

# Functional form for representing all vibrational eigenenergies of a diatomic molecule state. IV. Application to the $\text{Br}_2 B(^3\Pi_{0u}^+)$ state<sup>a)</sup>

Charles L. Beckel, Robin B. Kwong,<sup>b)</sup> and Ali-Reza Hashemi-Attar<sup>c)</sup>

*Department of Physics and Astronomy, The University of New Mexico, Albuquerque, New Mexico 87131*

Robert J. Le Roy

*Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada*

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A composite expression for diatomic vibrational energy levels is here tested by application to the  $B$  state of  $\text{Br}_2$ . The form is  $E_v = D - (v_D - v)^m [L/N]$ , where  $E_v$  is the energy of vibrational level  $v$ ,  $D$  the dissociation limit,  $v_D$  the value of  $v$  at dissociation, and  $[L/N]$  a ratio of polynomials in  $(v_D - v)$ . This functional form with a variety of  $[L/N]$  is fitted to experimental data for  $^{79,79}\text{Br}_2$ . The best fits, both with  $m$  variable and with  $m$  fixed at the value  $10/3$  predicted by near-dissociation theory, have an overall rms error of  $0.015 \text{ cm}^{-1}$ . The best fits with  $m \equiv 10/3$  all yield realistic estimates of the coefficient  $C_5$  (of  $R^{-5}$ , with  $R$  nuclear separation) in the long-range potential; moreover, fixing  $m$  at  $10/3$  offers computational and interpretational advantages. Analogous fits to Dunham polynomials in  $(v + 1/2)$  are found to be distinctly less reliable than these composite "near-dissociation expansion" (NDE) functions with  $m$  fixed or variable. In order to test the interpolation and low- $v$  extrapolation power of the composite functions, fits are made with 12 of the 56  $E_v$  excluded from the data set; the NDE functions again perform as well as or better than Dunham polynomials. In addition, use of Stwalley's mass-reduced quantum numbers in the best of the  $m = 10/3$  functions obtained for  $^{79,79}\text{Br}_2$  yields predicted vibrational spacings for  $^{81,81}\text{Br}_2$  with errors ( $< 0.03 \text{ cm}^{-1}$ ) only slightly larger than the experimental uncertainties.

## I. INTRODUCTION

For diatomic molecule vibrational levels  $E_v$  lying either near the potential minimum or very near dissociation, there are known functional dependences on vibrational quantum number  $v$ .<sup>1-3</sup> However, until recently<sup>4-7</sup> there were no general  $E_v$  expressions which both had the correct functional behavior in these two limiting regions and were able to provide compact representations over the whole range of level energies. The first paper in this series<sup>4</sup> proposed a formula satisfying these criteria and tested it by application to the ground state of  $\text{H}_2^+$ , a prototype for systems with attractive  $R^{-4}$  long-range potentials. Here  $R$  is nuclear separation. In a second paper,<sup>5</sup> it was applied to the ground state of  $\text{H}_2$ , a prototype of states with attractive  $R^{-6}$  potential tails; this functional form provided efficient representations of both experimental and theoretical vibrational energies and level spacings. It was also shown<sup>6</sup> that the use of Stwalley's<sup>8</sup> mass-reduced quantum numbers, plus minor least-squares fit adjustments to correct the first-order JWKB approximation, transformed these same expressions into excellent representations of ground-state  $\text{D}_2$  and  $\text{HD}$  data.

The present paper reports an application of the proposed expression to the  $B(^3\Pi_{0u}^+)$  state of  $\text{Br}_2$ , a prototype for realistic systems with an attractive  $R^{-5}$  limiting long-range

interaction potential. Unlike hydrogenic diatoms, this species has a large reduced mass. Furthermore, the state has experimentally observed high- $v$  levels for which the long-range inverse-power portion of the potential is relatively important. The latter property facilitates the testing of certain theoretically suggested constraints on the form of the proposed expressions. The 56 observed levels of this molecule<sup>9</sup> span virtually the whole region from the potential minimum to dissociation, so they should provide a significant test of the utility of any formula meant to represent the entire range of bound-state vibrational energies. The proposed formula is also examined for use in detecting apparent irregularities in experimental data and in providing reliable interpolations and extrapolations for missing data. The utility of the expression is systematically compared to that of the traditional polynomial expansions in  $(v + 1/2)$ . Application of the proposed formula, expressed in terms of mass-reduced quantum numbers, to converting  $^{79,79}\text{Br}_2(B)$  data into level spacing predictions for  $^{81,81}\text{Br}_2(B)$  is also investigated.

Note that as in previous publications in this series,<sup>4-6</sup> the focus of the present paper is the ability of the proposed functional form to provide efficient representations of experimental data. The explicit question of their utility for determining molecular dissociation energies and for extrapolating at high  $v$  to predict the number and energies of missing levels is examined elsewhere.<sup>7,10,11</sup>

## II. METHODS

The expressions considered here have the form

$$E_v = D - (v_D - v)^m [L/N], \quad (1)$$

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<sup>b)</sup> Present address: Hughes Aircraft Co., Albuquerque Engineering Center, P.O. Box 9301, Albuquerque, NM 87119.

