

Supplementary Information

“Effects of Hydrogen Bonding on the Ring Stretching Modes of Pyridine”

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S1. x-Marginal Spectra

The experimental data obtained in an I⁽²⁾CARS experiment comes directly as a spectrogram as an individual I⁽²⁾CARS spectrum is collected at each stepper motor (delay time) position. The spectrogram itself is then fit to Eq. (2) from the paper associated with this Supplementary Information:

$$I(\omega_D, \tau) = AJ'(\omega_D) \left[\begin{array}{l} e^{-2\gamma_1|\tau-\tau_0|} (\cos [(\omega_{D_1}^0 - \omega_D) |\tau - \tau_0|] + R_1 \sin [(\omega_{D_1}^0 - \omega_D) |\tau - \tau_0|]) \\ + A_2 e^{-2\gamma_2|\tau-\tau_0|} (\cos [(\omega_{D_2}^0 - \omega_D) |\tau - \tau_0|] + R_2 \sin [(\omega_{D_2}^0 - \omega_D) |\tau - \tau_0|]) \\ \vdots \\ + A_i e^{-2\gamma_3|\tau-\tau_0|} (\cos [(\omega_{D_i}^0 - \omega_D) |\tau - \tau_0|] + R_i \sin [(\omega_{D_i}^0 - \omega_D) |\tau - \tau_0|]) \\ + I_0 + m(\tau - \tau_0) \end{array} \right] \quad (2)$$

This yields quantitative results for the parameters of Eq. (2) (See Fig. S1).

The spectrograms, however, do not provide the most transparent physical representation of the I⁽²⁾CARS signal. To achieve a more visually appealing representation of the data carried in the spectrogram, the time axis is Fourier transformed into a frequency. This provides what is called the Fourier transformed spectrogram as shown in Fig. S1. The Fourier transformed spectrogram is very useful for visually assessing the data because real vibrational modes appear as x shaped patterns. The x patterns can be visually picked up on even at very poor signal to noise levels.

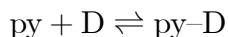
Although the Fourier transformed spectrograms are the most useful representation for the data for visually assessing vibrational modes, it is difficult to determine changes in relative signal strengths. The x-marginal technique provides a means for reducing the two dimensional Fourier transformed into a one dimensional spectrogram (Fig. S1). This is done by imitating how ones eyes perceive the x pattern. The Fourier transformed spectrogram is multiplied by an x shaped “mask” that is equal to unity inside a narrow x shape and zero elsewhere. The product of the data and the mask is then summed to yield a single datum on the x-marginal spectrum. The mask is moved along the horizontal frequency dimension and a new x-marginal datum is calculated. This is repeated until the x-marginal spectrum is obtained. Figure S2 illustrates this idea.

The x-marginal spectrum is very similar to a conventional CARS spectrum, however the convolution of the mask with the data artificially broadens the peaks. Qualitative values of the theoretical model parameters are not obtained from the x-marginal spectra.

S2. Thermodynamic Information

One is able to extract the thermodynamic values, ΔG^\ominus , ΔH^\ominus and ΔS^\ominus for hydrogen bonding from the data in temperature studies of pyridine mixtures. Unfortunately the thermodynamic information extracted from I⁽²⁾CARS data cannot be considered as precisely measured as from other methods, including conventional Raman scattering. In spite of this, it is worthwhile to provide the thermodynamic information carried in these data.

The first operating approximation is that the hydrogen bonding reaction is



which has an equilibrium constant expressed as

$$K_X = \frac{X_{\text{py-D}}}{X_{\text{py}} X_{\text{D}}}.$$

Note that the use of K_X implies a Raoult's law reference state (denoted with a superscript \ominus). This is the most convenient reference state for describing binary mixtures. Unfortunately this poses some practical problems when comparing to thermodynamic values collected in, for example, Vinogradov and Linnell¹ and Pimentel and McClellan.² Those references use the unit molarity convention for the reference state. This is a common reference state used because much of the tabulated data is collected in situations where the hydrogen bonding pair is diluted with an inert (non-hydrogen bonding) solvent. Of course, in principle, one can readily convert between reference states, but that is not easily done in this case because of the lack of information on activity coefficients for pyridine, water and the pyridine-water complex in this mixture. The pyridine/water system is non-ideal and deviates from Raoult's law.³ The same could well be expected for the pyridine/formamide system.

