Measuring vibrational coherence lifetimes in liquid methanol using transient coherent Raman scattering

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Abstract. We demonstrate the measurement of vibrational coherence in liquids using transient coherent Raman scattering. This technique measures the coherence lifetime of vibrational states through the interference of time-delayed coherent Raman-scattered photons using low-power, non-resonant optical pulses. We measure the vibrational lifetime of the 1033 cm\(^{-1}\) mode in liquid methanol. The resulting lifetime agrees with frequency-domain lineshape measurements. This technique is a complementary and in some cases simpler alternative to standard nonlinear spectroscopy techniques.

1. Introduction
Vibrational spectroscopy is a useful tool to study molecular structure in the condensed phase, as the vibrational resonances of molecules are quantized and bond-specific. The study of vibrational modes in liquids is often undertaken using inelastic-scattering of optical photons, such as Raman scattering [1]. In the process of Raman scattering (see Figure 1(a)) an incident photon causes a molecule to make a transition from its ground state to a vibrational excited state by interacting non-resonantly with an electronic excited state. The scattered photon has an energy equal to the incident photon energy minus the resulting vibrational state energy. By spectrally resolving these so-called Stokes photons, it is possible to measure directly the vibrational modes of a complex system in the condensed phase.

A typical Raman Stokes spectrum of methanol, taken using a continuous-wave (CW) laser, is shown in Figure 2. The vibrational resonances appear as peaks in the spectrum. Their frequencies and lineshapes contain structural and dynamical information about the molecular bonds. In particular, the resonances at \(\sim3000\) cm\(^{-1}\) correspond to O-H and C-H vibrations, while the 1000-1500 cm\(^{-1}\) peaks correspond to C-O and C-H vibrations [2]. The results shown in Fig. 2 are in the spontaneous regime, in which the intensity of the scattered photons is linear with the incident light intensity and the photons are scattered isotropically. Nonlinear optical techniques [3] can provide greater signal-to-noise ratio and selectivity of which bonds are excited by using a second incident photon at the Stokes photon energy to stimulate the process (see Figure 1(b)). As a result a so-called anti-Stokes photon is emitted as a fourth field in a phase-matched direction. The directionality and enhanced emission rate of the stimulated process results in better signal-to-noise ratios compared to the spontaneous regime. Using ultrashort...
pulses, one can obtain directly the temporal dynamics of the excited vibrational state. Thus nonlinear techniques such as coherent anti-Stokes Raman spectroscopy (CARS) are often used to reveal the underlying vibrational dynamics associated with complex spectra [4, 5, 6, 7, 8, 9]. Nevertheless, in the case of molecular liquids where inhomogeneous broadening is substantial, the full interpretation of nonlinear spectra can be difficult. When the incident pulses overlap in time, coherent artifacts can arise due to overlapping transition pathways. In addition, the choice of Stokes pulse frequency limits the frequency range of excitations that can be probed simultaneously and requires a separate light source.

Recently it was demonstrated that the interference of spontaneously-scattered Stokes photons can be used to measure vibrational coherence dynamics in solid-state systems [10, 11, 12]. This technique uses two ultrashort pulses with a time delay between them to set up a kind of two-slit experiment. The pulses are in the same spatial mode and are low-intensity such that the probability of both pulses generating Stokes photons at the same time is negligible. Thus any emitted Stokes photon will exist in a superposition of having been created by one pulse and by the other. Measuring the emitted Stokes photons on an optical spectrometer reveals an interference pattern whose visibility depends on the coherence remaining in the system when the second pulse arrives. Thus the interference visibility as a function of time delay provides a direct measure of the coherence lifetime. In this work we extend this technique to the study of vibrational
coherence in liquids, providing another tool to gain insight into the intermolecular dynamics that result in loss of coherence. Unlike frequency-domain spontaneous Raman scattering, the method works in the transient regime, in which the pulse duration is less than the coherence lifetime but greater than the period of the vibrational modes excited. Thus it provides a direct time-domain measurement of the dynamics. In contrast to nonlinear techniques, this method can probe the coherence dynamics of multiple vibrational states with widely separated frequency shifts simultaneously without the need for additional light sources. Coherent artifacts that are present in CARS are eliminated in the technique due to the low single-photon-level Stokes emission. The low single-photon-level excitation also eliminates excitation-induced line broadening that can be problematic in stimulated experiments [11]. Thus the technique, which we refer to in this paper as transient coherent Raman scattering, complements existing methods by providing an alternative and in some cases simpler setup that may be more suitable for applications in which available light sources are limited. In this work, we apply the technique to measure the coherence lifetime of an isolated vibrational resonance in methanol.

