Gas-phase Reactivity of OH Radicals Towards NH_3: A Considerable Enhancement of the Rate Coefficients at Interstellar Temperatures

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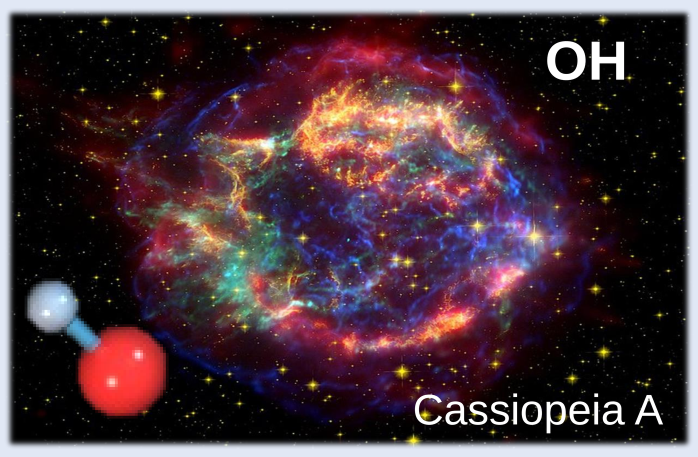
1. Introduction

1st detection: 1963 by Weinreb *et al.* [1]



Hydroxyl radical (OH) is a crucial intermediate in combustion, atmospheric and interstellar chemistry. Although, it is known that these radicals are ubiquitous in the Interstellar Medium (ISM), kinetic data for gas-phase OH-reactions with IS species are still scarce at ultra-low temperatures (10-100 K). Particularly for nitrogen-bearing species, which could form amino acids in the ISM, the literature is very limited.

1st detection: 1968 Cheung *et al.* [2]

Kinetics $OH+NH_3$

T=22-2360 K — Experiments

Positive temperature dependence of k(T)
Acceleration of k(T) at 22 K.

Theory — T=5-4000 K

Positive temperature dependence of k(T) in the entire T-range

In this work, the kinetics of the reaction between **OH** and **NH_3** have been studied experimentally at ultra-low temperatures (11.7-177.5 K).

2. Experimental Set-up and CRESU Technique

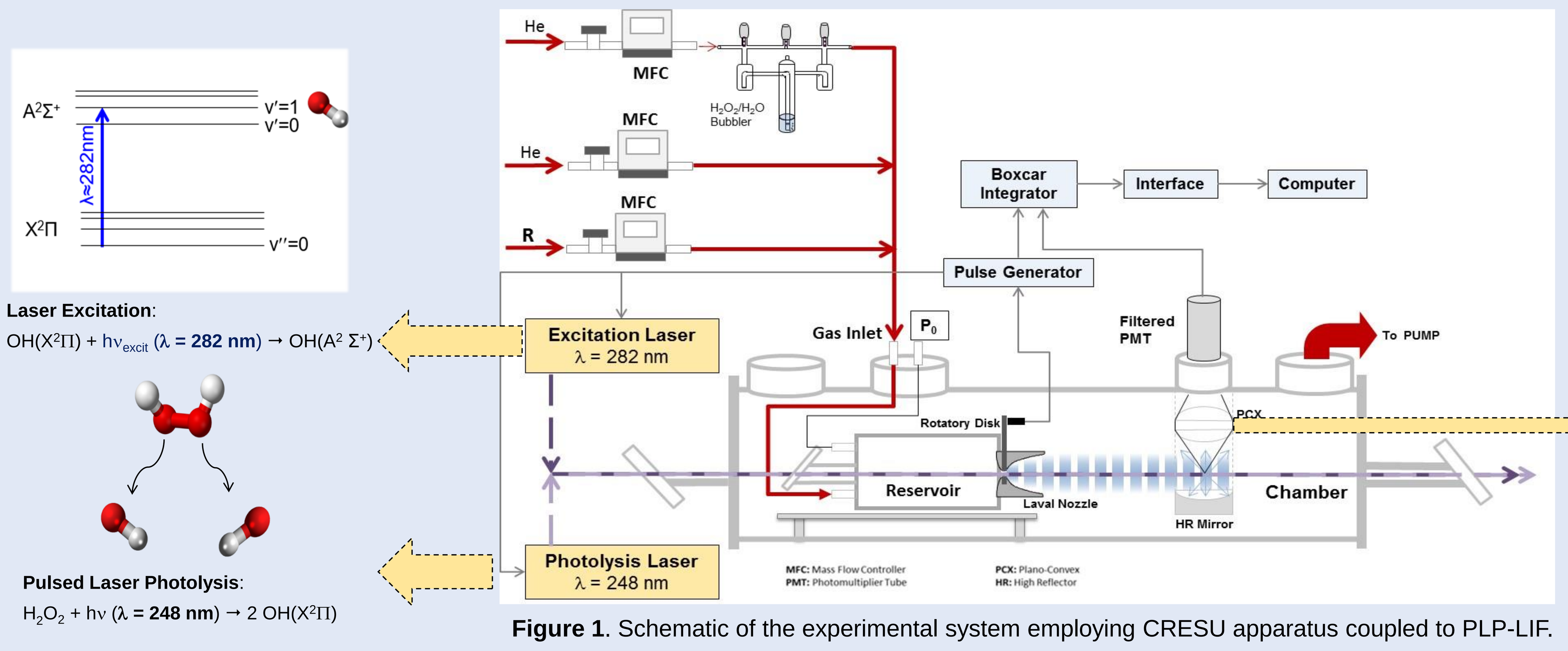
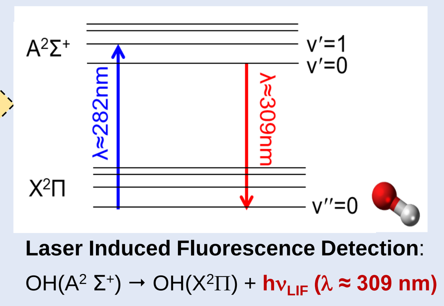


