

## Long-Range Potential Coefficients From RKR Turning Points: $C_6$ and $C_8$ for $B(^3\Pi_{ou}^+)$ -State $Cl_2$ , $Br_2$ , and $I_2$ <sup>1</sup>

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Methods of analyzing long-range RKR turning points to determine inverse-power potential coefficients have always required an implicit assumption about the relative magnitudes of higher-power coefficients. However, its effect on the derived constants has never been examined. A generalization of a method of Goscinski is introduced in which this assumption is explicitly introduced as the parameter  $\alpha$ . Application of the new procedure to  $B$ -state  $Cl_2$ ,  $Br_2$ , and  $I_2$  yields improved estimates of their  $C_6$  and  $C_8$  constants, but shows that such results may be strongly dependent on the assumed value of  $\alpha$ . A search for an *a priori* estimate of  $\alpha$  uncovered the intriguing *empirical* relationship  $(C_{10}/C_8)/(C_8/C_6) \approx 4/3$  between the theoretically known potential constants for a certain class of molecular states. However, its origin is not yet understood.

Les méthodes d'analyse des points tournants RKR, pour la détermination des coefficients dans les expressions du potentiel en termes de puissances de l'inverse de la distance, ont toujours nécessité une supposition implicite à propos des valeurs relatives des coefficients d'ordres plus élevés. Cependant, l'influence de cette supposition sur la valeur des constantes déduites n'a jamais été étudiée. La généralisation d'une méthode de Goscinski par laquelle cette supposition est explicitement introduite sous la forme d'un paramètre  $\alpha$ , est présentée. L'application de ce nouveau procédé au  $Cl_2$ , au  $Br_2$  et au  $I_2$  dans l'état  $B$  permet d'obtenir une estimation des constantes  $C_6$  et  $C_8$ , mais indique aussi que de tels résultats peuvent être fortement influencés par la valeur assignée à  $\alpha$ . La recherche d'une estimation *a priori* de la valeur d' $\alpha$  a permis de formuler la relation empirique:  $(C_{10}/C_8)/(C_8/C_6) \approx 4/3$  entre les constantes connues théoriquement pour une certaine classe d'états moléculaires. Toutefois, l'origine de cette relation demeure encore inconnue. [Traduit par le journal]

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### I. Introduction

It has long been known (see Margenau (1939) or Hirschfelder, Curtiss, and Bird (1964)) that if two atoms are sufficiently far apart their electron clouds overlap negligibly and their interaction potential may be expressed (ignoring electronic degeneracy and fine-structure effects) as a sum of inverse-power terms:

$$[1] \quad V(R) = D - \sum_{m \geq \bar{n}} C_m/R^m$$

where  $D$  is the dissociation limit and the powers  $m$  have positive integer values. The nature of the electronic states of the atoms produced by the dissociation of a given diatomic species determines which powers contribute to its [1], and Le Roy (1973) has presented a convenient summary of the rules governing this behavior. Furthermore, expressions for the coefficients  $C_m$  are readily obtained from perturbation theory, and considerable theoretical effort has been directed towards the development of practical techniques

by which they may be calculated (see Dalgarno and Davison (1966), Dalgarno (1967), Hirschfelder and Meath (1967), Margenau and Kestner (1971), and Certain and Bruch (1972)).

Within the past decade, reasonably reliable *experimental* values of the  $C_m$  constants of [1] have also begun to become available (see Bernstein and Muckerman (1967), Bernstein and LaBudde (1973), and Le Roy (1973)). Unfortunately, while the real intermolecular potential depends on a *sum* of inverse-power terms, the analysis of experimental data has usually involved the use of an effective single term potential:

$$V(R) \approx D - C_n/R^n$$

for the whole of the "long-range region". If the observable under consideration depends only on the asymptotic potential tail, then a reliable value of the coefficient  $C_{\bar{n}}$  of the leading term in [1] may be obtained. However, the traditional techniques of molecular beam scattering and the analysis of bulk properties of gases have not as yet been able to yield the coefficients of any but this leading term. Indeed, in recent years the

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tendency in analyzing such data has been to assume the accuracy of theoretical  $C_m$  constants, and then to utilize the predicted long-range tail as a constraint in the analysis of the measurements (see Barker and Pompe (1968), Parson, Siska, and Lee (1972), or Farrar and Lee (1972)).

The RKR method of determining diatomic potential energy curves by numerical inversion of spectroscopic level energies and  $B_v$  values has by now been routinely applied to many species (see Mason and Monchick (1967), Le Roy (1973), and Albritton, Schmeltekopf, and Zare (1974)). However, such results have seen surprisingly little use as a means of determining long-range potentials. This seems particularly strange in view of their point-by-point form, which is ideally suited to an analysis based on [1]. The present paper attempts to provide better means of exploiting results of this type.

The first really proper analysis of long-range RKR turning points was that which Stwalley (1970) applied to ground state  $Mg_2$ . One of the innovative features of this work was the fact that he paused to examine the question of whether or not [1] was actually valid for the region under consideration. This question will be examined in detail in Sect. II.A below.

Stwalley (1970) and Cummings (1972) have both presented simple graphical methods of analyzing turning points to obtain values of the first two unknown constants on the right-hand side of [1]. The former considered cases where the leading coefficient  $C_{\bar{n}}$  is known, and introduced a linear plot which yields values of  $D$  and of the second  $C_m$  constant. The latter was concerned with situations in which both  $D$  and  $C_{\bar{n}}$  are known, and his plots yield values of the next two  $C_m$  constants. However, both these techniques and all earlier attempts to obtain potential constants from RKR turning points (see the review of Le Roy, (1973)) assumed that all inverse-power coefficients, other than those explicitly considered, were precisely zero.

Recently, Goscinski (1972) has proposed an interesting new type of expression for use in analyzing long-range turning points. While it explicitly considers only the two leading unknown  $C_m$  constants, his expression implicitly takes account of additional contributions to the interaction potential. The present paper generalizes his approach by making the strength of these implicit higher-order potential terms a variable parameter. Applications to  $B$ -state  $Cl_2$ ,

$Br_2$ , and  $I_2$  show that RKR turning point analyses are very sensitive to the assumed value of this parameter, and hence emphasize the need for some *ab initio* theoretical knowledge of it.

