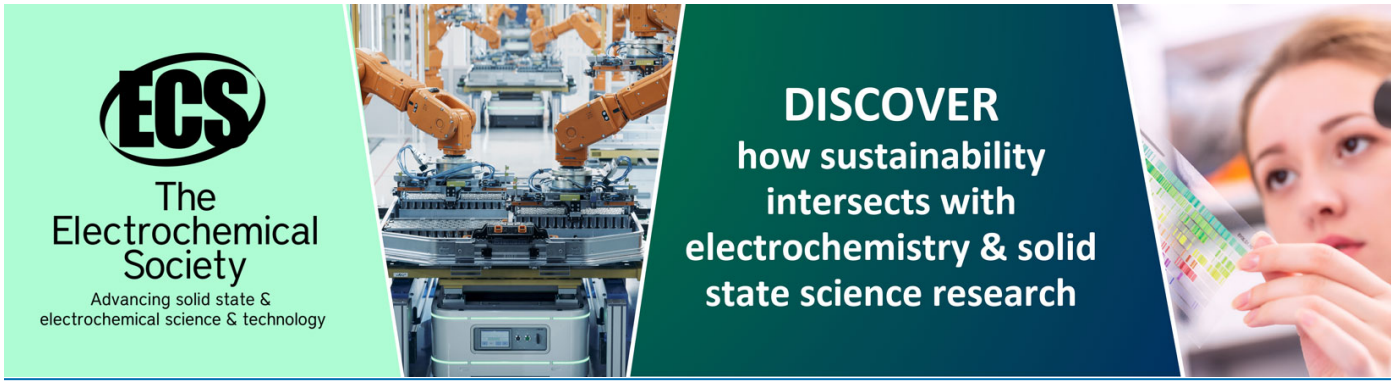
Ab *initio* quantum calculations of collisional effects in molecular spectra



Ab initio quantum calculations of collisional effects in molecular spectra

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Synopsis We present the methodology of obtaining the dataset of the beyond-Voigt line-shape parameters for spectroscopic databases from fully *ab initio* quantum-scattering calculations. It provides not only the pressure broadening and shift coefficients, but also their speed dependencies and the complex Dicke parameter. This approach is based on the calculations of the generalized spectroscopic cross section, resulting from the close-coupling equations solved for a given scattering system. The calculations were validated on accurate experimental spectra of the helium-perturbed hydrogen molecule.

In molecular spectroscopy, the collisions manifest themselves as a perturbation of the spectral line shapes. Proper treatment of these effects is crucial in the interpretation of highly accurate molecular spectra [1], analyses of the planetary atmospheres [2, 3] or studies of *ab initio* molecular interactions [4, 5, 6, 7]. Recently, a new structure of the most commonly-used spectroscopic database HITRAN [1, 8] has been proposed, enabling the beyond-Voigt line-shape effects to be represented. However, populating the entire database (all the bands, branches or temperature ranges) with purely experimental parameters is very difficult.

We present a new methodology of obtaining the line-shape parameters beyond the Voigt profile, based on *ab initio* quantum-scattering calculations. The process begins with the ultra-accurate potential energy surface (PES), calculated by means of the state-of-art quantum chemistry methods [5, 7]. Dynamical calculations on the PES are used to solve the close-coupling equations for a wide range of kinetic energies of the colliding pair. From the solutions of the close-coupling equations, the scattering matrices are constructed. Afterwards, the generalized spectroscopic cross sections are calculated for a given spectroscopic transition. Finally, the line-shape parameters are determined, taking into account various effects, such as the speed-dependence or the influence of the velocity-changing collisions. We provide the temperature dependence of the pressure broadening and shift coefficients, of their speed dependencies, as well as the complex Dicke parameters.

The methodology was successfully tested on the H_2-He system [7, 9], for which the calculations were validated by the ultra-accurate experimental data [10]. This approach was also used for several transitions of the helium- or self-perturbed D_2 [11, 12], and is currently being implemented on the systems of atmospheric interest, like CO-N_2 or O_2-N_2.

References

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