# Ultraviolet photoelectron spectroscopy analysis of lithium and deuterium interactions with graphite

**BP9.44**


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## Abstract

### Objectives

- Determine whether or not ultraviolet photoelectron spectroscopy (UPS) is a suitable method for assessing surface chemistry.
- Identify binding energies in the ultraviolet photoelectron spectrum characteristic of Li, O, C, D interactions.

### Background

- X-ray photoelectron spectroscopy (XPS)
  - Li-O-D interactions occur at 533.0 ± 0.6 eV
  - Li-C-D interactions occur at 291.4 ± 0.6 eV
  - Post-mortem NSTX tiles and control studies show that lithiated graphite reacts readily with oxygen to form additional chemical bonds.
- Ultraviolet photoelectron spectroscopy (UPS)
  - UPS probes the outer top 1 nm of the surface, ejecting the outermost valence electrons.
  - Technique is more surface sensitive and can potentially yield more chemical relevant information.


## 1 Surface Characterization Methods

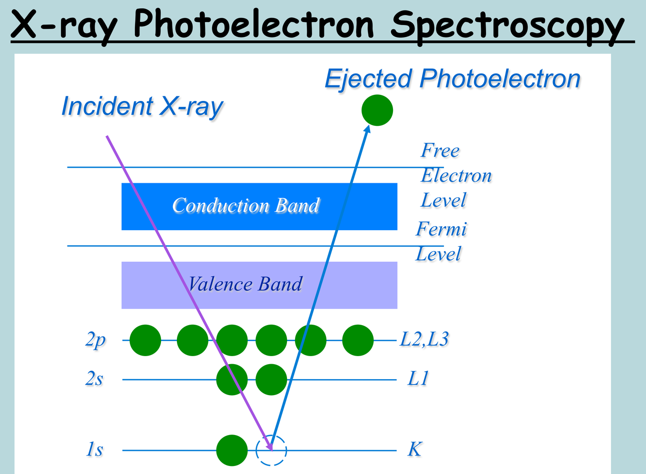
### Photoelectron spectroscopy: The photoelectric process

- *XPS/UPS spectral lines are identified by the shell from which the electron was ejected (1s, 2s, 2p, etc.).*
- *The ejected photoelectron has kinetic energy:*

$$KE = h\nu - Binding\ E - Work\ Function$$

- *Energy of ejected photoelectron reveals characteristic information regarding the elemental composition of the substrate.*

### X-ray Photoelectron Spectroscopy




**Why XPS?**

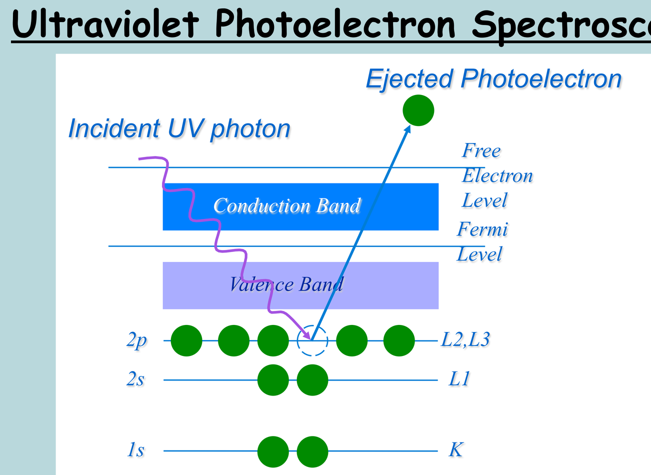
The probing depth for XPS is typically <10 nm. X-rays cause photoelectrons to be released from the deep core orbitals. XPS provides a robust technique for elemental identification.

**Omicron surface characterization Cluster**
(Birck Nanotechnology Center)

**XPS Specs:**
- Non-monochromatic Mg Kα (1253.6 eV)
- Dwell time = 0.8ms
- Step size = 0.05eV
- Pass energy = 20 eV

**Experiment includes:**
- Li deposition via lithium evaporator.
- $D_2^+$ irradiation (500 eV/amu)
- Ar cleaning (1keV, 30°)

