

## CHEMISTRY

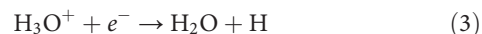
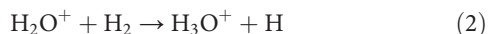
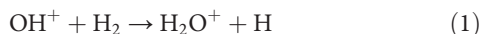
## Low temperature rates for key steps of interstellar gas-phase water formation

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The gas-phase formation of water molecules in the diffuse interstellar medium (ISM) proceeds mainly via a series of reactions involving the molecular ions OH<sup>+</sup>, H<sub>2</sub>O<sup>+</sup>, and H<sub>3</sub>O<sup>+</sup> and molecular hydrogen. These reactions form the backbone for the chemistry leading to the formation of several complex molecular species in space. A comprehensive understanding of the mechanisms involved in these reactions in the ISM necessitates an accurate knowledge of the rate coefficients at the relevant temperatures (10 to 100 K). We present measurements of the rate coefficients for two key reactions below 100 K, which, in both cases, are significantly higher than the values used in astronomical models thus far. The experimental rate coefficients show excellent agreement with dedicated theoretical calculations using a novel ring-polymer molecular dynamics approach that offers a first-principles treatment of low-temperature barrierless gas-phase reactions, which are prevalent in interstellar chemical networks.

## INTRODUCTION

Water—one of the most important molecules for life as we know it—has been observed in the interstellar medium (ISM) in gaseous and solid forms (1–3). In the diffuse ISM, ion-neutral reactions at low temperature (10 to 100 K) are the driving force for the formation of more complex molecules in space. Under these conditions, water is formed mainly via a chain of exothermic gas-phase processes with no intrinsic barriers (4)



where the hydroxyl ion OH<sup>+</sup> is formed either by the reaction of O<sup>+</sup> with molecular hydrogen or by the reaction of atomic oxygen with H<sub>3</sub><sup>+</sup>. The O<sup>+</sup> ions are created by charge-transfer reactions between atomic oxygen and atomic hydrogen ions that are produced by cosmic ray ionization, whereas the H<sub>3</sub><sup>+</sup> formation is initiated by cosmic ray ionization of H<sub>2</sub>. Consequently, the formation of OH<sup>+</sup>, H<sub>2</sub>O<sup>+</sup>, and H<sub>3</sub>O<sup>+</sup> are all essentially cosmic ray-driven, and one can use their abundance to constrain the cosmic ray ionization rate in the diffuse ISM and the fraction of atomic to molecular hydrogen (4, 5).

All three molecular ions, OH<sup>+</sup>, H<sub>2</sub>O<sup>+</sup>, and H<sub>3</sub>O<sup>+</sup>, have been observed in the ISM, often in surprisingly high abundance. OH<sup>+</sup> was first detected using the Atacama Pathfinder Experiment 12m telescope toward the massive star-forming region Sagittarius B2(M) (6). H<sub>2</sub>O<sup>+</sup> was found using the Herschel satellite toward the star-forming regions DR21, Sagittarius B2(M), and NGC 6334 (7). The protonated water

molecule H<sub>3</sub>O<sup>+</sup> was first detected much earlier, using the National Radio Astronomy Observatory 12m telescope toward Orion KL and OMC-1 (8, 9). Furthermore, all of these molecular ions were found along the line of sight toward the submillimeter continuum source G10.6-0.4 (W31C) using the Herschel Heterodyne Instrument for the Far Infrared (10). Since OH<sup>+</sup> and H<sub>2</sub>O<sup>+</sup> are known to react exothermically with H<sub>2</sub>, both ions are believed to reside in environments with a low fraction of molecular to atomic hydrogen. The observed velocity profiles support this assumption (11). Apart from their crucial role in the gas-phase water chain, both OH<sup>+</sup> and H<sub>2</sub>O<sup>+</sup> play key roles in the formation of oxygen-bearing molecules such as OH, CO, and other polyatomic molecules in the ISM (4).

