Radek Plašil*¹, Thuy Dung Tran*, Štěpán Roučka*, Pavol Jusko*, Dmytro Mulin*, Illia Zymak*, Petr Dohnal*, and Juraj Glosík* ¶

* Department of Surface and Plasma Science, Faculty of Mathematics and Physics, Charles University in Prague, 180 00 Prague, Czech Republic

Synopsis The reaction of O⁻ anions with molecular deuterium D_2 has been studied experimentally using a cryogenic 22-pole radiofrequency ion trap. There were observed two reaction channels. In the associative detachment D_2O is formed and for atom transfer formation $OD^- + D$ was observed. The rate coefficients of the reactions have been determined at temperatures ranging from 10 K to 300 K.

The reaction of O^- with D_2 has two exothermic channels corresponding to associative detachment and deuterium atom transfer

$$O^- + D_2 \rightarrow D_2O + e^-, \qquad \Delta H = -3.65 \text{ eV},$$

 $O^- + D_2 \rightarrow OD^- + D, \qquad \Delta H = -0.28 \text{ eV}.$

Energetically possible are also reactions leading to the formation of metastable D_2O^- anion in three body or radiative association. However these processes have not been detected experimentally. Studies of gas-phase processes involving water and especially those leading to isotopic fractionation [1] is essential for understanding of the water formation in the Universe.

The reactions were studied using a 22-pole radiofrequency ion trap. It was mounted on a cryo-cooler in an ultra-high vacuum system. The measuring procedure was based on iterative filling of the trap with a well-defined number of primary ions O^- where they react with molecular deuterium. The content of the trap were analyzed after chosen times using a quadrupole mass spectrometer and a micro-channel plate detector. Further detail may be found in [2] and references therein.

We studied previously analogous reactions involving O^- and H_2 . At first we measured electron energy spectrum originating from associative detachment [3] at 300 K. Later on we studied both reactions using the 22-pole ion trap [4].

Very interesting dependence on temperature is shown on Figure 1. Up to now the associative detachment has been measured mostly at temperatures higher than 300 K and the observed reaction rate coefficient was about $\frac{1}{3}$ of the Langevin rate. It is explained by the fact that trajectories on only one of three electronic surfaces of the collision system can lead directly to autodetachment.

At lower temperatures we observed unexpectedly high value of the associative detachment rate coefficient. Theoretical model in our paper [4] for the reaction $O^- + H_2$ explained this behavior by rearrangement of the collisional system in a shallow local minimum. The increase of the reaction rate coefficient at low temperatures is in qualitative agreement with the theoretical predictions. The presented data will be compared with classical trajectory simulation model. An isotopic effect will be evaluated.



Figure 1. Measured temperature dependencies of the reaction rate coefficients for both channels of $O^- + D_2$ reaction. The open circle indicates results of our previous experiment [4].

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References

- [1] L. I. Cleeves et al. 2014 Science 345 1590
- [2] D. Gerlich and G. Borodi 2009 *Faraday Discussions* **142** 57
- [3] P. Jusko et al. 2013 Int. J. Mass Spectr. 352 19
- [4] P. Jusko et al. 2015 J. Chem. Phys. 142 014304

¹E-mail: Radek.Plasil@mff.cuni.cz