Molecular Constants of the Ground State of I₂†

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The molecular constants of the ground state of the I_2 molecule have been determined making use of the interferometric measurements of Rank and Baldwin for the green line resonance series combined with the ultraviolet resonance data obtained by Verma. In order to fit the data, values of D_e, γ_e, and β_e are calculated from theory since in the opinion of the authors the data are not sufficiently good to yield realistic values for these constants. It is shown that the molecular constants obtained here are consistent with both the green line series and ultraviolet series measurements within the precision of both sets of measurements. Calculations are made using Sandeman's relations derived from Dunham's potential function to estimate certain molecular constants not accurately derivable directly from the spectroscopic data.

Some years ago Rank and Baldwin (*1*) gave a brief report on their determination of the molecular constants of the ground state of the iodine molecule derived from their interferometric measurements of Wood's resonance doublets. Verma (*2*) has published the results of his very complete work on several ultraviolet resonance series which he was able to observe nearly to the dissociation limit of the ground state of the molecule. In view of the total situation it is of interest to present the original data of Rank and Baldwin (*1*) and correlate it with the data obtained by Verma (*2*) to produce as complete as possible determination of the ground-state constants. It will be demonstrated later that the frequencies measured by Rank and Baldwin (*1*) by means of the interferometer in the red green region of the spectrum have a precision 20 times as great as those measured by Verma (*2*) in the ultraviolet. However Verma (*2*) has observed his doublets to values of v'' up to more than 80 contrasted with the interferometric measurements to only $v'' = 22$. The values of the molecular constants obtained from analysis of the both sets of data must be consistent with the precision of both the sets of data.

We can write the following equations to represent a resonance series:

$$R(J_r - 1) = A - [G''(v) + F''(J_r - 1)], \tag{1}$$

where

$$G''(v) = \omega_e(v + \tfrac{1}{2}) + x_e\omega_e(v + \tfrac{1}{2})^2 + y_e\omega_e(v + \tfrac{1}{2})^3 \\ + z_e\omega_e(v + \tfrac{1}{2})^4 + t_e\omega_e(v + \tfrac{1}{2})^5 \tag{2}$$

and

$$F''(J_r - 1) = [B_e + \alpha_e(v + \tfrac{1}{2}) + \gamma_e(v + \tfrac{1}{2})^2 + \delta_e(v + \tfrac{1}{2})^3 \\ + \varphi_e(v + \tfrac{1}{2})^4]J_r(J_r - 1) \tag{3} \\ + [D_e + \beta_e(v + \tfrac{1}{2})]J_r^2(J_r^2 - 1).$$

Then

$$R(J_r - 1) = A' - \left[\omega_e + x_e\omega_e + \tfrac{3}{4}y_e\omega_e + \tfrac{1}{2}z_e\omega_e + \tfrac{5}{16}t_e\omega_e \right.$$
$$\left. + \{\alpha_e + \gamma_e + \tfrac{3}{4}\delta_e + \frac{\varphi_e}{2} + \beta_e J_r(J_r - 1)\}J_r(J_r - 1) \right]v$$
$$- [x_e\omega_e + \tfrac{3}{2}y_e\omega_e + \tfrac{3}{2}z_e\omega_e + \tfrac{5}{4}t_e\omega_e + \{\gamma_e + \tfrac{3}{2}\delta_e \tag{4}$$
$$+ \tfrac{3}{2}\varphi_e\}J_r(J_r - 1)]v^2$$
$$- [y_e\omega_e + 2z_e\omega_e + \tfrac{5}{2}t_e\omega_e + (\delta_e + 2\varphi_e)J_r(J_r - 1)]v^3$$
$$- [z_e\omega_e + \tfrac{5}{2}t_e\omega_e + \varphi_e J_r(J_r - 1)]v^4 - t_e\omega_e v^5,$$

where

$$A' = A - \left\{ \frac{\omega_e}{2} + \frac{x_e\omega_e}{4} + \frac{y_e\omega_e}{8} + \frac{z_e\omega_e}{16} + \frac{t_e\omega_e}{32} \right\}$$
$$- \left\{ B_e + \frac{\alpha_e}{2} + \frac{\gamma_e}{4} + \frac{\delta_e}{8} + \frac{\varphi_e}{16} + \left(D_e + \frac{\beta_e}{2} \right) J_r(J_r - 1) \right\} J_r(J_r - 1).$$

