Updated line-list of $^{16}O_3$ in the range 5860 – 7000 cm^{-1} deduced from CRDS spectra.

A. Barbe, M.R. De Backer-Barilly, Vl.G. Tyuterev, A. Campargue[1], S.Kassi[1]

Groupe de Spectrométrie Moléculaire et Atmosphérique, UMR CNRS 6089

Université de Reims Champagne – Ardenne

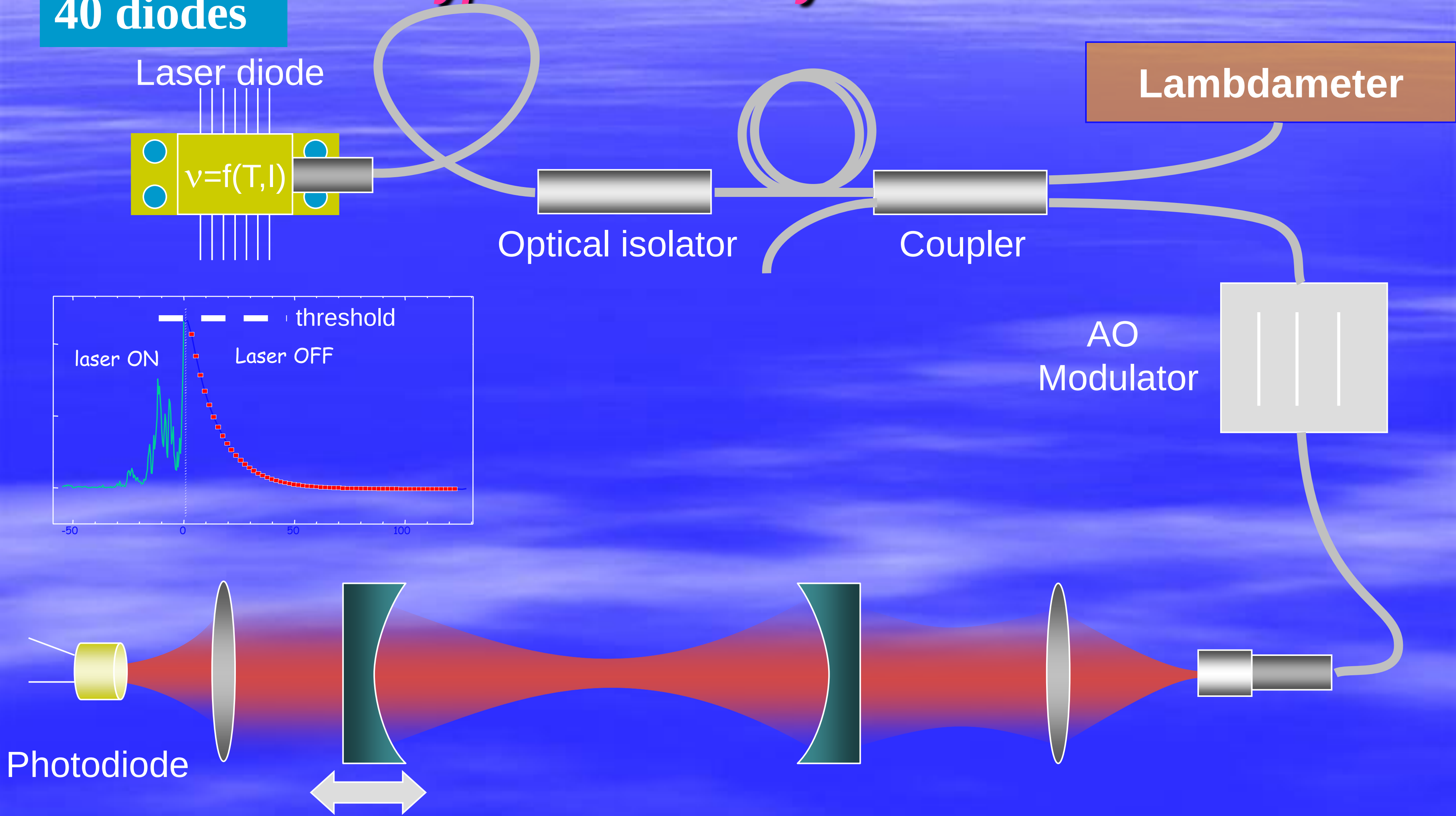
France

[1] Laboratoire de Spectrométrie Physique, UMR CNRS 5588, Université Joseph Fourier, Saint Martin d'Hères, France

The compact fibered CW-CRDS spectrometer (Grenoble) 1480-1687 nm (5800-7000 cm^{-1})

6nm/diode
40 diodes

Typical sensitivity 3×10^{-10} cm^{-1}



HAMILTONIAN

Diagonal block

$$H^{VV} = E^{VV} + \left[A - \frac{1}{2}(B+C)\right]J_z^2 + \frac{1}{2}(B+C)\mathbf{J}^2 + \frac{1}{2}(B-C)J_{xy}^2 - \Delta_K J_z^4 - \Delta_{JK} J_z^2\,\mathbf{J}^2 - \Delta_J\left(\mathbf{J}^2\right)^2$$
$$-\delta_K\left\{J_z^2, J_{xy}^2\right\} - 2\delta_J J_{xy}^2\,\mathbf{J}^2 + H_K J_z^6 + H_{KJ} J_z^4\,\mathbf{J}^2 + H_{JK} J_z^2\left(\mathbf{J}^2\right)^2 + H_J\left(\mathbf{J}^2\right)^3 + h_K\left\{J_z^4, J_{xy}^2\right\}$$
$$+ h_{KJ}\left\{J_z^2, J_{xy}^2\right\}\mathbf{J}^2 + 2h_J J_{xy}^2\left(\mathbf{J}^2\right)^2 + L_K J_z^8$$

where $\{A,B\} \equiv AB + BA$ and $J_{xy}^2 = J_x^2 - J_y^2$

Extradiagonal blocks

$$H_{Coriolis}^{VV'} = C_{001}(J_+ - J_-) + C_{011}\left(J_+(J_z + 1/2) + (J_z + 1/2)J_-\right) + C_{021}\left(J_+(J_z + 1/2)^2 - (J_z + 1/2)^2 J_-\right)$$
$$+ C_{201}\,\mathbf{J}^2(J_+ - J_-) + C_{003}\left(J_+^{\,3} - J_-^{\,3}\right) + C_{031}\left(J_+(J_z + 1/2)^3 - (J_z + 1/2)^3 J_-\right)$$
$$+ C_{211}\,\mathbf{J}^2\left(J_+(J_z + 1/2) + (J_z + 1/2)J_-\right) + \ldots$$

where $J_\pm = J_x \pm \frac{1}{i} J_y$

$$H_{Anharm}^{VV'} = F_{000} + F_{200}\,\mathbf{J}^2 + F_{020} J_z^2 + F_{002}\left(J_+^2 + J_-^2\right) + F_{022}\left[J_+^2 (J_z + 1)^2 + (J_z + 1)^2 J_-^2\right] + F_{202}\mathbf{J}^2\left(J_+^2 + J_-^2\right) + \ldots$$

Assignments :

- ♦ **vibration** : predictions from Vl. G. Tyuterev – keep the usual label $v_1\ v_2\ v_3$.
- ♦ **rotation** : use of ASSIGN program (Chichery A.) based on Ground State Combination Differencies (GSCD) - J Ka Kc
- ♦ **calculation of energy levels, transitions, and intensities :** GIP program. (S. A. Taskhun)

Intensity calculations

The linestrenghths are calculated using the following effective transition moment operators :

