Intensities of the 1397 cm^{-1} (ν_3) band of HO_2NO_2 and feasibility of atmospheric detection

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Abstract

Absorption coefficients of the 1397 cm^{-1}, V_3, band of peroxynitric acid ($H0_2N0_2$) have been measured at 225-230 K in order to calculate the feasibility of detecting this spectral feature in atmospheric spectra. High-resolution (0.0078 cm^{-1}) Fourier transform spectra (1370-1430 cm^{-1}) of low pressure gas-mixtures containing $H0_2N0_2$ were analyzed to determine the absorption coefficient, $k(\upsilon)$. The maximum absorption coefficient was found to be 1.0×10^{-18} $cm^2/molec$ at the peak of the 1397 cm^{-1} Q-branch. An average pressure broadening coefficient of 0.1 (± 0.02) cm^{-1}/atm was also measured using a tunable diode laser spectrometer (resolution 0.001 cm^{-1}) and a convolution technique. The high resolution spectrum and pressure broadening coefficient were used to simulate the atmospheric transmission spectrum at an altitude where $H0_2N0_2$ is expected to have it's peak in the vertical concentration profile (27 km).

Introduction

Model calculations of atmospheric ozone depletion dueto chlorofluorocarbon degradation, and possible commercial operation of stratospheric aircraft, are particularly sensitive to processes that effect the partitioning between reactive NO_x (NO, NO_2, and NO_3) and reservoir NO_y (HNO_3, N_2O_5, HO_2NO_2, $ClONO_2$, and $CH_3CO_3NO_2$) species. Peroxynitric acid (l'NA), HO_2NO_2, serves as a temporary reservoir for HO_2 and NO_2 in the Earth's upper troposphere and lower stratosphere. It is also a precursor to formation of nitrous acid (HONO) and has recently been postulated to play an important role in the unexpectedly large increase in hydroxyl radical (OH) concentrations observed at sunrise near 20 km altitude [1,2]. As our understanding of atmospheric chemistry and photochemistry increases, it is necessary to improve the accuracy of experimental measurements of the concentrations of trace gases and radicals so that photochemical models used to interpret the experimental observations can be critically tested.

PNA has been observed in atmospheric spectra recorded by the Atmospheric Trace Molecule Spectrometer (ATMOS) operating from the Space Shuttle [3], and in spectra recorded by Fourier Transform Spectrometers (FTS) flown on high-altitude balloons [4]. The only spectral feature of this molecule identified to date in atmospheric spectra is the strong Q-branch of the ν_6 band at 803 cm^{-1} [3,4]. In previous work, we have reported absorption coefficients for the ν_6 band at a temperature of 220 K [5], and derived preliminary molecular constants for the upper state of the band obtained from high-resolution FTS spectra [6]. In this paper we report additional low temperature studies of the 1397 cm^{-1} band undertaken to assess the feasibility of detecting absorption by this band in atmospheric spectra. Although the V_3 band at 1397 cm^{-1} is weaker than the 803 cm^{-1} band, it is the only other fundamental band that is not obscured by strong interfering absorption in the atmosphere, and thus it is potentially detectable in atmospheric spectra. We also report an average pressure broadening coefficient which was measured from high-resolution tunable diode laser (TDL) spectra.

Experimental details

The method used to prepare and handle PNA have been described previously [5,7]. Briefly, HO_2NO_2 was prepared in the liquid phase using the method of Kenley *et al.* [8]:

$$H_2O_2(90\%) + NO_2BF_4(s) \rightarrow HO_2NO_2 + HBF_4 \qquad (1)$$

Samples were prepared in 3-ml quantities and transferred to a glass bubbler attached to the inlet of either a multipass (White-type) absorption cell (optical pathlength 36 m) coupled to a Bomem DA3-O02 FTS, or to a multipass Herriott cell (optical pathlength 39 m) coupled to a tunable diode laser spectrometer. PNA vapor was entrained by He or Ar carrier gas and flowed through the bubbler and into the absorption cell, The bubbler was immersed in an ice-bath to reduce PNA decomposition during the transfer process.