The resonance doublet separation $\Delta\nu = R(J_r - 1) - P(J_r + 1)$ may be expressed by the equation

$$\Delta\nu = (4J_r + 2)\left[B_e + \frac{\alpha_e}{2} + \frac{\gamma_e}{4} + \frac{\delta_e}{8} + \frac{\varphi_e}{16} \right.$$
$$\left. + \left(D_e + \frac{\beta_e}{2} \right)(2J_r^2 + 2J_r + 2) \right]$$
$$+ (4J_r + 2)[\alpha_e + \gamma_e + \tfrac{3}{4}\delta_e + \tfrac{1}{2}\varphi_e + \beta_e(2J_r^2 + 2J_r + 2)]v \tag{5}$$
$$+ (4J_r + 2)[\gamma_e + \tfrac{3}{2}\delta_e + \tfrac{3}{2}\varphi_e]v^2$$
$$+ (4J_r + 2)(\delta_e + 2\varphi_e)v^3 + (4J_r + 2)\varphi_e v^4.$$

Table I. The calculated-observed values of the lines in R and P branches of the green series and in the R branch of ultraviolet series.

v"	ν_0 of Green Series = 18,307.4712 cm⁻¹				ν_0 of U.V Series = 54,633.22 cm⁻¹		
	R(J_r-1) Obs. cm⁻¹	Calc.-Obs. cm⁻¹	P(J_r+1) Obs. cm⁻¹	Calc.-Obs. cm⁻¹	v" R(J_r-1) Calc.-Obs. cm⁻¹	vⁿ	R(J_r-1) Calc.-Obs. cm⁻¹
1	18,094.309	− 0.0019	18,089.179	− 0.0049	2 + 0.36	44	− 0.27
3	17,671.664	+ 0.0027	17,666.563	+ 0.0037	4 + 0.06	46	− 0.42
4	462.205	+ 0.0017	457.122	+ 0.0017	5 + 0.09	49	− 0.18
5	253.992	+ 0.0051	248.938	− 0.0059	6 + 0.13	50	− 0.27
6	047.054	− 0.0045	041.999	+ 0.0005	8 + 0.05	52	+ 0.09
8	16,636.969	− 0.0005	16,631.943	+ 0.0092	9 + 0.37	55	+ 0.25
10	232.036	+ 0.0007	227.052	+ 0.0019	10 + 0.06	56	+ 0.68
11	031.524	+ 0.0029	026.561	− 0.0001	11 − 0.03	58	+ 0.41
12	15,832.335	− 0.0005	15,827.387	− 0.0025	12 + 1.02	59	+ 0.29
13	634.470	+ 0.0023	629.539	− 0.0019	13 − 0.05	62	+ 0.46
15	242.770	+ 0.0003	237.870	+ 0.0013	15 − 0.10	63	+ 0.51
17	14,856.520	+ 0.0005	14,851.651	+ 0.0036	17 − 0.04	66	+ 0.91
18	665.479	− 0.0086	660.635	− 0.0136	19 − 0.20	67	+ 1.18
20	287.584	+ 0.0021	282.768	+ 0.0021	21 − 0.41	71	+ 4.20
22	13,915.397	+ 0.0162	13,910.632	− 0.0018	24 − 0.48	75	+ 12.34
23	731.8	− 0.29	727.0	− 0.29	26 + 0.08	76	+ 15.19
25	368.2	− 0.07	363.8	− 0.37	28 + 0.03	77	+ 18.95
27	011.0	− 0.22	006.0	+ 0.08	30 − 0.29	83	+ 60.34
29	12,659.9	− 0.29	12,655.7	− 0.79	31 − 0.38	84	+ 71.06
30	486.5	− 0.12	481.7	− 0.02	33 − 0.27		
32	144.6	+ 0.15	140.3	− 0.15	35 − 0.60		
34	11,809.5	+ 0.20	11,805.1	0.00	36 − 0.47		
35	644.2	+ 0.49	640.0	+ 0.09	38 − 0.41		
36	481.4	0.00	476.9	− 0.10	40 − 0.66		
37	319.6	+ 0.24	315.4	− 0.05	41 − 0.44		
39	11,001.4	+ 0.64	10,997.4	+ 0.15	43 − 0.35		

In Eqs. (2)–(5) $v \equiv v''$ and the other constants have their usual spectroscopic significance.

ANALYSIS OF DOUBLETS EXCITED BY THE GREEN LINE

The data obtained for the green line series are given in Table I. Doublets from $v'' = 1$ to 22 were measured with the interferometer. Doublets corresponding to $v'' = 23, 25,$ and 27 were measured by Wood and Kimura (3) using a one-meter plane grating. The remainder of the doublets were measured by Rank (4) with a one-meter concave grating.

