SAND2019-2346C

Uncertainty Limits in Raman Derived Values of Temperature and Stress

PRESENTED BY

Elbara Ziade, 9144

March 4th 2018

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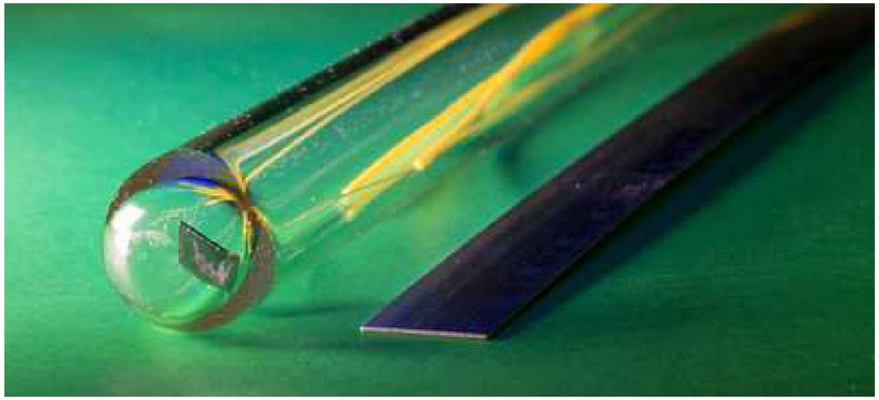
Outline

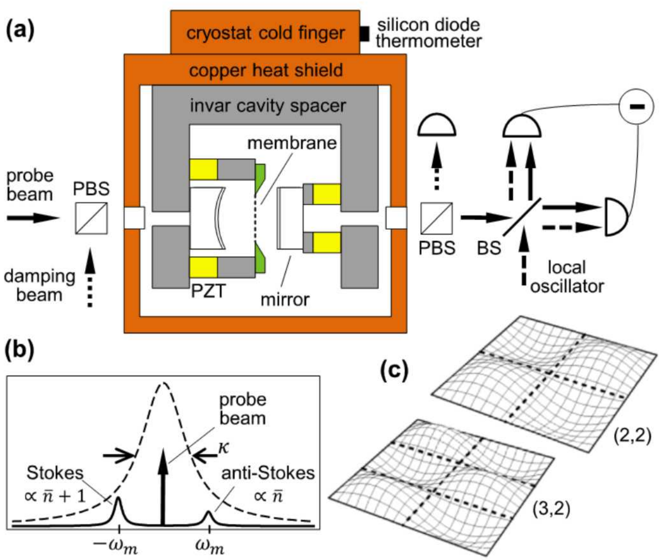
1. Physics of the Raman Measurement
2. Voigt Function
3. Traceability to SI
4. Uncertainty in Raman data fitting (Temperature)
5. Uncertainty in Spectrometer calibration

Impact of Raman Microscopy

NIST-on-a-chip: Photonic Thermometry



https://www.nist.gov/pml/nist-chip-photonic-sensors-temperature-and-light



Purdy, T. P., Yu, P. L., Kampel, N. S., Peterson, R. W., Cicak, K., Simmonds, R. W., & Regal, C. A. (2015). Optomechanical Raman-ratio thermometry. *Physical Review A*, *92*(3), 031802.

Residual Stress in Additive Manufactured Components

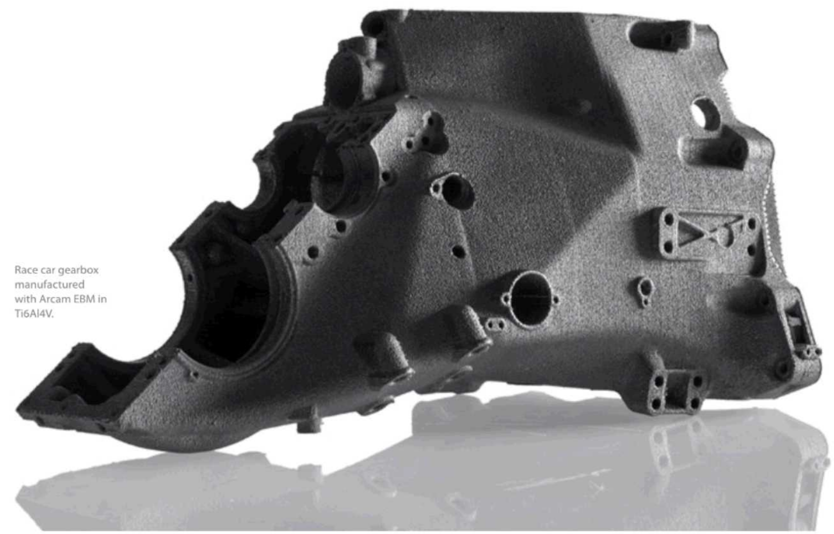
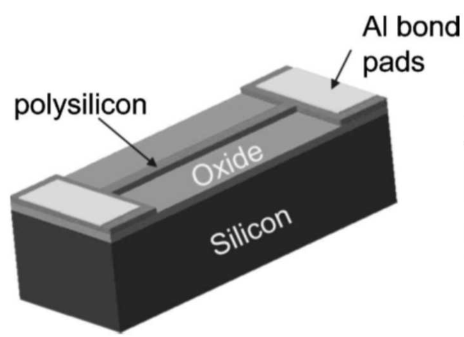
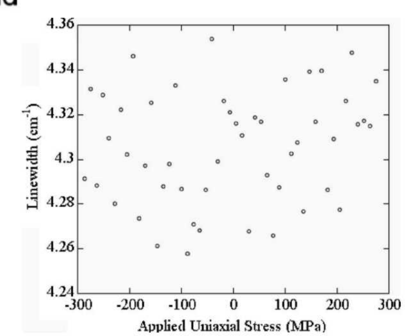


Photo from GE Arcam EBM Ti6Al4V brochure

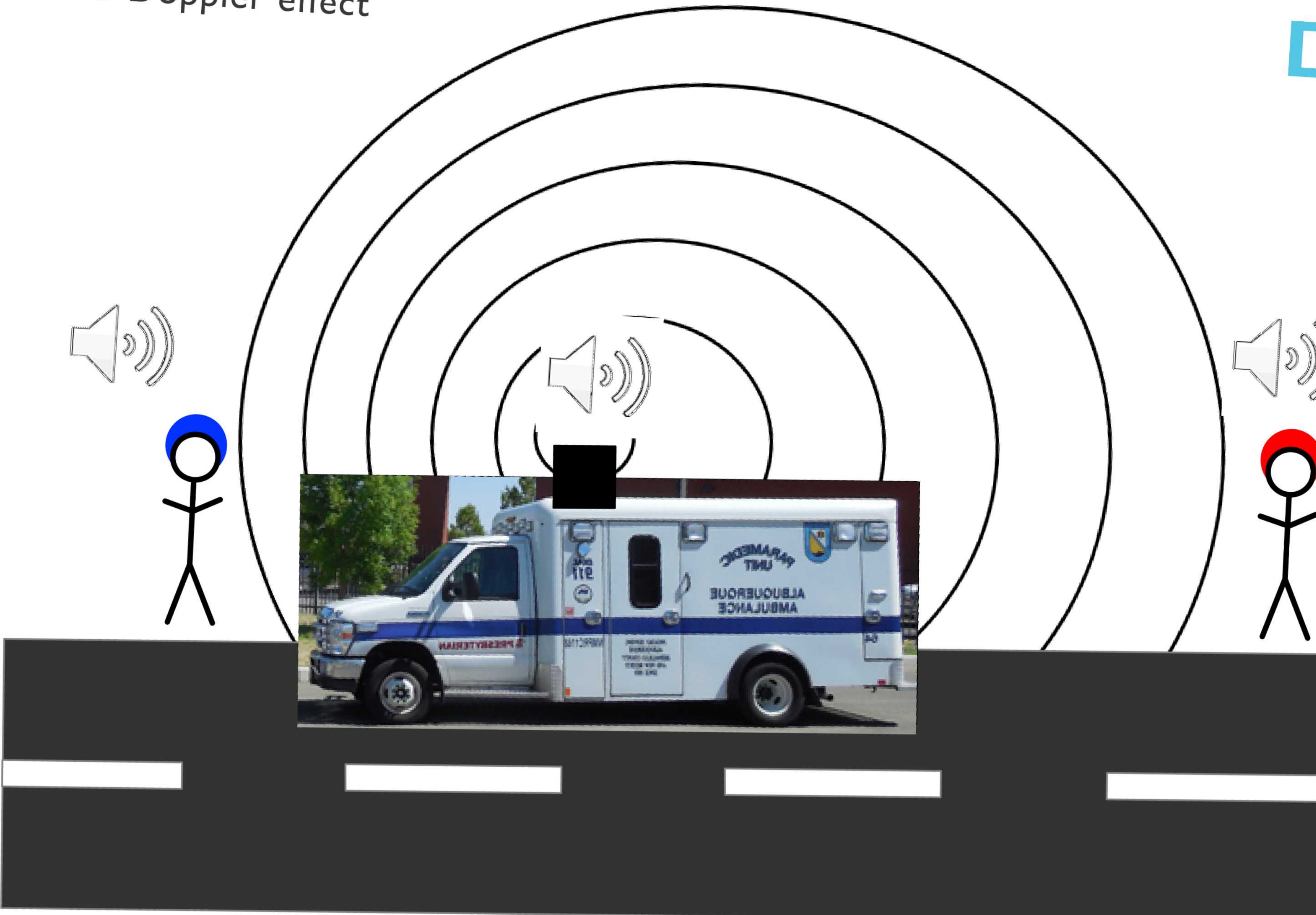




NISTIR 8036

Abel, M. R., Graham, S., Serrano, J. R., Kearney, S. P., & Phinney, L. M. (2007). Raman thermometry of polysilicon microelectro-mechanical systems in the presence of an evolving stress. *Journal of Heat Transfer*, *129*(3), 329-334.

