SLAC-WP-100

A mechanistic study of CO_2 reduction at the interface of a gallium phosphide (GaP) surface using core-level spectroscopy

Kristen Flynn

Office of Science, Science Undergraduate Laboratory Internship (SULI) Program

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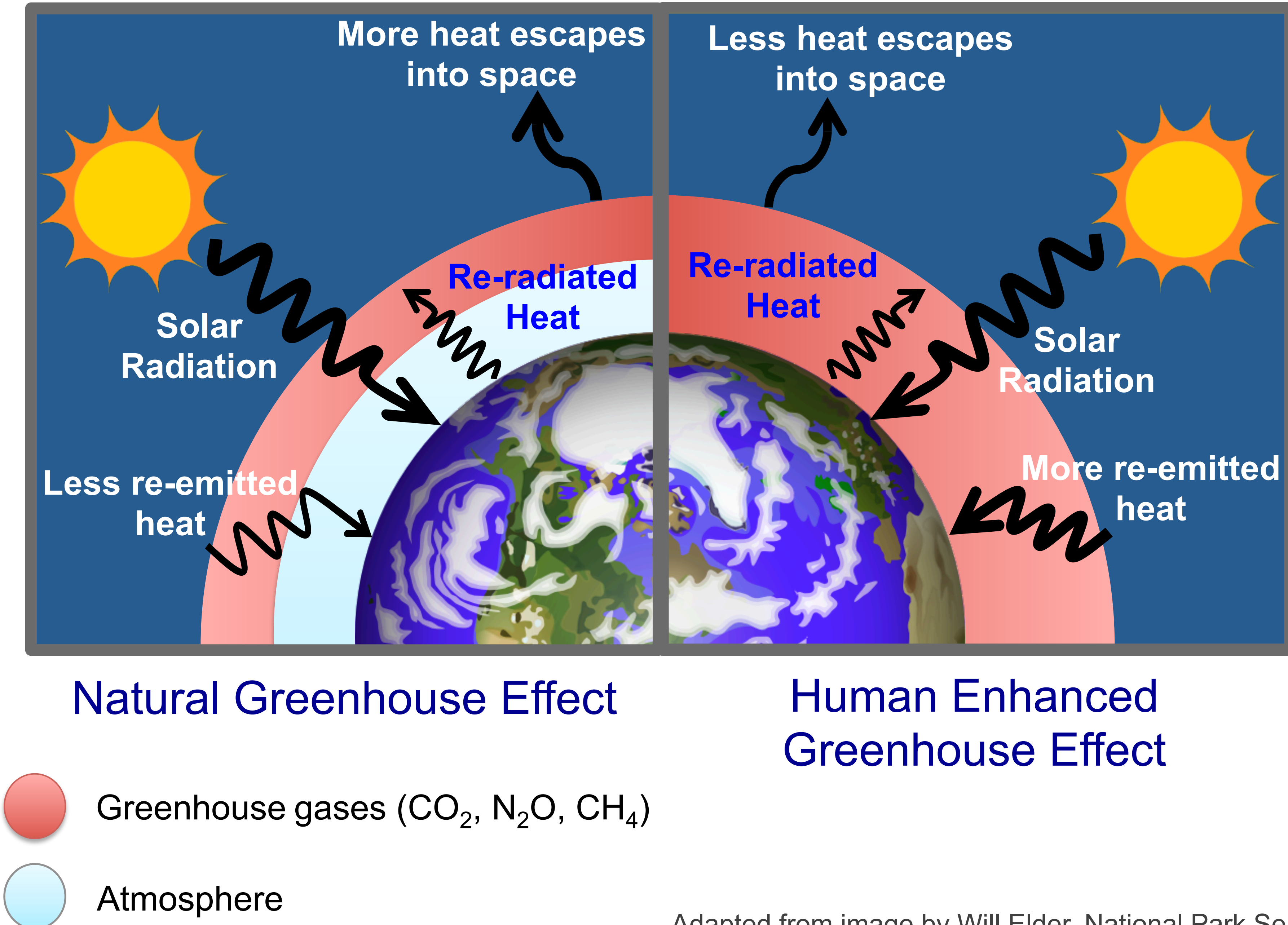
Abstract