The doublet separations obtained from the interferometric measurements were fitted to Eq. (5) using only a constant and linear term. Up to $v'' = 22$ no trace of quadratic term could be observed.[1]

[1] From the Kratzer approximation $\gamma_e = 6D_e$, we get $\gamma_e = 2.7 \times 10^{-8}$ cm⁻¹, a quantity much too small to be observed up to $v'' = 22$. The experience of the authors is that in few cases where γ_e has been accurately determined for diatomic molecules, the γ_e is probably somewhat smaller than the prediction of the Kratzer approximation. From the relations given by Sandeman (5), we have calculated $\gamma_e = +1.90 \times 10^{-8}$. The value of c_3 in Sandeman's (5) paper was obtained by interpolation. No experimental value of D_e from the analysis of iodine absorption bands is available in literature. Verma (2) has demonstrated that the potential function for the ground state of iodine agrees very well with the Morse potential function for low values of v. The diatomic molecules CO and HCl both yield
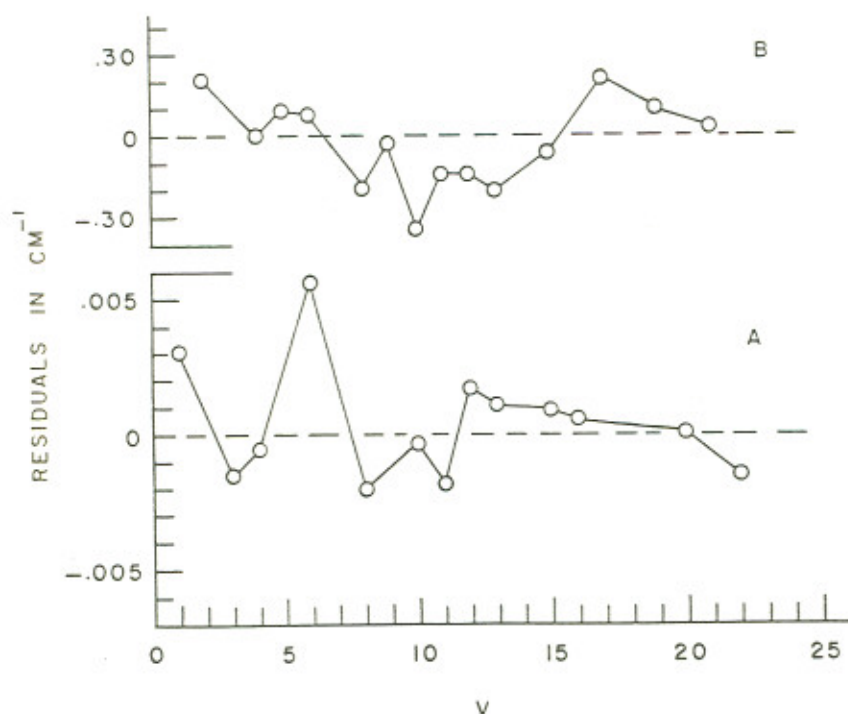
FIG. 1. Deviations of the experimental values of the doublet separations from the predictions of empirical equations: A from Eq. (6) and B from Eq. (7).

The empirical equation which gives the best approximation of the green line doublets is

$$\Delta\nu = 5.14987 - 0.016699v \tag{6}$$

which for $J_r = 34$ and $D_e = -4.54 \times 10^{-9}$ yields $B_e = 0.037389$ and $\alpha_e = -0.0001210$ both in cm^{-1}. In Fig. 1 the deviations of the experimental values of the doublet separations from the predictions of Eq. (6) are shown. It may be noted that the value of α_e computed from the approximation of the Morse potential function is -0.0001185 cm^{-1} which only differs by 2% from the experimentally determined value of α_e.

