Ftir spectroscopy of so2

Abstract

In this lab, the IR spectrum of SO2 gas was taken. The spectrum was then used to determine which peaks corresponded to the vibrational modes of SO2. Once the modes had been determined, the experimental wavenumbers of the v1 and v3 modes and the overtones were used to determine the anharmonicity of the two different modes. While there was a difference between the two modes' anharmonicity, overall there was not a significant difference. The modes and their corresponding wavenumbers were also used to calculate the force constants of SO2. The experimental data produced a force constant k1 with 3. 112% error while the kδ/l2 constant had a 2. 963% error.

Introductions

IR spectroscopy is the detection of a transmittance or absorption intensity of change as a function of frequency1. In recent years, Fourier transform spectrometers replaced the traditional dispersive spectrometer because they are faster and more sensitive. They have made it possible to analyze many areas which were not possible with the dispersive spectrophotometer. The difference is the simultaneous examination of all frequencies. The three basic spectrometer components in a FT system are the radiation source, interferometer and detector. The radiation source in precision FTIR instruments is often water-cooled in give it more power and stability2.

Figure 1. shows a diagram of the interferometer and the schematics of the spectrophotometer as a whole. The interferometer has the following three components: a moving mirror, fixed mirror, and a beamsplitter.. The beamsplitter is a semireflecting geranium thin film of small particles

deposited on flat KBr substrate. Radiation from the broadband IR source is focused into the interferometer, and hits the beamsplitter. Once the beam hits the beam splitter, half of it is transmitted to the fixed mirror while the other half is transmitted to the moving mirror. The changing position of the moving mirror relative to the fixed one generates an interference pattern and causes the two beams to oscillate in and out of phase. When the beams are in phase, there is a constructive interference resulting in the maximum detector response. However, when the beam is out of phase, there is a deconstructive interference between the two beams. Once they have been reflected from both mirrors, they recombine at the beam splitter. The recombined beam passes through the sample and then focuses on the detector2.

The intensity of the radiation hitting the detector will vary in a sinusoidal manner while the mirror is moving at constant velocity. The record of the interference signal is the interferogram and is a time domain spectrum. The detector’s response changes versus time within the mirror scan are recorded. When a sample absorbs at a certain frequency, the amplitude of the sinusoidal wave reduces proportionally to the amount of sample in the beam. In an IR spectrophotometer, this process happens in three component frequencies, which creates a more complex interferogram2.

To convert these interferogram recordings to the IR spectrum, a Fourier transformation is used. Small, precise intervals are used during the mirror scan. The rate of the sampling behavior is controlled by a monochromatic beam produced by a helium neon laser focused on a separate detector2.

For this analysis, the mid IR spectrophotometer utilized a KBr beamsplitter and a mercury cadmium telluride (MCT) detector. MCT detectors are photon detector with a dependence on the quantum nature of radiation. They also exhibit very fast responses. They must be at a constant temperature of 77^(o)K, the temperature of liquid nitrogen. It is faster and more sensitive than the alternative detector, the deuterated triglycine sulfate (DTGS) 2, which was used for the far IR analysis. The cell used to hold the SO2 gas can be seen in Figure 2.

A molecule’s energy can be split into three components: the electrons motion, the constituent atom’s vibrations and the whole rotation of the molecule. While electronic transitions happen on a short timescale, rotational transitions happen on a longer time scale. When a molecule is placed in an electromagnetic field, such as light, energy from the light is transferred from the field to the molecule. This happens upon the satisfaction of Bohr’s frequency condition:

$\Delta E = hv$

When a molecule is excited from one state to another, the energy difference between the two states is absorbed by the molecule. When the molecule reverts back to the previous state, the change in energy which was absorbed upon excitation is then emitted1*. A molecule will be excited by photons which possess the appropriate energy3.

Vibrational transitions are observed in the infrared (IR) spectra which are about the 103 ~ 104 cm-1 region. These transitions are caused by the vibration of the nuclei constituting the molecule. The rotational transitions occur at 1-103 cm-1 region, the microwave region, while the electronic transitions occur at 104-106 cm-1 region, the UV-visible region. As the vibrational quantum number v increases, the rotational intervals tend to decrease. The vibrational fine structure of electronic transitions can give insight to the structural and bonding information about molecules which are electronically excited1*.

