

H. H. Willard, L. L. Merritt, Jr., J. A. Dean, and F. A. Settle: "Instrumental Methods of Analysis," 6th ed., Van Nostrand-Reinhold, New York (1981).

EXPERIMENT 36 INFRARED SPECTROSCOPY: VIBRATIONAL SPECTRUM OF SO₂

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: $\bar{\nu}(\text{cm}^{-1}) = 1/\lambda = \nu/c$, where c is the speed of light in 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 ν'') to a different rotational level (quantum number J') in an excited vibrational state (quantum number ν'). 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. 38 and 39 for the case of linear molecules and will not be considered here.

In this experiment we shall be concerned with the infrared bands of SO₂ gas at medium resolution, i.e., with only the vibrational spectrum. Electron diffraction studies show that SO₂ is a symmetrical, nonlinear molecule.¹ For a nonlinear molecule containing N atoms there are $3N - 6$ vibrational degrees of freedom. Thus, SO₂ 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 SO₂ all three fundamentals are infrared-active; they will

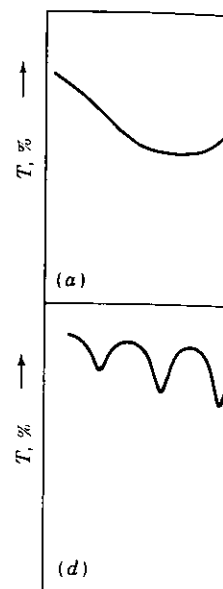


FIGURE 1
Schematic infrared band structure. (a) shows a single broad absorption band shown in (b) then (c) and (d) have Q branch

correspond to the fundamentals (ν_1, ν_2, ν_3) may be the bending frequency antisymmetric stretch

The structure of the fundamentals in the spectrum have a center of symmetry such as O—O—S rotational band ends beyond the scope of

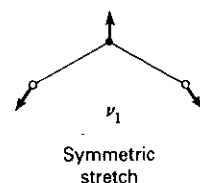
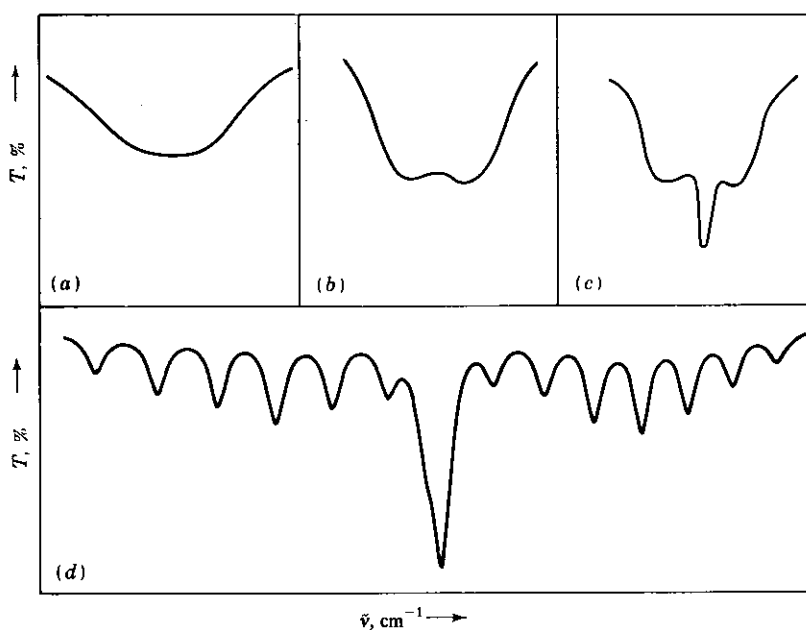


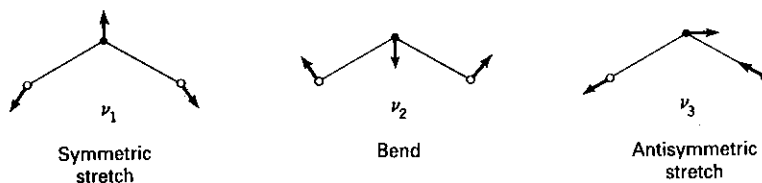
FIGURE 2
Normal modes of vibration of the equilibrium configuration

**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.

correspond to the three most intense bands in the spectrum. The fundamentals (ν_1 , ν_2 , ν_3) may be assigned by analogy with the spectra of other molecules: the bending frequency ν_2 should be that of the lowest frequency band, and the antisymmetric stretch ν_3 should be that of the highest frequency band.

