

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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