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New H₂O–H₂O collisional rate coefficients for cometary applications

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ABSTRACT

We re-introduce a semiclassical methodology based on theories developed for the determination of broadening coefficients. We show that this simple and extremely fast methodology provides results that are in good agreement with results obtained using the more sophisticated MQCT approach. This semiclassical methodology could be an alternative approach which allows to provide large sets of collisional data for very complex molecular systems. It saves time both on the determination of potential energy surfaces and on the collisional dynamical calculations. In addition, this paper provides more complete sets of rotational de-excitation cross-sections and rate coefficients of H₂O perturbed by a thermal average of water molecules. Those data can be used in the radiative transfer modelling of cometary atmospheres.

Key words: molecular data – molecular processes – comets: general.

1 INTRODUCTION

The scientific context of this work is related to the interpretation of water spectra in cometary atmospheres. Water is the main constituent of cometary ices, and molecules released in the coma by the sublimation of cometary ices undergo a wealth of excitation processes. These include collisions with water, collisions with electrons, infrared excitation of the fundamental bands of vibration by solar radiation, and radiative decay. Radiative transfer codes based on the escape probability method and on the accelerated Monte Carlo algorithm of Hogerheijde & van der Tak (2000) have been developed to interpret optically thick H₂O rotational lines (Bockelée-Morvan 1987; Bensch & Bergin 2004; Zakharov et al. 2007), and as far as radio observations are concerned, their interpretation relies on assumptions on collisional cross-sections since in most cases the field of view encompasses the regions out of equilibrium.

The task of obtaining sets of collisional rate coefficients for the de-excitation of water by water is currently an impossible task if one wishes to use the traditional close-coupling (CC) (Arthurs & Dalgarno 1960) or coupled states (CS; McGuire & Kouri 1974; Pack 1974) methods. Indeed CS calculations have been performed by Dubernet & Quintas-Sánchez (2019) for the HCN–H₂O system: the calculations were extremely lengthy and the final CS rate coefficients were converged at best at 20–30 per cent. We need to access whether it is necessary to use sophisticated methods to obtain collisional rate coefficients for the analysis of water spectra in cometary atmospheres, indeed other methods such as the semiclassical mixed quantum/classical theory (MQCT) method (Ivanov, Dubernet & Babikov 2014; Semenov, Dubernet & Babikov 2014; Semenov & Babikov 2017; Semenov, Mandal & Babikov 2020) or statistical methods (Loreau, Faure & Lique 2018a; Loreau, Lique

& Faure 2018b) could be used. Currently, the radiative transfer models (Bockelée-Morvan 1987; Bensch & Bergin 2004; Zakharov et al. 2007) use a global constant cross-section for excitation of water by water, and do not take into account any possible differences in state-to-state inelastic rate coefficients.

Therefore, the objective of this work is to re-introduce a fast and simple analytical semiclassical and statistical methodology (Boursier et al. 1993; Boursier, Ménard-Bourcin & Boulet 1994) in order to obtain the rotational de-excitation rate coefficients of H₂O perturbed by a thermal average of water molecules. The analytical semiclassical methodology uses the Robert–Bonamy (RB) method (Robert & Bonamy 1979) for the determination of broadening coefficients, this is the best and most used semi-analytical method for the determination of broadening coefficients. With such approaches, it is straightforward to calculate with the same parameters both the broadening coefficients and the de-excitation rate coefficients, and then to compare the theoretical broadening coefficients with the available experimental data. Buffa et al. (2000) already calculated H₂O–H₂O rotational inelastic rate coefficients, they used a semiclassical methodology adapted from the Tsao–Curnutte approach (Tsao & Curnutte 1962) and they limited the interaction to dipole–dipole interaction. Our approach uses a more sophisticated method and it extends the interaction to quadrupole interactions. In addition, the validity of the current results is tested against some preliminary results obtained with the more sophisticated MQCT method (Semenov et al. 2020) and the broadening calculations are tested against experimental results (Podobedov, Plusquellic & Fraser 2004). In the following section, we review in detail our methodology while the last section presents and discusses the results.

2 METHODS

We recall that the water molecules are asymmetric top molecules whose rotational energy levels are characterized by the rotational

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quantum number j_i , $\tau_i (=k_a - k_c)$. Identical to our previous publications involving the water molecule (Dubernet & Grosjean 2002; Grosjean, Dubernet & Ceccarelli 2003; Dubernet et al. 2006, 2009; Daniel et al. 2010; Daniel, Dubernet & Grosjean 2011; Dubernet & Quintas-Sánchez 2019), the H_2O energy levels and eigenfunctions are obtained by diagonalization of the effective Hamiltonian of Kyrö (1981), compatible with the symmetry of the potential energy surface used in the current work.

2.1 Outline of the collisional method

2.1.1 Transition probability

The dynamics of the collision is treated with a semiclassical approach in which the relative motion of the colliding molecules is handled classically when internal degrees of freedom, here only rotations of the two molecules, are treated quantum mechanically. We use the impact approximation that decouples the rotations from the relative motion, and to follow the approach described by Murphy & Boggs (1967). This approach leads to the de-excitation probability $P_{1,2}$ from a given (j_1, τ_1) rotational level of the target molecule, when the colliding molecule is characterized by (j_2, τ_2) , for a relative collision velocity v and an impact parameter b :

$$P_{1,2}(b, v) = 1 - \exp(-S_{j_1, \tau_1; j_2, \tau_2}(b, v)). \quad (1)$$

It can be shown that the expression of $S_{j_1, \tau_1; j_2, \tau_2}(b, v)$ corresponds to twice the efficiency function of Anderson's theory (Anderson 1949) [with $(j'_1, \tau'_1) = (j_1, \tau_1)$; Murphy & Boggs 1967], or to twice the outer term of Tsao & Curnutte (1962), or to twice the $S_{2,i}$ of Robert & Bonamy (1979).¹ From those expressions, the $S_{j_1, \tau_1; j_2, \tau_2}(b, v)$ term can be re-written as $\sum_{j'_1 \tau'_1} \sum_{j'_2 \tau'_2} S(j_1, \tau_1; j_2, \tau_2 \rightarrow j'_1, \tau'_1; j'_2, \tau'_2)(b, v)$. In the region of weak interaction where the $S_{j_1, \tau_1; j_2, \tau_2}(b, v)$ and the $S(j_1, \tau_1; j_2, \tau_2 \rightarrow j'_1, \tau'_1; j'_2, \tau'_2)$ are small, one can take the limit of the Taylor expansion of the exponential and

