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Line parameters for the 4-0 band of carbon monoxide by high sensitivity cavity ring down spectroscopy near 1.2 μm

--Manuscript Draft--

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Abstract:	<p>The room temperature spectrum of the very weak third overtone band of carbon monoxide in natural isotopic abundance is recorded by cavity ring down spectroscopy (CRDS) referenced to a frequency comb, between 8206 and 8465 cm^{-1}. The sensitivity of the recordings (noise equivalent absorption on the order of $\text{min} \sim 5 \times 10^{-12} \text{ cm}^{-1}$) allowed for measuring lines with intensity as weak as $1 \times 10^{-30} \text{ cm}^2/\text{molecule}$ at a recording pressure limited to 10.0 Torr. The use of low pressure values (1.0 and 10.0 Torr) helped to minimize the impact of profile effects on the derived line positions and line intensities. The line profile analysis was performed using the speed dependent Nelkin-Ghatak model for the 10 Torr recordings while the Voigt profile was found sufficient to account for the line shapes recorded at 1.0 Torr. Overall, line parameters of 227 transitions are derived. The observed transitions belong to the 4-0 band of the $^{12}\text{C}^{16}\text{O}$, $^{13}\text{C}^{16}\text{O}$, $^{12}\text{C}^{18}\text{O}$ and $^{12}\text{C}^{17}\text{O}$ isotopologues present in natural abundance in the sample and to the 5-1 hot band of $^{12}\text{C}^{16}\text{O}$. For a large part of the observations, line positions are reported with accuracy as good as $4 \times 10^{-6} \text{ cm}^{-1}$ ($\sim 120 \text{ kHz}$). The self-induced line shift of the 4-0 band is reported for the first time from the position values at 1 and 10 Torr. Using literature values of the 1-0, 2-0 and 3-0 bands, the vibrational dependence of the self-induced pressure shift in CO is discussed. The experimental values of the $^{12}\text{C}^{16}\text{O}$ $v=4$ energy levels $J < 26$ are reproduced with a standard deviation of $2.5 \times 10^{-6} \text{ cm}^{-1}$ (75 kHz). The intensities of the $^{12}\text{C}^{16}\text{O}$ lines reported with an accuracy better than 1% show an overall good agreement with literature values in particular with those included in the HITRAN database.</p>
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Response to Reviewers:	see attached answers to the reviewers

Response to the reviewers

Ref: JQSRT_2020_794

Title: Line parameters of the 4-0 band of carbon monoxide by high sensitivity cavity ring down spectroscopy near 1.2 μm

We want to thank the two reviewers for their useful comments which were taken into account as detailed below.

-Reviewer 1

The room temperature spectra of the very weak third overtone band of carbon monoxide in natural isotopic abundance are recorded by cavity ring down spectroscopy referenced to a frequency comb, between 8206 and 8465 cm^{-1} . Using these spectra, the spectral line parameters (line position, line intensity) were recovered for the 4-0 band of the $^{12}\text{C}^{16}\text{O}$, $^{13}\text{C}^{16}\text{O}$, $^{12}\text{C}^{18}\text{O}$ and $^{12}\text{C}^{17}\text{O}$ isotopologues and for the 5-1 hot band of $^{12}\text{C}^{16}\text{O}$. The unprecedented high accuracy for the line positions was achieved (uncertainty about 100 kHz). Using the spectra recorded at two pressures (1 Torr and 10 Torr) the self-pressure induced broadening and shift coefficients were determined. It is necessary to emphasize that the very careful analysis of the spectra and comparison to the existing data were performed. The paper is well written. It can be published in the Journal of Quantitative Spectroscopy and Radiative Transfer after addressing below minor remarks.

1) The authors have to look carefully through the text of the manuscript and correct some misprints, for example:

a) Introduction, second line: overtone band of carbon dioxide -- overtone band of carbon monoxide

Thank you! The same error has been corrected in the title of Table 1.

b) Page 9, second paragraph, second line: please, change the following sentence: Statistical error bars as provided by the fitting program are provided for the fitted VP and qsdNGP parameters while
Corrected

c) Page 11, third line: HITRAN values for in our region -- HITRAN values in our region
Done

2) Fig.4. I think that the comparison to the empirically extrapolated differences of the line positions has to be excluded from this figure. The comparison has to be done to the real experimental data for $m < 27$.

The large dispersion of the shift values for $m > 27$ is mainly due to the uncertainty on the position values at 1 Torr. To make use of the 10 Torr values, they have to be corrected from the pressure shift and the empirical correction is more suitable than the direct use of the 1 Torr value. The adopted linear law is consistent with the general m dependence observed for the other vibrational bands (see Fig. 6).

Reviewer #2: The manuscript describes experimental results of spectroscopic parameters of carbon monoxide lines in a weak 4-0 band and provide new data of line positions, intensities and self-broadened line shapes. Authors use their well-developed cavity ring-down spectrometer with improved accuracy of frequency axis, comparing to earlier papers. The manuscript is well written and provides line parameters that are clearly more accurate than previously available data for CO 4-0 band. There is also exhaustive comparison of new results with previous literature data. Therefore the manuscript clearly should be published in JQSRT.

I don't have any remarks that requires major revision. I would only suggest some minor improvements to consider by authors:

1) "Accurate" in the title seems unnecessary, as any new published data should be more accurate than previous one.

The title has been modified as suggested

2) Page 4: "positions are determined with an accuracy on the order of $5 \times 10^{-6} \text{ cm}^{-1}$ (or 150 kHz)" This is inconsistent with an abstract sentence "line positions are reported with accuracy as good as $3 \times 10^{-6} \text{ cm}^{-1}$ ($\sim 100 \text{ kHz}$)"

The first value $-5 \times 10^{-6} \text{ cm}^{-1}$ (or 150 kHz)- is an average value while the second $-3 \times 10^{-6} \text{ cm}^{-1}$ ($\sim 100 \text{ kHz}$)- concern "a large part of the observations". To be consistent, we now indicate $4 \times 10^{-6} \text{ cm}^{-1}$ ($\sim 120 \text{ kHz}$) in the two places.

3) Figure 2: A vertical axes on the right side are not well described. I suppose "Line intensity" scale refers to blue dots in figure, but they are present only in the second and third plot while intensity scale is on all plots without any corresponding data points.

The intensity scale on the right side was added to give an idea of the intensities of the displayed lines. The corresponding stick spectrum (corresponding to the blue dots noted by the reviewer) is not plotted for clarity. We have deleted the blue dots and added: "The right-hand intensity scale is adjusted to correspond approximately to the peak heights."

4) Page 7: "The line parameters were converted to the 296 K reference value". Does it refer to line intensities or any other parameters were also corrected?

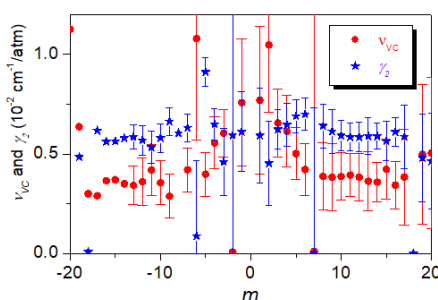
Only line intensities were converted

5) Page 11: "... positions are larger by about to 2×10^{-5} and $3 \times 10^{-5} \text{ cm}^{-1}$...". Here "to" is unnecessary. Corrected. Thank you.

6) Section 5: what about fitted speed dependence parameters of pressure broadening and shift. Were they both fitted. Some explanation would be needed here. Even if they have high uncertainties, showing it would maybe allow to see if a mentioned problem of correlated parameters (correlation with ν_{vc}) occurs. Also, have authors tried to fit quadratic SDVP instead of NGP? Would it be also significantly worse (like NGP) than $qsdNGP$?

Yes, the 10 Torr recordings allowed us to determine to fit the speed dependence parameters of pressure broadening and shift for the lines with good signal-to-noise ratios. It is clearly indicated in the text: *In addition to the Doppler width and pressure broadening parameters, the quadratic speed-dependent NGP ($qsdNGP$) [16,17] includes the Dicke narrowing parameter (ν_{vc}) [18] and the quadratic speed dependence of the pressure width and shift.* The corresponding fitted values are provided as Supplementary Material together with their error bars.

As concerned the correlation between ν_{vc} and g_2 , it is not obvious as illustrated on the following figure where they are both plotted versus m :



We have tried to use SDVP instead of NGP and the obtained residuals were slightly worse for most of the tested lines.

We hope that the amended version is now suitable for publication in JQSRT.

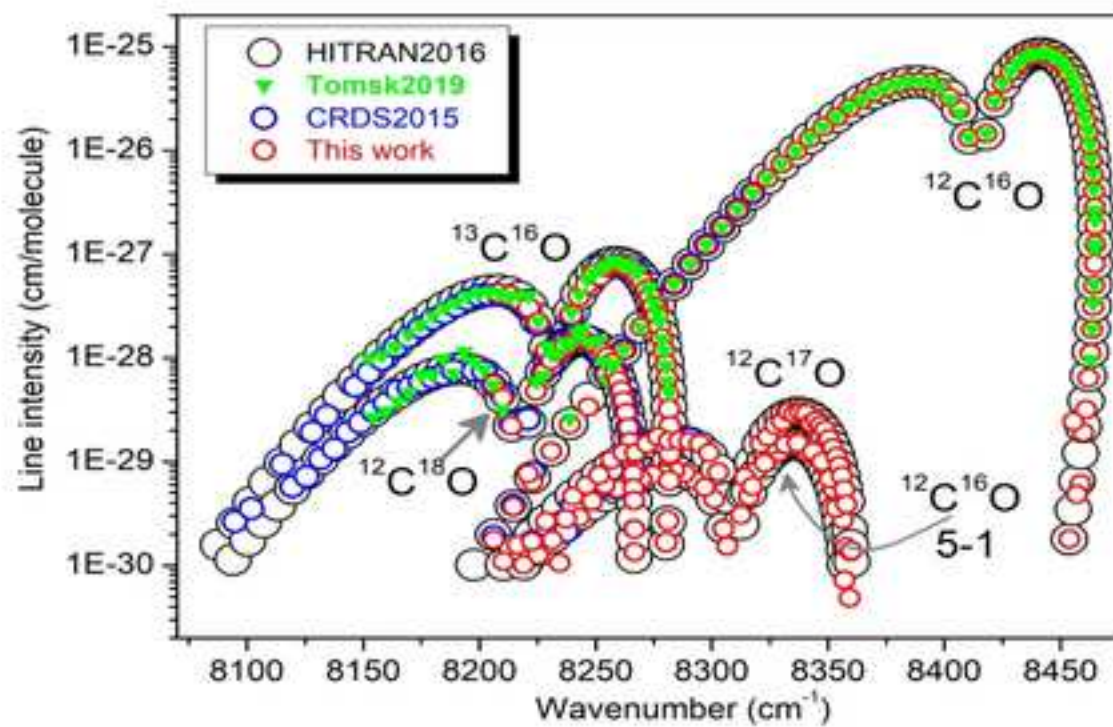
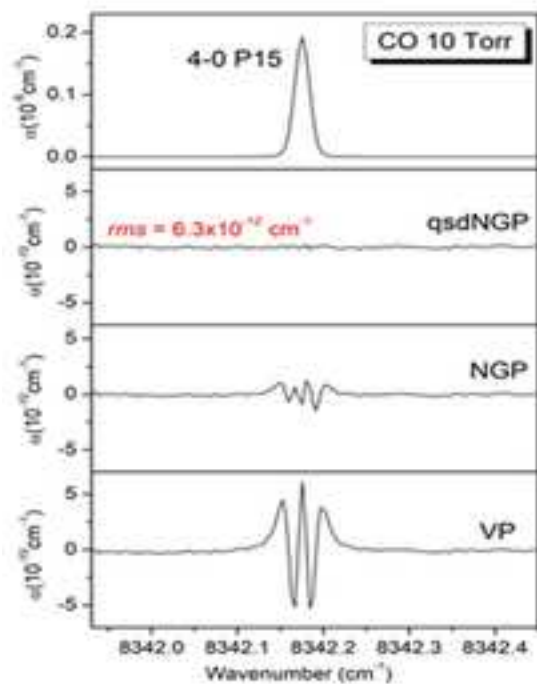
High sensitivity CRDS of the 4-0 band of CO at low pressure (1 and 10 Torr)

Line profile analysis using the speed dependent Nelkin-Ghatak model

First determination of the self-induced line shift of the 4-0 band

Line positions are reported with accuracy as good as $3 \times 10^{-6} \text{ cm}^{-1}$ (~90 kHz).

Accurate line intensities are used for critical evaluation tests of literature values



Line parameters of the 4-0 band of carbon monoxide
by high sensitivity cavity ring down spectroscopy near 1.2 μm

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25 November 2020

Number of tables: 3

Number of figures: 10

Key words: Molecular spectroscopy; Carbon monoxide; CO; line intensity; line profile, self-induced line shift; HITRAN.

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Abstract

The room temperature spectrum of the very weak third overtone band of carbon monoxide in natural isotopic abundance is recorded by cavity ring down spectroscopy (CRDS) referenced to a frequency comb, between 8206 and 8465 cm^{-1} . The sensitivity of the recordings (noise equivalent absorption on the order of $\alpha_{\text{min}} \sim 5 \times 10^{-12} \text{ cm}^{-1}$) allowed for measuring lines with intensity as weak as $1 \times 10^{-30} \text{ cm/molecule}$ at a recording pressure limited to 10.0 Torr. The use of low pressure values (1.0 and 10.0 Torr) helped to minimize the impact of profile effects on the derived line positions and line intensities. The line profile analysis was performed using the speed dependent Nelkin-Ghatak model for the 10 Torr recordings while the Voigt profile was found sufficient to account for the line shapes recorded at 1.0 Torr.

