

ABSOLUTE INTENSITY OF THE BENDING MODE
OF CHLOROFORM IN n-HEXANE

by

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ADVANCE BOND

Ch. L. Brown Paper

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ABSOLUTE INTENSITY OF THE BENDING MODE OF CHLOROFORM IN n-HEXANE

INTRODUCTION

William Herschel is credited with the discovery of Infrared radiation in 1800. The identity of this "heat" radiation with "light" radiation was established by about 1840.

That this radiation could be an important tool in chemical researches was indicated by the work of W. W. Coblentz during the period 1900-1910 when he obtained the absorption spectra of many organic liquids as well as the absorption, emission, and reflection spectra of numerous inorganic materials. Work in infrared spectroscopy received an impetus with the discovery in 1913 of rotational absorption spectra, and the development of the concept of the vibrating molecule in 1916. The importance and versatility of infrared absorption in the fundamental calculations of molecular structure, chemical bonds, and the thermodynamic constants is, at present, well-established and of growing importance.

Electromagnetic Radiation and the Infrared Spectrum

Electromagnetic radiation may be regarded simply as a traveling field of electric force whose direction oscillates with the characteristic frequency. It is

known to exist throughout a wave-length range falling in between 10^{+6} to 10^{-12} cm. There are, however, no significant qualitative differences between infrared radiation and other kinds of radiations, such as x-rays, visible light and radio waves. The different radiations are characterized by the different methods used for the production and the measurement of these radiations, and their interaction with matter. For example, the irradiation of matter with radiation of wavelength shorter than 10^{-5} cm results in either the dissociation of the molecule or the scattering of the radiation quantum; but in molecular spectroscopy we are more interested in the simple absorption, and emission of radiation.

Units of Measurement

A position in the infrared range of the electromagnetic spectrum is described usually by two interchangeable units. These are a wavelength (λ), the micron (μ) $1\mu = 10^{-4}$ cm = 10^4 A, and a frequency, or wave-number (ν), waves per cm, which is written as cm^{-1} . These two are interrelated by a simple reciprocal relationship, namely, $\nu (\text{cm}^{-1}) = 1/\lambda (\text{cm}) = 10^4/\lambda (\mu)$. The reciprocal centimeter unit, that is, the wave-number, is thus defined as the reciprocal of λ_{vac} in cm. Hence ν (frequency) = c (velocity of light) $\times \lambda$. As the

wave-number is proportional to the frequency it has the advantage that it is proportional to the energy of the radiation quanta and independent of the medium. One reciprocal centimeter is thus equivalent to 1.9863×10^{-16} erg per molecule or 2.86 calories per mole. This as well as the fact that the wave-number scale permits both infrared and Raman spectra to be measured in the same units facilitating the inter-comparison of Raman and infrared data present a cogent argument in favour of the wave-number scale (14, vol. IX, p. 261-263).

The primary region of fundamental infrared interest is the range $\nu = 4000 - 200 \text{ cm}^{-1}$ or $\lambda = 2.5 - 50 \mu$. The range between this and visible, $0.7 - 2.5 \mu$, is called the overtone or the near infrared, while the region beyond 50μ is spoken of as the far infrared.

Significance of Infrared Absorption

The versatility of infrared absorption spectrophotometry in the determination of molecular structure becomes obvious when we compare this method with some of the other techniques available for that purpose. While the electron-diffraction technique is limited to materials in the gaseous state, and work with x-ray diffraction is confined to substances in the solid state, infrared absorption method can be applied equally well to

absorbing molecules whether in the solid, liquid, or the gaseous state. This method, however, cannot give us any direct information such as the bond distances on the structure of the molecule involved; the information provided are about the symmetry of the molecule, and the nature of the various chemical bonds in it. Nowadays the determination of the absolute intensities of molecules in the solid, liquid, or the gaseous state is giving some knowledge on the environment of the molecule, or the molecular groups under consideration. The absorption spectra of substances in the gaseous state are less complicated when compared with those of the materials in the solid, or liquid state. In the gaseous state, provided the pressure of the gas is not too high, the molecules are free from external influences, whereas in the condensed states the spectra show complications due to perturbations resulting from the environments. The nature of such perturbations are, however, not well-understood at present.

The interpretation of molecular spectra in terms of molecular properties is important in understanding molecular mechanics. In this connection the frequency relationship

$$\Delta E = E_2 - E_1 = h \nu' = hc \nu$$

by Neils Bohr, is of fundamental significance. The emission or absorption of radiation of frequency ν , implies that the molecule is capable of existing in two stationary states with an energy difference ΔE .

Experimental molecular spectroscopy leads one to the conclusion that for every pure compound, neglecting those without a permanent dipole moment, strong spectral activity occurs somewhere in the visible ultra violet region, somewhere in the infrared region, and somewhere in the microwave region (1, p. 2-21). This takes place irrespective of the physical state of the compound, pressure, and temperature. The evaluation of this result in the light of the Bohr's frequency condition points towards the existence of three types of molecular stationary states, each type differing from the other in the separation of the energy levels; it also leads to the concept of the quantization of energy.

In the quantum-mechanical treatment of the molecules in the gas phase it is assumed that each molecule possesses translational, rotational, and vibrational energy, and that the latter two energies are quantized. Radiation takes place only when there is a quantum jump, each such jump corresponding with the emission or absorption of a quantum of energy, or photon of energy, $h\nu = hc\lambda$. Radiation is absorbed when a molecule

undergoes a transition from a lower state (E_1) to a higher state (E_2) and is emitted in the reverse process. The wave-number of the emitted or absorbed radiation, which follows from the frequency relationship of Bohr, is

$$\nu = \frac{E_2}{hc} - \frac{E_1}{hc}$$

The spectral activity in the prism infrared ($2 - 2.5 \mu$) has been found to be due to the quasi-elastic properties of the molecules. But since the infrared absorption bands of substances measured in the liquid state exhibit no rotational fine structure with the sole exception of the Raman spectrum of liquid hydrogen (12, vol. IX, p. 279-280), such spectral activity as results from changes in molecular rotational energy will be neglected here. Considering a diatomic molecule as a harmonic oscillator of mass μ , where μ , the reduced mass, $= m_1 m_2 / m_1 + m_2$, m_1 and m_2 being the masses of the atoms involved, quantum-mechanical calculation allows only those energy values for the elastic or the vibrational energy of the harmonically oscillating molecule as are given by

$$E(\nu) = \frac{h}{2\pi} \sqrt{\frac{k}{\mu}} \left(\nu + \frac{1}{2} \right) = h\nu_{osc} \left(\nu + \frac{1}{2} \right)$$

where the vibrational quantum number ν can take only integral values 0, 1, 2, and ν_{osc} , the vibrational

frequency of the oscillator is equal to

$$\frac{1}{2\pi} \sqrt{\frac{k}{m}}$$

For the transition $v = 0$ to $v = 1$, which represents an absorption process, the change in energy is

$$\Delta E(v) = \frac{h}{2\pi} \sqrt{\frac{k}{m}}$$

If Bohr's frequency rule is applied to this, one gets

$$h\nu = \frac{h}{2\pi} \sqrt{\frac{k}{m}}$$

or

$$\nu = \frac{1}{2\pi c} \sqrt{\frac{k}{m}}$$

This interpretation of the infrared spectra has been confirmed by a large amount of experimental materials, especially by the observed absorption spectra of the hydrogen halides (5, p. 86-87). The absorption frequencies found in the infrared region are, therefore, often called the vibration frequencies of the molecule.

