

Measurement of the relative populations of $I(2\ P\ 0\ 1/2)$ and $I(2\ P\ 0\ 3/2)$ by laser induced vacuum ultraviolet fluorescence

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Measurement of the relative populations of $I(^2P_{1/2}^0)$ and $I(^2P_{3/2}^0)$ by laser induced vacuum ultraviolet fluorescence

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The ground ($^2P_{3/2}^0$) and first excited ($^2P_{1/2}^0$) states of iodine atoms can absorb two photons at 304.7 and 306.7 nm, respectively, to reach $^2D_{5/2}^0$ and $^2D_{3/2}^0$ states. The excited atoms fluoresce twice, emitting an IR and then a VUV quantum. This is the basis of a new method for measuring the relative quantum yields of the two fine structure states at very short times after the atoms are formed. Quantum yields for I^* production are reported for a number of alkyl halides and HI upon photodissociation.

Iodine atoms form weak chemical bonds. As a consequence they are frequently products of exothermic displacement reactions. Also, they and their radical partners can be generated by photodissociation at easily accessible wavelengths. Since the development of the iodine atom photodissociation laser¹ at the 7603 cm^{-1} transition between $I(^2P_{1/2}^0)$ and $I(^2P_{3/2}^0)$ there has been considerable interest in determining the nascent ratios of the populations of these two states.

Three methods have been used to determine the fraction of atoms generated as I and I^* : (1) VUV absorption,² (2) infrared emission,³ and (3) photofragment translational energy measurement.⁴⁻⁸ The VUV absorption method uses an iodine atom resonance lamp usually self-reversed. The absorption does not always follow Beer's law and the weak intensity limits measurement to the time scale of tens of microseconds during which time substantial quenching of the I^* atoms may occur. The infrared emission method suffers from the weak emission intensity per unit time (0.13 s radiative lifetime) and the slowness of infrared detectors. Thus the time scale for detection of the I^* population is limited to microseconds or longer. Extension to I^* atoms produced in a chemical reaction is not obvious and the ground state I atoms are not detected.

The method of photofragment translational energy measurement exploits the 0.942 eV energy difference between I^* and I . As long as the width of the internal energy distribution of the companion radical is less than this value the method works well. It has been used for I_2 ,⁴ HI ,⁵ ICN ,⁶ and CH_3I ⁷ but begins to fail for the molecule C_2H_5I .⁸ Thus its use is limited to relatively small molecules. The same limitation will apply to iodine atoms produced in a crossed beam reaction. This method does have the advantage over all other methods discussed here that it furnishes an absolute ratio of number densities of I^* and I atoms.

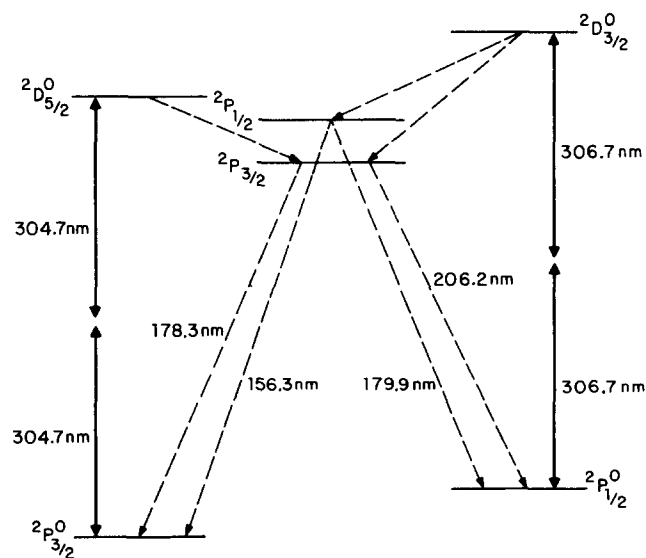
We report a new method for the detection of atomic iodine in both fine structure states based on two photon laser induced fluorescence. As shown in Fig. 1 the transition involved in the two photon absorption step for the I atom is $^2D_{5/2}^0 \leftarrow ^2P_{3/2}^0$ and for the I^* atom is $^2D_{3/2}^0 \leftarrow ^2P_{1/2}^0$. The excited atoms decay to the ground state, first by emission of an infrared photon and then by emission of a VUV photon which is detected. This method can be applied at short times to iodine atoms pro-

duced by chemical reactions or photodissociation. It is a happy coincidence that the two excitation wavelengths 304.7 (I atoms) and 306.7 nm (I^* atoms) are so close together that on the same scan emission signals from atoms in both states can be compared.

