

An improved method of representing and extrapolating diatomic molecule rotational constants

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It is shown that "near-dissociation expansions", empirical functions constrained to have the correct theoretically-predicted limiting behaviour at dissociation, provide representations of rotational and centrifugal distortion constants of diatomic molecules which are often much more compact, and which *always* provide much more reliable extrapolations beyond the range of available experimental data than comparable Dunham ($\nu + 1/2$) expansions. The capabilities of these expansions are illustrated by applications to the extensive data for the $B(^3\Pi_{0u}^+)$ state of I_2 .

On montre que les "développements de quasi-dissociation", en termes de fonctions empiriques contraintes à reproduire les prédictions théoriques à la limite de dissociation, fournissent, pour les constantes rotationnelles et centrifuges des molécules diatomiques, des représentations qui sont souvent plus compactes et qui donnent *toujours* des extrapolations plus fiables, en dehors du domaine où les données expérimentales sont disponibles, que les développements ($\nu + 1/2$) comparables de Dunham. Les possibilités de ces développements sont illustrées par des applications à l'ensemble considérable de données qu'on possède pour l'état $B(^3\Pi_{0u}^+)$ de I_2 .

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I. Introduction

In the familiar expression for the vibrational (ν) and rotational (J) levels of a diatomic molecule (1),

$$[1] \quad E(\nu, J) = G(\nu) + B_\nu[J(J+1)] - D_\nu[J(J+1)]^2 + H_\nu[J(J+1)]^3 + \dots$$

the ν -dependence of the vibrational energy $G(\nu)$, the rotational constant B_ν , and the centrifugal distortion constants D_ν, H_ν, \dots etc., have traditionally been represented by a power series in $\nu + 1/2$ (or Dunham expansion). While such polynomials can adequately represent available data over a given range of ν , they are inherently unreliable for extrapolating significantly beyond the range of the known values. Moreover, since the magnitudes of the centrifugal distortion constants approach infinity for levels approaching dissociation (refs. 2 and 3 and unpublished work (1976) by M. G. Barwell and R. J. Le Roy), the traditional Dunham-type polynomials in $\nu + 1/2$ cannot adequately represent their behaviour in that region.

An alternative to these simple power series expansions is suggested by recent studies (refs. 4 and 5 and unpublished work (1980) by R. J. Le Roy) of representations for the vibrational energies $G(\nu)$. They showed that a "near-dissociation expansion" which explicitly incorporates the known (6) limiting near-dissociation behaviour of the molecule provides much more reliable extrapolations (4) and can yield a more compact representation (i.e., involving fewer empirical parameters) of the experimental data (5). The present paper extends the use of these "near-dissociation expansions" to a representation of the rotational and centrifugal dis-

torion constants, and tests them by comparing the utility of near-dissociation vs. Dunham expansions for representing those properties of levels of the $B(^3\Pi_{0u}^+)$ state of I_2 .

II. Method

A. Background

The basis of the near-dissociation expansion method is the fact that for vibrational levels lying near dissociation the vibrational eigenvalue distribution (6), rotational (7) and centrifugal distortion constants (2, 3), and many other properties (8) depend mainly on the long range part of the intermolecular potential. At sufficiently large distances the long-range potential takes on the limiting form:

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

Substituting this approximation for the potential into the semiclassical expressions for various molecular properties (3) yields simple analytic expressions for their limiting near-dissociation behaviour. For the vibrational energies and rotational and centrifugal distortion constants these expressions are (2, 3, 6, 7):

$$[3] \quad [\mathcal{D} - G(\nu)]^\infty = X_0(n)(\nu_{\mathcal{D}} - \nu)^{2n/(n-2)}$$

$$[4] \quad B_\nu^\infty = X_1(n)(\nu_{\mathcal{D}} - \nu)^{2n/(n-2)-2}$$

$$[5] \quad D_\nu^\infty = -X_2(n)(\nu_{\mathcal{D}} - \nu)^{2n/(n-2)-4}$$

$$[6] \quad H_\nu^\infty = X_3(n)(\nu_{\mathcal{D}} - \nu)^{2n/(n-2)-6}$$

$$[7] \quad L_\nu^\infty = X_4(n)(\nu_{\mathcal{D}} - \nu)^{2n/(n-2)-8}$$

where $\nu_{\mathcal{D}}$ is the effective vibrational index at dis-

sociation, and $X_i(n) = \bar{X}_i(n)/[(C_n)^2 \mu^n]^{1/(n-2)}$, where μ is the reduced mass of the diatom and $\bar{X}_i(n)$ an explicitly known numerical constant (2, 3, 6, 7). The superscript “ ∞ ” is used here to denote the fact that these are *limiting* near-dissociation expressions which in general are only quantitatively reliable at energies very close to dissociation (except for the vibrational energy expression which, due to a fortuitous cancellation of errors (9), can sometimes be trusted over a somewhat more extended range). However, the fact that these functions incorporate the correct behaviour at this limit is still a very powerful constraint, especially for the centrifugal distortion constants for which this limiting behaviour is singular. Note that for the familiar case of neutral molecules dissociating into neutral atoms, $n = 5$ or 6 (6, 10, 11) and all the centrifugal distortion constants become singular at dissociation (i.e., as $v \rightarrow v_{gr}$) since the powers of $(v_{gr} - v)$ appearing in [5]–[7] are negative.