The diode laser spectra were recorded using the spectrometer described by May and Webster [9] which was coupled to a multipass Herriott cell, This was used for measurements in selected regions of the P, Q, and R branches of the 1397 cm^{-1} V_3 band at 0.001 cm^{-1} resolution. Tunable diode laser spectra were recorded over a range of temperatures from room temperature to 220 K. The absorption cell was maintained at 220 K by means of a cooler circulating methanol through an outer jacket on the cell. At the lower temperatures PNA condensed on the walls of the absorption cells, and the gas-phase PNA concentration remained approximately constant at the 22o K equilibrium vapor pressure (3.5 mTorr). Total cell pressures were <0.25 Torr, measured using capacitance manometers (MKS instruments) covering O-1 and 0-1000 torr ranges.

Infrared spectra were obtained using the FTS system described previously by May and Friedl [5] with the following modifications: a narrow-band interference filter (OCLI N07298-9) was placed directly in front of the detector element and cooled to 4 K. This filter limited the detector responsitivity to 1374-1429 cm-l, FWHM, with total transmission, $T \geq 80$ %, between 1387 and 1416 cm^{-1}. Total cell pressures ranged from 0.05 to 0.25 Torr. For all FTS spectra the instrumental resolution was 0.0078 cm^{-1} (unanodized) and spectra were recorded at temperatures in the range 225-230 K.

Results

Band Intensity

Figure 1 shows the measured absorption coefficient for the ν_3 band of PNA obtained from the FTS spectrum. The total band intensity was normalized to the value 1.25 x 10^{-17} $cm^2/molec$ reported by May and Fried] [5]. Individual rotational transitions are largely unresolved even at the Doppler limit. However, some structure is evident. In general, the spectrum is much more congested and irregular than the ν_6 band at 803 cm^{-1} [6], and thus more difficult to analyze. The Q-branch of the 1397 cm^{-1} band is also much broader than the sharp Q-branch of the 803 cm^{-1} band and therefore will be more difficult to identify in atmospheric spectra.

Since the integrated band intensity for the 1397 cm^{-1} band has been measured previously [51, conversion of the measured transmission spectrum to absorption coefficient could be carried out without knowledge of the PNA partial pressure or the optical pathlength:

$$B = \frac{1}{K_{pL}} \int \ln\tau(\upsilon)d\upsilon \qquad (2)$$

where $\tau(\upsilon)$ is the observed transmission, υ is the wavenumber, and the parameter K_pL was adjusted iteratively so that B corresponded to the integrated band intensity reported in reference [5]. The maximum absorption coefficient for the Q-branch is about 1.0 x 10^{-18} $cm^2/molec$ whereas the maximum absorption coefficient for the P- and R-branches are 0.8 x 10^{-18} and 0.9 x 10^{-18} $cm^2/molec$, respectively. The Q-branch value is about a factor of two larger than reported by Molina and Molina [7]. However their measurements were carried out at higher pressure and lower resolution (1 atm and 1 cm^{-1}, respectively).

Contributions from interfering water lines were handled in two ways. First, direct integration and summation of the strongest observed water lines showed that their contribution to the integrated PNA band intensity was less than O. l%. Secondly, the 22 strongest water lines in the region 1370-1430 cm^{-1}, according to the 1992 version of the

HITRAN data base [10], were subtracted from the recorded spectra and similar results were obtained. No other molecules that were produced during the preparation of PNA, (HNO_3, H202, NO_2, HF, SiF_4), contributed significantly to absorption over the 1370-1430 cm^{-1} region.

Pressure broadening measurements

An average pressure broadening coefficient was determined for the PNA 1397 cm^{-1} band by convolving low pressure spectra with Lorentzian functions of varying half width until the best match to observed air-broadening spectra were obtained. This approach gives only an average broadening coefficient, but for heavy molecules such as PNA, where it is not possible to resolve the rotational structure in the infrared, the procedure provides a useful parameter for use in atmospheric transmission calculations. In previous work on $HN0_3$ and COF_2 this technique was employed successfully to obtain average air-broadening coefficients [9,1 1].

