Absorption of strong infrared radiation by polyatomic molecules in a buffer gas under conditions of saturation of vibrational transitions

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A calculation is made of the total observed cross section for the absorption of strong infrared radiation by polyatomic molecules in a high-pressure buffer gas, subject to an allowance for the excitation and relaxation processes. The solutions of the kinetic equations are obtained for such molecules in the limit of very high radiation intensities. It is shown that in some physical situations the observed absorption cross section is related directly to the microscopic relaxation parameters of the molecules.

1. INTRODUCTION

We shall calculate the cross section for the absorption of strong infrared radiation by polyatomic molecules in a buffer gas. We shall solve the kinetic equation which allows for two main competing processes: vibrational excitation of molecules by radiation and collisional relaxation.

The process of radiative excitation will be described by a microscopic cross section $\sigma(E,\omega)$ of the interaction of a molecule in a vibrational energy state E with a field of frequency ω; in dealing with the process of collisional relaxation we shall use a function $R(E)$, which by definition is the rate of relaxation of the total vibrational energy E of a molecule which is in a state with an energy E: $R(E) = d\langle E \rangle /dt$.

The energy E will be the only quantum number used to describe the state of a molecule, so that the excitation cross section $\sigma(E,\omega)$ and the relaxation rate $R(E)$ should be regarded as quantities averaged over a group of states with energies close to E.

Nonlinear absorption of strong infrared radiation by polyatomic molecules in a buffer gas has been investigated experimentally on a number of occasions (see, for example, Ref. 1–4). However, in general, the observed absorption cross section σ_t (ω,p,I) depends on the parameters of an experiment (such as the buffer gas pressure p, the frequency ω, and the radiation intensity I) and on the microscopic characteristics of a molecule $\sigma(E,\omega)$ and $R(E)$ in a manner too complex for the utilization of the information carried by σ_t (ω,p,I) in a reliable determination of these microscopic characteristics.

It is nevertheless found that in the case of saturation of vibrational transitions the observed cross section σ_t practically ceases to depend on $\sigma(E,\omega)$ and is governed mainly by the relaxation rate $R(E)$. We shall identify the conditions under which this regime is observed in experiments on polyatomic molecules and provide a simple method for the determination of the relaxation parameters of excited vibrational states of molecules. Moreover, we shall compare the calculations with the published experimental data for SF_6 in He to estimate the rate of relaxation of the SF_6 molecule and to draw some conclusions on the properties of vibrationally excited polyatomic molecules in a buffer gas.

2. DESCRIPTION OF A PHYSICAL MODEL

We shall consider a quantity $W(E,\omega) = I\sigma(E,\omega)$, which can be called the excitation rate, as well as the relaxation rate $R(E) = pK(E)$, where p is the buffer-gas pressure and $K(E)$ is a relaxation parameter which is governed solely by the microscopic properties of the investigated molecule.

We shall assume that the radiation intensity I is so high and its frequency ω is selected so that there are constraints which limit at least from above the range of energies (known as the absorption band of energies), where the excitation is much stronger than the relaxation:

$$W(E, \omega) \gg R(E) \quad \text{for} \quad E_a \lesssim E \lesssim E_b, \tag{1a}$$

whereas outside the absorption band, the reverse condition is obeyed:

$$W(E, \omega) \ll R(E) \quad \text{for} \quad 0 < E \lesssim E_a \text{ and } E_b \lesssim E \tag{1b}$$

(see Fig. 1). Such a situation is fully realizable if the infrared radiation frequency ω is in the so-called "red wing" of the linear absorption profile of a molecule, i.e., if ω is less than the characteristic frequencies of the transitions from the ground to the first vibrationally excited state. The existence of a bounded absorption band is due to a departure (because of the anharmonic shift outside this band) from the resonance of the laser radiation frequency ω with the absorption frequency of the molecule in a vibrational energy state E.
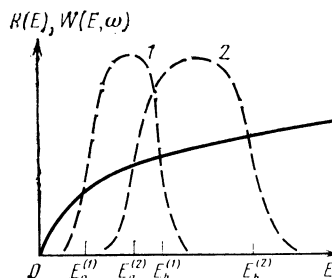

FIG. 1. Relaxation rate $R(E) = pK(E)$ (continuous curve) and excitation rate $W(E,\omega) = I\sigma(E,\omega)$ (dashed curves) plotted as a function of the vibrational energy E of a molecule excited by laser radiation of different frequencies ω $(\omega_1 > \omega_2)$.

