

Comparison of the effectiveness of excitation of various modes in the CCl_4 molecule in a strong IR field

B. I. Vasil'ev, N. A. Vishnyakov, V. T. Galochkin, A. Z. Grasyuk, A. P. Dyad'kin, A. K. Zhugalkin, V. A. Kovalevskii, V. N. Kosinov, A. N. Oraevskii, A. N. Sukhanov, and N. F. Starodubtsev
P. N. Lebedev Physics Institute, USSR Academy of Sciences

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The energy required to excite the CCl_4 molecule by an IR field to the dissociation level is experimentally shown to depend on the excitation modes.

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In the current studies of laser-induced chemical reactions the problem of activating a reaction along a single branch or a group of selected branches, by exciting appropriate modes for the multiphoton absorption of IR quanta, remains open. This work is dedicated to the experimental comparison of the effectiveness of activation by a field of different vibrational modes of a molecule.

The multiphoton dissociation of CCl_4 has been sufficiently well studied.^{1,2} In our work, we compared experimentally the average values of energy that was absorbed by a CCl_4 molecule when the ground ν_3 and hybrid $\nu_1 + \nu_2 + \nu_4$ states were excited to the dissociation level. Excitation of the $\nu_1 + \nu_2 + \nu_4 = 980 \text{ cm}^{-1}$ state was by CO_2 laser radiation [$P(26)$ line, $00^\circ 1-02^\circ 0$ band]. The conventional shape of a CO_2 -laser pulse was characteristic of TEA lasers, with an overall length not exceeding $3 \mu\text{sec}$. The fundamental mode $\nu_3 = 794 \text{ cm}^{-1}$ (triple degenerate deformation mode) was excited by an NH_3 laser pulse ($\nu = 771 \text{ cm}^{-1}$) with a baseline width of $1.5 \mu\text{sec}$. The time dependent output shape from both lasers was qualitatively similar. The cell containing CCl_4 was a stainless cylinder 10 cm long and 10 mm in diameter, its total volume being 14 cm^3 . The gas pressure in the experiments was 0.5 mm Hg. Laser radiation was focused inside the cell by means of an $f = 10 \text{ cm}$ lens. Energy absorption in the cell was measured with an acousto-optic receiver that was designed to permit a direct measurement in the focal region of the lens.

To compare the magnitude of absorbed energy for different modes of the CCl_4 molecule, it was necessary to provide the same level of excitation for all the modes. This was accomplished in the following manner.¹⁾ In selecting the intensity of the excitation field to be such that the molecule attains the dissociation level, we achieve a common excitation level for the molecule. Figure 1 shows plots of the dependence of the degree of dissociation of CCl_4 $w = n^{-1} \ln(N_0/N)$ on the energy incident on a cell (n is a number of incident pulses, N_0 is total number of particles before illumination, and N is number of illuminated particles). We should note that the "threshold" energy density was 1.2 J/cm^2 for the excitation of mode ν_3 and 120 J/cm^2 for the hybrid mode. These results are in agreement with earlier data.^{1,2}

Our experiments were designed to determine the fraction q of the captured particles by means of a method of two-frequency dissociation yield saturation. Unlike Ref.

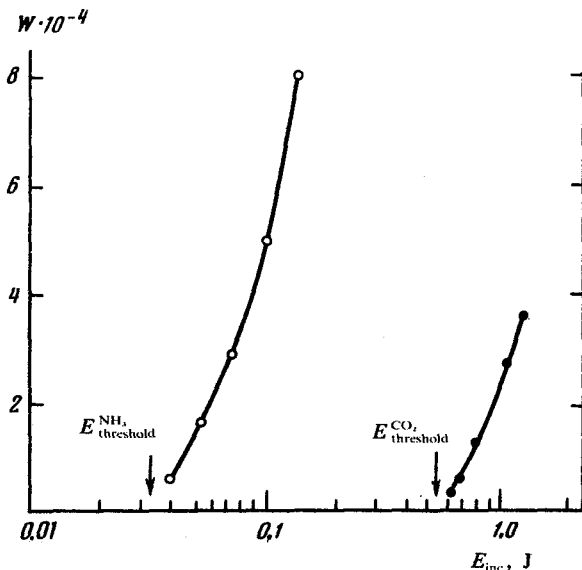


FIG. 1. Dependence of the dissociation yield of CCl_4 molecule w on the laser energy incident on a cell.

