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Calibration of Raman Spectrometer for Gas Phase Measurements

Patrick E. O'Rourke
May 2020
SRNL-STI-2020-00202
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Calibration of Raman Spectrometer for Gas Phase Measurements

Patrick E. O'Rourke

May 2020
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EXECUTIVE SUMMARY

Raman spectroscopy is currently used at SRNL to measure the concentration of gaseous species evolved from chemical reactions. This report documents the methods used to calibrate the spectroscopic systems in both frequency and intensity spaces.
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Introduction

Raman spectroscopy is currently used at SRNL to measure the concentration of gaseous species evolved from chemical reactions. The Raman spectrometers used for this work are manufactured by TSI Inc., model GasRaman NOCH-1. This model instrument incorporates a 532 nm diode pumped solid state laser and fiber optic sampling probe. This memo details the methods used to calibrate Raman spectrometers.

Calibration of spectroscopic instruments is usually accomplished by measuring the response of known standard substances and using these responses to model the quantity of substance through a mathematical equation. For Raman spectroscopic instruments, the measured response is the intensity of light inelastically scattered from molecules by the Raman process, and the mathematical equation is a linear expression:

\[ \text{[Concentration(i)]} = \Omega \times \text{Raman Line Intensity(i)} \]

Where [Concentration] has units of pressure, Raman Line Intensity has units of counts, and \( \Omega \) is a proportionality constant determined by measuring the counts of a known pressure of gas under fixed spectrometer conditions. In this work, \( \Omega \) is expressed as a product of three factors: the Raman scattering cross-section of each measured species i (RSC\(_i\)), the spectrometer response function at the measured frequencies of species i (SRF\(_i\)), and a Laser energy correction factor (PCF), which is the ratio of a reference power and time to the actual laser power and time used in the experiment. This factoring of \( \Omega \) allows for correction of short-term laser power drift, long-term spectrometer response drift, and sample integration time adjustment.

\[ \text{[Concentration(i)]} = \text{PCF} \times \text{SRF(i)} \times \text{RCS(i)} \times \text{Raman Line Intensity(i)} \]

The RCS values were taken from literature values \(^{(2)}\). The PCF is calculated by \((300\text{mw} \times 5\text{ sec}) / (\text{Laser-Power} \times \text{Integration-Time})\). The SRF values are determined from measurements of gas standards with the NOCH-1:

\[ \text{SRF(i)} = \frac{\text{[Concentration(i)]}}{\text{PCF} \times \text{RCS(i)} \times \text{Raman Line Intensity(i)}} \]

Gas compositions used in the spectrometer calibration are listed in Table 1.

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>CAS</th>
<th>MW</th>
<th>Target Conc</th>
<th>Stabilizer</th>
<th>Balance Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>N(_2)</td>
<td>7727-37-9</td>
<td>28.01</td>
<td>100.00%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxygen (Air)</td>
<td>O(_2)</td>
<td>7782-44-7</td>
<td>32.00</td>
<td>20.95%</td>
<td>(Air)</td>
<td></td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>CO(_2)</td>
<td>124-38-9</td>
<td>44.01</td>
<td>100.00%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitrous oxide</td>
<td>N(_2)O</td>
<td>10024-97-2</td>
<td>44.01</td>
<td>20.00%</td>
<td>5% N(_2)</td>
<td>Ar</td>
</tr>
<tr>
<td>Nitric oxide</td>
<td>NO</td>
<td>10102-43-9</td>
<td>30.01</td>
<td>20.00%</td>
<td>5% N(_2)</td>
<td>Ar</td>
</tr>
<tr>
<td>Nitrogen dioxide</td>
<td>NO(_2)</td>
<td>10102-44-0</td>
<td>46.01</td>
<td>5.00%</td>
<td>20% O(_2)</td>
<td>Ar</td>
</tr>
<tr>
<td>Hydrogen_High</td>
<td>H(_2)</td>
<td>1333-74-0</td>
<td>2.02</td>
<td>10.00%</td>
<td>5% N(_2)</td>
<td>Ar</td>
</tr>
<tr>
<td>Hydrogen_Low</td>
<td>H(_2)</td>
<td>1333-74-0</td>
<td>2.02</td>
<td>2.67%</td>
<td>Ar</td>
<td></td>
</tr>
</tbody>
</table>

