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The Energy Levels of a Rotating Vibrator

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The energy levels of a rotating vibrator are calculated in considerable detail by means of the Wentzel-Brillouin-Kramers method. The new terms determined are $\omega_e z$ and a set of correction terms which appear in the earlier members of the equation. These correction terms enter in such a way that ω_e is not exactly the coefficient of $(v+\frac{1}{2})$; B_e is not exactly the coefficient of $K(K+1)$, etc. However the differences are small and are detectable only in the case of light molecules. The correction terms are of the magnitude of B_e^2/ω_e^2. Formulas for the effect of the correction terms on isotope shifts are given, and for the calculation of the correction terms themselves. Also a method is given for obtaining actual potential functions from band spectrum data, based on Morse's potential function. Finally the numerical magnitude of the correction terms for several states of H_2 and for NaH is discussed.

INTRODUCTION

RECENT work on the measurement of isotope masses by means of band spectra[1,2,3] has led to the necessity of examining in more detail the theory of a rotating vibrator. The energy levels of this sytem were thoroughly investigated by Kratzer,[4] Born and Hückel,[5] Kemble[6] and Birge[7] on the basis of the Bohr theory, but no detailed quantum mechanical treatment of this system has been published. This seems to be at least partly because the potential function suggested by Morse[8] has energy levels which agree exactly with those predicted for it by the Bohr theory[9] (apart from the matter of half quantum numbers), and which fit the empirical energy levels remarkably well. Furthermore, the early work of Fues[10] indicated an almost complete agreement between the two theories for quite general potential functions, the difference between Fues' result and that of the Bohr theory being merely a constant term, spectroscopically undetectable. Calculation of the higher approximations, however, shows that this constant term is one of a set of terms which in general depend on the vibrational and rotational quantum numbers, adding small corrections to the familiar terms in the energy level formula. It happens that for Morse's potential function the corrections to the pure vibra-

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[1] R. T. Birge, Phys. Rev. **37**, 841, 227, and 233 (1931).
[2] F. A. Jenkins, Phys. Rev. **39**, 549 (1932).
[3] Mecke and Wurm, Zeits. f. Physik **61**, 37 (1930).
[4] A. Kratzer: Zeits. f. Physik **3**, 289 (1920).
[5] M. Born and Hückel, Phys. Zeits. **24**, 1 (1923).
[6] E. C. Kemble, J. Opt. Soc. Am. **12**, 1 (1926).
[7] R. T. Birge, Nature **116**, 783 (1925) and Phys. Rev. **27**, 245 (1926). See also W. C. Pomeroy, Phys. Rev. **29**, 67 (1927).
[8] P. M. Morse, Phys. Rev. **34**, 57 (1929).
[9] P. M. Davidson and W. C. Price, Proc. Roy. Soc. **A130**, 105 (1931).
[10] E. Fues, Ann. d. Physik **80**, 367 (1926).

tion terms are exactly zero which leads us to expect they will be small in actual molecules. But the predictions of Morse's function for the corrections to the rotational terms are not zero, so we cannot expect these to be small.

The analysis shows that the coefficients of the various powers of $(v+\frac{1}{2})$ and $K(K+1)$ in the energy level formula are really a series in powers of the ratio B_e^2/ω_e^2. This ratio is, for most molecules, of the order of magnitude of 10^{-6} so that all of the terms beyond the first (given by the Bohr theory) are negligible. However, for hydrogen molecules and some of the hydrides this ratio is more nearly 10^{-3}, so that in these cases they cannot be neglected.

In this paper the energy levels of a rotating vibrator will be calculated in detail using a perfectly general type of potential function. To find the characteristic values of Schrödinger's equation we shall use the Wentzel-Brillouin-Kramers[11] method (hereafter called the W. B. K. method) because it solves our problem in a very simple fashion. The particular advantage of this method is that it uses the Bohr theory energy levels as its first approximation, correcting for higher quantum effects by its later approximations. Now according to the correspondence principle point of view, quantum effects become small not only for large quantum numbers, but also for large masses, and the nuclei of molecules have large masses compared to electronic masses. We would therefore expect the Bohr energy levels to be good approximations in this case. The W. B. K. method can make use of this fact by starting with the Bohr levels and calculating any further terms as small corrections. The details of the W. B. K. method necessary for application to this problem have been developed in the preceding paper and we shall apply them here to the solution of the rotating-vibrator, and then discuss applications to a few actual molecular states.

