Quantum Effects on the $D + H_3^+ \rightarrow H_2D^+ + H$ Deuteration Reaction and Isotopic Variants.

Niyazi Bulut,[†] Alfredo Aguado,[‡] Cristina Sanz-Sanz,[‡] and Octavio Roncero*,[¶]

[†]*Firat University, Department of Physics, 23169 Elazig, Turkey*

[‡]*Unidad Asociada UAM-IFF-CSIC, Departamento de Química Física Aplicada, Facultad de Ciencias, Módulo 14, Universidad Autónoma de Madrid, 28049, Madrid, Spain*

[¶]*Instituto de Física Fundamental (IFF-CSIC), C.S.I.C., Serrano 123, 28006 Madrid, Spain*

E-mail: octavio.roncero@csic.es

Abstract

The title reaction and its isotopic variants are studied using quasi-classical trajectory (QCT) (without taking into account corrections to account for the possible zero point energy breakdown) and ring polymer molecular dynamics (RPMD) methods with a full dimensional and accurate potential energy surface which presents an exchange barrier of approximately 0.144 eV. The QCT rate constant increases when the temperature decreases from 1500 to 10 K. On the contrary, the RPMD rate constant decreases with decreasing temperature, in semi-quantitative agreement with recent experimental results. The present RPMD results are in between the thermal and translational experimental rate constants, extracted from the measured data to eliminate the initial vibrational excitation of H_3^+ , obtained in an arc discharge. The difference between the present RPMD results and experimental values is attributed to the possible existence of non thermal vibrational excitation of H_3^+ , not completely removed by the semi-empirical model used for the analysis of the experimental results. Also, it is found that below 200 K the RPMD trajectories are trapped, forming long lived collision complexes, with lifetimes longer than 1 ns. These collision complexes can fragment by either redissociating back to reactants or react to products, in the two cases tunneling through the centrifugal and reaction barriers, respectively. The contribution of the formation of the complex to the total deuteration rate should be calculated with more accurate quantum methods, as it has been found recently for reactions of larger systems, and the present four atoms system is a good candidate to benchmark the adequacy of RPMD method at temperatures below 100 K.

September 18, 2019

Introduction

H_3^+ is considered to be the universal protonator of the Universe through the proton-hop reaction^{1,2}

The formed HM^+ cations, also very reactive, trigger many chemical networks giving rise to most of the molecular systems detected in space.^{3–8} H_3^+ survives in cold environments, because the M colliders deposit on ices. Under these circumstances, the exchange reaction

becomes important transforming H_3^+ , and it is generally admitted that this is the main reaction responsible for the ortho/para ratio of H_3^+ , and controlled by nuclear spin statistics.^{9–15} Reaction (2) also produces the deuteration of H_3^+ when replacing H_2 by HD . H_2D^+ can then trigger the formation of deuterated species, which are observed in high abundances in different media, $\approx 10^4$ times higher than the D/H ratio of the galaxy.^{16–19} The deuteration fraction is an important tracer of molecular clouds in the interstellar medium.

$\text{HD} + \text{H}_3^+$ has been widely studied experimentally.^{10,14,20–25} The efficiency of the deuteration of H_3^+ is attributed to zero-point energy differences which are important at the low temperatures of the interstellar medium.^{23,26} It is commonly accepted that this reaction occurs through a statistical mechanism below 100 K, and several models have been developed that provide state-to-state rate constants.^{14,25,27} In this statistical mechanism the ratio between the proton hop and the full scrambling (in which several proton exchanges are produced) is $\alpha = 0.5$. Crabtree *et al.*²⁵ measured a value $\alpha = 0.5 \pm 0.1$ at 135 K. However, this ratio increases gradually with increasing temperature reaching a value of 2.4 ± 0.6 at 400 K, as reported by Cordonnier *et al.*²² This is explained by a transition to a direct

mechanism at higher temperature where only the proton hop is possible, as obtained with a statistical model including a dynamical bias using quasi-classical trajectories (QCT),²⁸ in which zero-point energy (ZPE) leakage was avoided by correcting the initial ZPE. This was recently confirmed by Ring Polymer Molecular Dynamics (RPMD) calculations,²⁹ which include quantum effects such as ZPE and tunneling, and reproduce very satisfactorily the variation of the experimental α ratio with temperature.

The $\text{H}_2 + \text{H}_2^+ \rightarrow \text{H}_3^+ + \text{H}$ reaction is highly exothermic and has been widely studied experimentally^{30–36} as well as theoretically.^{37–43} The reaction cross section increases with decreasing energy,^{30,32,37} leading to a rate constant close to the Langevin limit.

The $\text{D} + \text{H}_3^+$ and isotope exchange reactions are, however, less studied. The first theoretical study of Moyano *et al.*⁴⁰ uses a QCT treatment, and the cross section obtained increases with decreasing the collision energy, between 1.31 and 19.69 kJ/mol. This result is surprising since this reaction has a barrier of 0.144 eV (see Fig. 1). Very recently, measurements of the title reaction were performed using a dual-source, ion-neutral, merged-fast-beams apparatus.⁴⁴ A careful analysis was done of the effect of initial vibrational excitation of the H_3^+ reactant obtained in the discharge, allowing to present mixed experimental-theoretical thermal reaction rate constants, which increases with temperature in the interval 10–3981 K. Moreover, in this work⁴⁴ tunneling effects were taken into account by using a Transition State Theory (TST) treatment. The tunneling-corrected thermal rate constants obtained also increases with increasing temperature.

The aim of this work is to perform QCT and RPMD calculations on the title reaction and some isotopologues. A recently proposed potential energy surface (PES) is used,³⁸ full dimensional with long-range interactions and analytical derivatives.³⁷ The paper is distributed as follows. In section 2, the main features of the PES and the zero-point energy (ZPE) of the isotopologues of reactants and at the saddle point are shown. Section 3 describes QCT results while section 4 shows the RPMD results. Finally, in section 5 some conclusions are extracted.

Potential energy surface and zero-point energies

The minimum energy path (MEP) of the PES used in this work is presented in Fig. 1, where the zero of energy is set in the reaction channel. The saddle point, of 0.144 eV, presents a planar geometry. The well, 0.25 eV deep, corresponds to a slightly deformed equilateral triangle H_3^+ with the fourth hydrogen pointing to one of the vertices, in the plane of H_3^+ .

Figure 1: Minimum energy path for the $\text{H} + \text{H}_3^+ \rightarrow \text{H}_3^+ + \text{H}$ exchange reaction for the PES of Ref. ³⁸. Energies are in eV. The ZPE shown are for $\text{H} + \text{H}_3^+$ system.

The ZPE of reactants (H_3^+) and full tetratomic system at the saddle point (H_4^+) are shown in eV, on the top of the blue vertical arrows (all values corresponding to the fully hydrogenated isotopologue). For the other isotopologues the ZPE are listed in Table 1. For the isotopologues with more than one deuterium there are several ZPE for the saddle point, depending on the relative positions of hydrogen and deuterium atoms. All HZPE correspond to harmonic ZPE, extracted from normal modes calculated at either the TS or at the minimum of the triatomic system.

