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Intramolecular vibrational dynamics of ν_1 mode in $(CF_3)_2C=C=O$ molecule induced by resonant IR femtosecond radiation

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Abstract. Intramolecular dynamics of the vibrational levels (up to v = 5) of the ν_1 mode in $(CF_3)_2CCO$ molecule, induced via multiphoton selective excitation of this mode by resonant femtosecond IR radiation, was studied. The times of intramolecular vibrational energy redistribution (*IVR*) of each vibrational level v to the remaining modes of the molecule were measured. In accordance with the theory predictions the decrease of *IVR* time with increasing v is observed. A sharp reduction of the *IVR* time (up to 1 ps) at a wavelength of 2130 cm^{-1} of transition v=3 $\rightarrow$ v=4 was found. It was shown that with a negative chirp of a femtosecond radiation pulse the population of high-lying vibrational levels of ν_1 modes significantly increases.

At a multiphoton excitation of selected vibrational modes in the molecule an implementation of photochemical bond-selective processes (or group of bonds) is possible. However, this possibility is limited due to effect of rapid intramolecular energy redistribution (*IVR*) from the excited mode to other vibrations of the molecule [1]. It is therefore important to study the process of *IVR* for different vibrational levels of the excited molecule. The aim of this work was to study vibrational dynamics in bis (trifluoromethyl) molecule $(CF_3)_2CCO$, resulting from multiphoton excitation of the ν_1 =2194 cm^{-1} mode of the C=C=O bond vibration by resonance IR femtosecond radiation.

In the experiments the IR pump-probe method with a spectral analysis of the probing radiation was used. For this purpose the new IR detector, namely high-sensitive and low-noise linear array on the basis of CdHgTe, developed with the participation of the authors, was employed for the first time. Measurements were carried out in the gas phase at low pressure, which made it possible to completely avoid the influence of intermolecular interaction. The duration of the pump and probe pulses was 120 fs with a spectral width of ~230 cm^{-1}. The spectra of induced transmission/absorption ΔOD depending on the delay

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time Δt between pump and probe pulses were measured in the range of wavelengths 2240–2040 cm^{-1}.

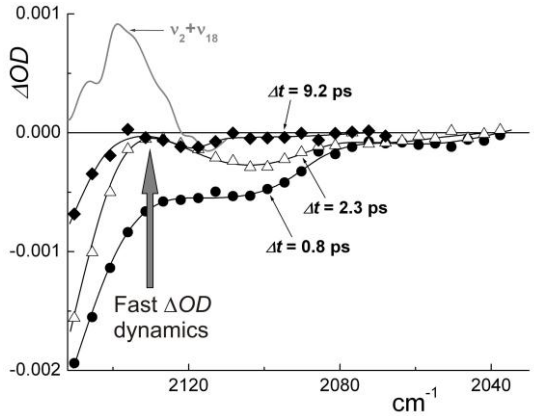

Fig. 1. "Tails" of ΔOD spectra in dependence on time delay Δt and fast dynamics at 2138 –2129 cm^{-1}.

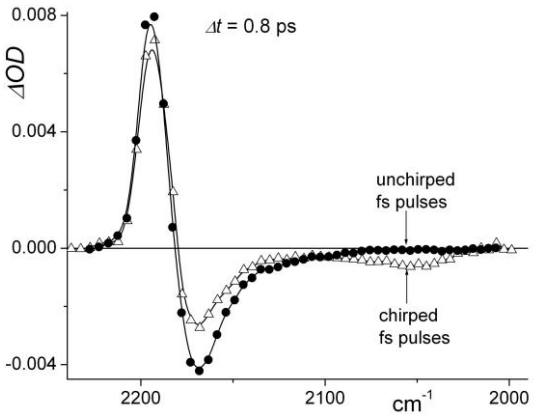

Fig. 2. ΔOD spectra for nonchirped (1.5×10^{12} W/cm^2) and negative chirped (1.8×10^{11} W/cm^2) laser femtosecond pulses.

The experiments confirmed a selective excitation of the resonant mode ν_1 up to vibrational level v = 5, which was previously registered by another way [2]. As the level of vibrational excitation of the resonant mode grows up the exponential decrease of the ΔOD signal was observed with characteristic times from τ = 6 ps for the transitions 0–1 and 1–2 to τ = 3.5 ps for the transitions 4–5 and 5–6. This corresponds to a reduction of *IVR* time from 6 to 1.2 ps in proportion to the quantum number v, which confirms the predictions of the theory [1]. At the same time, a sharp decrease of time τ to 1 ps at wavelengths of 2138–2129 cm^{-1}, approximately corresponding to the vibrational transition v=3→v=4 was found (see Fig. 1), which may be due to the resonance of the frequency of the excited vibrational level with the frequency of composite vibration $\nu_2+\nu_{18}$. Increasing the fluence/intensity of femtosecond pulses causes close to a proportional the growth of signal ΔOD and has virtually no effect on the dynamics of long "tail" of ΔOD spectrum. With a negative chirp of femtosecond radiation, when the frequency of the pulse decreases with time and thus adjusts to reduction of frequency of successive vibrational transitions due to the anharmonicity [3], it was found that the population of the high-lying vibrational states of molecules has increased considerably, although the radiation intensity has decreased by ~ 8 times (see Fig. 2).

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