ROTATIONAL QUENCHING OF ROTATIONALLY EXCITED H$_2$O IN COLLISIONS WITH He

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ABSTRACT

Theoretical rotational quenching cross sections and rate coefficients of ortho- and para-H$_2$O due to collisions with He atoms are presented. The complete angular momentum close-coupling approach as well as the coupled-states approximation for the angular momentum decoupling was applied to solve the scattering problem for a large range of rotationally excited states of water. Results are obtained for quenching from initial levels $l_{1,0}$, $2_{1,2}$, $2_{1,1}$, $3_{0,3}$, $3_{1,2}$, $4_{1,4}$, $3_{3,0}$, and $4_{2,3}$ of ortho-H$_2$O and from initial levels $l_{1,1}$, $2_{0,2}$, $2_{1,1}$, $2_{2,0}$, $3_{1,3}$, $3_{2,2}$, $4_{0,4}$, $4_{1,3}$, and $3_{3,1}$ of para-H$_2$O for kinetic energies from $10^{-3}$ to $10^{4}$ cm$^{-1}$. State-to-state and total deexcitation cross sections and rate coefficients for temperatures between 0.1 and 3000 K are reported. The present state-to-state rate coefficients are found to be in good agreement with previous results obtained by Green and coworkers at high temperatures, but significant discrepancies are obtained at lower temperatures likely due to differences in the adopted potential energy surfaces. Astrophysical applications of the current rate coefficients are briefly discussed.

**Key words:** ISM: molecules – molecular data – molecular processes

**Online-only material:** color figures

1. INTRODUCTION

Water is one of the most important molecules in a large variety of astrophysical environments. As such it is the focus of a Key Program for the Herschel Space Observatory. Water in Star-forming regions with Herschel (WISH). WISH is designed to probe the physical and chemical structures of young stellar objects using water and related molecules and to follow the water abundance from collapsing clouds to planet-forming disks (van Dishoeck et al. 2011). Water has been detected in observations with Herschel in the massive star-forming region W3 IRS5 (Chavarria et al. 2010), in dark regions (Caselli et al. 2011), and in protoplanetary disks (Carr & Najita 2008; Salyk et al. 2011), for example. Water was also detected in earlier observations by the Submillimeter Wave Astronomy Satellite (SWAS), the Infrared Space Observatory (ISO), Odin, and the Spitzer Space Telescope. For example, SWAS observed the 1$_{10}$–1$_{01}$ 556.936 GHz transition of ortho-water, which revealed the presence of widespread emission and absorption by water vapor around the strong submillimeter continuum source Sagittarius B2 (Neufeld et al. 2003). Detections of thermal water vapor absorption lines were made toward Orion IRc2 using the Short Wavelength Spectrometer on board ISO (Wright et al. 2000). Franklin et al. (2008) presented detections of the 1$_{10}$–1$_{01}$ line in 18 molecular outflows with SWAS, while Spitzer presented the first clear signature of water vapor on a hot, gas planet outside our solar system, HD 189733b (Grillmair et al. 2008; Barman 2008). A large number of H$_2$O lines were also observed with Spitzer from the outflow of NGC 2071 (Melnick et al. 2008) and studied with shock models by Flower & Pineau des Forêts (2010).

The significance of water arises primarily due to its importance as a coolant (e.g., Doty & Neufeld 1997), but it is also responsible for observed maser action. Water observations serve as an important tool for studying long-sought details of the planet formation process (Ehrenreich et al. 2007). It is the most abundant molecule frozen on grain surfaces and is found to change the optical properties of grains and to aid in the coagulation process that ultimately produces planets (Whittet et al. 2001).

To interpret observations of water emission lines, accurate line frequencies and oscillator strengths are needed, but also key are the availability and accuracy of collisional rate coefficients. Collisional state-to-state rate coefficients are of great importance to describe energy exchange processes responsible for thermal balance and line formation, particularly in low-density gas. In such situations, the molecular level populations may be out of equilibrium or driven to non-local thermodynamic equilibrium (NLTE) via external energy sources.

