Collisional excitation of water by hydrogen atoms

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ABSTRACT

We present quantum dynamical calculations that describe the rotational excitation of H$_2$O due to collisions with H atoms. We used a recent, high accuracy potential energy surface, and solved the collisional dynamics with the close-coupling formalism, for total energies up to 12 000 cm$^{-1}$. From these calculations, we obtained collisional rate coefficients for the first 45 energy levels of both ortho– and para–H$_2$O and for temperatures in the range T = 5–1500 K. These rate coefficients are subsequently compared to the values previously published for the H$_2$O / He and H$_2$O / H$_2$ collisional systems. It is shown that no simple relation exists between the three systems and that specific calculations are thus mandatory.

Key words: molecular data – molecular processes – scattering

1 INTRODUCTION

In astrophysical studies, water is an important molecule which has been observed in many different media, ranging from cold prestellar cores (Caselli et al. 2011, 2012), to warm intermediate and high mass star–forming regions (Cernicharo et al. 1994, 2006), circumstellar envelopes (see e.g. González-Alfonso & Cernicharo 1999; Decin et al. 2010) or extra–galactic sources (González-Alfonso et al. 2004). In these media, the emission observed for H$_2$O is often associated with shocked gas (Cernicharo et al. 1999; Flower & Pineau Des Forêts 2010; Neufeld et al. 2014). An extensive view of the water component in these regions can be found in the reviews by Cernicharo & Crovisier (2005) and by van Dishoeck et al. (2011, 2013).

In order to interpret the H$_2$O line intensities and infer the physical and chemical properties of the observed regions, the most reliable methodology relies on radiative transfer calculations. Indeed, for most of these objects, the water energy levels are often populated under non–LTE conditions. It is thus necessary to know the H$_2$O collisional rate coefficients with the relevant collisional partners, namely H$_2$, He, e$^-$ and H. Extensive collisional data sets are now available for the three former colliders (Daniel et al. 2011, Green et al. 1993; Faure et al. 2004; Faure & Josselin 2008). The collision between a H$_2$O molecule and H atom has been the subject of many studies (see e.g. Jiang et al. 2011; Fu & Zhang 2013). However, most of these works were only focused on reactive collisions and in the formation of the OH and H$_2$ molecules. To the best of our knowledge, no quantum state–to–state rate coefficients have been published for the inelastic collisions.

The molecules for which rate coefficients have been obtained with H as a collisional partner are limited. Indeed, in the case of molecules which have been detected in the interstellar medium, the only available calculations consider CO (Chu & Dalgarno 1973; Green & Thaddeus 1976; Balakrishnan et al. 2002; Shenler et al. 2007; Yang et al. 2013), CO$^+$ (Andersson et al. 2008), N$_2$ (Stoecklin & Voronin 2007), H$_2$ (Forrey et al. 1997; Flower & Roueff 1998; Wrathmall & Flower 2006; Lique et al. 2012) and HD (Flower & Roueff 1999; Roueff & Flower 1999). To date, no data are available for the inelastic rate coefficients of the H$_2$O / H collisional system. Therefore, these quantities are usually inferred by scaling either the H$_2$O / He (Nesterenok & Varshalovich 2014, e.g.) or H$_2$O / H$_2$ (Flower & Pineau Des Forêts 2010, e.g.) collisional rate coefficients, when needed. In the current study, we provide rate coefficients for the H$_2$O / H system and comment on the possibility of scaling the rates from other collisional systems to have an estimate of such rates. These collision rates are of particular importance in predicting and interpreting H$_2$O line emission in shocks propagating in the molecular interstellar medium. Indeed, in J–type shocks with velocities greater than 15–20 km/s, the temperature behind the shock front is sufficient to dissociate molecular hydrogen and there is a large range of temperature (300–2000K) where H$_2$O and atomic hydrogen coexist and where the cool-
ing can be dominated by H$_2$O line emission (Flower et al. 2003; Flower & Pineau Des Forêts 2010). Finally, in such regions, some water lines may exhibit population inversion. In order to interpret the emission from these masers, it is necessary to describe accurately the rates at which the upper and lower states are populated, which thus depends on the collisional rate coefficients used (Daniel & Cernicharo 2013; Hollenbach et al. 2013).