There is one experimental problem intrinsic to this method. In order to observe the two photon induced fluorescence the dye laser light must be focused and this may result in photodissociation. This problem was circumvented by reducing the probe light intensity until only about 5% of the observed signal was due to probe laser dissociation. This amount was subtracted from the total observed signal. Generally ten scans were made for each compound and the error quoted is the rms deviation from the mean of the ten ratios.

EXPERIMENTAL

The apparatus used in these experiments is illustrated in Fig. 2. A sample gas is contained at 25–100 mTorr in a stainless steel cell which is diffusion pumped and



ENERGY LEVELS OF THE IODINE ATOM

FIG. 1. Relevant energy levels of the iodine atom.

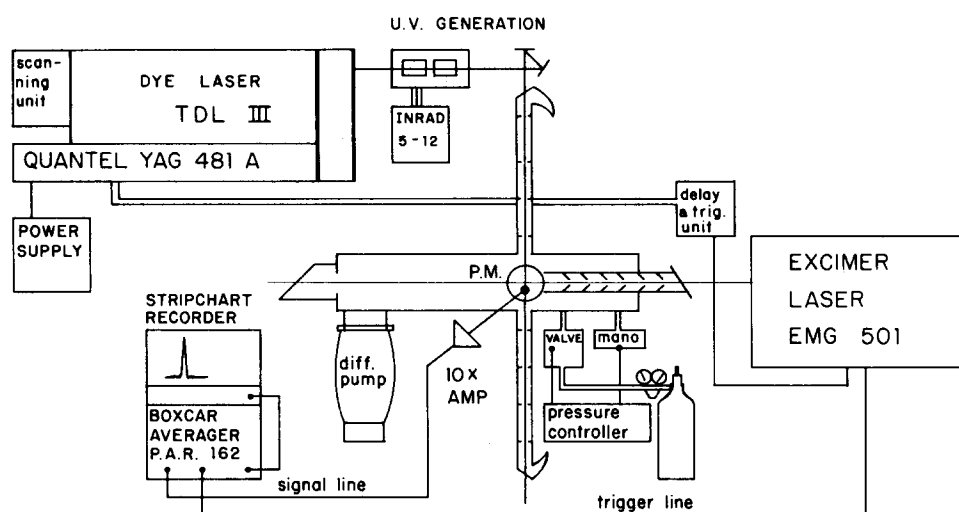


FIG. 2. Schematic diagram of the apparatus.

held at a constant pressure by means of an MKS pressure controller. Photolysis at 248 nm is accomplished by using a KrF excimer laser (EMG 501) with typical pulse energies of 100 mJ in 15 ns. The linearly polarized probing laser light of a YAG pumped dye laser (pulse width: 10 ns, bandwidth: 0.12 cm^{-1}) delayed by 100–200 ns after the excimer laser pulse, is doubled by a KDP crystal, bent into the stainless steel cell perpendicular to the photolyzing light beam and focused with a 38 mm Suprasil lens. Typical pulse energies of 0.1 mJ were used throughout the experiments. To cover the excitation of the $^2P_{3/2}^0$ and $^2P_{1/2}^0$ states at 304.7 and 306.7 nm, respectively, small concentrations of Rh 640 were added to Rh 610 so as to obtain equal intensities at the two wavelengths. Fluorescence was observed through a MgF_2 window by a solar blind photomultiplier tube (EMR 542G-09-18). The space between the window and the PMT was continuously flushed with dry nitrogen. Signals were amplified ($\times 10$) and sent to a boxcar averager (PAR 162) and recorded on a strip chart recorder. The iodine compounds were purified by a standard procedure⁹ and dried with magnesium sulfate. In the case of HI, a dry ice/acetone bath was used first to freeze the HI and pump off H_2 and I_2 impurities.

RESULTS

The suitability of the two photon laser induced fluorescence method for the determination of the relative quantum yields ϕ^* ($\phi^* = I^*/(I + I^*)$) depends upon an initial calibration of the signals obtained for I and I^* atoms from a well known standard. By measuring the ratio of the signals at 304.7 nm for I atoms and 306.7 nm for I^* atoms, one obtains the proportionality constant k in the equation below. Here S and S^* refer to the experimental signal intensities while $[I]$ and $[I^*]$ are number densities.

$$\frac{S^*(306.7\text{ nm})}{S(304.7\text{ nm})} = k \frac{[I^*]}{[I]}$$

As a standard molecule for calibration we chose CH_3I for which the quantum yield for I^* production has been determined by the infrared emission method² and by the photofragment translational energy method.¹⁵ The

two values are 0.81 ± 0.03 and 0.71 ± 0.04 , respectively, and we have adopted the average value 0.76 for determination of k . If $\phi^* = 0.76$, then $[I^*]/[I] = 3.17$ and from the experimental ratio $S^*/S = 3.54$, we obtain $k = 1.12$. Thus, by coincidence, the raw experimental signal ratios are close to the ratios of concentrations of I^* and I atoms. The signal ratios listed in Table I have been corrected for the $\sim 5\%$ dissociation effect caused by the dye laser. The experimental uncertainty in ϕ^* is probably mainly due to fluctuations in the relative intensities of the dye laser at the two wavelengths.

