

Investigation of the dissociation of BCl_3 molecules in the field of an intense CO_2 laser pulse

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Visible luminescence produced upon dissociation of BCl_3 molecules in the intense field (10^7 - 10^9 W/cm^2) of a pulse from a CO_2 laser of frequency close to that of one of the molecular vibrations is investigated. It is found that down to very low pressures (<0.1 Torr) and at in fields of 10^9 W/cm^2 the luminescence is excited without any delay relative to the laser pulse. There are two luminescence stages, "instantaneous" due to dissociation of single molecules in the intense laser field, and "delayed" due to collisions between highly excited molecules and observable also in weaker fields (10^7 - 10^8 W/cm^2). Dissociation of BCl_3 molecules in an intense field can be used to produce an isotopically-selective chemical reaction between the BCl_3 dissociation products and oxygen, resulting in an enrichment coefficient of the order of 10 for ^{10}B . Possible mechanisms of the phenomenon under investigation are discussed.

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1. INTRODUCTION

Dissociation of NH_3 and $\text{C}_2\text{F}_3\text{Cl}$ molecules by a high-power CO_2 -laser pulse was observed in ^[1-3] and the visible luminescence accompanying this dissociation was investigated. These phenomena were observed in fields $\sim 10^7$ - 10^9 W/cm^2 , in the pressure range 20-500 Torr, with the laser emission frequency close to the frequency of one of the vibration-rotational transitions of the molecule. A study of the luminescence has shown it to differ in principle from the visible glow of gas acted upon by continuous CO_2 radiation ^[4-6], and also from the glow produced in optical breakdown of a gas. ^[1] High-power continuous radiation causes thermal heating of the gas to high temperatures, accompanied by glow of the gas and by decomposition of the molecules ^[4,5]. In optical breakdown of a gas in fields 10^{10} - 10^{11} W/cm^2 , the glow intensity is by 10^3 - 10^5 times larger than the intensity of the luminescence that accompanies dissociation. In addition, in optical breakdown, a plasma is produced and spectral lines of the ions are observed, whereas the luminescence spectrum contains bands of radicals. ^[1,3]

The dissociation and luminescence of molecules in a strong pulsed infrared (IR) field is of physical interest, since the mechanism whereby it is produced is not trivial. One might assume that the strong field excites one or several lower vibrational levels of the molecule, and then exchange of vibrational excitation transfers the molecules to higher-lying vibrational levels, and ultimately, dissociation of the molecule takes place in collisions of the highly-excited molecules ^[7]. The visible luminescence, however, is produced without a delay (accurate to 3×10^{-8} sec ^[3]) relative to the CO_2 -laser pulse, and there is not enough time for realization of the V-V relaxation process. In addition, the vibrational energy acquisition by the molecule in a resonant field is even more delayed if account is taken of the "bottle-neck" effect when molecules that are excited via a small number of rotational sublevels interacting with the field. ^[8,9] It is therefore impossible to explain the instantaneous onset of luminescence observed in ^[3] within the framework of such a collision model.

Another possible explanation might lie in successive radiative excitation of vibrational levels as a result of cancellation of the anharmonicity of the oscillations in a

strong resonant field. ^[10] This, too, cannot explain why the pulse intensities are patently insufficient for so strong a broadening of the levels in NH_3 .

According to a hypothesis advanced in ^[3], the low-lying levels of the molecules are instantaneously excited by collision with the electrons that are heated by the strong IR field, i.e., the gas luminescence is excited below (but near) the optical-breakdown threshold. Certain experimental data favoring this hypothesis were advanced in ^[11] for NH_3 , so that the role of collisions with electrons could not be excluded. Within the framework of the "electron" mechanism, however, it is difficult to explain the resonant character of the luminescence excitation.

Taking all the foregoing into account, we undertook an investigation of the excitation of the visible luminescence of molecules in a strong pulsed IR field, using an object capable of answering two basic questions, namely, (1) whether collisions play an important role in the production of instantaneous luminescence, and (2) whether the dissociation of a molecule at resonance with the field in a mixture of molecules is a selective process.

We chose for the experiments the BCl_3 molecule, since its absorption bands coincide well with the CO_2 -laser emission lines even at gas pressures lower than 10^{-3} Torr. In addition, the natural mixture consists of two isotopes, $^{10}\text{BCl}_3$ and $^{11}\text{BCl}_3$, which have almost non-overlapping absorption bands. This makes it possible to act selectively on the chosen sort of molecule in the mixture.

