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## Dependence of the Diatomic Rotational Constant $B_v$ on the Long-Range Internuclear Potential<sup>1</sup>

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A simple expression is derived which explicitly relates the rotational constant  $B_v$  for vibrational levels near the dissociation limit  $D$  of a diatomic molecule, to the nature of the long-range interatomic potential. Assuming a long-range potential of the form  $V(R) = D - C_n/R^n$ , the expression  $B_v = Q_n(v_D - v)^{4/(n-2)}$  is obtained, where  $v_D$  is the effective vibrational index at the dissociation limit, and  $Q_n$  is a constant depending only on  $n$ ,  $C_n$ , and the reduced mass. This result is slightly less accurate than an analogous recently developed relation for the vibrational level distribution near  $D$ . Its utility and accuracy are demonstrated by application to experimental data for the  $B^3\Pi_{0,u}^+$  states of  $\text{Cl}_2$ ,  $\text{Br}_2$ , and  $\text{I}_2$ .

On déduit une expression simple qui relie explicitement la constante de rotation  $B_v$  des niveaux de vibration situés près de la limite de dissociation  $D$  d'une molécule diatomique à la nature du potentiel inter-atomique de longue portée. En supposant que le potentiel à longue portée a la forme  $V(R) = D - C_n/R^n$ , on obtient l'expression  $B_v = Q_n(v_D - v)^{4/(n-2)}$ , où  $v_D$  est l'indice effectif de vibration à la limite de dissociation,  $Q_n$  est une constante qui ne dépend que de  $n$  et  $C_n$  est la masse réduite. Ce résultat est comparativement un peu moins précis qu'une relation analogue mise au point récemment pour la distribution des niveaux de vibration près de  $D$ . On démontre son utilité et sa précision en l'appliquant à des données expérimentales correspondant aux états  $B^3\Pi_{0,u}^+$  de  $\text{Cl}_2$ ,  $\text{Br}_2$  et  $\text{I}_2$ .

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### I. Introduction

Prediction of rotational constants  $B_v$  for highly excited vibrational levels for which experimental data are not available is a continuing problem in diatomic spectroscopy. This question assumes a wider significance in view of the current interest (Dickinson and Bernstein 1970; Baylis 1970; Mahan 1970; Mahan and Lapp 1969; Bernstein 1966) in the densities and total numbers of bound and quasibound levels of diatomics. The difficulty is that aside from the generally accepted assumption that  $B_v \rightarrow 0$  as the level energy  $E(v)$  approaches the dissociation limit  $D$ , there is no known "natural" form for

$B_v$  as a function of  $v$  or  $E(v)$ .<sup>3</sup> The determination of some such functionality is the object of this paper.

The nature of the distribution of the highest vibrational levels of diatomic molecules has been recently elucidated by Le Roy and Bernstein (1970*a*, *b*, 1971). They showed that for levels sufficiently near the dissociation limit that the potential at their outer turning points has the theoretically expected long-range form (*e.g.*, see Hirschfelder, Curtiss, and Bird 1954; Margenau and Kestener 1969):

$$[1] \quad V(R) = D - C_n/R^n$$

the level distribution is closely approximated by

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

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<sup>3</sup>Throughout, the rotationless vibrational eigenvalue  $E(v, J=0)$  will be written as  $E(v)$ .

where the constant

$$[3] \quad K_n = \frac{K'_n}{(\mu)^{1/2}(C_n)^{1/n}} = \left[ \frac{14.55487}{(\mu)^{1/2}(C_n)^{1/n}} \right] \left[ \frac{n\Gamma\left(1 + \frac{1}{n}\right)}{\Gamma\left(\frac{1}{2} + \frac{1}{n}\right)} \right]$$

$\mu$  is in [a.m.u.], and  $\Gamma(x)$  is the familiar gamma function (e.g., Abramowitz and Stegun 1964, Chap. 6). Equation 2 is often used in its integrated form (Le Roy and Bernstein 1970a, b, 1971),

$$[4] \quad E(v) = D - [(v_D - v)H_n]^{2n/(n-2)}, \quad n \neq 2$$

where  $H_n = [(n-2)/2n]K_n = H'_n/[(\mu)^{1/2}(C_n)^{1/n}]$ , and for  $n > 2$  the integration constant  $v_D$  is the effective vibrational index (in general noninteger) at the dissociation limit:  $E(v_D) = D$ .