For almost any diatomic species the integer n appearing in [2]–[7] is readily obtained from a knowledge of the electronic states of the atomic dissociation products (6, 10, 11) and reliable theoretical or semi-empirical estimates of C_n can often be generated (10). Thus, the limiting near-dissociation behaviour of these spectroscopic constants is often known even in the *complete absence* of experimental data. This is a necessary condition for the application of the method described below.

While requiring a knowledge of n , C_n , and v_{gr} may appear to be a fairly severe condition, in practice it often presents little difficulty. As was stated above, the appropriate value for n is usually provided by the identity of the species in question. At the same time, the value of C_n used to determine the $X_i(n)$ need *not* be known with any great precision, both because $X_i(n)$ depends on a fractional power of C_n , and because the functional behaviour of [4]–[7] is their most important feature. Moreover, the functional form used below for the near-dissociation expansions also helps minimize the effect of uncertainty in C_n . The third parameter, the vibrational index associated with the dissociation limit, v_D , can only be determined from experiment. However, for any state for which one might wish to use the present method, a near-dissociation expansion analysis of the corresponding vibrational energies will always define v_D with more accuracy than is required for the desired rotational constant analysis (4).

Recent work has shown that the presence of additional higher inverse-power terms in the long-range potential can lead to significant deviations from the limiting near-dissociation behaviour, even at energies fairly close to dissociation (9). Moreover, the explicit form of the leading deviations from limiting behaviour due to the presence of a second inverse-power term in

the long-range potential of [2] have been derived for a number of cases (9).¹ While the bulk of this paper is concerned only with utilizing the limiting behaviour of [4]–[7], it is shown in Sect. IIID that a knowledge of the leading deviations from limiting behaviour can yield further substantial improvements in the accuracy of extrapolations based on this approach.

B. Near-dissociation expansions for rotational and centrifugal distortion constants

The essence of the present method is that the functional form used to represent the rotational or centrifugal distortion constants should be constrained to have the correct limiting behaviour at dissociation. As in the vibrational energy analysis (4, 5), use of this approach in no way presumes the availability of data for highly excited vibrational levels. On the contrary, the ability of the method to provide realistic extrapolations is most dramatically illustrated when no such data are available. The type of expansion proposed here is:²

$$[8] \quad K_v = K_v^\infty \exp \left[\sum_{i=1} a_i (v_{gr} - v)^i \right]$$

where K_v is one of the constants B_v , D_v , H_v , ... etc., K_v^∞ is the expression for its limiting near-dissociation behaviour (one of [4]–[7]), and the $\{a_i\}$ are empirical constants to be determined from fits to the experimental data. In the studies of the use of near-dissociation expansions for the vibrational energies (4, 5), the exponential function appearing in [8] was replaced by a ratio of polynomials in $(v_{gr} - v)$. However, in the present work on the rotational and centrifugal distortion constants the exponential expansion of [8] was found to both be relatively more stable in the extrapolation region and to yield more compact representations (i.e., fewer empirical parameters were required to obtain a given quality of fit).

An apparent limitation of [8] is the fact that it implicitly assumes that all of the experimental K_v values have the same sign as K_v^∞ . However, when this is not the case the actual behaviour may be readily accounted for by multiplying [8] by a function such as

$$[9] \quad \prod_j [1 - (v_{gr} - v)/(v_{gr} - v_j)] = \prod_j [(v - v_j)/(v_{gr} - v_j)]$$

where v_j is(are) the empirically determined v -value(s) at which K_v/K_v^∞ changes sign.

¹Results for a number of cases not treated in ref. 9 have been obtained by the present authors and will be published in due course.

²Note that there can be no constant term in the power series expansion appearing here or the quantity K_v would not achieve the correct limiting behaviour (K_v^∞) as $v \rightarrow v_{gr}$.

