Atom Tunneling in the Water Formation
Reaction $H_2 + OH \rightarrow H_2O + H$ on an Ice Surface

Jan Meisner,* Thanja Lamberts, and Johannes Kästner

Institute for Theoretical Chemistry, University of Stuttgart, Pfaffenwaldring 55, 70569 Stuttgart, Germany
E-mail: meisner@theochem.uni-stuttgart.de

Abstract

OH radicals play a key role as an intermediate in the water formation chemistry of the interstellar medium. For example the reaction of OH radicals with $H_2$ molecules is among the final steps in the astrochemical reaction network starting from $O$, $O_2$, and $O_3$. Experimentally it was shown that even at 10 K this reaction occurs on ice surfaces. As the reaction has a high activation energy only atom tunneling can explain such experimental findings.

In this study we calculated reaction rate constants for the title reaction on a water-ice $I_h$ surface. To our knowledge, low-temperature rate constants on a surface are not available in the literature. All surface calculations were done using a QM/MM framework (BHLYP/TIP3P) after a thorough benchmark of different density functionals and basis sets to highly accurate correlation methods. Reaction rate constants are obtained using instanton theory which takes atom tunneling into account inherently, with constants down to 110 K for the Eley–Rideal mechanism and down to 60 K for the Langmuir–Hinshelwood mechanism. We found that the reaction is nearly temperature independent below 80 K. We give kinetic isotope effects for all possible deuteration patterns for both reaction mechanisms. For the implementation in astrochemical networks, we also give fit parameters to a modified Arrhenius equation. Finally, several different binding sites and binding energies of OH radicals on the $I_h$ surface are discussed and the corresponding rate constants are compared to the gas-phase case.

Keywords: astrochemistry, interstellar medium molecules, water formation, kinetics, tunneling, isotopes

Introduction

Water ice was first detected in 1973[1] and is meanwhile known to be the main component of most interstellar ices[2–4]. Therefore, the surface formation of water in space was studied extensively experimentally in ultra-high vacuum setups[5–15] and through modeling studies with different varieties of Kinetic Monte Carlo[16–21] and rate equation models.[22–24] Although water can also be formed via gas-phase reactions, it is the formation on the surface of dust grains in dense molecular clouds that can explain the observed abundances. One of the crucial factors is that the surface provides an efficient way for the reaction products to lose their excess energy.[25] In other words, addition reactions which yield only one reaction product cannot take place in the gas phase, but can take place on the surface. For more insight on the gas-phase
routes we refer the reader to the recent review by Van Dishoeck et al. and focus on surface chemistry from hereon. An involved network of surface reactions in the interstellar medium (ISM) was originally proposed by Tielens and Hagen and has been updated incorporating the experimental results mentioned above.

Three main water formation routes constitute this network: hydrogenation of atomic oxygen, molecular oxygen ($O_2$), and ozone ($O_3$). Depending on the interstellar region of interest different routes dominate. In each pathway the hydroxyl radical is formed and subsequently reacts with either atomic or molecular hydrogen.

The barrierless direct hydrogenation of $O$ atoms by $H$ atoms is believed to be important in translucent and diffuse clouds in which $H$ atoms are more abundant than $H_2$ molecules and was experimentally studied by different groups.

$$O + H \rightarrow OH \quad (R\,1)$$

Alternatively, $O_2$ can be hydrogenated twice and the resulting hydrogen peroxide ($H_2O_2$) reacts with another $H$ atom to form water and a hydroxyl radical:

$$O_2 + H \rightarrow HO_2 \quad (R\,2)$$

$$HO_2 + H \rightarrow H_2O_2 \quad (R\,3)$$

$$H_2O_2 + H \rightarrow H_2O + OH \quad (R\,4)$$

These reactions have been shown to proceed even at temperatures as low as $12\,K$. The last reaction again proceeds via a barrier and has been shown to take place via tunneling both experimentally and using instanton theory. Note that the sequential hydrogenation of $O_2$ up to $H_2O_2$ is not possible in the gas phase, because of the reasons mentioned above. The reaction between $H$ and $HO_2$ can also result in two $OH$ radicals via a decomposition of activated $H_2O_2$.

$$H_2O_2 \rightarrow 2\,OH \quad (R\,5)$$

The resulting $OH$ radicals can recombine to $H_2O_2$ or form water and an $O$ atom:

$$2\,OH \rightarrow H_2O + O \quad (R\,6)$$

Microscopic kinetic Monte Carlo modeling found that experiments can be best described by the sequence $R\,2$, $R\,3$ leading to $H_2O_2^*$ and $R\,5$ with $OH$ radical recombination to $H_2O_2$ dominating over reaction $R\,6$.

