Dissociation and bleaching of a multilevel molecular gas by high-power CO_2 laser radiation

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A theoretical analysis is made of the interaction between high-power infrared radiation and resonantly absorbing gases. A multistage radiation-collisional mechanism of the vibrational excitation of a resonant molecular system, resulting in the dissociation and bleaching of a gas, is considered. The propagation of the incident radiation in a gaseous medium is accompanied by bleaching, dissociation, and recombination waves. Experiments carried out on the absorption of 10.6 μ radiation in BCl_3 and SF_6 gases made it possible to calculate the characteristic excitation transfer times for a multistage process and to estimate the distribution of the population of molecules over the vibrational levels and their degree of dissociation, which amounted to 97–99% at $\sim$ 10 kW/cm^2 radiation power densities. The dependences of the velocities of bleaching waves on the radiation power were determined and it was found that a steady-state bleaching occurred when practically all the molecules were dissociated.

1. INTRODUCTION

It is known that the energy of CO_2 laser photons is equal to the vibrational energies of many molecular gases. The interaction of high-power CO_2 laser radiation with such gases may give rise to interesting effects such as the selective excitation of certain types of molecular vibrations, laser photodissociation of the molecules, breaking of certain chemical bonds, and initiation of chemical reactions. The dissociation of ammonia molecules, evidently of thermal origin, under the action of the CO_2 laser radiation was observed back in 1966.[1] The dissociation of boron trichloride molecules was reported later[2] and attributed to the excitation of the vibrational spectrum by a radiation-collisional multistage process. Carbon dioxide laser radiation was found to initiate chemical reactions in mixtures of boron trichloride and hydrogen[3] and in several other gas mixtures.[4] Experiments of this type provided a stimulus for a study of the interaction of high-power CO_2 laser radiation with resonantly absorbing gases. The interest in these investigations is enhanced by the possibility of isotope separation with the aid of laser radiation of $\lambda = 2.7\ \mu$ which was achieved by illuminating a mixture of methanol and deuteromethanol with radiation generated in an HF chemical laser.[5]

The present paper reports a study of the interaction of high-power (up to 12 kW/cm^2) CO_2 laser radiation with the molecular gases BCl_3 and SF_6.

At high incident radiation power densities ($\sigma\tau J \approx 1$) the contribution of purely collisional processes to the transfer of the excitation to higher vibrational levels is slight. Monochromatic radiation excites a resonant rotational sublevel of the first vibrational level. The excitation spreads from the resonant sublevel throughout the vibrational level and to the sublevels of other vibrational modes of similar energies. This is due to the vibration-vibrational (V–V) exchange. This is followed by a radiative transition to a resonant rotational sublevel of a higher vibrational level, and so on. Since polyatomic gases are characterized by a weak anharmonicity of the vibrational spectrum, a large width of the vibrational levels, and many vibration modes, this process is efficient even in the case of high vibrational levels and in a wide range of pressures. If the frequency of the incident radiation does not resonate with the lowest-frequency vibration mode of a polyatomic molecule, the dissociation threshold lies below the threshold of the resonant vibration and a molecule splits under the action of infrared radiation because of predissociation as a result of vibration. In this case, the radiation-collisional multistage process predominates right up to the stage when dissociation takes place.

A molecule acquires the dissociation energy E_d in K interactions with the field of the incident radiation ($K \approx E_d/h\nu$). In other words, the process consists of K excitation stages. Under steady-state conditions in the presence of high-power radiation this multistage process reduces the number of absorbing centers with increasing radiation power. A large number of molecules is dissociated and the transmission of the system increases (the system is "bleached") not only because of the redistribution of the molecules over the vibrational spectrum but also because of their dissociation.

