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Mikkel Bregnhøj

The Electronic Transitions of Molecular Oxygen

Doctoral Thesis accepted by
Aarhus University, Aarhus, Denmark

Springer

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Supervisor's Foreword

In his Ph.D. research program, Mikkel Bregnhøj systematically examined how optical transitions among the three lowest-lying electronic states in molecular oxygen respond to perturbation, principally from a liquid organic solvent. This is an important topic given that we live in a world of light, oxygen, and organic molecules. Indeed, for this very reason, this topic has a long history. Nevertheless, despite volumes of published data and interpretations, a consistent and unified picture of the pertinent phenomena has heretofore been lacking. Using a variety of state-of-the-art spectroscopic techniques, Mikkel Bregnhøj was able to move the field forward.

Mikkel's work is certainly important from a fundamental perspective. Understanding how a given organic molecule perturbs radiative and, independently, non-radiative transitions in oxygen is a difficult problem that addresses fundamental tenets of science. Among other things, Mikkel's data, recorded as a function of temperature, point an intriguing finger at the role that tunneling likely plays in these processes. In this way, he has opened the door for a whole new generation of theoretical/computational chemists and physicists.

Mikkel's work is also important from a practical sense, with ramifications from polymer science to biology. For example, Mikkel nicely showed that singlet delta oxygen, the excited state of oxygen that exhibits unique chemical reactivity, can be selectively made in meaningful yields via direct irradiation of ground-state oxygen at 765 nm. This reactive state of oxygen is commonly prepared in a sensitized process wherein the energy of excitation is transferred to oxygen from an organic molecule. In the least, Mikkel's sensitizer-free approach will certainly be a boon in mechanistic studies of photooxygenation reactions. Mikkel also demonstrated that this sensitizer-free approach can perturb living cells differently depending on the light "dose." This result has appreciable ramifications in the medical field of light-mediated therapies.

In conclusion, Mikkel Bregnhøj has had a productive program of Ph.D. research that puts him at the cutting edge of internationally competitive science.

Aarhus, Denmark
July 2018

Prof. Peter R. Ogilby

Abstract

The three lowest electronic states of molecular oxygen, $O_2(X^3\Sigma_g^-)$, $O_2(a^1\Delta_g)$, and $O_2(b^1\Sigma_g^+)$, are an omnipresent part of life on earth. Although they differ only by the occupancy of two electrons in degenerate orbitals, they each have their own unique chemistry and photophysics. For example, singlet oxygen, $O_2(a^1\Delta_g)$, is a well-established oxidant, important in fields ranging from polymer degradation across chemical synthesis to the photodynamic treatment of cancer. Controlling the reactions of $O_2(a^1\Delta_g)$ in a given solution invariably involves understanding and controlling the processes by which the excited states of oxygen are formed and deactivated. These solvent-mediated radiative and non-radiative processes are the unifying theme of this thesis.

The radiative transitions among $O_2(X^3\Sigma_g^-)$, $O_2(a^1\Delta_g)$, and $O_2(b^1\Sigma_g^+)$ are "forbidden" by the selection rules of quantum mechanics. It is, therefore, highly improbable to form the excited states, $O_2(a^1\Delta_g)$ and $O_2(b^1\Sigma_g^+)$, by irradiation of the ground state, $O_2(X^3\Sigma_g^-)$. Nevertheless, an important goal of this work has been to show that it is indeed possible to produce and detect singlet oxygen using only the light-induced and emitting transitions among $O_2(X^3\Sigma_g^-)$, $O_2(a^1\Delta_g)$, and $O_2(b^1\Sigma_g^+)$. This provides an alternative way to produce $O_2(a^1\Delta_g)$ in systems where photosensitizers and chemical sources of $O_2(a^1\Delta_g)$ are undesirable. As a demonstration, we apply this new tool in a biological context to induce proliferation, apoptosis, or necrosis in mammalian cancer cells.

The electronic transitions in oxygen are very sensitive to the immediate environment surrounding the oxygen molecule. This sensitivity to solvation has so far almost exclusively been quantified for the $O_2(a^1\Delta_g)$–$O_2(X^3\Sigma_g^-)$ transition. Since our work has provided easier spectroscopic access to $O_2(b^1\Sigma_g^+)$, one important goal of this work has also been to quantify the effects of solvent on the $O_2(b^1\Sigma_g^+)$–$O_2(a^1\Delta_g)$ and $O_2(b^1\Sigma_g^+)$–$O_2(X^3\Sigma_g^-)$ transitions. Most interestingly, our data show that each of these three transitions in oxygen, and the radiative and non-radiative parts of that given transition, responds very differently to changes in solvent and temperature. These observations allow us to test and refine the currently accepted theories regarding the electronic transitions in oxygen.

