On the possible formation and destruction of the OD^+ ions in the interstellar medium

Niyazi Bulut,[†] Octavio Roncero,[‡] and François Lique*,[¶]

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

[‡]*Instituto de Física Fundamental, CSIC, C/ Serrano, 123, 28006 Madrid, Spain*

[¶]*LOMC - UMR 6294, CNRS-Université du Havre, 25 rue Philippe Lebon, BP 1123, F-76063 Le Havre, France.*

E-mail: francois.lique@univ-lehavre.fr

Abstract

The OH^+ ion is an important constituent of the interstellar medium (ISM). It can be used as a probe of cosmic ray and X-ray ionization rates in molecular clouds as well as a tracer of oxygen chemistry. The deuterated variant of OH^+ , the OD^+ ion, may also be present in the ISM despite it has not been detected yet. In this paper, we aim at providing a quantitative insight into the OD^+ chemistry and at accurately studying the possible formation and destruction processes of OD^+ in the ISM. We study the formation and destruction of OD^+ through the $\text{O}^+ + \text{HD} \rightarrow \text{OD}^+ + \text{H}$ and $\text{OH}^+ + \text{D} \leftrightarrow \text{OD}^+ + \text{H}$ reactions that can occur in diffuse ISM. Reactive rate constants have been obtained from exact state-to-state quantum wave packet calculations for temperatures ranging from 10 to 1000 K. The new theoretical data are validated through a detailed comparison with available experimental data. The formation of OD^+ is found to be less efficient than that of OH^+ . As a first application, the OD^+/OH^+ abundance ratio in ISM has been evaluated from a simple astrochemical model and we found that this ratio can be larger than D/H abundance ratio only at low temperatures. This calculations may help in an astrochemical search of OD^+ in cold ISM.

1 Introduction

The OH^+ ion has been first detected in the interstellar medium (ISM) in absorption against the strong continuum source Sagittarius B2(M)¹ in 2010. Since then, OH^+ has been frequently observed both in absorption and emission in a variety of interstellar environments including diffuse ISM,²⁻⁴ hot and dense photodissociation regions (PDR),⁵ the nuclei of active galaxies,^{6,7} planetary nebulae⁸ and PDRs associated to ultra compact HII regions.⁹

The OH^+ ion is known to act as tracer of oxygen chemistry¹⁰ and as a probe of cosmic ray (CR) and X-ray ionization rates¹¹⁻¹³ as well as a probe of molecular hydrogen fractions in molecular clouds.^{11,14} In addition, the OH^+ ions play an important role in the interstellar chemistry as they act as precursors to the H_2O molecule.^{15,16}

The chemistry of OH^+ in interstellar clouds is rather well understood. As the depth into the cloud increases and the Far-UltraViolet (FUV) flux decreases, the formation of OH^+ successively follows two different pathways.¹⁷ At the border of the cloud where most of the hydrogen is atomic, the production of OH^+ proceeds through

Conversely, deeper in the cloud where most of the hydrogen is molecular, the production of OH^+ proceeds through

As a result the abundance of OH^+ predicted by the chemical models displays two peaks whose positions and amplitudes depends on the ratio of the incident UV radiation field and the gas density.¹⁷

The deuterated variant of OH^+ , the OD^+ ion, may also be formed in interstellar clouds from the same chemical mechanism than OH^+ but implying deuterated species (HD , H_2D^+ or D_2H^+). Indeed, in space, the abundance of deuterated species often exceed the D/H abundance ratio because of an efficient fractionation process.¹⁸ Hence, deuterated species are important constituent of the interstellar matter and many deuterated molecules have been detected both in the dense and diffuse ISM.¹⁹ Surprisingly, the OD^+ ion has not been detected yet whereas many deuterated hydrides have been detected so far.²⁰ It is then important to have a quantitative insight into the OD^+ chemistry and to accurately study the possible formation and destruction processes of OD^+ in the ISM. This may open the way towards the detection of the OD^+ ion.