The sensitivity of the method can be roughly inferred from the known excimer laser intensity, the molar extinction coefficient of the iodine atom parent and the apparent signal to noise ratios. From these numbers it would appear that I atoms at a concentration of $10^{11}/\text{cm}^3$ can be detected without extensive signal averaging.

The test of any new method is the range of its applicability. We have applied the two photon LIF method to a wide range of simple iodine containing compounds including HI, CD_3I , CF_3I , and alkyl iodides up to four carbons. Representative spectra are shown in Fig. 3.

TABLE I. Relative quantum yields of I^* .^a

Compound	Signal ratio S^*/S	ϕ^* (248 nm)	ϕ^* Broadband
CH_3I	3.54 ± 0.35	0.81 ± 0.03^b 0.71 ± 0.04^c	0.76 ± 0.08^d
CD_3I	3.35 ± 0.34	0.75 ± 0.02	0.99
CF_3I	9.00 ± 0.90	0.89 ± 0.01	0.91 ± 0.03
$\text{C}_2\text{H}_5\text{I}$	2.33 ± 0.23	0.68 ± 0.02	0.69 ± 0.05
$n\text{-C}_3\text{H}_7\text{I}$	1.70 ± 0.17	0.60 ± 0.02	0.67 ± 0.04
$i\text{-C}_3\text{H}_7\text{I}$	0.39 ± 0.04	0.26 ± 0.02	< 0.10
$n\text{-C}_4\text{H}_9\text{I}$	1.27 ± 0.13	0.53 ± 0.03	0.82 ± 0.04
$2\text{-C}_4\text{H}_9\text{I}$	0.28 ± 0.03	0.20 ± 0.02	< 0.10
$t\text{-C}_4\text{H}_9\text{I}$	0.04 ± 0.02	0.03 ± 0.02	< 0.10
HI	1.00 ± 0.10	0.47 ± 0.03 0.5^e	0.10 ± 0.05

^aAll data in column four after the first entry are from Ref. 2.

^bReference 3.

^cReference 15.

^dReference 16.

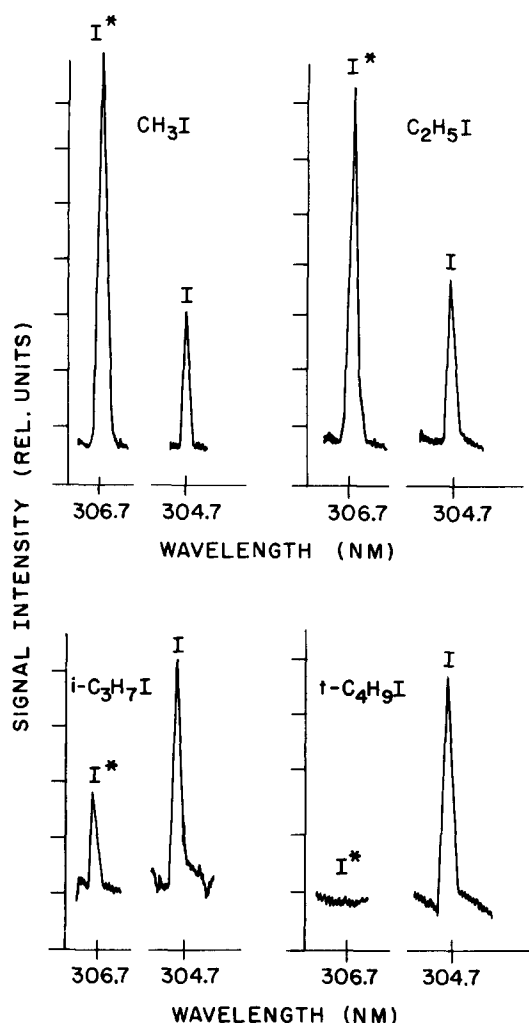


FIG. 3. I and I* fluorescence excitation spectra from CH_3I , $\text{C}_2\text{H}_5\text{I}$, $i\text{-C}_3\text{H}_7\text{I}$, and $t\text{-C}_4\text{H}_9\text{I}$.

