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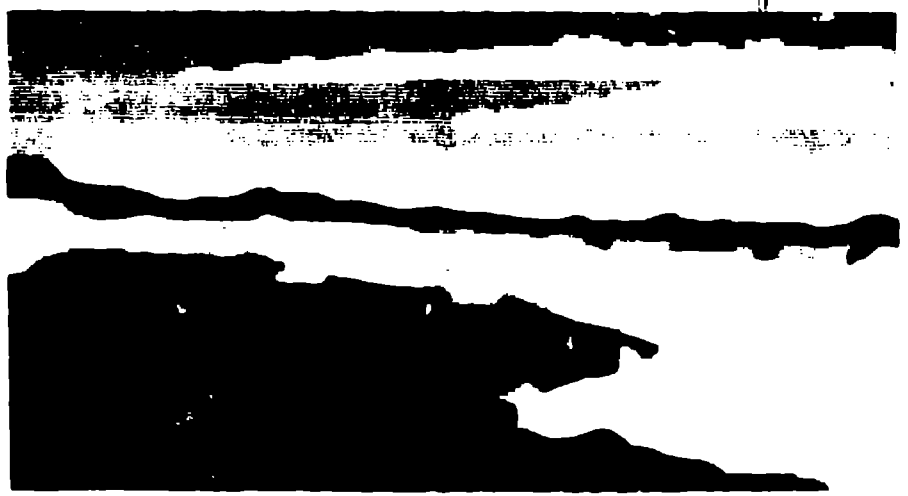
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HOOK SPECTROSCOPY AS AN ATOMIC NUMBER DENSITY DIAGNOSTIC APPLIED TO LASER-ABLATED COPPER PLASMAS

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Abstract

Hook spectroscopy has been used to determine the absolute number density of ground state copper atoms in laser-ablated plasma plumes. An ablation laser power flux of $\sim 1.5 \text{ GW/cm}^2$ is applied to a solid copper target in a background gas, producing a plasma plume suitable for studying homogeneous copper vapor condensation. Density is measured at post-ablation time delays ranging from $10 \mu\text{s}$ to 3 ms with 25 torr of argon as the background gas. Planar laser-induced fluorescence (PLIF) images containing relative density information are used in conjunction with the hook spectra to resolve spatially the absolute density within the plume. Copper atom densities thus measured ranged from $1.9 \times 10^{15} \text{ cm}^{-3}$ at a delay of $10 \mu\text{s}$ to $2.7 \times 10^{13} \text{ cm}^{-3}$ at 3 ms delay in 25 torr of argon. The decrease in density is due to the condensation of copper vapor to form fine particulate. As a combustion diagnostic, the hook method may prove extremely useful for the determination of metal impurity density in coal fired flames as well as a single - shot OH density and temperature diagnostic.

Introduction

The purpose of this work is to determine the ground state copper atom number density in dense, condensing laser-ablated copper plasma plumes. Absolute number density is a key quantity in the study of condensation reactions of gas phase copper. The ultimate goal is to determine values for the condensation reaction rate coefficients which govern copper cluster growth.

The copper plasma plumes studied are produced via laser ablation of a solid copper target in an inert backing gas at a pressure of 25 torr. In low density plumes a technique such as direct absorption is useful for determining absolute number density. In the low density regime, copper line transitions are predominantly Doppler broadened and one can calculate a line center absorption coefficient.¹ However, at background gas pressures above 10-25 torr, pressure broadening of the transition begins to distort the Gaussian line shape of the Doppler broadened profile. In addition, the large copper atom density at these pressures requires a high laser fluence to overcome absorption of the beam. This causes additional distortion of the Gaussian line shape due to power broadening. Direct absorption measurements are not easily analyzed because of the resultant Voigt line shape,² thus a different number density diagnostic is required for dense plasma plumes.

