

Multipulse polarisation selective spectroscopy of rotational and vibrational responses of molecules in a liquid

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Abstract. The amplitude control of time-resolved optical responses in a liquid is theoretically analysed under nonresonant irradiation of the system by a train of femtosecond pulses with parallel and orthogonal polarisations. The control parameters, specifying the excitation scenarios, are the duration of pulses, their relative intensities, polarisation, and the delays between the pulses. It is shown that the choice of specific excitation scenarios transfers the system into a state in which only one response is detected from a set of responses of coherent intramolecular Raman active vibrational modes, coherent molecular librations and orientational rotations.

Keywords: polarisation selective spectroscopy, rotational and vibrational responses of molecules in a liquid, optical Kerr effect.

1. Introduction

Currently, femtosecond laser technology is widely used to study the processes with femtosecond and picosecond relaxation times. One of the main methods to study time-resolved optical responses is the use of an exciting pulse–probe pulse scheme. Typically, a femtosecond pulse has a sufficient spectral width for the simultaneous excitation of a train of optical responses. In turn, recording the superposition of responses makes it difficult to decompose an aggregate signal into components. Recording individual responses can be solved by selective multipulse excitation [1]. In this case, a particular excitation scenario is given by pulse train parameters: the pulse intensity, the delay between the pulses, etc. The excitation scenarios are chosen so that in a given state of the system only one response is recorded from a set of optical responses. For the first time this technique was used to extract the response of individual modes in the molecular crystal of α -perylene [2] and LiTaO₃ crystal [3].

In a liquid, rovibrational responses at room temperature have subpicosecond relaxation times. This leads to some difficulties when multipulse excitation is widely used to study intramolecular vibrations, molecular rotations and librations. Recently, two-pulse excitation has been implemented to control the amplitude of the vibrational response in chloroform [4] and carbon tetrachloride [5]. In these experiments use was

made of the pulses with identical linear polarisation and the excitation scenarios were set by varying the relative intensity of the pulses and the delay between them. The medium was probed by a third pulse to observe the optical Kerr effect (OKE) [6–8]. Experiments [4, 5] showed that the two-pulse excitation can amplify/suppress the response of the vibrational modes; as a result, the response of the specified mode can be extracted from the OKE signal. In addition, in the case of delays in the order of a half period of intramolecular vibrations, the vibrational response can be completely suppressed and the rotational response can be observed.

It should be noted that the scenarios with the pulses having identical polarisation do not allow one to control the amplitude of rotational responses, because the action of each pulse leads to an increase in the intensity of these responses. Nikiforov et al. [9] have shown experimentally that the use of orthogonally polarised pulses reduces the amplitude of the rotational responses. Thus, experimental papers [4, 5, 9] suggest that for the selective spectroscopy of molecular vibrational and rotational responses in liquids, pulses with both parallel and orthogonal polarisations should be used in the case of nonresonant excitation. The above-said has motivated this work, i.e., a theoretical analysis of molecular responses in the OKE signal under excitation by a train of pulses with parallel and orthogonal polarisations. We also give examples of modelling the scenarios of excitation by pulse trains for selective spectroscopy of time-resolved responses in a liquid.

2. Theory

The OKE-signal analysis is based on simulation of the superposition of the electronic response and the response of coherent molecular vibrations and rotations. There are several approaches to calculate the OKE signal (see, for example, Refs [10–13]). In our case, the description of the time-resolved optical response of a medium is based on the model of independent vibrational and rotational motions of the molecules in a liquid [14], which allows one to calculate the optical response during multipulse excitation. Modelling of the excitation scenarios by a train of pulses with identical linear polarisation is described in [4, 5, 15]. Note that the theoretical analysis of the OKE signal in a liquid excited by orthogonally polarised pulses is absent in the literature.

When recording the OKE in a liquid according to the pump–probe scheme, the signal $S(\tau)$ is measured, which is determined by the probe pulse $E_0(t-\tau)$ and the local oscillator field $E_{l0}(t-\tau)$ after passing through the sample and crossed polariser and analyser:

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$$S(\tau) \propto \int_{-\infty}^{\infty} dt E_0(t - \tau) E_{lo}(t - \tau) [\alpha_{yy}(t) - \alpha_{xx}(t)] \\ \propto \int_{-\infty}^{\infty} dt E_0(t - \tau) E_{lo}(t - \tau) R(t), \quad (1)$$

where τ is the delay between the probe pulse and the response of the local oscillator; $\alpha_{yy}(t)$ and $\alpha_{xx}(t)$ are the components of the medium polarisability; and the x and y axes are specified in the medium by the direction of polarisation of the excitation pulses. The response function $R(t)$ is proportional to the anisotropy of the medium, which is formed by the electronic and rovibrational molecular responses as a result of the pump pulse action. The nonresonant optical response $R(t)$ is a linear function of the pump pulse intensity $I_p(t)$:

$$R(I_p^{(1)}(t), I_p^{(2)}(t), I_p^{(3)}(t), \dots) = R(I_p^{(1)}(t)) \\ + R(I_p^{(2)}(t)) + R(I_p^{(3)}(t)) + \dots \quad (2)$$

