

energy function is also important in its own right, as it often greatly facilitates the analysis of experimental data.

2. SPECTROSCOPIC PROPERTIES OF A GIVEN POTENTIAL ENERGY FUNCTION

The two-term (or third-order) JWKB quantization condition for a particle of mass μ with energy E bound by the one-dimensional potential energy function $U(r)$ may be written as (1):

$$v + \frac{1}{2} = \left(\frac{2\mu}{\hbar^2} \right)^{1/2} \int_{r_1}^{r_2} dr [E - U(r)]^{1/2} + \frac{1}{96\pi} \left(\frac{\hbar^2}{2\mu} \right)^{1/2} \int_{\Gamma} dr U''(r) / [E - U(r)]^{3/2} \quad (1)$$

where primes denote differentiation with respect to the distance coordinate r and the contour Γ encloses the segments of the real line (see Fig. 1) on which $E > U(r)$. While eq. (1) may be applied much more generally, the present chapter will only consider cases such as that shown in Fig. 1 where there exists only one "classically accessible" interval $[r_1, r_2]$ enclosed by the contour Γ .

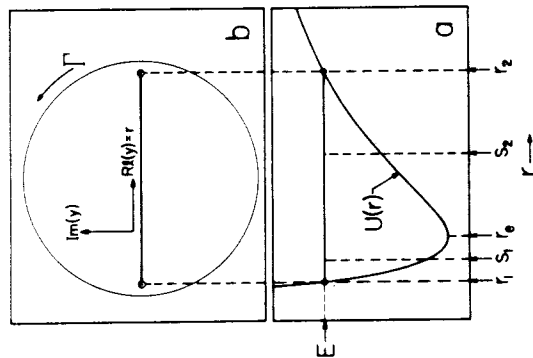


Figure 1. Schematic drawing of quantities associated with the JWKB contour integrals of eq. (1) (Reproduced by permission of the American Institute of Physics)

APPLICATIONS OF BOHR QUANTIZATION IN DIATOMIC MOLECULE SPECTROSCOPY

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Use of the first- and higher-order JWKB quantization conditions for determining the diatomic molecule level energies and rotational constants implied by any given potential energy function is described. The widely used first-order RKR inversion procedure for determining the potential energy function implied by a given set of experimental vibrational energies and rotational constants is then derived and a procedure for including the effect of higher-order terms is outlined. Finally, simple analytic expressions for the limiting near-dissociation behaviour of vibrational energies and rotational constants are derived and their use for determining accurate molecular dissociation energies and long-range potential energy constants is described.

1. INTRODUCTION

Elsewhere in this volume, Fröman (1) has discussed the basis of the JWKB approximation and derived the first- and higher-order JWKB quantization conditions for the allowed eigenvalues of a one-dimensional potential. The present chapter will describe certain applications of these expressions in diatomic molecule spectroscopy, paying special attention to the problem of determining the molecular dissociation energy and potential energy curve implied by a given set of observed vibration-rotation level energies. As in any inversion problem, it is essential to first understand the properties of the equation one is trying to invert, so we will begin with an examination of the JWKB quantization condition and of the way in which the spectroscopic properties of a given system may be calculated from a knowledge of its potential energy function. This ability to calculate properties of an assumed-known potential

To obtain the one-term quantization condition, the second integral is deleted from the right hand side of eq. (1), while the higher-order eigenvalue equations are obtained by adding appropriate higher-order contour integrals to this equation. However, with a few notable exceptions (2), it is the single-term or first-order version of the JWKB quantization condition which has been used in most practical applications to diatomic molecule spectroscopy. Much of the discussion in this chapter is therefore based on this simple case. However, since the greater accuracy provided by the higher-order expressions is becoming increasingly important in modern work, the theory is formulated in so as to make extension to the higher-order approximations quite straightforward.

Within any chosen order of the JWKB approximation, the allowed eigenvalues of the potential $U(r)$ are defined as the values of E for which the sum of terms on the right hand side of eq. (1) yields an exact integer for the vibrational index v ($=0, 1, 2, \dots$ etc.). For a diatomic molecule, $\mu = m_1 m_2 / (m_1 + m_2)$ is the reduced mass associated with the stretching and rotation of the molecular axis, while the total potential energy function

$$U(r) = V(r) + J(J+1)\hbar^2/2\mu r^2 \quad (2)$$

is the sum of the electronic potential energy $V(r)$ plus the centrifugal potential term due to the rotational motion characterized by total angular momentum quantum number J . Thus, values of v calculated from eq. (1) in general depend on the two independent variables E and J .

