CONTENTS

INTRODUCTION

Some low-pressure gases selectively absorb electromagnetic radiation of particular wavelengths in the millimeter and centimeter range. This type of absorption can be observed in an experiment broadly represented by Fig. 1.

The source of microwaves (electromagnetic radiation of wavelength between 1 and 1000 mm) is usually an electronic tube, which emits radiation through a hollow metal pipe called a waveguide. The microwaves are detected after passage through a region of low-pressure gas (10 mm to 10^{-4} mm Hg pressure) by a silicon "crystal" or other detecting device. This detector produces an electrical signal proportional to the
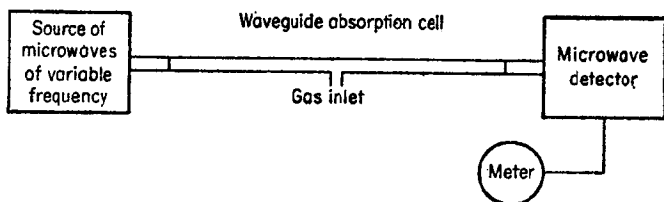
FIG. 1. Experiment for measuring microwave absorption.

microwave power which, after possible amplification, is observed on a meter or oscilloscope. As the frequency of the microwaves is varied, absorption appears as a sudden decrease in the voltage output of the detector.

Electronic techniques are characteristic of microwave spectroscopy, being involved in the production, detection, and amplification of microwaves. In some cases very sensitive electronic circuits are needed for proper detection and amplification, since the fractional power decrease may be quite small—as small as one part in 10^8 in an absorption path of 1 meter. In a few cases the absorption may be as much as 90 per cent in 1 meter path, and very easily detectable.

At gas pressures near 1 atm, a small microwave absorption may occur over a wide range of frequency. As the pressure is lowered, the range of frequency absorbed decreases proportionally down to pressures near 10^{-3} mm Hg, where the range is so small that the term absorption "line" is well merited. Very significantly, and contrary to experience in most

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other types of spectroscopy, the intensity of absorption in the center of the line does not appreciably decrease with this enormous decrease in pressure.

Because of the narrowness of absorption lines at low pressures, and the flexibility and sensitivity of electronic techniques, this type of experiment and its many refinements and ramifications form a basis for the precise, widely applicable microwave spectroscopy of gases which is the subject of this volume.

Consider now the frequencies absorbed. These must be interpretable in terms of the structure and behavior of the absorbing molecules. The motions (or transitions) of electrons in atoms and molecules are known to produce characteristically spectra in the optical and ultraviolet region. The slower vibrational motions of atoms in molecules are primarily responsible for the rich infrared spectra. It is the still slower end-over-end rotation of molecules which have characteristic frequencies so low that they lie in the microwave range and dominate microwave spectra.

Discussion of the interpretation of microwave spectra will begin with the rather simple diatomic molecules and progress in following chapters to successively more complex cases of linear polyatomic molecules, symmetric-top molecules, and asymmetric-top molecules.

Superimposed on the frequencies associated with molecular rotation are many interesting fine and hyperfine effects, some of which have been observed clearly for the first time by microwave techniques. These will be discussed after the broader outlines of rotational spectra have been treated.

ROTATIONAL SPECTRA OF DIATOMIC MOLECULES

1-1. The Rigid Rotor. If the distance between nuclei in a diatomic molecule is considered fixed, the possible frequencies of the end-over-end rotation of this "rigid rotor" can be rather simply obtained. Using assumptions of the "old" quantum mechanics, the angular momentum must be some integral multiple of $h/2\pi$, so that

$$2\pi\nu I = \frac{Jh}{2\pi}$$

where h is Planck's constant, I is the molecular moment of inertia about axes perpendicular to the internuclear axis, ν is the frequency of rotation, and J is a positive integer giving the angular momentum in units of $h/2\pi$. Hence the frequencies expected from such a system are

$$\nu = \frac{Jh}{4\pi^2 I} \tag{1-1}$$

The moment of inertia I comes largely from the nuclei, where most of the molecular mass is concentrated, and for diatomic molecules of ordinary masses is of such size that for small integral values of J, the frequency ν is of the order 10,000 to 100,000 Mc, or the wavelength in the region 3 cm to 3 mm.

