COLLISION INDUCED VELOCITY CHANGES FROM MOLECULAR DYNAMIC SIMULATIONS. APPLICATION TO THE SPECTRAL SHAPE OF THE Q(1) RAMAN LINES OF H_2/H_2

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Collision induced velocity changes for pure H_2 have been computed from classical dynamic simulations. The results have been compared with the Keilson-Storer[a] model from four different points of view. The first involves various autocorrelation functions associated with the velocity. The second and third give more detailed information, and are time evolutions of some conditional probabilities for changes of the velocity modulus and orientation and the collision kernels themselves. The fourth considers the evolutions, with density, of the half widths of the Q(1) lines of the isotropic Raman (1-0) fundamental band and of the (2-0) overtone quadrupole band. These spectroscopic data enable an indirect test of the models since velocity changes translate into line-shape modifications through the speed dependence of collisional parameters and the Dicke narrowing of the Doppler contribution to the profile. The results indicate that, while the KS approach gives a poor description of detailed velocity-to-velocty changes, it leads to accurate results for the correlation functions and spectral shapes, quantities related to large averages over the velocity. It is also shown that the use of collision kernels directly derived from MDS lead to an almost perfect prediction of all considered quantities (correlation functions, conditional probabilities, and spectral shapes). Finally, the results stress the need for very accurate calculations of line-broadening and -shifting coefficients from the intermolecular potential to obviate the need for experimental data and permit fully meaningful tests of the models.

[a] H. Tran, J.M. Hartmann *J. Chem. Phys.* **130**, 094301, 2009.