A high-power resonant radiation disturbs a gaseous medium. In our case, this disturbed state is transparent to the incident radiation. Therefore, if the incident radiation is applied continuously from some moment, the perturbed state travels in the medium. In this way, bleaching, photodissociation, and photochemical waves are produced.[6–8] In a complex multilevel molecular medium with a strong radiative and collisional coupling between the waves a steady-state bleaching wave corresponding to any given transition arises because of the formation of an equilibrium distribution wave throughout the vibrational molecular spectrum. In those cases when the incident radiation dissociates the molecules, a bleaching wave arises because of a wave-like establishment of equilibrium throughout the system comprising the molecules and their dissociation products; in the case of an irreversible dissociation reaction, such a bleaching wave is due to a chemical wave. The velocity of a bleaching wave is governed by the intensity of the transmitted radiation. In our case, we are dealing with a complex multilevel system in which multistage processes are important and the delay time of this wave is inversely proportional to the square of the radiation power.

2. DISTRIBUTION OF MOLECULES OVER VIBRATIONAL ENERGY LEVELS UNDER STEADY-STATE ILLUMINATION CONDITIONS

We shall now consider a steady-state excitation process. In collisional energy exchange we can identify two processes: 1) the exchange of energy between closely spaced vibrational levels, characterized by a time constant τ_3; 2) the exchange of energy between neighboring levels in one vibration, accompanied by the conversion of the excess energy into heat (characteristic time τ_1). It is assumed that τ_1 is the same for all the levels and that this is also true of τ_3. It is also assumed that the recombination occurs only because of collisions between the dissociation products (time constant τ_2) and after recombination a molecule is in the predissociation state, i.e., it is in the (K − 1)-th stage. In view of the strong V–V coupling ($\tau_3 \ll \tau_1$) between the levels of one stage, we shall consider only the relaxation from one level in a given state. We shall also postulate that the relaxation of the molecules from this level is solely due to the collisions with the molecules which are in the next stage below, because under strong illumination conditions all the vibrational levels are strongly populated and the probability of a collisional transition is highest if this transition corresponds to an allowed radiative transition.

Since the vibrational spectra of polyatomic molecules are complex and the levels have many vibrational sublevels, radiative transitions from one excitation stage to another occur along many parallel paths, so that the probabilities of induced transitions can be assumed to be the same for all the steps and for upward and downward directions.

If we now derive a system of rate equations for all the K excitation stages, we can find the dependence of the normalized density of molecules in each stage n_i as a function of the illumination power J and the density in the first step n_i : $n_i = n_i(n_1, J)$. Substituting these densities into the equation for J

$$\partial J / \partial x = -\sigma N n_1 J, \tag{1}$$

where σ is the radiative capture cross section, N is the molecular density, and the normalization condition is

$$\sum_{i=1}^{K} n_i = 1, \tag{2}$$

we can find the dependence J(x).

The equations for the densities in the various stages and their solutions are very cumbersome. Therefore, we shall consider only the case of high-power radiation $J \gg n_1 \tau_3 / \sigma\tau_1^2$. Bearing in mind also that $\tau_1 \gg \tau_3$, the system of equations can be written in the form

$$\begin{gathered}
0 = -\sigma n_1 J + \sigma n_2 J + \frac{n_1 n_2}{\tau_1}, \\
0 = -2\sigma n_2 J + \sigma n_1 J + \sigma n_3 J + \frac{n_2 n_3}{\tau_1} - \frac{n_1 n_2}{\tau_1}, \ldots, \\
0 = -2\sigma n_i J + \sigma n_{i-1} J + \sigma n_{i+1} J + \frac{n_i n_{i+1}}{\tau_1} - \frac{n_i n_{i-1}}{\tau_1}, \ldots, \\
0 = -2\sigma n_{K-1} J + \sigma n_{K-2} J - \frac{n_{K-2} n_{K-1}}{\tau_1} + \frac{n_K^2}{\tau_2}, \\
0 = \sigma n_{K-1} J - \frac{n_K^2}{\tau_2}.
\end{gathered} \tag{3}$$

Thus, at high radiation powers the problem reduces to the solution of the equations of a harmonic oscillator with a truncated spectrum (K − 1 levels) and with relaxation-type collisional terms.