To analyze the gas-phase water chain, most astronomical models use the rates that are reported in the University of Manchester Institute of Science and Technology (UMIST) database (12), which lists  $k_1 = 1.01(\pm 0.20) \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  for reaction (1) and  $k_2 = 6.4(\pm 3.2) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  for reaction (2). These values are based on the experiments of Jones *et al.* (13) and Rakshit and Warneck (14), although the original work is almost never cited in the astronomical literature. The rate coefficients were measured in flow tube and drift chamber studies at 300 K, and typically, they are assumed to be independent of temperature. However, the measured values differ significantly from the energy-independent classical Langevin rate coefficient approximation (15), which yields values around  $k_{1,2} \sim 1.5 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  for both reactions. Besides the experiments mentioned above, a number of additional room temperature values can be found in the literature, most of them being obtained in flow tube or drift chamber measurements. The published values show a significant scatter, and we refrain from addressing all of the individual measurements here (we will discuss the overall trends in Results and Discussion). In summary, the rate coefficients published for reaction (1) range from  $k_1 = 8.6 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  (16) to  $k_1 = 1.5 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  (17), while rate coefficients for reaction (2) range from  $k_2 = 4.0 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  (18) to  $k_2 = 1.4 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  (17), with additional values between these two extremes (14, 19, 20).

There is renewed interest in both reactions in recent years. Modern temperature-variable selected-ion flow-tube (SIFT) measurements were carried out between 200 to 600 K for reaction (1) (21) and from 100 to 600 K for reaction (2) (22). Both measurements show only a small variation of the rate coefficients with temperature, and in essence, the measured values agree with the rate coefficients listed in the UMIST database.

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Ng and co-workers (23–25) recently used a quite different experimental approach to shed light on reaction (2). They produced the  $\text{H}_2\text{O}^+$  ion in specific rovibrational states using a state-of-the-art laser-pulsed field ionization method in the vacuum ultraviolet. These measurements mark a clear step forward as they provide state-selective absolute cross sections. However, since the translational energies are above 300 K, the implications for astronomical applications are not straightforward. Nevertheless, note that the absolute cross sections obtained for reaction (2), at energies near room temperature, are much higher than the commonly accepted values. The series of recent experiments have also sparked theoretical work (26–28), resulting in quasi-classical trajectory (QCT) and quantum dynamics (QD) calculations for both reactions.

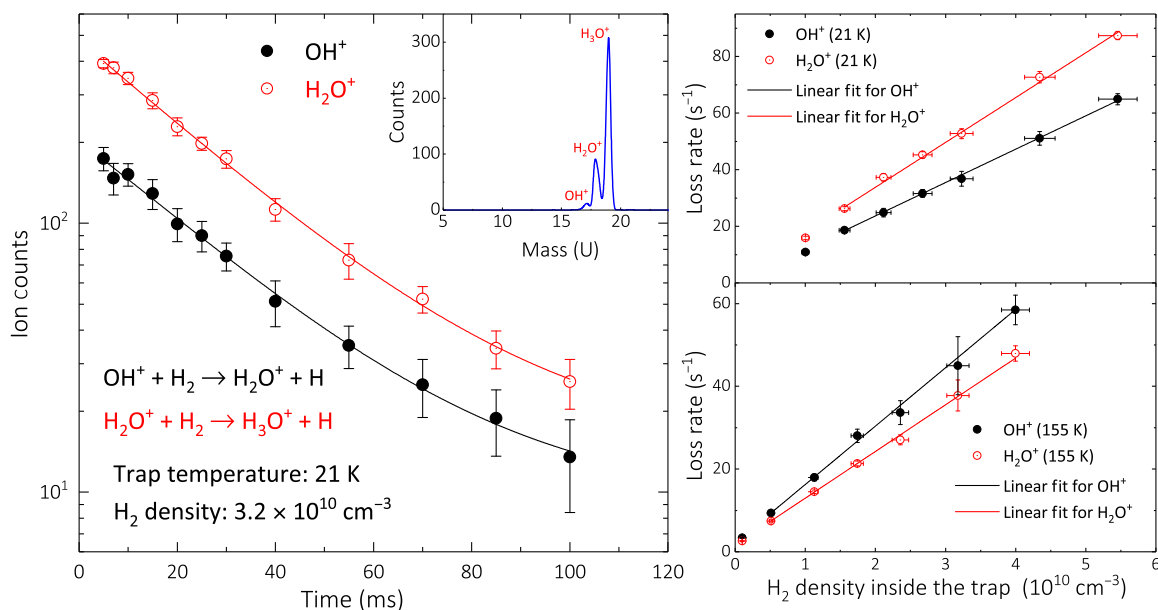
It is generally acknowledged, however, that despite the fact that gas-phase water formation is a much-studied reaction chain, none of the previous techniques has reached sufficiently low temperatures to be truly applicable for interstellar conditions. Here, we present the first dedicated rate coefficient measurements for reactions (1) and (2) at temperatures below 100 K, performed in a temperature-variable radio-frequency ion trap. Ring-polymer molecular dynamics (RPMD) calculations accompany these measurements, taking into account quantum mechanical effects of nuclear motions that were absent in previous theoretical rate calculations.

