

Isotopic selective chemical reaction of BCl_3 molecules in a strong infrared laser field

R.V. Ambartsumyan, V.S. Letokhov, E.A. Ryabov, and N.V. Chekalin

Spectroscopy Institute, USSR Academy of Sciences

(Submitted October 1, 1974)

ZhETF Pis. Red. 20, No. 9, 597-600 (November 5, 1974)

We report the first observation of an isotopically selective chemical reaction induced in a mixture of gases by a strong pulse of infrared radiation.

1. As is well known, when a pulse of high-power resonant IR radiation is focused in an absorbing gas, at a power on the order of 10^9 W/cm^2 , molecule dissociation takes place and is accompanied by visible luminescence of the dissociation product.^{11,21} It was observed in¹² that luminescence sets in without a delay relative to the laser pulse. A more detailed investigation, carried out independently in¹³ (on the BCl_3 molecule) and in¹⁴ (on the SiF_4 molecule) has shown that there exist two distinct luminescence phases, a rapid phase connected with the collision dissociation of the isolated molecules in the high-power IR field, and a delayed phase that follows the termination of the laser pulse and seems to be of collision origin.

The observed effect of instantaneous collisionless dissociation of molecules in a strong infrared laser field¹²⁻⁴¹ has uncovered one more way of laser stimulation of chemical reactions that can, in principle, be isotopically selective in the case of a well-resolved isotopic shift in the IR spectrum. In this article we describe experiments that prove this assumption directly for the first time. At the same time, the described experiment is the first successful separation of isotopes in a natural mixture by using IR radiation.

2. We used in the experiment an atmospheric-pressure pulsed CO_2 laser with energy up to 0.5 J in the pulse, at a pulse duration 100 nsec. The laser radiation was focused into a cell with the gas by a short-focus lens ($f=5 \text{ cm}$). The luminescence radiation from the focal region was projected through a side window, with a magnification 1.5, onto the entrance slit of an MDR-2 monochromator, which was used to record the emission spectra of the radicals and molecules produced by dis-

sociation and by subsequent chemical reactions. The obtained spectra were used to identify the chemical reaction products.

The experiment was performed with a natural mixture of B^{10}Cl_3 and B^{11}Cl_3 molecules ($\text{B}^{10}:\text{B}^{11}=1:4.32$). The spectrum of the instantaneous phase of the luminescence in pure BCl_3 lies in the visible region up to 4400 Å and is continuously accurate to 15 Å. When an $\text{O}_2 + \text{N}_2$ mixture ($\text{O}_2:\text{N}_2=1:4$) was added to the BCl_3 , an intense system of bands was produced in the spectrum and was identified as the α -band of the BO radical.¹⁵ In addition, the waveform of the luminescence pulse was strongly altered. Figure 1 shows the luminescence pulses in pure BCl_3 and in a mixture of BCl_3 with $\text{O}_2 + \text{N}_2$. The leading front of the pulse in the latter case corresponds to the rate of the BO production reaction. The CO_2 laser employed in the experiment was tuned to the absorption band of the ν_3 oscillation of either the B^{11}Cl_3 molecule or B^{10}Cl_3 . To investigate the selectivity of the collisionless dissociation of BCl_3 and of the subsequent reaction of the dissociation products with the oxygen, we used the shift in the spectrum of B^{10}O and B^{11}O . It is known¹⁵

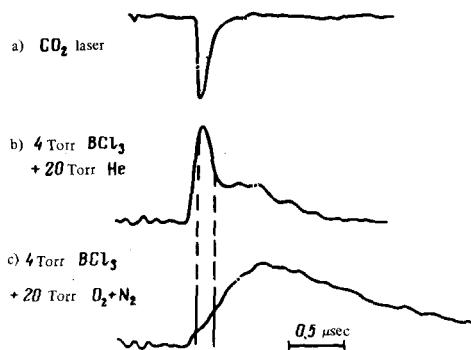


FIG. 1. Luminescence in pure BCl_3 and in BCl_3 mixed with $\text{O}_2 + \text{N}_2$: a— CO_2 -laser pulse, b—luminescence pulse in BCl_3 , c—luminescence pulse in BO.

