Mode-Selective Optical Kerr Effect Spectroscopy

Xiang Zhu,† Richard A. Farrer,† Erez Gershgoren,‡ Henry C. Kapteyn,‡ and John T. Fourkas*,†

Eugene F. Merkert Chemistry Center, Boston College, Chestnut Hill, Massachusetts 02467, and JILA, University of Colorado, and the National Institute of Standards and Technology, Boulder, Colorado 80309

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We demonstrate that by using two pump pulses with independently controllable polarizations, intensity, and timing, different contributions to the optical Kerr effect (OKE) signal in liquids can be enhanced and suppressed. When both pump pulses have the same polarization, intramolecular vibrations can be enhanced or suppressed without affecting the reorientational diffusion contribution to the signal significantly. Similar control can be exerted over intramolecular vibrations when the pump pulses are perpendicularly polarized, and under these conditions it is also possible to suppress the reorientational diffusion component of the signal completely. When two intramolecular vibrational modes are present in the signal, it is possible to enhance one while completely suppressing the other if the pump polarizations and timing are chosen appropriately. This technique should be a useful means for enhancing contrast in OKE microscopy.

Ultrafast optical Kerr effect (OKE) spectroscopy has found broad use in probing low-frequency, Raman-active modes of liquids.[1−4] OKE spectroscopy has been used to study collective intermolecular modes, low-frequency intramolecular modes, and collective reorientational diffusion in liquids. On time scales of up to a few picoseconds all three of these phenomena contribute significantly to the OKE signal, whereas on longer time scales the latter two effects dominate. However, interferences in the data can often make it difficult to separate contributions due to individual processes, for example the dynamics of a particular intramolecular vibrational mode or of reorientational diffusion.

Nelson, Weiner, and co-workers showed that by using phase masks to create trains of appropriately timed, evenly spaced pulses for excitation in an impulsive stimulated scattering[5] (transient grating[6]) geometry, they could strongly enhance the OKE signal from selected vibrational modes of a crystal.[7,8] When the period between the pulses matches the vibrational period, the selected mode is resonantly and preferentially excited. Recent work demonstrated that for OKE spectroscopy such pulse trains can be generated using a combination of a dispersive delay line and an interferometer.[9] However, all this past work used pulse trains of constant linear polarization.

In principle, excitation pulse trains can be used to control the contributions to the OKE signal in liquids. However, if all of the pulses have the same polarization, the contribution from collective reorientational diffusion will be enhanced roughly as strongly as that from any intramolecular vibrational mode of interest. Here we demonstrate that, similar to what has been demonstrated for lattice vibrations in crystalline quartz,[10] intramolecular vibrational contributions to the OKE signal in liquids can be controlled using two pump pulses with independently controlled polarization, intensity and timing in an optical-heterodyne-detected polarization-spectroscopy geometry.[11] We further demonstrate that by using a pair of perpendicularly polarized pump pulses it is possible to enhance a desired vibration while eliminating the reorientational component of the signal.

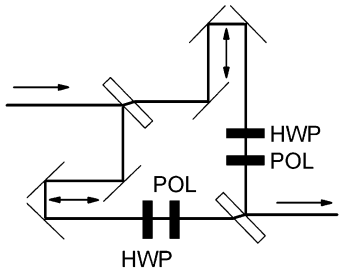

Figure 1. Schematic of the optics for creation of dual pump pulses. HWP = half-wave plate, POL = polarizer.

Our basic experimental setup for optical-heterodyne-detected OKE spectroscopy has been described in detail elsewhere.[4,12] Briefly, a Ti:sapphire laser produces 60 fs pulses at a center wavelength of 800 nm with a repetition rate of 76 MHz and an average power of 500 mW. The output is split into a pump beam and a weaker probe beam, each of which is chopped at a different frequency. The pump beam is polarized vertically and focused into the sample. The probe beam traverses a computer-controlled delay line, a polarizer and a quarter-wave plate before being focused onto the sample by the same lens as the pump. The probe is then recollimated and polarization-analyzed. To implement optical heterodyne detection, the polarizer is set slightly off of 45°, the fast axis of the quarter-wave plate is set at 45°, and the analyzer is set at −45°. The polarization-analyzed light is focused onto a low-noise amplified photodiode connected to a digital lock-in amplifier referenced to the sum of the two chopping frequencies.

