

MOLECULAR LINE-SHAPE MODELING FROM FIRST PRINCIPLES

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We present an *ab initio* approach to spectral line-shape modeling and the comparison of the results with experimental data. The most important collisional effects responsible for the formation of the shape of molecular lines are the phase- or state-changing collisions and velocity-changing collisions. Our calculations of these two contributions originate from the interaction potential.

We consider the case of molecular hydrogen perturbed by much heavier noble gas atoms (Ar). This system is atypical due to a strong Dicke narrowing and the strong speed dependence of broadening and particularly shifting. It is noteworthy that the first comparison of experimental data and *ab initio* calculations for this system (Raman Q(1) fundamental line) was made 25 years ago and resulted in fundamental discrepancy between the broadenings. Despite several attempts this problem has remained unresolved. We show that this discrepancy is caused by the use of oversimplified description of the model of the velocity-changing collisions¹. In our approach, instead of using phenomenological model, we describe the velocity-changing collisions by approximating the H₂-Ar interaction with a hard-sphere potential. The line-shape profile originating from this approach is called speed-dependent billiard ball profile (SDBBP)². We show, by referring to the collisional kernel derived from *ab initio* classical molecular dynamics simulations, that this approach reproduces the kinetics of the velocity-changing collisions much better than commonly used phenomenological models³. The description of the phase- or

¹[doi:10.1103/PhysRevA.91.052505](https://doi.org/10.1103/PhysRevA.91.052505), P. Wcisło, F. Thibault, H. Cybulski, R. Ciuryło, *Phys. Rev. A*, **91**, 052505, (2015).

²[doi:10.1103/PhysRevA.65.012502](https://doi.org/10.1103/PhysRevA.65.012502), R. Ciuryło, D. A. Shapiro, J. R. Drummond, A. D. May, *Phys. Rev. A*, **65**, 012502, (2002).

³[doi:10.1063/1.4892414](https://doi.org/10.1063/1.4892414), P. Wcisło, H. Tran, S. Kassi, A. Campargue, F. Thibault, R. Ciuryło, *J. Chem. Phys.*, **141**, 074301, (2014).

state-changing collisions was determined from quantum close-coupling calculations. Finally, we directly compare our *ab initio* profiles with experimental Raman spectra⁴ demonstrating agreement not only for the broadenings, but also for the whole line shapes.

⁴[doi:10.1063/1.480570](https://doi.org/10.1063/1.480570), F. Chaussard, X. Michaut, R. Saint-Loup, H. Berger, P. Joubert, B. Lance, J. Bonamy, D. Robert, *J. Chem. Phys.*, **112**, 158, (2000).
