

COMPUTATIONAL SPECTROSCOPY OF NCS IN THE RENNER-DEGENERATE ELECTRONIC STATE $\tilde{X}^2\Pi$

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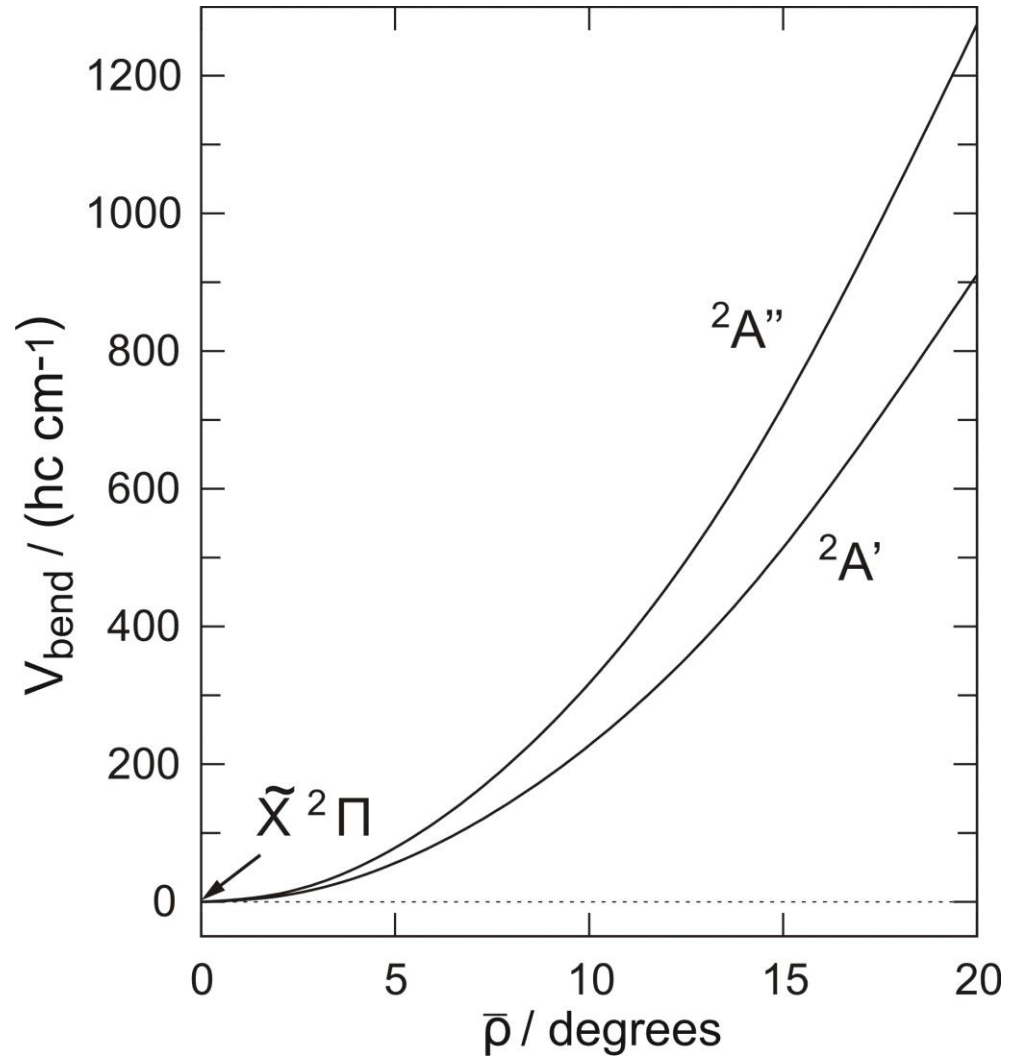
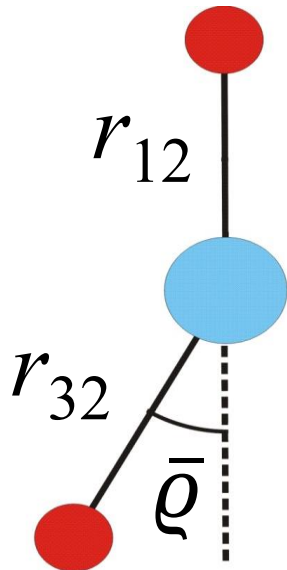
Why NCS?

