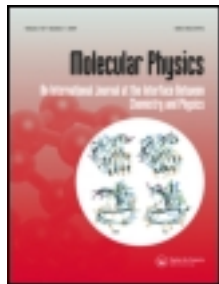


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### Raman and Infrared spectra of the $\nu_1$ band of oxirane

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## **Raman and Infrared spectra of the $\nu_1$ band of oxirane**

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## Abstract

Fourier transform spectra of oxirane (ethylene oxide (c-C<sub>2</sub>H<sub>4</sub>O)) have been recorded in the 3.17  $\mu\text{m}$ -3.50  $\mu\text{m}$  region with a resolution of 0.005  $\text{cm}^{-1}$ . In addition, a Raman spectrum covering the same spectral region was recorded at a resolution of 0.44  $\text{cm}^{-1}$ . Using the Raman spectrum, it was possible to determine the band center of the  $\nu_1$  band to within 0.5  $\text{cm}^{-1}$ . This determination was essential to assign the infrared region transitions of the B-type  $\nu_1$  band since this weak band is masked by the much stronger A-type bands  $\nu_2 + \nu_{10}$  and  $\nu_9$  and  $\nu_{13}$  C-type band. Using a Watson-type Hamiltonian for an asymmetric-top molecule, it was possible to reproduce the observed energy levels to within  $2 \times 10^{-3}$   $\text{cm}^{-1}$  and the Raman spectrum could be satisfactorily modeled. The band center was determined to be  $\nu_0(\nu_1) = 3018.3454(10)$   $\text{cm}^{-1}$  (1  $\sigma$  uncertainty).

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## 1) Introduction

Oxirane (ethylene oxide ( $c\text{-C}_2\text{H}_4\text{O}$ )) has been previously detected in the interstellar medium, especially in star-forming regions [1,2]. Moreover laboratory studies [3] have shown the possibility that oxirane may exist in the atmosphere of Titan. Oxirane has then been the subject of a number of both low- and medium-resolution infrared and Raman studies [4-7], but only the  $\nu_3$  band located at  $1270.4\text{ cm}^{-1}$  [8,9] and, more recently, the  $\nu_{15}$ ,  $\nu_{12}$ ,  $\nu_5$ ,  $\nu_{10}$  and  $\nu_2$  bands located at  $808.1$ ,  $822.3$ ,  $876.7$ ,  $1471.4$  and  $1497.8\text{ cm}^{-1}$  have been studied at high resolution [9]. In this paper, we present the first detailed analysis of the  $\nu_1$  band which is a weak B-type band which has never been observed in the infrared since it is masked by the much stronger A-type bands  $\nu_2 + \nu_{10}$  and  $\nu_9$  as well as the C-type band  $\nu_{13}$ . The  $1^1$  ( $\nu_1 = 1$ ) upper state rotational levels were reasonably fit using a Watson-type Hamiltonian for an asymmetric-top molecule written in the  $I^r$  ( $x = b$ ,  $z = a$ ,  $y = c$ ) representation [10-12].

## 2) Experimental details.

### *Fourier transform spectra*

The high-resolution infrared absorption spectra of oxirane were recorded with the Bruker IFS125HR Fourier transform spectrometer<sup>1</sup> located at the LISA facility in Creteil. A KBr beamsplitter, Globar source (Silicon Carbide, SiC) and a liquid nitrogen-cooled Indium Antimonide (InSb) detector were employed for these experiments. The optical path of the spectrometer was continuously evacuated to below  $6.7\text{ Pa}$  for the duration of all spectral measurements. Spectra were recorded with an aperture diameter of  $1.3\text{ mm}$ , scanner frequency  $40\text{ kHz}$ , and a maximum optical path difference ( $d_{\text{MOPD}}$ ) of  $180\text{ cm}$ . According to the Bruker definition ( $\text{Resolution} = 0.9/d_{\text{MOPD}}$ ), these settings correspond to a resolution of  $0.005\text{ cm}^{-1}$ . The White-type multipass absorption cell, made of pyrex glass and equipped with CsBr windows, was connected to the Fourier transform spectrometer with a dedicated optical interface (six mirrors) inside the back sample compartment of the Bruker spectrometer. Its base length is

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<sup>1</sup> 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.

