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First measurements of nitrous oxide self-broadening and self-shift coefficients in the 0002-0000 band at 2.26 μm using high resolution Fourier transform spectroscopy

Viktor Werwein [a,*], Jens Brunzendorf [a], Anton Serdyukov [a], Olav Werhahn [a], Volker Ebert [a,b]

[a] Physikalisch-Technische Bundesanstalt, Bundesallee 100, 38116 Braunschweig, Germany
[b] Centre of Smart Interfaces, Technische Universität Darmstadt, Jovanka-Bontschits-Straße 2, 64287 Darmstadt, Germany

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ABSTRACT

Nitrous oxide (N_2O) is one of the most important greenhouse gases in the terrestrial atmosphere and is routinely measured with ground-based FTIR networks like the Total Carbon Column Observing Network (TCCON). A spectral window for the TCCON retrievals is the $^{14}N_2{}^{16}O$ 0002-0000-band region from 4375 to 4445 cm^{-1} (2.250–2.285 μm). In our study, we present the first high-resolution Fourier transform spectrometer measurements of self-broadening and self-shift coefficients in the range of 53–1019 hPa for the lines R0e–R40e of this band. The line parameters were determined at 296 K using metrologically validated temperature, and pressure values, which were traced back to the SI-units. The averaged estimated relative uncertainties for the coverage factor of $k = 2$ (two times the standard deviation) are 0.3% and 9.5% with a standard deviation of 0.1% and 5.3% for the self-broadening and the self-shift coefficients, respectively. Vacuum line positions, determined for the first time by taking the self-shift coefficients into account are also reported with an estimated averaged relative uncertainty of $1.1 * 10^{-8}$ for $k = 2$ and a standard deviation of $3 * 10^{-9}$. A well-defined uncertainty assessment for the measured line parameters is given.

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1. Introduction

Besides water (H_2O), carbon dioxide (CO_2) and methane (CH_4), which are mostly associated with the atmospheric greenhouse effect, nitrous oxide (N_2O) is an important greenhouse gas in the terrestrial atmosphere. According to the Intergovernmental Panel on Climate Change (IPCC), its contribution to the "dry" global greenhouse effect amounts to 6% [1]. It is hence the main contributor after CO_2 and CH_4. N_2O is also the anthropogenic emission with the highest ozone-depleting potential in the 21st century due to its high emission rate compared to halogenated hydrocarbons [2].

During the last decades, many efforts to monitor the concentration of the major atmospheric trace gases have been undertaken. The Network for the Detection of Atmospheric Composition Change (NDACC) [3,4] and the Total Carbon Column Observing Network (TCCON) [5,6] are some of the most prominent facilities working in this field. NDACC and TCCON use ground-based high resolution Fourier transform infrared (FTIR) spectrometers distributed all over the world to measure atmospheric absorption spectra using sun as radiation source. Total column densities or vertical concentration profiles of the examined species are determined through fitting of synthetic spectra to the observed path-integrated atmospheric absorption spectra [7–16] using almost exclusively Voigt-line profiles as line shape models [6]. This purpose requires accurate spectral line parameters of the specific target molecules for the relevant wavelength ranges. The quality of the extracted species concentration strongly depends on the uncertainty of the spectral line parameters like vacuum line position, line strength, pressure-induced shift and pressure-broadening coefficients as well as their temperature dependencies.

The TCCON network monitors N_2O via the 0002-0000-band region of the most abundant isotopologue $^{14}N_2{}^{16}O$ from 4376.65 to 4414.35 cm^{-1} (P-branch) and from 4418.00 to 4441.60 cm^{-1} (R-branch) [11]. For the vibrational mode description we use henceforth the common notation v1v2l2v3 with the upper state given first. The TCCON network uses [11] the HITRAN spectroscopic database [17] for the N_2O line parameters. These are derived from several Fourier transform spectrometer studies performed by Toth and Lacome et al. from 1984 to 2000 [18–21].

* Corresponding author.
E-mail address: viktor.werwein@ptb.de (V. Werwein).

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The HITRAN 2012 N_2O self-broadening coefficients originate from FTIR measurements of Toth [19]. In this study, Toth measured, with a nominal spectral resolution of 0.011 cm^{-1}, an extensive set of self-broadening coefficients in the spectral range from 1800 to 2360 cm^{-1} determined through a multi-band, non-linear least squares fitting procedure using Voigt-profiles, followed by a linear regression of the obtained Lorentzian widths with respect to the total pressure. A pressure range from 67 to 672 hPa – 5 pressure levels in total – was covered. Subsequently, the determined broadening coefficients were averaged over different vibrational states for the same quantum number m ($m = -J$ for the P-branch and $m = J + 1$ for the R-branch lines) and smoothed afterwards over neighboring m values. Self-broadening coefficients from a third order polynomial fit to Toth's interpolation model are implemented in the HITRAN compilation [17].

Except for older low-resolution FTIR measurements by Margolis [22], where metrologically defined uncertainties were not given and therefore the results are difficult to assess, to the best of our knowledge, no direct measurements of self-broadening coefficients in the 0002-0000-band of N_2O have been reported so far. Therefore, we carried out an experimental verification of Toth's interpolation method [19] for this band.

