ABSTRACT

This dissertation presents a study of theoretical molecular spectroscopy, aiming to provide highly-accurate spectral line profiles derived from first principles. Central to this work is the development and refinement of a methodology for simulating spectral line profiles using parameters obtained from *ab initio* quantum scattering calculations, and testing it for several molecular systems, including H_2-He, HD-He D_2-H_2 H_2-Ar and CO-Ar.

Our methodology bridges theoretical calculations with experimental results by allowing one to compare simulated and measured lines, thereby validating its accuracy against highly-accurate experimental spectra. This dissertation features a series of experimental tests, proving the accuracy of the simulated spectral line-shape profiles with several molecular collisional systems, at pressures spanning six orders of magnitude. With our quantum-scattering calculations and careful modelling of the spectral line shape, we reproduce these high-accuracy experimental spectra at sub-percent level of agreement.

In addition to validating the methodology against experimental data, this dissertation contributes to the field by generating expansive datasets of spectral line-shape parameters. We apply our methodology to create the first datasets of spectral line-shape parameters based entirely on the *ab initio* calculations. Our datasets allow one to simulate the shapes of the spectral lines beyond the Voigt model, taking into account the speed dependence of the broadening and shift, as well as the Dicke effect. This dissertation presents complete sets of rovibrational transitions of the helium-perturbed H_2 and HD molecules, as well as the most important lines of the HD-H_2 system.

The dissertation presents a novel approach of description the spectral lines in the regime of frequent velocity-changing collisions. Using the previous methods to simulate the spectral lines under these conditions requires carrying out exhaustive numerical simulations. This dissertation shows, that the line profiles in these conditions can be described by a simple Lorentz profile. We provide analytical expressions for effective width and shift of this profile.