

limiting value for the correlation correction per unit volume.

$$\lim_{D \rightarrow 0} (E_{\text{corr}} / \frac{4}{3}\pi D^3) = -(1/32\pi)\zeta^3 = -0.0477 \text{ hartree/bohr}^3. \quad (12)$$

One can try to estimate the magnitude of the error arising from the lack of a small cusp in Φ_{CI} around $r_{12}=0$. Table IV contains absolute improvements, $E_D - E_{D=0}$, for small D for three wavefunctions. Notice that for a particular value of D these improvements are of the same order of magnitude, although the total expected improvements ΔE differ greatly. Thus the error due to a missing small cusp is not too dependent on the wavefunction. How large would a cusp have to be to correct the remaining error in the energies calculated from some of the best available configuration interaction functions? The 35-term function of Weiss,⁶ con-

taining angular terms through $l=4$, differs by 5×10^{-4} hartree from the nonrelativistic value of Pekeris.¹⁹ Assuming that this function is in error by only a missing cusp, one might hope, from the values in Table IV, to capture the remaining error by including a cusp of $D \sim 0.2$ bohr. In the most extensive helium configuration interaction calculation to date, with a wavefunction containing angular terms through $l=8$, Tycko, Thomas, and King²⁰ computed an energy that differed by 2.8×10^{-4} hartree from the Pekeris value. To correct this deficiency would require a cusp of $D \sim 0.15$ bohr. It seems probable, therefore, that even pushing configuration interaction to its practical limits would still leave out a cusp of $D \sim 0.1$ and yield an energy too high by $\sim 1 \times 10^{-4}$ hartree.

¹⁹ C. L. Pekeris, Phys. Rev. **112**, 1649 (1958).

²⁰ D. H. Tycko, L. H. Thomas, and L. M. King, Phys. Rev. **109**, 369 (1958); see the critique of this paper by C. Schwartz, Phys. Rev. **126**, 1015 (1962).

Spectroscopic Constants and Vibrational Assignment for the $B \ ^3\Pi_{0_u}+$ State of Iodine*

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Portions of the iodine $B \ ^3\Pi_{0_u}+\leftarrow X \ ^1\Sigma_g+$ absorption spectrum have been remeasured under high resolution. A new analysis of 719 lines in the 3-6, 4-7, 5-4, 7-5, 11-1, 12-2, 13-2, 25-0, and 29-0 bands, combined with previous measurements by Mecke, Loomis, and Brown, gives the following revised constants:

$\omega_e' = 125.273 \text{ cm}^{-1}$	$T_e' = 15770.59$	$\gamma_e' = -4.0 \times 10^{-7}$
$\omega_e x_e' = 0.7016$	$B_e' = 0.028969$	$\delta_e' = -3.5 \times 10^{-8}$
$\omega_e y_e' = -0.00567$	$r_e' = 3.0276 \text{ \AA}$	$D_e' = 3.5 \times 10^{-9}$
$\omega_e z_e' = +0.000032$	$\alpha_e' = 0.0001562$	$\beta_e' = 3.9 \times 10^{-10}$
$D_e' = 4391.0$		

Constants for ground state rotational levels were found to be in good agreement with Rank's latest determinations.

Using these new constants for the B state, Franck-Condon factors for this system were computed. The vibrational numbering originally assigned by Mecke and Loomis to the B state was decreased by one unit to bring calculated intensity distribution into complete agreement with all observed fluorescence data, including new photoelectric measurements on a number of bands. No systematic variation of the electronic transition moment could be derived from these data. These revised Franck-Condon factors were also used to recalculate radiative lifetimes from absolute absorption data which are in fair agreement with the phase-shift determination of Brewer, Berg, and Rosenblatt.

INTRODUCTION

MOLECULAR iodine has often been used as a model system for energy transfer studies by monochromatically excited fluorescence,¹ most re-

cently in this laboratory.² A knowledge of the correct relative radiative transition probabilities for the different fluorescence bands is required in order to obtain meaningful vibrational energy transfer cross sections from the observed spectroscopic data. Since it is preferable to observe fluorescence of bands that are not extensively self-absorbed, absolute absorption measurements for bands of interest in energy transfer work are difficult to obtain. Therefore, it is necessary to obtain

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† National Science Foundation Predoctoral Fellow.

¹ J. Franck and R. W. Wood, Phil. Mag. **21**, 314 (1911). (b) M. Eliahevitch, Physik. Z. Sowjetunion **1**, 510 (1932). (c) F. Rössler, Z. Physik **96**, 251 (1935). (d) J. C. Polanyi, Can. J. Chem. **36**, 121 (1958). (e) C. Arnot and C. A. MacDowell, *ibid.*, p. 114.

² (a) R. L. Brown, thesis, Harvard University (1963); R. L. Brown and W. Klemperer, J. Chem. Phys. (to be published); (b) J. I. Steinfeld and W. Klemperer (to be published). A preliminary account was given at the Molecular Spectroscopy and Structure Symposium, Columbus, Ohio, 1964.

