

Theory of deviations from the limiting near-dissociation behavior of diatomic molecules

Robert J. Le Roy^{a)}

Theoretical Chemistry Department, University of Oxford, 1 South Parks Road, Oxford, OX1 3TG, England
(Received 17 July 1980; accepted 28 August 1980)

The nature of the deviations from the limiting near-dissociation behavior of diatomic molecule properties is investigated. It is shown that for strongly bound species the leading deviations from the limiting behavior associated with the asymptotically dominant C_n/r^n potential energy term can be quantitatively attributed to the higher inverse power terms contributing to the long-range potential. The properties of the derived expressions show that experimental vibrational energies should often obey the limiting near-dissociation equation even when the term C_n/r^n is responsible for only a fraction of the potential strength at the levels' outer turning points. In contrast, B_v values (and other properties) are quite sensitive to the presence of additional contributions to the long-range potential, and deviations from their predicted limiting behavior should provide a sensitive new means of determining values of higher-order potential coefficients. The theory is illustrated by and tested against results for $B(^3\Pi_{0g}^+)$ -state I_2 and for simple model potentials.

I. INTRODUCTION

The past ten years have seen the derivation of a number of simple analytic expressions which quantitatively explain the limiting near-dissociation behavior of vibrational level spacings,¹ rotational constants,² and many other properties^{3,4} of diatomic molecules. Their validity is based on the fact that extreme potential anharmonicity makes molecules in highly excited vibrational levels spend most of their time in the neighborhood of their outer turning points. As a result, the properties of such levels depend mainly on this part of the potential energy function. For a level lying sufficiently near dissociation, the potential in this region has the characteristic inverse-power form⁵

$$V(r) = \mathcal{D} - \sum_{m>n} C_m/r^m, \quad (1)$$

where the (positive integer) powers m appearing in this sum are determined by the nature of the interacting particles.^{5,6} As the vibrational energy approaches dissociation, the potential at the levels' outer turning points becomes dominated by the leading ($m=n$) inverse-power term in Eq. (1). Substituting the ensuing approximation for the potential

$$V(r) \approx \mathcal{D} - C_n/r^n \quad (2)$$

into the appropriate first-order semiclassical expressions for various molecular properties^{7,8} then yields simple analytic expressions for their limiting near-dissociation behavior. For the vibrational energy derivative and the rotational constant B_v , the resulting equations are

$$\omega_v^\infty \equiv [dE(v)/dv]^\infty = K_n [\mathcal{D} - E(v)]^{(n+2)/2n}, \quad (3)$$

$$B_v^\infty = P_n [\mathcal{D} - E(v)]^{2/n}, \quad (4)$$

where K_n and P_n are known constants^{1,2,6} depending only on n , C_n , and the reduced mass μ , and the superscript

∞ denotes the fact that these expressions are based on the limiting single-term approximation to the potential, given by Eq. (2).

The limiting equations mentioned above have proved very useful for explaining and interrelating a wide variety of molecular phenomena and for predicting the properties of unobserved levels. Moreover, applying Eq. (3) and expressions obtained from it to experimental data has proved to be a powerful method for determining accurate molecular dissociation energies^{6,9} and when data are available for levels lying sufficiently near dissociation, also for determining the asymptotically dominant potential energy constant C_n .^{6,10} However, a number of questions have arisen about the nature and implications of deviations from this predicted limiting behavior. In particular, the derivation described above explicitly assumes¹⁻⁴ that near the outer turning points of the levels in question, the long-range potential of Eq. (1) is accurately approximated by Eq. (2). However, the observed spacings of highly excited vibrational levels of B state I_2 appear to display exactly the predicted limiting behavior, even when half of the potential strength at their outer turning points is due to higher-power ($m>n$) contributions to Eq. (1).^{6,11,12} In other words, Eq. (3) appears to be much more accurate than it should be. Moreover, while its derivation does suggest that Eq. (4) should be somewhat less reliable than Eq. (3),² the magnitude of the errors in its predictions seem surprisingly large.

In view of the above, the present paper examines the nature of deviations from the limiting near-dissociation behavior. Attention is focused on the vibrational energy derivative ω_v and the rotational constant B_v , but analogous results may be readily obtained for other properties. In the following, Sec. II presents an extended near-dissociation theory which explains the deviations from the limiting behavior caused by higher-power ($m>n$) contributions to the long-range potential of Eq. (1). Section III then describes the general spectroscopic implications of this theory and examines its predictions for the $B(^3\Pi_{0g}^+)$ state of I_2 . Finally, Sec. IV examines the importance of other types of contributions to deviations from the limiting behavior, in order to ascertain the

^{a)}John Simon Guggenheim Foundation Fellow, 1979-80; present and permanent address: Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1.

limitations of the present extended near-dissociation theory.

II. EXTENDED NEAR-DISSOCIATION THEORY FOR DIATOMIC MOLECULES

Within the first-order semiclassical or phase integral approximation, the derivative of the vibrational energy $E(v)$ with respect to vibrational quantum number v is given by

$$\omega_v \equiv dE(v)/dv = 2\pi\beta/I_0(E) \quad (5)$$

and the rotational constant B_v by

$$B_v = \beta^2 I_2(E)/I_0(E), \quad (6)$$

where $\beta = \sqrt{\hbar^2/2\mu}$,

$$I_l(E) = \int_{r_1}^{r_2} dr/r^l [E - V(r)]^{1/2}, \quad (7)$$

and the inner and outer classical turning points $r_1 = r_1(E)$ and $r_2 = r_2(E)$, respectively, are defined by the requirement that $E = V(r_i)$.¹³ It was previously shown^{1,2} that for energies E lying near the potential asymptote \mathcal{D} , integrals of this type depend mainly on the integrand in the neighborhood of the outer turning point $r_2(E)$. In the earlier work, this observation instigated the replacement of the exact $V(r)$ appearing in these integrals by Eq. (2). The present study begins by replacing it by a two-term approximation for the long-range potential

$$V(r) = \mathcal{D} - C_n/r^n - C_m/r^m, \quad (8)$$

where $m > n$ and both C_n and C_m are positive, and examines the ensuing deviations from the limiting behavior of Eqs. (3) and (4).

By the definition of the outer turning point,

$$E = \mathcal{D} - C_n/(r_2)^n - C_m/(r_2)^m, \quad (9)$$

and hence

$$r_2 = (C_n/[\mathcal{D} - E])^{1/n} \{1 + \alpha\}^{1/n}, \quad (10)$$

where α is the ratio of the two inverse-power terms, evaluated at $r_2(E)$:

$$\begin{aligned} \alpha &\equiv C_m/C_n(r_2)^{m-n} \\ &= C_m/(C_n)^{m/n} \{[\mathcal{D} - E]/[1 + \alpha]\}^{(m-n)/n}. \end{aligned} \quad (11)$$

Making the change of variables $x = r/r_2$, Eqs. (8)–(11) transform Eq. (7) into the form:

$$\begin{aligned} I_l(E) &= (C_n)^{-1/2} (r_2)^{1-l} \\ &\times \int_{r_1/r_2}^1 dx/x^l \{(x^{-n} - 1) + \alpha(x^{-m} - 1)\}^{1/2}. \end{aligned} \quad (12)$$