Overall, line parameters of 227 transitions are derived. The observed transitions belong to the 4-0 band of the $^{12}\text{C}^{16}\text{O}$, $^{13}\text{C}^{16}\text{O}$, $^{12}\text{C}^{18}\text{O}$ and $^{12}\text{C}^{17}\text{O}$ isotopologues present in natural abundance in the sample and to the 5-1 hot band of $^{12}\text{C}^{16}\text{O}$. For a large part of the observations, line positions are reported with accuracy as good as $4 \times 10^{-6} \text{ cm}^{-1}$ ($\sim 120 \text{ kHz}$). The self-induced line shift of the 4-0 band is reported for the first time from the position values at 1 and 10 Torr. Using literature values of the 1-0, 2-0 and 3-0 bands, the vibrational dependence of the self-induced pressure shift in CO is discussed. The experimental values of the $^{12}\text{C}^{16}\text{O}$ $\nu=4$ energy levels $J < 26$ are reproduced with a standard deviation of $2.5 \times 10^{-6} \text{ cm}^{-1}$ (75 kHz). The intensities of the $^{12}\text{C}^{16}\text{O}$ lines reported with an accuracy better than 1% show an overall good agreement with literature values in particular with those included in the HITRAN database.

I. Introduction

The present work is devoted to an improvement of the line parameters of the third overtone band of carbon monoxide, 4-0. The rapid decrease of the band intensities *versus* the vibrational excitation (more than two orders of magnitude for each increase of vibrational quantum number, ν) makes the considered band, more than 10^6 times weaker than the fundamental band near 2150 cm^{-1} .

The first detection of the 4-0 band was reported by Herzberg and Narahari Rao in 1949 [1]. These authors used a pressure of 1 atm and path lengths of 500 to 1000 m to detect transitions up to $J=20$ on their photographic plates. The first intensity measurements were performed in 1976 by Chackerian and Valero using a grating spectrograph, with a path length of 2.1 km and a pressure of 49.3 Torr [2]. In 2002, Ogilvie et al. measured the P(20)-R(25) lines by Fourier transform spectroscopy (FTS) with an absorbing pass of 107 meters and a CO pressure of about 1 atm [3]. A few years ago, we reported low pressure measurements of 94 transitions below 8317 cm^{-1} by high sensitivity cavity ring down spectroscopy (CRDS) [4]. The external cavity diode laser (ECDL) at disposal at that time allowed covering only the low energy range ($7910\text{-}8320\text{ cm}^{-1}$) of the 4-0 band system. Thus most of the reported observations belonged to the CO minor isotopologues, in natural abundances, and only the P34-P19 transitions of the $^{12}\text{C}^{16}\text{O}$ band centered at 8414 cm^{-1} could be measured. In their, semi-empirical intensity calculations, Li et al. [5] used the reported $^{12}\text{C}^{16}\text{O}$ CRDS intensity values to fit the expansion coefficients of their dipole moment function. The resulting calculated intensities are those reproduced in the present version of the HITRAN database [6]. The high J P34-P19 transitions reported in Ref. [4] have their intensity very sensitive to the temperature as their lower state energy range between 730 and 2279 cm^{-1} . This may affect the uncertainty of the reported intensities and makes suitable a complete CRDS coverage of the P and R branches of the 4-0 band of $^{12}\text{C}^{16}\text{O}$. This is the subject of the present contribution performed with a newly purchased ECDL. Similar arguments of validation of HITRAN line intensities have motivated a very recent FTS study of the 4-0 band performed in Tomsk with a 30-m long cell providing a pathlength on the order of 1 km [7]. The high resolution spectra recorded at 146 and 374 Torr were used to derive line intensities with uncertainties between 2 and 3% for the strongest lines and to fit the 4-0 effective dipole moment parameters of the $^{12}\text{C}^{16}\text{O}$ isotopologue. The obtained FTS intensities will be compared below to our results.

In the present work, the very high sensitivity provided by the CRDS technique allows us to record high signal-to-noise ratio spectra of the 4-0 band with pressure values limited to 10 Torr. The quality of the retrieved spectral parameters is expected to benefit from the use of

low pressures values as potential biases linked to the choice of the line profile used to reproduce the experimental line shape are minimized [see *e.g.* Ref. [8]). In addition, compared to our previous CRDS study [4], an important gain on the frequency accuracy is presently achieved by linking the CRDS setup to a frequency comb referenced to a GPS referenced 10 MHz rubidium clock [9,10]. As a result, for the “strong” unblended lines, positions are determined with an accuracy on the order of $4 \times 10^{-6} \text{ cm}^{-1}$ (or 120 kHz) and the relative uncertainty on the intensities is below 1%. These performances make possible to derive the self-induced line shifts from the difference of the line centers at 10 and 1 Torr obtained using a speed dependent Nelkin-Ghatak profile and a Voigt profile, respectively.

We present in **Fig. 1** an overview of the HITRAN2016, Tomsk [7], previous [4] and present CRDS measurements. In the following part 2, the setup, spectra recordings, line profile fitting procedures are described. Parts 3-5, are devoted to the analysis of the obtained line positions, line intensities and line profile parameters and their comparison with literature results.

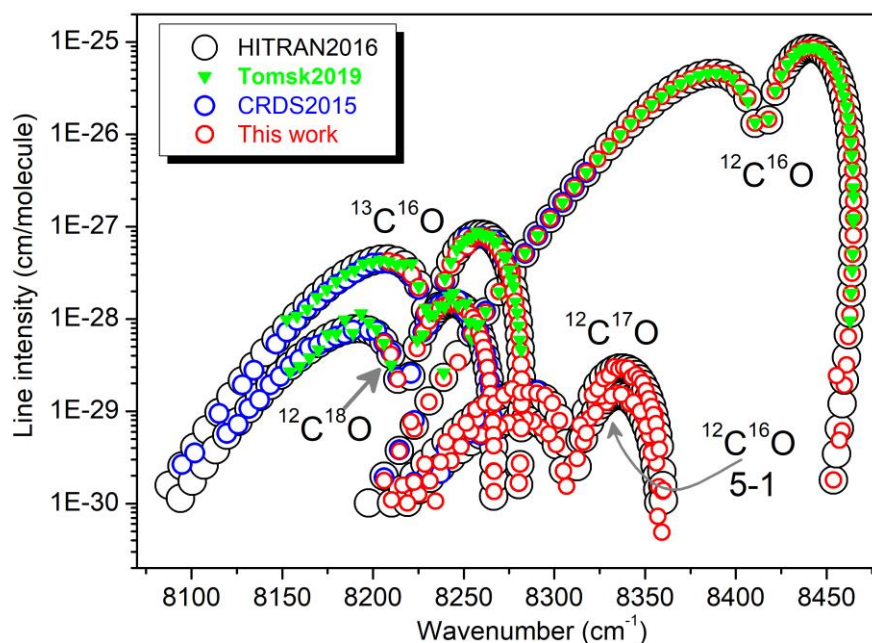


Figure 1.

Overview of the spectrum of carbon monoxide in natural isotopic abundance, in the region of the 4-0 band. The displayed spectrum includes the 4-0 band of $^{12}\text{C}^{16}\text{O}$, $^{13}\text{C}^{16}\text{O}$, $^{12}\text{C}^{18}\text{O}$ and $^{12}\text{C}^{17}\text{O}$ and the 5-1 hot band of $^{12}\text{C}^{16}\text{O}$. The transitions measured by FTS in Tomsk [7], by CRDS in Ref. [4] and in this work (green, blue and red symbols, respectively) are superimposed to the HITRAN2016 line list [6] (black circles).

2. Experimental set-up and line list construction

2.1. Spectra acquisition

The reader is referred to Refs. [11-13] for a detailed description of the cavity ring down spectrometer. Briefly, the Polarization-Maintaining (PM) fiber collimated beam emitted by the ECDL (Toptica, DL-PRO) is split using a fiber coupler. About 10% of the power is used for accurate frequency measurement purpose. The remaining 90% are first going through a fibered acousto-optic modulator (AOM) before optically exciting the 1.4-meter-long high-finesse cavity ($F \approx 130,000$). The AOM is used as a fast optical switch used to initiate ring down (RD) event, measured with an InGaAs photodiode. The frequency measurement port optical power is shared between a Fizeau type wavemeter (High Finesse WS-U-30 IR) and a self-referenced frequency comb (FC) beat note detection setup, providing sub-100 kHz accuracy to the instantaneous frequency readings. The Fizeau wavemeter provides a first determination of the ECDL emission frequency that allows for an unambiguous determination of the tooth n of the FC, which is beating with the laser. The latter measurement permits an accurate optical frequency measurement, potentially at sub-kHz level [14]. Presently, the beat note frequency is refreshed 1000 times per second, permitting active ECDL emission frequency control with 300 kHz *rms* dispersion. This value sets the frequency scale uncertainty of the spectra.

Classically, the frequency tuning of the ECDL was achieved by acting simultaneously on its internal grating angular position and the laser chip current (see Ref. [12] for details). Mode-hop-free tuning range of up to 1.3 cm^{-1} could be obtained with a step by step linear scan of the PZT voltage. The broadband spectra covering the $8206\text{-}8465 \text{ cm}^{-1}$ range were obtained by concatenation of a series of partly overlapping, 1.1 cm^{-1} wide individual spectra, recorded with about $1.3 \times 10^{-3} \text{ cm}^{-1}$ step resolution, to be compared to the CO Doppler line width of about $9 \times 10^{-3} \text{ cm}^{-1}$ (HWHM) in the considered region. Additional spectra were recorded around the strongest $^{12}\text{C}^{16}\text{O}$ lines, between 8310 and 8465 cm^{-1} .

Each baseline point was obtained by averaging 40 individual events. This number was increased according to the local absorption of the gas, in order to achieve a constant noise equivalent absorption, even on the absorption lines profiles. The noise equivalent absorption evaluated as the *rms* of the baseline fluctuations is around $5 \times 10^{-12} \text{ cm}^{-1}$. **Fig. 2** illustrates the sensitivity and high dynamical range on the intensity scale. It also reveals a number of water vapor interfering lines, with a relative concentration of about 0.1 %.

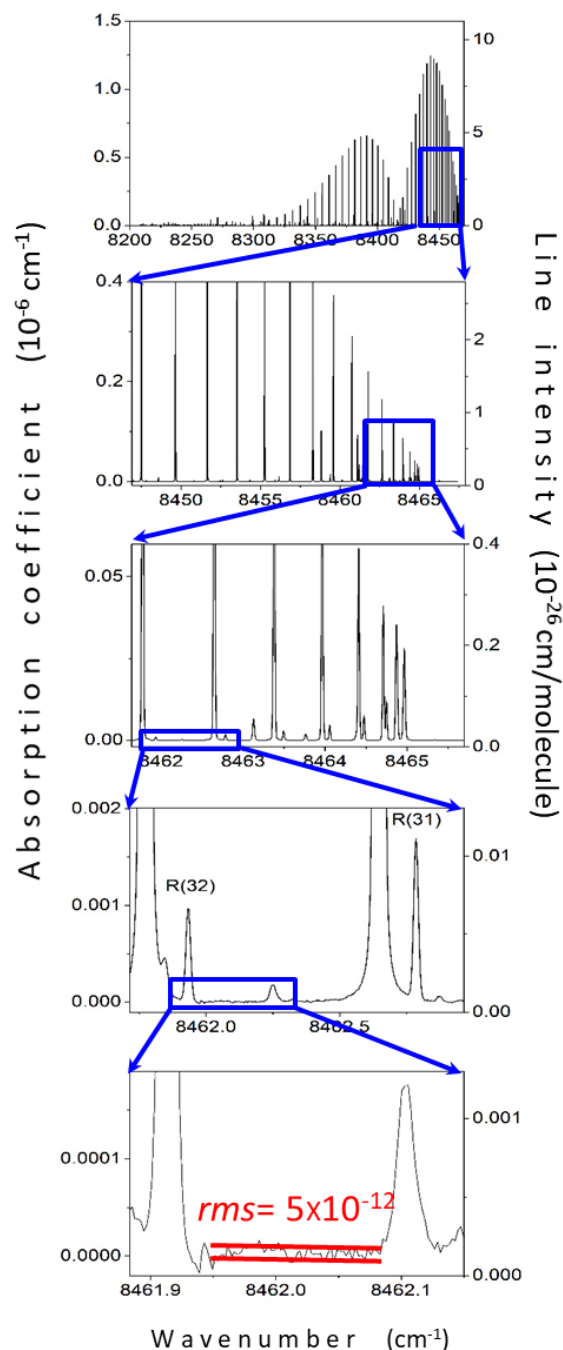


Fig. 2.

CRDS spectrum of the carbon monoxide in the region of the *R* branch head of the 4-0 overtone band of the $^{12}\text{C}^{16}\text{O}$ main isotopologue, recorded at a pressure of 10.0 Torr. The right-hand intensity scale is adjusted to correspond approximately to the peak heights. The enlargements illustrate the dynamics achieved on the intensity scale and the noise equivalent absorption ($\alpha_{\min} \approx 5 \times 10^{-12} \text{ cm}^{-1}$). The spectrum includes a number of interfering lines due to water vapor present in the CRDS cell as an impurity.

In order to minimize the amount of water degassing from the CRDS cell, the spectra were recorded in flow regime. The flow of CO (Air Liquide 99.997% stated purity) was roughly adjusted to 1 sccm with a downstream manual needle valve and the pressure was

actively regulated, acting on a solenoid valve according the readings of a capacitance gauge (MKS Baratron, 10 Torr range, 0.15% accuracy of the reading) recording the total pressure. The temperature of the outer wall of the stainless steel gas cell was monitored with a PT 1000 resistive probe (class Y, ± 0.15 K accuracy at room temperature) and an analog temperature sensor (TSic 501, IST-AG, ± 0.1 K accuracy) both fixed on the cell surface, the whole being surrounded by a thermal insulator. In the data treatment, for each line, spectroscopic parameters were derived using the temperature value at the recording time of the considered line. The line parameters were converted to the 296 K reference value, the originating energy level being well known. Over the whole spectrum recording, the temperature evolved in the 295.66-285.98 K and 295.68 and 296.03 ranges for the recordings at 1 and 10 Torr, respectively.

