

Ultraviolet Resonance Spectrum of the Iodine Molecule*

R. D. VERMA

Laboratory of Molecular Structure and Spectra, Department of Physics, The University of Chicago, Chicago 37, Illinois

(Received October 2, 1959)

The ultraviolet resonance spectrum of I_2 observed in electric discharges in the region 1830–2370 Å has been photographed at high resolution with a 21-ft vacuum grating spectrograph, and a thorough and complete analysis of the data in this region is given. The five doublet resonance series are shown to be excited from five rotational levels of vibrational level $v''=0$ of the ground state of I_2 to three vibrational levels (v_n' , v_{n+1}' , v_{n+4}') of an upper electronic state by a single iodine atomic line 1830.4 Å. The rotational constants for the ground state of I_2 may be represented:

$$B_v = 0.03734 - 0.0001208(v + \frac{1}{2}) + 0.444 \times 10^{-6}(v + \frac{1}{2})^2 - 1.839 \times 10^{-8}(v + \frac{1}{2})^3 - 0.057 \times 10^{-10}(v + \frac{1}{2})^4 \quad (1)$$

$$D_v = 1.99 \times 10^{-9} + 1.236 \times 10^{-10}(v + \frac{1}{2}). \quad (2)$$

The ground-state $\Delta G(v + \frac{1}{2})$ values have been obtained from $v''=0$ up to the dissociation limit. A precise value of the dissociation energy of I_2 , has been found to be $12\,452.5 \pm 1.5$ cm $^{-1}$ as against the previous value of 12439 ± 8 cm $^{-1}$.

The potential energy curve of $X^1\Sigma_g^+$ has been computed by using the Rydberg-Klein-Rees method after modifying its final expressions, right up to the dissociation limit, and certain curious features in the neighbourhood of the dissociation limit are pointed out. The curve follows the van der Waals force law c/r^6 between $r=4.6$ Å and $r=6.4$ Å with $c=3.7 \times 10^6$. Various possibilities for the nature of the upper electronic state are discussed.

INTRODUCTION

OLDENBERG¹ studied the fluorescence spectrum of I_2 in the ultraviolet region, excited by various atomic lines, and discussed the results in a qualitative way. From the work of Asagoe,² and Kimura and Tonomura³ it has been known for a long time that in the same region as that studied by Oldenberg, a series of I_2 resonance lines, excited by iodine atom emission lines, are observed in electric discharges through iodine vapor. Kimura and Tonomura gave an analysis of this spectrum after photographing it in the region 2050–2370 Å with a Hilger E_1 quartz spectrograph and reported this resonance spectrum as excited by the iodine atomic lines 1830.4 Å and 1844.5 Å. They also photographed the spectrum down to 1783 Å with a small fluorite spectrograph and indicated in the published spectrum short and weak resonance series excited by iodine atomic lines 1782.9, 1799.2, and 1876.4 Å, together with the extension of those excited by 1830.4 and 1844.5 Å. No data were given below 2050 Å. The process of excitation could not be decided uniquely. The present author also repeated the experiment in India by using a Hilger E_1 quartz spectrograph. The preliminary analysis of the spectrum showed that the analysis could be improved and further definite knowledge about the ground electronic state of I_2 could be

obtained, if the spectrum were photographed with a high resolution instrument down to 1700 Å. Hence the study of this spectrum was continued in this laboratory and the results are discussed in this paper.

EXPERIMENTAL

Various conditions of the discharge were tried to excite this resonance spectrum and a high-frequency (2450 Mc/sec) discharge was found to be an efficient method. The source of iodine vapor was kept at 0°C and the vapor was pumped off continuously by a mechanical pump during the exposure time and the discharge tube was cooled with a fan. The exposure time ranged from 10 to 90 minutes. Ilford Q_2 photographic plates were used. The spectrum was photographed in the region 1700–2060 Å in the third order of a 21-ft vacuum grating spectrograph having a grating with 30 000 lines/inch. The Ge atomic spectrum⁴ was used as the standard for the measurements. The region 2000–2400 Å was photographed in the 2nd order of the same instrument and copper and iron atomic lines were used as reference spectra for measurements. The measurements were made with an SIP comparator. The accuracy for sharp lines was ± 1 mÅ, but for the weak lines and for those which were overlapped by other lines, the error ranged from ± 3 mÅ to ± 6 mÅ. The wavelengths measured were vacuum wavelengths (λ_{vac}); λ_{vac} values for the standard lines above 2000 Å were obtained with the help of Edlen's table.⁵ The wave numbers of the resonance lines, along with their analysis, are given in Tables I to IV.

* This work was assisted by the Geophysics Research Directorate of the Air Force Cambridge Research Center under Contract No. AF 19(604)-3478 with the University of Chicago, and the preliminary work by the Council of Scientific and Industrial Research, Government of India, under the research scheme sanctioned to Dr. P. Venkateswarlu at the Muslim University, Aligarh, India.

¹ O. Oldenberg, *Z. Physik* **18**, 1 (1923).

² K. Asagoe, *Sci. Repts. Tokyo Bunrika Daigaku* **2**, 9 (1935).

³ M. Kimura and K. Tonomura, *Pieter Zeeman* (Martinus Nijhoff, The Hague, Netherlands, 1935), p. 241.

⁴ Meissner, Van Veld, and Wilkinson, *J. Opt. Soc. Am.* **48**, 1001 (1958).

⁵ B. Edlen (private distribution, 1952).

RESULTS

The spectrum consists of groups of sharp lines which are repeated at intervals from 1830 Å to 2370 Å. On the lower frequency side, the spectrum converges to a sharp limit [Fig. 1(g)] followed by a maze of lines. Each group of lines consists of doublets which form doublet resonance series. The intervals between the members of the individual series correspond to the vibrational quanta of the ground electronic state of iodine molecule. In all, five doublet series are found to be excited. In individual resonance series, a number of the members are very weak or missing in accordance with the wave-mechanical formulation of the Franck-Condon principle. It is found that these resonance series involve the ground state of I_2 for their lower electronic state. The resonance doublets in some of the

TABLE I. Doublet series I.^a

v''	$R(86)$ cm ⁻¹	$P(88)$ cm ⁻¹	$\Delta\nu_{\text{obs}}$	$\Delta\nu_{\text{calc}}$
0	54 632.93 ^b	54 619.23	13.70	13.04
2	54 209.30	54 196.55	12.75	12.95
4	53 790.97	53 778.10	12.87	12.87
5	53 583.50	53 570.76	12.74	12.83
6	53 377.29	53 364.58	12.71	12.79
8	52 968.82	52 955.92	12.90	12.70
9	52 766.16	52 753.47	12.69	12.66
10	52 565.43	52 552.47	12.96	12.62
11	52 365.78	52 353.06	12.72	12.58
12	52 166.31	52 153.63	12.68	12.53
13	51 970.30	51 957.61	12.69	12.49
15	51 580.21	51 567.74	12.47	12.41
17	51 195.47	51 183.36	12.11	12.32
19	50 816.52	50 804.39	12.13	12.23
21	50 443.30	50 431.19	12.11	12.14
24	49 894.17	49 882.10	12.07	12.01
26	49 534.87	49 523.07	11.80	11.91
28	49 182.37	49 170.35	12.02	11.81
30	48 836.42	48 824.88	11.54	11.71
31	48 665.78	48 654.08	11.70	11.66
33	48 329.16	48 317.90	11.26	11.55
35	47 999.69	47 998.28	11.41	11.44
36	47 837.25	47 826.02	11.23	11.39
38	47 517.86	47 506.68	11.18	11.27
40	47 206.02	47 194.70	11.32	11.15
41	47 052.54	47 041.38	11.16	11.08
43	46 751.65	46 740.77	10.88	10.95
44	46 604.10	46 593.24	10.86	10.89
46	46 315.32	46 304.61	10.71	10.75
49	45 897.25	45 886.80	10.45	10.53
50	45 762.36	45 751.81	10.55	10.45
52	45 498.72	45 488.46	10.26	10.29
55	45 120.97	45 110.92	10.05	10.04
56	44 999.48	44 989.84	9.64	9.96
58	44 765.08	44 755.49	9.59	9.78
59	44 651.59	44 641.76	9.83	9.68
62	44 326.95	44 317.52	9.43	9.39
63	44 224.19	44 214.76	9.43	9.29
66	43 932.89	43 923.92	8.97	8.97
67	43 841.59	43 832.64	8.95	8.86
71	43 505.78	43 497.36	8.42	8.39
75	43 218.10	43 210.25	7.85	7.88
76	43 154.21	43 146.63	7.58	7.74
77	43 093.10	43 085.64	7.46	7.60
83	42 789.32	42 783.02	6.30	6.72
84	42 749.26	42 742.79	6.47	6.56

^a For explanation of the missing lines, see the text.^b Exciting line.