Doppler effect



Doppler Shift of Light: Raman

Rayleigh:
Photon reflects with same energy

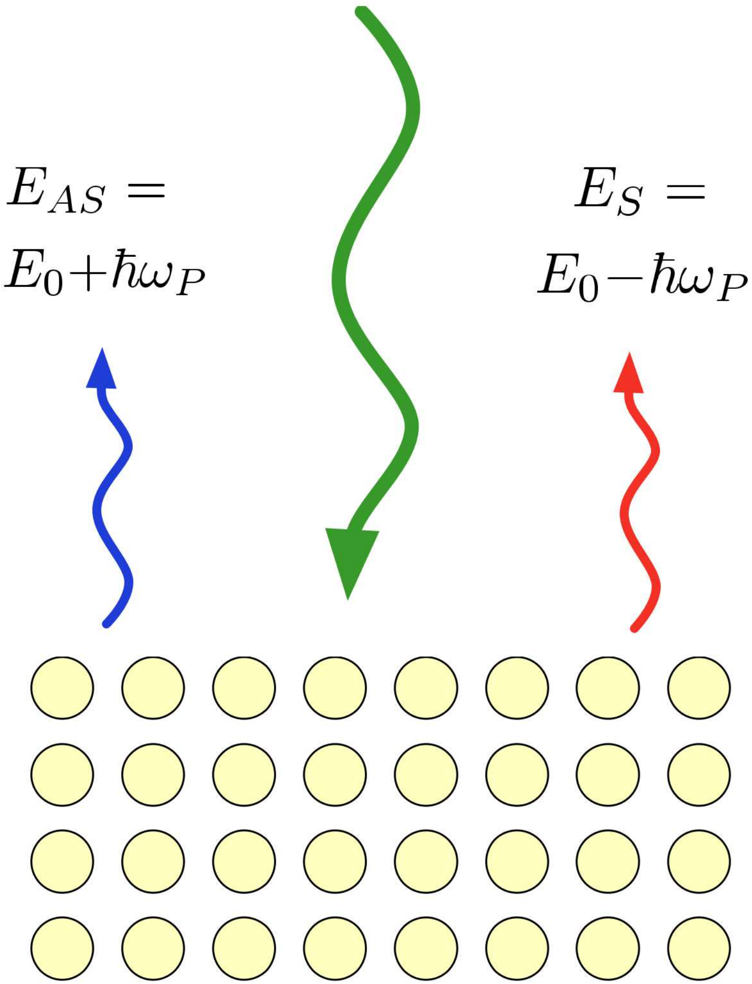
$$E_0 = \hbar\omega_0$$

Anti-Stokes:
photon gains energy from lattice

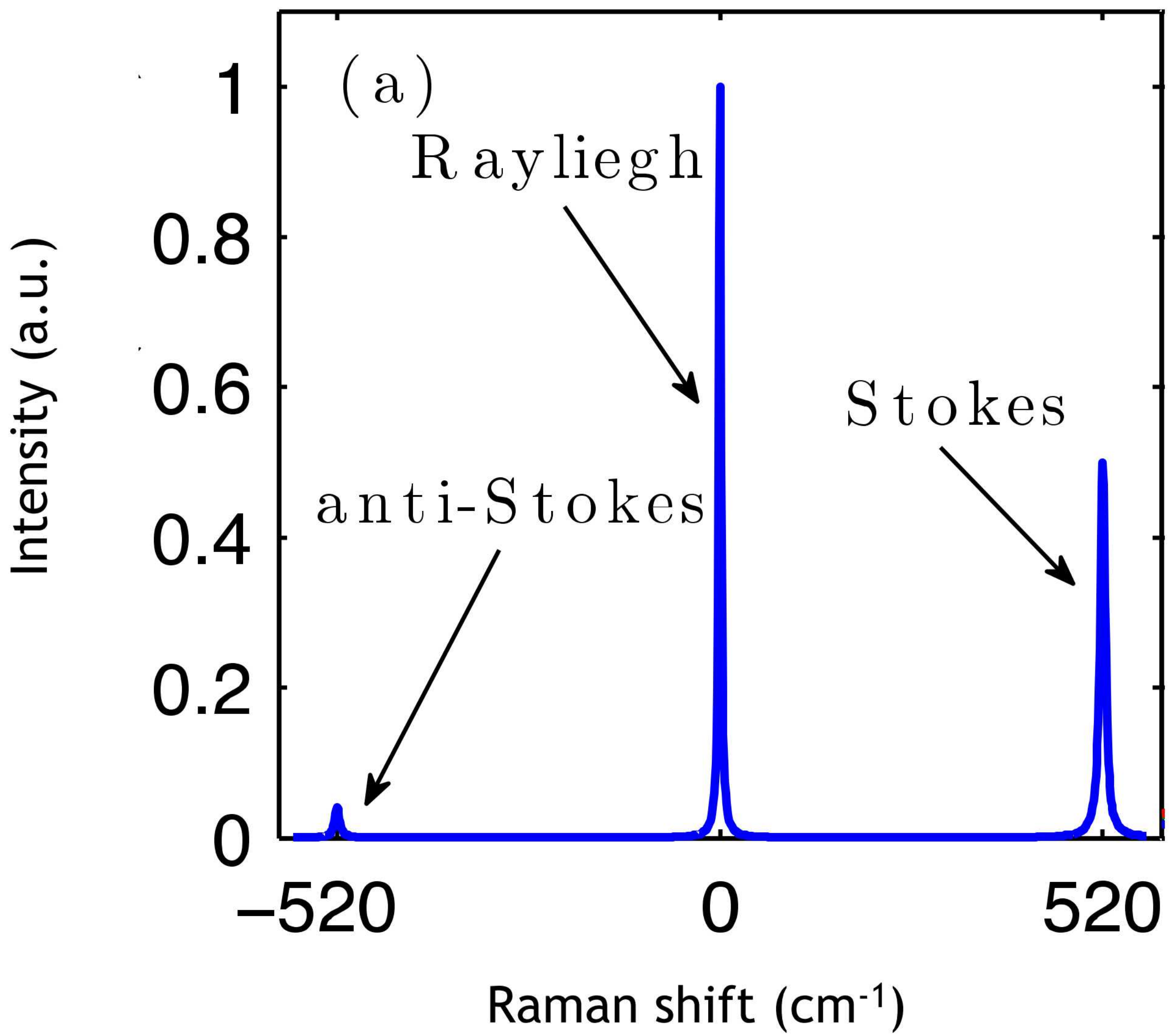
$$E_{AS} = E_0 + \hbar\omega_P$$

$$E_S = E_0 - \hbar\omega_P$$

Stokes:
photon loses energy to lattice



Raman: Doppler Shift of Light



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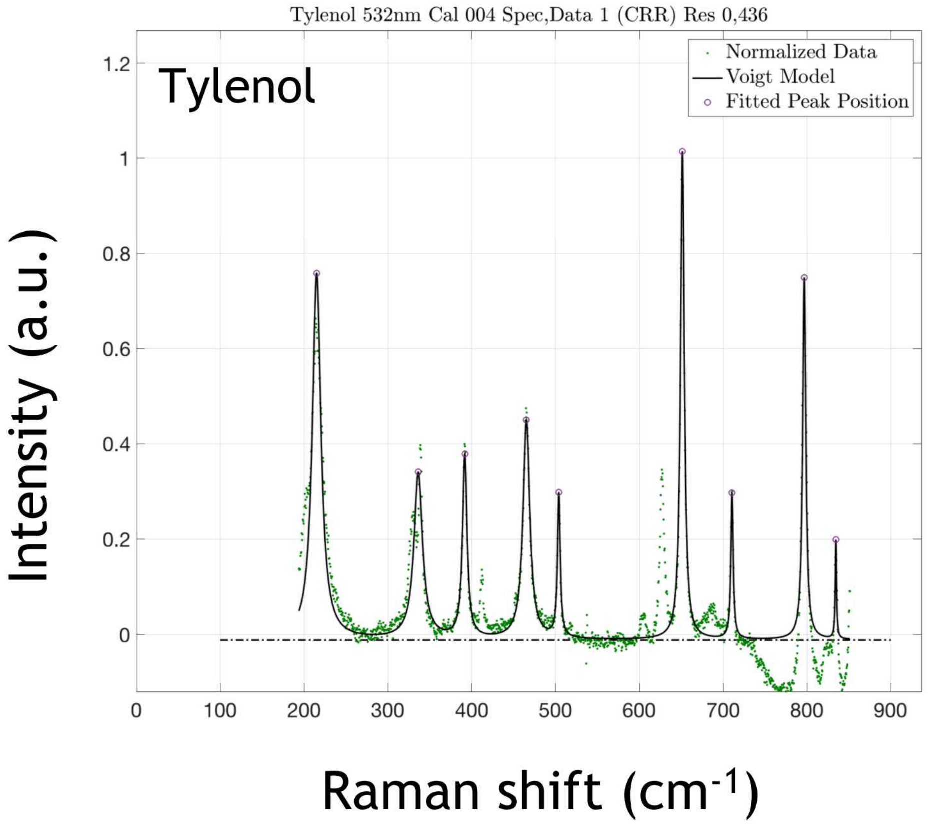
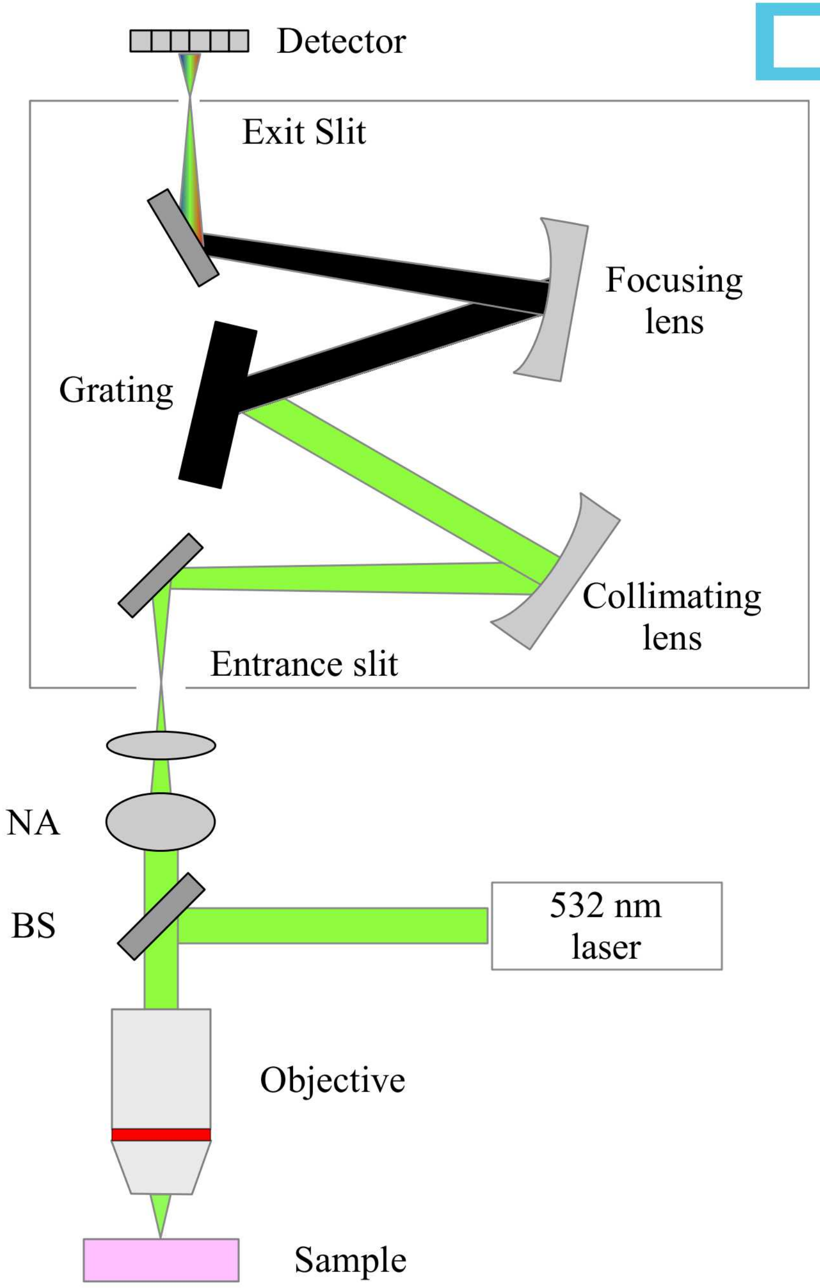
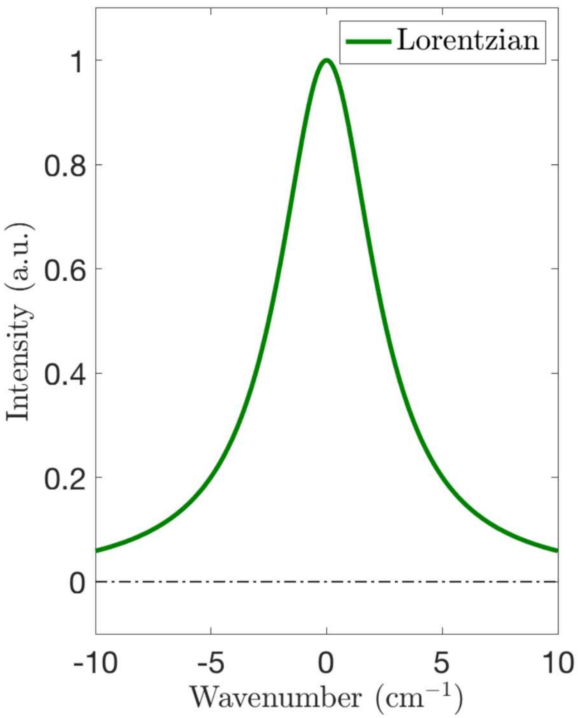
Raman Setup


Tylenol 532nm Cal 004 Spec,Data 1 (CRR) Res 0,436
Tylenol
Normalized Data
Voigt Model
Fitted Peak Position
Intensity (a.u.)
Raman shift (cm^{-1})
0
0.2
0.4
0.6
0.8
1
1.2
0
100
200
300
400
500
600
700
800
900


Detector
Exit Slit
Focusing lens
Grating
Collimating lens
Entrance slit
NA
BS
532 nm laser
Objective
Sample

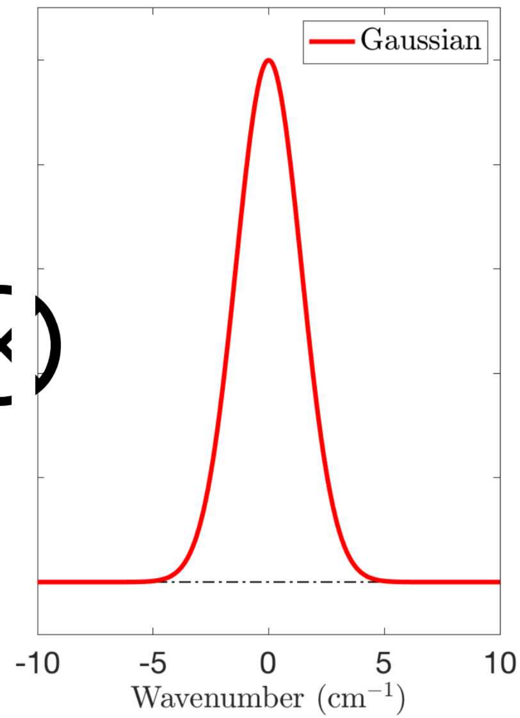
Voight: Gaussian Convolution with Lorentzian

Pure Raman signal:
Lorentzian



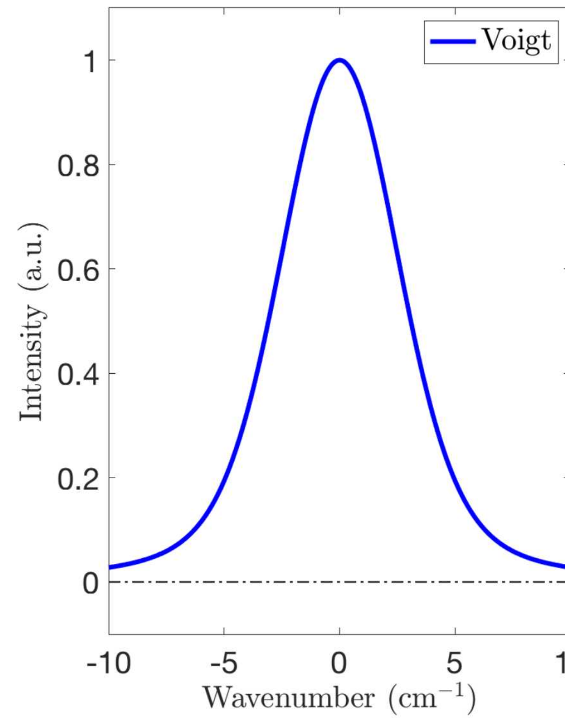
$\otimes$

Gaussian noise
from measurement



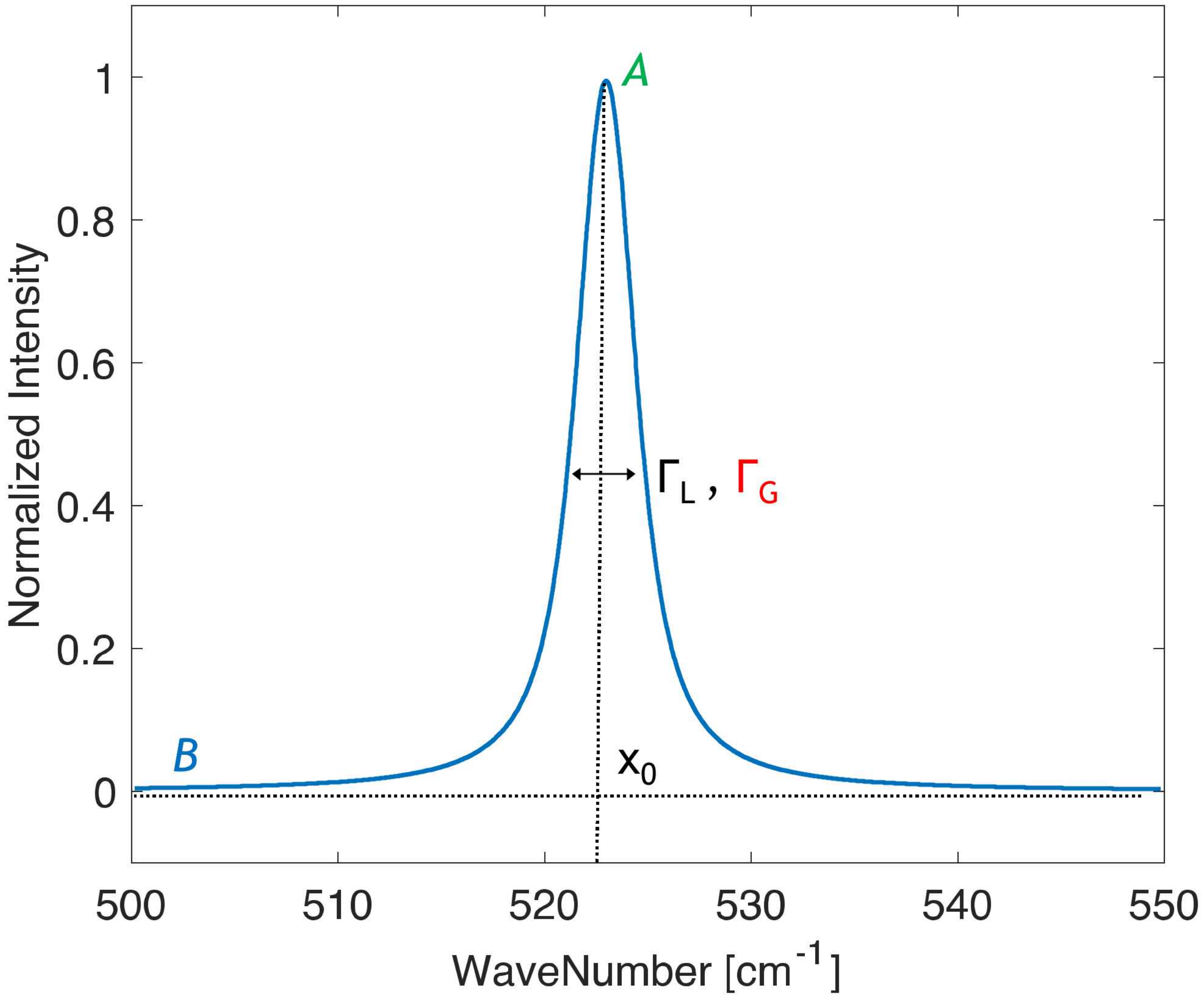
=

Measured signal:
Voigt



Voigt function: Gaussian & Lorentzian convolution

$$V(x) = f(\Gamma_L, \Gamma_G, x_0, A, B)$$



Γ_L - Lorentzian FWHM
x_0 - Peak Position
Γ_G - Gaussian FWHM
A - Integrated area
B - Background level

Posener, D. W. "The shape of spectral lines: Tables of the Voigt profile." *Australian Journal of Physics* 12.2 (1959): 184-196.