Finally, $O_3$ can be hydrogenated which leads to an $O_2$ molecule and $OH$ radical and has been experimentally studied in the solid state at $10\,K$.

$$O_3 + H \rightarrow O_2 + OH \quad (R\,7)$$

In all of these reaction pathways, $OH$ radicals are formed. Subsequent reaction to form water can take place via reaction $R\,8$ or $R\,9$:

$$H + OH \rightarrow H_2O \quad (R\,8)$$

$$H_2O + OH \rightarrow H_2O + H \quad . \quad (R\,9)$$

Reaction $R\,8$ is barrierless, since it is a radical recombination reaction, but the reaction with $H_2$ proceeds via a barrier. It is the topic of this paper. A hydrogen atom is transferred from the $H_2$ molecule to the $OH$ radical to finally form water. In the ISM the competition between reactions $R\,8$ and $R\,9$ is determined by the interstellar environment, the relative abundances of $H$, $H_2$, and $O$ in the gas phase, and the reaction rates. Modeling this process in dense molecular clouds – where ice layers are thick and the $H_2$ abundance is high – therefore requires detailed knowledge of the low-temperature reaction rate constant. Reaction $R\,9$ in the gas phase was studied extensively experimentally and computationally.

The high activation energy of $2000\,K$ (experimentally determined by laser-induced fluorescence after photolysis) to $3000\,K$ (computationally determined) shows that atom tunneling is crucial for the reaction rate at low temperatures. Oba et al. found experimental evidence that the reaction of $H_2$ and $OH$ to wa-
ter and hydrogen atoms also occurs on surfaces even at 10 K due to atom tunneling.\textsuperscript{43} Recently, we published an extensive study on the reaction of molecular hydrogen and hydroxyl radicals (equation (R9)) in the gas phase including all possible isotope patterns down to 80 K.\textsuperscript{42} Here, we extend this work to the adsorption of OH radicals onto crystalline I\textsubscript{h} water ice and the subsequent reaction with H\textsubscript{2}. We present binding sites, energies, reaction paths and reaction rate constants for the reaction of H\textsubscript{2} with OH on the surface. This includes the effect of atom tunneling at low temperatures via the use of instanton theory.

This paper is structured as follows: In the methods section we present a benchmark to find a suitable density functional and basis set by comparing the quality with highly correlated calculations on UCCSD(T)-F12\textsuperscript{45,46} level. Furthermore, the water ice surface and the organization of the QM/MM setup, as well as the methodology of the reaction rate calculations are described. In the results section we show binding sites and binding energies of the OH radical on the ice surface as well as accompanying activation energies, transition state structures and intrinsic reaction coordinates (IRC). We give reaction rate constants for the Eley–Rideal and the Langmuir–Hinshelwood mechanism using multidimensional atom tunneling via semiclassical instanton theory\textsuperscript{47–51} and make a comparison to the analytical solution of an Eckart shaped barrier. The results are compared to those in the gas phase and the impact of surfaces on the reactivity is discussed. Kinetic isotope effects for all eight possible permutations of exchanging hydrogen for deuterium are shown as well. The last section discusses the implications to astrochemistry, gives fits of to a modified Arrhenius equation and concludes the study.

Methods

Choice of Electronic Potential

In order to obtain reliable reaction rate constants, the method to calculate the underlying electronic potential has to be as accurate as possible. Instanton calculations using highly correlated wave function methods are too time consuming so we applied density functional theory (DFT) throughout this work. For this purpose, an extensive benchmark of the most common functionals and basis sets has been performed, as can be seen in the Supplementary Information. The BHLYP functional\textsuperscript{52–55} in combination with the def2-SVPD basis set\textsuperscript{57} is found to describe the reaction well. The BHLYP functional has previously been found to describe astrochemical reactions with open-shell molecules properly.\textsuperscript{58,59} It was also found appropriate for water-water interactions (see Supplementary Information). Thus BHLYP is used in the remainder of this paper. All DFT calculations were performed with Turbomole version 7.0\textsuperscript{60} SCF energies were converged to an accuracy of $10^{-9}$ Hartree on a $m5$ grid.\textsuperscript{61}

To include the environment, i.e., the water surface, we used a QM/MM framework for which we used the ChemShell interface.\textsuperscript{62,63} The QM part can be polarized by means of electrostatic embedding into the MM charges. All geometry optimizations and reaction rate calculations were done with DL-FIND.\textsuperscript{64} The visualisation of the molecules and ice surface was done using Visual Molecules Dynamics (VMD).\textsuperscript{65}

Surface Model and QM/MM setup

We used the (0001) surface of hexagonal ice I\textsubscript{h} that minimizes the surface free energy as described by Fletcher.\textsuperscript{66} The structure of the bare surface can be seen in Fig. 1. In that phase, the protons are ordered. Equivalent sites for rows (vertical in the top image in Fig. 1). While the majority of solid water in the ISM is expected to be amorphous, the crystalline phase is easier to model because only a limited number of distinct adsorption sites is available.
Figure 1: QM/MM setup of the Fletcher surface. The solid ball-and-stick-molecules represent the QM region while the transparent ones represent the MM region. All MM water molecules within a radius of 15 Å are allowed to move and rotate.