The integrand in Eq. (12) has an integrable singularity at $x=1$, and for small l (more particularly, for $l < 1 + n/2$) the value of the integral depends mainly on the nature of the integrand near $x=1$. For the highly excited levels in question $r_2 \gg r_1$, and in any case the only situations in which the present approach has any relevance are those in which the small- r behavior of the potential is unimportant. It is therefore a natural approximation to replace the lower limit of integration in Eq. (12) by $r_1/r_2 = 0$, yielding

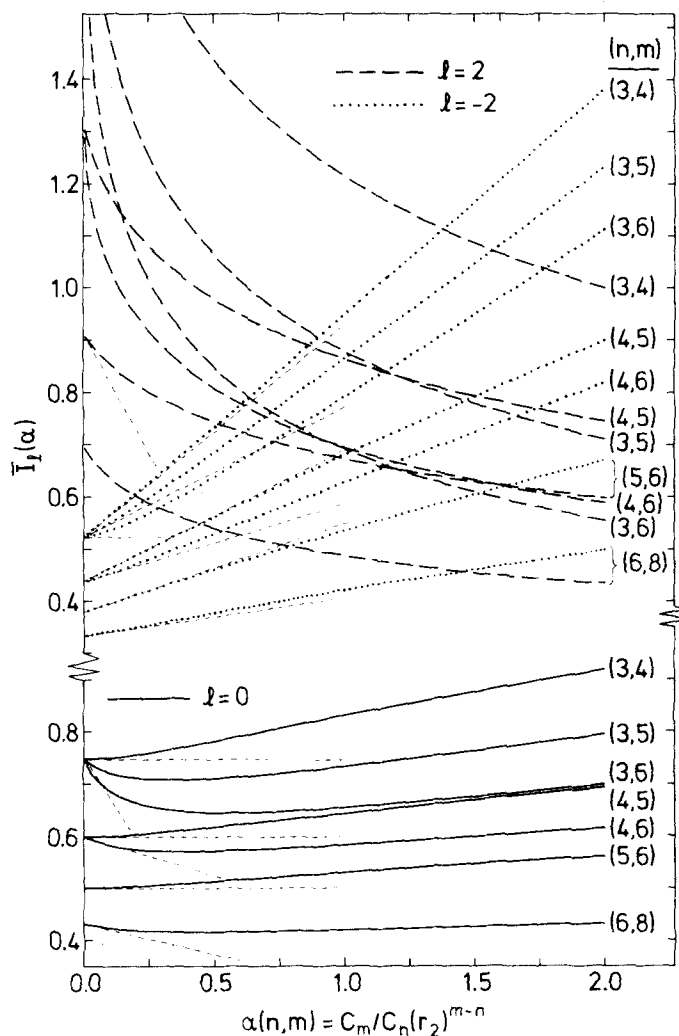


FIG. 1. For (n, m) combinations of most physical interest, dependence of the $\bar{I}_l(\alpha)$ integrals of Eq. (14) on the relative strength $\alpha(n, m)$ of the second inverse-power term in the long-range potential; the fine short-dash lines are tangents at $\alpha = 0$ to the corresponding curves.

$$I_l(E) = \{(C_n)^{(1-l)/n}/[\mathcal{D} - E]^{1/2+(1-l)/n}\} \bar{I}_l(\alpha), \quad (13)$$

where

$$\begin{aligned} \bar{I}_l(\alpha) &= (1 + \alpha)^{1/2+(1-l)/n} \\ &\times \int_0^1 dx/x^l \{(x^{-n} - 1) + \alpha(x^{-m} - 1)\}^{1/2}. \end{aligned} \quad (14)$$

For $\alpha = 0$, the limiting case considered in the earlier work,^{1-4,6,8} $\bar{I}_l(\alpha)$ may be expressed in terms of elementary functions,¹⁴

$$\bar{I}_l(\alpha = 0) = (\sqrt{\pi}/n) \Gamma\left(\frac{1}{2} + \frac{1-l}{n}\right) / \Gamma\left(1 + \frac{1-l}{n}\right), \quad (15)$$

where $\Gamma(y)$ is a gamma function. Moreover, for any $\alpha \geq 0$ it may be readily evaluated to arbitrary precision using appropriate (Gaussian-type¹⁵) quadrature techniques.¹⁶ For the (n, m) combinations of most practical importance, Fig. 1 shows how $\bar{I}_l(\alpha)$ depends on α for $l = 0$ (lower segment) and $l = \pm 2$ (upper segment).

In order to illustrate the detailed behavior of $\bar{I}_l(\alpha)$ for small α , the integral in Eq. (14) may be expanded as a

Taylor series about $\alpha = 0$, yielding

$$\bar{I}_l(\alpha) = (1 + \alpha)^{1/2 + (1-l)/n} \{ T_{l,0}(n, m) - (\alpha/2) T_{l,1}(n, m) + (3\alpha^2/8) T_{l,2}(n, m) + \dots \}, \quad (16)$$

where the integrals

$$T_{l,k}(n, m) = \int_0^1 dx (x^{-m} - 1)^k / x^l (x^{-n} - 1)^{k+1/2} \quad (17)$$

may be readily evaluated using the same type of quadrature techniques mentioned above. Of course, $T_{l,0}(n, m) \equiv T_l(n) = \bar{I}_l(\alpha = 0)$ is independent of m ; values of this quantity [see Eq. (15)] are listed in Table I.

The integral of Eq. (14) is a continuous function of α for all $\alpha \geq 0$, and all its derivatives exist and are continuous for $\alpha > 0$. However, the fact that $T_{l,k}(n, m)$ is infinite unless

$$k(m - n) < 1 - l + n/2 \quad (18)$$

shows that derivatives of order $(1 - l + n/2)/(m - n)$ or higher are all singular at $\alpha = 0$. Thus, this series expansion may be of limited utility unless α is very small, and for $l \geq \frac{3}{2}n - m + 1$ it is completely invalid since even the first derivative at $\alpha = 0$ does not exist. Nonetheless, $\bar{I}_l(\alpha)$ may still be formally expanded as a power series in α to obtain

$$\bar{I}_l(\alpha) = T_l(n) \left\{ 1 + \alpha \left[\frac{1}{2} + \frac{1-l}{n} - \frac{1}{2} R_{l,1} \right] + \frac{1}{2} \alpha^2 \left[-\frac{1}{4} + \left(\frac{1-l}{n} \right)^2 - \left(\frac{1}{2} + \frac{1-l}{n} \right) R_{l,1} + \frac{3}{4} R_{l,2} \right] + \dots \right\}, \quad (19)$$

where $R_{l,k}(n, m) \equiv T_{l,k}(n, m)/T_l(n)$. For the $\{n, m, l\}$ cases of most physical interest, Table II presents values of $R_{l,k}(n, m)$ for all k satisfying Eq. (18). The linear version of Eq. (19) is the source of the tangents at $\alpha = 0$ to the curves in Fig. 1 (fine short-dash lines); curves for which no tangent is drawn have singular first derivatives at this intercept.

The linear version of Eq. (19) appears to provide a fairly realistic representation of the α dependence of the $l = -2$ integrals for small $(m - n)$, but for the spectroscopically important [see Eqs. (5) and (6)] $l = 0$ and 2 integrals its accuracy is clearly very limited. Thus, even without considering the difficulties pointed out by Stwalley,¹⁹ it is clear that the kind of analytic correction factors for Eqs. (3) and (4) envisioned in the discussion of Ref. (6) cannot adequately account for the deviations of Eq. (1) from the limiting behavior of Eq. (2). However, in spite of its limitations Eq. (19) does confirm that⁶

TABLE I. Values of $\bar{I}_l(\alpha = 0) = T_{l,0}(n, m) = T_l(n)$.

