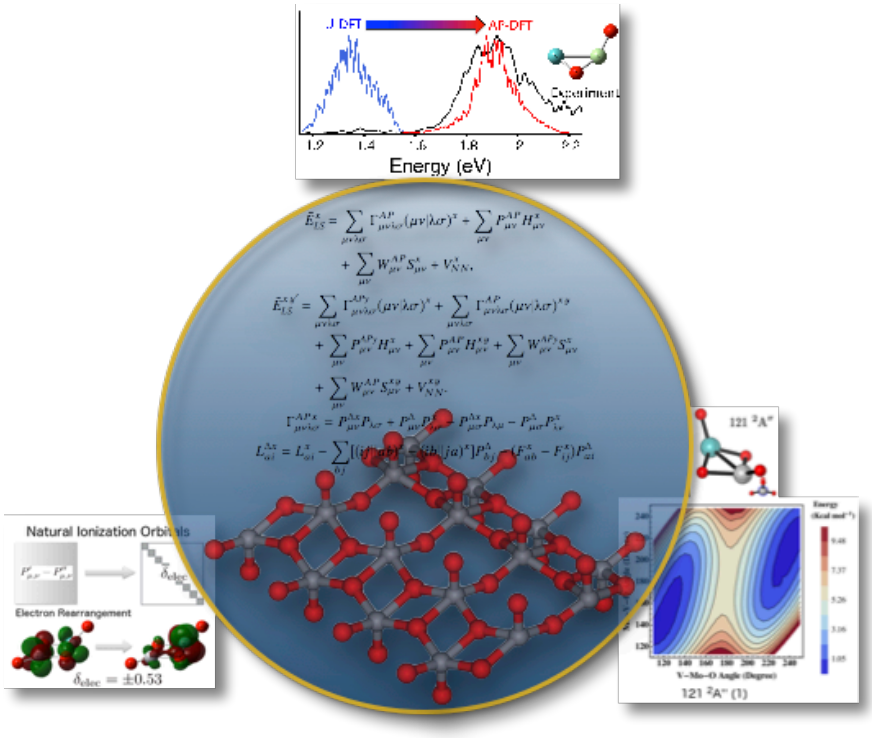
# *Modeling Electron Detachment with Efficient Electronic Structure Methods*


***Hrant P. Hratchian***

***University of California, Merced***

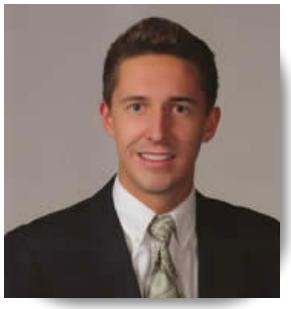




UCMERCED

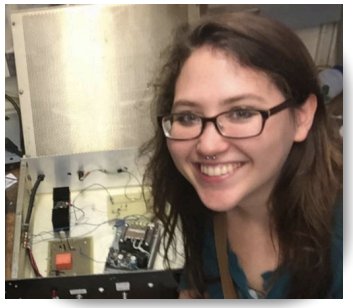
# *Modeling Electron Detachment with Efficient Electronic Structure Methods*

**Caroline Jarrold**
**Indiana U**

**Dan Neumark**
**UC Berkeley**



**Jarrett Mason**



**Jessalyn DeVine**

**Mark Babin**

# *Modeling Electron Detachment with Efficient Electronic Structure Methods*

Hassan Harb

Bryce Fairless
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Dan Neumark
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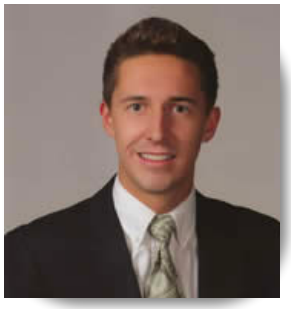

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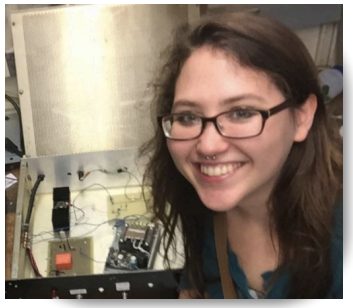

Jessalyn DeVine

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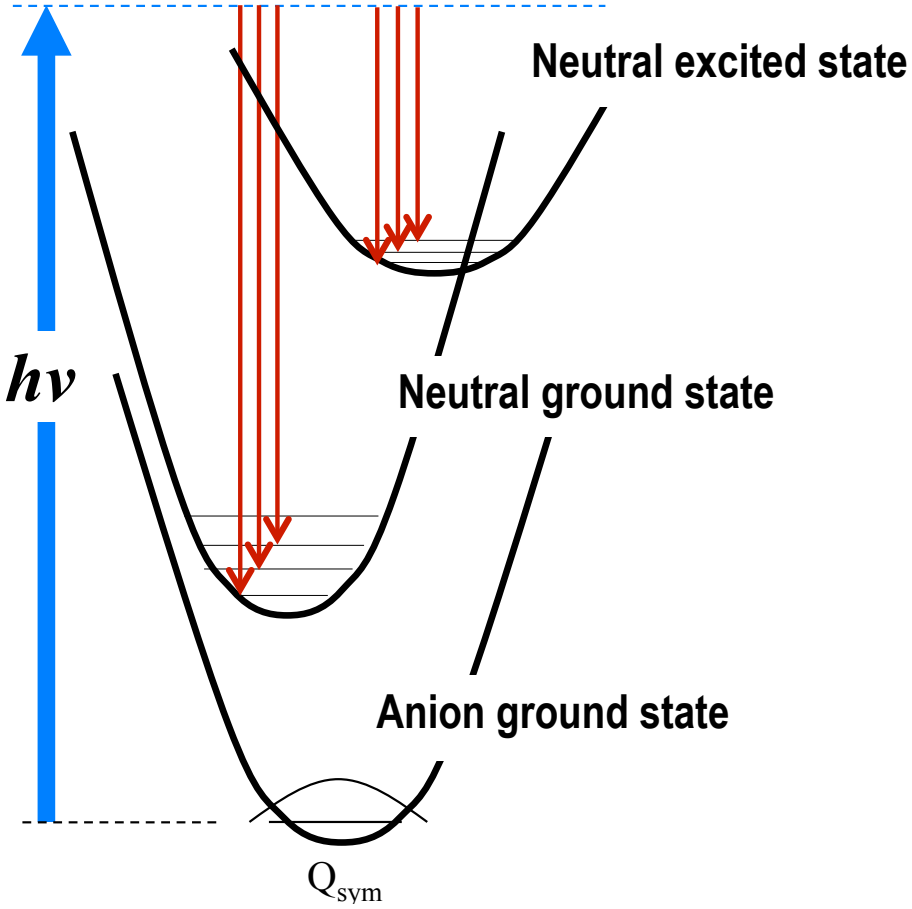
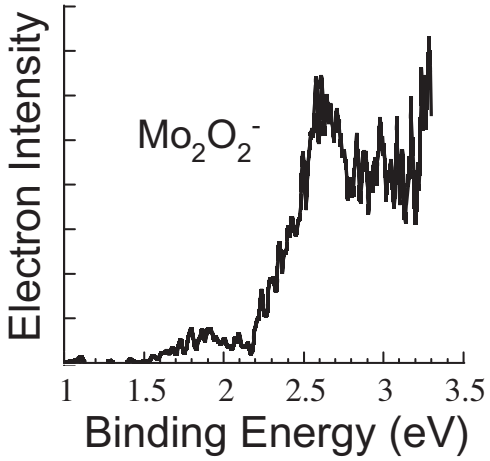
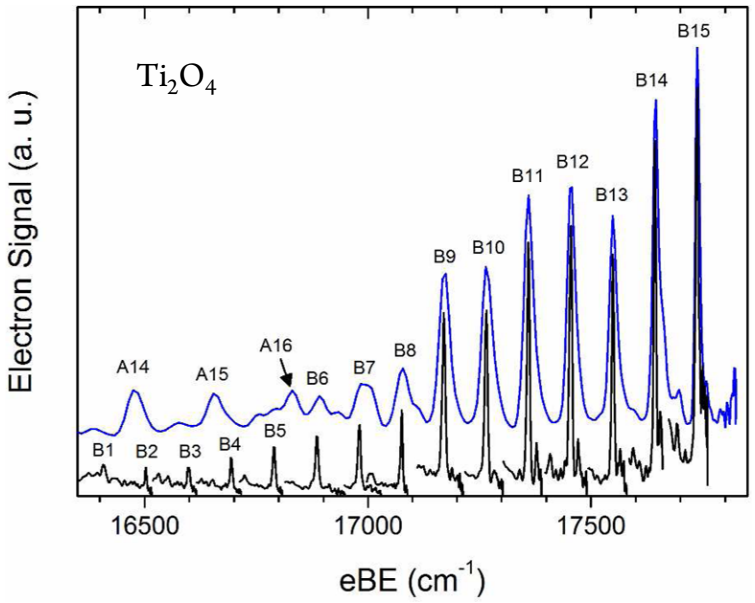
# Modeling PE Spectra




