Measurements of spectral parameters for nitrous oxide near 4.56 μm using a quantum cascade laser

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Line strengths and nitrogen ($N_2$)-broadening coefficients for six nitrous oxide transitions were measured using a continuous-wave quantum cascade laser (cw-QCL) operating near 4.56 μm. The temperature dependence of the exponent $n$ for the $N_2$-broadening coefficients was determined over the range 298–800 K using a sapphire-sealed optical cell. Spectral parameters were determined by fitting absorption spectra with multi-peak Voigt profiles. The line strengths for the six transitions are 0–3% larger than those in the HITRAN 2012 database, while the $N_2$-broadening coefficients at the reference temperature are 2–5% smaller than the HITRAN 2012 values.

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1. Introduction

Laser absorption diagnostics using quantum cascade lasers (QCLs) have enabled non-intrusive, real-time, in situ measurements of gas temperatures and species concentration under various flow-fields [1–5]. Laser-based measurements depend on accurate spectral parameters for target transitions, including line strengths, broadening coefficients, and temperature-dependent exponents. Those parameters obtained from spectroscopic databases such as HITRAN [6] and GEISA [7] are mostly derived from quantum-mechanical calculations and lack experiment validations. In particular, the accuracies of the spectral parameters for triatomic molecules such as H$_2$O and N$_2$O are questionable. Accurate experimental measurements of H$_2$O vapor transitions have been reported from fully resolved absorption measurements in the near-IR [8–11].

Nitrous oxide (N$_2$O, also known as laughing gas) is important to greenhouse issue because it is 300 times more effective than CO$_2$ with regard to global warming [12]. It is generally produced through industrial fossil-fuel combustion and is used as an energetic oxidizer for chemical reactions at elevated temperatures. In addition, it is widely studied as a rocket propellant for aerospace applications, such as small satellites [13–17]. Laser absorption methods may be used for N$_2$O quantification in harsh environments, such as that found in combustion engines [5]. Mid-infrared (IR) laser-based sensors provide more sensitive measurements of N$_2$O relative to those in the near-IR, because the mid-IR line strengths are at least two orders of magnitudes greater [6]. Meanwhile, line-shape broadening and temperature exponents are crucial parameters that should be calibrated experimentally for engine diagnostics under high-pressure and/or high-temperature conditions.

Spectral parameters for N$_2$O lines between 500 cm$^{-1}$ and 7500 cm$^{-1}$ are presented in HITRAN [6]. Toth has reported much on N$_2$O spectra: line strengths over 900–3600 cm$^{-1}$ and self-broadened line widths over 1800–2360 cm$^{-1}$ [18–20], line strengths over 3515–7800 cm$^{-1}$, and N$_2$- and air-broadened line widths over 1800–4800 cm$^{-1}$ [21]. Line strength measurements were obtained by Daumont et al. for the 10-μm region [22], over 4300–5200 cm$^{-1}$ [23],...
and over 5400–11,000 cm\(^{-1}\) [24]. Rachet et al. measured line strengths over 2400–2850 cm\(^{-1}\) [25,26]. Absolute intensities of \(\text{N}_2\text{O}\) transitions were measured in the 4-\(\mu\)m and 3-\(\mu\)m regions by Barbe et al. [27]. Line strengths, \(\text{N}_2\text{O}\), \(\text{O}_2\text{O}\), and air-broadening of \(\text{N}_2\text{O}\) were obtained in the 4.5-\(\mu\)m region by Nemchinov et al. [28], and in the 4-\(\mu\)m and 8-\(\mu\)m region by Lacome et al. [29]. Previous studies were performed with a broad-bandwidth Fourier-transform spectrometer at room temperature, and the results were compared with the HITRAN and GEISA databases. Meanwhile, line strengths near 8 \(\mu\)m [30] and 2 \(\mu\)m were obtained with narrow-line-width diode laser systems at room temperature. The strongest vibrational band of \(\text{N}_2\text{O}\) is in the 4.5-\(\mu\)m region, which offers great potential for sensitive detection [6]. However, few measurements of spectral parameters have been performed for the \(v_3\) fundamental band near 4.5 \(\mu\)m. Loewenstein et al. performed preliminary measurements using a tunable diode laser spectrometer at 297 K [31,32], but there is a lack of data for high-temperature conditions.

