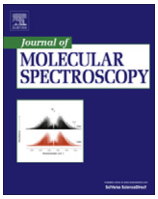
Journal of Molecular Spectroscopy 271 (2012) 38–43

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Spectroscopy

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



First high-resolution analysis of the ν_{15}, ν_{12}, ν_5, ν_{10} and ν_2 bands of oxirane

J.-M. Flaud [a], W.J. Lafferty [b,*], F. Kwabia Tchana [a], A. Perrin [a], X. Landsheere [a]

[a] *Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), UMR CNRS 7583, Universités Paris Est Créteil et Paris Diderot, Institut Pierre Simon Laplace, 61 Avenue du Général de Gaulle, 94010 Créteil Cedex, France*

[b] *Optical Technology Division, National Institute of Standards and Technology, Gaithersburg, MD 20899-8440, USA*

ARTICLE INFO

Article history:
Received 12 October 2011
In revised form 22 November 2011
Available online 2 December 2011

Keywords:
Oxirane
Ethylene oxide
High resolution IR spectrum

ABSTRACT

Fourier transform spectra of oxirane (ethylene oxide, c-C_2H_4O) have been recorded in the 730–1560 cm^{-1} (6.4–13.7 μm) spectral region using a Bruker IFS125HR spectrometer at a resolution of 0.0019 cm^{-1}. A total of six vibration bands, ν_{15}, ν_{12}, ν_5, ν_3, ν_{10} and ν_2, have been observed and analyzed. The corresponding upper state ro-vibrational levels were fit using Hamiltonian matrices accounting for various interactions. Satisfactory fits were obtained using the following polyads $\{15^1,12^1,5^1\}$ and $\{10^1,2^1\}$ of interacting states. As a result, an accurate and extended set of Hamiltonian constants were obtained. The following band centers were derived: ν_0 (ν_{15}) = 808.13518(60) cm^{-1}, ν_0 (ν_{12}) = 822.27955(37) cm^{-1}, ν_0 (ν_5) = 876.72592(15), ν_0 (ν_3) = 1270.37032(10) cm^{-1}, ν_0 (ν_{10}) = 1471.35580(50) cm^{-1} and ν_0 (ν_2) = 1497.83309(15) cm^{-1} where the uncertainties are one standard deviation.

1. Introduction

Oxirane(ethylene oxide, c-C_2H_4O) has been the subject of a number of both low- and medium-resolution infrared studies [1–3] but, to the best of our knowledge, only one band, the ν_3 band located at 1270.4 cm^{-1}, has been analyzed at high-resolution [4]. However, there have been quite a few microwave studies on both the ground state and excited states of this molecule [5–9]. Because of this a very accurate set of rotational and centrifugal distortion constants have been derived for the ground state leading to the possibility of using combination differences to check the assignments of the infrared bands, a majority of which are perturbed. Despite the number of infrared studies there is still some uncertainty of the correct vibrational assignment of a few of the IR bands.

In this paper we present an extensive high-resolution analysis of the three interacting bands ν_{15}, ν_{12} and ν_5 which fall in the 750 cm^{-1} to 950 cm^{-1} range, of the ν_3 band between 1200 cm^{-1} and 1350 cm^{-1} and of the interacting ν_2 and ν_{10} bands which absorb between 1420 cm^{-1} and 1560 cm^{-1}.

The upper state rotational levels were fit using Hamiltonian (written in the I^r ($x = b$, $z = a$, $y = c$) representation) models taking into account the numerous interactions affecting the various states. In this way, very satisfactory fits were obtained which lead to accurate Hamiltonian constants. The oxirane molecule possesses C_{2v} symmetry. In order to simplify the following discussions, its structure as well as its symmetry properties and nuclear spin statistical weights are illustrated in Fig. 1.

