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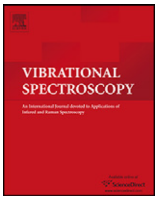

Short communication

A simple asymmetric lineshape for fitting infrared absorption spectra

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Almost exclusively, lineshape functions used to model infrared (IR) absorption peaks are based on symmetric frequency distributions. However, in complex systems such as large biological macromolecules in aqueous solutions, the distribution of vibrational frequencies may in fact be asymmetric. In this communication, we show that asymmetry can be introduced to the standard symmetric Lorentzian and Gaussian lineshapes using a simple, easy to implement method. Our technique involves replacing the static width parameter of the symmetric profiles with a smoothly varying function that is wave number dependent. In this way, the width varies across the IR band resulting in an asymmetric peak. In our model, the width varies sigmoidally with wave number. As a demonstration, we fit experimental spectra of adenosine 5′-monophosphate (AMP).

1. Introduction

Infrared (IR) absorption spectra of large biological macromolecules in aqueous solutions are frequently comprised of broad, overlapping peaks. When spectral congestion is substantial, the interpretation of the data is difficult. Curve fitting of IR absorption spectra is a useful technique that can be used to facilitate data interpretation [1]. In curve fitting, the experimental spectrum is modeled as a sum of individual spectral contributions. For obvious reasons, the choice of lineshape for the component spectra has a profound impact on the outcome of the fitting procedure. Mathematically, the lineshape is a statistical function that describes the distribution of frequencies within a given transition. Symmetric distribution functions are used almost exclusively. Typically these functions are firmly grounded in theory and usually provide reliable results. However, in complex systems (e.g., large molecules in condensed phases), the frequency distributions may in fact be asymmetric. When symmetric lineshapes are used to fit asymmetric data, the results will be unsatisfactory. All too often, the temptation is to add additional symmetric components to the model to improve the fit. However, if the number of peaks in the model exceed the actual number of underlying transitions in the data, the results will be misrepresented. In this communication, we present a straightforward modification of well known symmetric lineshapes that introduces asymmetry.

2. Experimental

The disodium salt of adenosine 5′-monophosphate (AMP) was purchased from Sigma and used without further purification. Reported purity was greater than 99.0%. Samples were lyophilized against D_2O three times to exchange the labile protons. The lyophilized samples were dissolved in 100 mM deuterated phosphate buffer (pD = 7.2) to a final nucleotide concentration of ~150 mM. Transmission infrared spectra were recorded on an Oriel MIR8025 FTIR spectrometer using custom built sample cells. The cells are comprised of two CaF_2 windows separated by a 50 μm thick Teflon spacer that defines the cell path length. The spacer also divides the cell into two compartments, one for the sample (AMP + buffer) and the other for the reference (buffer only). The CaF_2 windows are held together in a copper housing. The copper housing is then mounted to a temperature controlled platform. All spectra were recorded at 25 °C ± 0.01 °C and a spectral resolution of 2 cm^{-1}. The interferograms were apodized using a triangular function prior to Fourier transformation.

2.1. Lineshape models

In principle, the number of functions that could be used to fit spectral data is limitless [2]. However, to be truly meaningful, the parameters of the lineshape model should have a direct correspondence with physical phenomena. For example, parameters such as peak width, peak area, and peak position are the relevant quantities when dealing with symmetric spectra. As we will show shortly, one additional parameter is necessary to characterize asymmetry. The asymmetry parameter is an indication of the extent of asymmetry and the direction of skew (i.e., whether the spectrum is skewed toward higher or lower wave

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numbers). In addition to having physically meaningful parameters, we would also argue that the lineshape functions are firmly rooted in theory. For example, an *n*th order polynomial can be used to fit some peaks with satisfactory results. However, such a model is purely empirical and has no theoretical basis.

