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Evaluation report on the Doctoral Dissertation submitted by Wassie Mersha Takele, entitled: "*Molecular Properties in an Optical Microcavity: From Ensembles to Single Molecules"* submitted to the Scientific Council of the Institute of Physical Chemistry, Polish Academy of Sciences in Warsaw.

The dissertation submitted by Wassie Mersha Takele concerns several demonstrations of the influence of optical microcavity modes on the properties of several optically active systems. Particular attention is given to influencing the optical spectra of molecular ensembles in a vibrational strong coupling regime, observation of the Purcell effect for single molecules embedded in a microcavity, and controlling tautomerization of single molecules in a microcavity. Judging already from this list, it is quite obvious that the spread of the topics addresses in the dissertation is rather broad, with the only common denominator being the microcavity itself. Definitely, the scope of the dissertation is highly important and the context of this research is well embedded in current efforts of implementing advanced structures in controlling the optical response of molecular systems. This research has the potential of influencing many fields of optics and nanoscience, as it is located at the interface between chemistry, biology, and advanced spectroscopy techniques. In addition, progress in straightforward fabrication of optical microcavities suitable for precise controlling of the response of optically active materials may find numerous implementation in quantum optics, sensing, optoelectronics, and alike. The research project, which led to the PhD thesis was a collaborative effort of two renowned groups led by prof. Jacek Waluk at the Institute of Physical Chemistry Polish Academy of Sciences in Warsaw, Poland, and prof. Alfred Meixner at the Institute of Physical and Theoretical Chemistry, University of Tubingen, Germany. The experience and expertise of both groups should provide close to ideal environment for tackling challenging problems related to applying advanced optical spectroscopy and microscopy for understanding interactions in molecular systems.

Before I discuss the details of this work, I find it necessary to give a birds-eye view of the thesis. While most of the results obtained within the project are of high quality and must have required substantial effort and determination combined with deep understanding of the interactions between molecular levels and modes of optical microcavities, the thesis itself – regretfully – falls far below this standard. From the point of view of the structure of this work, there is no easy and straightforward flow, which would lead a reader through these rather separated topics, such as strong coupling regime, Raman spectroscopy, tautomerization, and Purcell effect. There is essentially no connection between these chapters, giving the feeling that these experiments are to a large degree weakly related to each other, with the exception of the optical cavity structure used in each case. Any indication of more general context of bringing these four experiments together is missing, giving an impression of a patchwork-type of accidentally collected results. In a case of highly interdisciplinary work, as the one included in the PhD dissertation of Wassie Mersha Takele, it is extremely important to keep the cohesion of the content and coherence in presentation and discussion of the experimental results.

Furthermore, at least three writing styles can be easily identified in this dissertation. Initial chapters and Chapter 5 were written to large extent by Wassie Mersha Takele, the language is rather rough, the connection between following sentences is often missing, so is the flow of the discussion. On the other hand, Chapter 4, the only one, which is based on a published article, closely follows this publication, in particular in the sequence of presenting and discussing the results. Also, almost all of the figures included in this Chapter are taken directly, with essentially no modifications, from this publication. The language, however, was to some degree altered, and many sentences were paraphrased, while keeping the meaning thereof. Finally, the writing style of Chapter 6 (and perhaps also Chapter 7) resembles a classic style found in publications. It reads very well, there are no strange or simply incorrect terms included, the results are presented in a coherent logical way. In this case, the manuscript has not been published, but is presumably submitted. The contrast between Chapter 5 and Chapter 6 is rather striking. I leave this observation without any further comment.

As already mentioned, the results included in the dissertation appeared in one publication (Journal of Physical Chemistry B in 2020), while three (or two) manuscripts are in the submission process. This is rather weak publication record, not accompanied with extensive conference activity.

The structure of the dissertation submitted by Wassie Mersha Takele is rather classic. First, theoretical aspects relevant to the optical properties of molecular systems and interaction with modes of optical cavities are described. Particular attention is paid to distinguish between weak and strong coupling regime, as well as separate discussion of vibrational and electronic energy levels of molecules. While most of the content of this part is a textbook knowledge, I find it justified to present all these aspects before discussing the experimental results. This section is followed directly by description of materials used in the research project and experimental techniques, after which the results are presented in four separate chapters. A major shortcoming of such a structure is the absence of any description of the state-of-the-art of the research field associated with studying interactions between molecular systems and optical microcavities. Again, in the case of highly interdisciplinary dissertation, which covers many aspects of science, including such a chapter would help – and very significantly – in placing the original results in an appropriate context. Presumably, such a comparison would result in much stronger, more solid appreciation of the outcome of the PhD project.

