

## Quantum efficiencies for the production of electronically excited iodine atoms $I(5p^5^2P_{1/2})$ following laser photolysis of $I_2$ near $5000 \text{ \AA}$ <sup>†</sup>

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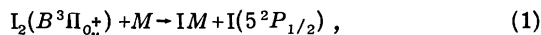
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The production of electronically excited iodine atoms is observed by time-resolved atomic absorption spectroscopy following the dissociation of molecular iodine excited by a tunable dye laser to the  $B^3\Pi_{0_u^+}$  state above and below the thermochemical dissociation limit. The quantum efficiency is independent of excitation wavelength above the dissociation limit. Substantial yields of  $I(5^2P_{1/2})$  are found for excitation as much as  $4.5kT$  below the dissociation limit.

The irradiation of mixtures of hydrocarbons and iodine vapor at wavelengths in the banded region of the  $I_2(B^3\Pi_{0_u^+} \rightarrow X^1\Sigma_g^+)$  system below the thermochemical dissociation limit can result in the production of excited iodine atoms which may react with the hydrocarbons to form alkyl iodides.<sup>1</sup> It has been proposed that the appearance of  $I(5^2P_{1/2})$  following excitation below the dissociation limit of the  $I_2(B^3\Pi_{0_u^+})$  state is a consequence of the formation of a molecular complex  $IM$ ,



and an excited atom. The process of "collisional release"<sup>1</sup> was found experimentally to proceed with a similar quantum yield, i.e., number of  $I(5^2P_{1/2})$  formed per photon absorbed, when  $M = \text{He}$  or  $\text{Xe}$ . This observation is not in agreement with the expectation<sup>1</sup> that He would be much less efficient than Xe or other gases, because the attractive interaction of He with atomic iodine should be comparatively weak. Using trajectory calculations leads to a similar conclusion.<sup>2</sup> The fact that other collision partners  $M = \text{C}_3\text{H}_8, \text{H}_2, \text{N}_2, \text{Ar},$  and  $\text{CO}_2$  gave similar results led Broadbent and Callear<sup>1</sup> to conclude that the energy available in all of the degrees of freedom of the  $I_2(B^3\Pi_{0_u^+})$

+  $M$  collision complex contributes efficiently to surmounting of the dissociational barrier.

This paper reports the observation of the time development of the appearance and disappearance of  $I(5^2P_{1/2})$  atoms following the excitation of  $I_2(^1\Sigma_g^+)$  molecules with a short monochromatic light pulse at selected wavelengths between 4700 and 5250  $\text{\AA}$ . As expected, the quantum yield for the production of excited atoms is constant for excitation wavelengths shorter than 4995  $\text{\AA}$  corresponding to the thermochemical dissociation energy. At longer wavelengths our results, like those reported previously,<sup>1</sup> show substantial quantum yields for photon energies several  $kT$  below the thermochemical threshold. In the present experiments, however, no additional gas was present in our system and any collisional processes must involve  $I_2$  species only.

Figure 1 shows a block diagram of the experiment. The molecular  $I_2$  was contained in a cell having a rectangular section  $1 \times 1 \times 7 \text{ cm}$ . Two opposite sides were externally coated with aluminum to form a pair of parallel mirrors. The laser light was introduced at an angle to establish a series of multiple reflections between the mirrors, resulting in relatively uniform absorption of the

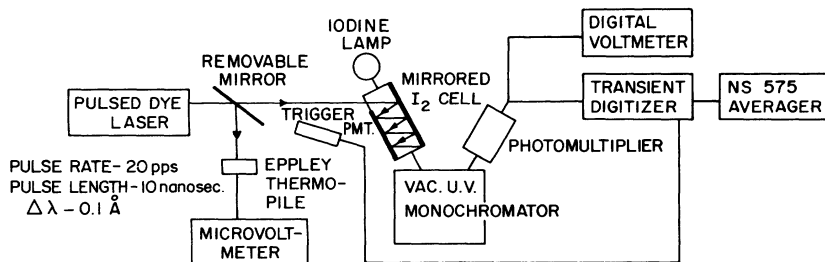


FIG. 1. Block diagram of the experimental apparatus.

laser radiation by  $I_2$  along the cell length. The presence of excited iodine atoms was detected by monitoring the absorption of atomic line emission transmitted through the cell from a microwave-excited electrodeless discharge lamp containing 0.030 Torr iodine and 1 Torr argon. A McPherson model 225 monochromator selected the line at 2062 Å, corresponding to the  $I(6^2P_{1/2} - 5^2P_{1/2})$  transition, which was monitored to provide a direct measurement of  $I(5^2P_{1/2})$  population as a function of time following the laser pulse.