## RESULTS AND DISCUSSION

### Laboratory measurements in a cryogenic ion trap

For our low-temperature measurements, we used a cryogenic 22-pole ion trap (29). Details on the experimental procedure and a schematic of the setup can be found in Methods. Briefly,  $\text{OH}^+$ ,  $\text{H}_2\text{O}^+$ , and  $\text{H}_3\text{O}^+$  ions are created inside a radiofrequency ion source (30) by electron impact on water vapor. The inset in Fig. 1 shows a typical mass spectrum. Owing to fast reactions of  $\text{OH}^+$  and  $\text{H}_2\text{O}^+$  with  $\text{H}_2\text{O}$  already

inside the source, the  $\text{H}_3\text{O}^+$  peak was usually dominant. Two consecutive quadrupole ion guides lead the ions into the 22-pole ion trap, facilitating efficient differential pumping and thus preventing  $\text{H}_2\text{O}$  or unwanted trace gases from traveling from the source region to the ion trap. Inside the 22-pole trap, we stored the ions in a large field-free central region to minimize radiofrequency heating. During storage, we continuously bled in unreactive helium buffer gas for cooling through precooled lines, reaching a typical number density of  $10^{13} \text{ cm}^{-3}$ . Since the 22-pole trap does not discriminate between different masses (for the mass range of interest in the present work), we simultaneously stored all ions coming from the source. To initiate the reactions of  $\text{OH}^+$  and  $\text{H}_2\text{O}^+$  with  $\text{H}_2$ , we let in small amounts of hydrogen gas through a precision valve. After a predefined time interval, we extracted the stored ions and analyzed them using a mass spectrometer. We took special care to calibrate the neutral  $\text{H}_2$  density inside the trap, which is essential for determining absolute rate coefficients. For a given trap temperature and  $\text{H}_2$  density, we monitored the decay of  $\text{OH}^+$  and  $\text{H}_2\text{O}^+$  as a function of storage time (Fig. 1, left) over many trap fillings. We fitted the resulting decay curves averaged over the trap fillings by a set of coupled differential equations (see the Supplementary Materials) to obtain the loss rates for each ion. Varying the  $\text{H}_2$  density at a given temperature reveals a linear dependence, shown for two examples in the righthand panel of Fig. 1. For our low-temperature measurements presented here, we did not observe any contaminations in the mass spectra, and the dependence of the ion loss rates as a function of the hydrogen number density remained linear, with virtually no need for an axis offset (which would suggest an alternative loss mechanism). At higher temperatures ( $\geq 200 \text{ K}$ ), where the trap conditions become less “clean,” we started to observe deviations, most likely from  $\text{H}_2\text{O}$  residual gas that is cryopumped less effectively at higher temperature. The linear fits to the loss rates yield the experimental rate coefficients for a fixed temperature. Table 1 lists the resulting values with relative  $1\sigma$  statistical uncertainties. The determination of the  $\text{H}_2$  number density