If the molecule consists of more than two atoms, the actual form of the vibrational pattern may be quite complicated since such a molecule could carry out an infinite number of different vibrations about its equilibrium position. If these vibrations are not too

violent, that is, if they are harmonic, it is always possible to regard any such vibration as formed by suitable superposition of two or more simple vibrations called the normal vibrations. In a normal vibration each particle carries out a simple harmonic motion, and all the particles constituting the system have the same frequency of oscillation and, in general, move in phase. For a molecule containing N atoms there are $(3N - 6)$ normal vibrations ($(3N - 5)$, if the molecule is linear). The $(3N - 6)$ frequencies associated with them are called the fundamental frequencies of the molecule. If the molecule has few elements of symmetry, the molecule would show $(3N - 6)$ different fundamental absorption bands all of which might be allowed both in the infrared and Raman spectra. Inasmuch as the symmetry property of the molecule determines whether a certain number of these frequencies occurs in pairs or triples the forms of the normal vibrations are strongly dependent on the symmetry of the molecule. For all the $(3N - 6)$ different modes of vibration, the energy-level scheme is given by

$$E(v) = \sum_{i=1}^{3N-6} \left(v_i + \frac{1}{2} \right) h\nu_{i\text{osc}}$$

If the vibrations were harmonic the energy-levels of a single frequency would be equally spaced, the separation

being $h\nu'$, and that the lowest energy-level ($\nu = 0$) is not at zero energy but at the zero-point energy $\frac{1}{2}h\nu'$.

The normal vibrations for a non-linear triatomic molecule are shown qualitatively in the following picture:

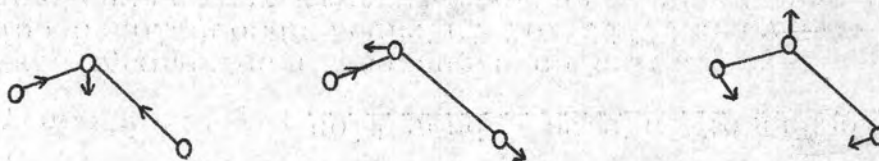


Figure 1

The actual vibrational pattern for any given electronic state of any diatomic molecule, or polyatomic molecule shows that the upper energy-levels are somewhat crowded together, that is, are not equally spaced due to anharmonicity.

EXPERIMENTAL METHODS

The Spectrometer

The instrument used for obtaining the spectra was a Perkin-Elmer model 21 double beam spectrophotometer. The absorption curve as obtained for the various samples represent the percentage transmission of the radiation incident in it. The percentage transmission is a simple ratio of the energy which passes through the absorption cell containing the sample and that for a similar cell containing the solvent only when a parallel beam of monochromatic radiation is incident normally on it. The absorption curve, therefore, is a ratio of two curves: the spectrum for the sample, and the spectrum which would have been obtained, had the spectrum been run, under exactly similar conditions, with the solvent only.

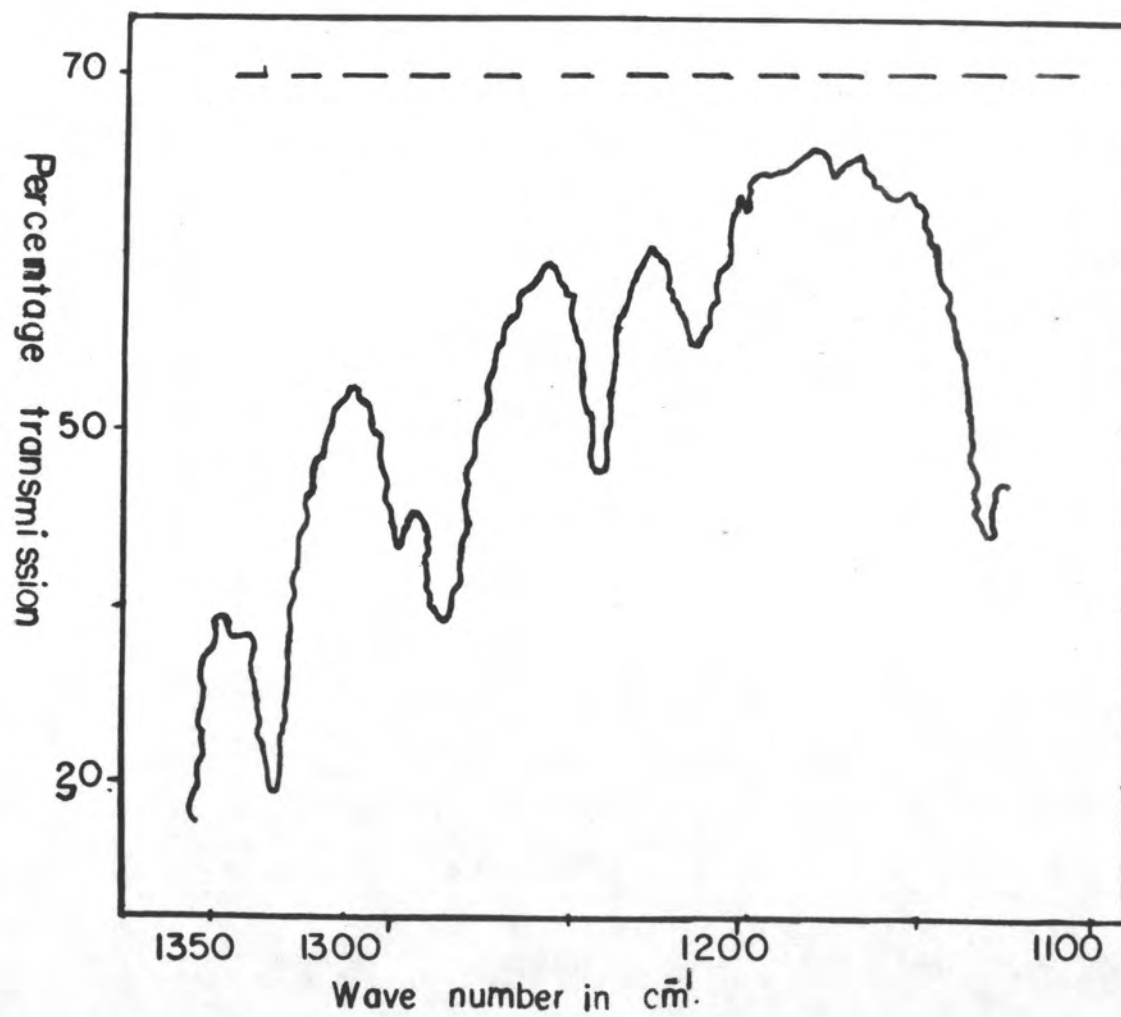
In the instrument used to obtain the absorption spectra, that is, the double beam spectrometer, the beam of the incident radiation is divided into two parts, one-half of which goes through the sample and the other half, the reference beam, through the cell containing the solvent only. For the latter purpose, the variable thickness liquid absorption cell is used, with the cell set approximately to a thickness calculated to be equivalent to the solvent content of the sample. For

obtaining the best compensation the spectrometer is set to the wave-length of a moderately weak absorption peak of the solvent, and the thickness of the variable space cell in the reference cell is so adjusted that the deflection corresponds to the 100% value. This setting is then checked by running the compensated condition through the spectral range of the absorption band.

Preparation of the Sample

The solvent, n-hexane, was chosen because it was only weakly absorbing in the wave-length region of the absorption band for the solute. The absorption spectrum of hexane in the range of the wavelength considered is shown in Figure 2. Solutions of the solute, chloroform, in this solvent was then prepared by weighing in a Mettler gravimetric balance. The solution was contained in a small glass vial which was closed by inserting firmly a small glass rod in a narrow Teflon tube attached tightly to the tapering neck of the vial. To keep the loss due to evaporation of the volatile solute and the solvent at the barest minimum, these vials were kept, whenever not used, in a Dewar flask containing a desiccant, and stored in the dark at low temperatures. Since chloroform is susceptible to air-oxidation in the presence of day-light, or other kinds of bright

Figure 2
Absorption spectrum of Hexane in the range of wavelength indicated



lights (13, p. 153-155), all operations connected with the sample were carried out as far as possible in the absence of such lights. For carrying the out the experiment, the sample, thus prepared, is then filled in a fixed thickness cell with sodium chloride window.

Calibration of the Instrument

After carrying out each series of experiment, the instrument was calibrated by running a polystyrene vs. air spectrum in the instrument. The spectrum obtained was then compared with the standard spectrum provided in the literature for that purpose. The correct frequencies were then assigned for the region of the absorption band.

Comparison of the Results

The results obtained from the Perkin-Elmer model 21 were compared by running the spectra for some of the same solutions in a Beckman IR4 spectrometer. A comparison of both results is shown in Figures 3 and 4.