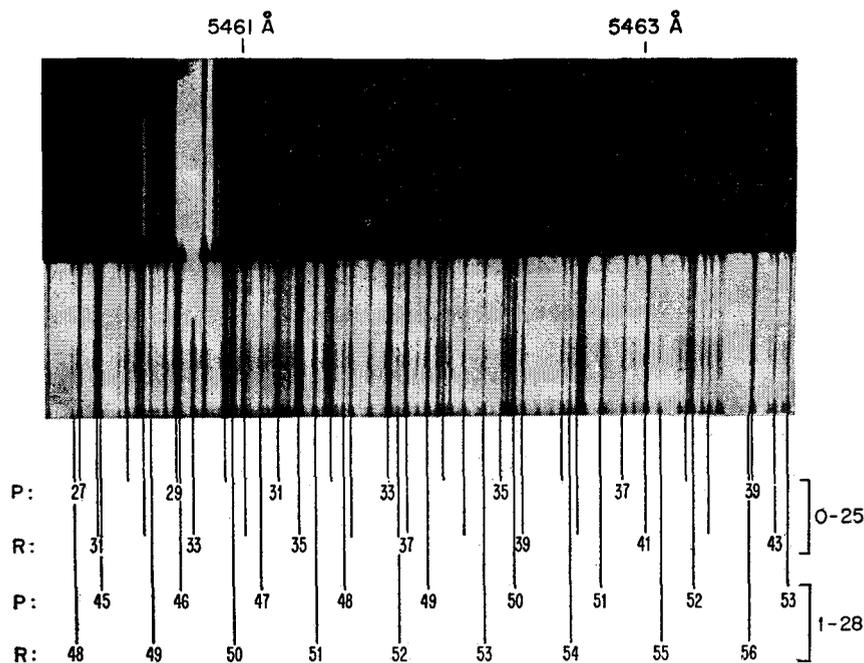


FIG. 1. Portion of iodine $B-X$ absorption system and mercury 5460.75- \AA line, showing hyperfine structure in latter. This exposure was taken on a III-F plate to reduce graininess. Note the overlapping of the central Hg line with a single feature in the I_2 absorption spectrum.

accurately calculated values of the Franck-Condon coefficients. The test of the accuracy of such a calculation is its agreement with observed intensity data for the primary resonance fluorescence series.

Intensity measurements on the fluorescence series excited by the mercury green line at 5460.75 \AA , first observed by Wood,³ have been recorded by Lenz⁴ and Oldenberg⁵ and more recently by Arnot and McDowell.⁶ All these measurements were taken from photographic plates. We have redetermined relative intensities photoelectrically, out to the 19th fluorescence doublet.

Using the customary assignment^{7,8} for the state excited at 5460.75 \AA , viz., electronic state $B^3\Pi_{0_u^+}$, $v'=26$, $J'=34$, and the tabulated spectroscopic constants,⁹ Zare¹⁰ was unable to obtain agreement between his calculations and the experimental data. He found that a small adjustment of the rotational constants of the upper state within the uncertainties allowable on the basis of the very incomplete spectroscopic data available at the time (so that, for example, B'_{26} had the value 0.02388 cm^{-1}) sufficed to bring calculated and experimental intensities into agreement. In addition, Brown^{2a} found that the accepted^{7,9} B state

constants did not reproduce the absorption spectrum in the vicinity of the sodium D lines. Furthermore, it was learned that the unpublished measurements on the I_2 absorption spectrum made by Wood, Loomis, *et al.* many years ago, and never fully analyzed, have since been discarded and are no longer available.¹¹ These facts led us to undertake a new analysis of the $B-X$ absorption spectrum, in order to obtain a consistent set of spectroscopic constants for this molecule, and to repeat the previous calculations of fluorescence intensity distributions and radiative lifetimes.

EXPERIMENTAL

The iodine sample had been distilled and sealed under vacuum by Brown into a 60-cm tube with flat Pyrex end windows. It was heated to about 100°C by "Glas-Col" heating tapes when the "hot bands" were to be measured. The spectrometer is a 10-m Littrow mounting. A newly installed Bausch & Lomb diffraction grating, having 73.25 lines/mm, and blazed at 63°26', was operated in this optical system at nearly its full resolving power of 500 000 with a plate dispersion of approximately 1 $\text{\AA}/\text{cm}$. The optical system included a small modified Perkin-Elmer prism system as a predisperser, and adjustable slits which were operated at a width of approximately 75 μ . The illumination used was a 2500-W Hanovia xenon arc lamp, with external ballast. Using this system, an exposure of approximately one minute or less was sufficient with Eastman Kodak I-F plates. A typical spectrum, taken in the neighborhood of the mercury green line, is shown in Fig. 1. The reference employed was a thorium line spectrum produced by an electrode-

³ R. W. Wood, *Physical Optics* (Macmillan and Company, New York, 1934), 3rd ed., pp. 616-647.

⁴ W. Lenz, *Z. Physik* **25**, 299 (1924).

⁵ O. Oldenberg, *Z. Physik* **45**, 451 (1927).

⁶ C. Arnot and C. A. McDowell, unpublished data reported by F. E. Stafford, thesis, University of California, UCRL-8854 (1959).

⁷ F. W. Loomis, *Phys. Rev.* **29**, 112 (1927).

⁸ P. Pringsheim, *Fluorescence and Phosphorescence* (Interscience Publishers, Inc., New York, 1949), p. 151 ff.

⁹ G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company, Princeton, New Jersey, 1950), 2nd ed., p. 541.

¹⁰ R. N. Zare, *J. Chem. Phys.* **40**, 1935 (1964). A complete documentation of the computer programs employed may be found in R. N. Zare, UCRL-10925 (Lawrence Radiation Laboratory, Berkeley, California, 1963).

¹¹ F. W. Loomis (private communication).

less discharge in an Ophthos ThI₄ lamp¹² excited by a Raytheon 2.4 kMc/sec diathermy generator. A 15-min exposure generally sufficed to develop a good thorium spectrum. All line positions were measured from the plates on a Mann traveling-microscope comparator which is accurate to 0.0002 cm, corresponding to 0.002 cm⁻¹ in the spectrum.

The photoelectric measurements of primary fluorescence intensities were made with the high-resolution photoelectric spectrometer described elsewhere.^{2b}

Computations of Franck-Condon factors, radiative lifetimes, and spectroscopic assignments were performed with the use of the IBM 7094 installations at Harvard and at MIT, and the IBM 1620 in this Department.