	$l = 0$	2
$n = 6$	0.431 184 926 538	0.701 091 052 663
5	0.501 159 115 268	0.910 888 617 592
4	0.599 070 117 368	1.311 028 777 146
3	0.746 834 200 222	2.428 650 647 888
2	1.0	a
1	$\pi/2$	a

^aThis integral does not exist.

TABLE II. For various (k, n, m) , values of $R_{l,k}(n, m)$ for all k satisfying Eq. (18).

n	m	k	$l = 0$	$l = 2$
6	8	1	1.875 321 24	a
5	6	1	7/5	2.588 930 24
		2	2.168 287 05	a
		3	5.162 029 98	a
4	5	1	3/2	a
		2	2.661 849 84	a
4	6	1	2.594 219 81	a
3	4	1	5/3	a
		2	3.964 105 16	a
3	5	1	3.384 618 31	a
3	6	1	a	a

^aThe integral $T_{l,k}(n, m)$ does not exist.

the leading (i.e., linear in α) deviation from the limiting $\alpha = 0$ value of the $l = 0$ integrals which determine the vibrational level spacings is exactly zero when $m = n + 1$.²⁰ The exact cancellation of the $R_{0,1}(n, n + 1)$ factor which leads to this result is one manifestation of a property of the overall α -dependence of these integrals which has considerable practical significance (see below).

Consideration of Eqs. (12)–(14) shows that increases in α affect the values of $I_l(E)$ in two different ways. The first is that it increases the value of the outer turning point $r_2(E)$ and hence, for $l < 1 + n/2$, multiplies the integral by the monotonically increasing factor $(1 + \alpha)^{1/2 + (1-l)/n}$; the second is that it decreases the magnitude of the integrand and hence decreases the value of the integral itself. For $l < 0$ the first of these effects is usually dominant and $\bar{I}_l(\alpha)$ [and hence $I_l(E)$] is a monotonic increasing function of α ²¹; for $l \geq 2$ the second factor is dominant and $\bar{I}_l(\alpha)$ is a monotonic decreasing function of α ; for $l = 1$ an initial sharp drop in $\bar{I}_l(\alpha)$ is followed by its leveling off and approaching a limiting value of $T_l(m)$ as $\alpha \rightarrow \infty$. However, for the physically most important $l = 0$ case, substantial cancellation of these two effects occurs for all physically significant values of α . This explains why all of the $l = 0$ curves appearing in Fig. 1 are relatively flat. The practical implications of this cancellation are demonstrated below.

Note that while the preceding discussion is based on the use of the simple two-term potential of Eq. (8), its extension to take account of the expanded potential

$$V(r) = D - C_n/r^n - C_{m_1}/r^{m_1} - C_{m_2}/r^{m_2} - \dots \quad (20)$$

is accomplished simply by replacing $\bar{I}_l(\alpha)$ of Eq. (14) by

$$\bar{I}_l(\{\alpha_i\}) = (1 + \alpha_1 + \alpha_2 + \dots)^{1/2 + (1-l)/n} \times \int_0^1 dx / x^l \{ (x^{-n} - 1) + \alpha_1(x^{-m_1} - 1) + \alpha_2(x^{-m_2} - 1) + \dots \}^{1/2}, \quad (21)$$

where

$$\begin{aligned} \alpha_i &= C_{m_i} / C_n (r_2)^{m_i - n} \\ &= [C_{m_i} / (C_n)^{m_i/n}] [(D - E) / (1 + \alpha_1 + \alpha_2 + \dots)]^{(m_i - n)/n} \\ &= [(C_{m_i})^{m_i - n} (C_n)^{m_i - m_i} (\alpha_1 / C_{m_1})^{m_i - n}]^{1/(m_i - n)}. \end{aligned} \quad (22)$$

Since any realistic long range potential consists of a sum of several inverse-power terms, this generalized expression Eq. (21) is required in most practical applications of the present extended theory of near-dissociation behavior.

III. SPECTROSCOPIC IMPLICATIONS OF THE PRESENT THEORY

A. Treatment of experimental data

For $n \neq 2$ the integrated form of Eq. (3) is^{1,22}

$$D - E(v) = X_0(n)[v_D - v]^{2n/(n-2)}, \quad (23)$$

where $X_0(n) = [(n-2)K_n/2n]^{2n/(n-2)}$, and for $n > 2$ the integration constant v_D corresponds to the effective (non-integer) vibrational index at the dissociation limit. Substituting Eq. (23) into Eqs. (3) and (4) then yields expressions for ω_v^∞ and B_v^∞ in which the vibrational quantum number v , rather than the energy $E(v)$, is the independent variable. In most previous applications of limiting near-dissociation equations it was more convenient to treat v as the independent variable.^{1-4,6,8-12} However, the absence of simple analytic expressions for the energy dependence (as buried in the α -dependence) of the integrals of Eqs. (14) and (21) prevents a simple analog of Eq. (23) from being used here. As a result, $E(v)$ is used as the independent variable throughout the present work.

In the following, the present theory is tested by comparing predicted values of the quantities ω_v and B_v , with experiment. However, it is important to remember that while the vibrational energy $E(v)$ and rotational constant B_v are directly obtained from the spectral data, the vibrational energy derivative ω_v is not. A reasonable estimate of the latter may be obtained from first differences:

$$\omega_{v+1/2} \approx \Delta G_{v+1/2} = E(v+1) - E(v) \quad (24)$$

or

$$\omega_v \approx \Delta \bar{G}_v = \frac{1}{2}[E(v+1) - E(v-1)]. \quad (25)$$

However, for accurate work this approximation is not entirely satisfactory, especially for species with small μ and/or small C_n values.

A simple way of improving upon Eq. (25) is suggested by the exact expression

$$\Delta \bar{G}_v = \omega_v + (d^3E/dv^3)/3! + (d^5E/dv^5)/5! + \dots \quad (26)$$

The third derivative term appearing here is certainly responsible for most of the difference between ω_v and $\Delta \bar{G}_v$, and in the near-dissociation region a good estimate of it may be obtained from Eqs. (23) and (25). The resulting improved estimate of ω_v is therefore

$$\omega_v \approx \Delta \bar{G}_v - A_n (\Delta \bar{G}_v)^{(6-n)/(n+2)}, \quad (27)$$

where the constant A_n is

$$A_n = \frac{4n(n+2)}{3(n-2)^3} \left(\frac{n-2}{2n} \right)^{(6-n)/(n+2)} [X_0(n)]^{2(n-2)/(n+2)}. \quad (28)$$

The simple $n=6$ version of this expression was previously introduced in the near-dissociation analysis of the vibrational spacings of Kr_2 .²³