The experiment was carried out at room temperature. Sufficient  $I(5^2P_{1/2})$  was produced with each laser pulse to produce an absorption at 2062 Å on the order of several percent. The very large photon statistic noise present on the photomultiplier output was of the same order of magnitude as the absorption signal. At each wavelength approximately  $10^4$  pulses were recorded using a Biomation model 8100 transient digitizer and were digitally transferred for accumulation of the waveform in a Northern Scientific model 575 signal averager. Figures 2(a)–2(d) show the  $I(5^2P_{1/2})$  population as a function of time following the 10-nsec laser pulse for excitation at 4950 and at 5100 Å. In Figs. 2(a) and 2(b) the display represents a total time of 20 μsec. The removal of  $I(5^2P_{1/2})$  is predominantly due to collision with  $I_2$  molecules,<sup>3</sup> diffusion being negligible at the  $I_2$  pressure used. A later paper will report our determination of a second-order quenching rate constant for this process which we find to be substantially faster than previously reported.<sup>3,4</sup> Figures 2(c) and 2(d) show an expanded display

(total time  $\approx 2$  μsec) of the leading edges of Figs. 2(a) and 2(b). Individual sampling points are spaced by 10 nsec. As the Hamamatsu type R106UH photomultiplier which was employed was sensitive to visible light, a small amount of laser radiation scattered into the monochromator is seen in the initial channels as a negative signal.

The response time of our system was measured by observing this scattered laser light through the monochromator. It was determined that the display required no more than two sample points in going from 10 to 90% of the maximum laser pulse amplitude and this sets a lower limit on signal rise times which can be measured. The significance of the delay to reach maximum atomic absorption is discussed below.

Measurements were made as a function of excitation wavelength of the relative yield of  $I(5^2P_{1/2})$  atoms per photon absorbed by the  $I_2$  which leads to the production of a  $B^3\Pi_{0_u^+}$  molecule. It was necessary to correct for the fact that experiments of this kind using absorption techniques require a modified form of Beer's law,<sup>5</sup>

$$I = I_0 e^{-\epsilon(CL)^\gamma},$$

to describe the intensity of radiation transmitted through a sample of length  $L$ , containing species density  $C$  and with an atomic extinction coefficient  $\epsilon$ . The quantity  $\gamma$  accounts for self-reversal in the iodine lamp and is an empirically determined parameter.<sup>5</sup> By varying the concentration of iodine atoms using different laser powers it was found that for the particular lamp used in this study,

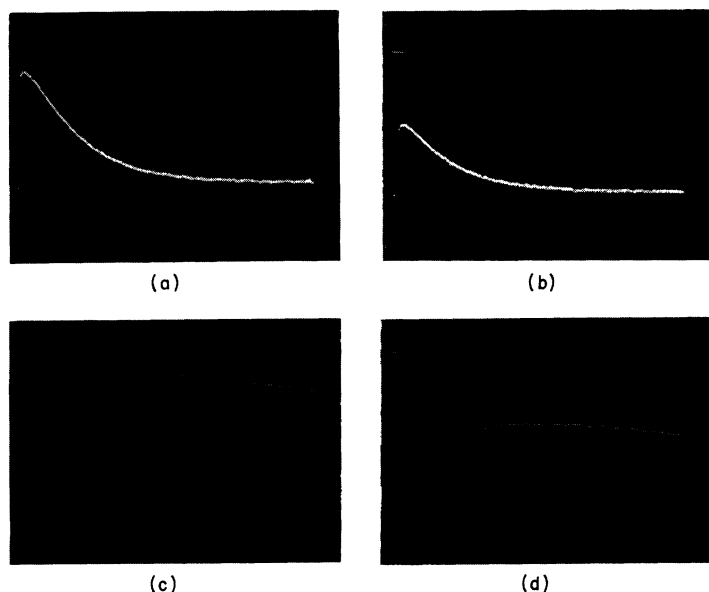


FIG. 2.  $I^*$  population after 10-nsec laser pulse: (a), (c) 4950-Å excitation; (b), (d) 5100-Å excitation. Scattered laser light appears as a negative signal in first few channels. The channel spacing is 10 nsec.

$$\gamma = 0.89 \pm 0.07,$$

and subsequent data analysis employs this value.