TABLE II. Doublet series II.

v''	$R(45)$ cm ⁻¹	$P(47)$ cm ⁻¹	$\Delta\nu_{\text{obs}}$	$\Delta\nu_{\text{calc}}$
0	54 640.09	54 632.93 ^b	7.16	6.93
2	a	54 208.12 ^a		
4	53 795.14	53 788.31 ^a	6.83	6.84
6	53 380.37	53 373.53	6.84	6.80
7	53 174.92	53 167.90	7.02	6.78
8	52 970.54	52 963.77 ^a	6.77	6.76
10	52 565.43	52 558.96 ^a	6.47	6.71
11	52 365.45	52 358.60 ^a	6.85	6.69
12	52 166.31	52 159.93	6.38	6.67
13	51 968.68	51 962.20 ^a	6.48	6.64
15	51 577.60	51 570.80 ^a	6.80	6.60
17	51 191.32	51 184.77 ^a	6.55	6.55
19	50 810.84	50 804.39 ^a	6.45	6.51
21	50 436.17	50 429.86 ^a	6.31	6.46
23	50 067.14	50 060.80 ^a	6.34	6.41
24	49 884.77	49 878.35 ^a	6.42	6.39
26	49 524.02	49 517.75 ^a	6.27	6.34
28	49 170.35	49 164.16 ^a	6.19	6.29
30	48 822.50	48 816.30 ^a	6.20	6.23
31	48 650.93	48 644.92 ^a	6.01	6.20
33	48 312.96	48 306.86 ^a	6.10	6.15
35	47 981.42	47 975.53 ^a	5.89	6.09
36	47 818.31	47 812.39 ^a	5.92	6.06
38	47 497.03	47 491.09 ^a	5.94	6.00
40	47 183.10	47 177.31 ^a	5.79	5.93
41	47 028.90	47 023.09 ^a	5.81	5.90
43	46 726.16	46 720.37	5.79	5.83
46	46 286.74	46 280.96	5.78	5.72
48	46 003.70	45 998.12	5.58	5.65
49	45 865.42	45 859.84	5.58	5.61
51	45 595.23	45 589.66	5.57	5.53
52	45 463.47	45 457.89	5.58	5.48
54	45 206.40	45 201.30	5.10	5.40
55	45 081.98	45 076.64	5.34	5.35
58	44 722.08	44 716.84	5.24	5.21
61	44 385.07	44 379.95	5.12	5.06
62	44 278.00	44 272.94	5.06	5.01
65	43 973.17	43 968.41	4.76	4.85
66	43 877.32	43 872.50	4.82	4.79
69	43 606.52	43 601.90	4.62	4.61
70	43 522.22	43 517.62	4.60	4.55
74	43 214.56	43 210.25	4.31	4.29
75	43 145.16	43 141.05	4.11	4.22
76	43 078.75	43 074.56	4.19	4.15
80	42 842.88	42 838.88	4.00	3.86
81	42 791.24	42 787.45	3.79	3.78
82	42 742.79	42 738.92	3.87	3.70

^a This line is masked by the atomic line 1844.5 Å.^b Exciting line (iodine atomic line 1830.4 Å).^c These lines are blended with those as marked * in series III.

series, could be identified up to the vibrational level $v''=84$ of the ground state without any difficulty. Though the resonance series extend up to the dissociation limit of the ground state, v'' values could not be independently identified above $v''=84$ because of the overlapping of the various series and also because of larger gaps due to missing doublets in the series.

Microphotometric traces of the resonance doublets for certain v'' values are given in Fig. 1. The five doublet series are marked I, II, III, IVa, and IVb. The P line of series II and the R line of series III overlap each other for lower v'' values and could be resolved only after $v''=42$. Thus below $v''=43$ the doublets of series II and III together give the appearance of triplets. A similar kind of overlap is observed for the

TABLE III. Doublet series III.

v''	$R(48)$ cm^{-1}	$P(50)$ cm^{-1}	$\Delta\nu_{\text{obs}}$	$\Delta\nu_{\text{calc}}$
0	54 632.93*	54 625.76	7.17	7.38
2	54 208.12*	54 200.84	7.28	7.33
4	53 788.31*	53 781.05	7.26	7.29
8	52 963.77*	52 956.45	7.32	7.19
9	52 760.68	52 753.47	7.21	7.17
10	52 558.96*	52 551.73	7.23	7.14
11	52 358.60*	52 351.36	7.24	7.12
13	51 962.20*	51 955.02	7.18	7.07
15	51 570.80*	51 563.80	7.00	7.03
17	51 184.77*	51 177.83	6.94	6.98
19	50 804.39*	50 797.44	6.95	6.93
21	50 429.86*	50 422.97	6.89	6.88
23	50 060.80*	50 054.06	6.74	6.83
24	49 878.35*	49 871.78	6.57	6.80
26	49 517.75*	49 511.18	6.57	6.75
28	49 164.16*	49 158.02	6.14	6.69
30	48 816.30*	48 809.82	6.48	6.64
31	48 644.92*	48 638.32	6.60	6.61
33	48 306.86*	48 300.52	6.34	6.55
35	47 975.53*	47 969.32	6.21	6.48
36	47 812.39*	47 806.13	6.26	6.45
38	47 491.09*	47 485.28	5.81	6.39
40	47 177.31*	47 171.10	6.21	6.32
41	47 023.09*	47 017.09	6.00	6.28
43	46 720.89	46 714.67	6.22	6.21
46	46 281.51	46 275.47	6.04	6.10
48	45 998.65	45 992.66	5.99	6.02
49	45 860.43	45 854.54	5.89	5.97
51	45 590.30	45 584.38	5.92	5.89
52	45 458.60	45 452.73	5.87	5.84
54	45 202.03	45 196.31	5.72	5.75
55	45 077.37	45 071.52	5.85	5.71
58	44 717.58	44 711.96	5.62	5.56
61	44 380.77	44 375.36	5.41	5.40
62	44 273.84	44 268.43	5.41	5.35
65	43 969.27	43 964.12	5.15	5.17
66	43 873.47	43 868.42	5.05	5.11
69	43 603.04	43 598.18	4.86	4.93
70	43 518.79	43 513.94	4.85	4.86
74	43 211.48	43 207.00	4.48	4.59
75	43 142.24	43 137.62	4.62	4.52
76	43 075.97	43 071.63	4.34	4.44
80	42 840.77	42 836.57	4.20	4.14
81	42 789.32	42 785.33	3.99	4.05
82	42 740.67	42 736.80	3.87	3.97

* Exciting line.

other two doublet series IVa and IVb which could be resolved only for the last member identified ($v''=74$). The separation between the P line of series II and the R line of series III is found to increase slowly with v'' . This feature together with the fact that the P line of II and the R line of III coincide for the lower values of v'' , shows that the doublet series II and III are excited to the same vibrational level of the upper electronic state by monochromatic radiation which coincides with the P line of II and the R line of III for a certain low v'' value. A similar conclusion is valid for the doublet series IVa and IVb. According to the analysis it was found that all the five doublet series are excited by the single iodine atomic line 1830.4 Å which is the resonance line of the iodine atom and is strongly excited in electric discharges. The 1830.4 Å atomic line excites the five doublet series from five rotational levels of the vibrational level $v''=0$ to the rotational levels of

three different vibrational levels (v_n', v_{n+1}', v_{n+4}') of the upper electronic state. Unfortunately the resonance doublets at 1830.4 and 1844.5 Å are overrun by the Rowland ghosts of these atomic lines of the iodine atom and hence only a few resonance series lines could be measured in this region and others were masked by the ghosts.

The process of excitation is explained in the energy level diagram (Fig. 2). This process of excitation requires that the following relations hold good:

$$F''(24) - F''(23) = F'(25) - F'(22)$$

or

$$48 B_0'' = 144 B_n'$$

$$F''(48) - F''(47) = F'(49) - F'(46)$$

or

$$96 B_0'' = 288 B_{n+1}' = 288 B_n'$$

(The effect of α' falls within the width of the exciting line) and

$$F''(47) - F''(23) = \omega_n' - (\omega x)_n' + F'(46) - F'(22)$$

$$F''(86) - F''(48) = \{4\omega_n' - 16(\omega x)_n' + F'(87)\}$$

$$- \{\omega_n' - (\omega x)_n' + F'(49)\}.$$

TABLE IV. Doublet series IVa and IVb.

