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Ion–to–neutral-atom measurements within an ablation plasma through laser selective-excitation spectroscopy

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A direct measurement of the ion–to–neutral-atom density ratio has been made in a rapidly expanding ablation plasma by means of laser selective-excitation spectroscopy. Evidence of an ionization freeze out at a degree of ionization of about 0.1% is presented.

INTRODUCTION

Laser selective-excitation spectroscopy (often referred to as laser saturation spectroscopy in the literature) involves momentarily locking the population of two atomic levels in the ratio of their degeneracies by an intense pulse of laser radiation, as first suggested by Measures.[1-3] The subsequent burst of *intensified spontaneous emission* from the overpopulated level represents a spectroscopic signal that is both spatially and temporally resolved. This powerful diagnostic technique has been used in a wide range of applications, that include (i) atomic lifetime measurements,[3-6] (ii) trace element analysis,[7,8] (iii) single-atom detection,[9-12] (iv) combustion and flame studies,[13-16] (v) neutral-hydrogen measurements in Tokamaks,[17,18] and (vi) fusion-plasma–impurity diagnostics.[19,20] A broad review of time-resolved laser-fluorescence spectroscopy has been written by Gauthier and Delpeck.[21]

Laser ablation of a solid is central to many diverse areas of endeavour including laser fusion,[22] x-ray–laser development,[23-26] trace-element analysis,[7,8,27] ion-beam generation,[28] and laser sputtering.[29] In addition, some interest has recently been shown in using laser vaporization of thin metal films for chemical kinetic studies.[29,30] Although there have been several investigations of the ablated material, some concerned with the electrons and ions,[31,32] others with the neutrals,[33,34] these measurements were either spatially or temporally integrated.

In the present paper we demonstrate that laser selective-excitation spectroscopy can provide a direct means of evaluating, with spatial and temporal resolution, the density ratio of two consecutive stages of ionization in a rapidly expanding ablation plasma. This diagnostic approach uses two short pulse, appropriately tuned lasers to produce a burst of *intensified spontaneous emission* (ISE) on one resonance line from each of the two stages of ionization of the species of interest.

THEORETICAL BASIS OF MEASUREMENTS

In accordance with the basic ideas of *selective-excitation spectroscopy*[1] the resonance–to–ground-level population ratio, for an ensemble of atoms excited by a steplike pulse of laser radiation tuned to the resonance transition, approaches the corresponding degeneracy ratio (equivalent to an effective infinite-temperature distribution) once the rate of stimulated emission plus absorption dominates the decay rate of the resonance level (in the absence of laser radiation). This requirement for *saturation of the transition* can be expressed in the form

$$(1+g)R_{21} \gg 1/\tau_2 , \tag{1}$$

where the rate of stimulated emission

$$R_{21} = B_{21} \int I^{l}(\nu)\mathfrak{L}_{21}(\nu)d\nu/4\pi , \tag{2}$$

$I^{l}(\nu)$ is the laser spectral irradiance, $\mathfrak{L}_{21}(\nu)$ is the resonance transition profile function, B_{21} is the Milne stimulated emission coefficient for the resonance transition, g is the ratio of the resonance to ground level degeneracies, and τ_2 is the resonance level lifetime in the absence of laser radiation.

In the case of broad-band laser radiation, this criterion for saturation can be expressed in the form

$$I^{l}(\nu) \gg I_s , \tag{3}$$

where the *saturated spectral irradiance*

$$I_s = \frac{8\pi h\nu^3}{c^2(1+g)}\left(\frac{\tau_2^{\mathrm{rad}}}{\tau_2}\right). \tag{4}$$

Here, h is Planck's constant, ν is the laser (i.e., resonance transition) frequency, c is the velocity of light, and τ_2^{rad} is the radiative lifetime of the resonance transition.

For a steplike laser pulse the resonance–to–ground-level population ratio N_2/N_1 approaches the degeneracy ratio g with an exponential time constant[1]

$$\tau_s = [(1+g)R_{21}]^{-1}. \tag{5}$$

Consequently, saturation is only achieved if the laser pulse duration $\tau^l \gg \tau_s$. For an experimental broad-band fast-rising laser pulse, saturation can be expected if: (i) the half-maximum duration of the laser pulse $\tau^l_{1/2} \gg \tau^p_s$, where

$$\tau^p_s = [(1+g)R^p_{21}]^{-1} \tag{6}$$

and R^p_{21} is the peak stimulated emission rate; and (ii) the peak laser irradiance $I^l_p \gg I_s \Delta\nu^l$, where $\Delta\nu^l$ is the laser bandwidth. Saturation of the resonance transition implies that $N_2 = GN_0$, where $G \equiv g/(1+g)$ and N_0 is the original (prior to laser irradiation) ground-level atom density, provided the laser pulse duration does not exceed the time for collisional excitation or multiphoton ionization of the resonance population. Recent theoretical[35] and experimental work[36] has clearly demonstrated that laser saturation of a resonance transition for an extended period can lead to appreciable perturbation (ionization) of the laser pumped species.