Table 1: Zero point energies, harmonic (HZPE) and exact (ZPE), for triatomic fragments and at the saddle point of each indicated isotopic reaction. The effective barrier including ZPE, E_b^{ZPE} , is also listed, to compare with the potential barrier of 0.144 eV. All energies are in eV.

system	HZPE	ZPE	Reaction	HZPE at TS	E_b^{ZPE}
H_3^+	0.556	0.518	$\text{H} + \text{H}_3^+$	0.521	0.115
			$\text{D} + \text{H}_3^+$	0.493	0.087
H_2D^+	0.506	0.472	$\text{D} + \text{H}_2\text{D}^+$	0.447	0.108
HD_2^+	0.452	0.422	$\text{D} + \text{HD}_2^+$	0.401	0.099
D_3^+	0.393	0.369	$\text{D} + \text{D}_3^+$	0.369	0.125

For the triatomic systems, the exact ground vibrational state is calculated using hyperspherical coordinates following the method described elsewhere.^{45,46} Since the permutation symmetry is not included in the present dynamical calculations, the ground state for H_3^+ for total angular momentum equals to zero, of A_1 symmetry (totally symmetric) is listed in Table 1. This state is not antisymmetric under nuclear permutation and therefore does not exist, but is included for consistency with dynamical calculations.

In the QCT calculations presented below, the ground vibrational state, (0,0,0), of the triatomic system is considered, unless explicitly stated. The adiabatic switching (AS) method^{47–50} is used to calculate the initial conditions. For each case the procedure is as follows: about 500 trajectories are run, and the one chosen is that with the lowest angular momentum and with energy between the harmonic and exact ZPE. Following this procedure, the initial vibrational energy of H_3^+ in the QCT calculations is 0.538 eV.

Quasi-classical calculations

The QCT cross section for each triatomic reactant (H_3^+ , H_2D^+ , HD_2^+) are calculated considering the ground vibrational state and angular momentum equals to zero. The total reaction cross section are shown in Fig. 2, compared with previous calculations.⁴⁰ The total reaction cross section includes any atom exchange, corresponding to exchange and deuteration processes. Batches of 10^5 trajectories are calculated for each collision energy, varying randomly

the initial impact parameter and the point along the AS trajectory describing the vibrational motion. The initial distance between the two reactants is 66 Å, and trajectories are ended when any distance between the atoms exceeds 70 Å.

Figure 2: QCT cross section for the $\text{H} + \text{H}_3^+(0,0,0) \rightarrow \text{H}_3^+ + \text{H}$ exchange reaction and its isotopologues. The data from Moyano *et al.*⁴⁰ are included for comparison. The total exchange includes H exchange and deuteration processes.

The total cross sections in Fig. 2 show a significant isotope effect when comparing the different reactions. However, the qualitative behavior is the same for all of them, showing a minimum at $\approx 0.2\text{-}0.4$ eV, and an important increase of the cross section, of nearly 2-3 orders of magnitude as energy decreases. As an example, for the $\text{H} + \text{H}_3^+$ case, the maximum impact parameter increases monotonically from 4.3 bohr at 1 eV to 42.6 bohr at 0.1 meV, while the reaction probability, however, presents a minimum of 0.5% at 0.1 eV, with maximum values at 0.1 and 1000 meV, with reaction probabilities of 1.2 and 2.1 %, respectively. This behavior is similar for all the isotopic variants and demonstrate that the increase of the reaction cross section with decreasing collision energy is due to the increase of the maximum

impact parameter due to the long range ion-induced dipole interactions.

The reaction barriers, including the zero point energies of reactants and saddle point (see Table 1), are in the interval between 0.087 (for $\text{D}+\text{H}_3^+$) and 0.115 eV (for $\text{H}+\text{H}_3^+$), slightly below the minima of the calculated cross section. The increase of the reaction cross section below the ZPE corrected reaction barriers clearly indicates that classical mechanics introduces energy redistribution among all modes due to the similarity of the atomic masses involved, without introducing any constraint about the ZPE at the saddle point, in the so called ZPE leakage. This energy redistribution is attributed to the well in the entrance channel, which makes that at low energies many trajectories lead to the formation of a collision complex, $\text{H}-\text{H}_3^+$, which live long enough to favor energy transfer among all the vibrational modes. Thus, for 0.1 eV the longest collision complex lives ≈ 40 ps, while for 1 meV this time increases to 150 ps.

These results are very close to those reported previously by Moyano *et al.*⁴⁰ for $\text{H}+\text{H}_3^+$ and $\text{D}+\text{H}_3^+$ with another PES, and also shown in Fig. 2. For collision energies higher than 0.02-0.03 eV the agreement is rather good. Below this energy, the present results show larger cross section values. This is considered to be due to the long range ion-induced dipole interaction, which is introduced more accurately in the PES used here.^{37,38}

The formation of two diatomic fragments opens at ≈ 1.82 eV (1.65 eV including HZPE), above the energies considered here. There are four $\text{A} + \text{BCD}^+$ channels, and the number of deuteration channels varies with the reaction: for $\text{D}+\text{H}_3^+$ there are 3, for $\text{D}+\text{H}_2\text{D}^+$ there are 2 and for $\text{D}+\text{HD}_2^+$ there is only one. This ratio of 3:2:1 only holds for collision energies above 0.3 eV, as can be seen in Fig. 3. Below 0.1 eV, the deuteration cross section for the $\text{D}+\text{H}_3^+$ reaction is about 9 times larger than that of the $\text{D}+\text{HD}_2^+$, showing that there are important dynamical effects. The ratio between the deuteration cross sections for the $\text{D}+\text{H}_3^+$ / $\text{D}+\text{H}_2\text{D}^+$ is always larger than 3/2, but it varies with collision energy: for 0.1 meV this ratio gets close to 3/2 while for 0.1 eV it is 6/2.

Figure 3: QCT deuteration cross section for the $D + H_3^+(0,0,0) \rightarrow H_2^+D + H$ reaction and its isotopologues.

The deuteration rate constants have been calculated with the QCT method for the ground vibrational state of the triatomic system and for a thermal distribution of translational and rotational energies. Batches of 3×10^6 trajectories have been run for each temperature, and the results are shown in Fig. 4. The calculated rate constants show a slight increase when decreasing temperature. The Langevin rate for these reaction is $10^{-9} \text{ cm}^3/\text{s}$ and all these QCT rate constants are between 10 or 100 times smaller, depending on the temperature.

Also the deuteration rate ratio between the $D+H_3^+ : D+H_2D^+ : D+HD_2^+$ is always larger than the expected 3:2:1 ratio obtained by simply considering the number of deuteration channels.

Figure 4: QCT deuteration reaction rate constants for the $D + H_3^+(0,0,0)$ reaction and isotopologues, versus temperature.