In an attempt to enhance the low transition probabilities in oxygen, we investigated the effect of metal nanoparticles on the photophysics of oxygen. Unfortunately, our results show that metal nanoparticles, at least in bulk solution, do not provide a viable path to enhance the radiative transitions in oxygen. However, our results highlight some of the challenges that need to be addressed in future studies of interactions between nanoparticles and chromophores in general.

Despite the fact that molecular oxygen in solution represents a system that has been studied intensely for over half a century, our results show that there is still much to be learned about the interaction between oxygen and its surroundings.

Preface

Ninety years have passed since Robert Mulliken predicted the existence of a meta-stable electronic state of molecular oxygen called $O_2(a^1\Delta_g)$ or singlet oxygen. Since then, many scientific careers have been spent unearthing, rationalizing, and taming the properties of this omnipresent excited state. The list encompasses a wide fraction of photochemistry's Hall of Fame: Kautsky, Kasha, Terenin, Foote, to name but a few. Accordingly, the photophysics of oxygen has been investigated to the point, where one would not expect to find earthshaking new sources of singlet oxygen science. Instead, my approach has been to step back and take a grander perspective. What are the unifying themes in this wealth of knowledge? And where are the holes that need to be filled?

It is likely that I will be the last person able to spend an entire Ph.D. scholarship in the subject of fundamental singlet oxygen photophysics. I sense that the future of singlet oxygen science concerns the applications and the mechanisms of singlet oxygen biochemistry. How, why, when, and where does singlet oxygen exert its influence on biological organisms and humans? And, more importantly, can we control and manipulate the action of singlet oxygen to the benefit of mankind?

Aarhus, Denmark
July 2018

Mikkel Bregnhøj

Parts of this thesis have been published in the following journal articles:

I. Bregnhøj, M., Blázquez-Castro, A., Westberg, M., Breitenbach, T., & Ogilby, P. R. (2015). Direct 765 nm optical excitation of molecular oxygen in solution and in single mammalian cells. *The Journal of Physical Chemistry B*, *119*(17), 5422–5429.

II. Bregnhøj, M., & Ogilby, P. R. (2015). Effect of Solvent on the $O_2(a^1\Delta_g) \rightarrow O_2(b^1\Sigma_g^+)$ Absorption Coefficient. *The Journal of Physical Chemistry A*, *119*(35), 9236–9243. (Cover article).

III. Westberg, M., Bregnhøj, M., Blázquez-Castro, A., Breitenbach, T., Etzerodt, M., & Ogilby, P. R. (2016). Control of singlet oxygen production in experiments performed on single mammalian cells. *Journal of Photochemistry and Photobiology A: Chemistry*, *321*, 297–308. (Cover article).

IV. Westberg, M., Bregnhøj, M., Banerjee, C., Blázquez-Castro, A., Breitenbach, T., & Ogilby, P. R. (2016). Exerting better control and specificity with singlet oxygen experiments in live mammalian cells. *Methods, 109*, 81–91.

V. Bregnhøj, M., Westberg, M., Jensen, F., & Ogilby, P. R. (2016). Solvent-dependent singlet oxygen lifetimes: temperature effects implicate tunneling and charge-transfer interactions. *Physical Chemistry Chemical Physics*, *18*(33), 22946–22961.

VI. Bregnhøj, M., Krægpøth, M. V., Sørensen, R. J., Westberg, M., & Ogilby, P. R. (2016). Solvent and Heavy-Atom Effects on the $O_2(X^3\Sigma_g^-) \rightarrow O_2(b^1\Sigma_g^+)$ Absorption Transition. *The Journal of Physical Chemistry A*, *120*(42), 8285–8296.

VII. Bregnhøj, M., Westberg, M., Minaev, B. F., & Ogilby, P. R. (2017). Singlet Oxygen Photophysics in Liquid Solvents: Converging on a Unified Picture. *Accounts of Chemical Research*, *50*(8), 1920–1927.

VIII. Bregnhøj, M., Rodal-Cedeira, S., Pastoriza-Santos, I. & Ogilby, P. R. (2018). Light Scattering versus Plasmon Effects: Optical Transitions in Molecular Oxygen near a Metal Nanoparticle, *The Journal of Physical Chemistry C*, *122*(27), 15625–15634.

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