COMPUTATIONAL CHEMISTRY OF EXPERIMENTALLY CHARACTERIZED ORGANOMETALLICS

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Computational Quantum Chemistry

- Start from a basis set of combined Gaussian functions to mimic exponential atomic orbital wavefunctions.
- Linear combinations of these make a basis set of molecular orbital (MO) wavefunctions. The product of these is the simplest many-electron wavefunction.
- Solve the many-body Schrödinger equation for the electrons by some approximate means, usually involving a mean-field for electronelectron repulsion and the variational principle.

Ab initio quantum chemistry.

Computational Quantum Chemistry

OR

Computational Quantum Chemistry

- Realize that wavefunctions are only mathematical constructs, and should not be required to predict physical properties. So forget the Schrödinger equation entirely.
- Instead, find how the energy and other functions depend directly on the electron density.
- Unfortunately, this relationship is unknown, so use another mathematical construct (a makebelieve gas of non-interacting electrons) and some empirical expressions to approximate it.
- Solve variationally.

Density Functional Theory (DFT).

My history with computational chemistry

N⁺ fine structure spectrum by laser magnetic resonance



FIG. 2. Observed LMR spectra of the $\Delta M_J = -1 {}^{3}P_2 \leftarrow {}^{3}P_1$ (a) ${}^{14}N(II)$ and (b) ${}^{15}N(II)$ transitions at 2447.9685 GHz and 5.4 kG magnetic field.

Leif Veseth (Phys Rev 1985) successfully predicts isotope shift.

What else happened in the 80s

George Washington elected president (1789)





Duran Duran on MTV (1982)

Copper dimer

Electronic transition C-X by cavity ring-down Spectroscopy, 1990.



Contemporary theoretical prediction for this transition was 514 nm (Nakamura JCP **78** 815).

And copper's one of the *simplest* of the *transition metals*.

Periodic Table

1 H																	2 He
з Ц	4 Be											5 B	ωU	7 N	8 0	9 F	10 Ne
ll Na	12 Mg		Tr	an	sit	io	n r	ne	ta	S		13 Al	14 Si	15 P	16 5	17 d	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Min	26 Fe	27 Co	28 Ni	29 Ca	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 경	49 In	50 Sn	51 Sb	52 Te	53 -	54 Xe
55 Cs	56 Ba		72 Hf	73 Ta	74 W	75 Re	76 0s	77 Ir	78 Pt	79 Au	80 Hg	81 Tİ	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra		104 R∱	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo
			57	58	59 8-	60 N-1	61 Bar	62 5 m	63	64 Gd	65 TL	66	67	68	69 Turr	70 VL	71
			89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	но 99 Ез	Er 100 Fm	101 M d	102 No	103 Lr

The problem with transition metals

Partially filled d subshell leads to

- A high energy density of electronic states,
- Possibility of extremely strong spin-orbit interactions,
- Need for high angular momentum components in basis set (so a larger basis)

Plus, the atoms are heavy enough that relativistic effects may be significant.

Bohr speed of the Zn²⁹⁺ 1s electron

$$v = \frac{2\pi Z e^2}{nh} = 6.5 \cdot 10^7 \mathrm{m/s}$$

So we can reasonably expect the 1st row transition metals to have relativistic inner electrons.

Back to low atomic #s: HCCCO

Lewis structures: computations by Gus Scuseria predicted structure II



FIG. 1. Two canonical structures for HCCCO: the (I) propynonyl and (II) propadienonyl radicals. The unpaired electron is represented as a single dot.

HCCCO

Rotational spectrum with isotopic substitutions



FIG. 3. The $N = 18 \leftarrow 17$ transition in the $K_a = 1$, $K_c = N$ stack of HCCCO, showing the well resolved proton hyperfine splitting. The line-shape is approximately the second derivative of a Lorentzian due to the modulation scheme. The observed relative intensities are predicted by the eigenfunctions from the frequency fit.

HCCCO

Experimental structures find geometry I



FIG. 4. The geometry of HCCCO in the ${}^{2}A'$ ground state, determined from the present experimental results, based on the $r_m^{(1)}$ structures reported in Table III and assuming the HCCC chain to be (a) *trans* or (b) *cis.* The *trans* structure is preferred (see Sec. IV).

CuCH₃ with Grotjahn & Ziurys

Cu-C (Å)	С-Н (Å)	Н-С-Н	
1.881	1.085	109.9	Expt (Ziurys)
1.873	1.092	108.1	QCISD/6-311G** (us)
1.921	1.089	111.3	B3LYP/TZ2P (Barone)
1.921	1.096	110.0	CCSD(T)/DZP (Lee)

Reasonable method and basis set seem to work well. No relativistic corrections.