CALCULATION OF THE ENERGY LEVELS

Our first problem is to find the energy levels of a rotating vibrator. To do this we calculate the characteristic values of Schrödinger's equation for this system, which is:

$$\frac{d^2\psi}{d\xi^2}+\frac{8\pi^2 m r_e^2}{h^2}\left[E-V-\frac{h^2K(K+1)}{8\pi^2 r_e^2 m(1+\xi)^2}\right]\psi=0. \tag{1}$$

Here $\xi=(r-r_e)/r_e$, r_e being the equilibrium nuclear separation; m is the reduced nuclear mass; V the potential function with a minimum at r_e; and the last term in the bracket, which we shall call V_r, is due to the centrifugal force of rotation.

It would be convenient to use a potential function based on that of Morse, because this gives a very good approximation to actual energy levels. However, it is difficult to include the effect of rotation in Morse's potential function. In the end the simplest procedure is to use a power series expansion of

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[11] G. Wentzel, Zeits. f. Physik **38,** 518 (1926); L. Brillouin, Comptes Rendus **183,** 24 (1926); H. A. Kramers, Zeits. f. Physik **39,** 828 (1926). For a good short account see A. Sommerfeld: Ergänzungsband, p. 158.

V around the point $\xi=0$, as V_r has a particularly simple expansion about this point. Having found the energy levels in terms of this sort of expansion, it is not difficult then to rewrite the formulas in terms of any simple expression for the potential function by expanding the latter in a power series about $\xi=0$ and equating coefficients. We shall therefore use

$$V = hca_0\xi^2(1 + a_1\xi + a_2\xi^2 + a_3\xi^3 + \cdots) \tag{2}$$

where $a_0=\omega_e^2/4B_e$; ω_e is the classical frequency of small oscillations expressed in cm^{-1} and $B_e=h/(8\pi^2 m r_e^2 c)$.

We shall first calculate the energy levels neglecting rotation (i.e., for the case $K=0$). The effect of rotation can then be found by rewriting the whole effective potential function in the form of Eq. (2) and comparing coefficients.

In the preceding paper I showed that the energy levels of a potential function with a single minimum could be found by evaluating a generalized phase integral (Eq. (23) of that paper). It will be convenient to express all quantities involving energy in this equation in terms of wave numbers. This involves replacing E by hcF and V by hcU. Eq. (23) then becomes

$$\oint (F - U)^{1/2}d\xi - (B_e/32)\oint U'^2(F - U)^{-5/2}d\xi + \cdots = 2\pi B_e^{1/2}(v + \tfrac{1}{2}). \tag{3}$$

The first integral on the left has been evaluated many times.[4,5,6] However, the method necessary to evaluate the second integral is also applicable to the first, and handles it in a particularly simple fashion, so we shall use it here.

The first step is to transform to the independent variable U. The integral becomes

$$\oint (F - U)^{1/2}d\xi = \oint (F - U)^{1/2}(U')^{-1}dU. \tag{4}$$

Here the integral is taken in the U plane twice around the two points $U=0$ and $U=F$ (the origin of energy being so chosen that $U=0$ for $\xi=0$). The cut in the ξ plane between the two turning points goes over into a cut in the U plane between the origin and the point $U=F$.

The integral can be evaluated if we know U' as a function of U, so we expand U'

$$U' = A_1U^{1/2} + A_2U + A_3U^{3/2} + A_4U^2 + \cdots, \tag{5}$$

from which we can calculate $(U')^{-1}$ in a series of the form

$$(U')^{-1} = A_1^{-1}U^{-1/2}[1 + B_1U^{1/2} + B_2U + B_3U^{3/2} + \cdots]. \tag{6}$$

We can therefore write the integral as:

$$\begin{aligned} &\oint (F - U)^{1/2}d\xi \\ &= \oint iA_1^{-1}[1 - F/2U - F^2/8U^2 + \cdots][1 + B_1U^{1/2} + B_2U + \cdots]dU. \end{aligned} \tag{7}$$

