Innovation in the Production of Singlet Oxygen

Professor
Aristides Marcano Olaizola

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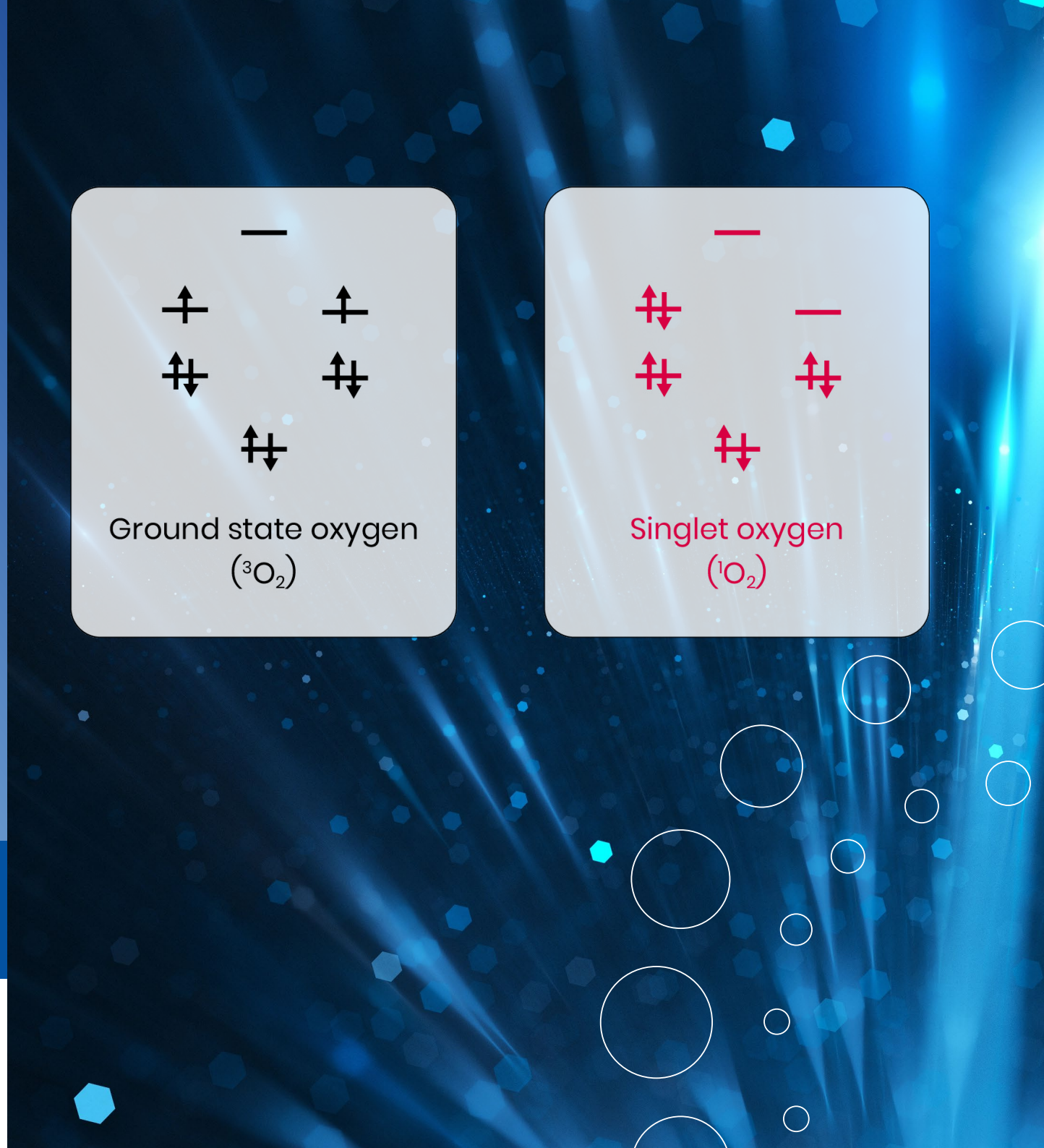


Innovation in the Production of Singlet Oxygen

A novel method for producing singlet oxygen via stimulated Raman scattering (SRS) offers an innovative alternative to traditional photosensitizer-based techniques, promising safer and more efficient applications in disinfection, cancer treatment, and beyond. Professor Aristides Marcano Olaizola at Delaware State University is driving innovation in this critical field.

