The role of transition metals in the structure and reactivity of astrochemicals

Nathan J. DeYonker

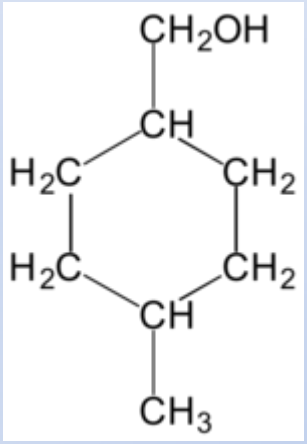
The University of Warwick Centre for Scientific Computing

6/5/2017


WE'VE GOT YOUR SIZE IN FRIES!
McDonald's
McDonald's
McDonald's
Now our biggest!
astrochem
inorganic
biochem

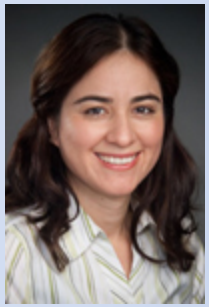
Medium fries

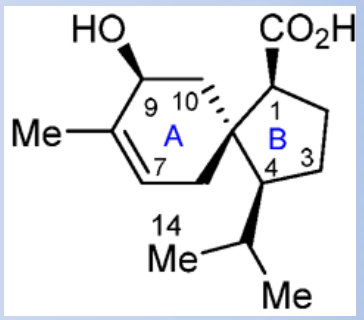
Environmental



Prof. William Alexander @ U. Memphis

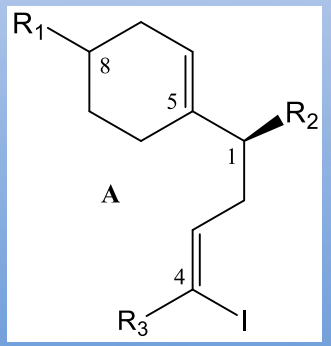
& organometallic chemistry





Retrosynthesis of Pharmaceutical scaffold

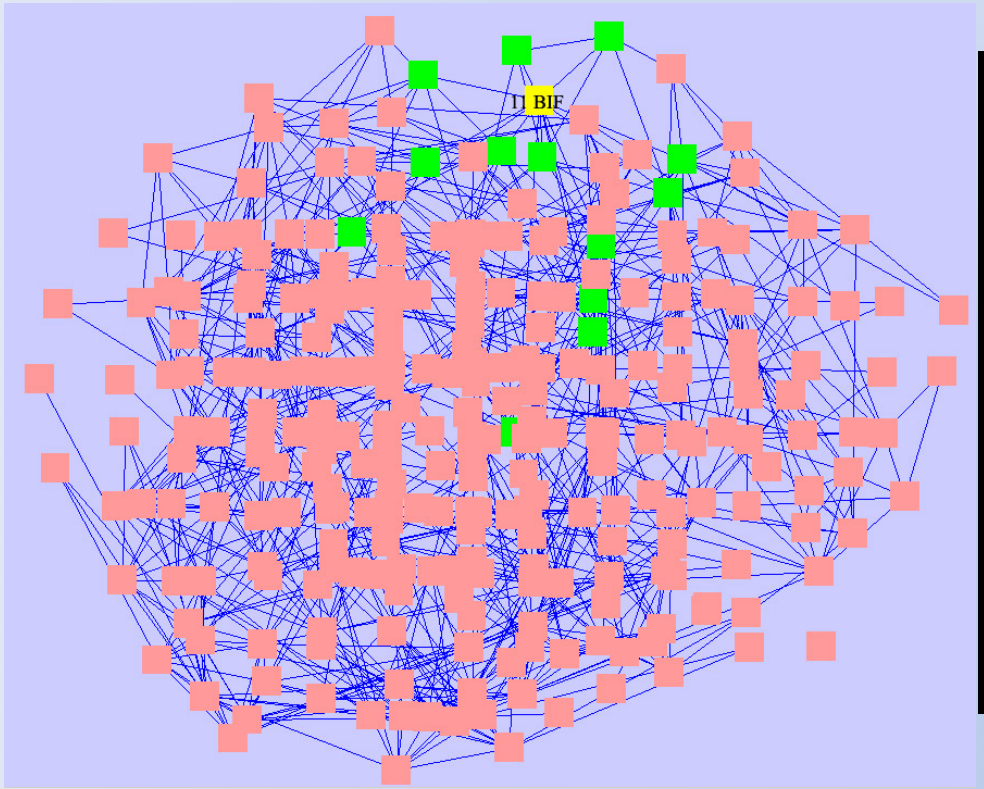
(Intramolecular Pd-catalyzed Heck)

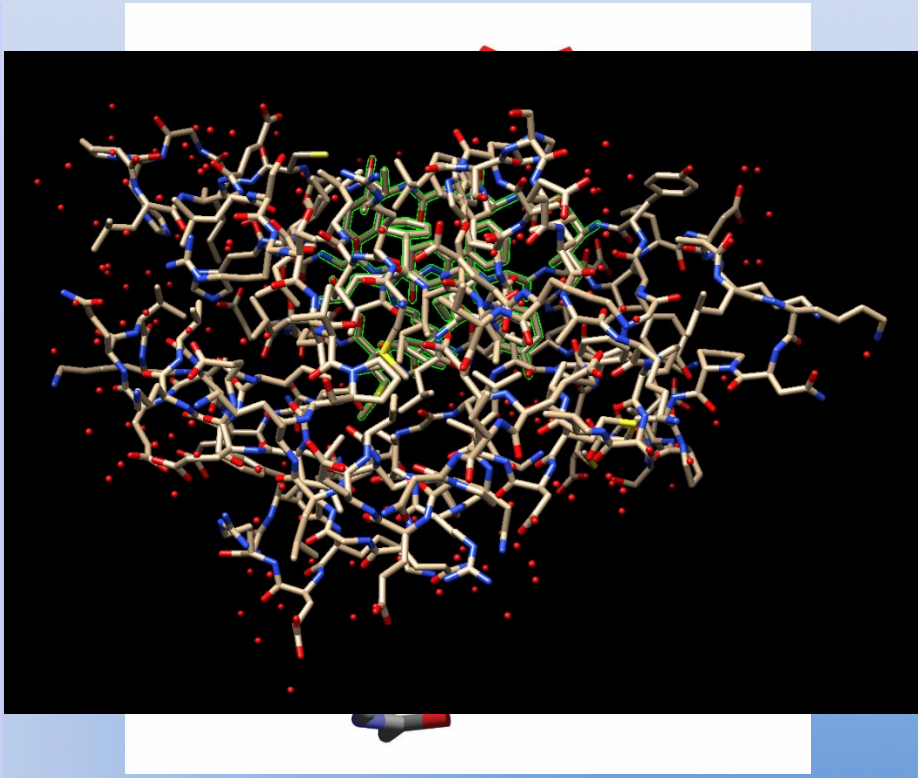


Dr. Fatima Rivas @ St. Jude Children's Hospital

Large fries

Reproducible/systematically constructed QM enzyme models





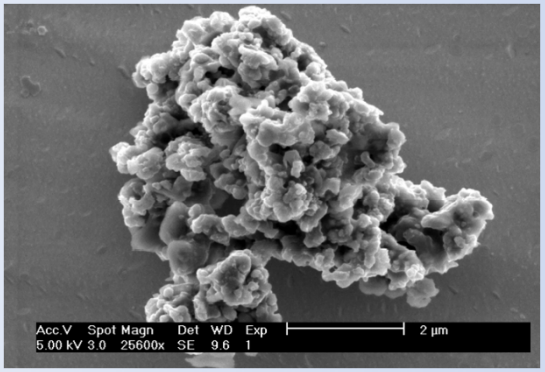
Are we alone in the Universe?

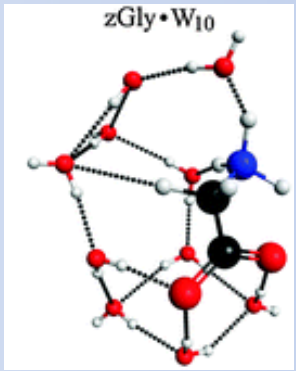
“I think we’re going to have strong indications of life beyond Earth within a decade, and I think we’re going to have definitive evidence within 20 to 30 years. We know where to look. We know how to look. In most cases, we have the technology, and we’re on a path to implementing it.”

-Dr. Ellen Stofan

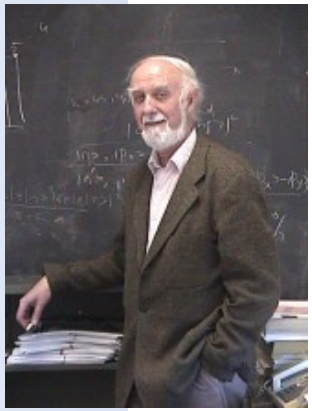
Previous NASA Chief Scientist

Before astrobiology, astro**chemistry**





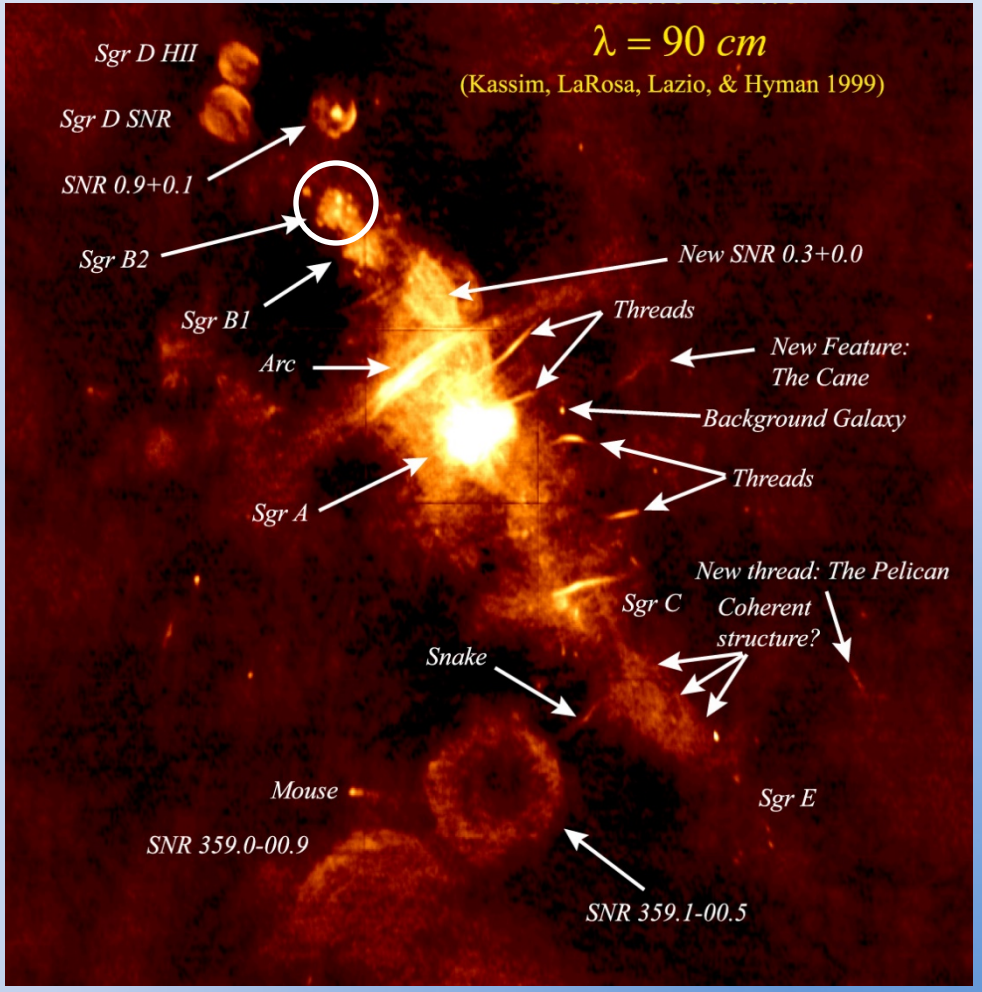
Molecules **are** out there



From “Astrochemistry and Astrobiology”, Smith, Cocknell, Leach, Ed., Springer, 2013

Sagittarius B2

- ~50% of known interstellar molecules directly observed
- Dense cloud: 300 million x mass of Sun
- Cold! -390 to 80 ºF
- Weird, reactive molecules
- Origin of life?