Subsequent tests on other 1^{st} row transition metals MCH₃'s show that this is a lucky cancellation of errors. These require a better basis set *and* relativistic corrections.

Beginning of collaboration

Grotjahn group gathers lots of quantitative data:

- Molecular structures from x-ray diffraction
- Nuclear magnetic interaction energies from NMR
- Reaction rates from time-dependent NMR

Our contribution:

- Justify structures based on details of electron distribution
- Model reaction pathways involving unobserved intermediates
- Perhaps guide future experiments by identifying promising targets

Methods

- The molecules have too many electrons for useful ab initio, so use DFT.
- Most popular DFT method, B3LYP, benchmarks very well against experimental geometries.
- Closed shell complexes, so no spin-orbit to worry about
- Recently developed basis sets provide quality and convergence tests not previously available
- Effective core potentials replace explicit treatment of dozens of core electrons *and incorporate relativistic corrections* empirically.

Alkyne hydration catalysis

















































Why does the first step occur?



Standard approach is Polarizable Continuum Method (PCM).



Calculate structure of molecule independently (gas-phase).

Standard approach is Polarizable Continuum Method (PCM).



Calculate molecular electric field.

Standard approach is Polarizable Continuum Method (PCM).



Generate a smooth cavity that surrounds the molecule (solvent).

Standard approach is Polarizable Continuum Method (PCM).



Calculate dielectric response of solvent cavity to molecular field.

Standard approach is Polarizable Continuum Method (PCM).



Iteratively optimize molecular wavefunction in presence of solvent.

COSMO-RS

Solvent model based on PCM but including stochastic algorithm with empirical factors for approximating dynamic nature of solvent-solute interactions.



COSMO-RS benchmarks well with explicit solvent

pK_a comparison to experiment

acid	expt	B3LYP/COSMO	BP86/COSMO-RS
Acetic acid	4.8	5.4	4.0
Pyrindine-H⁺	5.2	8.9	7.6
Pyrrolidine-H⁺	11.4	12.9	10.7
Cobalt-pyridine –H ⁺ complex	10.7		12.0

...but has no more than ~3 kcal/mol effect on relative energies in alkyne hydration reaction pathway.

Also add explicit solvent molecules



COSMO-RS + explicit solvent strongly affects steps involving H₂O

ΔG (kcal/mol)

Step	Gas phase	+ 2 H ₂ O	+2 H ₂ O + COSMO-RS
M-H2O to M-HCCH activation	41.5	26.8	26.2
M-H2O to M-HCCH equilibrium	16.2	<7.8	<6.2
H transfer from pyr to form aldeyde activation	17.9	22.7	21.5

Activation barrier for displacement of water drops 15 kcal/mol.

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Predicts at equilibrium [M-HCCH]/[M-H2O] > 10^{-5} .

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Relatively little shift in steps that don't directly involve water.

Oxygen atom transfer

Carl Carrano's group observes O atom transfer from a molybdenum complex, a model for enzyme-catalyzed O transfer.

Unlike previous studies, this complex has competing configurations and sites for reaction.

cis





Why the observed preference for reaction at trans, when cis is predicted to be more stable?

Qualitative agreement with experiment on first pass





O atom transfer to PMe₃

Displacement by solvent





Relative Energies

Rate Constants

	k_1 (s ⁻¹)	
Mo-O-PMe ₃	Computational	Experimental
Cis	2.64 x 10 ⁻⁹	6.96 x 10 ⁻⁴ s ⁻¹
Trans	1.87 x 10 ⁻⁴	4.18 x 10 ⁻² s ⁻¹
	k ₂ (s ⁻¹)	
Mo-Pyridine	Computational	Experimental
Trans	2.91 x 10 ⁻⁹	1.82 x 10 ⁻⁴

Each order of magnitude error in k is error of 1.4 kcal/mol in free energy. Still some work to do, improving calcs with solvent modeling, etc.