As for any nonlinear fit, fits of experimental data to [8] require realistic initial trial estimates of the free parameters $\{a_i\}$. Since the functions K_v^∞ and the intercept $v_{\mathcal{D}}$ are known, these trial parameters are readily obtained from fits to the linearized equation:²

$$[10] \quad \ln(K_v/K_v^\infty) = \sum_{i=1} a_i(v_{\mathcal{D}} - v)^i$$

As in any least-squares fit, the weight associated with each datum K_v should be proportional to $(\Delta K_v)^{-2}$, where ΔK_v is the uncertainty in the experimental value of K_v . The analogous weights associated with the fits to the values of $\ln(K_v/K_v^\infty)$ appearing in [10] are therefore $(K_v/\Delta K_v)^2$. An annotated listing of a FORTRAN programme which automatically generates the required trial parameters and performs the desired nonlinear fits of [8] to experimental data, may be obtained from the authors on request.

III. Trial applications of the method to $I_2(B^3\Pi_{0u}^+)$

A. Nature of the data

One of the most extensive and most accurate sets of vibrational energies and rotational constants ever reported is that obtained by Luc (12) for the $B^3\Pi_{0u}^+$ state of I_2 . While even better results for this system are becoming available,³ his data may still be used as a model system for illustrating and testing the present method. For this species it is known (6, 10, 11) that $n = 5$, and in independent work Danyluk and King (13) measured the energies of levels $v = 77-82$ and used a near-dissociation theory analysis of them to determine $C_5 = 2.776 \times 10^5 \text{ cm}^{-1} \text{ \AA}^5$ and $v_{\mathcal{D}} = 87.18$. This $v_{\mathcal{D}}$ value does not differ significantly from that yielded by a near-dissociation expansion analysis of Luc's vibrational energies (R. J. Le Roy, unpublished work, 1980), and relative to the accuracy required by the present procedure their C_5 value does not differ significantly from theoretical estimates of it (11, 14). Thus, for the sake of simplicity the Danyluk-King (13) C_5 and $v_{\mathcal{D}}$ values were used to define the K_v^∞ functions used in the present study; the ensuing values of $X_1(5)$, $X_2(5)$, and $X_3(5)$ are 2.74×10^{-4} , -3.58×10^{-6} , and $-4.13 \times 10^{-8} \text{ cm}^{-1}$, respectively.

Luc (12) reported vibrational energies and B_v , D_v , and H_v constants for $I_2(B)$ levels $v = 1-62$, the highest of which is bound by only 100 cm^{-1} (or 2.3% of the well depth). While Luc also reported the results of Dunham expansion fits to his rotational and centrifugal distortion constants, his fits cannot readily be reproduced as they were performed subject to certain

additional constraints.^{3, 4} Thus, in order to provide an objective test of the present method, new Dunham expansion fits are performed here which are precisely analogous to our near-dissociation expansion fits. Since Luc did not report uncertainties for the various constants listed in his Table V, the most appropriate choice of weights for his data is not immediately apparent. In the absence of other information, we chose to weight the tabulated B_v values equally (i.e., ΔB_v was assumed to be a constant). At the same time, in view of the relatively rapid growth in magnitude of the centrifugal distortion constants over the range $v = 1-62$ (e.g., H_v increases by almost 3 orders of magnitude) and the fact that the observed rotational progressions die off at lower J for the higher vibrational levels, it seemed more appropriate to assume an equal *relative* weighting for D_v and H_v . In other words, the present analysis assumed that the uncertainties associated with the reported centrifugal distortion constants are a constant (unspecified) fraction of the value of the constant itself: $\Delta K_v = f \times K_v$. While this weighting scheme may not be truly optimum, its use allows the present Dunham and near-dissociation expansion fits to be compared on an equal footing.

A final point here concerns the fact that at low v Luc's tabulated H_v values showed considerable scatter (see Fig. 2c). In order to prevent the worst of these points from unduly influencing the statistics of the fits, his H_v values for $v = 1, 8, 12$, and 13 (points drawn as "+" in Fig. 2c) were therefore omitted from the fits.

B. Tests of expansion compactness

The first point of comparison between Dunham and near-dissociation expansions is their compactness, i.e., the number of empirical parameters required to achieve a given quality of fit. To examine this point, Fig. 1 plots the standard errors (σ) of near-dissociation (NDE: round points) and Dunham (triangular points) expansion fits to the experimental B_v , D_v , and H_v values vs. the number of fitting parameters N . Note that because

⁴The Dunham expansion parameters in Luc's (12) Table VII were determined sequentially in the following manner.³ First the $Y_{\ell 0}$ constants were determined from a fit to the $G(v)$ values in Table V plus the estimated $v = 0$ energy $15\,724.589 \text{ cm}^{-1}$. With the vibrational energies held fixed at the values defined by this polynomial, a new fit to the raw data then yielded modified B_v , D_v , and H_v values. These B_v 's were then used to determine the $Y_{\ell 1}$ coefficients in Table VII and their associated predicted values held fixed (together with the $G(v)$'s) in fits to the data which yielded further sets of D_v and H_v values. The $Y_{\ell 2}$ coefficients were then determined from a fit to the former, and a fit to the raw data holding $G(v)$, B_v , and D_v all fixed at the values determined by the appropriate polynomials then yielded the final empirical H_v constants, which in turn yielded Luc's $Y_{\ell 3}$ coefficients.