In the case of K − 1 levels, we have

$$n_i = \frac{\sigma\tau_1 J n_1}{\sigma\tau_1 J + (i-1) n_1}. \tag{4}$$

For the K-th level, which corresponds to the density of dissociated molecules, we have

$$n_K = \sigma J \left[\frac{\tau_1 \tau_2 n_1}{\sigma\tau_1 J + (K-2) n_1} \right]^{1/2}. \tag{5}$$

The value of n_1 can be found from a transcendental equation obtained by substituting Eqs. (4) and (5) into Eq. (2):

$$1 = \sigma\tau_1 J \sum_{i=1}^{K-1} \frac{n_1}{\sigma\tau J + (i-1) n_1} + \sigma\tau_1 J \left[\frac{\tau_2 n_1}{\sigma\tau_1^2 J + (K-2)\tau_1 n_1} \right]^{1/2}. \tag{6}$$

The condition for the validity of the relationships obtained above is $n_1 \ll 1$.

In the special case when $J \gg K n_1 / \sigma\tau_1$, the expression for n_K simplifies to

$$n_K = (\sigma\tau_2 J n_1)^{1/2}. \tag{7}$$

Equation (6) now becomes

$$K n_1 + (\sigma\tau_2 J n_1)^{1/2} = 1, \tag{8}$$

which gives

$$n_1 = \frac{1}{2K^2}(2K + \sigma\tau_2 J - R), \tag{9}$$

$$R = [4K\sigma\tau_2 J + (\sigma\tau_2 J)^2]^{1/2}. \tag{10}$$

It follows that when $J \gg 4K/\sigma\tau_2$ the density n_1 is low and vanishes for $J \to \infty$.

Integration of Eq. (1) subject to the condition $J \gg K n_1 / \sigma\tau_1$ yields the absorption of the radiation in a layer of gas of thickness l:

$$\alpha l = {}^1/_2[\sigma\tau_2 J_0 + R_0 - \sigma\tau_2 J - R] + 2K \ln\left[\frac{\sigma J_0 \tau_2 + R_0}{\sigma\tau_2 J + R} \right] \tag{11}$$

where $R_0 \equiv R(J_0)$ and J_0 is the incident radiation power. As expected, whereas $n_1 \to 0$, the absorption also vanishes $\alpha l \to 0$.

Equation (11) differs from the well-known expression for the saturation of absorption in a two-level system with a homogeneous broadening because of the presence of the terms R and R_0 and of the coefficient 2K in front of the logarithmic term. We note that, in our case, the bleaching conditions $J \gg K n_1 / \sigma\tau_1$ and $J \gg 4K/\sigma\tau_2$ have the same structure as the condition for the saturation of two vibrational levels having a large number of rotational sublevels (see, for example, [9]).

We investigated experimentally the interaction between high-power 10.6 μ radiation and the resonantly absorbing gases BCl_3 and SF_6. In these experiments we used a CO_2 laser emitting powers up to 600 W and operating quasicontinuously. A radiation pulse was in the form of a single step. The duration of the leading edge was 100 μsec. The radiation was collimated into a narrow parallel beam of 2-mm diameter, which was practically homogeneous over its cross section. A calibrated pyroelectric barium titanate detector was placed directly in a cell containing the investigated gas. A special system enabled us to measure the intensity of the transmitted 10.6-μ radiation in the gas at distances of 0 to 6 cm. The absorption was investigated at gas pressures from 0.01 to 1 atm.

