

systems such as the Cu_2Cl_6^- unit which is present in KCuCl_3 .

ACKNOWLEDGMENTS

We wish to thank B. C. Gerstein and G. M. Cole, Jr., for some helpful discussions, H. P. Hoen III and R. McEwen for their aid in the chemical and x-ray analyses of our samples, and E. D. Sanford for help with the cryogenic equipment.

* This work was supported by the Air Force Office of Scientific Research, Office of Aerospace Research Under Grant No. AFOSR 928-681. The computations were supported by the National Science Foundation (Grant NSF-GJ-367).

† This paper was taken from part of a dissertation by J. E. Hynes in partial fulfillment of the requirements for the Ph.D. degree.

‡ Present address: Pitney Bowes, Stamford, Conn.

¹ B. C. Guha, Proc. Roy. Soc. (London) **A206**, 3353 (1951).

² B. Bleaney and K. D. Bowers, Phil. Mag. **43**, 372 (1952).

³ B. Bleaney and K. D. Bowers, Proc. Roy. Soc. (London) **A214**, 145 (1952).

⁴ B. Bleaney, Rev. Mod. Phys. **25**, 161 (1953).

⁵ M. Kato, Chem. Rev. **64**, 99 (1964).

⁶ F. Keffer and T. Oguchi, Phys. Rev. **115**, 1428 (1959).

⁷ N. L. Huang and R. Orbach, J. Appl. Phys. **39**, 426 (1968).

⁸ N. L. Huang and R. Orbach, Phys. Rev. **154**, 487 (1967).

⁹ N. L. Huang and R. Orbach, Phys. Rev. **157**, 378 (1967).

¹⁰ P. H. Vossos, L. D. Jennings, and R. E. Rundle, J. Chem. Phys. **32**, 1590 (1960).

¹¹ R. D. Spence and C. R. K. Murty, Physica **27**, 850 (1961); S. C. Abrahams and H. J. Williams, J. Chem. Phys. **39**, 2923 (1963).

¹² N. J. Poulis and G. E. C. Hardeman, Physica **18**, 201 (1952).

¹³ G. J. Maass, B. C. Gerstein, and R. D. Willett, J. Chem. Phys. **46**, 401 (1967).

¹⁴ R. D. Willett, Ph.D. dissertation, Iowa State University, 1962. R. D. Willett, C. D. Wiggins, R. F. Krueh, and R. E. Rundle, J. Chem. Phys. **38**, 2429 (1963).

¹⁵ M. Groger, Anorg. Chem. **19**, 328 (1899).

¹⁶ H. Bayer, Z. Physik **130**, 227 (1951).

¹⁷ J. E. Hynes, Ph.D. dissertation, Florida State University, 1969.

¹⁸ F. E. Cotton, Ann. Chim. (Paris) **4**, 9 (1925).

¹⁹ R. D. Willett and O. L. Liles, Jr., Inorg. Chem. **6**, 1666 (1967).

²⁰ C. H. Townes and B. P. Dailey, J. Chem. Phys. **17**, 782 (1949).

²¹ J. H. M. Thornley, B. W. Mangum, J. H. E. Griffiths, and J. Owen, Proc. Phys. Soc. (London) **78**, 1263 (1961).

²² C. H. Townes and B. P. Dailey, J. Chem. Phys. **20**, 35 (1952).

²³ S. Kojima, K. Tsukada, S. Ogawa, A. Shimauchi, and Y. Abe, J. Phys. Soc. Japan **9**, 805 (1954).

²⁴ A. Dalgarno, Advan. Phys. **11**, 281 (1962).

²⁵ G. Burns and E. G. Wikner, Phys. Rev. **121**, 155 (1961).

²⁶ S. L. Carr, B. B. Garrett, and W. G. Moulton, J. Chem. Phys. **47**, 1170 (1967).