**Fig. 1. Exemplary ion counts of  $\text{OH}^+$  and  $\text{H}_2\text{O}^+$  as a function of storage time and loss rates versus  $\text{H}_2$  density.** (Left) Decay curves of  $\text{OH}^+$  and  $\text{H}_2\text{O}^+$  as observed in the 22-pole trap at 21 K with a  $\text{H}_2$  number density of  $3.2 \times 10^{10} \text{ cm}^{-3}$ . The inset shows a spectrum of a typical initial mass distribution produced by the ion source. (Right) Loss rates for  $\text{OH}^+$  and  $\text{H}_2\text{O}^+$  as a function of  $\text{H}_2$  density at two different temperatures. The data points at the lowest densities resulted from the residual  $\text{H}_2$  in the trap, which varied with trap conditions and temperature. Those points, while fully consistent with the trend, were not included in the fit.

inside the ion trap dominates the uncertainty for the absolute scale of 20% (see the Supplementary Materials).

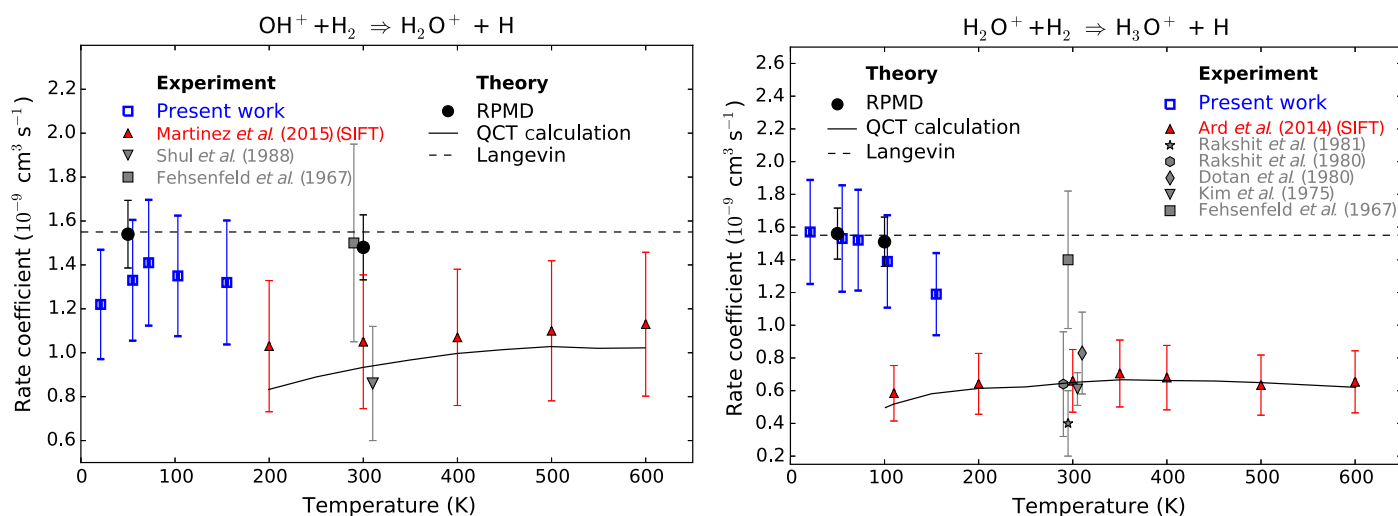
### Theoretical calculation of the rate coefficients using RPMD