2.2. Line parameter retrieval

The line centers and intensities were determined using a homemade interactive least squares multi-line fitting program written in LabVIEW and C++. The spectra recorded at 1.0 and 10.0 Torr were treated independently.

Voigt profile at 1 Torr

Line parameters of the P18-R35 transitions transitions of the main isotopologue, $^{12}\text{C}^{16}\text{O}$, were retrieved from the 1 Torr spectra. The considered lines being weak, a Voigt profile (VP) was found sufficient to reproduce the line shape at 1.0 Torr. The ECDL line width (~ 100 kHz HWHM) is much smaller than the Doppler width ($\sim 9 \times 10^{-3} \text{ cm}^{-1}$ HWHM) leading to a line profile mostly Doppler limited (the pressure broadening at 1 Torr is about 10^{-4} cm^{-1}). The mass was fixed according to the isotopologue in the calculation of the Doppler width. The small Lorentzian width could be generally adjusted. Otherwise, it was constrained to the pressure broadened width calculated using the HITRAN self-broadening coefficient [6]. A number of CO lines are blended with water vapor lines which were included in the fit assuming a Voigt profile, too. The multi-line fit provides the line center, line intensity, Lorentzian width and the corresponding local baseline (assumed to be a linear function of the wavenumber). The obtained list of 53 transitions of the main isotopologue, $^{12}\text{C}^{16}\text{O}$, is included in a Supplementary Material.

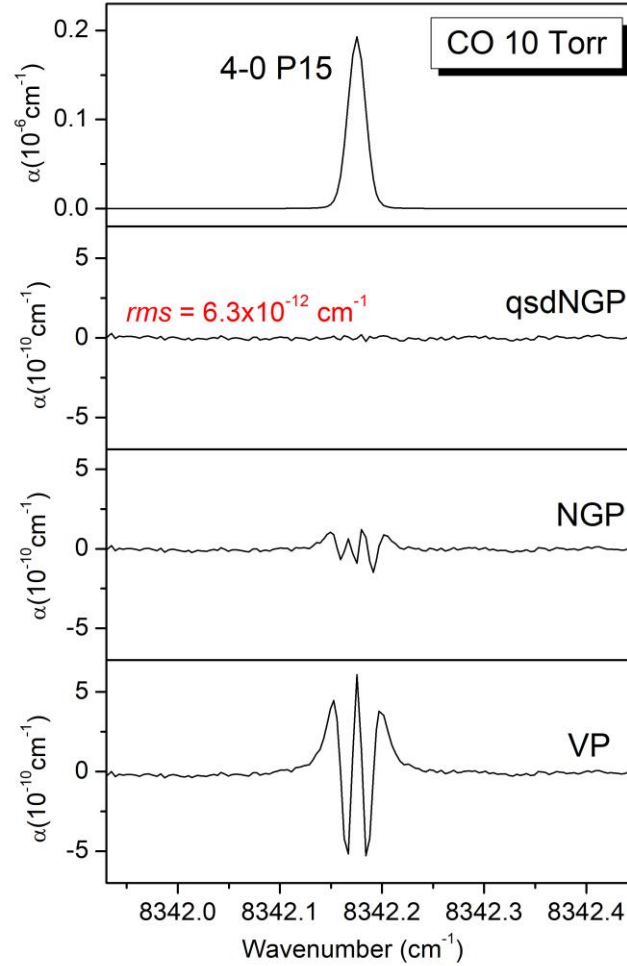


Fig. 3

Example of fit residuals of the P15 line of $^{12}\text{C}^{16}\text{O}$ at 10 Torr for different line profiles. The quadratic speed-dependent Nelkin-Ghatak profile (qsdNGP) allows for reproducing the observed line profile at the noise level ($\alpha_{min} \sim 6.3 \times 10^{-12} \text{ cm}^{-1}$).

qsdNG profile at 10 Torr

As illustrated in **Fig. 3**, the VP is not sufficient to reproduce the line profiles at 10 Torr and a more sophisticated line shape is required. The VP residuals (lower panel) exhibit a W shape which is the usual signature of collisional narrowing effects. Indeed, most of the residuals vanish by using a Nelkin-Ghatak profile (NGP) [15] which accounts for the collisional narrowing assuming a hard-collision model. Nevertheless, speed-dependent effects have to be taken into account to achieve a line shape reproduction at the experimental noise level ($\alpha_{min} \sim 6.3 \times 10^{-12} \text{ cm}^{-1}$). In addition to the Doppler width and pressure broadening parameters, the quadratic speed-dependent NGP (qsdNGP) [16,17] includes the Dicke narrowing parameter (v_{vc}) [18] and the quadratic speed dependence of the pressure width and shift. The Doppler width was fixed to its theoretical value calculated according to the temperature value measured at the time of the recording of the considered line and the

isotopologue mass. The line intensity was then converted to the 296 K reference temperature according to the lower state energy value and partition functions provided by the HITRAN2016 database [6].

The obtained list of the 227 transitions measured at 10 Torr is provided as Supplementary Material. Statistical error bars as obtained from the fitting program are given for the fitted VP and qsdNGP parameters while, when profile parameters had to be constrained to a default value, the adopted value is given without error bar. As illustrated on the overview plot of **Fig. 1**, the measured transitions summarized in **Table 1** belong to the 4-0 band of the $^{12}\text{C}^{16}\text{O}$, $^{13}\text{C}^{16}\text{O}$, $^{12}\text{C}^{18}\text{O}$ and $^{12}\text{C}^{17}\text{O}$ isotopologues and to the 5-1 hot band of $^{12}\text{C}^{16}\text{O}$. Measurements relative to the $^{12}\text{C}^{17}\text{O}$ isotopologue and to the 5-1 hot band are mostly new while for the other bands, high J transitions extend further previous studies.

Table 1

Summary of the transitions analyzed in the CRDS spectrum of carbon monoxide at 1.0 and 10.0 Torr between 8206 and 8465 cm^{-1} .

	$^{12}\text{C}^{16}\text{O}$ (4-0)	$^{13}\text{C}^{16}\text{O}$ (4-0)	$^{12}\text{C}^{18}\text{O}$ (4-0)	$^{12}\text{C}^{17}\text{O}$ (4-0)	$^{12}\text{C}^{16}\text{O}$ (5-1)
10.0 Torr	P34-R38	P6-R31	P3-R 28	P20-R34	P18-R22
1.0 Torr	P18-R35				

3. Line positions and self-pressure shifts

3.1. Zero-pressure positions and comparison with literature

In a first step, we compared the $^{12}\text{C}^{16}\text{O}$ line positions obtained at 1 Torr and 10 Torr, which were derived using a VP and a qsdNGP, respectively. In the upper panel of **Fig. 4**, the corresponding position differences are plotted *versus* m where $m = -J$ and $m = J + 1$ for P - and R - branch transitions, respectively. Clear deviations with smooth and symmetric m dependence are observed. In order to check that the position shifts are not related to the choice of the line profile, **Fig. 4** includes the differences between the positions at 10 Torr derived with a VP and a qsdNGP. These differences are very small (as expected from the symmetry of the VP residuals displayed on **Fig. 3**) and we conclude that the deviations between the positions at 1 and 10 Torr measure the self-induced line shifts.

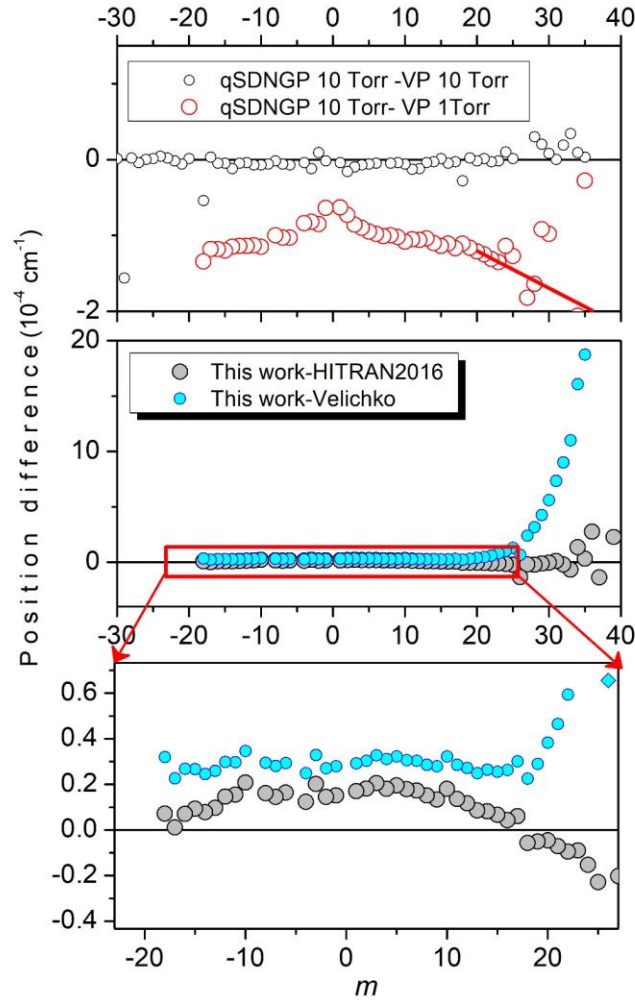


Fig. 4

Comparison of line positions of the 4-0 band of $^{12}\text{C}^{16}\text{O}$

(a) Differences of line centers retrieved using the qsdNGP and VP at 10 Torr (black circles) and between the centers values at 10 and 1 Torr (red circles). The red line corresponds to the empirical law used for $m > 26$ to extrapolate the 10 Torr line centers at zero-pressure,

(b) Differences of line centers extrapolated at zero-pressure (This work) and HITRAN2016 values and calculated values of Velichko et al. [19] (grey and blue symbols, respectively),

(c) Zoom of the middle panel by a factor of about 20 on the ordinate scale.

In order to compare to literature values, the zero-pressure positions were extrapolated from the positions at 1 and 10 Torr. For $m > 26$, estimated values of the pressure shifts were used as either the 1 Torr positions were missing or the 10 Torr positions were affected by line overlapping near the R branch head. On the two lowest panels of **Fig. 4**, the obtained zero-pressure line centers are compared to HITRAN2016 values and to values calculated by using the set of mass-independent Dunham parameters of the CO energy levels derived by Velichko, Mikhailenko and Tashkun (VMT hereafter) [19]. The HITRAN2016 positions originate from the work of Li et al. [5] which uses the potential energy function computed by Coxon and Hajigeorgiou [20] but they were corrected compared to the original values of Ref.

[5]. **Fig. 4** shows that the agreement between the CRDS and HITRAN values within 3×10^{-5} cm^{-1} up to $m=35$, much better than the 10^{-3} cm^{-1} uniform error bar attached to HITRAN values in our region. The deviations of the VMT values show a rapid increase for m larger than 20. No error bars are attached to VMT values but from the Supplementary Material of Ref. [19], it appears that VMT fit of the Dunham parameters used about 800 line positions involving the $\nu=4$ upper state of $^{12}\text{C}^{16}\text{O}$ available in the literature with accuracy ranges from 10^{-4} to 7×10^{-3} cm^{-1} , which is consistent with the observed deviations. For low m values, our zero-pressure positions are larger by about 2×10^{-5} and 3×10^{-5} cm^{-1} compared to HITRAN2016 and VMT, respectively. The observed symmetry of the m dependence indicates that ground state combination differences (GSCD) relations are fulfilled within an even better accuracy. The observed deviations are thus due to differences in the $\nu=4$ upper energy levels as confirmed hereafter by the quality of their empirical fit.

Table 2. Experimental and fitted values of the energy levels of the $\nu=4$ vibrational state of $^{12}\text{C}^{16}\text{O}$ derived from P and R -branch transitions.

J	P branch		R branch	
	Exp. (cm^{-1})	Exp.- Calc. (10^{-6} cm^{-1})	Exp. (cm^{-1})	Exp.- Calc. (10^{-6} cm^{-1})
0			8414.46930251	-1.71
1	8418.17432775	-2.68	8418.17433000	-0.43
2	8425.58423911	3.17	8425.58423651	0.57
3	8436.69872198	-4.99	8436.69872985	2.88
4			8451.51736401	1.16
5	8470.03955527	-0.77	8470.03955818	2.14
6	8492.26457024	-1.89	8492.26457256	0.43
7	8518.19152932	-0.56	8518.19153007	0.19
8			8547.81939994	-1.31
9	8581.14701697	5.57	8581.14700952	-1.88
10	8618.17303995	1.23	8618.17304173	3.01
11	8658.89601679	1.90	8658.89601487	-0.02
12	8703.31432347	-1.45	8703.31432415	-0.77
13	8751.42620521	-1.94	8751.42620469	-2.46
14	8803.22975415	0.79	8803.22975307	-0.29
15	8858.72290982	1.07	8858.72290811	-0.64
16	8917.90346895	-3.10	8917.90347215	0.10
17	8980.76910116	5.61	8980.76909872	3.17
18			9047.31727915	-6.03
19			9117.54539776	-2.78
20			9191.45065568	0.67
21			9269.03011550	-0.32
22			9350.28070406	-0.02
23			9435.19919714	2.22
24			9523.78222118	3.63
25			9616.02625183	-3.49
26			9711.92770657*	60.68
27			9811.48261058*	29.36
28			9914.68710698*	-0.80

Note

The asterisks mark energy values excluded from the fit.