Spectroscopic Reassignment and Ground-State Dissociation Energy of Molecular Iodine*

ROBERT J. LEROY

Theoretical Chemistry Institute and Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706

(Received 3 September 1969)

Reanalyzing some early bandhead data for $\text{I}_2[B\ 0_u^+(^3\Pi)]$, an improved value of the ground-state dissociation energy is found to be $D_0 = 12\,440.9 \pm 1.1\text{ cm}^{-1}$, differing significantly from the previously accepted value of Verma, $12\,452.5 \pm 1.5\text{ cm}^{-1}$. This result implies that the final state of one of the uv resonance series reported by Verma must have a rotationless potential maximum some $13.1 \pm 1.4\text{ cm}^{-1}$ high. It is further shown that the original electronic assignment of this state as ground-state $X\ 0_g^+(^1\Sigma)$ is implausible. A reassignment as $0_g^+(^3\Pi)$ is proposed, and the nature of the $0_g^+(^3\Pi)$ potential is considered.

I. INTRODUCTION

Verma observed¹ six series of uv resonance emission doublets which were excited by absorption of the 1830.4-Å iodine atomic line by molecules in five rotational levels of the $v''=0$ level² of the ground electronic state of I_2 . This absorption corresponded to transitions into five resonant vibrational-rotational levels of an excited 0_u^+ electronic state, and the subsequent emission from these levels yielded the observed series. Verma concluded¹ that this emission always produced molecules in the ground electronic state. This is unquestionably true for those final levels to which he assigned vibrational quantum numbers $v'' \leq 84$. However, the separate set of levels at the convergence limit of the emission spectrum (Verma's $v''=98-115$) causes a strange flattening of the Birge-Sponer plot

for the ground state. Furthermore, their sharp convergence-limit cutoff lies above a value of the ground-state dissociation energy obtained from other data, which implies that the state to which they belong has a potential maximum. This suggests that the present best value of the dissociation energy,¹ which is based on the position of this cutoff, is too large by an amount equal to the height of the barrier. The present paper presents a new value of the ground-state dissociation energy and proposes that the levels in question be reassigned to the $0_g^+(^3\Pi)$ state.

II. DISSOCIATION ENERGY OF GROUND STATE

$$\text{I}_2[X\ 0_g^+(^1\Sigma)]$$

Two main approaches to the determination of the dissociation energy are considered. In the first, an

estimate for D_0 is obtained by subtracting the ${}^2P_{3/2}$ - ${}^2P_{1/2}$ spin-orbit splitting of iodine atoms from the convergence limit of the $B\ 0_u^+({}^3\Pi)$ - $X\ 0_g^+({}^1\Sigma)$ band spectrum.^{3,4}

Brown⁵ has reported bandhead measurements for levels $v'=48$ -72 of the $B\ 0_u^+({}^3\Pi)$ state. Careful extrapolation from these data places the B -state dissociation limit $20\ 044.0\pm 1.1\ \text{cm}^{-1}$ above the $v''=0, j''=0$ level of the ground state.^{7,8} Subtracting from this the 7603.15-cm^{-1} ${}^2P_{1/2}$ - ${}^2P_{3/2}$ spin-orbit splitting energy⁹ yields $D_0=12\ 440.9\pm 1.1\ \text{cm}^{-1}$.¹⁰ This result corresponds to the $B=1$ state having 89 ± 1 vibrational levels.⁸

A second approach to D_0 , that used by Verma,¹ is based on the sharp low-energy cutoff of the uv resonance series at the convergence limit. The electronic assignment of the lower state of this series is immaterial since it could only dissociate to yield two ground-state ${}^2P_{3/2}$ atoms. Furthermore, the original rotational assignment of this resonance series ($J_r=25$) is based on the rotational constants for the emitting levels and hence is valid independent of the electronic assignment of the final state. Utilizing the data in essentially the same manner as Verma¹ yields a D_0 estimate of $12\ 452.4\pm 1.8\ \text{cm}^{-1}$.¹¹

In general, the final electronic states of the two transitions considered above may have repulsive potential barriers as well as attractive wells. Therefore, the two estimates of D_0 are both upper bounds, being equal to the true D_0 plus the height of the appropriate barrier. Since the first value obtained is $11.5\pm 3\ \text{cm}^{-1}$ smaller than the second, the state giving rise to the latter must have a rotationless ($J=0$) potential barrier at least $11.5\pm 3\ \text{cm}^{-1}$ high.

