

# Fully coupled photochemistry of the deuterated ionosphere of Mars and its effects on escape of H and D

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## Abstract

Although deuterium (D) on Mars has received substantial attention, the deuterated ionosphere remains relatively unstudied. This means that we also know very little about non-thermal D escape from Mars, since it is primarily driven by excess energy imparted to atoms produced in ion-neutral reactions. Most D escape from Mars is expected to be non-thermal, highlighting a gap in our understanding of water loss from Mars. In this work, we set out to fill this knowledge gap. To accomplish our goals, we use an upgraded 1D photochemical model that fully couples ions and neutrals and does not assume photochemical equilibrium. To our knowledge, such a model has not been applied to Mars previously. We model the atmosphere during solar minimum, mean, and maximum, and find that the deuterated ionosphere behaves similarly to the H-bearing ionosphere, but that non-thermal escape on the order of 8000–9000 cm<sup>-2</sup>s<sup>-1</sup> dominates atomic D loss under all solar conditions. The total fractionation factor,  $f$ , is 0.04–0.07, and integrated water loss is 147–158 m GEL. This is still less than geomorphological estimates. Deuterated ions at Mars are likely difficult to measure with current techniques due to low densities and mass degeneracies with more abundant H ions. Future missions wishing to measure the deuterated ionosphere *in situ* will need to develop innovative techniques to do so.

1           **Fully coupled photochemistry of the deuterated**  
2           **ionosphere of Mars and its effects on escape of H and**  
3           **D**

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8           **Key Points:**

- 9
- We present the first photochemical modeling study of the deuterated ionosphere  
10           of Mars.
  - Non-thermal escape dominates D loss under all solar conditions, and the processes  
11           producing hot D are similar to those producing hot H.
  - The combined D/H fractionation factor is  $f = 0.04\text{--}0.07$ , indicating 147–158 m  
12           GEL of water loss, still less than geological estimates.  
13
- 14

15 **Abstract**

16 Although deuterium (D) on Mars has received substantial attention, the deuterated iono-  
 17 sphere remains relatively unstudied. This means that we also know very little about non-  
 18 thermal D escape from Mars, since it is primarily driven by excess energy imparted to  
 19 atoms produced in ion-neutral reactions. Most D escape from Mars is expected to be non-  
 20 thermal, highlighting a gap in our understanding of water loss from Mars. In this work,  
 21 we set out to fill this knowledge gap. To accomplish our goals, we use an upgraded 1D  
 22 photochemical model that fully couples ions and neutrals and does not assume photo-  
 23 chemical equilibrium. To our knowledge, such a model has not been applied to Mars pre-  
 24 viously. We model the atmosphere during solar minimum, mean, and maximum, and find  
 25 that the deuterated ionosphere behaves similarly to the H-bearing ionosphere, but that  
 26 non-thermal escape on the order of  $8000\text{--}9000 \text{ cm}^{-2}\text{s}^{-1}$  dominates atomic D loss under  
 27 all solar conditions. The total fractionation factor,  $f$ , is  $f = 0.04\text{--}0.07$ , and integrated  
 28 water loss is 147–158 m GEL. This is still less than geomorphological estimates. Deuter-  
 29 ated ions at Mars are likely difficult to measure with current techniques due to low den-  
 30 sities and mass degeneracies with more abundant H ions. Future missions wishing to mea-  
 31 sure the deuterated ionosphere *in situ* will need to develop innovative techniques to do  
 32 so.

33 **Plain Language Summary**

34 Our knowledge of ions in the martian atmosphere that contain deuterium (D) is extremely  
 35 limited, lacking measurements and dedicated computer models. This is a problem be-  
 36 cause the expectation is that most D that escapes to space does so “non-thermally”, by  
 37 gaining extra energy from ion reactions. H and D mostly exist in water on Mars, so iden-  
 38 tifying how much H and D have escaped non-thermally is an important piece of the puz-  
 39 zle of water loss from Mars. Here, we present the first one dimensional model of the Mars  
 40 atmosphere that includes D-bearing ions. This new model avoids many common approx-  
 41 imations that might change our results in unclear ways. We report the amounts of ther-  
 42 mal and non-thermal escape of H and D and confirm that most D escapes non-thermally.  
 43 We also identify the specific chemical reactions that are most important, and show how  
 44 many D-bearing ions we expect to find at different altitudes in the atmosphere that might  
 45 be detectable by future missions. Finally, we calculate that a layer of water 147–158 m  
 46 deep has been lost from Mars. This is still less than the amount calculated by geolog-  
 47 ical studies.

48 **1 Introduction**

49 Mars is a natural laboratory to study how atmospheric escape shapes planetary habit-  
 50 ability. It is now well established that a significant amount of the Mars atmosphere has  
 51 been lost to space (Jakosky et al., 2018). This escape is fractionating—the relative es-  
 52 cape efficiency is different for members of an isotope pair, such as deuterium (D) and  
 53 hydrogen (H). Because on Mars, D and H are found primarily in water, D/H fraction-  
 54 ation indicates a history of water loss (Owen et al., 1988). Understanding escape frac-  
 55 tionation therefore contributes to understanding the long-term loss of the atmosphere  
 56 and desiccation of the planet.

57 Geological studies indicate that Mars has likely lost 500+ meters global equivalent layer  
 58 (GEL) of water (Lasue et al., 2013, and references therein), but atmospheric modeling  
 59 studies typically do not find the same result, instead arriving at a smaller number of 100–  
 60 250 m GEL (Cangi et al., 2020; Alsaeed & Jakosky, 2019; V. A. Krasnopolsky, 2002; V. Krasnopol-  
 61 sky, 2000). A key step in retrieving water loss estimates from atmospheric models is to  
 62 quantify both thermal and non-thermal escape.

63 Thermal escape occurs for particles with a thermal velocity in the high-energy tail of the  
 64 velocity distribution above the planet’s escape velocity. Non-thermal escape comprises

all other processes that grant extra kinetic energy to atmospheric particles, which are variously dubbed “suprothermal” or “hot”; most of these processes involve ion chemistry or interaction with ions. Thermal escape of H has been well-studied at Mars with atmospheric models, observations from missions, and mixes of the two (Chaffin et al., 2021; Stone et al., 2020; Mayyasi et al., 2018; Rahmati et al., 2018; Zahnle et al., 2008; V. A. Krasnopolsky, 2002). Thermal escape of D has also been modeled (Cangi et al., 2020; Kass & Yung, 1999; Yung et al., 1988), but non-thermal escape of D from Mars has not been directly modeled, despite expectations that it should be the dominant loss process (Gacesa et al., 2012; V. A. Krasnopolsky, 2002). V. A. Krasnopolsky (2002) and V. A. Krasnopolsky et al. (1998) calculated non-thermal escape velocities for a few select processes (solar wind charge exchange, electron impact ionization, and photoionization), but their model did not include a deuterated ionosphere, and so missed a portion of the production of hot atoms.

Cangi et al. (2020) used a 1D photochemical model of Mars’ neutral atmosphere to calculate the D/H fractionation factor  $f$  as a function of atmospheric temperatures. The model only calculated thermal escape directly; non-thermal escape was approximated by scaling the non-thermal effusion velocities given by V. A. Krasnopolsky (2002) and multiplying them by the densities of H and D at the exobase. This estimation indicated that  $f$  is several orders of magnitude larger when non-thermal escape processes are considered, motivating a more complete calculation of non-thermal escape of H and D. Here, we present this more complete treatment. The key questions about the deuterated martian ionosphere that we address are as follows.

1. What are the atmospheric densities of deuterated ions?
2. What are the dominant production mechanisms of hot H and hot D, and are they analogous or dissimilar?
3. What is the magnitude of non-thermal escape of D, and is it the dominant type of escape during quiet solar conditions?
4. Can inclusion of non-thermal escape in the model yield an estimation of water loss similar to the amount calculated in geomorphological studies?

To answer these questions, we have upgraded our existing 1D photochemical model of the neutral martian atmosphere to include a self-consistent ionosphere and deuterated ions. Because ions and neutrals have substantially different behaviors and chemistry, the problem of modeling both at the same time turns out to be an expensive and computationally difficult one, even in 1D. Most recent ion-neutral photochemical models use one or more of three common approaches: (1) a fixed (either wholly or partially) background neutral atmosphere (Fox et al., 2021, 2017, 2015; Matta et al., 2013; Molina-Cuberos et al., 2002); (2) placing the lower boundary of the model near the bottom of the ionosphere (Fox et al., 2021; V. A. Krasnopolsky, 2019; Fox et al., 2015; Matta et al., 2013; V. A. Krasnopolsky, 2002); or (3) the assumption of photochemical equilibrium for chemically short-lived species (Vuitton et al., 2019; Banaszkiewicz et al., 2000) and/or neglect of ion diffusion (Dobrijevic et al., 2016). But because we did not want to lose any subtle ion-neutral feedbacks, we have upgraded our photochemical model such that it does not use any of the above simplifications. In this way, we obtain a more complete understanding of the coupling of the lower to upper atmospheres, which has been recently shown to be key to understanding water transport, destruction, and escape during the Mars dusty season (Villanueva et al., 2021; Chaffin et al., 2021; Holmes et al., 2021; Stone et al., 2020; A. A. Fedorova et al., 2020; Vandaele et al., 2019; Aoki et al., 2019; Heavens et al., 2018).

Our new model spans surface-to-space and fully couples ions and neutrals without assumption of photochemical equilibrium. We use this enhanced model to present a first

theoretical analysis of D ion chemistry at Mars, which includes an updated quantification of non-thermal escape of D and H, the most critical reactions for production of hot H and D, and the implications for water loss.

## 2 Model description

Here we describe changes made to the 1D photochemical model as described by Cangi et al. (2020). In addition to the upgrades to physics and chemistry described below, this update incorporates computational improvements, such as extensive encapsulation, vectorization of functions, and performance tuning. The only species that we hold constant in our model is argon and lower atmospheric water (see Section 2.1.3). The absolute tolerance is  $1 \times 10^{-12}$ , or 1 ppt, and the relative tolerance is  $1 \times 10^{-6}$ .

### 2.1 New features

#### 2.1.1 Ion reaction network

Our updated model contains  $\sim 600$  total ion and neutral reactions. We enumerate the deuterated reactions in Table 1. The full network of chemical reactions is available in the Supporting Information, Table S1; rate coefficients of H-analogue reactions are generally the same as those used by Vuitton et al. (2019).

**Scope of deuterated reactions.** We define a deuterated analogue reaction as a reaction in which one H atom in one of the reactants has been replaced with D; for example,  $D + O_2 \rightarrow DO_2$  instead of  $H + O_2 \rightarrow HO_2$ . We do not consider doubly deuterated reactions or species, e.g., we do not include reactions like  $DO_2 + D \rightarrow OD + OD$  nor species like  $D_2O$ . Our deuterated reaction network includes the deuterated analogues of the top 23 fastest H-bearing reactions (according to the column rate), including neutral reactions used by (Cangi et al., 2020) and many deuterated analogues of ion-neutral reactions. All told, the H-bearing analogues of these deuterated reactions make up 99.99997% of the integrated column rate of all H-bearing reactions. For this reason, it is unlikely we have missed any significant deuterated reactions.

Table 1: Deuterated reactions used in the model. Reactions 1-6b: column rate  $\nu$  in  $\text{cm}^{-2}\text{s}^{-1}$ . Reactions 7-125: rate coefficients in units of  $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$  for bimolecular reactions and  $\text{cm}^6 \text{molecule}^{-1} \text{s}^{-1}$  for termolecular reactions. BR = branching ratio; MS = mass scaling.

		Reaction	BR	MS	Rate coefficient	Ref
Photodissociation and photoionization						
1	D	$\rightarrow D^+$			$\nu_{\text{col}} = 0.3$	†
2	DO <sub>2</sub>	$\rightarrow OD + O$			$\nu_{\text{col}} = 2779$	†
3a	HD	$\rightarrow HD^+$			$\nu_{\text{col}} = 0.5$	†
3b		$\rightarrow H + D$			$\nu_{\text{col}} = 0.15$	†
3c		$\rightarrow H^+ + D$			$\nu_{\text{col}} = 0.03$	†
3d		$\rightarrow D^+ + H$			$\nu_{\text{col}} = 0.03$	†
4a	HDO	$\rightarrow D + OH$			$\nu_{\text{col}} = 17.4$	C0499
4b		$\rightarrow H + OD$			$\nu_{\text{col}} = 17.4$	C0499
4c		$\rightarrow HD + O(^1D)$			$\nu_{\text{col}} = 2.3$	C0499
4d		$\rightarrow HDO^+$			$\nu_{\text{col}} = 1.3$	†
4e		$\rightarrow OD^+ + H$			$\nu_{\text{col}} = 0.3$	†
4f		$\rightarrow OH^+ + D$			$\nu_{\text{col}} = 0.3$	†
4g		$\rightarrow D^+ + OH$			$\nu_{\text{col}} = 0.1$	†
4h		$\rightarrow H^+ + OD$			$\nu_{\text{col}} = 0.1$	†

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		Reaction	BR	MS	Rate or rate coefficient	Ref
4i		$\rightarrow \text{O}^+ + \text{HD}$			$\nu_{\text{col}} = 0.02$	†
4j		$\rightarrow \text{H} + \text{D} + \text{O}$			$\nu_{\text{col}} = 0$	†
5a	HDO <sub>2</sub>	$\rightarrow \text{OH} + \text{OD}$			$\nu_{\text{col}} = 451$	†
5b		$\rightarrow \text{DO}_2 + \text{H}$			$\nu_{\text{col}} = 12.5$	†
5c		$\rightarrow \text{HO}_2 + \text{D}$			$\nu_{\text{col}} = 12.5$	†
5d		$\rightarrow \text{HDO} + \text{O}(\text{¹D})$			$\nu_{\text{col}} = 0$	†
6a	OD	$\rightarrow \text{O} + \text{D}$			$\nu_{\text{col}} = 44.7$	NL84
6b		$\rightarrow \text{O}(\text{¹D}) + \text{D}$			$\nu_{\text{col}} = 0.6$	NL84
Deuterated neutral-neutral reactions						
					See text	
7	CO + D	$\rightarrow \text{DCO}$			$k_\infty = 1.00e + 00 \left(\frac{T_n}{300}\right)^{0.2}$ $k_0 = 2.00 \times 10^{-35} \left(\frac{T_n}{300}\right)^{0.2}$	Est.
8a	CO + OD	$\rightarrow \text{CO}_2 + \text{D}$	$\sqrt{\frac{17}{18}}$		$k_\infty = 1.63 \times 10^{-6} \left(\frac{T_n}{300}\right)^{6.1}$ $k_0 = 4.90 \times 10^{-15} \left(\frac{T_n}{300}\right)^{0.6}$	Est.
8b		$\rightarrow \text{DOCO}$	$\sqrt{\frac{17}{18}}$		See text $k_\infty = 6.62 \times 10^{-16} \left(\frac{T_n}{300}\right)^{1.3}$ $k_0 = 1.73 \times 10^{-29} \left(\frac{T_n}{300}\right)^{-1.4}$	Est.
9	D + H <sub>2</sub>	$\rightarrow \text{HD} + \text{H}$			$2.73 \times 10^{-17} \left(\frac{T_n}{300}\right)^{2.0} e^{-2700/T_n}$	N15
10a	D + H <sub>2</sub> O <sub>2</sub>	$\rightarrow \text{H}_2\text{O} + \text{OD}$	0.5		$1.16 \times 10^{-11} e^{-2110/T_n}$	C10
10b		$\rightarrow \text{HDO} + \text{OH}$	0.5		$1.16 \times 10^{-11} e^{-2110/T_n}$	C10
11a	D + HO <sub>2</sub>	$\rightarrow \text{DO}_2 + \text{H}$			$1.00 \times 10^{-10}$	Y88
11b		$\rightarrow \text{HD} + \text{O}_2$			$2.45 \times 10^{-12}$	Y88
11c		$\rightarrow \text{HDO} + \text{O}(\text{¹D})$			$1.14 \times 10^{-12}$	Y88
11d		$\rightarrow \text{OH} + \text{OD}$			$5.11 \times 10^{-11}$	Y88
12	D + O <sub>2</sub>	$\rightarrow \text{DO}_2$	$\sqrt{\frac{1}{2}}$		$k_\infty = 2.40 \times 10^{-11} \left(\frac{T_n}{300}\right)^{0.2}$ $k_0 = 1.46 \times 10^{-28} \left(\frac{T_n}{300}\right)^{-1.3}$	Est.
13	D + O <sub>3</sub>	$\rightarrow \text{OD} + \text{O}_2$			$9.94 \times 10^{-11} e^{-470/T_n}$	Y89, N15
14	D + OH + CO <sub>2</sub>	$\rightarrow \text{HDO} + \text{CO}_2$	$\sqrt{\frac{1}{2}}$		$1.16 \times 10^{-25} \left(\frac{T_n}{300}\right)^{-2.0}$	Est.
15	DCO + H	$\rightarrow \text{CO} + \text{HD}$	$\sqrt{\frac{29}{30}}$		$1.50 \times 10^{-10}$	Est.
16a	DCO + O	$\rightarrow \text{CO} + \text{OD}$	$\sqrt{\frac{29}{30}}$		$5.00 \times 10^{-11}$	Est.
16b		$\rightarrow \text{CO}_2 + \text{D}$	$\sqrt{\frac{29}{30}}$		$5.00 \times 10^{-11}$	Est.
17a	DCO + O <sub>2</sub>	$\rightarrow \text{CO}_2 + \text{OD}$	$\sqrt{\frac{29}{30}}$		$7.60 \times 10^{-13}$	Est.
17b		$\rightarrow \text{DO}_2 + \text{CO}$	$\sqrt{\frac{29}{30}}$		$5.20 \times 10^{-12}$	Est.
18	DCO + OH	$\rightarrow \text{HDO} + \text{CO}$	0.5	$\sqrt{\frac{29}{30}}$	$1.80 \times 10^{-10}$	Est.
19	DO <sub>2</sub> + HO <sub>2</sub>	$\rightarrow \text{HDO}_2 + \text{O}_2$	$\sqrt{\frac{33}{34}}$		$3.00 \times 10^{-13} e^{460/T_n}$	Est.
20	DO <sub>2</sub> + N	$\rightarrow \text{NO} + \text{OD}$	$\sqrt{\frac{33}{34}}$		$2.20 \times 10^{-11}$	Est.
21	DO <sub>2</sub> + O <sub>3</sub>	$\rightarrow \text{OD} + \text{O}_2 + \text{O}_2$	$\sqrt{\frac{33}{34}}$		$1.00 \times 10^{-14} e^{-490/T_n}$	Est.
22	DOCO + O <sub>2</sub>	$\rightarrow \text{DO}_2 + \text{CO}_2$	$\sqrt{\frac{45}{46}}$		$2.09 \times 10^{-12}$	Est.
23	DOCO + OH	$\rightarrow \text{CO}_2 + \text{HDO}$	$\sqrt{\frac{45}{46}}$		$1.03 \times 10^{-11}$	Est.

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		Reaction	BR	MS	Rate or rate coefficient	Ref
24	H + D + M	$\rightarrow$ HD + M		$\sqrt{\frac{1}{2}}$	$6.62 \times 10^{-27} (\frac{T_n}{300})^{-2.27}$	Est.
25a	H + DO <sub>2</sub>	$\rightarrow$ HD + O <sub>2</sub>		$\sqrt{\frac{33}{34}}$	$3.45 \times 10^{-12}$	Est.
25b		$\rightarrow$ HDO + O( <sup>1</sup> D)		$\sqrt{\frac{33}{34}}$	$1.60 \times 10^{-12}$	Est.
25c		$\rightarrow$ HO <sub>2</sub> + D			$1.85 \times 10^{-10} e^{-890/T_n}$	Y88
25d		$\rightarrow$ OH + OD		$\sqrt{\frac{33}{34}}$	$7.20 \times 10^{-11}$	Est.
26	H + HD	$\rightarrow$ H <sub>2</sub> + D			$1.15 \times 10^{-11} e^{-3041/T_n}$	N15
27a	H + HDO <sub>2</sub>	$\rightarrow$ H <sub>2</sub> O + OD	0.5		$1.16 \times 10^{-11} e^{-2110/T_n}$	C10
27b		$\rightarrow$ HDO + OH	0.5		$1.16 \times 10^{-11} e^{-2110/T_n}$	C10
28	H + OD + CO <sub>2</sub>	$\rightarrow$ HDO + CO <sub>2</sub>		$\sqrt{\frac{17}{18}}$	$1.16 \times 10^{-25} (\frac{T_n}{300})^{-2.0}$	Est.
29	HCO + D	$\rightarrow$ CO + HD		$\sqrt{\frac{1}{2}}$	$1.50 \times 10^{-10}$	Est.
30	HCO + OD	$\rightarrow$ HDO + CO	0.5	$\sqrt{\frac{29}{30}}$	$1.80 \times 10^{-10}$	Est.
31a	HD + O	$\rightarrow$ OD + H			$1.68 \times 10^{-12} e^{-4400/T_n}$	N15
31b		$\rightarrow$ OH + D			$4.40 \times 10^{-12} e^{-4390/T_n}$	N15
32	HO <sub>2</sub> + DO <sub>2</sub> + M	$\rightarrow$ HDO <sub>2</sub> + O <sub>2</sub> + M		$\sqrt{\frac{33}{34}}$	$4.20 \times 10^{-33} e^{920/T_n}$	Est.
33	HOCO + OD	$\rightarrow$ CO <sub>2</sub> + HDO		$\sqrt{\frac{17}{18}}$	$1.03 \times 10^{-11}$	Est.
34	O + D	$\rightarrow$ OD		$\sqrt{\frac{1}{2}}$	$8.65 \times 10^{-18} (\frac{T_n}{300})^{-0.38}$	Est.
35	O + DO <sub>2</sub>	$\rightarrow$ OD + O <sub>2</sub>		$\sqrt{\frac{33}{34}}$	$3.00 \times 10^{-11} e^{200/T_n}$	Est.
36a	O + HDO <sub>2</sub>	$\rightarrow$ OD + HO <sub>2</sub>	0.5	$\sqrt{\frac{34}{35}}$	$1.40 \times 10^{-12} e^{-2000/T_n}$	Est.
36b		$\rightarrow$ OH + DO <sub>2</sub>	0.5	$\sqrt{\frac{34}{35}}$	$1.40 \times 10^{-12} e^{-2000/T_n}$	Est.
37	O + OD	$\rightarrow$ O <sub>2</sub> + D		$\sqrt{\frac{17}{18}}$	$1.80 \times 10^{-11} e^{180/T_n}$	Est.
38a	O( <sup>1</sup> D) + HD	$\rightarrow$ D + OH			$4.92 \times 10^{-11}$	Y88
38b		$\rightarrow$ H + OD			$4.92 \times 10^{-11}$	Y88
39	O( <sup>1</sup> D) + HDO	$\rightarrow$ OD + OH		$\sqrt{\frac{18}{19}}$	$1.63 \times 10^{-10} e^{60/T_n}$	Est.
40	OD + H	$\rightarrow$ OH + D			$4.58 \times 10^{-9} (\frac{T_n}{300})^{-0.63} e^{-717/T_n}$	Y88
41	OD + H <sub>2</sub>	$\rightarrow$ HDO + H			$2.80 \times 10^{-12} e^{-1800/T_n}$	Y88
42	OD + H <sub>2</sub> O <sub>2</sub>	$\rightarrow$ HDO + HO <sub>2</sub>		$\sqrt{\frac{17}{18}}$	$2.90 \times 10^{-12} e^{-160/T_n}$	Est.
43	OD + HO <sub>2</sub>	$\rightarrow$ HDO + O <sub>2</sub>		$\sqrt{\frac{17}{18}}$	$4.80 \times 10^{-11} e^{250/T_n}$	Est.
44	OD + O <sub>3</sub>	$\rightarrow$ DO <sub>2</sub> + O <sub>2</sub>		$\sqrt{\frac{17}{18}}$	$1.70 \times 10^{-12} e^{-940/T_n}$	Est.
45a	OD + OH	$\rightarrow$ HDO + O		$\sqrt{\frac{17}{18}}$	$1.80 \times 10^{-12}$	Est.
45b		$\rightarrow$ HDO <sub>2</sub>		$\sqrt{\frac{17}{18}}$	See text  $k_{\infty} = 2.60 \times 10^{-11}$ $k_0 = 2.69 \times 10^{-28} (\frac{T_n}{300})^{-1.0}$ $3.30 \times 10^{-9} (\frac{T_n}{300})^{-0.63}$	Est.
46	OH + D	$\rightarrow$ OD + H			$4.20 \times 10^{-13} e^{-1800/T_n}$	Y88
47	OH + DO <sub>2</sub>	$\rightarrow$ HDO + O <sub>2</sub>		$\sqrt{\frac{33}{34}}$	$4.80 \times 10^{-11} e^{250/T_n}$	Est.
48a	OH + HD	$\rightarrow$ H <sub>2</sub> O + D			$5.00 \times 10^{-12} e^{-2130/T_n}$	S11
48b		$\rightarrow$ HDO + H			$2.90 \times 10^{-12} e^{-160/T_n}$	Est.
49a	OH + HDO <sub>2</sub>	$\rightarrow$ H <sub>2</sub> O + DO <sub>2</sub>	0.5	$\sqrt{\frac{34}{35}}$	$2.90 \times 10^{-12} e^{-160/T_n}$	Est.
49b		$\rightarrow$ HDO + HO <sub>2</sub>	0.5	$\sqrt{\frac{34}{35}}$	$2.90 \times 10^{-12} e^{-160/T_n}$	Est.
Deuterated ion-neutral reactions						
50	ArD <sup>+</sup> + CO	$\rightarrow$ DCO <sup>+</sup> + Ar			$1.25 \times 10^{-9}$	A03

Continued on next page

		Reaction	BR	MS	Rate or rate coefficient	Ref
51	ArD <sup>+</sup> + CO <sub>2</sub>	$\rightarrow$ DCO <sub>2</sub> <sup>+</sup> + Ar			$1.10 \times 10^{-9}$	A03
52a	ArD <sup>+</sup> + H <sub>2</sub>	$\rightarrow$ ArH <sup>+</sup> + HD			$4.50 \times 10^{-10}$	A03
52b		$\rightarrow$ H <sub>2</sub> D <sup>+</sup> + Ar			$8.80 \times 10^{-10}$	A03
53	ArD <sup>+</sup> + N <sub>2</sub>	$\rightarrow$ N <sub>2</sub> D <sup>+</sup> + Ar			$6.00 \times 10^{-10}$	A03
54	ArH <sup>+</sup> + HD	$\rightarrow$ H <sub>2</sub> D <sup>+</sup> + Ar			$8.60 \times 10^{-10}$	A03
55a	Ar <sup>+</sup> + HD	$\rightarrow$ ArD <sup>+</sup> + H			$3.84 \times 10^{-10}$	A03
55b		$\rightarrow$ ArH <sup>+</sup> + D			$3.68 \times 10^{-10}$	A03
55c		$\rightarrow$ HD <sup>+</sup> + Ar			$4.80 \times 10^{-11}$	A03
56a	CO <sub>2</sub> <sup>+</sup> + D	$\rightarrow$ DCO <sup>+</sup> + O			$6.38 \times 10^{-11}$	A03
56b		$\rightarrow$ D <sup>+</sup> + CO <sub>2</sub>			$2.02 \times 10^{-11}$	A03
57a	CO <sub>2</sub> <sup>+</sup> + HD	$\rightarrow$ DCO <sub>2</sub> <sup>+</sup> + H	0.5	$\sqrt{\frac{2}{3}}$	$2.35 \times 10^{-10}$	Est.
57b		$\rightarrow$ HCO <sub>2</sub> <sup>+</sup> + D	0.5	$\sqrt{\frac{2}{3}}$	$2.35 \times 10^{-10}$	Est.
58a	CO <sub>2</sub> <sup>+</sup> + HDO	$\rightarrow$ DCO <sub>2</sub> <sup>+</sup> + OH	0.5	$\sqrt{\frac{18}{19}}$	$3.00 \times 10^{-10}$	Est.
58b		$\rightarrow$ HCO <sub>2</sub> <sup>+</sup> + OD	0.5	$\sqrt{\frac{18}{19}}$	$3.00 \times 10^{-10}$	Est.
58c		$\rightarrow$ HDO <sup>+</sup> + CO <sub>2</sub>		$\sqrt{\frac{18}{19}}$	$1.80 \times 10^{-9}$	Est.
59	CO <sup>+</sup> + D	$\rightarrow$ D <sup>+</sup> + CO			$9.00 \times 10^{-11}$	A03
60a	CO <sup>+</sup> + HD	$\rightarrow$ DCO <sup>+</sup> + H	0.25	$\sqrt{\frac{2}{3}}$	$7.50 \times 10^{-10}$	Est.
60b		$\rightarrow$ DOC <sup>+</sup> + H	0.25	$\sqrt{\frac{2}{3}}$	$7.50 \times 10^{-10}$	Est.
60c		$\rightarrow$ HCO <sup>+</sup> + D	0.25	$\sqrt{\frac{2}{3}}$	$7.50 \times 10^{-10}$	Est.
60d		$\rightarrow$ HOC <sup>+</sup> + D	0.25	$\sqrt{\frac{2}{3}}$	$7.50 \times 10^{-10}$	Est.
61a	CO <sup>+</sup> + HDO	$\rightarrow$ DCO <sup>+</sup> + OH	0.5	$\sqrt{\frac{18}{19}}$	$8.40 \times 10^{-10}$	Est.
61b		$\rightarrow$ HCO <sup>+</sup> + OD	0.5	$\sqrt{\frac{18}{19}}$	$8.40 \times 10^{-10}$	Est.
61c		$\rightarrow$ HDO <sup>+</sup> + CO		$\sqrt{\frac{18}{19}}$	$1.56 \times 10^{-9}$	Est.
62	C <sup>+</sup> + HD	$\rightarrow$ CH <sup>+</sup> + D	0.17		$1.20 \times 10^{-16}$	A03
63a	C <sup>+</sup> + HDO	$\rightarrow$ DCO <sup>+</sup> + H	0.5	$\sqrt{\frac{18}{19}}$	$7.80 \times 10^{-9} \left(\frac{T_i}{300}\right)^{-0.5}$	Est.
63b		$\rightarrow$ DOC <sup>+</sup> + H	0.5	$\sqrt{\frac{18}{19}}$	$1.08 \times 10^{-9}$	Est.
63c		$\rightarrow$ HCO <sup>+</sup> + D	0.5	$\sqrt{\frac{18}{19}}$	$7.80 \times 10^{-9} \left(\frac{T_i}{300}\right)^{-0.5}$	Est.
63d		$\rightarrow$ HDO <sup>+</sup> + C			$2.34 \times 10^{-10}$	Est.
63e		$\rightarrow$ HOC <sup>+</sup> + D	0.5	$\sqrt{\frac{18}{19}}$	$1.08 \times 10^{-9}$	Est.
64	DCO <sub>2</sub> <sup>+</sup> + CO	$\rightarrow$ DCO <sup>+</sup> + CO <sub>2</sub>		$\sqrt{\frac{45}{46}}$	$7.80 \times 10^{-10}$	Est.
65a	DCO <sub>2</sub> <sup>+</sup> + e <sup>-</sup>	$\rightarrow$ CO + O	0.68		$4.62 \times 10^{-5} \left(\frac{T_i}{300}\right)^{-0.64}$	G05
65b		$\rightarrow$ CO + OD	0.27		$4.62 \times 10^{-5} \left(\frac{T_i}{300}\right)^{-0.64}$	G05
65c		$\rightarrow$ CO <sub>2</sub> + D	0.05		$4.62 \times 10^{-5} \left(\frac{T_i}{300}\right)^{-0.64}$	G05
66	DCO <sub>2</sub> <sup>+</sup> + H <sub>2</sub> O	$\rightarrow$ H <sub>2</sub> DO <sup>+</sup> + CO <sub>2</sub>		$\sqrt{\frac{45}{46}}$	$2.65 \times 10^{-9}$	Est.
67	DCO <sub>2</sub> <sup>+</sup> + O	$\rightarrow$ DCO <sup>+</sup> + O <sub>2</sub>		$\sqrt{\frac{45}{46}}$	$5.80 \times 10^{-10}$	Est.
68a	DCO <sup>+</sup> + e <sup>-</sup>	$\rightarrow$ CO + D	0.92		$9.02 \times 10^{-5} \left(\frac{T_i}{300}\right)^{-1.1}$	GK
68b		$\rightarrow$ OD + C	0.07		$9.02 \times 10^{-5} \left(\frac{T_i}{300}\right)^{-1.1}$	GK
69	DCO <sup>+</sup> + H	$\rightarrow$ HCO <sup>+</sup> + D			$1.50 \times 10^{-11}$	A03
70	DCO <sup>+</sup> + H <sub>2</sub> O	$\rightarrow$ H <sub>2</sub> DO <sup>+</sup> + CO		$\sqrt{\frac{29}{30}}$	$2.60 \times 10^{-9}$	Est.
71	DOC <sup>+</sup> + CO	$\rightarrow$ DCO <sup>+</sup> + CO		$\sqrt{\frac{29}{30}}$	$6.00 \times 10^{-10}$	Est.