The first investigations have shown that luminescence is present also at low pressures (to 0.03 Torr). The luminescence pulse at low pressures has a complicated time structure and consists of two stages - "instantaneous" occurring simultaneously with the laser pulse, and "delayed," whose lag after the pulse depends on the pressure and on the field intensity. ^[12]

Two phases of luminescence were observed ^[13] also in SiF_4 at pressures 5-20 Torr. However, the fast phase observed there differed greatly in its properties from the instantaneous luminescence in BCl_3 , namely a different dependence on the pressure of the investigated gas in the presence of a buffer gas, strong

broadening of the pulse in the region of the focus, etc. On the other hand, in the case of BCl_3 , as shown in ^[12], the instantaneous stage of the luminescence is a result of the interaction of the IR field with an isolated molecule, while the delayed luminescence is governed to a considerable degree by collisions of highly-excited molecules. One could therefore expect selective action of the radiation either on the $^{10}\text{BCl}_3$ molecules or on $^{11}\text{BCl}_3$, depending on the frequency of the CO_2 laser. Such a selectivity of the action was demonstrated experimentally in an observation of an isotope-selective chemical reaction of the BCl_3 dissociation products with oxygen. The preliminary results of these experiments were published in ^[14].

We present in this paper the entire aggregate of data on the action of a strong IR field on BCl_3 molecules, and describe the experiments on the selectivity of its decay. We discuss the possible mechanisms of the observed phenomena.

2. EXPERIMENTAL SETUP

A block diagram of the experimental setup is shown in Fig. 1. To excite the molecules we used an atmospheric-pressure CO_2 laser with transverse discharge. A homogeneous discharge was ensured by a system of preliminary photoionization of the gas between specially shaped electrodes. The electrode length was 40 cm, the width 2.5 cm, and the distance between them about 2 cm. The laser generated pulses with energy up to 1.5 J of 150 nsec duration at half-width and 400 nsec at the base. The rise time of the pulse did not exceed 25 nsec. This laser-pulse waveform was made possible by a special choice of the $\text{CO}_2:\text{N}_2:\text{He}$ mixture (4:1:10). With the aid of a diffraction grating used as the output mirror, the laser was tuned to any of the CO_2 -laser generation lines in the range 10.2–10.9 μ , where the absorption bands of the molecules $^{10}\text{BCl}_3$ and $^{11}\text{BCl}_3$ are located.

The CO_2 -laser radiation was focused into the cell with BCl_3 by an $f = 40$ mm NaCl lens. The beam diameter at the lens focus did not exceed 0.2 mm. At sufficiently high radiation power, yellow-green glow was produced in the cell. The dimensions of the glowing region depended on the gas pressure and the cell; in particular its length along the beam direction ranged from 5 to 20 mm under various conditions. The luminescence was observed through a quartz window in a direction perpendicular to the laser beam. A lens was used to project, with 5 \times magnification, the image of the glowing region on to the photocathode of a photomultiplier, in front of which a diaphragm of 5 mm diameter was placed. By moving the photomultiplier parallel to the

cell axis we could register the luminescence signals from various points of the glowing region.

The luminescence pulses and the CO_2 -laser generation pulses, registered with a photodetector, were displayed simultaneously on the screen of an S1-42 two-beam oscilloscope. The registration time constants were determined by the oscilloscope bandwidth and amounted to 30–40 nsec. The photomultiplier-pulse delay relative to the photodetector did not exceed 90 nsec. In the spectral investigations of the luminescence, the image of the glowing region, magnified 1.5 times, was projected on the entrance cell of an MDR-2 monochromator, the output radiation of which was registered with a photomultiplier (FÉU-39A or FÉU-79). The signal from the photomultiplier output was fed to the input of a stroboscopic amplifier and then to a pulse-accumulation system and from there to an automatic recorder. The use of a stroboscopic amplifier of adjustable width and of a strobe delay made it possible to investigate spectra of various time intervals of the luminescence pulse.

The luminescence in the pure BCl_3 was registered down to pressures 0.03 Torr, and the emission characteristics were investigated in the region 0.1–20 Torr. Two series of experiments were performed, with an ordinary laser pulse (150 nsec at half-height, 400 nsec at the base), and with a shortened laser pulse (50 nsec at the base). The laser pulse was shortened with a system of two confocal lenses. The focal distance was chosen such that optical breakdown occurred in the focal region at the instant when the pulse maximum was reached. The produced plasma absorbed the remaining part of the pulse completely. The power of the shortened pulse remained the same as that of the ordinary one. We shall consider separately the results obtained with each of the pulses.