The structural model consisted of a hemisphere with a radius of 25 Å comprising 1151 water molecules. The MM part was described by the TIP3P potential. For the QM part, we used five adjoining water hexagons of the top layer: 19 water molecules and the adsorbed atoms. Geometry optimisations included all water molecules within a radius of 15 Å around the center of the hemisphere (261 molecules) as active atoms, the other H2O molecules were frozen. This leads to a proton disordereding of the surface. All in all, 2349 variables are to be optimised for the bare surface. Instantons and the corresponding Hessians have been calculated with a reduced dimensionality: here, only the adsorbed atoms/molecules and the hexagon of six closest water molecules were flexible.

Reaction Rate Calculations and Tunneling

To calculate reaction rate constants including atom tunneling we use instanton theory, which is increasingly used to calculate chemical reaction rate constants. In instanton theory, a closed Feynman path spans the barrier region. At low temperatures it extends towards the reactant state. At temperatures above the crossover temperature

$$T_c = \frac{\hbar \omega_{TS}}{2\pi k_B}$$

the instanton path generally collapses to one single point on the potential energy surface. Here, $\hbar$ is Planck’s constant divided by 2π, $k_B$ is Boltzmann’s constant and $\omega_{TS}$ is the absolute value of the imaginary frequency at the transition state structure in the harmonic approximation. The crossover temperature gives a first and simple estimate at which temperature atom tunneling becomes important. The mass dependence of $\omega_{TS}$ also causes mass dependence of $T_c$.

For the reaction on the Fletcher surface, the closed Feynman path was discretized with 40 images down to 175 K and with 78 images down to 80 K. For the gas phase reaction (of all isotopologues), 200 images were used for the whole temperature range. Vibrational modes are included harmonically around the Feynman path. The rotational partition functions of the reactants and the images of the instantons were approximated by those of rigid rotors. The translational partition function was included within the approximation of an ideal gas, which is identical to the quantum particle in a box. The rotational partition function of the whole instanton was calculated to be the geometric mean value of the rotational partition functions of all images. The symmetry number $\sigma = 2$ was taken into account when calculating the rotational partition function of the H2 and D2 molecules for bimolecular reaction rates. For the reactions with HD and for unimolecular reaction rates in general, $\sigma = 1$ was used because the rotation of adsorbed molecular hydrogen is
hindered by the surface.

Besides the structural model which includes the surface atoms explicitly, we alternatively mimic the effect of the ice surfaces on the partition function for reactions calculated in a gas-phase model in an approach we successfully applied previously.\(103\) For unimolecular reaction rate constants, the rotational partition function is assumed to be constant during the reaction just as the surface suppresses the rotation in the reactant as well as in the transition state. For bimolecular reaction rate constants, only the translation and rotation of the \(\text{H}_2\) fragment is considered in the reactant state. Rotational and translational motion of the \(\text{OH}\) radical and transition state structure are suppressed, just it is the case when \(\text{OH}\) is adsorbed on the surface. It has to be mentioned that while this approach properly approximates the suppressed motion of the species on the surface, it neglects any influence of the surface on the potential energy along reaction path and therefore the corresponding potential activation energy. Hereinafter, this methodology is referred to as implicit surface model.

Instantons were considered to be converged when all components of the nuclear gradient are smaller than \(1 \cdot 10^{-8}\) a.u.. Instanton calculations were performed at temperatures below the crossover temperature of \(280 \pm 5\) K (depending on the binding site). Because of the existence of a pre-reactive minimum, below a particular, mass-dependent temperature, the tunneling energy is lower than the potential energy of the separated products for bimolecular reaction rates. At that temperature, canonical instanton theory becomes unreliable.\(106\) Therefore, bimolecular reaction rates can only be provided for \(110\) K and higher temperatures for the reaction \(\text{H}_2 + \text{OH} \rightarrow \text{H} + \text{H}_2\text{O}\).

Calculations of intrinsic reaction coordinates (IRCs) have been performed using a modified version of Schlegel’s Hessian-Predictor-Corrector method\(107-109\) with a step size of 0.05 mass-weighted atomic units.

### Results

#### Binding Sites and Energies

We identified three different binding sites of \(\text{OH}\) on the Fletcher surface, which are shown in Fig. 2. We calculated the corresponding adsorption energies with and without harmonically approximated vibrational zero-point energies. The values are given in table 1. For all binding sites, zero-point energy reduces the binding energy by around 16 kJ mol\(^{-1}\) (1920 K) because the OH–surface complex has additional vibrational modes. The harmonic approximation can be assumed to overestimate the zero-point energy which leads to an underestimation of the corresponding adsorption energy.

In the first binding site, the \(\text{OH}\) radical is located directly in the middle of a water hexamer where it accepts hydrogen bonds from two of the dangling hydrogen atoms and donates a hydrogen bond to the O atom of a water molecule of the surface. We call this binding site hollow. The binding energy is 40.5 kJ mol\(^{-1}\) (4870 K) including zero-point energy.

In a similar binding site the \(\text{OH}\) radical is also hydrogen-bound to the oxygen atom of a water molecule and to one dangling hydrogen atom of the surface, see Fig. 2. The third hydrogen bond is absent, \(i.e.,\) the \(\text{OH}\) radical bridges two surface water molecules. We call this binding site bridged. As this binding site is rather similar to the hollow one, the binding energy is with 39.7 kJ mol\(^{-1}\) (4770 K) only slightly smaller.

