ASYMMETRIES AND CORRELATIONS IN SPEED-DEPENDENT DICKE-NARROWED SPECTRAL PROFILES

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Asymmetric line shapes are known to result from correlations between velocity-changing (Dicke-narrowing) and dephasing (pressure-broadening) collisions [a] and from speed-dependent broadening and shifting coefficients arising from relative kinetic-energy-dependent collision cross-sections [b c d]. Here, we superpose the uncorrelated and correlated strong collision models of Rautian and Sobelman, similar to Joubert et al. [e], combined with various speed-dependent models in order to determine the contributions of these effects in measured spectral profiles. The sense of the asymmetries and the pressure and temperature dependencies of the detailed shapes, as well as physical constraints from diffusion and state-to-state rate measurements, all provide clues to the line shape parameters, their correlation and their speed dependence.

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