The moderately long-range interaction of two 2P (${}^2P_{3/2}$ or ${}^2P_{1/2}$) iodine atoms may be expressed as¹³

$$V(R) = \frac{C_5}{R^5} + \frac{C_6}{R^6} + \frac{C_8}{R^8} + \frac{C_{10}}{R^{10}} + \dots, \quad (1)$$

where the first term arises from the first-order perturbation energy, and the next three terms from the second order. It may readily be shown that C_6 , C_8 , and C_{10} are negative (attractive) for all molecular states formed from two ground-state (${}^2P_{3/2}$) atoms.¹⁴ Furthermore, theoretical values of C_5 have been calculated for all the states formed on combining ${}^2P_{3/2}+{}^2P_{3/2}$ or ${}^2P_{3/2}+{}^2P_{1/2}$ atoms.^{13,15} These values show which states are attractive and which are repulsive at the large distances at which the R^{-5} term dominates the interaction.

The theoretical C_5 for the $B\ 0_u^+({}^3\Pi)$ state, which dissociates to ${}^2P_{3/2}+{}^2P_{1/2}$, is negative (attractive).^{13,15} Furthermore, in Ref. 8 it is shown that the potential at the outer turning points of the highest observed B -state levels is dominated by this R^{-5} term. Therefore, the $B\ 0_u^+({}^3\Pi)$ potential cannot have a barrier maximum, $D_0=12\ 440.9\pm 1.1\ \text{cm}^{-1}$ for the ground elec-

tronic state, and the state giving rise to the uv convergence-limit resonance series must have a potential barrier $\approx 11.5\pm 3\ \text{cm}^{-1}$ high.

III. Reassignment of the uv Resonance Series at the Convergence Limit

A. The Need for a Reassignment

The data considered for reassignment are the lines in the convergence limit portion of Verma's resonance series IVb, presented in his Table V.¹ He concluded that the lower state of this series was the ground electronic state. While this is unquestionably the case for the other five uv resonance series observed, it is shown below that this assignment is quite implausible for the series in question.

The theoretical C_5 for the ground $X\ 0_g^+({}^1\Sigma)$ state of I_2 is zero^{13,15}; hence, the moderately long-range forces are dominated by the attractive second-order perturbation terms (C_6 , C_8 , and C_{10}). Since the exchange forces are also attractive (as is evidenced by the deep potential well), this state cannot have a potential maximum. Therefore, the final state of the uv convergence-limit resonance series cannot be the ground state.

A more qualitative objection to the original assignment is based on the Franck-Condon accessibility of the final levels. Verma's Fig. 1(g)¹ shows that the emission into the 18 adjacent levels at the dissociation limit has roughly constant intensity. Therefore, it seems strange that none of the 13 levels immediately below his $v''=98$ would be sufficiently accessible from the upper state to allow measurable emission. The observed behavior suggests that Verma's $v''=98$ is actually the lowest vibrational level of some excited electronic state.

A final argument against the $X\ 0_g^+({}^1\Sigma)$ assignment is based on the expected behavior of a Birge-Sponer plot for vibrational levels lying near the dissociation limit. It has been shown that when the outer branch of the potential in this region is a short sum of attractive inverse-power terms, the plot should have positive (upward) curvature.^{8,16} For the ground state of I_2 this positive curvature is observed above $v''=73$ and increases from there up to $v''=82$ (the highest well-known level below the convergence-limit resonance series), where it equals $0.060\ \text{cm}^{-1}$.¹² For this state, the theory suggests⁸ that above the point of inflection at $v''=73$ the curvature $[d^3G(v)/dv^3]$ should increase, perhaps pass through a slight maximum, and asymptotically approach a constant value of $94/(C_6)^{1/2}\ \text{cm}^{-1}$ (where C_6 is in $\text{cm}^{-1}\ \text{\AA}^6$).¹⁷ For a reasonable C_6 of $3.0\times 10^{+6}\ \text{cm}^{-1}\ \text{\AA}^6$, this asymptotic curvature would be $0.054\ \text{cm}^{-1}$. On the other hand, the level spacings in the convergence limit resonance series show negligible curvature ($\lesssim 0.001\ \text{cm}^{-1}$; see

