Understanding the vibrational mode-specific polarization effects in femtosecond Raman-induced Kerr-effect spectroscopy

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Optically heterodyne-detected femtosecond Raman-induced Kerr-effect spectroscopy (OHD-FRIKES) was observed in neat cyclohexane. In this Letter, an examination of the effect of the Raman pump ellipticity on the multiplex OHD-FRIKES spectra is discussed. The Raman pump ellipticity scanned OHD-FRIKES results reproduce anomalous observables from previous OHD-FRIKES experiments and suggest new methods of tracking transient vibrational mode polarization in complex systems. © 2016 Optical Society of America

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Coherent Raman scattering (CRS) is a well-established field of vibrational spectroscopy. In particular, femtosecond stimulated Raman scattering (FSRS) has been established as a versatile form of CRS that can deliver simultaneous high temporal and spectral resolutions on the order of tens of femtosecond and wavenumbers. However, transient FSRS signals can have low signal to noise, making positive identification of dynamic vibrational features difficult. Hence, developing methods of improving experimental techniques in FSRS by increasing the interaction length of the mixing process and improving the sensitivity by lowering the noise floor is important.

Similar to rotating polarization coherent anti-Stokes Raman scattering (RP-CARS) [1–4], polarization dependent excitation and detection schemes have been applied to FSRS. Using an optical Kerr effect, where the plane of polarization in light is rotated by a transient birefringence in a sample induced by an intense pump beam, the Raman-induced Kerr-effect scattering (RIKES) has been thoroughly studied in single-mode stimulated Raman scattering (SRS) [5–11]. RIKES occurs where the rotation of light occurs at a stimulated Raman resonance, allowing for a polarization sensitive excitation and detection scheme to be applied to FSRS.

Based on the success of FSRS, the Mathies group developed a multiplex RIKES experiment: femtosecond Raman-induced Kerr-effect scattering (FRIKES). In the work of Shim and Mathies [12], the FRIKES experiment was performed using a circularly polarized Raman pump and a linearly polarized Stokes field. The FRIKES signal was observed by recording the scattering that transmitted through a linear polarizer set perpendicular to the polarization of the Stokes field. This experiment still observed residual Stokes field which necessitated background removal. In subsequent FRIKES experiments [13,14], the background removal of the transmitted Stokes field has been performed by keeping a chopper in the Raman pump path, making FRIKES data acquisition analogous to FSRS.

FRIKES has been used to suppress background signals of non-interacting Stokes fields and other polarization sensitive background signals [13–19]. However, outside of the work of Balakrishnan et al. [14] and a collection of Fourier-transform time domain experiments [20–23], FRIKES research has focused on single-mode detection when performed in the frequency domain. In addition, the work of Balakrishnan et al., observed unexplained dispersive and negative lineshapes in an optically heterodyne-detected FRIKES (OHD-FRIKES) experiment. As most frequency domain FRIKES experiments are currently being treated as OHD-FRIKES experiments [13,14], further investigation into the anomalous lineshapes is of strong interest if the polarization sensitive technique is to be applied in future frequency domain studies.

By performing an OHD-FRIKES experiment and treating the data acquisition identically to FSRS experiments, we determine the functional dependence of OHD-FRIKES lineshapes on the Raman pump ellipticity. In a FSRS experiment, data are typically collected in a gain measurement:

\[ I_{\text{FSRS}} = \frac{I_{\text{Stokes, pump on}} - I_{\text{background}}}{I_{\text{Stokes, pump off}} - I_{\text{background}}} \]
where the Stokes field covers the frequency domain of interest relative to the Raman pump, and the background intensity is a measure of any homodyne signal component (normal Raman scattering, fluorescence, etc.). Thus, FSRS spectral lineshapes are very similar to those seen in spontaneous Raman scattering (see Fig. 1), provided the experiments are performed far from the molecular resonance [24].

