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Absorption cross-sections and pressure broadening of rotational lines in the $3v_3$ band of N₂O determined by diode laser cavity ring-down spectroscopy

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Abstract

Diode laser cavity ring-down spectroscopy (CRDS) has been used to measure rotational line intensities and air pressure broadening coefficients for the $3v_3$ (N–N stretching) vibrational overtone band of N₂O. The line intensity measurements are in quantitative agreement with previously reported Fourier transform spectroscopy results [J. Mol. Spectrosc. 197 (1999) 158]. The air pressure broadening coefficients increase from 0.086 ± 0.015 cm⁻¹ atm⁻¹ for the P(34) line to 0.139 ± 0.010 cm⁻¹ atm⁻¹ for the P(3) line, and are greater than values reported for other ro-vibrational bands of N₂O observed at lower frequencies. The effects of pressure broadening on line-centre absorption cross-sections, and thus for the sensitivity of CRDS detection of N₂O using narrow bandwidth near-IR lasers are quantified.

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1. Introduction

Nitrous oxide is a trace constituent of the Earth's atmosphere, present at mixing ratios in the troposphere of \sim 315 parts per billion by volume (ppbv). It is a potent greenhouse gas with a global warming potential that, per molecule, is more than 300 times that of CO₂, and has a half-life to loss from the atmosphere of 120 years [1]. Levels have risen over the last century at an average rate of

0.8 ppbv per annum because of both industrial and agricultural sources [2].

N₂O has three fundamental modes of vibration, the N–O stretch (Σ^+ , $v_1 = 1284.9 \text{ cm}^{-1}$), the N–N– O bend (Π , $v_2 = 588.8 \text{ cm}^{-1}$) and the N–N stretch (Σ^+ , $v_3 = 2223.8 \text{ cm}^{-1}$). There are a number of combination and overtone bands that show absorption spectra in the mid and near-infrared, and which have been the subject of considerable spectroscopic investigation, much of which is summarised in the HITRAN 2000 database [3]. A detailed Fourier transform spectroscopy (FTS) study of the frequencies and intensities of rotational lines of the $3v_3$ band, with origin at 6580.85 cm⁻¹, derived integrated absorption cross-sections

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for *P*- and *R*-branch lines up to J'' = 52 [4], and Tanoura et al. [5] also reported FTS studies of the line positions in this band. The effects of pressure of bath gases on the spectral features of the $3v_3$ band, however, remain unexplored, but will have consequences for its role in radiative forcing in the atmosphere.

We have used cw diode laser cavity ring-down spectroscopy (CRDS) [6,7] to obtain spectra of selected individual rotational lines in the P-branch of the $3v_3$ band of N₂O from P(3) to P(34). The ${}^{1}\Sigma^{+}-{}^{1}\Sigma^{+}$ vibrational symmetry of the band dictates that it shows only P- and R-branches and the lines are well separated. Spectra obtained for known partial pressures of N₂O under conditions of low overall pressure were used to derive line intensities (i.e., line-integrated absorption crosssections, σ_{line}) that are compared with previously reported FTS data. Spectra of N₂O in various pressures of air up to 200 Torr exhibit substantial pressure broadening, and fits to rotational line profiles reveal rotational level-dependent pressure broadening coefficients. The effects of pressure broadening on the limiting sensitivity of diode laser CRDS for measurement of N₂O in ambient air via the $3v_3$ absorption band are discussed.

