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Development of coherent Raman measurements of temperature in condensed phases

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We report theoretical considerations and preliminary data on various forms of coherent Raman spectroscopy that have been considered as candidates for measurement of temperature in condensed phase experiments with picosecond time resolution. Due to the inherent broadness and congestion of vibrational features in condensed phase solids, particularly at high temperatures and pressures, only approaches that rely on the ratio of anti-Stokes to Stokes spectral features are considered. Methods that rely on resolution of vibrational progressions, calibration of frequency shifts with temperature and pressure in reference experiments, or detailed comparison to calculation are inappropriate or impossible for our applications. In particular, we consider femtosecond stimulated Raman spectroscopy (FSRS), femtosecond/picosecond hybrid coherent Raman spectroscopy (multiplex CARS), and optical heterodyne detected femtosecond Raman induced Kerr Effect spectroscopy (OHD-FRIKES). We show that only FSRS has the ability to measure temperature via an anti-Stokes to Stokes ratio of peaks.

Nomenclature

I_{AS} = anti-Stokes signal intensity (square of the electric field)
I_S = Stokes signal intensity (square of the electric field)
$Im()$ = imaginary part
k = Boltzmann constant
$n(\omega)$ = thermal occupation number of phonon mode with frequency ω
T = temperature
$\chi^{(3)}$ = third order Raman susceptibility

I. Introduction

THERE are many problems of condensed phase and chemical physics that could be advanced with detailed time resolved observation of vibrational energy flow on molecular timescales. While our particular interest focuses on measuring vibrational energy flow and chemical dynamics in shocked explosives,[1-4] the ability to measure vibrational temperatures on picosecond time scales[5] could also be useful for fields such as temperature jump protein folding experiments or measurements of molecular scale thermal conductivity. We seek to measure nonequilibrium temperatures with picosecond to sub-picosecond time resolution in samples as thin as 100 nm.

Several methods exist for measuring temperature through Raman spectroscopy. The simplest conceptually is the temperature dependence of the spontaneous Raman anti-Stokes to Stokes ratio.[5-7] Essentially, the anti-Stokes peaks are weighted by the thermal population of the first excited vibrational state. This is a function of temperature and mode frequency only. There are no material specific parameters. There are no modeling parameters. There are no significant assumptions. Unfortunately, the scattering efficiency of spontaneous Raman is typically very small, approximately 1 photon in 100 million is inelastically scattered. Collection is difficult due to scattering in all directions. Competing emissions such as fluorescence are often much stronger, overwhelming the spontaneous Raman signals. We need a coherent Raman analog of the anti-Stokes to Stokes temperature measurement of spontaneous Raman that overcomes these limitations while maintaining the material independent, no assumptions interpretation.

II. Brief theoretical overview of the anti-Stokes to Stokes ratio in coherent Raman

Here, we consider only the part of the Raman scattering that explicitly depends on the temperature. A full consideration of all the factors that contribute to the spontaneous and nonlinear Raman intensities can be found in the references.[8-10] Also note that some of the factors not discussed, in particular refractive indices, may have implicit temperature dependences that are expected to be minor contributions to the measured intensity changes with temperature. Our experimental results thus far support this assumption.

For spontaneous Raman, the Stokes and anti-Stokes intensities have temperature dependences given by Eq. 1[11].

$$\begin{aligned} I_S^{spon} &\propto n(\omega) + 1 \\ I_{aS}^{spon} &\propto n(\omega) \end{aligned} \tag{1}$$

Where $n(\omega)$ is given by standard Bose-Einstein statistics

$$n(\omega) = 1/(\exp(\hbar\omega / kT) - 1) \tag{2}$$

and ω is the phonon frequency. The spontaneous Raman ratio is then

$$I_{AS}^{spon} / I_S^{spon} \propto \exp(-\hbar\omega / kT) \tag{3}$$

The various forms of coherent Raman discussed are all sensitive to the imaginary part of the third order susceptibility, which contains a phonon population factor as shown in Eq. 4, following Eesley.[8] In addition, there is a conjugate symmetry between the anti-Stokes and Stokes susceptibilities[9, 10] which leads to a sign change in the imaginary part when transitioning from the Stokes to anti-Stokes frequencies.

