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Fourier Transform Spectroscopy of two trace gases namely Methane and Carbon monoxide for planetary and atmospheric research application

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Abstract. Two atmospheric trace gases, namely methane and carbon monoxide have been considered in this study. Fourier transform absorption spectra of the 2–0 band of $^{12}$C$^{16}$O mixed with CO$_2$ have been recorded at total pressures from 156 to 1212 hPa and at 4 different temperatures between 240 K and 283 K. CO$_2$ pressure-induced line broadening and line shift coefficients, and the associated temperature dependence have been measured in an multi-spectrum non-linear least squares analysis using Voigt profiles with an asymmetric profile due to line mixing. The measured CO$_2$-broadening and CO$_2$-shift parameters were compared with theoretical values, calculated by collaborators. In addition, the CO$_2$-broadening and shift coefficients have been calculated for individual temperatures using the Exponential Power Gap (EPG) semi-empirical method. We also discussed the retrieved line shape parameters for Methane transitions in the spectral range known as the Methane Octad. We used high resolution spectra of pure methane and of dilute mixtures of methane in dry air, recorded with high signal to noise ratio at temperatures between 148 K and room temperature using the Bruker IFS 125 HR Fourier transform spectrometer (FTS) at the Jet Propulsion Laboratory, Pasadena, California. Theoretical calculations for line parameters have been performed and the results are compared with the previously published values and with the line parameters available in the GEISA2015 [1] and HITRAN2012 [2] databases.

1. Introduction

The success of spectroscopic planetary atmospheric remote sensing studies often relies on having highly accurate sets of laboratory data for line parameters of the majority of atmospheric trace constituents, to interpret them. Advances in remote sensing instrumentation are pushing the requirements for accuracy of spectroscopic line parameters included in databases such as GEISA [1] or HITRAN2012 [2]. Today’s state of the art line shape models go beyond the Voigt model, and include subtle effects such as line mixing, correlation between collisional narrowing, the velocities of molecules, the ro-vibrational relaxation mechanisms [3-7].

Besides being an active greenhouse gas present in the terrestrial atmosphere, carbon monoxide is also present as trace constituent in the atmosphere of Venus [8]. Understanding its sources, sinks and
distribution in the Venusian atmosphere can help scientists better understand the dynamics taking place in the mesosphere and the lower thermosphere (from 70 to 120 km). The Venusian atmosphere is probed by the “Solar Occultation in the InfraRed” (SOIR) instrument on board of the ESA “Venus Express” spacecraft [9]. Precise spectroscopic line shape parameters of this species perturbed by CO₂ are required to retrieve CO concentrations from SOIR or NOMAD spectra on the first overtone (2–0) band of CO, located near 4260 cm⁻¹ (2.3 μm). Our study, published in Ref. [10] is intended to extend the knowledge for line parameters of CO broadened by CO₂ over a range of temperatures.

For this propose, we have used number of 21 spectra of CO/CO₂ mixtures recorded using Fourier transform spectrometer at University of Brussels. Different line shape models have been used to reproduce the observed spectra: The Voigt profile (VP) [11], the Rautian profile (RP) [12] to account for the Dicke narrowing effects [13], and the quadratic Speed Dependent Voigt profile (qSDV) [14,15] to account for the dependence of line shape parameters on the relative speed of the molecules. CO₂ pressure induced broadening and shift coefficients of the lines of 12C¹⁶O have been determined, together with the temperature dependence of the CO₂ broadening parameters. We were able to retrieve the line mixing (LM) coefficients [16], as well. The retrieved parameters were then compared with CO₂ broadening and shift coefficients calculated using a semi-empirical method.

Due to the importance of methane as a trace atmospheric gas and a greenhouse gas and its contributions to the terrestrial Carbon Cycle, we have carried out a precise line shape study to obtain the self- and air half-width coefficients, self- and air-shift coefficients and the off-diagonal relaxation matrix element coefficients for methane transitions in the spectral range known among spectroscopists as the "methane octad". In addition, the temperature dependences of these coefficients have been measured. The results have been published in Ref. [17].

2. Experimental details

The experimental sessions for the two experiments presented here were carried out in different locations. The high resolution absorption spectra of the 2–0 band of carbon monoxide mixed with carbon dioxide at total pressures ranging from 156 to 1212 hPa and at 4 different temperatures between about 240 K and 283 K have been recorded using a Bruker IFS 125 HR Fourier transform spectrometer. The instrument was fitted with a Tungsten source, a CaF₂ beam-splitter, a band-pass filter limiting the transmission to the 3980–5100 cm⁻¹ range, and an InSb detector cryogenically cooled to 77 K. The gas mixtures were prepared in the 19.7(2) cm long double jacketed stainless steel cell, closed by CaF₂ windows and located inside the evacuated spectrometer.