The structure of SO₂ is confirmed by the presence of all three fundamentals in the infrared spectrum. When this is true, the molecule cannot have a center of symmetry¹ as in O—S—O. Linear unsymmetric structures, such as O—O—S or O—S—O, can be 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.

**FIGURE 2**

Normal modes of vibration for SO₂. The lengths of the arrows which indicate displacements from the equilibrium configuration have been exaggerated for clarity.

In addition to the fundamentals, other much weaker bands may be observed in the spectrum at high pressure. Such weak bands are either overtones ($2\nu_i, 3\nu_i, \dots$) or combination bands ($\nu_i \pm \nu_j, 2\nu_i \pm \nu_j, \dots$) 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_2 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.¹ In the case of SO_2 , none of the combinations are forbidden by symmetry. This is not generally true for molecules of higher symmetry; see the discussion in Exps. 37 and 39.

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 (2α), 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,² we can write the potential energy of SO_2 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 δ is the change in the bond angle 2α . The quantities k_1 and k_δ/l^2 are force constants for stretching and bending motions, respectively. Using the classical mechanics of harmonic oscillators, one can obtain² for SO_2

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

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

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

If one expresses the frequencies in wavenumber units $\tilde{\nu}(\text{cm}^{-1})$ and uses $m_O = 16$ and $m_S = 32$, $4\pi^2$ should be replaced by $4\pi^2 c^2/10^3 N_0 = 5.892 \times 10^{-5}$ to obtain k_1 and k_δ/l^2 in units of N m^{-1} . For SO_2 , $2\alpha = 119.5^\circ$ and $l = 1.432 \text{ \AA} = 0.1432 \text{ nm}$.³

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Combining Eqs.

where $u_i = hv_i/k$
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EXPERIMENT

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Vibrational partition function⁴. 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 independent of temperature. For SO₂ (a nonlinear polyatomic molecule), the molar quantities are

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

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

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

The partition function q_{vib} is well approximated by

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

where q_i^{HO} is the harmonic-oscillator partition function for the i th normal mode of frequency ν_i . Since the energy levels of a harmonic oscillator are given by $(v + \frac{1}{2})h\nu$, one obtains⁴

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

Combining Eqs. (5)–(7), we find

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

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 XVIII. 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 SO₂ 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

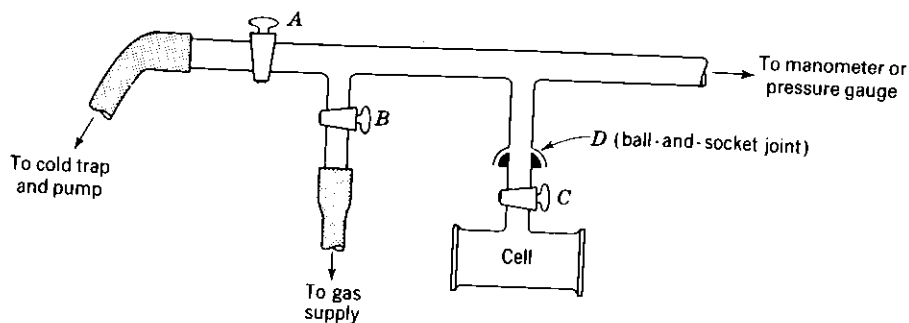


FIGURE 3
Gas-handling system for filling infrared cell.

cell or are sealed on the ends with Glyptal resin. Since SO_2 spectra should be recorded down to 400 cm^{-1} , KBr windows are needed. For studies concentrating on the region 4000 to 700 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.

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_2 cylinder is closed. Then open *B* and continue pumping.

