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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Contents of this file

1. Figure S1: Vertical density profiles of all modeled species

2. Figure S2: Density profiles of neutral deuterated species and their H-bearing analogues as a function of solar cycle

3. Figure S3: Comparison of densities with Fox, Benna, McFadden, Jakosky, and Maven Ngims Team (2021)

4. Figure S4: Water loss as a function of fractionation factor

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

6. Text S1: Using the reaction network spreadsheet

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

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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_{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_2 or HD by virtue of being exothermic.

• hotH, hotD, hotH2, 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:

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

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

$$\frac{v_1}{v_2} = \sqrt{\frac{R}{R+1}}, \tag{2}$$

where $R = m_{product2}/m_{H,D}$. If the product set consists of H and the heaviest species in the model, O_3, 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_3 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

Burkholder, J., Sander, S., Abbatt, J., Barker, J., Cappa, C., Crounse, J., ... Wine, P. H. (2019). *Chemical kinetics and photochemical data for use in atmospheric studies, evaluation no. 19* (JPL Publication No. 19-5). Pasadena: Jet Propulsion Laboratory.

Fox, J. L., Benna, M., McFadden, J. P., Jakosky, B. M., & Maven Ngims Team. (2021, April). Rate coefficients for the reactions of CO_2^+ with O: Lessons from MAVEN at Mars. *Icarus*, *358*, 114186. doi: 10.1016/j.icarus.2020.114186

Vuitton, V., Yelle, R. V., Klippenstein, S. J., Hörst, S. M., & Lavvas, P. (2019). Simulating the density of organic species in the atmosphere of Titan with a coupled ion-neutral photochemical model. *Icarus*, *324*, 120–197. Retrieved from

