

Understanding the potential energy surface of CO oxidation with O₃ and Au atoms utilizing DFT and AIMD



Angela N. Smith, David T. Moore

Department of Chemistry, Lehigh University, Bethlehem, PA 18015



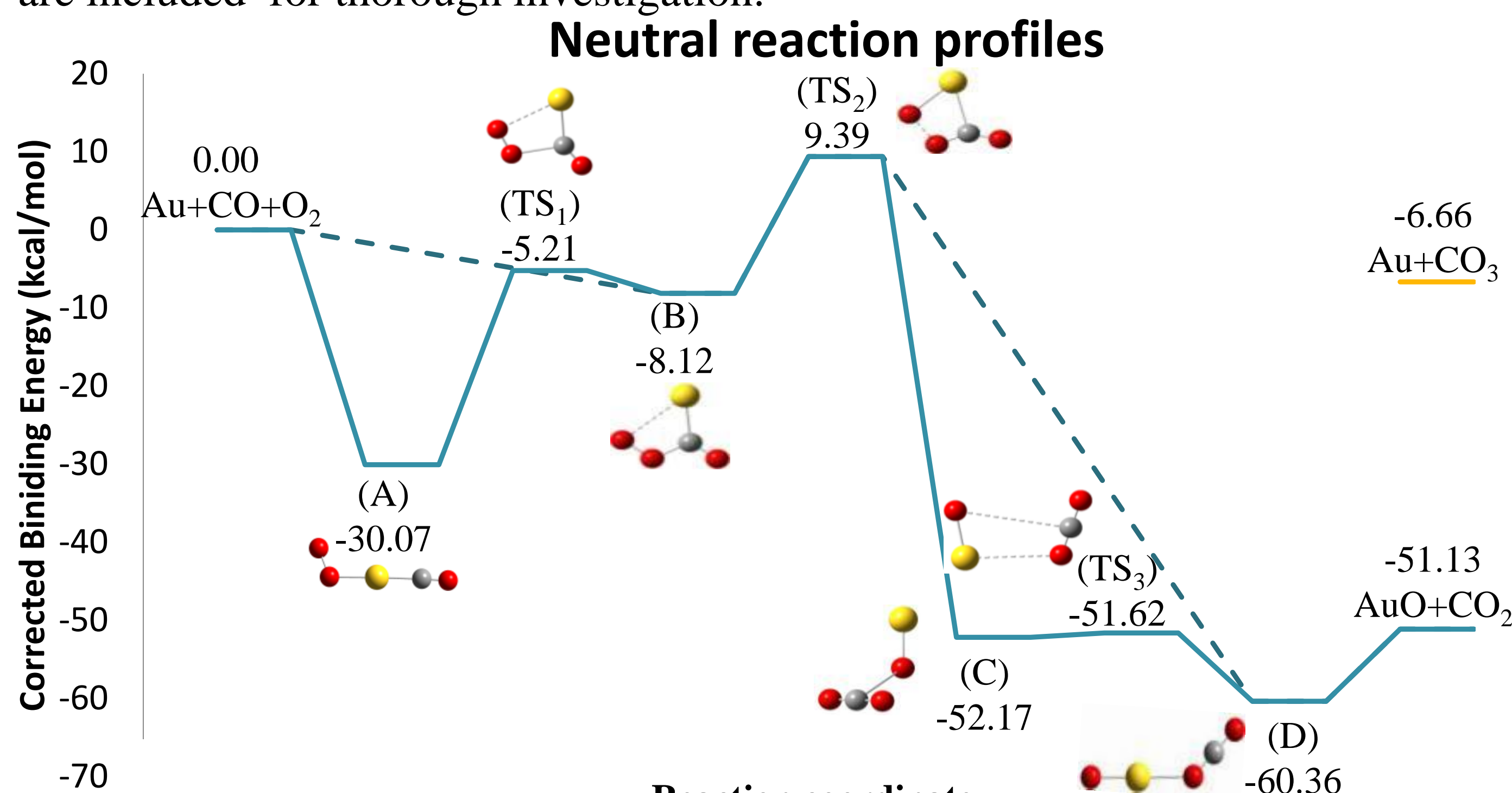
Introduction

Ozone decomposition has been observed over supported Au nanoparticles & single crystal Au surfaces; many of these catalysts have been utilized in CO oxidation.¹⁻⁴ Several of these experiments have focused on kinetics and, to some extent, gas phase intermediates of [Au_nO₃]^q (q=+1,-1 & n=1-9), where Castleman *et al.* identify two binary complexes; however, they focus on ground state O₂AuO (triplet) complex for reaction profiles.^{5,6} DFT calculations can provide evidence for the structure of the [Au+O₃+CO]^q complexes with respect to connectivity, energy & vibrational frequencies. Here we present results on the [Au+O₃+CO]^q reaction profiles to compare with the [O₂+Au+CO]^q systems, where q=+1,0,-1.

