Resetting Tropospheric OH and CH_4 Lifetime with UV H_2O Absorption

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Abstract

The decay of methyl chloroform, a banned ozone-depleting substance, has provided a clear observational metric of mean tropospheric OH abundance. Almost all current global chemistry models calculate about 15% too much OH, and thus too rapid methane loss. Methane is a short-lived climate forcer, critical to achieving global warming targets, and this error impacts our model projections of climate change. New observations of water vapor absorption in the ultraviolet region (290-350 nm) imply reductions in sunlight with key photolysis rates decreasing by 8-12% in the near-surface tropical atmosphere. Incorporation of this new mechanism in a chemistry-transport model reduces OH and methane loss by only 4%, but combined with other proposed mechanisms, such as tropospheric halogen chemistry (7%), we may be able to resolve this conundrum.

Projecting the efficacy of climate change mitigation efforts involving short-lived climate forcers such as the greenhouse gas methane (CH_4) (*1*) requires accurate modeling of its atmospheric loss, which is a function of its lifetime, i.e., the total atmospheric burden divided by the loss rate. A long-standing problem with most current global chemistry models (*2*-*3*) is that the lifetime of methane (CH_4) with respect to loss by tropospheric OH, which constitutes about 82% of the total loss, is systematically lower than that scaled from the observed OH-driven decay of methyl chloroform (CH_3CCl_3) (*4*). Here, we identify a missing component in current chemistry models, viz. ultraviolet absorption by water vapor (H_2O) (*5*), and show that its inclusion in a photochemistry model will reduce OH levels, increasing the CH_4 lifetime, thus partly resolving the discrepancy found in most models (*2*).

A combination of recent laboratory studies, field measurements, and satellite observations presents a convincing case for significant absorption of radiation by water vapor at ultraviolet wavelengths (*5*-*6*). Previously, only negligibly small ultraviolet H_2O absorption was found (*7*-*8*). Both sides of that disagreement present plausible cases and the difference remains unresolved. Here, we take the recently measured H_2O cross sections, implement them in a photolysis code, and examine the first-order impacts on tropospheric chemistry.

Water vapor absorbs ultraviolet sunlight (290- to 350-nm) in the troposphere but does not photodissociate, and thus it reduces the overall photochemical activity. This tropospheric ultraviolet window coincides with that where photolysis of ozone (O_3) produces the metastable excited state of atomic oxygen, $O(^1D)$ (R1). Some of this $O(^1D)$ reacts with H_2O (R2) becoming the primary source of atmospheric hydroxyl radicals (OH). These OH radicals are responsible for the photochemical destruction of many pollutants, including CH_4 (R3).

$$O_3 + h\nu\ (\lambda < 340\ \text{nm}) \rightarrow O_2 + O(^1D) \qquad \text{(R1)}$$

$$O(^1D) + H_2O \rightarrow OH + OH \qquad \text{(R2)}$$

$$OH + CH_4 \rightarrow CH_3 + H_2O \quad (R3)$$

Here we adopt the measured ultraviolet spectrum for H_2O absorption from (*5*) as shown by the thin black line in Figure 1a. This high-resolution (1-nm) absorption is mapped onto the broader wavelength bins used in the photolysis calculations of the Cloud-J module (*9*) and shown as blue bars. These average H_2O cross sections are weighted by the variations in solar flux across each bin. Even these 'large' H_2O cross sections are relatively small, only about eight times larger than the Rayleigh scattering cross section for air, shown as black bars. The cross section for R1, scaled down by 10^6, is shown as red bars. R1 occurs only for wavelengths less than 340 nm, i.e., the five leftmost bars in the figure, which have mid-point wavelengths of 295, 303, 310, 316, and 333 nm.

Photolysis Results

The photolysis rate for R1, J_{O1D} (s^{-1}), is calculated here using Cloud-J 7.6 (*10*) updated to version 8.0 to include H_2O absorption in the ultraviolet region (Fig. 1a). Calculations in Fig. 1 are for overhead sun, clear sky, and a tropical atmosphere, see caption. The contribution to J_{O1D} from the five ultraviolet wavelength bins are shown in Fig. 1b. The 295-nm bin has the largest cross section for R1, but 99.5 % of the photons in this bin are absorbed in the stratosphere and so it contributes little to J_{O1D} (<5%). The 333-nm bin has very low cross sections for R1 and also contributes less than 5% to J_{O1D}. The dominant production of $O(^1D)$ comes from the 303-, 310-, and 316-nm bins.

