ATMOSPHERIC SPECTROSCOPY APPLICATIONS

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The $3\nu_3$ bands of isotopic ozone 668 and 686

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Introduction :

Using 0.003 cm^{-1} resolution Fourier transform spectra of ^{18}O-enriched ozone around 3.5 µm, the first high-resolution analysis of the $3\nu_3$ bands of $^{16}O^{18}O^{16}O$ and $^{16}O^{16}O^{18}O$ has been performed. The experimental rotational levels derived from the analysis were very satisfactorily calculated using a Hamiltonian model which takes into account the involved interactions. More precisely, for $^{16}O^{16}O^{18}O$, the Coriolis and anharmonic-type interactions coupling the levels of (003) with those of (031), were taken into account.

We present also evidence of the $^{16}O^{18}O^{16}O$ and $^{16}O^{16}O^{18}O$ ozone absorptions in the 3.5 µm region from FTIR solar occultation spectra obtained from the Jungfraujoch Solar Observatory (47°N, 8°E, 3580m) in Switzerland at a spectral resolution of 0.00496 cm^{-1} (res. = 1/2L).

Experimental details for laboratory spectra :

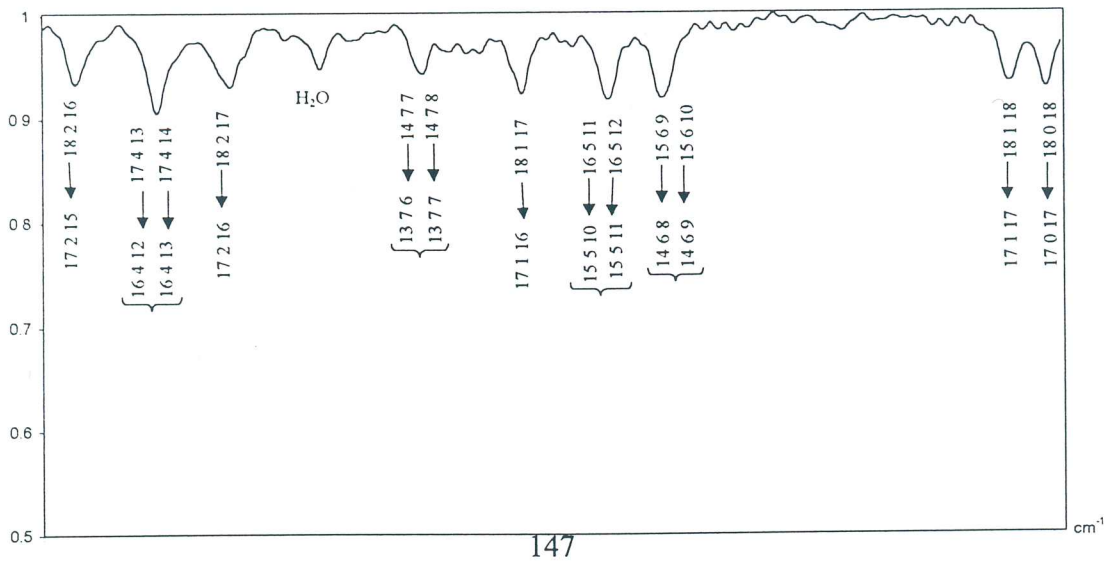
We used the FTS built in the Groupe de Spectrométrie Moléculaire et Atmosphérique (G.S.M.A) laboratory in Reims (*). The beam splitter and beam mixer used here are two half-disks of CaF_2. We used a Globar as the source and InSb as the detector. The FTS was associated with a cell operating at a pathlength of 30 cm.

To generate ozone, we used the silent electric discharge technique (12000 V, 400Hz), the generator being trapped at liquid nitrogen temperature. At 77 K, the vapor pressures of O_3 and O_2 are so different that the generation is quasi-complete. The ozone was formed from a sample containing 43 % of $^{18}O_2$ and 57 % of $^{16}O_2$. The O_3-O_2 mixture was, respectively, 29.85 Torr of O_3 and 0.61 Torr of O_2.

(*) : J.J.Plateaux, A.Barbe, and A.Delahaigue, Spectrochim.Acta, 51A,1153-1169 (1995).

Results :

Laboratory spectrum : P branch of $3\nu_3$ band of the 16-16-18 isotope.
Assignment (J' Ka' Kc' ← J'' Ka'' Kc'') are reported.



