

WH07

Computational Molecular Spectroscopy of FeCN in the ${}^6\Delta$ Electronic Ground State

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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 (PES)

	Exp. Spectroscopy	Comp. Spectroscopy
Starting point	Spectral Lines	<i>Ab Initio</i> PES
Strong points	Accurate B_0 Elect. Excited states	Electronic states Force constants (Renner constant) Unperturbed Spin-splitting Large Amplitude Bending Motion

Our Strategy in Computational Molecular Spectroscopy

1) Three-dimensional **potential energy surface**

by the *ab initio* MO method:

$$\text{MR-SDCI} + \text{Q} + E_{\text{rel}}$$

2) **Fit** the potential to an analytical potential function

3) The 2nd-order **perturbation** treatment

4) **Variational** calculations with MORBID or RENNER

- FeNC: Hirano *et al.*, *J. Mol. Spectrosc.*, **236**, 234 (2006)
- CoCN: Hirano *et al.*, *Mol. Phys.*, **105**, 599 (2007)
- CoH: Tomonari *et al.*, *J. Chem. Phys.*, **144**, 144307 (2007); WH08

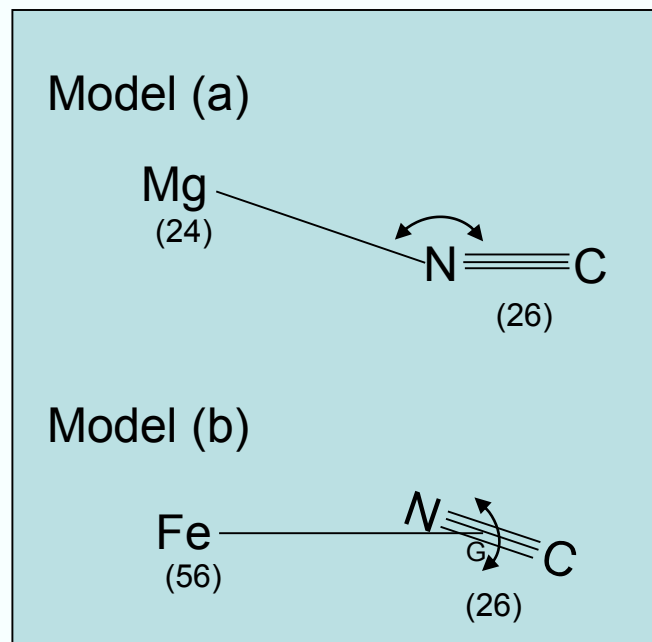
Large Amplitude Bending Motion



Too-short experimental $r_0(\text{C-N})$

Ionic Cyanides and Isocyanide with a heavy atom

FeNC
CoCN
NiCN
BrCN⁺
CrCN
...



FeNC

Exp. (LIF) Lie & Dagdian (2001)

$$B_0 = 0.1452(2) \text{ cm}^{-1}$$

$$B_0 (^6\Delta_{9/2}) = 0.14447(13) \text{ cm}^{-1}$$

$$2.01(5) \text{ \AA} \quad \underline{1.03(8) \text{ \AA}}$$



Calc. 1.935 \AA 1.182 \AA r_e

$$B_e = 0.14250 \text{ cm}^{-1}, B_0 = 0.14278 \text{ cm}^{-1}$$

CoCN

Exp. (MW) Sheridan and Ziurys (2004)

$$B_0(^3\Phi_4) = 4208.827(23) \text{ MHz}$$

$$1.88270 \text{ \AA} \quad \underline{1.13133 \text{ \AA}}$$



Calc. 1.854 \AA 1.168 \AA r_e

$$B_e = 4210 \text{ MHz}$$

NiCN

Exp. (LIF) Kingston, Merer, Varberg (2002)

$$B_0 (^2\Delta_{5/2}) = 0.1444334(30) \text{ cm}^{-1}$$

(MW) Sheridan, Ziurys (2003)

$$B_0 (^2\Delta_{5/2}) = 0.14443515(5) \text{ cm}^{-1}$$

LIF 1.8292(28) \AA 1.1591(29) \AA $r_0(^2\Delta_{5/2})$

MW 1.8293(1) \AA 1.1590(1) \AA $r_0(^2\Delta_{5/2})$



Calc. 1.811 \AA 1.166 \AA r_e

$$B_e = 0.14590 \text{ cm}^{-1}, B_0(^2\Delta_{5/2}) = 0.14595 \text{ cm}^{-1}$$

However,
difference in B_0 is small:

$$\text{FeNC}_{\text{calc}} \quad -1.2 \%$$

$$\text{NiCN}_{\text{calc}} \quad 1.1 \%$$

DeYonker, *et al.* (2004, *JCP*)