Figure 3
 $\text{Log}_e (T_o / T)$ vs $\nu \text{ (cm}^{-1}\text{)}$
(Perkin Elmer)

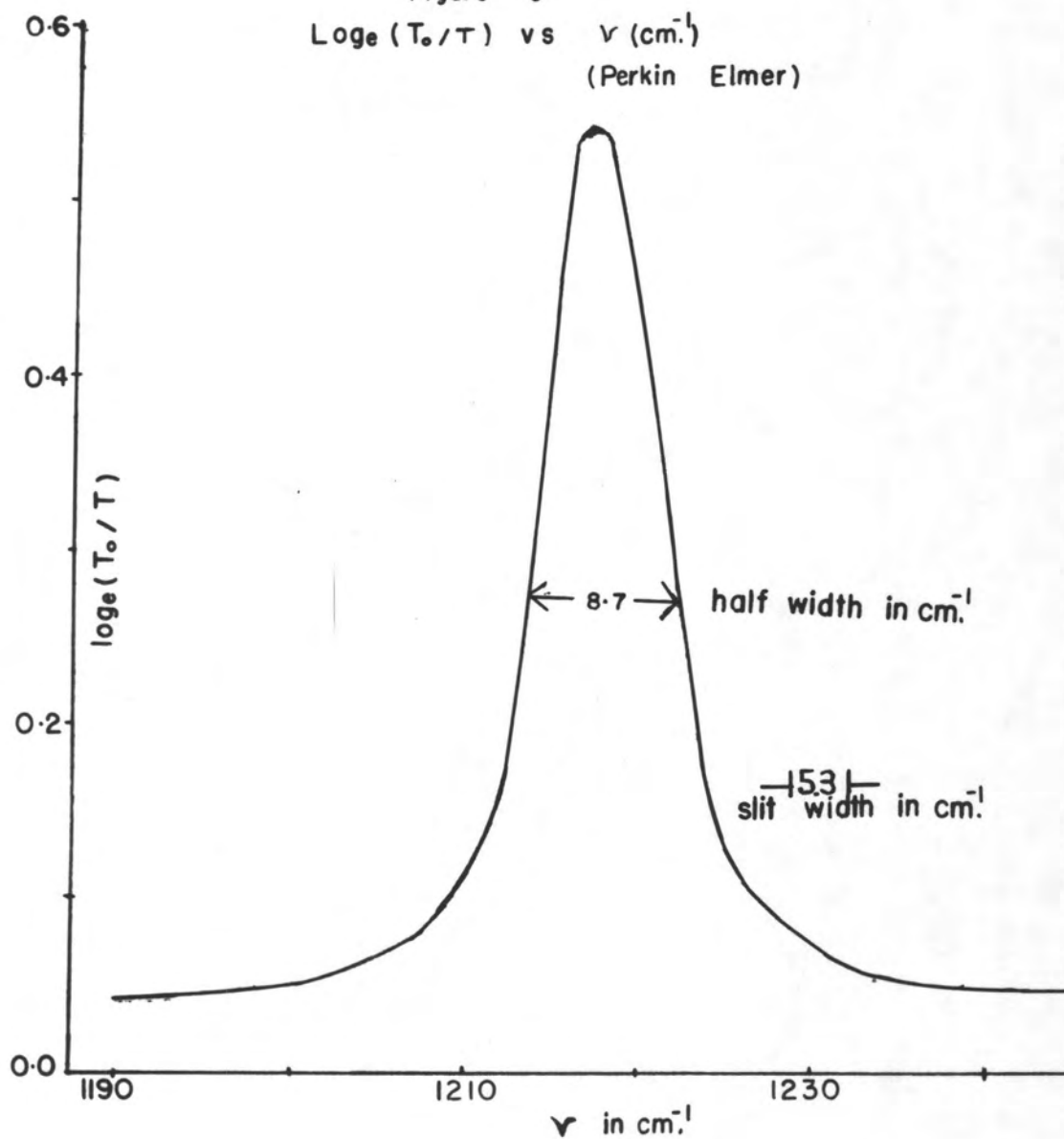
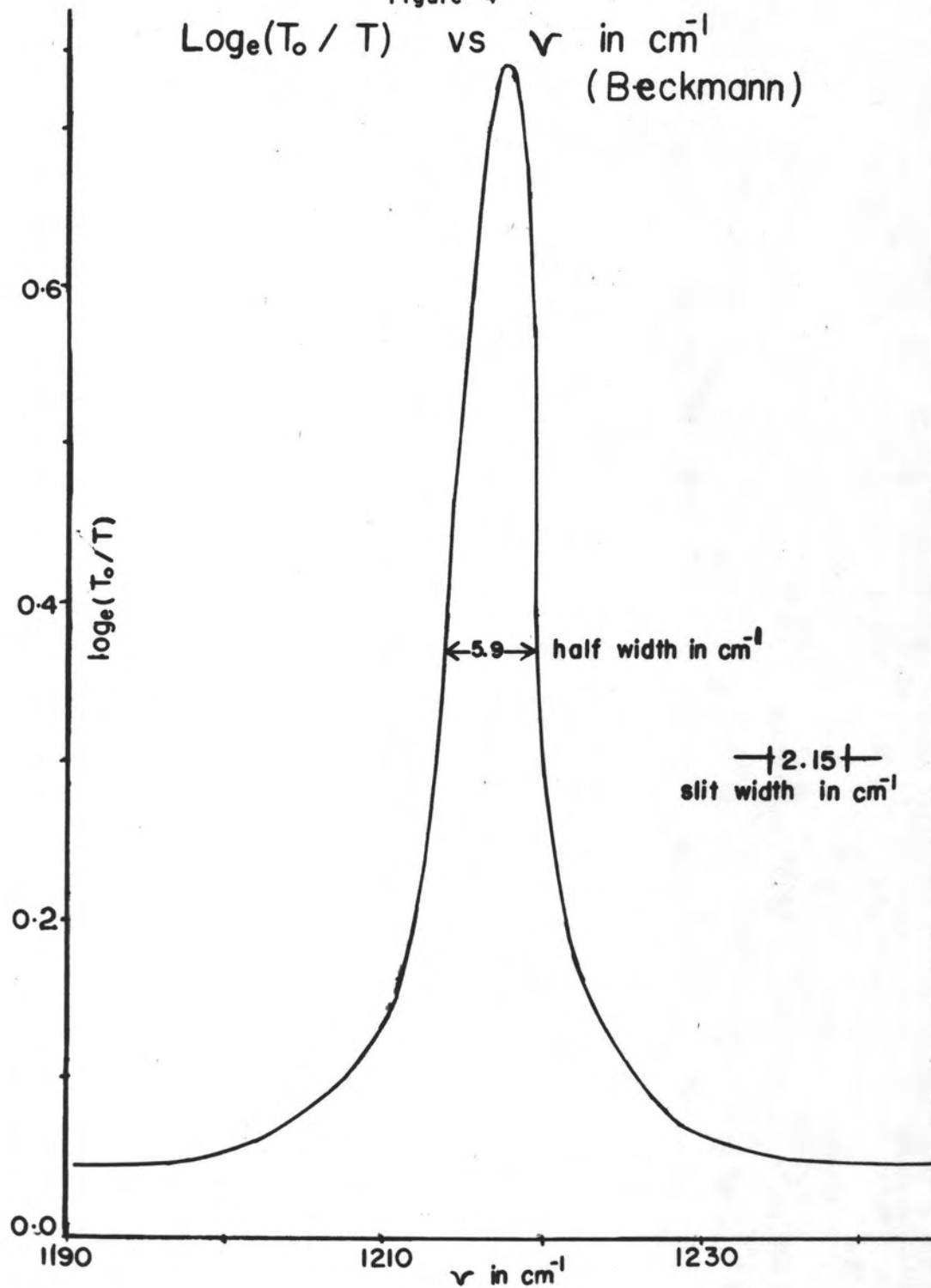


Figure 4



THEORY OF THE EXPERIMENT

For monochromatic radiation of frequency ν cm^{-1} , the fundamental law assumed to hold good for liquids and solutions is the Lambert-Beer law

$$I = I_0 e^{-\alpha_\nu c l}$$

where I_0 and I are the incident and the transmitted intensities of monochromatic radiation, α_ν is the absorption coefficient for the frequency ν , c is the concentration of the solute in moles per liter, and l is the cell length in cm.