RESULTS AND DISCUSSION

A. Spectroscopic Constants

A total of 719 lines were measured and assigned in the 3-6, 4-7, 5-4, 7-5, 11-1, 12-2, 13-2, 25-0, and 29-0 bands.¹³ The vibrational assignment given for these bands is the one made for the reasons cited in Sec. B of the Results. The thorium reference lines were

TABLE I. B_v' values for I₂ B ³Π_u⁺ state.

v'	band	B_v' (polynomial fit) (cm ⁻¹)	B_v' (combination differences) (cm ⁻¹)	Source
3	3-6	...	0.02841	a, b
4	4-7	0.02828	0.02823	a, b
5	5-4	0.02808	0.02802	a
7	7-5	0.02780	0.02781	a
11	11-1	0.02710	0.02701	a
12	12-2	0.02692	0.02688	a
13	13-2	0.02670	0.02669	a
14	14-1	0.02655	...	c
15	15-1	...	0.02628	d
16	16-2	0.02615	...	c
17	17-0, 17-2	...	0.02589	d
18	18-1	...	0.02578	d
19	19-1	...	0.02554	d
25	25-0	0.02412	0.02413	a
	25-1	...	0.02416	e
28	28-0	...	0.02337	e
29	29-0	0.02312	0.02301	a

^a This work.

^b Reference 17 (Mecke, 1923).

^c Reference 2a (R. L. Brown, 1963).

^d R. L. Brown and D. Griffiths (unpublished data, 1961); uncertainty ±0.0001 cm⁻¹.

^e Reference 7 (Loomis, 1927).

¹² The narrow-tube design originally furnished by the Ophthos Company, was found to give a weak, unstable discharge. We are indebted to Ophthos for a gift of a new lamp, incorporating a considerably larger discharge region, which proved to be very satisfactory.

¹³ A listing of all assigned lines with their frequency and air wavelength has been deposited as Document No. 8187 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. A copy may be secured by citing the Document number and by remitting \$5.00 for photoprints, or \$2.25 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to Chief, Photoduplication Service, Library of Congress.

TABLE II. B_v'' values for I₂X ¹Σ_g⁺ state.

v''	band	B_v'' (combination differences) (cm ⁻¹)	B_v'' (calc. from Rank's consts.) (cm ⁻¹)
0	25-0, 29-0	0.03729	0.03733
1	11-1	0.03706	0.03721
2	12-2, 13-2	0.03702	0.03709
5	7-5	0.03672	0.03672
7	4-7	0.03654	0.03648

assigned with the aid of compilations of Zalubas¹⁴ and Littlefield¹⁵; a second-order polynomial function was generally required to represent the plate dispersion to within the accuracy of the line position measurements. Measurements of the same line on different plates generally agreed to within ±0.03 cm⁻¹.

Two separate analyses were applied to the absorption data. First, ground state energy levels were generated by an IBM 1620 computer, using the latest data available from Rank.¹⁶ The term values for the excited state were then computed using the observed absorption frequencies, and the rotation constants fitted as the coefficients of a function in $J(J+1)$ using an IBM 1620 SHARE program for least-squares polynomial curve fitting. Since complete P and R progressions were not always determined, this method did not waste any of the data. The second method was the standard procedure of combination differences, which yielded independent determinations of both X - and B -state spectroscopic constants. The result of the rotational analysis for the B state is shown in Table I, which includes data obtained from previous studies^{1,7,17} as well. It is estimated that these constants are reliable to better than ±0.00004 cm⁻¹. Table II compares the ground state rotational constants obtained from combination differences with those computed from Rank's constants.¹⁶ These are mostly in excellent agreement, although there seems to be a slight systematic deviation, of so small a magnitude as to be within our error limits, and which is certainly not significant for the vibrational overlap calculations. This deviation may be due to centrifugal distortion effects, which had not been accounted for in analyzing the fluorescence data for ground state rotational constants.

From the level-fitting procedure for the excited state, it was also possible to obtain values for D_v' , the centrifugal distortion coefficient. These are shown in Fig. 2. The scatter of the points bears out the fact that all residual errors tend to be incorporated into the D_v' by this procedure; nevertheless, the general trend of the data is evident. No reliable information on D_v'' could be elicited, since the addition of a $[J(J+1)]^2$

¹⁴ R. Zalubas, "New Description of Thorium Spectra," National Bureau of Standards Monograph 17 (Washington, D. C., 1960).

¹⁵ W. A. Wood and T. A. Littlefield (private communication). Abstracts, Molecular Structure and Spectroscopy Symposium (Columbus, Ohio, 1963), p. 63.

¹⁶ D. H. Rank and B. S. Rao, *J. Mol. Spectry*, **13**, 34 (1964).

¹⁷ R. Mecke, *Ann. Physik* **71**, 104 (1923).

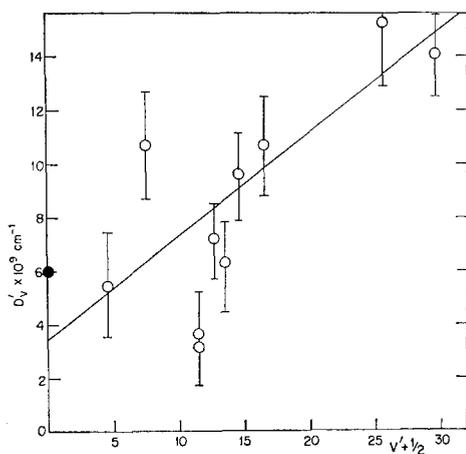


FIG. 2. Experimental values for D_v' . The filled point at $v=0$ is the Dunham predicted value, $D_e=4B_e^3/\omega_e^2$.

term to the ground state combination differences produced no reduction in the standard error.