A few of the lines and doublet separations show much larger deviations than the majority of the measurements from the best smooth functions. It is believed

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experimental D_e values for the ground state agreeing with the prediction of the Morse function within a very small experimental error. It seems certain that the value of $D_e = -4.54 \times 10^{-9}$ cm^{-1} calculated from the Morse function would be far more accurate than values which would be determined from the spectrum. It can be presumed that approximate theory will also give the right order of magnitude for β_e, namely, -1.8×10^{-11} cm^{-1}. Although the probable precision of this calculated β_e value is low it can be reasonably presumed that the effect of this constant will be too small to be significant even in the ultraviolet resonance series within the precision of measurement. We have also determined β_e from Sandeman (5) relationships and find $\beta_e = -1.20 \times 10^{-11}$.

that these few large residuals are not the result of experimental error in measuring the wavelengths since the measured values are consistent on different plates. These deviations probably arise from accidental perturbations produced by reabsorption of part of the resonance line by the prolific overlapping absorption system. The difference in the B_e value quoted above from that quoted in the earlier note (*1*) arises largely from the fact that the centrifugal distortion constant correction had been applied with the wrong algebraic sign. However, these statistical procedures always yield probable errors which are absurdly small, and a much more realistic approach is to triple the statistically calculated probable error.

With regard to the pioneer work of Loomis (*6*) on the analysis of the iodine absorption spectrum the authors have been unable to find the promised detailed publication. From the Loomis (*6*) paper it is impossible to decide whether his B_0 value quoted took adequate account of centrifugal distortion. The method of analysis described in the above reference does not take into account the centrifugal distortion.

RESONANCE DOUBLETS EXCITED BY λ*1830* Å

Of the resonance series observed by Verma (*2*) the one excited by λ1830 Å for which $J_r = 87$ is by far the best one to analyze, in order to obtain precise molecular constants. Making use of the values of B_e and α_e determined from the green line series and the values of D_e, β_e, and γ_e calculated from the theory, the $J_r = 87$ series has been used to evaluate the constants δ_e and φ_e. The resulting empirical equation is

$$\Delta\nu = 13.0445 - 0.04241v + 6.65 \times 10^{-6}v^2 - 1.00 \times 10^{-7}v^3$$
$$- 6.50 \times 10^{-8}v^4 \tag{7}$$

which yields values for $\delta_e = +8.57 \times 10^{-11}$ cm^{-1} and $\varphi_e = -1.86 \times 10^{-10}$ cm^{-1}. The residuals for the doublet separations up to $v = 21$ as observed compared to the values computed from Eq. (7) are shown in Fig. 1. It should be noted that the $J_r = 87$ doublet series has only been used to determine two of the molecular constants, namely, δ_e and φ_e.[2]

DETERMINATION OF VIBRATIONAL CONSTANTS

The $R(J_r - 1)$ series of lines excited by the green line were fitted to an equation of the 5th degree in v. The fitting was accomplished by a method of approximation which first fitted the interferometrically measured $R(J_r - 1)$ lines to an equation of the 4th degree in v. By means of a differential method a 5th degree equation was then passed through the experimental point for $R(J_r - 1)$ corresponding to $v = 36$. This point was chosen because of the reliability of its abso-

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[2] It is seen that δ_e and φ_e as determined above have a smaller magnitude than γ_e. However we do not place any appreciable confidence in these constants since φ_e is larger than δ_e and the algebraic signs of both constants we believe from theoretical reasons should have reversed signs.

lute value since the doublet $v = 36$ in the first order of the grating fell between two known Hg lines which appear in the 2nd order. This fact tended to minimize any displacement error between known and unknown wavelengths.

The empirical equation obtained was

$$R(J_r - 1) = 18,307.4712 - 213.774747v + 0.6093235v^2$$
$$+ 0.00130848v^3 + 0.0000056441v^4 + 0.0000001589v^5 \tag{8}$$

A sufficient number of significant figures has been carried in the fitting process so that the $R(J_r - 1)$ lines can be calculated from Eq. (8) to 1 or 2×10^{-4} cm^{-1}. This does not imply that the molecular constants calculated from Eq. (8) making use of the relationships given in Eq. (4) can realistically be expressed to a similar number of significant figures. The $P(J_r + 1)$ lines are then computed from the values of $R(J_r - 1)$ lines calculated from Eq. (8) and the doublet separations calculated from Eq. (6). The comparison of the observed and calculated values for $R(J_r - 1)$ and $P(J_r + 1)$ lines is given in Table I, columns 3 and 5. The fit seems to be eminently satisfactory.

