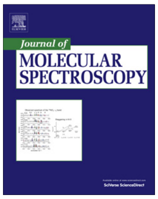
Journal of Molecular Spectroscopy 286–287 (2013) 5–11

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Spectroscopy

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



Line broadening, shifting and mixing parameters of OCS perturbed by O_2 in the $\nu_3 + \nu_2 - \nu_2$ and $5\nu_2 - \nu_2$ bands

S. Galalou [a,*], H. Aroui [a], F. Kwabia Tchana [b,*]

[a] *Laboratoire de Dynamique Moléculaire et Matériaux Photoniques, Université de Tunis, Ecole Supérieure des Sciences et Techniques de Tunis, 5 Avenue Taha Hussein, 1008 Tunis, Tunisia*

[b] *LISA, Laboratoire Interuniversitaire des Systèmes Atmosphériques, UMR CNRS 7583, Université Paris Est Créteil (UPEC) et Université Paris Diderot (UPD) 61 Avenue du Général de Gaulle, 94010 Créteil Cedex, France*

ARTICLE INFO

Article history:
Received 21 December 2012
In revised form 17 February 2013
Available online 27 February 2013

Keywords:
OCS
Fourier transform spectrometer
O_2-pressure shift
O_2-pressure broadening
Line mixing

ABSTRACT

Molecular spectroscopic parameters are useful for the interpretation of high-resolution infrared spectra of gaseous species in the Earth's atmosphere and those of giant planets.

In this work line broadening, shifting and mixing parameters have been measured for the $\nu_3 + \nu_2 - \nu_2$ and $5\nu_2 - \nu_2$ bands of the primary isotopologue of carbonyl sulfide ($^{16}O^{12}C^{32}S$), perturbed by O_2 at room temperature. Measurements have been made using a high-resolution Fourier transform spectrometer (Bruker IFS125HR, resolution = 0.004 cm^{-1}) at the LISA Laboratory in France. A total of six pressures between 5.80 and 83.2 Torr of O_2 perturbing gas were recorded. The measurements cover the P and R branches of the studied bands, located in the 5 μm spectral region. The line broadening, shifting and mixing parameters were derived using a multi-pressure fitting method, applied to the measured shapes of the lines, including line-mixing effects.

The results are compared with values calculated using a semi-classical model based on the Robert and Bonamy formalism that reproduces rather well the observed *m* rotational dependence of the O_2 broadening coefficients.

1. Introduction

Carbonyl sulfide (OCS) is one of the principal and most long-lived reservoirs of sulfur in the Earth's troposphere [1] and has been detected in different astrophysical objects (the Venus atmosphere [2], the Orion molecular clouds [3], the Hyakutake and Hale–Bopp comets [4,5] and the starburst galaxies [6,7]).

For transitions with small rotational energy separation, or when the gas pressure increases, inelastic collisions transfer population from one radiative state to another. If, at low pressure, when the lines are isolated, this effect just gives a line broadening proportional to the pressure, at high pressure the lines overlap, and rotational energy exchanges induced by collisions can mix these lines, transferring populations between close spectral components and altering their shapes.

Previous studies at high spectral resolution have reported line-mixing effects for various molecules such as CH_4 [8]. Later, line-mixing effects have been analyzed for CH_3F, perturbed by rare gases using a dynamical model [9]. A simple model was proposed by Hartmann et al. [10] for the ν_5 band of CH_3Cl perturbed by N_2. Recently, another model was used by Tran et al. to predict line mixing effects in the ν_6 band of CH_3Br perturbed by N_2 and self-perturbed [11]. Also, line mixing of a large set of inversion doublets of NH_3 self-perturbed has been measured in the ν_2, $2\nu_2$ and ν_4 bands by Aroui et al. [12].

As far as carbonyl sulfide is concerned, line mixing effects have been studied in only a few works: Broquier and Picard-Bersellini [13] studied the mixing effects due to inelastic collisions in the hot-band doublets of OCS–Ar in the infrared (5 μm region), using a diode-laser spectrometer. Line mixing coefficients have been measured by Blanquet et al. for 15 doublets in the P and R branches for the $\nu_1 + \nu_2 - \nu_2$ hot band [14]. However, to our knowledge, no measurement has yet been published for line mixing coefficients of OCS perturbed by O_2, for the $\nu_3 + \nu_2 - \nu_2$ and $5\nu_2 - \nu_2$ bands.