Theoretical calculations of the rate coefficients complement the experiment using a novel RPMD method (31). The accurate calculation of

rate coefficients of reactions at low temperatures is still extremely difficult because of quantum effects such as tunneling, zero-point energy (ZPE), and resonances (32, 33). Here, we computed the rate coefficients using the RPMDrate code (34), which takes advantage of the isomorphism between a statistical property of a quantum system and that of a fictitious classical ring polymer made of harmonically connected beads. Although RPMD calculations are performed by running classical trajectories, it offers an accurate account of quantum effects, which are particularly important for low-temperature reactions. Careful comparison between the RPMD approximation and exact quantum dynamical theory has been carried out recently for many prototypical reactions (35), including several barrierless complex-forming reactions similar to reactions (1) to (3), and the agreement has been very encouraging. Here, we focus on reactions (1) and (2), using recently developed full-dimensional potential energy surfaces based on fitting a large number of high-level ab initio data and augmented with analytical long-range interaction terms (26, 36). Note that we did not distinguish the ortho- and para- $\text{H}_2$  in our calculations, and we assumed the  $\text{H}_2$  rotational distribution to be Boltzmann. The details of the RPMD calculation can be found in the Supplementary Materials.

### Comparison of experiment/theory and with previous work

Table 1 and Fig. 2 show the results of the present experiment and calculations, together with previous measurements and calculations. Our low-temperature measurements, as well as theoretical calculations, indicate high rate coefficients for both reactions, almost approaching the classical Langevin collision limit. The present measurements of reaction (1) show higher values than the recent results of Martinez *et al.* (21), which only extend down to 200 K. Within the combined error bars, however, they can be regarded consistent. The RPMD results at 50 K are in excellent agreement with the current experimental values, and at 300 K RPMD, the error bar overlaps with the previous



**Fig. 2. Comparison of the present measured and calculated rate coefficients for the reactions of  $\text{OH}^+$  and  $\text{H}_2\text{O}^+$  with  $\text{H}_2$  and previous measurements, QCT calculations, and the Langevin rate coefficient.** For the present experimental work and the SIFT results of (21) and (22), we added the respective relative and absolute uncertainties in quadrature to depict absolute uncertainties for a fair comparison. The uncertainties for the present RPMD calculations represent the convergence limit within two SDs. Also shown are previous room temperature measurements; for clarity, they are shifted in steps of 10 K. Theoretical calculations (RPMD and QCT) were performed using potential energy surfaces (PEs) from (26, 36). References for previous room temperature data are as follows: Shul *et al.* (1988) (16), Fehsenfeld *et al.* (1967) (17), Rakshit *et al.* (1981) (18), Rakshit *et al.* (1980) (14), Dotan *et al.* (1980) (20), and Kim *et al.* (1975) (19). Note that the measurements of Dotan *et al.* are actually energy-resolved, extend to kinetic center-of-mass collision energies of up to 0.3 eV (corresponding to  $k_B T = 3500$  K), and show a slow monotonic decrease. Since the present work is concerned primarily with the low-temperature regime, we only show their lowest energy data point for clarity.

experimental results. As shown in the Supplementary Materials (fig. S2), the free-energy barrier for reaction (1) is very small (below 0.1 kcal/mol) at this temperature, suggesting a loose bottleneck. At the same time, the ring polymer transmission coefficients (or real-time recrossing factor) require picoseconds of propagation to reach plateau values, which are significantly below unity when reaching the product region (see the Supplementary Materials), underscoring its importance in the total RPMD rate coefficient calculation. The QCT calculations presented in (21) are distinctly lower at both low and room temperatures. QCT's reliability is sometimes uncertain (35, 37), particularly at low energies and temperatures, as this approximation completely ignores important quantum effects such as tunneling, resonances, and—presumably more importantly for the present essentially barrierless reactions (1) and (2)—ZPE conservation along the reaction path (see the energy diagrams in the Supplementary Materials). For instance, for another complex-formation astrochemical reaction in the  $\text{H}_5^+$  system, it was recently shown that the ZPE leakage in QCT simulations can lead to strong deviations from experimental data at low temperatures (37). By contrast, RPMD was shown to be immune to these shortcomings as it accurately treats the ZPE along the reaction coordinate. As discussed in the Supplementary Materials, the higher temperature gives rise to a slightly higher free-energy barrier (0.6 kcal/mol) in the entrance channel, but it is offset by a smaller recrossing factor. The temperature dependence of  $k_1$  is negligible, again in agreement with the experiment.