The true integrated absorption intensity (A) of an absorption band is then defined as

$$A = \int \alpha_\nu \cdot d\nu = \frac{1}{cl} \int \log e \left(\frac{I_0}{I} \right)_\nu \cdot d\nu$$

the integral being measured over the limits of the absorption band. In practice the energy which passes through the exit slit of a monochromator illuminated with continuous radiation is never truly monochromatic because of the finite width of the slit (9, p. 73-74). The quantity measured is, therefore, not the true integrated absorption intensity but the apparent integrated intensity (B) given by

$$B = \frac{1}{cI} \int \log_e \left(\frac{T_0}{T} \right)_{\nu_i} d\nu$$

where T_0 and T are the apparent intensities of the incident and transmitted radiation respectively with the spectrometer set at frequency ν_i . Ramsay (9, p. 73-74) has pointed out that with prism instruments at present in use in the infrared, since the spectral slit widths are of the same order as the half-widths of the absorption bands of liquids, the band intensities, instead of being the true physical constants of the absorbing molecules, depend upon the instrumental conditions employed. He has shown that with a slit-width equal to one-half the true half-width of the absorption, the true and apparent integrated intensities differ by about 2-3%, assuming the Lorentz shape for the absorption curves. The decrease in peak intensity produced by the finite slit width is compensated roughly by an increase in the band width.

The envelopes of the infrared absorption bands of liquids, assumed to be symmetrical about the frequency of the absorption maximum, is fitted by an equation of the form analogous to that derived theoretically by Lorentz to fit the infrared absorption bands of gases observed under high pressures, where the rotational fine

structure is largely suppressed, and hence called the Lorentz function. Such a function which has been used to describe the shape of the vibrational bands is given by

$$\log e \left(\frac{I_0}{I} \right)_\nu = \frac{a}{(\nu - \nu_0)^2 + b^2}$$

where ν_0 is the frequency of the band center and a and b are constants. It has been observed that for suitably isolated bands, the agreement with the Lorentz curve, suitably modified by mathematically scanning with a triangular slit function, is very close. Because of the finite slit widths the energy which passes through the exit slit of the spectrometer set at any frequency ν_1' instead of being monochromatic, contains a range of frequencies on either side of ν_1 . The energy distribution can, however, be represented by a function $\ell(\nu, \nu_1')$, called the slit function. The apparent absorption band which is obtained by scanning an absorption band, assumed to be exactly represented by the Lorentz equation mentioned above, by a spectrometer of finite resolving power can be expressed by means of the equation

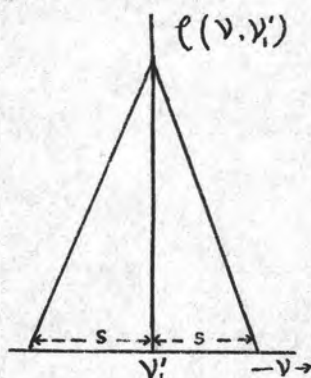
$$\left(\frac{I}{I_0} \right)_{\nu_1'} = \frac{\int \ell(\nu, \nu_1') e^{\frac{-a}{(\nu - \nu_0)^2 + b^2}} d\nu}{\int \ell(\nu, \nu_1') d\nu}$$

On the assumption that the intensity of the incident radiation is constant over the entrance slit, the dispersion is constant over the exit slit and that the widths of the entrance and exit slits are equal, the slit function for prism spectrometers for which the resolution of the prism in cm^{-1} is small compared with the mechanical widths of the slits also in cm^{-1} , can be represented to a first approximation by a triangle with a half energy spectral slit width given by

$$S = \frac{\nu^2 (1 - n^2 \sin^2 \alpha / 2)^{1/2}}{8 \sin \alpha / 2 \frac{dn}{d\lambda}} \frac{s_1 + s_2}{f} + F(s) \frac{\nu}{2b \frac{dn}{d\lambda}}$$

where ν is the frequency in cm^{-1} , n is the refractive index of the prism at the frequency ν , α is the prism angle, $dn/d\lambda$ is the dispersion of the prism material in cm^{-1} , f is the focal length in cm, b the length of the prism base in cm, and $F(s)$ a quantity varying from about 0.9 for $s = 0$ to 0.5 for $s = \nu / 2b \frac{dn}{d\lambda}$. The spectral slit width (s), defined as a quantity that represents the separation in wave number units of two monochromatic lines such that they fail to be resolved, may then be taken as the sum total of two contributions, a contribution due to the finite slit widths, represented by the

first term of the above equation, and another contribution due to the finite resolving power of the prism, represented by the second term. The following figure shows the triangular spectral energy distribution ($\ell(\nu, \nu')$) for the energy passing through the exit slit of the spectrometer set at a frequency ν' , s being the spectral slit width.



Furthermore, the assumption of the Lorentz curve shape has been found to give useful corrections for the areas under the wings of the absorption bands beyond the limits of the experimental measurements which range to about 50 cm^{-1} on either side of the band center. The assumption that the band extends indefinitely may make the area under the wings a significant fraction of the total area of the band which necessitates this correction.

Calculation of the True Integrated Absorption Intensity

Various investigators have examined the problem of determining the true integrated absorption intensity

of the absorbing molecule from the experimentally measured quantity, B for known values of the spectral slit width (s).

Wilson-Wells Extrapolation Method

The method used here is due to Wilson-Wells (15, p. 578-581). They studied the absorption bands of gases under pressures so as to eliminate the effects of the rotational fine structure. Wilson and Wells established that the true integrated absorption intensity could be obtained by measuring B at several concentrations and extrapolating the band areas so obtained to zero concentration. For obtaining a good extrapolation, since several points are needed, it becomes necessary to measure B at low optical densities which, unfortunately, involve rather large experimental errors.

Thus, according to Wilson and Wells,

$$\lim_{cl \rightarrow 0} (B/cl) = A$$

True Integrated Absorption Intensities in the Gas and Solution Phases

The positions of the atoms in the molecule are equilibrium positions, and hence one can consider a

molecule as a configuration of mass-points representing the nuclei of the constituent atoms, bound together in an equilibrium state. On the application of some distorting force, the atoms can be forced closer together or pushed farther apart, and the bond angles can be increased or decreased. And provided the distorting force is not too great, the restoring force which binds the atoms together in the molecule and which is assumed to vary linearly with the displacements of the mass-points from the center of origin of any suitable co-ordinate system fixed within the molecule, will bring the mass-points back to their original equilibrium positions on removal of the distorting force.

Interaction of the molecule with incident electromagnetic waves serves to intensify the vibrations of the mass-points owing to the electric field associated with the waves. If this vibration causes a change in the dipole moment of the molecule, then according to classical electrodynamics, radiation is either absorbed or emitted. The vibrational motion of the molecule assumed to be a simple periodic motion, can be resolved into a sum of one or more of the fundamental modes of vibration, $(3N - 6)$ for a non-linear molecule consisting of N atoms. Hence the frequencies of the absorbed or emitted radiation are those of the modes composing the motion. For molecular

vibrations these frequencies are found to lie in the infrared region of the electromagnetic spectrum (4, p. 239-240). Those vibrations which are associated with a change of the dipole moment and thus cause the absorption of light in the infrared region are called infrared active. Whereas for non-symmetrical molecules all normal vibrations cause a change of dipole moment and are infrared active, for symmetrical molecules, because of the possibility that some of the vibrations may cause neither a change in the magnitude nor in the direction of the dipole moment, all vibrations may not be infrared active.

The dipole moment μ of a system is

$$\mu_x = \sum e_k x_k$$

where e_k is the charge on the mass-point, and x_k is the vector distance of the point from the origin of a suitable co-ordinate system fixed in the molecule. In a Cartesian system,

$$\mu^2 = \mu_x^2 + \mu_y^2 + \mu_z^2$$

Since for vibrational transitions the vector distances x_k , y_k , etc. change during vibrations the dipole moments considered must change with distances. For small displacements, that is, when the nuclei are not

displaced too much from their equilibrium positions during the vibration, the dipole moment μ can be expanded in a power series

$$\mu = \mu^0 + \sum \left[\left(\frac{\partial \mu_x}{\partial x_k} \right)_0 x_k + \left(\frac{\partial \mu_y}{\partial y_k} \right)_0 y_k + \left(\frac{\partial \mu_z}{\partial z_k} \right)_0 z_k \right] + \dots$$

where x_k, y_k, z_k refer to the displacement co-ordinates of the nucleus k , and the subscript zero means that the derivatives are evaluated at the equilibrium positions of the mass-points. If the Taylor expansion is done in normal co-ordinates in Q_1, Q_m, Q_n, \dots , then

$$\mu_x = \mu_x^0 + \sum_1 \left(\frac{\partial \mu_x}{\partial Q_1} \right)_0 Q_1 + \dots \quad (2)$$

μ_y and μ_z can be expanded in the same way.

