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MULTIPHOTON LASER IONIZATION MASS SPECTROMETRY OF CESIUM IODIDE AND ATOMIC IODINE

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## Abstract

Using the technique of laser ionization mass spectrometry, a study of multiphoton ionization (MPI) of atomic iodine and cesium iodide was conducted with a tunable dye laser. One of the objectives was to determine if this technique provides more selective ionization of the components of such a mixture than does conventional electron bombardment. It was found that under intense photon irradiation, CsI fragments to  $I^+$  by a multistep process. The first step is dissociation of CsI which is followed by multiphoton ionization of the liberated atomic iodine. Because of this mechanism, the atomic iodine in a CsI + I mixture with less than 10% iodine cannot be detected by MPI at the available photon wavelenths (2800 - 3000 Å). However, operation at wavelengths which preclude dissociation of CsI should greatly improve the selectivity. The cross section for two-photon excitation of iodine at 3047 Å was determined to be  $4 \times 10^{-50} \text{ cm}^4\text{-s}$ .

## 1. INTRODUCTION

An important aspect of the behavior of fission products in nuclear reactor fuel elements is the chemistry of cesium and iodine. Because the ratio of the stable isotopes of cesium to those of iodine produced by fission is  $\sim 10$ , thermodynamics predicts that essentially all of the iodine should be in chemically combined form CsI(1). This species is non-volatile and chemically nonaggressive in the fuel. However, there is indirect evidence that elemental iodine may be released from irradiated fuel(2). The actual chemical nature of iodine released from hot irradiated uranium dioxide has profound consequences in a reactor accident involving severe core damage as well as in the understanding and mitigation of the operational problem of failure of the Zircaloy cladding by fission product stress corrosion cracking. As a result, there is a great practical interest in a method of detecting CsI and atomic iodine during fission product release tests on irradiated reactor fuel specimens. Because of the substantial dissociative ionization of CsI under electron bombardment, electron impact (EI) mass spectrometry may not be suitable for this application. The purpose of the present study was to investigate multiphoton ionization (MPI) with a tunable dye laser as a means of selectively ionizing CsI and I for subsequent mass analysis.

For the practical application discussed above, knowledge of the sensitivity and selectivity of the MPI technique compared to conventional EI mass spectrometry is desired. From a fundamental viewpoint, the study represents an application of multiphoton ionization to two species which have heretofore not been investigated. Although considerable work on molecular iodine has

appeared in the literature(3,4), nothing is known about MPI of atomic iodine. Similarly, the only pertinent data on gaseous CsI is from a total optical absorption investigation reported by Davidovits and Brodhead(5). Since the species of interest cannot be contained in conventional optical cell, beams of atomic iodine and molecular CsI generated by high-temperature Knudsen cells were crossed with the laser beam in the ionizer cage of a quadrupole mass spectrometer. The ions produced were collected and mass analyzed by the mass filter.

## 2. EXPERIMENTAL

Figure 1 shows a schematic of the apparatus. The vacuum chamber housing the mass spectrometer is pumped by a well-trapped 1500 lit/s oil diffusion pump to a base pressure of  $5 \times 10^{-9}$  Torr. The mass spectrometer is tuned to different ions by using conventional electron impact ionization. The laser ionization tests are done with the same mass spectrometer settings. Following the analyzer section, the mass spectrometer is equipped with an off-axis electron multiplier on one side and a Faraday cup on the other. Either one of these detection methods can be employed by application of appropriate voltages to steer the analyzed ion beam to the desired location. The magnitude of the current pulse produced by the electron multiplier is proportional to the number of ions created during the laser pulse interacting with the steady neutral beam. The electron multiplier output is fed via a preamplifier and amplifier to a multichannel analyzer. Hence the channel number in which the pulse is stored is proportional to the number of ions in the pulse. Calibration of the electron multiplier is accomplished by utilizing the Faraday cup and the amplification train is calibrated by inserting a variable pulse height generator and a 1 M $\Omega$  resistance before the preamplifier.

A quartz Knudsen cell is used to generate the molecular beam of CsI. Heating is accomplished by a platinum filament wrapped around the quartz cell, whose temperature is measured by a thermocouple. Maximum cell temperatures are  $\sim 850\text{K}$ , and no reaction of the CsI with the crucible occurred. For generating an atomic iodine beam, molecular iodine vaporizes from a source held in a constant temperature path and passes through a 3 mm diameter, 12 mm long platinum tube with a 1 mm diameter orifice at the exit. This cell is heated resistively by tungsten filaments. The temperature of the tip is measured by an optical pyrometer and maintained at  $\sim 1400\text{K}$  to ensure essentially complete dissociation of iodine molecules at the pressure upstream of the orifice ( $\sim 5 \times 10^{-3}$  Torr). For both CsI and I, application of simple gas kinetic theory to the source pressures, orifice geometries and beam paths permitted calculation of the density of atoms or molecules in the volume of interaction of the neutral beams with the laser. Typical densities are  $6 \times 10^{10}\text{ cm}^{-3}$  for atomic iodine and  $4 \times 10^{11}\text{ cm}^{-3}$  for CsI.