Ring polymer molecular dynamics calculations

To check how the reaction rate constant varies with temperature, it is of great importance to include quantum effects. In recent experiments,⁴⁴ it has been observed that the deuteration rate constant for the $D+H_3^+$ reaction decreases monotonically below 1000 K, consistent with the presence of a barrier as it happens in these reactions. In order to include quantum effects, such as tunneling and ZPE, in this work we use the Ring Polymer Molecular Dynamics (RPMD) method.^{51–55} RPMD is a semiclassical formalism based on Path Integral Molecular Dynamics (PIMD) which includes quantum effects as ZPE⁵⁶ and tunneling,⁵⁷ and it is a very powerful technique to describe reaction dynamics.⁵⁵ In this work we use the dRPMD program,^{29,58} a direct version of the RPMD method based on the RPMDrate code,⁵⁹ which has been applied to $H_2 + H_3^+$ ²⁹ and $OH + CH_3OH$ ⁵⁸ reactions at low temperatures.

The dRPMD method consist in two steps: thermalization and real dynamics. In the thermalization, a pure PIMD calculation is performed using the Andersen thermostat⁶⁰ for the two reactants constrained to be separated by 35 Å. The number of beads (n_{beads}) is determined by converging the mean energy at each temperature. Following this procedure

$n_{beads} = 64$ for temperatures higher than 600 K, and $n_{beads} = 512$ and 256 for 50 and 100 K, respectively, and so on, *i.e.* n_{beads} is approximately inversely proportional to the temperature. For each RPMD-trajectory (consisting on $n_{beads} \times n_{atoms}$ pseudo-particles) 30 thousand integration steps are performed in the thermalization step.

After the thermalization, the thermostat and the restrictions are removed, and the system is rotated so that the relative velocity vector is set parallel to the z-axis. Furthermore, a maximum impact parameter between centroids is also set, as in QCT approaches, to improve the statistics. The RPMD-trajectories are propagated up to a maximum of 10^7 iterations, with a time step of 0.1 fs. This makes a maximum time of 1 ns, so that if the RPMD-trajectory is not finished it is considered to be trapped. This situation was also found in reactions with similar MEPs, a reaction barrier and a well in the entrance channel such as OH with H₂CO and CH₃OH.⁵⁸ In those cases it was found that the fragmentation of the complexes is very slow, so that integrating up to 100 ns in some cases was not enough to end them. In this case the maximum propagation time is set to 1 ns to make the calculations affordable.

The ending RPMD-trajectories are analyzed, using their centroids, to determine if they are reactive or not and in which products channel. By doing so, the rate constant for the different processes is defined as

$$k_{\beta}(T) = \sqrt{\frac{8k_B T}{\pi \mu}} \times \pi [b_{max}^{\beta}(T)]^2 \times P_{\beta}(T). \quad (3)$$

The index $\beta = 2, 3, \dots, 10$ refers to the reaction channel (being $\beta = 1$ the inelastic channel), or trapping ($\beta = trap$), where $P_{\beta}(T) = N_{\beta}/N_{max}$ is the probability for channel β , with N_{max} being the total number of RPMD trajectories and N_{β} the number of trajectories leading to products or trapped in the entrance channel. The four first reaction channels yield to ABC⁺ + D products, while the remaining correspond to channels dissociation into two diatomic fragments, which only open at temperatures higher than 1000 K.

For $D + H_3^+$, between 10^4 and 2×10^4 trajectories are run for each of the temperatures above 200 K. Below 200 K, many trajectories become trapped, and only 2000 trajectories were run. The results obtained for the $D + H_3^+$ reaction are shown in Fig. 5

Figure 5: Deuteration reaction rate constants for the $D + H_3^+$ reaction versus temperature obtained with the RPMD and QCT methods, and the three rate constants, $k_{tr}^{exp}(T)$, $k_{mod}^{exp}(T)$, $k_{tun}^{exp}(T)$, defined in the experimental study of Ref.,⁴⁴ given in their Table 5. The RPMD rate constant called k_{dir}^{RPMD} is the sum over channels $\beta = 2, 3$ and 4, and k_{trap}^{RPMD} is that corresponding to the trapped trajectories, all defined in the text. The QCT results correspond to the ground vibrational state of $H_3^+(0,0,0)$

The RPMD results are completely different from the QCT results, and the direct rate constant at temperatures above 300 K shows a clear decrease with decreasing temperature, as a consequence of the reaction barrier. Concerning the experiments, it is important to note that in the discharge reaction H_3^+ is obtained vibrationally excited. For this reason, the experimental conditions are varied to minimize the vibrational excitation, and then a semiempirical model is done to eliminate the contribution of the vibrational excitation. This treatment, allowed Hillenbrand *et al.*⁴⁴ to define three different temperature rate constants, all plotted in Fig. 5: $k_{tr}^{exp}(T)$, in which all vibrational excitation is removed and is defined as purely translational; $k_{mod}^{exp}(T)$ the thermal rate constant in which a thermal vibrational

distribution is considered; and finally $k_{tun}^{exp}(T)$, obtained from $k_{mod}^{exp}(T)$ by including the tunneling using an Eckart monodimensional barrier along the reaction mode. The decrease of the RPMD rate constant with decreasing temperature is qualitatively in agreement with the three experimental values, but there are some differences that we discuss below. Also, at temperatures below 200 K the trapping mechanism dominates. These two regimes are discussed separately below. In order to present a more detailed quantitative comparison we list the RPMD rate constants in Table 2, to be compared with the three experimental values listed by Hillenbrand *et al.*⁴⁴

Table 2: Rate constants for the $D + H_3^+$ reaction (in cm^3/s) obtained for different temperatures with the RPMD method, (k_{dir} and k_{trap}) and QCT method for three different initial vibrational states of $H_3^+(v_1, v_2, v_3)$.

T (K)	k_{dir}	k_{trap}	QCT(0,0,0)	QCT(1,0,0)	QCT(0,1,0)	QCT(0,0,1)
50	$< 10^{-15}$	2.88×10^{-9}	3.07×10^{-10}			
100	$2. \times 10^{-14}$	1.73×10^{-9}	2.75×10^{-10}			
200	1.30×10^{-12}	3.00×10^{-10}	2.48×10^{-10}			
300	1.67×10^{-11}	2.16×10^{-12}	2.01×10^{-10}			
400	2.98×10^{-11}	2.68×10^{-13}	1.95×10^{-10}			
600	4.52×10^{-11}	$< 10^{-15}$	1.63×10^{-10}	6.38×10^{-10}	6.62×10^{-10}	6.63×10^{-10}
800	7.14×10^{-11}	0.00	1.62×10^{-10}	5.68×10^{-10}	6.90×10^{-10}	6.71×10^{-10}
1000	1.69×10^{-10}	0.00	1.67×10^{-10}	6.60×10^{-10}	6.55×10^{-10}	6.65×10^{-10}
1400			1.51×10^{-10}	5.55×10^{-10}	6.43×10^{-10}	6.31×10^{-10}
1500	2.61×10^{-10}	0.00		5.46×10^{-10}	6.52×10^{-10}	6.10×10^{-10}

T > 300 K

The decrease of the direct RPMD rate constant with decreasing temperature is in qualitative agreement with the experimental findings. This is taken as a clear evidence that RPMD accounts properly for quantum effects, while QCT method does not. The quantitative difference between RPMD and experimental results, a factor of 2 approximately, also deserves some discussion.

