# Anion Photoelectron Spectroscopy of $NbW^-$ and $W_2^-$

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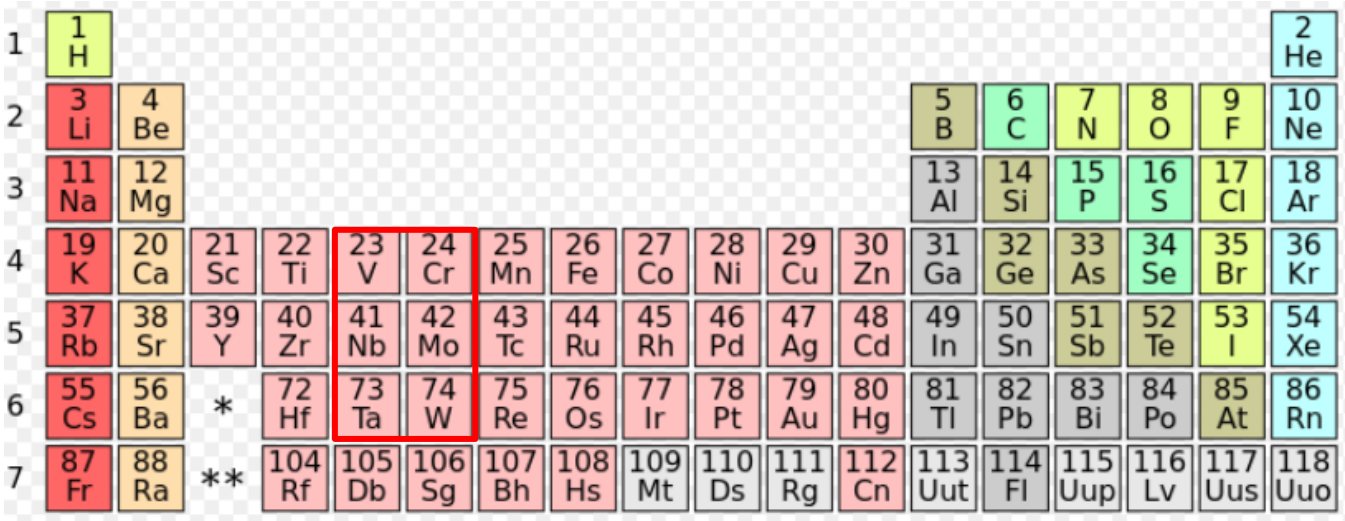
6-23-2015

# Why NbW and $W_2$?




V: $3d^3 4s^2$

Nb: $4d^4 5s^1$

Ta: $4f^{14} 5d^3 6s^2$

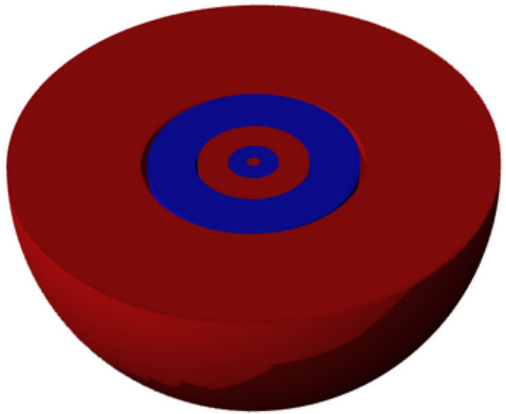
Cr: $3d^5 4s^1$

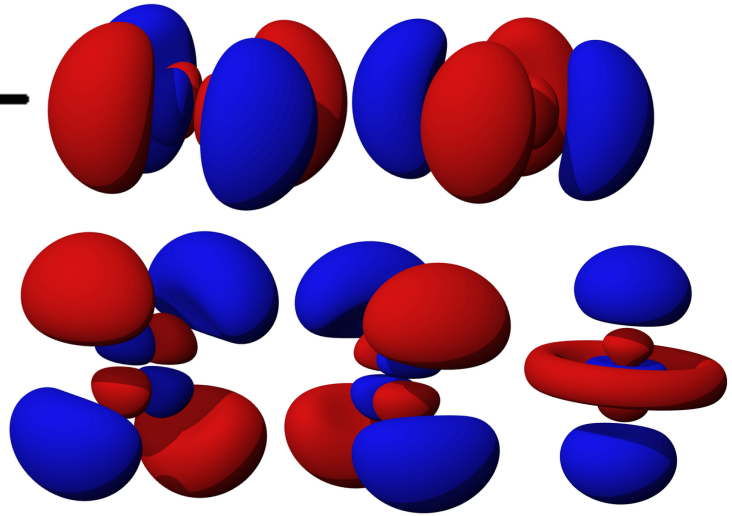
Mo: $4d^5 5s^1$

W: $4f^{14} 5d^4 6s^2$

Nb: 4d: ↿ ↿ ↿ ↿ —

5s: ↿





# High Order Bonding

$W_2$: Formal Bond Order of 6 W  W

NbW: Formal Bond Order of 5.5

Group V and VI metal dimers:

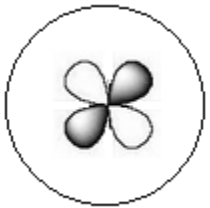
High bond orders, low force constants

e.g., $Cr_2$: 3.54 mdyn/ Å

HCl: 4.80 mdyn/ Å CO: 18.6 mdyn/ Å

# Orbital Overlap

In metal-metal bonding, participating s-orbitals have much larger radial extents than d-orbitals



| e.g. | $Cr_2$ | $W_2$ |
|---|---|---|
| Bond Length: | 1.68 Å | 2.05 Å * |
| | $\langle r_{3d} \rangle$ = 0.75 Å | $\langle r_{5d} \rangle$ = 1.08 Å |
| | $\langle r_{4s} \rangle$ = 2.00 Å | $\langle r_{6s} \rangle$ = 1.80 Å |

*calculated

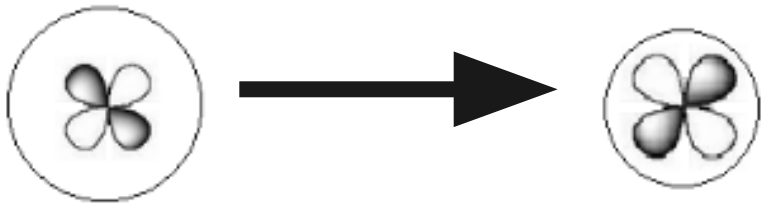
*Desclaux, J. P. Atomic Data and Nuclear Data Tables, 12, 311-406 (1973)*

*Kraus, D.; Lorenz, M.; Bondybey, V. E., PhysChemComm, 2001, 4, 44-48*

# Relativistic Effects in Heavy Atoms

Electrons near nucleus (s and p orbitals) reach relativistic speeds, contracting the orbital