The above results were based on the semiclassical WKB quantum condition for vibrational eigenvalues (e.g., Merzbacher 1961, Chap. 7), and on the theoretically known form of the long-range potential (Hirschfelder, Curtiss, and Bird 1954; Margenau and Kestner 1969). The latter is actually a sum of inverse-power terms, which may be locally approximated by [1] with some effective  $n$  corresponding to a weighted average of the powers of the contributing terms. As  $R$  increases, this local power  $n$  gradually decreases, and in the limit it approaches  $\tilde{n}$ , the power of the asymptotically dominant term. This  $\tilde{n}$  is theoretically known to be determined by the nature of the atoms to which the given molecular state dissociates, and a summary of the rules determining it is given elsewhere (see Le Roy and Bernstein 1970b, Appendix B).

Equations 2 to 4 show that the distribution of the highest vibrational levels depends explicitly on the nature of the long-range internuclear potential. In the following, analogous results are derived for the rotational constants  $B_v$ . These new expressions are examined and tested, and then used to predict as-yet-unobserved  $B_v$  values for the highest vibrational levels of  $B(^3\Pi_0^-)$  Cl<sub>2</sub>, Br<sub>2</sub>, and I<sub>2</sub>. Throughout, the units of length and energy are taken to be [Å] and [cm<sup>-1</sup>], respectively.

## II. Behavior of $B_v$ for Levels very near $D$

### A. Derivation

It is well known that the diatomic rotational constant  $B_v$  may be expressed in terms of the expectation value of  $R^{-2}$  for the given vibrational level (Herzberg 1950). Expressing this expectation value classically yields (Rydberg 1931)

$$[5] \quad B_v = \left( \frac{\hbar}{4\pi\mu c} \right) \frac{\int_{R_1(v)}^{R_2(v)} R^{-2} [E(v) - V(R)]^{-1/2} dR}{\int_{R_1(v)}^{R_2(v)} [E(v) - V(R)]^{-1/2} dR}$$

where  $R_1(v)$  and  $R_2(v)$  are the classical turning points of level  $v$ :

$$E(v) = V(R_1(v)) = V(R_2(v))$$

The integral in the denominator of [5] also appeared in the derivation of [2] (Le Roy and Bernstein 1970b), and the approach followed here precisely parallels the earlier work.

At this point it is appropriate to examine the nature of the integrands of the two integrals in [5]. These are shown in Fig. 1 for three levels of a chosen model LJ(12,6) potential.<sup>4</sup> The solid curves there ( $k=0$ ) are the integrands of the integral in the numerator of [5], and the dashed curves ( $k=2$ ) are the integrands from the denominator; the dot-dash curve is the approximate  $k=0$  integrand for  $v=20$ ,  $R^{-2}[E(v) - (1 - 2/R^6)]^{-1/2}$ , obtained when the repulsive part of the potential is omitted.<sup>4</sup> As was noted in the derivation of [2], the value of an integral of this type ( $k=0$  or 2) depends mainly on the nature of the integrand near the outer turning point, and this becomes increasingly true as

<sup>4</sup>This is the same 24-level Lennard-Jones (12,6) model potential used in the earlier work (Le Roy and Bernstein 1970b):  $V(R) = D_e[(R_e/R)^{12} - 2(R_e/R)^6]$ , with (Harrison and Bernstein 1963)  $B_z = 2\mu D_e R_e^2 / \hbar^2 = 10\,000$ , where  $D_e$  is the well depth and  $R_e$  the position of the potential minimum. Throughout the discussion of this model, energies are scaled relative to  $D_e$  and lengths with respect to  $R_e$ .