An empirical equation for the λ1830 Å resonance series for which $J_r = 87$ can now be easily determined making use of the coefficients of the powers of v given in Eq. (8) and the rotational constants determined from Eqs. (6) and (7). Thus it is now only necessary to determine A' from the ultraviolet resonance data. First $R(J_r - 1)$ was computed from the observed value of $P(J_r + 1)$ and $\Delta \nu$ calculated from Eq. (7). This computed value of $R(J_r - 1)$ was then averaged with the observed value of $R(J_r - 1)$. It is certainly true that $\Delta \nu$ can be calculated from Eq. (7) with very much higher precision than the absolute value of either $R(J_r - 1)$ or $P(J_r + 1)$ has been measured. The empirical equation then obtained for $J_r = 87$ series is

$$R(J_r - 1) = 54,633.22 - 213.0048223v + 0.60920361v^2$$
$$+ 0.001310297v^3 + 0.0000068252v^4 + 0.0000001589v^5 \tag{9}$$

The comparison between the "average" value observed for the $R(J_r - 1)$ lines with the values of $R(J_r - 1)$ calculated from Eq. (9) is given in columns 7 and 9 of Table I. It seems certain that up to at least $v = 21$ the calculated values of $R(J_r - 1)$ must be correct to at least 0.02 cm^{-1} and thus the residuals in column 7, Table I are an indication of the magnitude of the experimental error of the frequency determinations in the ultraviolet series. It can be seen that above $v = 50$ the residuals in column 9, Table I rapidly increase, showing clearly that powers of v as high as 7 would have to be used to fit the $R(J_r - 1)$ series to $v = 84$. It is problematical as to the feasibility of fitting to such high powers of v since there are no highly precise data available in the $v = 20$ to 40 region to "control" the fitting process. It can be stated that the molecular constants derivable from Eq. (8) give a satisfactory representation of both the green line series and the presently analyzed ultraviolet series up to $v = 40$. Of course the

Table II. Rotational and vibrational constants
of the ground state of iodine.

$$a_e = -0.0001210$$

$$\gamma_e = +1.90 \times 10^{-8} \quad \text{calculated}$$

$$\delta_e = +8.57 \times 10^{-11}$$

$$\varphi_e = -1.86 \times 10^{-10}$$

$$B_e = +0.037389$$

$$D_e = -4.54 \times 10^{-9} \quad \text{calculated}$$

$$\beta_e = -1.20 \times 10^{-11} \quad \text{calculated}$$

$$\omega_e = 214.51886$$

$$x_e\omega_e = -0.60738$$

$$y_e\omega_e = -1.307 \times 10^{-3}$$

$$z_e\omega_e = -5.04 \times 10^{-6}$$

$$t_e\omega_e = -1.6 \times 10^{-7}$$

value of $t_e\omega_e$ obtained will not be realistic since Eq. (8) must be an infinite series. The values obtained for the rotational and vibrational constants of the ground state of iodine are given in Table II in cm^{-1} units.

INTERRELATIONSHIP OF THE MOLECULAR CONSTANTS

The theory of relationships between the various molecular constants is almost as old as the theory of band spectra itself. Many potential functions for the diatomic molecule have been proposed and tested. Probably the most general potential function is the one proposed by Dunham (7) who has given the detailed expressions relating the ordinary band spectrum constants to the constants of the potential function. Unfortunately it is nearly impossible to make calculations to evaluate the potential constants from the equations given by Dunham because of the algebraic complexity of these equations.

Sandeman (5) has critically discussed the nature of Dunham's potential function. Sandeman inverts Dunham's potential equation and thus is able to express the spectroscopically observable quantities in terms of certain constants c_1, c_2, c_3, etc. which bear definite relationships to Dunham's a_1, a_2, a_3, etc. Sandeman has split Y_{lj} into first-order and higher order correction terms.

