

Physical Mechanisms of Generation and Deactivation of Singlet Oxygen

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I. Introduction

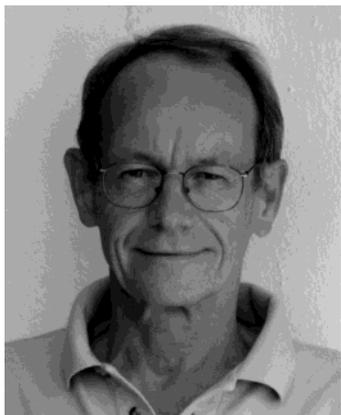
For more than 70 years, researchers in several areas of science have been intrigued by the physical and chemical properties of the lowest excited states of molecular oxygen. With two singlet states lying close above its triplet ground state, the O₂ molecule possesses a very unique configuration, which gives rise to a very rich and easily accessible chemistry, and also to a number of important photophysical interactions. In particular, photosensitized reactions of the first excited state, O₂(¹Δ_g), play a key role in many natural photochemical and photobiological processes, such as photodegradation and aging processes including even photocarcinogenesis. Reactions of O₂(¹Δ_g) are associated with significant applications in several fields, including organic synthesis, bleaching processes, and, most importantly, the photodynamic therapy of cancer, which has now obtained regulatory approval in most countries for the treatment of several types of tumors. The development of both applications and novel observation techniques has strongly accelerated during the past few years. Significant recent advances include, for example, the development of novel luminescent singlet oxygen probes,^{1–4} the time-resolved detection of O₂(¹Δ_g) in a transmission microscope,⁵ the first time-resolved measurements of singlet oxygen luminescence in vivo,⁶ and the observation of oxygen quenching of triplet-excited single molecules.⁷

Experimental and theoretical studies on the mechanisms of photosensitized formation of excited O₂ states and of their deactivation have been performed for almost 40 years. While most early liquid-phase studies were exclusively concerned with O₂(¹Δ_g), recent technological advances also made possible time-resolved investigations of the second excited state, O₂(¹Σ_g⁺), which can be formed in competition with O₂(¹Δ_g) in many cases. A significant number of

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Claude Schweitzer was born in Luxembourg in 1975. He studied chemistry in Luxembourg and in Strasbourg, where he graduated from the Ecole Européenne de Chimie Polymères et Matériaux in 1999, working with Charles Tanielian on photochemistry of free radicals and singlet oxygen. After receiving his Ph.D. degree with Reinhard Schmidt from the Johann Wolfgang Goethe-Universität in 2001, for mechanistic research on singlet oxygen photophysics, Claude joined Tito Scaiano's group at the University of Ottawa to do postdoctoral research on fluorescent probes for DNA damage detection.



Reinhard Schmidt was born 1944 in Reichenberg/Sudeten. He studied chemistry at the J. W. Goethe-Universität in Frankfurt/M, where he received the Dr. Phil. Nat. degree in 1972 with Prof. H.-D. Brauer for investigating the magnetic properties and the association behavior of some biradicaloids. Afterward, he joined the group of Prof. H. Kelm at the same institute, doing research in high-pressure kinetics and kinetic investigations of chemiluminescent systems based on dioxetanes. He later moved with H.-D. Brauer into the field of photochemistry. His habilitation occurred in 1989, with a thesis on the deactivation of singlet oxygen by solvent molecules. In 1995, he was appointed as professor at the J. W. Goethe-Universität. He was visiting professor at the University of Grenoble in 1987, and at the ECPM, University of Strasbourg, in 1993. His present research interests are photochemistry and photophysics, particularly of singlet oxygen.

studies have been carried out during the past 10 years, and it has become clear that a full discussion of all photophysical processes involving $O_2(^1\Sigma_g^+)$, $O_2(^1\Delta_g)$, and ground-state oxygen, $O_2(^3\Sigma_g^-)$, is required to achieve a complete understanding of photosensitized reactions of molecular oxygen.

Starting with a short presentation of the most important features of the $O_2(^1\Sigma_g^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g^-)$ states, we propose here an overview of experimental and theoretical studies on the mechanisms of physical deactivation of $O_2(^1\Sigma_g^+)$ and $O_2(^1\Delta_g)$ to $O_2(^1\Delta_g)$ and/or $O_2(^3\Sigma_g^-)$ in the gas and liquid phases, and in the absence and presence of physical and/or chemical quenchers. This includes radiative,

electronic-to-vibrational, charge transfer, and electronic energy-transfer processes, which all may compete in a given chemical system. We also cover the physical mechanisms of generation of $O_2(^1\Sigma_g^+)$ and $O_2(^1\Delta_g)$, focusing mainly on the quenching of excited singlet and triplet states by $O_2(^3\Sigma_g^-)$. Both processes can proceed via energy-transfer and charge-transfer pathways, and we explain here how the physical properties of the quencher and of the medium influence the mechanisms, rate constants, efficiencies, and products of the individual deactivation processes.

Our review will conclude with a short presentation of the most recent advances in the field of singlet oxygen detection, and with a guide to the utilization of the mechanistic knowledge presented here, showing, for example, how to evaluate the contribution of individual physical and/or chemical mechanisms to the generation or deactivation of $O_2(^1\Sigma_g^+)$ and $O_2(^1\Delta_g)$ in a given situation, or how to design molecules in order to maximize or minimize their $O_2(^1\Sigma_g^+)$ and/or $O_2(^1\Delta_g)$ photosensitization ability in a given medium.

The review is strictly limited to physical mechanisms of generation and deactivation of singlet oxygen. Chemical processes are discussed only in those cases where they compete with the physical processes and/or proceed via common intermediates. It should be noted that most chemical reactions of singlet oxygen are well understood, and only a few fundamentally new aspects have been revealed since the publication of previous reviews.^{8–11} The only significant exception seems to be the antibody-catalyzed singlet oxygenation of water, which was suggested in 2001.^{12,13} An introduction to applications of photosensitized reactions of singlet oxygen was also published very recently.¹⁴

The solvent dependence of singlet oxygen formation and deactivation parameters is discussed to the extent to which it provides relevant mechanistic information; a more detailed review of the solvent dependence of singlet oxygen deactivation can be found elsewhere.¹⁵ Also, extensive data collections of quantum yields of $O_2(^1\Delta_g)$ generation¹⁶ and of rate constants for its deactivation¹⁷ were published in 1993 and 1995, respectively, and are freely accessible on the Internet.¹⁸ A recent (1999) update of singlet oxygen yields from biologically relevant molecules is also available.¹⁹ The present review considers the literature published through the end of November 2002.