There is now a cut in the U plane extending from the point $U=0$ to ∞, introduced by the expansion Eq. (5). Consequently when the integration is performed all of the terms in $U^{n/2}$ for which n is odd will vanish because the integrand will have opposite signs on the two circuits around the point $U=0$. Of the remaining terms only those in U^{-1} will have a residue. The integration yields:

$$\oint (F-U)^{1/2}d\xi = (2\pi/A_1)[F + B_2F^2/4 + B_4F^3/8 + 5B_6F^4/64 + \cdots]. \quad (8)$$

The second integral in Eq. (3) can be evaluated similarly. As before we transform to U as independent variable. On substituting the expansion Eq. (5) for U' and expanding the denominator, we have

$$\oint U'(F-U)^{-5/2}dU = 4\pi[A_3 + 5A_5F/2 + 35A_7F^2/8 + 105A_9F^3/16 + \cdots]. \quad (9)$$

We have now evaluated the integrals of Eq. (3) in terms of the coefficients A_n of Eq. (5), and it remains to find these A_n's in terms of the a_n's of Eq. (2). If we expand $U^{n/2}$ and U' as power series in ξ and substitute all of these in Eq. (5), we can equate coefficients of like powers of ξ on both sides of the equation and obtain enough relations to determine the coefficients A_n.

The results of this procedure are:

$$\begin{aligned}
A_1 &= 2a_0^{1/2};\ A_2 = 2a_1;\ A_3 = a_0^{-1/2}(3a_2 - 7a_1^2/4)\\
A_4 &= a_0^{-1}(4a_3 - 6a_1a_2 + 5a_1^3/2)\\
A_5 &= a_0^{-3/2}(5a_4 - 19a_1a_3/2 - 17a_2^2/4 + 105a_1^2a_2/8 - 273a_1^4/64)\\
A_6 &= a_0^{-2}(6a_5 - 14a_1a_4 - 12a_2a_3 + 22a_1^2a_3 + 20a_1a_2^2 - 30a_1^3a_2 + 8a_1^5)\\
A_7 &= a_0^{-5/2}(7a_6 - 39a_1a_5/2 - 33a_2a_4/2 - 31a_3^2/4 + 279a_1^2a_4/8 + 75a_2^3/8\\
&\quad + 243a_1a_2a_3/4 - 825a_1^3a_3/16 - 2277a_1^2a_2^2/32 + 9009a_1^4a_2/128\\
&\quad - 8151a_1^6/512).
\end{aligned} \quad (10)$$

. . . .

We are now ready to go back to Eq. (3) and substitute the results we have obtained for the integrals. We shall at first express these in terms of the A_n's and B_n's for simplicity, using the a_n's only at the end.

Substituting Eqs. (8) and (9) in Eq. (3) we have

$$\begin{aligned}
&(2\pi/A_1)[F + B_2F^2/4 + B_4F^3/8 + 5B_6F^4/64 + \cdots]\\
&\qquad - (2\pi B_e/16)[A_3 + 5A_5F/2 + 35A_7F^2/8 + \cdots] = 2\pi B_e^{1/2}(v+\tfrac{1}{2}).
\end{aligned} \quad (11)$$

By the inversion of this series we find F as a power series in $(v+\frac{1}{2})$. The result is:

$$\begin{aligned}
F = {} & B_eA_1A_3/16 + A_1B_e^{1/2}(v+\tfrac{1}{2}) + (B_e^{3/2}A_1^2/32)(5A_5 - B_2A_3)(v+\tfrac{1}{2})\\
& - (B_eB_2A_1^2/4)(v+\tfrac{1}{2})^2 + (B_e^2A_1^3/128)(35A_7 - 15B_2A_5 + 3A_3B_2^2\\
& - 3A_3B_4)(v+\tfrac{1}{2})^2 + (B_e^{3/2}A_1^3/8)(B_2^2 - B_4)(v+\tfrac{1}{2})^2\\
& + (B_e^2A_1^4/64)(10B_2B_4 - 5B_2^3 - 5B_6)(v+\tfrac{1}{2})^4 + \cdots.
\end{aligned} \quad (12)$$

Substituting Eqs. (10) gives us the term value equation for an oscillator having Eq. (2) for a potential function up to and including terms in B_e^4/ω_e^4. (One term, not depending on $(v+\frac{1}{2})$, has been omitted.)

