An Advanced Treatise on Physical Chemistry

by

J. R. PARTINGTON

AN ADVANCED TREATISE ON PHYSICAL CHEMISTRY

VOLUME FIVE

Molecular Spectra and Structure
Dielectrics and Dipole Moments

by

J. R. PARTINGTON

M.B.E., D.Sc.

Emeritus Professor of Chemistry
in the University of London

LONGMANS, GREEN AND CO
LONDON · NEW YORK · TORONTO

LONGMANS, GREEN AND CO LTD
6 & 7 CLIFFORD STREET LONDON W 1

ALSO AT MELBOURNE AND CAPE TOWN

LONGMANS, GREEN AND CO INC
55 FIFTH AVENUE NEW YORK 3

LONGMANS, GREEN AND CO
20 CRANFIELD ROAD TORONTO 16

ORIENT LONGMANS LTD
BOMBAY CALCUTTA MADRAS

First published 1954

Printed in Great Britain by Jarrold and Sons, Limited, Norwich

AN ADVANCED TREATISE ON PHYSICAL CHEMISTRY

By J. R. Partington, M.B.E., D.SC.

AN ADVANCED TREATISE
ON PHYSICAL CHEMISTRY

Vol. 1. Fundamental Principles.
The Properties of Gases.
Vol. 2. The Properties of Liquids.
Vol. 3. The Properties of Solids.
Vol. 4. Physico-Chemical Optics.

PREFACE

The subjects considered in the present volume, which are set out in detail in the Contents, fall into four main sections. Section X G, the part held over from Vol. IV, is an account of the theories of molecular spectra and molecular structure, treated in an elementary manner with the requirements of non-specialists in mind. The treatment comes between the over-simplified accounts of the subject in some books, and the detailed expositions in books written for specialists, which for the student of chemistry are perhaps too difficult yet nevertheless omit full consideration of some parts of the theory. Only typical examples are dealt with, the detailed treatment of the visible and ultraviolet absorption spectra of organic compounds, and their relation to chemical constitution, being outside the scope of the work. The general theoretical principles underlying infrared absorption and Raman spectra are the main interest.

Part of Section X G is based on lectures given to chemistry students over a period of years, and several points which seemed to offer difficulty have been explained in more detail than is usual. The part on molecular structure gives an account of the main methods of treatment, including the so-called valency-bond and molecular-orbital methods. The mathematical apparatus, including elementary accounts of spherical and ellipsoidal harmonics, matrix theory, and group theory, is incorporated in appropriate parts of the text, as was done in Vol. I, rather than in appendices.

Section XI A deals with the methods used for the measurement of dielectric constants. Some older methods are not neglected, since the author (who has done work in this field) feels able to assess the value of such information to the present-day worker more accurately than non-specialists. The most modern methods are also included. This section was in pages when Vol. IV was issued, but every effort was made to bring it up to date. This resulted in the information on microwaves appearing in three places, fully cross-referenced and indexed; since the two books on this subject had not been published when the text was written, it is based on the original sources. Quite a small part of the text deals with alternating-current theory, which is not usually very well comprehended by chemistry students. The nomenclature and symbols here, as in the rest of the book, are those used by specialists. Some information is given on imperfect dielectrics and dielectric loss, with a rather full bibliography, but it was felt that more detail would be outside the scope and interest of the volume.

Section XI B on dipole moments includes in some detail the methods used with solutions, since the most interesting and useful applications are to compounds which cannot be obtained in the gaseous state. The theories of the solvent effect are treated in some detail, since they have an importance and interest in other fields. A careful and critical selection of the literature has been made, and the treatment is not intended to be exhaustive.

Section XI C on hyperelectrics ("ferroelectrics"), although concise, covers most of the important aspects and, with the bibliographies in Vol. IV referred to, covers practically all the literature available at the time of writing, including the Japanese publications.