The data provide I⁽²⁾CARS intensities which are very complicated function of the mole fractions involved. However, with reasonable, but not strictly correct,⁴ approximations ($\chi_{\text{py-D}} = \chi_{\text{py}}$) fortuitous cancellations occur, leaving the ratio of the intensities simply related to the moles as

$$\frac{I_{\text{py-D}}}{I_{\text{py}}} = \left(\frac{n_{\text{py-D}}}{n_{\text{py}}} \right).$$

Interestingly, the ratio of intensities is proportional to linear powers of the moles rather than the square powers as one might expect since CARS is a passive class II spectroscopy.⁵

Rearranging the above ratio and defining $\frac{I_{\text{py-D}}}{I_{\text{py}}} \equiv \Lambda$ gives

$$n_{\text{py-D}} = \Lambda n_{\text{py}}.$$

By conservation of pyridine

$$n_{\text{py-D}} + n_{\text{py}} = n_{\text{py}}^{(0)},$$

where $n_{\text{py}}^{(0)}$ is the initial moles of pyridine. Also,

$$n_{\text{D}} + n_{\text{py-D}} = n_{\text{D}}^{(0)}.$$

Simplifying these equations results in

$$n_{\text{py}} = \frac{n_{\text{py}}^{(0)}}{1 + \Lambda},$$

$$n_{\text{py-D}} = \frac{\Lambda}{1 + \Lambda} n_{\text{py}}^{(0)},$$

and

$$n_{\text{D}} = n_{\text{D}}^{(0)} - \frac{\Lambda}{1 + \Lambda} n_{\text{py}}^{(0)}.$$

Additionally,

$$\begin{aligned} n_{\text{tot}} &= n_{\text{D}} + n_{\text{py-D}} + n_{\text{py}} \\ &= n_{\text{D}}^{(0)} + \frac{n_{\text{py}}^{(0)}}{1 + \Lambda}. \end{aligned}$$

Casting the equations in terms of mole fractions yields,

$$\begin{aligned} X_{\text{py}} &= \frac{X_{\text{py}}^{(0)}}{(1 + \Lambda) X_{\text{D}}^{(0)} + X_{\text{py}}^{(0)}}, \\ X_{\text{py-D}} &= \frac{\Lambda X_{\text{py}}^{(0)}}{(1 + \Lambda) X_{\text{D}}^{(0)} + X_{\text{py}}^{(0)}}, \end{aligned}$$

and

$$X_D = \frac{(1 + \Lambda) X_D^{(0)} - \Lambda X_{py}^{(0)}}{(1 + \Lambda) X_D^{(0)} + X_{py}^{(0)}}.$$

Substituting these mole fraction expressions in for the equilibrium constant and simplifying gives

$$K_X = \frac{\Lambda \left((1 + \Lambda) X_D^{(0)} + X_{py}^{(0)} \right)}{(1 + \Lambda) X_D^{(0)} - \Lambda X_{py}^{(0)}}.$$

ΔG^\ominus is obtained directly from K_X and ΔH^\ominus and ΔS^\ominus from the temperature variation in ΔG^\ominus

References

- (1) Vinogradov S.N.; Linnell, R.H. *Hydrogen Bonding* **1971** Van Nostrand Reinhold, New York.
- (2) Pimentel, G.C.; McClellan, A.L. *The Hydrogen Bond* **1960** W.H. Reeman, San Fransisco, CA.
- (3) Abe J-I.; Nakanishi, K.; Touhara, H. *J. Chem. Thermodynamics* **1978**, *10*, 483.
- (4) Mierzecki, R. *J. Raman Spectrosc.* **1986**, *17*, 35.
- (5) Kirkwood, J.C.; Ulness, D.J. Albrecht, A.C. *J. Phys. Chem. A* **2000**, *104*, 4167.

