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Multispectrum measurements of spectral line parameters including temperature dependences of N_2- and self-broadened half-width coefficients in the region of the ν_9 band of $^{12}C_2H_6$

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ABSTRACT

Ethane is a prominent contributor to the spectrum of Titan, particularly in the ν_9 region centered near 822 cm^{-1}. To improve the spectroscopic line parameters at 12 μm, 41 high-resolution (0.0016–0.005 cm^{-1}) absorption spectra of C_2H_6 were obtained at sample temperatures between 211 and 298 K with the Bruker IFS 120HR at the Pacific Northwest National Laboratory (PNNL) in Richland, Washington. Two additional spectra were later recorded at ~150 K using a new temperature-stabilized cryogenic cell designed for the sample compartment of the Bruker IFS 125HR at the Jet Propulsion Laboratory (JPL) in Pasadena, California. A multispectrum nonlinear least-squares fitting program was applied simultaneously to all 43 spectra to measure the line positions, intensities, N_2- and self-broadened half-width coefficients and their temperature dependences. Reliable pressure-induced shift coefficients could not be obtained, however, because of the high congestion of spectral lines (due to torsional-split components, hot-band transitions as well as blends). Existing theoretical modeling of this very complicated ν_9 region permitted effective control of the multispectrum fitting technique; some constraints were applied using predicted intensity ratios, doublet separations, half-width coefficients and their temperature dependence exponents in order to determine reliable parameters for each of the two torsional-split components. For $^{12}C_2H_6$, the resulting retrievals included 17 ^pQ and ^rQ sub-bands of ν_9 (as well as some ^pP, ^rR sub-bands). Positions and intensities were measured for 3771 transitions, and a puzzling difference between previously measured ν_9 intensities was clarified. In addition, line positions and intensities were obtained for two $^{12}C_2H_6$ hot bands ($\nu_9+\nu_4-\nu_4$, $\nu_9+2\nu_4-2\nu_4$) and the ν_9 band of $^{13}C^{12}CH_6$, as well as several hundred presently unidentified transitions. N_2- and self-broadened half-width coefficients were determined for over 1700 transitions, along with 1350 corresponding temperature dependence exponents. Similar to N_2- and self-broadened half-width coefficients, their temperature dependence exponents were also found to follow distinctively different patterns. However, while the self- and N_2-broaded widths differed by 40%, the temperature dependence exponents of the two broadening gases were similar.

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The variations of the observed half-width coefficients and their temperature dependences with respect to *J*, *K* quantum numbers were modeled with a set of linear equations for each *K*. The present broadening coefficients compared well with some of the prior measurements.

1. Introduction

The 12-μm emission features of ethane are readily seen in atmospheric spectra of Jupiter, Saturn, Neptune and Titan (e.g. [1]). Ethane is also an important constituent in the atmosphere of the Earth and in comets [2–5]. The measured spectral line parameters of ethane reported in this work are important since its ν_9 band at 822 cm^{-1}, as well as transitions from the ν_6 and ν_8 fundamental bands near 1400 cm^{-1}, appear at all latitudes in the CIRS stratospheric spectra of Titan [6]. Titan's atmosphere largely consists of nitrogen, but it has measurable quantities of organic molecules such as methane and ethane. Nitrogen broadening and its temperature dependence are thus essential for studies of Titan's atmosphere. In laboratory studies, self-broadened half-width coefficients are also needed because N_2-broadened spectra generally have significant ethane volume mixing ratios. At 12-μm, the ethane positions, intensities and broadening at room temperature are already available (see Ref. [7]), but the information for the temperature dependence of widths is very limited (e.g. Ref. [7] and the references therein). The recent rovibrational analyses of the 12-μm bands are already described [7], so that only those studies that are directly relevant to present study will be referenced here.