Suppose that the medium is excited by pump pulses, which are linearly polarised along the axes x [$I_{px}^{(i)}(t)$] and y [$I_{py}^{(i)}(t)$]. Because the response of the medium to the action of the pulse is determined by the induced anisotropy of the medium polarisability, $R(t) \propto \alpha_{yy}(t) - \alpha_{xx}(t)$, then the responses to identical pulses with intensities $I_{px}(t)$ and $I_{py}(t)$, differing only in the polarisation, will be equal in amplitude and opposite in sign:

$$R(I_{px}(t)) = -R(I_{py}(t)). \quad (3)$$

Thus, expression (3) determines the response of the medium to the action of the pump pulses with intensities $I_{px}(t)$ and $I_{py}(t)$. Hence, based on the linearity of the response function $R(t)$, the response of the medium to a pulse train with intensity

$$I_p(t) = \sum_i I_{py}^{(i)}(t) + \sum_j I_{px}^{(j)}(t) \quad (4)$$

will be described by the expression

$$R(I_{py}^{(1)}(t), I_{py}^{(2)}(t), \dots, I_{px}^{(1)}(t), I_{px}^{(2)}(t), \dots) = \sum_i R(I_{py}^{(i)}(t)) \\ - \sum_j R(I_{px}^{(j)}(t)) = R\left(\sum_i I_{py}^{(i)}(t) - \sum_j I_{px}^{(j)}(t)\right). \quad (5)$$

To model the result of multipulse excitation, following [14], let us consider briefly the vibrational and rotational responses of molecules in a liquid. The response of intramolecular vibrations has the form

$$R_{osc}(t) \propto \sum_{m=1}^M r_{osc}(\Omega_{osc}^{(m)}, \tau_{osc}^{(m)}, \alpha_{osc}^{(m)}, t), \\ r_{osc}(\Omega_{osc}, \tau_{osc}, \alpha_{osc}, t) = \alpha_{osc}^2 (\Omega_{osc}^2 - \tau_{osc}^{-2})^{-1/2} \\ \times \int_0^{\infty} I_p(t - t') \exp(-t'/\tau_{osc}) \sin[(\Omega_{osc}^2 - \tau_{osc}^{-2})^{1/2} t'] dt', \quad (6)$$

where M is the number of Raman-active vibrational modes; $\alpha_{osc}^{(m)}$ is the coefficient characterising the change in polarisabil-

ity of molecules upon excitation of the m th mode; and $\Omega_{osc}^{(m)}$ and $\tau_{osc}^{(m)}$ are the oscillation frequency and the relaxation time of the m th mode. For the qualitative analysis we consider the action of a train of delta-pump pulses on a medium:

$$I_p(t) = \sum_{i=1}^n I_p^{(i)} \delta(t - \tau_{li}), \quad (7)$$

where $I_p^{(i)}$ is the intensity of the i th pulse and τ_{li} is the delay of the i th pulse. In this case, the response of the molecular modes $r_{osc}(t)$ is described by the expression

$$r_{osc}(t) \propto \alpha_{osc}^2 (\Omega'_{osc})^{-1} \\ \times \sum_{i=1}^n H(\tau_{li}) I_p^{(i)} \exp[-(t - \tau_{li})/\tau_{osc}] \sin[\Omega'_{osc}(t - \tau_{li})], \quad (8) \\ \Omega'_{osc} = (\Omega_{osc}^2 - \tau_{osc}^{-2})^{1/2},$$

where $H(\tau)$ is the Heaviside function. Expression (8) shows that the dependence of response amplitude on the multipulse excitation scenario can be used in the spectroscopy of molecular vibrations. For example, for two-pulse excitation

$$I_p(t) = I_{py}^{(1)} \delta(t) + I_{py}^{(2)} \delta(t - \tau_{12}), \quad (9)$$

the intensity of the second pulse can be chosen such that the amplitude of the oscillations excited by this pulse was equal to the amplitude of the oscillations excited by the first pulse at the time of action of the second pulse: $I_{py}^{(2)} = I_{py}^{(1)} \exp(-\tau_{12}/\tau_{osc})$. Then, after the action of the second pulse the vibrational response is described by the expression

$$r_{osc}(t > \tau_{12}) \propto A_{osc}(t, \tau_{12}) \sin\left[\Omega'_{osc}\left(t - \frac{1}{2}\tau_{12}\right)\right], \quad (10)$$

$$A_{osc}(t, \tau_{12}) = 2I_{py}^{(1)} \exp(-t/\tau_{osc}) \cos\left(\frac{1}{2}\Omega'_{osc}\tau_{12}\right).$$

