

# Topic Outline

## VB2a. Initial State Effects

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### Chemical State Effects

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Ti Implanted with N

Poly(ethylene glycol) on Ti

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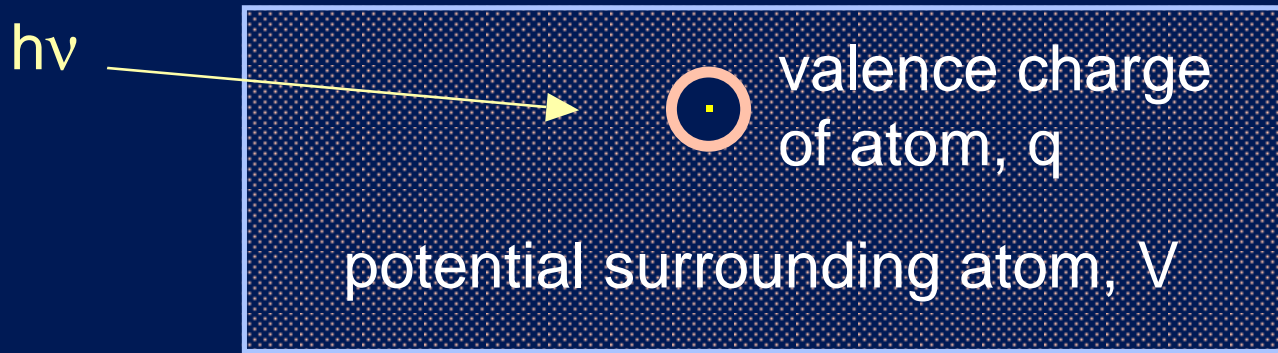
### Madelung Potential

Cause

Example

# Definition

Initial state effects are those factors that influence the charge state of the atom **before** the photon strikes it.



- $q_i/r_i$  - potential due to orbital charge
- $V$  - potential due to external fields

Comparison of atoms in two different cases gives

$$BE_2 - BE_1 = K(q_2/r_2 - q_1/r_1) + (V_2 - V_1)$$

# Causes

Any change in bonding of an atom that changes the binding energy of the electron of interest will cause a corresponding shift in the peak position.

Factors include changes in

## hybridization

example - C in  $\text{H}_2\text{C}=\text{CH}_2$  versus C in  $\text{H}_3\text{C}-\text{CH}_3$

## oxidation state

example - Fe in FeO versus Fe in  $\text{Fe}_2\text{O}_3$

## degree of polar covalent or ionic bonding

examples - \*C in  $[\text{C}-^*\text{CCl}]_n$  versus \*C in  $[\text{C}-^*\text{CF}]_n$   
- Cl in NaCl versus Cl in KCl

# Effects

## hybridization

How the BE of an electron in a given orbital changes due to a change in hybridization state of the atom must be determined in each case (via quantum mechanics).

## oxidation state

In general, the BE of an electron in any orbital of an atom increases as the oxidation state of the atom increases.

## degree of polar covalent or ionic bonding

In general, as the atom loses valence electrons, the BE of all remaining electrons increases.

# Magnitudes

When an electronic change occurs in an atom, the change in potential felt by an electron in an orbital at radius  $R$  from the nucleus goes as  $1/R$ .

Chemical state effects can be as significant for core electrons (small  $R$ ) as they are for valence levels (larger  $R$ ).

Shifts in BE due to chemical state effects decrease going down a group in the periodic table (because  $R$  increases) ...

... and may increase going to larger atomic number across a period in transition metals (because  $R$  decreases).

# General Examples

## hybridization

The BE of the C 1s levels may shift as much as that for the C 2sp<sup>x</sup> valence level.

## oxidation state

The extent of shift in BE clearly tracks with 1/R for the three metals listed, but the trend is not linear.

## degree of polar covalent or ionic bonding

Electronegativity differences, atom sizes, and number of neighboring bonds will be important in determining the magnitude of the shift in BE.

