POSSIBILITY OF OBTAINING EXCITED IODINE IONS AS A RESULT OF CHEMICAL REACTIONS

T. L. Andreeva, V. I. Malyshev, A. I. Maslov, I. I. Sobel'man, and V. N. Sorokin
P. N. Lebedev Physics Institute, USSR Academy of Sciences
Submitted 23 September 1969
ZhETF Pis. Red. 10, No. 9, 423 - 427 (5 November 1969)

The working transitions in the presently known chemical lasers are the vibrational-rotational transitions of molecules excited during the course of chemical reactions (cf., e. g., [1]. In so far as we know, there are still no chemical lasers based on the electronic transitions of molecules, or on atomic transitions.

We consider in this paper the possibility of obtaining excited atoms of iodine ($^2P_{1/2}$) and a population inversion $N(^2P_{1/2})/N^2P_{3/2}) > 1/2$ as a result of the chemical reactions

$$CF_3 + CF_3J \rightarrow C_2F_6 + J(^2P_{1/2}), \qquad (1a)$$

$$CF_3 + CF_3J \rightarrow C_2F_6 + J(^2P_{3/2}). \qquad (1b)$$

Both reactions (1a) and (1b) are energetically feasible, since the corresponding binding energies are $E(CF_3\text{-}I) = 57$ kcal/mole and $E(CF_3\text{-}CF_3) = 92$ kcal/mole, while the excitation energy of the iodine atom is $E(^2P_{1/2}) - E(^2P_{3/2}) \approx 22$ kcal/mole.

The assumption that chemical reactions of the type (1a) and (1b) play a role in the population inversion of the iodine levels $^2P_{1/2}$ and $^2P_{3/2}$ arose during the course of investigations of the photolysis of the CF_3I molecules and the photodissociation iodine laser based on CF_3I molecules. According to these data, the most active in the reactions (1a) and (1b) may be the "hot" radical CF_3 produced directly during the photodissociation of the CF_3I

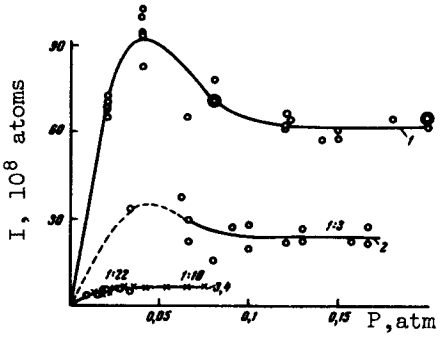

Fig. 1. Total number of I atoms vs. partial pressure of CF_3I (V = 170 cm^3, E_p = 900 J, C = 50 μF; 1) pure CF_3I gas; 2) CF_3I:Xe = 1:3; 3) x - CF_3I:Xe = 1:10; 4) o - CF_3I:Xe = 1:22.

molecules if the wavelength of the incident radiation is short enough.

The performed experiments can be arbitrarily divided into two groups, one dealing with the decomposition of the initial CF_3I molecules during the photolysis, and the other with the behavior of the interted population of the iodine levels $^2P_{1/2}$ and $^2P_{3/2}$ during the photolysis of the CF^3I molecules.

Figure 1 shows plots of the total number of I atoms produced in the photolysis of the CF_3I molecules vs. the partial CF_3I pressure, for the pure gas and for CF_3I-Xe mixtures of various proportions. All plots were obtained at the same pump-lamp energy. The following can be concluded from Fig. 1: 1) the number of produced I atoms, at the same lamp energy, decreases very strongly (by approximately one order of magnitude) on going from the non-diluted gas to dilute mixtures 1:10 and 1:22; 2) the number of I atoms exhibits saturation if the mixture dilution is sufficiently large (1:10 and 1:22).

Figures 2 and 3 show examples of the spectral investigations of the photolysis of the molecules with a time sweep. The spectral region corresponding to the absorption of the CF_3I molecules is shown. Fig. 2 shows the absorption band of pure CF_3I at various instants of photolysis, and Fig. 3 shows the same band for a mixture CF_3I:Xe = 1:9. It is seen that the

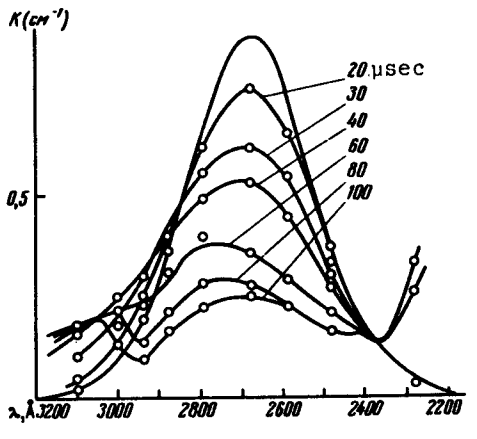

Fig. 2. Appearance of CF_3I absorption band at various instants of photolysis (E_p = 900 J, C = 50 μF, $\tau_{\gamma 2}$ ≈ 25 sec).

