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Quantum Yield for Unimolecular Dissociation
of I_2 in Visible Absorption

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ABSTRACT

An atomic fluorescence technique has been used to observe iodine atoms under conditions of steady-state irradiation of I_2 between 5000 Å and 6300 Å. Photodissociation quantum yields are reported for narrow-band excitation at twelve wavelengths within this range. The yield exceeds 90% at both ends of this region with a minimum of 33% near 5900 Å and a subsidiary maximum of 72% at 5460 Å. These results are further resolved into contributions from direct dissociation via the $A[lu(^3\Pi)] \leftarrow X[O^+g(^1\Sigma)]$ and $lu(^1\Pi) \leftarrow X$ transitions, and a spontaneous predissociative decay, $B[O^+u(^3\Pi)] \rightarrow lu(^1\Pi)$. The rate for this predissociation fluctuates with v' in a manner which accounts for the previously reported erratic behavior of the B-state lifetime. The total radiative decay rate varies smoothly but strongly with v' , implying that the $B \leftrightarrow X$ electronic transition moment attains a maximum for some internuclear distance in the region 3.0-3.2 Å.

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I. INTRODUCTION

Spontaneous predissociation in I_2 has been the subject of a number of studies since Chutjian, Link, and Brewer¹ suggested that this process competes with radiative decay in depopulating the B [$O^+u(^3\Pi)$] state. Absorption measurements² and theoretical work³ demonstrated that a strong v' dependence in the predissociation was entirely plausible, and I atoms were observed by ESR methods under conditions of steady-state photolysis of I_2 .⁴ Molecular-beam photodissociation experiments⁵ indicated that excitation to the B state in the vicinity of $v' = 33$ produces atoms by at least two, possibly three different mechanisms. An atomic fluorescence technique was used by us to measure the quantum yield for unimolecular dissociation at several wavelengths in the banded region of the spectrum.⁶ A number of the questions raised in this last work have been answered in recent investigations^{7,8} of the underlying continuum transitions in the visible absorption, and we present here the dissociative yield results, interpreted in accord with these recent findings.

The I_2 electronic states of primary concern in the present work are illustrated in the abbreviated potential diagram of Fig. 1, which is taken from Ref. 8. The $lu(^1\Pi)$ state, which accounts for most of the continuum absorption overlapping the bands of the predominating $B \leftarrow X[O^+g(^1\Sigma)]$ transition, is presumably also responsible for the spontaneous predissociation of the B state.⁹ This lu state is now estimated to behave as r^{-9} in the vicinity of r_e ($=2.666 \text{ \AA}$) rather than r^{-12} as assumed by Chutjian,³ and it probably crosses the left branch of the B curve at low v' levels instead of near the dissociation

limit. The $A[lu(^3\Pi)]$ state is somewhat steeper near r_e than illustrated earlier,⁶ and the $A \leftarrow X$ continuum absorption is accordingly more spread out and also stronger than estimated previously.^{10,11} The illustrated location of the repulsive branch of the B-state curve is considered more reliable than in previous work,¹² and the X curve is based on the most recent study of the ground state.¹³

The measurements presented in this work were obtained at twelve wavelengths in the region 5000 - 6300 Å, using the previously described^{6,14} atomic fluorescence technique to monitor I-atom concentrations under conditions of steady-state irradiation of I_2 . The quantum yields are based on a comparison of atom production in the banded region with that for excitation to the purely dissociative continuum at ~4920 Å. These results are resolved into contributions from direct dissociation via the $lu \leftarrow X$ continuum transitions, and spontaneous predissociation from the B state. Existing lifetime measurements for B-state decay are discussed in terms of the competitive radiative and predissociative decay modes.

II. EXPERIMENTAL

The I-atom detection system^{6,14} consisted briefly of a solar-blind photomultiplier sensitive to 1783-Å resonance fluorescence, which was excited by an iodine discharge lamp affixed directly to the photolysis cell. The I_2 was photolyzed with light from a tungsten continuum source used in combination with a number of interference filters. Measurements were made in the limit of zero pressure, where only unimolecular dissociative

processes give atoms, and at high foreign-gas pressures, where the dissociative yield is 1.00 throughout the visible spectrum.¹⁵ (See Section III.) The data were referenced against the atom production for a filter with peak transmission at $\sim 4920 \text{ \AA}$, where the dissociative yield is 1.00 under all conditions.

