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ABSTRACT
Coherent Raman scattering (CRS) spectroscopy techniques have been widely developed and optimized for different applications in biomedicine and fundamental science. The most utilized CRS technique has been coherent anti-Stokes Raman scattering (CARS), and more recently, stimulated Raman scattering. Coherent Stokes Raman scattering (CSRS) has been largely ignored mainly because it is often strongly affected by fluorescence, particularly for resonance enhanced measurements. However, in the cases of resonant excitation, the information contained in the CSRS signal can be different and complementary to that of CARS. Here, we combine the approaches of pulse shaping, interferometric heterodyne detection, 8-step phase cycling, and Fourier-transform of time-domain measurements, developed in CARS and 2D electronic spectroscopy communities, to measure resonant CSRS and CARS spectra using a titanium:sapphire oscillator. The signal is essentially background-free (both fluorescent and nonresonant background signals are suppressed) with high spectral resolution and high sensitivity and can access low-energy modes down to $\sim 30$ cm$^{-1}$. We demonstrate the ability to easily select between CSRS and CARS schemes and show an example in which acquisition of both CSRS and CARS spectra allows vibrational modes on the excited electronic state to be distinguished from those on the ground electronic state.

INTRODUCTION

Understanding the nature of low-energy (<200 cm$^{-1}$) vibrational modes is of high significance in several disciplines and can allow insights into the systems under investigation. In biological sciences, for example, low-frequency vibrations may be associated with large-scale nuclear motions in proteins, which can be associated with proteins’ ability to tune their reactivity or enhance energy transfer in photosynthetic light-harvesting.1 In condensed matter physics, low-frequency vibrations can, for example, characterize details of polycrystalline structures,3,4 determine the size of nanomaterials (e.g., 1D single-wall carbon nanotubes, 2D materials), and may assist with identification of a low-temperature noncentrosymmetric phase of matter, such as those that host exotic type-II Weyl fermions. Low-frequency vibrations are typically measured by far-infrared (FIR)/terahertz (THz) spectroscopy,5,6 or by various Raman scattering spectroscopy (RSS) techniques.7–9,10,11 FIR/THz spectroscopy directly probes optically active low-energy vibrations; however, working in this spectral range poses several challenges: broad
and strong water absorption can swamp the system response; generating and detecting light in this spectral range is difficult and lies in what is known as the terahertz gap. On the other hand, Raman techniques typically utilize visible, near-infrared (NIR), or near-ultraviolet (NUV) radiation, allowing the use of standard optical components and greater capabilities for measuring water-containing samples. However, acquiring Raman spectra in low-energy spectral regions usually requires sending the signal through triple-grating spectrographs that have extremely low throughput and detection sensitivity, or by using expensive notch filters, based on ultrathin coatings and volume holographic gratings, with fixed laser wavelengths.\textsuperscript{26–28}

Our approach to access low-energy vibrational modes is based on several ideas that have been separately implemented in coherent anti-Stokes Raman scattering (CARS) techniques\textsuperscript{15} and multidimensional electronic spectroscopy (MDES)\textsuperscript{16–17} (see the section titled Experiment). CARS is part of the family of coherent Raman spectroscopy (CRS) techniques that also includes coherent Stokes Raman scattering (CSRS)\textsuperscript{18} and stimulated Raman scattering (SRS)\textsuperscript{29–31} approaches. There are many similarities between CARS and CSRS schemes: both take advantage of coherent four-wave mixing processes that generate a signal only in specific directions defined by the phase matching condition, which drastically increases the detection sensitivity. Both CARS and CSRS spectra, however, suffer from the presence of nonresonant background (NRB). This background interferes with the signal of interest and complicates the analysis,\textsuperscript{11} although with proper quantification the NRB response can be deconvoluted\textsuperscript{19} and in some circumstances can even enhance sensitivity.\textsuperscript{28,30,31} In many cases, however, the noise from the NRB signal can reduce the sensitivity and resolution of the resonant Raman response, and hence, eliminating the NRB is often desirable.\textsuperscript{14} The contributions from the NRB are even more pronounced in the low-energy region\textsuperscript{22–24} since most of the third-order NRB quantum pathways increase in efficiency with decreasing frequency. SRS methods were initially suggested to be intrinsically free from NRB, and while they are substantially better than CARS in this regard, there are still ubiquitous sources of parasitic signal, which have necessitated the development of specific approaches to realize background-free SRS.\textsuperscript{25}

