A full nine-dimensional potential energy surface for hydrogen molecule−water collisions

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Abstract

The hydrogen and water molecules are ubiquitous in the Universe. Their mutual collisions drive water masers and other line emission in various astronomical environments, notably molecular clouds and star forming regions. We report here a full nine-dimensional interaction potential for H_2O-H_2 calibrated using high-accuracy, explicitly correlated wavefunctions. All degrees of freedom are included using a systematic procedure transferable to other small molecules of astrophysical or atmospherical relevance. As a first application, we present rate constants for the vibrational relaxation of the v_2 bending mode of H_2O obtained from quasi-classical trajectory calculations in the temperature range 500−4000 K. Our high temperature ($T \geq 1500$ K) results are found compatible with the single experimental value at 295 K. Our rates are also significantly larger than those currently used in the astrophysical literature and will lead to a thorough re-interpretation of vibrationally excited water emission spectra from space.

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I. INTRODUCTION

Since its discovery in interstellar space in 1969 [1], water vapor has been detected in a great variety of astronomical objects using both Earth-based and spaceborn observations (for a review, see [2]). Water is now known to be the third most abundant molecule in the Universe, after H_2 and CO. Many rotational and rotation-vibration transitions have been detected including many which yield spontaneous microwave amplified stimulated emission of radiation (maser). Masers are prominent in star-forming regions where water plays a central role in the chemistry and cooling of the molecular gas during protostellar collapse [3]. The modeling of water line emission has thus received particular attention for many years. Collisional rates are essential for describing energy exchange processes responsible for thermal balance and line formation in astronomical environments. Spectral features, such as maser emissions, are generally produced in low-density conditions far from thermodynamic equilibrium and through a complex competition between radiative and collisional processes. A detailed knowledge of rates for all microscopic processes that drive the populations of the emitting levels is thus necessary to interpret the observed spectra. Despite some recent progress in laboratory measurements of state-to-state collision rates [4], astrophysical models still rely heavily on theoretical predictions owing to the vast network of relevant states which span a wide range of excitation energies.

The present work is particularly motivated by the mission of the European Space Agency's Herschel Space Observatory 3.5 m telescope to be launched in mid-2007. Herschel will observe water lines in regimes from the cold interstellar medium to stellar, planetary and cometary atmospheres, with unprecedented sensitivity, spectral resolution and calibration precision. The detailed interpretation of these spectra will critically depend on the accuracy of the available collisional rate constants. Here we report calculations of rates for vibrational relaxation of water by hydrogen molecules, the dominant collision partners in molecular clouds [44]. The H_2O-H_2 collision complex is also of fundamental interest since it is one of the simplest systems in which water exhibits a dual identity as either proton donor or acceptor [5]. Moreover, the vibrational relaxation of water is of great interest for modeling atmospheric processes and for understanding high temperature dynamics of combustion product gases [6].

The only available theoretical collisional rates for H_2O-H_2 collisions were obtained by Phillips et al. [7] for rotational excitation in the temperature range $20-140$ K. Recently, Dubernet and Grosjean [8] extended these calculations down to 5-20 K where resonances were found to greatly influence the excitation rates. At such temperatures, collisional cross sections are particularly sensitive to the details of the potential energy surface (PES) [9]. Here, a new PES is computed for H_2O-H_2 which significantly improves the earlier PES's [10–12]. In particular, the Van der Waals minimum region of the interaction is determined with a near-spectroscopic precision (≈ 1 cm^{-1}). To achieve this accuracy, we not only performed very elaborate non-relativistic electronic structure calculations, but also considered the vibrational effects resulting from the four internal degrees of freedom of the molecules (three for H_2O and one for H_2). This latter correction is routinely neglected in high-dimensional ($n>3$) PES calculations. Only recent advances in theoretical chemistry and computer technology enabled us to calculate the full nine-dimensional intermolecular potential with such precision.