3. KINETICS OF VISIBLE LUMINESCENCE

A. Ordinary pulse. At low pressures, up to 3–4 Torr, one can see clearly two stages of luminescence (Fig. 2a). An "instantaneous" luminescence peak appears simultaneously with the laser pulse (with allowance for the photomultiplier delay time), independently of the pressure. The second luminescence peak—"the delayed" stage—appears at pressures above 1 Torr (at lower pressures it is seen as the tail of the instantaneous glow and has no clearly pronounced maximum). The delay τ of the maximum of this peak relative to the laser pulse decreases with increasing pressure in accord with the relation $p\tau = 2.3 \mu\text{sec-Torr}$. The peaks cannot be resolved at pressures above 5 Torr.

Addition of a buffer gas (helium) affects the different stages of the luminescence differently. The instantaneous stage remains practically unchanged when the pressure of the helium is varied from 0 to 40 Torr; amplitude of the delayed stage decreases sharply with the buffer-gas pressure, and the maximum of the delayed luminescence disappears at pressures ≈ 20 Torr (Fig. 3).

The character of the luminescence pulse depends significantly on the region from which the luminescence is observed. The results shown in Fig. 2 were observed both in a strong field in the focal region (a) and in a weaker off-focus field (b). In case b there is no instantaneous luminescence, and the maximum of the delayed

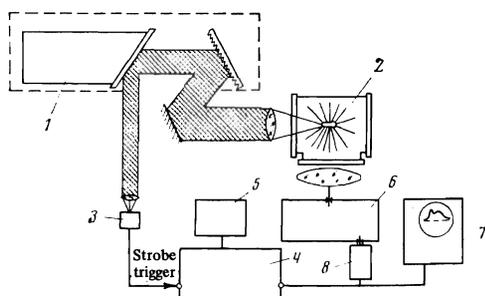


FIG. 1. Block diagram of experimental setup: 1— CO_2 laser, 2—cell, 3—photoreceiver, 4—recording system, 5—ÉPP-09 automatic recorder, 6—MDR-2 monochromator, 7—S-1-42 oscilloscope, 8—photomultiplier.

luminescence lags the laser pulse by 1–2 μsec , while the dependence of the delay on the pressure becomes very weak.

To confirm the connection between the instantaneous glow and the strong field, a special experiment was performed in which the radiation was focused into the cell by a long-focus lens. Its focus was located behind the cell in a way that the diameter beam in the cell did not exceed 4 mm. Under these conditions, the field intensity was $\sim 10^7 \text{ W/cm}^2$, i.e., smaller by a factor of 100 than at the focus (case a), and by a factor 7–8 than near the focus (case b). As seen from Fig. 4, no instantaneous luminescence is observed in this case. The delayed luminescence begins 0.7–0.8 μsec after the exciting pulse. Its maximum is delayed relative to the start of the excitation by 3–4 μsec and is independent in the investigated pressure range (4–40 Torr) of both the gas pressure and of the displacement of the photomultiplier along the luminescence region. Thus, in spite of the fact that the delayed luminescence phase appears after the termination of the excitation pulse and is patently due to molecule collisions, the kinetics of its development is governed in many respects by the field in which the molecular system was situated in the preceding instants of time.

B. Shortened pulse. Work with such a pulse has made it possible to observe luminescence under conditions when the time between collision (40 nsec-Torr) can be much longer than the duration of the laser pulse (50 nsec), since the measurements were performed at BCl_3 pressures starting with 0.1 Torr. In addition, this has made it possible, working at large gas pressures, to measure the characteristics of the instantaneous luminescence.