On this simple basis one might expect a rotation about the molecular axis to occur also and to have characteristic frequencies a few thousand times greater because the moment of inertia about this axis is produced by electrons, which are very much lighter than the nuclei. These frequencies lie then near the optical region, and in a very rough way the electronic frequencies may be regarded as due to this type of rotation about the molecular axis. Since these frequencies are very high, they lie far beyond the microwave range and are not ordinarily excited at room temperature. They will therefore be neglected in most of the following treatment. A somewhat more sophisticated and rigorous determination of the frequencies produced by a rigid diatomic molecule can be obtained by finding the permitted energy levels from wave mechanics (see [62], p. 271, or [305], p. 60). As the molecule rotates about its center of gravity, its orientation in space may be specified by the spherical

polar coordinates θ and ϕ. The wave equation may then be written

$$\frac{h^2}{8\pi^2 I}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right] + W\psi = 0 \qquad (1\text{-}2)$$

where ψ is the wave function and W the rotational energy of the molecule. The variables θ and ϕ may be separated by substituting

$$\psi = \Theta(\theta)\Phi(\phi)$$

which gives

$$\frac{d^2\Phi}{d\phi^2} = -M^2\Phi \qquad (1\text{-}3)$$

and

$$\frac{h^2}{8\pi^2 I}\left[\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) - \frac{M^2\Theta}{\sin^2\theta}\right] + W\Theta = 0 \qquad (1\text{-}4)$$

where M^2 is an arbitrary constant.

Solutions of these equations which are single-valued and normalized can be obtained only when

$$W = \frac{h^2}{8\pi^2 I}J(J+1)$$

where J is a positive integer and M is an integer such that $|M| \leq J$. Such solutions are

$$\Phi_M = \frac{1}{\sqrt{2\pi}}e^{iM\phi} \qquad (1\text{-}5)$$

$$\Theta_{MJ} = \left[\frac{(2J+1)(J-|M|)!}{2(J+|M|)!}\right]^{\frac{1}{2}} P_J^{|M|}(\cos\theta) \qquad (1\text{-}6)$$

where $P_J^{|M|}(\cos\theta)$ is an associated Legendre function. $[J(J+1)](h^2/4\pi^2)$ is the square of the total angular momentum, so that the angular momentum may for convenience be designated by J. Similarly the projection of the angular momentum on the polar axis is given by $M(h/2\pi)$, or simply by the integer M.

The frequency observed when the molecule makes a transition between a lower state of energy W_1 and an upper state of energy W_2 is given by

$$\nu = \frac{W_2 - W_1}{h} = \frac{h}{8\pi^2 I}[J_2(J_2+1) - J_1(J_1+1)] \qquad (1\text{-}7)$$

From the correspondence principle, these frequencies may be expected to approximately equal the frequencies given by expression (1-1); hence J_2 should equal $J_1 + 1$, and

$$\nu = 2B(J+1) \qquad (1\text{-}8)$$

where J is the angular-momentum quantum number for the lower state (J_1), and $B = (h/8\pi^2 I)$ is called the rotational constant. The quantity

B is often expressed in units of cm^{-1} for infrared spectroscopy. In that case $B = (h/8\pi^2 Ic)$. For microwave spectroscopy, B will generally be given in cycles per second, or $B = h/8\pi^2 I$. However, numerical values will usually be quoted in megacycles, or 10^6 cycles/sec. The selection rule that $J_2 = J_1 + 1$ or $\Delta J = \pm 1$ for dipole radiation of a diatomic molecule will be more rigorously demonstrated in the discussion of intensities later in this chapter.