(MR-SDCI+Q)

$$r_e(\text{Fe-N}) = 1.940 \text{ \AA}$$

$$r_e(\text{C-N}) = 1.182 \text{ \AA}$$

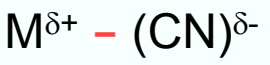
$$\rightarrow B_e = 0.1420 \text{ cm}^{-1}$$

C-N Bond length / Å			
	FeNC	CoCN	NiCN
Obs. (r_o)	1.03(8)	1.131	1.159
Calc. (r_e)	1.182	1.168	1.166
Difference/Å	-0.15	-0.037	-0.007

Our Calc. level:
 FeNC, CoCN, and NiCN
 MR-SDCI+Q + E_{rel}

cf. Exp.
 r_o (NC): 1.15 – 1.19 Å
 AINC 1.171 Å
 CN 1.172 Å

- **Ionicity** (Metal-Ligand) can be estimated from the C-N bond length:



The transferred electron goes into $\sigma^*(CN)$ orbital \rightarrow weaken the CN bond.
 (i.e. lengthen the CN bond).

Hence, the ionicity of the Metal-Ligand bond should be in this order,

$$Fe-NC > Co-CN > Ni-CN \quad (\text{from } ab \text{ initio } r_e)$$

- **And, hence, floppiness in bending motion should be**

$$Fe-NC > Co-CN > Ni-CN ,$$

since the more ionic, the more floppy.

- **Wavefunction**

- Construction of MCSCF guess by merging Fe^+ (6D) and CN^- (${}^1\Sigma$) MCSCF orbitals
- Multi-Reference Single and Double Configuration Interaction (MR-SDCI)
- Davidson's type corrections were added to the MR-SDCI calculation (denoted as +Q).
- The relativistic corrections (E_{rel}) have been included using the Cowan-Griffin approach by computing expectation values of the mass-velocity and one-electron Darwin terms.

- **Active space**

- 3s, 3p, 3d and 4s shells of Fe, and 2s and 2p shells of CN

- **Program**

- MOLPRO 2002

Molecular constants of ${}^6\Delta_i$ FeCN and FeNC

MR-SDCI+Q+Erel/[Roos ANO(Fe), aug-cc-pVQZ(C,N)]

	FeCN	FeNC	
	Calc.	Calc.	Exp. (Lie & Dagdigian)
$r_e(\text{Fe-N, Fe-C}) / \text{\AA}$	2.0484	1.9354	$2.01 \pm 0.05 (r_0)$
$r_e(\text{N-C}) / \text{\AA}$	1.1681	1.1823	$1.03 \pm 0.08 (r_0)$
$a_e(\text{Fe-C-N, Fe-N-C})/\text{deg}$	180.0	180.0	180.0
B_e/cm^{-1}	0.1239	0.14250	
B_e/MHz	3714.0	4272.2	
$B_{0,\Omega=9/2}/\text{cm}^{-1}$	0.12380	0.14276 (-1.2%)	0.14447(13)
E_e/E_h	<u>-1364.1951508</u>	-1364.1941735	
D_J/MHz	0.00123	0.00145	
$D_J * 10^8/\text{cm}^{-1}$	4.12	4.83	
$\alpha_1 / \text{cm}^{-1}$	0.00055	0.00055	
$\alpha_2 / \text{cm}^{-1}$	-0.00091	-0.00147	
$\alpha_3 / \text{cm}^{-1}$	0.00053	0.00061	
ω_1/cm^{-1}	2179	2090	
ω_2/cm^{-1}	173	109	
ω_3/cm^{-1}	420	476	464.1 ± 4.2

Continued ...