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

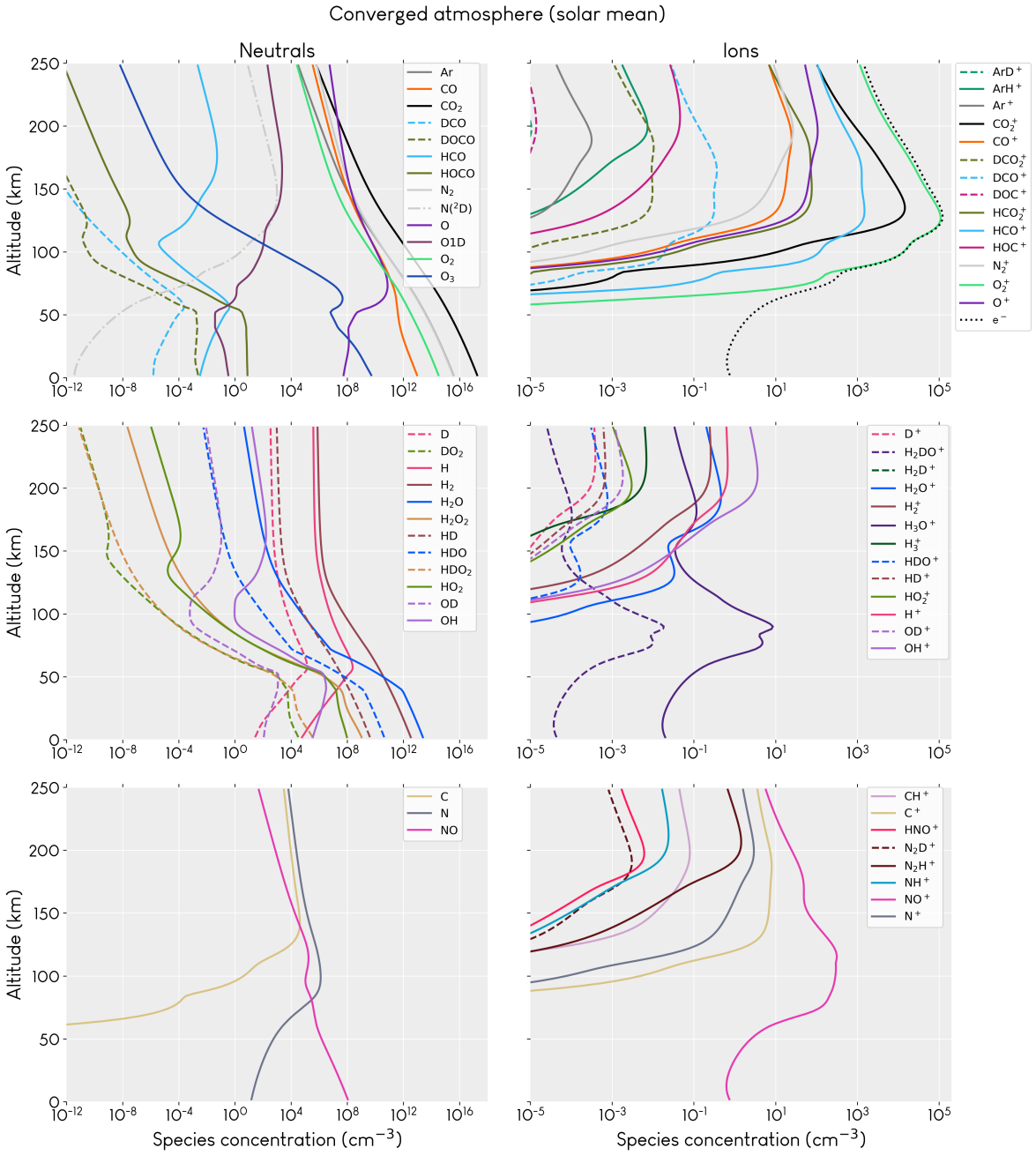

Figure S1. The complete atmosphere, with all species, at the end of the solar mean simulation.

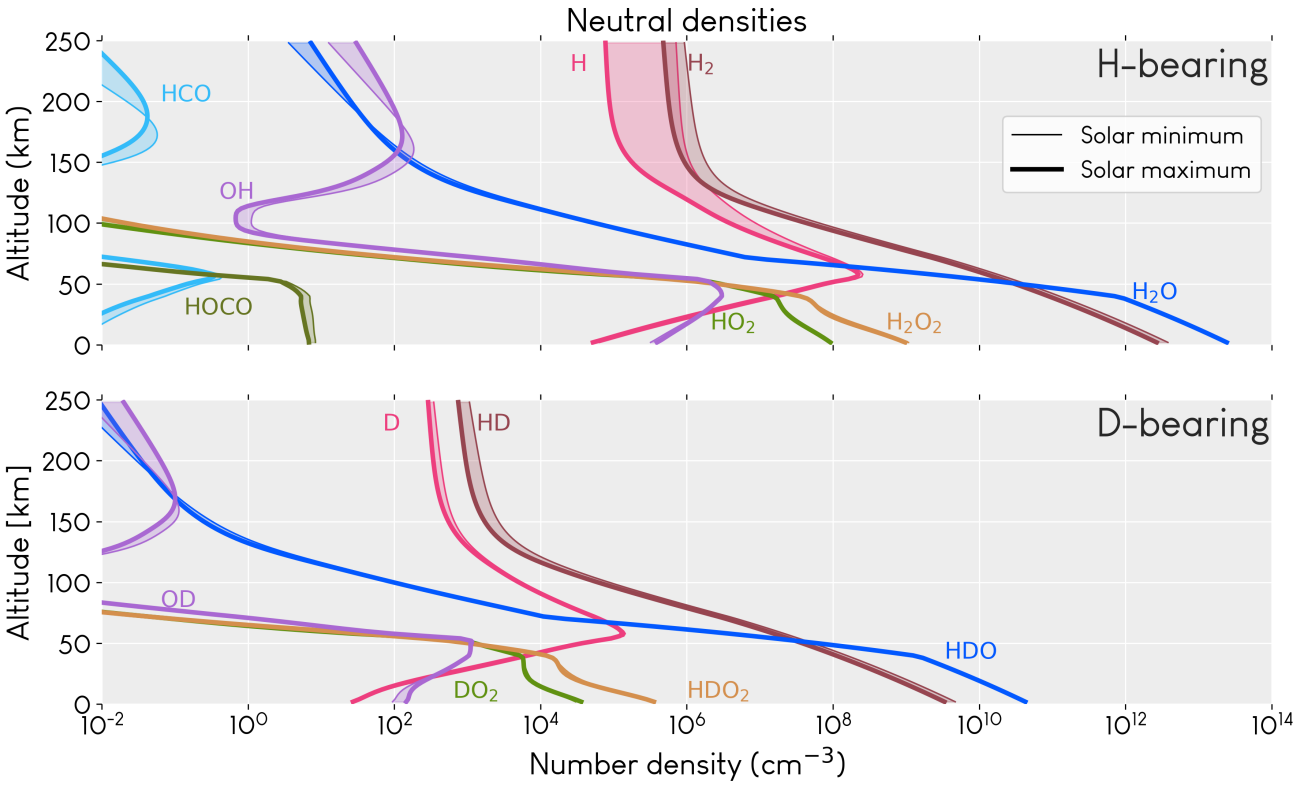

Figure S2. Densities of neutral deuterated species and their H-bearing analogues. Some minor species are not plotted in order to maintain legibility of the more abundant species.