1-2. Energy Levels of the Diatomic Molecule. From Eq. (1-8) it is seen that the spectrum of a rigid rotor consists of absorption lines equally spaced in frequency with an interval $2B$. Although the rigid rotor is an idealization to which actual molecules conform to a good approximation, accurate spectroscopic measurement reveals many deviations from this approximation. As J increases and the molecule rotates faster, it stretches so that the moment of inertia increases. Moreover, the nuclei vibrate back and forth along the line joining them even in the lowest vibrational state. A much greater difficulty from the point of view of obtaining a complete theoretical treatment is that the entire molecular system, composed of interacting electrons as well as nuclei, is so complicated that an exact quantum-mechanical solution is impossible.

However, since the electrons are very much lighter than the nuclei and move in electric fields of approximately the same intensity, the electron motion is very much faster than that of the nuclei; i.e., many cycles of the electronic motion occur during a small portion of a cycle of the nuclear motion. It is therefore reasonable to treat first the electronic motion, considering the nuclei as fixed. Then the internuclear distance r appears as a parameter. In this way the electrons are found to be capable of occupying several states, each giving the molecule a particular value of the energy U, for each internuclear distance. Generally in microwave spectroscopy only the lowest of these electronic states is important.

As the internuclear distance is slowly varied, the electronic energy varies. Because the electronic motion is so fast in comparison with the nuclear motion, at each instant the electronic energy may be considered to have reached its equilibrium value corresponding to that distance. Thus we are justified in treating the vibration and rotation of the nuclei separately from the electronic motion. In this treatment $U(r)$, which is the sum of the electron energy plus energy of electrostatic interaction between the two nuclei, appears as the potential energy. The validity of this approximation was discussed by Born and Oppenheimer ([8]; see also [62], pp. 259–274, and [21], Chap. I). They showed that the entire molecular energy, including that due to electronic motion, can be expanded in powers of $(m/M)^{\frac{1}{4}}$, where m is the electronic mass and M an average nuclear mass. Separation of nuclear and electronic motions hence corresponds to selecting the larger terms of the series expansion

and neglecting those which are smaller by $(m/M)^{\frac{1}{2}}$ or more. In some cases the neglected terms lead to observable effects, but they can only with difficulty be taken into account.

Using the approximation that the variation in electron energy with nuclear motion may be included in the potential $U(r)$, the wave equation for vibration and rotation of a diatomic molecule becomes

$$\frac{1}{M_1} \nabla_1^2 \psi + \frac{1}{M_2} \nabla_2^2 \psi + \frac{8\pi^2}{h^2} [W - U(r)]\psi = 0 \qquad (1\text{-}9)$$

in which ψ is the wave function for the nuclear motion, M_1 and M_2 are the nuclear masses, and

$$\nabla_i^2 = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \qquad \text{where } i = 1 \text{ or } 2 \qquad (1\text{-}10)$$

x_i, y_i, and z_i being Cartesian coordinates of the ith nucleus relative to axes fixed in space.

Transforming to spherical polar coordinates r, θ, ϕ of the second nucleus relative to the first as origin (cf. [62], p. 264),

$$\frac{1}{r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial \psi}{\partial r}\right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta}\left(\sin \theta \frac{\partial \psi}{\partial \theta}\right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2}$$
$$+ \frac{8\pi^2 \mu}{h^2}[W - U(r)]\psi = 0 \quad (1\text{-}11)$$

where μ is the reduced mass, $M_1 M_2/(M_1 + M_2)$. The variables may be separated by the substitution

$$\Psi = R(r)\Theta(\theta)\Phi(\phi) \qquad (1\text{-}12)$$

$\Theta(\theta)$ and $\Phi(\phi)$ turn out to be the same as the wave functions found above for the rigid rotor.

The radial wave function $R(r)$ obtained by the separation process is given by

$$\frac{1}{r^2} \frac{d}{dr}\left(r^2 \frac{dR}{dr}\right) + \left\{\frac{8\pi^2 \mu}{h^2}[W - U(r)] - \frac{J(J+1)}{r^2}\right\} R = 0 \quad (1\text{-}13)$$

The term $J(J+1)/r^2$ may be regarded as a potential energy associated with the centrifugal force due to the rotational angular momentum J. Substituting the expression

$$R(r) = \frac{1}{r} S(r) \qquad (1\text{-}14)$$

we get

$$\frac{d^2 S}{dr^2} + \left\{-\frac{J(J+1)}{r^2} + \frac{8\pi^2 \mu}{h^2}[W - U(r)]\right\} S = 0 \qquad (1\text{-}15)$$

The solutions of Eq. (1-15) will obviously depend on the form of $U(r)$. Since it is seldom possible actually to solve the electronic wave equation, it is customary to use an empirical expression for $U(r)$.