	FeCN	FeNC ⁴⁾	
	Calc.	Calc.	Exp (Lie & Dagdigian)
$\omega_e x_e(11)/\text{cm}^{-1}$	-12.2	-11.8	
$\omega_e x_e(22)/\text{cm}^{-1}$	-5.9	-4.0	
$\omega_e x_e(33)/\text{cm}^{-1}$	-1.6	-3.7	
$\omega_e x_e(12)/\text{cm}^{-1}$	-3.5	-4.9	
$\omega_e x_e(13)/\text{cm}^{-1}$	-1.4	-3.7	
$\omega_e x_e(23)/\text{cm}^{-1}$	22.4	8.6	
g_{22}/cm^{-1}	5.7	2.7	
ν_1/cm^{-1}	2150	2060	
ν_2/cm^{-1}	170	102	
ν_3/cm^{-1}	438	475	468
Zero-Point $E./\text{cm}^{-1}$	1472	1385	
$\zeta_{12}/\text{cm}^{-1}$	-0.98	-0.97	
$\zeta_{23}/\text{cm}^{-1}$	-0.22	-0.24	
Λ -doubling/ cm^{-1}	0.00019	0.00038	
μ_e / D^*	-4.59 (-4.57)	-4.59 (-4.74)	
$A_{\text{SO}}/\text{cm}^{-1**}$	-83	-83	[cf. FeF (⁶ Δ_j) -78.15]***

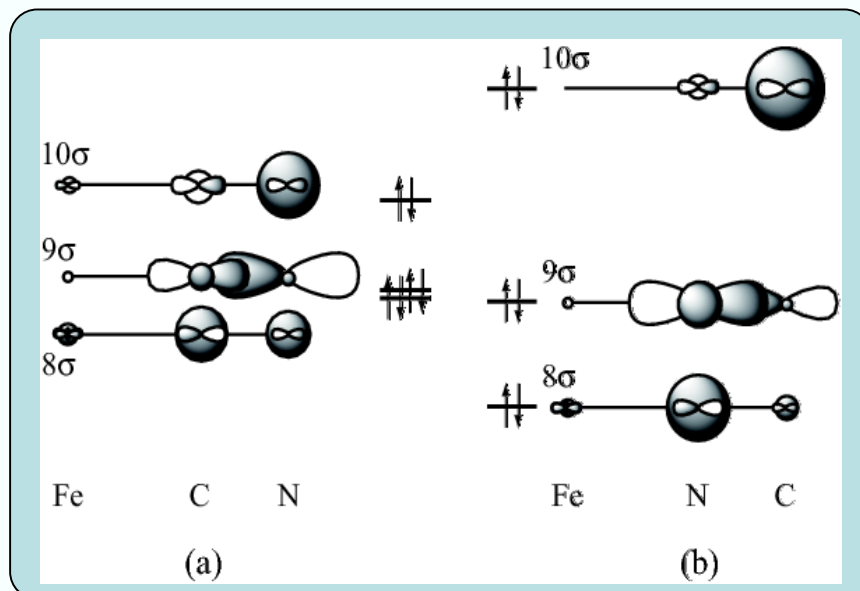
* Electric field derivative of Energy ** Basis sets: Wachters+f (Fe), aug-cc-pVTZ (C,N) *** Allen and Ziurys (1997)

$\text{Fe}^{\delta+}(\text{CN})^{\delta-}$ vs $\text{Fe}^{\delta+}(\text{NC})^{\delta-}$

	FeCN	FeNC
Mulliken Charge (Fe)	0.682	0.946
Ionicity		<
$r_e(\text{Fe-C/N}) / \text{\AA}$	2.048	> 1.935
$\omega_3(\text{Fe-C/N}) / \text{cm}^{-1}$	420	< 476
$r_e(\text{C-N}) / \text{\AA}$	1.168	< 1.182
$\omega_1(\text{C-N}) / \text{cm}^{-1}$	2179	> 2090

← ionic Fe—C/N bond

← e-transfer to CN^*
10 σ orbital



Comparison with Variational Method (MORBID)

	Fe ¹² CN /cm ⁻¹		Fe ¹³ CN /cm ⁻¹	
	Perturb.	MORBID	Perturb.	MORBID
(0,1 ^{e,f} ,0)	170.3	170.4	165.4	165.4
(0,2 ⁰ ,0)	317.1	329.8	311.3	321.2
(0,0 ⁰ ,3)	438.1	423.2	429.3	417.6
(1,0 ⁰ ,0)	2150.3	2153.4	2103.4	2106.14
B_0	0.12426	0.12456	0.12295	0.12323

Averaged bond lengths in Å from MORBID

	$\langle r(\text{Fe-C}) \rangle$	$\langle r(\text{C-N}) \rangle$	$\langle r(\text{C-N}) \cos \tau \rangle$	$\langle \Delta(\text{Fe-C-N}) \rangle$
r_e	2.048	1.168		0
(0,0,0)	2.082	1.172	1.158	10(5)
(0,1 ^{e,f} ,0)	2.088	1.173	1.146	15(6)
(0,2 ⁰ ,0)	2.083	1.173	1.311	18(9)
(1,0 ⁰ ,0)	2.089	1.178	1.155	10(5)
(0,0 ⁰ ,1)	2.093	1.172	1.158	10(5)

Now we can make quantitative arguments....

