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ED SPECTROSCOPY AND MOLECULAR STRUCTURE

# INFRA-RED SPECTROSCOPY AND MOLECULAR STRUCTURE

AN OUTLINE OF THE PRINCIPLES

*Edited by*

MANSEL DAVIES

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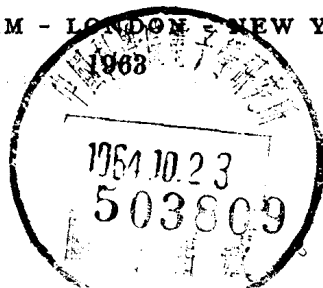
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ELSEVIER PUBLISHING COMPANY

AMSTERDAM - LONDON - NEW YORK



SOLE DISTRIBUTORS FOR THE UNITED STATES AND CANADA  
AMERICAN ELSEVIER PUBLISHING COMPANY, INC.  
52 VANDERBILT AVENUE, NEW YORK 17, N.Y.

SOLE DISTRIBUTORS FOR GREAT BRITAIN  
ELSEVIER PUBLISHING COMPANY LIMITED  
12B, RIPPLESIDE COMMERCIAL ESTATE  
RIPPLE ROAD, BARKING, ESSEX

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## Preface

This volume is intended to provide an introduction to the principles and practice of those aspects of infra-red spectroscopy which are of major interest in the study of molecular structure and molecular behaviour.

It is only since 1945 and the commercial production of recording spectrometers that the infra-red field has become generally accessible for routine investigation and use. The result has been a great proliferation of research studies and applications, so that the region has acquired major status in the broad area of spectroscopy. The greatest number of participants have been in laboratories devoted to chemical studies, whilst inevitably many of the basic developments have been made by physicists. Recent advances in the use of interferometric spectrometers, far infra-red techniques, and dispersion and reflection methods will be permanent influences in future studies. The advent of the computer, too, has awakened a renewed interest in the problem of defining the force-field within polyatomic molecules. This problem, despite its difficulties, cannot be side-stepped in the elucidation of the bonding conditions within molecules. Whilst the recognition of such characteristic aspects as group frequencies has made infra-red spectra of outstanding value in the qualitative definition of molecular structures, it is to be hoped that their quantitative evaluation can equally help in the precise representation of valency conditions.

The present chapters, however, have not been written to provide a survey of recent advances. Their particular aim is to outline the basic principles, to illustrate such success as is possible with current methods, and to indicate their potential scope and present limitations. Accordingly, there is no attempt to provide anything in the nature of an encyclopaedic coverage, but rather, after a general survey of infra-red studies, each specialist has emphasized what he regards as the essential bases of his topic.

It will be no surprise to those familiar with infra-red studies to find the Herzberg volume *Infrared and Raman Spectra of Polyatomic Molecules* frequently referred to for further theoretical detail. Few physical topics developed in the last forty years have been as fortunate in having so masterly a presentation of fundamental aspects as Herzberg provides.

One particular problem in planning the present volume was that of deciding whether specific introductions should be included to the relevant aspects of group theory and wave mechanics. It will be seen that this has not been done. However, adequate references are provided for those who

are not familiar with the symbolic languages of those mathematical methods. A further explanation is due in the general sense that the authors were restricted in the space available to them, and thus, to mention a specific instance, Dr. Martin originally illustrated many of his points by presentation of details from a variety of commercial infra-red spectrometers: most such variants have been omitted.

Finally, the editor wishes to record his thanks to the authors for their co-operation. Their contributions have cost them valuable time which they must have been loath to spare from their research and other activities. However – and despite some disadvantages in a multi-author work – the virtues of fundamental accounts by active leaders in each topic were successfully pressed upon them. In this respect it was a particular pleasure for the editor to be able to call upon three of his former research students as contributors. In addition, Dr. Norman Sheppard of Cambridge is gratefully thanked for his interest and help.

“If to do were as easy as to know what were good to do, chapels had been churches and poor men’s cottages princes’ palaces”.