Most studies of collisional excitation begin with the consideration of He impact as the resulting collision complex is weakly bound and of low dimensionality. As such, the H$_2$O–He collisional system has been investigated in a number of experimental (Bickes et al. 1975; Slankas et al. 1979; Brudermann 1980, 1989; Palma et al. 1988a, 1988b; Green et al. 1991, 1993; Maluendes et al. 1992; Tao et al. 1996; Kukawska-Tarnawska et al. 1993; Calderoni et al. 2003; Hodges et al. 2002; Patkowski et al. 2002; Yang et al. 2010a, 2010b) and theoretical (Green 1980, 1989; Palma et al. 1988a, 1988b; Green et al. 1991, 1993; Maluendes et al. 1992; Tao et al. 1996; Kukawska-Tarnawska et al. 1993; Calderoni et al. 2003; Hodges et al. 2002; Patkowski et al. 2002; Yang & Stancil 2007; Makarewicz 2008; Dagdigian & Alexander 2010) studies. For numerical astrophysical models, quantitative determinations of state-to-state rate coefficients for collisions of water are crucial.

As direct measurements of collisional rate coefficients are generally difficult, numerical models often rely on calculations. However, other types are measurements can be performed to give some insight to the process and the reliability of calculations. For example, pressure broadening of five transitions of water due to helium and molecular hydrogen was investigated for temperatures relevant to the cold interstellar medium by Dick et al. (2010). In the case of He, they found a significant temperature dependence that is in agreement with
results deduced from previous theoretical inelastic studies. The situation for H₂ is less satisfactory and requires further study both experimentally and theoretically (see, for example, van der Tak 2011).

Recently, state-to-state differential cross section (DCS) measurements have been performed for rotational excitation of water by He and H₂ (Yang et al. 2010a, 2010b). The experimental data were compared to DCS calculations obtained with the close-coupling (CC) method using the potential energy surfaces (PESs) for H₂O–He (Hodges et al. 2002) and H₂O–H₂ (Faure et al. 2005; Valiron et al. 2008). Very good agreement was found for most transitions providing some confidence in the reliability of the adopted PESs.

Four PESs (Calderoni et al. 2003; Hodges et al. 2002; Patkowski et al. 2002; Makarewicz 2008) have been developed recently for the H₂O–He complex. The potentials of Hodges et al. (2002) and Patkowski et al. (2002) were constructed using symmetry-adapted perturbation theory (SAPT), referred to as SAPT-H and SAPT-P, respectively. Calderoni et al. (2003) reported their potential based on valence bond (VB) calculations. Detailed comparison of the dynamic performance on the first three potentials, SAPT-H, SAPT-P, and VB, was performed by Yang & Stancil (2007), who concluded that the SAPT-P potential (Patkowski et al. 2002) was likely the most reliable. The PES of Makarewicz (2008) is expected to be of a similar quality, but has not been adopted in scattering calculations to the best of our knowledge.

In this work, we extend the previous rotational quenching calculations of Yang & Stancil (2007) to higher levels of rotational excitation primarily utilizing the SAPT-P (Patkowski et al. 2002) PESs for both para- and ortho-water. H₂O–He rate coefficients are presented for a large range of temperature which will be applicable to modeling a wide variety of astrophysical and atmospheric environments.

2. THEORETICAL METHOD

The theory for scattering of a asymmetric top, such as H₂O, with a spherical atom can be found in Garrison et al. (1976) and Green (1976). The center of the coordinate system is fixed at the center of mass of H₂O. The water molecule is located in the x–z-plane, with oxygen on the positive z-axis. H₂O is taken to be rigid with the O–H bonds and H–O–H angle fixed at their equilibrium positions. The interaction then depends only on the position of the He atom which is described in the usual polar coordinates: R, θ, and φ. In the scattering calculations, it is convenient to expand the angle dependence of the potential V in spherical harmonics Yₗμ(θ, φ) as

\[
V(R, \theta, \phi) = \sum_{\lambda \mu} v_{\lambda \mu}(R)(1 + \delta_{\mu 0})^{-1} \times [Y_{\lambda \mu}(\theta, \phi) + (-1)^{\mu} Y_{\lambda \mu, -\mu}(\theta, \phi)].
\]

Owing to the C₂ᵥ symmetry of water, only even values of μ enter the expansion. The rotational levels of H₂O are labeled by jk₋, k±1, where k₋ and k±1 are the k quantum numbers in the prolate and oblate limits, respectively. Rotational wave functions were obtained by diagonalizing the rigid-rotor Hamiltonian using rotational constants, \(A = 27.881\, \text{cm}^{-1}\), \(B = 14.522\, \text{cm}^{-1}\), and \(C = 9.278\, \text{cm}^{-1}\), with rotational energy levels taken from Kyrö (1981) and Lanquetin et al. (1999). Energy levels of the first 12 rotational states of ortho- and para-H₂O are given in Table 1.