No list of publications is given; these are contained in earlier volumes, and since the symbols are those used by specialists, a list of symbols would serve no useful purpose, the same symbols being used with different meanings by actual workers in the different fields. There are 4056 literature references, distributed among countries of publication as follows:

United States of America, 1441
Great Britain and Ireland, 1007
Germany, 971
France, 192
Holland, 101
Japan, 98
India and Pakistan, 68
Russia, 61
Switzerland, 36
Italy, 20
Austria, 13
Denmark, 11
Poland, 8
Belgium, 6
Norway, 6
Sweden, 6
Australia, 4
Canada, 3
Finland, 2
Spain, 2

The author wishes to thank Professor T. S. Wheeler for reading part of Section X G in proof and making helpful comments, and those colleagues who sent him reprints of their papers or drew his attention to matters which otherwise might have been overlooked.

CAMBRIDGE, *August, 1954.*

ACKNOWLEDGMENTS

For permission to redraw diagrams we are indebted to the following:

Messrs. Macmillan & Co. Ltd. for Fig. 49.X G from Partington, *General and Inorganic Chemistry*; the author and the Oxford University Press for Figs. 50, 51, 53–55.X G from Coulson, *Valence*; the author and Messrs. Wepf & Co. for Figs. 34, 35, 37 and 39.X G from Jellinek, *Wellenmechanik*; Messrs. John Wiley & Sons, Inc. for Fig. 68.X G from Eyring, Walter and Kimball, *Quantum Chemistry*.

CONTENTS

SECTION X—Physico-chemical Optics

G—Elementary Theory of Molecular Spectra

SECTION XI—The Properties of Dielectrics

A—The Measurement of Dielectric Constants

B—Dipole Moments

C—Hyperelectrics

SECTION X

PHYSICO-CHEMICAL OPTICS

G. ELEMENTARY THEORY OF MOLECULAR SPECTRA

§ 1. Absorption and Extinction Coefficients

The law expressing the absorption of radiation by a material is usually called *Lambert's law,*[1] although it seems first to have been discovered experimentally by Bouguer.[2] If radiation of intensity I, the energy passing through unit area in unit time, passes through a length $\mathrm{d}l$ of a pure substance the change of intensity is:

$$-\mathrm{d}I=\varkappa I\mathrm{d}l, \tag{1}$$

where $\varkappa$ is called the *absorption coefficient.* The value of $\varkappa$ is independent of I and $\mathrm{d}l$ but depends on the wave-length λ of the radiation and on the chemical nature of the pure substance. By integration of (1):

$$\int \mathrm{d}I/I=-\varkappa\int \mathrm{d}l,$$

$$\ln I=-\varkappa l+\text{const.}, \tag{2}$$

where const. $=\ln I_0$, I_0 being the intensity of the radiation entering[3] the substance, and hence, by writing (2) in the exponential form (§ 13.I):

$$I=I_0\mathrm{e}^{-\varkappa l}. \tag{3}$$

Bunsen and Roscoe[4] used an *extinction coefficient* a defined by:

$$I=I_0 10^{-al}, \tag{4}$$

and hence related to $\varkappa$ by the equation:

$$a=\varkappa\log_{10}\mathrm{e}=0{\cdot}4343\varkappa. \tag{5}$$

$1/\varkappa$ is the length in which the intensity is reduced to $1/\mathrm{e}$ of its initial value, and $1/a$ the length in which it falls to $1/10$ of its initial value; $a<\varkappa$.

An important result, called *Beer's law,*[5] states that the fractional absorption, for a given cross-section, is independent of the length in which a fixed amount of absorbing substance is present. For example,[6] a length of 10 cm. of chlorine gas at 0·1 atm. pressure will absorb the same amount of radiation as a length of 5 cm. at 0·2 atm. pressure. If c is the concentration (e.g. in mols/lit.) of a substance, and $\varkappa'$ the absorption coefficient, then $\varkappa=\varkappa' c$, and:

$$I=I_0\mathrm{e}^{-\varkappa' cl}=I_0 10^{-a' cl}, \tag{6}$$

where a' is the *molar extinction coefficient.*

---

[1] J. H. Lambert, "Photometria sive de Mensvra et Gradibvs Luminis, Colorvm et Vmbrae," Augsburg, 1760, 394; Ostwald's *Klassiker*, 1892, **32**, 68.

[2] "Essai d'Optique," 1729; "Traité d'Optique sur la Gradation de la Lumiere, Ouvrage posthume," publ. by de la Caille, 1760, 306; Anding, in Ostwald's *Klassiker*, 1892, **33**, 59.