Traceability to International System of Units (SI)

1 Spectrometer Calibration

Process	ASTM E1840	Environmental Control
Type B	Type B	Type B

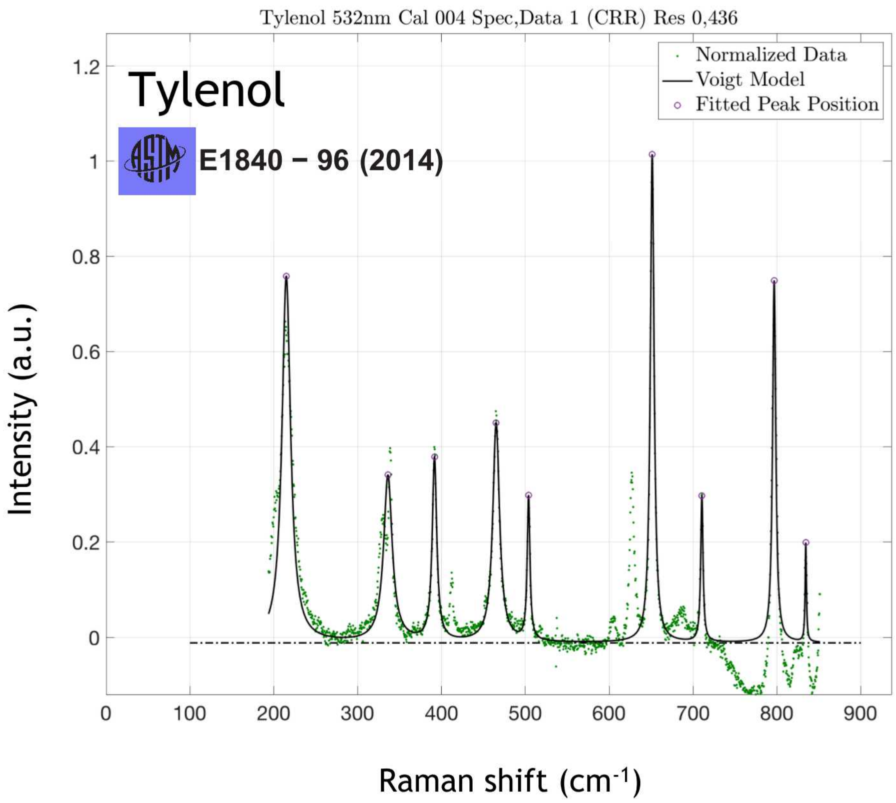
2 Process Uncertainty

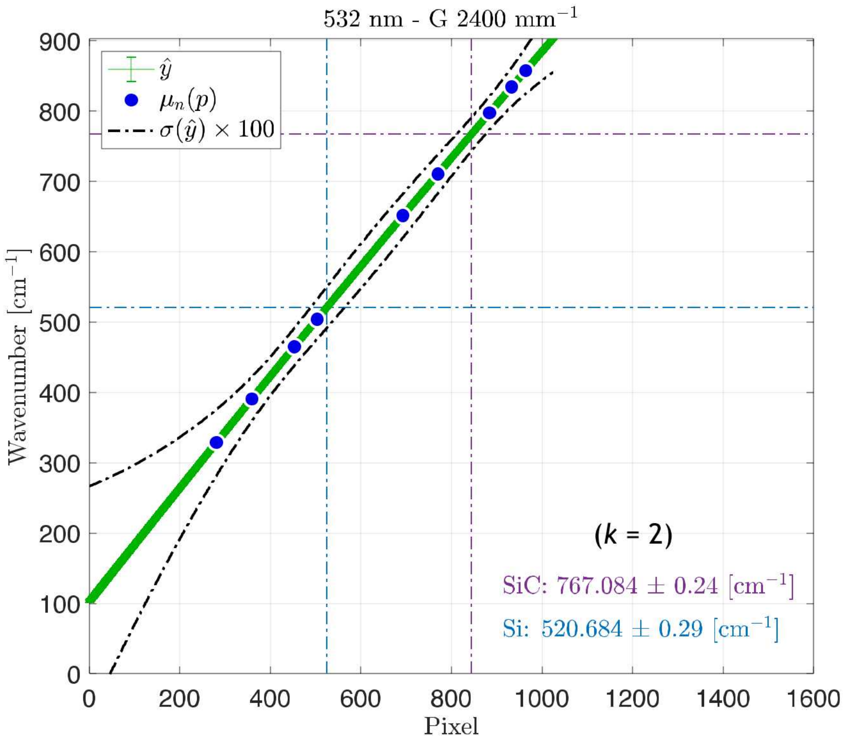
Signal to Noise Ratio	Type A	H - Peak Height A - Integrated Area B - Background
Resolution	Type B	Γ_G - FWHM Gaussian N - Number of points under peak
Variability of Sample	Type B	Γ_L - FWHM Lorentzien x_0 - Peak Position

What is the lowest achievable uncertainty for:

1. **Relative Peak position** for stress and temperature measurements
2. **Absolute peak position** for stress and temperature measurements

Spectrometer Calibration: Traceability to SI



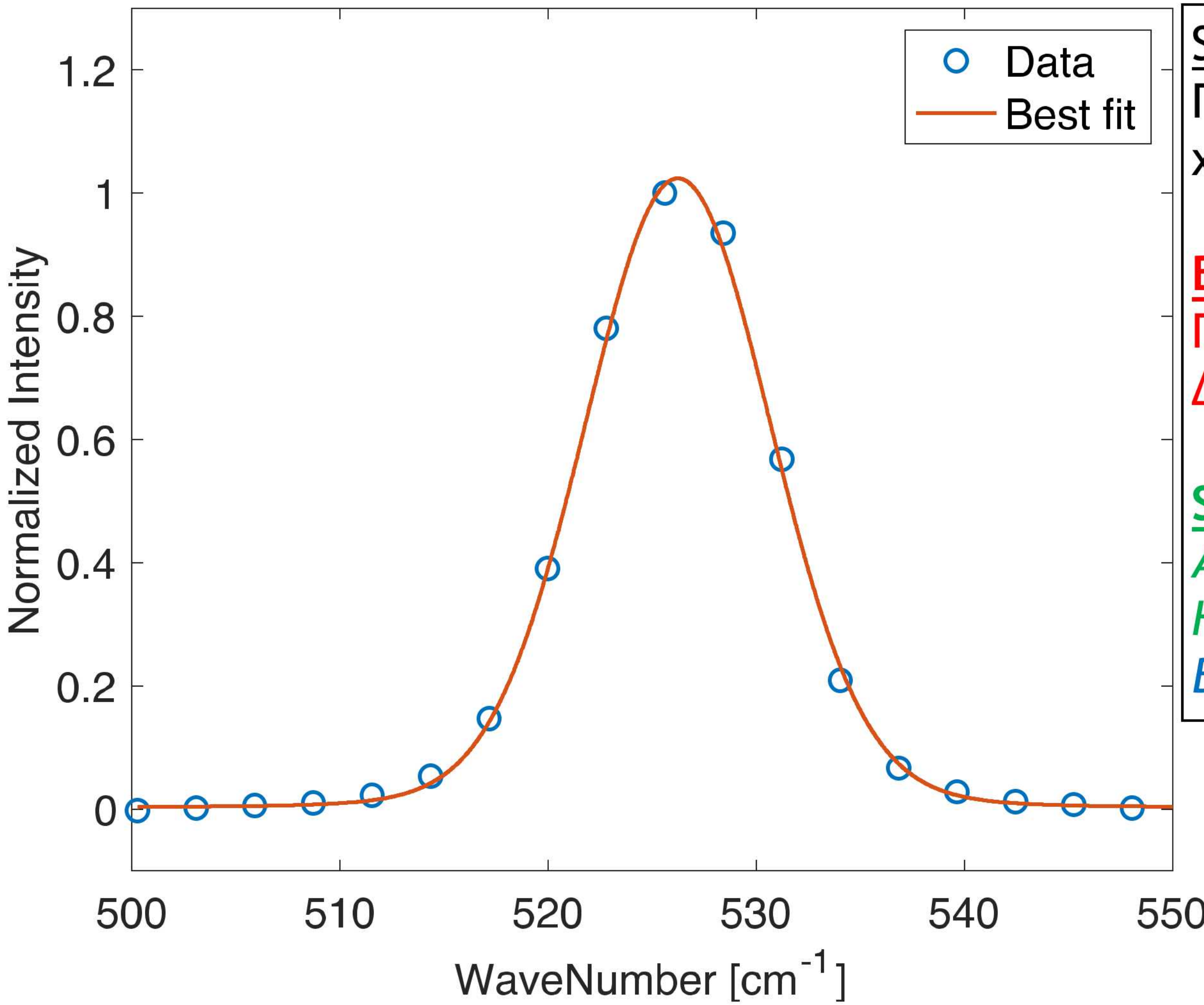


$$y_n = c_0 + c_1 x_n + c_2 x_n^2$$

where y_n is wavenumber of observation n; c_0, c_1 and c_2 are the best estimate fitting constants; and x is the pixel number.

Raman Measurement:

$$V(x) = f(\Gamma_L, \Gamma_G, x_0, A, B)$$



Signal of Interest:

Γ_L - Lorentzian FWHM

x_0 - Peak Position

Binning:

Γ_G - Gaussian FWHM

Δ - Resolution

Signal to Noise Ratio (SNR):

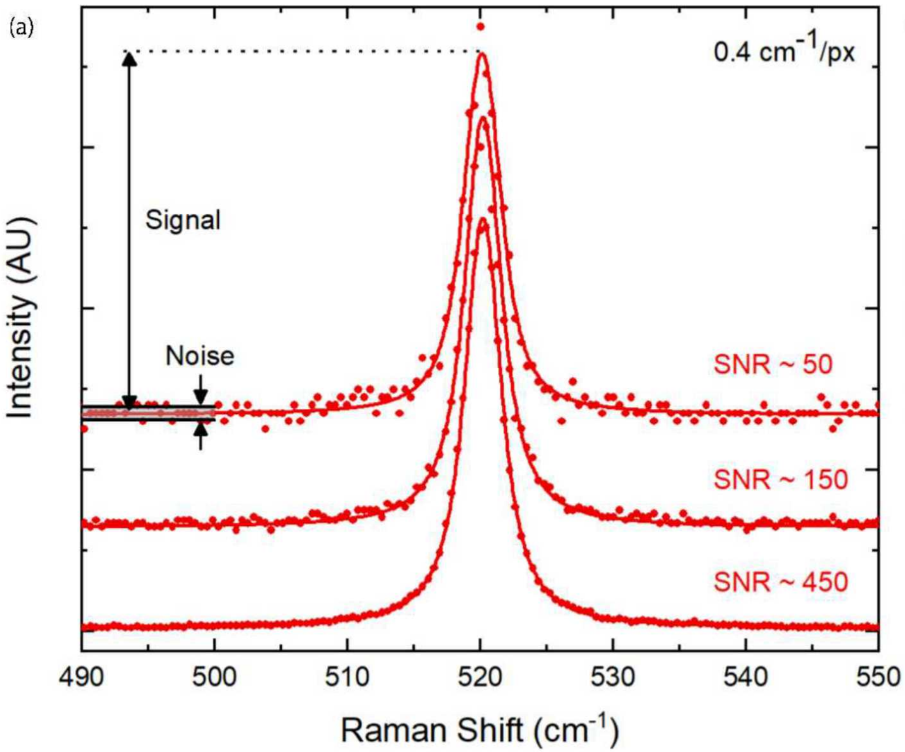
A - Integrated area

H - Peak height

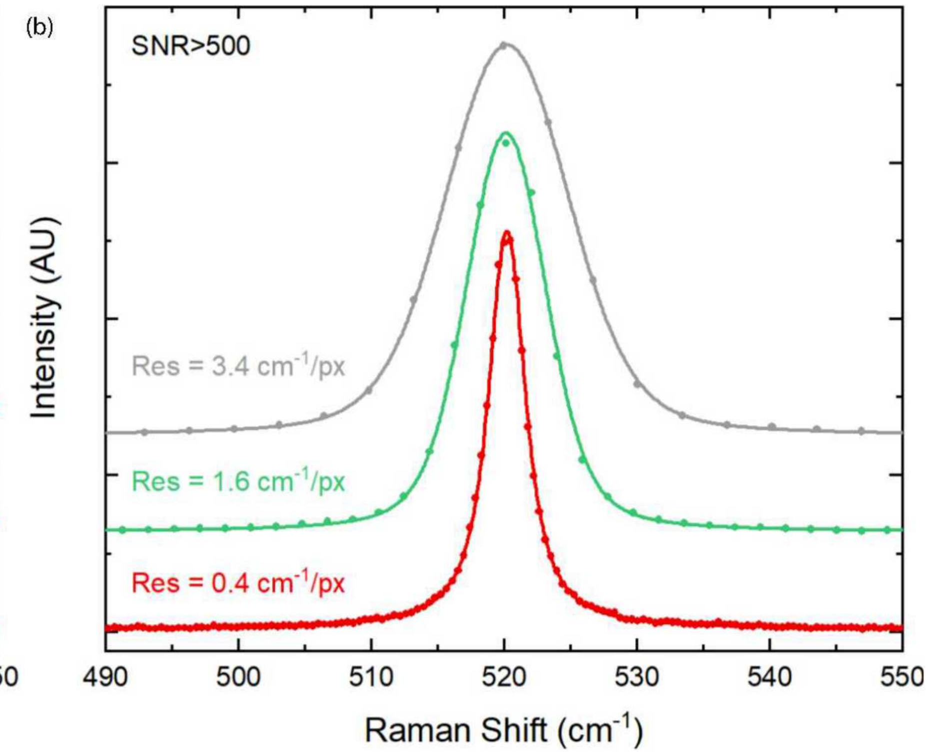
B - Background level

Raman Measurement

Signal to Noise Ratio (SNR)



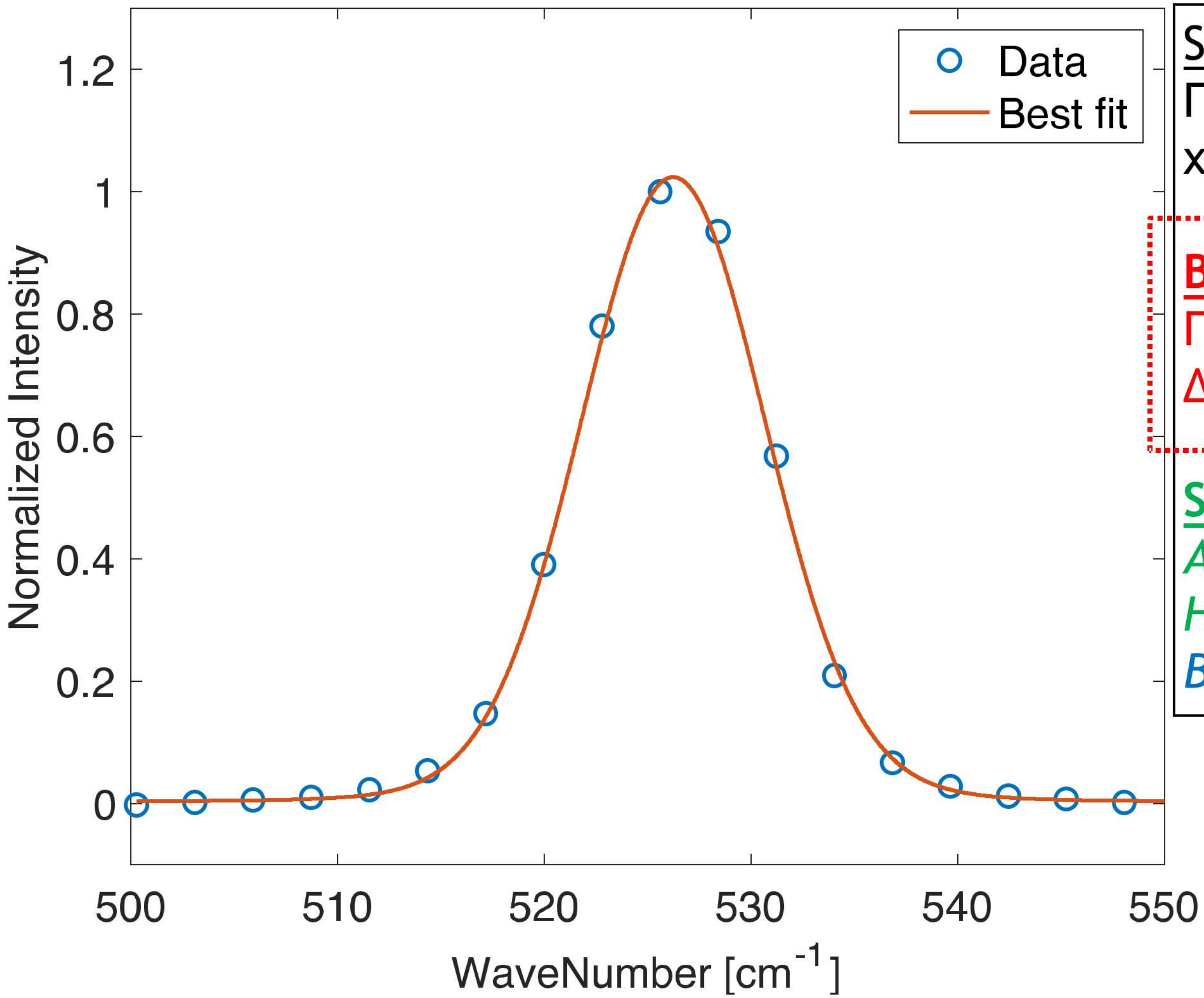
Binning



$$V(x) = f(\Gamma_L, \Gamma_G, x_0, A, B)$$

Raman Measurement:

$$V(x) = f(\Gamma_L, \Gamma_G, x_0, A, B)$$



Signal of Interest:

Γ_L - Lorentzian FWHM

x_0 - Peak Position

Binning:

Γ_G - Gaussian FWHM

Δ - Resolution

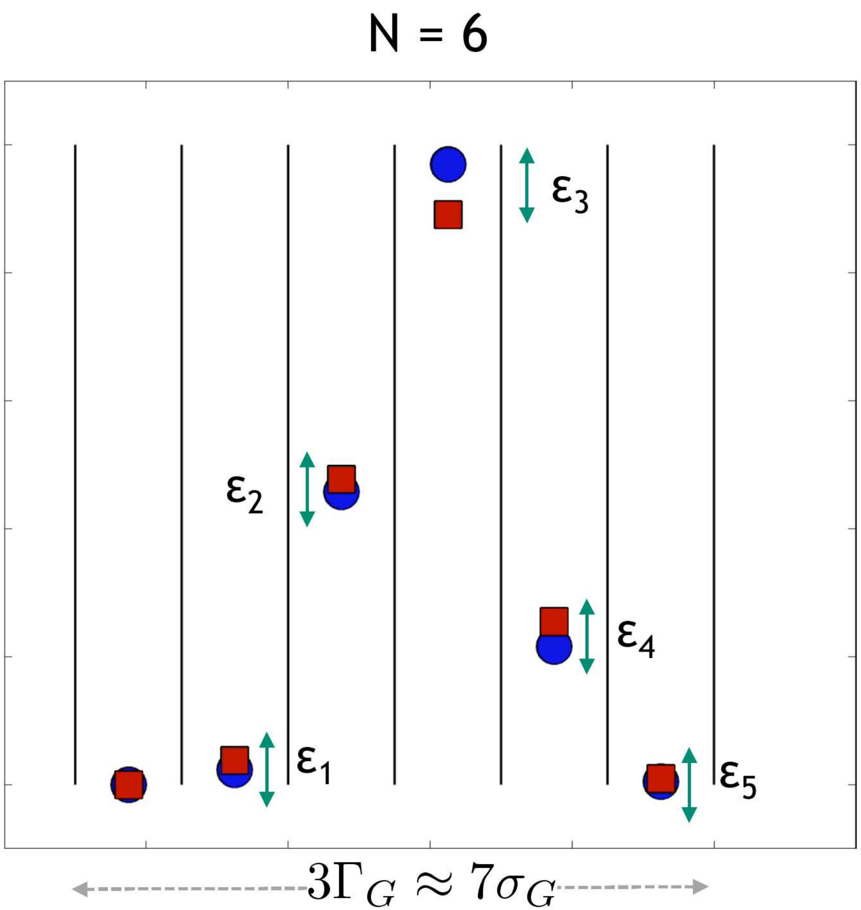
Signal to Noise Ratio (SNR):

A - Integrated area

H - Peak height

B - Background level

Error due to Binning



$$\sigma^2_{\Delta,V} = \sum_i^N \frac{\epsilon_i - \bar{\epsilon}}{N-1} \approx \frac{1}{(N-1)^3}$$

$$x_{\text{start}} = x_0 - 3\Gamma_V(\Gamma_G, \Gamma_L)$$
$$x_{\text{end}} = x_0 + 3\Gamma_V(\Gamma_G, \Gamma_L)$$

$$N = \frac{3\Gamma_V(\Gamma_G, \Gamma_L)}{\Delta}$$

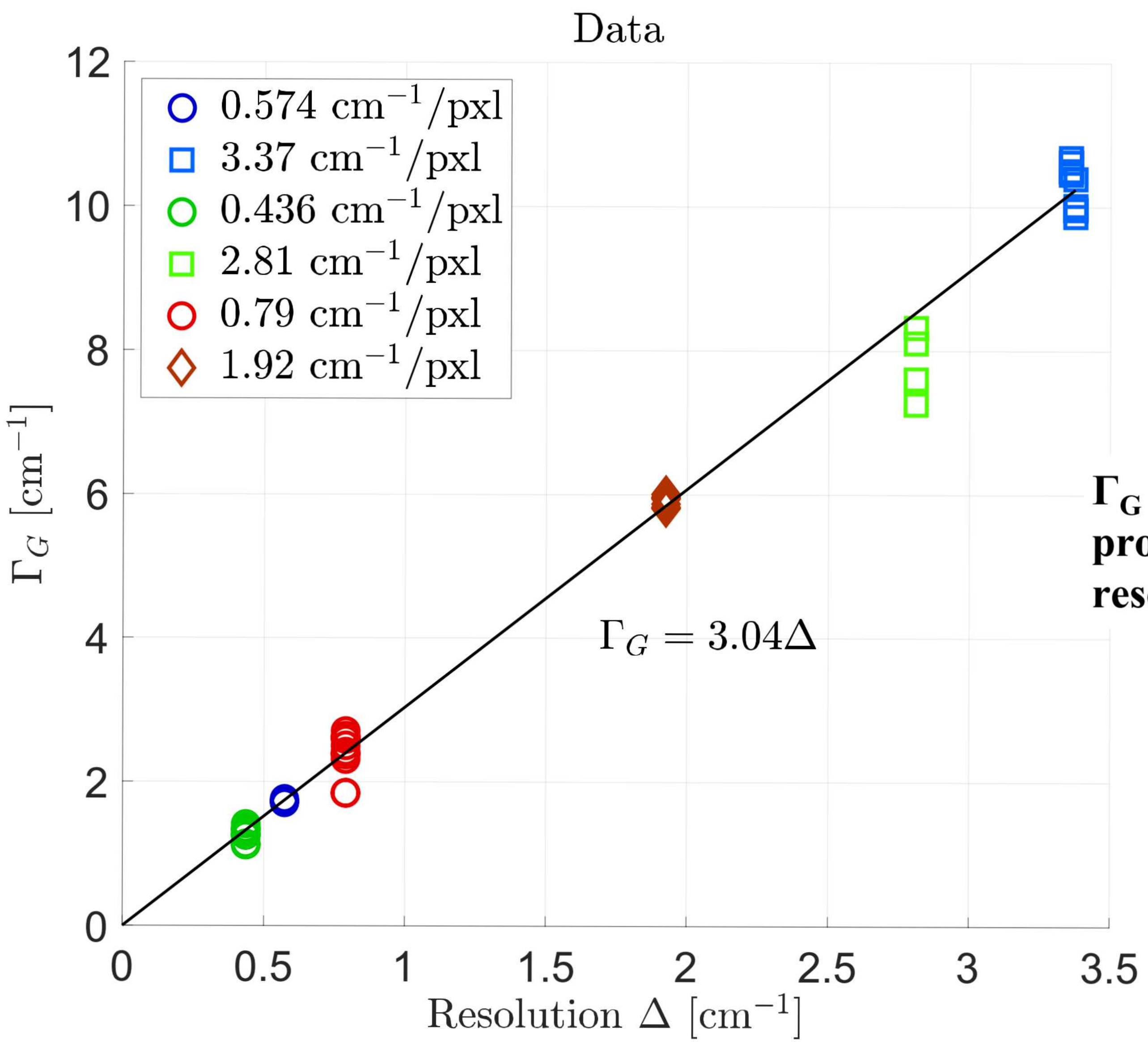
Convert pixilation error into wavenumber error

$$\boxed{\sigma^2_{\Delta,x} = (\boldsymbol{J}'\boldsymbol{J})^{-1}\boldsymbol{J}'[(\mathbf{1}\cdot\sigma_{\Delta,V}\cdot H)^2]\boldsymbol{J}(\boldsymbol{J}'\boldsymbol{J})^{-1}}$$

● $V(x) = v(x)$ True value of Voigt function at position *x*

■ $V_P(x) = \int_{x-\Delta/2}^{x+\Delta/2} v(x)dx$ Integrated value (measured value)

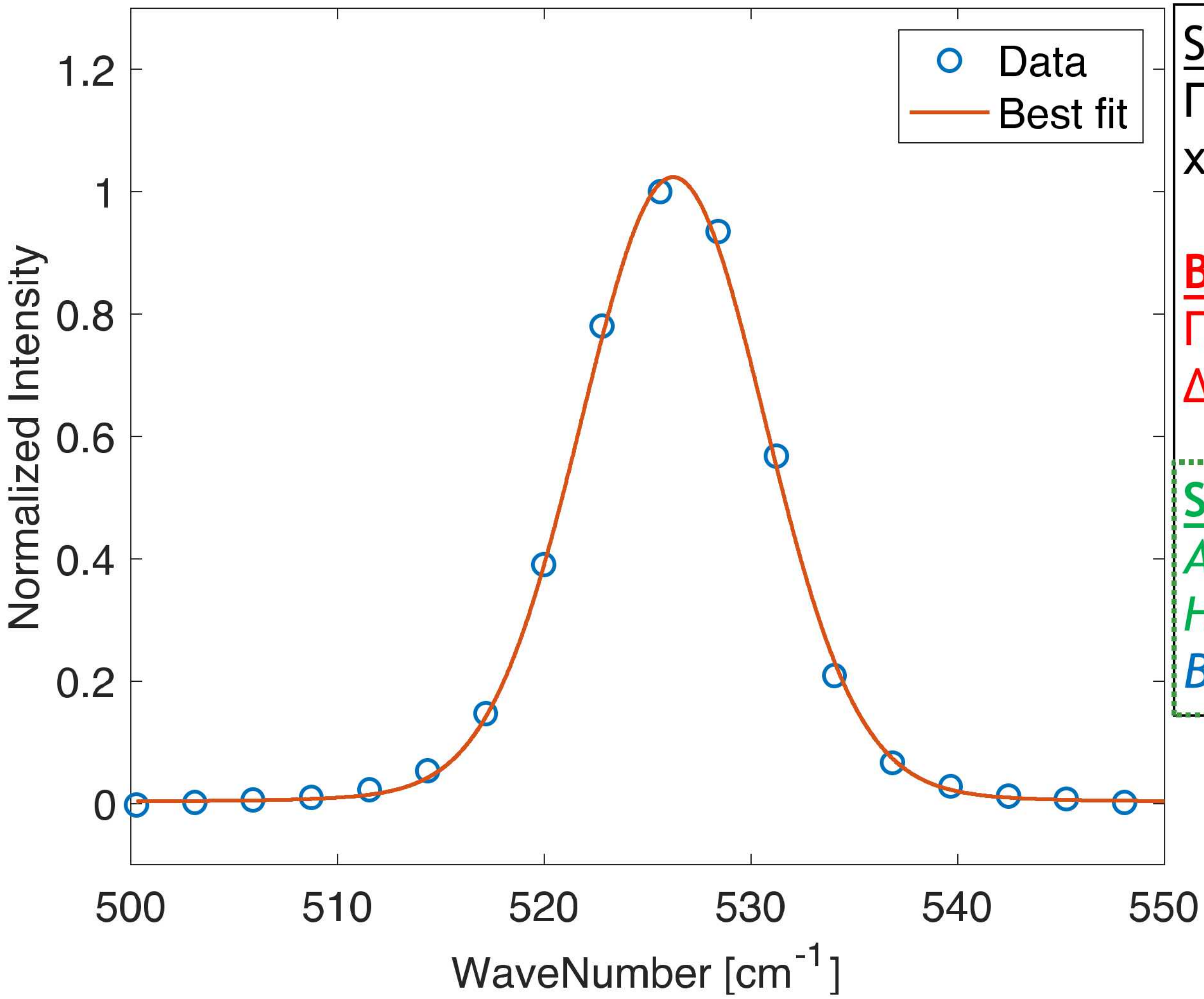
Binning: $\Gamma_G(\Delta)$



Γ_G is directly proportional to resolution (Δ)!

Raman Measurement:

$$V(x) = f(\Gamma_L, \Gamma_G, x_0, A, B)$$



Signal of Interest:

Γ_L - Lorentzian FWHM

x_0 - Peak Position

Binning:

Γ_G - Gaussian FWHM ✓

Δ - Resolution

Signal to Noise Ratio (SNR):

A - Integrated area

H - Peak height

B - Background level

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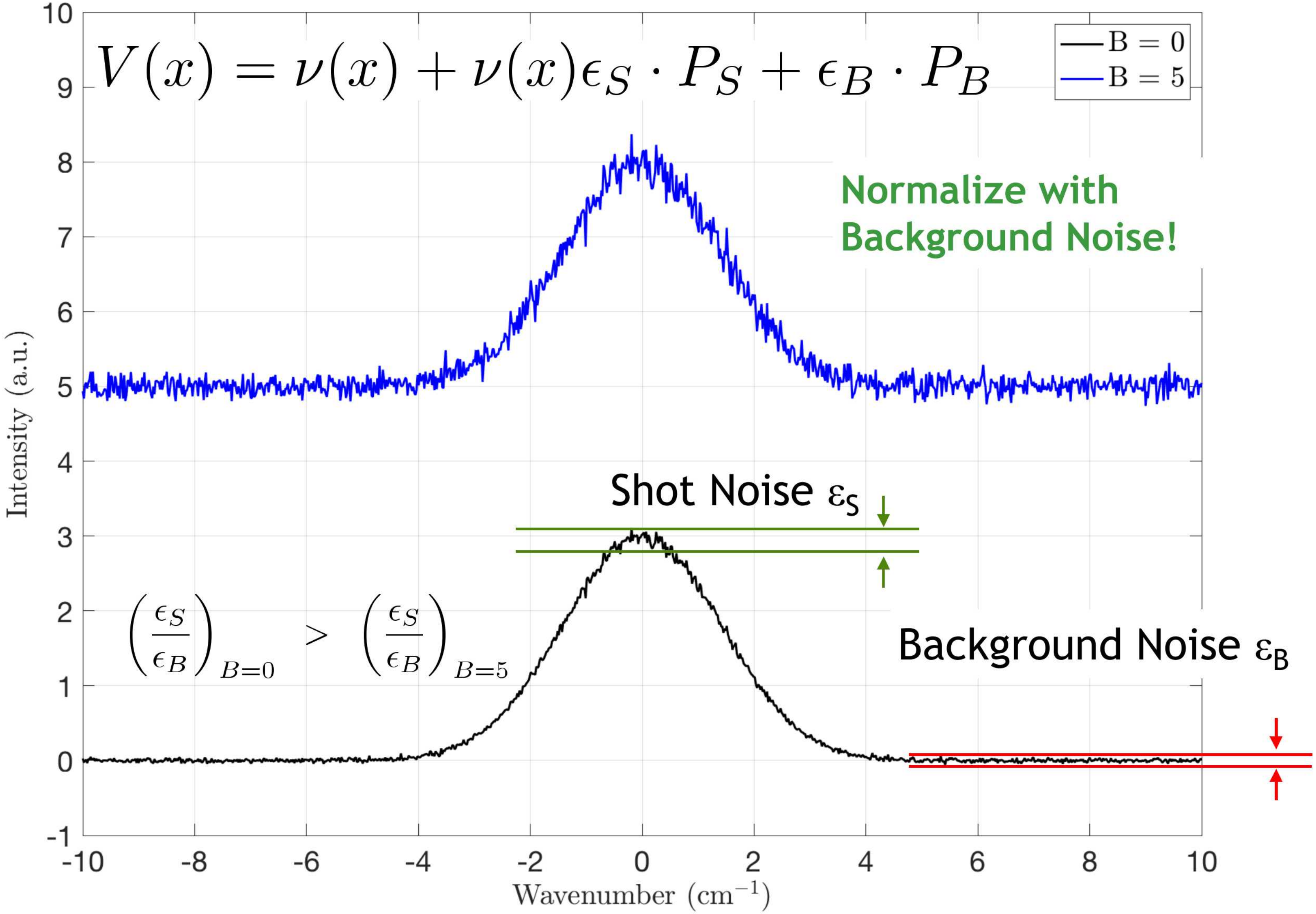
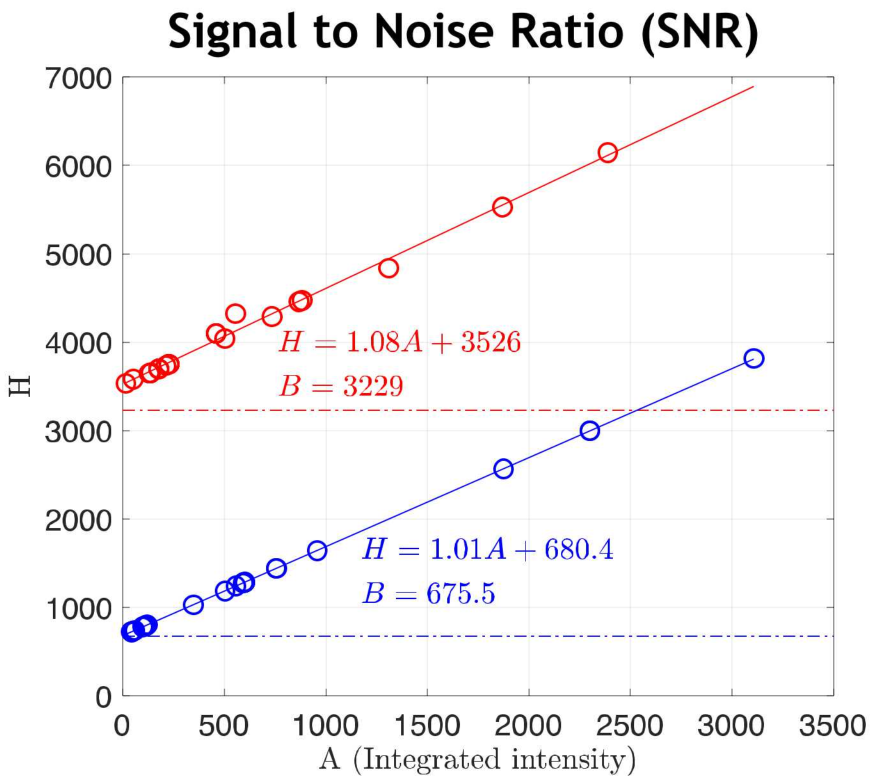
Signal to Noise Ratio (SNR)