³S. Gerstenkorn and P. Luc. Private communication, 1981.

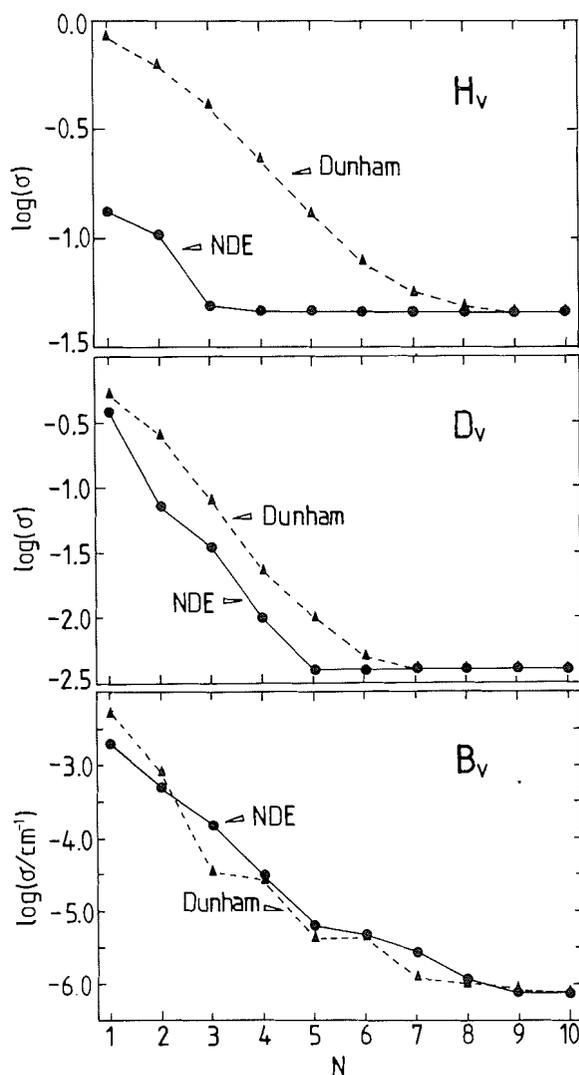


FIG. 1. Dependence of standard error of fit (σ) on number of free parameters (N) in Dunham (triangular points) and near-dissociation ("NDE", round points) expansion fits to Luc's (12) reported constants for levels $\nu = 1-62$ of B -state I_2 .

of the weighting scheme used, for D_ν and H_ν σ is the relative or fractional standard error and hence is dimensionless, while for B_ν it is the absolute standard error and has units cm^{-1} . It is immediately clear that while the two types of expansion for the B_ν constants are virtually equivalent in this regard, the near-dissociation expansions are much more compact than the traditional $(\nu + 1/2)$ power series representations of the centrifugal distortion constants.

As might have been expected, the degree of preference for the near-dissociation expansions depends on the order of the singularity at dissociation (2, 3) of the

property in question. In particular, for this ($n = 5$) $I_2(B)$ case the limiting behaviour of these constants as $\nu \rightarrow \nu_{\text{cf}}$ is (see [4]–[6]): $B_\nu \propto (\nu_{\text{cf}} - \nu)^{4/3}$, $D_\nu \propto (\nu_{\text{cf}} - \nu)^{-2/3}$, and $H_\nu \propto (\nu_{\text{cf}} - \nu)^{-8/3}$. Since the rate at which $B_\nu \rightarrow 0$ at this limit deviates only slightly from linearity (i.e., $4/3$ is fairly close to 1) it is no surprise that imposing this limiting behaviour as a constraint yields no substantial advantages over a simple polynomial expansion. On the other hand, the singularities of the D_ν and H_ν constants typify behaviour which cannot be readily mimicked by any polynomial, and the deficiencies of polynomial representations should increase with the order of this singularity. Note too that for the other common neutral molecule \rightarrow neutral atoms case, $n = 6$, the limiting behaviour of B_ν is predicted to be precisely linear while the singularities in D_ν and H_ν are of slightly higher order than those encountered here, so the effects seen in Fig. 1 should be exaggerated there.