The resulting values of Hamiltonian parameters are given in the form adapted to GIP(*) program used for the fit.

$$H_{vv} = {}^{d}H_{rot} + {}^{n.d}H_{rot} = \sum_{nm} C_{nm}(\mathbf{J}^2)^n J_z^{2m} + \sum_{nm} N_{nm}(\mathbf{J}^2)^n \left\{ J_+^2 (J_z+1)^{2m} + (J_z+1)^{2m} J_-^2 \right\}$$

$$\text{with} \quad J_\pm = J_x \pm (1/i) J_y$$

$$\text{and n, m} = 0,1,2,3\ldots$$

Parameter of interaction blocks were chosen as follows :

$$H^{c}_{v'v} = C_{001}(J_+ - J_-) + C_{011}(J_+(J_z+1/2) + (J_z+1/2)J_-) + C_{201}\mathbf{J}^2(J_+ - J_-) +$$
$$+ C_{021}(J_+(J_z+1/2)^2 - (J_z+1/2)^2 J_-) + \ldots$$

$$H^{a}_{v'v} = A_{002}(J_+^2 + J_-^2) + \ldots$$

(*) : High-Resolution Molecular Spectroscopy, SPIE 2205 (1993) 188-191

a) $^{16}O^{16}O^{18}O$

Range of observed transitions for the $3\nu_3$ band :

- $\{J_{min}, J_{max}\}$: {3, 29}
- $\{K_{amin}, K_{amax}\}$: {0, 8}
- number of transitions : 284

Statistics of the fit :

rms = 1.580×10^{-3} cm^{-1}

$0 < \delta E < 0.00158$ cm^{-1} (211 transitions)

0.00158 cm^{-1} $< \delta E < 0.00316$ cm^{-1} (61 transitions)

0.00316 cm^{-1} $< \delta E < 0.00474$ cm^{-1} (12 transitions)

b) $^{16}O^{18}O^{16}O$

Range of observed transitions for the $3\nu_3$ band :

- $\{J_{min}, J_{max}\}$: {3, 34}
- $\{K_{a\,min}, K_{a\,max}\}$: {0, 7}
- number of transitions : 186

Statistics of the fit :

rms = 1.41×10^{-3} cm^{-1}

$0 < \delta E < 0.00141$ cm^{-1} (138 transitions)

0.00141 cm^{-1} $< \delta E < 0.00282$ cm^{-1} (37 transitions)

0.00282 cm^{-1} $< \delta E < 0.00423$ cm^{-1} (11 transitions)

Note :

$$\delta E = E_{obs} - E_{cal}$$

Vibrational Energies and rotational and coupling constants for the $3\nu_3$ band of 16-16-18 (in cm^{-1})

	(0,0,3)		(0,3,1)	
	Value	St.err.	Value	δ
E_v	2998.85764	0.00045	3025.39	0.630
A	3.37289	0.00050	3.587102	e
B	0.40903	0.00040	0.412695	e
C	0.35985	0.00040	0.364637	e
$\Lambda_K \times 10^3$	0.22470	0.00037	0.180881184	g
$\Lambda_{JK} \times 10^5$	-0.1902291	g	-0.1902291	g
$\Lambda_J \times 10^6$	0.31	0.11	0.4478478	g
$\delta_K \times 10^5$	0.720	0.097	0.3115599	g
$\delta_J \times 10^6$	0.139	0.053	0.07290516	g
$H_K \times 10^7$	0.3520083	g	0.3520083	g
$H_{KJ} \times 10^8$	-0.158923	g	-0.158923	g
$H_{JK} \times 10^{10}$	-0.14066	g	-0.14066	g
$H_J \times 10^{12}$	0.30051	g	0.30051	g
$h_K \times 10^8$	0.15996	g	0.15996	g
$h_{JK} \times 10^{11}$	0.2081	g	0.2081	g
$h_J \times 10^{12}$	0.11280	g	0.11280	g

Coupling parameters of Coriolis-type resonance

	(0,3,1) <=> (0,0,3)	
	Value	St.err.
C_{001}	-0.048	0.027
$C_{011} \times 10^1$	-0.124	0.048
$C_{021} \times 10^3$	-0.589	0.077
$C_{201} \times 10^4$	-0.187	0.086
$C_{003} \times 10^3$	0.117	0.095

Coupling parameters of anharmonic-type resonance

	(0,3,1) <=> (0,0,3)	
	Value	St.err.
$A_{002} \times 10^3$	0.109	0.019

e: extrapolated value

g : fixed to the ground state value.