<sup>c)</sup> Present address: Bell Telephone Laboratories, 1255 Cedar Crest Blvd., Allentown, PA 18103.

with

$$[L/N] = \frac{p_0 + p_1(v_D - v) + \dots + p_L(v_D - v)^L}{1 + q_1(v_D - v) + \dots + q_N(v_D - v)^N}. \quad (2)$$

In the most general case  $D$ ,  $v_D$ ,  $m$ ,  $\{p_i\}$ , and  $\{q_i\}$  may all be treated as adjustable parameters. The basis for this type of formula is that Eq. (1) becomes equivalent<sup>4-7</sup> to Dunham's<sup>1</sup> polynomial in  $(v + 1/2)$  at low  $v$  and to the limiting near-dissociation theory result<sup>2,3</sup> near the dissociation limit  $D$ . Because of the latter property, Eq. (1) can be called<sup>7</sup> a "near-dissociation expansion" (NDE). For molecules whose long-range potential takes on the asymptotic form

$$V(R) \simeq D - C_n/R^n, \quad (3)$$

the power  $m = 2n/(n - 2)$  is known, the constant  $p_0$  is determined by the value of the potential constant  $C_n$ , and (for  $n > 2$ )  $v_D$  is the (noninteger) effective vibrational index at dissociation. The question of whether  $m$  and  $p_0$  should be held fixed at their theoretically predicted values, as recommended in Ref. 7, is discussed below.

Equation (1) is not a linear function; hence, iterative nonlinear least-squares fitting techniques are required for determining its variable parameters. Since we are dealing with multidimensional parameter spaces, each of which could have multiple minima, the present fits began from a large number of starting points; in addition, each minimum is checked for spurious zeros and poles. For a given  $[L/N]$  case, we report on only the best fit that has no spurious numerator or denominator zeros.

In general, Eq. (1) may be fitted either to the level energies themselves, or to the level spacings  $\Delta E(v + 1/2)$ . In the latter case,  $D$  is no longer explicitly present as a parameter and the function minimized by the least-squares procedure is

$$F = \sum_v [\Delta E_{\text{obs}}(v + 1/2) - \Delta E_{\text{calc}}(v + 1/2)]^2. \quad (4)$$

This was the case for most of the results reported below.

In reducing data to obtain spectroscopic constants it is, of course, best to fit directly to raw experimental data,<sup>11</sup> rather than to a set of partially reduced spectroscopic constants such as a set of energy differences. When this is not possible (as in the present case where the raw data were not published), the dependent variable used in fits should be as closely related as possible to experimental observables. For example, if the data consist of a series of infrared  $\Delta v = -1$  lasing transitions, the vibrational spacings are the most appropriate dependent variable; in contrast, if the data are a series of fluorescence doublets, the energy itself is the more appropriate dependent variable. For the  $\text{Br}_2$  system considered below, the raw data consist of a large number of visible absorption bands;<sup>9</sup> the vibrational energies themselves may well be the more natural fitting variable. However, the primary objective of the present work is to examine the utility of NDE functional forms, rather than to provide an optimal archival set of spectroscopic constants for this particular system. For consistency with the previous papers in this series,<sup>4-6</sup> most of the fits reported below again used the vibrational spacings as dependent variable. However, it is shown in Sec. IV that the essential conclusions of the present work do not depend on the choice of dependent variable used in the fits.

On introducing Stwalley's<sup>8</sup> mass-reduced vibrational quantum number  $\eta = (v + 1/2)/\mu^{1/2}$ , where  $\mu$  is the reduced mass, Eq. (1) may be rewritten as

$$E(\eta) = D - (\eta_D - \eta)^m \times \frac{[p'_0 + p'_1(\eta_D - \eta) + \dots + p'_L(\eta_D - \eta)^L]}{[1 + q'_1(\eta_D - \eta) + \dots + q'_N(\eta_D - \eta)^N]}, \quad (5)$$

where  $\eta_D = (v_D + 1/2)/\mu^{1/2}$ ,  $p'_i = p_i\mu^{(m+i)/2}$ , and  $q'_j = q_j\mu^{j/2}$ . Alternatively, a version of Eq. (1) determined for isotope (1) of a given species may be converted into an expression for isotope (2) by the relationships

$$v_D(2) + 1/2 = [v_D(1) + 1/2]/(\mu_r)^{1/2}, \quad (6)$$

$$p_i(2) = p_i(1)(\mu_r)^{m+i/2}, \quad (7)$$

$$q_j(2) = q_j(1)(\mu_r)^{j/2}, \quad (8)$$

where  $\mu_r = \mu(1)/\mu(2)$  is the ratio of reduced masses. In the following, the accuracy of this type of conversion is tested for <sup>81,81</sup>Br<sub>2</sub> and <sup>79,79</sup>Br<sub>2</sub>. (A similar procedure was used for D<sub>2</sub> and HD ground states in paper III.)

### III. APPLICATION TO THE $B(^3\Pi_{0u}^+)$ STATE OF Br<sub>2</sub>

#### A. Experimental data and predicted limiting behavior

For  $B$  state<sup>79,79</sup> Br<sub>2</sub> Barrow *et al.*<sup>9</sup> reported energies for the first 56 vibrational levels, the highest of which lies only  $\sim 1 \text{ cm}^{-1}$  from dissociation. The standard error reported for these experimental energies was  $0.02 \text{ cm}^{-1}$ . Unless otherwise stated all of the fits reported below were performed on the 55 vibrational spacings between pairs of adjacent levels  $\Delta E(v + 1/2)$ .

