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Laboratory Experiment

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Determining the Energetics of the Hydrogen Bond through FTIR: A Hands-On Physical Chemistry Lab Experiment

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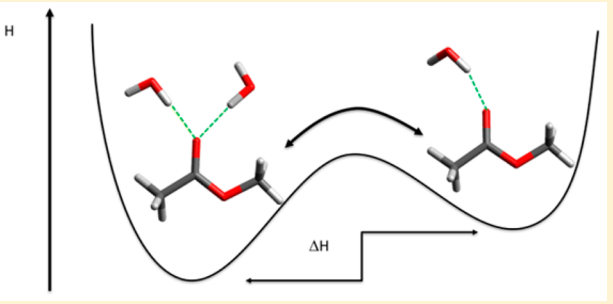
Supporting Information

ABSTRACT: Hydrogen bonds are very important chemical structures that are responsible for many unique and important properties of solvents, such as the solvation power of water. These distinctive features are directly related to the stabilization energy conferred by hydrogen bonds to the solvent. Thus, the characterization of hydrogen bond energetics has been vital for many areas of science. We present a laboratory experiment for physical chemistry in which the hydrogen bond energetics between methyl acetate and water is investigated by Fourier transform infrared spectroscopy (FTIR). The experiment consists of measuring the temperature dependent IR spectra of methyl acetate to determine the changes in the enthalpy and entropy of making/breaking hydrogen bonds. This experiment aims at providing the students with hands-on experience in the following topics: solution and sample cell preparation, IR spectra collection and analysis, and data modeling and thermodynamic calculations. The overall objective of this experiment is to familiarize chemistry students with a methodology used to extract meaningful and up-to-date physical chemistry properties from real experimental data.



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Hydrogen bonds impact many different areas of science, including, but not limited to, chemistry, biology, and biophysics.[1,2] In particular, they play a major role in determining the properties of water[3] and defining the structure of proteins[4,5] and DNA,[6] and recently, they have been used for the design of large molecular assemblies in supramolecular[7] and polymer chemistry.[8] Thus, the hydrogen bond is a very important concept that should be present in any college Chemistry curricula.

The formation of a hydrogen bond occurs when a hydrogen covalently bonded to an electronegative atom, such as oxygen, interacts with another electronegative atom. This interaction confers a stabilization energy to the molecular system of a few kilojoules per mole, but not greater than 25 kJ/mol.[9] The formation and rupture of a hydrogen bond occurs on an ultrafast time scale, i.e., on the order of a few picoseconds (10^{-12} s).[10] The fast interchange dynamics complicates the characterization of the hydrogen bond by most conventional techniques, such as NMR.[9,11,12] Methodologies relying on the absorption of light are not limited to any particular dynamic time scale because they quantify the different species in a sample by measuring the number of photons that they absorb.[13] However, the drawback of light absorption methodologies is that most of them do not provide structural information about the species being detected.

Fourier transform infrared spectroscopy (FTIR) is a spectroscopic methodology that measures the infrared light absorbed by a sample[14] as a consequence of their molecules being promoted from vibrational ground states to vibrational excited states.[15] Some vibrational modes, such as the carbonyl stretch, are well localized modes, allowing one to investigate confined regions of the molecule. In addition, vibrational modes are very good probes of the molecular environment because their associated vibrational frequency is sensitive to the different interactions with the environment.[16] In particular, vibrational modes are very susceptible to the formation of hydrogen bonds because hydrogen bonds significantly alter the electronic structure of the molecular system and, consequently, their associated vibrational transitions.[17] The effect of the hydrogen bond on vibrational transitions is directly observed in the IR spectrum as a shift of the central frequency of the vibrational transition.[17] Thus, IR spectroscopy can be used to measure the different hydrogen bonded states of a molecule. However, it has been very difficult to unequivocally assign the different peaks in the IR spectrum to the different vibrational modes due to the presence of other vibrational transitions, such as those arising from overtones and combinational modes.[18] Recently, the introduction of nonlinear ultrafast IR spectroscopy has allowed the interpretation and assignment of the peaks observed in the IR spectrum to specific vibrational

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transitions.[19] Therefore, it is now possible to study the energetics of the hydrogen bond directly by FTIR spectroscopy.[20−23]

In this work, FTIR spectroscopy is used to investigate the hydrogen bond energetics between methyl acetate and deuterium oxide by probing the carbonyl stretch of the acetate at ∼1700 cm^{-1}.[24] Our approach presents a different hands-on experience to familiarize students with the concept of hydrogen bond thermodynamics by experimenting with FTIR spectroscopy, which is a methodology currently utilized in many research laboratories worldwide. In addition, the FTIR spectrometer is an apparatus that is present in nearly every, if not all, departments of Chemistry, making this laboratory experiment accessible to a worldwide undergraduate student audience.

