

Molecular Constants and Internuclear Potential of Ground-State Molecular Iodine*

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A reanalysis of the spectroscopic data for ground-state iodine yields improved rotational constants and vibrational energies which are used to compute a new RKR potential. Polynomial representations of the vibrational energies and rotational constants are presented which fit all the data to within the respective experimental precision of Verma and of Rank and Baldwin. New approaches are introduced for separately obtaining the rotational B_v and D_v constants and for estimating error bounds for computed RKR turning points.

INTRODUCTION

In 1960 Verma¹ reported some remarkable measurements of several series of uv-resonance emission doublets in the spectrum of I_2 , excited in an electric discharge. Although the final state of one of these resonance series has recently been reassigned as $0_v^+(^3\Pi)$,² the remaining lines thoroughly catalogue the levels of ground-state $X\ 0_v^+(^1\Sigma)I_2$ up to within 4% of the dissociation limit. Because of this remarkably complete set of data, the ground state of I_2 has become almost a touchstone of RKR potential calculations.^{1,3-5}

In the present work, the data for the ground state are handled somewhat differently than was done previously, and discrepancies of up to 6.6 cm^{-1} were found between the vibrational energies obtained here and the earlier results.¹ Since the reported ground-state RKR potential curves^{1,3-5} are based on this earlier energy spectrum,¹ all will be somewhat in error. Furthermore, most of these curves^{1,3,4} were calculated all the way to the dissociation limit by utilizing the energies of a set of levels which recently has been reassigned to another electronic state.² An improved energy spectrum and RKR potential will be presented which are based on both the uv-resonance data¹ and the more accurate, but restricted (to $v \leq 22$), green-line resonance data of Rank and Baldwin.⁶

SELECTION OF EXPERIMENTAL DATA

The raw data used in the present analysis consisted of the green-line resonance doublets measured by Rank and Baldwin⁶, and five of the six uv-resonance doublet series reported by Verma.^{1,8} The former measurements are relatively accurate, being reported to 0.001 cm^{-1} , though they only describe levels $v = 0-22$. On the other hand, while the uv measurements span the region from $v = 0-84$, they were reported only to an accuracy of 0.01 cm^{-1} . Because of this difference in precision, only the green-line data were used in determining the vibrational energies and rotational B_v constants for $v \leq 22$. In addition, all of the blended uv lines were omitted from consideration⁹, as well as three lines which the present analysis suggests were misassigned.¹⁰

THE ROTATIONAL CONSTANTS

Values of B_v constants are obtained from the experimental $P-R$ doublet branch splittings

$$\Delta\nu_{P-R}(v, J_r) = (4J_r + 2)[B_v - 2(J_r^2 + J_r + 1)D_v], \quad (1)$$

where $\Delta\nu_{P-R}(v, J_r)$ is the observed doublet splitting for vibrational level v , in the resonance series characterized by rotational quantum number J_r . In the original analysis of the uv data,¹ Verma tried to obtain a polynomial representation for the D_v constants by fitting the splittings for different J_r directly to (1). However, in Ref. 7 it was pointed out that this approach is not very meaningful, because the effect of the D_v values on the splittings is less than the experimental precision. On the other hand, significant information on the D_v 's can still be obtained, because while the effect of this term on the doublet splittings varies as $\approx 8 \times J_r^3$, its effect on the vibrational energies varies as $\approx J_r^4$. For the $J_r = 87$ resonance series this difference is particularly significant.

Since the D_v constants are known to be small,^{1,7} they will affect the observed splittings only slightly. Hence, to a first approximation they can be replaced by any plausible set of trial values $\{D_v^{(n)}\}$, yielding

$$B_v^{(n)} = [\Delta\nu_{P-R}(v, J_r)/(4J_r + 2)] + 2(J_r^2 + J_r + 1)D_v^{(n)} \\ = B_v - 2(J_r^2 + J_r + 1)(D_v - D_v^{(n)}) \approx B_v. \quad (2)$$

These estimates of the exact D_v and B_v values may then be applied to the data for resonance series $J_r = J_2$ to yield an apparent vibrational energy for level v , $G_{J_2}^{(n)}(v)$. Comparison of the apparent vibrational energies obtained from the data for two different resonance series then yields improved estimates of D_v :

$$D_v^{(n+1)} = D_v^{(n)} + \left(\frac{G_{J_1}^{(n)}(v) - G_{J_2}^{(n)}(v)}{(J_2^2 + J_2)^2 - (J_1^2 + J_1)^2} \right) \\ = D_v - (D_v - D_v^{(n)}) \left(\frac{2\langle J_r^2 + J_r + 1 \rangle_v}{J_2^2 + J_2 + J_1^2 + J_1} \right). \quad (3)$$

Here $\langle J_r^2 + J_r + 1 \rangle_v$ is an average for the \bar{n} different resonance series contributing splittings at levels near v .¹¹

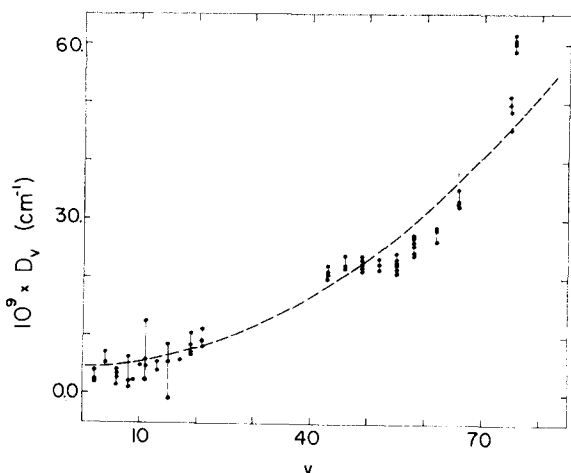


Fig. 1. D_v vs v for ground-state $X^1\Sigma_g^+ I_2$. ●, empirical points; ---, curve from expression (5).

