Quantum Electronics **42** (4) 332–336 (2012) ©2012 Kvantovaya Elektronika and Turpion Ltd

FEMTOSECOND LASER SPECTROSCOPY

PACS numbers: 42.62.Fi; 42.65.Hw; 82.53.–k
DOI: 10.1070/QE2012v042n04ABEH014796

Femtosecond laser control of induced anisotropy in a liquid: selective spectroscopy of intramolecular vibrations of carbon tetrachloride

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Abstract. **Two-pulse control of time-dependent anisotropy in liquid carbon tetrachloride at room temperature is implemented by using femtosecond polarisation spectroscopy. The liquid is excited by a train of two linearly polarised laser pulses, and the state of anisotropy is probed by a weak third pulse with registration of the optical Kerr effect. It is shown that by varying the delay between the exciting pulses and their relative intensity, selection of contributions of individual intramolecular modes into the recorded signal is achieved.**

Keywords: *multipulse laser control, ultrafast optical Kerr effect, vibrational–rotational molecular dynamics in a liquid.*

1. Introduction

Laser control of the medium's state is one of the research priority areas focused on theoretical and experimental investigations. Currently, the most effective instrument for the implementation of laser control is femtosecond technique [1], which makes it possible to excite a system by pulses comparable (in duration) to the period of molecular oscillations. It has been shown experimentally that laser control allows one to solve fundamental problems of controlling the product yield of chemical reactions [2–4], energy transfer in photosynthetic complexes [5, 6], selective photoionisation of isotopes of molecules [7], selective photodissociation and creation of new bonds in molecules [8], photoisomerisation of molecules [9], etc.

One of the laser control schemes is based on the use of multipulse excitation. A wave packet in a medium is formed by sequential interaction of pulses and free evolution of the system. Optimisation of pulse parameters (duration, intensity, frequency spectrum of pulses, delay between pulses, etc.) enables achieving a given state of the medium. This technique has been first used for selective amplification of individual modes in a molecular crystal of α-perylene [10]. Two-pulse and four-pulse trains were employed to control coherent phonon oscillations in solids [11–18]. In a liquid two-pulse excitation enabled control of orientational anisotropy in orthodichlorobenzene [19] and implementation of selective spectroscopy of molecular dynamics in chloroform [20]. Using paper [21], which theoretically examined application of multipulse nonresonant excitation in a liquid, we used a two-pulse train for selective spectroscopy of intramolecular vibrations. In order to manipulate the time-dependent anisotropy of the liquid, we varied the intensity of the excitation pulses and the time delay between them. The medium's state was probed by using the time-resolved heterodyne-detected optical Kerr effect (OKE) technique [22–24].

The OKE signal detected in a liquid is a superposition of the electronic response and the response of coherent molecular vibrations and rotations. The vibrational–rotational response in turn contains contributions of the modes of intramolecular vibrations, orientational and librational rotations. Simultaneous recording of these responses creates certain difficulties for definite separation of the total signal into its constituent components with femtosecond and picosecond relaxation times. The mentioned circumstances impose high technical requirements on the experimental technique, which, in our opinion, is one of the obstacles to widespread use of multipulse excitation in the liquid. In this paper we show how, using two-pulse nonresonant excitation, to control the intensities of the contributions of individual intramolecular modes into the recorded signal, which allows selection of intramolecular responses and provides qualitatively new possibilities of the analysis of molecular dynamics in the experiment.

To implement the two-pulse control, we have chosen liquid carbon tetrachloride (CCl_4), widely used as a solvent. It is transparent in the visible region and in the 790-nm region (the carrier frequency of the laser radiation) and has low-frequency Raman-active intramolecular modes which are excited by 30-fs laser pulses. In addition, the symmetry of the CCl_4 molecule ensures weak excitation of rotational responses, which is convenient for selective recording of responses of the intramolecular modes.

In analysing the OKE signal it is required to simulate the third-order optical response in the case of single-pulse excitation and the fifth-order response in the case of two-pulse excitation. There are several approaches to the analysis of the OKE signal [25–28]. In this paper, simulation is based on the phenomenological model presented in [20, 21, 29], which allows us to analyse the total OKE signal in the case of single- and multipulse excitation of the medium. Planning and conducting the experiments are carried out in view of [21], which considered theoretically the scenarios of application of a train of excitation pulses to manipulate the vibrational response of the molecules in a liquid in the subpicosecond range.

