Journal of Quantitative Spectroscopy & Radiative Transfer 113 (2012) 840–849

Contents lists available at SciVerse ScienceDirect

Journal of Quantitative Spectroscopy & Radiative Transfer

journal homepage: www.elsevier.com/locate/jqsrt

Predissociation and spectroscopy of the $^3A_2(0\,0\,0)$ state of $^{18}O_3$ from CRDS spectra of the $^3A_2(0\,0\,0)\leftarrow X^1A_1(1\,1\,0)$ hot band near 7900 cm^{-1} ☆

Didier Mondelain [a],*, Rémy Jost [a], Samir Kassi [a], Richard H. Judge [b], Vladimir Tyuterev [c], Alain Campargue [a]

[a] *Université Grenoble 1/CNRS, UMR5588 LIPhy, Grenoble, F-38041, France*
[b] *University of Wisconsin-Parkside, Kenosha, WI 53141, USA*
[c] *Groupe de Spectrométrie Moléculaire et Atmosphérique, UMR CNRS 6089, UFR Sciences Exactes et Naturelles, BP 1039, 51687 Reims, Cedex 2, France*

ARTICLE INFO

Available online 30 January 2012

Keywords:
Ozone
O3
Line width
Predissociation
Absorption spectroscopy
CRDS
Isotopologue

ABSTRACT

The spectroscopy and predissociation of the $^3A_2(0\,0\,0)$ state of $^{18}O_3$ are investigated from the analysis of the absorption spectrum of the $^3A_2(0\,0\,0)\leftarrow\tilde{X}^1A_1(1\,1\,0)$ hot band recorded by high sensitivity cw-CRDS between 7600 and 7920 cm^{-1}. The noise equivalent absorption of the recordings is on the order of 1×10^{-10} cm^{-1}. Forty transitions could be rotationally assigned and their line positions were used to derive approximate spectroscopic parameters of the $^3A_2(0\,0\,0)$ upper state. Most of the transitions exhibit a clear broadening due to the predissociation of the $^3A_2(0\,0\,0)$ upper state at 9573.61 cm^{-1}. The width of the Lorentzian component (from 0.02 up to more than 0.5 cm^{-1}) was retrieved for some of the assigned transitions. The variation of the corresponding predissociation rates is due to the dependence of the spin–orbit coupling between the $^3A_2(0\,0\,0)$ level and high lying dissociative vibrational levels of the $\tilde{X}^1A_1$ electronic ground state, with (i) the J and K_a rotational quantum numbers and (ii) the energy gap between the coupled pair of rotational levels. From the predicted energies of the $\tilde{X}^1A_1$ vibrational states and their vibrational overlap with the $^3A_2(0\,0\,0)$ state, a few of these $\tilde{X}^1A_1$ vibrational levels are identified as possibly responsible for the $^3A_2(0\,0\,0)$ predissociation. The predissociative mechanism in $^{18}O_3$ is compared to that taking place in $^{16}O_3$.

1. Introduction

The $^3A_2$ triplet electronic state of ozone is a predissociative state which contributes to the Wulf band. It was previously observed by Fourier Transform Spectroscopy (FTS) through the $^3A_2(0\,0\,0)\leftarrow\tilde{X}^1A_1(0\,0\,0)$ [1] and the $^3A_2(0\,1\,0)\leftarrow\tilde{X}^1A_1(0\,0\,0)$ [2] cold bands with an origin at 9553.02(8) and 10082.01(3) cm^{-1} for $^{16}O_3$, and 9573.61(6) and 10074.95(3) cm^{-1} for $^{18}O_3$, respectively. The $^3A_2(0\,0\,0)\leftarrow\tilde{X}^1A_1(0\,0\,0)$ band of $^{16}O_3$ was also recorded by high sensitivity techniques like Intracavity Laser Absorption Spectroscopy (ICLAS) [3] and pulsed-Cavity Ring Down Spectroscopy (CRDS) [4] in order to determine lifetimes of the $^3A_2(0\,0\,0)$ predissociative state through the study of the broadening of the absorption lines. In these studies, the spectral resolution was 0.014 cm^{-1} at best, making difficult the profile analysis of the narrow lines. In the present work, the $^3A_2$ (0 0 0) vibronic level of $^{18}O_3$ was accessed through the $^3A_2(0\,0\,0)\leftarrow\tilde{X}^1A_1(0\,0\,0)$ hot band near 7877 cm^{-1}. The very high sensitivity of the

