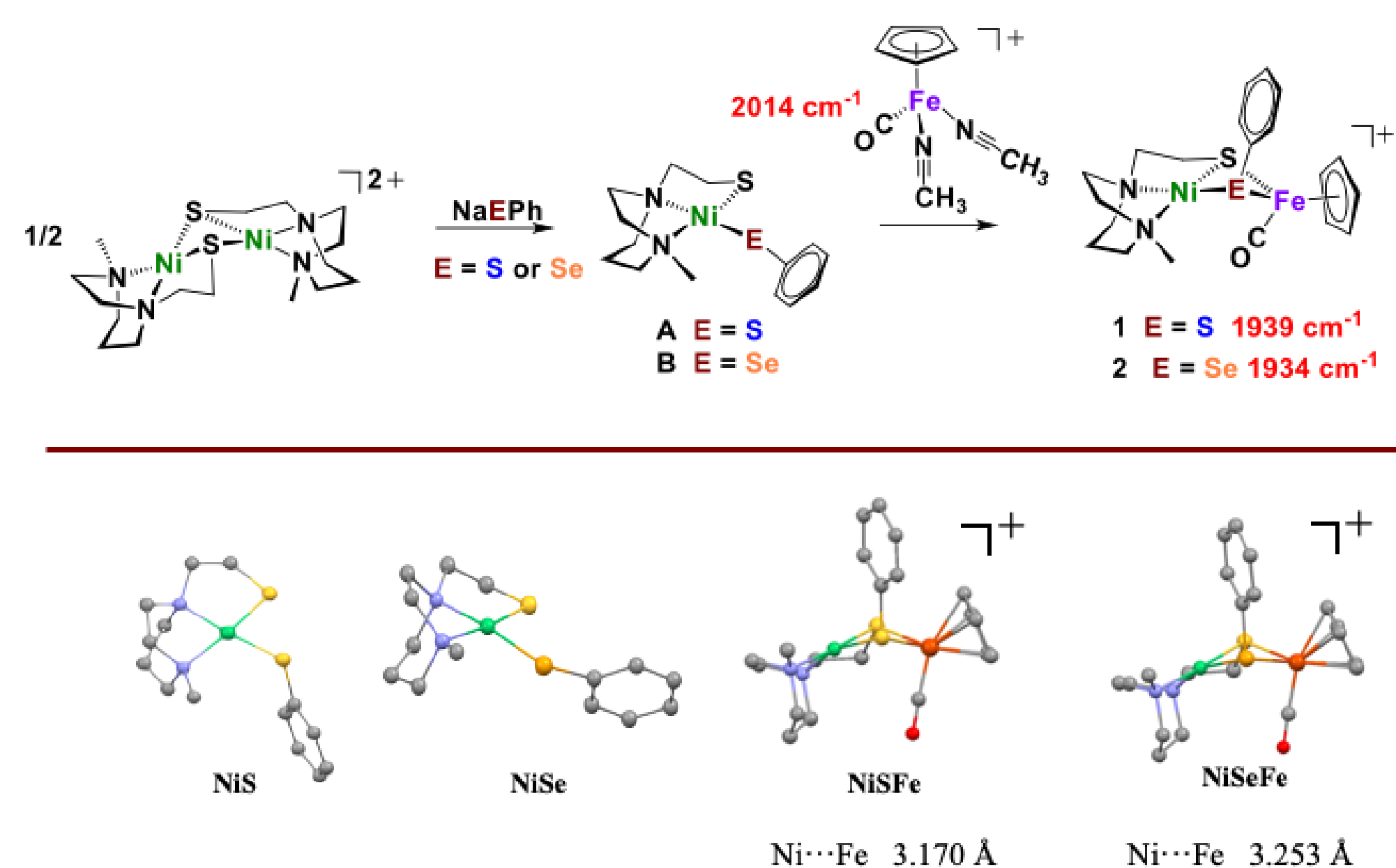