For reaction (2), the experiment-theory agreement near 50 and 100 K is also excellent. As shown in the Supplementary Materials, the free-energy barrier for this reaction is again almost null, supporting the capture model. However, we see a distinct discrepancy between our results and the previous SIFT measurements (22), which are lower in the overlapping temperature regime. Most of the previous room temperature experiments (also shown in Fig. 2) resulted in lower rate coefficients; however, the temperature trend observed in the current results may be consistent with these findings. One potentially significant difference between our data and almost all previous studies [except for the room temperature ion cyclotron resonance measurements of Kim *et al.* (19)] is the pressure regime. While the number densities in all experiments are orders of magnitude higher than in interstellar space, the  $\text{H}_2$  density in our studies was below  $10^{11} \text{ cm}^{-3}$ , and the helium buffer gas density was on the order of  $10^{13} \text{ cm}^{-3}$ . These conditions are safely within the two-body regime. Most studies in flow tubes and drift chambers are carried out at helium pressures around 1 torr, resulting in densities on the order of  $10^{16} \text{ cm}^{-3}$ , at least three orders of magnitude higher than in the present work. For some critical reactions (that have a long-lived collision complex), high number densities can influence the rate coefficients significantly; for example, the electron recombination of  $\text{H}_3^+$  in flow tubes seems to be dominated by ternary effects (38, 39). However, in the present case, one would probably expect that collisions with helium would stabilize the collision complex and increase the rate coefficient rather than decrease it. Therefore, we presently have no compelling explanation for the discrepancy between the present work and the recent SIFT experiments (22) at temperatures below room temperature.

As we have not used a dedicated catalytic converter to modify the  $\text{H}_2$  ortho/para ratio in the experiment, we expect ortho- $\text{H}_2$  to be somewhat overpopulated for the low-temperature experimental points in both reactions, when compared to the Boltzmann distribution that we assumed in the calculations. However, a previous QD study of reaction (1) showed that the ortho and para forms of  $\text{H}_2$  have similar reactivity

(28). Furthermore, since we observe for both reactions rate coefficients that are very close to the classical capture rate and vary only weakly with temperature, we do not anticipate a strong influence of the nuclear spin.

## CONCLUSION

Countless astronomical models and observational analyses have used the rate coefficients for reactions (1) and (2). Assessing the impact of the much higher rate coefficient for reaction (2) (compared to the previously accepted room temperature value) for different astronomical environments is beyond the scope of this work. On a broader scope, the combined experimental and theoretical study of the prototypical ion-molecule reactions considered here has implications even beyond the interstellar gas-phase water and oxygen networks. While modern interstellar chemistry codes often contain hundreds of rate coefficients (most of them for ion-neutral processes), only a handful of these reactions have been measured at the relevant temperatures. Consequently, interstellar gas-phase models continue to rely on extrapolated or guessed values for most of the reactions, rendering them vulnerable to the propagation of large errors and uncertainties. Here, we present laboratory measurements and accurate calculations for two key astrophysical ion-neutral reactions using methods for both experiment and theory that are suitable for the extreme temperatures and densities of interstellar environments. Accurate measurements of absolute rate coefficients under true interstellar conditions still pose a great challenge. In view of the growing molecular complexity that is uncovered by modern instruments such as the Atacama Large Millimeter/submillimeter Array, it is therefore crucial to benchmark promising theoretical methods, as it is apparent that the laboratory efforts alone will be outpaced by the observational demands.

In summary, our low-temperature measurements find that both  $\text{OH}^+$  and  $\text{H}_2\text{O}^+$  ions react very fast with molecular hydrogen, with rate coefficients very close to the Langevin limit. The rate coefficients for both reactions are well reproduced by our RPMD calculations. These findings corroborate the assumption that both molecular ions have to reside in interstellar environments with low  $\text{H}_2$  density. The perfect agreement of the low-temperature experimental and theoretical data is very promising. Contrasted by the discrepancy with previous QCT calculations, it indicates that it is essential to include quantum effects when considering reactions at interstellar temperature, even for seemingly nondiscriminative exothermic ion-neutral processes.