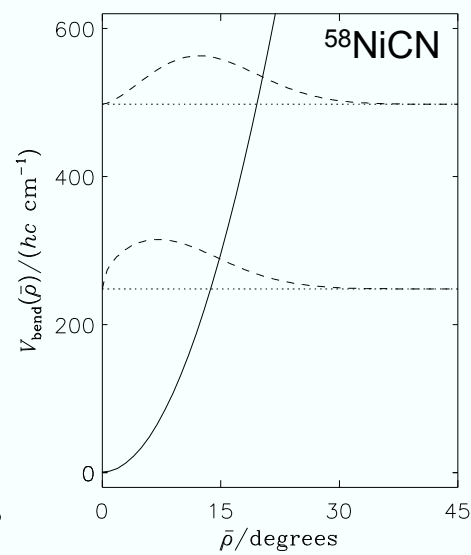
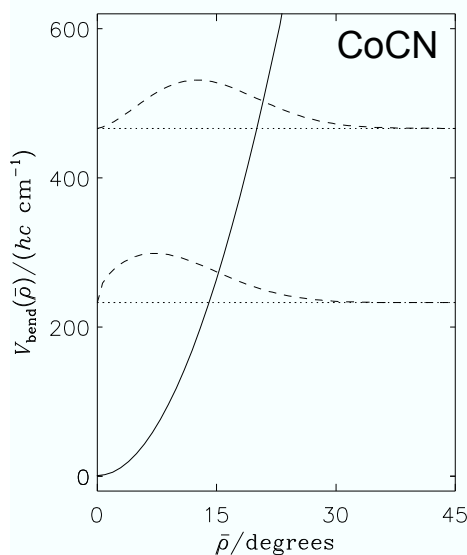
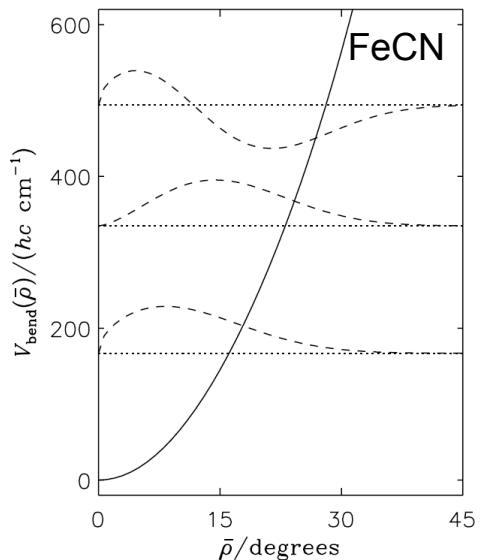
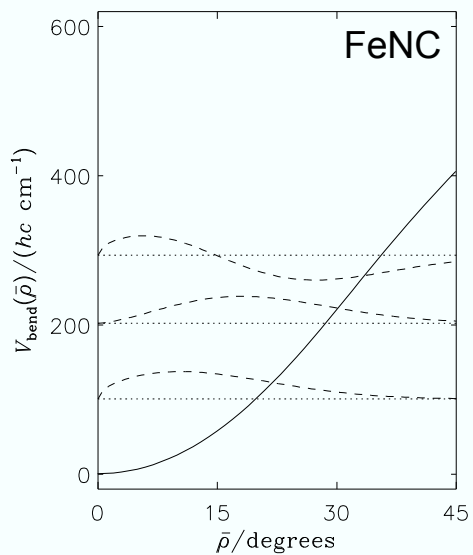
Floppiness in bending motion

- Bending force constant (aJ) from the 3-D PES

FeNC > FeCN > CoCN > NiCN

0.036 0.085 0.151 0.180

- Bending potential: **FeNC > FeCN > CoCN > NiCN**



C-N bond lengths

C-N Bond length / Å				
	FeNC	FeCN	CoCN	NiCN
Obs. (r_0)	1.03(8)	?	1.131	1.159
Calc. (r_e)	1.182	1.168	1.168	1.166
(r_0)	1.187	1.172	1.172	1.171
Difference	-0.15	?	-0.041	-0.012
(%)	-12.9	?	-3.4	-1.0

Then, **WHAT** does the experimentally obtained r_0 values mean ?

