
1NASA Langley Research Center, Science Directorate, MS 401A, Hampton, VA 23681-2199 (E-mail: Mary.Ann.H-Smith@nasa.gov), 2Department of Physics, College of William and Mary, Box 8795, Williamsburg, VA 23187-8795, 3Pacific Northwest National Laboratory, Battelle Boulevard, MS K8-88, P.O.Box 999, Richland, WA 99352.

Abstract: N2-broadening and N2-pressure-induced shift coefficients and their temperature dependences have been measured for transitions in the ν2 band of HCN from analysis of high-resolution absorption spectra recorded with two different Fourier transform spectrometers. A total of 34 laboratory spectra recorded at 0.0013-0.005 cm⁻¹ resolution and at temperatures ranging from 211 to 300 K were used in the determination of the spectral line parameters. A multispectrum nonlinear least squares fitting technique was used to obtain line positions, intensities, broadening and shift parameters and their temperature dependences. In analyzing the Q branch transitions, in was necessary to also solve for the off-diagonal relaxation matrix elements that characterize line mixing. Present results are compared to previous measurements reported in the literature.

Introduction: The molecular bands of HCN are prominent features in the infrared spectra of Titan. The 14-μm band of HCN is of interest not only for measurements of HCN itself, but also because it overlaps the spectra of other atmospheric molecules. Knowledge of the temperature dependence of N2-broadened widths and N2 pressure-induced shifts is needed for interpretation of infrared spectra of Titan’s atmosphere.

We earlier reported measurements of air- and N2-broadening and pressure-induced shift coefficients for HCN lines, along with their temperature dependences, for the ν1 band lines in the 3-μm region[1]. More recently we reported similar measurements of air- and self-broadening and pressure-induced shift coefficients and their temperature dependences for P and R branch transitions in the ν2 band in the 14-μm region[2].

Experiment: Room temperature as well as low temperature spectra used in the analysis were recorded using two different Fourier transform spectrometers (FTS); the McMath-Pierce FTS located on Kitt Peak, Arizona and the Bruker IFS 120 HR FTS situated at the Pacific Northwest National Laboratory (PNLNL) in Richland, Washington. A total of 34 spectra were used in the analysis. The resolution of the spectra varied from 0.0013 to 0.005 cm⁻¹. One low pressure high purity (99.8%) HCN spectrum included in the analysis was recorded at PNNL (0.0013 cm⁻¹ resolution) with a short (<1cm) path length absorption cell. The spectra from Kitt Peak were recorded using a 50-cm long Pyrex coolable cell and those from PNNL were obtained using a 19.95-cm (stainless steel but electroplated and gold coated) long coolable cell. Details about these cells are given in several previous publications [1, 3].

Analysis: Wavenumber scales of all spectra were calibrated using the lines of residual H2O and 12C16O2 present in the optical paths outside the sample cells.

An interactive multispectrum nonlinear least squares fitting technique[4] was used to analyze limited wavenumber intervals (20 to 25 cm⁻¹ each) of 17 to 30 spectra simultaneously, depending on the spectral region. A Voigt line shape was assumed; small (<0.5%) but systematic discrepancies between observed and calculated spectra appeared near line centers, particularly in the P- and R-branches. However, including speed-dependence in our spectral line shapes slightly improved these residuals.

Line mixing (off-diagonal relaxation matrix elements) was necessary to accurately model the absorption in Q-branch regions.

Initial values for all HCN parameters were taken from the HITRAN 2004 database[5]. Self- and N2-shift coefficients had initial values of zero. The temperature-dependence exponents of self-broadening were taken from Malathy Devi et al. [2] or were assumed to be 0.7 for transitions where no data were available.

Spectral backgrounds (including some channeling), zero transmission levels, FTS phase errors, and FTS line shapes for both instruments were appropriately modeled.

Results: The present work is the first known experimental determination of N2-shifts and of line mixing coefficients in the HCN ν2 band system.

Positions, absolute intensities, N2-broadening and line shift coefficients, and the temperature dependences of both broadening and shifts, were determined for P, Q and R branch transitions in the ν2 band of H12C14N. Parameters were also determined for some transitions of H13C14N.

The N2-broadening coefficients agree with previous measurements in the ν2 and other HCN bands within measurement uncertainties.

The temperature-dependence of N2-broadening in ν2 agrees with recent results in ν1[1] but not so well with a previous ν2 N2-broadening study[6].
The $\nu_2$ band intensity determined in the present work is 10.5% smaller than the value used in the 2004 HITRAN database [5].

References:


