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# Water Vapor does not Catalyze the Reaction between Methanol and OH Radicals

Wen Chao,<sup>[b]</sup> Jim Jr-Min Lin,<sup>[b]</sup> Kaito Takahashi,<sup>[b]</sup> Alexandre Tomas,<sup>[c]</sup> Lu Yu,<sup>[d]</sup> Yoshizumi Kajii,<sup>[d]</sup> Sébastien Batut,<sup>[a]</sup> Coralie Schoemaeker<sup>[a]</sup>, and Christa Fittschen\*<sup>[a]</sup>

**Abstract:** Recent works [Jara-Toro *et al.*, *Angew. Chem. Int. Ed.* **2017**, *56*, 2166 and *PCCP* **2018**, *20*, 27885] suggest that the rate coefficient of OH reactions with alcohols would increase by up to 2 times from dry to high humidity. This finding would have an impact on the budget of alcohols in the atmosphere and that it may explain differences in measured and modeled methanol concentrations. The results were based on a relative technique carried out in a small Teflon bag, which might suffer from wall reactions. We have re-investigated this effect using a direct fluorescence probe of OH radicals, and no catalytic effect of H<sub>2</sub>O could be found. Experiments in a Teflon bag were also carried out, but we were not able to reproduce the results of Jara-Toro *et al.* Further theoretical calculations show that the water-mediated reactions have negligible rates compared to the bare reaction and that even though water molecules can lower the barriers of reactions, it cannot make up for the entropy cost.

Methanol (CH<sub>3</sub>OH) is one of the most abundant oxygenated volatile organic compounds (OVOC) in the atmosphere<sup>[1, 2]</sup>. Direct emissions are the main source, but some oxidation pathways of methane also contribute to its abundance, especially in the remote troposphere<sup>[3, 4, 5]</sup>. Concentrations range from 1-15 ppbv in the continental boundary layer and up to 1 ppbv in the remote troposphere<sup>[6, 7]</sup>. Despite numerous efforts, global atmospheric chemical models are presently unable to reconcile the modeled and measured methanol concentrations<sup>[7, 8, 9]</sup>.

The atmospheric degradation of CH<sub>3</sub>OH is governed by its reaction with OH radicals, which proceeds by abstraction of H-atoms from either the methyl or the hydroxyl site<sup>[10]</sup>. The rate coefficient shows a non-Arrhenius behavior and increases at

temperatures below 200 K, due to enhanced stabilization of a pre-reactive H-bonded complex that can undergo tunneling<sup>[10]</sup>. The rate coefficient at room temperature (298 K) has been measured many times<sup>[11, 12]</sup> and is recommended<sup>[13]</sup> to be  $k_1 = 9.0 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ .

Very recently, Jara-Toro *et al.*<sup>[14]</sup> reported that the reaction of OH with CH<sub>3</sub>OH is significantly catalyzed by water (enhanced by a factor of 2 between 20 to 95% of relative humidity) even at 294 K. The same group also reported the water catalysis effect on reactions of OH with ethanol and n-propanol<sup>[15]</sup>. Their results are based on a well-known relative method, where the consumption of the alcohol is measured relative to the consumption of a reference compound (C<sub>5</sub>H<sub>12</sub>) following their simultaneous reactions with OH radicals. The reactions took place in a 80 liter Teflon bag, and OH radicals were generated continuously from the 254 nm photolysis of H<sub>2</sub>O<sub>2</sub>. The ratio of the consumption of CH<sub>3</sub>OH versus the consumption of C<sub>5</sub>H<sub>12</sub> gives the ratio of the rate coefficients,  $k_{\text{CH}_3\text{OH}+\text{OH}} / k_{\text{Ref}+\text{OH}}$ . This type of experiments was carried out at different relative humidity (RH) up to 95%, and it was found that the ratio increased with increasing RH. Under the assumption that the rate of the OH reaction with unpolar C<sub>5</sub>H<sub>12</sub> is independent on RH, this increased ratio was assigned to an increased rate of OH reaction with CH<sub>3</sub>OH due to water catalysis. More surprisingly, they found a quadratic dependence of the rate enhancement with RH, and speculated that this effect was dismissed in earlier works, because earlier experiments were commonly carried out under low RH, where the water effect would be too weak to observe. Accompanying theoretical work proposed a mechanism of reaction barrier lowering by adding H<sub>2</sub>O. However, no rate coefficient has been calculated to estimate the impact of this lowering in the reaction barrier heights.

