Low-Temperature Kinetic Isotope Effects in 
$\text{CH}_3\text{OH} + \text{H} \rightarrow \text{CH}_2\text{OH} + \text{H}_2$ Shed Light on 
the Deuteration of Methanol in Space

April M. Cooper and Johannes Kästner

Institute for Theoretical Chemistry, University of Stuttgart, Pfaffenwaldring 55, 70569

Stuttgart, Germany

E-mail: kaestner@theochem.uni-stuttgart.de

Phone: +49-711-685-64473
Abstract

We calculated reaction rate constants including atom tunneling for the hydrogen abstraction reaction $\text{CH}_3\text{OH} + \text{H} \rightarrow \text{CH}_2\text{OH} + \text{H}_2$ with the instanton method. The potential energy was fitted by a neural network, that was trained to UCCSD(T)-F12/VTZ-F12 data. Bimolecular gas-phase rate constants were calculated using microcanonic instanton theory. All H/D isotope patterns on the CH$_3$ group and the incoming H atom are studied. Unimolecular reaction rate constants, representing the reaction on a surface, down to 30 K, are presented for all isotope patterns. At 30 K they range from 4100 for the replacement of the abstracted H by D to $\sim$8 for the replacement of the abstracting H to about 2–6 for secondary KIEs. The $^{12}$C/$^{13}$C kinetic isotope effect is 1.08 at 30 K, while the $^{16}$O/$^{18}$O kinetic isotope effect is vanishingly small. A simple kinetic surface model using these data predicts high abundances of the deuterated forms of methanol.

Introduction

Methanol, CH$_3$OH, has been detected in several environments in the interstellar medium, e.g. in dark clouds, pre-stellar cores, in the gas phase as well as in ices. Like several other molecules, it is found to be heavily deuterated. For example the ratio between CH$_3$OH and CD$_3$OH was found to be merely 125 towards IRAS 16293-2422. With a cosmic D/H abundance ratio of $\sim 1.5 \times 10^{-5}$ this corresponds to a deuterium enrichment by a factor of over 13 orders of magnitude. Moreover, deuteration is almost exclusively found on the C atom rather than on the OH group.

The reasons for that have been discussed in the past. Methanol is mostly synthesized in the solid state on the surface of dust grains by successive hydrogenation of carbon monoxide. In that process, the slowest reaction is the initial hydrogenation of CO to form HCO or DCO. Here, formation of HCO is faster than the formation of DCO by factors between 10 and $> 250$ at low temperatures. Formaldehyde, H$_2$CO, is preferentially hydrogenated
at the carbon end to form CH$_3$O.\footnote{10} Also in this reaction, H-addition is much faster than D-addition,\footnote{10} as are the majority of reactions that exhibit a barrier. Overall, we must assume that methanol is initially produced even in a deuterium-depleted manner with respect to the cosmic H/D ratio.

One way to explain the high degree of deuteration is the lower zero point vibrational energy (ZPE) of, e.g., CD$_3$OH vs. CH$_3$OH. However, the majority of deuterium is stored in the form of HD in the interstellar medium, which has an even lower ZPE per hydrogen atom. Alternatively, H-D exchange in solid methanol was suggested as an explanation for the selective deuteration.\footnote{15} Hydrogen atoms may abstract H or D from methanol. This reaction will be the focus of this study. Here, the H-abstraction is much faster than the D-abstraction, leading to a D-enrichment.\footnote{15,17} The resulting CH$_2$OH can, again, react with H or D in a barrier-less process to reform methanol. Since the process is barrier-less, both H and D are expected to react almost equally fast. Both, abstraction and addition, are expected to happen on the surface of dust grains, since the dust grain allows for the dissipation of the excess energy from the radical-radical recombination, which is impossible in the gas phase.