$E(v) \rightarrow D$ . Thus, it seems reasonable to replace  $V(R)$  in [5] by the long-range form [1] which is appropriate at the outer turning points. However, this approximation is not nearly so accurate for the  $k=0$  integral in the numerator of [5] as it is for  $k=2$ , the latter being the only integral appearing in the derivation of [2]; this point will bear further scrutiny later.

The remainder of the derivation proceeds by substituting [1] into [5] and replacing the variable of integration by  $y \equiv R_2(v)/R$ , yielding

$$[6] \quad B_v = \left( \frac{\hbar}{4\pi\mu c} \right) \left[ \frac{D - E(v)}{C_n} \right]^{2/n} \left\{ \int_1^{R_2/R_1} [y^n - 1]^{-1/2} dy / \int_1^{R_2/R_1} y^{-2} [y^n - 1]^{-1/2} dy \right\}$$

The final approximation of letting  $R_1(v) \rightarrow 0$  (i.e.,  $R_2(v)/R_1(v) \rightarrow \infty$ ) is relatively minor. In this limit the above integrals are well known (see Gradshteyn and Ryzhik 1965, Section 3.251), and [6] becomes (for  $n > 2$ )<sup>5,6</sup>

$$[7] \quad B_v = \left( \frac{\hbar}{4\pi\mu c} \right) \left[ \frac{\Gamma\left(1 + \frac{1}{n}\right)\Gamma\left(\frac{1}{2} - \frac{1}{n}\right)}{\Gamma\left(\frac{1}{2} + \frac{1}{n}\right)\Gamma\left(1 - \frac{1}{n}\right)} \right] \left[ \frac{D - E(v)}{C_n} \right]^{2/n} \\ = P_n [D - E(v)]^{2/n} = \{P'_n / \mu (C_n)^{2/n}\} [D - E(v)]^{2/n}$$

While [7] displays the desired dependence on the long-range potential, a better form of this result is obtained on substituting [4] into it and defining  $Q_n = P_n (H_n)^{4/(n-2)}$ :

$$[8] \quad B_v = Q_n [v_D - v]^{4/(n-2)} \\ = \{Q'_n / [(\mu)^{n/(n-2)} (C_n)^{2/(n-2)}]\} [v_D - v]^{4/(n-2)}$$

The constants  $Q'_n$ ,  $P'_n$ ,  $H'_n$ , and  $K'_n$  occurring in [8], [7], [4], and [2] are all just collections of numerical factors and depend only on  $n$ ; values of them are given in Table 1 for divers integer  $n$ . Equations 7 and 8 are clearly the desired analogs of [2] and [4].

TABLE 1. Numerical factors from eqs. 2, 4, 7, and 8 for divers  $n$

$n$	$K'_n$	$H'_n$	$P'_n$	$Q'_n$
1	16.4234	-8.21171	<sup>a</sup>	<sup>a</sup>
2	25.7978	0.0	<sup>a</sup>	<sup>a</sup>
3	34.5429	5.75715	54.8210	60225.244
4	43.0631	10.76578	36.8928	4275.947
5	51.4763	15.44290	30.6405	1178.333
6	59.8301	19.94336	27.4105	546.658
8	76.4406	28.66524	24.0754	225.498
10	92.9819	37.19274	22.3544	136.330

<sup>a</sup>See footnote 5.

<sup>5</sup>For  $n \leq 2$  the  $k=0$  integral in the numerator of [6] is infinite, and hence the present approach is not viable. In the remainder of this discussion it is implicitly assumed that  $n > 2$ .

<sup>6</sup>The result [7] was also independently obtained by M. S. Child (1971) (private communication).