Signal to Noise Ratio (SNR)



$$\mathrm{SNR} = H/B$$

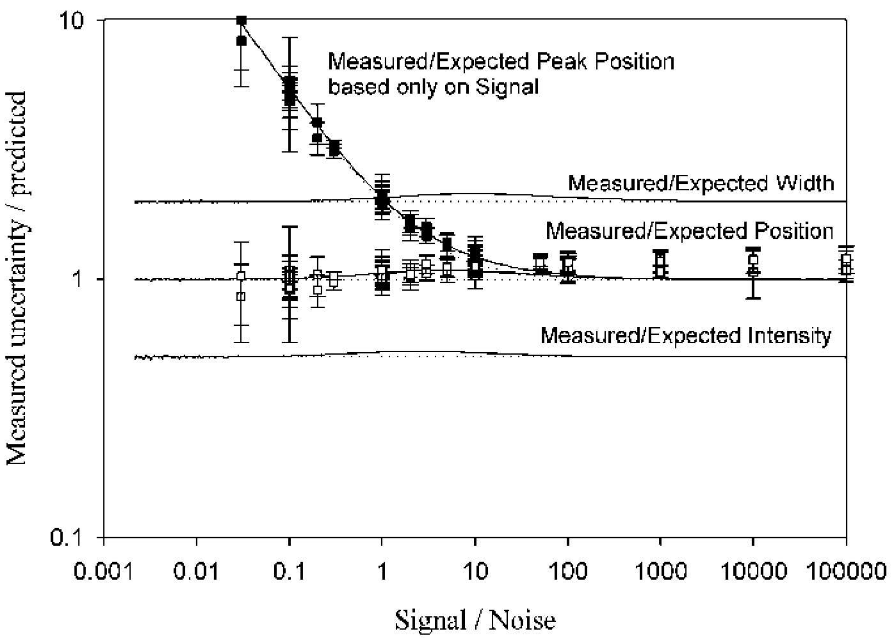
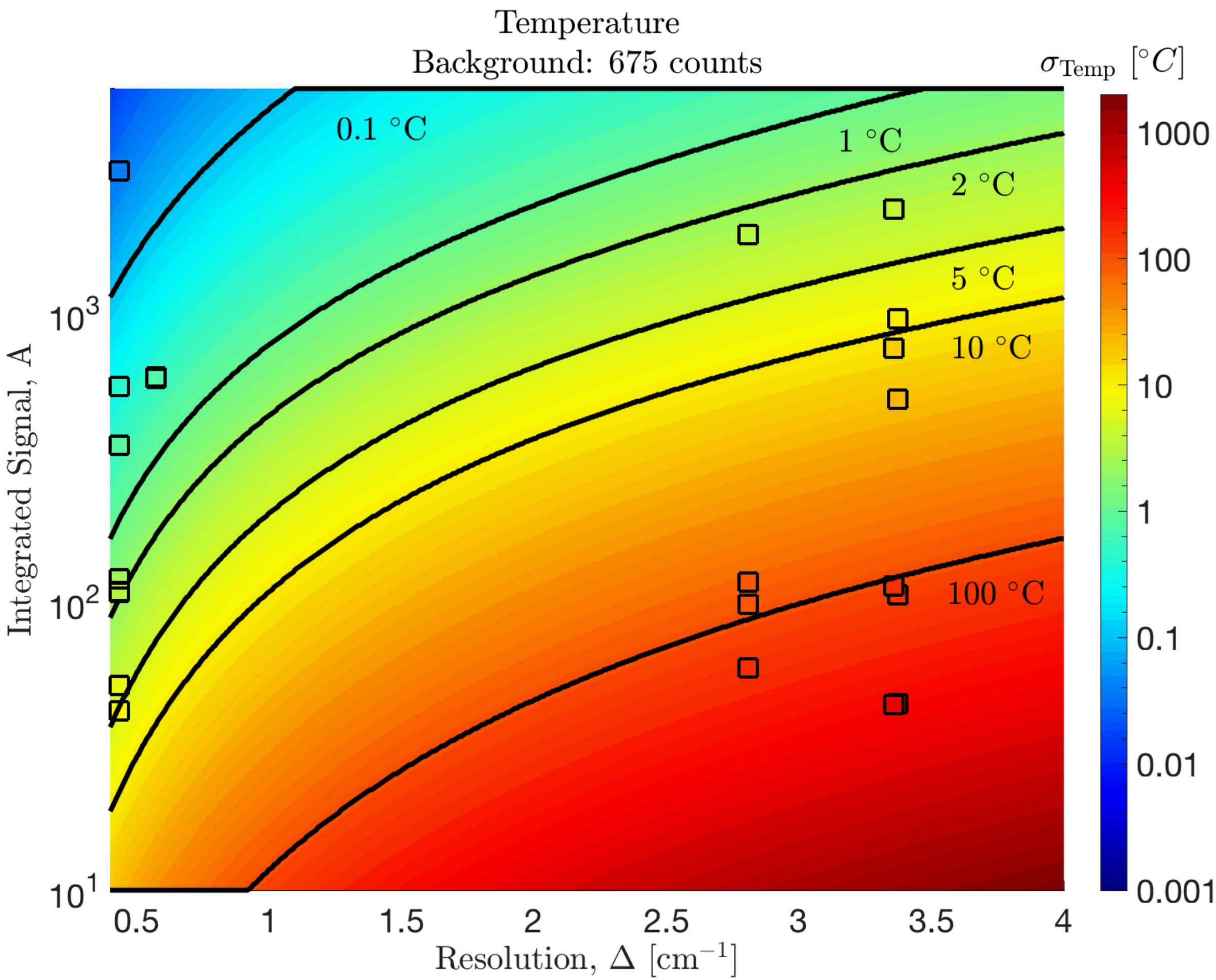


Figure 2. Plot of measured uncertainty in peak position, normalized by Γ_G^2/A without background (full symbols) or with background (open symbols), of the simulated data as a function of signal to noise (H/B). Four parameter weighted uncertainty fit.

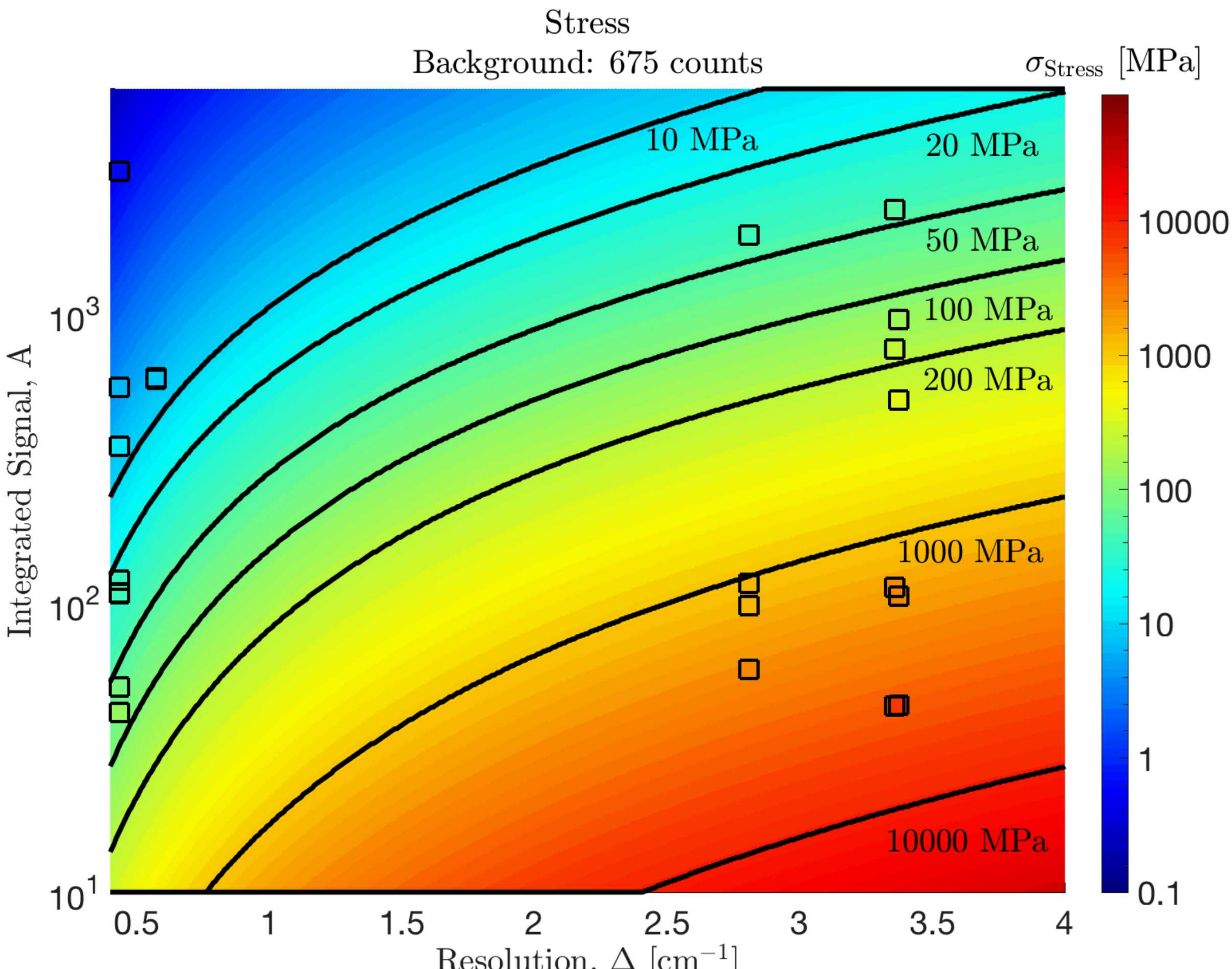
$$\boxed{\sigma^2_{\mathrm{SNR},x} \approx \frac{\Gamma_T(\Gamma_L,\Gamma_G)^2}{A}\left[1 + 2\sqrt{2}\left(\frac{H}{B} - 1\right)^{-1}\right]}$$

Appl. Phys. A 74 [Suppl.], S112–S114 (2002) / Digital Object Identifier (DOI) 10.1007/s003390201392

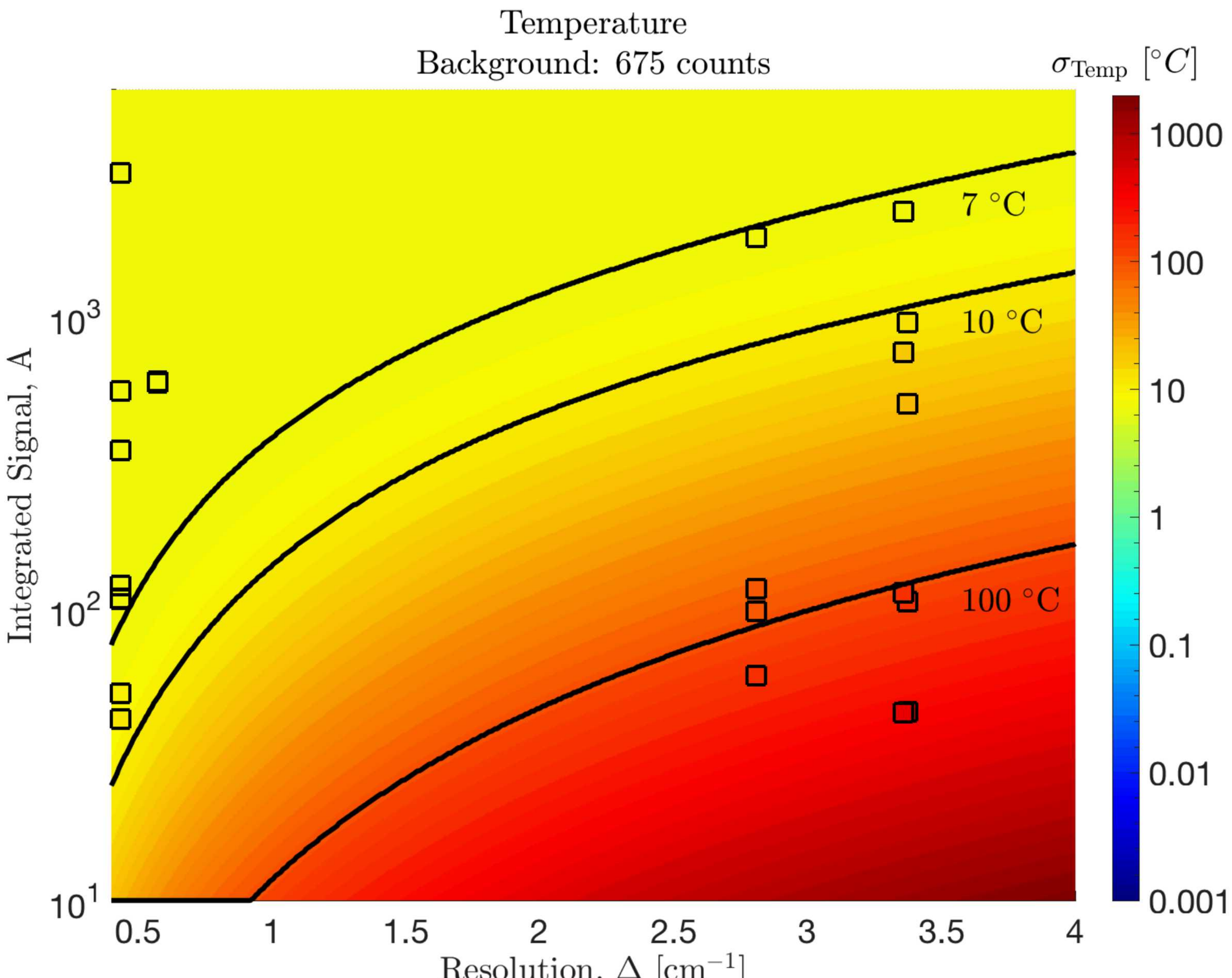
Relative Temperature Capabilities (B = 675) (*k* = 1)