Before we carry out this substitution, however, it will be convenient to take account of rotation. In this case the effective potential function is $U+U_r=U_K$, which is of the form

$$\begin{aligned} U_K = a_0\xi^2(1 + a_1\xi + a_2\xi^2 + \cdots) \\ + B_eK(K+1)(1 - 2\xi + 3\xi^2 - 4\xi^3 + \cdots). \quad (13) \end{aligned}$$

We can introduce a new variable η such that $\xi=\eta+\epsilon$, ϵ being a constant, and choose ϵ so that the minimum of U_K falls at the point $\eta=0$. If we then express U_K as a power series in η of the same form as Eq. (2), and use the coefficients of this new series in Eq. (12) instead of the a_n's, we shall have the energy levels of a rotating vibrator.

The detail of determining these coefficients is rather tedious but quite straightforward, so we shall not reproduce it here. The energy level equation which one finds is most conveniently written in the following form

$$F_{vK} = \sum_{lj} Y_{lj}(v+\tfrac{1}{2})^l K^j(K+1)^j. \quad (14)$$

The first subscript under Y refers to the power of the vibrational quantum number, the second to that of the rotational quantum number.

The first fifteen Y_{lj}'s are found to be [12]

$$Y_{00} = (B_e/8)(3a_2 - 7a_1^2/4)$$

$$\begin{aligned} Y_{10} = \omega_e[1 + (B_e^2/4\omega_e^2)(25a_4 - 95a_1a_3/2 - 67a_2^2/4 + 459a_1^2a_2/8 \\ - 1155a_1^4/64)] \end{aligned}$$

$$\begin{aligned} Y_{20} = (B_e/2)[3(a_2 - 5a_1^2/4) + (B_e^2/2\omega_e^2)(245a_6 - 1365a_1a_5/2 - 885a_2a_4/2 \\ - 1085a_3^2/4 + 8535a_1^2a_4/8 + 1707a_2^3/8 + 7335a_1a_2a_3/4 \\ - 23865a_1^3a_3/16 - 62013a_1^2a_2^2/32 + 239985a_1^4a_2/128 \\ - 209055a_1^6/512)] \end{aligned}$$

$$Y_{30} = (B_e^2/2\omega_e)(10a_4 - 35a_1a_3 - 17a_2^2/2 + 225a_1^2a_2/4 - 705a_1^4/32)$$

$$\begin{aligned} Y_{40} = (5B_e^3/\omega_e^2)(7a_6/2 - 63a_1a_5/4 - 33a_2a_4/4 - 63a_3^2/8 + 543a_1^2a_4/16 \\ + 75a_2^3/16 + 483a_1a_2a_3/8 - 1953a_1^3a_3/32 - 4989a_1^2a_2^2/64 \\ + 23265a_1^4a_2/256 - 23151a_1^6/1024) \end{aligned}$$

$$Y_{01} = B_e[1 + (B_e^2/2\omega_e^2)(15 + 14a_1 - 9a_2 + 15a_3 - 23a_1a_2 + 21(a_1^2 + a_1^3)/2)]$$

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[12] Eq. (14) can be changed to a set of power series in $(K+1/2)^2$ instead of $K(K+1)$ by using the formulas

$$K^n(K+1)^n = [(K+\tfrac{1}{2})^2 - \tfrac{1}{4}]^n$$

This will affect only the second order terms (of the order of B_e^2/ω_e^2) in each of the Y's.

