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Time-resolved heme protein intermediates¹

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To determine the enzymatic mechanisms of heme proteins, it is necessary to identify the intermediates along the catalytic pathway and measure the times of their formation and decay. Resonance Raman scattering spectra are especially powerful for obtaining such information as the electronic structure of the heme group and the nature of the ligand coordinated to the heme iron atom may be monitored. The oxygen intermediates of two physiologically important enzymes will be presented. Nitric oxide synthase (NOS) uses oxygen to convert arginine to NO and citrulline; and cytochrome c oxidase (CcO) reduces oxygen to water to support oxidative phosphorylation. The fate of the oxygen in each of these enzymes has been followed by resonance Raman scattering. In NOS the oxygen is slowly converted to an activated species that then reacts fast, whereas in CcO the oxygen is rapidly converted to a reactive species that subsequently reacts slowly. The properties of the intermediates and the origin of the differences between these enzymes will be discussed.

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