

CONTROLLING MOLECULAR FRAGMENTATION IN POSTIONIZATION EXPERIMENTS OPERATED AT kHz REPETITION RATES WITH FEMTOSECOND LASER PULSES

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1. Introduction

Ultrashort pulsed lasers are promising new ionization sources for the detection of neutral atoms and molecules desorbed from surfaces. Early experiments using an eximer based system delivering 248 nm photons with a 500 fs pulse width illustrated that molecular ion signals could be generated by postionization of sputtered materials such as sinapinic acid, tryptophan and polystyrene with efficiencies much higher than found with ns lasers. These workers also demonstrated, because of this high efficiency, that ultrashort pulsed lasers are useful in molecular imaging experiments [1]. Other groups have shown similar trends using 200 fs [2] pulses and ps [3] pulses. The results are somewhat surprising because of the intense fields that are involved. Molecular ions are seen with power densities as high as 10^{12} - 10^{13} W/cm².

Another interesting point associated with these types of lasers involves studies using near IR radiation where photoionization may require more than 6 photons. Levis et al. [4] have suggested, for aromatic molecules, that the high fields distort the potential energy surface such that electrons may simply tunnel out of the molecule (tunnel ionization) and at higher fields the barrier to ionization is completely removed (barrier suppression ionization). This group found strong molecular ion signals using laser power densities in the 10^{13} - 10^{14} W/cm² range.

Recently, technological advances have further expanded the prospects for these types of lasers for use as sources in postionization experiments. Using a Ti:sapphire regenerative amplifier-based system, 150 fs pulses at 800 nm with 1.6 mJ of pulse energy can be produced at a repetition rate of 1 kHz, a rate comparable to typical TOF-SIMS experiments. Moreover, it is straightforward to double or triple the fundamental energy to yield pulses of 400 nm and 266 nm, respectively. Mild focusing provides power densities of $>10^{11}$ W/cm². Here we illustrate the photoionization properties of dopamine [(HO)₂C₆H₃CH₂CH₂NH₂], an important neurotransmitter, when exposed to intense fields of various wavelengths. Moreover, we show how the high repetition rate of this type of laser greatly increases the possibilities for molecular imaging in the static mode.

2. Experimental

The experiments presented here were performed on a reflectron based TOF-SIMS apparatus manufactured by Kratos, Inc. Desorption was initiated using a 600 pA 25 keV pulsed Ga^+ ion beam. The sample stage was kept at 90 K for all experiments to avoid a background signal from thermally evaporating molecules. The apparatus is configured so that it is possible to directly compare SIMS yields with yields obtained using laser postionization. More details of the apparatus have been described previously [2].

The femtosecond laser source for these experiments is shown in Figure 1. The Ti:sapphire oscillator is pumped with 3.3 W from an Ar^+ ion laser and generates

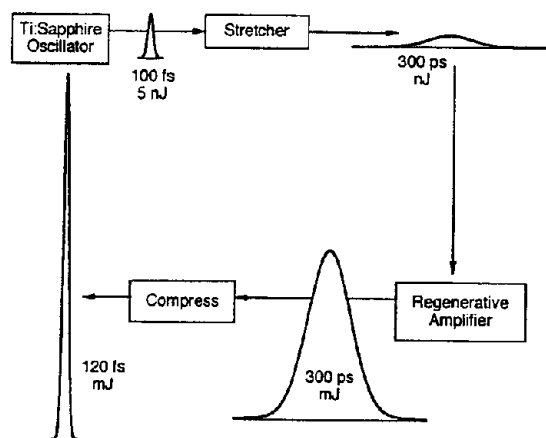


Figure 1. Block diagram of laser system.

100 fs pulses at 100 MHz with an output of 5 nJ per pulse at 800 nm. This pulse is then stretched to 300 ps by multiple passes on a single grating before re-entering an isolator for redirection into the regeneration amplifier. It acts as a seed pulse in a Ti:sapphire regenerative amplifier, which is pumped with 12 W of the second harmonic from a Nd:YAG laser operating at repetition rates of up to 5 kHz. At this point the energy of each pulse is vastly increased from the nJ range to ~2 mJ per pulse at 1 kHz. The amplified pulse is finally compressed by a grating pair to 120 fs with an output power in excess of 1.5 mJ per pulse. The 2nd harmonic (400 nm) of the fundamental (800 nm) is generated using an LBO crystal, while the third harmonic (266 nm) is produced by spatially and temporally overlapping the fundamental and the 2nd harmonic in a BBO crystal. We currently are producing about 600 μJ at 400 nm and 200 μJ at 266 nm, with a pulse width of ~250 fs. More details about this setup have been reported previously [2].