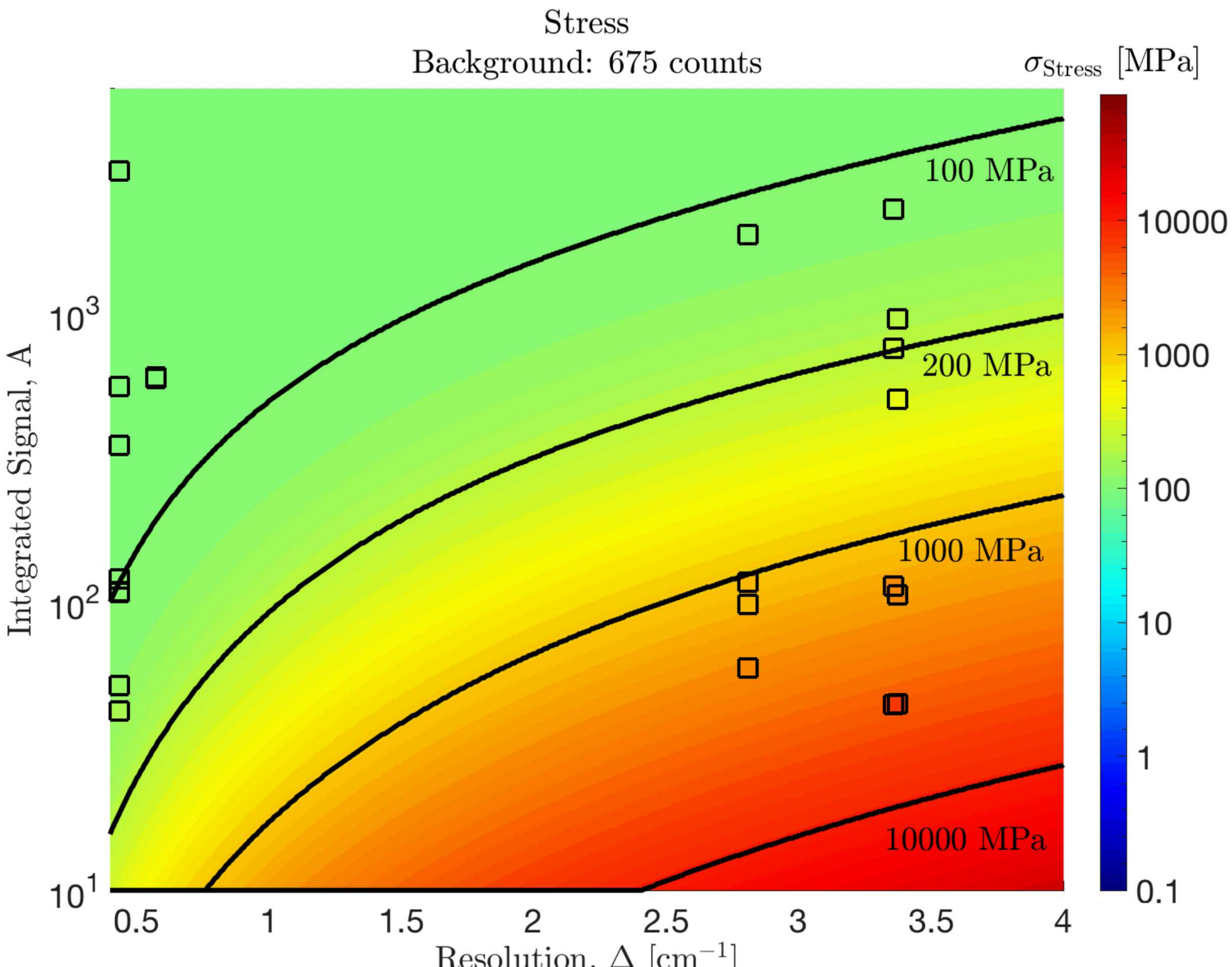
Relative Stress Capabilities (B = 675) (k = 1)



Absolute Temperature Capabilities (B = 675) (k = 1)



Absolute Stress Capabilities (B = 675) (k = 1)



Summary

- SNR = H/B
- $\Gamma_G \approx 3.04\ \Delta$
- Higher accuracy standard needed for Raman spectrometer calibration

Uncertainty due to binning

$$\sigma^2_{\Delta,V} = \sum_i^N \frac{\epsilon_i - \bar{\epsilon}}{N-1} \approx \frac{1}{(N-1)^3}$$

$$x_{\text{start}} = x_0 - 3\Gamma_V(\Gamma_G, \Gamma_L)$$
$$x_{\text{end}} = x_0 + 3\Gamma_V(\Gamma_G, \Gamma_L)$$

$$N = \frac{3\Gamma_V(\Gamma_G, \Gamma_L)}{\Delta}$$

$$\boxed{\sigma^2_{\Delta,x} = (\boldsymbol{J}'\boldsymbol{J})^{-1}\boldsymbol{J}'[(\mathbf{1}\cdot\sigma_{\Delta,V}\cdot H)^2]\boldsymbol{J}(\boldsymbol{J}'\boldsymbol{J})^{-1}}$$

Uncertainty due to SNR

$$\sigma^2_{\text{SNR},x} \approx \frac{\Gamma_T(\Gamma_L, \Gamma_G)^2}{A}\left[1 + 2\sqrt{2}\left(\frac{H}{B} - 1\right)^{-1}\right]$$

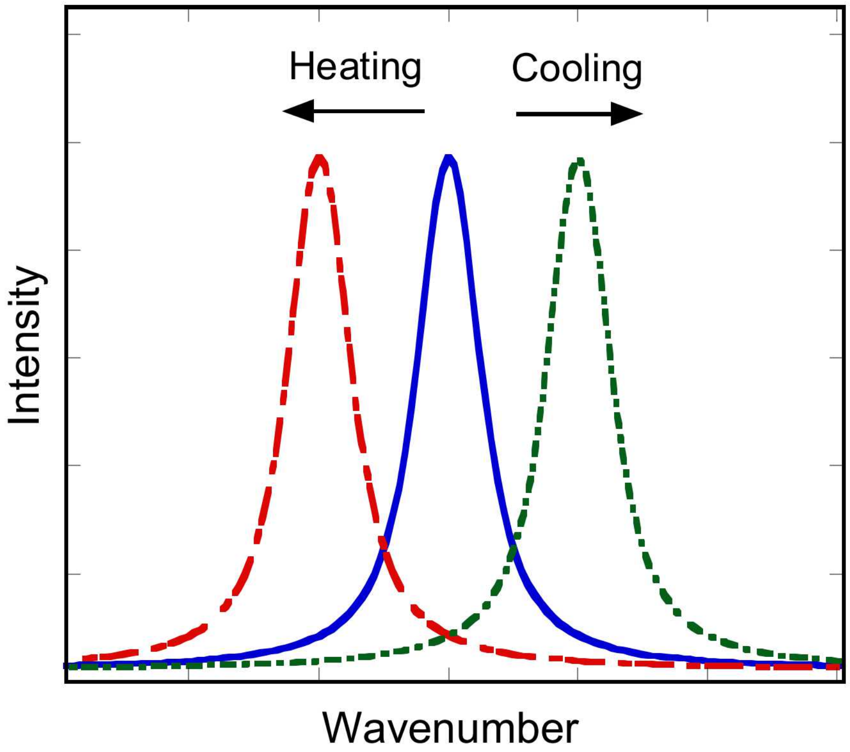
Uncertainty due to Standard

$$\sigma^2_{S,x} = \frac{1}{n^2}\sum_{p=i}^{n} \sigma_i^2(p)$$

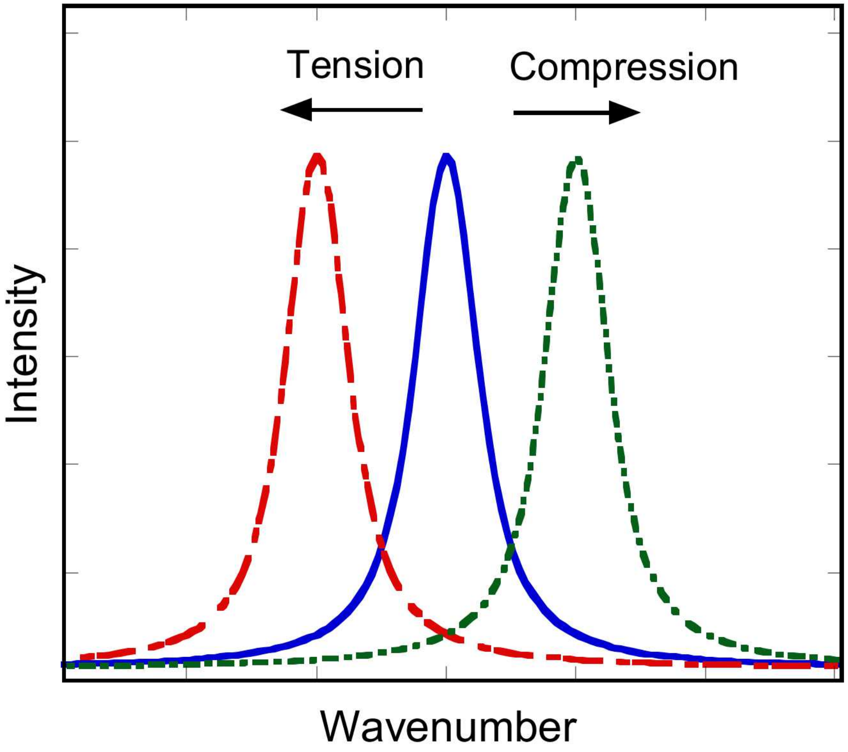
Questions?

What can we Measure with Peak Position?

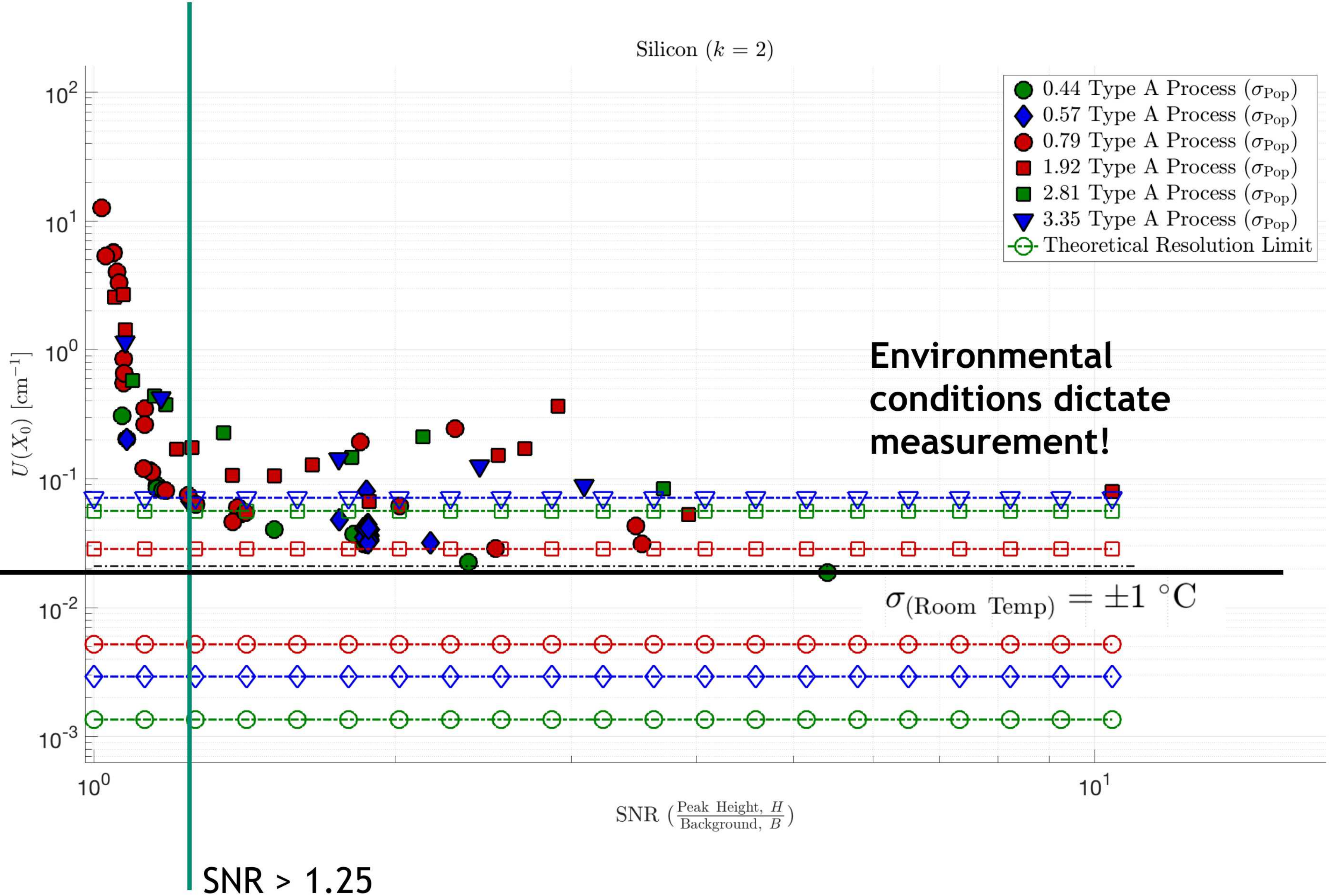
Temperature



Stress



Comparison of Analytical Model with **Population σ** (n = 500)



ASTM E1840 Standard: Tylenol

ASTM E1840

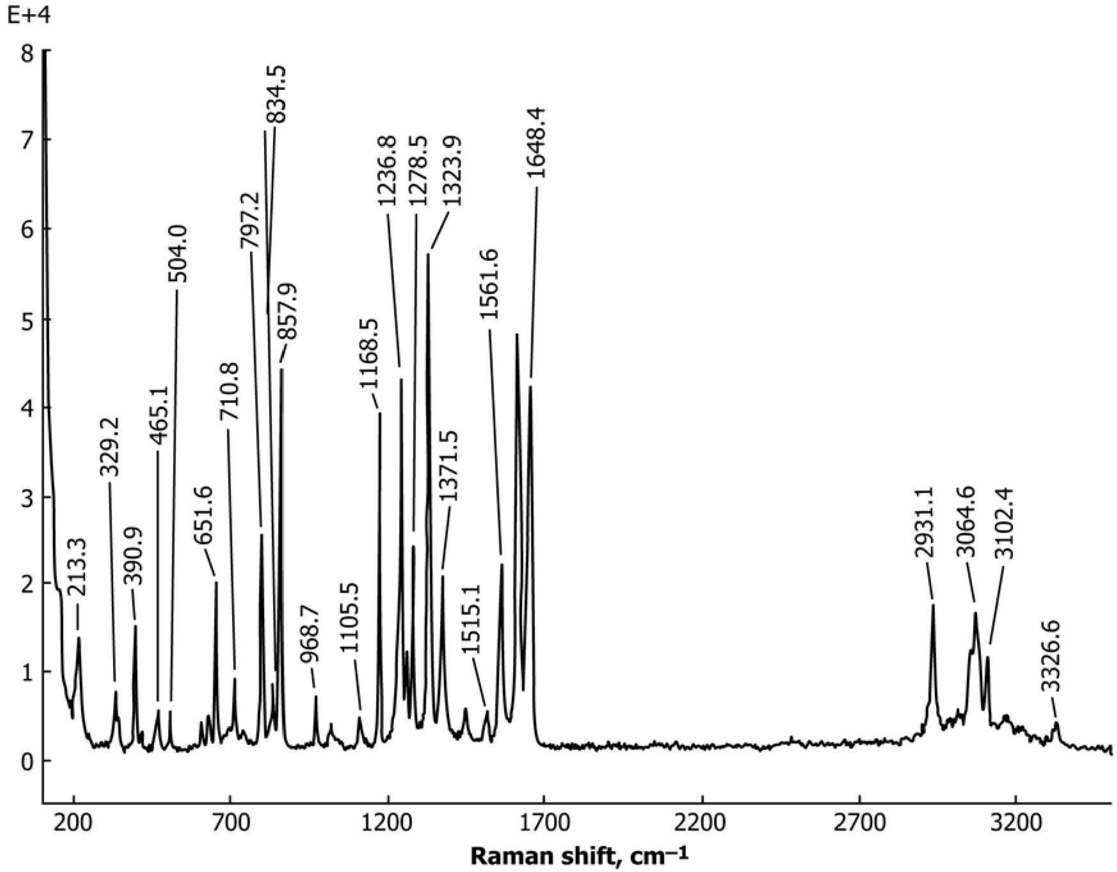


FIG. 5 4-Acetamidophenol (Tylenol)