Both the energy difference table for the experimental data and the residual discrepancies yielded by all fewer-parameter "good" fits suggest that there are unusually large experimental errors in the values of  $E_v$  for  $v = 10, 37$ , and  $51$ . To insure that these apparently bad points did not lead to misinterpretation of trends in the present study, these three data points were adjusted by adding  $0.05 \text{ cm}^{-1}$  to  $E_{10}$ ,  $-0.03 \text{ cm}^{-1}$  to  $E_{37}$ , and  $0.03 \text{ cm}^{-1}$  to  $E_{51}$  and so used in all of the better fits reported below.

The theory of long-range intermolecular forces indicates that for the  $B(^3\Pi_{0u}^+)$  state of Br<sub>2</sub>, the power of the asymptotically dominant inverse-power term in the potential [Eq. (3)] is  $n = 5$ .<sup>12</sup> According to near-dissociation theory,<sup>2,3,13</sup> this implies that the energies of levels lying sufficiently close to dissociation will be accurately described by the [0/0] version of Eq. (1) with  $m = 2n/(n - 2) = 10/3$  and

$$p_0 = 9170.9/\mu^{5/3}(C_5)^{2/3}. \quad (9)$$

Here  $C_5$  (in  $\text{cm}^{-1} \text{ \AA}^5$ ) is the potential constant of Eq. (3) and  $\mu$  is in amu. On using this expression to analyze their highest observed vibrational levels, Barrow *et al.*<sup>9</sup> concluded that  $v_D = 59.56$  and  $p_0 = 0.00625 \text{ cm}^{-1}$  (or  $C_5 = 1.818 \times 10^5 \text{ cm}^{-1} \text{ \AA}^5$ ). This empirical  $p_0$  value is certainly quite reasonable, as it is only 6%–17% larger than estimates obtained from Eq. (9) using various theoretical estimates of this  $C_5$  constant.<sup>14</sup> One objective of the present study is to examine the effect on the utility of Eq. (1) of fixing  $m$  and  $p_0$  at these theoretically predicted values.

no. free parameters	5	6	7	8	9
					0.018 [6/0] 5.39 1.25 63.01
				0.024 [5/0] 4.59 1.08 61.43	0.023 [5/1] 5.03 1.13 62.06
		0.13 [3/0] 3.34 1.21 60.06	0.05 [4/0] 3.51 0.76 59.12	0.048 [4/1] 3.96 0.83 59.78	0.015 [4/2] 3.81 1.04 60.42
0.14 [2/0] 3.86 1.48 61.40		0.10 [2/1] 3.58 1.19 60.32	0.08 [3/1] 3.03 0.81 58.68	0.032 [3/2] 3.31 0.75 58.90	0.022 [3/3] 3.86 0.92 60.04
0.16 [1/1] 3.83 1.24 60.85		0.10 [1/2] 2.64 0.53 57.49	0.05 [2/2] 3.03 0.60 58.13	0.043 [2/3] 3.50 0.72 58.99	0.015 [2/4] 3.59 1.03 60.17
0.11 [0/2] 3.04 0.81 58.68		0.08 [0/3] 2.57 0.36 56.92	0.07 [1/3] 2.76 0.47 57.47	0.055 [1/4] 3.27 0.62 58.39	0.028 [1/5] 4.40 1.44 64.08
			0.07 [0/4] 3.04 0.49 57.77	0.029 [0/5] 5.11 1.47 65.25	0.020 [0/6] 3.32 1.16 60.65
-----					
	0.21 0 [5/0] ∞	0.12 0 [6/0] 55.88	0.05 0 [7/0] ∞	0.045 0 [8/0] ∞	0.020 0 [9/0] 56.98

FIG. 1. Results of Eq. (1), variable- $m$  fits to  $^{79,79}\text{Br}_2(B)$  experimental vibrational spacings. Properties shown are  $\frac{\text{rms error}}{D - E_{55}} [L/N]_{v_D}^m$ . The last row contains Dunham polynomial least-squares fits. Energies are in  $\text{cm}^{-1}$ .

## B. Fits with $m$ and $p_0$ variable

The upper portion (above the dashed horizontal line) of Fig. 1 summarizes the results of nonlinear least-squares fits of the 55 experimental vibrational spacings to diverse forms of Eq. (1). The result of each fit is characterized there by the quantity

$$\frac{\text{rms error}}{D - E_{55}} [L/N]_{v_D}^m \quad (10)$$

The symbol  $[L/N]$  indicates the polynomial degrees in the rational fraction,  $m$  and  $v_D$  are the optimized values yielded by the fit,  $(D - E_{55})$  is the predicted binding energy in  $\text{cm}^{-1}$  of the highest level used in the fit, and "rms error" is the root mean square error  $(F/M)^{1/2}$  in  $\text{cm}^{-1}$  associated with the fit, where  $M$  is the number of spacings. The listed rational fractions have no poles or spurious zeros on the real axis for  $-1/2 < v < v_D$ . For  $[L/N]$  cases for which the  $F$  hypersurface was found to have more than one local minimum, the case listed is that which yields the smallest value of  $F$ .

