INTRODUCTION

An immense amount of experimental data has been accumulated from investigations of the infrared absorption spectra and of the Raman effect in polyatomic molecules. Only an extremely small fraction of this material has been subjected to analysis, although the theoretical tools for such an analysis are quite well developed and the results which could be obtained are of considerable interest. One reason for this situation is the amount of labor required to unravel the spectrum of a complex molecule, but an additional deterrent has been the unfamiliar mathematics, such as group theory, in terms of which the most powerful forms of the theory of molecular dynamics have been couched. When only the necessary parts of these mathematical techniques are considered, the difficulty of understanding the theory of the vibrational and rotational spectra of polyatomic molecules is greatly reduced.

In this first chapter, a short general survey of the background of the subject will be given, to serve as an introduction to the more mathematical treatment which follows.

1-1. Infrared Spectra

The absorption or emission spectrum arising from the rotational and vibrational motions of a molecule which is not electronically excited is mostly in the infrared region. A small molecule having an electric moment emits and absorbs light of frequency below about 250 wave numbers[1] because of its rotational motion. Molecules which are absorbing or emitting 1 quantum of vibrational energy show bands in the region from about 200 to 3,500 cm^{-1}, while bands due to several vibrational quantum jumps are detected all the way from a few hundred to many

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[1] The symbol ω will be used throughout to represent the reciprocal of the wavelength λ. The unit for ω is the reciprocal centimeter (cm^{-1}) or the wave number, since ω represents the number of waves per centimeter. Inasmuch as the frequency ν is connected with ω by the relationship $\nu = \omega c$, where c is the velocity of light, it will frequently be said that the frequency is ω wave numbers. Experimentalists often express their results in terms of the wavelength in microns (μ), 1 micron being 10^{-4} cm. If λ_μ is the wavelength in microns, $\omega = 10^4/\lambda_\mu$. Recently the symbol K, for Kayser, has been proposed to replace cm^{-1}.

thousand wave numbers, sometimes being observable in the visible portion of the spectrum (13,000 to 26,000 cm^{-1}). See Fig. 1-1.

Infrared spectra may be observed either in emission or in absorption, although the latter method is by far the more common. In absorption experiments light from a suitable source is passed through a tube containing the gas to be studied and thence into the spectrograph.[1] If the spectrograph is of low resolving power, a series of wide bands is observed which correspond to the vibrational transitions, but if a spectrograph of
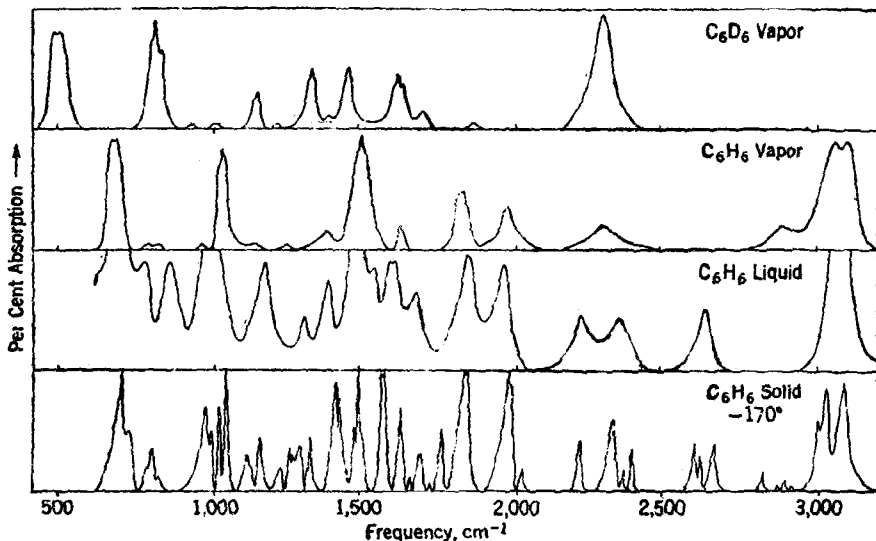
FIG. 1-1. Vibrational absorption spectra in the infrared as illustrated by benzene.

higher resolution is used, these bands may break up into lines which can be correlated with the energy levels of rotation. In practice, only a few light molecules (H_2O, NH_3, CH_4, CO_2, etc.) have been observed in the

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[1] Information concerning experimental methods can be obtained from the following sources:

W. W. Coblentz, "Glazebrook's Dictionary of Applied Physics," Vol. 4, p. 136, Macmillan, London, 1923.

G. R. Harrison, R. C. Lord, and J. R. Loofbourow, "Practical Spectroscopy," Prentice-Hall, New York, 1948.

G. Laski, "Handbuch der Physik," Vol. 19, p. 802, Springer, Berlin, 1928.

J. Lecomte, "Le Spectre infrarouge," Recueil des conférences-rapports de documentation sur la physique, Vol. 14, Les Presses Universitaires de France, Paris, 1928.

