Femtosecond spectroscopy of optical Kerr effect with multipulse excitation in chloroform

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Abstract. Optical Kerr effect in the spectrum of chloroform is investigated by the method of two-pulse pumping. Here it's shown that during one-pulse pumping hyperpolarizability response, libration, the orientation response and the response of the intramolecular vibrations take place. Also we have achieved the suppression of intramolecular vibrations by two-pulse pumping with corresponding intensity and time delay.

1. Introduction
The femtosecond laser control nowadays is the object of intensive theoretical and practical research. The main aim of laser control is to manipulate the molecular dynamics, which can create the necessary molecular state. This state is determined by the conditions of the problem which is being solved: electronic, oscillatory or rotatory state, the necessary way of dissociation or ionization, the beginning of the chemical reaction [1] etc. At present the femtosecond technique is actively used for realization of laser control. The reason for the use of ultrashort pulses is their duration, which is comparable to molecular oscillation period.

2. Experimental setup
The experimental setup is showed at Fig. 1.
Mode-locked Ti:Sapphire femtosecond generator of laser pulses (1) has got the following characteristics: pulse duration 35 fs, wavelength 790 nm, output power 400 mW, pulse rate 80 MHz. Mirror 2 divides laser beam in ratio 98:2, mirror 4 – in ratio 50:50. Lines of delay (3) allow to control delay time between the pulses. Polarizers (5) allow to detect the changes in isotropism of analyzed liquid with detector (7). Optical Kerr effect (OKE) concludes in registration of the light transmitted through crossed polarizers and investigated liquid between them [2,3,4].

3. Investigated liquid and sample preparation
Chloroform was selected for demonstrating the control of the vibrational dynamics of the molecules. The laser pulse duration was maximally reduced to 35 fs since this fluid has a Raman-active modes near 400 cm\(^{-1}\). The direction of the linear polarization is in accord with pump pulses. Vibrational-rotational wave packets are created in the medium by the pump pulse. Thus the effect of non-stationary polarizability anisotropy is induced into the liquid. The wave packets evolution is fixed by the low probe pulse, acting on medium after a specified delay.

![Figure 2. Chloroform molecule](image)

Chloroform is widely used in the practice of chemical laboratories as a dissolver. In normal conditions it's a transparent easily evaporating liquid, not soluble in water. Chloroform molecule has comparatively small dipole momentum (1.08 Deby). As it's shown in Fig. 2, the molecule has a structure of a tetrahedron with a shortened top, resulting to small contribution of rotational diffusion and librational movements in the OKE spectrum. It's possible to excite two Raman-active modes (273 cm\(^{-1}\) and 375 cm\(^{-1}\)) by laser pulses with a duration of 35 femtoseconds. Thereby this liquid allows to learn and control the vibration dynamics by the experiments with OKE registration.

Only high purity liquids were used in the experiment. The quartz cuvette was abundantly washed with acetone. The cuvette was washed first with distilled water (in the case if the substances poorly soluble in acetone were in the cuvette before). After the drying the cuvette was washed with filtered acetone and dried again. Afterwards the filtered liquid was poured into the cell and the cuvette was sealed. The surface of the cuvette was washed with acetone and wiped with the special soft paper for optical elements soaked in acetone. After that the cell was placed in a holder. The holder was put onto the table, so that it became possible to move the cell in two directions (the cuvette was moved so that the focus lens was in the thick liquid which helped to minimize dispersion made by cuvette surfaces), and to rotate the cuvette around its vertical axis (to avoid spurious reflections).

4. OKE spectrum analysis
OKE spectrum analysis is based on the kinetic theory of fluids. OKE signal can be decomposed into four components (different in dynamics) [5]. Firstly, it's non-inertion response, which can be described by an easy scaling of the autocorrelation function. Secondly, it's the response (main contribution in OKE signal) which is associated with the rapid libration motion of the molecule. Thirdly, after a long time (1 picosecond and more) the main contribution comes from the rotational diffusion response. If the molecule has Raman-active modes, and stimulating pulse duration allows to excite it, the following effect takes place: well-visible OKE signal oscillations with a frequency corresponding to excited Raman-active modes superimposed on all previous responses. So, it should be obvious that to demonstrate the control of vibrational-rotational dynamics of the molecules we have to find molecules and experimental parameters for which the corresponding contribution to the OKE signal (e.g. response of rotational diffusion or coherent oscillations) would be maximized.
5. OKE spectroscopy and vibrations suppression of chloroform

At Fig. 3 the OKE signal with one-pulse excitation of the medium grade is shown. The analysis of experimental data shows that in chloroform all the molecular responses discussed above (response of hyperpolarisability, libration, the orientation response and the response of the intramolecular vibrations) are presented. The subject of major interest is the response of coherent intramolecular oscillations, because the molecules of chloroform in our experiment (two Raman-active modes with frequencies of 273 cm\(^{-1}\) and 375 cm\(^{-1}\)) are excited. The main contribution is made by low-frequency mode, as the excitation of the intramolecular oscillations in the region of 400 cm\(^{-1}\) by pulses about 35 fs is less effective. We should note that there occurred the integration of the molecular response and the probe pulse at the coherent oscillations registration. Also it reduces the amplitude of higher frequency response in the aggregate OKE signal.

![Figure 3. OKE signal spectrum with one-pulse pumping (duration 35 fs).](image)

Fig. 4 shows examples of the suppression scenarios of coherent intramolecular oscillations in chloroform. Appropriate settings of the mode is the delay between the first and second exciting pulses and the relative intensity of the pump pulse. In any case the contributions related to the molecular rotations (libration and the orientation anisotropy of the molecule) are amplified as a result of the second pump pulse. For long delays it’s necessary to reduce the intensity of the second pump pulse because of the damped oscillatory response for reduction mode. Thus, the method of two-pulse pumping enables the manipulation of vibrational dynamics of molecules with different delays between the exciting pulses up to a time of full oscillatory response damping.

![Figure 4. Two-pulse pumping (35 fs), a – delay between pulses 60 fs, intensity ratio 0,7; b – delay between pulses 260 fs, intensity ratio 2,5.](image)
6. Conclusion
The control of coherent intramolecular vibrations was carried out in pure chloroform liquid at room temperature. For this purpose, non-resonant excitation by sequences of the two linearly polarized laser pulses (duration of 35 fs) was used. Probing the medium state was achieved by the weak third pulse with the use of recording ultrafast optical Kerr effect. It's shown that by using two parameters (delay between exciting pulses and their relative intensity) the control of the molecular vibrational dynamics in the subpicosecond range is achieved. The control of the vibrational dynamics in the subpicosecond range and even with long delays (compared to the decay time of the intramolecular vibrations) between the pump pulses is possible. The intensity of the second pump pulse must be reduced. When we use a double-pulse pumping, quantity of controlled parameters increases (relative to single-pulse excitation), and the number of constants for medium behavior modeling isn't changed. It results in the simplification of the OKE spectrum analysis.

References
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