This article is organized as follows. In Sect. 2, we discuss the potential energy surface used in the current work. In Sect. 3, we present the quantum dynamical calculations and in Sect. 4, we discuss the current rate coefficients with respect to other collisional systems involving the water molecule.

## 2 POTENTIAL ENERGY SURFACE

A high accuracy potential energy surface (PES) for the interaction of H$_2$O with a hydrogen atom was computed recently by Dagdigian & Alexander (2013). The rigid-rotor approximation was employed with the water geometry kept fixed at its vibrationally averaged geometry. The reactive channel leading to OH + H is thus ignored and the PES is three-dimensional. The rigid-rotor approximation is valid at the temperatures investigated here since the activation energy for the reaction is high (~ 9300 K) and the rate coefficient is only $\sim 2 \times 10^{-14}$ cm$^3$ s$^{-1}$ at 1500 K (Baulch et al. 1992). Dagdigian & Alexander (2013) employed restricted coupled cluster calculations with inclusion of single and double excitations, augmented by a perturbative estimate of the connected triple excitations [RCCSD(T)]. A quadrupole zeta quality basis set was used, with the addition of mid–bond functions, and a counterpoise correction was applied to correct for basis set superposition error (BSSE). By exploiting symmetry, a total of 3800 nuclear geometries only were computed for atom-molecule separations ranging from 3 to 10 bohr. Full details about the PES and the H$_2$O–H system can be found in Dagdigian & Alexander (2013).

In order to interface the H$_2$O–H potential of Dagdigian & Alexander (2013) with the MOLSCAT scattering program (see below), it was necessary to perform a new angular expansion of the PES. Indeed, the coordinates used by Dagdigian & Alexander (2013) to describe the H$_2$O–H PES (see Fig. 1 of their paper) are different from those required by MOLSCAT for an atom-asymmetric top system. As a result, the 3800 nuclear geometries were converted to the MOLSCAT coordinate system where the z axis is the symmetry axis of water. This conversion corresponds in practice to a single rotation by an angle of 90° about the z axis, which is common to both sets of coordinates. The resulting new spherical coordinates were found in Dagdigian & Alexander (2013) with the MOLSCAT scatterer program (see Fig. 1 of their paper) are di

## 3 COLLISIONAL DYNAMICS

In order to solve the collisional dynamics, we used the MOLSCAT$^2$ code. Benchmark calculations were also performed with the HIBRIDON$^2$ code using the original fit of the H$_2$O–H PES by Dagdigian & Alexander (2013). We tested both codes at a few total energies and the cross sections were found to be essentially similar, within 5%. We performed the calculations in order to provide rate coefficients for the first 45 energy levels of the ortho– and para–H$_2$O symmetries, i.e. up to $J_{\text{K, \text{K'}}} = 7_{10}$ (E $\sim$ 1395 cm$^{-1}$) for o–H$_2$O and up to $J_{\text{K, \text{K'}}} = 7_{11}$ (E $\sim$ 1395 cm$^{-1}$) for p–H$_2$O. Calculations have been performed up to a total energy of 12 000 cm$^{-1}$ and we have used the close–coupling formalism over the whole energy range. This enables to provide converged rate coefficients for the range of temperature $T = 5 – 1500 K$. The parameters of the calculations, i.e. the number of H$_2$O energy levels, the integration step and the step between two consecutive energies were determined in order to ensure an accuracy better than 5% for the rate coefficients. These parameters are given in Tables 1 and 2. Additionally, we included a cut in energy for the H$_2$O energy levels, set to $E_{\text{max}} = 3000$ cm$^{-1}$ below total energy of 5000 cm$^{-1}$ and $E_{\text{max}} = 4000$ cm$^{-1}$ above this threshold.

