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## EXPERIMENT 35

### Infrared Spectroscopy: Vibrational Spectrum of SO<sub>2</sub>

The infrared region of the spectrum extends from the long-wavelength end of the visible region at 1  $\mu\text{m}$  out to the microwave region at about 1000  $\mu\text{m}$ . It is common practice to specify infrared frequencies in wavenumber units:  $\tilde{\nu}(\text{cm}^{-1}) = 1/\lambda = \nu/c$ , where  $c$  is the speed of light in  $\text{cm s}^{-1}$  units. Thus this region extends from 10 000  $\text{cm}^{-1}$  down to 10  $\text{cm}^{-1}$ . Although considerable work is now being done in the far-infrared region below 400  $\text{cm}^{-1}$ , the spectral range from 4000 to 400  $\text{cm}^{-1}$  has received the greatest attention because the vibrational frequencies of most molecules lie in this region.

## THEORY

Almost all infrared work makes use of absorption techniques in which radiation from a source emitting all infrared frequencies is passed through a sample of the material to be studied. When the frequency of this radiation is the same as a vibrational frequency of the molecule, the molecule may be vibrationally excited; this results in loss of energy from the radiation and gives rise to an absorption band. The spectrum of a molecule generally consists of several such bands arising from different vibrational motions of the molecule.

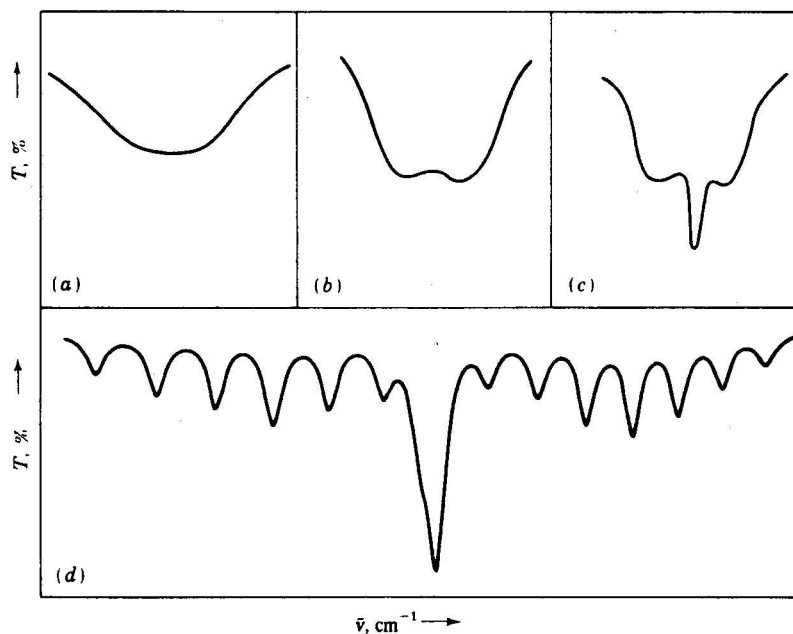
Associated with each vibrational energy level there are also closely spaced rotational energy levels. In general, transitions occur from a particular rotational level (quantum number  $J''$ ) in a given vibrational state (quantum number  $v''$ ) to a different rotational level (quantum number  $J'$ ) in an excited vibrational state (quantum number  $v'$ ). The appearance of this rotational fine structure will depend on the resolution of the spectrometer used, as shown schematically in Fig. 1. Vibrational-rotational spectra are discussed in Exps. 37 and 38 for the case of linear molecules and will not be considered here.

In this experiment we shall be concerned with the infrared bands of  $\text{SO}_2$  gas at medium resolution, i.e., with only the vibrational spectrum. Electron diffraction studies show that  $\text{SO}_2$  is a symmetric, nonlinear molecule.<sup>1</sup> For a nonlinear molecule containing  $N$  atoms there are  $3N - 6$  vibrational degrees of freedom. Thus,  $\text{SO}_2$  has three basic patterns of vibration called "normal modes." These are shown in Fig. 2. All vibrations of the molecule may be expressed as linear combinations of these normal modes.

The frequencies of the normal modes of vibration are called *fundamentals*. For  $\text{SO}_2$  all three fundamentals are infrared-active; they will correspond to the three most intense bands in the spectrum. The fundamentals ( $\nu_1, \nu_2, \nu_3$ ) may be assigned by analogy with the spectra of other molecules: the bending frequency  $\nu_2$  should be that of the lowest frequency band, and the antisymmetric stretch  $\nu_3$  should be that of the highest frequency band.