Electrons in d and f orbitals become more shielded and expand

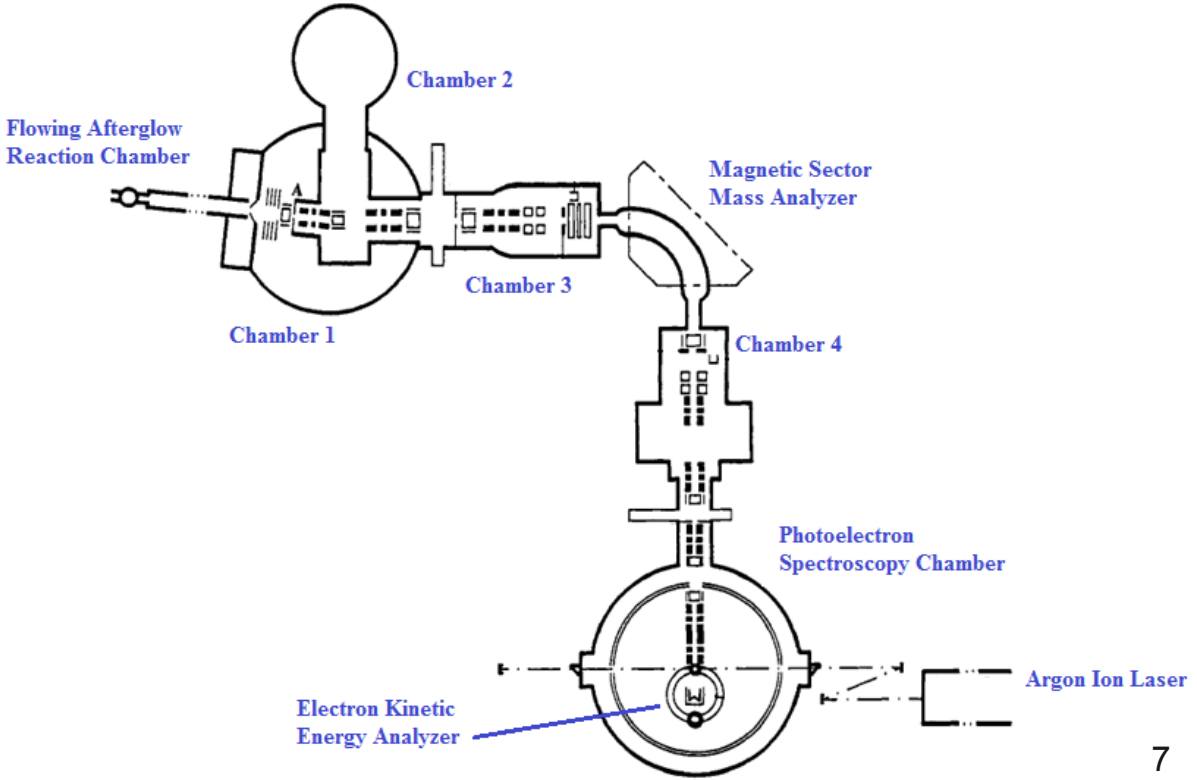


# Minnesota Anion Photoelectron Spectrometer - MAPES

Nb or W cathode

$W(CO)_6$ added to flow tube

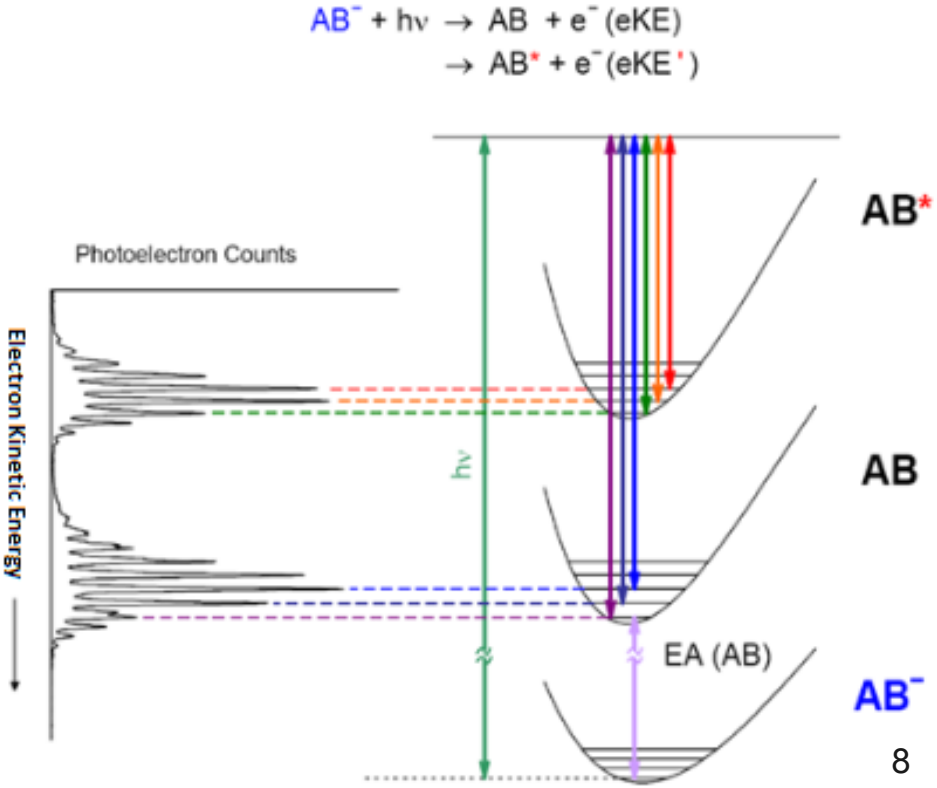
488 nm argon ion laser



# Anion Photoelectron Spectroscopy

$AB^- + h\nu \rightarrow AB + e^-$

Transitions from anion to neutral



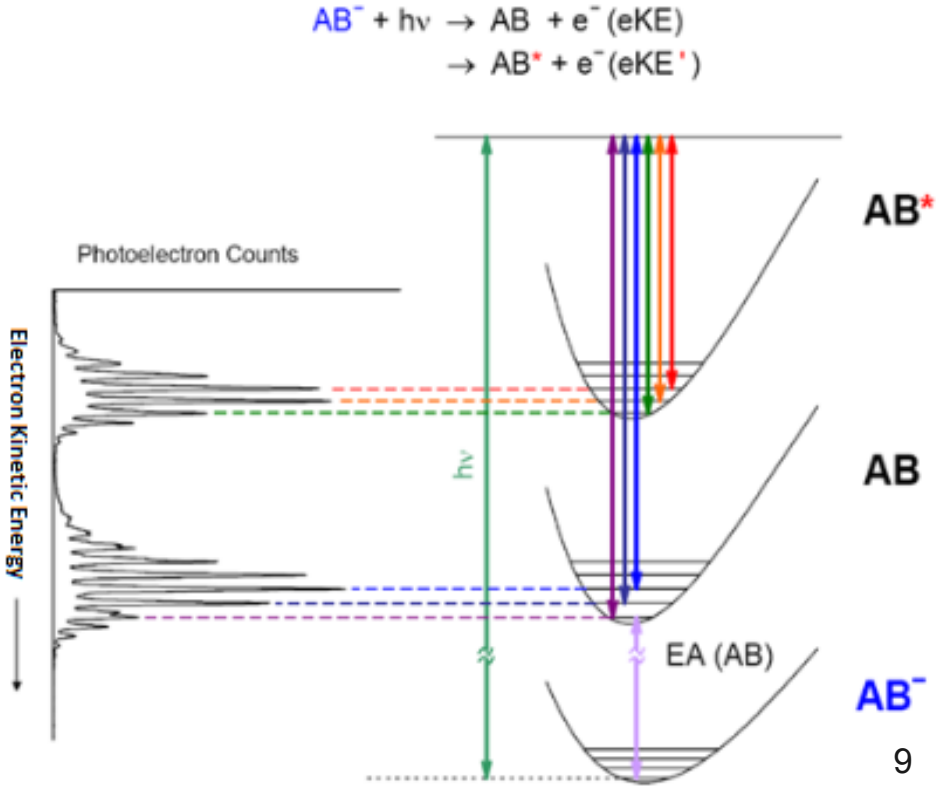
# Anion Photoelectron Spectroscopy

$AB^- + h\nu \longrightarrow AB + e^-$

eBE = hv - eKE

eBE: electron binding energy

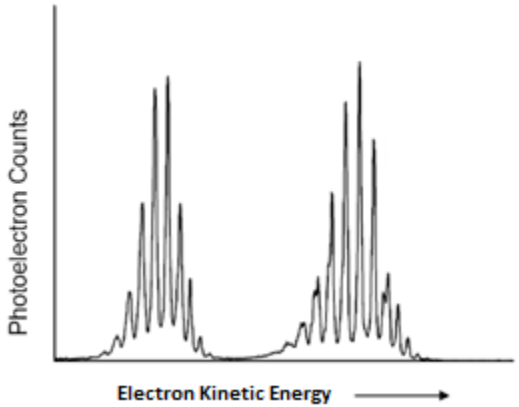
eKE: electron kinetic energy



# Anion Photoelectron Spectroscopy

Franck-Condon Fitting:

- Vibrational Frequencies
- Electron Affinities
- Energies of Excited States
- Changes in Bond Length



# Computational Interest in APES Information

Computational Methods -

Struggle with metal-metal bonding

Experimental results provide model for testing new computational methods

# $W_2$ - Previous Work

| | DFT Calculations | CASSCF/CASPT2 Calculations | Experiment |
|---|---|---|---|
| Electron Affinity | 1.07-1.18 eV | n/a | 1.46 eV |
| Vibrational Frequency | 388-410 $cm^{-1}$ | 354 $cm^{-1}$ | 337 $cm^{-1}$ |


*Z.J. Wu, X.F. Ma / Chemical Physics Letters 371 (2003) 35–39*

*Sun, X.; Du, J.; Zhang, P.; Jiang, G. J. Clust. Sci. (2010)* ***21****:619-636*

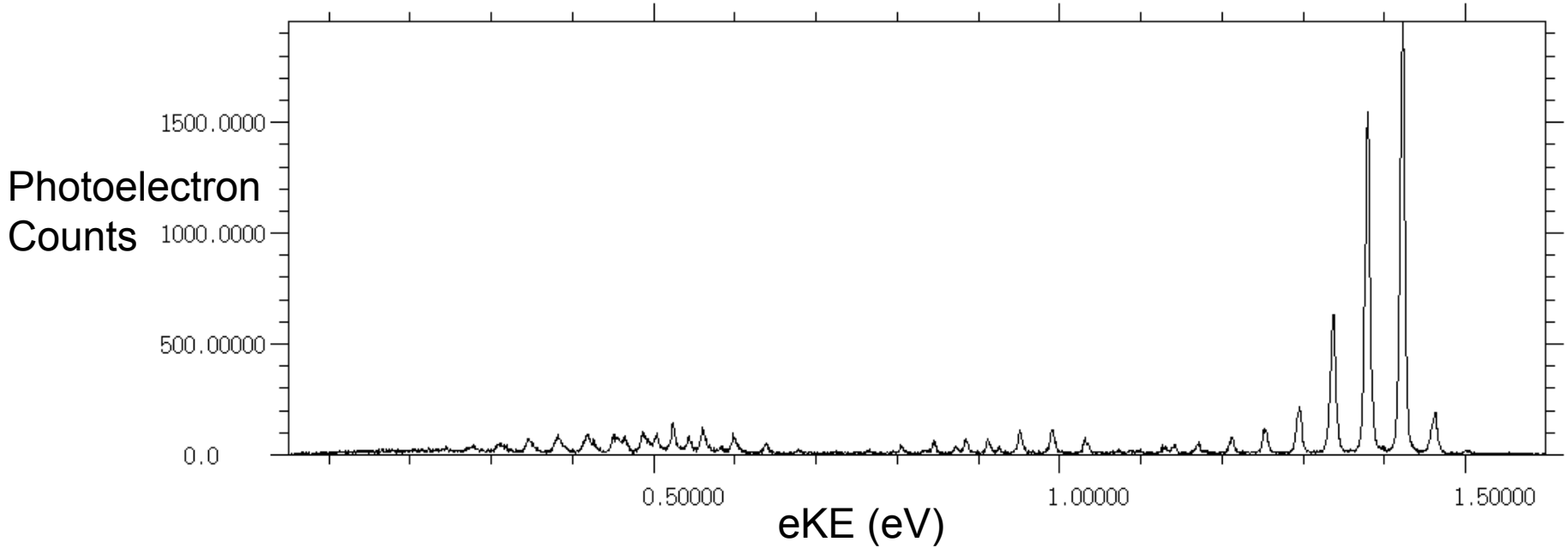
*Z.J. Wu / Chemical Physics Letters 370 (2003) 510–514*