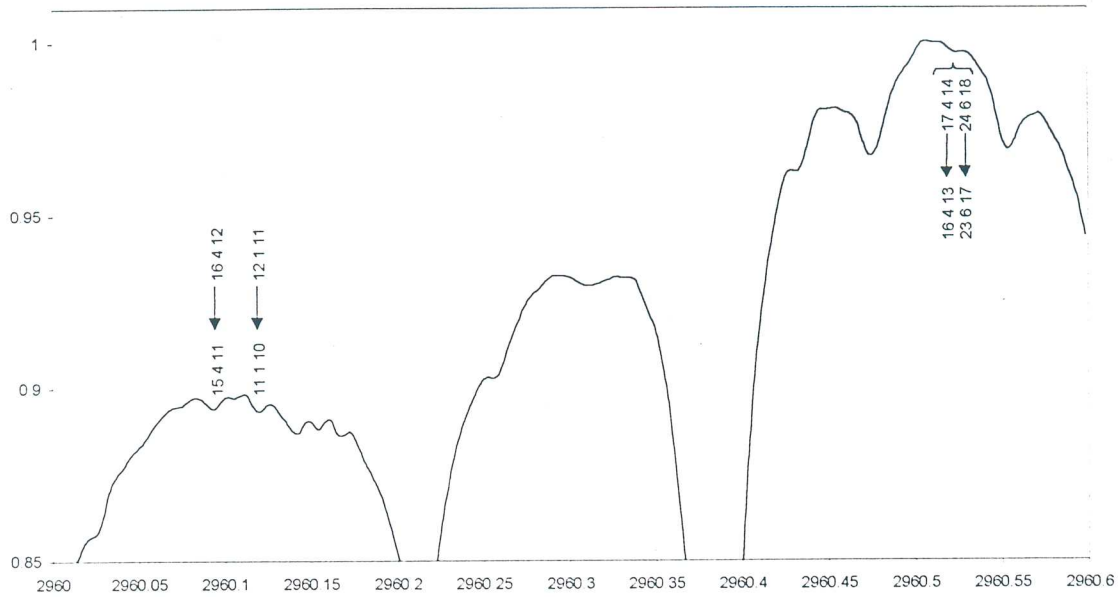
δ : we quote uncertainties delta estimated by taking into account also model errors

Vibrational Energies and rotational and coupling constants for the $3\nu_3$ band of 16-18-16 (in cm^{-1})

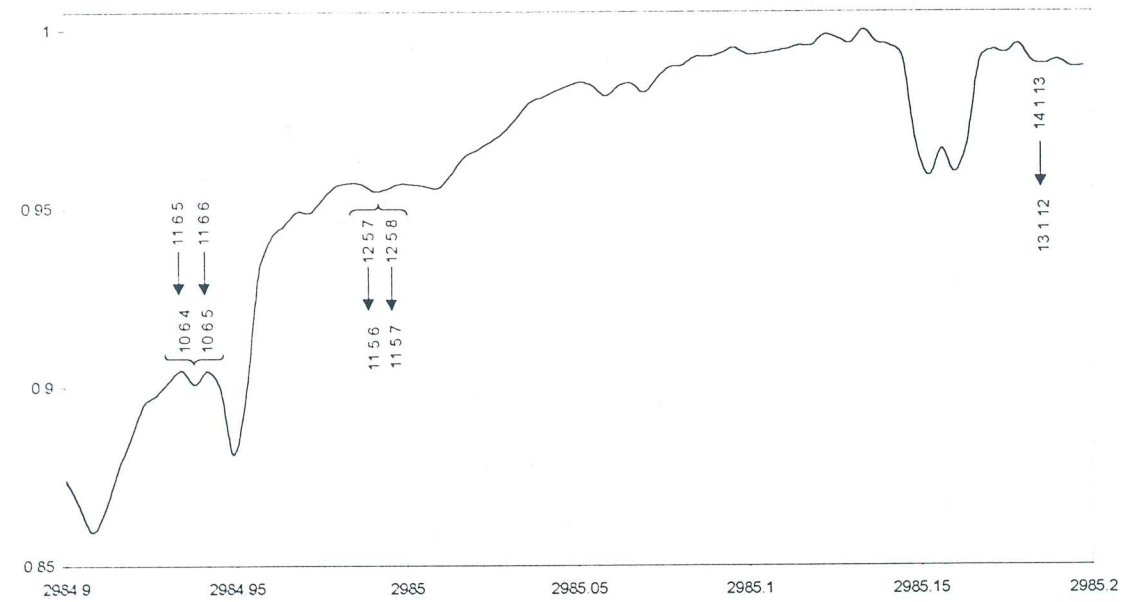
	(0,0,3)	
	Value	St.err.
E_v	2952.41424	0.00033
A	3.164347	0.000285
B	0.4339118	0.0000039
C	0.3769153	0.0000039
$\Delta_K \times 10^3$	0.18583	0.00053
$\Delta_{JK} \times 10^5$	-0.1290	0.0033
$\Delta_J \times 10^6$	0.4302	0.0020
$\delta_K \times 10^5$	0.280	0.022
$\delta_J \times 10^6$	0.1037	0.0014
$H_K \times 10^7$	0.2955062	g
$H_{KJ} \times 10^8$	-0.147549	g
$H_{JK} \times 10^{10}$	-0.12117	g
$H_J \times 10^{12}$	0.43919	g
$h_K \times 10^8$	0.16147	g
$h_{JK} \times 10^{11}$	0.1181	g
$h_J \times 10^{12}$	0.16029	g

Identification of ozone isotopes in high resolution ground-based FTIR spectra :

Solar spectrum : Absorption lines of ozone : $3\nu_3$ band of the 16-18-16 isotope



Solar spectrum : Absorption lines of ozone : $3\nu_3$ band of the 16-16-18 isotope.



A high resolution (0.00496 cm-1 apodized) solar occultation spectrum was collected on 5 august 1998 at a solar zenith angle of 86.435°, with a high resolution Fourier Transform Infrared Spectrometer developed in the Department of Astrophysics at the University of Liege, Belgium. The S/N ratio was 2718.