

Line Mixing in Water Vapor and Methane

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Abstract. A multispectrum fitting algorithm has been used to identify line mixing and determine mixing parameters for infrared transitions of H₂O and CH₄ in the 5-9 μ m region. Line mixing parameters at room temperature were determined for two pairs of transitions in the ν_2 fundamental band of H₂¹⁶O, for self-broadening and for broadening by H₂, He, CO₂, N₂, O₂ and air. Line mixing parameters have been determined from air-broadened CH₄ spectra, recorded at temperatures between 210 K and 314 K, in selected R-branch manifolds of the ν_4 band. For both H₂O and CH₄, the inclusion of line mixing was seen to have a greater effect on the retrieved values of the line shifts than on the retrieved values of other parameters.

Keywords: Infrared, line mixing, water vapor, methane, line broadening, line shifts.

PACS: 33.20.-t, 33.20.Ea, 33.70.Jg

INTRODUCTION

A multispectrum fitting algorithm [1], used to analyze pressure-broadening and line shift parameters for transitions of H₂O and CH₄ in the 5-9 μ m region, has revealed the characteristic residual patterns due to line mixing between specific transitions within each band. In this paper we will describe observations and quantitative analyses of line mixing in the ν_2 fundamental band of H₂¹⁶O and in the ν_4 fundamental band of CH₄. These are the first laboratory measurements of line mixing parameters in each band.

WATER VAPOR

For two pairs of transitions in the ν_2 fundamental band of H₂¹⁶O, the characteristic residuals of line mixing were observed very distinctly in least-squares fits of high-resolution FTS spectra of self-broadened H₂O at pressures up to 29 Torr and mixtures of H₂O with H₂, He, CO₂, N₂, O₂ and air at pressures up to 999 Torr [2]. The positions

and rotational assignments of the four lines (in terms of the rotational quantum numbers J , K_a and K_c) are given as follows:

P branch: $(1\ 0\ 1) \leftarrow (2\ 1\ 2)$ at 1539.061 cm^{-1} mixing with $(2\ 1\ 2) \leftarrow (3\ 0\ 3)$ at 1540.300 cm^{-1} ;

R branch: $(3\ 0\ 3) \leftarrow (2\ 1\ 2)$ at 1652.400 cm^{-1} mixing with $(2\ 1\ 2) \leftarrow (1\ 0\ 1)$ at 1653.267 cm^{-1} .

Note that in each pair of lines, the rotational quantum numbers of the upper state of one transition $(2\ 1\ 2)$ are the same as those of the lower state of the other transition.

For each broadening gas, groups of three to seven spectra were analyzed [2] to determine line positions, intensities, halfwidths, pressure-induced shifts and off-diagonal relaxation matrix elements. Each group of spectra was analyzed first using the multispectrum algorithm assuming Voigt line shapes and no line mixing, and then the analysis was repeated with line mixing implemented, allowing the off-diagonal relaxation matrix elements [3] to be determined in the least-squares fit. The observed spectra and residuals from the fits of self-broadened spectra are shown in Fig. 1.

