

# FULLY-COUPLED PHOTOCHEMICAL MODELING OF THE DEUTERATED IONOSPHERE AND NON-THERMAL ESCAPE OF D.

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## Introduction

**Context:** The Mars water D/H ratio is  $5\text{-}6 \times$  the Earth ratio, and is considered to be an indicator of past water loss on Mars. Because the isotope D is heavier than H, thermal escape is less effective for D, and escape of D is expected to occur primarily via non-thermal escape driven by ion processes. Neutral H loss from both thermal and non-thermal processes is well-studied at Mars, but the deuterated ionosphere is relatively unstudied. This leaves us with a lack of understanding of the true scale of non-thermal D escape and its variation throughout time.

**Aims:** To fill this knowledge gap, we have performed a modeling study of the deuterated ionosphere at Mars. Our primary goals are to characterize the overall composition of the deuterated ionosphere, quantify the thermal and non-thermal escape of H and D, and understand associated changes to the exchangeable water inventory over time.

**Methods:** To accomplish our goals, we simulated a long-term equilibrium state of the atmosphere using a 1D photochemical model and atmospheric parameters representing the present-day mean atmosphere on Mars. Studying the atmosphere in equilibrium allows us to establish a mean probable magnitude of non-thermal escape of D. To do this effectively, we have upgraded our existing 1D photochemical model to be the first such model to couple the lower and upper atmospheres and the neutral and ion chemistry—without assuming photochemical equilibrium or fixing a background atmosphere.

**Results:** We find that  $\text{DCO}^+$  is the dominant deuterated ion at all altitudes, with  $\text{D}^+$ ,  $\text{OD}^+$ ,  $\text{HDO}^+$ , and  $\text{DCO}_2^+$  also important, similar to their H-bearing analogues. Our density profiles for the H-bearing analogue ions are generally in agreement with Fox (2015). For non-thermal escape of D during solar mean conditions, we find an upper limit of  $\sim 1.6 \times 10^4 \text{ cm}^{-2}\text{s}^{-1}$ . A detailed analysis of the contributions of different processes and implications for water loss will be discussed in the presentation.

## Motivating questions about non-thermal D escape

Many open questions remain about D at Mars. The MAVEN mission is addressing questions about the upper

atmospheric D/H ratio measured in the atomic species (Clarke et al., 2021), and past results from many missions have characterized the D/H ratio in water (Alday et al., 2021; Encrenaz et al., 2018; Fedorova et al., 2020; Vandaele et al., 2019; Villanueva et al., 2021). D ions must exist on Mars, but have been neither modeled nor observed. In this work, we seek to use our 1D model to simulate the detailed D chemistry and answer the following:

- What are the abundances of deuterated ions in the martian atmosphere?
- Which chemical reactions dominate D escape?
- How do non-thermal processes affect D/H in the martian atmosphere?
- What are the relative contributions of thermal and non-thermal processes to D escape, and how does this balance differ from H escape?

## 1D photochemical modeling of deuterium ions

Neutrals and ions behave very differently: they have vastly different equilibration timescales, different density distributions, and different primary production pathways. 1D photochemical models that include both neutrals and ions must thus find ways to solve large systems of coupled equations for these very different populations. Most tend to either (1) have a lower boundary in the middle atmosphere (80-100 km) (V. A. Krasnopolsky, 2019, and references therein), (2) hold many species in the background neutral atmosphere fixed (Fox, 2015), or (3) assume that some or all short-lived species (such as ions) are in photochemical equilibrium (Banaszkiewicz et al., 2000; Dobrijevic et al., 2016; Fox, 2015). These approaches improve computation time, but risk losing fine details, precluding a complete understanding of the connections between D and H chemistry, escape, and lower-upper atmospheric coupling on Mars.

To achieve our goals and answer our scientific questions, we have extended the model from our previous paper (Cangi et al., 2020) to be the first fully coupled, surface-to-upper-atmosphere model of the neutral atmosphere and ionosphere that does not require any of the three previously described modeling approaches. The

model is built in Julia 1.7 (Bezanson et al., 2017), a language designed to combine the fast numerical modeling of languages like MATLAB and FORTRAN and the user-friendliness of Python. The original version of the model included 23 neutral species, a fixed background ionosphere of  $\text{CO}_2^+$ , a fixed water profile, and 117 chemical reactions. Our recent improvements include 13 new neutral and 43 new ion species, 900 new ion and neutral reactions, ambipolar diffusion for ion vertical transport, optional photochemical equilibrium for user-specifiable species, a water profile that is fixed in the lower atmosphere but freely solved in the middle and upper atmosphere, and of course, calculation of non-thermal escape for H and D. Computation-specific improvements include updated ODE solver algorithm options, vectorization of repeatedly called functions, and other general best-practice optimizations. Using the model, we simulate the atmospheric chemistry, photochemistry, and vertical diffusion in 2 km slices between 0-250 km. We choose a set of parameters and boundary conditions for the nominal Mars atmosphere (intended to represent a baseline). As the model runs, the simulated atmosphere evolves forward in time until it reaches a state of chemical and diffusive equilibrium, usually within 10 million years.