These $D_v^{(n+1)}$ values may then be substituted into the first part of (2) to yield improved $B_v^{(n+1)}$ values, ... etc. The error in a $D_v^{(n)}$ value obtained after n such iterations is

$$D_v^{(n)} - D_v = (D_v^{(0)} - D_v) \left(\frac{2\langle J_r^2 + J_r + 1 \rangle_v}{J_2^2 + J_2 + J_1^2 + J_1} \right)^n.$$

Clearly the sequence $\{D_v^{(0)}, B_v^{(0)}\}$, $\{D_v^{(1)}, B_v^{(1)}\}$, ... etc. will converge to the exact $\{D_v, B_v\}$ as long as

$$f \equiv 2\langle J_r^2 + J_r + 1 \rangle_v / (J_2^2 + J_2 + J_1^2 + J_1) < 1.$$

In applying (3), apparent vibrational energies from the $J_2=87$ resonance series were compared in turn to those yielded by each of the $J_1=49, 46, 25$, and 23 series, for all levels $0 \leq v \leq 82$.¹² In applying (2), for $v < 22$ only the green-line resonance splittings were used (i.e., $J_r=34$ only)¹³; therefore, in this region $f \lesssim 0.3$ and the $\{D_v^{(n)}, B_v^{(n)}\}$ sequence will converge quite quickly. Analogously, for $v \geq 43$ the $J_r=87, 49$, and 46 splittings are weighted about equally; hence $f \approx 0.85$, and the sequence will converge here also. However, $f \approx 2$ for $22 < v < 43$, since in this region only the $J_r=87$ splittings were measured with high precision.¹⁴ Therefore, Eq. (3) was only applied to the data for $v \leq 22$ and $v \geq 43$, while $D_v^{(n)}$ values in the intermediate region were obtained by interpolation.

In applying the above stepwise convergence procedure, the individual values of $D_v^{(n)}$ and $B_v^{(n)}$ were always represented by polynomials in $(v + \frac{1}{2})$ before utilizing them in the next step. The values of $D_v^{(n)}$ were represented by

$$D_v^{(n)} = D_e^{(n)} + \beta_e^{(n)}(v + \frac{1}{2}) + d_2^{(n)}(v + \frac{1}{2})^2,$$

where $D_e^{(n)}$ and $\beta_e^{(n)}$ were calculated from the other spectroscopic constants using the expressions given by Herzberg,¹⁵ and $d_2^{(n)}$ was obtained from a least-

squares fit to the data.¹⁶ The convergence of $d_2^{(n)}$ to an asymptotic value was used as the criterion of convergence for the $\{D_v^{(n)}, B_v^{(n)}\}$ sequence.

The high accuracy of the green-line splitting for $v < 22$ relative to the uv splittings used for $v > 22$ was retained in the polynomial representation of the $B_v^{(n)}$ constants. First, a second-order least-squares fit to the green-line data for $v < 22$ ¹⁷ yielded approximate values of the three lowest-order polynomial coefficients, B_e , α_e , and γ_e . Next, the contributions of these terms [i.e., $B_e - \alpha_e(v + \frac{1}{2}) + \gamma_e(v + \frac{1}{2})^2$] were subtracted from the 79 individual $B_v^{(n)}$ values¹⁸ and the remainders fitted to an expression of the form

$$R(v) = \delta_e(v + \frac{1}{2})^3 + \epsilon_e(v + \frac{1}{2})^4.$$

Then the contributions of these initial δ_e and ϵ_e values were subtracted from the $B_v^{(n)}$ values for $v < 22$ and these remainders fitted to a quadratic, yielding improved estimates of B_e , α_e , and γ_e . This cycle was then repeated until the polynomial coefficients converged.¹⁹

The above $\{D_v^{(n)}, B_v^{(n)}\}$ convergence procedure was applied three times, using polynomial representations of the $B_v^{(n)}$ constants with maximum order $M=3, 4$, and 5 , respectively.¹⁹ In each case, the initial trial D_v values were $\{D_v^{(0)}=0\}$. The results are shown in Table I.