Each column in the upper portion of Fig. 1 corresponds to a fixed value of  $L + N$  and the entries in each column correspond to fits with the same number of adjustable parameters,  $L + N + 3$ . Entries along a diagonal have either a common  $L$  or common  $N$  value. Throughout the following, all entries with eight or more parameters correspond to fits which used the corrected first differences obtained from the adjusted values of  $E_{10}$ ,  $E_{37}$ , and  $E_{51}$  mentioned above, while fits with less than eight parameters used the raw data of Ref. 9.

One apparently puzzling aspect of the results in Fig. 1 is the fact that the fitted  $m$  values range from 2.57 to 5.39, and in general are not particularly close to the theoretical value of  $10/3$  appropriate for this state. This contrasts sharply with Ref. 5's study of the ground state of  $\text{H}_2$ , where all of the better fits yielded optimized  $m$  values quite close to the theoretical value. It also is counter to the finding of Barrow *et al.*<sup>9</sup> that the  $m = 10/3$  version of the limiting  $[0/0]$  form of Eq. (1) provides a much better representation of the spacings of the highest observed  $\text{Br}_2(B)$  levels  $v = 45-55$  than do analogous expressions with  $m = 3, 3.14$ , and 4.

The resolution of this paradox appears to be the fact that when a large number of levels from *all* parts of the potential well are fitted simultaneously, the physical significance of the parameters yielded by the fits is substantially altered by the effects of interparameter correlation. In particular, the significance of  $m$  at low  $v$  is quite different from that at high  $v$  (see Sec. IV A of Ref. 5); in many-parameter fits to large data sets, an "incorrect" value (according to near-dissociation theory) of the power  $m$  is compensated for by corresponding changes in parameters such as  $v_D$  and  $p_0$ . This conclusion is confirmed by the rather discordant  $v_D$  values yielded by the fits with  $m$  free (see, e.g., the last column of Fig. 1). In contrast, the results presented in the following section show that when  $m$  is held fixed at the predicted limiting value (here  $10/3$ ),  $v_D$  values yielded by the "better" fits are all very similar. This suggests that it may be better to fix  $m$  at its theoretically predicted value, rather than treat it as a parameter to be determined by the fit.

no. free parameters	4	5	6	7	8	9
						*
					*	
			0.05 <sub>[4/0]</sub> <sup>10/3</sup> 0.66 <sub>58.62</sub>	0.05 <sub>[5/0]</sub> <sup>10/3</sup> 0.67 <sub>58.65</sub>		*
		0.13 <sub>[3/0]</sub> <sup>10/3</sup> 1.21 <sub>60.04</sub>		0.05 <sub>[4/1]</sub> <sup>10/3</sup> 0.66 <sub>58.64</sub>		0.015 <sub>[5/2]</sub> <sup>10/3</sup> 0.95 <sub>59.57</sub>
0.20 <sub>[2/0]</sub> <sup>10/3</sup> 0.68 <sub>58.83</sub>			0.08 <sub>[3/1]</sub> <sup>10/3</sup> 1.00 <sub>59.52</sub>		*	
		0.17 <sub>[2/1]</sub> <sup>10/3</sup> 1.17 <sub>60.81</sub>		0.03 <sub>[3/2]</sub> <sup>10/3</sup> 0.77 <sub>59.00</sub>		*
0.20 <sub>[1/1]</sub> <sup>10/3</sup> 0.65 <sub>58.78</sub>			0.07 <sub>[2/2]</sub> <sup>10/3</sup> 0.96 <sub>59.42</sub>		*	
		0.12 <sub>[1/2]</sub> <sup>10/3</sup> 1.15 <sub>59.87</sub>		0.05 <sub>[2/3]</sub> <sup>10/3</sup> 0.68 <sub>58.71</sub>		0.015 <sub>[3/4]</sub> <sup>10/3</sup> 0.99 <sub>59.72</sub>
0.15 <sub>[0/2]</sub> <sup>10/3</sup> 1.47 <sub>60.48</sub>			0.10 <sub>[1/3]</sub> <sup>10/3</sup> 0.58 <sub>58.02</sub>		0.018 <sub>[2/4]</sub> <sup>10/3</sup> 0.88 <sub>59.36</sub>	
		0.12 <sub>[0/3]</sub> <sup>10/3</sup> 1.06 <sub>59.65</sub>		0.06 <sub>[1/4]</sub> <sup>10/3</sup> 0.63 <sub>58.47</sub>		0.015 <sub>[2/5]</sub> <sup>10/3</sup> 0.98 <sub>59.69</sub>
			0.07 <sub>[0/4]</sub> <sup>10/3</sup> 0.53 <sub>58.07</sub>		*	
				0.05 <sub>[0/5]</sub> <sup>10/3</sup> 0.81 <sub>59.17</sub>		*
					0.020 <sub>[0/6]</sub> <sup>10/3</sup> 1.16 <sub>60.66</sub>	*
						*
0.44 <sub>[4/0]</sub> <sup>0</sup> ∞	0.21 <sub>[5/0]</sub> <sup>0</sup> ∞	0.12 <sub>[6/0]</sub> <sup>0</sup> 0.17 <sub>55.88</sub>	0.05 <sub>[7/0]</sub> <sup>0</sup> ∞	0.045 <sub>[8/0]</sub> <sup>0</sup> ∞	0.020 <sub>[9/0]</sub> <sup>0</sup> 0.48 <sub>56.98</sub>	

FIG. 2. Results of Eq. (1), fixed- $m$  fits to  $^{79,79}\text{Br}_2$  ( $B$ ) experimental vibrational spacings. Format, notation, and units are the same as in Fig. 1.