Continued on next page

		Reaction	BR	MS	Rate or rate coefficient	Ref
72	$\text{DOC}^+ + \text{e}^-$	$\rightarrow \text{OD} + \text{C}$		$\sqrt{\frac{29}{30}}$	$1.19 \times 10^{-8} \left(\frac{T_i}{300}\right)^{1.2}$	Est.
73a	$\text{DOC}^+ + \text{H}_2$	$\rightarrow \text{H}_2\text{D}^+ + \text{CO}$	0.57		$6.20 \times 10^{-10}$	A03
73b		$\rightarrow \text{HCO}^+ + \text{HD}$	0.43		$6.20 \times 10^{-10}$	A03
74a	$\text{D}^+ + \text{CO}_2$	$\rightarrow \text{CO}_2^+ + \text{D}$			$3.50 \times 10^{-9}$	A03
74b		$\rightarrow \text{DCO}^+ + \text{O}$			$2.60 \times 10^{-9}$	A03
75	$\text{D}^+ + \text{H}$	$\rightarrow \text{D} + \text{H}^+$	0.87		$6.50 \times 10^{-11} \left(\frac{T_i}{300}\right)^{0.5}$	Y89
76	$\text{D}^+ + \text{H}_2$	$\rightarrow \text{H}^+ + \text{HD}$			$2.20 \times 10^{-9}$	A03
77a	$\text{D}^+ + \text{H}_2\text{O}$	$\rightarrow \text{H}_2\text{O}^+ + \text{D}$			$5.20 \times 10^{-9}$	A03
77b		$\rightarrow \text{HDO}^+ + \text{H}$	0.5	$\sqrt{\frac{1}{2}}$	$8.20 \times 10^{-9}$	Est.
78	$\text{D}^+ + \text{NO}$	$\rightarrow \text{NO}^+ + \text{D}$			$1.80 \times 10^{-9}$	A03
79	$\text{D}^+ + \text{O}$	$\rightarrow \text{D} + \text{O}^+$			$2.80 \times 10^{-10}$	A03
80	$\text{D}^+ + \text{O}_2$	$\rightarrow \text{O}_2^+ + \text{D}$			$1.60 \times 10^{-9}$	A03
81a	$\text{H}_2\text{DO}^+ + \text{e}^-$	$\rightarrow \text{H}_2 + \text{O}$	0.5	$\sqrt{\frac{19}{20}}$	$9.68 \times 10^{-8} \left(\frac{T_i}{300}\right)^{-0.5}$	Est.
81b		$\rightarrow \text{H}_2\text{O} + \text{D}$	0.5	$\sqrt{\frac{19}{20}}$	$1.86 \times 10^{-6} \left(\frac{T_i}{300}\right)^{-0.5}$	Est.
81c		$\rightarrow \text{HD} + \text{O}$	0.5	$\sqrt{\frac{19}{20}}$	$9.68 \times 10^{-8} \left(\frac{T_i}{300}\right)^{-0.5}$	Est.
81d		$\rightarrow \text{HDO} + \text{H}$	0.5	$\sqrt{\frac{19}{20}}$	$1.86 \times 10^{-6} \left(\frac{T_i}{300}\right)^{-0.5}$	Est.
81e		$\rightarrow \text{OD} + \text{H}$	0.5	$\sqrt{\frac{19}{20}}$	$4.47 \times 10^{-6} \left(\frac{T_i}{300}\right)^{-0.5}$	Est.
81f		$\rightarrow \text{OD} + \text{H}_2$	0.5	$\sqrt{\frac{19}{20}}$	$1.04 \times 10^{-6} \left(\frac{T_i}{300}\right)^{-0.5}$	Est.
81g		$\rightarrow \text{OH} + \text{D}$	0.5	$\sqrt{\frac{19}{20}}$	$4.47 \times 10^{-6} \left(\frac{T_i}{300}\right)^{-0.5}$	Est.
81h		$\rightarrow \text{OH} + \text{HD}$	0.5	$\sqrt{\frac{19}{20}}$	$1.04 \times 10^{-6} \left(\frac{T_i}{300}\right)^{-0.5}$	Est.
82a	$\text{H}_2\text{D}^+ + \text{CO}$	$\rightarrow \text{DCO}^+ + \text{H}_2$	0.33		$1.60 \times 10^{-9}$	A03
82b		$\rightarrow \text{HCO}^+ + \text{HD}$	0.67		$1.60 \times 10^{-9}$	A03
83	$\text{H}_2\text{D}^+ + \text{H}_2$	$\rightarrow \text{H}_3^+ + \text{HD}$			$5.30 \times 10^{-10}$	A03
84a	$\text{H}_2\text{O}^+ + \text{HD}$	$\rightarrow \text{H}_2\text{DO}^+ + \text{H}$	0.5	$\sqrt{\frac{2}{3}}$	$3.80 \times 10^{-10}$	Est.
84b		$\rightarrow \text{H}_3\text{O}^+ + \text{D}$	0.5	$\sqrt{\frac{2}{3}}$	$3.80 \times 10^{-10}$	Est.
85	$\text{HCO}_2^+ + \text{HDO}$	$\rightarrow \text{H}_2\text{DO}^+ + \text{CO}_2$		$\sqrt{\frac{18}{19}}$	$2.65 \times 10^{-9}$	Est.
86	$\text{HCO}^+ + \text{D}$	$\rightarrow \text{DCO}^+ + \text{H}$			$4.25 \times 10^{-11}$	A03
87	$\text{HCO}^+ + \text{HDO}$	$\rightarrow \text{H}_2\text{DO}^+ + \text{CO}$		$\sqrt{\frac{18}{19}}$	$2.60 \times 10^{-9}$	Est.
88a	$\text{HDO}^+ + \text{CO}$	$\rightarrow \text{DCO}^+ + \text{OH}$	0.5	$\sqrt{\frac{18}{19}}$	$2.12 \times 10^{-10}$	Est.
88b		$\rightarrow \text{HCO}^+ + \text{OD}$	0.5	$\sqrt{\frac{18}{19}}$	$2.12 \times 10^{-10}$	Est.
89a	$\text{HDO}^+ + \text{e}^-$	$\rightarrow \text{HD} + \text{O}$		$\sqrt{\frac{18}{19}}$	$2.64 \times 10^{-6} \left(\frac{T_i}{300}\right)^{-0.74}$	Est.
89b		$\rightarrow \text{O} + \text{D}$		$\sqrt{\frac{18}{19}}$	$2.08 \times 10^{-5} \left(\frac{T_i}{300}\right)^{-0.74}$	Est.
89c		$\rightarrow \text{OD} + \text{H}$	0.5	$\sqrt{\frac{18}{19}}$	$5.86 \times 10^{-6} \left(\frac{T_i}{300}\right)^{-0.74}$	Est.
89d		$\rightarrow \text{OH} + \text{D}$	0.5	$\sqrt{\frac{18}{19}}$	$5.86 \times 10^{-6} \left(\frac{T_i}{300}\right)^{-0.74}$	Est.
90a	$\text{HDO}^+ + \text{H}_2$	$\rightarrow \text{H}_2\text{DO}^+ + \text{H}$	0.5	$\sqrt{\frac{18}{19}}$	$3.80 \times 10^{-10}$	Est.
90b		$\rightarrow \text{H}_3\text{O}^+ + \text{D}$	0.5	$\sqrt{\frac{18}{19}}$	$3.80 \times 10^{-10}$	Est.
91a	$\text{HDO}^+ + \text{N}$	$\rightarrow \text{HNO}^+ + \text{D}$	0.5	$\sqrt{\frac{18}{19}}$	$5.60 \times 10^{-11}$	Est.
91b		$\rightarrow \text{NO}^+ + \text{HD}$		$\sqrt{\frac{18}{19}}$	$2.80 \times 10^{-11}$	Est.
92	$\text{HDO}^+ + \text{NO}$	$\rightarrow \text{NO}^+ + \text{HDO}$		$\sqrt{\frac{18}{19}}$	$4.60 \times 10^{-10}$	Est.

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		Reaction	BR	MS	Rate or rate coefficient	Ref
93	HDO <sup>+</sup> + O	$\rightarrow \text{O}_2^+ + \text{HD}$		$\sqrt{\frac{18}{19}}$	$4.00 \times 10^{-11}$	Est.
94	HDO <sup>+</sup> + O <sub>2</sub>	$\rightarrow \text{O}_2^+ + \text{HDO}$		$\sqrt{\frac{18}{19}}$	$3.30 \times 10^{-10}$	Est.
95a	HD <sup>+</sup> + Ar	$\rightarrow \text{ArD}^+ + \text{H}$	0.45	$\sqrt{\frac{2}{3}}$	$2.10 \times 10^{-9}$	A03
95b		$\rightarrow \text{ArH}^+ + \text{D}$	0.55	$\sqrt{\frac{2}{3}}$	$2.10 \times 10^{-9}$	Est.
96a	HD <sup>+</sup> + CO	$\rightarrow \text{DCO}^+ + \text{H}$	0.5	$\sqrt{\frac{2}{3}}$	$1.45 \times 10^{-9}$	Est.
96b		$\rightarrow \text{HCO}^+ + \text{D}$	0.5	$\sqrt{\frac{2}{3}}$	$1.45 \times 10^{-9}$	Est.
97a	HD <sup>+</sup> + CO <sub>2</sub>	$\rightarrow \text{DCO}_2^+ + \text{H}$	0.5	$\sqrt{\frac{2}{3}}$	$1.17 \times 10^{-9}$	Est.
97b		$\rightarrow \text{HCO}_2^+ + \text{D}$	0.5	$\sqrt{\frac{2}{3}}$	$1.17 \times 10^{-9}$	Est.
98	HD <sup>+</sup> + e <sup>-</sup>	$\rightarrow \text{H} + \text{D}$			$1.93 \times 10^{-6} \left(\frac{T_i}{300}\right)^{-0.853} e^{-43.3/T_i}$	K19
99	HD <sup>+</sup> + HD	$\rightarrow \text{H}_2\text{D}^+ + \text{D}$			$8.42 \times 10^{-10}$	A03
100a	HD <sup>+</sup> + N <sub>2</sub>	$\rightarrow \text{N}_2\text{D}^+ + \text{H}$	0.5	$\sqrt{\frac{2}{3}}$	$1.00 \times 10^{-9}$	Est.
100b		$\rightarrow \text{N}_2\text{H}^+ + \text{D}$	0.5	$\sqrt{\frac{2}{3}}$	$1.00 \times 10^{-9}$	Est.
101a	HD <sup>+</sup> + O	$\rightarrow \text{OD}^+ + \text{H}$	0.5	$\sqrt{\frac{2}{3}}$	$7.50 \times 10^{-10}$	Est.
101b		$\rightarrow \text{OH}^+ + \text{D}$	0.5	$\sqrt{\frac{2}{3}}$	$7.50 \times 10^{-10}$	Est.
102	HD <sup>+</sup> + O <sub>2</sub>	$\rightarrow \text{HO}_2^+ + \text{D}$	0.5	$\sqrt{\frac{2}{3}}$	$9.60 \times 10^{-10}$	Est.
103	H <sup>+</sup> + HD	$\rightarrow \text{D}^+ + \text{H}_2$			$1.10 \times 10^{-10}$	A03
104a	H <sup>+</sup> + HDO	$\rightarrow \text{H}_2\text{O}^+ + \text{D}$	0.5	$\sqrt{\frac{18}{19}}$	$8.20 \times 10^{-9}$	Est.
104b		$\rightarrow \text{HDO}^+ + \text{H}$	0.5	$\sqrt{\frac{18}{19}}$	$8.20 \times 10^{-9}$	Est.
105	N <sub>2</sub> D <sup>+</sup> + CO	$\rightarrow \text{DCO}^+ + \text{N}_2$		$\sqrt{\frac{29}{30}}$	$8.80 \times 10^{-10}$	Est.
106	N <sub>2</sub> D <sup>+</sup> + e <sup>-</sup>	$\rightarrow \text{N}_2 + \text{D}$		$\sqrt{\frac{29}{30}}$	$6.60 \times 10^{-7} \left(\frac{T_i}{300}\right)^{-0.51}$	Est.
107	N <sub>2</sub> D <sup>+</sup> + H	$\rightarrow \text{N}_2\text{H}^+ + \text{D}$			$2.50 \times 10^{-11}$	A03
108	N <sub>2</sub> D <sup>+</sup> + O	$\rightarrow \text{OD}^+ + \text{N}_2$		$\sqrt{\frac{29}{30}}$	$1.40 \times 10^{-10}$	Est.
109	N <sub>2</sub> H <sup>+</sup> + D	$\rightarrow \text{N}_2\text{D}^+ + \text{H}$			$8.00 \times 10^{-11}$	A03
110	N <sub>2</sub> <sup>+</sup> + D	$\rightarrow \text{D}^+ + \text{N}_2$			$1.20 \times 10^{-10}$	A03
111a	N <sub>2</sub> <sup>+</sup> + HD	$\rightarrow \text{N}_2\text{D}^+ + \text{H}$	0.51		$1.34 \times 10^{-9}$	A03
111b		$\rightarrow \text{N}_2\text{H}^+ + \text{D}$	0.49		$1.34 \times 10^{-9}$	A03
112a	N <sub>2</sub> <sup>+</sup> + HDO	$\rightarrow \text{HDO}^+ + \text{N}_2$		$\sqrt{\frac{18}{19}}$	$1.90 \times 10^{-9}$	Est.
112b		$\rightarrow \text{N}_2\text{D}^+ + \text{OH}$	0.5	$\sqrt{\frac{18}{19}}$	$5.04 \times 10^{-10}$	Est.
112c		$\rightarrow \text{N}_2\text{H}^+ + \text{OD}$	0.5	$\sqrt{\frac{18}{19}}$	$5.04 \times 10^{-10}$	Est.
113	N <sup>+</sup> + HD	$\rightarrow \text{NH}^+ + \text{D}$	0.25		$3.10 \times 10^{-10}$	A03
114	OD <sup>+</sup> + CO	$\rightarrow \text{DCO}^+ + \text{O}$		$\sqrt{\frac{17}{18}}$	$8.40 \times 10^{-10}$	Est.
115	OD <sup>+</sup> + CO <sub>2</sub>	$\rightarrow \text{DCO}_2^+ + \text{O}$		$\sqrt{\frac{17}{18}}$	$1.35 \times 10^{-9}$	Est.
116	OD <sup>+</sup> + e <sup>-</sup>	$\rightarrow \text{O} + \text{D}$		$\sqrt{\frac{17}{18}}$	$6.50 \times 10^{-7} \left(\frac{T_i}{300}\right)^{-0.5}$	Est.
117a	OD <sup>+</sup> + H <sub>2</sub>	$\rightarrow \text{H}_2\text{O}^+ + \text{D}$	0.5	$\sqrt{\frac{17}{18}}$	$9.70 \times 10^{-10}$	Est.
117b		$\rightarrow \text{HDO}^+ + \text{H}$	0.5	$\sqrt{\frac{17}{18}}$	$9.70 \times 10^{-10}$	Est.
118	OD <sup>+</sup> + N	$\rightarrow \text{NO}^+ + \text{D}$		$\sqrt{\frac{17}{18}}$	$8.90 \times 10^{-10}$	Est.
119	OD <sup>+</sup> + N <sub>2</sub>	$\rightarrow \text{N}_2\text{D}^+ + \text{O}$		$\sqrt{\frac{17}{18}}$	$2.40 \times 10^{-10}$	Est.
120	OD <sup>+</sup> + O	$\rightarrow \text{O}_2^+ + \text{D}$		$\sqrt{\frac{17}{18}}$	$7.10 \times 10^{-10}$	Est.
121	OD <sup>+</sup> + O <sub>2</sub>	$\rightarrow \text{O}_2^+ + \text{OD}$		$\sqrt{\frac{17}{18}}$	$3.80 \times 10^{-10}$	Est.

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	Reaction	BR	MS	Rate or rate coefficient	Ref
122a	$\text{OH}^+ + \text{HD} \rightarrow \text{H}_2\text{O}^+ + \text{D}$		$\sqrt{\frac{2}{3}}$	$9.70 \times 10^{-10}$	Est.
122b	$\rightarrow \text{HDO}^+ + \text{H}$		$\sqrt{\frac{2}{3}}$	$9.70 \times 10^{-10}$	Est.
123	$\text{O}^+ + \text{D} \rightarrow \text{D}^+ + \text{O}$		$\sqrt{\frac{1}{2}}$	$6.40 \times 10^{-10}$	Est.
124a	$\text{O}^+ + \text{HD} \rightarrow \text{OD}^+ + \text{H}$	0.46		$1.25 \times 10^{-9}$	A03
124b	$\rightarrow \text{OH}^+ + \text{D}$	0.54		$1.25 \times 10^{-9}$	A03
125	$\text{O}^+ + \text{HDO} \rightarrow \text{HDO}^+ + \text{O}$		$\sqrt{\frac{18}{19}}$	$2.60 \times 10^{-9}$	Est.

NL84: Nee and Lee (1984). Y88: Anicich (2003). Y89: Yung et al. (1989). A03: Anicich (2003).  
C0499: Cheng et al. (2004); Cheng et al. (1999). G05: Geppert et al. (2005). K09: Korolov et al. (2009).  
GK: Rate from K09, branching ratio from G05. C10: Cazaux et al. (2010). S11: Sander et al. (2011).  
N: Manion et al. (2015). K19: Wakelam and Gratier (2019). Est: Estimated with mass scaling.  
†: Assumed same as H-analogue.

**Photodissociation and photoionization:** Photodissociation and ionization of deuterated species is calculated using the solar spectrum (see Section 2.2.2), so the entry in the table under ‘Rate or rate coefficient’ represents the integrated column rate. The ‘Ref’ column refers to the source of the cross sections used. For photoionization cross sections of the H-analogue reactions, see Vuitton et al. (2019, and references therein).

**Neutral and ion bimolecular and termolecular reactions:** The rate coefficient used for a given reaction is the product of the ‘BR’, ‘MS’ and ‘Rate coefficient’ columns (empty fields are taken to be 1). ‘BR’, or branching ratio, accounts for the fact that deuteration of a reaction can create two or more branches with differing products where only one branch would exist for the H-analogue reaction. ‘MS’, or mass scaling, is a scaling factor equal to the square root of the mass ratio,  $\sqrt{m_1/m_2}$ , where  $m_2$  is the mass of the deuterated species and  $m_1$  the H-bearing species. This factor is applied to reactions for which we were not able to find a measurement in the literature to account for replacement of one reactant H atom with one D atom; a similar approach was used previously by V. A. Krasnopolsky (2002) for reactions of neutral HD with dominant ions and minor H-bearing ions.

Most reactions in these tables proceed using the listed rate coefficients. A few exceptions apply; the categorization Types and formulae mentioned below are the same as used by Vuitton et al. (2019). A more complete description of the formulae used can be found in their Appendix B.

*Reaction 7:* Similar to its analogue  $\text{CO} + \text{H} \rightarrow \text{HCO}$ , this is a Type 4 (pressure dependent association) reaction. The Troe parameter for this reaction is 0, so we use the form:

$$k = k_R + \frac{(Mk_0k_\infty)}{Mk_0 + k_\infty} \quad (1)$$

Where  $k_R$  is 0 in this case and M is the background atmospheric density.

*Reactions 8a, 8b, 12, and 45b:* These are Type 6 ( $\text{CO} + \text{OD} \rightarrow \text{CO}_2 + \text{D}$ ) and Type 5 ( $\text{CO} + \text{OH} \rightarrow \text{DOC}_2$ ,  $\text{D} + \text{O}_2 \rightarrow \text{DO}_2$ ,  $\text{OD} + \text{OH} \rightarrow \text{HDO}_2$ ) pressure dependent bimolecular reactions, with the formulae originally given by Burkholder et al. (2019); Sander et al. (2011). We use the same forms here, but multiplied by our mass scaling factor.

167 Ion reactions which produce a lone D or H atom have the potential to cause the produced  
 168 atom to be “hot”, that is, gaining enough excess energy from the reaction that they can  
 169 escape. We describe this in more detail in Section 2.1.4.

### 170 **2.1.2 Ambipolar diffusion**

171 The model employs ambipolar diffusion for all ions, using the Langevin-Gioumousis-Stevenson  
 172 equation (Bauer, 1973):

$$D_{ai} = \frac{k(T_i + T_e)}{m_i \sum \nu_{ij}} \quad (2)$$

$$\nu_{ij} = 2\pi \left( \frac{\alpha_j e^2}{\mu_{ij}} \right)^{1/2} n_j \quad (3)$$

173 Where  $D_{ai}$  is the ambipolar diffusion coefficient for ion  $i$ ,  $\nu_{ij}$  is the collision frequency  
 174 of ion  $i$  with neutral  $j$ ,  $\alpha_j$  is the polarizability,  $e$  is the fundamental charge, and  $n$  is the  
 175 neutral density. Polarizability values for neutrals are collected from Manion et al. (2015).  
 176 Where polarizability was not available either in data or models for a deuterated species  
 177 we include, we assumed the same value as the H-bearing analogue.

### 178 **2.1.3 Partially fixed water profile**

179 We assume a constant abundance of water in the lower atmosphere, which approximates  
 180 the average water available due to seasonal cycles of polar cap sublimation and trans-  
 181 port. The mixing ratio is  $1.3 \times 10^{-4}$  up to the hygropause (which we take to be 40 km,  
 182 between 25 km by V. A. Krasnopolsky (2002) and its enhanced altitude of 50-80 km dur-  
 183 ing dust storms (Heavens et al., 2018)). The hygropause on Mars represents the altitude  
 184 at which water begins to condense; in our model, which does not include microphysics  
 185 or phase changes, the hygropause altitude is the point at which the water mixing ratio  
 186 begins to follows the saturation vapor pressure curve. At 72 km, a minimum of satura-  
 187 tion is reached; above that level, the abundance of water is a free variable. This allows  
 188 a more holistic understanding of water and water ion chemistry in the upper atmosphere,  
 189 which has been shown to be an important tracer of seasonal H escape (Stone et al., 2020).  
 190 The total amount of water in the atmosphere is 10.5 pr  $\mu\text{m}$ , in accordance with obser-  
 191 vations (Smith, 2004; Lammer et al., 2003).

### 192 **2.1.4 Non-thermal escape**

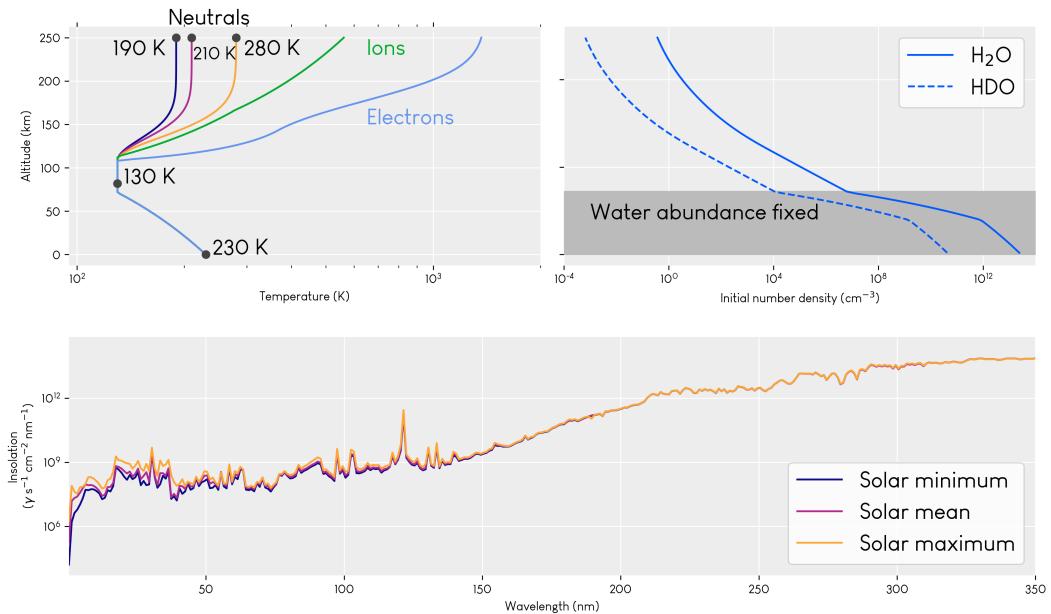
193 Although there are many non-thermal escape mechanisms, in this work, we focus on pho-  
 194 tochemical loss, i.e. the contribution to escape from chemistry and photochemistry. We  
 195 neglect processes involving the solar wind such as sputtering, ion pickup, and charge ex-  
 196 change with the solar wind. Processes which depend upon the solar wind will primar-  
 197 ily occur above the bow shock (which is far above our top boundary), where the solar  
 198 wind can interact with the corona before being mostly deflected around the planet (Halekas  
 199 et al., 2017). By focusing on planetary ionospheric reactions, we capture the non-thermal  
 200 escape of H and D sourced from the atmosphere below the exobase.

201 We calculate the non-thermal escape of hot atoms created via ion-neutral chemistry as  
 202 the product of the probability of escape and the volume production rate of hot atoms  
 203 using the procedure described by Gregory et al. (2022). We have evaluated all ion-neutral  
 204 reactions that produce H, D,  $\text{H}_2$ , or HD in the model for their exothermicity (following  
 205 Fox (2015)) and only use those where the excess energy exceeds the escape velocity en-  
 206 ergy. In reality, the excess heat produced can be split between the two products accord-  
 207 ing to conservation of energy. Information about these heat branching ratios is sparse,  
 208 even for H species; for this reason, we assume that all excess energy produced ends up  
 209 in the atomic H or D (see the Supporting Information). We use the escape probability  
 210 curve calculated by Gregory et al. (2022) for a particle of excess energy 5 eV; this is a  
 211 reasonable approximation of the actual mean excess energy in our model, with is 3.6 eV.

The resulting volume escape rate can be integrated to obtain an escape flux for the top boundary of the model. Although our focus is escape of atomic H and D, some loss does occur via loss of the molecular form, so we also include non-thermal escape of  $\text{H}_2$  and HD. In these cases, we assume that  $\sigma_{\text{H}_2}$  is the same as for D due to the similar masses, and that  $\sigma_{\text{HD}}$  is larger than  $\text{H}_2$  by the same amount that D is larger than H.

## 2.2 Model inputs

Because the importance of non-thermal escape is expected to vary with solar activity, we have constructed three sets of inputs representing solar minimum, mean, and maximum conditions. The only properties which we vary between these cases are the neutral exobase temperatures and the incoming solar flux. Figure 1 shows these inputs in the navy, purple, and yellow colors. The inputs represent a dayside mean atmosphere (solar zenith angle [SZA]= $60^\circ$ ).



**Figure 1.** Main model inputs. a) Temperature profiles, with separate neutral exobase temperatures for each solar condition. Ion and electron temperatures are fits to data from MAVEN/STATIC as reported by Hanley et al. (2022) and MAVEN/LPW as reported by Ergun et al. (2015). b) Initial water profile. Above 72 km, water densities evolve according to the chemistry and transport. c) Insolation profiles from 0–300 nm for solar minimum, mean, and maximum. The full input spectrum goes out to 2400 nm, but the insolation there is relatively flat, with no variation due to solar cycle.

### 2.2.1 Atmospheric temperature profiles

Standard neutral temperatures were obtained from the Mars Climate Database (Millour & Forget, 2018) by several layers of averaging, in order of first to last: by longitude, local time (9, 12, and 3 pm local times, night excluded), latitude (weighted by encompassed surface area), and  $L_s$ . Over the solar cycle, the only significant change is to the exobase temperature, so we hold the surface and mesospheric temperature constant at 230 K and 130 K respectively.

In order to support modeling of ion chemistry, we use a piecewise fit to the new ion temperature profiles obtained at SZA= $60^\circ$  with the STATIC instrument by Hanley et al. (2022). These new data have overturned long-standing assumptions that the neutrals, ions, and

234 electrons thermalize to the same temperature around 125 km (Schunk & Nagy, 2009),  
 235 and thus represent a significant update in Mars photochemistry. We also include a fit  
 236 to the electron profile from MAVEN/LPW (Ergun et al., 2015). Because it is difficult  
 237 to associate ion temperatures with contemporary neutral temperatures due to the av-  
 238 eraging required for the neutral profiles, and because the data are limited in time, we  
 239 do not change the ion or electron profiles for the different solar cycle scenarios, although  
 240 in the real atmosphere, enhanced solar activity would likely lead to enhanced ion and  
 241 electron temperatures.

### 242 **2.2.2 Insolation**

243 Incoming solar photons are key reactants in photochemical reactions. For each solar case,  
 244 we include photon fluxes from 0.5–2400 nm, binned in 1 nm increments. Total flux, once  
 245 obtained, is scaled to Mars’ orbit and SZA=60°.

246 We determined the dates of recent representative solar conditions by looking for peri-  
 247 ods when Ly  $\alpha$  irradiance in the Lyman-alpha Model Solar Spectral Irradiance data set  
 248 (Woods et al., 2019) reached a peak, average, or trough. Because solar maximum and  
 249 mean in recent decades have been historically quiet, we chose dates from the early 2000s  
 250 to get a more representative photon flux for maximum and mean (solar minimum has  
 251 not changed much). The dates we used were February 25, 2019 for solar minimum; Febru-  
 252 ary 7, 2004 for mean; and March 22, 2002 for maximum.