Hook spectroscopy is a line-of-sight interferometric diagnostic technique which utilizes the anomalous dispersion in the wings of an electronic line transition, and therefore is not significantly affected by various line broadening mechanisms.³ The diagnostic is made even more powerful if a broad-band pulsed laser is used to illuminate the interferometer; the precise temporal resolution achieved by a pulsed laser allows one to follow the decay rates of copper atom density in the plume. Additionally, limited one-dimensional spatial resolution is achieved directly with the hook technique if the optics are properly designed.⁴

The experiments described here include measurement of the time dependent absolute ground state copper atom density in argon background gas at a nominal pressure of 25 torr. The hook method is a line-of-sight diagnostic which results in absolute densities, but they are averaged over the plume diameter. For uniform (or nearly uniform) density distributions, the average density is very close to the peak density. However, this is the case with only a fraction of our data. Consequently, it is desirable to determine absolute peak density. To accomplish this, the density distribution along the hook method probe beam path must be determined. A PLIF diagnostic is applied as described in Ref. 5 to reveal the density distribution. The average relative density from PLIF images is related to the average absolute density determined from the hook spectrum, and a constant of proportionality is calculated. This constant can then be applied to any point in the two-dimensional PLIF image to determine absolute density.

Hook spectroscopy makes use of the region of anomalous dispersion near electronic transitions in atoms. The hook experiment consists of a Mach-Zehnder interferometer used in conjunction with a high resolution stigmatic spectrometer. Broad band pulsed laser light is expanded, collimated and passed through the interferometer. In one arm of the interferometer is placed the gas sample of

interest, in this case the laser-ablated plasma plume. In the other arm compensating optics are placed to account for path length differences introduced by windows or other optics placed in the sample arm. The fringe pattern resulting from the recombined beams is imaged onto the slit of a spectrometer. The spectrally resolved fringe pattern at the exit plane of the spectrometer exposes the characteristic 'hooks' (see Figures 1 and 2).

The hooks form because the light passing through the plume experiences a wavelength dependent phase shift due to the anomalous dispersion near the absorption line. This variation is observable only after the fringe pattern has been spectrally resolved. The spectral separation of the hook normal points on either side of the line is directly related to the number density of atoms in the lower level of the electronic transition.

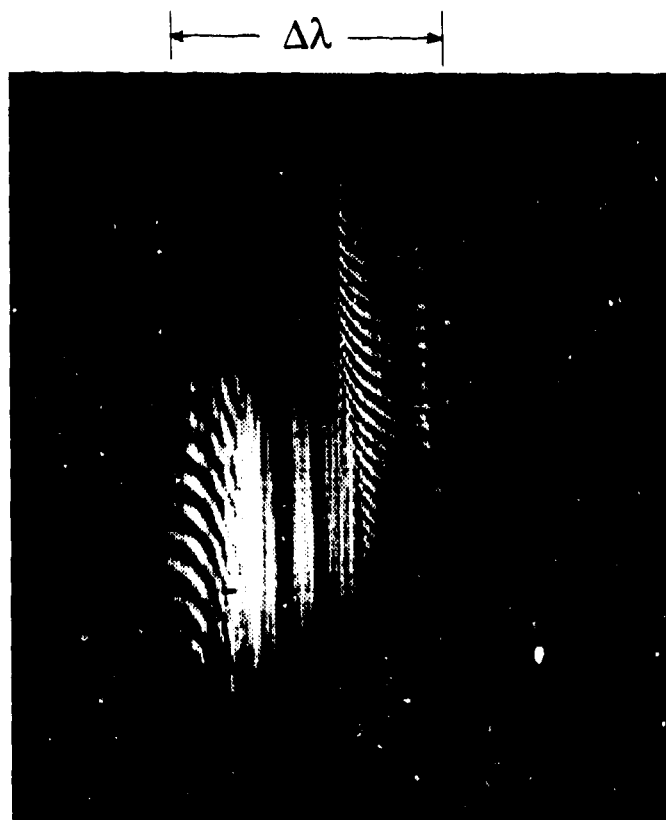


Figure 1. Copper atom hook spectrum taken at 100 μ s delay time in 25 torr of argon background gas. The large hook separation corresponds to a ground state copper density of $1.0 \times 10^{15} \text{ cm}^{-3}$.

