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Ro-vibrationally averaged structure of $^2\Pi$ NCS: Re-interpretation of the B_0 values

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$\tilde{X}\ ^2\Pi$ NCS

In 2003, ISMS 2003, Ohio

- Maeda, Habara, Amano, reported B_0 values (Submilli.-wave). RG05
- Hirano, Nagashima, Jensen,
  2D PES (Core-valence MR-SDCI/[aCV(Q+d)Z (S), aCVQZ (C,N)]). RG02

	B_0/MHz (Exp.: Amano et al)	B_0/MHz (Calc.)	Difference
$NC^{32}S$	6106.62195(16)	6106.47	-0.002%
$NC^{34}S$	5962.857(52)	5962.77	-0.001%

⇨

B_e = 6108.9 MHz, D_J = 0.00171 MHz

r_e(N-C) = 1.1777 Å, r_e(C-S) = 1.6338 Å

ω_1 = 1998 cm^{-1}, ω_2 = 352 cm^{-1}, ω_3 = 737 cm^{-1}

Renner const ε = -0.158

A_{SO} = -341 cm^{-1}

μ_e = 2.496 D ….

However, how about r_0 structure ? We need 3D PES.

NCS: 3D PES

MR-SDCI+Q/[aug-cc-pCVQZ (N, C, S)]

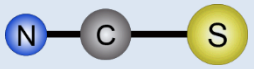
T.Hirano, U. Nagashima, P. Jensen, *J. Mol. Spectrosc.*, **346**, 4 (2008) .

Electronic state: $^2\Pi$ (Renner molecule)

Geometry of NCS

Equil. Structure: r_e(N-C) = 1.1778 Å, r_e(C-S) = 1.6335 Å, $\angle_e$(N-C-S) = **180°**

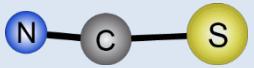
→ Linear molecule



r_0 structure: r_0(N-C) = 1.1836 Å, r_0(C-S) = 1.6356 Å, $\angle_0$(N-C-S) = **172.5°**

(DVR3D)

→ Bent



N≡C≡S· (Cumulative π, 84% ↑ on S)

A_{SO} = -342.2 cm^{-1}

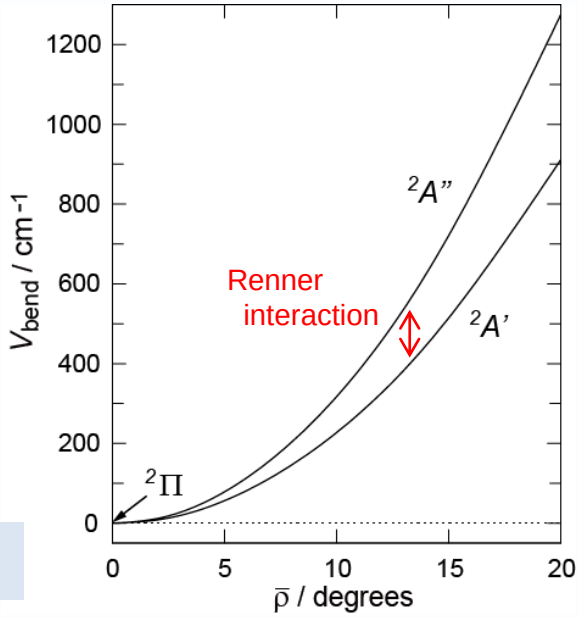
Mulliken Charge : N C S

(-0.409) (0.210) (0.199)