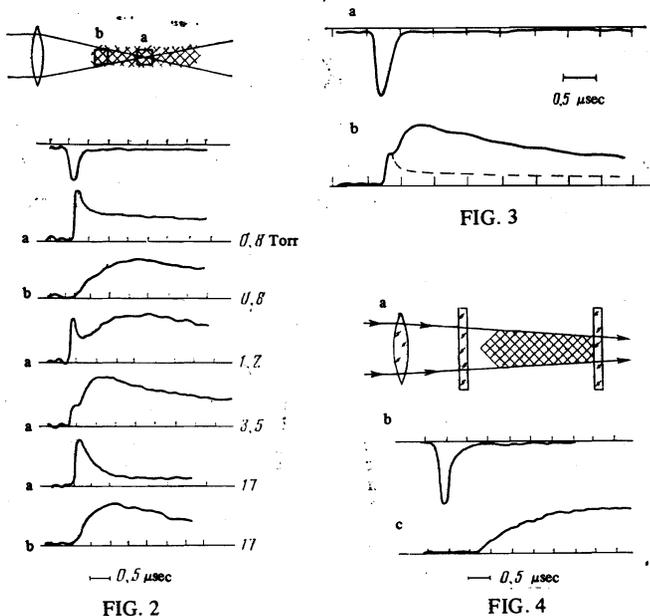


FIG. 2. Luminescence pulses produced at various BCl_3 pressures in the cell. 150-nsec excitation pulse. The observations were performed: a) from the region of the focus (IR field intensity 10^9 W/cm^2), b) from a region away from the focus (IR field intensity $1.5 \times 10^8 \text{ W/cm}^2$).

FIG. 3. Influence of buffer gas (He) on the luminescence signal: a) CO_2 laser pulse, b) luminescence signal at BCl_3 pressure 5.5 Torr (solid line) and following addition of 40 Torr of He (dashed).

FIG. 4. Observation of luminescence in weakly-focused beam (IR field intensity 10^7 W/cm^2): a) irradiation geometry, b) CO_2 laser pulse, c) luminescence pulse at BCl_3 pressure 13 Torr.

The waveform of the luminescence pulse from the focal region at 1.5 Torr is shown in Fig. 5 by the solid line, and the dashed line shows the luminescence pulse in the case when the laser pulse is not shortened. It turned out that the time behavior of the pulse is described by two different characteristic times, τ_1 and τ_2 . The pressure dependences of τ_1 and τ_2 were measured at fixed laser power. The following relations hold true with good accuracy: $p\tau_1 = 400 \text{ nsec-Torr}$ and $p\tau_2 = 73 \mu\text{sec-Torr}$.

In addition, we investigated the dependence of the intensity I_f of the instantaneous luminescence peak on the BCl_3 pressure. As seen from Fig. 6, I_f varies linearly with pressure in the range 0.3–3 Torr, and $I_f \propto p^2$ at higher pressures. It must be noted, however, that at a BCl_3 pressure of approximately 3 Torr the lag of the delayed luminescence is small, its intensity is comparable with that of the instantaneous luminescence, and the subsequent stronger dependences I_f on p at $p > 3$ Torr is due to the contribution made to I_f by the delayed luminescence.

Finally, we measured the dependence of the intensity I_f of the luminescence of the instantaneous phase on the intensity I_L of the laser pulse. This dependence is shown in Fig. 7 for a BCl_3 pressure 1.6 Torr in that range of I_L in which the luminescence intensity could be reliably measured. We see that as I_L changes by a

FIG. 5. Comparison of the luminescence pulses in BCl_3 (1.5 Torr) for the ordinary excitation pulse (150 nsec at half-height—dashed curve) and shortened excitation pulse (50 nsec at the base—solid line); $p\tau_1 = 400 \text{ nsec-Torr}$, $p\tau_2 = 73 \mu\text{sec-Torr}$.

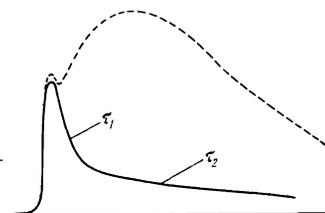


FIG. 6. Dependence of the intensity of the instantaneous stage of luminescence on the BCl_3 pressure: line a— $\tan \alpha_1 = 0.94 \pm 0.1$, line b— $\tan \alpha_2 = 1.8 \pm 0.1$.

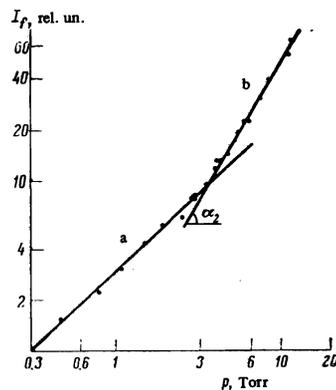
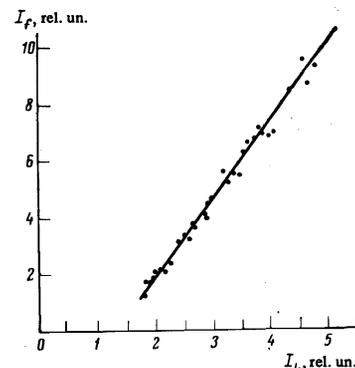


FIG. 7. Dependence of the intensity of the instantaneous stage of luminescence on the laser intensity; the BCl_3 pressure is 1.6 Torr.



factor 2.5, the luminescence intensity depends linearly on I_L and that the instantaneous luminescence seems to have a threshold.