In this paper, we study the formation and destruction of the OD^+ ions in the interstellar medium. We focus on interstellar cloud where most of the hydrogen is atomic. Hence, we study the formation and destruction of OD^+ through the $\text{O}^+ + \text{HD} \longrightarrow \text{OD}^+ + \text{H}$ and

$\text{OH}^+ + \text{D} \longleftrightarrow \text{OD}^+ + \text{H}$ reactions that can occur in diffuse ISM. To the best of our knowledge, the $\text{OH}^+ + \text{D} \longleftrightarrow \text{OD}^+ + \text{H}$ reaction has never been studied from both a theoretical and experimental point of view. At the opposite, the $\text{O}^+ + \text{HD} \longrightarrow \text{OD}^+ + \text{H}$ has been intensively studied experimentally²¹⁻²³ and theoretically.^{24,25} Many of these studies focused on the OH^+/OD^+ branching ratio. **Previous theoretical studies were done either using the adiabatic capture approximation (ACA),²⁴ quasi-classical trajectory (QCT) approach²⁵ and wave packet calculations in the helicity decoupling approach (HD-WP).²⁶** Those studies focused mainly in the calculation of the integral cross section, and here we present detailed exact calculations focused on low energies **for the calculation of state-to-state cross sections and rate constants.** This is even crucial for astrochemical applications where quantum effects can be prevalent because of the low temperatures in interstellar clouds. This is why, we present here a complete quantum study of these reactions and provide state-to-state rate constants for temperature relevant for astrophysical applications.

The paper is organized as follows : Sec. 2 provides a brief description of the employed potential energy surface and of the scattering calculations. In Sec. 3, we present the results and in Sec. 4, we discuss the OH^+ and OD^+ chemistry in the interstellar medium. Concluding remarks are drawn in Sec. 5.

2 Computational methodology

In this work, we closely follow the previous study performed for the formation $\text{O}^+(^4\text{S}) + \text{H}_2 \longrightarrow \text{OH}^+(^3\Sigma^-) + \text{H}(^2\text{S})$ and exchange $\text{OH}^+(^3\Sigma^-) + \text{H}(^2\text{S}) \longrightarrow \text{H}(^2\text{S}) + \text{OH}^+(^3\Sigma^-)$ reactions.²⁷⁻²⁹ In those studies, the ground quartet²⁵ and doublet³⁰ H_2O^+ potential energy surfaces (PESs) were used, (whose minimum energy paths (MEPs) are represented in Fig. 1), and where their validity was assessed by comparing scattering results to available experimental data.

Figure 1: Minimum Energy Paths (MEPs) for the $\text{O}^+ + \text{HD} \rightarrow \text{OD}^+ + \text{H}$ reaction in the $1^4A''$ (obtained at collinear O-H-H configuration) and $1^2A''$ (at OHH angle of 40°) electronic states

The formation reaction can only take place on the quartet PES while the exchange reaction may take place in both, quartet and doublet PESs. The calculated cross section for the formation reaction in the 0.01 - 1 eV energy interval was found to be in good agreement with the experimental values reported by Burley *et al.*³¹ More recent experiments reported rate constants for temperatures ranging from 20 to 200 K. The overall agreement was found to be good but, below 50 K, the measured values are larger than the simulated ones.^{27,28} This was explained by a change of the behavior of the simulated cross section²⁸ as it will be further discussed below.

In this work we extend these studies to the deuterated analogue, *i.e.* the formation reaction

in the ground quartet electronic state H_2O^+ , and the exchange reactions, that can produce deuteration or hydrogenation as

that take place in both, the ground quartet and doublet electronic states.

The doublet PES presents a very deep insertion well (~ 6 eV), while the quartet PES shows a much shallower well of ~ 1 eV. Scattering calculations were performed on the two PESs independently.

We have studied the formation [Eq. (3)] and exchange [Eq. (4)] reactions from a full

quantum wave packet (WP) method, using the MADWAVE3 program.³²⁻³⁵

The calculation of the state-to-state cross sections is performed using the partial wave expansion over total angular momentum J as follows

$$\sigma_{vj,v'j'}(E) = \frac{\pi}{k_{vj}^2(E)} \sum_J (2J+1) P_{vj,v'j'}^J(E), \quad (5)$$

where the reaction probabilities are given by

$$P_{vj,v'j'}^J(E) = \frac{1}{2j+1} \sum_{\Omega,\Omega'} |S_{vj\Omega,v'j'\Omega'}^J(E)|^2, \quad (6)$$

where $S_{vj\Omega,v'j'\Omega'}^J(E)$ are the scattering matrix elements. v and j designate the vibrational and rotational levels, respectively, of the molecule (HD, OD⁺ or OH⁺). In this work, we restrict the reactant in their ground vibrational state $v = 0$. Ω and Ω' are the projection of total angular momentum on the reactant and product body-fixed z-axis, respectively.