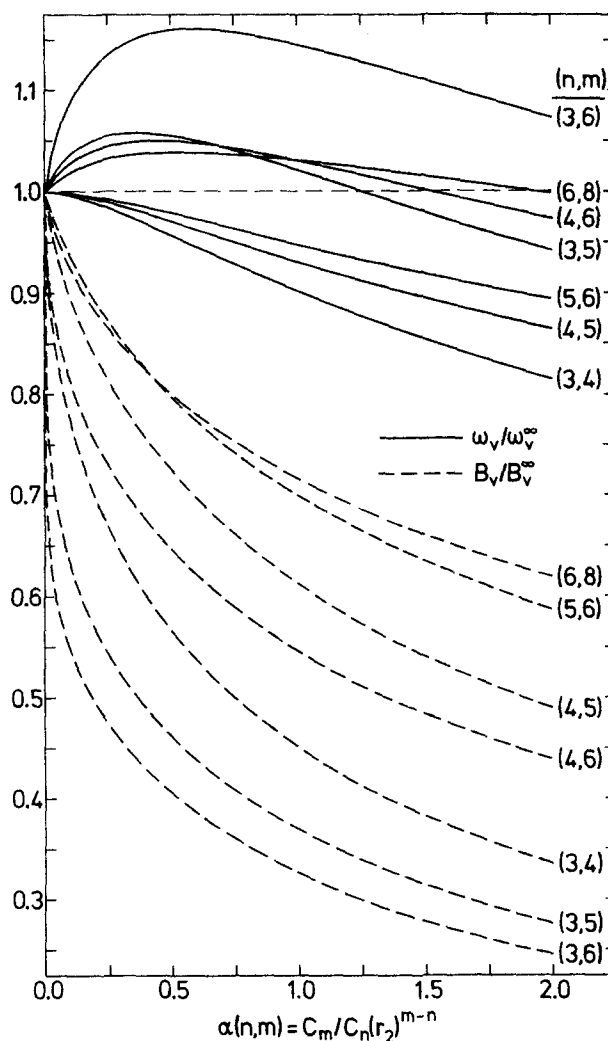


FIG. 2. For the (n, m) combinations of most practical importance, dependence of ω_v/ω_v^∞ and B_v/B_v^∞ , as predicted by Eqs. (29) and (30), on $\alpha(n, m)$.

B. General spectroscopic implications

Substitution of Eqs. (13) and (15) into the general semiclassical expressions for ω_v and B_v , Eqs. (5) and (6), immediately yields the limiting (i.e., $\alpha = 0$) near-dissociation expressions for ω_v^∞ and B_v^∞ given in Eqs. (3) and (4), the constant factors in the latter being defined as $K_n = 2\pi\beta(C_n)^{-1/n}/T_0(n)$ and $P_n = \beta^2(C_n)^{-2/n}T_2(n)/T_0(n)$. The deviations from this limiting behavior predicted by the present generalized near-dissociation theory may therefore be expressed in terms of the ratios

$$\omega_v/\omega_v^\infty = T_0(n)/\bar{I}_0(\{\alpha_i\}), \quad (29)$$

$$B_v/B_v^\infty = T_0(n)\bar{I}_2(\{\alpha_i\})/T_2(n)\bar{I}_0(\{\alpha_i\}). \quad (30)$$

For the same set of two-term long-range potentials considered in Fig. 1, these predicted deviations are shown in Fig. 2.

The ω_v/ω_v^∞ curves in Fig. 2 clearly illustrate the effect of the fortuitous cancellation of competing contributions to the $\bar{I}_0(\alpha)$ integral, described above. Since ω_v depends only on the $I_0(E)$ integral, this cancellation means that the limiting expression ω_v^∞ will accurately

describe a much wider range of levels than the breakdown of the $\alpha = 0$ approximation on which it is based would appear to allow. Moreover, deviations from the limiting behavior of Eq. (3) are smallest for just those cases $(n, m) = (5, 6)$ and $(6, 8)$, which most commonly characterize the long-range potentials of neutral molecules. In particular, when $\alpha = 1$ the predicted deviations for these two cases are only -5.3% and $+3.0\%$, respectively; since this situation corresponds to the single-term potential of Eq. (2) being in error by a factor of 2, this cancellation is clearly remarkably complete. In view of the way in which a knowledge of the limiting behavior of ω_v can facilitate the determination of accurate molecular dissociation energies,^{6,9} the existence of this extended region of validity of Eq. (3) is very propitious.

In contrast with the ω_v results discussed above, Fig. 2 clearly shows that B_v values for levels lying very near dissociation are very sensitive to deviation of the long-range potential from the single-term form of Eq. (2). Since realistic potentials at normally accessible distances virtually always have significant contributions from more than one inverse-power potential term, this means that experimental B_v values can virtually never be expected to quantitatively obey Eq. (4). For a set of neighboring levels over which the value of α does not change drastically, the correction factors of Eq. (30) will be roughly constant, so that the observed B_v values may appear to display approximately the predicted limiting functional dependence on $E(v)$ or v . However, the value of a C_n constant determined from such data would be substantially in error. Since $E(v)$ (and hence ω_v) values will always be available for levels for which B_v is known, it is therefore clear that fits to Eq. (4) should virtually never be used for determining experimental dissociation energies and C_n values.²⁴ On the other hand, the sensitivity of B_v values to deviations from the limiting single-term potential of Eq. (2) suggests that analyzing data in terms of Eqs. (29) and (30) should be a good way of determining the higher-power ($m > n$) potential coefficients C_{m_1} .

The results presented above correspond to a case in which the long-range potential consists of only two inverse-power terms. While this virtually never occurs in nature, the contributing higher-power terms are usually relatively weak, so in spite of their larger m values they should be somewhat less important. However, whenever possible they should not be neglected.

To a first approximation, the effects of all higher-power ($m > n$) contributions to the long-range potential will be roughly additive. The fact that $B_v/B_v^\infty < 1$ for all two-term potentials therefore means that inclusion of additional higher-power terms simply increases the predicted (negative) deviations from B_v^∞ . For cases in which the power of the leading $m > n$ term in the long-range potential is $m_1 \geq n + 2$, the inclusion of higher-power terms also simply increases the magnitude of the predicted (positive, as long as $\alpha(n, m_1)$ is not too large) deviations from ω_v^∞ . However, if $m_1 = n + 1$, the term C_{m_1}/r^{m_1} causes negative deviations from ω_v^∞ while the higher-power $m > m_1$ terms tend to cause positive deviations (as long as $\alpha(n, m)$ is not too large). In this case,

TABLE III. Long-range potential constants for B state I_2 determined by Danyluk and King.¹²

$\mathcal{D} = 4381.15 \text{ cm}^{-1}$	
$C_5 = 2.776 \times 10^5 \text{ cm}^{-1} \text{ \AA}^5$	$C_8 = 243 \times 10^5 \text{ cm}^{-1} \text{ \AA}^8$
$C_6 = 17.8 \times 10^5 \text{ cm}^{-1} \text{ \AA}^6$	$C_{10} = (C_8)^2 / 2C_6$

therefore, some cancellation between the effects of the $m_1 = n + 1$ and $m > m_1$ terms will further decrease the already small deviations of ω_v from its limiting ω_v^∞ behavior. In other words, increased error in the assumption that the potential is accurately described by Eq. (2) leads to *increased accuracy* in the expression for ω_v based on this assumption. An example of this behavior is presented below.