In the third binding site the \(\text{OH}\) radical is located on top of one of the water molecules. Because of that we call this binding site top. The \(\text{OH}\) radical also accepts two hydrogen bonds from the surface and donates one. The binding energy of this site is with 32.1 kJ mol\(^{-1}\) (3860 K) lower than for the hollow and bridged binding sites. These values lie nicely in the range of experimentally determined desorption energies on silicate surfaces of 1656–4760 K.\(110\)

#### Reaction Barriers

One possibility for the reaction of the \(\text{OH}\) radical with molecular hydrogen on the ice surface
Figure 2: Structures of the adsorbed OH radical (blue) on the Fletcher surface. All binding sites are shown from top and side perspectives. Left: Hollow, Middle: Bridged, Right: Top

Table 1: Adsorption energies of OH on the Fletcher surface and hydrogen bond distances. \( V_{\text{ads}} \) and \( E_{\text{ads}} \) denote the adsorption energy without and with zero point energy, respectively. The hydrogen-bond lengths \( d_1 \) to \( d_4 \) are explained in Fig. 2. Energies are given in kJ mol\(^{-1}\), distances in Å.

|       | \( V_{\text{ads}} \) | \( E_{\text{ads}} \) | \( d_1 \)  | \( d_2 \)  | \( d_3 \)  | \( d_4 \)  |
|-------|---------------------|---------------------|------------|------------|------------|------------|
| Hollow| 57.0                | 40.5                | 1.77       | 2.22       | 2.27       |            |
| Bridge| 55.6                | 39.7                | 1.77       | 1.99       | 3.89       |            |
| Top   | 48.1                | 32.1                | 2.11       | 2.36       | 1.78       |            |

In this work, we restrict ourselves to the chemical reaction forming \( \text{H}_2\text{O} \) molecules and ignore the physical processes after that. Therefore, for the products the label indicating the aggregate state was omitted. For each binding site of OH we found one corresponding transition state structure. These transition state structures are called direct hereinafter. The vibrational adiabatic reaction barriers with respect to the separated reactants (potential energy barriers including zero-point energy) of these transition state structures lie between 24.2 and 24.7 kJ mol\(^{-1}\), (2910 and 2970 K), see table 2. This is just slightly lower than the adiabatic reaction barrier of the gas phase reaction of 25.4 kJ mol\(^{-1}\) (3055 K, from separated reactants). Here we want to stress that all reaction barriers are very similar, independently of the corresponding adsorption energies, although the latter vary over 8 kJ mol\(^{-1}\). This is in agreement with what is found for reactions on amorphous solid water.

We found another type of transition state structures in which the hydrogen atom of the OH radical points away from the surface and the \( \text{H}_2 \) molecule approaches via a path closer
to the surface. The [OH ••• H₂] complex possesses similar internal coordinates as in the direct transition state structures but is rotated with respect to the ice surface. For these rotated transition state structures, the adiabatic reaction barriers are 49.3 and 45.7 kJ mol⁻¹ (5930 K and 5500 K) for the hollow and the top binding site, respectively. No rotated transition state structure was found for the bridged binding site. Since the barriers via rotated transition states are much higher than those via the direct transition states, the latter have resulted in much higher rates and the former are not considered further.

We calculated the potential energy along the intrinsic reaction coordinates (IRCs) of the different binding sites. The end of the IRCs define pre-reactive complexes (PRCs). Those are geometries in which an H₂ molecule is loosely bound to the surface in the vicinity of the OH radical. These structures are used as reactant states to calculate the unimolecular activation energies shown in table 2.

The potential energy curves along the IRCs belonging to the different binding sites are almost indistinguishable from the one of the gas-phase reaction, see Fig. 4. This shows again that the surface has negligible influence on the potential energy along the reaction path. During the reaction, any changes in the hydrogen bond length remain below 0.2 Å, see Fig. S3 of the Supplementary Information. Overall, a classical catalytic effect is absent: the activation barrier is unaltered, neither is the reaction mechanism changed. This can be explained by the adsorption energy during the reaction. In typical heterogeneous catalysis the molecules are activated through interactions with the surface in a way that the energy of the transition state with respect to the energy of the reactant state is reduced. These interactions are either forming new chemical bonds or causing a shift in electron density. In our case, the OH radical forms three hydrogen bonds in the adsorption

Table 2: Reaction barriers including zero-point energies. The label bi denotes that the barrier is given with respect to the separated reactants, i.e., OH(ads) and H₂(g). The label uni indicates barriers with respect to the respective pre-reactive complexes. All values are in kJ mol⁻¹.

|                      | Hollow | Bridged | Top | Gas Phase |
|----------------------|--------|---------|-----|-----------|
| $E_{\text{direct}}^\text{A,bi}$ | 24.2   | 24.7    | 24.3 | 25.4      |
| $E_{\text{rotated}}^\text{A,bi}$ | 49.3   | —       | 45.7 | —         |
| $E_{\text{direct}}^\text{A,uni}$   | 22.5   | 24.1    | 22.4 | 24.4      |

Figure 3: Transition state structure of the direct-hollow binding site. QM atoms are shown as balls and sticks, MM atoms as transparent sticks.