- Complicated rovibronic spectrum due to:
 - Renner effect – two lowest electronic states degenerate at linear geometries
 - All-pervading resonances: $2\omega_2 \approx \omega_3$
 - Spin-orbit coupling constant $A_{SO} \approx \omega_2$

Rovibronic spectrum much less experimentally characterized than that of NCO.

First observation of NCS: R.N. Dixon, D.A. Ramsay, *Canadian J. Phys.* **46** (1968) 2619–2631.

Renner effect



Ab initio calculation

- Program MOLPRO
- Method & basis set: core-valence, full-valence
MRSDCI+Q/[aug-cc-pCVQZ(S, C, N)]
- Spin-orbit coupling constant $A_{SO} = -342.2 \text{ cm}^{-1}$
- Renner parameter $\varepsilon =$
$$[(\omega_{2,A'})^2 - (\omega_{2,A''})^2] / [(\omega_{2,A'})^2 + (\omega_{2,A''})^2] = -0.1653.$$

RENNER calculation

- Variational program RENNER
- Parameterized representation of the potential energy function

$$V_{\pm}(\Delta r_{12}^{(\text{ref})}, \Delta r_{32}^{(\text{ref})}, \bar{\rho}) = \sum_{jkl} G_{jkl}^{(\pm)} \left(y_1^{(\text{ref})}\right)^j \left(y_3^{(\text{ref})}\right)^k (1 - \cos \bar{\rho})^l$$

where the ‘−’ (‘+’) refers to the lower (upper) component $1^2A'$ ($1^2A''$), and $G_{jkl}^{(\pm)}$ are expansion coefficients. We have

$$y_i^{(\text{ref})} = 1 - \exp(-a_i \Delta r_{i2}^{(\text{ref})})$$

where $i = 1$ or 3 . The function $y_1^{(\text{ref})}$ is associated with the C–N bond, whereas $y_3^{(\text{ref})}$ is associated with the S–C bond.

- Parameter values obtained by least-squares fitting.

Parameter values

Table 1: The fitted potential energy surface parameters for the electronic $^2A'$ and $^2A''$ states of NCS (Eq. (1))

Absolute energy, molecular parameters, standard deviation		
V_e^a/cm^{-1}	$-186165.29(14)^b$	
$r_{12}^{(\text{ref})}/\text{\AA}$	$1.1776970(60)$	
$r_{32}^{(\text{ref})}/\text{\AA}$	$1.633467(10)$	
$a_1/\text{\AA}^{-1}$	2.433^c	
$a_3/\text{\AA}^{-1}$	1.885	
Std. dev. $^d/\text{cm}^{-1}$	1.87	
Parameters of the pure stretching potential energy		
$G_{200}^{(\pm)}/\text{cm}^{-1}$	$63906.4(88)$	
$G_{020}^{(\pm)}/\text{cm}^{-1}$	$33422(32)$	
$G_{110}^{(\pm)}/\text{cm}^{-1}$	$14842(30)$	
$G_{300}^{(\pm)}/\text{cm}^{-1}$	$-1252(68)$	
$G_{210}^{(\pm)}/\text{cm}^{-1}$	$13427(169)$	
$G_{120}^{(\pm)}/\text{cm}^{-1}$	$-9769(332)$	
$G_{040}^{(\pm)}/\text{cm}^{-1}$	$17450(1326)$	
$G_{310}^{(\pm)}/\text{cm}^{-1}$	$37538(2053)$	
$G_{220}^{(\pm)}/\text{cm}^{-1}$	$39166(4281)$	
	$^2A' (\sigma = -)$	$^2A'' (\sigma = +)$
Parameters of the pure bending potential energy		
$G_{001}^{(\sigma)}/\text{cm}^{-1}$	$15004(12)$	$20981(12)$
$G_{002}^{(\sigma)}/\text{cm}^{-1}$	$2196(199)$	$5078(199)$
$G_{003}^{(\sigma)}/\text{cm}^{-1}$	20000	20000
Parameters of the stretch-bend potential energy		
$G_{101}^{(\sigma)}/\text{cm}^{-1}$	$-7843(34)$	$-10806(34)$
$G_{011}^{(\sigma)}/\text{cm}^{-1}$	$-13898(183)$	$-21067(172)$
$G_{012}^{(\sigma)}/\text{cm}^{-1}$	$-12869(2944)$	$-20767(2944)$
$G_{201}^{(\sigma)}/\text{cm}^{-1}$	$3132(358)$	$-3758(325)$
$G_{021}^{(\sigma)}/\text{cm}^{-1}$	$4830(518)$	
$G_{111}^{(\sigma)}/\text{cm}^{-1}$	$-7936(892)$	$3123(892)$
$G_{031}^{(\sigma)}/\text{cm}^{-1}$	$15031(4736)$	

