

Infrared Spectroscopy of SO₂

The infrared spectrum extends from about 1 μm to about 1000 μm . However, it is most common refer to infrared frequencies in terms of wavenumbers. The spectrum encompasses the region from 12,800 cm^{-1} to 10 cm^{-1} , although most work has been done in the region from 4000 cm^{-1} to 400 cm^{-1} . Infrared frequencies are comparable in magnitude to that of stretches and bends in molecules. Allowing molecules to interact with IR radiation often causes them to become vibrationally excited. The loss of energy from the radiation changes the transmittance of the applied radiation, which becomes an absorption band in the IR spectrum.

IR spectroscopy can be used as a fingerprint for molecules. Every molecule has a different spectrum. In Figure 1, the spectra for butane and isobutene are shown; both have the structural formula C₄H₁₀. They show distinctly different spectra. Due to much research in the area, it is possible to obtain an IR spectrum of an unknown compound and compare it to a database to definitively identify the compound. It is also possible to classify a compound by its functional group by quick inspection of a spectrum. For example, an intense peak at approximately 1700 cm^{-1} suggests there is a C=O in the compound, -OH stretches have characteristic peaks which occur at approximately 3200 cm^{-1} , and saturated C-H stretches characteristically occur around 2900 cm^{-1} .

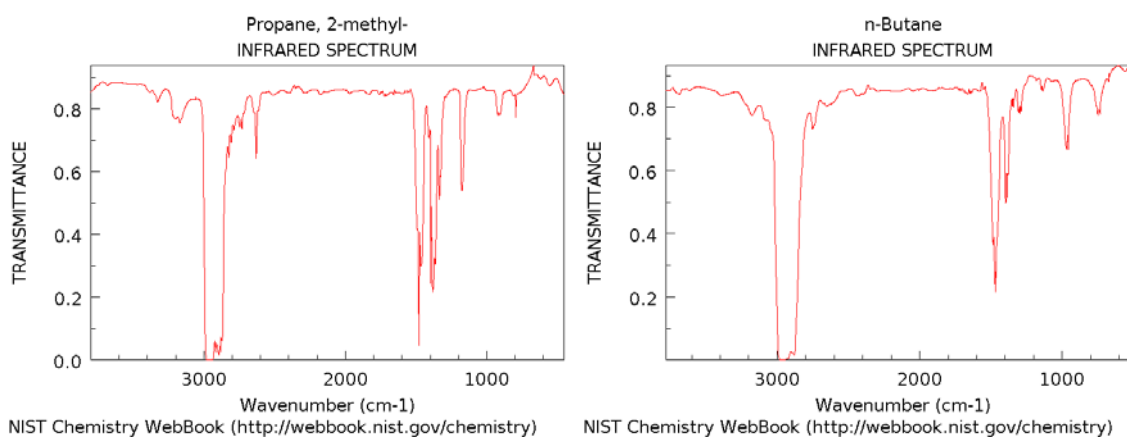


Figure 1. Infrared spectra

Infrared spectra show us characteristics of vibrational energy levels. Within each vibrational energy level there are rotational energy levels. That is, upon excitation, transitions typically occur from a particular rotational level within a vibrational level (J'' ,

v'' respectively) to a different rotational level in an excited vibrational state (J' and v' respectively.) This rotational information can be examined if the spectrometer being used is high resolution. For the purposes of this experiment, it will not be necessary to worry about rotational information. The energy of these vibrational transitions are given by

$$E = (v + \frac{1}{2})$$

and transitions occur at

$$\Delta E = \hbar \sqrt{\frac{k}{\mu}}$$

where the selection rule for the transition is $\Delta v = \pm 1$.

The subject of this experiment is to study the vibrations of SO_2 , a nonlinear, symmetric molecule. For this type of molecule, containing N atoms, there are $3N-6$ vibrational degrees of freedom. This means that an SO_2 molecule has 3 different normal modes. They are shown in Figure 2. All possible vibrations of the molecule are made up of linear combinations of these normal modes.

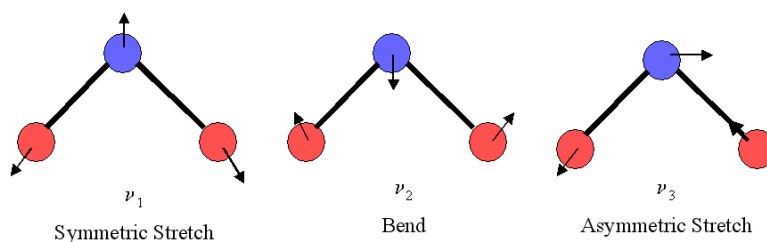


Figure 2. Normal modes of SO_2 .