In the above manner, the following mutually consistent expressions were found to best represent the rotational constants B_v and D_v (in cm^{-1}):

$$B_v = 3.7395 \times 10^{-2} - 1.2435 \times 10^{-4}(v + \frac{1}{2}) \\ + 4.498 \times 10^{-7}(v + \frac{1}{2})^2 - 1.482 \times 10^{-8}(v + \frac{1}{2})^3 \\ - 3.64 \times 10^{-11}(v + \frac{1}{2})^4, \quad (4)$$

$$D_v = 4.54 \times 10^{-9} + 1.7 \times 10^{-11}(v + \frac{1}{2}) \\ + 7 \times 10^{-12}(v + \frac{1}{2})^2. \quad (5)$$

Expression (4) represents the experimental B_v values [obtained by substituting (5) into (1)] within a standard error of $\pm 0.24 \times 10^{-4} \text{ cm}^{-1}$ for $v < 22$, and $\pm 3.2 \times 10^{-4}$ for $v \geq 22$. Figure 1 contrasts a plot of expression (5) with the final D_v values obtained from expression (3). Utilizing the first term of (4) in the

TABLE I. Results of $\{D_v^{(n)}, B_v^{(n)}\}$ convergence using different polynomial fits to the $B_v^{(n)}$ values.¹⁹ ERR is the standard error of the D_v representation. All quantities are in cm^{-1} .

Order M	B_v representation		D_v representation	
	$10^9 \times B_e$	$10^4 \times \alpha_e$	$10^9 \times \text{ERR}$	$10^9 \times d_2$
3	3.7397	1.2519	6.7	0.004 ₈
4	3.7395	1.2435	4.4	0.007 ₂
5	3.7399	1.2652	4.4	0.007 ₀

TABLE II. Absorption lines exciting observed resonance series. $R(33)$ is for the green-line series⁶ and the others for the uv series.¹

Line	$R(33)$	$P(47)$	$R(48)$	$P(23)$	$R(24)$
ν_e (cm ⁻¹)	18 307.487	54 633.216	54 633.155	54 633.203	54 633.182

usual manner,¹⁵ one obtains an equilibrium internuclear distance of $R_{\text{EQ}} = 2665_7$ Å for ground state I_2 .

THE VIBRATIONAL CONSTANTS

A shift of B_v values for $v > 22$ generated from expression (4) by one standard error, $\pm 3.2 \times 10^{-4}$ cm⁻¹, changes vibrational energies obtained from the resonance series characterized by $J_r = 87$ by $\approx \mp 2.5$ cm⁻¹, while affecting energies obtained from the other (uv) series by between ∓ 0.15 and ∓ 0.8 cm⁻¹ (corresponding to $J_r = 22$ and 49, respectively). In view of this, the $J_r = 87$ data were not utilized at all in the determination of the vibrational spectrum and constants for the ground state. This means that the highest level fitted is $v = 82$, although the highest level observed is $v = 84$.

Utilizing expressions (4) and (5), a vibrational ladder may be constructed from the data for each of the five remaining resonance series, $J_r = 49, 46, 34, 25$, and 22. Unfortunately, the emission lines corresponding to the inverse of the five molecular transitions exciting the various series are masked by the intense atomic lines. Also, the atomic emission and molecular absorption lines have a significant width,²⁰ so that the peaks of the latter need not coincide with those of the former.

In the present work, improved values for the peak energies of the exciting molecular transitions were obtained by shifting the five independent vibrational ladders so as to minimize disagreement,²¹ yielding the frequencies given in Table II. A weighted average value for the 4 uv series is $54\,633.18$ cm⁻⁶. This lies between the center of the atomic line which is the source of the uv light, $54\,633.46$ cm⁻¹,²² and the value $\nu_e = 54\,632.93$ cm⁻¹ used in the original analysis¹ as the single excitation frequency for all 6 uv resonance series.

The above procedure, combined with the method of obtaining the D_v values,¹² yields a fairly high degree of internal consistency between the results for different resonance series. The statistical scatter in the B_v values for $v > 22$, $\pm 3.2 \times 10^{-4}$ cm⁻¹, could give rise to differences of ∓ 0.6 cm⁻¹ between vibrational energies calculated from the $J_r = 49$ and 22 series. However, the disagreement actually found is always less than 0.15 cm⁻¹ for $v < 74$, while for $74 \leq v \leq 82$, where the rotational data is least reliable, the spread never exceeds 0.5 cm⁻¹.

Vibrational energies obtained by applying expres-

sions (4) and (5) to the data were fitted to a polynomial in $(v + \frac{1}{2})$ to yield the customary representation ($\omega_e, \omega_e x_e \dots$ etc.). An iterative procedure was used to obtain a single self-consistent set of constants which reflected the higher accuracy of the green-line data used for $v \leq 22$. The approach was similar to that used for obtaining the B_v representation. The coefficients of terms of order up to five were based mainly on the $v \leq 22$ data and those of order six to nine mainly on the uv data ($22 \leq v \leq 82$). In addition, an external constraint²³ was applied to force the vibrational constants to yield roughly the known dissociation limit.²

The final expression obtained for the vibrational energies is²⁴ (in cm⁻¹)

$$\begin{aligned}
 G(v) = & 214.5481(v + \frac{1}{2}) - 0.616259(v + \frac{1}{2})^2 \\
 & + 7.507 \times 10^{-5}(v + \frac{1}{2})^3 - 1.263643 \times 10^{-4}(v + \frac{1}{2})^4 \\
 & + 6.198129 \times 10^{-6}(v + \frac{1}{2})^5 - 2.0255975 \times 10^{-7}(v + \frac{1}{2})^6 \\
 & + 3.9662824 \times 10^{-9}(v + \frac{1}{2})^7 - 4.6346554 \times 10^{-11}(v + \frac{1}{2})^8 \\
 & + 2.9330755 \times 10^{-13}(v + \frac{1}{2})^9 - 7.61000 \times 10^{-16}(v + \frac{1}{2})^{10}.
 \end{aligned}
 \tag{6}$$

This fits the 30 green-line data for $v \leq 22$ with a standard error of $\pm 0.004_6$ cm⁻¹, and the 146 (uv) data for $22 < v \leq 82$ with a standard error of ± 0.14 cm⁻¹, within the ranges of the respective experimental uncertainties. However, the extrapolated eigenvalues are probably not reliable much beyond $v \approx 85$.

