Adam Mickiewicz University in Poznań
Faculty of Chemistry
Chemical Physics Department

Prof. dr. hab. Bronisław Marciniak

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Review
of the dissertation
"*Molecular Properties in an Optical Microcavity: From Ensembles to Single Molecules*"
by
Wassie Mersha Takele

The presented dissertation has been prepared within the International Doctoral Studies of the Institute of Physical Chemistry of the Polish Academy of Sciences, Warsaw, Poland in collaboration with the Institute of Physical and Theoretical Chemistry, University of Tuebingen, Tuebingen, Germany. It has been conducted under the supervision of Professor Jacek Waluk (Institute of Physical Chemistry of the Polish Academy of Sciences) and Professor Alfred J. Meixner (the Institute of Physical and Theoretical Chemistry, University of Tuebingen).

The subject of the thesis is a continuation and further extension of very successful research work that has been developed for several years by professors Waluk and Meixner and their research teams (including joint research). It contains the study of spectral, photophysical and photochemical properties of single molecules and modulations of their properties using the electromagnetic field of an optical microcavity. This research topic is very ambitious and correlates well with the current prevailing trends in spectroscopy, photophysics and photochemistry.

The dissertation contains 103 pages and comprises of 8 chapters: 1. Introduction, 2. Theoretical Foundation, 3. Materials ads Methods, 4. Multimode Vibrational Strong Coupling Using a Tunable Microcavity, 5. Raman Scattering Under Vibrational Strong Coupling, 6. Controlling of Photophysical Properties of Single Molecules by the Purcell Effect of an Optical Microcavity, 7. Tailoring the Tautomerization Properties of Single Phthalocyanine Molecules

ul. Umultowska 89b, Collegium Chemicum,61-614 Poznań, Poland
tel. +48 61 829 15 87, mobile +48 519 340 500
marcinia@amu.edu.pl

by Vacuum Electromagnetic Field of an Optical Microcavity, 8. Summary and Outlook, abstract (in English and Polish) and the reference section with more than 200 references. The main part of thesis – the results and discussion, is presented in chapters no. 4-7. Before moving into details, I would like to admit that the dissertation contains a lot of very interesting and new results presented in a logical and clear manner, and the text is written in precise English.

A substantial part of the thesis (chapter 4 - Multimode Vibrational Strong Coupling Using a Tunable Microcavity) has been already published in a very prestigous journal (J. Phys. Chem. B 2020, 124, 5709), and the results from chapters (5-7) were summarized in two additional articles (submitted or ready to submit) :

1. Wassie Mersha Takele, Frank Wackenhut, Lukasz Piatkowski, Alfred J. Meixner, and Jacek Waluk; *Multimode Vibrational Strong Coupling of Methyl Salicylate to a Fabry−Pérot Microcavity, J. Phys. Chem. B* 2020, *12*4, 5709−5716.
2. Wassie Mersha Takele, Frank Wackenhut, Quan Liu, Lukasz Piatkowski, Jacek Waluk, and Alfred J. Meixner; *Tailoring Tautomerization of Single Phthalocyanine Molecules Through Modification of Chromophore Photophysics by the Purcell Effect of an Optical Microcavity*, submitted.
3. Wassie Mersha Takele, Lukasz Piatkowski, Frank Wackenhut, Sylwester Gawinkowski, Alfred J. Meixner, and Jacek Waluk*; Scouting for Strong Light-Matter Coupling Signatures in Raman Spectra*, ready for submission.

Unfortunately, the reviewer could not find via the Web of Science any information on the present status of the submitted papers.

In the first chapter - Introduction the background and motivation of the research described in the thesis are presented in a simple and logical manner. As it was summarized at the end of Introduction "This thesis addresses the influence of confined optical fields of an optical microcavity on the spectral, photophysical, and tautomeric properties of molecules". In the Chapter 2, typical for PhD thesis in chemistry, there is a description of the methods, theories, terminologies used in the thesis, e.g. the basics of electromagnetic radiation, molecular spectroscopies (IR, Raman and electronic), energy level diagram of ground and excited states and the main theories of weak and strong light-matter coupling. Chapter 3, Materials and Methods, is divided into three paragraphs: Chemicals and Materials, Sample Preparation,

ul. Umultowska 89b, Collegium Chemicum,61-614 Poznań, Poland
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marcinia@amu.edu.pl

Optical Setups and Measurements. Chapters 1-3 are written in a very clear manner and constitute a very good introduction for readers of this thesis, including those who are not experts in this field. However, I would like to note the lack of a list of abbreviations. A list of abbreviations would be very useful for general readers who are not familiar with the specific terminology in this field.