For A-Type band : $v_3' - v_3$ odd

$$^{(v_1v_2v_3)(v_1'v_2'v_3')}\tilde{\mu}_z = d_1\varphi_z + d_2\{\varphi_z, J^2\} + d_3\{\varphi_z, J_z^2\} + d_4\frac{1}{2}[\{\varphi_x, iJ_y\} - \{i\varphi_y, J_x\}] + d_5\frac{1}{2}[\{\varphi_x, \{J_x, J_z\}\} - \{i\varphi_y, i\{J_y, J_z\}\}] + d_6\frac{1}{2}[\{\varphi_x, iJ_y\} + \{i\varphi_y, J$$

$$+ d_7[\{\varphi_x, \{J_x, J_z\}\} + \{i\varphi_y, i\{J_y, J_z\}\}] + d_8\{\varphi_z, J_{xy}^2\}$$

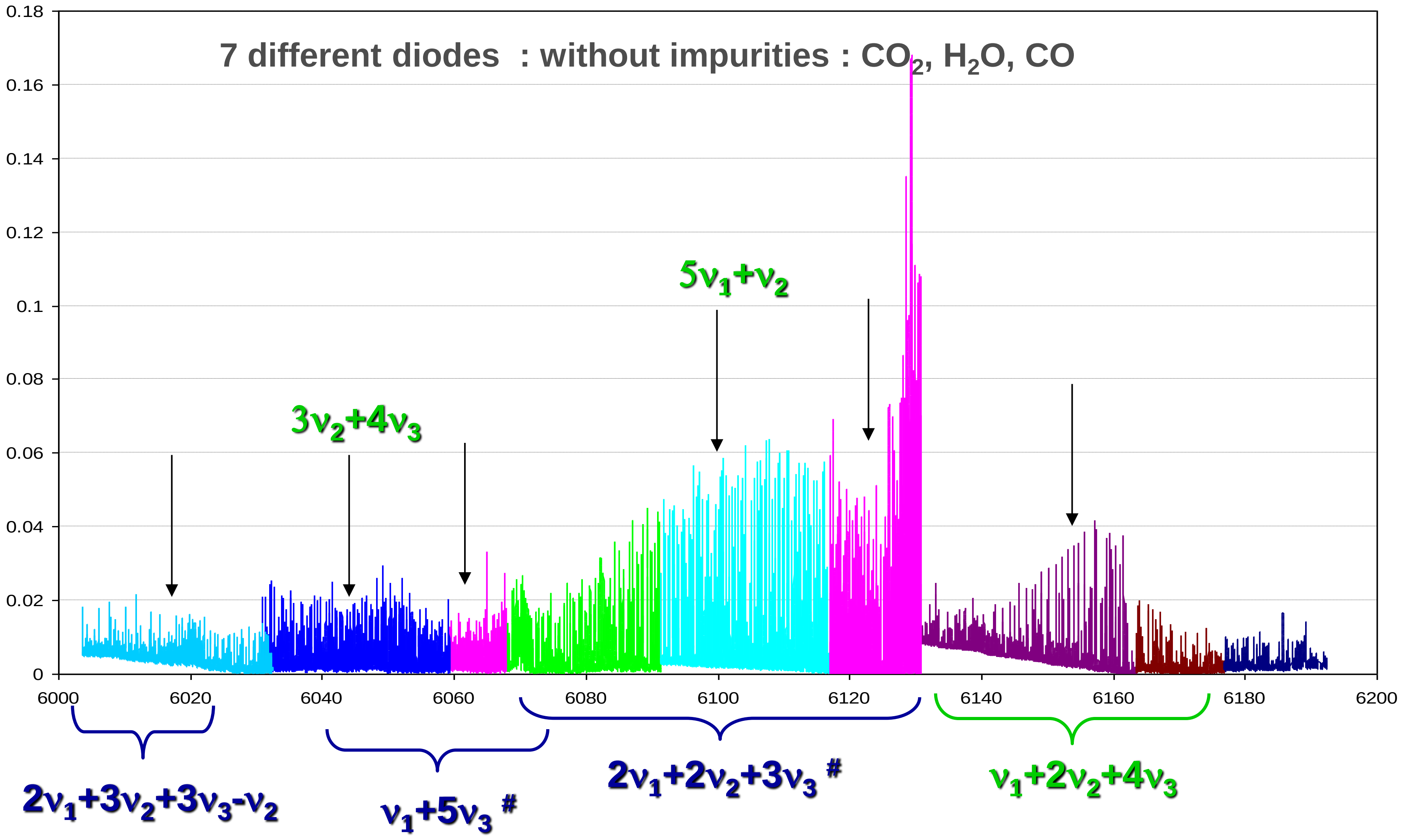
For B-Type band : $v_3' - v_3$ even

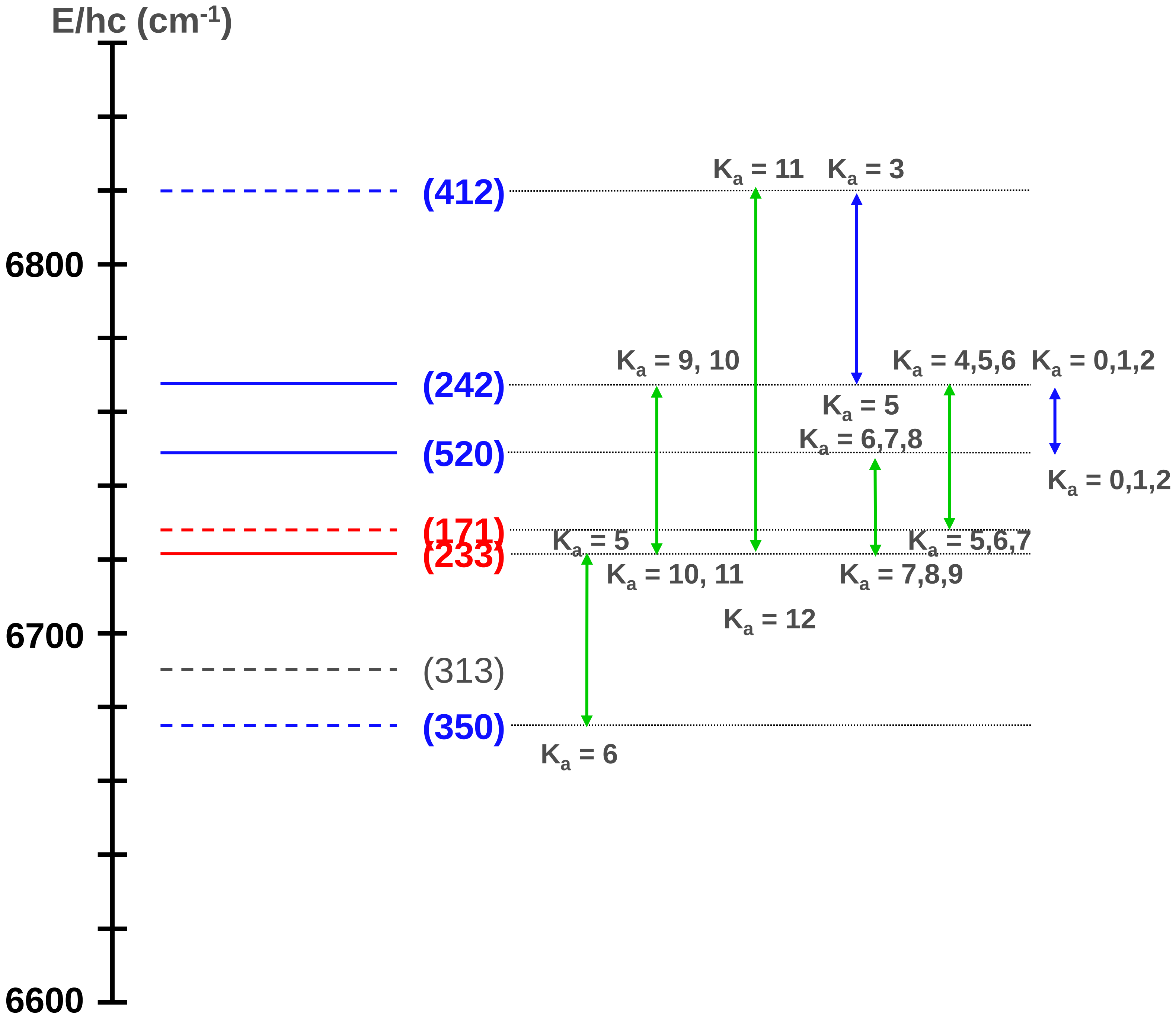
$$^{(v_1v_2v_3)(v_1'v_2'v_3')}\tilde{\mu}_z = d_1\varphi_x + d_2\{\varphi_x, J^2\} + d_3\{\varphi_x, J_z^2\} + d_4\{i\varphi_y, J_z\} + d_5\{\varphi_z, iJ_y\} + d_6\{\varphi_z, \{J_x, J_z\}\} + d_7\frac{1}{2}[\{\varphi_x, J_{xy}^2\} - \{i\varphi_y, i\{J_x, J_y\}\}]$$

