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Infrared Spectroscopy of Diatomic Molecules-the First Century

J. F. Ogilvie Academia Sinica, Institute of Atomic and Molecular Sciences Taipei IO 764, Taiwan R. O. C. P. O. Box 23-166 (Received July 18, 1989)

A survey of the progress in the experimental measurement and theoretical interpretation of the vibration-rotational spectra of diatomic molecules during the period 1889-1988 is made, with special reference to the spectra of HCl and CO as illustrative molecules.

I. INTRODUCTION

Although there was in the preceding decades a steady if erratic development of research in the infrared region of the electromagnetic spectrum, we may take the year 1889 to make the effective beginning of infrared spectroscopy. In that year the first spectra within the range of wavelengths between 2.5 μ m and 25 μ m were recorded in the laboratory of Knut Ångström. That wavelength range, now known as the mid infrared region, contains most fundamental modes of vibration of all molecules (or materials) but the most massive and the least massive (1H2). Furthermore because almost all this range is beyond the transmission limit of traditional optical glasses and even silica, the ability to make optical measurements throughout this range requires a different technology. During the past century there have of course been achieved immense advances in the instrumental technology that now make possible routine measurements from the radio-frequency region to the visible. During the first half of this period since 1889, there was also developed a mechanical formalism which in association with the quantum-mechanical methods permitted a broad interpretation of the nature of the vibrational and rotational spectra of diatomic and polyatomic molecules. The first monograph' to provide a coherent and thorough description of the existing treatments of the vibration-rotational spectra of polyatomic molecules appeared in 1939; although prepared under difficult conditions (in time of war), nevertheless Wu's book evidently had a significant influence on the content and treatment in Herzberg's later, enduring monograph*.

In this essay we review some features of the development of vibration-rotational spectroscopy, with emphasis. on the physical principles and applications. Because poly-

atomic molecules now represent far too broad a topic for any brief review that could be meaningful. we take as our particular subject the infrared spectroscopy of diatomic molecules. especially referring to HCl and CO. Diatomic molecules have always had a special attraction for physicists because the abundant data and the relative simplicity of the system of effectively a single oscillator, even though anharmonic, have provided scope for increasingly sophisticated theoretical treatments. By 1923, Randall had already recognised³ the importance both of the theoretical description of vibrational and rotational motions and of the experimental information about HCl in particular that could serve as a test of any new theory. We also refer to pertinent information from other experimental methods in order to complement the picture of a mature discipline within physical science.

11. THE EARLY YEARS

Knut Angstrom (1857-1 9 10) became 'Laborator' (roughly equivalent to associate professor) in the Institute of Physics in Stockholm in 1885, the year of the institute's foundation. He was the son of the more renowned scientist Anders Jonas Angstrom who, during appointments in Uppsala University as Observator in astronomy from 1843 and professor of physics after 1858, prepared a detailed atlas of the wavelengths of solar radiation; every spectral line used as a standard was specified to the precision 10^{-10} m, a unit later named in his honour. His son Knut also became professor of physics in Uppsala in 1896, but his pioneering studies of infrared radiation, later from the sun as well, were done in Stockholm. An appreciated lecturer, he designed and constructed himself the instruments he used, even the most complicated.

In 1800 F. W. Herschel discovered the infrared region in a classic' experiment in which solar radiation dispersed by a glass prism was detected by means of thermometers (mercury in glass) having blackened bulbs; the movement of one such thermometer across the visible projection of the solar spectrum from violet to red led to progressively greater readings of temperatures, relative to another thermometer kept aside as a control, with a still further temperature rise beyond the visible. In 1834, with the aid of a thermopile having 27 elements, Melloni in France noticed the high transparency of the mineral rocksalt (NaCl) in the infrared. Bunsen and Kirchhoff constructed the first proper spectrometers for the visible region about 1850, and spectrosocopy as a distinct scientific activity may be considered to date from that time. One of the founders of modern photography, William Abney also deserves credit for the discovery of the first applications of infrared spectroscopy in chemical analysis when with Festing in 188 1 he studied the infrared absorption by 46 organic liquid substances in the photographic infrared region by means of a Hilger spectrograph; together they clearly understood the potential applications of characteristic vibrations of molecular fragments in organic chemistry. Of major importance to the further progress of infrared spectroscopy was the invention of the bolometer as a detector of infrared radiation beyond the photographic limit; S. P. Langley made this achievement in

188 1 at the Allegheny Observatory in Pittsburgh U.S.A.