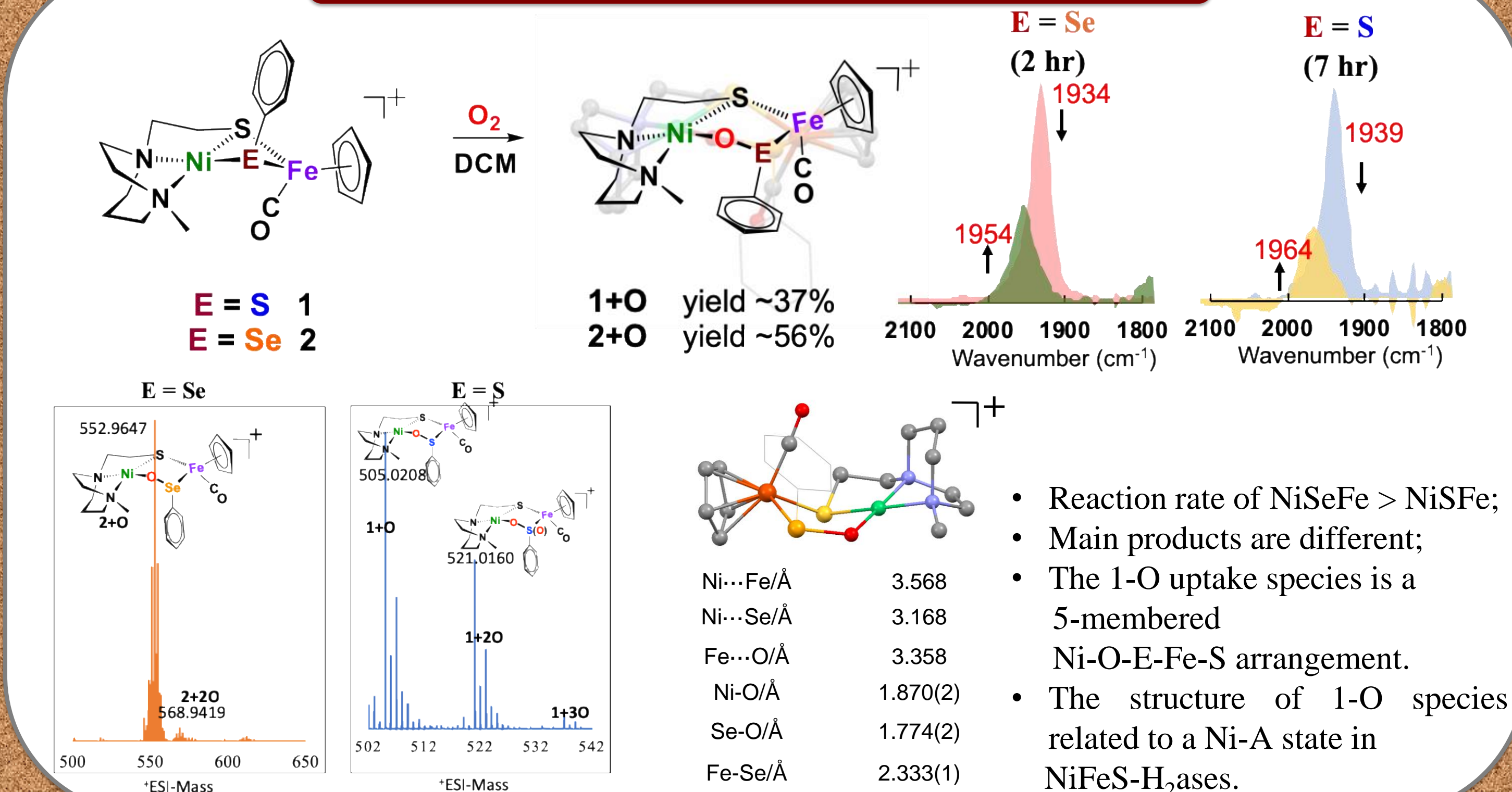