It was shown previously that abstraction from the CH$_3$ group of methanol, resulting in CH$_2$OH, is much more likely than abstraction from the OH group,\footnote{18–21} which would result in CH$_3$O. This explains the selective deuteration. Moreover, CH$_2$OH is thermodynamically more stable than CH$_3$O. A conversion from CH$_2$OH to CH$_3$O is unlikely.\footnote{22,23}

While the hydrogenation reactions of CO have been studied extensively, studies of hydrogen abstraction from CH$_3$OH are rarer. Gas-phase kinetic measurements for temperatures of 200 K and above are available,\footnote{24,25} as well as simulations.\footnote{20,21,26–28} In previous work,\footnote{17} the title reaction was investigated to low temperature using instanton theory based on density functional theory. To improve on the limits of that method, we now describe the reaction based on coupled cluster theory. We provide rate constants for several isotope patterns using instanton theory. Since on-the-fly coupled cluster calculations would be computationally too demanding, especially since we aim at multiple isotope patterns, we fitted the potential
energy surface by a neural network, as described previously.\cite{29} We now explicitly study all H/D isotope patterns on the CH$_3$ group as well as for the incoming H or D atom. Moreover, we investigated the $^{12}$C/$^{13}$C and $^{16}$O/$^{18}$O kinetic isotope effects (KIE). Since all the reactions are expected to happen on the surface of dust grains, we provide unimolecular rate constants, which describe the decay of a pre-reactive complex between H and methanol on the surface in a Langmuir–Hinshelwood process.\cite{30} There are four main effects of adsorption on a surface on such a reaction: (1) a higher concentration of reactive species, (2) dissipation of excess energy of the reaction into the surface, (3) influence of the surface environment on the reaction barrier (catalytic effect), and (4) restriction of the rotation and translation of the reactants on the surface. Effects 1 and 2 are handled implicitly by our approach, since we calculate canonical rate constants, which are independent of the concentrations and assume a thermalized ensemble. A catalytic effect of the surface is expected to be small for the rather apolar surfaces on which methanol is expected (dirty CO ice). Even for water ice surfaces, which are much more polar, such effects were found to be small.\cite{16,30-33} Thus, we neglect catalytic surface effects here. The rotation and translation of the methanol molecule are restricted by keeping its rotational and translational partition functions constant between the reactant and the instanton. Such an implicit surface model, which allows the description of surface reactions by a gas-phase structural model, was used successfully previously.\cite{30}

The different deuteration patterns result in the following reactions, where the incoming atom X can be H or D. The first three reactions involve H abstraction, reactions R4 to R6 involve D abstraction.

\begin{equation}
\text{CH}_3\text{OH} + X \rightarrow \text{CH}_2\text{OH} + \text{XH} \quad (\text{R}1)
\end{equation}

\begin{equation}
\text{CH}_2\text{DOH} + X \rightarrow \text{CHDOH} + \text{XH}. \quad (\text{R}2)
\end{equation}

\begin{equation}
\text{CHD}_2\text{OH} + X \rightarrow \text{CD}_2\text{OH} + \text{XH}. \quad (\text{R}3)
\end{equation}
CDH₂OH + X → CH₂OH + XD. (R4)

CD₂HOH + X → CDHOH + XD. (R5)

CD₃OH + X → CD₂OH + XD. (R6)

¹³CH₃OH + H → ¹³CH₂OH + H₂ (R7)

CH₃¹⁸OH + H → CH₂¹⁸OH + H₂ (R8)

Computational Details

Neural-Network Potential Energy Surface

The neural-network potential energy surface (NN-PES) used in this paper has been constructed as described in reference 29 where reaction R₁ was studied to prove the applicability of a NN-PES for the accurate calculation of reaction rate constants with the instanton method. Therefore we will only report the essential computational details on the training of the NN-PES here and refer to Ref. 29 for further details.

The training and test set used in this work were constructed on the basis of the reference data used previously. The reference energies for the training and test set structures were calculated with unrestricted explicitly correlated coupled-cluster theory, where single and double excitations were considered and triple excitations were treated perturbatively, UCCSD(T)-F12/VTZ-F12, on a restricted Hartree-Fock basis. Compared to our previous
some slight adjustments have been made: First all redundant structures, whose overall coordinates differed less than $10^{-2}$ Bohr were deleted. Subsequently several structures from the minimum regions were added to the training set. In total the training set consists of 70 and the test set of 18 structures. In order to obtain a NN-PES that is suitable for the calculation of reaction rate constants it is beneficial to directly include gradient and Hessian information in the training process. Therefore, gradients and Hessians were calculated for all reference structures by finite differences of the coupled cluster energies employing a $4^{th}$ order scheme. All energy calculations were performed using Molpro 2012.7 via ChemShell with an energy threshold of $10^{-10}$ Hartree. The gradients and Hessians were calculated in DL-FIND via ChemShell.

