

Supporting Information:
Infrared Spectroscopy of 2-Oxo-Octanoic Acid in Multiple Phases

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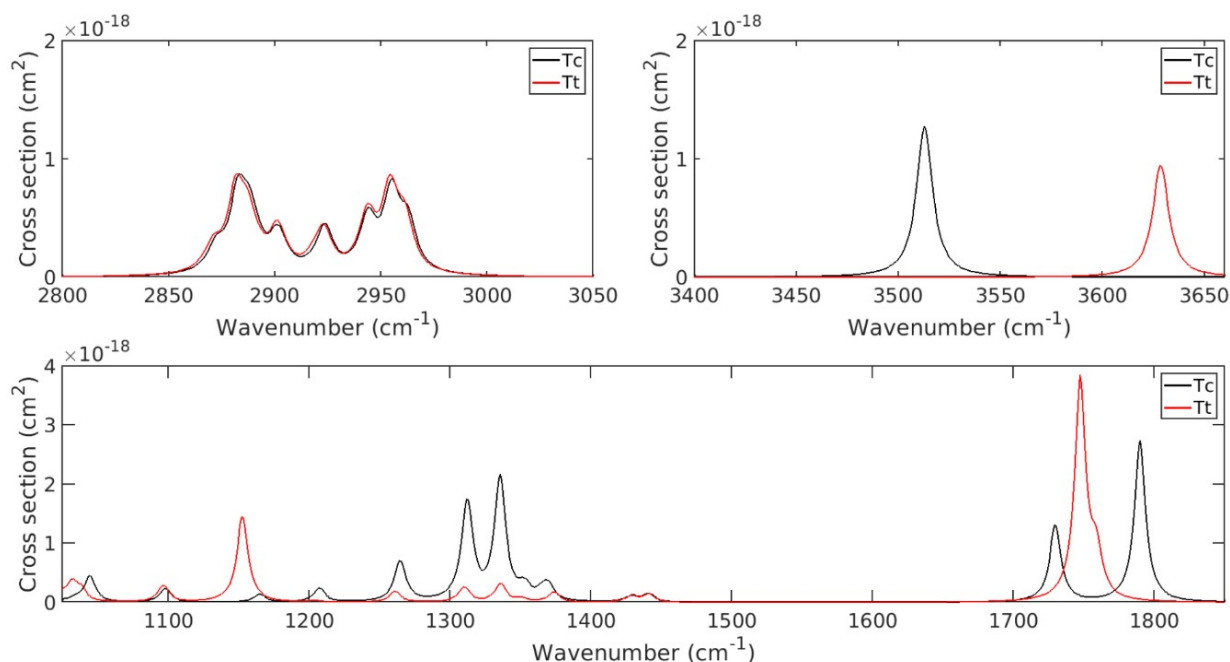


Figure S1. A comparison of the calculated gas phase IR spectra of the single lowest energy Tc and Tt 200A conformer.

Calculated Saturated Vapor Pressure. The theory derived oscillator strengths were used in combination with the experimental spectra to calculate the saturated vapor pressure for 200A using the equation

$$p = 7.9458 \cdot 10^{-7} [\text{Torr m cm}] \frac{\int A(\tilde{\nu}) d\tilde{\nu}}{f \cdot l} \quad (1)$$

which is taken from the literature.^{1,2} The constant is given at 295 K, p is the pressure given in Torr, f is the calculated oscillator strength which is unitless, l is the experimental path length in meters, A is the experimental absorbance, which in the equation is integrated over the experimental bands giving the unit cm^{-1} .

Several peaks in the IR spectrum are suitably isolated and clearly assigned to be used for calculating the saturated vapor pressure of 200A with Equation 1. This includes the sum of the OH stretches (hydrogen bonded and free), the sum of CH stretches, the two C=O stretches and the CH₂ bending peaks. Integrations of experimental peaks were done using a straight line as baseline. Straight baseline integration avoids contribution to the integrated absorbances from the sloping baseline in the OH stretch region. The saturated vapor pressure calculated as a mean value using the listed peaks is $6.1 \cdot 10^{-3}$ Torr, with a standard deviation of $2.1 \cdot 10^{-3}$ Torr. The standard deviation does not accurately reflect the uncertainty on the saturated vapor pressure, but it does show that our calculation is consistent across the different peaks used to calculate it. The integrations of measured absorbances has an uncertainty of about 10%, while the uncertainty on the calculated oscillator strength is not simple to estimate.³ It should also be mentioned that the oscillator strengths used for calculating saturated vapor pressures come from just the lowest energy Tc and Tt conformers which are the all *trans* Tt and Tc conformers not from a weighted contribution of the 66 unique conformers used for spectral simulation. As an alternative way of determining the saturated vapor pressure of 200A we compared it to the saturated vapor pressure of Pyruvic acid (PA), which has spectra that have been reported in the literature.⁴⁻⁶ Equation 1 can be rearranged as a ratio between infrared transition intensities, which in practice is the integrated absorbances, that are similar between 200A and PA. The OH and C=O stretches are used here. Since PA pressures were directly measured in those prior experiments,⁴⁻⁶ we can derive an absolute pressure using the equation