F. I. G. Rawlins and A. M. Taylor, "Infrared Analysis of Molecular Structure," Cambridge, New York, and London, 1929.

C. Schaefer and F. Matossi, "Das ultrarote Spektrum," Springer, Berlin, 1930.

G. B. B. M. Sutherland, "Infrared and Raman Spectra," Methuen, London, 1935.

V. Z. Williams, *Rev. Sci. Instr.*, **19**: 135 (1948).

infrared region with high enough resolving power to resolve the rotational structure.   Figure 1-1 shows some observed spectra.

Liquids and solids are also studied, and they yield interesting results, but except in so far as they give vibrational spectra in close agreement with those found for the corresponding gases they will not be discussed in this book, in which interactions between separate molecules will be neglected.

1-2. Raman Spectra[1]

If the substance being studied (as a gas, liquid, or solid) is strongly illuminated by monochromatic light in the visible or ultraviolet region and the scattered light observed in a spectrograph,[2] a spectrum is obtained (see Fig. 1-2) which consists of a strong line (the *exciting line*) of the same frequency as the incident illumination together with weaker lines on either side shifted from the strong line by frequencies ranging from a few to about 3,500 wave numbers.   The pattern of lines is symmetrical about the exciting line except with regard to intensities, the lines on the high-frequency side being considerably weaker than the others.   In fact, they are frequently too weak to be observed.   The lines of frequency less than the exciting lines are called Stokes lines, the others anti-Stokes lines.

These lines differing in frequency from the exciting line, the Raman lines, have their origin in an interchange of energy between the light quanta and the molecules of the substance scattering the light.   The lines which appear very near the exciting line are correlated with changes in the

[1] The original papers dealing with this effect are:

A. Smekal, *Naturwissenschaften*, **11**: 873 (1923).

H. A. Kramers, *Nature*, **113**: 673 (1924).

H. A. Kramers and W. Heisenberg, *Nature*, **114**: 310 (1924).

C. V. Raman, *Indian J. Phys.*, **2**: 1 (1928).

G. Landsberg and L. Mandestamm, *Naturwissenschaften*, **28**: 557 (1928).

[2] Information concerning the experimental methods for the study of the Raman effect can be obtained from the following sources:

S. Bhagavantam, "Scattering of Light and the Raman Effect," Chemical Publishing, New York, 1942.

P. Daure, "Introduction à l'étude de l'effêt Raman," Éditions de la Revue d'optique, théorique et instrumentale, 1933.

G. Glockler, *Revs. Mod. Phys.*, **15**: 112 (1943).

J. H. Hibben, "The Raman Effect and Its Chemical Applications," Reinhold, New York, 1939.

G. Joos, "Handbuch der Experimentalphysik," Vol. 22, p. 413, Akademische Verlagsgesellschaft, Leipzig, 1929.

K. W. F. Kohlrausch, "Der Smekal-Raman-Effekt," Springer, Berlin, 1931. See also "Erganzungsband 1931–37," Springer, Berlin, 1938.

K. W. F. Kohlrausch, "Ramanspektren," Vol. 9, Sec. VI of Eucken-Wolf. "Hand- und Jahrbuch der Chemischen Physik," Akademische Verlagsgesellschaft, Leipzig, 1943.   Reprinted by Edwards, Ann Arbor, Mich., 1945.

Symposium, *Trans. Faraday Soc.*, **25**: 781 (1929).

rotational energy states of the molecules without changes in the vibrational energy states and form the *pure rotation* Raman spectrum. The lines farther from the exciting line are really bands of unresolved lines and are associated with simultaneous changes in the vibrational and rotational energy states.

