Journal of Molecular Spectroscopy 333 (2017) 19–22

Contents lists available at ScienceDirect

Journal of Molecular Spectroscopy

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

First analysis of the rotationally-resolved v_2 and $2v_2$-v_2 bands of sulfur dioxide, $^{33}S^{16}O_2$

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ARTICLE INFO

Article history:
Received 18 September 2016
In revised form 27 December 2016
Accepted 29 December 2016
Available online 3 January 2017

Keywords:
Sulfur dioxide
Sulfur-33 isotope
High resolution Fourier transform infrared spectroscopy
Ro-vibrational constants

ABSTRACT

A Fourier transform spectrum of sulfur dioxide $^{33}S^{16}O_2$ has been recorded in the 18.3 μm spectral region at a resolution of 0.002 cm^{-1} using a Bruker IFS 125HR spectrometer leading to the observation of the v_2 and $2v_2$-v_2 vibrational bands of the $^{33}S^{16}O_2$ molecule. The corresponding upper state ro-vibrational levels were fit using Watson-type Hamiltonians. In this way it was possible to reproduce the upper state ro-vibrational levels to within the experimental uncertainty; i.e., $\sim 0.20 \times 10^{-3}$ cm^{-1}. Very accurate rotational and centrifugal distortion constants were derived from the fit together with the following band centers: v_0 (v_2) = 515.659089(50) cm^{-1}, v_0 ($2v_2$) = 1030.697723(20) cm^{-1}.

1. Introduction

Sulfur dioxide plays an important role in the atmospheres of various planets [1–4]. Providing laboratory spectroscopic information on the less abundant isotopic species is then of interest for detecting them in those atmospheres. The fundamental bands of several isotopic species of SO_2 have been widely studied both in the microwave (see Refs. [5–13] and references therein) and infrared regions (see Refs. [14–21] and references therein). The $^{33}S^{16}O_2$ species has been the subject of spectroscopic studies in the microwave region [5,9,11,13], but to our knowledge no high resolution study has been performed in the infrared region. In this paper we present the first detailed extensive analysis of the spectrum of this molecule in the 18.3 μm spectral region where the v_2 and the $2v_2$-v_2 bands absorb. The work was performed using a high-resolution Fourier transform spectrum (0.002 cm^{-1} resolution) recorded at room temperature. The transition assignments have been extended to very high quantum numbers both for the v_2 and the $2v_2$ - v_2 bands. The upper state rotational constants were derived through the fit of the upper state levels using a Watson-type Hamiltonian written in the I^r (x = b, y = c, z = a representation) [22]. It is also worth noting that the ground state constants were slightly improved through a simultaneous fit of the existing microwave data and the ground state combination differences derived in this work.

2. Experimental

The $^{33}S^{16}O_2$ ro-vibrational spectra were recorded using a Bruker IFS 125HR spectrometer.[1] The instrument was configured to operate between 400 and 900 cm^{-1} using a KBr beamsplitter and a resistively heated silicon carbide infrared source. The spectrometer was evacuated below 0.015 Torr for these measurements. The sulfur dioxide sample was held in an adjustable path length White cell, the fore optics of which are seated in a sample compartment of the spectrometer. Wedged cesium iodide windows are used to separate the interior of the White cell from the interior of the spectrometer. The White cell optical path length for these measurements was 1604 cm ± 10 cm. Infrared light can be directed into the sample compartment without breaking vacuum. The White cell is hard-plumbed to a vacuum manifold that is used to evacuate the cell and introduce metered amounts of sample into the cell. Sample pressures were

[1] Certain commercial equipment instruments or materials are identified in this paper to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

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http://dx.doi.org/10.1016/j.jms.2016.12.011
0022-2852/

Table 1
Watson-type Hamiltonian used to calculate the 2^1 and 2^2 ro-vibrational levels of sulfur dioxide $^{33}S^{16}O_2$.