$$+ d_8\frac{1}{2}[\{\varphi_x, J_{xy}^2\} + \{i\varphi_y, i\{J_x, J_z\}\}]$$

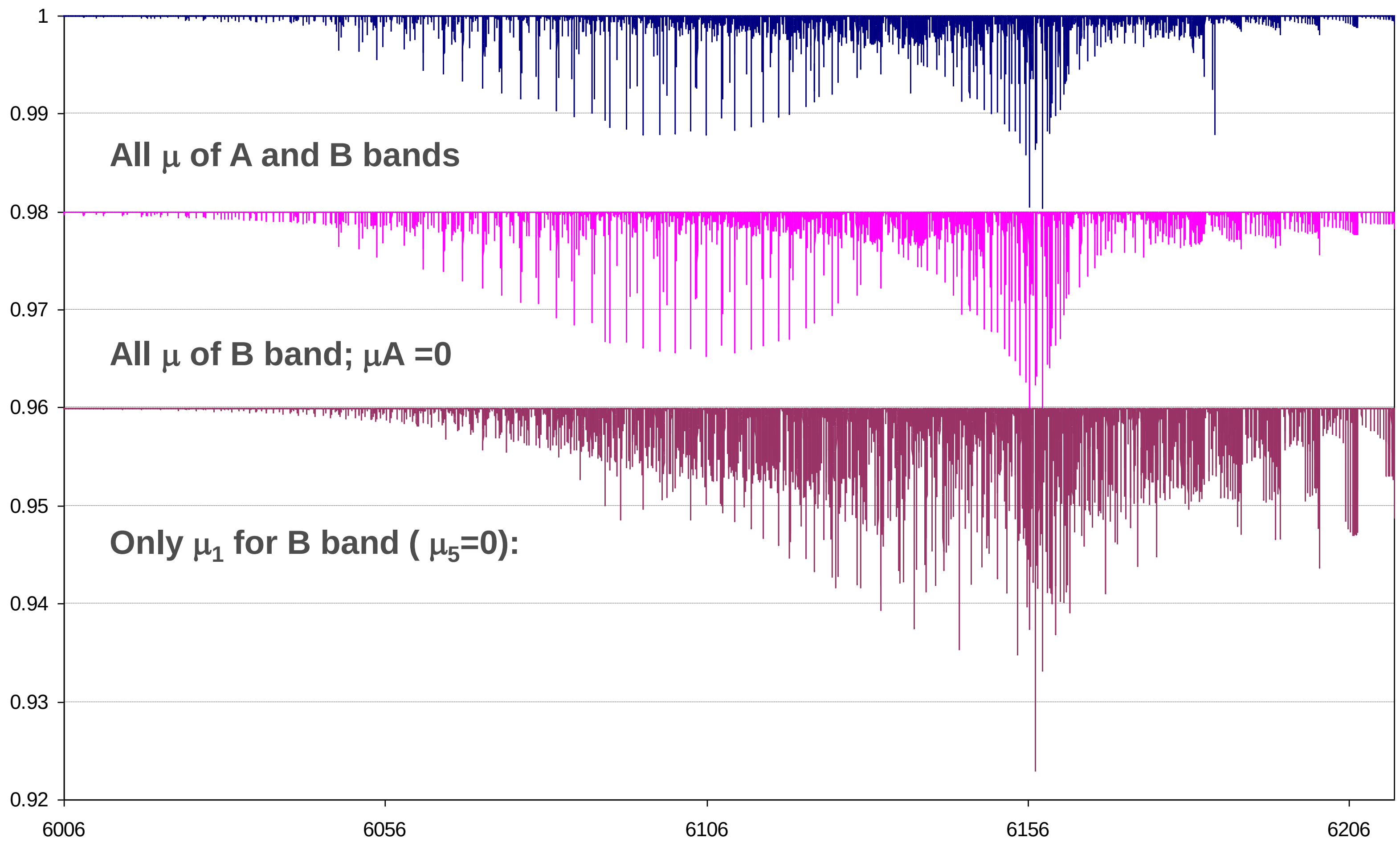
$\{A, B\} = AB + BA$ $\qquad$ $d_i = {}^{vv'}d_i$

Global survey of the 6000 – 6200 cm^{-1} spectral range




E/hc (cm-1)
6800
6700
6600
(412)
(242)
(520)
(171)
(233)
(313)
(350)
Ka = 11
Ka = 3
Ka = 9, 10
Ka = 4,5,6
Ka = 0,1,2
Ka = 5
Ka = 6,7,8
Ka = 0,1,2
Ka = 5
Ka = 5,6,7
Ka = 10, 11
Ka = 7,8,9
Ka = 12
Ka = 6

Calculated spectra of $\nu_1+2\nu_2+4\nu_3$ in 3 cases (normalisation on observed lines in the 6155 cm^{-1} region)