A system displaced from its equilibrium force will be restored due to a restoring force provided by the elasticity of the system. However, there is a property of inertia which causes the system to over correct for the displacement. The back and forth actions of elasticity and inertia cause the system to have oscillatory motion4. When the potential energy is graphed versus the internuclear separation, a perfect harmonic oscillator forms a parabola. The energy spacing in a harmonic oscillator does not change throughout the well of the parabola and is equal to

$h\omega$ where $\omega= km12$

and the zero point energy is

$Eo= 12h\omega$

When a system is not a perfect harmonic oscillator, it is considered anharmonic. Anharmonicity forces the right side of the parabola to widen and asymptotically approach zero. The spaces between the permitted states are not evenly spaced as they were in the harmonic system5. The comparison of the two graphs can be seen if Figure 3.

One of the possible ways to calculate xe, a term which shows the anharmonicity of a system is to graph ? G/? versus (?+1). This yields a graph with an equation as follows

$\Delta Gv= v+ 1xeve+ ve$

By dividing the xeve term by ve, the xe term is found. The larger this number, the more anharmonic the system is and vise versa5.

Covalent bonds of molecules are not rigid as ball and stick models would suggest, but rather they can be compared to stiff springs which are capable of stretching and bending. More energy is required to stretch and compress a bond than it does to bend it. There is a direct relationship between the energy or frequency which characterizes the stretching vibration of a bond and the bond dissociation energy3.

The major factors which are influencial in the stretching frequency of a covalent bond can be seen in the following equation:

$v = 12rck(m1+m2)m1+m2$

where v is the frequency, k is the force constant, c is the speed of light, and m1 and m2 are the masses of the two atoms on each end of the bond. This equation corresponds to the rigidness of the oscillation. However, it should be noted that not all molecular vibrations are capable of being observed in the infrared region. In order to be seen in an IR spectrum, a vibration must cause a change in the dipole of a molecule. This change in charge distribution allows the molecule to absorb infrared light. There is a proportional relationship between the change in charge distribution and the absorption: the greater the change, the stronger the absorption3.

All vibrating physical objects have a set of normal modes6. A normal mode can be defined as a simple harmonic oscillation which occurs about an area which is local and low in energy. The normal modes are determined by the system’s structure R and it’s energy function V(R). Any motion can be expressed as a superposition of normal modes when a pure harmonic V(R) is being considered. However, the near minimum potential can still be approximated by a harmonic potential for an anharmonic V(R). Also, small-amplitude motions can still be described by the sum of normal modes. This means that all systems behave harmonically at low temperatures7.

For SO2, it is necessary to have nine Cartesian coordinates in order to determine the positions of all three nuclei. Therefore, the molecule is considered to have nine nuclear degrees of freedom. The first three are necessary to describe the position of the center of mass of the molecule. If these three degrees change, it represents the translational movement of the molecule in space. The next three degrees of freedom refer to the orientation of the molecule. These three degrees can be described as the angles of the molecule. If these three degrees change, then the molecule has rotated. The three remaining coordinates are those used to describe the relative positions of the three atoms. These are called vibrational coordinates8.

To describe the vibrations of a bent trigonal molecule, it makes sense to use the valence coordinates. The valence coordinates consist of the two bond lengths and the bond angle. However, they do possess a drawback. If energy is put into a bond so that it stretches, to observe how the molecule reacts is difficult due to the energy put into the stretched bond quickly flowing into the vibrations of the other bond in the molecule. Because of this, it is said that the stretching of a single bond and other vibrational motions are coupled8.

By varying the coordinates, which are the linear combinations of changes in the bond lengths and bond angles, a good uncoupled approximation can be made. These coordinates are called the normal coordinates. Motions which take place in these coordinates are appropriately called normal modes of vibration. The center of mass does not move in these coordinates8.

A non symmetric molecule with N number of atoms will have 3N-6 normal modes. This means SO2 will have 3(3)-6 = 3 normal modes. The normal modes for SO2 can be seen in Figure 3. The symmetric stretch is labeled as v1, the bend is labeled v2, and the asymmetric stretch is labeled v3. When a molecule is exhibiting one of the vibrational modes, it travels the path indicated by the arrow, stops, and then returns back to its starting position8.

