Physiological autoxidation behaviour of vitamin C

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The study of vitamin C and its reducing capacity is of great importance for the understanding of the human defense mechanism against radical species and crucial to a wide range of medical applications. Due to the antioxidative effect of vitamin C, aggressive radicals, like reactive oxygen species, that are under suspicion to benefit cancer generation, can be rendered harmless. On the other hand induced autoxidations of vitamin C may actually produce reactive oxygen species and allow a controlled generation of the latter at cancerous cells leading to apoptosis. The development of possible catalysts, triggering this autoxidation, is an ongoing challenge in modern cancer research.

Oxidation and autoxidation reactions of vitamin C have been investigated using quantum chemical first-principle and ab initio methods. Reaction energies and Gibbs energies of the reactions were calculated at the DFT level, applying the gradient-corrected BP and the hybrid B3LYP functionals together with basis sets of triple zeta quality. Based on these calculations adiabatic and vertical ionisation potentials as well as electron affinities were determined for all biologically active vitamin C species. Additionally, single-point CC2, CCSD and CCSD(T) calculations were used for calibration of the DFT data.[1]
Since the investigated reactions take place in a physiological environment, modelling of an aqueous vitamin C solution is mandatory. Several approaches have been accounted for, employing continuum models and explicit water molecules, approximated as effective fragment potentials. These were expressed by Coulomb interactions of multipolar charge distributions, dipole polarizability and empirical repulsive potentials.

[1] Herrmann, N., Heinz, N., Dolg, M., Cao, X, *J. Comput. Chem.* **2016**, 37, 1914.