The WP is represented in reactant Jacobi coordinates in a body-fixed frame, including Ω projections up to a maximum of $\Omega = 15$. The calculation of the state-to-state reaction probabilities, $P_{vj,v'j'}^J(E)$, for each partial wave J is very demanding computationally, and it is performed for all J 's in the 0-20 interval, and for $J = 30, 40, \dots, 80$. For intermediate J values, $P_{vj,v'j'}^J(E)$ are obtained using an interpolation method based on the J -shifting approximation as described previously.^{29,32} The parameters used in the WP propagation on both the quartet and doublet PESs are listed in Table 1.

Initial-state selected rate constants are obtained by numerically averaging the corresponding integral cross-sections over translational energy as

$$k_{vj,v'j'}(T) = \sqrt{\frac{8}{\pi\mu(k_B T)^3}} \int dE E \sigma_{vj,v'j'}(E) e^{-E/k_B T} \quad (7)$$

where k_B is the Boltzmann constant and μ is the reduced mass of the reactive system.

Table 1: Parameters used in the WP calculations (all distances are given in Å). r_{abs} , R_{abs} define the position at which absorption starts in each of the radial Jacobi coordinates. R_0 is the center of the gaussian describing the initial wave packet, E_{col} being its mean energy. R_∞ is the distance at which the flux of products is analyzed.

Parameters	Quartet PES	Doublet PES
$r_{\min}, r_{\max}, N_r$	0.01, 30.0, 256	0.001, 25.0, 512
r_{abs}	16.0	15.0
$R_{\min}, R_{\max}, N_R$	0.01, 36.0, 620	0.01, 32.0, 620
R_{abs}	16.0	22.0
N_θ	300	200
R_0, E_{col}	15.0, 0.3	21.0, 0.3
R_∞	11.0	12.0
Ω, Ω'	15, 30	19, 25
Number of Chebyshev iterations:	80000	200000

3 Results

3.1 $O^+ + HD \longrightarrow OD^+ + H / OH^+ + D$ formation reaction

The calculated cross sections for the formation of OD^+ and OH^+ products in the $O^+(^4S) + HD(v=0, j=0)$ collisions are shown in Fig. 2. The overall reactive cross sections are obtained by summing state-to-state cross sections over all values of v' and j' , namely

$$\sigma_{vj} = \sum_{v'j'} \sigma_{vj \rightarrow v'j'} \quad (8)$$

The cross sections of the two reactions increase with decreasing energy as expected for exothermic reactions, following a Langevin behavior in the 0.01-0.4 eV interval, in very good agreement with the experiment in the whole energy interval.²¹ However, below 0.01 eV the slope of the cross sections decreases, as previously reported for the $O^+ + H_2$ reaction.^{27,29} The “Langevin model” is attributed to reactions involving an ion and a neutral molecule,³⁶ which depends on the intermolecular distance as $\alpha/2R^4$, leading to a

cross section $\sigma(E) = \pi\sqrt{2\alpha/E}$ and to a constant rate constant $K(T) \propto \sqrt{\alpha}$. This concept can be generalized to long-range interactions depending on a general power of R , as C_s/R^s , giving a cross section³⁷

$$\sigma(E) = \pi q(s) (C/E)^{2/s} \quad \text{with} \quad q(s) = \frac{s/2}{[(s-2)/2]^{(s-2)/s}}. \quad (9)$$

Full dimensional potentials with good long-range behavior present a leading C_s/R^s dependence at very long distances, and this also depends on the collision energy at which the “capture” is produced.

At low collisional energies, in order to be fully converged, wave packet calculations require very long propagations and careful absorption parameters and are hence challenging to be performed. However, for exothermic reaction, these problems are attenuated and the comparison made by Bulut and co-workers²⁹ between wave packet and quantum time-independent calculations for the $\text{O}^+ + \text{H}_2$ reaction showed an excellent agreement even at collision energies below 1 meV. This demonstrates that wave packet calculations are fully reliable at low energies for exothermic reactions.