2. Experiment

The experiments were performed using the polarisation spectroscopy technique with the OKE registration. Unlike conventional experiments on OKE registration [22–24], the

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Received 9 December 2011; revision received 3 March 2012
Kvantovaya Elektronika **42** (4) 332–336 (2012)
Translated by I.A. Ulitkin

medium was excited by a train of two pulses with identical polarisation. In the experiment, different scenarios of excitation were realised by varying the delay between the pump pulses and their relative intensities. Femtosecond pulses were generated by a standard Ti:sapphire laser (JSC 'Avesta-project'), pumped by the second harmonic of a diode-pumped Nd:YAG laser. The output power of the pump laser was 3.9 W. The average energy of the 30-fs pulse at a carrier wavelength of 790 nm was $4. \times 10^{-9}$ J. In the experiment we used the standard scheme of OKE registration [22–24, 29], when the intensity of the probe beam passing through a polariser, sample and analyser is measured. To improve the signal-to-noise ratio, optical heterodyne detection and a lock-in amplifier were used. The sample was a pure filtered liquid (the filter pore size of 0.2 μm) in a 3-mm-thick quartz cuvette.

Figures 1, 3–5 show normalised intensities of OKE signals. The signal intensity characterises the state of induced optical anisotropy of the medium during pulse probing. The probing time is determined by the delay between the effects of the first exciting pulse and probe pulse on the medium. The parameters of the experiment (the delay between the exciting pulses, their relative intensities and durations) are shown in these figures.

3. Analysis of experimental results

The OKE signal is simulated by using the phenomenological approach presented in [21, 29], a brief description of which is as follows. The OKE signal $S(\tau)$ detected in the experiment is a time-averaged instantaneous response of the medium $s(\tau, t)$:

$$S(\tau) = \int_{-\infty}^{\infty} s(\tau, t)\,\mathrm{d}t, \tag{1}$$

where τ is the delay between the pump pulse and probe pulse. The function $s(\tau, t)$ includes the molecular responses $R(t)$, recorded in the experiment:

$$s(\tau, t) \propto E_{\mathrm{lo}}(t-\tau)E_0(t-\tau)[R_{\mathrm{e}}(t) + R_{\mathrm{osc}}(t) + R_{\mathrm{or}}(t) + R_{\mathrm{lib}}(t)]. \tag{2}$$

The exciting pulse $E_{\mathrm{p}}(t)$, the probe pulse $E_0(t)$ and the local oscillator field pulse $E_{\mathrm{lo}}(t)$ have a duration τ_{p} (full width at half maximum), the envelope of their intensity is modelled by the function

$$I_{\mathrm{p}}(t) \propto I_0(t) \propto I_{\mathrm{lo}}(t) \propto \mathrm{sech}\left(\frac{t}{0.38\tau_{\mathrm{p}}}\right).$$

In the case of two excitation pulses the expression for $I_{\mathrm{p}}(t)$ consists of two components:

$$I_{\mathrm{p}}(t) = I_{\mathrm{p}}^{(1)}\mathrm{sech}\left(\frac{t}{0.38\tau_{\mathrm{p}}}\right) + I_{\mathrm{p}}^{(2)}\mathrm{sech}\left(\frac{t-\tau_{12}}{0.38\tau_{\mathrm{p}}}\right), \tag{3}$$

where $I_{\mathrm{p}}^{(k)}$ is the intensity of the kth pulse; τ_{12} is the delay between the pulses.

The response of electronic hyperpolarisability $R_{\mathrm{e}}(t)$ is proportional to the coefficient of the 'instantaneous' electronic cubic hyperpolarisability γ and the exciting pulse intensity $I_{\mathrm{p}}(t)$:

$$R_{\mathrm{e}}(t) \propto \gamma I_{\mathrm{p}}(t). \tag{4}$$

The response function of the intramolecular vibrations $R_{\mathrm{osc}}(t)$ has the form:

$$R_{\mathrm{osc}}(t) \propto \sum_{i=1}^{N} r_{\mathrm{osc}}(\Omega_{\mathrm{osc}}^{(i)}, \tau_{\mathrm{osc}}^{(i)}, \alpha_{\mathrm{osc}}^{(i)}, t), \tag{5}$$