The polynomial curve-fitting program mentioned above, recompiled in double precision on an IBM 7094 system, was used to fit spectroscopic constants to the rotational data, using the formula

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

The results are

$$B_e' = 0.028969 \pm 0.00007 \text{ cm}^{-1},$$

$$\alpha_e' = 0.0001562 \pm 0.00002 \text{ cm}^{-1},$$

$$\gamma_e' = -(4.0 \pm 13) \times 10^{-7} \text{ cm}^{-1},$$

$$\delta_e' = -(3.5 \pm 3) \times 10^{-8} \text{ cm}^{-1}.$$

Also, $D_e' \cong 3.5 \times 10^{-9} \text{ cm}^{-1}$, and $\beta_e' \cong 3.9 \times 10^{-10} \text{ cm}^{-1}$. The curve generated by these constants is compared with the experimental B_v' values in Fig. 3. Finally, from the B_e' value obtained, it is possible to calculate a value for r_e' of $3.0276 \pm 0.004 \text{ \AA}$.

The error estimates given for the spectroscopic constants refer to the absolute determination of these numbers, and are calculated from the least-squares

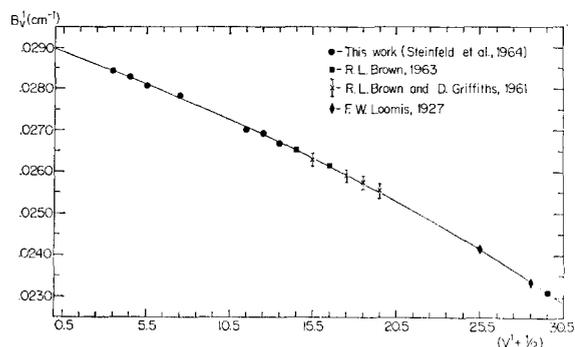


FIG. 3. Experimental B_v' values, and curve generated by least-squares-fitted spectroscopic constants.

formula¹⁸

$$\epsilon_j = \sigma(A_{jj}/D)^{\frac{1}{2}}, \quad (2)$$

where ϵ_j is the error estimate for the j th coefficient in the power series, σ is the computed standard deviation of fitting, D is the determinant of the normal equations, and A_{jj} is the cofactor of that determinant corresponding to the j th coefficient. It should be emphasized that only *correlated* variations of the constants within these limits are permissible; that is, the complete set of numbers given above, with all the significant figures quoted, must be employed to reproduce the measured B_v' values, but there are many other sets of constants within the computed error limits which can be constructed, which will also reproduce the data to within the same standard deviation.

The Dunham relations for α_e and D_e in a Morse potential¹⁰ are satisfied surprisingly well by these values, although, not unexpectedly, the more general Dunham-

TABLE III. Band heads for $I_2B^3\Pi_{0u}^+$ state.

v'	band	Rotationless term value (cm ⁻¹) ^a	Source
4	4-7	16 319.05	b
5	5-4	16 436.97	b
7	7-5	16 667.91	b
11	11-1	17 109.70	b
12	12-2	17 215.89	b
13	13-1, 13-2	17 320.35	b, c
14	14-1	17 422.87	c
15	15-1	17 523.81	c
16	16-2	17 622.73	c
25	25-0	18 427.80	b
29	29-0	18 733.54	b

^a Relative to zero of X -state potential.

^b This work.

^c Reference 2a (R. L. Brown, 1963).

Sandeman relations fail to predict γ_e and β_e nearly as well.

For those bands in which a sufficiently long rotational progression was observed, a rotationless energy term value could be obtained by extrapolating to $J=0$. These values are approximately five to ten times more accurate than the corresponding band-head measurements of Mecke,¹⁷ i.e., to about 0.1 cm⁻¹ or less, and are given in Table III. From the pooled band-head data, the following vibrational constants were obtained by polynomial fitting:

$$\omega_e' = 125.273 \pm 0.1 \text{ cm}^{-1},$$

$$\omega_e x_e' = 0.7016 \pm 0.01 \text{ cm}^{-1}$$

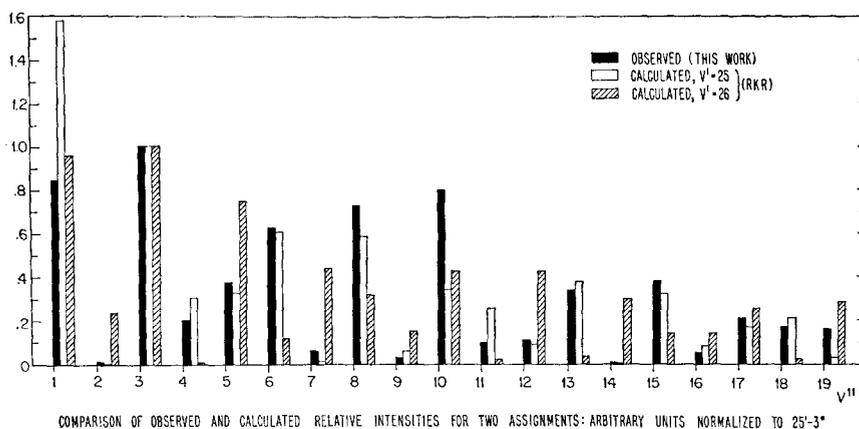
$$\omega_e y_e' = -0.00567 \pm 0.0004 \text{ cm}^{-1},$$

$$\omega_e z_e' = +0.000032 \pm 0.000005 \text{ cm}^{-1}.$$

The same remarks concerning the error limits given, as were made following the listing of the rotational constants, apply here as well.

¹⁸ E. Whittaker and G. Robinson, *The Calculus of Observations* (Blackie and Son, Ltd., London, 1944), 4th ed., p. 241.

FIG. 4. Comparison of experimental and calculated fluorescence intensity distributions for assignments $v'=25$, $v'=26$.



