NIR strong field ionization and imaging of C_{60} sputtered molecules: overcoming matrix effects and improving sensitivity

Andrew Kucher,† Lauren M. Jackson,† Jordan O. Lerach,† A. N. Bloom,† N. J. Popczun,† Andreas Wucher,‡ Nicholas Winograd,†*

†Chemistry Department, The Pennsylvania State University, 104 Chemistry Building, University Park, Pennsylvania 16802

‡Fachbereich Physik, Universitaet Duisburg-Essen, 47048 Duisburg, Germany

ABSTRACT

The supporting information provides additional details alluded to in the Experimental and Results and Discussion sections of the publication. Ion extraction methods are discussed first, followed by detector gain saturation, a description of the laser system and its implementation, and additional sample preparation details. Finally Figure S-1 from the Results and Discussion section is presented, showing the molecular structures investigated in this study.

EXPERIMENTAL SECTION

Ion Extraction

The instrument was operated in delayed extraction mode, with the sample at ground potential during the ion bombardment, and the ion extraction field being switched on at the end of the primary ion pulse. Ion extraction was operated in two modes, one for standard SIMS and the other for LPI SNMS. For secondary ion detection, the sample stage is positively pulsed in order to extract positive ions into the mass spectrometer. In LPI SNMS mode, on the other hand, a negative pulse of 150 ns duration is applied to the stage prior to the start of positive ion extraction and subsequent introduction of the laser, in order to accelerate positive secondary ions back to the surface. This procedure reduces the secondary ion background in the LPI spectra. The laser pulse is fired shortly (50-80 ns) after the start of the positive extraction pulse. This way the signals arising from post-ionization are slightly displaced from the remaining secondary ion background peaks in the TOF spectrum, since the flight time zero for the post-ionized neutrals is defined by the arrival of the laser pulse. For the secondary ions the zero is defined by the start of the ion extraction pulse.

Detector Gain Saturation

In the mouse brain tissue and algae experiments, detector gain saturation[1] by low mass ions was encountered. This is a phenomenon which severely deteriorates the sensitivity for the detection of intact molecules. The problem was remedied by deflecting the m/z 1 - 100 mass range away from the multichannel plate detector by positively pulsing a metal grid mounted above it just prior to the arrival of the ions. The grid voltage is adjusted to a value above the

starting potential of the photoions produced in the post-ionization process, in order to overcome the kinetic energy imparted to them by the extraction field.

Laser System for LPI

The commercially available laser system employed for LPI SNMS operates based on the concept of chirped pulse amplification (Coherent Legend Elite Duo) and pumps an optical parametric amplifier (OPA, Light Conversion TOPAS C-HE). The pump laser produces pulses of 40 fs duration at a wavelength of 800 nm, a repetition rate of 1 kHz and an average power of 10 W. The repetition rate of the entire experiment is limited by this laser. Frequency resolved optical gating (Swamp Optics Grenouille 8-20-USB) is used to confirm the pulse-width of the pump laser.[2]

The OPA's overall conversion efficiency (combined signal and idler) is 30-40%. It produces a tunable wavelength beam between 1160 - 2580 nm, with its output filtered by dichroic mirrors. The wavelength was checked by an Ocean Optics USB 4000 spectrometer after frequency doubling in a BBO crystal. The final output beam delivered by the OPA was focused using a 150 mm focal length lens (at 587.6 nm) on an xyz translation stage and introduced into the analysis chamber through a CaF_2 window. The laser intensity was calibrated by comparison with the well known saturation behavior of Xe gas, which was introduced into the analysis chamber through a leak valve.[3,4]

Recently, we developed a procedure to map the detectable plume of point source sputtered indium atoms in our instrument, and determined that our tightly focused laser beam (75 ± 25 μm diameter) overlaps ~ 3% of it.[5] In general, it is possible to defocus the laser to achieve better plume overlap, as the maximum intensity of the beam (~ 10^{15} W/cm^2 at 1350 nm) is significantly

higher than that needed to saturate the ionization process for most organic molecules (10^{13} - 10^{14} W/cm^2).[3] As described in detail elsewhere,[6] optimum experimental conditions are established when the laser is defocused to an intensity slightly above the (molecule specific) *saturation intensity* (I_{sat}), which can in principle be determined from fundamental laser intensity dependent ionization measurements. For the example of sputtered β-estradiol molecules, a post-ionized molecular ion signal about an order of magnitude greater than the corresponding secondary ion signal was achieved employing this strategy, using a defocused laser beam with an effective diameter of ~ 320 μm.[6] From the indium data,[5] it can be inferred that about 25% of a point source sputtered detectable plume is sampled under these conditions, with rastering of the primary ion beam in an 600 μm^2 area decreasing this value to ~ 5% at the edges of the field of view.[6]

