

Analysis Of The Long-range Internuclear Potentials Of $B(^3\Pi_{0u}^+)$ -State Br_2 And Cl_2^1

Recently calculated RKR potentials for the $B(^3\Pi_{0u}^+)$ states of Cl_2 and Br_2 are combined with theoretical C_5 potential constants to yield estimates of the C_6 coefficients for these states. The approach used is analogous to that which Stwalley recently applied to ground-state ($X^1\Sigma_g^+$) Mg_2 . The implications of the present results with regard to a recently developed method of determining dissociation limits and long-range potentials from vibrational spacings are discussed.

It is known theoretically that for the $B(^3\Pi_{0u}^+)$ -state halogens, the long-range internuclear potential may be expanded as $(1-4)^2$

$$V(R) = D - C_5/R^5 - C_6/R^6 - C^8/R^8 - \dots \quad (1)$$

Values of the C_6 constants may be readily calculated for most species (2, 3, 6),³ and those for the states in question are given in Table I. Like the C_5 's, the C_6 and C_8 coefficients for these molecular states are also almost certainly positive (attractive), although they are much harder to evaluate theoretically.⁴ Although Eq. (1) is only valid at large R (see the discussion in Ref. (10)), its use in the present discussion is almost certainly appropriate, since the potentials are examined only in the region $R \gtrsim 5.5 \text{ \AA}$, where the internuclear interaction energy is $\lesssim 1\%$ of the potential well depth.

It was recently concluded (5, 7) that the distribution of the highest observed vibrational levels for each of B -state Cl_2 , Br_2 , and I_2 corresponds to the long-range potential in this energy range being dominated by the leading (R^{-5}) term in Eq. (1).⁵ On the other hand, the

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² The derivation of Eq. (1) is discussed in a number of sources, including Refs. (1, 2, 4). The lowest power term contributing to it is determined by the nature of the atoms to which the given molecular state dissociates; a summary of the theoretical rules governing this is given in Appendix B of Ref. (5).

³ The derivation of the expressions for C_5 coefficients is presented in Refs. (2 and 6), while the results are compactly summarized in Ref. (3) (also in Footnotes 41 and 12 of Refs. (5) and (7), respectively). Uncertainties in the theoretical C_5 's largely originate in the values chosen for the expectation values of the square of the electron radii in the unfilled atomic valence shells, and are probably of the order of a few per cent.

⁴ The second-order perturbation-theory expressions for interatomic dispersion forces (1, 4) show that in the present case, where the molecular states dissociate to one ground ($^2P_{3/2}$) and one excited ($^2P_{1/2}$) atom, there is only one repulsive (negative) term contributing to each of the C_6 and C_8 coefficients. Its magnitude depends on a matrix element coupling the $^2P_{3/2}$ and $^2P_{1/2}$ atomic states; this is known to be very small because of the forbiddenness of this atomic transition (8, 9), and it is certain to be overwhelmed by the contributions from terms corresponding to allowed transitions to higher excited states.

⁵ There is an error in Eq. (8) of Ref. (7); the vibrational quantum number v therein

TABLE I
ASYMPTOTIC POTENTIAL COEFFICIENTS OF $B(^3\Pi_{0u}^+)$ -state Cl_2 and Br_2

| | C_5 [$\text{cm}^{-1} \text{\AA}^5$] (theoretical) ^a | C_6 [$\text{cm}^{-1} \text{\AA}^6$] (empirical) ^b |
|---------------|---|---|
| Cl_2 | 1.44×10^5 | $0.42 (\pm 0.02) \times 10^6$ |
| Br_2 | 2.39×10^5 | $1.01 (\pm 0.24) \times 10^6$ |

^a See Refs. (2, 3, 6), and Footnote 3.

^b These values are the slopes of lines through the highest four points in Figs. 1 and 2 which were constrained to have the indicated intercepts. The uncertainties represent 95% statistical confidence intervals.

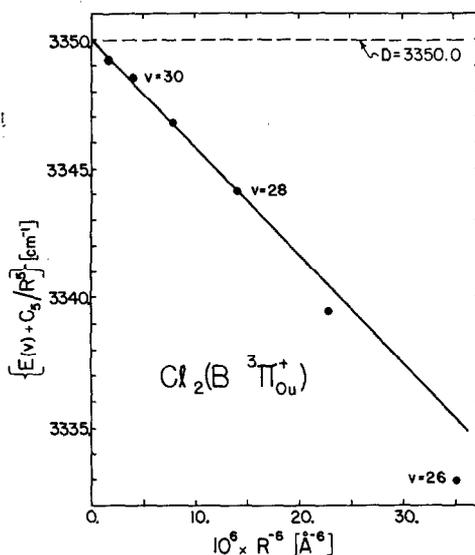


FIG. 1. $\{E(v) + C_5/[R_2(v)]^5\}$ vs $[R_2(v)]^{-6}$ for Cl_2 ($B\ ^3\Pi_{0u}^+$). The solid line is a least-squares fit to the four highest points, constrained to have its intercept at the previously obtained (5, 7) value of D (horizontal dashed line).

outer turning points of the vibrational levels in question (11) are not particularly large ($R \lesssim 9.2 \text{\AA}$), so that the contributions to the potential from some of the higher-power terms (particularly, C_6/R^6) may be significant. This question will now be examined using the graphical approach which Stwalley (10) applied to ground-state Mg_2 . Figures 1 and 2 show plots of $\{E(v) + C_5/[R_2(v)]^5\}$ vs. $[R_2(v)]^{-6}$ for B -state Cl_2 and Br_2 , where $E(v)$ are the

should be replaced by $[v + \frac{1}{2}]$, yielding

$$[v_D(j) + \frac{1}{2}]/[v_D(i) + \frac{1}{2}] = [\mu(j)/\mu(i)]^{1/2}. \quad (8)$$

However, this expression was used only to yield the interpolated v_D and predicted vibrational energies for the mixed isotopes^{79,81} Br_2 (7), for which case the effect of the above error is completely negligible. We are very grateful to Professor W. C. Stwalley for bringing this point to our attention.