2. Experimental details

The high-resolution absorption spectra of oxirane were recorded with the Bruker IFS125 SHR Fourier transform spectrometer[1] located at the LISA facility in Creteil. A KBr beam splitter, Globar source (silicon carbide, SiC) and a HgCdTe (MCT) photovoltaic liquid nitrogen cooled detector were used for these recordings. The spectrometer was evacuated to roughly 6.7 Pa (0.05 Torr) in order to minimize residual absorptions by H_2O and CO_2. An entrance aperture diameter of 1.3 mm and a maximum optical path difference (d_{MOPD}) of 473.68 cm was used. According to the Bruker definition, this corresponds to a resolution of 0.0019 cm^{-1} (Resolution = 0.9/d_{MOPD}). The White-type multipass absorption cell, constructed of Pyrex glass and equipped with CsBr windows, was connected to the FTS with a dedicated optical interface (six mirrors) inside the sample chamber of the instrument. Its base length is 0.80 m and, for the experiment described here, an optical path of 32.049 m was used. The oxirane sample of stated purity 99.8% was purchased from Sigma–Aldrich and used without further purification.

Six spectra were recorded at a stabilized room temperature of 295.2 K and with pressures of 8.399(13) Pa (0.0630(1) Torr),

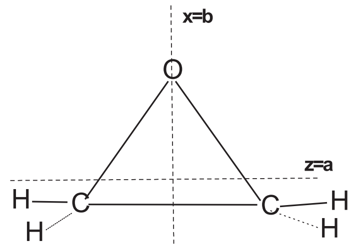
---

* Corresponding author. Fax: +1 301 975 2950.
E-mail address: walter.lafferty@nist.gov (W.J. Lafferty).

[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.

0022-2852/$ - see front matter © 2011 Elsevier Inc. All rights reserved.
doi:10.1016/j.jms.2011.11.005

Structure of the oxirane molecule



C_{2v} group character table

	I	C_{2x}	σ_{xz}	σ_{xy}	Polar vector	Axial vector	Vibrations
A_1	1	1	1	1	T_x		$\nu_1, \nu_2, \nu_3, \nu_4, \nu_5$
A_2	1	1	-1	-1		R_x	ν_6, ν_7, ν_8
B_1	1	-1	1	-1	T_z	R_y	$\nu_9, \nu_{10}, \nu_{11}, \nu_{12}$
B_2	1	-1	-1	1	T_y	R_z	$\nu_{13}, \nu_{14}, \nu_{15}$

Nuclear spin statistical weights for the ground state rotational levels

K_a	K_c	Weight
Even	Even	10
Even	Odd	6
Odd	Even	6
Odd	Odd	10

Fig. 1. Structure and symmetry properties of the oxirane (ethylene oxide) molecule.

33.86(40) Pa (0.2540(3) Torr), 16.40(13) Pa (0.1230(1) Torr) , 8.626(13) Pa (0.0647(1) Torr), 20.465(25) (0.1535(2) Torr), and 62.128(80) (0.4660(6) Torr) in order to get the best line positions for each band. Sample pressures in the multipass cell were measured using a high-accuracy capacitance manometer (266.65 Pa (2 Torr) full scale, MKS instruments type 627D Baratron) which has a stated uncertainty of 0.12% of full scale according to the manufacturer. Spectra were ratioed against an empty cell single-channel background spectrum which was taken at a resolution of 0.4864 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 300 interferograms. For the Fourier transform a Mertz-phase correction, 1 cm^{-1} phase resolution, zero-filling factor of 2 and boxcar apodization function were applied to the averaged interferograms. All the spectra were calibrated with residual CO_2 and H_2O lines observed in the spectra with their wavenumbers taken from HITRAN89 [10]. The resulting precision is ±0.00012 cm^{-1} (RMS) for well isolated lines. The absolute accuracy can be estimated as the RMS agreement of the CO_2 and H_2O lines, i.e. 0.0007 cm^{-1}. Figs. 2–4 give overviews of the 750 cm^{-1} –950 cm^{-1}, 1200 cm^{-1} –1350 cm^{-1} and 1420 cm^{-1} –1560 cm^{-1} spectral domains showing the high signal-to-noise ratios which were obtained. The band centers of the various bands are