*A. C. Borin, J. P. Gobbo, B. O. Roos (2010). Chem. Phys. Lett.,* ***490****, 24 - 28*

*H. Weidele et al. / Chemical Physics Letters 237 (1995) 425–431*

*Hu, Z.; Dong, J.-G.; Lombardi, J. R.; Lindsay, D. M.* ***J. Chem. Phys.*** *97 (11) 1992, 8811-8812*

# $W_2$ - Tungsten Dimer Photoelectron Spectrum



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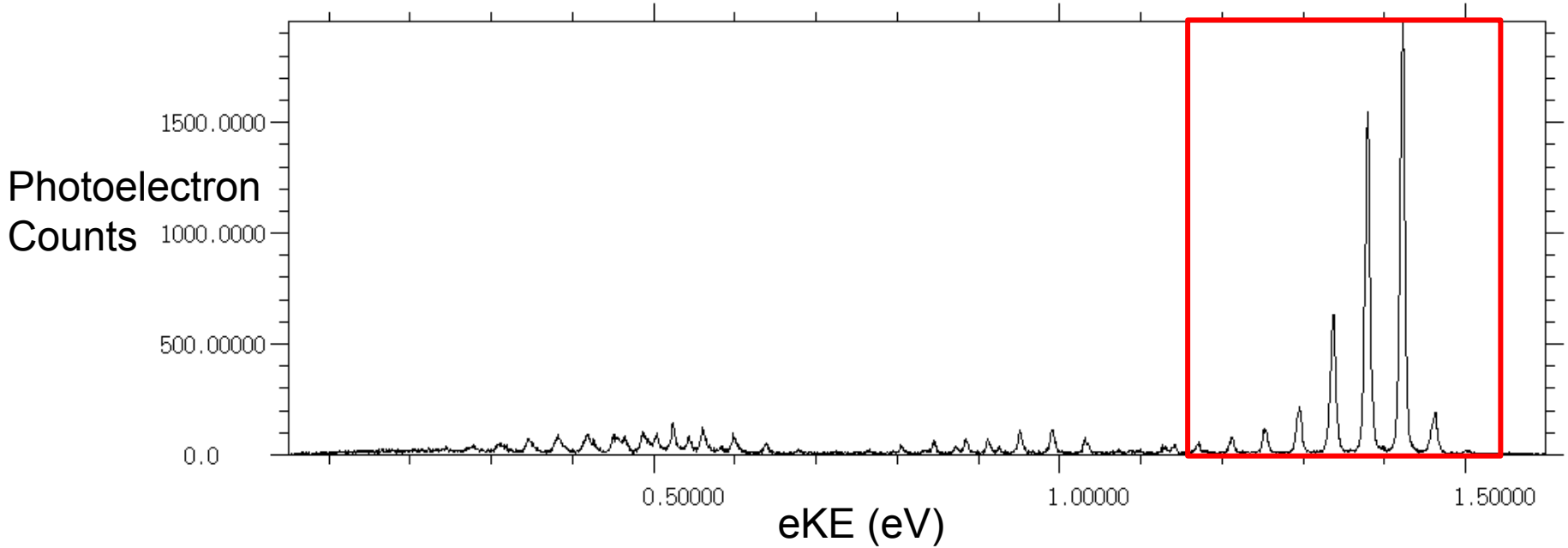
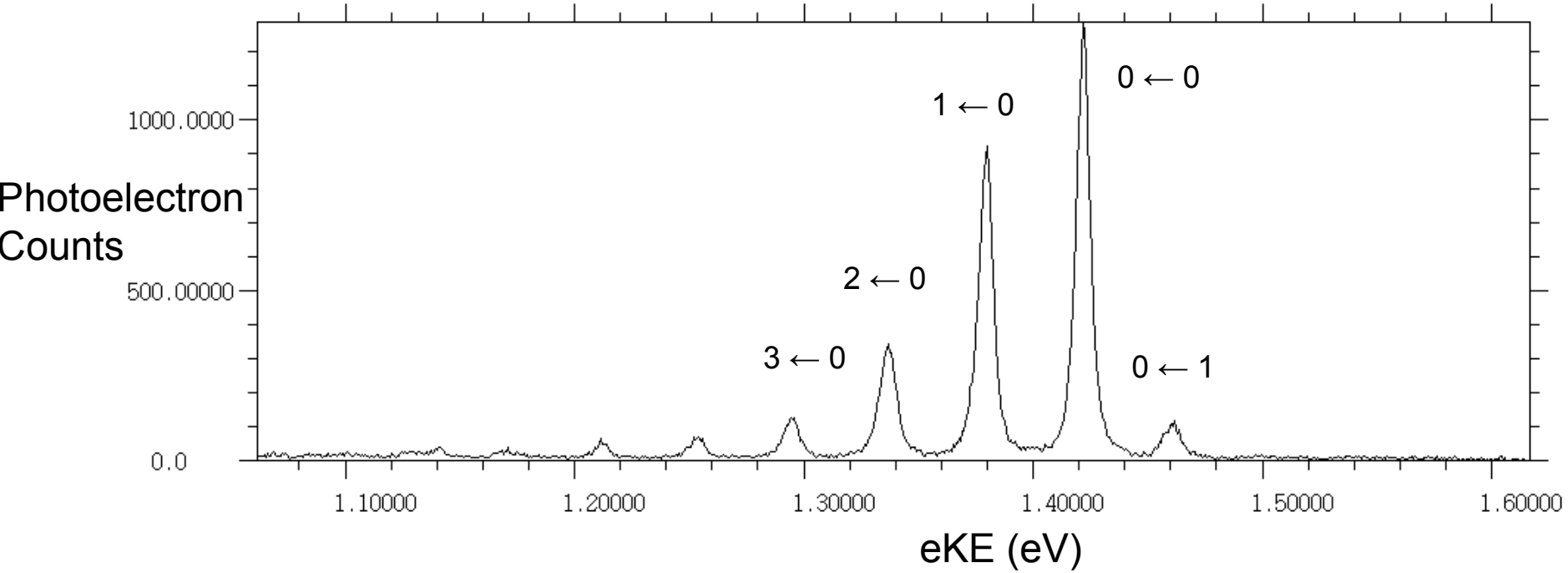
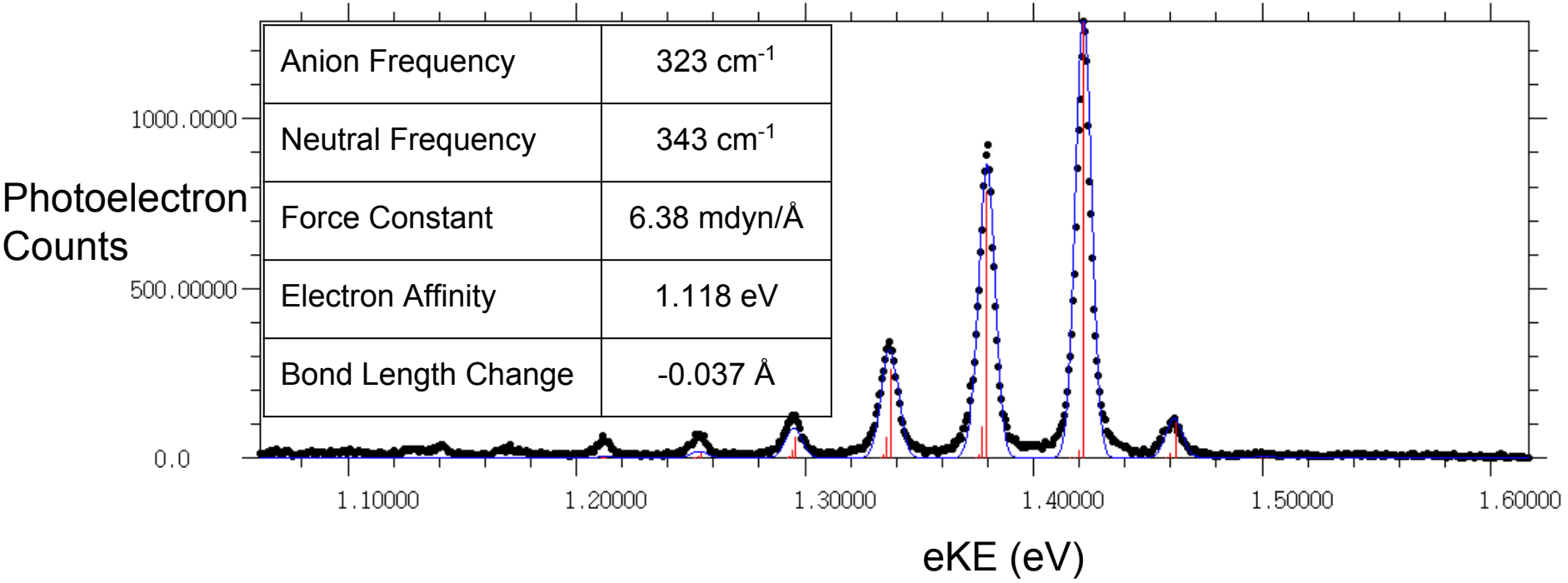