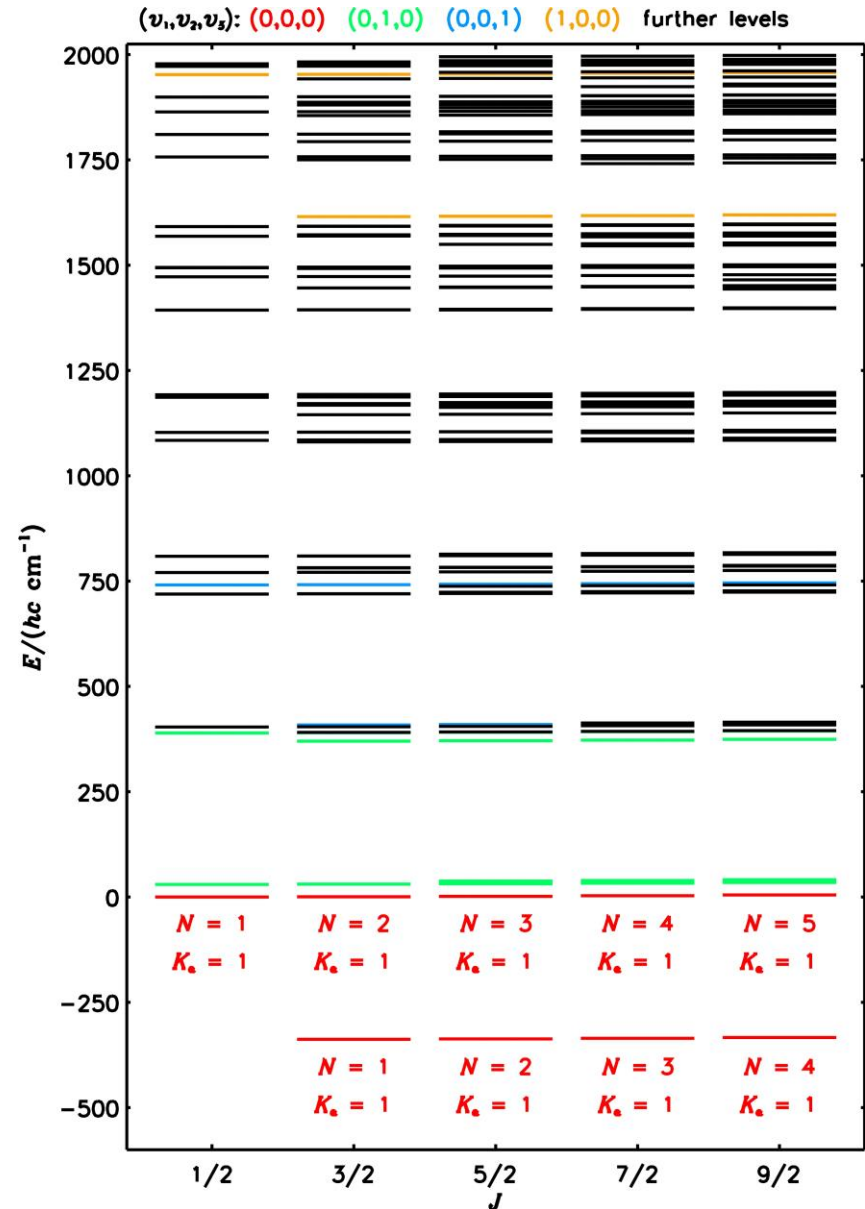
^a Absolute energy at the minimum of the $^2A'$ potential energy surface.