The laser system consists of a Quanta-Ray Nd/YAG laser generating pulses at a repetition rate of 10 Hz. After passing through a harmonic generator, the beam pumps a dye laser and then enters a wavelength extension system (WEX). The laser light is focused by a quartz lens of 15 cm focal length into the ionizer region of the mass spectrometer. The diameter of the beam at this point is  $\sim 0.1\text{ mm}$ , as estimated from its image on photographic paper. The length of the zone over which it interacts with the neutral beam is  $\sim 0.5\text{ cm}$ . The volume of laser-neutral interactions is  $\sim 5 \times 10^{-5}\text{ cm}^3$ . The maximum output power is 10 mJ, which corresponds to a photon flux of  $\sim 5 \times 10^{28}\text{ cm}^{-2}\text{ s}^{-1}$  at  $3000\text{ \AA}$ . The pulse width is 5 ns.

### 3. RESULTS

#### A. Atomic Iodine

The first allowed excited state of the iodine atom is too far from the



ground state (6.78 eV) to be populated by resonant absorption of a single photon from the laser used. In the present experiment, photon wavelengths around 2800 Å and in the vicinity of 3000 Å were used to reach states near the first allowed level by two-photon absorption. Atoms excited to these states were then ionized by a third photon before decaying to the ground state. Figures 2 and 3 show the MPI spectra near the two wavelength regions investigated for the largest laser pulse energies attainable. The results are displayed in terms of the ionization efficiency, defined as the ratio of the number of ions generated per pulse to the number of neutral atoms in the interaction volume. The spectra have not been corrected for the wavelength-dependence of the laser intensity, which is also shown on the plots. Except for the two peaks at  $\sim 2810$  and  $\sim 2820$  Å, the spectrum is consistent with known energy levels of the iodine atom reported in the literature(6). The ionization efficiency varies as  $I^2$  at high laser power levels, where  $I$  is the photon flux ( $\text{cm}^{-2}\text{s}^{-1}$ ). At low power levels, the exponent increased to between 2 and 3.

#### B. Cesium Iodide

Figures 4 and 5 show the ionization efficiencies of  $\text{I}^+$  and  $\text{CsI}^+$  from the neutral CsI beam in the interaction volume with the laser. The wavelength regions around 2800 and 3000 Å were chosen to enable comparison of the results with those for iodine atoms. Fortuitously, there is a minimum in the total absorptivity of CsI near 3000 Å (5), so that these two wavelengths are useful for distinguishing between I and CsI with high selectivity. At 2800 Å the efficiency for  $\text{I}^+$  production from CsI is only 10% of that for  $\text{I}^+$  formation from I. At 3000 Å, the ratio of the  $\text{I}^+$  production efficiencies from the two parents is 0.13. This efficiency comparison is for the same laser energies per pulse for the CsI and I target gases. The

$I^+$  spectra obtained from CsI are identical to that obtained from I in both wavelength regions.

Consistent with the absorption curve obtained in Ref. 5, the CsI<sup>+</sup> signal observed around 3000 Å is within the noise limits of the detection system. At 2800 Å, on the other hand, CsI production is appreciable and appears to exhibit some structure. The ionization efficiency for CsI<sup>+</sup> is proportional to photon flux at low laser power and varies as  $I^{0.8}$  at the highest pulse energies attainable.

The efficiency for production of Cs<sup>+</sup> from CsI is also shown on Figs. 4 and 5. It is large and wavelength-independent.