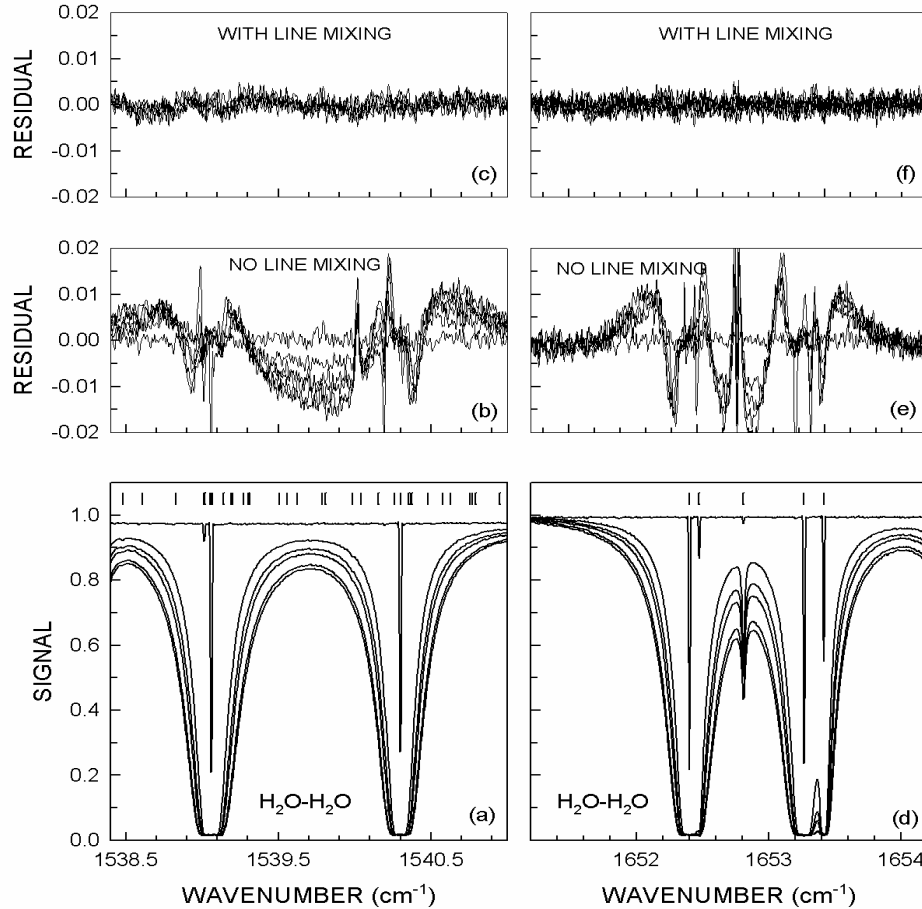


FIGURE 1. Multispectrum fits of mixed pairs of self-broadened H_2O lines in the P branch (left panels) and R branch (right panels) of the ν_2 band. Observed spectra, at six different water pressures ranging from 0.01 to 29 Torr, are plotted in the bottom panels (a, d) along with tick marks indicating the line positions. Middle panels (b, e) show (Obs. – Calc.) residuals for the Voigt line shape *without* line mixing, and the upper panels (c, f) show the corresponding residuals for the fits *with* line mixing [2].

The characteristic residuals of a pair of mixed lines are seen most clearly in the middle left panel of Fig.1, where the calculations without line mixing overestimate the absorption between the two strong P branch lines and underestimate the absorption in the wings of the mixed pair. The zig-zag residuals near the line centers also indicate that the line positions and/or pressure-induced shifts are not well-determined. For the R branch pair, which is overlapped by some other lines, the pattern of residuals is less obvious but still discernable.

Since all of the H₂O spectra had been recorded with samples near room temperature, the temperature dependences of the broadening, shift, and line mixing parameters could not be determined. However, it was possible to compare the mixing parameters retrieved for the various broadening gases. For the two pairs of ν_2 transitions analyzed, the largest mixing effects were observed for self-broadening and H₂-broadening, and the smallest effects were found for He-broadening.

While inclusion of line mixing in the fits did not significantly change the retrieved line intensities and widths (except for self- and H₂-broadening), the retrieved values of the pressure-induced shifts were affected by mixing for all broadeners except He.

Details of this study may be found in the journal article of Brown et al. [2].

METHANE

Multispectrum fits of air-broadened CH₄ spectra, recorded at temperatures between 210 K and 314 K and broadening gas pressures between 50 and 550 Torr, have been carried out for selected R-branch manifolds in the ν_4 band. An example of fits with and without line mixing in the R(11) manifold is shown in Fig. 2. In this figure it is apparent from the residuals that most of the line mixing is occurring between transitions on the low-wavenumber side of the manifold. Examination of the retrieved relaxation matrix elements verifies this initial observation, as the mixing parameters for transitions on the high-wavenumber side of the manifold are effectively zero. Some self-broadened CH₄ spectra were also included in this fit, but the results are very preliminary since only 15 spectra were included out of 64 possible spectra that can be used in the final analysis.

Another interesting spectral region is the R(3) manifold of ¹²CH₄, which is overlapped by the R(5) manifold of ¹³CH₄. A set of 31 spectra was fit in this region to determine broadening, shift, and line mixing parameters in both manifolds. The observed spectra and residuals from the fit with line mixing are shown in Fig. 3.