Before proceeding further, it is convenient to introduce the notation

$$I_{k,\ell}^{m,n} = I_{k,\ell}^{m,n}(E, J) = \oint_{\Gamma} dr [\partial^m U(r) / \partial r^m] / r^\ell [E - U(r)]^{k+\frac{1}{2}} \quad (3)$$

for integrals of the type appearing in eq. (1), and to note that for any well-behaved function $U(r)$ such integrals may be readily evaluated to arbitrary accuracy using either of two simple numerical quadrature procedures (3). The first of these procedures (3,4) makes use of the fact that any $I_{k,\ell}^{m,n}$ integral may be written as a numerical constant times the k -th partial derivative with respect to E (at constant J) of $I_{0,\ell}^{m,n}$. The integrand of the latter is integrable on the real line across the whole of the interval bounded by the classical turning points r_1 and r_2 . Subdividing this interval $[r_1, r_2]$ at points s_1 and s_2 defined such that $r_1 < s_1 < s_2 < r_2$ (see Fig. 1) and performing integration by parts on the subintervals $[r_1, s_1]$ and $[s_2, r_2]$ prior to each

of the k stages of differentiation with respect to E allows these $I_{k,\ell}^{m,n}$ integrals to be expressed as a linear combination of simple integrals across the subintervals $[r_1, s_1]$, $[s_1, s_2]$ and $[s_2, r_2]$, plus a few edge effect terms involving values of the integrand at s_1 and s_2 . The second integration method (3,5) is even simpler to use in that it involves a simple Gaussian-like quadrature formula for the integral as an appropriately weighted sum of values of the integrand evaluated at certain specified quadrature mesh points. The development of these methods is a matter of some significance, since while the $k=0$ integrals arising in many applications of the single-term quantization condition may be readily evaluated using a variety of techniques, difficulties associated with evaluation of such integrals for $k \geq 1$ had inhibited general use of the higher-order JWKB approximation.

Defining $\beta = (\hbar^2/2\mu)^{\frac{1}{2}}$, allows the two-term quantization condition of eq. (1) to be rewritten as

$$v + \frac{1}{2} = (1/2\pi\beta) I_{-1,0}^{0,0} + (\beta/96\pi) I_{1,0}^{2,1} \quad (4)$$

In applications of this expression, it is important to remember that the natural independent variables associated with the $I_{k,\ell}^{m,n}$ integrals are E and $[J(J+1)]$. The partial derivatives of $I_{k,\ell}^{m,n}$ with respect to these variables are readily expressed in terms of other integrals of this form:

$$\left[\frac{\partial I_{k,\ell}^{m,n}}{\partial E} \right]_J = -(k+\frac{1}{2}) I_{k+1,\ell}^{m,n} \quad (5)$$

$$\left[\frac{\partial I_{k,\ell}^{m,n}}{\partial [J(J+1)]} \right]_E = \beta^2 \left\{ (k+\frac{1}{2}) I_{k+1,\ell+2}^{m,n} + (-1)^m n(m+1)! I_{k,\ell+m+2}^{m,n-1} \right\} \quad (6)$$

However, in the calculation of many spectroscopic properties, it is more appropriate to hold v constant when taking partial derivatives with respect to $[J(J+1)]$, so we note that

$$\left[\frac{\partial I_{k,\ell}^{m,n}}{\partial [J(J+1)]} \right]_v = \left[\frac{\partial I_{k,\ell}^{m,n}}{\partial [J(J+1)]} \right]_E + \left[\frac{\partial I_{k,\ell}^{m,n}}{\partial E} \right]_v \quad (7)$$

For any given value of J , the vibration-rotation eigenvalues $E(v, J)$ are readily determined by evaluating the integrals on right hand side of eq. (3) at a sequence of trial energies until their sum converges on the desired value of $v + \frac{1}{2}$. The convergence of this search is greatly accelerated if at each trial energy the

partial derivative of v with respect to energy

$$1/\omega_v \equiv \left[\frac{\partial (v+\frac{1}{2})}{\partial E} \right]_J = (1/4\pi B) \{ I_{0,0}^{0,0} - (\beta^2/16) I_{2,0}^{2,1} \} \quad (8)$$

is calculated and used to estimate the required correction to E . Since both $(v+\frac{1}{2})$ and $1/\omega_v$ are smooth monotonically increasing functions of E , this convergence should be very rapid.

