

Which do you believe in ?

e.g. NiCN $r_0(\text{C-N})$

- Spectroscopy (Exp.) 1.1590(2) Å (MW: Sheridan, et al. 2003)
- Computational
Molecular Spectroscopy 1.171 Å (MORBID: Hirano, et al. 2007)

Which is the more **accurate** and **physically meaningful** number ?

Large Amplitude Bending Motion: Approach from Computational Molecular Spectroscopy

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T. Hirano



U. Nagashima



P. Jensen

Computational Molecular Spectroscopy



Computational Molecular Spectroscopy

- *ab Initio* Potential Energy Surface (PES)
- Solve ro-vibrational Schrödinger equation.
- Molecular constants as expectation values of the wavefunction
- Simulation of ro-vibrational spectrum



Experimental Molecular Spectroscopy

- Observation of ro-vibrational spectrum
- Analyses of the spectrum → Molecular structure and constants
- Inference of the Potential Energy Surface

Present status of Computational Molecular Spectroscopy

We **used to be** **helpers** for spectroscopy.

← Low computational accuracy and only qualitative suggestions

Now:

$\tilde{X}^2\Pi$ NCS (2009 Hirano, Nagashima, and Jensen)

Core-valence MR-SDCI/[a**CV**(Q+d)Z (S), a**CVQZ** (C,N)]

	B_0/MHz (Exp.: Amano et al ^a)	B_0/MHz (Calc.)	Difference
NC ³² S	6106.6 2195 (16)	6106.47	-0.002%
NC ³⁴ S	5962.8 57 (52)	5962.77	-0.001%

a) Maeda, Habara, Amano, Mol. Phys., **105**, 477- 495 (2007)



$$B_e = 6108.9 \text{ MHz}, D_J = 0.00171 \text{ MHz}$$

$$r_e(\text{N-C}) = 1.1777 \text{ \AA}, r_e(\text{C-S}) = 1.6338 \text{ \AA}$$

$$\omega_1 = 1998 \text{ cm}^{-1}, \omega_2 = 352 \text{ cm}^{-1}, \omega_3 = 737 \text{ cm}^{-1}$$

$$\text{Renner const } \varepsilon = -0.158$$

$$A_{\text{SO}} = -341 \text{ cm}^{-1}$$

$$\mu_e = 2.496 \text{ D} \dots$$

Molecular Spectroscopy is the most accurate science,
backed with laser wavelength accuracy.

e.g., NiCN $r_0(\text{C}\equiv\text{N}) = 1.1590(2) \text{ \AA}$

(MW: Sheridan, *et al.* 2003)

However, it is not all-mighty

Weak Point:

- Cannot treat large amplitude bending motion properly.

Because the analysis methods of analyses are generally based on perturbation theory.

For example,

- 1) Too short C $\equiv$ N bond length (FeNC, CoCN, ...).
- 2) If equilibrium structure is linear, the
ro-vibrationally averaged structure should also be linear (belief).
- 3) Coupling between bending and stretching modes
(due to 3rd order asymmetric PES-term)
Cases where bond elongates significantly with bending
(FeCO, HCO⁺, CaNC)

⇒ Jobs for Computational Molecular Spectroscopy
(complementary)

Large Amplitude Bending Motion: too short $\text{C}\equiv\text{N}$ bond length

With Per Jensen (Wuppertal, Germany)

The effects of **large amplitude bending motion** gave rise to a **longstanding** debate:

CsOH: D.M. Lide, R.L. Kuczkowski, *J. Chem. Phys.*, 46, 4768 (**1967**).

D.M. Lide, C. Matsumura, *J. Chem. Phys.*, 50, 3080 (**1969**)

RbOH: C. Matsumura, D.R. Lide, *J. Chem. Phys.*, 50, 71 (**1969**)

r_c : M. Nakata, K. Kuchitsu, *et al.*, *J. Mol. Spec.*, **83**,118 (1980) **OCCl₂**

J. Mol. Spec., **86**,241 (1981) **OCCl₂**

J. Mol. Struc., **320** ,179 (1994) **OCS, etc.**

$r_m^{(2)}$: J.K.G. Watson, *et al.*, *J. Mol. Spec.*, **196**,102 (1999)

K.A. Walker, *et al.*, *J. Mol. Spec.*, **209**, 178 (2001)

Theory

AlNC/AlCN, GaNC/GaCN,

InNC/InCN

However, mostly forgotten in recent experimental studies.

FeNC

Exp. (LIF) Lie & Dagdigan (2001)

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

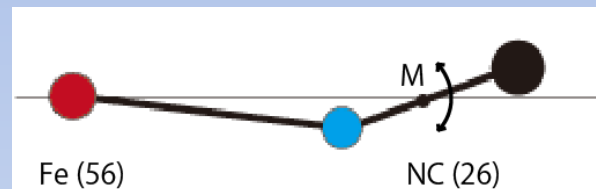
$$B_0 (^6\Delta_{9/2}) = \underline{0.14447(13)} \text{ cm}^{-1}$$

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



Calc. $1.935 \text{ \AA}$ $\underline{1.182 \text{ \AA}}$ r_e

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



$\text{N}\equiv\text{C}$ ligand (triple bond) $\rightarrow$ Strong and of almost constant bond length:
Should be $1.16 \sim 1.19 \text{ \AA}$ **Strange !**

Our calculation level: MR-SDCI+Q+ E_{rel} with error $\pm 1 \%$
 $\rightarrow$ Again **Strange !**

Fe $\cdots$ NC Ionic bond $\rightarrow$ Large amplitude bending motion

Experimental $r_0(\text{C-N})$ is too short !

