

# Molecular collisions : State-of-the-art calculations of inelastic collisions

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**Abstract.** We set up a framework for calculating in a precise and controlled way the collisional properties of several molecules of astrophysical meaning. The quantities that are relevant for astrophysics are rotational and vibrational quenching/excitation rates by means of collisions of H<sub>2</sub> with water and some organic molecules (HC<sub>3</sub>N, H<sub>2</sub>CO). We calculate those rates by means of successively determining a intermolecular potential energy surface and calculating inelastic cross sections and rates classically and/or quantum mechanically. These calculations are part of the European Union FP6 Molecular Universe program.

**Keywords.** Astrochemistry, molecular data

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## 1. Computational scheme

In order to understand the intensities of the various lines in molecular rotational spectra of astrophysical origin, we need to know rates of collisional excitation and deexcitation. Molecular hydrogen, H<sub>2</sub>, is by far the more frequent collision partner. Hence, in collaboration with several partners from the European Union 'Molecular Universe' FP6 program, we undertook in Grenoble a large computational program in order to determine some astrophysically relevant inelastic rates, including CO – H<sub>2</sub> rotational excitations, HC<sub>3</sub>N – H<sub>2</sub> and H<sub>2</sub>CO – H<sub>2</sub> rotational excitation and H<sub>2</sub>O – H<sub>2</sub> rotational and rovibrational excitations (see, e. g., Wiesenfeld *et al.* 2006). Calculating those rates is a twofold endeavor:

(a) Calculating the potential energy surface (PES) of the molecule *M* - molecular hydrogen collision. Since this PES is a non reactive PES, the *interaction* energy is very small compared with the internal energy of the two collision partners.

(b) Using this carefully calibrated PES to perform dynamical calculations in order to compute inelastic cross sections  $\sigma_{kk'}(E)$  or inelastic rates  $k_{kk'}(T)$ , where *k, k'* denote collectively the quantum numbers of the molecule under study, before and after collision.

## 2. Some Recent Results

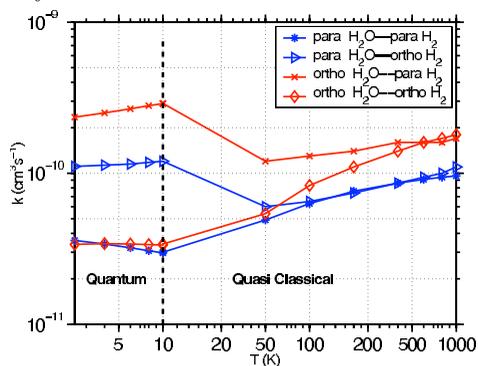
### 2.1. Water

The PES for the H<sub>2</sub>O – H<sub>2</sub> interaction was calculated in a very careful way (see Faure *et al.* 2005 and Valiron *et al.* 2008). The rigid body 5-dimensional interaction potential was determined first, in a very precise calculation, for *equilibrium* geometries of both the water and hydrogen molecules. Afterwards, a full 9-dimensional (including the vibrational coordinates of H<sub>2</sub> and H<sub>2</sub>O) was computed. It allowed us to determine firstly the collisional matrix elements and rates for vibrational quenching (Faure *et al.* 2005). Also, averaging the 9-dimensional PES over the ground state vibrational wavefunctions

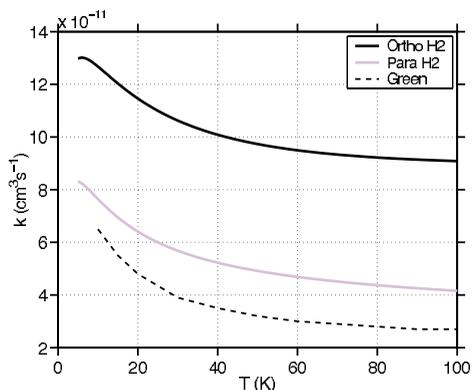
of hydrogen and water molecules allowed us to define PES with the two colliding partners in an *average* geometry, which differs significantly from the equilibrium geometry. The minimum of the PES was found to be at  $-235.14\text{ cm}^{-1}$ . This new, precise PES allowed us to compute rotational quenching rates, both quantum mechanically (Dubernet *et al.* 2006) and classically (Faure *et al.* 2007). A brief summary of some of our results may be found in Figure 1.

## 2.2. Formaldehyde

After CO and H<sub>2</sub>O, formaldehyde (H<sub>2</sub>CO) is the most common molecule in interstellar media, and the simplest to have both C and O atoms. Many reasons make the observation of formaldehyde in space important, but all can be resumed in one sentence: observation of formaldehyde rotational lines is one of the best tools we have to study astrophysical sources. We undertook the study of the H<sub>2</sub>CO–H<sub>2</sub> rotational (de)excitation. Like H<sub>2</sub>O, H<sub>2</sub>CO comes in ortho and para nuclear spin states. We compare our calculation with earlier ones by Green (1991), on the H<sub>2</sub>CO–He system. Properly scaled, it used to be employed as a model for the excitation by hydrogen molecules, because of its much lighter computational cost. Figure 2 shows that proper rates with H<sub>2</sub> are vastly different and may lead to some reassessments of formaldehyde line excitation processes.



**Figure 1.** Deexcitation rates for the fundamental transition in various ortho/para configurations. Ortho H<sub>2</sub>O  $1_{10} \rightarrow 1_{01}$  transition; para H<sub>2</sub>O :  $1_{11} \rightarrow 0_{00}$  transition. Para H<sub>2</sub>,  $J = 0$  only; ortho H<sub>2</sub>,  $J = 1$  only. Quantum calculations,  $T \leq 20$  K, Dubernet *et al.* (2006); Quasi classical calculations,  $T \geq 20$  K, Faure *et al.* (2007).



**Figure 2.** Deexcitation rates for the 2 cm transition  $2_{11} \rightarrow 2_{12}$  of ortho-H<sub>2</sub>CO. Comparison with scaled He calculations of Green *et al.* are included. See Troscompt *et al.* (2008).

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