The difference between experimental and predicted values indicates the *existence of large-amplitude bending motion*.

However, experimentally derived r_0 value, in this case, has **No-physical meaning** for the understanding of the chemical bond.

We need to explore a new method to derive physically-sound, and meaningful r_0 from experiments for this type of floppy molecule !!!

We used to be **Helpers** (助っ人).

Now, we are one of the **Main-players** in Molecular Spectroscopy

Acknowledgements

- All calculations were carried out on **AIST Super Clusters**
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- **CREST** project “Development of MO calculation system for large molecules on grid.”

Thank you for your attention !



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Computational Molecular Spectroscopy is

a Spectroscopy of Molecules using Computational Methods.

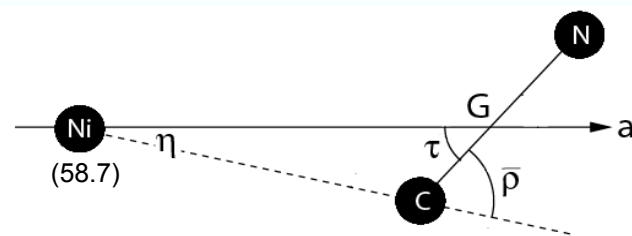
Experimental spectroscopy --- **Laser, Microwave, ...**

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

For example: $r_0(\text{C-N})$ of NiCN

- Experimental $1.1591(29) \text{ \AA}$ (Visible LIF: Kingston, et al. 2002)
 $1.1590(2) \text{ \AA}$ (MW: Sheridan, et al. 2003)
- Computational 1.171 \AA (MORBID: Hirano, et al. 2007)
cf. 1.160 \AA (averaged z-axis projection)

Which is more accurate, and more physically sound?

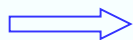


ii) CN bond lengths: MORBID Expectation value

Ro-vibrationally averaged MORBID structure

	FeNC	CoCN	NiCN	BrCN ⁺
$r_e(\text{C-N}) / \text{\AA}$	1.182	1.168	1.166	1.199
$r_0(\text{C-N}) / \text{\AA}$	1.187	1.172	1.171	1.204
$\langle \bar{\rho} \rangle / \text{deg.}$	13(7)	8(5)	9(5)	8(4)

- Both $r_e(\text{C-N})$ and $r_0(\text{C-N})$ fall inside of the normal C-N bond length 1.16-1.19 Å. BrCN⁺ is a cation, and hence gives a little longer C-N bond.
- MORBID expectation value of the bond length r_0 :
a little longer than the equilibrium bond length r_e .
keeps almost constant unless the associated bond is vibrationally excited.
→ physically sound bond length to characterize a chemical bond even for molecules showing large amplitude bending motion.
- Although the equilibrium structure is linear, the ro-vibrationally averaged structure is bent.



This is our answer to the longstanding debate :
How to treat a large amplitude bending motion.

Why the Conventional method to derive r_0 value is inadequate ?

Observe B_0 's for isotopomers

- derive r_0 's, assuming linear structure for the moment of inertia calc.
- **interpret** thus derived r_0 's as the projection average onto the a -axis in the bending motion.

However, **NO average over bending motion is taken into account** in this procedure !

NiCN case:

Experimentally decided r_0 agrees with MORBID $\langle r(\text{C-N}) \cos \tau \rangle_0$, since B_0 's for $^{58}\text{NiCN}$ and $^{60}\text{NiCN}$ are corrected for the rotation-vibration interaction α_j .

Now, the turn is in the experimental side.

Explicit treatment of large amplitude bending motion is necessary.

