Hamiltonian model for $3\nu_2$ and $\nu_4 + \nu_2$ states of ammonia

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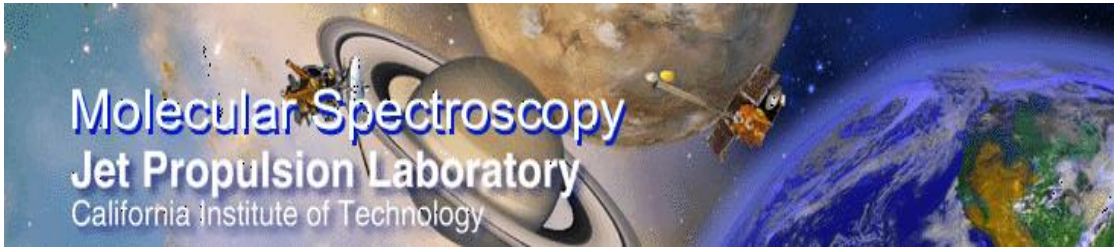

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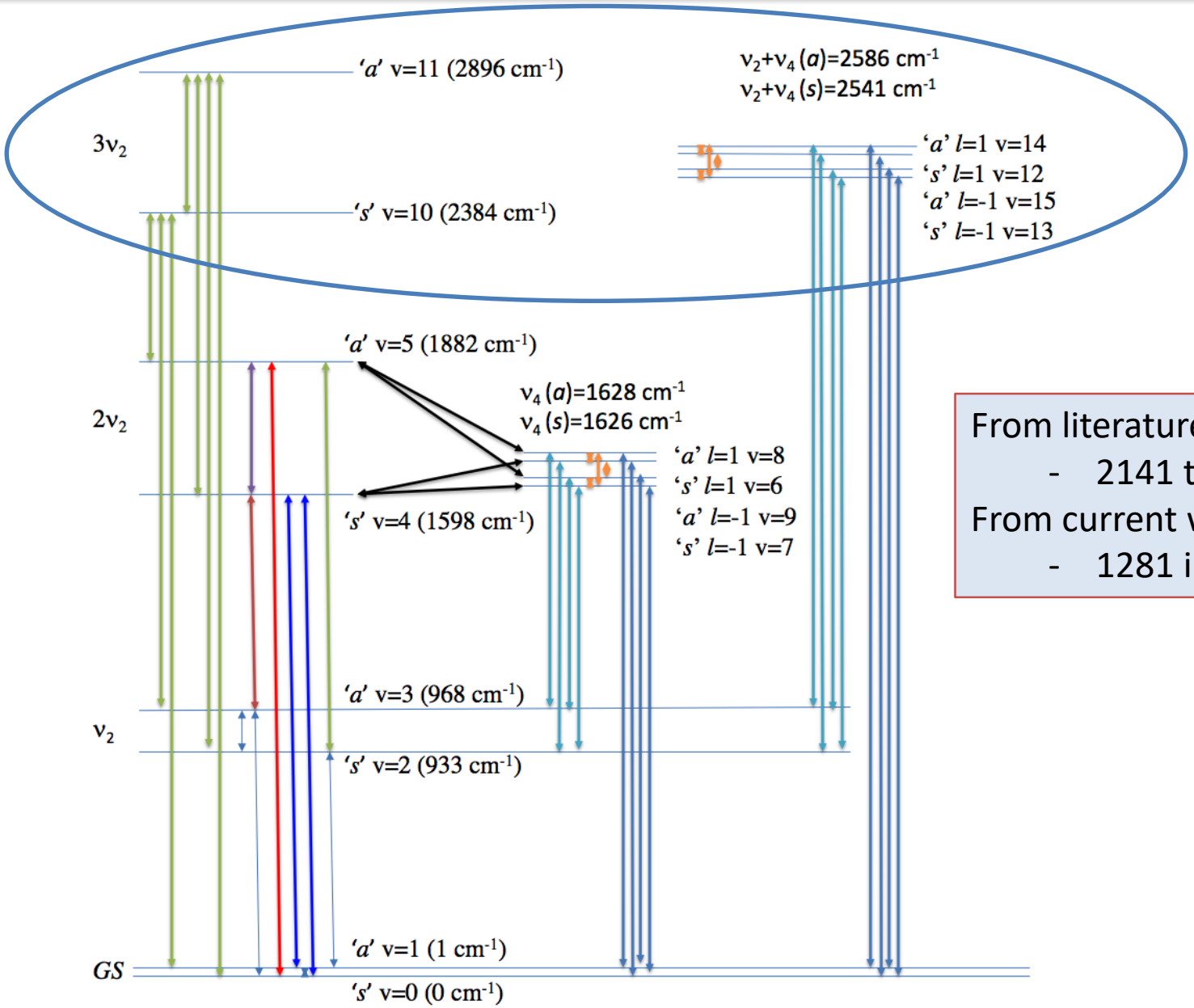
Dataset for the current analysis of NH_3 $3\nu_2/\nu_2+\nu_4$



