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Water Photolysis and its Contributions to the Hydroxyl Dayglow Emissions in the Atmospheres of Earth and Mars

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Abstract

Airglow is a well-known phenomenon in the Earth's upper atmosphere, which arises from the emissions of energetic atoms and molecules. The Meinel band emission from high vibrationally excited OH(X) radicals is one of the more important contributors to the airglow from the mesosphere/lower thermosphere. The $\text{H} + \text{O}_3$ reaction has long been regarded as the dominant source of these OH(X, high ν) radicals. Here we demonstrate that vacuum ultraviolet (VUV) photolysis of water vapor at $\lambda \sim 112.8$ nm represents another source of exceptionally highly vibrationally excited OH(X) radicals, with a nascent vibrational state population distribution that maximizes at $\nu = 9$ and extends to at least the $\nu = 15$ level. Atmospheric chemistry modelling indicates that OH(X, high ν) radicals from H_2O photolysis might be detectable in the OH Meinel band dayglow in the upper atmosphere of Earth, and should dominate the corresponding emission from the Martian atmosphere. VUV photolysis of H_2O also produces electronically-excited OH(A) radicals, and simultaneous detection of emissions from OH(X, high ν) and OH(A) is shown to offer a route to identifying high-oxygen exoplanetary atmospheres.

TOC Graphic:

Keywords: Photodissociation, VUV free electron laser, OH airglow, high vibrational excitation

The Earth's sky exhibits a faint luminescence known as airglow, which is caused by solar radiation initiated chemical reactions between atoms and molecules present in the upper atmosphere. Though weaker than the bright auroral display, the airglow provides important optical signatures of processes occurring in the atmosphere and studies of the airglow have driven the field of upper atmospheric science known as aeronomy.¹

The OH Meinel band emission² is an important contributor to the airglow in the Earth's mesosphere/lower thermosphere and has also been observed from the upper atmospheres of Mars³ and Venus.⁴ First identified in the Earth's atmosphere at night (*i.e.* as part of the nightglow) using a ground-based spectrometer,⁵ selected spectral regions of the Meinel band emission have since been studied using balloon-borne spectrometers⁶ and the TIMED⁷ (Thermosphere-Ionosphere-Mesosphere Energetic and Dynamics) and Odin⁸ satellites during both night and day. More than 1700 OH Meinel lines have now been identified and assigned to transitions from high vibrational levels (with vibrational quantum number $v \leq 9$) of the ground ($X^2\Pi$) state of the OH radical.⁹

Such vibrationally excited OH(X) radicals in the Earth's upper atmosphere have long been ascribed to products of the highly exothermic reaction of H atoms with O₃.¹⁰⁻

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The H and O₃ reactants are formed by, respectively, H₂O photolysis and the three-body association $\text{O} + \text{O}_2 + \text{M}$ (where $\text{M} = \text{N}_2, \text{O}_2, \text{etc.}$). Energy conservation dictates that the highest vibrational level of the OH(X) products from reaction (1) will be $v = 9$; the

(very weak) emission from OH(X, $v = 10$) radicals observed in the Earth's nightglow has been attributed to reactions involving vibrationally excited O₃ molecules.¹²⁻¹³ The higher background light levels make studies of the OH dayglow more challenging, but this emission has been found to exhibit a double-layer structure – peaking at heights $z \sim 88$ km (near the mesopause) and in the range $70 \leq z \leq 85$ km (which mimics the double-peaked daytime O₃ concentration profile).¹⁴

H₂O photolysis is an important source of OH radicals in the interstellar medium (ISM),¹⁵ and the photochemistry of H₂O has been the subject of many prior experimental and theoretical studies summarized in refs.16-18 and in the Supporting Information (*SI*). The electronic absorption spectrum of H₂O is entirely in the vacuum ultraviolet (VUV) region, at wavelengths $\lambda < 190$ nm.¹⁹ Excitation in the range $150 \leq \lambda \leq 190$ nm populates the first excited singlet state (the $\tilde{A}^1B_1$ state). The ensuing direct dissociation yields H atoms and OH(X) radicals in a range of (low) vibrational states; 72% of the OH(X, v) products from the $\lambda = 157.6$ nm photolysis of H₂O, for example, are formed in levels with $0 < v \leq 4$.²⁰