2. Experimental

The cw diode laser cavity ring-down spectrometer used for this study has been described in detail elsewhere [8,9], so only a brief description of key elements is presented here. The ring-down cavity (RDC) comprises two high reflectivity mirrors (Layertec GmbH) located 47 cm apart within finely adjustable mounts held on an assembly of four stainless steel rods and situated within a vacuum chamber. One mirror was mounted on a piezo-electric transducer and its position was continuously modulated at 50 Hz to sweep the cavity mode frequencies back and forth over one free spectral range. Near-infrared laser radiation from an external cavity diode laser (ECDL, Sacher Lasertechnik TEC 500), operating at air wavelengths near 1.525 µm with a bandwidth of \sim 4 MHz, was injected into the RDC using TEM₀₀ spatial mode coupling optics when the laser frequency matched the frequency of a cavity mode. An acousto-optic modulator (AOM, Isle Optics 80 MHz) was used as a fast switch to extinguish the laser to initiate cavity ring-down events, and the time-dependent light intensity escaping from the cavity was monitored using a high gain near-IR sensitive photodiode (New Focus IR-DC 150 MHz) and amplifier, and digitised with an 8-bit vertical resolution digital oscilloscope (LeCroy 9361). In vacuo the measured RDT was $\tau_0 = 8.80$ us, corresponding to mirror reflectivities of R = 0.99982. The stability of the ring-down times was determined to be 1.86% (1 SD) from analysis of numerous individual decay traces, giving a minimum detectable absorption coefficient of $\alpha_{min} = 7.1 \times 10^{-8} \text{ cm}^{-1}$ (corresponding to 1 SD of the baseline noise level) [6].

Samples of dilute N₂O (BOC Medical Grade, 99.98%) in argon (BOC Research Grade, 99.998%) were prepared in glass bulbs using an all-glass vacuum line, and the N2O was used without further purification. Typical dilutions were between 1% and 5% N_2O and pressures of ~1.5 Torr were introduced to the evacuated RDC, with all pressures measured using capacitance manometers. For pressure broadening studies, laboratory air was admitted to the vacuum chamber through a glass inlet to pressures up to 200 Torr. In all experiments the laboratory temperature was maintained at 295 K. Spectra of N₂O were obtained by applying a ramp voltage to the diode laser controller, and wavelengths were continuously monitored using a wavemeter (Burleigh WA-1000) with a manufacturer quoted precision of ± 0.01 cm⁻¹. A personal computer running a custom-written LabView program was used to fit to the natural logarithm of each individual ring-down trace, average the resultant ring-down rates, step the laser wavelength and record readings from the wavemeter.

3. Results and discussion

Several isolated rotational lines in the *P*-branch of the N₂O $3v_3$ band absorption spectrum were located and spectra recorded using the diode laser spectrometer. In the absence of air as a bath gas,



Fig. 1. CRD spectra of the P(10) rotational line of the $3v_3$ band of N₂O obtained at partial pressures of N₂O of 23, 37 and 57 mTorr (using a 5% N₂O/Ar gas mixture). The solid lines are Gaussian fits to the line profiles. The inset shows a plot of linecentre absorption coefficients against N₂O partial pressure, from the gradient of which a line-centre absorption cross-section is derived.

fits to N₂O absorption lines using Gaussian functions to model the expected low-pressure, Doppler-limited line broadening gave full-widths at half maximum height (FWHM) of $0.0123 \pm$ 0.00011 cm^{-1} , in accord with expectations at a temperature of 295 K. Numerous spectra were obtained of the P(J'') lines with J'' = 3, 5, 8, 10, 15, 21, 26 and 34 at a variety of partial pressures of N₂O in the range 15–75 mTorr and both peakand line-integrated absorption coefficients were plotted against partial pressure of N₂O to obtain line-centre absorption cross-sections and integrated line intensities (denoted, respectively, as σ_{λ} and σ_{line}) from straight line fits. Fig. 1 contains representative N₂O spectra of the P(10) line at three partial pressures of N₂O and the inset shows a plot of the linear variation of the peak absorption coefficient with pressure of N_2O . The values of σ_{line} obtained from such measurements are summarised in Table 1, along with corresponding line intensity values from FTS measurements by Toth [4]. The agreement is generally excellent between the two methods, with five of our measurements lying well within the specified uncertainties of the FTS data, a further two agreeing within the uncertainties in our data set, and the value for the P(8) line within the mutual uncertainties. The FTS and CRDS data are also in good agreement with line intensity ratios calculated from spectral simulations performed using the PGOPHER program [10] and spectroscopic constants from [4].