Concerning the RPMD results, we consider that the PES is very accurate in this system and can not explain the differences. It is based in multi-reference configuration interaction

(CI) calculations with large basis sets, that for this 3 electrons system is close to full CI. The analytical fit is based on a triatomic-in-molecule treatment plus a permutationally invariant polynomials fit,^{38,61} with an overall error of few wave numbers. This PES was used to study the $\text{H}_2 + \text{H}_2^+ \rightarrow \text{H}_3^+ + \text{H}$ formation reaction leading to very good results as compared with the experimental data.³⁷

RPMD has proven to be well adapted to describe ZPE and tunneling in many reactions,⁵⁵ yielding to accurate results for reactions with deep wells.^{62–65} This approximation does not take into account the permutation symmetry, which in this case may produce unbalance effects between reactants and products. H_3^+ rovibrational states can be separated in three permutation groups A_1 , A_2 and E , that when combined with the nuclear spin functions, only A_2 and E eigenfunctions can be fully antisymmetric under nuclear permutation, while levels of A_1 symmetry are non-physical. Since A_2 and E levels are not connected without a proton exchange, this reduces the density of H_3^+ levels, roughly speaking, by a factor of 4. On the contrary, H_2D^+ vibrational levels are separated in ortho and para levels and these two sets of states can be formed in the reaction, and therefore RPMD is considering the density of levels for products correctly, approximately. In order to overcome this factor, fully quantum calculations should be done.

To check the role of the permutation symmetry, we can argue that the $\text{D} + \text{H}_2\text{D}^+ \rightarrow \text{HD}_2^+ + \text{H}$ reaction shows a balanced situation, and a comparison between RPMD and experimental results can bring some light. For this purpose, RPMD calculations above 200 K have been performed for the $\text{D} + \text{H}_2\text{D}^+$ reaction and the deuteration rate constants obtained are shown in Fig. 6. The same behavior as for the $\text{D} + \text{H}_3^+$ is observed: the direct deuteration rate shows a monotonous decrease with decreasing temperature below 1000 K. The trapping also is very important below 200 K. The ratio of the deuteration rate constants for $\text{D} + \text{H}_3^+$ and $\text{D} + \text{H}_2\text{D}^+$ reactions is $\approx 3/2$ above 600 K, as expected from the number of deuteration channels, in contrast with the QCT results which show a higher ratio. The trapping for $\text{D} + \text{H}_2\text{D}^+$ occurs at slightly higher temperature than for $\text{D} + \text{H}_3^+$, probably because its effective

Figure 6: Deuteration reaction rate constants for the $D + H_2D^+$ reaction versus temperature obtained with the RPMD and QCT methods. The QCT results correspond to the ground vibrational state of $H_3^+(0,0,0)$

E_b^{ZPE} barrier is higher (see Table 1). The similarity between the results of the two reactions indicates that the permutation symmetry produces minor effects on the reaction rates for these two reactions.

It is worth mentioning that also experimental values are subject to some uncertainty. The RPMD rate constant is in between k_{tr}^{exp} and k_{mod}^{exp} , while the k_{tun}^{exp} presents more clear differences below 200-300 K. In the RPMD results we have distinguished between k_{dir}^{RPMD} and k_{trap}^{RPMD} , and the effect of tunneling is expected to be more important in the k_{trap}^{RPMD} , which only appears to be significant below 200-300 K, as will be discussed below.

The fact that k_{dir}^{RPMD} is in between k_{tr}^{exp} and k_{mod}^{exp} is taken as an evidence that the vibrational excitation of the H_3^+ plays an important role. In k_{tr}^{exp} it is expected that all vibrational excitation is removed, and therefore may be considered as a lower bound of the “real” rate constant. k_{mod}^{exp} seems to be a factor of 2 higher than the k_{dir}^{RPMD} , both of them considering a thermal vibrational excitation of H_3^+ .

In order to analyze the effect of vibrational excitation of the H_3^+ reactants, initially

Figure 7: Deuteration reaction rate constants for the $D + H_3^+$ reaction obtained with a QCT method for several initial vibrational excitations of H_3^+ , denoted as (v_1, v_2, v_3) , corresponding to the normal modes of frequencies $(3419.65, 2776.19, 2776.19) \text{ cm}^{-1}$, respectively, used in the AS procedure to calculate the initial conditions. These vibrations correspond to symmetric stretch, and the degenerate asymmetric stretch, respectively.

vibrational selected rate constants are calculated, and are shown in Fig. 7. In the RPMD method the initial conditions are thermalized in all degrees of freedom, and therefore a Boltzmann distribution of initial vibrational states of H_3^+ is used in the calculations. On the contrary, in QCT calculations, the initial vibrational state is selected for each set of calculations, and a Boltzmann distribution is done in the rotational and translation degrees of freedom. Vibrational state selected deuteration rate constants are calculated with the QCT in the 600-1500 K interval, where the QCT method seems to work correctly, and the calculated QCT rate constants give approximately the same as k_{tr}^{exp} . The reaction rate constants obtained for all the internal vibrations, with only one vibrational quantum of excitation, $(1,0,0)$, $(0,1,0)$ and $(0,0,1)$, is a factor of nearly 4 larger than that obtained for the ground $(0,0,0)$ state. This explains why the QCT rate constant is lower than that obtained for the RPMD method above 800 K. Also, this strong dependence with vibrational excitation would introduce errors in the determination of the vibrational excitation of H_3^+

reactants, and could explain why the experimental k_{mod}^{exp} is a factor of ≈ 2 higher than the present $k_{dir}^{RPM D}$ results above 300 K.

$T \leq 200$ K

At temperatures below 200 K the trapping process dominates, with the formation of long lived collision complexes. In order to show the nature of these long lived complexes, in Fig. 8 two typical trapped trajectories obtained at 200 K are shown, corresponding to high impact parameter (left panels) and low impact parameter (right panels).

Figure 8: Evolution of the vector $\mathbf{R}$, between the centers-of-mass of reactants using the centroid for a RPMD trajectory at 200 K with initial impact parameter $b^{trap}=9.5$ bohr (left panels), and at 200 K with $b^{trap}= 0.8$ bohr (right panels). In the lower right panels, the evolution of the norm of $\mathbf{R}$ (the vector between the center of mass of H_3^+ and the deuterium atom), versus time is shown. In the upper right panels, the evolution of $\theta_{H_3^+-R}$ (the angle between $\mathbf{R}$ and the vector perpendicular to the H_3^+ plane) and $\theta_{H_1-H_2-H_3}$ (the angle formed by the three hydrogen atoms of H_3^+) are displayed for a short period of time.

The two reactants can be attracted from rather long distances due to the long range

ion-induced dipole interactions. This originates a circular orbit of one with respect to each other. Along this orbit the stretching motions do not seem to be excited, but the rotation of one reactant with respect to the other is accompanied by the rotation of the H_3^+ subunit, to keep the $\theta_{\text{H}_3^+-R}$ nearly constant at $\approx \pi/2$, corresponding to the four atoms in a plane. The angle of the three atoms of H_3^+ is not $\pi/3$, the equilateral configuration, but corresponds to a deformed triangle close to the equilibrium configuration in the well.