The frequency shifts, that is, the differences between the frequencies of the Raman lines and the exciting line, are independent of the frequency of the exciting line. A mercury arc is usually used for illumination, and there are a number of the strong mercury lines which are used to excite
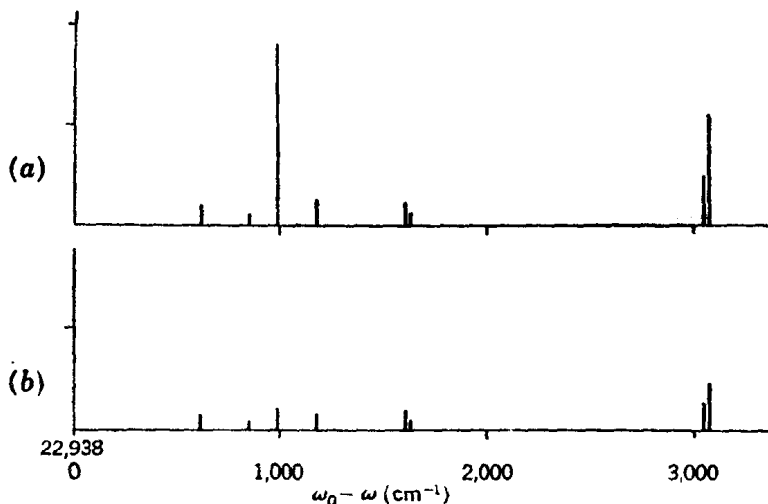
FIG. 1-2. Plot of the Raman spectrum of benzene. The heights of the lines indicate relative intensity, (a) being the parallel spectrum and (b) the perpendicular spectrum ($b/a = \rho_n$; see Sec. 3-6). The scale is in cm^{-1} and the Raman shift is measured from the mercury exciting line at 22,938.04 cm^{-1} (4,358 A). (*These data, used in the example discussed in Chap.* 10, *are from Angus, Ingold, and Leckie, J. Chem. Soc.*, 1936, *p.* 925.)

Raman spectra. The frequencies for a given molecule found in infrared absorption frequently agree with the frequency *shifts* found in the Raman effect, but this is not always true and depends on the symmetry of the molecule in a way which is now well understood.

By polarizing the incident light or in other ways, it is possible to find the *degree of depolarization* of each frequency shift in the Raman spectrum, a quantity which will be important in the interpretation of the experimental results. This quantity is the ratio, for the scattered light, of the intensities of the components polarized perpendicular and parallel, respectively, to the direction of polarization of the incident illumination.

1-3. The Molecular Model

In attempting to account for the observed infrared and Raman spectra of real molecules, a certain simplified model for such molecules is adopted,

and then the spectra which this model would exhibit are calculated. The specification of the model involves certain parameters such as size, stiffness of valence bonds, etc., which can be varied within limits set by other types of experimental evidence until the best agreement with experiment is obtained. An attempt is usually made to select a number of such parameters which is much smaller than the number of experimental quantities so that the success of the theory can be tested by the agreement which it provides with experiment.

The model which will be used in this book consists of particles held together by certain forces. The particles, which are to be endowed with mass and certain electrical properties, represent the atoms and are to be treated as if all the mass were concentrated at a point. It is assumed that the atoms may be electrically polarized by an external electrical field, such as that of a beam of light, and that they may or may not be permanently polarized by their mutual interactions in such a manner that the whole molecule has a resultant electric moment.[1] Both the polarizability and the electric moment of the model may vary as the particles (hereafter called atoms) change their relative positions. Finally, the atoms may possess an internal degree of freedom or nuclear spin which introduces certain symmetry restrictions.

The forces between the particles may be crudely thought of as weightless springs which only approximately obey Hooke's law and which hold the atoms in the neighborhood of certain configurations relative to one another. This picture of the forces as springs is useful for visualization, but is not sufficiently general for all cases. For example, it does not cover cases of restricted rotation about single bonds such as may occur in ethane. The nature of these interatomic forces is one of the chief problems still being studied and will be discussed in Chap. 8. The search for a potential function which involves a small number of parameters and which at the same time permits good agreement with experiment is by no means ended.

The statement that the model obeys the laws of quantum mechanics is an essential part of its specification. However, since atoms are fairly heavy particles (compared to electrons), it will sometimes be true that classical mechanics when properly used gives results which are good approximations to those of quantum mechanics.

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[1] The *electric moment* μ of an electrically neutral molecule is a vector quantity whose direction is that of a line joining the center of charge of the negative charges with the center of charge of the positive charges and whose magnitude is the length of that line multiplied by the total negative or the total positive charge, these being equal. An atom or molecule is said to be *polarized* by an electric field when the displacements of charges caused by the electric field produce or alter the electric moment of the atom or molecule. If the electric field strength is $\mathcal{E}$ and the induced moment is μ, then $\mu = \alpha\mathcal{E}$ defines the *polarizability* α for an isotropic molecule.