The absorption cross-sections, σ_{λ} , at wavelengths corresponding to the centres of the spectral lines, are also listed in Table 1. With $\sigma_{\lambda} = 1.86 \times 10^{-21}$ cm² molecule⁻¹ at the centre frequency of the P(15) line, and a limiting absorption coefficient of 7.1×10^{-8} cm⁻¹ for our experimental conditions, the detection limit for N₂O is estimated to be

Table 1

Line-integrated (σ_{iine}) and line-centre (σ_{λ}) absorption cross-sections from the CRDS measurements, compared with the Fourier transform spectroscopy (FTS) results from [4]

	Spectral line ^a (cm ⁻¹)	$\sigma_{\text{line}} (\text{CRDS})/10^{-23}$ (cm ² molecule ⁻¹ cm ⁻¹)	$\sigma_{\text{line}} \text{ (FTS)/10}^{-23}$ (cm ² molecule ⁻¹ cm ⁻¹)	% Difference ^b	σ_{λ} (CRDS)/10 ⁻²¹ (cm ² molecule ⁻¹)
	P(3) 6578.277	0.69 ± 0.04	0.71 ± 0.04	+2.8	0.48 ± 0.02
	P(5) 6576.456	1.21 ± 0.09	1.14 ± 0.06	-6.0	$0.91\pm0.07^{\circ}$
	P(8) 6573.569	1.51 ± 0.15	1.69 ± 0.08	+10.4	1.22 ± 0.04
	P(10) 6571.540	2.02 ± 0.23	1.96 ± 0.10	-2.9	1.51 ± 0.02
	P(15) 6566.107	2.29 ± 0.15	2.25 ± 0.11	-1.9	1.86 ± 0.02
	P(21) 6558.904	1.99 ± 0.13	2.02 ± 0.10	+1.9	1.50 ± 0.04
	P(26) 6552.334	1.64 ± 0.17	1.53 ± 0.08	-7.3	$1.27\pm0.09^{\circ}$
	P(34) 6540.749	0.74 ± 0.04	0.75 ± 0.05	+0.4	0.54 ± 0.01

The final column lists line-centre absorption cross-sections derived from the current study. Uncertainties on the CRDS values are obtained as 1 SD of repeated measurements.

^a Line-centre frequencies are from [4].

^b The % difference is defined as $100 \times \{\sigma_{\text{line}}(\text{FTS}) - \sigma_{\text{line}}(\text{CRDS})\} / \sigma_{\text{line}}(\text{FTS})$.

^c Uncertainties estimated from signal to noise ratios of limited data sets.

 3.80×10^{13} molecules cm⁻³ (i.e., 1.2 mTorr, 1 SD of the baseline noise), which could be substantially improved with greater cavity stability and higher mirror reflectivities.

With addition of air to the RDC, the N₂O rotational lines showed pronounced broadening, as illustrated in Fig. 2 for the P(8) spectral line. Spectra of such unblended rotational lines were fitted to Voigt functions, with the width of the Lorentzian component and the area of the function floated, but the line-centre frequency and the FWHM of the Gaussian component held fixed at values derived from the spectra taken in the absence of any bath gas. Fixing these two parameters of the line shape function was found to be necessary to ensure reliable fitting of the experimental data. No pressure-induced line-centre frequency shifts can be resolved from our spectra. The inset to Fig. 2 shows the variation with pressure of air of the half-widths at half maximum height (HWHMs) of the Lorentzian components of the best-fit Voigt profiles. Linear fits to such data sets give pressure broadening coefficients, γ_{air} in units of cm⁻¹ atm⁻¹. Measurements for the various *P*-branch lines listed previously reveal a J''-dependence to the pressure broadening coefficients, as illustrated in Fig. 3, that is particularly pronounced at low values of J''. The trend evident in



Fig. 3. (Upper panel) The J''-dependence of the air pressure broadening coefficients, γ_{air} . Error bars are 1 SD, obtained from the linear fits to data sets such as that shown in the inset to Fig. 2. The solid line is a fit of the J''-dependent broadening coefficients to a 1,1-Padé approximant as described in the text. (Lower panel) A simulated stick spectrum (with arbitrary intensity units) of the *P*-branch of the N₂O $3v_3$ band obtained using the rotational constants from [4] and a temperature of 296 K.