The 14 high signal to noise ratio spectra of pure Methane and of dilute mixtures of Methane in dry air with 0.005 cm⁻¹ resolution, have been recorded at temperatures from 148 K to room temperature using the Bruker IFS 125 HR Fourier transform spectrometer (FTS) at the Jet Propulsion Laboratory, Pasadena, California. The coolable absorption cell used in this experiment has an optical path of 20.38 cm and has been built to fit inside the sample compartment of the Bruker FTS [18] and [19]. The spectrometer setup consisted of a Globar source, a CaF₂ beam-splitter and a liquid-N₂ cooled InSb detector. Of the 14 spectra, 8 spectra were recorded with pure methane samples and 6 of the spectra were obtained with dilute mixtures of ¹²CH₃ in dry air.

3. Analysis of both set of the spectra and results

The analysis of both sets of spectra was done using the multispectrum nonlinear least-squares curve fitting technique. The CO₂ broadening and shift coefficients of the P(22) to R(21) lines and their temperature dependences and first-order line mixing coefficients, have been retrieved. For methane we have focused on the 4300–4500 cm⁻¹ spectral region for the range of terrestrial atmospheric temperatures. The off-diagonal relaxation matrix element coefficients and quadratic speed dependence were taken into account for several transitions.

The following expressions were used to determine the half-width and shift coefficients:

\[ b_L = \frac{P_{tot}}{T_0} \left( b_L^{(foreign)} (1 - \chi) \left( \frac{T_0}{T} \right)^{n_1} + b_L^{(self)} \chi \left( \frac{T_0}{T} \right)^{n_2} \right) \]
\[ \Delta \nu = P_{\text{tot}} \left[ d^{\text{foreign}}(1 - \chi) + d^{\text{self}}(s) \chi \right] \]

where \( P_{\text{tot}} \) is the total sample pressure, \( T_0 = 296 \text{ K} \), \( \chi \) is the mole fraction, and \( b_l \) is the Lorentz half-width at pressure \( P \) and temperature \( T \), \( b_0^l \) is the Lorentz half-width coefficient of the line at the reference pressure \( P_0 \) and temperature \( T_0 \), \( \delta^0 \) represent the shift coefficient (in \( \text{cm}^{-1} \text{atm}^{-1} \)). \( n_1 \) and \( n_2 \) are the temperature dependence exponents of the foreign and self broadening coefficients, respectively. \( \delta \) quantifies the temperature dependence of the shift coefficients.

Figure 1 presents the sample fit obtained for CO spectra corresponding to the high total pressure achieved in this work. The residuals show that, at high pressure, the qSDV line shape model, with or without first-order line mixing, best reproduces the observed line profiles.

3.1 Sample of results obtained for Carbon monoxide

We measured the CO\(_2\)-pressure broadening and CO\(_2\)-pressure shift coefficients. The temperature dependence of the CO\(_2\) broadening coefficients measured in this work using the 3 line shape models are presented in figure 2. Interestingly, the present measurements exhibit an intensity dependence, similar for the 3 line shape models. The results reported by Nakazawa and Tanaka [20] for the R branch of the fundamental band do exhibit a minimum for the same \( m \) value as in the present work, but strongly disagree at higher \( J \). These comparisons may suggest that the temperature dependence of the CO\(_2\) broadening coefficients are the same for the fundamental and first overtone bands.
Figure 2. The temperature dependence exponent of CO₂ broadening coefficients for the 2–0 band of $^{12}$C$^{16}$O measured in this work with the VP (1), RP (2) and qSDV (3) line shape models. The error bars associated with these measurements represent the uncertainty of measurement, estimated by the least squares fitting algorithm. Measurements reported for the fundamental band of $^{12}$C$^{16}$O by Nakazawa and Tanaka using the Lorentz profile [20] (4) and by Sung and Varanasi [21] using the VP (5), and values calculated using a semi-classical method are also shown. (Figure taken from [10].)

Figure 3. Comparison of CO₂ broadening coefficients measured at 2 temperatures in the 2–0 band of $^{12}$C$^{16}$O with semi-classical calculations. (Figure taken from [10].)

Theoretical calculations were also performed to obtain line CO₂-broadening and CO₂-shift coefficients [22]. To allow comparisons with the theoretical calculations, the CO₂ broadening coefficients were also measured separately at each of the 4 temperatures, using the qSDV line shape model, including first-order line mixing. The retrieved parameters were then compared with CO₂ broadening (figure 3) coefficients calculated using a semiempirical method. The semi-classical method used is based on the impact theory of broadening and includes correction factors, the parameters of which being determined by fitting the calculated broadening or shift coefficients to the experimental data.