### Ultraviolet Photoelectron Spectroscopy

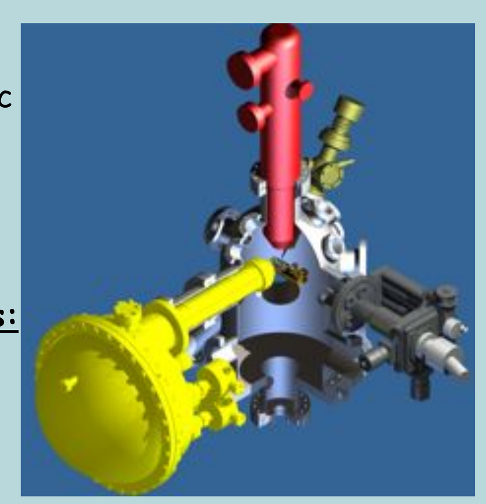



**Why UPS?**

UPS probes the top ~1 nm of a surface. The UV photons eject photoelectrons from the outermost valence electronic shells. Chemical bonding occurs between valence electrons. UPS exploits these bonding signatures.

**UPS Specs:**
- Non-monochromatic He I (21.2 eV)
- Dwell time = 0.2ms
- Step size = 0.05eV
- Pass energy = 2 eV

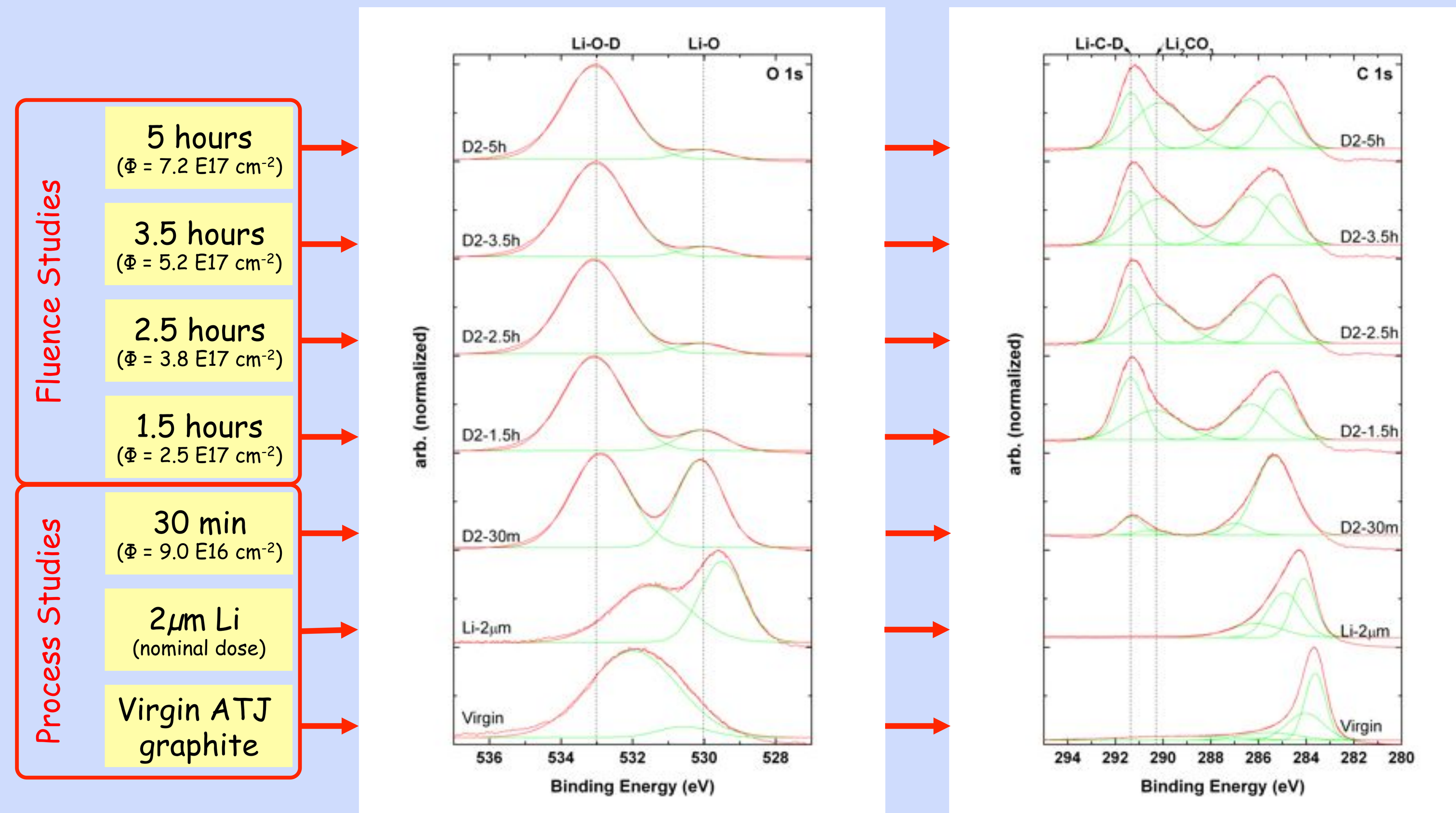
**Experiment includes:**
- Ar cleaning (1keV, 30°)