The traditional way of expressing the dependence of diatomic molecule level energies on the rotational quantum number J is via the expression

$$E(v,J) = G(v) + B_v [J(J+1)] - D_v [J(J+1)]^2 + H_v [J(J+1)]^3 + \dots \quad (9)$$

The rotational constant B_v and the centrifugal distortion constants D , H , ... etc. are therefore defined as derivatives of the energy with respect to $[J(J+1)]$ at constant v , all evaluated at $J=0$. Application of eqs. (4)-(6) and (9) then yields:

$$B_v = \left[\frac{\partial E}{\partial [J(J+1)]} \right]_v = - \left[\frac{\partial (v+\frac{1}{2})}{\partial [J(J+1)]} \right]_E \left/ \left[\frac{\partial (v+\frac{1}{2})}{\partial E} \right]_J \right. \quad (10)$$

$$= (\beta/4\pi) \omega_v \{ I_{0,2}^{0,0} - (\beta^2/16) [I_{2,2}^{2,1} + 4I_{1,4}^{0,0}] \}$$

Expressions for the centrifugal distortion constants are then obtained by repeated partial differentiation of eq. (10) with respect to $[J(J+1)]$ at constant v (using eqs. (5-7)). In particular, within the single-term quantization condition, the leading centrifugal distortion constant is (4):

$$D_v = -(\beta^4/4) [I_{1,4}^{0,0} / I_{0,0}^{0,0} - 2I_{0,0}^{0,0} / I_{0,2}^{0,0} + I_{0,0}^{0,0} / I_{0,0}^{0,0}] \\ + I_{1,0}^{0,0} (I_{0,2}^{0,0})^2 / (I_{0,0}^{0,0})^3 \quad (11)$$

and analogous expressions for H_v , L_v , ... etc. are readily obtained (4) by repeated differentiation of eq. (9).

The ability to calculate reliable values of the centrifugal distortion constants associated with any given potential energy function is often essential for optimizing the analysis of experimental data. In practise, it is often difficult to determine reliable values of these constants from direct fits of experimental data to eq. (9). This is particularly true for

highly excited vibrational levels for which relatively few rotational sublevels are often observed, but for which the distortion constants have the largest magnitude. This in turn introduces uncertainties into the values of $G(v)$ and B_v obtained from these fits and into the potential energy curve generated from them (see section 3 below). However, in the absence of curve crossings or other perturbations, centrifugal distortion constants calculated from eq. (11) and its analogs using any reasonably good trial potential will usually be quite reliable. Holding D , H , ... etc. fixed at these calculated values in a subsequent fit of experimental data to eq. (9) should yield improved $G(v)$ and B_v values, and thence an improved potential energy curve. The latter can then be used to calculate new centrifugal distortion constants and the procedure iterated to convergence. While a number of other quantum mechanical and semiclassical methods of calculating centrifugal distortion constants have been proposed (6)-(12), the present approach is unique in that it is equally stable and reliable for vibrational levels lying near dissociation and for those lying near the potential minimum, since the $I_{k,\ell}^{m,n}$ integrals may be computed equally readily in either region (3).

3. THE RKR INVERSION PROCEDURE

The first general inversion procedure for determining a diatomic molecule potential energy curve from a set of experimental vibration-rotation level energies is that due to Dunham (2). He showed that if the potential energy expansion

$$V(r) = a_0 \xi^2 [1 + a_1 \xi + a_2 \xi^2 + \dots] \quad (12)$$

where $\xi \equiv (r-r_e)/r_e$, is substituted into the two-term JWKB quantization condition, the level energies are given by

$$E(v,J) = \sum_{\ell,m} Y_{\ell m} (v+\frac{1}{2})^\ell [J(J+1)]^m \quad (13)$$

where the "Dunham coefficients" $Y_{\ell m}$ are explicitly-known (2) functions of the potential energy parameters a_0, a_1, a_2, \dots etc. Values of $Y_{\ell m}$ obtained from a fit of eq. (13) to experimental data may then be used to determine these potential parameters.

One limitation of the Dunham procedure is the fact that the potential expansion of eq. (12) diverges at large r , rather than approach an asymptote. To remove this difficulty, Simons et al. (13) and Thakkar (14) replaced Dunham's variable ξ by the expansion parameters $(r-r_e)/r$ and $[1-(r_e/r)]^p$, respectively, and used the

two-term quantization condition to determine the relationships between their new potential expansion coefficients and the Y_{Qm} constants of eq. (13). However, all three of these Dunham-type methods are rather complicated to apply when more than a few terms are included in the potential expansion. Moreover, while the second type of potential (13) may in principle be constrained to have the correct theoretically-known long-range behaviour, introduction of the necessary constraints makes the resulting formulation sufficiently complex to discourage its use. Thus, potentials obtained from this type of analysis usually do not have the correct long-range functionality, and hence they cannot be extrapolated reliably beyond the range of the data used in the analysis.