When the laser radiation frequency is reduced, i.e., when ω is shifted to the red wing, the absorption band shifts because of the anharmonicity toward higher vibrational energies E, i.e., $E_a(\omega)$ and $E_b(\omega)$ increase on reduction in ω. The width of the band may in general change (Fig. 1).

Introduction of the lower E_a and upper E_b limits of the absorption band is to some extent arbitrary because in the case of real molecules a change from the saturation (1a) to the thermalization (1b) regime is not abrupt but occurs in certain (sometimes quite wide) intervals which we shall call intermediate bands.

An accurate description of the dynamics of the excitation and relaxation of molecules requires the knowledge of the spectrum of vibrational-rotational transitions between excited vibrational states. However, since in the case of polyatomic molecules such a spectrum is frequently not known sufficiently accurately, it is usual to adopt a model approach. The whole process of multiphoton excitation is divided into two stages: resonant excitation of lower vibrational states (known as the region of the "discrete spectrum") and the subsequent excitation in the so-called "vibrational quasicontinuum" (see, for example, the review in Ref. 5). Usually the limit of the quasicontinuum corresponds to several CO_2 laser photons, but a situation is possible when a molecule reaches the quasicontinuum having absorbed just one or two photons[3,6] or, conversely, when an isolated mode is excited and after the absorption of up to ten photons the molecule is still in the region of the discrete spectrum.[7]

We shall make our treatment as general as possible by considering two limiting situations: the level-quasicontinuum model and the model of discrete levels (Fig. 2).

In the first model all the sufficiently strongly excited states form a quasicontinuum characterized by a continuous distribution of the energies E and by a total population P_{qc}. The lower limit of the quasicontinuum is separated, according to this model, by an energy E_S from the ground state and this energy is equal to the quantum energy of the "softest"

mode of the molecule ($E_S \ll \hbar\omega$) (see Ref. 5). The absorption of the incident radiation is described by the microscopic cross section $\sigma(E,\omega)$ and the absorption from the ground state as well as stimulated emission accompanied by transition to the ground state has the cross section $\sigma(E = 0,\omega) = \sigma_0(\omega)$. We shall ignore spontaneous emission. Relaxation to the ground state occurs from the lower limit of the quasicontinuum and is described by the parameter K_S. Inside the quasicontinuum the process of relaxation involves transitions between closely spaced levels, so that we can describe this process by the diffusion approximation (see, for example, Ref. 8), where the parameter $R(E)$ determines the diffusion coefficient in the vibrational energy space.

In the model of discrete levels the transitions occur only between the neighboring states of an excited mode (Fig. 2). The absorption cross section for the transition $n \to n + 1$ is denoted by $\sigma_n(\omega)$ and the relaxation parameter for the $n \to n - 1$ transition is represented by K_n. In both models the degree of excitation is such that there is no dissociation of molecules.

The level-quasicontinuum model seems to us sufficiently realistic and suitable for a quantitative description of polyatomic molecules under conditions when strong mixing of the vibrational modes takes place because of, for example, collisions with the buffer atoms. The model of discrete levels is of auxiliary nature.

3. KINETIC EQUATIONS AND THEIR SOLUTIONS

I. "Level-quasicontinuum" model

We shall describe a system of polyatomic molecules in a quasicontinuum by introducing a normalized population density function $N(E,t)$ $[\int_0^\infty N(E,t)dE = P_{qc}]$, so that $dN = N(E)dE$ is the fraction of the molecules that have an energy E in the interval dE. The ground-state population is $P_0 = 1 - P_{qc}$.

The balance equation relating the ground state to the quasicontinuum is

$$\frac{\partial P_0}{\partial t} = -W_0\left[P_0 - \frac{N(\hbar\omega)}{g(\hbar\omega)}\right]$$
$$+ R_s\left[\frac{N(E_s)}{g(E_s)} - P_0 \exp\left(-\frac{E_s}{T_0}\right)\right], \qquad (2)$$

where $g(E)$ is the density of vibrational states in the quasicontinuum.

The relaxation rate $R_S = pK_S$ is known to be considerably less than the rate of redistribution of energy in the quasicontinuum. Moreover, we shall assume that the absorption band is located completely in the quasicontinuum, i.e., that $W_0 = I\sigma_0$ is small, so that the following inequality is obeyed:

$$W_0 \ll R_s \ll R(E \approx \hbar\omega). \qquad (3)$$

In this case the pumping W_0 and the relaxation R_S do not distort the function $N(E,t)$ in the quasicontinuum, but simply alter the total population.