With the benefit of this experimental background Ångström was able to make the first measurements of the fundamental vibrational modes (transitions involving the change of a vibrational quantum number from zero to one). In this first experiments he showed that, because two different gaseous compounds of carbon and oxygen CO and CO, had different spectra, infrared absorptions in this region arose from molecular not atomic activity; of course practically all the modem applications of infrared spectrophotometry in analytical chemistry are based on this fact. Also in 1889 he recorded the infrared spectra of methane, ethene, diethyl ether, benzene and carbon disulphide, the latter compounds in both the liquid and vapour phases. Soon after, Julius in Holland recorded the spectra of 20 organic liquid substances as far as 10 μ m. Both investigators used prisms and lenses of NaCl and bolometers as detectors. Many more details of the general history of the early years of spectroscopy may be found in the delightful accounts by Bart⁴ and Jones'.

111. INFRARED SPECTROSCOPY OF **HCl** AND CO

We illustrate the progress over the years of both the experiments in infrared spectroscopy and the associated theory by reference to the particular chemical compounds hydrogen chloride HCI and carbon oxide CO as dilute gaseous samples. In a broad sense, the history of the studies of the diatomic molecules comprising these substances exemplifies the development of infrared spectroscopy of gaseous samples as a whole.

Ångström and Palmaer⁶ measured the first infrared absorption of gaseous HCl in 1893. At a wavelength 3.4 μ m they observed a single absorption peak. Noting in the same paper that gaseous Cl₂ lacked any such absorption in the infrared region, they had discovered the fundamental distinction between the infrared activity of vibrations of homonuclear and heteronuclear diatomic molecules, although the wavelength of the fundamental mode of Cl₂ actually lay beyond the spectral region in which they were then able to make measurements. The spectrum of HCl that they had detected might be imagined to resemble that in figure 1. The physical origin of this spectrum was initially enigmatic, but Julius



FIG. 1 Infrared absorption spectrum of the fundamental band of HCl at an effective resolution 2.56x10⁴ m⁻¹. The pressure of HCl in a cell of length 0.1 m was 1.6x10⁴ Pa, and the temperature of the sample was 296 K. The ordinate scale, although linear in absorbance, conveys no particular significance.

drew⁵ the general conclusion that the absorption is due to internal motions in the molecule and that the internal structure determines the spectrum. In 1904 Drude proposed⁷ the theory that such infrared absorption by many substances was associated with the vibration of electrically charged atoms, not the oscillations of electrons. In 1910 Eva von Bahr working in the laboratory of Professor Heinrich Rubens in the University of Berlin confirmed' the observation of the single broad line in the absorption spectrum of HCl. However, after Burmeister (1913) used a fluorite (CaF₂) prism to detect' two distinct maxima. similar to figure 2, in the absorption at 3.40 and 3.55 μ m, she extended his work



FIG. 2 As figure 1, except resolution $6.4 \times 10^3 \text{ m}^{-1}$

by means of a quartz prism and found" twelve maxima, similar to figure 3. These maxima were attributed to the quantised rotation associated with the same vibrational transition. Already at the First Solvay Conference in 1911, Nels Bjerrum, professor of physical chemistry in Copenhagen, had proposed the first quantum theory of molecules in which he introduced" the concept of three forms of molecular energy, translational, rotational and vibrational. In accordance with Lord Rayleigh's principle¹² (1892), Nernst had also concluded¹³ in i 911 that rotational model.



