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Computational Molecular Spectroscopy of NCS in the $\tilde{X}^2\Pi$ Electronic Ground State Jens Freund,^{*a*} Per Jensen,^{*a*} and Tsuneo Hirano^{*b*}

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Introduction

The electronic ground state of the NCS radical (and, in fact, those of all other 15-valence-electron triatomics such as BO_2 , N_2O^+ and NCO) exhibits the Renner effect. At linear geometries, the electronic state is doubly degenerate with ${}^{2}\Pi$ symmetry, but it splits into two separate states of $A' \oplus A''$ symmetries at bent geometries (Fig. 1). As a result of the Renner interaction in $\tilde{X}^2\Pi$ NCS and of the facts (1) that $2\omega_2 \approx$ ω_3 , leading to all-pervading Fermi resonances, and (2) that the spinorbit coupling constant is close in size to ω_2 , the resulting rovibronic spectrum is extremely complicated. This spectrum was first observed by Dixon and Ramsay [1] in 1968 with more recent experimental studies from Northrup and Sears [2, 3], Amano and Amano [4], Maeda et al. [5], McCarthy et al. [6], Tokue et al. [7], and Li and Iwata [8].



Figure 1: Bending potential energy functions for $\tilde{X}^2 \Pi$ NCS. The angle $\bar{\rho}$ is the supplement of the bond angle \angle (N–C–S), i.e., $\bar{\rho} = 180^{\circ} - \angle$ (N–C–S)



Figure 2: Term value diagram for $\tilde{X}^2 \Pi$ NCS.

Theoretical Work

Previous theoretical studies of $\tilde{X}^2\Pi$ NCS include the work by Szalay *et al.* [9] and by Ouazbir *et al.* [10]. The latter authors calculated *ab initio* the associated rovibronic energies. We extend their work by calculating also rovibronic intensities, thus producing simulated spectra. Our nuclear-motion calculations have been done with the REN-NER program system [11, 12]. These calculations are based on new

three-dimensional potential energy surfaces and dipole moment surfaces computed *ab initio* with the MOLPRO program [13] at the corecorrelated, full-valence MR-SDCI+Q/[aug-cc-pCVQZ(N, C,S)] level of theory.

Calculated Vibrational Term Values

Table 1: Calculated term values of NCS in the electronic Renner states ${}^{2}A'$ und ${}^{2}A''$ for J = 1/2 and $E/hc \le 2000 \text{ cm}^{-1}$

J	$J = 1/2, A'^a$				J = 1/2, A''				
(v_1, v_2, v_3)	N	K_a	E/cm^{-1}	(v_1, v_2, v_3)	N	K_a	E/cm^{-1}		
(0,0,0)	1	1	0.000	(0,0,0)	1	1	0.000		
(0,1,0)	0	0	29.837	(0,1,0)	1	0	29.977		
(0,1,0)	1	0	389.581	(0,1,0)	0	0	389.443		
(0,2,0)	1	1	403.576	(0,2,0)	1	1	403.576		
(0,3,0)	0	0	719.143	(0,3,0)	1	0	719.350		
(0,0,1)	1	1	740.930	(0,0,1)	1	1	740.930		
(0,2,0)	1	1	770.301	(0,2,0)	1	1	770.302		
(0,1,1)	0	0	808.743	(0,1,1)	1	0	808.913		
(0,4,0)	1	1	1084.165	(0,4,0)	1	1	1084.165		
(0,1,1)	1	0	1103.040	(0,1,1)	0	0	1102.872		
(0,2,1)	1	1	1186.529	(0,2,1)	1	1	1186.529		
(0,3,0)	1	0	1192.548	(0,3,0)	0	0	1192.350		
(0,5,0)	0	0	1393.240	(0,5,0)	1	0	1393.501		
(0,0,2)	1	1	1472.402	(0,0,2)	1	1	1472.402		
(0,0,2)	1	1	1493.822	(0,0,2)	1	1	1493.804		
(0,3,1)	0	0	1494.501	(0,3,1)	1	0	1494.719		
(0,4,0)	1	1	1568.726	(0,4,0)	1	1	1568.726		
(0,1,2)	0	0	1591.589	(0,1,2)	1	0	1591.791		
(0,6,0)	1	1	1756.869	(0, 6, 0)	1	1	1756.868		
(0,1,2)	1	0	1810.456	(0,1,2)	0	0	1810.261		
(0,4,1)	1	1	1863.796	(0,4,1)	1	1	1863.795		
(0,5,0)	1	0	1899.229	(0,5,0)	0	0	1899.044		
(1,0,0)	1	1	1952.424	(1,0,0)	1	1	1952.423		
(0,2,2)	1	1	1971.906	(0,2,2)	1	1	1971.906		
(1,1,0)	0	0	1978.113	(1,1,0)	1	0	1978.249		

 $^{a}A'$ und A'' denote the symmetry of the rovibronic wavefunction of the respective

We compare the calculated term values with the available experimental data in terms of the percentage deviation

$$\Delta_{\text{rel.}} = 100 \times \frac{|\nu^{(\text{lit.})} - \bar{\nu}^{(\text{calc.})}|}{\nu^{(\text{lit.})}} \tag{1}$$

Table 2: Comparison of the calculated vibrational term values for NCS in the elec tronic states ${}^{2}A'$ and ${}^{2}A''$ with experimental and calculated literature values