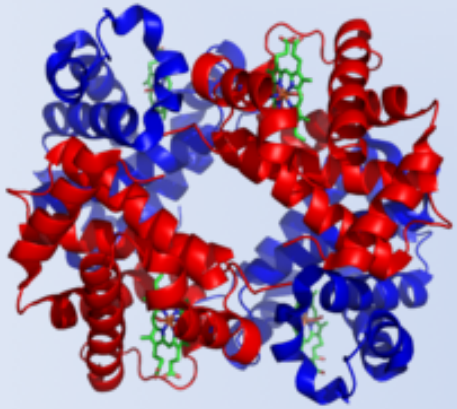


164 known interstellar molecules

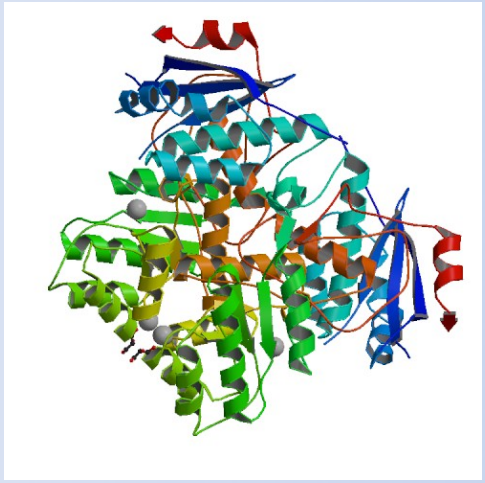
2		3		4		5	6	7	8	9
H_2	PN	C_3	OCS	c-C_3H	HCNO	C_5	C_5H	C_6H	CH_3C_3N	CH_3C_4H
AlF	SO	CCH	SO_2	CCCH	HOCN	C_4H	H_2C_4	CH_2CHCN	$HCOOCH_3$	CH_3CH_2CN
AlCl	SO^+	CCO	c-SiC_2	CCCN	HSCN	SiC_4	C_2H_4	CH_3CCH	CH_3COOH	$(CH_3)_2O$
C_2	SiN	CCS	CO_2	CCCO	HOOH	H_2C_3	CH_3CN	HC_5N	C_7H	CH_3CH_2OH
CH	SiO	CH_2	NH_2	CCCS	HMgNC	c-C_3H_2	CH_3NC	CH_3CHO	H_2C_6	HC_7N
CH^+	SiS	HCN	H_3^+	HCCH	HCCO	H_2CCN	CH_3OH	CH_3NH_2	CH_2OHCHO	C_8H
CN	CS	HNC	H_2D^+	NH_3		CH_4	CH_3SH	c-CH_2OCH_2	CH_2CCHCN	CH_3CONH_2
CO	HF	HCO	SiCN	HCCN		HC_3N	HC_3NH^+	CH_2CHOH		C_8H^-
CO^+	SH	HCO^+	AlNC	$HCNH^+$		HCCNC	HC_2CHO	C_6H^-		CH_3CHCH_2
CP	HD	HCS^+	KCN	HNCO		HCOOH	NH_2CHO	CH_3NCO		
SiC	CF^+	HOC^+	HCP	HNCS		CH_2NH	C_5N			
HCl	PO	H_2O	CCP	HCO_2^+		H_2CCO	HC_4N	**10**	**11**	**>12**
KCl	AlO	H_2S	AlOH	H_2CO		NH_2CN	C_5N^-	CH_3C_5N	HC_9N	$HC_{11}N$
NH	HCl^+	HNO	FeCN	H_2CN		HNCCC		CH_3COCH_3	CH_3C_6H	C_{60}
NO	SH^+	MgNC	HO_2	H_2CS		SiH_4		$(CH_2OH)_2$		C_{70}
NS	CN^-	MgCN	Si_2C	H_3O^+		H_2COH^+				C_{60}^+
NaCl	OH^+	NaCN	CCN	c-SiC_3		C_4H^-				
OH	TiO	N_2H^+	H_2O^+	CH_3		CH_3O				
ArH^+	NO^+	N_2O		PH_3		$NCCNH^+$				
O_2		H_2Cl^+		C_3H^+		NH_4^+				

# of known molecules on Earth: ~120 million!

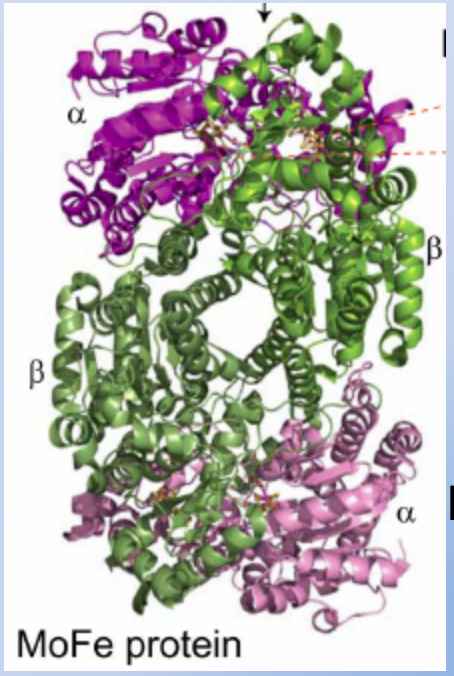
Complexity of bioinorganic molecules on Earth

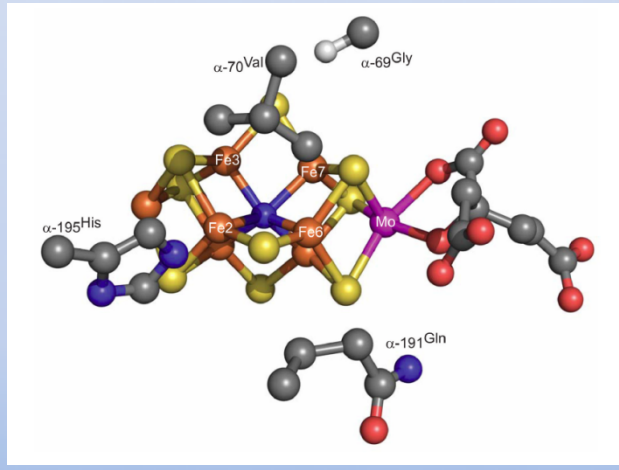


Hemoglobin (Fe)



Monomer of Dichloromuconate cycloisomerase (Mn)

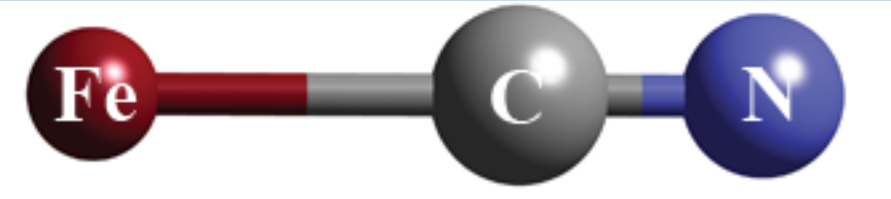




Mo-dependent nitrogenase (Fe and Mo)

Complexity of known organometallic molecules in ISM

- Fe-C-N
- Mg-C-N
- K-C-N
- Na-C-N



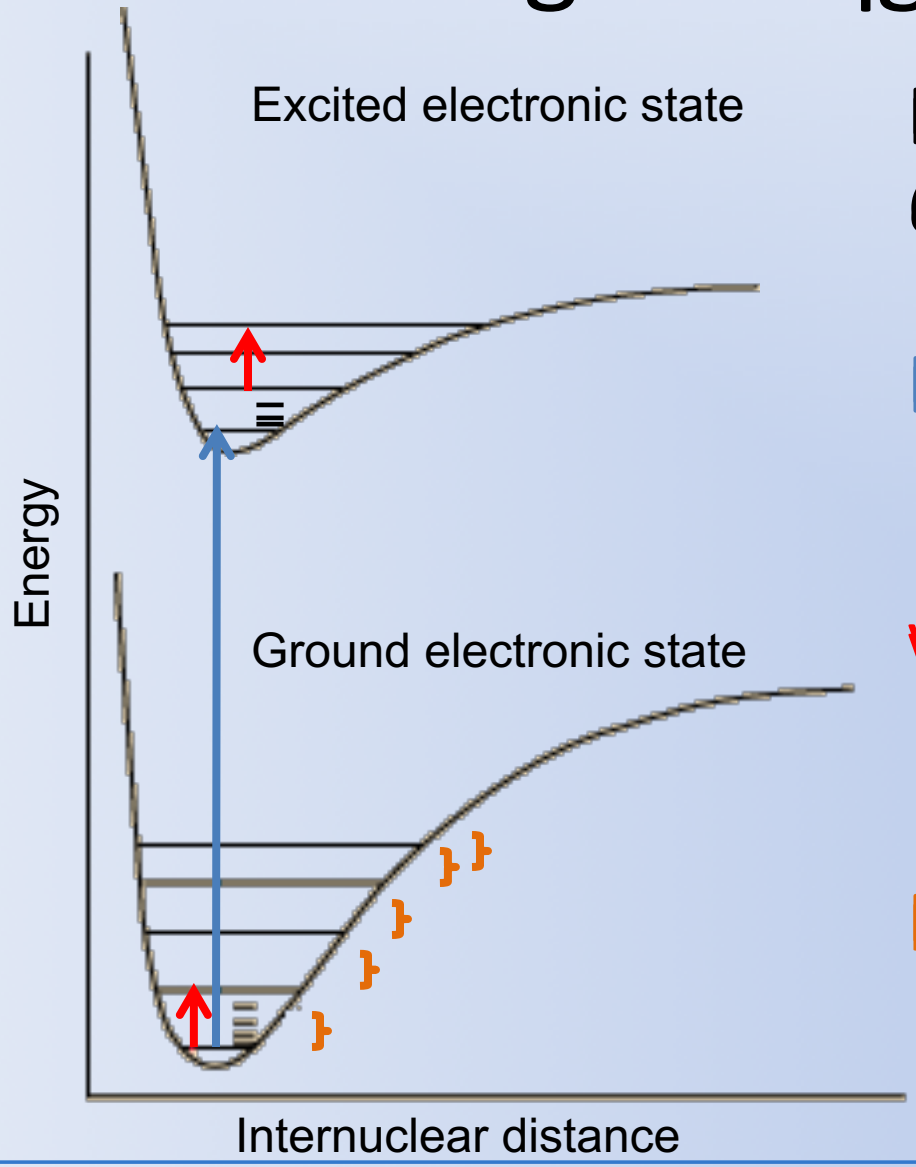
When does “astrochemistry” become “astrobiology”?

