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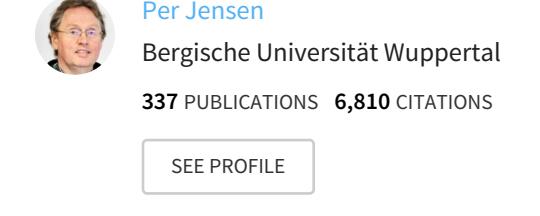
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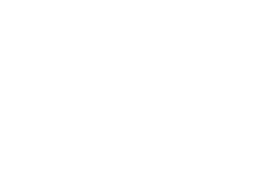
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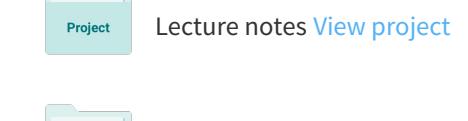
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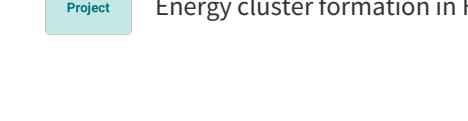
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Computational Molecular Spectroscopy of NCS in the $\tilde{X}^2\Pi$ Electronic Ground State

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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 BO₂, N₂O⁺ 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 $2\omega_2 \approx \omega_3$, leading to all-pervading Fermi resonances, and (2) that the spin-orbit 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].

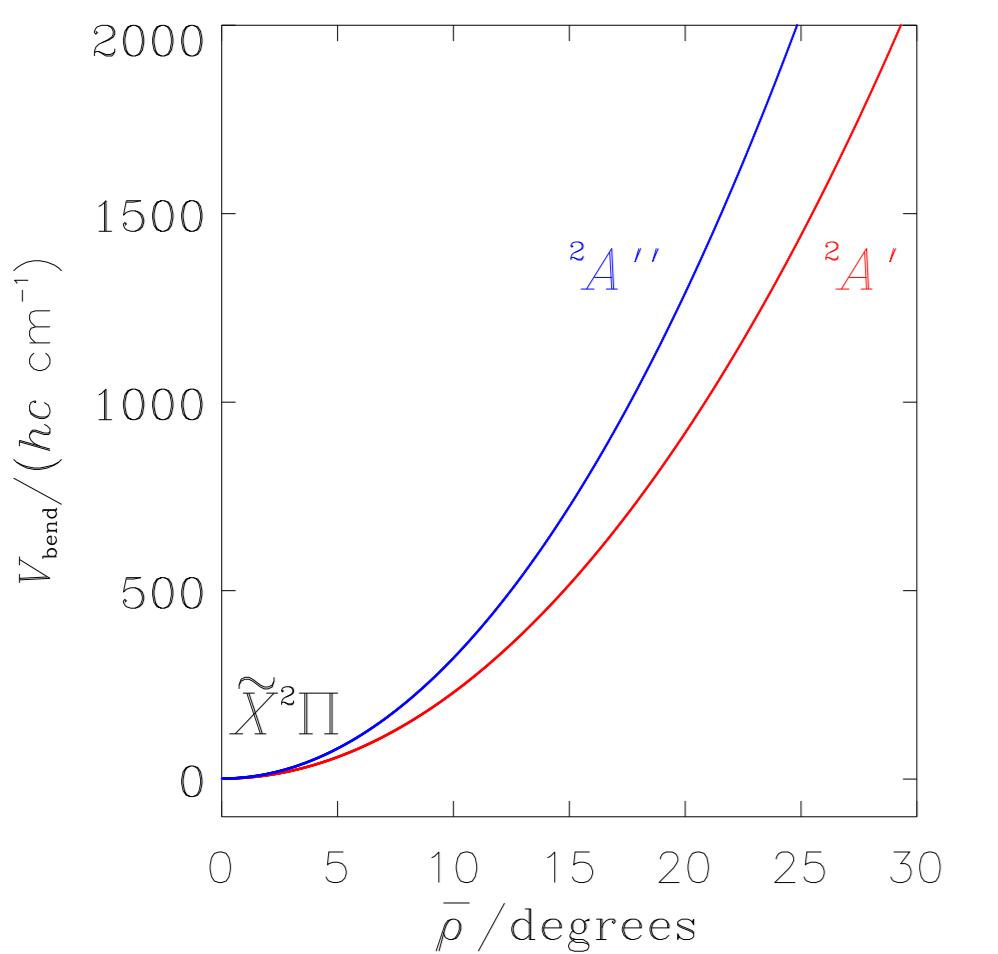


Figure 1: Bending potential energy functions for $\tilde{X}^2\Pi$ NCS. The angle $\bar{\rho}$ is the supplement of the bond angle $\angle(N-C-S)$, i.e., $\bar{\rho} = 180^\circ - \angle(N-C-S)$