*Table 1: Standard Gas Compositions*

This calibration technique works well for gases which remain chemically stable during the sampling and measuring process. Ideal gas behavior is assumed; specifically, the RSC values are assumed to be invariant with respect to the constitution of other gases in the sample. This assumption is validated by
observations. The reference laser power is 300 mw, and the reference detector integration time is 5 seconds. Longer integration times are useful provided the concentration of NO$_2$ gas is low enough so that its fluorescence did not saturate the detector.

**Raman Line Intensity Measurement**

Accurate determination of SRF values relies on reproducible extraction of Raman line intensities from Raman spectra. For these instruments and conditions, gas phase Raman spectra exhibit the characteristics of fixed Raman shifts and narrow line widths. The value of the Raman line shift for gases is determined by the vibrational/rotational energy levels of the molecule and is typically unaffected by chemical or environmental conditions near STP. The line width is typically narrower than the spectrometer instrument response function and so can be reliably modeled by the instrument shape function.

Raman lines in general are superimposed on a broad fluorescence background. This background must be removed to accurately measure line intensity. Figure 1 shows a typical Raman spectrum of air using a fiber optic Raman probe optimized for laser excitation at 532nm. The sharp line at 1555 cm$^{-1}$ is from oxygen and the line at 2331 cm$^{-1}$ is nitrogen.

![Figure 1: Raw Raman Spectrum of Air](image_url)

Other broader features in the spectrum are characteristic of the fiber optic probe and sample cell. Identification and quantification of the sharp Raman lines can be enhanced with respect to the broad background by digital processing of the spectrum using Gaussian derivative filters.

$$PS(v) = \sum_{(\rho-N)} G_0DF(\rho) * RS(v+\rho)$$
\[ G_0 \text{DF}(\rho) = \left( \frac{1}{\sqrt{2\pi}\sigma} \right) \exp\left( -0.5 \left( \frac{\rho}{\sigma} \right)^2 \right) \]

\[ G_1 \text{DF}(\rho) = \left( \frac{\rho}{\sigma^2} \right) G_0 \text{DF}(\rho) \]

\[ G_2 \text{DF}(\rho) = \left( \frac{(\rho^2 - \sigma^2)}{\sigma^4} \right) G_0 \text{DF}(\rho) \]

Where \( PS(\nu) \) is the processed spectrum, \( RS(\nu) \) is the Raw spectrum and \( G_d \text{DF}(\rho) \) is the derivative Gaussian filter (\( d \) is derivative order = 0, 1, or 2). \( \sigma \) is a filter parameter specifying the signal line width, and \( N \) is the range of the filter, typically greater than \( 4\sigma \). Sigma is assumed to be the half-width of the instrument function, typically 2 channels for this work, and \( N = 12 \). Table 2 lists the values for the zero order, first derivative and second derivative Gaussian filter function. Figure 2 shows the processed Raman spectrum of air. The second derivative Gaussian filter preserves a linear relationship to intensity among peaks with similar widths, but effectively eliminates broad background.

