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TO WHOM IT MAY CONCERN

This letter is to assess the PhD thesis “Photo-induced phase transitions in molecular materials” written by Wawrzyniec Kaszub under a joint supervision of professors Hevre Cailleau from University of Rennes 1 (France) and Ryszard Naskręcki from Adam Mickiewicz University (Poznań, Poland).

The dissertation is multi-lingual; its body is written in English while the abstract has three equivalent language version: English, French and Polish. The former two are rather short (3 pages + references) while the latter occupies 12 pages. The body of the dissertation contains 7 chapters. In addition, at the end of the dissertation one finds: (1) a list of scientific papers co-authored by Wawrzyniec Kaszub, (2) a list of his conference reports, (3) copies of 3 papers from the list given in (1) and (4) copies of 5 conference posters. I cannot see a good reason for the author to include all this data; in particular it seems a waste of resources to reprint the papers published in scientific journals and easily available to an interested reader.

The dissertation start with an Introduction (Chapter 1) followed by a Review (Chapter 2) discussing the basics of femtoscience and its applications in studies of phase transitions. The original material of the thesis, concerns 3 specific topics within a wide field of pulse laser induced transformations in molecular materials. Since the topics are only partially interconnected I will discuss each of them separately as they are presented in the chapters 3-5 of the thesis.

I. Dynamics of spin-crossover in metal-organic materials (Chapter 3)
The two metal-organic crystalline compounds: [(TPA)FeIIL(TCC)]PF6 and [(TPA)FeIII(TCC)]SbF6 studied in this thesis belong to catecholate iron (III) complexes and are known to undergo spin-crossover from S=1/2 to S=5/2 transition with the conversion temperatures 214 K and 237 K respectively. The thesis describes a number of studies on those compounds including SQUID measurements, steady state optical studies and last but not least time-resolved optical spectroscopic studies. The major experimental result of the latter is recording the time evolution of the sample’s magnetization for delays ranging from hundreds of femtoseconds to milliseconds. The experimental results falling within distinct time ranges have been interpreted as due to direct optical excitation of the sample followed by elastic and thermal effects; each leading to its own increase of the observed signal.

II. Insulator-to-metal transitions induced by an ultrafast laser (Chapter 4)
The system studied - (EDO – TTF)2SbF6 crystal belongs to a larger class of compounds (EDO – TTF)2XF6 of which (EDO – TTF)2PF6 has been investigated previously and shows a giant photo-
response. The materials undergo a phase transition leading to increased electric conductivity – Metal-Insulator (M-I) transition - with the control parameter being, typically, the temperature. The research performed within this PhD work concentrated on phase transitions induced by a short laser pulse. The authors of the research described in the thesis studied coherent oscillations of the crystal lattice (phonons) and, experimentally, performed two-color time-resolved reflectance measurements for a range of temperatures below and above the M-I phase transition temperature as well as stationary Raman spectroscopy in thermal equilibrium. The analysis of the experimental data shows a number of coherent lattice oscillations with frequencies in the range of about 1-3 THz and decay times of the order of a few picoseconds. They are used to form conclusions concerning the properties of the compound studied the major of which pertains the nature of the photo-induced M-I transition. In contrary to the giant photo-response of [(TPA)FeIII(TCC)]PF6, the crystal (EDO – TTF)2SbF5 studied here does not display a collective photo-induced transformation; rather the transformation is localized to within small volume with no long-range order being established.

III. A novel set-up for studies of laser induced irreversible transitions (Chapter 5)
The idea behind this part of the thesis concerns ultrafast optical spectroscopy using the standard pump-probe arrangement which allows one to study the effects of the usually stronger pump pulse on the sample at a range of time delays. This is, typically, achieved by employing a train of the laser pulse doublets with a varying delay between the pump and probe pulses. However, such a standard approach fails miserably when one deals with an irreversible process – the system that undergoes such transition on a given pump pulse never returns to the initial state and the consecutive pair of light pulses in the stroboscopic train does not interact with the same system. Thus, a method that will allow one to study irreversible phenomena in a "single shot" manner would be quite beneficial. The thesis describes a construction and performance of system built by its author and based on a simple time-frequency mapping in the probe pulse and independent spectral analysis of each probe pulse. By imparting a large frequency chirp on a white light probe pulse and spectrally resolving this pulse reflected from the sample one can "pinpoint" the moment of the irreversible process by simply searching for the colors that show significantly changed reflectivity. The system has been tested on a sample consisting of gold plated glass surface. The authors believe that, indeed, they can observe an irreversible change of the gold layer reflectivity. They could distinguish between the reflectivity of the molten gold surface when the short pump pulse damaging the gold layer coincided with a given color in the chirped probe pulse and the reflectivity of the surface excited and probed by the next pulse pair. It is a pity that the shutter used in the experiments did not allow to operate in truly "single pulse pair" regime so the number of the pump pulses could not be controlled precisely.

Chapter 6 of the thesis entitled "Experimental" describes the technical aspects of the experiments. In my opinion it is the weakest part of the dissertation. Large parts of this chapter contain information simply copied from the manuals of the equipment used in the experiments. For example, I find the description of lock-in amplifier superficial and not very instructive. It also has no bearing on the thesis itself.

Chapter 7 "General conclusions" is brief (2 pages) summary of the major results described in the thesis.
The editorial side of the thesis leaves a lot to be desired. The text quality varies significantly – some passages show a very good command of the topics described as well the English language while the other include basic language and editorial mistakes such as miss-numbered pictures, missing words, etc.

The thesis describes a series of results, obtained mostly with time-resolved techniques, on selected photo-induced processes in solid state materials. The problems studied are important both for our understanding of the basic science as well as for potential applications. The experiments described in the thesis required both very good technical capabilities and excellent understanding of the underlying physics and, as such, shall be considered of great value. Also, the dissertation contains a very large amount of data. Unfortunately, it fails to state clearly which of the work and results included can be attributed uniquely to its author. Of the two papers published on the topics described in the thesis one contains a list of 12 authors with Wawrzyniec Kaszub at the 3rd position and the other in which he is the leading author is actually a conference paper. Were the results included in the thesis achieved by its author solely I would call the thesis excellent. Since this is apparently not the case the overall grade has to be lowered.

To conclude, despite some drawbacks the dissertation assessed here fulfills the customary requirements for such works. Therefore, I propose to allow for the public defense of the PhD thesis "Photo-induced phase transitions in molecular materials" by Wawrzyniec Kaszub.

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