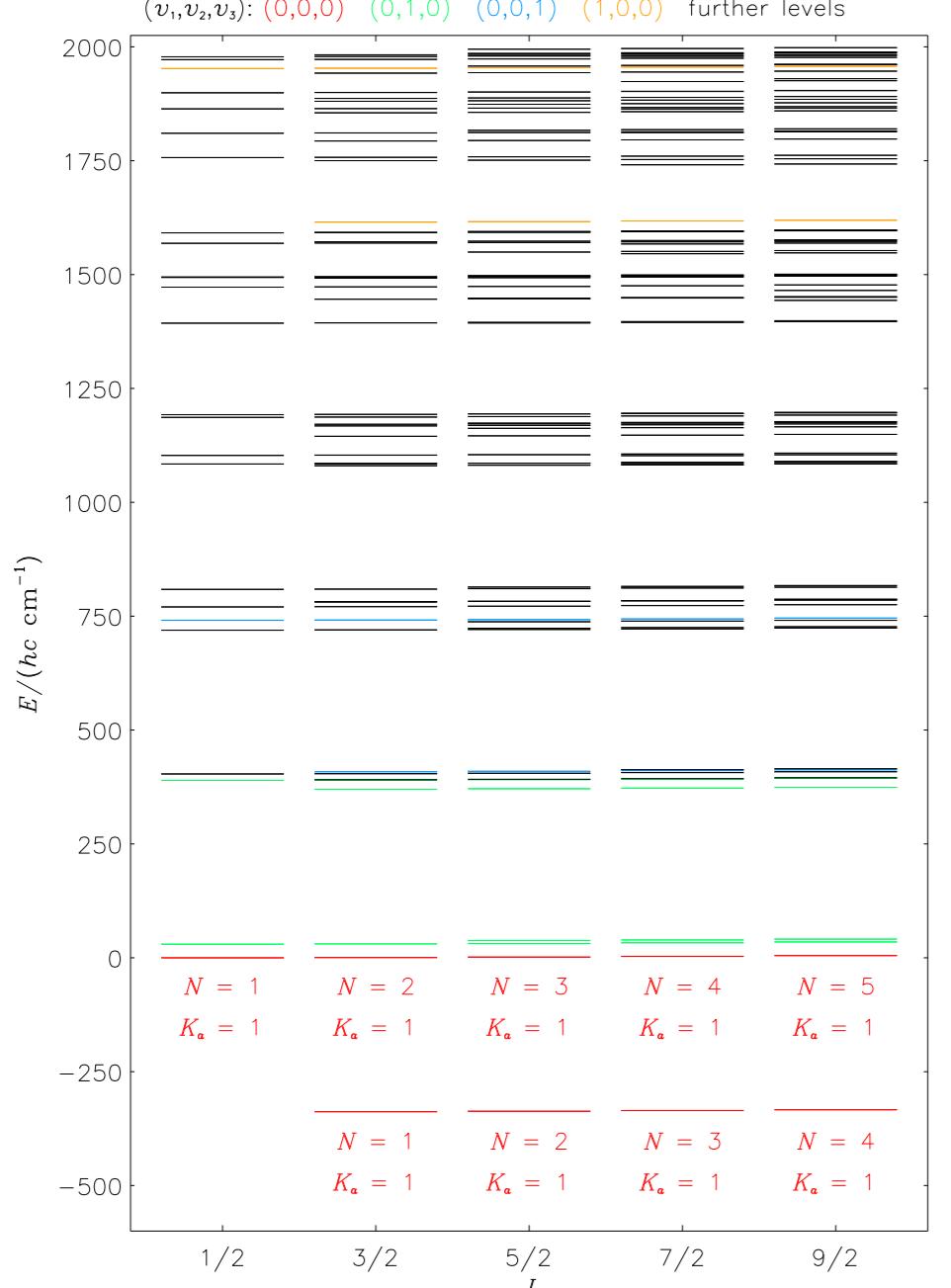


Figure 2: Term value diagram for $\tilde{X}^2\Pi$ NCS.

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 RENNER 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 core-correlated, full-valence MR-SCCI+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 $^2A'$ und $^2A''$ for $J = 1/2$ and $E/hc \leq 2000 \text{ cm}^{-1}$

$J = 1/2, A''$			$J = 1/2, A''$				
(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 state.

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

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

Table 2: Comparison of the calculated vibrational term values for NCS in the electronic states $^2A'$ und $^2A''$ with experimental and calculated literature values

$^2A'$ ^a	Literature	Ref.	$^2A''$	This work	$^2A'$	$^2A''$	$\bar{\nu}^{(\text{lit.})}$	$\bar{\nu}^{(\text{calc.})}$	$\Delta_{\text{rel.}}^d$
				e^b	f^c	e^f			
ν_1/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 ^c	[2]	316.8	—	—	440.4	378.6	0.71	0.97
	375 ^[3]	[3]							
	348.6 ^f	[10]						9.12	
	379 ^f							7.58	
	352 ^f	[8]						0.11	
	383.5 ^f	[8]						1.28	
	372 ^f	[9]						1.78	
	375 ^f	[7]						15.52	
	416 ^f	[7]						3.63	
ν_3/cm^{-1}	735.41 ^e	[2]	743.5	743.5	—	—	743.5	8.99	
	760 ^[3]	[3]							
	748.4 ^f	[10]						1.10	
	726 ^f	[8]						2.17	
	765 ^f	[7]						0.66	
	708 ^f	[9]						2.41	
								2.81	
								5.01	

^a $^2A'$ und $^2A''$ denote the electronic state. ^bAn e-state has the parity $+(-1)^N$. ^cAn f-state has the parity $-(-1)^N$. ^dSee equation (1). ^eExperimental literature value. ^fCalculated literature value. ^gAverage of the literature vibrational constants in the row above.

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Calculated Rotational Constants

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

(v_1, v_2, v_3)	K_a	$^2A''$		$^2A''$	
		$B_{\text{eff.}}^{(\text{calc.})}$ (e) ^b	$B_{\text{eff.}}^{(\text{calc.})}$ (f) ^c	$B_{\text{eff.}}^{(\text{calc.})}$ (e)	$B_{\text{eff.}}^{(\text{calc.})}$ (f)
(0,0,0)	II	0.20384	0.20384	—	—
(0,1,0)	Σ	0.20431	—	—	0.20378
(0,1,0)	Δ	0.20390	0.20390	—	0.