	2a	2b	2c	2e	3b	3e-(¹⁵ N) ₂	5b
$Ir-Cp^*$ ($Cp^* = centroid$)	1.844(2)	1.818(2)	1.827(8)	1.819(12)	1.869(2)	1.866(2)	1.800(2)
Ir-P	2.3957(6)	2.3140(7)	2.2972(7)	2.3171(13)	2.2645(11)	2.2788(10)	2.3841(8)
Ir-A (hydrogen bonded) (Ir-N for 5b)	2.4224(5)	2.4336(7	2.4263(7)	2.4419(14)	1.64(2) (Ir-H)	2.4072(11)	2.118(3) (Ir-N)
Ir-Cl or Ir-X (non-hydrogen-bonded)	2.4005(5)	2.4032(6)	2.4089(7)	2.4050(14)	2.4097(13)	1.664(19)	2.4001(9)
P-C2(Im)	1.835(2)	1.807(3)	1.820(3)	1.804(5)	1.821(3)	1.820(4)	1.799(3)
N-A	3.054(4)	3.177(8)	3.202(3)	3.141(4)	2.55(2)	3.039(4)	
N-H	0.88	0.88	0.79(3)	0.87(7)	0.900(1)	0.88	0.87
Н•••А	2.27(1)	2.44(1)	2.47(3)	2.40(7)	1.913	2.29(2)	
A to imidazole plane ^b	0.337	0.588	0.115	0.651	0.220	0.863	
Cl or X to imidazole plane ^b	2.593	0.797	2.741	0.723	2.538	1.722	
torsional angle C2(Im) P-Ir-Cp*	-175.65(0.36)	62.58(0.35)	-165.96(0.34)	-66.34(0.52)	163.58(0.53)	-179.59(0.37)	-134.55(0.34)
(θ_1) N-H···A	149.1(1)	141.1(1)	155(3)	143(6)	126.4	143.3(2)	1000 C
(θ_2) Cl-Ir-A, X-Ir-A, or Cl-Ir-N	85.898(19)	89.39(2)	88.74(2)	88.05(5)	84.8(1)	92.0(17)	83.58(8)
(θ_3) A-Ir-P or N-Ir-P	91.932(18)	86.39(2)	91.33(2)	87.10(5)	79.7(3)	95.31(4)	66.88(7)
(θ_4) Cl-Ir-P or X-Ir-P	88.090(19)	88.84(2)	86.84(2)	91.78(5)	90.5(4)	83.1(17)	87.64(3)
(θ_5) Cp*-Ir-Cl or Cp*-Ir-X	120.6(1)	123.5(1)	122.4(3)	122.1(4)	122.4(1)	121.19(4)	122.6(1)
(θ_6) Cp*-Ir-A	117.5(1)	122.2(1)	123.6(3)	124.0(4)	125(3)	117.55(2)	
(θ_7) Cp*-Ir-P	138.5(1)	133.5(1)	131.4(2)	131.1(4)	137.3(1)	136.03(3)	140.6(1)
(θ_8) P-C2(Im)-N(H)	124.29(16)	121.9(2)	121.9(2)	121.8(4)	124.6(6)	123.3(3)	145.2(3)
(θ_9) P-C2(Im)-N	125.20(16)	127.0(2)	125.8(2)	127.5(4)	124.7(6)	125.8(3)	105.2(2)

^{*a*} Cp^{*} = centroid. ^{*b*} Distance to mean plane defined by the three carbons and two nitrogens of the imidazole ring.

Lots of great data...(this is only page 1 of 3)...

1d

Cp*

2d



But there are 3 mysteries...

 Cp^{*} $CI \xrightarrow{I} Ir \qquad R$ $H \xrightarrow{P - R}$ $HN \xrightarrow{N}$ $R^{1} \qquad R^{1}$

3a-3c, 3e





3d



4b, 4e

1. Why are there two conformers for 2b, but not 2c?



2. X-ray shows 3b forms H-bond to hydride, but all the other H bonds are to Cl. Why?



3. Why is the N-H J coupling is larger in 3e than in 1e, even though the N-H distance is longer?



3e

1. Why are there two conformers for 2b, but not 2e?

Hypothesis A: two rotamers about the P-imidazole bond



Hypothesis B: two rotamers about the Ir-P bond



Amy Arita's calculations find that the exo is always less stable by 10-12 kcal/mol, so exo is not a likely contributor.

But then a new mystery: if the two conformers are anti and gauche, why not seen for 2c?

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1. Why are there two conformers for 2b, but not 2e?





The iPr groups in 2b bump into the Cp* more than the phenyls!

So anti/gauche in 2c interconvert too rapidly to observe distinct spectra.

2. X-ray shows 3b forms H-bond to hydride, but all the other H bonds are to Cl. Why?





Amy's calcs find that H-bond to hydride is always less stable by 6-7 kcal/mol than Hbond to Cl, and often not stable wrt the bond to Cl.

2. X-ray shows 3b forms H-bond to hydride, but all the other H bonds are to Cl. Why?

Because the crystal structure allows intermolecular H-bonding!



3. Why is the N-H J coupling is larger in 3e than in 1e, even though the N-H distance is longer?



Calcs show right away that H-bonding to Cl increases electron density at the H, which increases the J coupling.

Growing respect for ability of comp chem to model transition metal compounds

- 1. Qualitative agreement with experiment almost routine.
- 2. Quantitative agreement still challenging, especially for reaction rates and where solvent effects are big.
- 3. Powerful tool in interpretation of even highly detailed experimental data.

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