# Reactivity of Metal Oxalate EUV Resists as a Function of the Central Metal

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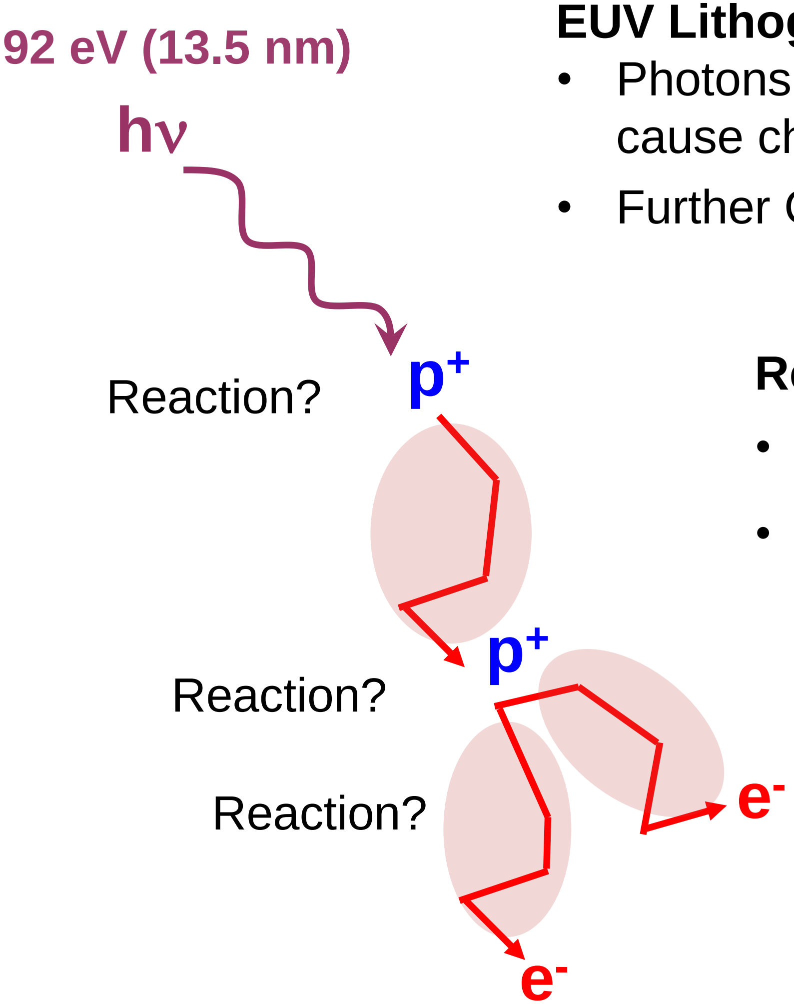
# EUV Lithography




**EUV Lithography**

- Photons liberate electrons in the resist and possibly cause chemistry to occur in the process
- Further Chemistry due to electron-resist interactions

**Resist chemistry can be improved by:**

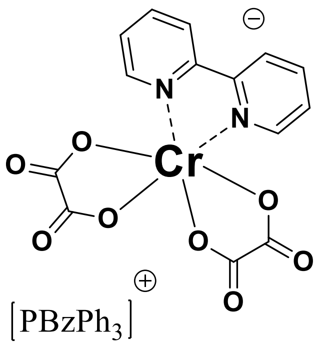
- Increasing the number of photons absorbed
- Efficient reactivity of secondary electrons

**References**

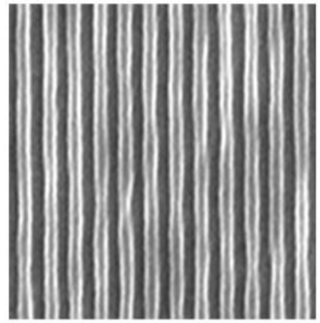
[1]T. Kozawa and S. Tagawa, *Jpn. J. Appl.Phys.*, **49 (3)** (2010) 030001.
[2]A. Narasimhan, S. Grzeskowiak, et al., *Proc. SPIE*, **9779** (2016) 97790F.
[3]J. Torok, et al., *J. Photopolym. Sci. and Technol.*, **26 (5)** (2013) 625–634.
[4]P. de Schepper, et al., *Proc. SPIE*, **9425** (2015) 942507.
[5]T. H. Fedynyshyn, et al., *Proc. SPIE*, **5039** (2003) 310.

Number of Electrons?
2-4 $e^-$/photon[1-5]

# Comparison of Metal Centers Previous Work

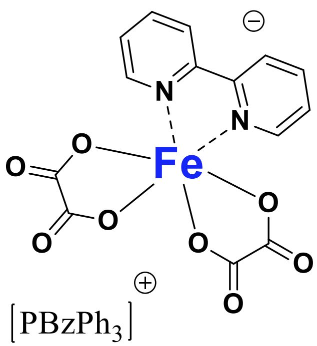



### NP4: Cr

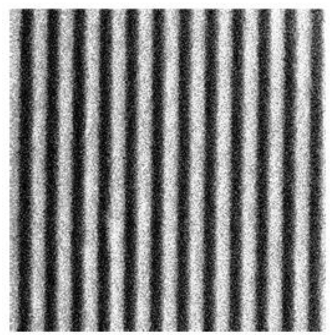


**$E_{size}$ = 70 mJ/cm$^2$**

- Number of d electrons = 3
- Oxidation State = (III)
- *Calculated EUV abs. = 5.8 μm$^{-1}$

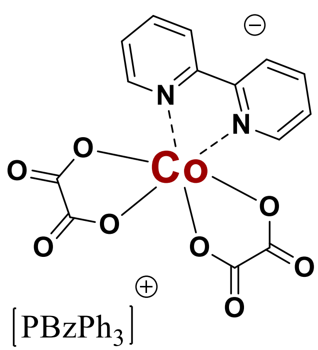



### NP3: Fe

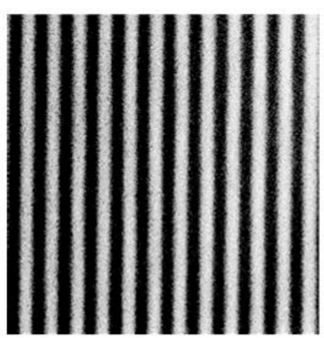


**$E_{size}$ = 48 mJ/cm$^2$**

- Number of d electrons = 5
- Oxidation State = (III)
- *Calculated EUV abs. = 6.0 μm$^{-1}$




### NP1: Co



**$E_{size}$ = 27 mJ/cm$^2$**

- Number of d electrons = 6
- Oxidation State = (III)
- *Calculated EUV abs. = 6.1 μm$^{-1}$