## II. Methods of Analyzing Turning Points

### A. Theoretical Constraints

As was pointed out by Stwalley (1970), any use of [1] should be preceded by a determination of whether or not this expression provides a valid representation of the intermolecular potential at the distances under consideration. Each of the terms in [1] arises from a particular type of atomic interaction, and can in principle be calculated by perturbation theory at all distances. However, while the individual interaction energies asymptotically take on the familiar inverse-power forms of [1], at shorter distances the latter grossly exaggerate the magnitudes of their contributions to the potential.

For a number of hydrogen and helium systems, Kreek and Meath (1969), Singh, Kreek, and Meath (1970), Kreek, Pan, and Meath (1970), and Pan and Meath (1971) examined the effect of this inverse-power approximation on the second-order interaction energies which give rise to the  $m = 6, 8, 10, \dots$  etc. terms in [1]. Among other things, they found that the term  $C_{m+2}/R^{m+2}$  no longer accurately represents the appropriate interaction energy at distances

$$[2] \quad R \lesssim (2C_{m+2}/C_m)^{1/2}$$

In other words, if it is half as large as the previous term arising in the same (second) order of perturbation theory, the inverse-power representation of the ' $m + 2$ ' term is unrealistically large. In practice, this means that in a region where the third ( $m = 10$ ) second-order perturbation term makes a reasonably large contribution to the potential, it cannot be adequately represented by the asymptotic  $C_{10}/R^{10}$  form. This in turn implies that it would not be wise to attempt to obtain reliable values of  $C_{10}$  or higher-power coefficients from an analysis of RKR turning points. However, it does *not* mean that their effect on the potential may necessarily be ignored.

In view of the above, the methods considered here do not explicitly involve the coefficients of terms with powers higher than  $m = 8$ . On the other hand, some of them do implicitly take account of higher-power terms, and on expansion give rise to an  $R^{-10}$  term whose coefficient is a function of the  $C_6$  and  $C_8$ . Therefore, it

TABLE 1. Ratios of theoretical potential constants for diverse inert gas and H<sub>2</sub> states<sup>a</sup>

Species	$\frac{C_{10}/C_8}{C_8/C_6}$	Species	$\frac{C_{10}/C_8}{C_8/C_6}$
Kr <sub>2</sub> (X <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> ): <sup>1</sup> S <sub>0</sub> + <sup>1</sup> S <sub>0</sub>	1.34	H <sub>2</sub> ( <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> , <sup>3</sup> Σ <sub>u</sub> <sup>+</sup> ):1s + 2p	0.659
Ar <sub>2</sub> (X <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> ): <sup>1</sup> S <sub>0</sub> + <sup>1</sup> S <sub>0</sub>	1.31	H <sub>2</sub> ( <sup>1</sup> Σ <sub>u</sub> <sup>+</sup> , <sup>3</sup> Σ <sub>g</sub> <sup>+</sup> ):1s + 2p	0.854
Ne <sub>2</sub> (X <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> ): <sup>1</sup> S <sub>0</sub> + <sup>1</sup> S <sub>0</sub>	1.40	H <sub>2</sub> ( <sup>1</sup> Π <sub>g</sub> , <sup>3</sup> Π <sub>u</sub> ):1s + 2p	4.048
He <sub>2</sub> (X <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> ): <sup>1</sup> S <sub>0</sub> + <sup>1</sup> S <sub>0</sub>	1.35	H <sub>2</sub> ( <sup>1</sup> Π <sub>u</sub> , <sup>3</sup> Π <sub>g</sub> ):1s + 2p	2.974
HeH(X <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> ): <sup>1</sup> S <sub>0</sub> + <sup>2</sup> S <sub>1/2</sub>	1.38		
H <sub>2</sub> (X <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> ):1s + 1s	1.380		
H <sub>2</sub> ( <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> , <sup>3</sup> Σ <sub>u</sub> <sup>+</sup> ):1s + 2s	1.339		
H <sub>2</sub> ( <sup>1</sup> Σ <sub>u</sub> <sup>+</sup> , <sup>3</sup> Σ <sub>g</sub> <sup>+</sup> ):1s + 2s	1.244		
Average	1.34 (±0.06)		

<sup>a</sup>Inert gas values from Starkschall and Gordon (1972), ground state H<sub>2</sub> from Hirschfelder and Meath (1967), other H<sub>2</sub> states from Bukta and Meath (1973), and HeH value from Kreek *et al.* (1970).

seems desirable to examine the *ab initio* C<sub>6</sub>, C<sub>8</sub>, and C<sub>10</sub> constants which are presently known to see if any inherent relationships are apparent. Table 1 presents values of the dimensionless ratio (C<sub>10</sub>/C<sub>8</sub>)/(C<sub>8</sub>/C<sub>6</sub>) for the ground-state diatomic inert gases, and for the ground and a number of excited states of H<sub>2</sub>. The results in the first column are for states correlating with two S-state atoms. The agreement seen there appears too good to be accidental, and hence suggests the empirical conclusion that

$$[3] \quad C_{10} \approx (4/3)(C_8)^2/C_6$$

for molecular states arising from pairs of S-state atoms. However, for other cases no simple correlation appears evident.

The breakdown at small distances of the inverse-power form of the long-range interaction potential is caused by the increasing overlap of the electron clouds on the two atoms. Thus, it seems reasonable to correlate this breakdown with some measure of the atomic radii. In this regard, a study of the results of Meath and co-workers previously (Le Roy 1973) led to the conclusion that for an interaction between atoms A and B, [1] should not be used at distances smaller than

$$[4] \quad R_b(AB) = 2[\langle r_A^2 \rangle^{1/2} + \langle r_B^2 \rangle^{1/2}]$$

Here,  $\langle r_X^2 \rangle$  is the expectation value of the square of the radius of the outermost electrons on atom X; these expectation values are known for all orbitals of all ground-state atoms (Lu *et al.* 1971; Froese Fischer 1968, 1972). This requirement is used throughout the present work.

### B. Compact Representations for Long-Range Turning Points

In the following, it is always assumed that an accurate value of the dissociation limit *D* is known. In practice this requirement is not very restrictive, since the existence of sufficient data to yield reliable turning points in the long-range region usually means that an accurate *D* is readily obtainable.<sup>2</sup>

At the outer RKR turning point *R<sub>v</sub>* of level *v*, its energy  $G(v) = V(R_v)$ , and hence [1] yields

$$[5] \quad D - G(v) = C_{m1}/(R_v)^{m1} + C_{m2}/(R_v)^{m2} + C_{m3}/(R_v)^{m3} + \dots$$

For the sake of simplicity, the present discussion will assume that all of the coefficients *C<sub>m</sub>* on the right-hand side of [5] are unknown. While not true for the examples considered in Sect. III, the appropriate generalizations are very straightforward, though the equations do become somewhat more cluttered.