RKR POTENTIAL FOR GROUND STATE I_2

RKR calculations reported here were performed using a slightly modified version of the computer program reported by Zare.²⁵ This program was previously tested and found to yield a potential which reflects the input vibrational energies and rotational B_v 's with an accuracy better than that warranted by the data used here.²⁶ Values of the physical constants, taken from Cohen and DuMond,²⁷ yielded

$$\hbar / (4\pi c \mu) = 16.85749 / \mu \text{ (} \text{Å} \text{ cm}^{-1} \text{)},$$

where $\mu = 63.4377$ amu²⁸ is the reduced mass of the two nuclei.²⁹

A check of the plausibility of the potential by evaluating its first and second derivatives over the range of the inner turning points²³ showed the second derivatives to be negative for $v > 56$. This must be due to inaccuracy in the B_v constants in this region,

TABLE III. RKR turning points (in angstroms) for ground-state I₂. The energies $G(v)$ are in cm⁻¹.

v	$G(v)$	$R_1(v)$	$R_2(v)$	v	$G(v)$	$R_1(v)$	$R_2(v)$
0	107.120	2.61784	2.71750	30	5 932.60	2.3689	3.2176
1	320.435	2.58504	2.75807	32	6 274.60	2.3618	3.2443
2	532.515	2.56348	2.78741	34	6 610.06	2.3550	3.2713
3	743.356	2.54653	2.81214	36	6 938.78	2.3487	3.2986
4	952.952	2.53228	2.83419	38	7 260.56	2.3427	3.3264
5	1 161.296	2.51983	2.85444	40	7 575.21	2.3370	3.3546
6	1 368.379	2.50871	2.87339	42	7 882.51	2.3316	3.3835
7	1 574.194	2.49862	2.89134	44	8 182.20	2.3265	3.4132
8	1 778.731	2.48933	2.90850	46	8 474.05	2.3217	3.4436
9	1 981.980	2.48072	2.92502	48	8 757.78	2.3171	3.4751
10	2 183.932	2.47268	2.94101	50	9 033.11	2.3128	3.5076
11	2 384.577	2.46511	2.95655	52	9 299.72	2.3087	3.5413
12	2 583.905	2.45796	2.97172	54	9 557.29	2.3049	3.5765
13	2 781.904	2.45119	2.98656	56	9 805.50	2.3012	3.6133
14	2 978.564	2.44473	3.00113	58	10 043.98	2.2978	3.6520
15	3 173.874	2.43857	3.01545	60	10 272.39	2.2946	3.6928
16	3 367.822	2.43268	3.02958	62	10 490.37	2.2916	3.7360
17	3 560.397	2.42702	3.04352	64	10 697.57	2.2888	3.7819
18	3 751.586	2.42159	3.05732	66	10 893.66	2.2862	3.8310
19	3 941.377	2.41635	3.07099	68	11 078.35	2.2837	3.8837
20	4 129.756	2.41130	3.08454	70	11 251.40	2.2815	3.9406
21	4 316.709	2.40643	3.09801	72	11 412.60	2.2794	4.0021
22	4 502.223	2.40172	3.11140	74	11 561.84	2.2775	4.0689
24	4 868.87	2.3927	3.1380	76	11 699.11	2.2758	4.142
26	5 229.58	2.3843	3.1645	79	11 882.75	2.2734	4.264
28	5 584.20	2.3764	3.1910	82	12 040.40	2.2715	4.406

since they largely determine the absolute positioning of the pair of turning points for a given level, while the distance between a pair of turning points depends only on the relatively more accurate vibrational spacings. However, a good approximation to the potential may still be obtained by adding the relatively more accurate differences between the pairs of turning points [$R_2(v) - R_1(v)$] to inner turning points obtained by extrapolation from the region in which the two derivatives are acceptable. Consideration of the derivatives of the repulsive branch of the potential for $22 \leq v \leq 50$ showed that the best (integer) inverse-power fit to it corresponded to R^{-12} .³⁰ The expression $A/R^{12} + B$ was then fitted to the computed inner turning points at $v=49$ and 50 , yielding

$$V(R) = 2.921166 \times 10^8 / R^{12} - 3438.00. \quad (7)$$

Expression (7) was then used with expression (6) to generate "extrapolated" inner turning points $R_1(v)$ for $v > 50$ (i.e., $R < 2.313 \text{ \AA}$). The differences between the extrapolated and RKR turning points increased from 0.00016 \AA at $v=60$, to 0.0020 at $v=70$, to 0.0094 at $v=82$. Because of the magnitude of this correction and the steepness of the potential, the probable errors in the resulting inner turning points are insignificant.