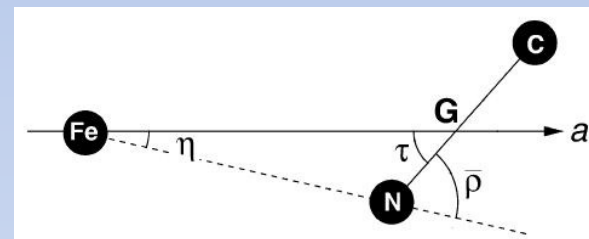
$\text{Fe}^{14}\text{N}^{12}\text{C} \quad \tilde{X}^6\Delta$ linear equilibrium structure

Three dimensional PES was calculated at the MR-SDCI + $Q + E_{\text{rel}}$ level.

J. Mol. Spectrosc., **236**, 234 (2006)

Exp. B_0 = 0.1452 (2) cm^{-1} ,
 Perturbation B_0 = 0.1434 cm^{-1} (1.2% difference)

It means something is wrong in deriving $r_0(\text{CN}) = 1.03(8) \text{ \AA}$!



Averaged bond lengths in $\text{\AA}$ from the variational MORBID

$(\nu_1, \nu_2^{l_2}, \nu_3)$	$\langle r(\text{Fe-N}) \rangle$	$\langle r(\text{CN}) \rangle$	$\langle r(\text{Fe-N}) \cos \eta \rangle$	$\langle r(\text{CN}) \cos \tau \rangle$	$\langle \bar{\rho} \rangle / \text{deg}$
(0, 0 ⁰ , 0)	1.967	1.187	1.964	1.164	13(7)
(0, 1 ^{1e,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)
Equil. Struct. r_e	1.935	1.182			0
Exp. r_0	2.01(5)	1.03(8)			0

Similar calculations have been done for

FeCN: *J. Mol. Spectrosc.*, **243**, 267 (2007)

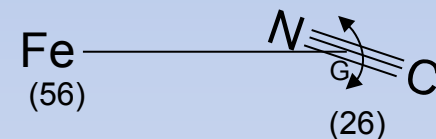
CoCN; *Mol. Phys.*, **105**, 599 (2007)

NiCN; *J. Mol. Spectrosc.*, **250**, 33 (2008)

In summary, ...

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** do the experimentally obtained r_0 values mean ?

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

However, the 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 values from experiments for this type of floppy molecule !!!

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Actually, 1.160 Å is an averaged z-axis projection (MORBID)

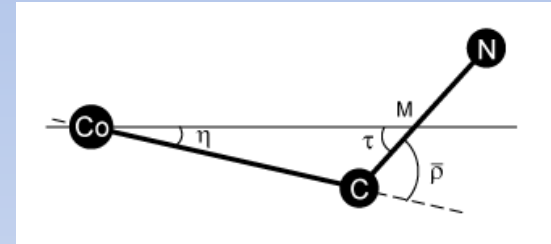
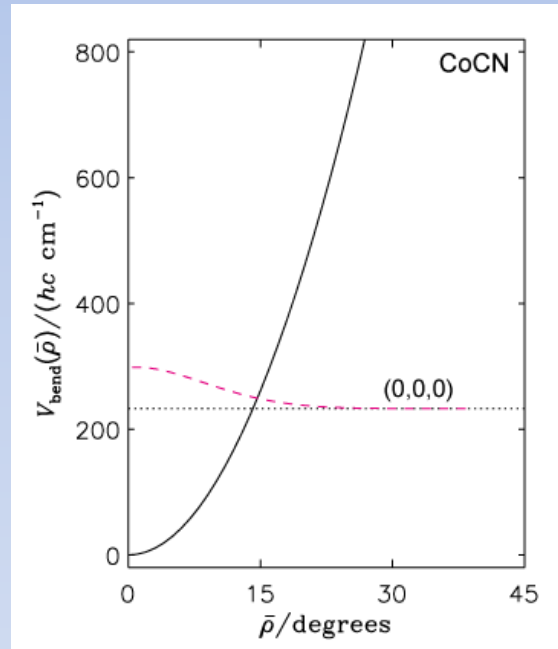
Large Amplitude Bending Motion: r_0 -structure is not linear

With Per Jensen (Wuppertal, Germany)

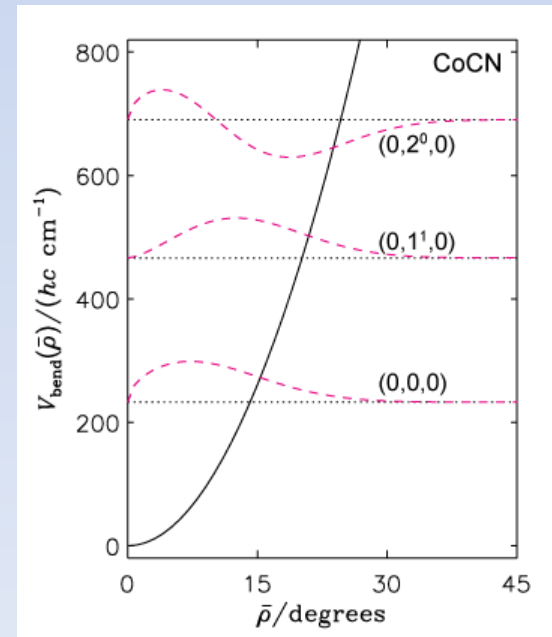
How do we distinguish linear and quasi-linear ?

- One-dimensional Harmonic Oscillator :
Maximum of wavefunction should be at the Origin. (imprinted with text book)

That is true !