[3] Not that falling on the boundary of the substance, since some may be reflected.

[4] *Ann. Phys.*, 1857, **101**, 235; Bunsen, "Gesammelte Abhandlungen," Leipzig, 1904, **3**, 89.

[5] Beer, *Ann. Phys.*, 1852, **86**, 78; Kayser, "Handbuch der Spectroscopie," Leipzig, 1905, **3**, 1f.

[6] Von Halban and Siedentopf, *Z. phys. Chem.*, 1922, **103**, 71.

Beer's law holds strictly only when the solvent, in the case of a solution, does not absorb, and the molecules of solute do not influence one another or the molecules of the solvent. If several molecular species are present, each has its own extinction coefficient and Beer's law will *apparently* not hold for the solution, although it applies to each species separately.[1]

§ 2. Light Absorption in Dilute Atomic Gases

The effects of light absorption in dilute atomic gases may be grouped into four main classes.

(i) *Resonance Radiation.*[2] A beam of sodium light from a salted flame when passed into sodium vapour present in an evacuated glass bulb containing some sodium at 100° C., under a vapour pressure of about 10^{-7} mm., shows a yellow luminous track. Most of the sodium atoms are in the ground state $3s$ ($n=3$, $l=0$), and by absorption of a quantum of radiation such an atom is raised to the next higher energy level $3p$ ($n=3$, $l=1$). Most of these excited atoms fall back to the original ground state by the emission of the same quantum as they absorbed, and hence sodium light is emitted.

This phenomenon occurs only with radiation of such frequency that the corresponding quantum $h\tilde{\nu}$ is sufficient to raise the atom from its normal state to the next higher excited state. The atom in the excited state can then lose the quantum $h\tilde{\nu}$ in passing back to its normal state, and hence in this reverse change it emits the same kind of radiation as it previously absorbed. Such emitted radiation is called *resonance radiation.*

Another example is shown when light from a mercury lamp is passed into an evacuated quartz flask containing mercury at room temperature (vapour pressure 10^{-3} mm.), when resonance radiation $\lambda=2537$ A. is emitted. In this case the mercury atom in the ground state $^1S_0$ is raised to the next higher excited state $^3P_1$ and the reverse change occurs when the resonance radiation is emitted. The average life of an excited atom or molecule is usually of the order of 10^{-7} to 10^{-8} sec.

In some cases an excited atom, before it returns to its normal state with emission of radiation, may collide with another atom and give up to this the whole or part of its excitation energy. If only part of the excitation energy is transferred the rest appears as kinetic energy in the form of heat. Such collisions are called *collisions of the second kind.*[3]

(ii) *Fluorescence Radiation.*[4] This type occurs when illumination with light of one wave-length, e.g. $\lambda=3303$ A. into sodium vapour, brings about the emission of light of longer wave-length (e.g. the sodium double D-line 5898 A. and 5892 A.) or lower frequency. The production of the longer wave-length is in accordance with *Stokes's law*[5] for fluorescence. The excited molecule now falls to an energy level higher than the original ground state, since the emitted quantum is smaller than the absorbed quantum, to account for the smaller frequency. The sodium atom in the ground state $3s$ passes into an excited state $4p$ and returns to $3s$ by way of an intermediate level $3p$. In the transition $4p \rightarrow 3p$ no radiation is emitted but the energy is used in collisions of the second kind, in which part of the excitation energy is converted into kinetic energy of the atoms (heat). The transition $3p \rightarrow 3s$ gives rise to the emission of the sodium

---

[1] Weigert and Pruckner, *Z. phys. Chem.*, 1931, *Bodenstein Festb.*, 775.

[2] Mitchell and Zemansky, "Resonance Radiation and Excited Atoms," Cambridge, 1934.

[3] Willey, "Collisions of the Second Kind," 1937.

[4] Hirschlaff, "Fluorescence and Phosphorescence," 1938.

[5] Stokes, *Phil. Trans.*, 1852, **153**, 463.

D-lines. Such *Stokes transitions* give rise to radiation of longer wave-length than that absorbed. In a few cases, the so-called *anti-Stokes transitions*, the emitted light is of shorter wave-length (higher frequency), and in such cases the energy of the molecule after absorption of radiation is further increased by conversion of kinetic energy into internal energy of the molecule, which may add to the absorbed energy and so become available for the emission of a shorter-wave fluorescence line.

