Yield of excited iodine atoms during many-photon dissociation of CF_3I and $(CF_3)_3CI$

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The yield of iodine atoms in the $^2P_{1/2}$ and $^2P_{3/2}$ states has been measured directly for the first time during many-photon dissociation of CF_3I and $(CF_3)_3CI$ by the beam from a CO_2 laser. The yield of excited iodine $I^*(^2P_{1/2})$ is essentially the same for the two molecules at comparable degrees of dissociation.

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Among the many questions which arise in research on collisionless many-photon dissociation of polyatomic molecules in intense IR laser beams, one which we feel is of fundamental importance is whether electronically excited molecules[1,2] or their fragments can form in the course of this dissociation. In a recent study[3] of the many-photon dissociation of $(CF_3)_3CI$ through observations of the luminescence in the spectral region ~ 1.3 μm [i.e., near the transition $I^*(^2P_{1/2}) \rightarrow I(^2P_{3/2})$] it was concluded that excited $I^*(^2P_{1/2})$ atoms can form directly during the many-photon dissociation. An estimate based on the luminescence intensity put the yield at $I^*(^2P_{1/2})$, $\gamma > 0.1$, at a power density $\Phi = 5$ J/cm^2 of the CO_2 laser beam. No luminescence was observed up to $\Phi = 8$ J/cm^2 in the many-photon dissociation of CF_3I.

Kozlov and Pravilov[4] have shown that in measurements of the $I^*(^2P_{1/2})$ yield during the UV photolysis of $(CF_3)_3CI$ the emission observed at $\lambda = 1.3$ μm is due primarily to the luminescence of electronically excited molecules formed in the reaction $(CF_3)_3C + I^*(^2P_{1/2}) \rightarrow (CF_3)CI^*$, from the state $^5\,^3Q_0$; this state has a shallow minimum at large C–I internuclear distances. The possibility that this state may also be populated during the many-photon excitation of the $(CF_3)_3CI$ molecules is not ruled out. Since the probability for a transition from the $^3Q_0$ state to the ground state is substantially higher than the probability for the magnetic dipole transition $I^*(^2P_{1/2}) \rightarrow I(^2P_{3/2})$, this method for observing the luminescence is incapable in principle of distinguishing atomic from molecular excitation.

For an unambiguous resolution of whether excited $I^*(^2P_{1/2})$ atoms are formed during the many-photon dissociation of CF_3I and $(CF_3)_3CI$ by a CO_2 laser beam, we indirectly measured the concentrations of the atoms $I(^2P_{3/2})$ and $I^*(^2P_{1/2})$ through the use of a resonance method sensitive to the iodine atoms exclusively.[6,7] By measuring the intensity attenuation $\varkappa$ of the probing pulse from an iodine laser [which works on the transition $I(^2P_{1/2}, F = 3) \rightarrow I(^2P_{3/2}, F = 4)$], passed through a cell holding RI [CF_3I or $(CF_3)_3CI$], we can find the actual yield of the many-photon dissociation, β_0, and the yield of excited atoms,[7] $I^*(^2P_{1/2})$, γ, after a time $\tau \ll \tau_R$, where τ_R is the scale time for the secondary chemical reactions:

$$\beta_0 = -\frac{24 \ln \kappa_1^{O_2}}{9\sigma_{4-3} L [RI]_0}; \qquad \gamma = \frac{1}{3}(1 - \ln \kappa_1^{N_2} / \ln \kappa_1^{O_2}) \tag{1}$$

Here $\kappa_1^{O_2}$ and $\kappa_1^{N_2}$, respectively, are the relative intensity attenuations when the mixture contains the strong quencher $I^*(^2P_{1/2}) - O_2$ and when this species is replaced by N_2; σ_{4-3} is the cross section for absorption of the beam from the iodine laser by an iodine atom; L is the length of the cell; and $[RI]_0$ is the initial RI concentration.