#### 4. DISCUSSION

##### A. Cross Section for Two-Photo Excitation of Iodine at 3047 Å

Multiphoton excitation can be described by rate equations provided that the sequence of transitions from the ground state to the ion exhibits successively increasing rates and the final step irreversibly removes the particle from the system(7). In the MPI process, the second condition is automatically satisfied by removal of ions. For the photon fluxes in the present experiments, the first condition is also met since the two-photon transition via a virtual state is much less probable than the single-photon transition which produces the ion. The transition probability for an n-photon absorption step can be written as(8):

$$W^{(n)} = \sigma^{(n)} I^n \quad (1)$$

where  $I$  is the photon flux ( $\text{cm}^{-2} \text{s}^{-1}$ ) and  $\sigma^{(n)}$  is the  $n^{\text{th}}$  order absorption cross section ( $\text{cm}^{2n} \text{s}^{-n-1}$ ). For example, Eq. (1) is applied to the two-photon

excitation of the  $6p^2D_{2\frac{1}{2}}^0$  state in iodine (designated as state 2) from the ground state (state 0). It is also used to describe the rate of the production (state 3) from the excited state. The low-lying  $5p^52P_{\frac{1}{2}}^0$  state of iodine is not involved in the process. For small ionization efficiencies, the concentration of ground state atoms is constant and the rate equations for the time-dependent densities  $N_2$  and  $N_3$  are:

$$\frac{dN_2}{dt} = \sigma^{(2)} I^2 N_0 - (\sigma^{(1)} I + \gamma) N_2 \quad (2)$$

$$\frac{dN_3}{dt} = \sigma^{(1)} I N_2 \quad (3)$$

where  $\gamma$  is the probability per unit time of nonradiative relaxation of the excited state. Integrating Eq(2) yields:

$$N_2(t) = \frac{N_0 \sigma^{(2)} I^2}{\sigma^{(1)} I + \gamma} [1 - \exp\{- (\sigma^{(1)} I + \gamma) t\}] \quad (4)$$

By inserting Eq(4) into Eq(3) and integrating, the ionization rate can be obtained. However, for the laser intensities used in the present experiments the argument of the exponential term in Eq(4) is large, so the population of state 2 builds up rapidly and remains constant during most of the pulse. In this case, the ionization efficiency, defined as the ratio of the number of ions produced during the pulse to the number of ground state atoms initially in the interaction volume, is given by:

$$\eta_{I^+} = \frac{N_3(\tau)}{N_0} = \frac{\sigma^{(2)} \sigma^{(1)} I^3 \tau}{\sigma^{(1)} I + \gamma} \quad (5)$$

where  $\tau$  is the duration of the laser pulse. For high laser power

( $I = 3 \times 10^{28} \text{ cm}^{-2} \text{ s}^{-1}$ ),  $\sigma^{(1)} I \gg \gamma$  and Eq(5) reduces to:

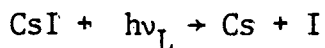
$$n_{I^+} = \sigma^{(2)} I^2 \tau \quad (6)$$

Using the measured ionization efficiency at  $3047 \text{ \AA}$  (Fig. 2) and  $\tau = 5 \text{ ns}$  gives  $\sigma^{(2)} = 4 \times 10^{-50} \text{ cm}^4 \text{ s}$ .

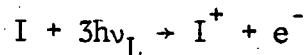
At low laser powers ( $I \approx 10^{27} \text{ cm}^{-2} \text{ s}^{-1}$ ),  $\gamma$  in Eq(5) becomes comparable to  $\sigma^{(1)} I$  and  $n_{I^+}$  approaches a cubic dependence on photon flux. This behavior was observed experimentally.

### B. Cesium Iodide Dissociative Ionization

The locations of the  $I^+$  peaks in the spectra obtained from laser irradiation of the CsI molecular beam are identical to those for atomic iodine. This observation suggests that the photons first dissociate CsI to produce neutral iodine, which is then ionized by the same three-photon process that was observed with the atomic iodine beam. This process is represented by:



where  $h\nu_L$  is the energy of the photon. This step is followed by:



The magnitudes of the ionization efficiencies of  $I^+$  from CsI are 10 - 13% of the efficiencies of producing  $I^+$  from I. The CsI dissociation probability  $\eta_D$ , which is the first step of the above mechanism, is thus equal to 0.13 at  $3000 \text{ \AA}$  and 0.1 at  $2800 \text{ \AA}$ .

C. Detection of Atomic Iodine in the Presence of Cesium Iodide

In analyzing a vapor mixture containing CsI and I, proper choice of laser wavelength can yield optimum response for the desired species. For detection of CsI, measurement of the number of  $\text{CsI}^+$  ions produced per pulse at a wavelength of  $2813 \text{ \AA}$  ( $N_{\text{CsI}^+}^{2813}$ ) can be combined with the ionization efficiency  $\eta_{\text{CsI}^+}^{2831}$  from Fig. 5 (corrected for laser intensity if necessary) to give the density of CsI molecules in the ionizer ( $n_{\text{CsI}}$ ):

$$n_{\text{CsI}} = \frac{\left(1 + \eta_{\text{D}}^{2813}\right) N_{\text{CsI}^+}^{2813}}{\eta_{\text{CsI}^+}^{2813} V} \quad (7)$$

where  $V$  is the laser-neutral beam interaction volume and  $\eta_{\text{D}}^{2813}$  is the fraction of CsI dissociated to Cs and I by the laser photons.

