with the second 0.6 nsec after the first (Fig. 5b). With the one-component coumarin solution, that interval was only 150-200 psec. With $E_p = 1.4\ E_t$, there was a third pulse separated from the first by $\Delta t = 150$ psec (Fig. 5c), and with $E_p > 1.4\ E_t$, there was a fourth pulse at 150 psec from the second one. There is thus a tendency to generate two bursts of pulses as the pumping increases. The run-up time for the first burst shortens to 0.89 nsec. The interval between the first and second pulses, i.e., between bursts, remains 0.6 nsec.

These two bursts with interval independent of the pumping mean that there are two distinct mechanisms for the inversion. The first, which is fairly fast, is radiationless energy transfer, which provides the first burst, while the second, which is much slower, is radiative and produces the second one.

The basic characteristics for these DFB binary-dye picosecond pulses show spectral dependence, which needs to be considered.

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COLLISIONAL DISSOCIATION FOR DIFLUOROMETHYLENE BISHYPOFLUORITE ON EXCITATION BY A PULSED CO_2 LASER

E. B. Aslanidi, N. K. Kalandadze,
and Yu. S. Turishchev

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Most polyatomic molecules (over 5 atoms) that absorb in the 10 micron range dissociate in collision-free mode on excitation by a pulsed CO_2 laser. The excitation is described by cascade or multiphoton transitions via real or virtual states, as the quasicontinuum in the vibrational states begins at a certain point. Sometimes, however, unimolecular decomposition under collision-free conditions does not occur. This has been observed [1, 2] for SiH_4 and CH_3CN. It is assumed that SiH_4 enters the quasicontinuum by V—V collision with unexcited or less excited molecules.

These molecules dissociate by subsequent radiative excitation. The same model has been applied to collisional dissociation of CH_3CN. V—V and V—T, R relaxation may influence the multiquantum excitation in mixtures containing buffer gases. The absorbed energy and the dissociation yield are increased. This is known as the rotational bottleneck effect [3].

Here we examine the excitation and dissociation of difluoromethylene bishypofluorite used with a pulsed CO_2 laser. $CF_2(OF)_2$ is a gas with a characteristic odor of fluorine. The latent heat of evaporation is 18.62 kJ/mole, while the standard heat of formation is 546.79 kJ/mole [4]. The vapor pressure is

$$\lg P = 7{,}530 - 971{,}6/T. \quad (1)$$

The exact O—F bond energy has not been determined, but it is not more than 170 kJ/mole. There are 15 major bands in the IR spectrum, which peak at [5]:

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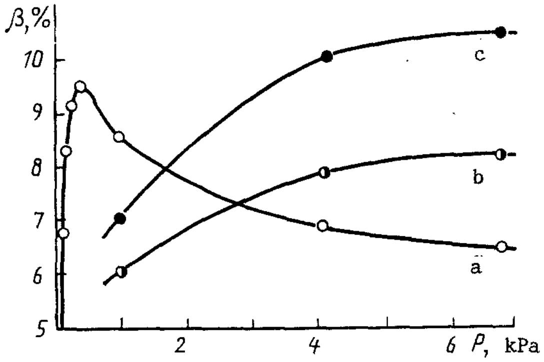

Fig. 1. Dissociation yield from $CF_2(OF)_2$ in relation to pressure ($\Phi_\ell \approx 3$ J·cm^{-2}, $\nu_\ell = 931$ cm^{-1}): a) $CF_2(OF)_2$; b) $CF_2(OF)_2$ with He in 1:1 ratio; c) $CF_2(OF)_2$ with O_2 in 1:1 ratio.

302 cm^{-1}; 603 cm^{-1} (CF_2); 659 cm^{-1} (CF); 692 cm^{-1} (CF);
866 cm^{-1}; 916 cm^{-1} (OF); 933 cm^{-1} (OF); 1080 cm^{-1};
1196 cm^{-1}; 1251 cm^{-1} (CF); 1271 cm^{-1} (CF); 1375 cm^{-1} (CF);
2491 cm^{-1}; 2046 cm^{-1}; 2197 cm^{-1}

The molecule belongs to symmetry group C_{2V}.

The compound does not decompose in several hours at 423 K, and 40% is recovered after 3 h at 523 K. The slow pyrolysis is [6] described by

$$CF_2(OF)_2 \rightarrow COF_2 + 1/2\,O_2 + F_2. \tag{2}$$

$CF_2(OF)_2$ was first treated with CO_2 laser pulses in [7]. The dissociation products were found to be COF_2, CO_2, and F_2.

