WG13

Large Amplitude Bending Motion: Computational Molecular Spectroscopy and Experiments of Transition-Metal Containing Isocyanide and Cyanides.

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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) **Theory**
K.A. Walker, et al., *J. Mol. Spec*., **209**, 178 (2001) **AlNC/AlCN, GaNC/GaCN, InNC/InCN**

However, mostly forgotten in recent experimental studies.

FeNC

Exp. (LIF) Lie & Dagdian (2001)

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

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

2.01(5) Å **1.03(8) Å**

Fe ---------- N ----- C

Calc. 1.935 Å **1.182** Å r_e

B_e= 0.14251 cm^{-1}, B_0 = 0.14341 cm^{-1}

CoCN

Exp. (MW) Sheridan and Ziurys (2004)

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

1.88270 Å **1.13133** Å

Co --------- C ----- N

Calc. 1.854 Å **1.168** Å r_e

B_e= 4209.9 MHz, $B_0(^3\Phi_4)$ = 4229.1 MHz

NiCN

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

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

(MW) Sheridan, Ziurys (2003)

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

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

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

Ni --------- C ------ N

Calc. 1.8141 Å **1.1665** Å r_e

B_e = 0.14552 cm^{-1}, $B_0(^2\Delta_{5/2})$ = 0.14559 cm^{-1}

However, **Difference in B_0 is small**:

$FeNC_{calc}$	-1.2 %
$CoCN_{calc}$	0.5 %
$NiCN_{calc}$	0.8 %

C-N Bond length / Å

	FeNC	CoCN	NiCN
Obs. (r_0)	1.03(8)	1.131	1.159
Calc. (r_e)	1.182	1.168	1.167
Difference/Å	-0.15 (13%)	-0.037	-0.008

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

cf. Exp.
r_0(NC): MgNC 1.169 Å
AlNC 1.171 Å
CN 1.172 Å

cf. Calc. (Hirano, *et al*. JMS, 2002)
r_e(NC) MgNC 1.1814 Å

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

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

  The transferred electron goes into σ^*(CN) orbital → weakens the CN bond.
  (*i.e*. lengthens this bond).

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

  Fe-NC > Co-CN > Ni-CN (from *ab initio* r_e)

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

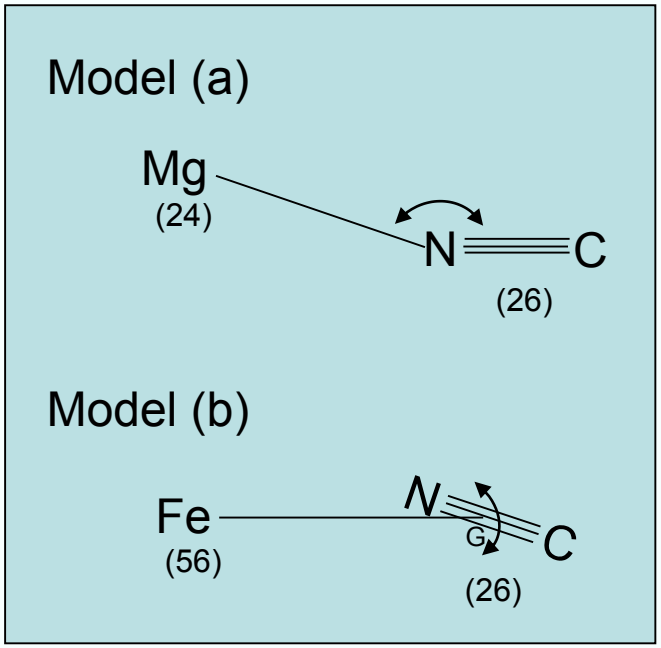
  Fe-NC > Co-CN > Ni-CN ,

  since the more ionic, the more floppy.

Now, we know Ionicity and, hence, floppiness:

Fe-NC > Co-CN > Ni-CN

r_0(Obs.): (1.03) (1.131) (1.159)



The more floppy, the shorter the CN bond length projected to the molecular axis becomes.

To go further, we need the knowledge of the
Three-dimensional Potential Energy Surfaces.