Figure 4: Above: Potential energy $V$ of the intrinsic reaction coordinates (IRCs) of the hollow, top, and the bridged binding site compared with the gas-phase reaction.
Table 3: Geometric parameters of the transition state structures for different binding sites in comparison to the gas phase transition state structure. The O–H distance of the newly formed bond, the H–H distance of the original H$_2$ molecule, and the H–O–H angle of the newly formed water molecule are denoted by $d_{\text{O-H}}$, $d_{\text{H-H}}$, and $\angle(\text{H-O-H})$, respectively. Distances are in Å and angles in degrees.

|        | $d_{\text{O-H}}$ | $d_{\text{H-H}}$ | $\angle(\text{H-O-H})$ |
|--------|------------------|------------------|-------------------------|
| Hollow | 1.33             | 0.83             | 99.2                    |
| Top    | 1.33             | 0.83             | 99.7                    |
| Bridged| 1.33             | 0.84             | 98.7                    |
| Gas    | 1.36             | 0.82             | 96.8                    |

process and these three hydrogen bonds are retained during the whole reaction. Therefore, the adsorption energies of the reactant state and the transition state structure are virtually the same and the potential energy of the reaction remains comparable to the gas phase. Reaction with an OH radical bound via four hydrogen bonds is impossible due to steric hindrance. Therefore, the maximal number of H-bonds to a reactive OH is always three, independent of the existence of e.g. cavities for surface defects. It can, therefore, be assumed that amorphous solid water ices behave similarly in terms of negligible catalytic effect.

Note, that any processes after the formation of the chemical bonds, like desorption or dissipation, are outside of the scope of this article because the do not influence the rate. The kinetic bottleneck in the water formation from H$_2$ molecules and OH radicals is the H–H bond breaking which is described here.

**Reaction Rate Constants for the Eley–Rideal Mechanism**

In the Eley–Rideal (ER) mechanism, one particle (a molecule or an atom) physisorbs on the surface and thermalizes there. Another particle comes and directly reacts with the pre-adsorbed particle to form the products. In this study, we want to focus on reaction (R 10) where an OH radical is adsorbed and the H$_2$ molecule comes in from the gas phase, since OH has a higher adsorption energy. The incoming H$_2$ molecule reacts with the OH-surface system in what can be formally seen as a bimolecular reaction. Instantons were calculated from 250 K to 110 K. For comparison, we calculated reaction rate constants using the approximation of an Eckart-shaped barrier.

As the reaction profiles of all three direct transition state structures and IRCs are nearly identical, we only calculated reaction rate constants of the direct-hollow transition state structure. Due to high computational costs the active region for the instanton calculations was reduced to the one water hexamer below the adsorbed OH radical. The resulting adiabatic activation energy of 24.11 kJ mol$^{-1}$ almost equal to the 24.19 kJ mol$^{-1}$ obtained for the full active region.

The resulting reaction rate constants are compared to the gas-phase data calculated on the same potential energy surface in the Arrhenius plot in Fig. 5. The rate constants including tunneling correction via the Eckart barrier and those obtained by transition state theory without tunneling are shown for comparison. The implicit surface model is able to reproduce the
rate constants of the explicit surface calculations up to factors of 3.6 and 2.7 at 275 K and 110 K, respectively. This indicates that for reactions without a classical catalytic effect, the implicit surface approach is a promising approximation. Numeric values for the rate constants are available in the Supplementary Information, table S II.

**Reaction Rate Constants for the Langmuir–Hinshelwood Mechanism**

In the Langmuir–Hinshelwood (LH) mechanism, both particles are adsorbed on the surface and diffuse until they meet. If they approach each other, they form a PRC. This PRC can either react or decay by diffusion or desorption of one or both reactants. The reaction of a PRC to the products is a unimolecular process. Thus, Langmuir–Hinshelwood reactions are characterized by unimolecular rate constants.

We calculated unimolecular reaction rate constants for the hollow binding site. The adiabatic activation barriers for the LH mechanism in all binding sites are given as \( E_{A,uni}^{\text{direct}} \) in table 2. The resulting unimolecular rate constants \( k_{\text{react}} \) are shown in Fig. 6 and table S II. Instantons were calculated down to 80 K. At even lower temperatures, more images would be required to obtain converged reaction rates which would render the computations too expensive.

The rate constants from the implicit surface model agree within one order of magnitude with those from the full ice surface model, see Fig. 6.

The main effects of a surface on catalysis are

1. An increase in the concentration of reactive species compared to the gas phase, especially in low-pressure environments like the ISM.

2. The removal of excess heat of reaction and, thus, the stabilization of reaction products of exothermic reactions.

3. Restricted mobility, in particular rotation.

Figure 6: Arrhenius plot of the unimolecular Reaction rate constants. Surface reaction rates were calculated around the direct-hollow reaction pathway.