In order to provide a reference against which to consider the utility of Eq. (1), these same  $\text{Br}_2$  vibrational spacings were fitted to the traditional Dunham polynomials in  $(v + 1/2)$ . Such fits are equivalent to fits to Eq. (1) performed with  $N = 0$  and  $m = 0$ . The results obtained are summarized in the last row of Fig. 1, where each entry corresponds to a fit with the same number of adjustable parameters as those above it. In this context, an entry with  $v_D = \infty = D - E_{55}$  identifies an unphysical situation in which the extrapolated vibrational spacings go through a minimum without ever changing sign. That this occurs for most of the  $m = 0$  cases seen in Fig. 1 emphasizes the fact that polynomials are very unreliable for extrapolating beyond the last observed level. In addition, the Dunham expansions are clearly no more "efficient" in that they require as many or more free parameters to achieve a given rms error as do the NDE functions.

### C. Fits with $m=10/3$ and $\rho_0$ variable

As was mentioned above, near-dissociation theory predicts that vibrational levels lying sufficiently close to the dissociation limit of  $B$  state  $\text{Br}_2$  will be described by the  $[0/0]$  version of Eq. (1) with  $m = 10/3$ . The 55 "experimental" vibrational spacings were therefore fitted to Eq. (1) with  $m$  fixed at this value, yielding the results summarized in the upper portion of Fig. 2; as in Fig. 1, the last row comprises the results of fits to Dunham expansions ( $m = 0 = N$ ).

Each entry in Fig. 2 characterizes the best fit obtained for that  $[L/N]$  space that had no spurious zeros or poles for

$-1/2 < v < v_D$ . Entries replaced by an asterisk indicate cases for which no independent  $m = 10/3$  fit could be obtained; the omitted results were either very similar to a fit with fewer parameters or tended to produce an effective  $m$  of  $13/3$ . For example, in the  $[0/7]^{10/3}$  fit the optimized  $q_7$  value is three orders of magnitude smaller than the optimized  $q_6$ . The contribution of the  $q_7$  term to Eq. (2) is therefore insignificant, indicating that this  $[0/7]^{10/3}$  expansion is essentially equivalent to the  $[0/6]^{10/3}$  one. Similarly, since the optimized  $p_0$  yielded by the  $[1/5]^{10/3}$  fit is more than three orders of magnitude smaller than the optimized  $p_1$ ,  $p_0 \ll p_1(v_D - v)$  for all relevant  $v$ . Consequently, this  $[1/5]^{10/3}$  fit effectively yields a  $[0/5]^{13/3}$  expansion. In contrast, the additional flexibility in the variable- $m$  fits associated with incrementing  $L$  or  $N$  by 1 generally produced a distinct fit, albeit at the cost sometimes of unreasonable  $m$  and  $v_D$  values.

Comparison of Figs. 1 and 2 shows that for the same number of variable parameters, variable- $m$  fits are similar in quality to fixed- $m$  ones, both achieving an overall rms error of  $0.015 \text{ cm}^{-1}$  with nine parameters. Fixing  $m$  does appear to reduce significantly the flexibility of the expansions, as is evidenced by the fact that no independent fits could be obtained for ten  $[L/N]^{10/3}$  cases in the range spanned by Fig. 2. This is perhaps to be expected, since the fact that  $m$  appears in the exponent in Eq. (1) means that it will have a dominant effect on the fitting process. However, it is also clear<sup>7,10,11</sup> that achieving reliable extrapolations beyond the highest observed level requires  $m$  to be fixed at its theoretically known

TABLE I. Parameters for the best five of the Fig. 1 and Fig. 2 fits to the 55  $^{79,79}\text{Br}_2$  experimental  $\Delta E$ 's. The  $\{q_i\}$ ,  $v_D$ , and  $m$  values are unitless while the  $\{p_i\}$  are in  $\text{cm}^{-1}$ .

Fit	[4/2] <sup>3,81</sup>	[2/4] <sup>3,59</sup>	[5/2] <sup>10/3</sup>	[3/4] <sup>10/3</sup>	[2/5] <sup>10/3</sup>
$p_0$	0.001 818 485 7	0.002 819 780 3	0.005 744 686 0	0.005 273 840 5	0.005 413 870 8
$p_1/p_0$	-6.245 955 7 $\times 10^{-2}$	-4.373 453 2 $\times 10^{-2}$	-4.256 277 9 $\times 10^{-2}$	-3.845 082 8 $\times 10^{-2}$	-4.652 990 3 $\times 10^{-2}$
$p_2/p_0$	1.594 916 0 $\times 10^{-3}$	7.660 450 5 $\times 10^{-4}$	4.577 359 9 $\times 10^{-5}$	5.548 027 6 $\times 10^{-4}$	9.087 705 6 $\times 10^{-4}$
$p_3/p_0$	-1.535 977 9 $\times 10^{-5}$		3.280 562 4 $\times 10^{-5}$	5.830 669 8 $\times 10^{-6}$	
$p_4/p_0$	5.475 455 4 $\times 10^{-8}$		-4.805 553 0 $\times 10^{-7}$		
$p_5/p_0$			2.132 201 8 $\times 10^{-9}$		
$q_1$	-4.714 000 7 $\times 10^{-2}$	-4.612 315 0 $\times 10^{-2}$	-5.357 272 6 $\times 10^{-2}$	-5.317 643 4 $\times 10^{-2}$	-5.899 699 5 $\times 10^{-2}$
$q_2$	8.196 828 2 $\times 10^{-4}$	1.186 043 3 $\times 10^{-3}$	1.012 408 6 $\times 10^{-3}$	1.567 229 4 $\times 10^{-3}$	1.830 468 4 $\times 10^{-3}$
$q_3$		-1.460 825 4 $\times 10^{-5}$		-2.119 286 2 $\times 10^{-5}$	-2.689 077 9 $\times 10^{-5}$
$q_4$		2.105 474 7 $\times 10^{-7}$		2.633 193 0 $\times 10^{-7}$	3.196 479 4 $\times 10^{-7}$
$q_5$					-7.782 805 7 $\times 10^{-10}$
$v_D$	60.424 201	60.171 223	59.570 753	59.720 208	59.687 760
$m$	3.807 559 8	3.590 199 9	10/3	10/3	10/3