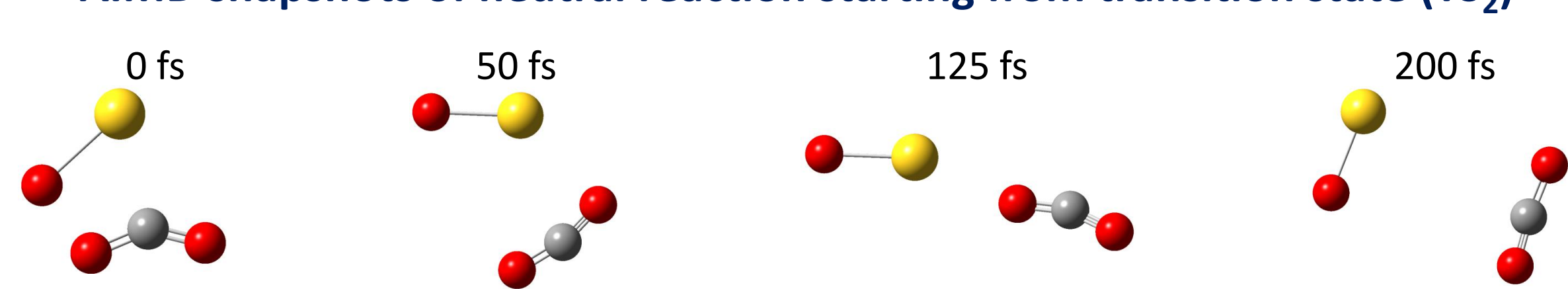
Computational Methods and Results

DFT geometry optimizations. Frequency, IRC and AIMD calculations were performed for the binary [AuO₃]^q complexes, and ternary [O₃AuCO]^q complexes, for charge states q=1,0, and -1. The results reported here are for B3LYP hybrid functional and mixed SDD/6-311+G(3df) basis set for Au/C,O respectively.