TABLE I. $I_2[0_v^+(^3\Pi)]$ vibrational energies (in cm^{-1}) expressed relative to the $v''=0, J''=0$ level of the ground state.

v'	E	v'	E	v'	E
0	12 362.4	6	12 413.6	12	12 444.0
1	12 372.5	7	12 420.1	13	12 447.2
2	12 381.9	8	12 426.0	14	12 449.7
3	12 390.5	9	12 431.4	15	12 451.5
4	12 399.0	10	12 436.1	16	12 452.9
5	12 406.6	11	12 440.4	17	12 453.7

Fig. 2).¹⁸ This strengthens the argument that these levels cannot belong to the ground state.

Theory shows⁸ that vibrational levels lying near the dissociation limit, which yield a linear Birge-Sponer plot, correspond to a long-range potential which is either exponential or is dominated by an effective inverse-power term R^{-n} with n being large ($n \gg 10$).¹⁹ This high effective power is qualitatively the type of behavior one would expect on the inner side of a potential barrier arising from a sum of attractive and repulsive inverse power terms.

B. The Reassignment

The final state to which the levels in question belong must have a potential barrier of height $\approx 11.5 \pm 3 \text{ cm}^{-1}$ as well as an attractive well, and must correlate with two ground-state $^2P_{3/2}$ atoms. Nine states in addition to the ground state correlate with two ground-state atoms; of these, three are nondegenerate and six are doubly Ω degenerate.²⁰ The nature of the emission and absorption spectrum of Verma's upper state clearly indicates that it is 0_u^+ .²¹ Therefore, the $\Delta\Omega = 0, \pm 1$ electronic selection rule immediately removes two possible assignments. In addition, the gerade-ungerade symmetry selection rules for electric dipole²³ transitions ($g \leftrightarrow u, g \leftrightarrow g, u \leftrightarrow u$)²⁴ leave the $0_v^+(^3\Pi)$ and $1g(^3\Pi)$ states as the only electronically allowed assignments.

The rotational selection rules for transitions from a 0_u^+ state into singly degenerate 0_g^+ or doubly

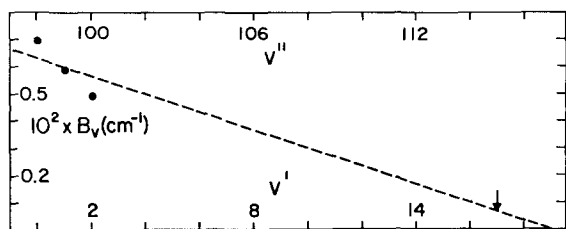


FIG. 1. Rotational constants for final state of convergence-limit resonance series. The v'' numbering corresponds to Verma's $X 0_v^+(^1\Sigma)$ assignment¹ and v' numbering to the present $0_v^+(^3\Pi)$ assignment. ● are Verma's experimental values, and the arrow denotes the highest observed level.

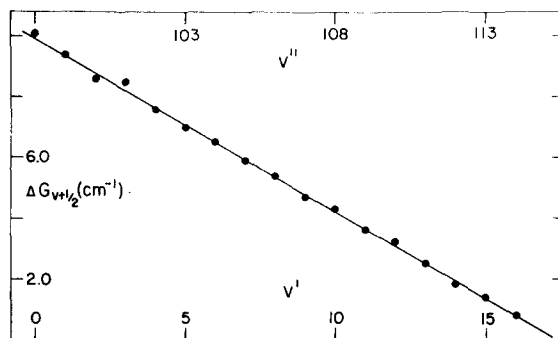


FIG. 2. Vibrational spacings of levels in convergence-limit resonance series. v'' represents the old $X 0_v^+(^1\Sigma)$ vibrational numbering¹ and v' the proposed $0_v^+(^3\Pi)$ numbering. The curve is generated from expression (2).