(iii) *Sensitised Fluorescence.* A quartz vessel containing thallium is heated to 800° C., when the thallium vapour has a pressure of 2 mm., and another quartz vessel containing mercury is heated to 100°, the two vessels being connected.

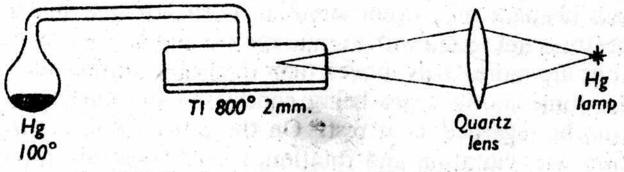

FIG. 1.X G. Apparatus for Sensitised Fluorescence

The mixture of thallium and mercury vapours is exposed to light from a mercury lamp focused by a quartz lens (Fig. 1.X G). The wave-length of the mercury light entering the vessel is $\lambda=2537$ A. The light emitted contains the mercury resonance line 2537 A. and also the thallium lines 2768, 3529, 3776, and 5350 A. The mercury vessel is now strongly cooled so that only thallium vapour is present, when it is found that no thallium lines are emitted, since thallium vapour does not absorb the line 2537 A. In the first experiment the mercury atoms are excited by the radiation 2537 A. An excited mercury atom collides with a thallium atom and gives it a smaller quantum than that corresponding with 2537 A. and the thallium atom is excited. The energy difference is transformed into kinetic energy. The excited thallium atoms then emit the lines as stated. Other examples of this sensitised fluorescence are found with mixtures of mercury and sodium vapours, when many sodium lines are emitted, especially the one corresponding with the transition of mercury from the excited to the ground state; and with mercury vapour and helium gas, when only mercury lines are emitted, since the energy of excitation of helium is high, 20 volts as compared with 4·86 volts for mercury.

Sensitised fluorescence may be used to detect collisions of the second kind. If an inert gas (e.g. argon) is added to the mixture of mercury and thallium vapours, the thallium fluorescence is greatly enhanced. A mercury atom is converted by absorption of 2537 A. into an excited state. It then collides with an inert gas atom and is brought into a somewhat lower excited state, which is metastable, i.e. cannot lose energy directly by radiation. In the metastable state the mercury atom can lose energy by collision with a thallium atom, and the excitation energy of the metastable mercury atom is practically quantitatively converted into fluorescence energy of the thallium.

(iv) *Quenching of Resonance Radiation.* Mercury vapour emits the line 2537 A. corresponding with an energy of 112,000 g.cal./mol, and addition of hydrogen gas quenches the emission, since the heat of dissociation of hydrogen is 100,000 g.cal./mol (H_2). Cadmium vapour emits 3262 A. and hydrogen also quenches the emission, but since 3262 A. corresponds with only 88,000 g.cal/mol, the hydrogen molecule in this case cannot be dissociated, as with mercury, but is raised to a higher rotational level of 3·84 volts, excited cadmium corresponding with 3·7 volts.

The above sketch may suffice to indicate some of the features of atomic absorption in so far as they may be required in what follows.

§ 3. Energy Levels and Quantum Numbers

In the emission or absorption of radiation by molecules, as contrasted with atoms, various kinds of energy changes may occur. An electron in the molecule may be raised to a higher energy level, giving *electronic spectra* (which are the only kind found with single atoms). There may also be processes in which the vibrational energy of the atomic nuclei changes, giving rise to *vibrational spectra.* The rotational energy of the molecule may also change, producing *rotational spectra.* These changes may occur simultaneously, so that molecular spectra show many features not found with atomic spectra and may be very complicated.

The electrons are more easily moved than the heavy atomic nuclei, and hence when the electronic motions are being considered the nuclei may, as a first approximation, be regarded as at rest. On the other hand, in considering the nuclear motion, viz. vibration and rotation, a mean position for the electrons may be assumed. The simplest case is the diatomic molecule, and this alone is considered until § 16.X G.