^b The values in parentheses are standard errors in units of the last digit given.

^c Parameters without standard errors were held fixed during the fitting process.

^d Standard deviation of the fitting.

Term values



Term values

Table 2: Calculated rovibronic term values (in cm^{-1}) for selected $(v_1, v_2^{\text{lin}}, v_3)$ states of $\tilde{X}^2\Pi$ NCS.^a

J	$(0,0,0) \ ^2\Pi_{3/2}$		$(0,0,0) \ ^2\Pi_{1/2}$		$(0,1,0) \ \mu^2\Sigma_{1/2}$		$(0,1,0) \ \kappa^2\Sigma_{1/2}$		$(0,1,0) \ ^2\Delta_{5/2}$	
	<i>e</i> states	<i>f</i> states	<i>e</i> states	<i>f</i> states	<i>e</i> states	<i>f</i> states	<i>e</i> states	<i>f</i> states	<i>e</i> states	<i>f</i> states
1/2			0.000	0.000	29.837	29.977	389.581	389.443		
3/2	-337.867	-337.867	0.612	0.612	30.379	30.659	390.260	389.986		
5/2	-336.849	-336.849	1.632	1.632	31.329	31.749	391.346	390.935	37.724	37.724
7/2	-335.423	-335.423	3.060	3.060	32.687	33.248	392.837	392.292	39.150	39.150
9/2	-333.589	-333.589	4.896	4.895	34.453	35.154	394.733	394.057	40.984	40.984

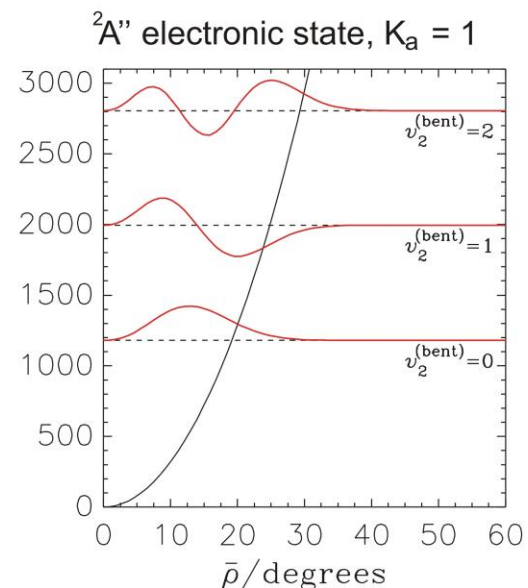
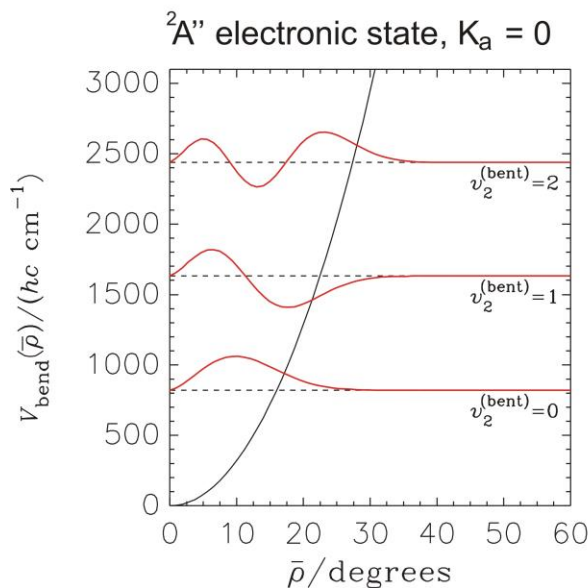
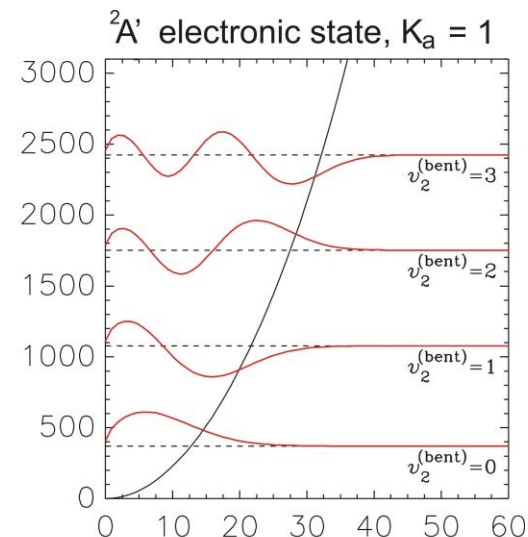
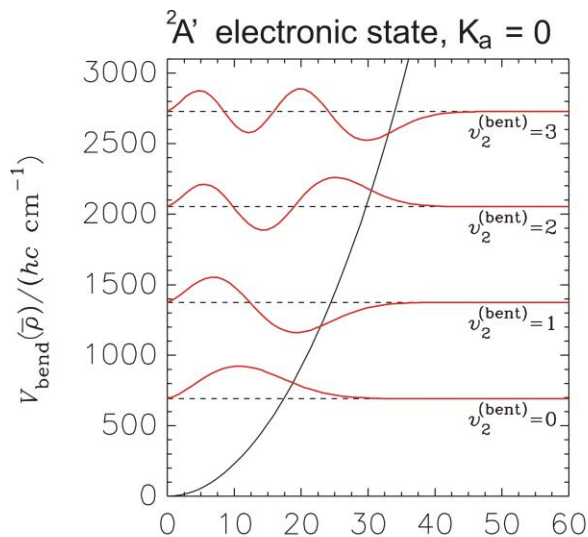
J	$(0,1,0) \ ^2\Delta_{3/2}$		$(0,2,0) \ \mu^2\Pi_{3/2}$		$(0,2,0) \ \kappa^2\Pi_{3/2}$		$(0,2,0) \ \mu^2\Pi_{1/2}$		$(0,2,0) \ \kappa^2\Pi_{1/2}$	
	<i>e</i> states	<i>f</i> states	<i>e</i> states	<i>f</i> states	<i>e</i> states	<i>f</i> states	<i>e</i> states	<i>f</i> states	<i>e</i> states	<i>f</i> states
1/2							403.576	403.576	770.302	770.301
3/2	370.084	370.084	390.771	390.771	781.844	781.844	404.191	404.190	770.914	770.913
5/2	371.104	371.104	391.794	391.792	782.871	782.871	405.216	405.214	771.934	771.933
7/2	372.533	372.533	393.228	393.222	784.308	784.308	406.650	406.648	773.363	773.362
9/2	374.370	374.370	395.072	395.061	786.156	786.156	408.494	408.491	775.199	775.198