Here, a narrow-line-width continuous-wave (cw) QCL near 4.56 \(\mu\)m was used to obtain \(\text{N}_2\text{O}\) spectral parameters over the temperature range 298–800 K and the pressure range 2–200 Torr. Line strengths, broadening coefficients, and temperature-dependent exponents were obtained to verify the HITRAN 2012 [6] and GEISA 2009 [7] molecular spectroscopic databases. The measurements were conducted in a sapphire-sealed optical cell and absorption spectra were fitted with Voigt line-shape profiles.

2. Fundamental spectroscopy

Laser absorption by a molecular transition at frequency \(\nu\) is expressed by the Beer–Lambert law in Eq. (1) for transmitted intensity \(I_t\) through a gas medium of optical path length \(l\) (cm) and incident intensity \(I_0\):

\[
l_t = \frac{I_t}{I_0} = \exp(-PX\varepsilon(T)\phi(\nu - \nu_0)L)
\]

where \(P\) (atm) is the pressure, \(X\) is the mole fraction of the target absorbing species, \(S(T)(\text{cm}^{-2}\text{atm}^{-1})\) is the line strength of the transition at temperature \(T\) (K), and \(\phi(\nu - \nu_0)\) (cm) is the line shape function at the center wavelength \(\nu_0\). The line-shape function is normalized such that \(\int_{-\infty}^{+\infty} \phi(\nu - \nu_0)\,d\nu = 1\) and the integrated absorbance \(A\) (cm\(^{-1}\)) can be expressed as:

\[
A = PX\varepsilon S(T)L
\]

Given the line strength at the reference temperature \(S(T_0=296\text{K})\) and the energy of the lower state for transition \(E\) (cm\(^{-1}\)), the line strength at an arbitrary temperature \(S(T)\) can be calculated by:

\[
S(T) = S(T_0)\frac{Q(T_0)}{Q(T)}\left[\frac{T_0}{T}\right]^5 \exp\left[-\frac{h c E}{k T}\right]
\]

\[
\times \left[1 - \exp\left(-\frac{h c v_0}{k T}\right)\right]^{-1}
\]

where \(h\) is Planck’s constant, \(c\) is the speed of light, \(k\) is Boltzmann’s constant, and \(Q(T)\) is the partition function of the molecule.

The line-shape function \(\phi(\nu - \nu_0)\) is determined by inhomogeneous broadening (or Doppler broadening) and homogeneous broadening (or collisional broadening) [4]. It offers significant information with regard to pressure, gas concentration, and temperature. A brief discussion of the broadening mechanisms is given below.

Doppler broadening is caused by the random thermal motion of the absorbing molecules. The Doppler lineshape function \(\phi_d(\nu)\) is described by a Gaussian profile:

\[
\phi_d(\nu) = \frac{2}{\Delta\nu D}\sqrt{\frac{\ln 2}{\pi}} \exp\left\{-4\ln 2\left(\frac{\nu - \nu_0}{\Delta\nu D}\right)^2\right\}
\]

where \(\Delta\nu D\) (cm\(^{-1}\)) is the Doppler full width at half maximum (FWHM):

\[
\Delta\nu D = \frac{8kT\ln 2}{m c^2} = 7.1623 \times 10^{-7} \nu_0 \sqrt{\frac{T}{M}}
\]

where \(M\) (g/mol) is the molecular weight.

Pressure broadening of spectral transitions is caused by binary collisions of the absorbing and non-absorbing species, where the duration of the collisions is assumed to be negligible. The pressure-broadened line shape has a Lorentzian profile:

\[
\phi_p = \frac{1}{\pi} \frac{2\Delta v_c}{\left(\nu - \nu_0\right)^2 + (\Delta v_c)^2}
\]

where \(\Delta v_c\) (cm\(^{-1}\)) is the collisional FWHM that is proportional to the pressure:

\[
\Delta v_c = P \sum_j X_j \gamma_j
\]

Here, \(\gamma_j\) (cm\(^{-1}\)atm\(^{-1}\)) is the broadening coefficient due to the collisions between perturbing species \(j\) and the absorbing species. The temperature dependence of \(\gamma_j\) can be expressed in terms of the temperature exponent \(n\):

\[
\gamma_j = \gamma_j(\nu_0)\left(\frac{T_0}{T}\right)^{n_j}
\]

