On the beam axis  $(\tau = 0)$  at  $I_0 = const$  we have

$$r = r_o - \frac{I_o T_d}{W_c} \ln \left( 1 + \frac{I}{T_d} \right) . \tag{12}$$

Obviously, the duration of that part of the pulse which clears the channel effectively is equal to the diffusion time  $T_d$ . In the case of turbulent diffusion we have  $T_d \simeq 1$  sec for a beam with a = 1 m. With decreasing cross section of the high-power beam, the role of diffusion blurring of the channel increases  $(T_d/T_w \approx av/D)$ .

6. Using the foregoing formulas it is possible to trace also the passage of the laser beam itself (Fig. 2b). In this case there is an analogy with the passage of a laser beam through a self-bleaching medium with inertial absorption mechanism. We note also that after clearing the cloud can act on the beam like a thermal lens and make it nonlinearly divergent [7, 8].

F.A. Williams, Int. J. Heat and Mass Transfer 8, 575 (1965).

[2] V.E. Zuev, Rasprostranenie vidimykh i infrakrasnykh voln v atmosfere (Propagation of Visible and Infrared Waves in the Atmosphere), Sov. Radio, 1970. G.L. Lamb and R.B. Kinney, J. Appl. Phys. 40, 416 (1969). G.I. Mullaney, W.H. Christiansen, and D.A. Russel, Appl. Phys. Lett. 13,

[3] [4] 145 (1970).

S.L. Glickler, Appl. Optics <u>10</u>, 644 (1971).

L.T. Matveev, Osnovy obshchel meteorologii (Principles of General Meteorology), Gidromet. izd., 1965.

A.P. Sukhorukov, Usp. Fiz. Nauk <u>103</u>, 81 (1970).

[8] J. Wallace and M. Camac, J. Optical Soc. Am. 60, 1587 (1970).

## STIMULATION OF CHEMICAL PROCESSES BY INFRARED LASER RADIATION

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In [1] we have observed the photochemical action of infrared radiation, wherein the vibrationally-excited molecules take direct part in a chemical reaction. The conclusion that vibrationally-excited molecules take part in the reaction follows also from the results of [2].

We have investigated the behavior of several inorganic chemical nonreacting systems under the influence of IR radiation of a CO2 laser. The radiation intensity ranged from 20 to 50 W in a beam of approximate diameter 9 mm. The irradiation time was shorter than 0.5 sec. The reactions were produced in cells 20 mm in diameter and 100 mm long, with windows of AgCl. The substances absorbing the IR radiation of 10.6  $\mu$  wavelength were N<sub>2</sub>F<sub>4</sub> (valent vibrations of the N-F bond v<sub>2</sub> = 934 cm<sup>-1</sup> and v<sub>8</sub> = 958 cm<sup>-1</sup>), BCl<sub>3</sub> (valent vibrations v<sub>3</sub> = 958 cm<sup>-1</sup>), SF<sub>6</sub> (deformation vibration v<sub>3</sub> = 943 cm<sup>-1</sup>), SiH<sub>4</sub> (deformation vibration range 910 - 1000 cm<sup>-1</sup>, frequency 914 cm<sup>-1</sup>), and PF<sub>5</sub> (valent vibration 948 cm<sup>-1</sup>).

We investigated the following systems:  $N_2F_4$ ;  $N_2F_4 - NO$ ;  $N_2F_4 - NO - N_2$ ;  $N_2F_4 - NO - CF_4$ ,  $N_2F_4 - NO - NF_4$ ;  $N_2F_4 - NO - Xe$ ;  $N_2F_4 - N_2O$ ;  $N_2F_4 - H_2$ ;  $N_2F_4 - CH_4$ ;  $N_2F_4 - BCI_3$ ; BCl 3; SiH4; SiH4 - BCl 3; SF6 - NO; SiH4 - SF6.

The experimental conditions and the reactions are listed in the table. Laser-chemical reactions occur at explosive rates and are accompanied by the emission of light.

The emission spectrum of the products of the reaction of N<sub>2</sub>F<sub>4</sub> with NO revealed two regions - infrared and visible. The visible spectrum is interpreted as the emission of the molecule FNO, produced in the reaction F + NO = FNO\*.