The remaining numbers required to characterize the molecular state are the dissociation energy D_e' and the electronic term value T_e . These constants must satisfy the relation

$$D_e' + T_e = E_{\text{diss}} + E_0'', \quad (3)$$

where E_{diss} is the frequency of the optical absorption series limit (onset of photodissociation), and E_0'' is the ground-state zero-point energy. Another requirement is that

$$D_e' + T_e = D_e'' + E_{\text{at}}, \quad (4)$$

where E_{at} is the difference in term values for the atomic iodine states $^2P_{3/2}$, $^2P_{1/2}$, which are the products of photodissociation. The most accurate determination of the ground-state dissociation energy D_e'' is that of Verma,¹⁹ who found the value $12559.6 \pm 1.5 \text{ cm}^{-1}$; the accepted value of E_{diss} is that of Mecke,¹⁷ who found $20\,014 \text{ cm}^{-1}$ (corresponding to $\lambda = 4995 \text{ \AA}$). A value of $E_{\text{at}} = 7603.15 \text{ cm}^{-1}$ is given by Moore.²⁰ With these values, expression (3) gives $D_e' + T_e = 20\,121 \text{ cm}^{-1}$, and Expression (4) gives $D_e' + T_e = 20163 \text{ cm}^{-1}$. The most likely source of the discrepancy is in E_{diss} , since the discrete absorption spectrum of I₂ becomes almost indistinguishable from a continuum near the dissociation limit. If λ_{diss} were 4985 \AA , then all the numbers would be consistent. We are currently attempting an improved experimental determination of E_{diss} , by a combination of high-resolution absorption and magnetic rotation experiments. With the data presently available, knowing, e.g., that the level $v'=4$, $J'=0$ is at $16\,319.05 \text{ cm}^{-1}$ (Table III), and that its vibrational energy is 548.46 cm^{-1} , we can determine $T_e = 15\,770.59 \text{ cm}^{-1}$, and thus estimate $D_e' \cong 4391 \text{ cm}^{-1}$.

B. Calculated Intensity Distribution and Revision of Vibrational Assignment

The vibrational assignment of the absorption bands in the B state of iodine was first made by Mecke.¹⁷ Since bands ending on low vibrational states had vanish-

ingly small intensity, and thus could not be observed, this assignment was somewhat arbitrary. Loomis,⁷ in his comprehensive correlation of the absorption and fluorescence spectra, decided on a band-numbering scheme such that the fluorescence excited by the Hg green line at 5460.75 \AA was labeled with $v'=26$. Although Loomis cautioned²¹ that this assignment might well be subject to future revision, it rapidly gained a general acceptance.

The vibrational overlap matrix which governs the intensity distribution in electronic transitions is, however, extremely sensitive to absolute vibrational quantum number, and may be made the basis for a vibrational assignment. A typical band intensity is given by

$$I(v', v'') = N(v') A(v', v''), \quad (5)$$

where $N(v')$ is the density of excited molecules and, as has been shown, the probability of emitting a photon is given by

$$A(v', v'') = \frac{64\pi^4\nu^3}{3c^3h} |M_{\text{el}}(\bar{r})|^2 \left| \int \langle v' | r | v'' \rangle dr \right|^2. \quad (6)$$

For transitions between two highly excited vibrational states, such as are involved in the I₂ resonance fluorescence, the resulting intensity distribution shows a quite irregular oscillatory pattern. A calculation employing the spectroscopic constants determined in Sec. A of these Results, and the assignment of Loomis *et al.*, gave essentially no agreement with the observed intensity pattern, as Fig. 4 shows. Therefore, we varied the only parameter remaining, viz., the vibrational assignment. The numbering of the levels was varied in unit intervals from +3 to -3 with respect to the previously accepted assignment without, of course, changing the values of any of the observed term levels. The only assignment which produced a calculated intensity distribution in agreement with the observed fluorescence was $\Delta v' = -1$, corresponding to,

²¹ "Mecke . . . concludes . . . that n_2 corresponds to n' , the upper level vibrational quantum number, but increases as $n' = n_2 - 26 \dots$. This is only an approximation and some future investigation may necessitate changing all the values of n' by a few units or half units. Since, however, only relative values of n' are needed in this paper, it is simplest to retain Mecke's assignments of n , for the present" (Ref. 7, p. 115).

¹⁹ R. D. Verma, J. Chem. Phys. **32**, 738 (1960).

²⁰ C. Moore, Natl. Bur. Std. (U.S.) Circ. No. 467, **3**, 106 (1958).

TABLE IV. Classical turning points of the potential-energy curve for the B state of I_2 .^{a,b}

v'	$r_-(\text{\AA})$	$r_+(\text{\AA})$	v'	$r_-(\text{\AA})$	$r_+(\text{\AA})$
0	2.967	3.097	23	2.708	3.752
1	2.925	3.153	24	2.704	3.780
2	2.898	3.193	25	2.700	3.808
3	2.878	3.228	26	2.696	3.836
4	2.860	3.260	27	2.692	3.865
5	2.845	3.290	28	2.688	3.895
6	2.832	3.318	29	2.685	3.926
7	2.820	3.345	30	2.682	3.957
8	2.809	3.371	31	2.679	3.990
9	2.799	3.397	32	2.676	4.023
10	2.790	3.422	33	2.673	4.057
11	2.781	3.447	34	2.671	4.093
12	2.773	3.472	35	2.669	4.129
13	2.766	3.497	36	2.667	4.167
14	2.758	3.521	37	2.665	4.206
15	2.752	3.546	38	2.663	4.247
16	2.745	3.571	39	2.661	4.289
17	2.739	3.596	40	2.660	4.333
18	2.733	3.621	41	2.658	4.379
19	2.728	3.647	42	2.657	4.427
20	2.723	3.672	43	2.656	4.477
21	2.717	3.699	44	2.655	4.530
22	2.713	3.725			

^a The repulsive "left end" of the potential is given by

$$V(r_-) = (1.343 \times 10^9) / r^{12} - 11\,496 \text{ cm}^{-1}, \quad r < 2.66 \text{ \AA}.$$

^b The long-range attractive "right end" of the potential is given by

$$V(r_+) = -(5.567 \times 10^6) / r^{6.086} \text{ cm}^{-1}, \quad r > 4.53 \text{ \AA}.$$

e.g., $v' = 25$ for the state excited at 5460.75 Å. All the constants reported in Sec. A are in accordance with this assignment. The classical turning points of the revised B state potential are given in Table IV.