Tunable diode laser spectra were recorded at low pressure, <0.25 Torr, and broadened by zero-air at pressures of 10, 20, 30 and 50 Torr, for determination of the air-broadening coefficient. Figure 2a shows an example of Doppler-limited (a) and pressure broadened (b) spectra recorded at 298 K over a portion of the Q-branch region, In Fig. 2b the total pressure was 20.8 Torr. The spectrum from Fig. 2a was then convolved with a Lorentzian function with a half width (HWHM) determined so that the outcome converged with the scan in Fig. 2b. The convolved result is shown in Fig. 2c. This procedure was then repeated for several spectra recorded at four different pressures from 10 to 50 Torr giving a pressure broadening coefficient of 0.1 (±0.02) cm^{-1}/atm. This figure was used in the synthetic transmission calculations described below.

Atmospheric transmission calculation

The primary purpose of undertaking the measurements presented here was to provide quantitative data for assessing the feasibility of observing the PNA 1397 cm^{-1} Q-branch in atmospheric spectra, Since the Q-branch of the 803 cm^{-1} band of PNA has been observed in both ATMOS spectra [3] and in spectra recorded using balloon-born spectrometers [4],

simulations were carried out for both the 803 cm^{-1} and 1397 cm- I Q-branches to obtain relative absorption levels. The calculations used con ditions appropriate for optimum detection of PNA at the peak of it's vertical profile in the northern hemisphere Spring, near 30"N latitude. Parameters used for the calculations are shown in table 1. The absorption pathlength adopted for the calculation was the pathlength that yielded the correct absorption observed for the 803 cm^{-1} band by Rinsland *et al.* [3], with the PNA mixing ratio fixed at 0.3 ppbv. This mixing ratio is the value reported at 27 km altitude [31.

The synthetic spectra are shown in Fig. 3. For a PNA volume mixing ratio of 0.3 ppbv, the maximum absorption in the calculated spectrum at 803 cm^{-1} (a) is 2.5 %, fixed to the observed ATMOS measurement [31. At the 1397 cm-1 Q-branch (b) the maximum absorption is calculated to be 0,9 %, about 30 % of the peak absorption at 803 cm^{-1}. It is also evident that the 1397 cm^{-1} Q-branch is much broader and has an even more complex rotational structure than the 803 cm^{-1} Q-branch. Thus, identification of this feature in atmospheric spectra will be difficult. However, the 1397 cm^{-1} Q-branch lies in a spectral region where subtraction of interfering lines should leave a residual showing the envelope of the PNA Q-branch provided the experimental signal-to-noise ratio is adequate (>100). This subtraction approach, used to identify many weak absorption in ATMOS spectra including the 803 cm^{-1} Q-branch [3,12], is possible in the present case because the interfering lines of H_20, $C0_2$, 0_3, and CH_4[10,13] are relatively weak, are well characterized in terms of their line positions and intensities, and are not saturated.

Parameter	Value
Mixing ratio	0.3 ppbv
Pressure	18.55 Torr
Temperature	226.2 K

***Table 1. Parameters used** for calculation of synthetic spectra.*

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Figure captions

Figure 1. Absorption coefficient for the 1397 cm-1, (ν_3), band of HO_2NO_2

(a) The 1370-1430 cm^{-1} region, P-, Q-, and R-branch, (b) Magnification of the Q- Branch, 1394-1400 cm^{-1}.

Figure 2. Tunable diode laser spectra of a portion of the Q-branch, (a) spectra at low pressure, 0.2 Torr, (b) spectra at a total pressure of 20.2 Torr, (c) same spectra as in (a) but convolved with a Lorentzian function with a half width of 0.003 cm^{-1}.

Figure 3. Calculated synthetic transmission spectra at the Q-branches for (a) the 803 cm^{-1}, ν_6, band and (b) the 1397 cm^{-1}, ν_3, band of HO_2NO_2.