The Rydberg-Klein-Rees or RKR method (15-20) is a semi-classical inversion procedure which is much easier to apply to cases in which the data are very extensive, and it is not restricted by the assumption of any particular analytic form for either the potential energy function or the vibrational energy level equation. It is based on a formal inversion of the one-term quantization condition of eqs. (1) or (4) to yield expressions for the values of the classical turning points associated with given values of the vibrational energy (or of the vibrational index v).

Following Vanderslice et al. (18), the present derivation of the RKR procedure begins by identifying the variable A as the area on Fig. 1a enclosed by the potential energy curve and the total energy,

$$A(E, J) = \int_{r_1}^{r_2} dr [E - U(r)] \quad (14)$$

where the turning points r_1 and r_2 are functions of E and J . Partial differentiation of eq. (14) then yields:

$$r_2 - r_1 = (\partial A / \partial E)_J \quad (15)$$

$$1/r_1 - 1/r_2 = -(1/\beta^2) (\partial A / \partial J)_{E,J} \quad (16)$$

However, the definition of an Eulerian integral of the first kind allows eq. (14) to be expressed as

$$A(E, J) = (1/\pi) \int_{U_0}^E dE' (E-E')^{1/2} I_{0,0}^{0,0}(E', J) \quad (17)$$

where $U_0 = U_0(J)$ is the energy at the potential minimum. Substituting eq. (17) into (15) and (16) then yields

$$r_2 - r_1 = (1/2\pi) \int_{U_0}^E dE' (E-E')^{-1/2} I_{0,0}^{0,0}(E', J) \quad (18)$$

and

$$\frac{1}{r_1} - \frac{1}{r_2} = -(1/2\pi) \int_{U_0}^E dE' (E-E')^{1/2} I_{1,2}^{0,0}(E', J) + (1/\pi\beta^2) (E-U_0)^{1/2} I_{0,0}^{0,0}(U_0, J) \frac{dU_0}{d[J(J+1)]} \quad (19)$$

Making use of eq. (5), eq. (19) may be integrated by parts and transformed into

$$\frac{1}{r_1} - \frac{1}{r_2} = \frac{1}{2\pi} \int_{U_0}^E dE' (E-E')^{-1/2} I_{0,2}^{0,0}(E', J) + (E-U_0)^{1/2} \Delta(U_0, J) \quad (20)$$

where

$$\Delta(U_0, J) = (1/\pi) \left\{ -I_{0,2}^{0,0}(U_0, J) + (1/\beta^2) I_{0,0}^{0,0}(U_0, J) \frac{dU_0}{d[J(J+1)]} \right\} \quad (21)$$

According to the one-term quantization condition, $v_0 = -1/2$ and $\Delta(U_0, J) = 0$; while this is not exact, the correction term $(E-U_0)^{1/2} \Delta(U_0, J)$ is always fairly small.

Substituting for $I_{0,0}^{0,0}$ from eq. (8) and noting that $(1/\omega_v) dE' = dv'$, eq. (18) becomes

$$r_2 - r_1 = 2\beta \int_{v_0}^v dv' [E(v) - E(v')]^{-1/2} \left\{ 1 + \frac{\beta \omega_v}{64\pi} I_{2,0}^{2,1}(E', J) \right\} \quad (22)$$

where v_0 is the non-integer vibrational index associated with the potential minimum and $E' = E(v', J)$. Similarly, substitution of $I_{0,0}^{0,0}$ from eq. (10) into eq. (20) yields:

$$\frac{1}{r_1} - \frac{1}{r_2} = \frac{2}{\beta} \int_{v_0}^v dv' B_v [E(v) - E(v')]^{-1/2} \left\{ 1 + \frac{\beta^3 \omega_v}{64\pi B_v} I_{2,2}^{2,1}(E', J) + 4I_{1,4}^{0,0}(E', J) \right\} + (E-U_0)^{1/2} \Delta(U_0, J) \quad (23)$$

reliable procedure for evaluating the $I_{k,\ell}^{m,n}(E',J)$ integrals at all energies. In particular, the methods k,ℓ which had been devised (22,23,24) for calculating the "correction factors" in the integrands of eqs. (22) and (23) are all numerically unstable for vibrational levels lying near the dissociation limit. Another difficulty was the fact that two of these methods (23,24) appear to have neglected the contribution of the term $[E-U_0]^{1/2}\Delta(U_0,J)$ to eq. (23). However, with the techniques now available, it appears that reliable two-term or three-term RKR procedures should soon be replacing the familiar one-term method in routine spectroscopic analysis.