It is possible that the measured post-ionization signal levels observed in this work may be improved further by more in-depth investigations, similar to the β-estradiol experiments.[6] However, a major goal of the present paper is to perform practical imaging experiments on complex multicomponent biological samples. Therefore, the molecular ion signals in this work were optimized empirically, by defocusing the laser to reach the maximum observable ionization efficiency which is likely similar, at least to first order, to that observed in the β-estradiol experiments. The optimal laser focal and intensity conditions determined were sample dependent and reproducible on subsequent analogous samples. Within experimental uncertainty, the optimized effective laser beam diameters used in these studies, as calculated from geometrical optics, were as follows: rubrene 500 ±170 μm (1350 nm), mouse brain tissue 350 ±50 μm (1700 nm) and 430 ±170 μm (1350 nm), and *B. braunii* algae 670 ±270 μm (1350 nm). Maximizing the ionization efficiency in this way was essential as a tightly focused 75 ±25 μm diameter laser

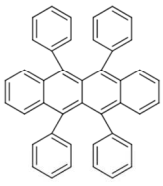
beam generated substantially lower signal levels, approaching the signal to noise threshold for some analytes.

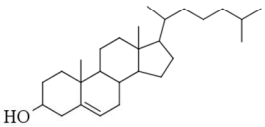
Sample Preparation

The rubrene (99% CAS 517-51-1) used in these experiments was purchased from Acros Organics. Spin-cast films were patterned using photolithographic techniques and plasma etching. Details of the exact methodology will be presented elsewhere.

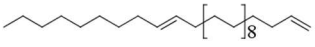
Gas phase and sputtered experiments were performed on cholesterol purchased from Sigma Aldrich (99% CAS 57-88-5). For gas phase experiments, cholesterol powder was pressed into In foil, mounted onto a Si shard, and attached to the sample block. The block was heated to 343 K by passing heated N_2 gas through the sample holder stage. Post-ionization experiments were performed on physical vapor deposited films, made in a home-built deposition chamber. During analysis the sample block was cooled to 100 K, as noted previously.

RESULTS AND DISCUSSION

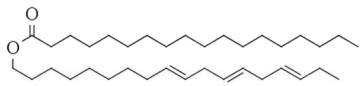

Rubrene



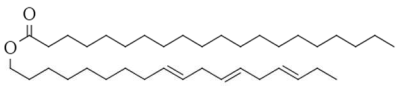
Cholesterol



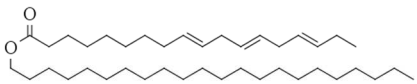
C_{31} diene



Linolenyl stearate*



Linolenyl arachidate*



Behenyl linolenate*

Figure S-1. Structures of the molecules investigated in this study. *Denotes a likely isomer.

REFERENCES

(1) Fraser, G. W. *Nucl. Instrum. Meth. A* **1990**, *291*, 595-606.

(2) Trebino, R.; Bowlan, P.; Gabolde, P.; Gu, X.; Akturk, S.; Kimmel, M. *Laser Photon. Rev.* **2009**, *3*, 314-342.

(3) Hankin, S. M.; Villeneuve, D. M.; Corkum, P. B.; Rayner, D. M. *Phys. Rev. A* **2001**, *64*.

(4) Gingras, G.; Tripathi, A.; Witzel, B. *Phys. Rev. Lett.* **2009**, *103*.

(5) Breuer, L.; Kucher, A.; Herder, M.; Wucher, A.; Winograd, N. *J. Phys. Chem. A* **in press, 2014**.

(6) Kucher, A.; Wucher, A.; Winograd, N. *Anal. Chem.* **submitted, 2014**.