*Courtesy of C. C. Jarrold*

# *Modeling PE Spectra*

- **Challenges**
  - Balancing Static & Dynamic Correlation
  - Anharmonicity
  - Interpretive Models
  - Relativistic Effects

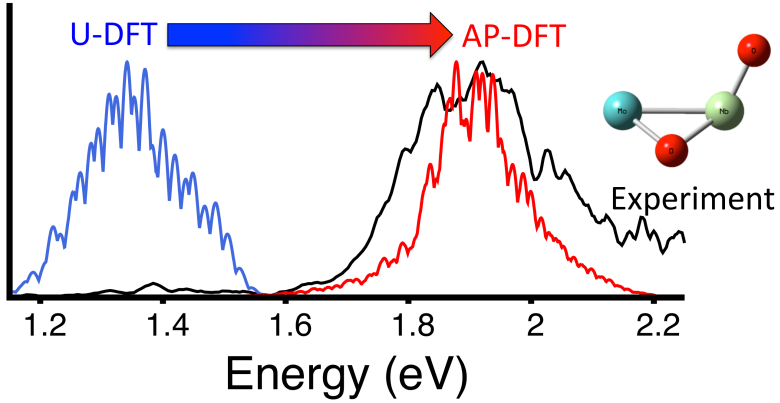
- **Objectives**
  - Multiple handles: Energies, force-fields, densities…
  - Affordable and efficient: Aim for SCF-like cost
  - Fully-defined model: Avoid user-defined parameters
  - Analytic derivatives: Geometry optimization, vibrational analysis, dynamics, etc.

# Supporting Methods Development

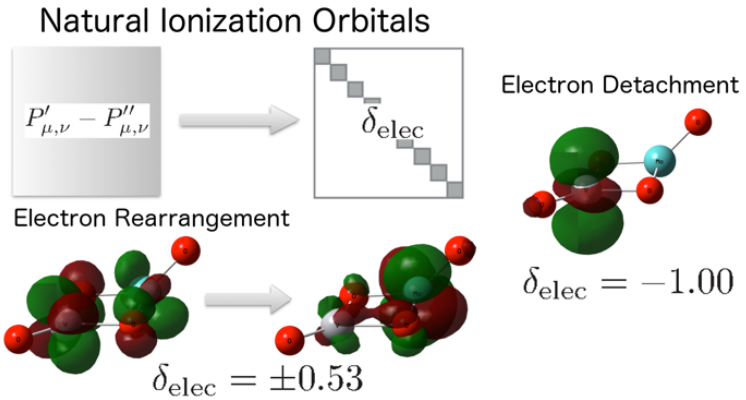
- **Spin projection**
  - *J. Chem. Phys.* **138**, 101101 (2013).
  - *J. Chem. Phys.* **141**, 034108 (2014).
  - *J. Chem. Phys.* **142**, 054106 (2015).
  - *J. Phys. Chem. A* **119**, 8744-8751 (2015).
  - *Mol. Phys.*, **117**, 1421-1429 (2019).

$$E = \alpha E_{LS} + (1-\alpha) E_{HS}$$

$$\alpha = \frac{\langle S^2_{HS} \rangle - s_{z,LS}(s_{z,LS}+1)}{\langle S^2_{HS} \rangle - \langle S^2_{LS} \rangle}$$




- **Natural Ionization Orbitals (NIOs)**
  - *J. Chem. Phys.* **144**, 204117 (2016).
  - *J. Chem. Phys.* **146**, 104301 (2017).



# Natural Ionization Orbitals

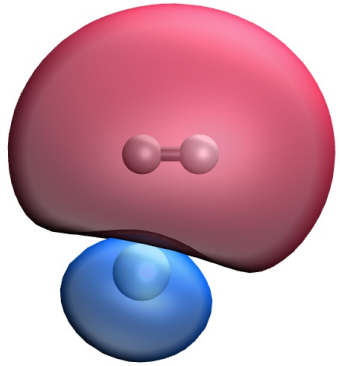
$$\mathbf{\Delta}_P = \mathbf{P}_i - \mathbf{P}_g$$

$$\langle \mathbf{\Delta}_P \mathbf{S} \rangle = \Delta_{\text{elec}}$$

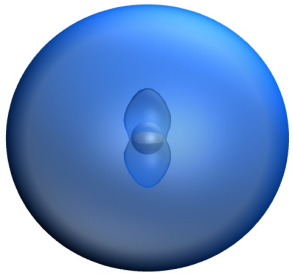
$$(\phi_1, \phi_2, \ldots, \phi_{N_{\text{basis}}}) = (\psi_1, \psi_2, \ldots, \psi_{N_{\text{basis}}})\mathbf{U}$$

$$\mathbf{U}^\dagger \mathbf{S}^{1/2} \mathbf{\Delta}_P \mathbf{S}^{1/2} \mathbf{U} = \delta_{\text{elec}}$$