4. Alternations of the barrier height and possibly the reaction path, *i.e.*, a classical catalytic effect.

In any atomistic models based on transition state theory, as used in the present work, effects (1) and (2) are included implicitly. Rate constants are independent of the concentrations. Thermal rate constants assume a canonic ensemble, *i.e.*, thermal equilibrium throughout the reaction. Excess heat is removed instantly. The implicit surface model we propose here also includes (3), the immobilization. Only (4), the classical catalytic effect, is neglected by the implicit model, but taken into account in an explicit surface model in which the surface atoms are actually included in the structural model.

The results of the standard gas-phase model and the gas-phase calculations using the implicit surface model are closer for the unimolecular reaction than for the bimolecular calculations. The reason is that in the unimolecular case, the implicit surface model merely assumes that the rotational partition function of the PRC is the same as the one of the transition state (*e.g.* that both do not rotate), while their rotation is taken into account in the gas phase. As both PRC and transition state have similar rotational partition functions (they include the same atoms), the neglect of this term is of minor effect. In the bimolecular case, the
implicit surface model removes translation and rotation of one reactant (OH) and the transition state, which is a much larger alternation of the rate constant. Note, that due to the inhibited rotation of the H₂ molecule in the PRC the symmetry number \( \sigma = 1 \) was used for the explicit and implicit surface calculations.

**Kinetic Isotope Effects**

We used the implicit surface model to calculate kinetic isotope effects (KIEs) for all eight possible deuteration patterns. Bimolecular and unimolecular reaction rate constants are shown in Fig. 7 and Fig. 8 respectively. When substituting protium atoms with deuterium atoms, the crossover temperature reduces significantly as a result of a smaller imaginary frequency and therefore a smaller crossover temperature. Thus, the rate constants are reported here for 200 K and below. For bimolecular reaction rates, the temperature below which the tunneling energy is lower than the potential energy of the asymptotic reactants changes with the mass, too. Here and in Fig. 7 and Fig. 8 the isotope patterns are labeled as in our previous work\(^{42}\) as H\(^1\)H\(^2\)OH\(^3\) such that the reaction reads H\(^1\)H\(^2\) + OH\(^3\) \(\rightarrow\) H\(^1\) + H\(^2\)O\(^2\)H\(^3\). DDOH therefore corresponds to a reaction of OH with D\(_2\) while HDOH corresponds to the reaction HD + OH \(\rightarrow\) H + DOH.

In both, the bimolecular and unimolecular cases, the primary KIE – the ratio between the rate constants of H-transfer and the corresponding D-transfer – is as big as two orders of magnitude but also depends on the isotope pattern of the other two hydrogen atoms.

For the bimolecular case, the KIEs are similar to the ones reported in the gas phase.\(^{42}\) The secondary KIEs play a smaller role as they are in all cases smaller than 10. When substituting OH by OD, an inverse KIE is found, i.e., the rate constant increases due to deuteration. This small inverse secondary KIE, about 2-3 is caused by differences in the zero-point energy.\(^{112,115}\) The inverse KIE for the deuteration of OH was also present in the gas-phase reaction rate constants where the difference in zero-point energy corrected activation barrier between the HHOH and the HHOD system is 1.3 kJ mol\(^{-1}\) (156 K).\(^{42}\)

In the unimolecular case, the primary KIEs are \(\approx 5\) at 200 K and increase to \(\approx 300\) at 60 K. The secondary KIEs play an even smaller role than in the bimolecular case and no inverse KIE is present, see Fig. 8.
Astrochemical Implications

In order to provide our calculated rate constants to astrochemical modelers in an easily implementable way, we have fitted all curves in Figs. 7 and 8 to the following analytical expression:

$$k(T) = \alpha \left( \frac{T}{300 \text{ K}} \right)^\beta \exp \left( -\frac{T + T_0}{T^2 + T_0^2} \right)$$

Here, the parameters $\alpha$, $\beta$, $\gamma$, and $T_0$ are all fitting parameters, where $\alpha$ has the units of the rate constant, $\beta$ regulates the low-temperature behavior, and $\gamma$ and $T_0$ can be related to the activation energy of the reaction. To obtain a realistic low-temperature extrapolation the value of $\beta$ has been fixed to 1. For the fitting procedure we use the Eckart approximation above the crossover temperature, equation (1), and the values calculated with instanton theory below $T_c$. The exact values for the fit parameters for all eight isotope-substituted reactions are given in the Supplementary Information along with the corresponding reaction rate constants.

We have found that the energy barrier is rather independent of the binding site. We have found the same trend for the reaction of HNCO with hydrogen atoms on amorphous solid water. Furthermore, from the figures in the previous Section it is apparent that the curves of the rate constants flatten off with decreasing temperature. Therefore, in order to be able to use our unimolecular rate constants in models that take the very low temperatures in dense molecular clouds (20 K) into account, we recommend to use the value of the rate constant at the lowest temperature given (60 K) with an approximate error bar of ± half an order of magnitude.

As mentioned above, there is a relation between bimolecular rate constants and the Eley–Rideal mechanism and unimolecular rate constants and the Langmuir–Hinshelwood mechanism. Given the typical low fractions of OH radicals available at the surface for direct H$_2$ impingement, the Langmuir–Hinshelwood mechanism where two species find each other via surface diffusion is expected to dominate.