Under most experimental conditions, both mechanisms are usually important and the broadened line shape, or Voigt profile [3], is a convolution of the Gaussian and Lorentzian line shapes:

\[
\phi_v(\nu) = \int_{-\infty}^{+\infty} \phi_d(u)\phi_l(\nu - u)\,du
\]

3. Experimental setup

Measurements were performed on two strong \(\text{N}_2\text{O}\) transitions near 2192.48 cm\(^{-1}\) and 2193.54 cm\(^{-1}\) and four weak neighboring transitions, belonging to the \(v_3\) fundamental and a combination band. The center wavelengths and lower-state energies of these transitions in the P-branch are listed in Table 1. Fig. 1 is a simulated absorption spectrum based on parameters from the HITRAN 2012 database and experimental conditions represented here. The peak absorbances range from 0.05–0.6 for a given optical path length, ensuring sufficient absorption in the experiments.
A cw distributed-feedback-mode QCL (ALPES LASERS), with a FWHM $\leq$ 3 MHz, was used to excite the N$_2$O near 4.56 $\mu$m. Previously, a three-section heated static cell was used for the near-IR [8–10,33]. Here, a different optical cell was used for mid-IR measurements; it is similar to those used by Rieker [34] and Rice [35]. Fig. 2 shows a detailed schematic of the cell. A pair of sapphire windows was installed inside a high-temperature resistant tube. The edges of the windows were machined (beveled) with a 45° sealing face so that each window could be mounted with two thin triangle copper seals compressed by a nut. The window faces were wedged to avoid etalon interference. In addition, two 5-cm-long sapphire rods were used to set the 5.86-cm optical path length.

The cell was heated with high-temperature heating tape (OMEGA, STH Series). The temperature of the gas was determined to within 0.75% with a type-K thermocouple (OMEGA) in the center of the cell. Up to 800 K, the cell had a maximum leakage rate of 0.1 Pa min$^{-1}$ (OMEGA) in the center of the cell. Up to 800 K, the cell had determined to within 0.75% with a type-K thermocouple (OMEGA, STH Series). The temperature of the gas was the 5.86-cm optical path length.

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the stability and improve the accuracy and precision. The integrated absorbance over the pressure range was fitted by a linear function, and the line strength \( S(T) \) at each temperature was derived from the slope using Eq. (2). The results for the \( P(32) \) transition at 2193.54 cm\(^{-1}\) are shown in Fig. 4(a). Based on 10 measured line strengths over the
temperature range 298–800 K, the line strength at the reference temperature $S(296 \text{ K})$ was derived from a non-linear fit according to Eq. (3).

To obtain broadening coefficients and temperature exponents, similar experiments were performed over the pressure range 10–200 Torr and at 10 temperatures over 298–800 K. The $N_2$-broadening coefficient $\gamma_{N_2}$ at a specific temperature was derived from the slope of a linear fit to the measured Lorentzian FWHM as a function of pressure using Eq. (7), as shown in Fig. 4(b). From the 10 $N_2$-broadening coefficients, the collisional pressure-broadening coefficient at the reference temperature $\gamma_{N_2}(296 \text{ K})$ and the temperature exponent $n$ were derived by fits according to Eq. (8).

5. Results and discussions

Fig. 5 plots the measured line strengths at 10 temperatures over 298–800 K for the $P(19f)$ transition at 2192.40 cm$^{-1}$. The line strength at the reference temperature $S(296 \text{ K})$ was obtained with an uncertainty of less than 1%. Also plotted are values from the HITRAN 2012 database: the measured line strengths are 1–5% larger at all temperatures. Fig. 6 plots measured line strengths for the six $N_2O$ transitions over the temperature range 298–800 K. Table 2 lists the measured line strengths, as well as corresponding HITRAN 2012 and GEISA 2009 values, at the reference temperature of 296 K. The measured line strengths are 1–5% larger at all temperatures.