- We are not close to knowing ☹
- Huge disconnect between molecular complexity
- **Slowly** learning more about composition of space and how chemistry is transported
- Fascinating new (experimental and theoretical) discoveries await us ☺
- <u>What is the role of inorganic chemistry in space?</u>

Difficulties in molecular astrochemistry

- Astrophysical observation
  - Low abundances of metals in ISM
  - Heavy atoms condense into ices and grains
- Human factors
  - Few people are searching for small inorganics
  - Perturbations in spectra from low-lying electronic states
  - Overlapping transitions from different molecules
  - Volatile / toxic molecules

Small radicals in Organic Spectroscopy



Detect signatures of molecules

Quantized transitions

Electronic states = UV-vis

Typically 10,000 – 35,000 cm^{-1}

Vibrational states = Infrared

300 – 3500 cm^{-1}

Rotational states = Microwave

0.1 – 10 cm^{-1}

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JOURNAL OF CHEMICAL PHYSICS VOLUME 114, NUMBER 5 1 FEBRUARY 2001

Observation of the FeNC molecule by laser fluorescence excitation spectroscopy

Jie Lie and Paul J. Dagdigian[a)]
Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218-2685

(Received 15 September 2000; accepted 7 November 2000)

- Dagdigian in 2001 – published experimental fluorescence study of FeNC

Lucy Ziurys
University of Arizona

H. Fritz Schaefer III
University of Georgia

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Cite this: *RSC Advances*, 2012, **2**, 7849–7859

www.rsc.org/advances

PAPER

Predicting the interactions of organometallic ruthenium ethylenediamine complexes with mononucleotides: insights from density functional theory†

Hanlu Wang,[a] Nathan J. De Yonker,[b] Hui Gao,[a] David Lee Phillips,*[c] Cunyuan Zhao,*[a] Liangnian Ji[a] and Zong-Wan Mao*[a]

JOURNAL OF CHEMICAL PHYSICS VOLUME 114, NUMBER 5 1 FEBRUARY 2001

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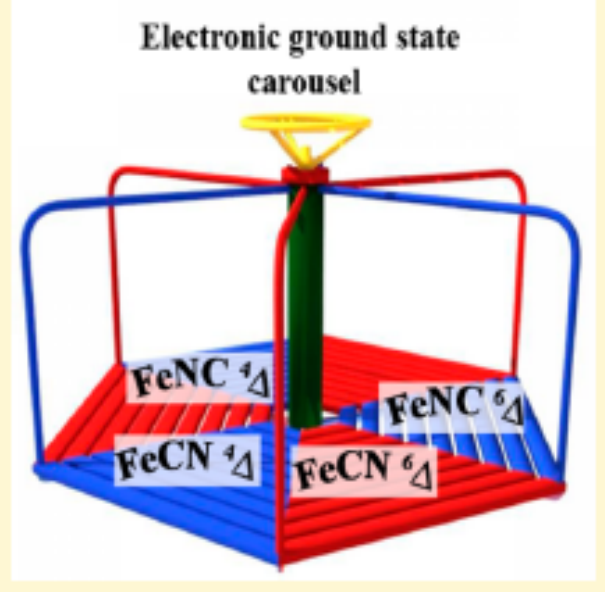
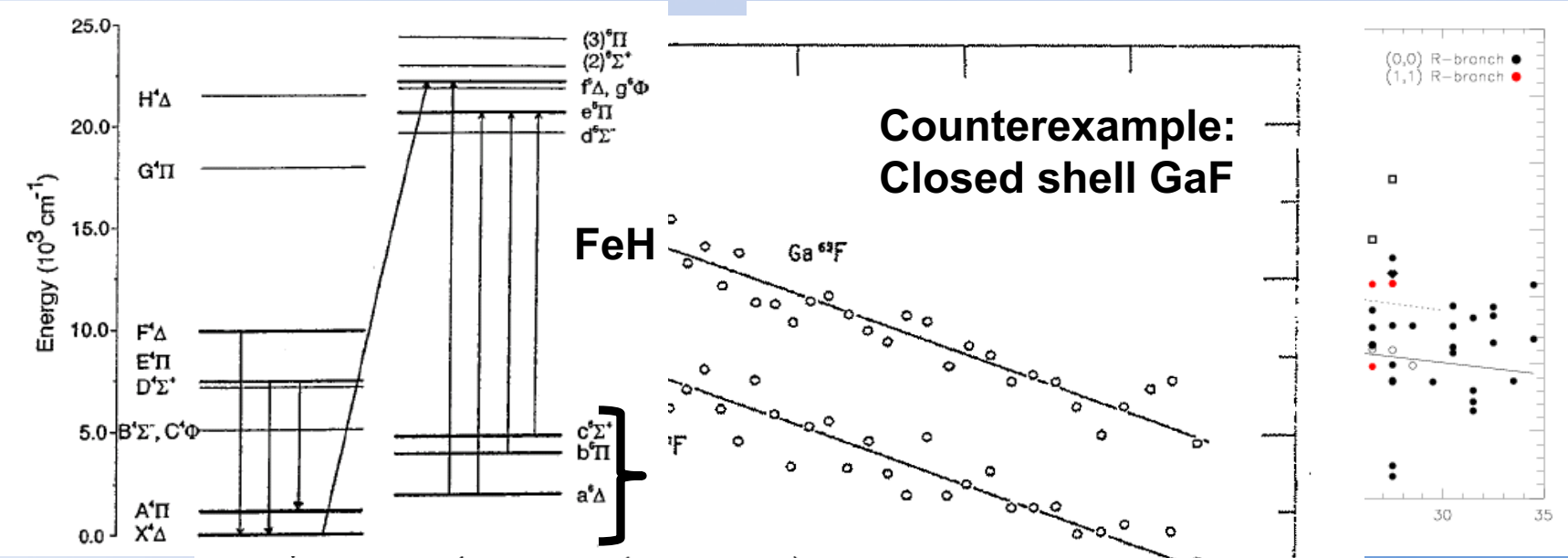
THE UNIVERSITY OF GEORGIA

- Dagdigian in 2001 – published experimental fluorescence study of FeNC
- First project in graduate school
  - Use computational chemistry to study properties of FeCN and FeNC
- "3 months"? No way, 3 years



Fe-containing molecules are a hot mess

- Fe – $1s^2 2s^2 2p^6 3s^2 3p^6 \underline{4s^2 3d^6 4p^0}$
- Electronic & vibrational energy levels are too close
- Leads to spectral perturbations



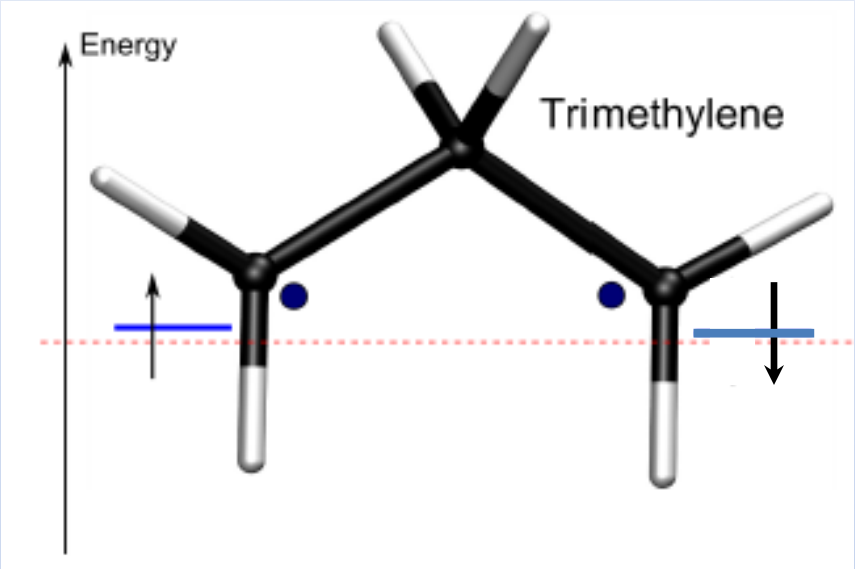
W. J. Balfour, J. M. Brown, and L. Wallace, *J. Chem. Phys*. **121** (16), 7735 (2004).

S. Wende, A. Reiners, A. Seifahrt, and P.F. Bernath *Astronomy & Astrophys.* **523** A58 (2010).

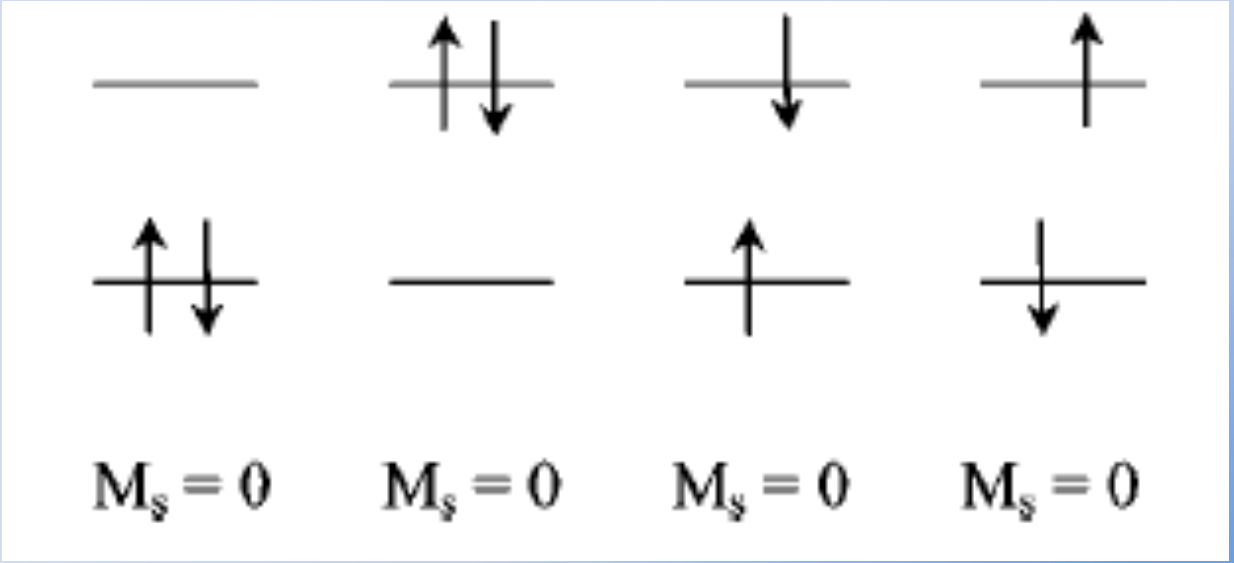
Multireference vs single reference

- Atoms and molecules are actually **linear combinations** of electronic configurations
- For most atoms and organic molecules,
  - From Hund's rules, Aufbau principle, Pauli exclusion principle, LCAO-MO, dominant config > 98 % of the wave function
  - Organic exceptions:
    - Carbon dimer (C_2)
    - Diradicals: molecules where two electrons occupy nearly degenerate molecular orbitals