# $W_2$ Photoelectron Spectrum Main Transition

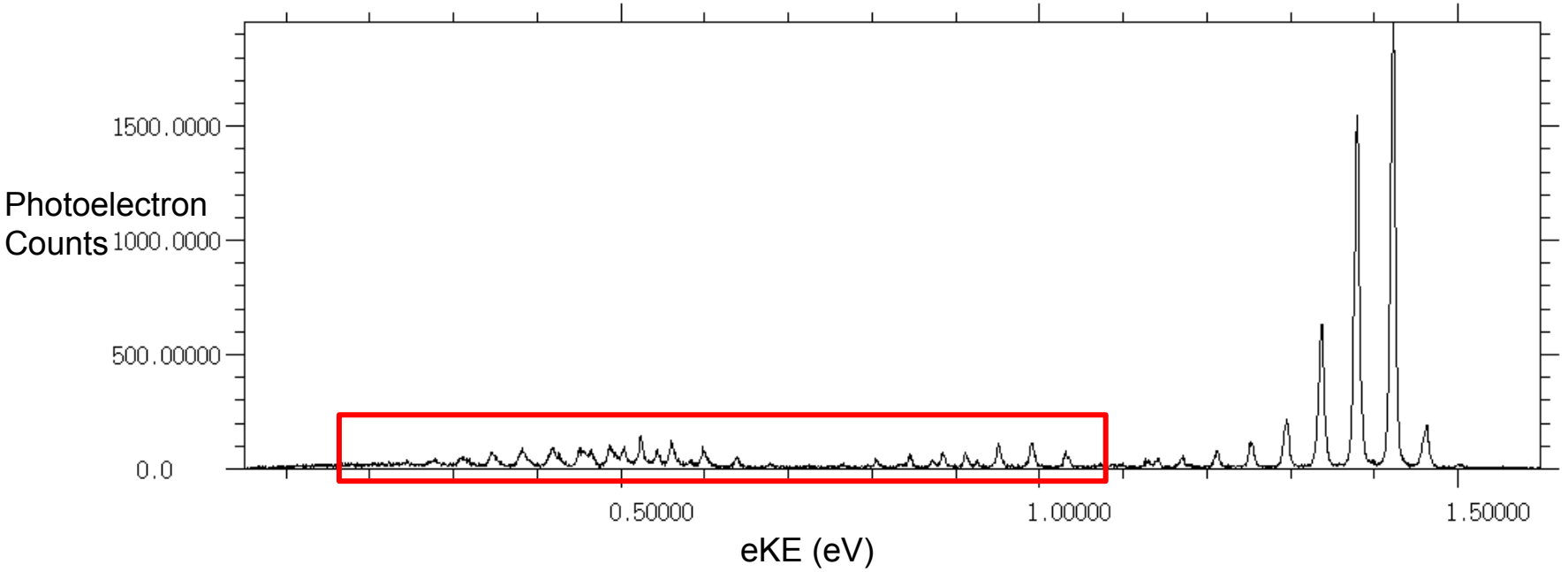


# $W_2$ Main Transition Franck-Condon Fit

| | |
|---|---|
| Anion Frequency | 323 $cm^{-1}$ |
| Neutral Frequency | 343 $cm^{-1}$ |
| Force Constant | 6.38 mdyn/Å |
| Electron Affinity | 1.118 eV |
| Bond Length Change | -0.037 Å |



# $W_2$ - Other Transitions



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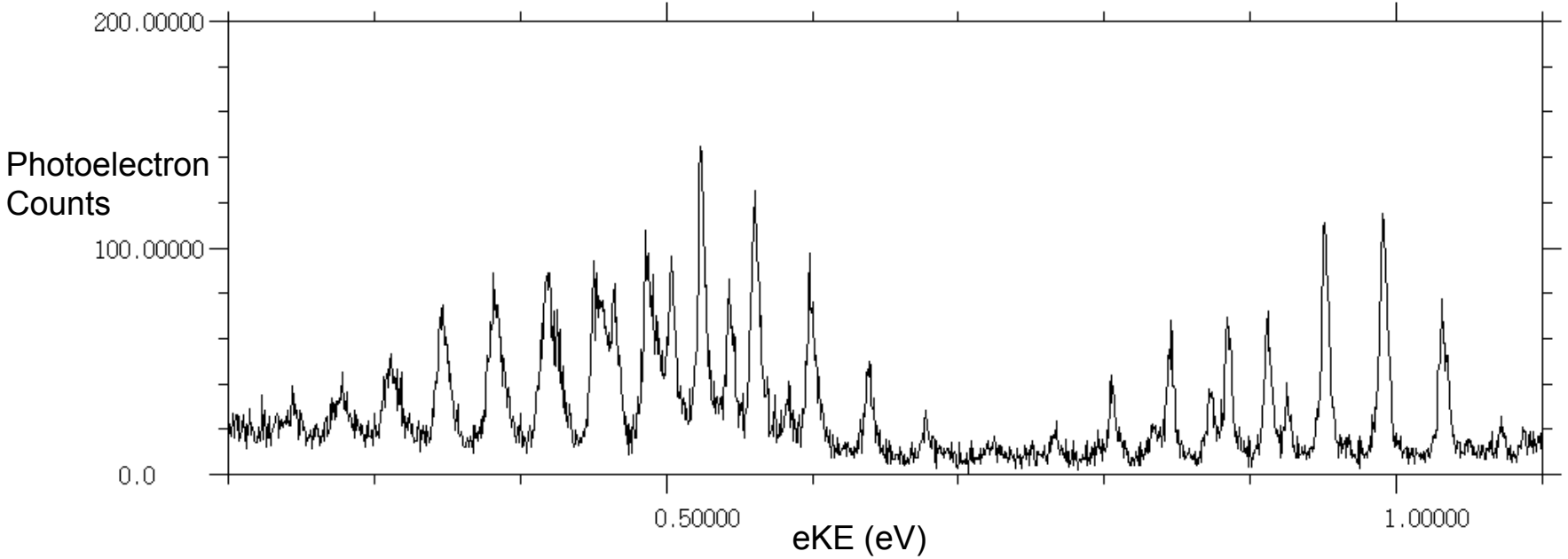