$$\begin{aligned} P_{1,2}(b, v) &= \sum_{j'_1 \tau'_1} \sum_{j'_2 \tau'_2} S(j_1, \tau_1; j_2, \tau_2 \rightarrow j'_1, \tau'_1; j'_2, \tau'_2)(b, v) \\ &= \sum_n S^{(n)}(b, v), \end{aligned} \quad (2)$$

with n is a simplified notation representing the n th transition $(j_1, \tau_1; j_2, \tau_2 \rightarrow j'_1, \tau'_1; j'_2, \tau'_2)$ for given values of $(j_1, \tau_1; j_2, \tau_2)$.

In the strong interaction region, for an impact parameter b smaller than a limit value b^* , there is no such 'natural partition' among state-to-state probabilities. Therefore, we adopt a method proposed by Rabitz & Gordon (1970) and already used by Boursier et al. (1993, 1994); this method is based on a 'statistical partition' which follows a simple partition rule: the sum of the state-to-state probabilities must be equal to the total probability and each individual state-to-state probability must be less than 1. This rule leads to defining arbitrary new $S^{(n)}(b, v)$ terms (Boursier et al. 1994) where

$$S^{(n)}(b, v) = \frac{\bar{S}^{(n)}(b, v)}{\sum_n \bar{S}^{(n)}(b, v)} (1 - \exp(-S_{j_1, \tau_1; j_2, \tau_2}(b, v))), \quad (3)$$

with $\bar{S}^{(n)}(b, v) = S^{(n)}(b, v)$ in the weak interaction region and with $\bar{S}^{(n)}(b, v) = 1$ for b smaller than b^* . Then in both interaction domain,

one can write equation (2) as

$$\begin{aligned} P_{1,2}(b, v) &= \sum_n S^{(n)}(b, v) \\ &= \sum_{j'_1 \tau'_1} \sum_{j'_2 \tau'_2} S'(j_1, \tau_1; j_2, \tau_2 \rightarrow j'_1, \tau'_1; j'_2, \tau'_2)(b, v). \end{aligned} \quad (4)$$

2.1.2 Cross-sections and rate coefficients

From this de-excitation probability (equation 4), one can calculate the total de-excitation cross-sections from the initial collider level j_1, τ_1 and initial perturber level j_2, τ_2 , at a given relative velocity v as

$$\sigma_{j_1, \tau_1; j_2, \tau_2}(v) = \int_0^\infty 2\pi db b P_{1,2}(b, v). \quad (5)$$

This total cross-section can be re-written as a function of state-to-state cross-sections $\sigma(j_1, \tau_1; j_2, \tau_2 \rightarrow j'_1, \tau'_1; j'_2, \tau'_2)(v)$ as

$$\sigma_{j_1, \tau_1; j_2, \tau_2}(v) = \sum_{j'_1 \tau'_1} \sum_{j'_2 \tau'_2} \sigma(j_1, \tau_1; j_2, \tau_2 \rightarrow j'_1, \tau'_1; j'_2, \tau'_2)(v), \quad (6)$$

with

$$\sigma(j_1, \tau_1; j_2, \tau_2 \rightarrow j'_1, \tau'_1; j'_2, \tau'_2)(v) = \int_0^\infty 2\pi db b S'(b, v), \quad (7)$$

where $S'(b, v)$ is defined in equation (4).

For the integral over the impact parameter we follow the kinematic model developed by Robert & Bonamy (1979). In that model the classical trajectory includes the influence of the isotropic potential at close range with the modulus of the relative distance given by

$$r(t) = [r_c^2 + v_c'^2 t^2]^{1/2} + o(t^2), \quad (8)$$

where r_c is the distance of closest approach and v_c' is the apparent relative velocity which is computed using the isotropic part of the potential [see equation 18 of Robert & Bonamy (1979) and section 2.2]. As a result the integral over the impact parameter can be replaced by

$$2\pi \int_0^\infty db b \rightarrow 2\pi \int_{r_{\min}}^\infty dr r_c \left(\frac{v_c'}{v}\right)^2, \quad (9)$$

where $r_{\min}(v)$ is the value of r_c for head-on collisions ($b = 0$). This formalism allows to treat both distant and close collisions on the same physical basis. A further approximation is used concerning the velocity Boltzmann average, where the cross-sections are considered as varying very little with velocity, so that the integral over relative velocity is reduced to the first moment of velocity at temperature T given by the usual expression $\bar{v} = (8k_B T / \mu \pi)^{1/2}$, with k_B the Boltzmann constant and μ the reduced mass of the collisional system. This leads to the following approximation for the integral over the impact parameter:

$$2\pi \int_0^\infty db b \rightarrow 2\pi \int_{r_{\min}}^\infty dr r_c \left(\frac{v_c'}{\bar{v}}\right)^2. \quad (10)$$

From the elementary state-to-state cross-sections (equation 7) one obtains the 'effective' state-to-state cross-sections between the target molecule's states, for a given state of the perturber $j_2 \tau_2$ and a given $\bar{v}$ (or temperature T) as

$$\hat{\sigma}_{j_2 \tau_2}(j_1 \tau_1 \rightarrow j'_1 \tau'_1)(\bar{v}) = \sum_{j'_2 \tau'_2} \sigma(j_1, \tau_1; j_2, \tau_2 \rightarrow j'_1, \tau'_1; j'_2, \tau'_2)(\bar{v}), \quad (11)$$

¹It should be noted that the S function of Buffa et al. (2000) (equation 1) corresponds to only once the efficiency function of Anderson (1949).