limiting value. Moreover, finding appropriate search starting points is considerably more difficult for the variable- $m$  fits than the fixed- $m$  ones. Indeed, the computing cost for generating the results summarized in Fig. 1 was more than four times greater than that required for filling in Fig. 2 (including the asterisk entries). Thus, while variable- $m$  fits may give some insight into why certain independent fixed- $m$  fits cannot be obtained, they appear to offer few other advantages.

#### D. Best fits achieved and the question of fixing $p_0$

Table I lists the optimized parameters for the five best fits from Figs. 1 and 2; each has an overall rms error of only  $0.015 \text{ cm}^{-1}$ . The fact that the best fits are of neither the  $[L/N]$  or  $[0/N]$  types agrees with the observation of Refs. 4–6 that polynomial ratios often provide the most efficient types of expansion functions.

Using theoretical  $C_5$  values from the literature,<sup>14</sup> the same theory of limiting near-dissociation behavior which predicts  $m = 10/3$  for  $B$  state  $^{79,79}\text{Br}_2$  yields predicted  $p_0$  values ranging from  $0.0052$  to  $0.0059 \text{ cm}^{-1}$ ; the experimentalists' analysis of their highest observed levels yielded an empirical value of  $0.0062 \text{ cm}^{-1}$ .<sup>9</sup> It is significant that the  $m \equiv 10/3$  fits summarized in Table I all yielded  $p_0$  values in this range. Thus, fixing  $m$  at this value seems to decouple  $p_0$  from other parameters so that resulting fits yield realistic estimates of the long-range potential coefficient  $C_5$  and presumably this is also true of the extrapolation intercept  $v_D$ .

This agreement means that fits performed with  $p_0$  held fixed at its near-dissociation theoretical value would have yielded expansions almost identical to the best ones obtained here, with *one fewer* free parameter. This would have re-

duced the computational effort. Essentially the same result is obtained in the present example because of the existence of data for levels lying very close to dissociation. However, when such data are not available, even fixing  $m$  at its theoretically predicted value will not assure that fits would yield the correct limiting value of  $p_0$ . This would make the resulting expansion much less reliable for performing extrapolations beyond the last observed level than would an analogous expansion with  $p_0$  held fixed at a realistic theoretical value.<sup>7,15</sup> It seems clear that for high- $v$  extrapolations,  $p_0$  should be held fixed at the best available theoretical value, particularly in fits to data sets which do not include levels lying extremely close to dissociation.

#### E. Interpolation and extrapolation to low $v$

A not uncommon experimental situation is that one has a moderately complete set of measured  $E_v$ 's, but with some missing values at low and intermediate  $v$ . It is appropriate, therefore, to examine the reliability of expansions of the form of Eq. (1) for interpolating and extrapolating for such missing data. To this end, the energies of the 12  $^{79,79}\text{Br}_2$  levels  $v = 0, 1, 2, 12, 13, 15, 16, 24, 25, 26, 27$ , and 28 were dropped, and the five fits of Table I and the  $[9/0]^0$  Dunham expansion were repeated using this reduced data set. Note, however, that the energy differences across the gaps  $E_{14} - E_{11}$ ,  $E_{17} - E_{14}$ , and  $E_{29} - E_{23}$  were included in the input to these fits.

Table II summarizes the results of these interpolation and extrapolation tests. For each type of fit, it compares the root mean square errors in the predicted  $\Delta E(v + 1/2)$  values for certain sets of levels implied by fits to the full (FULL) or reduced (M12) data sets. The results in the  $v = 11$ –16 and

TABLE II. Effect on rms errors in  $\Delta E_{\text{calc}}(v + 1/2)$  of excluding 12  $E_v$ 's from the data set used in the best fits of Figs. 1 and 2. The rms errors, in  $\text{cm}^{-1}$ , are tabulated for  $v$  ranges shown in column 1. Columns labeled M12 are for fittings with 12 data missing.