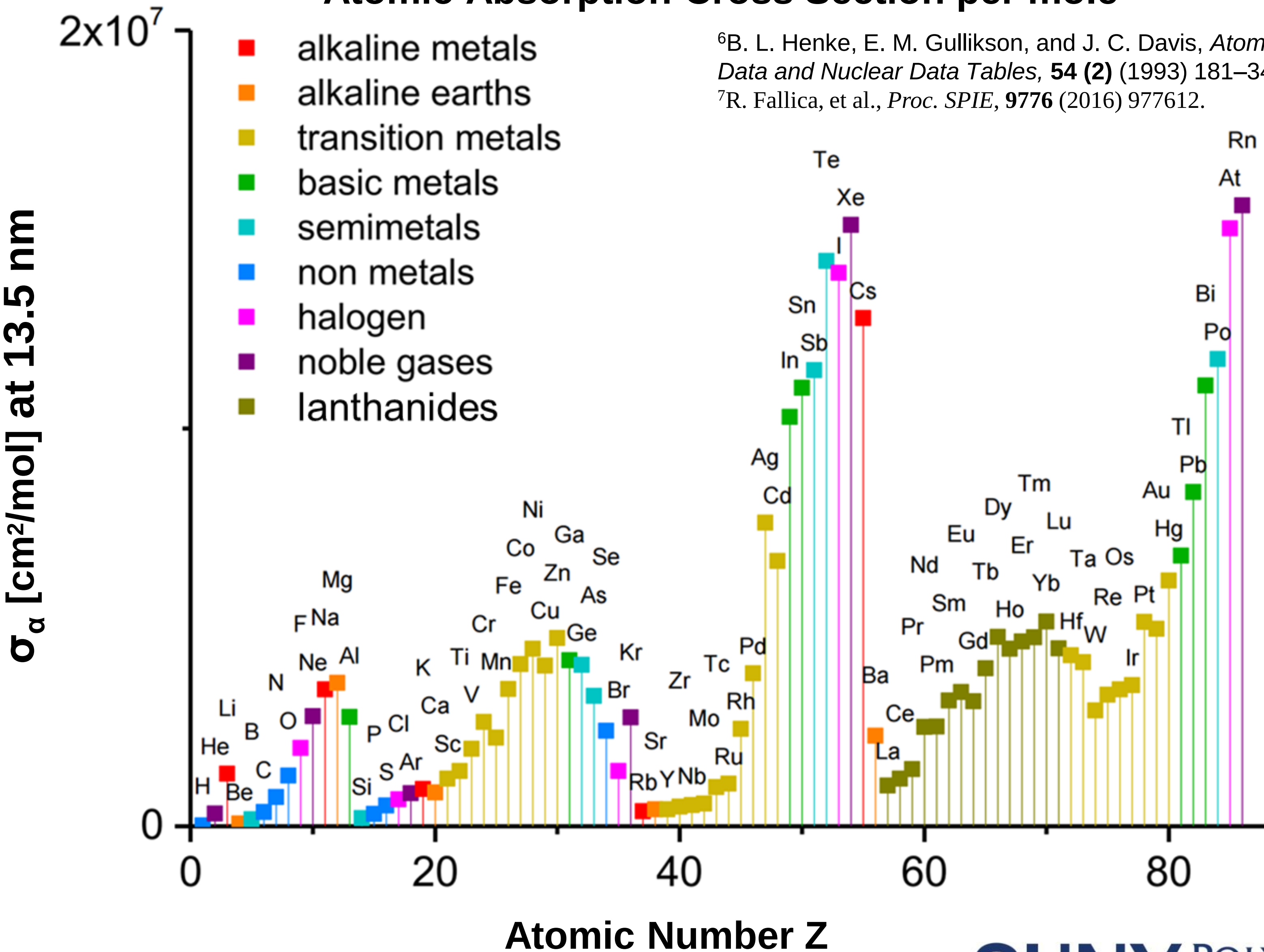
## Improved Sensitivity

**35 nm h/p lines**

*Calculated values are based on CXRO absorption using an assumed film density of 1.5 g/cm$^3$

[7]M. Marnell, et al., "***A Molecular Inorganic Approach to EUV Photoresists***", *presented at SPIE advanced lithography conference*, (February 2014), San Jose, CA.

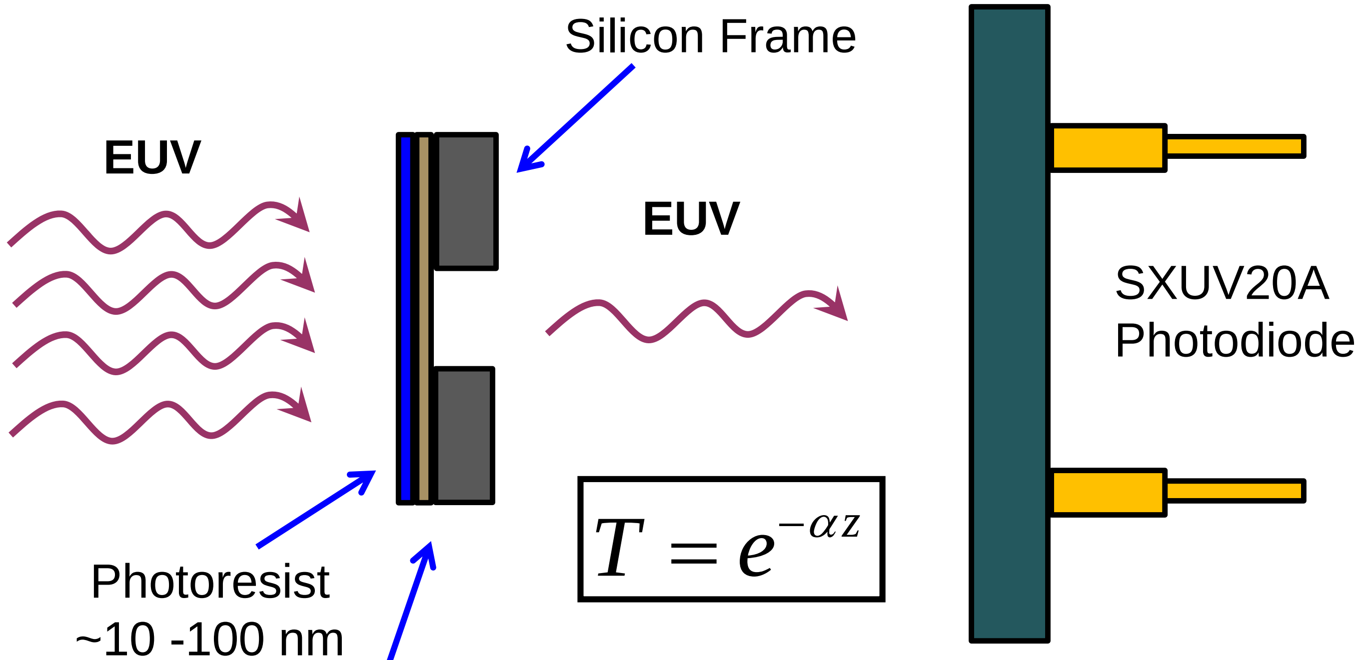
# EUV Atomic Absorption



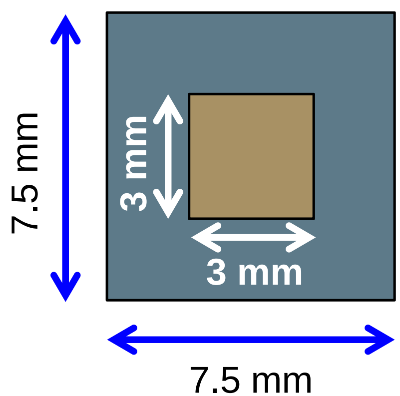

[6] B. L. Henke, E. M. Gullikson, and J. C. Davis, *Atomic Data and Nuclear Data Tables*, **54 (2)** (1993) 181–342.
[7] R. Fallica, et al., *Proc. SPIE*, **9776** (2016) 977612.

# EUV Absorption Measurements

EQ-10M
EUV Source



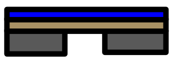

$$T = e^{-\alpha z}$$



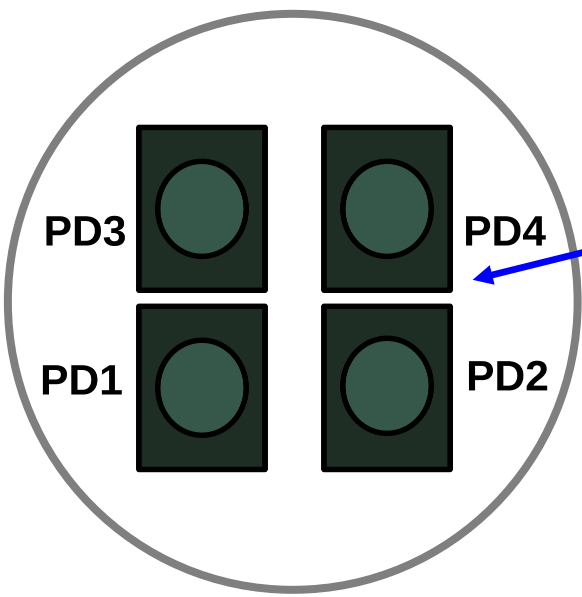

- Silicon nitride membranes used were 100 nm thick with a 525 µm thick silicon frame.
- SXUV20A photodiodes are coated with 100 nm zirconium and 200 nm silicon.
- A ~100 nm zirconium filter is used to block undesired wavelengths of light.

# EUV Absorption Experimental Design

- Measure relative transmission at identical times to avoid pulse to pulse variations.
- Resist thicknesses on the membrane are measured using a J. A. Woollam M-2000 fixed angle ellipsometer equipped with Complete Ease software.