The original results are presented in four chapters focused on: (1) vibrational strong coupling in methyl salicylate in a tunable microcavity (Chapter 4), (2) Raman scattering of polymer film in vibrational strong coupling regime (Chapter 5), (3) Purcell effect for single molecules placed in an optical microcavity (Chapter 6), and (4) tautomerization properties of single molecules in an optical microcavity (Chapter 7). The chapters are very uneven both with respect to the quality of the results as well as their presentation. Particularly valuable are the results associated with demonstration of vibrational strong coupling in methyl salicylate and observation of vibrational polaritons. In this case the experimental results are strongly supported by theoretical modeling of such structures, which strongly improves the scientific quality of this result. Another aspect of this dissertation which I find highly important for further development of this approach in manipulating interactions at the nanoscale is manipulation of radiative rates of individual molecules through optical modes in microcavities. This is quite an achievement, from the point of view of both fabrication of cavities as well as the single molecule experiment.

The high quality of – in particular – these two results is however overshadowed by the presentation and discussion of the experiments which comprise the dissertation. Here is the list of specific remarks, questions, critical comments:

Page 1: what is “quantum light”?

Page 2: “pathlength” or “path length”?

Page 3: there is no reference regarding the values of Q-factor in microcavities.

Page 3: what is “energy exchange” between cavity mode and molecular transition?

Page 4: “half-light half-matter … polariton” is not correct.

Page 6: “condensate physics” is jargon.

Fig. 2.2 a is wrong – the spacing between the energy levels for a harmonic oscillator potential are equal.

Page 14: I do not understand how direct absorption or emission of IR radiation can cause changes in vibrational energy levels.

Page 15: the Beer-Lambert law applies also to other spectral regions, not only to IR.

Fig. 2.4: why there are two dotted lines representing the virtual energy level?

Page: 18: last sentence of the first paragraph: there must be molecules emitting in the infrared spectral region.

Fig. 2.5. is completely wrong, including the spacing between the energy levels and the assignment of internal conversion process. What is geometry of S1 and T1?

Page: 19: molecule cannot decay, nor it can be promoted, electrons can.

Page 20: what is the concentration of S1?

Page 21: is it possible to provide an example of using the Purcell effect to reduce the spontaneous emission rate?

Page 21: excited state cannot decay.

Page 25: out of the sudden an exciton appears (the last paragraph) without any definition. On the following pages electron and exciton are used in a rather random way, although these are two completely different objects.

Page 26: “behavior” although previously “behaviour” was used, there are more examples of mixing British and American English.

Page 27: font is changed.

Page 27: figure caption is over to the next page, g denotes the ground state and the coupling strength.

Chapter 2 ends rather abruptly, with no summary, no connection to the next chapters.

Chapter 3 is very chaotic, lacking many details, containing a few wrong statements. Furthermore, some of the setups are presented in the next chapters (Fig. 6.2). Why? Some of the setups are not described at all (AFM for instance).

Page 32: what is “high voltage current”?

Fig. 3.1. Ag layers were also fabricated using this technique.

Page 35: excitation source cannot be focused.

Fig. 3.4. it looks like only red light is reaching the detector after the diffraction grating disperses the light in a rather unique way. I would expect that PhD dissertation should be more rigorous in

this regard. Why the excitation wavelength of 532 nm was used for Raman scattering experiments? What was the spatial resolution of the set-up? What was the spectral resolution of the set-up? What was the detector? The details are missing. It is also not clear why the averaging over 140 spectra was applied. If the spectra are identical, then the averaging is pointless. On the other hand, if the spectra are different, the averaging is senseless. Such a procedure should be better justified.

Page 36: there are many standard techniques for studying single molecules. Confocal fluorescence microscopy is one of them. However, standard confocal microscopy rarely uses epi-fluorescence configuration. A PhD student working with confocal microscopy should know that. Fortunately, the scheme of the confocal microscope displayed in Fig. 3.5 is correct in this respect.