From literature:

- 2141 transitions

From current work:

- 1281 infrared transitions

Summary of sources for our new data

	Spectrum 1	Spectrum 2	Spectrum 3
Range (cm^{-1})	50-700	50-700	500-2800
Spectra type	Absorption	Emission with an RF discharge	Emission with an RF discharge
Resolution (cm^{-1})	0.0011	0.004	0.004
Optical path (m)	180	0.7	0.7
Gas Pressure (Torr)	1	10	10
Gas Temperature (K)	300	900	900
accuracy	0.0006 cm^{-1}	0.001 cm^{-1}	0.001 cm^{-1}

* The Three FTS spectra from Synchrotron SOLEIL were recorded in 2010 and used in our data analyses of the ground state and ν_2 state (Yu et al. 2010), and the $2\nu_2$ and ν_4 states (Pearson et al. 2016)

Included interactions in NH_3 $3\nu_2/\nu_2+\nu_4$ (1)

	$3\nu_2$; s	$3\nu_2$; a	$\nu_2+\nu_4$; s	$\nu_2+\nu_4$; a
$3\nu_2$; s	Diagonal terms $\Delta(K-l)=0,\pm6,\pm12\cdots$ $\Delta K=\pm6,\Delta l=0: q_6{}^a$	$\Delta(K-l)=\pm3,\pm9\cdots$ $\Delta K=\pm3,\Delta l=0: \alpha_3{}^b$ $\Delta K=\pm9,\Delta l=0: \beta_9{}^c$ **(1)**	$\Delta(K-l)=\pm3,\pm9\cdots$ $\Delta K=\pm2,\Delta l=\mp1: C_2{}^d$ $\Delta K=\pm4,\Delta l=\pm1: C_4{}^e$ $\Delta K=\pm8,\Delta l=\mp1: C_8{}^f$ **(2a)**	$\Delta(K-l)=0,\pm6,\pm12\cdots$ $\Delta K=\pm1,\Delta l=\pm1: \alpha_1{}^g,\beta_1{}^h$ $\Delta K=\pm5,\Delta l=\mp1: \alpha_5{}^i,\beta_5{}^j$ $\Delta K=\pm7,\Delta l=\pm1: \alpha_7{}^k,\beta_7{}^l$ **(3a)**
$3\nu_2$; a		Diagonal terms $\Delta(K-l)=0,\pm6,\pm12\cdots$ $\Delta K=\pm6,\Delta l=0: q_6{}^a$	$\Delta(K-l)=0,\pm6,\pm12\cdots$ $\Delta K=\pm1,\Delta l=\pm1: \alpha_1{}^g,\beta_1{}^h$ $\Delta K=\pm5,\Delta l=\mp1: \alpha_5{}^i,\beta_5{}^j$ $\Delta K=\pm7,\Delta l=\pm1: \alpha_7{}^k,\beta_7{}^l$ **(3b)**	$\Delta(K-l)=\pm3,\pm9\cdots$ $\Delta K=\pm2,\Delta l=\mp1: C_2{}^d$ $\Delta K=\pm4,\Delta l=\pm1: C_4{}^e$ $\Delta K=\pm8,\Delta l=\mp1: C_8{}^f$ **(2b)**
$\nu_2+\nu_4$ s			Diagonal terms $\Delta(K-l)=0,\pm6,\pm12\cdots$ $\Delta K=\pm6,\Delta l=0: q_6{}^a$ Off-diagonal terms in l $\Delta K=\pm2,\Delta l=\pm2: q_2{}^m$ $\Delta K=\pm4,\Delta l=\mp2: q_4{}^n$ $\Delta K=\pm8,\Delta l=\pm2: q_8{}^o$ **(4a)**	$\Delta(K-l)=\pm3,\pm9\cdots$ $\Delta K=\pm3,\Delta l=0: \alpha_3{}^b,\beta_3{}^p$ $\Delta K=\pm1,\Delta l=\mp2: \alpha_1,\beta_1{}^q$ **(5)**
$\nu_2+\nu_4$ a				Diagonal terms $\Delta(K-l)=0,\pm6,\pm12\cdots$ $\Delta K=\pm6,\Delta l=0: q_6{}^a$ Off-diagonal terms in l $\Delta K=\pm2,\Delta l=\pm2: q_2{}^m$ $\Delta K=\pm4,\Delta l=\mp2: q_4{}^n$ $\Delta K=\pm8,\Delta l=\pm2: q_8{}^o$ **(4b)**