C. Illustrative results for $B(^3\Pi_{0u}^+)$ -state I_2

For the $B(^3\Pi_{0u}^+)$ state of I_2 , $n = 5$ and the long-range interaction potential has the form

$$V(r) \approx \mathcal{D} - C_5/r^5 - C_6/r^6 - C_8/r^8 - C_{10}/r^{10} - \dots \quad (31)$$

By fitting Eq. (3) to their observed energies for vibrational levels lying within a few cm^{-1} of dissociation, Danyluk and King¹² determined values of \mathcal{D} and C_5 for this species. For most of the levels thus used $\alpha(5, 6) \leq 0.7$, so in view of the small deviations of ω_v/ω_v^∞ from unity for this $(n, m) = (5, 6)$ case (see Fig. 2) and the additional compensating effects described above, these constants should be fairly reliable. Holding \mathcal{D} and C_5 fixed at these values, Danyluk and King¹² then used a fit of Eq. (31) to the outer RKR turning points of their highest observed levels to obtain estimates of C_6 and C_8 and an implicitly determined value of $C_{10} = (C_8)^2 / 2C_6$. The precise values for C_6 and C_8 obtained in this way are of course sensitive to the assumed values of \mathcal{D} and C_5 and to implicit assumptions about the nature of C_{10} and any additional contributions to the potential.^{26,27} However, Danyluk and King's constants (see Table III) do provide an excellent representation of the long-range part of this potential, so for the purpose of the following discussion they are assumed to be exact.

Figure 3 compares experimental^{11,12,28} ω_v and B_v values for B state I_2 [points, the former obtained using Eq. (27)] with predictions of the present theory generated from the potential energy constants in Table III. The different curves for each case correspond to the use of different numbers of potential terms when calculating the correction factors of Eqs. (29) and (30); note that the horizontal dotted line for $\{m\} = (5)$ applies to both ω_v/ω_v^∞ and B_v/B_v^∞ . On a plot of this type, it is clear that unless the assumed \mathcal{D} and/or C_5 values are substantially in error, the experimental points must approach a value of unity as $[\mathcal{D} - E(v)] \rightarrow 0$. Thus, the scatter of their ω_v values and the behavior of their B_v 's for $v = 78-82$ (square points) reflects the fact that Danyluk and King's data analysis¹² neglected centrifugal distortion constants, which are known to become increasingly important for levels approaching dissociation.^{8,29} It is illuminating to see how readily a plot of this type uncovers such irregularities.

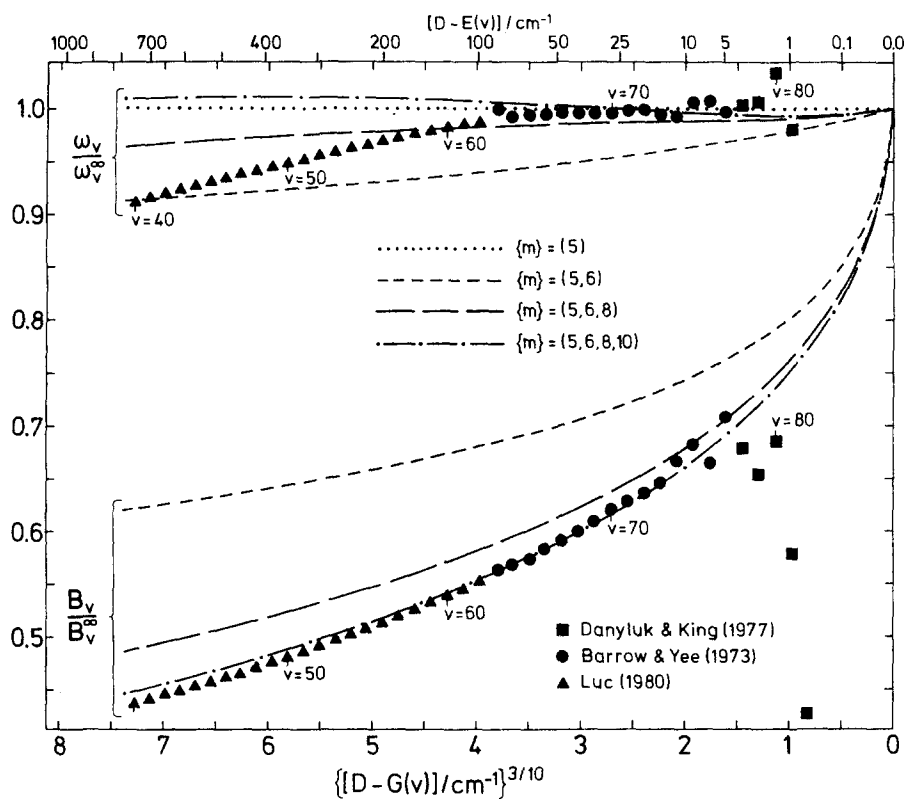


FIG. 3. For the $B(^3\Pi_{0u}^+)$ state of I_2 , comparisons of experiment (points) with the predictions of Eqs. (29) and (30) (curves) generated using the potential energy constants in Table III.

The curves in Fig. 3 illustrate all of the qualitative effects described in the preceding section. For example, the deviations of B_v/B_v^∞ from unity increase rapidly as the higher-order ($m > n$) terms in the long-range potential grow with increasing binding energy, while cancellation effects make the corresponding deviations from unity of ω_v/ω_v^∞ very much smaller. Similarly, the predicted B_v/B_v^∞ values decrease monotonically as successively higher power terms in the long range potential are taken into account, while the small negative deviations of ω_v/ω_v^∞ from unity caused by the $m=6$ potential term are largely canceled out by the effects of the higher power $m=8$ and 10 terms. The very close agreement with ω_v^∞ of the measured ω_v values for the higher observed levels is quite striking when one realizes that the asymptotically dominant $n=5$ potential term is responsible for less than half of the binding at the outer turning points of levels below $v=73$. However, the agreement with experiment of the predictions based on the full four-term potential (dot-dash curves) provides convincing evidence of the validity of the present theory.

The nature of the cancellation effects within the $l=0$ integral determining ω_v [see Eqs. (5) and (7)] is examined in more detail in Fig. 4. For the $v=60$ level of B state I_2 , for which $\alpha(5,6)=1.12$, the upper segment of Fig. 4 compares the exact integrand of the $l=0$ integral (solid curve, obtained from the RKR turning points of Refs. 11 and 12) to various approximations to it, while the lower segment contrasts the corresponding exact and approximate potentials. The striking feature about this plot is the fact that in spite of their rather disparate appearance, the areas under the various curves in the upper part of Fig. 4 all agree to within 8% (see Fig. 3),

indeed, for the $\{m\}=(5)$ and $\{m\}=(5,6,8,10)$ cases (dotted and dot-dash curves, respectively) these areas differ by only approximately 0.8%. The upper half of Fig. 4 illustrates the competition between the increase in the turning point and the decrease of the integrand which occurs when higher-order ($m > n$) terms in the long-range potential are taken into account. For the level in question, the almost perfect cancellation of these effects makes the experimental ω_v value²⁸ lie within 1.8% of the prediction ω_v^∞ yielded by Eq. (3), in spite of the fact that the $m=n=5$ potential term is responsible for only 37% of the binding at this level's outer turning point.

In concluding this discussion, one should note that some cancellation of the effects on ω_v/ω_v^∞ due to the leading ($m=m_1$) and additional ($m > m_1$) higher-power contributions to the long-range potential will occur in any case in which $m_1=n+1$. At the same time, it is important to realize that the almost exact cancellation which makes the upper dot-dash curve in Fig. 3 deviate so very little from unity reflects the particular potential energy constants used for this system and will not necessarily occur generally.

