Rotational Constants of $\tilde{X}\,^2\Pi$ NCS: Importance of the Core-Valence Correlation

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The electronic ground state of NCS is $^2\Pi$, and hence attention has been paid from the viewpoint of the Renner effect. In contrast to its isovalent sister radical NCO, much has not been known both experimentally and theoretically. Experimentally, the rotational constant B_0 was reported by Amano, *et al.* [1], but the N-C and C-S bond lengths in the radical have not been determined yet. Theoretically, Koch, *et al.* (1987), Tokue, *et al.* (1990), Yu, *et al.* (1997), Li and Iwata (1997), Szalay, *et al.* (1998), Ouazbir, *et al.* (1999), reported their *ab initio* molecular orbital studies. The validity of the spectroscopic constants predicted there, however, is not guaranteed since the errors in the predicted B_0 values are not small enough, *eg.* 0.8 % even in the hitherto highest level of calculation, full valence MR-SDCI/cc-pVQZ(-*g*), by Ouazbir, *et al.* [2].

We have carried out highly correlated *ab initio* molecular orbital calculations at various levels to obtain 'spectroscopic accuracy.' The results are summarized in Table 1. Entry 1 is those by

Table 1 Equilibrium Geometry and Rotational Constant of $\tilde{X}\,^2\Pi$ $NC^{32}S$ at Various Levels of Calculations

		Basis sets [a]				
Method	Active space	S	C and N	r_e(N-C)/Å	r_e(C-S) /Å	B_e /MHz
1) MR-SDCI [b]	Full valence	aVQZ(-*g*)	aVQZ(-*g*)	1.1735	1.646	6066.2
2) MR-ACPF	Full valence	V(Q+*d*)Z(-*g*)	VQZ(-*g*)	1.1810	1.6429	6053.6
3) MR-ACPF	9σ–11σ, 2π–4π [c]	V(Q+*d*)Z(-*g*)	VQZ(-*g*)	1.1784	1.6428	6063.3
4) MR-ACPF	9σ–11σ, 2π–4π [c]	V(Q+*d*)Z	VQZ	1.1785	1.6394	6079.1
5) MR-ACPF	9σ–11σ, 2π–4π [c]	V(Q+*d*)Z	aVQZ	1.1811	1.6367	6082.4
6) MR-ACPF	Full valence	aV(Q+*d*)Z	aVQZ	1.1815	1.6396	6067.5
7) MR-ACPF+E_{rel}	9σ–11σ, 2π–4π [c]	aV(Q+*d*)Z	aVQZ	1.1788	1.6390	6080.1
8) CCSD(T)	Full valence	V(Q+*d*)Z	aVQZ	1.1783	1.6424	6066.0
9) MR-SDCI	Core-val. Full-v. [d]	aCV(Q+*d*)Z	aCVQZ	1.1754	1.6349	6112.0 (B_0 = 6101.2)
10) **MR-SDCI+Q**	**Core-val. Full-v.** [d]	aCV(Q+*d*)Z	aCVQZ	**1.1785**	**1.6319**	**6115.2** (**B_0 = 6104.5**)
11) MR-SDCI+Q+E_{rel}	Core-val. Full-v.[d]	aCV(Q+*d*)Z	aCVQZ	1.1783	1.6321	6115.0 (B_0 = 6104.2)
Exp. Amano, *et al*. (1991) for $NC^{32}S$						**B_0 = 6106.62162(25)**

[a] (-*g*): without *g*-functions. [b] Quazbir, *et al*. (1999). [c] Dynamic correlation from closed 6σ-8σ orbitals are included. [d] Full-v.: Full valence.

Ouazbir, *et al.*, [2] for comparison.

Since we know tight *d*-functions are necessary for the basis set of S, we employed cc-pV(Q+*d*)Z, but significant improvement was not observed (Entries 2-8). Inclusion of the *g*-basis functions which were not included in Ouazbir *et al.*'s calculations, gave a slight improvement as shown in Entries 4-8, but still the errors in B_0 were of the order of 0.5 %.

A dramatic improvement has been observed, however, when the core-valence correlation was included in the full valence MR-SDCI and MRSDCI+Q levels of calculations (Entries 9 - 11). The error in B_0 becomes to be 0.03 % against the experimental B_0, for example, at the core-valence MR-SDCI+Q/[aug-cc-pCV(Q+*d*)Z (S), aug-cc-pCVQZ (C and N)] level of calculations (Entry 10). The effect of relativistic correction is proved to be negligible. The N-C and C-S equilibrium bond lengths are predicted to be 1.1785 and 1.6319 Å, respectively, at this level of calculation; and, therefore, the B_e and B_0 of the isotopomer $NC^{34}S$ could be 5971.1 and 5960.4 MHz, respectively.

1) T. Amano and T. Amano, *J. Chem. Phys.*, **95**, 2275 (1991).
2) M. Ouazbir, G. Chambaud, P. Rosmus and P.J. Knowles, *Phys. Chem. Chem. Phys.*, **1**, 2649-2655 (1999).

NCS ラジカルの回転定数：Core-valence 相関の重要性

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