Figure 1 shows the experimental dependences of the intensity of the transmitted radiation on the thickness of the gas layer at various pressures. These curves have nearly flat regions corresponding to strong bleaching. A dissociation "jet" emitted strong luminescence

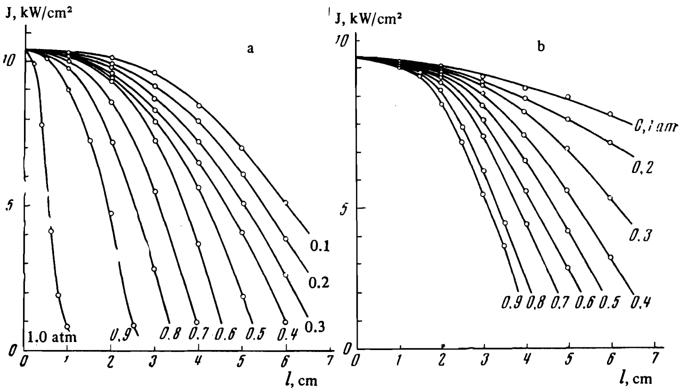

FIG. 1. Dependences of the intensity of the transmitted 10.6 μ radiation on the thickness of the gas layer: a—BCl_3; b—SF_6. $J_0 = 10.4$ kW/cm², S = 0.05 cm², pressures from 0.1 to 1.0 atm (given alongside the curves).

at the same pressures. The slope $\partial J/\partial l$ enabled us to find the values of n_1 in conjunction with Eq. (1). For radiation power density of about 10 kW/cm² we found that

$$n_1(BCl_3) \approx 10^{-2}, \quad n_1(SF_6) \approx 10^{-3}.$$

In these calculations we used the values $\sigma(BCl_3) = 6.5 \times 10^{-19}$ cm², $\sigma(SF_6) = 4.3 \times 10^{-18}$, K = 40. An increase in the number of stages to 100 altered the results of the calculations by less than one order of magnitude. The obtained values of n_1 indicated that under steady-state conditions at high radiation powers the low energy levels were emptied of the molecules and this reduced the absorption coefficient.

The experimental dependences $J(l)$ and $n_1(l)$ were used to calculate the relaxation times τ_1 and τ_2 with the aid of Eq. (6). The numerical calculations were performed on a Mir-2 computer. In the range of pressures from 0.01 to 1 atm the relaxation time τ_1 varied smoothly from 1.2×10^{-7} to 3.7×10^{-8} sec for BCl_3 and from 9.5×10^{-9} to 3.4×10^{-9} sec for SF_6. The constant τ_2 (representing the dissociation time of a molecule, the lifetime in the dissociated state, and the recombination time) varied—in the same range of pressures—from 2.6×10^{-3} to 5.7×10^{-3} sec for BCl_3 and from 5.8×10^{-4} to 1.9×10^{-3} sec for SF_6.

Knowing the values of τ_1, τ_2, and n_1, we could use Eqs. (4) and (5) to calculate the population densities of all the other levels. For example, for $J_0 \approx 10$ kW/cm², K = 40, we found for BCl_3 that $n_1 \approx 10^{-2}$, $n_{K-1} \approx 5 \times 10^{-4}$, $n_K \lesssim 1$, whereas for SF_6 we found that $n_1 \approx 10^{-3}$, $n_{K-1} \approx$ $\approx 3 \times 10^{-4}$, $n_K \approx 0.97$.

In these calculations we ignored changes in the gas density in the laser beam zone because the heating of the gas during the transmission measurements was slight.

Thus, in the dissociation (combustion) jet zone practically all the molecules were dissociated, which strongly reduced the absorption in this region. There was hardly any bleaching beyond this region.

3. BLEACHING WAVES

Bleaching and dissociation waves generated by 10.6μ radiation were observed in the BCl_3 and SF_6 gases at pressures from 0.01 to 1 atm. The experiments were carried out using the apparatus described in the preceding section. The time dependences of the 10.6μ transmission were recorded with a pyroelectric detector which was moved along the beam inside a gas-filled cell.