Close *A* and slowly open the valve on the SO_2 cylinder. Fill the system to about 900 Torr (1.2 atm) with SO_2 . 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 ν_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_2 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_s/l^2 from Eqs. (1) and (3) using your values of $\tilde{\nu}_1$, $\tilde{\nu}_2$,

and $\tilde{\nu}_3$. Compare the results with those obtained by comparing the observed frequencies with those calculated using 500 K from the experimental data. Express the results in $\text{J K}^{-1}\text{ m}^{-1}$.

APPARATUS

Infrared spectrometer with KBr window and vacuum valve.

REFERENCES

1. G. Herzberg, *Polyatomic Molecules*, pp. 168.
2. *Ibid.*, pp. 168.
3. G. Herzberg, *Electronic Structure of Molecules*, pp. 168.
4. P. W. Atkins and G. M. McQuarrie, *Quantum Theory of Molecular Structure*, ed., p. 419ff.
5. G. N. Lewis and R. S. Stein, *J. Chem. Phys.*, 1, 419ff.

GENERAL

G. Herzberg, *op. cit.*
J. I. Steinfeld, "Molecular Spectroscopy," p. 419ff.

RAN

In Exp. 36, the student is measuring the frequencies of the vibrational bands between vibrational levels caused by inelastic scattering (frequency) sh of the vibrational frequency from scattered light and the effect of the monochromator.

and $\bar{\nu}_3$. Check the valence-force model by calculating both sides of Eq. (2) and comparing them.

Using your values of $\bar{\nu}_1$, $\bar{\nu}_2$, and $\bar{\nu}_3$, calculate $\bar{C}_v(\text{vib})$ at 298 K and at 500 K from Eq. (8). Compare the spectroscopic value $\bar{C}_v = 3R + \bar{C}_v(\text{vib})$ with the experimental \bar{C}_v value obtained from directly measured values⁵ of \bar{C}_p and the expression $\bar{C}_v = \bar{C}_p - R$: $\bar{C}_v = 30.5 \text{ J K}^{-1} \text{ mol}^{-1}$ at 298 K and $37.7 \text{ J K}^{-1} \text{ mol}^{-1}$ at 500 K.

APPARATUS

Infrared spectrometer or Fourier transform (FTIR) instrument; gas cell with KBr windows; vacuum line for filling cell; cylinder of SO_2 gas with needle valve.

REFERENCES

1. G. Herzberg, "Molecular Spectra and Molecular Structure II. Infrared and Raman Spectra of Polyatomic Molecules," pp. 251-269, 285, Van Nostrand, Princeton, N.J. (1945).
2. *Ibid.*, pp. 168-172.
3. G. Herzberg, "Molecular Spectra and Molecular Structure III. Electronic Spectra and Electronic Structure of Polyatomic Molecules," p. 605, Van Nostrand, Princeton, N.J. (1966).
4. P. W. Atkins, "Physical Chemistry," 3d ed., chap. 22, Freeman, New York (1986); D. A. McQuarrie, "Statistical Thermodynamics," Harper & Row, New York (1976).
5. G. N. Lewis and M. Randall (revised by K. S. Pitzer and L. Brewer), "Thermodynamics," 2d ed., p. 419ff., McGraw-Hill, New York (1961).

GENERAL READING

- G. Herzberg, *op. cit.*, vol. II, chaps. II and III.
 J. I. Steinfeld, "Molecules and Radiation," 2d ed., chap. 8, MIT Press, Cambridge, Mass. (1985).

EXPERIMENT 37 RAMAN SPECTROSCOPY: VIBRATIONAL SPECTRUM OF CCl_4

In Exp. 36, the vibrational frequencies of a molecule were determined by measuring the direct absorption of infrared radiation due to transitions between vibrational energy levels. Such changes in molecular state can also be caused by inelastic scattering of higher-energy visible photons. The energy (or frequency) *shifts* in the scattered radiation then give a direct measure of the vibrational frequencies of the molecule. Although the intensity of this scattered light is quite low, Raman was able to observe such scattering in 1928 and the effect was later named after him. With the advent of extremely intense monochromatic laser sources, Raman spectroscopy has become much faster