$$
\begin{aligned}
Y_{11} = {} & (B_e^2/\omega_e)\,[6(1+a_1)+(B_e^2/\omega_e^2)(175+285a_1-335a_2/2+190a_3-225a_4/2 \\
& + 175a_5 + 2295a_1^2/8 - 459a_1a_2 + 1425a_1a_3/4 - 795a_1a_4/2 \\
& + 1005a_2^2/8 - 715a_2a_3/2 + 1155a_1^3/4 - 9639a_1^2a_2/16 + 5145a_1^2a_3/8 \\
& + 4677a_1a_2^2/8 - 14259a_1^3a_2/16 + 31185(a_1^4 + a_1^5)/128)\,] \qquad (15) \\
Y_{21} = {} & (6B_e^3/\omega_e^2)(5 + 10a_1 - 3a_2 + 5a_3 - 13a_1a_2 + 15(a_1^2 + a_1^3)/2) \\
Y_{31} = {} & (20B_e^4/\omega_e^3)(7 + 21a_1 - 17a_2/2 + 14a_3 - 9a_4/2 + 7a_5 + 225a_1^2/8 \\
& - 45a_1a_2 + 105a_1a_3/4 - 51a_1a_4/2 + 51a_2^2/8 - 45a_2a_3/2 \\
& + 141a_1^3/4 - 945a_1^2a_2/16 + 435a_1^2a_3/8 + 411a_1a_2^2/8 \\
& - 1509a_1^3a_2/16 + 3807(a_1^4 + a_1^5)/128) \\
Y_{02} = {} & -\,(4B_e^3/\omega_e^2)\,[1 + (B_e^2/2\omega_e^2)(163 + 199a_1 - 119a_2 + 90a_3 - 45a_4 \\
& - 207a_1a_2 + 205a_1a_3/2 - 333a_1^2a_2/2 + 693a_1^2/4 + 46a_2^2 \\
& + 126(a_1^3 + a_1^4/2))\,] \\
Y_{12} = {} & -\,(12B_e^4/\omega_e^3)(19/2 + 9a_1 + 9a_1^2/2 - 4a_2) \\
Y_{22} = {} & -\,(24B_e^5/\omega_e^4)(65 + 125a_1 - 61a_2 + 30a_3 - 15a_4 + 495a_1^2/4 - 117a_1a_2 \\
& + 26a_2^2 + 95a_1a_3/2 - 207a_1^2a_2/2 + 90(a_1^3 + a_1^4/2)) \\
Y_{03} = {} & 16B_e^5(3 + a_1)/\omega_e^4 \\
Y_{13} = {} & (12B_e^6/\omega_e^5)(233 + 279a_1 + 189a_1^2 + 63a_1^3 - 88a_1a_2 - 120a_2 + 80a_3/3) \\
Y_{04} = {} & -\,(64B_e^7/\omega_e^6)(13 + 9a_1 - a_2 + 9a_1^2/4).
\end{aligned}
$$

The new quantities are Y_{40}, Y_{13} and the second terms [13] in $Y_{10}Y_{20}Y_{01}Y_{11}$ Y_{02}.

The connection between the Y's and the ordinary band spectrum constants is as follows:

$$
\begin{array}{lll}
Y_{10} \sim \omega_e & Y_{20} \sim -\,\omega_e x & Y_{30} \sim \omega_e y \\
Y_{01} \sim B_e & Y_{11} \sim -\,\alpha_e & Y_{21} \sim \gamma_e \\
Y_{02} \sim D_e & Y_{12} \sim \beta_e & Y_{40} \sim \omega_e z \\
Y_{03} \sim F_e & Y_{04} \sim H_e &
\end{array}
$$

Throughout this paper the Y_{lj}'s will be used to denote the coefficients in Eq. (14), and the old coefficients will retain their mechanical significance. Thus B_e will be used only for $h/8\pi^2 I_e c$ and not for the coefficient of $K(K+1)$ in the energy level equation, etc.

DISCUSSION OF THE ENERGY LEVEL FORMULA

The most important point about Eq. (15) is that the Y's are not exactly equal to the coefficients given by the Bohr theory. For example, Y_{10}, which is the coefficient of $(v+\frac{1}{2})$, is not equal to ω_e, but differs from it by terms in B_e^2/ω_e^2. Similarly Y_{01} differs from B_e by small terms. In fact each of the Y's

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[13] The second term in Y_{00} has been omitted because it is not important. It has the same form as Y_{40} or the second term in Y_{20}.

is a power series in B_e^2/ω_e^2. Now for many molecules this ratio is of the order of magnitude of 10^{-6} so that the first term of the power series is adequate for all practical purposes. But for some molecules, notably H_2, B_e^2/ω_e^2 is more nearly 10^{-3}, and higher terms in several of the Y's must be taken into consideration. This correction arises from the presence of the second term on the left hand side of Eq. (3), and one can see from the fact that m appears in the denominator of this term that the corrections will be small for heavy systems and large for light ones. It is for this reason that these terms will be most easily detectable in H_2.