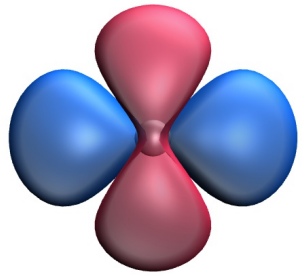
$$\mathbf{V} = \mathbf{S}^{-1/2}\mathbf{U}$$



***NIO EVal: -1.0***



***NIO EVal: -0.8***

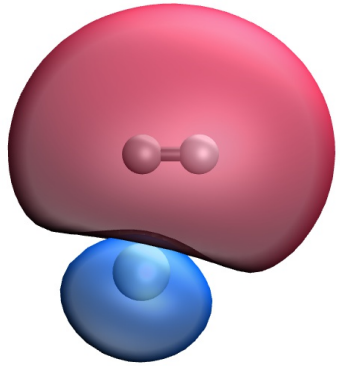


***NIO EVal: +0.8***

L. M. Thompson, H. Harb, HPH, *J. Chem. Phys.* **144**, 204117 (2016)

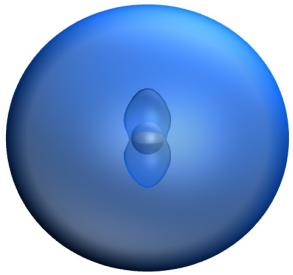
# Natural Ionization Orbitals

- **It can be shown that under Koopmans conditions, the NIO is rigorously equivalent to the corresponding Dyson orbital.**

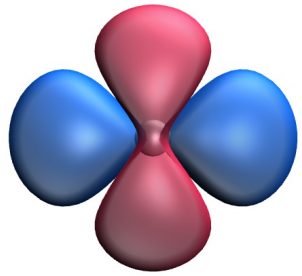


***NIO EVal: -1.0***
***Occ Population: 1.0***

- **Our initial interpretation under non-Koopmans conditions was *wrong*.**



***NIO EVal: -0.8***
***Occ Population: 0.92***
***Virt Population: 0.08***



***NIO EVal: +0.8***
***Occ Population: 0.08***
***Virt Population: 0.92***

# $MoVO_4$

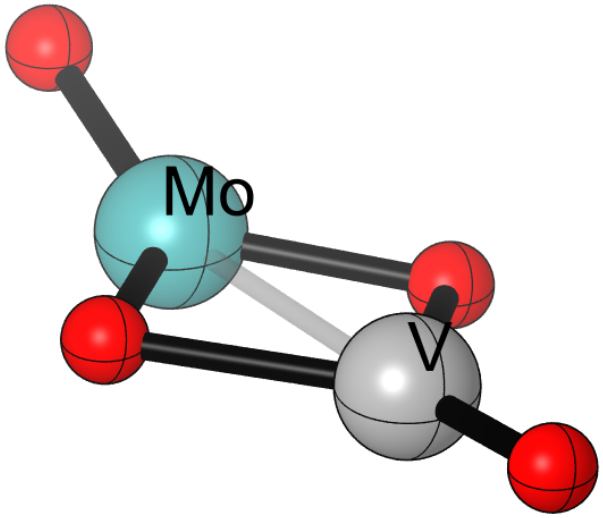
11312 J. Phys. Chem. A 2010, 114, 11312–11321

**Study of $MoVO_y$ ($y = 2-5$) Anion and Neutral Clusters using Anion Photoelectron Spectroscopy and Density Functional Theory Calculations†**

**Jennifer E. Mann, David W. Rothgeb, Sarah E. Waller, and Caroline Chick Jarrold***

*Department of Chemistry, Indiana University, 800 East Kirkwood Avenue, Bloomington, Indiana 47405, USA*

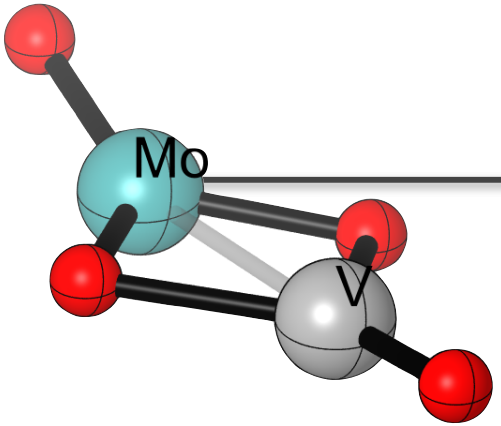
*Received: May 14, 2010; Revised Manuscript Received: August 4, 2010*

