TECHNICAL NOTE

Relative intensity calibration using broadband white light from tungsten lamps

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Introduction

Emission from heated tungsten lamps have been used as reference for the calibration of spectrometers for some time. In this case, the emission is modeled as broad-band emission from a black-body emitter.[1, 2]

However, choice of specific equation used for the purpose and pre-processing the photo count data is important here.

1. Theory

Emission from ideal black body with unit of photon counts per unit solid angle per unit wavenumbers is given by

$$I(\omega, T) = 2c\omega^2 \left(\frac{1}{e^{hc\omega}/k_B T - 1} \right) \tag{1}$$

It should be noted that the equation differs when considering radiant power emitted per unit solid angle, or the case for photons per unit solid angle per unit wavelength.

2. Method

2.1 Non-uniform photon counting

Many Raman spectrometers are based on imaging spectrographs with grating as the dispersive element mounted on a turret in a polychromator. The disperson of the grating is however wavelength dependent, and thus $\delta\lambda/\delta x$ is not uniform. Here, x is physical distance, which is the horizontal axis of the multi-channel detector such as a CCD/CMOS camera. Thus on the detector, photons are binned on a non-uniform wavelength scale. Subsequently, the photons are also non-uniformly binned across the wavenumber scale.

The correction for this is to normalize the raw photon counts to get photon counts per wavenumber. Such correction has been discussed in context of electronic spectroscopy where the measured spectral range is rather large.[3, 4] The correction is equal to a multiplicative factor of $\delta\vec{\nu}_s/\delta\nu_0$, where $\delta\vec{\nu}_s$ is the wavenumber spacing at certain wavenumber, a vector, while, $\delta\nu_0$ is the wavenumber spacing at a reference wavenumber, a scalar. Refer to Examples section for curve of this function determined from the dispersion data for a Raman spectrometer.

2.2 Correction assuming black-body emission

The raw spectrum of broad band white light is thus corrected for non-uniform photon counting using correction defined above. Next, the spectral profile is modeled as emission from a black body emitter using Eqn. 1. However, when evaluating Eqn. 1, temperature of the lamp should be known. A comparison of the white light spectrum with a simulated black-body emission profile gives the next correction curve.

If the correction for non-uniform spacing is termed as C_0, and the correction derived from white-light emission using Eqn. 1 is termed as C_1, then the net multiplicative correction applicable to an arbitrary Raman spectrum would be C_0/C_1.

2.3 Implementation as computer program

The defined scheme has been implemented as a python program and Igor procedure for rapid applications,[5] and openly available on the online repository.[6] When evaluating Equation (2), one may fix the temperature value if known. However, when temperature is unknown the value can be a fit parameter (which will enlarge the error in the determined curve). Programs for both cases have been implemented in the software repository. Refer to the file 'gen_correction.py' in the software repository for python programming language. A full usage is described online (see jupyter notebook on browser).

3. Examples

The C_0 curve (determined as $\delta\vec{\nu}_s/\delta\nu_0$) from the relative wavenumber vector (or RamanShift vector) for a Raman spectrometer operating with 532 nm is shown in Fig.1. Zero across the relative wavenumber axis corresponds to this wavelength. Surprisingly, over 20% change in the relative photon counts is observed.

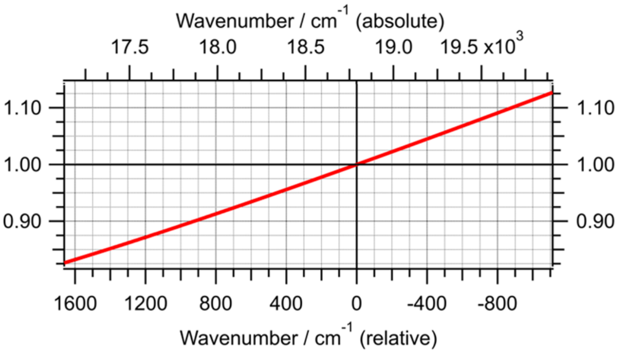

Figure 1. Correction to obtain photons per wavenumber for a non-uniformly sampled photon data on a Raman spectrometer designed for 532 nm excitation.

Broad band white light spectrum was measured on the same instrument and corrected using C_0 by multiplication. Next, it was fit to Eqn. 1 assuming temperature of about 3000 K. For fit function refer to the online resource.[6] The measured data together with the fit trace are in Fig. 2. Their ratio which is equal to C_1 is shown in black color. This correction accounts for channel-to-channel sensitivity of the Raman spectrometer.

If the temperature was known to high accuracy and used as a fixed parameter during the fit process, the so determined C_1 correction should ideally account for the wavelength dependent sensitivity of the Raman spectrometer. However, in practical cases this is very difficult to be achieved. Depending on the required accuracy, additional correction determined from Raman intensities themselves can be used to obtain a final correction for relative sensitivity.[5, 7]

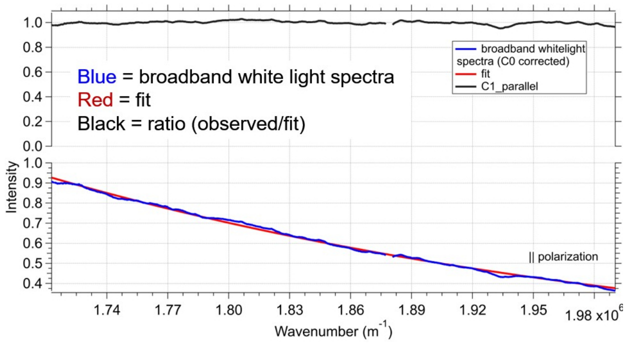

Figure 2. Correction to obtain correction for pixel-to-pixel correction from broad-band white light spectrum measured from tungsten lamp. Adapted from Ref. [5]

4. Limitations

There have been discussions on the applications of the heated tungsten lamp towards calibration of Raman spectrometer and the disadvantages.[8, 9] The emission spectrum can change significantly depending on the position of the lamp relative to the slit of the spectrometer, and hence, the experimental setup requires a precise placement of the lamp exactly at the sample position.[8]

Another limitation is that temperature of the lamp has to be known. Further, information about polarization dependent sensitivity is difficult to be derived from this approach. One may assume that the emission is purely random, and an optical diffuser may be used to account for this.

5. Sources of error

With proper wavenumber calibration, the determination of C_0 should be without an introduction of error. The determination of C_1 requires the temperature of the lamp. In the visible region, the slope of the emission profile as per Eqn. 1 changes rather slowly, and one will be able to assess the error in C_1 by analyzing $dI(\omega)/dT$ over the measured spectral range taking into account the uncertainty associated with the temperature of lamp.

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