Unfortunately the detection of the effect of these higher terms in actual spectra will be complicated by the fact that the nuclear potential function is defined only in so far as the nuclear and electronic wave functions are separable. This is ordinarily true to terms in B_e^2/ω_e^2, which means that this coupling will introduce terms of nearly the same size as the new terms which we have been discussing. In cases where the interaction is very large, such as l-uncoupling or when there are perturbations, the coupling effects will be much more important than the effects discussed here. This state of affairs can be detected by using the fact that for a simple rotator Y_{02} (D_e) is determined by the other Y's. The values of Y_{l0} and Y_{l1} determine all of the a_n's. Consequently Y_{02} can be found in terms of these Y's. If this theoretical value of Y_{02} does not agree with the observed value, the system is not a simple rotating vibrator, and we can expect that there is appreciable interaction. It is therefore important to find Y_{02} as accurately as possible from the data, as it is necessary to show that coupling effects are small before one can determine the size of the correction terms.

One of the chief uses of a detailed derivation of the energy level equation is to find how the terms depend on the nuclear mass. By definition we know that B_e is proportional to m^{-1} and that ω_e is proportional to $m^{-1/2}$, so we can find the mass dependence of the Y's if we assume that two isotopic molecules have identical potential functions.

The Bohr theory leads to the result suggested by Kemble[14] that

$$(Y_{lj}^i/Y_{lj}) = (m/m^i)^{(l+2j)/2} \tag{16}$$

the superscript i referring to one of the isotopes, but this equation takes account of only the first terms in the expressions for the Y's. The presence of the new correction terms will alter the mass dependence of the Y's, as they are now of the form

$$Y_{lj} = f_{lj}(B_e, \omega_e)\ [\alpha_{lj} - (B_e^2/\omega_e^2)\,\beta_{lj} + \cdots] \tag{17}$$

where $f_{lj}(B_e, \omega_e)$ contains that part of the first term in Y_{lj} which depends on m, whereas α_{lj} and β_{lj} do not depend on m. Since B_e^2/ω_e^2 is small, Eq. (16) now becomes

$$(Y_{lj}^i/Y_{lj}) = (m/m^i)^{l/2+j}[1 + (\beta_{lj}B_e^2/\alpha_{lj}\omega_e^2)((m - m^i)/m^i)] \tag{18}$$

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[14] R. S. Mulliken, Phys. Rev. **25**, 126 (1925).

This gives us a simple way of finding the correction to the isotope effect due to the presence of the new correction terms in the energy level formula.

We want to be able to find the coefficients β (in Eq. (17)) from the experimental data. This is simplified by the fact that these correction terms are small enough so that we can use a method of successive approximations. If we regard the Y's as being given experimentally, and if we neglect the correction terms, a set of approximate a_n's can be calculated from the Y_{l0}'s and the Y_{l1}'s. These a_n's can then be used to calculate the correction terms with sufficient accuracy for most purposes. Carrying out this procedure algebraically we find the following equations for the corrections which are designated by β_{lj}.

$$\begin{aligned}
\beta_{01} &= Y_{10}^2Y_{21}/4Y_{01}^3 + 16a_1Y_{20}/3Y_{01} - 8a_1 - 6a_1^2 + 4a_1^3 \\
\beta_{10} &= 5Y_{10}Y_{30}/4Y_{01}^2 + a_1Y_{10}^2Y_{21}/3Y_{01}^3 - 10a_1 - 20a_1^2 - 15a_1^3/2 \\
&\quad - 5a_1^4/2 + Y_{20}(4a_1 + 16a_1^2/3)/Y_{01} + Y_{20}^2/2Y_{01}^2 \\
\beta_{02} &= 73/2 + 37a_1 + 67a_1^2/2 + 33a_1^3 - 6a_1^4 - 9Y_{10}Y_{30}/2Y_{01}^2 \\
&\quad + Y_{10}^2Y_{21}(3 - 11a_1/6)/2Y_{01}^3 - Y_{20}(130/3 + 4a_1 + 74a_1^2/3)/2Y_{01} \\
&\quad + 31Y_{20}^2/9Y_{01}^2 \\
a_1 &= (Y_{11}Y_{10}/6Y_{01}^2) - 1
\end{aligned} \tag{19}$$

The other β's (β_{20}, β_{11}, and others not given in Eqs. (15)) are more complicated but can be calculated in the same fashion. Eqs. (19) are not as simple as the expressions for the corresponding β's in Eqs. (15). However to use Eqs. (19), it is not necessary to calculate all of the a_n's involved first.