For any normal vibration l with a frequency ν_l ,

$$Q_l = Q_l^0 \cos (2\pi \nu_l t + \varphi_l)$$

where Q_l^0 is the amplitude, t the time, and φ_l a phase constant. It follows from (2) that the dipole moment of the system will change with the frequency ν_l of a normal vibration only if at least one of the derivatives

$\left(\frac{\partial \mu_x}{\partial Q_1} \right)_0, \left(\frac{\partial \mu_y}{\partial Q_1} \right)_0, \left(\frac{\partial \mu_z}{\partial Q_1} \right)_0$ is different from zero. The intensity of this infrared fundamental band turns out to be proportional to the square of the vector representing

the change of the dipole moment for the corresponding normal vibration near the equilibrium position; that is, it is proportional to

$$\left(\frac{\partial \mu_x}{\partial Q_1}\right)_0^2 + \left(\frac{\partial \mu_y}{\partial Q_1}\right)_0^2 + \left(\frac{\partial \mu_z}{\partial Q_1}\right)_0^2$$

To calculate the exact form of the relationship between the integrated intensity of an infrared band and the square of the vector mentioned above, use is made of the time dependent perturbation theory. According to the latter theory, the intensities of transition between two energy states n and m of a molecule are determined theoretically, by integrals of the form

$$P_{nm} = \int \psi_n P \psi_m^* dv$$

where P is some physical vector quantity which depends upon the $(3N - 6)$ co-ordinates of the N particles in the system, and ψ_n and ψ_m are the eigenfunctions of the two states, the integral being taken over the whole space of the $3N$ co-ordinates.

In considering the infrared absorption spectra, the quantity P may be identified simply as the dipole moment μ . Using

$$\mu_x = \sum e_k x_k, \quad \mu_y = \sum e_k y_k, \quad \mu_z = \sum e_k z_k,$$

Substitution of this in the above expression gives

$$\mu_{\frac{nm}{x}} = \int \psi_n (\sum e_k x_k) \psi_m^* dv$$

$$\mu_{\frac{nm}{y}} = \int \psi_n (\sum e_k y_k) \psi_m^* dv$$

and
$$\mu_{\frac{nm}{z}} = \int \psi_n (\sum e_k z_k) \psi_m^* dv$$

where μ^{nm} is called the matrix element of the dipole moment of the system. For a dipole transition to be possible the matrix element μ^{nm} must differ from zero for the two states. In other words, if just one of the above integrals differs from zero the two states can combine with one another with a certain probability with emission or absorption of radiation, and the dipole transition is permitted. The probability of a transition between two energy states, according to the time dependent perturbation theory, turns out to be proportional to the square of the magnitude of the matrix element μ^{nm} . That is, proportional to

$$\sum |\psi_n \mu_c \psi_m^* dv|^2 \quad c = x, y, z$$

On the other hand, transition probabilities can be expressed by the Einstein coefficients. The expression for the Einstein coefficient of spontaneous absorption, B_{nm} , where the subscript m refers to the upper state, and the transition is from n to m (14, p. 162-164), is

$$B_{nm} = \frac{8\pi^3}{3h^2} \sum_x \left[(\mu_x)_{nm} \right]^2 \quad (3)$$

These absorption coefficients can be related to the decrease in the intensity of the infrared beam, $-dI$, in the following manner

$$-dI = -\frac{h\nu_{nm}}{c} B_{nm} (N_m - N_n) I dl$$

Also since $-dI = KI dl$

$$K = -\frac{h\nu_{nm}}{c} B_{nm} (N_m - N_n)$$

where K is the absorption coefficient.

Substitution of this value of K in (3) gives

$$\int_{\text{line } nm} K(\nu) d\nu = -\frac{8\pi^2}{3ch} (N_m - N_n) \nu_{nm} |\mu^{nm}|^2$$

This equation refers to a single transition from a rotation-vibration state m to n . By summing the line intensity over all rotational lines and using the

harmonic oscillator approximation and adding up all contributions of equal frequency vibrational transitions (15, p. 162-166), the following relationship is arrived at

$$A = \int_{\text{band } \Delta v_k=1} K(\nu) d\nu = \frac{N\pi}{3C} \left\{ \left[\mu_x^{(k)} \right]^2 + \left[\mu_y^{(k)} \right]^2 + \left[\mu_z^{(k)} \right]^2 \right\}$$

This relationship is, as aforesaid, true for the absorbing molecule in the gaseous phase. When one tries to obtain an analogous equation for the liquid or solution phase, one has to take note of the differences in the environments of the absorbing molecules in the two phases. Whereas in the gaseous phase (at sufficiently low pressures), the vibrating molecules being far from one another, and suffering relatively infrequent collisions may be considered as essentially independent systems, the situation in the liquid phase or in solution is fundamentally different. In the latter case the molecules are more crowded together, any one molecule being in general at closer distances from its neighbors, and as a result suffering more collisions. The vibration of any particular molecule would, therefore, be influenced by its neighboring molecules, such influences manifesting themselves through collisions and through intermolecular forces. Thus the dipole moment of the molecule in the

gas phase may be different from that in the solution. Also since the magnitude of the effective electric field in the solution may depend upon the dielectric properties of the solvent as well as upon the electric field associated with the infrared radiation absorbed, the change in the magnitude of the electric field during the infrared absorption measurement may be significantly different in the solution as compared with that in the gaseous phase.

Relation Between Intensities of an Infrared Band in the Gas and Liquid Phases

Polo and Wilson (8, p. 2376-2377) have related the intensities of an infrared absorption band in the liquid and the gas phases by the following expression

$$\frac{A_l}{A_g} = \frac{E_l^2}{E_g^2} \quad \text{or} \quad \frac{A_{\text{SOLN}}}{A_{\text{GAS}}} = \frac{E_{\text{SOLN}}^2}{E_g^2} = \frac{E_e^2}{E_o^2}$$

where E_l is the effective field acting in the unperturbed moment in the liquid phase and E_g is the field acting in the same moment in the gas phase; E_{soln} or E_e can be considered as the field acting upon the unperturbed moment of the solute.

According to Onsager (3, p. 260-265) the total effective field acting on a spherical molecule in a

polarized dielectric is

$$E_e = G + R$$

where G , called the cavity field, is the field which would be obtained in a spherical cavity containing the molecule under consideration if the latter were removed from this cavity, and R is the reaction field arising from the effect of the molecule on itself through the induced polarization of the surrounding dielectric by the dipole moment of the molecule in question. The reaction field is taken as being proportional to the total dipole moment (both induced and permanent) of the molecule, that is,

$$R = g \times p$$

where p is the total dipole moment, and g , a constant of proportionality, is given by the relation

$$g = \frac{2(n^2 - 1)}{2n^2 + 1} \frac{1}{a^3}$$

where a , the molecular radius, is defined by the expression $a^3 = 3/4\pi N$, N being the number of molecules per cc, and n is the refractive index of the medium.

According to Onsager the total electric field turns out to be

$$E_e = \frac{3\epsilon}{2\epsilon+1} E + \frac{2(\epsilon-1)}{2\epsilon+1} \cdot \frac{p}{a^3}$$

where E is the average macroscopic field within the dielectric, ϵ the dielectric constant, a the cavity radius. The first term on the right hand side of this expression is taken to be the contribution from the reaction field and the second term that due to the cavity field.