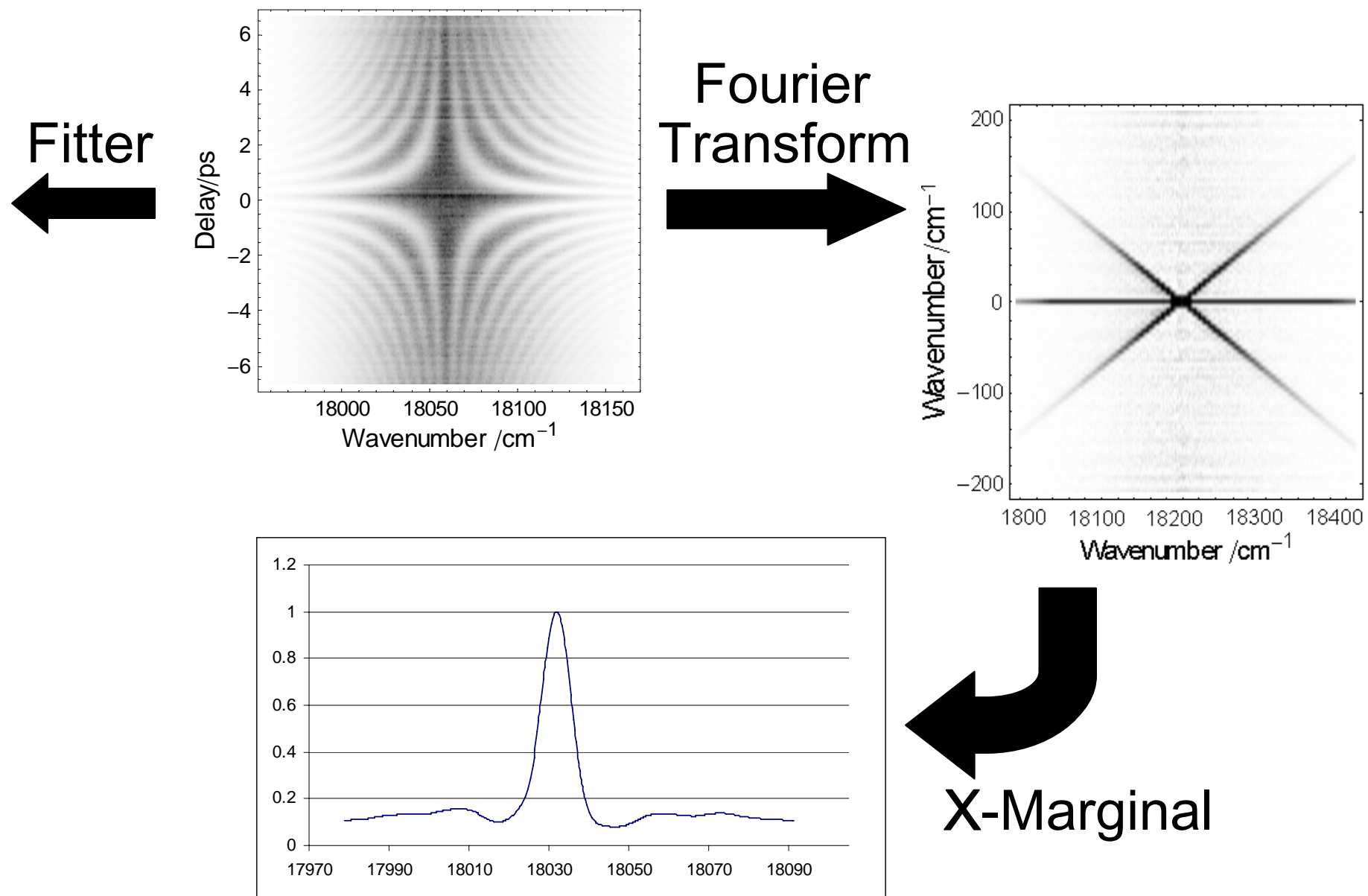


Figure S1