### B. Accuracy and Utility of [7] and [8]

Examination of Fig. 1 shows that there is a relatively much smaller contribution to the  $k=0$  (solid curves) integrals from their integrands in the immediate neighborhood of  $R_2(v)$

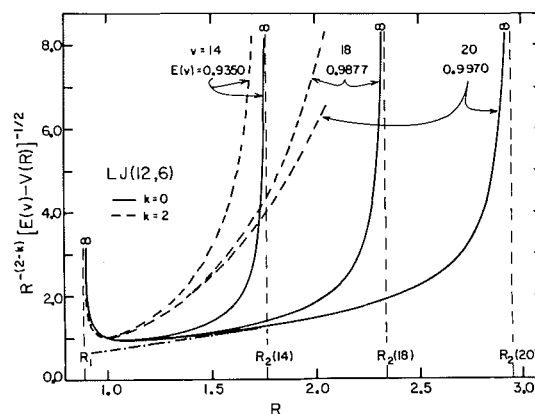


FIG. 1. Integrands of integrals in [5] for three levels of a model 24-level LJ(12,6) potential;<sup>4</sup>  $k=0$  corresponds to the integral in the numerator of [5] and  $k=2$  to that in the denominator. The dot-dash curve is the approximate  $k=0$ ,  $v=20$  integrand obtained on omitting the repulsive  $R^{-12}$  contribution to the model  $V(R)$ .

than is true for the  $k = 2$  case (dashed curves). Thus, the approximation of replacing the exact  $V(R)$  by [1] is worse for the  $k = 0$  integral in the numerator of [5] than for the  $k = 2$  integral which appeared in the derivation of [2] (and in the denominator of [5]). This means that the constant  $P_n$  is always a relatively poorer representation of the exact integral ratio in [5] than  $K_n$  is of the integral appearing in the derivation of [2]. As a result, parameter values  $n$ ,  $C_n$ ,  $D$ , and  $v_D$  obtained on fitting [7] and [8] to experimental data will be relatively less accurate than those obtained from application of [2]–[4]. On the other hand, for any real case in which experimental  $B_v$  values are available for levels near  $D$ , the energies  $E(v)$  will also be known. Hence, one need not rely on [7] and [8] to yield these parameters since they can be more accurately obtained from fits to [2]–[4]. As a result, the main role of [7]–[8] would appear to lie in qualitatively confirming the conclusions obtained from [2]–[4], and in extrapolating to estimate  $B_v$  values for levels for which they have not yet been observed. However, it turns out that this “weakness” of [7]–[8] is in fact a strength, facilitating the extraction of further information about long-range potentials from  $B_v$  data (see Section IV).

The final point considered here is the question of the direction of the error. The main approximation in the derivation of [7]–[8] was replacing the true  $V(R)$  in [5] by the approximate expression [1] which is appropriate only in the neighborhood of the outer turning points. Since the actual long-range potential is a sum of inverse-power terms of increasing power, the true  $V(R)$  drops below [1] as  $R$  decreases from  $R_2(v)$ , so that the approximate integrand is too large in this region. On the other hand, at  $R_1(v)$  the exact integrand has a singularity, while the approximate one is small and finite. As will be seen below, the former effect is much stronger than the latter, so that use of [1] yields an upper bound to the true values of the integrals in [5]. Since this effect is relatively much more pronounced for the  $k = 0$  than for the  $k = 2$  integrals, the constant  $P_n$  (i.e.,  $P'_n$ ) overestimates the true value of the integral ratio, and hence  $C_n$  values obtained from fitting [7–8] to experimental data will be too large. In Section III these qualitative conclusions are quantitatively exploited to yield bounds on unobserved  $B_v$  values for the levels closest to  $D$ .