The structure of  $\text{SO}_2$  is confirmed by the presence of all three fundamentals in the infrared spectrum. When this is true, the molecule cannot have a center of symmetry<sup>1</sup> as in  $\text{O}-\text{S}-\text{O}$ . Linear unsymmetric structures, such as  $\text{O}-\text{O}-\text{S}$  or  $\text{O}-\text{S}-\text{O}$ , can be

**FIGURE 1**  
Schematic infrared band contours at (a) low, (b) and (c) medium, and (d) high resolution. For the band shown in (b) there is no  $Q$  branch ( $\Delta J = 0$  transitions are forbidden); the bands shown in (c) and (d) have  $Q$  branches.



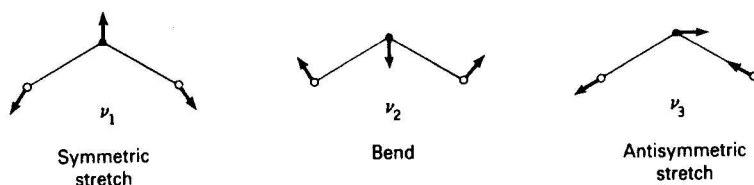


FIGURE 2

Normal modes of vibration for SO<sub>2</sub>. The lengths of the arrows which indicate displacements from the equilibrium configuration have been exaggerated for clarity.

ruled out by the shape of the rotational band envelopes in the infrared spectrum; discussion of this topic is beyond the scope of this book.

In addition to the fundamentals, other much weaker bands may be observed in the spectrum at high pressure. Such weak bands are either overtones ( $2\nu_i$ ,  $3\nu_i$ , . . .) or combination bands ( $\nu_i \pm \nu_j$ ,  $2\nu_i \pm \nu_j$ , . . .) that arise from the fact that small anharmonicities tend to couple the normal vibrations. On the basis of intensity, the transitions that involve binary overtones ( $2\nu_i$ ) and binary combinations ( $\nu_i \pm \nu_j$ ) are the most likely to be observed. Thus, any weak bands observed for SO<sub>2</sub> may be assigned as overtones or combinations of the strong fundamentals. Any such assignment should take into account rules that determine whether a given combination will be active in the infrared.<sup>1</sup> In the case of SO<sub>2</sub>, none of the combinations is forbidden by symmetry. This is not generally true for molecules of higher symmetry; see the discussion in Exps. 36 and 38.

**Valence-Force Model.** The normal modes of vibration can be expressed in terms of the atomic masses ( $m_S$  and  $m_O$ ), the O—S—O bond angle ( $2\alpha$ ), and several force constants that define the potential energy of the molecule. These force constants are analogous to the Hooke's-law constant for a spring. If a force model is chosen involving fewer force constants than the number of normal modes, the force constants are overdetermined and a check on the validity of the model is then possible. The valence-force model assumes that there is a large restoring force along the line of a chemical bond when the distance between the two atoms at the ends of this bond is changed from its equilibrium value. It also assumes a restoring force for any change in angle between two adjacent bonds. Adopting the notation used by Herzberg,<sup>2</sup> we can write the potential energy of SO<sub>2</sub> as

$$U = \frac{1}{2}[k_1(r_1^2 + r_2^2) + k_\delta \delta^2]$$

where  $r_1$  and  $r_2$  are changes in the S—O distances (whose equilibrium value is denoted by  $l$ ), and  $\delta$  is the change in the bond angle  $2\alpha$ . The quantities  $k_1$  and  $k_\delta/l^2$  are force constants for stretching and bending motions, respectively. Using the classical mechanics of harmonic oscillators, one can obtain<sup>2</sup> for SO<sub>2</sub>

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

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

$$16\pi^4\nu_1^2\nu_2^2 = 2 \left(1 + \frac{2m_O}{m_S}\right) \frac{k_1}{m_O^2} \frac{k_\delta}{l^2} \quad (3)$$

If one expresses the frequencies in wavenumber units  $\tilde{\nu}$  ( $\text{cm}^{-1}$ ) and uses appropriate isotopic masses (in amu)  $m_O = 15.995$  and  $m_S = 31.972$ ,  $4\pi^2$  should be replaced by  $4\pi^2 c^2/10^3 N_0 = 5.8918 \times 10^{-5}$  to obtain  $k_1$  and  $k_\delta/l^2$  in units of  $\text{N m}^{-1}$ . For SO<sub>2</sub>,  $2\alpha = 119.5^\circ$  and  $l = 1.432 \text{ \AA} = 0.1432 \text{ nm}$ .<sup>3</sup>