253 For the insolation flux data, we use SORCE/SOLSTICE at solar minimum and mean,  
 254 and a mix of SORCE/SOLSTICE and TIMED/SEE at solar maximum. There is an ad-  
 255 dditional complication for solar maximum: SORCE/SOLSTICE began a year after our  
 256 solar maximum date, but includes the longer wavelengths we need, while TIMED/SEE  
 257 began before our solar maximum date, but only includes fluxes at wavelengths shortwards  
 258 of 190 nm. We patched together these two datasets, using SORCE/SOLSTICE for wave-  
 259 lengths 190–2000 nm from June 4, 2015 and TIMED/SEE for wavelengths 0.5–189.5 nm  
 260 from March 22, 2002.

261 Figure 1a shows the fluxes only from 0.5 to 300 nm for simplicity; longwards of 300 nm,  
 262 the profile does not vary over the solar cycle. The region shortward of 300 nm is also more  
 263 important for photochemistry as the photodissociation and photoionization cross sec-  
 264 tions are largest there. We use the same cross sections as Cangi et al. (2020), with the  
 265 addition of new photoionization and a few neutral photodissociation cross sections, the  
 266 same used by Vuitton et al. (2019).

### 267 **2.3 Boundary conditions**

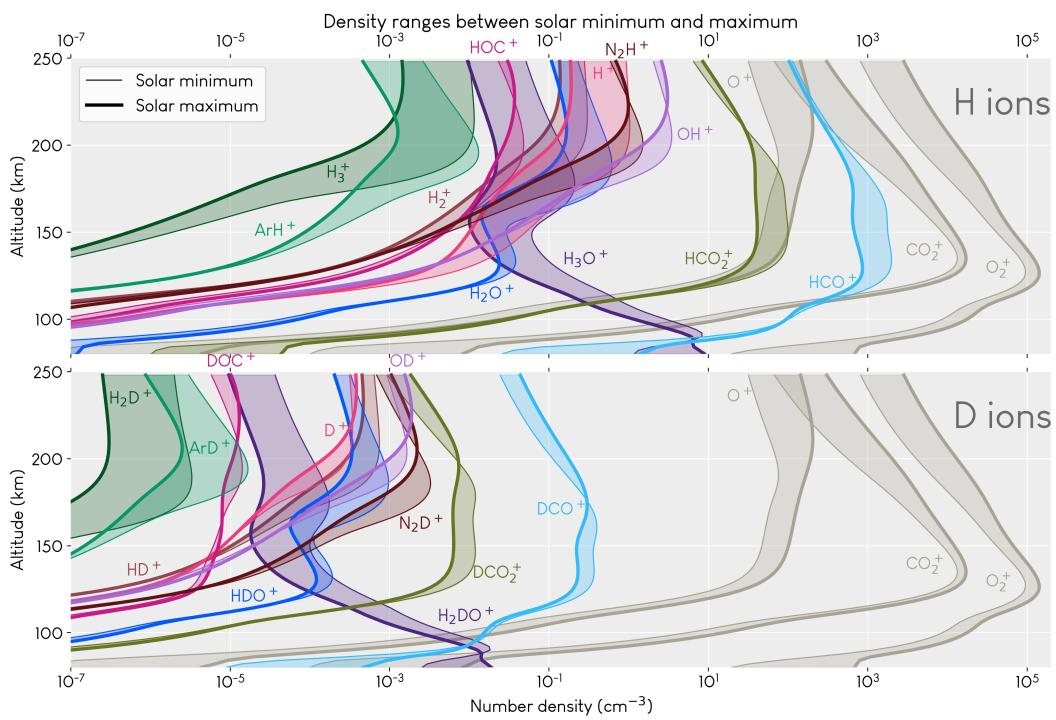
268 We use mostly the same boundary conditions as Cangi et al. (2020). The key addition  
 269 is an additional non-thermal flux boundary condition at the top of the model for H, D,  
 270 H<sub>2</sub>, and HD, according to the functional form described by (Gregory et al., 2022). Flux  
 271 is zero at the top and bottom of the model for all ion species and any neutral species with-  
 272 out a different boundary condition.

273 It is worth emphasizing that our flux boundary condition at the top of the model for atomic  
 274 O is fixed at  $1.2 \times 10^8 \text{ cm}^{-2}\text{s}^{-1}$ . Over long simulation times where the atmosphere reaches  
 275 equilibrium, the sum  $\phi_H + \phi_D$  will naturally evolve to equal twice the O escape flux, since  
 276 H<sub>2</sub>O and HDO are the primary source of H and D in the model. This is a feature of the  
 277 atmosphere in long-term equilibrium, but it does not necessarily occur over shorter timescales—  
 278 either on the real Mars or in the model.

## 279 **3 Results**

### 280 **3.1 What are the atmospheric densities of deuterated ions?**

281 The general distribution of the deuterated ionospheric species is similar to that of their  
 282 H-analogues. Vertical profiles for select species containing H or D are shown in Figure  
 283 2. Although they are calculated from surface to 250 km, the figure’s lower boundary is



**Figure 2.** Densities of a) H-bearing ions and b) D-bearing (deuterated). Density ranges are bounded by their values at solar minimum (thin line) and solar maximum (thick line). Gray lines show the primary ionospheric species for comparison. For most species and at most altitudes, densities at solar mean fall within these ranges.

placed at 80 km for legibility. The full image from surface to 250 km showing all species in the model appears in the Supporting Information (Figure S1).

Primary peaks in the densities of deuterated ions occur between 150 and 200 km, with a minor peak near the top of the mesosphere, around 90–125 km. This structure does not hold for all species.  $\text{H}_3\text{O}^+$  has its peak much lower down at about 90 km, which is in agreement with previous modeling (Fox et al., 2015; Molina-Cuberos et al., 2002). Unfortunately, comparisons with data are not feasible at this altitude because such data do not exist. Most ionic species, H- and D-bearing alike, also display a slight dip in density around 150 km, which is caused by a feature of the same shape in the electron temperature profile (see Figure 1a).

At solar maximum, greater insolation at short wavelengths enables more photoionization, increasing the abundances of primary species  $\text{CO}_2^+$ ,  $\text{O}_2^+$ , and  $\text{O}^+$  which are produced directly from the parent neutrals. But for the lighter (and often more minor) ions containing H and D, chemistry and/or transport is a more important driver than photoionization. Temperature-driven changes in the parent neutral densities propagate through to their ions; for example,  $\text{H}^+$  abundance at the top of the atmosphere decreases as the temperature goes up because H escape is diffusion-limited, whereas the same is not true for D abundance (Cangi et al., 2020; Zahnle et al., 2008). For other minor species that are not diffusion-limited, higher temperatures can also stimulate faster chemical reactions, slightly enhancing production and therefore density at higher temperatures.

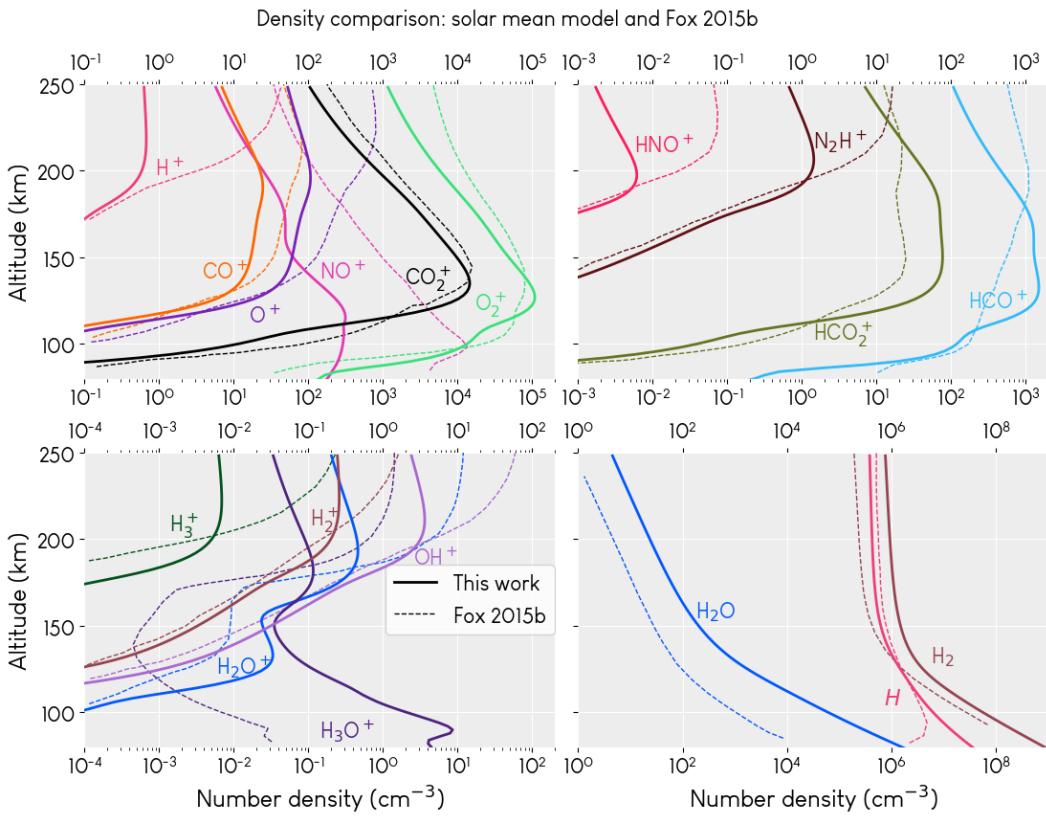
### 3.1.1 Comparisons with previous works

Here, we compare our results to modeling results by Fox et al. (2015, 2021) and measurements by MAVEN NGIMS (Benna et al., 2015; Fox et al., 2021). In this work, we have parameterized our atmosphere in order to obtain an understanding of the mean-field behavior in time and space. We have not attempted to match the same the modeling input or the relevant atmospheric conditions of those studies. Our models differ substantially from those by Fox et al. (2021, 2015) in temperature structure, boundary conditions (especially for ions at the upper boundary), vertical extent, use of photochemical equilibrium, background atmosphere, SZA, included species, mean Mars-Sun distance, assumed eddy diffusion profile, and included processes (we do not model electron impact ionization or dissociation). Because of these differences, we provide these comparisons primarily for the reader's orientation.

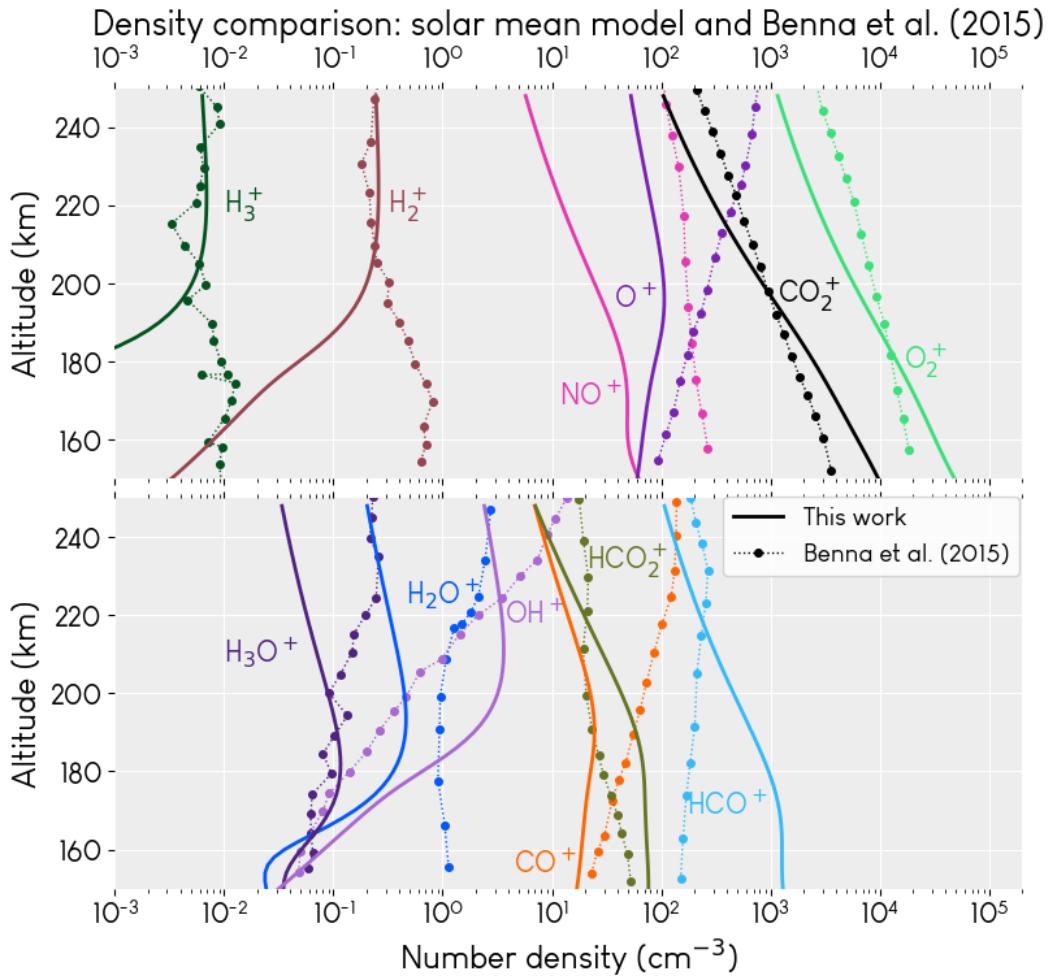
**Fox et al. (2015).** For the major ions such as  $\text{O}^+$ ,  $\text{CO}_2^+$ , and  $\text{O}_2^+$ , our density profiles are generally consistent with those modeled by Fox et al. (2015), as shown in Figure 3. They are also broadly similar for many of the minor ions, although in general, our profiles tend to show lower densities near 250 km by 1–2 orders of magnitude. There is a significant difference between our  $\text{H}_2\text{O}^+$ ,  $\text{H}_3\text{O}^+$ , and  $\text{NO}^+$  profiles; of these,  $\text{NO}^+$  has the largest density overall. It should be noted that many of the ions for which we show a significantly different profile are quite minor, with populations never exceeding  $100 \text{ cm}^{-3}$ , so the absolute differences as a percent of the total atmosphere are tiny, well within the absolute tolerance. Fox et al. (2015) make the point that their model calculates neutral  $\text{H}_2\text{O}$  produced only by ion-neutral reactions due to their choice of boundary conditions, whereas ours includes production by photodissociation; it is then perhaps not surprising that our results include more water than theirs (see Figure 3d).

In Figure S3, we also compare our results to Fox et al. (2021), which uses a similar model to Fox et al. (2015) and includes recent data from NGIMS for  $\text{CO}_2^+$ ,  $\text{O}_2^+$  and  $\text{O}^+$ . Compared to that paper, our results are more dissimilar.

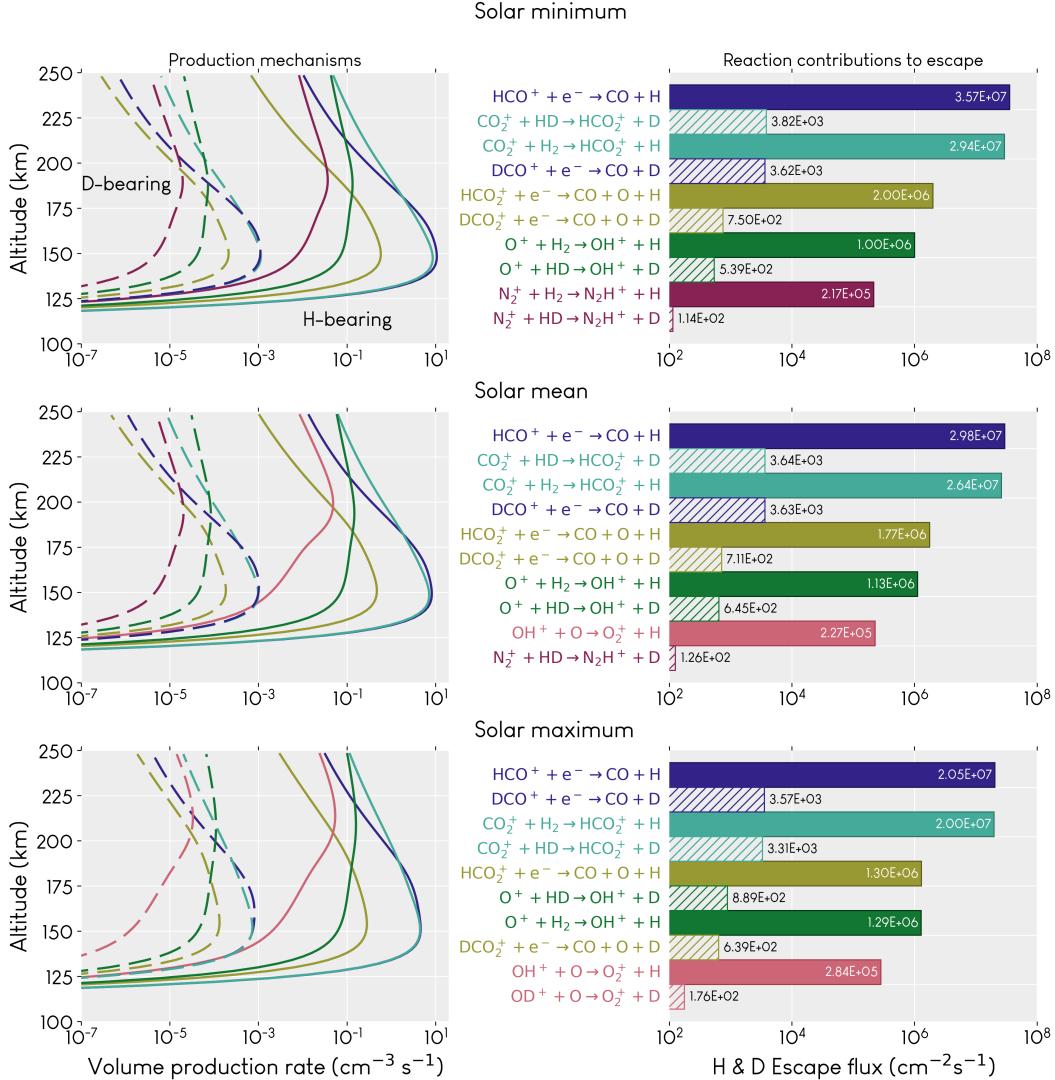
**Benna et al. (2015), using MAVEN NGIMS.** Our results show reasonably good agreement with the initial NGIMS measurements at Mars (Benna et al., 2015) (Figure 4), which occurred long enough into the mission that solar mean conditions would have prevailed. There continues to be a divergence between model and data for  $\text{O}^+$  in the up-



**Figure 3.** Ion and neutral densities computed by our model and compared with those computed by Fox et al. (2015). Species are divided amongst the four panels for legibility and compared with Figure 3 in Fox et al. (2015). Some minor species are omitted for clarity.



**Figure 4.** Ion and neutral densities computed by our model and compared with those computed by Benna et al. (2015). Species are divided amongst the two panels for legibility.  $\text{HNO}^+$  differs significantly from data and has been omitted; the measurements are known to be unreliable due to spacecraft potential.



**Figure 5.** Volume production rates of escaping atoms (panels a, c, e) and integrated escape flux of the produced atomic H or D (b, d, f) for the dominant five chemical pathways producing hot H (solid lines/solid bars) and hot D (dotted lines/dot-fill bars).

per atmosphere and an underprediction of  $\text{NO}^+$ , but considering we are using a 1D model that does not account for local and short-term variations and we have not made any model changes to match data, we find the output acceptable.

### 3.2 Are the dominant production mechanisms of hot H and D analogous or dissimilar?

Figure 5 shows the production mechanisms for hot H and D, which are mostly similar.

The most important reaction driving the production of hot D (H) below 200 km in solar mean and maximum is  $\text{DCO}^+(\text{HCO}^+)$  dissociative recombination (DR), with  $\text{CO}_2^+ + \text{HD}$  ( $\text{H}_2$ ) a close second.  $\text{HCO}^+$  DR dominates for hot H under all solar conditions, but for hot D,  $\text{CO}_2^+ + \text{HD}$  marginally dominates over  $\text{DCO}^+$  DR during solar minimum at certain altitudes, making it the dominant source of escaping hot D at solar minimum. This is because the density of HD relative to  $\text{DCO}^+$  is larger than  $\text{H}_2$  relative to  $\text{HCO}^+$ .

	Thermal escape ( $\text{cm}^{-2}\text{s}^{-1}$ )				Non-thermal escape ( $\text{cm}^{-2}\text{s}^{-1}$ )				Total escape ( $\text{cm}^{-2}\text{s}^{-1}$ )		
	H	D	$\text{H}_2$	HD	H	D	$\text{H}_2$	HD	H	D	H + D
Solar minimum	$1.75 \times 10^8$	80	$1.6 \times 10^5$	0.13	$6.5 \times 10^7$	9387	15351	19	$2.3996 \times 10^8$	9467	$2.4 \times 10^8$
Solar mean	$1.833 \times 10^8$	309	$5.0 \times 10^5$	0.89	$5.6 \times 10^7$	9219	12331	18	$2.39966 \times 10^8$	9529	$2.4 \times 10^8$
Solar maximum	$1.834 \times 10^8$	6740	$8.2 \times 10^6$	98	$4.0 \times 10^7$	8908	7669	16	$2.39969 \times 10^8$	15747	$2.4 \times 10^8$

**Table 2.** Amount of thermal and non-thermal escape of atomic and molecular H and D species for the three solar conditions. The total escape amounts to  $2.4 \times 10^8$  because in the equilibrium atmosphere, the ratio  $\phi_H/\phi_O$  approaches 2, as O escape is fixed at  $1.2 \times 10^8$  (see Section 2.3). Escaping atoms and molecules are sourced from the neutral species; densities for the associated species are shown in Figure S2.

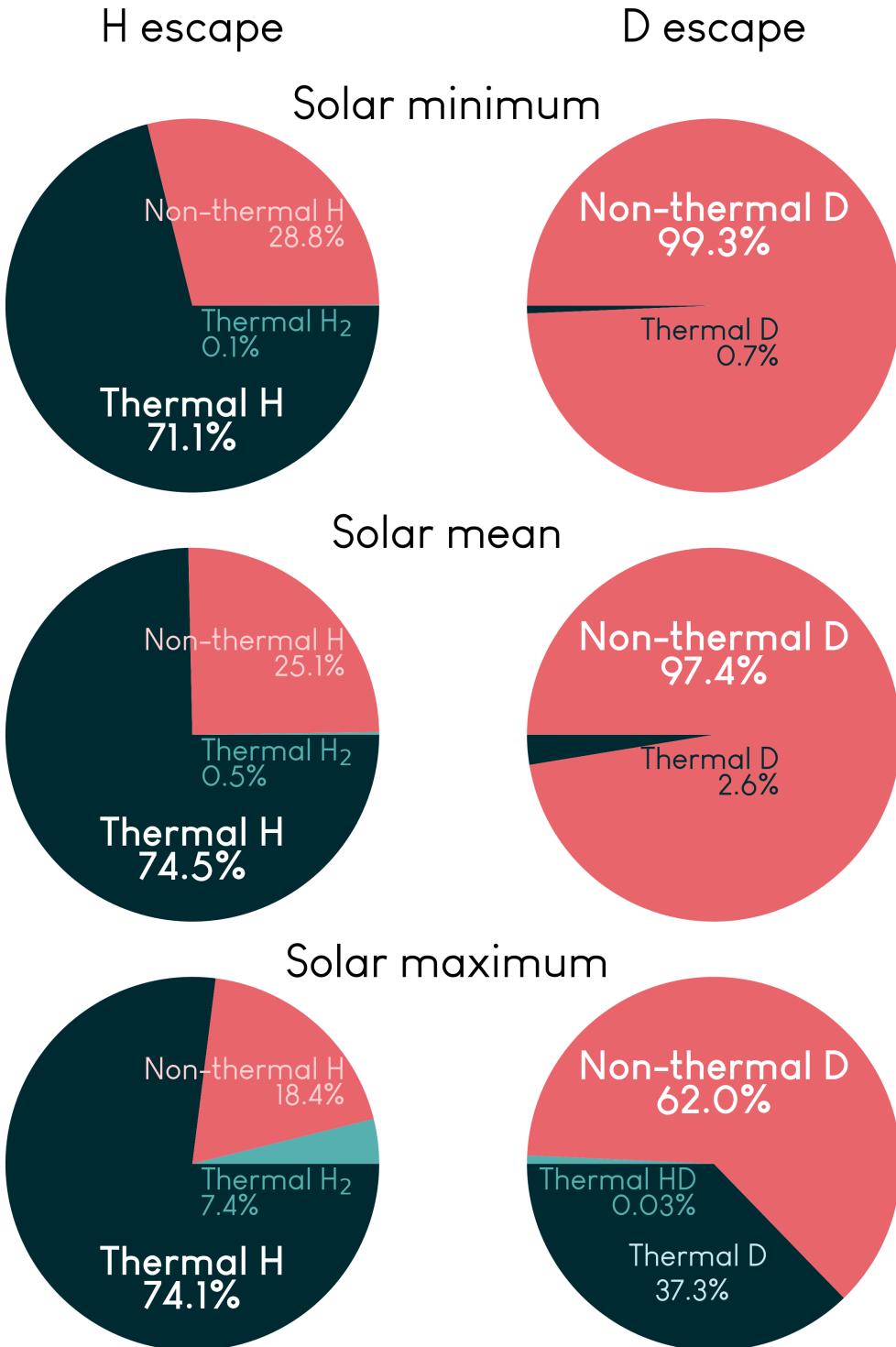
The rates of production from these two processes for hot D are very close; minor changes in conditions, including normal fluctuations in the real atmosphere, could likely change this relationship. Above 200 km,  $\text{CO}_2^+ + \text{H}_2$  dominates for hot H production, but high-altitude hot D comes mostly from  $\text{O}^+ + \text{HD}$ .

DCO<sub>2</sub><sup>+</sup>(HCO<sub>2</sub><sup>+</sup>) DR is the third most important reaction during quiet solar conditions, but it is eclipsed by O<sup>+</sup> + HD (H<sub>2</sub>) during solar maximum. Under quieter solar conditions, the fifth place position is seized by N<sub>2</sub><sup>++</sup> HD (H<sub>2</sub>). But as the thermosphere warms, OD (OH) + O claims the fifth place, first for the H species and then for the D species. This appears to be because the dominant reaction involving OH<sup>+</sup> and OD<sup>+</sup> is the reaction O<sup>+</sup> + H<sub>2</sub> (HD) → OH<sup>+</sup>(OD<sup>+</sup>) + H. This reaction also has a rate coefficient that is independent of temperature, whereas N<sub>2</sub><sup>++</sup> HD (H<sub>2</sub>) has a rate coefficient which decreases with temperature.

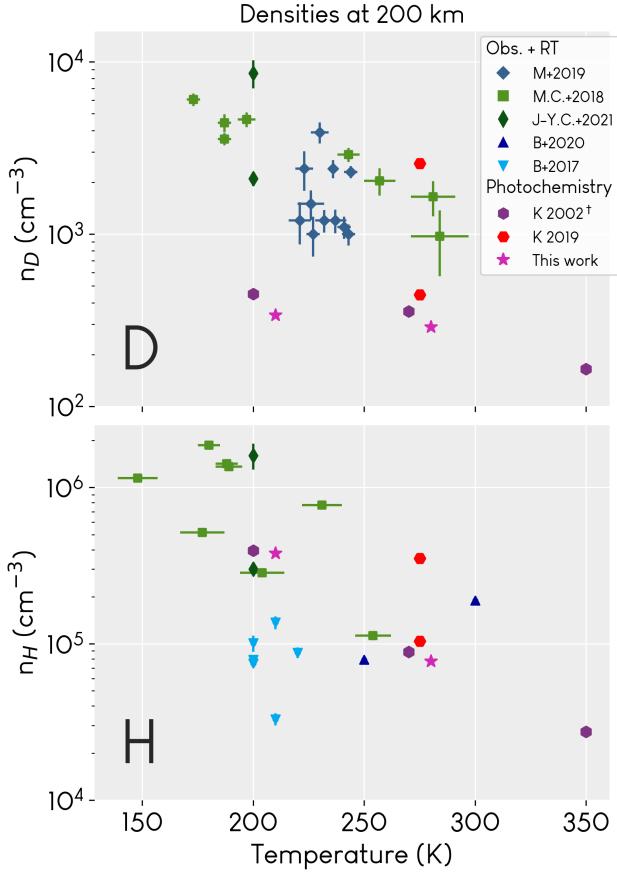
### 3.3 What is the magnitude of non-thermal escape of D, and under which conditions does it dominate thermal escape?

Figure 6 shows the relative contributions of thermal and non-thermal escape of atomic H and D and thermal escape of the molecular species; the associated escape fluxes to space are given in Table 2. The density profiles of the neutral species, from which the escape is sourced, appear in Figure S2; an upcoming publication will focus on variations in these neutral species and their D/H ratios. As has been asserted in the literature (V. A. Krasnopolsky, 2002), thermal escape is the dominant loss process for atomic H, with non-thermal escape of H making up a gradually reducing share across the solar cycle. The picture looks very different for D, for which 62-99.3% of escape is non-thermal depending on solar conditions. Note that, as shown in Table 2, the total escape of H and D adds to  $2.4 \times 10^8 \text{ cm}^{-2}\text{s}^{-1}$  under all solar conditions due to the boundary conditions (see Section 2.3).

Previous work has predicted that thermal escape of D should actually dominate at solar maximum (V. A. Krasnopolsky, 2002) and that non-thermal escape of D in the form of larger molecules such as HD, OD, and HDO could be up to 15% (Gacesa et al., 2018), whereas our results show that non-thermal escape of HD is so negligible as to not appear at all in Figure 6. Besides the fact that we do not account for excited rotational states of HD, the discrepancy also likely arises from our chosen methods. Our non-thermal escape probability curve is valid for hot atoms with 5 eV of energy, and we do not account at all for branching to excited internal states of the other product; we assume that all atomic H and D produced by exothermic reactions are produced “hot”. In reality, not all exothermic heat is dumped directly into the lone atoms all the time. With proper accounting for these intricate branching ratios, our calculated total of non-thermally escaping atomic D would likely decrease. We also do not calculate non-thermal OD escape.



**Figure 6.** Relative escape contributions for H and D. As expected based on the literature, thermal escape dominates for H during all solar conditions, but non-thermal escape dominates D escape, even at solar maximum. Although we do model non-thermal escape of H<sub>2</sub> and HD, their contributions are completely negligible (see Table 2).



**Figure 7.** D and H densities at 200 km (<sup>†</sup> 250 km) from multiple studies. Data represent multiple solar zenith angles, seasons, hemispheres, etc. M+2019: Mayyasi et al. (2019). M.C.+2018: Chaffin et al. (2018). J-Y.C.+2021: Chaufray et al. (2021). B+2020, 2017: Bhattacharyya et al. (2020, 2017). K 2002, 2019: V. A. Krasnopolsky (2002, 2019). Entries under “Obs. + RT” used brightness observations from either HST (Bhattacharyya et al., 2017) or MAVEN IUVS (all others) with radiative transfer modeling for density retrievals. For these studies, invisible density error bars indicate uncertainty smaller than the marker size. Temperature error bars indicate that temperature was retrieved from spacecraft data, while missing temperature error bars mean it was a model parameter or output. Uncertainties for photochemistry studies are not calculated. Photochemical modeling typically reports an order of magnitude less D than other methods, which may be due to observation biases toward times of brighter D emission. There is no similar discrepancy in H densities.