In view of the importance of Morse's[8] potential function for vibrational analysis we shall discuss briefly its relation to the formulas which we have used.

The most striking property of Morse's potential function is the simplicity of the energy level equation to which it leads. It is interesting to see how this simplicity arises in the method we have used for calculating energy levels. Morse's potential function can be written

$$U = D(1 - e^{-a\xi})^2. \tag{20}$$

From this it is easy to show that

$$U' = 2a(DU)^{1/2} - 2aU. \tag{21}$$

Comparing with Eq. (5) we see that for this case

$$A_1 = 2aD^{1/2} \quad A_2 = -2a \tag{22}$$

and that all the other A's are zero. Now all of the Y_{l0}'s, except Y_{10} and Y_{20}, involve A_n's with $n \geqq 3$ so that they vanish, and the same is true of all of the terms beyond the first in Y_{10} and Y_{20}. A similar but no so far reaching simplification can be found in the case of Kratzer's potential function. This accounts in detail for the fact that the Bohr theory with half quantum numbers gives Morse's energy levels exactly.[9]

Because of its simplicity and because it represents actual molecular energy levels so well, it would be convenient to have a relatively simple potential function based on that of Morse. One could then determine a potential curve from band frequencies more easily than at present. The most satisfactory way to do this seems to be to write the potential function in the following form. (The a used here is equal to Morse's a multiplied by r_e.)

$$U = D[(1 - e^{-a\xi})^2 + P_4(1 - e^{-a\xi})^4 + P_5(1 - e^{-a\xi})^5 + \cdots]. \tag{23}$$

This can be expanded about the point $\xi = 0$ in a power series and the a_n's so determined can be substituted in Eqs. (15) and then the P's determined in terms of the Y's. Morse determined a from the relation $a\,^2B_e = -\omega_e x$. We shall use

$$a = 1 - (Y_{10}Y_{11}/6Y_{01}^2). \tag{24}$$

Then the P_n's can be expressed as follows:

$$\begin{aligned} P_4 &= (2/3)[1 + Y_{20}/Y_{01}a^2] \\ P_5 &= [Y_{10}^2Y_{21}/6Y_{01}^3 - 5 + 10a - 23a^2/4 + 7a^3/6 - 3P_4a^2(a - 1)]/5a^3 \qquad (25) \\ P_6 &= Y_{10}Y_{30}/5a^4Y_{01}^2 + P_4/5 - 17P_4^2/20 - P_5. \end{aligned}$$

Now since the first term in Eq. (23) is a very good representation of actual potential functions we would expect the P_n's to be quite small and Eq. (23) should converge rapidly.

In calculating Eqs. (25) the new correction terms were *not* used. For obtaining graphical potential functions they are not of enough importance. It should also be mentioned that although the P_n's make corrections to the heat of dissociation predicted by Morse's potential function, it is not to be supposed that these corrections are very reliable. It has been repeatedly shown that the extrapolation of energy levels to dissociation can be used only when most of the energy levels are actually known.

DISCUSSION OF ACTUAL DATA

We turn now to the calculation of the correction terms for some actual molecular states. These terms are most important in the case of the H_2 molecule. The upper states are known to show a good deal of l-uncoupling,[15] as can be seen easily from the difference between the observed and calculated values of $Y_{02}(D_e)$. The normal state of the molecule should be quite free from such coupling effects, but unfortunately the vibrational analysis has not been carried through with enough precision to be able to tell definitely whether or not this is the case.[16]

Nevertheless it is possible to see how large the correction terms will be for

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[15] W. Weizel, Zeits. f. Physik **55**, 483 (1929) and **56**, 727 (1929); G. H. Dieke, Zeits. f. Physik **55**, 447 (1929).

