Dr. Stefan Müller
Institut für Physikalische und Theoretische Chemie
Am Hubland, 97074 Würzburg
☏ +49 931 31-86727
✉ stefan.mueller@uni-wuerzburg.de

Faculty of Mathematics and Physics
Charles University
Ke Karlovu 5, 121 16 Prague

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Report on a master thesis „Excited state dynamics in fluorescence-detected transient absorption" by Kateřina Charvátová (Study programme and branch: Biophysics and chemical physics), 2024

To whom it may concern,

The task of the thesis by Kateřina Charvátová was to investigate the general properties of the previously established experimental technique of "fluorescence-detected pump–probe spectroscopy" (F-PP). To achieve this goal, the existing Quantarhei library was extended accordingly and successfully to simulate F-PP experiments. One particular goal was to investigate how the F-PP signal behaves for negative pump–probe delays with the prospect of using the signal for negative delays for subtraction from the F-PP signal with positive pump–probe delays. Moreover, the properties of the F-PP signal near time zero between pump and probe pulses (in the case of finite pulse duration) and the influence of chirp of the pulses was investigated.
The professional level of the thesis is excellent. The work is well and sensibly structured.
The theoretical results are original and in very good agreement with existing experimental spectra and observations. The extent of the thesis is sufficient and the results contain important implications for further research adressing the issues of so-called incoherent mixing which was very recently discussed in the literature.
On the formal level, the work has weaknesses in terms of language and notation. Some explanations lack clarity. The definite or indefinite article has been omitted in several places. At a few occurences, the language was unprecise, see, e.g., p. 7: "incident lights" or p. 16: "electric intensity", or p. 20: "excited energies". Further, the use of the reference "this" or "it" is at some occurences used in such a way that it is not clear what "this" or "it" referes to, making it difficult for the reader to follow the flow of arguments and equations. However, the formal quality improves in the course of the work. In Section 3.1, some equations are used with insufficient notation, making it difficult for the reader to follow which situation applies to which equation. The F-PP signals that represent a particular scenario are often only indicated as "F-PP", but it would be helpful for the reader if suitable indexes were available that would correspond to the particular situations described in the text (i.e., with or without annihilation or for positive or negative pump–probe delays). At some occurences, notation is unprecise or misleading, for example, in Section 3.4 it is not clear what a coherence labelled as |A><13000| refers to, since "13000" does not seem to represent a state of the investigated system. Some statements and explanations lack clarity, for example it is difficult to understand what "|2⟩ is the excited state of the other molecule than in |1⟩" means.
The quality of the graphics and plots created is very good. Section 3.5.2 is descriptively and comprehensively written. Chapter 4, which was intended to compare the theoretical results with reference measurement data from the literature, is somewhat brief.

On the scientific level, the conclusions given in this thesis are signficant and correct within the framework of the methodologies used and provide valuable implications for experimentalists and thus future work. The summary is concise and well written.

In the following I provide possible questions which may be asked during the defence of the thesis and which may also serve as a suggestion for topics for discussion:

- The simulations have been conducted in a partly rotating frame of $\gamma = 0.2$ and 3×3 phase cycling of the probe pulses. Why have the simulations not been conducted in a fully rotating frame?
- Can cross-population ground-state bleach pathways also be formulated for coherence-based PP spectroscopy? Does the ratio between stimulated emission and ground-state bleach also decrease with increasing number of chromophores in coherence-based PP spectroscopy?
- In subsection 3.5.1, the “time-energy uncertainty relation” is mentioned. What is the actual reason why there is an uncertainty relation for time and energy? Can a canonical commutation relation be formulated for time and energy?

Concluding, I would recommend the work to be accepted as a master thesis. Overall, I recommend classification with the degree “very good (velmi dobře)”.

Kind regards,

Stefan Müller

Dr. Stefan Müller • Institut für Physikalische und Theoretische Chemie • Universität Würzburg • Am Hubland • 97074 Würzburg
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