Are Linear Molecules Really Linear?
I. Theoretical Predictions

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3D PES: Core-valence RCCSD(T)/aug-cc-pCV5Z
r_e(H-C) = 1.0915 Å, r_e(C-O) = 1.1057Å

B_0 = 44594.56 MHz   (DVR3D) 0.0003% error
(*cf*. Exp. 44594.4282 MHz)

$\Longrightarrow$ So, we have very accurate PESs (Potential Energy Surfaces)

Now, let's start the discussion
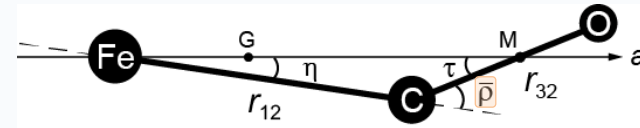on ro-vibrationally averaged structure of a linear molecule.

To be Linear or not to be, that is …

Linear molecule:

Definition:

A molecule which has PES minimum at the linear configuration !

Bending angle: supplement of bond-angle $\bar{\rho}$

What is the Ro-vibrationally averages structure of a linear molecule?

PES has minimum at the linear configuration.

$\Longrightarrow$ Max. Amplitude of bending wavefunction is at the linear configuration.
$\rightarrow$ Max. probability density is at the linear configuration.

$\Longrightarrow$ $\langle \bar{\rho} \rangle = 0$ ($\bar{\rho}$: Deviation angle from linearity)
This is Conventional Paradigm in molecular spectroscopy !!!

This is true in Nature (i.e., world of Schrödinger equation).

What will happen when we "observe" it ?

1) In 2006, we calculated *ab inito*,
$\langle \bar{\rho} \rangle$ = 13°   for (0,0^0,0) state of $^6\Delta$ FeNC . → bent structure

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

Note,
Expectation value is the theoretical observation of Nature.

However, conventional wisdom: r_0 structure has $\langle \bar{\rho} \rangle$ = 0,
since FeNC is a linear molecule.

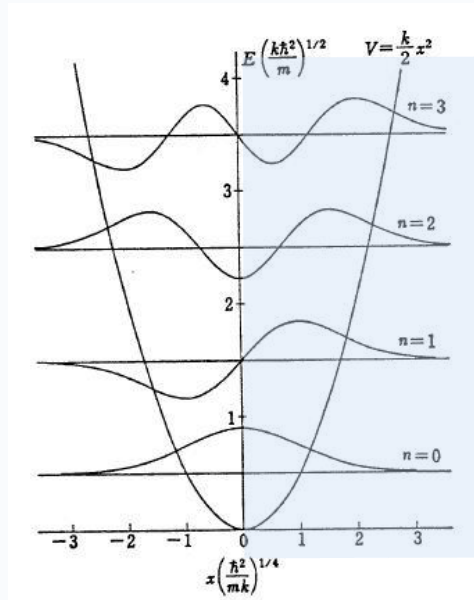2) In 2008, again, for (0,0^0,0) state of $^2\Delta$ NiCN,
$\langle \bar{\rho} \rangle$ = 9°.   (*J. Mol. Spectrosc.*, **236**, 234 (2006))
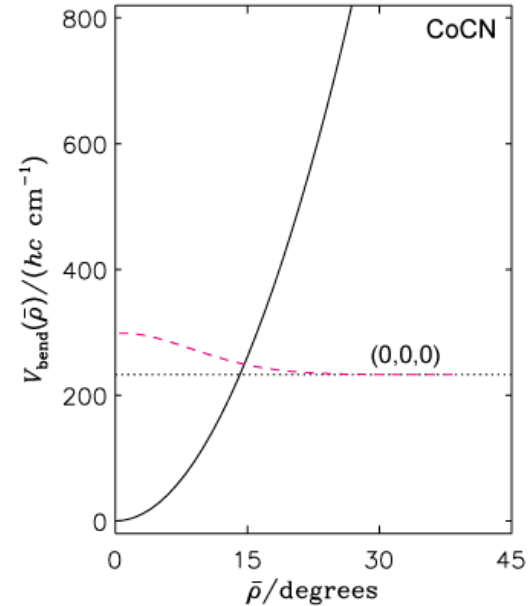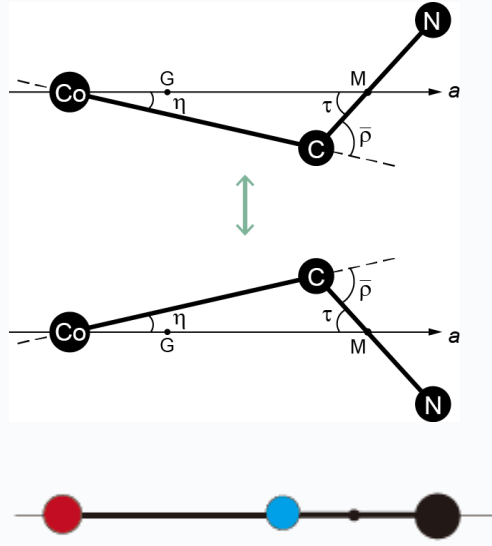
Why ?   We gave a short answer (2006):
- Bending motion is doubly degenerate ($3N$ – 5 vib. degrees of freedom),
  and so, should be described by a two-dimensional oscillator.
- We cannot separate bending motion
  from the rotation of the bending plane about the *a* axis.