- However, in an experiment,
 vibration and rotation **cannot separately** be observed !!!
 At least, should be treated as
 2-dimensional oscillator.
 ∴ Maximum of wavefunction (in pink) is not at the origin
 in the plot for the bending angle.
 (One-dimensional expression)



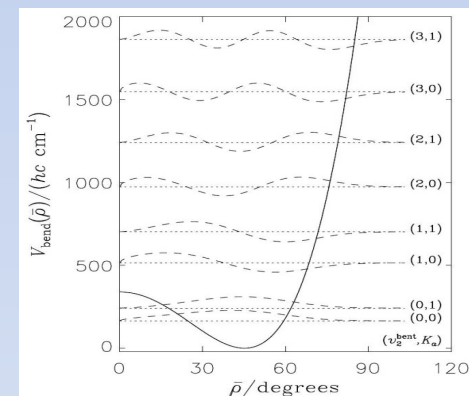
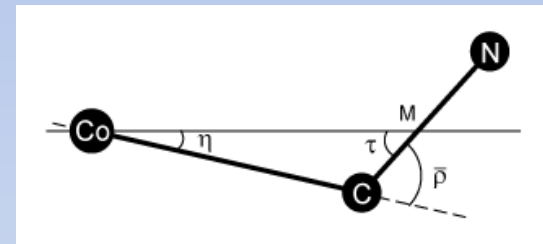
r_0 -structure of linear molecule (Linear at equilibrium structure)

Equilibrium structure		$\langle \bar{\rho} \rangle$ ($\delta \bar{\rho}$)
Linear	$^3\Phi$ CoCN	8° (5°)
	$^2\Delta$ NiCN	9° (5°)
	$^6\Delta$ FeCN	10° (5°)
	$^6\Delta$ FeNC	13° (7°)
	$^1\Sigma$ CsOH	17° (9°)
Quasi-linear (45.8°)	$^6\Delta$ FeOH	39° (14°)
Bent (65.1°)	$^2A'$ ZnOH	64° (10°)

$$\gamma_0 \approx -1$$

$$\gamma_0 \approx 0.10$$

$$\gamma_0 \approx 0.84$$



We have PES from the beginning. → No problem.
But, how can experimental people distinguish ?
Linear or quasi-linear ?

$$\gamma_0 = 1 - 4 \times \frac{E(v_2 = |\ell_2| = 1) - E(0)}{E(v_2 = 2, |\ell_2| = 0) - E(0)}$$

Yamada-Winnewisser index
J. Mol. Struct. **798**, 1 (2006)

Large Amplitude Bending Motion: Elongation with Bending

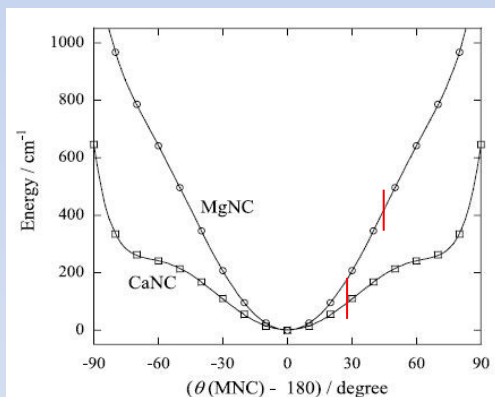
With Per Jensen (Wuppertal, Germany)

Large Amplitude bending Motion: Elongation with Bending (FeCO , HCO^+ , CaNC , ...)

In some molecules, bond significantly elongates on bending.

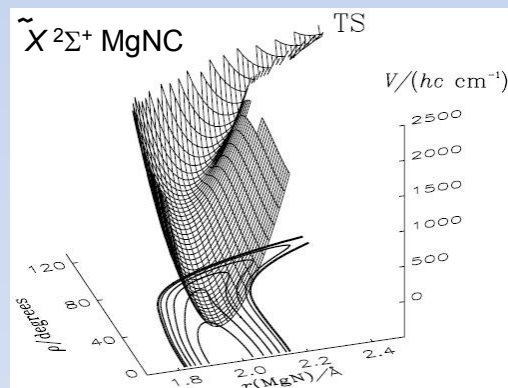
- **Ionic bond** ($^2\Sigma^+$ CaNC , $^2\Sigma^+$ MgNC),
due to the increasing difficulty in transferring electron to the ligand.

Ishii, Taketsugu, Hirano, CPL, **374**, 506 (2003)
Core-valence RCCSD(T)



Difficulty: Steimle et al., *Astrophys. J.*, **410** L49(1993).

Hirano, Ishii, Odaka, Jensen, JMS, **215**, 42 (2002)
Core-valence ACPF



Difficulty: Fukushima et al., *Bunshikagaku-Toronkai*, (2011)

- **Coordinate-covalent bond** ($^3\Sigma^-$ FeCO , $^1\Sigma^+$ H^+CO),

Conventional molecular spectroscopy cannot handle these features.

Bending Motion

Bonding type

- **Covalent** bond: **Small** amplitude bending motion, and **normal**.
- **Ionic** bond: **Large amplitude** bending motion, but **normal**.
- **Coordinate-covalent** bond:
Large amplitude bending motion
with significant elongation with bending.

Fe-CO

$\tilde{X} \ ^3\Sigma^-$ (Low-spin) : **Coordinate-covalent bond**
 $^5\Sigma^-$ (High-spin): **Ionic bond**

Fe-CN

$^4\Delta$ (Low-spin): **Coordinate-covalent bond**
 $\tilde{X} \ ^6\Delta$ (High-spin): **Ionic bond**

FeCO: [Exp. and Perturbation] vs. [MORBID] ?