From experimental studies of molecular spectra and from calculations on simple molecules, the general form of $U(r)$ is known to be that of Fig. 1-1 (see [471]). At large distances the atoms are independent, and the force between them is negligible. Their energy is then just the sum of the energies of the individual atoms. At very small distances, when the atoms are "in contact," they must repel each other. At some intermediate distance there must be a potential minimum, corresponding to the equilibrium distance of the atoms.
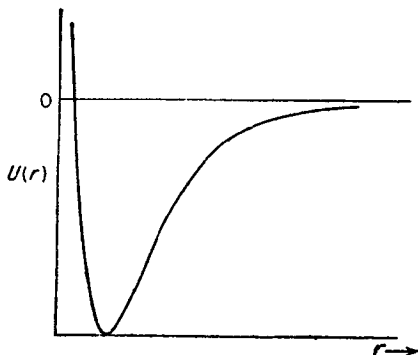
FIG. 1-1. Variation of molecular potential energy $U(r)$ with internuclear distance r.

Solution for Morse Potential. A potential which fulfills these requirements is the Morse function [16]

$$U(r) = D(1 - e^{-a(r-r_e)})^2 \tag{1-16}$$

where D = dissociation energy of the molecule
r_e = equilibrium distance between nuclei
a = a constant

The Morse function differs from the true potential at $r = 0$, where the actual potential would be extremely large. However, the Morse potential is also quite large at $r = 0$ and this is a region where the wave function of the vibrating rotor is expected to be small so that the discrepancy is not serious.

Using the Morse potential function, the radial equation (1-15) becomes

$$\frac{d^2S}{dr^2} + \left[- \frac{J(J+1)}{r^2} + \frac{8\pi^2\mu}{h^2}(W - D - De^{-2a(r-r_e)} + 2De^{-a(r-r_e)}) \right]S = 0 \tag{1-17}$$

The solution of this equation for $J = 0$ has been given by Morse [16] and for any J by Pekeris [52]. Substituting

$$y = e^{-a(r-r_e)} \quad \text{and} \quad A = J(J+1)\frac{h^2}{8\pi^2\mu r_e^2} \tag{1-18}$$

in Eq. (1-17), we obtain

$$\frac{d^2S}{dy^2} + \frac{1}{y}\frac{dS}{dy} + \frac{8\pi^2\mu}{a^2h^2}\left(\frac{W-D}{y^2} + \frac{2D}{y} - D - \frac{Ar_e^2}{y^2r^2} \right)S = 0 \tag{1-19}$$

For $A \neq 0$, it is necessary to expand r_e^2/r^2 in terms of y:

$$\frac{r_e^2}{r^2} = \frac{1}{[1 - (\ln y)/ar_e]^2} = 1 + \frac{2}{ar_e}(y - 1)$$
$$+ \left(-\frac{1}{ar_e} + \frac{3}{a^2 r_e^2}\right)(y - 1)^2 + \cdots \quad (1\text{-}20)$$

If the first three terms of this Taylor expansion are retained, Eq. (1-19) becomes

$$\frac{d^2 S}{dy^2} + \frac{1}{y}\frac{dS}{dy} + \frac{8\pi^2\mu}{a^2 h^2}\left(\frac{W - D - c_0}{y^2} + \frac{2D - c_1}{y} - D - c_2\right)S = 0 \quad (1\text{-}21)$$

in which

$$c_0 = A\left(1 - \frac{3}{ar_e} + \frac{3}{a^2 r_e^2}\right)$$
$$c_1 = A\left(\frac{4}{ar_e} - \frac{6}{a^2 r_e^2}\right) \quad (1\text{-}22)$$
$$c_2 = A\left(-\frac{1}{ar_e} + \frac{3}{a^2 r_e^2}\right)$$