In the same study Toth reported also self-shift coefficients of N_2O [19]. Besides the self-shift coefficients determination of four single lines by Pollock et al. using heterodyne frequency techniques [23], this effort is the only work on nitrous oxide self-shift in this band we are aware of. Toth inferred from his obtained results a very small J-dependence of the self-shift coefficients, but could not provide any evidence due to his too large uncertainties. Therefore, he simply averaged his measured self-shift coefficients and attributed the mean to all rovibrational transitions, giving rise to a single value for all coefficients in this band [19]. Directly measured self-shift coefficients for the 0002-0000-overtone band, however, are still missing.

The aim of this study was to provide high-resolution measurements of self-broadening and self-shift coefficients for the R-branch of the $^{14}N_2{}^{16}O$ 0002-0000-band including a well-defined uncertainty assessment. This study was performed in the framework of the EUMETRISPEC project [24], a joint effort of the Physikalisch-Technische Bundesanstalt (PTB) and other European national metrology institutes to establish a spectroscopy infrastructure for the generation of spectral line parameters traceable to the SI units.

2. Experimental details

The N_2O absorption spectra presented here were recorded with a Bruker IFS 125HR high-resolution Fourier transform spectrometer (FTS) at PTB in the spectral region from 3800 to 5200 cm^{-1}.

Table 1
Spectrometer settings for N_2O spectra measurements in the spectral region from 3800 to 5200 cm^{-1}.

Component	Specification
Spectrometer	Bruker IFS 125HR
Source	NIR tungsten lamp
Mirrors	Gold-plated
Beamsplitter	Calcium fluoride
Optical filter	2.25 μm band-pass (FWHM 0.5 μm)
Detector	InGaAs (room temperature)
Aperture	0.5 mm
Max. optical path difference	4.5 m
Nominal resolution	0.002 cm^{-1} (0.9/4.5 m)
Apodization	sinc ∗ boxcar (natural apodization)
Phase correction algorithm	Mertz
Zerofilling factor	2
Spectrometer vacuum	Better than 10^{-4} hPa

The details of the spectrometer settings are given in Table 1. Throughout this study, a beam aperture of 0.5 mm as well as a nominal spectral resolution of 0.002 cm^{-1} (0.9 divided by maximum optical path difference of 4.5 m) was chosen. In order to facilitate both, high spectral resolution and high signal-to-noise level of the spectra, measuring times of 8 h were used. Details are given in Section 3.1.

The spectrometer was evacuated by two turbo molecular pumps leading to a residual pressure always below 10^{-4} hPa. The exceptional quality of the spectrometer vacuum ensures a very smooth background spectrum, completely free of disturbing H_2O or CO_2 absorption lines.

A custom-made gas cell positioned inside the sample compartment of the spectrometer was used. The 20 cm long cell consists of a massive copper body with a built-in heat exchanger using ethanol as cooling fluid. The cell windows are 5 mm thick sapphire discs, 50 mm in diameter, with 6 mrad wedge angle. The optical path length of the utilized absorption cell was measured with a mechanical calliper by subtracting the thickness of the cell windows from the outer cell length. Furthermore, the wedge angle of the windows and the path difference of the on-axis and off-axis rays were included in the determination of the cell length of 20.70 ± 0.07 cm with an expanded uncertainty coverage factor of $k = 2$.

The used N_2O gas (Air Liquide) was a high purity sample with a volume concentration of $\geqslant$99.999 %. Spectral features due to sample impurities were not observed in the measured FTIR-spectra so that we assumed pure N_2O.

The cell filling procedure was as follows: The entire gas manifold was evacuated with a turbo molecular pump, purged with the N_2O sample gas three times and evacuated again before filling the sample gas into the cell to a certain pressure level. After filling about 30 min were given to achieve thermal equilibrium before starting the FTS measurement. For each pressure level, the cell was filled with new sample gas. During the complete filling procedure gas pressure and gas temperature were monitored continuously.

For this study, interferograms were recorded for seven different pressure levels from 53 to 1019 hPa. The gas temperature was always kept at 296.0 ± 0.2 K ($k = 2$). Sample pressure and temperature were recorded continuously. A summary of the measurement conditions is given in Table 2.

At each pressure level 160 interferograms were collected, each scan taken within about 3 min. After the sample measurements a background spectrum was measured recording 1200 interferograms (63 h) with an empty cell and identical spectrometer settings.

The gas pressure was measured using a capacitance diaphragm gauge (MKS Baratron 628D, full scale 1000 Torr), which was connected to the gas manifold next to the sample compartment. The pressure sensor was calibrated against PTB's national primary pressure standards in the range of 13 to 1300 hPa. The relative expanded uncertainty ($k = 2$) of a single pressure value amounts to 0.3–0.7% in the covered pressure range.

In order to process each average pressure level spectrum by its associated gas pressure value p_{gas}, p_{gas} had to be determined from the continuous pressure monitoring values p_{meas}. To this end, a three-step procedure was employed. First, all individual pressure values were corrected according to traceable sensor calibration resulting in traced back pressure values p_{cor}.

In the second step, the values p_{cor} were used to study the time dependency of the pressure behavior during a sample measurement. Its time series, shown in Fig. 1, revealed an exponential decrease at the beginning, turning into a quasi-linear behavior after 1–2 h as shown in Fig. 1 for 1019 hPa. The magnitude of the exponential pressure decrease showed a clear dependence on the

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