4. NEAR-DISSOCIATION BEHAVIOUR OF DIATOMIC MOLECULES

An extremely useful recent application of the JWKB quantization condition has been in the derivation of simple analytic expressions for the limiting near-dissociation behaviour of vibrational level spacings (25,26), rotational constants (4,27,28) and other properties (29-31). While most of these expressions are based on the one-term quantization condition, analogous near-dissociation expressions have been obtained for the second and third terms of the higher-order JWKB quantization condition (32),

These are the generalized RKR equations which include effects due to the second (i.e., third-order) term in the JWKB quantization condition.

Within the first-order JWKB approximation, the integrand factors in parentheses {...} appearing in eqs. (22) and (23) collapse to 1 and $\Delta(U_0,J)=0$. Evaluation of the resulting integrals therefore merely requires a knowledge of the experimental vibrational energies $E(v)$ and rotational constants B . While the integrands of these integrals are singular at the upper limit $v'=v$, the integrals are finite and may be readily evaluated using a variety of techniques. It is interesting to note that while the basic formulation of the "one-term" RKR procedure was developed by 1932, the method saw very little use for almost 30 years, at least partly because of the apparent difficulty of evaluating these improper integrals accurately. However, it is now clear (19,20) that with an appropriately chosen numerical integration technique, these integrals present no problem. In particular, making the change of variables $v'=v_0+(v-v_0)x$ reduces the integrals of eqs. (22) and (23) to the form

$$\int_0^1 dx F(x) [1-x]^{-1/2} \quad (24)$$

where the function $F(x)$ is well-behaved and finite across the whole range of integration $[0,1]$. Use of a quadrature procedure which explicitly takes account of the $[1-x]^{-1/2}$ weight function allows such integrals to be evaluated extremely efficiently. For example, using the Gauss-Mehler quadrature procedure (see eq. 25.4.36 of ref. 21), Tellinghuisen (19) showed that 4 integration mesh points often yield results accurate to one part in 10^4 !

The ordinary one-term RKR procedure described above has now become a standard spectroscopists' tool which is routinely used in the analysis of experimental data. However, although a general procedure for performing higher-order RKR calculations was reported by Vanderslice et al. (22) in 1965, it has not yet seen much use. In their approach, a single-term RKR calculation is first used to determine a realistic estimate of the potential energy function. This trial potential can then be used to evaluate the $I_{k,\ell}^{m,n}(E',J)$ integrals appearing in the integrands of eqs. (22) and (23) and the integration over v' repeated to give improved estimates of the turning points r_1 and r_2 . The resulting improved potential may then be used to give more realistic estimates of the $I_{k,\ell}^{m,n}(E',J)$ factors and the process repeated until convergence is achieved.

One factor inhibiting the general adoption of this procedure was the lack, until relatively recently (3-5), of any simple and

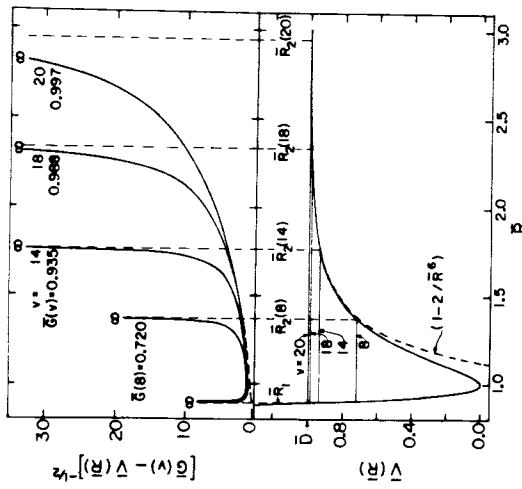


Figure 2. Lower: eigenvalues and turning points for 4 levels of a LJ(12,6) model potential. Upper: integrand of eq. (25) for these four levels. In both, energies and lengths are scaled by the potential well depth and equilibrium distance, respectively (Reproduced from J. Chem. Phys. 1970, 52, p. 3869).

and similar results can readily be obtained for any property defined in terms of $I_{m,n}^{k,l}$ type integrals corresponding to $k \geq 0$.

