

Mechanism of water oxidation in photosystem II

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Photosystem II sustains live on Earth by converting solar energy into chemical energy. Specifically, it utilizes the energy of visible light to split water into molecular oxygen, protons and electrons, of which the latter two are being employed by photosynthetic organism to reduce CO₂ into energy-rich compounds such as carbohydrates. In recent years the interest in understanding the details of photosynthetic water-splitting is also fueled by efforts to develop man-made systems that directly convert solar energy into chemical fuels such as molecular hydrogen or a low chain alcohols. I will begin my presentation by reviewing the latest information on the structure of photosystem II, including its catalytic site for water-splitting, and its overall reaction scheme. On

that basis the binding sites for the two substrate waters will be discussed. Key information in this regard comes from $H_2^{16}O/H_2^{18}O$ substrate water-exchange measured by time-resolved membrane-inlet mass spectrometry, a technique that I pioneered during my postdoc at RSBS, and by advanced electron paramagnetic resonance spectroscopy. These data result in a proposal for water-oxidation that also takes recent information on the structural flexibility of the catalytic Mn_4CaO_5 cluster into account. An emerging technique that may provide crucial information for deciding among various proposal for water oxidation maybe serial femtosecond X-ray crystallography of photosystem II. I will explain the basics and the potential of this technique that is performed with an X-ray laser and present first results. Finally, my group's latest results on the role of hydrogen carbonate (bicarbonate) in photosynthetic water oxidation will be presented.

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