The observed OHD-FRIKES intensity as a function of the Raman pump ellipticity ($\phi$) can be expressed as [25,26]

$$
\frac{I_\perp(\omega_s)}{I(\omega_s)I_{\perp}(\omega_{pu})} = 9(\chi^{NR})^2 \times \left[ (\omega_R - (\omega_S - \omega_{pu}))^2 \cos^4(2\phi) - (\omega_R - (\omega_S - \omega_{pu}))^2 + \Gamma^2 + \left( \Gamma \cos^2(2\phi) + \Delta(1 - 3\rho) \sin(2\phi) \right)^2 \right].
$$

(2)

In Eq. (2), the overall background amplitude is given by the nonresonant frequency independent Kerr-effect contribution, $\chi^{NR}$, which is modulated in the amplitude by the cos and sin functions of $\phi$. In addition, $\omega_R$ and $\Gamma$ are the Raman frequency and linewidth, $\Delta$ is the resonance parameter, and $\rho$ is the depolarization ratio [25,26]:

$$
\Delta = \frac{N(a_{11}^R)^2}{4\hbar c(\chi^{NR})^2},
$$

(3)

where $a_{11}^R$ is the diagonal Raman tensor element, $N$ is the number of oscillators, and $\hbar c$ is the product of Planck’s constant with the speed of light.

Thus, to understand the dependence of the lineshape on Raman pump ellipticity, one needs to map out the OHD-FRIKES intensity dependence on $\phi$. These are the exact experiments we have performed herein, and compared to simulated spectra from Eq. (2) where all parameters are derived from previous experimental data [2,3].

To perform the FSRS and OHD-FRIKES experiments, we used a spectrometer, as shown in Fig. 2.

Fig. 2. Experimental setup for FSRS and OHD-FRIKES.

Briefly, the 1 W, 800 nm output of a 100 kHz regenerative amplifier (Coherent RegA) is split into two paths for the FSRS experiment. Approximately 500 mW of the amplified output are used to generate a picosecond bandwidth Raman pump field by passing through two identical angle-tuned bandpass filters (CVI optics) at 795 nm. A portion of the remainder of the amplified output is used for white light continuum generation in a sapphire plate which is then temporally compressed by a prism pair. The compressed continuum is then filtered using a set of short- and long-pass filters to create a Stokes field in the spectral region of interest. The pulses are then overlapped spatiotemporally in a collinear geometry in a 2 mm cell. The pump pulse is mechanically chopped so that sequential pump-on and pump-off spectra are obtained in a home-built LabView program. A OHD-FRIKES signal is detected using a spectrograph (Princeton Instruments SP2538) and CCD (PIXIS:100F). The average powers were 500 µW and 20 µW for the Raman pump and the Stokes fields, respectively. Each experimental OHD-FRIKES spectrum shown has a total acquisition time of 100 s.

To control the polarization of both the Raman pump and Stokes fields, thin film linear polarizers and wave plates were used before recombining and focusing into the sample. In the Raman pump field, the linear polarizer removes any residual non-desirable polarization components before passing through a quarter-wave plate to create an elliptical field. To find the setting of most circular polarized light, a linear polarizer was placed in the sample position; then the quarter-wave plate was optimized to have minimized power fluctuations across $2\pi$ rotation of the analyzer at the sample. The Stokes field also passes through a thin film linear polarizer before the sample, then through a high-quality double Glan–Taylor calcite polarizer set to a perpendicular polarization of the Stokes field for extinction of $>1000:1$. The residual Stokes field intensity after the analyzer serves as the local oscillator for the optical heterodyning measured. As there is a portion of space between the two calcite blocks, effectively creating an air-space etalon, having a higher extinction after the sample, comes at the expense of interference fringes, as observed in Fig. 6.

Using this spectrometer, the pump ellipticity was mapped by rotating a quarter-wave plate in 5 deg increments over a full $2\pi$. All experimental and simulated data in Figs. 3–5 have had the modulating background given by the electronic Kerr-effect contribution flattened to better represent the changes in lineshape. The complete OHD-FRIKES dataset is displayed in Fig. 3.