Particle and Radiation Interaction with Hard and Soft Matter PRIHSM experiment is designed to be a versatile facility able to measure in-situ the surface evolution during energetic particle modification.

## 2 XPS Results: Deuterium-Lithium Surface Chemistry

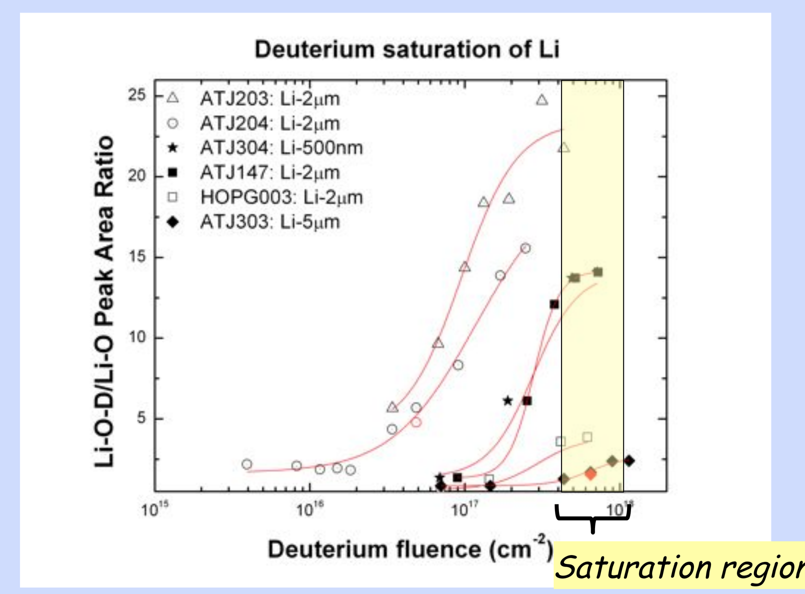
Surface chemistry of ATJ graphite with 2μm lithium deposition and $D^+$:




- Li-O-D peak (533.0 ± 0.6 eV) increases with D fluence
- Li-O peak (530.1 ± 0.6 eV) decreases with D fluence
- Li-C-D peak (291.4 ± 0.6 eV) increases

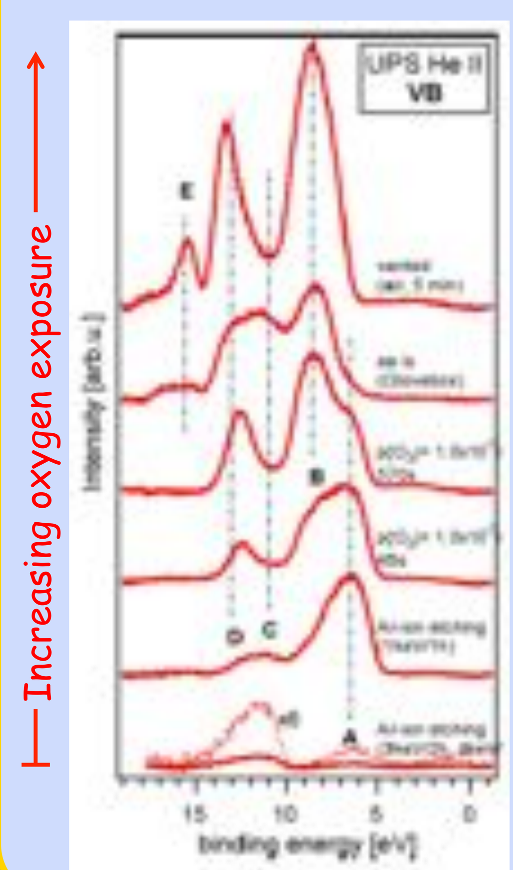
### Discussion

- Li and O interactions are manifest at 530.1 eV in the XPS spectrum.
- Li, O, and D interactions, on a graphite substrate, are manifest at 533.0 eV.
- Li, D, and C interactions are manifest at 291.4 eV.
- Taking the ratio of Li-O-D to Li-O peak areas (in O 1s spectra above) shows that at high fluences, Li-O-D/Li-O ceases to increase – an indication of saturation (seen at right). Data fit to logistic curve.
- Deuterium saturation occurs between $2 \times 10^{17}$ and $8 \times 10^{17}$ $cm^{-2}$.
- A given lithium dose is capable of "holding" a finite amount of deuterium.
- Deuterium added to the system after this threshold does not affect the surface chemistry (as observed through XPS).