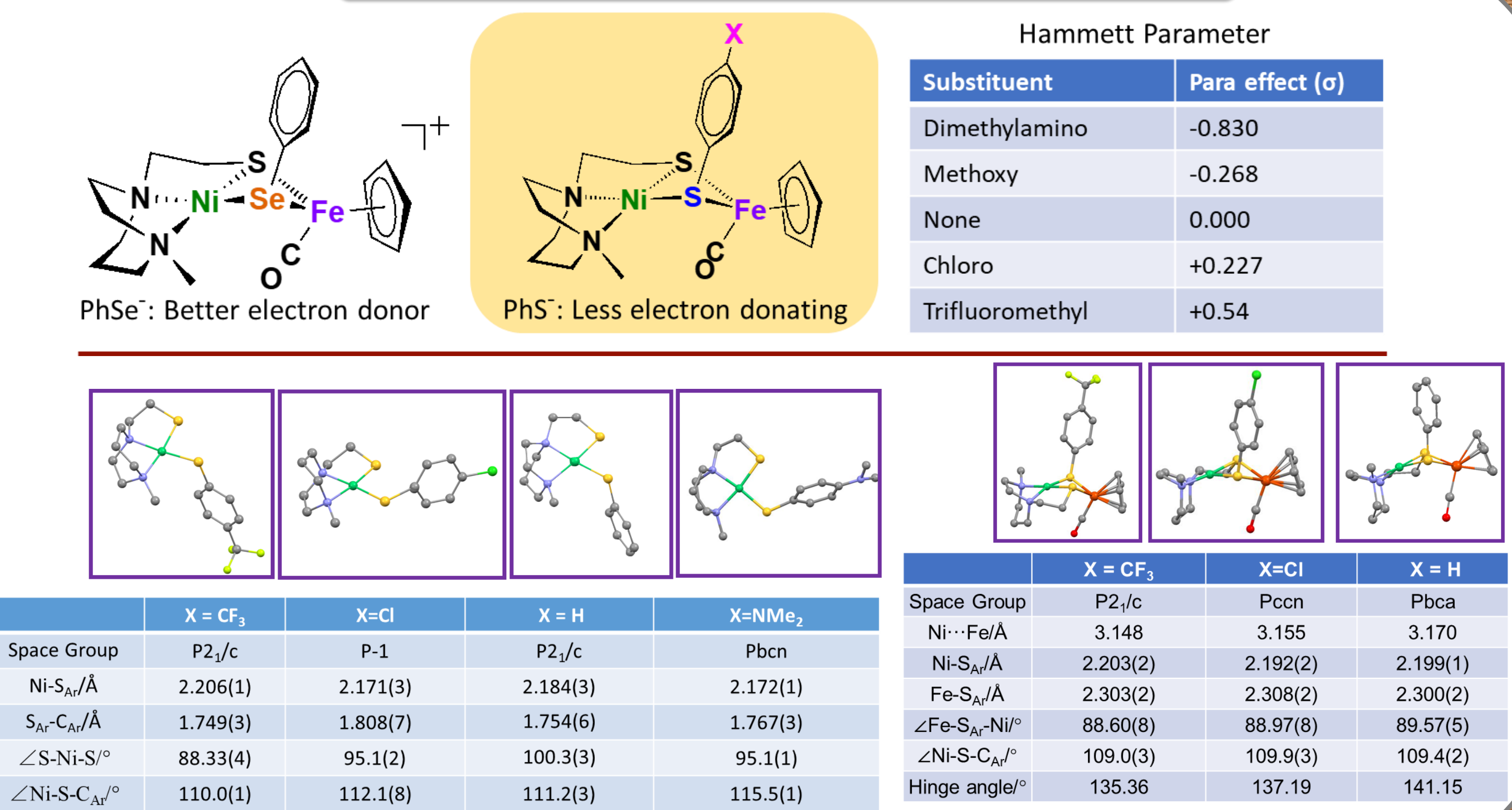
Synthesis of NiFe Complexes



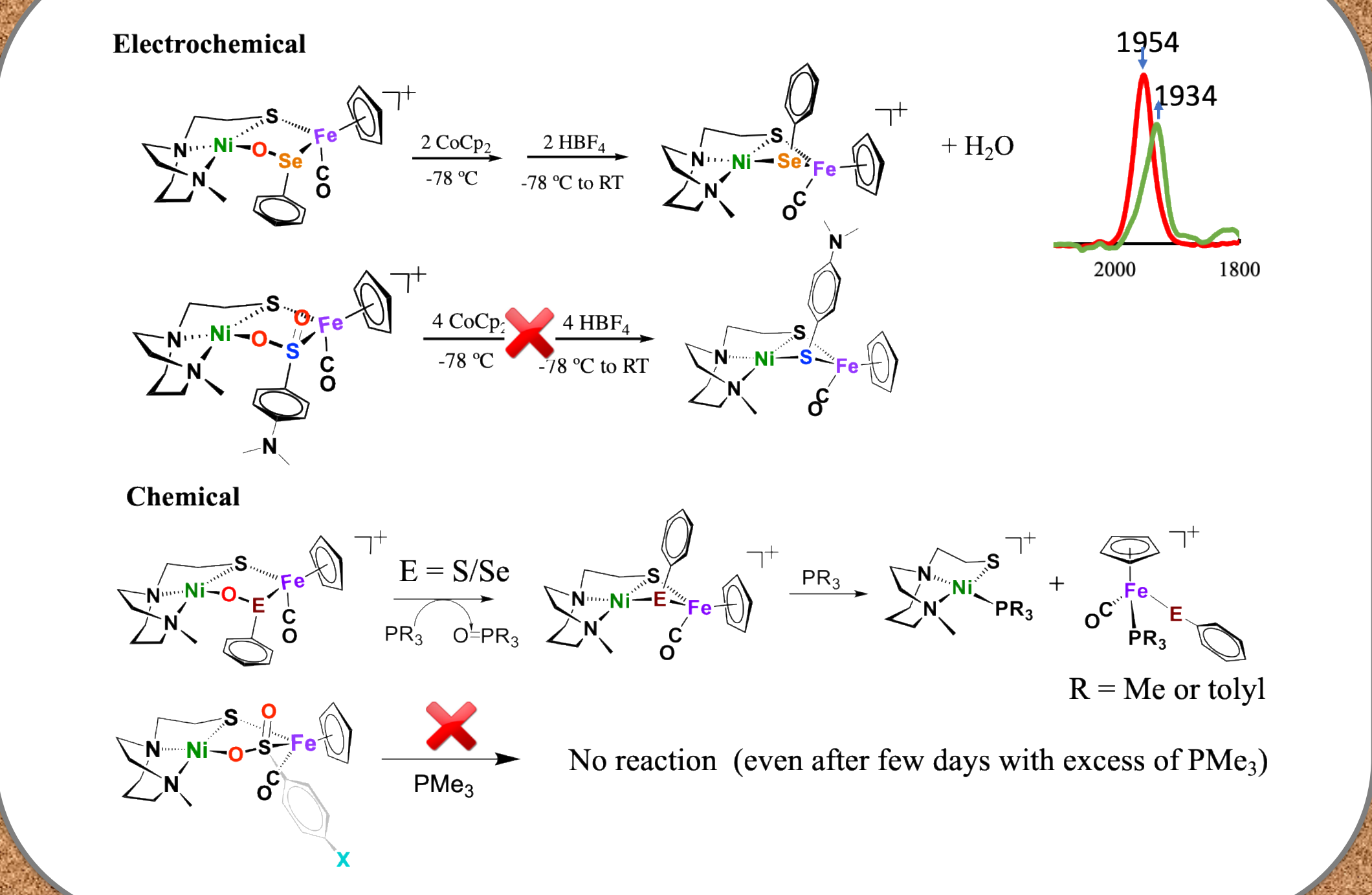
O₂ reaction with NiFe Complexes



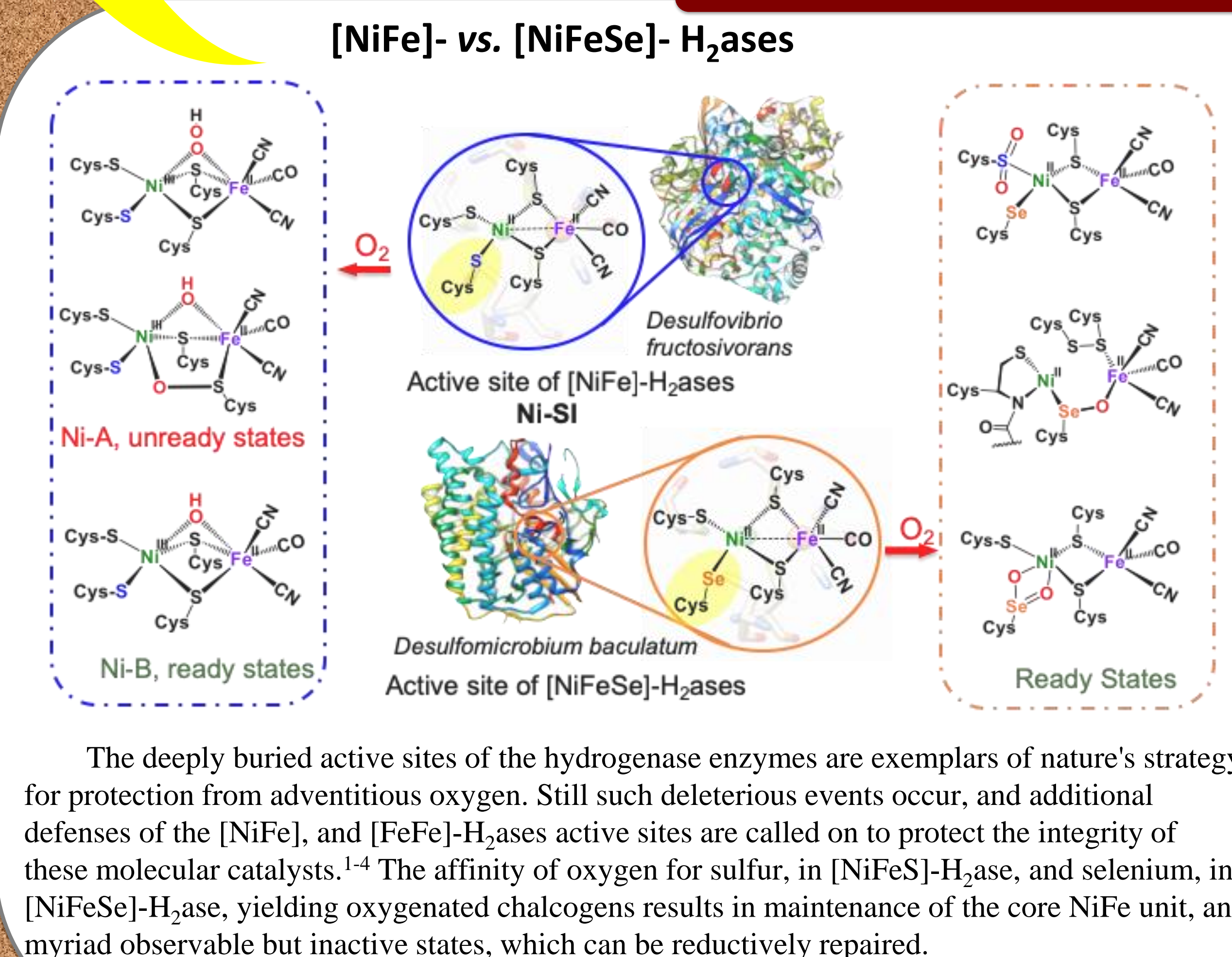