$$p_{200A} = p_{PA} \cdot \frac{f_{PA} \cdot l_{PA}}{f_{200A} \cdot l_{200A}} \cdot \frac{\int A(\tilde{\nu}) d\tilde{\nu}_{200A}}{\int A(\tilde{\nu}) d\tilde{\nu}_{PA}} \quad (2)$$

where p refers to partial pressure, f is the calculated oscillator strength of a transition, l is the path length of the cell used in the experiment and $A(\tilde{\nu})$ is the absorbance here expressed per wavenumber which is integrated over the specific band in the infrared spectrum in question. This eliminates most uncertainties associated with the calculated oscillator strengths because they are at most 10% different between PA and 200A for any two alike transitions in our calculations. This does add more experimental uncertainties including any uncertainty in the pressure measurements of PA. Using this method, a 200A saturated vapor pressure of 9.8×10^{-3} Torr and a standard deviation of 2.2×10^{-3} Torr was calculated. The two different saturated vapor pressures determined are taken and are added two standard deviations uncertainty, resulting in a range for 200A of 2×10^{-3} Torr to 2×10^{-2} Torr.

Discussion of 200A Impurity. An NMR analysis of our 200A stock, which was used unpurified, reveals an impurity with approximately 5% of the intensity of 200A, even though the purchased product was listed as $\geq 99\%$ pure. As shown in Figure S2, the chemical shift of the apparent impurity is 2.37 ppm, which is the expected shift and splitting of CH_2 hydrogens adjacent to a carbonyl. Given that a carboxylic acid is a likely impurity in alpha keto acid samples⁴, we also obtained an NMR spectrum of heptanoic acid, shown in Figure S3. The heptanoic acid spectrum exhibits the same triplet centered around 2.34 as the 200A impurity. Its other features would be obscured by 200A's other features in the 200A NMR spectrum. Therefore, there is likely a contribution from a fatty acid impurity to the gas phase spectrum of 200A. If the fatty acid impurity is comprised of higher saturated vapor pressure compounds than 200A, its gas phase spectral contribution could be more significant than the NMR analysis suggests. The impurity may account for why the Tc and Tt conformer OH stretch transitions suggest that a lot more of the Tt conformer is present than what has been reported in the literature for PA and calculated for 200A in this work. A carboxylic acid would exclusively contribute to the Tt OH stretch signal since it lacks the means of forming an internal hydrogen bond. Thus, the experimental Tt population of 200A cannot be accurately determined but can be inferred to be lower than what the experimental spectra would suggest.