The cross section below 0.01 eV for the formation of OD^+ and OH^+ products are very similar, close to a 1/1 ratio. However, for collision energies in the 0.01-0.9 eV interval, the cross section for the formation of OH^+ is significantly larger, in good agreement with the experimental data.²¹ This result is somehow unexpected, since the OD^+ channels is more exothermic and with a higher density of final states (see Fig. 1). Dateo & Clary²⁴ also reproduced this behavior using an adiabatic capture approach (ACA) and explained it as generated by the torque induced by the displacement of the center-of-mass with respect to the center-of-dispersion. This torque induces a rotation leading to a favorable approach of O^+ towards the H atom. The present quantum results confirm this behavior and extend it over 0.3 eV, where the ACA approach seems to fail.

Figure 2: Reactive cross section for the $\text{O}^+ + \text{HD}(v = 0, j = 0) \rightarrow \text{OD}^+ + \text{H} / \text{OH}^+ + \text{D}$ collisions (lines), compared with the experimental results of Sunderlin and Armentrout.²¹ Two analytical functions are also shown for extrapolation at low energies: A $E^{-1/2}$, the usual Langevin behavior for charge-induced dipole long-range interaction, and B $E^{-1/3}$ better adapted to the calculated cross section below 0.01 eV.

Figure 3: Reaction probabilities obtained for the $\text{O}^+ + \text{HD}(v = 0, j = 0) \rightarrow \text{OD}^+ + \text{H} / \text{OH}^+ + \text{D}$ at different partial waves, J , as indicated in each panel.

Three intervals can be established in terms of the interplay of collision energies and total angular momentum:

- For low collision energy, $E < 0.01$ eV, the long-range interaction dominates and guide the system to either OH^+ or OD^+ channels with nearly the same probability because the interaction is identical. In this regime, the end-over-end angular momentum is low ($\ell \approx J < 20$), and the top of the rotational barrier is at long intermolecular distance.
- At intermediate energies, $0.01 < E < 0.9$ eV, higher angular momentum ($J > 20$) contribute. For this higher J values and collision energies near the top of the rotational barrier, the rotational torque is able to reorient HD, favoring the approach of the O^+ to the H side, and hence the formation of OH^+ as explained by Dateo & Clary.²⁴ This is clearly seen in Fig. 3, for $J > 30$, for which near the threshold the probability of forming OH^+ is always larger than that of OD^+ .
- As collision energy increases, however, the torque has not time to reorient the HD reactant, and the OD^+ cross section increases and becomes dominant for all J 's studied (see Fig. 3). This behavior is consistent with an impulsive model, in which the lighter H atom is preferentially ejected, or with a statistical model, because the density of final states is higher in the OD^+ channel.

Rotational effects can also explain the dependence of the OH^+/OD^+ branching ratio. Indeed, the experimental temperature of the HD beam^{21,22,24} implies rotationally excited states of HD to be populated. The cross sections for $\text{O}^+(^4S) + \text{HD}(v=0, j=1)$ have also been calculated, and the total cross section is very similar to that obtained for collisions implying $\text{HD}(v=0, j=0)$. The effect of initial rotational excitation of HD can be seen in the helicity dependent total cross sections,³⁸ $\sigma_{vj\Omega}(E)$, that is shown in Fig. 4. For $\Omega = 0$, the cross section associated to the two products are very close to each other. However, for $\Omega = 1^\pm$, the cross section for OH^+ formation becomes larger than that of OD^+ formation, in good agreement with the results obtained for collisions implying $\text{HD}(v=0, j=0)$. After summing

Figure 4: Helicity dependent total reaction cross section (lines) to form OD^+ and OH^+ products in the collision $\text{O}^+(^4S) + \text{HD}(v=0, j=1, \Omega=0, 1^\pm)$, where the $\pm$ refers to even/odd parity under spatial inversion. The open circles are the experimental measurements of Sunderlin and Armentrout²¹ where the beam temperature is assumed to be 105 K.

