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Journal of Molecular Spectroscopy 229 (2005) 89–107

Journal of MOLECULAR SPECTROSCOPY

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Transferring the high accuracy of the 10 μm CO_2 laser bands to far infrared region with internal calibration of CS_2

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Received 10 June 2004; in revised form 18 August 2004

Abstract

The main aim of the work is to transfer the high accuracy of the CO_2 laser bands around 10 μm to far infrared regions around 400 and 250 cm^{-1} for secondary standards. The bands $\nu_1 + \nu_2$ and $3\nu_2$ of CS_2 were measured on the Bruker IFS 120 HR Fourier spectrometer in Oulu with special care and calibrated against CO_2. In the second stage the ν_2 region around 400 cm^{-1} was measured at a resolution of 0.001 cm^{-1}. This spectrum was calibrated against $3\nu_2$ internally with the CS_2 band system using ladders formed with rotational lines in the bands ν_2, $2\nu_2 - \nu_2$ and $3\nu_2 - 2\nu_2$. Further, the difference band $\nu_1 - \nu_2$ at 263 cm^{-1} together with accompanying hot bands was measured on a similar spectrometer in Lund, Sweden, but with a synchrotron radiation source. Using corresponding chains of lines as above this region was calibrated with $\nu_1 + \nu_2$. In this way, problems with conventional calibration could be avoided. Without the effect of the pressure shifts the absolute accuracy of 2.0×10^{-6} and 8.4×10^{-6} cm^{-1} has been achieved at 400 and 250 cm^{-1}, respectively. Simultaneously the same calibration accuracy is also transferred to residual water lines around the CS_2 far infrared bands and the best H_2O lines will be given with literature comparisons. In addition to the calibration new results from the observed hot bands of CS_2 in the region of the bands $\nu_1 + \nu_2$ and $3\nu_2$ will be given.

Keywords: Wavenumber calibration; High accurate infrared measurement; Carbon disulfide spectra

1. Introduction

Some years ago we measured the weak bands $\nu_1 + \nu_2$ and $3\nu_2$ of CS_2 [1]. The spectra in the region 1000–1300 cm^{-1} were carefully calibrated against CO_2 laser lines [2]. In addition to the investigation of the bands themselves the idea was to start a series of measurements with which the high accuracy around 10 μm could be transferred to the more troublesome far infrared region. The region of the fundamental band ν_2 (396 cm^{-1}), previously investigated, e.g., by Jolma and Kauppinen [3], was re-measured. The ν_2 band and several hot bands were assigned. Sums of suitable rotational lines in the bands ν_2, $2\nu_2^{0,2} - \nu_2$, and $3\nu_2^1 - 2\nu_2^{0,2}$ were formed. By comparing them with the direct transitions in the $3\nu_2$ band we calibrated the bands in the region of the fundamental ν_2. The principle and preliminary results were presented in different conferences [4–6]. When inspecting carefully the measured spectra to prepare the article some small shortcomings were observed. These errors had been of minor importance, if the spectra had only been applied to deduce molecular parameters. However, the phase errors and differences between strong and weak lines could not be accepted in calibration work. The situation is more difficult also because $3\nu_2$ band does not overlap any of the CO_2 bands, but an extrapolation is needed in the calibration. During the next years the spectrometer was renovated and improvements in alignment methods were developed. Now quite satisfying spectra have been obtained and the task can be completed.

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0022-2852/$ - see front matter
doi:10.1016/j.jms.2004.08.016

The primary sources for calibration spectra in the infrared are the books edited by Guelachvili and Rao [7]. The wavenumber standards recommended for calibration has been later given in the thorough report collected by an international commission [8]. In the far infrared (FIR) region the most accurate calibration sources with easily treatable gases are the pure rotational lines of CO [9] and the ν_2 lines of OCS [10–13]. The former lie in the region below 150 cm^{-1} and the latter band is between 500 and 550 cm^{-1}. So they are at different ends of the FIR region. Calibration errors from these sources to the middle of FIR region are often significant. Pure rotational lines of H_2O spread over the whole far infrared region and they are present practically always, see [14] and references there. The application of water lines can still be extended by using D_2O and HDO [14]. Water lines are easy to use in calibration. The accuracy is only moderate, however, because, e.g., the spectra in [14] have been calibrated with the OCS lines mentioned above. On the other hand some kind of asymmetries compared to lines of linear molecules have also been found in water lines [14]. At this time our opinion is that those lineshape asymmetries were caused by same kind of non-linear type phase errors in the measured spectrum, which has disturbed our accurate measurements with cube corner interferometers. By using interdependencies between transitions of one molecule in the way described above the calibration can be transferred over a long wavenumber range partially eliminating common calibration errors. One reason for problems to transfer calibration in the FIR region is the poor *S*/*N* in high resolution spectra. Signal to noise ratio limits also the accuracy of these measurements but one advantage is that the important initial calibration can be made in the region above 1000 cm^{-1}, where higher *S*/*N* is available. The second advantage in the present case is that the primary standard, CO_2 laser bands, are used as the source.

We have also measured the difference band $\nu_1 - \nu_2$ (262 cm^{-1}). With the aid of the fundamental ν_2, and the hot bands $\nu_1 - \nu_2$, $\nu_1 + \nu_2 - \nu_1$, $2\nu_2 - \nu_2$, and $\nu_1 + \nu_2 - 2\nu_2$ we formed sums, which could be compared with the direct transitions in the $\nu_1 + \nu_2$ band. In this way the calibration was transferred to the region of the band $\nu_1 - \nu_2$ too.

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 μm region as well as ν_2 together with the accompanying hot bands in the same region were recorded in Oulu. The measurement conditions have been collected in Table 1. After those measurements presented in [3–5] the spectrometer was renovated and the resolution due to the mirror movement was enhanced to 0.00085 cm^{-1}. Also many components were changed. The measurements in the $\nu_1 + \nu_2$/$3\nu_2$ region were repeated several times to get better spectra and also computational correction programs were tried. However, it was only after improvements in the moving mirror guides and alignment procedures that spectra, practically free of distortions, could be produced. The whole careful aligning and checking procedure is described in details by Horneman [13]. A remeasurement over the ν_2 region was also carried out. In the measurement of the weak $\nu_1 + \nu_2$ and $3\nu_2$ bands, the large White cell [1] was applied. For calibration, carbon dioxide was added in the sample gas (pressure 24 Pa). The CO_2 spectrum was recorded simultaneously with that of the CS_2 sample. In this region, the Doppler

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	200–350
Spectrometer	Bruker 120 HR Oulu	Bruker 120 HR Oulu	Bruker 120 HR Lund, Sweden
Source	Globar	Globar	Synchrotron radiation
Beamsplitter	Ge/KBr	Mylar 3.5 μm	Mylar 6 μm
Detector	MCT liquid N_2	Si-bolometer liquid He (1.4 K)	Si-bolometer liquid He (1.4 K)
Optical filter	Interference	Cold low-pass	Cold low-pass
Filter band (cm^{-1})	820–1400	0–650	0–370
Resolution (cm^{-1})*	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)	121.5	43	12.5
S/*N* ratio (100% absorption)	300–400	100	30
S/*N* in CS_2 peaks (max)	300	100	25
Path length (m)	173	16	9.6
Sample pressure (Pa)	410	1.0	120
Pressure of CO_2 (Pa)	24		

* Due to the maximum optical path length.