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Analysis of the CRDS spectrum of $^{18}O_3$ between 6950 and 7125 cm^{-1}

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ABSTRACT

The absorption spectrum of the $^{18}O_3$ isotopologue of ozone was recorded by CW-Cavity Ring Down Spectroscopy in the 6950–7125 cm^{-1} region. The typical noise equivalent absorption of the recordings is $\alpha_{min} \approx 1 \times 10^{-10}$ cm^{-1}. The spectrum is dominated by three very weak bands: $3\nu_1+5\nu_3$ near 7009 cm^{-1} and the $\nu_2+7\nu_3$ and $4\nu_2+5\nu_3$ interacting bands near 7100 cm^{-1}. In total 260, 206 and 133 transitions were assigned for the $3\nu_1+5\nu_3$, $\nu_2+7\nu_3$ and $4\nu_2+5\nu_3$ bands, respectively. The line positions of the $3\nu_1+5\nu_3$ band were modelled using an effective Hamiltonian (EH) model involving two dark states – (6 0 1) and (2 5 2) – in interaction with the (3 0 5) bright state. The EH model developed for the $\nu_2+7\nu_3$ and $4\nu_2+5\nu_3$ bands involves only the (0 1 7) and (0 4 5) interacting bright states. Line positions could be reproduced with *rms* deviations on the order of 0.01 cm^{-1} and the dipole transition moment parameters were determined for the three observed bands. The obtained set of parameters and the experimentally determined energy levels were used to generate a list of 984 transitions of the three bands which is provided as Supplementary Material.

1. Introduction

We are involved in a long term project aiming at investigating the very highly excited rovibrational levels of ozone in its ground electronic state, at energies approaching the dissociation energy *via* an extensive study of its extremely weak absorption spectrum. Our studies by high sensitivity Cavity Ring Down Spectroscopy (CW-CRDS) have provided a large amount of new observations from 5850 to 7920 cm^{-1}. Rovibrational bands of the main isotopologue have been assigned up to 7600 cm^{-1} [1–8] and detected up to 7912 cm^{-1} [9] i.e., only 6 % below the dissociation energy $D_0 \approx 8480$ cm^{-1}.

The study of the homogeneously substituted isotopologue, $^{18}O_3$, at high vibrational excitation [10–12] provides complementary information to test theoretical calculations of the Potential Energy Surface (PES). The average value of the shift for the band centres around 7000 cm^{-1} should be about 420 cm^{-1} but, while the $^{16}O_3 \rightarrow {}^{18}O_3$ substitution is homogenous, the centres of the highly excited bands are not homogenously shifted according to the usual $\sqrt{(m\,(^{18}O)/m\,(^{16}O))}$ scaling factor of the vibrational frequency [13]. The isotopic shifts appear to vary irregularly around the average value, even though the change in masses is small and homogeneous. This reflects the complexity of the anharmonic interactions in the ozone molecule and is expected to provide hints for new inter-polyad resonances. Such unusual behaviour was investigated from our previous CRDS studies of $^{18}O_3$ in the 5850–6850 cm^{-1} region [10–12]. The aim of the present study is to extend the $^{18}O_3$ observations at higher energy by the analysis of the 6950–7125 cm^{-1} region. In terms of quantum numbers,

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this spectral interval corresponds to the vibrational bands of the main isotopologue located in the 7300–7600 cm^{-1} interval, recently analysed in Ref. [8]. In the present work, three A-type bands with very compressed *R*-branches were detected and assigned to the $3\nu_1+5\nu_3$, $\nu_2+7\nu_3$ and $4\nu_2+5\nu_3$ bands on the basis of the theoretical predictions of Ref. [14] using the Potential Energy Surface (PES) of Refs. [15,16].

The experimental set-up and the theoretical approach, extensively described in our previous works [9,10,17], are summarized in Sections 2 and 3, respectively. The detailed analyses of the three observed bands are included in Section 3 where the effective Hamiltonian and transition moment operators are derived from the fits on measured line positions and intensities, respectively.

2. Experiment

The detailed description of the fibred CW-CRDS spectrometer using distributed feedback (DFB) diode lasers can be found in Refs. [2–4,6,9,17,18]. The typical sensitivity of the recordings is $\alpha_{min} \approx 1\times10^{-10}$ cm^{-1}. The presently analysed spectra were recorded between 6950 and 7125 cm^{-1} using six DFB diode lasers. Each diode laser allows covering a 35 cm^{-1} wide section of the spectrum by temperature variation from -10 °C to 60 °C. About 20 ring down events were averaged for each spectral data point and the duration of the scan was about 90 min for each DFB source. The cell was filled at an ozone pressure of 40 Torr produced from ^{18}O enriched oxygen with a silent electric discharge (12 kV, 400 Hz) at liquid nitrogen temperature [19]. The pressure, measured by a capacitance gauge as well as the ring down cell temperature was monitored during the spectrum acquisition. The ozone degradation in oxygen was limited to 1.5 Torr/h.