0.80 m, and, for the experiment described here, an optical path length of 32.05 (6) m was used. This value takes into account the distance between the surface of the field mirror and the windows of the cell ( $2 \times 2.45$  cm). 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 measurements: Initially, a background spectrum was collected while the cell was being continuously evacuated; next the infrared gas cell was treated with ethylene oxide several times and two ethylene oxide spectra were recorded at pressures of 3.41 (2) and 6.67 (3) Pa. Sample pressure in the cell was measured using a calibrated MKS Baratron gauge model 627 D (266.64 Pa full scale) with an accuracy reading of 0.12 %, according to the manufacturer. The absolute uncertainty for the sample pressure was estimated to be about 0.5 % taking into account the uncertainty reading and the variation of the pressure during the measurements. The spectra were recorded at a stabilized room temperature of  $295.2 \pm 1$  K. Both spectra were ratioed against the empty cell, single-channel background spectrum, which was taken at a resolution of  $0.32 \text{ cm}^{-1}$  in order to ensure the best possible signal-to-noise in the ratioed spectra. The spectra were the result of the co-addition of 800 interferograms. For the Fourier transform, a Mertz-phase correction,  $1 \text{ cm}^{-1}$  phase resolution, zero-filling factor of 2 and boxcar apodization function were applied to the averaged interferograms. The spectra were calibrated using residual  $\text{CO}_2$  and  $\text{H}_2\text{O}$  lines observed in the spectra with their wavenumbers taken from HITRAN [13] leading to a wavenumber uncertainty of  $0.0001 \text{ cm}^{-1}$  for a well isolated line.

Fig. 1 gives an overview of the ethylene oxide spectrum, between  $2860$  and  $3150 \text{ cm}^{-1}$ , showing the high signal-to-noise ratio which was obtained. The distinctive shape of the two A-type  $\nu_2 + \nu_{10}$  (around  $2930.8 \text{ cm}^{-1}$ ) and  $\nu_9$  (around  $3006.5 \text{ cm}^{-1}$ ) bands, as well as the  $\nu_{13}$  (around  $3066.0 \text{ cm}^{-1}$ ) C-type bands, appear clearly. The band center of the much weaker B-type  $\nu_1$  (around  $3018.3 \text{ cm}^{-1}$ ) band is indicated.

### ***Raman spectra***

For the Raman spectra, a cylindrical glass cell of 13 mm diameter was filled with 10000 Pa of distilled oxirane, from the same sample as the IR spectra. The Raman scattering was excited at room temperature by 5 W of linearly polarized radiation at 532 nm from a Coherent Verdi V-10 laser, sharply focused on the sample by an  $f = 35$  mm lens. Scattered radiation perpendicularly to both laser propagation and polarization was collected by an  $f = 55$  mm photographic objective at  $f/1.0$  aperture, and projected onto the entrance slit of the spectrograph

with a total magnification  $\times 10$ . The spectrograph consists of an additive double-monochromator equipped with two 2400 line/mm gratings and a CCD detector refrigerated by liquid nitrogen. The entrance slit was set to 150  $\mu\text{m}$ , yielding a spectral resolution of 0.44  $\text{cm}^{-1}$ . Only linearly polarized radiation parallel to the exciting one reached the detector, and thus only scattering due to the trace (mean) of polarizability tensor was observed. Four scans, with a total acquisition time of 12 min, were spike-filtered and averaged. The wavenumber scale was calibrated to  $\pm 0.15 \text{ cm}^{-1}$  against Ne emission lines recorded simultaneously with the Raman spectra.