An investigation of the spectral composition of the luminescence was carried out in the range 2000–6000 Å for both the instantaneous and delayed phases. In the region 4400–6000 Å, the spectra turned out to be identical with 15 Å, and continuous. It is clear that the source of luminescence in both cases is the same, although one cannot identify with assurance the molecule to which this spectrum belongs.

In the ultraviolet region of the spectrum (2700 Å), we observe bands belonging to the radical BCl. The maximum of this radiation, however, is delayed even in the region of the focus relative to a laser, and there is no instantaneous luminescence phase. It can therefore be assumed that the BCl radicals are the result of secondary processes, i.e., chemical reactions with participation of the BCl₃ dissociation products.

4. ISOTOPICALLY SELECTIVE REACTIONS IN A STRONG INFRARED-LASER FIELD

The observed effect of instantaneous collisionless dissociation of molecules in a strong IR field uncovers a possibility of laser stimulation of chemical reactions, which can be isotropically selective in the case of well-resolved isotopic shift in the IR spectrum.

It is natural first to raise the following question: is the dissociation process itself selective, i.e., is there any energy exchange between the molecules in the course of the "instantaneous" acquisition of energy by the molecule? This question can be answered in principle by investigating the isotopic effects in the emission spectrum of the dissociation products when the laser is tuned to the absorption line of one of the isotopes. Since the spectrum of the instantaneous phase of the luminescence in BCl₃ turned out to be continuous, and the apparatus could not resolve ¹⁰BCl and ¹¹BCl, we investigated the selectivity of the products using as an example other possible reactions with the radicals produced by dissociation. The most suitable for this purpose turned out to be the reaction with oxygen, the formation of BO in the excited state. When an O₂ + N₂ mixture is added to the cell with a BCl₃, a reaction takes place in the irradiated volume. This is clearly revealed by the appreciable increase of the luminescence intensity and by the change in its color. An intense system of lines appears in this spectrum and fully coincides with the α band of the BO radical.^[15,16] At the same time, an abrupt change takes place in the waveform of the luminescence pulse. The maximum of the luminescence is delayed relative to the laser pulse and its position is determined by the kinetics of the reaction.

The selectivity was verified in the following manner. The CO₂ laser was tuned to the absorption band of the ν₃ vibration of either the ¹⁰BCl₃ or the ¹¹BCl₃ molecule, and the intensities of the lines belonging to ¹⁰BO and ¹¹BO were investigated. The work was carried out with the natural isotope mixture (¹⁰B : ¹¹B = 1 : 4.32). It is known^[15,16] that the isotopic shift between the R branches of the transitions (0, 2) of the ²Π_{1/2} → Σ² band and (0, 2) ²Π_{3/2} → Σ² band equals ~30 Å (Fig. 8). This agrees with the splitting of the ²Π state by the spin-orbit interaction, so that the line resulting when both isotopes are excited is a triplet.

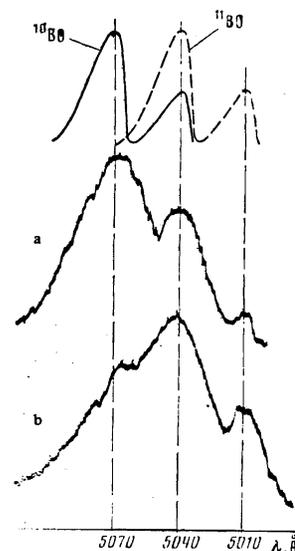


FIG. 8. Emission spectrum of BO on the (0, 2) transition of the ²π → Σ² band: a—excitation of ¹⁰BCl₃, b—¹¹BCl₃. The emission spectra of ¹⁰BO and ¹¹BO are shown schematically on the top.

