In Strasbourg, 06.03.2023

Report on the PhD thesis entitled: "Spectroscopy of single molecules in STM nanocavity" presented by Mr. Jiří Doležal to obtain a doctoral degree from the Charles University.

The doctoral thesis presented by Jiří Doležal focuses on experimental optical spectroscopy of individual molecules enabled by scanning probe microscopy. The author studies luminescence from several chromophores and addresses different parameters related to their optical properties and demonstrates several novel strategies for controlling them by the atomic scale environment. The work is clearly at the forefront of the field of STM-induced luminescence (STML), the results are outstanding and their interpretation well-supported. The manuscript is well-organized, clearly written, all illustrations are instructive, the literature is properly referenced, contributions (such as theory) are properly acknowledged and the data are well-represented.

The thesis features an introduction presenting the main focus and the broad relevance of performing optical spectroscopy of individual molecules. It is followed by two chapters discussing the physical principles key to the performed work and their instrumental implementation. Jiří Doležal started his PhD on a topic that was previously not developed in his Institute. This is an extremely challenging task that requires solving a lot of technical problems and constantly improving the experimental setup. He executed it in an absolutely exemplary way by developing and improving the optical detection, optimizing tip preparation, implementing a time-resolved setup, developing laser excitation and automatizing as many procedures as possible. As emphasized by the candidate in the conclusion, the technical part will be of great use to the readers of the thesis that wish to develop a similar setup.

The third chapter reports on the role of the tip in STML. One of the common tip functionalizations relies on attaching a CO molecule to the tip apex, a method applied in particular for the Pauli repulsion AFM imaging. Here, the same functionalization is applied to probe electroluminescence from ZnPc with sub-molecular precision, which is found to induce a different contrast due to the local change of charge carrier transport. In addition, the chapter also compares the molecules that are adsorbed on the substrate in both stable and dynamic configurations.

The next chapter focuses on STML from CuPc chromophores and discusses the environmental effects that affect molecular emission. Here it is demonstrated that the change of the molecular adsorption site from Na+ to Cl- changes the emission energy – an effect that would be ensemble-averaged if the usual optical techniques were used demonstrating the power of STML.

Chapters 5 and 6 focus on time-resolved studies using STML. The phase fluorometry technique developed by the candidate was used to probe the sub-ns dynamics of emission from an individual ZnPc molecule. Here, the data are reinterpreted with respect to the original publication using an improved understanding developed recently in the community that the lifetimes of molecules in the picocavity are in the picosecond regime. Therefore, the measurements are sensitive to the charge dynamics rather than to the exciton lifetime. The technical details (constant amplitude of the driving wave) of this novel technique, which can easily be applied to other systems, are discussed in detail in chapter 6.

The next chapter reports on studies on electroluminescence from molecular assemblies. The transition dipoles couple within such structures and, as found by the candidate, can be tuned by manipulating individual electrons attached (or not) to the molecule. This is a very elegant method of controlling optical properties with atomic precision.

The last experimental chapter reports on exploring the coupling between excited states and a specific type of vibrational motion – libration, which was not explored before with such resolution. The in-depth analysis of the measured linewidths provides new insight into the additional features observed in the emission of charged species and will help interpret the spectra measured by other groups. Eventually, Jiří Doležal resumes his work and proposes some perspectives for future studies.

As for any work that defines the state-of-the-art, some questions and open problems remain such as:

- Many of the photon maps presented in the thesis are shown in the absolute scale (Ch. 3, 5). As discussed in the manuscript, local transport affects these patterns. This effect can be partially removed by normalizing the maps by the current – is applying such treatment to the presented data yielding some interesting results regarding the role of the tip apex? For example, a different interaction of CO with the probed molecule. Following on that, what would be expected if the tip is functionalized by another entity, for example, a Cl- ion?
- The emission of CuPc is assigned to the emission of a doublet state. Usually, doublet emission energies for phthalocyanine molecules are much lower (for example, Doppagne et al., Science, 2018) – how could this difference between CuPc and ZnPc/H2Pc/etc be explained?
- As currently heavily debated in the field, the excitation mechanism of STML is also discussed in the thesis. However, some aspects of the discussion are not consistent, such as the difference between HOMO/LUMO and PIR/NIR in STS, the nature of the STS gap, and what are the factors that affect the position of states in STS. The thesis would benefit from improving these issues.
- Time-resolved measurements performed on a single PTCDA molecule seem to not reveal any time-constant. Following the reinterpretation proposed in Chapter 5 one could expect to observe some time constants related to the charge dynamics, what could be an explanation for the lack of such dynamics in this system?
- The theoretical model used to account for the spectra showing librational features includes effective temperature originating from inelastic tunneling that seems to be a fixed parameter for a given molecule. Can one imagine that, for example for measurements at different bias voltages, analysis of such spectra could be a way to measure the local temperature?
- The thesis would benefit from some more specific examples of future experiments and physical parameters related to the single-molecule luminescence that could be explored, which could be added to the final chapter. As of now, I found that such perspectives are rather vaguely summarized. For example, one interesting discussion that could be presented includes using molecular assemblies for quantum computing, which was mentioned in Chapter 7, however, without a specific proposition for a quantum device/circuit and discussion of benefits and problems related to such solutions.

To summarize, the results obtained by Jiří Doležal are novel, of a top-tier scientific level and the overall level of the thesis is outstanding. This is confirmed by a total of 6 first-author publications in leading journals – a truly remarkable result in the field. Thanks to his work, the research group has become one of the leaders in the international community of atomic-scale optics. This thesis proves the ability of the candidate for creative scientific work. Therefore, I accept unconditionally the thesis and fully support awarding the PhD title to Jiří Doležal. I am also happy to support a nomination of the thesis for a prize.

Sincerely,

Dr. Anna Rosławska

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