### 3) Line assignments and results

The absorption spectrum of oxirane in the 3.3  $\mu\text{m}$  region is dominated by two A-type bands,  $\nu_2 + \nu_{10}$  and  $\nu_9$ , located at 2930.8 and 3006.5  $\text{cm}^{-1}$ , respectively, as well as the C-type band  $\nu_{13}$  located at 3066.0  $\text{cm}^{-1}$  (Fig. 1). Note that  $\nu_2 + \nu_{10}$  is a strong band because it borrows its intensity through a strong Fermi resonance with  $\nu_9$ . These bands have been easily observed in low and medium resolution spectra [4-7], whereas the  $\nu_1$  band center was only roughly estimated by subtracting the mirror image of the R-branch of  $\nu_{13}$  from the observed spectrum [5].

In this paper, we present the first high resolution study of the  $\nu_1$  band. Such an analysis has been possible because of the availability of the gas-phase Raman spectrum taken at a resolution of 0.44  $\text{cm}^{-1}$ . This spectrum consists of a strong Q-branch which provides us with a good band center for  $\nu_1$  (Fig. 2). With this datum it was possible to generate an estimated spectrum and to spot series of lines in the P- and R-branches of the  $\nu_1$  band. The first transitions to be assigned were the  $J'd'J' \leftarrow J''d''J''$  transitions with  $\Delta J = \pm 1$ ,  $d' = 0, 1$  and  $d'' = 1, 0$ . This allowed us to obtain a better band center as well as a more accurate  $B'$  rotational constant. Next the  $J'J'd' \leftarrow J''J''d''$  transitions with  $\Delta J = \pm 1$ ,  $d' = 0, 1$  and  $d'' = 1, 0$  were spotted leading to an improved value of the  $A'$  rotational constant. Finally a much improved synthetic spectrum was generated and used to make further line assignments. This process was repeated until no further assignments could be made. Since we were expecting a large number of resonances to be found in this band, we were amazed that it was possible to fit the upper state rotational levels using a simple Watson-type Hamiltonian [10-12]. Indeed, it turned out that, except for a few levels, the observed levels could be fit reasonably well with a standard deviation of 0.003  $\text{cm}^{-1}$ , 61 % of the levels being calculated to within  $2 \times 10^{-3} \text{ cm}^{-1}$  with a maximum difference of  $15 \times 10^{-3} \text{ cm}^{-1}$ . The corresponding Hamiltonian constants are given in Table 1. Using these constants, we have

calculated a synthetic spectrum for the  $\nu_1$  band. A small region around  $3008\text{ cm}^{-1}$  that is not too obscured by the transitions from  $\nu_9$  is shown in Fig. 3; it shows a satisfactory comparison between the observed and calculated spectra. In addition, a synthetic Raman spectrum was calculated using a single mean-polarizability derivative parameter for the intensities. Fig. 2 gives the comparison of the observed and calculated spectra. The satisfactory modeling of the Raman spectrum leads to extra confidence in the rotational constants derived from the infrared spectrum.

#### 4) Conclusion

The simultaneous use of a medium resolution Raman spectra and of a high-resolution infrared absorption has led to the first observation and assignment of the  $\nu_1$  band of oxirane. Surprisingly, it appears that this band is only weakly perturbed, and the upper state rotational levels could indeed be reasonably fit using a single Watson-type Hamiltonian. This assignment of  $\nu_1$  will facilitate the analysis of the other absorption bands in this spectral region.