### III. Application to $B(^3\Pi_{0u}^+)$ -State Halogens

#### A. General

As was pointed out above, it is better to utilize values of  $D$ ,  $n$ ,  $C_n$ , and  $v_D$  obtained using [2]–[4] than to try to extract them from experimental  $B_v$  values using [7] or [8]. The energies of the highest observed vibrational levels of  $B$ -state  $\text{Cl}_2$ ,  $\text{Br}_2$ , and  $\text{I}_2$  were previously treated in terms of [2]–[4] and found to display the theoretically expected asymptotic  $n = \tilde{n} = 5$  behavior (Le Roy and Bernstein 1970a, b, 1971). In the present treatment of the  $B_v$  values for these levels,  $n$  will be fixed at  $\tilde{n} = 5$  and the previously obtained values of  $D$ ,  $C_5$ , and  $v_D$  assumed.

Equations 7 and 8 suggest that plots of  $(B_v)^{\tilde{n}/2}$  vs.  $E(v)$ , and of  $(B_v)^{(\tilde{n}-2)/4}$  vs.  $v$  should be linear for levels near  $D$ , and have intercepts  $D$  and  $v_D$  respectively. However, the  $P_n$  inaccuracy discussed in the previous section will reflect itself in the  $C_{\tilde{n}}$  values obtained from the slopes of such plots, causing them to be upper bounds to the “true” value obtained from application of [2]–[4].<sup>7</sup> Examination of [7] and [8] also shows that  $C_{\tilde{n}}[7]$  (i.e., the  $C_{\tilde{n}}$  value obtained from the slope of the plot suggested by [7]) varies as  $(P_{\tilde{n}})^{[\tilde{n}/2]}$ , while  $C_{\tilde{n}}[8]$  depends on  $(P_{\tilde{n}})^{[(\tilde{n}-2)/2]}$ , implying that  $C_{\tilde{n}}[7] > C_{\tilde{n}}[8] > C_{\tilde{n}}[\text{true}]$ , as is observed. An important result of the above conclusions is that  $B_v$  values predicted with [8] using the empirical constant  $Q_{\tilde{n}} = B_v/(v_D - v)^{4/(\tilde{n}-2)}$  obtained from an experimental  $B_v$  will be lower bounds to the true values for  $v > v'$ . Concomitant upper bounds in this extrapolation region are obtained on utilizing a  $Q_{\tilde{n}}$  calculated from the “true”  $C_{\tilde{n}}$  (obtained by application of [2]–[4]).<sup>7</sup> It should also be noted that  $B_v$  values calculated from the empirical  $Q_{\tilde{n}}$  value mentioned above are upper bounds to the true values for  $v < v'$ .

<sup>7</sup>It is implicitly assumed here that  $C_5$  values obtained on applying [2]–[4] to experimental data (Le Roy and Bernstein 1970, 1971) are more accurate than the *ab initio* theoretical  $C_5$ 's calculated for these species (see Table 2).<sup>8</sup> The basis for this conclusion will be discussed elsewhere (R. J. Le Roy, to be published).

<sup>8</sup>The derivation of theoretical  $C_5$  coefficients was first presented by Knipp (1938) and later expanded upon by Chang (1967), and its application to the present case is summarized in footnotes 41 and 46 of Le Roy and Bernstein (1970b). The values given here differ from those reported earlier because they were calculated using the improved relativistic Hartree–Fock–Slater expectation values of Lu *et al.* (1971).

TABLE 2. Estimates of  $C_5$  values for  $B$ -state halogens

Species	$10^{-5} \times C_5 \text{ cm}^{-1} \text{ \AA}^5$			
	From [7] <sup>a</sup>	From [8] <sup>a</sup>	From [2-4] <sup>b</sup>	Theoretical <sup>c</sup>
Cl <sub>2</sub>	2.67	1.99	1.29 ( $\pm 0.2$ )	1.2 <sub>3</sub>
Br <sub>2</sub>	4.31	3.03	1.79 ( $\pm 0.2$ )	2.0 <sub>1</sub>
I <sub>2</sub>	13.6	7.53	3.11 ( $\pm 0.2$ )	3.6 <sub>7</sub>

<sup>a</sup>Obtained on substituting the known  $v_D$  and the experimental  $B_v$  value for the highest level for which it is observed into this equation.