Eq. (1-21) can be further simplified by the substitutions

$$S(y) = e^{-z/2}z^{b/2}F(z) \qquad z = 2dy$$
$$d^2 = \frac{8\pi^2\mu}{a^2 h^2}(D + c_2) \qquad b^2 = -\frac{32\pi^2\mu}{a^2 h^2}(W - D - c_0) \quad (1\text{-}23)$$

so that it becomes

$$\frac{d^2 F}{dz^2} + \left(\frac{b + 1}{z} - 1\right)\frac{dF}{dz} + \frac{v}{z}F = 0 \quad (1\text{-}24)$$

where

$$v = \frac{4\pi^2\mu}{a^2 h^2 d}(2D - c_1) - \tfrac{1}{2}(b + 1) \quad (1\text{-}25)$$

As in the usual quantum-mechanical treatment of the simple harmonic oscillator or of the hydrogen atom (*cf.* [62]), for the solution of Eq. (1-24) to be finite and vanish at the ends of its range, it must be given by a terminating series, *i.e.*, a polynomial. In fact, Eq. (1-24) is identical in form with the equation for Laguerre polynomials found in the solution of the hydrogen atom. This requirement can be shown to restrict v to the values 0, 1, 2, ... Strictly speaking, the solutions thus obtained satisfy the boundary condition $S \to 0$ as $r \to -\infty$ rather than the proper condition $S \to 0$ as $r \to 0$. Ter Haar [156] has examined this approximation and shown that it is usually a good one.

It is possible to solve for W using Eqs. (1-25), (1-23), (1-22), and

(1-18), which give

$$W_{J_*} = D + c_0 - \frac{(D - \frac{1}{2}c_1)^2}{D + c_2} + \frac{ah(D - \frac{1}{2}c_1)}{\pi \sqrt{2\mu} \sqrt{D + c_2}} \left(v + \frac{1}{2} \right)$$
$$- \frac{a^2 h^2}{8\pi^2 \mu} \left(v + \frac{1}{2} \right)^2 \quad (1\text{-}26)$$

Expanding Eq. (1-26) in powers of c_1/D and c_2/D, it takes the form:

$$\frac{W_{J_*}}{h} = \omega_e(v + \tfrac{1}{2}) - x_e\omega_e(v + \tfrac{1}{2})^2 + J(J + 1)B_e - D_e J^2(J + 1)^2$$
$$- \alpha_e(v + \tfrac{1}{2})J(J + 1) \quad (1\text{-}27)$$

where

$$\omega_e = \frac{a}{2\pi} \sqrt{\frac{2D}{\mu}} \qquad x_e = \frac{h\omega_e}{4D} \qquad B_e = \frac{h}{8\pi^2 I_e}$$
$$D_e = \frac{h^3}{128\pi^4 \mu^3 \omega_e^2 r_e^6} = \frac{4B_e^3}{\omega_e^2} \quad (1\text{-}28)$$
$$\alpha_e = \frac{3h^2\omega_e}{16\pi^2\mu r_e^2 D} \left(\frac{1}{ar_e} - \frac{1}{a^2 r_e^2} \right) = 6\sqrt{\frac{x_e B_e^3}{\omega_e}} - \frac{6B_e^2}{\omega_e}$$

ω_e, α_e, B_e in (1-27) and (1-28) are expressed in cycles per second. The terms in Eq. (1-27) can be identified with the solutions of more specialized problems, so that each can be given a physical significance. Thus the first term involving $(v + \frac{1}{2})$ has the form of the solution of the wave equation of a pure vibrator with a harmonic potential. The second term is obtained when the vibrator potential is made anharmonic by the addition of a cubic term in the potential energy. A term of the form $BJ(J + 1)$ is just that obtained in Eq. (1-4), the solution of the rigid rotor problem, while the next to last term comes from centrifugal stretching of the rotating molecule. The last term allows for the change in average moment of inertia due to vibration and the consequent change in rotational energy.