For each excitation wavelength  $\lambda$ , the quantity

$$\left[ \ln \left( \frac{I_0}{I} \right) \right]^{1/\gamma} \frac{1}{\lambda \epsilon(B-X) P_{\text{laser}}},$$

which represents the required relative efficiency, was calculated. In this expression  $I_0$  is the atomic emission lamp signal in the absence of the laser pulse,  $I$  is the transmitted signal at maximum absorption,  $P_{\text{laser}}$  is the average laser power at 20 pulses/sec, and  $\epsilon(B-X)$  is the extinction coefficient for this system as determined by Tellinghuisen.<sup>6</sup> The data are plotted in Fig. 3, normalized to the mean of the values determined for wavelengths below 5000 Å, where the quantum yield of  $I(5^2P_{1/2})$  is indeed 1. The experimental data, the extinction coefficients, and the results are shown in Table I. As would be expected, the quantum efficiency remains constant for excitation above the dissociation limit. Since only  $I_2(B^3\Pi_{0_u^+})$  molecules are responsible for the appearance of  $I(5^2P_{1/2})$  atoms, the data support the wavelength dependence of  $\epsilon(B-X)$  determined by Tellinghuisen<sup>6</sup> for  $\lambda < 5000$  Å.

Also plotted in Fig. 3 are the results obtained with Xe as the collision partner reported in Ref. 1 corrected for the more recent values of the extinction coefficient used here. Although it is difficult to compare the results of experiments carried out using such different techniques, it would appear that a major fraction of the observed collisional release in the presence of inert gases may indeed be due to the process

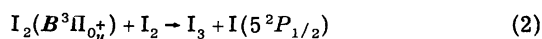


TABLE I. Quantum yield for the production of  $I(5^2P_{1/2})$  atoms.

Excitation wavelength (Å)	$\epsilon(B-X)^a$ (liter mole <sup>-1</sup> cm <sup>-1</sup> )	$\phi(\lambda)$		
		Run 1	Run 2	Average
4700	91	1.06	0.93	0.99
4750	124	(0.68) <sup>b</sup>	1.02	1.02
4800	157	1.01	0.86	0.93
4850	209	1.00	0.98	0.99
4900	261	0.95	1.14	1.05
4950	318	0.98	1.07	1.02
5000	375	0.90	1.04	0.97
5050	449	0.73	0.87	0.80
5100	523	0.38	0.43	0.41
5150	557	0.16	0.20	0.18
5200	591	0.09	0.12	0.11
5250	635	0.06	0.05	0.05

<sup>a</sup> Reference 6.

<sup>b</sup> Excluded from calculations.

as opposed to reaction (1). Such a view is in agreement with the suggested stability of the  $I_3$  complex as obtained from iodine atom recombination data.<sup>7</sup> Furthermore, the participation of process (2) reconciles the observation<sup>1</sup> of efficient production of  $I(5^2P_{1/2})$  from  $I_2(B^3\Pi_{0_u^+})$  as the result of collisions with He atoms with the theoretical prediction that such collisions lead primarily to vibrational relaxation of the highly excited molecule.<sup>2</sup> Measurements at greatly reduced  $I_2$  densities and high inert gas pressures will permit direct observation of release processes such as (1).

