

Elias M. Neeman,<sup>a,(\*)</sup> Daniel González,<sup>a</sup> Sergio Blázquez,<sup>a</sup> María Antiñolo,<sup>b</sup> Bernabé Ballesteros,<sup>a,b</sup> José Albaladejo,<sup>a,b</sup> and Elena Jiménez<sup>a,b,(\*)</sup>

<sup>a</sup> Departamento de Química Física, Facultad de Ciencias y Tecnologías Químicas, Universidad de Castilla-La Mancha, 13071 Ciudad Real (Spain).

<sup>b</sup> Instituto de Investigación en Combustión y Contaminación Atmosférica, Universidad de Castilla-La Mancha, 13071 Ciudad Real (Spain).

(\*): elias.neeman@uclm.es; Elena.Jimenez@uclm.es

## INTRODUCTION

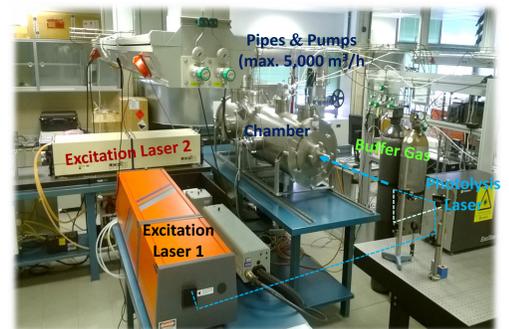
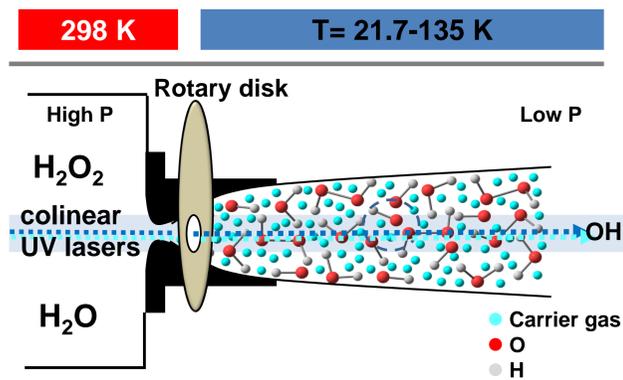
Water vapor, H<sub>2</sub>O, is one of the most abundant species in the Earth's atmosphere (T≈220-298 K, in the troposphere), but it can also be found in the atmosphere of many objects in the solar system at low temperature conditions (T≤150 K), such as Jupiter's and Saturn's moons. H<sub>2</sub>O can form hydrogen-bonded complexes with many atmospheric species and consequently influences the radiation balance on Earth and affects the atmospheric chemistry.

The purpose of this work is to determine **for the first time**, the formation and OH-reactivity rate coefficients of OH(H<sub>2</sub>O) and H<sub>2</sub>O<sub>2</sub>(H<sub>2</sub>O) complexes at ultra-low temperature.

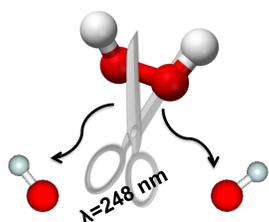


## EXPERIMENTAL SET-UP

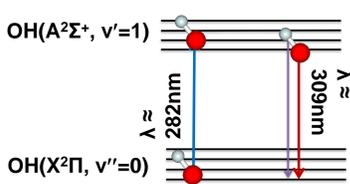
The pulsed CRESU (French acronym for *Cinétique de Réaction en Ecoulement Supersonique Uniforme*) technique was used to perform the ultra-low temperature gas phase kinetic experiments and create a gas jet with a uniform temperature and gas density. The technique is based on the **uniform supersonic expansion** of gas mixture from a relative high pressure in a pre-expansion reservoir through a Laval nozzle into a vacuum chamber which provokes the cooling of the gas. The **pulsed laser photolysis/laser induced fluorescence** (PLP-LIF) technique was used to generate OH radicals and to monitor their temporal profile.