FIG. 3 As figure 2, except resolution $1.6 \times 10^3 \text{ m}^{-1}$

As a result of this theoretical work, the rotational energy W_R was taken to be equal to an integer number n of photons, each of energy $h\nu$ (following Planck^{14,15}),

$$W_{\rm R} = \frac{1}{2} I (2\pi\nu)^2 = nh\nu \quad , \tag{1}$$

and the corresponding rotational frequencies were then given by

$$\nu = nh \ (2\pi^2 I)^{-1} \tag{2}$$

In these equations the symbols h, I and ν denote respectively the Planck constant, the moment of inertia about the molecular centre of mass, and the frequency (in Hz). Note that the second equation implies a constant difference of energy between adjacent rotational states. Aware o' f Rutherford' s then recent model¹⁶ of the nuclear atom, von Bahr used¹⁷ the measured frequency interval in HCl Av ~ 6.6 x 10¹¹ Hz to calculate the moment of inertia I ~ 5.1 x 10⁻⁴⁷ kg m², implying a bond length (internuclear distance) ~ 1.8 x 10⁻¹⁰ m. She also noted that the frequency interval was not constant, but varied regularly across the band, in accordance with Eucken' s suggestion¹⁸ that the moment of inertia might increase with an increasing speed of rotation because of centrifugal stretching of the chemical bond.

Two comments on Bjerrum's theory" and its application to HCI are pertinent. First, the factor one half, instead of one quarter, in the first equation leads to an incorrect value of the bond length; the latter number yields a value ~ 1.27×10^{-10} m that is remarkably similar to the most recent value¹⁹ (1.274603 ± 0.000003) × 10^{-10} m that has a nominal uncertainty smaller than the nuclear radius of either H or Cl. Second, this early theory predicted three prominent features (branches) of the band near $\lambda \sim 3.5 \,\mu$ m; the observation of only two maxima or branches was interpreted to imply the absence of nonrotating molecules. We now know of course that nonrotating molecules, those having the rotational quantum number' of value J = 0 do exist and are in fact essentially solely responsible*' for the polarisation effects in HCl (the temperature dependence of the relative permittivity). The absence of the central maximum in the absorption spectrum of the gaseous HCl at small pressures reflects the selection rule AJ = ±1, but not 0, for electric dipole transitions.

Also about 1911, Rubens and Wartenburg observed²¹ strong absorption of gaseous HCl, albeit unresolved into individual components, much farther into the infrared, in the range $21 < \lambda/\mu m < 35$. Some years later, Czemy resolved²² six lines in the adjacent region $42 < \lambda/\mu m < 100$. These absorptions were all associated with the motion of molecular rotation, and comprise what is commonly called the pure rotational band.

In 19 19 by means of a double monochromator incorporating both a prism and a diffraction grating, Imes not only obtained²³ a spectrum of the band at 3.4 μ m with greatly improved resolution, similar to figure 4, but also measured similarly a second band at 1.76 μ m previously detected²⁴ by Brinsmade and Kemble. Kemble had predicted²⁵ the occurrence of an harmonic band at half the wavelength of the fundamental absorption, and both Coblentz²⁶ and Burmeister⁹ had already detected such an harmonic band of CO. In

analysing his data for HCl. Imes applied the theory of Ehrenfest²⁷ and Eucken¹⁸, justified²⁸ by Kemble, that used $\frac{1}{2}h\nu$ as the energy quantum of rotation (instead of $h\nu$ of Bjerrum);



FIG. 4 As figure 3, except resolution $4.0 \times 10^2 \text{ m}^{-1}$.

thus Imes fortuitously obtained²³ an accurate value ~ 1.28×10^{-10} m of the bond length of HCl. Another interesting feature of the dvertone band, made possible by the improved resolution and the greater splitting of the adjacent pairs of lines than in the fundamental band, was the apparent doubling of each of the spectral lines, seen in the fundamental band in figure 5. Subsequently Kratzer²⁹ and Loomis³⁰ interpreted this doubling as evidence for the detection of the two isotopic species H³⁵Cl and H³⁷Cl.



FIG. 5 As figure 4, except resolution $1.0 \times 10^2 \text{ m}^{-1}$.

A further new feature in the absorption spectrum of HCl in the fundamental region appeared³¹ when Colby et al heated a gaseous sample to a temperature ~ 775 K. They observed near $\lambda \sim 3.8 \,\mu m$ an additional set (a 'hot' band) of weak lines that were attributed to molecules undergoing transitions from initial states that were vibrationally excited.

Several years after individual vibration-rotational lines were resolved and their wavenumbers (reciprocals of wavelengths) determined, measurements of the intensities of spectral lines were begun, the pure rotational transitions by Badger³², the lines in the

fundamental band by Kemblc and Bourgin³³ and by Bourgin³⁴, and the overtone band by Dunham³⁵. These measurements provided detailed information on the electrical properties of the HCl molecule, specifically on the variation of dipole moment with internuclear distance.