v''	$R(21)$ cm^{-1}	$\Delta\nu_{RP}$	$P(23)$ $R(24)$ cm^{-1}	$\Delta\nu_{RP}$	$P(26)$ cm^{-1}
2	54 211.21	3.09	54 208.12	4.05	54 204.07
4	53 790.97	3.35	53 787.62	3.79	53 783.83
6	53 375.75	3.30	53 372.45	3.76	53 368.69
7	...		53 166.83	3.79	53 163.04
8	52 965.48	3.31	52 962.17	3.70	52 958.47
11	52 359.87	3.41	52 356.46	3.65	52 352.81
12	52 160.49	3.16	52 157.33	3.70	52 153.63
15	51 570.80	3.06	51 567.74	3.89	51 563.85
17	51 184.77	3.35	51 181.42	3.59	51 177.83
19	50 803.56	3.10	50 800.46	3.61	50 796.85
21	50 428.52	3.18	50 425.34	3.43	50 421.91
23	50 059.02	3.11	50 055.91		
24	49 876.41	2.94	49 873.47	3.33	49 870.14
26	49 515.44	2.99	49 512.45	3.28	49 509.17
28	49 161.21	3.12	49 158.09	3.16	49 154.93
30	48 812.73	2.91	48 809.82	3.36	48 806.46
33	48 302.42	2.90	48 299.52	3.27	48 296.25
35	47 970.58	2.85	47 967.73	3.20	47 964.53
36	47 807.27	3.04	47 804.23	3.17	47 801.06
38	47 485.28	2.73	47 482.55	3.23	47 479.32
40	47 171.10	3.02	47 168.08	3.05	47 165.03
41	47 016.39	2.74	47 013.65	3.10	47 010.55
43	46 713.12	2.74	46 710.38	3.10	46 707.28
46	46 275.47	2.74	46 272.73	2.78	46 269.95
48	45 989.23	2.70	45 986.53	2.92	45 983.61
49	45 850.53	2.65	45 847.88	2.94	45 844.94
51	45 579.60	2.66	45 576.94	2.74	45 574.20
54	45 190.02	2.41	45 187.61	2.72	45 184.89
55	45 064.84	2.46	45 062.38	2.68	45 059.70
58	44 703.73	2.36	44 701.37	2.60	44 698.77
61	44 365.55	2.30	44 363.25	2.56	44 360.69
62	44 257.93	2.41	44 255.52	2.35	44 253.17
65	43 951.87	2.28	43 949.59	2.39	43 947.20
69	43 583.09	2.13	43 580.96	2.16	43 578.80
74	43 188.00	2.19	43 185.81		
			43 186.58	2.42	43 184.16

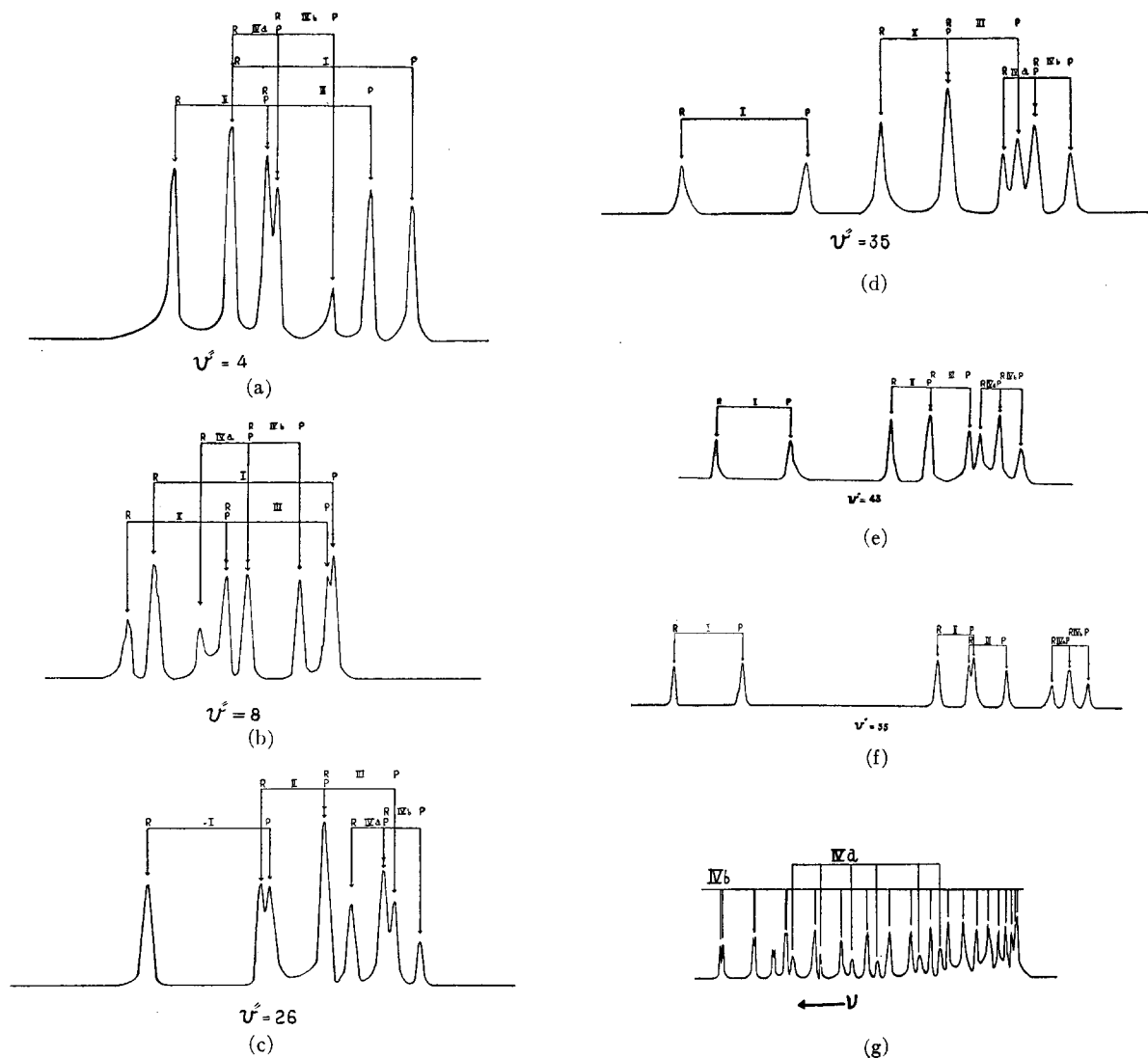


FIG. 1. (a)–(f). Microphotometric traces for the five resonance doublets at certain v'' values. (g) The resonance series IVb near the convergence limit.

Thus a single line is able to excite the molecule from five rotational levels of $v''=0$.

It may be pointed out that according to Kimura and Tonomura the doublet series I is excited by the 1830.4 Å atomic line and II, III, IVa, and IVb are excited by the 1844.5 Å atomic line. However, it may be noted that according to the present analysis the *R* line of II at $v''=2$ falls very close to the 1844.5 Å atomic line, giving rise to the probability of one mistaking 1844.5 Å as the exciting line, especially in a low dispersion spectrum. The calculations are based on the following theory.

The doublet separation $\Delta\nu$ in a doublet series can be shown to be given by

$$\Delta\nu = (4J_r + 2)[B_v'' - (2J_r^2 + 2J_r + 2)D_v''] \quad (1)$$

where J_r is the rotational quantum number of the level excited in the upper state. B_v'' and D_v'' are the rotational constants of the lower state (ground state in this

case) and are functions of the vibrational quantum number v'' . Expressing B_v'' and D_v'' in a polynomial in v'' and dropping off the primes, one gets

$$B_v = B_e - \alpha_e(v + \frac{1}{2}) + \gamma_e(v + \frac{1}{2})^2 + \delta_e(v + \frac{1}{2})^3 + \phi_e(v + \frac{1}{2})^4, \quad (2)$$

$$D_v = D_e + \beta_e(v + \frac{1}{2}). \quad (3)$$

On substitution in Eq. (1),

$$\begin{aligned} \Delta\nu = & (4J_r + 2)[B_e - \frac{1}{2}\alpha_e + \frac{1}{4}\gamma_e + \frac{1}{8}\delta_e + \frac{1}{16}\phi_e \\ & - (2J_r^2 + 2J_r + 2)(D_e + \frac{1}{2}\beta_e)] \\ & - (4J_r + 2)[\alpha_e - \gamma_e - \frac{3}{4}\delta_e - \frac{1}{2}\phi_e + (2J_r^2 + 2J_r + 2)\beta_e]v \\ & + (4J_r + 2)[\gamma_e + \frac{3}{2}\delta_e + \frac{3}{2}\phi_e]v^2 \\ & + (4J_r + 2)[\delta_e + 2\phi_e]v^3 + (4J_r + 2)\phi_e v^4. \quad (1') \end{aligned}$$

Thus $\Delta\nu$ is expressed in the form of a polynomial in v . Therefore $\Delta\nu$ versus v was plotted for the five doublet series (Figs. 3-7). The points which are too far off the smooth curves correspond to either very weak lines or blended lines and therefore were omitted from consideration in drawing the smooth curves. In drawing the