3D PES: [MR-SDCI + Q] _DK3

	$^3\Sigma^-$ (coordinate-covalent bond)			$^5\Sigma^-$ (ionic bond)	
	MORBID	Perturb.	Exp.	MORBID	Perturb.
B_0 / MHz	4381.5	4366.2	4363.88342(40) ^a	4028.0	4016.9
Error (%)	0.40	0.05			

Why is the error(%) different although the same 3D PES is employed ?

Note that Perturb. and Exp. give quite similar values in disagreement with the MORBID result.

α_1 / cm-1	0.000757	0.000747	0.000728 ^b	0.000440	0.000693
α_2 / cm-1	0.000230	-0.000379	-0.000350 ^b	-0.000157	-0.000654
α_3 / cm-1	0.000627	0.000686	0.000674 ^b	0.000244	0.000596

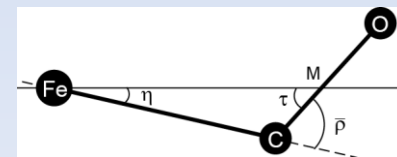
$^3\Sigma^-$: Why is the sign of α_2 from MORBID different from those from Perturb. and Exp. ?

Note that Perturb. and Exp. give quite similar values, while MORBID does not.

And, α_2 of $^5\Sigma^-$ state is a normal, negative value for both MORBID and Perturb.

a) Tanaka et al. (1997) b) Ikeda, Tanaka *et al.* (2007)

Positive $\alpha_2 \rightarrow B_{\text{eff}}(0,0,0) > B_{\text{eff}}(0,1,0)$ against common sense !



... continued

MORBID α_2 : positive (0.000230) for $^3\Sigma^-$ ← uncommon feature
negative (-0.000157) for $^5\Sigma^-$ ← normal feature

Why?

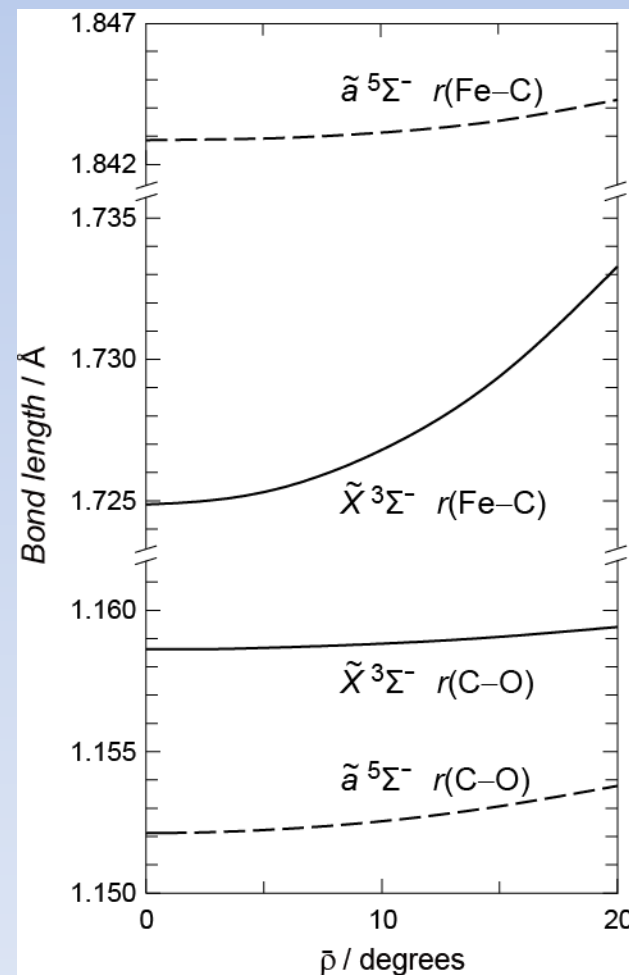
Force constants $f_{r(\text{Fe-C}), r(\text{C-O}), \angle(\text{Fe-C-O})}$

	$^3\Sigma^-$	$^5\Sigma^-$
f_{002} /aJ	0.362	0.180
f_{102} /aJ Å ⁻¹	-0.430	-0.060
Fe-C bond	coordinate-covalent	ionic

- When f_{102} is large, the Fe-C bond elongates significantly upon bending.

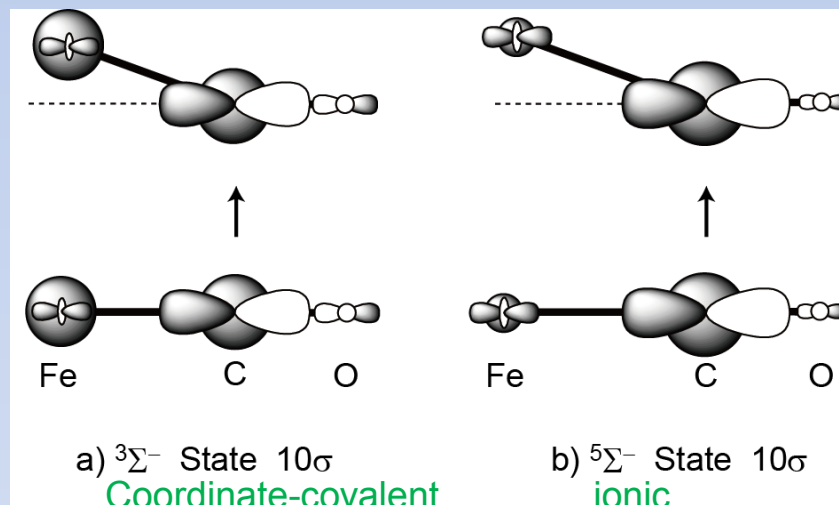


Thus, elongation of Fe-C bond upon bending is significant in the $^3\Sigma^-$ state, but normal in the $^5\Sigma^-$ state.