The total J_{O1D} tropospheric profile is shown in Fig. 1c with H_2O absorption (blue line) and without (red line). The decrease in J_{O1D} from previous models (without H_2O) is substantial, 11% near the surface falling to 5 % at 3 km altitude and 2 % by 10 km. Many other key tropospheric photolysis rates also decrease at the surface, see Table 1. For example, J_{H2CO} is driven by ultraviolet wavelengths, and the two channels decrease by 8-10 % (surface) to 4-5% (3 km) to 2% (10 km). In contrast, J_{NO2} with dominant cross sections at blue wavelengths decreases by only 1 % throughout the troposphere. An obvious atmospheric test of UV H_2O absorption would be through profiles of measured and modeled actinic fluxes in the UV region as in (*11*), but absolute fluxes vary with nearby clouds and are difficult to model at the 10% level.

The ultraviolet-visible heating rates calculated in Cloud-J 7.6c consider only O_3 absorption and not H_2O absorption, and thus these rates are small, < 0.02 K day^{-1} throughout most of the troposphere, see Fig. 1d. With the H_2O ultraviolet absorption adopted here, these rates jump to 0.05 K day^{-1} near the surface but this rate is inconsequential compared to solar heating by clouds (*12*, Fig. 3), infrared absorption by H_2O, or other sources of available potential energy (*13*). In terms of the overall radiative balance in this case, the atmospheric absorption increases by 1.5 W m^{-2} (0.1%), reducing surface ocean absorption by 1.25 W m^{-2} and reflected sunlight by 0.25 W m^{-2}.

The photolysis code and underlying cross sections for other chemical species are described in (*9*) for Cloud-J version 7.3c, in (*10*) for Cloud-J and Solar-J version 7.6. The new photolysis module including absorption by H_2O (Cloud-J version 8.0 including its code, figures and tables) is published in (*14*).

Chemistry Results

The updated Cloud-J (v8.0) was incorporated into thee current UC Irvine chemistry-transport model (CTM). The UCI CTM, including Cloud-J, has been used for a variety global chemistry studies (*11, 15-16*), and in direct comparisons with many global models, the O_3 and OH chemistry results are consistent with the other top models (*16-18*). A five-year simulation was made using the integrated forecast system (OpenIFS, cycle 38r1) meteorological data for years 2000-2004 but with annually repeating emissions for year 2000 from scenario RCP-6.0. The annual

chemical budgets averaged over the last four years for O_3, CO, and CH_4 are given in Table 2. We did not activate the extra diagnostics for stratosphere-troposphere exchange of O_3 in these CTM simulations, and so it is derived from mass balance.

The budgets in T-moles provide for some interesting comparisons. About 60% of the CO source is from in situ chemical production (64 Tm y^{-1}), about half of which is from CH_4 oxidation (34 Tm y^{-1}) and the rest from short-lived non-methane hydrocarbons. The primary OH production (101 Tm y^{-1}) matches the OH oxidation of CO (99 Tm y^{-1}), and thus the extra OH to oxidize CH_4 and other hydrocarbons must be part of OH amplification involving reactions of OH, HO_2, NO, NO_2, and hydrocarbons.

A parallel perturbation simulation was run with the H_2O absorption cross sections zeroed out and the % changes are given in Table 2. Because the H_2O absorption results in 8-12% boundary-layer reductions in photolysis rates for so many species (e.g., H_2CO, HOOH, CH_3OOH, acetaldehyde, acetone, see Table 1), we expect complex changes across the major tropospheric species. The largest perturbation caused by the H_2O absorption is still what we expected from the photolysis-only example above: primary OH production is reduced by 4.4% and the OH-driven loss of CH_4 decreases by 4.1%. This decrease results in a reduced CH_4-source of CO, but the CO sink is also reduced by 3.8%, so that overall CO increases by 2.1%. The OH reduction has a larger impact on CH_4 compared with CO (4.1% vs. 3.8%) because the CH_4 loss is highly temperature dependent, occurring more rapidly in the lowermost tropical troposphere where the H_2O absorption has the largest reduction in J_{O1D} (Fig. 1).