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

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]
r_e(Fe-N) /Å	1.9354	2.01(5) (r_0)
r_e(N-C) /Å	**1.1823**	**1.03(8)** (r_0)
a_e(Fe-N-C)/deg	180.0	180.0
B_e /cm^{-1}	0.1425	
$B_{0,\Omega=9/2}$ /cm^{-1}	**0.14278**[b]	**0.14447(13)**
D_J * 10^8/ cm^{-1}	4.83	
E_e /Eh	-1364.1941735	
α_1 / cm^{-1}	0.00055	
α_2 / cm^{-1}	-0.00147	
α_3 / cm^{-1}	0.00061	
ω_1(N-C) /cm^{-1}	2090	
ω_2(Fe-N-C) /cm^{-1}	109	
ω_3(Fe-N) /cm^{-1}	476	
A_{so} /cm^{-1}	-83	
[*cf.* FeF ($^6\Delta_i$) -78.15][c]		
μ_e /D	-4.59	
(Expec. Value	-4.74)	

	Calc.	Exp. $^6\Delta_i$ [a]
$\omega_e x_e$(11) /cm^{-1}	-11.8	
$\omega_e x_e$ (22) /cm^{-1}	-4.0	
$\omega_e x_e$ (33) /cm^{-1}	-3.7	
$\omega_e x_e$(12) /cm^{-1}	-4.9	
$\omega_e x_e$ (13) /cm^{-1}	-3.7	
$\omega_e x_e$ (23) /cm^{-1}	8.6	
g_{22} /cm^{-1}	2.66	
ν_1(N-C) /cm^{-1}	2060	
ν_2 (Fe-N-C) /cm^{-1}	102	
ν_3(Fe-N) /cm^{-1}	475	464.1(42)
Zero-Point *E*. /cm^{-1}	1385	
ζ_{12}/cm^{-1}	-0.97	
ζ_{23}/cm^{-1}	-0.24	
Λ-doubling/cm^{-1}	0.00038	

[a] (LiF) Lie, *et al.* (2001). [b] **Difference 1.2 %** [c] Allen and Ziurys (1997)

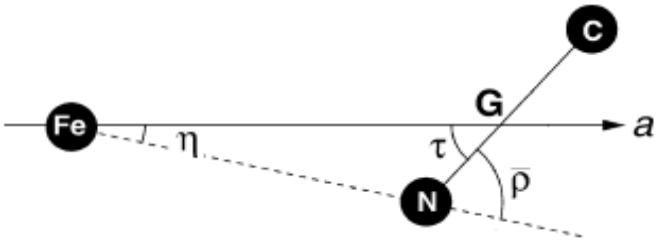
Expectation values from MORBID analysis: FeNC

(v_1, v_2^{l2}, v_3)	$\langle r$(Fe-N)$\rangle$/Å	$\langle r$(N-C)$\rangle$/Å	$\langle r$(Fe-N) cos(η)$\rangle$/Å	$\langle r$(N-C) cos(τ)$\rangle$/Å	$\langle\bar{\rho}\rangle$/degree
$(0,0^0,0)$	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)
cf.					
Equil. Struct.	1.935	1.182			0.0
Exp. r_0 (Lie *et al.*, 2001)	2.01(5)	1.03(8)			0.0

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

Exp. model is inadequate !!

Explicit treatment of large amplitude bending motion is necessary.



CoCN $X\,^3\Phi$ MR-SDCI+Q+E_{rel} , **Perturbation method**

	Calc.	Exp. $^3\Phi_4$ [a]
r_e(Co-C) /Å	1.8541	1.8827(7) (r_0)
r_e(C-N) /Å	**1.1677**	**1.1313(10)**(r_0)
a_e(Co-C-N)/deg	180.0	180.0
B_e /MHz	4209.9	
B_0 /MHz	**4234.8**[b]	**4208.827(23)**
D_J /MHz	0.00108	0.001451(10)
E_e /Eh	-1484.7591917	
α_1 /MHz	10.5	
α_2 /MHz	-24.7	
α_3 /MHz	-12.1	
ω_1(C-N) /cm^{-1}	2191	
ω_2(Co-C-N) /cm^{-1}	238	
ω_3(Co-C) /cm^{-1}	542	
A_{so} /cm^{-1}	**-242**	**-133.3** (assumed)
[*cf.* CoH ($^3\Phi$) -242.7][c]		
μ_e /D	-6.993	
(Expec. Value	-7.464)	