The calculations presented in this paper were performed by applying the CC approach and the coupled-states (CS) approximation (see, for example, Flower 2007) and using the SAPT-P PES, except where noted. The CC method was used to calculate rotational quenching cross sections for center-of-mass kinetic energies from \(10^{-3}\) to 450 cm\(^{-1}\), while the CS approximation was used from 500 to 10,000 cm\(^{-1}\). All the CC and CS calculations were performed using the nonreactive scattering code MOLSCAT (Hutson & Green 1994). In the quantum-scattering calculations, the coupled-channel equations were integrated using the modified log-derivative Airy propagator of Alexander & Manolopoulos (1987) with a variable step size. The propagation was carried out to a maximum intermolecular separation of \(R = 100\, \text{Å}\). At each energy, a sufficient number of total angular momentum partial waves was included to ensure convergence of the cross sections. The maximum value of the total angular momentum quantum number J employed in the calculations was 140. \(J = l + j\) and l is the orbital angular momentum of the complex. All calculations include 5–10 energetically closed channels to ensure converged cross sections. As a consequence of the nuclear spins of the two hydrogen atoms in H₂O, water exists in two forms: para-H₂O and ortho-H₂O. The ortho- and para-levels do not interconvert in nonreactive collisions and are therefore treated separately in the current inelastic calculations.

Cross sections were thermally averaged over a Maxwellian kinetic energy distribution to yield state-to-state rate coefficients from specific initial rotational states \(j_{k₋, k±1}\) as functions of the temperature \(T\),

\[
k_{j_{k₋, k±1} \rightarrow j'_{k₋, k±1}}(T) = \left(\frac{8}{\pi m \beta}ight)^{1/2} \beta^2 \times \int_0^{\infty} E_k \sigma_{j_{k₋, k±1} \rightarrow j'_{k₋, k±1}}(E_k) \exp(-\beta E_k) dE_k,
\]

where \(\sigma_{j_{k₋, k±1} \rightarrow j'_{k₋, k±1}}(E_k)\) is the rotational transition cross section with \(j_{k₋, k±1}\) and \(j'_{k₋, k±1}\) being, respectively, the initial and final rotational states of H₂O, \(m\) is the reduced mass of the He–H₂O complex, \(E_k\) is the kinetic energy, and \(\beta = (k_B T)^{-1}\), where \(k_B\) is Boltzmann’s constant.

3. RESULTS AND DISCUSSION

3.1. State-to-state and Total Deexcitation Cross Sections

State-to-state deexcitation cross sections were computed for initial rotational levels \(1, 0, 2, 1, 2, 2, 1, 3, 0, 3, 3, 1, 3, 2, 3, 1, 4, 1, 4, 3, 3, 0,\)
In their work, relative DCS measurements of H$_2$O state-to-state shown in Yang & Stancil (2007). Importantly, for astrophysical the resonances are sensitive to the details of the PES as interaction potential. The energy location and magnitude of

4 All state-to-state cross sections and rate coefficients for quenching are available on the UGA Molecular Opacity Project Web site (www.physast.uga.edu/ugamop/). The rate coefficients are also available in the format of the Leiden Atomic and Molecular Database (LAMDA; Schöier et al. 2005) on our Web site.

42, 3 of ortho-H$_2$O and initial levels 1$_{1,1}$, 2$_{0,2}$, 2$_{1,1}$, 2$_{2,0}$, 3$_{1,3}$, 3$_{2,2}$, 4$_{0,4}$, 4$_{1,3}$, and 3$_{3,1}$ of para-H$_2$O, extending the results from our earlier work (Yang & Stancil 2007) which was limited to $j \leq 2$. As examples, the state-to-state quenching cross sections from the initial level 3$_{0,3}$ of ortho-H$_2$O and 3$_{1,3}$ of para-H$_2$O are presented in Figures 1(a) and (b), respectively. The agreement between CC and CS calculations, as shown in Figure 1, is found to be excellent. We conclude that the CS approximation, which is computationally efficient, is reliable for the current collision system at high energies.