Tropospheric O_3 increases by 2.0%, and it is hard to explain simply with the budget terms we have available. The obvious explanation is that O_3 loss was reduced by 2-4% because the major terms are $O(^1D)+H_2O$, O_3+OH, and O_3+HO_2. The first two terms dropped 4% and HO_2 dropped only 1%. Production of O_3 is assigned to the rates of HO_2+NO and other peroxy radicals with NO. The HO_2 mass dropped only 1% while NO and NO_2 were unchanged. Thus, the photolysis changes reduced O_3 loss more than production and the abundance increased.

The lower tropical troposphere dominates both the CH_4 budget and the impact of H_2O absorption. The tropospheric loss of CH_4 to reaction with OH is weighted toward the lower troposphere with 40% of the total occurring in the 800-1000 hPa range, 84% in the 500-1000 hPa range, and about 8% at pressures < 400 hPa. The relative reduction in CH_4 loss from H_2O absorption is about 2.5% at pressures < 500 hPa, increasing linearly in pressure to 6.5% at 1000 hPa. Half (50%) of CH_4 loss occurs in the core tropics (±20° latitude), where the impact of H_2O absorption is largest (>5%); and most loss (90%) occurs within ±45° latitude, where the H_2O impact drops to about 3%. The longitudinal impact of H_2O varies about 4.3% with a standard deviation of 0.6%. Thus, the largest relative impact of UV absorption by H_2O occurs where the absolute loss of CH_4 is greatest.

Discussion

This process – UV absorption by H_2O – can only partially resolve one of the more enduring conundrums in modeling CH_4: use of the OH calculated in current models produces a much more rapid decay of atmospheric CH_3CCl_3 than is observed, 0.18 y^{-1} (±1%) over 1998-2008 (*15, 19*). From Table 1 of (*2*), the mean modeled CH_4 lifetime across 16 global chemistry models is biased 15% low (i.e., biased high in OH). Work by (*3*) examined 10 next-generation models and found their CH_4 lifetime for the 2000 period ranged from 6.6 to 8.5 y, with most having lifetimes below 8 y, which also falls well below an observationally based range of 9.1±0.9 yr (*14-15*). Reference (*3*) also identified the tropospheric O_3 abundances and J_{O1D} as the primary factors controlling model differences. Unfortunately, we can get only 4% of the 15% OH reduction by including H_2O absorption, and thus must continue to look elsewhere.

A number of chemistry models have added tropospheric halogen chemistry (*20-23*) and found that the ensuing chemical changes caused, typically, an 8% reduction in the $OH+CH_4$ rate, which was attributed to a 20% reduction in present day tropospheric O_3, e.g., from 30 to 24 DU. Calculations using the NASA Atmospheric Tomography mission (ATom) parcel data (*24*) show that O_3 controls CH_4 loss with a sensitivity factor of 0.46 over the Atlantic and Pacific Ocean basins, and combining this with a 20% reduction in tropospheric O_3 gives a 9% reduction in $OH+CH_4$. One challenge for the halogen model is that the major shift in tropospheric O_3 down to 24 DU may be incompatible with observations giving values closer to 30 DU (*25*, Table 1)

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Table 1. Reduction in key tropospheric photolysis rates (J-values) at the surface when UV absorption by H_2O (*5*) is included.

J-value	reduction @ surface	notes
O3(1D)	11%	O_3 photolysis yielding $O(^1D)$
H2COa	10%	H_2CO channel–a yields H + HCO;
H2COb	8%	channel-b yields H_2 + CO.
H2O2	9%	
CH3OOH	8%	
N2O5	8%	
HNO3	11%	
OCS	9%	
PAN	10%	
CH3NO3	11%	
ActAld	12%	Acetaldehyde
MeVK	8%	Methylvinyl ketone
MeAcr	5%	Methacrolein
GlyAld	11%	Glycol aldehyde
MEKeto	11%	Methylethyl ketone
PrAld	11%	Propionaldehyde, C_2H_5CHO-> C_2H_5+HCO
Glyxlb	9%	Glyoxal, $(CHO)_2$, channels–b and –c are equally affected;
Glyxlc	9%	channel–a (HCO+HCO, 61% of total) is much less affected (3%).