over Ω , the total cross section yields to a slightly lower $\sigma_{OH^+}/(\sigma_{OH^+} + \sigma_{OD^+})$ ratio, as shown in Fig. 5. This reduction of the ratio as rotational excitation is in qualitative agreement with the observed behavior of the ratio as (rotational) temperature is varied (see Fig. 2 of Ref.²¹), and follows the analysis of Dateo and Clary.²⁴ **Moreover, the present results are in good agreement with the previous results reported by Martinez *et al.*³⁹ for this quantity using the helicity decoupling approximation for $j=0$.** For a given Ω , the corresponding

Figure 5: $f(E) = \sigma_{OH^+}/(\sigma_{OH^+} + \sigma_{OD^+})$ ratio obtained for collisions with HD($v = 0, j = 0$) and HD($v = 0, j = 1$) state.

angular functions behave as $Y_{j\Omega}(\gamma, \phi) \rightarrow \sin^\Omega \gamma$, with $\cos \gamma = \mathbf{r} \cdot \mathbf{R}/rR$ being the angle between the HD internuclear vector, $\mathbf{r}$, and the vector $\mathbf{R}$ joining HD center of mass and O^+ . Therefore, for $\Omega \rightarrow j$, the angular function are peaked closely to $\gamma \approx \pi/2$, while for $\Omega \rightarrow 0$, the angular function presents preference towards the co-linear geometry. The charge-induced dipole/quadrupole long range interaction has maxima at these co-linear configurations, while it is attractive towards the center of the HD bond. The $OH^+/(OH^+ + OD^+)$ ratio of the reaction probabilities obtained for HD($v = 0, j = 1$) for several Ω at high J show that the OH^+ probability near the rotational threshold is higher for $\Omega = 1$ than for $\Omega = 0$, showing

that the attractive part of the long range interaction makes the difference among different Ω , and is the responsible for the rotational effect on the ratio.

In order to determine the reactive rate constants at low temperatures ($T \sim 10$ K), it is necessary to extrapolate the cross sections at collision energies below 1 meV, the lower energy calculated. In Fig. 2 two extrapolation approaches for the cross section at low energies are shown. The typical Langevin behavior for ion-induced dipole and quadrupole interactions, behaving as $A \cdot E^{-1/2}$, is valid for $E > 0.01$ eV. The calculated cross section in the 1-10 meV energy interval is however better fitted by a $B \cdot E^{-1/3}$ law. The total rate constants obtained with these two extrapolations are shown in Fig. 6. Using the Langevin extrapolation yields a nearly constant rate constant, as expected, while using $B \cdot E^{-1/3}$ the rate constant decreases with decreasing temperatures. Viggiano and co-workers²² reported a value of $1.2 \cdot 10^{-9}$ cm³/s independent of temperature and with an experimental error of $\pm 40\%$. The two rate constants obtained here are within this large error. However, we conclude that the Langevin extrapolation is better suited and will be used hereafter.

The $f(T) = k_{OH^+}/(k_{OH^+} + k_{OD^+})$ ratio for collisions implying HD($v = 0, j = 1$) in the top panel of Fig. 6 is lower than that for collisions implying HD($v = 0, j = 0$), while the total rate constants (in the lower panel) are nearly the same. For a beam temperature of 105 K, the distribution of HD($v = 0, j = 0$) and HD($v = 0, j = 1$) are 0.53 and 0.47%, respectively, (neglecting the contribution of higher j 's), and therefore the $f(T)$ ratio is in between collisions implying HD($v = 0, j = 0$) and collisions implying HD($v = 0, j = 1$). As rotational temperature increases, the $f(T)$ ratio is expected to decrease, as a consequence of the helicity effect discussed above, in good agreement with the arguments used before.^{21,22,24} The $f(T)$ ratio also increases with the translational temperature, as reported by Viggiano and co-workers,²² when discussing the behavior of the reaction cross sections with translational energy. In addition, recently Tran and coworkers⁴⁰ reported a value of $f(T) = 0.53$ at $T = 26$ K. **The value of $f(T=23K)$ obtained here is 0.512, 0.501 and 0.507 for $j= 0, 1$ and the average, respectively, what is considered to be rather good, specially**

Figure 6: Bottom panel: Total reaction rate constants for the $O^+(^4S) + HD(v=0, j=0)$ reaction obtained with two different extrapolations of the cross section for $E < 1$ meV, the Langevin behavior (A $E^{-1/2}$), and B $E^{-1/5}$. Top panel: $f(T) = k_{OH^+}/(k_{OH^+} + k_{OD^+})$ ratio .

when considering the experimental uncertainties.