The coordinates were described by normal vibrational coordinates relative to the transition state structure. A feed forward neural network with two hidden layers was used and the network architecture employed was 15-50-50-1, i.e. there are 15 nodes in the input layer (i.e. the 15 vibrational degrees of freedom), 50 nodes in both hidden layers and one node in the output layer. For training a batch training approach was chosen where the L-BFGS algorithm was used to minimize the cost function.

**Reaction Rate Constants**

Reaction rate constants including quantum mechanical tunneling were calculated using instanton theory, which is based on a semi-classical approximation of the Feynman path integral formalism. Instanton theory in its standard formulation is only applicable for temperatures below the crossover temperature $T_c = \frac{\hbar \omega_{TS}}{2\pi k_B}$, where $\hbar$ is the reduced Planck constant, $\omega_{TS}$ is the absolute value of the imaginary frequency at the transition structure and $k_B$ is Boltzmann’s constant. Thereby the crossover temperature $T_c$ is mass dependent since $\omega_{TS}$ is mass dependent. The instanton is at a given temperature the tunneling path with the highest statistical weight. The instanton was located using a modified Newton–Raphson method in DL-FIND. Close to $T_c$, instanton theory is known to overestimate the rate constant.
Thus, a correction was applied. When taking the rotational symmetry factors into account, the three hydrogen atoms at the CH$_3$ group were considered indistinguishable, unless they were different isotopes.

To model Langmuir–Hinshelwood processes, unimolecular rate constants were calculated for all isotope patterns considered using the implicit surface model. For completeness, the bimolecular gas-phase rate constants for R1 with an incoming H atom were also calculated. For these calculations, the rate constants were obtained from a microcanonical formulation of instanton theory, which is the appropriate model for the low-pressure limit, in which thermal equilibration in the pre-reactive complex is excluded. The microcanonical rate constants were obtained from solving the stability matrix differential equation. In this work the instantons were discretized to 200 images and the convergence criterion for the instanton was set to the gradient of the Euclidean action $S_E$ with respect to the mass-weighted coordinates being less than $5.0 \cdot 10^{-11}$ atomic units.

Results

![Graph of rate constants](image)

Figure 1: Rate constants for the reactions R1–R6 for an incoming H atom.

Temperature-dependent rate constants for the 12 H/D combinations of reactions were calculated. Graphs are shown in Figures 1 and 2, numbers for some temperatures are given in Tables 1 and 2. A more extensive list of rate constants is given in the Sup-
Figure 2: Rate constants for the reactions $R_1$–$R_6$ for an incoming D atom.

porting Information. Overall, one can see that the unimolecular rate constants are almost temperature-independent below 40 K. Below that temperature, all of the reactions are dominated by tunneling from the ground state of the reactant state complex. Primary KIEs are substantial: the replacement of the abstracted H by D decreases the rate constant by a factor of about 3000 to 4000 at 30 K, depending on the H/D pattern of the other atoms. This ratio has a direct consequence for the deuterium fractionation of methanol, as shall be discussed below. Changing the abstracting atom from H to D also decreases the rate constant, but to a much lesser degree, by factors of about 6 to 9 at 30 K. This is caused by two opposing contributions: while tunneling decreases the rate constant for abstraction by D, the vibrational zero point energy increases it, see Table 2. The increase in mass of the abstracting atom hardly changes the ZPE of the reactant, in which that atom is bound only weakly, while it reduces the ZPE of the transition state.

Secondary KIEs are smaller. The rate of abstracting a H atom from CH$_3$OH by a H atom is about 6 times higher than from CHD$_2$OH at 30 K. Of that, a factor of 3 originates merely from the rotational symmetry factor, which essentially captures the fact that there are three H atoms to abstract in CH$_3$OH, while there is only one in CHD$_2$OH. Only the remaining factor of 1.99 is caused by the different masses.