Ω -degenerate $1g$ states allow $\Delta J = \pm 1$ and $\Delta J = 0, \pm 1$ transitions, respectively. The first gives rise to doublet and the second to triplet structure. While transitions into the separate branches of the Ω doublet ($1g$) would correspond to $\Delta J = \pm 1$ and $\Delta J = 0$, respectively, the intensity of the Q branch ($\Delta J = 0$) is theoretically twice that of the P or R branches, so this spectrum would be observed as either the full triplet or as a singlet.²⁴ Verma was able to resolve the structure of the emission into the three lowest levels of the convergence-limit series, and it is clearly doublet in nature. Therefore, the only completely allowed reas-

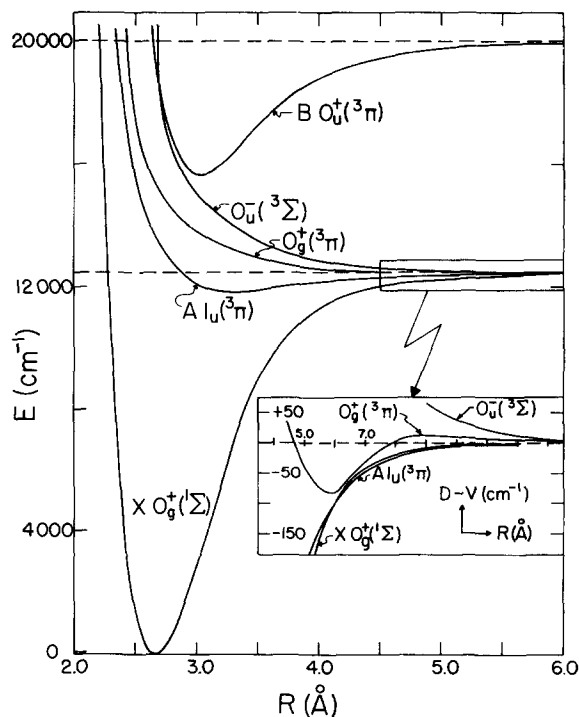


FIG. 3. Schematic potential curves for $0_v^+(^3\Pi)$ and some neighboring states. The zero of energy is the $v''=0, J''=0$ level of the ground electronic state.

signment of the levels in question is to the $0_g^+(^3\Pi)$ state.

The theoretical long-range R^{-5} term for the $0_g^+(^3\Pi)$ state is repulsive,^{13,15} while its R^{-6} , R^{-8} , and R^{-10} terms are attractive¹⁴; thus it seems plausible that it will have an attractive well bounded by a potential maximum. On the other hand, the theoretical C_5 for this state ($2.3 \times 10^5 \text{ cm}^{-1} \text{ \AA}^5$)^{13,15} is too small to yield a $11.5 \pm 3 \text{ cm}^{-1}$ barrier at large R , either alone or when the competing attractive R^{-6} term is taken into account.²⁵

Although the origin of the potential barrier is somewhat uncertain, the reassignment of the uv convergence-limit resonance series to the $0_g^+(^3\Pi)$ state still seems much more likely than its original assignment as $X 0_g^+(^1\Sigma)$. The validity of this reassignment will now be assumed and the concomitant properties of the $0_g^+(^3\Pi)$ state will be considered.