*The Edward Davies Chemical Laboratories,  
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Aberystwyth.  
June, 1963*

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## Chapter I

### Introductory Survey

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#### (1) The Infra-red Region

The infra-red region of the spectrum extends from the visible (say 8000 Å) until it overlaps the micro-wave or very short radar range at wavelengths of some millimetres. Perhaps its basic characteristic is that over this region of approximately eleven octaves the principal source of radiation is thermal emission from a hot source: this contrasts with the selective emission of discharge tubes and similar sources in the visible and ultra-violet, and even more so with the electronic generation of radiation by valves or klystron sources in the radio and radar regions.

The physical optics of the infra-red is identical with that of the visible, with minor modifications due to the increased wavelength. The operational limit of the "visible" region is perhaps best taken as that set by photographic sensitivity (*ca.* 13,000 Å). Beyond that wavelength, the radiation must be detected and measured by the response of a thermocouple, bolometer or radiometer.

Wavelengths in the (non-photographic) infra-red have usually been given in microns:  $1\mu = 10,000\text{Å} = 10^{-4}\text{ cm}$ . It has now been accepted that the wavelength unit throughout the spectroscopic regions shall be the nanometre (nm).  $1\text{ nm} = 10^{-9}\text{ m} = 10\text{Å} = 10^{-8}\mu = 1\text{ m}\mu$ . Thus,  $7.65\mu = 7650\text{ nm}$ . Alternatively, and more significantly, the wavenumber, *i.e.* the number of waves per cm, is used to characterize the radiation. The wavenumber unit is the reciprocal centimetre,  $\text{cm}^{-1}$ , and so has the convenient values of 10,000  $\text{cm}^{-1}$  to 10  $\text{cm}^{-1}$  in the infra-red.

$$\bar{\nu} \text{ (wavenumber in cm}^{-1}\text{)} = 1/(\text{wavelength in cm}) = 1/\lambda$$

$$\text{As } \nu \text{ (frequency in sec}^{-1}\text{)} = c/\lambda$$

where  $c$  = velocity of electromagnetic radiation

$$= 2.9978 \cdot 10^{10} \text{ cm sec}^{-1}$$

$$\nu = c\bar{\nu}$$

As the quantum of energy ( $h\nu$ ) is exchanged when a molecule absorbs or emits the corresponding frequency, the wavenumber is proportional to this energy. From the values of  $h$  = Planck's constant,  $J$  = mechanical equiv-

alent of heat;  $N$  = Avogadro's number, it follows that a quantum of radiation of frequency  $\nu$  sec<sup>-1</sup> or wavenumber  $1$  cm<sup>-1</sup> has energy  $1.9862 \times 10^{-16}$  erg. Then  $1$  cm<sup>-1</sup>  $\equiv 1.9862 \times 10^{-16}$  erg/molecule  $\equiv 2.8593$  cal/g mole  $\equiv 11.962$  joule/g mole. Owing to this proportionality and to the further circumstance that the frequency of radiation is normally unchanged in passing from one medium to another whilst its wavelength varies with the refractive index, there is every reason for using the wavenumber as the unit in infra-red spectroscopic data. Although the frequency and wavenumber should be clearly distinguished, it is common practice in infra-red spectroscopy to use the same symbol ( $\nu$ ) for both, and thus to write "an absorption band at  $\nu = 1673$  cm<sup>-1</sup>". Little uncertainty can arise when the unit (cm<sup>-1</sup>) is indicated, but this should not be spoken of "a frequency of 1673": it is "a wavenumber of 1673".

## (2) Diatomic Molecules

Many of the basic aspects of molecular spectra are clearly seen in the case of diatomic molecules, and it will be helpful, here, briefly to review the behaviour of the diatomic molecule.