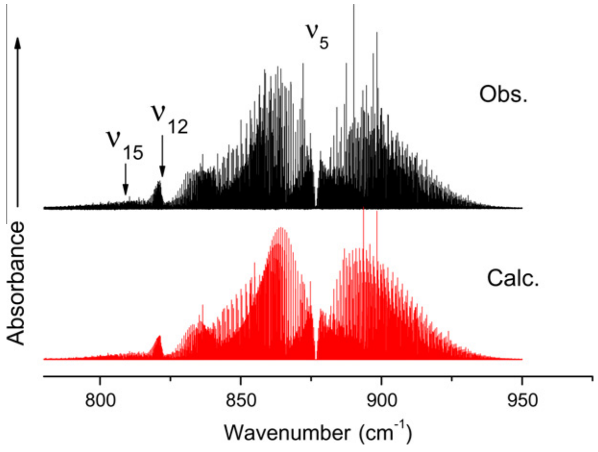


Fig. 2. Overview of the oxirane spectrum between 1.05 μm and 1.33 μm. The C-type ν_{15}, B-type ν_5 and A-type ν_{12} band centers are indicated. The upper trace is the observed spectrum recorded with a resolution of 0.0019 cm^{-1}. The lower trace is a synthetic spectrum calculated using the line list generated in this work. The observed and synthetic spectra are plotted in absorbance and are shifted vertically for clarity.

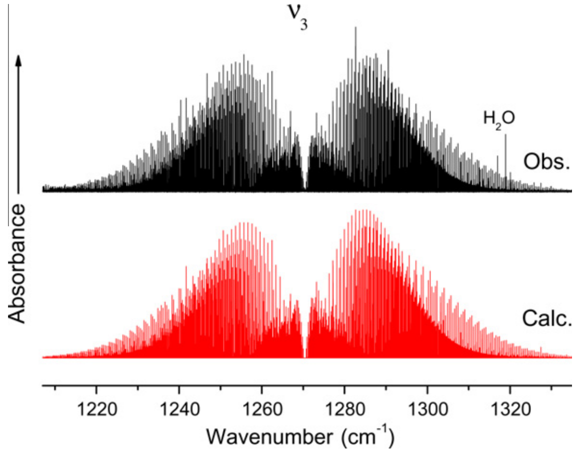


Fig. 3. Overview of the oxirane spectrum between 8.2 and 7.5 μm. The band center of the B-type ν_3 band is shown.

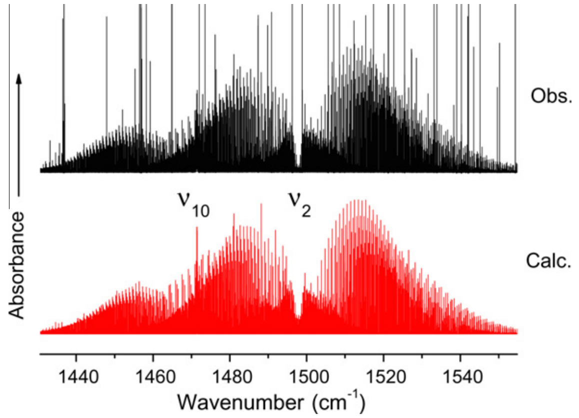


Fig. 4. Overview of the oxirane spectrum between 6.61 μm and 7.04 μm. The band centers of the A-type ν_{10} and B-type ν_2 bands are given. Note the presence of strong residual water lines in the observed spectrum. Most of them have been used for calibration.

Table 1
Range of quantum numbers observed for experimental energy levels and a statistical analysis of the results of the energy level calculation for the $\{15^1, 12^1, 5^1\}$, 3^1 and $\{10^1, 2^1\}$ ro-vibrational levels of oxirane.

Vibrational state	$\{15^1$	12^1	$5^1\}$	3^1	$\{10^1$	$2^1\}$
Number of levels	278	863	1199	1219	832	1087
J_{Max}	33	49	53	46	49	54
K_{Max}	29	35	40	28	31	37
$0.000 \leqslant \delta < 0.0006$ (%)	64.4	84.5	79.7	92.4	91.6	94.9
$0.0006 \leqslant \delta < 0.0012$ (%)	25.5	11.0	15.0	5.5	6.7	4.3
$0.0012 \leqslant \delta < 0.0032$ (%)	10.1	4.5	5.3	2.1	1.7	0.8
Std. deviation (10^{-3} cm^{-1})		0.75		0.59		0.33

$\delta = |E_{Obs.} - E_{Calc}|$in cm^{-1}.