Figure 1. Schematic of the experimental system employing CRESU apparatus coupled to PLP-LIF.

The **CRESU** (French acronym for *Cinétique de Réaction en Ecoulement Supersonique Uniforme* or *Reaction Kinetics in a Uniform Supersonic Flow*) technique was used to achieve ultra-low temperatures. It is based on an isentropic expansion of a gas mixture from a relative high-pressure reservoir to a low-pressure chamber through a perfectly designed Laval Nozzle (the heart of this technique) which creates a supersonic and cold gas jet uniform in temperature and gas density. This gas mixture is pulsed by a rotary disk which is placed in the divergent part of the Laval nozzle. The pulsed CRESU apparatus developed in our group has been described in detail elsewhere. [3]



Pulsed laser photolysis/laser induced fluorescence (PLP-LIF) technique was used to generate OH radicals and to monitor their temporal profile.In this work, the **PLP** of **gaseous H_2O_2** at 248 nm was the **source of OH radicals**. The **LIF from excited OH radicals** was detected at ca. 309 nm by a photomultiplier tube as a function of reaction time.

3. Kinetic Analysis

Under pseudo-first order conditions ($[NH_3]_0$, $[H_2O_2]$>>$[OH]_0$), the LIF signal from OH radicals decay due to the following reactions:

$OH + NH_3 \rightarrow H_2O + NH_2$	k(T)	k'
$OH + H_2O_2 \rightarrow H_2O + HO_2$	k_{prec}	k'_0
$OH \rightarrow$ Other losses	k_{diff}	