The water energy levels are described using the effective Hamiltonian of Kyrd (1981), as previously done in our quantum calculations that dealt with the H$_2$O / H$_2$ system (Dubernet & Grosjean 2002; Grosjean et al. 2003; Dubernet et al. 2006, 2009; Daniel et al. 2010, 2011). We used the hybrid modified log-derivative Airy propagator of Alexander & Manolopoulos (1987), the change of propagator being set at 20 a.u. The reduced mass of the collisional system is $\mu = 0.954418234$ amu.

## 4 RATE COEFFICIENTS

The collisional de-excitation rate coefficients are calculated by averaging the cross sections with a Maxwell–Boltzmann distribution

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1 We note that in the MOLSCAT coordinate system, the $C_2$$_0$, symmetry of H$_2$O requires that $\mu$ is even, while in the original coordinate system, symmetry restricts the expansion to terms with $\lambda + \mu$ even.

2 J. M. Hutson and S. Green, MOLSCAT computer code, version 14 (1994), distributed by Collaborative Computational Project No. 6 of the Engineering and Physical Sciences Research Council (UK).

3 HIBRIDON is a program of packages for the time-independent quantum treatment of inelastic collisions and photodissociation written by M. H. Alexander, D. E. Manolopoulos, H.-J. Werner, B. Follmeg, Q. Ma, and P. J. Dag digian, with contributions by P. F. Vohralik, D. Lemoine, G. Corey, R. Gordon, B. Johnson, T. Orlikowski, A. Berning, A. Degli-Esposti, C. Rist, B. Pouilly, G. van der Sanden, M. Yang, F. de Weerd, S. Gregurick, J. Klos and F. Lique. More information and/or a copy of the code can be obtained from the website http://www2.chem.umd.edu/groups/alexander/hibridon/hib43.
that describes the distribution of velocity of the molecules in the gas (see e.g. eq. (2) in Dubernet et al. 2006)

\[ R_{β,β′}(T) = \left( \frac{8}{μ_2} \right)^{1/2} \int_0^{∞} \sigma_{β,β′}(E) E^{-E/k_B T} dE \]

(1)

where \( β \) and \( β′ \) are a set of quantum numbers that describe the initial and final states of water, \( k_B \) is the boltzmann constant, \( μ \) is the reduced mass of the colliding system and \( E \) is the kinetic energy. In Table 3 we give the de–excitation rate coefficients for levels up to \( J_{K_e,K′_e} = 3_{10} \), and for temperatures in the range \( T = 20–1000 \) K. The whole set of rate coefficients, with higher temperatures and with a more extended set of molecular levels will be made available through the LAMDA (Schöier et al. 2005) and BASECOL (Dubernet et al. 2013) databases.

In astrophysical applications, it is rather common to need rate coefficients which are not available. Therefore, it is quite usual to infer the rate coefficients of a colliding system from the values calculated for closely related system. The methodology which is generally used, even if its theoretical basis are questionable (Walker et al. 2014), consist in assuming that the cross sections \( σ_{β,β′}(E) \) which appear in eq. (1), are similar for both systems. The rate coefficients are then derived by correcting for the change in reduced mass, which lead to the scaling relationships: \( R_{β,β′}(T) = \sqrt{μ_1/μ_2} \times R_{β,β′}^{He}(T) \). As an example, in the current case, we could apply this methodology to infer the H₂O / H rate coefficients from either the H₂O / He or H₂O / p–H₂ rate coefficients. This would lead to rate coefficients such that \( R_{p–H_2}^{He} \sim 1.8 \times R_{β,β′}^{He} \) or \( R_{p–H_2}^{H_2} \sim 1.4 \times R_{β,β′}^{H_2} \).