3. Results and Discussion

The photoionization properties of thermally evaporated dopamine molecules are shown in Figure 2 using the three available photoionization wavelengths. There are three major species observed including the molecular ion M^+ at $m/z=153$, a fragment ion $M^+-\text{CH}_2\text{NH}$ at $m/z=124$ arising from the McLafferty rearrangement (McL^+) and the side chain fragment CH_2NH_2^+ at $m/z=30$. Note that M^+ is observable at all ionization wavelengths including 800 nm where at least 5 photons are required for ionization. As the wavelength is reduced toward the UV, the relative amount of M^+ increases, suggesting that UV radiation will yield the best detection efficiency during ion desorption experiments. The ionization does not appear to involve tunnel or

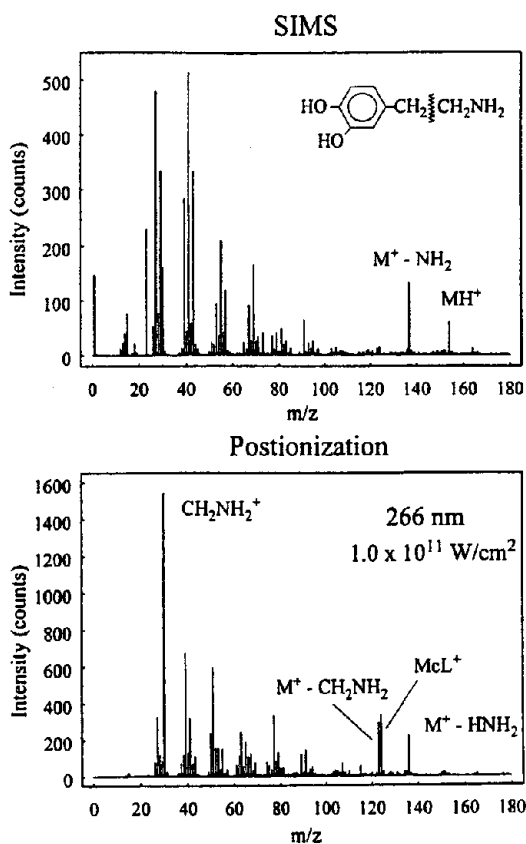
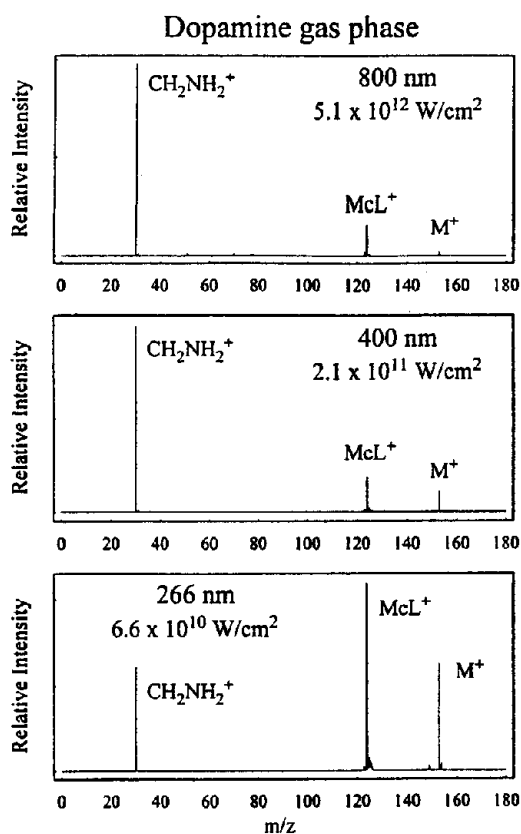


Figure 2. Photoionization of dopamine at various ionization wavelengths.