The Langmuir–Hinshelwood mechanism can be described as a reaction cascade:

$$\text{OH}_{(ads)} + \text{H}_2(g) \rightarrow \text{OH}_{(ads)} + \text{H}_2(ads)$$

$$\rightarrow \left[ \text{OH} \cdots \text{H}_2 \right]_{(ads)} \stackrel{k_{\text{react}}}{\rightarrow} \text{H}_2\text{O} + \text{H} \quad (R\, 11)$$

Diffusion forms the pre-reactive complex (PRC), which reacts to the products. The reaction rate of the last step is $R_{\text{react}} = k_{\text{react}}n([\text{OH} \cdots \text{H}_2]_{(ads)})$, i.e., a unimolecular process with the rate constant $k_{\text{react}}$. The rate of the overall LH process, $R_{\text{LH}}$, can be expressed as the probability to react, $P_{\text{react}}$, multiplied by the rate at which the particles meet, $R_{\text{diff}}$:

$$R_{\text{LH}} = R_{\text{react}} R_{\text{diff}}$$

$$= P_{\text{react}} \frac{k_{\text{diff,H}_2} + k_{\text{diff,OH}}}{N_{\text{sites}}} n(\text{H}_2)n(\text{OH})$$

The overall process is bimolecular, of course. It depends on the surface concentrations $n(\text{H}_2)$ and $n(\text{OH})$, as well as on the concentration of adsorption sites $N_{\text{sites}}$.

When surface diffusion and microscopic sites are not explicitly included in the model, such as is commonly the case for two-, three- or multiphase rate-equation models, the competition between reaction, diffusion, and desorption of the reactants after they reside next to each other has to be taken into account. This can be done by calculating the probability to react as the ratio between the rate constant for reaction and the total rate constant for all processes:

$$P_{\text{react}} = \frac{k_{\text{react}}}{k_{\text{react}} + k_{\text{diff,H}_2} + k_{\text{diff,OH}} + k_{\text{des,H}_2} + k_{\text{des,OH}}}$$

With this formulation of a LH rate, two limiting cases can be discussed. In both, we will assume for simplicity that the desorption is negligible compared to reaction and diffusion. The first case is a diffusion-limited reaction, in which the diffusion of both species is much slower than the reaction ($k_{\text{diff}} \ll k_{\text{react}}$). Then
Table 4: Reaction rate constants $k$ in cm$^3$ s$^{-1}$ and kinetic isotope effects for low-$T$ unimolecular reactions with different approaches.

| Rate constant | Rectangular barrier | Eckart barrier | Instanton theory |
|---------------|---------------------|----------------|------------------|
|               | ref [22]            | this work$^\dagger$ | ref [23]$^\ddagger$ | this work$^\circ$ |
| HHOH          | $1.40 \times 10^{+1}$ | $6.31 \times 10^{+2}$ | $4.07 \times 10^{+5}$ | $3.19 \times 10^{+5}$ | $5.12 \times 10^{+5}$ |
| DHOH          | $1.11 \times 10^{−1}$ | $6.31 \times 10^{+2}$ | $3.62 \times 10^{+5}$ | $1.16 \times 10^{+5}$ | $1.59 \times 10^{+5}$ |
| HDOH          | $1.11 \times 10^{−1}$ | $9.76 \times 10^{−2}$ | $1.00 \times 10^{+3}$ | $3.12 \times 10^{+2}$ | $1.41 \times 10^{+3}$ |
| HHOD          | $1.30 \times 10^{+1}$ | $6.31 \times 10^{+2}$ | $8.74 \times 10^{+5}$ | $4.62 \times 10^{+5}$ | $3.42 \times 10^{+5}$ |
| DDOH          | $2.51 \times 10^{−3}$ | $9.76 \times 10^{−2}$ | $8.07 \times 10^{+2}$ | $3.40 \times 10^{+2}$ | $3.99 \times 10^{+2}$ |

KIEs wrt. HHOH

|          |           |           |           |
|----------|-----------|-----------|-----------|
| DHOH     | 127       | 1.00      | 1.12      | 1.37      | 3.22      |
| HDOH     | 127       | 6465      | 407       | 511       | 363       |
| HHOD     | 1.08      | 1.00      | 0.466     | 0.69      | 1.50      |
| DDOH     | 5578      | 6265      | 504       | 938       | 1283      |

$^\dagger$ $a = 1$ Å, $m$ as the reduced mass, $E_{\text{reaction}} = 2100$ K

$^\ddagger$ $a = 1$ Å, $m$ as the mass of the transferring atom, $E_{\text{reaction}} = 2700$ K

$^\circ$ at 60 K

$^a$ Literature values$^{23}$ multiplied by $\nu_{\text{trial}} = 10^{12}$ s$^{-1}$

$k_{\text{diff}} + k_{\text{react}} \approx k_{\text{react}}$ and $P_{\text{react}} \approx 1$. Thus,

$$R_{\text{LH,diffusion-limit}} = \frac{k_{\text{diff,H}_2} + k_{\text{diff,OH}}}{N_{\text{sites}}} n(H_2)n(OH). \quad (6)$$