The experimental values of the upper energy levels listed in **Table 2** were calculated by adding the Ritz ground state energy values provided by Tashkun et al. [21] and fitted using the standard expression:

$$G_v + B_v J(J+1) - D_v J^2(J+1)^2 + H_v J^4(J+1)^4 \quad (1)$$

where G_v is the vibrational term value, B_v is the rotational constant, D_v and H_v are the centrifugal distortion constants. The *rms* values of the fit for the $J < 26$ levels is $2.5 \times 10^{-6} \text{ cm}^{-1}$ ($\sim 75 \text{ kHz}$) (see (meas.-calc) values included in **Table 2**). The derived constants listed in **Table 3** are compared to our previous determination based on the CRDS measurements referenced to a FC of the 4-1 hot band in the 6300 cm^{-1} range [22]. A gain of one order of magnitude is achieved on the *rms* deviation and the statistical error bars are significantly reduced. The two determinations of the vibrational term differ by $5 \times 10^{-5} \text{ cm}^{-1}$.

Table 3. Spectroscopic constants of the $\nu=4$ vibrational state of $^{12}\text{C}^{16}\text{O}$ and comparison with the results of Ref. [22] based on transition frequencies of the 4-1 hot band.

$^{12}\text{C}^{16}\text{O } \nu=4$	G_v (cm^{-1})	B_v (cm^{-1})	D_v (10^{-6} cm^{-1})	H_v (10^{-12} cm^{-1})	N^a	Range ^b	Stdev (10^{-6} cm^{-1})
This work	8414.46930423(88)	1.85252534(16)	6.12069(7)	0.5352(78)	41	P(17)-R(25)	2.5
Ref. [22]	8414.469255(14)	1.85252593(27)	6.1234(13)	9.1(1.5)	34	P(19)-R(20)	35.4

Notes ^a Number of input data used for the fit
^b Range of the transitions used in the fit

The 4-0 absorption lines of the minor isotopologues were measured only at 10 Torr. The direct comparison of the 10 Torr positions to the HITRAN values at zero-pressure is presented in **Fig. 5**. Overall, a very good agreement is achieved. In particular, for the $^{13}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{18}\text{O}$ species, the agreement is significantly better than the 10^{-3} cm^{-1} error bar attached to the corresponding HITRAN position values. On the panels of **Fig. 5** relative to the minor isotopologues, the deviations of the main isotopologue are added as a reference. Indeed, the self-induced line shifts are believed to be isotopically independent and the deviations of the minor isotopologues are thus expected to be similar to those of $^{12}\text{C}^{16}\text{O}$, dominated by the self-induced line shift (see above). **Fig. 5** indicates that no significant information can be drawn for the $^{12}\text{C}^{18}\text{O}$ and $^{12}\text{C}^{17}\text{O}$ species but for $^{13}\text{C}^{16}\text{O}$, the m dependence of the deviations follows that of $^{12}\text{C}^{16}\text{O}$ with a systematic shift on the order of 10^{-4} cm^{-1} , probably due to an overestimation of the same amount of HITRAN2016 position values.

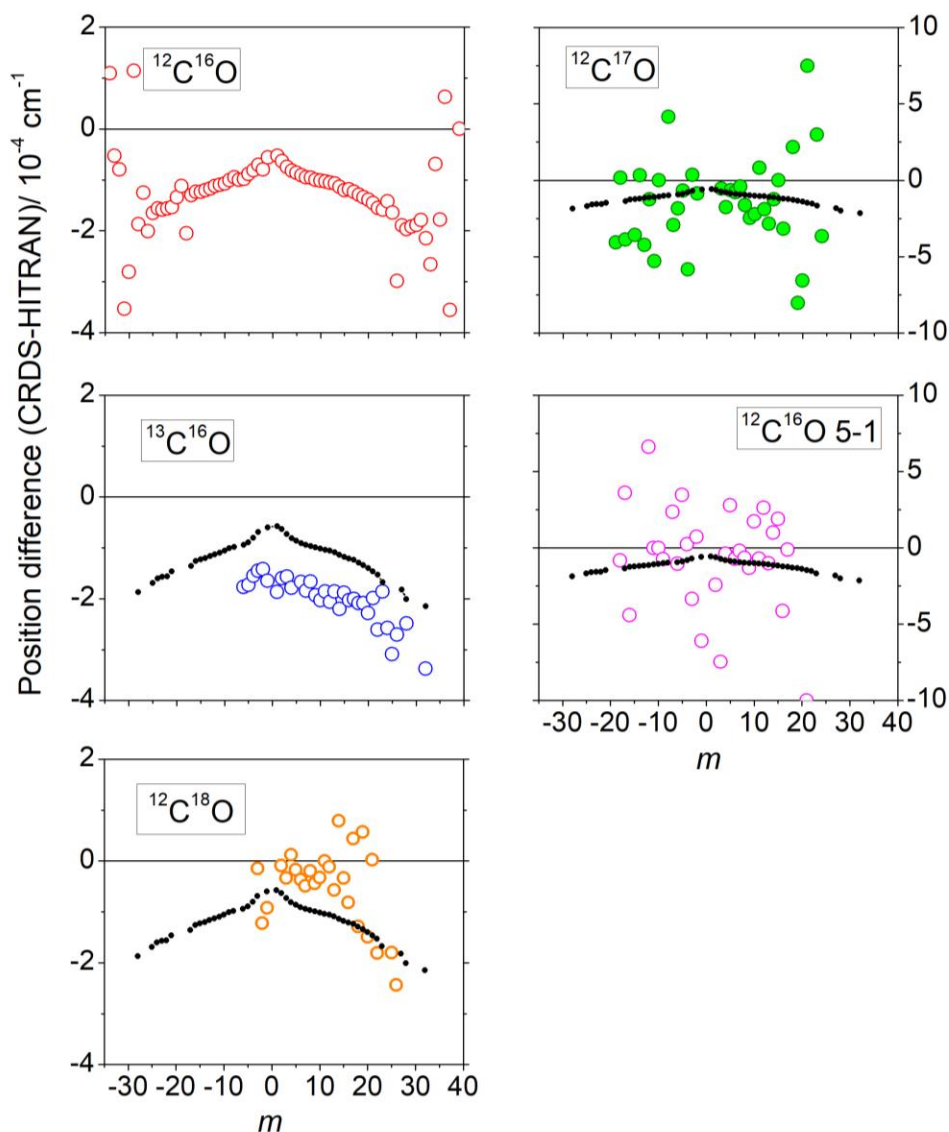


Fig. 5

Differences of line centers retrieved using the qsdNGP at 10 Torr and HITRAN2016 values for the various CO isotopologues. The self-induced line shift being mostly unchanged by isotopic substitution, $^{12}\text{C}^{16}\text{O}$ deviations which are due to the self-induced line shift at 10 Torr, are displayed as reference values on the other panels (see Text).

3..2. Self-pressure shifts

The 4-0 self-pressure shift coefficient ($\delta_{v,0}(m)$ in $\text{cm}^{-1}/\text{atm}$) were calculated from the line center at 1 and 10 Torr. The resulting values coefficient are compared to literature values relative to the 1-0 [23, 24], 2-0 [25] and 3-0 [26-29] bands of $^{12}\text{C}^{16}\text{O}$. All these previous determinations rely on FTS measurements which pressure values reaching up to 1 atm. The overview comparison presented in **Fig. 6** shows that the self-induced line shifts show similar m dependences with an amplitude increasing significantly with the vibrational excitation. The FTS measurement of the very small 1-0 self-pressure shifts was particularly challenging [23,24]. The 2-0 values from Zou et al. [25] seem to be robust as they confirm previous

measurements by Predoi-Cross et al. [30] and Bouanich et al. [31] within a few 10^{-4} $\text{cm}^{-1}/\text{atm}$ (see Fig. 14 of Ref. [25] and Fig. 6 of Ref. [24]). In the case of the 3-0 band, the most recent measurements by Sung et al. [29] and Jacquemart et al. [28] agree with each other but have amplitudes significantly larger than those of Picqué et al. [27] and Swann and Gilbert [26].

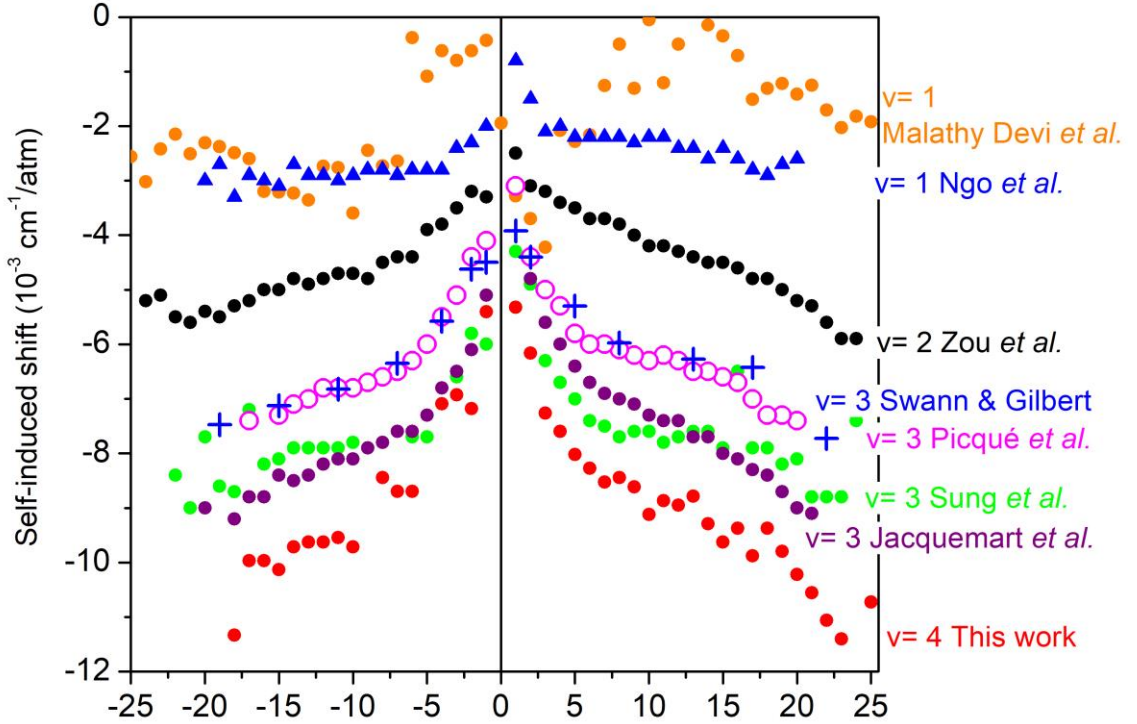


Fig. 6.

Vibrational dependence of the of $^{12}\text{C}^{16}\text{O}$ self-induced line shifts.

The present measurements of the 4-0 band are compared to literature data of the fundamental by Malathy Devi et al. [23] and Ngo et al. [24], of the 2-0 band by Zou et al. [25] and of the 3-0 band by Swann and Gilbert [26], Picqué et al. [27], Jacquemart et al. [28] and Sung et al. [29]

The empirical approach proposed by Hartmann for CO_2 [32] indicates that the self-shifts relative to the ν -0 band are roughly scaling with ν . Using the 2-0 values of Zou et al. [25] as references, we plotted in **Fig. 7** the scaled shifts $[2\delta_{\nu-0}(m)/\nu\delta_{2-0}(m)]$. The resulting ratios are close to unity for our 4-0 values and the 3-0 values of Refs. [26,27]. The largest deviations from unity (about 10%) are similar for these three studies and reflect the fact that the amplitude of the δ_{2-0} reference values of Zou et al. [2] show a mostly linear m dependence while the $\delta_{3-0}(m)$ and $\delta_{4-0}(m)$ dependences show an inflexion point around $m = \pm 8$. Note that the variation of $\delta_{\nu-0}$ with m is twice quicker for $\nu = 4$ than for $\nu = 2$.

Our low pressure 4-0 values show less consistency with the 3-0 values of Refs. [28,29] which show similar larger deviations. This observation already discussed in Sung et al. (see

Fig. 11 of Ref. [29]) remains largely unexplained. It could be related to (i) the treatment of the instrumental line shape (ILS) of the different FTS spectra (in particular the phase error), (ii) the pressure range of the analyzed spectra (FTS results were retrieved from relatively high pressure spectra, up to 1 atm), (iii) the choice of the line shape (we note that an asymmetric ILS was used in Ref. [27] to reproduce the measured line shape using a standard Voigt profile).

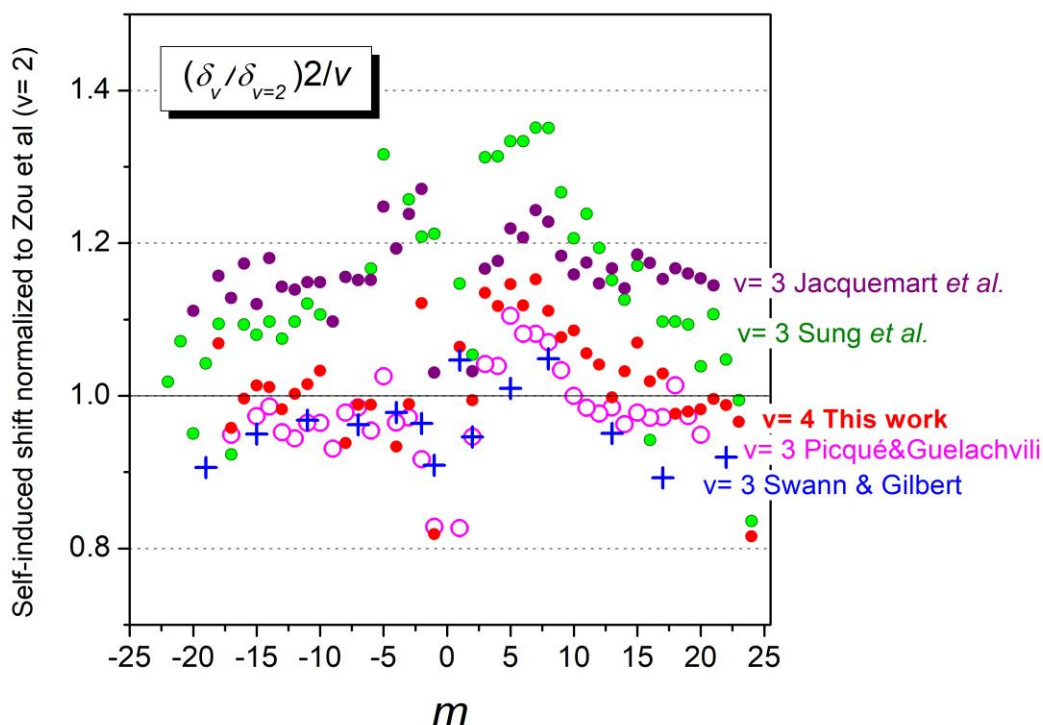


Fig. 7.

