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Measurements and theoretical calculations of self-broadening and self-shift coefficients in the v_2 band of CH_3D

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Abstract

In this paper, we report measured Lorentz self-broadening and self-induced pressure-shift coefficients of $^{12}CH_3D$ in the v_2 fundamental band ($v_0 \approx 2200\ cm^{-1}$). The multispectrum fitting technique allowed us to analyze simultaneously seven self-broadened absorption spectra. All spectra were recorded at the McMath-Pierce Fourier transform spectrometer of the National Solar Observatory (NSO) on Kitt Peak, AZ with an unapodized resolution of $0.0056\ cm^{-1}$. Low-pressure (0.98–2.95 Torr) as well as high-pressure (17.5–303 Torr) spectra of ^{12}C-enriched CH_3D were recorded at room temperature to determine the pressure-broadening coefficients of 408 v_2 transitions with quantum numbers as high as $J'' = 21$ and $K = 18$, where $K'' = K' \equiv K$ (for a parallel band). The measured self-broadening coefficients range from 0.0349 to $0.0896\ cm^{-1}\ atm^{-1}$ at 296 K. All the measured pressure-shifts are negative. The reported pressure-induced self-shift coefficients vary from about -0.004 to $-0.008\ cm^{-1}\ atm^{-1}$. 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 ^QP-, ^QQ-, and ^QR-branch, respectively) and K. On average, the empirical expressions reproduce the measured broadening coefficients to within 3.6%. A semiclassical theory based upon the Robert–Bonamy formalism of interacting linear molecules has been used to calculate these self-broadening and self-induced pressure-shift coefficients. In addition to the electrostatic interactions involving the octopole and hexadecapole moments of CH_3D, the intermolecular potential includes also an atom–atom Lennard–Jones model. For low K ($K \leqslant 3$) with $|m| \leqslant 8$ the theoretical results of the broadening coefficients are in overall good agreement (3.0%) with the experimental data. For transitions with K approaching $|m|$, they are generally significantly underestimated (8.8%). The theoretical self-induced pressure shifts, whose vibrational contribution is derived from results in the ^QQ-branch, are generally smaller in magnitude than the experimental data in the ^QP-, and ^QR-branches (15.2%).

Keywords: Monodeuterated methane; CH_3D; Self-broadening; Fourier transform infrared spectroscopy; Spectral lineshape

1. Introduction

The objective of the present study was to enhance our spectroscopic knowledge of monodeuterated methane in the v_2 fundamental band. Laboratory spectroscopic studies of CH_3D are needed for the correct interpretation of atmospheric spectra of Jupiter, Saturn, Titan, Neptune, and Uranus, planets known to contain CH_3D [1–5]. Of particular interest is the accurate determination of the CH_3D abundance and the D/H ratio in methane (via the CH_3D/CH_4 ratio) in the atmospheres of these solar system bodies. Significant differences in

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the thermodynamics and kinetics of various processes (e.g., chemical reactions, condensation, and thermal escape) result from the significant mass difference between H and its isotope D leading to an isotopic fractionation. For this reason, the D/H ratio in methane can provide invaluable insight into the formation and dynamics of the atmospheres of a number of solar system objects. In addition, the quantitative spectroscopic analysis of industrial and research gas samples containing methane and its isotopologues also requires a good knowledge of the CH_3D spectroscopic line parameters.

This paper is the latest of a series of detailed spectroscopic line parameters measurements involving the fundamentals of monodeuterated methane. The ν_2 band of $^{12}CH_3D$ is the lowest band of a polyad of nine interacting vibrational states analyzed by Nikitin et al. [6]. Foreign- and self-broadening and pressure-shift coefficients were obtained by Devi et al. [7–12] for a few thousand transitions in the ν_3, ν_5, and ν_6 bands of $^{12}CH_3D$. For the ν_2 fundamental, Chackerian and Guelachvili [13] measured the intensities and self-broadening of $R(0,0)$ and 7 P-branch transitions, while Suarez et al. [14] obtained widths of 18 P-branch transitions. At shorter wavelength, Boussin et al. [5] have reported line intensities and self-broadening coefficients for 221 transitions in the $3\nu_2$ band of CH_3D, 20 of which were reproduced to within 1.2% on average by Plateaux et al. [15].