The experiments were performed with an apparatus analogous to that described in [7]. When the $CF_2(OF)_2$ pressure was less than 66.5 Pa, there was no dissociation, but adding a buffer gas (Xe, Cl_2, Br_2, He, H_2) at lower pressures resulted in it. In a mixture of $CF_2(OF)_2$ (40 Pa) and Cl_2, the dissociation yield increased from 0.003 (P_{Cl_2} = 13.3 Pa) to 0.022 (P_{Cl_2} = 40 Pa). Higher chlorine pressure reduced the yield because the excited $CF_2(OF)_2$ molecules are deactivated by the Cl_2. The rotational bottleneck is important here. Raising the gas pressure increased the dissociation yield more sharply. Figure 1a shows the result. Increasing the pressure of a resonantly absorbing gas results in V–V, V–V', and V–T processes [3]. The probability of vibrational energy being transferred from a mode of higher frequency to one of lower frequency is higher by a factor exp(ΔE/kT) [8] than the probability of the reverse transfer.

We consider mild collisions, i.e., when there are only one-quantum transitions in V–V' collisions. $CF_2(OF)_2$ molecules excited by the IR laser beam can reach the dissociation energy also by V–V' transfer. The equation for the vibrational-state populations that incorporates this is

$$\frac{dZ_n}{dt} = \sigma_{n-1,n} I \left(Z_{n-1} - \frac{\rho_{n-1}}{\rho_n} Z_n \right) - \sigma_{n,n+1} I \left(Z_n - \frac{\rho_n}{\rho_{n+1}} Z_{n+1} \right) - \tag{3}$$
$$- Z_n K + K \sum_{i,V=0}^{N} (i+1)(V+1) Z_i Z_V \exp\left(\frac{E_{i+1} - E_i + E_V - E_{V+1}}{kT} \right),$$

in which $\sigma_{i,j}$ is the absorption cross section, I the laser intensity, $\rho_{i,j}$ the vibrational-state densities, and K the dissociation rate constant, which is defined from the ratio of the state densities for the activated complex and the molecule, with K_1 the rate constant for V–V' exchange between levels 1 and 2 and N the number of vibrational states up to the dissociation energy.

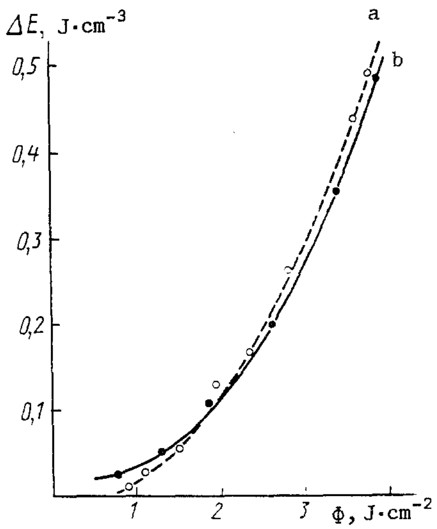

Fig. 2. Absorbed energy as a function of excitation density (ν_ℓ = 931 cm^{-1}): a) experiment; b) theory ($\Delta\nu_{anh}$ = 2 cm^{-1}, V_0 = 0.012).

The first three terms in (3) have been written in the symbols used in the Rice–Ramsberger–Kassel–Markus RRKM theory [9]. We assume that $CF_2(OF)_2$ has a high vibrational-state density and that resonant cascade transitions can occur. The anharmonicity may be compensated on several channels, one of which is Fermi resonance. The vibrational-state density is expressed in the Whitten–Rabinowicz approximation. The parameters of $CF_2(OF)_2$ determined from standard formulas [3] were as follows: rotational constant B = 0.219 cm^{-1}, zero-point energy ε_0 = 608 cm^{-1}, and vibrational dipole moment of the excited molecule $\mu \approx 0.1$ D. Then (3) is solved to derive the distribution over the vibrational states, from which one determines the absorbed energy. The unknown constants here are the anharmonicity $\Delta\nu$ and the Fermi interaction constant V_0. Simulation gave the most suitable values for $\Delta\nu$ and V_0 by fitting to experiment. Figure 2 shows the calculated and observed dependence of the adsorbed energy as a function of the laser energy density. The experimental curve saturates at higher energies and is not shown because absorption saturation is of known type. With $\Delta\nu$ = 1.5 cm^{-1} and constant $V_0 \geq 0.015$, there is a positive effect on the absorbed energy from V–V' processes, but a negative one for $\Delta\nu$ = 3 cm^{-1} and $V_0 \geq 0.009$. The observed dependence corresponds to the Treanor minimum, i.e., V–V' exchange has no effect on the absorbed energy. The observed curves in Fig. 1 show that the dissociation yields are dependent on the pressure of the compound and on the type of diluent gas. The dissociation product above 0.7 kPa is COF_2. A qualitative explanation is provided by the system