The $^{12}\text{C}^{16}\text{O}$ self-induced line shifts of the 3-0 and 4-0 bands normalized to the 2-0 values of Zou et al. [25]. The scaled shifts, $2\delta_{v-0}(m)/v\delta_{2-0}(m)$, where $v=3$ and 4 are plotted using literature sources: Swann and Gilbert [26], Picqué et al. [27], Jacquemart et al. [28] and Sung et al. [29] for 3-0 band and the present measurements for the 4-0 band.

4. Line intensities

4.1. Main isotopologue

In the same way as for line positions, we first examined the consistency of our intensity values retrieved from the 1 and 10 Torr spectra (**Fig. 8**). The intensity ratios between the $^{12}\text{C}^{16}\text{O}$ line intensities at 1 Torr and 10 Torr, derived using a VP and a qsdNGP, respectively show a systematic deviation limited to 0.25 % which is consistent with the 0.15% accuracy of the reading of the pressure values (temperature uncertainty, gas desorbing from the cell and the line profile could marginally contribute). The impact of the profile choice is examined from the qsdNGP/VP intensity ratios included in **Fig. 8**. A shift on the order of 0.5 % is noted, the VP intensities being systematically smaller. This is a usual bias of the VP (see e.g. Ref.

[8]). Note the small dispersion of the NGP10/VP10 and NGP10/VP1 ratios indicates that the observed deviations are due to systematic biases and that the experimental noise of the spectra is not the limiting factor.

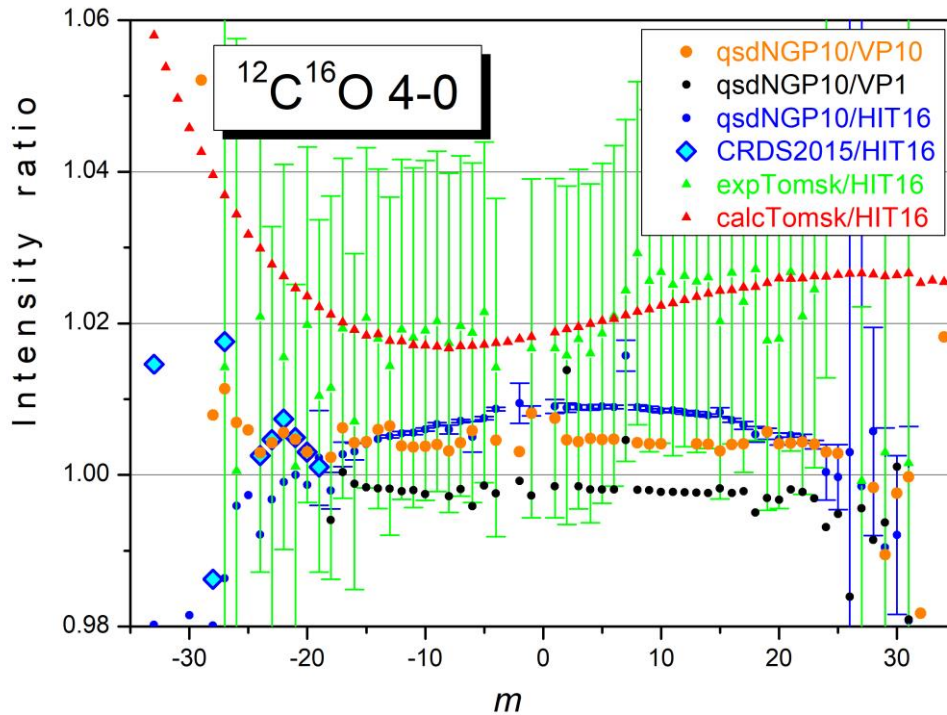


Fig. 8

Comparison of line intensities at 296 K of the 4-0 band of $^{12}\text{C}^{16}\text{O}$.

Black symbols correspond to the ratios of intensities retrieved using the recordings at 10 and 1 Torr. Orange symbols show the ratios of intensities obtained using the qsdNGP and VP at 10 Torr. The qsdNGP values at 10 Torr (blue circles), the CRDS values of Ref. [4] (blue diamonds), the FTS and calculated values of Ref. [7] (green and red triangles, respectively) are compared to HITRAN2016 values [6].

As reviewed in Refs. [4,5], previous intensity measurements of the 4-0 band are scarce. They include the work reported by Chackerian and Valero [2] who determined the transition moment and Herman-Wallis factors, from a fit of line intensities up to $J=24$. These parameters were used to calculate previous versions of the HITRAN database. As mentioned above, the HITRAN2016 version uses intensity values calculated by Li et al. [5] from a piecewise dipole moment function (DMF) and wavefunctions calculated from an experimentally-determined potential energy function from Coxon and Hajigeorgiou [20]. A selection of accurate intensity measurements, were used to adjust the semi-empirical DMF [5]. For the 4-0 band, our CRDS intensity values of the P(J) lines ($J=19-34$) [4] were used in the fit and were reproduced with a dispersion at the 1% level. As a result, the HITRAN2016 intensities of 4-0 band of $^{12}\text{C}^{16}\text{O}$ are given with uncertainties of 1 or 2% for J values below and above 30,

respectively. The satisfactory agreement with HITRAN values is illustrated by the qsdNGP10/HITRAN2016 intensity ratios included in **Fig. 8**: our qsdNGP10 values are slightly higher than HITRAN values with deviations, mostly symmetric in m , ranging between 0 and 0.9 % for low and high J values, respectively.

As mentioned in the introduction, very recently, new FTS recordings of CO were performed in Tomsk with a km absorption pathlength and dedicated to the measurements of the 4-0 line intensities [7]. Line intensities were reported with uncertainties between 2 and 3% for the strongest lines, from spectra recorded at 146 and 374 Torr analyzed with a quadratic seed-dependent Voigt profile (qsdVP). The overview of Tomsk observations is included in **Fig. 1**. The 4-0 effective dipole moment parameters of $^{12}\text{C}^{16}\text{O}$ were derived from a fit of the measured intensities. On average, Tomsk experimental and calculated intensities are larger than HITRAN values by about 2% (see **Fig. 8**) which is within the HITRAN2016 and Tomsk combined error bars. The agreement with our NGP10 values is even better at the 1% level for low J values (larger deviations are noted $P(J)$ lines with high J values). Finally let us note that we had some doubt about the real purity of the CO tank used for the present recordings (the same as used in the CRDS recording of Ref. [4], five years ago). The fact that Tomsk values are higher than our values seem to rule out a significant contamination of the sample used in the present recordings.

In conclusion, the reported qsdNGP10 intensities show an overall good agreement with literature values and are believed to be the most accurate values for the considered 4-0 band of $^{12}\text{C}^{16}\text{O}$.

4.2. Minor isotopologues

In spite of their small intensity values (less than 10^{-27} cm/molecule, in natural abundance), interesting information can be obtained for the 4-0 line intensities of the $^{13}\text{C}^{16}\text{O}$, $^{12}\text{C}^{18}\text{O}$ and $^{12}\text{C}^{17}\text{O}$ minor isotopologues. The overview comparison to HITRAN2016 values is presented in **Fig. 9**. The HITRAN2016 intensity values are those computed by Li et al. [5] using the DMF derived for the $^{12}\text{C}^{16}\text{O}$ species.

In the case of the $^{12}\text{C}^{18}\text{O}$ species, the FTS values from Tomsk [7], our CRDS values (both retrieved from natural CO spectra) and HITRAN2016 values show a very good agreement while Tomsk calculated values show a systematic overestimation by about 6%. Tomsk calculated intensity values were computed by applying isotopic substitution equations to the effective dipole moment parameters of the principal isotopologue (see Ref. [33]). In the case of $^{12}\text{C}^{17}\text{O}$, no FTS measurements were reported and Tomsk calculated intensities are

larger than HITRAN2016 values by about 4%, the agreement between the CRDS and HITRAN values being within the experimental error bars.

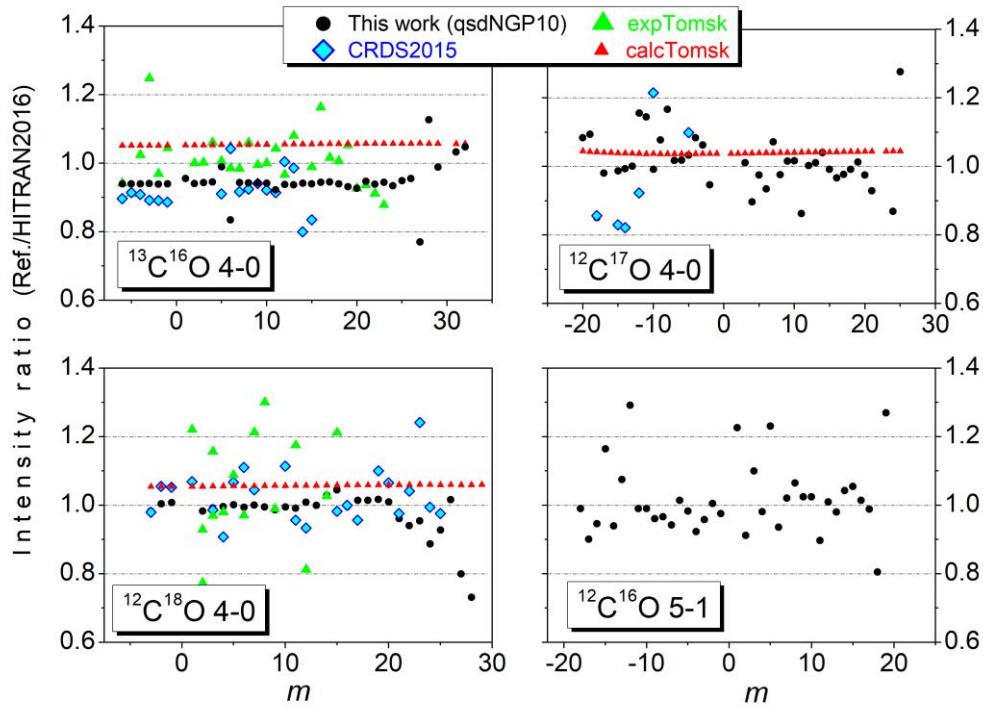


Fig. 9.

Comparison to HITRAN2016 of the line intensities of the 4-0 band of $^{13}\text{C}^{16}\text{O}$, $^{12}\text{C}^{18}\text{O}$ and $^{12}\text{C}^{17}\text{O}$ and of the 5-1 hot band of $^{12}\text{C}^{16}\text{O}$. The plots include our results (qsdNGP values at 10 Torr – black), the CRDS values of Ref. [4] (blue diamonds), the FTS and calculated values of Ref. [7] (green and red triangles, respectively).

Finally, a clear systematic 6% underestimation is noted for our $^{13}\text{C}^{16}\text{O}$ intensity values compared to both HITRAN2016 and Tomsk measurements. A similar deviation ($\sim 8\%$) with no m dependence was reported and discussed in our previous CRDS measurements [4]. (Note that similar results were reported by Wójtewicz et al. from their $^{13}\text{C}^{16}\text{O}$ intensity measurement in the 3-0 band with natural carbon monoxide [35]). Both a depletion of $^{13}\text{C}^{16}\text{O}$ in the used CO samples and a possible breakdown of the Born-Oppenheimer approximation in the intensity calculations by Li et al. [5] were proposed in Ref. [4] as tentative explanations. The good agreement between HITRAN2016 intensities and the very recent Tomsk FTS values favors the first option i.e. that the $^{13}\text{C}^{16}\text{O}$ relative concentration in our sample (the same as used in the 2015 [4]) is about 6% lower than HITRAN abundance value (1.10 %). Recordings performed with a CO sample with accurately known enrichment in ^{13}C are nevertheless suitable to confirm this explanation. Again, Tomsk calculated intensities of $^{13}\text{C}^{16}\text{O}$ appear to be slightly overestimated compared to HITRAN values, suggesting a possible small bias in the isotopic substitution equations derived in Ref. [33].

Finally, let us note that the very small intensities of the measured 5-1 hot band ($< 8 \times 10^{-30}$ cm/molecule) show a good agreement with HITRAN values (see **Fig. 9**).

5. Line profile parameters

Our qsdNGP values of the broadening coefficient, γ_0 , are compared to HITRAN recommended values and to Tomsk qsdVP values in **Fig. 10**. The HITRAN2016 database uses as source the results of the study of the 2-0 band reported by Malathy Devi et al. [35]. These authors performed a simultaneous treatment of 28 spectra recorded at pressures up to 600 Torr using speed-dependent line shapes with line mixing and Dicke narrowing. In spite of differences of profiles, our values and Tomsk values show a very good agreement with HITRAN values. The Lorentzian widths obtained from the VP fits are included in **Fig. 10**. As usual (see e.g. Ref. [8]), the obtained VP broadening coefficients are significantly smaller than those obtained with more advanced line profiles.