C_3H_6

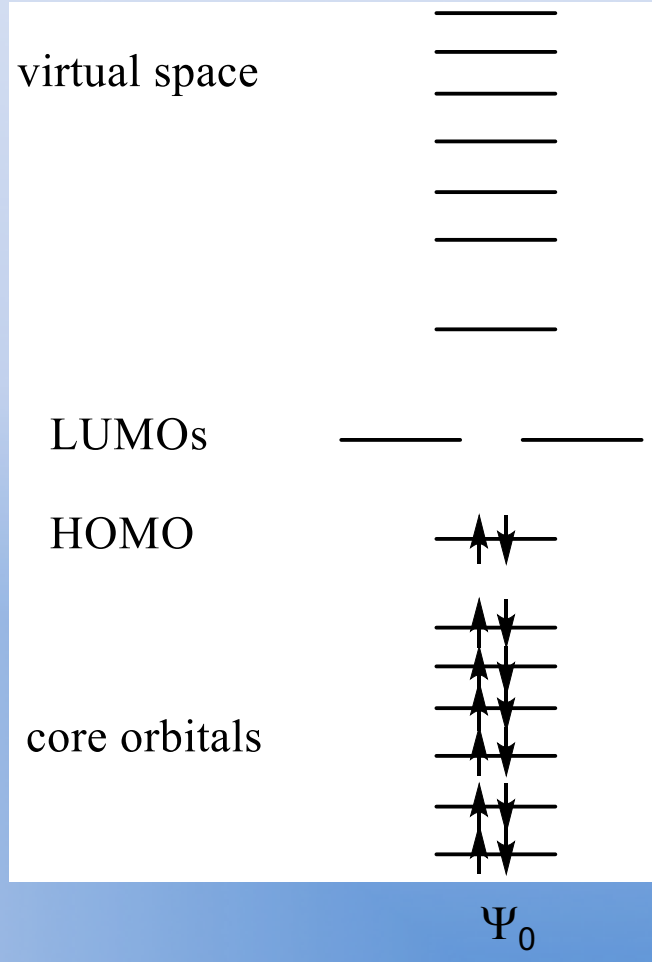


Singlet
Triplet
Single reference
Multireference



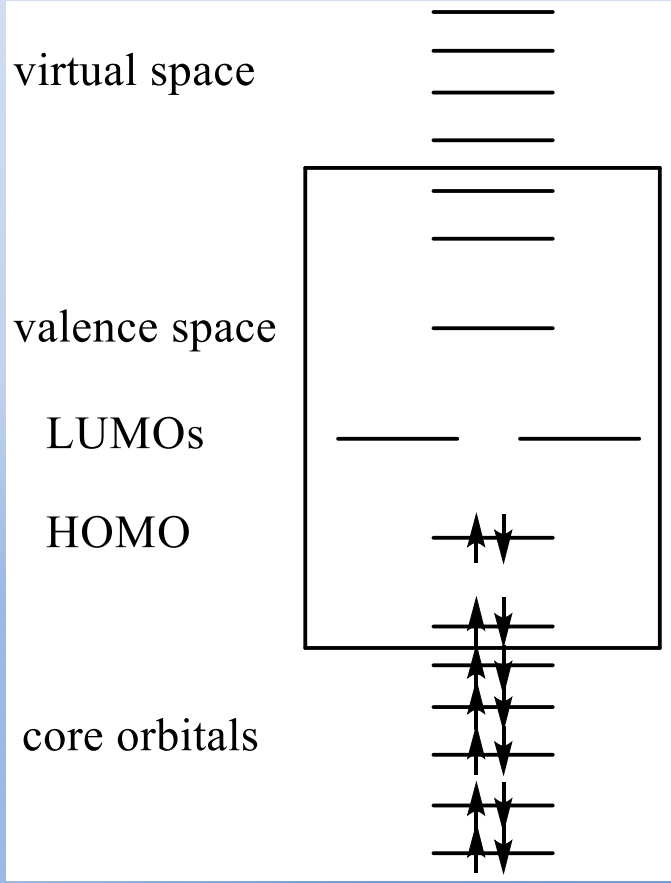
SR methods (coupled cluster)

- Single Hartree-Fock reference configuration (Ψ_0)
- Contribution of other configurations to Ψ
  - *n*-body substitutions of electrons into unoccupied MOs
  - Amplitudes of e^- substitutions and their products: **coupled cluster theory**
  - CCSD, CCSD(T), CCSDT, CCSDTQ, etc.
- Level of e^- - e^- interactions can be systematically improved
  - Increased substitution level = vastly increased computation time
  - **Short-range** or **dynamical** correlation

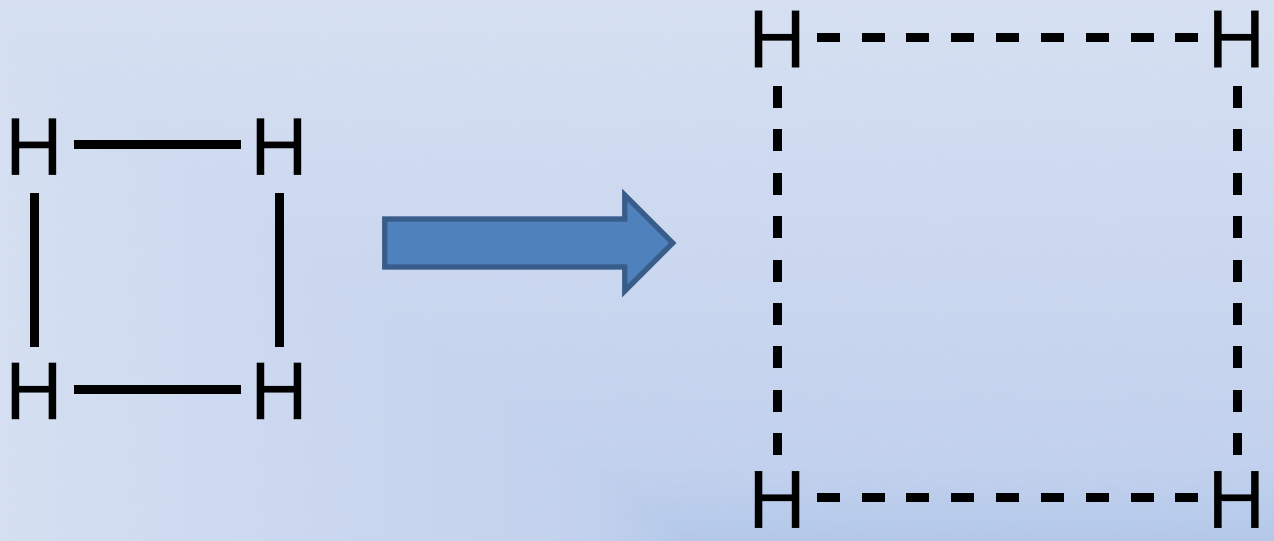


MR methods

- *All n-body* e^- - e^- interactions are accounted for in a limited "active space" (valence or frontier MOs)
- 1 and 2 e^- substitutions from valence electrons to virtual space (MRCISD)
- MR methods appropriate when near degeneracies exist in electronic Ψ
  - ***Long-range, strong, nondynamical, or static*** correlation



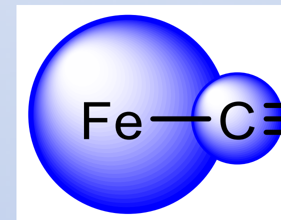
Degeneracies vs. *near* degeneracies



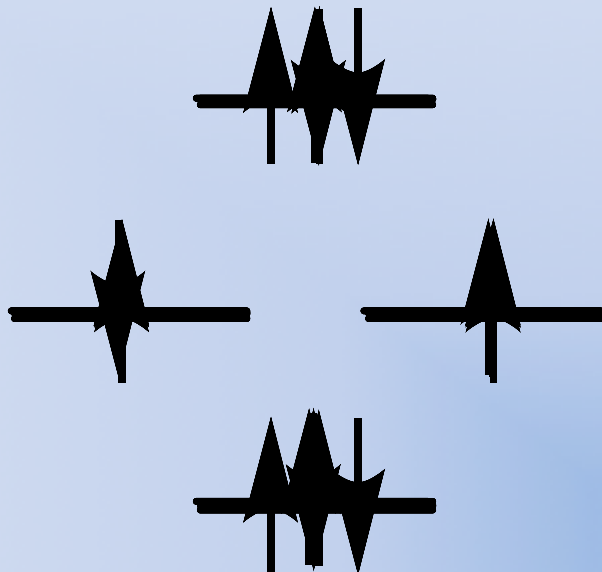
- Two different kinds of nondynamical electron correlation!

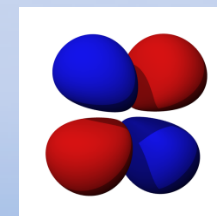
Frontier MO diagram of FeCN/FeNC

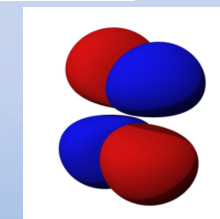
(Fe d_{xy} and $d_{x^2-y^2}$ not shown - always w/ 3 e^- in L = 2 MOs to form $^4\Delta$ or $^6\Delta$ state)



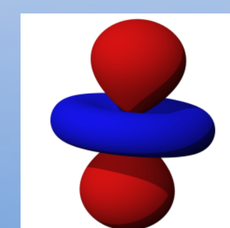
Fe 4*s* + C 2*s*





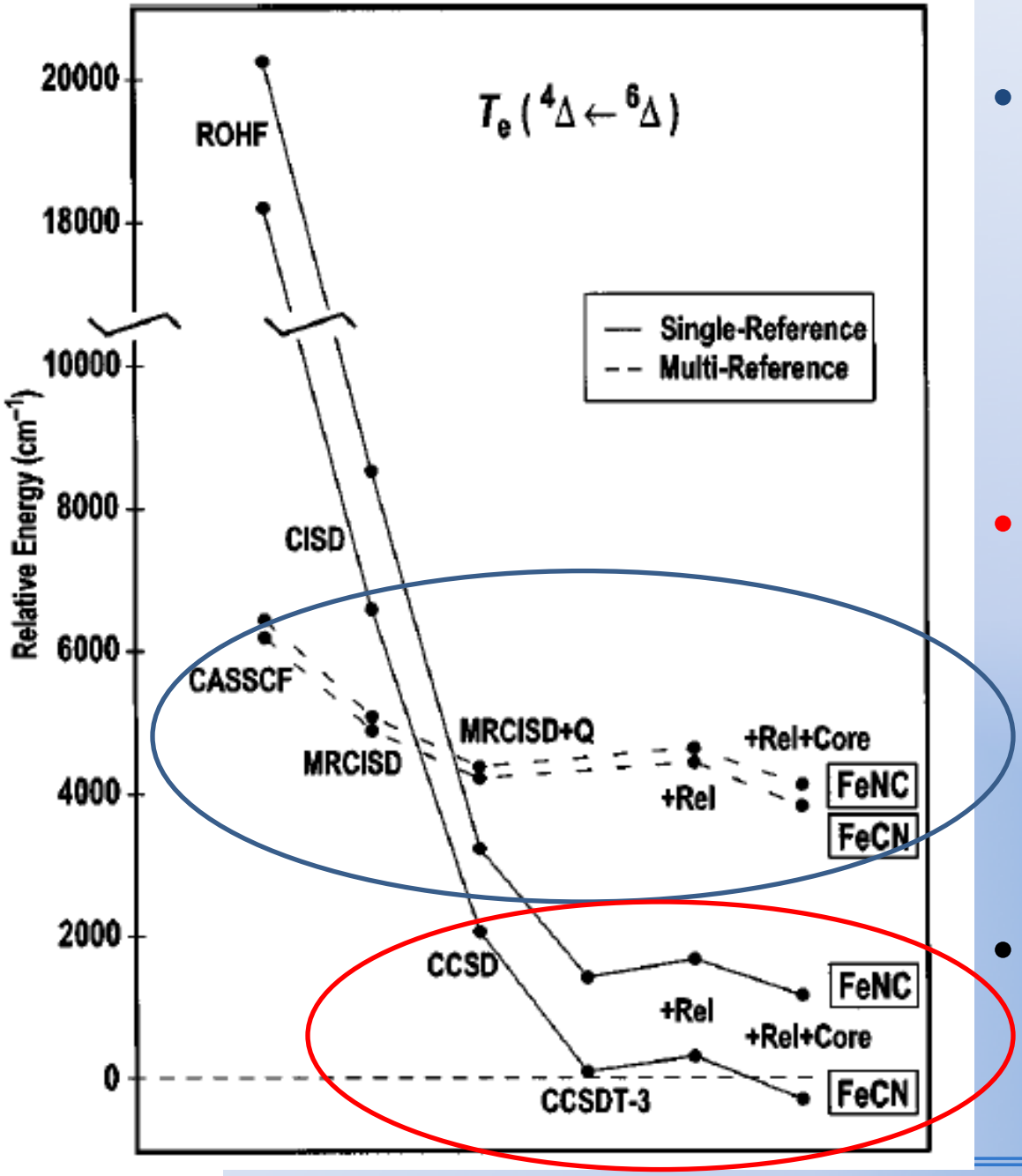


Fe d_{xz} & d_{yz}



Fe d_{z^2}

[illegible] 11 + 8 + 7% = 77%



- MRCISD+Q predicts high-spin FeCN & FeNC ground electronic states
- CCSD(T) & CCSDT-3 predicts **low-spin** FeCN & **high spin** FeNC
- MRCISD+Q is more reliable? *Status quo in 2004*