<sup>b</sup>See Le Roy and Bernstein (1971).

<sup>c</sup>See footnotes 7-8.

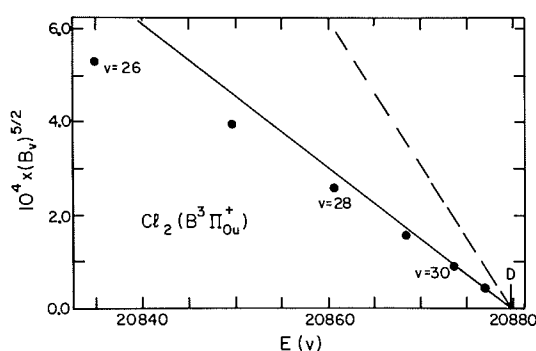


FIG. 2. Plot suggested by [7] for the  $B_v$  values of the highest observed vibrational levels of  $\text{Cl}_2(B^3\Pi_{0u}^+)$ .

### B. Chlorine

Experimental  $B_v$  values for  $B$ -state  $^{35,35}\text{Cl}_2$  have been reported by Douglas, Møller, and Stoicheff (1963) up to the highest observed level,  $v = 31$ . Figures 2 and 3 show the plots of these data suggested by [7] and [8]; the dashed lines on these figures are the limiting slopes predicted using the known  $C_5$  value. The differences between the slopes of the solid and dashed lines in Figs. 2 and 3 are thus a measure of the reduced accuracy of [7]-[8] relative to that of [2]-[4], and is reflected in the errors in the apparent  $C_5$  values obtained from the solid line slopes. These are compared in Table 2 to the experimental  $C_5$  value previously obtained using [2]-[4] (Le Roy and Bernstein 1970a, b, 1971), and to an *ab initio* theoretical  $C_5$ ,<sup>8</sup> analogous results for the other species discussed below are also given there. It is interesting to note that, as was suggested above,  $C_5$ [7] is always significantly more in error than is  $C_5$ [8]. Clearly the intercepts and slopes of Figs. 2 and 3 do qualitatively confirm the results obtained earlier from [2]-[4].

As suggested above, the solid line in Fig. 3

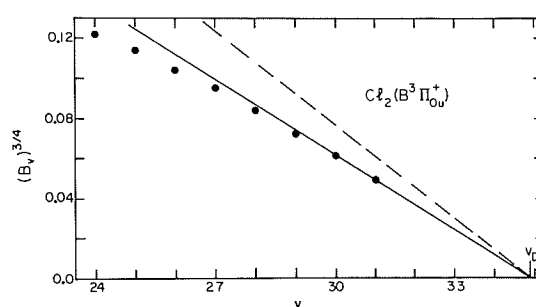


FIG. 3. Plot suggested by [8] for the  $B_v$  values of the highest observed vibrational levels of  $\text{Cl}_2(B^3\Pi_{0u}^+)$ .

TABLE 3. Lower bounds to unobserved  $B_v$  values for highest levels of  $^{35,35}\text{Cl}_2(B^3\Pi_{0u}^+)$ ; the corresponding upper bounds are given in parentheses

$v$	32	33	34
$B_v$	0.012 (0.016)	0.0069 (0.0092)	0.0025 (0.0034)

represents a lower bound and the dashed line an upper bound to the actual  $B_v$  values in the extrapolation region. Furthermore, it is clear that the former will probably lie relatively closer to the true values, except for levels very near  $D$  where the difference between these bounds is relatively small. In view of this, the present best estimates of these unobserved  $B_v$  values will be taken to be the lower bounds. They are presented in Table 3, with the concomitant upper bounds being given in parentheses.