II. POTENTIAL ENERGY SURFACE CALCULATIONS

Within the Born-Oppenheimer approximation, scattering cross sections or bound rovibrational states are obtained by solving for the motion of the nuclei on an "electronic" PES, which is independent of the masses of the nuclei. Recent studies have demonstrated that computational techniques employing advanced treatments for both electronic and nuclear motion problems have the ability to rival the accuracy of experimental data [13–15]. These studies all employed convergent hierarchies of basis sets and correlation methods to solve the electronic structure problem.

In contrast to conventional calculations, correlated methods that include explicitly the inter-electronic coordinates into the wave function can describe properly the electron-electron correlation cusp (as pioneered by [16]) and offer a direct way of reaching the basis set limit values within a single calculation, i.e. without extrapolation. Among various explicitly correlated methods [17], the R12 coupled cluster theory with singles, doubles and perturbative triples (CCSD(T)-R12) [18] is computationally practical [19] and proved highly accurate [15, 20–22], in particular using adequate R12-suited basis sets (as in [23, 24] for H to Ne). Generalizing the idea of Kutzelnigg [25], in CCSD(T)-R12 one takes care of the correlation cusp by inclusion of linear terms in the inter-electronic coordinates into the exponential wave function expansion. Assuming a fair saturation of the one-electron basis, the painful computation of 3- and 4-electron integrals is avoided by introducing a resolution-of-identity in the computational basis [18].

We constructed the full nine-dimensional H_2O-H_2 surface using the following three step procedure: (i) a five-dimensional rigid-rotor reference PES was computed at the (standard) CCSD(T) level of theory [26]; (ii) this reference surface was then calibrated using 812 "high-cost" CCSD(T)-R12 calculations; (iii) the R12 corrected rigid-rotor surface was finally extended to all nine-dimensions from a new set of CCSD(T) calculations. The strategy of splitting the calculations into two levels of accuracy is necessary because of the large computational cost of the R12 calculations ($\approx$ 40 hours on a IBM SP3 375 MHz machine for each nuclear geometry). Intermolecular energies were generated on grids using a combination of the 812 CCSD(T)-R12 calculations and 325,000 CCSD(T) calculations [45]. These grid points were chosen for 25 fixed intermolecular distances R (in the range $3-15$ a_0) via random sampling for the angular coordinates of H_2 relative to H_2O. Importance sampling was used for the internal coordinates based on high accuracy ground vibrational wavefunctions of H_2O [13] and H_2 [27]. At each intermolecular distance, the interaction energy was then least square fitted using the combination of a 149 terms expansion for the angular coordinates and a second-order Taylor-type series expansion for the internal coordinates. The accuracy of the angular expansion was monitored using a self-consistent Monte Carlo error estimator [28]. A cubic spline interpolation was finally employed over the whole intermolecular distance range and was smoothly connected with standard extrapolations to provide continuous expansion coefficients suitable for scattering calculations. The final accuracy of the nine-dimensional fit was found to be $\approx 1-2$ cm^{-1} in the long-range and minimum region of the interaction while the intrinsic accuracy of CCSD(T)-R12 calculations is also of the order of 1 cm^{-1}. In contrast to intramolecular studies [13, 15], the contribution of higher coupled cluster terms, relativistic and non-Born-Oppenheimer effects is minor for this intermolecular PES. Full details will be presented in a forthcoming article.

To compare with results available in the literature, the nine-dimensional surface was vibrationally averaged over the ground vibrational states [13, 27] of the monomers. As shown in table 1, the resulting five-dimensional surface gives a global minimum in good agreement with the recent results of Hodges and others based on the scaled perturbation theory (SPT) [29]. The best estimate of these authors, deduced from a complete basis set (CBS) extrapolation of CCSD(T) calculations, is even closer to our value, at -236.2 cm^{-1}. In its minimum-energy configuration, the H_2 approaches the oxygen atom along the water's symmetry axis, i.e. water acts as a proton acceptor. A secondary minimum, with the OH bond and H_2 in a T-shaped configuration, i.e. water as a proton donor, was also obtained in good agreement with earlier studies. Hodges et al. [29] used empirical vibrational ground state averaged geometries, in contrast to the customary choice of equilibrium geometries. The remarkable agreement with Hodges et al's CBS value is therefore not surprising. Indeed, our expansion is dominated by first-order terms in the Taylor-series which are exactly accounted for by state-averaged geometries; higher-order terms only account for a few cm^{-1} in the attractive region of the PES. We conclude that employing state-averaged geometries [46] is a reliable approximation for including vibrational effects within a rigid-rotor PES, as postulated by Mas and Szalewicz [30] (see also Jeziorska et al. [31]). Finally, our nine-dimensional surface is independent of nuclear masses and can therefore be used for any water isotopologue such as HDO.