Table III gives the RKR turning points computed from expressions (4) and (6) for $0 \leq v \leq 50$, and the adjusted turning points for $v > 50$ obtained by combining the extrapolated $R_1(v)$ values with the computed quantities [$R_2(v) - R_1(v)$]. The differences [$R_2(v) - R_1(v)$] depend solely on the vibrational spectrum and have approximate error bounds of $\pm 0.8 \times$

10^{-5} \AA for levels $v \leq 22$, and bounds ranging from ± 0.0003 to $\pm 0.003 \text{ \AA}$ as v increases from 23 to 82. On the other hand, the average of a pair of turning points $\frac{1}{2}[R_1(v) + R_2(v)]$ depends mainly on the less accurately known B_v constants. These averages have approximate error bounds of $\pm 0.0009 \text{ \AA}$ for $v \leq 22$, and bounds ranging from 0.01_3 to $\pm 0.02_3 \text{ \AA}$ for v increasing from 23 to 82.³¹ These bounds were obtained by applying the statistical standard errors of the fits of (4) and (6) to the data, to the expressions derived in the Appendix. It is important to note that the accuracies of the turning-point differences are significant, despite the relatively large uncertainties in the average values.

Consideration of the derivatives of the outer branch of the RKR potential for $v=80-82$ shows that in this region it is converging to the dissociation limit as $R^{-3.4}$.³⁰ On the other hand, the theoretical asymptotic long-range behavior of the potential for this state is $R^{-6.2}$. Therefore, the experimental results do not extend far enough to either confirm the long-range R^{-6} behavior or yield a value for the C_6 .³²

DISCUSSION

Vibrational energies generated from expression (6) differ significantly from those obtained by Verma in his original analysis of the uv spectrum.¹ His level spacings (see Table VI of Ref. 1)³³ yield energies relative to $v=0$ which are too high. The error ranges from 0.2 cm^{-1} at $v=10$ up to 6.6 cm^{-1} at $v=54$ and then decreases to 4.3 cm^{-1} by $v=82$. Verma appears to have based his vibrational spectrum on the spacings

TABLE IV. Comparison of calculated and observed disagreements with Zare's⁵ turning points. In all cases, δ represents subtraction of the present value from the previous value. $\Delta G_{v-1/2}$ and B_v are in cm^{-1} , while lengths are in angstroms.

v	$-\delta(\Delta G_{v-1/2})$	$10^5 \times \delta B_v$	$10^4 \times \delta [R_2(v) - R_1(v)]$		$10^4 \times \frac{1}{2} \delta [R_2(v) + R_1(v)]$	
			From (A1) and (A3)	Obs	From (A2) and (A4)	Obs
9	0.07	-2.4	0.8	0.0	8.	-2.2
19	-0.17	-1.0	-2.9	-2.4	4.	0.3
29	-0.24	-2.4	-5.7	-4.3	10.	1.4
39	-0.20	-6.9	-6.3	-7.5	31.	-1.6
49	-0.14	-14.2	-5.9	-6.4	65.	-3.4
59	0.21	-23.2	12.5	1.0	125.	9.7
69	-0.02	-31.9	-1.8	0.6	200.	60.0

of the 17 pairs of adjacent levels in the P branch of resonance series $J_v=49$. On the other hand, the present analysis fits 176 vibrational energies directly. The discrepancies between the results of these two approaches shows how a relatively large error can accumulate when attention is focused on the individual vibrational spacings, rather than on the vibrational ladder as a whole. These errors in the previously reported vibrational spectrum¹ are reflected in the previous RKR potentials^{1,3,5} in two ways. First of all, the differences $[R_2(v) - R_1(v)]$ are slightly in error (see Appendix); and more seriously, the turning points are correlated with incorrect energies.

The shift of the computed turning points above $v=50$, in the present work, has implications with regard to the accuracy of the B_v , D_v , and $G(v)$ representations [expressions (4)–(6)]. These shifts in the turning points actually correspond to small changes in the B_v values in this region. To be entirely consistent, new B_v values corresponding to the shifted turning points should have been derived and applied to yield new D_v values and vibrational energies. The maximum effect, occurring at $v=82$, would be a decrease of $1.04 \times 10^{-4} \text{ cm}^{-1}$ (0.5%) in B_{82} , and a concomitant decrease of $10 \times 10^{-9} \text{ cm}^{-1}$ (19%) in D_{82} and increase of 0.18 cm^{-1} in $G(82)$. However, aside from the change in D_{82} , these changes are effectively within the statistical standard error of the representations, and their effect on the turning point differences $[R_2(v) - R_1(v)]$ will be well within the stated bounds. Furthermore, these errors will drop quite sharply for lower vibrational levels and should be completely negligible for levels below $v \approx 74$.

Rotational B_v constants generated from (4) also differ with those reported previously.^{1,7} While the discrepancies are quite small for the lower levels, they increase steeply above $v \approx 60$. At $v=82$ the present $B_v=0.02190 \text{ cm}^{-1}$ is 1.4% larger than Verma's value and 5.7% larger than that of Rank and Rao.⁷ The main reason for this disagreement is the fact that the previous analyses used significantly smaller estimates for the D_v constants for the higher levels, while basing their B_v values in this region solely on the $J_v=87$ doublet splittings, which are relatively the

most sensitive to errors in D_v . While the preceding paragraph suggests that the present $B_{v=82}$ is too large by $\approx 0.5\%$, it will still be more accurate than values yielded by the previous analyses.