**Deuterium saturation**: The point at which deuterium no longer induces changes in surface chemistry. Defined as the fluence at which the normalized derivative < 10% between consecutive irradiations .

## 3 Review of Other UPS Work

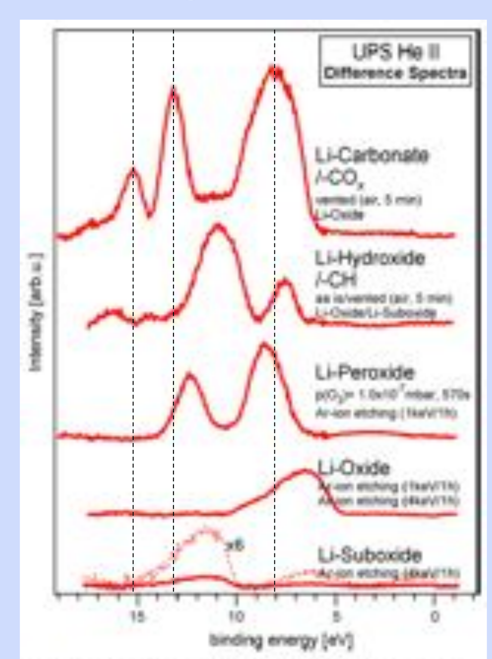



D. Ensling[1] examined lithium surfaces with UPS. Sample was loaded into vacuum under inert atmosphere, cleaned twice via Ar sputtering, and then exposed to two controlled amounts of $O_2$. Afterwards, the sample was exposed to air. UP spectra were collected at each stage of the experiment (*see figure at left*).

Identification of peaks lines (*left*):

- **A** (6 eV) and **C** (10.5eV): *O 2p*
- **B** (8.5 eV): *O 2p/C 2sp*
- **D** (11.5 eV): *C 2sp/O 2p*
- **E** (15.2 eV): *C 2s*

In addition, specific chemical bonds were identified that correspond to various lithium, carbon, oxygen, hydrogen interactions (see *right*). Bonds include lithium-carbonates, hydroxides, peroxides, oxides and sub-oxides.




## 4 Post-Mortem UPS Results

### Post-mortem samples:

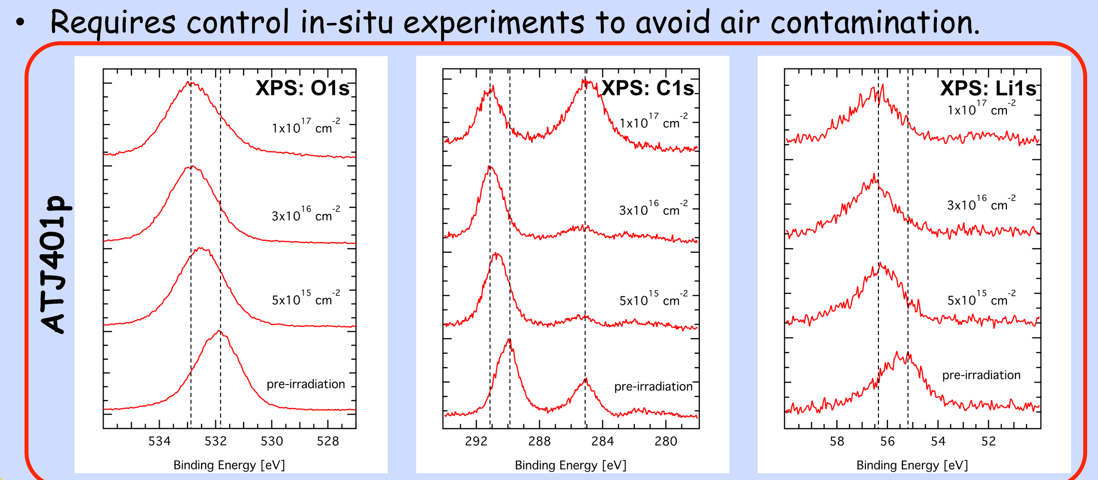
Mo205p – Porous molybdenum (same material as the NSTX liquid lithium divertor) exposed to ~1 week of NSTX plasmas via the sample analysis probe. Lithium conditioning preceded deuterium plasma discharge. Sample removed and analyzed at Purdue. Future probe upgrade, MAPP (Materials Analysis and Particle Probe) will allow for in-vacuo characterization at NSTX (see ***B. Heim, BP9.88***)