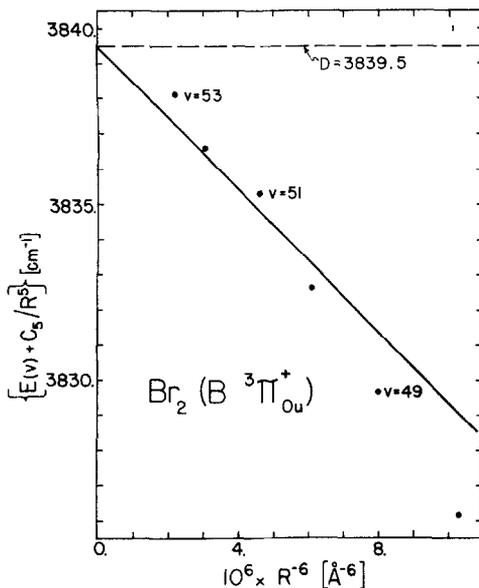


FIG. 2. $\{E(v) + C_5/[R_2(v)]^5\}$ vs $[R_2(v)]^{-6}$ for $\text{Br}_2 (B \ ^3\Pi_{0u}^+)$, as in Fig. 1.

energies and $R_2(v)$ Coxon's (11) outer RKR turning points for the highest observed vibrational levels, and the C_5 's are the theoretical values in Table I.⁶ Clearly, if the potential were purely R^{-5} these plots would be perfectly flat.

Consideration of Eq. (1) shows that the limiting slopes in Figs. 1 and 2 yield the C_5 coefficients and the intercepts at $[R_2(v)]^{-6} = 0$, yield the dissociation limits D . In practice, the lines fitted through the empirical points were constrained to yield the D values obtained in Refs. (5, 7), since the plots alone did not appear capable of yielding more reliable values. In particular, a best straight line through the four highest points in Fig. 2 would yield an estimate of the dissociation energy considerably larger than that obtained in Ref. (7). This is quite unacceptable, and suggests that there are small errors in these RKR turning points; the scatter of the highest points in Fig. 2 strengthens this conclusion.⁷

The C_5 constants corresponding to the slopes of the lines in Figs. 1, 2 are given in Table I, together with the theoretical C_5 values on which they are based. In addition to the inherent

⁶ A point corresponding to the outer RKR turning point calculated (11) for $v = 32$ was omitted from Fig. 1 because of its completely unreasonable disagreement with the others; it would have lain 0.8 cm^{-1} below the point for $v = 31$, at an abscissa of $10^6/R^6 = 0.07$. The only report of this level is in the thesis of Richards (12), and it is open to some doubt since it was not confirmed by the latter analyses of Refs. (13) and (14). The discrepancy, qualitatively, is expected if the $v = 31$ -32 level spacing assumed by Coxon (11) was too small, as is suggested by the fact that it is 33% smaller than that predicted in Ref. (5).

⁷ In an RKR calculation, small errors in interpolating over the eigenvalues and rotational constants for levels near a given vibrational level have relatively the largest effect on its calculated turning points if the level in question lies very close to the dissociation limit. Furthermore, for the highest observed levels, the absence of data for yet higher levels introduces relatively larger uncertainties into such interpolations.

interest in the C_6 coefficients, these results are interesting since they probe one of the approximations used in Refs. (5) and (7) in the determination of "experimental" C_5 coefficients for B -state Cl_2 , Br_2 and I_2 . The method used (5) is based on a simple expression for the vibrational energies of levels near the dissociation limit,

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

which is based on approximating the long-range potential of Eq. (1) by a single inverse-power term

$$V(R) = D - C_n/R^n. \quad (3)$$

In Eq. (2), H_n is a simple $\frac{1}{2}$ function of C_n , and v_D an integration constant.

In Refs. (5) and (7) it was concluded that the leading (R^{-5}) term dominated Eq. (1) for energies in the neighborhood of the four highest observed vibrational levels of Cl_2 and Br_2 . In view of this, the higher-power terms were neglected, and Eq. (2) was used with $n = 5$ to yield values of D , C_5 and v_D . However, the analysis of Figs. 1, 2 shows that the R^{-5} term is in fact responsible for only 65-75% of the potential over the range of the outer turning points of the four highest observed levels. Consideration of the derivation of Eq. (2) shows that this error would tend to make the C_5 values obtained from it somewhat small, as was found (7), although it would not significantly affect the concomitant D and v_D values. However, it is somewhat reassuring that the disagreement between the theoretical C_5 constants and the "experimental" values obtained from fits to Eq. (2) (with $n = 5$) were only 10% and 25% for the $B(^3\Pi_{0u}^+)$ states of Cl_2 and Br_2 , respectively (5, 7).

It appears that the nonnegligible influence of the higher power terms in Eq. (1) most seriously affects the C_n coefficients obtained using Eq. (2). However, this deficiency in the method of Refs. (5) and (7) should be ameliorated by an expansion of Eq. (2) to take account of contributions to the potential other than the first inverse-power term; this work will be reported elsewhere (15).

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