In the decades approaching the present, further measurements of increased accuracy and range of wavelength have been made. In 1979 Meyer and Levin made³⁶ accurate measurements of the isotopic splitting of the lines in the fundamental band. as in figure 5. Herzberg and Spinks³⁷, Lindholm³⁸, and Naudé and Verleger³⁹ photographed additional overtone bands in the near infrared, almost to the visible region. Benedict et al measured⁴⁰ not only the shapes of lines (broadened by HCl and foreign gases) in the fundamental, firstand second-overtone bands but also the intensities of lines in several hot bands. Rank et al made⁴¹ accurate and extensive measurements of HCl in an heated absorption cell, and Rank then combined⁴² the infrared measurements (in the units of vacuum wavenumber or inverse vacuum wavelength) with microwave data (in frequency units) in order to derive a precise value of the velocity of light in vacuum. In the same year that Toth et al measured⁴³ many lines in the second-overtone band, Kaiser reported accurate values of many spectral parameters obtained⁴⁴ by means of an electric-resonance spectrometer with a molecular beam. Using a long path of absorption, Gelfand measured⁴⁵ both the wavenumbers and intensities of lines in bands up to the sixth overtone (v' = 7 <- v'' = 0) extending into the green part of the visible spectrum. In contrast, Reddy measured⁴⁶ two of these visible bands by placing a gaseous sample within the optical cavity of a laser, thereby increasing the sensitivity of detection of the very weak absorption. The extension of microwave techniques into the millimetre-wave region has permitted the extremely precise measurements⁴⁷ of several transitions of HCl and DC1 in which the hyperfine structure, arising from the coupling of nuclear and rotational angular momenta, has been resolved. Such nuclear effects in vibration-rotational spectra have also been resolved, not for HCl but for HI⁴⁸.

Over the years, additional data on isotopic variants have become available. Not only for the most abundant species ${}^{1}H^{35}Cl$ and ${}^{1}H^{37}Cl$ have absorption spectra been measured in various spectral regions, but also for these chlorine nuclides in combination with ${}^{2}H$ (D) and ${}^{3}H$ (T) isotopes. The spectra of DC1 were measured first in natural abundance⁴⁹ then later in enriched samples⁵⁰, both with grating spectrometers, and more recently with an interferometer⁵¹, with resolution similar to that in figure 6. In contrast, the existing vibration-rotational spectra of TC1are⁵² of poor resolution and wavenumber accuracy according to modem standards, although one pure rotational line of each of T³⁵Cl and T³⁷Cl has been precisely measured⁵³.

Complementary to the these absorption spectra of HCl have been the emission spectra measured under various conditions. Cashion and Polanyi observed⁵⁴ chemiluminescence from the reaction of H atoms with gaseous Cl_2 , whereas Mould et al produced⁵⁵ the emission by means of an electric discharge in gaseous HCl. Precise measurements of emission from a hydrogen-chlorine flame were made⁵⁶ by Clayton et al. Stimulated emission processes in HCl have also been detected, in both vibrational⁵⁷ and rotational" * transitions. Earlier, Polanyi had proposed" that the vibrationally excited HCl from the



FIG. 6 As figure 5, except resolution 6.2 m⁻¹, pressure 1.6 X 10³ pa,

reaction of H with Cl, could be the basis of a chemical laser. Further information about vibrational states in the range up to v = 17 for HCl⁶⁰ and v = 23 for DCl⁶¹ has been obtained from electronic emission spectra in the far ultraviolet. A different type of vibration-rotational emission spectra occurs in Raman scattering. The first Raman spectrum of any gaseous sample showed⁶² for HCl a single strong line at a wavenumber shift from various Hg exciting lines midway between the two branches in the absorption spectrum of the fundamental band, plus series of weaker lines with spacing about double the separation of the infrared bands. These wavenumber displacements are well understood in terms of the Raman selection rules, $\Delta J = 0, \pm 2$.