## 4 Discussion

Figure 7 places our D and H densities in context with other studies. We have only consolidated reported densities; we make no attempt to filter by observation geometries. Nevertheless, there appears to be an inverse relationship of densities and temperature for both species. We can also see that photochemical models (red/purple/pink points) produce D densities that are an order of magnitude smaller than densities retrieved using observations and radiative transfer modeling; the same discrepancy does not occur for the H densities. Deuterium Lyman  $\alpha$  is difficult to separate from hydrogen Lyman  $\alpha$ ; the D density discrepancy may potentially be explained by a systematic bias toward anomalously bright D emissions. One exception is the density of D at  $\sim 2500$  and  $T = 275\text{K}$  in the work by V. A. Krasnopol'sky (2019); this point represents a model run with a high amount of water in the thermosphere, whereas all the other photochemical results have a comparatively lower water abundance. This comparison demonstrates that our model output is in reasonable agreement with other works.

As mentioned previously, we do not include cloud or dust microphysics, although these processes do have an important effect on the water cycle. These effects are explored in two recent papers using the Laboratoire de Météorologie Dynamique Planetary Climate Model (LMD-PCM) to study the creation of water ice clouds and their role in controlling the D/H ratio (Vals et al., 2022; Rossi et al., 2022).

### 4.1 Can inclusion of non-thermal escape in the model yield an estimation of water loss similar to the amount calculated in geological studies?

By considering both thermal and non-thermal escape, we can now compute the D/H fractionation factor, which represents the relative efficiency of D and H escape. It is defined as:

$$f = \frac{\phi_D / \phi_H}{[\text{HDO}]_s / 2[\text{H}_2\text{O}]_s} \quad (4)$$

Where  $\phi_X = \phi_{X,t} + \phi_{X,n}$  is the rate at which species X (D or H) escapes from the top of the atmosphere due to both thermal ( $t$ ) and non-thermal ( $n$ ) processes. The denominator represents the D/H ratio in water measured at the surface ( $s$ ), which is a proxy for the D/H ratio in the larger exchangeable reservoir.

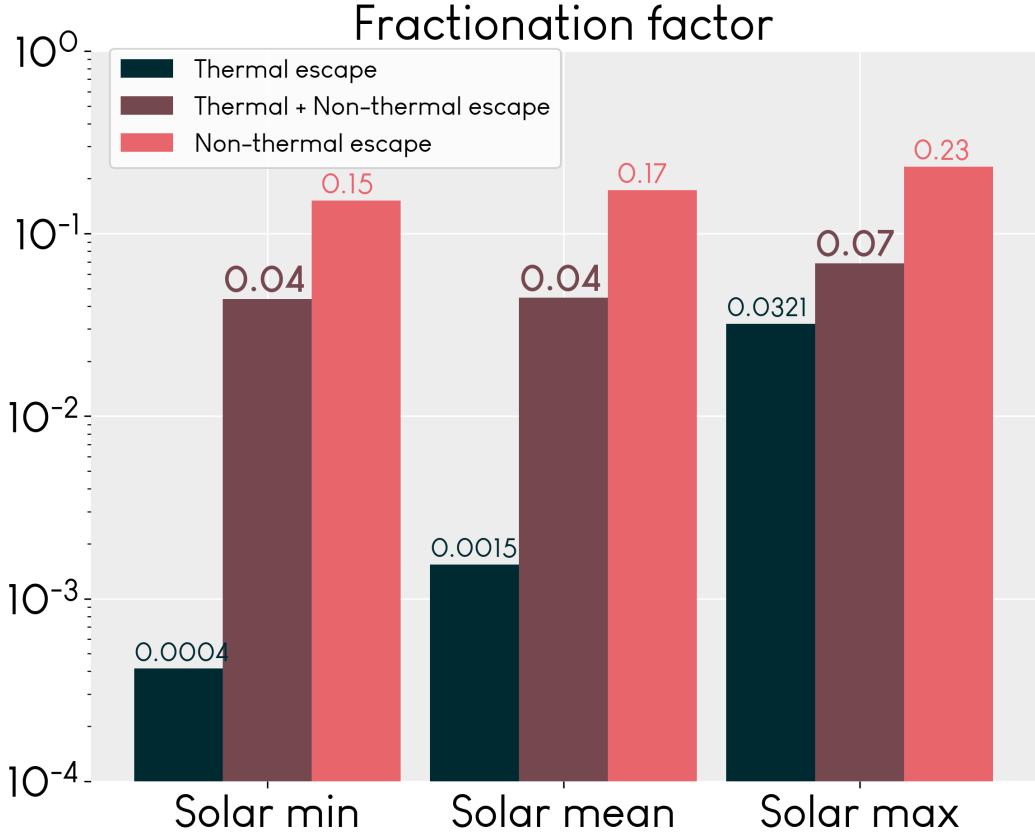
The fractionation factor is important not only because it tells us how efficient loss of D is compared to loss of H, but also because it is useful for calculating the integrated water loss from a planet. Long-term enrichment of the heavy isotope (D) due to differential escape of D and H can be modeled using Rayleigh fractionation (Chamberlain & Hunten, 1987; Yung & DeMore, 1998):

$$\frac{(\text{D}/\text{H})_{\text{now}}}{(\text{D}/\text{H})_{\text{past}}} = \left( \frac{[\text{H}]_{\text{past}}}{[\text{H}]_{\text{now}}} \right)^{1-f} \quad (5)$$

Equation 5 is used to calculate water loss from Mars. The D/H ratio on the left hand side represents the ratio measured in water in the exchangeable reservoir (the seasonal polar caps, near-surface ices, and atmospheric water vapor), and the ratio  $\text{H}_2\text{O}_{\text{past}}/\text{H}_2\text{O}_{\text{now}}$  can be substituted in on the righthand side and rearranged, obtaining (Cangi et al., 2020) (where W is water):

$$W_{\text{lost}} = W_{\text{now}} \left( \left( \frac{(\text{D}/\text{H})_{\text{now}}}{(\text{D}/\text{H})_{\text{past}}} \right)^{1/(1-f)} - 1 \right) \quad (6)$$

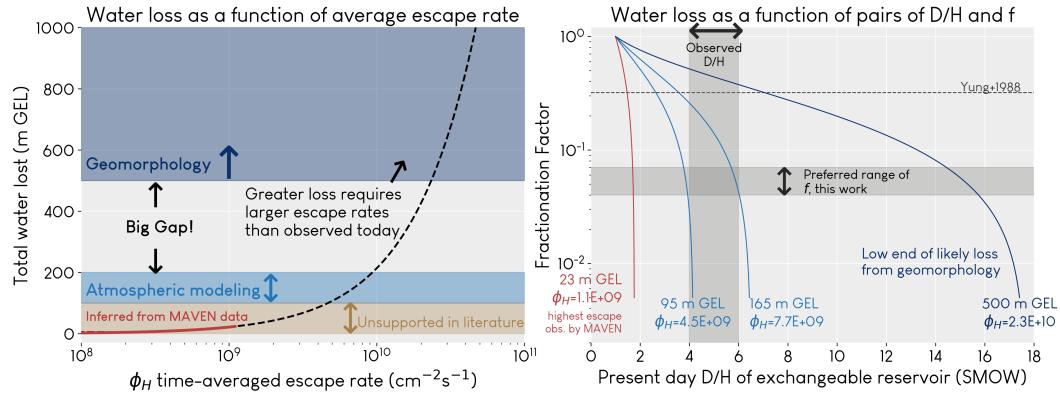
Implicit in these equations is the assumption that  $[\text{H}] \gg [\text{D}]$ , so that the past and present abundances of  $\text{H}_2\text{O}$  are reasonable representations of the entire water budget. In the present day, the ratio of D/H is well constrained by many observational studies to be approximately  $4\text{-}6 \times$  standard mean ocean water (SMOW) (Encrenaz et al., 2018; Villanueva



**Figure 8.** The fractionation factor  $f$  for three different modes of escape. Changing solar conditions lead to an orders of magnitude increase in  $f$ , as does inclusion of non-thermal escape in the calculation. Fractionation represents the escape efficiency of D compared to H, meaning that  $f = 0.04$  represents a 4% escape efficiency of D. Non-thermal escape is an effective escape method for D under all solar conditions.

et al., 2015, and references therein). Current research also has identified a likely present-day exchangeable reservoir water budget of 20-30 m GEL (Lasue et al., 2013, and references therein). By obtaining a reliable value for  $f$ , we can combine all these values to calculate the inventory of water on ancient Mars.

Cangi et al. (2020) suggested that the difference between the mean atmospheric  $f_t$  (considering only thermal escape) and  $f_{tn}$  (considering both thermal and non-thermal escape) was several orders of magnitude. Because they did not directly model non-thermal escape, they arrived at this conclusion by incorporating the non-thermal escape velocity given by V. A. Krasnopolsky et al. (1998) into their model. We are now in a position to compare with those estimates; our calculations of the fractionation factor are shown in Figure 8. Cangi et al. (2020) calculated  $f = 0.06$  for their standard atmosphere, based on their modeled thermal escape and estimated non-thermal escape. We calculate a total escape fractionation of  $f = 0.04$  for our solar mean atmosphere, which has the same insolation and similar temperatures, and is not far off from their 0.06. Our results are consistent with their thermal escape  $f = 0.002$  for the standard atmosphere (roughly equivalent to our solar mean atmosphere). Our results show that while overall D escape at Mars is around 4-7% as efficient as H escape, non-thermal D escape is much more efficient, between 15-23% that of H.



**Figure 9.** a): Possible water loss as a function of long-term average H escape rate  $\phi_H$ ,  $W_{\text{lost}} = \bar{\phi}_H t$ , where  $t = 4.5$  billion years. A significant gap separates the amount of water loss inferred from atmospheric modeling and geomorphological studies. Additionally, escape rates determined from MAVEN data enable very small amounts of water loss that are not consistent with the geological evidence. b): Water loss lines represent solutions to equation 6, assuming 30 m GEL in the present-day exchangeable reservoir. The regions matching the best values of D/H and  $f$  are shaded in gray, with the overlapped rectangle representing our best estimate of the present-day atmosphere. (The fractionation factor calculated by Yung et al. (1988) is shown for reference, though it is high due to the highly uncertain exospheric temperatures then used.)

Our results yield integrated water loss of 147–158 m GEL (present day exchangeable reservoir = 30 m GEL,  $f = 0.04\text{--}0.07$ , D/H=5.5×SMOW). This total loss still does not agree with the geological estimates of 500+ m GEL (Lasue et al., 2013). The discrepancy is summarized in Figure 9. Figure 9a shows the gap between the amount of water loss calculated by atmospheric models (Yung et al., 1988; Kass & Yung, 1999; V. Krasnopol'sky, 2000; V. A. Krasnopol'sky, 2002; Cangi et al., 2020) and that inferred from geomorphological observations (Lasue et al., 2013, and references therein). The time-averaged H escape rate curve suggests that the rates observed today (Jakosky et al., 2018) are unlikely to be near the average, and that escape was likely higher in the distant past, enabling greater water loss. Plausible explanations could include periods of hydrodynamic escape, a more EUV-active young sun driving greater photochemistry, extreme obliquities (Wordsworth, 2016; Laskar et al., 2004), or other as of yet unknown dynamics.

It is also possible that some water may have been sequestered into the surface. Recent work by Scheller et al. (2021) suggests that this amount may have accounted for between 30–99% of all missing water. More smaller-scale models and many observations will be needed to constrain this large range further. Hydrated minerals may contain 130–260 m GEL equivalent water Wernicke and Jakosky (2021), but the time of emplacement and any fractionation of the process is unclear. In general, due to the chaotic evolution of obliquity (Laskar et al., 2004) over Mars' history, it is extremely difficult to qualitatively describe escape rates in the past. Although it is difficult to extrapolate much from the present-day rates, high loss of water via escape to space is not ruled out.

Figure 9b also helps demonstrate when it is important to know the value of  $f$  rather precisely. Discriminating between  $f = 0.04$  or  $f = 0.07$  is not particularly important: below  $f = 0.1$ , water loss curves are relatively vertical, meaning that a change in  $f$  does not equate to a significant change in water loss, but this is less true the closer  $f$  gets to 1. (For another view, see Figure S4 for water loss as a function of  $f$  for a single D/H ratio.)

467 Considered together, these insights tell us that non-thermal escape processes for D are  
 468 important to model in order to accurately understand how D escapes from Mars. This  
 469 conclusion may not hold for other planets, moons, or exoplanets; on bodies which are  
 470 colder, larger, or otherwise less conducive to thermal escape, non-thermal escape may  
 471 have a greater role to play.

#### 472 **4.2 Other non-thermal processes**

473 We do not account for the collision of H or D with hot oxygen, which is another signif-  
 474 icant source of hot atoms in the martian atmosphere. Assuming an exospheric temper-  
 475 ature of 240 K, Gacesa et al. (2012) calculated that  $1.9 \times 10^5 \text{ cm}^{-2}\text{s}^{-1}$  H<sub>2</sub> molecules  
 476 escape as a result of collision with hot oxygen, which is larger than our non-thermal H<sub>2</sub>  
 477 flux by two orders of magnitude (see Table 2). They also estimate that 74 HD molecules  
 478  $\text{cm}^{-2}\text{s}^{-1}$  escape via this mechanism. This would bring our total HD escape to approx-  
 479 imately  $100 \text{ cm}^{-2}\text{s}^{-1}$ , an order of magnitude larger than our current result. Other species  
 480 may also play a role; Gacesa et al. (2017) calculate that the total non-thermal escape  
 481 of OH is  $1.07 \times 10^{23} \text{ s}^{-1}$ , i.e.  $7.4 \times 10^5 \text{ cm}^{-2}\text{s}^{-1}$ . Even added together, these numbers  
 482 are all still orders of magnitude smaller than the non-thermal atomic escape fluxes, and  
 483 will not significantly affect our results. If we included them, the net effect would be to  
 484 boost H escape, decreasing the fractionation factor and total water loss.

485 Energization of atomic H and D by collision with hot oxygen may be significant. Shematovich  
 486 (2013) estimates, for specific density profiles and temperatures, a total possible escape  
 487 flux of hot H produced this way to be  $6 \times 10^6 \text{ cm}^{-2}\text{s}^{-1}$  at low solar activity. This be-  
 488 gins to approach our non-thermal H escape (see Table 2). Our non-thermal D escape is  
 489 3 orders of magnitude lower than the H escape. If we crudely apply this scaling relation  
 490 to hot O collisions with D, we can expect that this pathway might produce D escape on  
 491 the order of  $10^3$ , which is the same order as our calculated non-thermal escape fluxes.  
 492 However, since it is not significantly larger, we can at least expect that the exclusion of  
 493 hot O collisions with H and D would not significantly change our primary conclusions.

#### 494 **4.3 Future opportunities and directions**

495 There are several things that could enhance our model. The first likely avenue worthy  
 496 of exploration would be to perform a similar study, but with a more physically-motivated  
 497 parameterization of atomic O escape. Fixing the O escape at  $1.2 \times 10^8 \text{ cm}^{-2}\text{s}^{-1}$  was suf-  
 498 ficient for the scope of this work; our results represent long-term equilibrium, when it  
 499 is possible to adopt reasonable means for parameters like O escape. Adding a dynam-  
 500 ically evolving escape flux boundary condition for atomic O would enable a more com-  
 501 prehensive understanding of shorter-term variations in H and D escape rates, such as a  
 502 result of regular seasonal cycles. This would better capture the interplay between the  
 503 hydrogen species and CO<sub>2</sub>, the main component of the atmosphere and a significant source  
 504 of O. This would also present an opportunity to include processes more important to O  
 505 loss, such as ion pickup, ion/polar outflow, and sputtering. We do not include these as  
 506 we focus on H and D loss, which are dominated by other processes.

507 We have also been forced to make some unavoidable assumptions about the basic chem-  
 508 istry, owing to a lack of laboratory data. While we have made a best attempt to use ex-  
 509 isting reaction rate coefficient data from several different papers and databases, a com-  
 510 prehensive catalogue of rate coefficients, branching ratios, and cross sections for deuter-  
 511 ated reactions is not available in the literature at this time. Most especially, future pho-  
 512 tochemical models would benefit from accurate photoabsorption cross sections for deuter-  
 513 ated neutrals other than HDO (including OD and HD in particular), and measured re-  
 514 action rate coefficients for as many of the deuterated reactions with estimated rates in  
 515 Table 1 as possible. While not all reactions will significantly affect the chemistry, cer-  
 516 tain rates that dominate production or loss of a species can have strong effects, affect-  
 517 ing densities up to a few orders of magnitude (see, for example, Fox et al. (2017)).

518 Photochemical modeling often entails excluding some important processes that are bet-  
 519 ter captured in higher-dimensional models. Our model is the first to couple the ion and  
 520 neutral atmospheres from the upper atmosphere down to the surface, but there is still  
 521 an opportunity for future work to give more attention to surface-atmosphere interactions.  
 522 Our inclusion of surface-atmosphere interactions is primarily relegated to surface den-  
 523 sity boundary conditions for certain species. A more detailed parameterization of pro-  
 524 cesses such as volcanic outgassing, major seasonal changes in the polar caps, water ad-  
 525 sorption and desorption on dust grains and dust lifting, deposition of volatiles, and the  
 526 role of non-volatiles such as perchlorates, salts, and other non-water ices could yield new  
 527 insights into the planetary climate system as a whole.

528 Our results also have implications for the detectability of deuterated ions by present and  
 529 future Mars missions. Using MAVEN's NGIMS instrument, the deuterated ions that we  
 530 model typically occupy the same mass/charge ratio bin as a more prevalent H-bearing  
 531 species. For example, D<sup>+</sup> occupies the same bin as H<sub>2</sub><sup>+</sup>, but the latter is far more abun-  
 532 dant. The deuterated species in our model which do not overlap with an H-bearing species  
 533 are H<sub>2</sub>D<sup>+</sup>(mass bin 4), HD<sub>2</sub><sup>+</sup>(5), H<sub>2</sub>DO<sup>+</sup>(20), HDO<sub>2</sub><sup>+</sup>(35), and ArD<sup>+</sup>(42). However,  
 534 several of these species are expected to be very rarefied and thus difficult to detect, and  
 535 others may overlap with species we do not model that do exist on Mars, such as helium  
 536 in mass bin 4. These degeneracies make obtaining deuterated ion densities challenging;  
 537 doing so will require inventive methods applied to existing data or new methods with  
 538 new instruments.

## 539 **5 Conclusions**

540 We have used a 1D photochemical model that fully couples ions and neutrals from sur-  
 541 face to space to study production of hot D from planetary ionospheric processes. We show  
 542 that the deuterated ionosphere behaves relatively similar to the H-bearing ionosphere.  
 543 This result is somewhat expected, as measurements of rate coefficients for deuterated  
 544 reactions are much less available than the H-bearing counterpart reaction rate coefficients.

545 For the first time, we have self-consistently quantified, in raw flux and in percent of to-  
 546 tal escape, the thermal and non-thermal escape fluxes of H and D in both the atomic  
 547 and molecular forms in equilibrium atmospheres under different solar conditions, and the  
 548 dominant chemical reactions responsible for producing hot D. Our results confirm ear-  
 549 lier suggestions that non-thermal escape dominates D escape at Mars, although our re-  
 550 sults have shown that this is true throughout the solar cycle rather than just during quiet  
 551 solar conditions.

552 We also confirm an earlier prediction (Cangi et al., 2020) that including non-thermal es-  
 553 cape when calculating the D/H fractionation factor will result in a fractionation factor  
 554 several orders of magnitude higher than if it is neglected. However, the resulting frac-  
 555 tionation factor is 0.04–0.07, meaning that D escape is only about 4–7% as efficient as  
 556 H escape. If the fractionation has consistently been this small, and we also assume that  
 557 the escape rate of H  $\phi_H$  has been similar to the value today through time, it is difficult  
 558 to ascribe the large amount of water loss that we see indicated in the rock record to at-  
 559 mospheric escape alone. On the other hand, the dust storm season on Mars, as well as  
 560 normal seasonal variations between perihelion and aphelion, are characterized by spa-  
 561 tially and temporally localized enhancements of the D/H ratio, water abundance, and  
 562 H escape (Villanueva et al., 2021; Daerden et al., 2022; A. Fedorova et al., 2021; Chaf-  
 563 fin et al., 2021; Holmes et al., 2021; A. A. Fedorova et al., 2020; Stone et al., 2020; Aoki  
 564 et al., 2019; Vandaele et al., 2019; Heavens et al., 2018; Chaffin et al., 2017, and refer-  
 565 ences therein). It is not yet clear if enhanced D escape or a heightened fractionation fac-  
 566 tor also occur along with these seasonal changes, although it seems likely (Alday et al.,  
 567 2021); if they do, then the assumption of a constant fractionation factor over time can-  
 568 not hold, and we will have to introduce some additional nuance to our use of Rayleigh  
 569 fractionation to estimate water loss.

570 Ongoing improvements in modeling, especially coupling between 1D and 3D models, as  
 571 well as continual advancements in instrumentation for planetary missions will be nec-  
 572 essary to continue putting together the puzzle of water on Mars throughout history.

## 573 6 Open Research Statement

574 The photochemical model used for this work is written for and compatible with Julia 1.7.1  
 575 (Bezanson et al., 2017). The model itself, in version 1.0 as used in this work, is avail-  
 576 able at Zenodo (Cangi & Chaffin, 2022).

577 A typical use-case of the model is to modify simulation parameters within `PARAMETERS.jl`  
 578 and to then call `julia converge_new_file.jl` at the command line.

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1           **Fully coupled photochemistry of the deuterated**  
2           **ionosphere of Mars and its effects on escape of H and**  
3           **D**

4           **Eryn Cangi<sup>1</sup>, Michael Chaffin<sup>1</sup>, Roger Yelle<sup>2</sup>, Bethan Gregory<sup>1</sup>, Justin**  
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8           **Key Points:**

- 9
- We present the first photochemical modeling study of the deuterated ionosphere  
10           of Mars.
  - Non-thermal escape dominates D loss under all solar conditions, and the processes  
11           producing hot D are similar to those producing hot H.
  - The combined D/H fractionation factor is  $f = 0.04\text{--}0.07$ , indicating 147–158 m  
12           GEL of water loss, still less than geological estimates.  
13
- 14

15 **Abstract**

16 Although deuterium (D) on Mars has received substantial attention, the deuterated iono-  
 17 sphere remains relatively unstudied. This means that we also know very little about non-  
 18 thermal D escape from Mars, since it is primarily driven by excess energy imparted to  
 19 atoms produced in ion-neutral reactions. Most D escape from Mars is expected to be non-  
 20 thermal, highlighting a gap in our understanding of water loss from Mars. In this work,  
 21 we set out to fill this knowledge gap. To accomplish our goals, we use an upgraded 1D  
 22 photochemical model that fully couples ions and neutrals and does not assume photo-  
 23 chemical equilibrium. To our knowledge, such a model has not been applied to Mars pre-  
 24 viously. We model the atmosphere during solar minimum, mean, and maximum, and find  
 25 that the deuterated ionosphere behaves similarly to the H-bearing ionosphere, but that  
 26 non-thermal escape on the order of  $8000\text{--}9000 \text{ cm}^{-2}\text{s}^{-1}$  dominates atomic D loss under  
 27 all solar conditions. The total fractionation factor,  $f$ , is  $f = 0.04\text{--}0.07$ , and integrated  
 28 water loss is 147–158 m GEL. This is still less than geomorphological estimates. Deuter-  
 29 ated ions at Mars are likely difficult to measure with current techniques due to low den-  
 30 sities and mass degeneracies with more abundant H ions. Future missions wishing to mea-  
 31 sure the deuterated ionosphere *in situ* will need to develop innovative techniques to do  
 32 so.

33 **Plain Language Summary**

34 Our knowledge of ions in the martian atmosphere that contain deuterium (D) is extremely  
 35 limited, lacking measurements and dedicated computer models. This is a problem be-  
 36 cause the expectation is that most D that escapes to space does so “non-thermally”, by  
 37 gaining extra energy from ion reactions. H and D mostly exist in water on Mars, so iden-  
 38 tifying how much H and D have escaped non-thermally is an important piece of the puz-  
 39 zle of water loss from Mars. Here, we present the first one dimensional model of the Mars  
 40 atmosphere that includes D-bearing ions. This new model avoids many common approx-  
 41 imations that might change our results in unclear ways. We report the amounts of ther-  
 42 mal and non-thermal escape of H and D and confirm that most D escapes non-thermally.  
 43 We also identify the specific chemical reactions that are most important, and show how  
 44 many D-bearing ions we expect to find at different altitudes in the atmosphere that might  
 45 be detectable by future missions. Finally, we calculate that a layer of water 147–158 m  
 46 deep has been lost from Mars. This is still less than the amount calculated by geolog-  
 47 ical studies.

48 **1 Introduction**

49 Mars is a natural laboratory to study how atmospheric escape shapes planetary habit-  
 50 ability. It is now well established that a significant amount of the Mars atmosphere has  
 51 been lost to space (Jakosky et al., 2018). This escape is fractionating—the relative es-  
 52 cape efficiency is different for members of an isotope pair, such as deuterium (D) and  
 53 hydrogen (H). Because on Mars, D and H are found primarily in water, D/H fraction-  
 54 ation indicates a history of water loss (Owen et al., 1988). Understanding escape frac-  
 55 tionation therefore contributes to understanding the long-term loss of the atmosphere  
 56 and desiccation of the planet.

57 Geological studies indicate that Mars has likely lost 500+ meters global equivalent layer  
 58 (GEL) of water (Lasue et al., 2013, and references therein), but atmospheric modeling  
 59 studies typically do not find the same result, instead arriving at a smaller number of 100–  
 60 250 m GEL (Cangi et al., 2020; Alsaeed & Jakosky, 2019; V. A. Krasnopolsky, 2002; V. Krasnopol-  
 61 sky, 2000). A key step in retrieving water loss estimates from atmospheric models is to  
 62 quantify both thermal and non-thermal escape.

63 Thermal escape occurs for particles with a thermal velocity in the high-energy tail of the  
 64 velocity distribution above the planet’s escape velocity. Non-thermal escape comprises

all other processes that grant extra kinetic energy to atmospheric particles, which are variously dubbed “suprothermal” or “hot”; most of these processes involve ion chemistry or interaction with ions. Thermal escape of H has been well-studied at Mars with atmospheric models, observations from missions, and mixes of the two (Chaffin et al., 2021; Stone et al., 2020; Mayyasi et al., 2018; Rahmati et al., 2018; Zahnle et al., 2008; V. A. Krasnopolsky, 2002). Thermal escape of D has also been modeled (Cangi et al., 2020; Kass & Yung, 1999; Yung et al., 1988), but non-thermal escape of D from Mars has not been directly modeled, despite expectations that it should be the dominant loss process (Gacesa et al., 2012; V. A. Krasnopolsky, 2002). V. A. Krasnopolsky (2002) and V. A. Krasnopolsky et al. (1998) calculated non-thermal escape velocities for a few select processes (solar wind charge exchange, electron impact ionization, and photoionization), but their model did not include a deuterated ionosphere, and so missed a portion of the production of hot atoms.

Cangi et al. (2020) used a 1D photochemical model of Mars’ neutral atmosphere to calculate the D/H fractionation factor  $f$  as a function of atmospheric temperatures. The model only calculated thermal escape directly; non-thermal escape was approximated by scaling the non-thermal effusion velocities given by V. A. Krasnopolsky (2002) and multiplying them by the densities of H and D at the exobase. This estimation indicated that  $f$  is several orders of magnitude larger when non-thermal escape processes are considered, motivating a more complete calculation of non-thermal escape of H and D. Here, we present this more complete treatment. The key questions about the deuterated martian ionosphere that we address are as follows.

1. What are the atmospheric densities of deuterated ions?
2. What are the dominant production mechanisms of hot H and hot D, and are they analogous or dissimilar?
3. What is the magnitude of non-thermal escape of D, and is it the dominant type of escape during quiet solar conditions?
4. Can inclusion of non-thermal escape in the model yield an estimation of water loss similar to the amount calculated in geomorphological studies?

To answer these questions, we have upgraded our existing 1D photochemical model of the neutral martian atmosphere to include a self-consistent ionosphere and deuterated ions. Because ions and neutrals have substantially different behaviors and chemistry, the problem of modeling both at the same time turns out to be an expensive and computationally difficult one, even in 1D. Most recent ion-neutral photochemical models use one or more of three common approaches: (1) a fixed (either wholly or partially) background neutral atmosphere (Fox et al., 2021, 2017, 2015; Matta et al., 2013; Molina-Cuberos et al., 2002); (2) placing the lower boundary of the model near the bottom of the ionosphere (Fox et al., 2021; V. A. Krasnopolsky, 2019; Fox et al., 2015; Matta et al., 2013; V. A. Krasnopolsky, 2002); or (3) the assumption of photochemical equilibrium for chemically short-lived species (Vuitton et al., 2019; Banaszkiewicz et al., 2000) and/or neglect of ion diffusion (Dobrijevic et al., 2016). But because we did not want to lose any subtle ion-neutral feedbacks, we have upgraded our photochemical model such that it does not use any of the above simplifications. In this way, we obtain a more complete understanding of the coupling of the lower to upper atmospheres, which has been recently shown to be key to understanding water transport, destruction, and escape during the Mars dusty season (Villanueva et al., 2021; Chaffin et al., 2021; Holmes et al., 2021; Stone et al., 2020; A. A. Fedorova et al., 2020; Vandaele et al., 2019; Aoki et al., 2019; Heavens et al., 2018).

Our new model spans surface-to-space and fully couples ions and neutrals without assumption of photochemical equilibrium. We use this enhanced model to present a first

theoretical analysis of D ion chemistry at Mars, which includes an updated quantification of non-thermal escape of D and H, the most critical reactions for production of hot H and D, and the implications for water loss.

## 2 Model description

Here we describe changes made to the 1D photochemical model as described by Cangi et al. (2020). In addition to the upgrades to physics and chemistry described below, this update incorporates computational improvements, such as extensive encapsulation, vectorization of functions, and performance tuning. The only species that we hold constant in our model is argon and lower atmospheric water (see Section 2.1.3). The absolute tolerance is  $1 \times 10^{-12}$ , or 1 ppt, and the relative tolerance is  $1 \times 10^{-6}$ .

### 2.1 New features

#### 2.1.1 Ion reaction network

Our updated model contains  $\sim 600$  total ion and neutral reactions. We enumerate the deuterated reactions in Table 1. The full network of chemical reactions is available in the Supporting Information, Table S1; rate coefficients of H-analogue reactions are generally the same as those used by Vuitton et al. (2019).

**Scope of deuterated reactions.** We define a deuterated analogue reaction as a reaction in which one H atom in one of the reactants has been replaced with D; for example,  $D + O_2 \rightarrow DO_2$  instead of  $H + O_2 \rightarrow HO_2$ . We do not consider doubly deuterated reactions or species, e.g., we do not include reactions like  $DO_2 + D \rightarrow OD + OD$  nor species like  $D_2O$ . Our deuterated reaction network includes the deuterated analogues of the top 23 fastest H-bearing reactions (according to the column rate), including neutral reactions used by (Cangi et al., 2020) and many deuterated analogues of ion-neutral reactions. All told, the H-bearing analogues of these deuterated reactions make up 99.99997% of the integrated column rate of all H-bearing reactions. For this reason, it is unlikely we have missed any significant deuterated reactions.