In the experiments we investigated precisely this section of the spectrum in two cases: when tuned to the absorption band of ¹¹BC₃ (the P(26)–P(28) lines of the CO₂ laser) or of ¹⁰BCl₃ (R(24)–R(26) lines of the CO₂ laser). The registration system made it possible to isolate individual 150-nsec time intervals on different sections of BO-molecule luminescence pulse. It was therefore possible to investigate the selectivity of BO formation at instants of time corresponding to both the instantaneous and the delayed stages of the luminescence in the pure BCl₃. Figure 8 shows sections of the luminescence spectrum of boron oxide at the maximum of the pulse (it corresponds to the delayed stage in pure BCl₃) following excitation of ¹⁰BCl₃ and ¹¹BCl₃. The BCl₃ pressure was 4 Torr, and that of O₂ + N₂ was 20 Torr. The spectrum was recorded with a resolution not worse than 8 Å. We see that tuning to the absorption band of ¹⁰BCl₃ produces in the main the radical ¹⁰BO, while ¹¹BO is produced in the case of ¹¹BCl₃. With further increase of the strobe delay relative to the laser pulse, up to 1.2 μsec, i.e., up to the end of the BO luminescence pulse, the shape of the spectrum does not change noticeably. The process of BO formation during the instantaneous luminescence phase, as shown in ^[14], is likewise selective.

In addition, we investigated the spectrum of BO emission from regions outside the focus. To this end, the edges of the luminescence region (5 mm ahead of the focus and 5 mm past the focus) were projected on the entrance slit of the monochromator, where only the delayed luminescence stages exist in pure BCl₃. In this case, too, the process turned out to be selective. Thus, the dissociation of the BCl₃ molecules is selective also in the delayed phase.

From the obtained data we can estimate the enrichment coefficient:

$$K = \frac{[^{10}\text{BO}][^{11}\text{BCl}_3]}{[^{11}\text{BO}][^{10}\text{BCl}_3]}$$

For the excitation of ¹⁰BCl₃ (R(24) line of the CO₂ laser), it was found that K ≈ 10.

5. DISCUSSION

The most significant, in our opinion, is the onset of the instantaneous luminescence, which is observed at a resonant IR field intensity of about 10⁹ W/cm² and is produced simultaneously with the laser pulse, even if

the time τ_{coll} between the molecule collisions greatly exceeds the laser pulse duration τ_p . The time between collisions in BCl_3 is given by $\tau_p = 40 \text{ nsec-Torr}$, so that the probability of the molecule experiencing one collision during the time of the pulse ($\tau_p \approx 40 \text{ nsec}$) at a pressure 0.03 Torr is equal to 0.03, and the probability of the experiencing several (4–5) collisions is $10^{-6} - 10^{-7}$. Thus, sufficient excitation of the molecules by collision to cause their dissociation is impossible during the time of the laser pulse, and the appearance of the instantaneous stage of luminescence is due to dissociation of an isolated molecule under the direct influence of the light field.

On the basis of the results we can certainly reject the electronic molecule excitation and dissociation mechanism discussed in [3,11]. This mechanism is not selective and cannot explain the observed isotopic selectivity of excitation and dissociation of the BCl_3 molecules.

The mechanism of BCl_3 molecule association in a strong resonant IR field is undoubtedly radiative in character. Let us discuss the possibilities that exist here.

In principle, the BCl_3 can become dissociated by radiative excitation of the ν_3 vibration on account of vibrational predissociation via the ν_2 vibration.^[6] To this end the molecule should be excited to the 42nd level of the ν_3 vibration, since the dissociation limit with respect to the ν_2 vibration is $39,000 \text{ cm}^{-1}$. However, direct radiative excitation on all the investigated vibrational-rotational transitions, without any relaxation on these levels at all, is impossible because of the anharmonicity, which amounts to 1.65 cm^{-1} in BCl_3 .^[6] Indeed, if the field is at resonance with the transition $v = 0 \rightarrow v = 1$, then for transitions for levels with $v \approx 40$ the detuning amounts to $\Delta\nu_{\nu}c = 65 \text{ cm}^{-1}$. The level broadening by the fields can, in principle, be offset by the anharmonicity^[10], but this calls for a field of intensity

$$E \approx \Delta\nu_{\nu}ch/\bar{\mu} = \Delta\omega_{\nu}ch/\bar{\mu}, \quad (1)$$

where $\bar{\mu}$ is the average value of the matrix element of the dipole moment for the succession of transitions $v = 0 \rightarrow \dots \rightarrow v = 40$. Assuming as an estimate $\bar{\mu} = \mu_{01}$ ($\mu_{01} = 0.2\text{D}$ for BCl_3 ^[17]), we obtain in our case $E = 1.8 \times 10^7 \text{ V/cm}$, or an intensity $4.5 \times 10^{11} \text{ W/cm}^2$ for the pulse whose action eliminates the detuning on account of the anharmonicity of the molecule. In the described experiments, the instantaneous luminescence phase was produced at an intensity 10^9 W/cm^2 . Even if we assume that the possible axial-mode locking of the laser (the width of the laser emission spectrum admits of generation of about 10 axial modes) increased the instantaneous value of the intensity by one order of magnitude (10^{10} W/cm^2), the model of direct radiative excitation of the molecule up to the dissociation limit cannot describe the phenomenon. A strong field on the order of 10^{10} W/cm^2 can excite within the framework of this model vibrational levels with $v_{\text{max}} \approx 7 - 10$.