[16] Birge and Jeppeson (Nature **125**, 463 (1930)) have found evidence for a "perturbation" of this lowest level, but there is not yet enough data on the constants of this state to determine the nature of the perturbation.

several states of this molecule, and they will give us some idea of what to expect.

For the normal state Hyman[17] has found the following values for the Y's

$$\begin{aligned} Y_{10} &= 4371 \qquad & Y_{11} &= 2.794 \\ Y_{01} &= 60.59 \qquad & Y_{21} &= 0.0105 \\ & & Y_{20} = 113.5. \end{aligned} \tag{26}$$

From these β_{01} can be calculated and turns out to be

$$\beta_{01} = -1.37.$$

Also

$$B_e^2/\omega_e^2 = 1/5200.$$

So we conclude that Y_{01} differs from B_e by one part in 3790. In a careful analysis this would be detectable.

Similarly, using data from the analyses of Richardson and Davidson,[18] we find that for the $2^1\Sigma$ state

$$\begin{aligned} Y_{01} &= B_e(1 - 1/778) \\ Y_{10} &= \omega_e(1 - 1/9240) \\ Y_{02} &= D_e(1 - 1/213). \end{aligned} \tag{27}$$

Although in Y_{10} the correction is very small, it is obviously not negligible in either of the other two.

The behavior of the corrections for this state is of some interest as it seems to be typical. The correction to Y_{10} is very small. If Morse's potential function were correct it would be zero, and the fact that it is small shows that Morse's function is a good approximation. Now Morse's function is known to be a better fit for most molecules than for H_2,[9] so we would expect β_{10} to be even smaller for other molecules than it is here.

The correction to Y_{02} is quite large. This appears to be a typical behavior as can be seen from the fact that the value of β_{02} predicted by Morse's potential function varies between 10 and 500 for moderate values of a. This is considerably larger than the other β's we have been discussing.

In the $2^3\Sigma$ state[18] we find that the corrections are quite small. β_{02} is the largest, being equal to 5.2 so that

$$Y_{02} = D_e(1 - 1/1165).$$

The other two are negligible.

The corrections to Y_{20} and Y_{11} demand a knowledge of Y_{40} and of Y_{31}, but as these coefficients have not been determined for the states of H_2 it is not possible to find the corresponding corrections.

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[17] H. H. Hyman, Phys. Rev. **36,** 187 (1930).

[18] O. W. Richardson and P. M. Davidson, Proc. Roy. Soc. **A125,** 23 (1929).

An interesting case arises in the alkali hydrides.[19] They are the only known bands for which Y_{20} is positive. We might therefore expect the correction terms to be abnormally large. Weizel[20] has tried to explain the strange behavior of these bands as due to l-uncoupling, but there also appears to be an abnormality in the pure vibration states, and it is therefore of interest to see how the corrections turn out in this case.

The best data available appear to be on NaH.[19] The value of B_e^2/ω_e^2 is 0.0000310 which is materially smaller than for the states of H_2. In this respect LiH would be the most suitable substance for finding large effects. The corrections are

$$\begin{aligned} Y_{01} &= B_e(1 - 1/2280) \\ Y_{10} &= \omega_e(1 - 1/3920) \\ Y_{02} &= D_e(1 - 1/886). \end{aligned} \tag{28}$$

In terms of β_{lj}'s one finds

$$\beta_{01} = -14.15 \qquad \beta_{10} = -8.23 \qquad \beta_{02} = -36.4.$$

These β's are, on the whole, larger than those for H_2 which indicates a slightly anomalous behavior of the potential function. The relatively small value of B_e^2/ω_e^2 prevents these large values of β from making large corrections to the Y's.

For molecules heavier than hydrides, the values of B_e^2/ω_e^2 are so small that unless the β's are abnormally large, the corrections will be undetectable.

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[19] LiH, G. Nakamura, Zeits. f. Physik **59**, 218 (1930); NaH, T. Hori, Zeits. f. Physik **62**, 352 (1930); KH, G. M. Almy and C. D. Hause, Phys. Rev. **39**, 178 (1932).

[20] W. Weizel, Zeits. f. Physik **60**, 599 (1930).