Available online at www.sciencedirect.com
SCIENCE DIRECT
Biochimica et Biophysica Acta 1757 (2006) 158–159
BIOCHIMICA ET BIOPHYSICA ACTA
BBA
http://www.elsevier.com/locate/bba

Discussion

Response to the "Comments to water-splitting activity of Photosystem II by far-red light in green plants" by H.-W. Trissl

Hugo Pettai [a], Vello Oja [a], Arvi Freiberg [a,b], Agu Laisk [a,*]

[a] *Institute of Molecular and Cell Biology, University of Tartu, Riia tn. 23, Tartu 51010, Estonia*
[b] *Institute of Physics, University of Tartu, Riia tn. 142, Tartu 51014, Estonia*

Received 2 February 2006; accepted 7 February 2006
Available online 13 March 2006

Two results of our papers [1,2] should be distinguished, one being an observation that surprisingly long-wavelength quanta up to 780 nm support oxygen evolution from plant leaves, and the second being a peculiar spectral behavior of the quantum yield of the PSII electron transport, showing a local maximum at ~745 nm. This is the quantum yield spectral dependence and its interpretation that has been questioned by H.-W. Trissl in his *Comments*. Several arguments were presented in favour of the absorption from thermally populated vibrational sublevels of PS II chlorophylls for explanation of the photosynthetic activity under extreme red light, without appellation to special far-red PSII chlorophylls, the presence of which was hypothesized in [1,2]. One of the arguments used was a good fit of our experimental oxygen evolution rates with the calculated PSII absorption spectrum shown in Fig. 1b of the *Comments*. This agreement is, unfortunately, deceptive, because only a limited number of experimental points and arbitrary normalization in a narrow spectral range was applied. When, however, the whole set of experimental points is presented, as shown in Fig. 1 of this letter, obvious discrepancies appear, clearly suggesting an extra absorbance with respect to PSII chlorophylls in the 720–760 nm region. Thus, while the proposed interpretation is certainly an option, which is also discussed in our works [1,2], the evidence given in the *Comments* is circumstantial, based upon an idealized computational model [3]. Amongst other things, this model, for example, uses the Kennard–Stepanov relation for the calculation of the fluorescence spectrum. Yet as noted in [4], the thermal equilibration assumed by Kennard–Stepanov (KS) is hardly ever seen in practice. The KS anomalies are observed in a wide variety of cases, including chlorophyll *a* in solution and in protein complexes [4,5], suggesting either departures from thermal equilibrium [4] or involvement of several electronic states [5]. The fact that a number of previous studies did not reveal these irregularities shows high "flexibility" of the "KS approach", well described in the context of photosystem I in [6].

In papers [1,2], the absorption from excited vibrational sublevels of PS II chlorophylls as a sole explanation for the increased photosynthetic activity at extreme red wavelengths was set apart on the quantitative basis of the data. The ratio of absorbencies at 680 nm and at 745 nm for PSII chlorophylls was estimated to be about 3000. A similar number can be deduced

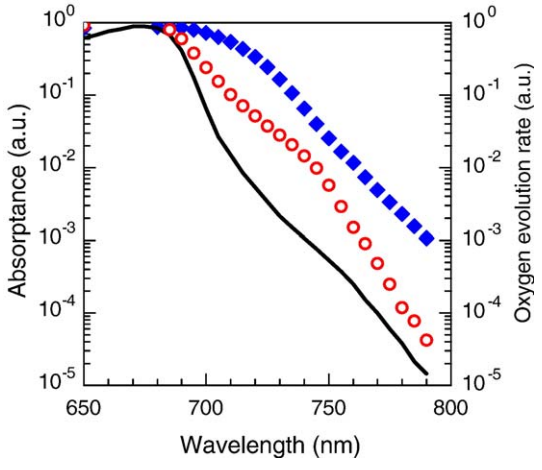

Fig. 1. Experimental absorptance spectrum of sunflower leaves (diamonds), that of PSII adopted from the *Comments* (solid line), and the oxygen evolution data of [1,2] scaled to the absorptance spectra (circles). The properly corrected experimental points are averaged over seven different leaves.

* Corresponding author. Fax: +372 7366 021.
E-mail address: agu.laisk@ut.ee (A. Laisk).

doi:10.1016/j.bbabio.2006.02.008

from the calculated absorption spectrum shown in Fig. 1b of the *Comments*. At the same time, the quantum yield value of oxygen evolution obtained for 745 nm assumes this ratio to be about 300. This discrepancy of almost an order of magnitude is difficult to explain, unless extra PSII absorption is present. In addition to the already proposed interpretations, the extra absorbance can be connected with the recently discovered weak long-wavelength absorption in the PSII reaction center of mixed exciton and charge transfer character [7].

To conclude, we have to admit that at the present stage of knowledge, the issue stays open. Referring to the conclusions of our paper [1]: more work should be done to meet the challenges brought up by this investigation. It should, however, be noticed that we have never stated that the far-red light does not directly excite vibrational sublevels of the bulk PSII chlorophyll *a* molecules. It certainly does. Yet the question remains as to whether the rate of this excitation is sufficient to explain the residual oxygen evolution observed far beyond 700 nm.

References

[1] H. Pettai, V. Oja, A. Freiberg, A. Laisk, Photosynthetic activity of far-red light in green plants, Biochim. Biophys. Acta 1708 (2005) 311–321.
[2] H. Pettai, V. Oja, A. Freiberg, A. Laisk, The long wavelength limit of plant photosynthesis, FEBS Lett. 579 (2005) 4017–4019.
[3] H.-W. Trissl, Modeling the excitation energy capture in thylakoid membranes, http://www.biologie.uni-osnabrueck.de/biophysik/trissl/Teaching/teaching.htm2003.
[4] R.S. Knox, P.D. Laible, D.A. Sawicki, M.F.J. Talbot, Does excited chlorophyll a equilibrate in solution? J. Luminescence 72–74 (1997) 580–581.
[5] R.S. Knox, J.S. Brown, P.D. Laible, M.F.J. Talbot, Part of the fluorescence of chlorophyll a may originate in excited triplet states, Photosynth. Res. 60 (1999) 165–177.
[6] R.C. Jennings, F.M. Garlaschi, G. Zucchelli, Excited state trapping and the Stepanov relation with reference to photosystem I, Biophys. J. 85 (2003) 3923–3927.
[7] V.I. Novoderezhkin, E.G. Andrizhiyevskaya, J.P. Dekker, R. van Grondelle, Pathways and timescales of primary charge separation in the photosystem II reaction center as revealed by a simultaneous fit of time-resolved fluorescence and transient absorption, Biophys. J. 89 (2005) 1464–1481.