Lineshape fitting of iodine spectra near 532 nm

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Problem

Given saturation absorption spectra of iodine[1], lineshape fitting to different models was done by non-linear regression. Lineshape parameters from all datasets were then analyzed to study temperature dependence, and how vapor cell depletion affected the spectra.

Data

Iodine spectra were measured by Hongquan Li in Hollberg Lab. The datasets were taken from 2 different iodine vapor cells, which were depleted or undepleted of iodine, at temperatures between 20-90 °C.

Lineshape fitting

- **Locally weighted regression** with Gaussian weight was applied to smooth out the data before fitting

$$w(i) = \exp(-\frac{(x - x(i))^2}{2\tau^2})$$

$\tau = 0.2$ was found to optimize the fitting error without overly underestimating signal height and width.

- **Least square non-linear regression** for the following lineshape models[2] were performed. Fitting parameters for each model were characteristic width(s), signal strength, horizontal offset, and vertical offset.

Model	Lineshape function	Characteristic widths
Lorentzian	$L(\omega) \propto \frac{\gamma/2}{(\omega-\omega_0)^2+\gamma^2/4}$	γ
Gaussian	$G(\omega) \propto \frac{1}{\sqrt{2\pi\sigma^2}}\exp(-\frac{(\omega-\omega_0)^2}{2\sigma^2})$	σ
Voigt	$V(\omega) \propto L(\omega;\gamma) * G(\omega;\sigma)$	γ, σ

Voigt function doesn't have an analytic form. Voigt shape is obtained by evaluating real part of Faddeewa function[3,4]

$$w(z) = w\left(\frac{\omega+i\gamma}{\sigma}\right) = e^{-z^2}(1 + \frac{2i}{\sqrt{\pi}}\int_0^z e^{t^2}dt)$$

References

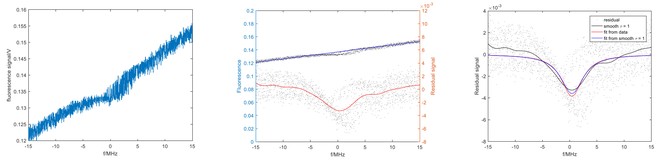
[1] Magyar, J. A., & Brown, N. (1980). High resolution saturated absorption spectra of iodine molecules 129I2, 129I127I, and 127I2 at 633 nm. *Metrologia*, *16*(2), 63.

[2] Chew, A. (2008). Doppler-free spectroscopy of iodine at 739nm. *undergraduate thesis, University of Maryland*.

[3] Ruzi, M. (2016, June 27). Voigt line shape fit. Retrieved November 30, 2017, from *https://www.mathworks.com/matlabcentral/fileexchange/57603-voigt-line-shape-fit*

[4] Abrarov, S. (2016, July 10). The Voigt/complex error function (second version). Retrieved November 30, 2017, from *https://www.mathworks.com/matlabcentral/fileexchange/47801-the-voigt-complex-error-function--second-version-*

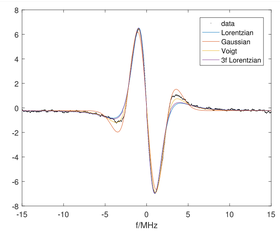
Original approach:



Linear baseline and Lorentzian curve fitting were performed on fluorescence data. Data noise resulted in 50 times higher error than fitting the 3rd derivative spectra directly.

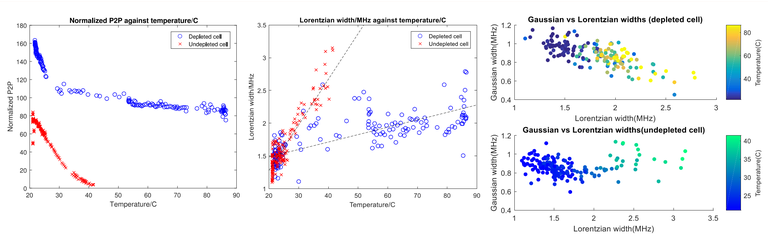
Better approach:
3rd derivative lineshape models

Model	RMS error	$\Delta P2P$(%)	$\Delta width$(%)
3rd derivative of Lorentzian	0.228	4.7	3.6
3rd derivative of Gaussian	0.248	0.2	12.6
3rd derivative of Voigt	0.126	3.5	6.3
3f Fourier component of Lorentzian x ref signal	0.232	4.6	0.9



Voigt model, a convolution of Lorentzian and gaussian functions, gave the best fit to spectral data.

Temperature dependence

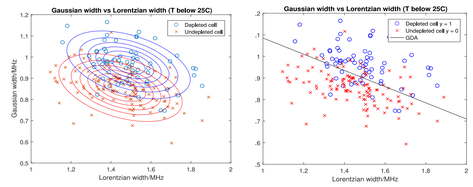


Weighted linear regression was used to fit temperature dependence of Lorentzian width. The weight was proportional to (peak-to-peak)^2 to prioritize stronger signals obtained at lower temperatures.

Vapor cell depletion comparison

For data taken near 25°C, 3 characteristic widths were extracted from Voigt fit: observed width w, Lorentzian width γ, and Gaussian width σ. We then reduced the number of features from 3 to 2 in the following ways:

- **Naïve choice of features:** γ and σ (assuming w is dependent on two independent widths)

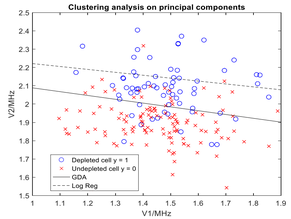


	Training set	Test set
size	303	75
Learning Accuracy(%)	80.5	73.3

Averaged over 5-fold cross validation

- **Principal Component Analysis**

2 principal components V1 and V2 were $V1 = \gamma$ and $V2 = 0.696w + 0.715\sigma$ with corresponding eigenvalues 1.14 and 1.86 respectively.



Learning accuracy averaged over 5-fold cross validation

	Training set	Test set
GDA(%)	81.1	80.8
Logistic Regression(%)	75.1	73.3

Discussion

- Our spectra were best fitted to Voigt model, which accounted for both intrinsic Lorentzian lineshape and external broadening mechanisms (Gaussian function)
- Lorentzian width increased with temperature as expected
- PCA: the sum of observed width and Gaussian width were independent of Lorentzian width
- The depleted iodine cell might be subjected to more external broadening than the undepleted cell

Future work

Detailed error analysis should be carried out to understand and eliminate major noises. Studies of temperature dependence can be improved with more data at 25-50°C