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A multispectrum analysis of the ν_2 band of $H^{12}C^{14}N$: Part I. Intensities, broadening, and shift coefficients

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Abstract

Absolute intensities, self- and air-broadening coefficients, self- and air-induced shift coefficients and their temperature dependences have been determined for lines belonging to the P- and R-branches of the ν_2 band of $H^{12}C^{14}N$ centered near 712 cm^{-1}. Infrared spectra of HCN in the 14-μm region were obtained at high resolution (0.002–0.008 cm^{-1}) using two different Fourier transform spectrometers (FTS), the McMath-Pierce FTS at the National Solar Observatory on Kitt Peak and the Bruker IFS 120HR FTS at the Pacific Northwest National Laboratory. Spectra were recorded with 99.8% pure HCN as well as lean mixtures of HCN in air at various temperatures ranging between +26 and −60 °C. A multispectrum nonlinear least squares technique was used to fit selected intervals of 36 spectra simultaneously to obtain the line positions, intensities, broadening, and shift parameters. The measured line intensities were analyzed to determine the vibrational band intensity and the Herman–Wallis coefficients. The measured self-broadening coefficients vary between 0.2 and 1.2 cm^{-1} atm^{-1} at 296 K, and the air-broadening coefficients range from 0.08 to 0.14 cm^{-1} atm^{-1} at 296 K. The temperature dependence exponents of self-broadening range from 1.46 to −0.12 while the corresponding exponents for air broadening vary between 0.58 and 0.86. The present measurements are the first known determination of negative values for the temperature dependence exponents of HCN-broadening coefficients. We were able to support our self-broadening measurements with appropriate theoretical calculations. Our present measurements are compared, where possible, with previous measurements for this and other HCN bands, as well as the parameters that are included in the 2000 and 2004 editions of the high-resolution transmission (HITRAN) database.

Keywords: HCN; Infrared spectra; Fourier transform infrared spectroscopy; Absolute intensity; Broadening and pressure shift coefficients

1. Introduction

Hydrogen cyanide (HCN) has been detected in the interstellar medium [1], in comets [2], in the atmospheres of the giant planets [3–6] and of Saturn's moon Titan [7,8], and in the terrestrial stratosphere [9] and troposphere [10]. HCN had been identified as a sensitive tracer of biomass burning emissions [11–13], and its tropospheric concentration has been observed to vary seasonally [12] and with the phase of El Nino [14]. Since the primary sources of HCN in the terrestrial atmosphere are at ground level, infrared remote sensing of atmospheric HCN [9,10,12–14] especially requires accurate knowledge of air-broadening and shift parameters.

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Recently [15–17] we reported intensities, self- and air-broadening and shift parameters determined from high-resolution laboratory infrared spectra of HCN in the ν_1 and $2\nu_2$ bands obtained with two different Fourier transform spectrometers. In the present work, we report similar measurements for transitions in the ν_2 band, including the temperature dependences of both the self- and air-broadening and shift coefficients.

A number of studies involving both low and high-resolution measurements are available in the literature for the ν_2 bending mode of HCN and its isotopologues [18–31]. Earlier absolute intensity measurements and determinations of the dipole moment [18–20] were based on spectra obtained with low-resolution recording instruments and at high gas pressures to reduce errors arising from saturation effects. Duxbury and Yu [21] have reported a comprehensive rotational analysis and relative integrated band intensities for several bands in the ν_2 region from spectra recorded with the McMath-Pierce FTS. Maki et al. [22–24] published extensive high-resolution measurements and calculations of intensities, vibrational transition moments and Herman–Wallis constants for fundamental and hot band transitions of several isotopologues of HCN in the 14-μm region.