The paper is organized as follows. The first section describes the theory behind the experiment. After this introduction, a section outlining the experimental procedure, hazards, and results is presented. Finally, the last sections summarize the concepts demonstrated and used in the experiment and the student response to the lab experiment.

THE THEORY BEHIND THE EXPERIMENT

The FTIR spectra of methyl acetate show that its carbonyl stretch is a high frequency singlet in tetrahydrofuran, but it is a low frequency doublet in deuterium oxide (Figure 1). While it

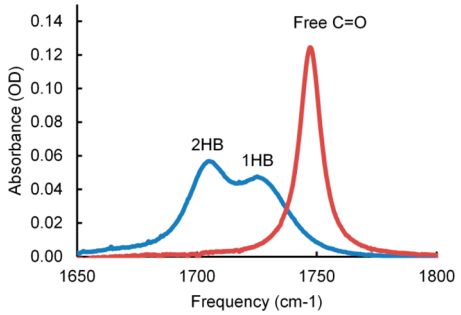

Figure 1. FTIR spectra of methyl acetate in different solvents. The blue and red lines correspond to the spectra of methyl acetate in D_2O and tetrahydrofuran, respectively.

is expected that methyl acetate will not form hydrogen bonds in tetrahydrofuran, hydrogen bonded species of methyl acetate are expected to account for the majority of the species in water (D_2O). Thus, it is safe to conclude that the split and shift of the carbonyl stretch band in D_2O (blue line, Figure 1) with respect to tetrahydrofuran (red line, Figure 1) are due to the formation of one and two hydrogen bonded species with the solvent (Figure 2).[24]

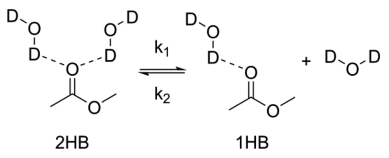

Figure 2. Scheme of the hydrogen bond making and breaking of methyl acetate in deuterium oxide. The [2HB] and [1HB] represent the double and single hydrogen bonded species of methyl acetate, respectively.

From a molecular perspective, the formation of a hydrogen bond implies a decrease in the electron density of the carbonyl group of methyl acetate, which not only stretches the C═O bond, but also lowers its associated vibrational frequency. Similarly, the presence of two hydrogen bonds further relaxes the C═O bond and lowers the carbonyl stretch frequency with respect to the hydrogen bonded species. Thus, the high and low frequency peaks in the FTIR of methyl acetate in D_2O (red line, Figure 1) represent the two populations of the methyl acetate with one and two hydrogen bonds, respectively, which are dynamically changing from one to the other (Figure 2).[24]

The interconversion between the two hydrogen bonded species (Figure 2) can be simply represented as

$$2HB \rightleftharpoons 1HB + D_2O \tag{1}$$

and its equilibrium constant is given by

$$K = \frac{a_{1HB} \cdot a_{D_2O}}{a_{2HB}} \tag{2}$$

where a is the activity of each of the components as shown in Figure 2. Given the low concentration of methyl acetate (∼0.3 M), it is reasonable to assume that the activity coefficients are unitary for all the species in solution, and that the water concentration is constant.[25] Thus, eq 2 can be simplified to

$$K' = \frac{[1HB]}{[2HB]} \tag{3}$$

where K' is $K/[D_2O]$.

