

\[
\lim_{D \to 0} \left( \frac{E_{corr}}{\frac{1}{2} \pi D^3} \right) = \frac{1}{\sqrt{3}} = 0.5773 \text{ hartree/bohr}^3 \tag{12}
\]

One can try to estimate the magnitude of the error arising from the lack of a small cusp in \( \Phi_{CI} \) around \( r_p = 0 \). 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 \( \Delta E \) 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, etc.

containing angular terms through \( l = 4 \), differs by \( 5 \times 10^{-4} \) hartree from the nonrelativistic value of Pekeris. 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 King computed an energy that differed by \( 2.8 \times 10^{-4} \) 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.

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**Spectroscopic Constants and Vibrational Assignment for the \( B \Pi_{0u}^+ \) State of Iodine**

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(Received 15 June 1964)

Portions of the iodine \( B \Pi_{0u}^+ \rightarrow X \Sigma^+ \) 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:

\[
\begin{align*}
\omega_0' &= 125.273 \text{ cm}^{-1} \\
\omega_a' &= 0.7016 \\
\omega_y' &= -0.00567 \\
\omega_z' &= +0.00032 \\
D_0' &= 439.1 \\
T_0' &= 15770.59 \\
T_a' &= 0.028969 \\
T_y' &= -3.0276 \\
T_z' &= -4.0 \times 10^{-7} \\
\gamma_0' &= -4.0 \times 10^{-7} \\
\gamma_a' &= -3.5 \times 10^{-8} \\
\gamma_y' &= -3.5 \times 10^{-9} \\
\gamma_z' &= -3.9 \times 10^{-10} \\
\delta_0' &= 0.0001562 \\
\delta_a' &= 0.0001562 \\
\delta_y' &= 0.0001562 \\
\delta_z' &= 0.0001562 \\
\end{align*}
\]

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.

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**INTRODUCTION**

MOLECULAR iodine has often been used as a model system for energy transfer studies by monochromatically excited fluorescence, most recently in this laboratory. 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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\[ (b) J. I. Steinfield and W. Klemperer (to be published). \]
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 Å, first observed by Wood, have been recorded by Lenz and Oldenberg and more recently by Arnot and McDowell. All these measurements were taken from photographic plates. We have redetermined relative intensities photoelectrically, out to the 19th fluorescence doublet.

Using the customary assignment for the state excited at 5460.75 Å, viz., electronic state \( \text{B}^2\Pi_{0}^{+} \), \( v'=26, J'=34 \), and the tabulated spectroscopic constants, Zare 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 found that the accepted \( \text{B}^2\Pi_{0}^{+} \) 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 \( \text{I}_2 \) absorption spectrum made by Wood, Loomis, et al. many years ago, and never fully analyzed, have since been discarded and are no longer available. These facts led us to undertake a new analysis of the \( \text{B} \rightarrow \text{X} \) 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 Å/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-
less discharge in an Ophthos ThI₄ lamp 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.²²

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 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 studies¹⁷.¹⁷ 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.¹⁸ 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 \( D' \), 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 \( D' \) by this procedure; nevertheless, the general trend of the data is evident. No reliable information on \( D'' \) could be elicited, since the addition of a \( [J(J+1)] \)

| TABLE I. \( B' \) values for \( I₂ B' \) state. |
|---|---|---|---|
| \( \nu' \) | band | \( B' \) \( \text{polynomial (fit) cm}^{-1} \) | \( B' \) \( \text{combination (diff) cm}^{-1} \) | Source |
| 3 | 3-6 | 0.02841 | | a, b |
| 4 | 4-7 | 0.02828 | 0.02823 | a |
| 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 | 0.02679 | 0.02669 | a |
| 14 | 14-1 | 0.02653 | | c |
| 15 | 15-1 | | | |
| 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 | 25-1 | | 0.02416 | e |
| 26 | 26-0 | | 0.02387 | e |
| 29 | 29-0 | 0.02312 | 0.02301 | a |

This work. ¹² Reference 17 (Mecke, 1923).
Reference 7 (Loomis, 1927).
Reference 17 (Loomis, 1927).
Reference 7 (Loomis, 1927).
Reference 16 W. A. Wood and T. A. Littlefield (private communication).
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

\[ B_\nu = B_\nu' - \alpha_\nu (v + \frac{1}{2}) + \gamma_\nu (v + \frac{1}{2})^2 + \delta_\nu (v + \frac{1}{2})^3 + \cdots. \]  