$$r_{\mathrm{osc}}(\Omega_{\mathrm{osc}}, \tau_{\mathrm{osc}}, \alpha_{\mathrm{osc}}, t) = \alpha_{\mathrm{osc}}^2(\Omega_{\mathrm{osc}}^2 - \tau_{\mathrm{osc}}^{-2})^{-1/2} \times \int_0^{\infty} I_{\mathrm{p}}(t-t')\exp\left(-\frac{t'}{\tau_{\mathrm{osc}}}\right)\sin[(\Omega_{\mathrm{osc}}^2 - \tau_{\mathrm{osc}}^{-2})^{1/2}t']\mathrm{d}t',$$

where N is the number of vibrational modes excited by the pump pulse; $\alpha_{\mathrm{osc}}^{(i)}$ is the coefficient characterising the change in polarisability of the molecule upon ith mode oscillation; $\Omega_{\mathrm{osc}}^{(i)}$ and $\tau_{\mathrm{osc}}^{(i)}$ are the oscillation frequency and the relaxation time of the ith mode.

If the molecules have anisotropic polarisabilities ($\Delta\alpha \neq 0$), the laser pulse creates orientational anisotropy of the molecules, whose relaxation occurs according to the mechanism of rotational diffusion. This molecular response is described by the expression:

$$R_{\mathrm{or}}(t) \propto \Delta\alpha^2 \int_0^{\infty} I_{\mathrm{p}}(t-t')\exp\left(-\frac{t'}{\tau_{\mathrm{or}}}\right)\mathrm{d}t', \tag{6}$$

where τ_{or} is the relaxation time of the orientational response.

In addition to the orientational anisotropy of the molecules, the librations of the molecules with a frequency Ω_{lib} are also excited. Description of the librational response is based on the distribution function of the libration frequencies $\rho(\Omega_{\mathrm{lib}})$, which reflects the local inhomogeneity of the medium:

$$R_{\mathrm{lib}}(t) \propto \int_0^{\infty} \mathrm{d}\Omega_{\mathrm{lib}}\rho(\Omega_{\mathrm{lib}})r_{\mathrm{lib}}(\Omega_{\mathrm{lib}}, t), \tag{7}$$

$$r_{\mathrm{lib}}(\Omega_{\mathrm{lib}}, t) = \Delta\alpha^2\Omega_{\mathrm{lib}}^{-1}\int_0^{\infty} I_{\mathrm{p}}(t-t')\sin[\Omega_{\mathrm{lib}}, t']\mathrm{d}t'.$$

To describe the distribution function of the libration response, we will use the results of [29], where it was shown that this function, in particular for molecules of chloroform in the liquid, is given by the Maxwell distribution:

$$\rho(\Omega_{\mathrm{lib}}) \propto \Omega_{\mathrm{lib}}^2\exp\left[-\frac{\Omega_{\mathrm{lib}}^2}{2(\Delta\Omega_{\mathrm{lib}})^2}\right], \tag{8}$$

where $\Delta\Omega_{\mathrm{lib}}$ is the parameter (width) of the distribution function.

In analysing the experimental data (Figs 1, 3–5) we have selected a single set of constants which are used to simulate the OKE signal in all scenarios of excitation: $\Omega_{\mathrm{osc}}^{(1)} = 216 \pm 4$ cm^{-1}, $\tau_{\mathrm{osc}}^{(1)} = 1.9 \pm 0.3$ ps, $\Omega_{\mathrm{osc}}^{(2)} = 312 \pm 6$ cm^{-1}, $\tau_{\mathrm{osc}}^{(2)} = 1.1 \pm 0.1$ ps, $\Omega_{\mathrm{osc}}^{(3)} \equiv 458$ cm^{-1}, $\tau_{\mathrm{osc}}^{(3)} \equiv 1.9$ ps, $\tau_{\mathrm{or}} = 0.5 \pm 0.07$ ps, $\Delta\Omega_{\mathrm{lib}} = 117 \pm 8$ cm^{-1}. Figure 2 shows the Raman-active modes of intramolecular vibrations of CCl_4 according to the data of the Raman scattering and the imaginary part of the Fourier transform of the OKE signal shown in Fig. 1a. One can see that the laser pulses effectively excite the modes 216 and 312 cm^{-1}. The mode 458 cm^{-1} in the OKE signal is not observed. To simulate the vibrational dynamics, the value of the frequency $\Omega_{\mathrm{osc}}^{(3)}$ was taken from Raman spectroscopy data and it was assumed that $\tau_{\mathrm{osc}}^{(3)} \equiv \tau_{\mathrm{osc}}^{(1)}$.