Hook spectroscopy, or the dispersion method, has long been used for the determination of atomic oscillator strengths.⁶ If a sample of known density is used in the experiment, oscillator strength can be calculated from Eqn. 1. The current experiment is a variation of the original, and follows closely the experiments of Molander.³

Experiments

The copper atom transition examined here is the $2P_{3/2} - 2S_{1/2}$ which occurs at 324.754 nm. Figure 3 represents a portion of the energy level diagram for the copper atom. The experimental apparatus is represented in Figure 4. It consists of a Lambda Physik LPX 105i XeCl excimer pump laser (308 nm, 150 mJ per pulse, 15 ns duration) and a LPD 3002 dye laser operating on DCM laser dye and fitted with a frequency doubling crystal. The nominal bandwidth of the doubled dye laser output is 0.5 cm^{-1} . Because the width of the copper atom transition can be as much as 2 cm^{-1} at high background gas pressure, the dye laser has to be modified to produce output broad enough to encompass the entire line. This is achieved by blocking the initial pass of the nominally double passed oscillator beam, and removing the feedback spoiler. In the nominal configuration, the initial pass illuminates a majority of the dye laser grating and is responsible for narrowing the bandwidth. The second pass serves mainly to eliminate amplified spontaneous emission. With the initial pass blocked, the laser produces visible output at nominally 650 nm with a bandwidth of $4\text{-}5 \text{ cm}^{-1}$, and frequency doubled output with a bandwidth of approximately $8\text{-}10 \text{ cm}^{-1}$. The potassium dihydrogen phosphate (KDP) doubling crystal used is 2.5 cm thick and does not adequately phase match the entire bandwidth of the fundamental beam. With a thinner crystal the doubling process could be made much more efficient.

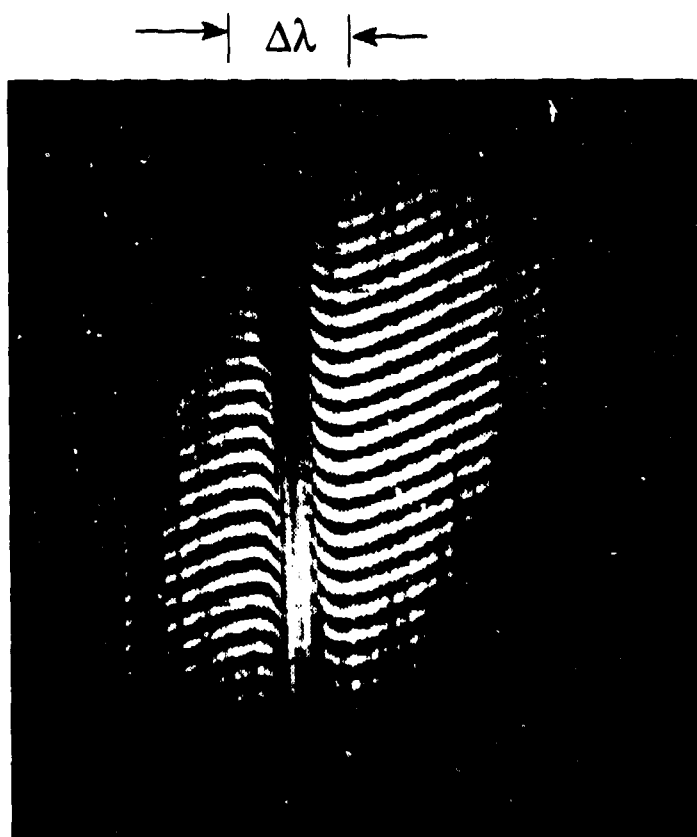


Figure 2. Copper atom hook spectrum taken at 1.5 ms delay time in 25 torr of argon background gas. The much smaller hook separation corresponds to a density of only $7.5 \times 10^{13} \text{ cm}^{-3}$.

The laser output is expanded with a Newtonian telescope to a diameter of ~8 mm, of which typically the central 4 mm is usable in the final interferograph. The Mach-Zehnder interferometer is fitted with dichroic mirrors (Acton, 99.5% reflectors at 45° for $\lambda=325$ nm) and beamsplitters (Acton, 50% at 45° for $\lambda=325$ nm) for ultraviolet operation, and is mounted on a graphite base plate for thermal and mechanical stability. Careful adjustment is made to the interferometer with no plasma plume in the test cell so that a sharp fringe pattern is produced at the exit. The interferometer output is focused by a cylindrical lens so that the collimated beam is imaged as a vertical line on the spectrometer entrance slit, thus preserving the limited spatial information in the beam. The spectrometer is a 1.25 m Spex with a 316 lines/mm echelle grating operated in 17th order. The cylindrical lens is chosen to f-number match the spectrometer in the horizontal dimension to maximize spectral separation. A CoHU CCD camera is mounted at the exit plane of the spectrometer to record the hook spectra. The CCD chip has 754 (horizontal) x 224 (vertical) active pixels, each measuring 11.5 x 24 μm . The resulting spectral resolution is 9.506×10^{-4} nm/pixel. Single shot hook spectra are obtained with a frame grabber (EPIX) board and analyzed with the associated software on an IBM 386 computer.

