Vibrational Stark effect probe as a tool for investigating SAM electrostatics

Schkolnik, G.; Salewski, J.; Millo, D.; Zebger, I.; Franzen, S. and Hildebrandt, P
Max Volmer Laboratorium
Instituet fuer Chemie - PC 14
Technische Universitaet Berlin
Str. des 17 Juni 135
D-10623 Berlin

Vibrational Stark effect probes are molecules which have a vibrational mode whose frequency is sensitive to external electric fields. We have shown [1,2] that 4-mercaptobenzonitrile (MBN), a Stark probe molecule, can be used to report the electric field on protein surfaces. Moreover, while attached to the protein surface, it can be used to monitor external electric fields the protein is exposed to, for example when bound to a charged SAM (self assembled monolayer). By comparing the nitrile stretching frequency in MBN bound to different positions on Cytochrome c surface, in solution and when the protein is attached to a charged SAM, we were able to show that reorientation of lysine residues on the protein surface may serve to decrease the electric field experienced by the protein as it approaches the SAM [2].
When the same Stark probe is used to form a SAM on a metal surface (Au or Ag), the changes to its nitrile stretch frequency in the presence of different solvents serves as a reporter of surface potential, while its response to a series of applied potentials may help elucidate SAM electrostatics and determine the effective potential of zero charge of the Metal/SAM/solvent system.

1. Schkolnik, G., Zhao, J., Jiang, S. Thompson, M. Hildebrandt, P. and Franzen, S. Catalytic efficiency of Dehaloperoxidase A is controlled by electrostatics – using the vibrational Stark effect to understand enzyme kinetics, submitted to J Phys Chem Lett.

2. Schkolnik, G., Utesch, T., Salewski, J., Tenger, K., Millo, D., Kranich, A., Zebger, I., Schulz, C., Zimányi, L., Rákhely, G., Mroginski, M.A. and Hildebrandt, P. Mapping local electric fields in proteins at biomimetic interfaces, Chem. Commun., 48, 70-72 (2012)