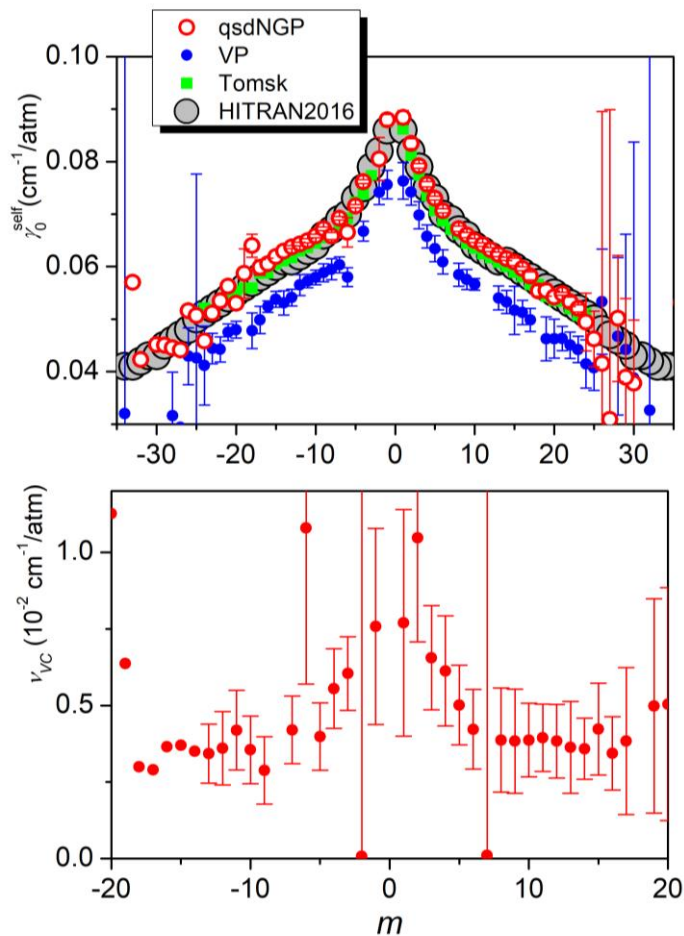


Fig. 10.

Variation of the pressure broadening coefficient and velocity change frequency parameter *versus* m (upper and lower panel, respectively). The upper panels include our results using a qsdNGP and a VP, HITRAN values and the FTS values of Ref. [7].

Although determined with a limited accuracy, the velocity change frequency parameter (or Dicke narrowing coefficient), w_C , shows a clear rotational dependence, mostly symmetric in the *P*- and *R*-branches. The overall dependence is similar to what reported by Wilzewski et al. in the ν_3 band of CO₂ from FTS spectra with pressure values up 1 atm [36]. Nevertheless, in the case of the low pressure recordings considered here, as underlined by Wójtcwicz et al. [34], it is very difficult to decorrelate Dicke narrowing and the speed dependence of collisional broadening. In addition, the observed *m*-dependence may be related to deviations of the speed dependence from the assumed quadratic dependence.

6. Conclusion

The absorption spectrum of carbon monoxide in natural isotopic abundance has been recorded between 8206 and 8465 cm⁻¹ by cavity ring down spectroscopy (CRDS) referenced to a frequency comb at two low pressure values of 1 and 10 Torr. An extensive set of 227 lines belonging to the 4-0 bands of the ¹²C¹⁶O, ¹³C¹⁶O, ¹²C¹⁸O and ¹²C¹⁷O and the 5-1 hot band of ¹²C¹⁶O was analyzed using a speed dependent Nelkin-Ghatak line shape. Line positions reported with an accuracy on the order of 100 kHz allowed for the determination of the ¹²C¹⁶O self-induced line shifts which have an amplitude limited to about 10⁻⁴ cm⁻¹ (3 MHz) at the recording pressure of 10 Torr. Considering previous literature values available for the 1-0, 2-0 and 3-0 bands and our 4-0 results, the proportionality of the self-induced line shifts with the upper state vibrational quantum number was discussed.

The line centers extrapolated at zero-pressure deviate by no more than 2×10⁻⁵ cm⁻¹ compared to HITRAN values. The experimental values of the ¹²C¹⁶O $\nu=4$ energy levels $J < 26$ were obtained by adding empirically determined values of the ground state levels [21] and could be reproduced with a standard deviation of 2.5×10⁻⁶ cm⁻¹ (75 kHz).

The reported intensities of the ¹²C¹⁶O lines improve the accuracy of previous measurements and show an overall good agreement with literature values. In particular, an agreement within 1% is achieved compared to HITRAN intensity values.

As concerned minor isotopologues, a systematic overestimation on the order of 10⁻⁴ cm⁻¹ was estimated for ¹³C¹⁶O line positions compared to HITRAN values. Systematic deviations were also noted for the intensities: our ¹³C¹⁶O intensity values relying on HITRAN isotopic abundances are about 6% below HITRAN intensity values and calculations based on isotopic substitution equations applied to effective dipole moment parameters of the principal isotopologue [33] leads to intensities larger than HITRAN values for ¹³C¹⁶O, ¹²C¹⁸O and

$^{12}\text{C}^{17}\text{O}$. New measurements with isotopically enriched samples with accurately known isotopic abundances are suitable to address these issues.