and then the ‘thermalized’ state-to-state de-excitation cross-sections at a given temperature T (or given $\bar{\nu}$), between the rotational states of the target molecule as

$$\bar{\sigma}(j_1\tau_1 \rightarrow j'_1\tau'_1)(T) = \sum_{j_2\tau_2} \rho(j_2\tau_2) \hat{\sigma}_{j_2\tau_2}(j_1\tau_1 \rightarrow j'_1\tau'_1)(T), \quad (12)$$

with $\rho(j_2\tau_2) = g_{j_2} e^{-\frac{E_{int}}{k_B T}} / Z(T)$, $Z(T) = Z_p(T) + 3Z_o(T)$ is the partition function over both para and ortho states of the colliding water molecule, g_{j_2} and E_{int} are the energy level degeneracy and the rotational energy related to rotational levels of the colliding H₂O molecule. These ‘thermalized’ state-to-state de-excitation cross-sections are functions of $\bar{\nu}$, thus of the temperature T . Those cross-sections are provided in table 1 of Buffa et al. (2000) and are the cross-sections that we give and discuss in the paper.

The thermalized state-to-state de-excitation rate coefficients between the rotational states of the target molecule at a temperature T are given by

$$\bar{R}(j_1\tau_1 \rightarrow j'_1\tau'_1)(T) = \bar{\nu} \times \bar{\sigma}(j_1\tau_1 \rightarrow j'_1\tau'_1). \quad (13)$$

The thermalized cross-sections and rate coefficients obtained with the above methodology do not satisfy the principle of detailed balance. Therefore, we introduce a further modification so that the principle of detailed balance be satisfied, this can be accomplished with either an arithmetic average

$$\bar{\sigma}_a^{av}(j_1\tau_1 \rightarrow j'_1\tau'_1)(T) = \frac{1}{2} \left(\bar{\sigma}(j_1\tau_1 \rightarrow j'_1\tau'_1) + \frac{\rho(j'_1\tau'_1)}{\rho(j_1\tau_1)} \bar{\sigma}(j'_1\tau'_1 \rightarrow j_1\tau_1) \right), \quad (14)$$

or a geometric average

$$\bar{\sigma}_g^{av}(j_1\tau_1 \rightarrow j'_1\tau'_1)(T) = \sqrt{\bar{\sigma}(j_1\tau_1 \rightarrow j'_1\tau'_1) \times \frac{\rho(j'_1\tau'_1)}{\rho(j_1\tau_1)} \bar{\sigma}(j'_1\tau'_1 \rightarrow j_1\tau_1)}, \quad (15)$$

with $\rho(j_1\tau_1)$ the energy level occupation probability of the target H₂O molecule, which is defined above for the colliding molecule. In both cases, the reverse thermalized collisional cross-sections $\bar{\sigma}^{av}(j'_1\tau'_1 \rightarrow j_1\tau_1)(T)$ can be obtained from forward rate coefficients by the usual formula:

$$\rho(j'_1\tau'_1) \bar{\sigma}^{av}(j'_1\tau'_1 \rightarrow j_1\tau_1) = \rho(j_1\tau_1) \bar{\sigma}^{av}(j_1\tau_1 \rightarrow j'_1\tau'_1). \quad (16)$$

The rate coefficients (equation 13) can be transformed with similar equations to equations (14), (15), and (16), replacing $\bar{\sigma}$ by $\bar{R}$. Those thermalized state-to-state rate coefficients can be directly used in the radiative transfer models of cometary atmospheres, as it is done in the study of the interstellar medium.

2.2 Analytical interaction potential

The interaction potential between the two asymmetric top molecules (labelled 1 and 2 for, respectively, the target and the colliding molecule), results from both long- and short-range forces. This interaction potential is modelled by the sum of atom–atom and an electrostatic contributions. The atom–atom potential is written as

$$V_{\text{at-at}} = 4 \sum_{i,j} \epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right],$$

where ϵ_{ij} and σ_{ij} are the Lennard–Jones (LJ) parameters for the interaction of the i th atom of the target molecule with the j th atom of the perturber molecule. The ϵ_{ij} and σ_{ij} of O–O and H–H are obtained

from tables 2 and 3 of Bouanich (1992), those of O–H are obtained by combination rules (Hirschfelder, Curtiss & Bird 1964) using the same O–O and H–H data. This leads to the following expression (Labani et al. 1987)

$$V_{\text{at-at}} = \sum_{i,j} \left(\frac{d_{ij}}{r_{ij}^{12}} - \frac{e_{ij}}{r_{ij}^6} \right), \quad (17)$$

with values $d(\text{O–O}) = 1.58 \times 10^{-15} \text{ J } \text{\AA}^{12}$, $e(\text{O–O}) = 2.12 \times 10^{-18} \text{ J } \text{\AA}^6$, $d(\text{H–H}) = 8.64 \times 10^{-17} \text{ J } \text{\AA}^{12}$, $e(\text{H–H}) = 2.32 \times 10^{-19} \text{ J } \text{\AA}^6$, $d(\text{O–H}) = 3.67 \times 10^{-16} \text{ J } \text{\AA}^{12}$, and $e(\text{O–H}) = 6.99 \times 10^{-19} \text{ J } \text{\AA}^6$.

The electrostatic contribution is expanded up to the quadrupole–quadrupole term and is given by equation 4 of Labani et al. (1987), with the dipole moment μ (D) = 1.8549 (Shostak & Muentner 1991; Antony, Neshyba & Gamache 2007) and the quadrupole moments (D $\text{\AA}$) along the principal axes of inertia being $Q_{aa} = 2.63$, $Q_{bb} = -0.13$, $Q_{cc} = -2.50$ (Verhoeven & Dymanus 1970; Labani et al. 1987; Antony et al. 2007). The isotropic potential parameters necessary for the trajectory calculations (equation 8) are obtained using a fit of the isotropic part of the above potential by an LJ function; the resulting LJ parameters are $\epsilon/k_B = 103 \text{ K}$ and $\sigma = 3.28 \text{ \AA}$.