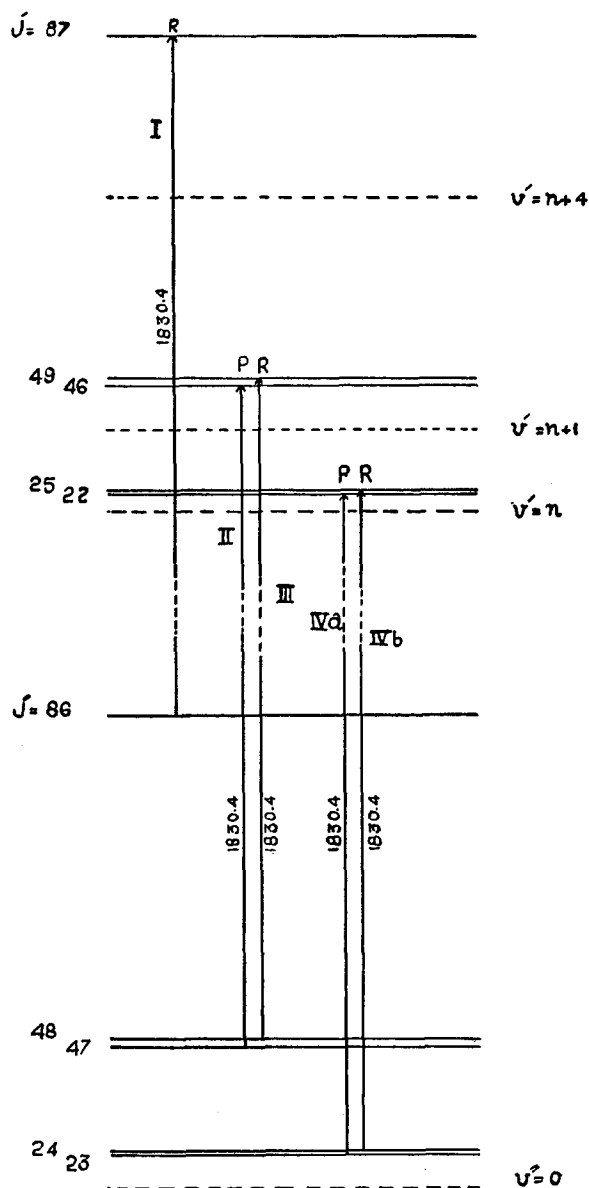


FIG. 2. Energy level diagram showing the process of excitation by a single iodine atomic line 1830.4 Å.

smooth curves for II and III, emphasis was given to the points below $v''=20$ and above $v''=42$. The points between are found to lie below the smooth curve, as is expected according to the analysis. The P line of II and the R line of III coincide for low v'' values and for higher v'' values they begin to separate out. But they could not be resolved by the instrument used

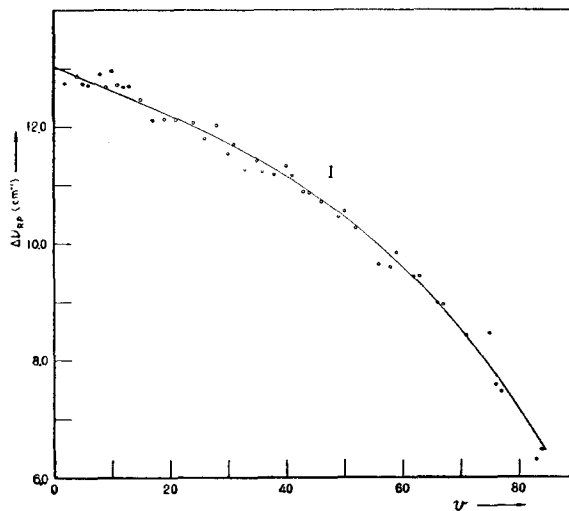


FIG. 3. $\Delta\nu$ versus v'' for series I.

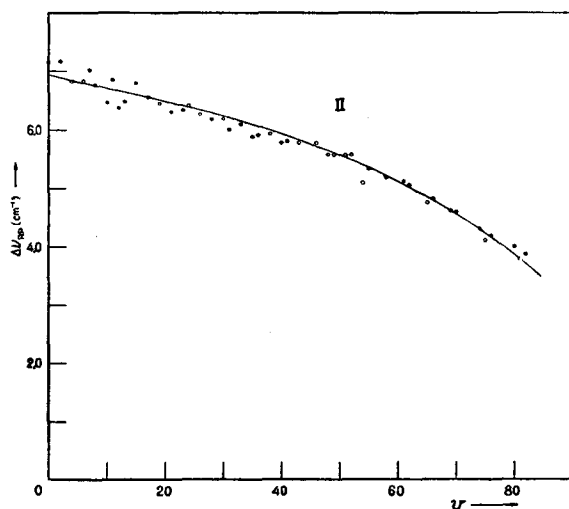


FIG. 4. $\Delta\nu$ versus v'' for series II.

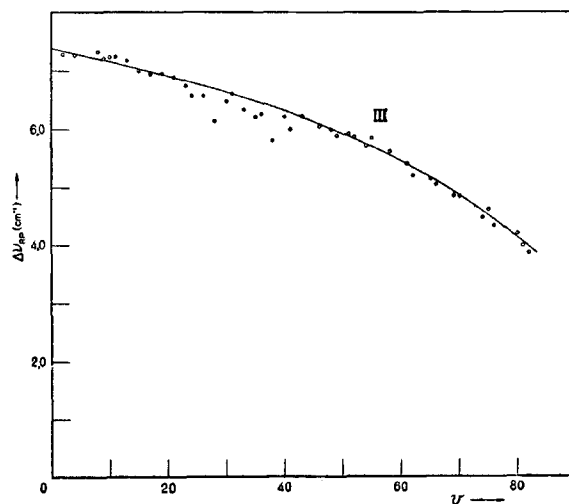


FIG. 5. $\Delta\nu$ versus v'' for series III.

below $v''=43$ and the measurements correspond to the mean of the positions of the two lines and hence this mean is larger than the true value of the P line of II and less than the true value of the R line of III. Thus $\Delta\nu$ for the two doublet series II and III falls below the true curves for the points below $v''=43$. The empirical equations developed for the three curves are given in the following:

For I,

$$\Delta\nu = 13.037 - 0.0428v + 1.52 \times 10^{-4}v^2 - 6.5 \times 10^{-6}v^3 - 0.20 \times 10^{-8}v^4. \quad (4)$$

For II,

$$\Delta\nu = 6.932 - 2.25 \times 10^{-2}v + 0.756 \times 10^{-4}v^2 - 3.43 \times 10^{-6}v^3. \quad (5)$$

For III,

$$\Delta\nu = 7.380 - 2.40 \times 10^{-2}v + 0.81 \times 10^{-4}v^2 - 3.60 \times 10^{-6}v^3. \quad (6)$$

On comparing the coefficients of equations (1') and (4) and on elimination one gets from series I,

$$(4J_r + 2)[B_e - (2J_r^2 + 2J_r + 2)D_e] = 13.0584 \quad (7)$$

$$(4J_r + 2)[\alpha_e + (2J_r^2 + 2J_r + 2)\beta_e] = 0.042937 \quad (8)$$

$$\left. \begin{aligned} (4J_r + 2)\gamma_e &= 1.61947 \times 10^{-4} \\ (4J_r + 2)\delta_e &= 6.496 \times 10^{-8} \\ (4J_r + 2)\phi_e &= 0.20 \times 10^{-8} \end{aligned} \right\} \quad (9)$$

B_e is known precisely from the interferometric work on the resonance spectrum in the visible region by Rank and Baldwin.⁶ Neglecting the term D_e in Eq. (7) and putting $B_e = 0.037364$ give

$$4J_r + 2 \simeq 349.5$$

$$J_r \simeq 86.9$$

$$= 87 \quad (\text{as } J_r \text{ has to be integer}).$$

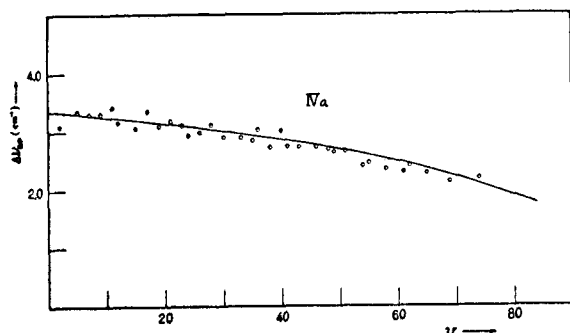


FIG. 6. $\Delta\nu$ versus v'' for series IVa.

⁶ D. H. Rank and W. M. Baldwin, J. Chem. Phys. 19, 1210 (1951).

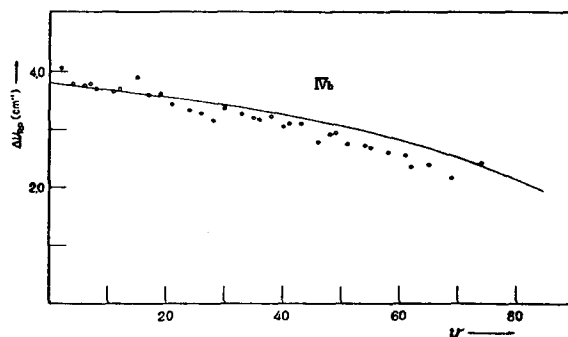


FIG. 7. $\Delta\nu$ versus v'' for series IVb.