In accord with our first theoretical constraint, only the first two unknown coefficients *C<sub>m1</sub>* and *C<sub>m2</sub>* are explicitly considered. Stwalley (1970) and Cummings (1972) satisfied this requirement by assuming that all higher-power coefficients were identically zero. In another approach, Goscinski (1972) introduced a "geometric or Padé approximant" representation for the right-hand side of [5]:

<sup>2</sup>Exceptions to this rule would mostly occur for weakly bound van der Waals molecules such as the X<sup>1</sup>Σ<sub>g</sub><sup>+</sup> state of Mg<sub>2</sub> (Stwalley 1970).

$$[6] \quad D - G(v) = \frac{C_{m1}/(R_v)^{m1}}{\{1 - C_{m2}/[C_{m1}(R_v)^{m2-m1}]\}}$$

The versatile generalized version of his expression which provides the framework for the present discussion is:

$$[7] \quad D - G(v) = \frac{C_{m1}/(R_v)^{m1}}{\{1 - \alpha C_{m2}/[C_{m1}(R_v)^{m2-m1}]\}^{1/\alpha}}$$

For  $\alpha = -1$ , [7] becomes the simple two-term version of [5] used by Stwalley and Cummings; similarly, when  $\alpha = +1$  it becomes Goscinski's expression. Less obviously, when  $\alpha = 0$  [7] corresponds to the exponential potential form introduced by Davis (1972):

$$[8] \quad D - G(v) = [C_{m1}/(R_v)^{m1}] \times \exp \{C_{m2}/[C_{m1}(R_v)^{m2-m1}]\}$$

The most convenient property of [7] (and of [6] and [8]) is (i) the fact that a binomial expansion of the right-hand side yields:

$$[9] \quad D - G(v) = C_{m1}/(R_v)^{m1} + C_{m2}/(R_v)^{m2} + \frac{1}{2}(1+\alpha)(C_{m2})^2/C_{m1}/(R_v)^{m2+m2-m1} + \dots$$

where the first two terms are independent of  $\alpha$  and identical to the leading terms in [5]. Thus, while explicitly depending on only  $C_{m1}$  and  $C_{m2}$ , [7] implicitly takes account of contributions from higher-power terms. Two additional noteworthy features of [9] are that: (ii) The powers of the successive implicit terms increase in steps of  $m2-m1$ ; and (iii) these subsequent terms are all of the same sign if  $C_{m2}/C_{m1}$  is positive, or are of alternating sign if this ratio is negative. Property (ii) makes the use of [7] particularly appropriate when the leading terms in [5] are the second-order perturbation energies corresponding to  $m = 6, 8$ , and  $10$  for neutral atoms (in addition to an  $m = 4$  term if one of them is charged). Furthermore, for species formed from ground-state atoms, all of these second-order terms are necessarily attractive (*i.e.* their  $C_m$ 's are all positive), a fact which correlates well with property (iii).

A prominent feature of expressions such as [7]–[9] is that their use requires the selection of a value for  $\alpha$ , which in turn corresponds to an explicit assumption about the higher-power ( $m > m2$ ) coefficients in [5]. In particular, it

assumes that  $m3 = m2 + m2 - m1$ , and that

$$C_{m3} = \frac{1}{2}(1+\alpha)(C_{m2})^2/C_{m1}$$

or in the notation of Table 1,

$$[10] \quad (C_{m3}/C_{m2})/(C_{m2}/C_{m1}) = \frac{1}{2}(1+\alpha)$$

Thus, the procedures of Cummings (1972) and Goscinski (1972) implicitly assume that the ratio in [10] is equal to 0 and 1 respectively. If we again consider the second-order interaction between neutral atoms (with  $m1, m2$ , and  $m3$  equal to 6, 8, and 10 respectively), [3] clearly implies that one should choose  $\alpha = 5/3$  when analyzing the potential curve of a species formed from two *S*-state atoms.

It is clear that the present approach becomes somewhat less than ideal if the true value of  $m3$  in [5] is not in fact equal to  $(m2 + m2 - m1)$ . This can occur when both first- and second-order interaction energies contribute to the potential<sup>3</sup>. However, as long as the implicit  $R^{-(m2+m2-m1)}$  coefficient has the right sign, a reasonable choice of  $\alpha$  would yield an approximate representation of the actual  $R^{-m3}$  term. Of course, in any case for which the leading  $m > m2$  term implicit in [7] has the wrong sign, one should force it to be zero by choosing  $\alpha = -1$ .

A set of RKR turning points could clearly be analyzed by performing nonlinear least-squares fits to [7] and [8]. However, it seems preferable to imitate Stwalley (1970), Cummings (1972), and Goscinski (1972) by providing a linear graphical procedure. To this end, [7] may be rearranged to yield:

$$[11] \quad \{(R_v)^{m1}[D - G(v)]\}^{-\alpha} = (C_{m1})^{-\alpha} - [\alpha C_{m2}/(C_{m1})^{(1+\alpha)}]/(R_v)^{(m2-m1)}$$

A plot of the left-hand side of [11] vs.  $1/(R_v)^{(m2-m1)}$  should clearly be linear with intercept  $(C_{m1})^{-\alpha}$  and slope  $-\alpha C_{m2}/(C_{m1})^{(1+\alpha)}$ . The analogous expression appropriate to the limit  $\alpha = 0$  is obtained from [8]:

$$[12] \quad \log \{(R_v)^{m1}[D - G(v)]\} = \log (C_{m1}) + (C_{m2}/C_{m1})/(R_v)^{(m2-m1)}$$

<sup>3</sup>Another possibility is when there is a nonzero  $R^{-9}$  third-order contribution to the energy. However, this term can only arise in resonant interactions between like atoms in different states, and even there it appears to be relatively much weaker than the neighboring second-order  $R^{-8}$  and  $R^{-10}$  terms (Bukta and Meath 1973).