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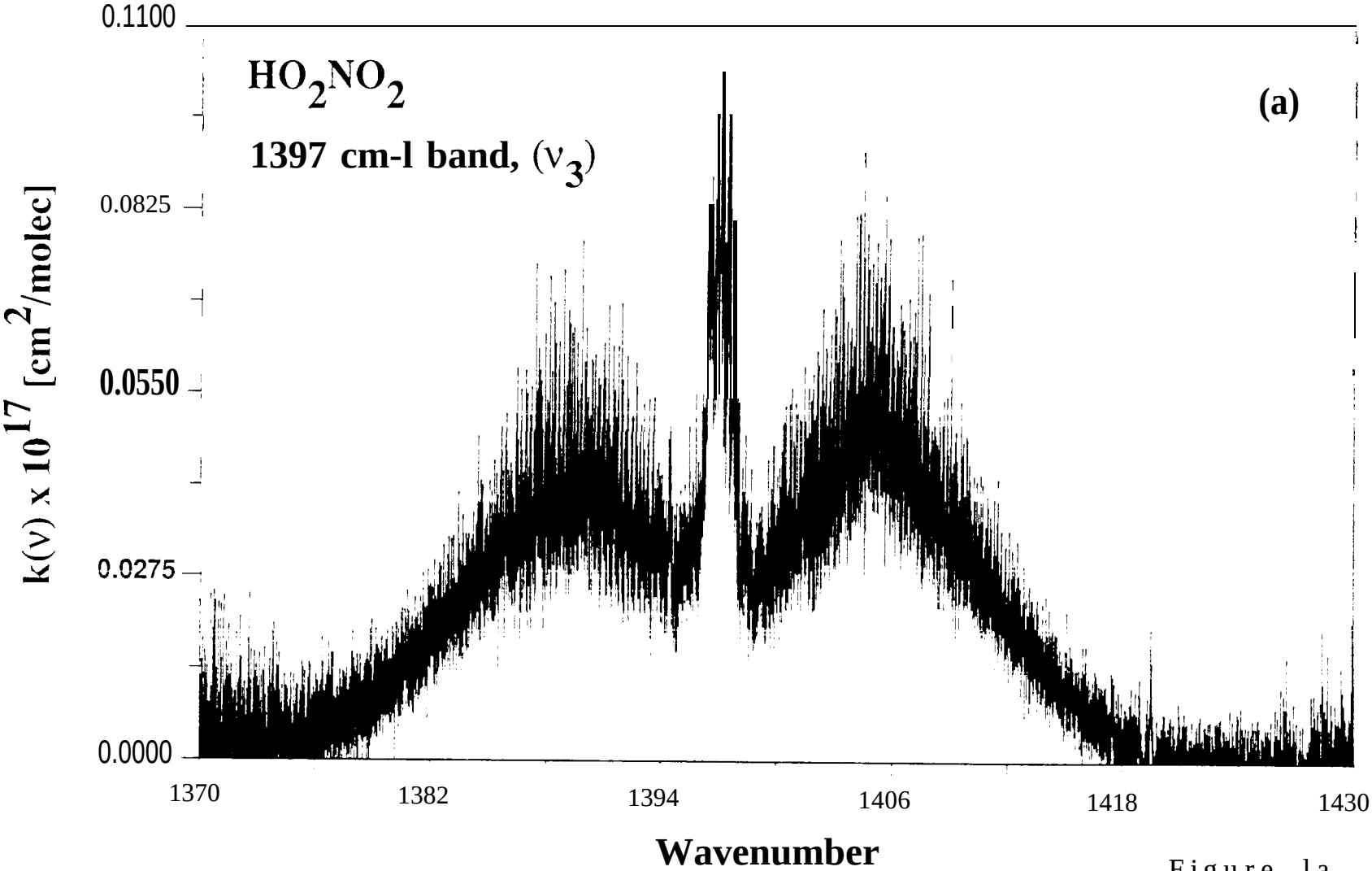
0.1100
0.0825
0.0550
0.0275
0.0000
HO_2NO_2
1397 cm-l band, (ν_3)
(a)
$k(\nu) \times 10^{17}$ [cm^2/molec]
1370
1382
1394
1406
1418
1430
Wavenumber

Figure la.