Experimental determinations of self-broadening coefficients and pressure-induced line shifts in the ν_2 band of HCN were first published by Foley [18,25] from data recorded with an echelle-type spectrometer. Several other more recent experimental studies on self- and foreign gas-broadening and pressure-induced shifts of HCN ν_2 transitions are available in the literature [26–31]. All of these recent studies analyzed spectra recorded with tunable diode laser spectrometers, to determine self-, N_2-, H_2-, and Ar-broadening coefficients as well as self-, H_2-, and He-pressure-induced shift coefficients for select transitions in the P-, Q-, and R-branches of the ν_2 band. All but one of these studies involved measurements only at room temperature. Schmidt et al. [27] made low temperature measurements of several P-, Q-, and R-branch transitions broadened by N_2 with the same tunable diode laser spectrometer system they had used to make room temperature measurements [26], and they reported the measured and calculated temperature dependence of N_2-broadening coefficients for 13 R-branch transitions.

Measurements of air-broadening and pressure-induced shift coefficients, most relevant to the interpretation of data used for remote sensing of HCN in the Earth's atmosphere, have not been reported for the ν_2 band. While we have previously determined these parameters in the $2\nu_2$ and ν_1 bands [16,17] it is not clear whether the results for these two parallel bands can be extrapolated to the perpendicular ν_2 band. Therefore, the primary purpose of the present study is to determine air-broadening and air-induced shift coefficients and their temperature dependences for lines in the ν_2 band of $H^{12}C^{14}N$. In addition, we were able to determine line intensities, self-broadening, and self-shift coefficients, and their temperature dependences. In our spectra, we also observed and measured a number of transitions belonging to the ν_2 bands of the $H^{13}C^{14}N$ and $H^{12}C^{15}N$ isotopologues, as well as several hot bands (such as $2\nu_2^0 - \nu_2^1$, $2\nu_2^2 - \nu_2^1$, $3\nu_2^1 - 2\nu_2^1$, and $3\nu_2^3 - 2\nu_2^1$) of the main isotopomer. These transitions are very weak and the parameters retrieved are not reliable enough to be reported at this time.

The self-broadening and shift coefficients and the variation of these parameters with temperature for the ν_2 HCN band been calculated using a semiclassical theory and are discussed in Part II of this series [32].

2. Experiment

The spectra analyzed in this study were recorded using two different Fourier transform spectrometers (FTS): the McMath-Pierce instrument located at the National Solar Observatory on Kitt Peak, Arizona and the Bruker IFS 120HR FTS at the Pacific Northwest National Laboratory (PNNL) in Richland, Washington. The resolution of each spectrum was about 0.005 cm^{-1} (see Table 1), except for two low-pressure self-broadened HCN spectra recorded at a resolution of about 0.002 cm^{-1}.

A total of 36 spectra obtained at various temperatures and path lengths were included in the analysis. We used three absorption cells, with path lengths of 50.0, 19.95, and 0.958 cm. All cells were used to obtain both room temperature and low temperature spectra. The first two cells were employed to obtain spectra of low pressure HCN and HCN broadened with dry air. The shortest cell (0.958 ± 0.003 cm) was used to record only self-broadened HCN spectra.

The gas sample used in recording the spectra at Kitt Peak was a nominal 0.1% mixture of HCN in N_2 purchased from Matheson-Trigas, Canada. The HCN–dry air mixtures used at Kitt Peak were prepared by adding proper quantities of dry O_2 to the HCN–N_2 mixture. A few low-pressure HCN spectra with more-concentrated (30–56%) HCN amounts were recorded with the Kitt Peak FTS to determine accurate reference line center positions for pressure-induced shift measurements. For these few low-pressure spectra the concentration of HCN in the sample was increased by condensing the purchased HCN–N_2 mixture (0.1% HCN in N_2) in liquid nitrogen, then pumping on it while thawing and repeating this processes a few times.

The HCN sample used with the FTS at PNNL was synthesized there. The major contaminants were found to be H_2O and CO_2. The H_2O contamination was removed by passing HCN through concentrated H_2SO_4, and the CO_2 was removed by pumping on the sample