The elucidation of *molecular spectra*[1] is very much facilitated by the use of

---

[1] A short bibliography of publications on molecular spectra, dealing with material considered in the text is: *Bull. Nat. Res. Counc.*, 1926, **11**, iii (molecular spectra in gases, various authors); Acly, *Z. phys. Chem.*, 1928, **135**, 251 (nitriles); Badger and Mecke, *ibid.*, 1929, **5 B**, 333 (NH_3); Barnes, Liddel, and Williams, *Ind. Eng. Chem. Anal.*, 1943, **15**, 659 (summary, experimental); Bartholomé and Teller, *Z. phys. Chem.*, 1932, **19 B**, 366; Bartholomé and Karweil, *ibid.*, 1938, **39 B**, 1; 1938, **40 B**, 396; Birge, *Astrophys. J.*, 1922, **55**. 273 (theory of band spectra); Bonner, *J.A.C.S.*, 1936, **58**, 34 (vibration modes of C_2H_4; force constants); Bowen, "The Chemical Aspects of Light," Oxford, 1942; Czerny and Röder, *Ergebn. exakt. Naturwiss.*, 1938, **17**, 70 (methods); Dennison, *Rev. Mod. Phys.*, 1931, **3**, 280; 1940, **12**, 175; Dieke, *Physica*, 1924, **4**, 193 (review); Discussion, *Trans. Faraday Soc.*, 1929, **25**, 611–949 (various authors); Finkelnburg, *Hand- u. Jahrb. chem. Phys.*, 1934, **9**, ii, 189; *idem*, "Kontinuierliche Spektren," Leipzig, 1938; Freymann, *Ann. de Phys.*, 1933, **20**, 243 (short infrared and relation to chemical structure); Glasstone, "Recent Advances in Physical Chemistry," 3rd edit., 1936, 183 (elementary); "Theoretical Chemistry," New York, 1945, 141, 203; Henri, "Structure des Molécules," 1925; Herzfeld, in Geiger and Scheel, "Handbuch der Physik," 1933, **24**, ii, 891; Herzberg, "Molekülspektren und Molekülstruktur," Dresden and Leipzig, 1939; transl. Spinks, "Molecular Spectra and Molecular Structure," New York, 1939; 2nd edit. (Herzberg), "Molecular Spectra and Molecular Structure. I. Diatomic Molecules," New York, 1950; "Infra-red and Raman Spectra of Polyatomic Molecules," New York, 1945; Herzberg and Teller, *Z. phys. Chem.*, 1934, **21 B**, 410; Hund, *Z. Phys.*, 1926, **36**, 657; 1927, **40**, 742; 1927, **42**, 93; 1927, **43**, 805; *Z. Elektrochem.*, 1930, **36**, 596; Hulthén, *Physica*, 1921, **1**, 365 (review); Jellinek, "Lehrbuch der physikalischen Chemie," 1937, **5**, 687; Jevons, "Report on the Band Spectra of Diatomic Molecules," 1932; Johnson, *Sci. Progr.*, 1927, **22**, 231; *idem*, "An Introduction to Molecular Spectra," 1949; Kemble, *J. Franklin Inst.*, 1928, **206**, 27 (elementary); Kronig, *Congr. Internat. Élec.*, 1932, **1**, No. 2 (isotope effect); "Band Spectra and Molecular Structure," Cambridge, 1930; "The Optical Basis of the Theory of Valency," Cambridge, 1935; Laski, *Ergebn. exakt. Naturwiss.*, 1924, **3**, 86; Lecomte, "Le Spectre infra-rouge," 1928; *Leipziger Vorträge*, 1931, Molekülstruktur (various authors); Matossi, *Ergebn. exakt. Naturwiss.*, 1938, **17**, 108 (results); Mecke, *Phys. Z.*, 1925, **26**, 217; *Z. Phys.*, 1927, **42**, 390; *Fortschr. Chem. Phys. phys. Chem.*, 1929, **20**, iii; *Nature*, 1930, **125**, 526; *Z. Elektrochem.*, 1930, **36**, 589; *Z. phys. Chem.*, 1930, **7 B**, 108; 1932, **16 B**, 409, 421; 1932, **17 B**, 1 (valency and deformation vibrations); *Hand- u. Jahrb. chem. Phys.*, 1934, **9**, ii, 281; Moelwyn-Hughes, "Physical Chemistry," Cambridge, 1940, 380, 448; Mulliken, *Proc. Nat. Acad.*, 1926, **12**, 338; *Z. Elektrochem.*, 1930, **36**, 603; *Rev. Mod. Phys.*, 1930, **2**, 60; 1932, **4**, 1; *J. Phys. Chem.*, 1937, **41**, 5, 159, 299 (historical and systematic); Olson and Kramers, *J.A.C.S.*, 1932, **54**, 136 (acetylene); Placzek, in Marx, "Handbuch der Radiologie," 1934, 6, ii; Planck, *Ann. Phys.*, 1917, **52**, 491; 1917, **53**, 241 (old quantum theory of rotation spectra); Rabinowitsch, *Z. Elektrochem.*, 1931, 37, 91; 1932, **38**, 370, 451 (review); Rawlins and Taylor, "Infra-Red Analysis of Molecular Spectra," Cambridge, 1929; Ruedy, "Bandenspektren auf experimenteller Grundlage," Brunswick, 1930;