Analysis of experimental data has shown that in carbon tetrachloride all the above molecular responses are excited. In this case, the intensity of the orientational and librational responses due to the symmetry of the molecule CCl_4 is small

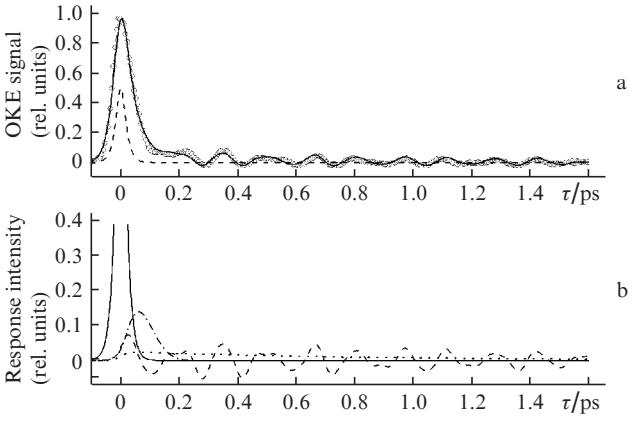

Figure 1. OKE signal in liquid CCl_4 under single-pulse excitation (τ_p = 30 fs): points are the experimental data, solid curve – simulation, dashed curve – envelope of the intensity of the exciting pulse (a) and simulation results of the OKE signal components: solid curve is the electronic response R_e, dashed curve – the vibrational response R_{osc}, dash-and-dot curve – the libration response R_{lib}, dotted curve – the orientational response R_{or} (b).

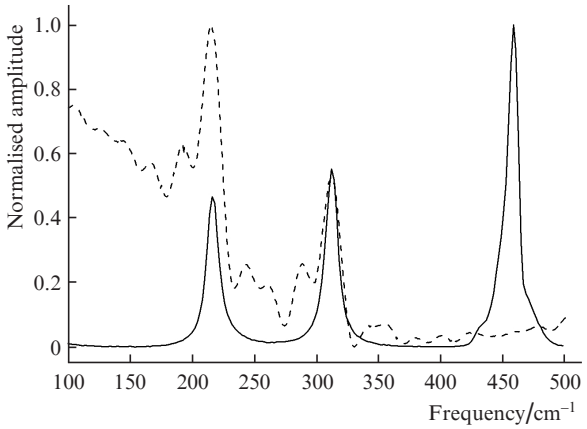

Figure 2. Raman-active modes of intramolecular vibrations of CCl_4. The solid curve is the data of Raman scattering, dashed curve – imaginary part of the Fourier transform of the OKE signal, shown in Fig. 1a.

compared, for example, with similar responses in chloroform $CHCl_3$ [20]. The subject of our primary interest are the responses of intramolecular coherent oscillations $r^{(i)}_{osc}$. Simulations show that the absence of response of the mode 458 cm^{-1} in the OKE signal is caused by the fact that the laser pulse duration is comparable with the period of molecular vibrations of the mode 458 cm^{-1}. As a result, first, there is no effective excitation of the mode, and secondly, in the process of registration of coherent oscillations of the mode 458 cm^{-1} integration of the molecular response $r^{(3)}_{osc}$ and the probe pulse [see (1) and (2)] leads to loss of information about the high-frequency component in the total OKE signal.

4. Discussion of the results

In this paper, experimental realisation of laser control of induced anisotropy in a liquid is based on two-pulse excitation of the medium. This control is achieved through constructive or destructive interference of vibrational packets, corresponding to the regime of amplification or suppression of vibrational responses in the OKE signal. Since the response of the vibrational modes 458 cm^{-1} in the OKE signal is not observed (Fig. 2), in the experiment we have focused on manipulating the intensities of the vibrational responses of the modes 216 and 312 cm^{-1}. We have analysed three scenarios of excitation: (i) strengthening of the response of the mode 216 cm^{-1} and suppression of the response of the mode 312 cm^{-1}; (ii) strengthening of the response of the mode 312 cm^{-1} and suppression of the response of the mode 216 cm^{-1}; and (iii) suppression of the responses of both low-frequency modes. The values of the relative pump-pulse intensity and of the delay between the pulses were selected directly in the experiment while monitoring the changes in the OKE signal. Amplification or suppression of the vibrational mode amplitude after the action of the second exciting pulse is considered in relation to the amplitude of this mode in the absence of the second pulse. Simulation of the vibrational response in the case of two-pulse excitation on the basis of (1)–(3) and (5) takes into account the pulse duration, their intensity and relaxation processes. If we assume that the laser pulses are identical and neglect the relaxation processes, the response of the individual mode will be the sum of two harmonic oscillations excited by the first and second pulses. Accordingly, changes in the amplitude A_{osc} of the response r_{osc} before the second pump pulse ($\tau < \tau_{12}$) and after the second pump pulse ($\tau > \tau_{12}$) can be estimated with the help of the ratio