4 where a CO_2 laser was used as a source of secondary excitation, we used an XeCl excimer laser. The measured value of q for both the CO_2 and NH_3 —lasers, equally capable of exciting various modes, was close to 1.

Radiation with the quantum energy of our XeCl laser is capable of capturing particles that are only 4–8 IR quanta below the dissociation level. This means that the bulk of particles excited by the IR field are distributed near the dissociation level, i.e., the particles are “hot.” We should note that a tunable UV laser may be used to measure experimentally the vibrational distribution function of the excited particles.

Figure 2 shows the dependence of the average number of quanta absorbed by the

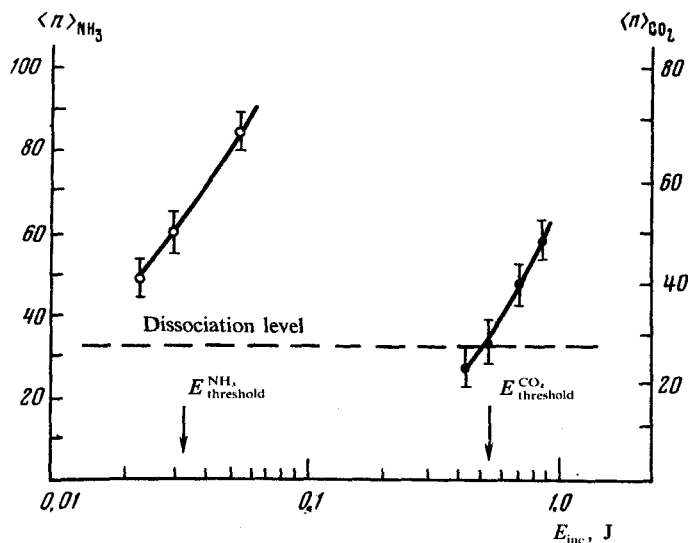


FIG. 2. Dependence of the average number of IR quanta absorbed by the CCl_4 molecule on the energy incident on a cell.

CCl_4 molecule on the IR energy incident on a cell. Clearly, the molecule absorbs twice the number of IR quanta when the ν_3 mode is excited to the dissociation level than for the excitation of the hybrid mode.

The nonequivalent absorption of energy in a molecule may imply the presence of processes that compete with the monomolecular decay reaction: $V-T$, $V-R$, $V-V$ and $V-V'$ relaxations, inverse monoradiative transitions.⁵ This may lead to differences in the energy requirements for the shaping of particle distribution functions for different modes. A possible explanation of the result obtained may be contained in the following. In the case of multiphoton excitation the vibrations of one of the C—Cl bonds attain a critical amplitude, causing this bond to break.^{6,7} The hybrid mode, which is excited by the CO_2 laser, contains the valent symmetrical mode ν_1 along the C—Cl bond, while the ν_3 mode, which is excited by the NH_3 laser, contributes to the vibration of this bond less significantly. Thus, the hybrid mode $\nu_1 + \nu_2 + \nu_4$ is more effective for the excitation of a molecule to the dissociation level.

Thus, we have shown experimentally that the energy required to excite a molecule to the dissociation limit depends substantially on the excitation mode. This fact, together with the necessary shift of the laser wavelength in the "red direction" with respect to the nonlinear absorption band,⁸ clearly constitutes the foremost condition for an increased quantum yield of the products of a reaction induced by a high-intensity IR field.

¹) It is known that the energy required to break the C—Cl bond in a CCl_4 molecule is 73.2 Kcal/mole and the detachment energy of a Cl_2 molecule is 106.6 Kcal/mole.³

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