In a discussion of the application of the Onsager theory to the determinations of the absolute infrared intensities, Polo and Wilson (8, p. 2376-2377) have given the relationship

$$E_o^2 = nE^2$$

where E_o is the electric field outside the dielectric, and is also called the vacuum field. By further writing out the dipole moment p as

$$p = \mu + (gp)\alpha$$

and by evaluating α by the use of the macroscopically derivable Clausium-Mossotti equation

$$\alpha = \frac{\epsilon - 1}{\epsilon + 2} a^3$$

they found out that for a liquid

$$\frac{E_e^2}{E_o^2} = \frac{1}{n} \left(\frac{n^2 + 2}{3} \right)^2$$

The refractive index was related with the dielectric constant by means of the Maxwell relationship, $n^2 = \epsilon$. By a simple modification of the Clausius-Mossotti relation, that is, by using the dielectric constants of the solute, ϵ , Person (7, p. 319-322) has given the analogous expression for a solution which is

$$\frac{E_e^2}{E_o^2} = \frac{1}{n} \left[\frac{n_o^2 + 2}{\left(\frac{n_o}{n}\right)^2 + 2} \right]^2$$

where n is the refractive index of the solvent, and n_o is that of the solute.

Buckingham (2, p. 32-39) has, by the introduction of the Clausius-Mossotti equation for the polarizability of the vibrating molecule, proposed another expression; his result may be stated as

$$\frac{A_{\text{SOLN}}}{A_{\text{GAS}}} = \frac{9n^3}{(2n^2+1)^2} \cdot \frac{k_i^2}{M_i^2}$$

By using the Onsagar model for p one obtains

$$p = \mu(1 - g\alpha)^{-1}$$

$$p' = \frac{1}{1 - g\alpha} \left(\mu' + \frac{g\alpha'}{1 - g\alpha} \right)$$

Provided that $\mu' \gg g\alpha'^\mu$ one obtains

$$\frac{A_{\text{SOLN}}}{A_{\text{GAS}}} = \frac{9n^3}{(2n^2+1)^2} \cdot \left(\frac{1}{1-g\alpha} \right)$$

which reduces to the Polo-Wilson or more properly to the Person expression if the Clausius-Mossotti expression is substituted for α .

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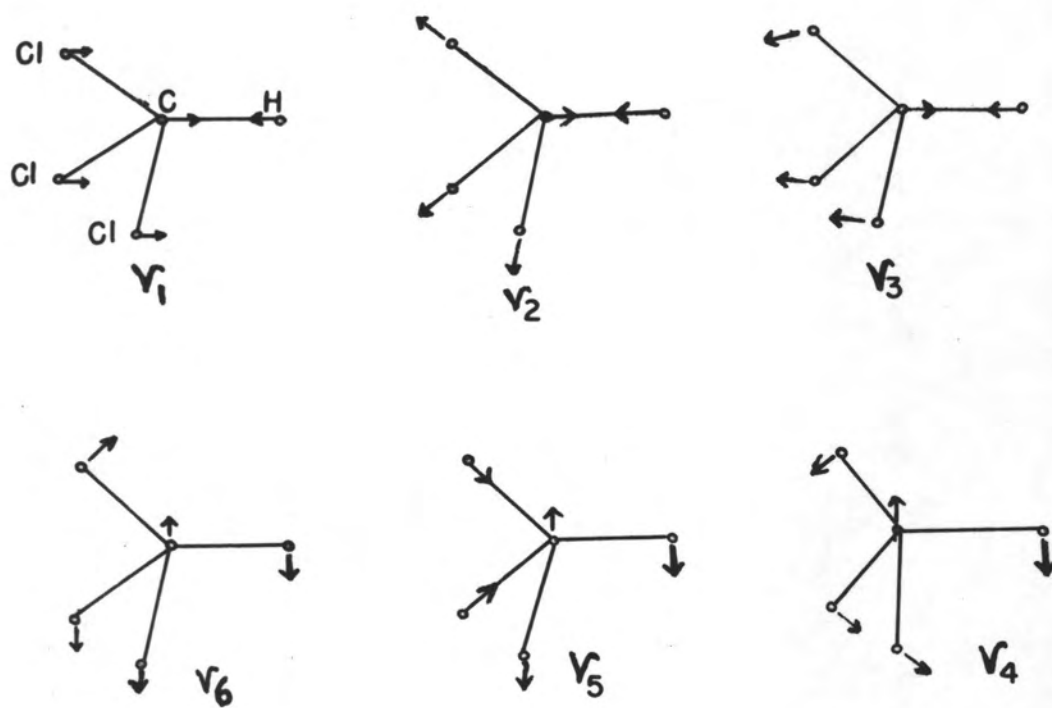
RESULTS AND DISCUSSION

The present work concerns itself with the determination and study of the absolute intensity of the ν_4 bending mode of the C-H group in chloroform dissolved in n-hexane. Table 1 gives the fundamental infrared vibration frequencies of chloroform in the region of the fundamentals. A schematic representation of the normal modes of vibration of CHCl_3 (4, p. 312-317) is given in Figure 5.

Table 1

FUNDAMENTAL FREQUENCIES OF CHLOROFORM

Assignment	Infrared vacuum in cm^{-1}	Description
$\nu_1 (A_1)$	3034	C-H stretching vibration
$\nu_2 (A_1)$	681	sym. C-Cl stretching vibration
$\nu_3 (A_1)$	364	sym. C-Cl_3 deformation
$\nu_4 (E)$	1221	Bending of C-H group against the rest of the molecule
$\nu_5 (E)$	769	Degenerate C-Cl stretching vibration
$\nu_6 (E)$	260	Degenerate C-Cl_3 deformation

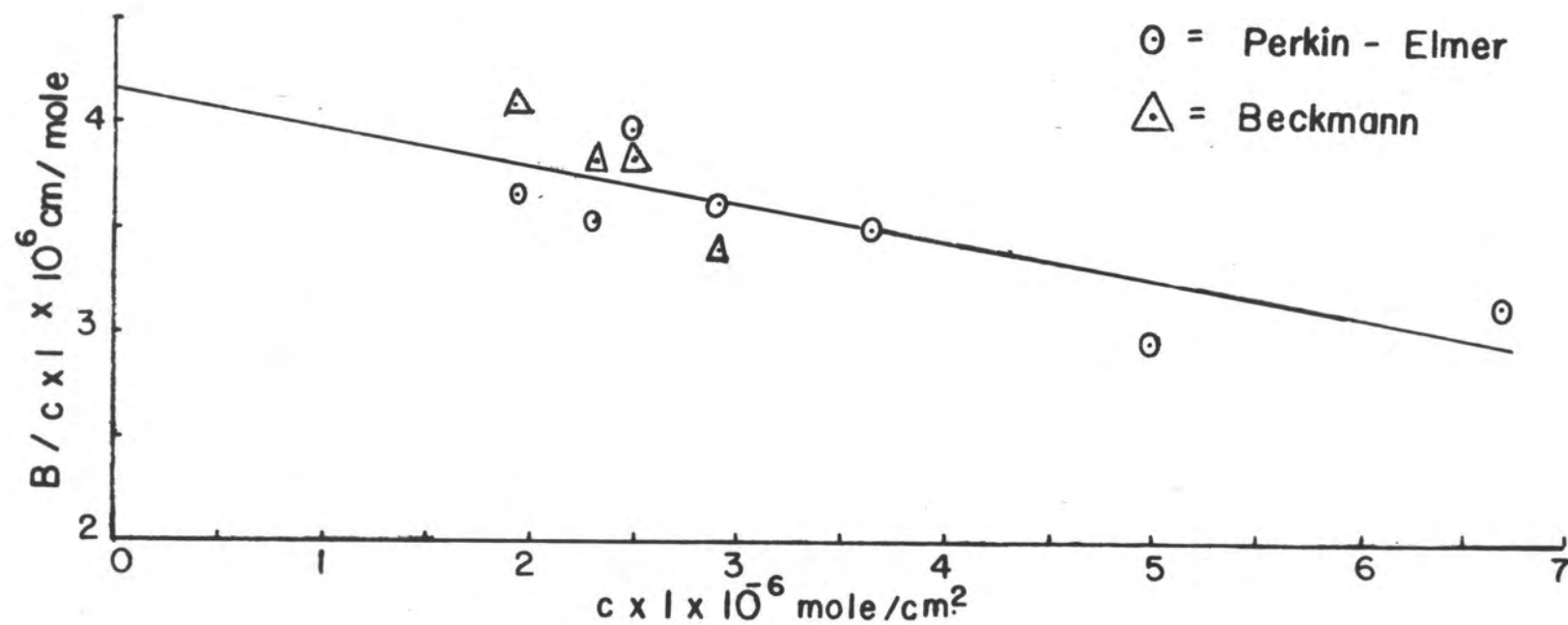


Normal vibrations of the Chloroform molecule
Figure 5

The absolute intensity as found out here was determined by using the principles laid down by Wilson-Wells, that is, by extrapolating the plot of $B/c \times l$ against $c \times l$ to zero concentration, in accordance with the assumptions of Ramsay regarding the shape of the infrared absorption band and the triangular spectral energy distribution across the exit slit of the spectrometer. On the basis of these assumptions Ramsay (9, p. 72-74) has shown that the extrapolation curve is a straight line with an almost negligible slope. The curve obtained in the final result in this work shows, however, a marked and significant deviation from that postulated by Ramsay, as can be seen from Figure 6. Also when the absolute intensities are computed by using the equation