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APPENDIX: ACCURACY OF RKR TURNING POINTS

RKR turning points for a $J=0$ potential curve are obtained from the spectroscopic data through the expressions

$$f(v) = \left(\frac{\hbar}{4\pi c \mu} \right)^{1/2} \int_{-1/2}^v [G(v) - G(x)]^{-1/2} dx$$

$$= \frac{1}{2} [R_2(v) - R_1(v)],$$

$$g(v) = \left(\frac{4\pi c \mu}{\hbar} \right)^{1/2} \int_{-1/2}^v B_x [G(v) - G(x)]^{-1/2} dx$$

$$= \frac{1}{2} \{ [R_1(v)]^{-1} - [R_2(v)]^{-1} \},$$

where B_x and $G(x)$ are the rotational constant and vibrational energy for level x . Hence, to a first approximation, errors δE_x in $G(x)$ yield an apparent value of $f(v)$:

$$\left(\frac{\hbar}{4\pi c \mu} \right)^{1/2} \int_{-1/2}^v [G(v) - G(x) - \delta E_x]^{-1/2} dx$$

$$\approx \left\{ 1 + \frac{1}{2} \left\langle \frac{\delta E_x}{G(v) - G(x)} \right\rangle \right\} \frac{1}{2} [R_2(v) - R_1(v)].$$

Similarly, combining this effect with errors δB_x in the rotational constant B_v , the apparent value of $g(v)$ is

$$\left(\frac{4\pi c \mu}{\hbar} \right)^{1/2} \int_{-1/2}^v (B_x + \delta B_x) [G(v) - G(x) - \delta E_x]^{-1/2} dx$$

$$\approx \left\{ 1 + \left\langle \frac{\delta B_x}{B_x} \right\rangle + \frac{1}{2} \left\langle \frac{\delta E_x}{G(v) - G(x)} \right\rangle \right\}$$

$$\times \frac{1}{2} \{ [R_1(v)]^{-1} - [R_2(v)]^{-1} \}$$

The average of a pair of turning points is

$$\frac{1}{2}[R_1(v) + R_2(v)] = f(v)[1 + f(v)^{-1}g(v)^{-1}]^{1/2},$$

where the portion in parenthesis is dominated by the last term. Therefore, the errors in the difference and average of the turning points calculated for level v are

$$\delta[R_2(v) - R_1(v)] \approx \frac{1}{2} \langle \delta E_x / [G(v) - G(x)] \rangle [R_2(v) - R_1(v)], \quad (\text{A1})$$

and

$$\frac{1}{2} \delta[R_1(v) + R_2(v)] \approx -\frac{1}{2} \langle \delta B_x / B_x \rangle \frac{1}{2} [R_1(v) + R_2(v)]. \quad (\text{A2})$$

In cases where the errors δE_x and δB_x are small, the average values in (A1) and (A2) may be replaced by

$$\langle \delta E_x / [G(v) - G(x)] \rangle \approx -\delta(\Delta G_{v-1/2}) / \Delta G_{v-1/2}, \quad (\text{A3})$$

and

$$\langle \delta B_x / B_x \rangle \approx \delta B_v / B_v. \quad (\text{A4})$$

Also, approximate turning point error bounds are obtained if the numerators on the right-hand sides of (A3) and (A4) may be replaced by $\langle \delta E_x \rangle$ and $\langle \delta B_x \rangle$.

Expressions (A1)–(A4) were tested by comparing the turning points calculated in the present work with those reported by Zare.⁵ The latter were calculated using essentially the same computer program as was used here, and are probably the most accurate previous results.²⁶ However, Zare utilized Verma's reported vibrational spacings and B_v representation which are believed to be slightly in error (see Discussion, above). The comparison is shown in Table IV. For the differences $[R_2(v) - R_1(v)]$ the agreement is quite good except for $v=59$ and 69 , and there the discrepancy is anomalously large only because $\delta(\Delta G_{v-1/2})$ changes sign at $v=55$ and at $v=68$. On the other hand, there is no readily apparent reason for the relatively large discrepancies between the calculated and observed errors in the turning point averages, other than the fact that Eq. (A4) is a relatively much worse approximation than is Eq. (A3).

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

² R. J. LeRoy, *J. Chem. Phys.* **52**, 2678 (1970) (preceding paper.)

³ S. Weissman, J. T. Vanderslice, and R. Battino, *J. Chem. Phys.* **39**, 2226 (1963).

⁴ W. G. Richards and R. F. Barrow, *Trans. Faraday Soc.* **60**, 797 (1964).

⁵ R. N. Zare, *J. Chem. Phys.* **40**, 1934 (1964).

⁶ D. H. Rank and W. M. Baldwin, *J. Chem. Phys.* **19**, 1210 (1951). While this reference did not list the raw data, they were presented later by Rank and Rao.⁷

⁷ D. H. Rank and B. S. Rao, *J. Mol. Spectry.* **13**, 34 (1964).

⁸ The sixth series is the portion of Verma's IVb (listed in his Table V) which was reassigned in Ref. 2.

⁹ In addition to the lines so designated in Ref. 1, this includes 29 other lines which appear to be blended, based on comparison of the data in Tables I–IV of Ref. 1.

¹⁰ It appears that $R(21)$ was inadvertently set equal to $P(50)$, and consequently the actual $R(21)$ and $P(23)$ lines were misassigned as $R(24)$ and $P(26)$, respectively.