Using the rate coefficients taking into account the water catalytic effect could decrease the atmospheric lifetime of CH<sub>3</sub>OH by a factor of 2 in tropical region with high RH, which would have a non-negligible effect on the global CH<sub>3</sub>OH budget. It is therefore important to verify this new finding by using different methods. Indeed, the experiments of Jara-Toro *et al.* have been carried out in a relatively small Teflon bag, where heterogeneous consumption of CH<sub>3</sub>OH on the walls may take place. This effect may increase with RH and may become complicated when photochemistry occurs (which produces radicals and radical reactions may change the wall property). They did not vary the surface to volume ratio to quantify this effect.

In this work, we have re-investigated the influence of H<sub>2</sub>O on the rate coefficient of OH reaction with CH<sub>3</sub>OH using a direct method: laser photolysis coupled to a time-resolved detection of OH radicals by laser induced fluorescence (LIF) after gas expansion (FAGE - Fluorescence Assay by Gas Expansion)<sup>[12, 16]</sup>. We have also repeated experiments using the same relative method as Jara-Toro *et al.*, and in addition to varying RH, we

[a] Sébastien Batut, Dr. Coralie Schoemaeker, Dr. Christa Fittschen  
Physical Chemistry of Combustion and Atmospheric Processes  
University Lille / CNRS UMR 8522

Cité Scientifique, Bât. C11, 59655 Villeneuve d'Ascq, France  
E-mail: Christa.Fittschen@univ-lille.fr

[b] Wen Chao, Dr. Jim Jr-Min Lin, Dr. Kaito Takahashi  
Institute of Atomic and Molecular Sciences  
Academia Sinica  
Taipei 10617, Taiwan

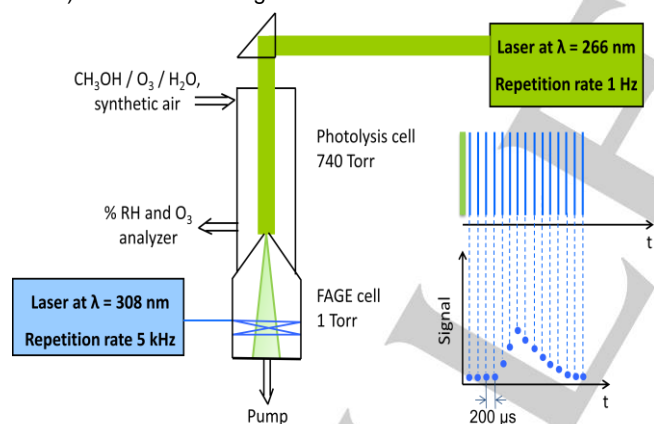
[c] Prof. Dr. Alexandre Tomas  
Sciences de l'Atmosphère et Génie de l'Environnement SAGE  
IMT Lille Douai  
941 Rue Charles Bourseul, 59508 Douai, France

[d] Lu Yu, Prof. Dr. Yoshizumi Kajii  
Atmospheric Chemistry, Department of Natural Sources  
University of Kyoto  
Yoshida-Honmachi, Sakyo-ku, Kyoto 606-8501, Japan

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1 have also largely varied the gas volume in the Teflon bag in  
2 order to vary the surface to volume ratio. Finally, theoretical  
3 calculations have been carried out for a refined analysis of  
4 possible H<sub>2</sub>O catalysis pathways.