TABLE 2. Known constants and turning point specifications for the *B*-state halogens

$X_2$	$D(\text{cm}^{-1})^a$	$10^{-5} C_5(\text{cm}^{-1} \text{Å}^5)$		$R_b(X_2)$	Turning points	
		Experimental	Theoretical <sup>b</sup>		Range	Reference
<sup>35,35</sup> Cl <sub>2</sub>	20 879.64(±0.14)	1.22 <sub>4</sub> (±0.04)	1.23 or 1.44	4.1	4.1 ≤ $R_v$ ≤ 9.2	Cummings (1972)
<sup>79,81</sup> Br <sub>2</sub>	19 580.78(±0.03)	1.79(±0.03)	2.00 or 2.39	4.7	4.7 ≤ $R_v$ ≤ 8.7	Todd <i>et al.</i> (1967)
<sup>127,127</sup> I <sub>2</sub>	20 043.20 <sub>8</sub> (±0.03)	2.8861(±0.006)	3.68 or 4.54	5.5	5.5 ≤ $R_v$ ≤ 10.0	Barrow and Yee (1973)

<sup>a</sup>Expressed relative to the ground-state  $v = 0, J = 0$  level.

<sup>b</sup>The first set of values calculated from the expectation values of Lu *et al.* (1971), and the second from those of Froese Fischer (1968, 1972).

The main drawback of [7] (and [6]) is the fact that for  $\alpha > 0$  it has an artificial singularity at the internuclear distance  $R = (\alpha C_{m2}/C_{m1})^{1/(m2-m1)}$ , where its denominator goes to zero. If terms  $m1$  and  $m2$  both arise in second-order perturbation theory, this problem is irrelevant, since the discussion associated with [2] and [4] implies that [1] and all expressions based on it are invalid at such small distances. On the other hand, if the  $m1$  term arises in first-order perturbation theory ( $m1 = 1, 3, 5$ ) and the  $m2$  term in second ( $m2 = 4, 6$ ), this singularity may occur in a region where [5] provides a perfectly valid representation of the turning points. It is also clear that use of large positive values of  $\alpha$  will tend to exaggerate any problems of this type. However, no such difficulties are encountered if  $\alpha$  is negative, or in the limit  $\alpha \rightarrow 0$  when [7] becomes [8].

While the preceding discussion has utilized the simplifying assumption that none of the coefficients  $C_m$  in [5] were known, it may readily be generalized to take advantage of any known constant  $C_k$ . In this case the term  $C_k/(R_v)^k$  is simply transferred to the left-hand sides of [5]–[9], and the quantities in square brackets on the left side of [11] and [12] become

$$[D - G(v) - C_k/(R_v)^k]$$

The examples considered below are all cases in which this modification was used.

### III. Applications to $B(^3\Pi_{Ou}^+)$ -State Cl<sub>2</sub>, Br<sub>2</sub>, and I<sub>2</sub>

#### A. Summary and Assessment of Known Quantities

For the  $B(^3\Pi_{Ou}^+)$ -state halogens, the leading inverse-power terms in the long-range interaction potential [1] correspond to  $m = 5, 6, 8, 10, \dots$  etc., and their coefficients are all positive (Le Roy 1971). For Cl<sub>2</sub>, Br<sub>2</sub>, and I<sub>2</sub>, the energies of the highest observed vibrational levels of this state have been analyzed using a new technique which appears to yield reliable values of the dissociation

energy  $D$  and the potential constant  $C_5$  (Le Roy and Bernstein 1970, 1971). A minor change in the original analysis has since (Le Roy 1973) yielded a slightly modified  $D$  and  $C_5$  for Cl<sub>2</sub>. Furthermore, elegant new measurements of levels lying very near dissociation have recently provided slightly better  $D$ 's for Br<sub>2</sub> and I<sub>2</sub>, and a much more accurate  $C_5$  for I<sub>2</sub> (Barrow and Yee 1973; Barrow, Broyd, Pederson, and Yee 1973). The present optimum values of these constants, and their uncertainties, are summarized in Table 2. Since the new  $D$  value for Br<sub>2</sub> (Barrow *et al.* 1973) was not accompanied by a revised  $C_5$ , the original value of Le Roy and Bernstein (1971) was used. However, the original uncertainty in their  $D$  for Br<sub>2</sub> was shown by the new results to be almost an order of magnitude too pessimistic. Hence, their reported  $C_5$  uncertainty was scaled down accordingly.

The turning-point analysis presented below is quite sensitive to the value of the assumed-known constants  $D$  and  $C_5$ . Thus, it is wise to pause and examine the significance of the values used here.

The formula used to obtain the experimental  $D$  and  $C_5$  values in Table 2 rests upon the assumption that the distribution of vibrational levels near dissociation depends only on the leading (here  $R^{-5}$ ) term in [1] (Le Roy and Bernstein 1970). On the other hand, both previous and present RKR analyses show that both the second and third ( $R^{-6}$  and  $R^{-8}$ ) terms also contribute significantly to the potential at the outer turning points of the levels in question. Since the  $R^{-6}$  contribution in this region is almost as large as the leading ( $R^{-5}$ ) potential term, this has led to some skepticism about the significance of the "experimental"  $C_5$  values obtained from the vibrational analyses (Tellinghuisen 1973; Barrow and Yee 1973; Yee 1973; Yee and Stone 1973). However, it has been pointed out (Le Roy 1973) that when this second inverse-power potential term is taken into account, the ensuing leading correction to the level distribution formula precisely vanishes.

Thus, the level spacings of a  $C_5/R^5 + C_6/R^6$  potential would behave the same as those for a pure  $C_5/R^5$  function, even if the second term contributes up to half the binding energy at the outer turning points. Unfortunately, this complete cancellation does not occur for the third ( $R^{-8}$ ) potential term. However, it is relatively weak; for the worst of the present cases ( $I_2$ ) it only contributes between 5 and 15% of the binding energy at the outer turning points of the levels used in the vibrational analysis. Furthermore, the vibrational analysis (Barrow and Yee 1973) determined  $C_5$  from the slope of a plot of  $(D - G(v))^{3/10}$  vs.  $v$ , and the power 3/10 effectively gives much greater weight to the levels nearest dissociation for which this discrepancy is smallest. The fact that the binding energies they used differ by factors of up to 15 makes the latter consideration fairly important. Qualitative evidence of the insignificant effect of the higher-order potential terms on the  $C_5$  determined for  $I_2$  is also provided by the way their accurate new data display precisely the functional behavior predicted by the "pure  $R^{-5}$  approximation" over this region.

The preceding arguments suggest that the  $C_5$  values obtained from the vibrational-spacing analyses should be fairly reliable. Furthermore, with the new data for  $Br_2$  and  $I_2$  (Barrow *et al.* 1973), the highest observed levels of all three species lie sufficiently close to dissociation that the  $D$  values obtained are not very strongly dependent on assumptions about the form of the long-range potential. We therefore conclude that the "experimental"  $D$  and  $C_5$  values in Table 2 are probably accurate to within the stated uncertainties. The discussion of  $I_2$  in Sect. III.C appears to provide additional confirmation of this point.