At  $3047 \text{ \AA}$ , iodine ionization is maximum, but the  $\text{I}^+$  contribution from CsI present must be subtracted from the total number of  $\text{I}^+$  ions produced per pulse ( $N_{\text{I}^+}^{3047}$ ). The number density of iodine atoms in the ionizer is:

$$n_{\text{I}} = \frac{N_{\text{I}^+}^{3047}}{\eta_{\text{I}^+}^{3047} V} - \eta_{\text{D}}^{3047} n_{\text{CsI}} \quad (8)$$

where  $\eta_{\text{I}^+}^{3047}$  is the ionization efficiency of atomic iodine by  $3047 \text{ \AA}$  photons (Fig. 2) and  $\eta_{\text{D}}^{3047}$  is the CsI dissociation probability at the same wavelength.

When combined with mass analysis, multiphoton ionization has the potential of providing a more highly selective means than electron impact ionization for detecting iodine atoms and cesium iodide in a mixture of these two vapors. A wavelength accessible to commercial pulse lasers ( $2813 \text{ \AA}$ ) ionizes CsI to produce

$\text{CsI}^+$  with reasonable efficiency. Iodine atoms can be detected in a mixture with a CsI/I ratio as large as  $\sim 10$  by operating at a wavelength of  $3047 \text{ \AA}$ . At wavelengths sufficiently long to avoid CsI dissociation, the selectivity should be much larger. The dissociation energy of CsI is  $3.57 \text{ eV}$ (9), so it is in principle possible to suppress CsI dissociation entirely yet still reach the first allowed excited state of atomic iodine by 2-photon absorption by using laser wavelengths between  $3475$  and  $3660 \text{ \AA}$ . However, because of the low repetition rate of the laser ( $10 \text{ Hz}$ ) and the short pulse time ( $5 \text{ ns}$ ), the duty factor is  $< 10^{-7}$ . This compares unfavorably to the 100% utilization factor of electron bombardment. In addition, the volume of the focused laser beam in the ionizer region of the mass spectrometer is considerably smaller than the volume of the electrons emitted from the filament of a conventional mass spectrometer ionizer. Defocusing the laser beam to increase the interaction volume decreases the photon flux. Because of the nonlinear dependence of the excitation cross section on this variable, defocusing the beam will result in poorer performance.

Consequently, the inherently higher selectivity of MPI cannot overcome the very low sensitivity characteristic of current commercial pulsed lasers. Application of the new techniques and the higher power lasers under development for Laser Isotope Separation (LIS) may improve this situation in the future. For detection of atomic iodine, development of a laser capable of producing photons with the energy of the first allowed state ( $1830 \text{ \AA}$ ) would result in a very much larger excitation cross section than is currently attainable with the two-photon process.