The most basic of these near-dissociation expressions is that for the distribution of vibrational energy levels, and its derivation illustrates the basic considerations which are involved in all such derivations. The natural starting point is the one-term JWKB expression for the density of vibrational levels (see eq. (8)) which may be rewritten as

$$\left(\frac{\partial v}{\partial E}\right)_J = \frac{1}{2\pi\beta} \int_{r_1}^{r_2} dr [E - V(r)]^{-1/2} \quad (25)$$

Fig. 2 shows the nature of the integrand of eq. (25) for four levels of a given model potential, where $\bar{R} = r/r_e$ and the potential energy function and vibrational eigenvalues are both scaled by the potential well depth. It is immediately clear that for the upper vibrational levels the dominant contribution to this integral comes from the region near the outer turning point. This suggests the fundamental approximation of this method, which involves replacing the exact potential by an approximate function which is accurate near the outer turning point though not necessarily highly reliable at shorter distances. As a justification of this approximation, the dashed curve seen in the upper portion of Fig. 2 shows the effect on the integrand of eq. (25) for the $v=20$ level of replacing the exact potential $V(r) = \epsilon [(r/r_e)^6 - 1]^2$ by its long-range part: $\epsilon [1 - 2(r_e/r)^6]$. While the extremely close agreement with the exact integrand (solid curve) for this case is partly due to the simplicity of the chosen model potential, it seems clear that for any potential this type of approximation will become increasingly exact the nearer the level in question lies to dissociation.

It has long been known that if two atoms lie sufficiently far apart that their electronic clouds overlap negligibly, their interaction energy may be expressed as a sum of inverse-power terms:

$$V(r) = D - \sum_{m \geq n} C_m / r^m \quad (26)$$

where D is the dissociation energy. The nature of the atoms to which the given molecular electronic state dissociates determines which (positive integer) values of m appear in eq. (26) (e.g., see ref. 33), and the perturbation theory has provided means by which many of these C_m coefficients may be calculated. Thus, for most molecular electronic states, the power n of the leading term in eq. (26) is known, and sometimes so is the associated C_n constant.

In view of the above, it seems appropriate to replace $V(r)$ in eq. (25) by the asymptotically dominant contribution to the long-range interaction potential: $V(r) = D - C_n / r^n$. Doing this and changing the variable of integration to $y = r_2^n(v) / r$ transforms eq. (25) into

$$\left(\frac{\partial v}{\partial E}\right)_J = \frac{1}{2\pi\beta} (C_n)^{1/n} [D - E(v)]^{-(n+2)/2n} \int_{r_2/r_1}^{r_2/r_1} dy y^{-2} (y^n - 1)^{-1/2} \quad (27)$$

For highly excited vibrational levels $r_2 \gg r_1$, and it is a very minor additional approximation to replace r_2/r_1 by ∞ ; in this limit the integral is well known and eq. (27) becomes

$$\frac{dE(v)}{dv} = K_n [D - E(v)]^{(n+2)/2n} \quad (28)$$

where the constant K_n is an exactly-known (25, 33) function of μ , n and C_n . In practice, it is often more convenient to use the integrated form of eq. (28), which for $n \neq 2$ is:

$$E(v) = D - X_0(n) [v_D - v]^{2n/(n-2)} \quad (29)$$

where (for $n > 2$) v_D is the non-integer effective vibrational index associated with the dissociation limit, $X_0(n) = [K_n(n-2)/2n]^{2n/(n-2)}$, and

$$X_1(n) = \bar{X}_1(n) / [\mu^n (C_n)^{2/n}]^{1/(n-2)} \quad (30)$$

while the constant $\bar{X}_1(n)$ depends only on the value of the integer n (see Table I). Another convenient form of these results is obtained on substituting eq. (29) into eq. (28) (or differentiating eq. (29)):

$$\frac{dE}{dv} = \left(\frac{2n}{n-2}\right) X_0(n) [v_D - v]^{(n+2)/(n-2)} \quad (31)$$

For practical applications of these results, it is useful to rewrite eqs. (28) and (31) in a form which facilitates graphical interpretation of the experimentally observed vibrational level spacings $\Delta G_{v+1/2} = E(v+1) - E(v)$. On making the approximation that

$$\Delta G_{v+1/2} \approx \frac{dE(v)}{dv} \Big|_{v+1/2} \quad (32)$$

Table 1. For energies in cm^{-1} , lengths in Å and mass in amu, numerical factors appearing in the limiting near-dissociation expressions for vibrational energies and rotational constants.