Several studies have been performed concerning O_2-pressure broadening and pressure induced shift coefficients. Among them, Bouanich et al. [15] reported pressure broadening coefficients for 25 lines belonging to the ν_1 band of OCS in collision with O_2 using a tunable diode-laser spectrometer. Domenech et al. [16] reported the first measurements of the pressure induced shift coefficients due to Ar, He, N_2 and O_2 perturbers for 22 ro-vibrational lines of the $2\nu_3$ band at 4100 cm^{-1}, using a tunable difference-frequency laser spectrometer. Koshelev et al. [17] have measured nitrogen

---

* Corresponding authors. Fax: +216 71391166 (S. Galalou), fax: +33 (0)1 45 17 15 64 (F. Kwabia Tchana).

E-mail addresses: souhailgalalou@yahoo.fr (S. Galalou), fridolin.kwabia@lisa.u-pec.fr (F. Kwabia Tchana).

0022-2852/$ - see front matter © 2013 Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.jms.2013.02.008

and oxygen pressure broadening and pressure induced shift coefficients for 42 transitions of OCS in the P and R branches of the ν_3 band at room temperature, using a high-resolution tunable diode-laser spectrometer. Air-broadening and shift parameters have also been determined from the N_2 and O_2 measurements [17]. N_2-, O_2- and self-broadening coefficients of OCS rotational lines for the $\nu_2 = 1$ and ground states were accurately studied at room temperature, using a radio-acoustic absorption spectrometer [18]. More recently, we studied the N_2 and O_2 pressure broadening and induced shift coefficients for 97 transitions of the $4\nu_2$ band at room temperature, using a high-resolution Fourier transform spectrometer [19].

The present work reports the first measurement of line mixing coefficients of OCS perturbed by O_2, as well as the pressure broadening and pressure induced shift coefficients in the $\nu_3 + \nu_2 - \nu_2$ and $5\nu_2 - \nu_2$ bands. Theoretical calculations of broadening coefficients have also been performed using the semi-classical Robert and Bonamy formalism.

2. Experimental details and data analysis

2.1. Experimental details

The IR absorption spectra of OCS and O_2 gaseous mixtures were obtained using a high-resolution Fourier transform spectrometer (FTS) Bruker IFS125HR located at the LISA facility, in Créteil. A KBr/Ge beamsplitter, a silicon carbide Globar source, a liquid nitrogen-cooled Indium Antimonide (InSb) detector and optical and electronic filters covering the spectral region 1850–2150 cm^{-1} were used. The optical path of the spectrometer was continuously evacuated below 0.05 Torr for the duration of all spectral measurements. Spectra were recorded with an aperture diameter of 1.15 mm, 40 kHz scanner frequency and a maximum optical path difference (d_{MOPD}) of 225 cm. According to the Bruker definition (resolution = $0.9/d_{MOPD}$) this corresponds to a resolution of 0.004 cm^{-1}.

A White-type multipass absorption cell, made of Pyrex glass and equipped with CsBr windows, was connected to the Fourier transform spectrometer with a dedicated optical interface (six mirrors) inside the back sample compartment of the spectrometer. Its base length is 0.80 m and, for the experiment described here, an optical path of 3.249 (6) m was used. The carbonyl sulfide and oxygen purities are 97.5% and 99.6% respectively.

The following procedure was used for measurements: first a background spectrum was collected while the cell was being continuously evacuated. Next, the cell was filled with OCS at a given pressure. Finally, O_2 was added in stages leading to the series of six pressures listed in Table 1. The sample pressure in the cell was measured using calibrated MKS Baratron capacitance manometers (2, 10 or 100 Torr full scale) with a stated uncertainty of 0.12% of full scale.