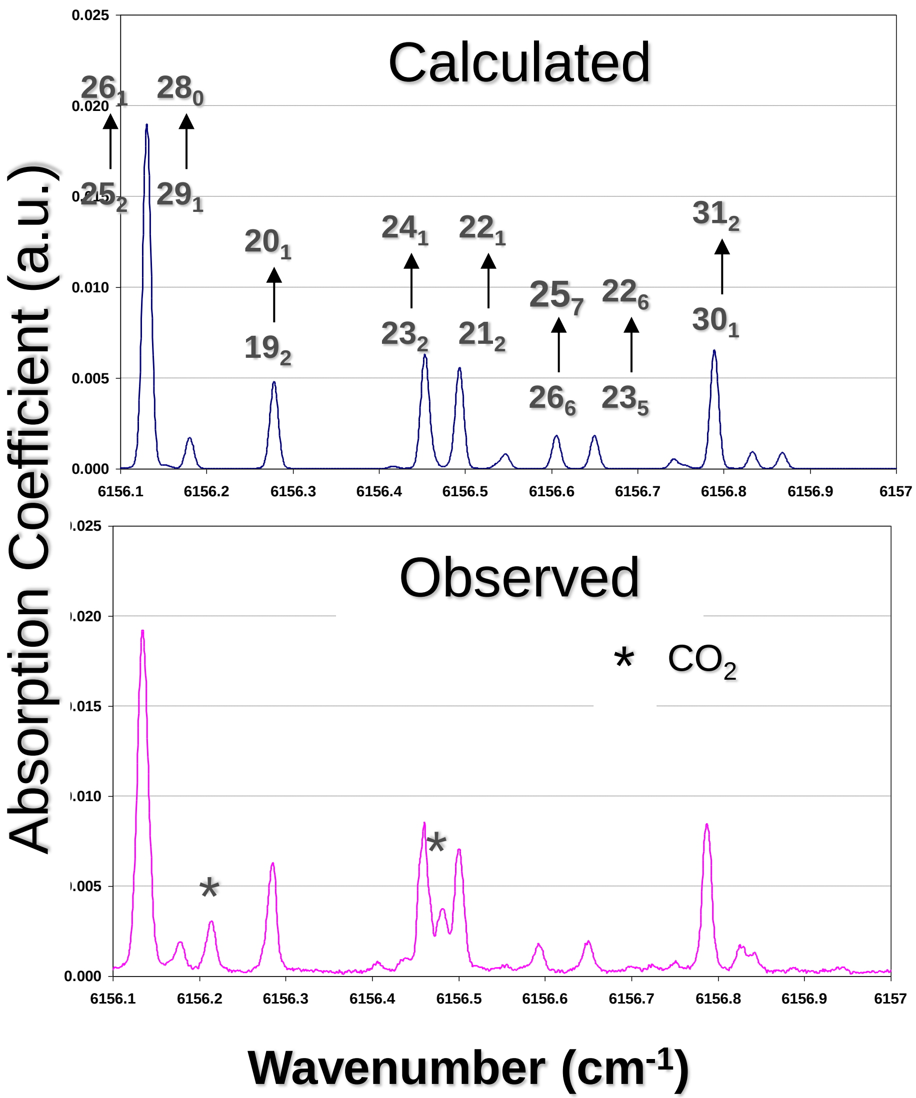
Assigned transitions in the range 6000—6900cm-1

Nature of the work	Vibrational Assignment	Band center	Number of transitions	J max	K_a max
completed	233-010	6015.605	350	37	11
completed	034-000	6046.970	138	40	4
completed	105-000	6063.933	531	43	10
completed	510-000 *	6100.216	122	29	4
completed	223-000	6124.286	520	44	14
completed	124-000*	6154.702	498	49	7
completed	331-000	6198.534	116	23	6
In progress	025-000	6305.039	992	39	12
In progress	501-000	6355.739	593	37	10
In progress	223-000	6386.981	548	36	11
In progress	421-000	6568.079	65	27	2
In progress	205-000	6586.969	398	37	6
completed	233-000	6716.536	483	37	12
completed	520-000 *	6751.246	22	33	7
completed	242-000 *	6764.456;	399	46	9
In progress	007-000	6895.493	284	29	11
			TOTAL :	5959	

Improvements since 2006

- 1. Theoretical predictions of rotational constants available
- 2.Experimental range extended
- 3.Model of B type bands improved
- 4. Obvious: a lot of work

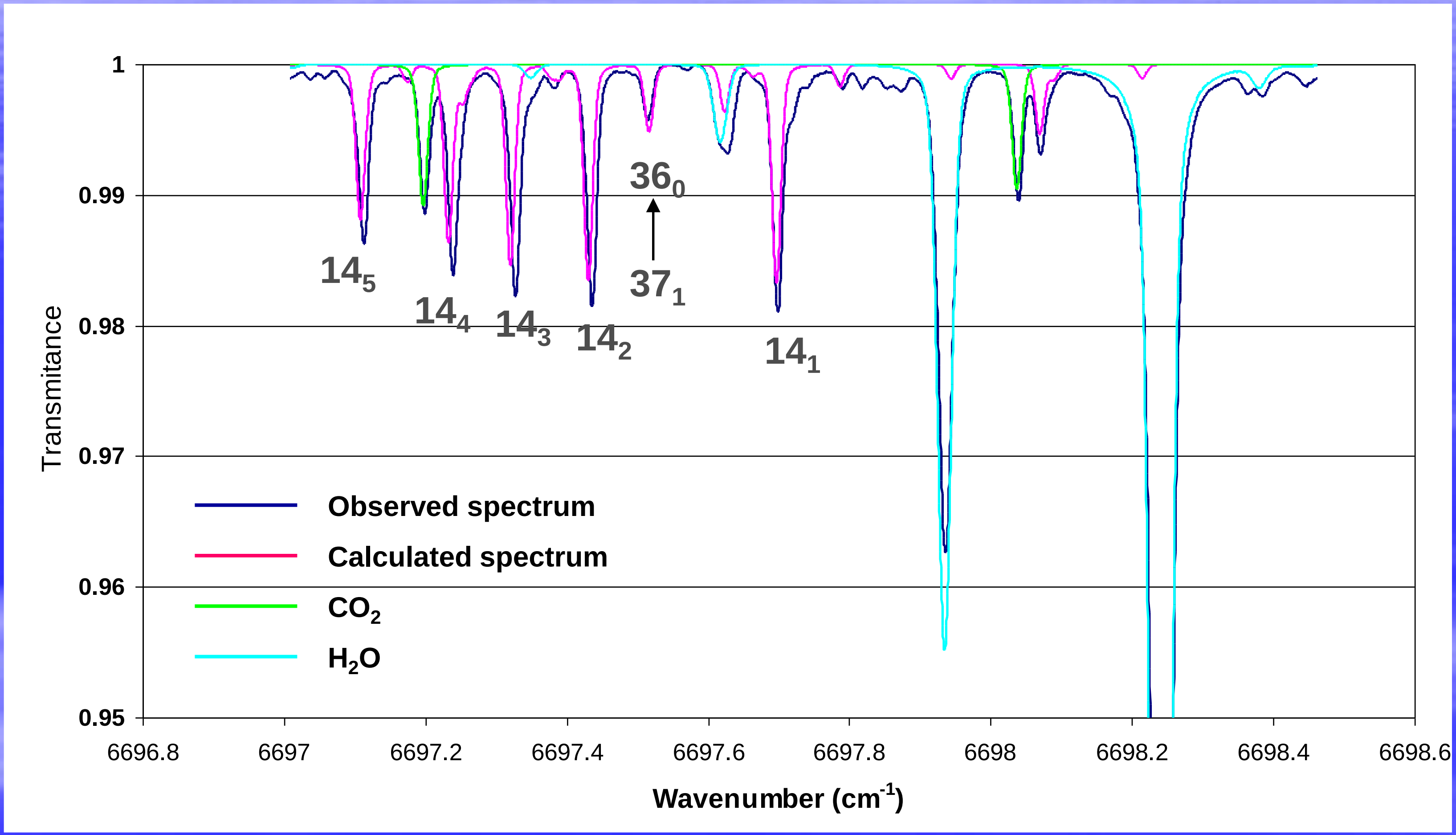
Observed and calculated spectrum of the $\nu_1 + 2\nu_2 + 4\nu_3$ band in the 6156 – 6157 cm^{-1} range