From Figure 1 it can be seen that the cross sections display resonances in the intermediate energy region from 0.1 to 100 cm$^{-1}$ due to the influence of the attractive part of the interaction potential. The energy location and magnitude of the resonances are sensitive to the details of the PES as shown in Yang & Stancil (2007). Importantly, for astrophysical applications, the properties of the resonances influence the quenching rate coefficients at low temperatures as discussed below. The $3_{0,3} \rightarrow 2_{1,2}$ transition is seen to dominate the quenching of the $3_{0,3}$ level and likewise for para-H$_2$O, the dominant quenching transition for the $3_{1,3}$ is $3_{1,3} \rightarrow 2_{0,2}$. Both transitions are seen to obey the propensity rule $|\Delta j| = |\Delta k_{+1}| = |\Delta k_{-1}| = 1$.

As a test of the accuracy of our results, we can compare to the recent measurements and calculations of Yang et al. (2010a). In their work, relative DCS measurements of H$_2$O state-to-state excitation due to He impact were performed at a kinetic energy of 429 cm$^{-1}$ for 12 different transitions. Differential and integral cross sections were also computed using MOLSCAT, but with the SAPT-H PES. They found good agreement between theory and measurement in all cases except for the 0$_{00} \rightarrow 2_{11}$ and 0$_{00} \rightarrow 3_{22}$ transitions (Yang et al. 2010a). As these transitions are weak (see Figure 2), the authors argued that the discrepancy may be due to contamination of their beam of ground-state molecules (0$_{00}$) with excited 1$_{11}$ water. For four dominant transitions, the relative DCSs were used to obtain relative integral cross sections which the authors normalized to the largest absolute cross section from their calculations, 0$_{00} \rightarrow 1_{11}$. These are reproduced in Figure 2 adopting the quoted experimental cross section uncertainty of $\pm 30\%$, while the uncertainty in the beam energy was $\pm 20\%$. Also shown in Figures 2 and 3 are the current calculations using the SAPT-P PES, as well as new results using the SAPT-H and VB surfaces, all performed at a kinetic energy of 429 cm$^{-1}$. As noted in Yang & Stancil (2007), the VB surface gives cross sections that typically differ significantly with results obtained on other surfaces and with available experimental data. This is further confirmed in the present work and with comparison to the Yang et al. (2010a) measurements. For all considered transitions, the current calculations using the SAPT-H and SAPT-P PESs result in similar cross sections. This is consistent with the study performed in Yang & Stancil (2007) which had difficulty in selecting a preferred PES between the two. Significant differences between the current calculations and those of Yang et al. (2010a) are noted, even though both sets of calculations adopted the same surface (SAPT-H) and the same scattering code. For the current calculations, all parameters were carefully checked to ensure convergence and we can offer no

Figure 1. State-to-state deexcitation cross sections of H$_2$O in collisions with He as a function of kinetic energy obtained with the CC method (lines) and the CS approximation (symbols). (a) 3$_{0,3}$ of ortho-H$_2$O and (b) 3$_{1,3}$ of para-H$_2$O.
Figure 2. Comparison of state-to-state H$_2$O-He excitation cross sections at 429 cm$^{-1}$ from the initial states (a) 000 and (b) 101. Open circle: CC calculations of Yang et al. (2010a); filled symbols: current CC calculations; boxes: experiment of Yang et al. (2010a). Note that in panel (a) the cross section magnitudes from other calculations to the 211 and 322 are smaller than the scale of the plot.

(A color version of this figure is available in the online journal.)

Figure 3. Same as Figure 2, but for the initial state 111. No experimental integral cross sections are available for this state.

(A color version of this figure is available in the online journal.)

determination for the difference. Finally, the agreement with experiment, regardless of normalization selection, is seen to be excellent for all the calculations for all adopted surfaces (except, of course, for the VB surface). The one exception occurs for the transition 101 $\rightarrow$ 221. Yang et al. (2010a) do not comment on this discrepancy and we can only speculate that their beam of 101 molecules may have been contaminated by other low-lying excited states which may have influenced the cross section measurement given its relatively small magnitude. We conclude that the current calculations using the SAPT-P surface give results of sufficient reliability for astrophysical needs.