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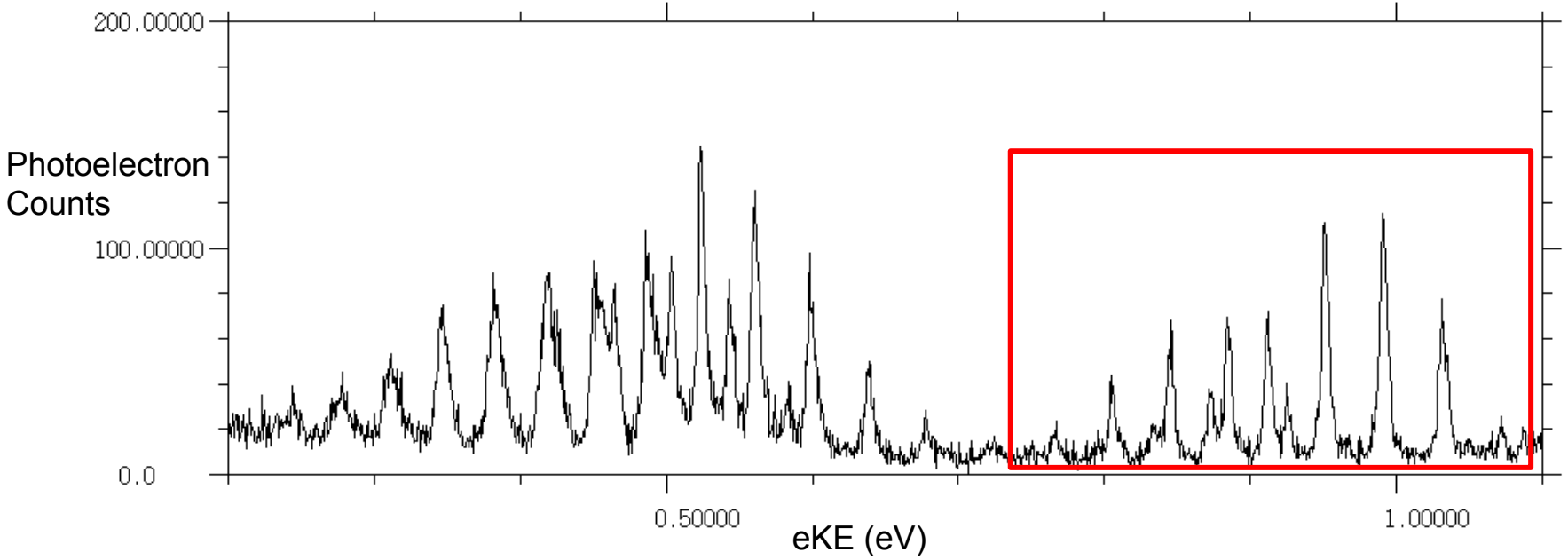
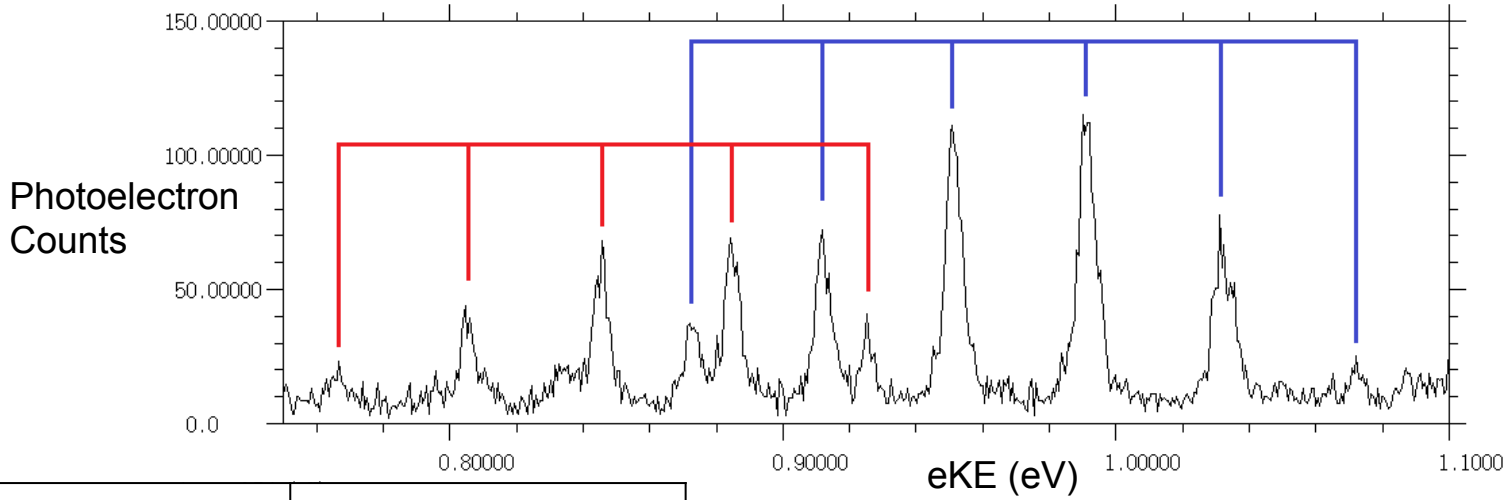
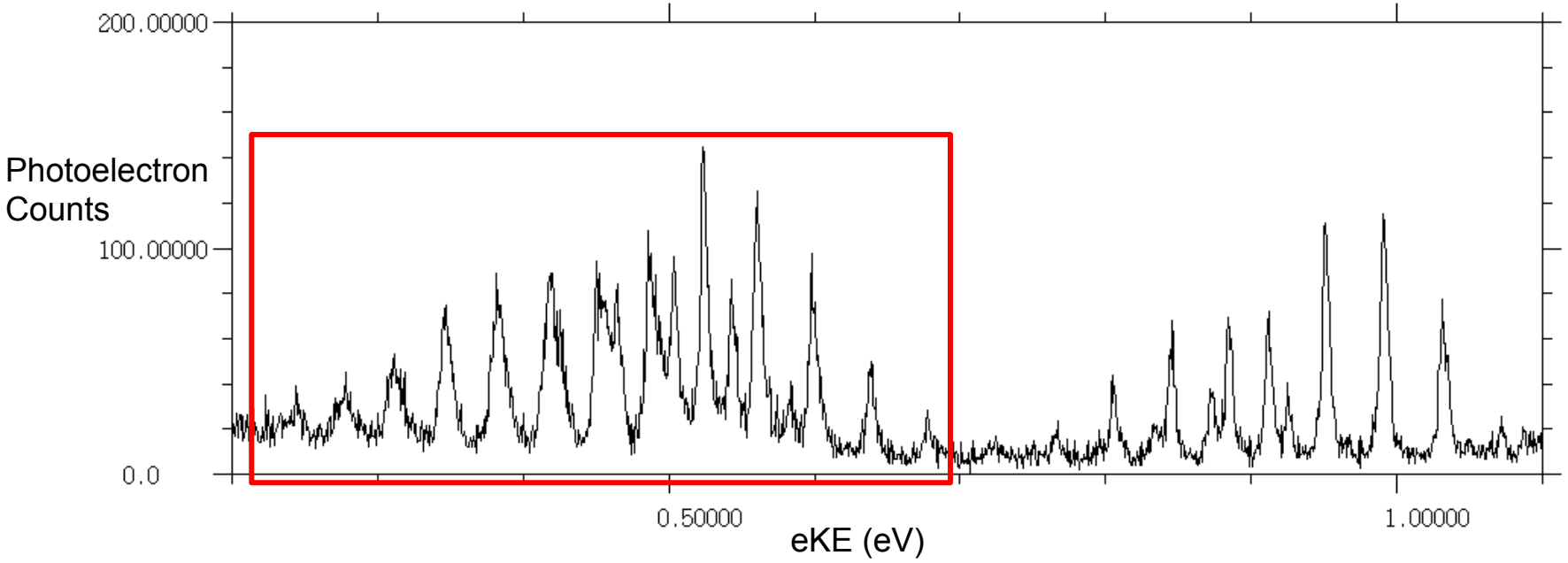


# $W_2$ - Transitions B and C

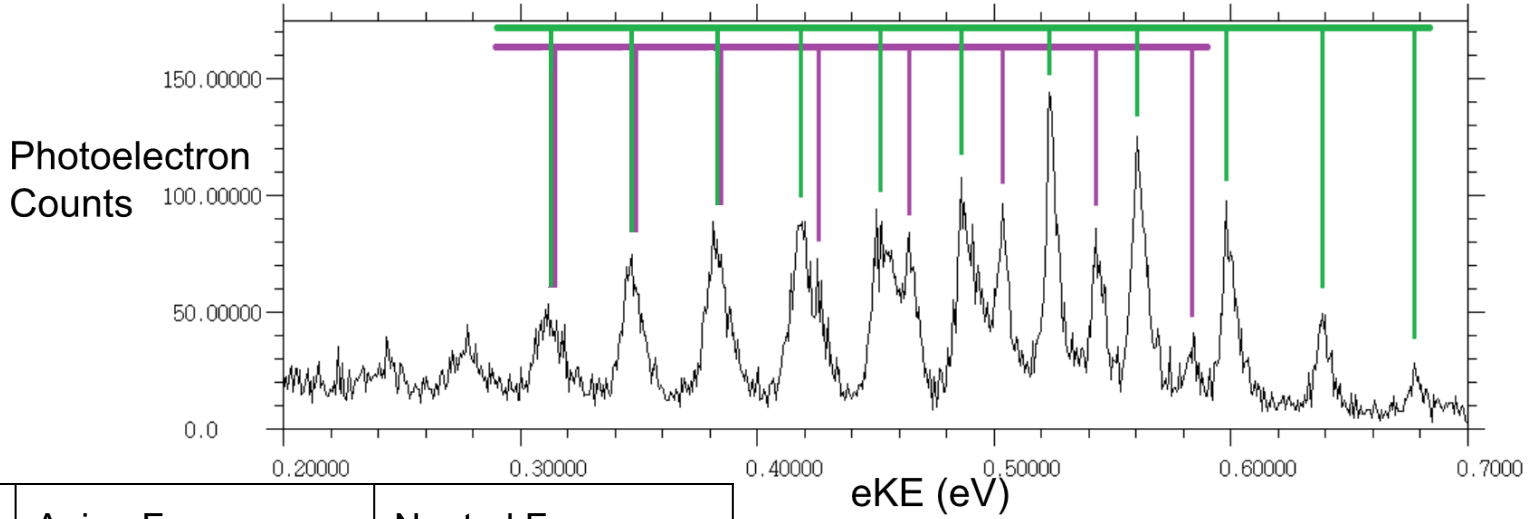



| | Anion Frequency | Neutral Frequency |
|---|---|---|
| Transition B | 323 $cm^{-1}$ | 330 $cm^{-1}$ |
| Transition C | 327 $cm^{-1}$ | 320 $cm^{-1}$ |