## PLP – LIF TECHNIQUE

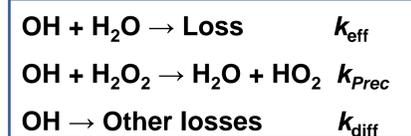
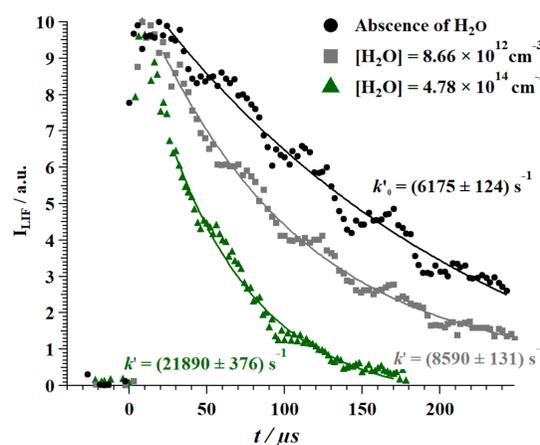


- To carry out the kinetic experiments, first, OH radicals are generated in situ using from gaseous H<sub>2</sub>O<sub>2</sub> at a wavelength of 248 nm (KrF excimer laser), generating two OH radicals.



- The OH radicals are excited at 282 nm, which after vibrational relaxation, emits fluorescence at around 309 nm. The laser induced fluorescence is detected a function of the reaction time using a filtered photomultiplier tube.

## TIME EVOLUTION OF OH IN THE PRESENCE OF H<sub>2</sub>O



$$I_{\text{LIF}}(t) = I_{\text{LIF}}(t=0) \exp(-k't)$$

$$k' - k'_0 = k_{\text{eff}} [\text{H}_2\text{O}]_0$$

$$k'_0 = k_{\text{Prec}}(T) [\text{H}_2\text{O}_2] + k_{\text{diff}}$$

$k_{\text{eff}}$  represents the loss of OH radicals which is a complex mechanism that involves many interdependent processes.

Fig 1. Temporal profiles of the LIF signal from OH.

## OH-REACTIVITY AND FORMATION OF THE OH(H<sub>2</sub>O) and H<sub>2</sub>O<sub>2</sub>(H<sub>2</sub>O) COMPLEXES AT 21.7 K - KINETIC MODEL

- Formation of binary complexes: OH(H<sub>2</sub>O), OH(H<sub>2</sub>O<sub>2</sub>), H<sub>2</sub>O<sub>2</sub>(H<sub>2</sub>O) and (H<sub>2</sub>O)<sub>2</sub>.
- Formation of water clusters (H<sub>2</sub>O)<sub>n=3-6</sub> larger than dimers was also considered in the model.
- Reactivity of OH with H<sub>2</sub>O<sub>2</sub> and binary complexes (OH(H<sub>2</sub>O), OH(H<sub>2</sub>O<sub>2</sub>), H<sub>2</sub>O<sub>2</sub>(H<sub>2</sub>O) and (H<sub>2</sub>O)<sub>2</sub>).

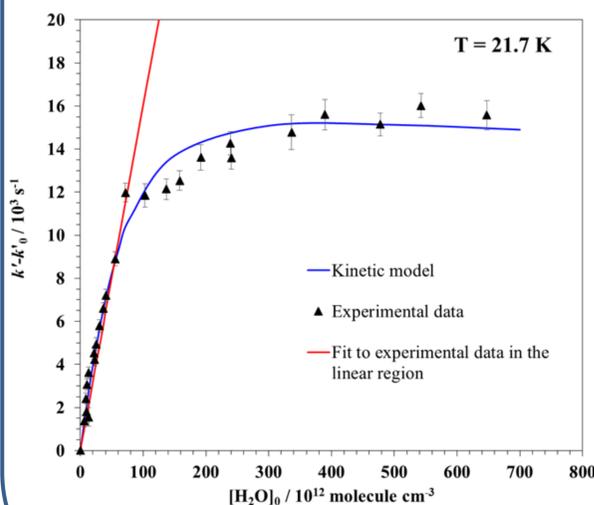


Fig 2. Loss rate coefficient for OH in the presence of an excess of added [H<sub>2</sub>O].