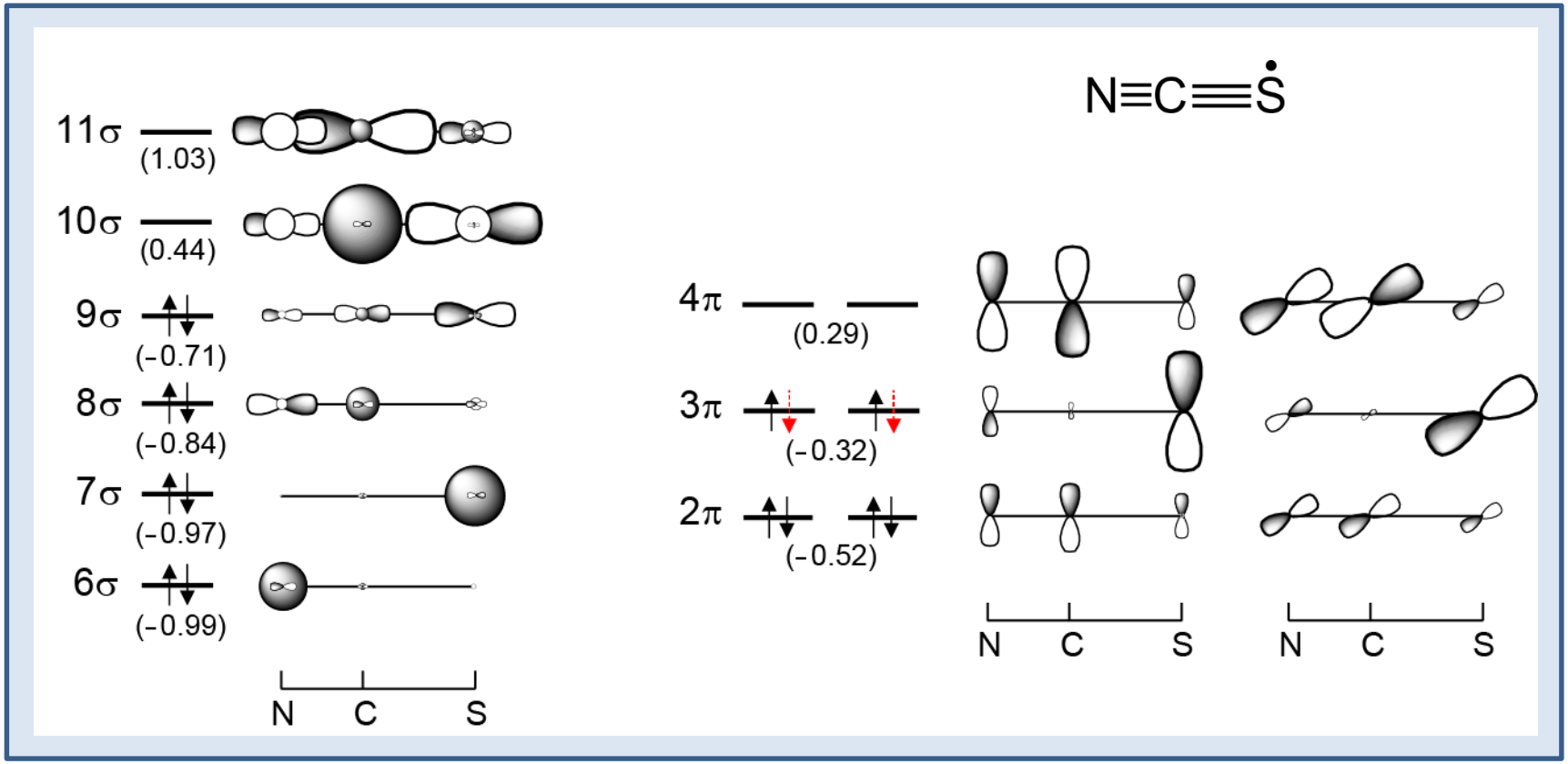
μ_e = 2.25 D

Renner const. ε = -0.1653

Yamada-Winnewisser γ = -1.05 → linear molecule

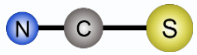
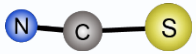
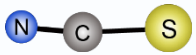


Two-state-averaged CASSCF NOs



Un-paired spin: N 2*p*π (15%), C 2*p*π (1%), S 3*p*π (84%)

NCS, Ro-vibrationally averaged structure (DVR3D)

$(v_1, v_2^{\ell_2}, v_3)^{a}$	$\nu_{A'}/\mathrm{cm}^{-1}$	$\nu_{A''}/\mathrm{cm}^{-1}$	$\langle r(\mathrm{N–C})\rangle/\text{Å}$	$\langle r(\mathrm{C–S})\rangle/\text{Å}$	$\langle\bar{\rho}\rangle/(\delta\bar{\rho})^{b}$ deg.
Equil. Struct. 			1.1778	1.6335	0.0
$NC^{32}S$ 					
$(0, 0^0, 0)$	0	0	1.1836	1.6356	7.5(3.8)
$(0, 1^{1e,f}, 0)$	349	412	1.1841	1.6371	11.2(4.0)
$(0, 2^0, 0)$	680	832	1.1847	1.6382	12.2(6.3)
$(0, 3^{1e,f}, 0)$	1019	1251	1.1852	1.6393	14.4(6.4)
$(1, 0^0, 0)$	1942	1930	1.1942	1.6279	7.4(3.8)
$(0, 0^0, 1)$	780	751	1.1854	1.6356	8.3(4.7)
$NC^{34}S$ 					
$(0, 0^0, 0)$	0	0	1.1837	1.6355	7.5(3.8)
$(0, 1^{1e,f}, 0)$	348	411	1.1841	1.6372	11.1(4.0)
$(0, 2^0, 0)$	677	828	1.1847	1.6383	12.2(6.3)
$(0, 3^{1e,f}, 0)$	1014	1246	1.1852	1.6396	14.4(6.4)
$(1, 0^0, 0)$	1944	1932	1.1942	1.6276	7.4(3.8)
$(0, 0^0, 1)$	771	742	1.1854	1.6357	8.3(4.7)

a) v_1: N-C antisym.-str., v_2: bending, v_3: C-S sym.-str.