It has been checked that neglect of the term D_e in the above calculation does not cause any error in J_r , and also any uncertainty in the last two figures of B_e are insignificant in the calculation of J_r . Having thus decided J_r , one could calculate γ_e , δ_e and ϕ_e directly from Eqs. (9). Equations (7) and (8) then reduce to the following:

$$B_e - 15314D_e = 0.037309797 \quad (7')$$

$$\alpha_e + 15314\beta_e = 0.000122677. \quad (8')$$

Similar calculations were followed for series II and III and the equations corresponding to (7') and (8') are obtained in the following:

For II,

$$B_e - 4326D_e = 0.03732933 \quad (7'')$$

$$\alpha_e + 4326\beta_e = 0.000121239 \quad (8'')$$

For III,

$$B_e - 4902D_e = 0.03733362 \quad (7''')$$

$$\alpha_e + 4902\beta_e = 0.000121483. \quad (8''')$$

The J_r values for II and III are found to be 46 and 49, respectively. γ_e and δ_e for these two series were calculated as for I. Equations (7'), (7''), and (7''') were solved by the least squares method and B_e and D_e were found. Similarly α_e and β_e were calculated. The average values of these constants are represented by the following two equations:

$$B_e = 0.03734 - 0.0001208(v + \frac{1}{2}) + 0.444 \times 10^{-6}(v + \frac{1}{2})^2 - 1.839 \times 10^{-8}(v + \frac{1}{2})^3 - 0.057 \times 10^{-10}(v + \frac{1}{2})^4 \quad (10)$$

$$D_e = 1.99 \times 10^{-9} + 1.236 \times 10^{-10}(v + \frac{1}{2}). \quad (11)$$

For the series IVa and IVb, the J_r values are calculated to be 22 and 25 and the solid curves IVa and IVb were drawn by using the following equations:

For IVa,

$$\Delta\nu = 3.355 - 1.083 \times 10^{-2}v + 3.751 \times 10^{-6}v^2 - 1.641 \times 10^{-6}v^3 \quad (12)$$

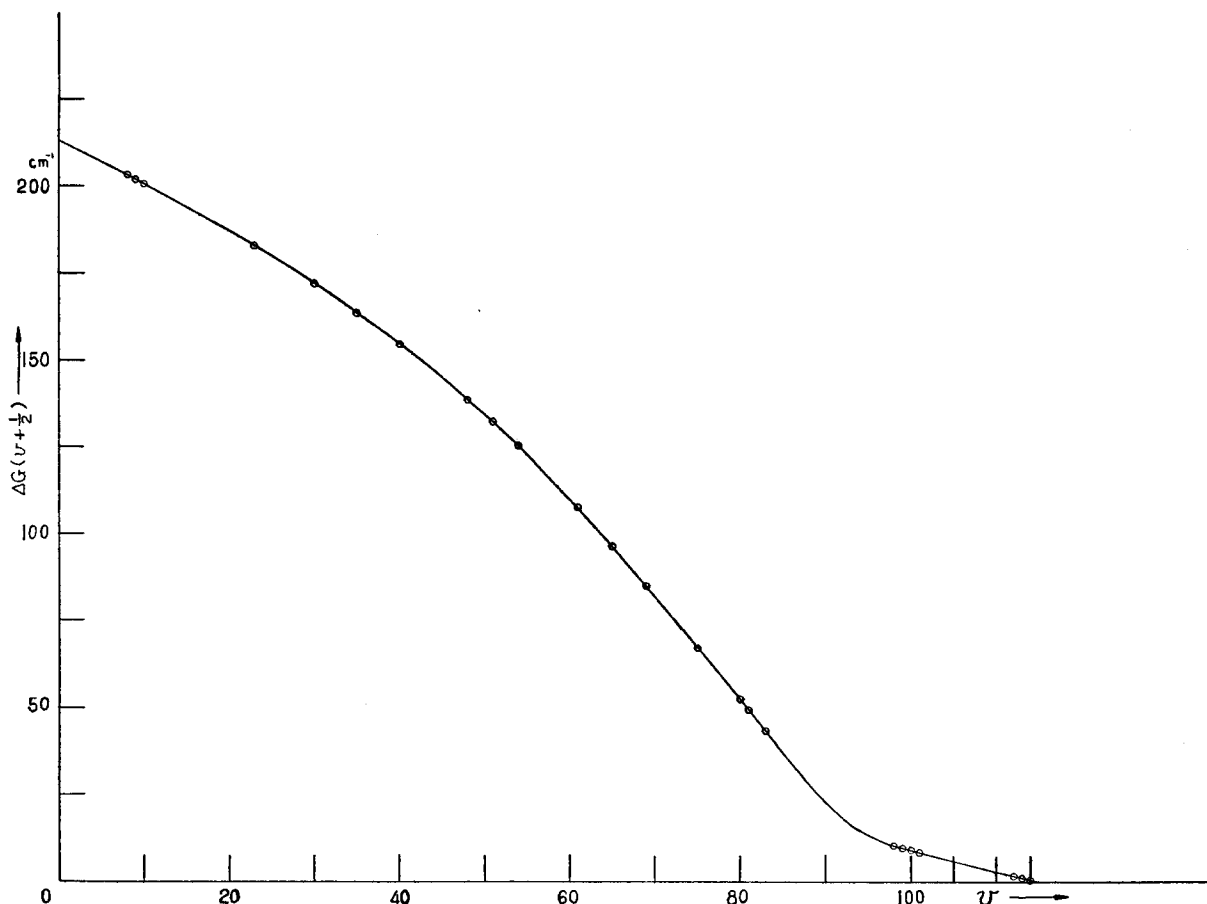


FIG. 8. $\Delta G(v + \frac{1}{2})$ versus v for the ground state of I_2 . For description see the text.

and

for IVb

$$\Delta\nu = 3.805 - 1.226 \times 10^{-2}v + 4.251 \times 10^{-5}v^2 - 1.859 \times 10^{-6}v^3. \quad (13)$$

These equations were developed from the constants given in Eqs. (10) and (11). The smooth curves so drawn represent the points for low v'' values as well as for the last point, for which the overlapping lines of the two doublets are resolved. The in-between points are below these curves in accordance with the reasons given for II and III.

Since three different vibrational levels are excited in the upper state as shown in Fig. 2, it was possible to calculate the vibrational and rotational constants of the upper state at those vibrational levels and the values found are given in the following:

$$\begin{aligned} \omega_n' &= 43.13 \text{ cm}^{-1} \\ (\omega x)_n' &= 0.19 \text{ cm}^{-1} \\ B_n' &= 0.01243 \text{ cm}^{-1} \end{aligned}$$

where n is unknown.

The series IVb is found to converge at 42201.41 cm^{-1} [Fig. 1(g)]. Therefore the dissociation energy of the ground electronic state of I_2 could be calculated as follows:

$$\begin{aligned} D_0 &= \text{exciting line (cm}^{-1}) - 42201.4 + F''(24) \text{ (for } v''=0) \\ &= 54632.9 - 42201.4 + 22.4 \\ &= 12453.9 \text{ cm}^{-1}. \end{aligned}$$

This value of D_0 may be slightly higher than the true value of D_0 by the amount of the height of the rotational level $J=24$ above the rotational level $J=0$ in the last vibrational level of the ground state. But the B_v value for this level is not known. However, out of the 18 doublets preceding the convergence limit, the first three were resolved and the B_v values for them could be calculated as 0.00696 cm^{-1} , 0.00588 cm^{-1} , and 0.00490 cm^{-1} . Taking $B_v = 0.00490 \text{ cm}^{-1}$, the height of the rotational level $J=24$ above $J=0$ was calculated to be 2.94 cm^{-1} which is more than its value for the last vibrational level. Thus the lower limit of D_0 is set at 12451.0 cm^{-1} and the higher limit at 12453.9 cm^{-1} , i.e., $D_0 = 12452.5 \pm 1.5 \text{ cm}^{-1}$. This value of D_0 can be contrasted with the previous value of $12439 \pm 8 \text{ cm}^{-1}$

determined from the convergence limit⁷ of the visible absorption bands.