Bond lengths along the bending MEP (Minimum Energy Path)

- **Why** does the Fe-C bond elongate significantly upon bending in the $^3\Sigma^-$ state? Because, the Fe 4s comes in off-centered position about the axis of σ_{CO} orbital, resulting in the smaller overlap (i.e., weaker bond) between Fe 4s and σ_{CO} . (cf. 10σ NO (natural orbital) contributing to the covalency of the Fe-C bond).



Thus, the Fe-C bond, coordinate-covalent, in the $^3\Sigma^-$ state elongates significantly upon bending.

While, the Fe-C bond, ionic, in the $^5\Sigma^-$ state does not, and behaves normally.

- MORBID includes this effect in the large amplitude bending motion correctly.
- Perturbation and Exp. are based on the small amplitude bending motion around the equilibrium structure. → Incorrect description of bending motion.

Differences in MORBID, Perturb, and Exp.

	MORBID	Perturb	Exp.
α_1, α_3	similar	similar	similar
α_2 (bending)	positive (0.000230)	negative (-0.000379)	negative (-0.000350)
Region of PES employed	whole	near-equilibrium.	near-equilibrium
Fe-C elongation (bending)	O	X	X

What to do ?

Term value of rotation;

$$F_v(J) = B_v (J(J+1) + l^2) - D_v (J(J+1) - l^2)^2 + \dots \quad (1)$$

$$\alpha_2 \text{ taken to be } B_0 - B_{(v\text{-bend}=1)} \text{ in experimental analysis} \quad (2)$$

Higher order expansion to include f_{102} ;

$$B_v = B_e - \sum \alpha_i u_i + \sum \gamma_{ij} u_i u_j + \sum \delta_{ijk} u_i u_j u_k + l^2(b_e + \sum b_i u_i)$$

$$u_i = v_i + 1/2 \quad (\text{Stretching})$$

$$v_i + 1 \quad (\text{Bending}) \quad (\text{Oka et al., 1944, 2012}) \quad (3)$$

Thank you for your attention !



T. Hirano



U. Nagashima



P. Jensen

Differences in MORBID, Perturb, and Exp.

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α_1, α_3	similar	similar	similar
α_2 (bending)	positive (0.000230)	negative (-0.000379)	negative (-0.000350)
Region of PES employed	whole	near-equilibrium.	near-equilibrium
Fe-C elongation (bending)	O	X	X

What to do ?

Term value of rotation;

$$F_v(J) = B_v^{\text{obs}} J(J+1) - D_v J^2(J+1)^2 + \dots \quad (1)$$

$$\alpha_2 \equiv B_0 - B_{(v\text{-bend}=1)} \quad (2)$$

$$I_v = I_v^{\text{eq}} + \Delta I_v \text{ (for Fe-C elongation due to } f_{102}) \quad (3)$$

$$B_v \equiv h / (8\pi^2 c I_v) = h / [8\pi^2 c (I_v^{\text{eq}} + \Delta I_v)] \approx [h / (8\pi^2 c I_v^{\text{eq}})] \cdot (1 - \Delta I_v / I_v^{\text{eq}}) \quad (4)$$

$$= B_v^{\text{eq}} (1 - \Delta I_v / I_v^{\text{eq}}) \quad (5)$$

When B_v^{obs} (i.e., probably = B_v^{eq}) is corrected against $\Delta I_v / I_v^{\text{eq}}$, $B_{(v\text{-bend}=1)}$ becomes smaller to give $\alpha_2 > 0$.

Now we can make quantitative arguments....

Floppiness (i.e. Ionicity)

- Qualitatively from **the C-N bond length**:

FeNC >> CoCN $\approx$ NiCN

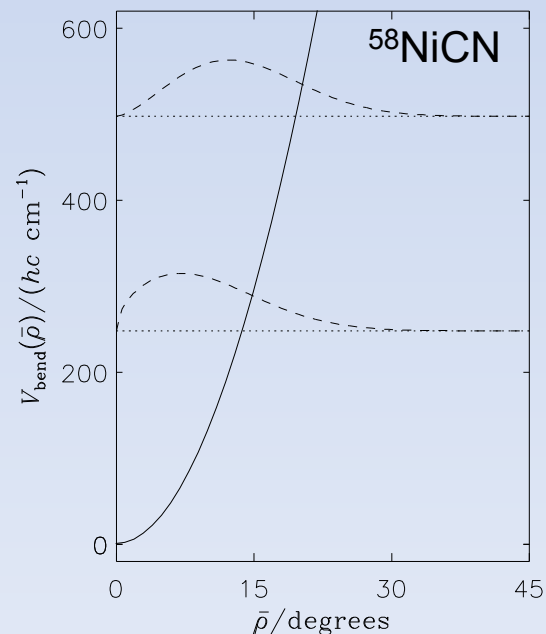
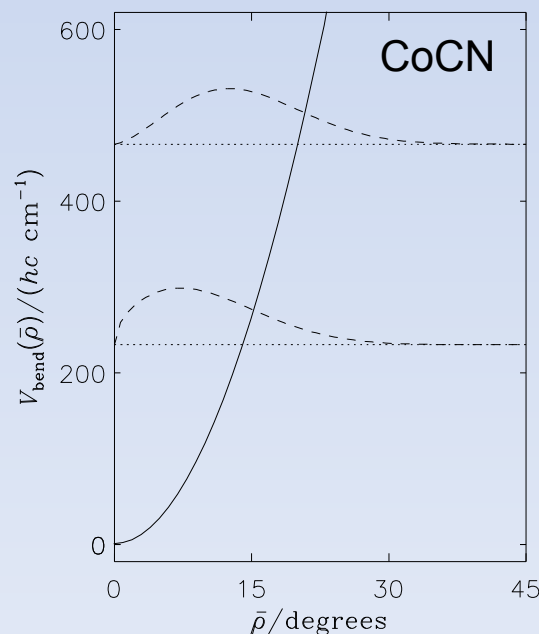
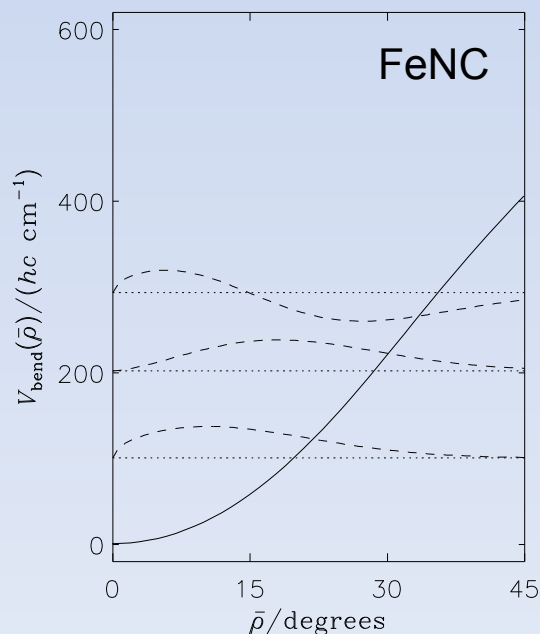
$(r_e(\text{C}\equiv\text{N})/\text{\AA})$ **1.182** **1.168** **1.167**

- Bending force constant** (aJ^{-1}) from the 3-D PES

FeNC >> CoCN > NiCN

0.036 **0.151** **0.180**

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



FeNC ${}^6\Delta_i$ MR-SDCI+Q+ E_{rel} /[Roos ANO(Fe), aug-cc-pVQZ(C,N)]

Perturbational Method

	Calc.	Exp. ${}^6\Delta_i$ ^{a)}		Calc.	Exp. ${}^6\Delta_i$ ^{a)}
$r_e(\text{Fe-N}) / \text{\AA}$	1.9354	2.01(5) (r_0)	$\omega_e x_e(11) / \text{cm}^{-1}$	-11.8	
$r_e(\text{N-C}) / \text{\AA}$	1.1823	1.03(8) (r_0)	$\omega_e x_e(22) / \text{cm}^{-1}$	-4.0	
$a_e(\text{Fe-N-C})/\text{deg}$	180.0	180.0	$\omega_e x_e(33) / \text{cm}^{-1}$	-3.7	
B_e / cm^{-1}	0.1425		$\omega_e x_e(12) / \text{cm}^{-1}$	-4.9	
$B_{0,\Omega=9/2} / \text{cm}^{-1}$	0.14278 ^b	0.14447(13)	$\omega_e x_e(13) / \text{cm}^{-1}$	-3.7	
$D_J * 10^8 / \text{cm}^{-1}$	4.83		$\omega_e x_e(23) / \text{cm}^{-1}$	8.6	
E_e / Eh	-1364.1941735		g_{22} / cm^{-1}	2.66	
$\alpha_1 / \text{cm}^{-1}$	0.00055		$\nu_1(\text{N-C}) / \text{cm}^{-1}$	2060	
$\alpha_2 / \text{cm}^{-1}$	-0.00147		$\nu_2(\text{Fe-N-C}) / \text{cm}^{-1}$	102	
$\alpha_3 / \text{cm}^{-1}$	0.00061		$\nu_3(\text{Fe-N}) / \text{cm}^{-1}$	475	464.1(42)
$\omega_1(\text{N-C}) / \text{cm}^{-1}$	2090		Zero-Point $E. / \text{cm}^{-1}$	1385	
$\omega_2(\text{Fe-N-C}) / \text{cm}^{-1}$	109		$\zeta_{12} / \text{cm}^{-1}$	-0.97	
$\omega_3(\text{Fe-N}) / \text{cm}^{-1}$	476		$\zeta_{23} / \text{cm}^{-1}$	-0.24	
$A_{\text{so}} / \text{cm}^{-1}$	-83		Λ -doubling/ cm^{-1}	0.00038	
[cf. FeF (${}^6\Delta_i$) -78.15] ^c					
μ_e / D	-4.59				
(Expec. Value -4.74)					

^a (LiF) Lie, *et al.* (2001).