IV. THE $0_g^+(^3\Pi)$ STATE

This state was previously observed by Venkateswarlu²² in diffuse bands arising as emission from discrete levels of the previously mentioned highly excited 0_u^+ state. Venkateswarlu concluded that its potential was repulsive in the neighborhood of the minimum of the ground-state potential, and that it lay below and to the left of the $B 0_u^+(^3\Pi)$ curve.²² This same conclusion was also inferred from considerations involving the quenching of B -state fluorescence.²⁶

Due to this intermediate-range repulsiveness of the $0_g^+(^3\Pi)$ curve, its potential minimum must lie at reasonably large R , and the well is unlikely to be very deep. The noncrossing rule which forbids it from crossing the ground-state $X 0_g^+(^1\Sigma)$ curve also implies that the well must be quite shallow. In view of this and of the roughly constant intensity of the emission into the observed levels, it seems probable that the lowest observed level is $v''=0$. If this numbering is incorrect, it seems unlikely that it would be more than one or two units too small.

The energies and assumed vibrational assignments of the convergence limit levels are given in Table I. The small rotational energy contributions to the observed lines were removed after extrapolating beyond the three experimental B_v values in the manner shown in Fig. 1. Utilizing Fig. 1 to obtain B_v values, rather than the approach of Ref. 1, places the convergence limit of this series at $12\,454.0 \pm 0.3 \text{ cm}^{-1}$ (1.6 cm^{-1} higher than the previous estimate). This yields $13.1 \pm 1.4 \text{ cm}^{-1}$ as a better estimate of the height of the potential maximum. Six of the 18 observed levels are metastable (for $J'=0$), being bound only by this potential barrier.

Using the above vibrational assignment, the vibrational energies may be represented within a standard error of $\pm 0.08 \text{ cm}^{-1}$ by

$$E(v'') = 12\,357.3 + 10.522(v' + \frac{1}{2}) - 0.2866(v' + \frac{1}{2})^2, \quad (2)$$

where the energy zero is the $v''=0, J''=0$ level of the ground state. This shows that this state has a potential well at least $83.6 \pm 1.1 \text{ cm}^{-1}$ deep (relative to the dissociation limit, not the potential maximum). Furthermore, the observed rotational splittings would place the potential minimum at $6.0 \pm 0.6 \text{ \AA}$. The experimental vibrational spacings are compared with those calculated from expression (2) in Fig. 2. The curve suggests that there may exist one more, as yet unobserved, quasibound state.

The potential curve for $0_g^+(^3\Pi)$ is shown schematically in Fig. 3, together with curves for a number of neighboring states. The ground-state potential up to $11\,933 \text{ cm}^{-1}$ and the $B 0_u^+(^3\Pi)$ -state potential up to $19\,705 \text{ cm}^{-1}$ are RKR potentials (taken from Ref. 12, and Refs. 4 and 6, respectively). The $0_u^-(^3\Sigma)$ curve was taken from Ref. 27 and the $A 1u(^3\Pi)$ curve is based on the conclusions of Brown.²⁸ At large distances the $A 1u(^3\Pi)$ and $X 0_g^+(^1\Sigma)$ curves must cross, since the latter dies off as R^{-6} and the former as R^{-5} . Furthermore, the $A 1u(^3\Pi)$ curve may also cut across the $0_g^+(^3\Pi)$ well. The theoretical C_5 for $0_u^-(^3\Sigma)$ is a third larger than that for $0_g^+(^3\Pi)$,^{13,15} so these curves should not cross at long range.

V. CONCLUSIONS

It has been shown that contrary to the original assignment, a portion of the uv resonance spectrum of I_2 does not correspond to emission into the ground electronic state. The most probable reassignment for the levels in question was found to be $0_g^+(^3\Pi)$. This state appears to be an example of a van der Waals²⁹ molecule (bound only by the moderately long-range dispersion forces³⁰) which has a potential barrier. An improved estimate of the ground-state dissociation energy is $D_0 = 12\,440.9 \pm 1.1 \text{ cm}^{-1}$.