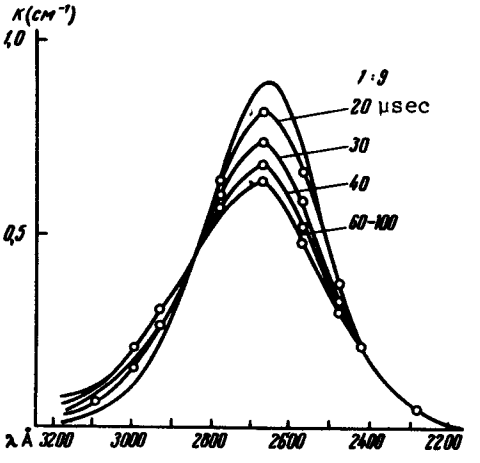

Fig. 3. Absorption band of CF_3I in a 1:9 CF_3I:Xe mixture at various instants of photolysis (E_p = 900 J, C = 50 F, $\tau_{\gamma 2}$ ≈ 25 sec).

decomposition of the CF_3I molecules in the pure gas is much more rapid than in the mixture, the difference being noticeable from the very start of the photolysis.

According to these data, it is to be expected that in strongly diluted mixtures, when the "hot" CF_3 radicals are sufficiently effectively thermalized in collisions with the buffer-gas molecules, the photolysis processes have the simplest form

$$CF_3J + \hbar\omega \rightarrow CF_3 + J(^2P_{1/2}) \tag{2a}$$

$$J + J \rightarrow J_2, \tag{2b}$$

$$CF_3 + CF_3 \rightarrow C_2F_6, \tag{2c}$$

and all the additional mechanisms of CF_3I decomposition (particularly reactions (1a), (1b), or some others) play no important role. To the contrary, in non-diluted CF_3I additional decomposition of the CF_3I molecules is clearly seen. The presented experimental data tell us nothing concerning the influence of the additional decomposition of CF_3I in the pure gas on the inverted population of the $^2P_{1/2}$ and $^2P_{3/2}$ levels of iodine. To this end, investigations were made of an iodine laser using CF_3I molecules. The investigations of the operating regime of the Q-switched laser have made it possible to select experimental conditions such that the lifetime of the inversion greatly exceeded the pump-pulse duration. The processes of production of the excited $I(^2P_{1/2})$ atoms were not masked by nonradiative deactivation. The diluent in these experiments was SF_6 gas, which termalizes the hot CF_3 radicals very effectively. It is known that the quenching constant of the $I(^2P_{1/2})$ state by the SF_6 molecules is negligibly small [2]. Under the experimental conditions, the radiation from the pump lamp was filtered with the aid of an additional gas filled with CF_3I gas. Since the pump intensity decreases sharply with decreasing wavelength in the region of the CF_3I absorption band, an increase of the filter density decreased the relative yield of the "hot" CF_3 radicals. The table shows the changes of the ratio of the threshold energy to the generation energy for CF_3I and for $CF_3I:SF_6$ = 1:1 as a function of the CF_3I pressure in the filter.

P_{filt}, atm	0	0.05	0.1	0.2	0.3	0.4	0.45	0.5
$\frac{E_{thr}CF_3J-SF_6}{E_{thr}CF_3J}$	2	–	1.4	1.3	1.3	1.07	–	1.1
$\frac{E_{gen}CF_3J}{E_{gen}CF_3J-SF_6}$	1.15	1.17	1.12	1.06	–	–	–	–

As seen from the table, both ratios decrease when the filter density is increased, and at sufficiently high density they approach unity.

A highly probable explanation of the obtained data is as follows: in pure CF_3I (without the filter), the excited $I(^2P_{1/2})$ atoms and the inverted population are produced both during the photolysis of the CF_3I molecules and simultaneously as a result of reaction (1a). With increasing filter density, the relative yield of the "hot" CF_3 radical decreases, and therefore the role of the reaction (1a) decreases. In the case of the CF_3I-SF_6 mixture the reaction

(1a) is apparently much less effective (even in the absence of the filter), owing to the fast thermalization of the CF_3 in collisions with the SF_8.

The question of the relative yield of excited and unexcited iodine atoms in reactions (1a) and (1b) still remain unclear. It is possible that there is a certain analogy between reactions (1a) and (1b) and the processes of photodissociation of the CF_3I molecules where, as is well known the yield of excited iodine atoms greatly predominates.

[1] K. L. Kompa, P. Gensel, and J. Wanner, Chem. Phys. Lett. 4, 210 (1969).
[2] R. I. Donovan and D. Husain, Trans. Far. Soc. 62, 2023 (1966).