diagrams of *energy levels*, and Fig. 2.X G shows such a diagram for a diatomic molecule. The lowest line in A represents the energy of the molecule in its *ground state*, when it has its lowest energy. In this case, the electrons are in their lowest energy levels, there is no vibration of the atomic nuclei (zero-point energy is, for the present, omitted), and there is no rotation of the molecule as a whole. Above v are written the *vibrational quantum numbers* of the molecule, $v=0$, 1, 2, 3, . . ., and the lines drawn from them represent increasing vibrational energies for an unchanged electronic energy of the molecule. The molecule with a given electronic energy level and a given vibrational energy level may have different

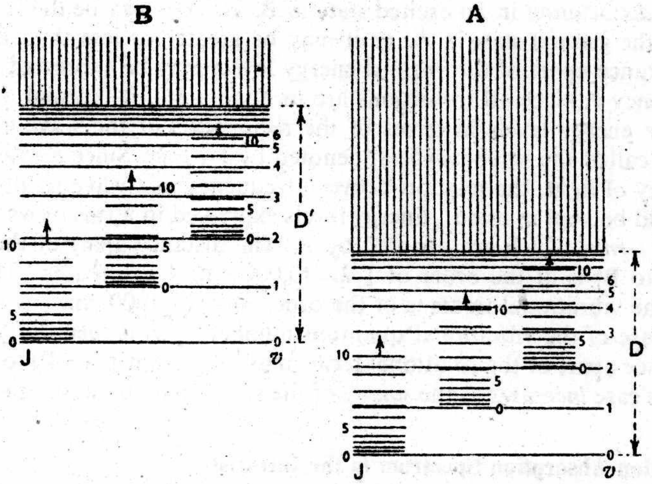

FIG. 2.X G. Energy Levels for Diatomic Molecule

rotational energies, and these are specified by the *rotational quantum number J*, the values of which are shown; these values are $J=0$, 1, 2, 3, . . ., and each vibrational level may have these values for the rotational energy. These levels give *fine structure* to the vibrational levels. Each vibrational level begins with $J=0$, and has higher values with increasing rotational energy, beginning with $J=1$. Each of the short lines, therefore, indicates a particular state of a molecule, e.g. it may have a vibrational energy corresponding with $v=2$, and a rotational energy corresponding with $J=4$, and this state would be represented by the fourth short line above the long line labelled $v=2$.

With increasing vibrational energy, the lines crowd closer together, as is seen, and the nuclei are then vibrating more and more intensely. When the energy of the molecule reaches a certain definite value, the vibration of the nuclei becomes so intense that they fly apart and the molecule dissociates into atoms. From this level the energy is absorbed continuously, as shown in the shaded portion of the diagram, no lines being detectable in this part. The case being considered, it is seen, is absorption of radiation by the molecule. On the other hand, if the molecule in a state above the ground state loses energy so that it