 = $Si_3N_4$ Membrane + Material

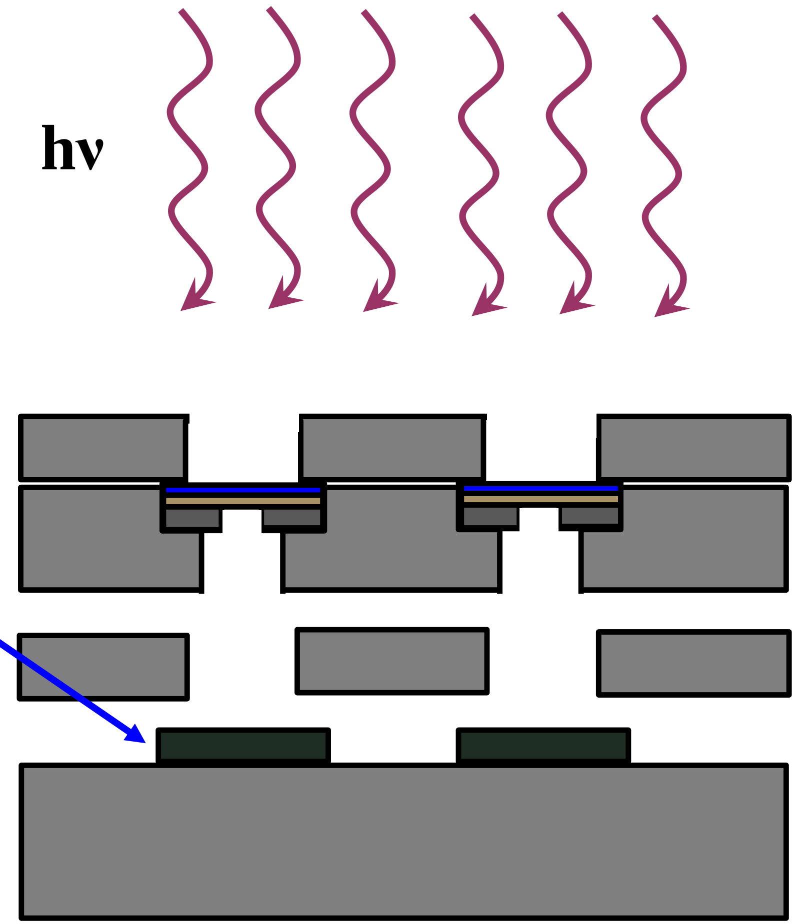
## Top Down View of Photodiodes



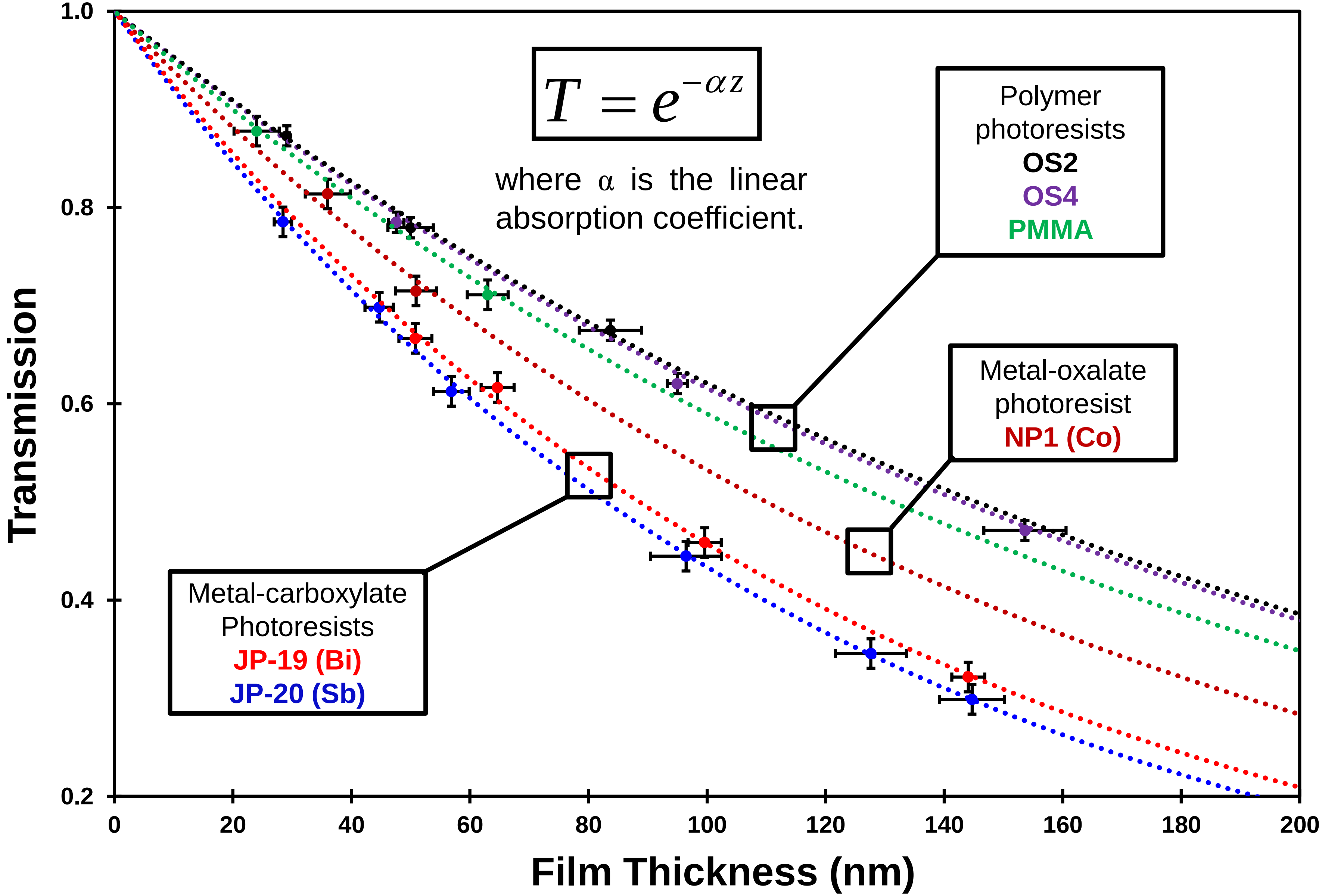

**SXUV20A Photodiodes**

## Cross-Sectional Side View

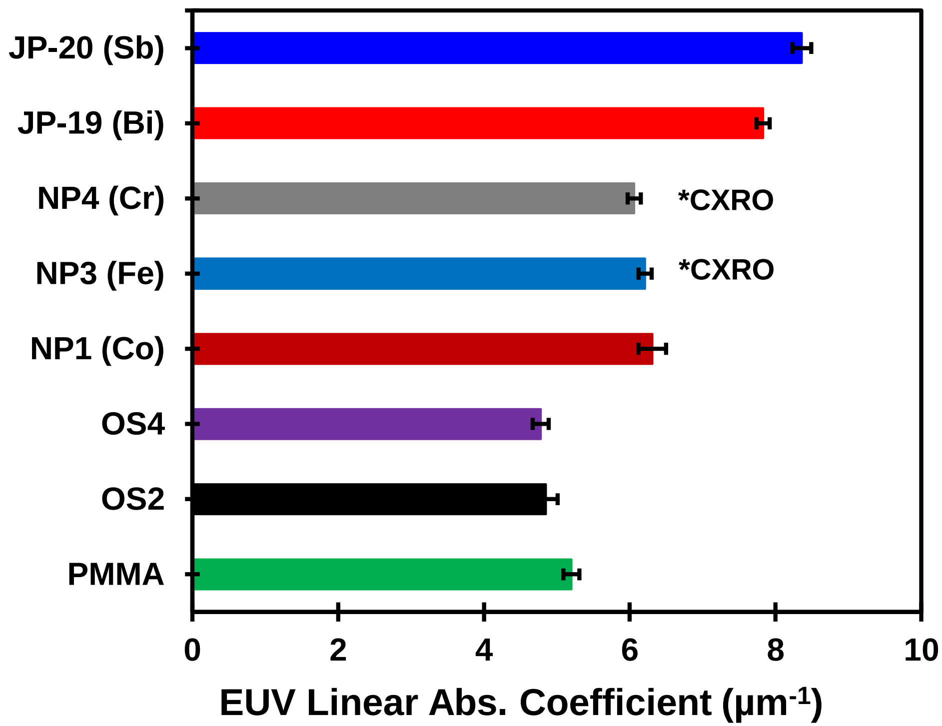
**EUV (13.5 nm)**



# EUV Absorption Measurements



# EUV Linear Absorption Coefficients




- Comparing the three metal oxalates (NP1, NP3, and NP4), there is only a small change in EUV absorption.
- Consequently, there must be very different reactivities to account for the change in sensitivity.

- Traditional photoresists have abs. coefficient of typically 5 $um^{-1}$.