The results are

\[ B_\nu' = 0.028969 \pm 0.00007 \text{ cm}^{-1}, \]
\[ \alpha_\nu' = 0.0001562 \pm 0.00002 \text{ cm}^{-1}, \]
\[ \gamma_\nu' = - (4.0 \pm 13) \times 10^{-7} \text{ cm}^{-1}, \]
\[ \delta_\nu' = - (3.5 \pm 3) \times 10^{-8} \text{ cm}^{-1}. \]

Also, \( D_\nu \approx 3.5 \times 10^{-9} \text{ cm}^{-1} \), and \( \beta_\nu \approx 3.9 \times 10^{-10} \text{ cm}^{-1} \). The curve generated by these constants is compared with the experimental \( B_\nu' \) values in Fig. 3. Finally, from the \( B_\nu' \) value obtained, it is possible to calculate a value for \( r_\nu' \) of 3.0276 ± 0.004 Å.

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

\[ e_j = \sigma (A_{jj}/D)^{1/2}, \]  

where \( e_j \) is the error estimate for the \( j \)th coefficient in the power series, \( \sigma \) 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 \( B_\nu' \) 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 \( \alpha_\nu \) and \( D_\nu \) in a Morse potential\(^9\) are satisfied surprisingly well by these values, although, not unexpectedly, the more general Dunham-Sandeman relations fail to predict \( \gamma_\nu \) and \( \beta_\nu \) 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:

\[ \omega_\nu' = 125.273 \pm 0.1 \text{ cm}^{-1}, \]
\[ \omega_\nu \omega_\nu' = 0.7016 \pm 0.01 \text{ cm}^{-1}, \]
\[ \omega_\nu \gamma_\nu' = -0.00567 \pm 0.00004 \text{ cm}^{-1}, \]
\[ \omega_\nu \delta_\nu' = +0.000032 \pm 0.000005 \text{ cm}^{-1}. \]

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

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

\[
D'_e + T_e = E_{\text{dis}} + E_0''
\]

where \( E_{\text{dis}} \) 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

\[
D'_e + T_e = D'_e + E_{at}
\]

where \( E_{at} \) is the difference in term values for the atomic iodine states \(^1P_1, ^3P_1\), which are the products of photodissociation. The most accurate determination of the ground-state dissociation energy \( D'_e \) is that of Verma,\(^{18}\) who found the value 12559.6 ± 1.5 cm\(^{-1}\); the accepted value of \( E_{\text{dis}} \) is that of Mecke,\(^{17}\) who found 20 014 cm\(^{-1}\), corresponding to \( \lambda = 4995 \) Å. A value of \( E_{at} = 7603.15 \) cm\(^{-1}\) is given by Moore.\(^{20}\) With these values, expression (3) gives \( D'_e + T_e = 20121 \) cm\(^{-1}\), and expression (4) gives \( D'_e + T_e = 20163 \) cm\(^{-1}\). The most likely source of the discrepancy is in \( E_{\text{dis}} \), since the discrete absorption spectrum of \( I_2 \) becomes almost indistinguishable from a continuum near the dissociation limit. If \( \lambda_{\text{dis}} \) were 4985 Å, then all the numbers would be consistent. We are currently attempting an improved experimental determination of \( E_{\text{dis}} \), 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 cm\(^{-1}\) (Table III), and that its vibrational energy is 548.46 cm\(^{-1}\), we can determine \( T_e = 15770.59 \) cm\(^{-1}\), and thus estimate \( D'_e \approx 4391 \) 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 vanishingly 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 Å was labeled with \( v' = 26 \). Although Loomis cautioned\(^{21}\) 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

\[
I(v', v'') = N(v') A(v', v'')
\]

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

\[
A(v', v'') = \frac{64\pi^2 L^2}{3\varepsilon^2 \hbar} | M_{al}(\vec{\mu}) |^2 \int \langle v' | r | v'' \rangle^2 dr
\]

For transitions between two highly excited vibrational states, such as are involved in the \( I_2 \) 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 \textit{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,

\[^{21}\text{Mecke... concludes... that } n_2 \text{ corresponds to } n', \text{ the upper level vibrational quantum number, but increases as } n' = n_2 - 20. \ldots \text{This is only an approximation and some future investigation may necessitate changing all the values of } n' \text{ by a few units or half units. Since, however, only relative values of } n' \text{ are needed in this paper, it is simplest to retain Mecke's assignments of } n, \text{ for the present}^{21} \text{ (Ref. 7, p. 115).} \]
The calculated intensity distribution be correct for the assignment
points, which are indicated with their associated standard devia­
tions. The lower curve represents the
em-I,
allowable in anyone measurement. The results of doing
em-I,
carrying out several systematic variations of the input
data to the Franck-Condon program, as indicated in
em-I,
this are indicated in Table
em-I,
IV. Classical turning points of the potential-energy
curve for the $B$ state of $I_a$.a,b