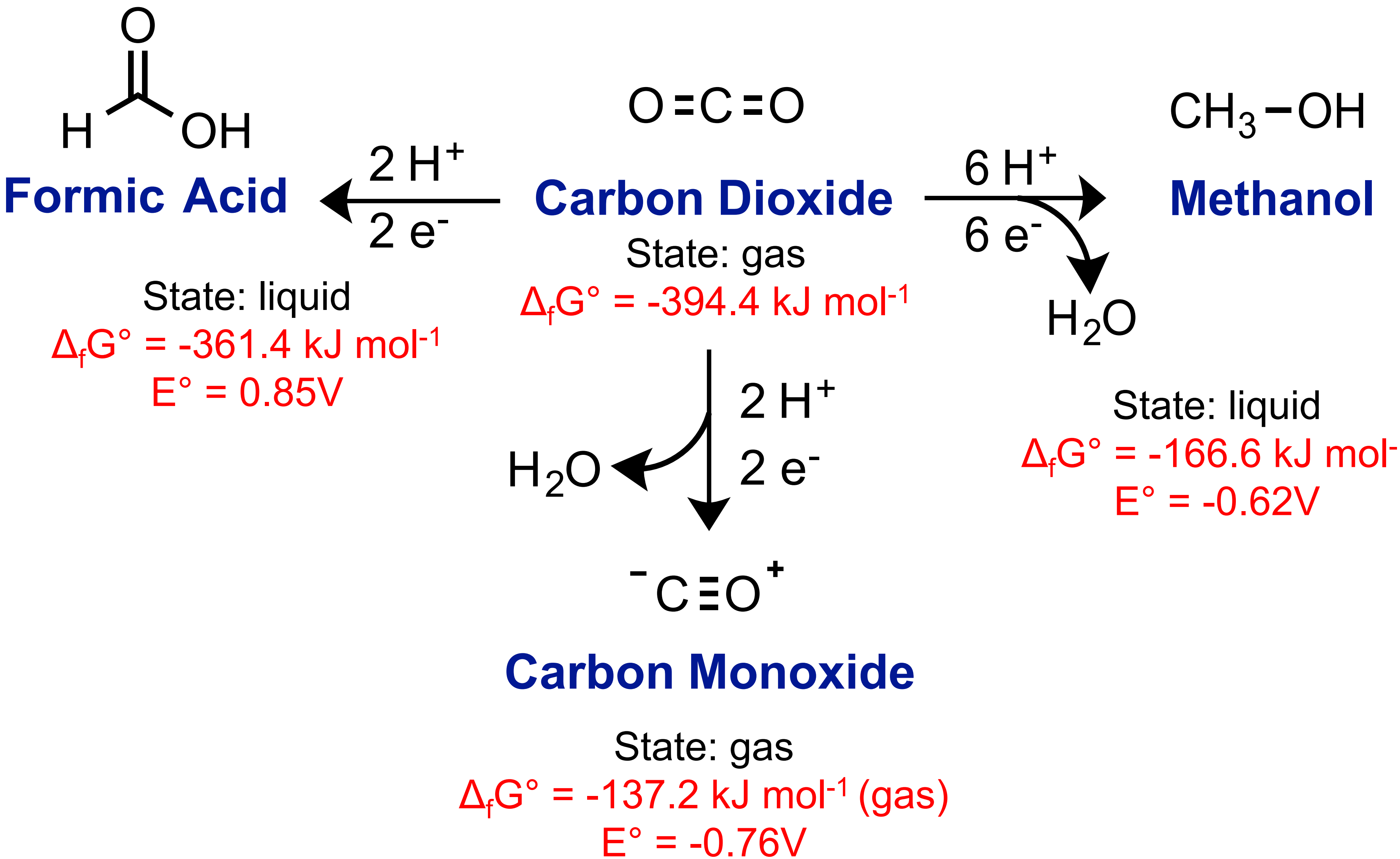
Carbon dioxide (CO_2) emission into the atmosphere has increased tremendously through burning of fossil fuels, forestry, etc.. The increased concentration has made CO_2 reductions very attractive though the reaction is considered uphill. Utilizing the sun as a potential energy source, CO_2 has the possibility to undergo six electron and four proton transfers to produce methanol, a useable resource. This reaction has been shown to occur selectively in an aqueous pyridinium solution with a gallium phosphide (GaP) electrode. Though this reaction has a high faradaic efficiency, it was unclear as to what role the GaP surface played during the reaction. In this work, we aim to address the fundamental role of GaP during the catalytic conversion, by investigating the interaction between a clean GaP surface with the reactants, products, and intermediates of this reaction using X-ray photoelectron spectroscopy. We have determined a procedure to prepare atomically clean GaP and our initial CO_2 adsorption studies have shown that there is evidence of chemisorption and reaction to form carbonate on the clean surface at LN2 temperatures (80K), in contrast to previous theoretical calculations. These findings will enable future studies on CO_2 catalysis.

