TEMPERATURE DEPENDENCE OF LINE MIXING IN THE ν_3 BAND OF $^{12}CH_4$

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The temperature dependence of off diagonal relaxation matrix elements has been measured directly from transmission spectra. To our knowledge, this is the first such measurement. Previously a means of solving for the off diagonal relaxation matrix elements from least squares fits to laboratory spectra was achieved. Such a fitting proceedure involving mixing for more than two lines requires either constraints relating the off diagonal matrix elements or else fitting numerous spectra simultaneously[a]. The latter technique with a model of line mixing involving air and self broadening and temperature dependence was successfully applied to 16 air broadened spectra at room temperature for the P branch of the ν_3 band of methane. The 0.01 cm^{-1} resolution spectra were obtained with the Fourier Transform spectrometer at the McMath-Pierce telescope on Kitt Peak. The improvement over Voigt profiles and Rosenkrantz mixing was substantial and the residuals in the fit were close to the noise levels of the spectra. Twenty seven additional self broadened or low temperature spectra from the same interferometer and 0.003 cm^{-1} resolution spectra from the Fourier transform spectrometer in Orsay were added to the fits. These spectra produced residuals considerably larger than the noise level.

A model of line mixing is now used which decouples the air and self coefficients for the off diagonal relaxation matrix elements. Temperature dependence exponents analogous to, but independant of the broadening temperature dependence exponent may also be fit. The temperature dependence of the broadening averages around 0.7, close to the values found earlier for methane (and many other gases). The temperature dependence exponents of the off diagonal relaxation matrix elements, however, are in the range of about 1.2 to 1.6, considerably larger than that of the widths.

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