If the data set used in these fits had included properties of levels lying above $\nu = 62$, it seems clear that the centrifugal distortion constants' preference for the near-dissociation expansions would have been enhanced, while the not-quite-linear behaviour of B_ν at ν_{cf} might have allowed a similar preference to become discernable for the B_ν fits as well. On the other hand, for a small set of centrifugal distortion constants which do not differ significantly in magnitude, the marked advantage of the near-dissociation expansion fits with regard to compactness may be expected to disappear. However, the fact that the near-dissociation expansions have the correct limiting behaviour means that they should always be able to provide more realistic extrapolations beyond the range of the observed data (see below).

C. Tests of extrapolation abilities

Figure 2 compares the present near-dissociation expansions (solid curves) and Dunham expansions (dashed curves) obtained from fits to the experimental constants (12) for levels $\nu = 1-62$ (solid points) of B -state I_2 . The four H_ν values omitted from the fits (see Sect. III.A) are denoted by plus signs (+), while the open circles represent recently obtained³ preliminary values of the various constants for levels $\nu = 63-75$; note that the latter (open circles) were not used in the fits. For the sake of comparison, the Dunham polynomials obtained by Luc (12) (dot-dash curves) are also shown. The quantity in parentheses in the label for each curve is the number of free parameters in the corresponding fit.

The choice of ordinate in Fig. 2 is suggested by the form of [8]. It provides a particularly convenient way of examining the extrapolation abilities of these functions, since the limiting near-dissociation theory tells us that a correctly extrapolated curve must necessarily

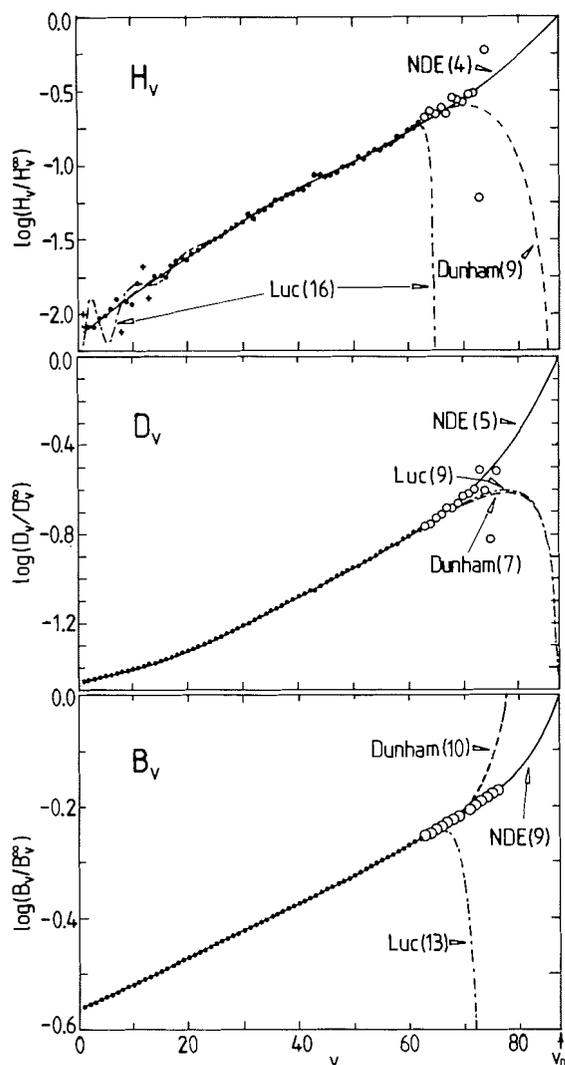


FIG. 2. Comparison of results of present near-dissociation (NDE, solid curves) and Dunham (dashed curves) expansion fits to Luc's (12) data for $v = 1-62$ (solid points); dot-dash curves represent the polynomials reported by Luc (12) while the open circles represent new experimental results³ (not used in the fits) for $v = 63-75$. The numbers in parentheses indicate the number of expansion parameters (N) associated with each fit.

approach zero (upper right-hand corner) as $v \rightarrow v_D$. For the singular centrifugal distortion constants it would be impossible to realistically illustrate these extrapolations on a plot which did not scale the actual K_v values by K_v^x .

The fact that both the present Dunham polynomials and those of Luc (12) become unreliable very shortly past the last point used in the fits ($v = 62$) is immediately apparent. This contrasts strongly with the way the near-dissociation expansions pass right through the new

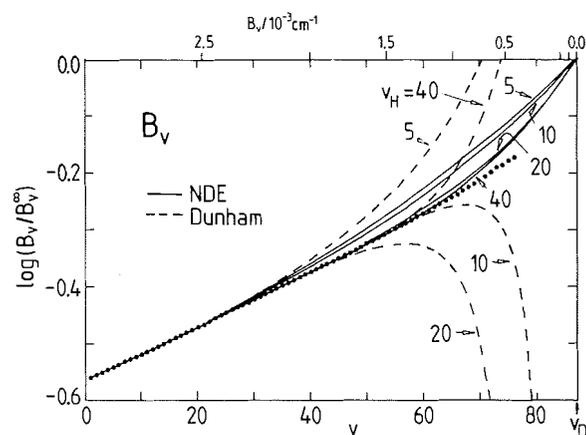


FIG. 3. Comparison of extrapolation abilities of near-dissociation (NDE, solid curves) and Dunham (dashed curves) expansions determined from fits to the experimental B_v values (solid points) for $v = 1$ to v_H , for $v_H = 5, 10, 20$, and 40 .