Background: Greenhouse Effect



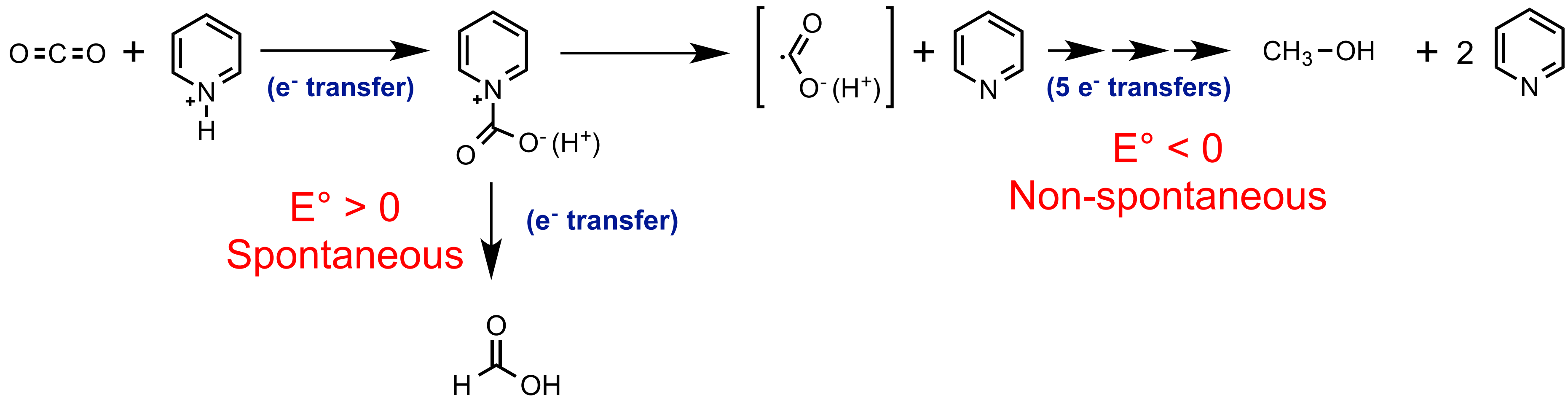
Adapted from image by Will Elder, National Park Service

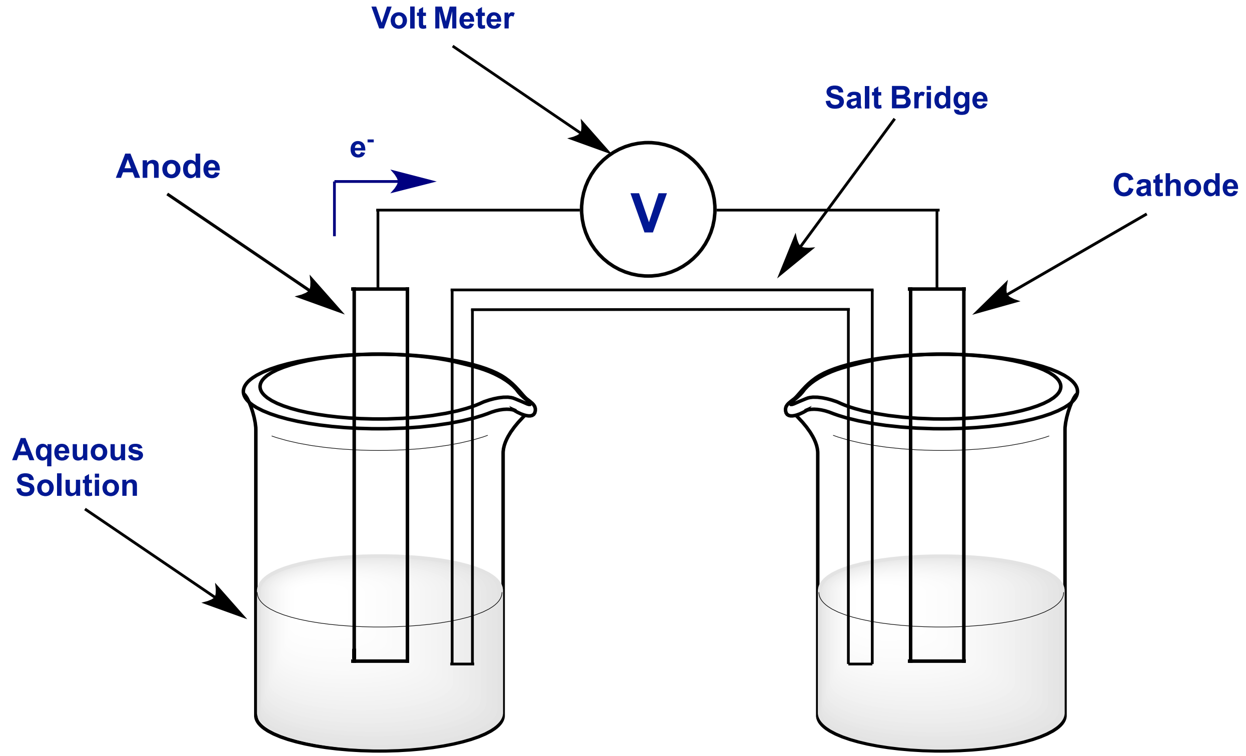
Background: Transformation of CO_2



Source: CRC Press Handbook of Chemistry and Physics (Internet Version 2005)