The main difference between CARS and CSRS processes is that they excite vibrational coherences that are complex conjugates of each other: first two pulses of the CARS process excite $|v_0\rangle$|vibrational coherences in the ground electronic state, while those for the CSRS process generate $|v_0\rangle|v_n\rangle$ coherences. As a consequence, the CSRS signal is detected on the low-energy side of the probe beam, where Raman features are often obscured by the presence of a strong fluorescence background. This is, in essence, the main reason for the preference of CARS over CSRS in the scientific community. In principle, both CSRS and CARS processes should lead to mostly equivalent information on Raman active vibrations, especially when the energies of the excitation beams are tuned far below any electronic transitions. However, in the case of resonantly enhanced RSS, where vibrational excitations on the excited electronic state are possible, the information contained in the CSRS signal can be different and complementary to that of CARS.\textsuperscript{15} Moreover, a simultaneous detection of CSRS and CARS can also be beneficial for the enhanced detection sensitivity.\textsuperscript{27}

Resonant excitation significantly enhances the sensitivity of a four-wave mixing experiment (including CARS and CSRS), but at the cost of added complications, such as generation of fluorescence, described above, and contributions from excited-state pathways. These can include vibrational modes on the excited electronic states, vibronic modes (where the electronic and vibrational degrees of freedom are strongly coupled), or electronic coherences, all of which can introduce additional peaks to the Raman spectrum. The challenge of identifying and separating coherences on ground or excited electronic states, as well as distinguishing between coherences of different nature (vibrational, vibronic, or electronic), has been discussed extensively in relation to CARS\textsuperscript{15} and MDES\textsuperscript{30–31} experiments.

In the case of CARS and CSRS, separating excited electronic state vibrations from the ground electronic state vibrations has been achieved through control over several degrees of freedom: timings between three excitation pulses, polarizations, wavelengths, and detection windows.\textsuperscript{30} Using MDES measurements, the nature of coherences can be identified by comparing peak amplitudes and locations in a 3D spectrum which can be very difficult and time consuming to acquire. In the recent work, pathway selective MDES has been developed to access the specific parts of the 3D spectrum that can reveal the nature of coherences, without having to acquire the full 3D spectrum. The approach we use here is based on these pathway selective MDES experiments.\textsuperscript{30,32–34}

With these measurements, we demonstrate the detection of low-energy vibrational modes with resonant enhancement without the fluorescent background and NRB, and the ability to easily switch between different signal generation pathways. Specifically, we show a direct comparison between CSRS and CARS schemes, which allow us to identify excited-state vibrations and isolate ground state contributions.

**EXPERIMENT**

Our experimental approach utilizes several ideas, developed within CARS and MDES. Specifically, we take advantage of an arrangement of the excitation beams in a box geometry, acquire spectral information in the time domain (i.e., Fourier transform spectroscopy), and use heterodyne detection with phase cycling and a pulse shaper to control the spectral and temporal properties of each individual pulse so that we can controllably access specific quantum pathways. Technical details on the experimental realization are described in the supplementary material, while the conceptual ideas are discussed below.

The box geometry [Figs. 1(a) and 1(c)], frequently used in CARS spectroscopy,\textsuperscript{35,36} spatially separates the signal from the excitation pulses, providing reduced spectral background and greater selectivity of the signal generation pathways. In this geometry, the pump, the Stokes, and the probe beams with wavevectors $k_{\text{pump}}$, $k_{\text{Stokes}}$, and $k_{\text{probe}}$, respectively, are placed at three corners of a square. The signal of interest is emitted on the fourth corner of the square in the direction, $k_{\text{CSRS}} = -k_{\text{pump}} + k_{\text{Stokes}} + k_{\text{probe}}$, for the CSRS signal (or $k_{\text{CARS}} = k_{\text{pump}} - k_{\text{Stokes}} + k_{\text{probe}}$ for CARS), defined by the phase-matching condition. Spatial separation of the signal in this way allows a greater dynamic range and sensitivity of the detection.
FIG. 1. Schematic representation of our pathway-selective CRS experiment. (a) Three spectrally shaped ultrashort laser pulses, arranged in the box geometry, are focused onto the sample to selectively excite different Liouville-space quantum pathways. (b) The first two pulses, the pump and the Stokes, arrive simultaneously, while the third, probe, pulse, delayed by the time $t_z$, generates a four-wave mixing signal, which interferes with the attenuated fourth pulse, referred to as local oscillator (LO). (c) Switching between different signal generation quantum pathways allows for the detection of CSRS and CARS signals in the same direction, defined by the wavevectors $k_{\text{CSRS}} = -k_{\text{pump}} + k_{\text{Stokes}} + k_{\text{probe}}$ and $k_{\text{CARS}} = k_{\text{pump}} - k_{\text{Stokes}} + k_{\text{probe}}$, respectively. In (d) and (e), Liouville-space pathway diagrams are illustrated alongside the schematic representations of CSRS and CARS dipole transitions between electronic singlet states $S_0$ and $S_1$, having the vibrational structure $v_0, v_1, \ldots$. Two distinct CARS pathways, CARS1 and CARS2, are measured in the present work to distinguish between the excited-state and the ground-state vibrations.