Interactions highlighted in orange are not included in previous studies.

Included interactions in NH_3 $3\nu_2/\nu_2+\nu_4$ (2)

a: $(q_6 + q_{6J}J^2 + q_{6K}J_z^2 + q_{6JJ}J^4 + q_{6JK}J^2J_z^2 + q_{6KK}J_z^4 + \cdots)(J_+^6 + J_-^6)$, rotation-inversion, SPFIT operator code: 600VV

b: $(\alpha_3 + \alpha_{3J}J^2 + \alpha_{3K}J_z^2 + \alpha_{3JJ}J^4 + \alpha_{3JK}J^2J_z^2 + \alpha_{3KK}J_z^4 + \cdots)[J_+^3 + J_-^3, J_z]_+$, rotation-inversion, SPFIT operator code: 2300VV

c: $i(\beta_9 + \beta_{9J}J^2 + \beta_{9K}J_z^2 + \beta_{9JJ}J^4 + \beta_{9JK}J^2J_z^2 + \beta_{9KK}J_z^4 + \cdots)(J_+^9 - J_-^9)$, rotation-inversion, SPFIT operator code: 2800VV

d: $(C_2 + C_{2J}J^2 + C_{2K}J_z^2 + C_{2JJ}J^4 + C_{2JK}J^2J_z^2 + C_{2KK}J_z^4 + \cdots)(J_+^2 + J_-^2)$, Coriolis interaction, SPFIT operator code: 400VV

e: $(C_4 + C_{4J}J^2 + C_{4K}J_z^2 + C_{4JJ}J^4 + C_{4JK}J^2J_z^2 + C_{4KK}J_z^4 + \cdots)(J_+^4 + J_-^4)$, Coriolis interaction, SPFIT operator code: 500VV

f: $(C_8 + C_{8J}J^2 + C_{8K}J_z^2 + C_{8JJ}J^4 + C_{8JK}J^2J_z^2 + C_{8KK}J_z^4 + \cdots)(J_+^8 + J_-^8)$, Coriolis interaction, SPFIT operator code: 700VV

g: $(\alpha_1 + \alpha_{1J}J^2 + \alpha_{1K}J_z^2 + \alpha_{1JJ}J^4 + \alpha_{1JK}J^2J_z^2 + \alpha_{1KK}J_z^4 + \cdots)[J_+ + J_-, J_z]_+$, Coriolis interaction, SPFIT operator code: 2100VV