Electrochemical Reduction of Carbon Dioxide Mechanism





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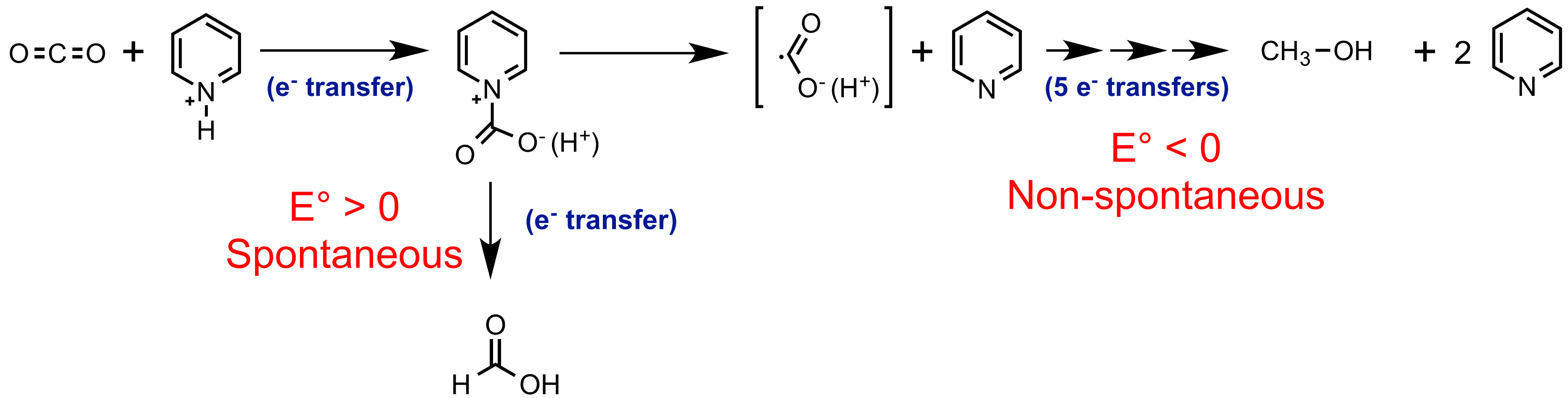
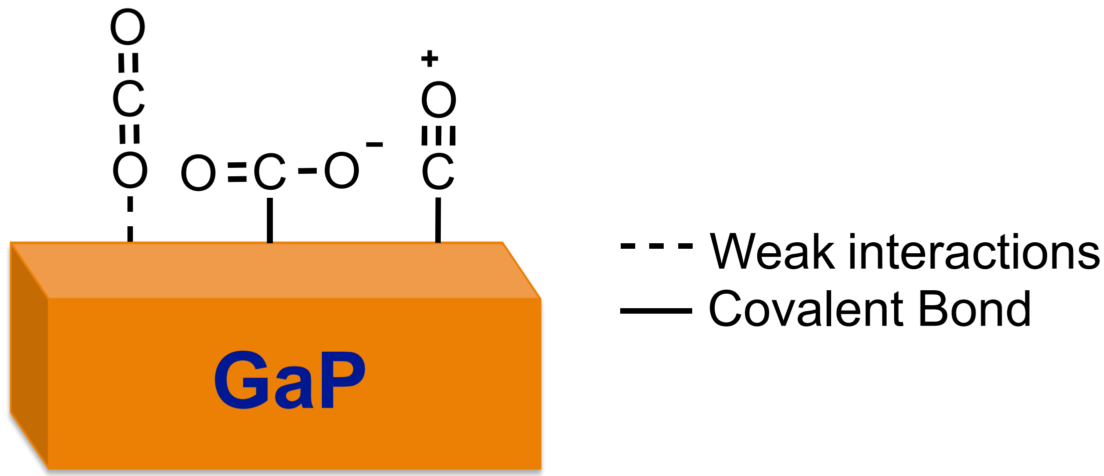


Electrode	E (V vs. SCE)[a]	Faradaic Efficiency Methanol ξ (%)
p-GaP	-0.20	96
p-GaP[b]	-1.40	~3
n-GaAs	-1.30	100
RuO_2/TiO_2	-0.8	60

[a]SCE: Saturated calomel electrode (reference electrode)
[b]p-GaP electrode was strictly an electrochemistry reaction

Source: Barton, E.E., et. *al. J. Am. Chem. Soc.* **2008**, *130*, 6342-6344

What is the nature of the intermediate(s) during electrochemical reaction on a gallium phosphide (GaP) surface?