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Fig. 1

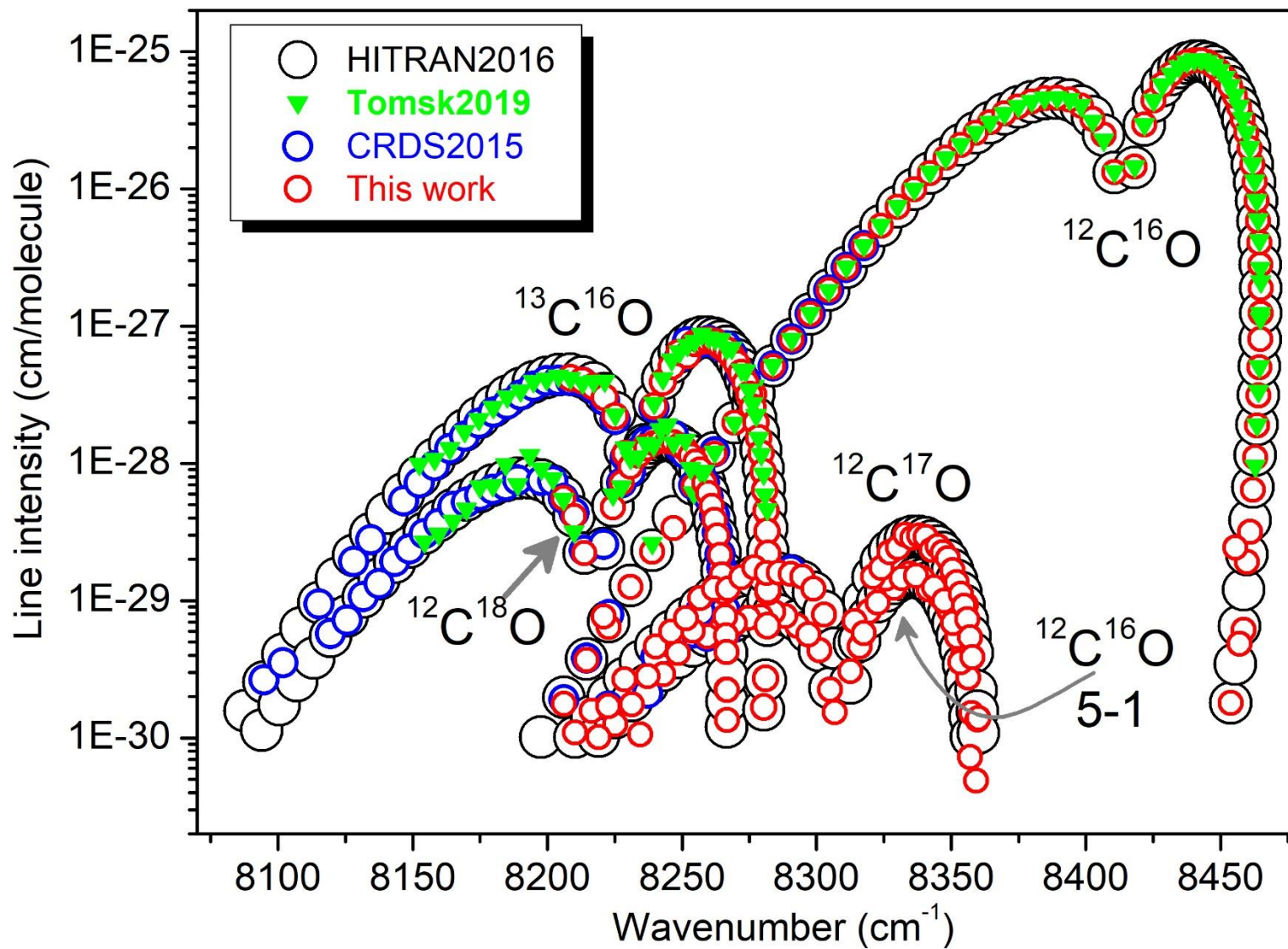


Fig. 2

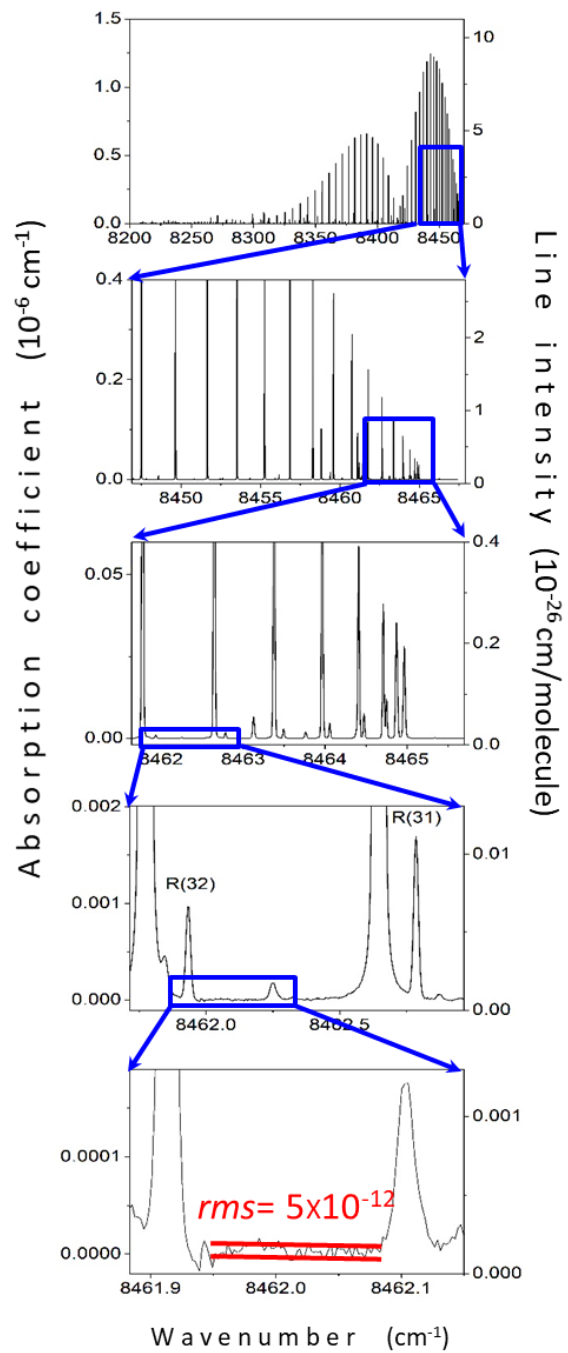


Fig. 3

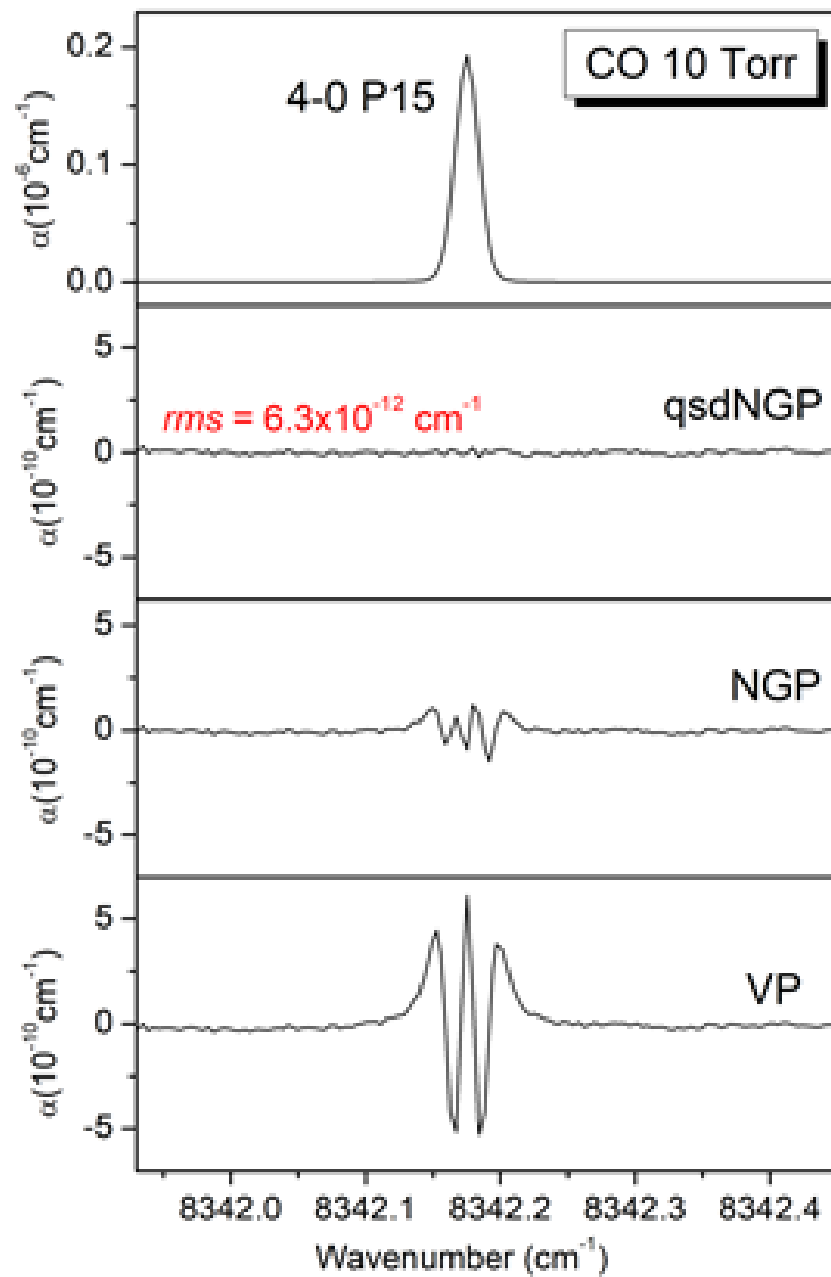


Fig. 4

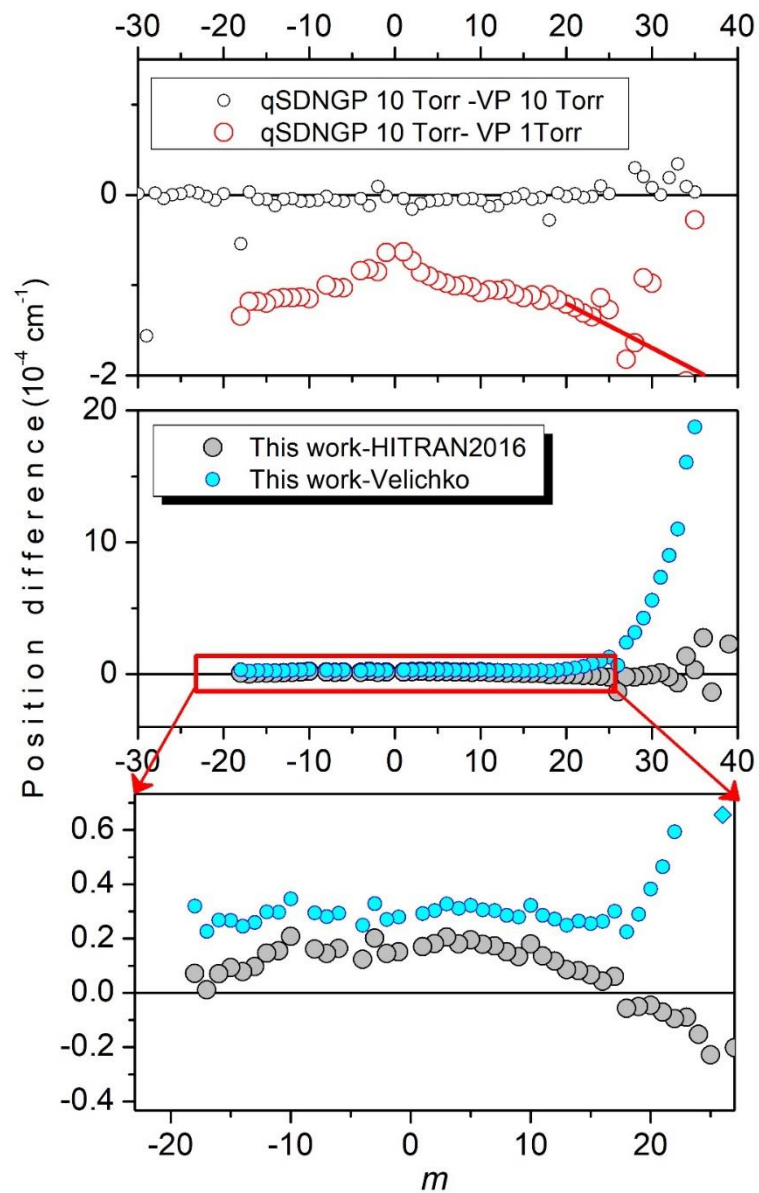


Fig. 5

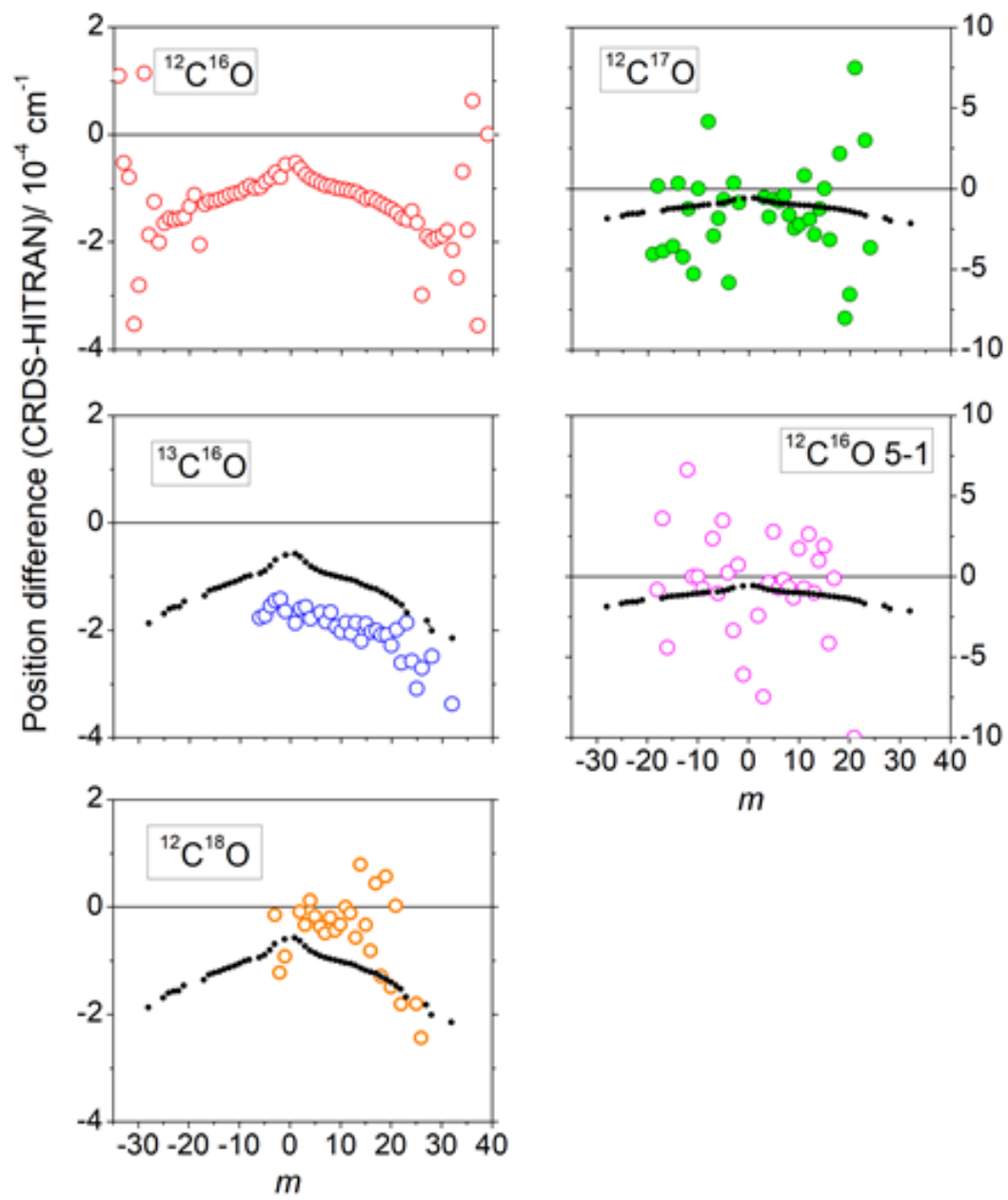


Fig. 6

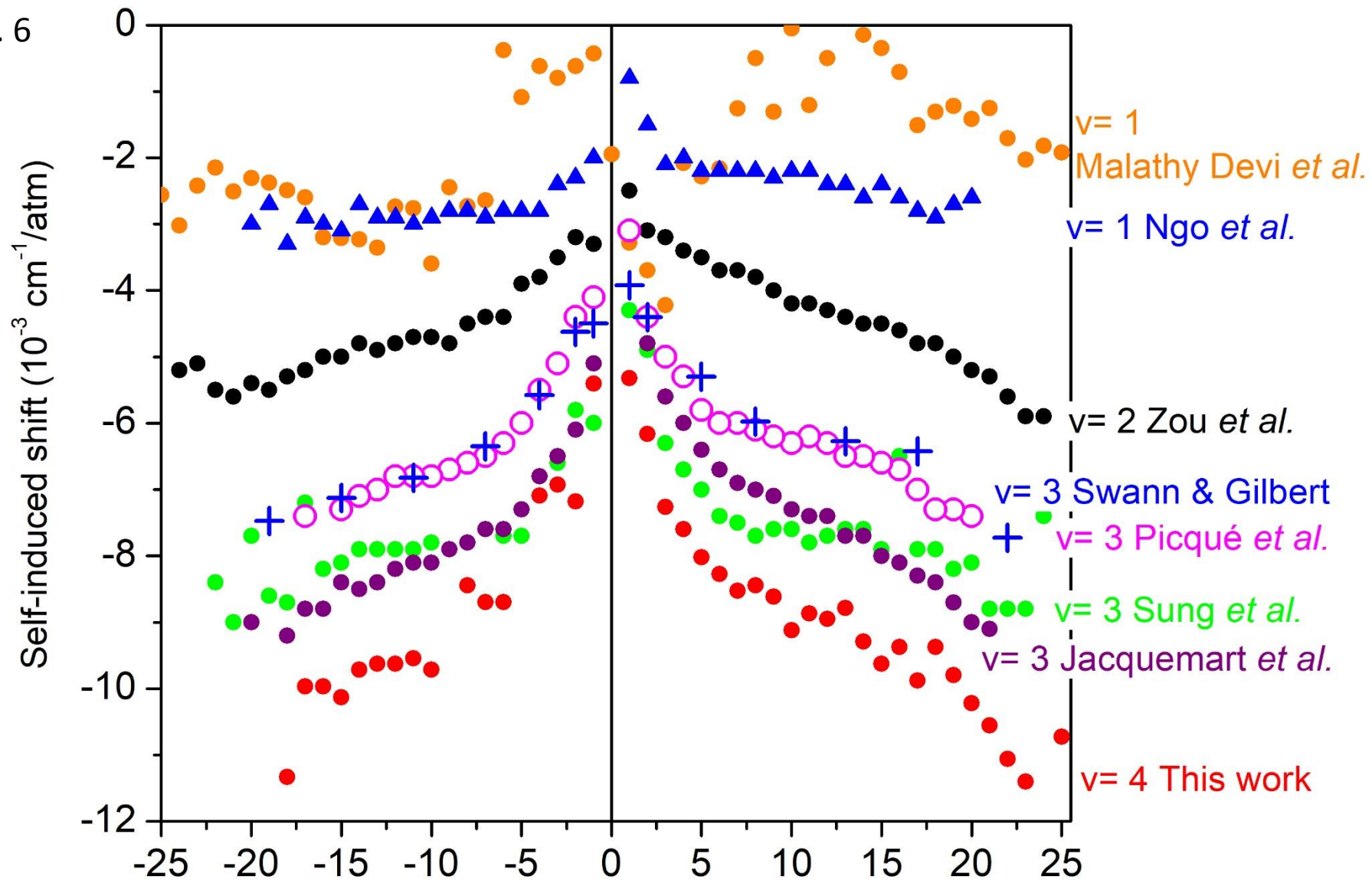


Fig. 7

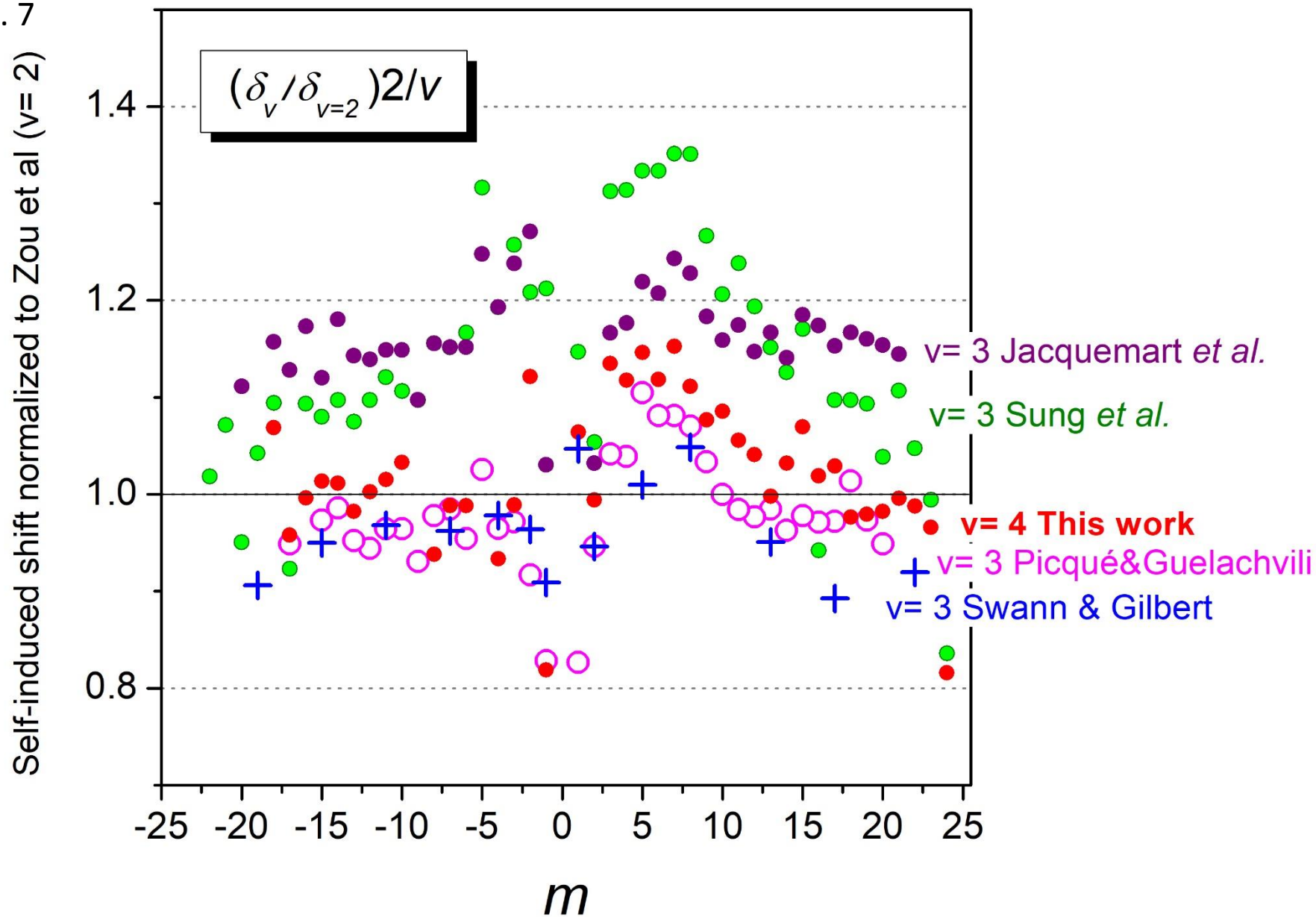


