J.Heyrovský Institute of Physical Chemistry

Dr. Otakar Frank
Czech Academy of Sciences
J. Heyrovský Institute of Physical Chemistry, v. v. i.
Dolejškova 2155/3, 182 23 Prague 8, Czech Republic
phone: +420 26605 3446, e-mail: otakar.frank@jh-inst.cas.cz

External review on doctoral thesis

Spectroscopy of single molecules in STM nanocavity

by Jiří Doležal

The thesis of Mr. Doležal describes his results on the investigation of single molecules by various spectroscopic methods based on near-field plasmonic nanocavity between an STM/AFM tip and the substrate. The thesis is anchored on the results of 6 publications in top-tier journals, in all of which the candidate is the first author, and the corresponding author in two of them.

The Introduction gives a brief overview of the field and defines some of its main scientific questions, which are also addressed in the work. The Introduction is followed by a thorough Theoretical background that discusses the principles of operation of the methods and physics behind the observed phenomena, at least in terms of what was known when he started and understood during the years he worked on the thesis. The next chapter covers the main Experimental details, also showing details of the STM and optical setups, with the commendable intention of enabling other researchers to follow up on them. The next six chapters encompass the main scientific results, each based on one of the aforementioned publications. Each chapter contains a brief introduction, the main scientific results and discussion, conclusion, and extra experimental details, when needed. Most of these results are also accompanied with supporting information in the appendices at the end of the thesis. A separate Conclusions chapter summarizes all the results and gives a brief outlook for further advancement in the field.

On the formal side, the work is meticulously prepared, with only very few minor flaws listed below. From the scientific and technological perspective, the work represents a considerable advancement in the field of atomically resolved spectroscopy. The individual chapters clearly document how the applicant contributed to the evolution of scientific theories behind the measurements and also brought forward some of previously not observed phenomena in the studied molecular systems.

Comments/questions:

J.Heyrovský Institute of Physical Chemistry

Dr. Otakar Frank
Czech Academy of Sciences
J. Heyrovský Institute of Physical Chemistry, v. v. i.
Dolejškova 2155/3, 182 23 Prague 8, Czech Republic
phone: +420 26605 3446, e-mail: otakar.frank@jh-inst.cas.cz

1) Page 10, 1.2.2. Principle of STM, 1st paragraph: it probably should state that electrons from occupied states tunnel to the unoccupied ones, not the other way round.
2) Pages 15 & 16, 1.2.5 Double-barrier tunneling junction: some of the less common (to a general scientific readership) abbreviations like ML, PIR, and NIR should better be defined at their first appearance, also because the list is only at the end of the work. That concerns especially NIR, as it more commonly refers to near infrared in the spectroscopy field.
3) In chapter 4, can it be that the static/dynamic behavior of the molecules can also be influenced by their proximity? It can be a coincidence, but in Figure 4.1, the two molecules with the static behavior are the closest (out of the 3 configurations shown in the figure), and in the intermediate distance case one molecule is static, one dynamic, while in the case where the separation is the largest, the behavior of both is dynamic.
4) In chapter 5, why do the intensities of the trion and neutral exciton emissions equalize at the most negative bias voltage? One could naively surmise that the probability of the trion emission would keep increasing with the number of excessive charge carriers.
5) In chapter 7, in the trimer where the central molecule is placed perpendicularly to the outer two, it is said that the central molecule acts merely as a spacer. Can it be estimated how wide the spacer can be (i.e. how many molecules arranged in that way) for it to keep functioning the way it does in the trimer?

Overall, the thesis presents original results that significantly advance the field. The results were achieved with the substantial contribution of the applicant, which is documented by the authorship of the connected 6 publications in excellent journals. The presented work thus fulfills the requirements of the doctoral thesis. I recommend this dissertation for public defense.

Prague, 27.2.2023

Otakar Frank