RIXS study on hydrogen bonding network of water at interfaces

Yoshihisa Harada[1,2,3,*], Kosuke Yamazoe[2], Jun Miyawaki[1,2,3], Yi-Tao Cui[2,3], Yuji Higaki[4,5], Yoshihiro Inutsuka[4], Daiki Murakami[4,5], Masaru Tanaka[4,5] and Atsushi Takahara[4,5]
[1]*Department of Advanced Materials Science, The University of Tokyo, Chiba 277-8561, Japan*
[2]*Institute for Solid State Physics, The University of Tokyo, Chiba 277-8581, Japan*
[3]*Synchrotron Radiation Research Organization, The University of Tokyo, Hyogo 679-5165, Japan*
[4]*Graduate School of Engineering, Kyushu University, Fukuoka 819-0395, Japan*
[5]*Institute for Materials Chemistry and Engineering, Kyushu University, Fukuoka 819-0395, Japan*
**harada@issp.u-tokyo.ac.jp*

Summary:

X-ray absorption (XAS) and emission (XES) spectroscopy of liquid water are one of the cutting-edge techniques to determine the local hydrogen bonding network of liquid water through observation of the valence electronic structure.[1] From ice to liquid water, substantial increase/decrease of the pre-/post-edge region of XAS occurs,[2] while in XES, resonant excitations to the pre-/post-edge in XAS are strongly related to the intensity of two distinct lone pair peaks,[3] thereby increasing the possibility that the lone pair peaks are originated from water molecules in different local hydrogen bonding configurations. In this context, an XES study of water at interfaces affords us a good opportunity to explore isolated or much more ordered water molecules than expected in bulk water. In this paper, XES studies on such "unique" water molecules are presented; an isolated extreme is water in a less hydrogen bonded network of acetonitrile or 3-methyl pyridine.[4] The other extreme is water encapsulated in a polyelectrolyte brush.[5] The apparent relationship between each lone pair peak in XES and a specific hydrogen bonding configuration is demonstrated through these extreme cases. From a point of practical view, unique hydrogen-bonding structure of water near polyelectrolytes should significantly affect the specific structure and functions of biomolecules[6] which consist of several biomolecular polyelectrolytes. Polyelectrolyte brushes,[7] which represent high-density polymer chains, are well suited for investigating the local structure of water that is not only near polyelectrolytes but also confined by these brushes. XAS and XES spectroscopies were used to investigate the strength of hydrogen bonding but also characterizing local symmetry of the hydrogen-bonding of water confined in a poly(2-(methacryloyloxy)ethyl trimethylammonium chloride) (PMTAC) brush. Detailed analyses of high resolution XAS and XES spectra provide constructive information about the hydrogen-bonding network of water. The results indicated that the confined water is highly hydrogen bonded like ice with a uniform distortion of hydrogen bonding,[5] which should be naturally connected to the function of the polyelectrolyte brushes.

References

1. T. Fransson, Y. Harada, N. Kosugi *et al.*, *Chem. Rev.* **116**, 7551 (2016).
2. S. Myneni, Y. Luo, L.-Å. Näslund *et al. J. Phys.: Condens. Matter* **14**, L213 (2002).
3. T. Tokushima, Y. Harada, O. Takahashi *et al.*, *Chem. Phys. Lett.* **460**, 387 (2008).
4. H. Arai, Y. Horikawa, K. Sadakane *et al.*, *Phys. Chem. Chem. Phys.* **14**, 1576 (2012).
5. K. Yamazoe, Y. Higaki, Y. Inutsuka *et al.*, *Langmuir* **33**, 3954 (2017).
6. M.-C. Bellissent-Funel, A. Hassanali, M. Havenith *et al.*, *Chem. Rev.* ***116***, 7673 (2016).
7. M. Kobayashi, Y. Terayama, H. Yamaguchi *et al.*, *Langmuir* **28**, 7212 (2012).