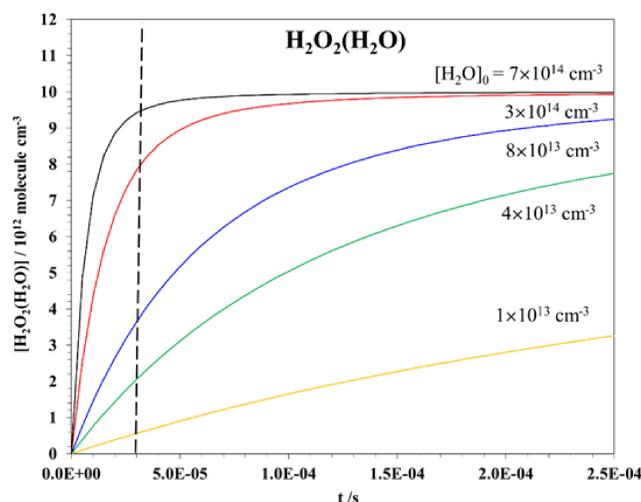


Fig 3. Formation of H<sub>2</sub>O<sub>2</sub>(H<sub>2</sub>O) complexes. [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub> = 10<sup>13</sup> cm<sup>-3</sup>; [OH]<sub>0</sub> = 10<sup>10</sup> cm<sup>-3</sup>

Reaction	k / 10 <sup>-10</sup> cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>
OH + H <sub>2</sub> O <sub>2</sub> → H <sub>2</sub> O + HO <sub>2</sub>	2.95 <sup>a</sup>
OH + H <sub>2</sub> O → OH(H <sub>2</sub> O)	1.0 <sup>a</sup>
H <sub>2</sub> O <sub>2</sub> + H <sub>2</sub> O → H <sub>2</sub> O <sub>2</sub> (H <sub>2</sub> O)	2.0 <sup>a</sup>
2 H <sub>2</sub> O → (H <sub>2</sub> O) <sub>2</sub>	0.121 <sup>b</sup>
(H <sub>2</sub> O) <sub>2</sub> + H <sub>2</sub> O → (H <sub>2</sub> O) <sub>3</sub>	3.25 <sup>b</sup>
(H <sub>2</sub> O) <sub>3</sub> + H <sub>2</sub> O → (H <sub>2</sub> O) <sub>4</sub>	4.46 <sup>b</sup>
(H <sub>2</sub> O) <sub>4</sub> + H <sub>2</sub> O → (H <sub>2</sub> O) <sub>5</sub>	5.76 <sup>b</sup>
(H <sub>2</sub> O) <sub>5</sub> + H <sub>2</sub> O → (H <sub>2</sub> O) <sub>6</sub>	5.59 <sup>b</sup>
OH + H <sub>2</sub> O <sub>2</sub> (H <sub>2</sub> O) → 2 H <sub>2</sub> O + HO <sub>2</sub>	8.5 <sup>a</sup>
OH + (H <sub>2</sub> O) <sub>2</sub> → H <sub>2</sub> O + OH(H <sub>2</sub> O)	9.0 <sup>a</sup>

<sup>a</sup> This Work

<sup>b</sup> Bourgalais et al. Phys. Rev. Lett. 2016, 116, 113401.

## CONCLUSIONS

- We present the first experimental evidence of the gas-phase formation and OH-reactivity of H<sub>2</sub>O<sub>2</sub>(H<sub>2</sub>O) and OH(H<sub>2</sub>O) complexes at ultralow temperature.
- We extended the measurement of the rate coefficient the OH+H<sub>2</sub>O<sub>2</sub> reaction from 64.1 to 21.7 K.
- We modeled the OH kinetics in the presence of a large excess of H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>O to provide information about the kinetics of the formation of these water clusters and their reaction with OH radicals.
- The formation of the H<sub>2</sub>O<sub>2</sub>(H<sub>2</sub>O) and OH(H<sub>2</sub>O) complexes is very fast at 21.7 K, ≈ 1 × 10<sup>-10</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.
- The OH-reactivity of the H<sub>2</sub>O<sub>2</sub>(H<sub>2</sub>O) complex and water dimers is even faster, ≈ 8 × 10<sup>-10</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.

## ACKNOWLEDGMENTS

All authors would like to thank the European Research Council (NANOCOSMOS project, REF: SyG-610256) and UCLM (*Ayudas para la financiación de actividades de investigación dirigidas a grupos* (REF: 2019-GRIN-27175) for funding this work.