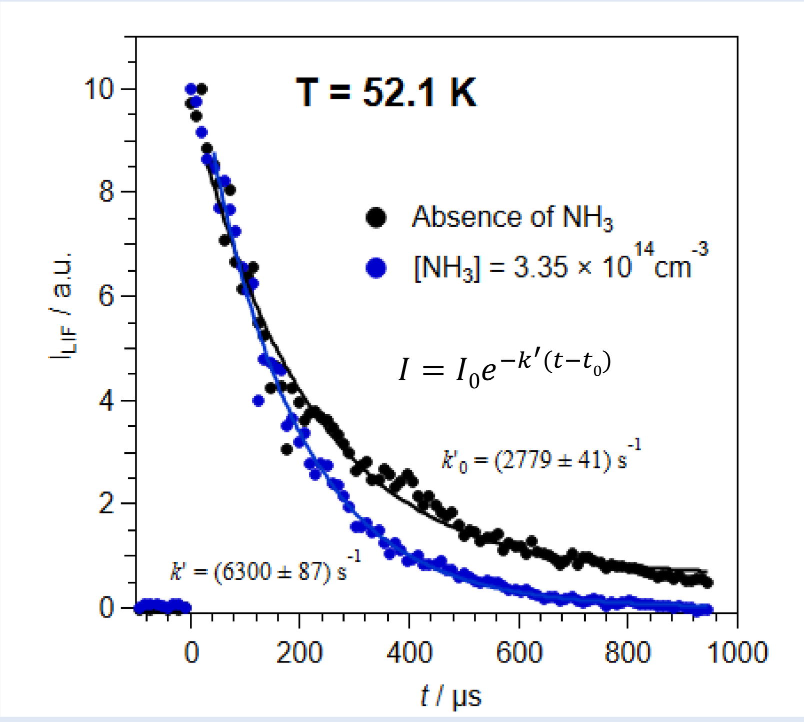


Figure 2. Temporal evolution of the laser induced fluorescence of OH radicals.

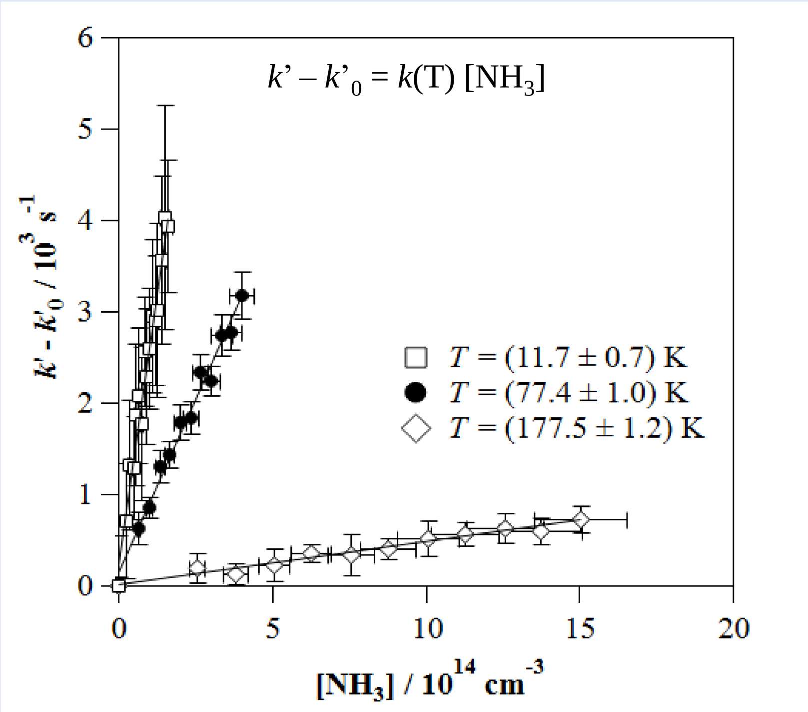


Figure 3. k'-k_0 versus $[NH_3]$ in the jet for 3 different temperatures.

4. Experimental Results of k(T=11.7-177.5 K)

The results of k(T) determined in the present study are the first experimental determination of k(T) for this reaction in the T<22 K and T=23-177.5 K ranges. These results are shown in a k(T) vs T plot along with previous works (T=230-500 K).

