SPEED-DEPENDENT Ar AND N_2 BROADENING OF CH_4 FROM MULTISPECTRUM FITS

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In a recent tunable difference-frequency laser study [a] of collisional line shapes in the Ar- and N_2-broadened P- and R-branch manifolds of the ν_3 band of CH_4, we observed the effects of Dicke narrowing and line mixing, analyzed in the Rosenkranz (linear pressure) regime with proper sum and selection rules [b] imposed on the mixing coefficients. The spectral traces recorded at pressures up to 67 kPa were individually fit with appropriate linear constraints on the parameters not well determined at some of the pressures. Previously, Benner et al [c] had shown that simultaneous multispectrum fits of FTIR spectra of CH_4 alleviated the requirement for such constraints, but they obtained noticeable deviations between observed and calculated spectra, implying a nonlinear pressure dependence of some of the parameters, thought to result from line mixing beyond the Rosenkranz regime. However, contrary to results presented here last year by Benner et al [d], we have found that multispectrum fitting directly for the relaxation matrix still does not adequately fit the data or yield reliable off-diagonal coupling elements. Indeed, systematic residuals well above the experimental noise level are observed for the R0, R1, R2 and P2 lines not subject to line mixing at the pressures studied. We will show that a simple model incorporating speed-dependent broadening and shifting parameters significantly improves the fits for these uncoupled lines as well as for the coupled lines in higher J manifolds within the Rosenkranz regime.

[a] A. S. Pine, JQSRT 57, 157 (1997).
[b] A. S. Pine, JQSRT 57, 145 (1997).
[c] D. C. Benner, C. P. Rinsland, V. Malathy Devi, M. A. H. Smith and D. Atkins, JQSRT 53, 705 (1995).
[d] D. C. Benner et al, WF10, WF11, WF12, WF13, 53rd Internat. Symp. Molec. Spectrosc., Columbus, OH (1998).