All atoms in the reaction contribute to the tunneling path, as can be seen from the instanton path for reaction $R_1$ with an incoming H atom, illustrated in Figure 3 for $T = 30$ K.
Table 1: Data for the reactions $\text{R1}$ to $\text{R8}$ for an incoming H atom. $E_{\text{uni,act}}$ refers to the unimolecular activation energy including ZPE, $T_c$ is the crossover temperature. The KIE is given with respect to H-$\text{R1}$, values in parentheses refer to powers of 10.

| Reactions | $E_{\text{uni,act}}$ (kJ/mol) | $T_c$ (K) | KIE w.r.t. H-$\text{R1}$ | $k$ at 30 K (s$^{-1}$) |
|-----------|-------------------------------|-----------|--------------------------|------------------------|
| $\text{R1}$: CH$_3$OH + H | 33.1 | 357 | 7.22(3) |
| $\text{R2}$: CH$_2$DOH + H | 33.2 | 356 | 2.11 | 2.24 | 3.23(3) |
| $\text{R3}$: CHD$_2$OH + H | 33.4 | 355 | 5.50 | 5.96 | 1.21(3) |
| $\text{R4}$: CDH$_2$OH + H | 37.9 | 269 | 1850 | 4170 | 1.73(0) |
| $\text{R5}$: CD$_2$OH + H | 38.1 | 269 | 1310 | 3230 | 2.23(0) |
| $\text{R6}$: CD$_2$HOH + H | 38.3 | 268 | 1180 | 3000 | 2.41(0) |
| $\text{R7}$: $^{13}$CH$_3$OH + H | 33.1 | 356 | 1.06 | 1.08 | 6.69(3) |
| $\text{R8}$: CH$_3^{18}$OH + H | 33.1 | 357 | 1.00 | 0.998 | 7.24(3) |

Table 2: Data for the reactions $\text{R1}$ to $\text{R8}$ for an incoming D atom. $E_{\text{uni,act}}$ refers to the unimolecular activation energy including ZPE, $T_c$ is the crossover temperature. The KIE is given with respect to D-$\text{R1}$, values in parentheses refer to powers of 10.

| Reactions | $E_{\text{uni,act}}$ (kJ/mol) | $T_c$ (K) | KIE w.r.t. D-$\text{R1}$ | $k$ at 30 K (s$^{-1}$) |
|-----------|-------------------------------|-----------|--------------------------|------------------------|
| $\text{R1}$: CH$_3$OH + D | 30.3 | 353 | 8.97(2) |
| $\text{R2}$: CH$_2$DOH + D | 30.4 | 351 | 2.08 | 2.30 | 3.90(2) |
| $\text{R3}$: CHD$_2$OH + D | 30.5 | 350 | 5.44 | 6.41 | 1.40(2) |
| $\text{R4}$: CDH$_2$OH + D | 35.0 | 265 | 1130 | 3380 | 2.66(1) |
| $\text{R5}$: CD$_2$OH + D | 35.2 | 264 | 791 | 2740 | 3.27(1) |
| $\text{R6}$: CD$_2$HOH + D | 35.4 | 263 | 709 | 2660 | 3.37(1) |

The instanton path is a closed Feynman path, which re-traces itself between two turning points. At low temperature, one turning point gets close to the reactant minimum. In Figure 3, this is given by the red geometry. The other turning point (blue) has the same energy as the first one, but is within the product valley. The changes of the C–H and H–H distances along the instanton are displayed in Figure 4. At high temperature, the instanton is short and close to the classical transition structure. Lowering the temperature leads to longer instnaton paths. The path length of the incoming H atom is 1.31 Å, while the path length of the abstracted H atom is 0.92 Å. The secondary hydrogen atoms have much shorter path lengths of 0.18, 0.22 and 0.32 Å. Replacing an atom with a heavier isotope results in an effective shortening of its contribution to the instanton path. While the path of the
incoming hydrogen atom can be shortened without raising the energy much (the potential
energy surface is rather flat in that area), changes to the abstracted atom’s path has a huge
influence on the energy. This is the reason why the KIE with respect to the incoming atom is
rather small (one order of magnitude), while the KIE with respect to changing the abstracted
atom is huge (3.5 orders of magnitude).