	Literature	This work					$\Delta_{\text{rel.}}^d$	
	${}^{2}A' {}^{a} {}^{2}A''$	Ref.	2	A'		${}^{2}A''$	$\bar{\nu}^{(\text{calc.})d}$	$^{2}A'$ $^{2}A''$
			e^{o}	f^c	е	f		
$ u_1/\mathrm{cm}^{-1} $	1950^{e}	[3]	1951.4	1951.4	_	_	1951.4	0.07
	2008.5^{f}	[10]						2.84
	2013^{f}	[8]						3.06
	2018^{f}	[9]						3.30
	2046^{f}	[7]						4.62
ν_2/cm^{-1}	375.96^{e}	[2]	316.8	_	—	440.4	378.6	0.71
	375 ^e	[3]						0.97
	348.6^{j} 409.4 ^j	[10]						9.12 7.58
	$3/9^9$	F01						0.11
	352^{g} 415 ^g 383.5^{g}	[8]						10.00 6.13
	372^{f}	[9]						1.78
	375^f 457^f	[7]						15.52 3.63
. 1	416^{g}							8.99
ν_3/cm^{-1}	735.41^{e}	[2]	743.5	743.5	—	—	743.5	1.10
	760 ^e	[3]						2.17
	748.4 ^j	[10]						0.66
	726^{J}	[8]						2.41
	765 ^J	[/]						2.81
	708	191						5.01

 $^{a2}A'$ and $^{2}A''$ denote the electronic state. $^{b}An e$ -state has the parity $+(-1)^{N}$. ^{c}An f-state has the parity $-(-1)^N$. ^d See equation (1). ^e Experimental literature value. ^{*f*}Calculated literature value. ^{*g*}Average of the literature vibrational constants in the row above.

Calculated Rotational Constants

Table 3: Calculated effective rotational constants $B_{eff}^{(calc.)}$ (in cm⁻¹) of NCS in its electronic states ${}^{2}A'$ und ${}^{2}A''$ and different vibrational states (v_1, v_2, v_3) . 2 1/a

We compare the calculated values of the rotational constant with the available experimental data in terms of the percentage deviation

Table 4: Comparison of the average effective rotational constants $\bar{B}_{eff}^{(calc.)}$ (in cm⁻¹) of NCS in its electronic states ${}^{2}A'$ und ${}^{2}A''$ and different vibrational states (v_1, v_2, v_3) with literature values $B_{\text{eff}}^{(\text{lit.})}$ (also in cm⁻¹)

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		\square		1		
		$B_{\rm eff.}^{\rm (calc.)}$	$B_{\rm eff.}^{\rm (calc.)}$	$B_{\rm eff.}^{\rm (calc.)}$	$B_{\rm eff.}^{\rm (calc.)}$	
$(v_1,\!v_2,\!v_3)$	K_a	$(e)^b$	$(f)^c$	(e)	(f)	$\bar{B}_{\text{eff.}}^{(\text{calc.})_d}$
(0,0,0)	Π	0.20384	0.20384	_	_	0.20384
(0,1,0)	\sum	0.20431	_	_	0.20378	0.20405
(0,1,0)	Δ	0.20390	0.20390	_	_	0.20390
(0,2,0)	Π	0.20488	0.20532	0.20469	0.20430	0.20480
(0,0,1)	Π	0.20279	0.20286	_	_	0.20283
(1,0,0)	Π	0.20323	0.20321	_	_	0.20322

 $a^{2}A'$ and A'' denote the electronic state. $^{b}An e$ state has the parity $+(-1)^{N}$. $^{c}An f$ state has the parity $-(-1)^N$. ^dAverage value of the rotational constants of the vibronic state.

$$\Delta_{\text{rel.}} = 100 \times \frac{|B_{\text{eff.}}^{(\text{lit.})} - \bar{B}_{\text{eff.}}^{(\text{calc.})}|}{B_{\text{eff.}}^{(\text{lit.})}}$$
(2)

<u> </u>		,			
(v_1, v_2, v_3)	K_a	$B_{\rm eff.}^{\rm (lit.)}$	Ref.	$\bar{B}_{\text{eff.}}^{(\text{calc.})_a}$	$\Delta^b_{\rm rel.}$
(0,0,0)	Π	0.20393 ^c	[2]	0.20384	0.05
		0.20369506(2) ^{c,d}	[6]		0.07
		0.203695016(5) ^c	[5]		0.07
		0.203694972(8) ^c	[4]		0.07
		0.2036 ^c	[1]		0.12
		0.20277^{e}	[9]		0.53
(0,1,0)	\sum	0.2033(10) ^c	[2]	0.20405	f
		0.20331^{e}	[9]		0.36
(0,1,0)	Δ	0.20491(36) ^c	[2]	0.20390	0.49
		0.20331^{e}	[9]		0.29
(0,2,0)	Π	0.2084(26) ^c	[2]	0.20480	1.73
		0.20385^{e}	[9]		0,47
(0,0,1)	Π	0.1984(30) ^c	[2]	0.20283	2.23
		0.20178^{e}	[9]		0.52
(1,0,0)	Π	0.204 ^c	[1]	0.20322	0.38
		0.20231^{e}	[9]		0.45

^{*a*}Individual values in Table 3. ^{*b*}See Eq. (2). ^{*c*} Experimental literature value. ^dThe values in parentheses are standard errors in units of the last digit given. ^eCalculated literature value. ^fThe average of the calculated values is in agreement with the literature value within the literature error margins.

Simulated Spectra









12 K.

Conclusion

The theoretical results obtained are in good agreement with the available experimental data. We hope that the wavenumbers and intensities predicted for transitions not observed so far will assist in the continued experimental investigation of this molecule.

2400

Wavenumber/cm⁻

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Figure 3: The absorption spectrum of $\tilde{X}^2 \Pi$ NCS, simulated at a temperature of T =

2800 3000

2600

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