To implement the multiple-pump scheme, we have modified the pump-beam portion of the setup as shown in Figure 1 to allow the timing, intensity, and polarization of each pump beam to be adjusted independently. The pump beam is split by a 50% beam splitter. The two halves of the pump beam each traverse an adjustable delay line, a half-wave plate, and a Polarcor polarizer before being recombined at a second beam splitter and sent on to the sample.

* To whom correspondence should be addressed; email: fourkas@bc.edu.
† Boston College.
‡ JILA.

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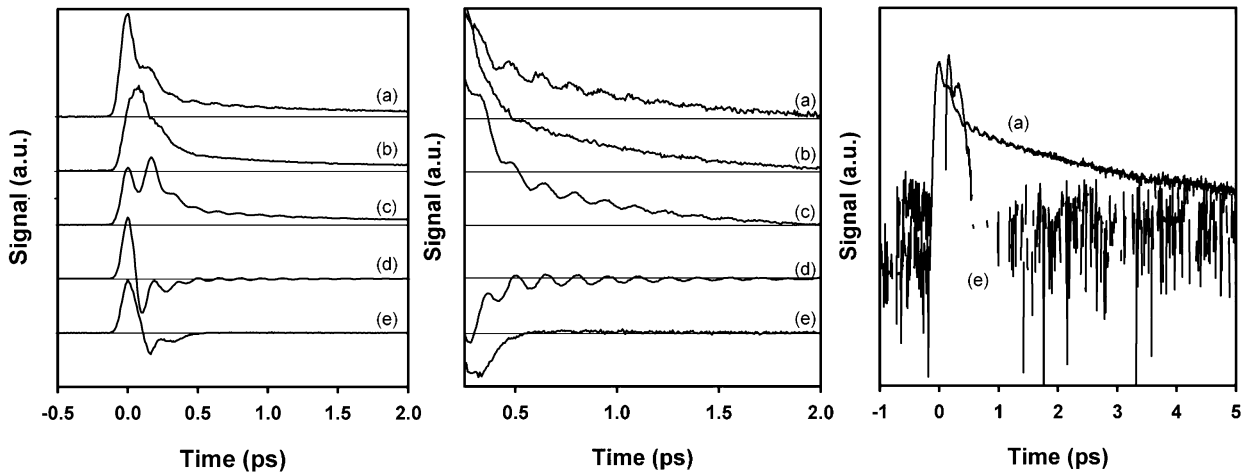

Figure 2. OKE decays for room-temperature propionitrile with (a) a single pump pulse, (b) parallel-polarized pump pulses separated by one-half period of the intramolecular vibration, (c) parallel-polarized pump pulses separated by one period of the intramolecular vibration, (d) perpendicularly polarized pump pulses separated by one-half period of the intramolecular vibration, and (e) perpendicularly polarized pump pulses separated by one period of the intramolecular vibration. The left panel shows the full decays, the middle panel shows a zoomed-in view of the decays after the electronic response, and the right panel shows semilog plots of trace (a) and the negative of trace (e), demonstrating the complete suppression of the reorientational signal. The horizontal lines in the left and center panels show the location of zero signal amplitude for each trace.