$$\begin{aligned} \mathrm{Im}(\chi_S^{(3)}) &\propto -1/(n(\omega)+1) = \exp(-\hbar\omega / kT) - 1 \\ \chi_{AS}^{(3)}(\omega_{AS}) &= \chi_S^{(3)}(\omega_S)^\dagger \\ \mathrm{Im}(\chi_{AS}^{(3)}) &= -\mathrm{Im}(\chi_S^{(3)}(\omega_S)) \end{aligned} \tag{4}$$

First consider coherent anti-Stokes Raman spectroscopy (CARS), coherent Stokes Raman spectroscopy (CSRS), and optically heterodyned Raman induced Kerr effect spectroscopy (OHD-RIKES) methods[8] that selectively observe the imaginary (resonant) part of the susceptibility. Examination of the functional forms shows no explicit temperature dependence of the anti-Stokes to Stokes ratio for CARS/CSRS or OHD-RIKES, as shown in Eq. 5.

$$\begin{aligned} I_{CARS} &\propto (-\mathrm{Im}(\chi_S^{(3)}))^2 \\ I_{CSRS} &\propto (\mathrm{Im}(\chi_S^{(3)}))^2 \\ I_{CARS} / I_{CSRS} &= 1 \\ I_{OHD-RIKES}^{AS} &\propto -\mathrm{Im}(\chi_S^{(3)}) \\ I_{OHD-RIKES}^{S} &\propto \mathrm{Im}(\chi_S^{(3)}) \\ I_{OHD-RIKES}^{AS} / I_{OHD-RIKES}^{S} &= -1 \end{aligned} \tag{5}$$

In contrast, stimulated Raman spectroscopy (SRS) does maintain a temperature dependent anti-Stokes to Stokes ratio.

$$
\begin{aligned}
I_{SRS}^{S} &\propto I_{probe}\exp(-\operatorname{Im}(\chi_S^{(3)})I_{pump}C_S) \\
I_{SRS}^{AS} &\propto I_{probe}\exp(\operatorname{Im}(\chi_S^{(3)})I_{pump}C_{AS}) \qquad (6) \\
I_{SRS}^{AS}\,/\,I_{SRS}^{S} &= \exp(\operatorname{Im}(\chi_S^{(3)})I_{pump}C_{AS})\,/\,\exp(-\operatorname{Im}(\chi_S^{(3)})I_{pump}C_S)
\end{aligned}
$$

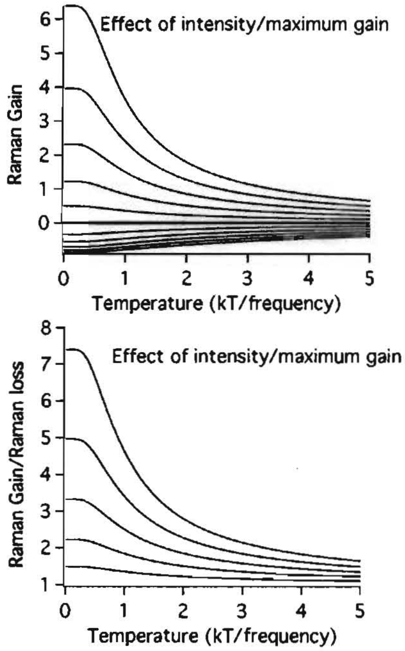

Figure 1. The stimulated Raman Stokes gain to anti-Stokes loss ratio is more temperature sensitive at high gain. The top panel is calculated Raman gain (negative for loss), the lower figure is gain to loss ratio. Each curve represents a different pump intensity.

