Coherent control for separation of the librational response through the ultrafast optically-heterodyne-detected optical-Kerr-effect (OHD-OKE)

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Abstract. We report the first experiment results on selective spectroscopy of librational response in ortho-dichlorobenzene at room temperature. By optimization of the controlling parameters we have achieved the suppression of the Raman-active vibrational and orientational responses. We have used the two-pulse excitation scheme. The controlling parameters were pulse duration, intensity and delay between two pump pulses.

1. Introduction
Femtosecond laser technique is one of the widest approaches for ultrafast processes studies. By using “pump-probe” method we can induce a certain excited state in the media by strong pump pulse and explore it by a weaker probe pulse. One of the methods is time-resolved ultrafast optical Kerr effect (OKE) spectroscopy of vibrational-rotational dynamics in liquids [1-3]. OKE signal consists of four different components [4,5]. The first, and the most rapid, is hyperpolarization response. The second one is rotation librational response. The third one is a longer orientational response. And the fourth is the vibrational response imposed on the whole spectrum (figure 1).

The frequency spectrum of the femtosecond laser pulse is very wide and allows to excite the above-mentioned responses. But a correct spectrum interpretation is a complex problem because of component superimposition. We have used the second pump pulse with certain parameters to suppress non-relevant responses and to distinguish the relevant one [6].

The delay times of vibrational-rotational responses are subpicosecond at room temperature. It can cause some difficulties for realization of multipulse experiment. Furthermore, laser coherent control of vibrational dynamics in chloroform and carbon tetrachloride is described in [7-12]. The cases of suppression and enhancement of the vibrational responses are realized for coherent laser control by the linearly polarized pulses. But the identical polarizations of the pump pulses don't allow to control the rotational dynamics.

The scenario of the suppression of the orientational and vibrational motions is realized in this work. Such a case allows us to perform the selective spectroscopy of the molecular librational motion response.
2. Experiment

We have used a femtosecond Ti:sapphire laser with 800 nm wavelength. The pulse duration varied from 30 fs to 100 fs. The single pulse energy was $4 \times 10^{-9}$ J. Two pump pulses were polarized linearly, and mutually orthogonal. Pulse duration, intensity and delay were varied for optimal suppression and enhancement of the vibrational-rotational dynamics.

The laser radiation of the femtosecond laser was divided into three parts: two pump beams and the probe beam. The delay times of each pulse were controlled by the optical delay line. Two pump beams and the probe beam were focused on the investigated liquid by the lens. After passing the liquid cell the probe beam was separated from the pump beams by the aperture hole. For the reduction of the impact of the scattering pump on the probe beam the optical path was extended up to 5 meters. The state of the investigated liquid was characterized by the intensity change of the probe pulse passing through the first polarizer, the liquid and the second polarizer, which was crossed with the first one. So, the amplitude of the OKE signal is directly dependent on the induced anisotropy in the medium.

Ortho-dichlorobenzene (figure 2) was selected as the investigated liquid. It possesses all of the aforementioned responses. Ortho-dichlorobenzene molecule is asymmetric and flat. The dipole moment of this molecule is 2.14 D.
3. Results
As we noted above, the OKE signal consists of the responses from electronic hyperpolarizability, Raman-active vibrations, orientation and libration motions. A typical spectrum of the single-pulse excitation OKE in liquid is depicted in figure 4. All four responses are represented. The main aim of this work was the implementation of selective spectroscopy of the librational response in ortho-dichlorobenzene. For the suppression of Raman-active vibrations we have used the second pump pulse with certain delay time. The polarization of the second pulse is the same as the polarization of the first pulse [8,13]. In [14] the possibility of the simultaneous suppression of the vibrational and orientational responses was theoretically illustrated. For this scenario the polarization of the second pulse must be orthogonal to that of the first.

![Figure 4. OKE signal in ortho-dichlorobenzene with single-pulse pumping.](image)

The OKE signals from the first and the second pump pulses are depicted separately (The registered OKE signal is curve 3 in figures 5 and 6).

![Figure 5. OKE signal in ortho-dichlorobenzene with pumping by the first pulse (1), the second pulse (2), the first and the second pulse simultaneously (3).](image)

![Figure 6. OKE signal in ortho-dichlorobenzene with pumping by the first pulse (1), the second pulse (2), the first and the second pulse simultaneously (3).](image)
As it can be seen from the figure we were able to suppress orientational and Raman-active vibrational responses. In spectrum 3 we can clearly identify the librational response. We have successfully realized two cases of librational response selective spectroscopy with the following controlling parameters: pulses duration of 80 fs, the delay between pump pulses is 280 fs, intensity ratio is 1:2; pulses duration of 50 fs, the delay between pump pulses is 310 fs, intensity ratio is 1:2. The polarizations of the pump pulses were orthogonal to each other.

4. Conclusion
The first selective detection of the librational response is realized with OKE signal detection. The method is based on two-pulse laser coherent control of Raman-active intramolecular vibrations and rotational movements of molecules. The suppression of the non-relevant molecular responses is realized in the experiment. The final spectrum of OKE signal contains librational response only.

References
[1] Ruhman S, Williams L R, Joly A G, Kohler B and Nelson K A 1987 *Journal of Physical Chemistry* 91 2237–40
[2] McMorrow D, Lotshaw W T and Kenney-Wallace G 1988 *IEEE Journal of Quantum Electronics* 24 443–54
[3] Righini R 1993 *Science – New York then Washington* 262 1386
[4] Steffen T, Fourkas J T and Duppen K 1996 *The Journal of chemical physics* 105 7364–82
[5] Nikiforov V G and Lobkov V S 2006 *Quantum Electronics* 36 984
[6] Zharkov D K, Shmelev A G, Nikiforov V G and Lobkov V S 2014 *Journal of Physics: Conference Series* 572 012043
[7] Nikiforov V G, Shmelev A G, Safiullin G M and Lobkov V S 2012 *Applied Physics Letters* 100 081904
[8] Nikiforov V G, Shmelev A G, Safiullin G M and Lobkov V S 2012 *Quantum Electronics* 42 332
[9] Nikiforov V G 2013 *Quantum Electronics* 43 177
[10] Nikiforov V G, Lobkov V V and Samartsev V V 2015 *Laser Physics* 25 075701
[11] Wiederrecht G P, Dougherty T P, Dhar L, Nelson K A, Leaird D E and Weiner A M 1995 *Physical Review B* 51 916
[12] Weiner A M, Leaird D E, Wiederrecht G P and Nelson K A 1990 *Science* 247 1317–9