In both CARS and CSRS spectroscopic schemes, the pump and the Stokes beams combine to excite the vibrational coherences [Figs. 1(d) and 1(e)] in either the ground or excited electronic state. The probe beam interacts with the vibrational coherences and is scattered into the signal direction with increased (CARS) or decreased (CSRS) energy. In time-domain measurements, the oscillating phases of the vibrational coherences are mapped onto the signal phase which is measured as a function of the delay of the probe beam, $t_z$ [Figs. 1(b) and 1(d)]. A Fourier transform of the data with respect to this time delay yields the spectral information on the vibrational modes. Such a Fourier transform CARS spectroscopy has been applied previously and has the advantage of being able to detect low-energy vibrations and having resolution limited only by the range of the delay. This relieves the need to have spectrally narrow pulses and/or filters with sharp edges. Measuring in the time domain can also help to remove NRB contributions, which persist only while all three pulses overlap in time.

To measure the phase of the signal electric field as well as the amplitude, we use heterodyne detection, which involves interfering the signal with a local oscillator (LO). To record the signal, we use a spectrometer and a CCD, where interference between the signal and the LO generates a spectral interferogram, from which we obtain the phase and the amplitude of the signal. By directly measuring the phase (as opposed to relying on interference between different signal contributions), we are able to get a unique solution to the Fourier transform, eliminating peaks that arise from linear combinations of the intrinsic vibrational modes. Another advantage of heterodyne detection is that the sensitivity of the experiment is further enhanced because the measured response depends linearly on electric field rather than intensity, as is normally the case.

One of the challenges of interferometric detection is that it requires interferometric phase stability between all pulses. This is achieved by generating the four beams using a two-dimensional spatial light modulator (2D-SLM) with a 2D phase grating, ensuring all beams are incident on common optics, or where delays are introduced, they are split into pairs in a particular way that eliminates any phase jitter in the interferogram (details can be found in Refs. 34 and 43 and in the supplementary material). These approaches have been developed particularly for multidimensional coherent electronic spectroscopy and have been applied for CARS spectroscopy as well.

The challenges of heterodyne detection are offset by many advantages. In addition to those mentioned above, measuring the
phase also allows phase cycling\textsuperscript{44–46} thus enabling significant suppression of contributions from undesired signals and enhancement of the signal of interest. In the simplest case, phase cycling involves shifting the phase of one pulse by π, which also shifts the phase of the signal (and the resultant interferogram) by π. Subtracting this from the signal without any phase shift doubles the signal, but removes any contributions (e.g., fluorescence) that do not have the same phase shift. In this case however, there remains a contribution from the interference of the beam that is phase cycled and the LO. To remove this contribution, and all others, we use an eight-step phase cycling, which involves 8 different combinations of pulses with phase shifts such that all that remains when combined in the right way is the interferogram of the signal and the LO. In this way, it is possible to eliminate all contributions from the pathways that do not depend on all four light-matter interactions and enhance the desired signal (see the supplementary material for details). This eliminates, for example, fluorescence background, scatter from the excitation beams, and third-order signals from any other quantum pathways.