Photoexcitation to the second ($\tilde{B}^1A_1$) excited singlet state, via the $\tilde{B} - \tilde{X}$ continuum absorption centred at $\lambda \sim 128$ nm, has served as a prototype for exploring and understanding non-adiabatic dissociation dynamics in polyatomic molecules.²¹⁻²³ Adiabatic dissociation on the $\tilde{B}$ state potential energy surface (PES) yields H atoms plus electronically excited OH(A²Σ⁺) radicals. However, the quantum yield of this process is much smaller than that for forming H + OH(X) products following non-adiabatic transfer from the $\tilde{B}$ state to the $\tilde{A}$ state or to the ground ($\tilde{X}$) state PESs.²⁴⁻

²⁶ Both the OH(X) and OH(A) fragments are formed highly rotationally excited – a consequence of the topography of the $\tilde{B}$ state PES, which encourages opening of the $\angle\text{HOH}$ bond angle in tandem with HO–H bond extension and fission.

The H₂O absorption spectrum at yet shorter wavelengths shows numerous resonances associated with excitations to Rydberg states, including the $\tilde{C} - \tilde{X}$, $\tilde{D} - \tilde{X}$ and $\tilde{E} - \tilde{X}$ transitions with origin bands at $\lambda \sim 124$, ~ 121 and ~ 112.8 nm.²⁷ Photodissociation at $\lambda \sim 124$ nm yields OH(X) products in a broad spread of vibrational levels with $v \leq 13$,¹⁶ whereas Lyman- α ($\lambda = 121.6$ nm) excitation favours highly rotationally excited OH(X) and OH(A) products.²³ The free-electron laser (FEL) at the Dalian Coherent Light Source (DCLS) allows studies of H₂O photolysis and OH radical formation at any atmospherically relevant wavelength. Here we report measurements of H₂O photodissociation via the $\tilde{E} - \tilde{X}$ origin band at $\lambda \sim 112.8$ nm using the VUV FEL laser together with the H-atom Rydberg tagging time-of-flight (HR-TOF) technique. The $\tilde{E} - \tilde{X}$ origin band displays partially resolved (but unassigned) rotational structure²⁸ (see *SI, Figure SI*). The present study reveals formation of extremely vibrationally excited OH(X) – henceforth termed ‘OH(X, high v)’ fragments, with an inverted vibrational state population distribution that maximizes at $v = 9$ and extends to at least $v = 15$ (*i.e.* to within 600 cm^{-1} of the dissociation limit of the OH(X) radical). **Supplementary Table 1** in the *SI* lists term values for all vibrational levels supported by the OH(X) state potential.

The present findings encourage us to pose, and answer, three questions of atmospheric relevance. Does H₂O photolysis contribute to the OH (X, v) radical yield,

both in the terrestrial atmosphere – where there is a strong biological source of O_2 – and in abiotic, O_2 -poor atmospheres such as found on Mars, Venus and the early Earth? If H_2O photolysis contributes, how might one detect $OH(X, \text{high } \nu)$ products that could only arise via the photolysis source? And, on a related theme, does the production of $OH(A)$ from H_2O photolysis make any significant contribution to the observed mesospheric $OH(A-X)$ resonance emission around 308 nm,²⁹ that is traditionally attributed to solar resonance pumping of $OH(X)$ radicals?

Figure 1A shows H atom TOF spectra measured following $\lambda = 112.81$ nm photolysis of a jet-cooled H_2O sample, with the polarization vector (ϵ) of the VUV FEL radiation aligned, respectively, parallel and perpendicular to the detection axis. These were converted to total kinetic energy release (TKER) spectra using eq. (2),

$$E_T = \frac{1}{2} m_H \left(1 + \frac{m_H}{m_{OH}}\right) \left(\frac{d}{t}\right)^2, \quad (2)$$

where E_T is the TKER, m_H and m_{OH} are the respective fragment masses, d is the distance between the photodissociation region and the detector, and t is the measured H atom TOF. Total energy and linear momentum must be conserved in the dissociation process, *i.e.*

$$h\nu + E_{\text{int}}(H_2O) - D_0(H-OH) = E_T + E_{\text{int}}(OH) \quad (3)$$

where h is the Planck constant, ν the photolysis photon frequency, $E_{\text{int}}(H_2O)$ is effectively zero given the jet-cooled parent sample and the dissociation energy $D_0(H-OH) = 41145.92 \pm 0.12 \text{ cm}^{-1}$.³⁰ Thus eq. (3) allows determination of the internal energy (E_{int}) distribution of the OH fragments from the TKER spectrum.