The parameter C is an accumulation of factors that do not depend explicitly on temperature, but cannot be removed due to their presence in the exponent. The temperature dependence of the Stokes to anti-Stokes ratio persists expressly because of the sign change in the susceptibility and the fact that the susceptibility is in the exponent. For small gains, the exponential can be expanded and only the linear term is significant. In this small gain limit, the temperature dependence of the SRS Stokes to anti-Stokes ratio becomes negligible. For temperature measurement, it is advantageous to maximize the Raman gain. The most facile manner of increasing the gain factor is through the exponential dependence on pump intensity. This is illustrated in Figure 1.

III. Experiments

The experiments were designed to test the basic premises of the predictions given in the theory section above. For simplicity, we used a cryostat to control temperature from 4-300 K. This range of temperatures will only affect modes at frequencies of a few hundred wavenumbers, which is within the spectral bandwidth of the 40 fs Ti:sapphire laser used for the experiments. Temperature was measured with a thermocouple and verified optically with spontaneous Raman anti-Stokes/Stokes ratio analysis.[6, 7, 11] Spontaneous Raman was excited with a 5 mW 532 nm laser. The samples used were various quartz single crystals. For our purposes here, the particular sample is unimportant, as long as the Raman signals could be separated from other emissions, the techniques should be universal.

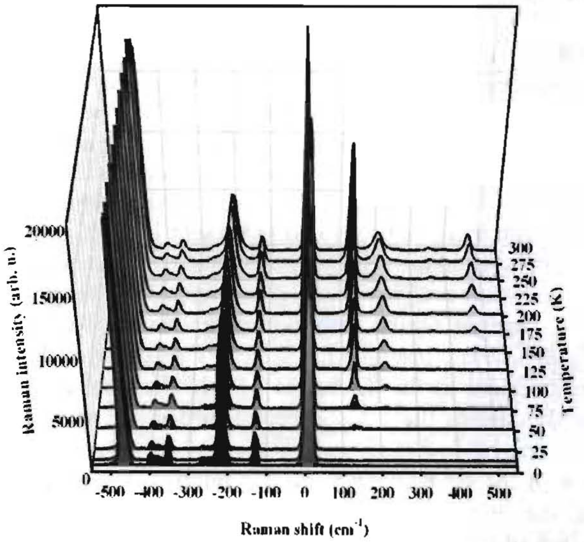

Figure 2. Spontaneous Raman scattering of quartz.

A. Spontaneous Raman results

The spontaneous Raman signals show the expected temperature dependence, as illustrated in Figs. 2 and 3.

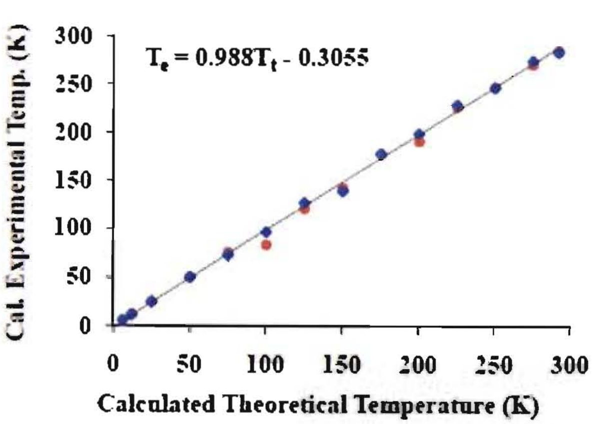

Figure 3. Temperature from spontaneous Raman scattering of quartz (206, 464 cm^{-1} modes) compared to the experimental thermocouple temperature.

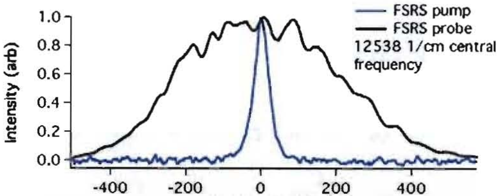

Figure 4. The FSRS pump and probe spectrum used to measure the low frequency modes of quartz.