The photolysis cell was fitted with a greaseless stopcock and taper to enable us to carry out the necessary charging and gas handling operations in a grease-free section of the utility vacuum line. To achieve a workable fluorescence signal level, it was necessary to treat the cell with acid to poison the walls against recombination and increase the steady-state I-atom concentration.^{4,16} After thorough cleaning, the cell was rinsed with dilute (1-3%) sulfuric acid, drained, and placed under vacuum, where it was kept for about a day at $\sim 10^{-5}$ torr. Then it was charged with excess reagent grade resublimed I_2 , which was subsequently processed through a series of subliming-recondensing cycles designed to remove any volatile impurities. When the ion gauge pressure readings showed no impurity peak during the warmup of the cold finger, the cell was removed for data collection. Because the acid-treated surfaces continued to degas slowly for weeks (giving a virtual leak rate of 0.2-.4 mtorr per hour), it was necessary to repeat the purification procedure immediately prior to each experimental run.

The photolysis lamps were 6-V, 18-A G.E. microscope illuminator bulbs (filament R6) operated from a DC power supply at currents up to 22 A. The brightness temperature at $6500 \text{ \AA}$ was measured for such a lamp at currents from 15 to 22 A using an optical pyrometer calibrated to the

1948 temperature scale. Thermodynamic filament temperatures were then taken from a nomogram given by Rutgers and De Vos.¹⁷ The optical characteristics of the Baird-Atomic interference filters (most of which were used in the lifetime study of Ref. 1) are summarized in Table I, together with corresponding vibrational distributions for the excitation process. Kodak Wratten neutral density filters were used at times to attenuate the visible exciting light. Calibrations of these filters singly and in various combinations with the interference filters indicated the optical densities were additive within 1%.

The experimental setup is shown schematically in Fig. 2. The box containing the tungsten lamp is covered with black cloth to reduce incidental visible light. Two 125-mm diameter condensing lenses focus the lamp radiation near the fluorescence port of the photolysis cell. The cell is covered with black paper to shield it from visible radiation from the iodine lamp. A rigid filter holder is located in the path of the light about 50 mm from the cell. A baffle placed between the filter holder and cell serves to further eliminate stray visible radiation from the tungsten lamp. With this arrangement the interference and neutral density filters could be inserted into the optical train without altering the geometry of the setup.

Fluorescence signals were recorded on two chart recorders. One of these measured the full signal while the other registered just the incremental signal when the visible source was on, the background being suppressed by a nulling circuit. For each measurement the lamp current was brought to 22 A and kept there for 10-12 seconds, long enough to

establish a steady chart recorder signal.¹⁸ The signals were recorded in a "sandwiching" fashion--reference (4919 Å), sample (λ), reference--in order to compensate for possible drifts in iodine-lamp power and cell pressure. They were subsequently normalized to a constant background before being converted to an experimental signal ratio ($\text{Sig}_\lambda / \text{Sig}_{\text{ref}}$). Every recorded data point then represented an average of 6-8 such measurements for the reference filter and 3-10 for the given sample filter. A correction for non-linearity, discussed below, was applied to produce each value of Y_λ , the experimental yield function.

The I_2 pressure in the cell was controlled by external cooling of a side tube, and values for the pressure were calculated from the thermodynamic data of Shirley and Giauque¹⁹ and the JANAF Tables.²⁰ Cylinder-grade N_2 was used to achieve the high-pressure limit of 100% dissociation. Pressures from 0.75 to 11 torr were employed, and were determined to ± 0.03 torr with an oil manometer. A dry ice/ethanol bath was used to cool the cold finger on the iodine lamp to -80°C . Several organic materials (o-xylene, benzyl alcohol, ethylene and diethylene glycols, methyl and n-butyl salicylates) were used as constant temperature slushes in the -6 to -30°C range.

III. KINETICS OF I₂ PHOTOLYSIS

A. Detailed Mechanism

The comparison method used in this work is similar in principle to that employed by Rabinowitch and Wood¹⁵ in their work on the dissociative yield for foreign-gas quenching of I₂*(B). For excitation to discrete levels of the B state we must consider at least six processes:

Here Φ_ν is the quantum flux at frequency ν (cm⁻¹); α_ν , the absorption coefficient in appropriate units; A_T , the total radiative decay rate to all lower levels; k_p , the rate constant for spontaneous predissociation; k_{q,I_2} and $k_{q,\text{M}}$, the constants for quenching by I₂ and foreign gas M, respectively; and k_w , the constant for wall removal of I atoms. The daggers in Eqs. (1) signify that the products of these reactions may retain some internal excitation energy.