Under conditions of momentary laser saturation of an atomic resonance transition the peak intensified spontaneous-emission signal is directly proportional to the ground-state population of the laser irradiation N_0, viz.,

$$S_p = GN_0A_{21}V\frac{\Delta\Omega}{4\pi}D, \tag{7}$$

where S_p represents the peak in the ISE signal obtained from the photodetector, A_{21} represents the Einstein transition probability of the observed transition, V represents the volume of excitation that is viewed by the receiving optics of the photodetector, $\Delta\Omega$ represents the acceptance solid angle of the receiving optics, and D represents the photodetector and receiving optics spectral sensitivity factor. This includes factors such as the spectral transmission factor for the receiving optics and monochromator, the photocathode quantum efficiency at the wavelength of the observed ISE, and the electronic gain of the dynode chain of the photomultiplier.

When two lasers are used to momentarily saturate, a resonance transition in the first ionized state (II) and one in the neutral atom (I) of a given species, the corresponding ISE peak signal ratio

$$\frac{S^{II}_p}{S^I_p} = \frac{G^{II}N^{II}_0A^{II}_{21}D^{II}}{G^IN^I_0A^I_{21}D^I} \tag{8}$$

can be seen to be directly proportional to the ratio of the ion to the neutral density ratio of the species of interest. The degree of ionization of the species $\alpha \simeq N^{II}_0/(N^I_0 + N_e)$, but for $\alpha \lesssim 1\%$ we can see that $\alpha \simeq N^{II}_0/N^I_0$. Equation (8) is valid provided the laser beams excite a common volume and that the receiver optics is common to both photodetectors. In general, the other quantities on the right-hand side of Eq. (8) can be calculated from knowledge of the transitions or evaluated by calibration, providing radiation trapping is negligible for both ISE signals.

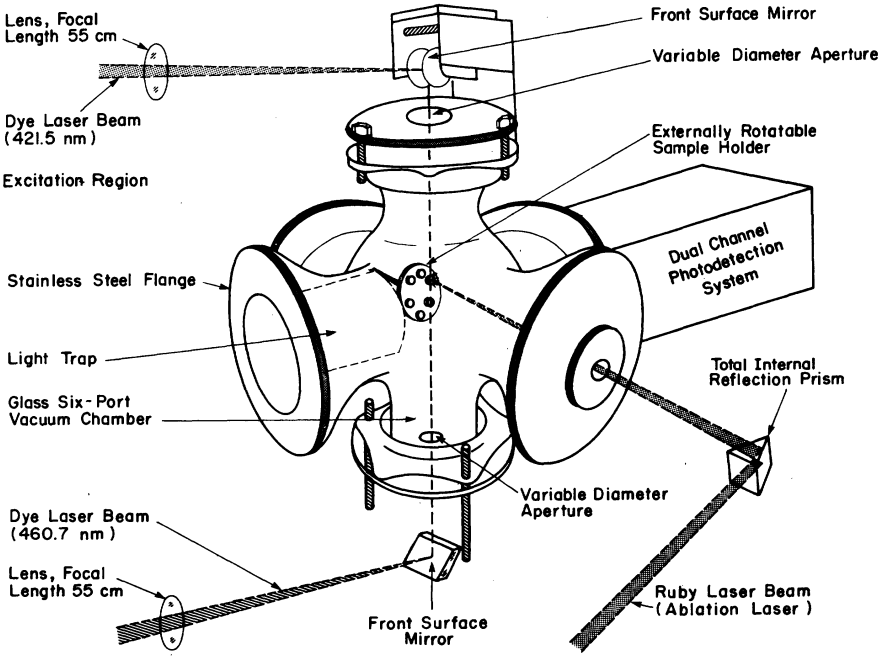

FIG. 1. Schematic view of laser ablation chamber.

