Using Instanton Theory to Study Quantum Effects in Photosensitization

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Photosensitization of O_2 is widely made use of in organic synthesis, photovoltaic cells and is a key step in photodynamic therapy. Despite its significance, its comprehensive mechanism is still unknown.

$$^3PS + {}^3O_2 \rightarrow {}^1PS + {}^1O_2$$

A previous theoretical study calculated O_2-photosensitization rates by thiothymines (2-thiothymine, 4-thiothymine and 2,4-dithiothymine) and found a speed up by several orders of magnitude when rates were calculated from Fermi's golden rule (FGR) compared to Marcus theory, thus establishing the importance of quantum effects in driving photosensitization [1]. However, even the smallest photosensitizers (PS) are too large for a quantum approach to be tenable. The gap between the need to account for quantum effects and computational cost can be bridged by semiclassical instanton theory (SCI), in particular, its extension to the inverted regime in the golden-rule limit [2]. SCI has been shown to give excellent results for ISC reactions [3]. While rate constants calculated from SCI are in excellent agreement with experiment, its central contribution is the elucidation of the reaction mechanism by locating the optimal tunnelling pathway [3]. For O_2-photosensitization, we start by extending SCI to a model system, which best describes the process, and obtain near-perfect agreement with exact (FGR) rates. Then, before applying the developed methodology to a real system, we take a closer look at the PSs – the thiothymines – themselves. This is because the mode which promotes photosensitization has been identified to be the one along which intersystem crossing (ISC) of the PS takes place [1]. Our calculations have shown evidence of room-temperature heavy-atom tunnelling in the ISC pathways of 4-thiothymine and 2,4-dithiothymine, while the tunneling effect in 2-thiothymine is negligible. We then extend the calculations to the O_2-photosensitization reaction by thiothymines.

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