To understand how it is possible to study a reaction that has very fast dynamics without a time-resolved spectroscopy, the relationship between the equilibrium constant and the kinetics of the reaction is used. At equilibrium, the ratio of $[2HB]_{eq}$ and $[1HB]_{eq}$ defines the equilibrium constant for the interconversion between the two species:

$$K' = \frac{[1HB]_{eq}}{[2HB]_{eq}} = \frac{k_1}{k_2} \tag{4}$$

since at this condition the rate of the forward and backward reactions are equal[25]

$$k_1[2HB]_{eq} = k_2[1HB]_{eq} \tag{5}$$

From eq 4, it is now clear that if the rate constants for the forward and backward reactions are similar in magnitude, the two species should be observed in solution since under these conditions K' is close to unity. This is exactly the case of the two hydrogen bonded states of methyl acetate, where the hydrogen bond making and breaking process has very large rate constants corresponding to dynamics of picoseconds,[25] but because the two rate constants (k_1 and k_2) are very similar in magnitude, the equilibrium constant is close to unity and the chemical process can still be investigated by conventional absorption spectroscopies.[24] Moreover, the two hydrogen bonded species are individually observed in the IR spectrum since the extra hydrogen bond imparts a significant and easily observable shift in the carbonyl stretching frequency, which is also fairly intense.[18,24]

To find the energetics of the hydrogen bond, the relationship between the absorption of the two vibrational transitions and the changes in the enthalpy and entropy of the chemical process is needed. This expression can be directly derived from the Gibbs free energy of reaction[25] and the Lambert−Beer

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Law.[26] The Gibbs free energy of any chemical process, such as that depicted in Figure 2, is defined as

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{6}$$

where ΔH^0 and ΔS^0 are the changes in the enthalpy and entropy, respectively, in standard conditions, and T is the temperature in Kelvin. Under equilibrium conditions, ΔG^0 can also be expressed as

$$\Delta G^0 = -RT\ln(K') \tag{7}$$

where R is the gas constant, T is the temperature, and K' is the equilibrium constant of the process (eq 4). When we combine eqs 6 and 7, the relationship between the equilibrium constant and the changes in the enthalpy and entropy of the process is found:

$$\ln(K') = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \tag{8}$$

Equation 8 shows that the equilibrium constant explicitly depends on the ΔH^0, ΔS^0, and T of the system. Thus, a small variation of the temperature, in which ΔH^0 and ΔS^0 can be assumed to be constant, will still change the equilibrium constant, or equivalently the ratio of concentrations of the two species (eq 4).

Finally, to relate the concentrations of the species with the infrared absorptions, the Lambert−Beer Law is used. The Lambert−Beer Law states that the absorption of a sample is given by[26]

$$A_i = \varepsilon_i \cdot b \cdot [i] \tag{9}$$

where A_i, ε_i, and $[i]$ are the absorbance, the molar absorptivity coefficient, and the concentration of the i species, respectively, and b is the path length of the sample cell. Combining eqs 8 and 9 leads to eq 10, which contains the relationship between the absorption of the species and the thermodynamics of the chemical process.

$$\ln\frac{A_{1HB}}{A_{2HB}} = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} - \ln\left(\frac{\varepsilon_{2HB}}{\varepsilon_{1HB}}\right) \tag{10}$$

It is now clear from eq 10 that, by measuring the absorption of the two hydrogen bonded species as a function of the temperature, it is possible to estimate the energetics (ΔH^0 and ΔS^0) of the hydrogen bond making and breaking process. In addition, eq 10 shows that $\ln\left(\frac{A_{1HB}}{A_{2HB}}\right)$ vs $\frac{1}{T}$ should produce a line if the temperature is varied in a small range, where ΔH^0 and ΔS^0 are fairly constant. Thus, eq 10 can be written in the form of

$$y = a + bx \tag{11}$$

where y is $\ln\left(\frac{A_{1HB}}{A_{2HB}}\right)$, x is $\left(\frac{1}{T}\right)$, b is the slope $\left(-\frac{\Delta H^0}{R}\right)$, and a is the intercept $\left(\frac{\Delta S^0}{R} - \ln\frac{\varepsilon_{2HB}}{\varepsilon_{1HB}}\right)$.

Note that the two parameters of eq 11, a and b, contain the thermodynamic parameters of the process which are the objective of this laboratory experiment.