There are three factors that contribute to the final lineshape of an IR band; Doppler broadening, radiation damping, and collision broadening. Doppler broadening results in Gaussian lineshapes [3,4]

$$G(\nu) = \frac{A}{\gamma_0}\sqrt{\frac{4\ln 2}{\pi}}\exp\left[-4\ln 2\left(\frac{\nu-\nu_0}{\gamma_0}\right)^2\right] \tag{1}$$

where ν is the frequency in wave numbers, ν_0 is the peak center and γ_0 is the full width at half maximum (FWHM). The term in front of the exponential is a normalization constant where A is the area under the peak. The latter two, radiation damping and collision broadening give Lorentzian distributions [3,4]

$$L(\nu) = \frac{2A/\pi\gamma_0}{1+4[(\nu-\nu_0)/\gamma_0]^2} \tag{2}$$

The parameters are defined as in Eq. (1) and the numerator is the normalization constant.

Since all three effects act on molecules, lineshapes are usually a convolution of the two symmetric profiles; this is the so-called Voigt function [5]. A true Voigt function is cumbersome and impractical for use in fitting routines so a pseudo-Voigt profile is frequently used. One form of a pseudo-Voigt that we will use here treats each peak as a sum of fractional contributions of the Gaussian and Lorentzian shapes

$$y(\nu) = fL(\nu) + (1-f)G(\nu) \tag{3}$$

Here, f is the fraction of Lorentzian character contributing to the net line shape. For example, when $f = 1$, the shape is a pure Lorentzian and when $f = 0$, the shape is a pure Gaussian. For a symmetric shape, the first and third derivatives at the peak center ($\nu = \nu_0$) are both equal to zero. In other words, the peak maximum exactly corresponds to the second derivative minimum. As will be shown shortly, this is not the case for an asymmetric band.

2.2. Asymmetric variation of the Lorentzian and Gaussian lineshapes

When the width is not uniform across an entire band, an asymmetric profile results. Our approach is to replace γ_0 in Eqs. (1) and (2) with a well behaved function, $\gamma(\nu)$ to introduce asymmetry. In the symmetric limit, the lineshape will reduce to a pure Lorentzian or Gaussian profile. While numerous possibilities exist, we obtain the best results when the width is allowed to vary sigmoidally,

$$\gamma(\nu) = \frac{2\gamma_0}{1+\exp[a(\nu-\nu_0)]} \tag{4}$$

The parameter a is a measure of asymmetry. Negative values of a skew the spectrum toward higher wave numbers while positive values of a skew it toward lower wave numbers. When a is zero, Eq. (4) reduces to γ_0 and the resulting band is a standard symmetric Gaussian or Lorentzian profile with a constant width (FWHM = γ_0). The sigmoid is advantageous since the width asymptotically approaches upper and lower bounds (i.e., 0 and $2\gamma_0$). In contrast, when other functions are used (e.g., linear) the width will increase and decrease without bound in opposite directions. If limits are not imposed, the width will eventually become non-physical (e.g., negative) or it will become so large that the peak will begin to increase after reaching a minimum. Fig. 1a shows the result of Eq. (4) substituted for γ_0 in a Lorentzian profile. The asymmetry parameter, a, is equal to $-1/5$. At $\nu = \nu_0$ the width is equal to γ_0 (see Fig. 1b).

