RO-VIBRATIONALLY AVERAGED STRUCTURE OF $^2\Pi$ NCS: RE-INTERPRETATION OF THE B_0 VALUES

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We have constructed *ab initio* 3D potential energy surfaces (PESs) for $\tilde{X}\ ^2\Pi$ NCS in core-valence SDCI+Q/[aCVQZ(N,C,S)] calculations. The B_0 value predicted from these PESs deviates only 0.05% from the corresponding experimental values for $NC^{32}S$ and $NC^{34}S$. Since we have quite accurate 3D PESs, we can determine both the equilibrium structure and the r_0 structure accurately: r_e(N–C) = 1.1778 Å, r_e(C–S) = 1.6335 Å, and $\angle_e$(N–C–S) = 180°. The ro-vibrationally averaged structure, determined as expectation values over DVR3D wavefunctions, has $\langle r(\text{N–C})\rangle_0$ = 1.1836 Å, $\langle r(\text{C–S})\rangle_0$ = 1.6356 Å, and $\langle \angle(\text{N–C–S})\rangle_0$ = 172.5°. The 3D PESs show that the $\tilde{X}\ ^2\Pi$ NCS has its potential energy minimum at a linear configuration, and hence it is a "linear molecule." Experimentally, B_0 values are reported for two isotopologues only.[a] Using the expectation values given above as the initial guess, a bent r_0 structure having an $\langle \angle(\text{N–C–S})\rangle_0$ of 172.2° is deduced from the experimentally reported B_0 values for $NC^{32}S$ and $NC^{34}S$. It shows that the linear molecule NCS has a "bent" ro-vibrationally averaged structure, confirming our previous predictions:[b] any linear molecule is observed as being bent on ro-vibrational average. See Ref. *c* [c] for further discussion of this molecule.

$^2\Pi$ NCS is a typical Renner molecule. The Renner spectroscopy of this molecule will be presented in a separate talk.[d]

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[a] A. Maeda, H. Habara, T. Amano, *Mol. Phys.*, **105**, 477–495 (2007).

[b] T. Hirano, U. Nagashima, *J. Mol. Spectrosc.*, **314**, 35–47 (2015); T. Hirano, U. Nagashima, P. Jensen, *J. Mol. Spectrosc.* **343**, 54–61 (2018).

[c] T. Hirano, U. Nagashima, P. Jensen, *J. Mol. Spectrosc.* (2018), https://doi.org/10.1016/j.jms.2017.12.011.

[d] J. Freund et al, "Computational spectroscopy of NCS in the Renner-degenerate Electronic state $\tilde{X}\ ^2\Pi$."