WH08

Computational Molecular Spectroscopy: The Equilibrium Bond Length of $\tilde{X}\ ^3\Phi$ CoH

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Computational Molecular Spectroscopy is

Spectroscopy of Molecules by Computational Methods.

Experimental spectroscopy --- Laser, Microwave, …

Computational spectroscopy --- *ab Initio* methods,
based on the potential energy surface

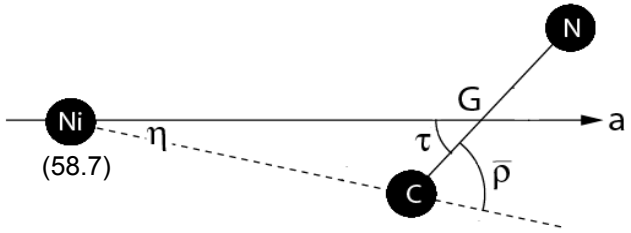
For example: r_0(C-N) of NiCN

- Experimental 1.1591(29) Å (Visible LIF: Kingston, et al. 2002)
  1.1590(2) Å (MW: Sheridan, et al. 2003)

- Computational 1.171 Å (MORBID: Hirano, et al. 2007)

  cf. 1.160 Å (averaged z-axis projection)

Which is more accurate, and more physically sound?



Our Strategy in Computational Molecular Spectroscopy

1) Three-dimensional potential energy surface
by the *ab initio* MO method:
MR-SDCI + Q + E_{rel}

2) Fit the potential to an analytical potential function

3) The 2nd-order perturbation treatment

4) Variational calculations with MORBID or RENNER

- Details for FeNC/FeCN in **the precedent talk** (WH07)
- FeNC: Hirano, *et al*., *J. Mol. Spectrosc*., **236**, 234 (2006)
- CoCN: Hirano, *et al*., Mol. Phys., **105**, 599 (2007)

There have been two distinctly different values for r_e(Co-H) of $^3\Phi$ CoH

r_e = 1.513 843 5(80) Å Beaton, et al. (1994) by LMR

$B_{0,\Omega=4}$ = **7.13680(16)** cm^{-1} **Hund's case (a) limit**

r_e = 1.531 291(8) Å Ram, *et al*. (1996) by IR-FT

$B_{0,\Omega=4}$ = **7.149160(57)** cm^{-1} **Hund's case (c)**

r_e = 1.532 664(16) Å Gordon, *et al*. (2006) by NearIR-FT

$B_{0,\Omega=4}$ = **7.136 591(160)** cm^{-1} **Hund's case (c)**

However, there should be ONE value within experimental error !!!

What will happen if we apply a spin-orbit correction to $B_{0,\Omega=4}$?

$$B_{0,\Omega} = B_0 + (2 B_0^2/A_{so}\Lambda)\,\Sigma, \qquad B_e = B_0 + 0.5\,(g\,\alpha)$$

	Ram, *et al*. (1996)	Gordon, *et al*. (2006)
$B_{0,\Omega=4}$ / cm^{-1}	7.149 160(57)	7.136 591(160)
A_{so} /cm^{-1}	-242.7 (Verberg, et al)	-242.3 (Gordon, et al)
B_0 /cm^{-1}	7.295 376	7.282 492
α / cm^{-1}	0.212444 (= $B_{0,\Omega=4} - B_{1,\Omega=4}$)	0.211 481 (= $B_{0,\Omega=4} - B_{1,\Omega=4}$)
B_e /cm^{-1}	7.401 598	7.388 232
r_e / Å	1.5161	1.5175
(original)	1.531 291(8)	1.532 664(16)
$B_{0,\Omega=3}$ / Å	7.286 10(18)	7.276 14(21)
r_e / Å (from $B_{0,\Omega=3}$)	1.5170	1.5181

← $\Sigma = 0$

r_e(Co-H) 1.513 843 5(80) Å (Beaton, et al. 1994)

r_e (Co-D) 1.5175 Å (Klyning,et al.1972)

Previous *ab Initio* studies

Method	State	r_e / Å	ω_e / cm^{-1}	T_e ($a\ ^5F - X\ ^3F$) / cm^{-1}
B3LYP[a]	^3F	1.510	1868	
MCSCF[b]	^3F	1.58	1998	
CISD[c]	^3F	1.529	1855	
MCPF[c]	^3F	1.532	1842	
CPF[c]	^3F	1.575	2000	
MR-SDCI+E_{rel}[d]	^3F	1.487	2026	
	^5F	1.640	1599	4597
Exp.	^3F	1.513-1.518	1926	6625

a) Barone and Adamo (1997), b) Das (1981), c) Chong, *et al*.(1986), d) Freindorf, *et al*. (1993)