J	$(0,2,0) \ ^2\Phi_{7/2}$		$(0,2,0) \ ^2\Phi_{5/2}$		$(0,0,1) \ ^2\Pi_{3/2}$		$(0,0,1) \ ^2\Pi_{1/2}$		$(0,0,2) \ ^2\Pi_{3/2}$	
	<i>e</i> states	<i>f</i> states	<i>e</i> states	<i>f</i> states	<i>e</i> states	<i>f</i> states	<i>e</i> states	<i>f</i> states	<i>e</i> states	<i>f</i> states
1/2							740.930	740.930		
3/2					408.526	408.526	741.539	741.539	1144.922	1144.922
5/2			737.706	737.706	409.544	409.544	742.554	742.555	1145.932	1145.932
7/2	413.120	413.120	739.139	739.139	410.969	410.969	743.976	743.976	1147.346	1147.346
9/2	414.960	414.960	740.983	740.983	412.802	412.801	745.803	745.804	1149.165	1149.165

J	$(0,0,2) \ ^2\Pi_{1/2}$		$(1,0,0) \ ^2\Pi_{3/2}$		$(1,0,0) \ ^2\Pi_{1/2}$		$(1,0,1) \ ^2\Pi_{3/2}$		$(1,0,1) \ ^2\Pi_{1/2}$	
	<i>e</i> states	<i>f</i> states	<i>e</i> states	<i>f</i> states	<i>e</i> states	<i>f</i> states	<i>e</i> states	<i>f</i> states	<i>e</i> states	<i>f</i> states
1/2	1472.402	1472.402			1952.424	1952.423			2703.773	2703.773
3/2	1473.011	1473.011	1615.131	1615.131	1953.033	1953.033	2373.969	2373.969	2704.381	2704.381
5/2	1474.027	1474.026	1616.148	1616.148	1954.048	1954.048	2374.962	2374.964	2705.394	2705.393
7/2	1475.448	1475.448	1617.571	1617.571	1955.470	1955.470	2376.352	2376.356	2706.811	2706.811
9/2	1477.276	1477.275	1619.401	1619.401	1957.298	1957.297	2378.139	2378.147	2708.634	2708.633

^aAn *e* state has the parity $+(-1)^{J-1/2}$ and an *f* state has the parity $-(-1)^{J-1/2}$ [27, 30].