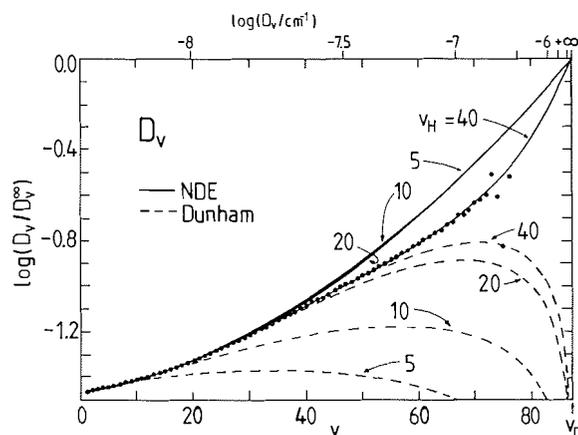


FIG. 4. For the D_v values, as in Fig. 3.

experimental points³ for $v = 63-75$ (not used in the fits) on their way to the correct limit. The oscillations of Luc's (12) H_v polynomial (dot-dash curve) at low v is apparently due to his use of a polynomial of higher order than is required to explain these data.⁴

As a further test of the extrapolation abilities of these functions, Figs. 3-5 compare the Dunham (dashed curves) expansion functions obtained from data sets truncated at $v = v_H$, for $v_H = 40, 20, 10$, and 5 . It is clear that although the near-dissociation expansion extrapolations are not perfect, they are virtually always much more reliable than polynomial extrapolations based on the same data. The fact that B_v decreases in magnitude with increasing v also means that the fairly large relative errors in the high- v values of these con-

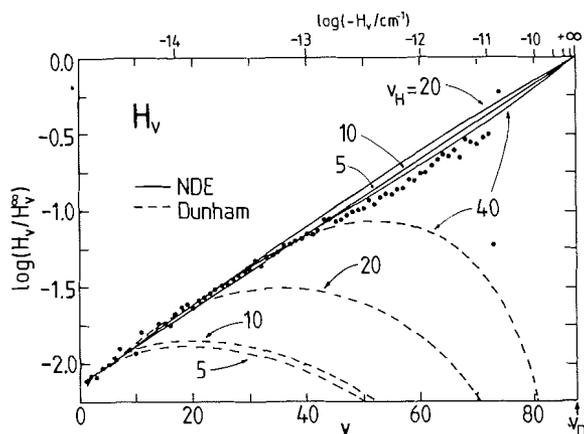


FIG. 5. For the H_v values, as in Fig. 3.

stants yielded by the longer extrapolations correspond to fairly small absolute errors in the predicted B_v values. Moreover, the mere fact that the near-dissociation expansions constrain B_v to go to zero exactly where the vibrational spacing does should reduce the anomalous behaviour often found for the inner walls of RKR potential energy curves calculated from extrapolated energy and B_v functions. For the D_v and H_v functions Figs. 4 and 5 show that the relative errors in the near-dissociation expansion predictions for some of the longer extrapolations become as large as 40%. However, relative both to the 2–3 orders of magnitude growth in these constants in the extrapolation to that point and to the errors in the analogous Dunham polynomial extrapolations, these errors are not too disturbing, particularly since they decrease for levels lying even closer to dissociation.

While the most significant property of near-dissociation expansions is their ability to provide realistic extrapolations at high v , they should also be reliable for extrapolating at small v to estimate potential minimum parameters (at $v = -1/2$) such as B_e , D_e , and H_e . Indeed for the vibrational energy case there is some evidence⁵ that they provide more reliable extrapolations at low v than would a simple polynomial in $(v + 1/2)$. This observation is in agreement with the results in Table 1 which compares our Dunham and NDE extrapolated values of D_e and H_e , together with those of Luc (12), with the predicted values of these quantities which Luc (12) generated from the Kratzer equation (1).

D. Utilizing the theory of deviations from the limiting near-dissociation behaviour

In ref. 9 it was shown that the addition of a second inverse-power term C_m/r^m ($m > n$) to the long-range

⁵C. L. Beckel, R. B. Kwong, and R. J. Le Roy. Unpublished work, 1981.

