Femtosecond redox-induced 2D-IR difference spectroscopy of proteins and biomolecules

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In analogy to redox-induced FTIR difference spectroscopy, we developed redox-induced 2D-IR difference spectroscopy to investigate ultrafast dynamics of redox-sensitive vibrational modes. Lifetimes, couplings, vibrational energy transfer and spectral diffusion can be investigated under redox control. The methodology and first applications including the protein cytochrome *c* are presented.

Electron transfer is an elementary reaction in chemistry and biology, where it is involved in cellular respiration, photosynthesis and catalysis.[1] Spectroelectrochemistry in the infrared can be used to probe redox-sensitive structural changes in chemical and biological samples.[2,3] Here we use a novel reflection mode spectroelectrochemical cell (see Fig. 1 a) in combination with 2D-IR spectroscopy to probe ultrafast redox-dependent processes.[4] We measure distinct redox-dependent vibrational lifetimes and anharmonicities in flavin mononucleotide and ferricyanide/ferrocyanide (Fig. 1 b),[4,5] as well as different anharmonic couplings and ultrafast vibrational dynamics in the protein cytochrome *c*.

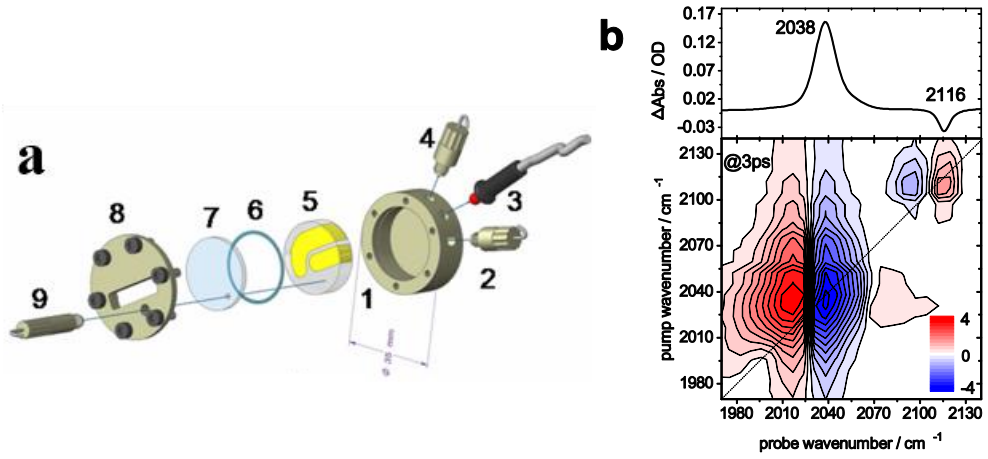

Fig.1 (a) Schematic drawing of the reflection mode spectroelectrochemical cell. The sample is contained between two windows, separated by a spacer (6). One window features gold coated areas (5) that serve as electrode and mirror at the same time. The other is a 2 mm CaF_2 window (7). A reference electrode (9) and a thermometer (3) are connected. The figure is generated using Solid Edge (http://www.solidedge.co.za/). (b) Reduced-minus-oxidized FTIR spectrum of ferricyanide/ferrocyanide in the νC≡N region (top), and the corresponding reduced-minus-oxidized-2D-IR difference spectrum (bottom; asinh(signal) is plotted in order to better visualize the small signals of the oxidized form). Reprinted with permission from [4]. Copyright 2015, AIP Publishing LLC.

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