## METHODS

### Measurement procedure

The initial  $\text{OH}^+$  and  $\text{H}_2\text{O}^+$  ions were produced in the storage ion source by electron impact on water vapor (for this purpose, a small reservoir of distilled water was connected to one of the gas inlets of the source). We typically accumulated and stored the ions for a few milliseconds inside the source before extraction to thermalize their translational motion after ionization, which increases the capture efficiency in the 22-pole trap. The mass spectrum of the ions generated in the source, and transported through the 22-pole trap without storing, is shown in the inset of Fig. 1.  $\text{OH}^+$ ,  $\text{H}_2\text{O}^+$ , and  $\text{H}_3\text{O}^+$  were readily produced inside the source, the latter being formed after ionized water  $\text{H}_2\text{O}^+$  or  $\text{OH}^+$  reacted with neutral  $\text{H}_2\text{O}$  inside the source. Therefore, the  $\text{H}_3\text{O}^+$  signal was typically the strongest peak coming from the source, and  $\text{OH}^+$  was the weakest. The mass spectrum remained unchanged when

we stored the ions for a short period of time inside the ion trap without letting in any gas. All of the ions coming from the source were stored simultaneously inside the 22-pole trap, as there is basically no mass separation in the trap for these comparatively light masses.

During the experiments, we continuously bled in nonreactive helium buffer gas for cooling (typical density,  $10^{13} \text{ cm}^{-3}$ ) and  $\text{H}_2$  reactant gas (typical densities,  $10^{10}$  to  $10^{11} \text{ cm}^{-3}$ ) while, at the same time, monitoring the decay of the  $\text{OH}^+$  and  $\text{H}_2\text{O}^+$  ions as a function of storage time (Fig. 1, left). For initial measurements, we kept the total number of stored ions low (approximately  $\sim 500$ ) to confirm that all  $\text{OH}^+$  and  $\text{H}_2\text{O}^+$  ions ended up as  $\text{H}_3\text{O}^+$  in reactions with  $\text{H}_2$ . For a larger number of ions, the  $\text{H}_3\text{O}^+$  signal—being the strongest peak right from the start—will saturate, as the ions were extracted from the trap in a bunch that is only several  $10 \mu\text{s}$  long. For more than a thousand ions per bunch, their signal piled up in the detector, and single-particle counting was no longer accurate. However, since the initial  $\text{OH}^+$  counts were too small to collect enough statistics in this mode, we increased the number of stored ions to a few thousand, at the expense of saturating the  $\text{H}_3\text{O}^+$  signal, which was not essential for determining the rate coefficients. We performed various cross-checks between measurements at small and large number of ions and observed no difference in the decay curves or resulting rate coefficients. The intrinsic lifetimes of the stored ions inside the trap were on the order of several seconds and thus much longer than the decay times that we aimed to determine.

For our measurements, we varied the trap temperature between  $\sim 20$  and  $\sim 150 \text{ K}$  and the  $\text{H}_2$  number density between  $1 \times 10^9$  and  $1 \times 10^{11} \text{ cm}^{-3}$ . For each temperature and density, we recorded the decay curves of  $\text{OH}^+$  and  $\text{H}_2\text{O}^+$ , averaging usually over at least 20 trap fillings per storage time bin.