Page 36: last sentence: it would be very difficult to collect an angle. Even with an objective lens.

Page 37: Eqn 3.3 yields a value of 170 nm as a diffraction limited spatial resolution. Why mentioning NA=1.4, while the objective with NA=1.46 is used. What was the filter used for the excitation beam? What was the dichroic mirror? What was the longpass filter? What APDs were used? How it is possible to obtain fluorescence images by raster scanning the sample through the focal spot? What was the spectral, spatial and temporal resolution of the setup? What values of the excitation power were used?

Page 38: there is no reference for the Hanbury – Brown – Twiss configuration.

Fig. 4.3. it is impossible to see that by chaning the voltage by 1V the cavity mode shifts by 5cm-1. It would also be good to determine the Q-factor of a typical cavity. This is shown in Chapter 6, two chapters too late.

Page 45, first line: what literature?

Fig. 4.5a: what was the voltage? What was the Q-factor for these cavities?

Fig. 4.5b: what are the error bars? It would be desirable to show original data for the boundary cases. What can be learned from the slope?

Page 56: why different thickness of Ag is used? Where the Ag nanoparticles (or nanospheres, as written a couple of pages later) were from? There is no mention about them in the Materials and Methods chapter. How the surface covered with Ag nanoparticles looks like? What gives a reason to use such a structure? This is not clear and is not explained in the text. In Fig. 5.3 chromium appears out of nowhere.

Page 57: second paragraph: why anyone should believe this information? Such statements must be accompanied with the presentation of experimental results. It is not clear what decrease the Authors refers to when discussing the influence of the transparency of the cavity. The comparison of the two spectra obtained for ON and OFF microcavities (blue and red lines)

yields rather substantial difference in relative intensities of the resonances. This effect is left without any comment, not to mention interpretation.

Fig. 5.6b: the lines are not described.

Fig. 5.8: there is no information on how the data was acquired. There is no discussion of the results and their implication on anything in this dissertation. Why the noise one the left side of the cross-section in (a) is much less compared to the remaining part of this cross-section? What are the errors in determining the surface roughness? The size of the islands seen in the AFM images is substantially less than 100 nm (the diameter of Ag nanoparticles used for probing any possible effect related to SERS). Comparing both structures should be better justified.

Page 61, last sentence: what is “the surface selection rule for the enhancement effect”?

Fig. 5.9: the spectra are certainly not normalized. The nomenclature used here is different: (a)…(e) were used previously for various panels within the same figure, here they are assigned to experimental curves.

Page 63: there is no section 2.6.2 in Chapter 2. Not in this dissertation. The whole paragraph is extremely vague in providing any explanation of the results measured for the structures discussed in Chapter 5. What is the cavity mode volume in the studied structures? How it relates to the spatial resolution of the Raman microscope? What is the fraction of the molecules within the focal spot that couple to the cavity mode volume? Without answering these questions, the summary of this experiment is incomprehensible.

Fig. 6.1: how the absorption was measured? With what instrument?

Page 66: why in the process of fabricating the microcavities used in these experiments a layer of SiO_2 was used?

Fig. 6.2: the setup is indeed simplified, as there is no a confocal pinhole present in it.

Fig. 6.5b: the units of Time delay are wrong.

Fig. 6.7b: what is the source of unexpectedly broad distribution of fluorescence lifetimes measured for the molecules in “free space”? It looks like the shortest values are around 1.5 ns, while the longest reach almost 8 ns. This is very surprising, and not commented in the dissertation. The narrowing of the distribution for molecules placed in a microcavity is also left without any discussion. It is also important to note, that the form of comparing histograms in a way shown in this figure is very misleading as the bins are shifted horizontally. Regretfully, this way of comparing histograms is followed through the remaining chapters of the dissertation.

After careful consideration, I highly value the results described in the thesis submitted by Wassie Mersha Takele, in particular related to vibrational strong coupling and Purcell effect of single molecules in microcavities. The scientific level of this work suppresses most of the

internal disappointment, which arose from the poor presentation and discussion of the results. Therefore, in my opinion, the dissertation submitted by Wassie Mersha Takele, fulfils all the formal requirements, it contains original results important for the field of optical spectroscopy and microscopy, several of the observations should be an inspiration for future, intensive research efforts. The application should be further processed according to appropriate procedures.