<table>
<thead>
<tr>
<th>Gaussian Filter Coefficients</th>
<th>Sigma = 2</th>
<th>Range = 12</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \rho )</td>
<td>Smooth</td>
<td>1st derivative</td>
</tr>
<tr>
<td>-12</td>
<td>0.000000003</td>
<td>-0.000000009</td>
</tr>
<tr>
<td>-11</td>
<td>0.000000054</td>
<td>-0.000000148</td>
</tr>
<tr>
<td>-10</td>
<td>0.000000743</td>
<td>-0.000001858</td>
</tr>
<tr>
<td>-9</td>
<td>0.000007992</td>
<td>-0.000017982</td>
</tr>
<tr>
<td>-8</td>
<td>0.000066915</td>
<td>-0.000133830</td>
</tr>
<tr>
<td>-7</td>
<td>0.000436341</td>
<td>-0.000763597</td>
</tr>
<tr>
<td>-6</td>
<td>0.002215924</td>
<td>-0.003323866</td>
</tr>
<tr>
<td>-5</td>
<td>0.008764150</td>
<td>-0.010955188</td>
</tr>
<tr>
<td>-4</td>
<td>0.026995483</td>
<td>-0.026995483</td>
</tr>
<tr>
<td>-3</td>
<td>0.064758798</td>
<td>-0.048569098</td>
</tr>
<tr>
<td>-2</td>
<td>0.120985362</td>
<td>-0.060492681</td>
</tr>
<tr>
<td>-1</td>
<td>0.176032663</td>
<td>-0.044008166</td>
</tr>
<tr>
<td>0</td>
<td>0.199471140</td>
<td>0.000000000</td>
</tr>
<tr>
<td>1</td>
<td>0.176032663</td>
<td>0.044008166</td>
</tr>
<tr>
<td>2</td>
<td>0.120985362</td>
<td>0.060492681</td>
</tr>
<tr>
<td>3</td>
<td>0.064758798</td>
<td>0.048569098</td>
</tr>
<tr>
<td>4</td>
<td>0.026995483</td>
<td>0.026995483</td>
</tr>
<tr>
<td>5</td>
<td>0.008764150</td>
<td>0.010955188</td>
</tr>
<tr>
<td>6</td>
<td>0.002215924</td>
<td>0.003323866</td>
</tr>
<tr>
<td>7</td>
<td>0.000436341</td>
<td>0.000763597</td>
</tr>
<tr>
<td>8</td>
<td>0.000066915</td>
<td>0.000133830</td>
</tr>
<tr>
<td>9</td>
<td>0.000007992</td>
<td>0.000017982</td>
</tr>
<tr>
<td>10</td>
<td>0.000000743</td>
<td>0.000001858</td>
</tr>
<tr>
<td>11</td>
<td>0.000000054</td>
<td>0.000000148</td>
</tr>
<tr>
<td>12</td>
<td>0.000000003</td>
<td>0.000000009</td>
</tr>
</tbody>
</table>

Table 2. Gaussian filter coefficients
Figure 2: Second Derivative Processed Raman Spectrum of Air

Raman Response Functions

The second derivative signal intensity from each molecule can be accurately determined by comparing the processed spectrum with normalized molecular response functions unique to the molecules of interest. The molecular response functions are calculated by assuming Gaussian peak shapes at the characteristic Raman shifts, relative intensities and line widths as verified from measurements of standard gas mixtures. Tables 3a-3c list characteristic peak features used to calculate molecular response functions. For those gases where a standard was not available, literature values for the peak position was used (in red).

Table 3a Raman Peak Shift

<table>
<thead>
<tr>
<th>Peak</th>
<th>NO2</th>
<th>N2</th>
<th>O2</th>
<th>N2O</th>
<th>NO</th>
<th>H2</th>
<th>CO2</th>
<th>CO</th>
<th>H2O</th>
<th>NH3</th>
<th>CH4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak1</td>
<td>422.0</td>
<td>752.0</td>
<td>2331.0</td>
<td>1555.0</td>
<td>1876.0</td>
<td>352.0</td>
<td>1285.0</td>
<td>2143.0</td>
<td>3654.0</td>
<td>3334.0</td>
<td>2914.0</td>
</tr>
<tr>
<td>Peak2</td>
<td>490.0</td>
<td>1321.0</td>
<td>2225.0</td>
<td>587.0</td>
<td>1388.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peak3</td>
<td>590.0</td>
<td>1500.0</td>
<td></td>
<td></td>
<td>815.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peak4</td>
<td>784.0</td>
<td>2068.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peak5</td>
<td>1942.0</td>
<td>2288.0</td>
<td></td>
<td></td>
<td>4155.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peak6</td>
<td>2430.0</td>
<td>2632.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peak7</td>
<td>4012.0</td>
<td>2816.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peak8</td>
<td>4354.0</td>
<td>3182.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peak9</td>
<td>4384.0</td>
<td>3554.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peak10</td>
<td>3928.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 3b