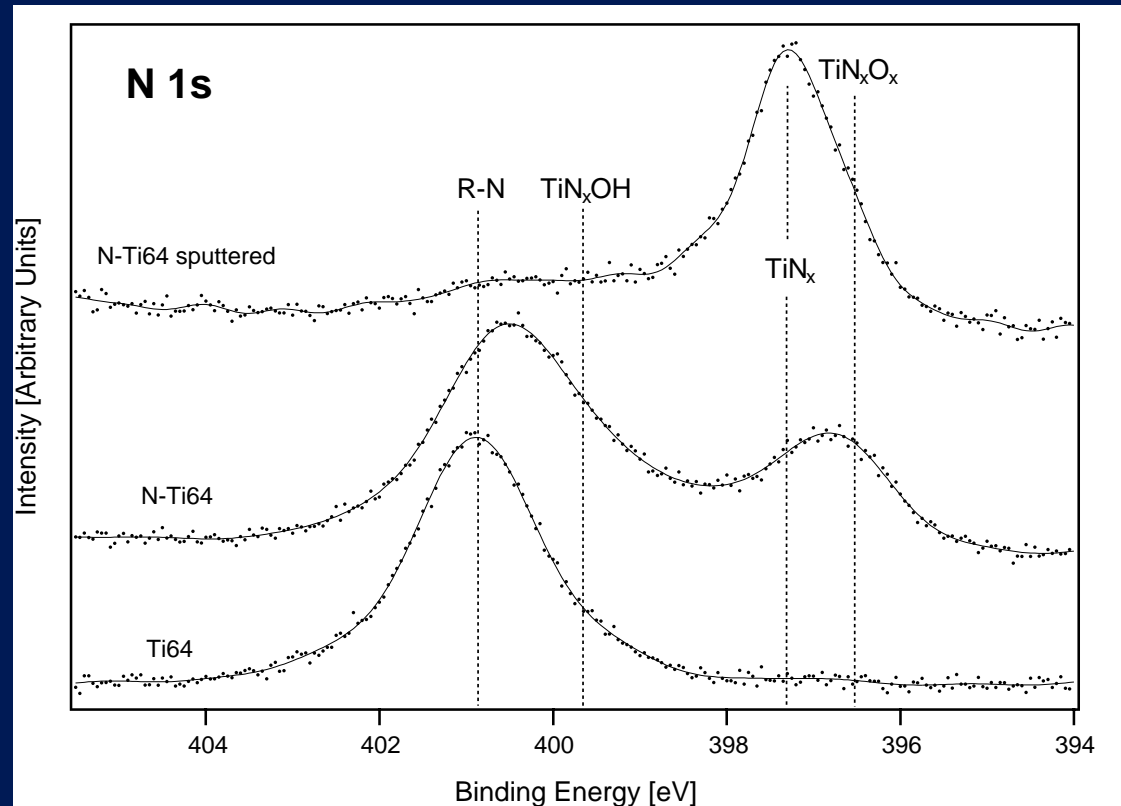
## Peak Positions (eV)

	Fe	FeO
Fe 2p <sub>3/2</sub>	706.74	709.6
Δ		2.9
R (nm)		0.1241
Δ / R		23
	Cu	CuO
Cu 2p <sub>3/2</sub>	932.6	934.4
Δ		1.8
R (nm)		0.1278
Δ / R		14
	Os	OsO <sub>2</sub>
Os 4f <sub>7/2</sub>	50.7	52.0
Δ		1.3
R (nm)		0.1367
Δ / R		9.5

# Ti Implanted with N

Ti was implanted with N. The N implanted Ti was sputtered to find the distribution of N.

This figure clearly shows how the various chemical states of N affect the position of the N 1s peak.