Fig. 8

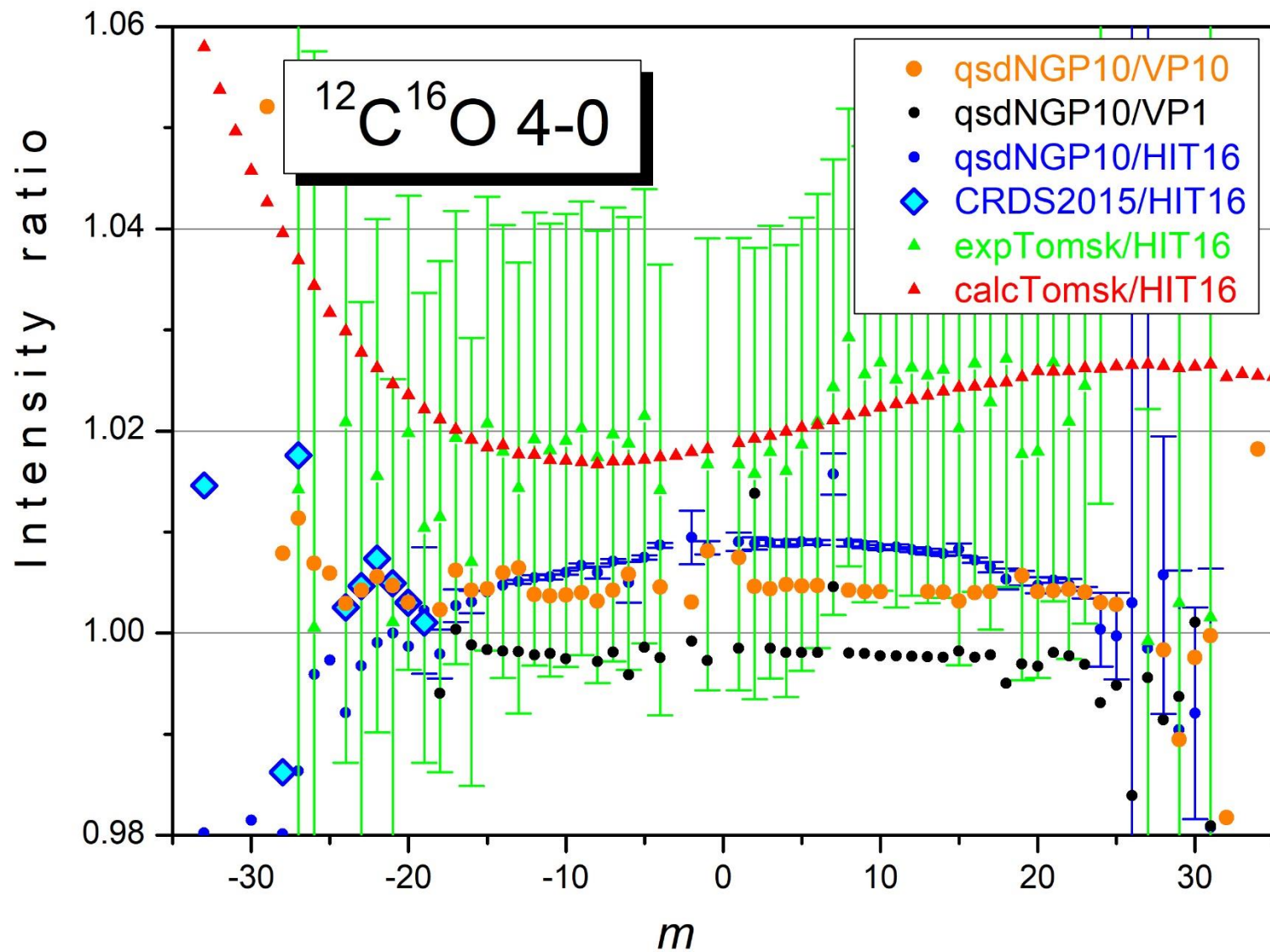


Fig. 9

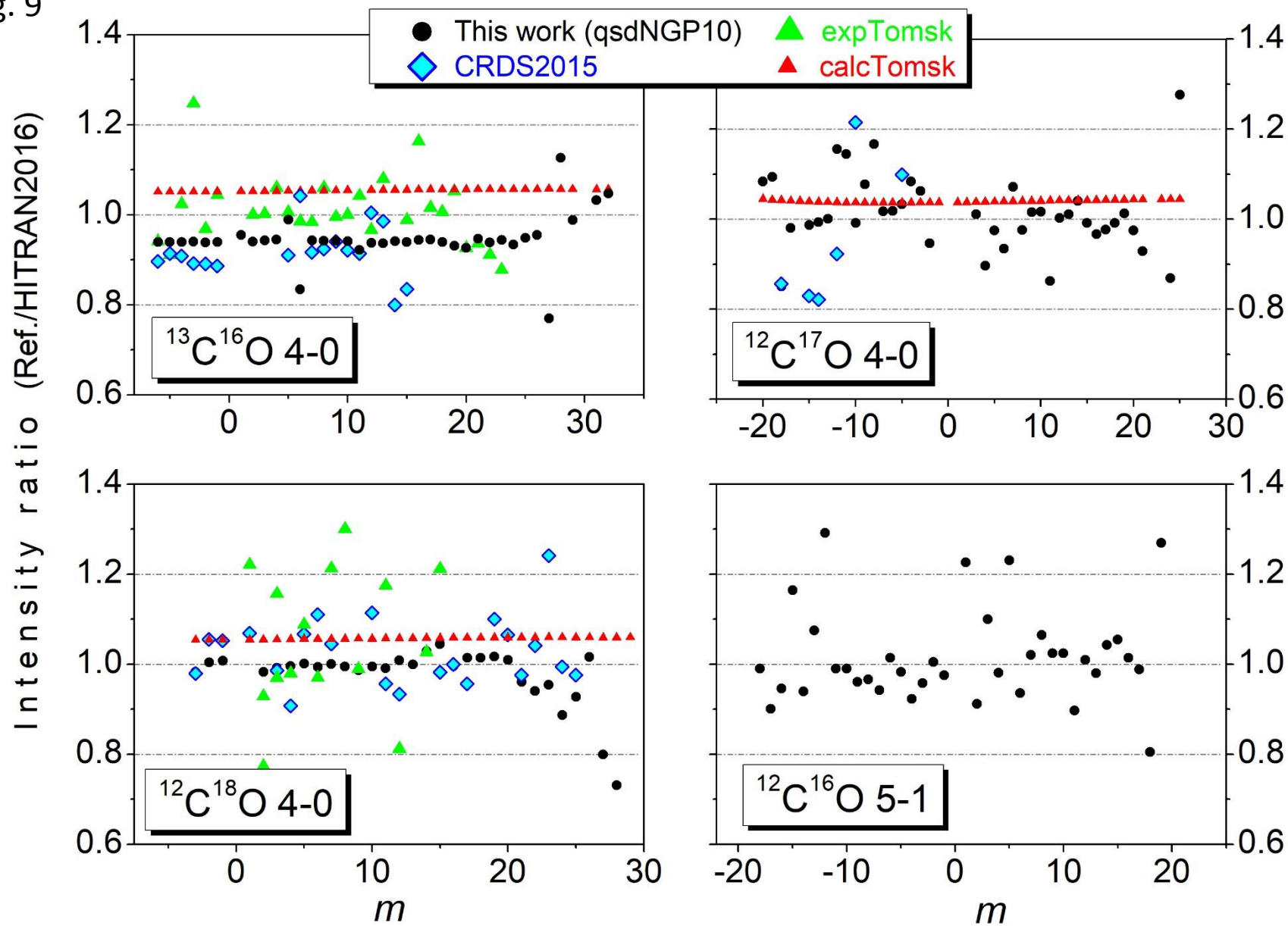
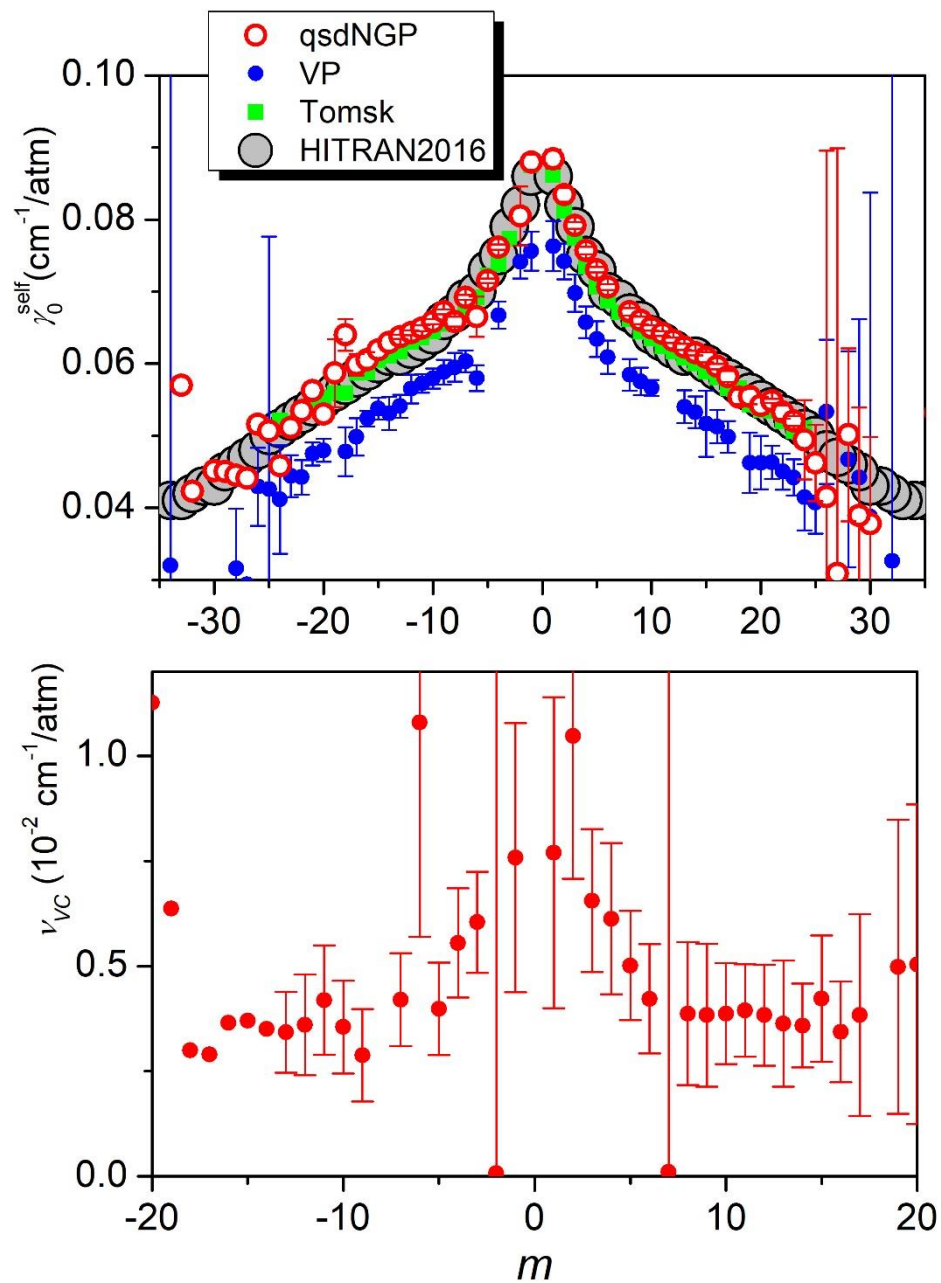


Fig. 10



The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

B. Bordet: Data analysis, **S. Kassi:** spectra recordings, **A. Campargue:** Data analysis,
Writing the paper



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