| Inten1 | 0.0000 | 0.3761 | 1.0000 | 1.0000 | 0.9701 | 1.0000 | 0.1800 | 0.0000 | 1.0000 | 1.0000 | 1.0000 |
| Inten2 | 0.9806 | 0.6268 | 0.0000 | 0.0000 | 0.2425 | 0.0000 | 0.7202 | 1.0000 | 0.0000 | 0.0000 | 0.0000 |
| Inten3 | 0.0000 | 0.3761 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.1440 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| Inten4 | 0.0000 | 0.4513 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0900 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| Inten5 | 0.0000 | 0.1504 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.6481 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| Inten6 | 0.0000 | 0.2256 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| Inten7 | 0.1961 | 0.1254 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| Inten8 | 0.0000 | 0.1003 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| Inten9 | 0.0000 | 0.0752 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| Inten10| 0.0000 | 0.1254 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |

Table 3c

| Width1 | 12.00 | 8.00 | 7.00 | 7.00 | 7.00 | 7.00 | 7.00 | 7.00 | 7.00 | 7.00 | 7.00 |
| Width2 | 8.00 | 8.00 | 7.00 | 7.00 | 7.00 | 7.00 | 7.00 | 7.00 | 7.00 | 7.00 | 7.00 |
| Width3 | 12.00 | 8.00 | 7.00 | 7.00 | 7.00 | 7.00 | 7.00 | 7.00 | 7.00 | 7.00 | 7.00 |
| Width4 | 12.00 | 8.00 | 7.00 | 7.00 | 7.00 | 7.00 | 7.00 | 7.00 | 7.00 | 7.00 | 7.00 |
| Width5 | 12.00 | 8.00 | 7.00 | 7.00 | 7.00 | 7.00 | 7.00 | 7.00 | 7.00 | 7.00 | 7.00 |
| Width6 | 12.00 | 8.00 | 7.00 | 7.00 | 7.00 | 7.00 | 7.00 | 7.00 | 7.00 | 7.00 | 7.00 |
| Width7 | 12.00 | 8.00 | 7.00 | 7.00 | 7.00 | 7.00 | 7.00 | 7.00 | 7.00 | 7.00 | 7.00 |
| Width8 | 12.00 | 8.00 | 7.00 | 7.00 | 7.00 | 7.00 | 7.00 | 7.00 | 7.00 | 7.00 | 7.00 |
| Width9 | 12.00 | 8.00 | 7.00 | 7.00 | 7.00 | 7.00 | 7.00 | 7.00 | 7.00 | 7.00 | 7.00 |

Molecular response functions are calculated from the equation:

$$\text{MRF}(\nu) = \sum_{i=1}^{10} \text{Inten}_i((\nu-\nu_i)^2-\sigma_i^2)/\sigma_i^4) \times \exp(-0.5*((\nu-\nu_i)/\sigma_i)^2)$$

Inten, are intensities from table 3b, $\nu_i$ are peak shifts from table 3a, and $\sigma_i$ are line widths from table 3c. Molecular response functions are calculated using the Excel macro MakePeak. Figure 3 shows the calculated response functions for the fiber optic cell, nitric oxide (NO$_2$), nitrogen (N$_2$) and oxygen (O$_2$). The response functions are calculated using a common-frequency pixel density of 2 cm$^{-1}$/point from 200 cm$^{-1}$ to 4200 cm$^{-1}$. Note that the raw pixel density from the Raman spectrometer is approximately 5.8 cm$^{-1}$/point. Native Raman spectra are interpolated to provide the 2 cm$^{-1}$/point data density, as described below.

