CORE LINE INTENSITY DEPLETION AND SUPER-LORENTZIAN FAR-WING ABSORPTION CAUSED BY THE FINITE DURATION OF COLLISIONS

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Physically realistic lineshape models that precisely describe molecular absorption spectra are critical to accurate spectroscopic intensity and amount-of-substance determination in both laboratory and remote sensing applications. We recently employed cavity ring-down spectroscopy to demonstrate a pressure-dependent broadening of the molecular lineshape that depletes intensity from the core of the line and redistributes it to its far wings leading to super-Lorentzian shapes [1]. This phenomenon is not modeled in the IUPAC-recommended Hartmann-Tran Profile [2], which was derived based on the impact approximation in which collision events are assumed to be instantaneous. However, molecular dynamics simulations show that the observed intensity depletion is due to the finite duration of collisions between the absorber and collision partner. Notably, typical collision time scales are orders of magnitude shorter than the characteristic time between collisions-the latter dominating the width of homogenously broadened lines. From Fourier analysis, the resulting spectral widths from these two mechanisms scale inversely with the respective time scales. Here we present high-precision cavity ring-down spectroscopy line intensity measurements of several transitions in the (3-0) band of N_2-broadened $^{12}C^{16}O$ exhibiting trends consistent with theoretical predictions. This effect is manifest as a pressure-dependent depletion in the experimental intensity obtained by integrating over only the core region of the absorption feature and its near wings.

This mechanism is expected to have a significant effect on the accuracy of molecular sensing across atmospherically relevant species. Here we discuss its physical basis and how it influences far-wing line shapes. We also consider how this effect may be included in remote sensing retrievals and line-by-line molecular databases.

[1] Z.D. Reed et al Phys. Rev. Lett. 130, 143001, 2023

[2] J. Tennyson et al Pure and Applied Chemistry 86, 12, 2014