Watson-type Hamiltonian:

$$H_W = E_v + [A^v - 1/2(B^v + C^v)]J_z^2 + 1/2(B^v + C^v)]J^2 + 1/2(B^v - C^v)]J_{xy}^2$$
$$-\Delta_K^v J_z^4 - \Delta_{JK}^v J_z^2 J^2 - \Delta_J^v (J^2)^2 - \delta_K^v \{J_z^2, J_{xy}^2\} - 2\delta_J^v J_{xy}^2 J^2$$
$$+H_K^v J_z^6 + H_{KJ}^v J_z^4 J^2 + H_{JK}^v J_z^2 (J^2)^2 + H_J^v (J^2)^3$$
$$+h_K^v \{J_z^4, J_{xy}^2\} + h_{KJ}^v \{J_z^2, J_{xy}^2\} J^2 + 2h_J^v J_{xy}^2 (J^2)^2 + \cdots$$

with $\{A, B\} = AB + BA$, $J_\pm = J_x \mp iJ_y$ and $J_{xy}^2 = J_x^2 - J_y^2$

Table 2
Vibrational band centers, rotational and centrifugal distortion constant (in cm^{-1}) for the ground state and the 2^1 and 2^2 vibrational states of sulfur dioxide $^{33}S^{16}O_2$.

	0^0	2^1	2^2
E_v/hc		515.659089(45)	1030.697723(20)
A	1.996595277(660)[a]	2.03519127(120)	2.0755724155 (510)
B	0.344181308(130)	0.344255311 (140)	0.3443181510 (720)
C	0.292873783(120)	0.292341697 (120)	0.2918044548 (760)
$\Delta_K \times 10^4$	0.83801438(5200)	0.92860380 (9100)	1.03008145(3000)
$\Delta_{JK} \times 10^5$	−0.38180636 (9300)	−0.3984898 (1000)	−0.41622140 (7000)
$\Delta_J \times 10^6$	0.21976967(4000)	0.22026261 (5500)	0.220776116 (4500)
$\delta_K \times 10^6$	0.837348(2400)	1.025294(1200)	1.2247786(9700)
$\delta_J \times 10^7$	0.5708293(1400)	0.5744184(3300)	0.577717(1000)
$H_K \times 10^7$	0.1190711(1000)	0.1454599(2400)	0.17619965(5000)
$H_{KJ} \times 10^9$	−0.671247(4300)	−0.768561(6500)	−0.866080(2000)
$H_{JK} \times 10^{12}$	2.214621415[b]	4.605(1500)	6.995[c]
$H_J \times 10^{13}$	3.827390459[b]	3.86274(8800)	4.06420(9400)
$h_K \times 10^9$	0.74134(1400)	0.89564(6500)	1.06534(1100)
$h_{KJ} \times 10^{13}$	−1.427642403[b]	−1.427642403[b]	−1.427642403[b]
$h_J \times 10^{13}$	1.795770464[b]	1.85734(6300)	1.91891[c]
$L_K \times 10^{12}$	−2.635612983[b]	−3.21188(2000)	−3.78815[c]
$L_{KKJ} \times 10^{13}$	1.444367432[b]	1.57021(8300)	1.69605[c]
$L_{KJ} \times 10^{16}$	8.466570753[b]	8.466570753[b]	8.466570753[b]
$L_{JK} \times 10^{17}$	−8.243466351[b]	−8.243466351[b]	−8.243466351[b]
$L_J \times 10^{18}$	−1.331348331[b]	−1.331348331[b]	−1.331348331[b]
$l_{JK} \times 10^{17}$	6.855534121[b]	6.855534121[b]	6.855534121[b]
$l_J \times 10^{19}$	−8.610696124[b]	−8.610696124[b]	−8.610696124[b]
$P_K \times 10^{16}$	6.531343786[b]	6.531343786[b]	6.531343786[b]
$P_{KKKJ} \times 10^{17}$	−3.393376689[b]	−3.393376689[b]	−3.393376689[b]
$P_{KKJ} \times 10^{17}$	3.800968760[b]	3.800968760[b]	3.800968760[b]
$R_{K12} \times 10^{19}$	−1.208536717[b]	−1.208536717[b]	−1.208536717[b]

[a] Uncertainties are given in parentheses in units of the last significant digits as stated, in terms of one standard deviation σ in the least squares adjustment (coverage factor k = 1, B.N. Taylor and C.E. Kuyatt, NIST Technical Note 1297, U.S. Government Printing Office, 1994, pp. 1–20. The publication may be downloaded from http://physics.nist.gov/Pubs/guidelines/contents.html). The number of digits in the uncertainties kept for the parameters (2 for the band centers, 3 for the rotational constants and 4 for the centrifugal distortion constants) are required to reproduce the results of the fit within the experimental uncertainty.