**Spectrometer Frequency Calibration**

In order to carry out the intensity calculation, the molecular response functions and the processed spectrum must be properly aligned with respect to Raman shift frequency ($\nu$). The Raman shift calibration for the spectrometer depends on its calibration with respect to absolute frequency and on the absolute frequency of the exciting laser. Since the Raman shift arises from the difference of the two absolute values, the spectrometer can be accurately calibrated in for Raman shift by fitting known Raman peak shift positions to detector pixel values using a cubic polynomial function, bypassing measurement of the individual absolute values. Table 4 lists Raman shift values and detector pixels used.
in the frequency calibration. These shift values were determined from measurements of samples with known composition.

![Calculated Molecular Response Functions](image)

**Figure 3: Calculated Raman Response Functions**

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Pixel</th>
<th>Frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2</td>
<td>55.0</td>
<td>352</td>
</tr>
<tr>
<td>H2</td>
<td>96.9</td>
<td>587</td>
</tr>
<tr>
<td>H2</td>
<td>138.3</td>
<td>815</td>
</tr>
<tr>
<td>H2</td>
<td>179.4</td>
<td>1036</td>
</tr>
<tr>
<td>N2O</td>
<td>226.9</td>
<td>1285</td>
</tr>
<tr>
<td>CO2</td>
<td>226.9</td>
<td>1285</td>
</tr>
<tr>
<td>CO2</td>
<td>246.9</td>
<td>1388</td>
</tr>
<tr>
<td>O2</td>
<td>279.9</td>
<td>1555</td>
</tr>
<tr>
<td>NO</td>
<td>345.3</td>
<td>1876</td>
</tr>
<tr>
<td>CO</td>
<td>401.8</td>
<td>2143</td>
</tr>
<tr>
<td>N2O</td>
<td>419.8</td>
<td>2226</td>
</tr>
<tr>
<td>N2</td>
<td>442.9</td>
<td>2331</td>
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<tr>
<td>CH4</td>
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</tr>
<tr>
<td>NH3</td>
<td>682.3</td>
<td>3334</td>
</tr>
<tr>
<td>Water</td>
<td>766.3</td>
<td>3654</td>
</tr>
<tr>
<td>H2</td>
<td>908.2</td>
<td>4155</td>
</tr>
</tbody>
</table>

*Table 4: Raman Lines and Estimated Channel Values Used for Wavelength Calibration*
Given an accurate pixel to frequency equation, the processed spectrum can be interpolated to a
common frequency scale as used for the molecular response functions. The interpolation is executed
using the Excel Macros SplineFit and Interpolate. SplineFit is a method to convert the discrete digital
data of the processed spectrum to a piece-wise continuous spectrum. Each discrete digital value in the
processed spectrum (PS) (pixel) is represented by a quadratic polynomial equation calculated by a least
squares fit to points on each side of the pixel. For each pixel in the derivative-processed-raw-spectrum
there are three values, the quadratic polynomial coefficients.

\[
\text{PS(pixel)} = a_0 + a_1 (\varepsilon - \text{pixel}) + a_2 (\varepsilon - \text{pixel})^2 \quad \text{for} \quad \{ \varepsilon : -1 < \varepsilon < 1 \}
\]

The \(a_i\)'s are the solution to the matrix equation:

\[
\begin{bmatrix}
2N+1 & 0 & \sum_{(n \to N)} n^2 & | & a_0 & | & \sum_{(n \to N)} \text{PS(pixel + n)} \\
0 & \sum_{(n \to N)} n^2 & 0 & | & X & | & \sum_{(n \to N)} n \cdot \text{PS(pixel + n)} \\
\sum_{(n \to N)} n^2 & 0 & \sum_{(n \to N)} n^4 & | & a_2 & | & \sum_{(n \to N)} n^2 \cdot \text{PS(pixel + n)}
\end{bmatrix}
\]