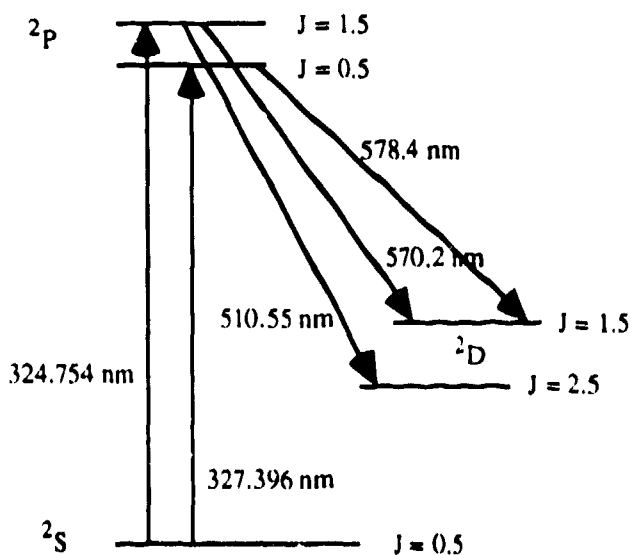


Figure 3. Partial energy level diagram for the copper atom. The dye laser probes the ultraviolet transition at 324.75 nm. The transition to the metastable $2D_{5/2}$ at 510.55 nm is monitored in PLIF experiments.

The ablation laser is a Lumonics EX-744 XeCl excimer laser (308 nm, 100 mJ per pulse, 15 ns pulse duration. Not shown in Fig. 4). The output is focused by a 25 cm lens onto a solid copper target rotating within a vacuum chamber. A slow flow of background gas is maintained to eliminate the buildup of copper particulate in the chamber. The flow is metered against the vacuum pump to maintain a pressure of 25 torr during experiments. The ablation beam is focused ~1 cm below the

target to diminish the interaction of the beam with newly ablated material. The resulting spot is approximately 0.08 x 0.05 cm resulting in a power flux of ~1.5 GW/cm².

The facility for the PLIF experiments is the same as that for the hook spectroscopy, except that the dye laser is operated in its nominal narrow band configuration, and the output is formed into a sheet rather than a collimated beam. There is no need for the interferometer/spectrometer arrangement in the PLIF experiment, so a gated Princeton Instruments CCD camera equipped with an appropriate interference filter is mounted at 90° to the probe beam. Fluorescence is detected at a wavelength of 510.55 nm and is due to the ²P_{3/2} - ²D_{5/2} transition. A complete description of the PLIF experiment can be found in Ref. 5.

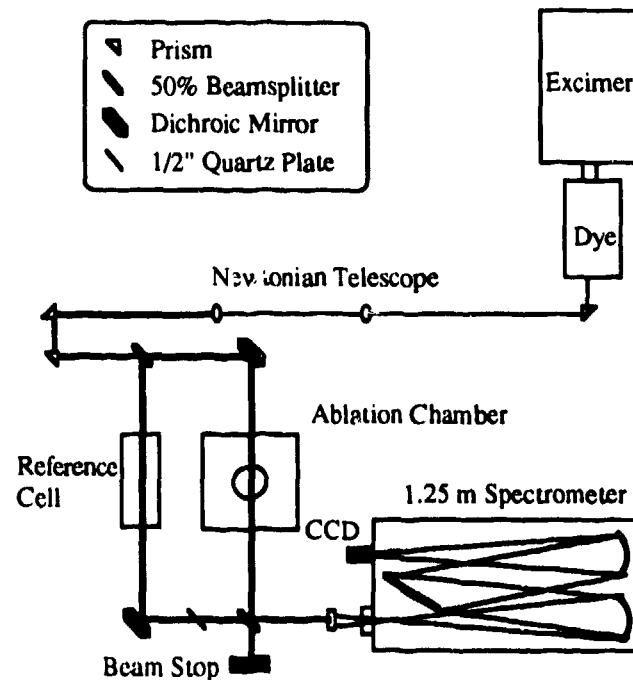


Figure 4. Hook spectroscopy apparatus (top view). The ablation laser (not shown) output enters vertically into the top of the ablation chamber.