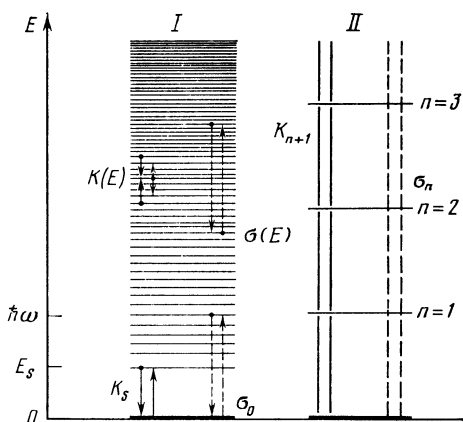The main kinetic equation for the quasicontinuum subject to Eq. (3) is

FIG. 2. Vibrational spectra and schematic representation of the excitation and relaxation processes in the level-quasicontinuum model (I) and in the model of discrete levels (II). The dashed arrows represent transitions accompanied by the absorption and stimulated emission of photons of energy $\hbar\omega$. The continuous arrows are the transitions which occur under the influence of collisions.

$$\frac{\partial N(E,t)}{\partial t} = -\frac{W(E,\omega)}{\hbar\omega}\left[N(E) - \frac{g(E)}{g(E+\hbar\omega)}N(E+\hbar\omega)\right]$$

$$+\frac{W(E-\hbar\omega,\omega)}{\hbar\omega}\left[N(E-\hbar\omega) - \frac{g(E-\hbar\omega)}{g(E)}N(E)\right]$$

$$+\frac{\partial}{\partial E}\left[R(E)\left(\left|\frac{\partial \ln N_g(E)}{\partial E}\right|^{-1}\frac{\partial N(E)}{\partial E} + N(E)\right)\right], \quad (4)$$

where $N_g(E) = \text{const } g(E)\exp(-E/T_0)$ is the equilibrium Gibbs distribution. The terms containing $W(E,\omega) = I\sigma(E,\omega)$ describe the absorption and stimulated emission processes. The last term corresponds to the relaxation processes.

The experimentally determined cross section $\sigma_t(\omega,p,I)$ is described in this model by

$$\sigma_t(\omega,p,I) = \sigma_0(\omega)\left[P_0 - \frac{N(\hbar\omega)}{g(\hbar\omega)}\right] + \int_0^\infty dE\, \sigma(E)\left[N(E)\right.$$

$$\left. - \frac{g(E)}{g(E+\hbar\omega)}N(E+\hbar\omega)\right],$$

i.e., we can calculate σ_t provided we know the steady-state population density function $N(E)$ and the quantity P_0, defined by Eqs. (2) and (4).

Equation (2) subject to Eq. (3) has the following steady-state solution

$$P_0 = (N(E_s)/g(E_s))\exp(E_s/T_0).$$

On the other hand, the solution of the differential-difference equation (4) is difficult to obtain even for the steady-state case. This equation is usually solved by going over to the diffusion approximation and expanding in $\hbar\omega$ the terms describing excitation, which—as pointed out by many authors[9-13]—is not quite correct. In our case we can use a different approach known as the method of arbitrary division described in detail in Ref. 14.

In this method the energy axis is divided into intervals of $\hbar\omega$ and the initial point of such a division is arbitrary; then, we formally integrate Eq. (4) in each interval and sum, which gives directly the cross section σ_t in terms of the relaxation contribution. [It is important to note the existence of an absorption band with an upper limit in which the condition $W(E) \gg R(E)$ is satisfied.] Using next the natural condition that the observed quantity σ_t be independent of the initial point of the division process and the smallness of the parameter $R(E)/W(E)$, we obtain a new equation for the function $N(E)$, which is much simpler than the initial equation and is easily integrated. Then, σ_t is obtained quite simply from the condition of normalization of the function $N(E)$.

The method of arbitrary division is particularly convenient in the case when the change between the regimes described by Eqs. (1a) and (1b) occurs abruptly and there is no absorption outside the absorption band. These simplifications are not of fundamental nature, but they make the solution clearer (a more general situation will be discussed in Sec. 4).