According to this image, we may conclude that these orbits correspond to high end-over-end angular momentum excitation of H atom with respect to the H_3^+ center of mass, and also a high rotational angular momentum of H_3^+ . This excitation is gradually acquired during the approach, when the initial linear trajectory is deviated thanks to the extra kinetic energy acquired by the presence of the well. Once the complex is formed in this kind of orbit, the system is trapped because in order to dissociate the system must evolve through tunnelling to either products (through the reaction barrier) or back to reactants (through the rotational barrier and/or rotational predissociation). These processes are slow, and the fact that they live for so long time allows the competition between the two processes. The long lifetime to redissociation back to reactants can be explained by the small number of accessible states of H_3^+ using the Rice–Ramsperger–Kassel–Marcus (RRKM) theory.

This kind of complexes are also formed in RPMD studies of the H_2+H_3^+ exchange reaction²⁹ (with no barrier) and the $\text{H}_2\text{CO} + \text{OH}$ and $\text{CH}_3\text{OH} + \text{OH}$ hydrogen abstraction reactions⁵⁸ (with barriers) at low temperatures. In the H_2+H_3^+ case, the trapping occurred below 200 K, and the RPMD calculations allowed to reproduce the experimental ratio between hop/exchange mechanism,^{22,25} as clear transition between statistical behavior below 100 K and a direct mechanism above 300 K.

In the $\text{H}_2\text{CO} + \text{OH}$ and $\text{CH}_3\text{OH} + \text{OH}$ hydrogen abstraction reactions the MEPs show similar behavior as the title reaction: strong long range interaction, a relatively deep well in the reactants channel followed by a reaction barrier. Moreover, considering that these long-lived complexes (who live more than 100 ns below 100 K) fragment, by either tunneling to

products or redissociating back to reactants, by tunneling through rotational barriers and/or by rotational predissociation, it was possible to reproduce⁵⁸ the experimental rise measured below 100 K^{66–74} assuming the zero-pressure limit. This was done assuming that part of the trapped complexes may react by tunneling in the deep regime, and the total reaction rate constant becomes the sum

$$k(T) = k_{dir}(T) + k_{CF}(T), \quad (4)$$

where $k_{dir}(T)$ is the direct reaction rate constant defined above and $k_{CF}(T)$ is the complex forming reaction rate constant given by

$$k_{CF}(T) = k_{trap}(T) \frac{k_{tunnel}(T)}{k_{tunnel}(T) + k_{rediss}(T)}. \quad (5)$$

The magnitude of this rise is still under debate, because several transition state theory (TST) calculations^{75–77} explain this increase of the rate constant at low temperature as been partially due to pressure effects. However, including the complex forming mechanism, it was also possible to obtain an increase of the rate constant by TST methods, but lower than the experimental one. The RPMD simulations made for the $\text{H}_2\text{CO} + \text{OH}$ and $\text{CH}_3\text{OH} + \text{OH}$ allowed to reproduce the experimental increase at zero-pressure.⁵⁸ Work to analyze the pressure effect with the buffer gas, He, is being done.⁷⁸

The challenge is to calculate the tunneling rate constant, $k_{tunnel}(T)$, and the redissociation rate, $k_{rediss}(T)$, under similar conditions, since they involve different processes and degrees of freedom. TST methods do not properly take into account the nature of these long lived resonances and more adapted multidimensional quantum method must be designed for this purpose.

With the purpose of analysing the importance of this effect at low temperatures of astrophysical interest, if the $k_{tunnel}(T)/[k_{tunnel}(T) + k_{rediss}(T)]$ is assumed to be only of 1%, $k_{CF}(T)$ contribution to the total reaction rate constant would be of $3 \times 10^{-11} \text{ cm}^3/\text{s}$ at 50

K, and even higher at lower temperatures. These values of rate constant are well below the Langevin value, but would be not negligible in astrophysical model, and therefore a combined experimental/theoretical effort must be done to elucidate this.

Conclusions

In this work we study the $\text{H} + \text{H}_3^+ \rightarrow \text{H}_3^+ + \text{H}$ exchange reaction and its deuterated isotopologues using quasi-classical trajectories (without taking into account corrections to account for the possible ZPE breakdown) and ring-polymer molecular dynamics methods. It is found that while QCT rate constants increase for temperatures below 1000 K, the RPMD results for the $\text{D} + \text{H}_3^+$ and $\text{D} + \text{H}_2\text{D}^+$ reactions decrease, showing that quantum effects play a significant role. These results are in rather good qualitative agreement with recent experimental results obtained for the $\text{D} + \text{H}_3^+$ reaction.⁴⁴

Above 300 K, the present k_{dir}^{RPMD} is in between the experimental k_{tr}^{exp} (with no vibrational excitation) and k_{mod}^{exp} (with thermal vibrational excitation). In the experiments the H_3^+ reactant is obtained vibrationally excited, and the thermal rate is obtained through the use of a semi-empirical model, whose accuracy also needs to be carefully analyzed. It is also found here, that only one initial quantum in any of the vibrational modes of H_3^+ yields to an increase in the rate constant of a factor of 4 higher than that from the ground vibrational state, yielding to values very close to the experimental ones. Therefore we conclude that the factor $k_{mod}^{exp}/k_{dir}^{RPMD} \approx 2$ is due to the vibrational excitation of the H_3^+ , and is considered to be rather satisfactory.

Also, a high trapping rate constant is found in the RPMD calculations below 200 K, corresponding to the formation of DH_3^+ collision complexes, with very long lifetimes, estimated here to be considerably longer than 1 ns. These complexes must fragment, by either redissociation back to reactants or by tunneling to form products. The ratio between these two fragmentation mechanism must be estimated using a full quantum method that estimaten

correctly the complex lifetimes. This may be very important in the present reactions, because it may yield to a significant increase of the reaction rate at low temperatures. Just as an estimation, if the tunneling probability is only of 1%, the reaction rate constant would be 3×10^{-11} cm³/s at 50 K, what could have some impact in astrophysical models. Also, this relatively simple reaction, involving only 4 atoms, may be taken as a benchmark system to check the RPMD results of complex forming reactions, such as OH with H₂CO and CH₃OH, which also show the trapping at temperatures below 200 K. In these cases, the tunneling branching ratio were estimated by using QCT and TST calculations,⁵⁸ and it was therefore possible to reproduce rather satisfactory the increase of the measured rate constant below 100 K using Laval expansion experiments,⁶⁶⁻⁷⁴ considering zero-pressure conditions.

Acknowledgement

This work is dedicated to the Festschrift of Prof. Javier Aoiz. CSS, AA, and OR acknowledge the support of the Ministerio de Ciencia e Innovación(SPAIN) under grant No. FIS2017-83473-C2. OR acknowledge the French-Spanish collaborative project PICS (Ref. PIC2017FR7). The calculations have been performed at SCAYLE (calendula) (under the Red Española de Supercomputación, grant no. AECT-2019-1-0001), at TUBITAK TR-Grid and at the trueno (CSIC) computer centers, which are acknowledged.