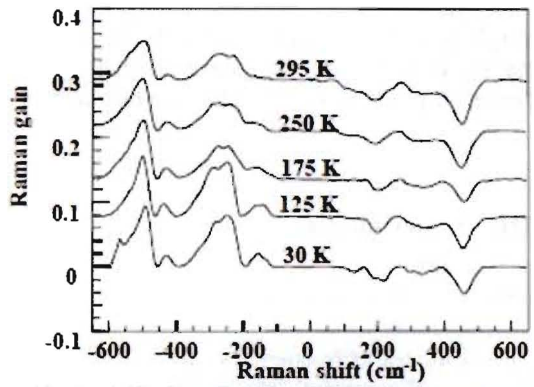

Figure 5. FSRS of quartz crystal versus temperature. Stokes gain at negative Raman shift frequencies and anti-Stokes loss at positive Raman shifts.

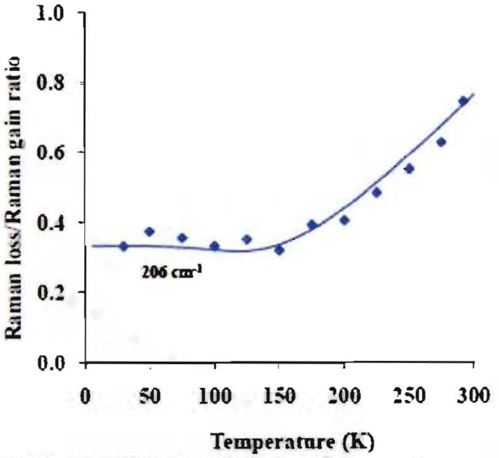

Figure 6. FSRS anti-Stokes loss to Raman gain ratio of quartz crystal for the mode at 206 cm^{-1}. The solid line is the theoretical prediction, matched well by the experimental points.

B. Femtosecond stimulated Raman spectroscopy (FSRS) results

The FSRS experimental pump and probe spectral characteristics are provided in Fig. 4. The probe is ~100 nJ of 40 fs Ti:sapphire spectrum. The pump of several μJ energy, traverses two 2.5 nm narrow band filters to achieve ~ 30 cm^{-1} resolution at ~ 700 fs duration. Spatial and temporal overlap of the pump and probe in the sample leads to stimulated Raman gain on the Stokes side and stimulated Raman loss on the anti-Stokes side. The Raman gain signal is defined as {(pump on-pump off)/pump off -1}, as seen in Fig. 5.

Figure 5 illustrates the difficulty with these FSRS(T) measurements. Spurious stimulated emissions compete with the Raman signals. Without the Raman pump the noise is random and Raman gain noise is < 1%. While the Stokes and anti-Stokes signals should look essentially the same spectrally, Fig. 5 shows that the spectra have structured artifacts, especially on the Stokes side. These complications may arise from a number of potential sources: stimulated emission, nonlinear pump induced pointing changes on the probe, stimulated absorption, cross phase modulation, and other third order nonresonant optical nonlinearities. In addition, the spectral shape is sensitive to fine adjustments of the pump-probe timing and spatial overlap. These difficulties have limited the fitting of the FSRS anti-Stokes to Stokes ratio to a single mode, shown in Fig. 6. The solid line in Fig. 6 is not a fit, but is the theoretical prediction of the temperature dependence. Even this mode has significant interference from pump induced emissions. Despite the difficulties of the measurements, all experimental indications support the agreement between the measured results and the theoretical predictions.