The spectra were recorded at a stabilized room temperature of 295 ± 1 K. They were ratioed against a single-channel background spectrum of the empty-cell which was taken at a resolution of 0.384 cm^{-1}, in order to ensure the best possible signal-to-noise in the ratioed spectra. The spectra were the result of the co-addition of 450 or 600 interferograms. For the Fourier transform calculations, a Mertz-phase correction with 0.5 cm^{-1} phase resolution and boxcar apodization function were used to the averaged interferograms. Fig. 1 shows a high resolution spectrum of pure OCS recorded at 0.0173 Torr pressure, that was used for calibration. Note that in the OCS spectra, there are significant absorption lines of H_2O and CO_2 residuals inside the FTS. Since the pressure inside the FTS chamber was less than 0.05 Torr, the observed line positions of the H_2O and CO_2 were good enough to serve as frequency standards without considering the pressure-induced shift. These line positions were in excellent agreement with those of HITRAN [20]. The resulting precision is ±0.0002 cm^{-1} for well isolated lines.

Table 1
Experimental data.

Optical path (m)		3.249
Resolution (cm^{-1})		0.004
Maximum optical path difference (cm)		225
Collimator focal length (mm)		418
Aperture diameter (mm)		1.15
Useful spectral domain (cm^{-1})		1850–2150
Spectrum number	OCS pressure (Torr)[a]	O_2 pressure (Torr)[a]
1	0.0754 (24)	5.80 (1)
2	0.0754 (24)	14.0 (1)
3	0.0754 (24)	22.1 (1)
4	0.0754 (24)	32.4 (1)
5	0.0754 (24)	51.8 (1)
6	0.0754 (24)	83.2 (1)

[a] The numbers in parentheses represent the absolute uncertainty in the units of the last digit quoted.

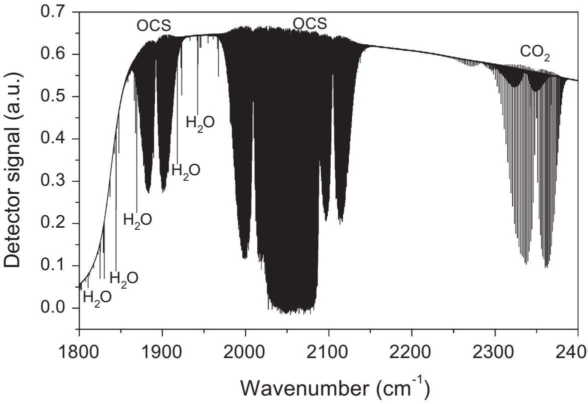


Fig. 1. Overview of the absorption spectrum of pure OCS between 1800 and 2400 cm^{-1} recorded using high-resolution Fourier transform spectroscopy. The spectrum was recorded with a spectral resolution of 0.004 cm^{-1} and an optical pathlength of 19.25 (4) m, at OCS pressure of 0.0173 (1) Torr and a stabilized room temperature of 295 ± 1 K. The lines appearing on the left and right of the spectrum are from residual H_2O and CO_2 inside the FTS and were used as frequency calibration reference.

Fig. 2 shows the transmittance spectrum of OCS–O_2 around 2032 cm^{-1} exhibiting some prominent lines of the P branch of the $\nu_3 + \nu_2 - \nu_2$ band. At low pressure the lines are separated, but when the pressure increases the lines broaden and begin to overlap.

2.2. Fitting procedures

The experimental spectra were analyzed by taking into account mixing effects. Thus, within the impact theory of the spectral shape and for moderately overlapping lines at low pressure, as considered in this work, the collisional absorption coefficient $\alpha(\sigma)$ is assumed to be described by a Rosenkranz profile, which can be expressed as the sum of a Lorentz and of a mixing term [21]:

$$\alpha(\sigma) = \frac{P_{OCS}}{\pi} \sum_k S_k \frac{Y_K(\sigma - \sigma_k) + \gamma_k}{(\sigma - \sigma_k)^2 + (\gamma_k)^2}, \tag{1}$$

where P_{OCS} is the OCS pressure, k represents the $v_iJ_i \rightarrow v_fJ_f$ line, S_k its intensity, σ_k its wave number including the collisional shift δ ($\delta = \sigma_k - \sigma_0$, σ_0 being the unperturbed or zero pressure wavenumber), γ_k its broadening coefficient and Y_k its mixing parameter.