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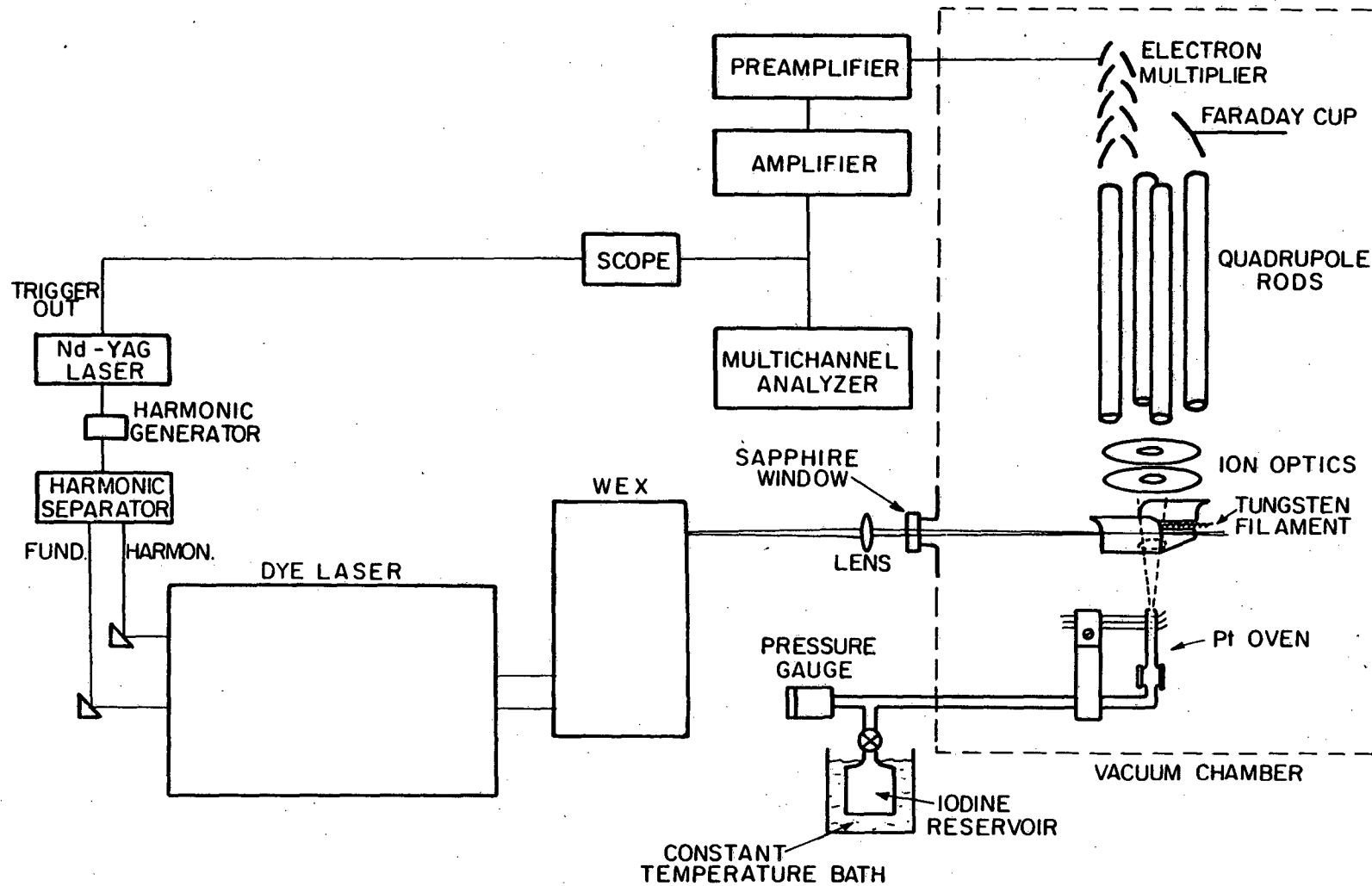
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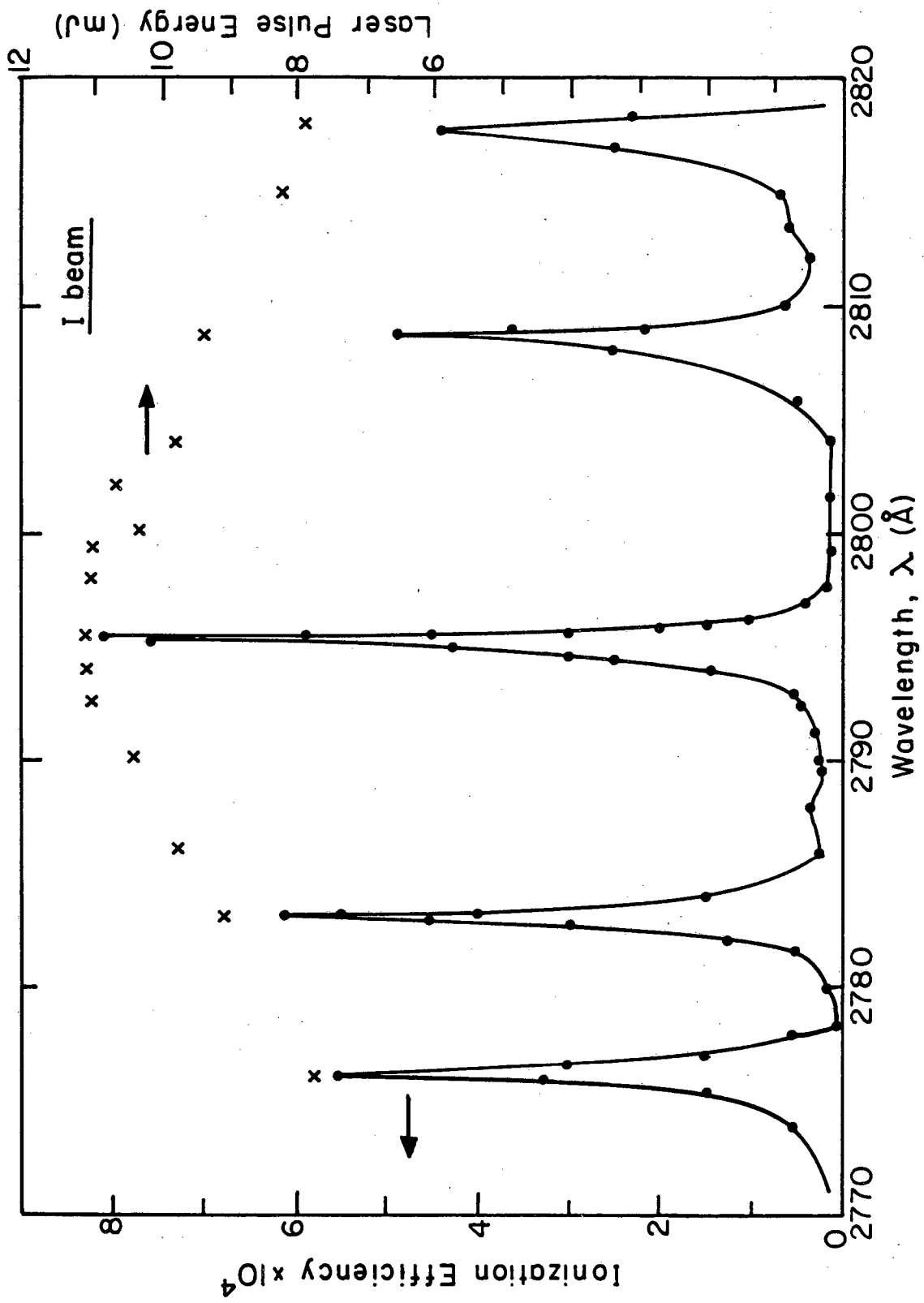
## Figure Captions

