Raman temperature measurement

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Abstract. We are examining the experimental trade-offs for the use of the spontaneous Raman Stokes/anti-Stokes intensity ratio as a fundamental temperature measurement at static and dynamic extreme conditions. The trade-off space includes spatial resolution and temperature range versus vibrational frequency, as well as heating of the sample and nonlinear damage caused by the excitation laser. The experiments are being performed under a range of experimental conditions from nanoseconds to seconds and from cryogenic (77 K) to elevated (ca. 1000 K) temperatures. The results are being compared to calculations for transparent metal oxide and polymer materials, with the aim to demonstrate their potential as temperature reporters when used as thin windows on opaque materials.

1. Introduction

Temperature is a thermodynamic variable of great current interest in studies of shock-compressed materials, not only because of its importance to equations of state, but also because it is extremely difficult to measure. There exist a number of experimental methods used to measure temperature. Radiometry of thermal emission from materials has been commonly used because it is experimentally easy to implement, but its accuracy relies on knowing the spectral emissivity of the material [1]. Usually the emissivity is not known and the grey body approximation is used. In shock compressed opaque materials, the measurement is also hindered by the short duration of the experiment due to release at the free surface, or shock interactions or thermal conduction with windows if they are used [2]. Neutron resonance spectroscopy has been used [3], wherein Doppler broadening of the neutron resonances allows the inference of the material temperature. There exist select materials with sufficiently large neutron absorption cross sections and sufficiently narrow line widths to allow the measurements, but the experiment requires doping of these materials into the material of interest, with accompanying concerns about perturbation of the material equation of state.

Other optical methods have also been used to measure temperature. Moore and Schmidt used coherent anti-Stokes Raman (CARS) to measure temperature via the vibrational hot band intensities in shock compressed condensed phase small molecules [4]. Dang et al. have demonstrated the temperature measurement capabilities of femtosecond stimulated Raman scattering in transparent materials [5].

The most prolific spectroscopic method used to measure temperature is common old ordinary Raman scattering (COORS), using the ratio of the anti-Stokes intensity to the Stokes intensity [6]. The advantage
of this method is that the anti-Stokes to Stokes intensity ratio depends only on $T$, permitting temperature measurements in dynamical systems, given sufficient excitation photon flux and spectral collection efficiency. This latter statement is the reason behind this study. We are examining the parameter space for use of Raman spectroscopy to measure temperature in dynamic compression experiments, including spatial and temporal resolution capabilities, temperature range, and sample perturbations caused by the excitation laser, such as heating and damage. This paper will discuss results obtained using a continuous wave (CW) Nd:YAG laser.

2. Experimental
The excitation lasers were either a frequency doubled diode-pumped solid state laser (DPSS; CNI model MGL-III-532) with up to 300 mW CW power, or a higher power DPSS (Spectra Physics Millennia). The laser beam diameter was expanded 2.5 times using a Galilean telescope, then passed through a polarizing beam splitter cube and a folding mirror off to the side of a 1" diameter f/2 achromat (ThorLabs), focusing on the sample of interest. The Raman emission was collected and collimated at 180° backscattering geometry using the same f/2 achromat, then passed through a holographic notch filter (Kaiser Optical Notch-Plus™), which reduced the available aperture to 15 mm, effectively limiting the collection system to f/3. Finally another f/2 achromat focused the Raman emission onto the 50-micron wide entrance slit of an f/1.8 spectrometer (Kaiser Holospec 1.8). The detector was a PI-MAX (Roper Scientific) cooled intensified CCD used at full gain and variable exposure time, typically 100 ms. A fifteen pixel tall region of interest covering the Raman emission was defined and binned, but the full 1340 pixels in the wavelength direction were utilized. The data acquisition and control program was written in LabView™ (National Instruments). A Ne rare gas penlamp (Oriel) were used for wavelength calibration of the spectrometer/CCD.

2.1. Spectral Radiance Calibration
To calibrate the spectral radiance efficiency of the entire optical system from sample to detector, a NIST traceable standard of spectral irradiance (Oriel Model 63355) was positioned a measured distance behind a 50 μm diameter pinhole placed at the sample position. The required lamp current of 6.5 A was provided by a regulated constant current power supply (Newport Model 69931). The measured spectrum on the CCD was then divided by the lamp spectral irradiance to give the correction, which we then applied to the Raman spectra in real time using the data acquisition and control program.