**Vibrational Partition Function.**<sup>4</sup> The thermodynamic quantities for an ideal gas can usually be expressed as a sum of translational, rotational, and vibrational contributions (see Exp. 3). We shall consider here the heat capacity at constant volume. At room temperature and above, the translational and rotational contributions to  $C_v$  are constants that are independent of temperature. For  $\text{SO}_2$  (a nonlinear polyatomic molecule), the molar quantities are

$$\begin{aligned}\tilde{C}_v(\text{trans}) &= \frac{3}{2}R \\ \tilde{C}_v(\text{rot}) &= \frac{3}{2}R\end{aligned}\quad (4)$$

The vibrational contribution to  $\tilde{C}_v$  varies with temperature and can be calculated from the vibrational partition function  $q_{\text{vib}}$  using

$$\tilde{C}_v(\text{vib}) = R \frac{\partial}{\partial T} \left( T^2 \frac{\partial \ln q_{\text{vib}}}{\partial T} \right) \quad (5)$$

The partition function  $q_{\text{vib}}$  is well approximated by

$$q_{\text{vib}} = \prod_{i=1}^{3N-6} q_i^{\text{HO}} \quad (6)$$

where  $q_i^{\text{HO}}$  is the harmonic-oscillator partition function for the  $i$ th normal mode of frequency  $\nu_i$ . Since the energy levels of a harmonic oscillator are given by  $(v + \frac{1}{2})h\nu$ , one obtains<sup>4</sup>

$$q_i^{\text{HO}} = \sum_{v=0}^{\infty} \exp \left[ \frac{-(v + \frac{1}{2})h\nu_i}{kT} \right] = \frac{e^{-h\nu_i/2kT}}{1 - e^{-h\nu_i/kT}} \quad (7)$$

Combining Eqs. (5)–(7), we find

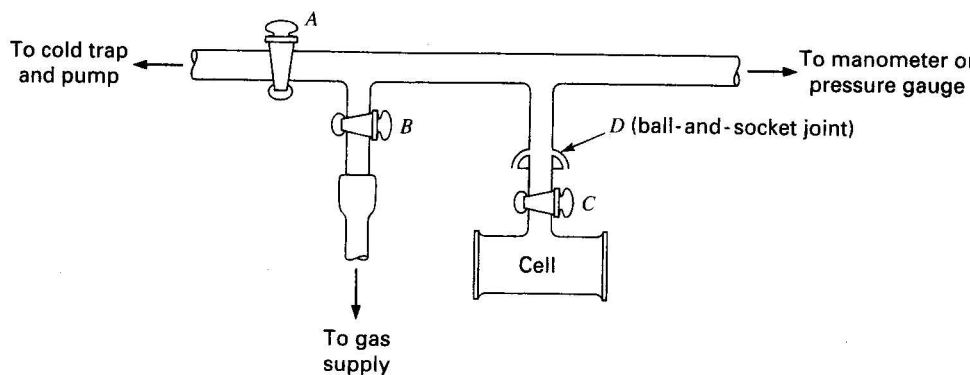
$$\tilde{C}_v(\text{vib}) = R \sum_i \frac{u_i^2 e^{-u_i}}{(1 - e^{-u_i})^2} \quad (8)$$

where  $u_i = h\nu_i/kT = hc\tilde{\nu}_i/kT = 1.4388\tilde{\nu}_i/T$  and the summation is over all of the normal modes.

## EXPERIMENTAL

There are many different infrared spectrometers in current use, almost all of which are suitable for this experiment. A general description of the characteristics of infrared grating and Fourier-transform infrared (FTIR) spectrometers is given in Chapter XX. Specific instructions should also be available for the operation of the instrument to be used in the laboratory. Before beginning the experiment, the student should review the pertinent material. **Use the spectrometer carefully;** if in doubt, ask the instructor.

The  $\text{SO}_2$  gas cell is constructed from a short (usually 10-cm) length of large-diameter (4 to 5 cm) Pyrex tubing with a vacuum stopcock attached. Infrared-transparent windows are clamped against O-rings at the ends of the cell or are sealed on the ends with Glyptal resin. Since  $\text{SO}_2$  spectra should be recorded down to  $400 \text{ cm}^{-1}$ , KBr windows are needed. For studies concentrating on the region  $4000$  to  $700 \text{ cm}^{-1}$ , NaCl windows will suffice. Both types of salt windows become “foggy” on prolonged exposure to a moist atmosphere and should be protected (e.g., stored in a desiccator) when not in use.