1. Apparatus used for laser ionization mass spectrometry of I and CsI.
2. MPI efficiency spectrum of iodine atom around  $2800 \text{ \AA}$  together with the wavelength dependence of the laser pulse energy.
3. MPI efficiency spectrum of iodine atom in the vicinity of  $3000 \text{ \AA}$  together with the wavelength dependence of the laser pulse energy.
4. Ionization efficiencies of  $\text{I}^+$ ,  $\text{Cs}^+$  and  $\text{CsI}^+$  from neutral CsI beam around  $2800 \text{ \AA}$ .
5. Ionization efficiencies of  $\text{I}^+$ ,  $\text{Cs}^+$  and  $\text{CsI}^+$  from neutral CsI beam around  $3000 \text{ \AA}$ .



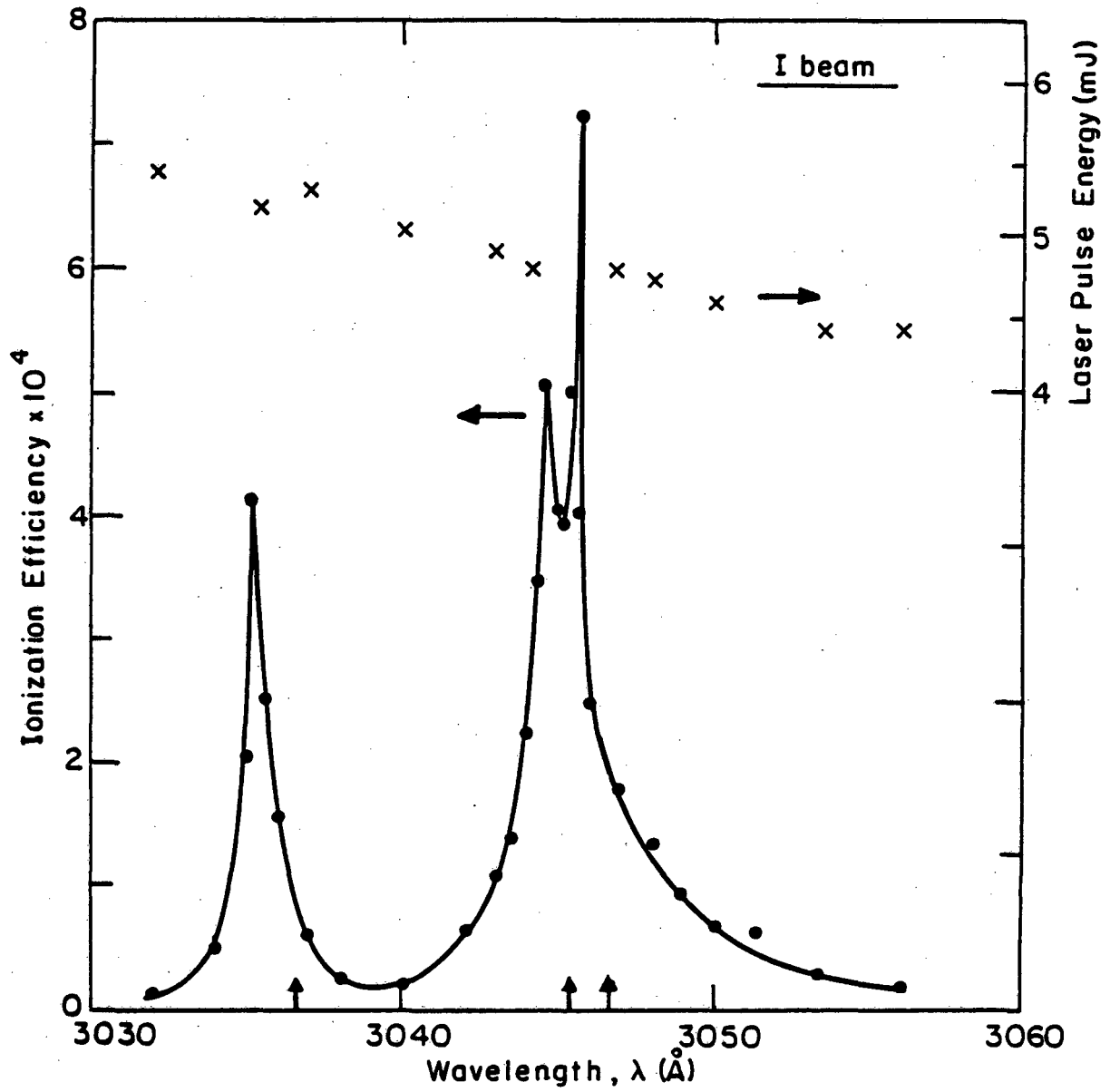
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Figure 1