In Table 3 we compare the current H₂O / H rate coefficients with the rate coefficients of the H₂O / He (Yang et al. 2013) and H₂O / p–H₂ (Dubernet et al. 2009) systems, for o–H₂O energy levels up to \( J_{K_e,K′_e} = 3_{10} \) (\( T \sim 285 \) K). In Fig. 1 we give the ratios of the current o–H₂O / H rate coefficients with the He rate coefficients of Green et al. (1993) and with the H₂ rates of Dubernet et al. (2009), for the first 45 o–H₂O energy levels. In the case of He, we used the rate coefficients from Green et al. (1993) since the most recent calculations by Yang et al. (2013) only consider the first 10 water energy levels. Additionally, as pointed out in the latter study, the impact of the new calculation is modest at high temperatures, the differences being lower than 30% above 200K. At lower temperatures, however, differences of up to a factor 3 can be found between the two sets. Considering the values taken by the ratios, it is obvious that no simple scaling relationship relate the various collisional rate coefficient sets, with differences that span various orders of magnitude. However, we note that the scatter of the ratios tends to decrease when increasing temperature. Moreover, for the largest rates at high temperature, the rate coefficients for the various colliders become similar, within a factor 2. This was expected since at high collision energy the scattering process becomes dominated by kinematics rather than specific features of the PES. Such conclusions were already reached for other collisional systems (see e.g. Roueff & Flower 1999 for the HD molecule). In summary, a dedicated calculation is a pre–requisite to accurately describe the collision with either H₂, He or H, especially at temperatures below ~1000 K.

5 CONCLUSIONS

We described quantum dynamical calculations performed at the close–coupling level of theory for the H₂O / H collisional system. As a result, we give collisional rate coefficients for the first 45 energy levels of both ortho– and para–H₂O and for temperatures in the range \( T = 5–1500 \) K. These calculations complete the sets already calculated for the water molecule, for which specific calculations are now available for all the colliders relevant to studies dealing with the interstellar medium, i.e. H₂, He, H and e⁻. In particular, we examined the possibility of emulating the H₂O / H rate coefficients by a simple scaling of either the H₂O / He or H₂O / H₂ sets and found that no simple relation enable to relate a set to another.

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Table 3. H$_2$O / H de-excitation rate coefficients ($R^H_{\beta,\beta'}$ in cm$^3$ s$^{-1}$, where the notation $x(y)$ stands for $x \times 10^y$) as a function of temperature and for H$_2$O levels up to $J_{K_a,K_c} = 3_{0,1}$. For each temperature, we give the ratio of the current rate coefficients with the He rate coefficients of [Yang et al. 2013] (second column), and with the para-H$_2$ rate coefficients of [Dubernet et al. 2009] (third column).

| Transition     | 20K | 40K | 60K | 80K | 100K | 120K | 140K |
|---------------|-----|-----|-----|-----|------|------|------|
| 1$_1,0$ → 0$_1,0$ |     |     |     |     |      |      |      |
| 2$_1,2$ → 0$_1,0$ |     |     |     |     |      |      |      |
| 2$_1,2$ → 1$_1,1$ |     |     |     |     |      |      |      |
| 2$_1,2$ → 0$_1,0$ |     |     |     |     |      |      |      |
| 2$_1,2$ → 1$_1,1$ |     |     |     |     |      |      |      |
| 3$_1,1$ → 0$_1,0$ |     |     |     |     |      |      |      |
| 4$_1,1$ → 0$_1,0$ |     |     |     |     |      |      |      |
| 5$_1,1$ → 0$_1,0$ |     |     |     |     |      |      |      |

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Figure 1. Ratios of the He (R_{He}^{β,β'} from Green et al. 1993) and H_{2} (R_{H_{2}}^{β,β'} from Dubernet et al. 2009) collisional rate coefficients with the o-H_{2}O rates calculated with H (R_{H}^{β,β'}) as a collider. These values are given as a function of the magnitude of R_{H}^{β,β'} and for temperatures of 20K (first column) 200K (second column) and 1000K (third column).

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