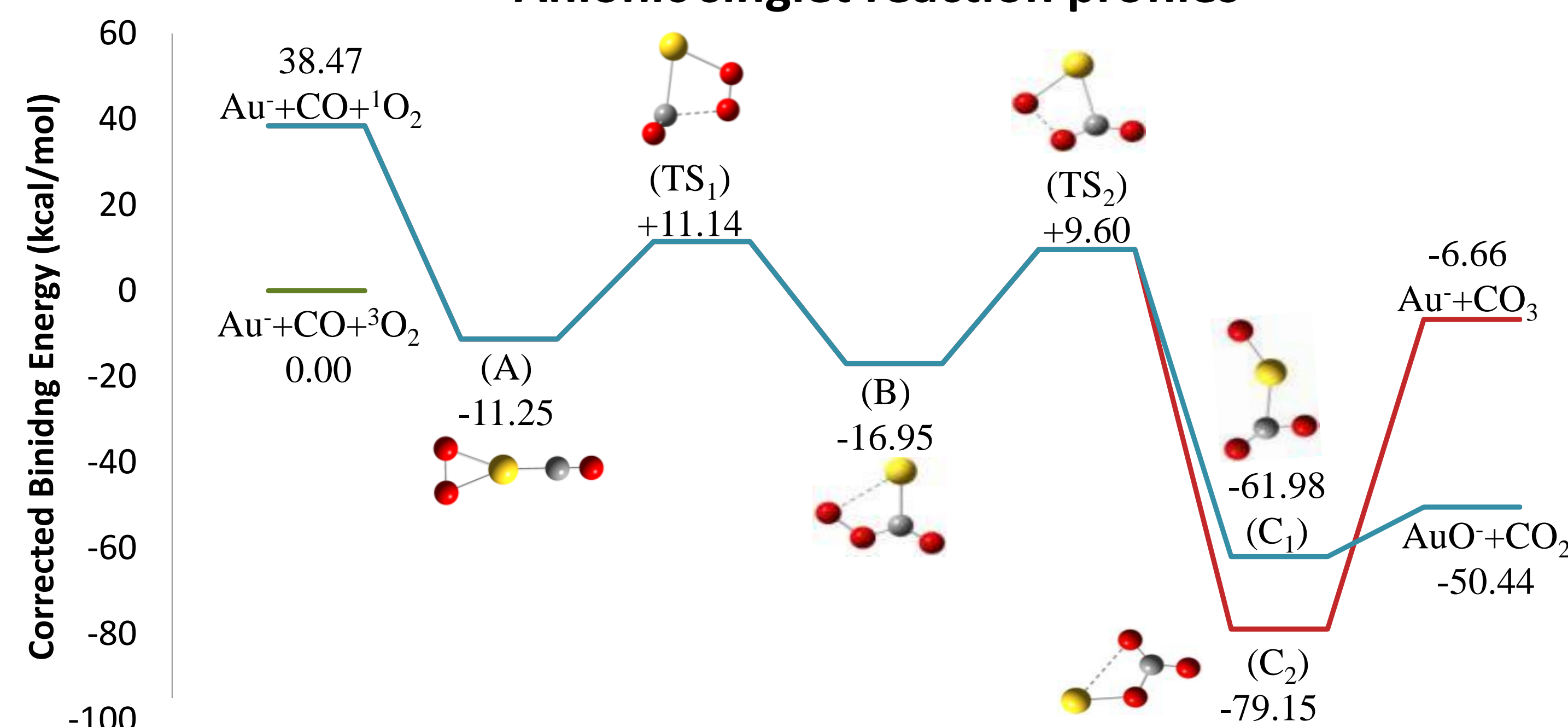
Spin-states: In general, for each complex there was a clearly identifiable “best” spin-state, giving a lower energy than all others, as noted in the tables below. Spin states within ~50 kcal/mol of lowest energy complex with the *same charge* are included for thorough investigation.