If the present reassignment is correct, Verma's uv spectrum¹ is the first observation of the discrete levels of the $0_g^+(^3\Pi)$ state. These levels clearly cannot be observed in absorption from the ground state because of the $g \leftrightarrow g$ symmetry selection rule. However, they may be observable in near ir fluorescence (at around 1.4μ) from some of the higher levels of the $B 0_u^+(^3\Pi)$ state. One restriction to this type of measurement is that the fluorescing state cannot have a very high rotational quantum number, as in this case the centrifugal potential would bury the shallow $0_g^+(^3\Pi)$ well. However, if appropriate $B 0_u^+(^3\Pi)$ levels can be excited, these $0_g^+(^3\Pi)$ levels may be observed together with neighboring $X 0_g^+(^1\Sigma)$ levels, giving direct confirmation of the proposed reassignment.

ACKNOWLEDGMENTS

I am pleased to acknowledge pertinent discussions with Dr. A. S. Dickinson; the comments, encouragement, and support of Professor R. B. Bernstein; and

helpful correspondence with Professor J. I. Steinfeld. I am also deeply indebted to Professor R. D. Verma for some very telling criticisms of an early version of this paper.

* Research supported by National Science Foundation Grant GP-7409 and National Aeronautics and Space Administration Grant NGL-50-002-001.

¹ R. D. Verma, *J. Chem. Phys.* **32**, 738 (1960).

² Throughout, double primed quantities will refer to the ground electronic state and single primed quantities to an excited electronic state.

³ This step is necessary because $B\ 0_u^+(^3\Pi)$ dissociates to $^2P_{3/2} + ^2P_{1/2}$, while the ground X state dissociates to $^2P_{3/2} + ^2P_{3/2}$.

⁴ In their recent measurements of the $B\ 0_u^+(^3\Pi) \leftarrow X\ 1\Sigma_g^+$ absorption spectrum, J. I. Steinfeld, J. D. Campbell, and N. A. Weiss [*J. Mol. Spectry.* **29**, 204 (1969)] reported long P and R branches for the 43-0 and 49-1 bands. However, the energy thus obtained for level $v'=49$ is 11 cm^{-1} smaller than that reported by Brown,⁵ and 8.5 cm^{-1} smaller than the earlier value of R. Mecke [*Ann. Phys.* **71**, 104 (1923)]. It appears [J. I. Steinfeld concurs in this conclusion (private communication, 1969)] that Steinfeld *et al.*'s 49-1 band should be reassigned as 57-2, since this assumption yields a $v'=57$ energy which is only 2.6 cm^{-1} smaller than Brown's⁵ value and 0.4 cm^{-1} larger than Mecke's.

⁵ W. G. Brown, *Phys. Rev.* **38**, 709 (1931). The accepted vibrational numbering for the B state has recently been revised,⁶ so the numbering used by Brown should be decreased by one.

⁶ J. I. Steinfeld, R. N. Zare, L. Jones, M. Lesk, and W. Klemperer, *J. Chem. Phys.* **42**, 25 (1965); R. L. Brown and T. C. James, *ibid.* **42**, 33 (1965).

⁷ The extrapolation procedure is based on a new method for determining long-range forces from vibrational spacings, which is reported elsewhere.⁸

⁸ R. J. LeRoy and R. B. Bernstein, *Wisc. Theoret. Chem. Inst. Tech. Rept. WIS-TCI-362* (1969); *J. Chem. Phys.* (to be published). The extrapolation to the dissociation limit of the B state is discussed in more detail by the same authors in *Chem. Phys. Letters* (to be published), and in *Wisc. Theoret. Chem. Inst. Tech. Rept. WIS-TCI-369* (1970).

⁹ C. Moore, *Natl. Bur. Std. (U.S.), Circ.* **467**, Vol. 3, 105 (1958). The results quoted are based on the data of C. C. Kiess and C. H. Corliss [*J. Res. Natl. Bur. Std.* **63A**, 1 (1959)].

¹⁰ This value agrees fairly well with Brown's⁵ $12439 \pm 8\ \text{cm}^{-1}$, because although his extrapolation to the dissociation limit is $\approx 7\ \text{cm}^{-1}$ too short, his value of the spin-orbit splitting (7598 cm^{-1}) was 5 cm^{-1} too small.