The influence of deuterium substitution on the C–H and H–H distances along the instan-
ton are displayed in Figure 5. An increase in the mass leads to a shortening of the path. The
H–H distance is noticeably reduced by an increase of the mass in the abstracting hydrogen
atom, especially in the reactant state region (upper left), where the potential energy is flat.

Heavy-atom KIEs were also calculated. They are, naturally, much smaller than the H/D
KIEs. Replacing $^{12}$C by $^{13}$C leads to a KIE of 1.0786 at 30 K. Somewhat smaller values
are found at higher temperature, see Figure 6. The difference in mass between the carbon
isotopes is small, but the atom is involved significantly in the tunneling process. During the
reaction, the C atom moves towards the abstracted H atom, afterwards it moves back. Its
path length is still 0.15 Å for $[\text{R}]_{1}$-$\text{H}$ at 30 K. Much smaller effects are seen for an $^{16}$O/$^{18}$O
replacement. At 30 K, we even obtain an inverse KIE of 0.9974. The oxygen atom hardly
moves during the reaction, with an instanton path length of only 0.03 Å.
The unimolecular rate constants presented so far refer to the thermalized surface process, i.e. a Langmuir–Hinshelwood mechanism on the surface. The abstraction reaction may, however, also happen in the gas phase. Reactions with a pre-reactive minimum lead to technical difficulties in canonical instanton theory, as that would assume that the pre-reactive complex is thermalized. At low pressure, however, such a thermalization is unlikely. The correct treatment of low-pressure bimolecular processes is to calculate microcanonical rate constants (cumulative reaction probabilities) and use those to calculate thermal rate constants using a thermal ensemble of the separated reactants. This was done to obtain the rate constants shown in Figure 7. The rate constants steeply decrease until tunneling sets
Figure 6: Heavy-atom KIEs for the title reaction, $^{12}\text{C}/^{13}\text{C}$ in green and $^{16}\text{O}/^{18}\text{O}$ in yellow.

Figure 7: Bimolecular rate constants for $\text{R}_1\text{H}$ obtained from a microcanonical formulation (solid lines). Literature data are also provided.

in at about the crossover temperature of 357 K. At very low temperature, the rate constant slightly increases again, a fact that can be seen for many bimolecular cases. It is caused by a delicate balance between the lost rotational and translational degrees of freedom and the additional vibrational degrees of freedom when the two reactants form one transition state. At high temperature our rate constants compare fairly well with the experimental data by Meagher et al.\cite{24} and the experiment-based recommendations by Baulch et al.\cite{25} Also at high temperature, we can compare to the simulation results by Kerkeni and Clary obtained using quantum dynamics,\cite{20} the VTST/ZCT values by Carvalho et al.\cite{26} or the expression fitted to VTST/µOMT data by Meana-Pañeda et al.\cite{21} and the DFT-based instanton data.\cite{17} The comparision is generally quite goood, see Figure 7. To the best of our knowledge, no data
are available in the literature below 180 K.

Discussion

In order to gauge the influence of the title reaction on the deuterium fractionation in methanol, we build a very small and simplistic chemical network, only consisting of hydrogen (H or D) abstraction from methanol and recombination of the resulting radical with hydrogen atoms. This is solved in a steady-state model. A similar attempt was made previously. Here, we use the new rate constants for reactions R1–R6, which are based on more accurate electronic structure calculations and which take secondary kinetic isotope effects into account. We, moreover take surface diffusion into account, albeit in a rather simple manner. The chemical network studied is shown schematically in Figure 8.

\[ R_{LH, \text{reaction-limited}} = k_1 \frac{n(H)n(\text{CH}_3\text{OH})}{n(\text{sites})}. \]

Here \( k_1 \) is the rate constant of R1, \( n(H) \) is the surface concentration of hydrogen atoms, \( n(\text{CH}_3\text{OH}) \) is the surface concentration of methanol, and \( n(\text{sites}) \) is the surface concentration.
of binding sites. Surface concentrations may be numbers of sites/species, number densities, or real concentrations. We neglect abstraction by D atoms, since they are much rarer than H atoms. Equations similar to (1) can be set up for R2 to R6.