### (2A) The vibrational frequency

The formation of a simple (X-Y) molecule (or, more generally, of any

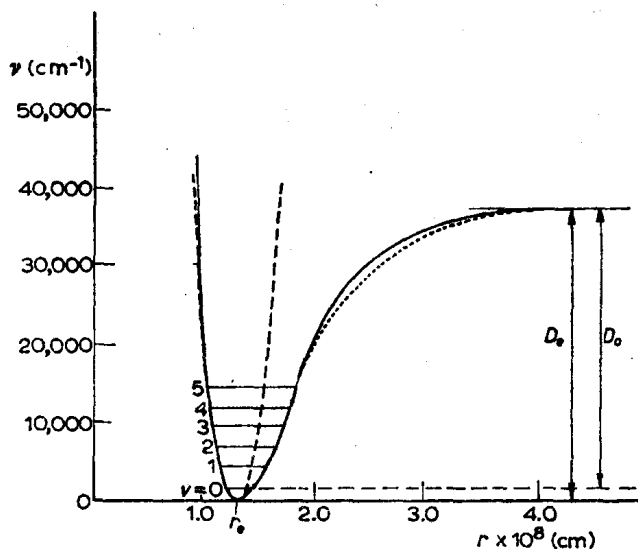


Fig. 1. 1. Potential energy curve for a diatomic molecule, drawn approximately to scale for hydrogen chloride. The full curve is drawn for the ground state of HCl. The broken line and the dotted curve are, respectively, the potential curves for the harmonic oscillator and the Morse function. The vibrational levels are drawn up to the level  $\nu = 5$ ;  $r_e = 1.2744$  Å.

chemical bond) can be envisaged energetically as arising from two forces: one of attraction which predominates at larger (X-Y) distances, and a second of repulsion which comes into play the more rapidly as the (X-Y) bond is compressed below its equilibrium length. These conditions give rise to the energy curve represented by the solid line in Fig. I, 1.

The minimum of the curve is taken as the arbitrary zero of energy. It is a reasonable first approximation (and the subsequent deductions confirm the adequacy of the assumption) to envisage the bonding force in the diatomic molecule as equivalent to the presence of an elastic spring. Quantitatively this means that any displacement, stretching or compressing, from the equilibrium bond length, will induce a restoring force proportional to the displacement and acting so as to reduce the displacement to zero: *i.e.* Hooke's Law is assumed to apply to the chemical bond near its equilibrium length. An immediate consequence is that slight displacement from equilibrium will lead to simple harmonic vibrations in the molecule. (See Fig. I, 2).

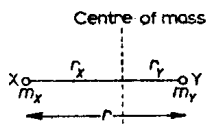


Fig. I, 2. A diatomic molecule XY.

The centre of mass (c.m.) is defined by  $m_X r_X = m_Y r_Y$ .

Using  $r = r_X + r_Y = r_X(1 + m_X/m_Y)$ ,

$$r_X = \left( \frac{m_Y}{m_X + m_Y} \right) r; \text{ and } r_Y = \left( \frac{m_X}{m_X + m_Y} \right) r.$$

If  $r_e$  is the equilibrium internuclear distance (see Fig. I, 1), stretching the bond will produce a displacement  $(r - r_e)$  and a restoring force  $-k(r - r_e)$ : the negative sign expresses the condition that the force operates against the displacement, and  $k$  is the (assumed elastic) force-constant, or rigidity modulus for the bond. Being the force for unit displacement, it is given in dyne per cm ( $\text{dyne cm}^{-1}$ ).

In the molecular vibrational mode of motion the centre of mass must not move – that would be introducing translational motion. Accordingly, the motion of the atoms is synchronized about the centre of mass and their equations of motion are

$$m_X \cdot \frac{d^2 r_X}{dt^2} = -k(r - r_e) = m_Y \cdot \frac{d^2 r_Y}{dt^2}$$