Data Analysis

The data analysis consists of two major procedures. First the hook spectra are analyzed by determining the wavelength separation of the hook normal points on either side of the absorption line. The number of pixels separating the hooks is converted to wavelength, and then average absolute number density is calculated from:

$$\bar{N} = \frac{\pi K \Delta\lambda^2}{f L r_0 \lambda_0^3} \quad (1)$$

Here, $\Delta\lambda$ is the spectral separation of the hooks, f is the oscillator strength of the transition excited,

L is the path length of the sample, r_0 is the classical electron radius, λ_0 is the center wavelength of the excited transition, and K is the calibration constant for the interferometer. Equation 1 was derived by Marlow⁶ from the expression for anomalous dispersion. For the spectrum in Fig. 1, $K = 22218$. The oscillator strength for the $\lambda_0 = 324.754$ nm copper transition is 0.64. The ground state hyperfine splitting of 0.4 cm^{-1} in this line is not resolved in the hook spectra and is neglected. The classical electron radius is 2.818×10^{-15} meters. The beam path length, L, is determined from PLIF images and is taken as the plume diameter. This procedure is performed for three spectra taken at each time delay and the mean of the three *average* densities is taken as the final result. As an example, the spectrum shown in Figure 1 has hooks separated by 115 CCD pixels, which corresponds to 0.109 nm. At 100 μs the plume head is 10.7 mm in diameter, and Eqn. 1 gives the *average* density across the plume to be $8.7 \times 10^{14} \text{ cm}^{-3}$. Error analysis indicates that there is an 11% uncertainty in the calculated absolute density using Eqn. 1 when $\Delta\lambda$ is relatively large, and a 16% uncertainty when $\Delta\lambda$ is small.

The second part of the data analysis is to calculate absolute density and requires analysis of PLIF images of the plume. The average absolute number density resulting from the hook separation equation can also be expressed in terms of the integral over the plume diameter of the relative number density distribution, $N_r(l)$, along the probe beam path:

$$\bar{N} = \frac{C}{L} \int_0^L N_r(l) dl \quad (2)$$

Here L is the plume diameter, $N_r(l)$ is the relative density along the diameter, and C is the constant of proportionality. This integral is approximated from numerically integrated PLIF data which provides the relative densities, and the constant of proportionality is then calculated from:

$$C = \left[\frac{\frac{\pi K \Delta \lambda^2}{f L r_0 \lambda_0^3}}{\frac{1}{L} \sum_{n=1}^{n(L)} N_r(n)} \right] \quad (3)$$

Here n is the pixel index of PLIF data across the plume diameter. With the constant of proportionality, absolute copper atom density at any point in the two-dimensional PLIF image can be found from:

$$N(n,m) = C_0 N_r(n,m) \quad (4)$$

Results and Conclusion

The primary result of this work is the determination of copper density in laser-ablated plasma plumes as a function of the time delay following the ablation event. Hook spectra and PLIF images are presented along with reduced data.

A series of PLIF images of the plume taken at increasing time delays in 25 torr of argon

background gas is shown in Fig. 5; the scale on the right hand side is in centimeters. In the hook experiment the probe beam propagated through the plume approximately 0.65 cm above the solid copper target, which is represented by the thick lines near the bottoms of the images. Because initial density and temperature are generally not uniform within the plume, the condensation rates can be different for different test volumes within the plume. So in the study of condensation kinetics using PLIF images it is important to follow the density decay at a particular location within the plume. This assures that the same test volume of vapor is analyzed at each of the time delays studied. For the case represented by the PLIF images in Fig. 5, a small volume in the dome of the plume approximately 0.65 cm above the target was analyzed, which is why the hook probe beam was aligned to pass through this region as well.