	Calc.	Exp. $^3\Phi_4$ [a]
$\omega_e x_e$(11) /cm^{-1}	-10.9	
$\omega_e x_e$ (22) /cm^{-1}	-7.7	
$\omega_e x_e$ (33) /cm^{-1}	-2.2	
$\omega_e x_e$(12) /cm^{-1}	-3.4	
$\omega_e x_e$ (13) /cm^{-1}	-4.4	
$\omega_e x_e$ (23) /cm^{-1}	35.6	
g_{22} /cm^{-1}	8.0	
ν_1(C-N) /cm^{-1}	2163	
ν_2 (Co-C-N) /cm^{-1}	239	
ν_3(Co-C) /cm^{-1}	571	~478 (?)
Zero-Point *E*. /cm^{-1}	1608	
ζ_{12}/cm^{-1}	-0.98	
ζ_{23}/cm^{-1}	-0.22	
Λ-doubling/cm^{-1}	0.00018	

[a] (MW) Sheridan, *et al.* (2004). [b] **Difference 0.6 %** [c] Varberg, *et al.* (1989)

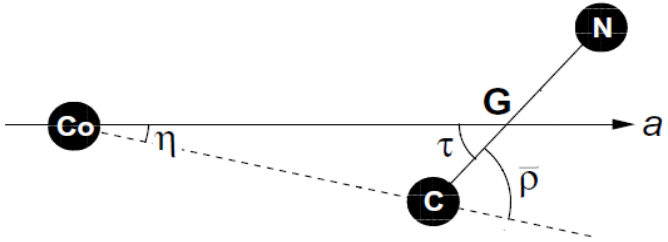
Expectation values from MORBID analysis: CoCN

(v_1, v_2^{l2}, v_3)	<r(Co-C)>/ Å	<r(C-N)>/ Å	<r(C-N) cos(τ)>/Å	<$\bar{\rho}$> / deg.
$(0,0^0,0)$	1.873	1.172	1.161	8(5)
$(0,1^{1e,f},0)$	1.877	1.173	1.152	13(5)
$(0,2^0,0)$	1.873	1.173	1.141	15(8)
$(1,0^0,0)$	1.874	1.180	1.164	8(5)
$(0,0^0,1)$	1.882	1.172	1.161	8(5)
cf.				
Equil. Struct.	1.854	1.168		0.0
Exp. $R_{0,\Omega=4}$ (Sheridan, et al., 2004)	1.8827(7)	1.1313(10)		0.0

- The <r(C-N)>, ~1.172 Å, a little longer than r_e(C-N), does not change unless the C-N bond is excited. → Physically meaningful, proper quantity.
- Exp. r_0 is not the averaged projection onto *a*-axis. → No physical meaning!

Exp. model is inadequate !!

Explicit treatment of large amplitude bending motion is necessary.



^{58}NiCN $X\,^2\Delta_i$ MR-SDCI+Q+E_{rel}, **Perturbation method**

	Calc.	Exp.
r_e(Ni-C) /Å	1.8141	1.8292(28) (r_0) [a]
		1.8293(1) (r_0)[b]
r_e(C-N) /Å	**1.1665**	**1.1591(29)** (r_0)[a]
		1.1590(2) (r_0)[b]
a_e(Co-C-N)/deg	180.0	180.0
B_e /cm^{-1}	0.14552	0.143681446(40)[b]
B_0 /cm^{-1}	0.14567	0.144638234(56)[b]
$B_{0,\Omega=5/2}$/cm^{-1}	**0.14559**[c]	**0.144443511(53)**[b]
D_J /cm^{-1}	4.49 x10^{-8}	4.99 x10^{-8} [a]
E_e /Eh	-1612.0269135	
α_1 /cm^{-1}	0.00052	
α_2 /cm^{-1}	-0.00072	-0.000712 [a]
		-0.00074636(4)[b]
α_3 /cm^{-1}	0.00060	
ω_1(C-N) /cm^{-1}	2199	
ω_2(Ni-C-N) /cm^{-1}	254	
ω_3(Ni-C) /cm^{-1}	511	