**FIGURE 3**  
Gas-handling system for filling infrared cell.

**Filling the Cell and Recording the Spectra.** An arrangement for filling the cell is given in Fig. 3. Attach the cell at *D*. With stopcock *C* open and *B* closed, open stopcock *A* and pump out the system. Make sure that the needle valve of the SO<sub>2</sub> cylinder is closed. Then open *B* and continue pumping.

Close *A* and slowly open the valve on the SO<sub>2</sub> cylinder. Fill the system to about 900 Torr (1.2 atm) with SO<sub>2</sub>. Close the valve on the cylinder and then close *B* and *C*. Remove the cell from the vacuum line and take a spectrum.

Return the cell to the line. With *B* closed and *C* closed, open *A* and pump out the line for a few minutes. Now close *A* and open *C*. Open *A* very slowly and carefully to reduce the pressure to about 300 Torr. Close *A* and *C*, remove the cell, and record the spectrum. Repeat this process and record the spectrum at pressures of 100, 20, and 5 Torr. Several spectra may be recorded on a single chart, using different colored inks to distinguish them. If it is not possible to observe  $\nu_2$ , the lowest frequency fundamental, owing to equipment limitations, a chart recording in the KBr region should be made available for reference.

## CALCULATIONS AND DISCUSSION

Assign the fundamental bands of SO<sub>2</sub> and report their frequencies. Then assign any other bands, comparing the observed frequencies with those calculated from combinations of the fundamental values  $\tilde{\nu}_1$ ,  $\tilde{\nu}_2$ , and  $\tilde{\nu}_3$ . If the  $\tilde{\nu}_2$  fundamental frequency was not measured directly, estimate it from a combination band. Is there any indication of rotational structure observed?

Calculate  $k_1$  and  $k_8/l^2$  from Eqs. (1) and (3) using your values of  $\tilde{\nu}_1$ ,  $\tilde{\nu}_2$ , and  $\tilde{\nu}_3$ . Check the valence-force model by calculating both sides of Eq. (2) and comparing them.

Using your values of  $\tilde{\nu}_1$ ,  $\tilde{\nu}_2$ , and  $\tilde{\nu}_3$ , calculate  $\tilde{C}_v(\text{vib})$  at 298 K and at 500 K from Eq. (8). Compare the spectroscopic value  $\tilde{C}_v = 3R + \tilde{C}_v(\text{vib})$  with the experimental  $\tilde{C}_v$  value obtained from directly measured values<sup>5</sup> of  $\tilde{C}_p$  and the expression  $\tilde{C}_v = \tilde{C}_p - R$ ;  $\tilde{C}_v = 30.5 \text{ J K}^{-1} \text{ mol}^{-1}$  at 298 K and  $37.7 \text{ J K}^{-1} \text{ mol}^{-1}$  at 500 K.

**Theoretical Calculations.** It would be instructive to calculate the vibrational frequencies and infrared intensities of SO<sub>2</sub> using an *ab initio* program such as Gaussian. Examples of such calculations at various levels are described in Foresman and Frisch<sup>6</sup> and in Hehre et al.<sup>7</sup> It should be noted that the calculated frequencies correspond to *harmonic* values that the molecule would have for motion about the equilibrium position. For SO<sub>2</sub>, the harmonic frequencies, derived by correcting the experimental values for anharmonicity, are 1167, 526, and 1381 cm<sup>-1</sup> for modes 1, 2, and 3, respectively.<sup>7</sup> Theoretical values

for these from *ab initio* calculations are generally high by about 10 percent, but agreement with experiment improves as the basis set and level of calculation increases. The vibrational frequencies can also be calculated using semiempirical methods such as PM3 in Gaussian and in programs such as HyperChem, which also provides an animated display of the form of the normal modes.

### SAFETY ISSUES

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The cylinder or lecture bottle of SO<sub>2</sub> gas must be strapped or chained securely to the laboratory bench. Work on a vacuum system requires preliminary review of procedures and careful execution in order to avoid damage to the apparatus and possible injury from broken glass (see Appendix C). Safety glasses must be worn.

### APPARATUS

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Infrared spectrometer or Fourier-transform (FTIR) instrument; gas cell with KBr windows; vacuum line for filling cell; cylinder of SO<sub>2</sub> gas with needle valve.

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