Table 1: Deuterated reactions used in the model. Reactions 1-6b: column rate  $\nu$  in  $\text{cm}^{-2}\text{s}^{-1}$ . Reactions 7-125: rate coefficients in units of  $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$  for bimolecular reactions and  $\text{cm}^6 \text{molecule}^{-1} \text{s}^{-1}$  for termolecular reactions. BR = branching ratio; MS = mass scaling.

		Reaction	BR	MS	Rate coefficient	Ref
Photodissociation and photoionization						
1	D	$\rightarrow D^+$			$\nu_{\text{col}} = 0.3$	†
2	DO <sub>2</sub>	$\rightarrow OD + O$			$\nu_{\text{col}} = 2779$	†
3a	HD	$\rightarrow HD^+$			$\nu_{\text{col}} = 0.5$	†
3b		$\rightarrow H + D$			$\nu_{\text{col}} = 0.15$	†
3c		$\rightarrow H^+ + D$			$\nu_{\text{col}} = 0.03$	†
3d		$\rightarrow D^+ + H$			$\nu_{\text{col}} = 0.03$	†
4a	HDO	$\rightarrow D + OH$			$\nu_{\text{col}} = 17.4$	C0499
4b		$\rightarrow H + OD$			$\nu_{\text{col}} = 17.4$	C0499
4c		$\rightarrow HD + O(^1D)$			$\nu_{\text{col}} = 2.3$	C0499
4d		$\rightarrow HDO^+$			$\nu_{\text{col}} = 1.3$	†
4e		$\rightarrow OD^+ + H$			$\nu_{\text{col}} = 0.3$	†
4f		$\rightarrow OH^+ + D$			$\nu_{\text{col}} = 0.3$	†
4g		$\rightarrow D^+ + OH$			$\nu_{\text{col}} = 0.1$	†
4h		$\rightarrow H^+ + OD$			$\nu_{\text{col}} = 0.1$	†

Continued on next page

		Reaction	BR	MS	Rate or rate coefficient	Ref
4i		$\rightarrow \text{O}^+ + \text{HD}$			$\nu_{\text{col}} = 0.02$	†
4j		$\rightarrow \text{H} + \text{D} + \text{O}$			$\nu_{\text{col}} = 0$	†
5a	HDO <sub>2</sub>	$\rightarrow \text{OH} + \text{OD}$			$\nu_{\text{col}} = 451$	†
5b		$\rightarrow \text{DO}_2 + \text{H}$			$\nu_{\text{col}} = 12.5$	†
5c		$\rightarrow \text{HO}_2 + \text{D}$			$\nu_{\text{col}} = 12.5$	†
5d		$\rightarrow \text{HDO} + \text{O}(\text{¹D})$			$\nu_{\text{col}} = 0$	†
6a	OD	$\rightarrow \text{O} + \text{D}$			$\nu_{\text{col}} = 44.7$	NL84
6b		$\rightarrow \text{O}(\text{¹D}) + \text{D}$			$\nu_{\text{col}} = 0.6$	NL84
Deuterated neutral-neutral reactions						
					See text	
7	CO + D	$\rightarrow \text{DCO}$			$k_\infty = 1.00e + 00 \left(\frac{T_n}{300}\right)^{0.2}$ $k_0 = 2.00 \times 10^{-35} \left(\frac{T_n}{300}\right)^{0.2}$	Est.
8a	CO + OD	$\rightarrow \text{CO}_2 + \text{D}$	$\sqrt{\frac{17}{18}}$		$k_\infty = 1.63 \times 10^{-6} \left(\frac{T_n}{300}\right)^{6.1}$ $k_0 = 4.90 \times 10^{-15} \left(\frac{T_n}{300}\right)^{0.6}$	Est.
8b		$\rightarrow \text{DOCO}$	$\sqrt{\frac{17}{18}}$		See text $k_\infty = 6.62 \times 10^{-16} \left(\frac{T_n}{300}\right)^{1.3}$ $k_0 = 1.73 \times 10^{-29} \left(\frac{T_n}{300}\right)^{-1.4}$	Est.
9	D + H <sub>2</sub>	$\rightarrow \text{HD} + \text{H}$			$2.73 \times 10^{-17} \left(\frac{T_n}{300}\right)^{2.0} e^{-2700/T_n}$	N15
10a	D + H <sub>2</sub> O <sub>2</sub>	$\rightarrow \text{H}_2\text{O} + \text{OD}$	0.5		$1.16 \times 10^{-11} e^{-2110/T_n}$	C10
10b		$\rightarrow \text{HDO} + \text{OH}$	0.5		$1.16 \times 10^{-11} e^{-2110/T_n}$	C10
11a	D + HO <sub>2</sub>	$\rightarrow \text{DO}_2 + \text{H}$			$1.00 \times 10^{-10}$	Y88
11b		$\rightarrow \text{HD} + \text{O}_2$			$2.45 \times 10^{-12}$	Y88
11c		$\rightarrow \text{HDO} + \text{O}(\text{¹D})$			$1.14 \times 10^{-12}$	Y88
11d		$\rightarrow \text{OH} + \text{OD}$			$5.11 \times 10^{-11}$	Y88
12	D + O <sub>2</sub>	$\rightarrow \text{DO}_2$	$\sqrt{\frac{1}{2}}$		$k_\infty = 2.40 \times 10^{-11} \left(\frac{T_n}{300}\right)^{0.2}$ $k_0 = 1.46 \times 10^{-28} \left(\frac{T_n}{300}\right)^{-1.3}$	Est.
13	D + O <sub>3</sub>	$\rightarrow \text{OD} + \text{O}_2$			$9.94 \times 10^{-11} e^{-470/T_n}$	Y89, N15
14	D + OH + CO <sub>2</sub>	$\rightarrow \text{HDO} + \text{CO}_2$	$\sqrt{\frac{1}{2}}$		$1.16 \times 10^{-25} \left(\frac{T_n}{300}\right)^{-2.0}$	Est.
15	DCO + H	$\rightarrow \text{CO} + \text{HD}$	$\sqrt{\frac{29}{30}}$		$1.50 \times 10^{-10}$	Est.
16a	DCO + O	$\rightarrow \text{CO} + \text{OD}$	$\sqrt{\frac{29}{30}}$		$5.00 \times 10^{-11}$	Est.
16b		$\rightarrow \text{CO}_2 + \text{D}$	$\sqrt{\frac{29}{30}}$		$5.00 \times 10^{-11}$	Est.
17a	DCO + O <sub>2</sub>	$\rightarrow \text{CO}_2 + \text{OD}$	$\sqrt{\frac{29}{30}}$		$7.60 \times 10^{-13}$	Est.
17b		$\rightarrow \text{DO}_2 + \text{CO}$	$\sqrt{\frac{29}{30}}$		$5.20 \times 10^{-12}$	Est.
18	DCO + OH	$\rightarrow \text{HDO} + \text{CO}$	0.5	$\sqrt{\frac{29}{30}}$	$1.80 \times 10^{-10}$	Est.
19	DO <sub>2</sub> + HO <sub>2</sub>	$\rightarrow \text{HDO}_2 + \text{O}_2$	$\sqrt{\frac{33}{34}}$		$3.00 \times 10^{-13} e^{460/T_n}$	Est.
20	DO <sub>2</sub> + N	$\rightarrow \text{NO} + \text{OD}$	$\sqrt{\frac{33}{34}}$		$2.20 \times 10^{-11}$	Est.
21	DO <sub>2</sub> + O <sub>3</sub>	$\rightarrow \text{OD} + \text{O}_2 + \text{O}_2$	$\sqrt{\frac{33}{34}}$		$1.00 \times 10^{-14} e^{-490/T_n}$	Est.
22	DOCO + O <sub>2</sub>	$\rightarrow \text{DO}_2 + \text{CO}_2$	$\sqrt{\frac{45}{46}}$		$2.09 \times 10^{-12}$	Est.
23	DOCO + OH	$\rightarrow \text{CO}_2 + \text{HDO}$	$\sqrt{\frac{45}{46}}$		$1.03 \times 10^{-11}$	Est.

Continued on next page

		Reaction	BR	MS	Rate or rate coefficient	Ref
24	H + D + M	$\rightarrow$ HD + M		$\sqrt{\frac{1}{2}}$	$6.62 \times 10^{-27} (\frac{T_n}{300})^{-2.27}$	Est.
25a	H + DO <sub>2</sub>	$\rightarrow$ HD + O <sub>2</sub>		$\sqrt{\frac{33}{34}}$	$3.45 \times 10^{-12}$	Est.
25b		$\rightarrow$ HDO + O( <sup>1</sup> D)		$\sqrt{\frac{33}{34}}$	$1.60 \times 10^{-12}$	Est.
25c		$\rightarrow$ HO <sub>2</sub> + D			$1.85 \times 10^{-10} e^{-890/T_n}$	Y88
25d		$\rightarrow$ OH + OD		$\sqrt{\frac{33}{34}}$	$7.20 \times 10^{-11}$	Est.
26	H + HD	$\rightarrow$ H <sub>2</sub> + D			$1.15 \times 10^{-11} e^{-3041/T_n}$	N15
27a	H + HDO <sub>2</sub>	$\rightarrow$ H <sub>2</sub> O + OD	0.5		$1.16 \times 10^{-11} e^{-2110/T_n}$	C10
27b		$\rightarrow$ HDO + OH	0.5		$1.16 \times 10^{-11} e^{-2110/T_n}$	C10
28	H + OD + CO <sub>2</sub>	$\rightarrow$ HDO + CO <sub>2</sub>		$\sqrt{\frac{17}{18}}$	$1.16 \times 10^{-25} (\frac{T_n}{300})^{-2.0}$	Est.
29	HCO + D	$\rightarrow$ CO + HD		$\sqrt{\frac{1}{2}}$	$1.50 \times 10^{-10}$	Est.
30	HCO + OD	$\rightarrow$ HDO + CO	0.5	$\sqrt{\frac{29}{30}}$	$1.80 \times 10^{-10}$	Est.
31a	HD + O	$\rightarrow$ OD + H			$1.68 \times 10^{-12} e^{-4400/T_n}$	N15
31b		$\rightarrow$ OH + D			$4.40 \times 10^{-12} e^{-4390/T_n}$	N15
32	HO <sub>2</sub> + DO <sub>2</sub> + M	$\rightarrow$ HDO <sub>2</sub> + O <sub>2</sub> + M		$\sqrt{\frac{33}{34}}$	$4.20 \times 10^{-33} e^{920/T_n}$	Est.
33	HOCO + OD	$\rightarrow$ CO <sub>2</sub> + HDO		$\sqrt{\frac{17}{18}}$	$1.03 \times 10^{-11}$	Est.
34	O + D	$\rightarrow$ OD		$\sqrt{\frac{1}{2}}$	$8.65 \times 10^{-18} (\frac{T_n}{300})^{-0.38}$	Est.
35	O + DO <sub>2</sub>	$\rightarrow$ OD + O <sub>2</sub>		$\sqrt{\frac{33}{34}}$	$3.00 \times 10^{-11} e^{200/T_n}$	Est.
36a	O + HDO <sub>2</sub>	$\rightarrow$ OD + HO <sub>2</sub>	0.5	$\sqrt{\frac{34}{35}}$	$1.40 \times 10^{-12} e^{-2000/T_n}$	Est.
36b		$\rightarrow$ OH + DO <sub>2</sub>	0.5	$\sqrt{\frac{34}{35}}$	$1.40 \times 10^{-12} e^{-2000/T_n}$	Est.
37	O + OD	$\rightarrow$ O <sub>2</sub> + D		$\sqrt{\frac{17}{18}}$	$1.80 \times 10^{-11} e^{180/T_n}$	Est.
38a	O( <sup>1</sup> D) + HD	$\rightarrow$ D + OH			$4.92 \times 10^{-11}$	Y88
38b		$\rightarrow$ H + OD			$4.92 \times 10^{-11}$	Y88
39	O( <sup>1</sup> D) + HDO	$\rightarrow$ OD + OH		$\sqrt{\frac{18}{19}}$	$1.63 \times 10^{-10} e^{60/T_n}$	Est.
40	OD + H	$\rightarrow$ OH + D			$4.58 \times 10^{-9} (\frac{T_n}{300})^{-0.63} e^{-717/T_n}$	Y88
41	OD + H <sub>2</sub>	$\rightarrow$ HDO + H			$2.80 \times 10^{-12} e^{-1800/T_n}$	Y88
42	OD + H <sub>2</sub> O <sub>2</sub>	$\rightarrow$ HDO + HO <sub>2</sub>		$\sqrt{\frac{17}{18}}$	$2.90 \times 10^{-12} e^{-160/T_n}$	Est.
43	OD + HO <sub>2</sub>	$\rightarrow$ HDO + O <sub>2</sub>		$\sqrt{\frac{17}{18}}$	$4.80 \times 10^{-11} e^{250/T_n}$	Est.
44	OD + O <sub>3</sub>	$\rightarrow$ DO <sub>2</sub> + O <sub>2</sub>		$\sqrt{\frac{17}{18}}$	$1.70 \times 10^{-12} e^{-940/T_n}$	Est.
45a	OD + OH	$\rightarrow$ HDO + O		$\sqrt{\frac{17}{18}}$	$1.80 \times 10^{-12}$	Est.
45b		$\rightarrow$ HDO <sub>2</sub>		$\sqrt{\frac{17}{18}}$	See text $k_{\infty} = 2.60 \times 10^{-11}$ $k_0 = 2.69 \times 10^{-28} (\frac{T_n}{300})^{-1.0}$ $3.30 \times 10^{-9} (\frac{T_n}{300})^{-0.63}$	Est.
46	OH + D	$\rightarrow$ OD + H			$4.20 \times 10^{-13} e^{-1800/T_n}$	Y88
47	OH + DO <sub>2</sub>	$\rightarrow$ HDO + O <sub>2</sub>		$\sqrt{\frac{33}{34}}$	$4.80 \times 10^{-11} e^{250/T_n}$	Est.
48a	OH + HD	$\rightarrow$ H <sub>2</sub> O + D			$5.00 \times 10^{-12} e^{-2130/T_n}$	S11
48b		$\rightarrow$ HDO + H			$2.90 \times 10^{-12} e^{-160/T_n}$	Est.
49a	OH + HDO <sub>2</sub>	$\rightarrow$ H <sub>2</sub> O + DO <sub>2</sub>	0.5	$\sqrt{\frac{34}{35}}$	$2.90 \times 10^{-12} e^{-160/T_n}$	Est.
49b		$\rightarrow$ HDO + HO <sub>2</sub>	0.5	$\sqrt{\frac{34}{35}}$	$2.90 \times 10^{-12} e^{-160/T_n}$	Est.
Deuterated ion-neutral reactions						
50	ArD <sup>+</sup> + CO	$\rightarrow$ DCO <sup>+</sup> + Ar			$1.25 \times 10^{-9}$	A03

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		Reaction	BR	MS	Rate or rate coefficient	Ref
51	ArD <sup>+</sup> + CO <sub>2</sub>	$\rightarrow$ DCO <sub>2</sub> <sup>+</sup> + Ar			$1.10 \times 10^{-9}$	A03
52a	ArD <sup>+</sup> + H <sub>2</sub>	$\rightarrow$ ArH <sup>+</sup> + HD			$4.50 \times 10^{-10}$	A03
52b		$\rightarrow$ H <sub>2</sub> D <sup>+</sup> + Ar			$8.80 \times 10^{-10}$	A03
53	ArD <sup>+</sup> + N <sub>2</sub>	$\rightarrow$ N <sub>2</sub> D <sup>+</sup> + Ar			$6.00 \times 10^{-10}$	A03
54	ArH <sup>+</sup> + HD	$\rightarrow$ H <sub>2</sub> D <sup>+</sup> + Ar			$8.60 \times 10^{-10}$	A03
55a	Ar <sup>+</sup> + HD	$\rightarrow$ ArD <sup>+</sup> + H			$3.84 \times 10^{-10}$	A03
55b		$\rightarrow$ ArH <sup>+</sup> + D			$3.68 \times 10^{-10}$	A03
55c		$\rightarrow$ HD <sup>+</sup> + Ar			$4.80 \times 10^{-11}$	A03
56a	CO <sub>2</sub> <sup>+</sup> + D	$\rightarrow$ DCO <sup>+</sup> + O			$6.38 \times 10^{-11}$	A03
56b		$\rightarrow$ D <sup>+</sup> + CO <sub>2</sub>			$2.02 \times 10^{-11}$	A03
57a	CO <sub>2</sub> <sup>+</sup> + HD	$\rightarrow$ DCO <sub>2</sub> <sup>+</sup> + H	0.5	$\sqrt{\frac{2}{3}}$	$2.35 \times 10^{-10}$	Est.
57b		$\rightarrow$ HCO <sub>2</sub> <sup>+</sup> + D	0.5	$\sqrt{\frac{2}{3}}$	$2.35 \times 10^{-10}$	Est.
58a	CO <sub>2</sub> <sup>+</sup> + HDO	$\rightarrow$ DCO <sub>2</sub> <sup>+</sup> + OH	0.5	$\sqrt{\frac{18}{19}}$	$3.00 \times 10^{-10}$	Est.
58b		$\rightarrow$ HCO <sub>2</sub> <sup>+</sup> + OD	0.5	$\sqrt{\frac{18}{19}}$	$3.00 \times 10^{-10}$	Est.
58c		$\rightarrow$ HDO <sup>+</sup> + CO <sub>2</sub>		$\sqrt{\frac{18}{19}}$	$1.80 \times 10^{-9}$	Est.
59	CO <sup>+</sup> + D	$\rightarrow$ D <sup>+</sup> + CO			$9.00 \times 10^{-11}$	A03
60a	CO <sup>+</sup> + HD	$\rightarrow$ DCO <sup>+</sup> + H	0.25	$\sqrt{\frac{2}{3}}$	$7.50 \times 10^{-10}$	Est.
60b		$\rightarrow$ DOC <sup>+</sup> + H	0.25	$\sqrt{\frac{2}{3}}$	$7.50 \times 10^{-10}$	Est.
60c		$\rightarrow$ HCO <sup>+</sup> + D	0.25	$\sqrt{\frac{2}{3}}$	$7.50 \times 10^{-10}$	Est.
60d		$\rightarrow$ HOC <sup>+</sup> + D	0.25	$\sqrt{\frac{2}{3}}$	$7.50 \times 10^{-10}$	Est.
61a	CO <sup>+</sup> + HDO	$\rightarrow$ DCO <sup>+</sup> + OH	0.5	$\sqrt{\frac{18}{19}}$	$8.40 \times 10^{-10}$	Est.
61b		$\rightarrow$ HCO <sup>+</sup> + OD	0.5	$\sqrt{\frac{18}{19}}$	$8.40 \times 10^{-10}$	Est.
61c		$\rightarrow$ HDO <sup>+</sup> + CO		$\sqrt{\frac{18}{19}}$	$1.56 \times 10^{-9}$	Est.
62	C <sup>+</sup> + HD	$\rightarrow$ CH <sup>+</sup> + D	0.17		$1.20 \times 10^{-16}$	A03
63a	C <sup>+</sup> + HDO	$\rightarrow$ DCO <sup>+</sup> + H	0.5	$\sqrt{\frac{18}{19}}$	$7.80 \times 10^{-9} \left(\frac{T_i}{300}\right)^{-0.5}$	Est.
63b		$\rightarrow$ DOC <sup>+</sup> + H	0.5	$\sqrt{\frac{18}{19}}$	$1.08 \times 10^{-9}$	Est.
63c		$\rightarrow$ HCO <sup>+</sup> + D	0.5	$\sqrt{\frac{18}{19}}$	$7.80 \times 10^{-9} \left(\frac{T_i}{300}\right)^{-0.5}$	Est.
63d		$\rightarrow$ HDO <sup>+</sup> + C			$2.34 \times 10^{-10}$	Est.
63e		$\rightarrow$ HOC <sup>+</sup> + D	0.5	$\sqrt{\frac{18}{19}}$	$1.08 \times 10^{-9}$	Est.
64	DCO <sub>2</sub> <sup>+</sup> + CO	$\rightarrow$ DCO <sup>+</sup> + CO <sub>2</sub>		$\sqrt{\frac{45}{46}}$	$7.80 \times 10^{-10}$	Est.
65a	DCO <sub>2</sub> <sup>+</sup> + e <sup>-</sup>	$\rightarrow$ CO + O	0.68		$4.62 \times 10^{-5} \left(\frac{T_i}{300}\right)^{-0.64}$	G05
65b		$\rightarrow$ CO + OD	0.27		$4.62 \times 10^{-5} \left(\frac{T_i}{300}\right)^{-0.64}$	G05
65c		$\rightarrow$ CO <sub>2</sub> + D	0.05		$4.62 \times 10^{-5} \left(\frac{T_i}{300}\right)^{-0.64}$	G05
66	DCO <sub>2</sub> <sup>+</sup> + H <sub>2</sub> O	$\rightarrow$ H <sub>2</sub> DO <sup>+</sup> + CO <sub>2</sub>		$\sqrt{\frac{45}{46}}$	$2.65 \times 10^{-9}$	Est.
67	DCO <sub>2</sub> <sup>+</sup> + O	$\rightarrow$ DCO <sup>+</sup> + O <sub>2</sub>		$\sqrt{\frac{45}{46}}$	$5.80 \times 10^{-10}$	Est.
68a	DCO <sup>+</sup> + e <sup>-</sup>	$\rightarrow$ CO + D	0.92		$9.02 \times 10^{-5} \left(\frac{T_i}{300}\right)^{-1.1}$	GK
68b		$\rightarrow$ OD + C	0.07		$9.02 \times 10^{-5} \left(\frac{T_i}{300}\right)^{-1.1}$	GK
69	DCO <sup>+</sup> + H	$\rightarrow$ HCO <sup>+</sup> + D			$1.50 \times 10^{-11}$	A03
70	DCO <sup>+</sup> + H <sub>2</sub> O	$\rightarrow$ H <sub>2</sub> DO <sup>+</sup> + CO		$\sqrt{\frac{29}{30}}$	$2.60 \times 10^{-9}$	Est.
71	DOC <sup>+</sup> + CO	$\rightarrow$ DCO <sup>+</sup> + CO		$\sqrt{\frac{29}{30}}$	$6.00 \times 10^{-10}$	Est.

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		Reaction	BR	MS	Rate or rate coefficient	Ref
72	$\text{DOC}^+ + \text{e}^-$	$\rightarrow \text{OD} + \text{C}$		$\sqrt{\frac{29}{30}}$	$1.19 \times 10^{-8} \left(\frac{T_i}{300}\right)^{1.2}$	Est.
73a	$\text{DOC}^+ + \text{H}_2$	$\rightarrow \text{H}_2\text{D}^+ + \text{CO}$	0.57		$6.20 \times 10^{-10}$	A03
73b		$\rightarrow \text{HCO}^+ + \text{HD}$	0.43		$6.20 \times 10^{-10}$	A03
74a	$\text{D}^+ + \text{CO}_2$	$\rightarrow \text{CO}_2^+ + \text{D}$			$3.50 \times 10^{-9}$	A03
74b		$\rightarrow \text{DCO}^+ + \text{O}$			$2.60 \times 10^{-9}$	A03
75	$\text{D}^+ + \text{H}$	$\rightarrow \text{D} + \text{H}^+$	0.87		$6.50 \times 10^{-11} \left(\frac{T_i}{300}\right)^{0.5}$	Y89
76	$\text{D}^+ + \text{H}_2$	$\rightarrow \text{H}^+ + \text{HD}$			$2.20 \times 10^{-9}$	A03
77a	$\text{D}^+ + \text{H}_2\text{O}$	$\rightarrow \text{H}_2\text{O}^+ + \text{D}$			$5.20 \times 10^{-9}$	A03
77b		$\rightarrow \text{HDO}^+ + \text{H}$	0.5	$\sqrt{\frac{1}{2}}$	$8.20 \times 10^{-9}$	Est.
78	$\text{D}^+ + \text{NO}$	$\rightarrow \text{NO}^+ + \text{D}$			$1.80 \times 10^{-9}$	A03
79	$\text{D}^+ + \text{O}$	$\rightarrow \text{D} + \text{O}^+$			$2.80 \times 10^{-10}$	A03
80	$\text{D}^+ + \text{O}_2$	$\rightarrow \text{O}_2^+ + \text{D}$			$1.60 \times 10^{-9}$	A03
81a	$\text{H}_2\text{DO}^+ + \text{e}^-$	$\rightarrow \text{H}_2 + \text{O}$	0.5	$\sqrt{\frac{19}{20}}$	$9.68 \times 10^{-8} \left(\frac{T_i}{300}\right)^{-0.5}$	Est.
81b		$\rightarrow \text{H}_2\text{O} + \text{D}$	0.5	$\sqrt{\frac{19}{20}}$	$1.86 \times 10^{-6} \left(\frac{T_i}{300}\right)^{-0.5}$	Est.
81c		$\rightarrow \text{HD} + \text{O}$	0.5	$\sqrt{\frac{19}{20}}$	$9.68 \times 10^{-8} \left(\frac{T_i}{300}\right)^{-0.5}$	Est.
81d		$\rightarrow \text{HDO} + \text{H}$	0.5	$\sqrt{\frac{19}{20}}$	$1.86 \times 10^{-6} \left(\frac{T_i}{300}\right)^{-0.5}$	Est.
81e		$\rightarrow \text{OD} + \text{H}$	0.5	$\sqrt{\frac{19}{20}}$	$4.47 \times 10^{-6} \left(\frac{T_i}{300}\right)^{-0.5}$	Est.
81f		$\rightarrow \text{OD} + \text{H}_2$	0.5	$\sqrt{\frac{19}{20}}$	$1.04 \times 10^{-6} \left(\frac{T_i}{300}\right)^{-0.5}$	Est.
81g		$\rightarrow \text{OH} + \text{D}$	0.5	$\sqrt{\frac{19}{20}}$	$4.47 \times 10^{-6} \left(\frac{T_i}{300}\right)^{-0.5}$	Est.
81h		$\rightarrow \text{OH} + \text{HD}$	0.5	$\sqrt{\frac{19}{20}}$	$1.04 \times 10^{-6} \left(\frac{T_i}{300}\right)^{-0.5}$	Est.
82a	$\text{H}_2\text{D}^+ + \text{CO}$	$\rightarrow \text{DCO}^+ + \text{H}_2$	0.33		$1.60 \times 10^{-9}$	A03
82b		$\rightarrow \text{HCO}^+ + \text{HD}$	0.67		$1.60 \times 10^{-9}$	A03
83	$\text{H}_2\text{D}^+ + \text{H}_2$	$\rightarrow \text{H}_3^+ + \text{HD}$			$5.30 \times 10^{-10}$	A03
84a	$\text{H}_2\text{O}^+ + \text{HD}$	$\rightarrow \text{H}_2\text{DO}^+ + \text{H}$	0.5	$\sqrt{\frac{2}{3}}$	$3.80 \times 10^{-10}$	Est.
84b		$\rightarrow \text{H}_3\text{O}^+ + \text{D}$	0.5	$\sqrt{\frac{2}{3}}$	$3.80 \times 10^{-10}$	Est.
85	$\text{HCO}_2^+ + \text{HDO}$	$\rightarrow \text{H}_2\text{DO}^+ + \text{CO}_2$		$\sqrt{\frac{18}{19}}$	$2.65 \times 10^{-9}$	Est.
86	$\text{HCO}^+ + \text{D}$	$\rightarrow \text{DCO}^+ + \text{H}$			$4.25 \times 10^{-11}$	A03
87	$\text{HCO}^+ + \text{HDO}$	$\rightarrow \text{H}_2\text{DO}^+ + \text{CO}$		$\sqrt{\frac{18}{19}}$	$2.60 \times 10^{-9}$	Est.
88a	$\text{HDO}^+ + \text{CO}$	$\rightarrow \text{DCO}^+ + \text{OH}$	0.5	$\sqrt{\frac{18}{19}}$	$2.12 \times 10^{-10}$	Est.
88b		$\rightarrow \text{HCO}^+ + \text{OD}$	0.5	$\sqrt{\frac{18}{19}}$	$2.12 \times 10^{-10}$	Est.
89a	$\text{HDO}^+ + \text{e}^-$	$\rightarrow \text{HD} + \text{O}$		$\sqrt{\frac{18}{19}}$	$2.64 \times 10^{-6} \left(\frac{T_i}{300}\right)^{-0.74}$	Est.
89b		$\rightarrow \text{O} + \text{D}$		$\sqrt{\frac{18}{19}}$	$2.08 \times 10^{-5} \left(\frac{T_i}{300}\right)^{-0.74}$	Est.
89c		$\rightarrow \text{OD} + \text{H}$	0.5	$\sqrt{\frac{18}{19}}$	$5.86 \times 10^{-6} \left(\frac{T_i}{300}\right)^{-0.74}$	Est.
89d		$\rightarrow \text{OH} + \text{D}$	0.5	$\sqrt{\frac{18}{19}}$	$5.86 \times 10^{-6} \left(\frac{T_i}{300}\right)^{-0.74}$	Est.
90a	$\text{HDO}^+ + \text{H}_2$	$\rightarrow \text{H}_2\text{DO}^+ + \text{H}$	0.5	$\sqrt{\frac{18}{19}}$	$3.80 \times 10^{-10}$	Est.
90b		$\rightarrow \text{H}_3\text{O}^+ + \text{D}$	0.5	$\sqrt{\frac{18}{19}}$	$3.80 \times 10^{-10}$	Est.
91a	$\text{HDO}^+ + \text{N}$	$\rightarrow \text{HNO}^+ + \text{D}$	0.5	$\sqrt{\frac{18}{19}}$	$5.60 \times 10^{-11}$	Est.
91b		$\rightarrow \text{NO}^+ + \text{HD}$		$\sqrt{\frac{18}{19}}$	$2.80 \times 10^{-11}$	Est.
92	$\text{HDO}^+ + \text{NO}$	$\rightarrow \text{NO}^+ + \text{HDO}$		$\sqrt{\frac{18}{19}}$	$4.60 \times 10^{-10}$	Est.