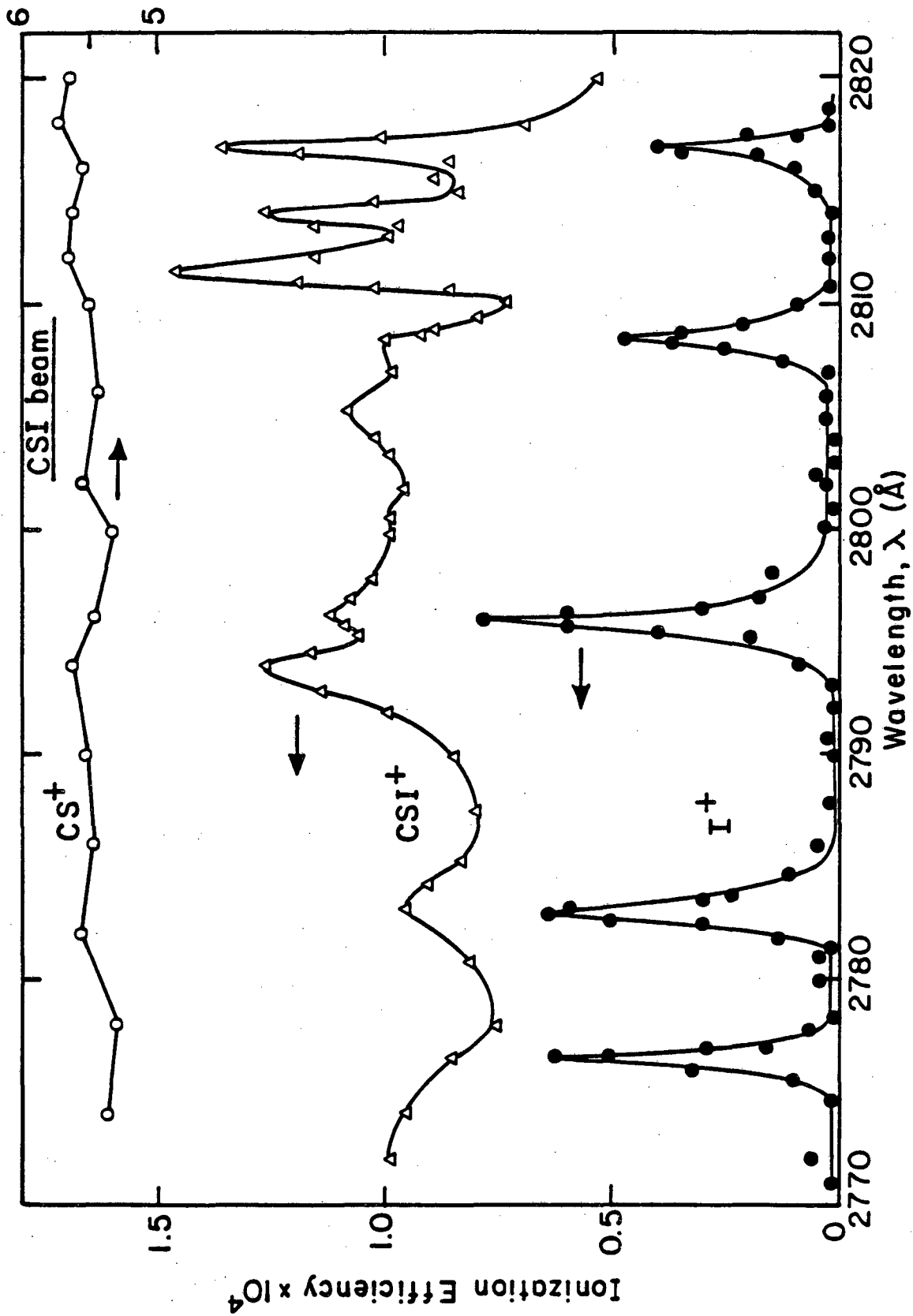
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Figure 2