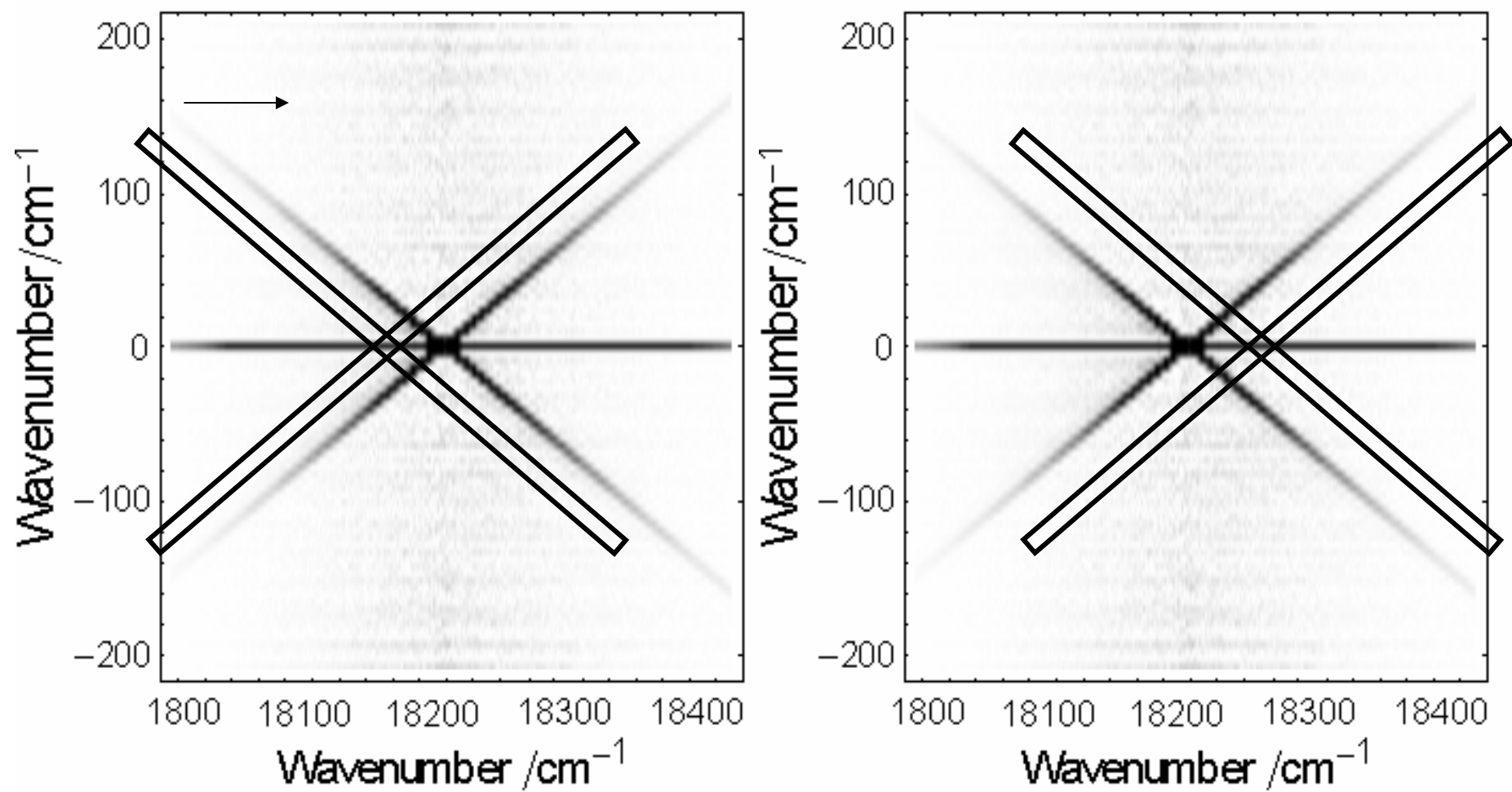


Figure S2