$$\frac{A_{osc}(\tau > \tau_{12})}{A_{osc}(\tau < \tau_{12})} = 2\left|\cos\left(\tau_{12}\frac{\Omega_{osc}}{2}\right)\right|. \quad (9)$$

The scenario of suppression of the response of the mode 312 cm^{-1} and amplification of the mode 216 cm^{-1} is shown in Fig. 3, where the delay between the pump pulses is 908 fs, and the phases of the intramolecular vibrations at the time of the second pulse action are as follows: 11.7π for the mode 216 cm^{-1}, 16.9π for the mode 312 cm^{-1} and 24.8π for the mode 458 cm^{-1}. Ratio (9), determining the amplification/suppression effectiveness for the given modes, is equal, respectively, to 1.8, 0.2 and 0.5.

An alternative scenario where the response of the mode 312 cm^{-1} is amplified and the response of the mode 216 cm^{-1}

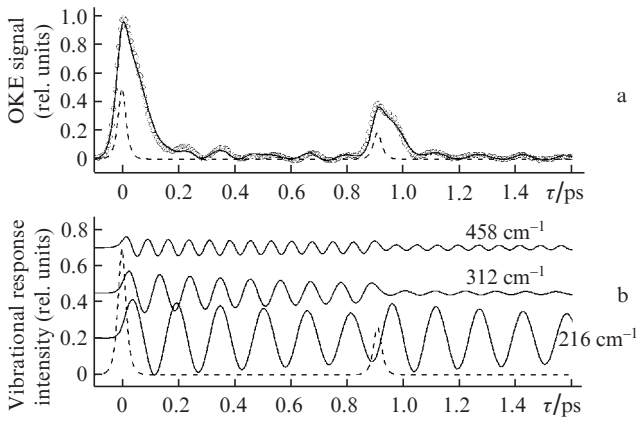

Figure 3. OKE signal in liquid CCl_4 under double-pulse excitation (τ_p = 30 fs, τ_{12} = 845 fs, $I_p^{(2)}/I_p^{(1)}$ = 0.38): points are the experimental data, solid curve – simulation, dashed curve – envelope of the intensity of the exciting pulse (a) and simulation results of the vibrational responses $r^{(i)}_{osc}$: dashed curve is the envelope of the intensity of the exciting pulse (b).

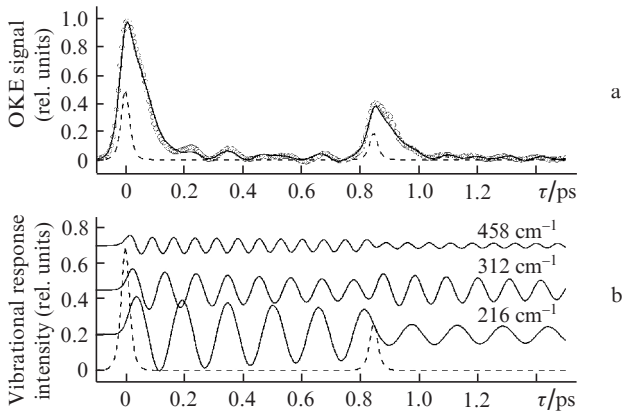

Figure 4. OKE signal in liquid CCl_4 under double-pulse excitation (τ_p = 30 fs, τ_{12} = 845 fs, $I_p^{(2)}/I_p^{(1)}$ = 0.38): points are the experimental data, solid curve – simulation, dashed curve – envelope of the intensity of the exciting pulse (a) and simulation results of the vibrational responses $r_{osc}^{(i)}$: dashed curve is the envelope of the intensity of the exciting pulse (b).

is suppressed is shown in Fig. 4. The delay between the exciting pulses is 845 fs, and the phases of the molecular vibrations during the action of the second pulse is 10.9π for the mode 216 cm^{-1}, 15.8π for the mode 312 cm^{-1} and 23.2π for the mode 458 cm^{-1}. Ratio (9) for these modes is equal, respectively, to 0.2, 1.9 and 0.5.