Comparison with Variational Method (MORBID)

	Rovibrational level /cm ⁻¹	
	SURFIT	MORBID
$v_2 = 1, L = 1$	102.3	102.3
$v_2 = 2, L = 0$	191.2	189.6
$v_3 = 1, L = 0$	480.7	486.0
$v_1 = 1, L = 0$	2061.0	2065.6
B_0	0.1434 (1.2%)	0.1434(1.2%)

Exp. $B_0 = 0.1452 \pm 0.0002$, $B_{0,\Omega=9/2} = 0.14447(13)$

Averaged bond lengths in Å from MORBID

	$\langle r(\text{CN}) \rangle$	$\langle r(\text{Fe-N}) \rangle$	<i>cf.</i> r_e		
r_0 (Ground state)	1.187	1.967	1.182	1.935	
$v_2 = 1, L = 1$	1.187	1.971	$r_0(\text{Obs})$ 1.03(8)	2.01(5)	
$v_2 = 2, L = 0$	1.188	1.970			
$v_3 = 1, L = 0$	1.187	1.976			
$v_1 = 1, L = 0$	1.195	1.969			

Expectation values from MORBID analysis: FeNC

(v_1, v_2^{f2}, v_3)	$\langle r(\text{Fe-N}) \rangle / \text{\AA}$	$\langle r(\text{N-C}) \rangle / \text{\AA}$	$\langle r(\text{Fe-N}) \cos(\eta) \rangle / \text{\AA}$	$\langle r(\text{N-C}) \cos(\tau) \rangle / \text{\AA}$	$\langle \bar{\rho} \rangle$
(0,0 ⁰ ,0)	1.967	1.187	1.964	1.164	13(7)
(0,1 ^{e,f} ,0)	1.971	1.187	1.965	1.141	20(7)
(0,2 ⁰ ,0)	1.970	1.188	1.960	1.113	25(12)
(1,0 ⁰ ,0)	1.969	1.195	1.965	1.169	13(7)
(0,0 ⁰ ,1)	1.976	1.187	1.972	1.159	13(7)

cf.

Equil. Struct. 1.935 1.182 0.0

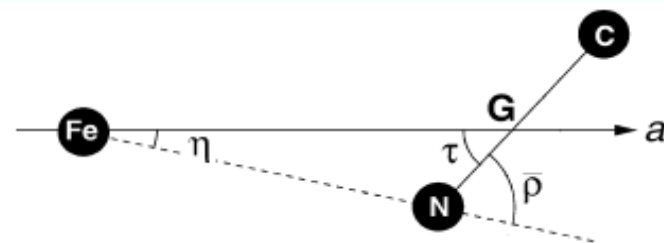
Exp. r_0 2.01(5) 1.03(8) 0.0

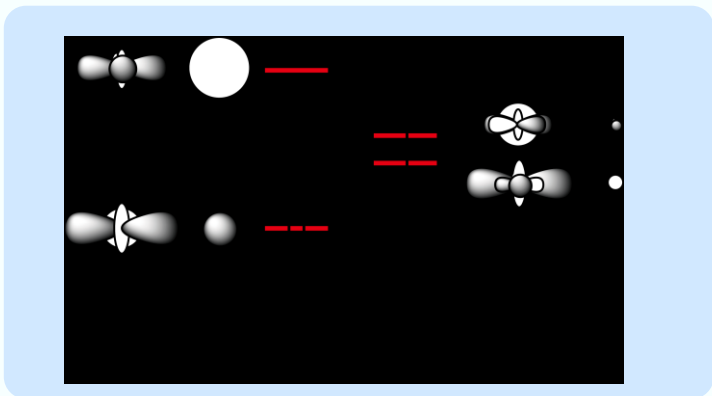
(Lie *et al.*, 2001)

- The $\langle r(\text{N-C}) \rangle$, $\sim 1.187 \text{ \AA}$, a little longer than $r_e(\text{N-C})$, does not change unless the C-N bond is excited. \rightarrow Physically meaningful, proper quantity.
- Exp. r_0 is **not** the averaged projection onto a -axis. \rightarrow No physical meaning !

Exp. model is inadequate !!

Explicit treatment of large amplitude bending motion is necessary.





CoH

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

	$\tilde{X}^3\Phi$	$^5\Phi$
CASSCF / mE_h	4.8	0.0
MRCPA(4)/ mE_h	0.0	28.8
Δ (Dynamical Electron Correlation) / mE_h	33.6	
Net Charge (Co)	+0.45	+0.12
Ionicity (Co-H)		>
$r_e(\text{Co-H}) / \text{\AA}$	1.510	1.632
$\omega_3(\text{Co-H}) / \text{cm}^{-1}$	1925	1756

Dynamical electron correlation

→ Low-spin

The same tendency is found for FeH, CoCN