P001 Photo-protective Function of Carotenoid Radical Cation in Photosynthesis

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Carotenoids are the crucial pigments involved in plant photo-protection and in scavenging dangerous free radicals. The underlying processes are charge transfer and free radical reactions, both of them leading to carotenoid radical cation ($Car^{\bullet+}$) formation. Thus, accurate knowledge of $Car^{\bullet+}$ properties is a precondition for a fundamental understanding of its role in plant photo-protection. Recently, we have generated and characterized $Car^{\bullet+}$ by means of resonant two-photon two-color ionisation (R2P2CI) spectroscopy both in solution and in light harvesting complexes of photosystem II (LHC II). Further two-photon two-color experiments in combination with chlorophyll (Chl) lifetime measurements on individual light-harvesting complexes (CP24, CP26 and CP29), allow for additional critical evaluation of the role of zeaxanthin radical cations in qE component of nonphotochemical quenching (NPQ). To shed more light onto those processes we performed experiments on $Car^{\bullet+}$ generated electrochemically by using ferric chloride ($FeCl_3$) as oxidizing agent. Our results clearly show a strong dependence of the $Car^{\bullet+}$ excited state dynamics on the polarizability of the solvent and on the number of conjugate double bonds of the carotenoids. Based on our findings a direct quenching of Chls excited state by Förster energy transfer $Q_y(Chl) \rightarrow D_2(Car^{\bullet+})$ is proposed. And indeed, a quenching of the Chl lifetime has been observed when $Car^{\bullet+}$ have been induced by R2P2CI in light harvesting complexes of plants.