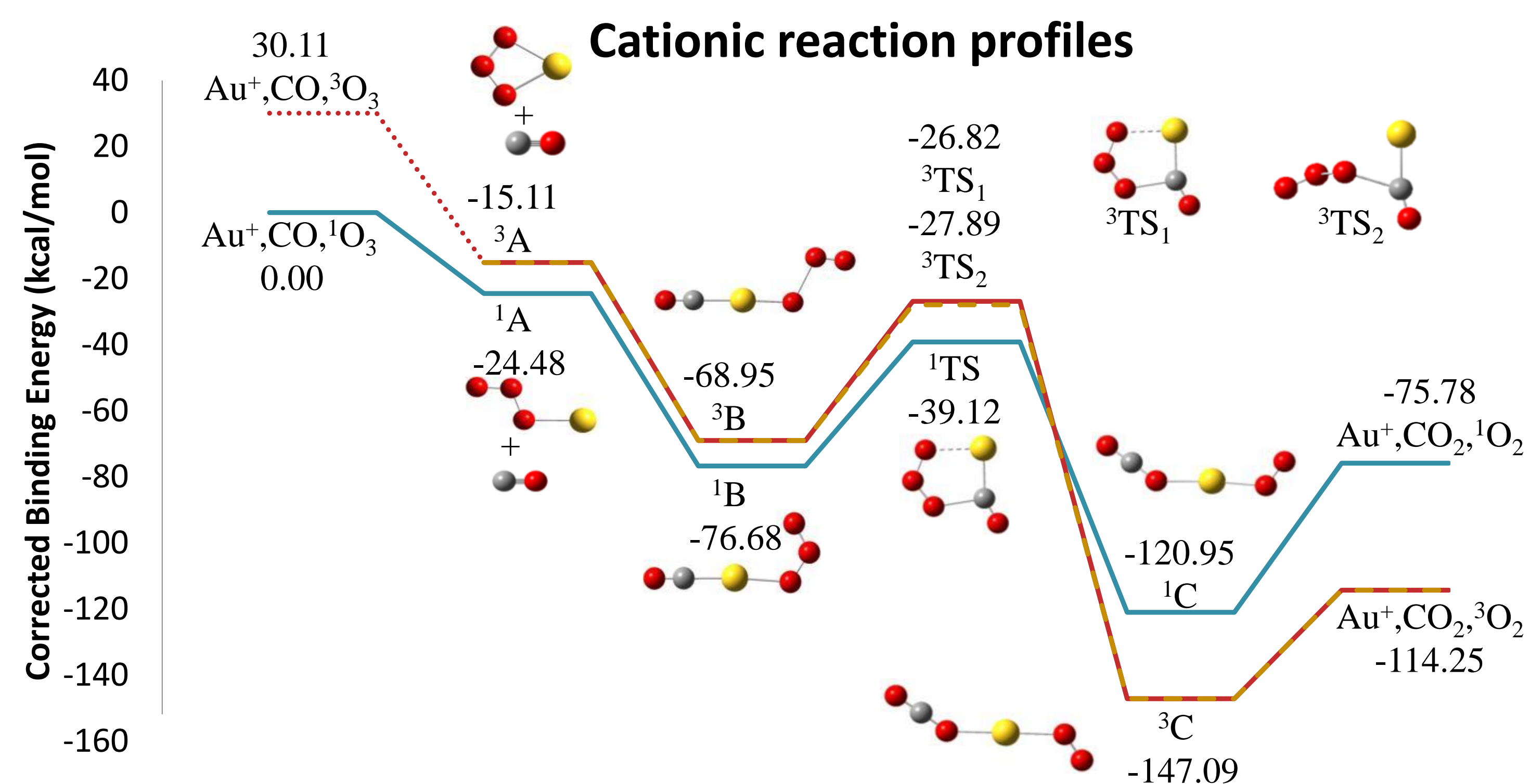
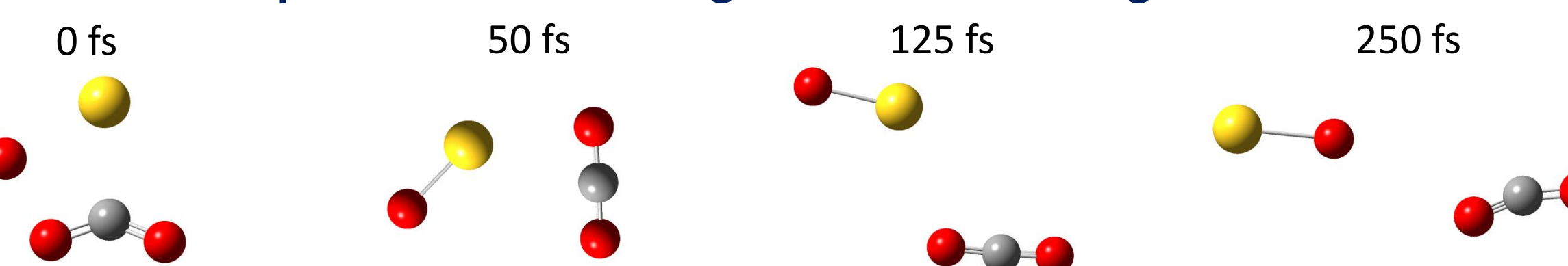
AIMD snapshots of neutral reaction starting from transition state (TS₂)