The gas is injected into a cell $L = 80$ cm long and 4 cm in diameter, fitted with NaCl windows. The beam from the CO_2 laser and that from the iodine laser are directed along the axis of this cell. We use mixtures RI, $O_2(N_2) = 1{:}6$ at a total pressue of 2.1 Torr. In the case of the CF_3I the average energy density of the CO_2 laser beam is $\Phi = 1.0$ J/cm^2 [$P(14)$,1075.6 cm^{-1}]; in the case of $(CF_3)_3$ the beam is compressed with a telescope to a power density $\Phi = 1.8$ J/cm^2 [$P(10)$,952.9 cm^{-1}]. The probing pulse is delayed a time $\tau = 10$ μs with respect to the CO_2 laser pulse. We also measure the intensity attenuation of the signal from the iodine laser after the nth pulse from the CO_2 laser, $\varkappa_n$; under the condition that the time between pulses is much longer than τ_R, this attenuation is given by

$$\ln \kappa_n = \ln \kappa_1 (1 - \alpha\beta_R)^{n-1}, \tag{2}$$

where α is the fraction of the cell volume illuminated by the CO_2 laser, and β_R is the yield of many-photon dissociation observed on the basis of the RI yield. We see from (2) that the dependence of $\ln|\ln \varkappa_n|$ on $n - 1$ should be linear.

Figure 1,a and b, shows the experimental results on $|n|\ln \varkappa_n^{O_2}|$ and $\ln|\ln \varkappa_n^{N_2}|$ vs $n - 1$, processed statistically in accordance with linear expression (2), for CF_3I and $(CF_3)_3CI$ molecules, respectively. Working from these curves of $\ln \varkappa_1^{O_2}$ and $\ln \varkappa_1^{N_2}$ and (1), we find

$$\gamma^{CF_3I} = (6{,}0 \pm 1.5)\% \quad \text{and} \quad \gamma^{(CF_3)_3CI} = (4.5 \pm 1.1)\%$$

$$\beta_0^{CF_3I} = (17{,}5 \pm 0{,}6)\% \text{ and } \beta_0^{(CF_3)_3CI} = (16.6 \pm 0.3)\%$$

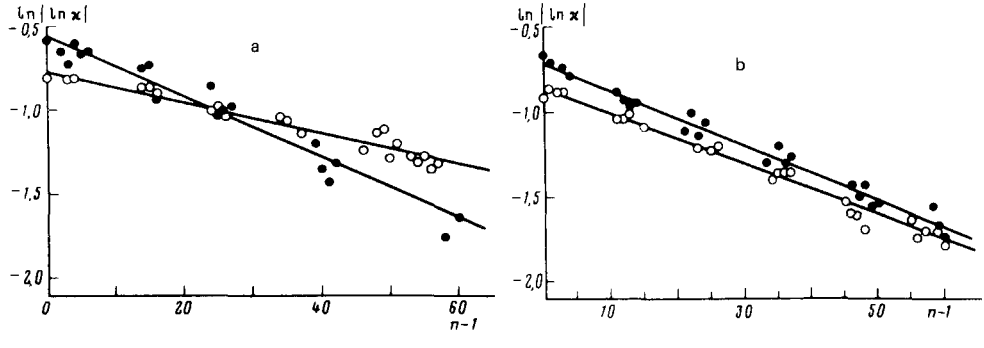

FIG. 1. Experimental results on $\ln|\ln \varkappa|$ vs the number of pulses from the CO_2 laser ($n - 1$). a—For CF_3I molecules; b—$(CF_3)_3CI$ molecules. ○—RI:N_2 = 1:6; ●—RI:O_2 = 1:6.

The approximate equality of these values of γ at essentially identical values of β_0 for molecules with such greatly different numbers of atoms is surprising to us and requires a special theoretical analysis. As for the difference between our results and those of Ref. 3, we believe that it is due to the ambiguity of the luminescence method for problems of this sort, as discussed above. The high emission intensity of the electronically excited $(CF_3)_3CI$ molecules in comparison with that of the CF_3I molecules is apparently a consequence of a higher optical-transition probability or a higher concentration of the luminescence spectrum near 1.3 μm.

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