The net effect of using multiple pump pulses is to create a linear superposition of third-order response functions at different times. In an optical-heterodyne-detected OKE experiment with a pump beam that is polarized vertically and a probe beam that is polarized at 45°, the signal of interest is proportional to the $R^{(3)}_{xyxy}(\tau)$ tensor element of the response function, where τ denotes the delay time and the subscripts denote lab-frame polarization components.[11] If the pump beam is instead polarized horizontally, the signal is proportional to $-R^{(3)}_{xyxy}(\tau)$. Thus, given two vertically polarized pump pulses separated by time t_p, the signal is proportional to $R^{(3)}_{xyxy}(\tau) + aR^{(3)}_{xyxy}(\tau - t_p)$, where a is a constant that depends on the relative intensities of the two pump pulses and the delay time τ is assumed to be measured relative to the first pump pulse. Similarly, when the first pump pulse is polarized vertically and the second is polarized horizontally, the signal is proportional to $R^{(3)}_{xyxy}(\tau) - aR^{(3)}_{xyxy}(\tau - t_p)$. Thus, the use of multiple pump pulses allows us to control the relative importance of different contributions to the depolarized signal by interfering the response function with itself at different delay times. This should be contrasted with techniques that use multiple beams of different polarizations to interfere different tensor elements of the response function at the same delay time.[13−15] Although the latter type of technique allows for discrimination among contributions to the response with different tensorial symmetry (e.g., depolarized vs isotropic modes), it cannot be used to control the relative contributions of modes with the same symmetry (e.g., depolarized vibrations and reorientational diffusion).

Given this background, the strategy for controlling the relative contribution of an intramolecular vibration to the OKE signal is straightforward. We consider first the case of parallel-polarized pump pulses. The contribution of an intramolecular vibrational mode to $R^{(3)}_{xyxy}(\tau)$ is approximately proportional to $\sin(\omega\tau)\exp(-\tau/\tau_d)$, where ω is the vibrational frequency and τ_d is the dephasing time. Thus, if the pump pulses are separated by a full period of the vibration, the responses arising from vibration for the two pump pulses will interfere constructively, and the vibration will be enhanced. If the pump pulses are separated by a half period of the vibration, the responses will interfere destructively, and by choosing the appropriate relative pump intensities it should be possible to suppress the contribution of the vibration entirely. We illustrate the implementation of this concept in Figure 2 in the case of propionitrile. Trace a in the left and center panels of Figure 2 shows the OKE decay for propionitrile when only a single pump pulse is employed. Following the electronic response at zero delay time, there is a contribution from coherently excited intermolecular modes that decays away over ∼2 ps, a contribution from collective reorientation that decays exponentially over many picoseconds, and a decaying oscillatory contribution from an intramolecular vibrational mode with a frequency of 220 cm^{-1} (corresponding to a period of 152 fs).[16] Trace b shows the propionitrile OKE decay for two pump pulses that are separated by 76 fs. The ratio of pump pulse intensities has been adjusted to eliminate the contribution of the intramolecular vibration completely while retaining the reorientational decay. Trace c shows the propionitrile OKE decay for two pump pulses that are separated by 152 fs. In this case the amplitude of the vibrational and reorientational portions of the signal remain comparable, as both of them are enhanced similarly by the second pump pulse.

We now turn to the case of perpendicularly polarized pump pulses. As discussed above, in this situation the response functions from each pump pulse are of opposite sign. For intramolecular vibrations, this reversal of sign is equivalent to a 180° shift in the sine-wave portion of their contribution to the response. Thus, perpendicularly polarized pulses separated by a full period of a vibration lead to a destructive interference of the response functions, whereas pulses separated by half a period lead to a constructive interference; this is exactly the opposite of what happens with parallel-polarized pump pulses.

We next consider the effect of perpendicularly polarized pump pulses on the diffusive reorientation component of the signal. For simple liquids composed of symmetric-top molecules, orientational relaxation is exponential, with a time constant τ_r on the order of picoseconds or longer. Thus, the reorientational contribution to the signal in this situation is proportional to $\exp(-\tau/\tau_r) - a\exp(-[\tau - t_p]/\tau_r) = [1 - a\exp(t_p/\tau_r)]\exp(-\tau/\tau_r)$. By adjusting the relative intensities of the two pulses, the quantity in brackets can be made to vanish, removing the contribution to the signal from diffusive reorientation. Note that for liquids composed of more complex molecules, the signal from diffusive reorientation is given by a sum of exponentials with different time constants and amplitudes, which makes it impossible to suppress the reorientational signal completely.