- A saying in computational chemistry: “The right answer for the wrong reason”
  - Parameterization
  - Picking one of hundreds of semi-quantitatively accurate methods (DFT) until finding agreement with experiment
- “**Wrong** answer for **right** reason?!”
  - MRCI versus CC
  - Unbalanced treatment of static vs dynamic correlation

JOURNAL OF CHEMICAL PHYSICS VOLUME 120, NUMBER 10 8 MARCH 2004

Low-lying electronic states of FeNC and FeCN: A theoretical journey into isomerization and quartet/sextet competition

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Kirk A. Peterson
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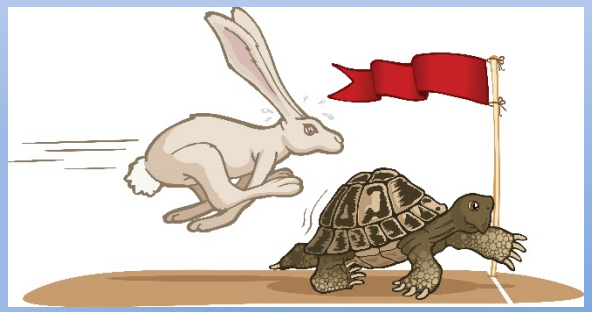
(Received 18 August 2003; accepted 4 November 2003)

N. J. DeYonker, H. F. Schaefer, K. A. Peterson, and coauthors *J. Chem. Phys.* **120**, 4726 (2004).

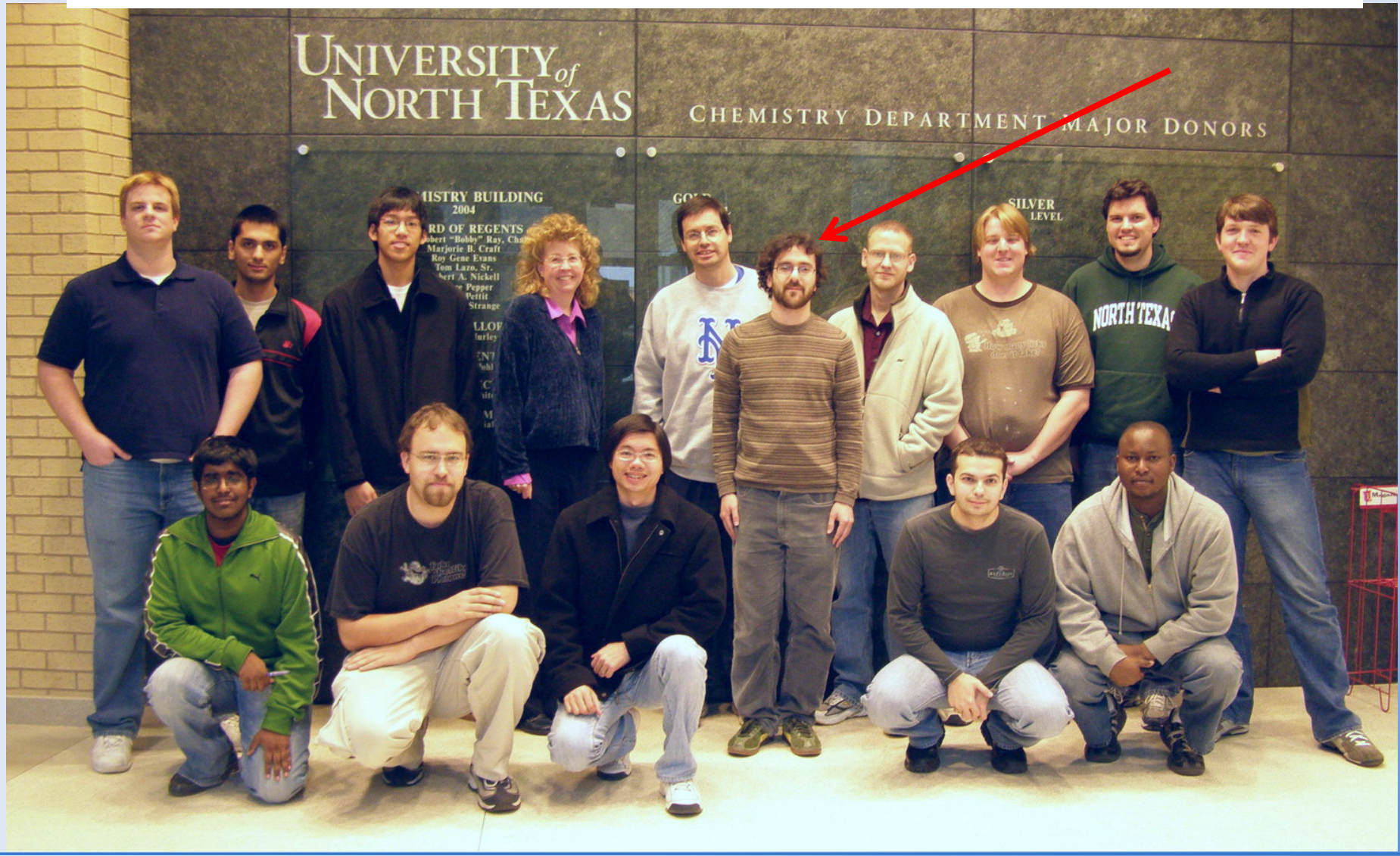
MRCI vs CC

- Many transition metal-containing radical molecules exhibit both static **and** dynamical correlation
  - "Pathological cases":
    - MRCISD treats enough static but not enough dynamical
    - Conventional CC treats enough dynamical but not enough static
- Over last 20 years
  - MRCI developments = slow
  - MRCC developments = VERY slow
  - CC developments = steady



Work since 2004

- Some experimental labs tried (and failed) to reproduce the Dagdigian work and synthesize FeCN and FeNC
  - L. Ziurys group (Arizona)
  - M. Heaven group (Emory)
- Some theoretical groups were skeptical of (and ignored) our coupled cluster results
  - MRCISD *must be* correct!
  - T. Hirano (Ochanomizu) and P. Jensen (Bergische)