$$A = \frac{K}{cl} \log_e \left(\frac{T_0}{T} \right)_{\nu_{\max}} \times \Delta \nu_{1/2}^a$$

in which K has a value determined by the ratio $s/\Delta \nu_{1/2}^a$ and is usually about 1.5, the values were found to be consistently lower than those obtained by the extrapolation method regardless of the variation in slit width as can be seen from the figures given in Table 2. Thompson (11, p. 145-160) casts doubt on the usefulness of the above equation for computing the absolute intensities since according to him the use of the integrated



Wilson - Wells extrapolation of apparent intensities of the bending mode of Chloroform in n - Hexane.

Figure 6

Table 2

Comparison of the values of absolute intensities in cm/mole for some of the solutions of the same concentration, in each case obtained from different spectrometers and calculated from Ramsay's equation.

Obtained from Perkin-Elmer instrument ($s=5.34 \text{ cm}^{-1}$)	Calculated from Ramsay's equation ($s=5.34 \text{ cm}^{-1}$)	Obtained from Beckmann instrument ($s=2.15 \text{ cm}^{-1}$)	Calculated from Ramsay's equation ($s=2.15 \text{ cm}^{-1}$)
3.61	3.09	3.40	3.05
3.98	3.29	3.84	3.26
3.54	2.90	3.84	3.12
3.68	3.06	4.12	3.05

band areas to obtain the K often gives values much below those predicted by Ramsay. He tends to ascribe this discrepancy to the fact that the infrared absorption band contour may not be represented exactly by the Lorentz equation. From what has been pointed out before, the present work also tends to support the observation of Thompson; either that or the assumption that the energy distribution across the exit slit of the spectrometer can be truly represented by a triangular slit function, or both may have to do with the observed discrepancies.

The absolute intensities of the various normal

vibrational modes of chloroform in the gaseous phase were determined by Morcillo, Herranz and Biarge in 1959 (6, p. 110-121). A comparison of their results with the results obtained in the course of the present work, as far as the ν_4 bending mode is concerned is shown in Table 3 and also in Figure 7. The results of Smirnov (10, p. 302-305), who determined the intensities of some of the vibrational modes of chloroform dissolved in non-polar solvents like carbon disulphide and carbon tetrachloride in low concentrations are also included in Table 3 for comparison. The Beer's law plot which turned

Table 3

Comparison of the absolute intensities of the bending mode of chloroform obtained in the gas phase and in solution by various workers. Absolute intensities are expressed in cm/mole.

Morcillo, Herranz, Biarge.

Absolute intensity in the gas phase	4.20×10^6
-------------------------------------	--------------------

Smirnov.

Intensity in CS ₂ solution of low concentration (0.6198 mole/liter)	3.07×10^6
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Absolute intensity as obtained in the present work	4.20×10^6
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out as anticipated to be a straight line passing through the origin is shown in Figure 7.

Comparison of the absolute intensities of
Chloroform in the gas phase and in
Hexane solution.

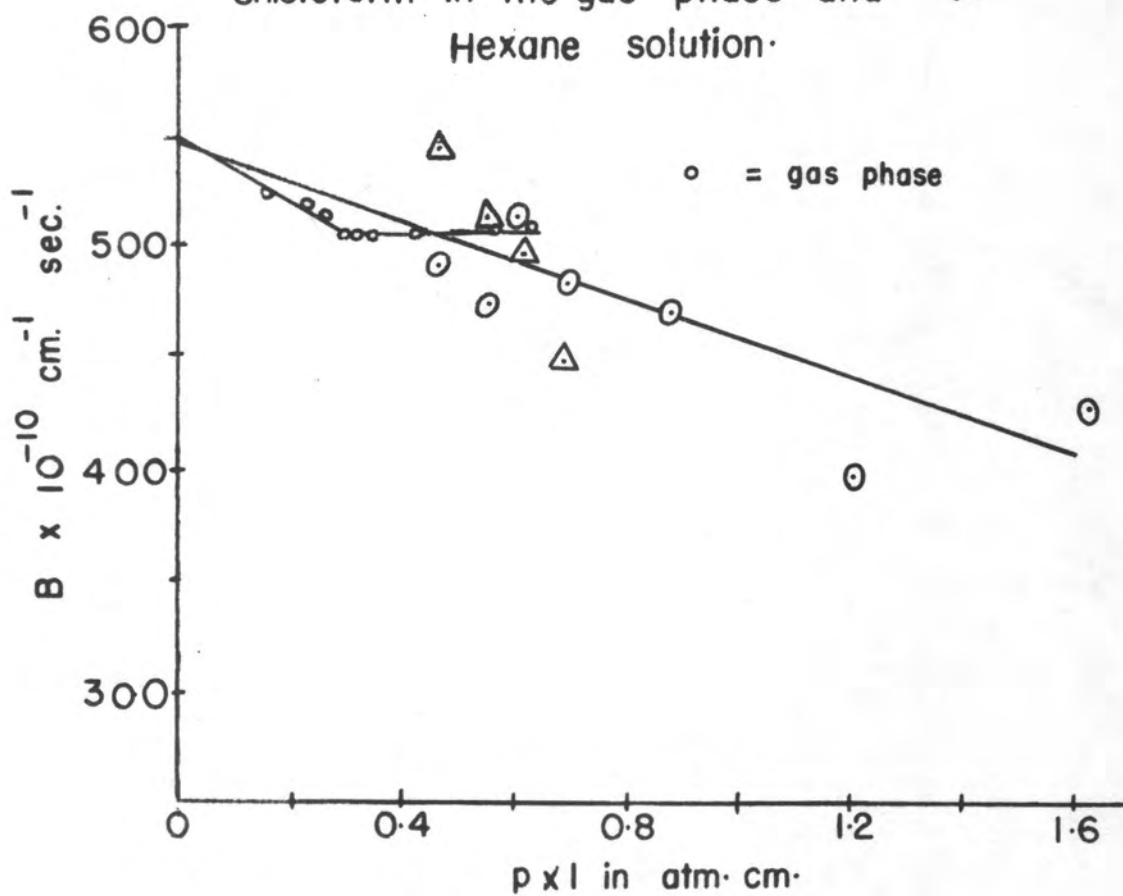


Figure 7

Some of the difficulties encountered in the use of the above equations particularly that of Buckingham, for calculating the ratio of the absolute intensities of liquid (or solution) and the gas phase of any particular molecule are due to uncertainties regarding the evaluation of ϵ and n which occur in these equations. Refractive indices of n-hexane in the region of the frequency of the infrared absorption could not be found in the literature because of which the values of the refractive indices referred to a wave-length of 656.3 μ were used in the calculations. The use of such values of the refractive indices may not, however, affect significantly the numerical values of the intensity ratio since the latter is not particularly susceptible to small changes in the values of the refractive indices. But the situation with regard to a which Onsager refers to as the molecular radius is different and still more uncertain. In the first place, it is not implicit in the literature as to whether a refers to the radius of a hole in the continuous dielectric with the solute molecule in the center of it, or is merely equal to the radius of the solute molecule caged in on all sides by the solvent molecules.

According to Onsager the size of the molecular radius, a , is given by the relation

$$a^3 = \frac{3}{4} \pi N$$

where N is the number of the molecules per unit volume. N was evaluated here from the expression, $N = N_A \times d/M$, N_A being Avogadro's number and d the density of the substance of molecular weight M .

