

Observation of electronic predissociation of vibrationally overexcited polyatomic molecules

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A new type of electronic predissociation of a polyatomic molecule has been observed for the particular case of $(\text{CF}_3)_3\text{CI}$. This predissociation results from the many-photon IR excitation of the molecule above the dissociation energy in the electronic ground state and from a mixing of the real vibrational continuum of the ground state with an unstable excited electronic state.

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If the vibrational energy E of a molecule exceeds its dissociation energy D , the molecule may spontaneously decay into fragments. The rate of the monomolecular decay, \mathbf{K} , is described in the semiclassical approximation¹ by

$$\mathbf{K}(E) \approx \mathcal{K} \left(\frac{E - D + E_0^A}{E + E_0^M} \right)^{s-1}, \quad (1)$$

where s is the number of vibrational degrees of freedom of the molecule: E_0^M and E_0^A are the zero-point vibration energies of the molecule and of the activated complex, respectively; and \mathcal{K} is a frequency factor, equal in order of magnitude to the molecular vibration frequency, 10^{13} – 10^{14} s^{-1} . The decay rate obviously imposes an upper limit on the extent to which a molecule can be excited above the dissociation energy ($E_{\text{max}} - D$) for a given vibrational-excitation rate w_0 . In many-photon IR excitation of a polyatomic molecule it is a simple matter to achieve an excitation rate $w_0 = 10^8$ – 10^9 s^{-1} (Ref. 2). Because of the rapid increase in the decay rate $k(E)$, the difference $E_{\text{max}} - D$ can be estimated from

$$w_0 \approx k(E_{\text{max}}). \quad (2)$$

Let us compare the values of the difference $E_{\text{max}} - D$ for two different molecules: CF_3I and $(\text{CF}_3)_3\text{CI}$. In the case of CF_3I ($s=9$), expression (2) yields $E_{\text{max}} - D \approx 0.1D$; i.e., only a slight overexcitation (excitation above the dissociation energy) is possible (~ 2000 cm^{-1}). For the molecule $(\text{CF}_3)_3\text{CI}$ ($s=36$), in contrast, we find $E_{\text{max}} - D \approx D$; i.e., there may be a significant overexcitation.

At such a pronounced overexcitation, the vibrational energy of the $(\text{CF}_3)_3\text{CI}$ molecule, $E \approx 40\,000$ cm^{-1} , is greater than the energy boundary of the first electronic term of this molecule ($E_0^* \approx 28\,000$ cm^{-1}). This term is unstable. It seemed to us that in this case, because of the nonadiabatic coupling of the electronic and vibrational motions, a many-photon IR overexcitation of the $(\text{CF}_3)_3\text{CI}$ molecule might lead to its electronic predissociation. It has been established that in the UV photoly-

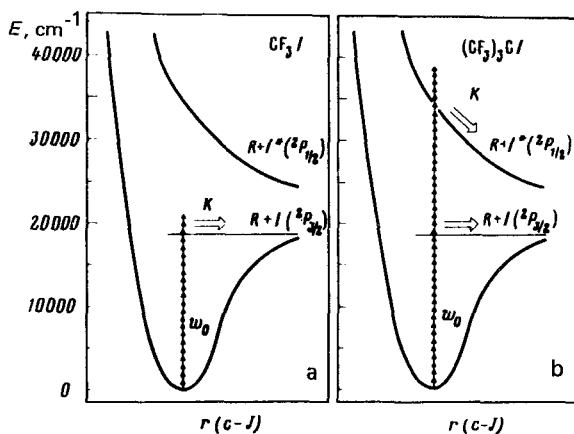


FIG. 1. Pathways for the monomolecular decay of the CF_3I molecule (a) and of the $(\text{CF}_3)_3\text{CI}$ molecule (b).

sis of many iodides, in particular $(\text{CF}_3)_3\text{CI}$, a substantial fraction of the iodine atoms are found in the $^2P_{1/2}$ excited state.³ If this predissociation of a vibrationally overexcited $(\text{CF}_3)_3\text{CI}$ molecule does in fact occur, then the many-photon IR dissociation should also lead to the formation of $I^*(^2P_{1/2})$, which luminesces at $\lambda = 1.315 \mu\text{m}$ (Fig. 1b). In contrast, the dissociation of a molecule in the electronic ground state leads to the formation of an iodine atom in its ground state ($^2P_{3/2}$).