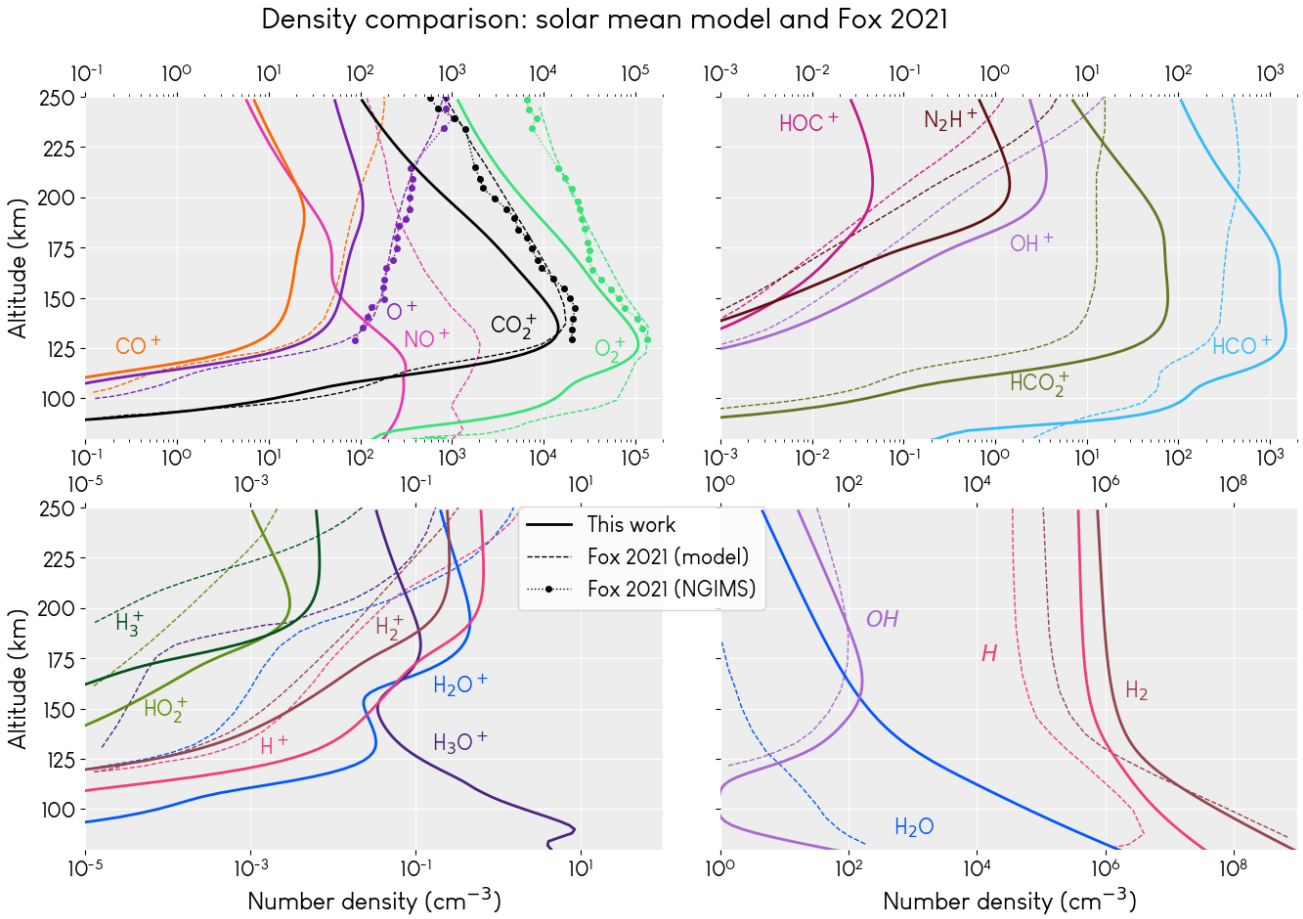

Figure S3. Comparison of model output with Fox et al. (2021), their model output and NGIMS densities for three principal ions.