5 The FAGE technique, initially developed for the quantification of  
6 OH radicals in the atmosphere, allows following OH  
7 concentrations in a selective and sensitive way even under  
8 atmospheric conditions, i.e. high O<sub>2</sub> and H<sub>2</sub>O concentrations,  
9 which proves difficult with in-situ LIF due to strong quenching of  
10 OH fluorescence by O<sub>2</sub> and H<sub>2</sub>O. Here, FAGE has been coupled  
11 to a laser photolysis reactor (Figure 1) [16, 17] for a pulsed  
12 initiation of the reaction between OH and CH<sub>3</sub>OH. Briefly, OH  
13 radicals were generated by pulsed photolysis of a mixture of  
14 ozone and water (O<sub>3</sub> + *hν* → O(<sup>1</sup>D) + O<sub>2</sub>; O(<sup>1</sup>D) + H<sub>2</sub>O → 2OH).  
15 The 266 nm photolysis laser beam (4th harmonic of Nd:YAG  
16 Laser, Quantel Brilliant, ~20 mJ) was expanded to a diameter of  
17 ~ 5 cm before entering the photolysis cell. The photolysed gas  
18 mixture was continuously expanded from near atmospheric  
19 pressure within the photolysis cell to around 1 Torr into the  
20 FAGE cell through a pinhole (1 mm diameter). OH radicals were  
21 resonantly excited at high repetition rate by the probe laser (308  
22 nm, Sirah Dye laser, 5000 Hz, ~3.5 mW). The LIF signal of OH  
23 was detected in a time resolved manner by a channel  
24 photomultiplier tube (Perkin Elmer) and recorded by a National  
25 Instrument DAQ card and computer. This way, temporal OH  
26 profiles were recorded from each photolysis shot with time  
27 stamps every 200 μs and, depending on the signal intensity,  
28 individual profiles were added from 30 up to 480 photolysis laser  
29 shots. We further binned 5 data points together (final time bin is  
30 1 ms) to enhance the signal-to-noise ratio.

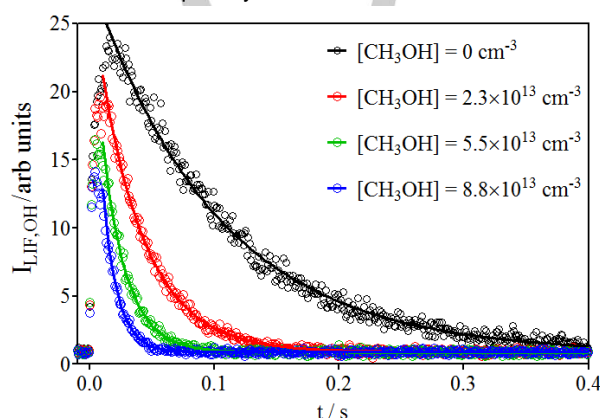


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**Figure 1.** Schematic view of the FAGE set-up

Water vapour was added to the reaction mixture by bubbling a  
fraction of the main flow (composed of synthetic air) through a  
glass bottle containing high purity water (TOC < 10 ppb). The  
H<sub>2</sub>O concentration was varied by changing the fraction of the  
main flow passing through the water bottle. A minimum H<sub>2</sub>O  
concentration of 1 × 10<sup>17</sup> cm<sup>-3</sup> (RH ≈ 17%) was necessary to  
generate enough OH radicals, the highest H<sub>2</sub>O concentration  
(6.1 × 10<sup>17</sup> cm<sup>-3</sup>, RH ≈ 92%) was reached by passing the entire  
air flow through the water bottle. The H<sub>2</sub>O concentrations were  
measured at the exit of the photolysis cell using a commercial  
dew point hygrometer (Mitchel S8000 Integrale).

Test experiments were carried out using CO as a reaction  
partner for OH. Different concentrations of CO were added to  
the main flow through calibrated flow meters and a rate constant  
of (2.3 ± 0.3) × 10<sup>-13</sup> cm<sup>3</sup>s<sup>-1</sup> was obtained, in good agreement with  
literature data [13] and no dependence on the water concentration  
was observed. See SI for more details.

The rate coefficient for the reaction of CH<sub>3</sub>OH with OH was then  
measured at RH up to 92%. Figure 2 shows typical OH decay  
profiles in the presence of different CH<sub>3</sub>OH concentrations. The  
OH loss in the absence of CH<sub>3</sub>OH (black symbols in Figure 2)  
is due to reaction of OH with impurities (trace amounts in the  
synthetic air or in the water) as well as through diffusion/dilution  
of OH into the non-photolysed volume.



**Figure 2.** Typical OH decay profiles in the presence of different CH<sub>3</sub>OH concentrations. [H<sub>2</sub>O] = 5.7 × 10<sup>17</sup> cm<sup>-3</sup>. Solid lines represent a fit to an exponential decay between 0.015 and 0.4 s.