Dunham's Solution for Energy Levels. Some other more refined potentials have been used for problems in optical spectra involving excited rotational or vibrational states ([471], pp. 102, 108). Dunham [34] has calculated the energy levels of a vibrating rotor, by a Wentzel-Kramers-Brillouin method, for any potential which can be expanded as a series of powers of $(r - r_e)$ in the neighborhood of the potential minimum. This treatment shows that the energy levels can be written in the form

$$F_{vJ} = \sum_{l,j} Y_{lj}(v + \tfrac{1}{2})^l J^j(J + 1)^j \quad (1\text{-}29)$$

where l and j are summation indices, v and J are, respectively, vibrational and rotational quantum numbers, and Y_{lj} are coefficients which depend on molecular constants. The effective potential function of the vibrating

rotor may be written in the form

$$U = a_0\xi^2(1 + a_1\xi + a_2\xi^2 + \cdots) + B_e J(J + 1)(1 - 2\xi + 3\xi^2 - 4\xi^3 + \cdots) \quad (1\text{-}30)$$

where $\xi = (r - r_e)/r_e$, $B_e = h/8\pi^2\mu r_e^2$. The term involving $B_e J(J + 1)$ allows for the influence of the rotation on the effective potential.

Dunham [34] shows that the first 15 Y_{ij}'s are

$$\left.\begin{aligned}
Y_{00} &= B_e/8(3a_2 - 7a_1^2/4) \\
Y_{10} &= \omega_e[1 + (B_e^2/4\omega_e^2)(25a_4 - 95a_1a_3/2 - 67a_2^2/4 \\
&\quad + 459a_1^2a_2/8 - 1155a_1^4/64)] \\
Y_{20} &= (B_e/2)[3(a_2 - 5a_1^2/4) + (B_e^2/2\omega_e^2)(245a_6 - 1365a_1a_5/2 \\
&\quad - 885a_2a_4/2 - 1085a_3^2/4 + 8535a_1^2a_4/8 + 1707a_2^3/8 \\
&\quad + 7335a_1a_2a_3/4 - 23{,}865a_1^3a_3/16 - 62{,}013a_1^2a_2^2/32 \\
&\quad + 239{,}985a_1^4a_2/128 - 209{,}055a_1^6/512)] \\
Y_{30} &= (B_e^2/2\omega_e)(10a_4 - 35a_1a_3 - 17a_2^2/2 + 225a_1^2a_2/4 \\
&\quad - 705a_1^4/32) \\
Y_{40} &= (5B_e^3/\omega_e^2)(7a_6/2 - 63a_1a_5/4 - 33a_2a_4/4 - 63a_3^2/8 \\
&\quad + 543a_1^2a_4/16 + 75a_2^3/16 + 483a_1a_2a_3/8 - 1953a_1^3a_3/32 \\
&\quad - 4989a_1^2a_2^2/64 + 23{,}265a_1^4a_2/256 - 23{,}151a_1^6/1024)
\end{aligned}\right\} \quad (1\text{-}31)$$

$$\left.\begin{aligned}
Y_{01} &= B_e\{1 + (B_e^2/2\omega_e^2)[15 + 14a_1 - 9a_2 + 15a_3 - 23a_1a_2 \\
&\quad + 21(a_1^2 + a_1^3)/2]\} \\
Y_{11} &= (B_e^2/\omega_e)\{6(1 + a_1) + (B_e^2/\omega_e^2)[175 + 285a_1 - 335a_2/2 \\
&\quad + 190a_3 - 225a_4/2 + 175a_5 + 2295a_1^2/8 - 459a_1a_2 \\
&\quad + 1425a_1a_3/4 - 795a_1a_4/2 + 1005a_2^2/8 - 715a_2a_3/2 \\
&\quad + 1155a_1^3/4 - 9639a_1^2a_2/16 + 5145a_1^2a_3/8 \\
&\quad + 4677a_1a_2^2/8 - 14{,}259a_1^3a_2/16 \\
&\quad + 31{,}185(a_1^4 + a_1^5)/128]\} \\
Y_{21} &= (6B_e^3/\omega_e^2)[5 + 10a_1 - 3a_2 + 5a_3 - 13a_1a_2 \\
&\quad + 15(a_1^2 + a_1^3)/2] \\
Y_{31} &= (20B_e^4/\omega_e^3)[7 + 21a_1 - 17a_2/2 + 14a_3 - 9a_4/2 + 7a_5 \\
&\quad + 225a_1^2/8 - 45a_1a_2 + 105a_1a_3/4 - 51a_1a_4/2 + 51a_2^2/8 \\
&\quad - 45a_2a_3/2 + 141a_1^3/4 - 945a_1^2a_2/16 + 435a_1^3a_3/8 \\
&\quad + 411a_1a_2^2/8 - 1509a_1^3a_2/16 + 3807(a_1^4 + a_1^5)/128]
\end{aligned}\right\} \quad (1\text{-}32)$$