Why Singlet Oxygen is Important

Singlet oxygen ($^1O_2$) is an electronically excited state of molecular oxygen (O_2) characterised by the paired electrons in its outermost molecular orbitals. Unlike the ground-state triplet oxygen ($^3O_2$), which has two unpaired electrons, singlet oxygen's electrons are paired, resulting in a higher energy state. This unique electronic configuration increases the molecule's reactivity compared to the relatively inert triplet oxygen.

Singlet oxygen plays a critical role in biological and chemical contexts due to its ability to engage in various oxidative reactions. It readily reacts with organic molecules, particularly those containing double bonds, forming peroxides and other oxidation products. This reactivity is exploited in several biological processes, such as cellular signalling and immune responses. For instance, singlet oxygen is produced by immune cells during the oxidative burst, a mechanism used to destroy pathogens.

The applications of singlet oxygen extend into the fields of disinfection, cancer treatment, and material science. In disinfection, $^1O_2$ effectively inactivates bacteria, viruses, and fungi by damaging their cellular components, including lipids, proteins, and nucleic acids. This property is harnessed in water treatment processes, surface sterilisation, and air purification systems.

In cancer treatment, singlet oxygen is a cornerstone of photodynamic therapy (PDT). PDT involves the administration of a photosensitizing agent, which accumulates selectively in cancerous tissues. Upon irradiation with light of a specific wavelength, the photosensitizer generates $^1O_2$ which induces cell death through oxidative damage to cellular structures.

In material science, it is used in the synthesis and functionalisation of various materials, including polymers and nanoparticles. The oxidative properties of $^1O_2$ facilitate the incorporation of functional groups into these materials, enhancing their performance and utility in applications such as drug delivery, catalysis, and sensor technologies.

Challenges with the Traditional Approach

Photosensitizers facilitate the generation of singlet oxygen ($^1O_2$) by absorbing light energy and transferring it to molecular oxygen (O_2). Typically, photosensitizers possess conjugated systems that allow them to absorb photons and transition to an excited electronic state. Upon relaxation from this excited state, the energy is transferred to triplet oxygen ($^3O_2$), converting it into the reactive singlet state ($^1O_2$). This process is known as photosensitization.

Despite their utility, photosensitizers are accompanied by significant limitations and drawbacks. One primary concern is phototoxicity. Photosensitizers can cause damage to non-target tissues due to their broad absorption spectra and the potential for off-target effects. This unintended phototoxicity can lead to adverse side effects, especially in medical applications where precise targeting is crucial. In addition, photosensitizers often induce uncontrolled reactions.

The chemical complexity of photosensitizers also poses challenges. Their synthesis and purification can be intricate and costly, which impacts the scalability and practicality of their use. Additionally, residual photosensitizers can persist in the environment or within biological systems post-treatment.

From a quantum mechanical perspective, direct one-photon excitation to the singlet oxygen state is inherently inefficient. The transition from the ground state ($^3O_2$) to the singlet state ($^1O_2$) is spin-forbidden, meaning that it violates the selection rules governing electronic transitions. This restriction necessitates using photosensitizers to mediate the process, as direct photon absorption by O_2 typically results in non-productive pathways. The inefficiency of this direct excitation underpins the reliance on photosensitizers, despite their associated drawbacks.

Professor Aristides Marcano Olaizola at Delaware State University has developed a novel approach to generating singlet oxygen that circumvents the need for photosensitizers altogether. Using blue laser light, his method leverages stimulated Raman scattering (SRS), a nonlinear optical process, to excite molecular oxygen directly to its singlet state. By exploiting the energy transfer dynamics inherent in Raman scattering, this technique provides a more controlled and efficient pathway to $^1O_2$ production.