The OH decays can be described as the sum of these losses:

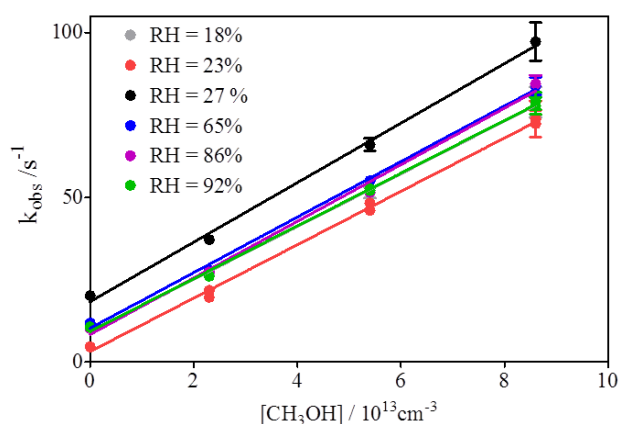
$$-\frac{d[\text{OH}]}{dt} = (k_{\text{loss}} + k_1[\text{CH}_3\text{OH}])[\text{OH}]$$

with  $k_1$  being the rate coefficient for the reaction between OH radicals and CH<sub>3</sub>OH. With [CH<sub>3</sub>OH] being in large excess over [OH], [CH<sub>3</sub>OH] can be considered as constant and the OH decay can be described by an exponential decay, with the observed decay rate being

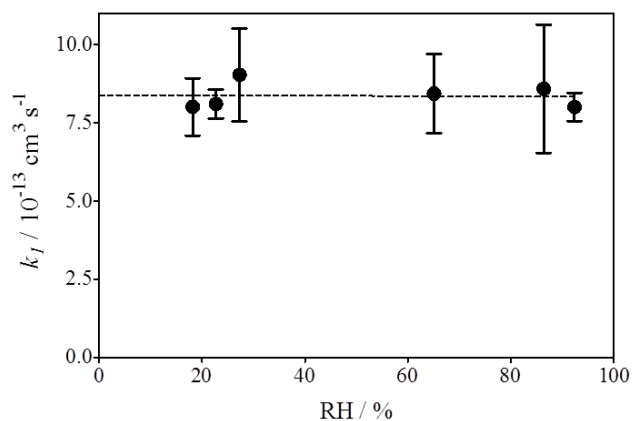
$$k_{\text{obs}} = k_{\text{loss}} + k_1[\text{CH}_3\text{OH}].$$

Plotting the decay rates of Figure 2-type signals as a function of [CH<sub>3</sub>OH] leads to a straight line, with the slope being the rate coefficient  $k_1$ , and the intercept  $k_{\text{loss}}$  representing the sum of all other losses. Figure 3 shows the decay rates of 6 series of experiments (see SI for detailed results) at different H<sub>2</sub>O concentrations (RH between 18 and 92%), where the CH<sub>3</sub>OH concentration has been varied for each RH between 2 – 9 × 10<sup>13</sup> cm<sup>-3</sup>.

It can be seen that the intercepts slightly differ for different series. This can be explained by the synthetic air gas cylinders of different quality used during the period of experiments, which lasted for weeks. However, the slopes are the same for all RH, which means that the rate coefficient obtained for conditions with different H<sub>2</sub>O concentrations are the same, no dependence of  $k_1$  on [H<sub>2</sub>O]. This is illustrated in Figure 4, where the slopes of the linear regressions from Figure 3 are plotted as a function of the RH.



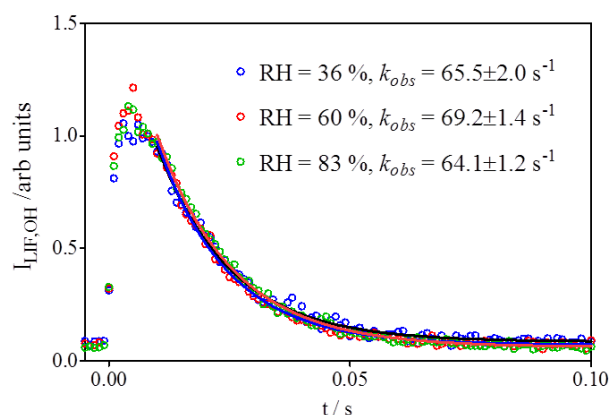
**Figure 3.** Plot of OH decay rates  $k_{obs}$  as a function of  $\text{CH}_3\text{OH}$  concentration for different RH. Error bars show statistical uncertainty only, full lines correspond to linear regression.



**Figure 4.** Plot of the rate coefficient  $k_1$ , such as obtained from the linear regression in Figure 3 as a function of RH. Error bars show statistical error only (95% confidence interval). Dashed line represents linear regression through all data points.

