Which do you believe in?

e.g. NiCN $r_0$(C-N)


Which is the more **accurate** and **physically meaningful** number?
Large Amplitude Bending Motion: Approach from Computational Molecular Spectroscopy

Ochanomizu Univ.*, AIST-Nanosystem**, Wuppertal Univ. (Germany) †

Tsuneo Hirano,* ** Umpei Nagashima,** Per Jensen †

T. Hirano  U. Nagashima  P. Jensen
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 \(\rightarrow\) 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:

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

Core-valence MR-SDCI/[\( \text{aCV}(Q+d)Z \) (S), \( \text{aCVQZ} \) (C,N)]

<table>
<thead>
<tr>
<th></th>
<th>( B_0/\text{MHz (Exp.: Amano et al(^a))} )</th>
<th>( B_0/\text{MHz (Calc.)} )</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>NC(^{32})S</td>
<td>6106.62195(16)</td>
<td>6106.47</td>
<td>-0.002%</td>
</tr>
<tr>
<td>NC(^{34})S</td>
<td>5962.857(52)</td>
<td>5962.77</td>
<td>-0.001%</td>
</tr>
</tbody>
</table>

\( B_e = 6108.9 \text{ MHz}, \quad D_J = 0.00171 \text{ MHz} \)
\( r_e(\text{N-C}) = 1.1777 \text{ Å}, \quad r_e(\text{C-S}) = 1.6338 \text{ Å} \)
\( \omega_1 = 1998 \text{ cm}^{-1}, \quad \omega_2 = 352 \text{ cm}^{-1}, \quad \omega_3 = 737 \text{ cm}^{-1} \)

Renner const \( \varepsilon = -0.158 \)
\( A_{SO} = -341 \text{ cm}^{-1} \)
\( \mu_e = 2.496 \text{ D} \quad \ldots \)
Molecular Spectroscopy is the most accurate science, backed with laser wavelength accuracy.

\[ r_0(\text{C≡N}) = 1.1590(2) \, \text{Å} \]


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≡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 $\text{C}≡\text{N}$ bond length

With Per Jensen (Wuppertal, Germany)
The effects of **large amplitude bending motion** gave rise to a **longstanding** debate:


\[ \text{OCCl}_2 \]
\[ \text{OCCl}_2 \]
\[ J. Mol. Struc., 320, 179 (1994) \]
\[ \text{OCS, etc.} \]


**Theory**
AlNC/AlCN, GaNC/GaCN, InNC/InCN

However, mostly forgotten in recent experimental studies.
**FeNC**

Exp. (LIF) Lie & Dagdigian (2001)

\[
B_0 = 0.1452 (2) \text{ cm}^{-1} \\
B_0 (^6\Delta_{9/2}) = 0.14447(13) \text{ cm}^{-1}
\]

2.01(5) Å  **1.03(8) Å**

**Fe ———— N ———— C**

Calc.

\[
\begin{align*}
1.935 \text{ Å} & \quad 1.182 \text{ Å} & \quad r_e \\
B_e &= 0.14250 \text{ cm}^{-1}, \quad B_0 = 0.14278 \text{ cm}^{-1}
\end{align*}
\]

N≡C ligand (triple bond)  →  Strong and of almost constant bond length:
Should be 1.16 ~ 1.19 Å  Strange!

Our calculation level: MR-SDCI+Q+E_{rel}  with error ±1 %
→  Again Strange!

**Fe···NC**  Ionic bond  →  Large amplitude bending motion

Experimental \( r_0(\text{C-N}) \) is too short!
\( \text{Fe}^{14}\text{N}^{12}\text{C} \ X^6\Delta \) linear equilibrium structure

Three dimensional PES was calculated at the MR–SDCI + \( Q + E_{\text{rel}} \) level.