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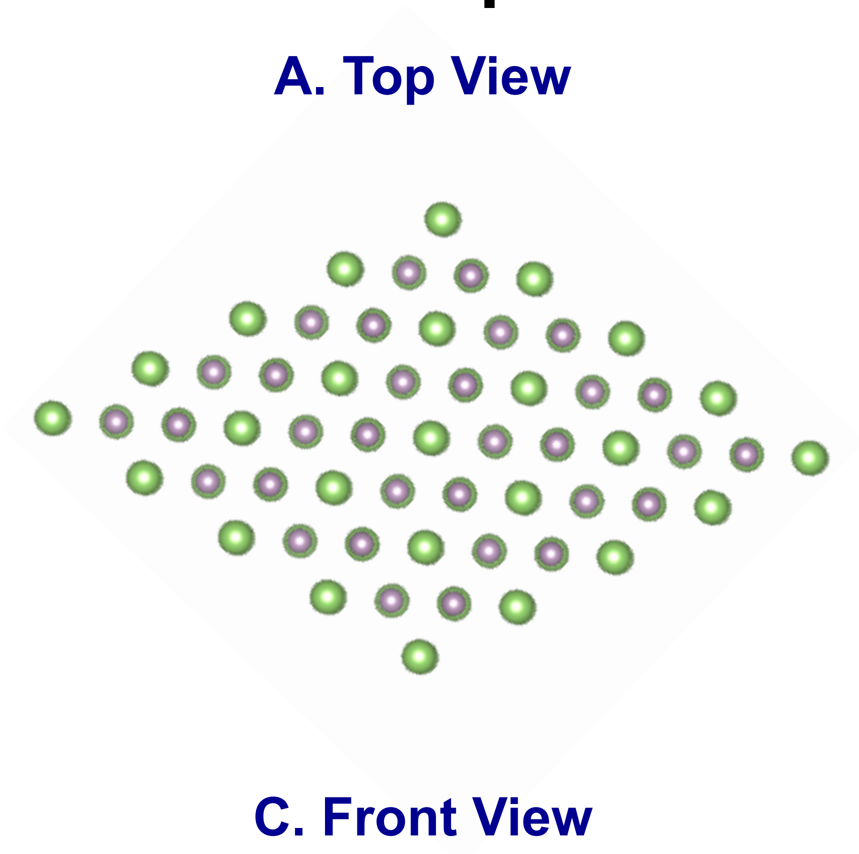
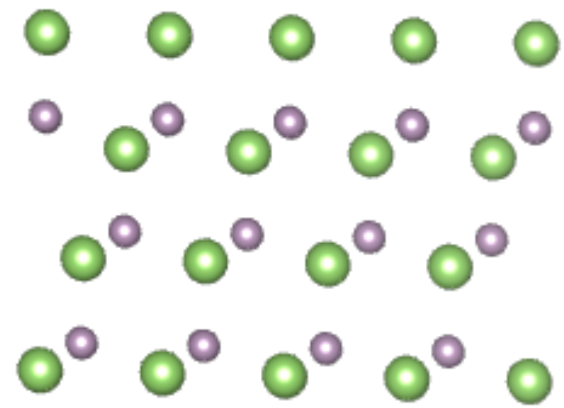
Gallium Phosphide Surface [GaP(111)]