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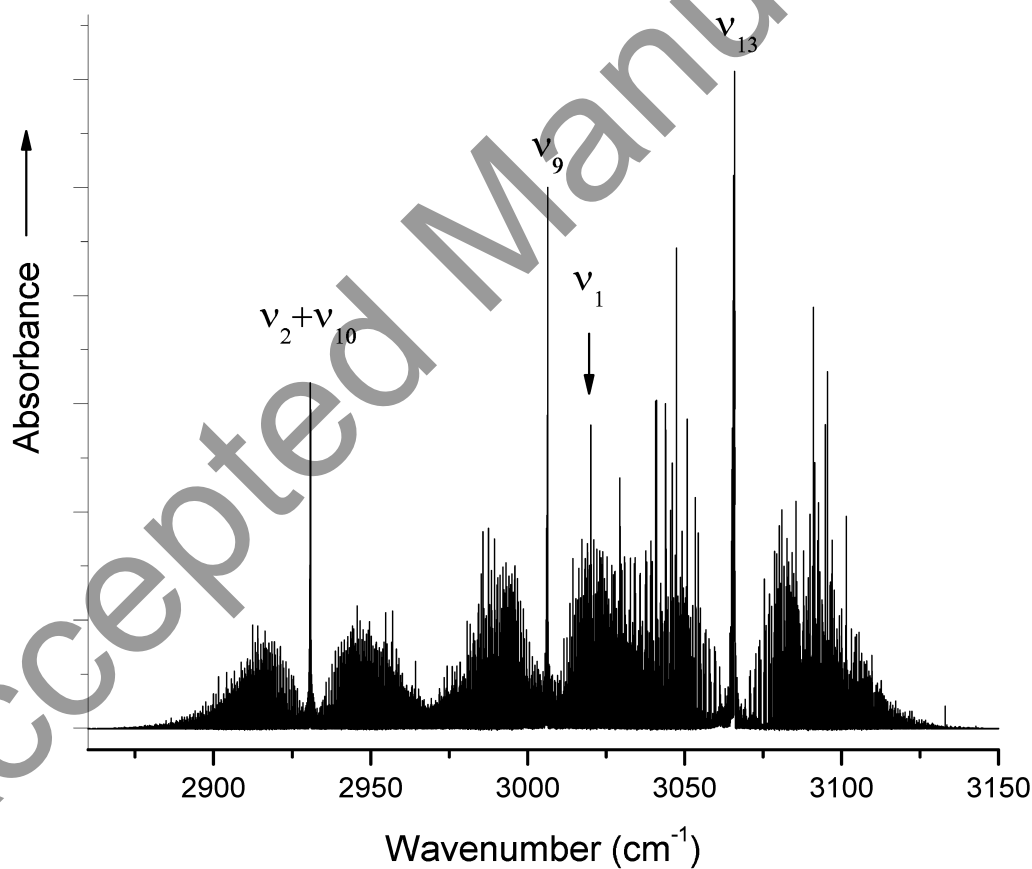
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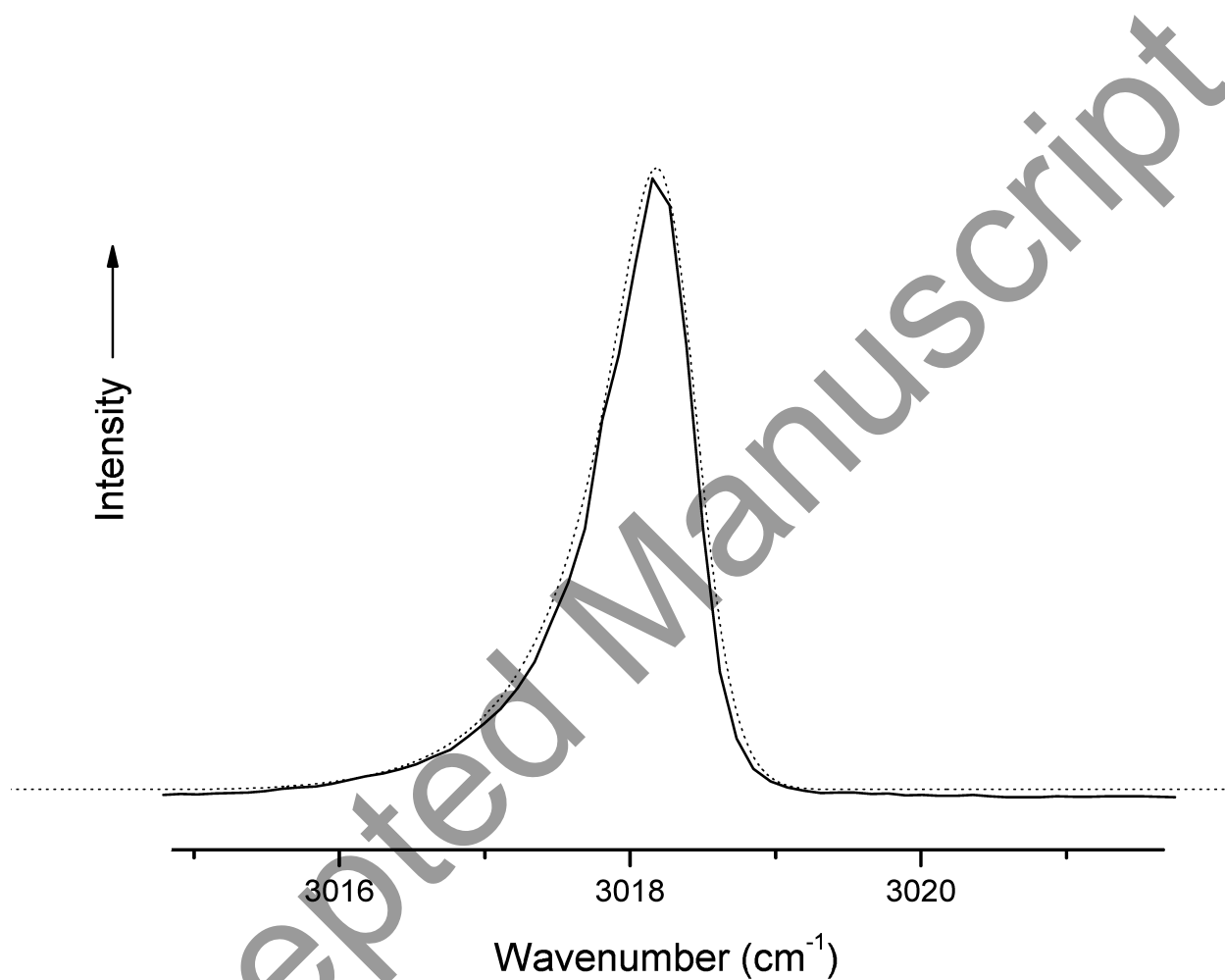