¹¹ This averaging is introduced by smoothing the individual $B_v^{(n)}$ values by representing them by a polynomial in $(v + \frac{1}{2})$ before using them to compute the $G_{J_r}^{(n)}(v)$ values. The individual $D_v^{(n)}$ values were similarly smoothed before use.

¹² The green-line ($J_r=34$) resonance data were omitted from these comparisons, since accurate relative positioning of these levels relative to those obtained from the uv measurements is impossible until good rotational constraints are obtained. $\nu_e = 54\,633.18 \text{ cm}^{-1}$ was used here as the single frequency exciting all the uv resonance series. Although this is slightly in error, the spread shown in Table II is considerably smaller than 0.27 cm^{-1} , the minimum effect of the D_v constant on $G(v)$ values.

¹³ This is on account of the higher accuracy of the green-line ($J_r=34$) as compared to the uv ($J_r=87, 49, 46, 25$, and 22) measurements.

¹⁴ At least one branch of every doublet of the other uv resonance series is blended in this region,¹ while the accurate green-line ($J_r=34$) data do not extend past $v=22$.⁷

¹⁵ G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Co., Inc., Toronto, Canada, 1950), 2nd. ed.

¹⁶ This rather simple representation was used because the scatter of the data both makes the theoretical values of D_e and β_e ¹⁶ somewhat more reliable than those obtained from a fit, and also precludes the use of a higher-order fit.

¹⁷ Since the analysis of Ref. 7 indicated that the uncertainties of the green-line splittings at $v=5, 8$, and 22 were considerably greater than those of other levels, the first two were omitted entirely from these fits, while the latter was included with the less precise uv splittings.

¹⁸ As was stated previously, the uv resonance data for $v < 22$ were excluded from these fits.

¹⁹ This approach of coupling a fit of order $0-N$ to the $B_v^{(n)}$ values based on the green-line data for $v < 22$, with a fit of order $(N+1)$ to M to the residuals for $0 \leq v \leq 82$, was tried for $N=1, 2$, and 3 and $M(>N)=3, 4, 5, 6$, and 7 . For all $M, N=2$ was much better than $N=1$ or 3 , while with $N=2$ the results were roughly equally good for $M=3, 4$, or 5 .

²⁰ Microphotometer traces of some uv emission lines (see Ref. 1) indicate that the reported molecular lines have a width at half-maximum of $\approx 0.8 \text{ cm}^{-1}$. Of this, the contribution from the Doppler effect is calculated to be 0.02 cm^{-1} (cf. 0.035 cm^{-1} for the absorbed atomic line). The remainder of the broadening must be due to collisional effects and Stark broadening in the discharge. Despite these effects, Verma was able to measure the peak positions of the molecular lines with an accuracy of $\pm 0.02 \text{ cm}^{-1}$ for sharp nonoverlapped lines, and from ± 0.07 to $\pm 0.14 \text{ cm}^{-1}$ for others.¹

²¹ In this procedure, the uv data for the whole range $0 \leq v \leq 82$ were used. On the other hand, the uv data for $v \leq 22$ were omitted from the analysis when the vibrational energies were being obtained.

²² C. C. Kiess and C. H. Corliss, *J. Res. Natl. Bur. Std.* **63A**, 1 (1959).

²³ R. J. LeRoy and G. Burns, *J. Mol. Spectry.* **25**, 77 (1968).

²⁴ The numbers of significant digits in the constants were chosen so that Eq. (6) would reproduce energies up to $v=82$ with a precision of $\pm 0.01 \text{ cm}^{-1}$, and energies up to $v=22$ with a precision of $\pm 0.001 \text{ cm}^{-1}$.

²⁵ R. N. Zare, University of California Lawrence Radiation Laboratory Rept. UCRL-10925, 1963.

²⁶ A given RKR potential may be tested by substituting it into the radial Schrödinger equation, solving exactly to get the vibrational energies $G(v)$ and expectation values $\langle v | R^{-2} | v \rangle$, and comparing these to the energies and B_v constants used as input in the RKR computations. Zare tested his program in this manner⁵ using Verma's results for the ground state of I_2 as the test case. He found that for the first thirty levels, the deviations of the vibrational energies were $\leq 0.09 \text{ cm}^{-1}$, while the deviations in the B_v values were $< 1 \times 10^{-6} \text{ cm}^{-1}$.

²⁷ E. R. Cohen and J. W. M. DuMond, *Rev. Mod. Phys.* **37**, 537 (1965).

²⁸ *Handbook of Chemistry and Physics*, R. C. Weast, Ed. (Chemical Rubber Publ. Co., Cleveland, Ohio, 1966), 47th ed.

²⁹ Using inexact values of the physical constants can have a real effect on the accuracy (through not the precision) of the RKR calculation. It was recently shown [R. J. LeRoy and R. B. Bern-

stein, J. Chem. Phys. 49, 4312 (1968)] that for the inverse problem of obtaining eigenvalues from a given potential, different authors obtained results differing by up to 0.7 cm^{-1} for the eigenstates of H_2 , on this account. Furthermore, use of the atomic reduced mass for H_2 rather than the nuclear reduced mass introduced errors of over $6. \text{ cm}^{-1}$.

³⁰ The potential was fitted to the expression $A/R^n + B$.