The recombinations of radicals with H or D atoms are barrier-less. Thus, they will be diffusion-limited. Their rate constants are

$$R_{LH,\text{diffusion-limited}} = [k_{\text{diff}}(H) + k_{\text{diff}}(\text{CH}_2\text{OH})] \frac{n(H)n(\text{CH}_2\text{OH})}{n(\text{sites})}$$

(2)

for reactions with H and

$$R_{LH,\text{diffusion-limited}} = [k_{\text{diff}}(D) + k_{\text{diff}}(\text{CH}_2\text{OH})] \frac{n(D)n(\text{CH}_2\text{OH})}{n(\text{sites})}$$

(3)

for reactions with D. Here, $k_{\text{diff}}$ are the hopping rate constants on the surface. At temperatures of 30 K or below, the diffusion of CH$_2$OH or its isotopologues is much slower than the diffusion of H or D, thus $k_{\text{diff}}(\text{CH}_2\text{OH})$ can be neglected.

Using these expressions, a set of differential equations can be constructed for the kinetics of the model illustrated in Figure 8:

$$\frac{dn(\text{CH}_3\text{OH})}{dt} = -k_1 \frac{n(H)n(\text{CH}_3\text{OH})}{n(\text{sites})} + k_{\text{diff}}(H) \frac{n(H)n(\text{CH}_2\text{OH})}{n(\text{sites})}$$

(4)

$$\frac{dn(\text{CH}_2\text{OH})}{dt} = k_1 \frac{n(H)n(\text{CH}_3\text{OH})}{n(\text{sites})} - k_{\text{diff}}(H) \frac{n(H)n(\text{CH}_2\text{OH})}{n(\text{sites})}$$

$$+ k_4 \frac{n(H)n(\text{CH}_2\text{DOH})}{n(\text{sites})} - k_{\text{diff}}(D) \frac{n(D)n(\text{CH}_2\text{OH})}{n(\text{sites})}$$

(5)

which can be continued in a similar manner for the other species. With all time-derivatives
vanishing in the steady-state assumption, the model simplifies significantly, resulting in:

\[
n(\text{CH}_2\text{DOH}) = \frac{k_1}{k_4} \frac{D}{H} n(\text{CH}_3\text{OH}) \quad (6)
\]

\[
n(\text{CHD}_2\text{OH}) = \frac{k_2}{k_5} \frac{D}{H} n(\text{CH}_2\text{DOH}) \quad (7)
\]

\[
n(\text{CD}_3\text{OH}) = \frac{k_3}{k_6} \frac{D}{H} n(\text{CHD}_2\text{OH}) \quad (8)
\]

where the short-hand notation \(D/H = \frac{k_{\text{diff}}(\text{D}) n(\text{D})}{k_{\text{diff}}(\text{H}) n(\text{H})}\) is the ratio of the availabilities of H and D. The ratio of diffusion constants was simulated on crystalline water and amorphous water and measured on different surfaces. It can be approximated to about 0.1. The concentrations of the isotopologues of methanol are independent of the diffusion constants and of the intermediate concentrations of the radical species. The concentrations of the radical species depend on the diffusion constants. Using our rate constants at 30 K from Table I we can relate the deuterium fractionations of methanol to the availability of H vs. D on the surface, see Figure 9.

![Figure 9](image_url)

Figure 9: Calculated abundances of \(\text{CH}_2\text{DOH}, \text{CHD}_2\text{OH},\) and \(\text{CD}_3\text{OH}\) relative to \(\text{CH}_3\text{OH}\) (solid lines).