Table 2

<table>
<thead>
<tr>
<th>Line Wavelength (cm$^{-1}$)</th>
<th>Measurements</th>
<th>Hitran 2012</th>
<th>ΔS/$S_{\text{Hitran}}$</th>
<th>GEISA 2009</th>
<th>ΔS/$S_{\text{GEISA}}$</th>
<th>Essenbar [32]</th>
</tr>
</thead>
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<tr>
<td></td>
<td>$S(296 \text{ K})$ (cm$^{-2}$atm$^{-1}$)</td>
<td>$S(296 \text{ K})$ (cm$^{-2}$atm$^{-1}$)</td>
<td>δ (%)</td>
<td>$S(296 \text{ K})$ (cm$^{-2}$atm$^{-1}$)</td>
<td>$S(296 \text{ K})$ (cm$^{-2}$atm$^{-1}$)</td>
<td>δ (%)</td>
</tr>
<tr>
<td>-----------------------------</td>
<td>--------------</td>
<td>-------------</td>
<td>-----------------------</td>
<td>------------</td>
<td>-----------------------</td>
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</tr>
<tr>
<td>1 2192.40</td>
<td>1.24</td>
<td>2.87</td>
<td>1.22</td>
<td>1.64</td>
<td>1.26</td>
<td>−1.59</td>
</tr>
<tr>
<td>2 2192.44</td>
<td>1.26</td>
<td>2.80</td>
<td>1.22</td>
<td>2.94</td>
<td>1.26</td>
<td>0</td>
</tr>
<tr>
<td>3 2192.48</td>
<td>8.54</td>
<td>0.96</td>
<td>8.37</td>
<td>2.03</td>
<td>8.45</td>
<td>1.07</td>
</tr>
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<td>4 2193.36</td>
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<td>1.25</td>
<td>2−5</td>
<td>0</td>
<td>8.40</td>
</tr>
<tr>
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<td>1.26</td>
<td>2.62</td>
<td>1.25</td>
<td>0.80</td>
<td>1.29</td>
<td>−3.30</td>
</tr>
<tr>
<td>6 2193.54</td>
<td>9.50</td>
<td>0.81</td>
<td>9.29</td>
<td>2.26</td>
<td>9.38</td>
<td>1.28</td>
</tr>
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</table>

Fig. 7. Measured $N_2$-broadening coefficients (symbol) vs. temperature for six $N_2O$ transitions.
strengths at the reference temperature for all lines of interest are 0–3\% larger than the HITRAN 2012 values, while the GEISA 2009 values are within ±3.1\%. The uncertainty δ for the measurements in Table 2 is the ratio of standard error and measured value derived from the nonlinear fit to the measured data. The uncertainties of the measurements derive from uncertainties in temperature (1\%), pressure measurements (0.12\%), gas mixture concentrations (0.5\%), optical path length determination (1\%), and fit error when determining the baseline and line-shape fits (1\%).

Fig. 7 plots the measured N₂-broadening coefficients vs. temperatures (298–800 K) for the six transitions. The N₂O concentration in the gas mixture was 0.42\%; thus there was a negligible contribution of self-broadening effect to the total collisional Lorentz width. The collisional pressure-broadening coefficients at the reference temperature γ₊₂(296K) and the temperature exponents n were obtained by fitting the data. The measured spectral parameters for the six lines are summarized in Table 3, along with air-broadening coefficients and temperature exponents from the HITRAN 2012 database. As can be seen, the measured N₂-broadening coefficients at the reference temperature of 296 K are 2–5\% smaller than the HITRAN 2012 air-broadening coefficients.

### Table 3

Comparison between measured N₂-broadening coefficients and HITRAN 2012 air-broadening coefficients of the six N₂O transitions.

<table>
<thead>
<tr>
<th>Line</th>
<th>Wavelength (cm⁻¹)</th>
<th>Measurements</th>
<th>Hitran 2012</th>
<th>Essebbar [32]</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>γ₊₂(296K) (cm⁻¹atm⁻¹)</td>
<td>δ (%)</td>
<td>n</td>
<td>Δ</td>
</tr>
<tr>
<td>1</td>
<td>2192.40</td>
<td>0.0718</td>
<td>2.52</td>
<td>0.721</td>
<td>0.96</td>
</tr>
<tr>
<td>2</td>
<td>2192.44</td>
<td>0.0721</td>
<td>4.23</td>
<td>0.634</td>
<td>1.52</td>
</tr>
<tr>
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<td>0.0685</td>
<td>4.38</td>
<td>0.715</td>
<td>1.61</td>
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<tr>
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<td>4.99</td>
<td>0.715</td>
<td>2.53</td>
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<tr>
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<td>0.0735</td>
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<td>0.702</td>
<td>2.65</td>
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<tr>
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<td>2193.54</td>
<td>0.0683</td>
<td>4.43</td>
<td>0.604</td>
<td>2.56</td>
</tr>
</tbody>
</table>

### Acknowledgments

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