3 RESULTS AND DISCUSSION

3.1 Detailed balance analysis

As indicated above the current method provides cross-sections (or thermalized rate coefficients) where the excitation and de-excitation processes do not satisfy the principle of detailed balance. This issue is also encountered for the infinite order sudden approximation (Secret 1975) used to obtain collisional rate coefficients and in the semiclassical methods. In order to provide detailed balance results, there are four ways to consider the results: we keep the raw calculated de-excitation cross-sections, we obtain the de-excitation cross-sections by detailed balance from the raw calculated endothermic cross-sections, we calculate either the arithmetic or the geometric averaged cross-sections (see equations 14 and 15). As there is no ‘perfect’ solution, for each exothermic transition we define a measure of errors by taking the relative difference between the arithmetic averaged cross-section and the maximum cross-section among the four cross-sections.

As expected the cross-sections are more sensitive to the detailed balance methodologies at the lowest temperature $T = 100 \text{ K}$. The red bullets on Fig. 1 generally display an error of less than 30 per cent for the largest de-excitation cross-sections (i.e. those above $50 \text{ \AA}^2$). More precisely for these transitions, the average of the relative errors (RM) is about 12 per cent with a standard deviation (STD) of 10 per cent at $T = 100 \text{ K}$. At higher temperatures, the RM is about 6 per cent with an STD of 5 per cent. It can be noted that the choice between arithmetic and geometric average is rather unimportant: the relative errors between those two methods for the largest cross-sections (blue crosses on Fig. 1) have an RM of 1 per cent with STD of 2 per cent at $T = 100 \text{ K}$; at higher temperature, the RM is about 0.5 per cent with an STD of 0.4 per cent. Therefore, in the following comparisons and results, we will use the cross-sections obtained by arithmetic averaging (equation 14). Tables 1 and 2 provide the subset of the arithmetic averaged cross-sections (equation 14) calculated with our full potential interaction; the complete calculated sets are provided as supplementary material. Tables 3 and 4 provide the corresponding rate coefficients; again the complete calculated sets are provided as supplementary material.

Figure 1. Relative errors as the function of the arithmetic cross-sections for the de-excitation transitions indicated in the supplementary documents. The four sub-figures correspond to the following temperatures: $T = 100$ K (a), $T = 200$ K (b), $T = 300$ K (c), $T = 400$ K (d). The red bullets are the relative difference between the arithmetic averaged cross-section and the maximum cross-section among the four cross-sections (see the text for further definitions). The blue crosses are the relative errors between the arithmetic and the geometric averaged cross-sections.

3.2 Comparison with Buffa et al. (2000) calculations

Buffa et al. (2000) calculations make a energy cut-off in the rotational states at 2000 cm^{-1} and include rotational wavefunctions with $j \leq 10$. This is not convenient for astrophysical applications as some rotational levels are missing below the rotational cut-off limit. Therefore, our strategy is to keep in the rotational basis set all the rotational levels below 2000 cm^{-1} , meaning that with the assurance of being able to calculate a correct detailed cross-section, the last transitions come from the level $j_2 = 11$, $k_a = 4$, $k_c = 7$ at $E = 1928.8201 \text{ cm}^{-1}$ for ortho- H_2O and from the level $j_2 = 10$, $k_a = 6$, $k_c = 4$ at $E = 1909.5252 \text{ cm}^{-1}$ for para- H_2O . Buffa et al. (2000) calculations do not include the quadrupole interaction, they estimate for their calculations that cross-sections below 20 Å^2 are irrelevant since it is likely that quadrupole interaction would be of that order. In order to access the influence of the quadrupole interactions, we performed test calculations of exothermic cross-sections with and without the quadrupole interactions. With the quadrupole interaction more collisional transitions are allowed and Table 5 shows that those additional cross-sections are usually small compared to the cross-sections induced by the dipole–dipole interaction. Nevertheless in the example of Table 5 we see that the magnitude of two quadrupole induced cross-sections are similar to dipole–dipole induced cross-sections, namely the $4_{31} \rightarrow 3_{31}$ and the $4_{32} \rightarrow 3_{30}$ transitions. Furthermore, Fig. 2 shows a general view of the cross-sections for the purely quadrupole transitions that we have kept (values above 0.1 Å^2). We see that they have significant values up to 100 Å^2 even at low values of the transition energies. Therefore, it is fully legitimate to take into account the quadrupole interactions. Fig. 3 shows that our results for the dipolar transitions are within 20–30 per cent of the results published by Buffa et al. (2000). As they do not provide a detailed description of their methodology we might consider the following differences: there appears to be an incorrect factor 2 of the denominator of their first equation (it is mentioned as a footnote in Section 2.1) and our statistical analysis (equation 3)

of transition probabilities does not exist in their methodology. In addition, the additional contribution from the quadrupole interactions has a 10 per cent effect on some of the dipolar transitions as is shown for some examples in Table 5. Finally increasing the isotropic well depth by 50 per cent we find that the cross-sections vary by less than 2 per cent: as expected for the water–water system the cross-sections are dominated by the long-range electrostatic interactions.