# $W_2$ - Other Transitions



# $W_2$ - Transitions D and E




| | Anion Frequency | Neutral Frequency |
|---|---|---|
| Transition D | n/a | 319 $cm^{-1}$ |
| Transition E | n/a | 323 $cm^{-1}$ |

# $W_2$ - Comparison with Previous Work

| | Our Experiment | Weidele APES | Hu R. Raman | (Various) DFT | Borin CASSCF |
|---|---|---|---|---|---|
| Anion Frequency | 323 $cm^{-1}$ | - | - | 357-374 $cm^{-1}$ | - |
| Neutral Frequency | 343 $cm^{-1}$ | - | 337 $cm^{-1}$ | 388-410 $cm^{-1}$ | 354 $cm^{-1}$ |
| Electron Affinity | 1.118 eV | 1.46 eV | - | 1.07-1.18 eV<br>1.121 eV* | - |

* *Z.J. Wu / Chemical Physics Letters 370 (2003) 510–514*

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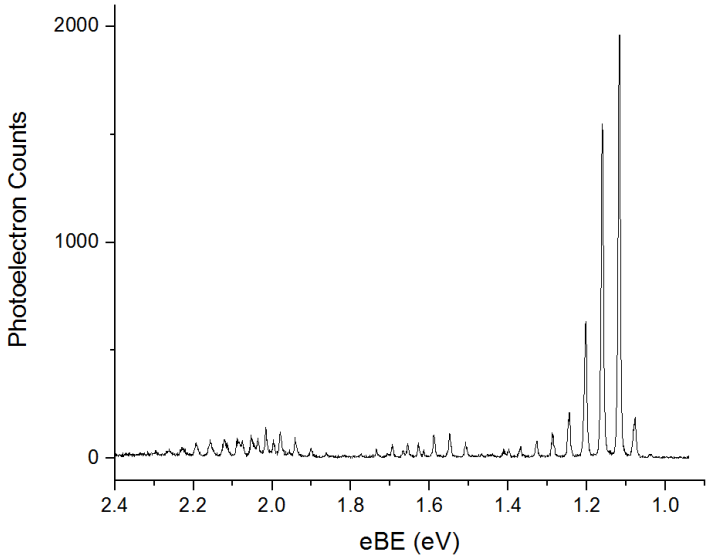
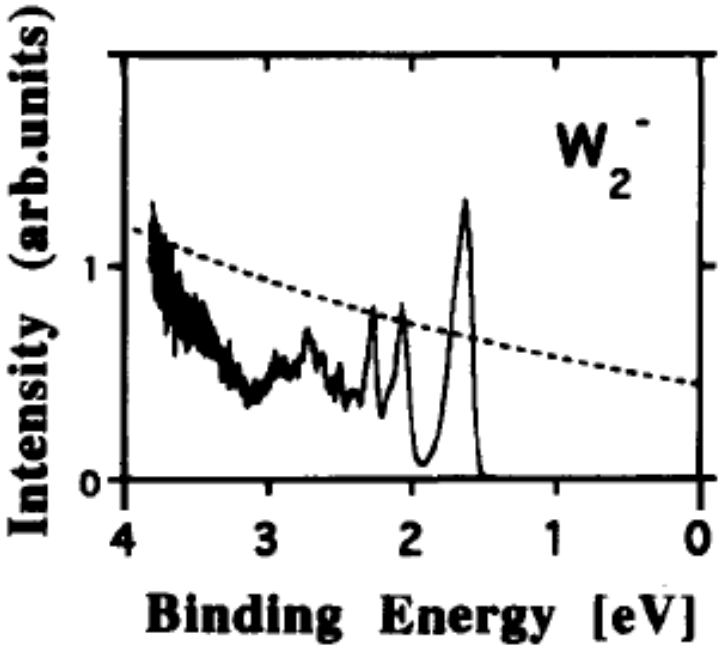
# Comparison of Photoelectron Spectra

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H. Weidele et al. / Chemical Physics Letters 237 (1995) 425–431

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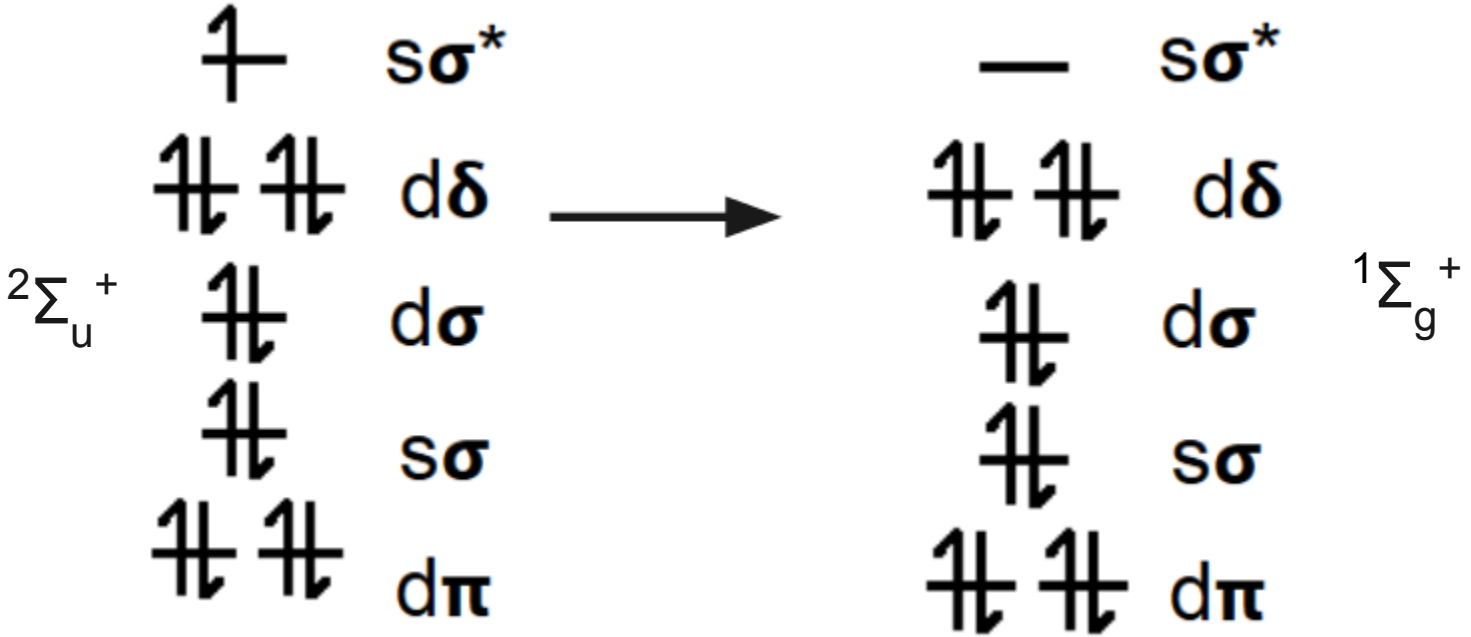
# $W_2$ - B3LYP/LANL2DZ Calculations

| | B3LYP/LANL2DZ | This Experiment |
|---|---|---|
| Electron Affinity | 1.121 eV | 1.118 eV |
| Anion Vibrational Frequency | 357 $cm^{-1}$ | 323 $cm^{-1}$ |
| Neutral Vibrational Frequency | 411 $cm^{-1}$ | 343 $cm^{-1}$ |
| Bond Length Change | -0.094 Å | -0.037 Å |

# $W_2$ - Electronic Configurations



# $W_2$ - B3LYP/LANL2DZ Calculations

B3LYP/LANL2DZ Calculation

| Transition | Energy (eV) |
|---|---|
| Doublet to Singlet | 1.121 |
| Doublet to Triplet | 1.25 |
| Quartet to Triplet | 1.00 |
| Quartet to Quintet | 1.11 |
| Sextet to Quintet | 0.52 |