### C. Bromine

The only  $B_v$  values measured for levels near the dissociation limit of  $\text{Br}_2(B^3\Pi_{0u}^+)$  are those which Horsley and Barrow (1967) reported for levels 50-53 of each of the pure isotopic forms

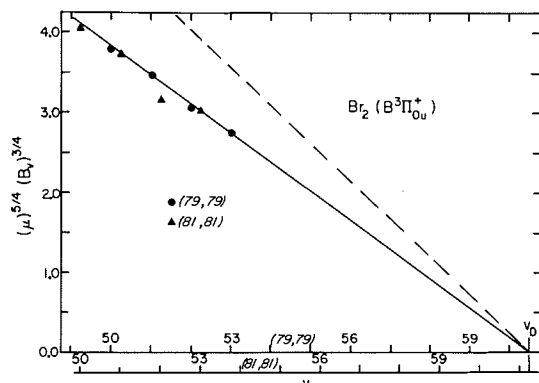


FIG. 4. As in Fig. 3 for the two isotopes (79,79) and (81,81) of  $\text{Br}_2(B^3\Pi_{0u}^+)$ .

(79,79) and (81,81).<sup>9</sup> Consideration of [8] shows that the data for these two species may be treated concurrently if the observed  $B_v$  values are multiplied by the appropriate power of the reduced mass  $\mu$ , and the abscissa axes shifted till the known intercepts  $v_D$  coincide. Figure 4 shows the combined plot thus suggested by [8]; as in the analogous plot for  $\text{Cl}_2$ , the dashed line is the theoretical limiting slope corresponding to the  $C_5$  value obtained from fits to [2]–[4]. The  $C_5$  value corresponding to the solid line on Fig. 4 is given in Table 2 together with the corresponding poorer estimate obtained from [7]. The apparent inconsistency of the (81,81)  $B_v$  value for  $v = 79$ , shown in Fig. 4, lies within the experimental uncertainty.

Predicted  $B_v$  values for as-yet-unobserved levels of  $\text{Br}_2$  are given in Table 4 for all three isotopic species (79,79), (79,81), and (81,81). As with  $\text{Cl}_2$ , the values given are the lower bounds corresponding to the solid line in Fig. 4, while the upper bounds calculated using the true  $C_5$  are given in parentheses.

#### D. Iodine

Upon analyzing the reported energies (Brown 1931) of the highest observed vibrational levels of  $^{127,127}\text{I}_2(B^3\Pi_{0u}^+)$ , Le Roy and Bernstein (1971) concluded that levels above  $v \approx 55$  were accurately described by [4] with  $n$  equal to its known asymptotic value  $\tilde{n} = 5$ . Unfortunately, most of the experimental results in this region

<sup>9</sup>The original analysis identified these levels as  $v = 49$ –52 respectively (Horsley and Barrow 1967), but it has since been shown that this numbering must be increased by one (Le Roy and Bernstein 1971; Coxon 1971).

TABLE 4. Lower bounds to unobserved  $B_v$  values for highest levels of isotopic  $\text{Br}_2(B^3\Pi_{0u}^+)$ ; the corresponding upper bounds are given in parentheses

$v$	$B_v(79,79)$	$B_v(79,81)$	$B_v(81,81)$
54	0.0069 (0.0099)	0.0073 (0.0104)	0.0077 (0.0110)
55	0.0056 (0.0079)	0.0060 (0.0085)	0.0063 (0.0090)
56	0.0043 (0.0060)	0.0046 (0.0066)	0.0050 (0.0072)
57	0.0030 (0.0043)	0.0034 (0.0049)	0.0038 (0.0054)
58	0.0019 (0.0028)	0.0023 (0.0033)	0.0027 (0.0038)
59	0.00099 (0.00141)	0.0013 (0.0019)	0.0016 (0.0023)
60	0.00023 (0.00033)	0.00048 (0.00068)	0.00076 (0.00108)
61	—	—	0.00010 (0.00014)