n	$\bar{X}_0(n)$	$\bar{X}_1(n)$	$\bar{X}_2(n)$	$\bar{X}_3(n)$	$\bar{X}_4(n)$
3	36410.	60221.	-24901.	1348.0	-73.367
4	13433.	4275.7	-205.65	-3.7691	-2.9067×10^{-1}
5	9170.9	1178.3	-15.377	-1.7742×10^{-1}	-5.3435×10^{-3}
6	7932.0	546.64	-2.7539	-1.9186×10^{-2}	-2.9942×10^{-4}

these expressions may be rewritten as

$$(\Delta G_{v+\frac{1}{2}})_{2n/(n+2)} = (K_n)^{2n/(n+2)} [D - E(v+\frac{1}{2})] \quad (33)$$

and
$$(\Delta G_{v+\frac{1}{2}})_{(n-2)/(n+2)} = [X_0(n)2n/(n-2)]^{(n-2)/(n+2)} (v_D - v - \frac{1}{2}) \quad (34)$$

They suggest that for vibrational levels lying sufficiently close to dissociation for eqs. (28) & (29) to be accurate, plots of the vibrational spacing, taken to the appropriate power, vs. $E(v+\frac{1}{2})$ or $v+\frac{1}{2}$ itself should be precisely linear and have intercepts corresponding, respectively, to the dissociation energy D and the vibrational index at dissociation, v_D . Moreover, the limiting slopes of these plots determine the constant $X_0(n)$ (or K_n), and hence define the value of the long-range potential constant C_n . In addition, once these three parameters (D , v_D and $X_0(n)$) are known, their substitution into eq. (29) yields reliable estimates of the energies of any vibrational levels lying above the highest one observed.

As an illustration of the utility of these results, Figs. 3 and 4 plot the vibrational spacings for the highest observed (prior to 1976) vibrational levels of the $B({}^1\Pi_{0u})$ state of I_2 (for which case it is known (25,33) that $n=5$) in the manner suggested by eqs. (33) and (34). The linearity of these plots and the internal consistency of their slopes attests to the appropriateness of these equations for characterizing such data, and suggests that the ensuing dissociation energy, C_5 constant and predicted energies for levels $v=73-87$ should be fairly reliable.

When applying these equations, it is important to remember the two fundamental assumptions on which they are based: (i) that the vibrational level density of eq. (25) depends mainly on the nature of the potential near the outer turning point of the level in question, and (ii) that the long-range potential may be

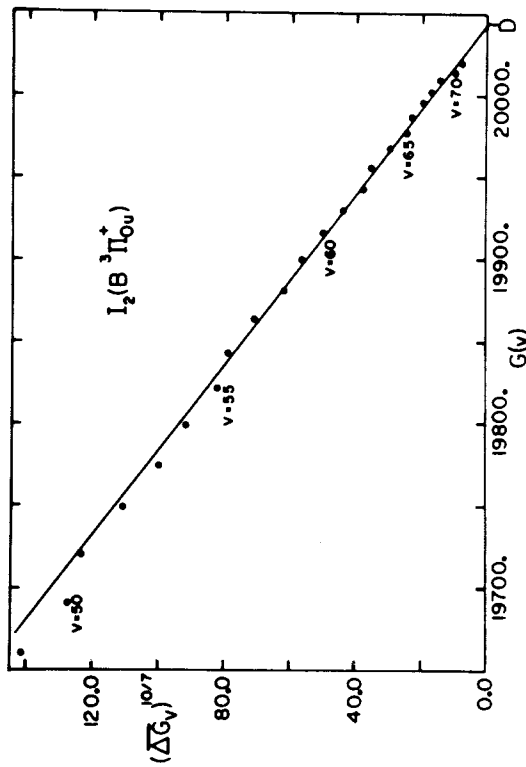


Figure 3. Data for B-state I_2 (34) plotted according to eq. (33) with $n=5$. (Reproduced from J. Mol. Spectrosc. 37 (1971), p. 109)

accurately represented by the single inverse-power term $V(r) = D - C/r^n$. Both of these assumptions are exactly true only for levels lying virtually right at dissociation. While experimental data will sometimes include observations of levels lying sufficiently near this limit that the errors in eqs. (28) and (29) are small (e.g., see Figs. 3 and 4), for most molecular states this is not the case. However, in the latter case the knowledge of the expected limiting behaviour of the distribution of vibrational eigenvalues may still greatly facilitate extrapolations to estimate molecular dissociation energies and predict the energies of unobserved levels, especially if a value of the appropriate C constant is provided by theory or some other experiment. In the long run, this transformation of an extrapolation beyond the observed vibrational levels into an interpolation between these data at low v and a known functional behaviour for $v \rightarrow v_D$ will probably prove to be the most significant feature of these results.