The change in the amplitude A_{osc} of the response r_{osc} immediately after the action of the second pulse can be estimated by the formula

$$A_{osc}(\tau = \tau_{12} + 0)/A_{osc}(\tau = \tau_{12} - 0) \\ = 2 \left| \cos\left(\frac{1}{2}\Omega'_{osc}\tau_{12}\right) \right|. \quad (11)$$

Equation (11) shows that at the delay $\tau_{12} = 2\pi k/\Omega'_{osc}$ (k is a positive integer), the second pulse will increase the response of the mode with the frequency Ω'_{osc} in the OKE signal. When the conditions

$$\tau_{12} = (\pi + 2\pi k)/\Omega'_{osc}, \quad (12)$$

$$I_{py}^{(2)} = I_{py}^{(1)} \exp[-(\pi + 2\pi k)/(\Omega'_{osc}\tau_{osc})]$$

are fulfilled, the second pulse will completely suppress the response of the mode with the frequency Ω'_{osc} in the OKE signal. When using a train of two orthogonally polarised pulses

$$I_p(t) = I_{\text{py}}^{(1)}\delta(t) + I_{\text{px}}^{(2)}\delta(t - \tau_{12}), \quad (13)$$

the vibrational response of a given mode, provided that $I_{\text{px}}^{(2)} = I_{\text{py}}^{(1)}\exp(-\tau_{12}/\tau_{\text{osc}})$, will be described by the expression

$$r_{\text{osc}}(t > \tau_{12}) \propto A_{\text{osc}}(t, \tau_{12}) \cos\left[\Omega'_{\text{osc}}\left(t - \frac{1}{2}\tau_{12}\right)\right], \quad (14)$$

$$A_{\text{osc}}(t, \tau_{12}) = 2I_{\text{py}}^{(1)}\exp(-t/\tau_{\text{osc}})\sin\left(\frac{1}{2}\Omega'_{\text{osc}}\tau_{12}\right).$$

The change in the amplitude after the action of the second pump pulse is determined by the expression

$$\begin{aligned} A_{\text{osc}}(\tau = \tau_{12} + 0)/A_{\text{osc}}(\tau = \tau_{12} - 0) \\ = 2\left|\sin\left(\frac{1}{2}\Omega'_{\text{osc}}\tau_{12}\right)\right|. \end{aligned} \quad (15)$$

In this case, at the delay $\tau_{12} = (\pi + \pi k)/\Omega'_{\text{osc}}$, the vibrational response will be amplified, and when the conditions

$$\tau_{12} = 2\pi k/\Omega'_{\text{osc}}, \quad (16)$$

$$I_{\text{px}}^{(2)} = I_{\text{py}}^{(1)}\exp[-2\pi k/(\Omega'_{\text{osc}}\tau_{\text{osc}})]$$

are fulfilled, the vibrational response will be suppressed.

The orientational response is given by the expression [14]

$$R_{\text{or}}(t) \propto \Delta\alpha^2 \int_0^\infty I_p(t - t')\exp(-t'/\tau_{\text{or}})dt', \quad (17)$$

where $\Delta\alpha$ determines the anisotropy of polarisability of a molecule and τ_{or} is the relaxation time of the orientational response. For multipulse excitation (7), the orientational response is described by the expression

$$R_{\text{or}}(t) \propto \Delta\alpha^2 \sum_i H(\tau_{1i})I_p^{(i)}\exp[-(t - \tau_{1i})/\tau_{\text{or}}]. \quad (18)$$

According to (5), pulses with parallel polarisation amplify the response, and pulses with orthogonal polarisation suppress the response. For example, when two orthogonally polarised pulses participate in excitation (13), expression (18) takes the form

$$R_{\text{or}}(t) \propto \exp(-t/\tau_{\text{or}})[I_{\text{py}}^{(1)} - I_{\text{px}}^{(2)}\exp(\tau_{12}/\tau_{\text{or}})]. \quad (19)$$

This shows that at the second pulse intensity $I_{\text{px}}^{(2)} = I_{\text{py}}^{(1)}\exp(-\tau_{12}/\tau_{\text{or}})$, the orientational response is completely suppressed.