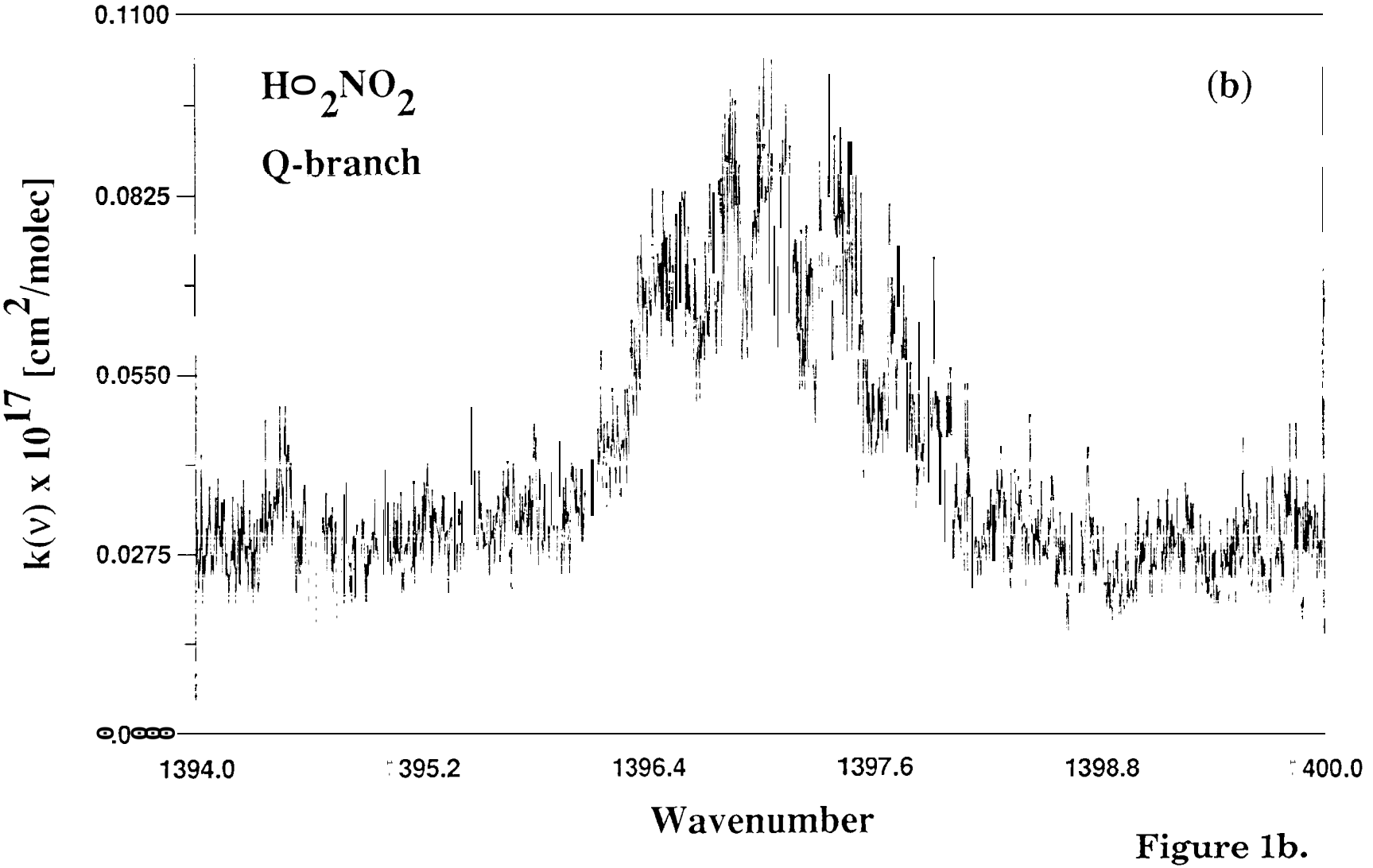
0.1100
0.0825
0.0550
0.0275
0.0000
HO2NO2
Q-branch
(b)
k(ν) x 10^17 [cm^2/molec]
1394.0
1395.2
1396.4
1397.6
1398.8
1400.0
Wavenumber

Figure 1b.