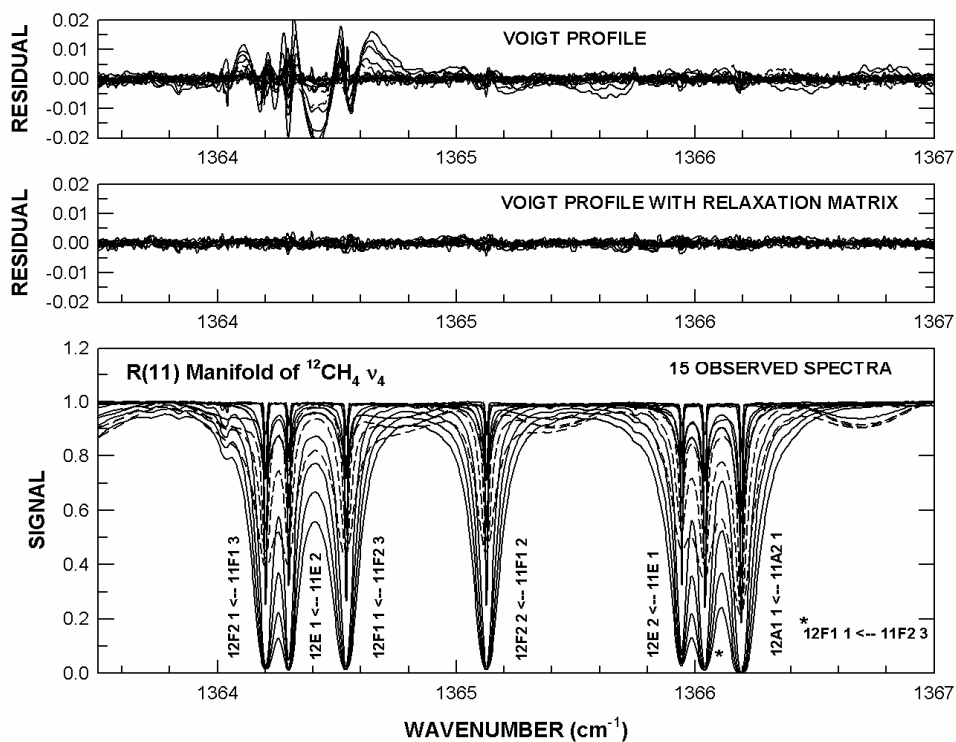


FIGURE 2. Fits of 15 air- and self-broadened room-temperature CH_4 spectra with and without line mixing. Maximum pressure is 550 Torr for air-broadening and 453 Torr for self-broadening.

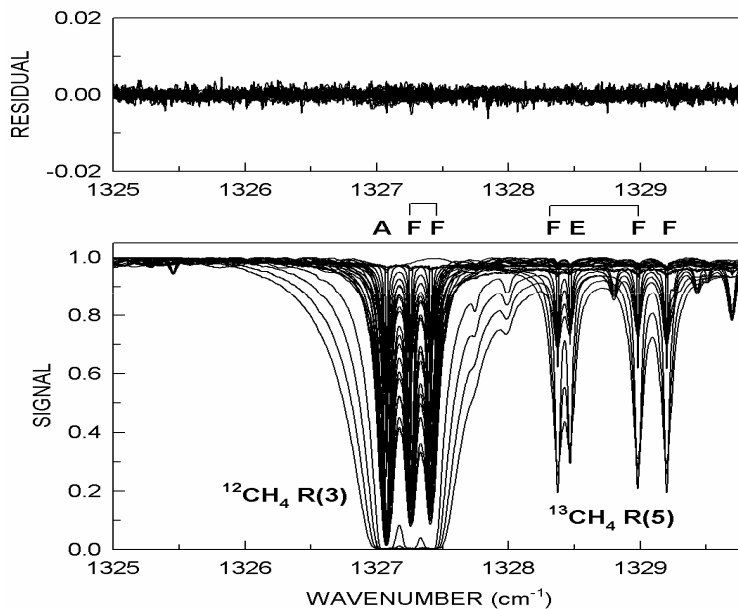


FIGURE 3. Fit, including line mixing, of 31 spectra in the region of the R(3) manifold of $^{12}\text{CH}_4$. The data set includes 3 room-temperature spectra of air-broadened $^{13}\text{CH}_4$, 26 spectra of air-broadened “natural” CH_4 at 210 K to 314 K, and one spectrum each of low-pressure pure $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$. Horizontal lines with ticks indicate which transitions are mixing with each other.

The parameters resulting from this fit of the R(3) region are shown in Table 1. The air-broadened widths and temperature dependences, as well as shifts of unmixed lines, retrieved using the multispectrum fits are in excellent agreement with earlier values determined from single-spectrum fits [4, 5]. Furthermore, the parameters determined from multispectrum fits show smaller statistical errors than the corresponding parameters resulting from single-spectrum fits of largely the same data set. Since the $^{13}\text{CH}_4$ spectra included in the fit were all recorded at room temperature, no information on the temperature-dependence of parameters for the $^{13}\text{CH}_4$ R(5) transitions could be determined, and these were held fixed to average values estimated from corresponding $^{12}\text{CH}_4$ R(5) transitions.