- One-dimensional Harmonic Oscillator for bending:
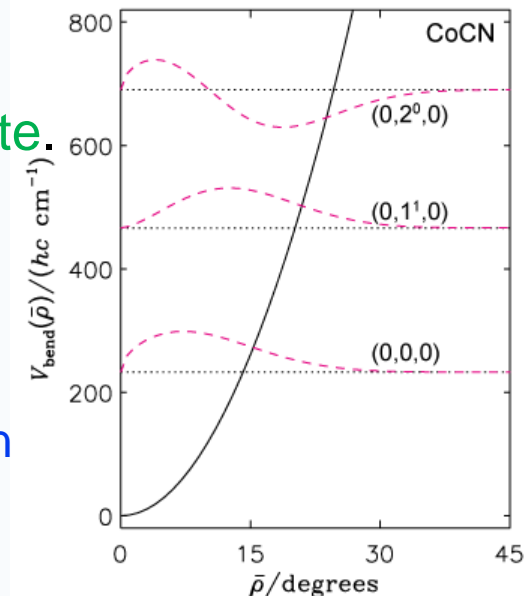   Maximum of wavefunction should be at the Origin. (imprinted in text-books)

That is true !

- However, bending motion has special features:
  1) linear molecule: bending motion is doubly degenerate.
     non-linear molecule: cannot be decoupled from rotation.
         ∴ 2-dimensional oscillator.
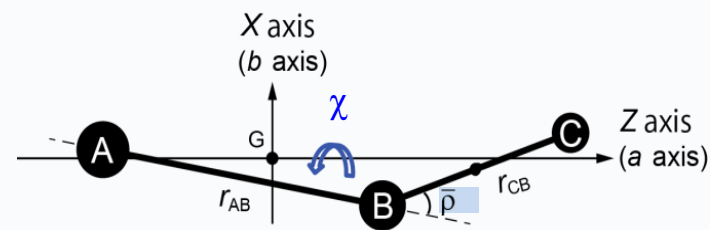 2) Only plus-value of $\bar{\rho}$ has meaning: $\bar{\rho} \geq 0$.
         We cannot fix a molecule in the space !!

