Journal of Molecular Spectroscopy 292 (2013) 1–4

Contents lists available at ScienceDirect

Journal of Molecular Spectroscopy

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

Absolute line intensities for oxirane from 1420 to 1560 cm^{-1}

F. Kwabia Tchana [a,*], M. Ngom [a,b], A. Perrin [a], J.-M. Flaud [a], W.J. Lafferty [c], S.A. Ndiaye [b], El.A. Ngom [b]

[a] 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

[b] Université Cheikh Anta Diop, Ecole Supérieure Polytechnique, Laboratoire de Physique de l'Atmosphère et l'Océan Simeon Fongang (LPAO-SF), BP 5085, Dakar, Senegal

[c] Sensor Science Division, National Institute of Standards and Technology, Gaithersburg, MD 20899-8440, USA

ARTICLE INFO

Article history:
Received 24 June 2013
In revised form 26 July 2013
Available online 8 August 2013

Keywords:
Oxirane
C_2H_4O
Infrared
Fourier transform spectra
Absolute intensities
Transition dipole moments

ABSTRACT

Absolute individual line intensities of numerous transitions of the fundamental ν_2 and ν_{10} bands of oxirane (ethylene oxide, cyc-C_2H_4O) have been measured in the 1420–1560 cm^{-1} region using seven high-resolution Fourier transform spectra recorded at 0.002 cm^{-1} resolution and various pressures. These line intensities were least-squares fit using a theoretical model which takes into account the vibration–rotation interactions linking the upper state rotational levels, and, therefore, accurate rotational expansion of the transition moments of the ν_2 and ν_{10} vibrational bands were derived. Using the coefficients obtained in the fitting, a line list of both bands has been generated. Comparisons with measurements taken at low resolution of the ν_2/ν_{10} dyad system show excellent agreement.

1. Introduction

Oxirane (ethylene oxide, cyc-C_2H_4O) has been detected in the interstellar medium especially in the star-forming regions [1]. Also Coll et al. [2] have suggested that this molecule could be present in the Titan atmosphere. Oxirane has been the subject of a number of low- and medium-resolution studies [3–5]. More recently, Russel and Wesendrup [6] have used a diode laser to study the ν_3 band located at 1270.4 cm^{-1} at high resolution. An analysis of a number of the vibrational bands of this molecule has been published by Flaud et al. [7]. In that work, the Fourier transform spectra were recorded in the 730–1560 cm^{-1} region at a resolution of 0.0019 cm^{-1} using the LISA Bruker IFS125HR spectrometer. In all, a total of six vibrational bands, ν_2, ν_3, ν_5, ν_{10}, ν_{12}, and ν_{15}, have been observed and analyzed. The upper state ro-vibrational levels of these states were fit using Hamiltonian matrices accounting for the various relevant interactions.

Specially, satisfactory fits were obtained using the polyads $\{15^1,12^1,5^1\}$ and $\{10^1,2^1\}$ of interacting states. In addition, as far as individual line intensities are concerned, a large set of individual ν_3 experimental line intensities was used to determine precisely the transition moment constants of this band. An accurate listing of line positions and intensities has been generated for ν_3 and comparisons with measurements at low resolution of the ν_3 intensity show a very good agreement [8].

The present study presents the measurement and modeling of the absolute infrared intensities for the two fundamental bands, ν_2 (CH_2 Scis mode) and ν_{10} (CH_2 Scis mode), of oxirane. The experimental individual line intensities were derived by analyzing seven Fourier transform spectra recorded at the LISA facility in Créteil. Modeling of the intensities was achieved using a model which accounts for the strong Coriolis coupling between these two states. Finally, a calculated spectrum of the 1430–1560 cm^{-1} oxirane bands has been generated using the dipole moment expansion determined in this work, and the molecular parameters and the Hamiltonian matrix given in a previous analysis [7]. Comparisons with band intensity measurements at low resolution of this dyad system, ν_2/ν_{10}, show very good agreement.

2. Experimental details and absolute intensity measurements

2.1. Experimental details

Seven absorption spectra of oxirane were recorded using the high-resolution Fourier transform spectrometer[1] Bruker IF125HR located at the LISA facility in Créteil. The instrument was equipped with a KBr/Ge beamsplitter, a silicon carbide Globar source, a low-pass filter with a cut-off wavenumber of 1970 cm^{-1} and a liquid

---

* Corresponding authors. Fax: +33 (0)1 45 17 15 64.
E-mail address: fridolin.kwabia@lisa.u-pec.fr (F. Kwabia Tchana).

[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 NIST nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

0022-2852/$ - see front matter © 2013 Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.jms.2013.07.006

nitrogen cooled HgCdTe photovoltaic detector. The entire optical path was evacuated in order to minimize H_2O and CO_2 absorptions. The aperture diameter (1.3 mm) of the spectrometer was set to maximize the intensity of IR radiation falling on the MCT detector without saturation or loss of spectral resolution. Spectra were recorded with a 40 kHz scanner frequency and a maximum optical path difference (d_{MOPD}) of 450 cm which corresponds to a resolution of 0.002 cm^{-1} according to the Bruker definition (Resolution = 0.9/d_{MOPD}). A short-path absorption cell (SPAC) made of Pyrex glass and equipped with CsBr windows was used for all the measurements. The SPAC is a White-type multipass cell with a base length of 0.20 m. In this experiment an optical path of 0.849(2) m was used. Transfer optics (six mirrors) located inside the sample compartment of the FTS were used to transfer the radiation from the spectrometer into the cell, and from the cell onto the MCT detector.