OH^+ and OD^+ are very reactive species and are therefore expected to disappear in a low number of collisions, with no opportunity to be thermalized. As a consequence, the rotational excitations observed in the ISM are related to chemical excitation, i.e. reaction products in ro-vibrationally excited states. Because H_2 is far more abundant than HD, chemically excited OH^+ are essentially produced by the $\text{O}^+ + \text{H}_2$ reaction, studied before.²⁷ Here, we focus on the ro-vibrational distribution of the OD^+ products. The final vibrationally resolved rate constants for $\text{O}^+(^4S) + \text{HD}(v, j = 0) \rightarrow \text{OD}^+(v') + \text{H}$ are shown in Fig. 7.

Figure 7: Vibrationally resolved state-to-state rate constants for the $\text{O}^+(^4S) + \text{HD}(v = 0, j = 0) \rightarrow \text{OD}^+(v') + \text{H}$ reaction.

The rate constants for the formation of OD^+ in its first 2 vibrational levels, $v' = 0$ and 1, are nearly constant rate constants, corresponding to a Langevin behavior, associated with exothermic reactions with no barrier (see Fig. 1). For $v' > 1$, the rate constants follow an Arrhenius behavior characteristic of reactions with a threshold, and their rate constants are more than 10 times lower. Since the rate for the formation of OD^+ in $v' = 1$ is only 2-3 times lower than that for the formation of OD^+ in $v' = 0$, it is obvious that these two

vibrational levels are significantly formed. In Fig. 8, the corresponding state-to-state reaction rate constants (rotational distribution in $v' = 0$ and $v' = 1$ manifold) are shown.

Figure 8: Rotationally resolved state-to-state rate constants for the $\text{O}^+(^4S) + \text{HD}(v = 0, j = 0) \rightarrow \text{OD}^+(v', j') + \text{H}$ reaction. Left/right panels correspond to $v' = 0$ and 1, and bottom/top panels describe low/high j' values

As it can be clearly seen, OD^+ products in highly excited rotational states are formed both in $v' = 0$ and $v' = 1$ manifold. The strongest rate constants is observed for the formation of OD^+ in $j' = 12$ and 8 for $v' = 0$ and 1, respectively. For $v' = 1$, the rate constants for the formation of OD^+ in rotational states $j' > 8$ decrease rapidly with increasing j' , because since the reaction becomes endothermic. For $v' = 0$, the same happens for rotational excitation $j' > 22$. For the formation of OD^+ in rotational levels in the $j' = 4 - 18$ interval, the rate constants are of the order of $2\text{--}3 \times 10^{-11} \text{ cm}^3/\text{s}$. This demonstrates that a significant part the excess of energy goes into final rotation of products.

3.2 $\text{OH}^+ + \text{D} \longleftrightarrow \text{OD}^+ + \text{H}$ exchange reactions

At energies below 0.5 eV, the $\text{OD}^+ + \text{H}$ or $\text{OH}^+ + \text{H}$ collisions can only produce the hydrogenation (destruction) or the deuteration (formation), respectively. These exchanges reactions were extensively study for the $\text{OH}^+ + \text{H}$ collisions,²⁹ where exchange gives the original products. For astrophysical applications where the interest is on the OH^+ collisional rotational excitation, data summed over inelastic and exchange contributions were provided.⁴¹ As discussed above, since OH^+ and H are open shell systems, there are several electronic states, a doublet and a quartet correlated to these reactants. In the quartet electronic state, with a shallow well, the exact inelastic and exchange state-to-state cross section were in rather good agreement with rigid rotor results. However this is not the case in the doublet electronic state, characterized by a deep well, for which exact excitation cross sections was found to be much higher than that obtained using the rigid rotor approximation.