The approximations used in the derivation of eq. (28) may also be applied to any other property defined in terms of $I_{m,n}$ integrals corresponding to $k \geq 0$. While these approximations become relatively less accurate with increasing k they will still be valid for vibrational levels lying extremely close to dissociation.

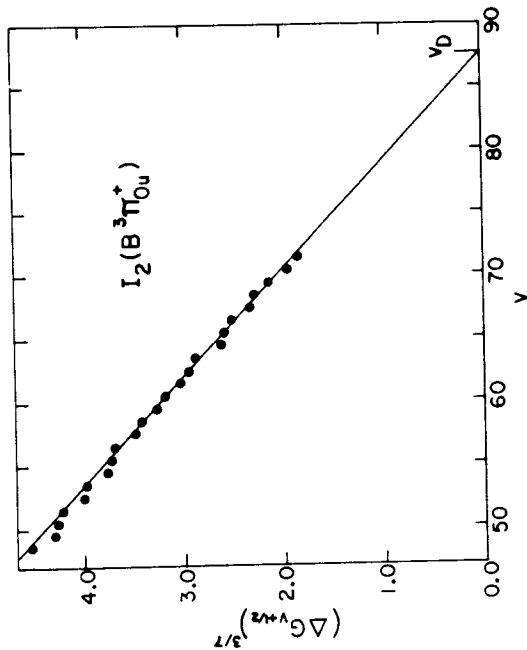


Figure 4. Data for B-state I_2 (34) plotted according to eq. (34) with $n=5$. (Reproduced from Molecular Spectroscopy I (1973), a Specialist Periodical Report of the Chemical Society (London), R.F. Barrow, D.A. Long and D.A. Millen editors).

For the rotational constants B_v, D_v, \dots etc. of eq. (9), the resulting expressions for their characteristic near-dissociation behaviour are (4,27,28):

$$B_v = X_1(n)(v_D - v) [2n / (n-2)] - 2 \quad (35)$$

$$D_v = -X_2(n)(v_D - v) [2n / (n-2)] - 4 \quad (36)$$

$$H_v = X_3(n)(v_D - v) [2n / (n-2)] - 6 \quad (37)$$

$$L_v = X_4(n)(v_D - v) [2n / (n-2)] - 8 \quad (38)$$

where $X_i(n)$ is given by eq. (30) and the associated $\bar{X}_i(n)$ constants are listed in Table 1. Analogous expressions for a number of other molecular properties have been derived by Stwally (29-31), and it seems clear that results of this type will play an increasingly important role in the interpretation of spectroscopic data in the years to come.

5. PROBLEMS

5.1 a) Derive equation (11).

b) Determine the generalized version of equation (11) which arises in the two-term (third-order) JWKB quantization condition.

5.2 Consider the potential $V(r) = -1/r + 1/4r^2$ where the energy and length units are chosen such that the factor $\beta = \sqrt{2\mu} = 1$.

a) Making appropriate use of known integrals (from tables) show that the first-order quantization condition yields the eigenvalues:

$$E(v, J) = -1/4(v + J + 1)^2$$

b) At $J = 0$ the vibrational energy is clearly given by $E(v, 0) = -1/4(v + 1)^2$ while the analogous expression for the rotational constant B_v is $B_v = 1/2(v + 1)^3$. Using these expressions as input to the first-order RKR equations (22) and (23), show that the expressions for $(r-r_1)$ and $(1/r_1 - 1/r_2)$ so obtained agree with the starting potential.

5.3 For a potential whose long-range attractive tail has the form $V(r) = D - A \exp(-br)$, derive the analog of eq. (28).

5.4 For the ground electronic state of Be^+ , $n=4$, $C_4 = 95340 \text{ cm}^{-1}$ and the four observed vibrational spacings are 344.98, 327.44, 310.06 and 292.91 cm^{-1} . Use the methods of section 4 to obtain estimates of the dissociation energy D and of v_D . (Hint: consider graphs analogous to Figs. 3 and 4).

5.5 Within the one-term quantization condition, show how the general expression for D_v given by eq. (11) gives rise to the limiting near-dissociation expression of eq. (36).

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