⟹ Maximum of the wavefunction (in pink) is not at the origin
     in the plot for the bending angle.
         (One-dimensional expression)

2D-Oscillator (Bending mode)

$\bar{\rho}$ is the supplement of the bond-angle (as x-axis),
χ is the rotation angle about a-axis (as y-axis)

Bending wavefunction: a Laguerre-Gauss wavefunction (Boháček *et al.*, *CPL*, 1976)

$$\varphi_{v,\ell}(\bar{\rho}, \chi) = N \exp(i\ell\chi)\,\phi_{v,\ell}(\bar{\rho}), \qquad (0 \le \chi \le 2\pi,\ 0 \le \bar{\rho} < \pi). \qquad (1)$$

Normalization of eq. (1),

$$
\begin{aligned}
\langle \varphi_{v,\ell}(\bar{\rho}, \chi) | \varphi_{v,\ell}(\bar{\rho}, \chi) \rangle &= \iint |\varphi_{v,\ell}(\bar{\rho}, \chi)|^2\, \bar{\rho}\, d\bar{\rho}\, d\chi & (2) \\
&= \int_0^{2\pi} |\exp(i\ell\chi)|^2\, d\chi \int_0^{\pi} N^2\, \phi_{v,\ell}(\bar{\rho})^2\, \bar{\rho}\, d\bar{\rho} \\
&= \int_0^{\pi} 2\pi\, N^2\, \phi_{v,\ell}(\bar{\rho})^2\, \bar{\rho}\ d\bar{\rho} = 1\,.
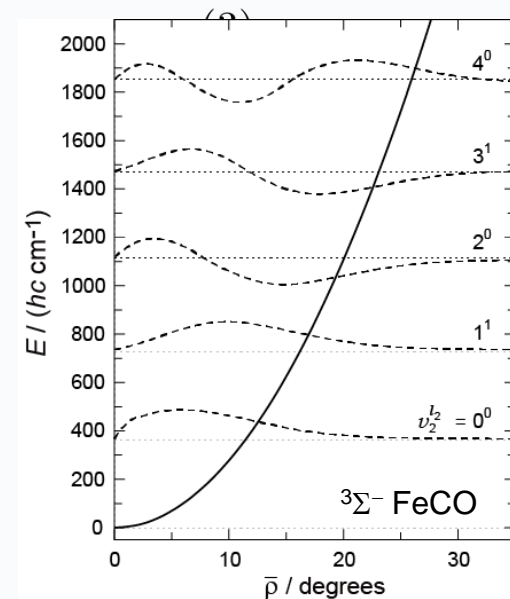\end{aligned}
$$

Thus, we get renormalized wavefunction:

$$\Phi_{v,\ell}(\bar{\rho}) = \sqrt{2\pi} N\, \phi_{v,\ell}(\bar{\rho})\, \sqrt{\bar{\rho}}\,, \qquad (0 \le \bar{\rho} < \pi)\,.$$

Expectation value $\langle \bar{\rho} \rangle$ using eq. (1) or eq. (4):

$$
\begin{aligned}
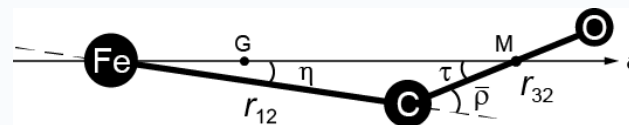\langle \bar{\rho} \rangle &= \langle \varphi_{v,\ell}(\bar{\rho}, \chi) | \bar{\rho} | \varphi_{v,\ell}(\bar{\rho}, \chi) \rangle = \langle \Phi_{v,\ell}(\bar{\rho}) | \bar{\rho} | \Phi_{v,\ell}(\bar{\rho}) \rangle \\
&= 2\pi\, N^2 \int_0^{\pi} \phi_{v,\ell}(\bar{\rho})^2\, \bar{\rho}^{\,2}\, d\bar{\rho}\,.
\end{aligned}
$$

Hence, for any bending states, $\langle \bar{\rho} \rangle > 0$.

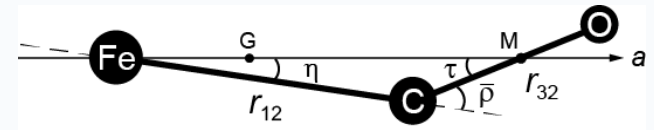# FeCO: Ro-vibrationally averaged structure in various states

Calc.: As an Expectation value of the wavefunction (DVR3D).