$$CF_2(OF)_2 + nh\nu \rightarrow CF_2(OF)_2^*, \qquad (4)$$

$$CF_2(OF)_2^* + CF_2(OF)_2(He,\ O_2,\ Cl_2,\ Br_2,\ H_2) \rightarrow CF_2(OF)_2^*\ , \qquad (5)$$

$$CF_2(OF)_2^* + CF_2(OF)_2^* \rightarrow CF_2(OF)_2^{**}, \qquad (6)$$

$$CF_2(OF)_2^{*\prime} + mh\nu \rightarrow CF_2(OF)_2^{**}, \qquad (7)$$

$$CF_2(OF)_2^{**} \underset{K_8'}{\overset{K_8}{\rightleftarrows}} CF_2O_2 + 2F^{\cdot}, \qquad (8)$$

$$F^{\cdot} + O_2 + M \xrightarrow{K_9} FO_2 + M, \qquad (9)$$

$$CF_2O_2 \rightarrow COF_2 + 1/2O_2. \qquad (10)$$

We estimated the V–T rates for the working conditions from standard formulas [8]; they can be neglected by comparison with the laser pulse length of ~1.5 μsec. Then (5) explains why the buffer gas has a positive effect on the dissociation yield. The molecule goes over to the quasicontinuum, with subsequent radiation excitation in reaction (7). Such reactions have not been incorporated into the above calculations. Oxygen differs from the other buffer gases in that it produces (9), i.e., is a fluorine atom acceptor. The competition between (8) and (9) means that Fig. 1 can be used to estimate the rate constant for the (8) recombination:

$$K_8' = K_9 \frac{[O_2]\,[M]\,[F^{\cdot}]}{[CF_2\dot{O}_2]\,[F^{\cdot}]\,[F^{\cdot}]}.$$

$K_9 = 1.49 \cdot 10^{-32}$ cm^6·sec^{-1} [10] for $M = O_2$. With $P_{CF_2(OF)_2} = 1995$ Pa, we get $K_5 = 3 \cdot 10^{-30}$ cm^6·sec^{-1}. The measurements enable one to estimate the efficiency in the use of the CO_2 laser energy in the dissociation of $CF_2(OF)_2$. The calculations give values from 5% for 1.33 kPa $CF_2(OF)_2$ + 1.33 kPa O_2 to 20% for 6.65 kPa $CF_2(OF)_2$ + 6.65 kPa O_2.

The dissociation energy of $CF_2(OF)_2$ is fairly low (≥ 2.5 J·cm^{-2}), and this efficiency is high, so the compound can be recommended as a source of atomic fluorine in laser chemistry.

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EFFECT OF DYNAMICS OF GENERATION ON THE PHOTOCHEMICAL STABILITY OF LASER DYES

O. I. Ivanenko and O. B. Cherednichenko

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One of the basic problems arising in development of effective dye lasers and increasing their operating lives, is photodegradation of the laser dye solutions. Photodegradation of dyes lasing in the blue-green spectral range is most significant.

One of the aspects of this problem is the effect of photodegradation of a laser dye on the emission characteristics of the laser. In [1, 2] an analysis of the kinetics of lasing in conditions of photodecay was performed on the basis of numerical solution of the balance equations, in which terms were introduced describing photodestruction of molecules and absorption of the generated radiation by the photoproduct. Analytically this question was discussed in [3, 4] for the case of a stationary single-pass amplifier with transverse pumping.

However, there exists an inverse effect of the conditions and dynamics of generation on the photochemical stability of laser dye solutions. In the experimental work [5] Kazmymov et al. noted that the photochemical stability of dyes in the resonator is 3-5 times higher than outside the resonator under the same conditions of irradiation with respect to pumping.

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