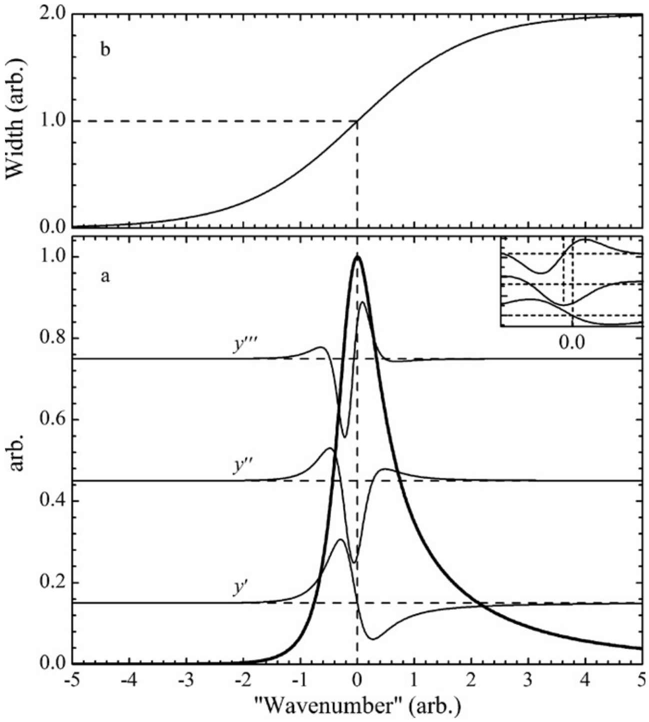

Fig. 1. (a) An asymmetric Lorentzian (thick black solid line) using Eq. (4) for γ_0, where $\nu_0 = 0$, $\gamma_0 = 1$ and $a = -1/5$. The derivative spectra are shown on an arbitrary y-axis for comparison and labeled accordingly. The horizontal dashed lines indicate $y = 0$ for each derivative. The inset shows the derivative spectra on an expanded wave number scale (−0.5 to 0.5). (b) A plot of Eq. (4), $\gamma(\nu)$.

A peak that appears to be asymmetric may in fact be comprised of two closely overlapped symmetric peaks. This is a condition that must be distinguished when dealing with asymmetric absorption bands. Up to a point, the two situations can be distinguished quantitatively. Consider a spectrum that is the sum of two symmetric component peaks of differing heights. When they are separated by a sufficient distance, the second derivative shows two distinct minima. However, as one approaches the other (all other variables being held constant, only the peak center is changing), the second derivative minimum corresponding to the weaker peak diminishes.[1] The point at which the minimum is tangent to zero is known as the *detection limit* [6]. Stated more rigorously, the detection limit is the point at which the second and third derivatives are equal to zero at the same wave number coordinate. Below this limit, the second derivative spectra cannot resolve two peaks. Higher derivatives can be used, but this is impractical for real data. When such a situation arises, *a priori* knowledge of the spectrum in question may provide the only clarification.

2.3. Fitting experimental spectra

The impetus for this paper arose from our efforts to model IR absorption spectra of nucleic acids. In many cases, using symmetric lineshapes to model the spectra failed to give satisfactory results. We concluded that the frequencies must be distributed asymmetrically. The IR active moieties on a large molecule in solution can experience numerous "microenvironments" that impact the vibrational frequencies of those species. If the frequencies differ by a sufficient amount, multiple, distinct bands will be resolved. Conversely, if the differences are small, a single band results and the individual frequencies of each of the absorbing species are

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[1] Equivalently, the weaker peak could increase in height or sharpen relative to the stronger peak.