3.3 Note on the validity of results

The way to assess the validity of theoretical results is to compare them with experimental results, and the comparison should include error bars for both the theoretical and the experimental results. The error bars of theoretical collisional calculated data are usually assessed on the basis of convergence of theoretical parameters or/and with comparisons to other theoretical calculations for both the determination of the potential energy surfaces and of the dynamical calculations. The usual technique of testing the theoretical accuracy of collisional calculations is to explore the behaviour of a few transitions (in average a maximum of five transitions) at a few given collisional energies (very often 3 or 4 energies), and to deduce that the whole set of collisional data (usually hundreds of transitions) are obtained with an accuracy of N per cent. For example, for the $\text{CO}-\text{H}_2\text{O}$ system the CC calculations were tested for a s-wave (Kalugina et al. 2018) for a few transitions at a few energies as it is impossible to perform (CC) calculations with J larger than 3 with the current numerical codes. It can be shown that the most contributing total angular momenta are non-zero, and it can be expected that the convergence with respect to basis sets is different from the convergence of a s-wave as it involves more CS. Nevertheless such comparisons provide some reassuring insight. Based on a s-wave comparison with (CC) calculations an approximate and efficient statistical method (Loreau et al. 2018b) was used to validate results for the $\text{CO}-\text{H}_2\text{O}$ system (Loreau et al. 2018a). For the $\text{CO}-\text{H}_2\text{O}$ system it is interesting to see that the state-to-state cross-sections for s-wave for two transitions as a function of energy (fig. 1 of Loreau et al. 2018a) showed factors up to 1000 between the statistical method and the (CC) method for some energies, and that such huge differences disappeared once summed over the final states of the collider (fig. 3 of Loreau et al. 2018a). This result is in agreement with the convergence procedure adopted for $\text{HCN}-\text{H}_2\text{O}$ (Dubernet & Quintas-Sánchez 2019): it was argued that the convergence of a single cross-section is of very limited interest because the numerous resonances in cross-sections are washed out by the kinetic Boltzmann average, and further washed out when summing and averaging over the states of the collider in order to obtain the meaningful data which are the state-to-state thermalized rate coefficients. Therefore, the state-to-state thermalized rate coefficients calculations were tested with respect to the convergence of the rotational basis sets using CS calculations for a few transitions at a few energies. The strong couplings in the interaction region and the depth of the potential energy surface meant that they did not reach a full convergence while increasing the size of the basis sets, and they assumed in the end that the CS results would vary within 20 per cent around the given CS data (educated guess based on observation of the oscillations of the results) (Dubernet & Quintas-Sánchez 2019). Then another educated guess would certainly say that CS calculations are expected to be more accurate at higher collision energy (Phillips, Maluendes & Green 1995), thus at higher temperature. For a system such as water–water one could argue that the approach of testing the global rate coefficients, such as the one used for the $\text{HCN}-\text{H}_2\text{O}$ system, would be even more relevant as the water–water system is more complex.

Table 1. Collisional de-excitation cross-sections (equation 14) of ortho- H_2O by thermalized H_2O . The first column indicates the initial state of water ($j_1 k_a k_c$), the second column the final state of water ($j_1' k_a' k_c'$), the following columns provide the cross-sections ($\text{\AA}^2$) from $T = 100$ K to $T = 800$ K.

Initial	Final	100 K	200 K	300 K	400 K	500 K	600 K	700 K	800 K
1 1 0	1 0 1	390.7	187.3	132.8	108.2	94.2	85.8	80.0	75.4
2 2 1	1 0 1	28.6	19.7	16.4	14.0	12.3	11.1	10.2	9.5
2 2 1	1 1 0	278.5	191.1	160.0	138.8	123.2	111.5	102.6	95.7
2 2 1	2 1 2	272.9	132.1	93.2	75.9	65.1	57.4	51.8	47.5
2 1 2	1 0 1	424.9	195.3	133.8	108.0	93.0	82.7	75.1	69.4
2 1 2	1 1 0	39.4	22.9	16.9	13.6	11.7	10.4	9.5	8.8

Table 2. Collisional de-excitation cross-sections (equation 14) of para- H_2O by thermalized H_2O . The first column indicates the initial state of water ($j_1 k_a k_c$), the second column the final state of water ($j_1' k_a' k_c'$), the following columns provide the cross-sections ($\text{\AA}^2$) from $T = 100$ K to $T = 800$ K.

Initial	Final	100 K	200 K	300 K	400 K	500 K	600 K	700 K	800 K
1 1 1	0 0 0	235.6	155.6	112.9	88.9	74.8	66.1	60.2	56.0
2 0 2	0 0 0	35.3	24.0	18.6	15.6	13.6	12.2	11.2	10.4
2 0 2	1 1 1	131.5	96.1	72.5	57.6	48.0	41.5	37.0	33.8
2 1 1	1 1 1	68.3	40.8	32.2	27.4	24.4	22.3	20.8	19.7
2 1 1	2 0 2	204.0	136.0	107.7	91.9	81.2	73.6	68.0	63.8
2 2 0	0 0 0	19.4	13.5	11.5	10.3	9.4	8.6	8.0	7.5
2 2 0	1 1 1	172.9	149.2	130.7	115.5	103.7	94.7	87.7	82.1
2 2 0	2 0 2	9.5	4.7	3.1	2.3	1.9	1.6	1.4	1.3
2 2 0	2 1 1	212.5	169.1	127.2	100.1	82.6	71.1	63.2	57.4

Table 3. Collisional de-excitation rate coefficients (corresponding to the arithmetic average similar to equation 14) of ortho- H_2O by thermalized H_2O . The first column indicates the initial state of water ($j_1 k_a k_c$), the second column the final state of water ($j_1' k_a' k_c'$), the following columns provide the rate coefficients ($\text{cm}^3 \text{s}^{-1}$) from $T = 100$ K to $T = 800$ K.

Initial	Final	100 K	200 K	300 K	400 K	500 K	600 K	700 K	800 K
1 1 0	1 0 1	1.8948E-09	1.2848E-09	1.1160E-09	1.0491E-09	1.0221E-09	1.0190E-09	1.0262E-09	1.0348E-09
2 2 1	1 0 1	1.3879E-10	1.3489E-10	1.3768E-10	1.3582E-10	1.3349E-10	1.3178E-10	1.3081E-10	1.3048E-10
2 2 1	1 1 0	1.3509E-09	1.3111E-09	1.3445E-09	1.3463E-09	1.3359E-09	1.3246E-09	1.3166E-09	1.3128E-09
2 2 1	2 1 2	1.3238E-09	9.0633E-10	7.8275E-10	7.3582E-10	7.0585E-10	6.8214E-10	6.6418E-10	6.5112E-10
2 1 2	1 0 1	2.0610E-09	1.3395E-09	1.1242E-09	1.0478E-09	1.0085E-09	9.8224E-10	9.6377E-10	9.5196E-10
2 1 2	1 1 0	1.9104E-10	1.5739E-10	1.4163E-10	1.3218E-10	1.2681E-10	1.2359E-10	1.2173E-10	1.2090E-10

Table 4. Collisional de-excitation rate coefficients (corresponding to the arithmetic average similar to equation 14) of para- H_2O by thermalized H_2O . The first column indicates the initial state of water ($j_1 k_a k_c$), the second column the final state of water ($j_1' k_a' k_c'$), the following columns provide the rate coefficients ($\text{cm}^3 \text{s}^{-1}$) from $T = 100$ K to $T = 800$ K.

