SUBPERCENT AGREEMENT BETWEEN AB INITIO AND EXPERIMENTAL COLLISION-INDUCED LINE SHAPES OF CARBON MONOXIDE PERTURBED BY ARGON

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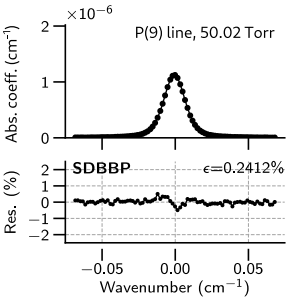
We present fully ab initio calculations of second-overtone rovibrational line shapes of carbon monoxide perturbed by argon[b]. The quantum mechanical scattering problem between the CO molecule and the Ar atom is solved numerically for an ab initio interaction potential. We use the generalized Hess method[c] to determine the spectroscopic cross sections which describe the effect of collisions on spectral lines. These cross section are then used to determine line-shape parameters of the Hartmann-Tran profile, its β-corrected[d] version and the speed-dependent billiard ball profile (SDBBP). We compare the generated line shapes with high-quality experimental line profiles[e] obtained at five pressures between 0.01 and 1 atm and obtain subpercent agreement in the whole pressure range. We show that the remaining discrepancies are mostly due to residual errors of ab initio pressure broadening and shift. We use the P(9) line data to compare two potential energy surfaces. We explain the differences in obtained pressure broadening and shift coefficients based on the properties of the surfaces.



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