References

- (1) Oka, T. Chemistry, astronomy and physics of H₃⁺. *Phil. Trans. R. Soc. A* **2012**, *370*, 4991.
- (2) Oka, T. Interstellar H₃⁺. *Chem. Rev.* **2013**, *113*, 8738.
- (3) Watson, W. D. The rate of formation of interstellar molecules by ion-molecule reactions. *Astrophys. J.* **1973**, *183*, L17.

- (4) Herbst, E.; Klemperer, W. The formation and depletion of molecules in dense interstellar clouds. *Astrophys. J.* **1973**, *185*, 505.
- (5) Millar, T. J.; Bernett, A.; Herbst, E. Deuterium fractionation in dense interstellar clouds. *Astrophys. J.* **1989**, *340*, 906.
- (6) Pagani, L.; Salez, M.; Wannier, P. The chemistry of H_2D^+ in cold clouds. *Astron. Astrophys.* **1992**, *258*, 479.
- (7) Tennyson, J. Spectroscopy of H_3^+ : planets, chaos and the Universe. *Rep. Prog. Phys.* **1995**, *58*, 412.
- (8) McCall, B. J.; Oka, T. H_3^+ an ion with many talents (perspective). *Science* **2000**, *287*, 1941.
- (9) Quack, M. Detailed symmetry selection rules for reactive collisions. *Mol. Phys.* **1977**, *34*, 21.
- (10) Uy, D.; Cordonnier, M.; Oka, T. Observation of ortho-para H_3^+ selection rules in plasma chemistry. *Phys. Rev. Lett.* **1997**, *78*, 3844.
- (11) Oka, T. Nuclear spin selection rules in chemical reactions by angular momentum algebra. *J. Mol. Spectros.* **2004**, *228*, 635.
- (12) Gerlich, D.; Windisch, F.; Hlavenka, P.; Plasil, R.; Glosik, J. Dynamical constraints and nuclear spin caused restrictions in collision systems. *Phil. Trans. R. Soc. A* **2006**, *364*, 3007.
- (13) Park, K.; Light, J. C. Nuclear spin selection rules for reactive collision systems by the spin-modification probability method. *J. Chem. Phys.* **2007**, *127*, 224101.
- (14) Hugo, E.; Asvany, O.; Schlemmer, S. $\text{H}_3^+ + \text{H}_2$ isotopic system at low temperatures: microcanonical model and experimental study. *J. Chem. Phys.* **2009**, *130*, 164302.

- (15) Crabtree, K. N.; Tom, B. A.; McCall, B. J. Nuclear spin dependence of the reaction of H_3^+ with H_2 . I. Kinetics and modelling. *J. Chem. Phys.* **2011**, *134*, 194310.
- (16) Millar, T. J. Modeling deuterium fractionation in interstellar clouds. *Planet. Space Sci.* **2002**, *50*, 1189.
- (17) Pagani, L.; Vastel, C.; Hugo, E.; Kokoouline, V.; Greene, C. H.; Bacmann, A.; Bayer, E.; Ceccarelli, C.; Peng, R.; Schlemmer, S. Chemical modeling of L183(L134MN): an estimate of the ortho/para ratio. *Astronomy and Astrophys.* **2009**, *494*, 623.
- (18) Bell, T. A.; Willacy, K.; Phillips, T. G.; Allen, M.; Lis, D. The influence of deuteration and turbulent diffusion on the observed D/H ratio. *Astrophys. J.* **2011**, *731*, 48.
- (19) Fontani, F.; Palau, A.; Caselli, P.; Sánchez-Monge, A.; Butler, M. J.; Tan, J. C.; Jiménez-Serra, I.; Busquet, G.; Leurini, S.; Audard, M. Deuteration as an evolutionary tracer in massive-star formation. *Astronomy and Astrophys.* **2011**, *529*, L7.
- (20) Adams, D. S. N. G.; Alge, E. Some H/D exchange reactions involved in the deuteration of interstellar molecules. *Astrophys. J.* **1982**, *263*, 123.
- (21) Giles, K.; Adams, N. G.; Smith, D. A study of the reactions of H_3^+ , H_2D^+ , HD_2^+ and D_3^+ with H_2 , HD and D_2 using a variable-temperature selected ion flow tube. *J. Phys. Chem.* **1992**, *96*, 7645.
- (22) Cordonnier, M.; Uy, D.; Dickson, R. M.; Kerr, K.; Zhang, Y.; Oka, T. Selection rules for nuclear spin modifications in ion-neutral reactions involving H_3^+ . *J. Chem. Phys.* **2000**, *113*, 3181.
- (23) Gerlich, D.; Schlemmer, S. Deuterium fractionation in gas-phase reactions measured in the laboratory. *Planet. Space Sci.* **2002**, *50*, 1287.
- (24) Gerlich, D.; Herbst, E.; Roueff, E. $\text{H}_3^+ + \text{HD} \rightarrow \text{H}_2\text{D}^+ + \text{H}_2$: low-temperature laboratory measurements and interstellar implications. *Planet. Space Sci.* **2002**, *50*, 1275.

- (25) Crabtree, K. N.; Kauffman, C. A.; Tom, B. A.; Becka, E.; McGuire, B. A.; McCall, B. J. Nuclear spin dependence of the reaction of H_3^+ with H_2 . II. Experimental measurements. *J. Chem. Phys.* **2011**, *134*, 194311.
- (26) Gerlich, D. Ortho-para transitions in reactive $\text{H}^+ + \text{H}_2$ collisions. *J. Chem. Phys.* **1990**, *92*, 2377.
- (27) Park, K.; Light, J. C. Microcanonical statistical study of ortho-para conversion in the reaction $\text{H}_3^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H}_2$ at very low energies. *J. Chem. Phys.* **2007**, *126*, 044305.
- (28) Gómez-Carrasco, S.; González-Sánchez, L.; Aguado, A.; Zanchet, A.; Roncero, O. Dynamically biased statistical model for the ortho/para conversion in the $\text{H}_2 + \text{H}_3^+ \rightarrow \text{H}_3^+ + \text{H}_2$ reaction. *J. Chem. Phys.* **2012**, *137*, 094303.
- (29) Suleimanov, Y. V.; Aguado, A.; Gómez-Carrasco, S.; Roncero, O. Ring polymer molecular dynamics approach to study the transition between statistical and direct mechanisms in the $\text{H}_2 + \text{H}_3^+ \rightarrow \text{H}_3^+ + \text{H}_2$ reaction. *J. Phys. Chem. Lett.* **2018**, *9*, 2133.
- (30) Allmendinger, P.; Deiglmayr, J.; Höveler, K.; Schullian, O.; Merkt, F. Observation of enhanced rate coefficients in the $\text{H}_2^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H}$ reaction at low collision energies. *The Journal of Chemical Physics* **2016**, *145*, 244316.
- (31) Allmendinger, P.; Deiglmayr, J.; Schullian, O.; Höveler, K.; Agner, J. A.; Schmutz, H.; Merkt, F. New method to study ion-molecule reactions at low temperatures and application to the $\text{H}_2^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H}$ reaction. *ChemPhysChem* **2016**, *17*, 3596–3608.
- (32) Glenewinkel-Meyer, T.; Gerlich, D. Single and merged beam studies of the reaction $\text{H}_2^+(v = 0, 1; j = 0, 4) + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H}$. *Israel J. Chem.* **1997**, *37*, 343.
- (33) Pollard, J. E.; Johnson, L. K.; Lichtin, D. A.; Cohen, R. B. State-selected reactive scattering. I. $\text{H}_2^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H}$. *J. Chem. Phys.* **1991**, *95*, 4877.