From Fig. 3, it is apparent that the relative intensities of the vibrational modes track with the degree of depolarization ($\rho$) to
the vibrational mode. Specifically, the highly polarized vibrational modes (801 and 1157 cm\(^{-1}\)) track, while the depolarized vibrational modes (1026, 1266, 1444 cm\(^{-1}\)) track together.

Focusing on just the 801 cm\(^{-1}\) mode, one can clearly see the \(\pi\) periodicity in Fig. 4.

To compare to Fig. 4, we simulate Eq. (2) with experimentally determined values [2] for \(\chi^{NR}\), \(\rho\), \(\alpha_{11}\), and \(\Gamma\) across \(\phi\), ranging from 0 to 2\(\pi\). For all simulations performed in this Letter, \(\omega_{pu} = 12578.61\) cm\(^{-1}\), \(\omega_{St} = \omega_{pu} - \omega_R\), and \(\chi^{NR} = 4.8 \times 10^{-14}\) esu. All vibrational mode-dependent properties, including the Raman linewidth (\(\Gamma\)), the depolarization ratio (\(\rho\)), and the Raman tensor element (\(\alpha_{11}\)) were used from the literature [2]. Figure 5 shows the resulting simulation, displaying identical periodicity and dispersive character.

The anomalous behavior observed at \(\phi = 135, 315\) is seen as a discontinuous value of the lineshape at perfectly circularly polarized light. As wave plates display strong wavelength dependent phase retardance, perfect circular polarization for broadband pulses is typically unobtainable.

To examine the behavior of the individual vibrational modes, we plot slices of the 2D mapping experiment, displayed in Fig. 6 and simulated in Fig. 7.

As evident by the agreement in Figs. 6 and 7, the experimental OHD-FRIKES spectra of cyclohexane are well reproduced by simulation of Eq. (2). Explicitly, the simulations show strong agreement on two points:

1. Accurate sign of positive or negative Lorentzian lineshapes at circularly polarized wave plate settings (45, 135, and 225 deg), reproducing the opposite trend of the sign between the highly polarized and the depolarized vibrational modes.
2. Correct phase of dispersive lineshapes at elliptically polarized positions of the quarter-wave plate (90 and 180 deg) for each vibrational mode, including the stronger dispersive character of the highly polarized vibrational modes at 801 and 1157 cm\(^{-1}\).
However, it should be noted that the linewidths in the simulated spectra for the polarized modes are much narrower than observed experimentally. This is likely due to the broader bandwidth of the Raman pump used here than that used in the RP-CARS experiment used for simulation parameters [2].

These results discussed herein suggest that the lineshapes in OHD-FRIKES are highly dependent on the Raman pump ellipticity and the vibrational mode character, particularly the value of the depolarization ratio. One interesting point is that the previous work of Shim and Mathies [12] showed only positive Lorentzian lineshapes. However, it was noted extensively in a more recent study by Balakrishnan et al. [14] that solvent OHD-FRIKES lineshapes were highly dependent on the Raman pump ellipticity.

The experiments and simulations shown here suggest that OHD-FRIKES in a multiplex experiment, such as the one demonstrated herein, can be a sensitive probe of vibrational polarization. By coupling OHD-FRIKES with time resolution dynamics from ultrafast spectroscopy, biological and materials systems that undergo large scale ordering changes can be probed. Of particular interest to biology are intrinsically disordered proteins (IDPs) [27]. IDPs include α-synucleins, αβ, and tau proteins, all of which exhibit fibril formation indicative of Alzheimer’s disease. From a materials perspective, the kinetics of supramolecular materials built from small molecule building blocks can be elucidated by tracking the vibrational polarization [28]. Due to OHD-FRIKES sensitivity to vibrational mode polarization, it is well situated to complement and perhaps improve on current vibrational optical activity techniques for studying large scale structural changes.

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