We investigated the reliability of this procedure by carrying out several systematic variations of the input data to the Franck-Condon program, as indicated in Fig. 5. The measured $B_{v'}$ values were uniformly displaced to both larger and smaller values by 0.00004 cm^{-1} , which was considered to be the largest error allowable in any one measurement. The results of doing this are indicated in Table V, in terms of the inner

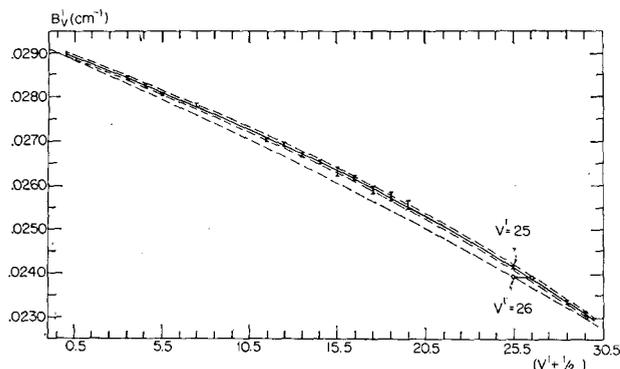


FIG. 5. The upper curve represents the experimental $B_{v'}$ points, which are indicated with their associated standard deviations. The lower curve represents the $B_{v'}$ values needed to make the calculated intensity distribution be correct for the assignment $v' = 26$. Note that the value of B_{26} , required is actually very near the true B value for the 26th vibrational level.

turning points for three different vibrational assignments for the level to which we assign $v' = 25$. Carrying through the calculations of intensity distributions showed that these shifts in the potential were insufficient to alter materially the predicted distribution for any one vibrational assignment. Figure 5 shows that the set of $B_{v'}$'s needed to produce the correct intensity distribution for the $v' = 26$ assignment is displaced from the actual set of $B_{v'}$'s by from two to four standard deviations over the range $v' = 0$ to 30. A systematic error is also excluded by the agreement of our measurements with other work done over the past forty years. These considerations indicate that it is highly unlikely that the vibrational assignment given above is not the correct one.

All calculated intensities and observed fluorescence data are given in Table VI. The data on fluorescence from $v' = 14$ and 15 are photoelectric measurements by Brown.^{2a} Data for the $v' = 25$ progression include photographic estimates by Lenz⁴ and Oldenberg,⁵ densitometric measurements by Arnot and McDowell,⁶ and

TABLE V. Sensitivity of inner turning point of the fluorescing state to variations in rotational constants.

$\delta B_{v'}$	Vibrational assignment of fluorescing state		
	24'	25'	26'
+0.00004 cm^{-1}	2.714	2.702	2.692
0	2.712	2.700	2.690
-0.00004 cm^{-1}	2.709	2.697	2.687

photoelectric measurements taken in this laboratory.^{2b} Of these three methods, the photoelectric measurements are surely the most accurate, except for a few bands ($v' = 11$ and 19) where the intensity response of the detection system was rapidly varying.²² The good agreement of the photoelectric and densitometric measurements shows that the latter method can, with care, be capable of giving reliable results too. The plate-blackening estimates are of value only for indicating the alternation of strong and weak bands where other data are lacking. Data for $v' = 23, 24, 26,$ and 27 were also taken photoelectrically, in connection with the energy-transfer work. All bands are corrected for the self-absorption of the fluorescent emission. A listing of all the Franck-Condon factors computed by us may be obtained as part of the supplementary material described in Ref. 13 above.

²² The spectrometer used to observe the fluorescence was operated in the ninth and tenth orders of the grating, and so it was necessary to separate the orders by the use of various filters. This made the intensity calibration relatively unreliable at the points at which the light was being passed through a "toe" of the transmission curve of a particular filter.

TABLE VI. Intensity distribution in iodine B-X fluorescence.

(a) ν''	Calculated intensity ^{a,b}	Observed intensity ^a			(b) Transition	Calculated intensity ^f	Observed intensity ^{f,g}
		Ref. c	Ref. d	Ref. e			
All fluorescence originating from $\nu' = 25$, R(33) line							
0	1.70	...	3.1	1.1	14-6	0.66	0.73
1	1.58	0.85	1.1	1.0	14-7	0.23	0.26
2	0.000	0.009	0.0	0.1	14-8	0.06	0.11
3	1.00	1.00	1.0	1.0	14-9	0.46	0.40
4	0.31	0.20	0.3	0.3	15-0, P(45)	0.21	0.16
5	0.33	0.38	...	0.9	15-1	1.03	0.80
6	0.61	0.63	0.7	0.9	15-2	1.77	...
7	0.016	0.067	0.06	0.2	15-3	1.00	1.00
8	0.59	0.73	0.8	1.0	15-4	0.01	0.00
9	0.063	0.029	0.03	0.0	15-5	0.55	0.76
10	0.34	0.80	0.6	0.9	15-6	0.78	0.80
11	0.26	0.10	0.3	0.3	15-7	0.05	0.00
12	0.093	0.11	0.2	0.2	15-8	0.33	0.50
13	0.38	0.34	0.5	0.8	15-9	0.57	0.46
14	0.000	0.006	0.0	0.0			
15	0.33	0.38	0.5	0.8			
16	0.078	0.048	0.06	0.0			
17	0.17	0.21	0.4	0.2			
18	0.21	0.17	0.3	0.1			
19	0.03	0.16	...	0.0			
20	0.27			
21	0.01	0.0			
22	0.19	1.0			
23	0.10	0.2			
24	0.06	0.3			
25	0.19	1.0			
26	0.00	0.0			
27	0.18	1.1			
28	0.05	0.1			
29	0.08	1.0			
30	0.13	1.0			
31	0.05	0.0			
32	0.15	1.1			
33	0.02	0.1			
34	0.08	1.0			
35	0.09	0.6			
36	0.01	0.2			
37 ^a	0.12	0.2			