Electronic Mutation of RS to RSe



Deoxygenation of NiE(O)_xFe



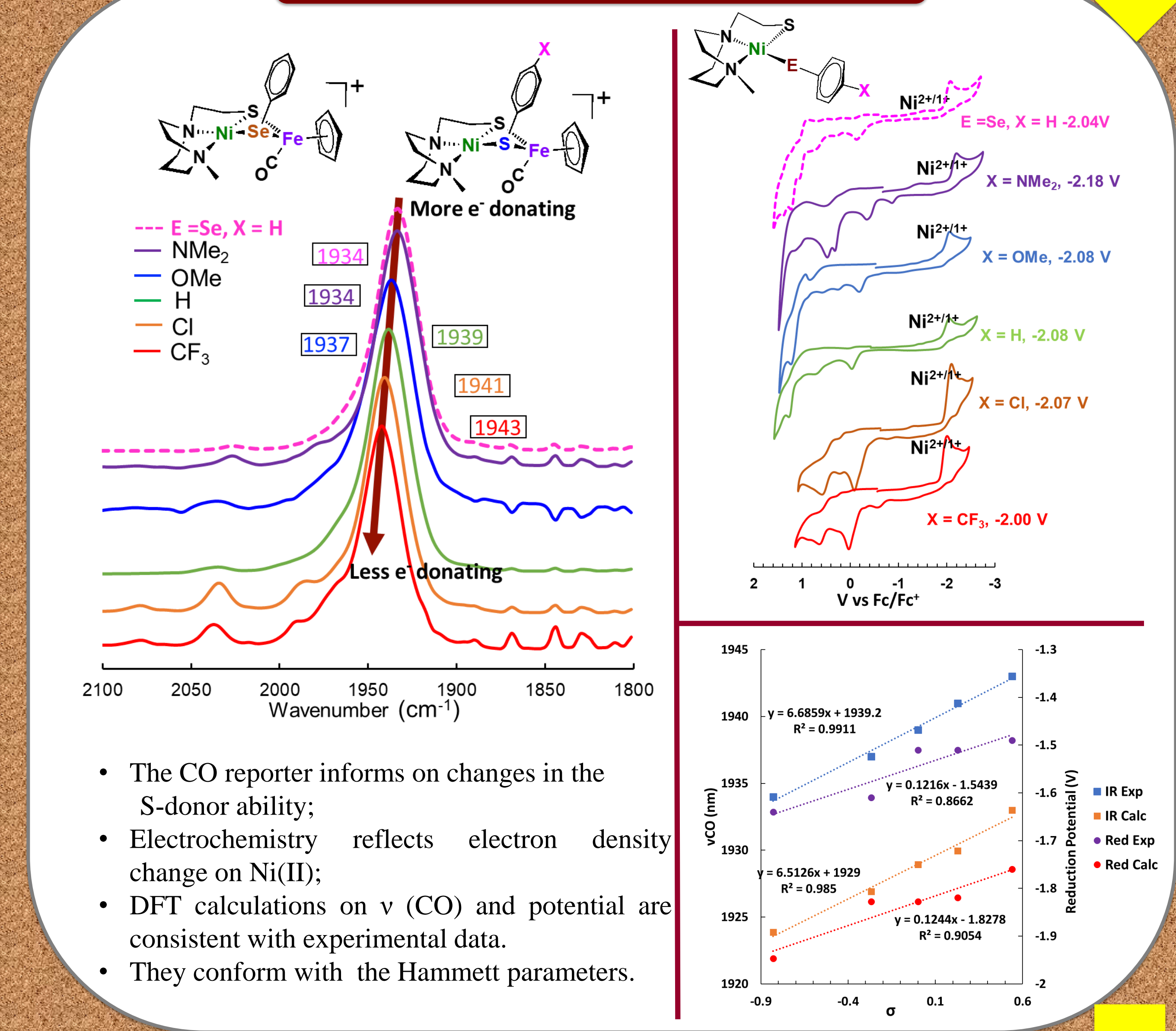
Introduction



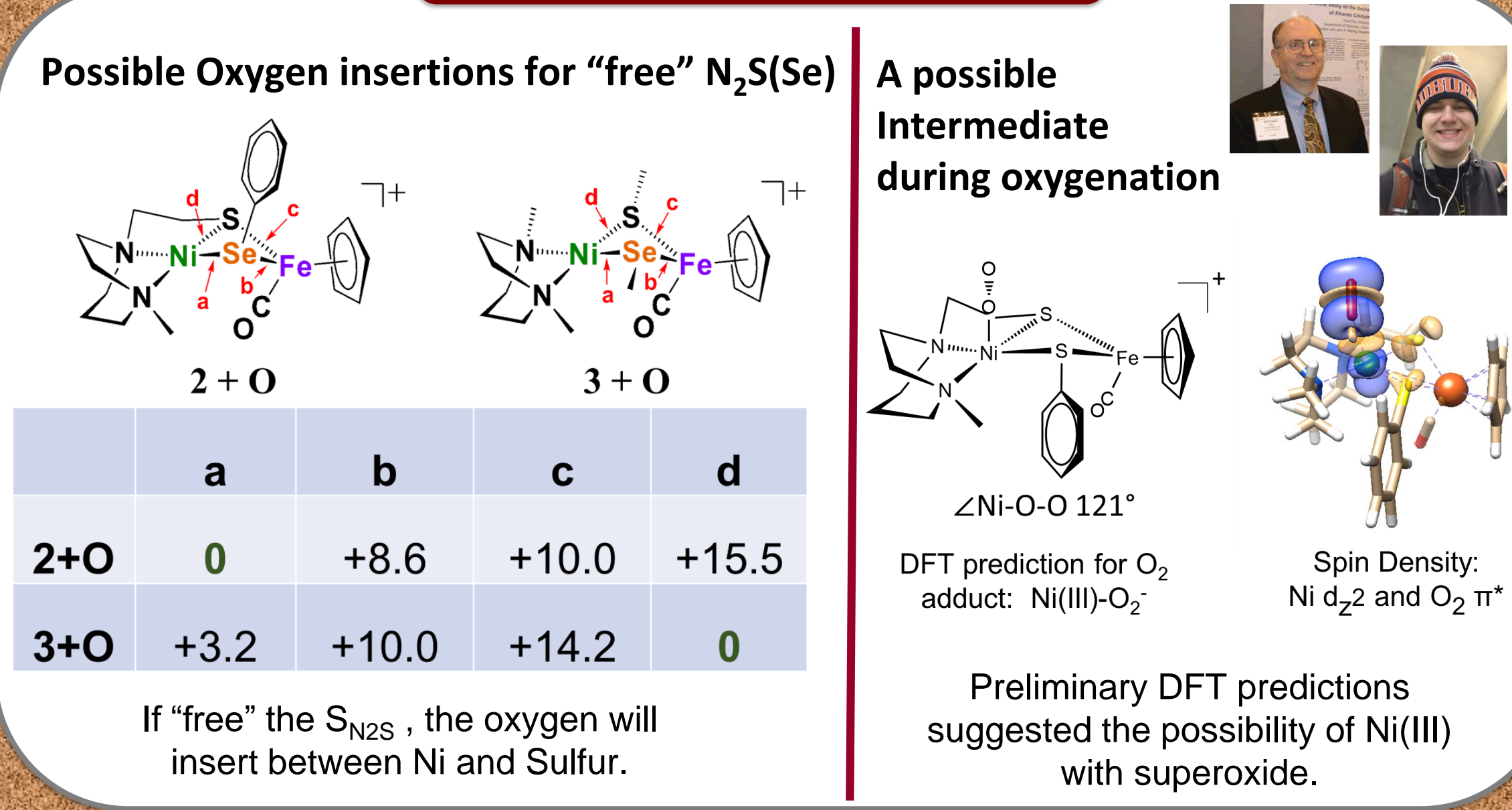
Question and Hypothesis

- Can oxygen uptake in [NiFe]-H₂ases be mimicked by small molecule analogues?
 - Is the biomimetic oxygenated S/Se able to accomplish reduction-induced repair processes?
 - What factor determines oxygen tolerance of complex and how can we overcome complexes' oxygen sensitivity?
- We have explored the difference in O₂ reactivity between small [NiFe] models containing SPh and SePh in bridging positions. Analysis of all the products of such reactions found multiple O-atom uptake, similar to the O-damaged [NiFe]-H₂ase active sites, indicating that the models might yield further information.