Bending wave- functions



Comparison with experiment

Table 3: Vibrational wavenumbers ω_i (in cm^{-1}) of NCS, calculated by RENNER for the $^2A'$ and $^2A''$ electronic states. Some previous theoretical predictions are also shown for comparison.

	ω_1	$\omega_2(A')$	$\omega_2(A'')$	ω_2^b	ω_3	$\Delta_{\text{rel}}(\omega_1)^a$	$\Delta_{\text{rel}}(\omega_2)^a$	$\Delta_{\text{rel}}(\omega_3)^a$
Exp. [8]	~ 1950	–	–	~ 375	~ 760			
Exp. [7]	–	–	–	375.96	735.41			
RENNER	1951.4	316.8	440.4	378.6	743.5	0.07	0.70	1.10
Perturbation ^c	1994.7	349.7	413.2	381.5	742.3	2.29	1.47	0.94
Optimised MRCI/ spdfg cc-pVQZ [31]	1987.6	343.4	408.3	375.8	743.4	1.93	–0.04	1.09
Optimised MRCI/ spdf cc-pVQZ [20]	2008.5	348.6	409.4	379	748.4	3.00	0.81	1.77

^a $\Delta_{\text{rel}} = 100 \times (\omega^{(\text{calc})} - \omega^{(\text{exp})})/\omega^{(\text{exp})}$ is the percentage deviation from the respective experimental value of $\omega_1 \approx 1950 \text{ cm}^{-1}$, $\omega_2 = 375.96 \text{ cm}^{-1}$, and $\omega_3 = 735.41 \text{ cm}^{-1}$.

^b Average value of $\omega_2(A')$ and $\omega_2(A'')$.

^c Quoted from Table 3 of Ref. [25].

Comparison with experiment

Table 4: Rotational constants B_{eff} of NCS for various vibrational states (v_1, v_2, v_3) , calculated by RENNER. Averaged values for those in its electronic states $^2A'$ and $^2A''$ are listed. For comparison, literature values are also quoted.

(v_1, v_2, v_3)	K_a	$B_{\text{eff}} / \text{cm}^{-1}$		$\Delta_{\text{rel}}^a / \%$
(0,0,0)	Π	0.20384	Present Work ^b	
		0.2039(1) ^c	Exp. ^d [6]	^e
		0.20369506(2)	Exp. [11]	0.07
		0.203695016(5)	Exp. [12]	0.07
		0.203694972(8)	Exp. [10]	0.07
		0.2036(1)	Exp. [5]	0.12
		0.206(1)	Exp. [6]	1.05
		0.20277	Calc. ^f [19]	0.53
(0,1,0)	Σ	0.20405	Present Work ^b	
		0.2033(10)	Exp. [7]	^e
		0.20331	Calc. ^f [19]	0.36
(0,1,0)	Δ	0.20390	Present Work ^b	
		0.20491(36)	Exp. [7]	0.49
		0.20331	Calc. ^f [19]	0.29
(0,2,0)	Π	0.20480	Present Work ^b	
		0.2084(26)	Exp. [7]	1.73
		0.20385	Calc. ^f [19]	0.47
(0,0,1)	Π	0.20283	Present Work ^b	
		0.1984(30)	Exp. [7]	2.23
		0.210(3)	Exp. [5]	3.42
		0.20178	Calc. ^f [19]	0.52
(1,0,0)	Π	0.20322	Present Work ^b	
		0.204	Exp. [5]	0.38
		0.20231	Calc. ^f [19]	0.45

^a $\Delta_{\text{rel}} = 100 \times |B_{\text{eff}}^{(\text{calc})} - B_{\text{eff}}^{(\text{lit})}| / B_{\text{eff}}^{(\text{lit})}$.