It is possibly to express the three normal modes as a potential-energy function written in terms of bond stretching and angle bending as shown in the following equation:

$V = 12k1(R1-Re)2+ 12k1(R1-Re)2+ 12kb(\theta-\theta e)2$

where R1 and R2 are the first and second bond length of S-O, Re is the equilibrium S-O bond length, ? is the bond angle of O-S-O, and ? e is the equilibrium value. The constants ks and kb are for the stretching and bending respectively9. Though the derivations are difficult, it was found that the following equations are derived from eq. (1) and are used to calculate both constants:

4r2v32 = 1+2momssin2αk1mo

16r4v12v22 = 21+2momssin2k1moαkδl2

4r2v12+v22 = 1+2momscos2αk1mo+2mo1+2momssin2αkδl2

where v# is the wavenumber of that particular mode, 4? 3 is expressed as 5. 8918E-5 in order to obtain units of Nm-1, mo is the mass of oxygen, ms is the mass of sulfur, ? is 59. 75^(o), and k?/l2 is the same as the kb constant used in equation (6)10.

Diatomic molecules possess only one vibrational coordinate which is quantized. This means that only specific results will be obtained for the value of the vibration. The quantum mechanical harmonic oscillator upon first approximation gives the allowed levels of a diatomic molecule. Polyatomic molecules are similar. Each normal mode has quantized energy, and can be approximated by the harmonic oscillator model when at low energy levels. The frequencies associated with bending tend to be lower than the frequencies associated with stretching10.

It is possible to see normal modes via IR spectroscopy if they have a change in dipole in the molecule when it stretches or bends10. All of the normal modes in SO2 are IR active and therefore can all be seen in the IR spectrum at the fundamental frequency. It is possible to observe other weak bands in the spectrum which are a result of overtones. Overtones occur because anharmonicities. They usually happen at integer multiples of 2 or 3 of the fundamental frequencies and are caused by two modes being simultaneously excited10. These bands are located at frequencies which are approximately the sum or difference of the two modes which were excited and are weak10.

Method

About 1. 5g of drierite was weighed out and placed in the barrel of a syringe and the plunger was inserted almost entirely into the barrel. A 3 cm piece of rubber tubing was attached to the tip of the syringe. A 1. 5 g of sodium hydrogen sulfite was measured and placed in a vial cap that was small enough to fit into the syringe barrel. The filled vial cap was then into the syringe using a bent spatula to prevent the sodium hydrogen sulfite from spilling into the barrel. The plunger was pushed into the syringe as far as it would go. To ensure that none of the sodium hydrogen sulfite was spilled, the syringe was placed tip down in a beaker.

The next step was placing 15 mL of 6 M HCl into a small beaker. All of the acid was then drawn into the syringe containing the vial cap very carefully as to not let any of the acid mix with the sodium hydrogen sulfite. The plastic lid was then screwed onto the syringe. Once the cap was secure on the tip, the syringe was shaken so that the acid and the sodium hydrogen sulfite mixed. As SO2 gas was being produced, the plunger on the syringe was pulled out simultaneously. The high pressure of the gas in the syringe caused the cap on the tip to leak so it was necessary to apply pressure to the tip to prevent it from spitting acid out.

Once the reaction had stopped producing gas, the syringe was inverted so that the tip was pointing up and the liquid was at the bottom of the barrel. The cap was removed and the tip was connected to the other end of the rubber tubing attached to the syringe containing drierite. At this point the syringe containing drierite was above the syringe containing the SO2 gas. As the plunger in the bottom syringe was being pushed in, the plunger in the top syringe was being pulled out; making sure no liquid was pushed through the tubing and into the top syringe. The top syringe, now containing the SO2 gas, was capped and allowed to sit for five minutes in order for the drierite to dry the SO2 gas.