These are equivalent to

$$\frac{m_X m_Y}{m_X + m_Y} \frac{d^2 r}{dt^2} = -k(r - r_e)$$

or

$$\mu \frac{d^2(r-r_e)}{dt^2} = -k(r-r_e)$$

where  $\mu$  = mass factor for the vibrator =  $\frac{m_x m_y}{m_x + m_y}$  and  $r_e$  is, of course, a constant. This is the equation for simple harmonic motion. Writing  $(r-r_e) = x$ , the solution is

$$x = x_0 \sin(2\pi\nu_e t + \phi)$$

$x_0$  is the amplitude of vibration,  $\phi$  a phase angle constant and

$$\nu_e = \text{molecular vibrational frequency (sec}^{-1}\text{)} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad (1)$$

As in circumstances where energy ( $V$ ) is conserved

$$-k(r-r_e) = \text{force in the system} = -\frac{dV}{dr} = -\frac{dV}{d(r-r_e)}$$

$$V = \frac{1}{2}k(r-r_e)^2 + \text{constant}$$

The "constant" represents the arbitrary factor in fixing the energy scale for  $V$ . It is taken as zero in Fig. I, 1, and so fitting a parabolic function for that curve near its minimum.

This simple model predicts that the molecule would, classically, emit or absorb radiation of frequency  $\nu_e$  if it possessed a dipole. The latter is certainly a pre-requisite for infra-red absorption by a diatomic molecule: the homonuclear species ( $\text{H}_2$ ,  $\text{O}_2$ ,  $\text{Cl}_2$ , etc.) show virtually no infra-red spectra. The polar species ( $\text{HCl}$ ,  $\text{CO}$ , etc.) not only show absorptions at a principal frequency  $\nu_e$  but also progressively weaker absorptions at their first, second, third, etc. overtones, *i.e.* at frequencies approximately  $2\nu_e$ ,  $3\nu_e$ ,  $4\nu_e$ , etc. For the interaction with radiation of a classically oscillating dipole this again is a consequence of the anharmonicity of the vibrations. The qualitative dissymmetry of the energy curve means that the function  $V = \frac{1}{2}k(r-r_e)^2$  can at best fit only near the minimum.

### (2B) The energy function

A simple empirical approximation for the energy function is to write the attractive and repulsive terms as inverse powers of the distance:

$$V = \frac{\alpha}{r^m} - \frac{\beta}{r^n} \quad (2)$$

$\alpha$  and  $\beta$  are constants and  $m > n$ , to fit the predominance of repulsion at the shortest distances. In this expression the energy zero is taken for  $r = \infty$ .

Using the conditions

$$\left(\frac{dV}{dr}\right)_{r=r_e} = 0; \quad \left(\frac{d^2V}{dr^2}\right)_{r=r_e} = k;$$

it is readily found (Sutherland) that

$$k = \frac{m\alpha(m-n)}{r_e^{m+2}}; \text{ and } D_e = kr_e^2/mn.$$

These expressions correspond to various empirical and approximate findings correlating  $k$ ,  $r_e$  and  $D_e$  in diatomic molecules of similar character, where  $m$  and  $n$  do not vary markedly. Thus, using Raman spectra frequencies for  $O_2$  and  $S_2$ , the following sequence can be constructed:

Molecule	$O_2$	$S_2$	SO	CN	NO
$D_e/kr_e^2$ in arbitrary units	0.098	0.111	0.093	0.096	0.080

A far more generally satisfactory expression for the energy is the empirical function put forward by Morse (in 1929):

$$V = D_e[1 - e^{-a(r-r_e)}]^2 \quad (3)$$

Here  $a$  is a constant characteristic of the bond and the energy zero reverts to the  $r = r_e$  value.  $D_e$  is the dissociation energy measured to the minimum in the curve. The simple Morse function can be seen to have the following appropriate properties:

- (i) It has a single minimum at  $r = r_e$ ;  $V(r_e) = 0$ .
- (ii) At large separations the dissociation limit is approached and  $V(r = \infty) = D_e$ .
- (iii) At small separations the energy rises steeply and for  $r = 0$  becomes, as  $e^{ar_e} \gg 1$ , essentially  $D_e(e^{2ar_e})$  which usually exceeds  $10^3 D_e$ . This is a reasonable approximation to the virtually infinite value it should attain.
- (iv) For very small displacements,  $(r - r_e)$ , the exponential term is adequately expanded as

$$V = D_e[1 - \{1 - a(r - r_e)\}]^2 = D_e \cdot a^2(r - r_e)^2$$

Whence

$$k = d^2V/dr^2 = d^2V/d(r - r_e)^2 = 2D_e \cdot a^2$$

This relation gives the value of  $a$  from the vibrational frequency ( $\nu_e = (1/2\pi)\sqrt{k/\mu}$ ),

$$a = \pi\nu_e \cdot \sqrt{\frac{2\mu}{D_e}}.$$

This is the only adjustable parameter if  $D_e$  and  $r_e$  are regarded as defined for the molecule.



(v) Inserted in the Schrödinger wave-equation the Morse function allows of a precise solution for the energy values of the permitted quantised vibrational states. The energy levels are given by

$$E_{\text{vib}} = h\nu_e(v + \frac{1}{2}) - \alpha h\nu_e(v + \frac{1}{2})^2 \quad (4)$$

Here  $v$  is the vibrational quantum number,  $h$  is Planck's constant, and  $\alpha$  is the anharmonicity factor.

### (2C) The vibrational levels

This expression is of the exact form found most generally suitable to represent the vibrational energy levels. The bands in the visible and ultra-violet spectra of diatomic molecules frequently allow a long sequence of such levels to be measured. Such expressions for the energy levels were established before the quantum theory clarified their origin. Occasionally terms in higher powers of  $(v + \frac{1}{2})$  are added to equation (4).

As  $\alpha$  is a small positive factor (*ca.*  $10^{-2}$ ), it is seen that with increasing  $v$  the vibrational energy levels come closer together. At the dissociation limit there will be no further increase of  $E_{\text{vib}}$  possible, *i.e.* the limiting value of  $v_L$  is given by  $dE_{\text{vib}}/d(v + \frac{1}{2}) = 0$ , or  $(v_L + \frac{1}{2}) = 1/2\alpha$ . Substituted in (4), this gives

$$E_{L(\text{vib})} = D_e = h\nu_e/4\alpha \quad (5)$$

This important relation allows an estimate of  $D_e$  to be made from  $\nu_e$  and  $\alpha$ , factors readily observed for the ground state of the diatomic molecule from its infra-red absorptions. The  $D_e$  value will be precise only insofar as the energy curve strictly follows the Morse function: a discrepancy of ten per cent from the correct value of  $D_e$  would not be uncommon. The applicability of this relation for determining bond energies in polyatomic molecules would be even further restricted, but it could lead to useful values in some cases of interest.

The dissociation energy  $D_e$  measured from the minimum in the energy relation, differs from  $D_0$ , the energy often directly assessable in band spectra. The latter has the ground vibrational state  $v = 0$  as its reference level, and  $(D_e - D_0) = (\frac{1}{2}h\nu_e - \frac{1}{4}\alpha h\nu_e)$ . This is the zero point energy and measures the residual amount present in each vibrational mode even at the absolute zero of temperature.

Equation (4) embodies the result that the fundamental and the successively much weaker overtones are not found at wavenumber values  $\omega_e (= \nu_e/c)$ ,  $2\omega_e$ ,  $3\omega_e$ , etc., but rather at the values given by  $\Delta E_{\text{vib}}/hc$ .

$$\begin{aligned} \nu \text{ (fundamental absorption)} &= \nu (v = 0 \rightarrow v = 1) = \omega_e - 2\alpha\omega_e; \\ \nu \text{ (first overtone absorption)} &= \nu (v = 0 \rightarrow v = 2) = 2\omega_e - 6\alpha\omega_e; \\ \nu \text{ } (\overline{v}-1 \text{ th overtone absorption)} &= \nu (v = 0 \rightarrow v = v) = v\omega_e[1 - \alpha(v+1)]; \\ \nu \text{ ("hot" band in absorption)} &= \nu (v = 1 \rightarrow v = 2) = \omega_e - 4\alpha\omega_e. \end{aligned}$$