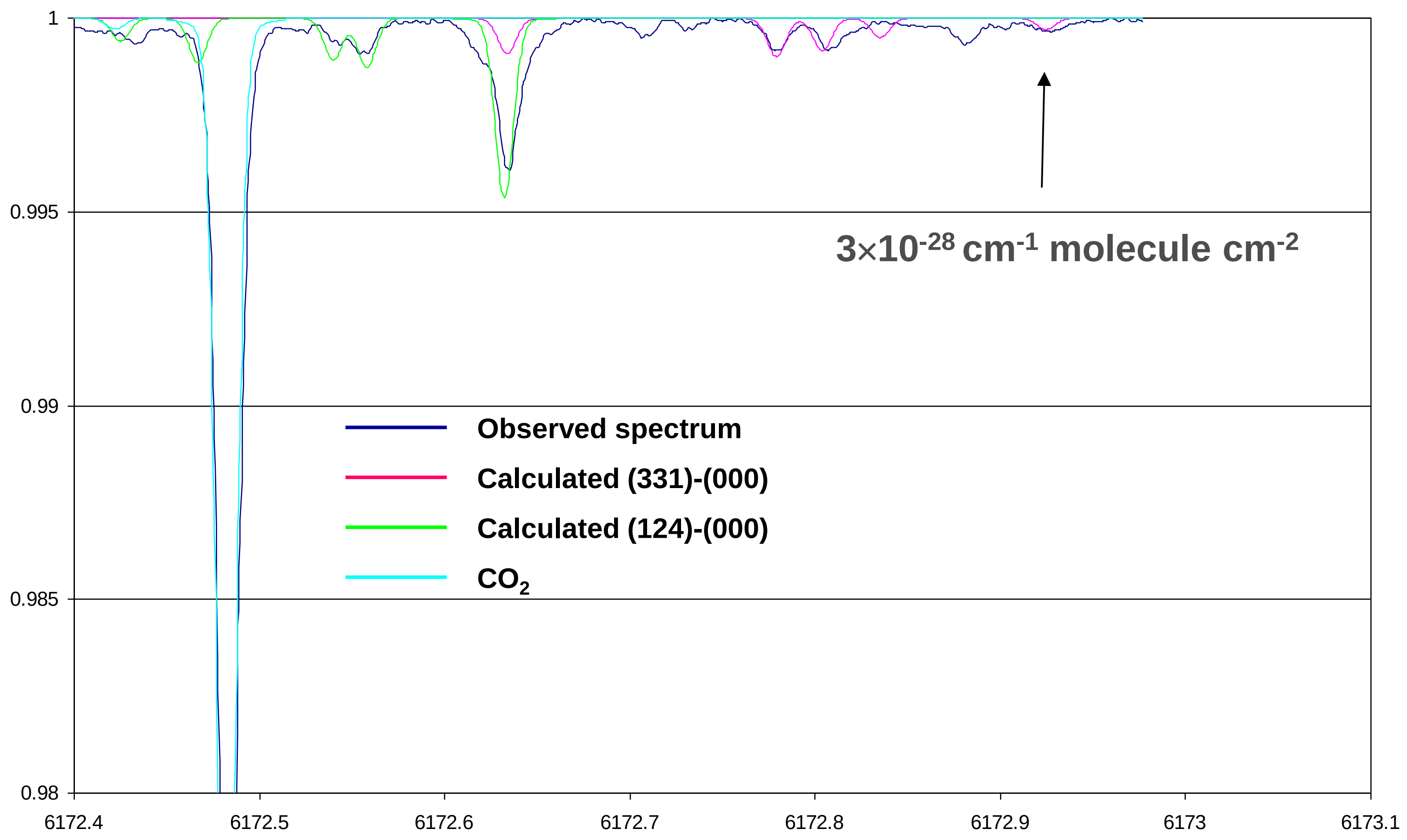
Summary of the observations and Spectroscopic parameters of the effective Hamiltonian model for the (511) and (233) vibrational states of $^{16}O_3$ (in cm^{-1}).

	(511)	(233)	(440)
Number of transitions	161	231	
Number of levels	126	168	
J max	25	25	
K_a *max*	10	9	
E^V	$6981.87040_0(94)$	$6990.0689_0(16)$	$6999.039_2(45)$
A-(B+C)/2	$3.080380_7(42)$	$3.14122_2(13)$	$3.3446_5(44)$
(B+C)/2	$0.3986179_9(74)$	$0.393062_7(86)$	$0.39850_3(14)$
(B-C)/2	$0.0247969_7(40)$	$0.02601_3(60)$	$0.02362_7(16)$
$D_K \times 10^3$	$0.32492_3(60)$	$0.2465_1(12)$	0.21168727(g)
$D_{JK} \times 10^5$	-0.1848469(g)	$-0.831_0(20)$	-0.1848469(g)
$D_J \times 10^6$	$0.884_3(13)$	$0.139_8(20)$	0.4541691(g)
		$C_{001}^{440,233} = 0.0924_7(21)$	
		$C_{011}^{440,233} = -0.00980_6(11)$	
rms (10^{-3} cm^{-1})	3.7	7.2	

Comparison between Obs. and Calc. spectrum in the P branch of $2\nu_1+3\nu_2+3\nu_3$ (J'= 14)



(331-000) the weakest band observed so far



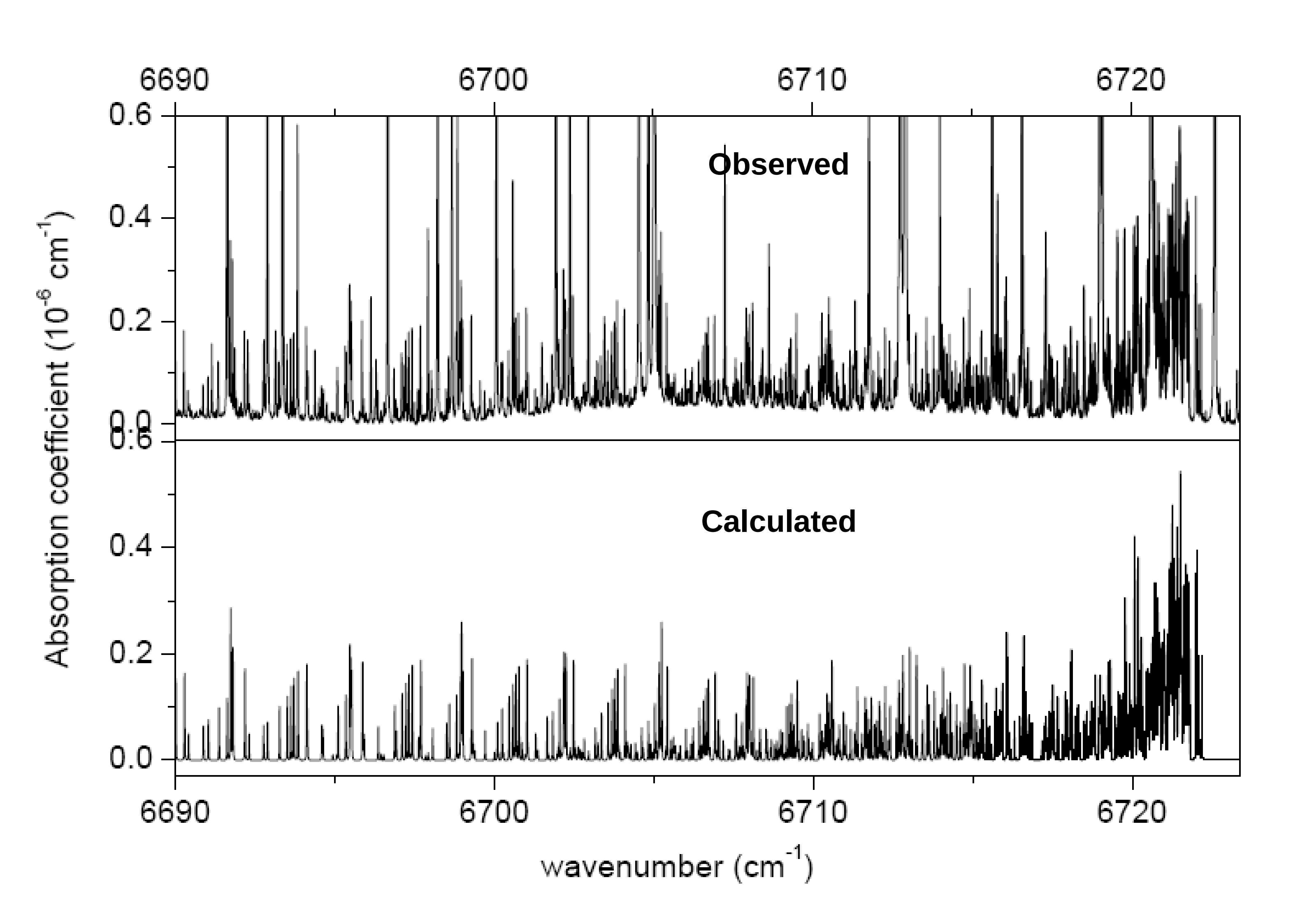
Example of derived energy levels with number of transitions, error and O-C in case of the (331) state