The derived $P(E_T)$ spectra (**Figure 1B**) reveal two clumps of peaks with different

angular distributions, suggesting that they arise via different dissociation mechanisms. The group with $E_T < 10,000 \text{ cm}^{-1}$ reveal formation of highly rotationally excited OH(A, $v = 0$ or 1) fragments, while the more widely spaced features at higher TKER indicate formation of OH(X) fragments in a broad distribution of vibrational states. The comparative narrowness of the latter features implies that these fragments carry little rotational excitation. The dominance of vibrationally excited, rotationally ‘cold’ OH(X) fragments has some parallels with the energy disposal observed when photolyzing H₂O at $\lambda = 124 \text{ nm}^{16}$ but is in marked contrast to that found at *e.g.* $\lambda = 121.6 \text{ nm}^{21}$ or 117.5 nm^{15} , where the dissociation dynamics favor formation of highly rotationally excited OH(X) fragments.

Very similar TKER spectra have been measured at neighbouring wavelengths ($\lambda = 112.89, 112.78$ and 112.70 nm , resonant with partially resolved rotational features in the $\tilde{E} - \tilde{X}$ origin band, see **Figure S2**), implying that the fragmentation dynamics are rather insensitive to parent rotational state. Thus the key photochemical finding of the present work is formation of OH(X, high v) fragments with a population distribution that extends to at least $v = 15$ (the vibrational energy content of which is >98% of the OH(X) potential well depth, $D_0(\text{O-H}) = 35593 \pm 24 \text{ cm}^{-1}$),³¹ that recoil preferentially along axes perpendicular to ϵ . Such recoil anisotropy is consistent with that expected for a perpendicular (*i.e.* $\tilde{E} \ ^1\text{B}_1 \leftarrow \tilde{X} \ ^1\text{A}_1$) photoexcitation and subsequent prompt (relative to the timescale of parent rotation) dissociation.

Quantum state population distributions for the OH photoproducts have been derived by simulating the TKER spectra, as described in the **SI**. **Figure 2A** shows the inverted

vibrational state population distribution of the OH(X) fragments from H₂O photolysis at $\lambda = 112.81$ nm, peaking at $v = 9$ and extending to the $v = 15$ level. The H + OH(X, high v) dissociation channel is dominant at this wavelength and ~95% of the total OH(X) fragment yield is formed in OH(X, $v > 0$) levels. The simulations provide branching ratio estimates: H+OH(X) : H+OH(A) : O(³P)+2H (*i.e.*, the three-body dissociation channel to atoms, characterized by a broad, structureless feature²³) of ~0.59 : 0.14 : 0.27 (see **Figure S3**), implying that the quantum yield, ϕ , for forming OH(X, $v > 0$) products when exciting the H₂O($\tilde{E}$) state is ~0.56 and that, of these, ~43% are formed in levels with $v > 9$ (*i.e.* $\phi[\text{OH(X, } v > 9)] \sim 0.24$).

The many prior studies of H₂O photodissociation at longer excitation wavelengths have revealed several non-radiative decay pathways, summarized in the **SI**. Analogy with these data suggest that the $\tilde{E}$ and $\tilde{C}$ states (both of which have ¹B₁ symmetry) display similar fragmentation dynamics and that the OH(X, high v) products arise via successive $\tilde{E} \rightarrow \tilde{I}^1\text{A}_2 \rightarrow \tilde{A}$ non-adiabatic couplings mediated by the asymmetric stretch vibration (of b_2 symmetry) in regions of configuration space where the respective PESs are near degenerate – *i.e.* at short and at extended O–H bond lengths, respectively; the OH(X, high v) products derive from the O–H bond that ‘survives’ after the final coupling to the $\tilde{A}$ state PES.