For CO, less extensive research has been carried out, but the wavenumbers and intensities of the second⁶³ and third⁶⁴ overtones have been measured. The fourth overtone of CO has apparently not yet yielded to detection, although the corresponding transition in the analogous molecule NO has been easily observed⁶⁵. Unlike HCl so far, the infrared absorption spectrum of CO expanded in a supersonic jet has been recorded⁶⁶ by means of an interferometer; the temperature, for instance -6 K downstream 11 mm from the nozzle, would be wholly impracticable to maintain in a static gas in conventional measurements in the laboratory, although molecular clouds in outer space from which microwave emission of CO has been detected are characterised by similar conditions.

Having almost 1000 discrete lines available from a few isotopic variants, the CO laser is an important source for various infrared experiments. The wavenumbers of thousands of vibration-rotational lines of several isotopic species have been analysed⁶⁷, as have also the intensities⁶⁸ of many hundreds of lines. Although all the measured lines were in sequences $\Delta v = 1$, 2 and 3, the highest vibrational and rotational states attained were v' = 41 and J' = 93 respectively.

Although this survey of the (mainly) infrared spectroscopy of HCI and CO is not meant to be exhaustive, we have intended to indicate the extent and the diversity of the kinds of

spectral measurements of HCl and CO that have been made since Angstrom's original experiments.

IV. RELATED THEORETICAL DEVELOPMENTS

Although in the earliest days of spectroscopy the metrological aspects were sufficiently challenging, soon the physical interpretation became more important. After the general accord that the infrared spectra (and their Raman counterparts) of gaseous samples at small densities provided information about the transitions between the vibrational and rotational states of the free molecules, such as the particular diatomic molecules that we here discuss, the attention soon shifted to the characterisation of the applicable radial functions. For instance, in 1920 Kratzer⁶⁹ introduced the first potential-energy function according to which the 'atoms' vibrated; Kratzer believed that the hydrogen halides (HF, HCl and HBr) to which he applied his theory consisted of ionic molecules and that the oscillations of the charged atoms, their centres a bond length apart, led to an interaction with the electric component of the radiation field such that radiant energy could be absorbed. According to modem notation, Kratzer's function⁶⁹ may be expressed

$$V(R) = \frac{\omega_{e}^{2}}{4B_{e}} \left[1 - \frac{2R_{e}}{R} + \frac{R_{e}^{2}}{R^{2}} - a_{3}x^{3} - a_{4}x^{4} - \dots \right], \qquad (3)$$

in which ω_e and B_e are the equilibrium harmonic vibrational, and rotational, parameters respectively, R and R_e are in turn the instantaneous and equilibrium internuclear distances, $x \equiv (R - R_e)/R_e$ is a reduced variable for internuclear displacement, and the coefficients a_j are arbitrary fitting parameters. Some terms in this equation have a simple physical interpretation. The constant term $\omega_e^2/4B_e$ is chosen such that $V(R_e) = 0$; the term proportional to R^{-1} is attributed to the coulombic attraction in the supposed ionic molecule, and the term with R^{-2} is related" to electronic kinetic energy. The additional terms containing the coefficients a_j permit additional flexibility in representing accurately the wavenumbers of the observed transitions. Later Fues solved⁷¹ the Schrodinger equation for Kratzer's function simplified by neglect of the terms containing the coefficients a_j . Lennard-Jones also introduced⁷² a potential-energy function containing inverse powers of R, that is expressed

$$V(R) = D_{e} + a_{m}, R^{-m} - a_{m}, R^{-n}$$
 (4)

in which D_e is the depth of the potential well, $m \ge n$ and generally the values n = 6, m = 12 have been used. Morse introduced⁷³ the first potential-energy function which gave a finite number of vibrational states (eigenvalues):

$$V(x) = D_{a}(1 - e^{-aMx})^{2}$$
(5)

Other forms of the potential-energy function developed later incorporated various combinations of these terms. including direct and inverse power series in R (or equivalent), exponential, and ordinary and hyperbolic trigonometric functions.