	Calc.	Exp.
$\omega_e x_e$(11) /cm^{-1}	-17.8	
$\omega_e x_e$ (22) /cm^{-1}	-96.3	
$\omega_e x_e$ (33) /cm^{-1}	0.1	
$\omega_e x_e$(12) /cm^{-1}	-4.2	
$\omega_e x_e$ (13) /cm^{-1}	3.6	
$\omega_e x_e$ (23) /cm^{-1}	383.7	
g_{22} /cm^{-1}	96.4	
ν_1(C-N) /cm^{-1}	2161	F.C. inactive[a]
ν_2 (Ni-C-N) /cm^{-1}	251	246.1(16)[a]
ν_3(Ni-C) /cm^{-1}	897	501.8(29)[a]
Zero-Point *E*. /cm^{-1}	1699	
ζ_{12}/cm^{-1}	-0.97	
ζ_{23}/cm^{-1}	-0.23	
Λ-doubling/cm^{-1}	0.00018	
A_{so} /cm^{-1}	**-613**	**-415.0(ass.)**[b]
μ_e /D	-7.23	
(Expect. value: -7.56)		
ε (Renner const.)	0.050	

[a] (LIF) Kingston, et al. (2002). [b] (MW) Sheridan, *et al.* (2003). [c] **Difference 0.8 %**

Expectation values from MORBID analysis: ^{58}NiCN

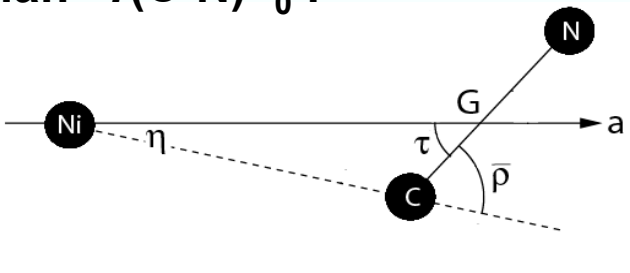
$(v_1, v_2^{l\,2}, v_3)$	<r(Ni-C)> / Å	<r(C-N)> / Å	<r(Ni-C) cos(η)> / Å	<r(C-N) cos(τ)> / Å	<$\bar{\rho}$> / degrees
$(0,0^0,0)$	1.842	1.171	1.839	1.160	9(5)
$(0,1^0,0)$	1.849	1.171	1.845	1.153	13(5)
$(0,2^0,0)$	1.846	1.171	1.841	1.145	15(8)
$(0,0^0,1)$	1.849	1.171	1.846	1.158	
$(1,0^0,0)$	1.844	1.178	1.841	1.168	
cf.					
Equil. Struct.	1.814	1.167			0.0
Exp. $r_{0,\Omega=5/2}$ (Sheridan, et al., 2003)	1.8293(1)	1.1590(2)			0.0

- The <r(C-N)>, ~1.171 Å, a little longer than r_e(C-N), does not change unless the C-N bond is excited. → Physically meaningful, proper quantity.

Again, experimental r_0(C-N) is much smaller than <r(C-N)>$_0$!

Exp. model is inadequate !!

Explicit treatment of large amplitude bending motion is necessary.



Now we can make quantitative arguments….