Anionic singlet reaction profiles

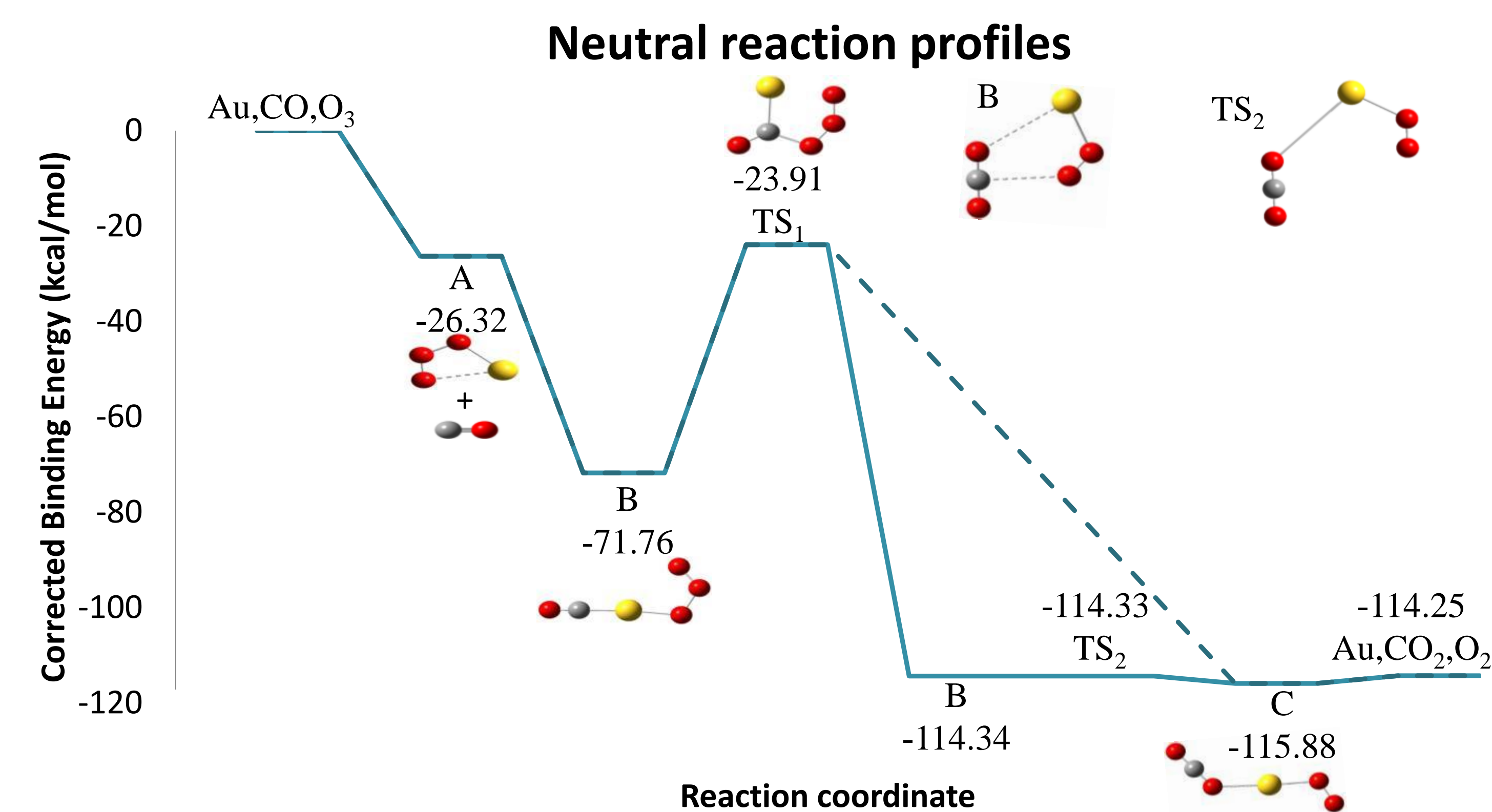
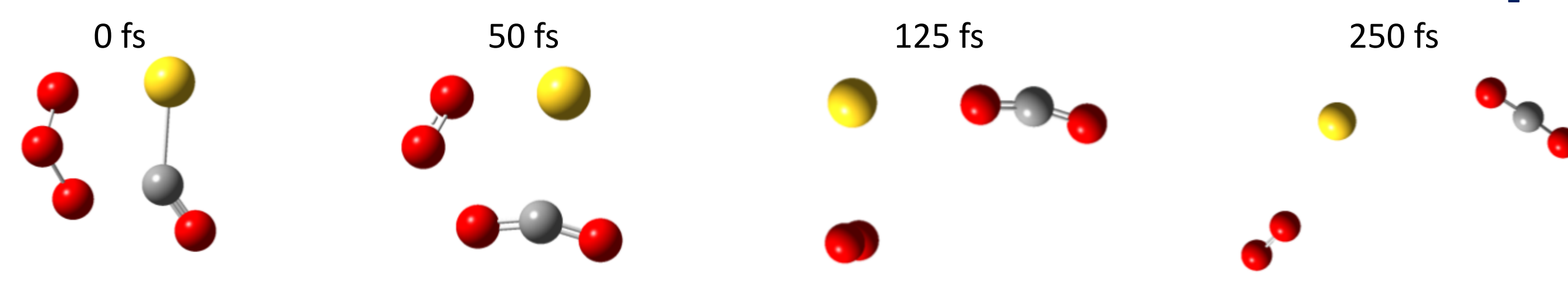


AIMD snapshots of anionic singlet reaction starting from transition state (TS₁)



