

Transferring calibration from CO₂ laser lines to far infrared water lines with the aid of the ν_2 band of OCS and the ν_2 , $\nu_1 - \nu_2$, and $\nu_1 + \nu_2$ bands of ¹³CS₂: Molecular constants of ¹³CS₂

V.-M. Horneman*, R. Anttila, S. Alanko, J. Pietilä

Department of Physical Sciences, P.O. BOX 3000, Fin-90014 University of Oulu, Finland

Received 22 June 2005; in revised form 8 September 2005

Available online 8 November 2005

Abstract

Water (H₂O) lines in the far infrared region from 210 to 600 cm⁻¹ have been calibrated against high accurate primary standard of the carbon dioxide (CO₂) laser lines with the aid of vibration–rotation transitions in the carbonyl sulfide (OCS) and ¹³C enriched carbon disulfide (¹³CS₂) molecules. The ν_2 band of ¹³CS₂ and the H₂O spectrum from 320 to 560 cm⁻¹ was calibrated with the OCS ν_2 band, which had earlier been calibrated against the 9.4 μ m CO₂ laser band that is lying in the same region as the OCS $2\nu_2$ band. The $\nu_1 + \nu_2$ and $3\nu_2$ bands of ¹³CS₂ were measured at the spectral resolution of 0.0032 cm⁻¹. The former band was also calibrated with the 9.4 μ m CO₂ laser band that is overlapping the ¹³CS₂ band. The calibration was then transferred to the ¹³CS₂ $\nu_1 - \nu_2$ difference band at 270 cm⁻¹ and to H₂O spectrum in the same region with the ¹³CS₂ fundamental ν_2 and associated hot bands and the internal information of the ¹³CS₂ vibration–rotation energy levels. The spectra for far infrared regions were measured at the instrumental resolution of 0.001 cm⁻¹. The range of the ν_2 band was measured with a Fourier transform spectrometer in the infrared laboratory at the University of Oulu using a conventional globar source and the lower lying range of the $\nu_1 - \nu_2$ band with a same kind of instrument in the Max laboratory in Sweden by utilizing a synchrotron radiation source. Molecular parameters for ¹³CS₂ were also updated from the analysis of all the available bands.

© 2005 Elsevier Inc. All rights reserved.

Keywords: High accurate wavenumbers; Vibration rotation analysis

1. Introduction

Recently, the high accuracy of the carbon dioxide (CO₂) laser bands around 10 μ m [1] was transferred to the far infrared region from 230 to 480 cm⁻¹ with the rotation vibration bands of carbon disulfide (¹²CS₂) [2]. The bands $3\nu_2$ and $\nu_1 + \nu_2$ were compared to laser lines. Next the region of the fundamental ν_2 was measured and it was internally calibrated against $3\nu_2$ using ladders formed by lines in the bands ν_2 , $2\nu_2 - \nu_2$, and $3\nu_2 - 2\nu_2$. The region of $\nu_1 - \nu_2$ was calibrated in a corresponding way starting from $\nu_1 + \nu_2$. The initial aim of the present work was to repro-

duce the same calibration procedure with the ¹³C enriched isotopic species of carbon disulfide and to ensure the results of the previous work. Concerning the primary calibration the situation for ¹³CS₂ is slightly more favorable because the $3\nu_2$ band (1169 cm⁻¹) is located about 40 cm⁻¹ lower than that of ¹²CS₂ and so the distance to be extrapolated from the higher laser band is shorter. Therefore, more accurate calibration could be expected—in principal. Unfortunately, as good spectrum as in the previous work [2] could not be produced. Because of the small amount of the sample the large cell with long absorption path length could not be used and the spectrum remained weak. Small line shape errors could also be found. The calibration of the ν_2 spectrum with the $3\nu_2$ band proved to lead to less accurate results than in the previous work. The region from 320 to 600 cm⁻¹ covers the ν_2 bands of ¹³CS₂

* Corresponding author. Fax: +358 8 5531287.

E-mail address: veli-matti.horneman@oulu.fi (V.-M. Horneman).

and OCS together with H₂O lines and so it was decided to apply the recent results from [3].

The region of the ¹³CS₂ ν_2 band (383 cm⁻¹) was measured at a resolution of about 0.010 cm⁻¹ by Kauppinen and Jolma [4] more than 20 years ago. They assigned and analyzed the fundamental, several hot bands, and an isotopic band as well as the difference band $\nu_1 - \nu_2$ (274 cm⁻¹). The ν_2 region was now re-measured together with OCS. As the ν_2 band of OCS has recently been calibrated against CO₂ laser band [3] it could be used for calibrating both the ¹³CS₂ spectrum and water lines in the wavenumber region from 320 to 600 cm⁻¹.