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

$$R_{\text{lib}}(t) \propto \Delta\alpha^2 \int_0^\infty d\Omega_{\text{lib}}\rho(\Omega_{\text{lib}})r_{\text{lib}}(\Omega_{\text{lib}}, t), \quad (20)$$

$$r_{\text{lib}}(\Omega_{\text{lib}}, t) = \Omega_{\text{lib}}^{-1} \int_0^\infty I_p(t - t')\sin(\Omega_{\text{lib}}t')dt'.$$

The form of the libration response is determined by the properties of the distribution function $\rho(\Omega_{\text{lib}})$. The response in the case of multipulse excitation (4) will be equal to the difference of responses excited by orthogonally polarised pulses:

$$R_{\text{lib}}(t) = \sum_i R_{\text{lib}}(I_{\text{py}}^{(i)}(t)) - \sum_j R_{\text{lib}}(I_{\text{px}}^{(j)}(t)). \quad (21)$$

Expression (21) also points to the possibility of controlling the libration response amplitude, by using a train of pulses with different polarisation and intensity.

The electronic response $R_{\text{el}}(t)$ is proportional to the coefficient of 'instantaneous' electronic cubic hyperpolarisability γ . In the case of multipulse excitation (4), its form will be determined by the intensity of the pump pulse envelope:

$$R_{\text{el}}(t) \propto \gamma \left[\sum_i I_{\text{py}}^{(i)}(t) - \sum_j I_{\text{px}}^{(j)}(t) \right]. \quad (22)$$

The considered properties of excitation of the responses of the ultrafast OKE by a train of orthogonally polarised pulses can be used for spectroscopy of molecular motions. Below, we present some examples of modelling multipulse excitation in the liquid for selective recording of individual molecular responses.

3. Modelling

To model a medium, we used the liquid chloroform characteristics presented in [5]. Chloroform is a liquid transparent in the visible region, whose molecules have polarisability anisotropy, Raman-active low-frequency oscillation modes with frequencies $\Omega_{\text{osc}}^{(1)} = 258 \text{ cm}^{-1}$ and $\Omega_{\text{osc}}^{(2)} = 362 \text{ cm}^{-1}$ with the relaxation times $\tau_{\text{osc}}^{(1)} = 1.5 \text{ ps}$ and $\tau_{\text{osc}}^{(2)} = 1.1 \text{ ps}$ at room temperature. The relaxation time of the orientational response τ_{or} is 1.28 ps. The distribution function of the libration frequencies is given by

$$\rho(\Omega_{\text{lib}}) \propto \Omega_{\text{lib}}^2 \exp[-\Omega_{\text{lib}}^2/(2\Delta\Omega_{\text{lib}}^2)], \quad (23)$$

where the parameter $\Delta\Omega_{\text{lib}}$, specifying the width of the contour, is 30 cm^{-1} . In the modelling it was assumed that the i th pulse intensity envelope has a Gaussian shape:

$$I_p^{(i)}(t) = A_p^{(i)}\exp[-(t - \tau_{1i})^2/\tau_0^2], \quad (24)$$

where $A_p^{(i)}$ is the intensity of the i th pulse, and the duration of all the pulses is the same and equal to τ_0 .

The simulation shows that the use of two pump pulses with orthogonal polarisation eliminates the orientational response in the OKE signal. This fact can be used to extract vibrational and libration responses. Figures 1 and 2 show the results of the OKE-signal calculation at different delays between the pump pulses. In the scenario with a delay $\tau_{12} = 2\pi/\Omega_{\text{osc}}^{(2)} = 91 \text{ fs}$ and an intensity ratio $I_{\text{px}}^{(2)}/I_{\text{py}}^{(1)} = 0.92$, orientational and vibrational (a mode with a frequency 362 cm^{-1}) responses are simultaneously suppressed. After the action of the pump pulses, the libration response and the

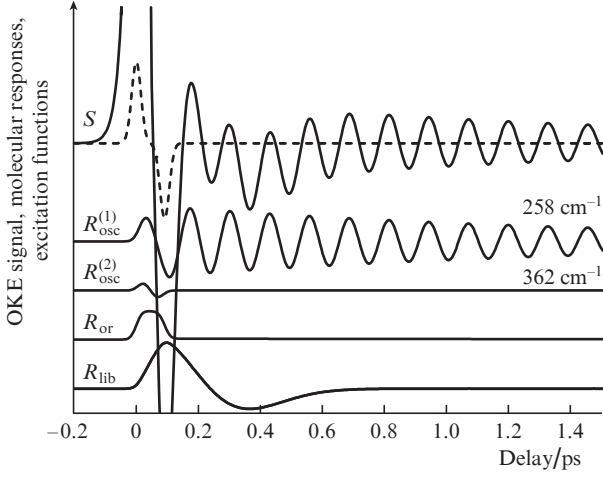


Figure 1. OKE signal S , vibrational responses $R_{\text{osc}}^{(1)}$ and $R_{\text{osc}}^{(2)}$, orientational response R_{or} and libration response R_{lib} (solid curves), and excitation function $f_{\text{ex}}(t) = I_{\text{py}}(t) - I_{\text{px}}(t)$ (dashed curve). The pulse duration is $\tau_0 = 20$ fs, the delay between the pulses is $\tau_{12} = 91$ fs, the intensity ratio is $I_{\text{px}}^{(2)}/I_{\text{py}}^{(1)} = 0.92$.