It must be noted, however, that at such field intensities the probability of induced transitions is $W_{\text{ind}} \gg 1/T_2$, where T_2 is the time required to randomize the phases of the wave functions; in BCl_3 we have $T_2 = 27 \text{ nsec-Torr}$.^[17] Therefore, in principle, the process of molecule excitation cannot be regarded as a succession of single-quantum transitions of the molecule in the field, and it is necessary to consider at least multi-

quantum quasis resonant transitions.

An attempt was made in [18] to treat the "instantaneous" dissociation of the molecule in a strong field as a result of multiphoton absorption. The calculation was carried out by perturbation theory, using as an example a diatomic molecule with equidistant levels. However, such a model is far from realistic, and applicability of perturbation theory, at least for the description of our results, is moot. Strictly speaking, it is necessary to solve the Schrödinger equation for a real anharmonic oscillator in a strong quasis resonant field. Since this problem has not yet been solved, but an exact solution is known for a harmonic oscillator in a strong field,^[19] we can proceed for a rough estimate in the following manner.

Consider a harmonic oscillator in a field whose frequency $\Delta\omega$ is detuned from exact resonance ω_0 by an amount $\Delta\omega$ approximately equal to the average detuning of the field relative to the sequence of transitions in the anharmonic oscillator. Thus, we are dealing with simulation of the excitations of the levels of an anharmonic oscillator in a strong field that is detuned relative to the field by the harmonic oscillator.

For a harmonic oscillator with frequency ω_0 , the probability W_v of excitation of the v -th vibrational level is

$$W_v = \frac{[P(t)]^v}{v!} \exp[-P(t)], \quad (2)$$

where in the case of a field in the form $E_0 \sin \omega t$ we have

$$P(t) = \frac{\mu^2 E_0^2}{\hbar^2} \frac{1 - \cos(\omega - \omega_0)t}{(\omega - \omega_0)^2} \quad (3)$$

which has the meaning of the average oscillator energy divided by the quantum energy $\hbar\omega$. Thus, at any instant of time, during the action of the field there exists a Poisson distribution of the probability of excitation of the levels of the harmonic oscillator, which itself oscillates in time at the detuning frequency $\Delta\omega$ between the levels $v = 0$ and $v_{\text{max}} = P_{\text{max}} = (\mu E_0 / \hbar \Delta\omega)^2$.

It should be noted that actually the energy is not absorbed by the oscillator under such excitations; if the field is turned off slowly in comparison with $1/\Delta\omega$, then the oscillator will return to the initial position. If we take a detuning $\omega - \omega_0$ equal to the average value of the anharmonicity for the sequence of transitions from $v = 0$ to $v = v_{\text{max}}$, i.e., $|\omega - \omega_0| = 1/2 \Delta\omega_{\nu}c$, then to excite the v_{max} level, according to [3], we need a field of intensity

$$E \approx \frac{\hbar \Delta\omega_{\nu}c}{2\mu} v_{\text{max}}^{1/2}. \quad (4)$$

This estimate agrees with (1) in order of magnitude.

Thus, all the considered schemes of molecule dissociation in a strong resonant field IR field cannot explain the observed instantaneous isotopically-selective dissociation of the BCl_3 molecules. Therefore, further theoretical and experimental investigations are needed to explain the mechanism of collisionless dissociation, all the more since this phenomenon is not restricted to the BCl_3 molecule, but is typical of many polyatomic molecules in strong fields. In particular, we have observed an instantaneous luminescence stage in the molecules C_2H_4 , CH_3OH , $\text{C}_2\text{F}_3\text{Cl}$, and others under the influence of a CO_2 -laser pulse.

As to the delayed luminescence stage, we can apparently state that it is connected with the collision

mechanism by which the molecules acquire energy. Favoring this assumption is the fact that at delay times $p\tau = \text{const}$ the intensity of this stage is proportional to p^2 . Addition of a buffer gas leads to a suppression of the delayed stage. This behavior is always typical of phenomena in which an important role is played by collisions, so that in this case we are dealing with a collision mechanism of dissociation of the excited molecules.