The results of the measurements of the relative quantum yields from the photolysis of these compounds at 248 nm are given in Table I together with previously measured values. The relative quantum yields of a series of alkyl iodides are striking. The straight chain alkyl iodide compounds in the series CH_3I , $\text{C}_2\text{H}_5\text{I}$, $n\text{-C}_3\text{H}_7\text{I}$, and $n\text{-C}_4\text{H}_9\text{I}$ show a 8% decrease in I* relative quantum yield per carbon added to the chain. However, in the case of the branched chain alkyl iodides, addition of carbon groups to the α carbon produce drastic decreases in the I* relative quantum yield with $t\text{-C}_4\text{H}_9\text{I}$ giving the lowest I* yield of 0.03. The relative quantum yield obtained from the wavelength specific photolysis at 248 nm of HI is compared with values obtained from other methods in Table I.

DISCUSSION

Alkyl iodides

All the data reported here were for the single wavelength 248 nm. We do not know if they are representative of the entire absorption band. On the one hand, studies of HgI_2^{10} and ICN^{11} show that the I*/I ratio can be

a sensitive function of wavelength. This is because the $n \rightarrow \sigma^*$ absorption band is in general a composite of several transitions only one of which correlates to I* atoms. For example, the allowed transitions in the alkyl iodides are labeled 3Q_1 , 3Q_0 , and 1Q in order of increasing energy.¹² The absorption spectrum of CH_3I has been resolved by magnetic circular dichroism measurements¹³ into three components and it was estimated that the total absorption strengths of the above three transitions were 1%, 75%, and 25%, respectively. As the strongest transition, 3Q_0 leads to I* atoms, we can understand the high quantum yield for I* production. Moreover, it appears that the quantum yield for production of I* is about the same at 248 and 266 nm showing that the 3Q_0 transition accounts for most of the absorption at these two wavelengths. One can make a stronger statement. Inasmuch as the angular distribution of the methyl radical partners of I atoms dissociated from a molecular beam at 266 and 248 nm¹⁵ are both parallel (typical of a 3Q_0 transition), the mechanism of production of I atoms at these wavelengths is only to a small extent by absorption to a different upper state and mainly by radiationless transitions from the only state with appreciable oscillator strength 3Q_0 .

Though the $n \rightarrow \sigma^*$ absorption spectrum in the 230–280 nm region is very similar for all alkyl iodides, the quantum yield for production of I*, ϕ^* varies sharply. It is 0.78 ± 0.05 for CH_3I but 0.04 ± 0.04 for $\text{C}(\text{CH}_3)_3\text{I}$. Donohue and Wiesenfeld² pointed out that there is a considerable difference in ionization potential in the series of radicals: methyl, ethyl, propyl, isopropyl, and t -butyl. The lower the ionization potential the more one might expect ionic states R^+I^- to approach the upper state of the transition. The resultant mixing might provide a mechanism for the nonradiative transition. There is a rough correlation between ionization potential and the quantum yield ϕ^* .

An alternative explanation is that while the upper state of the transition is relatively unaffected by the groups attached to the carbon atom, the mechanical differences, i. e., the number and nature of the vibrational modes affect the radiationless transition rate. For example, in the sequence $\text{C}_2\text{H}_5\text{I}$, $n\text{-C}_3\text{H}_7\text{I}$, and $\text{C}_4\text{H}_9\text{I}$ there can only be negligible changes in the upper electronic states but ϕ^* declines: 0.68, 0.60, and 0.53. A more striking change is from $i\text{-C}_3\text{H}_7\text{I}$ with ϕ^* close to unity³ to $i\text{-C}_3\text{H}_7\text{I}$ with $\phi^* = 0.26$ (present work). One could explain this effect on the basis of the 3 V difference in ionization potential of C_3F_7 and C_3H_7 or by postulating that the C–H stretch being of high frequency is the effective acceptor mode. It may be that both of the above mechanisms contribute to the quenching process as the fragments separate.

Photodissociation of HI at 248 nm

The first ultraviolet continuum of HI is broad, beginning near 300 nm and peaking at 220 nm. The absorption has been assigned¹⁴ to three transitions to $^3\Pi_0^+$, $^3\Pi_1$, and $^1\Pi_1$ states. Only the $^3\Pi_0^+$ dissociates to I* atoms. A resolution of the spectrum using the ϕ^* value of 0.36 ± 0.05 obtained at 266.2 nm leads to the prediction that

at 248 nm $\phi^* = 0.5$.⁵ A recent time of flight measurement of ϕ^* yielded the value 0.5 at 248 nm.¹⁵ Thus our value of 0.47 ± 0.05 agrees well and shows that either HI or CH₃I could be used to calibrate the method.¹⁷

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