Acet-a	11%	Acetone, both channel–a (CH_3CO+CH_3) and channel–b
Acet-b	12%	(CH_3+CH_3+CO) are affected almost equally.
Table notes: Calculated for tropical atmosphere, overhead sun; lower sun angles increase the % reduction. For all J-values, reduction % drops by ½ at ~3 km altitude, and by ¼ at ~7 km. Long-lived (stratospheric) trace gases not affected. Halogen species are not included. Other J-values are reduced by <5%.		

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Table 2. Reference case tropospheric chemical budgets (T-mole, T-mole y^{-1}, y) and change (%)

	tropospheric O_3 + O	global CO	global CH_4	OH via $O(^1D)+H_2O$
mass (Tm)	7.2	11.9	306.4	
emission (Tm y^{-1})	none	+45.54	l.b.c.	
chemical production (Tm y^{-1})	+507.34	+64.05	none	100.6
chemical loss (Tm y^{-1})	-501.64	-99.42	-33.73	
surface deposition (Tm y^{-1})	-13.24	-4.77	-1.88	
stratosphere-troposphere flux (Tm y^{-1})	+7.54	-5.38	-1.99	
net sum (Tm y^{-1})	0.00	0.02	37.60	
lifetime vs. OH (y)		0.120	9.08	
Relative change (%) in magnitude caused by UV H_2O absorption.				
mass	+2.05%	+2.09%	+0.02%	
chemical production	+0.90%	-2.48%	none	-4.42%
chemical loss	+0.85%	-1.77%	-4.09%	

Chemical production and loss refer to tropospheric chemistry only; stratospheric chemistry is counted as stratosphere-troposphere flux (units = T-moles per year). Results are the average of the last 4 years (2001-2004) of a UCI CTM simulation using constant year 2000 emissions from RCP6.0 scenario. The terms are taken from the budget tendencies except for the O_3 s-t flux, which is derived from mass balance. The O_3 production and loss terms assume that ground state atomic oxygen $O(^3P)$ and O_3 are equivalent and thus rates like $O+O_2+M\rightarrow O_3$ are not included, but the rate $NO_2+h\nu\rightarrow NO+O$ counts as the dominant O_3+O production (>99%) in these budgets. The rates $O(^1D)+H_2O$ (50 Tm y^{-1}) and $O(^1D)+CH_4$ (0.02 Tm y^{-1}) count as O_3+O loss, while O_2+hv counts as production of two O_3+O (0.6 Tm y^{-1}). CH_4 and CO chemical loss in these simulations is 99.9% due to tropospheric OH. Changes in radicals other than OH were smaller: NO and NO_2 tropospheric mass changed by <0.1%; HO_2 decreased by 0.9%. The lifetime versus OH is a simple burden:loss ratio, no chemical feedbacks are included.

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262 **Figure 1. Ultraviolet (UV) absorption by H_2O and its impact on photolysis and heating**
263 **rates. (a)** UV cross sections for H_2O absorption from laboratory measurements (*5*) (thin black
264 line), H_2O absorption as used by the wavelength bins in the Cloud-J (thick blue bars), Rayleigh
265 scattering by air (thick black bars), and O_3 absorption times quantum yield producing of $O(^1D)$
266 (scaled by 10^{-6}, red bars). **(b)** Altitude profiles of J_{O1D} (s^{-1}) from each of the 5 UV wavelength bins
267 in Cloud-J, centered on 295, 303, 310, 316, and 333 nm. Calculations are made with a tropical,
268 cloud-free, overhead-sun, oceanic atmosphere, and total ozone column of 274 DU. Plotted are
269 tropospheric values from surface (0 km, 1013 hPa, 299.5 K) to tropopause (16 km 110 hPa, 191
270 K). The H_2O profile has a scale height of about 2.2 km and a column density of 14 $\times10^{22}$
271 molecules. cm^{-2}, falling within the range of tropical atmospheres, 10-18 $\times10^{22}$ molecules cm^{-2}
272 (*26*). **(c)** Altitude profiles of total J_{O1D} (s^{-1}) calculated with (blue) and without (red) H_2O UV

absorption. **(d)** Altitude profiles of heating rates (K d^{-1}) calculated using only UV plus visible O_3 absorption (red) and then including UV H_2O absorption (blue).