Molecular Surface Analysis: Soft Ionization with Single Photons

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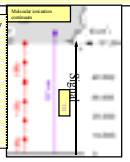
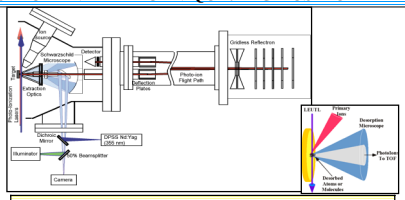
ANALYZING SOFT MATERIALS

- Surfaces of soft materials are analyzed by desorption mass spectrometry to determine their molecular components. Soft materials include:
  - self-assembled monolayers
  - polymers
  - biological materials (DNA).
- Ensures very high useful yield when performed with our state of the art instruments.
- Trace levels of molecules in micron-sized volumes can be measured.

- Single-photon ionization to a state just above the ionization potential can softly ionize a molecule, leaving the molecular ion intact
- Vacuum ultraviolet (VUV) lasers are needed to do single-photon ionization of most molecules :
  - **157nm** or **118nm** laboratory lasers
  - Free-electron laser (broadly tunable, powerful)



INSTRUMENTAL TECHNIQUE: HIGH USEFUL YIELD

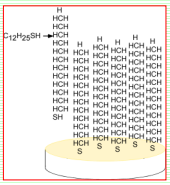


- Soft materials are desorbed with ion or laser beams.
- VUV lasers are used to postionize the desorbed flux.
- Ions are detected by time-of-flight mass spectrometry.

This approach gives a high number of detected molecules per molecule sampled (useful yield: 10^{-2} vs. 10^{-6} by SIMS).

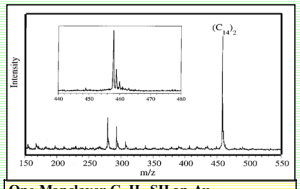
SELF ASSEMBLED MONOLAYERS

These studies were possible because of the strong parent ion signal and lack of fragmentation evident in the soft ionization process

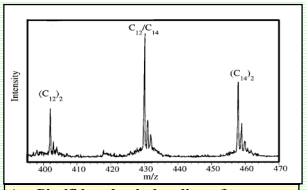


Organothiols absorb in a uniform self-assembled layer (SAM) on a gold substrate.

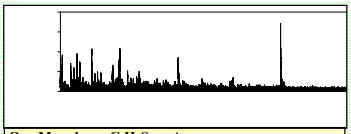
Desorption mechanism and mesostructure of various SAMs were determined using laser desorption followed by single photon ionization at 118nm (alkanes) or 157nm (aryl)



One Monolayer $C_{14}H_{27}SH$ on Au
ionized with 118nm
- Thiols desorb as **dimers!**
- Multilayers desorb as monomers
- S-S bond formation compensates for loss of two S-Au bonds

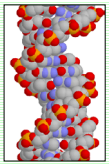


Are Disulfides adsorbed as dimers?
1/2 $(C_{14}H_{27}S)_2$ + 1/2 $(C_{12}H_{25}S)_2$ on Au
ionized with 118nm
- Homogeneous disulfides show randomized desorption products
  - Must adsorb as monomers.
  - Must not be in islands.



One Monolayer C_6H_5S on Au
ionized with 157nm
- Desorbs as dimer
- Lower ionization potential allowed F2 laser to be used – significantly more fluence than at 118nm.
- **Useful Yield 0.005 with F_2 Laser – world record for molecules!**

DNA ADDUCT AND MUTATION ANALYSIS (FUTURE)



ADDUCTS:

- Carcinogens can bind directly to DNA – forming an adduct.
- 7-methylchrysene guanine is a model compound for the chemical changes to DNA induced by smoke.
- Single photon ionization will allow **selective detection** of the adduct from a large background of guanine.
- Potential for *individual* diagnostic for carcinogenesis – early detection of cancer, improved epidemiology.

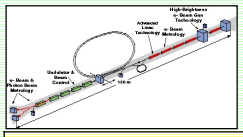
MUTATIONS:

- Mutations sometimes involve base pair deletions such as three successive guanines – 3g.
- Mutant mouse strains with these deletions on a specific gene are being studied in ANL-BIO (Woloschak).
- Difficult to analyze for with conventional techniques.
- Soft ionization will be used to differentiate 15 base pair (mutant) and 18 base pair (wild type) sequences. Only soft ionization can work since the parent molecular ions must be measured.

This methodology will enable trace level DNA adduct detection from small samples (e.g. individuals). Potential applications for this technique are abundant in fundamental cancer research, epidemiology and early detection of clinical cancer.

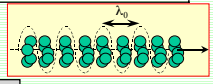
LEUTL FREE ELECTRON LASER: A POWERFUL, TUNABLE VUV SOURCE

Performing soft ionization of molecules requires powerful VUV lasers:
- mJ pulse energies
- 1% energy resolution
- <50ns pulse widths
- Tunable (for background subtraction) – not available in laboratory sources!

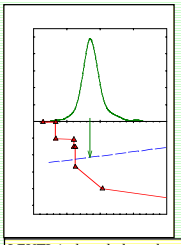


The Low-Energy Undulator Test Line (LEUTL) is capable of running as a free-electron laser **tunable** throughout the VUV. It was the first FEL to demonstrate gain saturation in the visible.

In the self-amplified spontaneous emission process, electrons are bunched at optical wavelengths, dramatically enhancing stimulated emission.



9/9/2001 LEUTL demonstrates 120nm lasing for the first time! (photo courtesy Steve Milton of ANL-ASD)



LEUTL is the only laser that can efficiently Single Photon Ionize most molecules (green curve).

A new instrument, SPIRIT, will use the VUV from LEUTL to establish excellent **background discrimination** combined with the highest **trace sensitivity** of any mass spectrometer.

SPIRIT (Single-photon ionization or resonant ionization to threshold) will be the first user experiment at LEUTL.

SUMMARY

Single-photon ionization has been found to produce 'soft' ionization of most molecules. This results in:

- Low fragmentation – simpler spectral interpretation.
- Strong molecular ion signal.
  - Trace molecule (e.g. DNA adduct) identification becomes possible.
- High ionization cross section

Soft ionization with single photons is therefore a powerful new analytical tool for trace analysis of small molecular samples.

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