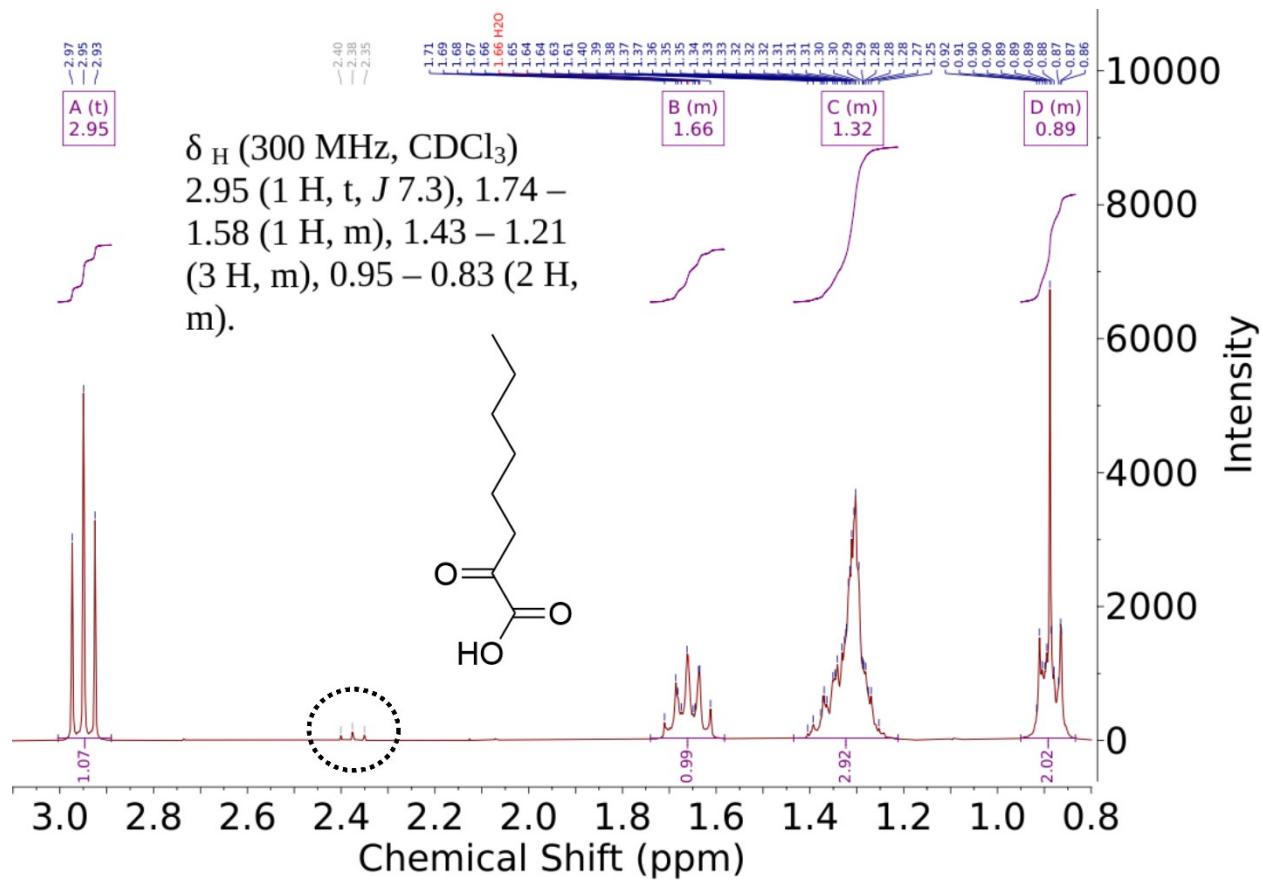


Figure S2. NMR spectrum of 200A in deuterated chloroform. The suggested impurity is circled in the spectrum.

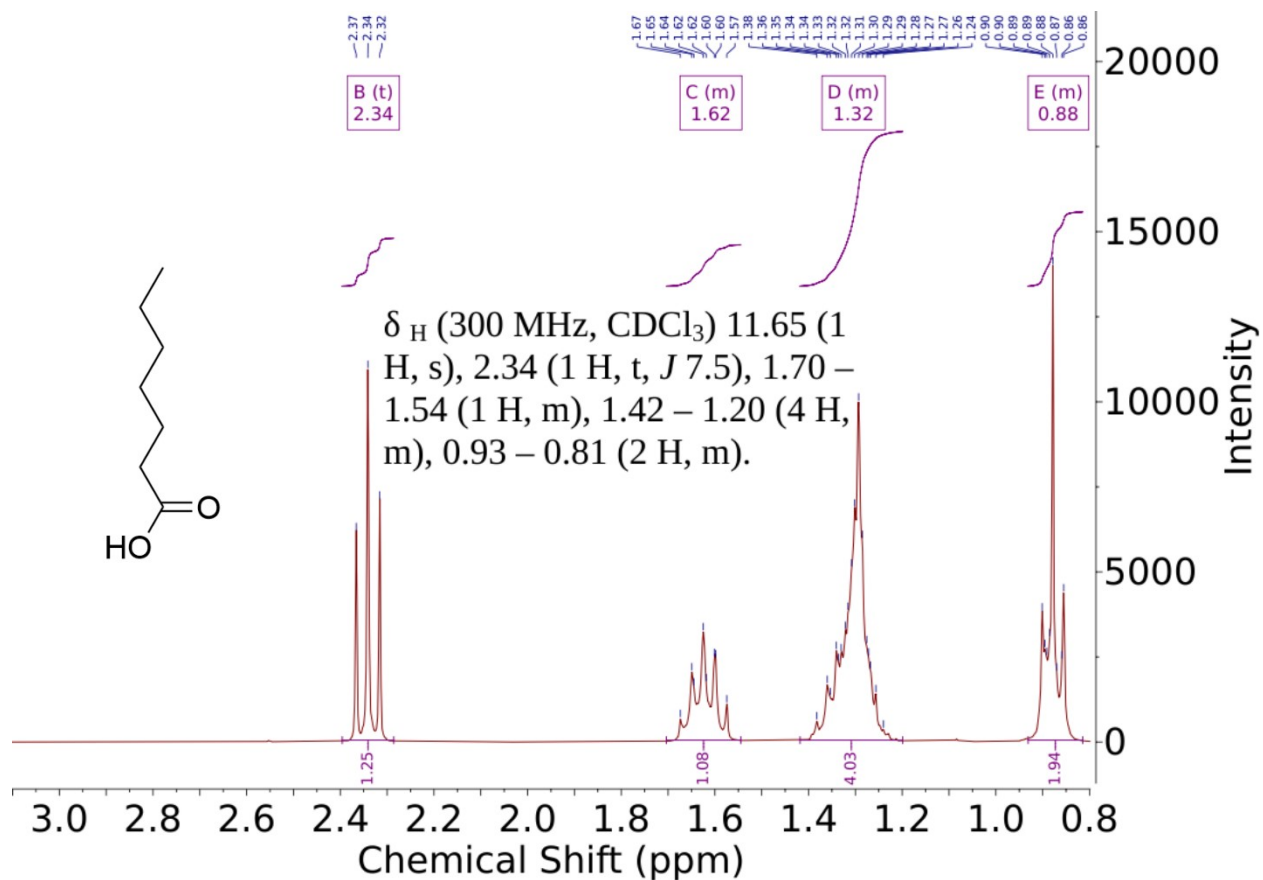


Figure S3. NMR spectrum of heptanoic acid in deuterated chloroform.

References

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