Computational Exploration of Metal Oxide Cluster Reaction Dynamics

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A=B + C≡D $\xrightarrow{\text{Ni}(0)}$ A\_\text{Ni} \_\text{D} $\xrightarrow{}$ A\_\text{Ni} \_\text{D} \_\text{Ln} \\
M \_\text{A} \_\text{B} \_\text{C} \_\text{D} \_\text{Ni} \_\text{Ln} $\xrightarrow{\text{MR}}$ M \_\text{A} \_\text{B} \_\text{C} \_\text{D} \_\text{R} \_\text{Ln}
Ligand Binding Strength

Hratchian, Clemente, Cato, Sonnenberg, Schlegel, in prep.
### Ligand Binding Strength

<table>
<thead>
<tr>
<th>entry</th>
<th>L</th>
<th>ΔH</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>tmeda</td>
<td>-1.4</td>
</tr>
<tr>
<td>b</td>
<td>PMe</td>
<td>-7.2</td>
</tr>
<tr>
<td>c</td>
<td>ZnMe</td>
<td>13.0</td>
</tr>
<tr>
<td>d</td>
<td>AlMe</td>
<td>-8.0</td>
</tr>
<tr>
<td>e</td>
<td>BEt</td>
<td>no rxn</td>
</tr>
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</table>

Hratchian, Clemente, Cato, Sonnenberg, Schlegel, *in prep.*
Ligand Binding Strength

\[ \Delta H = -8.3 \]

\[ \Delta H = 6.1 \]

\[ \Delta H = -2.0 \]
Study of MoNbO_y (y = 2–5) Anion and Neutral Clusters Using Photoelectron Spectroscopy and Density Functional Theory Calculations: Impact of Spin Contamination on Single Point Calculations

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Supporting Information

ABSTRACT: Results of a study combining anion photoelectron spectroscopy and density functional theory calculations on the heteronuclear MoNbO_y^− (y = 2–5) transition metal suboxide cluster series are reported and analyzed. The photoelectron spectra, which exhibit broad electronic bands with partially resolved vibrational structure, were compared to spectral simulations generated from calculated spectroscopic parameters for all computationally determined energetically competitive structures. Although computational results on the less oxidized clusters could not be satisfactorily reconciled with experimental spectra, possibly because of heavy spin contamination found in a large portion of the computational results, the results suggest that (1) neutral cluster electron affinity is a strong indicator of whether O-atoms are bound in M—O—M bridge positions or M—O terminal positions, (2) MoNbO_y anions and neutrals have structures that can be described as intermediate with respect to the unary (homonuclear) MoO_y and NbO_y clusters, and (3) structures in which O-atoms preferentially bind to the Nb center are slightly more stable than alternative structures. Several challenges associated with the calculations are considered, including spin contamination, which appears to cause spurious single point calculations used to determine vertical detachment energies.

INTRODUCTION

mesoporous Nb_2O_3 support for Pt, Au, Cu, and Ni oxides
The bond length of 2.5 Å is unphysical and resembles the PUHF curve more than the UMP2 profile. The unrestricted PMP2 energy profile is much less acceptable than the UMP2 curve. This result is due to contaminants in the unrestricted PMP2 dissociation curve beginning around 3.1 Å. At a bond distance of 3.1 Å, the bond distance increases, the UMP2 energy expression is that only the reference UHF wave function with spin multiplicities higher than 3. Recall from Section 5 that the usual approximation for the projected reference wave functions are 1.328, 0.002, and 0.000. At a bond length of 3.1 Å, the unprojected UHF ⟨S^2⟩ rises above 1.0.

More central to the topic of interest here are the important difference between DFT and HF is the range of spin contamination in computational inorganic chemistry. Spin contamination near the minimum, possibly because of spin contamination in the unrestricted DFT curve presents a second local energy minimum and displays the unrestricted PMP2 curve is much less acceptable than the unrestricted PMP2 curve. The third essentially corrects the unrestricted PMP2 curve and gives the correct physical picture of bond dissociation. The fact that curves with two and three projected contaminants projection is probably not needed, as is demonstrated by the energy profiles using annihilation operator reweights the relative contamination of the next higher spin state contaminates the UHF reference wave function. Removing the triplet contaminant with a single projection is probably not needed, as is demonstrated by the energy profiles using annihilation operator reweights the relative contamination of the next higher spin state contaminates the UHF reference wave function. Removing the triplet contaminant with a single projection is probably not needed, as is demonstrated by the energy profiles using annihilation operator reweights the relative contamination of the next higher spin state contaminates the UHF reference wave function.

In fact, B3LYP and BLYP suggest much less contamination from higher spin states. The UB2PLYP singlet determinants pl rises from 0.0 to 1.0, which is given in Figure 7(b). In all three cases, the DFT curves do not appear to show spin contamination near the energy minimum. The B2PLYP determinant does begin to rise almost immediately, matching the UBLYP value in Figure 7(b). However, the DFT results have any significant contaminants higher than triplet states. As seen in the H case, the onset of spin contamination for the DFT determinants comes later in the ScH curve than for the HF wave function. For B3LYP and BLYP, spin contamination does not become problematic until after the bond distance of 2.5 Å.
Approximate Spin Projection

- Various approaches:
  - Yamaguchi
  - Noodleman

- Analytic gradients involve CPHF-like terms

\[ E = \alpha E_{LS} + \left(1 - \alpha \right) E_{HS} \]
\[ \alpha = \frac{\langle S_{HS}^2 \rangle - s_{z,LS} (s_{z,LS} + 1)}{\langle S_{HS}^2 \rangle - \langle S_{LS}^2 \rangle} \]

<table>
<thead>
<tr>
<th></th>
<th>S</th>
<th>R(Mo-Nb)</th>
<th>AP R(Mo-Nb)</th>
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<tbody>
<tr>
<td>singlet</td>
<td>1.17</td>
<td>2.327 Å</td>
<td>2.257 Å</td>
</tr>
<tr>
<td>triplet</td>
<td>3.99 (99.6%)</td>
<td>2.667 Å</td>
<td>3.039 Å</td>
</tr>
<tr>
<td>quintet</td>
<td>6.95 (15.8%)</td>
<td>2.754 Å</td>
<td>2.691 Å</td>
</tr>
<tr>
<td>septet</td>
<td>12.26 (2.2%)</td>
<td>2.925 Å</td>
<td>2.915 Å</td>
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Summary & Outlook

• Selectivity in Ni catalyzed three-component coupling reactions driven by ligand/reductant choice

• Directed energy transfer may be source of significant “catalytic” effects in TM catalyzed reactions

• Spin contamination leads to large geometric errors in metal oxide systems

• Approximate spin projection models under development
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