IV. LIMITATIONS OF THE PRESENT THEORY

The theory of Sec. II explains the deviations from limiting near-dissociation behavior due to the fact that long-range intermolecular potentials consist of not one, but a sum of attractive inverse-power terms. However, its validity requires that the properties of the levels in question depend mainly on the long-range inverse-power part of the interaction potential. At energies sufficiently near dissociation this condition will always be satisfied,

but for the more strongly bound levels, effects due to deviations of the attractive part of the potential from the inverse-power expansion of Eq. (1) and the existence of a nonzero inner turning point are no longer negligible. The present section is concerned with identifying the factors governing the onset of the ensuing deviations from the predictions of the present extended near-dissociation theory. Throughout the following, the superscript label "ND" is used to identify quantities calculated from Eq. (21) using the full assumed inverse-power potential.

In order to better illustrate the following discussion, Figs. 5 and 6 compare the predictions of the present theory with the exact calculated properties of three model van der Waals-type potentials which all have exactly the same long-range tail,

$$V(r) \approx D - C_6/r^6 - C_8/r^8 - C_{10}/r^{10}, \quad (32)$$

where $C_6 = 6.69893 \times 10^5 \text{ cm}^{-1} \text{ \AA}^6$, $C_8 = 50.5006 \times 10^5 \text{ cm}^{-1} \text{ \AA}^8$, and $C_{10} = 426.289 \times 10^5 \text{ cm}^{-1} \text{ \AA}^{10}$. These three potentials are plotted (solid curves) and compared with their common long-range components (dotted and dashed curves) in the lower segment of Fig. 5. Potential a is

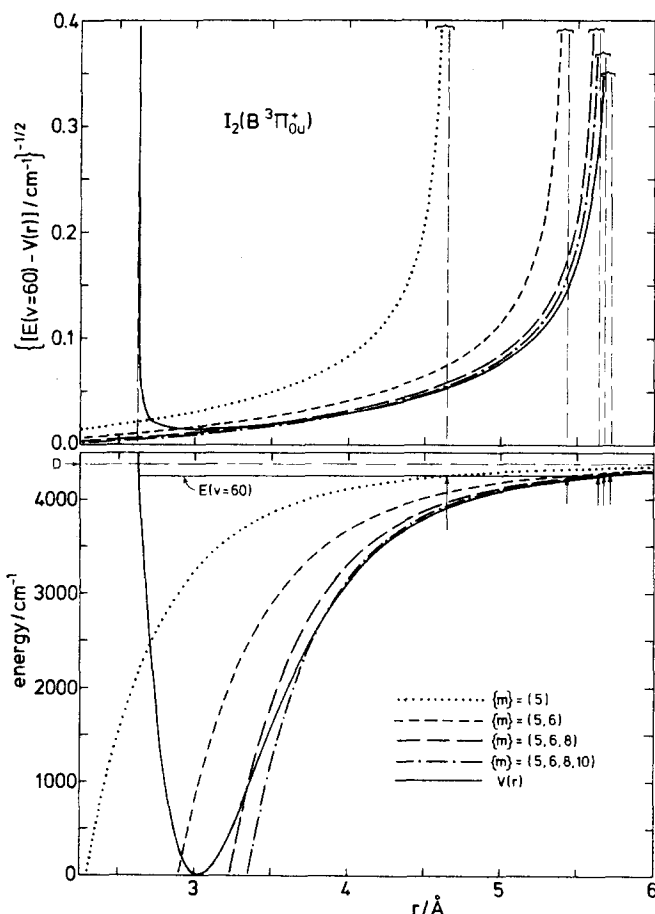


FIG. 4. Lower: comparison of full RKR potential^{11,12} (solid curve) with various inverse-power sum approximations (broken curves) to the long-range potential for B state I_2 . Upper: for the $v=60$ level of B state I_2 , integrand of the $l=0$ integral of Eq. (7) for the full potential (solid curve) and the various approximations to it (broken curves) shown below. Vertical dashed lines (upper) and vertical arrows (lower) denote turning point positions.

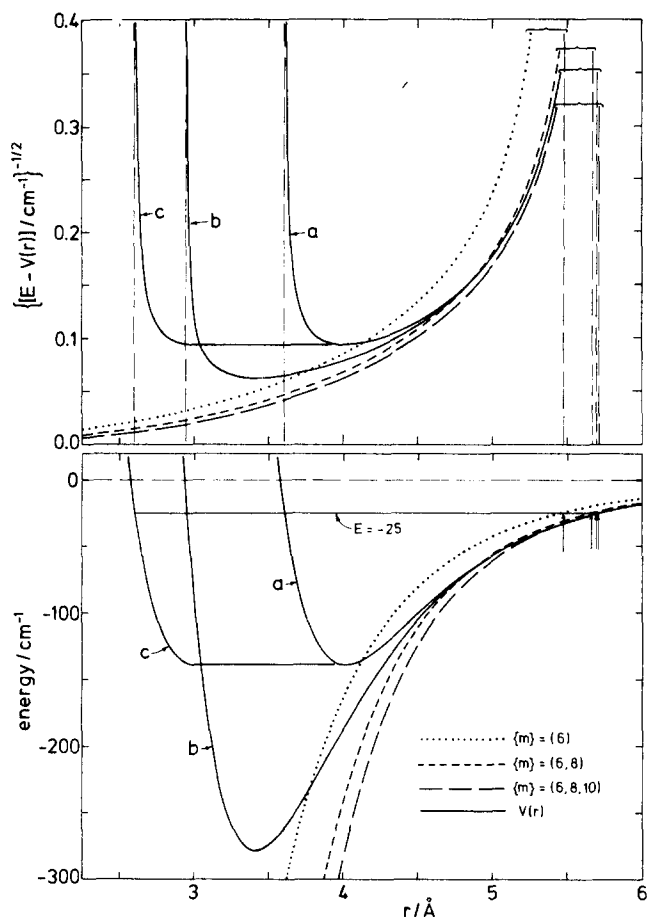


FIG. 5. Lower: comparison of recommended³⁰ potential curve for ground-state Kr_2 (curve a) and two related model potentials (curves b and c) with inverse-power sum approximations to their common long-range potential (broken curves). Upper: for $E = -25 \text{ cm}^{-1}$, integrand of the $l=0$ integral of Eq. (7) for the various potentials shown below. Vertical dashed lines (upper) and vertical arrows (lower) denote turning point positions.

Aziz's³⁰ HFGKR potential for ground-state Kr_2 ; potential b is a scaled version of it which has twice the well depth and an equilibrium distance r_e smaller by a factor of 0.85; potential c has exactly the same attractive and repulsive branches as curve a, except that the latter is shifted inward by $0.25r_e$ and a flat curve used to join the two segments. The "exact" ω_v and B_v values for these potentials, yielding the points in Fig. 6, were obtained by numerical integration of the radial Schrödinger equation for the reduced mass of $^{84,84}Kr_2$ and (for the former) application of Eq. (27).