In writing (1a) we have tacitly assumed that the absorption is weak enough to be considered linear in the molecular concentration [I₂]. As is discussed and demonstrated elsewhere,^{6,8} this assumption is a poor

one for the region of strong visible absorption by I_2 . However, our dissociative yields are based on observations taken to the limit of zero absorption, where such difficulties disappear.

Although there is no guarantee that the collisional quenching proceeds exactly as indicated in Eqs. (1d) and (1e), I atoms are known to be produced in this reaction.^{15,21} Our study¹⁴ of the recombination of I atoms in I_2 indicated that the I_3 complex is not very stable kinetically, and possible complexes of form MI and MI_2 should be even less a concern for the foreign gas (N_2) employed in these experiments. Hence, for our purposes (1d,e) should completely describe the quenching.

We have omitted from the mechanism processes which account for vibrational degradation of $I_2^+(X)$ from (1b) and (1d), because for the low intensity of our photolysis source, we consider it highly unlikely that the otherwise thermal distribution in the ground state can be perturbed by more than 1-2%. Accordingly we take $[I_2]$ as a constant with respect to the lamp intensity. Similarly, we have neglected energy transfer in the B state,²² because such processes are of no concern in the low-pressure limit, and in the high-pressure limit 100% quenching is effected regardless of how much energy transfer precedes it.²³

Equation (1f) is the only process given to account for the removal of I atoms. Previous studies have shown conclusively that recombination is predominantly a heterogeneous process at the low pressures employed in these experiments.^{4,14,24} The removal appears to occur through a mixture of first- and second-order processes, with the former dominating for containers characterized by high wall sticking efficiencies (0.01-0.1)¹⁴

and the latter prevailing for low (< 0.001).⁴ The recombination is diffusion hindered and can be represented approximately

$$-d[I]/dt = k_w[I](1+y[I])(1+z[I_2]+z'[M])^{-1} \quad (2)$$

where the terms in the denominator adequately reflect the diffusion dependence,¹⁴ and where we have assumed the process is primarily first order with a small corrective term $k_w y[I]^2$.

For absorption to a dissociative continuum, we need consider only two processes, the photodissociation

and I-atom removal (1f). Dissociation via the B-state continuum yields one ground-state ($^2P_{3/2}$) atom and one metastable ($^2P_{1/2}$) atom, in which case the relaxation of the metastables

is of interest, because the detection scheme sees only ground-state atoms. For now we will assume that relaxation of metastables (via quenching processes and radiative decay) is rapid and quantitative. (This assumption will be supported below.) Then we can compare quantitatively the I-atom concentration produced by steady-state irradiation of I_2 at frequency ν in the banded region with that produced at the reference frequency (filter at 4920 Å) above the dissociation limit of the B state. The resulting expression is

$$\frac{[I]_{\nu}(1+y[I]_{\nu})}{[I]_{\text{ref}}(1+y[I]_{\text{ref}})} = \frac{a_{\nu,b}}{a_{\text{ref}}} R_{\nu}([I_2], [M]) + \frac{a_{\nu,c}}{a_{\text{ref}}} \quad (5)$$

In Eq. (5) the a 's represent the integrated quantities

$$a_{\nu} = \int \Phi_{\nu} \alpha_{\nu} F(\nu', \nu) d\nu'$$

taken over the transmission region $F(\nu', \nu) > 0$, which in our case represents the bandpass of an interference filter with peak transmission at ν . The two terms on the right account for excitation to bound (b) and continuum (c) states; and R_{ν} is simply the fraction of B-state molecules produced by excitation at frequency ν which subsequently predissociate to atoms.

$$R_{\nu}([I_2], [M]) = \left(\frac{k_p + k_{q,I_2}[I_2] + k_{q,M}[M]}{A_T + k_p + k_{p,I_2}[I_2] + k_{q,M}[M]} \right) \quad (6)$$

In the high-pressure limit R_{ν} is unity; at low pressures it approaches $k_p/(A_T + k_p)$ or $k_p \tau$, where τ is the unimolecular lifetime. The expression on the right side of (5) is the quantity referred to earlier as the experimental yield function, $Y_{\nu}([I_2], [M]) = Y_{\nu,b} R_{\nu} + Y_{\nu,c}$. With this definition the quantum yield for unimolecular dissociation is $Y_{\nu,\text{min}}/Y_{\nu,\text{max}} = Y_{\nu}(0,0)/Y_{\nu}([I_2], \infty)$. As a consistency check on the experiments, the Y_{max} values can be calculated from measured extinction coefficients.