The results allow us to suggest that the dissociation of the molecular gas in a strong field proceeds in the following manner: During the laser pulse, some of the molecules acquire in the field an energy sufficient for dissociation, and the radiation of the obtained radicals gives the instantaneous phase of the luminescence. That fraction of the molecules which did not have time to acquire in the field an energy sufficient for dissociation, remains, following the action of the laser pulse, at high-lying vibrational levels. The V-V exchange processes between such strongly excited molecules cause some of them to become dissociated, and the luminescence of the resultant radicals constitutes the delayed phase of the luminescence. The character of the distributions of the molecules over the levels after the end of the laser pulse is determined by its intensity. This is apparently the reason why the maximum of the delayed stage lags the field intensity. Such a mechanism of the delayed stage is confirmed by the selectivity of the reaction of the radicals obtained not only during the instantaneous stage of the luminescence but also during the delayed one.

CONCLUSION

The described experiments show that the rapid dissociation of molecules in a strong infrared laser field is due only to the interaction of the radiation with the vibrational levels of the molecules and is purely radiative in character. The results uncover new possibilities of photochemistry research in strong IR laser fields, and also of isotope separation with lasers.

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- ¹N. R. Isenor and M. C. Richardson, *Appl. Phys. Lett.* **18**, 224 (1971).
- ²V. S. Letokhov, E. A. Ryabov, and O. A. Tumanov, *Optics. Comm.* **5**, 168 (1972).
- ³V. S. Letokhov, E. A. Ryabov, and O. A. Tumanov, *Zh. Eksp. Teor. Fiz.* **63**, 2025 (1972) [*Sov. Phys.-JETP* **36**, 1069 (1973)].
- ⁴C. Borde, A. Henry, and L. Henry, *C. R., Paris* **B262**, 1389 (1966).
- ⁵V. V. Losev, V. F. Papulovskii, V. P. Tychinskiĭ, and B. A. Fedina, *Khimiya vysokikh energii* **8**, 331 (1969).
- ⁶N. V. Karlov, Yu. N. Petrov, A. M. Prokhorov, and O. M. Stel'makh, *ZhETF Pis. Red.* **11**, 220 (1970) [*JETP Lett.* **11**, 135 (1970)].
- ⁷I. D. Artamonova, V. G. Platonenko, and R. V. Khokhlov, *Zh. Eksp. Teor. Fiz.* **58**, 2195 (1970) [*Sov. Phys.-JETP* **31**, 1185 (1970)].
- ⁸V. S. Letokhov and A. A. Makarov, *Zh. Eksp. Teor. Fiz.* **63**, 2064 (1972) [*Sov. Phys.-JETP* **36**, 1091 (1972)].
- ⁹V. S. Letokhov, A. A. Makarov, and E. A. Ryabov, *Dokl. Akad. Nauk SSSR* **212**, 75 (1973) [*Sov. Phys.-Doklady* **18**, 603 (1974)].
- ¹⁰A. N. Oraevskii and V. A. Savva, *Kratkie soobshcheniya po fizike (FIAN)*, No. 7, 50 (1970).
- ¹¹C. Rhodes, (Paper at 6th All-Union Conf. on Nonlinear Optics), Tashkent, May 1974.
- ¹²R. V. Ambartzumian, N. V. Chekalin, V. S. Doljikov, V. S. Letokhov, and E. A. Ryabov, *Chem. Phys. Lett.* **25**, 515 (1974).
- ¹³N. R. Isenor, V. Merchant, and R. S. Hallsworth, *Canad. J. Phys.* **51**, 1281 (1973).
- ¹⁴R. V. Ambartsumyan, V. S. Letokhov, E. A. Ryabov, and N. V. Chekalin, *ZhETF Pis. Red.* **20**, 597 (1974) [*JETP Lett.* **20**, 273 (1974)].
- ¹⁵F. A. Jenkins and A. McKellar, *Phys. Rev.* **42**, 464 (1932).
- ¹⁶R. S. Mulliken, *Phys. Rev.* **25**, 119 (1925).
- ¹⁷S. S. Alimpiev and N. V. Karlov, *Zh. Eksp. Teor. Fiz.* **66**, 542 (1973) [*Sov. Phys.-JETP* **39**, 260 (1973)].
- ¹⁸G. J. Pert, *IEEE J. Quant. Electr.* **QE-9**, 435 (1973).
- ¹⁹R. P. Feynman, *Phys. Rev.* **84**, 108 (1951).

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