[b] Fixed at ground state values from Refs. [11,23].

[c] Extrapolated from the corresponding constants of 0^0 and 2^1.

measured with a capacitance manometer (MKS Instruments model 690A01TRA; accuracy 0.05% of reading). The $^{33}SO_2$ sample pressure was 0.14483 hPa in the White cell. The temperature of the cell was not regulated, and was at room temperature, 25 °C ± 1 °C. For the 400–900 cm^{-1} range a liquid helium-cooled Si:Ga photodetector (Infrared Laboratories, Inc.) was used as the detector; it is fronted with a Winston cone and a 727–441 cm^{-1} passband filter. No other optical filters were used, the interferometer's aperture was set to 1.7 mm, and the scanner velocity was set to 40 kHz. Bruker's OPUS software (v7.0) was used to record the spectra.

A total of three-hundred twenty-eight coadded interferograms were processed by a Cooley-Tukey FFT with boxcar apodization, Mertz phase correction, and 1 cm^{-1} phase resolution. A zero filling factor of two was applied to the interferogram when it was initially recorded and an additional zero filling factor of eight was applied to bring the total zero filling factor to sixteen. Absorbance spectra were calculated as Abs = −ln(sample/background), where background spectra were recorded at sixteen times the instrument resolution and sixteen times the zero filling factor used for the associated sample spectrum. The White cell was being actively evacuated while background spectra were being recorded.

Wavenumber calibration was performed by recording the spectrum of a sample of OCS in the White cell using the same instrument parameters as those used for recording the $^{33}S^{16}O_2$ spectra. For the 400–900 cm^{-1} wavenumber region, 0.1433 hPa of OCS was placed in the White cell with the path length set to 1604 cm and the absorption spectrum recorded. The average of the wavenumber differences between the recorded spectrum and those given in the online NIST wavenumber tables (see https://www.nist.gov/pml/data/atlas-and-wavenumber-tables) for fifty-nine OCS transitions is 0.001002(107) cm^{-1}. This number was added to the wavenumber scale of the $^{33}SO_2$ spectrum for this wavenumber range.

The $^{33}S^{16}O_2$ sample was prepared by weighing out 0.026 g of sulfur-33 elemental powder (Trace Sciences International, Corp.; 99.8% ^{33}S enrichment) into a 100 mL vacuum Schlenk tube with a side arm (Kimble/Kontes model 218720-0100). The tube was then connected to the vacuum manifold, the air in the tube was evacuated, and the tube was then backfilled with 211 hPa of $^{16}O_2$ (Matheson). The tube was then wrapped with heat tape and baked at 488 °C for approximately 16 h. The sample was allowed to cool to room temperature and then was put through two freeze/pump/thaw cycles at liquid nitrogen temperature. As each spectroscopic measurement was finished, the sample was cryotrapped back into the Schlenk tube, and two freeze/pump/thaw cycles were performed prior to putting the sample into a gas cell for the next measurement.

3. Assignments and results

The line assignment process proved to be somewhat difficult given the density of lines in the spectrum. The analysis was started by analyzing the v_2 band which is the strongest infrared band in the 18.3 μm spectral region. The first estimation of the ground state rotational levels was made using the rotational constants quoted in Ref. [23]. As far as the 2^1 rotational levels are concerned, a first calculation was made using rotational constants estimated from the rotational constants of the $^{32}S^{16}O_2$ [16] and $^{34}S^{16}O_2$ [17] species. In this way it was possible to assign a few lines with rather low rotational quantum numbers. Then, as soon as a few lines were assigned, the corresponding upper state energy levels were fit with a computer program [24] using a Watson-type Hamiltonian (Table 1) and the refined upper state Hamiltonian constants were used to perform more reliable predictions allowing one to assign new lines. The process was repeated until it was no longer possible to locate and assign new lines with confidence.

However, it is worth noting that for high J and K_a quantum numbers the observed ground state combination differences were marginally different from those derived from the original calculation performed with the constants of Ref. [23]. Accordingly, we fit simultaneously the ground state microwave data together with the combination differences derived in this work and the corresponding ground state constants are given in Table 2. The 2^1 upper state rotational levels were fit together with the existing 2^1 microwave data [5,8] and the corresponding constants are given in Table 2. The results of the analysis are given in Table 3 showing that the fit was very satisfactory since the standard deviation is fully consistent with the experimental uncertainty.