the data in Fig. 3 is similar to that reported from FTS studies of rotational level-dependent pressure broadening of resolved spectral lines in the $v_1 + v_3$ and other lower-frequency bands [11–13], but the high-*J*" pressure broadening coefficients in air of



Fig. 2. Spectra of the P(8) rotational line obtained in different pressures of air: \bigcirc , 37 mTorr of N₂O in the absence of air; \spadesuit , 37 mTorr of N₂O in 45 Torr of air; \square , 37 mTorr of N₂O in 85 Torr of air. The solid lines are Voigt profile fits to the lineshapes from which HWHMs of the Lorentzian components plotted in the inset are obtained as a function of air pressure. The straight line fit gives the pressure broadening coefficient, γ_{air} (cm⁻¹ atm⁻¹).

 $\gamma_{air} = 0.086 \pm 0.015 \text{ cm}^{-1} \text{ atm}^{-1}$, increasing to $0.139 \pm 0.010 \text{ cm}^{-1} \text{ atm}^{-1} \text{ at } J'' = 3$ are larger than those reported bands at wavenumbers below 4800 cm⁻¹ (respective values for J'' = 34 and J'' = 3 are near 0.074 and 0.094 cm⁻¹ atm⁻¹ for N₂-induced broadening) [11–14]. Self-broadening by N₂O is known to have a greater effect on spectral linewidths than air or N₂ [14], but under our experimental conditions, partial pressures of N₂O less than 75 mTorr were employed and self-broadening effects are thus negligible. The greater observed broadening must, therefore, be a consequence of the interaction of the vibrationally excited $3v_3$ level with air.

The data shown in Fig. 3 were fitted to a 1,1-Padé approximant relating linewidths and ground vibrational state rotational quantum numbers, as employed for the v_1 fundamental band of N₂O. Higher-order Padé approximants have also been used to fit larger data sets for the $v_1 + v_3$ band [11]. Using a function of the form

$$\gamma$$
 (cm⁻¹ atm⁻¹) = $\frac{a_0 + a_1 J''}{1 + b_1 J''}$,

we obtain the parameters (in units of cm⁻¹ atm⁻¹) $a_0 = 0.217 \pm 0.022$, $a_1 = 0.0375 \pm 0.0023$ and $b_1 = 0.509 \pm 0.030$, with uncertainties of 1 SD from floating of all three parameters. The uncertainties in the fit parameters are a result of a combination of few data points and the restrictions of the model function.

At atmospheric pressure, the N_2O absorption line shapes will be dominated by the Lorentzian components from pressure broadening, with FHWM of ~0.18 cm⁻¹ (for $J'' \sim 15$ in the vicinity of the maximum intensity of the absorption band at 295 K). The associated reduction in the linecentre intensity will be a factor of ~ 15 compared to the low-pressure, Doppler-limited line shapes (with FWHM of 0.0123 cm⁻¹), with a correspondingly reduced sensitivity to N₂O detection by narrow bandwidth diode laser CRDS. The limiting sensitivity to N_2O via a single rotational line of the *P*-branch of the $3v_3$ band under the conditions of our experiment would thus be 5.7×10^{14} molecules cm^{-3} , or a mixing ratio in air at 1 atm of 23 ppmv, well above the average mixing ratio for N₂O of 315 ppbv.

4. Conclusion

Pressure broadening of various rotational lines in the $3v_3$ vibrational overtone absorption band of N₂O has been quantified in terms of *J*"-dependent pressure broadening coefficients. The consequences of this broadening are to reduce the sensitivity of cw CRDS detection of N₂O via this convenient near-IR absorption band by a factor of ~15 in ambient air, when compared to low-pressure conditions. Direct detection of atmospheric N₂O via this technique is thus not feasible with current performance levels of our spectrometer, but improved mirror reflectivities and cavity stability could, in principle, deliver the necessary sensitivity by CRDS.

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