EXPERIMENTAL FACILITY AND MEASUREMENTS

Our facility for undertaking these measurements comprise two nitrogen-laser-pumped dye lasers of the Hansch design[37] (excluding the etalon), a dual-wavelength photodetection system, and a low-pressure ablation chamber that has six optical ports and a rotatable multisample target (see Fig. 1) that allows us to change the target during an experiment without breaking the system's vacuum. A Q-switched ruby laser is used to create the ablation plasma. An RCA 8575 PMT and a SPEX 1700 monochromator are used in one channel, while an RCA 4526 PMT and a Jobin-Yvon H20 monochromator are used in the other channel. The background pressure in the chamber during the experiments was less than 10^{-4} torr.

Strontium was selected for this work since both the neutral and singly ionized form possesses resonance line wavelengths that conveniently fell within the operating range of our dye lasers. An example of the two intensified spontaneous emission signals generated about 1 cm out from the target surface and about 1 μsec from the moment of ablation is presented as Fig. 2. The upper trace corresponds to the ISE signal from the strontium atoms at 460.7 nm corresponding to

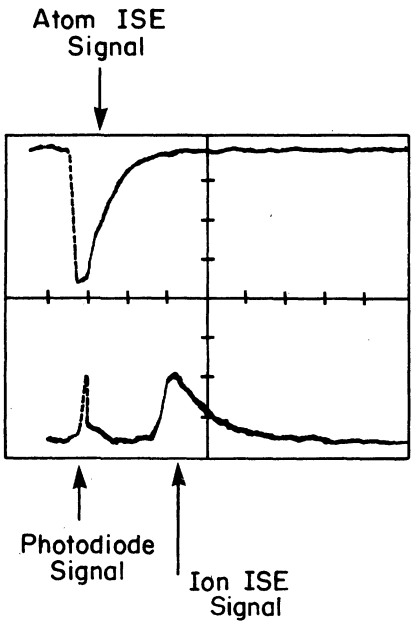

FIG. 2. Laser-intensified spontaneous-emission signals arising from an ablation plasma (1.2 μsec after ablation). The upper trace corresponds to the ISE signal from strontium atoms (at 460.7 nm) while the lower trace corresponds to the ISE signal from strontium ions (at 421.6 nm). The first pulse on the lower trace arises from a photodiode that monitors one of the dye lasers. Time scales are 20 nsec/division.

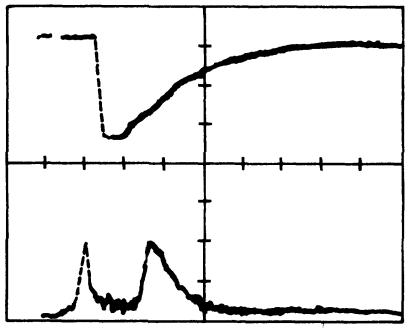

FIG. 3. Laser-intensified spontaneous-emission signals arising from an ablation plasma (1.2 μsec after ablation). The upper trace corresponds to the ISE signal from strontium atoms (at 460.7 nm) while the lower trace corresponds to the ISE signal from strontium ions (at 421.6 nm). The first pulse on the lower trace arises from a photodiode that monitors one of the dye lasers. Time scales are 20 nsec/division. N.B. The longer decay of the atom ISE signal relative to Fig. 2 arises from radiation trapping as density of strontium is higher in this experiment.

Sr I ($^1P_1 - {}^1S_0$) while the lower trace corresponds to the ISE signal from the strontium ions at 421.6 nm corresponding to Sr II ($^2P_{1/2} - {}^2S_{1/2}$). The first pulse (not clearly seen) on the lower trace arises from a photodiode that monitors one of the dye lasers.

In our preliminary experiments radiation trapping of the atom ISE signal was quite apparent since the radiative lifetime of the $^1P_1$ level of Sr I was known[38,39] to be about 5 nsec which was close to an order of magnitude smaller than the observed decay time for the 460.7-nm ISE signal as seen in Fig. 3. In order to eliminate the problem of radiation trapping, the strontium doping of the target material was reduced from 10% to below 1%. This had the unfortunate effect of also reducing the already weak ion ISE signal. To compensate for this the diameter of the 421.5-nm laser beam was increased from 0.25 to 0.8 mm, an effective increase in the excitation volume of close to a factor of 10. (The PMT used on the ion ISE signal was also changed from a degraded RCA 31034 to a new RCA 8575.) A comparison of Fig. 3 with Fig. 2 clearly reveals the elimination of radiation trapping on the atom 460.7-nm ISE signal in the latter work (Fig. 2). The residual difference between the observed decay time and the known radiative lifetime can be accounted for in terms of the finite duration of the laser pulse (about 5 nsec) and the combined temporal response time of the RCA 4526 PMT and the Tektronix 8744 oscilloscope.