III. VIBRATIONAL RELAXATION CALCULATIONS

Recently, several studies have shown that inaccuracies in the PES are the largest source of error in collisional rate calculations (see, e.g., Barnes et al. [32]). In principle, scattering calculations based on the close-coupling (CC) method [33] can provide an absolute accuracy of a few percent for a given PES. Unfortunately, the computational cost of CC calculations increases dramatically with temperature, especially when vibrational transitions are involved [47]. Approximate dynamical treatments of rotation by the coupled-state (CS) method, the infinite order sudden (IOS) approximation or methods based on classical mechanics have therefore provided useful alternatives [34, 35]. Here we have computed rate constants for the vibrational relaxation of water using quasi-classical trajectory (QCT) calculations. Rate constants and broadening coefficients for pure rotational excitation within the ground vibrational state of water are currently being computed at the CC level and will be published elsewhere by Dubernet et al. [36].

To investigate rovibrational (de)excitation processes, QCT calculations were carried out using the standard classical trajectory method (see, e.g., [35]). They were restricted to the vibrational relaxation of the lowest excited state of water, the v_2 bending mode (010) which lies 1594.7 cm^{-1} above the ground state [13]. In contrast to quantum approximate decoupling methods such as VCC-IOS (i.e. CC for vibration and IOS for rotation), QCT calculations can be performed without any dynamical approximation except the intrinsic limitations of classical mechanics at low temperatures where quantum effects are crucial. Some of us have recently shown that the standard bin histogram method, widely used in QCT calculations involving linear rotors, cannot be generalized to the case of rotational transitions in asymmetric top molecules owing to ambiguities in the assignment of the final rotational action [37]. To circumvent this problem, rovibrational rates were Boltzmann averaged over initial rotational states and summed over final rotational states. Collisional energies were sampled for a canonical distribution. All other variables were Monte Carlo selected from appropriate distributions. Stretching motions were neglected by freezing the OH and H_2 bonds at their effective rotational values. The bending potential of water was accurately represented by the simple analytic form of Wu et al. [38]. Because vibrational transitions are rare at low collision energy, reliable statistics could be obtained only for temperatures above 500 K. Detailed balance was checked by calculating the reverse transition from (000) to (010) and was found to be fulfilled within the quoted error bars. Figure 1 compares our results with the current best estimate which is based on an empirical equation derived from shock-tube measurements of diatomic systems [39, 40]. The single experimental result of Zittel and Masturzo [41] at 295 K is also shown. For temperatures above 1500 K, our results are about one order of magnitude greater than the empirical predictions. Below 1500 K, our rates are lower than 10^{-11} $\mathrm{cm^3s^{-1}}$ and must be considered only as lower limits since classical mechanics systematically underestimates rate constants at low temperature (see, e.g., [34]). Furthermore, it can be noticed that QCT results for $T \geq 1500$ K are compatible with the experimental point at 295 K. Vibrational relaxation was found to be mostly driven by the PES dependence on the bending coordinate, with a minor contribution of centrifugal and other dynamical effects. We also found a significant rotational enhancement of the total vibrational rates, suggesting that quantum VCC-IOS calculations might fail for molecule-molecule collision pairs with large rotational constants, as already observed for simpler systems (see, e.g., Krems et al. [42]). More elaborate schemes such as VCC-CS might thus be needed to compute reliable state-to-state rovibrational rates and also to check the low temperature dependence of the rate constant. Future studies will investigate this important issue.