***EUV linear absorption coefficients for NP3 and NP4 are based on the measured value of NP1 and the CXRO database.**

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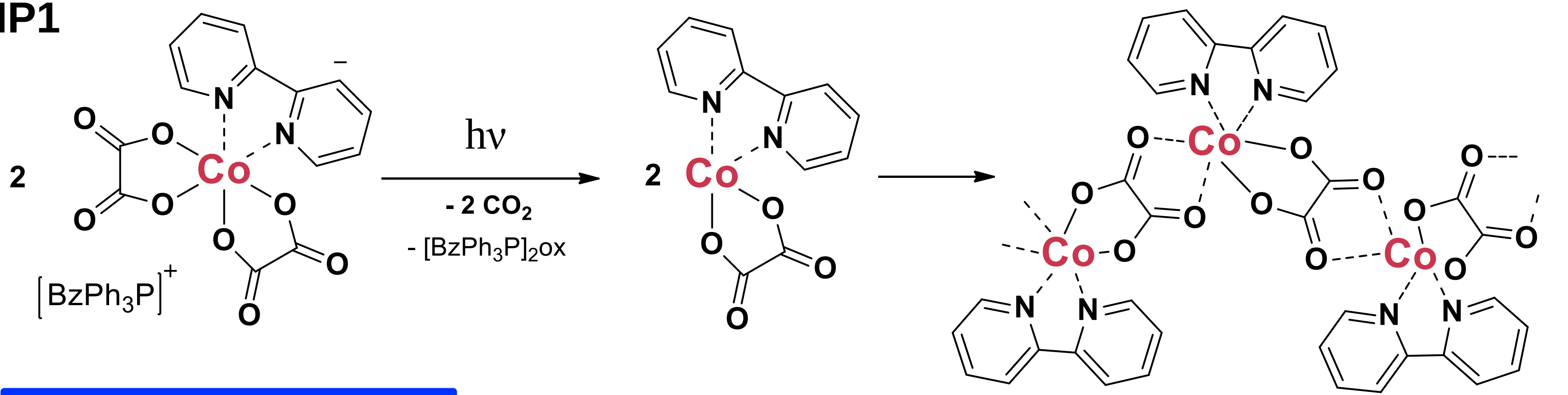
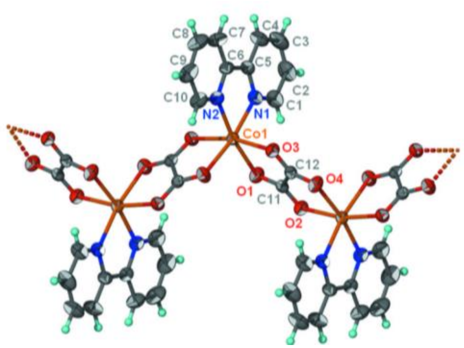
# Molecular Organometallic Resists for EUV (MORE): Cobalt Compound (NP1)

## Current understanding of photo-mechanism:

**NP1**



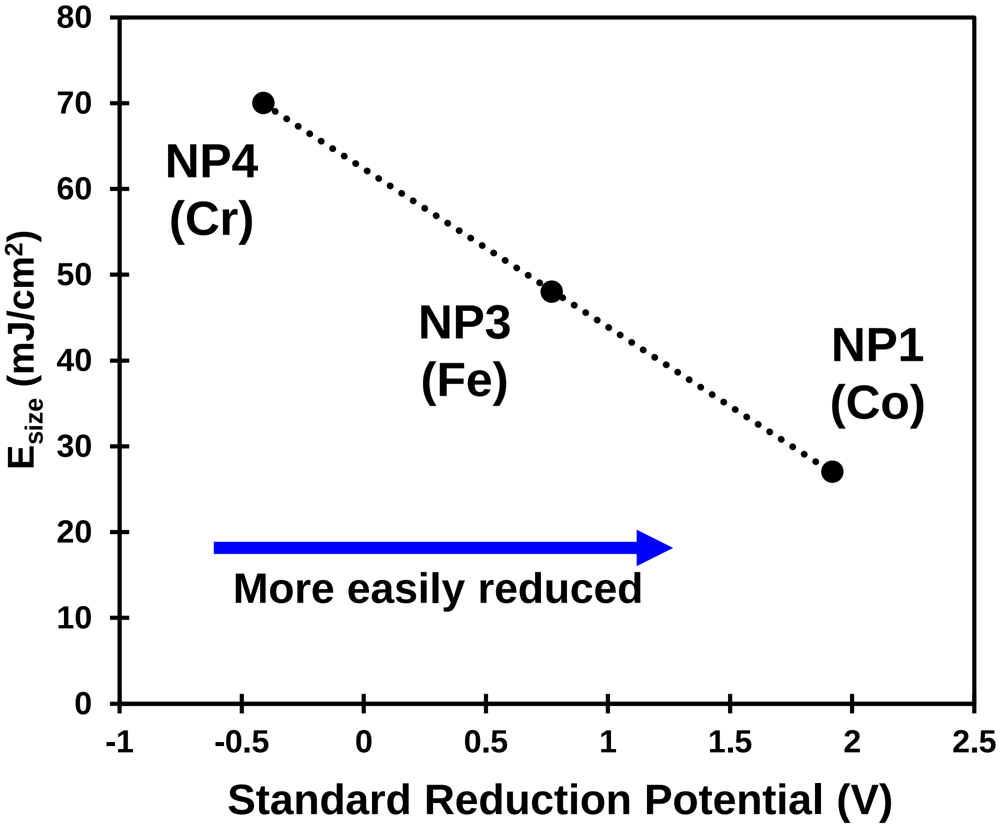

**Co(II)(bpy)(ox)**



*Acta Crystallographica, Section E: Structure Reports Online* **65 (10)** (2009).

- Upon Exposure to EUV light or electrons $CO_2$ is generated and outgassed from the resist.
- The photoproduct, Co(II)(bpy)(ox), is a coordination polymer that polymerizes through bridging oxalate ligands.
- This bridging occurs when one of the oxalate ligands is eliminated as $CO_2$

# $E_{size}$ *vs.* Metal Center Redox Potential



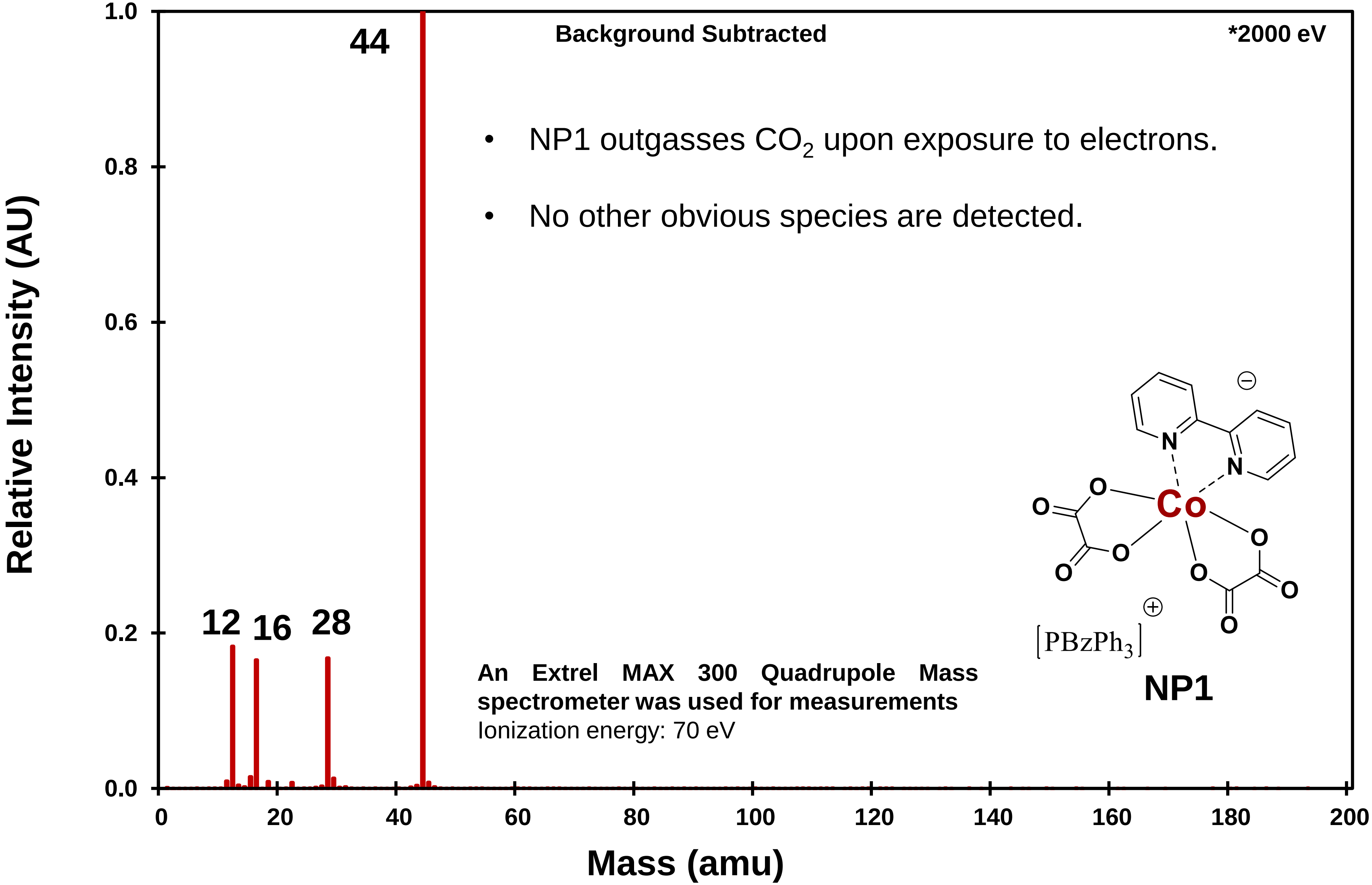

Literature Values[8-12]