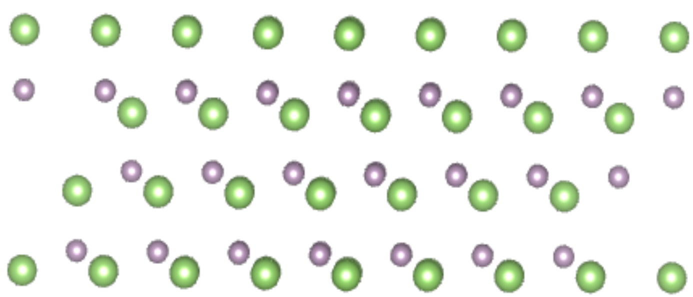
A. Top View



B. Side View



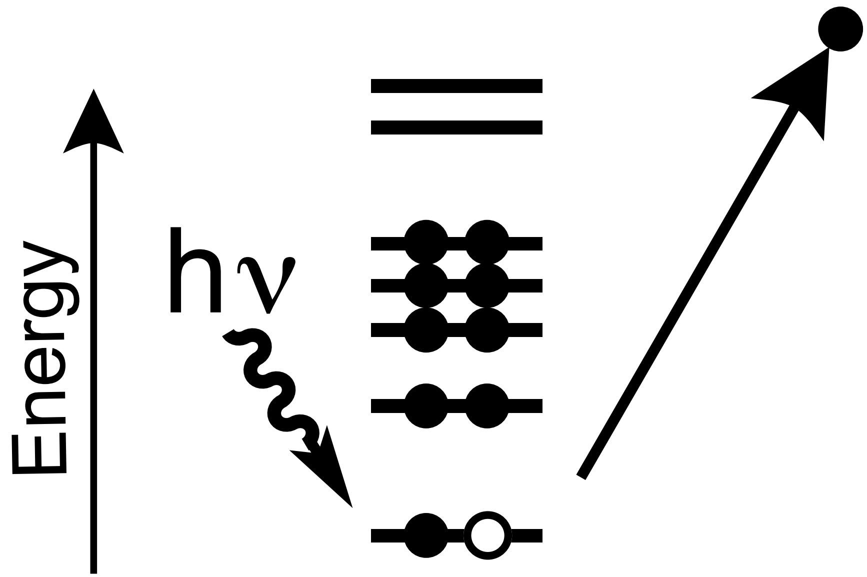
C. Front View



D. Wafer

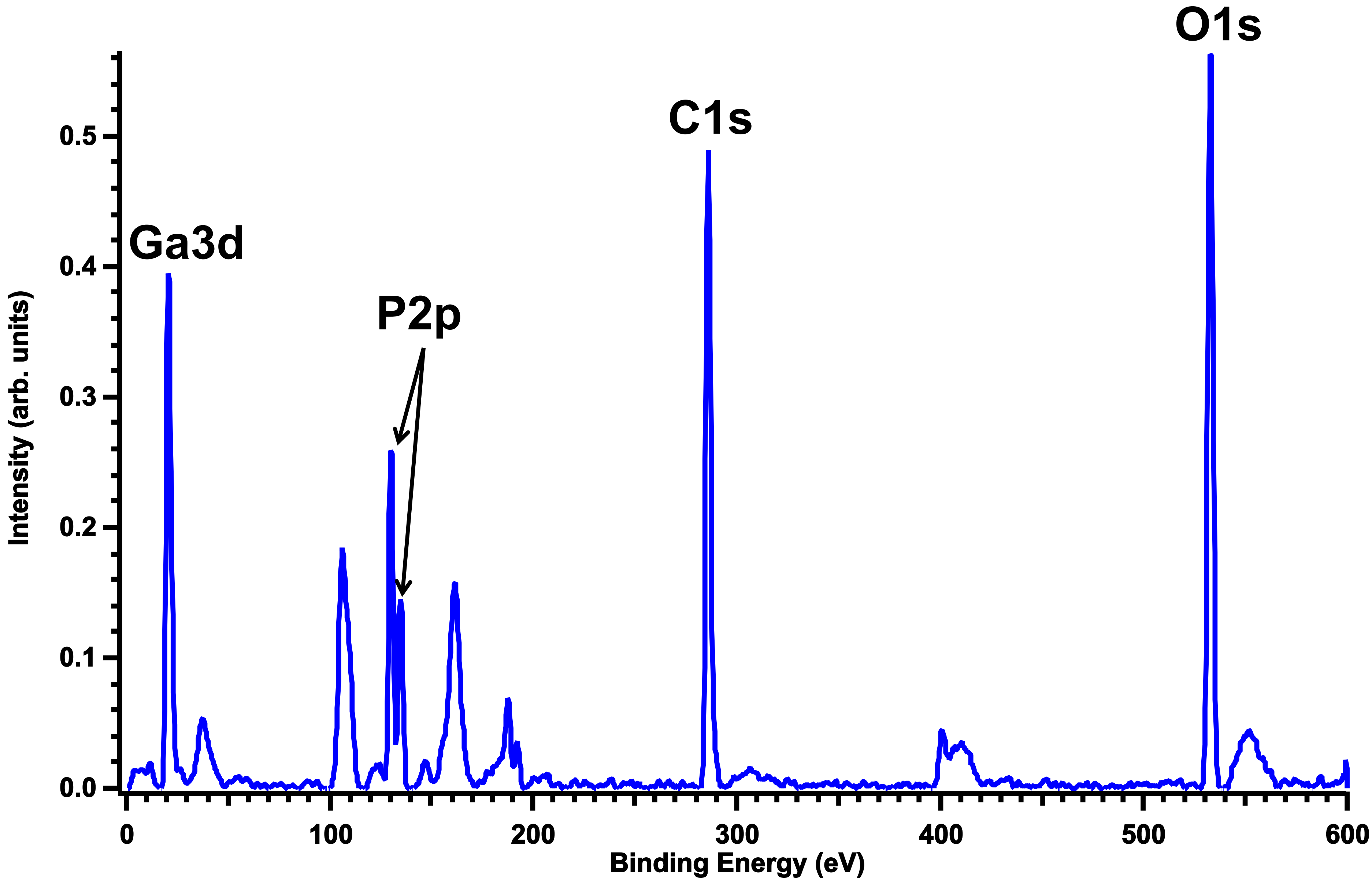
Core Level Spectroscopy: Theory

X-Ray Photoelectron Spectroscopy

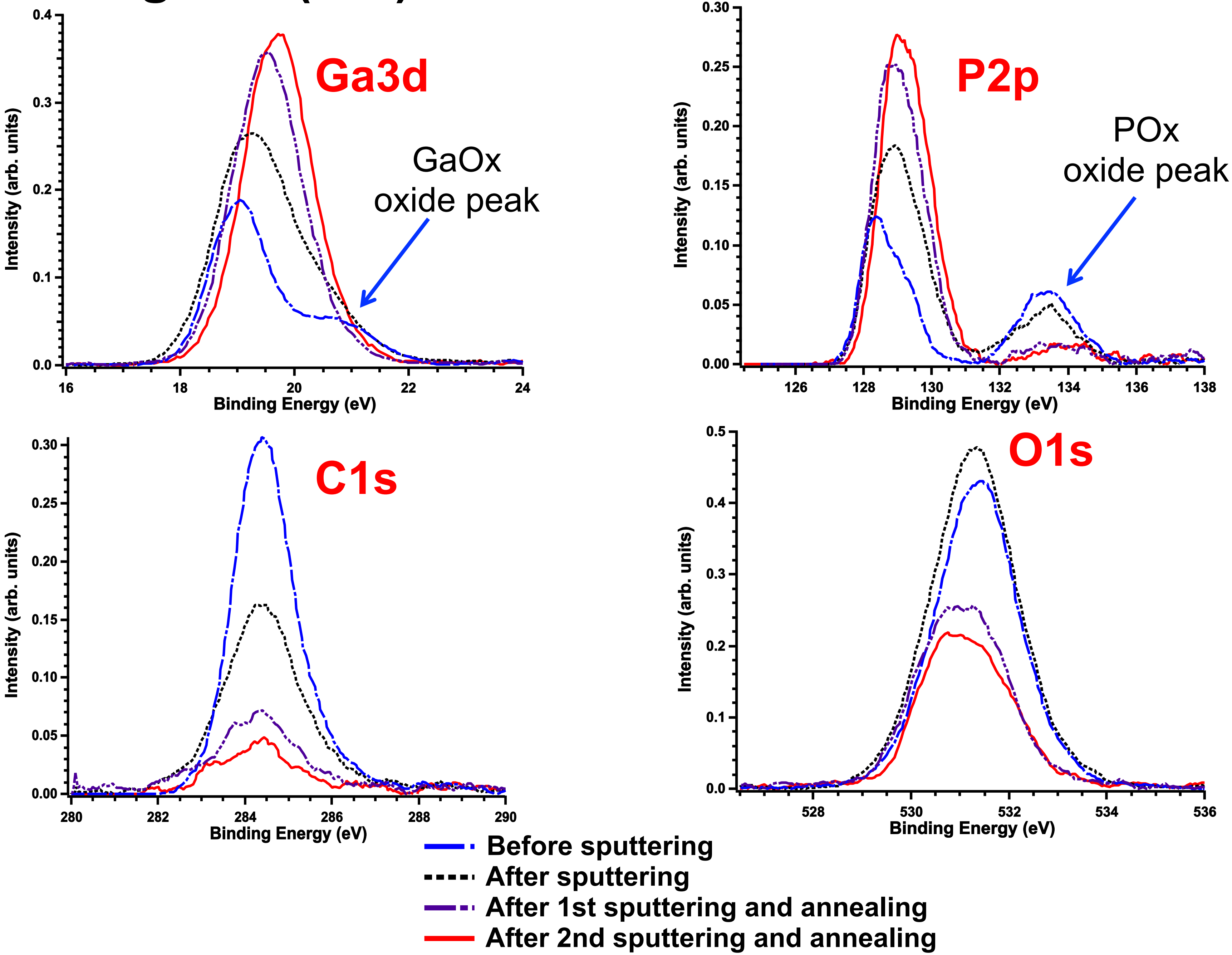


$$E_{binding} = E_{photon} - \left(E_{kinetic} + \phi\right)$$

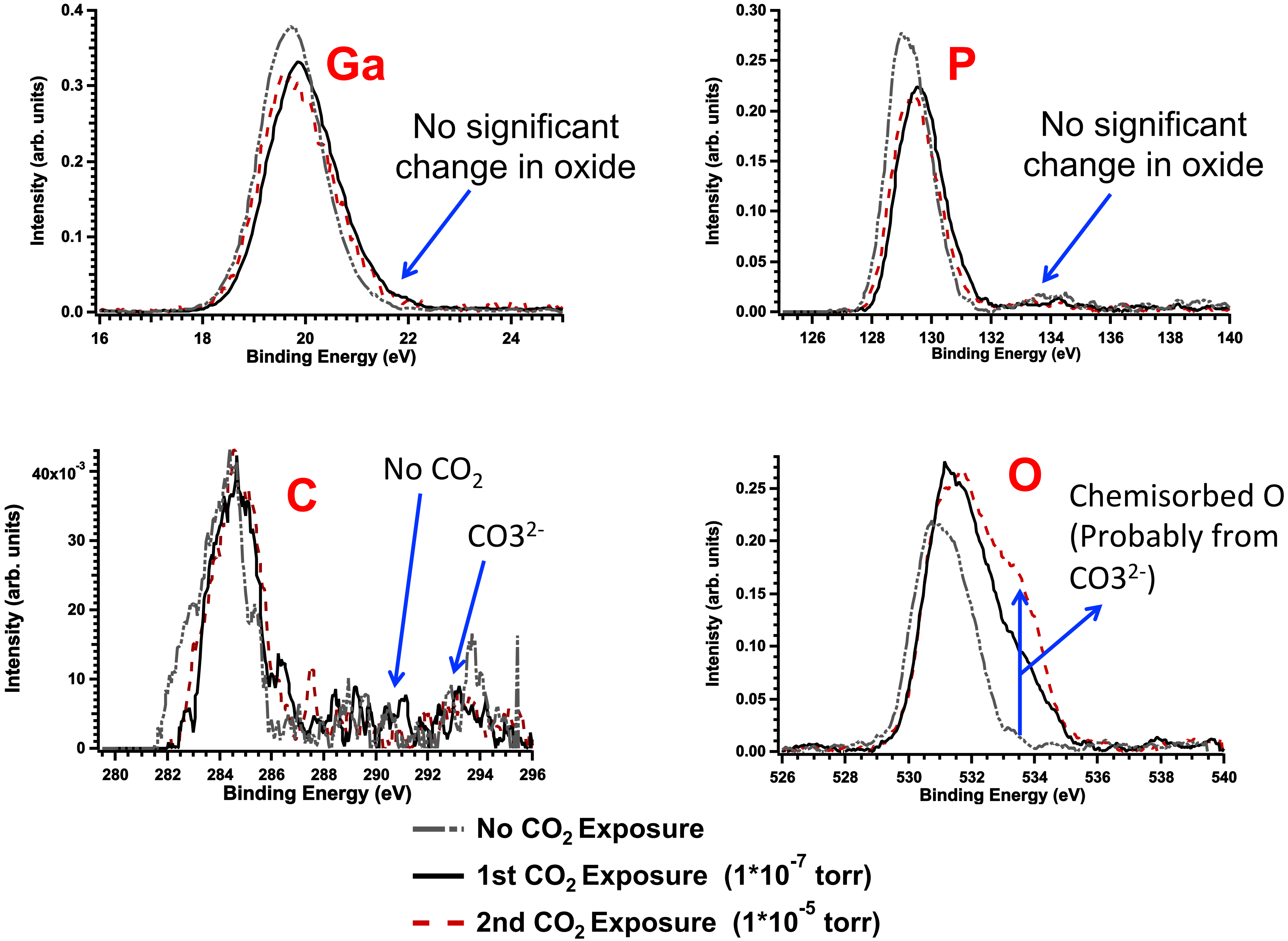
XPS Overview of GaP(111) (as is from distributor)



Cleaning GaP(111)



CO_2 Exposure on GaP(111) Surface



Conclusions

- ✧ Determined procedure for preparing atomically clean GaP
- ✧ CO_2 exposure occurs greater at higher pressure as confirmed by XPS
- ✧ CO_2 chemisorbs and forms $CO3^{2-}$ on surface

On-going/Future Studies

- ✧ Attainment of an atomically clean surface
  - ✧ Work function & “Fermi Level”
- ✧ CO_2 exposure studies
  - ✧ Longer Exposure
  - ✧ XPS and XAS of surface
  - ✧ Temperature Desorption Spectroscopy
  - ✧ Vibrational Spectroscopy (IR)
  - ✧ Ambient Pressure XPS
- ✧ Theoretical Simulations of Spectroscopic Signatures
  - ✧ DFT-based calculations of O1s, C1s XPS/XAS

Acknowledgements

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  - ✧Craig P. Schwartz
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