^b Average effective rotational constant calculated by RENNER.

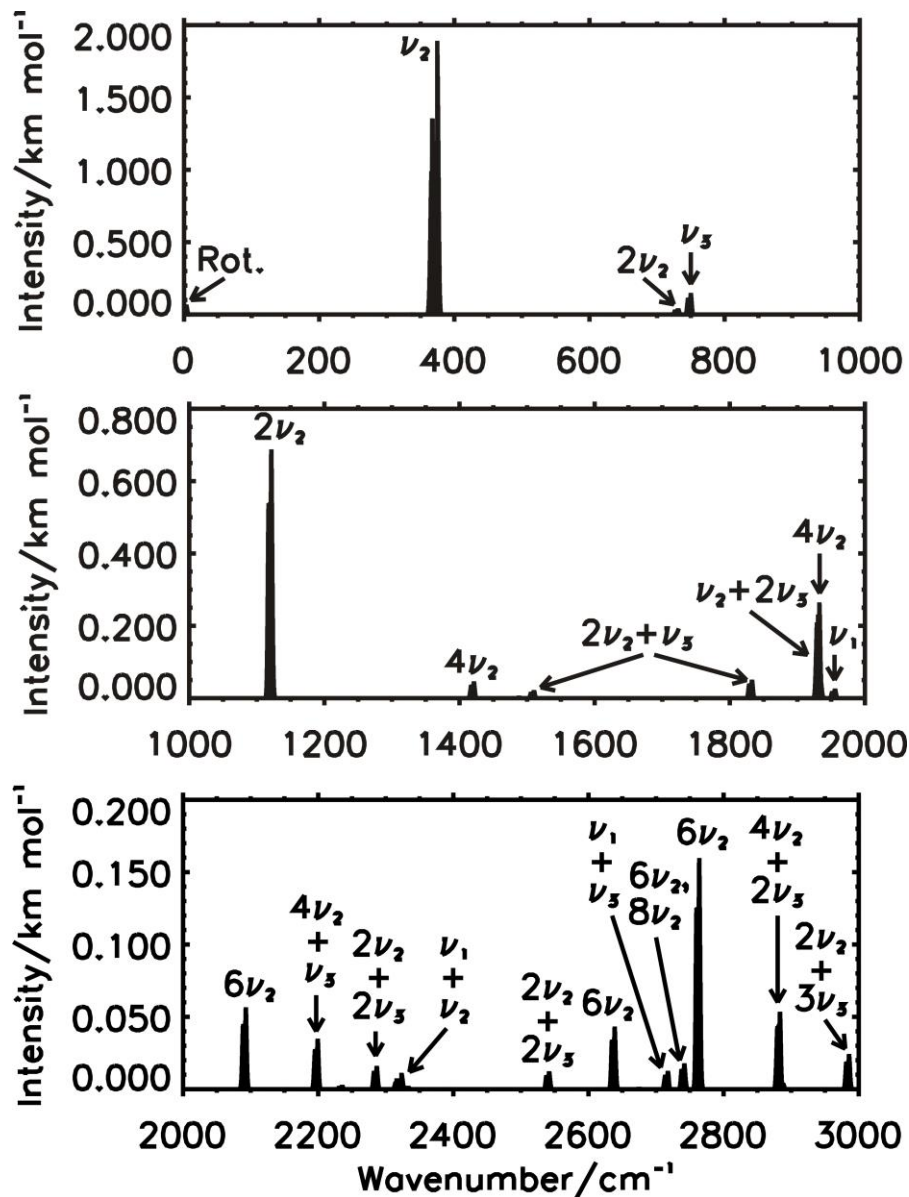
^c The values in parentheses are standard errors in units of the last digit given.

^d From Ref. [6]. Fit to the data of Ref. [5] with an alternative rotational energy model.

^e Theoretical value from the present work is in agreement with the literature value to within the quoted error margins.

^f From Ref. [19]. Obtained from CCSD(T)/cc-pVQZ equilibrium value with CCSD(T)/TZ2P vibration-rotation interaction constants.

Simulated spectra



Thank you for your attention!

- We hope that our new predictions will stimulate experimental work on NCS