

# XUV induced desorption from carbon containing interstellar ice analogues

John D. Thrower<sup>1</sup>, Tushar Suhasaria<sup>1</sup>, Robert Frigge<sup>1</sup>, Sebastian Roling<sup>1</sup>, Mathieu Bertin<sup>3</sup>, Xavier Michaut<sup>3</sup>, Jean-Hugues Fillion<sup>3</sup>, and Helmut Zacharias<sup>1</sup>

<sup>1</sup>*Physikalisches Institut, Westfälische Wilhelms Universität, Wilhelm-Klemm-Straße 10, 48149 Münster, Germany*

<sup>2</sup>*Sorbonne Université, Observatoire de Paris, PSL Research University, Laboratoire d'Etudes du Rayonnement et de la Matière en Astrophysique et Atmosphères, CNRS UMR 8112, 75005 Paris, France*

john.thrower@uni-muenster.de

Photon-induced processes play an important role in interstellar solid-state chemistry [1]. The interaction of VUV and XUV photons with the molecular ices that form mantles on sub-micron scale grains provides the necessary energetic input to drive chemical reactions and desorption in low temperature regions where thermal processes are inefficient. For example, the resonant excitation of CO in both pure CO [2] and mixed CO:N<sub>2</sub> [3] ice using VUV synchrotron radiation has been shown to result in the non-thermal desorption of CO molecules. To probe the underlying desorption dynamics, femtosecond duration pulses are required. The free-electron laser, FLASH, in Hamburg provides the means with which to perform such measurements at higher photon energies in the XUV regime. Previously, we investigated the UV induced desorption of fragment ions from D<sub>2</sub>O ice deposited on an HOPG substrate [4]. Here we have extended these investigations to interstellar ice analogues containing a simple carbon bearing species, namely CH<sub>4</sub>.

A mixed CH<sub>4</sub>:D<sub>2</sub>O (1:3.3) ice film was grown to a thickness of 8.4 nm on an HOPG substrate held at 15 K under ultrahigh vacuum conditions. The film was then exposed to photons with an energy of 40.8 eV ( $\lambda = 30.4$  nm), representative of the astrophysically relevant HeII emission line, with an average incident fluence of (33±8) mJ cm<sup>-2</sup>. Desorbing ionic species were detected with a linear time-of-flight mass spectrometer. A variety of desorption products were detected, with large H<sup>+</sup> and D<sup>+</sup> signals pointing to efficient deprotonation. In addition, fragment ions from both parent species, as well as recombination products were observed, consistent with our previous measurements on pure D<sub>2</sub>O. However, the presence of CH<sub>4</sub> in the ice mixture leads to the desorption of a series of C<sub>n</sub><sup>+</sup> ionic clusters with up to n=11. The fluence dependence of the desorption yield for each detected species was examined to provide insights into the underlying mechanism. Simple fragment ions exhibited either linear or slightly non-linear ( $m=2-3$ ) fluence dependences, consistent with direct ejection and few step mechanisms, respectively. On the other hand, the carbon cluster ions displayed a highly non-linear fluence dependence with up to  $m=10$ , suggesting a complex multi-step process involving the primary products of CH<sub>4</sub> fragmentation. The underlying reaction dynamics were further investigated through two-pulse correlation measurements employing the split-and-delay unit at FLASH. The simple fragment and carbon cluster ions showed very different temporal behaviours, again consistent with the presence of very different reaction pathways to these two families of desorption products.

## References:

- [1] K.I. Öberg, *Chem. Rev.*, **116**, 9631 (2016).
- [2] M. Bertin *et al.*, *Phys. Chem. Chem. Phys.*, **14**, 9929 (2012).
- [3] M. Bertin *et al.*, *Astrophys. J.*, **779**, 120 (2013).
- [4] B. Siemer, *et al.*, *Faraday Discuss.*, **168**, 553 (2014).
- [5] T. Suhasaria, *et al.*, *Phys. Chem. Chem. Phys.* (in press), DOI: 10.1039/C8CP00171E