TABLE 1. Comparison of various extrapolated D_e and H_e values with the theoretical values Luc (12) generated from the Kratzer equations (1)

	$D_e/10^{-9}$ (cm^{-1})	$H_e/10^{-15}$ (cm^{-1})
NDE	6.17	-1.89
Dunham	6.19	-2.98
Luc	6.13	-2.15 ^a
Theory	6.17	-1.97

^aIn view of the oscillations of the Luc H_v polynomial seen in Fig. 5, the reasonableness of this value may be fortuitous.

potential of [2] can lead to significant deviations from the limiting behaviour predicted by [3] and [4], even for energies fairly close to dissociation. Moreover, explicit expressions for the leading contribution to the deviation from the vibrational energy expression [3], were obtained for most common potential forms, and an analogous expression for the leading deviation from the limiting B_v expression, [4], was also obtained for the type of long-range potential ($n = 5$, $m = 6$) associated with the present sample problem. The latter implies that near dissociation

$$[11] \quad B_v = B_v^\infty [1 + a_0(v_{gr} - v)^{2/3} + \dots]$$

where the constant a_0 is determined by the values of the long-range potential constants C_5 and C_6 . In the case of the vibrational energy expansions it has been found (R. J. Le Roy. Unpublished work (1981).) that taking account of this leading deviation from limiting behaviour, in addition to the limiting behaviour itself, significantly improved the quality of the extrapolations. The present section examines this point for the near-dissociation expansion representation of the B_v constants.

In the following, the utilization of the extended near-dissociation behaviour implied by [11] is considered on two different levels. The first makes use of the functional form of [11], but treats the constant a_0 as an empirical parameter, which is what it would be in any case when no estimate of the C_6 constant was available. The near-dissociation expansion function used for this case is:

$$[12] \quad B_v = B_v^\infty \exp \left\{ (v_{gr} - v)^{2/3} \sum_{i=0} a_i (v_{gr} - v)^i \right\}$$

In the second case a_0 is held fixed at the value implied by the constant $C_6 = 17.8 \times 10^5 \text{ cm}^{-1} \text{ \AA}^6$ obtained by Danyluk and King (13), $a_0 = -0.150$, and the expansion function is:

$$[13] \quad B_v = B_v^\infty \exp \left\{ a_0 (v_{gr} - v)^{2/3} + \sum_{i=1} a_i (v_{gr} - v)^i \right\}$$

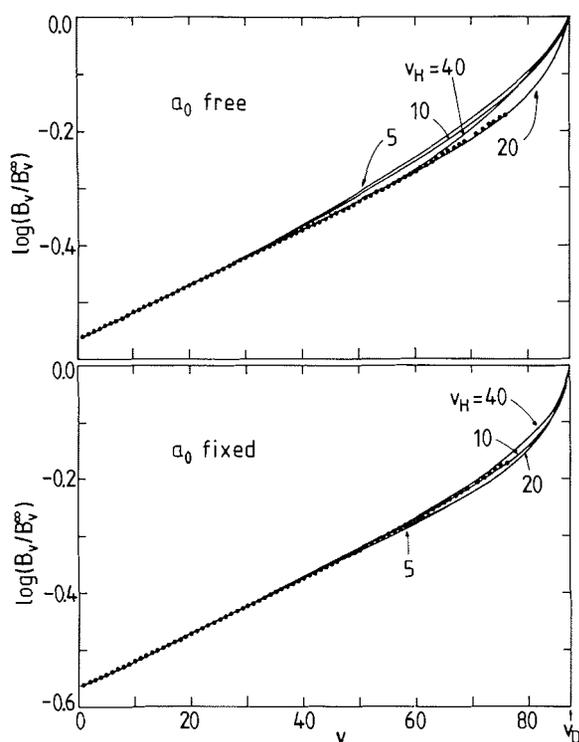


FIG. 6. Test of extrapolation abilities of the extended near-dissociation theory expansions of [12] (upper segment, " a_0 fitted") and [13] (lower segment, " a_0 fixed") determined from fits to the experimental B_v values (solid points) for $v = 1$ to v_H .

Figure 6 shows the results of fits to [12] and [13] performed using the same truncated data sets used for the fits summarized in Fig. 3. The dramatic improvements over the quality of the simple NDE extrapolations seen in Fig. 3 are immediately apparent. It is, therefore, clear that increasing the sophistication of the near-dissociation theory constraints can substantially improve the quality of rotational (and probably also centrifugal distortion) constant extrapolations performed using the present approach. This point should add impetus to efforts to derive extended near-dissociation theory expressions analogous to [11] for other B_v cases (i.e., for other combinations of n and m) and for the centrifugal distortion constants.

