FULLY *AB INITIO* SECOND-OVERTONE LINE SHAPES OF CARBON MONOXIDE PERTURBED BY ARGON: A COMPARISON WITH EXPERIMENT

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We present fully *ab initio* calculations of rovibrational line shapes of carbon monoxide perturbed by argon. 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 to determine the spectroscopic cross sections which describe the effect of collisions on a spectral line[a]. Using these cross sections, we determine line-shape parameters of the Hartmann-Tran profile and the speed-dependent billiard ball profile and generate the line profiles at the experimental conditions of the reference measurements. We compare the generated line shapes with high-quality experimental line profiles[b] obtained at five pressures between 0.01 and 1 atm and obtain sub-percent agreement in the whole pressure range. Calculations on the P(9) line are used to test the accuracy of a second Ar-CO interaction potential. The discrepancies between the results for both potentials and the experimental data are explained within the presented theoretical framework. Based on these results and quantum mechanical calculations of mass diffusion cross sections, we clarify the relations between the frequency of velocity-changing collisions and the complex Dicke parameter.

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[b] G. Kowzan, K. Stec, M. Zaborowski, S. Wójtewicz, A. Cygan, D. Lisak, P. Masłowski, and R. S. Trawiński, JQSRT 191, 46 (2017).