In the absence of foreign gas and for low I_2 concentrations Y can be represented

$$Y \approx Y_b(k_p \tau + k_{q,I_2} \tau^2 A_T [I_2]) + Y_c \quad (7)$$

which is a line with intercept $Y_{\min}$ and slope

$$Y_b k_{q,I_2} \tau^2 A_T = (Y_{\max} - Y_{\min}) k_{q,I_2} \quad (8)$$

Similarly at high foreign-gas pressures the following relationship will prove useful:

$$Y = Y_b \left(\frac{1 + A_1/[M]}{1 + A_2/[M]} \right) + Y_c \quad (9)$$

where

$$A_1 = (k_p + k_{q,I_2} [I_2]) / k_{q,M} \quad (10a)$$

$$A_2 = (A_T + k_p + k_{q,I_2} [I_2]) / k_{q,M} \quad (10b)$$

B. Relaxation of Metastable Iodine Atoms

In order for this comparison technique to yield valid results, there must be no significant reactions of form

which can tie up the metastable atoms formed by excitation to the B-state continuum. Furthermore processes (4) must be fast relative to the atom removal rate, so that in the steady state virtually all the I atoms are in the detectable ground state.

In a number of papers on $I(^2P_{1/2})$ reactions, Donovan, Husain, and co-workers²⁵ concluded that reactions of type (11) were significant in the cases $AM = Cl_2, Br_2, ICl,$ and IBr . In all other gases studied, collision-induced spin-orbit relaxation dominated the removal of $^2P_{1/2}$

atoms. The measured quenching rates may be used to estimate the fraction of metastable atoms persisting under steady-state conditions. Assuming the wall removal rate is identical for $^2P_{1/2}$ and $^2P_{3/2}$ atoms, the ratio of metastables to ground-state atoms (from dissociation via the B-state continuum) is

$$\frac{[I(^2P_{1/2})]}{[I(^2P_{3/2})]} = \tau_r^{-1} / (\tau_r^{-1} + 2k_R) \quad (12)$$

where τ_r is the I-atom recombination lifetime. (The wall removal of atoms is here assumed to be strictly first order.) The quantity τ_r was not measured directly for the acid-treated cell. However, from the before-and-after comparison of the steady-state I-atom fluorescence signals, we estimate that τ_r was an order of magnitude greater in the poisoned cell than in the clean cell; or $\tau_r \gtrsim 30$ msec, based on the minimum recombination time measured for the clean cell.¹⁴ Typical conditions for the high-pressure experiments were $P_{N_2} \sim 10$ torr and $P_{I_2} = 1.6$ mtorr. From Ref. 25 the corresponding value of k_R is $(8 + 67 + 260)$ sec, and the ratio in (12) is a tolerable 0.05. (The three terms represent radiative decay, quenching by N_2 , and quenching by I_2 , respectively.) When we consider that about 40% of the absorption at 4920 Å is to the $lu(^1\Pi)$ state (dissociating to two ground-state atoms),⁸ the likely error from persistence of metastable atoms is a negligible 3%. At low pressures the $I(^2P_{1/2})$ atoms are quenched predominantly through wall collisions.²⁵ In that case we must consider the possibility that the wall removal rates are different for $^2P_{1/2}$ and $^2P_{3/2}$ atoms. Although we were unable to locate any studies answering this question, the results themselves (Section IV) indicate that such effects can hurt the accuracy of the measured yields by at most 10%.

IV. RESULTS AND DISCUSSION

A. Dissociative Quantum Yield

1. Yield Function Plots

Terms of order two or higher in $[I]$ occur in the dependence of the atomic fluorescence signal on concentration,⁶ as well as in Eq. (5). Our observations were restricted to the region of the atomic fluorescence curve where only the linear and quadratic terms were significant, and we corrected for the non-linearities in the following way: The two contributions were lumped together to give a modified form of Eq. (5),

$$\frac{\text{Sig}_\lambda (1 + y' \text{Sig}_\lambda)}{\text{Sig}_{\text{ref}} (1 + y' \text{Sig}_{\text{ref}})} \approx Y_\lambda \quad (13)$$

Then y' was determined from the dependence of the signal on the intensity of visible exciting light at a given wavelength (usually at 5462 Å). To observe this dependence we used the calibrated neutral density filters to vary the intensity while the concentrations of I_2 and N_2 were held constant. The value of y' was slightly dependent on both $[I_2]$ and $[N_2]$, hence was determined separately for each experiment. The overall effect of this correction was small: it gave quantum yields which differed by at most ~4% from those determined using the simpler relation, $\text{Sig}_\lambda / \text{Sig}_{\text{ref}} \approx Y_\lambda$.

