Report on the Ph.D. thesis by Jakub Dostál (Photosynthetic Apparatus of Green Sulfur Bacteria Studied by Coherent Two-Dimensional Electronic Spectroscopy)

The dissertation thesis by Jakub Dostál is based on five papers either published or submitted in high-ranked journals while one paper is still reported as a manuscript. For four of these papers, Jakub Dostál is the first author with the dominant contribution to both experimental and theoretical parts of the papers. The thesis is of high quality, both from the content and presentation point of views. The content of the thesis demonstrates authors' expertise in various fields extending from theory of nonlinear spectroscopy to knowledge of various photosynthetic systems.

I especially value the introduction part in which the author nicely and patiently explains various aspects of the state-of-art experimental technique he has been using during his Ph.D. project. The introduction is very well written and serves precisely the purpose that a good Ph.D. thesis should do – it is a great reference material for potential successors in the field, containing many details concerning both the theory and experiment that the reader will not find in a 'standard' scientific paper. Any new Ph.D. student or postdoc will greatly benefit from reading the introduction of this thesis as the author slowly guides the reader through various aspects of the experiment, theory and the systems he has studied. The text flow in the introduction somehow reflects the obstacles and complications which the author must have faced during his own journey through this complicated field, which makes it very accessible and readable to any reader.

I also particularly like the explanation of some aspects of 2DES by using the references to Heisenberg, Einstein and to the 'famous' double-slit experiment. These parallels helps the reader to understand and to grasp the major essence of the complicated 2DES experiment. The author also does not hesitate to reveal some tricks that helped him to improve the experiment to a nearly perfect level. I am sure this will also save many days and nights of experimental work for his successors. In this respect I would like to see a bit more details concerning the phasing process that is described rather vaguely. The author admits that there are other ways than comparing the integrated 2DES spectrum with the conventional pump-probe spectrum, yet no other methods are mentioned even though the author consider the phasing as the 'bottleneck' of the 2DES experiment. Also, when illustrating various signals coming from the 2DES experiment, it might be more pedagogical to show the absorption spectrum first and not vice versa (Figs. 7 and 8 in the first chapter).

The second chapter nicely describes the whole photosynthetic apparatus of green sulfur bacteria, again in very pedagogical way explaining various aspects of both structural and dynamical properties of the system. When reading this chapter, the reader can only admire the bravery of the author (or here maybe of his supervisor) to choose such a complicated system for 2DES spectroscopy. While others in this field rather aims at simple systems with known structure, this thesis focuses on 2DES experiment applied to a large, inhomogeneous antenna with structure that varies from chlorosome to chlorosome. Yet, the results clearly demonstrates that the choice was excellent and 2DES spectroscopy can provide a vast amount of information even for such complex system.

The core of the results achieved during the work on this thesis is summarized in Chapter 3, in which the author pinpoints the crucial achievements of this thesis. Especially valuable is Chapter 4, popular summary, which makes the thesis available for a broad range of readers.

The rest of the thesis contains reprints of the papers. All papers demonstrate the power of the 2DES method, especially when in hand of a specialist. According to my opinion, the most important contribution to the field is provided in Papers IV and V that for the first time reveal excitonic structure of the chlorosome baseplate (Paper IV) and aims to track the path of energy through the whole photosynthetic system in vivo (Paper V). Especially the latter task was not so long time ago unthinkable to carry out, but the author of this thesis together with his supervisor and other collaborators clearly proved it is actually possible. It is even more admirable they managed to tackle this problem with experimentally very demanding method, 2D electronic spectroscopy.

To summarize, the whole thesis is clearly written in a very good English (in fact the highest density of misspellings I found in the Czech summary at the beginning), with excellent introduction understandable even for a non-specialist on one hand, and cutting edge science in the last chapters on the other hand. This thesis falls into the top 10% of Ph.D. theses I have seen so far.

Overall, I have no reservations that this thesis fulfills the requirements of the PhD work in any country or any university. The candidate did a great piece of scientific work and proved that he is able to contribute significantly to the development in the field. The thesis in my opinion fulfills (and in many aspects exceeds) the criteria for being accepted as a ground for awarding Jakub Dostál with the title PhD. and should be accepted for the defense.

Specific questions that could be discussed during the thesis defense:

1. On page 35 when discussing the higher-order contributions to the signal, it is mentioned that upon breaking the "linearity condition" the vertical cuts of 2DES spectrum do not correspond to pump-probe spectra anymore. How the phasing problem is tackled for such a case? At the end of this section, the author indicates that phasing cannot be even possible for some cases, but at the same time it is indicated that this might be the case for a number of photosynthetic systems. Thus, how this problem is solved in 2DES spectroscopy of photosynthetic systems?
2. Among advantages of 2DES over conventional pump-probe spectroscopy availability of other signals, such as transient changes in dispersion (in addition to the changes in absorption) is mentioned. What such signals are good for and what information can be extracted from them?

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