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TITLE: RIMS DIAGNOSTICS FOR LASER DESORPTION/LASER ABLATION

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RIMS Diagnostics for Laser Desorption, Laser Ablation

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Abstract. Laser desorption mass spectrometry is a useful method for interrogating materials and events at or near surfaces. Laser desorption ablation combined with Resonance Ionization Mass Spectrometry (RIMS) provides a powerful tool to obtain information on chemical composition and speciation and, in some cases, internal and translational energy distributions. The application of this technique to the interrogation of materials and interfaces is discussed for several systems, including the analysis of conventional analytical samples, and the study of optical damage events.

1. Introduction

RIMS is a powerful tool for elemental and isotopic analysis. The multistep laser photoionization process, when coupled with conventional mass analysis, can provide exceptional performance in detectivity, dynamic range, and discrimination against interfering species (Nogar et al 1985a, Fassett et al 1985). These properties can be used to great advantage both in the analysis of conventional materials (Bekov and Letokhov 1983) and in the interrogation of interfacial phenomena (Kimock et al 1983). In this report we will discuss the use of laser desorption/ablation in combination with RIMS analysis.

The motivations for this work are threefold. First, we desire to improve the effective duty cycle, relative to continuous sample evaporation, for the examination of routine analytical samples. Second, this method will allow the direct analysis of materials without extensive sample preparation. And third, we wish to study the mechanism of laser-material interactions, particularly optical damage, and characterize the desorption/ablation/damage process.

2. Experimental

The apparatus has been described previously (Nogar et al 1985b, Estler et al 1986), and will only be summarized here. Briefly, a Q-switched Nd:YAG laser equipped with beam-filling optics is used for desorption of a sample mounted on a manipulator in the source region of a time-of-flight mass spectrometer. Typical laser parameters include 10 nsec pulse length, 5 to 50 mJ pulses, 0.2 to 1 mm spot size at the sample, and 10 Hz repetition rate. After a variable time delay, the interrogation laser (XeCl excimer-pumped dye laser , typical parameters: ~12 nsec pulse, 1 mm diameter, 0.5 to 3 mJ, ~0.3 cm ^{1} bandwidth) is passed through the spalled plume. At a fixed time delay following the excimer trigger, ions are detected with a channel electron multiplier, and the signal processed with a gated integrator and standard analog signal processing electronics.

3. Results and Discussion

Two-photon excitation. In order to expedite diagnostics for our laser desorption ablation studies, we wished to minimize the complexity of the laser ionization process and associated hardware. We have therefore used single-color ionization processes at the fundamental output frequency of the interrogation dye laser. This, in turn, required n-photon excitation, n ·2, for moderate to high ionization potential elements. We have examined (Apel et al 1986) a number of atomic (and some molecular) systems ionizable via "2 - 1" processes. A list of observed transitions is shown in Table 1. For the atomic systems, the two-photon excitation typically saturated at ~2 mJ pulse, while the ionization step required somewhat higher energies.

TABLE 1
Observed Two-Photon Transitions

	Ground State		Excited State		Energy Difference[a]
Element	Configuration	Term	Configuration	Term	(cm ^{1})
Ca	($4s^2$)	$^1S_0$	($4s4d$)	$^1D_2$	37298
CaF		$X\ ^2\Sigma^{+}$		$F\ ^2\pi$	37550
Ta	($5d^36s^2$)	$^4F_{3/2}$	($5d^36s7s$)	J 3/2	44096
	($5d^36s^2$)	$^4F_{3/2}$	($5d^36s7s$)	$^4F_{3/2}$	43964

[a] T_0 is given for CaF.

Analytical Applications. The use of pulsed lasers with continuous sample evaporation can result in substantial loss of analyte because of the low effective duty cycle. For a probe laser beam diameter of 0.5 cm, and an atomic velocity of 5×10^4 cm sec, the rate of sample turnover in the beam volume is ~10^5 sec ^{1}. For a laser repetition rate of 10 sec ^{1}, the effective duty cycle is ~10 ^{4}. The use of lasers (or particle beams, Kimock et al 1984) to pulse desorb the sample can substantially improve this value. We have recently (Nogar et al 1985b) demonstrated laser desorption RIMS for tantalum samples. Tantalum atoms were detected via a "2 · 1" ionization through the $^2F_{3/2}$ state. The results were quite promising: the pulse of desorbed material was sufficiently narrow (· 4 μsec) that the effective duty cycle was improved to ~10 ^{1}, resulting in a substantial increase in sample utilization efficiency. The observed energy distributions were somewhat anomalous: for high intensities (10^8 W cm^{-2}) the hydrodynamic temperature was measured to be 8000 K, while the kinetic temperature was 400 K, and the internal (electronic) temperature was ~2000 K. At lower intensities (4×10^7 W cm^{-2}) the observed distributions were cooler, and more nearly thermal, as shown in Fig 1. These results are consistent with the existance of a thermal desorption barrier (Nogar et al 1985b).