The present and previous^{15,16,25} experimental studies of H₂O photolysis allow us to assess its significance in the upper atmosphere. Two whole atmosphere chemistry-climate models (see **SI** for further details) were used to explore the extent to which H₂O photochemistry, *i.e.*

could contribute to the Meinel band and OH(A–X) emissions in the dayglows of Earth and Mars (here taken as representative O₂-rich and O₂-poor atmospheres). The model outputs shown here are for roughly similar conditions, namely: midday, 40°N, northern hemisphere spring (April for Earth; solar longitude (Ls) = 0 - 30° for Mars). Vertical profiles of temperature (*T*) and H₂O, H, O₃, OH, O₂ and, for Mars, CO₂ concentrations from the respective models are shown in **Figure S4**. Details of the VUV solar irradiance flux used in the modelling are also provided in the **SI**.

VUV photodissociation of H₂O yields OH(X, ν) fragments with varying degrees of vibrational excitation at all wavelengths $\lambda < 190$ nm. Nascent OH(X, ν) population distributions determined at selected wavelengths are collected in the **Figure S5** and used to estimate the quantum yields, ϕ , for forming OH(X, $\nu > 0$) and OH(X, $\nu > 9$) fragments in the photodissociation of H₂O (**Supplementary Table 3**).

The false color plots in **Figure S6** show calculated photolysis rates, $J(\text{H}_2\text{O})$, and OH(X, $\nu > 0$) and OH(X, $\nu > 9$) production rates per unit wavelength, as functions of wavelength and altitude (*z*) for Earth and Mars, respectively. Integrating these data over λ yields the respective height-dependent OH(X, $\nu > 0$) and OH(X, $\nu > 9$) production rates, $R_{\text{OH}(\text{X}, \nu > 0)}$ and $R_{\text{OH}(\text{X}, \nu > 9)}$. As **Figure 3A** shows, this analysis indicates that H₂O photolysis in the middle mesosphere (67–76 km) of Earth will be a minor (1-3%) source of OH(X, $\nu > 0$) radicals, *cf.* the Meinel reaction (1). But it also suggests that ~1% of the OH(X) radicals at $z \sim 72$ km will be formed via H₂O photolysis and in levels with $\nu > 9$, which might provide a means of detecting this pathway. A very different situation

is predicted for the Martian atmosphere for which, as **Figure 3B** shows, H_2O photolysis should be the dominant daytime source of $\text{OH}(\text{X}, \nu > 0)$ species at $z > 64$ km. Further, since $>40\%$ of these $\text{OH}(\text{X})$ radicals are predicted to be formed in levels with $\nu > 9$, this should be a far more favorable environment in which to detect emission from these high ν levels.

Figure 2B compares the nascent $\text{OH}(\text{X}, \nu)$ vibrational state population distribution from the $\text{H} + \text{O}_3$ reaction³² with that observed in the Earth's nightglow.³³ Clearly, the latter distribution is partially relaxed as a result of collisions during the radiative lifetimes of the $\text{OH}(\text{X}, \nu)$ levels ($\tau_{\text{rad}} \sim 5$ ms for levels with $\nu = 9-13$, *cf.* $\tau_{\text{rad}} > 50$ ms for the $\nu = 1$ level³⁴). Current understanding of these collisional relaxation processes is summarized in the *SI*. The nascent $\text{OH}(\text{X}, \nu)$ population distribution from short wavelength photolysis of H_2O will similarly (partially) relax prior to emission, but the detection of any emission from $\text{OH}(\text{X}, \nu > 9)$ radicals in the dayglow from Earth or Mars should provide unambiguous confirmation of a photolytic contribution to the $\text{OH}(\text{X})$ Meinel emission.

Figures 4A and 4B show Meinel emission spectra predicted using the PGOPHER spectral simulation package³⁵ and assuming an $\text{OH}(\text{X})$ population distribution with respective vibrational and rotational temperatures of $T_{\text{vib}} = 11,500$ K and $T_{\text{rot}} = 180$ K. This rotational temperature is representative of the Earth's mesopause, while the vibrational state population distribution (shown in **Figure 2B**) is not intended to mimic that prevailing under any specific atmospheric conditions but provides a convenient way of mimicking the $\text{OH}(\text{X}, \nu = 9)/\text{OH}(\text{X}, \nu = 4)$ population ratio (~ 0.25) derived from

terrestrial OH nightglow measurements.³³

The overview OH Meinel emission spectrum shown in **Figure 4A** has been separated into contributions from levels with $v \leq 9$ (black), $10 \leq v \leq 13$ (red) and $14 \leq v \leq 16$ (blue). The three contributions are displayed on a common emission probability scale, which reflects the respective Einstein A coefficients and the relative populations of the levels. Even at quite modest resolution – achieved here by applying a 50 cm^{-1} full width half maximum (FWHM) Gaussian linewidth to each rovibrational transition – it is easy to recognize regions at low wavenumber and at $\sim 4000 \text{ cm}^{-1}$, associated with the $\Delta v = -1$ and $\Delta v = -2$ transitions, that only report on levels with $v \geq 10$.

