

# Room-temperature broadening and pressure-shift coefficients in the $\nu_2$ band of $\text{CH}_3\text{D}-\text{O}_2$ : Measurements and semi-classical calculations

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Received 1 December 2005; in revised form 16 December 2005

Available online 15 February 2006

## Abstract

We report measured Lorentz  $\text{O}_2$ -broadening and  $\text{O}_2$ -induced pressure-shift coefficients of  $\text{CH}_3\text{D}$  in the  $\nu_2$  fundamental band. Using a multispectrum fitting technique we have analyzed 11 laboratory absorption spectra recorded at  $0.011\text{ cm}^{-1}$  resolution using the McMath–Pierce Fourier transform spectrometer, Kitt Peak, Arizona. Two absorption cells with path lengths of 10.2 and 25 cm were used to record the spectra. The total sample pressures ranged from 0.98 to 339.85 Torr with  $\text{CH}_3\text{D}$  volume mixing ratios of 0.012 in oxygen. We report measurements for  $\text{O}_2$  pressure-broadening coefficients of 320  $\nu_2$  transitions with quantum numbers as high as  $J'' = 17$  and  $K = 14$ , where  $K'' = K' \equiv K$  (for a parallel band). The measured  $\text{O}_2$ -broadening coefficients range from  $0.0153$  to  $0.0645\text{ cm}^{-1}\text{ atm}^{-1}$  at 296 K. All the measured pressure-shifts are negative. The reported  $\text{O}_2$ -induced pressure-shift coefficients vary from about  $-0.0017$  to  $-0.0068\text{ cm}^{-1}\text{ atm}^{-1}$ . We have examined the dependence of the measured broadening and shift parameters on the  $J''$ , and  $K$  quantum numbers and also developed empirical expressions to describe the broadening coefficients in terms of  $m$  ( $m = -J''$ ,  $J''$ , and  $J'' + 1$  in the  $^{\text{O}}P$ -,  $^{\text{O}}Q$ -, and  $^{\text{O}}R$ -branch, respectively) and  $K$ . On average, the empirical expressions reproduce the measured broadening coefficients to within 4.4%. The  $\text{O}_2$ -broadening and pressure shift coefficients were calculated on the basis of a semiclassical model of interacting linear molecules performed by considering in addition to the electrostatic contributions the atom–atom Lennard-Jones potential. The theoretical results of the broadening coefficients are generally larger than the experimental data. Using for the trajectory model an isotropic Lennard-Jones potential derived from molecular parameters instead of the spherical average of the atom–atom model, a better agreement is obtained with these data, especially for  $|m| \leq 12$  values (11.3% for the first calculation and 8.1% for the second calculation). The  $\text{O}_2$ -pressure shifts whose vibrational contribution are either derived from parameters fitted in the  $^{\text{O}}Q$ -branch of self-induced shifts of  $\text{CH}_3\text{D}$  or those obtained from pressure shifts induced by Xe in the  $\nu_3$  band of  $\text{CH}_3\text{D}$  are in reasonable agreement with the scattered experimental data (17.0% for the first calculation and 18.7% for the second calculation).

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**Keywords:** Monodeuterated methane;  $\text{CH}_3\text{D}$ ;  $\text{O}_2$ -broadening; Fourier transform infrared spectroscopy; Spectral lineshape; Semi-classical calculation

## 1. Introduction

Laboratory spectroscopic studies of the  $\nu_2$  vibrational band of  $\text{CH}_3\text{D}$  are needed for the correct interpretation

of Earth's atmospheric spectra. The  $\nu_2$  band of  $\text{CH}_3\text{D}$  is the lowest band ( $\nu_0 \approx 2200\text{ cm}^{-1}$ ) of a polyad of nine interacting vibrational states. This paper is a continuation of our study of spectroscopic line parameters in this fundamental band [1,2]. Few measurements and calculations of  $\text{O}_2$ -broadening coefficients for  $\text{CH}_3\text{D}$  have been published and they refer only to the  $\nu_3$  fundamental [3,4]. To the best

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of our knowledge, no prior measurements of O<sub>2</sub>-induced pressure shift coefficients have been made.

