Non-Markovian formalism of rotational relaxation of irreducible spherical tensors extended to infrared absorption bands of linear molecules

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Reliable theoretical description of line-mixing effects in infrared absorption bands of atmospheric molecules is one of key points of radiative transfer modeling. In the spectrum calculation, these effects are accounted for via the off-diagonal elements of the so-called relaxation matrix which characterizes the interactions of the spectroscopically active molecule with the bath.

The standard approach of Energy-Corrected Sudden (ECS) type used in the literature for modeling this matrix (see [1] for CO_2-N_2 and [2] for CO_2-CO_2) employs a quite large set of empirical parameters as well as an artificial "renormalization procedure" to ensure simultaneously the correct isolated-line widths and the fundamental relations of detailed balance and sum rules. Moreover, this method operates with the frequency-independent (Markovian) relaxation matrix, so that it is applicable only near the band centers where the impact approximation is valid (the required spectral-wing intensities are modeled purely empirically).

An alternative approach going beyond the impact approximation and operating with an essentially non-Markovian (i.e. frequency-dependent) relaxation matrix was developed about fifteen years ago to interpret the far-wing intensities of high-density rototranslational Raman spectra of linear molecules [3,4]. In contrast with traditional theoretical models, it uses a specifically chosen *symmetric* definition of the scalar product in the Liouvillian space, so that all required basic properties for the relaxation matrix are satisfied automatically, and the Boltzmann relation (detailed balance) for the spectral density is easily ensured by introducing a quantum asymmetry factor.

In the present paper we present an extension of this non-Markovian ECS method to the case of infrared absorption by linear molecules with stretching and bending vibrational modes. Examples demonstrating the internal coherence and performances of the model (correct reproducing of isolated line widths, possibility of line-shift calculations, realistic band shapes up to very high densities, etc. [5]) are given for the case of pure CO_2 absorption.

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