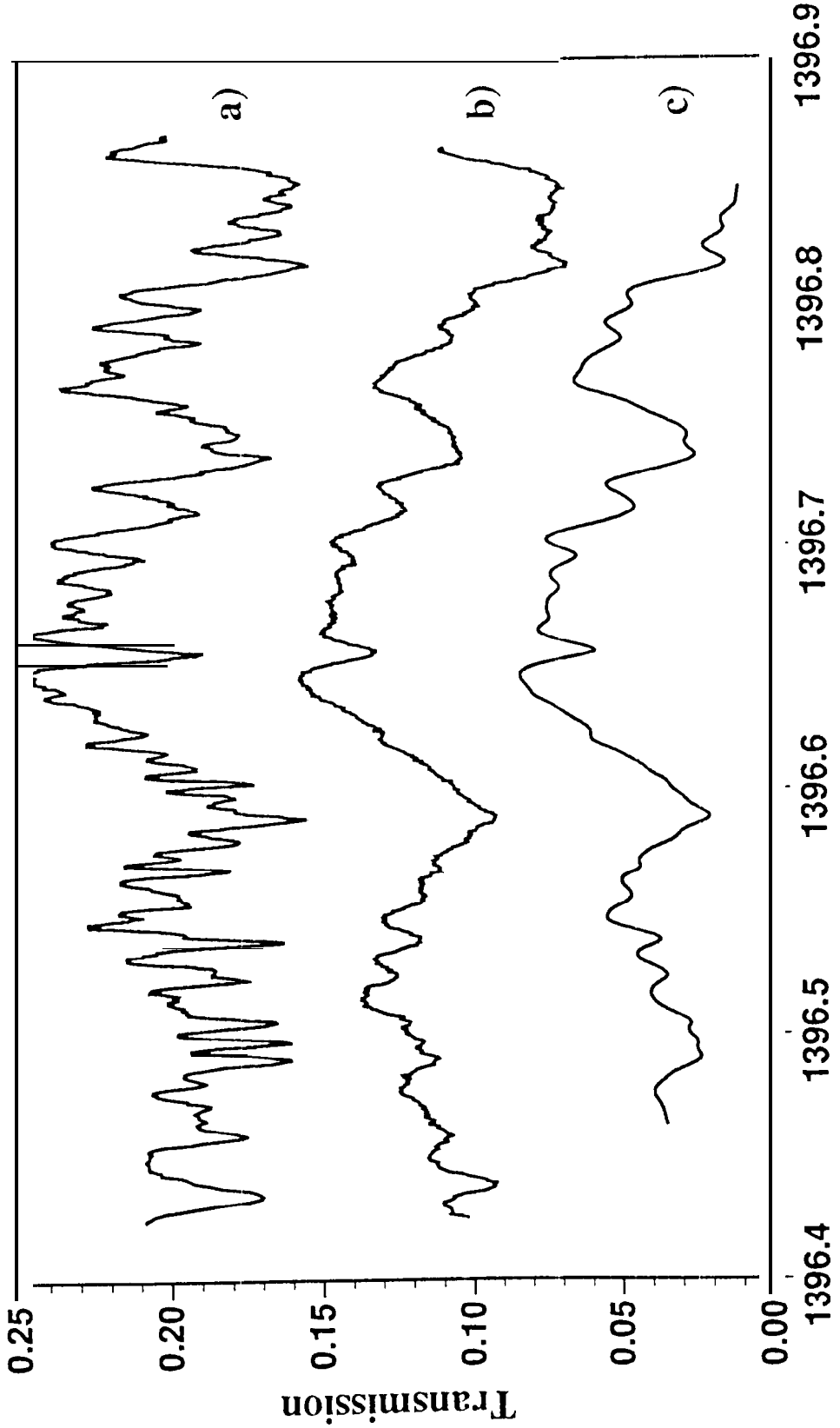
Transmission
0.25
0.20
0.15
0.10
0.05
0.00
1396.4
1396.5
1396.6
1396.7
1396.8
1396.9
Wavenumber
a)
b)
c)

Figure 2.