Experiment

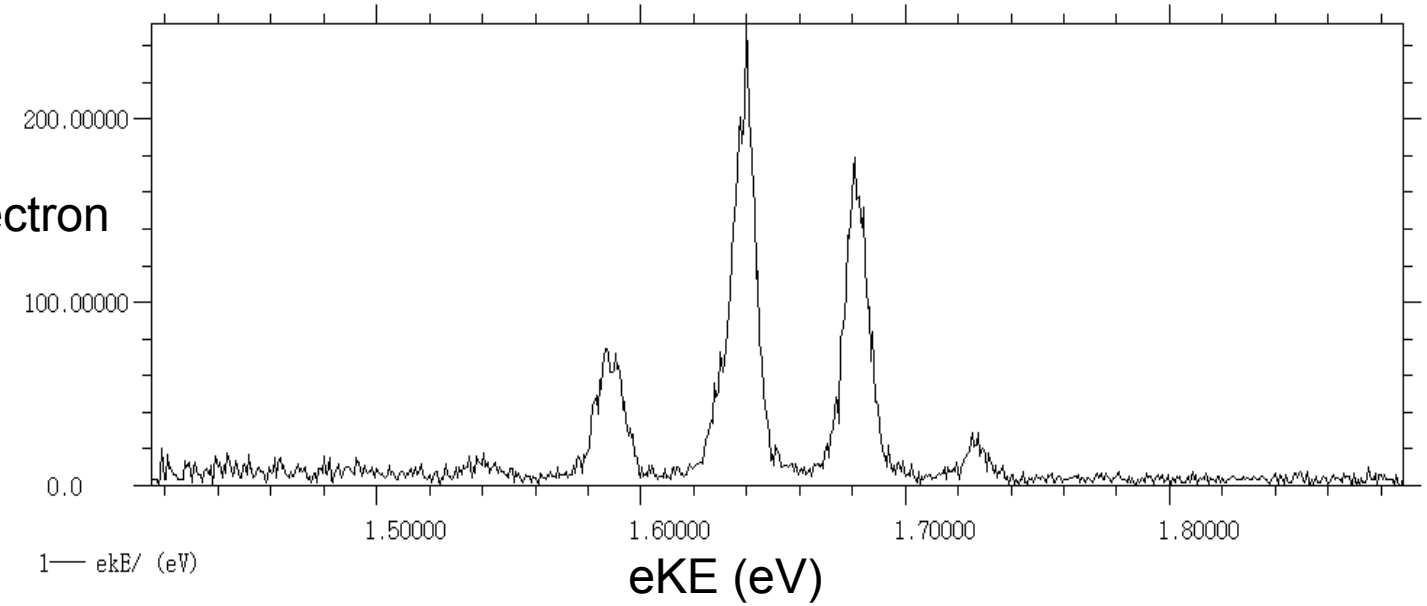
| Transition | Energy (eV) |
|---|---|
| Main | 1.118 |
| B | 1.51 |
| C | 1.67 |
| D | 1.90 |
| E | 1.99 |

# NbW - Niobium Tungsten
# Previous Work

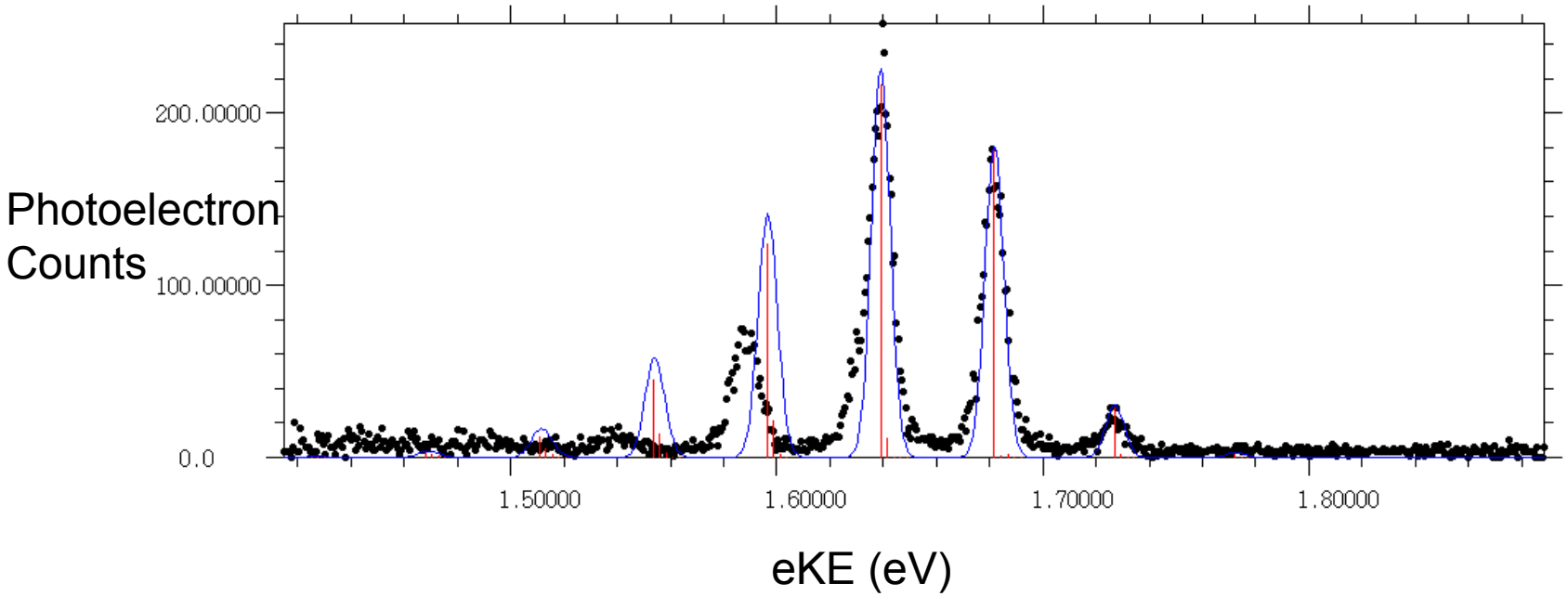
# NbW - Niobium Tungsten
# Previous Work

Nothing!

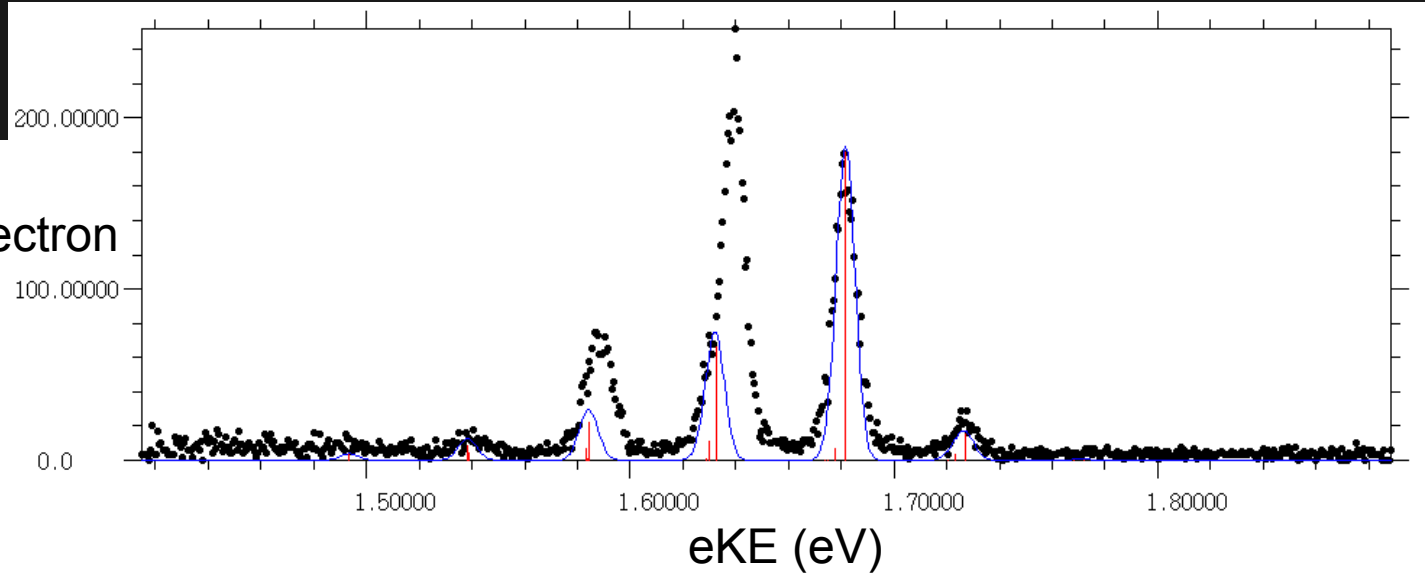
# NbW - Niobium Tungsten Photoelectron Spectrum