Exp. \( \Delta B_0 = 0.1452 \pm 0.002 \) cm\(^{-1}\),

Perturbation \( \Delta B_0 = 0.1434 \) cm\(^{-1}\) (1.2% difference)

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

Averaged bond lengths in Å from the variational MORBID

\[
\begin{array}{cccccccc}
\nu_1, \nu_2, \nu_3 & < |r(\text{Fe-N})| > & < |r(\text{CN})| > & < r(\text{Fe-N}) \cos \eta > & < r(\text{CN}) \cos \tau > & < \rho > / \deg \\
\hline
(0, 0^0, 0) & 1.967 & 1.187 & 1.964 & 1.164 & 13(7) \\
(0, 1^0e,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) \\
\hline
\text{Equil. Struct. \( r_e \)} & 1.935 & 1.182 & & & 0 \\
\text{Exp. \( r_0 \)} & 2.01(5) & 1.03(8) & & & 0
\end{array}
\]

Similar calculations have been done for


In summary, …
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 !!!

### C-N Bond lengths

<table>
<thead>
<tr>
<th>C-N Bond length / Å</th>
<th>FeNC</th>
<th>FeCN</th>
<th>CoCN</th>
<th>NiCN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Obs. $(r_0)$</td>
<td>1.03(8)</td>
<td>?</td>
<td>1.131</td>
<td>1.159</td>
</tr>
<tr>
<td>Calc. $(r_e)$</td>
<td>1.182</td>
<td>1.168</td>
<td>1.168</td>
<td>1.166</td>
</tr>
<tr>
<td>$(r_0)$</td>
<td>1.187</td>
<td>1.172</td>
<td>1.172</td>
<td>1.171</td>
</tr>
<tr>
<td>Difference (%)</td>
<td>-0.15</td>
<td>?</td>
<td>-0.041</td>
<td>-0.012</td>
</tr>
</tbody>
</table>

Fe–N–C

---

C-N bond lengths

Fe

(56)

N

(26)

C

---

C-N bond lengths
Which do you believe in?

e.g. NiCN $r_0$(C-N)

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

Which is more accurate and more physically meaningful number?

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)

<table>
<thead>
<tr>
<th>Equilibrium structure</th>
<th>$\langle \tilde{\rho} \rangle$ ((\delta \tilde{\rho}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear</td>
<td>( ^3\Phi ) CoCN 8° (5°)</td>
</tr>
<tr>
<td></td>
<td>( ^2\Delta ) NiCN 9° (5°)</td>
</tr>
<tr>
<td></td>
<td>( ^6\Delta ) FeCN 10° (5°)</td>
</tr>
<tr>
<td></td>
<td>( ^6\Delta ) FeNC 13° (7°)</td>
</tr>
<tr>
<td></td>
<td>( ^1\Sigma ) CsOH 17° (9°)</td>
</tr>
</tbody>
</table>

\[ \gamma_0 \approx -1 \]

| Quasi-linear (45.8°) | \( ^6\Delta \) FeOH 39° (14°)  |

\[ \gamma_0 \approx 0.10 \]

| Bent (65.1°)         | \( ^2\Delta \) ZnOH 64° (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

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** \((2\Sigma^+ \text{CaNC}, 2\Sigma^+ \text{MgNC})\),
due to the increasing difficulty in transferring electron to the ligand.

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

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

\[ \tilde{\chi}^{3\Sigma^-} \text{(Low-spin): Coordinate-covalent bond} \]
\[ ^5\Sigma^- \text{(High-spin): Ionic bond} \]

Fe-CN

\[ ^4\Delta \text{(Low-spin): Coordinate-covalent bond} \]
\[ \tilde{\chi}^{6\Delta} \text{(High-spin): Ionic bond} \]
**FeCO: [Exp. and Perturbation] vs. [MORBID] ?**

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

<table>
<thead>
<tr>
<th></th>
<th>( ^3\Sigma^- ) (coordinate-covalent bond)</th>
<th>( ^5\Sigma^- ) (ionic bond)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MORBID</td>
<td>Perturb.</td>
</tr>
<tr>
<td>( B_0 ) / MHz</td>
<td>4381.5</td>
<td>4366.2</td>
</tr>
<tr>
<td>Error (%)</td>
<td>0.40</td>
<td>0.05</td>
</tr>
</tbody>
</table>

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.