i) *Floppiness* in bending motion

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

FeNC >> CoCN ≈ NiCN

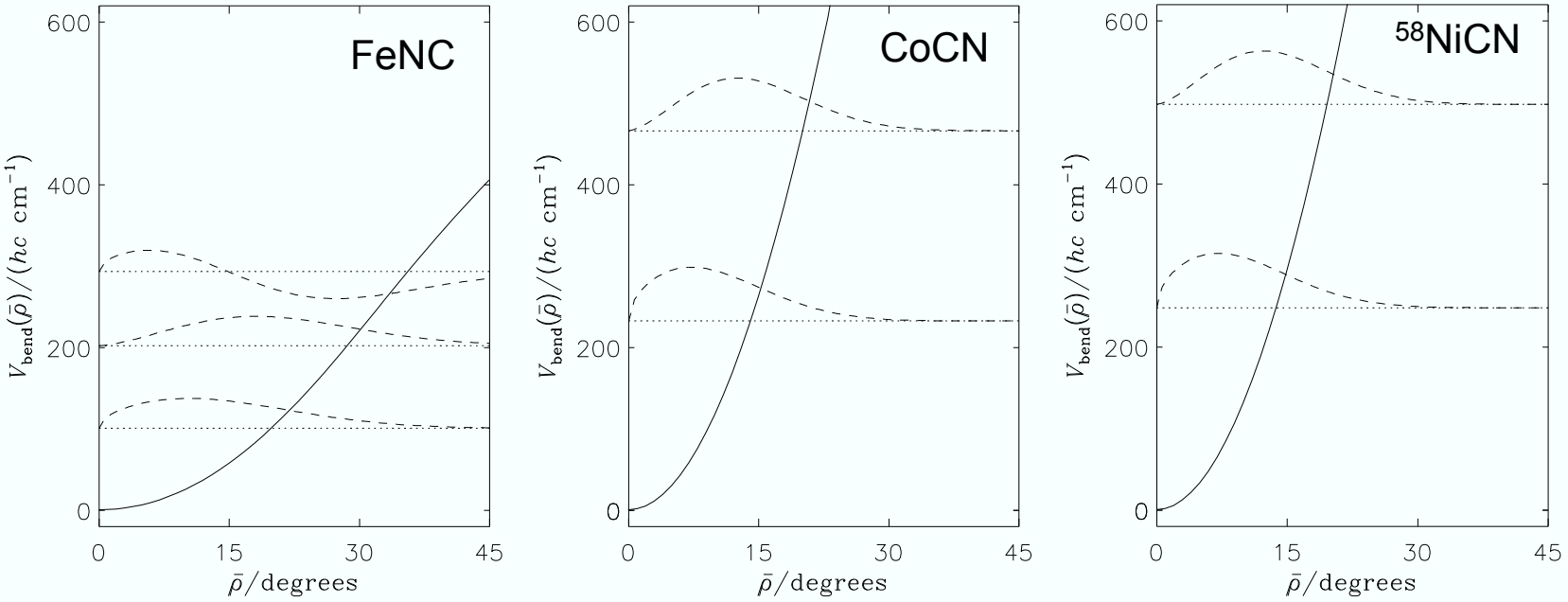
(r_e / Å) **1.182 1.168 1.167**

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

FeNC >> CoCN > NiCN ***cf.*** **FeCO**

0.036 0.151 0.180 0.364

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



ii) CN bond lengths: MORBID Expectation value

Ro-vibrationally averaged MORBID structure

	FeNC	CoCN	NiCN
r_e(C-N) /Å	**1.182**	**1.168**	**1.166**
r_0(C-N) /Å	**1.187**	**1.172**	**1.171**
$\langle \bar{\rho} \rangle$ / deg.	**13(7)**	**8(5)**	**9(5)**

- **Both r_e(C-N) and r_e(C-N) fall inside of the normal C-N bond length 1.16-1.19 Å.**

- 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.

Summary: Too-short CN bond lengths

C-N Bond length / Å

	FeNC	CoCN	NiCN
Obs. (r_0)	**1.03(8)**	**1.131**	**1.159**
Calc. (r_e)	1.182	1.168	1.166
(r_0)	**1.187**	**1.172**	**1.171**
Difference	-0.157	-0.041	-0.012
in r_0 (%)	**-13.2**	**-3.5**	**-1.0**

Then, **WHAT** does the experimentally derived r_0 values mean ?
No physical meaning !!!

- The difference between experimental and predicted values indicates the ***existence of large-amplitude bending motion***.
- **Conventional method to derive r_0 value is inadequate** for these molecules showing large-amplitude bending motion,

Why the Conventional method to derive r_0 value is inadequate ?

Observe B_0's for isotopologues.

→ derive r_0's, assuming linear structure in the moment of inertia calcs.

→ interpret the thus derived r_0's as the projection average onto the *a*-axis in the bending motion, because B_0's are employed.

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

Now, the turn is in the experimental side.

Explicit treatment of large amplitude bending motion is necessary.

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References;

FeNC: T. Hirano, R. Okuda, U. Ngashima, V. Špirko, P. Jensen, *J. Mol. Spectrosc*., **236** (2006) 234-247

CoCN: T. Hirano, R. Okuda, U. Nagashima, P. Jensen, *Mol. Phys*. **105** (2007) 599-611.

NiCN: T. Hirano, R. Okuda, U. Nagashima, P. Jensen, *Chem. Phys*., **346** (2008) 13-12.

Every linear poly-atomic (more than diatomic) molecule is *bent*, even when the equilibrium structure is *linear*.

Suppose the rovibronic wavefucntion be described by a **two**-dimensional harmonic-oscillator in bending and rotational normal coordinates, q_a and q_b.

When decoupled from rotation about the molecular axis, the averaged angle for bending motion becomes as

$$\langle \bar{\rho} \rangle \approx \langle \sqrt{q_a^2 + q_b^2} \ \rangle > 0 ,$$

$\langle \bar{\rho} \rangle$ is the bond angle supplement.