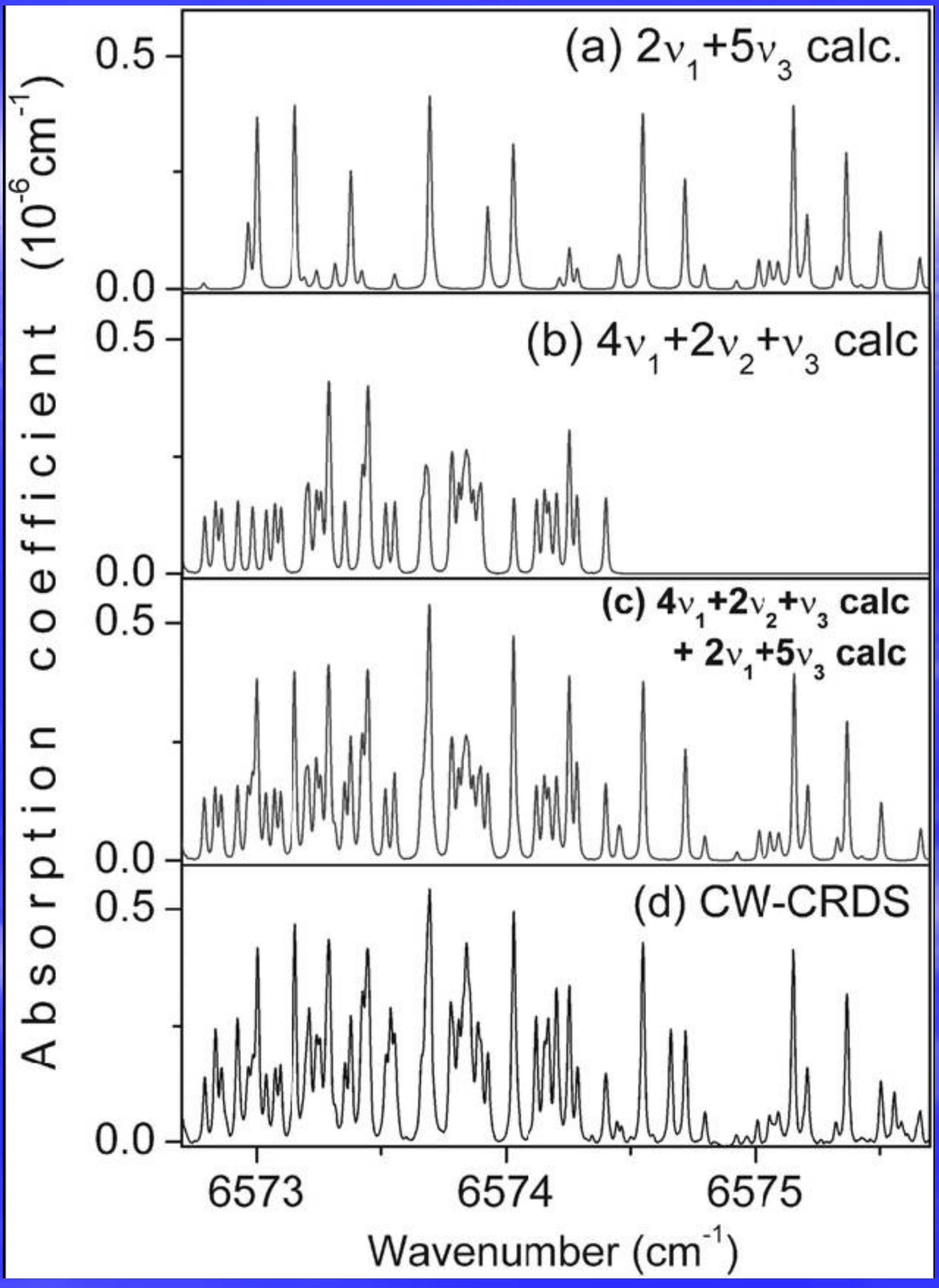
J	*Ka*	*Kc*	*Eobs*	*Nb*	*ΔE*	*o-c*
1	0	1	5919.9515	1		-2.8
3	0	3	5923.9178	2	0.3	-1.5
5	0	5	5931.0402	2	1.2	-1.2
7	0	7	5941.2951	2	0.2	-0.4
9	0	9	5954.6453	2	0.4	-1.9
11	0	11	5971.0547	2	1.0	-0.9
13	0	13	5990.4747	1		-4.0
15	0	15	6012.8779	1		-2.6
17	0	17	6038.2314	1		-3.0
19	0	19	6066.5240	1		-1.8
21	0	21	6097.7468	1		-1.9
23	0	23	6131.9023	1		-1.0
25	0	25	6168.9914	1		-0.8
27	0	27	6209.0190	2	0.6	0.5
29	0	29	6251.9865	2	0.9	0.9
31	0	31	6297.8949	2	0.6	-0.6

Example of final line-list for the $3\nu_1+3\nu_2+\nu_3$ band.