b) Uncertainty: $\delta\bar{\rho}\ (=\sqrt{\langle\bar{\rho}^2\rangle - \langle\bar{\rho}\rangle^2}\ )$

$f_{r(\mathrm{N\text{-}C}),r(\mathrm{C\text{-}S}),\bar{\rho}} = f_{012} = -0.52$ aJ/Å

Calculation of Rotational constant (DVR3D wavefunction)

$$
\begin{aligned}
\mathcal{B}_v &= \frac{\hbar}{4\pi c} \left\langle \psi_{v,\ell} \left| \frac{1}{2} \left(\frac{1}{I_{bb}} + \frac{1}{I_{cc}} \right) \right| \psi_{v,\ell} \right\rangle \; / \; \langle \psi_{v,\ell} \,|\, \psi_{v,\ell} \rangle \\
&= \left\langle \psi_{v,\ell} \left| \frac{1}{2}(B+C) \right| \psi_{v,\ell} \right\rangle \; / \; \langle \psi_{v,\ell} \,|\, \psi_{v,\ell} \rangle \qquad (1) \\
&= \frac{1}{2} \left(\langle \psi_{v,\ell} \,|B|\, \psi_{v,\ell} \rangle + \langle \psi_{v,\ell} \,|C|\, \psi_{v,\ell} \rangle \right) \; / \; \langle \psi_{v,\ell} \,|\, \psi_{v,\ell} \rangle \qquad (2) \\
&= \frac{1}{2} \left(B_v + C_v \right) \; . \qquad (3)
\end{aligned}
$$

I_{ii} : Moment of inertia for *ii* principal axis.

We cannot distinguish *b*- and *c*-axes,
due to the double degeneracy in bending motion.

$^2\Pi$ NCS

Exp. Maeda *et al*., *Mol. Phys*. (2007)

	B_0 / MHz
$NC^{32}S$	6106.6230(16)
$NC^{34}S$	5962.857(52)

Least-Squares Fit (LSQ) of Exp. B_0 values

3 roots for 2 B_0's

Residue	r(N-C)	r(C-S)	$\bar{\rho}$	→ B_0 (for $NC^{32}S$)
8 x10^{-13}	1.1836	1.6345	7.77°	6106.64

$\langle\bar{\rho}\rangle_0 = 0$ is assumed → projected bond-lengths.

Residue	r(N-C)	r(C-S)
79 x10^{-13}	1.1786	1.6336

cf. $\langle r(\text{N-C})\rangle_{proj}$	$\langle r(\text{C-}^{32}\text{S})\rangle_{proj}$
1.1784	1.6333

	Surfit		DVR3D (term value)		DVR3D Expectation value				
	B_0/MHz	%error	B_0/MHz	%error	$\langle r(\text{N-C})\rangle_0$	$\langle r(\text{C-S})\rangle_0$	$\langle\bar{\rho}\rangle_0$ ($\delta\rho$)	$\langle(B+C)/2\rangle$	%deviation
$NC^{32}S$	6105.5	-0.018	6109.4	-0.05	1.1836	1.6356	7.78 (1.9)	6109.4	-0.05
$NC^{34}S$	5961.9	-0.017	5965.8	-0.05	1.1837	1.6355	7.78 (2.0)	5965.8	-0.05

Units: B_0 (MHz), Distance (Å), Angle (degrees). r_e(N-C) = 1.1778 Å, r_e(C-S) = 1..6335 Å

Conclusion

	LSQ Residue	r_0(N-C) / Å	r_0(C-S) / Å	$\bar{\rho}_0$ / °	$\mathcal{B}_0$ / MHz	%Error
DVR3D		1.1836	1.6356	7.8	6109.4	-0.05
From Exp. $B_{eff,0}$ (LSQ)						
$\bar{\rho}_0$ as variable	8×10^{-13}	1.1836	1.6345	7.8	6106.6	-0.0004
$\bar{\rho}_0 = 0$ (fixed)	79×10^{-13}	1.1786	1.6336	0	6106.7	0.0013

Projected bond length (DVR3D)

$\langle r$(N-C) proj$\rangle_0$	$\langle r$(C-S) proj$\rangle_0$
1.1784	1.6333

Even for two isotopologues, we can carry out the LSQ fit with $\bar{\rho}_0$ as a variable.