Reagents, par- tial pressures, Torr	Irradiation cond., in- tensity (W), number of irradiations (n), fina pressure (P <sub>f</sub> ), Torr.	products,
N <sub>2</sub> F <sub>4</sub> 100 NO 100	40 W glow . P <sub>f</sub> = 262	FNO, N <sub>2</sub> , F <sub>2</sub>
N <sub>2</sub> F <sub>4</sub> 100 NO 200 N <sub>2</sub> 460	70 W glow	NO <sub>2</sub> , N <sub>2</sub> O, N <sub>2</sub>
N <sub>2</sub> F <sub>4</sub> 100 NO 100 CF <sub>4</sub> 200	30 W	NF <sub>3</sub> , NO, CO <sub>2</sub> (10%) CF <sub>4</sub> , N <sub>2</sub>
N <sub>2</sub> F <sub>4</sub> 300 N <sub>2</sub> O 150	40 W weak glow n = 3 Pf = 512	NO <sub>2</sub> (49%), NF <sub>3</sub> (38%) N <sub>2</sub> O(5%), FNO <sub>3</sub> , N <sub>2</sub>
N <sub>2</sub> F <sub>4</sub> 50 H <sub>2</sub> 100	50 W glow	$N_2$ , HF $N_2F_4 + 2H_2 = 4HF + N_2$
N <sub>2</sub> F <sub>4</sub> 228	50 W	CF <sub>4</sub> (22%), HF, N <sub>2</sub>
CH <sub>4</sub> 114∫	glow P <sub>f</sub> = 534	N <sub>2</sub> F <sub>4</sub> + CH <sub>4</sub> = CF <sub>4</sub> + 4HF + N <sub>2</sub> CF <sub>4</sub> and C produced in excess CH <sub>4</sub>
N <sub>2</sub> F <sub>4</sub> 114	50 W	BF, chlorine fluorides
BC1,114)	n = 3	N <sub>2</sub>
	glow at $n = 1 P_f = 289$	
SiH <sub>4</sub> 228	50 W	Si, H <sub>2</sub> (34%)
	n = 3	$SiH_4 = Si + 2H_2$ ,
	glow at	convers. 22%.
	$n = 1,2$ $P_{f} = 284$	
SiH 4 112	40 W	BCl, H, SiH,Cl
BCI ,112	n = 3	SiH <sub>4</sub> +BCl <sub>3</sub> =BCl <sub>2</sub> H+SiH <sub>3</sub> Cl
	glow at	B <sub>2</sub> H <sub>6</sub>
	$n = 1, 2, 3$ $P_{f} = 234$	
SiH <sub>4</sub> 300	40 W	SiF <sub>4</sub> , H <sub>2</sub> , S
SF <sub>6</sub> 100	glow $P_{f} = 698$	$SiH_4 + 2/3SF_6 = SiF_4 + 2H_2 + 2/3S$

The reaction between  $N_2F_4$  and NO is initiated by the interaction of the vibrationally-excited molecules of  $N_2F_4$  with NO:

$$N_2F_4^* + 4NO + 4FNO + N_2$$

 $(\Delta H_r = -149.2 \text{ kcal/mole for } N_2F_4 \text{ in the ground state})$ . The reaction takes place in the irradiated zone of the cell. The flash covers the entire volume of the reactor.

Excited products are produced during the course of the chemical reactions. The presence of intense luminescence gives ground for carrying out experiments aimed at detecting inverted populations of the products in laser-chemical reactions and at observing lasing effects.

Irradiation of  $N_2F_4$ , BCl<sub>3</sub>, SF<sub>6</sub>, PF<sub>5</sub>, and SiH<sub>4</sub> has shown that all substances with the exception of silane do not dissociate at intensities lower than  $\sim 40$  W and pressures lower than 200 Torr. This gives grounds for assuming that the investigated reactions (with the possible exception of reactions with silanes) begin not with a stage of dissociation of the vibrationally-excited molecules, but with an exothermal-reaction stage (for example, the reaction for the system  $N_2F_4$  - NO).

A comparison has revealed an appreciable difference between laser-chemical and thermal reactions. Thus, when mixtures of  $N_2F_4$  with NO and of  $N_2F_4$  with  $N_2O$  are heated, only decomposition of  $N_2F_4$  takes place, viz.,  $3N_2F_4=4NF_3+N_2$ , and there is no reaction with NO or  $N_2O$ . This can be attributed to the fact that the vibrationally-excited molecules produced upon absorption of the IR radiation have chemical properties different from those of the molecules in the ground state.

- [1] N.G. Basov, E.P. Markin, A.N. Oraevskii, and A.V. Pankratov, Dokl. Akad. Nauk SSSR 198, No. 5 (1971) [Sov. Phys.-Dokl. 16, No. 6 (1971)].
- [2] S.W. Mayer, M.A. Kwok, R.W.F. Cross, and D.J. Spenser, Appl. Phys. Lett. 17, 516 (1970).

## BIEXCITON IN Cu2O CRYSTAL

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An anomalous hydrogen-like series, converging not to the short-wave region of the spectrum, as usual, but to the long-wave region, was recently observed [1] in the luminescence spectrum of the crystal  $\text{Cu}_2\text{O}$ . The series was interpreted as the emission spectrum of a biexciton that becomes converted into an exciton of the green series (see the review [2]). The anomalous sequence of lines in the new series is due to the fact that the initial level in the emission of the quantum is the electronic excited state of the lattice (biexciton) with an excitation energy 33720 cm<sup>-1</sup>, which is approximately double the excitation energy of the main electrons of the yellow or green series.

A variant of the biexciton structure is also proposed in [1]. On the basis of the presented experimental information, the authors conclude that the biexciton in  $\text{Cu}_2\text{O}$  consists of two identical excitons of the green series with the frequency sum exceeding the level indicated above by 150 cm<sup>-1</sup>. The latter quantity is interpreted as the binding energy of the biexciton relative to its dissociation.