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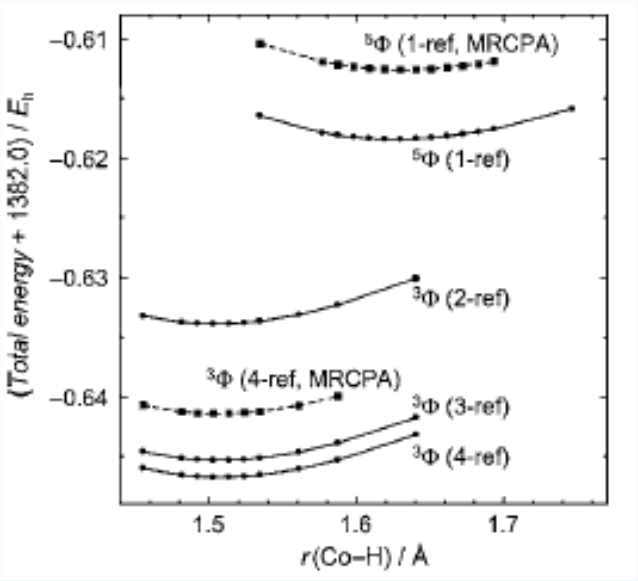
J. Chem. Phys., 126, 144307 (2007)

Calculations

Basis sets: STO
Symmetry: $C_{\infty v}$
MCSCF: 4 references or 5 references
MR-SDCI

MRCPA(4)



Method	State	r_e / Å	ω_e / cm^{-1}	T_e ($a\,^5\Phi - X\,^3\Phi$) / cm^{-1}
MR-SDCI (4-ref)	$^3\Phi$	1.507	1938	6218
	$^5\Phi$	1.626	1774	
MR-SDCI (5-ref)	$^3\Phi$	1.510	1925	
MRCPA(4)/4-ref	$^3\Phi$	1.507	1929	6331
	$^5\Phi$	1.632	1756	
Exp.	$^3\Phi$	1.513-1.518	1926	6625
	$^5\Phi$	1.67(5)[a]		

a) Miller (1987)

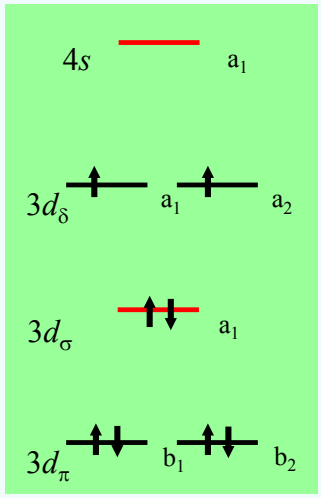
High-spin / Low-spin issue

FeNC $\tilde{X}\,^6\Delta < {}^4\Delta$
FeCO $\tilde{X}\,^3\Sigma^- < {}^5\Sigma^-$
FeH $X\,^4\Delta < a\,^6\Delta$

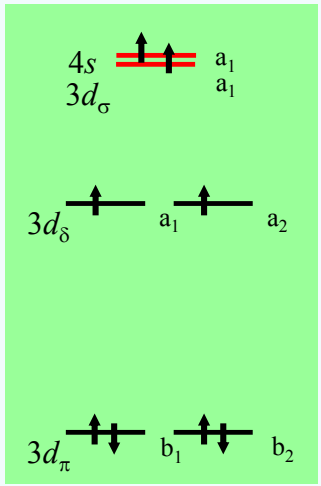
CoH $X\,^3\Phi < {}^5\Phi$
CoCN $\tilde{X}\,^3\Phi < {}^5\Phi$

NiCN $\tilde{X}\,^2\Delta < {}^4\Delta$

$\tilde{X}\,^6\Delta$ FeNC
(High-spin)

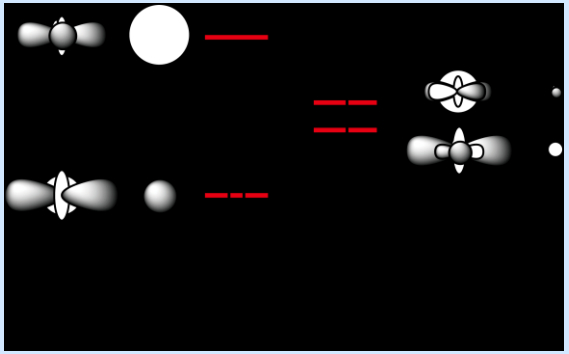


$\tilde{X}\,^3\Sigma^-$



$^5\Sigma^-$

FeCO
(Low-spin)



CoH $Co^{\delta+}\ H^{\delta-}$

	$\tilde{X}\,^3\Phi$	$^5\Phi$
CASSCF / mE_h	4.8	0.0
MRCPA(4)/ mE_h	0.0	28.8
Δ(Dynamical Electron Correlation) / mEh	33.6	
Net Charge (Co)	+0.45	+0.12
Ionicity (Co-H)	>	
r_e(Co-H) / Å	1.510	1.632
ω_3(Co-H) / cm^{-1}	1925	1756

Dynamical electron correlation → Low-spin

The same tendency is found for FeH, CoCN

The Aim of Spectroscopy is Understanding of Molecular Structure,
in Terms of Electronic, Vibrational, and Rotational Aspects.

↓

Cooperation between Experimental and Computational Mol. Spectroscopies should be promoted.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Discussion

The $^3F_4$ state is pure state.
The $^3F_3$ state should be perturbed by $^3D_3$.

The experimentally observed $^3F_3$ – $^3\Phi_4$ spin-splitting is perturbed.

Unperturbed spin-splitting should be larger than obs. 726.996 cm^{-1}.

Hence, true B_0 should be smaller than exp. B_0, and r_e should be smaller than 1.514 -1.518 Å