<table>
<thead>
<tr>
<th>$v'$</th>
<th>$r_-$ ($\lambda$)</th>
<th>$r_+$ ($\lambda$)</th>
<th>$v'$</th>
<th>$r_-$ ($\lambda$)</th>
<th>$r_+$ ($\lambda$)</th>
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<td>2.713</td>
<td>3.725</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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

$V(r_-) = (3.435 \times 10^7) r^{1/2} \text{ cm}^{-1}$, \( r < 2.66 \lambda \).

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

$V(r_+) = -(5.357 \times 10^7) r^{1/2} \text{ cm}^{-1}$, \( r > 4.53 \lambda \).

e.g., $v' = 25$ for the state excited at 5460.75 \( \lambda \). 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
em-I,
Fig. 5. The measured $B_{v'}$ values were uniformly dis­
placed 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
turning points for three different vibrational assignment
to the level for which we assign $v' = 25$. Carrying through the calculations of intensity distributions showed that these shifts in the potential were insuff­
icient 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 dis­
placed 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.\(^{26}\) Data for the $v' = 25$ progression include photo­
graphic estimates by Lenz\(^{4}\) and Oldenberg,\(^{6}\) densi­
tometric measurements by Arnol and McDowell,\(^{8}\) and

![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 $B_{v'}$, required is actually very near the true $B$ value for the 26th vibrational level.](image-url)

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

<table>
<thead>
<tr>
<th>$\delta B_{v'}$</th>
<th>$24'$</th>
<th>$25'$</th>
<th>$26'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$+0.00004 \text{ cm}^{-1}$</td>
<td>2.714</td>
<td>2.702</td>
<td>2.692</td>
</tr>
<tr>
<td>0</td>
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<td>2.700</td>
<td>2.690</td>
</tr>
<tr>
<td>$-0.00004 \text{ cm}^{-1}$</td>
<td>2.709</td>
<td>2.697</td>
<td>2.687</td>
</tr>
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</table>

\(^{26}\) 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 passing through a "toe" of the transmission curve of a particular filter.
Values of $|M_{41}(\bar{r})|$ 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 $M_{41}(\bar{r})$ is justified, as suggested by Zare, Larsson, and Berg.  

It is now clear how Zare was able to obtain almost...
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 determination \(^2\) 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

\[
\tau(v') = \sum_{v''} \frac{1}{A(v', v'')},
\]

where the sum extends over all bands having appreciable intensity.\(^3\)

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

\[
\tau(v') = \frac{\sum \nu(v'') \rho(v', v'') \nu(v', v'')}{\sum \nu(v') \rho(v', v')}.
\]

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

\[
\frac{1}{\tau(v')} = A_{v''} \int \frac{I_{\text{abs}}(v', v'')}{I_{\text{rel}}(v', v'')} dv''.
\]

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.\(^4\) 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 the 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 \(B^3\Pi_{\text{um}}^+\) 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 $I_2 B \Pi_{\nu u}^+$.  

<table>
<thead>
<tr>
<th>$\nu'$</th>
<th>Line</th>
<th>$A$ (sec$^{-1}$)</th>
<th>$\tau$ (from absorption) (sec)</th>
<th>$\tau$ (from Brewer et al.) (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>14–3</td>
<td>$(2.8 \pm 0.3) \times 10^5$ *</td>
<td>$3.2 \times 10^{-7}$</td>
<td>$6.2 \times 10^{-7}$,d</td>
</tr>
<tr>
<td>15</td>
<td>15–3</td>
<td>$(1.0 \pm 0.2) \times 10^5$ *</td>
<td>$6.8 \times 10^{-7}$</td>
<td>$6.3 \times 10^{-7}$,d</td>
</tr>
<tr>
<td>25</td>
<td>25–3</td>
<td>$(2.0 \pm 1.6) \times 10^5$ b</td>
<td>$3.5 \times 10^{-7}$</td>
<td>$7.2 \times 10^{-7}$,e</td>
</tr>
</tbody>
</table>

* Reference 1 (Brown, 1963).  
c Uncertain to ±15%.  
d Computed from $\nu (25')$ using Eq. (8).  
e Measured by Brewer et al., Ref. 25.

The state excited by the 5460.75-Å mercury line is found to be $\nu' = 25$, $J' = 34$.  
(3) There seems to be no systematic variation of $M_{el}(r)$ 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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