On the theoretical side, Tejwani and Fox [16] calculated self-, N_2-, O_2-, and H_2-broadening coefficients for CH_3D using the Anderson–Tsao–Curnutte (ATC) theory by considering interactions due to the dipole and octopole moments of CH_3D. They 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. Lance et al. [17] reported both measurements and theoretical calculations of self-broadening coefficients for CH_3D in the ν_3 band under small lineshift conditions (i.e., a pressure regime sufficiently low as to make the pressure shifts negligible in a first approximation).

Our present measurements of 408 transitions provide a large contribution to the current spectroscopic knowledge of self-broadening and self-shift coefficients for the ν_2 band of $^{12}CH_3D$. These results will be useful for developing reliable theoretical models of pressure-broadening and pressure-shift coefficients for symmetric top molecules. Aside from the experimental results, we also present theoretical self-broadening and self-shift coefficients calculated in the frame work of the semiclassical Robert–Bonamy (RB) model of interacting linear molecules [18]. The measured broadening and shift coefficients are compared to the theoretically calculated coefficients as a means of testing the theoretical model as well as the intermolecular potential used. Moreover, the line shift cross-sections in vibration–rotation spectra are a sensitive probe of the vibrational dependence of the potential [19]. The self-broadening coefficients were previously calculated in the ν_3 band by considering, in addition to electrostatic interactions, the dispersion contributions [17]. The results were very unsatisfactory probably because this potential does not include any repulsive interaction and also because the parameters of the dispersion energy (mainly the polarizability anisotropy and hyperpolarizabilities) are not available for CH_3D. Here, we consider a different theoretical approach recently applied to CH_3D–H_2 [20] as well as PH_3–H_2 [21] approximating CH_3D as a linear molecule for its self-interaction and involving the atom–atom Lennard–Jones potential, in addition to the electrostatic potential.

2. Experimental details

Seven absorption spectra at an unapodized resolution of 0.0056 cm^{-1} in the 2048–2318 cm^{-1} spectral range were obtained using the McMath-Pierce Fourier transform spectrometer (FTS) of the National Solar Observatory (NSO) on Kitt Peak. These spectra were used previously for studies involving the three lowest fundamentals [10–12]. A summary of the experimental conditions for each spectrum is given in Table 1. All CH_3D spectra were recorded using a 10.2 cm long glass absorption cell equipped with a 1 L ballast bulb and wedged KCl windows. The radiation generated by an infrared glower was detected between 800 and 2600 cm^{-1} using two helium-cooled arsenic-doped silicon detectors.

A 98% pure sample of CH_3D supplied by Icon Services was used without further purification. In addition to CH_3D lines, a few lines belonging to H_2O and CO were present in the spectra. The gas sample temperatures and pressures were monitored continuously during data recording. A thermocouple attached to the exterior of the ballast bulb was used to monitor the gas sample temperatures. The gas pressures in our data range from 0.98 to 303 Torr and were measured using either a 0–10 or a 0–1000 Torr capacitance gauge (Baratron). The wavenumber calibration for the CH_3D line positions was performed with respect to the well-

Table 1
Summary of experimental conditions of $^{12}CH_3D$ spectra

Temperature (K)	Broadener gas	Path (cm)	Pressure (Torr)
300.2	$^{12}CH_3D$	10.2	0.98
300.0	$^{12}CH_3D$	10.2	2.95
300.7	$^{12}CH_3D$	10.2	17.50
300.7	$^{12}CH_3D$	10.2	79.0
300.2	$^{12}CH_3D$	10.2	110.0
299.8	$^{12}CH_3D$	10.2	152.0
299.8	$^{12}CH_3D$	10.2	303.0

Note. 760 Torr = 1 atm = 101.325 kPa.