Approximating, for the sake of simplicity, the density-of-states function by an exponential expression

$$g(E) = g(E_s)\exp\left[(E-E_s)/D\right],$$

we obtain the general form of the dependence of the observed cross section on the parameters of the problem in the saturation regime:

$$\sigma_t(\omega,p,I) = \frac{p}{I}P_{qc}\hbar\omega\left\{\frac{1}{(1-\mu)}\int_0^{\hbar\omega}\frac{d\varepsilon}{S(\varepsilon)} - \mu^k\left[\frac{\mu}{(1-\mu)}\right.\right.$$

$$\times\int_0^{\hbar\omega}\frac{d\varepsilon}{S(\varepsilon)} + \int_0^\delta\frac{d\varepsilon}{S(\varepsilon)}\right] + \mu^k\exp\left(\frac{E_a-\delta}{T_e}\right)$$

$$\times\left[\frac{\mu\exp(-\hbar\omega/T_e)}{(1-\mu\exp(-\hbar\omega/T_e))}\int_0^{\hbar\omega}\frac{d\varepsilon\exp(\varepsilon/T_e)}{S(\varepsilon)}\right.$$

$$\left.\left. + \int_0^\delta\frac{d\varepsilon\exp(\varepsilon/T_e)}{S(\varepsilon)}\right]\right\}^{-1}, \quad (5)$$

where $\mu = \exp(-\hbar\omega D)$, $T_c = T_0 D/(D-T_0)$, the parameters k and δ are found from the relationship $E_b - E_a = k\hbar\omega - \delta$, and $S(\varepsilon)$ is a function determined entirely by the relaxation parameter $K(E)$:

$$S(\varepsilon) = \sum_{j=0}^k \mu^{k-j}K(E_b+(j-k)\hbar\omega+\varepsilon), \quad \delta\leqslant\varepsilon\leqslant\hbar\omega,$$

$$S(\varepsilon) = \sum_{j=1}^k \mu^{k-j}K(E_b+(j-k)\hbar\omega+\varepsilon), \quad 0\leqslant\varepsilon<\delta.$$

The population density function $N(E)$ can also be calculated and it is found that within the absorption band it has an unusual sawtooth shape, which corresponds to a periodic behavior of the distribution function per one state $f(E) = N(E)/g(E)$ in the absorption band (see Ref. 14). The sawtooth shape of $N(E)$ cannot be obtained within the framework of the frequently employed diffusion approximation with an expansion up to terms of the order of $(\hbar\omega)^2$ in Eq. (4).

II. Model of discrete levels

The main kinetic equation describing the dynamics of noncoherent excitation and relaxation in a system of discrete levels is

$$\hbar\omega\dot{x}_n = -W_n\left(x_n - \frac{g_n}{g_{n+1}}x_{n+1}\right) + R_{n+1}\left(x_{n+1} - \beta_n\frac{g_{n+1}}{g_n}x_n\right)$$

$$+W_{n-1}\left(x_{n-1} - \frac{g_{n-1}}{g_n}x_n\right) - R_n\left(x_n - \beta_{n-1}\frac{g_n}{g_{n-1}}x_{n-1}\right), \quad (6)$$

where x_0 is the population of the nth level; g_n is the statistical weight of the nth level; W_n is the rate of excitation from the level n to the level $n+1$; R_{n+1} is the rate of relaxation of the level $n+1$ to n (see Fig. 2); $\beta_n = \exp[-(E_{n+1}-E_n)/T_0]$; T_0 is the temperature of the buffer gas which acts as a thermostat.

The experimentally determined cross section $\sigma_t(\omega,p,I)$ is described by the following expression in the model of discrete levels:

$$\sigma_t = \sum_{n=0}^\infty \sigma_n[x_n - (g_n/g_{n+1})x_{n+1}].$$

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Under steady-state conditions, Eq. (6) yields the following recurrence relationship:

$$x_{n+1} = [W_n + R_{n+1}\beta_n g_{n+1}/g_n][W_n g_n/g_{n+1} + R_{n+1}]^{-1} x_n. \quad (7)$$

As in the preceding model, we shall assume that the change from the regime described by Eq. (1a) to that described by Eq. (1b) occurs abruptly, and then calculating x_n from Eq. (7) and the normalization condition $\Sigma_{n=0}^{\infty} x_n = 1$, we find that in the saturation regime the required cross section is given by

$$\sigma_l = \frac{p}{I}\left[\sum_{n=n_a}^{n_b} g_{n+1}K_{n+1}(1-\beta_n)\right]\left[\sum_{n=0}^{n_a-1} g_n \exp\left(\frac{E_{n_a}-E_n}{T_0}\right)\right.$$

$$\left. + \sum_{n=n_a}^{n_b} g_n + \sum_{n=n_b+1}^{\infty} g_n \exp\left(\frac{E_{n_b+1}-E_n}{T_0}\right)\right]^{-1}. \quad (8)$$