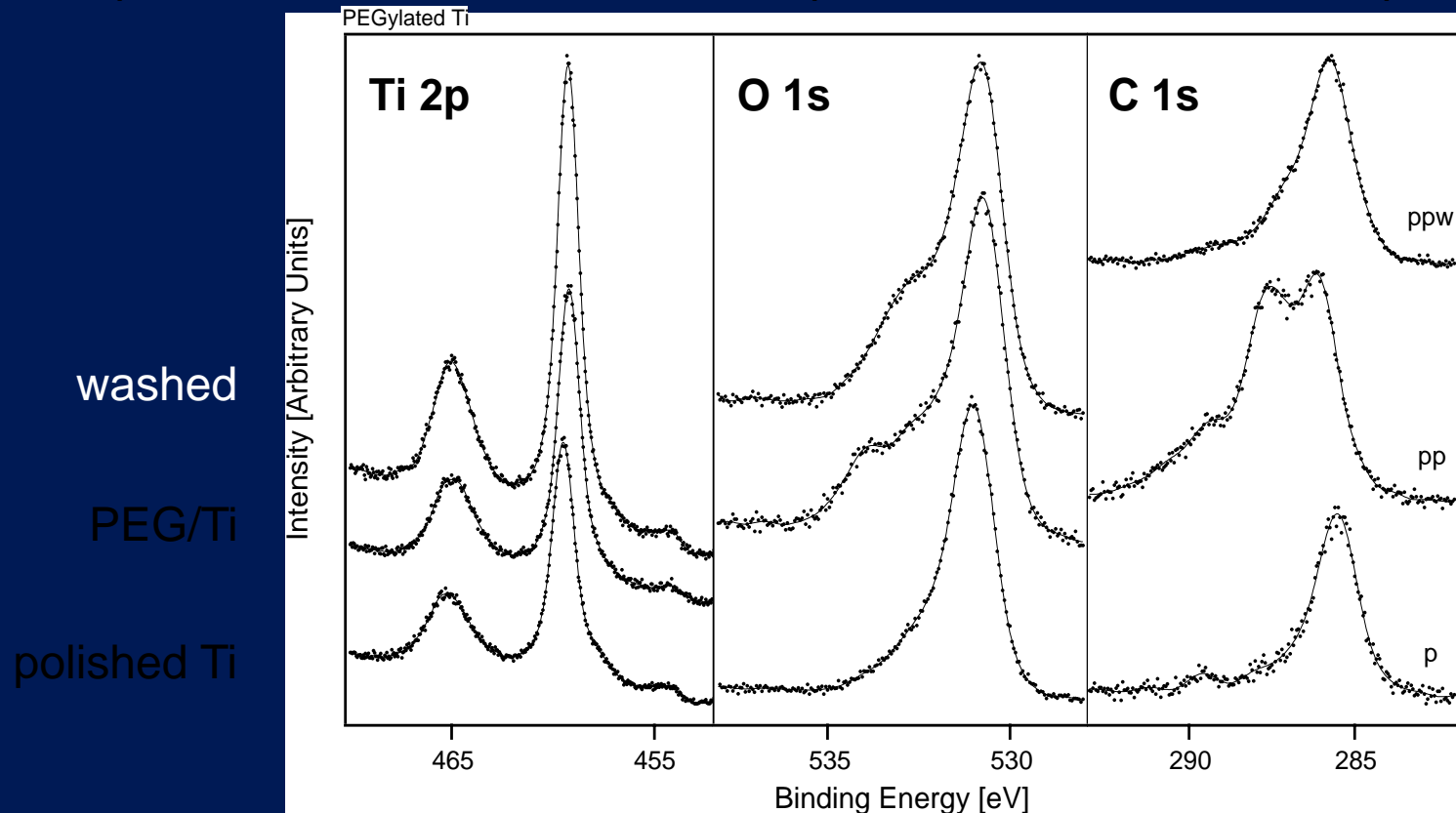


# Poly(ethylene glycol) on Ti

The Ti 2p peaks show  $\text{TiO}_2$ ,  $\text{TiO}_x$ , and Ti species.

The O 1s peaks show  $\text{TiO}_x$  and O-R species.

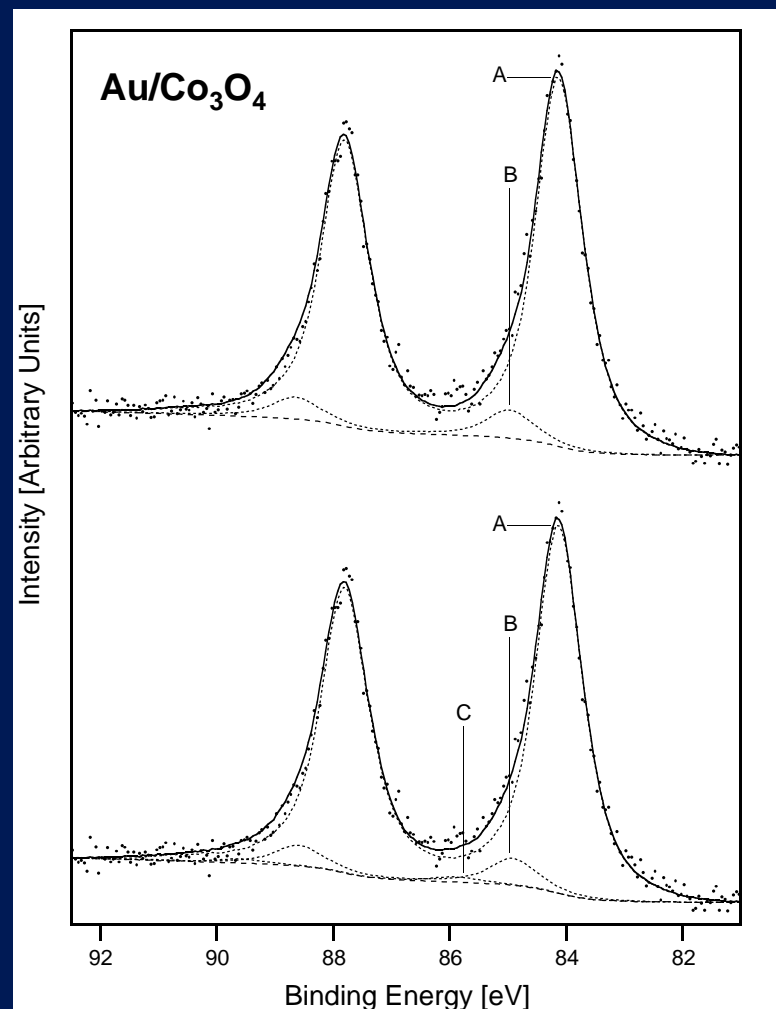
The C 1s peaks show C-C, C-O and C=O species.



# Au on Co Oxide Support

Au is deposited on Co oxide supports for use as catalysts.

The XPS spectra for the Au 4f levels are best fit by three peaks. The lowest BE peak is for Au metal and the highest BE peak is consistent with  $\text{Au}_2\text{O}_3$ . The intermediate peak is partially oxidized Au.



# Cause

The Madelung potential term gives rise to a stabilization of an ordered array of charges over a disordered array of the same charges.

This factor increases the binding energy of the electron in the orbital of an atom in an ordered lattice versus the same situation in a disordered lattice.

# Example

As CO is added to a K adlayer on a Ru(001) surface, the BE of the K 2p peak shifts to lower values even though we predict that K should be more positive in valence state. Some have argued the shift in the wrong direction is due to formation of an ordered  $\text{K}(\text{CO})_x$  compound on the surface (Madelung potential).