The excess HCl in the reaction syringe was expelled into a waste beaker. 15 mL of NaOH was placed in a beaker and then drawn up into the syringe in order to destroy any remaining SO2. The NaOH was then also expelled into the waste beaker. After the syringe containing the gas had sat for five minutes, the IR gas cell was placed in the hood. The syringe containing the SO2 was then attached connected to the gas cell using another piece of rubber tubing. Both stopcocks on the gas cell were opened and the gas was pushed into the cell. Both stopcocks were then immediately closed to prevent any of the SO2 from leaking out. A spectrum in the range of 700-2500 cm-1 was obtained using an FTIR spectrophotometer. In order to get a good spectrum from the mid IR range, the cell was undiluted. However, to obtain a good spectrum in the far IR range, it was necessary to dilute the gas cell.

Once the spectrum had been obtained, the gas cell was placed inside a fume hood. Both stopcocks were opened up and a syringe was used to flush air through the gas cell. The gas cell was then placed in a vacuum sealed dessicator with the stopcocks open in order to dry out any moisture that may have entered the cell during the experiment.

Results

The IR spectra of SO2 can be seen in Figure 5. By looking at what wavenumbers the peaks appeared at, it could be concluded which peak corresponded to each vibrational mode of SO2. The bending of a molecule happens at lower wavenumbers, so it was concluded that graph in the top right corner corresponds to the ? 2 vibration. It was known from literature that the stretches occur somewhere between 1000 and 1500 cm-1 so the graph in the bottom right must correspond to the overtones of SO2’s ? 3 and ? 1 modes.

It is known that asymmetric stretches always correspond to higher wavenumbers. So it was concluded that the next two peaks on the spectrum were ? 1 and ? 3 respectively. The actual experimental wavelengths of each mode can be seen it Table 1. There are two overtones present, one from the ? 1 mode and another from the ? 3 mode. The lower frequency overtone corresponds to the lower-frequency mode. Thus the lowest overtone is that of ? 1 while the second seen overtone comes from the ? 2 mode.

Using the experimental wavenumbers for each mode, both constants could be found using eq. (7) first to solve for k1. This values was calculated to be 1000. 858 Nm-1. The litereature value is 1033 Nm-1 and the percent error in the experimental value was 3. 112% The calculated value of k1 was then used in eq. (8) to find the k?/l3 constant. The second constant was calculated to be 78. 60 Nm-1. Literature value for this constant is 81 Nm-1 and the percent error in the experimental calculation was 2. 963%. To evaluate the effectiveness of this method for finding the constants, both sides of eq. (9) were solved for. The left side equaled 93. 77 Nm-1 while the right side equaled 95. 54 Nm-1. The percent difference between these two values is 1. 85%.

In order to determine the harmonicity of each of the modes of vibration, the ve and vexe values were calculated. This was done by graphing ? G/v versus (v + 1) in Microsoft Excel. The ? G corresponds to the wavenumber of the overtone seen on the IR spectrum. ? G was then divided by v. The overtones corresponded to v= 2 while the normal mode bands corresponded to ?= 1. Graphs for both the ? 1 mode and ? 2 mode can be seen in Figure 6.

Excel was then used to fit a trend line and produce a y = mx + b equation for the data. The slope of the equation was vexe and the intercept was ve. To determine the anharmonicity of the two modes, it was necessary to solve for xe. This was done using eq (4). The calculated values for xe in the ? 1 mode was 1. 0612 and for the ? 3 mode was 0. 07891. This means that the ? 1 mode is more anharmonic than the ? 3 mode.

Conclusion

For this lab, SO2 was prepared and then studied via FTIR spectroscopy. The three modes of SO2 were identified on the IR spectra obtained. It was determined that the lowest energy of bending correlated to the lowest frequency peak. The second highest frequency peak was determined to be ? 1 since the symmetric stretch is lower in energy than the asymmetric stretch

(? 3) which is the third highest frequency peak. The wavelengths determined from the IR spectra were used to calculate the constants k1 and k?/l3. It was determined from the numbers crunched from eq. (6) that the used method of determining the constants was an accurate method. Also, the anharmonicity of the modes ? 1 and ? 2 were calculated and compared. The graph of ? G/vversus (v + 1) produce an equation of y = mx + b which provided the values of xeve and ve. These values were then used to find xe, which described the anharmonicity of each mode. The ? 1 mode was found to be more anharmonic due to its greater xe value while the ? 3 was found to be more harmonic.

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