Chapters 4-7 describe the results obtained, and each chapter is divided into an introduction, methods, results, discussion and conclusion. Description of the influence of strong coupling between an IR-active molecular vibration and the vacuum field of a cavity on the spectral and vibrational energy levels of molecules is presented in the Chapter 4. Methyl salicylate was chosen as a model compound for this study (because of its strong C=O vibrational mode), and the obtained experimental spectra were in good agreement with the theoretical spectra.

Chapter 5 contains a study of the effect of strong coupling on the Raman scattering properties of molecules. For this study benzonitrile and methyl salicylate were used as model systems in the liquid phase, in addition to polyvinyl acetate as a model of a polymer film. The polaritonic states (results of strong coupling) were not observed in the Raman spectra although they were detected in the transmission IR spectra.

Chapter 6 demonstrates how the Purcell effect (weak coupling) can modulate photophysical properties of single molecules. Using phthalocyanine tetrasulfonate as an example, it was demonstrated that the confined optical fields in a microcavity can be used to control the blinking dynamics and photostability of single molecules. The same effect, but for tautomeric properties of single molecules of phthalocyanine tetrasulfonate, was presented in Chapter 7.

The thesis is presented in a good and simple way. The quality of figures, tables and equations is high, and the text is written in a clear and simple manner. There is a good balance between various chapters and various parts of the thesis. The references are carefully chosen and indicate the broad knowledge that Mr. Takele has in the topics covered by his PhD thesis.

It is worth noting that, in order to perform all of the experiments presented in the thesis, various sophisticated techniques (including time-resolved techniques) were used: FT IR spectroscopy, Raman spectroscopy (Surface Enhanced Raman Spectroscopy and micro-Raman setup), confocal microscopy (using home-build laser scanning confocal microscope), photon antibunching measurements, fluorescence decay measurements (using Time Correlated Single Photon Counting technique), and imaging single-molecule tautomerization (using confocal fluorescence microscopy and azimuthally (APDM) and radially (RPDM) polarized doughnut-modes excitations). In addition some special techniques were applied for sample preparations. Physical vapor deposition (PVD) techniques were used to prepare microcavity mirrors and spin coating method to prepare polymer films with organic molecules embedded in the polymer. The above-mentioned techniques indicate that the PhD student is an experienced and mature researcher.

I consider the following facts as the most important achievements of Mr. Takele's PhD thesis:

- during the study of the influence of strong coupling on the IR- absorption properties of selected organic compounds (e.g. methyl salicylate and benzonitrile) in the IR microcavity, it was proven that the cavity coupling can occur even for molecular vibrations that are off-resonance, but close to a cavity mode. This was confirmed by the theoretical description of multimode vibrational strong coupling. As a consequence, this work could open a new subject for a future study of the influence of the multimode coupling on the excited state intramolecular proton transfer of methyl salicylate
- it was confirmed that Raman scattering to the levels arising from the vibrational strong coupling effect was not observed (although the polaritonic peaks were observed in the IR spectra)
- it was found that weak coupling (the Purcell effect of an Optical Microcavity) could affect blinking dynamics, photobleaching properties and NH tautomerization of single phthalocyanine tetrasulfonate molecules. This was explained by an increase of the spontaneous emission rate due to a modification of the local optical density of states in the microcavity, and, as a consequence, by a reduction of the quantum yield of triplet formation.

In summary, taking into account that Mr. Wassie Mersha Takele's PhD thesis: (i) contains original and valuable scientific results that were discussed and interpreted at a high scientific level, (ii) concerns one of the most dynamically developed and attractive subject in modern molecular spectroscopy and photochemistry, (iii) was published, in part, in a top journal in the field of physical chemistry (and more publications are in the process of submission), (iv) has been written in a clear and logical way and carefully edited, I recommend it, without any doubt, to the Scientific Board of the Institute of Physical Chemistry of the Polish Academy of Sciences, Warsaw, Poland for a full acceptance.

Bronislaw Marciniak

ul. Umultowska 89b, Collegium Chemicum,61-614 Poznań, Poland
tel. +48 61 829 15 87, mobile +48 519 340 500
marcinia@amu.edu.pl