrational temperature which is established in the course of exchange of energy between excited and unexcited molecules. A similar pattern is observed also at other excitation intensities. Here the absorption in the initial band decreases with increase of Φ, and the shift of the new band towards longer wavelengths increases.

The observed evolution pattern of the absorption spectrum can be explained as follows. In infrared excitation in a strong infrared field a substantially nonequilibrium molecular system is excited, which consists of two ensembles: a cold ensemble of molecules which do not interact with the field, and hot molecules which have an excess of vibrational energy. We note that among the cold molecules in the case considered, in view of the high isotopic selectivity of the primary excitation event, are the unexcited molecules $^{33}SF_6$, $^{34}SF_6$, and $^{36}SF_6$. After termination of the action of the excitation pulse, exchange of vibrational energy begins in collisions between hot and cold molecules, and also a transition to equilibrium with a new supply of vibrational energy, i.e., with a new vibrational temperature T_{vib}. This naturally affects the absorption spectrum, and after establishment of vibrational equilibrium the spectrum differs substantially from the initial spectrum. Similar results and the same explanation for them were obtained recently by Ambartzumian et al.[7] with the molecule OsO_4.

From the spectra obtained, we can determine first of all the fraction of molecules q interacting with the field. This fraction was determined from the decrease of the integrated intensity of the R branch of the ν_3 band of the SF_6 molecule under the action of the CO_2 laser pulse:

$$q = \frac{S_0{}^R - S^R}{S_0{}^R}, \quad S^R = \int_R K(\nu) d\nu, \quad (4)$$

where S_0^R and S^R are the integrated intensities of the R branch of the SF_6 absorption band before and after the action of the laser pulse. This determination is valid, since the contribution to absorption in the R band immediately after the action of the pulse gives only excited molecules, in contrast to the P branch, where in addition to unexcited molecules, weakly excited molecules also contribute to the absorption as the result of the presence of anharmonicity.

In Fig. 3 we have shown the dependence of q on the incident energy density Φ. The value of q is already rather large (~0.34) at $\Phi = 0.05$ J/cm^2 and increases slowly with increase of the excitation intensity. In Fig. 3 we have shown also the dependence on Φ of the average number of absorbed photons $\langle n \rangle$ for any of the molecules in the strong-field region. The value of $\langle n \rangle$ was measured by the usual method on the basis of the decrease of the energy of the exciting field pulse after passing through cuvettes 1 and 2 (Fig. 1). Knowing $\langle n \rangle$ and q, we now can determine the average excitation level $\langle n_q \rangle = \langle n \rangle / q$; it increases with increase of Φ (Fig. 3).

With increase of the energy of the excitation pulse, the time of establishment of vibrational equilibrium also changes. In Fig. 4a we have shown oscillograms
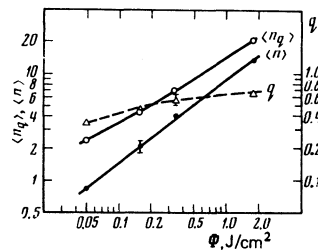

FIG. 3. Dependence of $\langle n \rangle$, q, and $\langle n_q \rangle$ on the energy density of the pulsed CO_2 laser: $\langle n \rangle$ is the number of absorbed photons per molecule with averaging of the absorbed energy over all molecules of the irradiated volume; q is the fraction of excited molecules; $\langle n_q \rangle$ is the average level of excitation of SF_6 molecules (quanta per molecule) absorbing CO_2 laser radiation.

of the change in absorption during establishment of equilibrium at different excitation energies in the region of those probing frequencies where the maximum of the equilibrium absorption spectrum is established in a characteristic time τ_e. It can be seen from the oscillograms that the total time for establishment of equilibrium τ_e, i.e., the time in which the absorption spectrum ceases to change, increases with increase of the excitation energy. In Fig. 4b we have shown the dependence of τ_e on the average excitation level $\langle n_q \rangle$. The increase of τ_e with increase of $\langle n_q \rangle$ can be explained qualitatively as follows.

With increase of $\langle n_q \rangle$ the displacement of the vibrational temperature of the hot molecules from the temperature of the cold molecules increases. If we assume that the transfer of vibrational energy from a hot molecule to a cold molecule cannot occur in large portions, i.e., can occur only by individual quanta corresponding, for example, to the quantum of the ν_3 mode (~1000 cm^{-1}), then in the case of large $\langle n_q \rangle$ for the transition to equilibrium more energy-transfer events are necessary, and consequently a longer time. Since the cold molecules include SF_6 molecules containing unexcited isotopes, the quantity τ_e determines the total time of loss of isotopic selectivity in the course of collisions after isotopically selective multiphoton excitation.