4. DISCUSSION OF THE SOLUTIONS

We shall now compare the solutions (5) and (8) obtained for fundamentally different representations of the vibrational transition spectrum. With this in mind we shall simplify as much as possible the solutions on the assumption that the density of states rises quite rapidly: $\mu(E) = g(E)/g(E+\hbar\omega) \ll 1$, but $\beta = \exp(-\hbar\omega/T_0) \ll \mu(E)$. [For example, for the SF_6 molecule with $E \approx (3-5) \times 10^3$ cm^{-1} at $T_0 = 300$ K we have $D \approx 400-600$ cm^{-1}, $\mu \approx 0.1$, and $\beta \approx 0.01$.] In this case Eq. (8) simplifies greatly and becomes

$$\sigma_l^{(11)} = \frac{p}{I}K_{n_b+1}\left\{1+\exp\left[\frac{E_{n_a}}{T_e}-\frac{E_{n_b}-E_{n_a}+\hbar\omega}{D}\right]\right\}^{-1}. \quad (9)$$

Moreover, assuming in Eq. (5) that the function $K(E)$ changes little in an interval representing a quantum in the region of E_b, and bearing in mind the link to the ground state, we obtain the expression

$$\sigma_l^{(1)} = \frac{p}{I}K(E_b+\hbar\omega)\left\{1+\alpha\exp\left[\frac{E_a}{T_e}-\frac{E_b-E_a+\hbar\omega}{D}\right]\right\}^{-1}, \quad (10)$$

where the parameter

$$\alpha = \left[\frac{T_e}{\hbar\omega}+\frac{1}{\hbar\omega g(E_s)}\exp\left(\frac{E_s}{T_0}\right)\right]\exp\left(-\frac{E_s}{T_e}\right)$$

is related to the specific model of the vibrational spectrum of a molecule. We can see that Eqs. (9) and (10) differ only by the parameter α of the order of unity [in the case of SF_6 we shall assume that $E_s \approx 350$ cm^{-1} and $g(E_s) \approx 0.01$ cm (Ref. 15), so that $\alpha \approx 0.3$]. In the most likely situation of a wide absorption band which is not too high on the energy scale (see below), such that

$$q = \exp[E_a/T_e - (E_b - E_a + \hbar\omega)/D] \ll 1,$$

the influence of the parameter α in the denominator is unimportant. Hence, we can conclude that the value of σ_l is affected very little by the selected model of the vibrational spectrum or by the method of describing a system of polyato-

mic molecules. Consequently, the model assumptions used above cannot affect the results significantly.

Since σ_l is governed entirely by the parameters E_a, E_b, and $K(E^*)$, where $E^* = E_b + \hbar\omega$, the nature of the solution obtained is related mainly to the model of a bounded absorption band. We shall ask the following question: what are the conditions which the width of the intermediate bands ΔE_a and ΔE_b must satisfy in the vicinity of E_a and E_b, respectively, to ensure that Eq. (10) for σ_l obtained formally for an absorption band with sharp limits can be extended to the more general case?

A rigorous analysis[14] shows that in the case of a wide absorption band characterized by $q \ll 1$ it is sufficient to satisfy two conditions. The first condition is $\Delta E_a \ll \hbar\omega/q$. If $q \ll 1$, the width ΔE_a can be of the order of several quanta $\hbar\omega$, i.e., σ_l is very little affected by the behavior of the parameters $\sigma(E,\omega)$ and $R(E)$ at the lower limit of the absorption band. Secondly, we have

$$\Delta E_b \ll \left[\frac{1}{K(E^*)}\left(\frac{\partial K(E)}{\partial E}\right)_{E=E_b}\right]^{-1}.$$

The quantity ΔE_b may also be fairly large if $K(E)$ is a slowly varying function in the vicinity of E^*.

The expressions (9) and (10) are obtained on the assumption that there is no excitation outside the absorption band. In reality, the cross section outside the absorption band may be small, but it is finite and consequently we cannot regard the intensity I as too high (otherwise a strong excitation occurs outside the absorption band). The restrictions on p/I due to the need to satisfy simultaneously two opposite conditions of Eq. (1) are of the form

$$\frac{\sigma \text{ (inside the band)}}{K \text{ (inside the band)}} \gg \frac{p}{I} \gg \frac{\sigma \text{ (outside the band)}}{K \text{ (outside the band)}}.$$

A range of permissible values of p/I exists if in the intermediate band the ratio $\sigma(E)/K(E)$ changes by at least an order of magnitude, which is quite realistic.