UNIVERSITY of NORTH TEXAS
CHEMISTRY DEPARTMENT MAJOR DONORS
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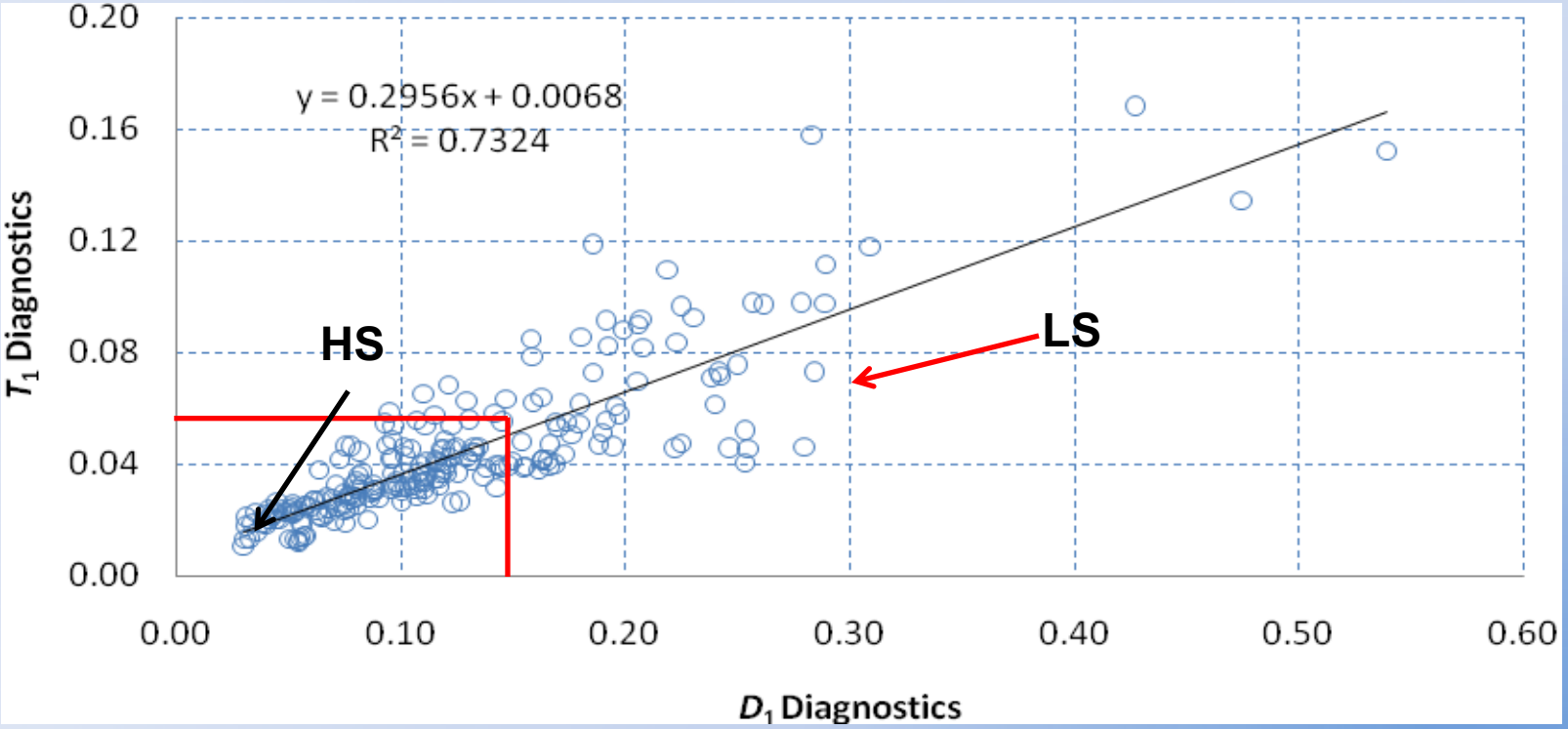
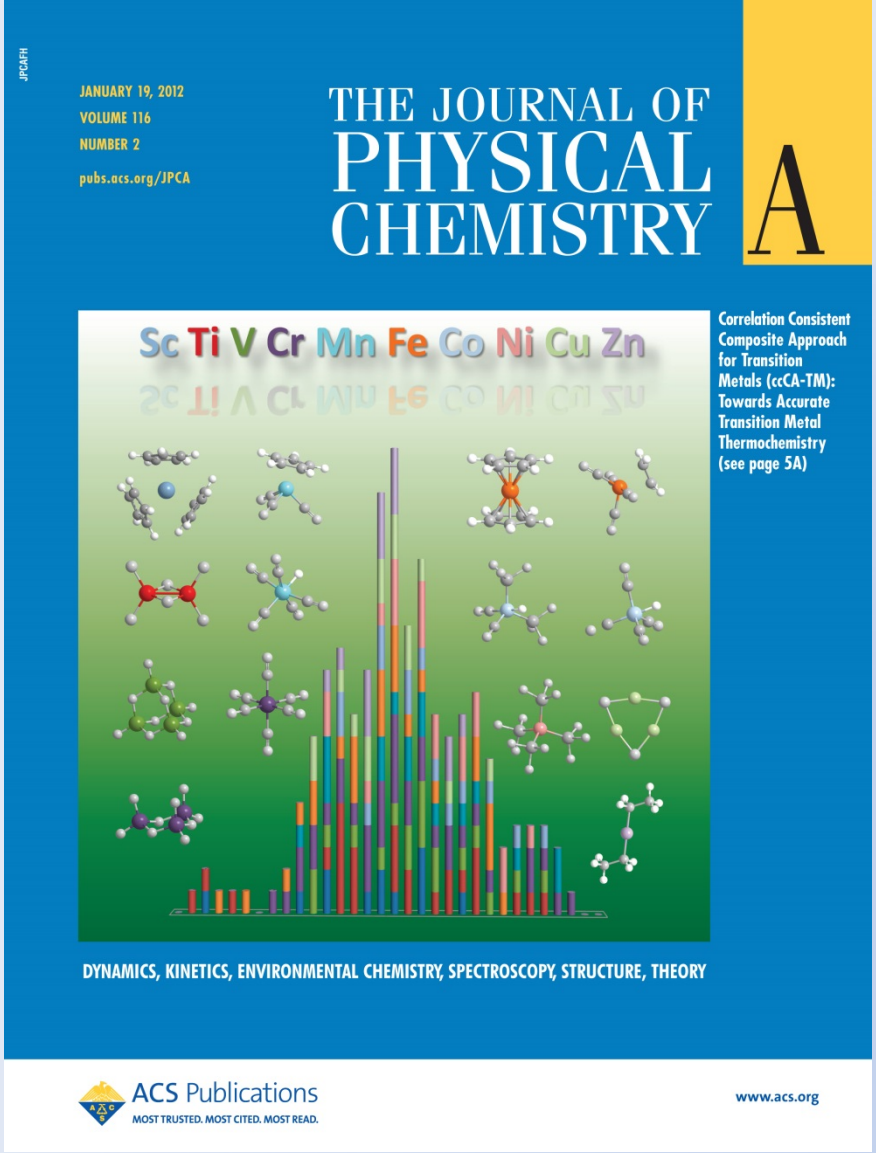
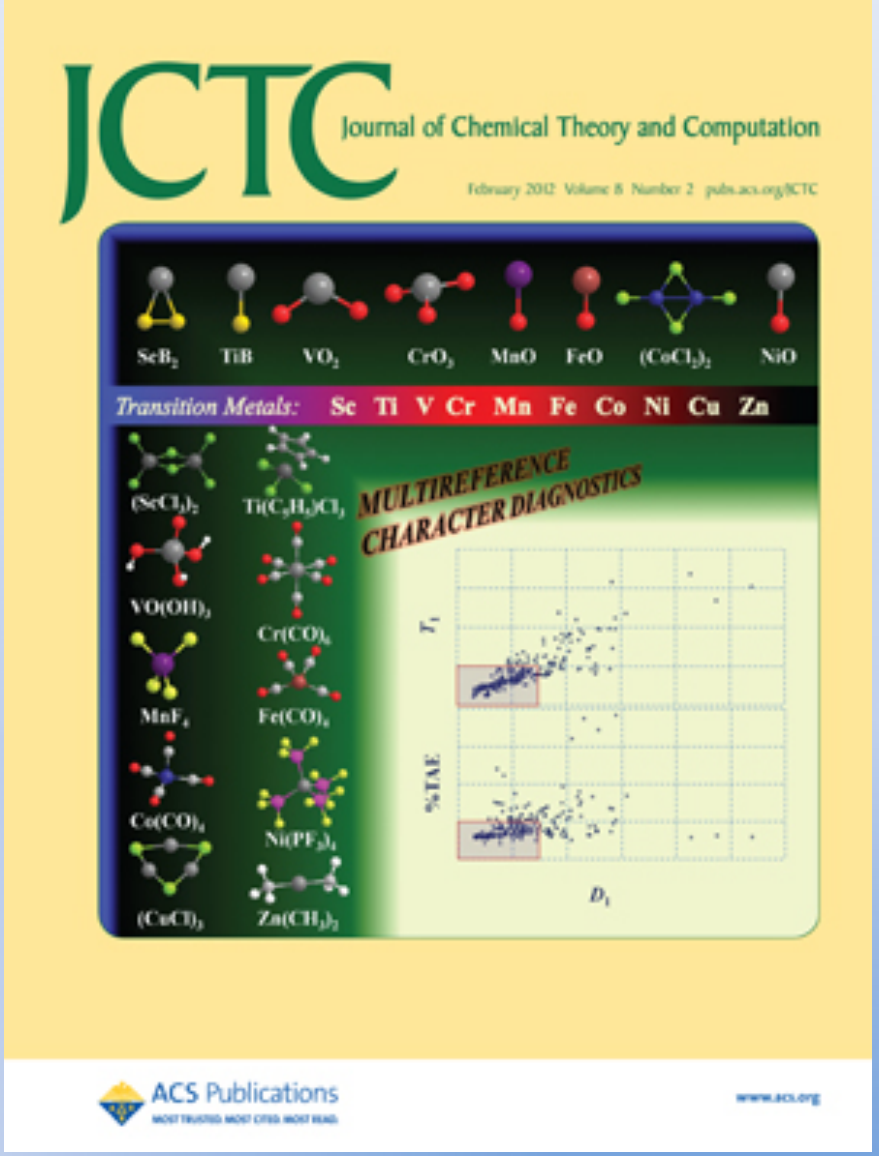
Assessing "pathology" of inorganic molecules





W. Jiang, N. J. DeYonker, J. J. Determan, A. K. Wilson, *J. Phys. Chem A.* **116**, 870 (2012).



W. Jiang, N. J. DeYonker, A. K. Wilson, *J. Chem. Theory Comput.* **8**, 460 (2012).

Fourier-transform microwave spectroscopy of FeCN ($X^4\Delta_i$): Confirmation of the quartet electronic ground state

L.N. Zack, J. Min, B.J. Harris [1], M.A. Flory [2], L.M. Ziurys *

Department of Chemistry, Department of Astronomy and Steward Observatory, 933 North Cherry Avenue, University of Arizona, Tucson, AZ 85721, USA

Millimeter-wave rotational spectroscopy of FeCN (X $^4\Delta_i$) and FeNC (X $^6\Delta_i$): Determining the lowest energy isomer

M. A. Flory and L. M. Ziurys[a)]

Department of Chemistry and Department of Astronomy, Steward Observatory, University of Arizona, 933 N. Cherry Ave., Tucson, Arizona 85721, USA

DETECTION OF FeCN ($X^4\Delta_i$) IN IRC+10216: A NEW INTERSTELLAR MOLECULE

L. N. ZACK[1], D. T. HALFEN[1,2], AND L. M. ZIURYS[1,2]

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[2] Department of Astronomy and Steward Observatory, Arizona Radio Observatory, University of Arizona, 933 North Cherry Avenue, Tucson, AZ 85721, USA

Received 2011 March 24; accepted 2011 April 20; published 2011 May 10

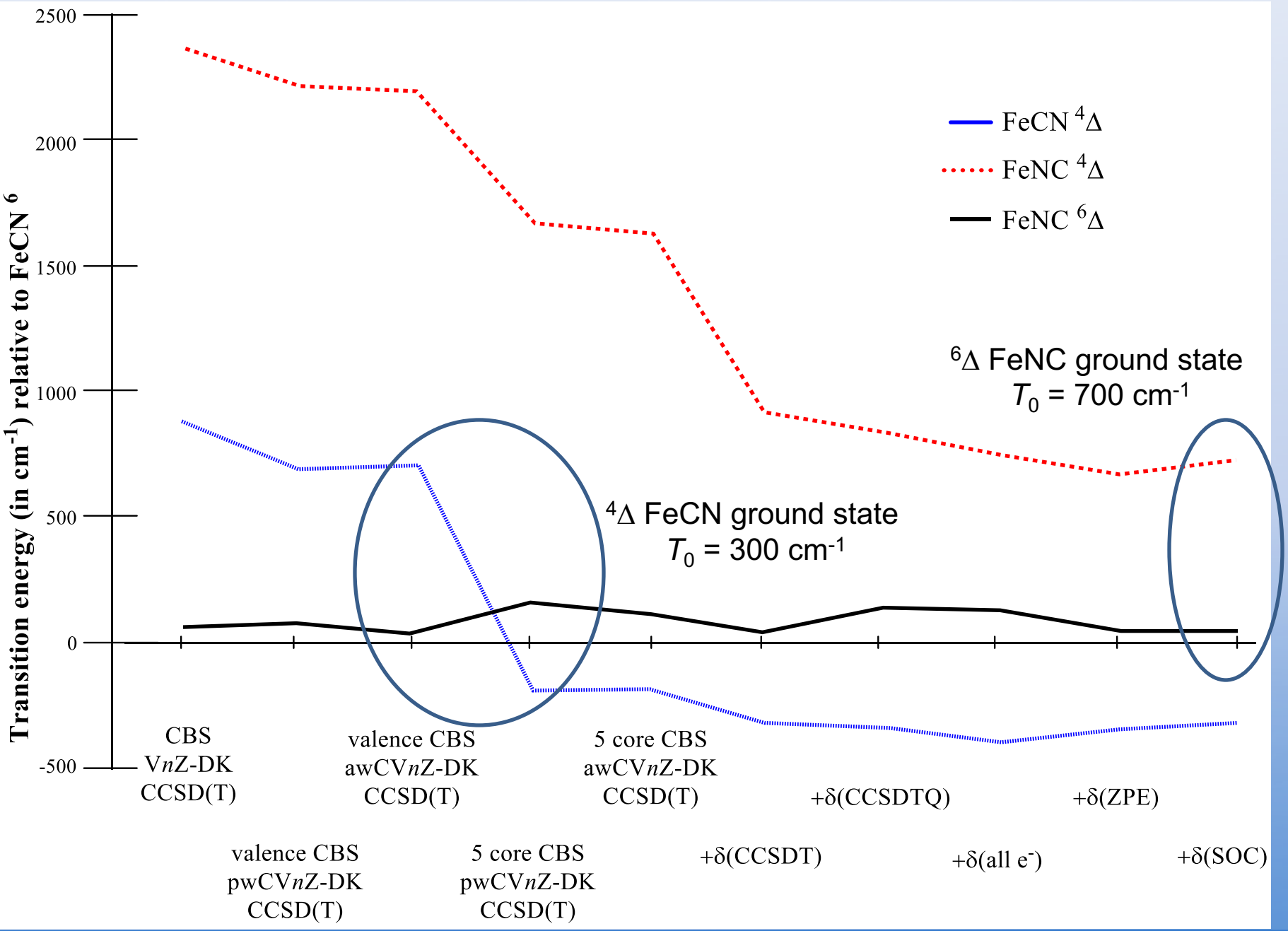
- FeCN (low spin) and FeNC (high spin) have a *different* ground state electronic configuration
- Our coupled cluster results were correct!