4. DISCUSSION OF RESULTS

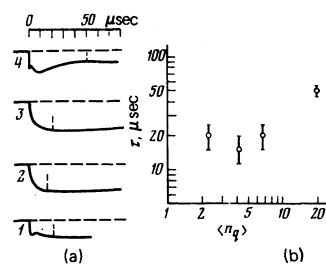Thus an important feature of the vibrational excitation of SF_6 molecules in a strong infrared field is the form-

FIG. 4. Time of establishment of equilibrium vibrational temperature. a—Signals of change of absorption: 1—Φ = 0.05 J/cm^2, frequency $P(22)$ of CO_2 laser; 2—Φ = J/cm^2, $P(26)$; 3—Φ = 0.34 J/cm^2, $P(28)$; 4—Φ = 1.8 J/cm^2, $P(42)$. b—Time of establishment of equilibrium τ_e as a function of the level of excitation of SF_6 molecules.

ation of two ensembles of molecules: cold, which do not interact with the field, and hot, which have an excess of vibrational energy. The evolution of the absorption spectra is determined by interaction of these ensembles in the collision process. The observed pattern is confirmed by the results of other studies,[8,9] in which it is shown that a significant fraction of polyatomic molecules from many rotational states can interact with a sufficiently strong infrared pulse of definite frequency. Possible mechanisms of this "emptying" of many rotational states are discussed in Refs. 8 and 10.

It is of interest to compare the equilibrium spectra obtained by us with laser excitation with the spectra obtained in Ref. 6 in thermal heating of SF_6 in shock tubes. Comparison with the results of Ref. 6 showed that the equilibrium spectrum at $\Phi = 0.16$ J/cm² corresponds to a temperature $T = 545 \pm 20$ K, and for $\Phi = 0.34$ J/cm² it corresponds to $T = 750 \pm 20$ K (Fig. 5). Here there is good agreement in the position of the absorption peak and the spectrum shape, and also in the magnitude of this peak. It is clear that the increase of the vibrational temperature is determined by the quantity of energy absorbed by molecules from the strong field $\langle n \rangle h\nu$ (Fig. 3). However, for determination of T_{vib} it is impossible to use the equipartition law, since in our case the level of excitation is insufficient and a molecule cannot be considered a system of classical oscillators. To determine the value of T_{vib} we shall use the formula for the quantum heat capacity of a polyatomic molecule[11] without taking into account electronic energy:

$$E_{vib} = \sum_i g_i h\nu_i \frac{1}{\exp(h\nu_i/kT) - 1}, \qquad (5)$$

$$E_{rot} + E_{trans} = 3kT. \qquad (6)$$

Here E_{vib}, E_{rot}, and E_{trans} are respectively the vibrational, rotational and translational energies of the molecule, and ν_i and g_i are respectively the eigenfrequencies and their degeneracy factors.

It is clear that T_{vib} depends substantially on what degrees of freedom come into equilibrium with each other: in heating only of vibrational degrees of freedom it will be higher than in heating of all degrees of freedom.

In the right-hand part of the Table we have given the results taken from Ref. 6 for two equilibrium temperatures T_{eq}, where the peaks of the absorption spectra of heated SF_6 are in the frequency region $P(24)$ and $P(28)$ of a CO_2 laser. In the left-hand part of the Table we have given the results obtained in the experiment and also the results of calculation of the vibrational temperatures from the measured value of $\langle n \rangle$ for two cases: heating of all degrees of freedom $(T_{V,T,R})$ and heating of only vibrational degrees of freedom (T_V). It can be seen that
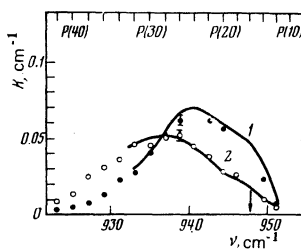

FIG. 5. Equilibrium SF_6 absorption spectra. Curves 1 and 2 are SF_6 absorption spectra at $T = 545$ K and $T = 750$ K (Ref. 6), $P = 0.18$ Torr; $\bigcirc$, $\bullet$ are the experimental absorption points after $\tau = 15$ μsec, $P = 0.18$ Torr; $\bullet$—$\Phi = 0.16$ J/cm², $\bigcirc$—$\Phi = 0.34$ J/cm².