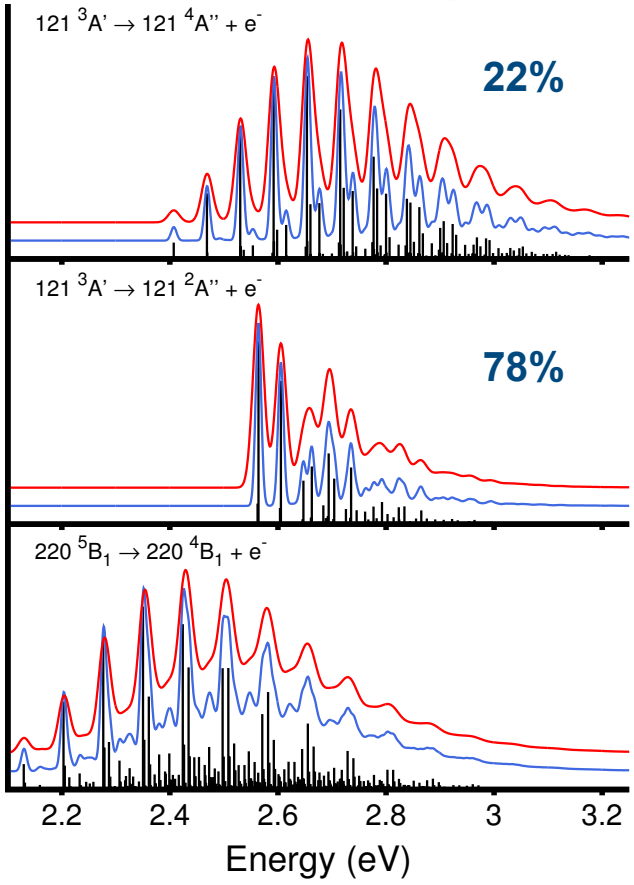


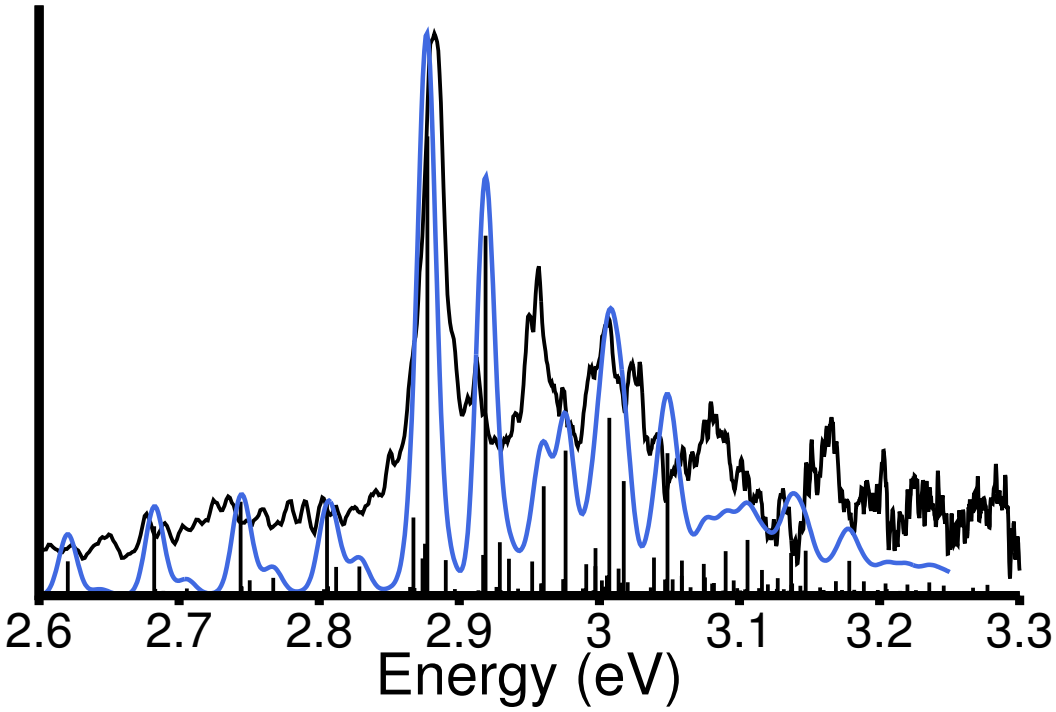

- **2 Candidate structures**
  - 220 $^5B_1$ and 121 $^3A'$
- **VDE/ADE exclude 220 $^5B_1$ → 220 $^6B_1$**
- **Hole burning: X/A bands from same initial state**
- **Assignment: 121 $^3A'$**
  - FC simulations ***not*** consistent with experiment
  - X band: 121 $^3A'$ –> 121 $^4A''$
  - A band: 121 $^3A'$ –> 121 $^2A''$

J. Mann, D. W. Rothgeb, S. E. Waller, & C. C. Jarrold *J. Phys. Chem. A*, **114**, 11312 (2010).

# $MoVO_4$

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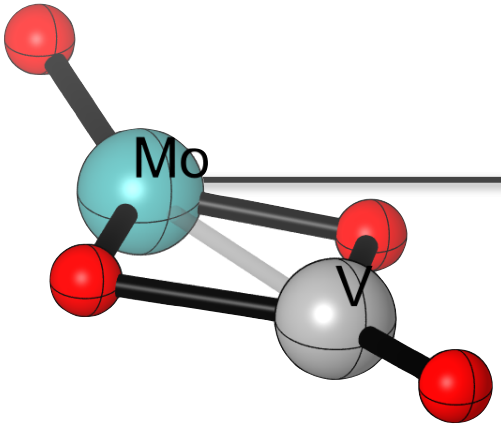
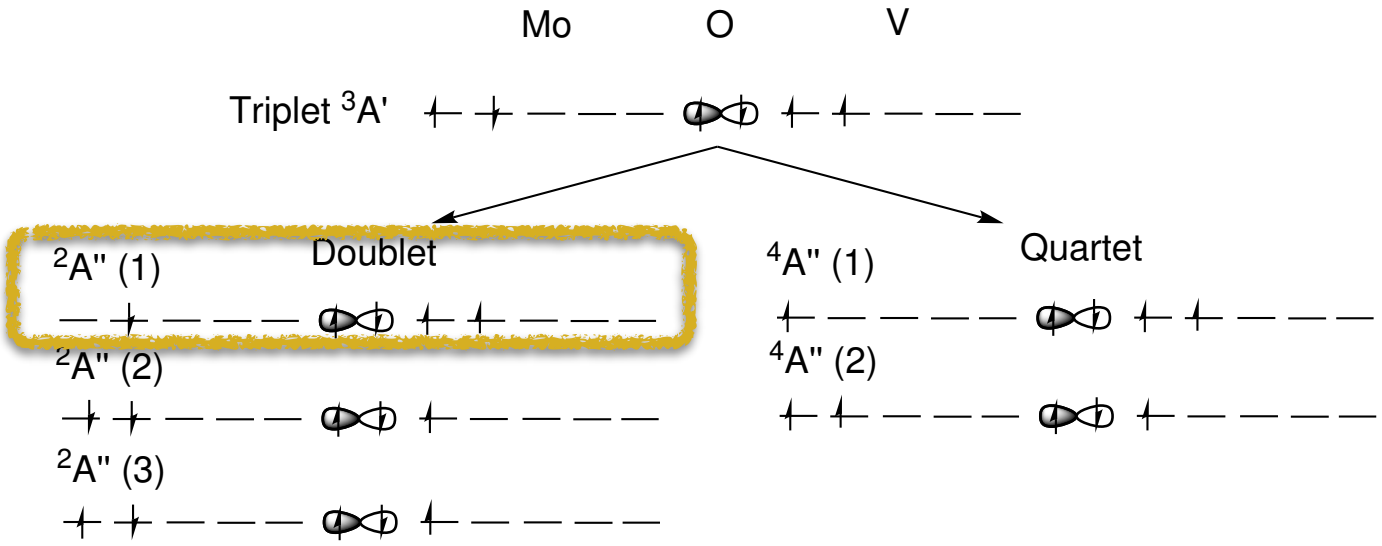
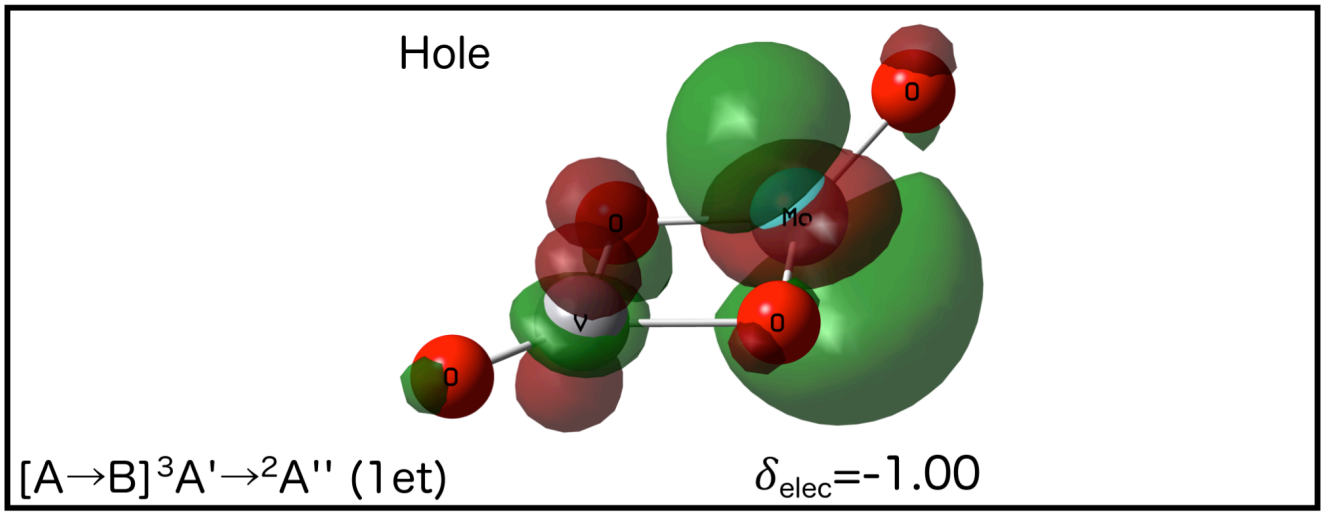