The temporal variation in the degree of ionization of the strontium in the ablation plasma (at

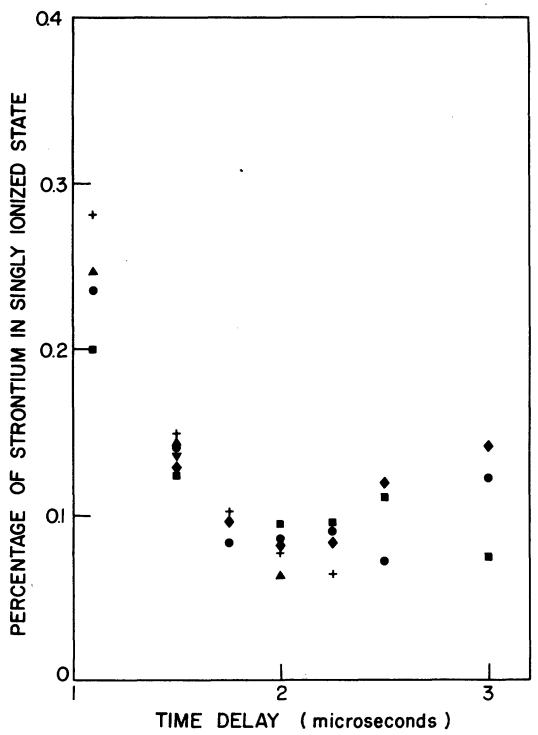

FIG. 4. The percentage of singly ionized strontium (to neutral strontium) as a function of time from the moment of ablation and at about 1 cm from the target as evaluated from the ratio of peak ISE signals from SR II and Sr I.

about 1 cm from the target surface) as determined from the ion to neutral ISE signal ratio is presented as Fig. 4. The lower limit of the time scale (about 1 μsec) was determined by the fixed delay in firing the nitrogen laser with respect to a photodiode signal from the ruby laser pulse. The upper limit was given by the weakness of the ion ISE signal. The relationship between the ISE peak signal ratio S_p^{II}/S_p^{I} and the ion to neutral density ratio (prior to laser irradiation) is given in our experiments by the expression

$$\frac{N_0^{II}}{N_0^{I}} = 2.3\times10^{-3}\frac{S_p^{II}}{S_p^{I}} . \tag{9}$$

In the case of our experiments, the saturated spectral irradiance equation (4) is estimated to be about 10^{-9} W cm^{-2} Hz^{-1} for each of the transitions (assuming negligible collision quenching), while the laser bandwidth is close to 7×10^{10} Hz. Consequently, saturation requires that the peak laser irradiance greatly exceeds 70 W cm^{-2}. Indeed, since the duration of the laser pulses was only 5 nsec, we would expect that a peak laser irradiance of closer to 10^3 W cm^{-2} is probably required to ensure that saturation is achieved within the period of laser excitation.

Unfortunately, the dye-laser power available to us was limited (by the output of the N_2 laser) and it was found that when the ion-dye-laser area was increased it led to only marginal saturation. The consequences of this were that the ion ISE signal had a stronger dependence on the laser irradiance than it would if true saturation occurred. Thus not only did the ion ISE signal vary as a result of the shot-to-shot irreproducibility of the dye laser, it was also vulnerable to some extent to the further shot-to-shot variation associated with attenuation of the dye-laser pulse in propagating through the ablation plasma. These effects contributed to the spread in the data presented in Fig. 4. An additional source of shot-to-shot variation was structure in the expanding plasma.

Previous work on this facility[7] has revealed that laser scattering from ablation generated particulates should not constitute a source of signal in these experiments due to the judicious choice of the space-time window of observation. It is quite clear that if a more powerful N_2 laser were available and a few other improvements made on our facility (such as better collection optics and better photomultipliers) substantial improvements in accuracy could be achieved. Nevertheless, it is apparent from our measurements that *ionization freeze-out*[31] occurs in our system at about 0.1% ionization in strontium. This represents the first such measurement of its kind and constitutes a reasonable *proof of principle* that laser selective-excitation spectroscopy can be applied to such transient ionization measurements. If the more powerful N_2 laser could also be fired closer in time to the moment of ablation a more comprehensive time history should be attainable.

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