The separation between successive R lines or P lines in a series is equal to the separation between two successive vibrational levels of the lower electronic state (ground state in this case) for a constant J value. Denoting this by $\Delta E^J(v+\frac{1}{2})$ it can be shown that

$$\Delta G''(v+\frac{1}{2}) = \Delta E^J(v+\frac{1}{2}) + J(J+1)(B_v'' - B_{v+1}'') - J^2(J+1)^2(D_v'' - D_{v+1}''). \quad (15)$$

The contribution by the last term is negligible, and therefore Eq. (15) reduces to

$$\Delta G''(v+\frac{1}{2}) = \Delta E^J(v+\frac{1}{2}) + J(J+1)(B_v'' - B_{v+1}''). \quad (15')$$

Thus it was possible to calculate the $\Delta G(v+\frac{1}{2})$ values for the ground electronic state of I_2 . The P lines of series III were chosen to obtain $\Delta E^J(v+\frac{1}{2})$. Missing lines were obtained from the graph plotted between ν_p and v'' . The $\Delta G''(v+\frac{1}{2})$ values were then calculated up to $v''=83$ using Eq. (15'). B_v'' in Eq. (15') was calculated from Eq. (10). The $\Delta G''(v+\frac{1}{2})$ values thus obtained are plotted against v'' (Fig. 8) and are shown by a smooth curve. The points marked in Fig. 8 are those for which the $\Delta E^J(v+\frac{1}{2})$ values were obtained directly. The $\Delta E^J(v+\frac{1}{2})$ values for the last 17 vibrational quanta were obtained from series IVb which converges to a sharp limit, but vibrational quantum numbers for them could not be identified independently. The doublet separation could be resolved only in the first three members as pointed out earlier. Therefore the B_v values for other members could not be found and hence the $\Delta G(v+\frac{1}{2})$ values for these vibrational

TABLE V. Doublet series IVb at convergence limit.

v''	ν_{vac} cm ⁻¹	$\Delta E^J(v+\frac{1}{2})$ cm ⁻¹
(98)	42 289.41 <i>R</i>	9.87
	42 288.70 <i>P</i>	
(99)	42 279.54 <i>R</i>	
	42 278.94 <i>P</i>	9.24
(100)	42 270.30 <i>R</i>	
	42 269.80 <i>P</i>	8.70
(101)	42 261.60 <i>R, P</i>	8.23
(102)	42 253.37 <i>R, P</i>	7.37
(103)	42 246.00 <i>R, P</i>	6.82
(104)	42 239.18 <i>R, P</i>	6.26
(105)	42 232.92 <i>R, P</i>	5.70
(106)	42 227.22 <i>R, P</i>	5.23
(107)	42 221.99 <i>R, P</i>	4.44
(108)	42 217.55 <i>R, P</i>	4.11
(109)	42 213.44 <i>R, P</i>	3.32
(110)	42 210.12 <i>R, P</i>	2.99
(111)	42 207.13 <i>R, P</i>	2.28
(112)	42 204.85 <i>R, P</i>	1.66
(113)	42 203.19 <i>R, P</i>	1.07
(114)	42 202.02 <i>R, P</i>	0.61
(115)	42 201.41 <i>R, P</i>	

⁷ W. G. Brown, Phys. Rev. **38**, 709 (1931).

TABLE VI. $\Delta G(v+\frac{1}{2})$ values for ground state of I_2 .

v''	$\Delta G(v+\frac{1}{2})$ cm ⁻¹	v''	$\Delta G(v+\frac{1}{2})$ cm ⁻¹
0	213.31	58	115.28
1	212.05	59	112.69
2	210.80	60	110.09
3	209.66	61	107.47
4	208.50	62	104.81
5	207.20	63	102.12
6	205.80	64	99.35
7	204.55	65	96.54
8	203.18	66	93.71
9	201.93	67	90.87
10	200.68	68	88.01
11	199.30	69	85.11
12	198.05	70	82.25
13	196.73	71	79.28
14	195.36	72	76.16
15	194.06	73	73.18
16	192.73	74	70.07
17	191.31	75	67.04
18	189.96	76	64.12
19	188.47	77	61.16
20	187.07	78	58.21
21	185.71	79	55.25
22	184.21	80	52.33
23	182.74	81	49.43
24	181.34	82	46.60
25	179.85	83	43.70
26	178.28	84	40.50
27	176.78	85	37.4
28	175.23	86	34.3
29	173.62	87	31.5
30	172.05	88	28.5
31	170.43	89	25.6
32	168.76	90	23.0
33	167.15	91	20.6
34	165.45	92	18.4
35	163.79	93	16.4
36	162.05	94	14.8
37	160.23	95	13.5
38	158.44	96	12.4
39	156.57	97	11.4
40	154.62	98	10.5
41	152.72	99	9.8
42	150.85	100	9.0
43	148.98	101	8.5
44	147.00	102	8.0
45	145.10	103	7.4
46	143.02	104	6.7
47	141.03	105	6.2
48	138.87	106	5.5
49	136.80	107	5.0
50	134.65	108	4.5
51	132.33	109	3.9
52	130.01	110	3.3
53	127.67	111	2.6
54	125.24	112	2.0
55	122.71	113	1.4
56	120.27	114	0.5
57	117.86		

levels could not be calculated according to Eq. (15'). However, taking the B_v values for the first three members out of 18, the $\Delta G(v+\frac{1}{2})$ values were calculated for the first four vibrational levels. The last three $\Delta E^J(v+\frac{1}{2})$ values were taken equal to the $\Delta G(v+\frac{1}{2})$ values which holds fairly well in the neighborhood of the dissociation limit. With the help of these seven $\Delta G(v+\frac{1}{2})$ values and the D_0 value calculated earlier, the curve after $v''=83$ could be adjusted without any difficulty and the v'' values for these 18 members

TABLE VII. Results of calculations for potential energy curve for ground state of I_2 .

v	$U(r)$ cm^{-1}	r_{\min} Å	r_{\max} Å
0	102.08	2.621	2.717
2	527.44	2.564	2.790
6	1 363.60	2.510	2.874
10	2 179.06	2.474	2.940
14	2 973.82	2.446	3.001
18	3 747.28	2.423	3.056
22	4 498.49	2.403	3.111
26	5 226.63	2.386	3.164
30	5 930.54	2.371	3.217
34	6 608.93	2.358	3.273
38	7 260.45	2.346	3.329
42	7 882.80	2.336	3.389
46	8 474.73	2.328	3.451
50	9 034.45	2.321	3.517
54	9 559.11	2.315	3.591
58	10 045.19	2.309	3.671
62	10 490.72	2.305	3.760
66	10 893.54	2.301	3.861
70	11 251.24	2.298	3.973
74	11 562.11	2.296	4.108
78	11 824.50	2.294	4.263
82	12 039.72	2.292	4.448
85	12 170.52	2.291	4.628
89	12 302.32	2.290	4.942
91	12 352.32	2.290	5.133
93	12 393.42	2.289	5.354
95	12 427.12	2.289	5.563
97	12 454.62	2.289	5.778
99	12 476.92	2.288	6.010
101	12 495.02	2.288	6.263
103	12 509.82	2.288	6.522
105	12 522.32	2.288	6.823
107	12 532.22	2.288	7.236
112	12 547.52	2.288	8.814

of IVb, thus identified, are shown in Table V. After adjusting the curve, the $\Delta G(v+\frac{1}{2})$ values were read off and all the values are collected in Table VI. The ω_e value for the ground state of I_2 according to these $\Delta G(v+\frac{1}{2})$ values is 214.52 cm^{-1} . It may be pointed out that the ω_e value of 214.248 cm^{-1} as given by Rank and Baldwin for I_2 has been calculated wrongly from their empirical equation⁸ and it should be 214.518 cm^{-1} which agrees very well with the present value.

POTENTIAL ENERGY CURVE

Since this work provides data for the positions of all the vibrational levels of the ground electronic state and for the values of the rotational constants, an attempt has been made to compute the potential energy curve right up to the dissociation limit by the Rydberg-Klein-Rees method.^{9,10} However, the final forms of the expressions for the computations of the RKR method have been changed into more convenient forms as discussed in the following

⁸ The author examined the data which Professor Rank kindly sent to him and this mistake has been confirmed by private communication.

⁹ A. L. G. Rees, Proc. Phys. Soc. (London) **59**, 998 (1947).

¹⁰ Vanderslice, Mason, and Maisch, J. Mol. Spectroscopy **3**, 17 (1959). (It is to be noted that a factor of $\frac{1}{2}$ in the expression for g should read 2. This has been confirmed by private communication with the authors.)