TABLE 1. Methane Air-broadening, Shift, and Line Mixing Parameters in the R(3) Region

Position (cm^{-1})	Isotope and HITRAN04 Assignment	Width ($\text{cm}^{-1} \text{ atm}^{-1}$ at 296 K)	n	Shift ($\text{cm}^{-1} \text{ atm}^{-1}$ at 296 K)	δ' ($\text{cm}^{-1} \text{ atm}^{-1} \text{ K}^{-1}$)	Mixing ($\text{cm}^{-1} \text{ atm}^{-1}$ at 296 K)	T- Dependence of Mixing
1327.074206(4)	12CH4 4A1 1 \leftarrow 3A2 1	0.05836(2) <i>0.0574(3)</i>	0.723(2) <i>0.81(3)</i>	$-0.00164(2)$ <i>$-0.0018(1)$</i>	$0.85(3) \times 10^{-5}$ <i>$0.7(2) \times 10^{-5}$</i>	none	none
1327.256817(5) *	12CH4 4F1 1 \leftarrow 3F2 1	0.06626(5) <i>0.0667(3)</i>	0.802(2) <i>0.64(2)</i>	$-0.00145(3)$ <i>$+0.0023(3)$</i>	$1.17(6) \times 10^{-5}$ <i>$1.0(3) \times 10^{-5}$</i>	0.00608(3)	1.32(2)
1327.409813(8) *	12CH4 4F2 1 \leftarrow 3F1 1	0.06689(3) <i>0.0662(3)</i>	0.818(2) <i>0.74(3)</i>	$-0.00157(3)$ <i>$-0.0050(2)$</i>	$0.60(5) \times 10^{-5}$ <i>$0.5(3) \times 10^{-5}$</i>	0.00608(3)	1.32(2)
1328.372213(9) **	13CH4 6F2 1 \leftarrow 5F1 2	0.05958(4) <i>0.0578(2)</i>	0.72 (fixed)	$-0.00190(4)$ <i>$-0.0016(2)$</i>	0.0 (fixed)	0.00978(27)	1.4 (fixed)
1328.467453(12)	13CH4 6E 1 \leftarrow 5E 1	0.05169(5) <i>0.0516(1)</i>	0.72 (fixed)	$-0.00198(4)$ <i>$-0.0026(1)$</i>	0.0 (fixed)	none	none
1328.982458(9) **	13CH4 6F1 1 \leftarrow 5F2 1	0.06180(4) <i>0.0611(0)</i>	0.72 (fixed)	$-0.00252(5)$ <i>$-0.0036(1)$</i>	0.0 (fixed)	0.00978(27)	1.4 (fixed)
1329.200880(9)	13CH4 6F2 2 \leftarrow 5F1 1	0.05894(4) <i>0.0584(1)</i>	0.72 (fixed)	$-0.00193(5)$ <i>$-0.0029(2)$</i>	0.0 (fixed)	Not measurable	Not measurable

Numbers in parentheses are statistical errors in units of the last digit quoted. Mixing parameter is the larger off-diagonal matrix element of the pair of mixed lines. Mixed pairs are indicated by * or ** in the first column. Results from previous spectrum-by-spectrum analyses [4, 5] are given in italics.

As was the case for H_2O , the inclusion of line mixing was seen to have a greater effect on the retrieved values of the line shifts than on the retrieved values of other parameters. We note that for the transition at $1327.2568 \text{ cm}^{-1}$, the inclusion of line mixing in the fit actually changes the sign of its pressure-induced shift; the magnitude of the shift of its mixing partner at $1327.4098 \text{ cm}^{-1}$ also changes significantly.

We have presented here only a sampling of line mixing results for a few transitions of H₂O and CH₄. Work is continuing on analysis of line mixing in these and other bands. As a larger database of experimentally-determined line mixing parameters is accumulated, there will be additional opportunities to compare experimental and theoretical mixing parameters, and to compare mixing parameters for different bands of the same molecule.

ACKNOWLEDGMENTS

The research described in this paper was carried out by the Jet Propulsion Laboratory, California Institute of Technology, Langley Research Center and the College of William and Mary under contracts with the National Aeronautics and Space Administration.

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