IV. Conclusions

The results presented above very clearly demonstrate the superiority of the near-dissociation expansions introduced here with regard to both economy of representation and extrapolation abilities. With regard to the former property, the advantage of the present scheme decreases with the range of the levels for which constants are available. Indeed, for the B_v constants this

superior compactness of the near-dissociation expansions may be difficult to discern unless values are available almost all the way to dissociation. However, even in the worst cases, near-dissociation expansions will not likely require significantly more parameters to achieve a given quality of fit than would equivalent Dunham expansions, while in more favourable situations, such as the H_v case considered in Fig. 2, the advantages of the former are considerable (e.g., 4 vs. 9 parameters in this particular case).

With regard to their ability to extrapolate reliably beyond the highest observed level, Dunham expansions clearly cannot begin to compete with near-dissociation expansions, especially for the centrifugal distortion constants which become singular at dissociation. Since the latter are constrained to have the correct behaviour at dissociation, this result is not too surprising. However, it is interesting to note that in extrapolations beyond the lowest observed levels to estimate the values of D_e and H_e , the near-dissociation expansions perform just as well, if not better than the traditional $(v + 1/2)$ power series expansions. Thus, while they do not appear as explicit parameters in the expansion expressions, it appears that the values of molecular constants such as H_e , D_e , B_e , α_e , ω_e , . . . etc., obtained from near-dissociation expansion extrapolations may be more accurate than those yielded by the traditional Dunham analysis.

The only apparent disadvantages of near-dissociation expansions are the fact that the molecular constants mentioned above do not appear as explicit parameters, and the fact that performing fits to [8], [12], or [13] is somewhat more complicated than simply fitting data to a power series in $(v + 1/2)$. However, this first difficulty is more apparent than real since these molecular constants can readily be determined from the properties of the expansion at $v = -1/2$. Similarly, to a user, a computer program for performing fits to [8], [12], or [13] (such a program may be obtained from the authors on request) is no more difficult to use than one which performs fits to $(v + 1/2)$ polynomials.

It is important to recall that the object of the tests reported in Sect. III was to demonstrate the superiority of near-dissociation expansions over the traditional Dunham $(v + 1/2)$ polynomials when the two are compared on an equal footing. Thus, no attempt was made there to take account of the correlation between the different constants for a given level in order to assure the best possible overall reproduction of the raw data. Moreover, the fact the weights used in the present fits (see Sect. III.A) may not correspond precisely to their actual uncertainties means that the expressions obtained here may not even provide the optimum representation of Luc's (12) tabulated constants. In spite of this, it seems appropriate to record our "best" near-

TABLE 2. Coefficients of present "best" near-dissociation expansions determined from fits of Luc's (12) constants for B -state I_2 to [8] and [13]

	B_v (from [13])	D_v (from [8])	H_v (from [8])
a_0	-0.150	—	—
a_1	2.465586×10^{-2}	-1.34962×10^{-1}	-9.657×10^{-2}
a_2	1.4980903×10^{-3}	4.08576×10^{-3}	1.64724×10^{-3}
a_3	$-1.30961784 \times 10^{-4}$	-7.82103×10^{-5}	-2.10743×10^{-5}
a_4	$5.08249846 \times 10^{-6}$	7.21116×10^{-7}	8.5287×10^{-8}
a_5	$-1.138850184 \times 10^{-7}$	-2.48121×10^{-9}	
a_6	$1.554945319 \times 10^{-9}$		
a_7	$-1.279752225 \times 10^{-11}$		
a_8	$5.85222138 \times 10^{-14}$		
a_9	$-1.1449662 \times 10^{-16}$		

dissociation expansions for his B -state I_2 rotational and centrifugal distortion constants. Table 2 therefore lists the expansion parameters obtained on fitting Luc's (12) Table V constants for levels $v = 1-62$ to [13] or [8], as indicated. Except for the rounded-off theoretical a_0 value associated with the B_v expansion, the number of significant digits quoted for the coefficients shown there was defined by requiring that the rounding error affect the predicted values of all the constants being fitted by less than $0.1 \times \sigma$, where σ is the standard error of the fit.

While the model problem considered in Sect. III consists of fits to sets of experimental B_v , D_v , and H_v values, it seems clear that the demonstrated superiority of near-dissociation expansions for representing such constants will also apply to sets of centrifugal distortion constants calculated (2, 3, 15-20) from a known potential energy curve. Thus, these expansions should also prove useful in compactly summarizing and extrapolating the results of self-consistent data analyses in which the $G(v)$ and B_v values are determined from fits in which the centrifugal distortion constants are held fixed at values computed from a previously determined potential energy curve (19, 21). In conclusion, therefore, it seems appropriate to suggest that near-dissociation expansions should eventually replace the traditional Dunham ($v + 1/2$) expansions for use in the routine analysis of spectroscopic data.

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