Emission measurements in the mid-IR are typically hampered by low detector sensitivities and unwanted attenuation by, for example, water vapor. The latter should not be a problem for satellite-based Meinel band measurements. Both the OH emission and the H₂O absorption spectra³⁶ consist of sharp lines, so complete attenuation of the former by the latter is unlikely. In the case of the $\sim 4000 \text{ cm}^{-1}$ emissions, the OH(X, $v = 11 \rightarrow v = 9$) band has some overlap with the stretch fundamentals of H₂O, but the OH(X, $v = 10 \rightarrow v = 8$) band is free from overlap.

It is also appropriate to identify signatures of emissions from high v levels at much shorter wavelengths. The 700–900 nm region displayed in **Figure 4B** highlights an obvious window at $\lambda \sim 870 \text{ nm}$ that contains emissions from levels with $v \geq 10$ only (specifically the $v = 13 \rightarrow v = 7$ band) and lies in a gap between weak H₂O overtone absorptions. *Supplementary Table 2* in the *SI* highlights reasonably intense and isolated features that might be suitable for detecting OH(X, v) radicals in each of the $v = 10 -$

14 levels.

VUV photodissociation of H₂O also produces electronically excited OH(A) fragments, with $\phi[\text{OH(A)}]$ measurements reported at $\lambda = 112.81$ nm (present work), 121.6 nm²³ and 131.0 nm.²⁵ The OH(A) production rates, $R_{\text{OH(A)}}$, were calculated in the same way as for $R_{\text{OH(X, } \nu>0)}$ (see **Supplementary Table 3**); the calculated emission rate at 308 nm was then compared with solar-pumped resonance fluorescence from ambient atmospheric OH(X). As **Figure 3C** shows, solar-pumped fluorescence dominates in the terrestrial atmosphere below ~ 78 km – though only by a factor of ~ 6 at the peak of the photolytic OH(A) layer at $z = 72$ km. This would imply that a significant fraction of the OH(A) emissions from the terrestrial upper atmosphere observed by Gattinger *et al.*²⁹ were produced by H₂O photolysis, which would have led to an overestimation of the ambient OH in the upper mesosphere. Even more strikingly, on Mars, the photolytic source of OH(A) is dominant throughout the range $43 \leq z \leq 122$ km, with a 6-times brighter integrated emission (**Figure 3D**). Note that the radiative lifetime of OH(A) is only ~ 700 ns,³⁷ which is shorter than the collisional lifetime above ~ 60 km on Earth and 35 km on Mars, so that the wavelength resolved spectrum of any photolytic OH(A) emission above these altitudes should be very different from that of a solar-pumped thermalized OH(X) distribution.

These results suggest a diagnostic for determining whether any exoplanetary atmosphere is highly oxygenated (*i.e.* like present-day Earth, as opposed to Mars): comparison of the signal from one of the strong OH overtone transitions in the near IR (700 – 900 nm region, **Figure 4B**) with the OH(A) signal at 308 nm. **Figure 5** shows

the vertical profile of the $R_{\text{OH(X, } \nu>0)}/R_{\text{OH(A)}}$ ratio, where emission from one of the OH overtone bands is taken as being roughly proportional to $R_{\text{OH(X, } \nu>0)}$. Excluding any contributions from H₂O photolysis to the OH(X, ν) and OH(A) emissions, this ratio on both Earth and Mars (dashed lines) display broad layers peaking at ~93 km on Earth and ~68 km on Mars. When H₂O photolysis is included (solid lines), however, the ratio for the terrestrial atmosphere still shows a layer (now peaking at ~87 km) – because the Meinel reaction (1) and OH solar pumping dominate (**Figures 3A and 3C**)). No such layered profile is predicted in the Martian atmosphere, however, because H₂O photolysis is the dominant contributor to both signals (**Figures 3B and 3D**). The predicted difference in this ratio for the atmospheres of Earth and Mars at 87 km is nearly 3 orders of magnitude. Observing such a large $R_{\text{OH(X, } \nu>0)}/R_{\text{OH(A)}}$ ratio would be a very clear signal of a high O₂/H₂O ratio (2×10^5 on Earth, *cf.* only 120 on Mars, at ~90 km altitude). For a planet in the habitable zone of a star, a high ratio would be compelling evidence for photosynthesis: when the Great Oxidation Event on Earth occurred around 2.5 Ga, the O₂ mixing ratio increased from $\sim 10^{-3}$ (similar to present-day Mars) to the present-day value of 0.2.³⁸