Data were collected at all wavelengths for fixed $[I_2]$ and $[N_2]$, corrected for non-linearity as described above, then pooled to determine Y_{min} and Y_{max} at each wavelength. The Y_{min} values resulted from a linear fit of 9-12 points²⁶ at I_2 pressures below 20 mtorr [Eqs. (7) and (8)]; and the Y_{max} values were obtained from a similar number of points recorded

with $P_{I_2} = 1.6$ mtorr and various pressures of N_2 up to 11 torr.²⁷ In the latter case the intercepts represented least-squares fits of the data to the equation, $Y = Y_{\max} (1 + C_1/P_{N_2}) / (1 + C_2/P_{N_2})$. This expression proved a useful mathematical form for obtaining the $Y_{\max}$ values; however, because of the continuum contribution Y_c at all wavelengths, C_1 and C_2 did not have the physical significance of A_1 and A_2 in Eqs. (10). (Values for k_{q,N_2} were taken from a separate computation mentioned below.)

Results for two of the excitation regions are displayed in Figs. 3 and 4. The upper plots show the behavior of Y in the high-pressure limit, and the lower graphs illustrate the low-pressure points. All of the low-pressure data gave good linear plots, but the slopes were in every case lower than calculated from constants in Ref. 1, with negative values resulting from the data at 5462, 5594, and 6239 Å. Possible reasons for these low slopes were considered in detail in Ref. 6. More recent work in Ref. 8 indicates that the effect of non-linear visible absorption by I_2 (due to partial saturation of individual rotational lines) is smaller by ~25% than estimated in the earlier work. However, this effect still accounts for most of the discrepancy in the region of strong absorption. Differences in the wall accommodation coefficients for $^2P_{1/2}$ and $^2P_{3/2}$ atoms and slight errors from residual concentrations of I atoms²⁷ possibly account for the rest. At 5091 Å and in the region around 6000 Å the deviation from linear absorption should be very small;⁸ and there the observed slopes in the low-pressure plots were roughly 2/3 the values calculated from Ref. 1. Hence we estimate that errors from the latter two effects can lead to $Y_{\min}$ values which are erroneously large by at most 10%.²⁸

Approximate values for $Y_{\max}$ may be calculated from the product of the I_2 extinction coefficient, the area of the filter transmission profile, and the black-body quantum flux (with emissivity correction) at the wavelength of peak transmission for each filter. When such computations were done in Ref. 6, they showed a systematic discrepancy of ~25% between calculated and observed $Y_{\max}$ values. However, when these numbers were recalculated with the more recent extinction coefficient measurements of Ref. 8, the disparity between calculated and observed $Y_{\max}$ values was random in nature and exceeded 10% at only one of the 12 wavelengths in question. Because of uncertainties in each of the factors required to calculate the $Y_{\max}$ values, we considered the experimental values more reliable and used them to obtain the dissociative yields.

Values of the dissociative yield ($Y_{\min}/Y_{\max}$) are summarized in Table II and displayed in Fig. 5. The yield is seen to approach unity at both ends of the region investigated, with a subsidiary maximum near 5450 Å. The values at 5462 and 5900 Å are in good agreement with the estimated predissociative fractions (67% and 33%, respectively) in Ref. 2. Because the contribution from direct dissociation via $lu \leftarrow X$ absorption is small, the agreement remains good when the yield is resolved into contributing processes, as discussed below. Wassermann and colleagues⁴ noted "parallel" production of atoms in continuum and banded-region excitation over a range of I_2 pressures from 10^{-4} to 10^{-1} torr. In terms of the mechanism presented in our paper, their results indicate practically 100% dissociation; however, their measurements should have been extended to somewhat higher I_2 pressures to observe more clearly the difference in the high- and

low-pressure limits. Alternatively, if their acid-treated cells were not freshly evacuated before each experiment, quenching by impurities could have given anomalously high yields. Results of an earlier study by this group²⁹ indicated a dissociative yield of 77% for 5460 Å excitation, in good agreement with the present findings.

2. Vibrational Excitation Distributions

The $v'-v''$ distributions involved in the $B \leftarrow X$ absorption process were calculated by summing the contributions of all I_2 rotational lines of significance falling within the transmission region of the interference filter in question. The transmission for each filter was taken as a Gaussian function of the wavelength. This form represented the transmission very well over the region $F_\lambda > 0.1 F_{\lambda, \text{max}}$. Bands involving v'' levels 0-5 and rotational levels 0-300 were included in the summation. The required Franck-Condon factors were those computed for rotationless RKR potential curves by Cunningham³⁰ using Zare's programs³¹ and the B-state spectroscopic data of Steinfeld, et al.³² (For $v' < 50$ the F-C factors differ only slightly from the values calculated using the revised B-state constants in Ref. 8.)