# $MoVO_4$




L. M. Thompson, C. C. Jarrold, & H. P. Hratchian, *J. Chem. Phys.* **146** 104301 (2017).

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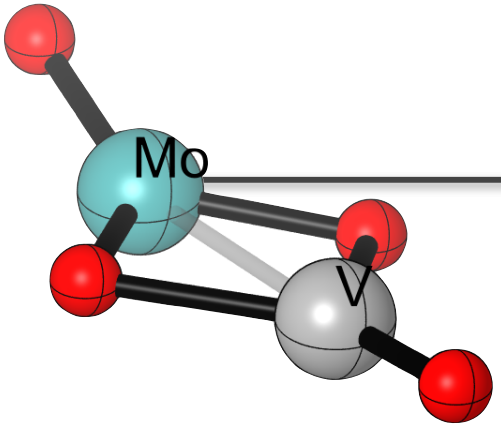


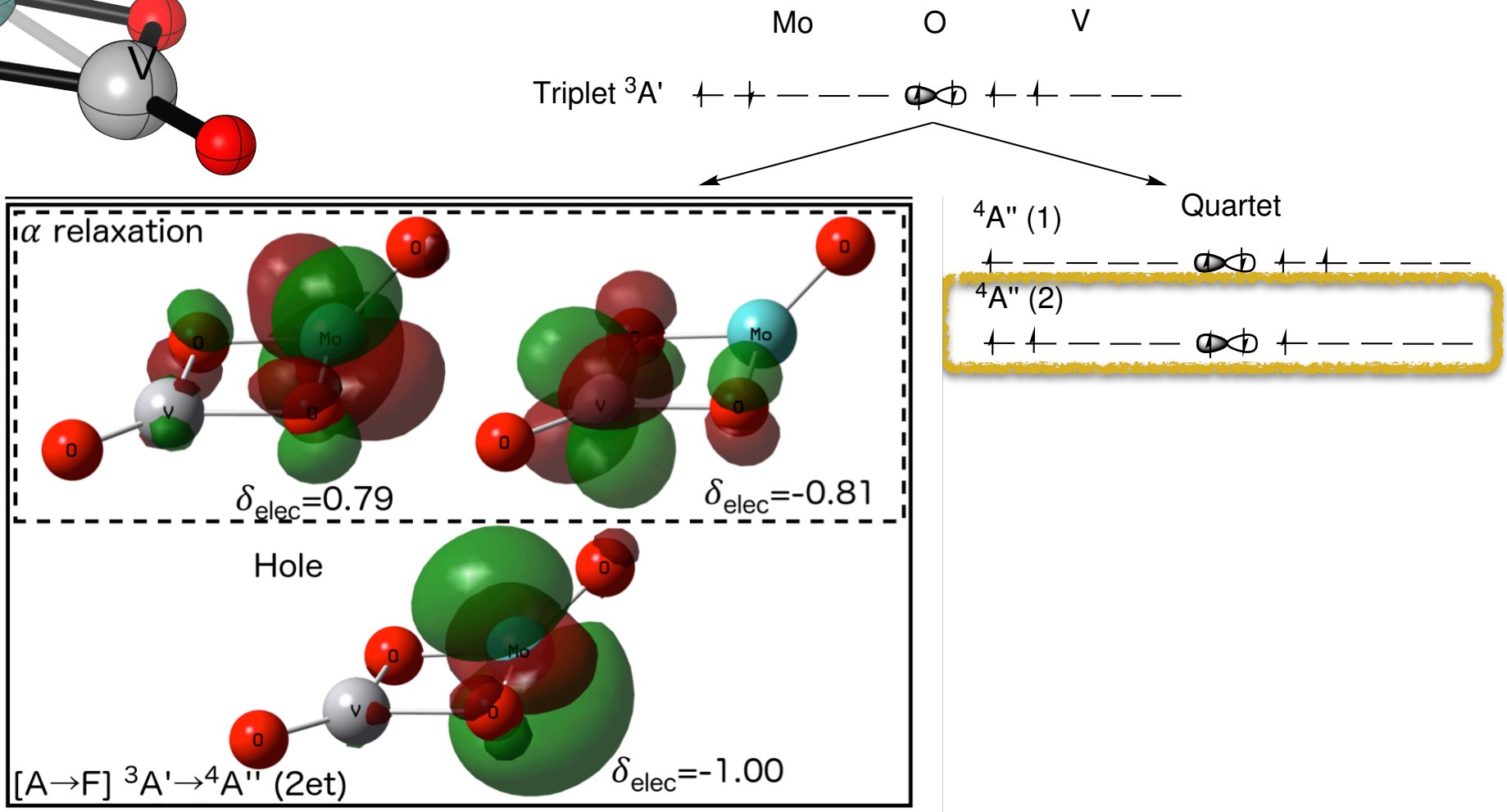


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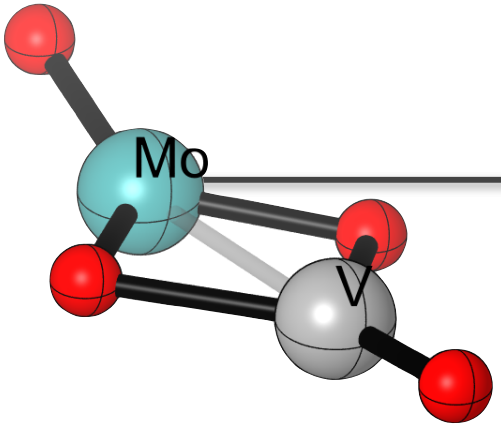
