

# Density-dependent intensity in CO<sub>2</sub> absorption spectra from requantized molecular dynamics simulations

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Intensity depletion, defined as the decrease of experimentally retrieved line intensities with gas density, is a significant non-impact effect in high-resolution molecular spectroscopy. Although the true line intensity is an intrinsic molecular property, experimentally determined values can be biased when standard line-shape profiles based on the impact approximation are used. This bias arises from the finite duration of intermolecular collisions, which redistributes part of the absorption from the line center to a broad underlying contribution, leading to an apparent reduction of the fitted intensity with density.

For carbon dioxide (CO<sub>2</sub>), a major atmospheric greenhouse gas, accurately characterizing this effect is essential for applications such as atmospheric remote sensing and precision gas metrology. Recent experimental studies have reported measurable intensity depletion in self-broadened CO<sub>2</sub> spectra in the near-infrared region, with typical values around 1% per atmosphere at room temperature and stronger effects at lower temperatures. These observations emphasize the need for a detailed physical understanding of density-dependent effects.

In this work, we investigate intensity depletion in self-broadened CO<sub>2</sub> spectra using requantized classical molecular dynamics simulations (rCMDS). This approach combines classical dynamics calculations based on accurate intermolecular potentials with a requantization procedure to generate absorption spectra for various pressure and temperature conditions. By analyzing these spectra using the Hartmann–Tran profile, we quantify the dependence of retrieved line intensities on gas density and temperature.

The simulations reproduce the main experimental trends, including the increase of depletion at lower temperatures and its dependence on rotational quantum number. The analysis provides insight into the underlying mechanisms, including the role of finite collision durations and the possible contribution of metastable dimers. Furthermore, the associated continuum absorption is characterized, and its evolution with temperature is determined and compared with available experimental data. Overall, these results highlight the limitations of impact-based line-shape models and the necessity of incorporating non-impact effects for accurate spectroscopic applications.

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