h: $i(\beta_1 + \beta_{1J}J^2 + \beta_{1K}J_z^2 + \beta_{1JJ}J^4 + \beta_{1JK}J^2J_z^2 + \beta_{1KK}J_z^4 + \cdots)(J_+ - J_-)$, Coriolis interaction, SPFIT operator code: 2000VV

i: $(\alpha_5 + \alpha_{5J}J^2 + \alpha_{5K}J_z^2 + \alpha_{5JJ}J^4 + \alpha_{5JK}J^2J_z^2 + \alpha_{5KK}J_z^4 + \cdots)[J_+^5 + J_-^5, J_z]_+$, Coriolis interaction, SPFIT operator code: 2500VV

j: $i(\beta_5 + \beta_{5J}J^2 + \beta_{5K}J_z^2 + \beta_{5JJ}J^4 + \beta_{5JK}J^2J_z^2 + \beta_{5KK}J_z^4 + \cdots)(J_+^5 - J_-^5)$, Coriolis interaction, SPFIT operator code: 2400VV

k: $(\alpha_7 + \alpha_{7J}J^2 + \alpha_{7K}J_z^2 + \alpha_{7JJ}J^4 + \alpha_{7JK}J^2J_z^2 + \alpha_{7KK}J_z^4 + \cdots)[J_+^7 + J_-^7, J_z]_+$, Coriolis interaction, SPFIT operator code: 2700VV

l: $i(\beta_7 + \beta_{7J}J^2 + \beta_{7K}J_z^2 + \beta_{7JJ}J^4 + \beta_{7JK}J^2J_z^2 + \beta_{7KK}J_z^4 + \cdots)(J_+^7 - J_-^7)$, Coriolis interaction, SPFIT operator code: 2600VV

m: $(q_2 + q_{2J}J^2 + q_{2K}J_z^2 + q_{2JJ}J^4 + q_{2JK}J^2J_z^2 + q_{2KK}J_z^4 + \cdots)(J_+^2 + J_-^2)$, *K*-type interaction, SPFIT operator code: 400VV

n: $(q_4 + q_{4J}J^2 + q_{4K}J_z^2 + q_{4JJ}J^4 + q_{4JK}J^2J_z^2 + q_{4KK}J_z^4 + \cdots)(J_+^4 + J_-^4)$, *K*-type interaction, SPFIT operator code: 500VV

o: $(q_8 + q_{8J}J^2 + q_{8K}J_z^2 + q_{8JJ}J^4 + q_{8JK}J^2J_z^2 + q_{8KK}J_z^4 + \cdots)(J_+^8 + J_-^8)$, *K*-type interaction, SPFIT operator code: 700VV

p: $i(\beta_3 + \beta_{3J}J^2 + \beta_{3K}J_z^2 + \beta_{3JJ}J^4 + \beta_{3JK}J^2J_z^2 + \beta_{3KK}J_z^4 + \cdots)(J_+^3 - J_-^3)$, rotation-inversion, SPFIT operator code: 2200VV

q: same as g and h, L-type interaction

Interactions highlighted in orange are not included in previous studies.

Fit statistics for datasets involving $3\nu_2$ and $\nu_2+\nu_4$

Reference	Band type	Experimental				Model			
		# of reference lines	J' range	K' range	Uncertainty	RMS (cm^{-1})	Reduced RMS	Avg residual	# of excluded lines
95KlTaBr	$3n_2$	694	0-12	0-12	0.0003-0.007	0.0008	1.2	0.0002	10
	n_4+n_2	1333	0-13	0-13	0.0003-0.005	0.001	2.4	-0.00002	82
13DoHiYuTe	$3n_2- 2n_2$	99	1-10	1-10	0.0004-0.005	0.003	0.7	0.0001	27
Present work	$3n_2$ inversion	317	0-13	0-13	0.0003-0.006	0.001	1.4	-0.0002	0
	$3n_2- 2n_2$	543	0-14	0-14	0.0003-0.003	0.001	2.0	-0.0005	0
	$3n_2- n_4$	12	8-13	0-12	0.001	0.0009	0.9	-0.0006	0
	$3n_2- n_2$	29	3-15	0-9	0.001	0.001	1.3	-0.0009	0
	n_4+n_2 inversion	313	3-15	1-14	0.0003-0.005	0.002	2.2	-0.00002	9
	$n_4+n_2- 2n_2$	36	3-14	0-13	0.001	0.001	1.5	-0.0007	0
	$n_4+n_2- n_4$	30	3-11	0-12	0.001	0.001	1.5	-0.001	0