Direct experimental confirmation of this predissociation of vibrationally overexcited molecules has come from the observation of IR luminescence at the $^2P_{1/2} \rightarrow ^2P_{3/2}$ transition of atomic iodine ($\lambda = 1.315 \mu\text{m}$) during the irradiation of $(\text{CF}_3)_3\text{CI}$ molecules by the pulsed beam from a CO_2 laser with a pulse length $\tau = 1 \mu\text{s}$ and a frequency $\nu = 949.48 \text{ cm}^{-1}$. Figure 2 shows the dependence of the IR luminescence intensity on the laser energy density Φ at a $(\text{CF}_3)_3\text{CI}$ pressure $P = 1 \text{ Torr}$. The IR

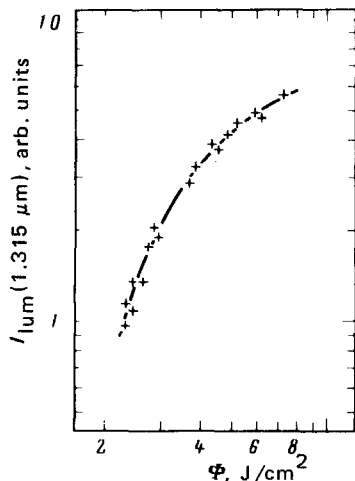
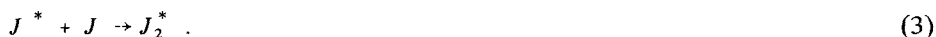


FIG. 2. Dependence of the luminescence intensity of I^* ($\lambda = 1.315 \mu\text{m}$) on the laser beam energy density. $P = 1 \text{ Torr}$, $\tau = 1 \mu\text{s}$, $\nu = 949.48 \text{ cm}^{-1}$.

luminescence signal was measured with a PbS photodetector. For an absolute intensity calibration of the IR luminescence of the excited iodine atoms, we carried out an UV photolysis of $(\text{CF}_3)_3\text{CI}$ molecules with the beam from a XeCl excimer ($\lambda = 308 \text{ nm}$). The irradiation and detection geometry for this calibration was the same as that for the many-photon IR photolysis. We then used the known quantum yield of I^* atoms, η^{UV} , to determine the absolute sensitivity of the detection system. Independently, we determined the yield (β) of the many-photon IR dissociation of the $(\text{CF}_3)_3\text{CI}$ molecules. The measurements yielded $\beta = 1$ at $\Phi = 5 \text{ J/cm}^2$; here at least 10% of the iodine atoms form in the $^2P_{1/2}$ state. The quantum yield for the formation of I^* atoms in the many-photon IR overexcitation of $(\text{CF}_3)_3\text{CI}$ by CO_2 laser pulses with $\Phi = 5 \text{ J/cm}^2$ is thus $\eta^{\text{IR}} \geq 0.1$. By way of comparison, we note that the yield for UV photolysis of these molecules at $\lambda = 308 \text{ nm}$ is $\eta^{\text{UV}} \approx 0.3$ (Ref. 3).

In addition to detecting the I^* atoms through their IR luminescence, we detected them through the visible luminescence at $\lambda \approx 580 \text{ nm}$ of electronically excited iodine molecules which form in the secondary chemical reaction



Measurements revealed that the temporal characteristics of this luminescence are completely identical to the corresponding characteristics during UV photolysis.⁴

From a comparison of data on the absorbed IR energy $\bar{\epsilon}$ and the dissociation yield β we conclude that there is a substantial many-photon IR overexcitation of the $(\text{CF}_3)_3\text{CI}$ molecule. At the same time, the estimates above and also direct measurements⁵ describe a very slight overexcitation for the simpler molecule CF_3I . In the present experiments as well, at the sensitivity of the particular detector used, we were not able to detect any IR luminescence signal at $\lambda = 1.315 \mu\text{m}$ (from CF_3I molecules) at laser energy densities Φ up to 8 J/cm^2 and at $P = 1 \text{ Torr}$. The dissociation yield for CF_3I is $\beta = 1$ at $\Phi \geq 4 \text{ J/cm}^2$. Taken together, these results imply that the predissociation of the $(\text{CF}_3)_3\text{CI}$ molecule is a direct consequence of its pronounced vibrational overexcitation, which is possible in molecules containing many atoms because the monomolecular decay from the electronic ground state is low.

We note in conclusion that these effects in vibrationally overexcited polyatomic molecules may occur not only upon excitation by intense IR light but also, apparently, with any sufficiently rapid vibrational heating, for example, in an electric discharge or through a fast exothermic reaction.

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