The values of a calculated for chloroform according to the Onsager expression as well as that obtained from consideration of the Van der Waals radii of the chlorine atom are compared together with the values of the intensity ratios obtained from the respective values of a . Since it is not certain whether the molecular radius to be used is definitely that of the solute only, a was calculated for hexane also according to the Onsager relation, and the intensity ratio was also determined for this value of a . The experimental value of the intensity ratio together with the value of a which would give the same ratio are also given for comparison (see Table 5). All the intensity ratios given in Table 5 were obtained by the use of the Buckingham equation. As can be seen from the calculations, the value of the intensity ratio, A_L/A_g , as obtained experimentally differs significantly from the values calculated either from the Person equation or from that of Buckingham. Apart from the uncertainties pointed out above in the use of the

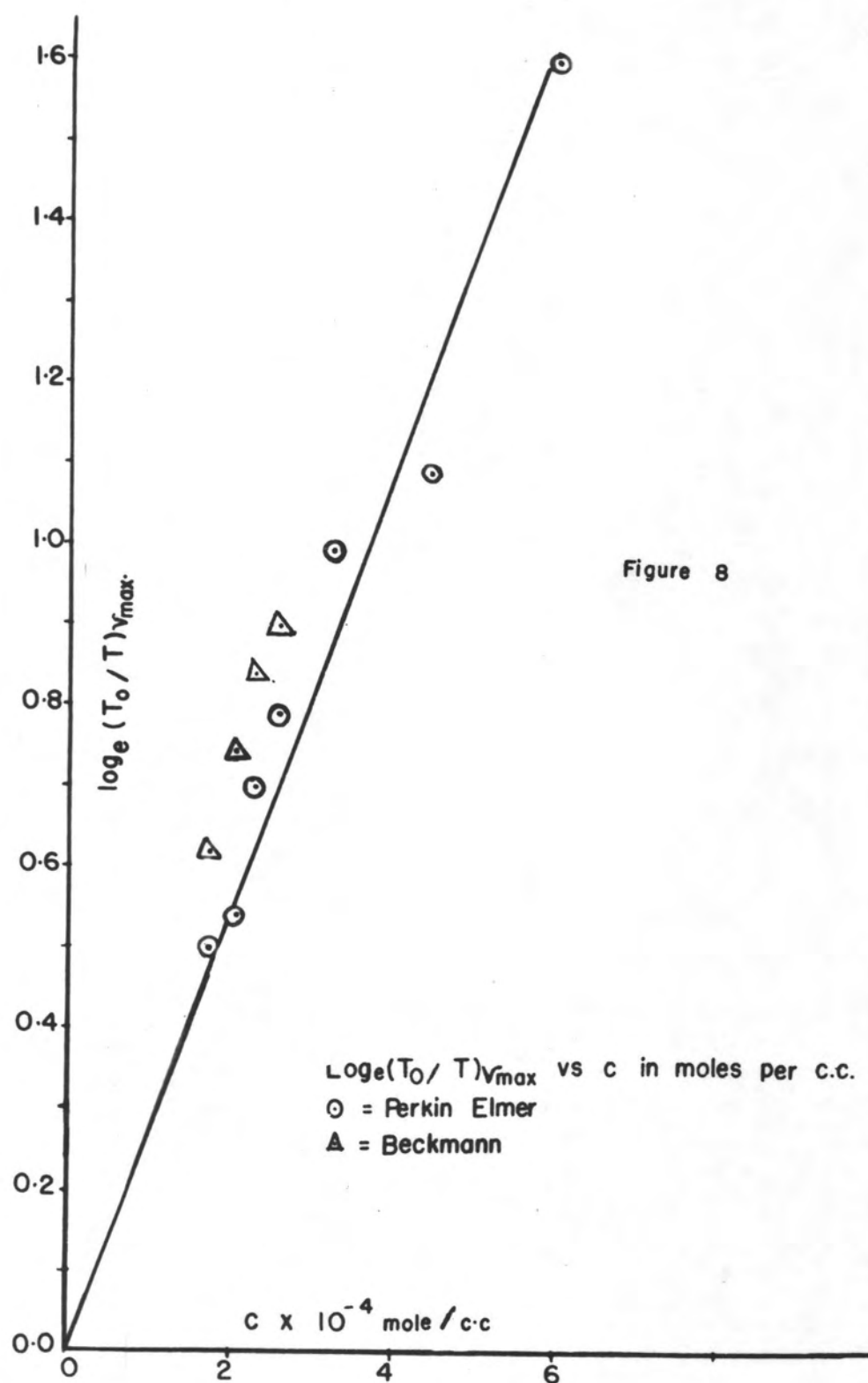
Table 4

Comparison of the absolute intensity ratios, theoretical and experimental.

Experimental	1.00
Calculated from Person equation	1.26
Calculated from Buckingham equation	1.28

Table 5

Chloroform			
a - Onsager	A_L/A_g	a - Van der Walls	A_L/A_g
3.2 Å	1.28	2.57 Å	1.58
Hexane			
a - Onsager	A_L/A_g		
3.73 Å	1.17		
Experimental			
A_L/A_g	a		
1.0	6.96 Å		



equations mentioned, it is just possible that the discrepancies observed in the calculated and the experimental values of the intensity ratios may be ascribed to some inadequacies in the Onsager equation for the total electric field acting on a spherical molecule in a polarized dielectric since both the Person and the Buckingham equations are derived from the Onsager equation.

The present situation with regard to the determination and study of the absolute intensities of simple molecules in gaseous, and in condensed phases, and in solution is not particularly a clear-cut one. Absolute intensities of very few simple molecules have been determined so far, and even in those few cases in which data is available, the results are conflicting. The aim of the present work was to obtain some more information concerning the absolute intensities by studying the bending mode of the chloroform molecule in n-hexane, and by comparing this data with the results of previous workers on the gaseous molecule.

BIBLIOGRAPHY

1. Bak, Borge. Elementary introduction to molecular spectra. New York, Interscience, 1954. 125 p.
2. Buckingham, A. D. A theory of frequency, intensity and band-width changes due to solvents in infrared spectroscopy. Proceedings of the Royal Society A 255:32-39. 1960.
3. Frenkel, J. Kinetic theory of liquids. New York, Dover, 1955. 488 p.
4. Herzberg, Gerhard. Infrared and Raman spectra. New York, Van Nostrand, 1945. 632 p.
5. . Molecular spectra and molecular structure. 1. Diatomic molecules. New York, Prentice-Hall, 1939. 592 p.
6. Morcillo, J., J. Herranz and J. Fernandez Biarge. Experimental determination of infrared intensities. Bond polar properties in CHF_3 and CHCl_3 . Spectrochimica Acta 14:110-121. 1959.
7. Person, Willis B. Liquid-gas infrared intensities, pressure-induced absorption and the temperature dependence of infrared intensities in liquids. The Journal of Chemical Physics 28:319-322. 1958.
8. Polo, S. R. and M. K. Wilson. Infrared intensities in gas and liquid phases. The Journal of Chemical Physics 23:2376-2377. 1955.
9. Ramsay, D. A. Intensities and shapes of infrared absorption bands of substances in the liquid phase. Journal of the American Chemical Society 74:72-80. 1952.
10. Smirnov, V. N. Study of the temperature dependence of the intensity of infrared absorption bands in solution. Optics and Spectroscopy 7:302-305. 1959.
11. Thompson, H. W. Vibrational band intensities and structural factors. Spectrochimica Acta 14:145-160. 1959.

12. Weissberger, A. (ed.) Technique of Organic Chemistry. Volume IX. Chemical applications of spectroscopy. New York, Interscience, 1956. 787 p.
13. Weissberger, A. and E. Proskaver. Organic Solvents. Oxford, The Clarendon Press, 1935. 212 p.
14. Wilson, E. B., Jr., J. C. Decius and P. C. Cross. Molecular Vibrations. New York, McGraw-Hill, 1955. 388 p.
15. Wilson, E. B. and A. J. Wells. The experimental determination of the intensities of infrared absorption bands. I. Theory of the method. The Journal of Chemical Physics 14:578-581. 1946.

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