---

☆ This article is dedicated to Prof. Alain Barbe, Dr. Claude Camy-Peyret and Dr. Jean-Marie Flaud for their valuable contributions to ozone spectroscopy.

* Corresponding author. Tel.: +33 4 76 51 43 29; fax: +33 4 76 63 54 95.
E-mail address: didier.mondelain@ujf-grenoble.fr (D. Mondelain).

0022-4073/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jqsrt.2012.01.015

cw-CRDS technique allowed for the detection of this hot band despite a much lower band intensity compared to the corresponding cold band (a factor of about 400 weaker). The cw-CRDS spectra are mostly Doppler limited permitting accurate line width analysis. The present work is then devoted to the detailed analysis of the broadening of the $^3A_2(0\,0\,0) \leftarrow \tilde{X}^1A_1(1\,1\,0)$ absorption lines in order to get further insight on the predissociation of the $^3A_2(0\,0\,0)$ upper state. Note that the ICLAS technique was also used to study the $^3A_2(0\,0\,2) \leftarrow \tilde{X}^1A_1(0\,0\,0)$ cold band for the $^{16}O_3$ and $^{18}O_3$ isotopologues, with an origin at 10 473(3) and 10 462(3) cm^{-1}, respectively [5].

The $^3A_2$ electronic state of ozone is the lowest of the three triplet states at the origin of the Wulf band [6,7] and thus plays a role for the ozone photodissociation in the near infrared [8]. The global potential energy surfaces (PES) of the $^3A_2$, $^3B_2$ and $^3B_1$ states have been calculated [8 and references there in]. The $^3A_2$ PES has a local minimum around 9500 cm^{-1} which is above the dissociation threshold corresponding to the $O(^3P)+O_2(\tilde{X}^3\Sigma_g^-)$ channel at about 8480 cm^{-1} [8]. This $^3A_2$ PES is one of the 27 PESs converging to this limit including the one of the ground electronic state [9]. Grebenshchikov et al. [10] and Xie et al. [11] mentioned that the observed predissociation rates of the $^3A_2(0\,0\,0)$ state are two orders of magnitude larger than expected from tunneling effect through the barrier of the $^3A_2$ PES. They conclude, in agreement with Bouvier et al. [2], that the observed predissociation rates are due to a spin–orbit (S–O) coupling inducing a singlet–triplet mixing of $^3A_2(0\,0\,0)$ with some highly excited vibrational metastable states of the $\tilde{X}^1A_1$ electronic ground state. As a result of the predissociation of the $^3A_2$ upper levels, the width of the absorption lines varies strongly with the upper rotational quantum numbers. The aim of the present contribution is then to get insight on the S–O coupling mechanism of the $^3A_2$ state with the high lying rovibrational resonant levels of the ground electronic state through the analysis of the broadening of the absorption lines.