**Captions to figures:**

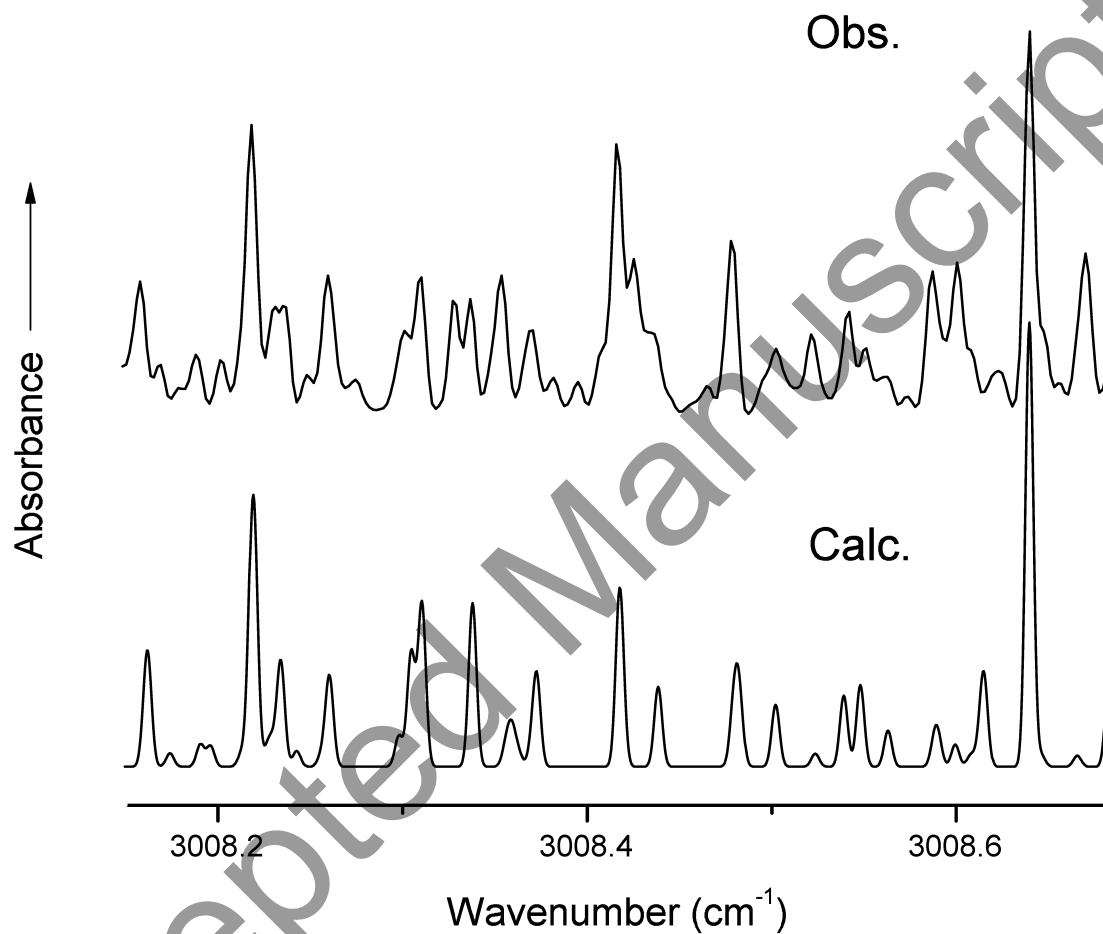
**Fig. 1.** Overview of the absorption spectrum of oxirane in the 3.3  $\mu\text{m}$  region recorded using high-resolution Fourier transform spectroscopy. The spectrum was recorded with a spectral resolution of  $0.005\text{ cm}^{-1}$  and an optical path length of  $32.05(6)\text{ m}$ , at a oxirane pressure of  $3.41(2)\text{ Pa}$  and a stabilized room temperature of  $295.2 \pm 1\text{ K}$ . The  $\nu_2 + \nu_{10}$  and  $\nu_9$  A-type bands as well as the  $\nu_{13}$  C-type bands appear clearly. The band center of the very much weaker B-type  $\nu_1$  band is indicated.