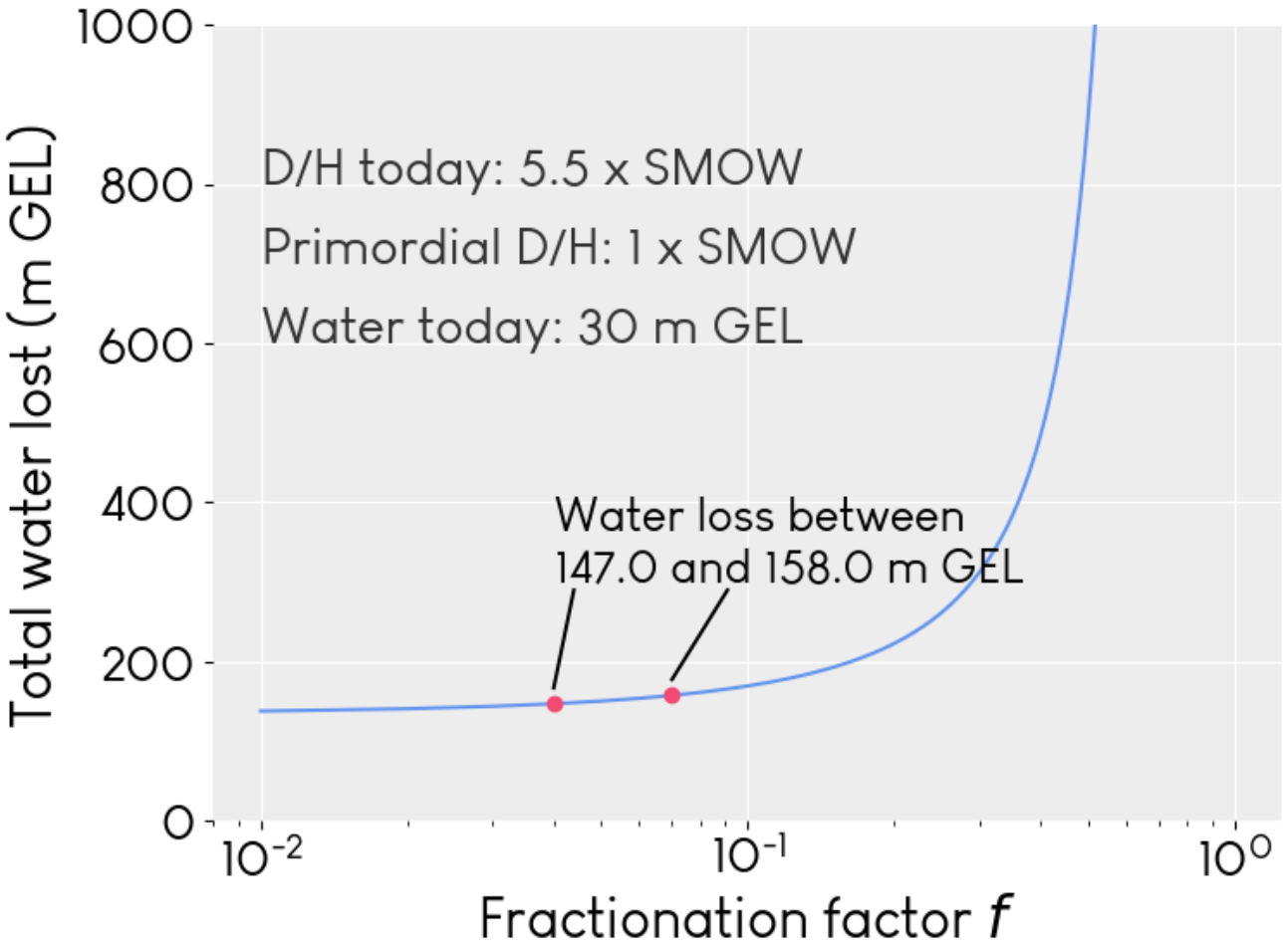

Figure S4. Water loss as a function of fractionation factor for D/H = 5.5× SMOW, primordial D/H = 1 × SMOW., and 30 m GEL present-day water inventory.