In general, three factors can contribute to error in the extended near-dissociation theory integrals of Eq. (21):

- (i) the sum of (attractive) inverse-power terms used does not accurately represent the attractive part of the true potential all the way to the potential minimum at r_e ;
- (ii) contributions to the integral associated with the repulsive part of the potential and the singularity of the exact integrand at the inner turning point $r_1(E)$ are neglected;

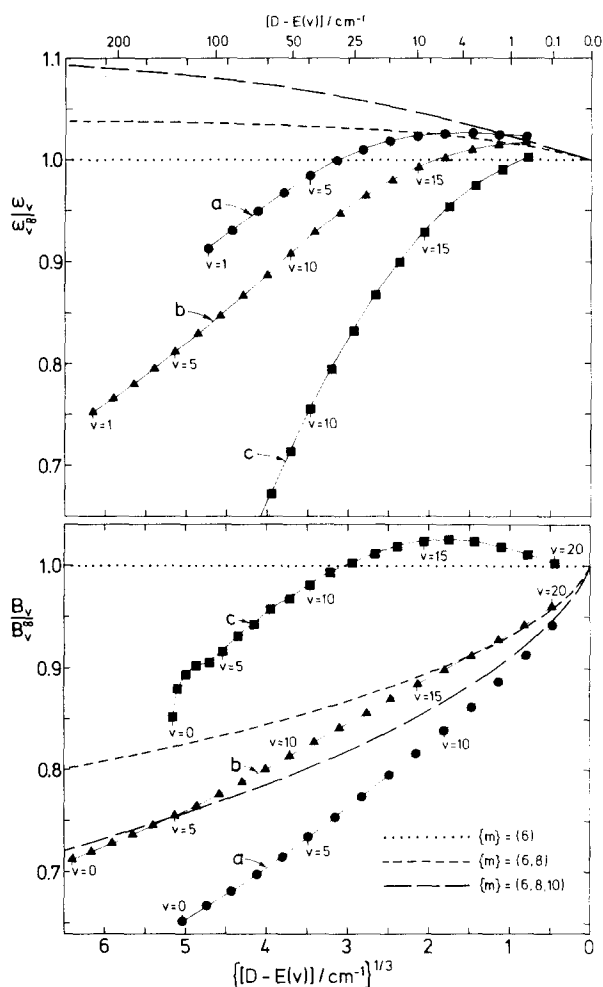


FIG. 6. For the three full potentials shown in the lower half of Fig. 5, comparison of "exact" ω_v/ω_v^∞ and B_v/B_v^∞ values (points) with the predictions of Eqs. (29) and (30) (broken curves, the same for all three cases).

(iii) the approximation that $r_1/r_2=0$ introduces a spurious positive contribution to the integral, associated with the interval $[0, r_1]$.

Factor (ii) will always tend to make $I_l^{\text{ND}}(E)$ too small, while (iii) will tend to make it too large, but the sign of the effect due to factor (i) depends on whether the species in question is chemically bound or is merely held together by van der Waals forces. If the former, factor (i) will tend to supplement the effects of (iii), while for the latter (i) will amplify the effects of (ii). This difference in the sign of the effects due to factor (i) for van der Waals vs non-van der Waals interactions is qualitatively illustrated by comparison of the differences between the solid and long-dash curves in the upper half of Fig. 5 with those between the solid and dot-dash curves in the upper part of Fig. 4.

Figure 3 shows that while the predicted $\omega_v^{\text{ND}}/\omega_v^\infty$ values based on the full four-term $\{m\}=(5, 6, 8, 10)$ long-range potential (dot-dash curve) for B state I_2 agree well with the experimental points for the highest observed levels, the latter eventually begin to drop increasingly farther below this curve with increasing binding energy. This shows that the dominant contribution to error in $I_0^{\text{ND}}(E)$

(at least initially) come from Factor (ii), since it is the only effect which tends to make this integral too small. The origin of the disagreement between the analogous $B_v^{\text{ND}}/B_v^\infty$ curve and experiment is somewhat more subtle, since the fact that B_v is defined as a ratio of two integrals means that even large errors in the ND approximations for these integrals will not significantly affect B_v^{ND} as long as the relative errors in the two integrals are approximately the same. This explains why agreement of the experimental B_v/B_v^∞ points with the appropriate dot-dash curve in Fig. 3 extends to much larger binding energies than is the case for ω_v/ω_v^∞ . The fact that the initial deviations of the B_v/B_v^∞ points from this curve are downward then reflects the relatively larger weighting given to errors of type (iii) by the $1/r^2$ term in the integrand of the numerator integral $I_2^{\text{ND}}(E)$, which causes its error to increase somewhat more slowly than that in $I_0^{\text{ND}}(E)$ as the binding energy increases.

For the model Kr_2 -like potentials of Fig. 5, the results in the upper half of Fig. 6 show that factor (ii), this time supplemented by factor (i), is again the leading source of error in the extended near-dissociation ω_v^{ND} values (long-dash curve). In this case, however, these errors are significant even for the highest bound levels. Though somewhat disappointing the latter is not a surprising result, since the relatively large inner turning points, shallow well depth, and flat repulsive wall characteristic of a van der Waals potential will tend to make all three sources of error much more important than is the case for a strongly bound species.

For potential-a in Fig. 5, the deviations of the B_v/B_v^∞ points in Fig. 6 from the long-dash curve yielded by the $\{m\}=(6, 8, 10)$ near-dissociation theory is explained in the same manner as the analogous deviations for B state I_2 in Fig. 3. For the modified potentials b and c, the analogous initial deviations are in the opposite direction. However, this is readily explained by the fact that the relatively small inner turning points of these potentials make errors of type (iii) quite unimportant (see Fig. 5), so that the additional $1/r^2$ weighting factor in the $l=2$ integral integrand mainly magnifies the relative effect of errors of types (i) and (ii) and makes the extended near-dissociation theory predictions distinctly too small.

The results described above suggest that in general, errors of type (ii), modulated by competition from errors of type (iii), are most important in determining the onset of deviations from predictions of the present theory. They also indicate that while this extended near-dissociation theory can be trusted a substantial distance below the dissociation limits of strongly bound species, it is of little practical use for van der Waals molecules. On the other hand, the fact that all sets of points in Fig. 6 approach unity as the binding energy approaches zero indicates that requiring experimental ω_v and B_v values to attain the limiting ω_v^∞ and B_v^∞ behavior at dissociation is a very important constraint even for shallow potentials.

In closing this discussion it is important to remember that the theory presented here explicitly assumes that all of the inverse-power potential terms taken into account are attractive.³¹ If C_n/r^n were repulsive and the

higher-power terms attractive, the potential would have a maximum and be repulsive at long range, so the limiting near-dissociation behavior of Eqs. (3) and (4) and their analogs would be completely invalid. The properties of the highest vibrational levels of such a system would still depend mainly on the shape of the outer branch of the potential and could be described by integrals analogous to that of Eq. (21). However, the dependence of such integrals on the competing contributions to the long-range potential would be quite complex, so this problem requires further study.

In contrast with the above, if C_n/r^n were attractive but one or more of the higher-power terms were repulsive, the integrand of the appropriately generalized version of Eq. (12) could have an integrable singularity at an inner turning point. While the resulting integrals could be readily evaluated, the fundamental assumption that the properties represented by these integrals depend mainly on the outer part of the potential becomes questionable and the generality of the method is lost. On the other hand, if a repulsive C_m/r^m term exists but is compensated for by an attractive higher-power term, such that the factor taken to the power $\frac{1}{2}$ in the denominator of the integral in Eq. (21) is always positive (and preferably a monotonic decreasing function of x), the present theory is satisfactory as it stands.