Figure 3. Comparison of SIMS and postionization spectra for dopamine.

Cr(CO)₆ gas phase

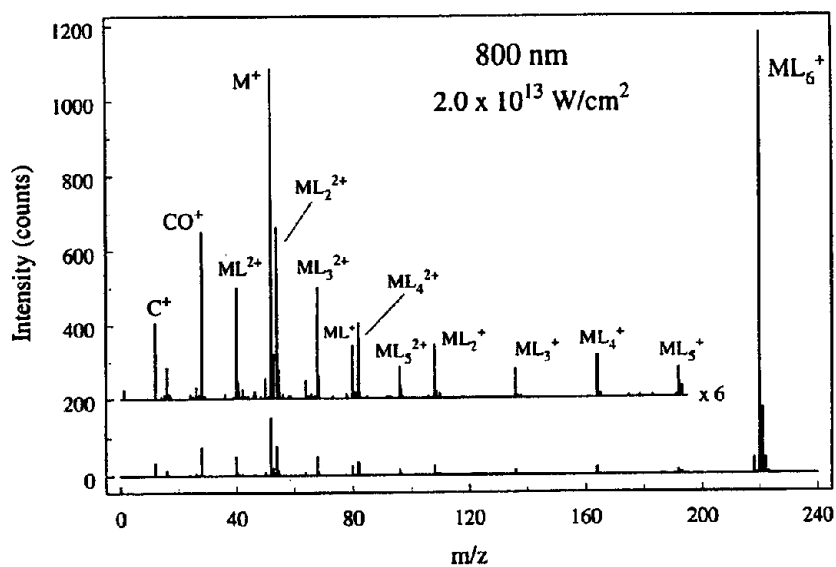


Figure 4. Photoionization spectra of thermally evaporated Cr(CO)₆.

barrier suppression ionization since better molecular photoionization is expected in the near IR than in the UV[4].

The corresponding spectral profile of dopamine sputtered from a thin film deposited onto a Si substrate is shown in Figure 3. Note that the M^+ signal is virtually undetectable via postionization but that MH^+ is a significant peak in the SIMS spectrum. The reasons for this discrepancy are unclear at the moment. It is possible that the sputtered molecule is formed in highly excited vibrational states and that photoionization leaves the ion on a dissociative potential energy curve. It is also possible, however, that there are fewer neutral dopamine molecules which are sputtered intact than there are protonated molecular ions formed during desorption. This is an interesting issue that merits further study. The intensity of the other fragment ions is, however, about 4 times greater than that found by SIMS.

We have found evidence for barrier suppression ionization for $Cr(CO)_6$. This molecule ionizes without significant fragmentation at 800 nm as shown in Figure 4. Moreover, only a few molecular ions are detected at 400 nm, and significant fragmentation is observed. There are no known absorption bands for $Cr(CO)_6$ at either wavelength. Hence, for this case much better photoionization behavior is observed at longer wavelengths. Obviously, there is a great deal to learn about the photophysics of high-field ionization events.

Finally, it is possible to take advantage of the high repetition rate of these lasers in imaging experiments. Shown below is the image of a film of benzo[a]pyrene with a line of diameter 1.0 micron etched into the surface using the Ga^+ ion beam. The image was recorded using $304 \times 256 = 77,824$ pixels with 10 pulses of 500 ns Ga^+ ion pulses at each pixel. The image required 13 min to acquire rather than the 7 hours and 12 minutes needed to acquire the same image at a 30 Hz repetition rate. The brightest pixel contains 85 counts. The benzo[a]pyrene was photoionized at 400 nm using a pulse energy of 200 μJ .

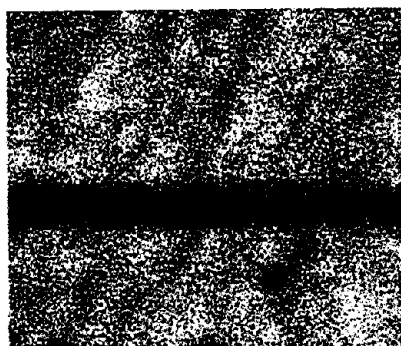


Figure 4. Postionization with 400 nm light of a 1.0 micron line etched into a thin film of benzo[a]pyrene.

Acknowledgement

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