The r_0-structure of a linear molecule is observed as being bent. Theory and Exp..

To get structure parameters from Exp. B_0,

1) Check the validity of a common set of geometry parameters among isotopologues.

2) Do not assume $\bar{\rho}_0 = 0$!!! → $\bar{\rho}_0$ should be treated as a variable !

$\bar{\rho}_0 = 0$ yields projected bond-length on *a*-axis. (r_s structure also).

⟹ Without projection angle, no physical meaning as a structure parameter !!!

Thanks to,

Koichi M. Yamada (AIST)

And, especially to,

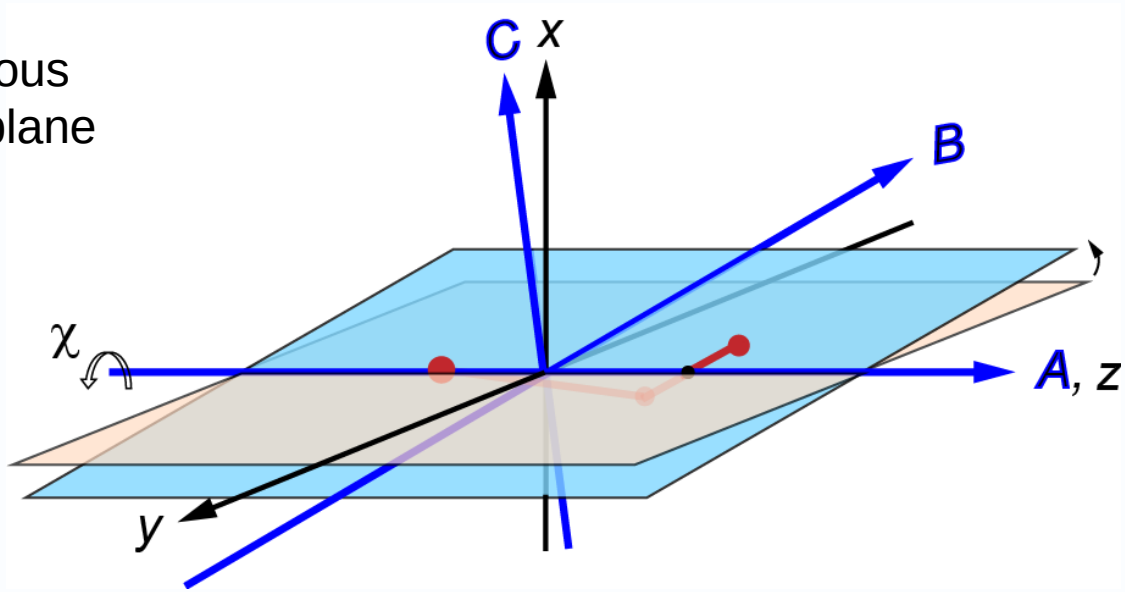
An anonymous Reviewer of our NCS paper !



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

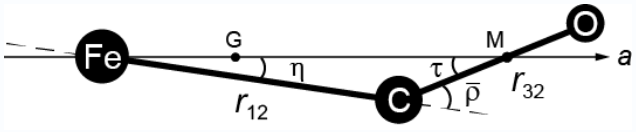


If rotation about the *a*-axis does not occur (*i.e.* if there is no double-degeneracy in the bending vibration), the spectrum pattern would become asymmetric top.

However, ….

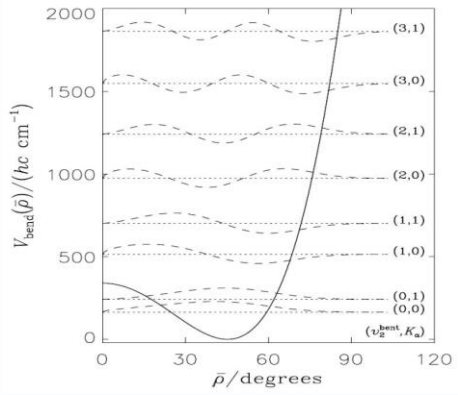
r_0-structure of linear molecule
(Linear at equilibrium structure)

Equilibrium structure		$\langle\bar{\rho}\rangle$ $(\delta\bar{\rho})$
Linear	$^3\Sigma^-$ **FeCO**	**7° (4°)**
	$^3\Phi$ 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°)	^{2}A' 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

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