EXPERIMENTAL PROCEDURE

Overview

The students will first prepare the sample and the sample cell (see Supporting Information for this procedure). Then, the students will measure the IR spectra of the solvent and the sample at a minimum of four different temperatures. Next, the students will analyze the IR spectra (see Supporting Information for the analysis and fitting of the IR spectra). It takes approximately 4 h to perform the measurements and an additional 4 h to analyze the spectra and do the calculations, so we recommend to have a group of two students.

IR Spectroscopy

This lab requires an FTIR spectrometer, a temperature controlled demountable liquid cell for transmission experiments, and a temperature controlled bath to modify the temperature of the sample cell. Our experiments were performed using a Bruker Tensor 27 FTIR spectrometer with a 0.5 cm^{-1} resolution, a Harrick temperature controlled sample cell, and a Pharmacia Biotech circulating bath (±0.1 °C temperature regulation). However, less expensive equipment can be used for this laboratory practice (see Supporting Information). The transmission sample cell (Harrick Scientific) consists of a pair of 2 mm calcium fluoride windows separated by a 15 μm Teflon spacer. Note that calcium fluoride windows are used because of their transparency in the infrared as well as their insolubility in water. The acquisition of one spectrum at one temperature, with an average of 40 scans, took approximately 10 min using this instrumentation.

HAZARDS

Methyl acetate is a highly flammable liquid and vapor. It causes serious eye irritation, and it may cause drowsiness or dizziness. Methanol is also a highly flammable liquid and vapor, and it causes damage to organs. It is toxic if swallowed or inhaled or if it comes in contact with skin.

RESULTS

The results of our FTIR experiment are presented in Figure 3. The FTIR spectrum with the background subtracted in the region of the carbonyl stretch (C═O) (between 1700 and 1800 cm^{-1}) presents two peaks. As previously mentioned, these two peaks correspond to the carbonyl asymmetric stretch of two different hydration states of methyl acetate in which the low and high frequency bands have been assigned to a doubly

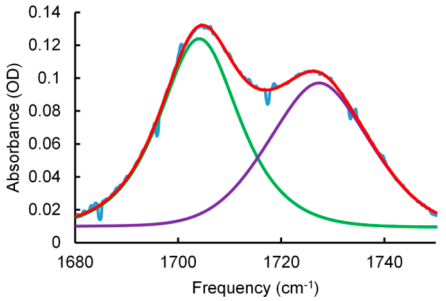

Figure 3. Measured IR spectra of methyl acetate in the region of the carbonyl asymmetric stretch. The blue and red lines represent the experimental data and the fitting of the spectra with two pseudo-Voigt profiles, respectively. The green and purple lines represent the individual pseudo-Voigt profiles.

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and singly hydrogen bonded species, respectively.[24] The IR spectrum also shows that the vibrational bands of the two hydration states have not only different central frequencies, but also different peak absorptions. At 283 K, the low frequency peak, centered at ~1710 cm^{-1}, has a peak absorption ~30% larger than the high frequency peak located at ~1730 cm^{-1} (Figure 3). The difference in peak heights is an indication of the equilibrium between the two hydrogen bonded species being shifted toward methyl acetate molecules with two hydrogen bonds.

To measure the energetics of the hydrogen bond formation, the change of the equilibrium between the different hydration states of the carbonyl stretch was measured by acquiring the FTIR spectrum at different temperatures. The results of our temperature dependence FTIR experiments are presented in Figure 4. Figure 4 shows that the shapes and locations of the

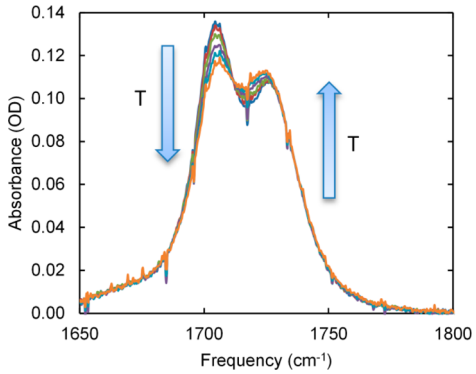

Figure 4. Temperature-dependent IR spectra of methyl acetate in the carbonyl region from 283 to 333 K in increments of 10 K. The arrows show the direction in which the peaks evolve when the temperature is increased. The various colors symbolize the different temperatures at which the IR spectra was recorded.

carbonyl stretch are not significantly altered with the change in temperature (see Supporting Information for the modeling of the IR bands). However, there is an appreciable variation in the peak absorbance as observed in the decline of the absorption of the low frequency band and the growth of the absorbance of the high frequency band when the temperature is increased. These observations are consistent with a change in the equilibrium conditions of the system in which the number of methyl acetate molecules hydrogen bonded to two water molecules decreases, while those with one hydrogen bond increase, when the temperature of the sample is increased.