For the sake of comparison, Table 2 also presents theoretical estimates of the  $C_5$  constants for these species. While the formula from which they were calculated (Knipp 1938; Chang 1967) is probably reliable, its use requires knowledge of the expectation value of the square of the radius of the electrons in the unfilled valence shell of each of the interacting atoms. Unfortunately, estimates of these expectation values obtained from different types of *ab initio* calculations differ significantly. Thus, Table 2 contains  $C_5$  values calculated using both the expectation values of Lu *et al.* (1971) (first set) and those of Froese Fischer (1968, 1972). While the former are certainly in better agreement with experiment, theoretical considerations suggest that the latter

should be the more accurate (P. R. Certain 1972, private communication). In view of this discrepancy, it seems reasonable to take the disagreement between the two theoretical estimates as a measure of their uncertainty. Within this rather broad limit, the theoretical and experimental constants may be said to be in agreement, but the latter are certainly to be preferred.

Table 2 also contains values of the critical distance  $R_b(X_2)$  defined by [4] and the range and source of the turning points used in the present fits. In all three cases, the turning points used extended from the bound at  $R_b(X_2)$  out to that for the highest observed vibrational level. While another RKR potential for  $Cl_2$  was reported by Coxon (1971), his turning points were not corrected to take account of irregularities in the inner branch of the potential. Even so, when analyzed in the same way as Cummings' (1972) results (see below), they yield virtually the same  $C_6$  and  $C_8$  values. Similarly, use of the  $I_2$  turning points of Brown *et al.* (1973) does not significantly affect the results of the fits for this case. It should also be pointed out that the older  $Br_2$  turning points of Todd *et al.* (1967) were deliberately used in preference to those obtained in Coxon's (1971) more precise calculations, because the use of a vibrational misassignment<sup>4</sup> makes the latter unreliable.

### B. Results

Since the coefficient  $C_5$  of the first-order interaction energy is known, the  $C_5/(R_v)^5$  term may be included in the left-hand side of [7] and [8]. In this case  $m_1 = 6$ ,  $m_2 = 8$ , and the "linearized" versions of these equations (analogous to [11] and [12]) are:

$$[13] \quad \{(R_v)^6 [D - G(v) - C_5/(R_v)^5]\}^{-\alpha} = (C_6)^{-\alpha} - [\alpha C_8/(C_6)^{(1+\alpha)}]/(R_v)^2$$

and

$$[14] \quad \log \{(R_v)^6 [D - G(v) - C_5/(R_v)^5]\} = \log(C_6) + (C_8/C_6)/(R_v)^2$$

Figures 1-3 plot the  $B$ -state halogen turning points in the manner suggested by [14] ( $\alpha = 0$ )

<sup>4</sup>A vibrational reassignment of the then highest observed levels, which was independently proposed by Coxon (1971) and by Le Roy and Bernstein (1971), has since been shown (Barrow *et al.* 1973) to have been spuriously based on excessive faith in the accuracy of the early measurements of Brown (1931).

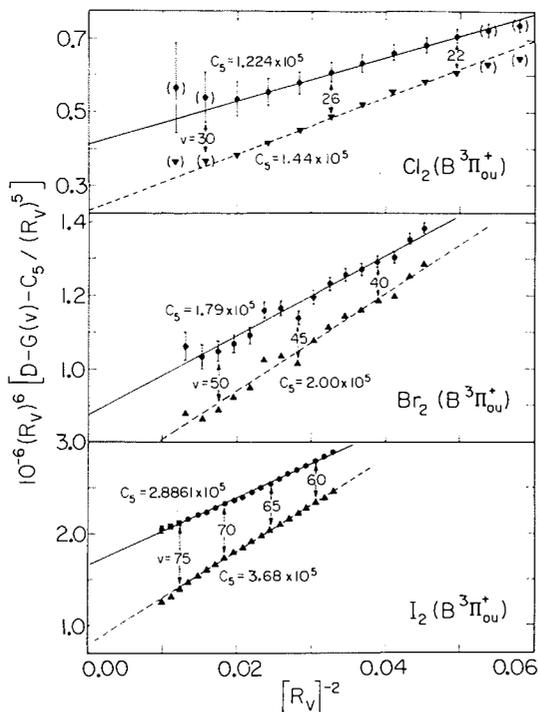


FIG. 1. RKR turning points for the  $B(3\Pi_{ou}^+)$ -state halogens plotted according to [13] with  $\alpha = -1$ .

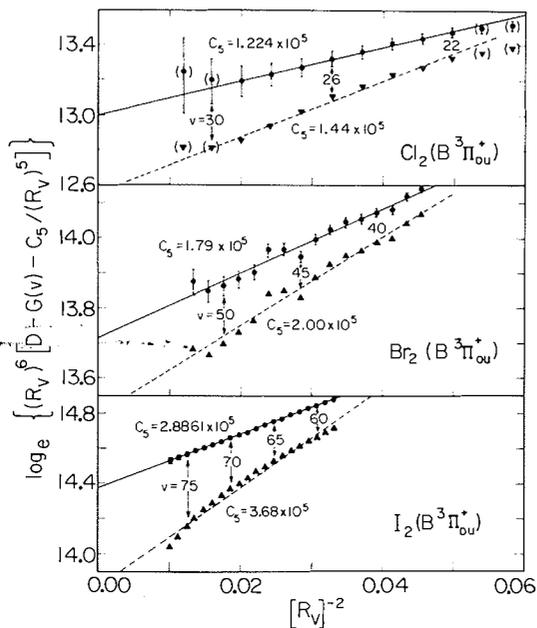


FIG. 2. As in Fig. 1, plotted according to [14] (corresponding to  $\alpha = 0$ ).

and by the  $\alpha = -1$  and  $5/3$  modes of [13]. The lines correspond to least-squares fits to the indicated points, and their intercepts and slopes give estimates of  $C_6$  and  $C_8$ .