However, the only way it is possible to see these normal modes in the spectrum is if they are IR active. In order to be IR active, there must be a change in dipole in the molecule when it stretches or bends. For SO_2 , all of the normal modes are IR active. These modes will appear in an IR spectrum at the frequency of the vibration, also known as the fundamental frequency. These frequencies should lead to the most intense bands in the spectrum. In addition to the fundamental vibration frequencies, other weak bands may be observed in the spectrum. These bands are a result of overtones or combination bands that can arise from anharmonicities. Overtones are bands that occur at integer multiples, usually 2 or 3, of the fundamental frequencies. Combination bands occur when two modes are excited simultaneously. These bands are seen at a frequency that is

approximately the sum or difference of the two excited modes. Any weak bands that are seen in the SO₂ spectrum can be taken as being a result of these anharmonicities.

Herzberg described the valence force model as a way to analyze the vibrations and determine the force constants of the stretches and bends. In this model, it is assumed that there is large restoring force along the chemical bond when the equilibrium position of this molecule is disturbed. This same type of restoring forces is assumed to affect any perturbations in the angle between two adjacent bonds. It is possible to derive the following formulas to describe the force constants of the SO₂ molecule, using the potential energy of the molecule and that classical harmonic oscillator mechanics apply. The derivation is long and complicated, so just the results will be shown here.

$$4\pi^2\nu_3^2 = \left(1 + \frac{2m_o}{m_s} \sin^2 \alpha\right) \frac{k_1}{m_o} \quad (1)$$

$$16\pi^4\nu_1^2\nu_2^2 = 2\left(1 + \frac{2m_o}{m_s}\right) \frac{k_1}{m_o^2} \frac{k_\delta}{l^2} \quad (2)$$

$$4\pi^2(\nu_1^2 + \nu_2^2) = \left(1 + \frac{2m_o}{m_s} \cos^2 \alpha\right) \frac{k_1}{m_o} + \frac{2}{m_o} \left(1 + \frac{2m_o}{m_s} \sin^2 \alpha\right) \frac{k_\delta}{l^2} \quad (3)$$

Information from the vibrational spectrum can also be used to calculate the heat capacity at constant volume of the substance. The heat capacity can be expressed as the sum of the translational, vibrational, and rotational contributions to the heat capacity. As temperatures of room temperature and above, the translational and rotational contributions to the heat capacity are constant. Each is equivalent to 3/2 R. However, the vibrational contribution varies considerably with temperature. This vibrational contribution can be calculated using the vibrational partition function, q_{vib} .

$$C_v(\text{vib}) = R \frac{\delta}{\delta T} \left(T^2 \frac{\delta \ln q_{\text{vib}}}{\delta T} \right) \quad (4)$$

Applying the harmonic oscillator approximation, the vibrational partition function can be written as

$$q_{\text{vib}} = \frac{e^{-h\nu_i/k_bT}}{1 - e^{-h\nu_i/k_bT}} \quad (5)$$

Combining equations 4 and 5

$$C_v(\text{vib}) = R \sum_i \frac{\left(\frac{h\nu_i}{k_b T} \right) e^{-h\nu_i/k_b T}}{\left(1 - e^{-h\nu_i/k_b T} \right)^2} \quad (6)$$

where the summation is over all normal modes.

CALCULATIONS

- Determine the fundamental frequencies of SO₂. Assign the normal modes to their corresponding bands. Also, assign any overtones or combination bands present.
- Calculate k_1 and k_8/l^2 in Nm⁻¹. To do this, express the frequencies in wavenumbers, the mass of sulfur and oxygen in amu, and replace $4\pi^2$ by $4\pi^2c^2/10^3N_0$. For SO₂, $2\alpha = 119.5^\circ$ and $l = 1.432 \text{ \AA}$.
- Check the effectiveness of the valence force model by solving for both sides of equation 3.
- Calculated C_v (vib) at 298 K and 500 K.
- Calculate C_v at 298 K and 500 K.
- No error propagation is necessary.
- Report percent errors.

DISCUSSION

- Make sure to include a discussion of the harmonic oscillator approximations and the valence force model.

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