response of a mode with the frequency 258 cm^{-1} are extracted in the OKE signal. In the scenario with the parameters $\tau_{12} = 2\pi/\Omega_{\text{osc}}^{(1)} = 128$ fs and $I_{\text{px}}^{(2)}/I_{\text{py}}^{(1)} = 0.91$, the libration response and the response of a mode with the frequency 362 cm^{-1} are extracted. If the pulse duration is increased up to $\tau_0 = 35$ fs, only the libration response will be observed in the OKE signal after the action of the pump pulse (Fig. 3), because, due to the comparability of the probe pulse duration to the period of oscillations, the vibrational response is weakly excited at the frequency 362 cm^{-1} and averaged during probing.

Analysis of the multipulse excitation scenarios showed the following. The trains of polarisation-alternating pulses, whose intensities are limited by a Gaussian profile of width Γ , provided that the delay between the pulses is much shorter than the relaxation time of the responses, do not excite orientational and libration responses:

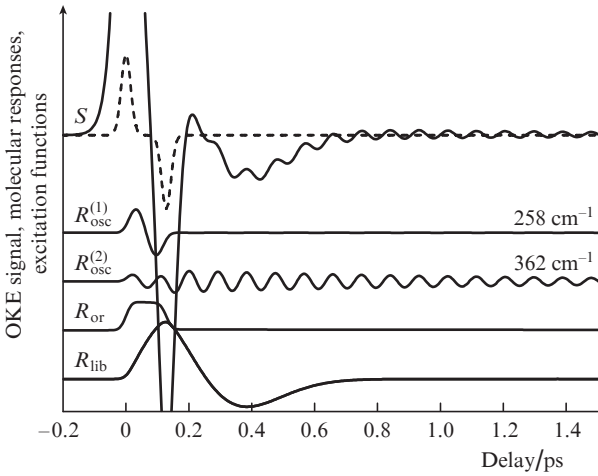


Figure 2. OKE signal S , vibrational responses $R_{\text{osc}}^{(1)}$ and $R_{\text{osc}}^{(2)}$, orientational response R_{or} and libration response R_{lib} (solid curves), and excitation function $f_{\text{ex}}(t) = I_{\text{py}}(t) - I_{\text{px}}(t)$ (dashed curve). The pulse duration is $\tau_0 = 20$ fs, the delay between the pulses is $\tau_{12} = 128$ fs, the intensity ratio is $I_{\text{px}}^{(2)}/I_{\text{py}}^{(1)} = 0.91$.

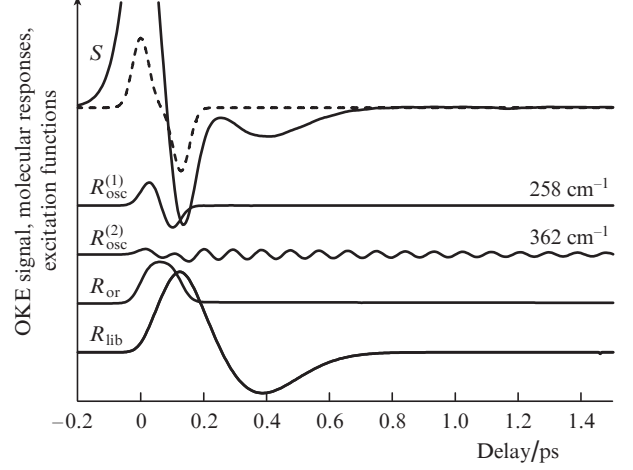


Figure 3. OKE signal S , vibrational responses $R_{\text{osc}}^{(1)}$ and $R_{\text{osc}}^{(2)}$, orientational response R_{or} and libration response R_{lib} (solid curves), and excitation function $f_{\text{ex}}(t) = I_{\text{py}}(t) - I_{\text{px}}(t)$ (dashed curve). The pulse duration is $\tau_0 = 35$ fs, the delay between the pulses is $\tau_{12} = 128$ fs, the intensity ratio is $I_{\text{px}}^{(2)}/I_{\text{py}}^{(1)} = 0.91$.

$$I_{\text{p}}(t) = I_{\text{py}}(t) + I_{\text{px}}(t),$$

$$I_{\text{py}}(t) = A_{\text{p}} \sum_{j=-N}^N \exp[-(2j\tau_{12}/\Gamma)^2] \exp\{-[(t - 2j\tau_{12})/\tau_0]^2\},$$

$$I_{\text{px}}(t) = A_{\text{p}} \sum_{j=-N}^N \exp\{-[(1 + 2j)\tau_{12}/\Gamma]^2\} \quad (25)$$

$$\times \exp\{-[t - (1 + 2j)\tau_{12}]/\tau_0\}^2\},$$

where $4N + 2$ is the number of pulses in the train, and A_{p} is a constant. According to (5), when use is made of a train of orthogonally polarised pulses, as an excitation function the molecular response argument has the difference between the intensity of pulses with y and x polarisations $f_{\text{ex}}(t) = I_{\text{py}}(t) - I_{\text{px}}(t)$ (Fig. 4).