The $\nu_1 + \nu_2$ spectrum is overlapping the 9.4 μ m CO₂ laser band and therefore the calibration could be performed more accurate for it than for $3\nu_2$. The calibration was then transferred to the region of the $\nu_1 - \nu_2$ band of ¹³CS₂ and H₂O lines around 270 cm⁻¹ with the fundamental ν_2 and associated hot bands of ¹³CS₂ together with the information about the structure of the vibration–rotation states in the ¹³CS₂ molecule. The result of the H₂O line positions form the calibration spectrum from 212 to 600 cm⁻¹ that is compatible with the CO₂ laser based previous results in [2,3]. As a final step the $3\nu_2$ band was calibrated backwards with the ν_2 and associated hot bands of ¹³CS₂ using the connection of the corresponding vibration–rotation transitions.

In addition to those bands needed in the calibration procedure a great number of ¹³CS₂ bands were analyzed. They resulted in an extended set of molecular parameters for low vibrational states of ¹³CS₂. These generally are more accurate than previous values or they are entirely new. Some results were also obtained for the isotopic species ³⁴S¹³C³²S and ³³S¹³C³²S. As impurity there was also ¹⁶O¹³C³²S in the sample, when the spectrum around 10 μ m was measured. The results for the band $2\nu_2^0$ of ¹⁶O¹³C³²S will also be given.

2. Experimental details

All the measurements were carried out with Bruker IFS 120 HR spectrometers at room temperature. The $\nu_1 + \nu_2$ and $3\nu_2$ bands in the 10 μ m region as well as the ν_2 band with the accompanying hot bands in the same region were recorded in Oulu. The measurement in the difference band $\nu_1 - \nu_2$ was performed in the MAX laboratory in Lund, Sweden by applying a synchrotron radiation source. In both far infrared measurements the maximum resolution 0.00085 cm⁻¹ due to the mirror movement was used. In the 10 μ m region the Doppler width is 0.0017 cm⁻¹. Therefore and also to get a good signal-to-noise (*S/N*) ratio in the weak spectrum a lower resolution of 0.0025 cm⁻¹ was used. A detailed list of the experimental conditions in all three measurements has been collected in Table 1. A White cell [5,6] that has been optimized for the optics of the Bruker IFS 120 HR spectrometer was used in all the measurements. The absorption spectrum of CO₂ laser lines was obtained simultaneously with the CS₂ spectrum.

3. Spectra

Both the bands $\nu_1 + \nu_2$ and $3\nu_2$ in the 10 μ m region are weak and they naturally resemble those of the more common isotopic species ¹²CS₂ [2]. Herman–Wallis effect causes remarkable intensity anomalies in the bands. In the combination band $\nu_1 + \nu_2$ around 1032 cm⁻¹ the *Q* branch is rather dense, as can be seen in Fig. 1. However, it was resolved almost from the beginning and it could be followed up to *J* = 90. The *P* branch is relatively strong and it could be assigned until *J* = 112. The *R* side is weaker and when *J* is smaller than 30 the intensity practically vanishes. The branch was detected until *J* = 114. The weak lines in high *J* tails were omitted from calculations as well as all blended lines. Hot bands starting from $\nu_2 = 1$, $\nu_2 = 2$, and $\nu_1 = 1$

Table 1
Measurement conditions for the different band regions

	$\nu_1 + \nu_2/3\nu_2$	ν_2	$\nu_1 - \nu_2$
Range (cm ⁻¹)	900–1300	320–610	200–360
Spectrometer	Bruker 120 HR Oulu	Bruker 120 HR Oulu	Bruker 120 HR Lund, Sweden
Source	Globalar	Globalar	Synchrotron radiation
Beamsplitter	Ge/KBr	Mylar 3.5 μ m	Mylar 6 μ m
Detector	MCT liq. N ₂	Si-bolometer liq. He (1.4 K)	Si-bolometer liq. He (1.4 K)
Optical filter	Interference	Cold low-pass	Cold low-pass
Filter band (cm ⁻¹)	820–1350	0–650	0–370
Resolution (cm ⁻¹) ^a	0.0017	0.00085	0.00085
Observed linewidth (cm ⁻¹)	0.0025–0.0035	0.0011–0.0014	0.0010–0.0014
Registration time (h)	59.3	68.3	18.4
<i>S/N</i> ratio (100% absorp.)	300	100	40
<i>S/N</i> in CS ₂ peaks (max)	100	100	32
Path length (m)	41.8	16	9.6
Sample pressure (Pa)	410.6	0.13	120
Pressure of CO ₂ (Pa)	114.7		
Pressure of OCS (Pa)		2.40	
Cell windows	KBr	KRS-5	KRS-5/WPE ^b

^a Due to the maximum optical path length.

^b The input and output windows KRS-5 and white polyethylene, respectively.

Download English Version:

<https://daneshyari.com/en/article/9589415>

Download Persian Version:

<https://daneshyari.com/article/9589415>

[Daneshyari.com](https://daneshyari.com)