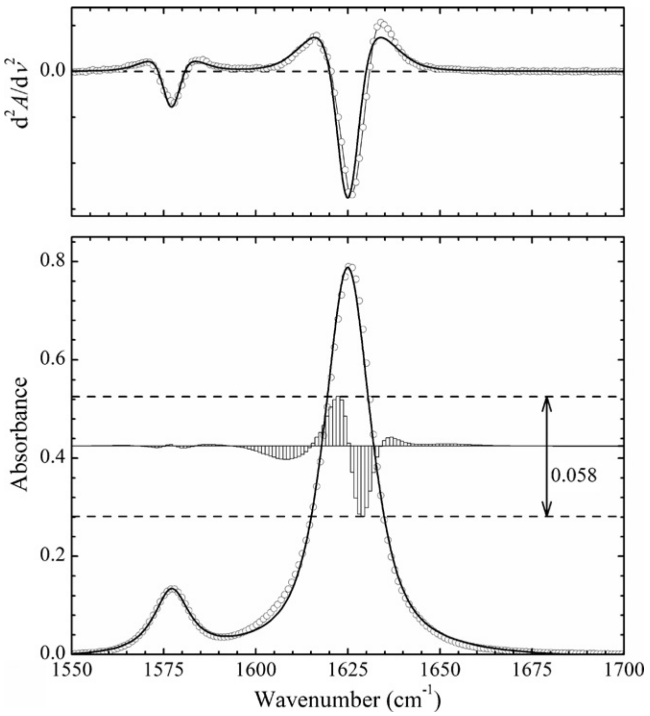

Fig. 2. Fitting of AMP IR absorption spectra using a symmetric pseudo-Voigt model. IR absorption spectra of AMP in D_2O (lower plot, circles) and its second derivative (upper plot, circles with thin black solid line). The solid black line is a fit to a symmetric pseudo-Voigt (Eq. (3)) profile (lower plot). The second derivative of the fit function is shown in the upper plot (solid black line). The residuals (fit–actual) are plotted on an expanded scale on the lower plot. The upper and lower limits are indicated.

Table 1
Summary of curve fitting results

		Symmetric	Asymmetric
Peak 1	ν_0, cm^{-1}	1577.14	1577.14
	$\langle\nu\rangle$, cm^{-1}	–	1576.50
	A	2.26	1.41
	γ_0, cm^{-1}	11.43	10.91
	a	–	0.01
	f	0.93	0.2
Peak 2	ν_0, cm^{-1}	1624.97	1625.44
	$\langle\nu\rangle$, cm^{-1}	–	1622.75
	A	17.86	17.75
	γ_0, cm^{-1}	15.30	15.04
	a	–	0.01
	f	0.84	0.86

distributed about a central frequency. In many cases, the distribution is symmetric. However, it is possible for the symmetry to break down resulting in a single asymmetric band. This is more pronounced in large macromolecules where inhomogeneities among the different microenvironments may be more evident. To demonstrate this and the need to consider asymmetric lineshapes, we have chosen to fit FTIR absorption spectra of 5′-monophosphate (AMP). This is an excellent system to use since its IR absorption spectrum and underlying transitions are known.

The spectrum of AMP and its second derivative are shown in Fig. 2. In agreement with what is expected based on previously published data, two transitions are observed [7]. A strong absorption centered around 1625 cm^{-1} is due to C=N and C=C vibrations of the purine ring. The corresponding in-plane ring vibration is weaker and is centered around 1577 cm^{-1}. Initially, the spectra were fit using a symmetric pseudo-Voigt model. The results are shown in Fig. 2 and tabulated in Table 1. While the fit is adequate, it clearly does not accurately model the spectra. In addition to the large residual, the second derivatives of the fit and the experimental data are substantially different, especially the region around the main peak ($\sim$1625 cm^{-1}). Quantitatively, the second derivative spectrum indicates only two peaks. However, we cannot unequivocally rule out the presence of a third peak based on these data alone. In fact, the addition of a third peak dramatically increases the agreement between the fit and the data (not shown). However, there is no precedent to indicate that a third transition is present [7]. We would conclude that, in reality, the strongest transition (and possibly to a lesser extent, the weak transition) is in fact asymmetric. Fig. 3 shows the fitting results using our asymmetric model. The quality of the fit is improved substantially when asymmetry is allowed for. In addition, the second derivative of the fit more closely reproduces the second derivative of the data. The results of both fits are tabulated in Table 1.

The introduction of asymmetry does more than improve the quality of the fit—there are significant practical implications as well. Most notably is the distinction between peak position and the mean wave number. The peak position, ν_0, simply reports the wave number having the maximum absorbance. When dealing with asymmetric peaks, further insight can be obtained if one considers the mean wave number of each transition in addition to the peak maximum. The mean wave number (for each isolated band) is defined according to

$$\langle\nu\rangle = \nu_0 + \frac{\int_{-5\gamma_0}^{+5\gamma_0} jy(j)\,\mathrm{d}j}{\int_{-5\gamma_0}^{+5\gamma_0} y(j)\,\mathrm{d}j} \qquad (5)$$