Initial	Final	100 K	200 K	300 K	400 K	500 K	600 K	700 K	800 K
1 1 1	0 0 0	1.1426E-09	1.0675E-09	9.4880E-10	8.6271E-10	8.1175E-10	7.8509E-10	7.7289E-10	7.6861E-10
2 0 2	0 0 0	1.7118E-10	1.6459E-10	1.5633E-10	1.5085E-10	1.4716E-10	1.4491E-10	1.4370E-10	1.4321E-10
2 0 2	1 1 1	6.3805E-10	6.5898E-10	6.0875E-10	5.5881E-10	5.2032E-10	4.9328E-10	4.7526E-10	4.6352E-10
2 1 1	1 1 1	3.3121E-10	2.7981E-10	2.7022E-10	2.6580E-10	2.6485E-10	2.6547E-10	2.6729E-10	2.6985E-10
2 1 1	2 0 2	9.8944E-10	9.3287E-10	9.0503E-10	8.9165E-10	8.8118E-10	8.7495E-10	8.7278E-10	8.7558E-10
2 2 0	0 0 0	9.4058E-11	9.2452E-11	9.6458E-11	9.9570E-11	1.0146E-10	1.0246E-10	1.0298E-10	1.0334E-10
2 2 0	1 1 1	8.3864E-10	1.0235E-09	1.0976E-09	1.1203E-09	1.1250E-09	1.1252E-09	1.1252E-09	1.1264E-09
2 2 0	2 0 2	4.5870E-11	3.2311E-11	2.5648E-11	2.2275E-11	2.0355E-11	1.9148E-11	1.8342E-11	1.7776E-11
2 2 0	2 1 1	1.0305E-09	1.1597E-09	1.0687E-09	9.7075E-10	8.9611E-10	8.4461E-10	8.1055E-10	7.8800E-10

Another way to validate an approximate method is to apply that method to simpler systems for which accurate calculations can be performed, then to use the same method with a more complex system and to infer its validity from the comparison on simpler systems (Loreau et al. 2018a, b). Though not providing any proved error bars for the more complex system the procedure is fair enough since there is no other way to provide insight on data error bars.

This short discussion shows on two examples of collisional systems involving water as one of the molecules, that the determination of error bars for theoretical calculations are far from being simple, that they are mostly educated guess provided for some transitions, that they are then generalized to a whole set of transitions, and that they are sometimes inferred from another system.

Experimental collisional cross-sections are hardly available, indeed 95 per cent of the published rate coefficients for inelastic

Table 5. De-excitation cross-sections ($\text{\AA}^2$) at $T = 200$ K from the $j_1 = 4 \tau_1 = -2$ ($k_a = 3 k_c = 1$) and $j_1 = 4 \tau_1 = -1$ ($k_a = 3 k_c = 2$) water levels. The $j'_1 k'_a k'_c$ are the final levels. ‘Our (All)’ stands for the cross-sections (equation 14) obtained with our model and our full interaction, ‘Our (Dip)’ stands for our model without the quadrupole interactions, ‘Buffa (Dip)’ stands for the cross-sections of Buffa et al. (2000) that includes the dipole interaction only.

$j'_1 k'_a k'_c$	Our (All)	Our (Dip)	Buffa (Dip)
Para-water initial level: $j_1 = 4 \tau_1 = -2$ ($k_a = 3 k_c = 1$)			
2 1 1	3.6	–	–
3 1 3	2.4	–	–
3 2 2	49.5	47.2	36.2
4 0 4	6.3	10.0	–
4 1 3	2.5	–	–
3 3 1	39.5	–	–
4 2 2	142.4	167.8	130.4
5 1 5	0.0	–	–
Ortho-water initial level: $j_1 = 4 \tau_1 = -1$ ($k_a = 3 k_c = 2$)			
2 1 2	2.1	–	–
3 0 3	1.9	2.4	–
3 1 2	6.2	–	–
3 2 1	65.5	65.7	49.5
4 1 4	0.8	–	–
3 3 0	39.6	–	–
4 2 3	139.8	159.3	110.4
5 0 5	3.5	5.5	–

Figure 2. Cross-sections ($\text{\AA}^2$) (equation 14) for purely quadrupole transitions as a function of the transition energy (in cm^{-1}) are displayed for different temperatures.

atom–molecule collisions (Dubernet et al. 2013) used in astrophysical applications lack of experimental comparisons. Nevertheless recently was reported a new molecular beam scattering experiments for the water–hydrogen system (Bergeat et al. 2020): the good agreement found with theoretical calculations validated both the employed potential energy surface (Faure et al. 2005) describing the $\text{H}_2\text{O}-\text{H}_2$ van der Waals interaction and the state-to-state rate coefficients (Dubernet et al. 2006; Daniel et al. 2011) calculated with this potential in the very low-temperature range needed for the modelling of interstellar media. This group has an excellent record (Bergeat et al. 2015, 2018, 2019; Chefdeville et al. 2015; Stoecklin et al. 2017; Klos et al. 2018; Naulin & Bergeat 2018) of producing useful comparisons to theoretical inelastic collisions that are of relevance to astrophysical applications, and hopefully they will be able to handle other collisional systems such as other molecule–water systems.

Figure 3. Relative differences (per cent) between our cross-sections (equation 14) and the cross-sections published by Buffa et al. (2000) as a function of our cross-sections ($\text{\AA}^2$). The data involve dipolar transitions only. The reference values are our cross-sections and 100 per cent difference corresponds to zero value of cross-section in the work of Buffa et al. (2000).