# NbW - Franck-Condon Fit

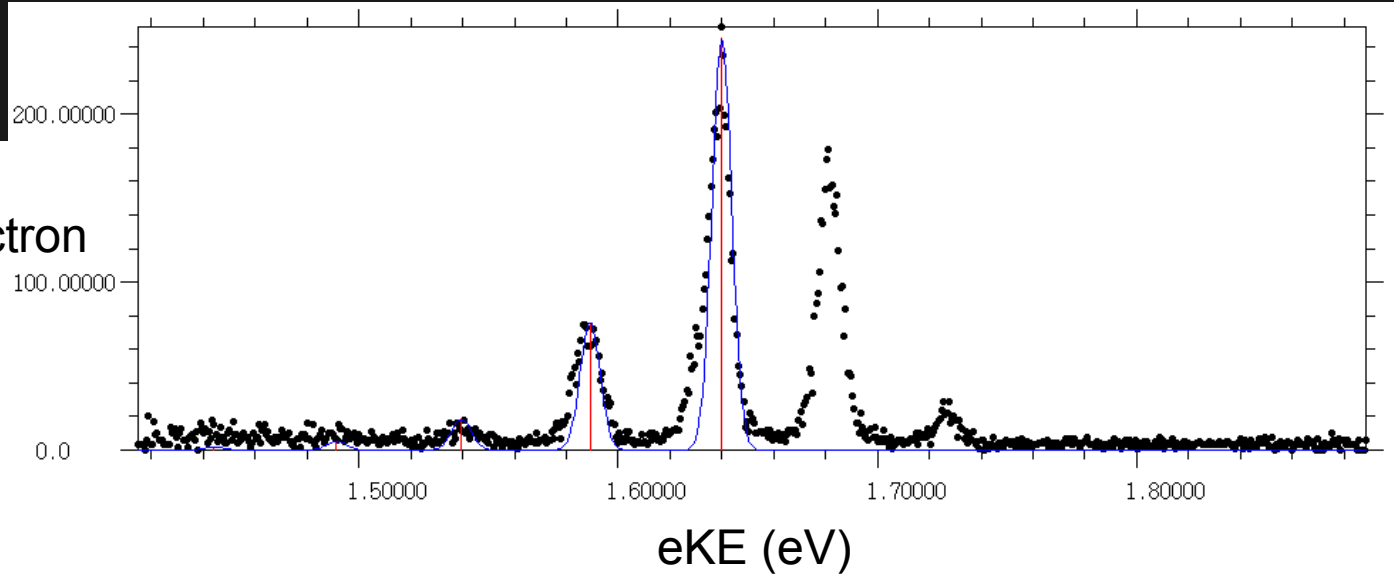


# NbW - Transition A



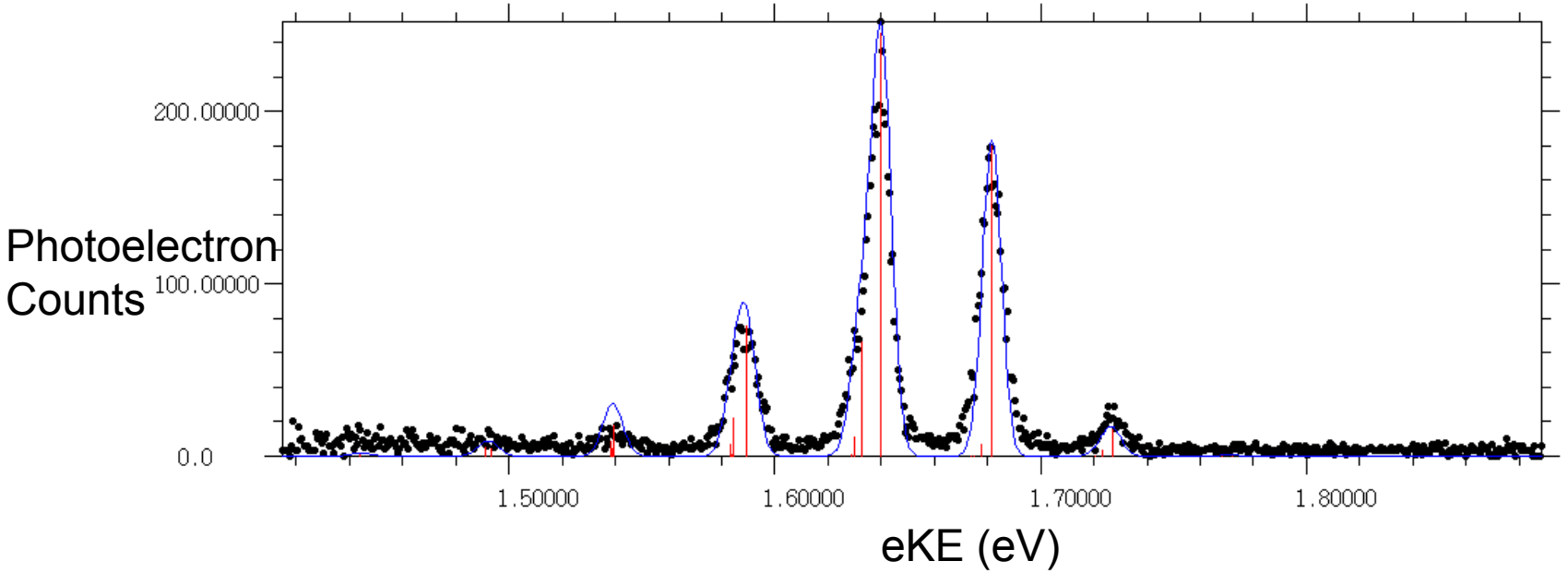

| | Anion Vibrational Frequency ($cm^{-1}$) | Neutral Vibrational Frequency ($cm^{-1}$) | Electron Affinity (eV) |
|---|---|---|---|
| Transition A | 365 | 410 | 0.858 |

# NbW - Transition B




| | Anion Vibrational Frequency ($cm^{-1}$) | Neutral Vibrational Frequency ($cm^{-1}$) |
|---|---|---|
| Transition B | n/a | 420 |

# NbW - Transitions A and B

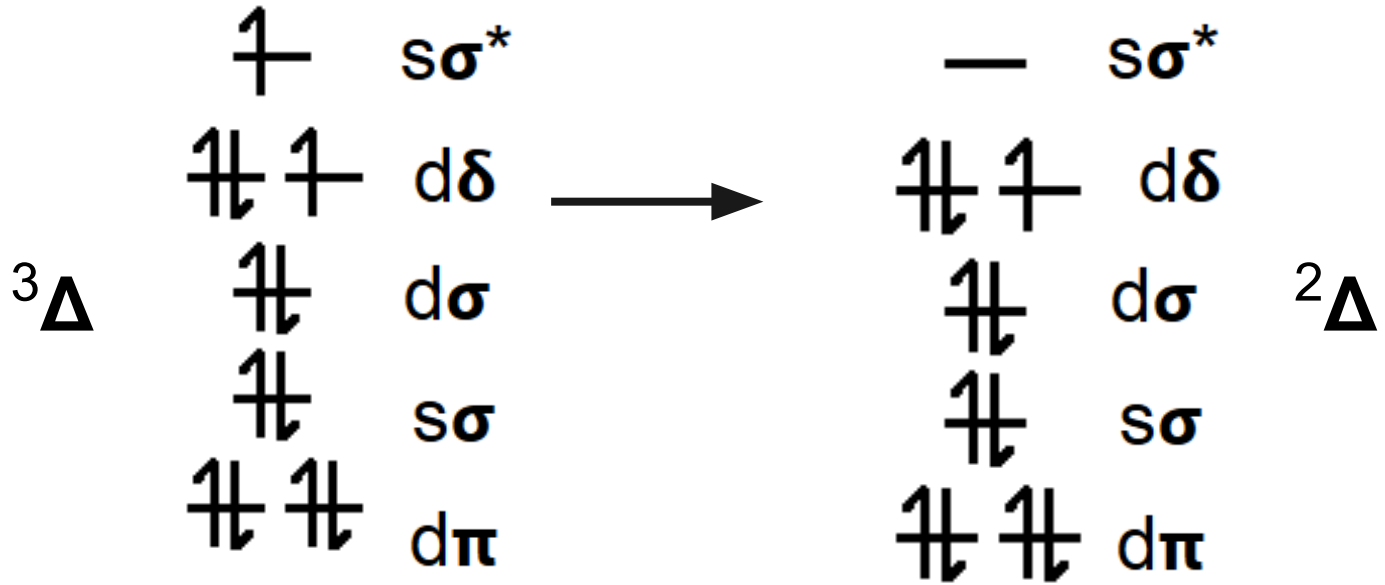


# NbW - DFT Calculations

B3LYP/LANL2DZ

| | DFT Calculation | Experiment |
|---|---|---|
| Electron Affinity | 0.526 eV | 0.858 eV |
| Anion Vibrational Frequency | 421 $cm^{-1}$ | 365 $cm^{-1}$ |
| Neutral Vibrational Frequency | 341 $cm^{-1}$ | 410 $cm^{-1}$ |

# NbW - Transition A



# NbW and $W_2$ - Comparison with other Transition Metal Dimers

| | VCr | VMo | NbCr | NbMo | NbW | $W_2$ | $Cr_2$ | $Mo_2$ |
|---|---|---|---|---|---|---|---|---|
| Electron Affinity (eV) | .521 | .932 | .793 | 1.131 | .858 | 1.118 | 0.505 | 0.733 |
| Neutral Vibrational Frequency ($cm^{-1}$) | 520 | 507 | 469 | 470 | 410 | 343 | 574 | 473 |
| Vibrational Force Constant (mdyn/Å) | 4.10 | 5.04 | 4.45 | 6.20 | 6.11 | 6.38 | 3.54 | 6.33 |

# Summary

$W_2$

More accurate electron affinity

Determined ground state and vibrational frequency of $W_2^-$

NbW

First ever observation

Determined electron affinity and vibrational frequencies of ground and first excited state

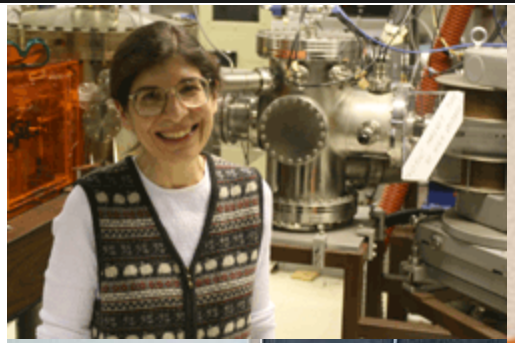
# Thanks to...

Doreen Leopold

Melissa Baudhuin

Sean Casey

NSF



# Questions?