| \( \alpha_1 \) / cm\(^{-1}\) | 0.000757 | 0.000747 | 0.000728\(^b\) | 0.000440 | 0.000693 |
| \( \alpha_2 \) / cm\(^{-1}\) | **0.000230** | **-0.000379** | **-0.000350**\(^b\) | -0.000157 | -0.000654 |
| \( \alpha_3 \) / cm\(^{-1}\) | 0.000627 | 0.000686 | 0.000674\(^b\) | 0.000244 | 0.000596 |

\( ^3\Sigma^- \): Why is the sign of \( \alpha_2 \) from MORBID different from those from Perturb. and Exp.?
Note that Perturb. and Exp. give quite similar values, while MORBID does not.
And, \( \alpha_2 \) 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 !**
MORBID $\alpha_2$: positive (0.000230) for $^3\Sigma^-$  \(\leftarrow\) uncommon feature
negative (-0.000157) for $^5\Sigma^-$  \(\leftarrow\) normal feature

Why?

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

<table>
<thead>
<tr>
<th>State</th>
<th>$f_{002}$ /aJ</th>
<th>$f_{102}$ /aJ Å$^{-1}$</th>
<th>Fe-C bond</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^3\Sigma^-$</td>
<td>0.362</td>
<td>-0.430</td>
<td>coordinate</td>
</tr>
<tr>
<td>$^5\Sigma^-$</td>
<td>0.180</td>
<td>-0.060</td>
<td>ionic</td>
</tr>
</tbody>
</table>

- 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.
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 $\sigma_{CO}$ orbital, resulting in the smaller overlap (i.e., weaker bond) between Fe 4s and $\sigma_{CO}$. (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.

<table>
<thead>
<tr>
<th></th>
<th>MORBID</th>
<th>Perturb</th>
<th>Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_1$, $\alpha_3$</td>
<td>similar</td>
<td>similar</td>
<td>similar</td>
</tr>
<tr>
<td>$\alpha_2$ (bending)</td>
<td>positive</td>
<td>negative</td>
<td>negative</td>
</tr>
<tr>
<td></td>
<td>$(0.000230)$</td>
<td>$(-0.000379)$</td>
<td>$(-0.000350)$</td>
</tr>
<tr>
<td>Region of PES employed</td>
<td>whole</td>
<td>near-equilibrium.</td>
<td>near-equilibrium</td>
</tr>
<tr>
<td>Fe-C elongation (bending)</td>
<td>$\bigcirc$</td>
<td>$\times$</td>
<td>$\times$</td>
</tr>
</tbody>
</table>

What to do?

Term value of rotation;

$$ F_v(J) = B_v (J(J+1) + l^2) - D_v (J(J+1) - l^2)^2 + \ldots $$  \hspace{1cm} (1)

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

Higher order expansion to include $f_{102}$;

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

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

$$ v_i + 1 \quad \text{(Bending)} $$

(Oka et al., 1944, 2012) \hspace{1cm} (3)
Thank you for your attention!
## Differences in MORBID, Perturb, and Exp.

<table>
<thead>
<tr>
<th></th>
<th>MORBID</th>
<th>Perturb</th>
<th>Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_1, \alpha_3$</td>
<td>similar</td>
<td>similar</td>
<td>similar</td>
</tr>
<tr>
<td>$\alpha_2$ (bending)</td>
<td>positive</td>
<td>negative</td>
<td>negative</td>
</tr>
<tr>
<td></td>
<td>(0.000230)</td>
<td>(-0.000379)</td>
<td>(-0.000350)</td>
</tr>
</tbody>
</table>

Region of PES employed

- whole
- near-equilibrium.
- near-equilibrium

Fe-C elongation (bending)

- ○
- X
- X

### What to do?

Term value of rotation:

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

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

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

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

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

When $B_v^{\text{obs}}$ (i.e., probably $= B_v^{\text{eq}}$) 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:
  \[
  \text{FeNC} \gg \text{CoCN} \approx \text{NiCN} \\
  (r_e(\text{C≡N})/\text{Å}) \quad 1.182 \quad 1.168 \quad 1.167
  \]

- Bending force constant (aJ⁻¹) from the 3-D PES
  \[
  \text{FeNC} \gg \text{CoCN} > \text{NiCN} \\
  0.036 \quad 0.151 \quad 0.180
  \]