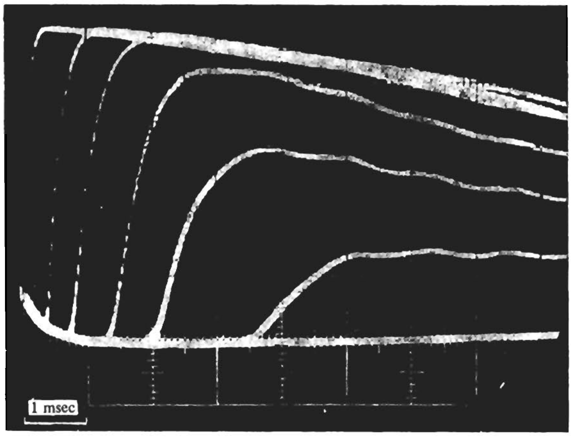

FIG. 2. Oscillograms of the intensity of the 10.6 μ radiation transmitted by BCl_3 ($J_0 \approx 12$ kW/cm², S = 0.05 cm², P = 0.4 atm), plotted for different thicknesses of the gas layer: from left to right l = 0, 1, 2, 3, 4, and 5 cm.

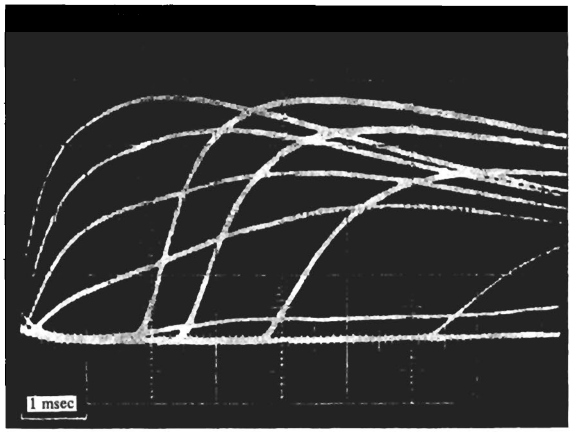

FIG. 3. Oscillograms of the intensity of the incident (J_0, the curves emerging from the origin of the coordinates) and the transmittted (J, the curves with a delay) 10.6 μ radiation obtained for SF_6: P = 0.5 atm, l = 2 cm, $J_0 \approx 5.0$, 4.5, 3.8, and 3.0 kW/cm² (from top to bottom of the figure).

Typical experimentally determined time dependences of the intensity of the transmitted radiation are shown in the form of oscillograms in Figs. 2 and 3. Figure 2 demonstrates the rise of the intensity of the 10.6μ radiation at various points along the beam for a given input radiation power density and pressure. Figure 3 gives examples of the dependence of the delay of a bleaching wave at a fixed point in a cell on the power density of the incident radiation.

The bleaching of a gas was a process with a definite threshold. The delay time of the appearance of bleaching, relative to the beginning of illumination, was defined as the time needed for the transmitted beam to reach a power of 2.5 W. We investigated the dependences of the bleaching delay time τ_b and the time taken by the system to reach steady-state conditions τ_s on the incident radiation power density J_0, the pressure of the gas P, and the thickness of the gas layer l in the dissociation-jet zone, i.e., in the strong-bleaching zone.

The expressions

$$\int_0^{\tau_b} SJ_0\, d\tau = E_b, \quad \int_0^{\tau_s} SJ_0\, d\tau - \int_0^{\tau_s} SJ\, d\tau = E_s$$

represent the energy absorbed in a gas before the onset of bleaching and before the establishment of steady-state conditions. Experimental determinations of the dependences of τ_b and τ_s on J_0 demonstrated that these time constants were inversely proportional to the square of the radiation power density. Consequently, for a fixed pressure and at a fixed point in the beam we found that, to within 5–10%,

$$E_bJ_0 / S = \text{const}, \quad E_sJ_0 / S = \text{const} \tag{12}$$

in the range $J_0 = 1 - 10$ kW/cm^2, P = 0.01 – 1 atm, and l lying in the dissociation-jet zone. A dependence of this type differed considerably from that discussed earlier for bleaching waves in a two-level system[6] and this was evidently due to the dissociation of molecules, which altered the number of the absorbing centers.