We note that although under saturation conditions the parameter p/I is small, the buffer gas pressure p should be sufficiently high to ensure that the distribution function is established during a laser pulse $\tau_l : p \gg 1/\tau_l k_{gas}$, where $k_{gas} = 1/(p\tau)_{gas}$ is the gaskinetic collision constant. For example, in the case of SF_6 molecules in He, we have

$$(p\tau)_{gas} = (T_0 m_{He}/8\pi)^{1/2}(R_{He}+R_{SF_6})^{-2}$$

$$\approx 1.3 \cdot 10^{-10} \text{ bar} \cdot \text{sec} \approx 0.1 \ \mu\text{sec} \cdot \text{Torr}.$$

For a typical laser pulse duration $\tau_l \approx 100$ nsec, we find that $p \gtrsim 10$ Torr. Hence, it follows that we need to use high intensities $I \gtrsim 10^6-10^7$ W/cm^2.

We shall now consider Eq. (10) in the limiting case of a wide absorption band, when

$$q = \exp[(E_a/T_e) - (E_b - E_a + \hbar\omega)/D] \ll 1.$$

Then,

$$\sigma_l \approx (p/I)K(E^* = E_b + \hbar\omega). \quad (11)$$

The expression (11) represents a direct relationship between

the observed quantity σ_t and the microscopic parameter $K(E)$. We note that Eq. (11) simply describes an energy balance. Since under the conditions of validity of this equation practically the whole population $N(E)$ is concentrated in the vicinity of $E^* = E_b + \hbar\omega$ (see Ref. 16), it follows from Eq. (11) that the total power of the absorbed radiation $I\sigma_t$ is equal to the relaxation power $pK(E^*)$ of molecules of energy E^*.

In spite of the fact that Eq. (11) is in a sense trivial, the more general expression (10) [or Eq. (5)] obtained above is useful also because it allows us to determine the conditions of validity of various simplified expressions for σ_t. The general expression (10) will also be used in the analysis of the experimental results.

It is found that the observed cross section for the absorption of radiation by molecules in the saturation regime described by Eq. (10) increases linearly on increase in the parameter p/I, i.e., on increase in $\sigma_t = (p/I)\gamma(\omega)$ with the coefficient

$$\gamma(\omega) = K(E^\cdot)\left\{ 1 + \alpha \exp\left[\frac{E_a}{T_e} - \frac{(E_b - E_a + \hbar\omega)}{D} \right] \right\}^{-1},$$

where $E_a(\omega)$, $E_b(\omega)$, and $E^*(\omega) = E_b(\omega) + \hbar\omega$ are functions of the frequency ω. The coefficient $\gamma(\omega)$ is determined directly in the course of an experiment. Knowing the dependence $\gamma(\omega)$, we can estimate $K[E^*(\omega)]$ and draw some conclusions on the behavior of the absorption band when the frequency ω is varied.

As pointed out already, a shift of the frequency ω from the blue to the red wing of the absorption profile of a molecule shifts the absorption band toward higher energies, i.e., $E_a(\omega)$ and $E_b(\omega)$ increase on reduction in ω. However, we can have two situations.

1) The absorption band expands in the course of its shift toward higher energies, i.e., the difference $E_b - E_a$ increases on reduction in ω. Then, the exponential function in Eq. (10) is unimportant and it follows from Eq. (11) that

$$\gamma(\omega) = K[E^*(\omega)]. \tag{12}$$

Since $K(E)$ is a nonrising function of the argument E, it follows that $\gamma(\omega)$ increases monotonically on reduction in the frequency ω, because there is an increase in $E^*(\omega)$.

2) The absorption band either becomes narrower or it retains its width. Then, if $K(E)$ does not rise too rapidly, when the detuning in the red wing is sufficiently large, the sign of the derivative of the dependence $\gamma(\omega)$ may be reversed: $\gamma(\omega)$ begins to decrease on increase in ω [see Eq. (10)].

The relationship (12) gives a simple link between the microscopic parameter $K[E^*(\omega)]$ and the observed quantity $\gamma(\omega)$. However, we cannot say exactly what is the value of the energy E^* that corresponds to the parameter $K(E^*)$ found from Eq. (12), because the dependence $E^*(\omega)$ is not known exactly. Nevertheless, variation of ω undoubtedly shifts the absorption band to different depths along the vibrational energy scale, i.e., the vibrational spectrum molecule is "probed" in this way.
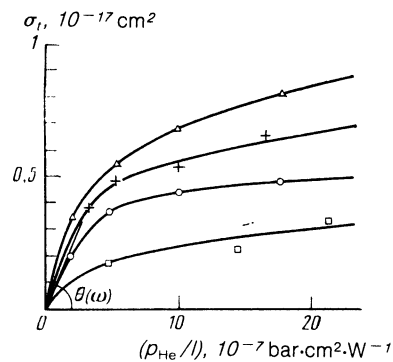

FIG. 3. Experimental curves showing the absorption cross section $\sigma_t(\omega, p/I)$ of radiation by SF_6 molecules in a buffer gas of He (Ref. 4); here, p is the buffer gas pressure, I is the intensity of the laser radiation, and ω is the frequency of this radiation. The curves are plotted for the following laser frequencies: $\square$) $\omega_1 = 951.1$ cm^{-1}; $\bigcirc$) $\omega_2 = 949.4$ cm^{-1}; $+$) $\omega_3 = 947.7$ cm^{-1}; $\triangle$) $\omega_4 = 945.9$ cm^{-1}. The angle between the experimental curves and the abscissa is $\theta(\omega) = \arctan[\gamma(\omega)]$.