2. Experimental details

We have recently recorded the absorption spectrum of $^{18}O_3$ between 7600 and 7920 cm^{-1} by cw-CRDS with a typical noise equivalent absorption of about 1×10^{-10} cm^{-1} [12]. The reader is referred to Ref. [12] for a detailed description of the recordings. Briefly, the cell was filled at an ozone pressure of 40 Torr produced from ^{18}O enriched oxygen (Cambridge Isotope Laboratories, 95% ^{18}O) with a silent electric discharge (12 kV, 400 Hz) at liquid nitrogen temperature. The unexpected observation of broad absorption lines was assigned to the $^3A_2(0\,0\,0) \leftarrow \tilde{X}^1A_1(1\,1\,0)$ hot band [12] from the (1 1 0) vibrational state at 1696.11 cm^{-1} to the $^3A_2(0\,0\,0)$ state at 9573.61(6) cm^{-1} far above the dissociation energy (D_0) at about 8480 cm^{-1} [8]. A large range of width values-from 0.02 cm^{-1} up to more than 0.5 cm^{-1}-was measured for the broadened lines. In addition, very weak vibrational combination bands within the ground electronic state appear superimposed on the broad features (Fig. 1). The vibrational cold bands and the $^3A_2(0\,0\,0) \leftarrow \tilde{X}^1A_1(1\,1\,0)$ hot band could be discriminated on the basis of CRDS spectra recorded from 294 K up to 327 K using the difference in the temperature dependence of their intensities. More precisely, the intensities of the hot band transitions are increased by a factor of 1.9 when the temperature increases from 294 K to 327 K [12] while the vibrational cold bands are mostly unaffected. Note that the corresponding hot band of $^{16}O_3$ shows similar broad features but the hot band spectrum is obscured by stronger vibrational cold bands, so that no useful information can be extracted [12].

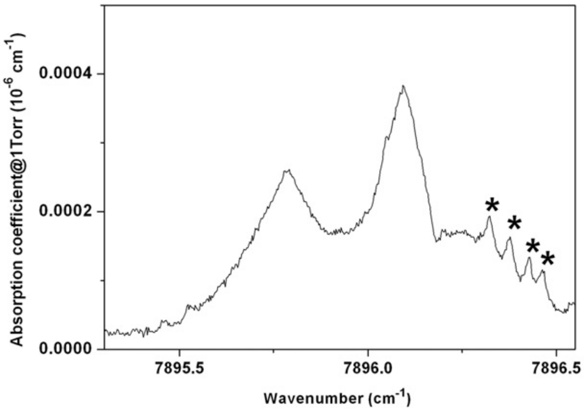

Fig. 1. Section of the CRDS absorption spectrum of $^{18}O_3$ recorded at 327 K showing the superimposition of broad features due to the $^3A_2(0\ 0\ 0) \leftarrow \tilde{X}^1A_1(1\,1\,0)$ hot band and narrow lines (marked with *) of very weak vibrational bands due to $\tilde{X}^1A_1(\nu_1\nu_2\nu_3) \leftarrow \tilde{X}^1A_1(0\,0\,0)$ transitions. The spectrum is normalized in density for a pressure of 1 Torr and a temperature of 296 K.

3. Rovibrational assignment and spectroscopic parameters for the $^3A_2(0\,0\,0)$ state of $^{18}O_3$

A prerequisite to analyze the coupling of the $^3A_2(0\,0\,0)$ state to the ground vibrational states is the rotational assignment of the $^3A_2(0\,0\,0) \leftarrow \tilde{X}^1A_1(1\,1\,0)$ hot band transitions. The spin S and the nuclear angular momentum N form the resultant total angular momentum, J, of the molecule. The rotational levels are thus defined by the quantum labels J, N, K_a and K_c. For a given value of N, the three spin components are: $F_1(J=N+1)$, $F_2(J=N)$, $F_3(J=N-1)$. The notation used for the different branches is $^{\Delta N}\Delta J_{F_{i=1,2,3}}(J'',K''_a)$ and the selection rules are $\Delta J=0, \pm1$ and $\Delta K_a=0$. The ′ and ″ subscripts refer to the high and low level of the transition, respectively.

The first assignments were based on the 26 assignments obtained by Bouvier et al. for the $^3A_2(0\,0\,0) \leftarrow \tilde{X}^1A_1(0\,0\,0)$ cold band [1]. In order to transfer the assignments from the cold to the hot band, we subtracted the difference between the lower state energy levels of the (1 1 0) and (0 0 0) vibrational states to the measured positions reported in Table 3 of Ref. [1]. The (1 1 0) and (0 0 0) energy values were taken from the S&MPO ("Spectroscopy and Molecular Properties of Ozone") information system [13]. It appears that only twelve transitions corresponding to the 26 transitions listed in Ref. [1] were clearly observed in our spectra, the other being either out