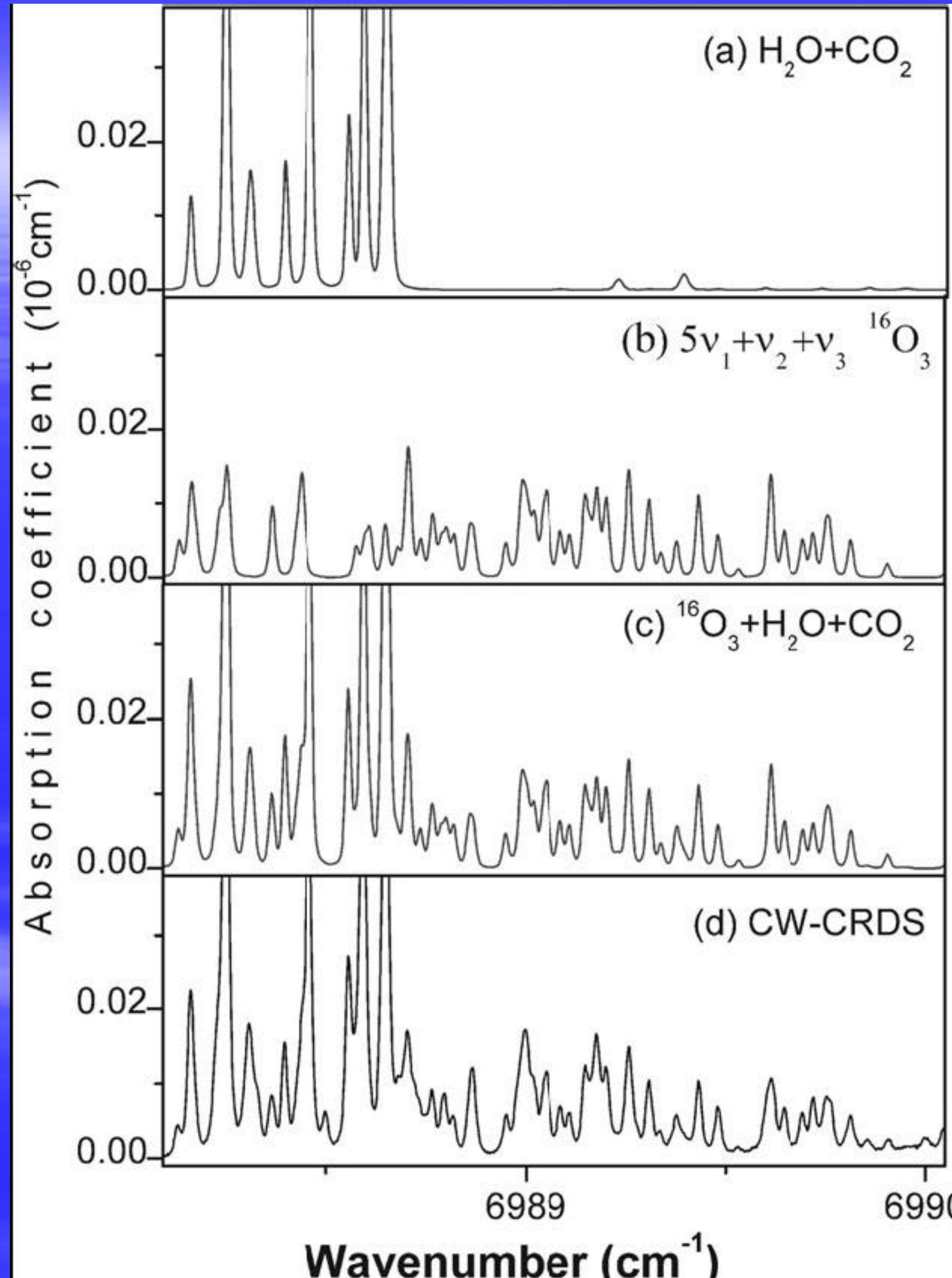
Freq.	Int.	E low	vup	J	Ka Kc	vlow	J	Ka Kc	isotope
6163.48607	0.747E-27	302.58362	3 3 1	25	1 24	0 0 0	26	1 25	31
6167.10164	0.850E-27	259.66969	3 3 1	23	1 22	0 0 0	24	1 23	31
6167.55099	0.912E-27	245.49835	3 3 1	23	0 23	0 0 0	24	0 24	31
6169.36300	0.959E-27	226.45186	3 3 1	22	1 22	0 0 0	23	1 23	31
6169.77600	0.711E-27	282.32885	3 3 1	22	4 19	0 0 0	23	4 20	31
6170.56671	0.946E-27	219.93833	3 3 1	21	1 20	0 0 0	22	1 21	31
6170.97789	0.838E-27	241.83170	3 3 1	21	3 18	0 0 0	22	3 19	31
6171.03200	0.101E-26	207.56234	3 3 1	21	0 21	0 0 0	22	0 22	31
6171.51095	0.745E-27	262.99506	3 3 1	21	4 17	0 0 0	22	4 18	31
6172.63313	0.962E-27	205.63536	3 3 1	20	2 19	0 0 0	21	2 20	31
6172.78000	0.104E-26	190.21251	3 3 1	20	1 20	0 0 0	21	1 21	31
6172.80706	0.877E-27	222.57162	3 3 1	20	3 18	0 0 0	21	3 19	31
6173.22670	0.776E-27	244.42024	3 3 1	20	4 17	0 0 0	21	4 18	31
6173.86912	0.103E-26	183.43074	3 3 1	19	1 18	0 0 0	20	1 19	31
6174.33459	0.108E-26	172.75680	3 3 1	19	0 19	0 0 0	20	0 20	31
6174.38445	0.906E-27	205.32847	3 3 1	19	3 16	0 0 0	20	3 17	31
6175.49300	0.684E-27	254.76284	3 3 1	19	5 14	0 0 0	20	5 15	31
6175.88932	0.103E-26	171.50149	3 3 1	18	2 17	0 0 0	19	2 18	31
6176.02192	0.111E-26	157.14710	3 3 1	18	1 18	0 0 0	19	1 19	31
6177.03057	0.109E-26	150.18998	3 3 1	17	1 16	0 0 0	18	1 17	31
6177.12529	0.104E-26	158.16527	3 3 1	17	2 15	0 0 0	18	2 16	31
6177.46871	0.114E-26	141.08198	3 3 1	17	0 17	0 0 0	18	0 18	31
6178.09768	0.839E-27	193.90699	3 3 1	17	4 13	0 0 0	18	4 14	31
6179.10400	0.115E-26	127.26394	3 3 1	16	1 16	0 0 0	17	1 17	31
6179.21033	0.967E-27	156.90332	3 3 1	16	3 14	0 0 0	17	3 15	31
6179.65200	0.848E-27	178.74687	3 3 1	16	4 13	0 0 0	17	4 14	31
6180.04180	0.112E-26	120.25713	3 3 1	15	1 14	0 0 0	16	1 15	31

Final comparison between Observed and Calculated spectrum ($2\nu_1+3\nu_2+3\nu_3$)





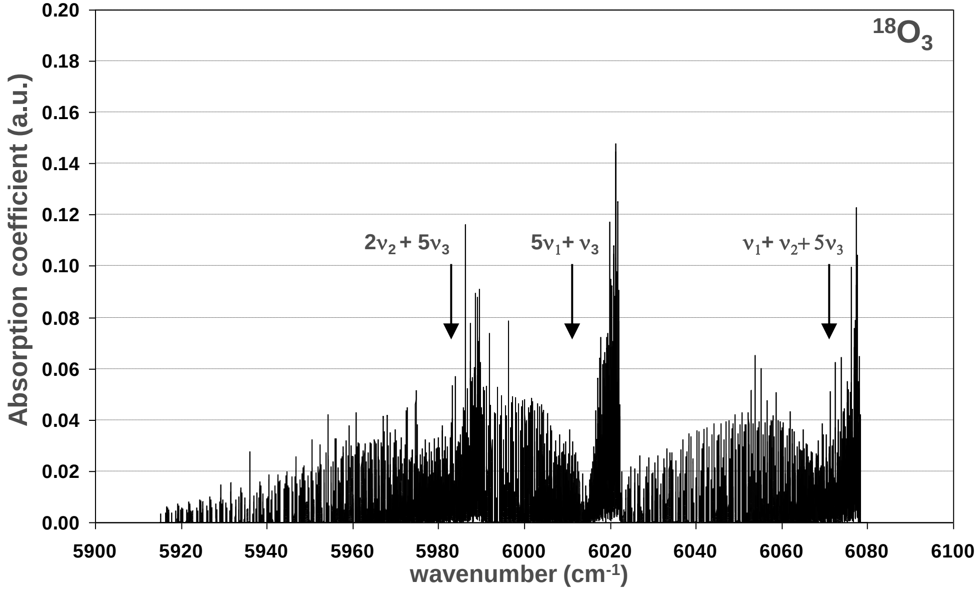
(a) $2\nu_1+5\nu_3$ calc.
(b) $4\nu_1+2\nu_2+\nu_3$ calc
(c) $4\nu_1+2\nu_2+\nu_3$ calc
+ $2\nu_1+5\nu_3$ calc
(d) CW-CRDS
Absorption coefficient (10^{-6}cm^{-1})
Wavenumber (cm^{-1})
0.5
0.0
6573
6574
6575