Several theoretical efforts concerned with O<sub>2</sub>-broadening coefficients of CH<sub>3</sub>D have been put forth. Tejwani and Fox [5] calculated N<sub>2</sub>-, O<sub>2</sub>-, self-, and H<sub>2</sub>-broadening coefficients for CH<sub>3</sub>D using the Anderson–Tsao–Curnutte (ATC) theory by considering only the electrostatic interaction between the quadrupole moment of the perturber and the octopole moment of CH<sub>3</sub>D, with an effective value of this octopole moment strongly overestimated (5.6 D Å<sup>2</sup>, instead of 3.1 D Å<sup>2</sup> in this study). They have computed pressure-broadening coefficients for the above broadening gases for a wide range of *J* and *K* values as well as the temperature dependence of the pressure-broadening coefficients in the 100–300 K range. The O<sub>2</sub>-broadening coefficients of CH<sub>3</sub>D in the ν<sub>3</sub> band reported in [3] were calculated using the theoretical model developed in [6]. For the intermolecular potential a simple formulation with two adjustable parameters [7] corresponding to dispersion, induction, and repulsive contributions has been used in addition to the electrostatic interactions. Although the calculated results are generally in reasonable agreement with the experimental data, except at high *J* values where they are underestimated, the two adjustable potential parameters used have probably no physical meaning. Here, we consider a different theoretical approach for the calculation of broadening coefficients that was recently applied to CH<sub>3</sub>D self-perturbed [1], CH<sub>3</sub>D–H<sub>2</sub> [8], and CH<sub>3</sub>D–N<sub>2</sub> [2] without any adjustable parameters. CH<sub>3</sub>D is approximated as a linear molecule for its interactions with O<sub>2</sub> and the potential involves the atom–atom Lennard-Jones model [9] in addition to the electrostatic contributions. The theoretical formulation is similar to that described previously [2] and only some features and characteristics of the potential used will be briefly presented.

## 2. Experimental details

The 11 absorption spectra used in this work were recorded at an unapodized resolution of 0.0056 cm<sup>-1</sup> using the McMath-Pierce Fourier transform spectrometer (FTS)

of the National Solar Observatory (NSO) on Kitt Peak. Two absorption cells with path lengths of 10.2 and 25 cm were used in the experiments. The spectra covering the 2048–2318 cm<sup>-1</sup> were simultaneously fit in segments of 5–10 cm<sup>-1</sup> wavenumber intervals using a multispectrum nonlinear least-squares procedure [10]. This analysis tool allowed us to combine spectra recorded with low pressures of 98% pure CH<sub>3</sub>D, self-broadened spectra, and lean mixtures (~1%) of CH<sub>3</sub>D in O<sub>2</sub> in a single least-squares solution. The experimental conditions for each spectrum are presented in Table 1. The experimental setup and data reduction methods were described in detail in our earlier study [1]. Residual water vapor lines appeared in all of our spectra as a combination of low pressure absorption due to small amounts (50 mTorr) of residual water vapor present in the vacuum tank enclosing the FTS, and H<sub>2</sub>O absorption arising from water vapor in the N<sub>2</sub>-purged atmospheric paths between the source and the absorption cell and between the absorption cell and the entrance aperture of the interferometer. The wavenumber calibration for the CH<sub>3</sub>D line positions was performed with respect to the well-known line centers [11] of residual water lines.

An example of a multispectrum fitted interval is presented in Fig. 1. The top panel shows 11 overlaid spectra of *Q*<sub>R</sub>-branch transitions with *J*' = 11 and *K* values from 0 to 10. The bottom panel indicates the fit residuals (observed minus calculated for all 11 spectra). The positions of transitions due to contaminants such as residual CO were determined prior to using the multispectrum fitting procedure. During the analysis these lines were included in the least-squares solution using 0.075 cm<sup>-1</sup> atm<sup>-1</sup> at 296 K as O<sub>2</sub>-broadening and –0.005 cm<sup>-1</sup> atm<sup>-1</sup> as O<sub>2</sub>-induced pressure shift coefficients, respectively.

## 3. Results and discussion

The results of our multispectrum analysis are presented in Table 2. The O<sub>2</sub>-broadening coefficients for CH<sub>3</sub>D transitions in the ν<sub>2</sub> band are given in units of cm<sup>-1</sup> atm<sup>-1</sup> at 296 K. For each transition we list the line center positions retrieved from the fits (in cm<sup>-1</sup>) and the transitions

Table 1  
Experimental conditions for the spectra using in this study

Temperature (K)	Broadening gas	<sup>12</sup> CH <sub>3</sub> D volume mixing ratio	Path (cm)	Pressure (Torr)
300.20	<sup>12</sup> CH <sub>3</sub> D	1.00	10.2	0.98
300.00	<sup>12</sup> CH <sub>3</sub> D	1.00	10.2	2.95
300.90	<sup>12</sup> CH <sub>3</sub> D	1.00	10.2	17.50
300.70	<sup>12</sup> CH <sub>3</sub> D	1.00	10.2	79.00
300.20	<sup>12</sup> CH <sub>3</sub> D	1.00	10.2	110.00
299.80	<sup>12</sup> CH <sub>3</sub> D	1.00	10.2	152.00
299.80	<sup>12</sup> CH <sub>3</sub> D	1.00	10.2	303.00
295.90	O <sub>2</sub>	~0.012	25.0	339.85
295.65	O <sub>2</sub>	~0.012	25.0	302.50
295.45	O <sub>2</sub>	~0.012	25.0	202.35
295.45	O <sub>2</sub>	~0.012	25.0	102.40

Note. 760 Torr = 1 atm = 101.325 kPa.

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