---

Schaefer and Matossi, "Das ultrarote Spektrum," Berlin, 1930; Scheibe and Frömel, *Hand- u. Jahrb. chem. Phys.*, 1936, **9**, iv, No. 4; Sponer, "Molekülspektren," 2 vols., Berlin, 1935–6; Sutherland, "Infra-Red and Raman Spectra," 1935; Teller, *Hand- u. Jahrb. chem. Phys.*, 1934, **9**, ii, 43; Tisza, *Z. Phys.*, 1933, **82**, 48; Thompson, "Chemical Spectroscopy," Oxford, 1938; Wall, *J.A.C.S.*, 1938, **60**, 71 (C_2H_6 and $CH_3.C{\equiv}CH$); Weizel, *Z. Elektrochem.*, 1930, **36**, 599; *idem*, Bandenspektren, supplement to Wien-Harms, "Handbuch der Experimentalphysik," 1931; Wu, "Vibrational Spectra and Structure of Polyatomic Molecules," Ann Arbor, 1946.

falls either into the ground state or into a lower state than its initial state, it will emit energy, and since the transition is always between definite quantum states, it will emit a spectrum line of given frequency, just as when its energy is raised above the ground state, it absorbs a line of given frequency.

The lowest level in B denotes a state of the molecule in which, by absorption of radiation, the electronic energy is altered by a single electron being in a higher energy level than in its ground state in A. In the lowest level in B it has no vibrational or rotational energy. Above, the vibrational and rotational levels are shown as in case A. Transitions from a level in A may occur to a level in B. The *energy of dissociation* in an excited state in B, viz. D', may be the same as that, D, above the ground state in A, or it may be greater or less than this.

The distance apart of the various energy levels may be expressed in terms of the frequency $\tilde{\nu}$, since all transitions are in quanta $h\tilde{\nu}$. It is usual, however, to specify the energy levels in terms of the reciprocals of the wave-lengths, $1/\lambda$, which are called the *wave-numbers*, denoted by $\nu = 1/\lambda$. Since $c = \tilde{\nu}\lambda$, where c is the velocity of light, the relation between frequency and wave-number is $\tilde{\nu} = c\nu$. This should be kept in mind. Energy levels expressed in terms of wave-numbers are called *terms*, which are denoted by T. The distance apart of the electronic terms (A to B) is of the order of $1/\lambda = 10{,}000$ cm.$^{-1}$ or greater. The distance apart of the vibrational terms is of the order of $1/\lambda = 1000$ cm.$^{-1}$ and *decreases* with increase of the vibrational quantum number v, as is seen on the diagram. The distance apart of the rotational terms may vary from $1/\lambda = 10$ to 100 cm.$^{-1}$, and in this case *increases* as the *square* of the rotational quantum number J.

§ 4. Rotation Absorption Spectrum in the Infrared

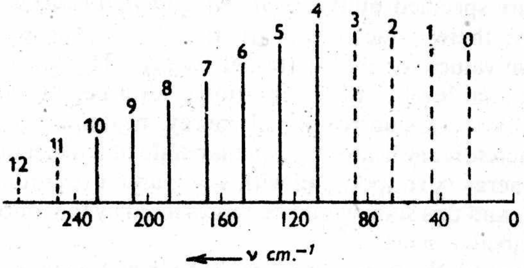

FIG. 3.X G. Pure Rotational Absorption Spectrum of Hydrogen Chloride

Transitions between purely rotational terms, i.e. changes of J without change of v and with fixed electronic energy, give rise to the lines constituting the so-called *pure rotational bands*. These are found only in the long (or far) infrared, $\lambda \simeq 100\ \mu$ or $\nu \simeq 100$ cm.$^{-1}$. This is because the heavy nuclear masses rotate relatively slowly. An important feature of pure rotational bands is that they are produced only by polar molecules, having a permanent electric moment, such as hydrogen chloride, HCl. Fig. 3.X G shows the lines of the pure rotational spectrum (for absorption) of hydrogen chloride, the height of the vertical line being proportional to the intensity of absorption. Dotted lines represent positions where rotational lines might be expected but are not observed. The distances between the lines is practically constant.[1]

The theory of pure rotational bands is based on the expression given by the new quantum theory (§ 19.IV) for the angular momentum of the diatomic molecule:

$$p_r = I\tilde{\omega} = (h/2\pi)\sqrt{[J(J+1)]}, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where $\tilde{\omega}$ is the rotational frequency, I the moment of inertia of the molecule,

---

[1] Bjerrum, *Z. Elektrochem.*, 1911, **17**, 731; *Nernst Festschr.*, 1912, 90.