Observations toward IRAS 16293-2422 lead to abundances of \(\text{CH}_2\text{DOH}, \text{CHD}_2\text{OH},\) and \(\text{CD}_3\text{OH}\) relative to \(\text{CH}_3\text{OH}\) of \(30 \pm 20\%\), \(6 \pm 5\%\), and \(0.8 \pm 0.6\%\), respectively. More recent observations towards the prototypical pre-stellar core L1544 lead to much smaller, but spa-
tially variable values of $8 \pm 2\%$ for CH$_2$DOH/CH$_3$OH.$^{59,60}$ All observations would correspond to somewhat high D/H ratios in our model.

Obviously, this is a very simplistic treatment. The steady-state assumption was made ad-hoc to simplify the analysis. A full kinetic model would take many more reactions into account, primarily hydrogen (H and D) abstraction by the radical-radical recombination. Several other effects were neglected, which may have an influence on the rate constants. Any influence of the surface that changes the reaction barrier was neglected in the implicit surface model.$^{30}$ All vibrations perpendicular to the instanton path were treated harmonically. Anharmonicity effects on the vibrational zero point energy were recently shown to influence the low-temperature rate constants of the reaction CH$_3$OH + OH.$^{61}$

Nevertheless, this chemical model represents correct trends in the abundances of deuterated species of methanol. These can be directly related to the strong primary kinetic isotope effects found for the exchange of the abstracted H atom with a D atom. Solving equation 6 for $n$(CH$_2$DOH)/$n$(CH$_3$OH) yields:

$$\frac{n(\text{CH}_2\text{DOH})}{n(\text{CH}_3\text{OH})} = \frac{k_1 D}{k_4 H},$$

(9)

where $k_1/k_4$ is the kinetic isotope effect for R4 with respect to H-R1 at 30 K. This reformulation shows clearly that the KIE defines the slope of the corresponding straight line shown Figure 9. Therefore it becomes obvious that the reason for the concentration of CH$_2$DOH relative to the concentration of CH$_3$OH being three orders of magnitude higher than the concentration one would expect for a statistical exchange of H with D according to a uniform distribution for a given D/H ratio is the strong kinetic isotope effect of 4170 at 30 K. Reformulations of equations 7 and 8 lead to the same conclusion that the KIE for R5 or respectively R6 with respect to H-R1 at 30 K dominates the slope of the corresponding straight line in Figure 9 and thus give a good qualitative explanation for the unintuitively high concentrations of deuterated methanol species, that were observed in the interstellar
medium.

Conclusions

We have studied the kinetics of $H + CH_3OH \rightarrow H_2 + CH_2OH$ and all H/D isotope patterns on the CH$_3$ group. This study provides unimolecular reaction rate constants relevant for surface reactions, that model Langmuir–Hinshelwood processes, down to temperatures as low as 25 K. Thereby the rate constants were calculated on a neural network potential energy surface that was fitted to UCCSD(T)-F12/VTZ-F12 data. For the unimolecular rate constants also kinetic isotope effects are given for all studied isotope patterns at 105 K and 30 K. Our study shows that primary KIEs are substantial for all isotope patterns. Replacing the abstracted H by D decreases the rate constants by a factor of 3000 to 4000 at 30 K. It was further shown that exchanging the abstracting H atom with a D atom leads to a decrease in the rate constant by a factor of 6–9 at 30 K. In this study also heavy-atom KIEs were computed. The KIE for replacing $^{12}$C by $^{13}$C is 1.0786 at 30 K whereas the KIE for exchanging $^{16}$O with $^{18}$O is vanishingly small. On top of that also secondary KIEs are given for all studied isotope patterns. Further, bimolecular rate constants derived from a microcanonic formulation, that are relevant for the description of reactions in the gas-phase in the low pressure limit, are given down to unsurpassedly low temperatures (10 K). With the help of a simplistic kinetic model it was found that the strong primary KIEs for replacing the abstracted H atom by D are a good qualitative explanation for the unexpectedly high concentrations of deuterated methanol species that were found experimentally in the interstellar medium.

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Supporting Information Available

The following files are available free of charge.

The following files are available free of charge.

- supporting_info.pdf: This file contains for all reactions discussed a detailed list of bimolecular as well as unimolecular reaction rate constants for the whole temperature range covered in this study.

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TOC Graphic

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\text{Methanol + H/D} \xrightarrow{\text{tunneling}} \text{Deuteration}
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