Experimental results for molecule–water systems are more commonly dealing with pressure broadening cross-sections as water is a central molecule to the planetary atmospheres such as the Earth (collisions with Earth atmospheric molecules such as N_2 , O_2), Jupiter (collisions with H_2 and He), and exoplanets. Therefore, many experimental and theoretical broadening results are available in the energy range pertinent to those applications. As an example useful for astrophysics, Faure et al. (2013) were able to test and prove the quality of collisional $\text{H}_2-\text{H}_2\text{O}$ rate coefficients by comparing above 200 K experimental broadening coefficients to approximate theoretical broadening coefficients obtained from those accurate de-excitation collisional rate coefficients (Dubernet et al. 2009; Daniel et al. 2011, 2010). Above 200 K they tested the validity of the approximate broadening coefficient versus exact quantum calculations of the broadening coefficients. It is interesting to note that they used the random phase approximation (Baranger 1958) that allows to write the broadening coefficients as half the sum of the total de-excitation rate coefficients from the initial and the final broadened transition; such concept underlies the theory used in the current semiclassical approach. Therefore, using the concept of inferring results from one system to another one would expect that the current semiclassical results and those of Buffa et al. (2000) had error bars decreasing with temperature.

Therefore, in order to give an honest insight into the validity of our current results, and not pretending to determine accurate error bars, we provide in the following sections a comparison with experimental results of self-broadening calculations and a comparison with a more accurate methodology directly designed to calculate inelastic collisional cross-sections and inelastic rate coefficients.

3.4 Comparison with experimental results for pressure broadening

As experimental state-to-state collisional cross-sections are not available, we calculate the self-broadening linewidth of water for all the pure rotational lines in the $12-52 \text{ cm}^{-1}$ range, that have experimentally been explored for three temperatures by Podobedov et al. (2004). As well outlined by these authors, measurements in the microwave or far-infrared region are difficult and very few experimental studies are reporting temperature dependence of self-

Table 6. FWHM (cm⁻¹ atm⁻¹) of H₂O broadened by H₂O with experimental results (Podobedov et al. 2004) (‘Obs’) and our calculated values (‘Full calc’). The relative percentage difference is given in the last column. The first column indicates the initial state of water ($j_1 k_a k_c$) and the second column the final state of water ($j_1' k_a' k_c'$).

Initial	Final	Obs	Full calc	Obs-calc (percent)
<i>T</i> = 263 K				
5 3 2	4 4 1	0.86 ± 0.02	0.8246	4.1
4 2 2	3 3 1	0.95 ± 0.02	0.9498	0.0
4 1 4	3 2 1	1.07 ± 0.01	1.0597	1.0
5 2 4	4 3 1	0.92 ± 0.02	0.9162	0.4
7 4 3	6 5 2	0.85 ± 0.02	0.7466	12.1
6 3 3	5 4 2	0.99 ± 0.02	0.8755	11.6
<i>T</i> = 300 K				
5 3 2	4 4 1	0.800 ± 0.003	0.7585	5.2
4 2 2	3 3 1	0.910 ± 0.009	0.8573	5.8
4 1 4	3 2 1	0.970 ± 0.008	0.9516	1.9
5 2 4	4 3 1	0.870 ± 0.005	0.8389	3.6
7 4 3	6 5 2	0.760 ± 0.005	0.6838	10.0
6 3 3	5 4 2	0.890 ± 0.005	0.7920	11.0
<i>T</i> = 340 K				
5 3 2	4 4 1	0.710 ± 0.004	0.6977	1.7
4 2 2	3 3 1	0.840 ± 0.007	0.7779	7.4
4 1 4	3 2 1	0.870 ± 0.005	0.8579	1.4
5 2 4	4 3 1	0.790 ± 0.003	0.7703	2.5
7 4 3	6 5 2	0.670 ± 0.004	0.6295	6.0
6 3 3	5 4 2	0.810 ± 0.004	0.7195	11.1

broadening of rotational lines of water. Table 6 shows that our theoretical pressure broadening linewidths are within 5 per cent of the experimental results for 4 transitions, and about 10 per cent for the transitions from the highest rotational levels for whichever temperature. It is expected (Antony et al. 2007) that the RB method (Robert & Bonamy 1979) provides excellent predictions for line broadening of water. These comparisons give an indirect assessment on the validity of our collisional results even if pressure broadening linewidths are more averaged than the thermalized state-to-state collisional rate coefficients. The results are reassuring with respect to the potential energy surface used in the calculations, at least in the temperature range tested by the experimental results, and with respect to the RB methodology. Indeed both the line-broadening calculations and the state-to-state cross-sections are obtained using this same formalism.

4 COMPARISON WITH MQCT CALCULATIONS

We decided to carry out one more independent test of our method by comparing versus an alternative recently developed MQCT (Semenov & Babikov 2017). Using MQCT code (Semenov et al. 2020), we carried out a set of auxiliary calculations of excitation and quenching of several states of para- and ortho-H₂O by collisions with another H₂O molecule. The target and quencher molecules in these MQCT calculations were considered distinguishable, and a thermal distribution of rotational states was assumed for the quencher H₂O at *T* = 800 K. Further details of our MQCT calculations are provided in Appendix A; the results are presented in Fig. 4. One can see that, overall, the results of semiclassical theory developed here and of the MQCT method are in good semiquantitative agreement. Importantly, both methods predict the same propensity pattern for state-to-state transitions in H₂O + H₂O collisions, namely: the transitions with odd $\Delta k_a = 1$ are characterized by systematically

Figure 4. Comparison of results of the semiclassical method developed in this work (red, Table 1) versus those obtained using MQCT method (black) for para-H₂O (left) and ortho-H₂O (right). The data of Buffa et al. (2000) are provided in green. Thermal distribution of the rotational states in the quencher H₂O and the collision energy correspond to *T* = 800 K.

larger cross-sections, whereas the transitions with even $\Delta k_a = 0$ and 2 always exhibit smaller cross-sections. Moreover, this trend is found in both para-H₂O and ortho-H₂O. For several transitions that describe quenching to the ground state, such as 111→000, 202→000 and 220→000 in para-H₂O and 212→101 in ortho-H₂O, the two methods gave very similar values of cross-sections (less than 5 per cent difference). Larger differences are typical for other transitions presented in Fig. 4. In particular, we found that for the transition 220→202 in para-H₂O the MQCT code gave much larger value of cross-section than the semiclassical method presented in this paper. However, we want to stress that one should not expect a perfect agreement because, first of all, the MQCT code uses a different built-in potential energy surface of Szalewicz and co-workers (Jankowski et al. 2015) and therefore some differences are expected. Secondly, MQCT calculations for H₂O + H₂O system are very demanding computationally and therefore they were carried out with a relatively small basis set and with relaxed convergence criteria (see Appendix A). For the sake of comparison, the results of Buffa et al. (2000) are included in Fig. 4. Transitions dominated by the quadrupole interaction ($\Delta k_a = 0$ and 2) are zero in Buffa et al. (2000) results and for most of the $\Delta k_a = 1$ transitions, but not all, our results seems closer to the MQCT results. One clear advantage of the analytical semiclassical method is its extremely low computational cost, which makes it a handy computational tool.