$$Y_{lj} = x_{lj} + y_{lj} + z_{lj}, \tag{10}$$

where $x_{lj}:y_{lj}:z_{lj} :: 1:\mu_e^2:\mu_e^4$ where $\mu_e = \dfrac{2B_e}{\omega_e}$. It is not hard to demonstrate that only x_{lj} values are experimentally significant for the ground state of iodine. Sandeman has shown that his c's would have values $c_n = \dfrac{a^n}{n+1}$ if Morse potential function was strictly valid
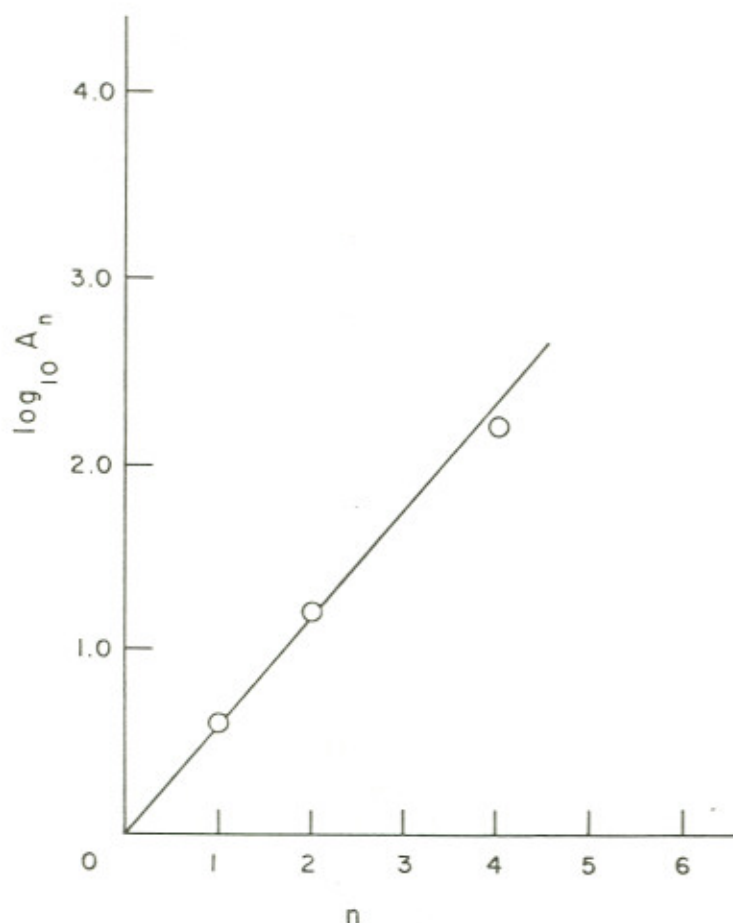
FIG. 2. Plot of $\log_{10} A_n$ versus n

Table III. Observed and calculated values of various molecular and potential constants.

Constant	Observed	Calculated	Observed Verma
Y_e		$+ 1.90 \times 10^{-8}$	4.44×10^{-7}
δ_e	$+ 8.57 \times 10^{-11}$		$- 1.839 \times 10^{-7}$
η_e		$- 4.54 \times 10^{-9}$	$+ 1.99 \times 10^{-9}$
μ_e		$- 1.80 \times 10^{-11}$	$+ 1.236 \times 10^{-10}$
c_1	2.047	2.048	
c_2	5.415	5.427	
c_3		14.53	
c_4	32.86	32.78	

We can now evaluate c_1 from the accurately experimentally determined value of $\alpha_e \sim x_{11}$ and obtain $c_1 = 2.047$. From $x_e\omega_e \sim x_{20}$ we obtain $c_2 = 5.415$. From $y_e\omega_e \sim x_{30}$ and previously determined value of c_2 we find $c_4 = 32.8_6$. It must be stated that this constant is considerably less precise than the values obtained

for c_1 and c_2. We cannot determine c_3 since γ_e could not be measured with any certainty.

Sandeman (5) has pointed out a striking relationship between his c's if the Morse potential function applies strictly. We might expect that the inclusion of an additional term might fit a modest deviation from the Morse function, e.g.,

$$c_n = [a^n/(n + 1)]f(n). \tag{11}$$

Denoting $(n + 1)c_n$ by A_n, we can write Eq. (11) in the particular form

$$\log_{10} A_n = Kn + Bn^k. \tag{12}$$

If we divide this equation (12) by n we find a value of $(k - 1) = 3$ makes the plot a straight line as portrayed in Fig. 2. It is not presumed that Eq. (12) has theoretical significance. This equation is simply a convenient device to interpolate and extrapolate to obtain estimates of potential constants not accurately determined directly from the experimental measurements.

Upon determination of K and B it is now possible to calculate c_3 with high precision since only interpolation is involved. c_5 and c_6 can be calculated by extrapolation but these values are subjected to large uncertainty.

In Table III the results obtained for the measured and calculated values of various molecular constants and potential constants are tabulated. The values calculated for D_e, γ_e, and β_e are undoubtedly very precise since only potential constants are involved which can be obtained with high precision. The values quoted in column 2 for c's have been determined from the appropriate x_{ij} values. In column 3 these constants have been determined from Eq. (12).

We feel that we have demonstrated that it is quite futile to solve for a large number of molecular constants from the experimental data making use of simultaneous equations because of the relationships existing between the molecular constants. The task of obtaining realistic values for molecular constants depending on high powers of $(v + \frac{1}{2})$ seems to be quite hopeless unless much more precise data derived from high values of v'' were available.

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