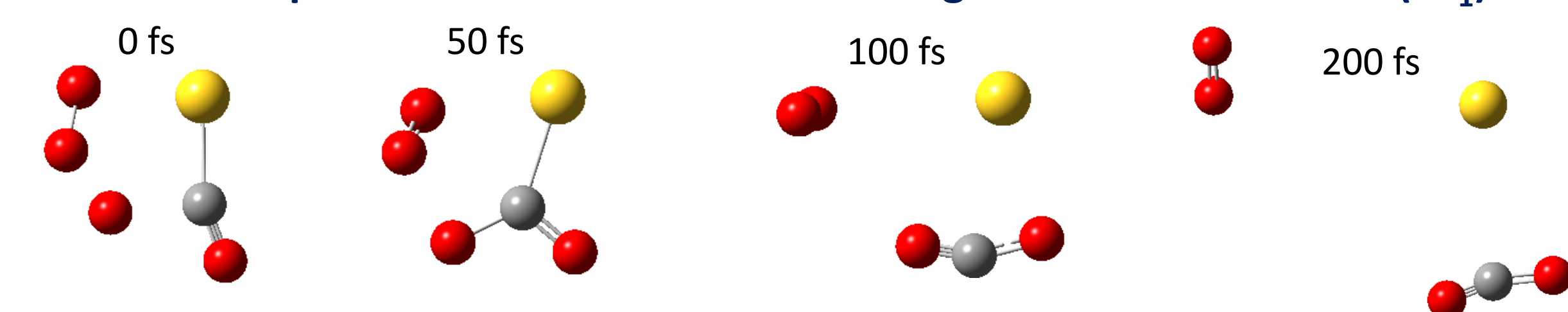
Reaction coordinate

AIMD snapshots of cationic singlet reaction starting from transition state (1TS₁)



Reaction coordinate

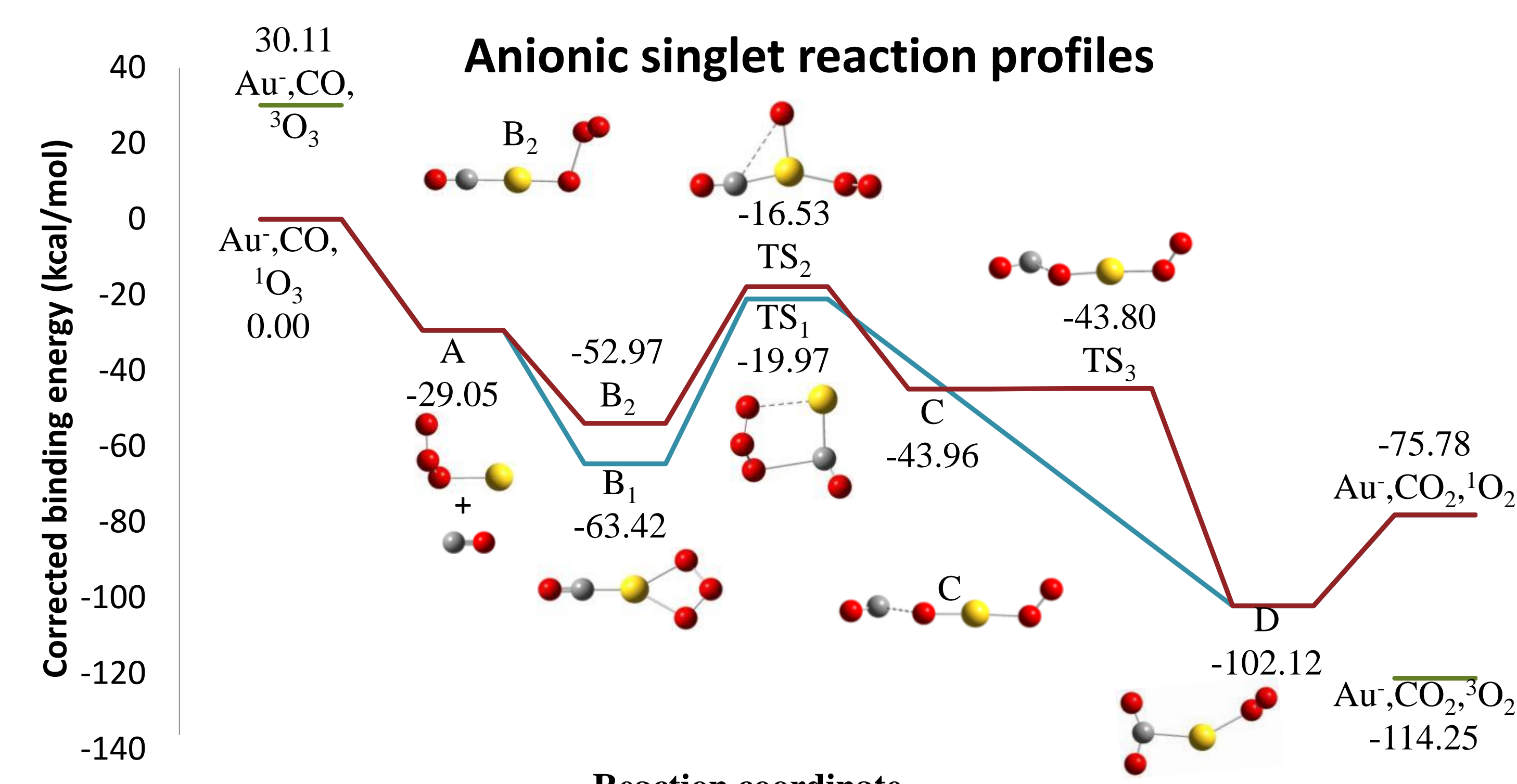
AIMD snapshots of neutral reaction starting from transition state (TS₁)