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		Reaction	BR	MS	Rate or rate coefficient	Ref
93	HDO <sup>+</sup> + O	$\rightarrow \text{O}_2^+ + \text{HD}$		$\sqrt{\frac{18}{19}}$	$4.00 \times 10^{-11}$	Est.
94	HDO <sup>+</sup> + O <sub>2</sub>	$\rightarrow \text{O}_2^+ + \text{HDO}$		$\sqrt{\frac{18}{19}}$	$3.30 \times 10^{-10}$	Est.
95a	HD <sup>+</sup> + Ar	$\rightarrow \text{ArD}^+ + \text{H}$	0.45	$\sqrt{\frac{2}{3}}$	$2.10 \times 10^{-9}$	A03
95b		$\rightarrow \text{ArH}^+ + \text{D}$	0.55	$\sqrt{\frac{2}{3}}$	$2.10 \times 10^{-9}$	Est.
96a	HD <sup>+</sup> + CO	$\rightarrow \text{DCO}^+ + \text{H}$	0.5	$\sqrt{\frac{2}{3}}$	$1.45 \times 10^{-9}$	Est.
96b		$\rightarrow \text{HCO}^+ + \text{D}$	0.5	$\sqrt{\frac{2}{3}}$	$1.45 \times 10^{-9}$	Est.
97a	HD <sup>+</sup> + CO <sub>2</sub>	$\rightarrow \text{DCO}_2^+ + \text{H}$	0.5	$\sqrt{\frac{2}{3}}$	$1.17 \times 10^{-9}$	Est.
97b		$\rightarrow \text{HCO}_2^+ + \text{D}$	0.5	$\sqrt{\frac{2}{3}}$	$1.17 \times 10^{-9}$	Est.
98	HD <sup>+</sup> + e <sup>-</sup>	$\rightarrow \text{H} + \text{D}$			$1.93 \times 10^{-6} \left(\frac{T_i}{300}\right)^{-0.853} e^{-43.3/T_i}$	K19
99	HD <sup>+</sup> + HD	$\rightarrow \text{H}_2\text{D}^+ + \text{D}$			$8.42 \times 10^{-10}$	A03
100a	HD <sup>+</sup> + N <sub>2</sub>	$\rightarrow \text{N}_2\text{D}^+ + \text{H}$	0.5	$\sqrt{\frac{2}{3}}$	$1.00 \times 10^{-9}$	Est.
100b		$\rightarrow \text{N}_2\text{H}^+ + \text{D}$	0.5	$\sqrt{\frac{2}{3}}$	$1.00 \times 10^{-9}$	Est.
101a	HD <sup>+</sup> + O	$\rightarrow \text{OD}^+ + \text{H}$	0.5	$\sqrt{\frac{2}{3}}$	$7.50 \times 10^{-10}$	Est.
101b		$\rightarrow \text{OH}^+ + \text{D}$	0.5	$\sqrt{\frac{2}{3}}$	$7.50 \times 10^{-10}$	Est.
102	HD <sup>+</sup> + O <sub>2</sub>	$\rightarrow \text{HO}_2^+ + \text{D}$	0.5	$\sqrt{\frac{2}{3}}$	$9.60 \times 10^{-10}$	Est.
103	H <sup>+</sup> + HD	$\rightarrow \text{D}^+ + \text{H}_2$			$1.10 \times 10^{-10}$	A03
104a	H <sup>+</sup> + HDO	$\rightarrow \text{H}_2\text{O}^+ + \text{D}$	0.5	$\sqrt{\frac{18}{19}}$	$8.20 \times 10^{-9}$	Est.
104b		$\rightarrow \text{HDO}^+ + \text{H}$	0.5	$\sqrt{\frac{18}{19}}$	$8.20 \times 10^{-9}$	Est.
105	N <sub>2</sub> D <sup>+</sup> + CO	$\rightarrow \text{DCO}^+ + \text{N}_2$		$\sqrt{\frac{29}{30}}$	$8.80 \times 10^{-10}$	Est.
106	N <sub>2</sub> D <sup>+</sup> + e <sup>-</sup>	$\rightarrow \text{N}_2 + \text{D}$		$\sqrt{\frac{29}{30}}$	$6.60 \times 10^{-7} \left(\frac{T_i}{300}\right)^{-0.51}$	Est.
107	N <sub>2</sub> D <sup>+</sup> + H	$\rightarrow \text{N}_2\text{H}^+ + \text{D}$			$2.50 \times 10^{-11}$	A03
108	N <sub>2</sub> D <sup>+</sup> + O	$\rightarrow \text{OD}^+ + \text{N}_2$		$\sqrt{\frac{29}{30}}$	$1.40 \times 10^{-10}$	Est.
109	N <sub>2</sub> H <sup>+</sup> + D	$\rightarrow \text{N}_2\text{D}^+ + \text{H}$			$8.00 \times 10^{-11}$	A03
110	N <sub>2</sub> <sup>+</sup> + D	$\rightarrow \text{D}^+ + \text{N}_2$			$1.20 \times 10^{-10}$	A03
111a	N <sub>2</sub> <sup>+</sup> + HD	$\rightarrow \text{N}_2\text{D}^+ + \text{H}$	0.51		$1.34 \times 10^{-9}$	A03
111b		$\rightarrow \text{N}_2\text{H}^+ + \text{D}$	0.49		$1.34 \times 10^{-9}$	A03
112a	N <sub>2</sub> <sup>+</sup> + HDO	$\rightarrow \text{HDO}^+ + \text{N}_2$		$\sqrt{\frac{18}{19}}$	$1.90 \times 10^{-9}$	Est.
112b		$\rightarrow \text{N}_2\text{D}^+ + \text{OH}$	0.5	$\sqrt{\frac{18}{19}}$	$5.04 \times 10^{-10}$	Est.
112c		$\rightarrow \text{N}_2\text{H}^+ + \text{OD}$	0.5	$\sqrt{\frac{18}{19}}$	$5.04 \times 10^{-10}$	Est.
113	N <sup>+</sup> + HD	$\rightarrow \text{NH}^+ + \text{D}$	0.25		$3.10 \times 10^{-10}$	A03
114	OD <sup>+</sup> + CO	$\rightarrow \text{DCO}^+ + \text{O}$		$\sqrt{\frac{17}{18}}$	$8.40 \times 10^{-10}$	Est.
115	OD <sup>+</sup> + CO <sub>2</sub>	$\rightarrow \text{DCO}_2^+ + \text{O}$		$\sqrt{\frac{17}{18}}$	$1.35 \times 10^{-9}$	Est.
116	OD <sup>+</sup> + e <sup>-</sup>	$\rightarrow \text{O} + \text{D}$		$\sqrt{\frac{17}{18}}$	$6.50 \times 10^{-7} \left(\frac{T_i}{300}\right)^{-0.5}$	Est.
117a	OD <sup>+</sup> + H <sub>2</sub>	$\rightarrow \text{H}_2\text{O}^+ + \text{D}$	0.5	$\sqrt{\frac{17}{18}}$	$9.70 \times 10^{-10}$	Est.
117b		$\rightarrow \text{HDO}^+ + \text{H}$	0.5	$\sqrt{\frac{17}{18}}$	$9.70 \times 10^{-10}$	Est.
118	OD <sup>+</sup> + N	$\rightarrow \text{NO}^+ + \text{D}$		$\sqrt{\frac{17}{18}}$	$8.90 \times 10^{-10}$	Est.
119	OD <sup>+</sup> + N <sub>2</sub>	$\rightarrow \text{N}_2\text{D}^+ + \text{O}$		$\sqrt{\frac{17}{18}}$	$2.40 \times 10^{-10}$	Est.
120	OD <sup>+</sup> + O	$\rightarrow \text{O}_2^+ + \text{D}$		$\sqrt{\frac{17}{18}}$	$7.10 \times 10^{-10}$	Est.
121	OD <sup>+</sup> + O <sub>2</sub>	$\rightarrow \text{O}_2^+ + \text{OD}$		$\sqrt{\frac{17}{18}}$	$3.80 \times 10^{-10}$	Est.

Continued on next page

	Reaction	BR	MS	Rate or rate coefficient	Ref
122a	$\text{OH}^+ + \text{HD} \rightarrow \text{H}_2\text{O}^+ + \text{D}$		$\sqrt{\frac{2}{3}}$	$9.70 \times 10^{-10}$	Est.
122b	$\rightarrow \text{HDO}^+ + \text{H}$		$\sqrt{\frac{2}{3}}$	$9.70 \times 10^{-10}$	Est.
123	$\text{O}^+ + \text{D} \rightarrow \text{D}^+ + \text{O}$		$\sqrt{\frac{1}{2}}$	$6.40 \times 10^{-10}$	Est.
124a	$\text{O}^+ + \text{HD} \rightarrow \text{OD}^+ + \text{H}$	0.46		$1.25 \times 10^{-9}$	A03
124b	$\rightarrow \text{OH}^+ + \text{D}$	0.54		$1.25 \times 10^{-9}$	A03
125	$\text{O}^+ + \text{HDO} \rightarrow \text{HDO}^+ + \text{O}$		$\sqrt{\frac{18}{19}}$	$2.60 \times 10^{-9}$	Est.

NL84: Nee and Lee (1984). Y88: Anicich (2003). Y89: Yung et al. (1989). A03: Anicich (2003).  
C0499: Cheng et al. (2004); Cheng et al. (1999). G05: Geppert et al. (2005). K09: Korolov et al. (2009).  
GK: Rate from K09, branching ratio from G05. C10: Cazaux et al. (2010). S11: Sander et al. (2011).  
N: Manion et al. (2015). K19: Wakelam and Gratier (2019). Est: Estimated with mass scaling.  
†: Assumed same as H-analogue.

**Photodissociation and photoionization:** Photodissociation and ionization of deuterated species is calculated using the solar spectrum (see Section 2.2.2), so the entry in the table under ‘Rate or rate coefficient’ represents the integrated column rate. The ‘Ref’ column refers to the source of the cross sections used. For photoionization cross sections of the H-analogue reactions, see Vuitton et al. (2019, and references therein).

**Neutral and ion bimolecular and termolecular reactions:** The rate coefficient used for a given reaction is the product of the ‘BR’, ‘MS’ and ‘Rate coefficient’ columns (empty fields are taken to be 1). ‘BR’, or branching ratio, accounts for the fact that deuteration of a reaction can create two or more branches with differing products where only one branch would exist for the H-analogue reaction. ‘MS’, or mass scaling, is a scaling factor equal to the square root of the mass ratio,  $\sqrt{m_1/m_2}$ , where  $m_2$  is the mass of the deuterated species and  $m_1$  the H-bearing species. This factor is applied to reactions for which we were not able to find a measurement in the literature to account for replacement of one reactant H atom with one D atom; a similar approach was used previously by V. A. Krasnopolsky (2002) for reactions of neutral HD with dominant ions and minor H-bearing ions.

Most reactions in these tables proceed using the listed rate coefficients. A few exceptions apply; the categorization Types and formulae mentioned below are the same as used by Vuitton et al. (2019). A more complete description of the formulae used can be found in their Appendix B.

*Reaction 7:* Similar to its analogue  $\text{CO} + \text{H} \rightarrow \text{HCO}$ , this is a Type 4 (pressure dependent association) reaction. The Troe parameter for this reaction is 0, so we use the form:

$$k = k_R + \frac{(Mk_0k_\infty)}{Mk_0 + k_\infty} \quad (1)$$

Where  $k_R$  is 0 in this case and M is the background atmospheric density.

*Reactions 8a, 8b, 12, and 45b:* These are Type 6 ( $\text{CO} + \text{OD} \rightarrow \text{CO}_2 + \text{D}$ ) and Type 5 ( $\text{CO} + \text{OH} \rightarrow \text{DOC}_2$ ,  $\text{D} + \text{O}_2 \rightarrow \text{DO}_2$ ,  $\text{OD} + \text{OH} \rightarrow \text{HDO}_2$ ) pressure dependent bimolecular reactions, with the formulae originally given by Burkholder et al. (2019); Sander et al. (2011). We use the same forms here, but multiplied by our mass scaling factor.

167 Ion reactions which produce a lone D or H atom have the potential to cause the produced  
 168 atom to be “hot”, that is, gaining enough excess energy from the reaction that they can  
 169 escape. We describe this in more detail in Section 2.1.4.

### 170 **2.1.2 Ambipolar diffusion**

171 The model employs ambipolar diffusion for all ions, using the Langevin-Gioumousis-Stevenson  
 172 equation (Bauer, 1973):

$$D_{ai} = \frac{k(T_i + T_e)}{m_i \sum \nu_{ij}} \quad (2)$$

$$\nu_{ij} = 2\pi \left( \frac{\alpha_j e^2}{\mu_{ij}} \right)^{1/2} n_j \quad (3)$$

173 Where  $D_{ai}$  is the ambipolar diffusion coefficient for ion  $i$ ,  $\nu_{ij}$  is the collision frequency  
 174 of ion  $i$  with neutral  $j$ ,  $\alpha_j$  is the polarizability,  $e$  is the fundamental charge, and  $n$  is the  
 175 neutral density. Polarizability values for neutrals are collected from Manion et al. (2015).  
 176 Where polarizability was not available either in data or models for a deuterated species  
 177 we include, we assumed the same value as the H-bearing analogue.

### 178 **2.1.3 Partially fixed water profile**

179 We assume a constant abundance of water in the lower atmosphere, which approximates  
 180 the average water available due to seasonal cycles of polar cap sublimation and trans-  
 181 port. The mixing ratio is  $1.3 \times 10^{-4}$  up to the hygropause (which we take to be 40 km,  
 182 between 25 km by V. A. Krasnopolsky (2002) and its enhanced altitude of 50-80 km dur-  
 183 ing dust storms (Heavens et al., 2018)). The hygropause on Mars represents the altitude  
 184 at which water begins to condense; in our model, which does not include microphysics  
 185 or phase changes, the hygropause altitude is the point at which the water mixing ratio  
 186 begins to follows the saturation vapor pressure curve. At 72 km, a minimum of satura-  
 187 tion is reached; above that level, the abundance of water is a free variable. This allows  
 188 a more holistic understanding of water and water ion chemistry in the upper atmosphere,  
 189 which has been shown to be an important tracer of seasonal H escape (Stone et al., 2020).  
 190 The total amount of water in the atmosphere is 10.5 pr  $\mu\text{m}$ , in accordance with obser-  
 191 vations (Smith, 2004; Lammer et al., 2003).

### 192 **2.1.4 Non-thermal escape**

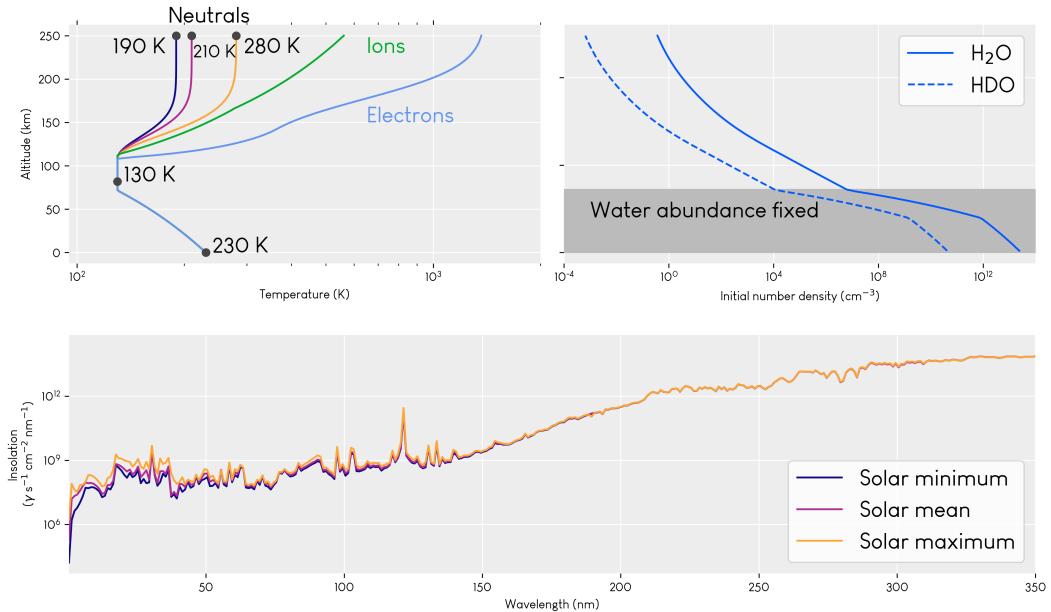
193 Although there are many non-thermal escape mechanisms, in this work, we focus on pho-  
 194 tochemical loss, i.e. the contribution to escape from chemistry and photochemistry. We  
 195 neglect processes involving the solar wind such as sputtering, ion pickup, and charge ex-  
 196 change with the solar wind. Processes which depend upon the solar wind will primar-  
 197 ily occur above the bow shock (which is far above our top boundary), where the solar  
 198 wind can interact with the corona before being mostly deflected around the planet (Halekas  
 199 et al., 2017). By focusing on planetary ionospheric reactions, we capture the non-thermal  
 200 escape of H and D sourced from the atmosphere below the exobase.

201 We calculate the non-thermal escape of hot atoms created via ion-neutral chemistry as  
 202 the product of the probability of escape and the volume production rate of hot atoms  
 203 using the procedure described by Gregory et al. (2022). We have evaluated all ion-neutral  
 204 reactions that produce H, D,  $\text{H}_2$ , or HD in the model for their exothermicity (following  
 205 Fox (2015)) and only use those where the excess energy exceeds the escape velocity en-  
 206 ergy. In reality, the excess heat produced can be split between the two products accord-  
 207 ing to conservation of energy. Information about these heat branching ratios is sparse,  
 208 even for H species; for this reason, we assume that all excess energy produced ends up  
 209 in the atomic H or D (see the Supporting Information). We use the escape probability  
 210 curve calculated by Gregory et al. (2022) for a particle of excess energy 5 eV; this is a  
 211 reasonable approximation of the actual mean excess energy in our model, with is 3.6 eV.

The resulting volume escape rate can be integrated to obtain an escape flux for the top boundary of the model. Although our focus is escape of atomic H and D, some loss does occur via loss of the molecular form, so we also include non-thermal escape of  $\text{H}_2$  and HD. In these cases, we assume that  $\sigma_{\text{H}_2}$  is the same as for D due to the similar masses, and that  $\sigma_{\text{HD}}$  is larger than  $\text{H}_2$  by the same amount that D is larger than H.

## 2.2 Model inputs

Because the importance of non-thermal escape is expected to vary with solar activity, we have constructed three sets of inputs representing solar minimum, mean, and maximum conditions. The only properties which we vary between these cases are the neutral exobase temperatures and the incoming solar flux. Figure 1 shows these inputs in the navy, purple, and yellow colors. The inputs represent a dayside mean atmosphere (solar zenith angle [SZA]= $60^\circ$ ).



**Figure 1.** Main model inputs. a) Temperature profiles, with separate neutral exobase temperatures for each solar condition. Ion and electron temperatures are fits to data from MAVEN/STATIC as reported by Hanley et al. (2022) and MAVEN/LPW as reported by Ergun et al. (2015). b) Initial water profile. Above 72 km, water densities evolve according to the chemistry and transport. c) Insolation profiles from 0–300 nm for solar minimum, mean, and maximum. The full input spectrum goes out to 2400 nm, but the insolation there is relatively flat, with no variation due to solar cycle.

### 2.2.1 Atmospheric temperature profiles

Standard neutral temperatures were obtained from the Mars Climate Database (Millour & Forget, 2018) by several layers of averaging, in order of first to last: by longitude, local time (9, 12, and 3 pm local times, night excluded), latitude (weighted by encompassed surface area), and  $L_s$ . Over the solar cycle, the only significant change is to the exobase temperature, so we hold the surface and mesospheric temperature constant at 230 K and 130 K respectively.

In order to support modeling of ion chemistry, we use a piecewise fit to the new ion temperature profiles obtained at SZA= $60^\circ$  with the STATIC instrument by Hanley et al. (2022). These new data have overturned long-standing assumptions that the neutrals, ions, and

234 electrons thermalize to the same temperature around 125 km (Schunk & Nagy, 2009),  
 235 and thus represent a significant update in Mars photochemistry. We also include a fit  
 236 to the electron profile from MAVEN/LPW (Ergun et al., 2015). Because it is difficult  
 237 to associate ion temperatures with contemporary neutral temperatures due to the av-  
 238 eraging required for the neutral profiles, and because the data are limited in time, we  
 239 do not change the ion or electron profiles for the different solar cycle scenarios, although  
 240 in the real atmosphere, enhanced solar activity would likely lead to enhanced ion and  
 241 electron temperatures.

### 242 **2.2.2 Insolation**

243 Incoming solar photons are key reactants in photochemical reactions. For each solar case,  
 244 we include photon fluxes from 0.5–2400 nm, binned in 1 nm increments. Total flux, once  
 245 obtained, is scaled to Mars’ orbit and SZA=60°.

246 We determined the dates of recent representative solar conditions by looking for peri-  
 247 ods when Ly  $\alpha$  irradiance in the Lyman-alpha Model Solar Spectral Irradiance data set  
 248 (Woods et al., 2019) reached a peak, average, or trough. Because solar maximum and  
 249 mean in recent decades have been historically quiet, we chose dates from the early 2000s  
 250 to get a more representative photon flux for maximum and mean (solar minimum has  
 251 not changed much). The dates we used were February 25, 2019 for solar minimum; Febru-  
 252 ary 7, 2004 for mean; and March 22, 2002 for maximum.

253 For the insolation flux data, we use SORCE/SOLSTICE at solar minimum and mean,  
 254 and a mix of SORCE/SOLSTICE and TIMED/SEE at solar maximum. There is an ad-  
 255 dditional complication for solar maximum: SORCE/SOLSTICE began a year after our  
 256 solar maximum date, but includes the longer wavelengths we need, while TIMED/SEE  
 257 began before our solar maximum date, but only includes fluxes at wavelengths shortwards  
 258 of 190 nm. We patched together these two datasets, using SORCE/SOLSTICE for wave-  
 259 lengths 190–2000 nm from June 4, 2015 and TIMED/SEE for wavelengths 0.5–189.5 nm  
 260 from March 22, 2002.

261 Figure 1a shows the fluxes only from 0.5 to 300 nm for simplicity; longwards of 300 nm,  
 262 the profile does not vary over the solar cycle. The region shortward of 300 nm is also more  
 263 important for photochemistry as the photodissociation and photoionization cross sec-  
 264 tions are largest there. We use the same cross sections as Cangi et al. (2020), with the  
 265 addition of new photoionization and a few neutral photodissociation cross sections, the  
 266 same used by Vuitton et al. (2019).

### 267 **2.3 Boundary conditions**

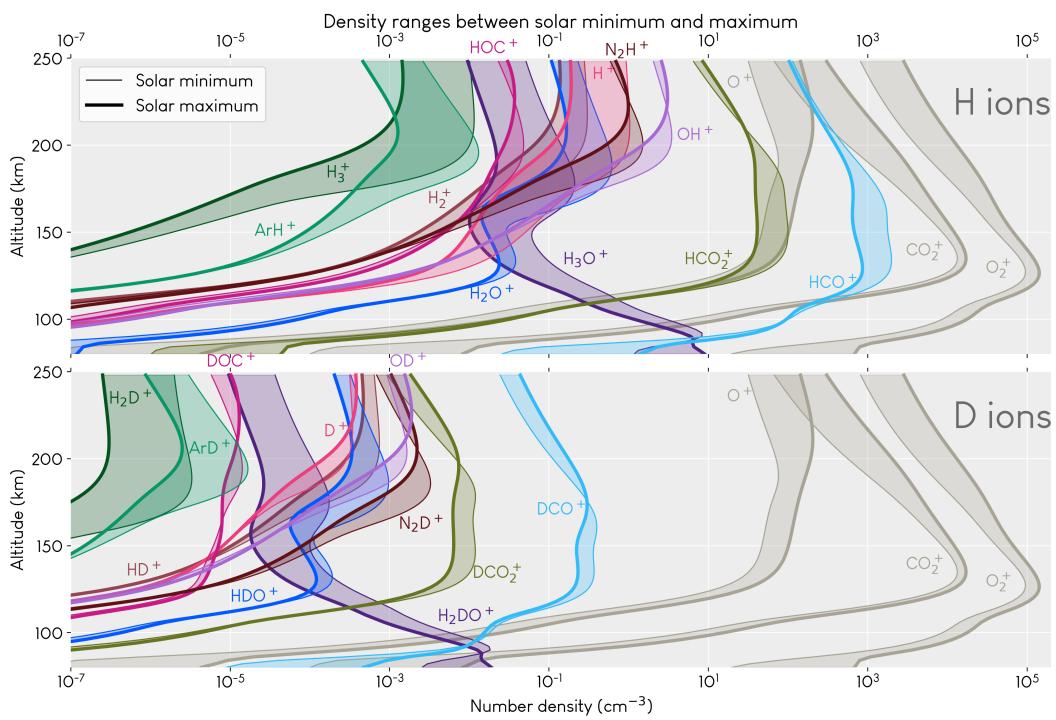
268 We use mostly the same boundary conditions as Cangi et al. (2020). The key addition  
 269 is an additional non-thermal flux boundary condition at the top of the model for H, D,  
 270 H<sub>2</sub>, and HD, according to the functional form described by (Gregory et al., 2022). Flux  
 271 is zero at the top and bottom of the model for all ion species and any neutral species with-  
 272 out a different boundary condition.

273 It is worth emphasizing that our flux boundary condition at the top of the model for atomic  
 274 O is fixed at  $1.2 \times 10^8 \text{ cm}^{-2}\text{s}^{-1}$ . Over long simulation times where the atmosphere reaches  
 275 equilibrium, the sum  $\phi_H + \phi_D$  will naturally evolve to equal twice the O escape flux, since  
 276 H<sub>2</sub>O and HDO are the primary source of H and D in the model. This is a feature of the  
 277 atmosphere in long-term equilibrium, but it does not necessarily occur over shorter timescales—  
 278 either on the real Mars or in the model.

## 279 **3 Results**

### 280 **3.1 What are the atmospheric densities of deuterated ions?**

281 The general distribution of the deuterated ionospheric species is similar to that of their  
 282 H-analogues. Vertical profiles for select species containing H or D are shown in Figure  
 283 2. Although they are calculated from surface to 250 km, the figure’s lower boundary is



**Figure 2.** Densities of a) H-bearing ions and b) D-bearing (deuterated). Density ranges are bounded by their values at solar minimum (thin line) and solar maximum (thick line). Gray lines show the primary ionospheric species for comparison. For most species and at most altitudes, densities at solar mean fall within these ranges.

placed at 80 km for legibility. The full image from surface to 250 km showing all species in the model appears in the Supporting Information (Figure S1).

Primary peaks in the densities of deuterated ions occur between 150 and 200 km, with a minor peak near the top of the mesosphere, around 90–125 km. This structure does not hold for all species.  $\text{H}_3\text{O}^+$  has its peak much lower down at about 90 km, which is in agreement with previous modeling (Fox et al., 2015; Molina-Cuberos et al., 2002). Unfortunately, comparisons with data are not feasible at this altitude because such data do not exist. Most ionic species, H- and D-bearing alike, also display a slight dip in density around 150 km, which is caused by a feature of the same shape in the electron temperature profile (see Figure 1a).

At solar maximum, greater insolation at short wavelengths enables more photoionization, increasing the abundances of primary species  $\text{CO}_2^+$ ,  $\text{O}_2^+$ , and  $\text{O}^+$  which are produced directly from the parent neutrals. But for the lighter (and often more minor) ions containing H and D, chemistry and/or transport is a more important driver than photoionization. Temperature-driven changes in the parent neutral densities propagate through to their ions; for example,  $\text{H}^+$  abundance at the top of the atmosphere decreases as the temperature goes up because H escape is diffusion-limited, whereas the same is not true for D abundance (Cangi et al., 2020; Zahnle et al., 2008). For other minor species that are not diffusion-limited, higher temperatures can also stimulate faster chemical reactions, slightly enhancing production and therefore density at higher temperatures.

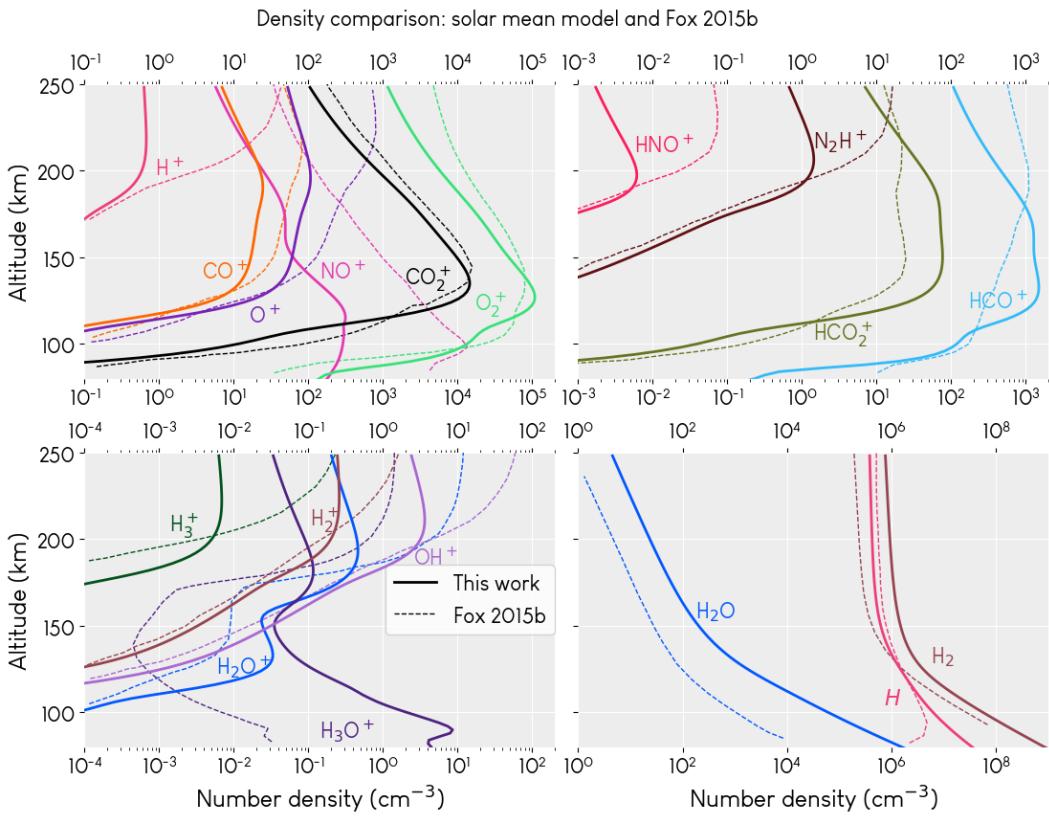
### 3.1.1 Comparisons with previous works

Here, we compare our results to modeling results by Fox et al. (2015, 2021) and measurements by MAVEN NGIMS (Benna et al., 2015; Fox et al., 2021). In this work, we have parameterized our atmosphere in order to obtain an understanding of the mean-field behavior in time and space. We have not attempted to match the same the modeling input or the relevant atmospheric conditions of those studies. Our models differ substantially from those by Fox et al. (2021, 2015) in temperature structure, boundary conditions (especially for ions at the upper boundary), vertical extent, use of photochemical equilibrium, background atmosphere, SZA, included species, mean Mars-Sun distance, assumed eddy diffusion profile, and included processes (we do not model electron impact ionization or dissociation). Because of these differences, we provide these comparisons primarily for the reader's orientation.