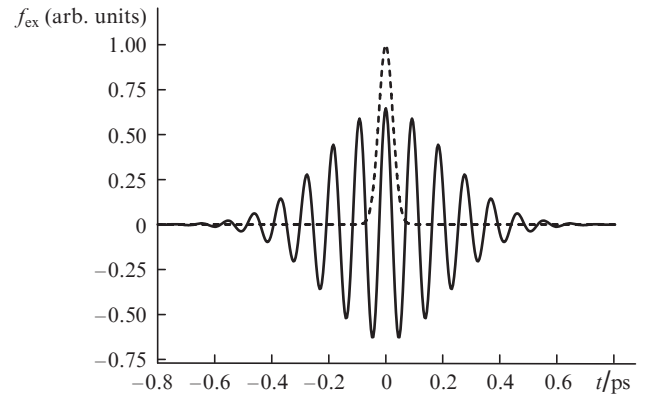


Figure 4. Excitation function $f_{\text{ex}}(t)$ for a train of pulses (25) with parameters $N = 10$, $\Gamma = 300$ fs, $\tau_{12} = 46$ fs, $\tau_0 = 35$ fs (solid curve) and excitation function for a single pulse $f_{\text{ex}}(t) = I_{\text{py}}(t)$ of duration $\tau_0 = 35$ fs (dashed curve).

The spectrum of the $f_{\text{ex}}(t)$ function with the parameters $N = 10$, $\Gamma = 300$ fs, $\tau_{12} = \pi/\Omega_{\text{osc}}^{(2)} = 46$ fs, $\tau_0 = 35$ fs is shown in Fig. 5. One can see that in the frequency region of 362 cm^{-1} there is a maximum, which causes the effective excitation of a mode with the frequency $\Omega_{\text{osc}}^{(2)} = 362 \text{ cm}^{-1}$. In this case, in the frequency region of 258 cm^{-1} , the amplitude spectrum is close to zero. Thus, the pulse train from the whole set of molecular responses extracts only the vibrational response of a mode with the frequency $\Omega_{\text{osc}} = 362 \text{ cm}^{-1}$. It follows from Fig. 5, which shows the real part of the Fourier transform of a single 35-fs pump pulse, that it simultaneously excites all the responses (Fig. 6). The effectiveness of the excitation of a mode with the frequency 362 cm^{-1} is much less than in the case of excitation by a pulse train (25), so that the observation of a weak response against the background of other responses is difficult. The results of modelling of the OKE signal excited by a pulse train (25) are shown in Fig. 7. It is clearly seen that the OKE signal after the action of the pulse train includes only the response of a mode at the frequency 362 cm^{-1} .

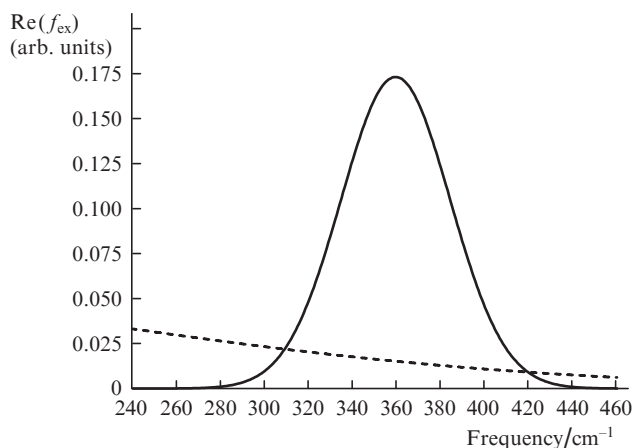


Figure 5. Real part of the Fourier transform of the excitation function f_{ex} , shown in Fig. 4.