The round points in each figure were obtained using the experimental  $D$  and  $C_5$ , while the error bars indicate the effect of the quoted uncertainties in these constants. For  $\text{Br}_2$ , this source of uncertainty is less important than the scatter due to small inaccuracies in the reported turning points. On the other hand, the  $v = 30$  and  $31$   $\text{Cl}_2$  points had to be omitted from the least-squares fits because of their inordinate sensitivity to possible errors in the experimental  $D$  and  $C_5$ . The parentheses around the  $v = 20$  and  $21$   $\text{Cl}_2$  points indicate that they too were omitted from these fits. This step was taken because for all  $\alpha$ , they appear to deviate systematically from a straight line through the remaining eight points. Although their omission does not have a large effect on the slope and intercept of such a line, it causes a considerable decrease in the standard error of the fit. This deviation could be due to systematic errors in the RKR turning points, but it is more likely caused by a breakdown of the inverse-power form of the long-range potential in this region. The latter possibility should not be surprising, since

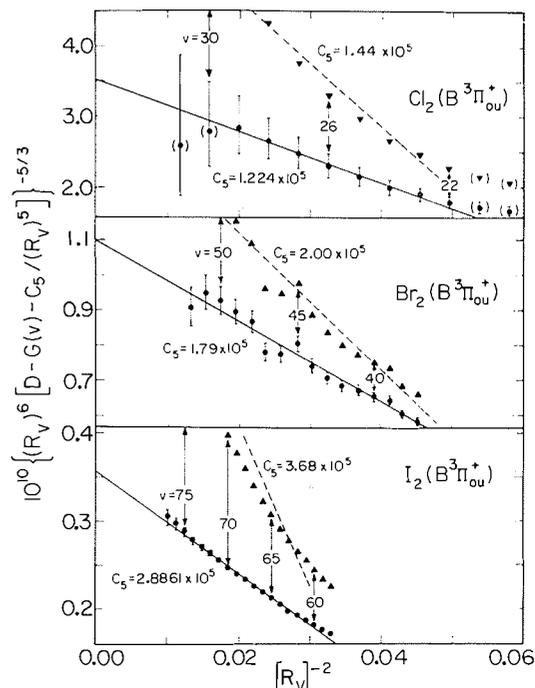


FIG. 3. As in Fig. 1, with  $\alpha = 5/3$ .

TABLE 3. Results of fits to [13] and [14] with  $D$  and  $C_5$  held fixed at the experimental values in Table 2<sup>a</sup>

$\alpha$	$\frac{C_{10}/C_8}{C_8/C_6}$	$\sigma(\text{cm}^{-1})$			$10^{-5} C_6 (\text{cm}^{-1} \text{Å}^6)$			$10^{-5} C_8 (\text{cm}^{-1} \text{Å}^8)$		
		$\text{Cl}_2$	$\text{Br}_2$	$\text{I}_2$	$\text{Cl}_2$	$\text{Br}_2$	$\text{I}_2$	$\text{Cl}_2$	$\text{Br}_2$	$\text{I}_2$
-2	-0.500	0.16	0.85	0.48	3.61	8.16	14.5	102	160	629
-1	0.000	0.13	0.71	0.27	4.13	8.72	16.4	59.7	109	372
		[0.33]	[0.59]	[0.16]	[2.29]	[6.72]	[7.68]	[78.0]	[133]	[516]
-1/2	0.250	0.20	0.65	0.15	4.29	8.91	17.0	49.7	94.1	310
0 <sup>b</sup>	0.500	0.30	0.59	0.06	4.41	9.07	17.5	42.7	82.9	267
		[0.84]	[0.60]	[1.00]	[2.85]	[7.28]	[10.0]	[45.2]	[91.9]	[283]
1/2	0.750	0.42	0.54	0.17	4.51	9.20	17.9	37.4	74.1	234
1	1.000	0.55	0.53	0.35	4.60	9.32	18.2	33.3	67.0	209
5/3	1.333	0.76	0.58	0.64	4.69	9.45	18.6	29.1	59.4	182
		[2.35]	[1.47]	[4.30]	[3.27]	[7.79]	[11.7]	[27.2]	[60.8]	[165]
3	2.000	1.33	1.00	1.49	4.84	9.65	19.1	23.2	48.3	145
Theoretical values of Cummings (1972)					4.5	8.3	18.5	—	—	—
					(±0.5)	(±0.8)	(±2)			
Recommended values					4.41	9.07	17.5	42.7	82.9	267
					(±0.56)	(±0.55)	(±0.5)	(±6.9)	(±11)	(±24)

<sup>a</sup>Results in brackets correspond to use of the experimental  $D$  with the theoretical  $C_5$  used in Figs. 1-3.

<sup>b</sup>Recall that  $\alpha = 0$  corresponds to use of the logarithmic expression [14].

the present  $R_b(X_2)$  criterion is only expected to provide an approximate lower bound to the "long-range region".

Fits analogous to those shown on Figs. 1-3 were performed for a wide range of  $\alpha$ 's, and the results are summarized in Table 3. The numbers in brackets were obtained using theoretical  $C_5$  values and correspond to the triangular points in the figures, while the rest were obtained using the experimental  $D$  and  $C_5$ . The error term  $\sigma$  is a root mean square deviation associated with use of the fitted  $C_6$  and  $C_8$  constants in [7] and [8]. Note, however, that care must be taken in any attempt to use  $\sigma$  to ascertain an optimum value of  $\alpha$ , since the effect of small errors in the assumed-known values of  $D$  and  $C_5$  may be of paramount importance.

For pairs of  $S$ -state atoms, the results in Table 1 clearly indicate that  $\alpha \approx 5/3$  should be most appropriate. However, for the present case of species dissociating to two  $P$ -state atoms, we know no analogous preference. The only constraints for the  $B$ -state halogens are that they should all have the same  $\alpha$ , and that it must *not* lie in the region  $\alpha \leq -1$ , which corresponds to zero and negative implicit  $C_{10}$  values.

A cursory examination of the  $\sigma$ 's in Table 3 indicates that for  $\text{I}_2$  there is a very marked preference for  $\alpha = 0$ , and for  $\text{Cl}_2$  a distinct preference for  $\alpha \approx -1$ , while the  $\text{Br}_2$  results are relatively insensitive to changes in  $\alpha$ . In order to ascertain its effect on the positions of the  $\sigma$  minima, this set

of fits was repeated as the experimental  $D$  and  $C_5$  were varied over the ranges of the uncertainties given in Table 2. When this was done, the sharp  $\sigma$  minimum for the  $\text{I}_2$  case was found to vary across the range  $-1/4 \lesssim \alpha \lesssim 1/4$ , while for  $\text{Cl}_2$ , it ranged between  $\alpha \approx -2$  and 0. While the analogous  $\sigma$  minimum for  $\text{Br}_2$  is too shallow to be very useful in defining  $\alpha$ , the low end of its range,  $\alpha \approx 1/4$ , almost overlaps the other two. In evaluating these results, it should also be noted that the  $\text{I}_2$  turning points used here are believed to be much more accurate than those for  $\text{Br}_2$  and  $\text{Cl}_2$ .