^b Difference 1.2 %

^c Allen and Ziurys (1997)

C-N Bond length / Å

	FeNC	CoCN	NiCN
Obs. (r_o)	1.03(8) ^a	1.1313(10) ^b	1.1591(29) ^c 1.1590(1) ^d
Calc. (r_e)	1.182	1.168	1.166
Difference	-0.15	-0.037	-0.007

実験

FeNC

^a) (LIF) Lie and Dagdian (2001)

CoCN

^b) (MW) Sheridan and Ziurys (2004)

NiCN

^c) (LIF) Kingston, Merer, Varberg (2002)

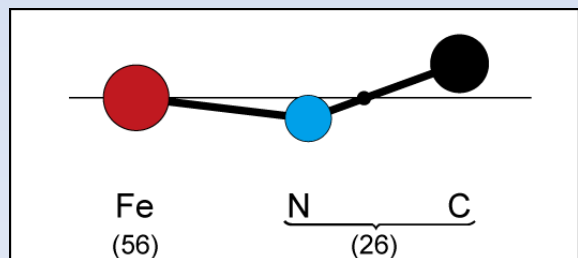
^d) (MW) Sheridan and Ziurys (2003)

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

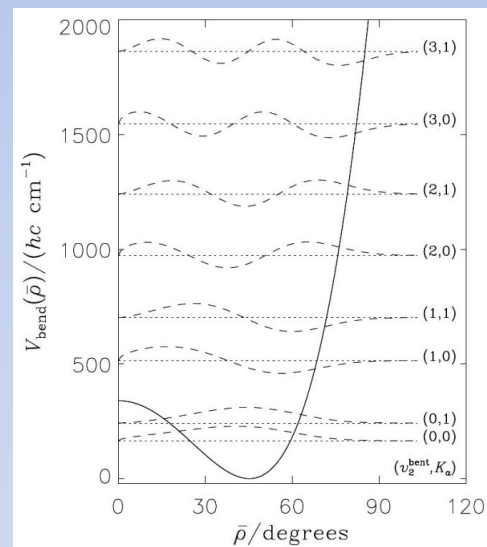
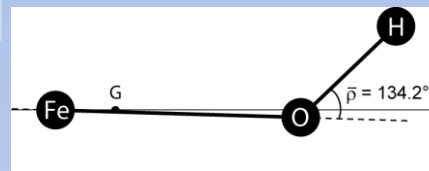
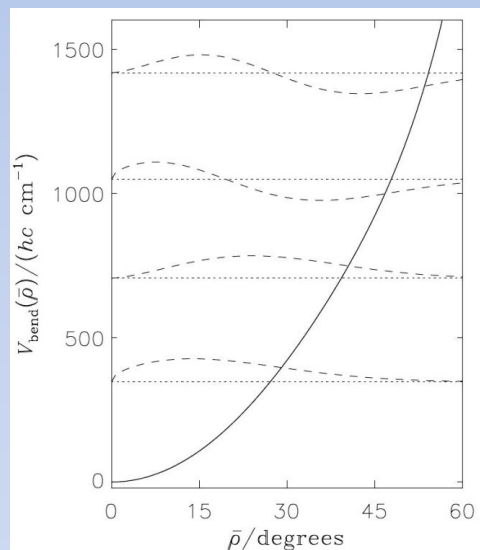


The transferred electron goes into $\sigma^*(CN)$ orbital $\rightarrow$ weaken the CN bond.
(i.e. lengthen the CN bond).

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



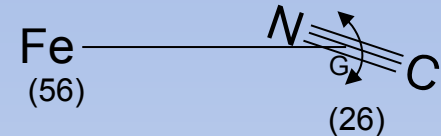
Linear ($^1\Sigma$ CsOH) vs. Quasi-linear ($^6\Delta$ FeOH)



			$\langle \bar{\rho} \rangle$ ($\delta \rho$)
Linear	$^3\Phi$ CoCN	8° (5°)	} $\gamma_0 \approx -1$
	$^2\Delta$ NiCN	9° (5°)	
	$^6\Delta$ FeCN	10° (5°)	
	$^6\Delta$ FeNC	13° (7°)	
	$^1\Sigma$ CsOH	17° (9°)	
Quasi-linear	$^6\Delta$ FeOH	39° (14°)	$\gamma_0 \approx 0.10$

$$\gamma_0 = 1 - 4 \times \frac{E(v_2 = |\ell_2| = 1) - E(0)}{E(v_2 = 2, |\ell_2| = 0) - E(0)}$$

Yamada-Winnewisser index
J. Mol. Struct. **798**, 1 (2006)



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 constants α_j .

Now, the turn is in the experimental side.

Explicit treatment of large amplitude bending motion is necessary.

Linear と Quasi-linear

1) $^1\Sigma$ CsOH (Linear)

a) D.R. Lide, Jr., and R.L. Kuczkowski, J. Chem. Phys., 46, 4768 (1967).

r_0 values obtained by extrapolating the bending mode to zero amplitude

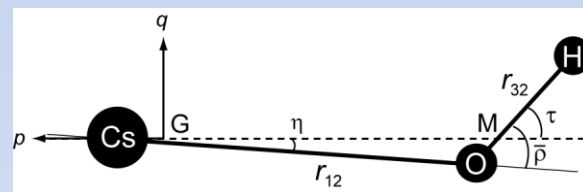
b) D.R. Lide, Jr., and C. Matsumura, J. Chem. Phys., 50, 3080 (1969).

r_e values

40 years later:

c) T. Hirano, V. Derpmann, U. Nagashima, P. Jensen (*J. Mol. Spectrosc.*, **263**, 150 (2010))

CCSD(T)_DK3 / [QZP Roos ANO-RCC (Cs, O, H)]