The Raman-based Generation Method

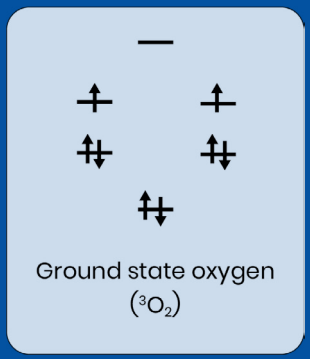
When light interacts with a molecule, most photons are elastically scattered, maintaining their original energy. However, a small fraction of the light is scattered inelastically, meaning the photons either gain or lose energy. This energy shift results in scattered light at different wavelengths. Raman scattering, discovered by Raman in 1928, is a two-photon process where the incident photon energy is partially transferred to a molecular vibrational mode, resulting in the scattered photon having reduced energy.

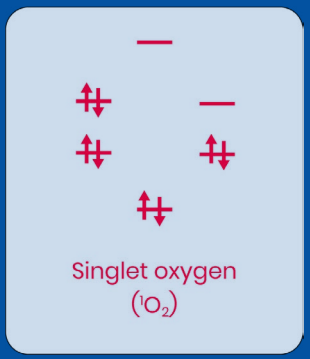
Professor Marcano utilises a blue laser light, typically within the wavelength range of 410–440 nm, to induce Raman scattering in a sample. The experimental setup includes a high-intensity blue laser directed through a focusing lens onto the sample contained within a cell. As the laser light interacts with the sample, it produces a spectrum of scattered light, including both elastic and Raman (inelastic) components. In this context, the energy difference matches the excitation energy required to transition oxygen from its ground state ($^3O_2$) to its singlet state ($^1O_2$).

The experimental results are presented through Raman spectra and photographs of the characteristic ring patterns formed by the scattered light. The Raman spectra display distinct peaks corresponding to the energy shifts indicative of singlet oxygen production. The presence of these peaks confirms the successful generation of $^1O_2$ via the SRS process. Photographs of the ring patterns further validate these findings, as the patterns are consistent with the expected distribution of Raman-scattered light.

Control experiments were conducted to strengthen the validation of the results. By reducing the oxygen concentration in the sample cell, the intensity of the Raman signal corresponding to singlet oxygen decreased proportionally. This reduction in signal intensity with lower oxygen concentrations provides strong evidence that the observed Raman peaks are indeed due to singlet oxygen generation. Additionally, varying the laser intensity and wavelength confirmed the specificity of the Raman process in producing $^1O_2$, as deviations from the optimal parameters resulted in diminished or absent Raman signals.

By exploiting the energy transfer dynamics inherent in Raman scattering, this technique provides a more controlled and efficient pathway to $^1O_2$ production.





A Significant Step Forward

The broader implications of this Raman-based method for singlet oxygen generation are substantial for photodynamic applications. Environmental conservation efforts could also benefit from this technology. The safe and efficient production of singlet oxygen could be applied in water treatment processes, air purification systems, and other environmental applications requiring oxidative reactions.

The Raman-based method offers significant advantages over traditional photosensitizer methods, including reduced complexity, increased safety, and potentially lower costs due to eliminating chemical sensitizers. As such, this novel approach represents a significant step forward in the practical and widespread application of singlet oxygen in various scientific and industrial domains.

MEET THE RESEARCHER

Professor Aristides Marcano Olaizola
Delaware State University, Dover, DE, USA

Professor Aristides Marcano Olaizola obtained his in Physics and Mathematical Sciences from Moscow State University (Russia) in 1980. After this, he worked at Instituto Venezolano de Investigaciones Cientificas, Caracas, Venezuela, and joined Delaware State University in 2006 as an Associate Professor. In his time at Delaware State University, Professor Marcano has served as Chair of the former Department of Physics and Engineering (2011–2015) and as a member of committees in other departments, the college, and the university. As a physicist specialising in experimental photophysics and molecular spectroscopy, Professor Marcano has published extensively and been awarded significant funding to support his research. In addition to his active research activities, Professor Marcano undertakes teaching and mentoring of undergraduate and graduate students.

CONTACT

amarcano@desu.edu

https://cast.desu.edu/about/faculty-profiles/aristides-marcano-olaizola-phd

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FURTHER READING

AM Olaizola, R Kuis, A Johnson, D Kingsley, Stimulated Raman generation of aqueous singlet oxygen without photosensitizers, *Journal of Photochemistry and Photobiology B: Biology*, 2022, 235, 112562. DOI: https://doi.org/10.1016/j.jphotobiol.2022.112562