there is good agreement in the case when, up to the moment of establishment of vibrational equilibrium, heating of only vibrational degrees of freedom occurs, and the rotational and translational degrees of freedom have their initial temperature. This can occur, since it is known that the V-T or V-R relaxation time for an SF_6 molecule at $P = 0.18$ Torr is several hundred microseconds and significantly exceeds τ_e. We note that in comparison of the spectra obtained with the data of Ref. 6 (Fig. 5) we did not take into account the fact that in our case $T_{rot} \neq T_{vib}$, while in the case of Ref. 6 $T_{rot} = T_{vib}$. However, as shown in Ref. 12, the shape and width of the absorption spectrum of a sufficiently heated SF_6 gas are determined mainly by T_{vib} and depend weakly on T_{rot}; the higher T_{vib}, the weaker this dependence.

Let us consider now the spectrum of vibrational excitation of molecules immediately after the action of an exciting infrared pulse (Fig. 6). We know the fraction q of the molecules which dominates this spectrum, and also the average level of excitation $\langle n_q \rangle$ in units of the quantum of the exciting infrared field. However, in contrast to the equilibrium case, we do not know the form of the distribution function of the vibrational energy $N(E_{v_i})$. At the present time there is intensive discussion in the literature[12,15] of the question of the possibility of selective excitation in the multiphoton regime and dissociation of polyatomic molecules in a strong infrared field. Unfortunately, it is difficult to judge uniquely from the shape of the spectrum whether a mode-selective excitation is occurring or there is a thermalization of the absorbed energy over many modes. The difficulty is that the anharmonic shift of a transition from some level of energy E wherein the photons of the mode ν_3 are decreased by unity depends practically only on E and depends only weakly on the distribution of E over the vibrational modes.[6]

In Fig. 6 the dashed lines show the equilibrium absorption spectra from Ref. 6 at temperatures corresponding to the measured supply of vibrational energy

TABLE I.

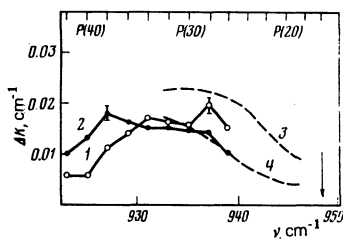|	Experiment						Results of Novak and Lyman[6]		
Φ, J/cm²	$\langle n \rangle$, quanta/molecule	ν_{max}	K_{max}, cm⁻¹	$T_{V,T,R}$, K	T_V, K		ν_{max}	K_{max}, cm⁻¹	T_{eq}, K
0.05	0.8±0.2	–	–	330±20	430±20		–	–	–
0.16	2±0.4	$P(24)$	0.065	450±50	550±50		$P(24)$	0.07	545
0.34	3.9±0.8	$P(28)$	0.05	610±60	750±60		$P(28)$	0.052	750
1.8	13±2	–	–	1370±200	1650±200		–	–	–

FIG. 6. Spectrum of variation of SF_6 absorption immediately after CO_2 laser excitation pulse $(\tau = 0)$: 1—$\Phi = 0.16$ J/cm^2, 2—$\Phi = 0.34$ J/cm^2, 3 and 4—equilibrium absorption spectra[6]: 3—$T = 800$ K, $P = q \times 0.18 = 0.086$ Torr, $q = 0.48$; 4—$T = 1050$ K, $P = 0.1$ Torr, $q = 0.57$.

$\langle n_q \rangle$ (800 and 1050 K). It is evident that the spectra obtained by us differ qualitatively from the equilibrium spectra in that they have a certain structure. It is clear that in the equilibrium case there should in principle be no structure, since the spectrum at such temperatures is formed by overlap of a large number of thermal bands. In the case of mode-selective excitation there should appear in the spectra sequences of P, Q, and R transitions, since the magnitude of the anharmonic shift in SF_6 is greater than the width of the rotational branches of an individual vibrational transition: $\Delta\nu_{anh} \gtrsim \Delta\nu_{P,Q,R}$. Thus, the presence of structure in a spectrum may serve as an indication of the possibility of mode-selective excitation for $\langle n_q \rangle \lesssim 10$. In this respect it is of interest to study such spectra with a smoothly tunable diode laser and at low temperatures (in order to reduce $\Delta\nu_{P,Q,R}$).

This technique may be applicable for study of many other molecules.

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