are band-head data which yield vibrational energies, but no estimates of the corresponding  $B_v$  values. Although level energies up to  $v = 72$  have long been known (Brown 1931), the only experimental  $B_v$  values above  $v = 30$  are those reported by Steinfeld, Campbell, and Weiss (1969) for  $v = 43$  and 57,<sup>10</sup> and a value for  $v = 62$  obtained from fluorescence measurements of Halldorsson and Menke (1970). Furthermore, it has recently been concluded<sup>11</sup> that rotational assignments in the bands measured by Steinfeld *et al.* (1969) may need to be changed, which means that their  $B_v$  values for  $v = 43$  and 57 may be somewhat in error. As a result, the present analysis will utilize only a  $B_v$  value for  $v = 62$  obtained from the fluorescence measurements.

Halldorsson and Menke (1970) observed  $B$ - $X$  state emission doublets in  $\text{I}_2$  excited by a coincidence between the 5017 Å argon laser line and the  $R(26)$  transition from the  $v'' = 0$  level of the ground state to a highly excited vibrational level of the  $B$  state. Adding the ground state  $J'' = 26$  rotational energy to the laser frequency shows that the emitting  $J = 27$  level lies 19952.3  $\text{cm}^{-1}$  above the  $v'' = 0, J'' = 0$  level of the ground state. Comparing this with the smoothed ( $J = 0$ )  $B$ -state vibrational energies (Le Roy and

<sup>10</sup>The band which these authors identified as 49–1 has since been vibrationally reassigned as 57–2 (Le Roy 1970).

<sup>11</sup>D. G. Brown, R. J. Le Roy, and G. Burns, to be published.

Bernstein 1971) shows that its vibrational quantum number must be  $v = 62$ , and that  $B_{62} = 0.0107 (\pm 0.0005) \text{ cm}^{-1}$ . Substituting this and the known  $v_D = 87.7$  into [8] yields the apparent  $C_5$  value in column 3 of Table 2, and a lower bound expression for  $B_v$  values for levels  $v > 62$ :

$$[9] \quad B_v(\text{lower}) = 1.41 \times 10^{-4} (87.7 - v)^{4/3}$$

Similarly, substituting the experimental  $C_5 = 3.11 \times 10^5 \text{ cm}^{-1} \text{ \AA}^5$  into [8] yields an equation for upper bounds to these quantities:

$$[10] \quad B_v(\text{upper}) = 2.54 \times 10^{-4} (87.7 - v)^{4/3}$$

Of course [9] also yields lesser upper-bound estimates of  $B_v$  values for  $v < 62$ .

#### IV. Discussion

Expressions have been derived here which quantitatively relate the rotational constant  $B_v$  for vibrational levels near  $D$  to the nature of the long-range internuclear potential. It was seen that these eqs. 7–8 are relatively less accurate than analogous relations [2]–[4] derived previously (Le Roy and Bernstein 1970*b*) for the vibrational level distribution near  $D$  (e.g., compare columns 2 and 3 in Table 2 to column 4). This is because the integral in the numerator of [5] is relatively more sensitive to the nature of the integrand at  $R < R_2(v)$  than was true for the corresponding integral appearing in the derivation of [2]–[4]. As a result, only upper and lower bounds could be given, rather than accurate predicted values for unobserved  $B_v$ 's for levels near  $D$ . On the other hand, the relatively higher sensitivity of  $B_v$ 's to contributions to  $V(R)$  other than the limiting asymptotic  $R^{-\bar{n}}$  term, suggests that they may be more readily used to obtain quantitative information about the higher-power terms. This fact will be exploited elsewhere in

expansions of [2]–[4] and [7]–[8] to take account of additional terms in the general expression for the long-range potential (R. J. Le Roy, unpublished).

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