In 1932 Dunham introduced⁷⁴ the general flexible potential-energy function:

$$V(x) = a_0 x^2 \left(\frac{1}{j=1} + \sum a_j x^j \right).$$
(6)

in which the various terms convey no particular physical meaning. However, he expressed the general vibration-rotational energies of a diatomic molecule in a ${}^{1}\Sigma$ electronic state in the systematic form of a double sum

$$E(v, J) = \sum_{k=0}^{\infty} \sum_{k=0}^{\infty} Y_{k\ell} (v + \frac{1}{2})^{k} [J(J+1)]^{\ell} , \qquad (7)$$

in which the term coefficients Y_{kl} were expressed as analytic (algebraic) functions of the potential-energy coefficients a_j . Appropriately extended, this theory has prevailed into recent years. For instance, the values of the coefficients a_j up to j = 8 have been determined¹⁹ for HCI to describe the potential-energy function up to half the energy of the dissociation limit. The argument x in Dunham's potential-energy function however suffers from a serious flaw, namely that it is not well behaved as $R \rightarrow \infty$. To overcome this limitation, a further argument z has been devised⁷⁵,

$$z \equiv 2 \left(R - R_e \right) / \left(R + R_e \right) , \qquad (8)$$

which treats entirely equivalently the two limits of molecular existence, namely at z = 2 the separate atoms (corresponding to the dissociation products as $R \rightarrow \infty$) and at z = -2 the united atom (as $R \rightarrow 0$). The corresponding radial functions for potential energy⁷⁵.

$$V(z) = c_0 z^2 (1 + \Sigma c_1 z^1) , \qquad (9)$$

and any other property 76 ,

$$K(z) = \sum_{j=0}^{\infty} h_j z^j , \qquad (10)$$

thus lend themselves to the application⁷⁷ of boundary conditions; in this way the theoretically correct asymptotic behaviour may be imposed on each function in order to extend the range of applicability beyond the region near $R = R_e$ to which the spectral data generally pertain. Methods of computer algebra⁷⁸ have been employed to form and test the large collections of the analytic expressions of the term coefficients⁷⁹ Y_{kQ} and the related expectation values and matrix elements⁸⁰ (required for the analysis of spectral intensities) that are in both cases available in machine-readable form (FORTRAN code).

If for a single isotopic species of a molecule in a ${}^{1}\Sigma$ electronic state, wavenumber data are available that can be fitted to the form of equation 7. then the adiabatic potential-

energy function according to equations 6 or 9 can be determined directly from the transition wavenumbers, as was done⁸¹ for A1F. If in addition there are intensity data, then the electric-dipole moment function⁸² from absorption or emission spectra or the electric polarizability function⁸³ from the Raman scattering spectra may be determined. If there are available wavenumber data for isotopic variants of a given molecule, then the deviation from mass scaling of the leading contribution to each term coefficient $Y_{k\varrho}$ provides information on collectively the adiabatic and nonadiabatic effects that may be used to determine the appropriate radial function, as has been achieved⁸⁴ for HCl.

If in addition to these effects there are net molecular angular momenta due to unpaired electrons, then further branches of lines exist in a given band and correspondingly further sets of spectral parameters can be defined. The analogous radial functions may be determined according to the general method 76 . Instances of this method for $^{2}\Sigma$ states 76 , for which six branches appear in a given vibration-rotational band, and for ${}^{3}\Sigma$ states⁸⁵ have been published in two cases in which there is net electronic spin angular momentum but no orbital angular momentum, for ¹II states⁸⁶ in which there is only net orbital angular momentum, and for ² II states⁸⁷ in which there are both spin and orbital angular momenta due to unpaired electrons. A given vibration-rotational band of a ${}^{2}\Pi$ electronic state consists of a main band having twelve branches and two further, weak, satellite bands. If the atomic nuclei have intrinsic angular momenta (nuclear spins), there are several possible couplings of these angular momenta with rotational and or electronic angular momenta; some applicable radial functions have been determined⁸⁸ for NaBr from experiments on molecular beams at radio frequencies. These nuclear angular momenta would lead to further complications in vibration-rotational bands if their effects could be resolved, but generally such effects lie within the Doppler width of the spectral lines. A collection of various radial functions to illustrate the various effects has been published⁸⁹.