The ν_9 fundamental of ethane is the strongest band in Titan in the 10-μm terrestrial window and is often used to detect and monitor its abundance in planetary atmospheres. Because torsional splittings arise from various perturbing interactions within ν_9 and with $3\nu_4$, each vibration–rotation line can be doubled into a strong and a weak component having intensity patterns which depend strongly upon the quantum number *K* (and also *J* for *K*=0); these splittings in ν_9 have marked *J* and *K* dependence [8]. For retrieving the ethane abundance, its sharpest sub-band, $^rQ_0$, is commonly used. However, the structure of the $^rQ_0$ sub-band is also more complex than the other ^rQ and ^PQ sub-band structures. Although the *J*-, *K*-dependent torsional splittings are large enough to be observed in several sub-bands, the two split components of $^rQ_0$ are often completely obscured by a torsional component of the nearby *J*. Each apparent spectral *line* in $^rQ_0$ is in reality two transitions with different *J* values, different relative intensities and even two different symmetry species in the quantum assignments. Thus, even at the lowest sample pressure and Doppler-limited resolution, retrieving $^rQ_0$ spectral line parameters, especially the pressure-broadened half-width coefficients and their temperature dependences, becomes all the more difficult and challenging.

Nevertheless, several past laboratory studies considered Lorentz broadening coefficients for a small number of ν_9 transitions broadened by self-, N_2-, H_2-, He-, Ar-, O_2- and CH_4 [9–13]. Chudamani et al. [9] measured N_2-broadened half-width coefficients at 150 K for transitions in select spectral intervals and reported a constant value of 0.168 cm^{-1} atm^{-1} for the entire spectral region. They did predict that the half-widths should be *J*-dependent but were unable to confirm that conjecture with their own data. Blass et al. [10] later used a tunable diode laser spectrometer system to determine ν_9 self- and foreign-gas broadening, giving a single half-width coefficient for each of six broadening gases (self-, N_2, He, Ar, H_2 and CH_4; see Table 2 in Ref. [10]). Then Halsey et al. [11] measured H_2 broadening for the entire $^rQ_0$ sub-band, reporting a constant half-width=0.1150(54) cm^{-1} atm^{-1} with a temperature dependence exponent n=0.942(26). The authors concluded that their measured temperature dependence exponent *n* revealed no detectable rotational state (*J*, *K*) dependence, contrary to the theoretical expectation. Nguyen et al. [12] obtained self-broadened half-width coefficients at three different temperatures (246.2, 226.2 and 150.2 K) for 11 spectral lines, using a tunable diode laser spectrometer operating between 798 and 817 cm^{-1}. They assumed a Rautian line profile to fit their data and reported that the temperature dependence exponent was constant (=0.676) within their experimental uncertainties. Finally, Blanquet et al. [13] measured N_2-broadening coefficients at room temperature for 15 lines (796–817 cm^{-1}) using the same diode laser spectrometer system of Nguyen et al. [12]; again, no variation of the temperature dependence exponents on broadening with the *J*, *K* quantum numbers was observed, contrary to what we observed in this work.

In the present work, new C_2H_6 measurements between 750 and 880 cm^{-1} were obtained using a simultaneous nonlinear multispectrum analysis technique. The new results are reported for 17 Q sub-bands; $^PQ(J, K=9)$ to $^PQ(J, K=1)$ in the P branch and $^rQ(J, K=0)$ to $^rQ(J, K=7)$ in the R branch and several other regions involving ^PR, ^rR, ^rP and ^PP sub-bands. The spectra were recorded at various experimental conditions of pressures, path lengths and temperatures. The experimental details and analysis procedure, as well as room-temperature measurements for a smaller subset (three ^PQ and four ^rQ sub-bands) of spectra were reported earlier [7]. The present effort expands our knowledge of ethane self- and N_2-broadening by analyzing both room- and low-temperature spectra, providing values for more assigned transitions (to ν_9, $\nu_9+\nu_4-\nu_4$, $\nu_9+2\nu_4-2\nu_4$ of $^{12}C_2H_6$ and ν_9 of $^{13}C^{12}CH_6$), along with several hundred unidentified transitions.

2. Experiment

The experimental spectra used in this study were obtained using two different high-resolution Fourier transform spectrometers (FTS). Most of the spectral data