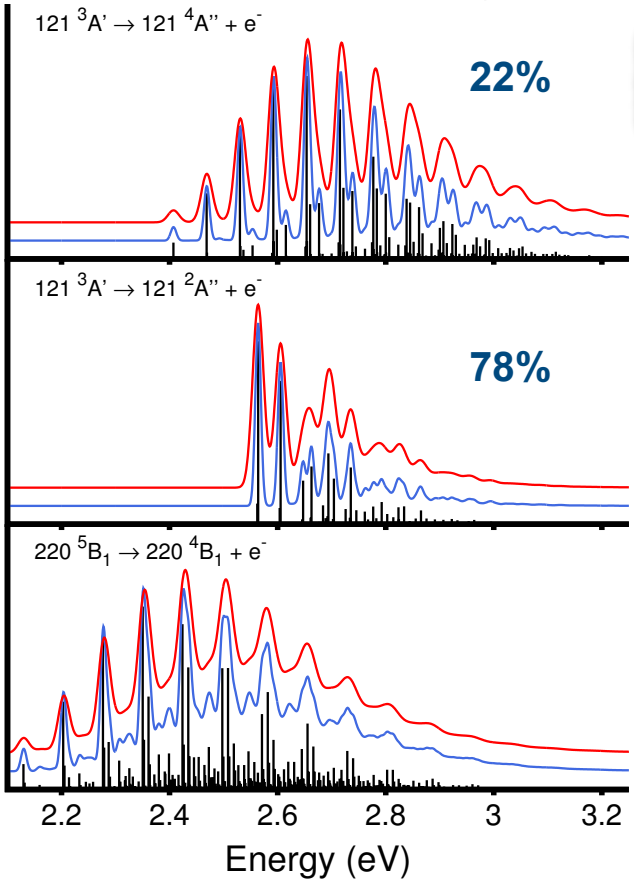
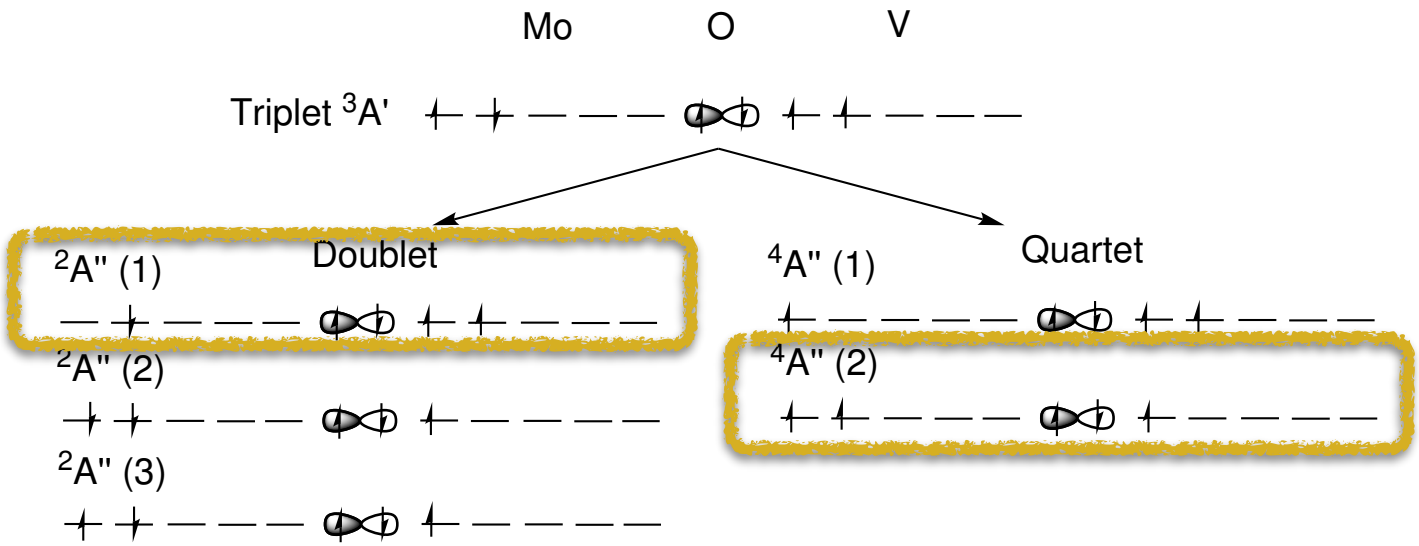
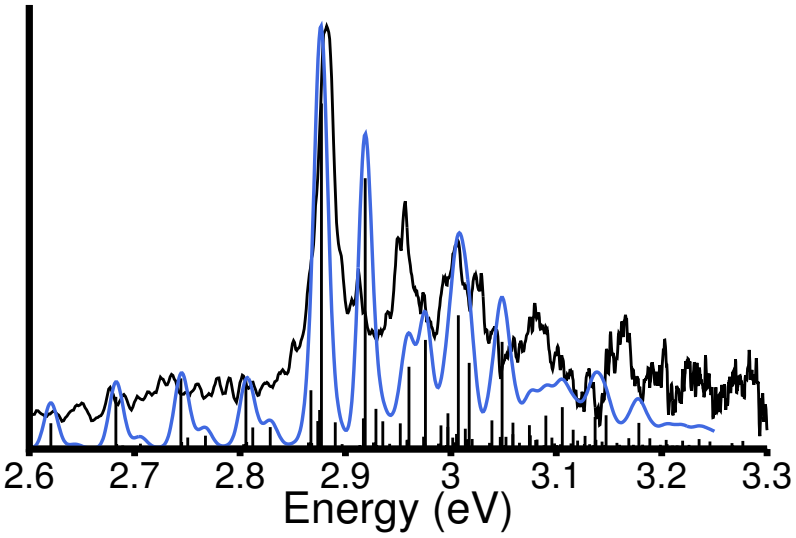



L. M. Thompson, C. C. Jarrold, & H. P. Hratchian, *J. Chem. Phys.* **146** 104301 (2017).

THE JOURNAL OF CHEMICAL PHYSICS **122**, 054313 (2005)