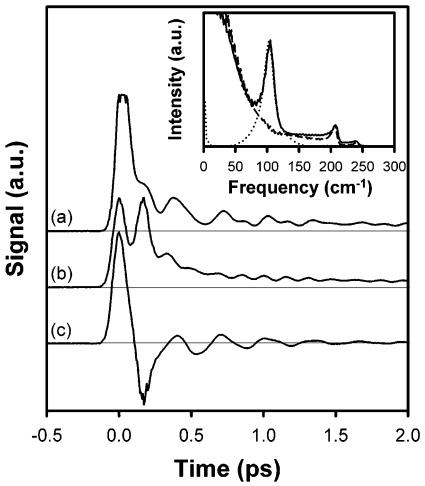

Figure 3. OKE decays for room-temperature S_2Cl_2 with (a) a single pump pulse, (b) parallel-polarized pump pulses separated by one cycle of the higher-frequency intramolecular vibration, and (c) perpendicularly polarized pump pulses separated by one cycle of the higher-frequency intramolecular vibration. The horizontal lines indicate the location of zero signal level for each trace. The inset shows the square of the imaginary portion of the Fourier transform of the portion of the decays after the electronic responses; the solid line is the single-pump data, the dashed line is the parallel-pump data, and the dotted line is the perpendicular-pump data. The two-pump spectra have been scaled such that the enhanced vibration is equal in intensity to that in the single-pump spectrum in each case. These data demonstrate the strong mode selectivity of the two-pulse pumping scheme.

However, so long as t_p is considerably shorter than the smallest τ_r, it should still be possible to suppress the reorientational contribution to the signal almost completely.

We demonstrate these effects in the left and center panels of Figure 2. In the traces labeled (d), the pump pulses are separated by half of a vibrational period, whereas in the traces labeled (e) they are separated by a full vibrational period. Note that, as discussed above, the second pulse generates a negative-going signal. The intensities of the two pulses have been adjusted such that the reorientational component is absent in both of these decays, as is confirmed in the right panel of Figure 2 by a comparison of semilog plots of the data with a single pump pulse and the negative of the data from trace (e). The intramolecular vibrational mode contributes strongly to the decay in trace (d), but only the intermolecular and electronic responses are evident in trace (e).

When more than one intramolecular vibration contributes to the OKE signal, paired pump pulses can also be used to select among them. Shown in Figure 3a is the room-temperature OKE decay for S_2Cl_2 with a single pump pulse. Two strong vibrational modes are evident, one[17] at 105 cm^{-1} (with a corresponding period of 318 fs) and another[17] at 206 cm^{-1} (with a corresponding period of 162 fs). By using two parallel-polarized pump pulses separated by 159 fs with appropriate relative intensities, it is possible to suppress the lower-frequency mode nearly completely (Figure 3b). However, because the higher-frequency mode is at nearly twice the frequency of the other mode, it is not possible to enhance the lower-frequency mode selectively with parallel-polarized pump pulses. This can be accomplished instead with perpendicularly polarized pump pulses separated by 162 fs, as shown in Figure 3c. As demonstrated by the power spectra of each of these decays in the inset of Figure 3, the mode selectivity from the pump pairs is excellent.

Nonlinear optical techniques are finding increasing use in optical microscopy,[18−22] in part because they can provide both three-dimensional resolution and unique types of contrast. OKE spectroscopy is only just beginning to be added to the arsenal of nonlinear optical techniques used in microscopy, however.[23] OKE spectroscopy has the potential to generate contrast based on a number of different mechanisms, including Raman-active intramolecular vibrations and collective reorientation. To attain maximal contrast in OKE microscopy, it would be useful to be able to suppress any unwanted contributions to the signal. For instance, for imaging of biological samples it would be desirable to suppress the reorientational contribution to the signal to focus on low-frequency vibrational modes of proteins, which appear at frequencies of 600 cm^{-1} and higher.[24] This can be accomplished using the technique described here, which can be implemented readily in an OKE microscopy setup.

Although the experiments described here employ two pulses, effecting control over *n* contributions to the OKE signal will generally require the use of *n* pulses. Our work underscores the utility of using polarization as a factor in the control scheme. Ultimately, the use of pulse-shaping technology with amplitude and polarization control[25] should provide the means for inducing a strong enhancement of any desired OKE contribution with the simultaneous suppression of all other modes.

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