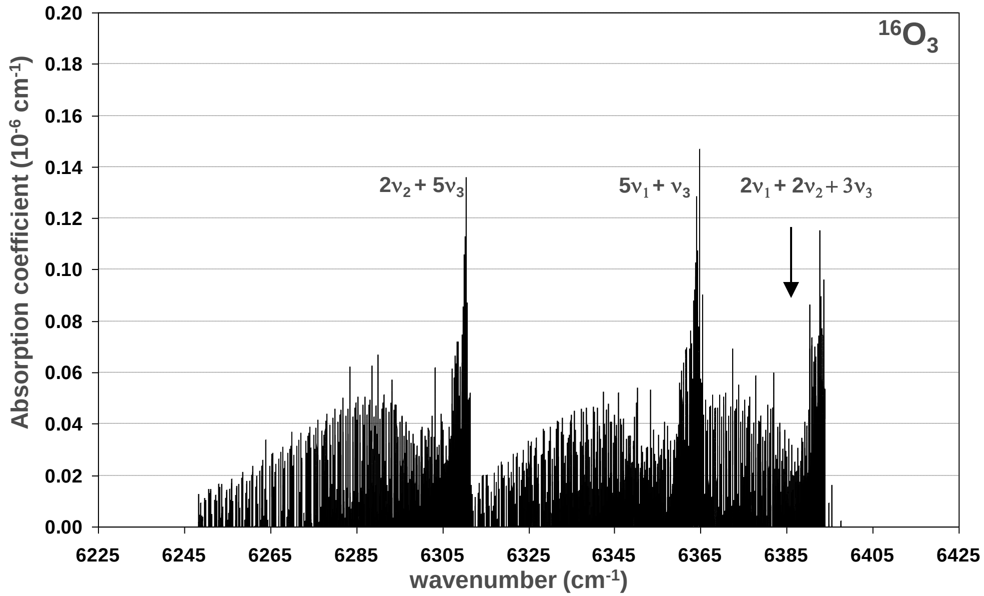


(a) H_2O+CO_2
(b) $5\nu_1+\nu_2+\nu_3$ $^{16}O_3$
(c) $^{16}O_3+H_2O+CO_2$
(d) CW-CRDS
Absorption coefficient ($10^{-6}cm^{-1}$)
0.02
0.00
6989
6990
Wavenumber (cm^{-1})

Sym.	Exp.	$(v_1v_2v_3)_0$ [a]	$S(10^{-24}$ cm/mol) [b]	Transitions [c]	*J* max	K_a max	Levels
B	5919.161	$(133)_0$	2.80/4.68	291/433	32/38	9/9	173/264
B	5947.070	$(411)_0$	1.38	287/294	34/34	11/11	168/179
A	6046.076	$(034)_0$	1.18	135	43	4	77
B	6063.922	$(105)_0$	2.46	531	43	10	265
A	6100.216	$(510)_0$	0.40	22	31	4	17
B	6124.288	$(223)_0$	13.2	507	44	14	338
A	6154.702	$(124)_0$	0.31	479	49	7	227
B	6198.534	$(331)_0$	0.31	115	25	5	80
B	6305.047	$(025)_0$	7.65	734	40	13	368
A	6343.983	$(124)_0$	0.34	46	42	3	31
B	6355.722	$(501)_0$	6.33	506	35	12	271
A	6365.264	$(430)_0$	2.98	53	35	4	36
B	6386.997	$(223)_0$	6.76	596	37	13	284
A	6509.279	$(044)_0$	0.25	325	49	6	151
B	6567.841	$(421)_0$	0.94	63/270+156 [d]	34/36	2/8	34/169
B	6586.967	$(205)_0$	2.00	331/419	35/35	6/11	156/220
B	6716.536	$(233)_0$	1.75		37	12	308
A	6751.246	$(520)_0$	-	797+322 [e]	33	7	16
A	6764.457	$(242)_0$	0.48		46	9	171
B	6895.511	$(035)_0$	0.23	552	35	11	281
B	6981.870	$(511)_0$	0.24	161	25	10	126
B	6990.069	$(233)_0$	0.46	231	25	9	168
				Total :7684			Total :4057

Synthetic spectra for $^{16}O_3$ and $^{18}O_3$ corresponding to the same bands





Comparison between observed and predicted band centers for $^{18}O_3$ and $^{16}O_3$ corresponding to the previous figure

$^{18}O_3$

Sym.	Exp. (cm^{-1})	(Obs.-Calc.) ^{a}	P_1 (%) ^{b}	W_1	P_2 (%)	W_2	P_3 (%)	W_3
B	5984.439	- 0.4	48.7	$(025)_0$	10.9	$(223)_0$	9.1	$(313)_0$
A	6011.836	0.1	72.2	$(430)_0$	9.8	$(322)_0$	8.7	$(124)_0$
B	6013.304	0.3	74.5	$(501)_0$	21.9	$(303)_0$	3.0	$(105)_0$
B	6072.132	1.5	27.8	$(115)_0$	27.1	$(313)_0$	22.5	$(223)_0$

$^{16}O_3$

Sym.	Exp. (cm^{-1})	(Obs.-Calc.) ^{a}	P_1 (%) ^{b}	W_1	P_2 (%)	W_2	P_3 (%)	W_3
B	6305.047	- 0.8	46.3	$(025)_0$	14.3	$(313)_0$	12.2	$(115)_0$
A	6365.264	-1.3	48.3	$(430)_0$	17.4	$(214)_0$	8.8	$(322)_0$
B	6355.722	- 0.2	73.4	$(501)_0$	22.6	$(303)_0$	3.3	(105)0
B	6386.997	- 0.9	28.0	$(223)_0$	20.4	(313)0	18.8	(115)0

Notes:

a **Difference between the vibrational energy values obtained from the experimental data reduction with variational predictions calculated [1] from the PES of Ref. [2].**

b **Columns 4-9 represent three major contributions for the decomposition of corresponding wave functions derived from the potential function [2, 3] in normal mode coordinates q_1, q_2, q_3 using 10th order Contact Transformations [1]. Columns Pn's indicate the mixing coefficients (in %) of Ψ*eff* in the harmonic normal mode basis. Columns Wn's indicate the corresponding vibration normal mode quantum numbers $(v_1v_2v_3)_0$. *n is the order of the contribution. The subscript "0" of* $(v_1v_2v_3)_0$ *means the normal mode representation.***

Conclusion

- **As the energy increases, the number of interacting levels becomes larger and larger. Then a confident assignment accounting for interacting "Dark" states is almost impossible without good predictions of the band centers and rotational constants. The point is that these good predictions allow the assignments of weaker and weaker bands (lines of a few 10^{-28} cm/molecule become possible). The observation of the $4\nu_2 + 4\nu_3$ band is a typical example.**
- **With this work, near dissociation, we may say that O_3 is now one of the most studied molecule, where the energy levels of 74 rovibrational states are obtained up to 7500 cm^{-1} for $^{16}O_3$, and as much for $^{18}O_3$.**
- **For all this work, including isotopomers studies, and in addition to the precise knowledge of molecular properties of ozone (Potential energy surface and Dipole Moment Surface), there are at least two direct fields of applications:**
  - **Non L.T.E**
  - **Progress in the understanding of the anomalous enrichment of ozone isotopes in the atmosphere.**