The narrowing coefficients measured using the RP line shape model and the dynamic friction coefficient also deduced. At the lowest (240.5 K) and highest (283.4 K) temperatures the dynamic friction coefficient obtained to be 0.0368 and 0.0320 cm⁻¹atm⁻¹, respectively. The measured narrowing coefficients indicated that the narrowing effect induced by velocity changing collisions decreases as the molecule rotates faster. However, except at high J, the measured narrowing coefficients are larger than the theoretical value, which indicates that the broadening coefficients may be affected by speed dependence [23] and that the Rautian line shape model with line mixing does not reproduce our spectra.
completely. The speed dependence of the CO$_2$-broadening coefficients and the first-order line mixing coefficients obtained in this work using the qSDV profile. The first-order line mixing coefficients determined for the 3 line shape models are presented in figure 4. Even though the obtained values are small, taking the line mixing effects into account was important as they affect the measured CO$_2$ shift coefficients.

![Figure 4. Weak line mixing coefficients in the 2–0 band of $^{12}$C$^{16}$O, measured and calculated using the EPG law at the same temperatures. (Figure taken from [10].)](image)

3.2 Sample of obtained results for Methane study
For methane, short spectral intervals (2-5 cm$^{-1}$) were fitted at a time using the multi-spectrum analysis program of Benner et al. [24]. We added the spectra one by one starting from the ones recorded at the lowest pressure until all 14 spectra were included in the fits. We retrieved line positions and intensities, the Lorentz CH$_4$–CH$_4$ and CH$_4$–air-half-width and shift coefficients, and their temperature dependences. The initial value for speed dependence parameter was fixed to 0.08. Our goal was to minimize the difference between the observed spectra and the simulated spectra by adjusting different line parameters. The background also was fitted to a first order Chebyshev polynomial and there was no need to add channel spectra.

The line positions and intensities have been measured and compared to our theoretically calculated values and to the values in the databases [1,2]. The comparisons of positions and intensities suggest that our results agree well with these datasets. For line positions, the agreement is in the order of 10$^{-4}$ cm$^{-1}$. For the intensities, we have obtained the percentage difference and it is less than 4% for most of the cases compared to HITRAN2012 [2] and GEISA [1] databases.

The temperature dependences of CH$_4$–CH$_4$ and CH$_4$–air half-width coefficients in the 4300–4500 cm$^{-1}$ region are plotted in Figure 5 as a function of $|m|$. We used the power law model from Eq. (1) to obtain the temperature exponents of CH$_4$–CH$_4$ and CH$_4$–air half-width coefficients. In the top panel, the temperature exponents for CH$_4$–CH$_4$ half-width coefficients are shown and in the bottom panel are shown the results of temperature dependence of air-width coefficients.
Figure 5. Temperature dependence exponents of CH$_4$–CH$_4$ and CH$_4$–air half-width coefficients in the $\nu_3+\nu_4$ band of methane. (Figure taken from [17].)

The Voigt profile was not able to fit the spectra within the experimental noise levels at higher pressures. This was also the case where the selected interval included pairs of transitions involved in collisional line mixing. To remedy the fault, line mixing for both CH$_4$–CH$_4$ and CH$_4$–air half-width coefficients was modeled using the off-diagonal relaxation matrix formalism [25]. Figure 6 shows the graph of the CH$_4$–air and CH$_4$–CH$_4$ coefficients from the present work, and corresponding values from the $\nu_4$ and $\nu_2$ bands [26] and [27] are shown for comparison.
4. Conclusions
In the first part of this study, we performed analysis of high-resolution Fourier Transform Spectra of CO mixed with CO$_2$ using a multispectrum least squares fitting technique. The quadratic speed-dependent Voigt profile with weak line mixing properly modeled the observed molecular line shapes, to within the noise level. We measured the CO$_2$ broadening and shift coefficients for transitions in the 2–0 band of $^{12}$C$^{16}$O, up to J=22. The temperature dependence of the broadening parameters, as well as the weak line mixing coefficients were also obtained. Theoretical semi-empirical calculations were carried out to obtain CO$_2$ broadening and CO$_2$ shift parameters. Comparison with the corresponding observed coefficients showed that the calculated values are comparable at 296 K. Also, the weak CO$_2$ line mixing coefficients were obtained using the EPG method.

Then, the accurate line shape parameters such as CH$_4$–CH$_4$ and CH$_4$–air half-width coefficients, CH$_4$–CH$_4$ and CH$_4$–air shift coefficients, their temperature dependence and line mixing coefficients were determined in the $v_3+v_4$ band of methane. For several transitions the temperature exponents for self half-width coefficients were slightly higher than those for air half-width coefficients. The quadratic SDV profile including line mixing through the off-diagonal relaxation matrix elements formalism was used in the retrievals. The results of this laboratory study addressed the broad objectives of the Atmospheric Composition Laboratory Research Program to develop further the understanding of terrestrial atmospheric and planetary composition [28] and to provide improved prognostic capability for environmental issues.

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