In the present case, $\text{OH}^+ + \text{D} \longleftrightarrow \text{OD}^+ + \text{H}$ exchange reactions can either destroy or form OD^+ , and the exchange is therefore of higher interest. The reaction probabilities for the two collisions and the two electronic states are shown in Fig. 9. In all cases the reaction probability associated with the exchange processes, both hydrogenation or deuteration, is rather low, as compared to that for the formation of OH^+ or OD^+ in $\text{O}^+ + \text{HD}$ collisions. Hydrogenation is endothermic while deuteration is exothermic, due to the lower zero point energy (ZPE) of OD^+ compared to that of OH^+ . As a consequence, the deuteration probabilities are also higher than the hydrogenation. In the two cases, there are many resonances, the resonant structure being denser in the doublet because the presence of a deeper well. However, the exchange probability is always larger for the quartet state with a much slower well.

The reaction cross section for the two reactions in the two electronic states are depicted in Fig. 10. As expected, the deuteration reaction in the two electronic states show the typical behavior of exothermic reactions, increasing with decreasing collision energy, while hydrogenation presents a threshold at ≈ 0.05 eV, associated to the endothermicity due to

Figure 9: Reaction probability for $J = 0$ obtained for the $\text{OD}^+ + \text{H}$ (left panels) and $\text{OH}^+ + \text{D}$ (right panels) for the quartet (lower panels) and doublet (top panels) electronic states.

Figure 10: Reaction cross section for the $\text{OD}^+(v=0, j=0) + \text{H}$ (left panels) and $\text{OH}^+(v=0, j=0) + \text{D}$ (right panels) for the quartet (lower panels) and doublet (top panels) electronic states.

the higher ZPE of OH^+ .

The cross sections for the doublet state are larger than that for the quartet state, while at $J = 0$ the reaction probabilities show the reverse behavior. This is explained by the deeper well of the doublet state, which reduce the effect of the rotational barrier, so that high J 's contribute significantly in the partial wave expansion.

The reaction individual rate constants display the same behavior than the cross sections. The total contribution of the exchange reactions are depicted in Fig. 11 after summing the contribution of the two electronic states with the appropriate degeneracy. It shows, that below 150 K the hydrogenation (destruction of OD^+) is very slow, while the deuteration (formation of OD^+) keeps being rather fast, nearly three order of magnitudes faster. The effect of these rate constants on the abundance of OD^+ , and the OD^+/OH^+ ratio, is studied below under different conditions, associated to different astrophysical environments.

Figure 11: Exchange rate constants for the $\text{OD}^+ + \text{H}$ (destruction) and $\text{OH}^+ + \text{D}$ (formation) reactions.

3.3 OH⁺ and OD⁺ chemistry in the interstellar medium

It is finally interesting to discuss the possibility of OD⁺ formation in space and to crudely estimate the [OD⁺]/[OH⁺] abundance ratio in interstellar clouds as a function of the physical conditions (temperature and D/H abundance ratio).

The chemistry of OH⁺ in molecular clouds is rather well understood. At the border of the cloud where most of the hydrogen is atomic, the production of OH⁺ proceeds through

In parallel, O⁺ ions can react with HD and form both OH⁺ and OD⁺ as follow

If one assumes that both OH⁺ and OD⁺ are similarly destroyed through collisions with $[\alpha]$ with a rate constant of k_4 (α can be electrons or all atoms or molecules that will efficiently react with OH⁺ and OD⁺), one can use the steady state approach to derive the [OD⁺]/[OH⁺] abundance ratio.

$$[\text{OH}^+] = \frac{k_1[\text{O}^+][\text{H}_2] + k_2[\text{O}^+][\text{HD}]}{k_4[\alpha]} \quad (13)$$

$$[\text{OD}^+] = \frac{k_3[\text{O}^+][\text{HD}]}{k_4[\alpha]} \quad (14)$$

So that:

$$\frac{[\text{OD}^+]}{[\text{OH}^+]} = \frac{k_3}{k_2 + k_1 \frac{[\text{H}_2]}{[\text{HD}]}} \quad (15)$$

For the k_1 , k_2 and k_3 rate constants, for consistency, we used those obtained only for H_2 and HD in their ground ro-vibrational state.