The results are summarized along with the filter characteristics in Table I. (The distributions for the 5010 and 5091 filters are estimates based on conclusions in Refs. 8 and 13.) It is worth noting the difficulty of exciting low v' levels at the red end of the spectrum. For the 6037, 6129, and 6239 filters, the v' distribution changes only slightly, while the v'' distribution shifts to higher levels as the absorption "climbs" up the outer branch of the X-state potential curve.

According to Kronig's³³ derivation the predissociative rate for the transition $O^+u \rightarrow lu$ should be proportional to $J(J+1)$. In that case the "effective" v' distribution might more properly be computed by including this J dependence in the sum. The effect would be to shift the distributions to slightly higher v' levels, with perhaps $\Delta v' = +1$. In the present study spectral resolution was too low to allow for a meaningful analysis of k_p in terms of individual rates $k_p(v')$, so this modification was not considered worthwhile.

B. Analysis of Contributing Processes

Estimates of the strengths of the $lu \leftarrow X$ continuum transitions are now precise enough⁸ to permit a more reliable resolution of the dissociative yield into contributing processes than was possible before.⁶ The new analysis is presented in Table III. The values for per cent continuum absorption are felt to be accurate within ~20% (relative) for the region investigated. The tabulated total decay rates ($1/\tau$) for the B state represent rough averages of the measurements of Chutjian,^{1,34} Wolff,³⁵ Cunningham,³⁰ and Grimes.³⁶ These lifetime experiments employed continuum sources in combination with the same interference filters that were used in the present work. More recent measurements of Broida and co-workers³⁷ are in general accord with these results, but should not be compared quantitatively, as they were obtained for visible excitation of much greater resolution, where the vibrational and rotational dependence of the decay is expected to be more pronounced.

For our purposes the τ^{-1} values in Table III are probably reliable to no better than ~20%, even though the individual determinations appear to be much more precise. With broad-band excitation the overall decay is some superposition of the individual decays for the numerous (v', J') levels involved. As Cunningham³⁰ has demonstrated, the observed lifetime under such conditions can be explicitly dependent on the method of observation. In his work, phase-shift measurements on the decay of $I_2^*(B, v' \sim 25)$ gave distinctly different lifetimes for different modulation frequencies.

The quantities in parentheses in Table III are based on a smooth interpolation of the resolved A_T values, illustrated in Fig. 6.

Theoretically the radiative decay rate may be represented²

$$A_{T, v'} = \frac{64\pi^4}{3h} \sum_{v''} |\langle v' | R_e(r) | v'' \rangle|^2 \nu_{v', v''}^3 \quad (14)$$

In the r-centroid approximation³⁸ the term in the summation becomes

$$|\langle v' | R_e(r) | v'' \rangle|^2 \nu_{v', v''}^3 = |\langle v' | v'' \rangle|^2 |R_e(\bar{r}_{v', v''})|^2 \nu_{v', v''}^3 \quad (15)$$

where $|\langle v' | v'' \rangle|^2$ is the Franck-Condon factor and $\bar{r}_{v', v''}$ the r-centroid for the given band. The observed dependence on A_T on v' (Fig. 6) is much too steep to be explained in terms of the ν^3 dependence alone, hence must be due to a strong variation of the dipole strength with internuclear distance. In order to accommodate the results of absorption measurements^{2,8} (giving $|R_e|^2$ for the limited range $\bar{r} \sim 2.60$ - 2.80 Å) and still account for the observed A_T behavior, the $|R_e|^2$ curve must be peaked sharply around $\bar{r} \sim 3.0$ - 3.2 Å (the region of maximum Franck-Condon density for

low v' levels) and decrease rapidly at larger $\bar{r}$ (where a large fraction of the F-C density is associated with the right-hand turning points for high v' levels). Thus, for example, the dashed curve in Fig. 6 shows the fair agreement with experimental results which was obtained for the $|R_e|^2$ curve displayed in Fig. 7. While the latter curve decreases toward zero at large r , as it must for the extremely weak $^2P_{1/2} \leftrightarrow ^2P_{3/2}$ atomic transition in the limit of dissociation, the quantitative behavior of the transition moment must remain somewhat speculative at present.