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

Perturbational Method

<table>
<thead>
<tr>
<th></th>
<th>Calc.</th>
<th>Exp. $^6\Delta_i$ a)</th>
<th>Calc.</th>
<th>Exp. $^6\Delta_i$ a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r_e(\text{Fe-N})$ /Å</td>
<td>1.9354</td>
<td>2.01(5) ($r_0$)</td>
<td>$\omega_e x_e(11)$ /cm$^{-1}$</td>
<td>-11.8</td>
</tr>
<tr>
<td>$r_e(\text{N-C})$ /Å</td>
<td>1.1823</td>
<td>1.03(8) ($r_0$)</td>
<td>$\omega_e x_e(22)$ /cm$^{-1}$</td>
<td>-4.0</td>
</tr>
<tr>
<td>$a_e(\text{Fe-N-C})$/deg</td>
<td>180.0</td>
<td>180.0</td>
<td>$\omega_e x_e(33)$ /cm$^{-1}$</td>
<td>-3.7</td>
</tr>
<tr>
<td>$B_e$/cm$^{-1}$</td>
<td>0.1425</td>
<td></td>
<td>$\omega_e x_e(12)$ /cm$^{-1}$</td>
<td>-4.9</td>
</tr>
<tr>
<td>$B_{0,\Omega=9/2}$/cm$^{-1}$</td>
<td><strong>0.14278</strong> b</td>
<td><strong>0.14447(13)</strong></td>
<td>$\omega_e x_e(13)$ /cm$^{-1}$</td>
<td>-3.7</td>
</tr>
<tr>
<td>$D_{J} \times 10^8$/cm$^{-1}$</td>
<td>4.83</td>
<td></td>
<td>$\omega_e x_e(23)$ /cm$^{-1}$</td>
<td>8.6</td>
</tr>
<tr>
<td>$E_e$/Eh</td>
<td>-1364.1941735</td>
<td></td>
<td>$g_{22}$/cm$^{-1}$</td>
<td>2.66</td>
</tr>
<tr>
<td>$\alpha_1$/cm$^{-1}$</td>
<td>0.00055</td>
<td></td>
<td>$\nu_1(\text{N-C})$/cm$^{-1}$</td>
<td>2060</td>
</tr>
<tr>
<td>$\alpha_2$/cm$^{-1}$</td>
<td>-0.00147</td>
<td></td>
<td>$\nu_2(\text{Fe-N-C})$/cm$^{-1}$</td>
<td>102</td>
</tr>
<tr>
<td>$\alpha_3$/cm$^{-1}$</td>
<td>0.00061</td>
<td></td>
<td>$\nu_3(\text{Fe-N})$/cm$^{-1}$</td>
<td>475</td>
</tr>
<tr>
<td>$\omega_1(\text{N-C})$/cm$^{-1}$</td>
<td>2090</td>
<td></td>
<td><strong>Zero-Point E.</strong> /cm$^{-1}$</td>
<td>1385</td>
</tr>
<tr>
<td>$\omega_2(\text{Fe-N-C})$/cm$^{-1}$</td>
<td>109</td>
<td></td>
<td>$\zeta_{12}$/cm$^{-1}$</td>
<td>-0.97</td>
</tr>
<tr>
<td>$\omega_3(\text{Fe-N})$/cm$^{-1}$</td>
<td>476</td>
<td></td>
<td>$\zeta_{23}$/cm$^{-1}$</td>
<td>-0.24</td>
</tr>
<tr>
<td>$A_{so}$/cm$^{-1}$</td>
<td>-83</td>
<td></td>
<td>$\Delta$-doubling/cm$^{-1}$</td>
<td>0.00038</td>
</tr>
</tbody>
</table>

[c.f. FeF ($^6\Delta_i$) -78.15] c

$\mu_e$/D

(Expec. Value -4.74)

a (LiF) Lie, et al. (2001).  b Difference 1.2 %  c Allen and Ziurys (1997)
### C-N Bond length / Å

