

TEMPERATURE DEPENDENCE OF LINE MIXING IN THE P BRANCH OF THE ν_3 BAND OF METHANE

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The ν_3 band of methane is important for atmospheric experiments such as HALOE, but Voigt profiles are inadequate to model long atmospheric paths. Line mixing is the primary cause of the problem, but the Rosenkrantz approximation is violated. This means that the calculation of the spectrum must be performed with the full relaxation matrix. This has been done for much of the P branch with the multispectrum, nonlinear least squares fitting technique^a. The solution fitted over 60 spectra simultaneously and included spectra with a natural mix of isotopomers, spectra enriched in $^{13}\text{CH}_4$, spectra enriched in CH_3D , temperatures ranging from 210 K to room temperature, pressures from 1 Torr to 500 Torr, path lengths from 18 mm to 24 m, air broadened spectra and self broadened spectra. Direct minimization of the residuals as a function of self induced off diagonal relaxation matrix element coefficients, air induced off diagonal relaxation matrix element coefficients and the temperature dependence exponent of the air induced off diagonal relaxation matrix element coefficients was performed simultaneously with the spectral line position, intensity, width and shift parameters. The temperature dependence coefficients of the off diagonal relaxation matrix element coefficients range from 0.5 to 1.2, averaging about 0.8. Relationships between these coefficients and other spectral line parameters will be discussed.

^aD. Chris Benner, C. P. Rinsland, V. Malathy Devi, M. A. H. Smith, and D. Atkins, *JQSRT* **53**, 705-721 (1995).