For the determination of transition-moment functions from spectral intensities, we have to employ somewhat special methods. For many effects in the analysis of data from measurements of wavenumbers or frequencies of transitions, the parameters in the applicable equations appear linearly. However the intensities of spectral lines are proportional to the squares of matrix elements involving the transition-moment functions; hence there are obvious difficulties in the determination of the signs of the pertinent coefficients in the applicable functions. For vibration-rotational transitions the transition-moment functions express the variation of the dipole or quadrupole moments with distance for the particular electronic state within which the vibration-rotational transitions occur. Although the Stark effect also provides information on the electric dipole-moment function, here again the shift of frequency on the application of an external electric field is proportional to the square of the expectation value of the electric dipole moment in a pure rotational transition or to the difference of the squares of the expectation values for a vibration-rotational transition. The solution of this problem makes use of the interaction between vibration and rotation that generates small increases, but linear in the parameters it is desired to determine, of the intensities of the lines in one branch of a given band relative to those of another branch. The quantitative treatment of these effects was first described⁹⁰ by Herman and Wallis. If we suppose. following Dunham' *. that we express the transition moment function as a power series in x (or alternatively in z).

$$\mathbf{M}(\mathbf{x}) = \sum_{\mathbf{j}=\mathbf{0}} \mathbf{M}_{\mathbf{j}} \mathbf{x}^{\mathbf{j}}$$
(11)

then the problem is transformed into the determination of the values of the coefficients M_j . For electric-dipole functions the procedures are well developed⁹², and the signs of all the coefficients M_j , j > 0, are readily thereby determined. For HCl this function has been determined up to the seventh power", for CO up to the fourth power⁹³, and for HBr up to even the eighth power⁹⁴. To determine the sign of M_0 , meaning the sense of the permanent electric dipole moment relative to the internuclear axis, a method was developed⁹⁵ by Townes et al, based on the molecular Zeeman effect; the measurement relies on the isotopic dependence of the magnetic dipole moment induced by the rotation of an electrically polar molecule about its centre of mass. By this means Townes et al determined⁹⁵ that the sense of the dipole in CO was -CO+, contrary to the common expectation of chemists. The transition-moment functions for both the magnetic dipole and electric quadrupole have been determined⁸⁹ for ¹⁶O₂, and the latter for ¹⁴N₂; as these molecules lack by symmetry a permanent electric dipole moment, the extremely weak infrared absorption spectra of these molecules are attributed to these mechanisms^{96,97} of interaction with the radiation field.

V. CONCLUSION

In this review we have both described the development of experimental methods to measure vibration-rotational spectra during the past century and emphasised the concomitant algebraic approach to the analysis of these spectra. For most effects encountered in such spectra of diatomic molecules, this analytic approach is readily applicable and yields considerable insight into the mechanism of each physical effect quite apart from the numerical values of the particular parameters that have been determined in specific cases. There exist of course alternative approaches that are wholly numerical, such as those originated by Rydberg⁹⁸, Klein⁹⁹ and Rees¹⁰⁰, and succeeding developments therefrom. Eventually the extreme complications possible in even diatomic molecular spectra make an analytic treatment intractable. In that case the numerical approaches must prevail, but our understanding of the physics is likely to suffer in the process.

The determination of the applicable radial functions, in either analytic or numerical form, represents for spectroscopists and physicists the ultimate objective of spectral analysis, because such functions constitute the most compact form of results. Therefore they are the most sensitive test of self consistency in the analysis and the final achievement in data reduction⁸⁹. During the second century of infrared spectrosocopy of diatomic molecules, the experiments will undoubtedly be extended to more reactive and transitory species, including free radicals and ions for which indeed many data have already appeared.

As instances of ions, the cation¹⁰¹ OH+ and anion¹⁰² OH- of the hydroxyl species are available, whereas the neutral hydroxyl radical¹⁰³ OH itself is an excellent instance of a reactive free radical only transitorily produced in the gaseous phase; the infrared spectra of these three species indicate the progress in the detection of such exotic species, but it seems that the theory necessary to interpret their spectra. like those of any other diatomic molecule, has already reached a mature state of development.

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APOLOGY

Volume 27, Number 3, "Quantitative Results of X-Ray Fluorescence Spectrometric Analysics of Chinese Ceramics by Photon Source Excitation" Author, C.T. Yap

Due to misprint, the erroneous Chinese Name (蘇德潤) is attached. We hereby apologize to both of the prefessors for the mistake!

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