| Metal Reduction from (III to II) | Standard Redox Potential (V) |
|---|---|
| $Co^{3+} + e^- \rightleftarrows Co^{2+}$ | +1.92 |
| $Fe^{3+} + e^- \rightleftarrows Fe^{2+}$ | +0.77 |
| $Cr^{3+} + e^- \rightleftarrows Cr^{2+}$ | -0.41 |


[8]D. R. Lide (Editor-in-Chief), "***CRC Handbook of Chemistry and Physics, 83rd edition***," *CRC Press,* (2002-2003).
[9]Nobuyuki Tanaka, and Michio Nanjo, "***The Thermal Decomposition of Metal Oxalato Complexes***." *Bull. Chem. Soc. Jpn.* **40 (2)** (1967) 330-333.
[10]A. J. Bard, R. Parsons, and J. Joseph, "***Standard potentials in aqueous solution***," *CRC Press* **6**, (1985).
[11]G. Milazzo and S. Caroli, "***Tables of Standard Electrode Potentials***," *Analytica Chimica Acta* **105** (1979) 459.
[12]D. C. Harris, "***Quantitative chemical analysis***, ***8th edition***," *Macmillan* (2010).


- There appears to be a correlation between the reducibility of the metal and $E_{size}$.
- **Hypothesis:** There may be a correlation between reducibility of the metal and $CO_2$ outgassing based upon the photo-mechanism.

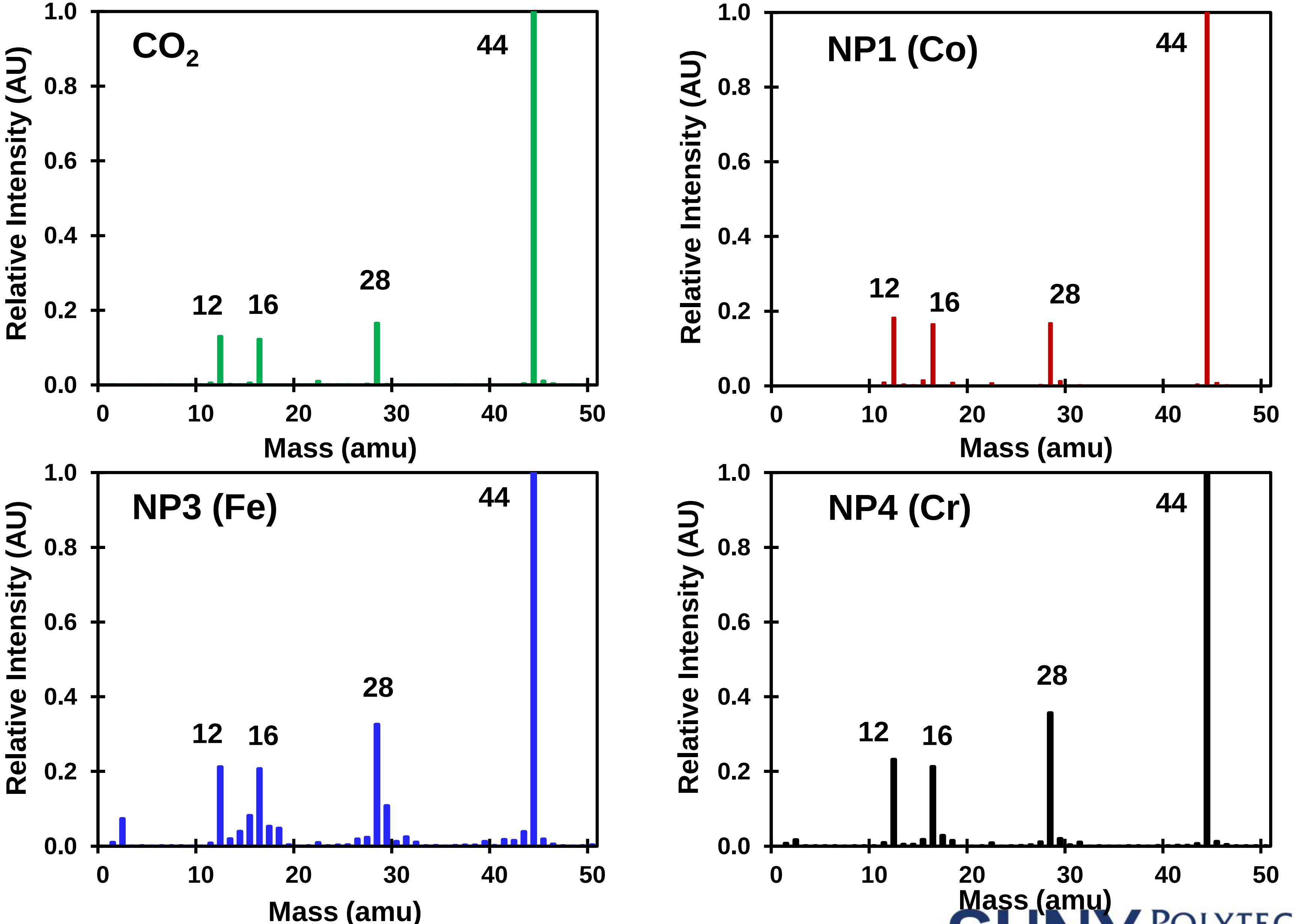
# Outgassing Spectrum of NP1 (electrons)




- NP1 outgasses $CO_2$ upon exposure to electrons.
- No other obvious species are detected.