Since the atoms of this model have been regarded as point masses with certain electrical properties, there is an apparent disagreement with the fact that many experiments require that atoms be made of electrons and nuclei. It is possible to reconcile these two points of view. If the wave equation for a molecule made up of electrons and nuclei is set up, a procedure[1] exists whereby this equation may be separated into two equations, one of which governs the electronic motions and yields the forces between the atoms, whereas the other is the equation for the rotation and vibration of the atoms and is identical with the equation for the model adopted here. In principle, therefore, the forces between the atoms can be calculated *a priori* from the electronic wave equation, but in practice this is not mathematically feasible (except for H_2), and it is necessary to postulate the forces in such a manner as to obtain agreement with experiment. Therefore, although it is theoretically possible to start with a model consisting of electrons and nuclei interacting coulombically and obeying the laws of quantum mechanics, in practice it is necessary to assume the nature of the equilibrium configuration and of the forces between the atoms, so that it seems more desirable to start with the model in which the atoms are the units.

This separation of the electronic motion and the nuclear motions is only an approximation which may break down in certain cases, especially for high electronic states. If there were no interaction between the two types of motions, there would be no Raman effect of any importance. However, the coupling is small for the lowest electronic state.

1-4. Classical Theory of Vibrational and Rotational Spectra

Classical electromagnetic theory[2] requires that an accelerated charged particle emit radiant energy. On this basis a rotating molecule with an electric moment should emit light of the same frequency as the frequency of rotation. Because of the Maxwellian distribution of rotational velocities, a collection of gas molecules should emit a band of frequencies possessing an intensity maximum which is related to the most probable frequency of rotation. In practice, this prediction of classical theory

[1] M. Born and J. R. Oppenheimer, *Ann. Physik*, **84**: 457 (1927).

R. L. Kronig, "Band Spectra and Molecular Structure," Cambridge, New York and London, 1930.

[2] For presentations of classical radiation theory, see the following:

L. Page, "Introduction to Theoretical Physics," Chap. 12, Van Nostrand, New York, 1934.

F. K. Richtmyer and E. H. Kennard, "Introduction to Modern Physics," Chap. 2, McGraw-Hill, New York, 1947.

A. E. Ruark and H. C. Urey, "Atoms, Molecules, and Quanta," Chap. 6, McGraw-Hill, New York, 1930.

F. Zerner, "Handbuch der Physik," Vol. 12, p. 1, 1927, Springer, Berlin.

is quite closely verified experimentally for heavy molecules and low resolution.

The molecular model of the previous section can move as a whole, rotate about its center of mass, and vibrate. The translational motion does not ordinarily give rise to radiation. Classically, this follows because acceleration of charges is required for radiation. The rotational motion causes practically observable radiation if, and only if, the molecule has an electric (dipole) moment. The vibrational motions of the atoms within the molecule may also be associated with radiation if these motions alter the electric moment. A diatomic molecule has only one fundamental frequency of vibration so that if it has an electric moment its infrared emission spectrum will consist of a series of bands, the lowest of which in frequency corresponds to the distribution of rotational frequencies for nonvibrating molecules. The other bands arise from combined rotation and vibration; their centers correspond to the fundamental vibration frequency and its overtones. A polyatomic molecule has more than one fundamental frequency of vibration so that its spectrum is correspondingly richer.

The Raman effect can also be explained classically. The electric vector of the incident illumination induces in the molecule an oscillating electric moment which emits radiation. If the molecule is at rest, the induced moment, and therefore the scattered light, has the same frequency as the incident light. If, however, the molecule is rotating or vibrating, this is not necessarily the case, because the amplitude of the induced electric moment may depend on the orientation of the molecule and the relative positions of its atoms. Since the configuration changes periodically because of rotation and vibration, the scattered radiation is "modulated" by the rotational and vibrational frequencies so that it consists of light of frequencies equal to the sum and to the difference of the incident frequency and the frequencies of the molecular motions, in addition to the incident frequency.

Thus, the classical theory of radiation and classical mechanics provides an explanation of the general features of both infrared and Raman spectra. It cannot, however, account for the details and is to be regarded as only a rough approximate method of treatment.