Comparison of some parameters (in cm^{-1})

Parameter name[a]			$3\nu_2$ (s)			$\nu_2+\nu_4$ (s)	
This work	Cottaz 2001		This work	Cottaz 2001		This work	Cottaz 2001
B	same		9.5221268(84)	9.49981(29)		10.324520(18)	10.31504(12)
C	same		6.195903(48)	6.19169(39)		6.015636(34)	6.01800(15)
$D_J \times 10^3$	same		-0.23049(30)	-0.2639(42)		1.33433(49)	1.3122(11)
$D_{JK} \times 10^2$	same		0.07620(73)	0.1282(10)		-0.31760(45)	-0.27747(69)
$D_K \times 10^3$	same		-0.4788(67)	-0.9440(78)		2.1029(55)	1.6843(75)
$C\zeta_4$	same		-	-		-1.30722718(13)	-1.30276(51)
$\eta_J \times 10^2$	same		-	-		-0.3339(16)	-0.2111(30)
$\eta_K \times 10^2$	same		-	-		0.2484(16)	0.1184(33)
$\alpha_3 \times 10^3$	$q_{3v} \times 10^3$		-0.5618 (78)	-0.278(26)		-0.25753(73)	-0.2258(33)
α_1	q_1		-	-		0.21978(27)	0.11074(26)
$\alpha_{1J} \times 10^3$	$q_{1J} \times 10^3$		-	-		-0. 1719(12)	-0.1316(26)
$\alpha_{1K} \times 10^4$	$q_{1K} \times 10^4$		-	-		-3.48(18)	0.636(44)
β_1	-		-	-		0.06188(46)	-
q_2	same		-	-		0.131555(19)	0.124686(90)
$q_{2J} \times 10^4$	same		-	-		-0.65427(77)	-0.8220(84)
$q_{2K} \times 10^4$	same		-	-		-1.99(18)	-0.632(34)
$q_4 \times 10^4$	same		-	-		0.18461(43)	0.1718(66)
C_2	same		-	-		0.032755(96)	0.01158966)