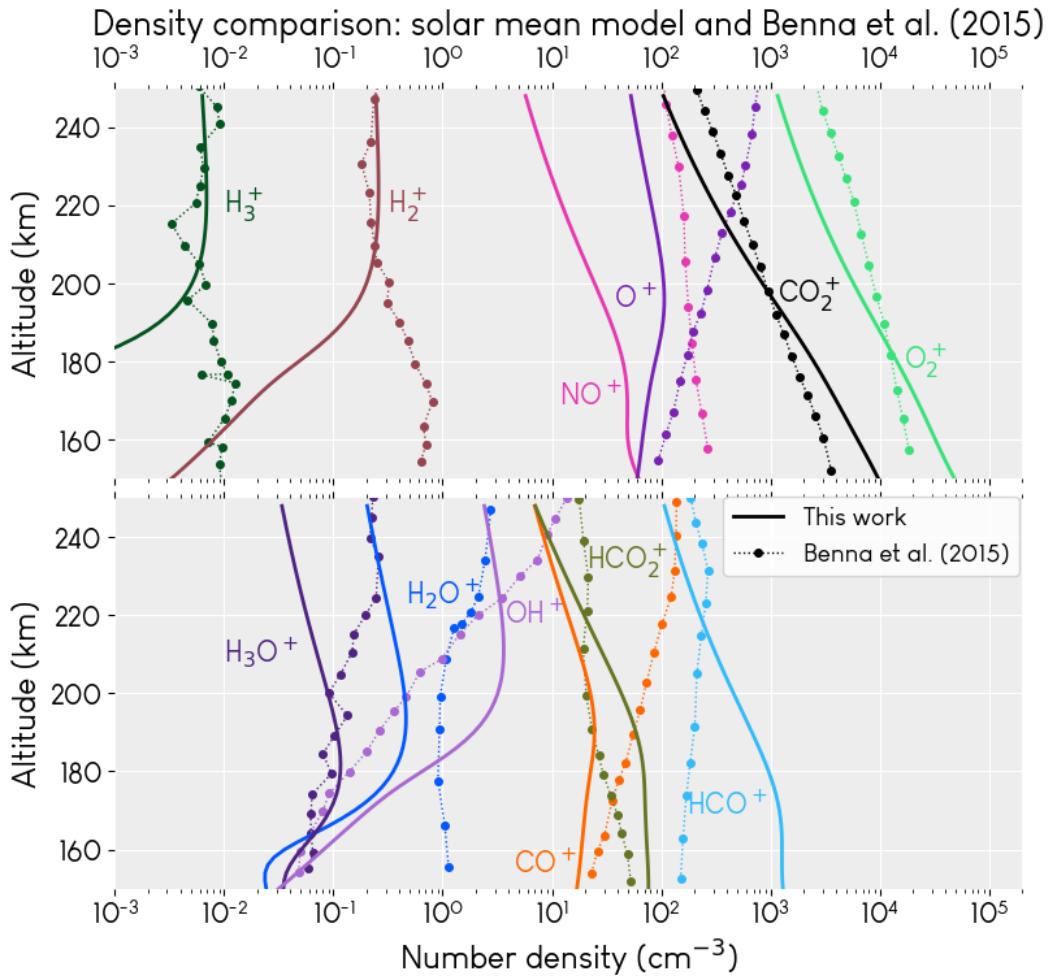
**Fox et al. (2015).** For the major ions such as  $\text{O}^+$ ,  $\text{CO}_2^+$ , and  $\text{O}_2^+$ , our density profiles are generally consistent with those modeled by Fox et al. (2015), as shown in Figure 3. They are also broadly similar for many of the minor ions, although in general, our profiles tend to show lower densities near 250 km by 1–2 orders of magnitude. There is a significant difference between our  $\text{H}_2\text{O}^+$ ,  $\text{H}_3\text{O}^+$ , and  $\text{NO}^+$  profiles; of these,  $\text{NO}^+$  has the largest density overall. It should be noted that many of the ions for which we show a significantly different profile are quite minor, with populations never exceeding  $100 \text{ cm}^{-3}$ , so the absolute differences as a percent of the total atmosphere are tiny, well within the absolute tolerance. Fox et al. (2015) make the point that their model calculates neutral  $\text{H}_2\text{O}$  produced only by ion-neutral reactions due to their choice of boundary conditions, whereas ours includes production by photodissociation; it is then perhaps not surprising that our results include more water than theirs (see Figure 3d).

In Figure S3, we also compare our results to Fox et al. (2021), which uses a similar model to Fox et al. (2015) and includes recent data from NGIMS for  $\text{CO}_2^+$ ,  $\text{O}_2^+$  and  $\text{O}^+$ . Compared to that paper, our results are more dissimilar.

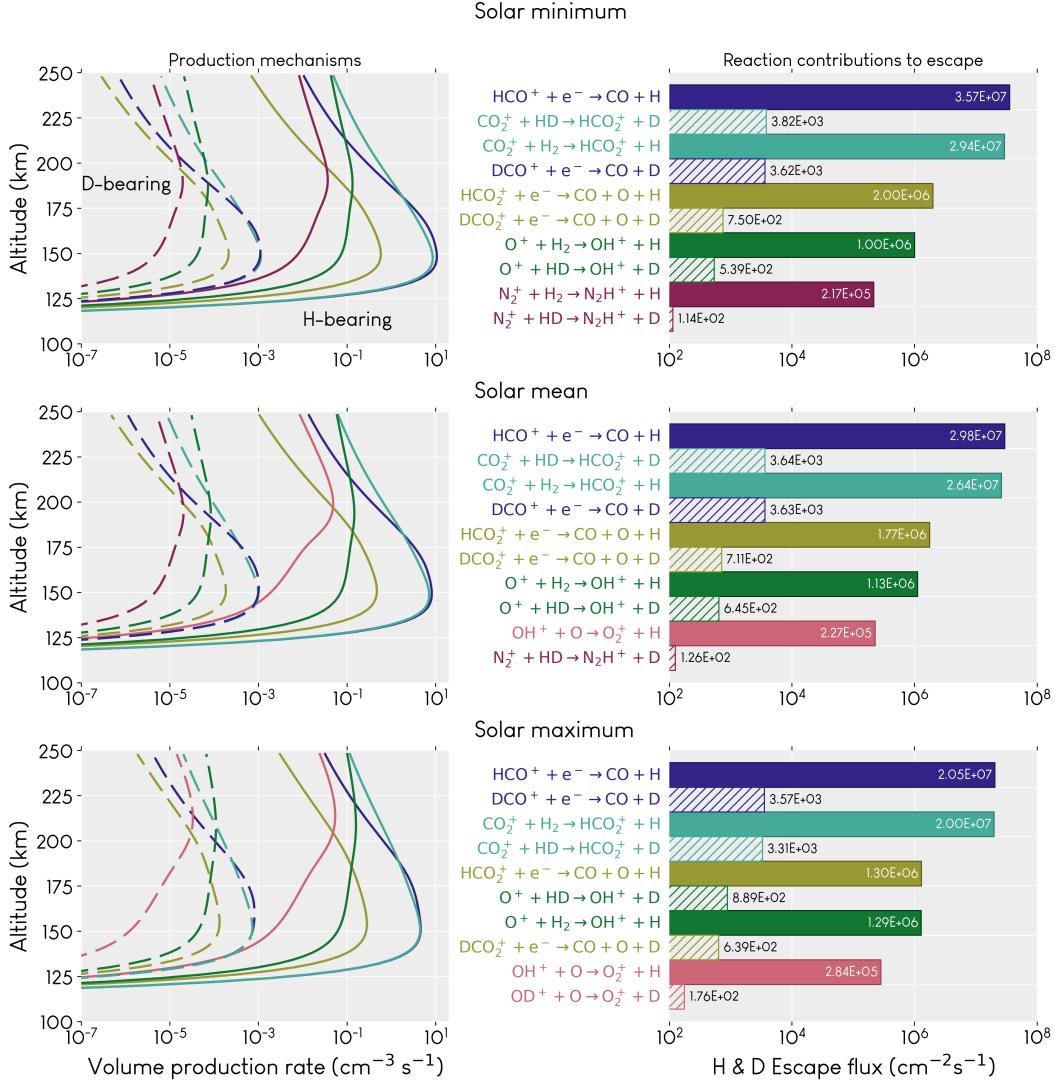
**Benna et al. (2015), using MAVEN NGIMS.** Our results show reasonably good agreement with the initial NGIMS measurements at Mars (Benna et al., 2015) (Figure 4), which occurred long enough into the mission that solar mean conditions would have prevailed. There continues to be a divergence between model and data for  $\text{O}^+$  in the up-



**Figure 3.** Ion and neutral densities computed by our model and compared with those computed by Fox et al. (2015). Species are divided amongst the four panels for legibility and compared with Figure 3 in Fox et al. (2015). Some minor species are omitted for clarity.



**Figure 4.** Ion and neutral densities computed by our model and compared with those computed by Benna et al. (2015). Species are divided amongst the two panels for legibility.  $\text{HNO}^+$  differs significantly from data and has been omitted; the measurements are known to be unreliable due to spacecraft potential.



**Figure 5.** Volume production rates of escaping atoms (panels a, c, e) and integrated escape flux of the produced atomic H or D (b, d, f) for the dominant five chemical pathways producing hot H (solid lines/solid bars) and hot D (dotted lines/dot-fill bars).

per atmosphere and an underprediction of  $\text{NO}^+$ , but considering we are using a 1D model that does not account for local and short-term variations and we have not made any model changes to match data, we find the output acceptable.

### 3.2 Are the dominant production mechanisms of hot H and D analogous or dissimilar?

Figure 5 shows the production mechanisms for hot H and D, which are mostly similar.

The most important reaction driving the production of hot D (H) below 200 km in solar mean and maximum is  $\text{DCO}^+(\text{HCO}^+)$  dissociative recombination (DR), with  $\text{CO}_2^+ + \text{HD}$  ( $\text{H}_2$ ) a close second.  $\text{HCO}^+$  DR dominates for hot H under all solar conditions, but for hot D,  $\text{CO}_2^+ + \text{HD}$  marginally dominates over  $\text{DCO}^+$  DR during solar minimum at certain altitudes, making it the dominant source of escaping hot D at solar minimum. This is because the density of HD relative to  $\text{DCO}^+$  is larger than  $\text{H}_2$  relative to  $\text{HCO}^+$ .

	Thermal escape ( $\text{cm}^{-2}\text{s}^{-1}$ )				Non-thermal escape ( $\text{cm}^{-2}\text{s}^{-1}$ )				Total escape ( $\text{cm}^{-2}\text{s}^{-1}$ )		
	H	D	$\text{H}_2$	HD	H	D	$\text{H}_2$	HD	H	D	H + D
Solar minimum	$1.75 \times 10^8$	80	$1.6 \times 10^5$	0.13	$6.5 \times 10^7$	9387	15351	19	$2.3996 \times 10^8$	9467	$2.4 \times 10^8$
Solar mean	$1.833 \times 10^8$	309	$5.0 \times 10^5$	0.89	$5.6 \times 10^7$	9219	12331	18	$2.39966 \times 10^8$	9529	$2.4 \times 10^8$
Solar maximum	$1.834 \times 10^8$	6740	$8.2 \times 10^6$	98	$4.0 \times 10^7$	8908	7669	16	$2.39969 \times 10^8$	15747	$2.4 \times 10^8$

**Table 2.** Amount of thermal and non-thermal escape of atomic and molecular H and D species for the three solar conditions. The total escape amounts to  $2.4 \times 10^8$  because in the equilibrium atmosphere, the ratio  $\phi_H/\phi_O$  approaches 2, as O escape is fixed at  $1.2 \times 10^8$  (see Section 2.3). Escaping atoms and molecules are sourced from the neutral species; densities for the associated species are shown in Figure S2.

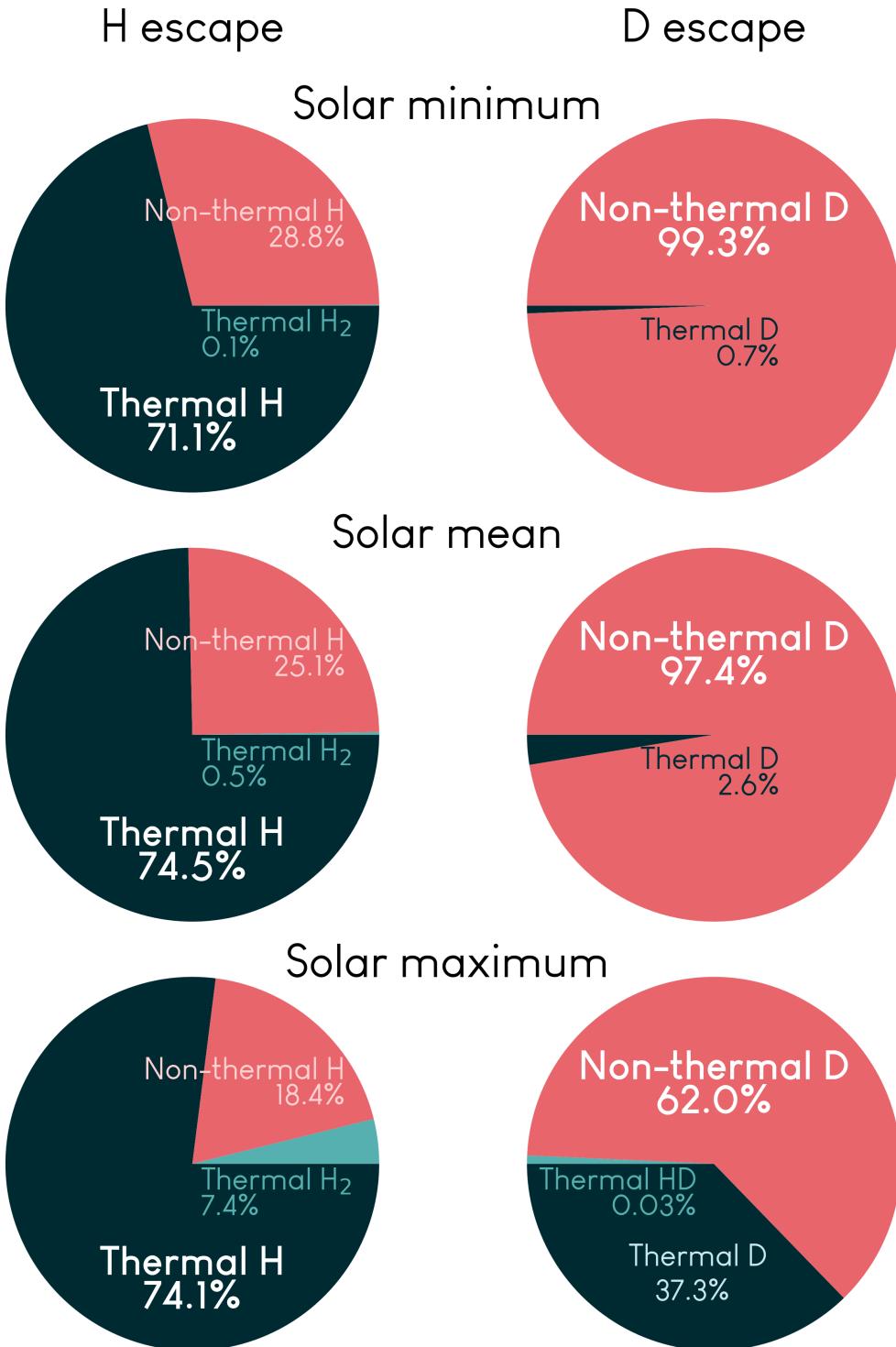
The rates of production from these two processes for hot D are very close; minor changes in conditions, including normal fluctuations in the real atmosphere, could likely change this relationship. Above 200 km,  $\text{CO}_2^+ + \text{H}_2$  dominates for hot H production, but high-altitude hot D comes mostly from  $\text{O}^+ + \text{HD}$ .

DCO<sub>2</sub><sup>+</sup>(HCO<sub>2</sub><sup>+</sup>) DR is the third most important reaction during quiet solar conditions, but it is eclipsed by O<sup>+</sup> + HD (H<sub>2</sub>) during solar maximum. Under quieter solar conditions, the fifth place position is seized by N<sub>2</sub><sup>++</sup> HD (H<sub>2</sub>). But as the thermosphere warms, OD (OH) + O claims the fifth place, first for the H species and then for the D species. This appears to be because the dominant reaction involving OH<sup>+</sup> and OD<sup>+</sup> is the reaction O<sup>+</sup> + H<sub>2</sub> (HD) → OH<sup>+</sup>(OD<sup>+</sup>) + H. This reaction also has a rate coefficient that is independent of temperature, whereas N<sub>2</sub><sup>++</sup> HD (H<sub>2</sub>) has a rate coefficient which decreases with temperature.

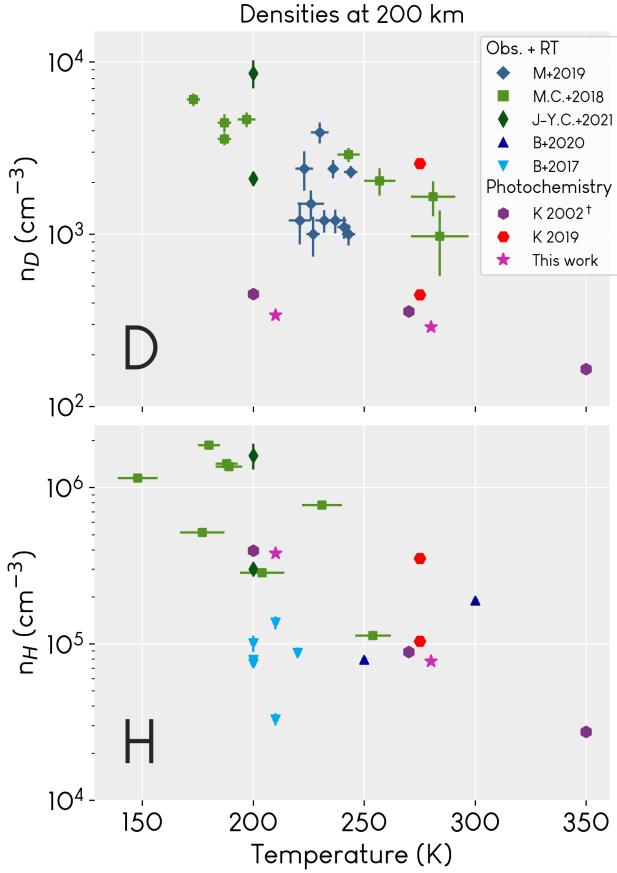
### 3.3 What is the magnitude of non-thermal escape of D, and under which conditions does it dominate thermal escape?

Figure 6 shows the relative contributions of thermal and non-thermal escape of atomic H and D and thermal escape of the molecular species; the associated escape fluxes to space are given in Table 2. The density profiles of the neutral species, from which the escape is sourced, appear in Figure S2; an upcoming publication will focus on variations in these neutral species and their D/H ratios. As has been asserted in the literature (V. A. Krasnopolsky, 2002), thermal escape is the dominant loss process for atomic H, with non-thermal escape of H making up a gradually reducing share across the solar cycle. The picture looks very different for D, for which 62-99.3% of escape is non-thermal depending on solar conditions. Note that, as shown in Table 2, the total escape of H and D adds to  $2.4 \times 10^8 \text{ cm}^{-2}\text{s}^{-1}$  under all solar conditions due to the boundary conditions (see Section 2.3).

Previous work has predicted that thermal escape of D should actually dominate at solar maximum (V. A. Krasnopolsky, 2002) and that non-thermal escape of D in the form of larger molecules such as HD, OD, and HDO could be up to 15% (Gacesa et al., 2018), whereas our results show that non-thermal escape of HD is so negligible as to not appear at all in Figure 6. Besides the fact that we do not account for excited rotational states of HD, the discrepancy also likely arises from our chosen methods. Our non-thermal escape probability curve is valid for hot atoms with 5 eV of energy, and we do not account at all for branching to excited internal states of the other product; we assume that all atomic H and D produced by exothermic reactions are produced “hot”. In reality, not all exothermic heat is dumped directly into the lone atoms all the time. With proper accounting for these intricate branching ratios, our calculated total of non-thermally escaping atomic D would likely decrease. We also do not calculate non-thermal OD escape.



**Figure 6.** Relative escape contributions for H and D. As expected based on the literature, thermal escape dominates for H during all solar conditions, but non-thermal escape dominates D escape, even at solar maximum. Although we do model non-thermal escape of H<sub>2</sub> and HD, their contributions are completely negligible (see Table 2).



**Figure 7.** D and H densities at 200 km (<sup>†</sup> 250 km) from multiple studies. Data represent multiple solar zenith angles, seasons, hemispheres, etc. M+2019: Mayyasi et al. (2019). M.C.+2018: Chaffin et al. (2018). J-Y.C.+2021: Chaufray et al. (2021). B+2020, 2017: Bhattacharyya et al. (2020, 2017). K 2002, 2019: V. A. Krasnopolsky (2002, 2019). Entries under “Obs. + RT” used brightness observations from either HST (Bhattacharyya et al., 2017) or MAVEN IUVS (all others) with radiative transfer modeling for density retrievals. For these studies, invisible density error bars indicate uncertainty smaller than the marker size. Temperature error bars indicate that temperature was retrieved from spacecraft data, while missing temperature error bars mean it was a model parameter or output. Uncertainties for photochemistry studies are not calculated. Photochemical modeling typically reports an order of magnitude less D than other methods, which may be due to observation biases toward times of brighter D emission. There is no similar discrepancy in H densities.

## 4 Discussion

Figure 7 places our D and H densities in context with other studies. We have only consolidated reported densities; we make no attempt to filter by observation geometries. Nevertheless, there appears to be an inverse relationship of densities and temperature for both species. We can also see that photochemical models (red/purple/pink points) produce D densities that are an order of magnitude smaller than densities retrieved using observations and radiative transfer modeling; the same discrepancy does not occur for the H densities. Deuterium Lyman  $\alpha$  is difficult to separate from hydrogen Lyman  $\alpha$ ; the D density discrepancy may potentially be explained by a systematic bias toward anomalously bright D emissions. One exception is the density of D at  $\sim 2500$  and  $T = 275\text{K}$  in the work by V. A. Krasnopolksy (2019); this point represents a model run with a high amount of water in the thermosphere, whereas all the other photochemical results have a comparatively lower water abundance. This comparison demonstrates that our model output is in reasonable agreement with other works.

As mentioned previously, we do not include cloud or dust microphysics, although these processes do have an important effect on the water cycle. These effects are explored in two recent papers using the Laboratoire de Météorologie Dynamique Planetary Climate Model (LMD-PCM) to study the creation of water ice clouds and their role in controlling the D/H ratio (Vals et al., 2022; Rossi et al., 2022).

### 4.1 Can inclusion of non-thermal escape in the model yield an estimation of water loss similar to the amount calculated in geological studies?

By considering both thermal and non-thermal escape, we can now compute the D/H fractionation factor, which represents the relative efficiency of D and H escape. It is defined as:

$$f = \frac{\phi_D / \phi_H}{[\text{HDO}]_s / 2[\text{H}_2\text{O}]_s} \quad (4)$$

Where  $\phi_X = \phi_{X,t} + \phi_{X,n}$  is the rate at which species X (D or H) escapes from the top of the atmosphere due to both thermal ( $t$ ) and non-thermal ( $n$ ) processes. The denominator represents the D/H ratio in water measured at the surface ( $s$ ), which is a proxy for the D/H ratio in the larger exchangeable reservoir.

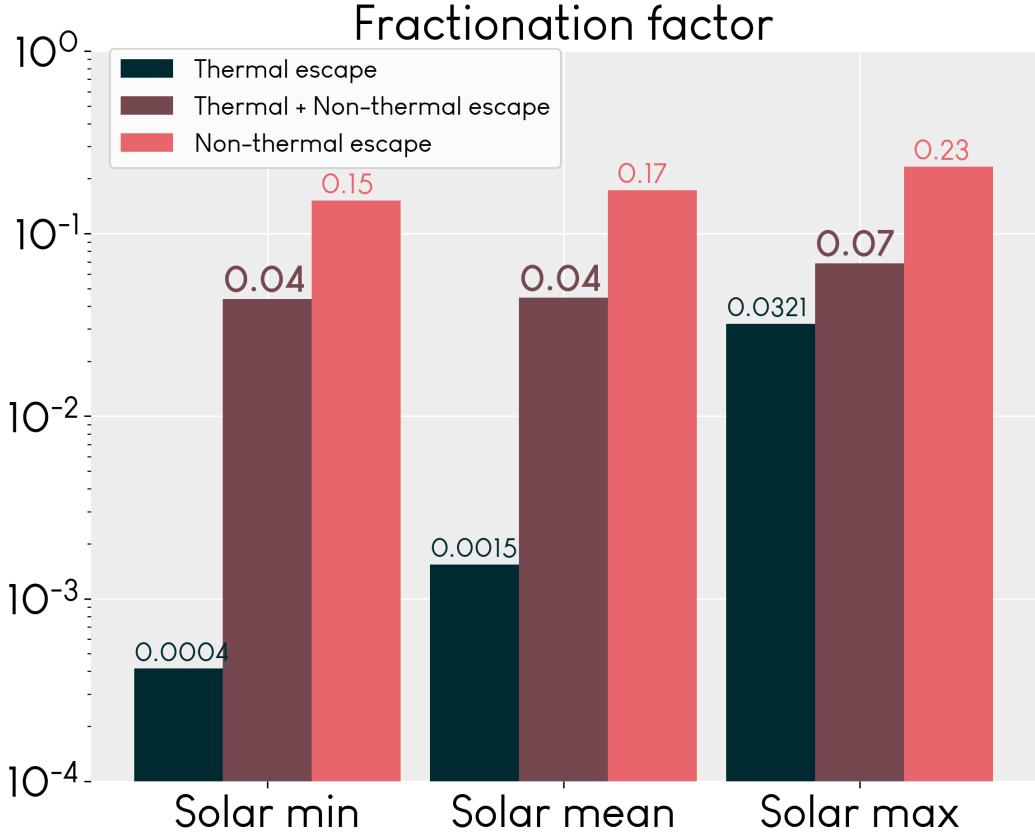
The fractionation factor is important not only because it tells us how efficient loss of D is compared to loss of H, but also because it is useful for calculating the integrated water loss from a planet. Long-term enrichment of the heavy isotope (D) due to differential escape of D and H can be modeled using Rayleigh fractionation (Chamberlain & Hunten, 1987; Yung & DeMore, 1998):

$$\frac{(\text{D}/\text{H})_{\text{now}}}{(\text{D}/\text{H})_{\text{past}}} = \left( \frac{[\text{H}]_{\text{past}}}{[\text{H}]_{\text{now}}} \right)^{1-f} \quad (5)$$

Equation 5 is used to calculate water loss from Mars. The D/H ratio on the left hand side represents the ratio measured in water in the exchangeable reservoir (the seasonal polar caps, near-surface ices, and atmospheric water vapor), and the ratio  $\text{H}_2\text{O}_{\text{past}}/\text{H}_2\text{O}_{\text{now}}$  can be substituted in on the righthand side and rearranged, obtaining (Cangi et al., 2020) (where W is water):

$$W_{\text{lost}} = W_{\text{now}} \left( \left( \frac{(\text{D}/\text{H})_{\text{now}}}{(\text{D}/\text{H})_{\text{past}}} \right)^{1/(1-f)} - 1 \right) \quad (6)$$

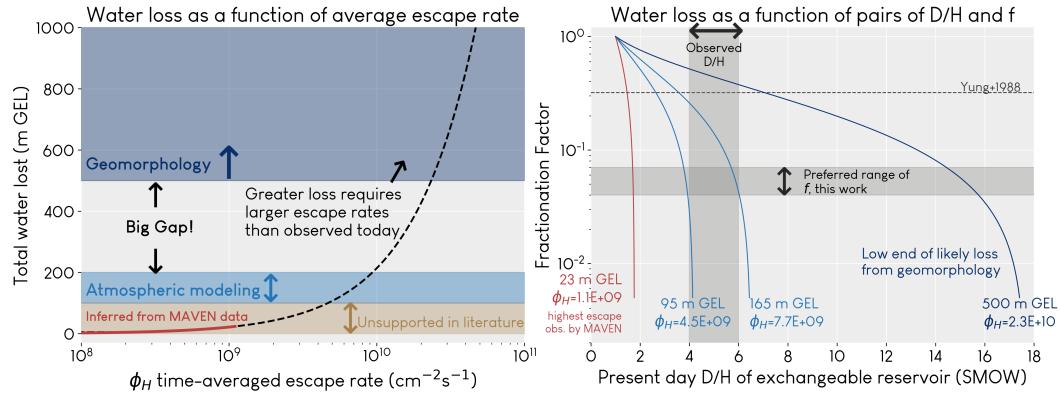
Implicit in these equations is the assumption that  $[\text{H}] \gg [\text{D}]$ , so that the past and present abundances of  $\text{H}_2\text{O}$  are reasonable representations of the entire water budget. In the present day, the ratio of D/H is well constrained by many observational studies to be approximately  $4\text{-}6 \times$  standard mean ocean water (SMOW) (Encrenaz et al., 2018; Villanueva



**Figure 8.** The fractionation factor  $f$  for three different modes of escape. Changing solar conditions lead to an orders of magnitude increase in  $f$ , as does inclusion of non-thermal escape in the calculation. Fractionation represents the escape efficiency of D compared to H, meaning that  $f = 0.04$  represents a 4% escape efficiency of D. Non-thermal escape is an effective escape method for D under all solar conditions.

et al., 2015, and references therein). Current research also has identified a likely present-day exchangeable reservoir water budget of 20-30 m GEL (Lasue et al., 2013, and references therein). By obtaining a reliable value for  $f$ , we can combine all these values to calculate the inventory of water on ancient Mars.

Cangi et al. (2020) suggested that the difference between the mean atmospheric  $f_t$  (considering only thermal escape) and  $f_{tn}$  (considering both thermal and non-thermal escape) was several orders of magnitude. Because they did not directly model non-thermal escape, they arrived at this conclusion by incorporating the non-thermal escape velocity given by V. A. Krasnopolsky et al. (1998) into their model. We are now in a position to compare with those estimates; our calculations of the fractionation factor are shown in Figure 8. Cangi et al. (2020) calculated  $f = 0.06$  for their standard atmosphere, based on their modeled thermal escape and estimated non-thermal escape. We calculate a total escape fractionation of  $f = 0.04$  for our solar mean atmosphere, which has the same insolation and similar temperatures, and is not far off from their 0.06. Our results are consistent with their thermal escape  $f = 0.002$  for the standard atmosphere (roughly equivalent to our solar mean atmosphere). Our results show that while overall D escape at Mars is around 4-7% as efficient as H escape, non-thermal D escape is much more efficient, between 15-23% that of H.



**Figure 9.** a): Possible water loss as a function of long-term average H escape rate  $\phi_H$ ,  $W_{\text{lost}} = \bar{\phi}_H t$ , where  $t = 4.5$  billion years. A significant gap separates the amount of water loss inferred from atmospheric modeling and geomorphological studies. Additionally, escape rates determined from MAVEN data enable very small amounts of water loss that are not consistent with the geological evidence. b): Water loss lines represent solutions to equation 6, assuming 30 m GEL in the present-day exchangeable reservoir. The regions matching the best values of D/H and  $f$  are shaded in gray, with the overlapped rectangle representing our best estimate of the present-day atmosphere. (The fractionation factor calculated by Yung et al. (1988) is shown for reference, though it is high due to the highly uncertain exospheric temperatures then used.)

