The **25th** International Conference on

High Resolution Molecular Spectroscopy

Bilbao 2018 September 3rd–7th

Bizkaia Aretoa – UPV/EHU

www.hrms-bilbao2018.com

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Classical trajectory simulation of collision–induced absorption spectra

Daniil N. Chistikov[3], Artem A. Finenko[1], Yulia N. Kalugina[2], Sergei E. Lokshtanov[1], Sergey V. Petrov[1], Andrey A. Vigasin[3]

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Various theoretical approaches (see e.g. [1–4]) are used in order to simulate collision- induced absorption (CIA) spectra, reliable knowledge of which is required nowadays for planetary climate modeling. Among these approaches the use of classical trajectory simulation is particularly promising since it makes possible relatively cheap evaluation of the spectral profiles using presently available ab initio calculated potential energy (PES) and induced dipole (IDS) surfaces.

The goal of the current paper consists of development and numerical realization of the procedure that enables simulation of the rototranslational CIA band profile for interacting monomers of arbitrary symmetry. We start by constructing a classical intermolecular Hamiltonian in a chosen body–fixed frame. Then the equations of motion are derived along with the trajectory density function. Methods of computer algebra are used to ensure correct results. Finally extensive classical trajectory calculations are carried out to compute the resulting CIA spectrum. Markov chain technique is applied to generate a set of initial points properly distributed in the phase space.

Simple anisotropic CO_2–Ar prototype system was first taken as an example. The spectra for this system were considered recently in Ref. [4] using classical trajectory analysis, though the formalism in Ref. [4] is significantly at variance from our approach.

Our trajectory simulation for concrete molecular pairs is supported by extensive ab initio PES and IDS calculations on a grid of angles and intermolecular separations followed by their analytical fit.

[1] Frommhold, L. Collision–induced absorption in gases. Cambridge University Press, 2006.
[2] Karman, T., et al. J. Chem. Phys. 2015, 142(8), 084306.
[3] Hartmann, J.M., et al. J. Chem. Phys. 2011, 134(9), 094316.
[4] Oparin, D., et al. J. Quant. Spectrosc. Radiat. Transfer, 2017, 196, 87.

The use of spectral moments to simulate rototranslational collision-induced bandshapes

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Reliable knowledge of collision-induced absorption (CIA) is presently in demand for climate modeling. Traditional theories of CIA bandshapes [1] are inadequate to fully take into account intermolecular anisotropy, though this is indispensable provided polyatomic monomers are considered. Recent advances in quantum and classical theory (see e.g. refs. [2-4]) are impressive though extremely expensive as both human and computer resources are concerned. Irrespective to theoretical formalism chosen to simulate the spectrum the use of spectral moments is important to quantify dipole-forbidden absorbance. On the one hand, spectral moments are defined as integrals of the properly weighted binary absorption coefficient. On the other hand, the zeroth and second moments can be calculated directly via statistical average of either squared induced dipole or Poisson bracket composed of the dipole and Hamiltonian derivatives, respectively.

Current paper aims at rigorous derivation of classical expression for the second spectral moment followed by its use in the spectral absorption bandshape simulation. Several pair systems are considered as examples, such as CO_2-Ar, CH_4-Ar, N_2-H_2, CO_2-H_2. For each of these systems rigorous classical Hamiltonians are first derived assuming rigid monomers. Explicit *ab initio* potential energy and induced dipole surfaces for the above mentioned pairs are either newly calculated or borrowed from the literature. Then the zeroth and second moments of rototranslational CIA bands are calculated as functions of temperature. These theoretically found values are then compared with the experimental ones, which are available for a limited number of molecular pairs at some selected temperatures only. For heteromolecular systems the CIA profiles are simulated assuming that the CIA band can be represented as a sum of properly weighted CIA profiles for pure gases as was previously attempted in ref. [5]. The importance of spectrum desymmetrization procedure is demonstrated in order to take into account quantum effects when light hydrogen molecule is part of a pair under consideration. Special attention is paid to analysis of the CO2-H2 rototranslational band, for which first experimental data were recently obtained [6].

[1] L. Frommhold. Collision-induced absorption in gases. Cambridge University Press, 2006
[2] T. Karman, E. Meliordos, *et al.* J. Chem. Phys., 2015, 142(8), p. 084306
[3] J.M. Hartmann, C. Boulet, and D. Jacquemart. J. Chem. Phys., 2011, 134(9), p. 094316
[4] D.V. Oparin, N.N. Filippov, *et al.* JQSRT, 2017, 196 p. 87
[5] R. Wordsworth, Y. Kalugina, *et al.* Geophys. Res. Lett., 2017, 44(2), p. 665
[6] M. Turbet, H. Tran, *et al.* submitted to Icarus, 2018