**An Extrel MAX 300 Quadrupole Mass spectrometer was used for measurements**
Ionization energy: 70 eV

# Outgassing Spectra (electrons)

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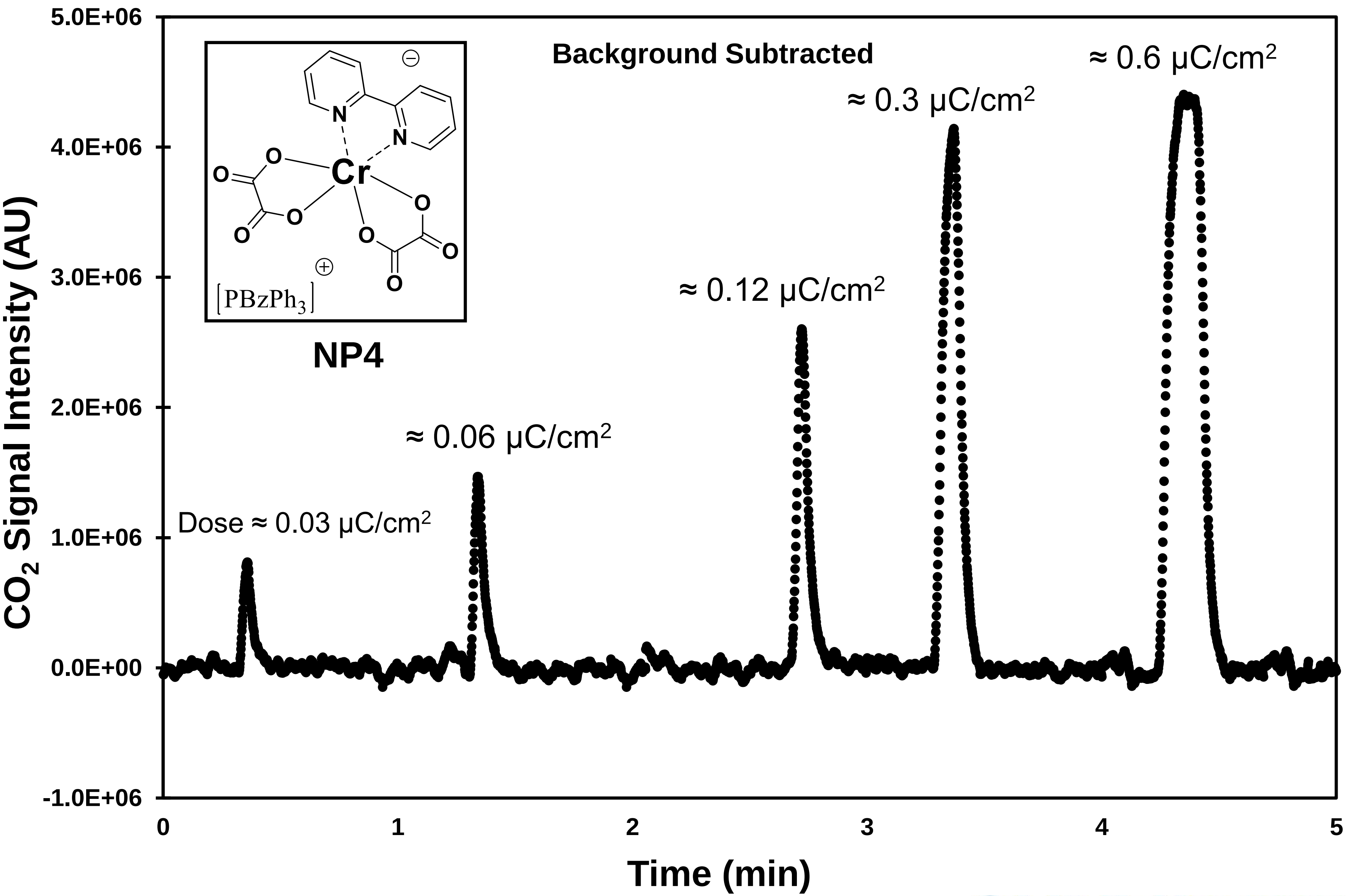
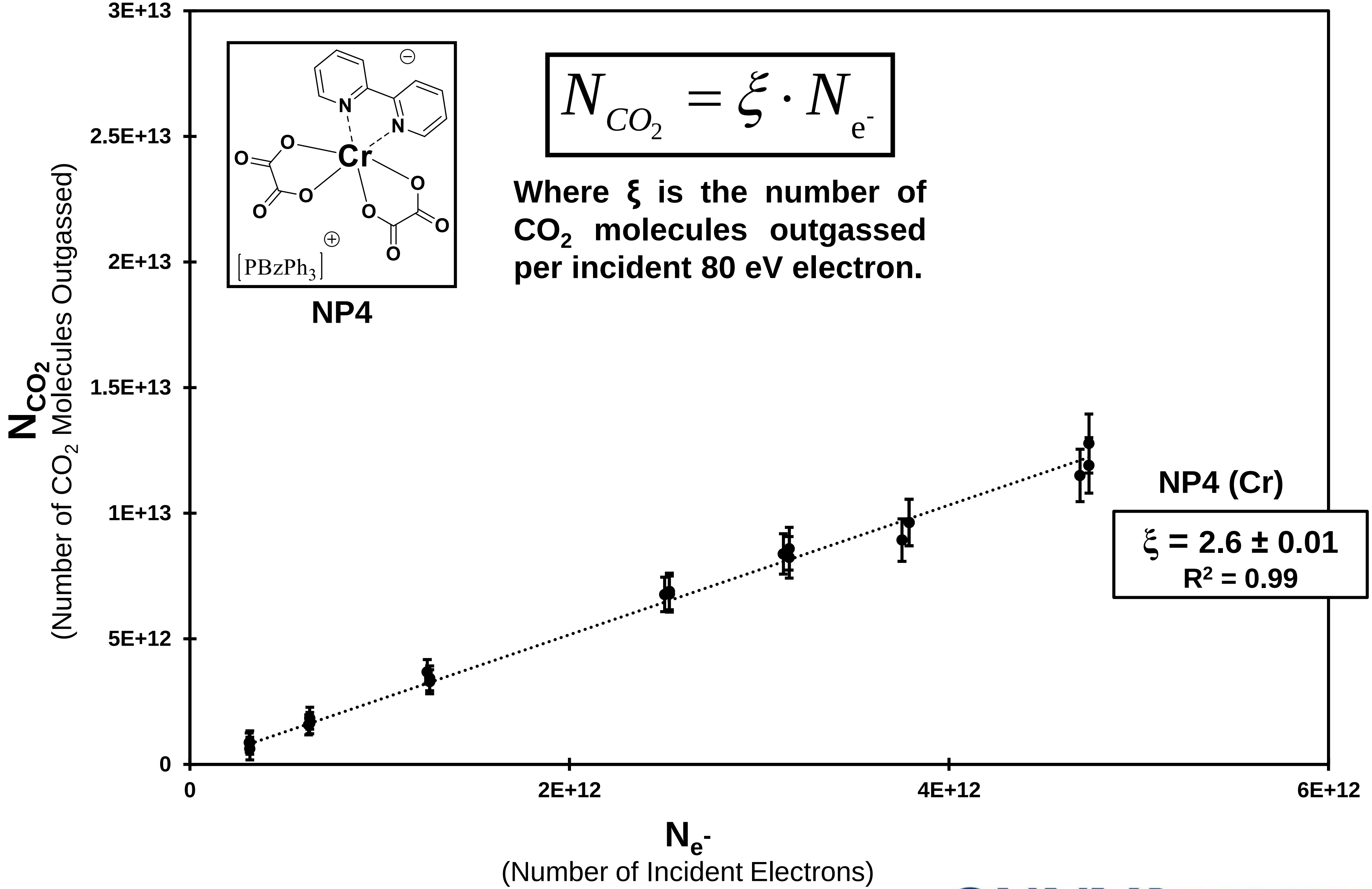
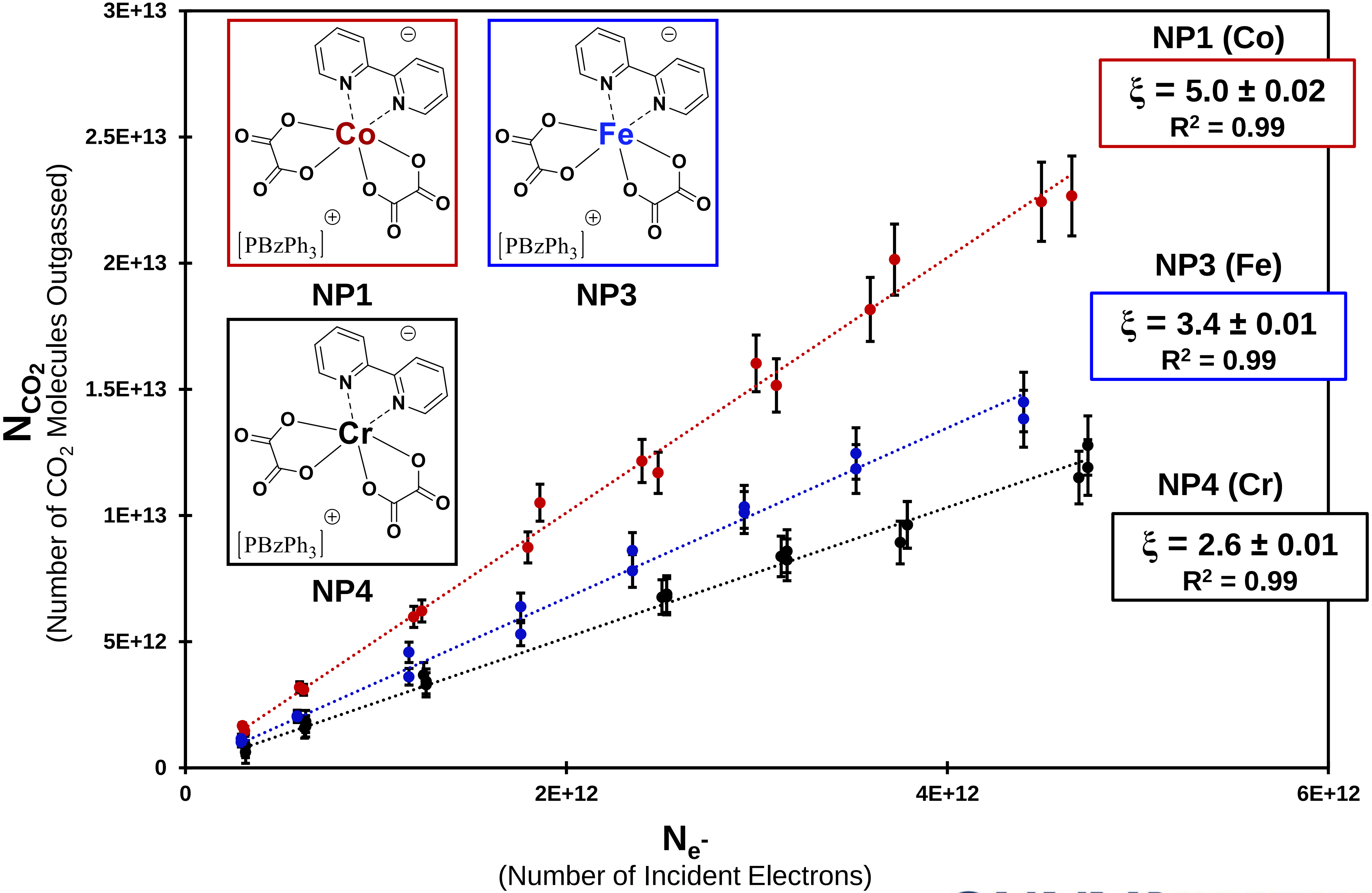
# $CO_2$ Outgassing Signal NP4: 80 eV Electrons