Recall that the hook diagnostic results in the absolute density averaged along the probe beam path. In order to arrive at an analogous quantity from the PLIF images, the denominator of Eqn. 3 is calculated along a path 0.65 cm above the target surface. The results of this calculation are shown in Fig. 6 and compared to the relative density in a small volume near the dome center for time delays ranging from 10 μs to 3 ms in argon. This central volume is the one analyzed in the study of copper atom density decay and corresponds to the peak density along the path of the probe beam through the dome. Notice that the peak relative density is always higher than the average density across the path through the dome. This indicates that the copper vapor test volume with the highest initial density does not condense significantly faster than the remainder of the plume.

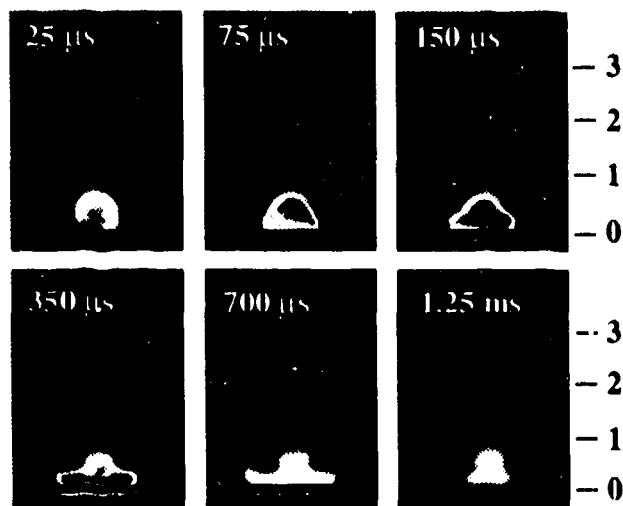


Figure 5. A series of copper atom PLIF images taken at increasing time delays in 25 torr of argon. All the images are normalized to the maximum signal level at 400 μs delay. The scale is in centimeters.

As mentioned above, the average relative density calculated from the PLIF images is analogous to the hook density result and should be proportional in value as indicated by Eqn. 3. A comparison of

these two density values is shown in Fig. 7 with the scale altered to arbitrary units so that the comparison is meaningful. Two items of importance are immediately clear from the figure. First is the outstanding match between the two curves over the majority of the time delays studied. This type of agreement between two such different diagnostic techniques is expected only under the most ideal experimental circumstances. Given that the two diagnostics were implemented over seven months apart indicates that the plume reproducibility is excellent, and that the hook probe beam and the PLIF test volume coincide quite well. It is also important to note from the figure the extremely poor match between the curves at delay times earlier than 250 μ s. It had been assumed that the increase in relative density in the PLIF images at early times was due to the relaxation of a highly nonequilibrium electronic state in the ablated copper atoms down to the ground state. But because the hook diagnostic also probes the ground state and yet results in a much higher initial density than does the PLIF diagnostic, it is clear that the original assumption is incorrect. Presumably the low density observed in the PLIF images at early times is due primarily to absorption of the fluorescence signal before it escapes the plume volume.

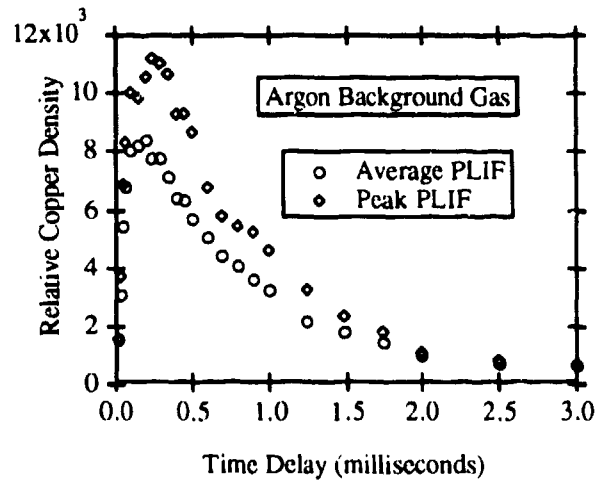


Figure 6. A plot of PLIF signal in 25 torr of argon vs. delay time for both a specific test volume (peak) and the average across the plume diameter. The PLIF signal is proportional to density for a given background gas and pressure.