For any given value of \(N\), which defines how many points on each side of the pixel to use in the least
squares fit, the inverse matrix of sums is easily calculated once for all pixels. Typically \(N = 2\), and the
solution for \(N=2\) is:

\[
\begin{bmatrix}
34/70 & 0 & -1/7 & | & \sum_{(n \to N)} \text{PS(pixel + n)} & | & a_0 \\
0 & 1/10 & 0 & | & X & | & \sum_{(n \to N)} n \cdot \text{PS(pixel + n)} & = & a_1 \\
-1/7 & 0 & 1/14 & | & \sum_{(n \to N)} n^2 \cdot \text{PS(pixel + n)} & | & a_2
\end{bmatrix}
\]

The spline fit coefficients for each pixel can be quickly calculated by construction the sums of the products of derivative-processed-raw-spectrum values with power integer values between -\(N\) and \(N\).

With the piece-wise continuous polynomial functions, it is a simple matter to interpolate the
derivative-processed-raw-spectrum to the common-frequency array as found in the molecular response functions.

\[
\text{IPS}(v_j) = a_0(v_j) + a_1(v_j) \cdot [(v_j - v_i) / v_j] + a_2(v_j) \cdot [(v_j - v_i) / v_j]^2 \quad \text{for} \quad \{ v_j : v_i < v_j < v_{i+1} \} \quad \text{and for} \quad \{ v_j : (v_j - v_{i-1}) > \text{Abs}(v_j - v_i) \} \quad \text{and for} \quad \{ v_j : (v_{i+1} - v_j) > \text{Abs}(v_j - v_i) \}
\]

Where \(\text{IPS}(v_j)\) is the interpolated-derivative-processed-raw-spectrum at the discrete common frequency
values used in the molecular response functions.

Inputs for SplineFit and Interpolate are the order of the spline-fit polynomial (typically=2), the
number of pixels used in the spline fits (typically \(2N+1 = 5\)), the derivative-processed-raw-spectrum, the
pixel-to-frequency polynomial calibration coefficients, and the molecular response function common-
frequency array. The accuracy of the Raman line intensity determination is sensitive to the pixel-to-
frequency calibration, so it is important to verify the calibration by measuring air composition before
and after a Raman experiment. The frequencies of the oxygen and nitrogen peaks should be at 1555 cm$^{-1}$ and 2331 cm$^{-1}$, respectively. The composition of air should measure 78.1% nitrogen and 20.9% oxygen (+/-2%). Raman intensities for each molecule of interest are calculated from the processed Raman spectrum as:

$$RLI(i) = \sum_{(v \text{ to } 4200)} MRF_i(v) * PS(v)$$

**Spectrometer Response Function Determination**

Molecular concentrations are calculated from Raman intensities by multiplying by proportionality constants. The proportional constant values are determined by absolute molecular cross-sections, laser power, integration time and the spectrometer intensity response function. The proportionality constants for each analyte of interest are modeled as a product of the molecular Raman cross-section and the spectrometer-response-function to allow easier correction to the calibration should the spectrometer-response-function change. In Table 5, the Raman-cross-sections, entered as diagonal elements in the calibration matrix, are taken from literature values, referenced to the nitrogen cross-section.

In general, where spectral overlaps occur, interferences can be accounted for by off-diagonal matrix elements which are the negative product of the relative intensity of the interferent times the cross-section of the analyte. For example, the interference of the 1285 cm$^{-1}$ CO$_2$ line on primary N$_2$O line is $-(0.61 * 0.51) = -.311$. In the case of NO$_2$ interference, the off diagonal elements were determined experimentally because of the complexity of the NO$_2$ spectrum. Figure 4 shows a nitrogen dioxide spectrum overlaid with MRF’s for NO$_2$, N$_2$O, and CO$_2$. Figure 5 shows the calculated concentrations of