We conclude that the long-range potentials of the  $B$ -state halogens are best represented by  $\alpha = 0.00 (\pm 0.25)$ . This is the source of the "recommended values" of  $C_6$  and  $C_8$  listed at the end of Table 3. The uncertainties in these preferred values have three sources. The smallest is that associated with the fit to obtain the slopes and intercepts of the solid lines shown in Fig. 2. The other two are uncertainties due to imprecision in our knowledge of the quantities  $D$  and  $C_5$  and of the parameter  $\alpha$ . Table 4 compares the relative magnitudes of these contributions to the final error estimates.

Table 3 also includes the theoretical  $C_6$  values for these species which were recently calculated by Cummings (1972). The agreement is quite gratifying and attests to the utility of both his theoretical, and the present empirical methods. Cummings (1972) also reported approximate

TABLE 4. Contributions (in %) to uncertainties in recommended  $C_6$  and  $C_8$  constants

	$\delta C_6(\text{fit})$	$\delta C_6(D, C_5)$	$\delta C_6(\alpha)$	$\delta C_8(\text{fit})$	$\delta C_8(D, C_5)$	$\delta C_8(\alpha)$
Cl <sub>2</sub>	0.7	10.9	1.1	1.3	7.8	7.1
Br <sub>2</sub>	1.4	3.9	0.8	3.6	3.9	6.0
I <sub>2</sub>	0.1	1.6	1.2	0.2	1.7	7.0

TABLE 5. Results obtained on fitting I<sub>2</sub> turning points to [16] and [17] with  $D$  fixed at the Table 2 value. Units are  $10^{-5} C_m (\text{cm}^{-1} \text{Å}^m)$ 

$\alpha$	$\sigma$	$5.5 \leq R_v \leq 10.0$ ( $58 \leq v \leq 77$ )			$\sigma$	$6.2 \leq R_v \leq 10.0$ ( $64 \leq v \leq 77$ )		
		$C_5$	$C_6$	$C_8$		$C_5$	$C_6$	$C_8$
-1	0.047	3.46(±0.16)	10.2(±1.5)	471(±19)	0.037	3.42(±0.29)	10.7(±3.1)	459(±51)
0	0.059	2.81(±0.13)	18.1(±1.0)	265(±3)	0.031	3.02(±0.17)	16.3(±1.5)	274(±8)
1	0.072	2.49(±0.13)	21.7(±1.0)	200(±2)	0.028	2.81(±0.13)	18.9(±1.1)	208(±3)
5/3	0.081	2.34(±0.14)	23.3(±1.0)	174(±2)	0.026	2.71(±0.11)	20.1(±0.9)	182(±2)
$\alpha = -1$ results of Barrow and Yee (1973)					—	3.43(±0.13)	10.6(±1.3)	460(±20)

theoretical  $C_8$  values for these states. However, they were obtained by combining his calculated halogen  $C_6$ 's with the  $C_8/C_6$  ratios reported for the corresponding diatomic inert gas. Since Table 1 shows that ratios of this sort are different for species formed from different types of atomic states, this extrapolation from an  $S$ - $S$  to a  $P$ - $P$  situation is probably ill founded. Hence, these "theoretical"  $C_8$ 's are deliberately omitted from Table 3.

### C. Comparisons and Discussion

The nature and inadequacies of earlier methods used for, and results obtained on analyzing halogen turning points were recently discussed by Le Roy (1973) and need not be belabored here. However, a couple of features of Goscinski's (1972) applications of [6] which were not noted earlier very aptly illustrate the types of difficulties which may arise when using the present procedure: Since he chose not to utilize the previously reported (Le Roy and Bernstein 1971) empirical  $C_5$ 's, Goscinski (1972) performed his fits to [13] (with  $\alpha = +1$ ) using  $m_1 = 5$  and  $m_2 = 6$ . As a result, the implicit third term of his expanded [6] varies as  $R^{-7}$  rather than the  $R^{-8}$  functionality of the third term in the actual long-range potentials, an approximation which tends to distort the  $C_5$  and  $C_6$  values so obtained.

A more serious problem, and one which could arise in any analysis using [7] or [11] with positive  $\alpha$ , is due to the singularity of [7] at  $R_v = [\alpha C_{m_2}/C_{m_1}]^{1/(m_2-m_1)}$ . Since the  $R^{-5}$  and  $R^{-6}$

potential terms arise in different orders of perturbation theory, the latter's becoming as large as the former is not associated with the breakdown of [1]. However, these terms do become equal within the ranges of the Br<sub>2</sub> and I<sub>2</sub> turning points used here, and only slightly outside the range of those for Cl<sub>2</sub>. Thus, Goscinski's (1972) analysis should not be reliable for these species. For I<sub>2</sub> this conclusion is apparently confirmed by Goscinski's report that he was unable to obtain meaningful results, while his Br<sub>2</sub> analysis was invalidated by his use of Coxon's (1971) mis-assigned-level turning points<sup>4</sup>.

In very recent work, Barrow and Yee (1973) and Yee (1973) presented long-range analyses of the same I<sub>2</sub> turning points used here, while Yee and Stone (1973) performed analogous studies of  $B$ -state Br<sub>2</sub> and Cl<sub>2</sub>. Unfortunately, the constants they obtained differ markedly with those determined here. For example, Barrow and Yee's (1973)  $C_6$  and  $C_8$  for I<sub>2</sub> (see Table 5) are respectively 40% smaller and 70% larger than the recommended values in Table 3. These discrepancies demand an explanation.

In their work, Barrow and Yee (1973), Yee (1973), and Yee and Stone (1973) fitted the level energies directly to the long-range potential expression:

$$[15] \quad G(v) = D - C_5/(R_v)^5 - C_6/(R_v)^6 - C_8/(R_v)^8$$

In spite of other differences with the present work,

it is their use of this  $C_{10} \equiv 0$ , or  $\alpha = -1$  type of expression which is responsible for most of the disagreement with the present results.