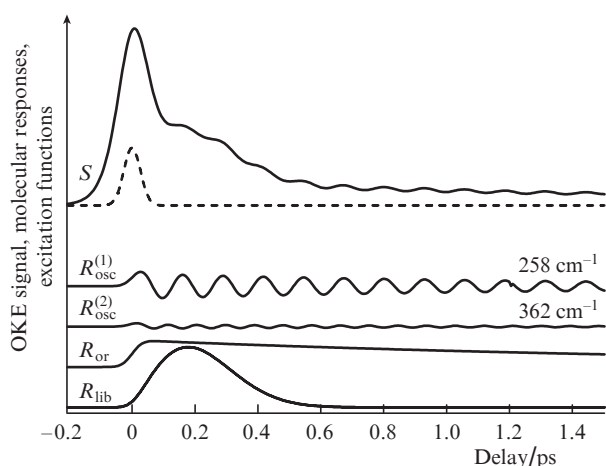


Figure 6. OKE signal S , vibrational responses $R_{\text{osc}}^{(1)}$ and $R_{\text{osc}}^{(2)}$, orientational response R_{or} and libration response R_{lib} (solid curves), and excitation function for a single pulse of duration $\tau_0 = 35$ fs (dashed curve).

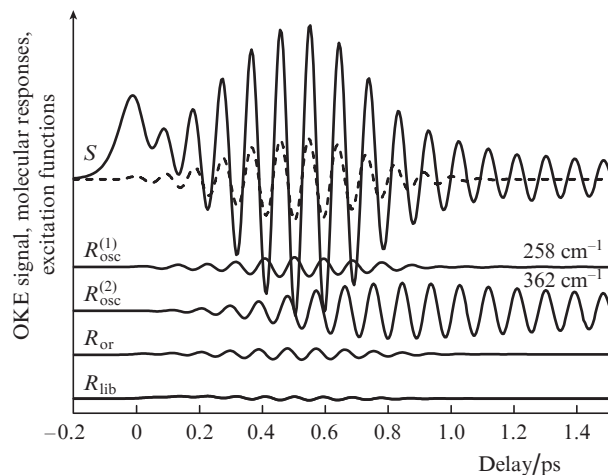


Figure 7. OKE signal S , vibrational responses $R_{\text{osc}}^{(1)}$ and $R_{\text{osc}}^{(2)}$, orientational response R_{or} and libration response R_{lib} (solid curves), and excitation function for a train of pulses (25) with the parameters $N = 10$, $\Gamma = 300$ fs, $\tau_{12} = 46$ fs, $\tau_0 = 35$ fs.

4. Discussion

The modelling shows that an orthogonally polarised pulse train in a liquid can control the amplitudes of vibrational and rotational molecular responses. This is due to the fact that the pulses that differ only in the direction of polarisation excite molecular responses (3) that are the same in amplitude and different in sign. By varying the duration, intensity, polarisation and number of pulses, the scenarios of the effective excitation of some and suppression of other molecular responses are specified. In other words, certain excitation scenarios implement selective polarisation spectroscopy of molecular vibrational and rotational motions.

For example, Nikiforov et al. [5] showed that a train of two parallel-polarised pulses extracts the orientational response in the OKE signal in chloroform. We considered above the examples in which two pump orthogonally polarised pulses extract the libration response and the responses of each vibrational mode in chloroform. Thus, the two-pulse scenarios are possible in chloroform for the selective spectroscopy of molecular motions.

In liquids, where rotational responses are effectively excited, the multipulse trains of form (25) are quite promising for the use in selective spectroscopy of intramolecular vibrations. These pulse trains do not excite rotational responses and can extract one of several vibrational modes in the OKE signal. The real part of the Fourier transform of the exciting function has the form

$$\begin{aligned} \text{Re}(f_y(\omega)) &= A_{py} \tau_0 \sqrt{\pi} \exp\left[-\left(\frac{1}{2}\tau_0\omega\right)^2\right] \\ &\times \sum_{j=-N}^N \exp\left[-(2j\tau_{12}/\Gamma)^2\right] \cos(2j\tau_{12}\omega), \\ \text{Re}(f_x(\omega)) &= A_{px} \tau_0 \sqrt{\pi} \exp\left[-\left(\frac{1}{2}\tau_0\omega\right)^2\right] \\ &\times \sum_{j=-N}^N \exp\left\{-[(1+2j)\tau_{12}/\Gamma]^2\right\} \cos[(1+2j)\tau_{12}\omega], \end{aligned} \quad (26)$$

$$f_p(\omega) = f_y(\omega) - f_x(\omega).$$

To extract some vibrational mode with the frequency $\Omega_{\text{osc}}^{(m)}$, the delay τ_{12} between the pulses must be equal to $\pi/\Omega_{\text{osc}}^{(m)}$. In this case, in the frequency region $\Omega_{\text{osc}}^{(m)}$ the spectrum of the exciting function has a maximum. The excitation efficiency is determined by this maximum, which depends, according to (26), on the ratio of the pulse duration τ_0 to the pulse delay τ_{12} : $f(\Omega_{\text{osc}}^{(m)}) \propto \exp[-(\tau_0/\tau_{12})^2]$. Thus, the effective excitation requires the pulse duration to be less than the delay between successive pulses. However, the pulse train with the parameters $\tau_0 \approx \tau_{12}$ should be used at $\tau_0 \approx \pi/\Omega_{\text{osc}}^{(m)}$, when single-pulse excitation of oscillations becomes ineffective.