<table>
<thead>
<tr>
<th></th>
<th>FeNC</th>
<th>CoCN</th>
<th>NiCN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Obs. $r_0$</td>
<td>1.03(8)$^a$</td>
<td>1.1313(10)$^b$</td>
<td>1.1591(29)$^c$</td>
</tr>
<tr>
<td>Calc. $r_e$</td>
<td>1.182</td>
<td>1.168</td>
<td>1.166</td>
</tr>
<tr>
<td>Difference</td>
<td>-0.15</td>
<td>-0.037</td>
<td>-0.007</td>
</tr>
</tbody>
</table>

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

  $$M^{\delta^+} - (CN)^{\delta^-}$$

  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,

  Fe-NC > Co-CN > Ni-CN (from *ab initio* $r_e$)
Linear ($^1\Sigma$ CsOH) vs. Quasi-linear ($^6\Delta$ FeOH)

<table>
<thead>
<tr>
<th></th>
<th>$^3\Phi$ CoCN</th>
<th>$^2\Delta$ NiCN</th>
<th>$^6\Delta$ FeCN</th>
<th>$^6\Delta$ FeNC</th>
<th>$^1\Sigma$ CsOH</th>
<th>Quasi-linear $^6\Delta$ FeOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\langle \rho \rangle$</td>
<td>8° (5°)</td>
<td>9° (5°)</td>
<td>10° (5°)</td>
<td>13° (7°)</td>
<td>17° (9°)</td>
<td>39° (14°)</td>
</tr>
<tr>
<td>$\delta \rho$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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

Yamada-Winnewisser index


$\gamma_0 \approx -1$

$\gamma_0 \approx 0.10$
Why the Conventional method to derive $r_0$ value is inadequate?

Observe $B_0$’s for isotopomers

$\rightarrow$ derive $r_0$’s, assuming linear structure for the moment of inertia calc.

$\rightarrow$ 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 $<r(C-N) \cos \tau>_0$, since $B_0$’s for $^{58}$NiCN and $^{60}$NiCN are corrected for the rotation-vibration interaction constants $\alpha_i$.

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)

   $r_0$ values obtained by extrapolating the bending mode to zero amplitude

   $r_e$ 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)]

<table>
<thead>
<tr>
<th></th>
<th>$r_e$(Cs-O)</th>
<th>$r_e$(O-H)</th>
<th>$r_0$(Cs-O)</th>
<th>$r_0$(O-H)</th>
<th>$\bar{\rho}$(δρ)/deg.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lide et al$^a)$</td>
<td>2.391(2)$^b)$</td>
<td>0.960(10)$^b)$</td>
<td>2.395</td>
<td>0.969</td>
<td>0.0</td>
</tr>
<tr>
<td>[Conventional method:]</td>
<td></td>
<td></td>
<td>2.403</td>
<td>0.920</td>
<td>0.0</td>
</tr>
<tr>
<td>CCSD(T)_DK3</td>
<td>2.4164</td>
<td>0.9575</td>
<td></td>
<td></td>
<td>0.0</td>
</tr>
<tr>
<td>MORBID</td>
<td></td>
<td></td>
<td>2.4231</td>
<td>0.9742</td>
<td>17 (9)</td>
</tr>
<tr>
<td>$a$-軸投影値</td>
<td></td>
<td></td>
<td>2.4227</td>
<td>0.9206</td>
<td></td>
</tr>
</tbody>
</table>
2) $^6\Delta$ FeOH (quasi-linear)

No experiment

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

<table>
<thead>
<tr>
<th></th>
<th>$r_e$(Fe-O)</th>
<th>$r_e$(O-H)</th>
<th>$r_0$(Fe-O)</th>
<th>$r_0$(O-H)</th>
<th>$&lt;\bar{\rho}&gt;$(\delta\bar{\rho})/deg.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MR-SDCI+Q+$E_{\text{rel}}$ $^6A'$ ($\Delta$)</td>
<td>1.8059</td>
<td>0.9520</td>
<td></td>
<td></td>
<td>45.8</td>
</tr>
<tr>
<td>MORBID</td>
<td>1.8049</td>
<td>0.9669</td>
<td></td>
<td></td>
<td>39 (14)</td>
</tr>
<tr>
<td>a-axis projection</td>
<td>1.8045</td>
<td>0.7320</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
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.


Core-valence RCCSD(T)
Core-valence ACPF