The ratio E_bJ_0/S or E_sJ_0/S depended on the gas pressure and on the path traveled by a bleaching wave or a wave representing the establishment of equilibrium in the system. An analysis of the experimental data yielded the following values of the ratios EJ/S for the investigated gases: for BCl_3

$$E_bJ_0 / S = (4.0 \pm 0.3) \cdot 10^{-13} M^{2.0}, \quad E_sJ_0 / S = (8.8 \pm 1.0) \cdot 10^{-4} M^{1.5} \tag{13a}$$

and for SF_6

$$E_bJ_0 / S = (4.6 \pm 0.5) \cdot 10^{-4} M^{1.5}, \quad E_sJ_0 / S = (1.9 \pm 0.1) \cdot 10^{-4} M^{1.1}. \tag{13b}$$

Here, J_0 is in W/cm^2; E_b and E_s are in eV; S is in cm^2; M is the total number of molecules in the path of the beam behind the front of a bleaching (equilibrium-establishment) wave.

Equations (13a) and (13b) can be used easily to calculate the average energy absorbed by a molecule in the path of a beam before the onset of bleaching or before the establishment of equilibrium in a given gas layer. Thus, for l = 1 cm, P = 1 atm, J_0 = 10 kW/cm^2, S = 0.05 cm^2, we found

$$E_b / M = 2.7\,\text{eV}, \quad E_s / M = 5.1\ \text{eV for } BCl_3,$$
$$E_b / M = 2.7\,\text{eV}, \quad E_s / M = 6.0\ \text{eV for } SF_6.$$

At the moment of establishment of an equilibrium in a given layer the value of E_s/M corresponds to the dissociation threshold, i.e., at this stage almost all the molecules are dissociated. The weak dependence of this ratio on l demonstrates that the processes of heat transfer and diffusion, and the escape of the excited molecules from the laser beam zone make only a small contribution. However, if such processes are ignored, the results obtained hold only for high radiation power densities (small values of τ_s).

Equations (13a) and (13b) can also be used to estimate the velocity of a bleaching wave ($v = \partial l/\partial t$) generated on illumination of a gas with a pulse characterized by a short leading edge. It is found that

$$v = \frac{1{,}1 \cdot 10^{-8} J_0^2}{(SP)^2 l}, \quad v = \frac{6{,}4 \cdot 10^{-8} J_0^2}{(SP)^{1{,}5} l^{0{,}5}} \tag{14}$$

for BCl_3 and SF_6, respectively; here, P is in atm and v is in cm/sec. For J_0 = 10 kW/cm^2, S = 0.05 cm^2, P = 1 atm, the velocity of a bleaching wave in BCl_3 is $v = 430/l$ cm/sec and the corresponding velocity in SF_6 is $v = 570/l^{0.5}$ cm/sec.

The more rapid attenuation of a bleaching wave in BCl_3 than in SF_6 was due to the more rapid escape of the excited molecules from the laser beam zone. The cross section of the dissociation jet in the 0.01 – 1 atm range of pressures in SF_6 exceeded only slightly the beam cross section, whereas in BCl_3 it exceeded this cross section by a factor of 4–2.

4. CONCLUSIONS

The results of the investigation reported above demonstrated that steady-state illumination of the BCl_3 and SF_6 gases with high-power 10.6μ radiation reduced the number of absorbing centers. A large proportion of the molecules became dissociated and this resulted in a very strong bleaching of the gases. Such steady-state bleaching was described quite accurately by the rate equations in which three relaxation times, identical for all the levels, were included: these were the relaxation times τ_1 and τ_3 and the recombination time τ_2. The experimental results justified the assumption that at high radiation power densities the radiation-induced filling of the higher vibrational levels of the gas molecules was more efficient than the collisional filling.

The delay time of a bleaching wave was inversely proportional to the square of the radiation power density. The energy absorbed in a molecular system before the establishment of steady-state bleaching represented the dissociation energy of the molecules. A steady-state bleaching was obtained when practically all the molecules were dissociated.

This investigation of the bleaching and dissociation of the molecular gases BCl_3 and SF_6 has a more general importance because of the considerable interest in the qualitative changes in the physical and chemical properties initiated by laser radiation.

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