The auxiliary function S as defined in earlier work,^{9,10} is

$$S(U, k) = (2\pi^2\mu)^{-\frac{1}{2}} \int_0^{I'} [U - E(I, k)]^{\frac{1}{2}} dI \quad (16)$$

where at $I = I'$, $U = E$ and $I = h(v+\frac{1}{2})$, $k = J(J+1)/b$, $b = 8\pi^2\mu/h^2$. Substituting the value of

$$E(I, k) = \omega_e(v+\frac{1}{2}) - \omega_e x_e(v+\frac{1}{2})^2 + B_e J(J+1) - D_e J^2(J+1)^2 - \alpha_e J(J+1)(v+\frac{1}{2})$$

in Eq. (16) and introducing the variables I and k , we have

$$S(U, k) = q \int_0^{I'} (A - lI + mI^2)^{\frac{1}{2}} dI \quad (16')$$

where

$$1/q = (2\pi^2\mu h)^{\frac{1}{2}},$$

$$A = h[U - B_e J(J+1) + D_e J^2(J+1)^2],$$

$$l = \omega_e - \alpha_e J(J+1),$$

$$m = \omega_e x_e / h.$$

Differentiating with respect to U and k under the integral sign, and then performing the integration, leads to the following expressions for f and g :

$$f = qh/2m^{\frac{1}{2}} \ln \{ (l - 2mI') / [l - (4mA)^{\frac{1}{2}}] \} \quad (17)$$

$$g = qb/2(m^{\frac{1}{2}})^{\frac{1}{2}} [\alpha_e (4mA)^{\frac{1}{2}} + 2mB_e h + 4mD_e h b k - \alpha_e l]$$

$$\cdot \ln \{ [l - 2mI'] / [l - (4mA)^{\frac{1}{2}}] \}. \quad (18)$$

For the rotationless state ($J=0$), applying the condition $U = E$ at $I = I'$ one gets

$$\begin{aligned} l - 2mI' &= \omega_e - 2\omega_e x_e(v+\frac{1}{2}) \\ &= \Delta G(v+\frac{1}{2}) + \omega_e x_e \end{aligned} \quad (19)$$

and

$$\begin{aligned} (4mA)^{\frac{1}{2}} &= [4\omega_e x_e \{ \omega_e(v+\frac{1}{2}) - \omega_e x_e(v+\frac{1}{2})^2 \}]^{\frac{1}{2}} \\ &= [\omega_e^2 - \{ \Delta G(v+\frac{1}{2}) + \omega_e x_e \}^2]^{\frac{1}{2}} = \chi^{\frac{1}{2}}. \end{aligned}$$

Therefore

$$\begin{aligned} f &= (8\pi^2\mu c/h)^{-\frac{1}{2}} \ln W / (\omega_e x_e)^{\frac{1}{2}} \\ g &= (2\pi^2\mu c/h)^{\frac{1}{2}} [(\alpha_e / (\omega_e x_e))^{\frac{1}{2}} \cdot \chi^{\frac{1}{2}} + (2B_e - \alpha_e \omega_e / \omega_e x_e) \\ &\quad \cdot \ln W / (\omega_e x_e)^{\frac{1}{2}}] \end{aligned}$$

where

$$\begin{aligned} W &= (\Delta G(v+\frac{1}{2}) + \omega_e x_e) / (\omega_e - \chi^{\frac{1}{2}}) \\ \chi &= \omega_e^2 - [\Delta G(v+\frac{1}{2}) + \omega_e x_e]^2. \end{aligned}$$

However, when a series of quadratics in the form of $E(I, k)$ are chosen to represent the entire experimental range, the auxiliary function S can be put in the

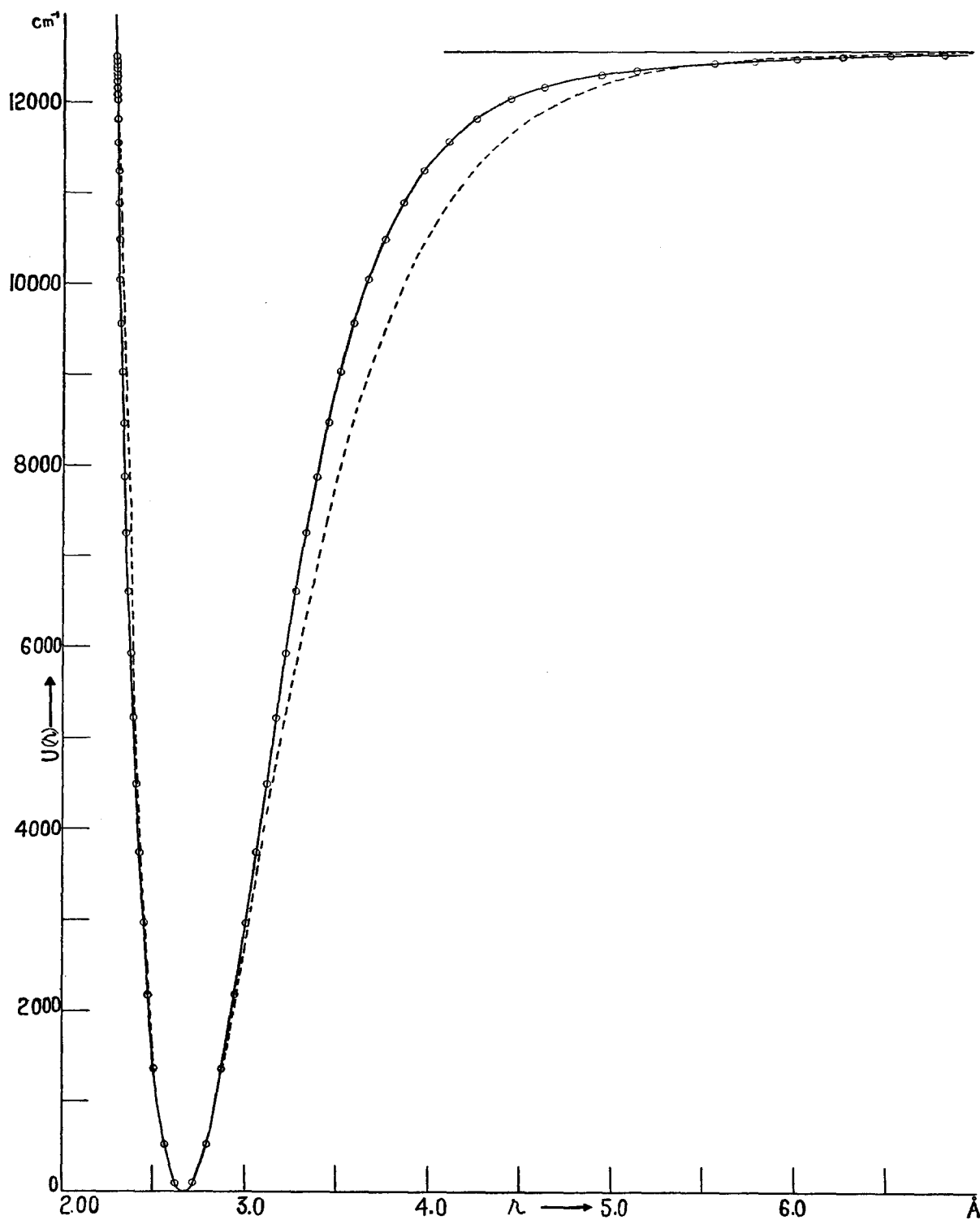


FIG. 9. The potential energy curve for the ground state of I_2 as computed by the RKR method. The dotted curve is the Morse curve.

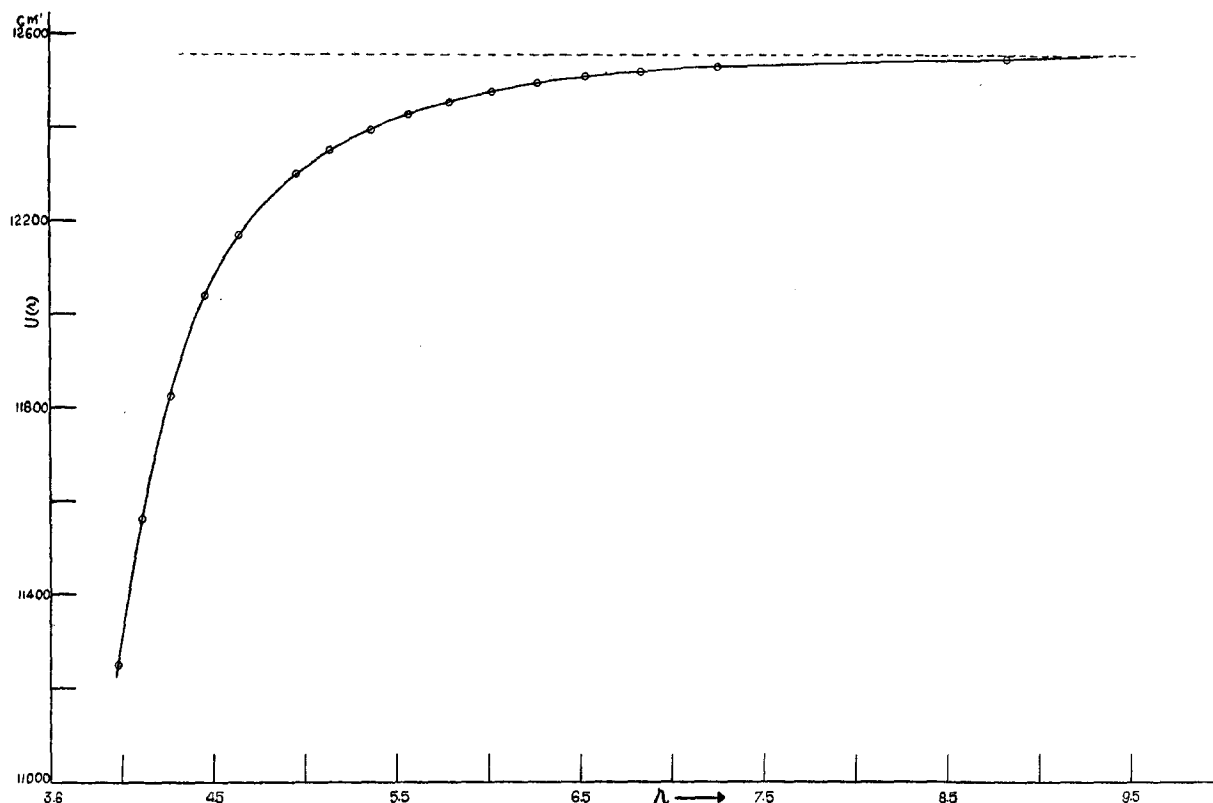


FIG. 10. The potential energy curve for the ground state of I_2 near the dissociation limit, drawn on a larger scale.