¹¹ The slight difference with Verma's¹ $12\ 452.5 \pm 1.5\ \text{cm}^{-1}$ arises from the use of a slightly different frequency for the line exciting the resonance series (see Ref. 12), and the use of the $J=26$ rotational energy rather than $J=24$.

¹² R. J. LeRoy, *J. Chem. Phys.* **52**, 2683 (1970), following paper.

¹³ T. Y. Chang, *Rev. Mod. Phys.* **39**, 911 (1967).

¹⁴ J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954). The expression for the second-order perturbation energy derived in Sec. 13.3b is negative for all states formed from two ground-state atoms.

¹⁵ J. K. Knipp, *Phys. Rev.* **53**, 734 (1938).

¹⁶ This was noted previously by H. Harrison and R. B. Bernstein [*J. Chem. Phys.* **38**, 2135 (1963)] for the cases of Lennard-Jones (12,6) and $\exp(\alpha,6)$ potentials, both of which have R^{-6} tails.

¹⁷ This is true because the long-range potential for the ground state is described by expression (1) with $C_3=0.0^{13,16}$ and $C_6, C_8,$ and C_{10} all attractive (negative).¹⁴

¹⁸ A third-order least-squares fit to these energies (see Table I) had the same standard error as a second-order fit (0.08 cm^{-1}) and yielded a curvature of only 0.0012 cm^{-1} . A curvature rate of 0.054 cm^{-1} over the 18 observed levels would add 7.8 cm^{-1} to $dG/dv[\Delta G(v)]$ for the highest observed level over the value obtained by linearly extrapolating from the lowest dG/dv values. For a curvature of 0.0012 cm^{-1} , this effect is reduced to 0.17 cm^{-1} .

¹⁹ The potential is assumed to be fitted to an expression of the form A/R^n+B .

²⁰ R. S. Mulliken, *Phys. Rev.* **36**, 599 (1930). Case c coupling is assumed.

²¹ This upper state has been previously observed in absorption by H. Cordes [*Z. Physik* **97**, 603 (1935)], and in emission by P. Venkateswarlu.²² This electronic assignment was not questioned in the later analyses by L. Mathieson and A. L. G. Rees [*J. Chem. Phys.* **25**, 753 (1956)] and by A. Nobs and K. Wieland [*Helv. Phys. Acta* **39**, 564 (1966)].

²² P. Venkateswarlu, *Proc. Indian Acad. Sci.* **24A**, 480 (1946). The author would like to thank R. D. Verma for bringing this reference to his attention.

²³ The intensity of the observed emission indicates that the transitions could only be electric dipole.

²⁴ G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Co., Inc., Toronto, Canada, 1950), 2nd ed.

²⁵ F. E. Cummings has developed a new method of calculating R^{-6} terms, and applied it to the different states of I_2 correlating with two ground-state atoms. This work was presented at the 24th Symposium on Molecular Structure and Spectroscopy, Ohio State University, Columbus, Ohio, September 1969; the present author is grateful to Dr. Cummings for making his results available in advance.

²⁶ J. E. Selwyn and J. I. Steinfeld, *Chem. Phys. Letters* **4**, 217 (1969).

²⁷ E. O. Degenkolb, J. I. Steinfeld, E. Wasserman, and W. Klemperer, *J. Chem. Phys.* **51**, 615 (1969).

²⁸ W. G. Brown, *Phys. Rev.* **38**, 1187 (1931).

²⁹ See Ref. 24, p. 377.

³⁰ This seems rather likely since the $0_v^+(^3\Pi)$ potential well is quite shallow, and its $R_{EQ} \approx 6\ \text{\AA}$ is considerably larger than the 2.66 \AA for the ground $X\ 0_v^+(^1\Sigma)$ state,¹² 3.03 \AA for the $B\ 0_u^+(^3\Pi)$ state,⁴ and $\approx 3.2\ \text{\AA}$ for the $A\ 1u(^3\Pi)$ state.²⁸