2. Experimental Setup

![Figure 3. Schematic of the transient coherent Raman scattering experiment.](image)

The experimental setup is shown in Figure 3. Optical pulses centered at 790 nm with a duration of ~150 fs are generated by a modelocked Ti:sapphire oscillator. The pulses are sent through an optical interferometer to create two identical time-delayed pulses, with the optical delay set by a computer-controlled mechanical stage. The average pump power in the two arms is approximately 280 mW. The time-delayed pulses are focused into a standard 1 cm thick quartz spectrometer cell filled with methanol, and the resulting scattered light is detected by an optical spectrometer with ~0.05 nm resolution. To isolate the Raman-scattered signal from the strong pump pulses, a series of bandpass filters are placed before the spectrometer. Ten independent time-delayed scans are collected for both the fundamental and Raman-scattered pulses, with an acquisition time of 2 seconds per spectrum.

In this experiment, the two time-delayed pump pulses can generate Stokes photons via off-resonant spontaneous Raman scattering. The resulting measured spectrum will display interference at both the laser and Stokes wavelengths. The visibility of the Stokes interference decays as a function of delay due to spontaneous fluctuations in the phase of the excited vibrational state due to intermolecular collisions. The spectrum can be written as a superposition of two spontaneous Raman scattering processes, $I_{\text{sig}}(t) = \left| R_S E_P(t) + R_S E_P(t - \tau)e^{i\phi} \right|^2$, where $E_P$ is the incident pump field, $R_S$ is the associated Stokes Raman tensor, and $\phi$ represents a continuously fluctuating phase, which when integrated over longer and longer delays results in greater loss of visibility [11]. Thus by measuring the spectral interference visibility of the emitted Stokes photons as a function of time delay, one can obtain information about the loss of coherence.
3. Results
As a proof-of-concept experiment we measure the coherence dynamics in liquid methanol, on which experimental investigations and theoretical structural calculations have been made [13, 14, 15, 16, 17, 18, 19, 20, 21]. We capture both the Stokes spectrum at the 1033 cm$^{-1}$ vibrational mode and the pump spectrum for a series of delays between the pumps. For each Stokes and pump spectrum we acquire a background signal by measuring the spectrum at a time delay at which the interference fringes are averaged out due to the finite resolution of the spectrometer. We take data across both positive and negative time delays, corresponding to one of the pulses arriving before the other and vice versa. Exemplary experimental results are shown in Fig. 4.

Figure 4. Exemplary background-subtracted spectra showing laser (top) and Stokes (bottom) interference at time delay $\tau = 0.7$ ps. Overlaid on the Stokes spectra is a numerical fit (in red). The separation between interference fringes corresponds to $1/\tau$.

We analyze the data by assuming that the pump pulse and subsequent Raman line have a Gaussian spectral profile. We subtract the long-time-delay background from the signal and fit the background-subtracted data via a nonlinear least squares method with a function of the form

$$A_1 \exp \left[ -\frac{(x - A_2)^2}{2\sigma^2} \right] \sin(A_3x + A_4)$$

in which $\sigma$ is fixed as the bandwidth of the laser pulse, and the $A_i$ are the fitting parameters. Figure 4 shows a fit result on exemplary background-subtracted Stokes data. After fitting the background-subtracted pump and Stokes spectra, we take a numerical weighted mean of the amplitude fitting parameter $A_1$ over the collected data sets at each delay for both the pump and Stokes spectra. We normalize the Stokes amplitudes by the pump amplitudes to address loss of visibility due to the finite resolution of the spectrometer [11]. The normalized amplitude of the Stokes fits as a function of time delay is then representative of the loss of visibility. We fit the amplitudes for both positive and negative delay with a simple exponential function of the form $B_1 \exp \left( -\frac{|x - B_2|}{B_3} \right)$, where the $B_i$ are the fitting parameters. The fit, shown in Fig. 5, yields a coherence lifetime of $449 \pm 16$ fs. This result is in agreement with the CW Raman frequency-domain linewidth shown in Fig. 2, providing proof-of-principle that transient coherent Raman scattering enables the direct time-domain measurement of coherence lifetimes in liquids.
Figure 5. Coherence lifetime measurements of the 1033 cm$^{-1}$ line of methanol. Plotted is the visibility of the Stokes interference fringes relative to the laser visibility, as a function of time delay $\tau$. The points are experimental data and the solid line is an exponential fit.

4. Conclusion
We have demonstrated that transient coherent Raman scattering is a useful spectroscopic tool for measuring vibrational coherence in liquids. This technique can be used at the single-photon level with low pump powers, does not require more than one laser, and is free of nonlinear artifacts. In addition, using this method it is possible to probe the coherence lifetimes of multiple vibrational excitations simultaneously by measuring the interference visibilities of each Stokes line on an optical spectrometer. This technique provides a complementary perspective and in some cases simpler setup for measuring coherence dynamics in molecular liquids.

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