The predissociative rate k_p fluctuates with v' , giving a maximum around $v' \sim 25$, a minimum near $v' = 15$, and apparently a radical increase for still lower v' levels. Such behavior is qualitatively consistent with the relative configuration of the B and $lu(^1\Pi)$ states shown in Fig. 1, because the bound and continuum wave functions should fall in and out of phase as the energy is increased. Calculations such as those of Chutjian³ should be applied to the new $lu(^1\Pi)$ state to provide more quantitative information on this matter. At the same time additional lifetime measurements for low v' levels of the B state would help locate more precisely the $lu(^1\Pi)$ potential curve in this region.

C. Collisional Predissociation of $I_2^*(B)$

Quenching rates for N_2 were calculated from the high-pressure data using the expression

$$k_{q,N_2} \tau[N_2] = \left(\frac{Y_{\max} - Y_{\min}}{Y_{\max} - Y} \right) - 1 - k_{q,I_2} \tau[I_2] \quad (16)$$

which is derived from Eqs. (5) and (6). Values for k_{q,I_2} in the last term on the right were taken from Ref. 1; this term was small for the I_2 pressure (1.6 mtorr) employed in most of these experiments. The measured $k_q \tau$ values were converted to quenching cross sections by means of the τ^{-1} values given in Table III and the relation

$$k_q = d^2(8\pi kT/\mu)^{1/2} \quad (17)$$

In Eq. (17) μ is the reduced mass for the collision partners and d^2 is the cross section.

The results are summarized in Table IV. For excitation to low v' levels ($\lambda \sim 5900 \text{ \AA}$) the agreement with previously published results^{22,39} is satisfactory. For $v' \gtrsim 25$ there appear to be no other published data for quenching by N_2 . However, one might expect the cross section to increase dramatically in this region as is indicated for other foreign gases.^{22,23,40} To the contrary, the rate appears to decrease somewhat. While we have no ready explanation for this apparent anomaly, we would emphasize the basically different nature of the present experiment--the detection of atoms--as compared with all other reported foreign-gas quenching studies of I_2 , which have relied upon fluorescence intensity measurements. In the present study all the quenching information is contained in the portion of the signal ($Y_{\max} - Y_{\min}$), which, for excitation in the green region, decreases to $\sim 30\%$ of the total signal. Because of possible small systematic errors in $Y_{\max}$ and $Y_{\min}$,⁶ the $k_q \tau$ values in Table IV are somewhat less reliable than the indicated standard deviations. However, we question that they can be in error by the magnitude

required to accommodate results such as those observed for the rare gases.⁴⁰ A study of the foreign-gas quenching by lifetime methods would be invaluable in sorting out discrepancies such as these, and in corroborating the information obtained from fluorescence quenching studies.

V. CONCLUSION

Dissociative processes account for a major portion of the unimolecular decay of I_2^* excited by visible radiation from 5000-6300 Å. A sizeable fraction of the dissociative yield is attributed to direct dissociation via the $lu \leftarrow X$ continuum transitions which underlie the stronger $B \leftarrow X$ band system. The remainder is accounted for in terms of spontaneous predissociation, $B \rightarrow lu(^1\Pi)$, which varies with v' in a manner that explains the vibrational dependence of the measured lifetimes for the first-order decay of the B state. The total radiative decay rate varies smoothly but strongly with v' , indicating that the dipole strength for the $B \leftrightarrow X$ transition must be peaked sharply at an internuclear distance near 3.0-3.2 Å.

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26. Approximately ten of the total ~250 recorded points were discarded on statistical and circumstantial grounds.
27. From the results for τ and k_{q,I_2} in Ref. 1, the deviation from the linear expression (7) should be less than 15% at $P_{I_2} = 20$ mtorr. The high-pressure limit could not be achieved using I_2 alone,

because at pressures greater than ~100 mtorr the atomic fluorescence signal decreased when the tungsten lamp was turned on. This effect we attribute to high residual concentrations of atoms from photolysis of I_2 by visible radiation from the iodine lamp. The residual concentration places the "zero" signal near the maximum in the characteristic fluorescence function. (See Ref. 6 for details.)

28. At 6239 Å the absorption was only ~30% of the reference value. Over such a range of visible intensities, flaws in the non-linearity correction for the I-atom detection could be large enough (~5%) to account for the observed negative slope.⁶
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these authors have given undue weight to the bands in the $v'' = 0$ progression at long wavelengths. As is pointed out in the present work (Section IV-A), v' levels lower than ~ 8 are exceedingly difficult to populate, because for $\lambda > 6000 \text{ \AA}$ the Franck-Condon prohibition for bands $v'-0$ far overbalances the Boltzmann prohibition for absorption from excited v'' levels. (G. Capelle has confirmed this point in a letter to us.)