Fit type	[4/2] <sup>3,81</sup>		[2/4] <sup>3,59</sup>		[5/2] <sup>10/3</sup>		[3/4] <sup>10/3</sup>		[2/5] <sup>10/3</sup>		[9/0] <sup>0</sup>	
	Full	M12	Full	M12	Full	M12	Full	M12	Full	M12	Full	M12
$v = 0$ –2	0.002	0.009	0.008	0.071	0.006	0.038	0.006	0.050	0.004	0.040	0.028	0.304
11–16	0.035	0.034	0.035	0.035	0.034	0.033	0.035	0.034	0.035	0.034	0.033	0.033
23–28	0.011	0.011	0.011	0.011	0.011	0.011	0.011	0.011	0.011	0.011	0.019	0.018
0–55	0.015	0.016	0.015	0.023	0.015	0.017	0.015	0.019	0.015	0.018	0.020	0.073

$v = 23$ – $28$  rows of this table clearly show that the Eq. (1) functions are able to perform very reliable interpolations and that they perform at least as well in this regard as a comparable Dunham expansion. The results in the first row also show that they perform reasonably well in extrapolating below the lowest-used level  $v = 3$ , down to  $v = 0$ , and that the Dunham expansion may be less reliable in this regard. As another test of the second point, Dunham polynomials and NDE functions were fitted to  $\text{Br}_2$  data sets which omitted the energies of levels  $v = 0$ – $9$ . The results showed that the errors in the predicted values of  $(E_{10} - E_0)$  were similar for fits of comparable quality.

One valid question that may be raised concerning Table II listings is “Does retention of the broad differences  $E_{14} - E_{11}$ ,  $E_{17} - E_{14}$  and  $E_{29} - E_{23}$  guarantee the reliable interpolation results (shown in Table II for  $v = 11$ – $16$  and  $23$ – $28$ ) from Eq. (1) expansions?” We checked this with the above listed 12 levels *and* the broad differences excluded as input data in what we call M15 fits. For  $[5/2]^{10/3}$ ,  $[3/4]^{10/3}$ , and  $[2/5]^{10/3}$  the  $v = 11$ – $16$  M15 rms errors are 0.034, 0.035, and 0.035  $\text{cm}^{-1}$ , respectively. Similarly, the M15 rms errors for  $v = 23$ – $28$  are each within 0.001  $\text{cm}^{-1}$  of the Table II M12 listings. Hence, the  $m = 10/3$  interpolations are equally reliable for M15 and M12. For M15 the  $v = 0$ – $2$  rms errors for  $m \equiv 10/3$  are 0.062, 0.008, and 0.009  $\text{cm}^{-1}$ . While individual low- $v$  extrapolation errors are changed, the range is the same as for M12. In comparison the M15 errors for the Dunham  $[9/0]^0$  are 0.259, 0.045, and 0.015  $\text{cm}^{-1}$  for  $v = 0$ – $2$ ,  $11$ – $16$ , and  $23$ – $28$ , respectively. Therefore, our conclusions on interpolation and low- $v$  extrapolation are unaffected by exclusion of the broad differences as input data.

In conclusion, it seems clear that Eq. (1) expansions are very reliable for interpolating and fairly reliable for extrapolating at low  $v$  to estimate missing data; they perform at least as well in this regard as the traditional Dunham expansions. Moreover, as was pointed out earlier, when  $m$  and (when no data exist for levels extremely close to dissociation)  $p_0$  are held fixed at their theoretical values, near-dissociation expansions also provide the most reliable procedure known for extrapolating above the highest observed levels.<sup>7,10,11</sup>

#### F. Mass-reduced quantum number predictions for $^{81,81}\text{Br}_2(B)$

Equations (5)–(8) allow expansions obtained for  $^{79,79}\text{Br}_2$  to be converted into expressions for  $^{81,81}\text{Br}_2$ ; this was done for the three  $m \equiv 10/3$  expansions of Table I. Table III compares the predictions of the directly converted functions

(first entry for each case) with those obtained by direct fitting to the  $^{81,81}\text{Br}_2$  data (second entry). The agreement with experiment (rms error) for the directly converted functions is only slightly worse than that yielded by the fits; the differences between the two are much smaller than the factor of 10 which appeared in comparisons of this type for the isotopes of ground state  $\text{H}_2$ .<sup>6</sup> This is not surprising because the mass-reduced quantum number method is based on the first-order JWKB quantization condition; it should produce more accurate results for heavier molecules. Note that the changes in  $v_D$  and in the binding energy of the highest observed level ( $D - E_{54}$ ) produced by fitting to the mass-81 data are quite small. These changes are similar in magnitude to variations associated with different  $[L/N]$  functions.

#### IV. DISCUSSION AND CONCLUSIONS

The present study agrees with our earlier work in demonstrating the suitability of product functional forms for representing diatomic vibrational<sup>4–7</sup> and rotational<sup>18</sup> properties. These forms, with theoretically justified near-equilibrium and near-dissociation behavior, have been applied here to vibrational level spacings of a state with an attractive  $C_5/R^5$  long-range potential. Results indicate that Eq. (1) representations can be used to:

(i) expose apparently erroneous experimental results through consistent discrepancy from experiment among a variety of functional form fittings;

(ii) represent level spacings from lowest to near-dissociation energies with an accuracy comparable to that of experimental spacings; and

(iii) interpolate missing levels very reliably and extrapolate to missing low- $v$  levels although with somewhat greater error than in interpolation.

For each of these tasks the present functional forms are no less and sometimes distinctly more efficient and reliable than traditional Dunham expansions. In addition one can:

(iv) use the composite forms, mass-reduced quantum numbers, and experimental level spacings of one isotope to predict vibrational spacings of another isotopic species in the same molecular state. Present results indicate that the predicted spacings can have an rms error close to experimental error for a heavy molecule like  $\text{Br}_2$ .