**Fig. 2.** The Raman spectrum of the  $\nu_1$  Q-branch of oxirane at a resolution of  $0.44\text{ cm}^{-1}$ . The experimental spectrum (continuous line) was recorded at 10000 Pa and 295K. The spectrum calculated using the molecular constants derived from the IR analysis is shown as a dashed line.



**Fig. 3.** A small portion of the infrared absorption spectrum of oxirane around  $3008.4\text{ cm}^{-1}$ . The lines belonging to the  $\nu_1$  band are clearly visible. The other lines belong to the  $\nu_9$  A-type band and to the  $\nu_{13}$  C-type band.



**Table 1:** Vibrational band center, rotational and centrifugal distortion constants for the  $1^1$  vibrational state of oxirane.

*Note.* All values are given in  $\text{cm}^{-1}$ .

<sup>a</sup> Uncertainties are  $1\sigma$ . They are statistical and do not account for possible systematic effects.

<sup>b</sup> Fixed at ground state values [9].

**Table 1**

	$1^1$
$E_v$	3018.3454 (10) <sup>a</sup>
A	0.8494540(130)
B	0.7345814(170)
C	0.47070962(640)
$\kappa \times 10^6$	1.3664(1000)
$\kappa_{JK} \times 10^6$	0.3601(1100)
$J \times 10^6$	0.72182(2400)
$\delta_{\kappa} \times 10^6$	0.48805(3300)
$\delta_J \times 10^6$	0.24200(1200)
$H_{\kappa} \times 10^{10}$	b
$H_{\kappa J} \times 10^{10}$	b
$H_{JK} \times 10^{10}$	b
$H_J \times 10^{12}$	b
$h_{\kappa} \times 10^{11}$	b
$h_{\kappa J} \times 10^{11}$	b
$L_{\kappa} \times 10^{15}$	b
$L_{\kappa \kappa J} \times 10^{15}$	b
$L_{JK} \times 10^{15}$	b
$l_{\kappa} \times 10^{15}$	b