5. ANALYSIS OF EXPERIMENTS. CONCLUSIONS

Although experimental determinations of the total absorption cross section $\sigma_t(\omega, p/I)$ of polyatomic molecules in buffer gases have been made on a number of occasions,[1–4] there is as yet no experimental data which would satisfy fully the requirements stated above. Nevertheless, the experimental conditions in the study reported in Ref. 4 best fit the situation considered by us and the relevant data can be used by way of illustration of our method. Molecules of SF_6 in a high-pressure He gas ($p_{He} \approx 1$–40 bar) absorb high-intensity (up to 10^7 W/cm^2) CO_2 laser radiation of different frequencies ($\omega = 936.8$–952.8 cm^{-1}). Some typical experimental curves are shown in Fig. 3. We shall be interested only in the region of the linear rise of $\sigma_t(\omega, p/I)$ in the saturation regime, i.e., the region where the parameter p/I is small. Here, the observed quantity is $\gamma(\omega)$ or, more accurately, the angle $\theta = \arctan[\gamma(\omega)]$ (see Fig. 3). The values of $\gamma(\omega)$ for the four best resolved (near zero) experimental curves are listed in Table I. These data alone are sufficient to draw some conclusions about the properties of the parameters $\sigma(E, \omega)$ and $K(E)$ of the SF_6 molecule.

1) The experiments described in Ref. 4 reveal a monotonic rise of $\gamma(\omega) = K(\omega)$ on reduction of the radiation frequency ω, which shows that under these experimental conditions the absorption band of the SF_6 molecule expands on reduction in ω.

2) The relaxation rate $R(E) = pK(E)$ represents the energy transferred by a molecule to buffer atoms per unit time. The constant $k_{VT}(E) = 1/(\rho\tau_{VT})$ (τ_{VT} is the characteristic time between energy-transferring collisions) and the energy $\langle \Delta E(E) \rangle$ transferred by a collision of this type are both functions of E. We cannot determine each of the quantities $\langle \Delta E(E) \rangle$ and $k_{VT}(E)$ separately, because they are obtained experimentally in the combination $K(E)$, which—according to Eq. (12)—is related directly to the observed quantity $\gamma(\omega)$. Therefore, further interpretation of the results depends on the model.

(I) In the level-quasicontinuum model the quantity

TABLE I. Results of analysis of experimental data reported in Ref. 4.

ω, cm^{-1}	$10^{-11}\ \frac{\gamma(\omega)}{\text{W/bar}}$	Model I		Model II	
		$\langle\Delta E\rangle(\omega)$, cm^{-1}	$E^*(\omega)$, cm^{-1}	$\frac{k_{VT}^{-1}(\omega)}{k_{gas}^{-1}}$ collis.	$n^*(\omega)$
951.1	0.45±0.12	30±10	1000–1500	32±12	1 or 2
949.4	1.2±0.4	80±35	1400–1900	12±5	2 or 1
947.7	1.3±0.3	85±30	1800–2400	11±4	2 or 3
945.9	1.9±0.4	125±40	2200–2800	7.5±2.5	3 or 2

Note. The slopes of the experimental curves in the range of low values of p/I were used to determine $\gamma(\omega)$ for different laser frequencies ω. Depending on the interpretation, the average energy per one collision (for $k_{VT}^{-1} = k_{gas}^{-1} = 0.1\ \mu\text{sec}\cdot\text{Torr}$) was determined in the model I; the average number of elastic collisions per one collision accompanied by energy transfer ($\langle\Delta E\rangle = \hbar\omega$ was assumed to be fixed) was found in the model II. The column headed $E^*(\omega)$ gives all possible values of the energy $E^*(\omega) = E_b(\omega) + \hbar\omega$ corresponding to the values of $\langle\Delta E\rangle(\omega)$ in the model I; the column $n^*(\omega)$ gives all possible values of the quantum number n in the model II.