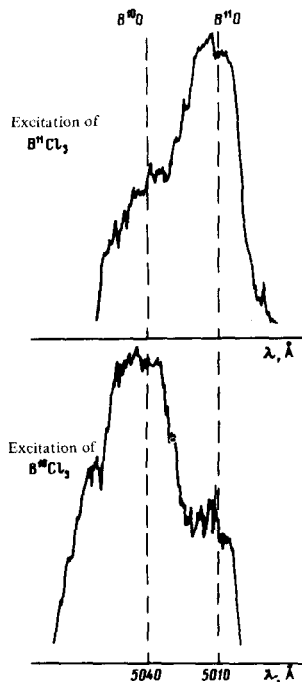


FIG. 2. Emission spectra of B^{10}O and B^{11}O on the transition $(0, 2) {}^2\pi_{1/2} \rightarrow {}^2\Sigma$ upon excitation of B^{11}Cl_3 (top) and B^{10}Cl_3 (bottom).

that the isotopic shift between the R branches of the transition $(0, 2) \ ^2\pi_{1/2} \rightarrow \ ^2\Sigma$ of the $B^{10}O$ and $B^{11}O$ radicals reaches 30 Å. We have therefore analyzed in the experiment precisely this section of the spectrum in two cases, when tuned either to the absorption band of the $B^{11}Cl_3$ (938.7 cm^{-1} $P(26)$ line of CO_2 laser) or to the $B^{10}Cl_3$ band ($R(24)$, 978.5 cm^{-1}). To measure the spectrum, the registration system separated in the BO emission pulse a time interval 150 nsec corresponding to the instantaneous phase of the luminescence in pure BCl_3 (Fig. 1). Figure 2 shows the obtained spectrum in these two cases. The BCl_3 pressure and the $O_2 + N_2$ pressure were 4 and 20 Torr respectively. The resolution was not worse than 8 Å. We see that $B^{11}O$ is obtained predominantly when $B^{11}Cl_3$ is excited, and $B^{10}O$ is obtained when $B^{10}Cl_3$ is excited.

Thus, collisionless dissociation of molecules in a high-power resonant IR field is a selective process (at least in the case of BCl_3 , when the isotopic shift in the absorption bands of the two different molecules exceeds 40 cm^{-1}).

The results reveal one more way of separating isotopes upon action of laser radiation of the molecules;

this method differs significantly from the two-step photodissociation¹⁶¹ and photopredissociation¹⁷¹ methods previously proposed and realized.

The authors thank E. L. Mikhailov and V. S. Dolzhikov for help with the preparation of the experiment.

¹N. R. Isenor and M. Richardson, Appl. Phys. Lett. 18, 225 (1971).

²V. S. Letokhov, E. A. Ryabov, and O. A. Tumanov, Zh. Eksp. Teor. Fiz. 63, 2025 (1972) [Sov. Phys. -JETP 36, 1069 (1973)].

³R. V. Ambartzumian, V. S. Dolijikov, V. S. Letokhov, E. A. Ryabov, and N. V. Chekalin, Chem. Phys. Lett. 25, 515 (1974).

⁴N. K. Isenor, V. Merchant, R. S. Hallsworth, and M. C. Richardson, Canad. J. Phys. 51, 1281 (1973).

⁵F. A. Jenkins and A. McKellar, Phys. Rev. 42, 464 (1932).

⁶R. V. Ambartzumian and V. S. Letokhov, IEEE Journ. Quant. Electr., QE-7, 305 (1971); Appl. Optics 11, 354 (1972); R. V. Ambartsumyan, V. S. Letokhov, G. N. Makarov, and A. A. Puretskiĭ, ZhETF Pis. Red. 17, 91 (1973) [JETP Lett. 17, 63 (1973)].

⁷V. S. Letokhov, Chem. Phys. Lett. 15, 221 (1972); E. S. Yeung and C. B. Moore, Appl. Phys. Lett. 21, 109 (1972).