Our results yield integrated water loss of 147–158 m GEL (present day exchangeable reservoir = 30 m GEL,  $f = 0.04\text{--}0.07$ , D/H =  $5.5 \times \text{SMOW}$ ). This total loss still does not agree with the geological estimates of 500+ m GEL (Lasue et al., 2013). The discrepancy is summarized in Figure 9. Figure 9a shows the gap between the amount of water loss calculated by atmospheric models (Yung et al., 1988; Kass & Yung, 1999; V. Krasnopol'sky, 2000; V. A. Krasnopol'sky, 2002; Cangi et al., 2020) and that inferred from geomorphological observations (Lasue et al., 2013, and references therein). The time-averaged H escape rate curve suggests that the rates observed today (Jakosky et al., 2018) are unlikely to be near the average, and that escape was likely higher in the distant past, enabling greater water loss. Plausible explanations could include periods of hydrodynamic escape, a more EUV-active young sun driving greater photochemistry, extreme obliquities (Wordsworth, 2016; Laskar et al., 2004), or other as of yet unknown dynamics.

It is also possible that some water may have been sequestered into the surface. Recent work by Scheller et al. (2021) suggests that this amount may have accounted for between 30–99% of all missing water. More smaller-scale models and many observations will be needed to constrain this large range further. Hydrated minerals may contain 130–260 m GEL equivalent water Wernicke and Jakosky (2021), but the time of emplacement and any fractionation of the process is unclear. In general, due to the chaotic evolution of obliquity (Laskar et al., 2004) over Mars' history, it is extremely difficult to qualitatively describe escape rates in the past. Although it is difficult to extrapolate much from the present-day rates, high loss of water via escape to space is not ruled out.

Figure 9b also helps demonstrate when it is important to know the value of  $f$  rather precisely. Discriminating between  $f = 0.04$  or  $f = 0.07$  is not particularly important: below  $f = 0.1$ , water loss curves are relatively vertical, meaning that a change in  $f$  does not equate to a significant change in water loss, but this is less true the closer  $f$  gets to 1. (For another view, see Figure S4 for water loss as a function of  $f$  for a single D/H ratio.)

467 Considered together, these insights tell us that non-thermal escape processes for D are  
 468 important to model in order to accurately understand how D escapes from Mars. This  
 469 conclusion may not hold for other planets, moons, or exoplanets; on bodies which are  
 470 colder, larger, or otherwise less conducive to thermal escape, non-thermal escape may  
 471 have a greater role to play.

#### 472 **4.2 Other non-thermal processes**

473 We do not account for the collision of H or D with hot oxygen, which is another signif-  
 474 icant source of hot atoms in the martian atmosphere. Assuming an exospheric temper-  
 475 ature of 240 K, Gacesa et al. (2012) calculated that  $1.9 \times 10^5 \text{ cm}^{-2}\text{s}^{-1}$  H<sub>2</sub> molecules  
 476 escape as a result of collision with hot oxygen, which is larger than our non-thermal H<sub>2</sub>  
 477 flux by two orders of magnitude (see Table 2). They also estimate that 74 HD molecules  
 478  $\text{cm}^{-2}\text{s}^{-1}$  escape via this mechanism. This would bring our total HD escape to approx-  
 479 imately  $100 \text{ cm}^{-2}\text{s}^{-1}$ , an order of magnitude larger than our current result. Other species  
 480 may also play a role; Gacesa et al. (2017) calculate that the total non-thermal escape  
 481 of OH is  $1.07 \times 10^{23} \text{ s}^{-1}$ , i.e.  $7.4 \times 10^5 \text{ cm}^{-2}\text{s}^{-1}$ . Even added together, these numbers  
 482 are all still orders of magnitude smaller than the non-thermal atomic escape fluxes, and  
 483 will not significantly affect our results. If we included them, the net effect would be to  
 484 boost H escape, decreasing the fractionation factor and total water loss.

485 Energization of atomic H and D by collision with hot oxygen may be significant. Shematovich  
 486 (2013) estimates, for specific density profiles and temperatures, a total possible escape  
 487 flux of hot H produced this way to be  $6 \times 10^6 \text{ cm}^{-2}\text{s}^{-1}$  at low solar activity. This be-  
 488 gins to approach our non-thermal H escape (see Table 2). Our non-thermal D escape is  
 489 3 orders of magnitude lower than the H escape. If we crudely apply this scaling relation  
 490 to hot O collisions with D, we can expect that this pathway might produce D escape on  
 491 the order of  $10^3$ , which is the same order as our calculated non-thermal escape fluxes.  
 492 However, since it is not significantly larger, we can at least expect that the exclusion of  
 493 hot O collisions with H and D would not significantly change our primary conclusions.

#### 494 **4.3 Future opportunities and directions**

495 There are several things that could enhance our model. The first likely avenue worthy  
 496 of exploration would be to perform a similar study, but with a more physically-motivated  
 497 parameterization of atomic O escape. Fixing the O escape at  $1.2 \times 10^8 \text{ cm}^{-2}\text{s}^{-1}$  was suf-  
 498 ficient for the scope of this work; our results represent long-term equilibrium, when it  
 499 is possible to adopt reasonable means for parameters like O escape. Adding a dynam-  
 500 ically evolving escape flux boundary condition for atomic O would enable a more com-  
 501 prehensive understanding of shorter-term variations in H and D escape rates, such as a  
 502 result of regular seasonal cycles. This would better capture the interplay between the  
 503 hydrogen species and CO<sub>2</sub>, the main component of the atmosphere and a significant source  
 504 of O. This would also present an opportunity to include processes more important to O  
 505 loss, such as ion pickup, ion/polar outflow, and sputtering. We do not include these as  
 506 we focus on H and D loss, which are dominated by other processes.

507 We have also been forced to make some unavoidable assumptions about the basic chem-  
 508 istry, owing to a lack of laboratory data. While we have made a best attempt to use ex-  
 509 isting reaction rate coefficient data from several different papers and databases, a com-  
 510 prehensive catalogue of rate coefficients, branching ratios, and cross sections for deuter-  
 511 ated reactions is not available in the literature at this time. Most especially, future pho-  
 512 tochemical models would benefit from accurate photoabsorption cross sections for deuter-  
 513 ated neutrals other than HDO (including OD and HD in particular), and measured re-  
 514 action rate coefficients for as many of the deuterated reactions with estimated rates in  
 515 Table 1 as possible. While not all reactions will significantly affect the chemistry, cer-  
 516 tain rates that dominate production or loss of a species can have strong effects, affect-  
 517 ing densities up to a few orders of magnitude (see, for example, Fox et al. (2017)).

518 Photochemical modeling often entails excluding some important processes that are bet-  
 519 ter captured in higher-dimensional models. Our model is the first to couple the ion and  
 520 neutral atmospheres from the upper atmosphere down to the surface, but there is still  
 521 an opportunity for future work to give more attention to surface-atmosphere interactions.  
 522 Our inclusion of surface-atmosphere interactions is primarily relegated to surface den-  
 523 sity boundary conditions for certain species. A more detailed parameterization of pro-  
 524 cesses such as volcanic outgassing, major seasonal changes in the polar caps, water ad-  
 525 sorption and desorption on dust grains and dust lifting, deposition of volatiles, and the  
 526 role of non-volatiles such as perchlorates, salts, and other non-water ices could yield new  
 527 insights into the planetary climate system as a whole.

528 Our results also have implications for the detectability of deuterated ions by present and  
 529 future Mars missions. Using MAVEN's NGIMS instrument, the deuterated ions that we  
 530 model typically occupy the same mass/charge ratio bin as a more prevalent H-bearing  
 531 species. For example, D<sup>+</sup> occupies the same bin as H<sub>2</sub><sup>+</sup>, but the latter is far more abun-  
 532 dant. The deuterated species in our model which do not overlap with an H-bearing species  
 533 are H<sub>2</sub>D<sup>+</sup>(mass bin 4), HD<sub>2</sub><sup>+</sup>(5), H<sub>2</sub>DO<sup>+</sup>(20), HDO<sub>2</sub><sup>+</sup>(35), and ArD<sup>+</sup>(42). However,  
 534 several of these species are expected to be very rarefied and thus difficult to detect, and  
 535 others may overlap with species we do not model that do exist on Mars, such as helium  
 536 in mass bin 4. These degeneracies make obtaining deuterated ion densities challenging;  
 537 doing so will require inventive methods applied to existing data or new methods with  
 538 new instruments.

## 539 **5 Conclusions**

540 We have used a 1D photochemical model that fully couples ions and neutrals from sur-  
 541 face to space to study production of hot D from planetary ionospheric processes. We show  
 542 that the deuterated ionosphere behaves relatively similar to the H-bearing ionosphere.  
 543 This result is somewhat expected, as measurements of rate coefficients for deuterated  
 544 reactions are much less available than the H-bearing counterpart reaction rate coefficients.

545 For the first time, we have self-consistently quantified, in raw flux and in percent of to-  
 546 tal escape, the thermal and non-thermal escape fluxes of H and D in both the atomic  
 547 and molecular forms in equilibrium atmospheres under different solar conditions, and the  
 548 dominant chemical reactions responsible for producing hot D. Our results confirm ear-  
 549 lier suggestions that non-thermal escape dominates D escape at Mars, although our re-  
 550 sults have shown that this is true throughout the solar cycle rather than just during quiet  
 551 solar conditions.

552 We also confirm an earlier prediction (Cangi et al., 2020) that including non-thermal es-  
 553 cape when calculating the D/H fractionation factor will result in a fractionation factor  
 554 several orders of magnitude higher than if it is neglected. However, the resulting frac-  
 555 tionation factor is 0.04–0.07, meaning that D escape is only about 4–7% as efficient as  
 556 H escape. If the fractionation has consistently been this small, and we also assume that  
 557 the escape rate of H  $\phi_H$  has been similar to the value today through time, it is difficult  
 558 to ascribe the large amount of water loss that we see indicated in the rock record to at-  
 559 mospheric escape alone. On the other hand, the dust storm season on Mars, as well as  
 560 normal seasonal variations between perihelion and aphelion, are characterized by spa-  
 561 tially and temporally localized enhancements of the D/H ratio, water abundance, and  
 562 H escape (Villanueva et al., 2021; Daerden et al., 2022; A. Fedorova et al., 2021; Chaf-  
 563 fin et al., 2021; Holmes et al., 2021; A. A. Fedorova et al., 2020; Stone et al., 2020; Aoki  
 564 et al., 2019; Vandaele et al., 2019; Heavens et al., 2018; Chaffin et al., 2017, and refer-  
 565 ences therein). It is not yet clear if enhanced D escape or a heightened fractionation fac-  
 566 tor also occur along with these seasonal changes, although it seems likely (Alday et al.,  
 567 2021); if they do, then the assumption of a constant fractionation factor over time can-  
 568 not hold, and we will have to introduce some additional nuance to our use of Rayleigh  
 569 fractionation to estimate water loss.

570 Ongoing improvements in modeling, especially coupling between 1D and 3D models, as  
 571 well as continual advancements in instrumentation for planetary missions will be nec-  
 572 essary to continue putting together the puzzle of water on Mars throughout history.

## 573 6 Open Research Statement

574 The photochemical model used for this work is written for and compatible with Julia 1.7.1  
 575 (Bezanson et al., 2017). The model itself, in version 1.0 as used in this work, is avail-  
 576 able at Zenodo (Cangi & Chaffin, 2022).

577 A typical use-case of the model is to modify simulation parameters within `PARAMETERS.jl`  
 578 and to then call `julia converge_new_file.jl` at the command line.

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# Supporting Information for “Fully coupled photochemistry of the deuterated ionosphere of Mars and its effects on escape of H and D”

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5. Table S1: Complete reaction network (Excel file)
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## Introduction

These supplementary figures and table add additional details about the model inputs and results. We hope that other photochemical modelers looking for rate coefficient sources, or anyone interested in the details of the chemistry, will find the complete table of reactions and rate coefficients useful.

**Text S1: Using the reaction network spreadsheet.** The reaction network for this work is large enough that to display it in a printed table would be unwieldy. All reactions used in the model are shown in the attached spreadsheet.

The spreadsheet has four sheets: **Neutral reactions**, **Ion reactions**, **Photodissociation**, and **Photoionization**.

The column name meanings common to all sheets are as follows:

- R1, R2, R3: Reactant species names
- P1, P2, P3: Product species names
- M2, M1, pow: Heavy isotope mass, light isotope mass, and power, used for estimating unmeasured reaction rate coefficients of deuterated reactions by assuming proportionality to the mass ratio of the deuterated isotope and its hydrogen partner (see main text).

Please note that in the spreadsheet, “pow” is usually equal to -0.5 because the calculation as performed in our model’s codebase is  $\left(\frac{M_2}{M_1}\right)^{-0.5}$ , but we print it in the main paper text as the more easily readable  $\sqrt{\frac{M_1}{M_2}}$ .

- BR: Branching ratio, used for reactions with identical reactants but differing products to identify percent of reactions which lead to each unique product set.
- kA, kB, kC: coefficients used for the standard Arrhenius equation (see below), i.e.  $k_{\text{inf}}$ , the rate in the high-pressure limit.

- k0A, k0B, k0C: coefficients for the low-pressure limit used with certain equations which use either the Troe form or the termolecular expression (Burkholder et al., 2019).

- kradA, kradB, kradC: coefficients used for the Troe form
- F: Troe parameter
- Trange: Range of temperatures for which reaction is valid. Not always guaranteed to match perfectly with Mars temperatures.

- Reference: Citation for rate in short form (AuthorYear, method description, or database acronym)
- Notes: Additional caveats or usage notes

The neutral spreadsheet contains the following information in the type column:

- 1: Pressure-independent unimolecular reactions, such as spontaneous de-excitation.
- 2: Pressure-independent bimolecular neutral-neutral reactions.
- 4: Pressure-dependent association reactions, as described by Vuitton, Yelle, Klippenstein, Hörst, and Lavvas (2019)
- 5 and 6: OH + CO or OD + CO bimolecular, pressure-dependent association reactions, as described by Vuitton et al. (2019)

For the Troe form and termolecular equations, the reader is directed to Appendix B of Vuitton et al. (2019).

The ion reaction sheet also contains:

- Type:
  - -2: Bimolecular ion-neutral reactions
  - -4: Dissociative recombination reactions

- excessE: excess energy computed by taking the difference  $\Delta H_f^{products} - \Delta H_f^{reactants}$ ,

in order to determine exothermicity. This excess energy is in eV and positive indicates an exothermic reaction.

- NTEscape: Whether the reaction contributes to non-thermal escape of H, D, H<sub>2</sub> or HD by virtue of being exothermic.

- hotH, hotD, hotH<sub>2</sub>, hotHD: Flags to indicate what types of hot atoms/molecules are produced by the reaction, for use internally by the model.

Bimolecular reaction rate coefficients for neutrals and ions are computed using the entries in the columns described above with the equation:

$$k = BR \left( \frac{M_2}{M_1} \right)^{pow} AT^B e^{C/T} \quad (1)$$

For non-deuterated reactions, M2=M1=1 and pow=0. For reactions with only one unique product set, BR=1.

Photodissociation and photoionization reactions do not have specific rate coefficients because they are computed for a given altitude as a function of incoming insolation and overhead column density. Some, however, will use the mass scaling term and the branching ratio term.

### **Text S2: Reasonableness of the assumption that all excess energy in a non-thermal reaction ends up in produced atomic H or D**

We can show this to be reasonable by calculating a ratio of the velocity of the light product (atomic H or D) in the case where (1) it gains all the excess energy to a case where (2) both products acquire excess energy. By assuming conservation of energy and

momentum, the ratio of the light product velocity in case (1) to case (2) can be shown to be

$$\frac{v_1}{v_2} = \sqrt{\frac{R}{R+1}}, \quad (2)$$

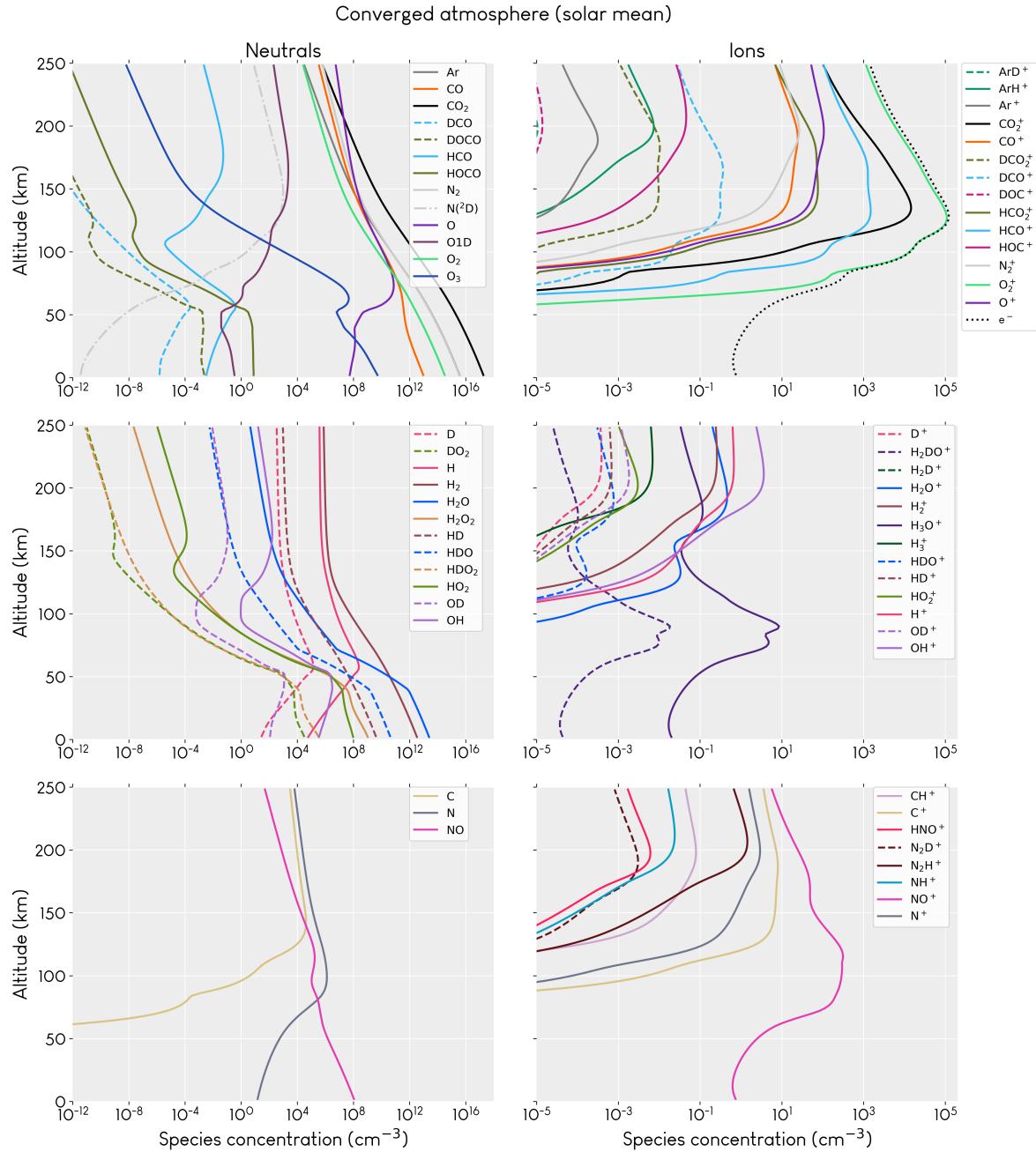
where  $R = m_{\text{product2}}/m_{\text{H,D}}$ . If the product set consists of H and the heaviest species in the model, O<sub>3</sub>, then  $v_1/v_2 = 0.99$ , that is, the velocity of atomic H if it gains all excess energy is 99% of what we would otherwise calculate if we allowed O<sub>3</sub> to also gain excess energy. On the other end of the spectrum, the product set with the smallest value of  $R$  would be H and H ( $R = 1$ ). In that case, energy is shared equally between the two produced H atoms, but  $v_1/v_2 = 0.70$ , which is close to what it would be if energy were not split at all.

## References

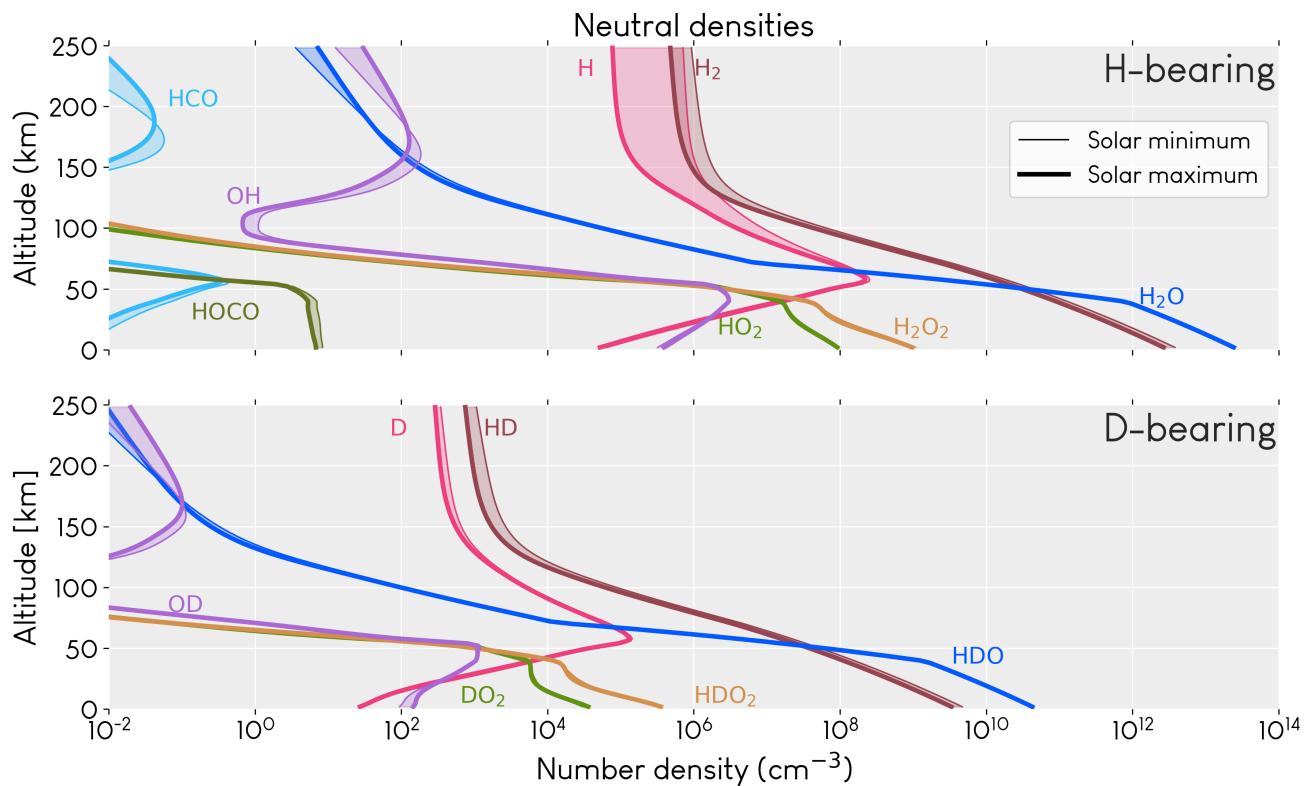
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X - 6 CANGI, CHAFFIN, YELLE, GREGORY, DEIGHAN: DEUTERATED IONOSPHERE OF MARS

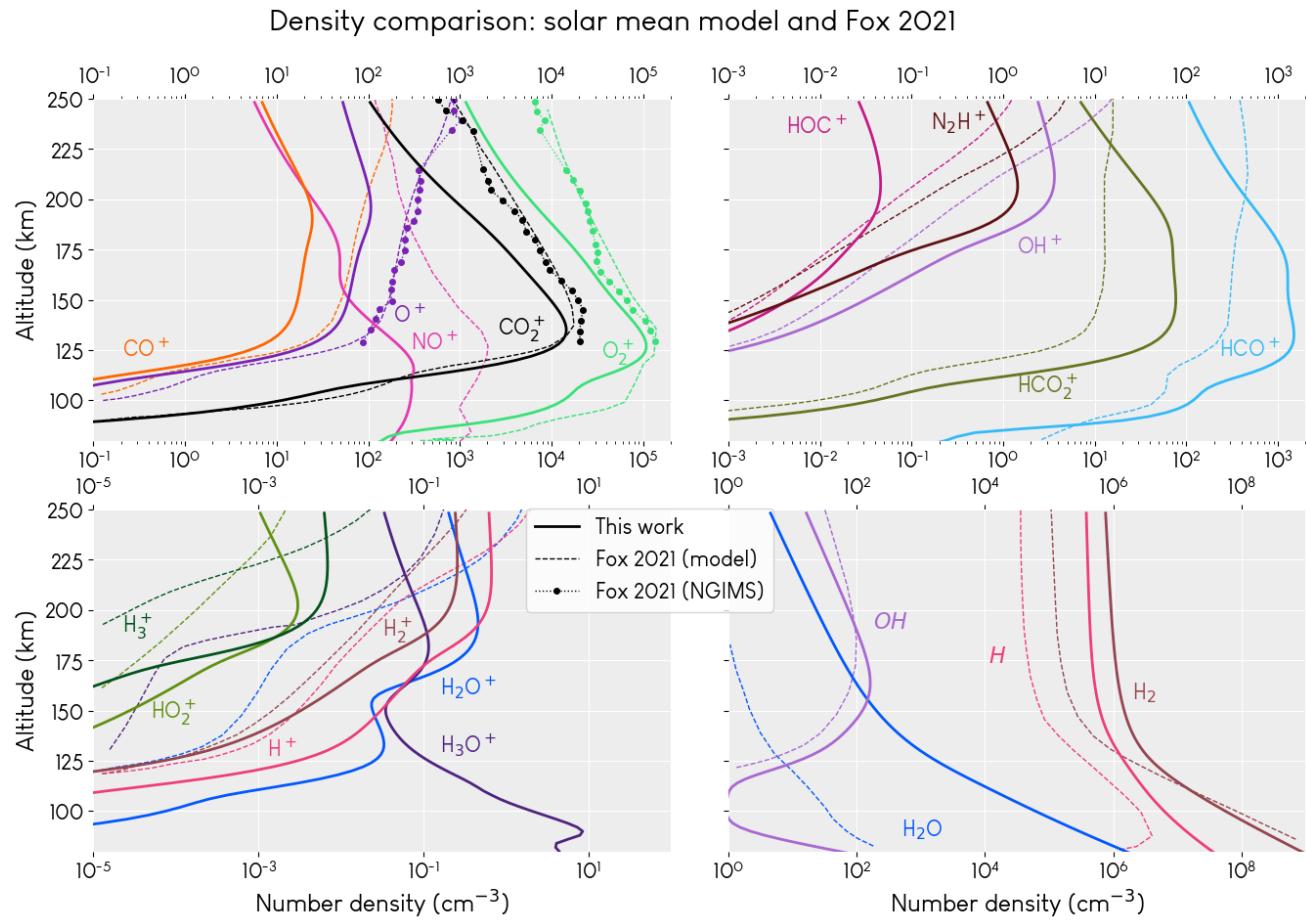
<https://doi.org/10.1016/j.icarus.2018.06.013> (Publisher: Elsevier Inc.) doi:  
10.1016/j.icarus.2018.06.013



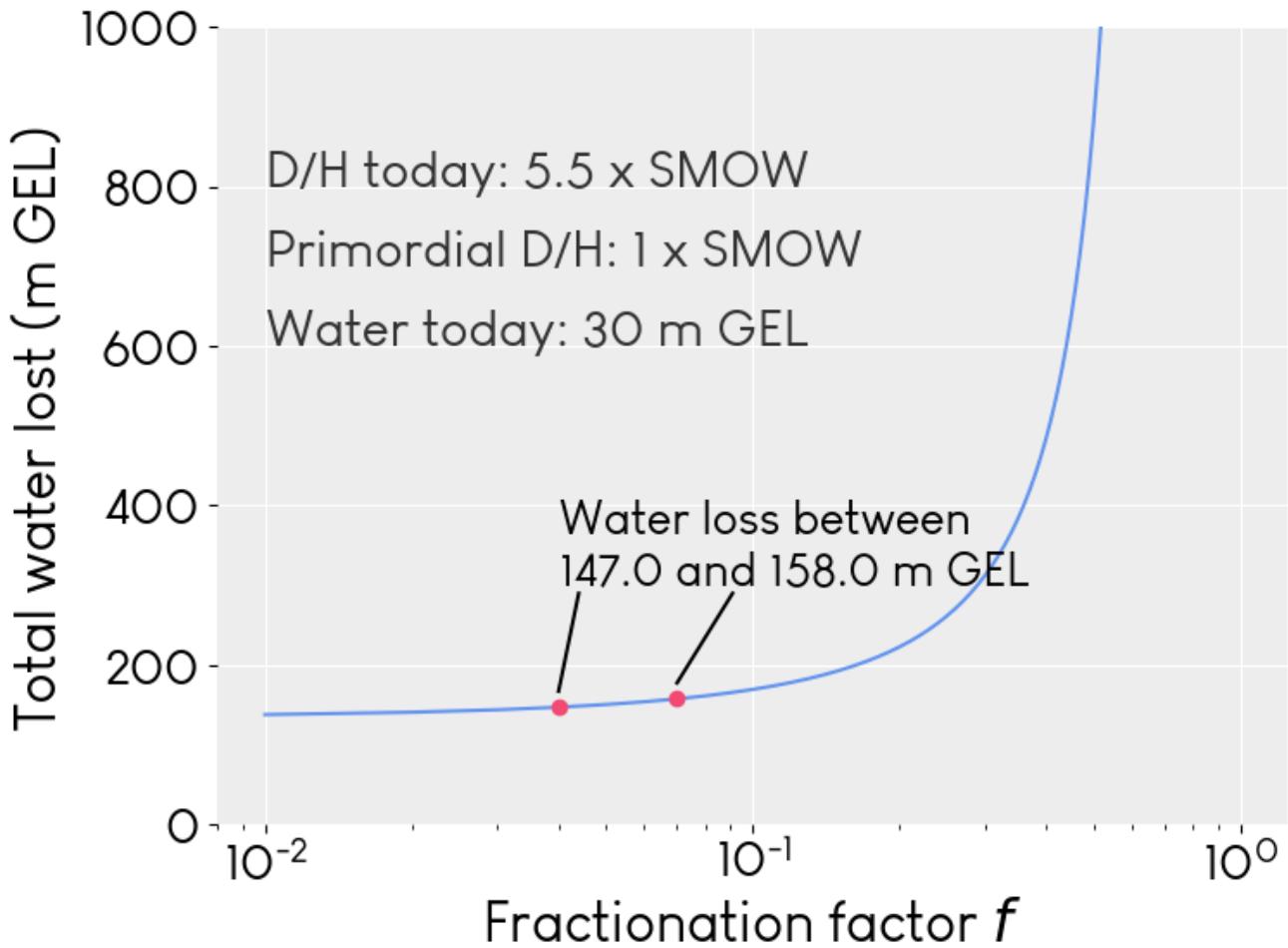
**Figure S1.** The complete atmosphere, with all species, at the end of the solar mean simulation.



**Figure S2.** Densities of neutral deuterated species and their H-bearing analogues. Some minor species are not plotted in order to maintain legibility of the more abundant species.



**Figure S3.** Comparison of model output with Fox et al. (2021), their model output and NGIMS densities for three principal ions.



**Figure S4.** Water loss as a function of fractionation factor for  $\text{D}/\text{H} = 5.5 \times \text{SMOW}$ , primordial  $\text{D}/\text{H} = 1 \times \text{SMOW}$ , and 30 m GEL present-day water inventory.