$K(E)$ is described by[8]:

$$K(E) = (\langle\Delta E^2(E)\rangle/2T_e)k_{VT}(E) = \langle\Delta E(E)\rangle k_{VT}(E). \quad (13)$$

Since the vibrational spectrum in the quasicontinuum is quite dense, we can assume that each collision with a buffer gas atom transfers energy, i.e., that $k_{VT} = k_{gas}$, where the gaskinetic collision constant is $k_{gas}^{-1} \approx 0.1\ \mu\text{sec}\cdot\text{Torr}$. In our case we have $T_0 = 210\ \text{cm}^{-1}$ and the parameter representing the rise of the density of states in SF_6 at $E \approx 2 \times 10^3\ \text{cm}^{-1}$ is $D \approx 600 \pm 200\ \text{cm}^{-1}$ (Ref. 15), so that we find that $T_e \approx 330 \pm 60\ \text{cm}^{-1}$. We can now use Eq. (13) to find $\langle\Delta E^2(E)\rangle$, which is frequently discussed in the literature, as well as $\langle\Delta E(E)\rangle$, which represents the energy transferred by one collision to a buffer atom by a molecule with a vibrational energy E. In our case when the molecules are excited by radiation of frequency ω, each value of ω can be matched by a specific energy E in Eq. (13). Following Eqs. (11) and (12), we shall assume that the energy in Eq. (13) is given by $E = E^*(\omega) = E_b(\omega) + \hbar\omega$, because in our case practically the whole population is near the energy $E^*(\omega)$. The limit of the absorption band $E_b(\omega)$ can be determined bearing in mind that the anharmonicity constant of the mode ν_3 of SF_6 is $\sim 4\ \text{cm}^{-1}$. It follows that the conversion from ω to E^* results in the greatest error in our calculations. For example, according to Table I, if $E \approx (2-3)\hbar\omega$, we have $\langle\Delta E\rangle \approx 80 - 130\ \text{cm}^{-1}$, which is in order-of-magnitude agreement with similar data obtained by much more complicated methods (see, for example, the review in Ref. 17).

(II) In the model of discrete levels the quantity $\langle\Delta E\rangle = \hbar\omega$ is fixed, since energy cannot be transferred in smaller portions. We then have $K_n(\omega) = \hbar\omega k_{n,n-1}(\omega)$, where $k_{n,n-1}$ is the constant for the relaxation from the level n to the level $n-1$. It follows from Table I that $k_{1,0}^{-1} \approx 2.0\text{–}4.4\ \mu\text{sec}\cdot\text{Torr}$ and $k_{2,1}^{-1} \approx 0.7\text{–}1.2\ \mu\text{sec}\cdot\text{Torr}$, in full agreement with the results obtained by a more complicated method used in Ref. 18 ($k_{1,0}^{-1} \approx 4.5\ \mu\text{sec}\cdot\text{Torr}$, $k_{2,1}^{-1} \approx 0.85\ \mu\text{sec}\cdot\text{Torr}$).

The published experimental data are insufficient to apply the above method and calculate $K(E)$ at higher energies E. Although experimental curves with a sufficient detuning

in the red wing (ω up to 936.8 cm^{-1}) are given in Ref. 4, the poor resolution in the range of low values of the parameter p/I prevents accurate determination of $\gamma(\omega)$. Experiments of the type described in Ref. 4 can be analyzed by our method only if in measurements at frequencies $\omega < 945\ \text{cm}^{-1}$ the value of the parameter p/I is reduced to $10^{-8}\text{–}10^{-9}$ bar·cm^2·W^{-1}, which is attainable when the buffer gas pressure is $p \approx 100$ Torr and the laser radiation intensity is $I \approx 10^7\text{–}10^8\ \text{W/cm}^2$.

Measurements in the red wing under saturation conditions have not yet attracted the due attention of experimentalists. Our results show that measurements of this kind make it possible to determine quite simply the important data on some properties of polyatomic molecules.

Conclusions. 1) When the laser radiation frequency is shifted toward lower values, the absorption band not only shifts toward higher energies, but also expands.

2) The dependence of the observed absorption cross section σ_t on the buffer gas pressure p, and on the frequency ω and the intensity I of the laser radiation under saturation conditions is of the form $\sigma_t(\omega,p,I) = (p/I)\gamma(\omega)$, where the coefficient $\gamma(\omega)$ is governed simply by the relaxation properties of the molecule that absorbed radiation. Determination of $\gamma(\omega)$ at different frequencies provides a new and relatively simple method for the determination of the parameters describing relaxation. The results obtained by this method are in good agreement with those deduced earlier by more complex methods.

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