Comment to the Editor

Kinetic Models of Photosystem II Should Incorporate a Role for Q_B-Nonreducing Reaction Centers

In their article, ''Evidence for Intermediate S-States as Initial Phase in the Process of Oxygen-Evolving Complex Oxidation'' (1), Jiri Jablonsky and Dusan Lazar used a kinetic model of photosystem II for analysis and simulation of the period-four oscillation pattern of oxygen evolution and fluorescence induction in 1.5–2 Hz single turnover flash (STF) trains. Their model is a modified version of an earlier model (2) after incorporation of so called intermediate S-states defined as $[S_n\, Y_z^{ox}]$ in the electron transport chain at the donor side of PSII.

It can easily be argued that the modified model (see Scheme 2 in Jablonsky and Lazar (1)), like the original one (2), is inadequate to simulate the kinetics of the primary PSII reactions upon individual STF trains in the 10 ns to 500 ms time range. This inadequacy is best illustrated when one considers STF-induced fluorescence responses in this time range (3–5). It follows from the authors' model (see the left hand upper part in section A of their scheme) that, after one STF and with $k_{AB1} \approx (500\ \mu s)^{-1}$, the final state L-PHAB$^-$ with F/Fo = 1 is reached after approx. 1–2 ms. However, experimental curves (3–5) show an intermediate quasi-steady state with F/Fo $\approx$ 1.3 after 1–2 ms. This state has been ascribed to originate from single reduced Q_B-nonreducing reaction centers (RCs) (5). An intermediate quasi-steady state with F/Fo $\approx$ 1.3 suggests the presence of an ~30% fraction of these RCs. This value is in the range of 15–35% at which a fraction of Q_B-nonreducing RCs is usually found in 5–30 min dark-adapted samples of various origins. The presence of a sizeable fraction of these RCs after the first STF-excitation and the likely contribution thereof to the period-four oscillatory variable fluorescence signal and to the population and de-population of S-states in subsequent STFs of a 1.5–2 Hz train (see for instance Vredenberg et al. (5,6)) is ignored in the authors' kinetic model. In addition, but probably of little effect on the oscillatory patterns, the rise of variable fluorescence, which in the authors' model is assumed to occur in parallel with the reduction of P^+ (release of P^+-quenching), will take place in the time domain of $(k_{Pred}^{02})^{-1}$ s $\approx$ 20 ns (see section D in scheme). However the experimental curves show that the rise takes at least 20 μs (3,4). A much better agreement between experimental and simulated STF responses is found when quenching by Y_z^{ox} is assumed to occur (7,8).

The model of Jablonsky and Lazar (1) is incomplete in its present form and inadequate to simulate STF-induced responses of variable fluorescence. Ignorance of a Q_B-nonreducing RC fraction, which has been shown to be 1), susceptible to double excitation; and 2), responsive with a period-four oscillatory pattern in repetitive STFs (6), has consequences for the mathematical modeling. It remains to be proven, when based on a complete kinetic model, whether or not the proposed rapid formation (with k_{iSn}) of the intermediate S-states ($Y_z^{ox}S_n$) is required for fitting the oscillatory pattern of O_2 evolution. It can be demonstrated that the oscillatory pattern of variable fluorescence before and 80 ms after an STF in a 12.5 Hz train (5) can be approximated (simulated) with the period-four modulated response of the Q_B-nonreducing RC fraction without assuming the involvement of intermediate S-states ($Y_z^{ox}S_n$).

To summarize, application and validation of the kinetic model presented in the article by Jablonsky and Lazar (1) is impossible because of the failure to find or to define conditions at which the kinetic profile of single flash-induced fluorescence induction is comparable to that predicted by the model.

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