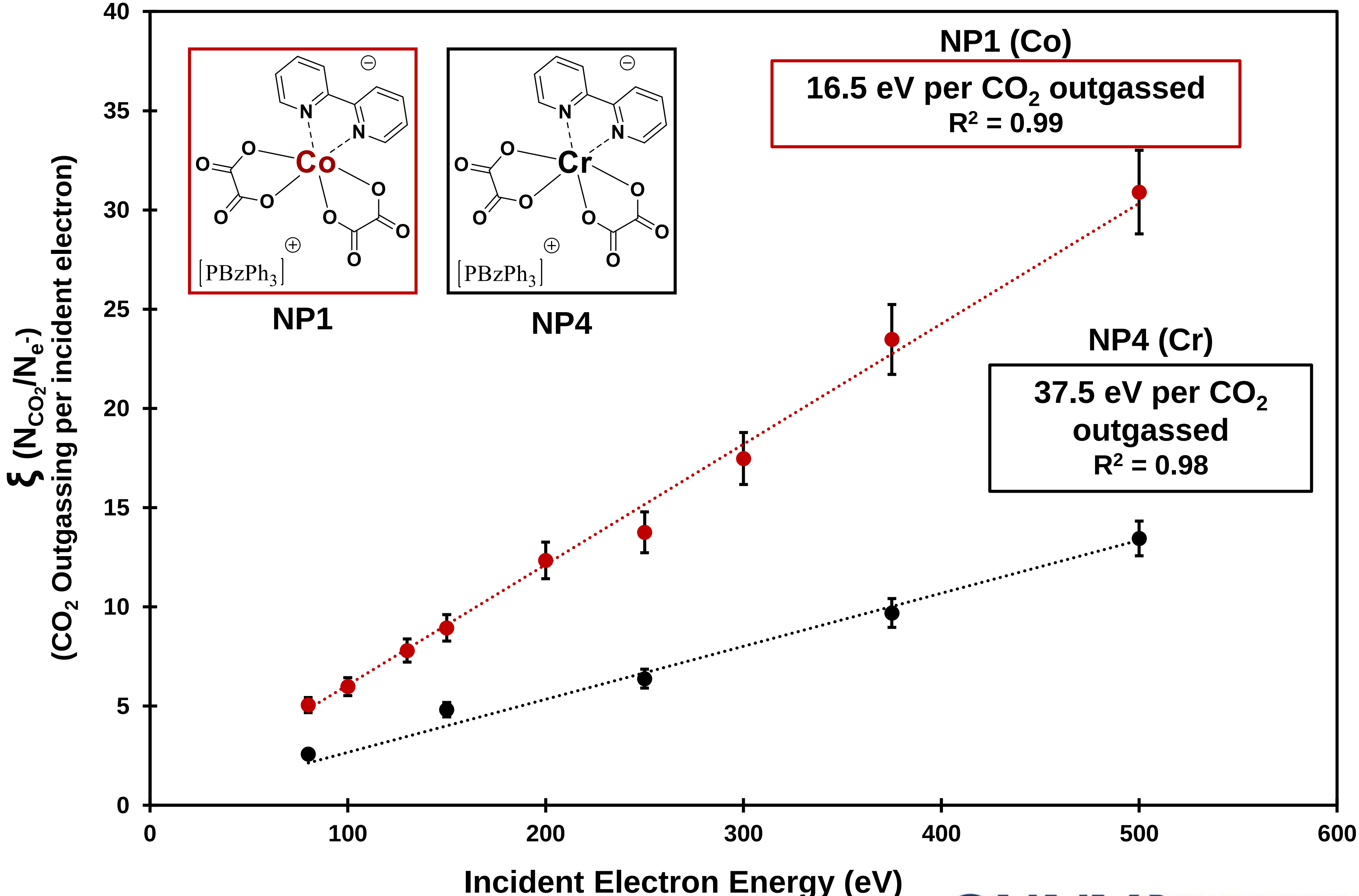
# $CO_2$ Liberated per Incident Electron: 80 eV



# $CO_2$ Liberated per Incident Electron: 80 eV



# $CO_2$ Outgassing *vs.* Electron Energy

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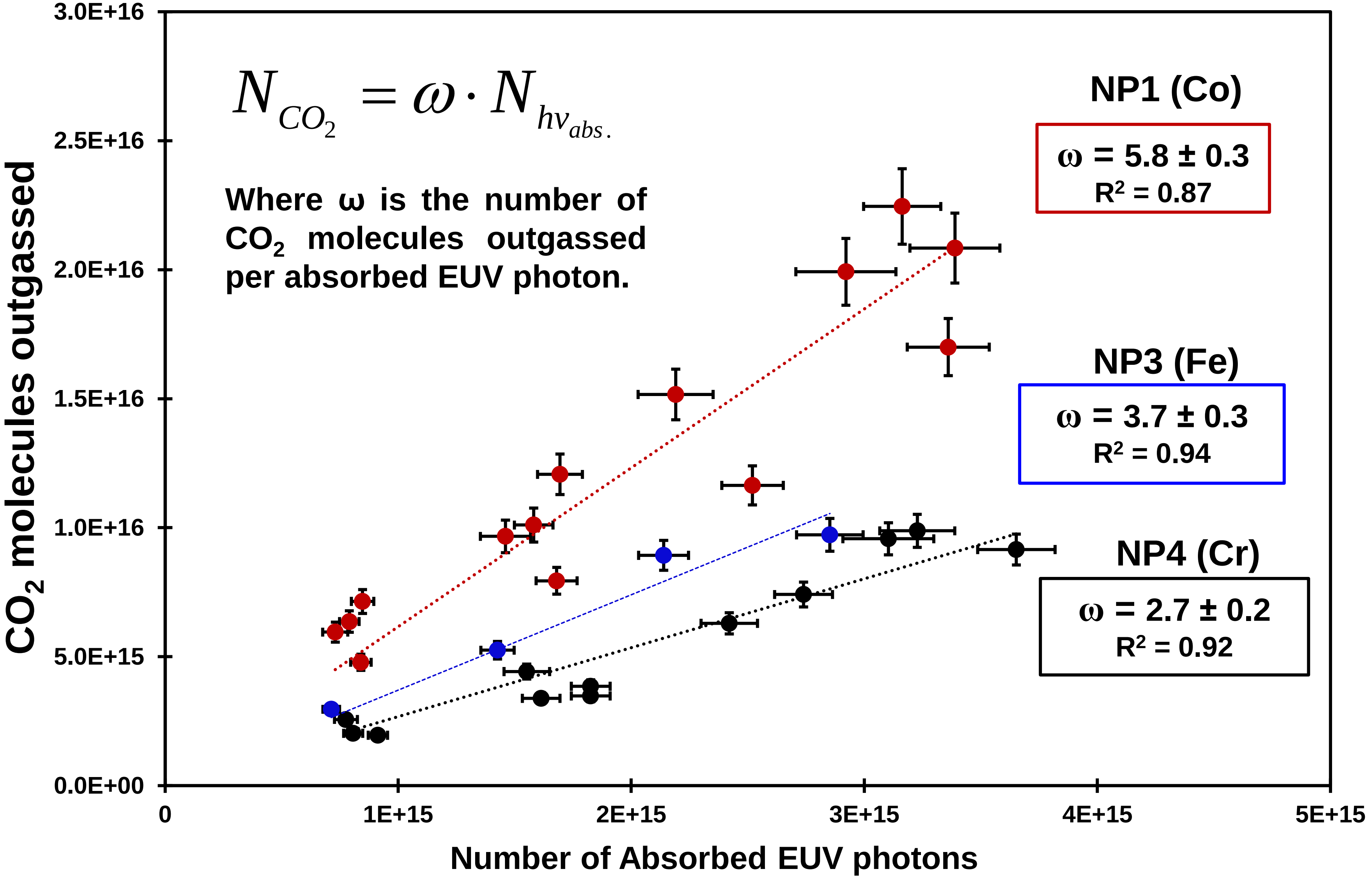
# $CO_2$ Liberated per Absorbed EUV Photon

