Energy- and Frequency-Corrected Rotational Relaxation Matrix for Binary Collisions between Linear Molecules

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From the pioneering work of Anderson [1] on, a variety of fully quantum and semi-quantum versions of line broadening theory has been elaborated that fostered progress in many spectroscopic applications (analysis of hot gases, combustion, planetary atmospheres, etc). Yet, in these approaches collisions are treated as instantaneous Markov events (scattering theory) whereas many well-known spectral signatures can be adequately interpreted only when collisions are supposed to evolve within a finite duration. The relaxation matrix Γ, a fundamental quantity of modern theory, then becomes dependent on frequency ω and its spectrum reflects the intracollisional dynamics [2]. However, the computational complexity makes the $\Gamma(\omega)$-matrix presently unattainable for direct first-principle calculations and, hence, development of its simplified dynamically-based models has the pivotal role for further progress.

So far, the $\Gamma(\omega)$ spectrum has been mimicked by two similar approaches, the frequency-extended, energy-corrected sudden approximation (ECSA) [3] and the fast-collision model [4], which tackled the relaxation problem of a linear rotator immersed into a monoatomic gas. Favourably, both models can be applied to arbitrary rotational spectra, i.e., ones associated with molecular scalars (isotropic polarizability), vectors (dipoles) and tensors (quadrupoles, etc) thus opening the way to multi-property fittings.

Here, extensions of these models to an important case of the nonMarkov collisions between two linear rotators are reported. These approaches allow straightforward generalizations to similar collisions between any molecular tops whose rotation is substantially slower than the relative translational motion.

References

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