The third scenario (Fig. 5) is implemented at a delay τ_{12} = 1025 fs and phases of the molecular vibrations during the action of the second pulse 13.2π for the mode 216 cm^{-1}, 19.1π for the mode 312 cm^{-1} and 28π for the mode 458 cm^{-1}. These values lead to suppression of the responses of the vibrational modes 216 and 312 cm^{-1} for which ratio (9) is equal, respectively, to 0.6 and 0.2; for the mode 458 cm^{-1}, this ratio is 2.

As shown above, in the OKE signal the vibrational response of the mode 458 cm^{-1} is not registered. However, simulation indicates that the double-pulse excitation also controls the intensity of the response of the given mode. The scenarios of excitation at delays 908 and 845 fs (Figs 3 and 4) correspond to suppression of the response amplitude. In the scenario with a delay of 1025 fs (Fig. 5) the response amplitude is efficiently amplified. Another important factor is the fact that suppression of the vibrational mode response at delays comparable to the relaxation time requires a decrease in the intensity of the second pump pulse. This is consistent with the results of [20, 21], in which, provided the complete suppression of the response of the vibrational mode, the dependence of the relative intensity of the pump pulse on the delay time between them is used to define the relaxation constant. Note also that in liquids, where intensive rotational vibrational responses are registered along with vibrational responses in the OKE signal, the scenario of complete suppression of the vibrational response at the lowest possible delay between the exciting pulses can be used to extract the rotational response.

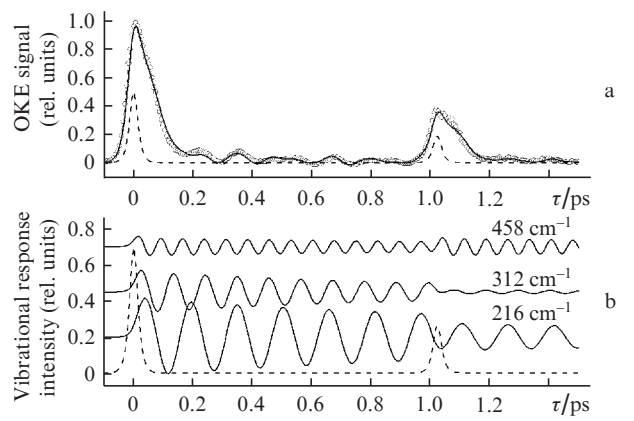

Figure 5. OKE signal in liquid CCl_4 under double-pulse excitation (τ_p = 30 fs, τ_{12} = 1025 fs, $I_p^{(2)}/I_p^{(1)}$ = 0.38): points are the experimental data, solid curve – simulation, dashed curve – envelope of the intensity of the exciting pulse (a) and simulation results of the vibrational responses $r_{osc}^{(i)}$: dashed curve is the envelope of the intensity of the exciting pulse (b).

An important feature of double-pulse excitation as compared to single-pulse excitation is a larger number of monitored parameters. Nevertheless, the number of constants used to simulate the optical response of the medium remains unchanged. This leads to a significant refinement of the procedure of separation of the total OKE signal into its constituent components in the simulation of different scenarios of excitation. Note that our results confirm the applicability of the model [21, 29] for interpretation of the OKE signals with multipulse excitation, as well as confirm experimentally the main results of [21], where the scenarios multipulse control of time-dependent anisotropy in a liquid have been considered theoretically.

In conclusion, we emphasise again the main result of our work – an experimental demonstration of selective spectroscopy of intramolecular vibrations of carbon tetrachloride by double-pulse control of the induced anisotropy of the liquid.

Acknowledgements. This work was supported by a grant from the Centre for the Collective Use of the Planning and Financial Department, by Grant No. NSh-4531.2008.2 of the President of the Russian Federation for Support of the Leading Scientific Schools, and by the Russian Foundation for Basic Research (Grant No. 09-02-00136a).

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