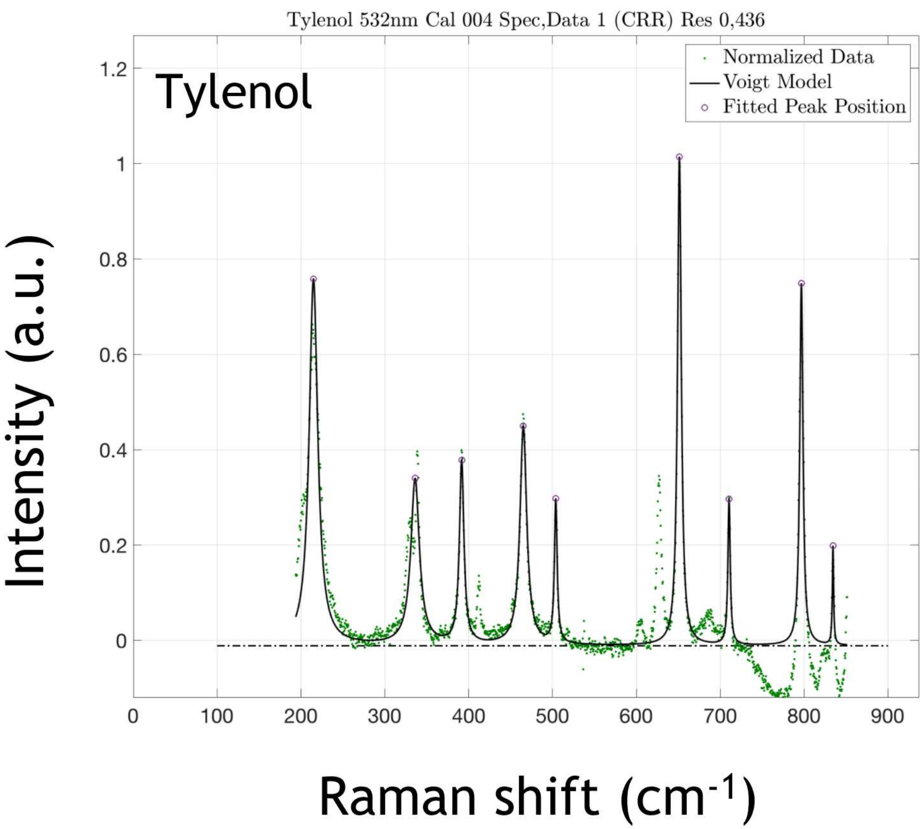
E1840 − 96 (2014)

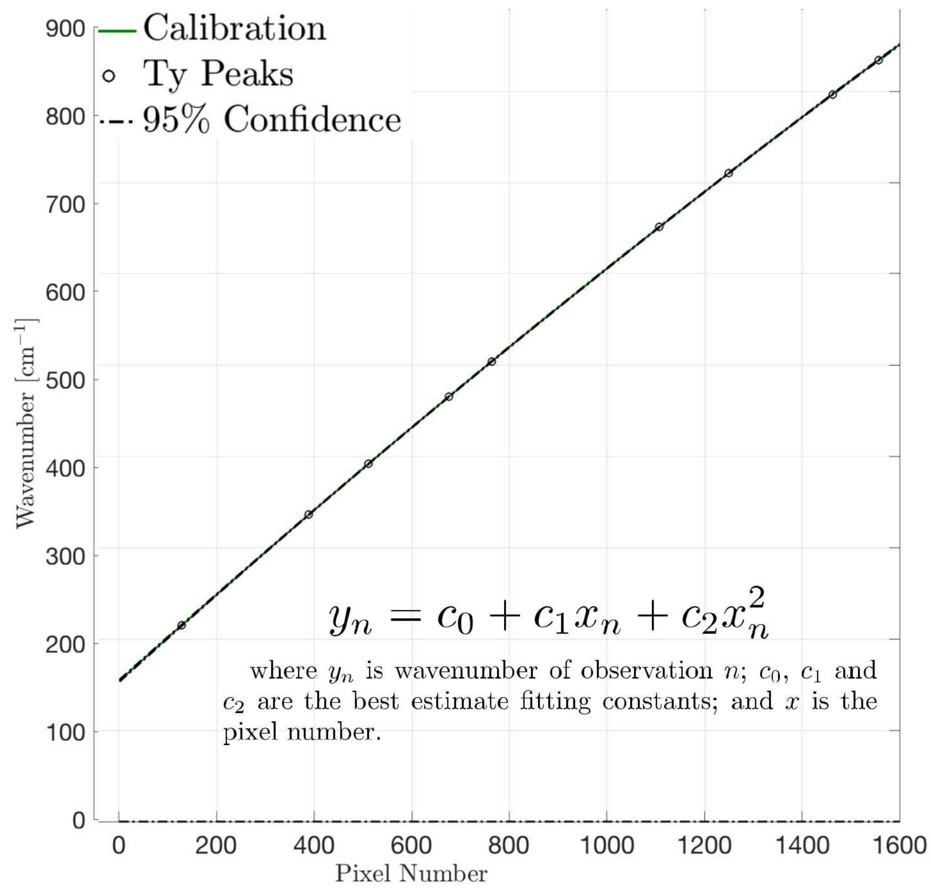
TABLE 5 4–Acetamidophenol[A]

Average (cm-1) ± Standard Deviation	Relative Intensity
213.3 ± 1.77	17
329.2 ± 0.52	11
390.9 ± 0.76	25
465.1 ± 0.30	11
504.0 ± 0.60	11
651.6 ± 0.50	33
710.8 ± 0.68	17
797.2 ± 0.48	45
834.5 ± 0.46	14
857.9 ± 0.50	82
968.7 ± 0.60	12
1105.5 ± 0.27	7
1168.5 ± 0.65	70
1236.8 ± 0.46	75
1278.5 ± 0.45	42
1323.9 ± 0.46	100
1371.5 ± 0.11	38
1515.1 ± 0.70	9
1561.5 ± 0.52	37
1648.4 ± 0.50	73
2931.1 ± 0.63	29
3064.6 ± 0.31	26
3102.4 ± 0.95	20
3326.6 ± 2.18	7

[A] Active ingredient of Tylenol (see Footnote 6).

Spectrometer Calibration: Traceability to SI





Uncertainty due to Standard

$$y_n = c_0 + c_1 x_n + c_2 x_n^2$$

where y_n is wavenumber of observation n; c_0, c_1 and c_2 are the best estimate fitting constants; and x is the pixel number.

$$\mathbf{y} = \mathbf{M}\boldsymbol{\kappa} + \boldsymbol{\epsilon}$$

$$\mathbf{y} = \begin{bmatrix} y_1 \\ y_2 \\ \vdots \\ y_N \end{bmatrix} \quad \mathbf{M} = \begin{bmatrix} 1 & x_1 & x_1^2 \\ 1 & x_2 & x_2^2 \\ \vdots & \vdots & \vdots \\ 1 & x_N & x_N^2 \end{bmatrix} \quad \boldsymbol{\kappa} = \begin{bmatrix} \kappa_0 \\ \kappa_1 \\ \kappa_2 \end{bmatrix} \quad \boldsymbol{\epsilon} = \begin{bmatrix} \epsilon_1 \\ \epsilon_2 \\ \vdots \\ \epsilon_N \end{bmatrix}$$

where $\mathbf{y}$ is a vector of $[N \times \mathbf{1}]$ measured peaks; N is the total number of measured peaks; κ is the true value of the fitted constants; and $\boldsymbol{\epsilon}$ is the error at each observation y_n, where $n = 1.2, ...N$.

$$\mathbf{c} = (\mathbf{M}'\mathbf{M})^{-1}\mathbf{M}'\mathbf{y}$$

best estimate of κ

$$\hat{\boldsymbol{y}} = \mathbf{Mc} + \mu_\epsilon$$

best estimate of **y**

$$\sigma^2(\hat{\boldsymbol{y}}_s) = \mathrm{Var}[\hat{\boldsymbol{y}}_s] = \mathrm{diag}\left(\boldsymbol{M_0} \times \mathrm{Var}[\mathbf{c}_s] \times \boldsymbol{M_0'}\right)$$

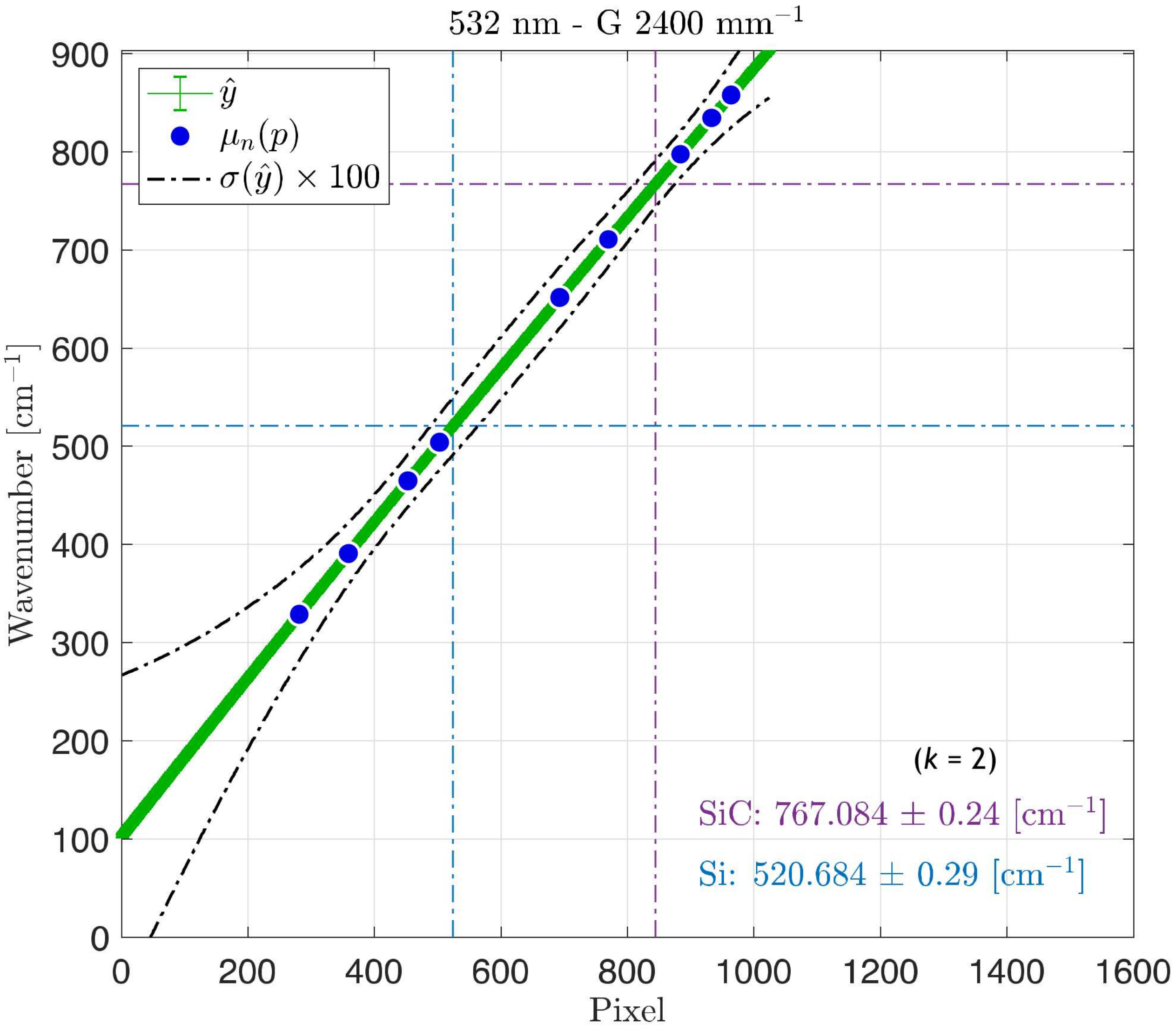
$$\mathrm{Var}[\mathbf{c}_s] = \mathbf{AM}' \times \mathrm{Var}[\mu_n(p)] \times \mathbf{MA}$$

$$\mathbf{A}{=}(\mathbf{M}'\mathbf{M})^{-1}$$

$$\mathrm{Var}[\mu_n(p)] = \begin{bmatrix} \sigma^2_{(\mathrm{S},1)} & 0 & 0 & \dots & 0 \\ 0 & \sigma^2_{(\mathrm{S},2)} & 0 & \dots & 0 \\ 0 & 0 & \sigma^2_{(\mathrm{S},3)} & \dots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \dots & \sigma^2_{(\mathrm{S},\mathrm{P})} \end{bmatrix}$$

Uncertainty from ASTM E1840

Uncertainty in Spectrometer Calibration



Estimate of Uncertainty due to Standard

E1840 – 96 (2014)

Resolution [k/pxl]		0.44	0.57	0.74	1.6	2.34	3.36
μ_ASTM	σ_ASTM	532	488	785	785	532	488
[cm^(-1)]		2400	2400	1200	600	600	600
213.3	1.77	213.30	213.30	213.30	213.30	213.30	213.30
329.2	0.52	329.20	329.20	329.20	329.20	329.20	329.20
390.9	0.76	390.90	390.90	390.90	390.90	390.90	390.90
465.1	0.3	465.10	465.10	465.10	465.10	465.10	465.10
504	0.6	504.00	504.00	504.00	504.00	504.00	504.00
651.6	0.5	651.60	651.60	651.60	651.60	651.60	651.60
710.8	0.68	710.80	710.80	710.80	710.80	710.80	710.80
797.2	0.48	797.20	797.20	797.20	797.20	797.20	**797.20**
834.5	0.46	834.50	834.50	834.50	834.50	834.50	834.50
857.9	0.5	857.90	-	857.90	857.90	857.90	857.90
968.7	0.6	-	-	-	968.70	968.70	968.70
1105.5	0.27	-	-	-	1105.50	1105.50	1105.50
1168.5	0.65	-	-	-	1168.50	1168.50	1168.50
1236.8	0.46	-	-	-	1236.80	1236.80	1236.80
1278.5	0.45	-	-	-	1278.50	1278.50	1278.50
1323.9	0.46	-	-	-	1323.90	1323.90	1323.90
1371.5	0.11	-	-	-	1371.50	1371.50	1371.50
1515.1	0.7	-	-	-	1515.10	1515.10	1515.10
1561.5	0.52	-	-	-	1561.50	1561.50	1561.50
1648.4	0.5	-	-	-	1648.40	1648.40	1648.40
2931.1	0.63	-	-	-	-	2931.10	2931.10
3064.6	0.31	-	-	-	-	3064.60	3064.60
3102.4	0.95	-	-	-	-	3102.40	3102.40
3326.6	2.18	-	-	-	-	3326.60	3326.60
U (s) (*k* = 2) cm^{-1}		**0.37**	**0.39**	**0.37**	**0.30**	**0.31**	**0.31**

(*k* = 2)