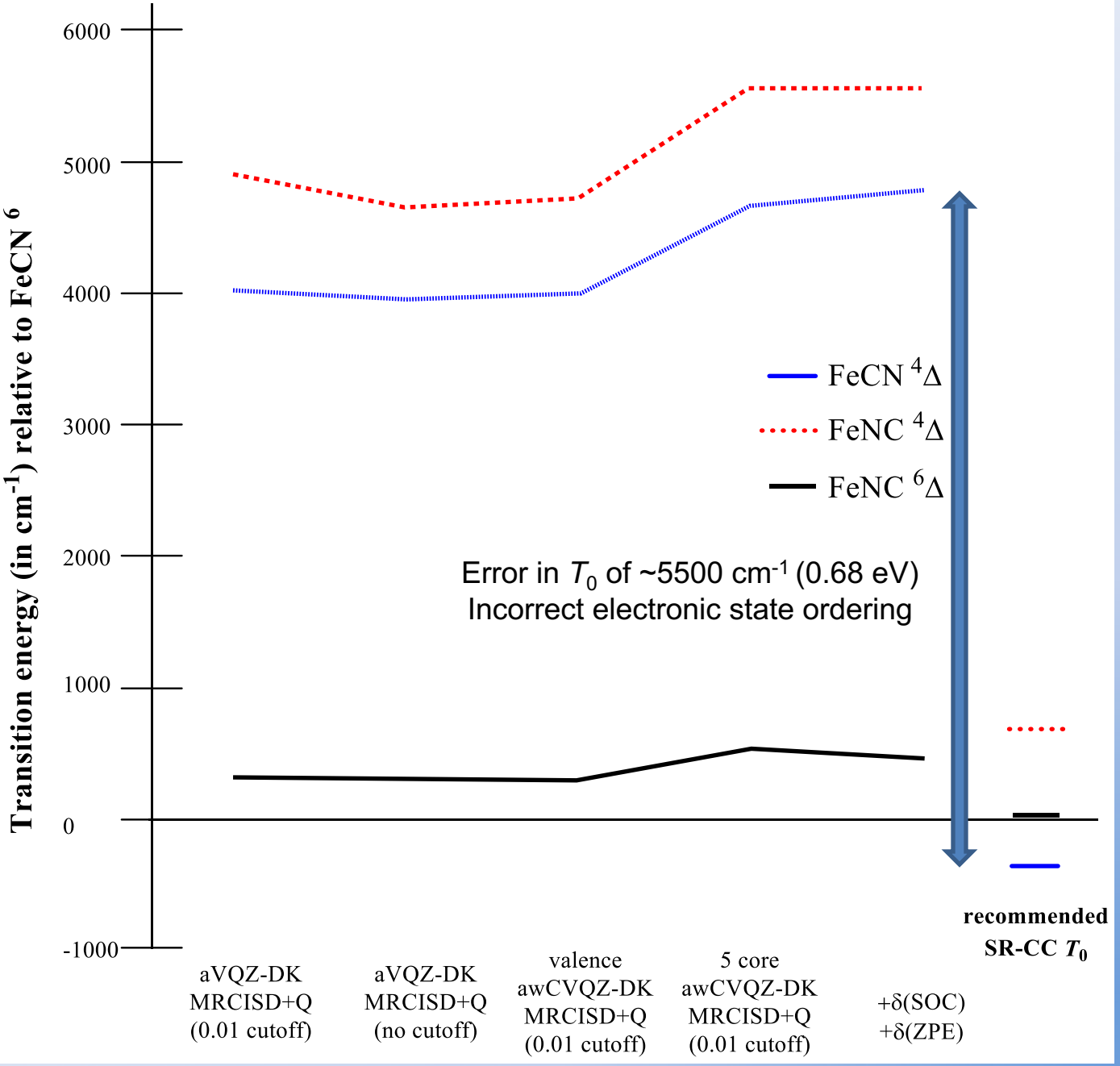
Zack, L. N.; Min, J.; Harris, B. J.; Flory, M. A.; Ziurys, L.M.; *Chem. Phys. Lett.* **2011,** *514* (4-6), 202-206.
Flory, M. A.; Ziurys, L. M.; *J. Chem. Phys.* **2011,** *135* (18), 184303.
Zack, L. N.; Halfen, D. T.; Ziurys, L. M., *Astrophys. J. Lett.* **2011,** *733* (2), L36.

10 years later, revisit FeCN/FeNC

- Calibration of inorganic chemistry and spectroscopy
- Confident that CC can often outperform MRCI
- New technological developments
  - Improved basis sets – treatment of 1-electron space
  - *Better treatment of core/valence (CV) interactions*
  - Scalar relativistic effects
  - *Arbitrary order coupled cluster (CCSDTQ and beyond)*
  - Parallel computing
  - Spin-orbit coupling

FeH: N. J. DeYonker, W. D. Allen, *J. Chem. Phys.*, **137**, 234303 (2012).
VCl^+: N. J. DeYonker, D. T. Halfen, W. D. Allen, L. M. Ziurys, *J. Chem. Phys.*, **141**, 204302 (2014).


2500
2000
1500
1000
500
0
-500
Transition energy (in cm-1) relative to FeCN 6
FeCN 4Δ
FeNC 4Δ
FeNC 6Δ
6Δ FeNC ground state
T0 = 700 cm-1
4Δ FeCN ground state
T0 = 300 cm-1
CBS
VnZ-DK
CCSD(T)
valence CBS
awCVnZ-DK
CCSD(T)
5 core CBS
awCVnZ-DK
CCSD(T)
+δ(CCSDTQ)
+δ(ZPE)
valence CBS
pwCVnZ-DK
CCSD(T)
5 core CBS
pwCVnZ-DK
CCSD(T)
+δ(CCSDT)
+δ(all e-)
+δ(SOC)

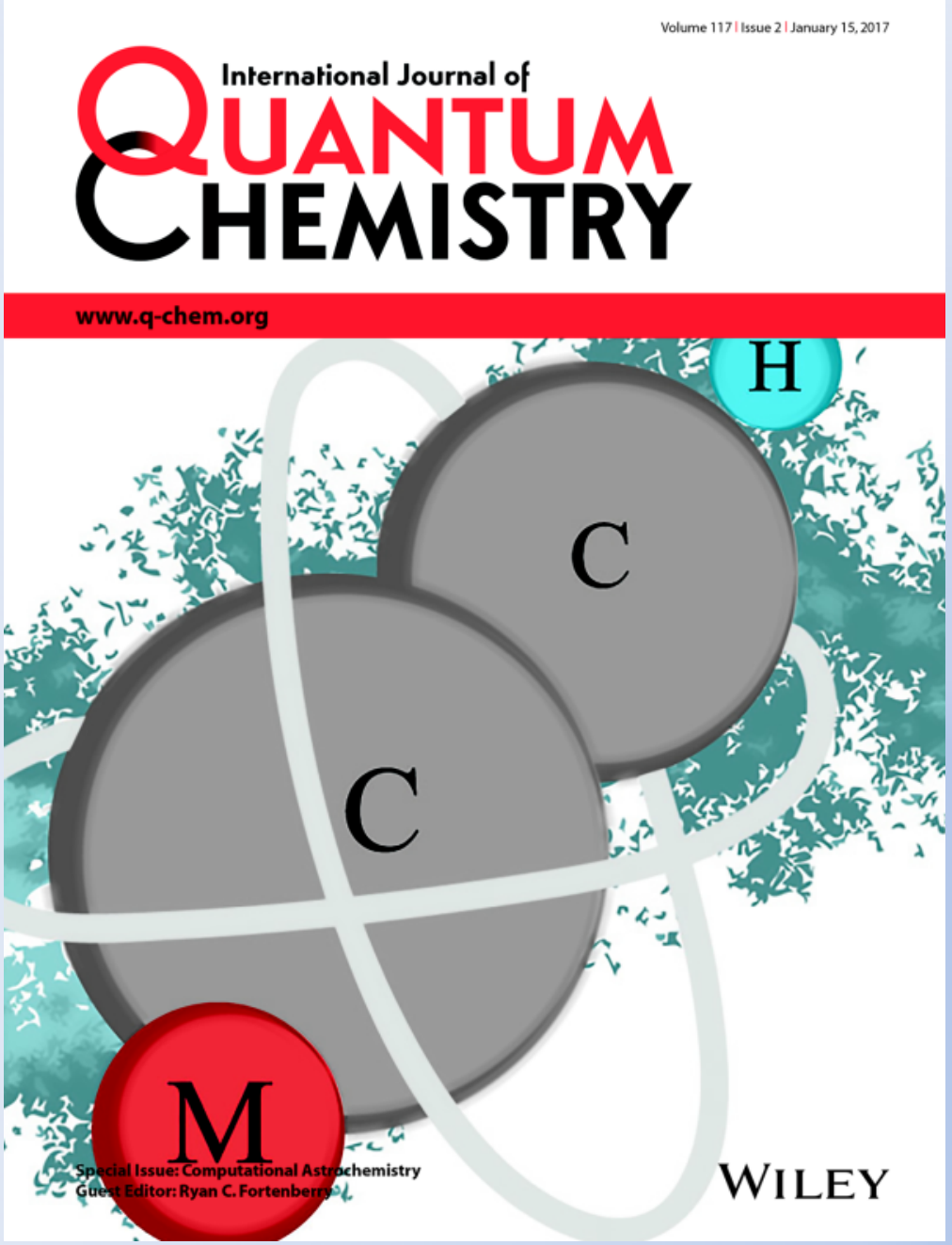


DeYonker, N. J.; *J. Phys. Chem. A* **2015**, *119* (1), 215.

Current work: TM monoacetylides

- M-C≡CH isoelectronic with MCN/MNC
  - Many polyynes (CC_nR, R = H,C,N,P) known in ISM
  - Organometallic catalysis
- Expt. data for M = Cr, Ni, Cu, Zn
- More discrepancies between CCSD(T) and MRCISD+Q
- 10 MCCH – 18 months vs. FeCN&FeNC - 3 years