ATJ147a – ATJ graphite with 2μm lithium deposition and $D_2^+$ irradiation at Purdue University. Post-mortem UPS analysis follows long term air exposure and includes Ar sputtering for surface cleaning.

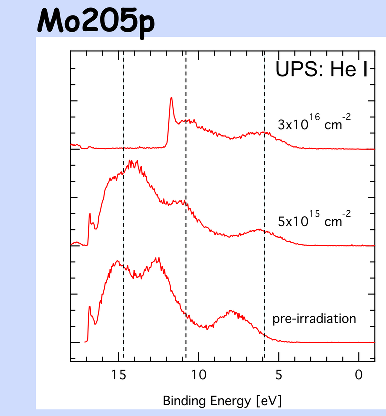
ATJ401p – ATJ graphite sample exposed to simultaneously with Mo205p to NSTX plasmas.

### Preliminary results:

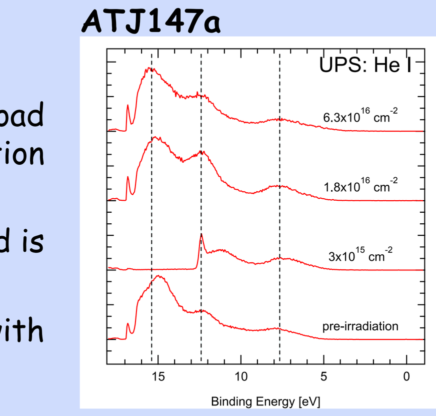
- XPS spectra of long-term air exposed samples (below) show a broad shoulder after 15 min Ar sputtering ($6.3 \times 10^{16}$ $cm^{-2}$). This is an indication of the Li-O and Li-O-D peaks from in-situ experiments (section 2).
- Strong peak at ~15.3 eV in UPS spectra is present for ATJ samples and is characteristic of C 2p bonds.
- Peaks resemble Li-Carbonate peaks shown in section 3, although not with perfect agreement.
- Requires control in-situ experiments to avoid air contamination.



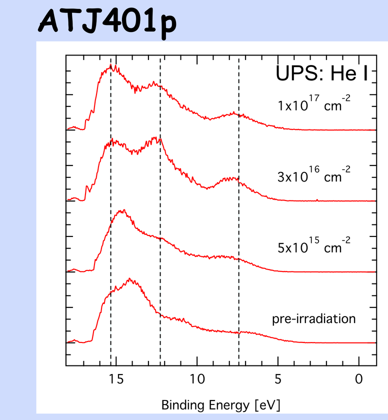

**Mo205p**




**ATJ147a**




**ATJ401p**




## 5 Conclusions

Ultraviolet photoelectron spectroscopy

- ❑ UPS provides data complementary to XPS for determining the chemical binding state of lithiated graphite and deuterium.
- ❑ UPS spectra of all post-mortem samples shows strong lithium **carbonate** presence even after Ar sputtering, thus motivating the need for in-situ control experiments.

X-ray photoelectron spectroscopy

- ❑ The point at which lithiated graphite saturates with deuterium can be observed in XPS spectra by comparing ratios of integrated peak areas.
- ❑ A nominal lithium thickness of 2μm becomes saturated with D at ~$10^{17}m^{-2}$. NSTX lithium depositions (10s-100s nm per cycle) likely saturate after a single discharge ($10^{17}$ $cm^{-2}$).
- ❑ Deuterium does not bind directly with lithium (LiD) in lithiated graphite, but forms multibody complexes with Li-O-D and Li-O-C. Lithium always binds with ***oxygen and carbon***, when present.

Future work

- ❑ Upgrade equipment to accommodate in-situ UPS studies of lithiated graphite
- ❑ Study surface morphology effects (roughness) via SEM on saturation .


## Acknowledgements

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[1] D. Ensling, A. Thissen, W. Jaegermann, Applied Surface Science 255 (2008) 2517–2523



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