To quantify the change in the equilibrium conditions, the peak amplitudes of the two bands as a function of temperature were determined by fitting the spectra with two pseudo-Voigt profiles (see Supporting Information Fitting methodology section). The result of the spectral fitting is illustrated in Figure 5. The fitting results quantitatively show, through the area, that as the temperature is increased, the amount of doubly hydrogen bonded species of methyl acetate (area of the low frequency band) decreases, while the number of singly hydrogen bonded species (area of the high frequency band) increases.

In addition, our observation shows that $\ln\left(\frac{A_{1HB}}{A_{2HB}}\right)$ has a linear relation with $\frac{1}{T}$ (Figure 6), validating the assumptions previously made for the derivation of eq 11. Moreover, the

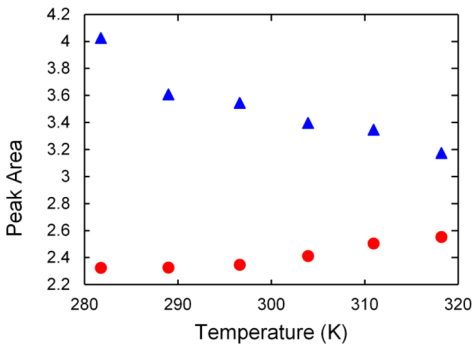

Figure 5. IR peak area versus temperature. The blue triangles and red circles show the change in peak area due to the increase in temperature for the low and high frequency bands, respectively.

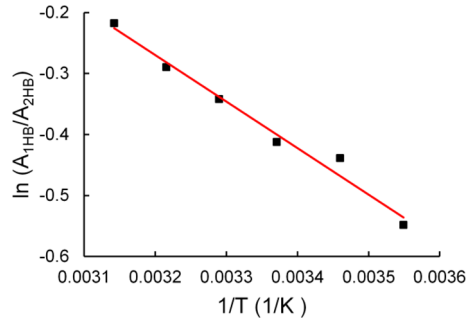

Figure 6. Relationship between $\ln\left(\frac{A_{1HB}}{A_{2HB}}\right)$ and $\frac{1}{T}$. The squares are the experimental data, and the red line represents the fit with a line.

slope of the least-squares fitting of the data with a line (b = −760 ± 50 K) provides an estimate for the change in enthalpy of breaking a hydrogen bond of ΔH^0 = 6.3 ± 0.4 kJ/mol, which is in agreement with previous experimental values.[3] From this analysis, it is also possible to estimate, from the intercept $\left(\frac{\Delta S^0}{R}\right)$, the change of entropy for breaking a hydrogen bond. For this purpose, it is required to assume that the molar absorptivity coefficients of the two carbonyl hydrogen bonded states (ε_{1HB} and ε_{2HB}) are equal. Thus, under the approximation of ε_{1HB} = ε_{2HB}, the entropy change for the process is estimated to be 18 ± 1 J/(K·mol). It is important to note that the positive signs of the changes in the enthalpy and entropy derived from the results are consistent with the physical chemistry of the hydrogen bond process. The change in enthalpy being greater than zero indicates that to break hydrogen bonds, energy in the form of heat is required by the system. Moreover, this directly demonstrates that the hydrogen bond confers a stabilization energy to the system. In the case of the change in entropy, the positive sign shows that the system increases its disorder when a hydrogen bond is broken. In other words, when one water molecule hydrogen bonded to methyl acetate breaks its hydrogen bond, the three-molecule arrangement becomes a two-molecule arrangement plus one water molecule (Figure 2) which is more disorganized than the three-molecule system.[27]