Although the temporal resolution of the signal-averaging apparatus is not sufficient to permit detailed observation of the rising portion of the  $I(5^2P_{1/2})$  absorption, it is clear from Fig. 2(d) that photolysis below the 4995-Å dissociation limit results in a rise time to the maximum excited atom population of approximately 100 nsec. Such a time scale is consistent with a reactive cross section for process (2) that is much larger than that measured for the corresponding decay of  $I_2(B-X)$  fluorescence excited at similar wavelengths.<sup>8</sup> As those fluorescence measurements were made over time scales relatively long compared to the rise time of the absorption signal described here and without sufficient spectral resolution to exclude fluorescence from lower-lying vibrational levels of the  $B^3\Pi_{0_u^+}$  state, it is difficult to accurately compare the results so obtained with our measurements. It should be noted, however, that very large cross sections have also been noted in collisional processes leading to dissociation of  $D_2CO$  following excitation of vibronically excited states.<sup>9</sup>

The  $I(5^2P_{1/2})$  absorption signal resulting from laser excitation above the dissociation limit displays a rapid initial rise followed by a slower

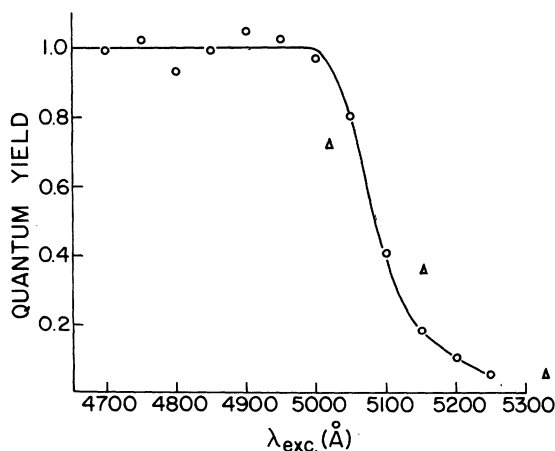


FIG. 3. Quantum yield  $\phi(\lambda)$  as a function of exciting wavelength: O, this work;  $\Delta$ , Xe data of Ref. 1.

build up to the maximum. This behavior would be expected from an ensemble of excited molecules with a distribution of rotational energies which would give rise to a rotational barrier to dissociation.<sup>2</sup> As expected, the fraction of the maximum concentration produced in the rapid initial dissociation increases as the energy of the actinic photons increases.

Collisional inverse predissociation via  ${}^1\Pi_u \rightarrow {}^3\Pi_{0u}^+ \rightarrow {}^2P_{3/2} + {}^2P_{1/2}$  as suggested in Ref. 2 seems to be an unlikely route for the production of  $I(5^2P_{1/2})$  atoms. Under the conditions of the

present experiment  $I_2$  molecules in the repulsive  ${}^1\Pi_u$  state are certainly being produced but will dissociate to give two  $I(5^2P_{3/2})$  atoms in a time very much shorter than that required for a collision to occur.

Time-dependent studies on the ground-state iodine atom are being undertaken to explore the details of the known predissociation<sup>10</sup> of the  $B^3\Pi_{0u}^+$  state due to a crossing of its potential curve by the  ${}^1\Pi_u$  state. For this experiment it will be necessary to use longer excitation wavelengths than those employed in this work.

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<sup>10</sup>L. Brewer and J. Tellinghuisen, *J. Chem. Phys.* **56**, 3929 (1972).

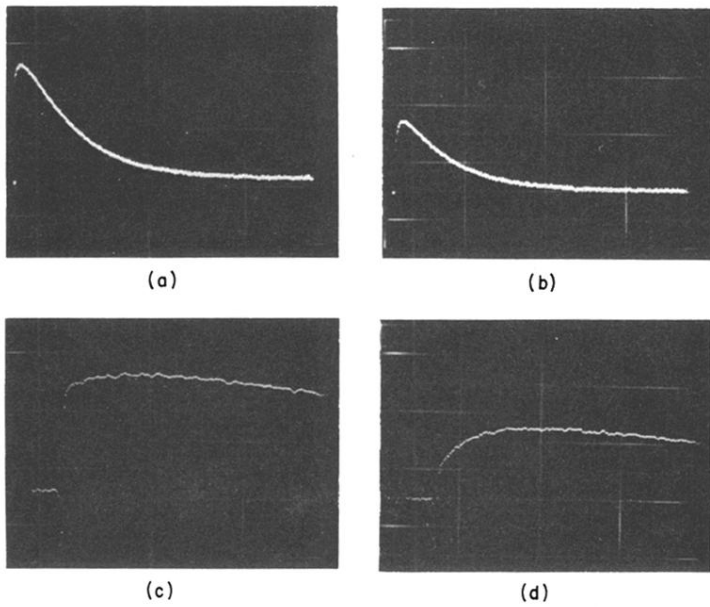


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