A single pump pulse excites intense rotational responses, and recording of weak vibrational responses against their background is technically challenging. For example, the simulation shows that when chloroform is excited by a single pulse with $\tau_0 = 35$ fs, the vibrational response of a mode with the frequency $\Omega_{\text{osc}}^{(2)} = 362 \text{ cm}^{-1}$ ($\pi/\Omega_{\text{osc}}^{(2)} = 46$ fs) is superimposed on the response mode with the frequency $\Omega_{\text{osc}}^{(1)} = 258 \text{ cm}^{-1}$ and intensive rotational responses (see Fig. 6). This leads to the fact that the amplitude ratio of the response of a mode with the frequency 362 cm^{-1} to the amplitude of other responses is of the order of 10^{-3} . Therefore, in an experiment the signal-to-noise ratio should be much greater than 10^3 for a confident recording of the response of a mode with the frequency 362 cm^{-1} . Under excitation by a pulse train (25) with the above parameters, only one response of a mode with the frequency 362 cm^{-1} is observed in the OKE signal.

The excitation selectivity is determined by the width of the maximum in the region of the frequency $\Omega_{\text{osc}}^{(m)}$ of interest. Figure 8 shows the dependence of the excitation function amplitude on the detuning $d\omega = \omega - \Omega_{\text{osc}}^{(m)}$. It can be seen that the selectivity in using a train of pulses increases with increasing parameter Γ , which specifies the width of the envelope contour and, hence, the number of pulses incident into it. It is possible to increase the width of the contour and improve the excitation selectivity until the width of the contour is much smaller than the relaxation time of the response: $\Gamma \ll \tau_{\text{osc}}^{(m)}$. If the width of the contour is comparable to the relaxation time or larger, the increase in Γ does not lead to higher selectivity.

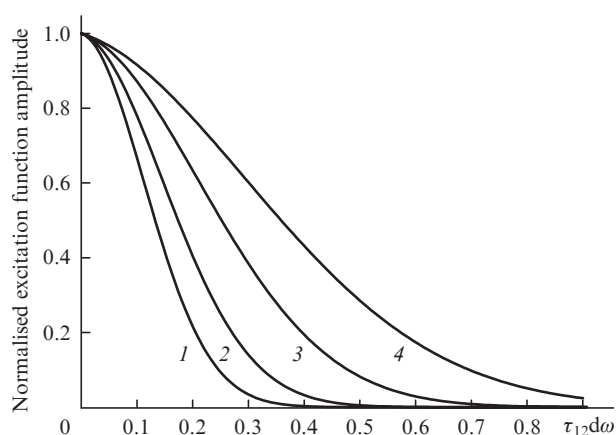


Figure 8. Excitation function amplitude for the train of pulses (25) as a function of detuning $d\omega = \omega - \Omega_{\text{osc}}^{(m)}$ at $\tau_{12}/\tau_0 = 1.82$, $\Gamma/\tau_{12} = 12$ (1), 9 (2), 6 (3) and 4 (4).

5. Conclusions

Theoretical analysis of the OKE signal under excitation by a train of pulses with different linear polarisation showed the possibility of selective control of the amplitudes of vibrational and rotational responses. This possibility is based on the following facts. Vibrational responses are amplified or suppressed, depending on the delay between the pulses. The main criterion is the difference between the phases of the vibrations caused by each pump pulse. In this case, the vibrational response is amplified or suppressed by the train of pump pulses with both parallel and orthogonal polarisation. In controlling the rotational response amplitudes, the main criterion is polarisation of pulses. Pulses with parallel polarisation amplify rotational responses, and pulses with orthogonal polarisation suppress them.

The OKE-signal simulation in liquid chloroform showed the following. The two-pulse excitation scenarios, where the control parameters are the relative intensity of the pulses, the delay between them, their duration and polarisation, allow observation of all the molecular responses: the response of one of the two Raman-active vibrational modes, the orientational and libration responses. This greatly improves the accuracy of analysis of data on the OKE compared with single-pulse excitation when superposition of all the molecular response is observed. Thus, the two-pulse excitation scenarios can be successfully applied for selective spectroscopy of vibrational and rotational motions of the molecules in a liquid.

If the molecule has a number of Raman-active vibrational modes, the response of one of them is advisable to extract by using a train of orthogonally polarised pulses of form (25). The simulation shows that the trains of form (25) have a narrow spectral band of excitation of molecular vibrations, and they do not excite the rotational response. Note also that the absence of rotational responses in the OKE signal greatly increases the possibility of observation of weak high-frequency vibrational responses when the pulse duration is comparable with the period of oscillations.

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