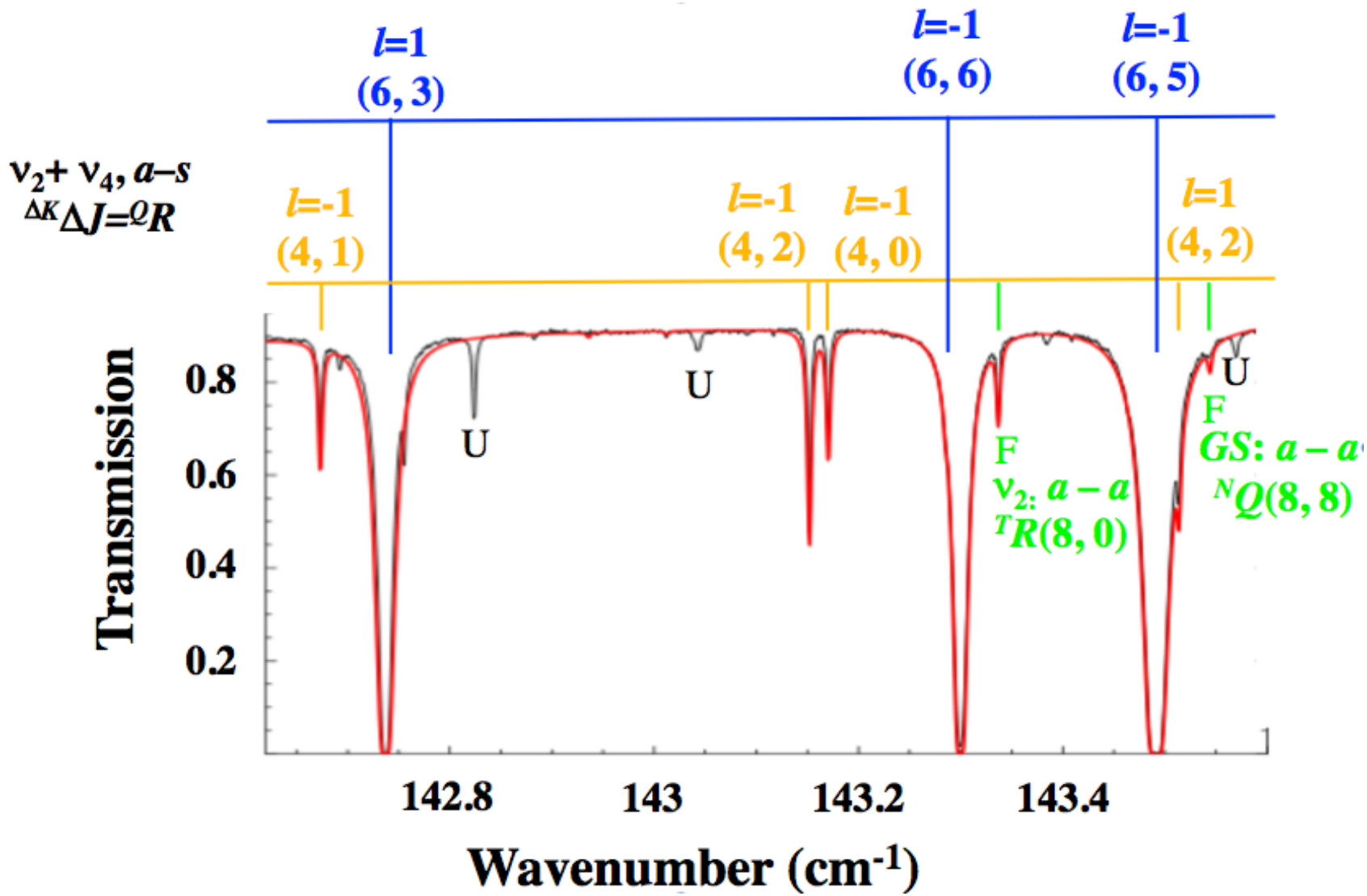
[a] The names for some Coriolis interactions were defined differently in the current work and in Cottaz et al. 2001.