The oxirane sample was purchased from Sigma Aldrich with a stated purity of 99.8% and was used without further purification. The following procedure was used for each measurement. Initially a background spectrum was collected while the cell was being continuously evacuated. The infrared gas cell was treated with C_2H_4O several times until the surfaces of the cell were saturated. For the pressure measurements, a calibrated MKS Baratron gauge model 627 *D* (1333.224 Pa full scale) was used. According to the manufacturer, it has an accuracy of 0.12%. The actual uncertainty for the sample pressure was estimated to be about 0.5% taking into account the accuracy and the pressure variation which occurred during the recording. The spectra were recorded at a stabilized room temperature of 295 ± 1 K. All spectra were ratioed against a single channel background spectrum of the empty cell which was recorded at a resolution of 0.256 cm^{-1} in order to ensure the best possible signal-to-noise in the ratioed spectra. For the Fourier transform, a Mertz-phase correction, 0.5 cm^{-1} phase resolution, a zero-filling factor of 2 and a boxcar apodization function were applied to the averaged interferograms. The FTS instrumental parameters and settings are summarized in Table 1, and details of the pressures and the number of scans taken for each sample are given in Table 2. All the spectra were calibrated with residual CO_2 and H_2O lines observed in the spectra with their wavenumbers taken from HITRAN [9] leading to an accuracy of 0.00040 cm^{-1} for a well isolated line.

2.2. Absolute intensity measurements

The individual line intensities were measured using the computer program and procedure described in a previous paper [10]. In brief, the measurements involved the adjustment of a calculated spectrum to the observed spectrum using a Levenberg–Marquardt non-linear least squares fitting procedure [11]. The calculated spectrum was computed as the convolution of a Voigt line profile and an instrumental line shape function which models the contributions of the finite maximum optical path difference and of the finite source aperture diameter of the interferometer [12]. No line mixing was introduced. For each line, the position, the $S * P$ (S is the integrated absorption coefficient per unit pressure and P is the pressure) product and the Lorentzian widths of the Voigt profile are fitted (in this work the Gaussian width was held fixed at the value calculated for the Doppler width). In addition, for the background, a slope and a curvature can also be varied. An example of the quality of the fitting procedure is given in Fig. 1. The upper panel shows the observed and calculated spectra overlaid; the lower panel gives the difference between the two in percent. A typical plot of the $S * P$ products derived from the fittings versus the C_2H_4O pressures, P, is shown in Fig. 2 for the ${}^qP_3(16)$, ${}^qR_4(13)$ lines of the ν_2 band and the ${}^qP_1(12)$ line of the ν_{10} band. The straight line obtained from the fitting show a good verification of the linearity of the $S * P$ product against P. The line intensities S (in cm^{-2}/atm) can be derived from the slopes of these straight lines. A total of 139 individual line intensities were obtained.

Table 1
FTS and SPAC configurations.

Source	SiC Globar
Detector	HgCdTe (MCT)
Beam Splitter	KBr/Ge
Maximum optical path difference (d_{MOPD})	450 cm
Resolution = 0.9 / d_{MOPD}	0.002 cm^{-1}
Aperture diameter	1.3 mm
Apodization function	Boxcar
Phase correction	Mertz
Phase resolution	0.5 cm^{-1}
Transfer optics mirror coatings	Gold
Cell windows	CsBr
Cell Mirror coatings	Gold
Pressure gauge	MKS-627 D Baratron (1333,224 Pa)

Table 2
Summary of experimental conditions used to record the Fourier transform infrared spectra of oxirane.

Spectrum no.	Oxirane pressure (hPa)	No. of scans
1	3.209(16)[a]	365
2	4.016(20)	354
3	4.746(24)	318
4	5.349(27)	378
5	6.061(30)	384
6	6.710(34)	414
7	7.339(37)	348

All spectra are recorded with a path length of 0.849 (2) m at stabilized room temperature of 295.2 ± 1 K. The path length value takes into account the distance between the surface of the field mirror and the windows of the cell (2 × 2.45 cm).

[a] The numbers between parentheses represent the absolute uncertainty in the units of the last digit quoted. It includes the variation of the pressure during the recording of the spectra.

The precision of the measurements (2σ) can be judged by examining the residuals of the fits. They are generally less than 1%. However, a better estimate of the accuracy of the line intensities requires taking into consideration the uncertainties on the physical parameters, the purity of the sample and contributions from possible systematic errors [13]. The dominant contributions to the systematic errors was found to arise from offsets in the 0% transmission level and nonlinearities in the response of the MCT detector. We estimate that the actual accuracy of the line intensities measured in this work is approximately 5%.

3. Line intensity calculations

The intensity of a line is given in cm^{-1}/(molecule cm^{-2}) by [14,15]:

$$k_{\tilde{\nu}}^{N} = \frac{8\pi^3\tilde{\nu}}{4\pi\varepsilon_0 3hcZ(T)} g_n \left(1-\exp\left(-\frac{hc\tilde{\nu}}{kT}\right)\right)\exp\left(-\frac{hcE_A}{kT}\right)R_A^B \qquad (1)$$

where A and B are respectively the lower and upper levels of the transition and $\tilde{\nu} = (E_B - E_A)/hc$ is the wavenumber of the transition. For the total partition function, $Z(T)$ we used $Z(296\text{ K}) = 84025.30$. Also, g_n is the nuclear spin statistical weight, with $g_n = 10$ (6) for the ground state rotational levels with $(K_a + K_c)$ = even (odd) respectively [7]. Finally, R_A^B is the square of the matrix element of the transformed transition moment operator μ'_Z. μ'_Z is expanded as:

$$\mu'_Z = \sum\nolimits_{v' \in B'} |0\rangle^{v'} \mu_z \langle v'| \qquad (2)$$

where v' belongs to the upper polyad of interacting states B'.