$$\left.\begin{aligned}
Y_{02} &= -(4B_e^3/\omega_e^2)\{1 + (B_e^2/2\omega_e^2)[163 + 199a_1 - 119a_2 + 90a_3 \\
&\quad - 45a_4 - 207a_1a_2 + 205a_1a_3/2 - 333a_1^2a_2/2 + 693a_1^2/4 \\
&\quad + 46a_2^2 + 126(a_1^3 + a_1^4/2)]\} \\
Y_{12} &= -(12B_e^4/\omega_e^3)(\tfrac{19}{2} + 9a_1 + 9a_1^2/2 - 4a_2) \\
Y_{22} &= -(24B_e^5/\omega_e^4)[65 + 125a_1 - 61a_2 + 30a_3 - 15a_4 \\
&\quad + 495a_1^2/4 - 117a_1a_2 + 26a_2^2 + 95a_1a_3/2 - 207a_1^2a_2/2 \\
&\quad + 90(a_1^3 + a_1^4/2)]
\end{aligned}\right\} \quad (1\text{-}33)$$

$$Y_{03} = 16B_e^5(3 + a_1)/\omega_e^4$$
$$Y_{13} = (12B_e^6/\omega_e^5)(233 + 279a_1 + 189a_1^2 + 63a_1^3 - 88a_1a_2$$
$$- 120a_2 + 80a_3/3)$$
$$Y_{04} = -(64B_e^7/\omega_e^3)(13 + 9a_1 - a_2 + 9a_1^2/4) \tag{1-34}$$

It should be noted that B_e is generally much smaller than ω_e. For most molecules the ratio B_e^2/ω_e^2 is of the order of 10^{-6}, although for light molecules such as H_2 it approaches more nearly to 10^{-3}. In such cases more terms are required in the expressions for the various coefficients.

If B_e/ω_e is small, the Y's can be related to the ordinary band spectrum constants as follows:

$$
\begin{aligned}
Y_{10} &\approx \omega_e & Y_{20} &\approx -\omega_e x_e & Y_{30} &\approx \omega_e y_e \\
Y_{01} &\approx B_e & Y_{11} &\approx -\alpha_e & Y_{21} &\approx \gamma_e \\
Y_{02} &\approx -D_e & Y_{12} &\approx \beta_e & Y_{40} &\approx \omega_e z_e \\
Y_{03} &\approx H_e
\end{aligned} \tag{1-35}
$$

where these symbols refer to the coefficients in the Bohr theory expansion for the molecular energy levels:

$$F_{vJ} = \omega_e(v + \tfrac{1}{2}) - \omega_e x_e(v + \tfrac{1}{2})^2 + \omega_e y_e(v + \tfrac{1}{2})^3 + \omega_e z_e(v + \tfrac{1}{2})^4$$
$$+ B_v J(J + 1) - D_e J^2(J + 1)^2 + H_e J^3(J + 1)^3 + \cdots \tag{1-36}$$

where $B_v = B_e - \alpha_e(v + \tfrac{1}{2}) + \gamma_e(v + \tfrac{1}{2})^2 \ldots$ (cf. [471], p. 92, pp. 107–108).