Comparison of interactions in $2\nu_2/\nu_4$ and $3\nu_2/\nu_2+\nu_4$

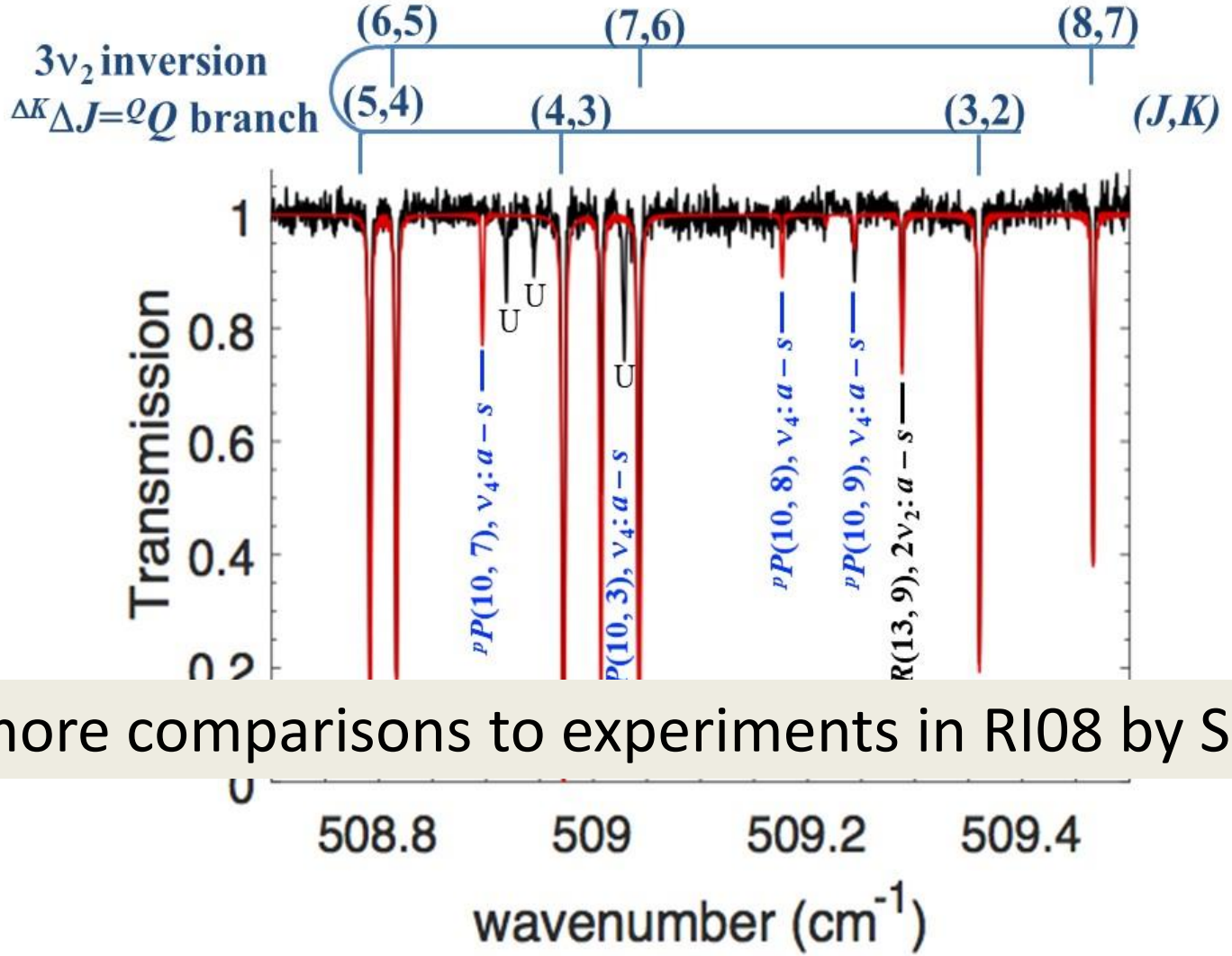
Parameter		$2n_2/n_4$ (Pearson et al 2016)	$3n_2/n_2+n_4$ (this work)	Ratio
Block #[a]	name			
1	a_3	-4.407(166)	-16.841(233)	3.8
	b_9	0.1580(57)E-06	-0.2862(269)E-06	-1.8
2a/2b	C_2	514.85(45)	981.96(287)	1.9
	C_4	-0.9023(95)	0.5745(140)	-0.6
	C_8	-3.071(180)E-06	-3.02(34)E-06	1.0
3a/3b	a_1	127.87(293)	-4650(47)	-36.4
	b_1	74603.62(257)	96861(45)	1.3
	a_5	-0.6074(260)E-03	0.02742(38)	-45.1
	b_5	-0.02680(32)	0.10614(156)	-4.0
	a_7	1.853(133)E-06	-1.858(311)E-06	-1.0
	b_7	-1.21(74)E-06	0.1758(79)E-03	-145.3
4a/4b	q_2	-4608.0900(307)	-3943.93(56)	0.9
	q_4	-0.3274(69)	-0.55345(128)	1.7
	q_8	-1.772(205)E-06	0.892(73)E-06	-0.5
5	a_1	6648.0(39)	6588.7(82)	1.0
	b_1	343.86(97)	1855.2(137)	5.4
	a_5	1.511(78)	-7.7205(220)	-5.1
	b_5	-6.921(35)	0.988(86)	-0.1

[a] Block numbers were defined in Slide #4

Observed and simulated spectrum (1)



Observed and simulated spectrum (2)



See more comparisons to experiments in RI08 by Sung

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