1-5. The Quantum Viewpoint

When the molecular spectra of a few light molecules are observed with spectrographs of high resolving power, the bands previously discussed are resolved into a series of closely spaced lines. Classical theory is unable to explain this phenomenon. The explanation, of course, depends on the use of quantum theory, in which the molecule is restricted to definite, discrete energy levels of rotation and vibration. Radiation

occurs only when a molecule undergoes a transition from one stationary state to another of different energy. The Bohr frequency rule gives the frequency ν of the light radiated or absorbed on transitions between states of energies $W_{n''}$ and $W_{n'}$. It is

$$\nu_{n''n'} = \nu_{n'n''} = \frac{W_{n'} - W_{n''}}{h} \tag{1}$$

where h is Planck's constant.[1]

Not every transition can occur with the emission or absorption of radiation. The rules which tell which transitions may occur are called *selection rules.*

Although the classical theory is not correct in predicting that the observed radiation will consist of frequencies occurring in the motion of the system, there is an asymptotic relationship between the frequencies predicted by the classical and by the quantum theory, known as Bohr's correspondence theorem for frequencies.[2] According to this theorem the frequencies emitted and absorbed by a quantum system approach asymptotically the classical frequencies of the system as the quantum numbers of the initial and final states are increased. The intensities of the quantum transitions will likewise asymptotically approach the intensities calculated classically, as the quantum numbers increase.

From the quantum viewpoint, the band of lowest frequency in the infrared spectrum (it may extend into the microwave region) of a molecule with an electric moment consists of discrete lines, each of which corresponds to a transition between two different rotational energy levels of the nonvibrating molecule (or rather, of the molecule in its lowest vibrational energy level). The other bands with higher frequencies correspond to transitions involving simultaneous changes of rotational and vibrational energies. The spacing between adjacent vibrational levels is considerably greater than that between adjacent rotational levels so that, although the various vibrational bands are usually fairly

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[1] Throughout this book, in dealing with transition phenomena, the general array of quantum numbers specifying the *upper* state will be indicated by n' and that specifying the lower state by n''. Whenever a double subscript is used to specify a transition, the symbols will be written in the order initial, final. Equation (1) thus states that the frequency, $\nu_{n''n'}$, of the absorption process $n'' \rightarrow n'$ is equal to the frequency, $\nu_{n'n''}$, of the emission process $n' \rightarrow n''$, and that this frequency is given by $(W_{n'} - W_{n''})/h$.

[2] See the following sources:

N. Bohr, *Z. Physik*, **2**: 423 (1920); **13**: 117 (1923).

W. Pauli, "Handbuch der Physik," Vol. 23, p. 1, Springer, Berlin, 1926.

A. Sommerfeld, "Atombau und Spektrallinien," 5th ed., Vol. 1, pp. 671*ff.*, Vieweg, Brunswick, 1931.

J. H. Van Vleck, "Quantum Principles and Line Spectra," Bulletin of the National Research Council, No. 54, Chap. 3, Washington, D.C., 1926.

widely spaced, it requires a spectrograph of very high resolving power to separate the rotational lines.

The fundamental frequency of the classical explanation corresponds to a quantum transition from one vibrational state to the next, while the overtone frequencies correspond to transitions to other than adjacent levels. Since the vibrational levels are nearly but not quite evenly spaced, the vibrational bands will fall into series with frequencies which are almost but not quite multiples of the fundamental frequencies.

The quantum picture of the Raman effect is that a photon of energy $h\nu_0$ (ν_0 being the frequency of the incident light) comes up to a molecule in a given stationary state, causing a transition to another higher (or lower) energy level different in energy by an amount $h\nu_{n''n'}$. This amount of energy is subtracted from (or added to) the incident photon so that the emitted or "scattered" photon then has the energy $h\nu_0 \mp h\nu_{n''n'}$ and therefore has the frequency $\nu_0 \mp \nu_{n''n'}$. Since in general more molecules are in the lower than in the higher energy states, there will be more cases in which the photon gives up some of its energy than vice versa, so that the Stokes lines will be stronger than the anti-Stokes lines.

In calculating the energy levels and selection rules, the principles of quantum mechanics must be used. This is usually done through the medium of the Schrödinger equation and wave mechanics, but the equivalent mathematical techniques of matrix mechanics and the operator calculus are frequently useful.[1]

1-6. Applications

There are three main applications of the interpreted results of infrared and Raman studies. These are the study of the nature of the forces acting between the atoms of a molecule, the determination of molecular structure, and the calculation of thermodynamic quantities.