- (34) Shao, J.; Ng, C. Y. A vibrational state-selected study of the reaction $\text{H}_2^+(\nu'_0)+\text{H}_2(\nu''_0=0)\rightarrow\text{H}_3^++\text{H}$ using the tandem photoionization mass spectrometry and radio frequency ion guide methods. *J. Chem. Phys.* **1986**, *84*, 4317.
- (35) Koyano, I.; Tanaka, K. State-selected ion-molecule reactions by a threshold electron-secondary ion coincidence (TESICO) technique. I. Apparatus and the reaction $\text{H}_2^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H}$. *J. Chem. Phys.* **1980**, *72*, 4858.
- (36) Krenos, J. R.; Lehmann, K. K.; Tully, J. C.; Hierl, P. M.; Smith, G. P. Crossed beam study of the reactions of H_2^+ with D_2 and D_2^+ with H_2 . *Chem. Phys.* **1976**, *16*, 109.
- (37) Sanz-Sanz, C.; Aguado, A.; Roncero, O.; Naumkin, F. Non-adiabatic couplings and dynamics in proton transfer reactions of H_n^+ systems: Application to $\text{H}_2+\text{H}_2^+ \rightarrow \text{H}+\text{H}_3^+$ collision. *J. Chem. Phys.* **2015**, *143*, 234303.
- (38) Sanz-Sanz, C.; Roncero, O.; Paniagua, M.; Aguado, A. Full dimensional potential energy surface for the ground state of H_4^+ system based on triatomic-in-molecules formalism. *J. Chem. Phys.* **2013**, *139*, 184302.
- (39) Alijah, A.; Varandas, A. J. C. H_4^+ : what we do know about it? *J. Chem. Phys.* **2008**, *129*, 034303.
- (40) Moyano, G. E.; Pearson, D.; Collins, M. A. Interpolated potential energy surface and dynamics for atom exchange between H and H_3^+ and D and H_3^+ . *J. Chem. Phys.* **2004**, *121*, 12396.
- (41) Baer, M.; Ng, C. Y. A three-dimensional quantum mechanical study of the H_2+H_2^+ system: Calculation of reactive and charge transfer cross sections. *J. Chem. Phys.* **1990**, *93*, 7787.
- (42) Eaker, C. W.; Schatz, G. C. A Quasiclassical trajectory study of the $\text{H}_2^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H}$ reaction. *J. Phys. Chem.* **1985**, *89*, 2612.

- (43) Stine, J. R.; Muckerman, J. T. Charge exchange and chemical reaction in the $\text{H}_2^+ + \text{H}_2$ system. I. Characterization of the potential energy surfaces and non-adiabatic regions. *J. Chem. Phys.* **1978**, *68*, 185.
- (44) Hillenbrand, P.-M.; Bowen, K. P.; Liévin, J.; Urbain, X.; Savin, D. W. Experimental and theoretical studies of the isotope exchange reaction $\text{D} + \text{H}_3^+ \rightarrow \text{H}_2\text{D}^+ + \text{H}$. *Astrophys. J.* **2019**, *877*, 38.
- (45) Aguado, A.; Roncero, O.; Tablero, C.; Sanz, C.; Paniagua, M. Global potential energy surface for the H_3^+ system: Analytical representation of the adiabatic ground state $1^1A'$ potential. *J. Chem. Phys.* **2000**, *112*, 1240.
- (46) Sanz, C.; Roncero, O.; Tablero, C.; Aguado, A.; Paniagua, M. The lowest triplet $^3A'$ of H_3^+ : Global potential energy surface and vibrational calculations. *J. Chem. Phys.* **2001**, *114*, 2182.
- (47) Grozdanov, T. P.; Solov'ev, E. A. Semiclassical quantisation of the hydrogen atom in crossed electric and magnetic fields. *J. Phys. B* **1982**, *15*, 1195.
- (48) Johnson, B. R. Semiclassical vibrational eigenvalues of $\text{H}_3^+, \text{D}_3^+$ and T_3^+ by the adiabatic switching method. *J. Chem. Phys.* **1987**, *86*, 1445.
- (49) Qu, C.; Bowman, J. M. Revisiting adiabatic switching for initial conditions in quasi-classical trajectory calculations: application to CH_4 . *J. Phys. Chem. A* **2016**, *120*, 4988.
- (50) Nagy, T.; Lendvay, G. Adiabatic switching extended to prepare semiclassically quantized rotational-vibrational initial states for quasi-classical trajectory calculations. *J. Phys. Chem. Lett.* **2017**, *8*, 4621.
- (51) Craig, I. R.; Manolopoulos, D. E. Quantum statistics and classical mechanics: Real time

- correlation functions from ring polymer molecular dynamics. *J. Chem. Phys.* **2004**, *121*, 3368.
- (52) Craig, I. R.; Manolopoulos, D. E. Chemical reaction rates from ring polymer molecular dynamics. *J. Chem. Phys.* **2005**, *122*, 084106.
- (53) Craig, I. R.; Manolopoulos, D. E. A refined ring polymer molecular dynamics theory of chemical reaction rates. *J. Chem. Phys.* **2005**, *123*, 034102.
- (54) Suleimanov, Y. V.; Collepardo-Guevara, R.; Manolopoulos, D. E. Bimolecular reaction rates from ring polymer molecular dynamics: application to $\text{H} + \text{CH}_4 \rightarrow \text{H}_2 + \text{CH}_3$. *J. Chem. Phys.* **2011**, *134*, 044131.
- (55) Suleimanov, Y. V.; Aoiz, F. J.; Guo, H. Chemical reaction rate coefficients from Ring polymer molecular dynamics: theory and practical applications. *J. Phys. Chem. A* **2016**, *120*, 8488.
- (56) Pérez de Tudela, R.; Aoiz, F. J.; Suleimanov, Y. V.; Manolopoulos, D. E. Chemical reaction rates from ring polymer molecular dynamics: zero point energy conservation in $\text{Mu} + \text{H}_2 \rightarrow \text{MuH} + \text{H}$. *The Journal of Physical Chemistry Letters* **2012**, *3*, 493–497, PMID: 26286053.
- (57) Pérez de Tudela, R.; Suleimanov, Y. V.; Richardson, J. O.; Sáez Rábanos, V.; Green, W. H.; Aoiz, F. J. Stress test for quantum dynamics approximations: deep tunneling in the muonium exchange reaction $\text{D} + \text{HMu} \rightarrow \text{DMu} + \text{H}$. *The Journal of Physical Chemistry Letters* **2014**, *5*, 4219–4224, PMID: 26278957.
- (58) del Mazo-Sevillano, P.; Aguado, A.; Jiménez, E.; Suleimanov, Y. V.; Roncero, O. Quantum roaming in the complex forming mechanism of the reactions of OH with formaldehyde and methanol at low temperature and zero pressure: a ring Polymer molecular dynamics approach. *J. Phys. Chem. Lett.* **2019**, *10*, 1900.