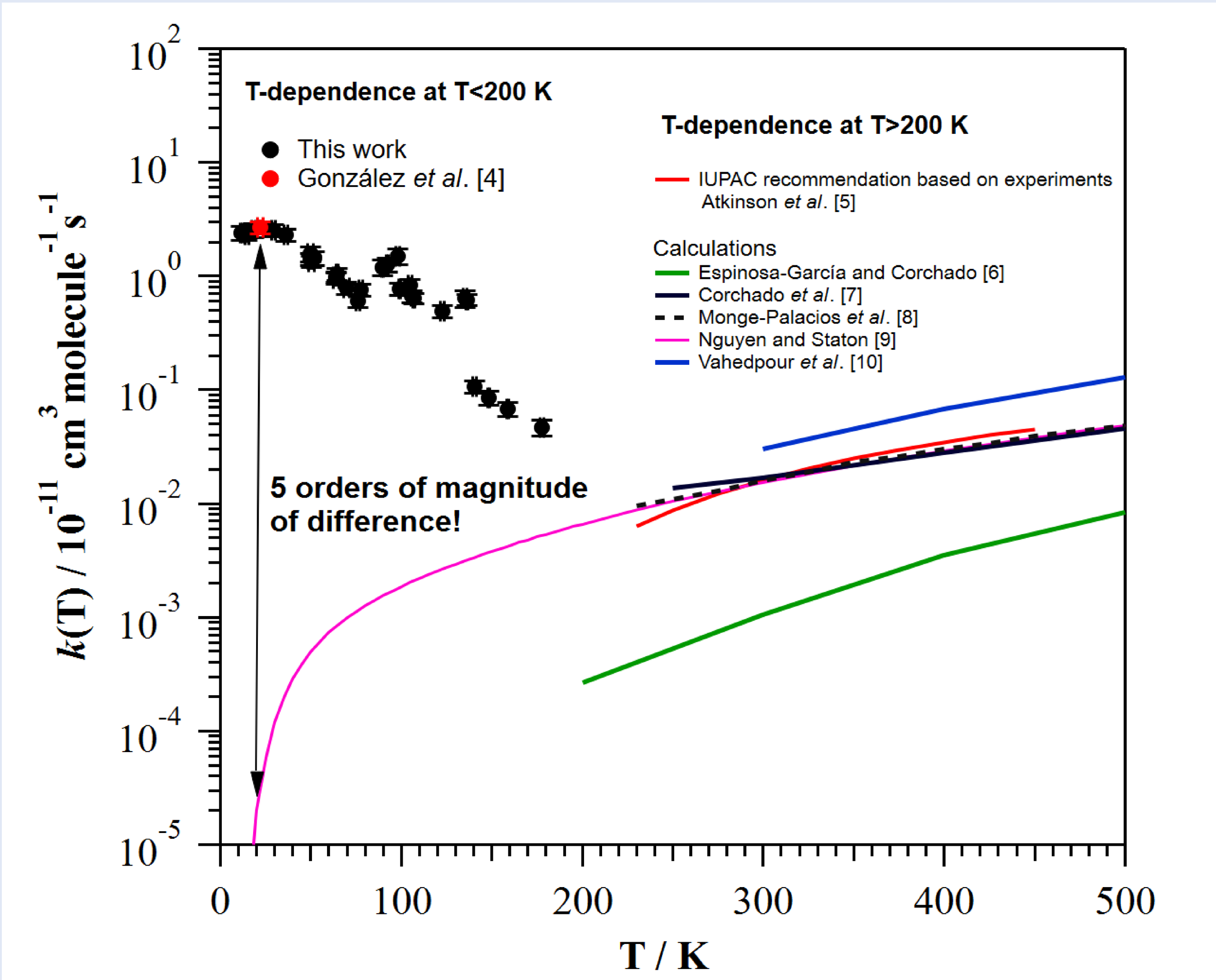


Figure 4. Comparison of the T-dependence of k(T) observed in our work with previous studies.

We observe a fast increase of k(T) between 177.5 K and 29.2 K, while k(T) is almost constant in the range 11.7-29.2 K,

However, theoretical calculations predict a decrease in the OH-rate coefficient with temperature. As shown in Figure 4, there is a huge difference between the experimental k(20K) and the calculated one by Nguyen and Staton [9].

5. Pressure Dependence of k(T)

The pressure dependence of k(T) has been studied at some temperatures. No pressure dependence of k(T) was observed in the density range investigated.