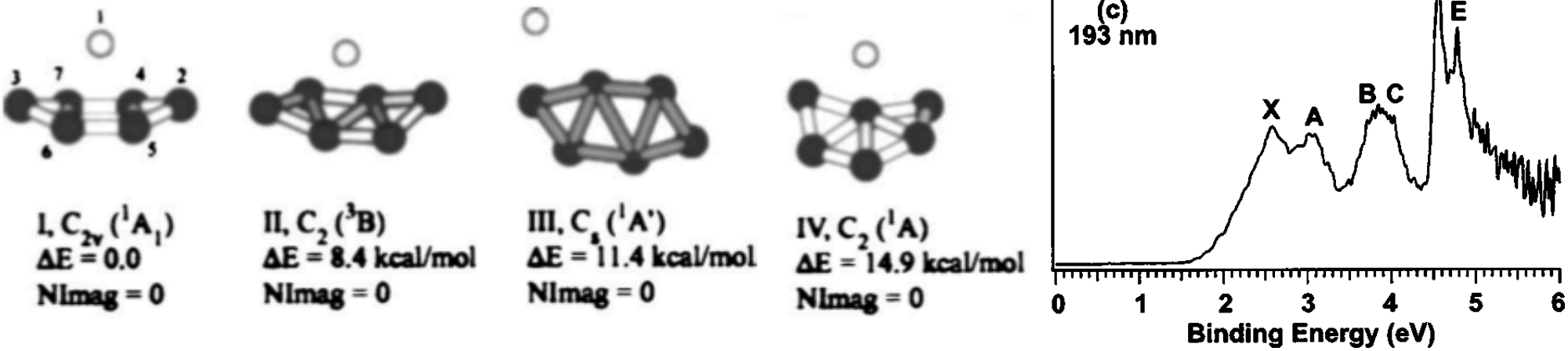
# Photoelectron spectroscopy and *ab initio* study of the doubly antiaromatic $B_6^{2-}$ dianion in the $LiB_6^-$ cluster

Anastassia N. Alexandrova and Alexander I. Boldyrev[a)]
*Department of Chemistry and Biochemistry, Utah State University, Logan, Utah 84322-0300*

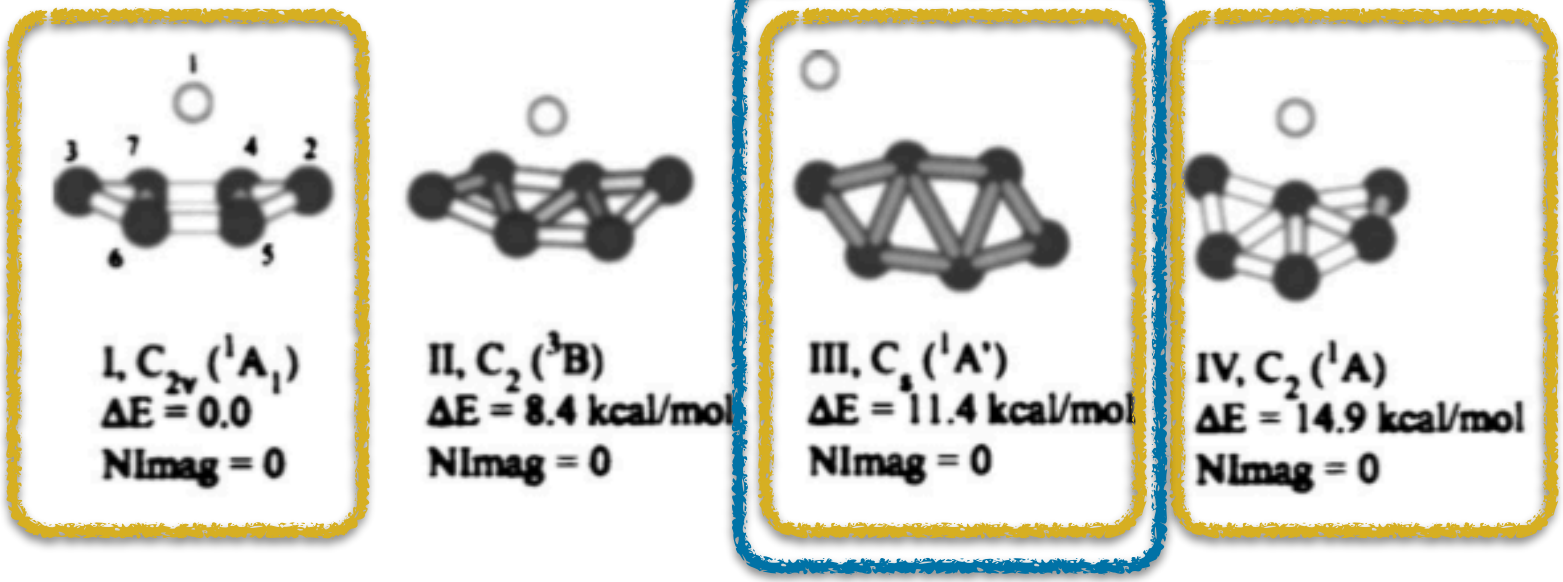
Hua-Jin Zhai and Lai-Sheng Wang[b)]
*Department of Physics, Washington State University, Richland, Washington 99352 and W. R. Wiley Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, MS K8-88, Richland, Washington 99352*

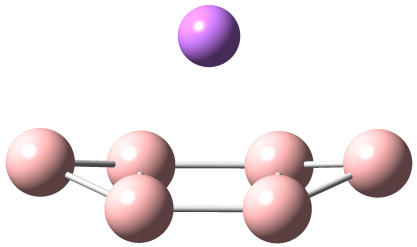
(Received 13 October 2004; accepted 3 November 2004; published online 20 January 2005)

A metal-boron mixed cluster $LiB_6^-$ was produced and characterized by photoelectron spectroscopy and *ab initio* calculations. A number of electronic transitions were observed and used to compare with theoretical calculations. An extensive search for the global minimum of $LiB_6^-$ was carried out via an *ab initio* genetic algorithm technique. The pyramidal $C_{2v}(^1A_1)$ molecule was found to be the most stable at all levels of theory. The nearest low-lying isomer was found to be a triplet $C_2$ ($^3$B) structure, 9.2 kcal/mol higher in energy. Comparison of calculated detachment transitions from $LiB_6^-$ and the experimental photoelectron spectra confirmed the $C_{2v}$ pyramidal global minimum structure. Natural population calculation revealed that $LiB_6^-$ is a charge-transfer complex, $Li^+B_6^{2-}$, in which $Li^+$ and $B_6^{2-}$ interact in a primarily ionic manner. Analyses of the molecular orbitals and chemical bonding of $B_6^{2-}$ showed that the planar cluster is twofold ($\pi$- and $\sigma$-) antiaromatic, which can be viewed as the fusion of two aromatic $B_3^-$ units. 
[DOI: 10.1063/1.1839575]