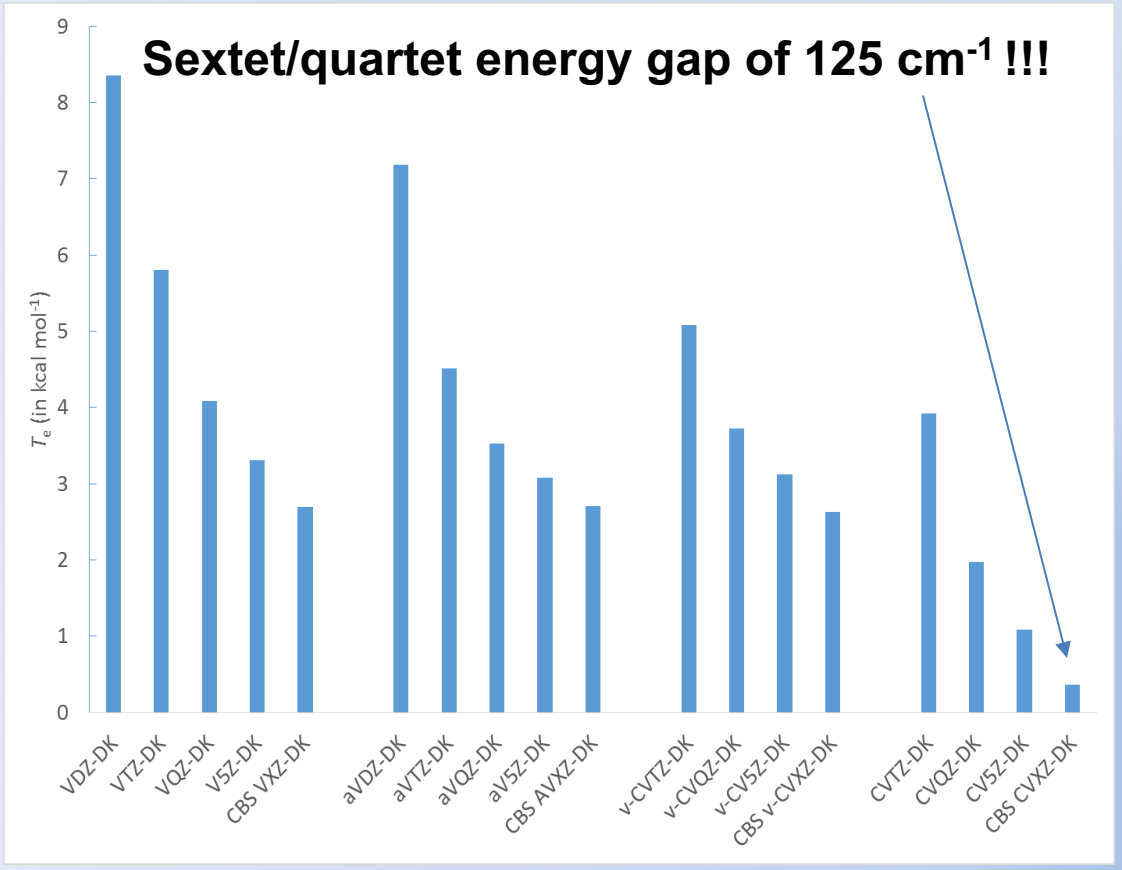
Metal	MCN ground state	Computed MCCH ground state
Sc	$^3\Delta$	$^1\Sigma^+$
Ti	$^4\Phi$	$^4\Phi$
V	$^5\Delta$	$^5\Delta$
Cr	$^6\Sigma^+$	$^6\Sigma^+$
Mn	$^7\Sigma^+$	$^7\Sigma^+$
Fe	$^4\Delta$	$^6\Delta$?
Co	$^5\Phi$	$^3\Phi$, $^5\Phi$
Ni	$^2\Delta$	$^2\Delta$
Cu	$^1\Sigma^+$	$^1\Sigma^+$
Zn	$^2\Sigma^+$	$^2\Sigma^+$

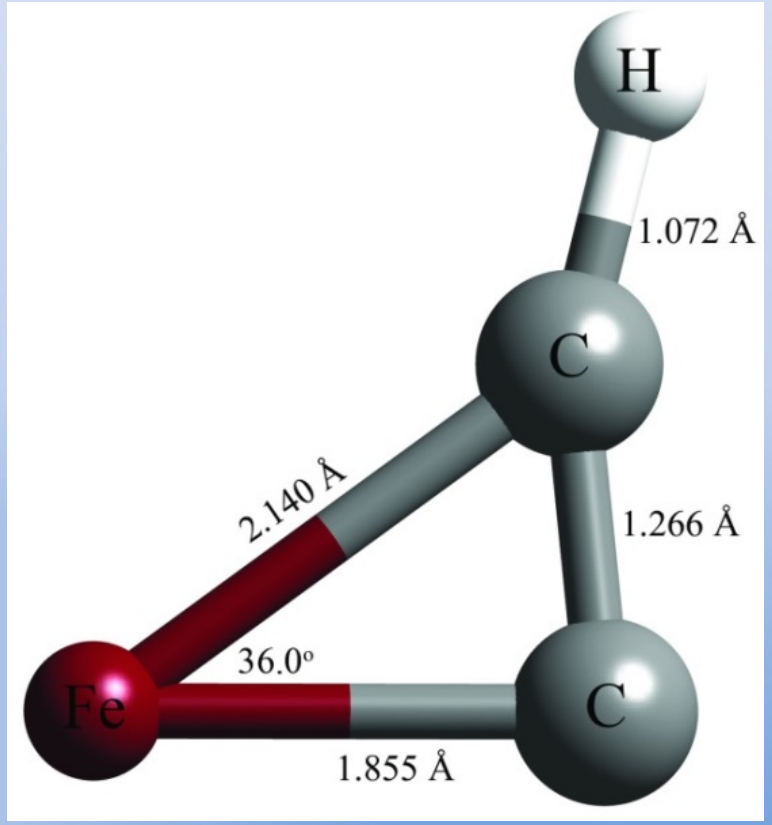


DOI: 10.1002/qua.25206

w/ Shelby Dickerson
(now at U. South Carolina)

FeCCH *déjà vu*

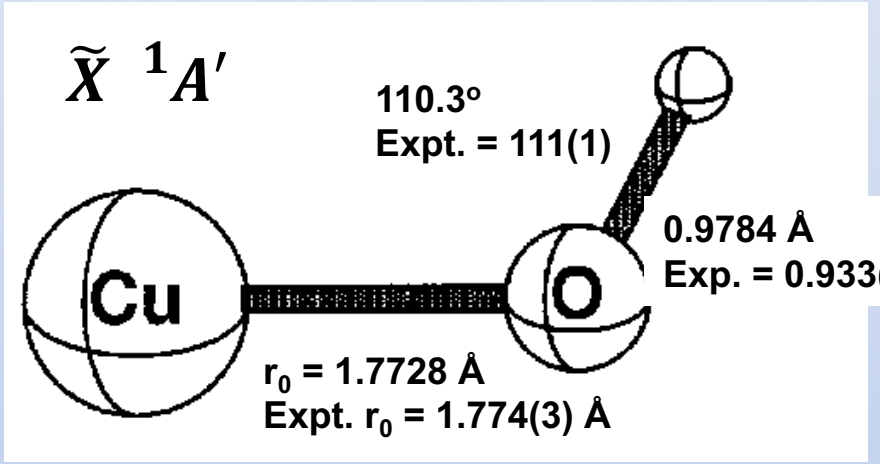




S. D. Dickerson, N. J. DeYonker, *Int. J. Quantum. Chem.*, **117**, 104 (2017).

TM rovibrational spectroscopy

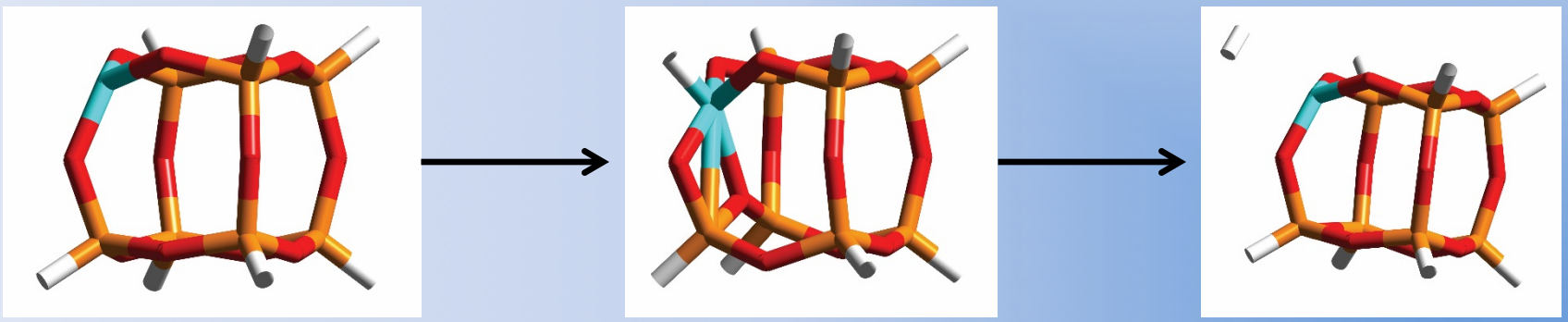
- CuOH, CuCN, CuCCH w/ Ryan Fortenberry (Georgia Southern)
- "Black box" vibrational quartic force fields
- Different prescription for inorganic species
  - Relativistic effects
  - Improved CV treatment



	Comp. (cm^{-1})	Expt.
ν_{OH}	3662.1	
ν_{CuO}	625.3	625(1)
ν_{bend}	735.1	743(1)

POSS reactions

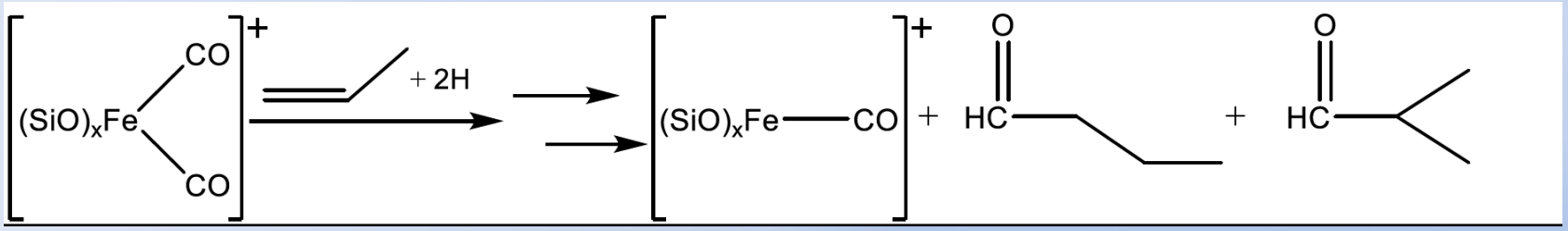
- Exploration of reactions on ice/grain surfaces with ionic metal defects (Ni^+, Co^+, Fe^+)
  - **P**oly**O**ligo**S**il**S**esquioxanes (siliceous clusters)
  - Interstellar rxns on grain/ice/mineral surfaces
  - Heterogeneous catalysis
  - Double-hybrid DFT & MP2-F12b calculations



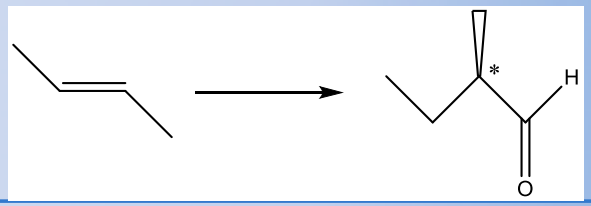
M. Fioroni, N. J. DeYonker, *ChemPhysChem,* **17**, 3390 (2016).

From astrochemistry to astrobiology!

- Building molecular complexity
- Regioselectivity
  - Mechanism of butyraldehyde from propene



- Enantioselectivity
  - Non-racemic mixtures of origin-of-life chemicals
  - Mechanism of methyl butanal from butene



Outlook

- Studying gas phase TM-containing radicals is quite challenging
- **Reactivity** of inorganics to produce more complex bio-relevant molecules will chronically stretch *ab initio* theory to its limits
- We **can** assess single reference & multireference methods

- Calibration of high-accuracy rovibrational and vibronic spectroscopy techniques is underway
- Multiscale modeling of reactions on grain & ice surfaces

Computational astrochemistry is awesome!

- Building trust
  - Terrestrial experimentalists need to believe in computations
    - Finally working together to understand and characterize undiscovered molecules
    - Increased throughput in astronomical observation
- How can we always efficiently get "**right** answer for **right** reason"?

- DeYonker Lab:

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Hannah Lozano

Kate Charbonnet

Dr. Qianyi Cheng

Lucy Ziurys

Ryan Fortenberry

Marco Fioroni

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