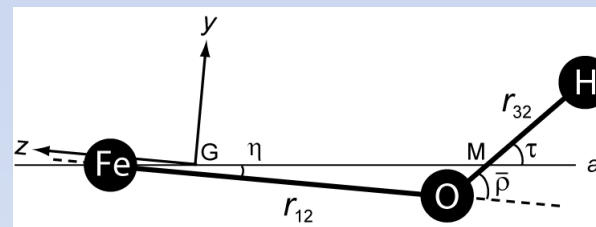
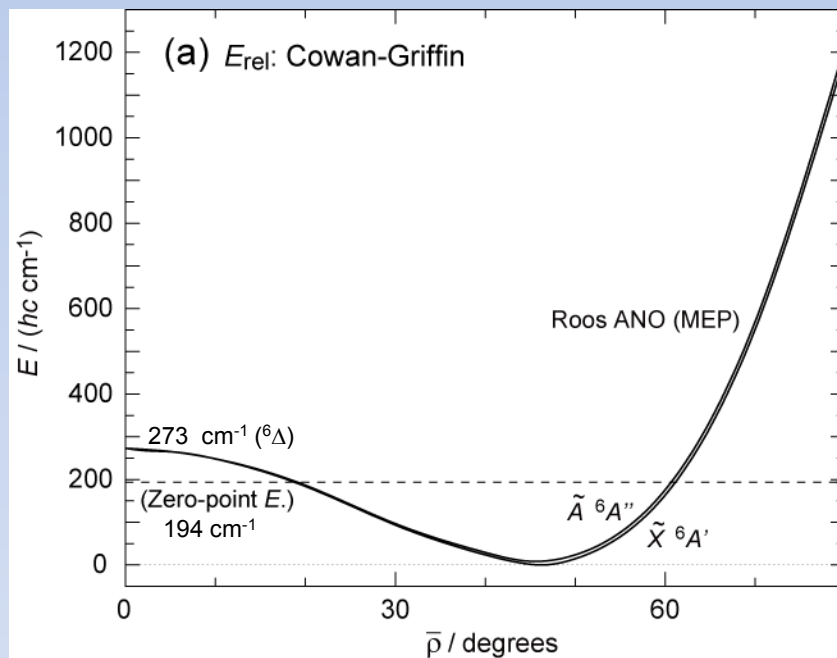


	$r_e(\text{Cs-O})$	$r_e(\text{O-H})$	$r_0(\text{Cs-O})$	$r_0(\text{O-H})$	$\langle \bar{\rho} \rangle (\delta \bar{\rho}) / \text{deg.}$
Lide et al ^{a)}	2.391(2) ^{b)}	0.960(10) ^{b)}	2.395	0.969	0.0
[Conventional method:			2.403	0.920	0.0]
CCSD(T)_DK3	2.4164	0.9575			0.0
MORBID			2.4231	0.9742	17 (9)
a -軸投影値			2.4227	0.9206	

2) ${}^6\Delta$ FeOH (quasi-linear)

No experiment

MR-SDCI+Q+ E_{rel} /[Rooa ANO (Fe),aVQZ(O, H)]



	$r_e(\text{Fe-O})$	$r_e(\text{O-H})$	$r_0(\text{Fe-O})$	$r_0(\text{O-H})$	$\langle \bar{\rho} \rangle (\delta \bar{\rho}) / \text{deg.}$
MR-SDCI+Q+ E_{rel} ${}^6A'$ (Δ)	1.8059	0.9520			45.8
MORBID			1.8049	0.9669	39 (14)
a-axis projection			1.8045	<u>0.7320</u>	

Bending Motion

- Bonding type

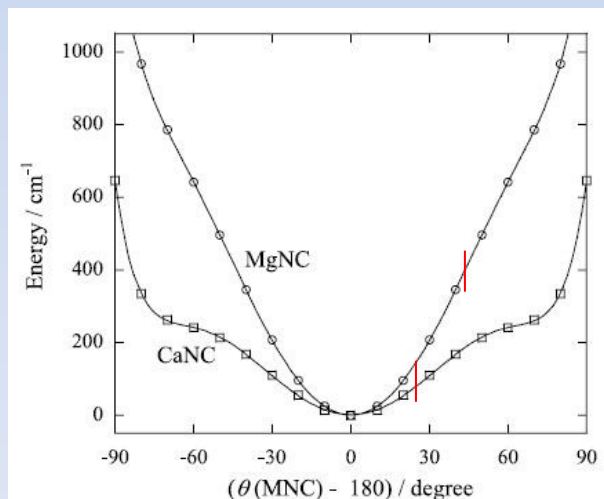
covalent bond: Small amplitude bending motion, and **normal**.

ionic bond: Large amplitude bending motion, but **normal**.

coordinate-covalent bond:

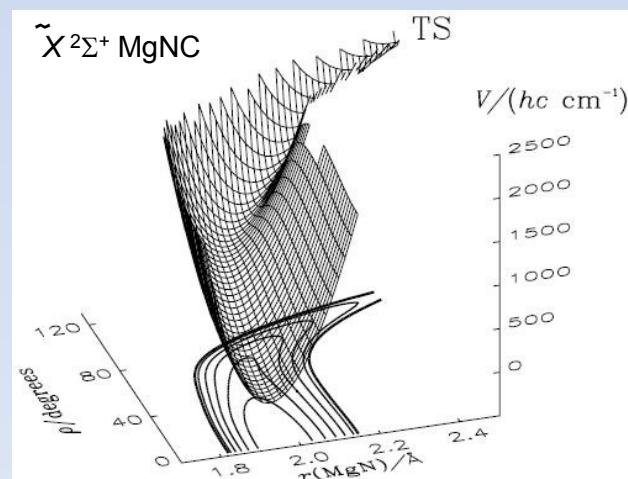
Large amplitude bending motion
with significant elongation with bending.

Ishii, Taketsugu, Hirano, CPL, **374**, 506 (2003)



Core-valence RCCSD(T)

Hirano, Ishii, Odaka, Jensen, JMS, **215**, 42 (2002)



Core-valence ACPF