A rearrangement of [13] and [14] yields the generalized versions of [15]:

$$[16] \quad G(v) = D - C_5/(R_v)^5 - \frac{C_6/(R_v)^6}{\{1 - \alpha C_8/[C_6(R_v)^2]\}^{1/\alpha}}$$

for  $\alpha \neq 0$ , and

$$[17] \quad G(v) = D - C_5/(R_v)^5 - [C_6/(R_v)^6] \exp \{C_8/[C_6(R_v)^2]\}$$

Imitating the Barrow and Yee (1973) and Yee (1973) approach by fitting the  $I_2$  turning points directly to [16] and [17] (with  $D$  held fixed at the Table 2 value) then yields the results in Table 5. The  $\alpha = -1$  fit to 14 turning points is effectively the same as their fit to [15], so the resulting  $C_m$  constants are naturally very similar to their values. However, combining their approach with a more realistic  $\alpha > -1$  yields markedly different results! In particular, a fit of the turning points of the 20 highest observed levels to [17] (for  $\alpha = 0$ ) yields a  $C_5$  in very good agreement with that obtained from their vibrational-spacing analysis (and a  $C_6$  and  $C_8$  in good accord with those in Table 3). The fact that this agreement is effected merely by modifying the Barrow and Yee method to allow for small high-order contributions to the potential would seem to be an additional reason for trusting the experimental  $C_5$ 's in Table 2.

One of the pitfalls of Barrow and Yee's (1973) approach is the fact that the constants obtained from these fits are very sensitive to the number of turning points used. In this regard, the differences in Table 5 between the 20- and 14-point results for  $\alpha > -1$  are typical, while the apparent stability of the  $\alpha = -1$  results for these two cases is quite misleading. This is demonstrated by the fact that the  $C_5$  values obtained from the 16-, 12-, and 10-point  $\alpha = -1$  fits are  $3.61(\pm 0.25) \times 10^5$ ,  $3.15(\pm 0.20) \times 10^5$ , and  $2.85(\pm 0.32) \times 10^5 \text{ cm}^{-1} \text{ \AA}^5$  respectively, differing markedly from the 20- and 14-point values in Table 5. Thus, it seems that a judicious choice of the number of turning points would allow one to obtain almost any desired result.<sup>5</sup>

<sup>5</sup>Note that this is not the case for the fits to [13] and [14] which yielded the results in Table 3 and Figs. 1-3.

For  $\text{Br}_2$  and  $\text{Cl}_2$ , Yee and Stone (1973) obtained their final  $C_6$  and  $C_8$  values from fits to [15] with the  $C_5$ 's held fixed at the first of the theoretical values shown in Table 2. For  $\text{Cl}_2$  this  $C_5$  is very close to the experimental value, and hence their ensuing  $C_6$  and  $C_8$  are very close (within 3 and 6% respectively) to the  $\alpha = -1$  values in Table 3. Thus, just as in the  $I_2$  case, the disagreement of their constants with the present recommended values is almost solely due to the different assumed values of  $\alpha$ .

For  $\text{Br}_2$ , Yee and Stone's (1973) assumed  $C_5$  is the same as that yielding the triangular points in Figs. 1-3 and the results in brackets in Table 3. Thus, in spite of their use of different, and presumably more accurate turning points, it is no surprise that their  $C_6$  and  $C_8$  for this case are quite similar to the bracketed  $\alpha = -1$  results in Table 3. Thus, the discrepancy in this case is due partly to the different assumed  $C_5$ , and partly to the different  $\alpha$ .

It is clear that the disagreement between the present results and those of Barrow, Yee, and Stone is largely due to their implicit assumption that  $\alpha = -1$  (or  $C_{10} \equiv 0$ ). This probably also applies to the part of the  $\text{Br}_2$  discrepancy caused by the different assumed  $C_5$ , since their faith in the smaller of the theoretical values of this constant is probably partly based on its reasonable agreement with their fitted  $\alpha = -1$   $C_5$  for  $I_2$ . In any case, the present  $\alpha = 0$  assumption is certainly much more realistic. Indeed, the concomitant value of the ratio  $(C_{10}/C_8)/(C_8/C_6) = 1/2$  is quite modest compared to its values for the species considered in Table 1.

#### IV. Conclusions

The present work shows that apparently innocuous implicit assumptions about the form of the long-range potential can drastically affect values of inverse-power potential coefficients determined from RKR turning points. In particular, assumptions about small contributions to the potential from  $R^{-10}$  and higher-order potential terms were shown to significantly affect the  $C_6$  and  $C_8$  values obtained for  $B$ -state  $\text{Cl}_2$ ,  $\text{Br}_2$ , and  $I_2$ . For these species, the most appropriate assumption about these terms was found to be that characterized by  $\alpha = 0.00 (\pm 0.25)$ , which correspond to assuming that  $(C_{10}/C_8)/(C_8/C_6) = 0.50 (\pm 0.13)$ . Note, however, that a  $C_{10}$  calculated from this ratio and the derived  $C_6$  and  $C_8$  should not be taken too seriously, since it may effectively

represent both higher inverse-power terms and any incipient exchange contribution to the potential.

Within the quoted uncertainties, the present recommended  $C_6$  and  $C_8$  constants for  $B$ -state  $\text{Cl}_2$  and  $\text{I}_2$  (see Table 3) are believed to be reliable. However, the origin and scatter of the  $\text{Br}_2$  turning points make the results for this case somewhat less certain. Their lower accuracy is qualitatively attested to by the nonmonotonic behavior of the ratio  $(C_8/C_6)$ , which equals  $9.7(\pm 2.8)$ ,  $9.1(\pm 1.8)$ , and  $15.3(\pm 1.8) \text{ \AA}^2$  for  $\text{Cl}_2$ ,  $\text{Br}_2$ , and  $\text{I}_2$  respectively. However, the imminent publication of a better experimental  $C_5$  and improved RKR curve for  $\text{Br}_2$  (see Barrow *et al.* 1973) should remedy this situation in the near future.

The results in Table 1 gave rise to an additional empirical conclusion which may be of some significance; that is, that for interactions of pairs of  $S$ -state atoms, the ratio  $(C_{10}/C_8)/(C_8/C_6) \approx 4/3$ . Within the notation of [7] and [9], this corresponds to  $\alpha = 5/3$ . While the origin of this correlation is not yet understood, it should be taken into account in interactions of this sort (*e.g.*, for the ground-state of  $\text{Mg}_2$ ; see Stwalley (1970)).

One final point deserving mention is the fact that while the quantity  $R_b(\text{AB})$  defined by [4] provides a reasonable lower bound to the region of validity of the long-range potential expansion [1], it is not necessarily the *greatest* lower bound, and should be used with some caution.

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