The ^{18}O atomic enrichment of the O_2 sample used (from Cambridge Isotope Laboratories) was stated to be larger than 95%. The same sample was used in a recent study of the $a^1\Delta_g$–$X\ ^3\Sigma_g^-$ band of $^{18}O_2$ near 1.27 μm and the relative abundances of the $^{18}O_2$ and $^{16}O^{18}O$ isotopologues were determined to be 94% and 4.9%, respectively (see Table 1 of Ref. [20]). These O_2 isotopologue abundances lead to an ^{18}O atomic abundance of 96.45%, in agreement with the stated ^{18}O enrichment. Assuming a statistical distribution of the oxygen atoms during the ozone synthesis, we calculated a 91.1% relative abundance for the homogeneously substituted $^{18}O_3$ isotopologue in our ozone sample. This value will be used below for the determination of the absolute line intensities.

Each individual spectrum was calibrated on the basis of the wavelength values provided by a Fizeau type wavemeter (WSU-30 Highfinesse, 5 MHz resolution and 20 MHz accuracy). The absolute calibration provided by the wavemeter is better than 1×10^{-3} cm^{-1} (30 MHz). Lines due to impurities (mainly water) present in the ozone sample were used to check and refine the absolute wavenumber calibration [21].

The investigated spectral region falls in the centre of the rather strong bands of the first hexade region of water. The strongest water transitions of the region have intensity on the order of 1×10^{-20} cm/molecule while the strongest ozone lines to be detected are about eight orders of magnitude weaker. The superposition of

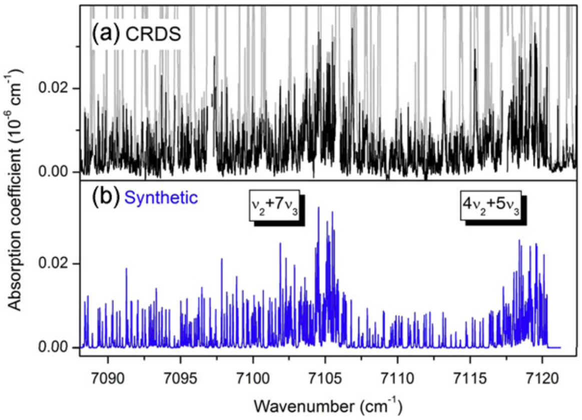

Fig. 1. Comparison of the experimental and calculated spectra of $^{18}O_3$ in the region of the $\nu_2+7\nu_3$ and $4\nu_2+5\nu_3$ bands near 7100 cm^{-1}. (a) CRDS spectrum recorded with a pressure of ozone of 40 Torr. The $^{18}O_3$ spectrum appears superimposed to a strong background (grey lines) of lines of water present as an impurity (partial pressure less than 1 mTorr) (b) synthetic spectrum of ozone calculated with the effective Hamiltonian approach.

Table 1
Theoretical predictions and experimental values for the centres of the bands relevant in the present analysis and corresponding normal mode assignments.

Band centre (cm^{-1})					Three major normal mode contributions[c]					
Obs	Calc_1[a]	O − C (1)	Calc_2[b]	O − C (2)	*P*1 (%)	*W*1	*P*2 (%)	*W*2	*P*3 (%)	*W*3
6997.21	6996.33	0.88	6997.22	−0.01	70	(6 0 1)	24	(4 0 3)	4	(2 0 5)
7005.81	7007.64	−1.83	7009.49	−3.68	44	(2 5 2)	9	(2 3 4)	9	(3 6 0)
7009.08	7014.67	−5.59	7011.80	−2.72	39	(3 0 5)	20	(5 0 3)	15	(2 1 5)
7101.48	7106.16	−4.68	7105.62	−4.14	40	(0 1 7)	30	(4 1v3)	8	(1 2 5)
7115.37	7112.84	2.53	7119.00	−3.63	25	(0 4 5)	12	(3 3 3)	12	(3 5 1)

[a] Global variational predictions from the potential function V^M of Ref. [15] in internal coordinates (r_1,r_2,θ).

[b] Non-empirical effective Hamiltonian predictions derived from the potential function of Ref. [16] in normal mode coordinates q_1,q_2,q_3 using 10th order contact transformation (CT) [14].

[c] Columns *Pn*'s indicate the squares of Ψ^{eff} expansion coefficients (in %) in the harmonic normal mode basis for the lowest rovibrational state [$J=1,K_a=0,K_c=1$] allowed by nuclear spin statistics (see Ref. [13] for more comments). Columns *Wn*'s indicate the corresponding vibration normal mode quantum numbers($v_1v_2v_3$), where *n* is the order of the contribution. These expansions are obtained using CT method$^{(b)}$. Grey backgrounds correspond to "dark" perturber states.