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Table I. Filter characteristics and I_2 B ← X excitation distributions.

Wavelength (Å)	Maximum Transmittance	Half-width (Å)	'v' levels*	v'' levels
4919	60%	66	continuum	0(40%), 1(25%), 2(25%)
5010	59	30	> 58 and continuum	0(60%), 1(25%), 2(10%)
5091	73	28	50 - 60	0(70%), 1(20%)
5166	78	47	40 - 46; 43 (11%)	0(80%), 1(15%)
5277	77	50	33 - 38; 35 (21%)	0(93%)
5462	77	51	24 - 29; 26 (25%)	0(81%), 1(13%)
5594	73	56	19 - 24; 21 (21%)	0(56%), 1(40%)
5690	45	138	16 - 22; 19 (18%)	0(39%), 1(53%), 2(5%)
5896	78	58	12 - 16; 15 (24%)	0(8%), 1(44%), 2(42%)
5922	72	85	11 - 16; 14 (21%)	0(6%), 1(41%), 2(45%)
6037	81	86	9 - 14; 12 (24%)	1(20%), 2(51%), 3(25%)
6129	54	84	8-13; 10&11(24% each)	1(8%), 2(39%), 3(45%)
6239	37	96	6 - 11; 9 (26%)	2(19%), 3(50%), 4(28%)

* Tabulated levels are those accounting for at least 50% of the total absorption.

Table II. Quantum yield for photodissociation of I_2 .
(Listed uncertainties are least-squares standard deviations.)

Wavelength ($\text{\AA}$)	Dissociative Quantum Yield
5010	$.926 \pm .020$
5091	$.698 \pm 0.34$
5166	$.623 \pm .018$
5277	$.66 \pm .04$
5462	$.723 \pm .016$
5594	$.667 \pm .025$
5690	$.591 \pm .028$
5896	$.332 \pm .014$
5922	$.346 \pm .010$
6037	$.537 \pm .018$
6129	$.673 \pm .043$
6239	$.878 \pm .053$

Table III. Analysis of Visible absorption and B-state decay processes.

Wavelength (Å)	Absorption		$I_2^*(B)$ Decay		τ^{-1} ($10^5/\text{sec}$)	A_T ($10^5/\text{sec}$)	k_p ($10^5/\text{sec}$)
	Continuum ($lu \leftarrow X$)	Discrete ($B \leftarrow X$)	Predissociation	Fluorescence			
5010	55%*	45%	85%	15%	6.7	1.0	5.7
5091	27	73	59	41	6.2	2.5	3.7
5166	22	78	51	49	4.7	2.3	2.4
5277	17	83	59	41	9.7	4.0	5.7
5462	13	87	68	32	14.9	4.8	10.1
5594	12	88	63	37	15.8	5.8	10.0
5690	13	87	53	47	(13.8)	(6.5)	(7.3)
5896	18	82	18	82	9.4	7.7	1.7
5922	19	81	20	80	(9.8)	(7.8)	(2.0)
6037	24	76	39	61	13.7	8.4	5.3
6129	35	65	49	51	(17.5)	(8.9)	(8.6)
6239	50	50	76	24	(39)	(9.4)	(30)

() - based on smooth interpolation of A_T values from measured τ^{-1} values.

* - includes contribution from $B \leftarrow X$ continuum, involving absorption from excited v'' levels.

Table IV. Results for collisional quenching by N₂.

Wavelength (Å)	$k_q \tau$ (torr ⁻¹)	d^2 (Å ²)
5010	—	—
5091	3 ± 2	3.6
5166	2 ± 1	1.9
5277	0.7 ± 0.3	1.4
5462	0.5 ± 0.2	1.4
5594	0.35 ± 0.1	1.1
5690	0.65 ± 0.3	1.7
5896	2.1 ± 0.6	3.8
5922	2.2 ± 0.8	4.3
6037	1.7 ± 0.7	4.5
6129	0.6 ± 0.3	1.7
6239	0.1 ± 0.2	0.9

XBL-7110-7353

Fig. 1

XBL 6910-5836

Fig. 2

$\lambda 5462$

XBL 6910-5823

Fig. 3

$\lambda 5896$

XBL 6910-5817

Fig. 4

XBL 6910-5815

Fig. 5

XBL7110-4523

Fig. 6

XBL7110-4522

Fig. 7

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