following form:

$$S(U, k) = (2\pi^2\mu h)^{-\frac{1}{2}} \sum_{i=1}^n \int_{I_{i-1}}^{I_i} (A_i - l_i I + m_i I^2)^{\frac{1}{2}} dI$$

and the expressions for f and g for the n th vibrational level become

$$f_n = (8\pi^2\mu c/h)^{-\frac{1}{2}} \sum_{i=1}^n \ln W_i / (\omega x)_i^{\frac{1}{2}}$$

$$g_n = (2\pi^2\mu c/h)^{\frac{1}{2}} \sum_{i=1}^n [\alpha_i / (\omega x)_i^{\frac{1}{2}} \cdot (\chi_i^{\frac{1}{2}} - \chi_{i-1}^{\frac{1}{2}}) + (2B_i - \alpha_i \omega_i / (\omega x)_i \ln W_i / (\omega x)_i^{\frac{1}{2}})]$$

where

$$W_i = [\Delta G(v + \frac{1}{2})_i + (\omega x)_i] / [\Delta G(v + \frac{1}{2})_{i-1} + (\omega x)_{i-1}] \cdot [\omega_i - \chi_{i-1}^{\frac{1}{2}}] / [\omega_i - \chi_i^{\frac{1}{2}}]$$

$$\chi_i = \omega_i^2 - [\Delta G(v + \frac{1}{2})_i + (\omega x)_i]^2$$

and $v = i - 1$ for the i th level.

The energy zero is chosen as the minimum of the $U(r)$ curve (i.e., $U_0 = 0$). Therefore $\chi_0 = 0$ and $\Delta G(v + \frac{1}{2})_0 + (\omega x)_1 = \omega_1$. The constants ω , ωx , B , and α are allowed to vary from quadratic to quadratic. This form involves the $\Delta G(v + \frac{1}{2})$ instead of U and hence avoids the confusion about zero reference point for each

quadratic, and also computations of the factor W_i are much simpler than previously.

The potential energy curve for the ground state of I_2 has been computed by using the data given in this paper, and the results are tabulated in Table VII and plotted in Figs. 9 and 10. Figure 10 shows the potential energy curve near the dissociation limit on a larger scale. The calculations above $v'' = 84$ could not be carried out directly as the constants B and α could not be obtained from the experimental data above $v'' = 84$. However, short extrapolation of the curve passing through the points representing r_{\min} below $v'' = 84$ is justified and r_{\min} could be obtained above $v'' = 84$. For these points above $v'' = 84$, the quantity f could be calculated from the experimental data as it does not involve B and α . Thus r_{\max} could be calculated as

$$r_{\max} = r_{\min} + 2f.$$

The potential energy curve so plotted shows the interesting feature of approaching the asymptote very slowly and it appears to show that at larger r values, the van der Waals forces are predominating over the valence forces. It is found that the potential energy curve follows the c/r^6 force law between $r = 4.6$ Å and $r = 6.4$ Å. The van der Waals force constant c was calculated to be 3.7×10^6 , if $U(r)$ and r are in cm^{-1} and Å respectively. The curve could be fitted within $\pm 3 \text{ cm}^{-1}$. It may be pointed out that the theoretical

value¹¹ of '*c*' for the HI molecule is 2.24×10^6 and is a little less than that for I₂ as expected.

ELECTRONIC TRANSITION

The lower state of this transition is the well-known $\sigma_g^2 \pi_u^4 \pi_g^4 {}^1\Sigma_g^+(O_g^+)$ the ground state of the molecule. There is no direct experimental evidence for deciding the nature of the upper electronic state, but a very good prediction can be made by considering the structure of the resonance series observed in this transition. According to the analysis only doublet series are excited and hence if upper state obeys Hund's case *c* (which is very likely) it has to be O_u^+ . There are a number of possibilities for the electron configurations¹² which can be associated with this state. However, the long resonance series observed suggest that the transition involved has a very high transition probability and may correspond to the transition which is responsible

for the Cordes¹³ absorption bands. From these considerations, one may propose one possibility as the *V* state, $\sigma_g \pi_u^4 \pi_g^4 \sigma_u$, ${}^1\Sigma_u^+(O_u^+)$ for the upper state. However, the possibility of the electronic states ${}^1\Sigma_u^+(O_u^+)$ and ${}^3\Sigma_u^-(O_u^+)$ arising from the electron configuration $\sigma_g^2 \pi_u^3 \pi_g^3 \sigma_u^2$ cannot be ruled out easily. It may be pointed out that one of these two states has been tentatively associated with the upper state at $T_e = 47207 \text{ cm}^{-1}$ of the emission band system¹⁴ 2730–2486 Å.

ACKNOWLEDGMENTS

The author expresses his thankfulness to Dr. P. G. Wilkinson for his helpful suggestions and encouragement while working with the vacuum spectrograph. Sincere thanks are extended to Dr. Putcha Venkateswarlu for his interest in the work. The author is highly thankful to Professor R. S. Mulliken for his kind interest in the work and for his valuable suggestions and discussions.

¹¹ F. London, Trans. Faraday Soc. **33**, 8 (1937).

¹² R. S. Mulliken, Phys. Rev. **46**, 549 (1934).

¹³ H. Cordes, Z. Physik **97**, 603 (1935).

¹⁴ R. D. Verma, Proc. Indian Acad. Sci. **48**, 197 (1958).

Thermodynamic Properties of Nonstoichiometric Urania-Thoria Solid Solutions

S. ARONSON AND J. C. CLAYTON

Bettis Atomic Power Laboratory, Pittsburgh 30, Pennsylvania

(Received September 28, 1959)

A solid state electrochemical technique has been used to obtain thermodynamic information on urania-thoria solid solutions of compositions $U_yTh_{1-y}O_{2+x}$ with values of *y* of 0.9 to 0.3 and values of *x* of 0.02 to 0.16. The electrochemical cells were of the type Fe, FeO | (ZrO₂+CaO) | $U_yTh_{1-y}O_{2+x}$, Pt. Measurements were made at temperatures of 1150–1350°K.

Partial molar free energies, entropies, and enthalpies of solution of oxygen in the solid solutions were calculated. The partial molar free energy decreases negatively with increasing thorium content for thorium concentrations greater than 30 atomic percent. The partial molar entropy increases negatively with increasing oxygen content or with increasing thorium content.

The experimental results are discussed in connection with a mechanism of interstitial solution of oxygen ions in the fluorite lattice. A thermodynamic equation for the entropy is developed which gives semiquantitative agreement with the experimental data.

I. INTRODUCTION

URANIUM dioxide and thorium dioxide form a continuous series of solid solutions in which the fluorite structure is maintained.¹ Anderson *et al.*² studied the oxidation of these solid solutions. They found that, for uranium contents greater than 50 atomic percent, the solid solutions, $U_yTh_{1-y}O_{2+x}$, could incorporate into interstitial sites in the lattice up to a value of *x* equal to 0.32–0.34 without destroying the

fluorite structure. At higher thorium contents, the maximum uptake of oxygen decreased with increasing thorium content.

Thermodynamic information on the nonstoichiometric solid solutions having high thorium contents (*y* < 0.25) have been reported by Anderson *et al.*² and by Roberts *et al.*³ The pressures of oxygen in equilibrium with the solid solutions increased with decreasing uranium content.² The partial molar heats of solution of oxygen in the solid decreased negatively with de-

¹ W. Trzebiatowski and P. W. Selwood, J. Am. Chem. Soc. **72**, 4504 (1950).

² Anderson, Edgington, Roberts, and Wait, J. Chem. Soc. **1954**, 3324.

³ Roberts, Russell, Adwick, Walter and Rand, "Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy," Geneva, September 1–13, 1958, Vol. 28, p. 215.