The fundamental frequencies of vibration obtained from infrared and Raman spectra have provided considerable information about the interatomic forces in various molecules. It is found that different types of valence bonds exhibit different degrees of resistance to stretching and bending which are roughly independent of the molecule in which the bond occurs. Further, empirical relations between the length of a bond and

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[1] In this book an elementary knowledge of quantum mechanics will be assumed. Any material, however, which is not covered in L. Pauling and E. B. Wilson, Jr., "Introduction to Quantum Mechanics," McGraw-Hill, New York, 1935, will be developed in the text or appendixes. For a more advanced treatment of the subject, see E. C. Kemble, "Fundamental Principles of Quantum Mechanics," McGraw-Hill, New York, 1937; also L. I. Schiff, "Quantum Mechanics," 2d ed., McGraw-Hill, New York, 1955; or K. S. Pitzer, "Quantum Chemistry," Prentice-Hall, New York, 1953.

its resistance to stretching have been found which promise to have useful applications.[1]

There are several ways in which information about molecular structure can be obtained from infrared and Raman spectra. Probably the most important is the determination of moments of inertia from the spacing of the rotational lines. This remains one of the most reliable methods known for the determination of molecular sizes of simple molecules although with present experimental techniques it cannot be used for any but very light molecules. In recent years this method has been enormously extended by the development of techniques for the use of the millimeter and centimeter wavelength regions, *i.e.*, the regions of microwave spectroscopy. The vibrational spectrum can also be used to provide clues as to the structure of a molecule, especially with regard to its symmetry.

In many ways the most valuable application of the data of infrared and Raman studies is to the calculation of the heat capacity, entropy, and free energy of gaseous molecules. For such calculations a knowledge of the moments of inertia and vibration frequencies of the molecule is necessary. Calculations of this sort have been carried out for a large number of simple molecules with results which usually surpass in accuracy those of any other method. If the value for the heat of reaction is known at any temperature, spectroscopic data can be used to find the heat of the reaction at any other temperature, the free energy and entropy changes, and the equilibrium constant at any temperature.

All these applications require a careful consideration of the principles underlying the interpretation of the spectral data. Because of the failure to recognize the importance of some of these principles. many false conclusions have been drawn in the past from spectroscopic experiments.

[1] R. M. Badger, *J. Chem. Phys.*, **2**: 128 (1934); **3**: 710 (1935).
W. Gordy, *J. Chem. Phys.*, **14**: 305 (1946).

CHAPTER 2

THE VIBRATION OF MOLECULES

The study of molecular vibrations will be introduced by a consideration of the elementary dynamical principles applying to the treatment of small vibrations. In order that attention may be focused on the dynamical principles rather than on the technique of their application, this chapter will employ only relatively familiar and straightforward mathematical methods, and the illustrations will be simple. This will serve adequately as an introduction to the applications of quantum mechanics and group theory to the problem of molecular vibrations. Since, however, these straightforward methods become cumbersome and impractical, even for simple molecules, equivalent but more powerful techniques using matrix and vector notations will be discussed in Chap. 4.

2-1. Separation of Rotation and Vibration[1]

The logical way to begin the mathematical treatment of the vibration and rotation of a molecule is to set up the classical expressions for the kinetic and potential energies of the molecule in terms of the coordinates of the atoms, and then to use these expressions to obtain the wave equation for vibration, rotation, and translation. Following this, it should be proved that when the proper coordinate system is used, the complete wave equation can be approximately separated into three equations, one for translation, one for rotation, and one for vibration. Unfortunately, this procedure is not a very simple one and utilizes more quantum-mechanical technique than is required for the discussion of the vibrational equation itself. Consequently, the actual carrying out of the separation will be deferred until Chap. 11, and only a summary of the results thus obtained will be presented at this point. The reader who prefers to follow the more logical order may turn to Chap. 11 before continuing with the present sections.

It is found that the proper coordinates to use are the following: the three cartesian coordinates of the center of mass of the molecule, the three Eulerian angles[2] of a rotating system of cartesian coordinates, the axes of which coincide with the principal axes of inertia of the undistorted molecule, and finally the cartesian coordinates of the atoms with respect

[1] References to the original papers dealing with this topic will be found in Chap. 11
[2] Eulerian angles are described in Appendix I.

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to the rotating coordinate system. Since there are only $3N$ degrees of freedom for a molecule of N atoms, there are six too many coordinates in the above list, so that all of them cannot be independent; six conditions connecting them must exist. However, just six conditions are required (for nonlinear molecules) to define the rotating coordinate system. Three of these locate the origin of the rotating system at the center of mass of the molecule, thus assuring that the rotating system moves with the molecule. The other three conditions tie the coordinate system to the molecule so that they rotate together.

The effect of these conditions is to enable the vibrations to be treated in terms of the coordinates of the moving system of axes just as if the molecule were not rotating or undergoing translation. The $3N$ cartesian coordinates of the moving system are used, together with the six conditions above which prevent translation or rotation with respect to the moving axes.