The other limiting case is a reaction-limited process in which the reaction is much slower than the diffusion of both reactants, *i.e.*, $k_{\text{react}} \ll k_{\text{diff,H}_2} + k_{\text{diff,OH}}$. Then, $P_{\text{react}} \approx k_{\text{react}}/(k_{\text{diff,H}_2} + k_{\text{diff,OH}})$ and

$$R_{\text{LH,reaction-limit}} = \frac{k_{\text{react}}}{N_{\text{sites}}} n(H_2)n(OH). \quad (7)$$

Reaction rate constants, like the ones calculated in this work, influence the overall Langmuir–Hinshelwood rate in the general case and in the reaction-limited case. Since $H_2$ is assumed to diffuse fast, this is likely to be the case for the reaction discussed in this paper.

Usually, for diffusion and desorption the approximation for the rate constant

$$k_{\text{process}} = \nu_{\text{trial}} \, e^{-E_{\text{process}}/k_B T} \quad (8)$$

is made, where $\nu_{\text{trial}}$ is the trial frequency and $E_{\text{process}}$ the activation energy for diffusion or desorption.

The reaction rate constant $k_{\text{react}}$ is provided by our instanton calculations. In models, however, often two approaches are tried and the rate constant that is the highest is chosen to be used in the model run: (a) the rate constant is calculated classically, analogous to equation (8) substituting $E_{\text{process}}$ with the reaction barrier and (b) tunneling is taken into account via a semiclassical approximation to the rectangular barrier approximation

$$k_{\text{react}} = \nu_{\text{trial}} \, e^{-2a/h/\sqrt{2\mu E_{\text{reaction}}}}. \quad (9)$$

Here, $a$ is seen as the barrier width, but in fact can not be directly linked to any physical observable and $\mu$ is an effective mass. Another way to take into account tunneling is the use of the Eckart barrier approximation instead.

We want to conclude with a specific comparison between values for the reaction rate constants and kinetic isotope effect calculated with the rectangular barrier approximation, the Eckart approximation (all with $\nu_{\text{trial}}$ kept constant), and instanton theory, taking into account the values published by Furuya et al.$^{22}$ and Taquet et al.$^{23}$ The values for the rate constants and KIE are given in Table 4. Firstly, it is clear that the choice for the value of the
reduced mass has a strong influence on the rate constants and therefore on the KIEs, too. Furthermore, the rectangular barrier approximation is very crude and can underestimate the rate constants by several orders of magnitude. This in turn can lead to wrong predictions of isotope fractionation in the ISM. Moreover, the rate constants themselves also span a large range between the different approaches and parameter choices which can have an effect on the thickness of the ice, the competition of OH reactivity with other species, and on the main route leading to water formation in dense molecular clouds. The Eckart barrier approximation works reasonably for this reaction although the reaction between H and H₂O₂ shows that an order of magnitude difference can appear between rate constants calculated with the Eckart approximation and the instanton method. Also the KIEs calculated in this way give surprisingly good agreement with the KIEs obtained with the instanton theory.

With this in mind, we wish to stress that it is important to realize when standard choices of parameter settings such as barrier width and reduced mass may not be enough to describe a reaction properly. In the case where better approximations are available, such as our instanton calculations, $k_{\text{react}}$ in equation (5) can directly be taken as the unimolecular rate constant or the fit thereof (see Supplementary Information).

### Conclusions

In this study, we computed chemical reaction rate constants of the reaction of hydroxyl radicals with molecular hydrogen (reaction $R\,9$) on an $I_h$ ice surface. For this purpose, we used instanton theory on highly accurate potential energy surfaces. We provide reaction rate constants from 275 K down to 110 K for the ER mechanism (bimolecular) and down to 60 K for the LH mechanism (unimolecular). For both mechanisms, a fit of parameters of a modified Arrhenius equation was performed to obtain a continuous expression of $k(T)$.

To summarize the most important results:

- For the reaction of H₂ and OH radicals, an ice surface just barely influences the potential energy along the reaction path, i.e., there is no classical catalytic effect. Therefore, the surface effects can be included by using an implicit surface model.
- A surface can be implicitly mimicked by a structural gas-phase model, using the same rotational partition function for reactant and transition state. The reaction rate constants obtained in this way differ by a factor of 9.3 from the ones calculated on a full ice surface model.
- We found three different binding sites on our $I_h$ surface. The binding energy lies between 32 and 41 kJ mol⁻¹ (3850 and 4930 K).
- The most important transition state structures and reaction paths are comparable to the ones in the gas phase. It follows that the adiabatic energy barriers (24–25 kJ mol⁻¹) are similar to the barrier of the gas phase reaction (25.4 kJ mol⁻¹, 3055 K).
- Kinetic isotope effects have been calculated for all possible isotope substitution patterns. Exchanging the H to be transferred to D leads to a decrease in the rate constant of 2–3 orders of magnitude. Secondary KIEs are at most half an order of magnitude.

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