Effect of depletion of many rotational states in vibrational excitation of molecules in a strong IR field

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Collisionless excitation of polyatomic molecules from the ground vibrational state independently of their rotational state was experimentally observed in a laser IR field of moderate intensity. This capture of many rotational states should be invoked in the analysis of collisionless dissociation of polyatomic molecules.

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1. Thorough investigations of radiative excitation of high vibrational levels of polyatomic molecules in strong IR fields (see the reviews[1]) have shown that this phenomenon can be qualitatively attributed to the presence of a quasi-continuum of vibrational levels of the polyatomic molecules and cancellation of the anharmonicity at lower vibrational levels. The cancellation mechanisms proposed in[2–4] are based on the assumption that molecules having a narrow range of quantum numbers take part in the successive excitation. However, a number of the latest experimental investigations, connected with the effectiveness of the acquisition of vibrational energy by polyatomic molecules,[5,6] cannot be satisfactorily explained within the framework of this "bottleneck,"[7] which is connected with the distribution of the molecules over the rotational states. This distribution limits the number of excited rotational states to a

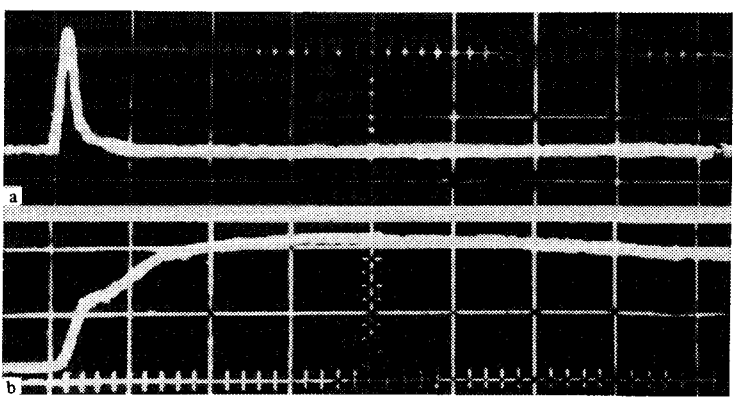

FIG. 1. Oscillograms of laser pulse (a) and of the change in the transmission of the gas-filled cell (b). Sweep 500 nsec/div.

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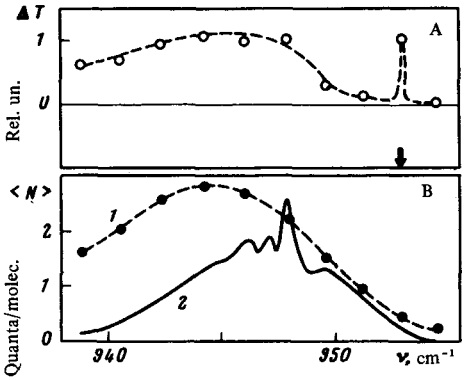

FIG. 2. A) Dependence of the amplitude of the instantaneous bleaching of a cell with SF_6 gas on the exciting-field frequency. Probing on the $P(10)$ laser line (indicated by vertical arrow). Exciting-field intensity $I_{exc} = 2.5$ MW/cm^2; SF_6 pressure 0.1 Torr. B) Spectrum of the absorbed energy of SF_6 from the exciting field at $I_{exc} = 2.5$ MW/cm^2 (curve 1) and spectrum of linear absorption of SF_6.

value $Ed/2hcB$, where E is the intensity of the IR radiation field, d is the dipole moment of the transition, and B is the rotational constant.

We report here a direct experimental observation of vibrational excitation of a large number of the rotational states ($\Delta J_{exc} \gg Ed/2hcB$) of the polyatomic molecules SF_6, SiF_4, and C_2H_4 in a laser field of moderate intensity.

2. We measured in the experiment the change in the transmission of a weak probing radiation from a cw CO_2 laser through a gas-filled cell acted upon by the radiation of a pulsed CO_2 laser. The intensity of the probing radiation did not exceed 300 mW/cm^2. The exciting-pulse duration was 150 nsec, the intensity was 0.2—3 MW/cm^2, and the spectral width was 0.03—0.04 cm^{-1}. The frequencies of the probing and exciting CO_2 lasers could be tuned over the lasing lines with the aid of diffraction gratings. The change of the transmission of the probing radiation was measured with an IR receiver having a time revolution of 100 nsec.

3. Figure 1 shows an example of collisionless bleaching of a cell with SF_6 for a probing radiation having a frequency 952.9 cm^{-1} and exciting radiation with frequency 944.2 cm^{-1}. The probing radiation was at resonance with the $R(109)$ line of the ν_3 band of the SF_6 molecule, while the exciting radiation was at resonance with the $P(63)$ line of the same band. The lifetime of the bleaching was equal to the duration of the exciting pulse and was independent of the SF_6 pressure in the range 0.03—0.7 Torr. This time, at 0.03 Torr, was shorter by a factor of 10 than the time of the rotational relaxation of the SF_6 molecules. The bleaching comes distinctly into view at an excitation intensity exceeding 300 kW/cm^2, and its value (ΔT) increases approximately in proportion to this intensity.

Figure 2 shows the dependence of the bleaching on the frequency of the exciting field in the case of probing at a frequency 952.9 cm^{-1}. The lower part shows the spectrum of the linear absorption and the spectral dependence of the

absorbed energy. A correlation is observed between the spectra of the bleaching and of the absorbed energy. It should be noted that when the molecule is excited in the Q branch of the absorption bands, no anomalously large bleaching signal is observed.

Analogous regularities are observed when the frequency of the probing radiation is shifted towards shorter wavelengths. When the probing radiation is shifted toward the long-wave side ($\nu < 953$ cm^{-1}), collisionless increase of the absorption (darkening) is observed. The reason why its bleaching gives way to darkening is apparently that the main contribution to the absorption of the probing radiation on the short-wave wing of the R branch of the SF_6 molecule is made by the vibrational transitions $v=0 \rightarrow v=1$ of the ν_3 mode, whereas in the case of longer wavelengths the transitions $v=1 \rightarrow v=2$, $v=2 \rightarrow v=3$ etc., become significant.

The presence of collisionless darkening is also evidence of the capture of many rotational states, but a quantitative interpretation is difficult in this case.

The observed effect cannot be attributed to the role of thermal bands. This follows from an analysis of the curves of Fig. 2, inasmuch as the bleaching signal changes insignificantly following an appreciable shift of the frequency of the exciting field. In addition, as shown by experiment, cooling the gas to the temperature of dry ice did not change the character of the observed effect.

It should be noted that this effect is apparently a common one; it was observed in our experiments also for the molecules SiF_4 and C_2H_4.

4. The observed depletion of the lines of rotational states can be attributed only to pure radiative processes. In our opinion, the quadratically small excitation probability of the strongly detuned rotational sublevels $[Ed/2hcB\Delta J_{exc}]^2$ can be offset by a rapid transfer of the excited molecules to higher vibrational states.[3,8] If the transfer probability is w and the emission-pulse time is τ, the number of captured rotational sublevels is $\Delta J_{exc} = Ed\sqrt{w\tau}/2hcB$. Assuming by way of estimate that w is of the order of Ed/h we obtain at a laser-radiation intensity 10^6 W/cm^2 a value $\Delta J_{exc} = \pm 30$ for molecules of the SF_6 type. Under the same conditions, but without allowance for the rapid upward transfer of the excited molecules, the molecules should interact effectively with the field only in the band $\Delta J_{exc} \pm 2$.

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