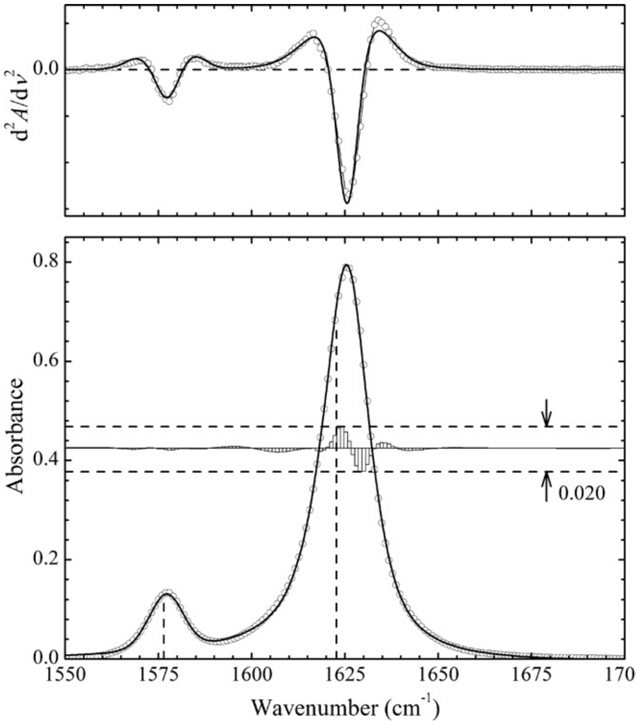

Fig. 3. Fitting of AMP IR absorption spectra using an asymmetric pseudo-Voigt model. IR absorption spectra of AMP in D_2O (lower plot, circles) and its second derivative (upper plot, circles with thin black solid line). The solid black line in the lower plot is a fit to an asymmetric pseudo-Voigt using Eq. (4) for γ_0. The second derivative of the fit function is shown in the upper plot (solid black line). The residuals (fit–actual) are plotted on an expanded scale on the lower plot. The upper and lower limits are indicated. The vertical dashed lines show the mean wave number for each of the peaks, $\langle\nu\rangle$ = 1576.50 and 1622.75 cm^{-1}.

where $j = \nu - \nu_0$. The limits of integration, $\pm 5\gamma_0$, are chosen to encompass the majority of the band area. Without limits, the mean frequency of an asymmetric band would increase (or decrease) without bound. The mean wave number for a symmetric peak is simply equal to the maximum wave number, ν_0. However, this is not the case for an asymmetric peak. If the peak is skewed toward higher wave numbers, the mean wave number will be greater than the peak maximum. Likewise, if the peak is skewed toward lower wave numbers, the mean will be less than the peak maximum. For example, our model indicates that the weakest peak is slightly asymmetric and its mean is shifted by less than a wave number (toward lower frequencies) from the peak position (see Fig. 3 and Table 1). The asymmetry in the stronger transition is more pronounced and the mean is shifted by $-2.69\ \mathrm{cm}^{-1}$ from 1625.44 to $1622.75\ \mathrm{cm}^{-1}$.

The most marked difference between the symmetric and asymmetric fits is the fraction of Lorentzian character, *f*, for the weak peak ($\sim 1577\ \mathrm{cm}^{-1}$). In the symmetric model, this peak is 93% Lorentzian. When asymmetry is accounted for, the fraction of Lorentzian character decreases to 20%. The reason for this is that the asymmetry of the stronger peak is skewed toward shorter wave numbers. As such, the tail of this peak on the short wave number side is more pronounced and contributes to the baseline of the weaker peak. One of the features that distinguishes a Gaussian from a Lorentzian is that the former drops off to zero very rapidly, while the latter approaches zero much more slowly. Thus, a Lorentzian peak with a substantial portion of its baseline negated will appear more “Gaussian”. However, we note that other than this difference, the other parameters for the weaker peak are not impacted when asymmetry is introduced.

3. Conclusion

In short, we have established a straightforward method to account for asymmetric IR absorption lineshapes. By replacing the static width of a standard Lorentzian or Gaussian profile with a smoothly varying function, asymmetry is introduced. In our model, the width varies sigmoidally with wave number across the band. The model fits experimental spectra of AMP well. In addition, the sigmoid function asymptotically approaches upper and lower limits and therefore gives a physically meaningful result.

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