State-to-state cross sections from each initial state are summed over all final states to obtain the total deexcitation cross section. In Figure 4, we compare the total deexcitation cross sections from select initial levels 21, 31, 20, 30, and 42, 3 of ortho-H$_2$O and 20, 31, 1, and 41, 3 of para-H$_2$O, while cross sections from some of the lower $j$ levels are given in Yang & Stancil (2007). Generally, the total deexcitation cross sections from different initial levels have similar behavior and are of similar magnitude over the considered energy range. Each of the total cross sections exhibits the behavior predicted by Wigner’s threshold law (Wigner 1948) at ultra-low collision energies, where only $s$-wave scattering contributes and the cross sections vary inversely with the relative velocity. In the intermediate energy region, between 0.1 and 100 cm$^{-1}$, the cross sections display scattering resonances. As a consequence of the diverse behavior of the resonances, no trends are evident except at the highest energies where the cross sections increase with rotational excitation.
3.2. State-to-state and Total Deexcitation Rate Coefficients

Deexcitation rate coefficients for temperatures ranging from 0.1 to 3000 K are shown in Figures 5–8 for some selected levels of ortho-H$_2$O and para-H$_2$O. The rate coefficients are given below 3 K to illustrate their behavior as they approach the zero-temperature limit. Unfortunately, we are unaware of any experimental rate coefficient data for rotational transitions of H$_2$O due to collisions with He. Therefore, we can only compare our computations with the theoretical results of Green et al. (1993), which were calculated with the potential of Maluendes et al. (1992). The Green et al. (1993) calculations were carried out using the potential energy surface of Maluendes et al. (1992).
out using MOLSCAT, with the modified log-derivative Airy propagator, and using the CC method for a total energy up to 470 cm$^{-1}$. For para-H$_2$O (ortho-H$_2$) as many as 17 (16) rotational levels were included in their basis. For higher total energies, Green et al. (1993) used the CS approximation up to 5000 cm$^{-1}$. The primary difference between the current calculations and those of Green et al. (1993) is the adopted PES.

Figures 5 and 6, which display state-to-state quenching rate coefficients for ortho-H$_2$O from initial levels $3_0,3$ and $4_2,3$.  

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**Figure 6.** Same as Figure 5, but for ortho-H$_2$O initial state $4_2,3$.

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**Figure 7.** Same as Figure 5, but for para-H$_2$O initial state $3_1,3$. 

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respectively, show that between 0.1 and 50 K, the rate coefficients exhibit an oscillatory temperature dependence due to the presence of resonances. For temperatures above ∼50 K, the rate coefficients generally increase with increasing temperature. Comparison with the rate coefficients of Green et al. (1993) shows generally good agreement at temperatures above ∼200 K. The results of Green et al. (1993) are smaller than the present rate coefficients for lower temperatures with the discrepancy increasing with decreasing temperature. The differences are primarily related to the adopted PESs since all other aspects of the two sets of calculations appear to be similar, though different choices of convergence parameters are possible. Further, the bumps in the present-rate coefficients are absent from the results of Green et al., likely due to resonances not produced for scattering on the Maluendes et al. (1992) PES.

Considering scattering of para-H$_2$O by He, the trends noted for ortho-H$_2$O are also evident in the state-to-state deexcitation rate coefficients as shown in Figures 7 and 8 for some example initial states. Oscillations due to resonances and a general increase in the rate coefficients above 50 K are similar. Comparisons to the work of Green et al. generally show good agreement, but again only for temperatures above ∼200 K.

The total deexcitation rate coefficients from all considered initial states (including those given in Yang & Stancil 2007) are shown in Figure 9. They exhibit similar oscillatory behavior, but the varying oscillation dependencies reflect different resonance energies. For temperatures above ∼50 K, the total deexcitation rate coefficients smoothly increase with increasing temperature, a trend which may be useful in scaling arguments to estimate rate coefficients for more highly excited states not explicitly computed.