$(\nu_1, \nu_2^\ell, \nu_3)$	$\langle r_{Fe\text{-}C}\rangle$	$\langle r_{C\text{-}O}\rangle$	$\langle r_{Fe\text{-}C}\cos\eta\rangle$	$\langle r_{C\text{-}O}\cos\tau\rangle$	$\langle\bar\rho\rangle$ /deg [a]
$\tilde X\,^3\Sigma^-$ (eq.)	1.7247	1.1587			
$(0, 0^0, 0)$	1.7303	1.1631	1.7292	1.1581	**7.4**(3.6)
$(0, 1^{1e,f}, 0)$	1.7319	1.1635	1.7295	1.1524	11.0(3.8)
$(0, 2^0, 0)$	1.7328	1.1639	1.7295	1.1486	12.9(5.9)
$(0, 3^{1e,f}, 0)$	1.7348	1.1643	1.7303	1.1431	15.1(6.3)
$(1, 0^0, 0)$	1.7313	1.1717	1.7302	1.1666	7.4(3.6)
$(0, 0^0, 1)$	1.7391	1.1629	1.7379	1.1576	7.5(3.7)
$\tilde a\,^5\Sigma^-$ (eq.)	1.8429	1.1522			
$(0, 0^0, 0)$	1.8471	1.1568	1.8457	1.1497	8.6(4.3)
$(0, 1^{1e,f}, 0)$	1.8476	1.1574	1.8444	1.1417	12.8(4.5)
$(0, 2^0, 0)$	1.8495	1.1574	1.8464	1.1421	12.7(7.1)
$(0, 3^{1e,f}, 0)$	1.8509	1.1579	1.8461	1.1345	15.6(7.1)
$(1, 0^0, 0)$	1.8485	1.1652	1.8470	1.1580	8.7(4.4)
$(0, 0^0, 1)$	1.8509	1.1571	1.8486	1.1457	10.9(6.1)

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

Equil. struct	r_0 struct.	$\langle\bar\rho\rangle$ ($\delta\bar\rho$)
Linear	$^1\Sigma$ CO_2	7° (3°)
	$^3\Sigma^-$ FeCO	7° (4°)
	$^2\Pi$ NCS	8° (4°)
	$^2\Pi$ NiCN	8° (2°)
	$^2\Delta$ $BrCN^+$	8° (4°)
	$^3\Phi$ CoCN	8° (5°)
	$^2\Delta$ NiCN	9° (5°)
	$^6\Delta$ FeCN	10° (5°)
	$^1\Sigma$ HCN	12° (6°)
	$^6\Delta$ FeNC	13° (7°)
	$^1\Sigma$ CsOH	17° (9°)
	$^1\Sigma$ C_3	20° (10°)

$\gamma_0 \approx -1$

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

Yamada-Winnewisser index
Z. Naturforsch., **31a**, 139 (1976);
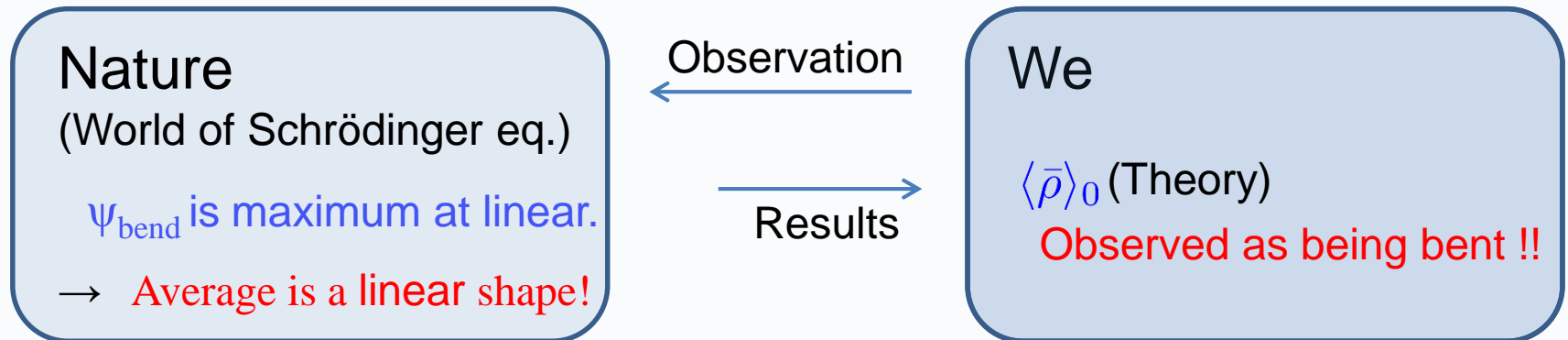*J. Mol. Struct.* **798**, 1 (2006)