³¹ The actual errors in the $[R_1(v) \pm R_2(v)]$ values are probably somewhat smaller than is indicated by these bounds. The results in the Appendix suggest that this may be especially true for the average values $\frac{1}{2}[R_2(v) + R_1(v)]$.

³² The previously reported "experimental" C_6 values^{1,4} were

based on the data for the levels which have recently been re-assigned to the $0_g^+(^3\Pi)$ state. Furthermore, even ignoring this reassignment, they appear to have been rather inconsistently obtained. Verma¹ obtained the asymptotic C_6 from his RKR curve in the interval $4.6 < R < 6.4 \text{ \AA}$, while his potential for $6.4 < R < 8.8 \text{ \AA}$ converges significantly more slowly than his C_6/R^6 . On the other hand, the deviation between the observed (RKR) and calculated (based on their C_6) curves of Richards and Barrow⁴ shows that their RKR potential has distinctly sharper curvature than is explained by their C_6 .

³³ As reported previously,⁵ the $G(v)$ values given in Table VII of Ref. 1 are all 5 cm^{-1} too small.

Possible $\text{O}_8^+ - \text{O}_{12}^+$ Structures Obtained by Use of Classical Electrostatic Theory

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The interaction energy in the series $\text{O}_2 - \text{O}_6^+$ through $3\text{O}_2 - \text{O}_6^+$ is approximated as the sum of the van der Waals interactions between the neutral species and the following electrostatic interactions: monopole-quadrupole, quadrupole-quadrupole, and (monopole+quadrupole)-induced dipole+induced dipole-induced dipole. Two planar O_6^+ structures and charge distributions obtained by the CDO-IBM method were used in the O_8^+ computations. The computed dissociation energy $D_e(\text{O}_2 - \text{O}_6^+)$ is certainly too large for the O_6^+ structure with the larger charge on the central O_2 . The D_e values computed for the O_6^+ structure of smaller charge are as follows: $D_e(\text{O}_2 - \text{O}_6^+) = 3.42$, $D_e(\text{O}_2 - \text{O}_8^+) = 3.26$, and $D_e(\text{O}_2 - \text{O}_{10}^+) = 3.12 \text{ kcal/mole}$. Although these values are larger than the experimental ΔH° data, they are in reasonable agreement considering the uncertainties in the van der Waals potential and the quadrupole moments and the lack of data concerning the higher moments and polarizabilities, e.g., the quadrupole polarizability. The $\text{O}_8^+ - \text{O}_{12}^+$ have been studied at $T < 100^\circ\text{K}$. The barriers to internal rotation by the attached O_2 molecules are computed to be 1.2 kcal , much larger than RT for $T < 100^\circ\text{K}$.

I. INTRODUCTION

There is now much evidence, both experimental and theoretical, that the bond between a diatomic molecule and its molecular ion is too strong to be caused by classical electrostatic (CE) interactions, but rather is the result of charge delocalization between the ion and the molecule.¹⁻⁶ The large decrease in bond energy of 4 kcal^1 from $\text{O}_2 - \text{O}_4^+$ to $\text{O}_2 - \text{O}_6^+$ appears to be too large for the $\text{O}_2 - \text{O}_4^+$ bond to be the result of CE interactions,⁷ so an attempt was made to compute the O_6^+ bond energy⁸ by the CDO-IBM method,⁴ a semiempirical SCF MO approach. Unfortunately, several structures were computed to have $\frac{2}{3}$ the experimental total dissociation energies (to $2\text{O}_2 + \text{O}_2^+$), and the method is not sufficiently accurate to determine which, if any, of these corresponds to the potential minimum. However, one of the reasons for developing these models is to provide methods to estimate rotational entropies, which turned out to be the same to within 3 e.u. for all the O_6^+ structures.

It has been argued that the $\text{O}_2 - \text{O}_6^+$ bond is probably due to CE-type interactions.⁸ The argument will not be repeated here, but the conclusion from the O_6^+ computations is that the intermolecular repulsive interactions increase faster than the (attractive) charge delocalization interactions as n increases in the series

X_{2n}^Z . Therefore, a CE model is expected to be valid for X_{3n}^Z or X_{4n}^Z , depending on the series.⁹ In the model applied here,⁸ which is an extension of an earlier model,³ the interaction energy is approximated as the sum of the van der Waals interaction potential between the neutral species (VR+VD) and such electrostatic interactions as can be computed from classical electrostatic theory. Because of the empirical parameters available for O_2 , the electrostatic interaction potential is considered to be the sum of the following potentials: the initial (monopole+quadrupole) field-induced dipole and induced dipole-induced dipole (VPC), monopole-quadrupole (VMQ), and quadrupole-quadrupole (VQQ).

II. CLASSICAL ELECTROSTATIC (CE) MODEL

For a complex of n molecules the repulsive (VR) and attractive (VD) parts of the van der Waals interaction are taken to be

$$\text{VR} = \sum_{A < B} \sum_{\alpha} \sum_{B=n'} \sum_{\beta} a_{\alpha\beta} \exp(-b_{\alpha\beta} r_{\alpha\beta}), \quad (1)$$

$$\text{VD} = - \sum_{A < B} \sum_{\alpha} \sum_{B=n'} \sum_{\beta} c_{\alpha\beta} r_{\alpha\beta}^{-6}, \quad (2)$$