(b) Transition	Calculated intensity ^f	Observed intensity ^{f,g}
14-0, P(144)	0.11	...
14-1	0.61	...
14-2	1.25	1.09
14-3	1.00	1.00
14-4	0.13	0.26
14-5	0.19	0.32

(c) Band	Calculated intensity ^h	Observed intensity ^{h,i}
27-0	1.76	...
27-1	1.07	...
27-2	0.12	0.0
27-3	1.00	1.0
27-4	0.02	0.0
27-5	0.65	0.24
27-6	0.23	0.37
26-0	1.65	...
26-1	1.25	(0.3) ^j
26-2	0.03	0.0
26-3	1.00	1.0
26-4	0.12	0.08
26-5	0.50	0.27
26-6	0.41	0.49
24-0	1.75	0.29 ^j
24-1	2.02	1.01
24-2	0.04	0.0
24-3	1.00	1.0
24-4	0.63	0.28
24-5	0.17	0.28
24-6	0.88	1.08
23-0	2.13	0.95 ^j
23-1	2.95	2.36
23-2	0.24	0.0
23-3	1.00	1.0
23-4	1.17	0.95
23-5	0.03	0.0
23-6	1.13	1.40

^a Normalized to 25-3 band intensity=1.00; units are energy/second.

^b Nonzero intensity calculated out to 25-68 band, but no experimental data exists beyond 25-37 band.

^c Photoelectric measurements, Ref. 2b (Steinfeld, 1964); average of P and R branch intensities.

^d Densitometric measurements, Ref. 6 (Arnot and McDowell, 1958).

^e Photographic estimates, Ref. 4 (Lenz, 1924; Bands 25-1 through 25-18); and Ref. 5 (Oldenberg, 1927; Bands 25-21 through 25-37).

^f Normalized to 14-3 and 15-3, respectively; units are energy/second.

^g Photoelectric measurements, Ref. 2a (Brown, 1963).

^h All bands normalized to $\nu' = 3$, respectively; intensity calculated for R(33) line; units are energy/second.

ⁱ Photoelectric measurements, Ref. 2b (Steinfeld, 1964).

^j Relatively uncertain due to large self-absorption.

Values of $|M_{01}(\bar{r})|$ were computed from the intensity data of Tables VI(a) and VI(b), for a range of r -centroids from 2.7 to 2.9 Å. No systematic variation could be discerned; indeed, an inspection of Fig. 6 indicates that the values form a normal distribution about a mean of 1.0. We therefore conclude that, for

this system, the Condon approximation regarding the constancy of $M_{01}(\bar{r})$ is justified, as suggested by Zare, Larsson, and Berg.²³

It is now clear how Zare¹⁰ was able to obtain almost

²³ R. N. Zare, E. O. Larsson, and R. A. Berg, J. Mol. Spectry. (to be published).

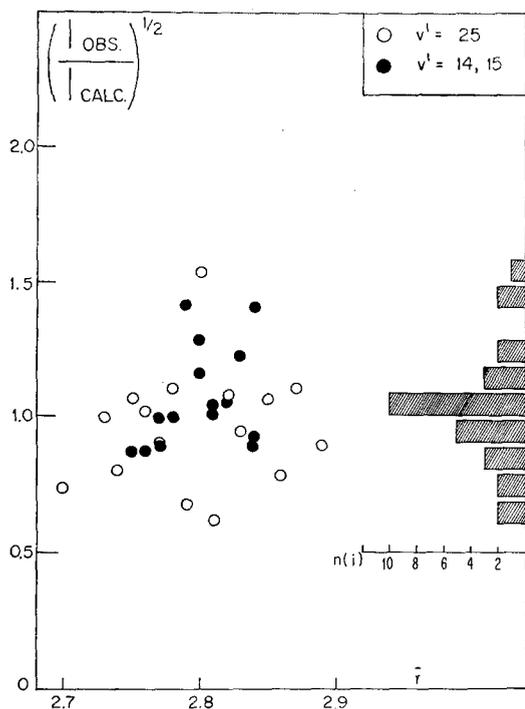


FIG. 6. Absolute value of electronic moment versus r centroid. Arbitrary units, normalized to the value for the 25'-3'' band.

as satisfactory a fit to the fluorescence distribution with the old values $v'=26$, $B_{26}'=0.02388$ cm⁻¹, instead of the newer results here reported: $v'=25$, $B_{25}'=0.02412$ cm⁻¹. Decreasing the rotational constant had the effect of "stretching" the 26-node radial wavefunction so that it matched very closely the true 25-node wavefunction over the region of importance. This indicates that the ability to give the correct vibrational overlap matrix is a *necessary* but not *sufficient* condition on a set of spectroscopic constants, and that this method should be applied with caution as a criterion for the accuracy of spectroscopic constants and assignments.

C. Radiative Lifetime

The radiative lifetime is important in the interpretation of energy transfer data, since this quantity fixes the time scale of the system. Also, it is of interest to check the phase-shift determination²⁴ of $\tau(25') = (7.2 \pm 1.0) \times 10^{-7}$ sec for this molecular state by comparison with absorption data. The radiative lifetime is given by

$$\tau(v') = \sum_{v''} [1/A(v', v'')], \quad (7)$$

where the sum extends over all bands having appreciable intensity.²⁵

²⁴ L. Brewer, R. A. Berg, and G. M. Rosenblatt, *J. Chem. Phys.* **38**, 1381 (1963).

²⁵ More detailed discussion of all the points mentioned in this section is given by Zare, Ref. 10.

