

THEORY OF SPECTRAL MOMENTS FOR NON-MARKOVIAN RELAXATION MATRIX AND LARGE-BAND SPECTRA MODELLING

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Despite inarguable effects of collisions with finite durations on spectral signatures of molecular gases, their quantitative picture remains deficient and sets obstacles to the progress of terrestrial and venusian atmospheric studies urgently demanding higher and higher accuracy of spectroscopic data modelling. The currently used theoretical description of large infrared absorption bands including line mixing [1] is still based on the impact approximation viewing the molecular collisions as a Markovian process with no memory effects and valid solely near the line centres. Proper simulations of such collisional effects, in particular in the far spectral wings, should operate with the frequency-dependent relaxation matrix $\Gamma(\omega)$ [2] satisfying the double-sided fundamental sum rules [3] which hold only in the non-Markov domain.

Assuming fast dynamics patterns for colliding pairs of linear rotators, we have recently derived [4] a general formula for non-Markovian Γ -matrix elements expressed via the Laplace-transforms of the time-correlations functions of anisotropic interaction terms. Practical computations can be either done directly from the intermolecular potential energy surfaces (tedious procedure with a high CPU-cost) or based on shape models including some molecular characteristics as parameters. In particular, a simple and rapid way to Γ -matrix computations is indicated by the collision-induced shapes [5] which suggest suitable functional forms of the Laplace-transforms (successfully tested in the past for the case of a linear active molecule perturbed by atoms [6]) and contain the leading spectroscopic moments.

In the present paper, for the case of the linear active molecule colliding with another linear molecule, we use the theory of spectral moments to strictly fix parameters of the trial Laplace-transform functions. To this aim, the formulae of leading spectral moments, M_0 and M_2 are derived classically, with the full allowance for the anisotropy of interaction potential and distribution function. Computer codes are elaborated, taking advantage of the new moments' expressions much more simple than those appearing for the collision-induced spectra. The method is applied first to high-pressure Raman depolarized spectra of N_2 - N_2 characterized by a small number of anisotropic potential components and provides results comparing favourably with available measurements. After that, the much more anisotropic CO_2 - CO_2 interaction is considered, which is of fundamental interest for Venus atmosphere modelling.

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