**Model inputs:** The primary model inputs include atmospheric temperatures at the surface, mesosphere, and base of the exosphere (i.e., roughly the neutral exobase) and the total atmospheric water content. Many other model parameters are modifiable, but typically don't change once we have arrived at reasonable choices for each, such as solver-specific options (e.g. number of timesteps, tolerance limits).

For a baseline, mean atmosphere, we assume a neutral temperature with  $T_{\text{surface}} = 216$  K,  $T_{\text{mesosphere}} = 130$  K, and  $T_{\text{exobase}} = 205$  K (Cangi et al., 2020), with ion and electron temperature profiles based on the Deep Dip 8 MAVEN data as described by Hanley et al. (2021, Figure 7a). The baseline water content of the atmosphere is 10 pr  $\mu\text{m}$ .

**Model outputs:** Our model output comprises atmospheric species densities ( $\text{cm}^{-3}$ ) at each layer of the atmosphere at discrete simulation times and for the final converged state. From this output, we can calculate and plot quantities relevant to answering our science questions, including:

- Densities of deuterated ions by altitude and species
- Chemical reaction rates by altitude and species
- Final resulting thermal and non-thermal escape rates of D, either cumulative or broken down by process

The escape rates are the primary output of interest. While the model does support calculation of hot H escape, we focus in this work on hot D escape. For

thermal escape, we consider Jeans escape only and assume that all atoms with a velocity falling in the tail of the Maxwell-Boltzmann distribution ( $v \geq v_{\text{esc}}$ ) will escape. Non-thermal escape is a bit more complicated, as it depends on collisions, and therefore the ever-changing density distributions of other species.

### How we calculate non-thermal escape

Although non-thermal H escape at Mars has been studied before (Nagy et al., 1990), there are no studies available in the literature that quantify production of superthermal (sometimes called “hot”) D atoms (those with high velocities that are not well described by the standard Maxwell-Boltzmann distribution). V. A. Krasnopolsky (2002) has provided estimates of certain non-thermal escape processes affecting this population, but only includes a few processes and excludes a detailed explanation of the calculations. This presents an opportunity, as non-thermal escape of D is expected to be far more important than thermal escape (Gacesa et al., 2018; V. Krasnopolsky, 2000). By applying the non-thermal escape velocity values from V. A. Krasnopolsky (2002) to their own model output, Cangi et al. (2020) showed that including non-thermal escape of D in calculations of the fractionation factor could change it by an order of magnitude and alter the estimation of integrated water loss by 10s of m GEL, indicating a need for updated, targeted modeling of non-thermal D loss.

Work to characterize the hot H production mechanisms in detail is presently underway (see Gregory et al., 2022, this meeting). In this study, we consider hot D produced via four main processes: (1) charge exchange reactions such as  $\text{D}^+ + \text{H} \rightarrow \text{D}_{\text{hot}} + \text{H}^+$ , (2) photoionization reactions such as  $\text{H}_2\text{O} + h\nu \rightarrow \text{H}^+ + \text{O}_2$ , and (3) dissociative recombination such as  $\text{DCO}^+ + e^- \rightarrow \text{CO} + \text{D}$ , and (4) other exothermic bimolecular ion reactions that produce a lone atomic D. To calculate how much escaping hot D is produced, we first calculate (from the model output) the volume production rate  $V_{\text{produced}}$  of any and all atomic D produced by exothermic reactions (Fox, 2015), generally falling under one of the four categories described previously. We then estimate the probability  $P$  of that atomic D to both be hot and to escape as follows:

$$P = Ae^{-a\sigma N(z)} \quad (1)$$

Where  $\sigma$  is a mean collisional cross section (Zhang et al., 2009),  $N(z)$  is the column density above altitude  $z$ , and  $A$  and  $a$  are parameters determined using by fitting to Monte Carlo simulations of hot H escape (see Gregory et al., this meeting). The volume production rate  $V_{\text{produced}}$  multiplied by this probability gives a volume production rate of escape-capable hot H and D:

$$V_{\text{esc}}[\text{cm}^{-3}\text{s}^{-1}] = PV_{\text{produced}} \quad (2)$$

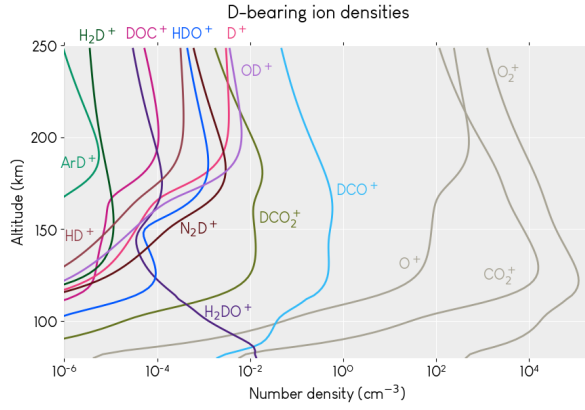


Figure 1: Volume production rates of escaping hot D from the top 5 chemical reactions.  $\text{DCO}^+$  dissociative recombination is the most important mechanism up to 180 km, at which point charge exchange of  $\text{D}^+$  with  $\text{CO}_2$  briefly takes over before giving way to  $\text{O}^+$  charge exchange with HD.

We perform this calculation for each chemical reaction, and the results can also be totaled. The expressions are vectors in altitude; by integrating them (summing over all altitudes), we arrive at a total non-thermal escape flux ( $\text{cm}^{-2}\text{s}^{-1}$ ) that we use to define an additional flux boundary condition at the upper boundary of the model. This flux is a function of the atmospheric conditions, so it constantly updates as the model runs, and its value at the end of the simulation reflects non-thermal loss in an equilibrium state.

## Results

Density profiles for D-bearing ions in our model are shown in Figure 1. For our mean atmosphere, we find that  $\text{DCO}^+$  is the dominant deuterated ion at all altitudes, with  $\text{D}^+$ ,  $\text{OD}^+$ , and  $\text{HDO}^+$  the most common deuterated ions near the base of the exosphere.  $\text{DCO}_2^+$  is also present in non-negligible concentrations at most altitudes. The order of these ions' appearances is similar to their H-bearing analogues, and the presented density profiles are useful for guiding possible future detection attempts.

The dominant chemical reactions contributing to non-thermal D escape are shown in Figure 2, and the total production of escaping non-thermal H and D in Figure 3. We find an upper limit for non-thermal escape of D to be  $\sim 1.7 \times 10^4 \text{ cm}^{-2}\text{s}^{-1}$ , double the  $2 \times 10^2 \text{ cm}^{-2}\text{s}^{-1}$  thermal escape reported by Cangi et al. (2020) for similar atmospheric conditions (Figure S5). The solar cycle conditions are for solar mean (Woods et al., 2019); it

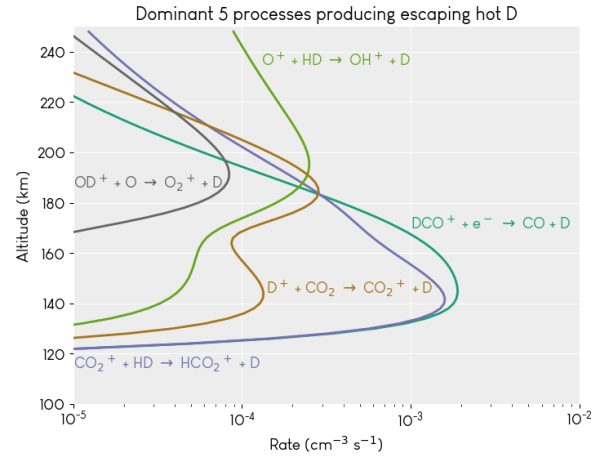


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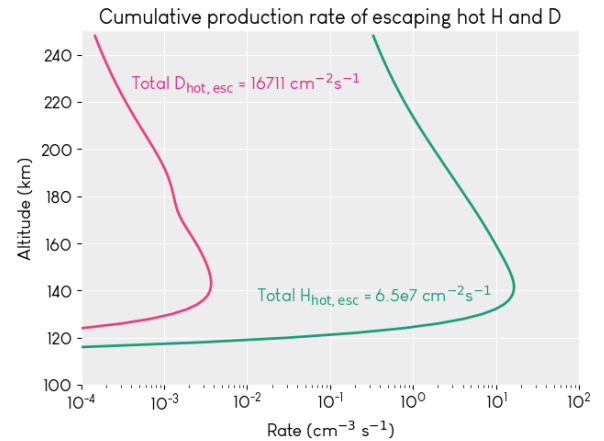


Figure 3: Volume production rate of escaping hot H and D from all contributing chemical reactions.

## REFERENCES

has been predicted (V. A. Krasnopolsky et al., 1998) that non-thermal escape should dominate for D at solar minimum only. Our model does not account for hot H and D that receive less than all the excess heat produced in exothermic reactions. With this thermal branching ratio included, we expect our calculation of non-thermal escape of D to be less, and likely more comparable to thermal escape at solar mean as predicted.

### Ongoing work

A more thorough discussion of the results and methods will occur at the in-person presentation at the meeting. Ongoing and future work will include similar modeling generated for solar minimum and solar maximum conditions, as well as seasonal cycling.

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