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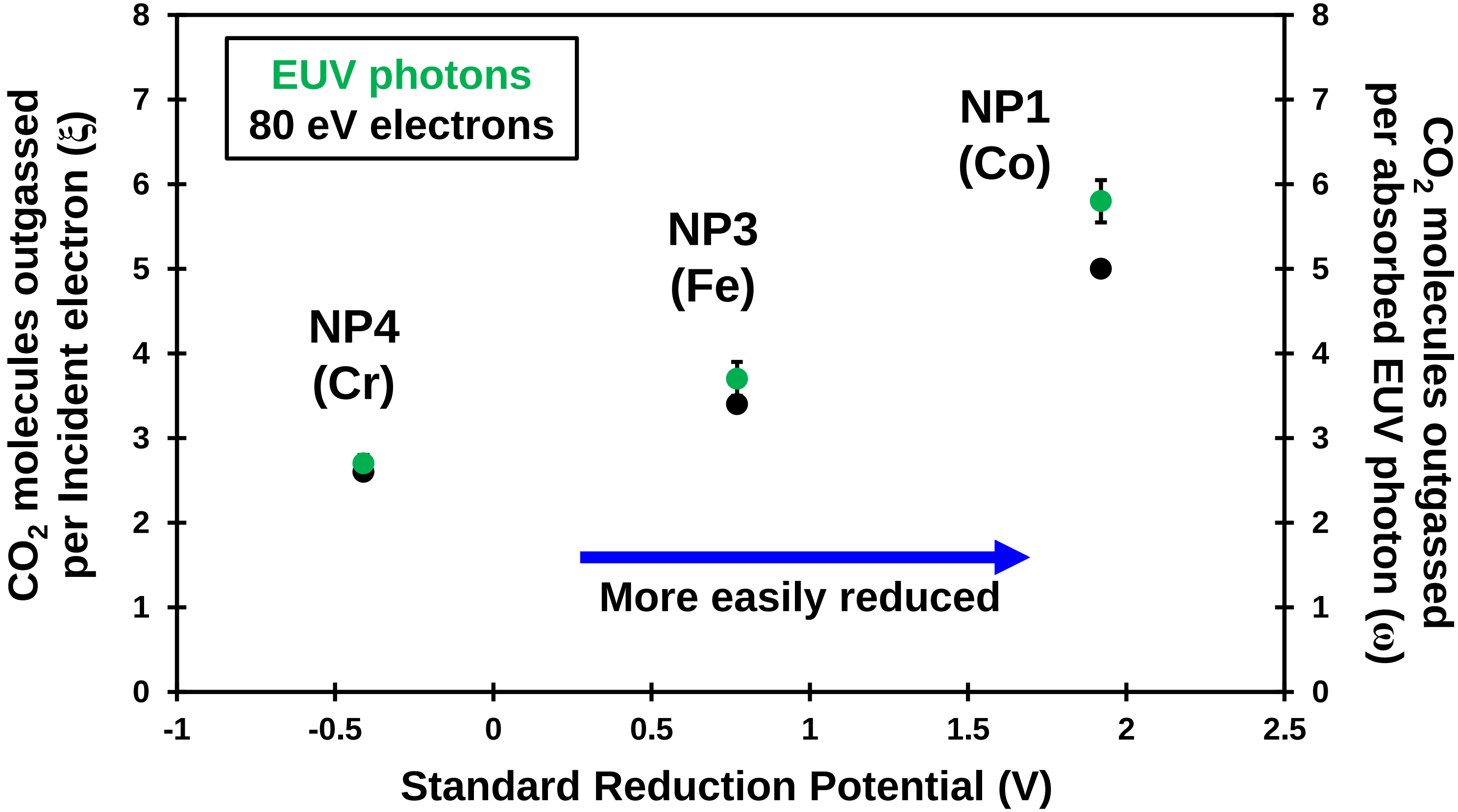
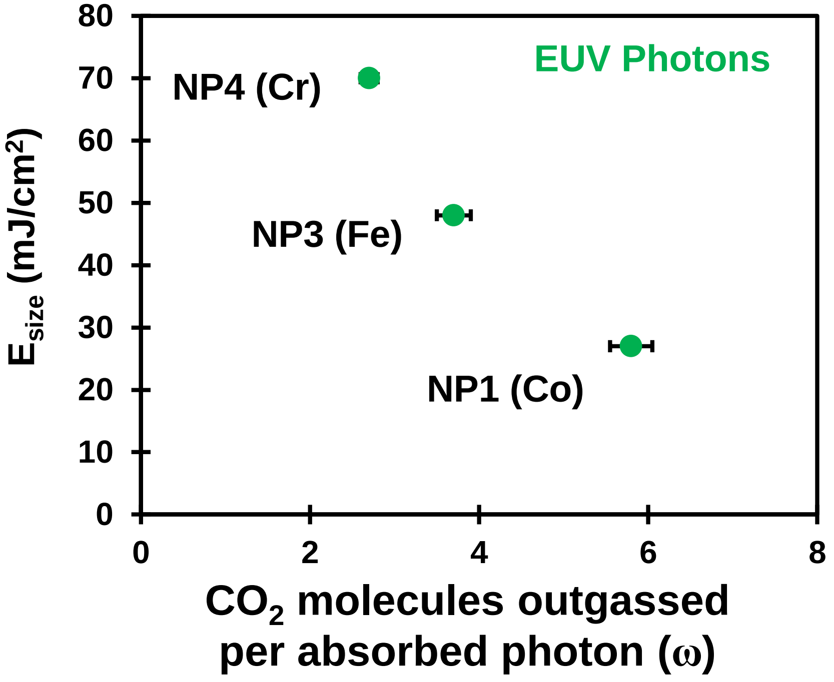
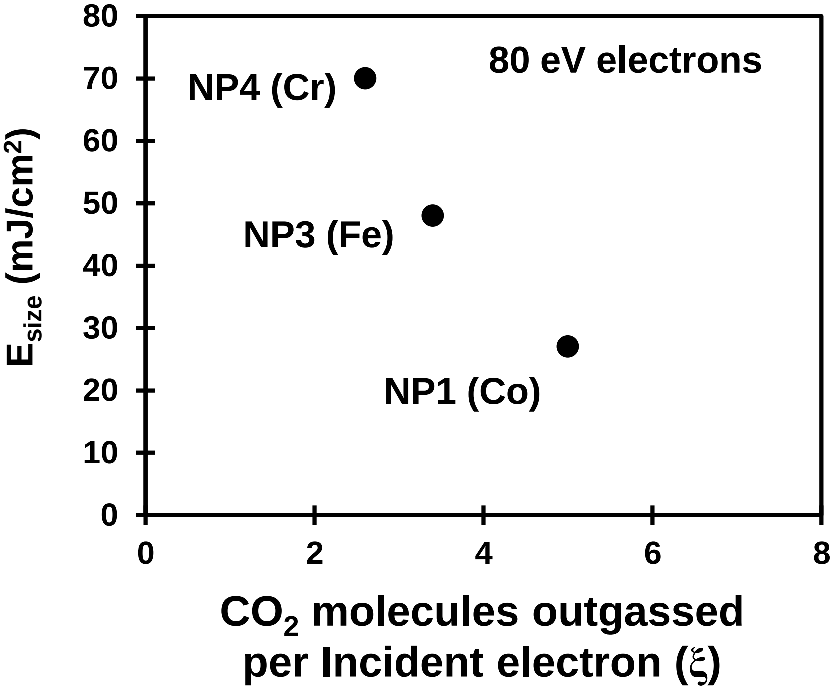
# $CO_2$ Outgassing *vs. Metal Reducibility*




- More easily reduced molecule outgasses more $CO_2$.
- This could explain the change in $E_{size}$ when varying the central metal.

# Conclusions




- Between the three photoresists, a small change in EUV absorption does not account for the large change in $E_{size}$.
- Based upon our understanding of the photo-mechanism increased $CO_2$ outgassing should improve sensitivity.
- The rate of $CO_2$ outgassing seems to be correlated to the reducibility of the central metal.

# Acknowledgements

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