Let x_α, y_α, z_α be the coordinates of the αth atom in terms of the moving system, and a_α, b_α, c_α be the values of the coordinates of the equilibrium position of the αth atom; $i.e.$, the values assumed by x_α, y_α, z_α when the molecule is at rest in its equilibrium position. Displacements from equilibrium will be measured by $\Delta x_\alpha = x_\alpha - a_\alpha$, $\Delta y_\alpha = y_\alpha - b_\alpha$, and

$$\Delta z_\alpha = z_\alpha - c_\alpha$$

The condition that the origin be at the center of mass yields the equations

$$\sum_{\alpha=1}^{N} m_\alpha x_\alpha = 0$$
$$\sum_{\alpha=1}^{N} m_\alpha y_\alpha = 0 \tag{1}$$
$$\sum_{\alpha=1}^{N} m_\alpha z_\alpha = 0$$

in which m_α is the mass of the αth atom. Similar expressions must hold for the equilibrium configuration, in which $x_\alpha = a_\alpha$, $y_\alpha = b_\alpha$, $z_\alpha = c_\alpha$. Consequently, the following relations will be valid:

$$\sum_{\alpha=1}^{N} m_\alpha \, \Delta x_\alpha = 0$$
$$\sum_{\alpha=1}^{N} m_\alpha \, \Delta y_\alpha = 0 \tag{2}$$
$$\sum_{\alpha=1}^{N} m_\alpha \, \Delta z_\alpha = 0$$

The other three conditions on the moving system are not as simple and obvious as the three just given.   They are chosen so that the axes will rotate with the molecule, but it is not easy to define what is meant by "rotating with the molecule" when all the atoms in the molecule are moving relative to one another in their vibrational motions.   It might, for example, be specified that there should be no angular momentum with respect to the translating-rotating coordinate system.   This is not a convenient definition of the rotating system, but the definition which is adopted, for reasons given in Chap. 11, is closely related.   Thus, the components $\mathfrak{m}_x$, $\mathfrak{m}_y$, and $\mathfrak{m}_z$ of the angular momentum in the moving system are

$$\mathfrak{m}_x = \sum_{\alpha=1}^{N} m_\alpha(y_\alpha \dot{z}_\alpha - z_\alpha \dot{y}_\alpha)$$

$$\mathfrak{m}_y = \sum_{\alpha=1}^{N} m_\alpha(z_\alpha \dot{x}_\alpha - x_\alpha \dot{z}_\alpha) \qquad (3)$$

$$\mathfrak{m}_z = \sum_{\alpha=1}^{N} m_\alpha(x_\alpha \dot{y}_\alpha - y_\alpha \dot{x}_\alpha)$$

A dot over a symbol means the time derivative, that is, $\dot{x}_\alpha = dx_\alpha/dt$, etc.   For small displacements, Δx_α, Δy_α, etc., are small, so that x_α, y_α, and z_α can be replaced by a_α, b_α, and c_α, respectively, these being the coordinates of the equilibrium position of the atom α.   Under these circumstances,

$$\mathfrak{m}_x \cong \sum_{\alpha=1}^{N} m_\alpha(b_\alpha \dot{z}_\alpha - c_\alpha \dot{y}_\alpha)$$

$$\mathfrak{m}_y \cong \sum_{\alpha=1}^{N} m_\alpha(c_\alpha \dot{x}_\alpha - a_\alpha \dot{z}_\alpha) \qquad (4)$$

$$\mathfrak{m}_z \cong \sum_{\alpha=1}^{N} m_\alpha(a_\alpha \dot{y}_\alpha - b_\alpha \dot{x}_\alpha)$$

The conditions actually employed in defining the rotating system of axes are (see also Sec. 2-5)

$$\sum_{\alpha=1}^{N} m_\alpha(b_\alpha \Delta z_\alpha - c_\alpha \Delta y_\alpha) = 0$$

$$\sum_{\alpha=1}^{N} m_\alpha(c_\alpha \Delta x_\alpha - a_\alpha \Delta z_\alpha) = 0 \qquad (5)$$

$$\sum_{\alpha=1}^{N} m_\alpha(a_\alpha \Delta y_\alpha - b_\alpha \Delta x_\alpha) = 0$$

If these are differentiated with respect to the time, it is seen that they become equivalent to the equations obtained when the approximate expressions for m_x, m_y, and m_z in (4) are equated to zero, since

$$\left(\frac{d\,\Delta x_\alpha}{dt}\right) = \dot{x}_\alpha$$

2-2. Small Vibrations in Classical Mechanics[1]

As a consequence of the conclusions set forth in the previous section, the problem of the vibration of a molecule may be treated independently of its rotation[2] by using a system of coordinates moving with the molecule and satisfying the six conditions of Eqs. (2) and (5), Sec. 2-1. Since classical mechanics yields a solution of the problem of small vibrations which is easier to visualize than the quantum mechanical solution, it will be employed first.