Conclusion:

Man recognizes Nature by Observation (quantum mechanics).

When we observe Nature through expectation value (theoretical observation), a linear molecule is observed as being bent on ro-vibrational average.

i.e., $\langle\bar\rho\rangle > 0$, against the conventional paradigm $\langle\bar\rho\rangle = 0$.

To avoid misunderstanding;

What is the averaged zero-point structure of a linear molecule ??

Nature
(World of Schrödinger eq.)

ψ_{bend} is maximum at linear.

→ Average is a linear shape!

← Observation

Results →

We

$\langle \bar{\rho} \rangle_0$ (Theory)

Observed as being bent !!

Why?   Because of double degeneracy of bending motion of a linear molecule.

E.g.: 1*s* orbital of H atom

Max. on the nucleus

Theoretical observation

←

→

Electron Density:
  Max. at Bohr radius.

Boháček *et al. ,* presented a Laguerre-Gauss 2D bending wavefunction in 1976.

Then, it is an easy task for a theoretician to calculate $\langle \bar{\rho} \rangle$ value.

However, nobody would have paid attention to $\langle \bar{\rho} \rangle$ until we did in 2006.

30 years later since that time !!!

For a linear molecule,
we need a paradigm shift from $\langle \bar{\rho} \rangle = 0$ to $\langle \bar{\rho} \rangle > 0$!!!

Thanks to,

    Keiichi Tanaka (Kyusyu Univ.)
    Kensuke Harada (Kyusyu Univ.)
    Koichi M. Yamada (AIST)
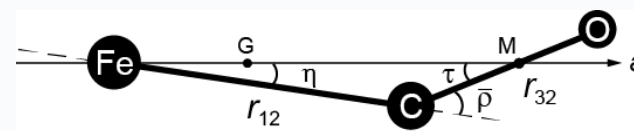   Kentaro Kawaguchi (Okayama Univ.)

    And, especially to,
      An anonymous Professor (?? Univ.)

E pur la terra si muove !