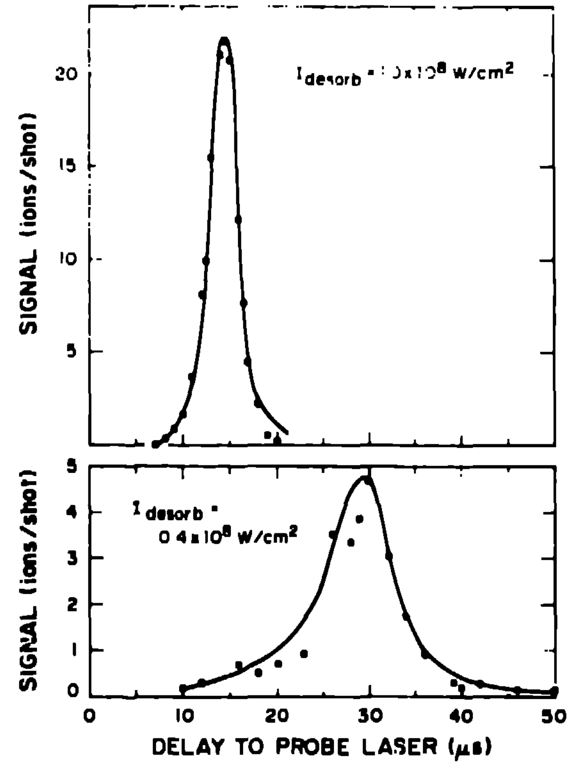

Fig. 1. Tantalum atom flight time distributions for high intensity (~10^8 W cm^{-2}) and low intensity (~4×10^7 W cm^{-2}) laser desorption.

Laser Damage Studies. RIMS has also been used as a monitor of the interaction between lasers and dielectric materials (Estler et al 1986). In initial experiments, optical damage on uncoated CaF_2 substrates was initiated with 1.06 μm pulses at fluences of 1 to 10 J cm^{-2}. Interrogation of the spalled plume revealed Ca atoms and CaF radicals only when damage events occured. Both species are monitored by "2 + 1" ionization processes through the $^1D_2$ and F $^2\pi$ states, respectively. This choice of intermediates states was made so that both species could be detected with a single laser dye. In subsequent experiments, CaF_2 damage was also induced at 355 nm and 266 nm. For 1.06 μm irradiation, we observed thermal (850 K) velocity distributions for both Ca and CaF. In addition, the CaF radical exhibited significant amounts of internal (rotational and translational) excitation. For both 355 nm and 266 nm irradiation, the velocity distributions were bimodal, with a fraction (~50%) of the spalled material exhibiting very high (4000 K) kinetic temperatures (see Fig. 2), while the remainder exhibited a temperature similar (800 to 1000 K) to that observed for the 1.06 μm experiments. In addition, both the vibrational and rotational temperatures of the CaF radicals decreased with decreasing damage wavelength. Lastly, the threshold for damage decreased slightly with decreasing wavelength.

These results suggest that while the 1.06 μm experiments can be adequately modeled in terms of a single damage mechanism (likely avalanche breakdown), the short-wavelength results suggest the onset of second mechanism, perhaps multiphoton absorption. This is consistent with both the bimodal velocity distribution, and with the decrease in CaF vibrational and rotational excitation.

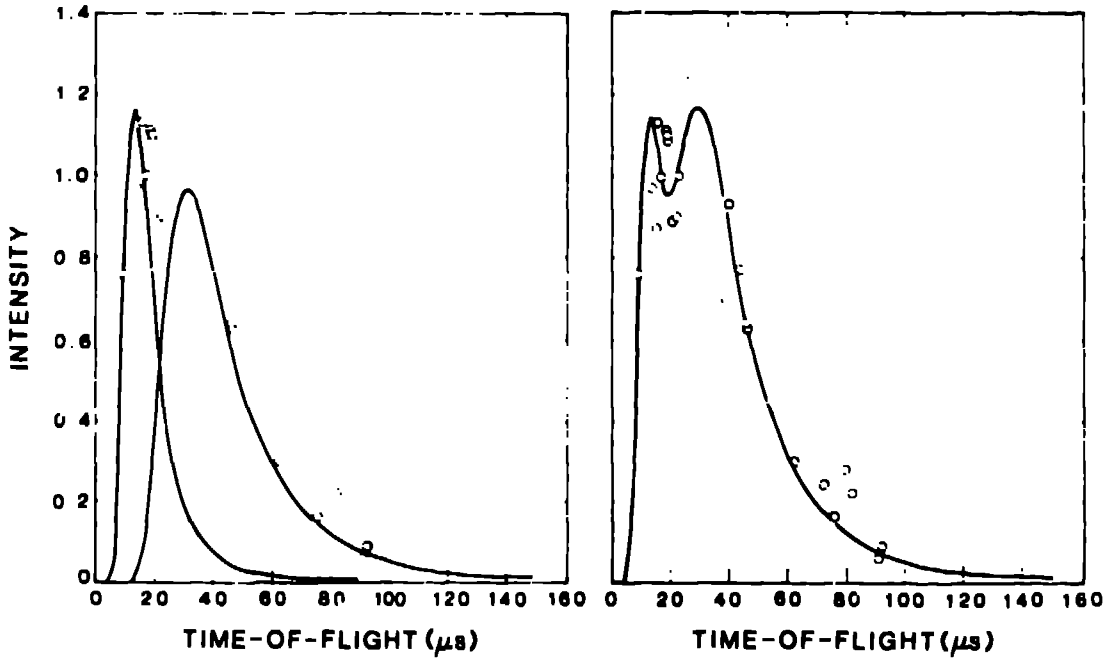

Fig. 2. (a) Calcium atom flight time distributions (dots) for damage induced at 266 nm, 25 J cm^2. The solid lines are Boltzmann fits for 4000 K and 850 K distributions. (b) Same as (a), where the solid line now represents a composite of the fast (33%) and slow (67%) contributions.

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