V. CONCLUSIONS

The most important conclusion yielded by the present work is that experimental vibrational energies are often expected to obey the limiting near-dissociation equations (3) and (23) even when the single term C_n/r^n is responsible for only a fraction of the total potential at their outer turning points. This strengthens the argument that application of these expressions (or the generalized versions of them provided by the present work) to appropriate experimental data is the most accurate method known for determining diatomic molecule dissociation energies. Moreover, the existence of this extended region of validity of the limiting equations (3) and (23) further justifies the proposal of Ref. 9 that fitting energies to "near-dissociation expansions" constrained to have the correct limiting behavior is the best way of determining dissociation energies and performing energy level extrapolations when none of the observed levels lie in the extended near-dissociation region. The results in Fig. 6 show that use of the latter procedure is the best that can be done for weakly bound van der Waals molecules.

A second important conclusion is that while observed B_v values can virtually never be expected to quantitatively obey the simple limiting behavior of Eq. (4), for strongly bound species the deviations from this characteristic limiting behavior may prove to be an accurate way of determining reliable experimental values of the higher-order ($m > n$) potential coefficients C_m . While the reliability of such a procedure remains to be tested, the fact that the various higher-power coefficients affect ω_v^{ND} and B_v^{ND} in qualitatively different ways suggests that this approach to their determination may be somewhat less impeded by statistical correlation effects than the traditional procedure of performing fits to RKR turning

points.²⁶ In addition to their inherent interest, the availability of reliable experimental C_m coefficients for comparison should facilitate the further development of reliable theoretical and semiempirical methods for predicting these constants. This in turn has implications for the utility of the near-dissociation expansion method of Ref. 9, since having a realistic value of the asymptotically dominant coefficient C_n is a prerequisite to its use.

ACKNOWLEDGMENTS

I am pleased to acknowledge the contributions of Mr. G. C. Corey, who helped demonstrate the inadequacy of the Taylor series expansion approach, and especially those of Dr. M. S. Child who independently tested those expansions and whose shrewd comments have helped shape the course of this work. I am also grateful to Dr. M. D. Tobey and Dr. R. G. Buschman for their comments on the mathematical properties of the $I_1(E)$ integrals, and in particular to Dr. D. F. Andrews whose suggestion that their behavior should be treated using numerical quadrature techniques I foolishly ignored for almost a decade. Finally, I would like to thank the Theoretical Chemistry Department at the University of Oxford for its warm hospitality and generous provision of computer time during the course of this work.

- ¹(a) R. J. Le Roy and R. B. Bernstein, *Chem. Phys. Lett.* **5**, 42 (1970); (b) R. J. Le Roy and R. B. Bernstein, *J. Chem. Phys.* **52**, 3869 (1970).
- ²R. J. Le Roy, *Can. J. Phys.* **50**, 953 (1972).
- ³W. C. Stwalley, *J. Chem. Phys.* **58**, 3867 (1973).
- ⁴W. C. Stwalley, in *Energy, Structure, and Reactivity*, edited by D. W. Smith and W. B. McRae, (Wiley, New York, 1973), p. 259.
- ⁵J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1964).
- ⁶R. J. Le Roy, *Molecular Spectroscopy 1* (a Specialist Periodical Report of the Chemical Society of London), edited by R. F. Barrow, D. A. Long, and D. J. Millen (Chem. Soc., London, 1973), Chap. 3, pp. 113-176.
- ⁷N. Fröman, in *Semiclassical Methods in Molecular Scattering and Spectroscopy*, edited by M. S. Child (D. Reidel, Dordrecht, 1980), Chap. 1, pp. 1-44.
- ⁸R. J. Le Roy, in *Semiclassical Methods in Molecular Scattering and Spectroscopy*, edited by M. S. Child (D. Reidel, Dordrecht, 1980), Chap. 3, pp. 109-126.
- ⁹R. J. Le Roy and W.-H. Lam, *Chem. Phys. Lett.* **71**, 544 (1980).
- ¹⁰R. J. Le Roy, *Surf. Sci.* **59**, 541 (1976).
- ¹¹R. F. Barrow and K. K. Yee, *J. Chem. Soc. Faraday Trans. 2* **69**, 684 (1973).
- ¹²M. D. Danyluk and G. W. King, *Chem. Phys.* **25**, 343 (1977).
- ¹³The notation used here differs slightly from that of Ref. 8 in that the present $I_1(E)$ is equal to $(1/2)I_{0,1}^{0,0}(E, J=0)$ from Ref. (8).
- ¹⁴I. S. Gradshteyn and I. M. Ryzhik, *Table of Integrals, Series and Products* (Academic, New York, 1965), p. 294.
- ¹⁵M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions*, Natl. Bur. Std. Appl. Math. Ser. **55** (1964); also (Dover, New York, 1965).
- ¹⁶For a few special cases such as $m=2n$ or $m=3n/2$, $\bar{I}(\alpha)$ may be expressed in terms of known higher transcendental functions such as hypergeometric functions or incomplete elliptic integrals.^{17,18} However, since these functions are difficult to evaluate and their analytic behavior at small α is not readily

approximated in terms of elementary functions, their use provides no real advantage over the quadrature procedures employed here.

¹⁷S. Tani and M. Inokuti, *J. Chem. Phys.* **54**, 2265 (1971).

¹⁸(a) M. D. Tobey (private communication, 1972); (b) R. G. Buschman (private communication, 1973).

¹⁹W. C. Stwalley, *Contemp. Phys.* **19**, 65 (1978).

²⁰Similarly, for $l = -1$ the leading deviation is zero when $(m - n) = 2$, and for $l = -2$ it is zero when $(m - n) = 3$.

²¹A minor exception to this monotonic increase occurs at small α for large $(m - n)$ where there is a small initial dip in the value of the $l < 0$ integrals.

²²For $n = 2$, the analogous expression is¹

$$D - E(v) = \{D - E(v_0)\} \exp[-\pi\hbar(v - v_0)(2/\mu C_2)^{1/2}] .$$

²³Y. Tanaka, K. Yoshino, and D. E. Freeman, *J. Chem. Phys.* **59**, 5160 (1973).

²⁴One exception to the rule, a case in which C_n is known but only one vibrational level lies in the limiting region, yielded the present best estimate of the dissociation energy of ground state D_2 .²⁵

²⁵R. J. Le Roy and M. G. Barwell, *Can. J. Phys.* **53**, 1983 (1975).

²⁶R. J. Le Roy, *Can. J. Phys.* **52**, 246 (1974).

²⁷While Danyluk and King's¹² long-range potential implicitly contains yet higher order $m > 10$ inverse-power terms, in the present study their series was truncated after $m = 10$.

²⁸P. Luc, *J. Mol. Spectrosc.* **80**, 41 (1980).

²⁹Independent confirmation of the fact that their B_v values for their highest observed levels¹² are substantially too small has been recently obtained by S. Gerstenkorn (private communication, 1980).

³⁰R. A. Aziz, *Mol. Phys.* **36**, 177 (1979).

³¹In the sense of Eq. (1), this is equivalent to requiring all of the C_m coefficients to be positive.