4. ASTROPHYSICAL APPLICATIONS

As discussed in Section 1, water has been observed in emission and absorption in a variety of astronomical environments. For example, in the past decade there has been increasing interest in the properties of protoplanetary disks (PPDs) and considerable effort has gone into the modeling of PPDs in general and the spectral features of water, in particular (Gorti & Hollenbach 2004; Meijerink et al. 2008, 2009; Glassgold et al. 2009; Salyk et al. 2011). The observation of water in PPDs has become very common (Carr & Najita 2008, 2011; Salyk et al. 2011) with interest focused on the inner-planet-forming region. Dullemond & Monnier (2010) point out that water is one of dominant coolants in the inner regions.

Because the critical densities of water are typically greater than $10^8$ cm$^{-3}$, models that assume a Boltzmann level population distribution, or local thermodynamic equilibrium (LTE), are generally not valid. Full NLTE models are necessary to predict the rotational and vibrational spectrum of water in most emitting regions of PPDs, above the plane of the disk, as demonstrated by Meijerink et al. (2009) and in a variety of other environments. NLTE models require knowledge of state-to-state rotational (and vibrational) rate coefficients for the kinetic modeling of the internal level populations. Important colliders may include H$_2$, H, He, H$^+$, and $e^-$, and for comets, H$_2$O (Bensch & Bergin 2004). A review of the status of collisional rate coefficients for water can be found in van der Tak (2011). Because of the complexity in considering H$_2$ collisions, there is a long history of initial collisional excitation calculations being performed with He collisions. The He rate coefficients are then often mass-scaled to emulate para-H$_2$ collisions. We certainly do not advocate such
a procedure here and it has been pointed out by Dubernet et al. (2009) that mass scaling does not result in reliable H$_2$O–H$_2$ rate coefficients. As a consequence, a considerable amount of effort has been expended to directly compute rate coefficients for rotational excitation of water by H$_2$ (Phillips, Maluendes, & Green 1995, 1996; Dubernet & Grosjean 2002; Faure et al. 2006, 2007; Dubernet et al. 2009; Daniel et al. 2010, 2011)\(^5\), while the rate coefficients for vibrational excitation are limited to the quasi-classical calculations of Faure et al. (2005), with extrapolations proposed by Faure & Josselin (2008). We are unaware of any collisional data for H$^+$ impact, we have performed some preliminary calculations for H collisions (Yang & Stancil, in preparation), while Faure & Josselin (2008) have compiled the available electron collision data. However, except for the set of calculations done for temperatures between 20 and 2000 K by Green et al. (1993) on the earlier, and presumably less accurate PES of Maluendes et al. (1992), our previous work (Yang & Stancil 2007), and the small set of calculations in support of the experiments of Yang et al. (2010a, 2010b), no other computations for rate coefficients due to He impact have been published. Therefore, the current rate coefficient calculations, which extend from $10^{-1}$ K to 3000 K, are the most comprehensive to date for He and can be utilized in a variety of applications augmenting the data sets developed for H$_2$ and electrons (see also the LAMDA Web site and BASECOL Web site; Schöier et al. 2005; Dubernet et al. 2006). We note that in NLTE models of water in PPDs, Meijerink et al. (2009) mass-scaled the available H$_2$O–H$_2$ rate coefficients to estimate values for H$_2$O–He.

5. CONCLUSION

Cross sections and rate coefficients for rotational quenching of ortho- and para-H$_2$O due to He collisions have been studied using the CC method and the CS approximation on the ab initio PES of Patkowski et al. (2002). State-to-state and total deexcitation cross sections and rate coefficients for the first nine initial excited rotational levels of para- and ortho-H$_2$O are obtained over a wide temperature range from 0.1 to 3000 K and are available in tables formatted for astrophysical applications. Numerous orbiting resonances result in undulations in the temperature dependence of the rate coefficients. For temperatures less than $\sim$200 K, the current state-to-state rotational rate coefficients are found to depart from the results of Green et al. (1993) obtained with the earlier PES of Maluendes et al. (1992). Discrepancies are primarily related to differences in the adopted PESs as all other aspects of the current calculations are similar to those of Green et al. (1993).

We dedicate this manuscript to the memory of Professor Mi-neo Kimura who passed away during the completion of the work presented here. B.H.Y. and P.C.S. acknowledge support from NASA under Grants No. NNX07AP12G and NNX12AF42G.

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\(^5\) In particular, for H$_2$O–H$_2$, the latest state-to-state rate coefficients of Daniel et al. (2011), with a package to calculate effective and thermal rates, can be found on BASECOL.