In the experiments reported here, the phase cycling is achieved by a 2D-SLM-based pulse shaper. The pulse shaper is configured so that each of the four beams are spectrally dispersed by a diffraction grating and a cylindrical lens in the horizontal direction and are incident on different vertical positions on the 2D-SLM matrix.\textsuperscript{32} This configuration allows control of the spectral amplitude and phase of the pulses. In addition to phase cycling, the phase control allows optimal compression of the pulses to their Fourier-transform limit, ensuring a flat spectral phase over the whole bandwidth which helps with analyzing the spectral interferograms.

Control of the spectral amplitude allows the pulses to be shaped so that specific pathways can be excited. In particular, we begin with broad pulses (covering spectral region of ∼760–870 nm and having FWHM of ∼70 nm) and shape the spectra of the individual beams, as shown in Fig. 2, after which we compress all pulses down to ∼65 fs. Making the pump and the Stokes pulses nondegenerate ensures that any detected signal arises from coherence pathways. In the context of nonresonant Raman spectroscopy, this may seem trivial since all vibrational pathways involve a coherence between vibrational levels. However, in resonant experiments where electronic excitations also occur, a part of the signal can arise from pathways involving excited (or ground) state populations. Indeed, this contribution can dominate the signal and swamp the desired vibrational pathways. Shaping the probe pulse further allows us to select specific resonant pathways and, as a consequence, to generate a signal that is spectrally well separated from the excitation pulses. Pulse shaping provides a flexible and straightforward way of changing between different pathways excited. Instead of tuning the wavelength of different optical parametric amplifiers (OPAs) or changing filters, all that is required is selecting between different amplitude modulation functions applied to the pulse shaping 2D-SLM. In particular, this allows us to easily switch between CARS and CSRS schemes [Figs. 1(c) and 2], both of which can affect ground and excited state vibrational coherences differently. This approach of incorporating pulse shaping in 3rd order spectroscopy has been previously adopted in MDES in order to isolate coherence pathways\textsuperscript{44–46} and is very similar to the approach of the present work.

To demonstrate this technique and its capabilities, we measure the spectra of near-infrared (NIR) cyanine dyes as test samples (see the supplementary material for more description of the samples). Here, we present the results for the NIR cyanine dye IR-813; similar results for other dyes, IR-806 and IR-140, are presented in the supplementary material. The absorption and fluorescence spectra of IR-813 are shown in Fig. 3 together with the broadband laser spectrum (gray) on the background. For convenience, the corresponding energy level diagrams and the dipole transitions are shown in insets.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig2.png}
\caption{The shaped pulse spectra of the pump, the Stokes, the probe (red) and the LO (orange) beams used for the (a) CSRS, (b) CARS1, and (c) CARS2 signal generation pathways. The absorption spectrum of IR-813 is shown shaded in gray on the background. For convenience, the corresponding energy level diagrams and the dipole transitions are shown in insets.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3.png}
\caption{Normalized absorbance (blue) and fluorescence emission (red) spectra of IR-813, and the broadband laser spectrum (gray) on the background.}
\end{figure}
that the signal predominantly arises from the coherence pathways (see the supplementary material for more details on the effect of having greater spectral overlap between the first two pulses). The range of vibrational energies that can be excited is limited by the bandwidth of and energy separation between the pump and the Stokes pulses; namely, it is mostly defined by the spectral cross correlation of the pump and the Stokes pulses, which is imprinted into the relative intensities of the detected Raman features. The probe and the LO spectra are chosen so that the signal overlaps with the spectrum of the LO, which leads to the additional scaling of the relative signal intensities by the spectral shapes of the last two pulses. To reconstruct the relative strengths of the detected Raman peaks it is then necessary to take into account the spectral shapes of all four pulses (see more details on the intensity calibration in the supplementary material).

The quantum pathways being excited in these measurements are shown in Fig. 4. In both the CSRS [Figs. 4(a) and 4(b)] and CARS1 [Figs. 4(c) and 4(d)] experiments, the combination of pulse energies, set by the pulse shaper, allows resonant excitation of vibrational coherences in both ground $S_0$ [Figs. 4(a) and 4(c)] and excited $S_1$ electronic singlet states [Figs. 4(b) and 4(d)]. However, in the CARS2 experiment with a similar resonant enhancement, the pathway involving vibrational coherences in the excited electronic state $S_1$ is expected to have reduced amplitude. This is because to access the same transitions as in the CSRS and CARS1 schemes, the initial state has to be the $|S_0,v_n\rangle$ state, as shown in Fig. 4(f). This state will have some thermal population at equilibrium, but for modes $>200$ cm$^{-1}$, this population will be minimal. Therefore, if there is a substantial contribution to the signal from vibrational modes on the excited electronic state, $S_1$, a significant difference in the detected spectra would be expected between CARS2 and the other two experiments. Other pathways beginning from the ground $|S_0,v_0\rangle$ state are possible in the CARS2 scheme, but these excited-state absorption pathways are equally possible in the CARS1 and CSRS schemes.