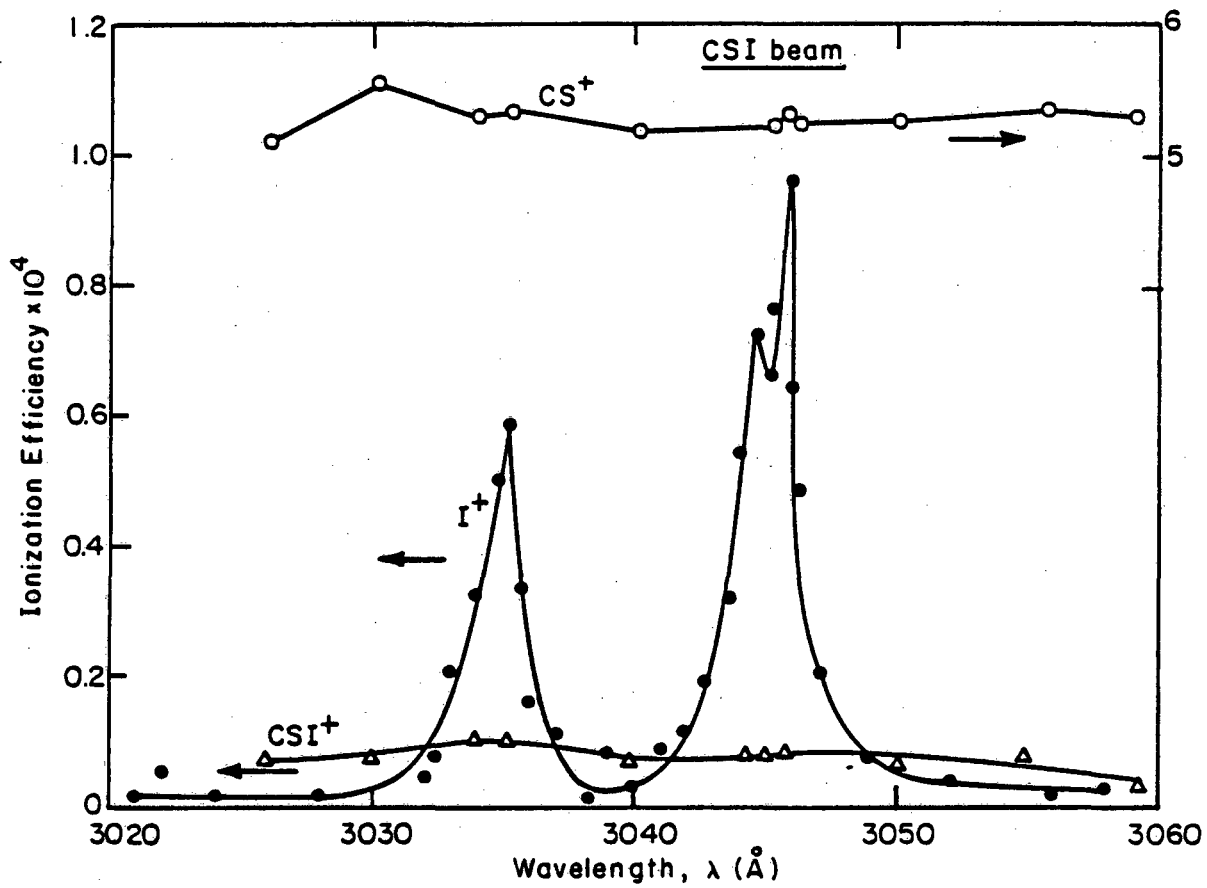
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Figure 3.



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Figure 4.



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Figure 5.

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