To probe how robust is this laboratory experiment, the experiment was performed with a sample three times less concentrated than the original experiment and with fewer temperature points. The results obtained after analyzing the data are illustrated in Figure 7. While the plot shows that the data has a lower quality (less linear) than that obtained in the

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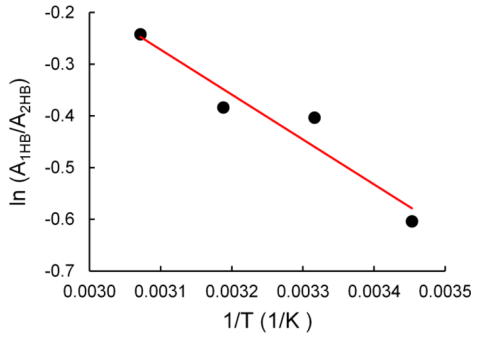

Figure 7. Relationship between $\ln\left(\frac{A_{1HB}}{A_{2HB}}\right)$ and $\frac{1}{T}$ when measured at four temperatures with a 3-fold concentration decrease. The circles are the experimental data, and the red line represents the fit with a line.

original experiment, the values of the enthalpy and entropy changes derived from this experiment (7 ± 1 kJ/mol and 20 ± 5 J/(K·mol), respectively) are within 20% from those determined before. Since this laboratory practice is designed to provide students with the opportunity of measuring the magnitude of the energetics of the hydrogen bond, a 20% error in the determination of the mean values of the energetics is within a reasonable experimental error. Thus, this last experiment proves that the present experiment is very robust and adequate to be performed in any physical chemistry laboratory.

CONCEPTS DEMONSTRATED BY THE EXPERIMENT

The physical concepts demonstrated by the experiment are as follows:

- *Effect of the hydrogen bond on the transition frequency*. This experiment shows that the carbonyl stretch is sensitive to the number of hydrogen bonds as seen in the different frequencies of the two carbonyl stretch bands.
- *Equilibrium constant*. The experiment demonstrates that the two peaks observed in the IR spectra correspond to the different hydrogen bonded species of methyl acetate where the ratio of the two species populations (peak absorptions) is the equilibrium constant.
- *Equilibrium constant and temperature dependence*. The experiment demonstrates that the population of the two hydrogen bonded methyl acetate species varies with temperature. This is a direct demonstration of the temperature dependence of the equilibrium constant.
- *Hydrogen bond energetics*. The experiment shows that the most abundant species at lower temperatures is methyl acetate with two hydrogen bonds, indicating that these species have less energy than the singly hydrogen bonded species. Moreover, it also demonstrates that the energetics of the hydrogen bond can be determined from the change in the different hydrogen bond populations with temperature.
- *Changes in the enthalpy and entropy of a hydrogen bond*. Here, it is determined that the changes in the enthalpy and entropy are +6.3 ± 0.4 kJ/mol and +18.0 ± 1 J/(K.mol), respectively, for breaking a water hydrogen bond from the carbonyl group of methyl acetate. The positive sign of both thermodynamic quantities indicates that breaking a hydrogen bond is an endothermic reaction which increases the overall disorder of the system.

STUDENT RESPONSE

Undergraduate students enrolled in the physical chemistry lab course performed this experiment. The students were given the handouts and supporting information prior to the experiment, and were able to complete the experiment and data analysis in two class periods. They were familiarized with the procedure for preparing a sample cell and the data collection process when using a Fourier transform infrared spectrometer. The students found the experiment extremely beneficial in providing practice with data modeling, since they had minimal prior experience. Understanding the process of fitting experimental data is a valuable tool for the students to have, as they move forward in their studies. Additionally, the students were asked to find improvements that could be made. Surprisingly, the students were very engaged with this assignment and they developed an alternative method for heating the sample, which consisted of using an electric heater and thermocouple to measure and control the temperature of the IR sample cell (see Supporting Information).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.5b01014.

The process used to prepare the sample and the sample cell, alternative equipment options, the procedure for analyzing and fitting the IR spectra, the table of parameters used in the fitting of the IR spectra; a student handout for completing the experiment and additional resources for the instructor (PDF, DOCX)

Excel file demonstrating how to analyze the raw data (XLSX)

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Notes

The authors declare no competing financial interest.

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