![Diagram showing energy levels and Feynman-Liouville diagrams for different pulse sequences.](image)

**FIG. 4.** The generic pathways showing the energy levels and Feynman-Liouville diagrams for the different pulse sequences used. The pathways exciting vibrational coherences in the ground electronic $S_0$ state are shown in (a), (c), and (e), and the pathways leading to vibrational coherences in the excited electronic state $S_1$ are illustrated in (b), (d), and (f).
RESULTS AND DISCUSSION

The Raman intensity spectra, acquired from our measurements, are represented in Fig. 5, where the relative intensities of spectral features have been calibrated and the effects of the different excitation pulse spectra have been taken into account. The positions of Raman peaks, above 200 cm\(^{-1}\) and their widths, are in excellent agreement with surface-enhanced Raman scattering (SERS) spectra reported previously.\(^{47,48}\) The present measurements, however, extend the lower detection limit below 200 cm\(^{-1}\) (down to \(\sim 30\) cm\(^{-1}\)) and reveal additional peaks (all detected Raman signatures are listed in Table II in the supplementary material). The Raman line shapes obtained are slightly asymmetric due to the initial thermal population of the vibrational modes below \(\sim 200\) cm\(^{-1}\) (thermal energy) and asymmetries in the confinement potential.

The comparison of the Raman signals, generated by driving electrons through CSRS, CARS1, and CARS2 quantum pathways, is shown in Fig. 3(a), where all three spectra were acquired sequentially in nearly identical experimental conditions. There is a number of differences between the CSRS and CARS spectra observed. First, the CARS features exhibit lower intensities than those of CSRS: the intensity of the CAR1 signal is lower than the intensity of the CSRS peaks by a factor of \(\sim 2\). More strikingly, the features of the CARS2 spectrum are \(\sim 1200\) times weaker than those of the CSRS spectrum. These numbers take into account differences in integration times and in spectral shapes of the excitation pulses. Since CSRS and CAR1 schemes are driven with the same laser pulses, which interact with the exact same transitions, it is expected that the strengths of the two signals should be of the same order of magnitude. The CARS2 pathway involving the vibrational modes on S0 [Fig. 4(e)] also involves the exact same transitions as CSRS and CAR1, but as discussed above, the pathway involving vibrational coherences on S1 [Fig. 4(f)] are expected to be significantly less efficient than the equivalent pathways in CAR1 and CSRS [Fig. 4(b)]. From this stark difference, we conclude that the dominant contribution to the differences in the signals measured here is vibrational coherences on the S1 excited electronic state. This is further confirmed by the observation that the difference between CAR1 and CARS2 signal amplitudes appears to decrease as the energy of the mode decreases, and the thermal population of these modes at equilibrium increases (see, e.g., the peak at \(138.5 \pm 1.3\) cm\(^{-1}\)).

Another observed difference between the CSRS and CARS spectra is that the spectral tails of individual Raman features are on different sides: in the CARS spectra, the tails are observed on the low-energy side of the spectral features, whereas in the CSRS spectrum, the tails are observed on the high-energy side (see also the amplitude spectra in the supplementary material). This is because the Liouville subspace describing CARS quantum pathways has been folded into its conjugate half to represent both CSRS and CARS spectra in the same spectral domain (with positive Raman shifts).

To highlight the importance of the interferometric detection of the phase information, we compare our data to the equivalent case where only intensity is measured [Fig. 5(b)] by taking the modulus square of our data in the time domain \(t_2\). This keeps the benefits of phase-cycling and interferometric detection for removing the various background signals but introduces additional spurious frequency components. In the case of intensity measurements [shaded in gray in Fig. 5(b)], when the phase information is absent, the acquired Raman spectra are congested with spectral features that are linear combinations of the peaks A–D. This is especially problematic in the low-energy region where rectified Raman features (differences of fundamental Raman modes, including nonoscillating contributions) dominate over intrinsic vibrational modes, making interpretation of the Raman modes challenging.