As one can see, the $[\text{OD}^+]/[\text{OH}^+]$ will increase with increasing $[\text{HD}]/[\text{H}_2]$ and obviously, OD^+ can be more easily detected in media with a large HD abundance. Figure 12 present the temperature variation of the $[\text{OD}^+]/[\text{OH}^+]$ abundance ratio derived from Eq. 15 with a $[\text{HD}]/[\text{H}_2]$ abundance ratio of $2 \cdot 10^{-5}$ which corresponds to the typical ratio in diffuse ISM.⁴²

Figure 12: Temperature variation of the $[\text{OD}^+]/[\text{OH}^+]$ abundance ratio. The $[\text{HD}]/[\text{H}_2]$ abundance ratio is $2 \cdot 10^{-5}$.

At the exception of the very low temperatures, because of a less efficient formation of OD^+ than OH^+ through the $\text{O}^+ + \text{HD}$ reaction, the $[\text{OD}^+]/[\text{OH}^+]$ abundance ratio is below than that of the $[\text{HD}]/[\text{H}_2]$ abundance ratio. As the temperature in the external part of interstellar clouds is generally above 100-200 K,²⁷ it is unlikely to expect a favorable formation of OD^+ through $\text{O}^+ + \text{HD}$ reaction and the $[\text{OD}^+]/[\text{OH}^+]$ abundance ratio will remain below (a factor

2 to 4) the $[\text{HD}]/[\text{H}_2]$ abundance ratio. The abundance of OH^+ in such media is expected to be at the most 10^{-8} the abundance of atomic hydrogen.²⁷ Then, the abundance of OD^+ would be below 10^{-13} the abundance of atomic hydrogen and would probably escape to detection because of a too weak signal.

Alternatively, OD^+ can be formed through collision of OH^+ and D and destroyed through collisions with H:

Using steady state chemistry and assuming that the $[\text{OD}^+]/[\text{OH}^+]$ abundance ratio is simply driven by this reaction, one obtains

$$\frac{[\text{OD}^+]}{[\text{OH}^+]} = \frac{k_5[\text{D}]}{k_6[\text{H}]} \quad (18)$$

Figure 13 presents the temperature variation of the $[\text{OD}^+]/[\text{OH}^+]$ abundance ratio derived from Eq. 18. The $[\text{D}]/[\text{H}]$ abundance ratio is $1 \cdot 10^{-5}$.

As one can see, at temperature below 100 K, the $[\text{OD}^+]/[\text{OH}^+]$ abundance ratio reaches a value up to 0.3, a value four orders of magnitude larger than the $[\text{D}]/[\text{H}]$ abundance ratio. Such increase can be explained by the inefficient destruction of OD^+ through collision with H at low temperature because of a significant endothermicity. At temperature around 200 K, the $[\text{OD}^+]/[\text{OH}^+]$ abundance ratio is still two orders of magnitude larger than the $[\text{D}]/[\text{H}]$ abundance ratio and could lead to a significant deuterium enrichment. Then, the abundance of OD^+ would be around 10^{-11} the abundance of atomic hydrogen and this gives a better hope for detection. Of course, the astrochemical model presented here is very crude since it neglects many possible formation and destruction processes. However, they clearly indicate that OD^+ could be searched in cold parts of interstellar clouds where the OH^+ are found to be

Figure 13: Temperature variation of the $[\text{OD}^+]/[\text{OH}^+]$ abundance ratio. The $[\text{D}]/[\text{H}]$ abundance ratio is $1 \cdot 10^{-5}$ transitions.

in significant abundance.

4 Conclusions

In this work, the state-to-state rate constants for the formation of OD^+ in the $\text{O}^+ + \text{HD}$ and $\text{OH}^+ + \text{D} \rightleftharpoons \text{OD}^+ + \text{H}$ reactions have been obtained using an accurate quantum WP treatment. The theoretical data were validated through a detailed comparison with experimental measurements. A less efficient formation of OD^+ than OH^+ through the $\text{O}^+ + \text{HD}$ reaction was found. At the opposite, the $\text{OH}^+ + \text{D} \rightleftharpoons \text{OD}^+ + \text{H}$ reaction will favor the OD^+ formation because of ZPE effects.

The new data were used in simple astrochemical models in order to estimate the $[\text{OD}^+]/[\text{OH}^+]$ abundance ratio in interstellar clouds. The results indicate that the abundance of OD^+ is expected to be low and that, if detectable, OD^+ could be search in cold part of interstellar clouds where the OH^+ are found to be in significant abundance.

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Graphical TOC Entry