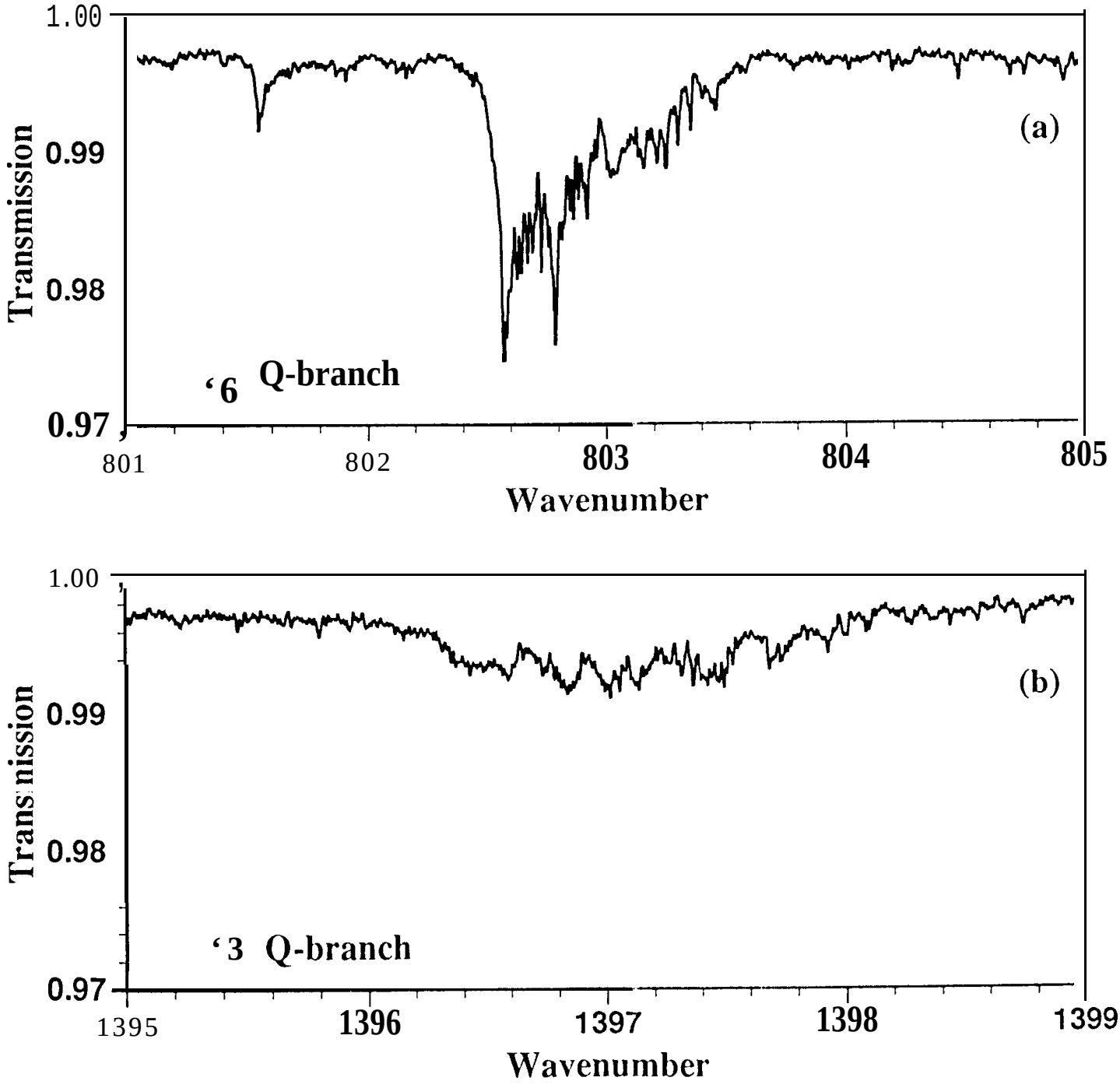
1.00
0.99
0.98
0.97
Transmission
(a)
ν6 Q-branch
801
802
803
804
805
Wavenumber
1.00
0.99
0.98
0.97
Transmission
(b)
ν3 Q-branch
1395
1396
1397
1398
1399
Wavenumber

Figure 3.