2.2. Collection Efficiency
The Raman collection efficiency was determined using liquid benzene, a material whose Raman cross section is well known [7]. The benzene sample was placed into a 1 mm thick cuvette and positioned at the sample position. The Raman signal expected can be calculated from equation 1 [8].

$$\frac{F}{P_p} = \frac{\sigma_R \eta_c N L}{\hbar \nu_p}$$

where $F/P_p$ is the ratio of Raman signal (in counts) to pump energy (J), $\sigma_R$ is the Raman cross section (cm²/molecule), $\eta_c$ is the optical system collection efficiency, $NL$ is the number of molecules per square centimeter (density times path length), and $\hbar \nu_p$ is the excitation photon energy ($3.7 \times 10^{-19}$ J at 532 nm). From the signal obtained from the benzene sample and the published Raman cross-section ($2.5 \times 10^{-29}$ cm²/molecule/steradian), we calculate $\eta_c = 6.3 \times 10^4$ counts/photon. Collecting 0.035 steradians in the
sample limits the maximum value of $\eta_c$ to $<2.8 \times 10^{-3}$, suggesting the detection efficiency of the optics, spectrometer and detector are 0.23.

2.3. Treatment of Raman Spectra
Most Raman spectra are accompanied by a broad background, usually from fluorescence, either native or from impurities or other materials in the sample. This background must be removed before the anti-Stokes to Stokes Raman intensity can be calculated. A number of methods have been examined and compared for their ability to remove fluorescence backgrounds without distorting the Raman spectral features [9]. We utilize the rolling circle method described by Brandt et al. [10] because it produces very little distortion of the Raman features. In all cases, the anti-Stokes and Stokes spectral regions are treated separately. The rolling circle filter and polynomial fitting methods of background removal are compared in figure 1 for a Teflon sample.

![Figure 1. Comparison of two fluorescence background removal algorithms. Both operated on the Stokes sides and anti-Stokes sides separately. Note the 4th order polynomial procedure produces an undulating baseline, particularly in regions of high background curvature (especially note anti-Stokes side). Lower and higher polynomial orders produced worse effects.](image)

We incorporated two different methods to calculate the anti-Stokes to Stokes Raman intensity ratio. The spectra as recorded on the CCD have uneven wavenumber spacing along the abscissa, which is corrected by interpolating onto an evenly spaced frequency grid to allow accurate peak integration. The “peak” method involves numerically integrating an arbitrary single peak in both anti-Stokes and Stokes regions. The “integral” method involves calculating $T$ from the anti-Stokes to Stokes intensity at each Raman frequency, applying a threshold to the intensity to discard spurious temperatures from low intensity regions, and averaging, weighted by the Stokes intensity as in the following equation:

$$T = \frac{\sum_{\omega} I_{\text{Stokes}} \omega}{\sum_{\omega} I_{\text{Stokes}}}.$$ 

The temperatures obtained using each method are compared in the results section below.

3. Results
We have examined several different kinds of materials using the above methodology, including metal oxides (MgO, quartz, calcite, sapphire) and polymers (polymethylmethacrylate, Teflon). The quartz results are significant, because the $\alpha-\beta$ phase transition has observable Raman features indicative of each
phase, has little or no hysteresis, and occurs at a well-known temperature, so it can be used to compare to the Raman temperature results, as shown in Figure 2 below.

**Figure 2.** Raman temperature measurement in quartz, showing the spectral differences between the α and β phases (left side) used in the comparison of the phase transition temperature to the Raman temperature (right side). The dashed vertical lines denote phase transitions observed spectrally, which intersect the red line denoting the phase transition temperature. Note also the agreement between the temperature from the “peak” and “integral” methods.

We also performed a similar study using Teflon (PTFE), comparing the Raman temperature to the known melting temperature. The agreement in this case was not as good as obtained for quartz, and also the “from peak” and “from integral” temperatures did not agree. We believe the disagreement is due to

**Figure 3.** Raman temperature measurement in Teflon (PTFE), compared to the known solid/liquid phase transition temperature. The Raman temperature “T from peak” using the largest peak at 731 cm\(^{-1}\) is in fair agreement with the phase transition, but ~35 K low. However, the “T from integral” method gives temperatures that are far too low, indicating possible inadequate fluorescence baseline removal even using the rolling circle filter method.
inadequate fluorescence background removal, even using the rolling circle filter. We are investigating procedures to improve that process. Preliminary results are given in figure 3.

4. Discussion
The accurate removal of the baseline from whichever cause (thermal, fluorescence, etc.) is vitally important to achieve reliable temperatures from the anti-Stokes to Stokes Raman intensity ratio. Figure 2 above for quartz shows how accurate the temperatures can be, comparing to the known phase transition temperature within about 1% at 846 K, when the baseline removal methods result in negligible artefacts. On the other hand, inadequate baseline removal can result in temperature inaccuracies as demonstrated in figure 3, where at 600 K the precision is < 1%, but accuracy (compared to the melt temperature) is > 5%.

The considerations reported here have been limited to CW Raman experiments, but are easily applied to dynamic measurements. Further studies are underway to determine the limits to which Raman spectroscopy can be used to measure sample temperature, particularly limitations due to sample perturbations caused by the excitation laser, such as heating and damage. The results reported here are a first step in identifying the trade-offs between spatial resolution, time resolution, and thermometric accuracy relevant to dynamic experiments.

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