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<th>RCS</th>
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<th>O$_2$</th>
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<th>NO</th>
<th>H$_2$</th>
<th>CO$_2$</th>
<th>CO</th>
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Table 5: Raman Cross-section Matrix and Spectrometer Response Values
Figure 4. Spectrum with 1% NO$_2$ with N$_2$O, CO$_2$, and NO$_2$ Molecular Response Functions

Figure 5. Mixed Gas Concentrations

The Spectrometer-response-functions in Table 5 are determined experimentally from known gas standards where possible. Figure 6 shows data from experiment 7 conducted on 23June2016. The test starts with 100% nitrogen in the cell which is displaced by Hydrogen over 75 minutes. The PCF is set to 0.874 to give 100% Total reading when averaged over the first 10 data points. As time progresses the nitrogen reading drops to 33% and the hydrogen reading increases to 65% with the balance being water at 2%. The average Total pressure is 100% +/-1.5% (1 sigma).
Molecular and Spectrometer Response by Difference

The Species concentrations can be modeled by straightforward calibration using measured intensities of gas standards with known composition. The assumption of fixed laser power, integration time and spectrometer configuration should be verified before and after experiments by measuring room air as a check standard. In the case of laser power drift, the PCF should be applied. In the case of instrument modification, a new set of SRF’s should be applied. Analyte gas concentration is determined by:

\[
[\text{Concentration}(i)] = \text{PCF} \times \text{SRF}_i \times (\sum_j \text{RCS}_{ij} \times \text{RLI}(j))
\]

There are cases when gas standards are not available for some species. Ammonia is one species that is difficult to characterize because a stable high concentration standard is difficult to obtain. It is possible to estimate the SRF for ammonia by difference. Figure 7, experiment Test_6A_Check again shows nitrogen in the Raman cell being displaced by hydrogen. The nitrogen SRF = 0.185 was established by measurements on 100% nitrogen gas at 1 atmosphere pressure. The hydrogen SRF = 0.38 was established by measurements of a 10% H2 standard gas at 1 atmosphere pressure. During the course of the test, the sum of nitrogen and hydrogen remain constant.
Figure 7. Hydrogen and Nitrogen SRF stability

Figure 8, experiment CDISS-6B shows a mixture of nitrogen, hydrogen and ammonia. The measured values of the gases are constant with the nitrogen concentration = 12.6% (+/- 0.5%), hydrogen = 52.3% (+/- 0.7%), water = 1.2% (+/-0.2%) and N₂O = 0.9% (+/-0.3%). If the balance of concentration = 33.0 (+/-0.9) was assigned to ammonia, the SRF for ammonia = 0.38.

Figure 8: Hydrogen, Ammonia and Nitrogen in Raman Cell

Figure 9, experiment CDISS-6A shows mixtures of hydrogen and ammonia displacing nitrogen. In this experiment the flow cell was partially plugged causing pressure buildup. The cell was vented near measurements 28, 77 and 135. The effect of pressure increase is evident in the total pressure value trending above 100%.
Appendix: Calibration Procedure Outline

Summary of Instrument Calibration Procedure:
1. Power up instrument and allow to stabilize for at least 20 minutes.
2. Start Raman control software and set to:
   a. Raw pixel output
   b. 5 second exposure
   c. 10 exposure average
   d. 300 mw laser power
   e. 25 micron entrance slit
3. Fill gas cell with air
4. Begin data collection into Excel spreadsheet
5. Open data processing spreadsheet and verify link to data collection sheet.
   The data processing sheet automatically:
   a. Reads frequency calibration from Model sheet
   b. Reads Molecular-Response-functions from Model sheet
   c. Reads common-frequency array from Model sheet
   d. Reads Intensity-calibration constants from Model sheet
   e. Reads spline fit parameters from Model sheet
   f. When available from instrument, load Raw-Raman-spectrum from RawData Sheet
   g. Process Raw-Raman-spectrum
   h. Spline fit
   i. Interpolate
   j. Calculate Raman Intensities
   k. Calculate Molecular Concentration
1. Write processed data to Results sheet
2. Go to f
References:

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Alfons Weber
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