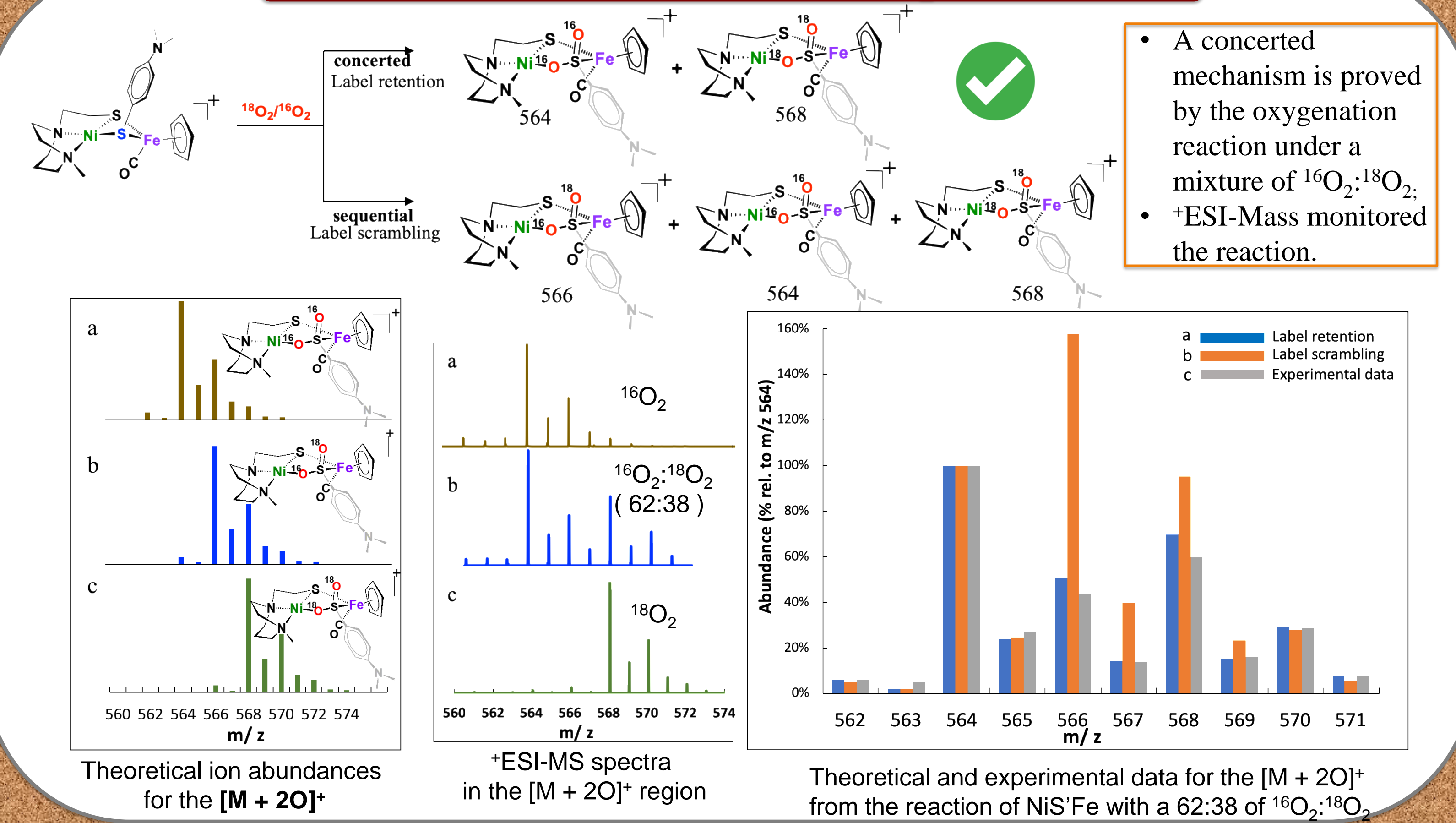
Modified NiS'Fe Complexes



DFT Calculation



Concerted vs. Sequential O₂ Addition



Conclusion

- The system has provided opportunity to examine O₂ reactivity that yields isolable complexes based on sulfur and selenium oxygenates.
- Consistent with the enzyme studies, selenium displays more rapid reactions for O₂ uptake, as well as O-atom removal. The chalcogenides play as "soldiers" to protect the NiFe heterobimetallic.
- The question of why nature chose heavier elements in the chalcogen relate to their intricate interactions with oxygen.

Oxygenation of NiS'Fe

X	React time	Main Product	Yield
NMe ₂	3.5 h	2-Oxygen uptake	~55 %
H	7 h	Mixture of 1-Oxygen and 2-Oxygen uptake	~37%
CF ₃	24 h	Mixture of 1-Oxygen, 2-Oxygen uptake complexes	~30%

Ni...Fe Distance	Value
Ni-O / A	1.880(3)
Fe-S _{ph} / A	2.169(1)
Fe-S _{ph} -O ₂ / A	1.536(3)
S _{ph} -O ₂ / A	1.464(3)
S _{ph} -O ₂ / A	1.776(4)
∠O-Ni-S _{ph}	91.96(10)
∠Ni-S-C _{ph}	82.63(16)