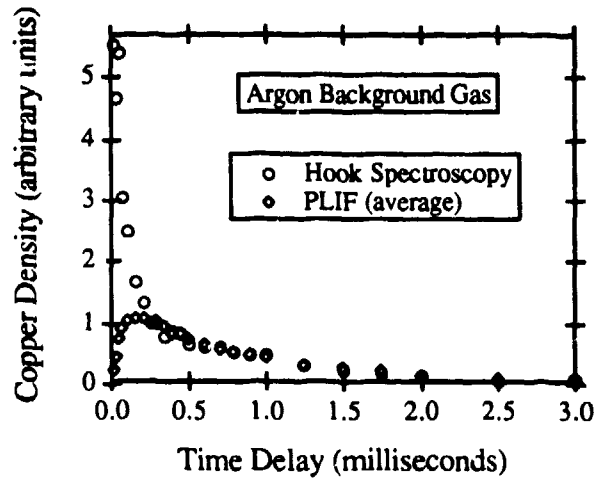


Figure 7. A plot of density from the hook diagnostic and average PLIF signal vs. delay time in 25 torr of argon. The curves are scaled so that they coincide over a majority of time delays. The proportionality constant for scaling PLIF signals comes from this plot.

The lower level of the transition monitored in the PLIF experiment is the metastable $^2D_{5/2}$. This level is deactivated to the ground state almost exclusively through collisions, and so may maintain a significant population for some time in the hot newly ablated plume. Chen and Erbert⁷ have measured the deactivation collision cross section for the $^2D_{5/2} - ^2S_{1/2}$ transition in the copper atom to be $4.8 \times 10^{-17} \text{ cm}^2$ for $\text{Cu}^* - \text{Cu}$ collisions. The cross section for $\text{Cu}^* - \text{Ar}$ collisions is four orders of magnitude smaller and does not significantly effect the overall deactivation rate, despite the much higher argon density. The deactivation rate equation is written:

$$\frac{-dn_m}{dt} = \sigma v n_m n_1 \quad (5)$$

where n_m is the population of the metastable state, σ is the deactivation collision cross section, v is the mean relative particle velocity, and n_1 is the population of the copper ground state. Solving this equation gives:

$$\ln \left[\frac{n_{mi}}{n_{mf}} \right] = \sigma v n_1 \Delta t \quad (6)$$

where n_{mi} and n_{mf} are the initial and final metastable populations, respectively, v and n_1 are assumed constant for simplicity, and Δt is the elapsed time. Taking n_1 to be $2 \times 10^{15} \text{ cm}^{-3}$ and the temperature to be 3000 K (v is a function of temperature), a tenfold decrease in the metastable population requires 170 μs . This approximation corresponds well with the observed delay time before the hook and PLIF diagnostics begin to result in the same average density. It will be shown that the absolute density used above is quite reasonable. There is no verification of the assumed temperature at a background gas pressure of 25 torr, but measurements made using a Doppler technique at 1 and 10 torr in both argon and helium⁵ support the assumption.

The results of the hook diagnostic in the 25 torr argon plume are shown in Fig. 8 in units of absolute density. The portion of the PLIF data set not corrupted by absorption is scaled with a constant of proportionality according to Eqns. 3 and 4 and plotted with the hook data. Again, because the hook diagnostic gives the average density across the plume diameter, and the PLIF curve is scaled from the peak density along the diameter, the hook curve lies below the scaled PLIF curve. The highest calculated absolute peak density (scaled from PLIF data) in this plume is $5.0 \times 10^{14} \text{ cm}^{-3}$, taken at 250 μs delay time. The highest average absolute density is $1.9 \times 10^{15} \text{ cm}^{-3}$, measured in the hook experiment at 10 μs delay time. It is very likely that the peak absolute density at 10 μs is somewhat higher than the average density, possibly $3 \times 10^{15} \text{ cm}^{-3}$ or higher, but due to the absorption of the PLIF signal at early time delays, it is not possible to determine the peak density precisely with this technique.