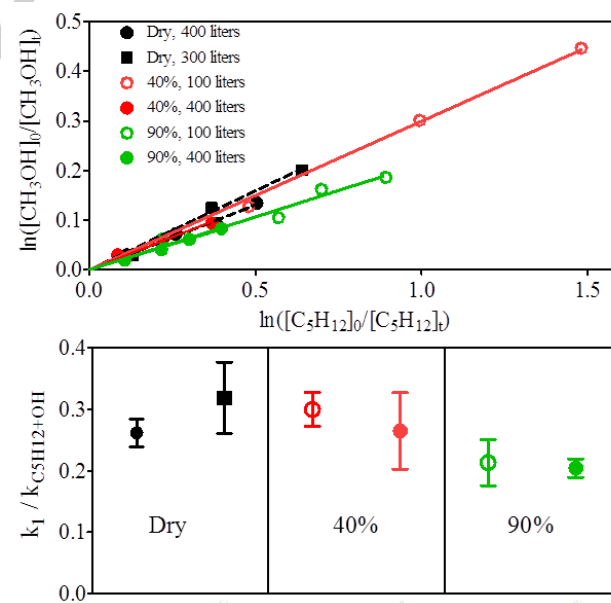
Additional series of experiments have been carried out by keeping the  $\text{CH}_3\text{OH}$  concentration stable and varying the  $\text{H}_2\text{O}$  concentration. Figure 5 shows the normalized OH decays for 3 different RH between 36 and 83 %, no systematic increase in the OH decay rate can be observed.

Teflon bag experiments have been carried out in order to try to reproduce and understand the water effect in the bag experiments such as observed by Jara-Toro *et al.* Experiments have been carried out in a 400 liter Teflon bag<sup>[18]</sup> using the relative rate method with n-pentane as reference compound:  $\text{CH}_3\text{OH}$  has been quantified by FTIR spectroscopy, while n-pentane was quantified by GC/FID, OH radicals have been generated by the photolysis of  $\text{CH}_3\text{ONO}$ , a common precursor for OH radicals in chamber experiments. Compared to  $\text{H}_2\text{O}_2$  (which has been used by Jara-Toro *et al.*), NO (and  $\text{NO}_2$  from the oxidation of NO) is a by-product of this precursor. However, it is not expected to influence the result of this study, as neither NO nor  $\text{NO}_2$  will react with  $\text{CH}_3\text{OH}$  or with  $\text{C}_5\text{H}_{12}$ . The bag was filled with either 400 liters or with 100 liters in order to vary the surface to volume ratio, and experiments with 3 different RH have been carried out: dry air (RH<5%), 40 and 90%.



**Figure 5.** Normalized OH LIF intensities as a function of time for 3 experimental conditions with identical  $\text{CH}_3\text{OH}$  concentrations ( $5.4 \times 10^{13} \text{ cm}^{-3}$ ), but different RH. Decay rate was obtained by fitting traces to an exponential decay between 0.01 and 0.2 s.

Figure 6 summarizes the results: the upper graph shows the plot of the consumption of  $\text{CH}_3\text{OH}$  versus the consumption of  $\text{C}_5\text{H}_{10}$  for the 6 different experiments, the lower graph shows the slopes of the linear regressions. The average of all experiments yields a slope of 0.26, leading with the rate coefficient of  $k_{\text{C}_5\text{H}_{12}+\text{OH}} = 3.8 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$  to a rate coefficient  $k_1 = 9.9 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ , in agreement with literature. This slope would increase with increasing RH if  $k_1$  increases with RH, however in our experiments we observed, if anything, a small decrease with increasing RH. We also do not see any effect when changing the surface to volume ratio by a factor of 4, indicating that our results are not affected by heterogeneous processes in our Teflon bag. No explanation can be given why Jara-Toro *et al.* observed an increase in the ratio.



**Figure 6.** Upper graph: plot of the decay of  $\text{CH}_3\text{OH}$  ( $\ln([\text{CH}_3\text{OH}]_0/[\text{CH}_3\text{OH}]_t)$ ) versus the decay of  $\text{C}_5\text{H}_{12}$  ( $\ln([\text{C}_5\text{H}_{12}]_0/[\text{C}_5\text{H}_{12}]_t)$ ) for different gas volumes and different RH. Lower graph: slopes of the linear regression of the experiments in the upper graph. Error bars represent 95% confidence interval.



