Prof. dr hab. Bolesław Kozankiewicz
Institute of Physics, Polish Academy of Sciences,
Al. Lotników 32/46, 02-668 Warsaw

Review of the PhD Thesis elaborated by M.Sc. Wassie Mersha Takele on

"Molecular Properties in an Optical Microcavity: From Ensemble to Single Molecules"

Hybrid light-matter states, which can be created if to place molecular material inside an optical cavity, are nowadays a subject of extensive studies in the field of quantum science and technology. Doctoral Thesis of Wassie Mersha Takele contributes to this field. The work was performed under supervision of two prominent scientists, Professor Jacek Waluk (Institute of Physical Chemistry, Warsaw) and Professor Alfred J. Meixner (University of Tubingen), and continues efficient collaboration between their scientific groups.

Maximum coupling between molecular and optical modes can be obtained if the length of a Fabry-Pérot microcavity, given by $m \cdot \lambda/2n$ (where: m - integer, λ – wavelength of the applied light, n – refractive index of the matrix), is in resonance with the molecular transition. For technical reasons it is easier to make cavities with a length of some microns, than in a submicron range, and investigate coupling of vibrational transitions in a molecular with the appropriate infrared (IR) light. Therefore, Wassie Mersha Takele concentrated on the IR spectra, before more difficult experiments performed within the visible light range. The chosen system was methyl salicylate (MS) dissolved in methylcyclohexane, and microcavity which he was able to piezo-tune to resonance with several vibrations of this molecule. He concentrated on a case of vibrational strong coupling (VSC) for the C=O streching vibration (~1685 cm^{-1}) and was able to observe upper and lower polaritonic modes. The proposed theoretical description of the observed spectra based on a model of coupled damped harmonic oscillators. To fit the data he had to consider not only the resonance molecular vibration but also some of the off-resonance vibrations with the nearest frequencies. The study of the multimode VSC of MS to a microcavity was already published in J. Phys. Chem. B **2020**, 124, 5709.

Raman scattering experiments, he performed, were not as successful as the above mentioned IR studies. The cavities for the experiments were created by placing thin polyvinyl acetate (PVA) films between the Ag mirrors. PVA films were obtained by spin casting of PVA dissolved in toluene, with the thickness controlled by the spinning condition, the speed and time. Appropriate thickness was chosen experimentally by monitoring the IR transmission spectrum the C=O stretching frequency (~1740 cm^{-1}) and trying to match the cavity length to either the on- or off- resonance. Several different samples were prepared and investigated, but the final conclusion was that in the Raman spectra under the VSC condition the polaritonic splitting of the

hybrid states was not observed, probably because of dominant contribution from uncoupled molecules.

Single-molecule experiments were performed with a confocal microscopy set-up and microcavity tuned to $\lambda/2$ for the absorption of the Q-band of phthalocyanine tetrasulfonate (PcS_4) in PVA film ($\lambda/2$ = ~350 nm). Comparing the fluorescence decay times and time traces of several single molecules located inside the resonant microcavity it was experimentally demonstrated operation of the Purcell effect, enhancement of the spontaneous fluorescence emission rate in the cavity. Shorter residence time in the excited singlet state reduced transition to the non-fluorescent (and often more reactive) triplet state. Consequently, PcS_4 molecules were more photostable inside the microcavity.

Tautomerization properties of single phthalocyanine molecules were extensively studied in passed by the Tubingen and Warsaw groups. It was thus not surprising that Wassie Mersha Takele tried to look at the dynamics of NH tautomerization in the $\lambda/2$ microcavity. In these experiments the confocal fluorescence images of molecules excited by using azimuthally (APDM) or radially (RDPM) polarized light reflected orientation of the transition dipole moment. Comparing the consecutively measured images Wassie Takele observed that in the microcavity the tautomerization process was considerably slower. Taking into account that the Purcell effect, operating in the $\lambda/2$ microcavity shortened lifetime of the excited singlet state and the lower lying triplet state of phthalocyanine molecules were less frequently visited, the result suggest that tautomerization happened in the triplet state. In my opinion it is the most important and interesting result of the Thesis.

Summarizing the work of Wassie Mersha Takele. He did a very extensive work, using several experimental, spectroscopic techniques. I'd like to stress difficulty of technical aspects of his work. Preparation of microcavities, deposition of mirrors and appropriate films, required not only knowledge but also many, time consuming trials. Thesis were prepared in a traditional way, where elaboration of the results was preceded with theoretical background and description of materials and methods. I'm sure that the results of this work can be useful for researchers, who will continue work on hybrid light-matter states.

The Thesis contains extensive and professionally elaborated material which improves our understanding of the hybrid light - organic molecule states. By the same the work is highly valuable and fulfils requirements for applying for the degree of Doctor according to the custom and low regulations (art. 187 ustawy z dnia 20 lipca 2018 r. Prawo o szkolnictwie wyższym i nauce, Dz. U. z 2018 r., poz. 1668 ze zm.). I recommend to pass Wassie Mersha Takele to next steps of the doctoral procedure.

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