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	$^1\Sigma$	HCN	12° (6°)
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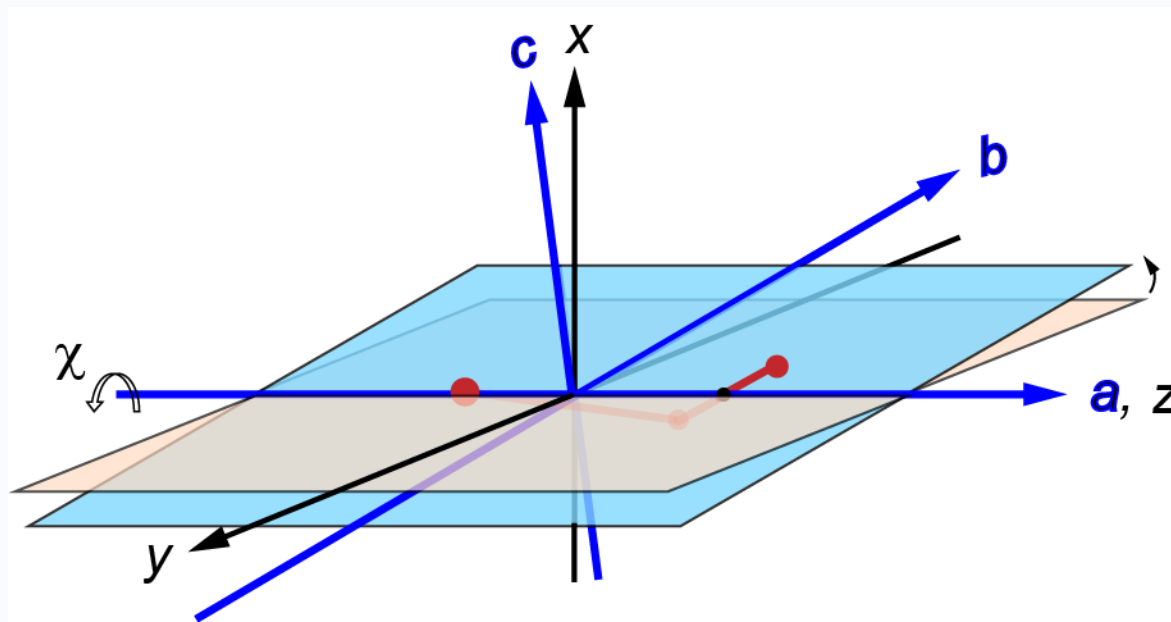Man recognizes Nature by Observation (quantum mechanics).

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i.e., $\langle\bar{\rho}\rangle > 0$, against the conventional paradigm $\langle\bar{\rho}\rangle = 0$.

In the case of linear molecule, always $(B+C)/2$ is observed
due to the double degeneracy.

 Even $\langle\bar{\rho}\rangle_0 > 0$, rotational constants B and C are never observed
as separate values.
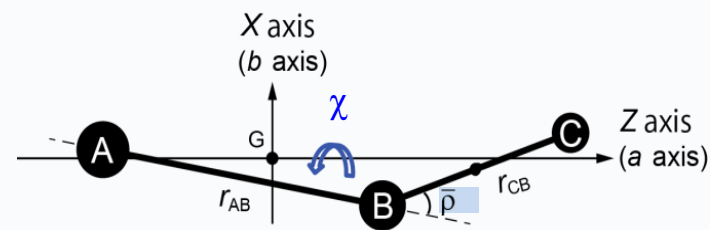

Instantaneous
bending plane

If rotation about the a-axis does not occur (*i.e.* if there is no double-degeneracy
in the bending vibration), the spectrum pattern would become asymmetric top.
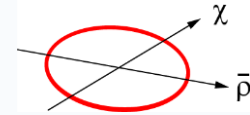 However, ….

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&= \int_0^{\pi} 2\pi\,N^2\,\phi_{v,\ell}(\bar{\rho})^2\,\bar{\rho}\ d\bar{\rho} = 1. &(3)
\end{aligned}
$$

Thus, we get renormalized wavefunction:

$$\Phi_{v,\ell}(\bar{\rho}) = \sqrt{2\pi}N\,\phi_{v,\ell}(\bar{\rho})\,\sqrt{\bar{\rho}}, \qquad (0 \le \bar{\rho} < \pi).$$

Expectation value $\langle\bar{\rho}\rangle$ using eq. (1) or eq. (4):

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\langle\bar{\rho}\rangle &= \langle\varphi_{v,\ell}(\bar{\rho},\chi)|\bar{\rho}|\varphi_{v,\ell}(\bar{\rho},\chi)\rangle = \langle\Phi_{v,\ell}(\bar{\rho})|\bar{\rho}|\Phi_{v,\ell}(\bar{\rho})\rangle\\
&= 2\pi\,N^2 \int_0^{\pi} \phi_{v,\ell}(\bar{\rho})^2\,\bar{\rho}^{\,2}\ d\bar{\rho}.
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$$

Hence, for any bending states, $\langle\bar{\rho}\rangle > 0$.