C. Coherent (anti-)Stokes Raman spectroscopy (CARS) results

The CARS experiment has been detailed elsewhere.[12] Briefly two broadband ~100 nJ pulses are overlapped in the sample in space and time and a third spectrally filtered pulse is delayed by 1 ps to avoid nonresonant signal contributions, selectively probing only the imaginary part of the susceptibility. The CARS and CSRS are measured simultaneously. Figure 7 illustrates the much higher signal to noise present in the CARS experiments compared to the FSRS experiments. Unfortunately, the CARS experiments are very sensitive to dephasing changes, and dephasing changes significantly with temperature. This is illustrated by the middle panel of Fig. 7. The 1 ps delay of the probe is insignificant at 26 K, but at 251 K the dephasing significantly diminishes the CARS spectra in a mode specifc manner.

Figure 8 demonstrates the observed temperature dependence of the CARS/CSRS ratio in quartz. Despite the systematic decrease in the ratio as the temperature increases, the two modes show identical behavior despite differing in frequency by a factor of two. In conjuction with the lack of temperature dependence expected by theory, pursuit of CARS/CSRS ratios for temperature measurement does not look promising despite the ease of achieving high signal to noise data with few spectral artifacts.

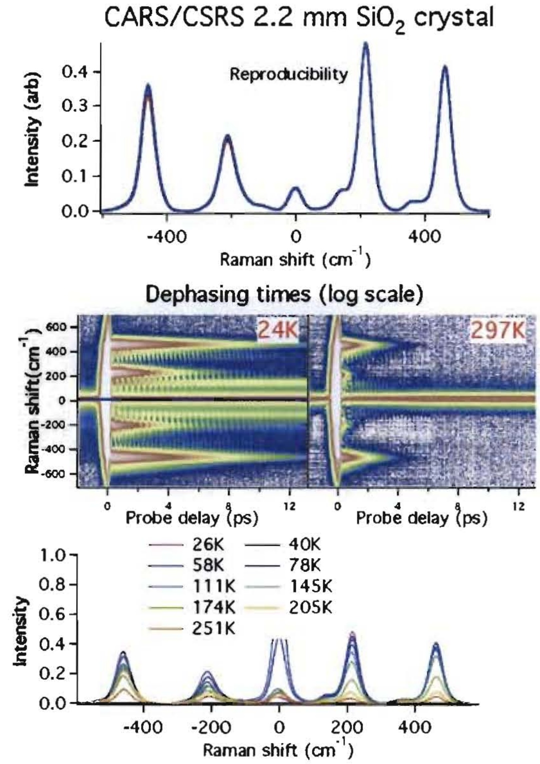

Figure 7. CARS/CSRS of quartz crystal as a function of temperature.

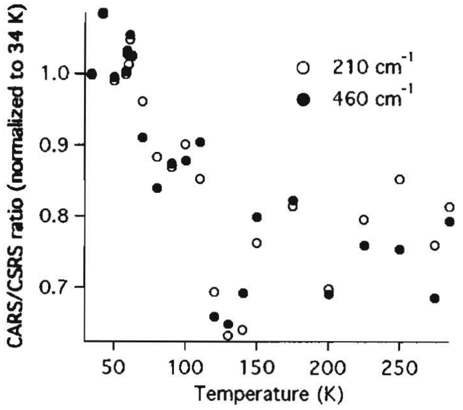

Figure 8. CARS/CSRS ratio versus T. While there is sytematic change, there is no indication of the characteristic frequency dependence. The apparent ratio change is likely dominated by artifacts arising from drastic dephasing time changes.

IV. Conclusion

We have shown that FSRS can be used to measure temperature without any additional material specific paramters in a manner analogous to the spontaneous Raman anti-Stokes to Stokes ratio. While the experiments are difficult due to inferring emissions, preliminary results support the theoretical expectations. Experiments measuring CARS/CSRS ratios do not show such promise of temperature measurements, and are not expected to based on theory. It is the peculiar exponential dependence of the FSRS signal on the third order Raman susceptibility that allows determination of temperature from a ratio of anti-Stokes to Stokes intensities.

Acknowledgments

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