5 CONCLUSIONS

An analytical, semiclassical and statistical methodology has been re-introduced in order to provide large sets of collisional inelastic rate coefficients for cometary applications at a very low computational cost. This method has been applied to the water–water system which is both central and one of the most complicated system for cometary applications. The method is more sophisticated than the one proposed by Buffa et al. (2000), and could be used for other systems. The inelastic rate coefficients obtained with our method compare well with MQCT calculations at the temperature where the MQCT calculations were feasible, and some comparison with broadening cross-sections are quite good. Of course those comparisons do not

give any accurate error bars, but they still show that our method is reasonable. Our sets of collisional rate coefficients are more complete than Buffa et al. (2000)'s results because they include the quadrupole interactions and they compare in general better with MQCT calculations for the restrained comparison performed in this paper. As mentioned the complete sets of de-excitation cross-sections and rate coefficients are provided as supplementary documents and the rate coefficients will be available in the BASECOL data base (Dubernet et al. 2013). It would be useful to modify the radiative transfer models of cometary atmospheres in order to take into account these state-to-state rate coefficients. This way, we would be able to assess the need to calculate more sophisticated cross-sections.

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DATA AVAILABILITY

The cross-sections and rate coefficients tables are available online as supplementary materials. The rate coefficients data and the rotational energy levels will be made available on the BASECOL data base (basecol.vamdc.org). This data base is accessible from the VAMDC infrastructure (www.vamdc.org, Dubernet et al. 2016) that follows FAIR (Findability, Accessibility, Interoperability, and Reuse) and open access principles.

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SUPPORTING INFORMATION

Supplementary data are available at [MNRAS](https://www.mnras.org) online.

Table 3. Collisional de-excitation rate coefficients (corresponding to the arithmetic average similar to equation 14) of ortho-H₂O by thermalized H₂O.

Table 4. Collisional de-excitation rate coefficients (corresponding to the arithmetic average similar to equation 14) of para-H₂O by thermalized H₂O.

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Figure A1. Opacity functions for $m = 0$ (red) and $m = 1$ (black) for the initial state $1_{11}0_{00}$.

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APPENDIX A: NUMERICAL DETAILS OF MQCT CALCULATIONS

A set of MQCT calculations was carried out for one collision energy $U = 533.3 \text{ cm}^{-1}$ that corresponds to thermal energy at $T = 800 \text{ K}$, which is the last column in Tables 1 and 2. We focused on transitions between the states $j = 0, 1$, and 2 of the target water molecules (in order to compare with Tables 1 and 2). Since cross-sections are summed over the final states of the quencher molecule, the ‘Billing correction’ of the collision energy U was not employed. ODEINT integrator was used to propagate MQCT trajectories. First of all, we found that largest contributions to the transition probability come from the relatively large impact parameters b and correspond to the long-range interaction between the two water molecules. We determined that in these conditions we can include only 1 out of 20 values of the orbital angular momentum quantum number, i.e.

$\Delta L = 20$ (1 out of 20 trajectories is propagated, skipping 19). The error associated with this approximation is about 6 per cent of the cross-section value on average (4–8 per cent for various individual transitions). We found, however, that we must start these trajectories relatively far, at a distance of $R_{\text{max}} = 100 \text{ Bohr}$ between the molecules, and we must cover a broad range of impact parameters, up to $b_{\text{max}} = 60 \text{ Bohr}$. Examples of opacity functions are presented in Fig. A1.

To be consistent with the semiclassical method we have opted to treat the two water molecules as distinguishable and count their degenerate states as belonging to the same channel. Namely, if before the collision the initial states are 0_{00} and 1_{11} for molecules 1 and 2, but after the collision the states are 1_{11} and 0_{00} for molecules 1 and 2 (i.e. swapped), we say that the corresponding probability contributes to the elastic channel, and is not counted in the inelastic transition probability. Note that normally the probability of such transitions (i.e. $0_{00} 1_{11} \rightarrow 1_{11} 0_{00}$) is large since the states are degenerate. With this ansatz, we tested convergence of the thermally averaged cross-sections with respect to the basis set size of the target molecule and found that if we are looking at the transitions between $j = 0, 1$, and 2 then excluding the states with $j = 3$ and above leads to the differences of cross-section values about 5 per cent on average (0.3–13 per cent for individual transitions). It is therefore safe to exclude $j = 3$ and above from the basis set of the target molecule. Then we tested convergence of cross-sections with respect to the basis set size of the projectile molecule and found that this is the most demanding aspect. First, we included the states up to $j = 2$, then up to $E = 200, 250$, and finally 300 cm^{-1} , but we cannot really claim that the result is converged. Indeed, this part of spectrum is within the collision energy. Adding more states to the basis set of the quencher does affect cross-sections. Including more states is computationally expensive, so we stopped without reaching convergence. The results presented in the paper were obtained with the basis set that includes six lowest lying states for the target H_2O (up to $E = 200 \text{ cm}^{-1}$) and 10 lowest lying states of the quencher H_2O (slightly above $E = 300 \text{ cm}^{-1}$). The overall convergence is estimated to be of the order of 25 per cent of the cross-section values. Numerical cost of these calculations exceeded 100 000 CPU hours at the Cori machine at NERSC.

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