Sandeman [103] has extended Dunham's treatment to include other terms of the same order of magnitude which involve higher powers of the vibrational quantum number.

For the special case of the Morse potential function, Dunham shows that all the Y_{l0}'s except Y_{10} and Y_{20} vanish and all but the first terms in the expressions for Y_{10} and Y_{20} are zero. Because of the simplicity of the expressions obtained with the Morse function, and because it does give a quite good fit to the actual potential in the region of $r = r_e$, the Morse function has been widely used.

Dependence of Energy on Isotopic Masses. Since the frequencies of lines in microwave spectra can be measured with great precision, and since they can be used to evaluate the molecular moment of inertia, they permit an accurate evaluation of atomic or nuclear masses, or rather the mass ratios of isotopic nuclei.

To a good approximation we can use the Morse potential solution. The usual expansion for energy levels, appropriate to the Morse potential or other similar potentials, is given by (1-27), from which the frequency of a microwave rotational transition, where J changes by one unit, is easily shown to be

$$\nu = \frac{W_{J+1} - W_J}{h} = 2B_e(J + 1) - 2\alpha_e(v + \tfrac{1}{2})(J + 1) - 4D_e(J + 1)^3$$
$$= 2B_v(J + 1) + 4D_e(J + 1)^3 \tag{1-37}$$

The constants B_e, α_e, and D_e are usually expressed in cm^{-1} in optical work. In the above formula they, and therefore the frequency, are in cycles per second, which may be divided by 10^6 to convert to megacycles, the most usual unit for microwave work.

B_e and α_e can be evaluated directly from microwave spectra if two lines can be measured with different values of v; for instance, the same rotational transition in the ground vibrational state and the first excited vibrational state. The term in $(J + 1)^3$ is often negligible because $D_e = (4B_e^3/\omega_e^2)$ is smaller in magnitude than B_e by $4(B_e/\omega_e)^2$, or approximately 10^{-6} for most molecules. However, for very light molecules or large J this term may be rather prominent. When required it can be calculated with sufficient accuracy from $B_0 \approx B_e$ and ω_e, which is usually obtainable from optical spectra.

If the nuclear masses are known from mass spectrographic or other measurements, a determination of B_e allows an evaluation of the internuclear distance r_e, since B_e is related to the moment of inertia I_e.

$$r_e = \sqrt{\frac{I_e}{\mu}} = \sqrt{\frac{h}{8\pi^2 B_e \mu}} \tag{1-38}$$

where $\mu = M_1 M_2/(M_1 + M_2)$ is the reduced mass. The accuracy with which r_e can be determined for a diatomic molecule is limited mainly by the error in Planck's constant h, which is required to calculate I_e from B_e. The best available value of this constant is

$$h = (6.6252 \pm 0.0005) \times 10^{-27} \text{ erg-sec}$$

[795] so that r_e can be determined to an accuracy of about 1 part in 6000. It is often convenient to have B_e in megacycles, r_e in angstroms, and μ in atomic mass units. In these units

$$I_e = \frac{5.055 \times 10^5}{B_e} = \frac{I_e \text{ in cgs units}}{1.6598 \times 10^{-40}} \tag{1-39}$$

and

$$r_e = \sqrt{\frac{5.055 \times 10^5}{\mu B_e}} \qquad \text{angstrom units} \tag{1-40}$$

Table 1a gives the constants of a number of representative diatomic molecules. Table 1b lists certain constants of one isotopic species of all diatomic molecules whose microwave rotational spectrum have been studied.

If the spectroscopic constants have been measured for one isotopic species of a molecule, their values for other species may be found from the following relations which are deducible from Eq. (1-28):

$$\omega_e \propto \frac{1}{\sqrt{\mu}} \qquad B_e \propto \frac{1}{\mu} \qquad \alpha_e \propto \frac{1}{\mu^{\frac{3}{2}}} \qquad D_e \propto \frac{1}{\mu^2} \tag{1-41}$$

The values in Table 1a have been calculated with the aid of these relations in some cases.