One significant conclusion of the present work is that NDE with the power  $m$  fixed at the theoretically predicted value, are as effective for representing experimental data as expansions with  $m$  free. Moreover, performing fits to the

TABLE III. Comparison of predictions for  $^{81,81}\text{Br}_2(B)$  of expansions obtained by isotopic conversion of  $^{79,79}\text{Br}_2(B)$  expansions from Table I (“converted”) with those obtained from least-square fits (“fitted”). For the mass-81 isotope,  $v = 54$  is the last observed level. Energies in  $\text{cm}^{-1}$ .

	$[5/2]^{10/3}$		$[3/4]^{10/3}$		$[2/5]^{10/3}$	
	Converted	Fitted	Converted	Fitted	Converted	Fitted
rms error in $\Delta E(v + \frac{1}{2})$	0.029	0.016	0.025	0.016	0.025	0.016
$D - E_{54}$	2.72	2.80	2.78	2.78	2.77	2.78
$v_D$	60.33	60.39	60.48	60.33	60.45	60.31

TABLE IV. Parameters yielded by fits of the three  $m = 10/3$  expansion functions of Tables I and II to the 56  $^{79,79}\text{Br}_2$  experimental energies. The  $\{q_i\}$  and  $v_D$  values are unitless while the  $\{p_i\}$ , the dissociation energy  $D$ , and the rms error are in  $\text{cm}^{-1}$ .

Fit	$[5/2]^{10/3}$	$[3/4]^{10/3}$	$[2/5]^{10/3}$
$p_0$	0.005 601 641 4	0.005 064 360 0	0.005 275 050 9
$p_1/p_0$	$-4.093\ 669\ 5 \times 10^{-2}$	$-3.726\ 508\ 6 \times 10^{-2}$	$-4.667\ 243\ 6 \times 10^{-2}$
$p_2/p_0$	$-5.272\ 056\ 7 \times 10^{-5}$	$5.257\ 965\ 1 \times 10^{-4}$	$9.319\ 983\ 5 \times 10^{-4}$
$p_3/p_0$	$3.627\ 068\ 5 \times 10^{-5}$	$6.862\ 071\ 6 \times 10^{-6}$	
$p_4/p_0$	$-5.245\ 617\ 2 \times 10^{-7}$		
$p_5/p_0$	$2.329\ 858\ 0 \times 10^{-9}$		
$q_1$	$-5.353\ 133\ 9 \times 10^{-2}$	$-5.395\ 476\ 5 \times 10^{-2}$	$-6.016\ 308\ 0 \times 10^{-2}$
$q_2$	$1.028\ 347\ 8 \times 10^{-3}$	$1.642\ 463\ 2 \times 10^{-3}$	$1.914\ 529\ 3 \times 10^{-3}$
$q_3$		$-2.269\ 178\ 8 \times 10^{-5}$	$-2.864\ 664\ 2 \times 10^{-5}$
$q_4$		$2.811\ 140\ 8 \times 10^{-7}$	$3.394\ 526\ 7 \times 10^{-7}$
$q_5$			$-8.596\ 304\ 7 \times 10^{-10}$
$v_D$	59.615 521	59.799 704	59.744 006
$D$	19 579.699	19 579.767	19 579.752
rms error	0.015	0.013	0.013

resulting expressions is computationally much easier and less expensive. These same conclusions also appear to apply to the possibility of holding the expansion constant  $p_0$  fixed at its theoretically predicted (in terms of the long-range potential constant  $C_n$ ) value. These two points are of particular importance when data are not available for levels lying near dissociation and one wishes to have an eigenvalue expression which can provide a "most realistic" extrapolation into this region.

One final point deserving comment here concerns the use of level spacings (rather than level energies themselves) as the dependent variable in the fits described above. As was pointed out in Sec. II, this is desirable from the viewpoint of consistency with the earlier papers in this series<sup>4-6</sup>; however, for the  $\text{Br}_2$  data considered herein level energy may be the better fitting variable. To test the effect of the choice of fitting variable on the conclusions of the present study, we have performed fits to the 56 experimental energies themselves using the three  $m = 10/3$  NDE functional forms considered in Tables I and II; the results obtained are summarized in Table IV. It is clear that the values of corresponding expansion parameters obtained from fits to the level energies (see Table IV) are very similar to those yielded by fits to the level spacings (see Table I). Indeed, corresponding parameters agree to within the (highly correlated) 95% confidence limit uncertainties yielded by the fits. (It is precision requirements that make it necessary to quote these parameters to the additional number of significant digits shown.) Moreover, the rms errors of the fits to the energies are if anything slightly smaller than those yielded by the fits to the level spacings. The fact that corresponding expansion functions from Tables I and IV are identical to within the uncertainties associated with interparameter correlation therefore clearly demonstrates that the above conclusions regarding the utility of the Eq. (1) functional form should be valid independent of whether level energies or level spacings are used as the dependent variable

in the fits. Moreover, although we expect the data used<sup>9</sup> to be superseded in the near future,<sup>19</sup> the expansions of Table IV may be taken as the current best overall functional representations of the vibrational level energies of  $B$  state  $\text{Br}_2$ .

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