This study demonstrates that VUV photolysis of H₂O vapor can form highly vibrationally excited OH(X) radicals as well as OH(A) radicals. The modelling predicts that these OH(X, high ν) radicals might be detectable in the OH Meinel band dayglow in the upper atmosphere of Earth and should dominate the corresponding emission from the Martian atmosphere. Further, OH(A) emission has been shown to be an indicator of H₂O photolysis in the upper atmosphere of Earth and, more importantly, the OH(X,

high ν /OH(A) emission ratio should be a direct diagnostic of the oxidation state of exoplanetary atmospheres.³⁹

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Supporting Information

Supporting Information Available: Detailed description of the experimental methods, OH term values and transitions, spectral fitting procedures, and atmospheric chemistry-climate modelling. Figures S1-S6 and Supplementary Tables 1-3.

Notes

The authors declare no competing financial interest.

Figures and Captions:

Figure 1 (A) Time-of-flight (TOF) spectra of the H atom fragments from photodissociation of H₂O at $\lambda = 112.81$ nm with the FEL laser polarization vector aligned parallel (red) and perpendicular (blue) to the detection axis. (B) TKER spectra obtained from the TOF data shown in (A). The sharp features can be assigned to population of rovibrational states of OH(X) and OH(A) radicals, as shown by the combs festooned above the spectra.

Figure 2 Relative OH(X, ν) vibrational state population distributions, P_ν , resulting from: (A) H₂O photodissociation at $\lambda = 112.81$ nm; (B) the H + O₃ reaction under single collision conditions (from Ref. 32) and observed in the Earth's airglow (from Refs. 33 and 12) with, in each case, the highest displayed population normalized to unity. (Note, the OH(X, $\nu=10$) level population in B (identified with an asterisk *) has been plotted on a 1000× expanded vertical scale). The dashed curve (blue) shows the P_ν distribution for $T_{\text{vib}} = 11500$ K used in generating the spectra shown in Figure 4.

Figure 3 Calculated vertical profiles of the production rates of $\text{OH}(\text{X}, \nu > 0)$ and $\text{OH}(\text{X}, \nu > 9)$ radicals by H_2O photolysis and for forming $\text{OH}(\text{X}, \text{all } \nu)$ through the $\text{H} + \text{O}_3$ reaction (1) at midday on **A:** Earth (40°N, April) and **B:** Mars (40°N, Ls = 30°). Calculated vertical profiles of the OH(A) production rates from H_2O photolysis and by solar-pumping of ambient atmospheric OH(X) under the same conditions on **C:** Earth and **D:** Mars.

Figure 4. OH Meinel emission spectrum simulated using PGOPHER, assuming an OH(X, v) population distribution described by $T_{\text{vib}} = 11,500$ K and $T_{\text{rot}} = 180$ K, plotted to illustrate contributions from levels with $v \leq 9$ (black), $10 \leq v \leq 13$ (red) and $14 \leq v \leq 16$ (blue). **A:** ‘low-resolution’ overview spectrum, plotted using a 50 cm^{-1} (FWHM) Gaussian linewidth for each rovibrational transition. **B:** higher resolution spectrum of the 700 – 900 nm region shaded in A, plotted with a 1 cm^{-1} effective resolution.

Figure 5. The ratio of the total OH(X, $\nu > 0$) versus OH(A) radical emissions as a function of altitude, for Earth (black) and Mars (red). The solid (dashed) lines show the ratio with (and without) inclusion of H₂O photolysis along with the Meinel reaction and solar-pumped resonance fluorescence.

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