IV. CONCLUDING REMARKS

A full nine-dimensional PES for hydrogen molecule−water collisions has been computed at high accuracy using explicitly correlated calibration calculations. Its average over the ground vibrational wavefunctions of the monomers compares very well with the best available literature results. QCT calculations for the vibrational relaxation of the water bending mode have been presented as a first application of this PES. Our results in the temperature range

1500−4000 K confirm that the vibrational relaxation process is very fast and our rates are compatible with the single experimental point at 295 K. The astrophysical consequences of the present study have now to be investigated. A particularly important issue that needs detailed modelling is the connection between rate constants and line intensities in radiative transfer models. A recent study by Grosjean et al. [43] has shown a strong correlation between differences in rate constants and predicted line intensities. For maser transitions, predicted intensities should be even more sensitive to collisional rates. The present results therefore suggest important changes in the interpretation of vibrationally excited water emission spectra from space. Laboratory measurements, even for limited temperature ranges or for Van der Waals dimers, are also of crucial importance to further test our predictions. Finally, the methodology described here is fully transferable to the study of other molecule-molecule collision pairs of astrophysical or atmospherical relevance.

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[44] In other environments such as cometary's comae, the excitation of water molecules can be dominated by self-collisions of water, i.e., H_2O-H_2O collisions, as well as collisions with electrons.

[45] CCSD(T) calculations employed Dunning's aug-cc-pVDZ basis sets augmented by the most diffuse higher orbital borrowed from the aug-cc-pVTZ set. The calibration CCSD(T)-R12 calculations employed 9s6p4d and 19s14p8d6f4g R12 suited basis sets for H and O respectively and were fully correlated. All calculations were counterpoise corrected.

[46] For water, the ground state-averaged geometry was obtained by averaging internal Radau

coordinates. This choice is consistent with both the vibrational wavefunction computation and the Taylor-type series expansion of the PES. This procedure is slightly different from the empirical correction used by Mas and Szalewicz [30].

[47] The computational cost of a CC calculation for a given energy and orbital angular momentum scales roughly as the cube of the number of channels required for convergence.

TABLE I: Rigid-rotor geometries of molecules and global minimum energy, E_{min}, for the H_2O-H_2 complex. R is the distance between the molecular centers of mass at the mimimum. Results are presented for five different theoretical models: PMMG, fourth-order perturbation theory (MP4) calculations of Phillips et al. [12] for experimental geometries; HWSH, SPT calculations of Hodges et al. [29] for empirical averaged geometries in the ground vibrational states; this work, (a) CCSD(T)-R12 calculations for theoretical equilibrium geometries; (b) CCSD(T)-R12 calculations for theoretical averaged geometries in the ground vibrational states; (c) average of the nine-dimensional fit over the ground vibrational wavefunctions.

	PMMG	HWSH	This work (a)	This work (b)	This work (c)
r_{HH} (au)	1.402	1.449	1.400	1.449	–
r_{OH} (au)	1.809	1.836	1.809	1.843	–
HOH (degrees)	104.52	104.69	104.22	104.41	–
E_{min} (cm^{-1})	-201.10	-240.72	-221.19	-234.88	-235.14
R (au)	6.01	5.80	5.90	5.82	5.82

Figure captions

Fig. 1: Rate constant (in cm^3s^{-1}) as a function of temperature for the vibrational relaxation of $H_2O(v_2)$ by H_2. QCT results are plotted as filled circles for $T \geq 1500$ K (with error bars corresponding to 2 Monte-Carlo standard deviations) and as arrows (lower limits) for $T < 1500$ K. The dotted curve denotes empirical rates reported by González-Alfonso et al. [40]. The empty circle gives the experimental value of Zittel and Masturzo [41] at 295 K. The solid line corresponds to a standard interpolation of the high temperature ($T \geq 1500$ K) QCT results.

Figure 1, Faure et al., Journal of Chemical Physics