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Referee's report on dissertation thesis by **Mgr. Zoltán Mics**

Dynamics of delocalized states in molecular systems studied by time-resolved THz spectroscopy

The proposed thesis focuses on the study of the behavior of both equilibrium and excited carriers in several nanocrystalline materials as well as in water and water-based solutions of salts. The tool almost exclusively used throughout this thesis is an experimentally demanding and novel technique of THz spectroscopy. The experiments performed on each material are complemented with the development of a suitable theoretical model describing and interpreting the measured data.

The thesis consists of 130 pages and is divided into 8 chapters including a preface and conclusions. Chapter 2 gives a theoretical background of charge transport and introduces theoretical models used further on for the fitting procedures. Chapter 3 describes in detail the applied experimental setups and the analysis of data. The following four chapters present results of THz-spectroscopy measurements performed on four types of materials. The thesis cites 100 references including three of which the candidate co-authored and which were published in journals specializing in chemical physics. The thesis contains 78 figures out of which about 50 present the original results.

The text is well-structured. The thesis is written in good academic-style English with only a small number of mistakes (perhaps the most common one is the referencing of a formula in the form of "the equation 2.0.1" instead of "Equation 2.0.1"). The form and literary presentation is on a high level, the candidate logically and pedagogically transfers from the description of measured results to discussion and the explanation of the underlying physics, author's reasoning is clear and concise.

Each of the result-presenting chapters opens with a paragraph commenting on the application prospects of the studied material and closes with a short conclusion summarizing the main observations. The presented original results consist of the following measurements: firstly, steady-state THz permittivity of titania nanoparticles prepared at different temperatures with varying levels of Nb doping and annealing, secondly, electron states of water and water-based salt solutions shortly after photo-ionization, thirdly, temperature-dependent dynamics of photo-excited carriers in bulk and nanocrystalline ZnO, and lastly, ultrafast carrier dynamics in CdS nanocrystals with different diameter. The main findings are aptly summarized in Chapter 8 and, therefore, I believe that they do not need to be repeated here. Although all these topics represent areas of intense research, personally, I think that the study of photo-ionized electronic states of water deserves high regard. Even though the corresponding chapter might feel like it lacks a firm conclusion on first reading, the candidate was clearly confronted with a number of experimental difficulties and setbacks, but managed to overcome the non-inherent ones and to quantify the limits imposed by the utilized experimental setup, which yielded physically meaningful estimates of the investigated parameters.

There are only a few minor issues which I found somewhat confusing or which could be improved:

- The choice of a slightly different font for the figure captions than for the rest of the text would sometimes simplify the orientation in the text.
- The unit used for the description of excitation intensity, photons.cm^{-3}, is, in my opinion, quite unusual. Although I understand its usefulness in connection with kinetic equations, I believe that what is actually meant by the value are absorbed photons.cm^{-3} *per the duration of the excitation pulse*. This slight inaccuracy could have been clarified in the text.
- One thing that seems to be lacking is at least an order-of-magnitude estimate of error both for the measured mobilities and for fits of the data. Only a few graphs in the thesis have explicit error bars. Although I certainly would not insist on the error bars being present in each figure, I think that for example a short paragraph commenting on the expected errors could have been included. Without any information on the expected error whatsoever (especially e.g. in the case of Monte-

Carlo-simulation-based fits, Fig. 7.19–7.22) it is quite difficult to judge what trends the presented dependencies really follow.

I propose that the following issues are discussed at the thesis defense:

1. This thesis is of high quality considering both the physics and the presentation of results. Where I find its main weakness, however, is the unclear candidate's contribution to the presented work, especially given the broad range of topics and the fusion of experimentally demanding technique and theoretical modeling. For example, when Monte-Carlo simulations are introduced as a suitable fitting procedure to describe the measured data, the author of the thesis states that "Monte-Carlo simulations were proposed by our group". In this case, it is possible to look up the authorship of the cited references, but the candidate's contribution seems somewhat vague in a similar way throughout the whole thesis. Could you specify on which tasks you focused during your thesis?
2. In my opinion, the measurements of photo-ionized electron states in water were probably the most experimentally demanding part of your work. The reported result of these measurements lies in the non-observance of THz signal. In theory, it is possible to enhance signal-to-noise ratio by extending the timespan of the measurement, but in reality the acquisition time is usually limited by stability. Could you tell us how long the measurements were and what limited extending their duration?
3. The next question is aimed at the measurements of CdS nanocrystals. In nanocrystalline materials, the studies of the excitation-intensity-dependent optical response is often interpreted in terms of the number of generated excitons per nanocrystal. This is because the presence of more than one exciton in a nanocrystal may cause new phenomena to set in (e.g. free carrier absorption or Auger recombination are present only above the 1 exc/nc threshold) and, consequently, switching to a completely different behavior than below the 1 exc/nc threshold is often observed. In your work, this threshold can be roughly estimated, considering the presented description of your samples, to be around 10^{18} photons.cm^{-3}.
   (a) In the dynamics of the mobility of carriers in Fig. 7.13, an ultrafast component attributed to the thermalization of carriers is present at lower excitation intensities. Its disappearance with increasing excitation intensity is attributed to filling of (unspecified) trap states. However, the excitation intensity at which this ultrafast component disappears shifts towards *higher* values with *decreasing* diameter of the nanocrystals (i.e. in agreement with the 1 exc/nc threshold). Could you qualitatively discuss if it is possible that a free-carrier-absorption-like process is responsible for the disappearance of the ultrafast component instead of the trap filling?
   (b) I suspect a similar aspect might play an important role in the excitation-intensity vs. mobility dependencies presented in Figs. 7.19–7.22. Is it possible that above the 1 exc/nc threshold (where the carriers clearly need to be described using Fermi–Dirac statistics, below this threshold, Boltzmann statistics could in theory suffice) a different "effective scattering time" than below this threshold has to be used to characterize the motion of carriers in such a tightly confined system? Are the Monte-Carlo simulations flexible enough to include such behavior?
4. Supposing isolated nanocrystals (i.e. those that do not form clusters of aggregates) were studied using THz spectroscopy, what would be the lower limit of a nanocrystal size (assuming these were present at some reasonable volume density) still giving reasonable amount of signal?

This thesis presents a large number of original results, focusing on both THz-spectroscopy experiments and theoretical models explaining the measured carrier dynamics. This novel technique allowed the candidate to probe processes which might be very difficult to access using other, more conventional, methods, such as the spectroscopy in the visible spectral region. Moreover, the application of THz spectroscopy on nanomaterials is a pioneering work as only a few of such studies exist. Based on these observations, I recommend that the candidate be awarded the degree of Doctor of Philosophy.

Prague, March 6, 2012

RNDr. Kateřina Kůsová, Ph.D.