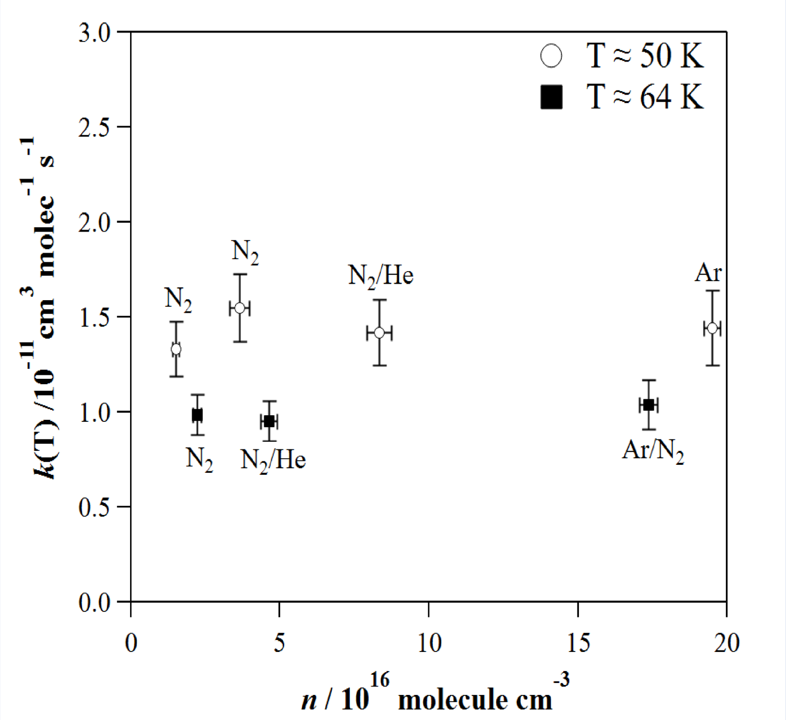


Figure 5a. Pressure dependence of k(T) at 50 and 64 K.

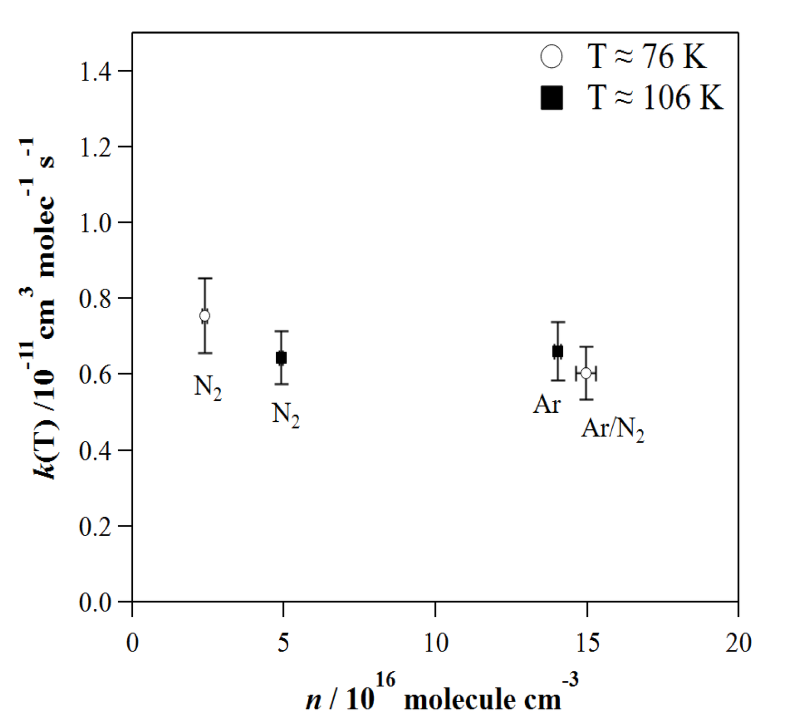


Figure 5b. Pressure dependence of k(T) at 76 and 106 K.

6. Conclusions

- Although, there is a huge increase of k(T) in the range 29.2-177.5 K, in general, is continuously increasing when temperature decreases in the explored temperature range (11.7-177.5 K), reaching a maximum around 22 K [4].
- No pressure dependence of k(T) has been observed at the selected temperatures reachable with our current CRESU apparatus.

References

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Acknowledgments

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