### RPMD rate theory

The RPMD rate theory is a relatively new approach to approximate quantum mechanical effects of nuclear motions in chemical dynamics studies, developed (31) and extensively benchmarked over the past decade (35). This method is based on the isomorphism between a quantum system and its  $n$  classical copies forming a necklace and coupled to the nearest neighbors via harmonic interactions. The classical isomorphism allows switching from purely quantum formalism to purely classical formalism and is formally an exact approach to calculate various static properties in which  $n$  (number of beads in the necklace) is a convergence parameter. The real-time dynamics of this necklace (“ring polymer”) represents an ad hoc idea of RPMD (31) to calculate approximately real-time correlation functions responsible for describing various dynamical processes, including chemical reactions (35). Through extensive study of various small gas-phase chemical reactions, it has been shown (35) that such an approximation to real-time dynamics allows accurate treatment of quantum mechanical effects of nuclear motions and provides very reliable and accurate estimates of thermal rate constants for different energy profiles along chemical reaction paths and temperatures. The key features of RPMD that lead to this success are (i) exact classical high-temperature limit, (ii) independence of the choice of transition state dividing surface, and (iii) connection to various transition state theories in the short-time limit (35). Here, we used the PESs for the title reactions (1) and (2) from (26, 36).

### SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at <http://advances.sciencemag.org/cgi/content/full/4/6/eaar3417/DC1>  
Supplementary Materials and Methods

fig. S1. Schematic of the experimental setup.

fig. S2. Potential of mean force  $[W(\xi)]$  and ring polymer recrossing factor  $[\kappa(t)]$  for the  $\text{OH}^+ + \text{H}_2$  reaction at 50 and 300 K.

fig. S3. Potential of mean force  $[W(\xi)]$  and ring polymer recrossing factor  $[\kappa(t)]$  for the  $\text{H}_2\text{O}^+ + \text{H}_2$  reaction at 50 and 100 K.

fig. S4. Histograms of final distances between the centers of mass of the products.

fig. S5. Schematic illustration of the reaction paths.

table S1. Rate coefficients (in  $10^{-9} \text{ cm}^3 \text{ s}^{-1}$ ) for the  $\text{OH}^+ + \text{H}_2$  and  $\text{H}_2\text{O}^+ + \text{H}_2$  reactions calculated using centroid-density quantum transition state theory ( $k_{\text{QST7}}$ ) and RPMD ( $k_{\text{RPMD}}$ ).

table S2. Input parameters for the RPMDrate calculations on the  $\text{OH}^+ + \text{H}_2$  and  $\text{H}_2\text{O}^+ + \text{H}_2$  reactions. References (40, 41)

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**Acknowledgments:** We thank A. A. Viggiano for the helpful comments and stimulating discussion. **Funding:** S.S.K. was supported by the Deutsche Forschungsgemeinschaft (DFG) within the DFG Priority Program 1573 “Physics of the Interstellar Medium” (contract no. KR 4617/1-1). F.G. and H.K. were supported by the European Research Council under grant agreement “Astrolab” no. StG 307163. Y.V.S. thanks the European Regional Development Fund and the Republic of Cyprus for the support through the Research Promotion Foundation (Project Cy-Tera NEA YΠOΔOMH/ΣTPATH/0308/31). Y.V.S. also acknowledges the support of the European Cooperation in Science and Technology Chemistry and Molecular Sciences and Technologies–Action CM1401 (Our Astro-Chemical History). H.G. acknowledges support from the U.S. Air Force Office of Scientific Research (FA-9550-15-1-0305). The support by the Max Planck Society is gratefully acknowledged. **Author contributions:** S.S.K. and H.K. designed and conceived the experimental research. S.S.K. and F.G. carried out the preparation of the setup and performed the measurements. H.G. and Y.V.S. devised the theoretical strategy and parameters and verified and interpreted the theoretical results. Y.V.S. wrote the RPMD code and carried out the rate coefficient calculations. **Competing interests:** The authors declare that they have no competing interests. **Data and materials availability:** All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Additional data related to this paper may be requested from the authors.

Submitted 27 October 2017

Accepted 15 May 2018

Published 22 June 2018

10.1126/sciadv.aar3417

**Citation:** S. S. Kumar, F. Grussie, Y. V. Suleimanov, H. Guo, H. Kreckel, Low temperature rates for key steps of interstellar gas-phase water formation. *Sci. Adv.* **4**, eaar3417 (2018).