- (59) Suleimanov, Y.; Allen, J.; Green, W. RPMDrate: Bimolecular chemical reaction rates from ring polymer molecular dynamics. *Computer Physics Communications* **2013**, *184*, 833 – 840.
- (60) Andersen, H. C. Molecular dynamics simulations at constant pressure and/or temperature. *The Journal of Chemical Physics* **1980**, *72*, 2384–2393.
- (61) Aguado, A.; Barragan, P.; Prosmiti, R.; Delgado-Barrio, G.; Villarreal, P.; Roncero, O. A new accurate full dimensional potential energy surface of H_5^+ based on triatomics-in-molecule analytical functional form. *J. Chem. Phys.* **2010**, *133*, 024306.
- (62) Espinosa-Garcia, J.; Fernandez-Ramos, A.; Suleimanov, Y. V.; Corchado, J. C. Theoretical kinetics study of the $\text{F}(^2\text{P}) + \text{NH}_3$ hydrogen abstraction reaction. *J. Phys. Chem. A* **2014**, *118*, 554.
- (63) Li, Y.; Suleimanov, Y. V.; Guo, H. Ring-polymer molecular dynamics rate coefficient calculations for insertion Reactions: $\text{X} + \text{H}_2 \rightarrow \text{HX} + \text{H}$ ($\text{X} = \text{N}, \text{O}$). *J. Phys. Chem. Lett.* **2014**, *5*, 700.
- (64) Suleimanov, Y. V.; Kong, W. J.; Guo, H.; Green, W. H. Ring-polymer molecular dynamics: rate coefficient calculations for energetically symmetric (near thermoneutral) insertion reactions $(\text{X} + \text{H}_2) \rightarrow \text{HX} + \text{H}$ ($\text{X} = \text{C}(^1\text{D}), \text{S}(^1\text{D})$). *J. Chem. Phys.* **2014**, *141*, 244103.
- (65) Hickson, K. M.; Loison, J.-C.; Guo, H.; Suleimanov, Y. V. Ring-polymer molecular dynamics for the prediction of low-temperature rates: An investigation of the $\text{C}(^1\text{D}) + \text{H}_2$ reaction. *J. Phys. Chem. Lett.* **2015**, *6*, 4194.
- (66) Shannon, R. J.; Blitz, M. A.; Goddard, A.; Heard, D. E. Accelerated chemistry in the reaction between the hydroxyl radical and methanol at interstellar temperatures facilitated tunnelling. *Nature Chem.* **2013**, *5*, 745.

- (67) Gómez-Martín, J. C.; Caravan, R. L.; Blitz, M. A.; Heard, D. E.; Plane, J. M. C. Low temperature kinetics of the $\text{CH}_3\text{OH} + \text{OH}$ reaction. *J. Phys. Chem. A* **2014**, *118*, 2693.
- (68) Caravan, R. L.; Shannon, R. J.; Lewis, T.; Blitz, M. A.; Heard, D. E. Measurements of rate coefficients for reactions of OH with ethanol and propan-2-ol at very low temperatures. *J. Phys. Chem. A* **2015**, *119*, 7130.
- (69) Antiñolo, M.; Agúndez, M.; Jiménez, E.; Ballesteros, B.; Canosa, A.; Dib, G. E.; Albadalejo, J.; Cernicharo, J. Reactivity of OH and CH_3OH between 22 and 64 K: modeling the gas phase production of CH_3O in Barnard 1b. *AstroPhys. J.* **2016**, *823*, 25.
- (70) Shannon, R. J.; Taylor, S.; Goddard, A.; Blitz, M. A.; Heard, D. E. Observation of a large negative temperature dependence for rate coefficients of reactions of OH with oxygenated volatile organic compounds studied at 86-112 K. *Phys. Chem. Chem. Phys.* **2010**, *12*, 13511.
- (71) Jimenez, E.; Antiñolo, M.; Ballesteros, B.; Canosa, A.; Albaladejo, J. First evidence of the dramatic enhancement of the reactivity of methyl formate ($\text{HC}(\text{O})\text{OCH}_3$) with OH at temperatures of the interstellar medium: a gas-phase kinetic study between 22 K and 64 K. *Phys. Chem. Chem. Phys.* **2016**, *18*, 2183.
- (72) Ocaña, A. J.; Jiménez, E.; Ballesteros, B.; Canosa, A.; Antiñolo, M.; Albadalejo, J.; Agúndez, M.; Cernicharo, J.; Zanchet, A.; del Mazo, P. et al. Is the gas phase $\text{OH} + \text{H}_2\text{CO}$ reaction a source of HCO in interstellar cold dark clouds? A kinetic, dynamics and modelling study. *AstroPhys. J.* **2017**, *850*, 28.
- (73) Ocaña, A. J.; Blazquez, S.; Ballesteros, B.; Canosa, A.; Antiñolo, M.; Albaladejo, J.; Jimenez, E. Gas phase kinetics of the $\text{OH} + \text{CH}_3\text{CH}_2\text{OH}$ reaction at temperatures of the interstellar medium ($T = 21\text{-}107$ K). *Phys. Chem. Chem. Phys.* **2018**, *20*, 5865.

- (74) Heard, D. E. Rapid acceleration of hydrogen atom abstraction reactions of OH at very low temperatures through weakly bound complexes and tunneling. *Accounts of Chemical Research* **2018**, *51*, 2620–2627.
- (75) Gao, L. G.; Zheng, J.; Fernández-Ramos, A.; Truhlar, D. G.; Xu, X. Kinetics of the methanol reaction with OH at interstellar, atmospheric, and combustion temperatures. *Journal of the American Chemical Society*. **2018**, *140*, 2906–2918.
- (76) Ocaña, A. J.; Blázquez, S.; Potapov, A.; Ballesteros, B.; Canosa, A.; Antiñolo, M.; Vereecken, L.; Albaladejo, J.; Jiménez, E. Gas-phase reactivity of CH₃OH toward OH at interstellar temperatures (11.7–177.5 K): Experimental and theoretical study. *PCCP* **2019**, *21*, 6942.
- (77) Nguyen, T. L.; Ruscic, B.; Stanton, J. F. A master equation simulation for the OH + CH₃OH reaction. *The Journal of Chemical Physics* **2019**, *150*, 084105.
- (78) Naumkin, F.; del Mazo-Sevillano, P.; Aguado, A.; Suleimanov, Y.; Roncero, O. Zero- and high-pressure mechanisms in the complex forming reactions of OH with methanol and formaldehyde at low temperatures. *ACS Earth and Space chem.* **2019**, *published on line*, doi:10.1021/acsearthspacechem.9b00051.

Graphical TOC Entry

Bottom panel: minimum energy path for the $\text{H}+\text{H}_3^+$ reactions

Top Right panel: $\text{D}+\text{H}_3^+$ deuteration rates

Top left panel: RPMD geometry of the collision complex