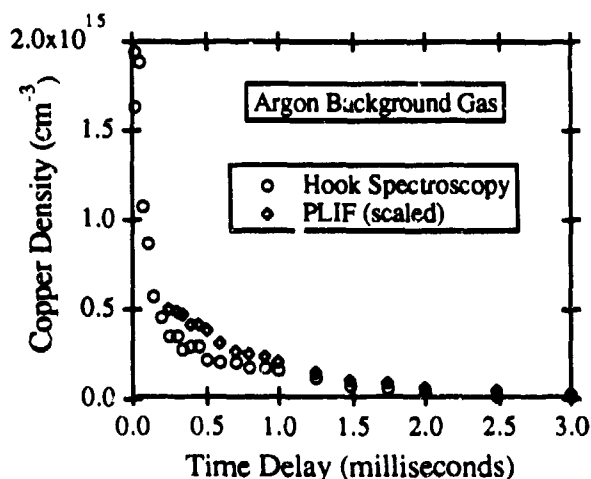


Figure 8. Average Cu density from Hook method show with peak density from scaled PLIF images in 25 torr of argon backing gas.

Earlier work using the hook spectroscopy to measure copper atom density in laser-ablated plasma plumes produced some preliminary results.⁸ The data in that work is not spatially resolved to any significant extent, nor is it used in conjunction with PLIF data. The expanded scope of the current experiments along with the improvements due to the integration of PLIF imaging provide some of the absolute densities needed for accurate empirical modeling of the condensation process.⁹ The scope of this work will be expanded even further to include background gas pressures of 1, 10, 50, and 100 torr. This should provide a nearly full set of quantitative information, and allow for the accurate determination of copper condensation rate coefficients from an ongoing modeling effort.⁹

Hook Spectroscopy as a Combustion Diagnostic

As a potential combustion diagnostic, hook spectroscopy has decided advantages over techniques such as LIF for the quantitative detection of flame constituents. First and foremost, hook

spectroscopy gives density directly. No approximations need be made to account for quenching or optical thickness, even at elevated pressures. In addition, non-fluorescent radicals such as CH_3 can be detected quantitatively with relative ease. This represents the holy grail for combustion diagnostics. There are two potential drawbacks of hook spectroscopy relative to LIF. First, LIF measurements can be spatially resolved along the laser beam propagation direction whereas hook spectroscopy integrates the signal across this dimension. This may or may not be a problem depending on the situation. If the distribution of species along the laser beam is known or if one desires only an average density, hook spectroscopy may be superior to LIF. Second, the hook method will be useful only for major species concentrations unless long path lengths are employed in contrast to LIF which can be used for trace species detection. A possible application of hook spectroscopy as a combustion diagnostic would be for the detection of impurity metals in coal fired flames. In particular, the hook method could be used to measure absolute sodium atom concentration in a coal furnace.

However, the hook method may have a much more profound effect in the field of combustion as a quantitative, single-shot OH density and temperature diagnostic with excellent temporal, and one-dimensional spatial resolution. Although hook spectroscopy has never been used for molecular systems, theoretically there is no reason to prevent such a diagnostic from working. Implemented as an OH diagnostic, hook spectroscopy would have the advantage of complete insensitivity to high optical density, quenching, and other line broadening mechanisms even in high pressure combustion applications such as automobile engines. We are currently setting up a demonstration experiment which will utilize a Raman-shifted KrF excimer laser (one Stokes in H_2 and one Stokes in HD) to produce broadband output at approximately 308 nm. The resulting interferogram will contain hooks from electronic transitions in the $Q_1(1) - Q_1(7)$ region. The major lines in this region are separated sufficiently ($\sim 10 \text{ cm}^{-1}$) to avoid significant overlap of hooks from different transitions. Satellite transitions will not be resolved, but can be taken into account via Honl - London factors. Calculations for an atmospheric pressure flame indicate that hook separations similar to those observed for the lower densities in the Cu atom work can be achieved with only a 2 cm path length (assuming $1 \times 10^{17} \text{ cm}^{-3}$ OH, 1700 K, an oscillator strength for the A - X (0,0) band of 0.002, and the appropriate Honl-London factors.) The only potential problem for molecular systems is insufficient dispersion in the monochromator to separate hooks from overlapping rotational lines. This problem can be defeated simply by utilizing a longer focal length monochromator. The technique should be extremely useful in real systems such as rocket nozzle exhaust or jet aircraft engines.

Acknowledgments

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