**FIG. 5.** (a) Comparison of the 1D CSRS, CAR1, and CARS2 (scaled by a factor of 200 in the >200 cm\(^{-1}\) region) calibrated intensity spectra. The most intense CARS2 feature is \(\sim 1200\) times weaker than the corresponding CSRS peak. The Raman features below 200 cm\(^{-1}\) are scaled by a factor of 50 (CSRS), 500 (CAR1), and 200 \(\times\) 20 (CARS2). (b) Comparison of the calibrated 1D CSRS intensity spectra (blue) of the IR-813 with analogous spectra, generated by time-resolved intensity measurements (gray): intensity measurements lead to congested spectra, having additional peaks, corresponding to linear combinations of intrinsic Raman modes. (c) Comparison of the calibrated 1D CSRS spectra (blue) with the spontaneous Raman line shapes (gray), obtained by the conventional Raman spectroscopy apparatus (Renishaw confocal Raman microscope) using the 488 nm excitation wavelength. The fluorescence background in the spontaneous measurements was subtracted. The integration time was set to 50 s to observe noticeable signal. See more information on these measurements in the supplementary material.
Figure 5(c) shows a further comparison of the CSRS spectrum with the results acquired by means of commercial spontaneous Raman spectroscopy instrument (see the supplementary material for details). As expected for a resonance-enhanced coherent Raman spectrum, the signal-to-noise ratio is significantly higher, by a factor of ~250. This is based on the RMS noise in the data and does not take into account the different acquisition parameters, such as the 50 s integration time required for the spontaneous Raman measurements and different volumes probed. In our CRS measurements, the integration time for each step was 30 ms (CSRS), 20 ms (CARS1), and 8 ms (CARS2) with overall integration times per spectrum being ~39 s, ~26 s, and ~10 s, respectively. The comparison also shows that spontaneous Raman features are narrower than those acquired in the CSRS/CARS measurements: the FWHM of the intense Raman feature obtained from the spontaneous Raman experiment was measured to be ~6.5 ± 0.6 cm⁻¹ (compared to ~12.5 ± 2.6 cm⁻¹ for the case of CSRS, ~10.9 ± 2.6 cm⁻¹ for the case of CARS1, and ~11.2 ± 2.6 cm⁻¹ for the case of CARS2). This may be because in the CSRS/CARS measurements we are probing the vibrations on the excited electronic state, which are typically broader, whereas the spontaneous Raman probes the vibrations on the ground electronic state. However, other experimental effects such as power broadening or the longer excitation wavelength may be artificially broadening the spectrum.

CONCLUSION

In conclusion, the approach described here combines several techniques that have been used for coherent Raman measurements previously in a manner that draws on recent developments in multi-dimensional coherent electronic spectroscopy. This approach allows detection of resonance-enhanced CSRS/CARS spectra with Raman shifts down to ~30 cm⁻¹, high sensitivity, and without the presence of fluorescence and nonresonant backgrounds. The intensity of the Raman features far below 200 cm⁻¹ could be enhanced by precise crafting of the spectral shapes of the excitation pulses. The ability to control precisely the spectral shape of each of the pump, Stokes, probe, and LO pulses gives added flexibility for coherent Raman spectroscopy, and allows straightforward interchange between CSRS and CARS experiments and between different quantum pathways in general. This is particularly useful in the cases, where the two schemes provide complementary information, such as in resonant experiments where excited state vibrations can be probed.24,25 Indeed, recent measurements have shown the ability to separate contributions from vibrational modes on ground and excited electronic states in resonant Raman experiments by shifting broadband pulses above and below resonance.26-28 Our ability to impart even greater control on the pulse spectra and available pathways provides even greater capacity to separate these contributions. Finally, the flexibility of the experiment leaves it well placed to extend these measurements to higher order experiments, such as the 2D resonant Raman29 and 2D-Raman 2D electronic34,35 spectroscopies recently reported.

SUPPLEMENTARY MATERIAL

See supplementary material for more details on the experimental apparatus, the dependence of the detection window on spectral overlap of the excitation pulses, the details on the intensity calibration procedure for the correction of relative intensities of the observed vibrational modes, CSRS measurements of IR-806 and IR-140, and spontaneous Raman measurements.

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