- [Au+CO+O₂] neutral & anionic reaction profiles have 9.39 & 9.60 kcal/mol barriers
- Ozone reaction profiles indicate barrier-less reactions to form CO₂ from CO & O₃
- Cationic and neutral profiles show oxidation of CO by molecular O₃
- Anionic singlet and triplet pathways appear to be entryways onto [O₂AuO+CO]⁻ pathways described previously by Castleman and co-workers⁶
- Ozone reaction profiles start from “separated” species, while O₂ reaction profiles have “pre-reactive” complexes as the starting structures
- AIMD of several reaction profiles display oxidation of CO by molecular O₃, when starting at or near the transition states

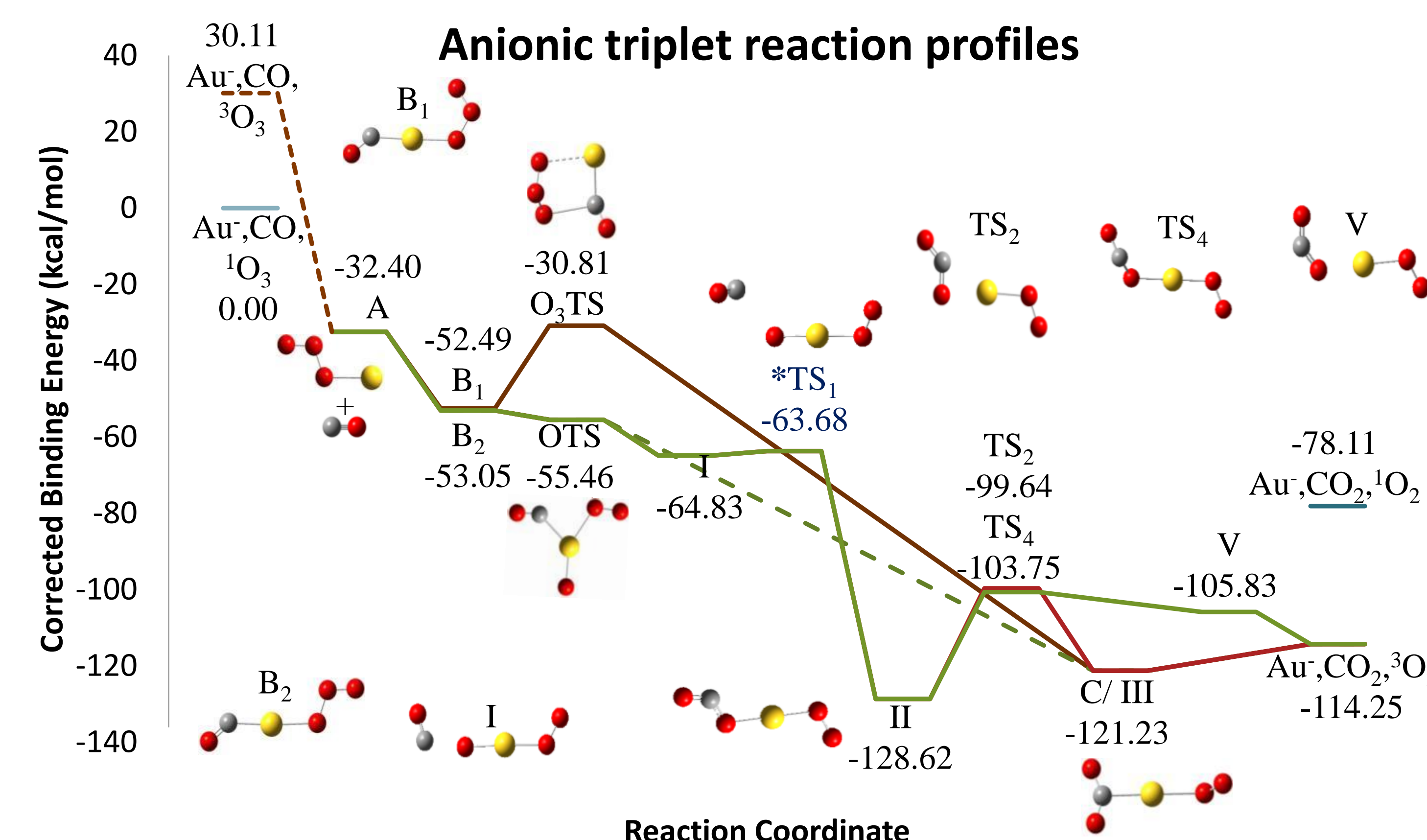
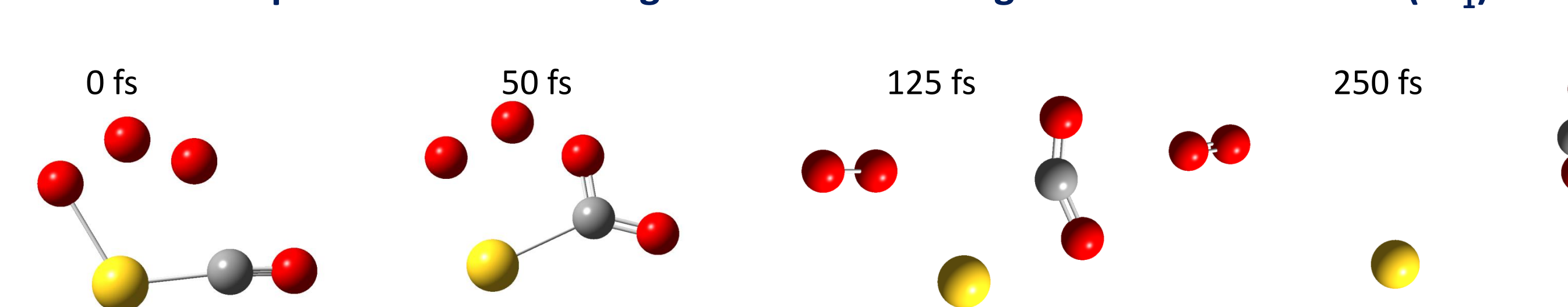
References

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Reaction coordinate

AIMD snapshots of anionic singlet reaction starting from transition state (TS₁)



* Energy reported in 6-31+G(d) basis set. Transition state has not been found in 6-311+G(3df) basis.

Conclusions and Future Work

Use of O₃ as a reactant leads to barrier-less reaction profiles relative to reactants. Cationic, neutral and anionic (to an extent) systems display oxidation by molecular O₃, while anionic systems also appear to be entryways onto [O₂AuO+CO]⁻ pathways, as previously shown by Castleman.⁶ Even with barrier-less profiles, stable “pre-transition” and “post-transition” complexes can be formed (and possibly isolated in experiments). We are also assuming that this system can be probed with a single reference calculations without regard to curve crossing, which can be dangerous with spin active species, like O₃. Future computational work includes AIMD calculations starting at minima/reactants and testing the dimer reaction pathways. We will also test these atomic pathways with higher level basis sets, such as aug-cc-pVQZ, and utilizing other computational methods (MP2 or B2PLYP) and DFT functionals (B3PW91 and mPW1PW91). We will complete experiments, using matrix isolation techniques, to probe the Au atom, CO, and ozone system.

Acknowledgements

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