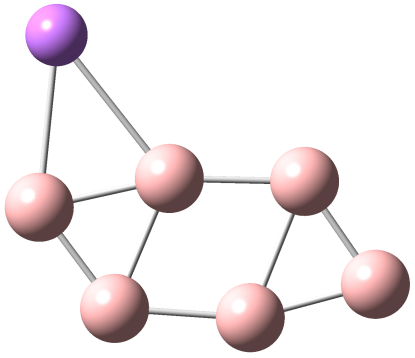


# $LiB_6$

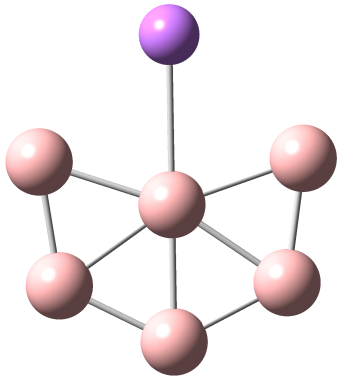


ΔE = 0.0 kcal/mol

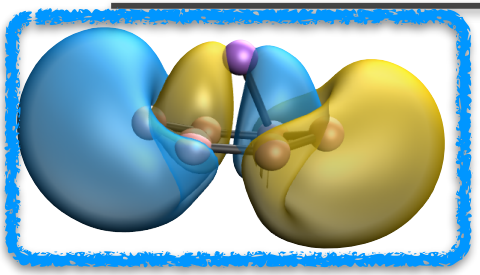


ΔE = 10.07 kcal/mol

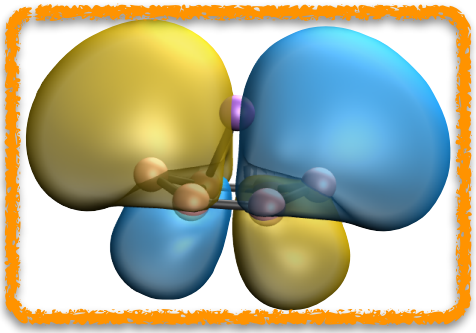


ΔE = 9.95 kcal/mol
ΔE(triplet) = 8.48 kcal/mol

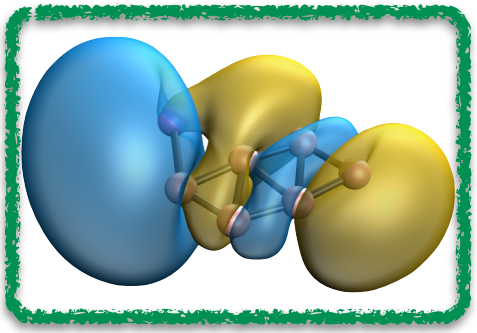
# $LiB_6$



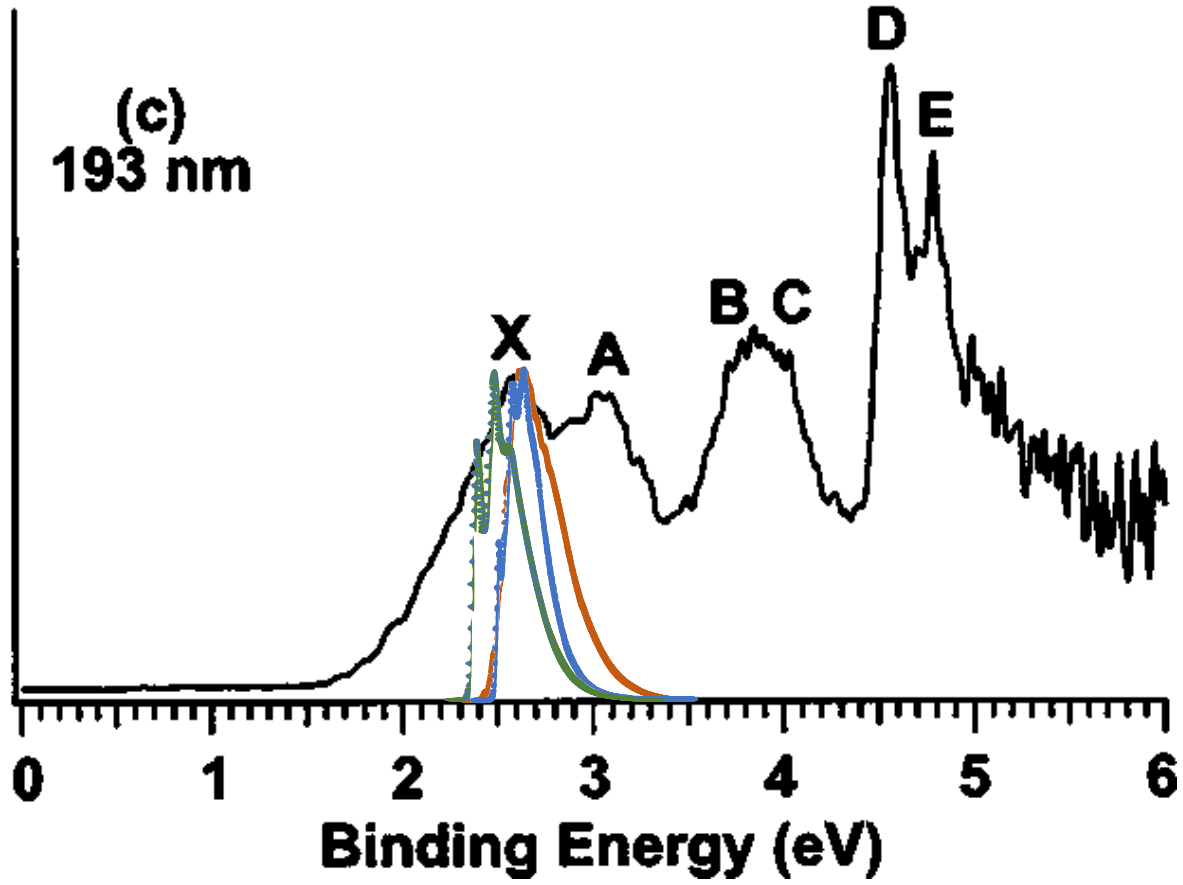
$^1|\rangle \rightarrow {}^2|\rangle + e^-$



$^3|\rangle \rightarrow {}^4|\rangle + e^-$



$^3|\mathrm{III}\rangle \rightarrow {}^4|\mathrm{III}\rangle + e^-$




A. N. Alexandrova, A. I. Boldyrev, H. J. Zhai, & L-S. Wang, *J. Chem. Phys.* **122** 054313 (2005).

# *Summary & Outlook*

- **$MoVO_4$**
  - Care required in treating soft modes
  - Natural Ionization Orbitals rationalize the PE spectrum

- **$LiB_6$**
  - Careful modeling is essential for making correct assignments
  - More experimental data is needed to make definitive assignment

- **Ongoing/Future work**
  - Other clusters: $LiB_6$, Ln containing systems, and more
  - Methods work: PADs, correlation, and TD models using NIOs

# Acknowledgments


- Hector Corzo
- Xianghai Sheng
- Sam Bidwell
- Hassan Harb
- Ali Abou Taka
- Abdul Zamani
- Bryce Fairless
- Yogev Gluzman

- Prof. Lee Thompson, U Louisville
- Prof. Caroline Jarrold, Indiana U
- Prof. Dan Neumark, UC Berkeley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