Quantum chemistry calculations (CCSD(T)/aug-cc-pVTZ//UMP2/aug-cc-pVTZ) and transition state theory (with vibrational perturbation theory including semiclassical tunneling model using the Multiwell program<sup>[19]</sup>) were used to simulate the rate coefficients for the  $\text{CH}_3\text{OH}+\text{OH}+n\text{H}_2\text{O}$  reactions. The obtained potential energy surfaces are very similar to those reported by Jara-Toro *et al.*; both showed lowering of the reaction barriers with increasing  $n$  (see SI for details). We obtained rate coefficients of  $2.7\times 10^{-12}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ ,  $1.4\times 10^{-32}\text{ cm}^6\text{ molecule}^{-2}\text{ s}^{-1}$ , and  $4.4\times 10^{-52}\text{ cm}^9\text{ molecule}^{-3}\text{ s}^{-1}$ , for the  $n = 0, 1$ , and 2 reactions, respectively at 298 K. Even at  $[\text{H}_2\text{O}] = 6\times 10^{17}\text{ cm}^{-3}$  (RH = 92% at 298 K), the effective bimolecular rate coefficient for  $\text{CH}_3\text{OH}+\text{OH}$  reaction with  $n=1$  will be  $8.4\times 10^{-15}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ , and that for  $n=2$  is  $1.6\times 10^{-15}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ , which are still orders of magnitude smaller than the  $n=0$  rate. That is, even though the reactant complexes are stabilized with the addition of water molecule(s), the decrease in enthalpy at the transition states is not large enough to overcome the large entropic effect of water complexation (for  $n=1, 2$ ) at room temperature. Similar reports on negligible water effect has been found for a number of OH reactions<sup>[20, 21]</sup>, it would require either low temperature<sup>[20, 22]</sup> or large stabilization in enthalpy<sup>[23]</sup> to observe significant water enhancement. For theoretical predictions and interpretations, it is important to calculate the reaction rates; only showing the electronic energy on the reaction path could often be misleading if one does not consider the associated entropy change.

It is interesting to mention that the reaction between  $\text{CH}_3\text{OH}$  and OH in liquid water has been well studied and is evaluated to be  $9.7\times 10^8\text{ M}^{-1}\text{ s}^{-1}$  ( $1.6\times 10^{-12}\text{ cm}^3\text{ s}^{-1}$ ) at 298 K and 1 atm<sup>[24]</sup>, which is close to the gas phase value, suggesting the water solvation does not enhance the rate dramatically.

In summary, our direct kinetic experiments, our relative rate measurements as well as the theoretical rate calculations all find that water catalysis in the  $\text{OH} + \text{CH}_3\text{OH}$  gas-phase reaction is insignificant at room temperature. No explanation can be given about the origin of the contradictory observations made by Jara-Toro *et al.*, but it can be speculated that unidentified heterogeneous reactions biased their results. This highlights the need of different approaches for getting reliable results.

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## Conflict of interest

The authors declare no conflict of interest.

**Keywords:** Alcohols • Atmospheric chemistry • Radical reactions • Reaction mechanism • OH radicals

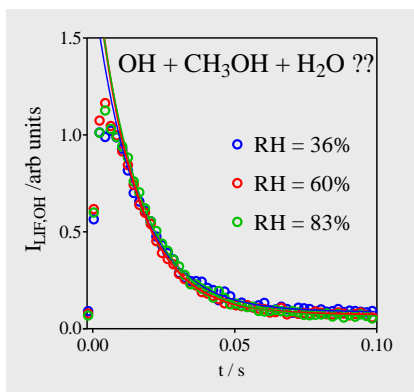
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## Entry for the Table of Contents

## COMMUNICATION

The reaction of OH radicals with CH<sub>3</sub>OH is the major removal path for CH<sub>3</sub>OH from the atmosphere. In recent works it was found, that this reaction is substantially catalyzed by water. Using direct methods, we re-investigated the influence of H<sub>2</sub>O on the reaction, and did not find any measurable influence of H<sub>2</sub>O on the rate coefficient.



Wen Chao, Dr. Jim Jr-Min Lin, Dr. Kaito Takahashi, Prof. Dr. Alexandre Tomas, Lu Yu, Prof. Dr. Yoshizumi Kajii, Sébastien Batut, Dr. Coralie Schoemaeker, Dr. Christa Fittschen\*

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**Water Vapor does not Catalyze the Reaction of Methanol and OH Radicals**

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