If the electronic moment variation is small for the different bands—as seems to be the case for this system—then a knowledge of τ for one vibrational state permits τ for any other vibrational state belonging to the same electronic state to be obtained from the Franck-Condon factors and the frequency dependence, since

$$\frac{\tau(v_1')}{\tau(v_2')} = \frac{\sum_{v''} \langle v_2' | v'' \rangle \nu(v_2', v'')^3}{\sum_{v''} \langle v_1' | v'' \rangle \nu(v_1', v'')^3}. \quad (8)$$

Some lifetime calculations by this method are given in the fifth column of Table VII. Alternatively, an absolute absorption measurement may give an independent determination of the radiative lifetime from

$$1/\tau(v') = A_{v'', J'', v' J'} \sum_{v''} I_{\text{rel}}(v', v'') / I_{\text{rel}}(v', v''), \quad (9)$$

where the relative intensities must be expressed in units of quanta per second; the relevant quantities for this calculation are displayed in the third and fourth columns of Table VII. The lifetimes calculated by this latter method are uncertain to within a factor of 2 or 3, from combined errors in the absorption measurement itself and the calculated value of $I_{\text{rel}}(v', v'')$. The radiative lifetime obtained from integrated band intensity measurements is not repeated here, since the mean fluorescence wavelength obtained does not differ from that used in the earlier calculation.¹⁰ To do better, absolute absorption measurements, preferably photoelectric, should be made on a number of resolved lines in a high-resolution absorption spectrum and the results averaged, and we are presently carrying out such experiments. But within the presently obtainable accuracy, the results are in reasonable agreement with the measurements of Brewer *et al.*

Another assumption implicit in this treatment is the validity of the rotational sum rules for all the lines in a band. However, the fact that a molecule is a nonrigid rotor is taken into account in the overlap calculations by adding a centrifugal distortion term to the potential curve, and the result of doing this is a variation of as much as $\pm 10\%$ in the Franck-Condon factors for the different rotational lines in a vibrational band. We have accepted this additional source of uncertainty in our results, rather than engage in the lengthy computations required to extend the sums in Eqs. (7) through (9) to include J .

CONCLUSIONS

(1) By combining previous measurements with new absorption data, a consistent set of spectroscopic constants for the $B^3\Pi_{0u^+}$ state of iodine has been determined.

(2) By comparing calculated and observed fluorescence intensity distributions, the assignment of vibra-

TABLE VII. Calculated radiative lifetimes for I₂B³Π_{0u}⁺.

<i>v</i> '	Line	<i>A</i> (sec ⁻¹)	<i>τ</i> (from absorption) (sec)	<i>τ</i> (from Brewer <i>et al.</i>) (sec)
14	14-3 P(114)	(2.8±0.3)×10 ⁶ ^a	3.2×10 ⁻⁷	6.2×10 ^{-7e,d}
15	15-3 P(45)	(1.0±0.2)×10 ⁶ ^a	6.8×10 ⁻⁷	6.3×10 ^{-7e,d}
25	25-3 R(33)	(2.0±1.6)×10 ⁶ ^b	3.5×10 ⁻⁷	7.2×10 ^{-7e,e}

^a Reference 1 (Brown, 1963).

^b C. Malamond and H. Boiteux, *Compt. Rend.* **238**, 778 (1954).

^c Uncertain to ±15%.

^d Computed from *τ*(25') using Eq. (8).

^e Measured by Brewer *et al.*, Ref. 25.

tional quantum numbers has been established. The state excited by the 5460.75-Å mercury line is found to be *v*'=25, *J*'=34.

(3) There seems to be no systematic variation of *M*_{el}(*r̄*) for the *r*-centroid range for which good data are available.

(4) Radiative lifetimes recalculated from absorption data are in fair agreement with the direct determination made by Brewer *et al.*

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Isotopic Determination of the Vibrational Numbering for the B³Π_{0u} State of Iodine

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A measurement of the vibrational isotope displacements between ¹²⁷I₂ and ¹²⁹I₂ has confirmed the revised vibrational numbering of the B³Π_{0u} state proposed by Steinfeld *et al.* They have observed that the traditional numbering must be decreased by one unit to bring their calculated fluorescence intensity distributions into agreement with experiment.

INTRODUCTION

RECENTLY Steinfeld, Zare, Jones, Lesk, and Klemperer¹ have remeasured a number of bands in the iodine B³Π_{0u}-X¹Σ_g⁺ absorption spectrum. Using the revised spectroscopic constants resulting from their analysis, they have calculated Franck-Condon factors for the band system. Rydberg-Klein-Rees potentials were derived for the two states involved, and from these, exact vibrational eigenfunctions were obtained by direct numerical solution of the radial Schrödinger equation. The electronic transition moment was assumed to be independent of internuclear distance. Details of the method have been described by Zare² who performed the calculation with the previously accepted B-state constants. He was able to obtain a satisfactory fit to a series of observed fluorescence intensity distribu-

tions. Steinfeld *et al.*, however, found that the calculated Franck-Condon factors based on their revised constants agreed satisfactorily with the experimental intensities only when the vibrational numbering of the B state was decreased by one unit from the previously accepted assignment.³

This technique of vibrational assignment depends upon three factors, namely, accurate knowledge of the spectroscopic constants, intensity measurements, and some assumption as to the constancy of the electronic transition moment. On the other hand, a vibrational analysis based on an isotope effect requires, at a minimum, only a knowledge of the vibrational constants. The correct vibrational numbering can be obtained simply by comparing the observed isotope shift of a

¹ J. J. Steinfeld, R. N. Zare, L. Jones, M. Lesk, and W. Klemperer, *J. Chem. Phys.* **42**, 25 (1965).

² R. N. Zare, *J. Chem. Phys.* **40**, 1935 (1964).

³ F. W. Loomis, *Phys. Rev.* **29**, 112 (1927). Since the 0-0 band of the system had not been observed, the assignment given by Loomis was actually somewhat arbitrary and was specified as such by him.