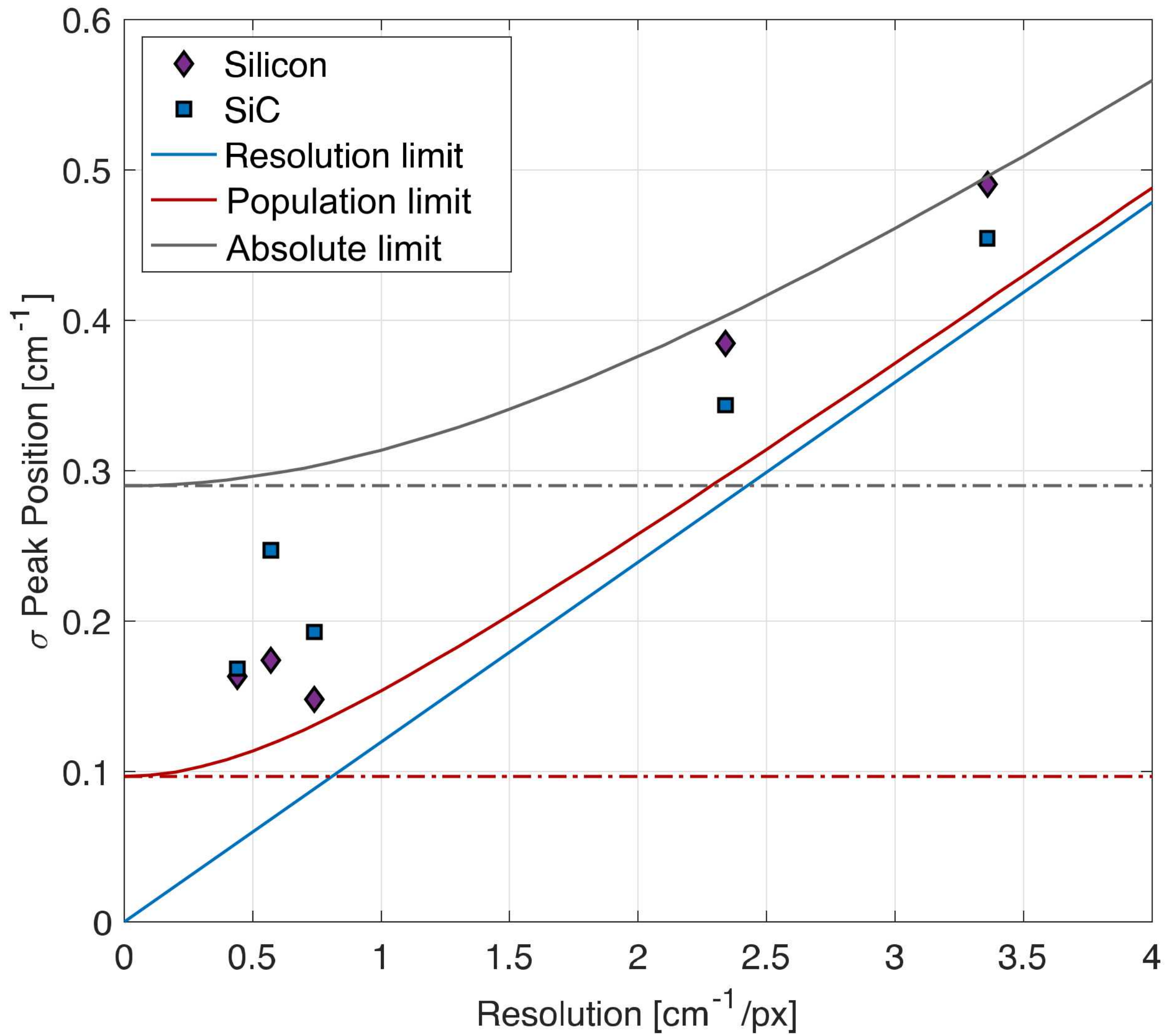
$\mathrm{SiC{:}}\ 767.084 \pm 0.24\ [\mathrm{cm}^{-1}]$

$\mathrm{Si{:}}\ 520.684 \pm 0.29\ [\mathrm{cm}^{-1}]$

$$\sigma^2_{S,x} = \frac{1}{n^2}\sum_{p=i}^{n} \sigma_i^2(p)$$

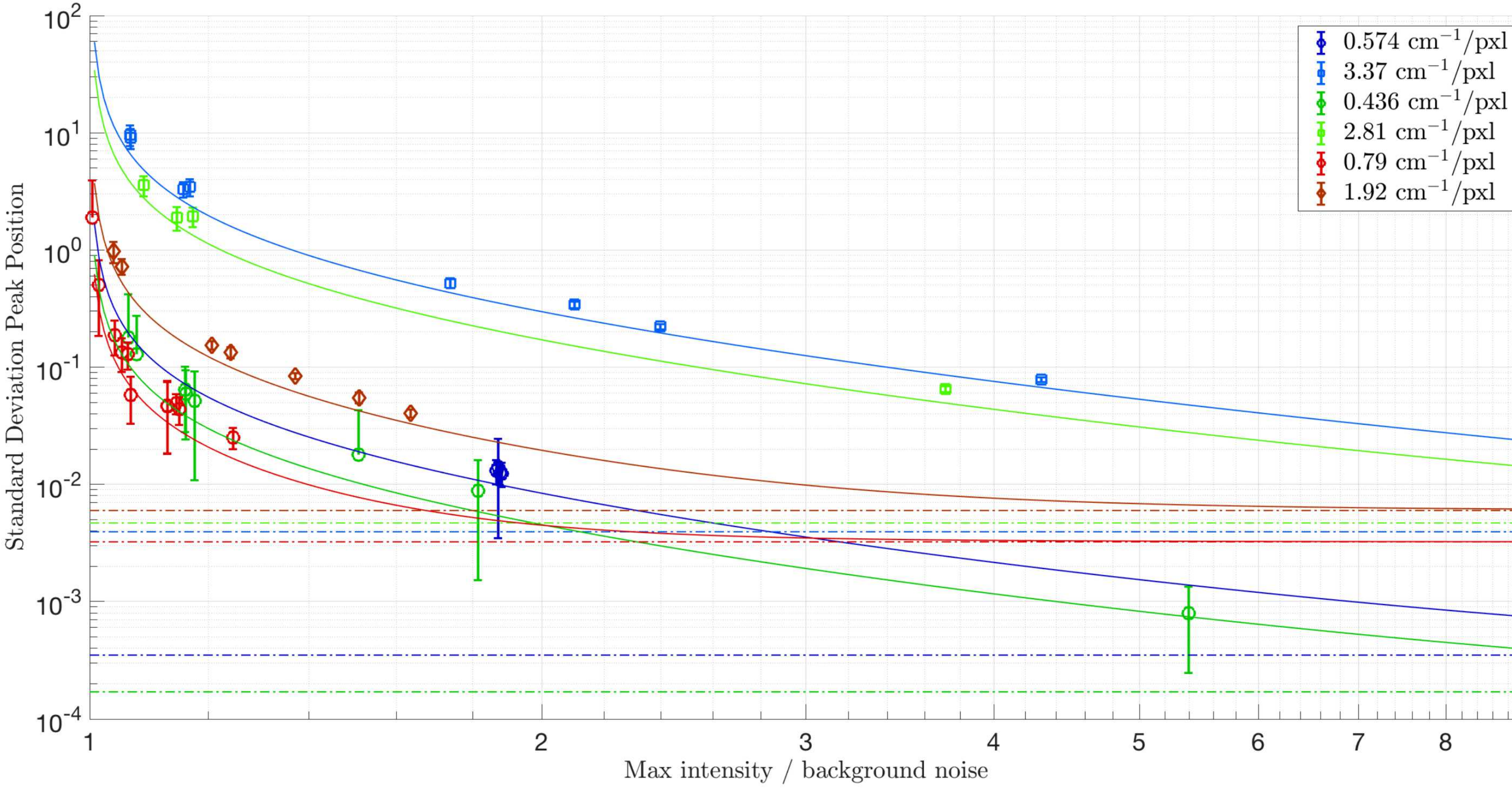
For absolute measurements, RSS uncertainty due to standard with Voigt uncertainty

Historical Measurements

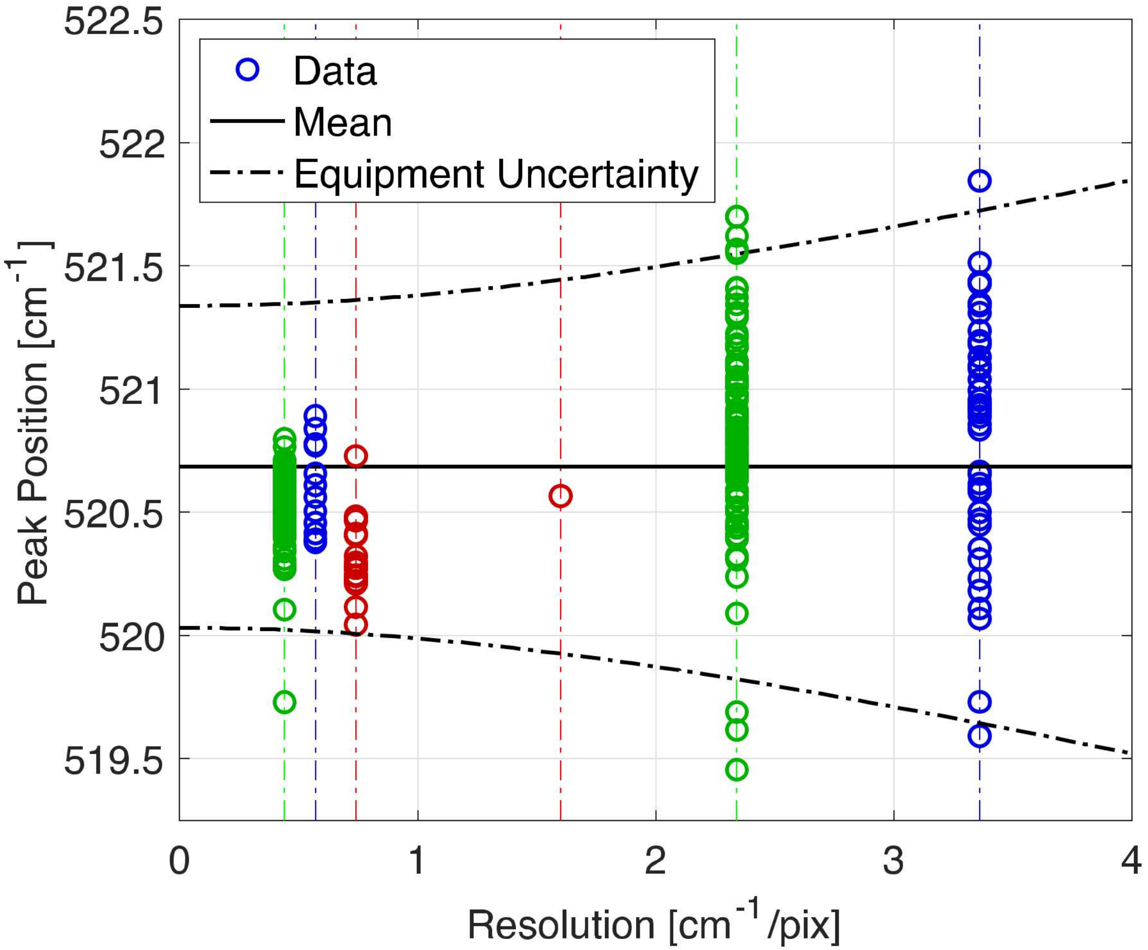


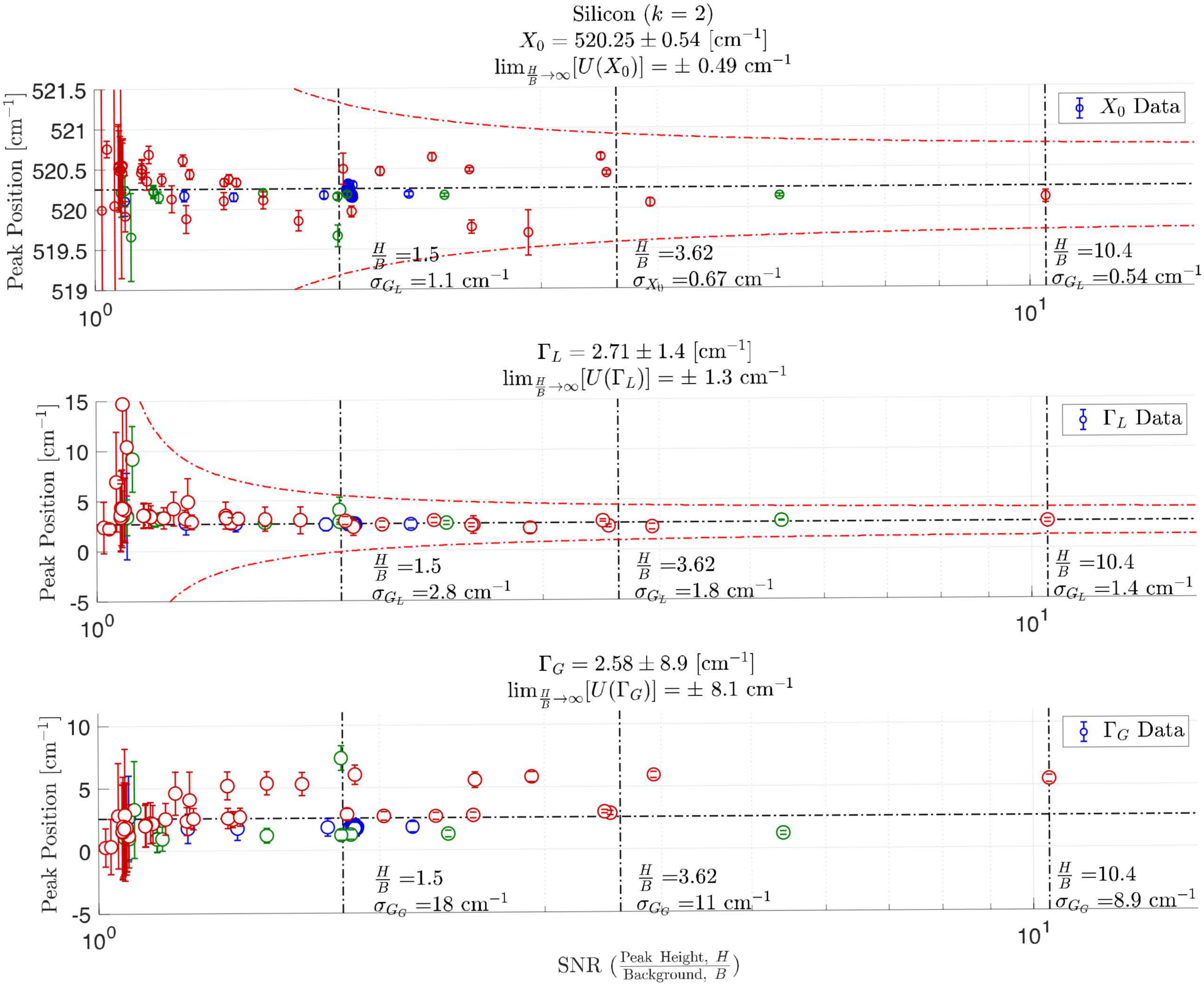
Comparison of Analytical Model with Data **Uncertainty of Fit**

n = 500



Historical Measurements of Silicon





Silicon ($k = 2$)
$X_0 = 520.25 \pm 0.54$ [cm^{-1}]
$\lim_{\frac{H}{B}\to\infty}[U(X_0)] = \pm\ 0.49$ cm^{-1}
X_0 Data
$\frac{H}{B}$ =1.5
σ_{G_L} =1.1 cm^{-1}
$\frac{H}{B}$ =3.62
σ_{X_0} =0.67 cm^{-1}
$\frac{H}{B}$ =10.4
σ_{G_L} =0.54 cm^{-1}
Peak Position [cm^{-1}]
$\Gamma_L = 2.71 \pm 1.4$ [cm^{-1}]
$\lim_{\frac{H}{B}\to\infty}[U(\Gamma_L)] = \pm\ 1.3$ cm^{-1}
Γ_L Data
$\frac{H}{B}$ =1.5
σ_{G_L} =2.8 cm^{-1}
$\frac{H}{B}$ =3.62
σ_{G_L} =1.8 cm^{-1}
$\frac{H}{B}$ =10.4
σ_{G_L} =1.4 cm^{-1}
Peak Position [cm^{-1}]
$\Gamma_G = 2.58 \pm 8.9$ [cm^{-1}]
$\lim_{\frac{H}{B}\to\infty}[U(\Gamma_G)] = \pm\ 8.1$ cm^{-1}
Γ_G Data
$\frac{H}{B}$ =1.5
σ_{G_G} =18 cm^{-1}
$\frac{H}{B}$ =3.62
σ_{G_G} =11 cm^{-1}
$\frac{H}{B}$ =10.4
σ_{G_G} =8.9 cm^{-1}
Peak Position [cm^{-1}]
SNR ($\frac{\text{Peak Height, } H}{\text{Background, } B}$)

Error due to Binning