The kinetic energy is given by

$$2T = \sum_{\alpha=1}^{N} m_\alpha \left[\left(\frac{d\,\Delta x_\alpha}{dt}\right)^2 + \left(\frac{d\,\Delta y_\alpha}{dt}\right)^2 + \left(\frac{d\,\Delta z_\alpha}{dt}\right)^2\right] \qquad (1)$$

It is very convenient to replace the coordinates Δx_1, . . . , Δz_N by a new set of coordinates q_1, . . . , q_{3N} defined as follows

$$q_1 = \sqrt{m_1}\,\Delta x_1 \quad q_2 = \sqrt{m_1}\,\Delta y_1 \quad q_3 = \sqrt{m_1}\,\Delta z_1 \quad q_4 = \sqrt{m_2}\,\Delta x_2, \text{etc.} \quad (2)$$

and known as mass-weighted cartesian displacement coordinates. In terms of the time derivatives of these coordinates the kinetic energy[3] is

$$2T = \sum_{i=1}^{3N} \dot{q}_i^2 \qquad (3)$$

The potential energy will be some function of the displacements and therefore of the q's. For small values of the displacements, the poten-

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[1] General treatments will be found in the following:

J. H. Jeans, "Theoretical Mechanics," p. 348, Ginn, Boston, 1907.

E. T. Whittaker, "Analytical Dynamics," 3d ed., Chap. 7, Cambridge, New York and London, 1927.

For the application to molecules, see the following:

N. Bjerrum, *Verhandl. deut. physik Ges.*, **16**: 737 (1914).

D. M. Dennison, *Revs. Mod. Phys.*, **3**: 280 (1931).

[2] For a further discussion of the justification of the method used in this section, see Appendix II.

[3] The subscripts α and β (running from 1 to N) will be used to enumerate *atoms*, while italic subscripts $i, j; k, l; m, n; q, r; s, t$; and u, v will be used to enumerate coordinates and will run from 1 to $3N$ or from 1 to $3N - 6$ or $3N - 5$.

tial energy V may be expressed as a power series in the displacement q_i:

$$2V = 2V_0 + 2\sum_{i=1}^{3N}\left(\frac{\partial V}{\partial q_i}\right)_0 q_i + \sum_{i,j=1}^{3N}\left(\frac{\partial^2 V}{\partial q_i\,\partial q_j}\right)_0 q_i q_j + \text{higher terms}$$

$$= 2V_0 + 2\sum_{i=1}^{3N} f_i q_i + \sum_{i,j=1}^{3N} f_{ij} q_i q_j + \text{higher terms} \tag{4}$$

By choosing the zero of energy so that the energy of the equilibrium configuration is zero, V_0 may be eliminated. Furthermore, when all the q's are zero, the atoms are all in their equilibrium positions so that the energy must be a minimum for $q_i = 0$, $i = 1, 2, 3, \ldots$. Therefore[1]

$$\left(\frac{\partial V}{\partial q_i}\right)_0 = f_i = 0 \qquad i = 1, 2, \ldots, 3N$$

For sufficiently small amplitudes of vibration, the higher terms (cubic, quartic, etc., in the q's) can be neglected, so that

$$2V = \sum_{i,j=1}^{3N} f_{ij} q_i q_j \tag{5}$$

in which the f_{ij}'s are constants given by

$$f_{ij} = \left(\frac{\partial^2 V}{\partial q_i\,\partial q_j}\right)_0 \tag{6}$$

with $f_{ij} = f_{ji}$.

Newton's equations of motion can be written in the form

$$\frac{d}{dt}\frac{\partial T}{\partial \dot{q}_j} + \frac{\partial V}{\partial q_j} = 0 \qquad j = 1, 2, \ldots, 3N \tag{7}$$

since T is a function of the velocities only (in this coordinate system) and V is a function of the coordinates only. Substitution of the expressions for T and V given above yields the equations

$$\ddot{q}_j + \sum_{i=1}^{3N} f_{ij} q_i = 0, \, j = 1, 2, \ldots, 3N \tag{8}$$

This is a set of $3N$ simultaneous second-order linear differential equations. One possible solution is

$$q_i = A_i \cos(\lambda^{\frac{1}{2}} t + \epsilon) \tag{9}$$

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[1] Here again the treatment disregards the fact that the coordinates q_i are not all independent. For justification of this method, see Appendix II.