Report of a thesis

submitted at the Faculty of Science, University of South Bohemia

❑ supervisor's report ☑ opponent's report
❑ bachelor thesis ☑ master thesis

Author:	**Bc. Patrik Musil**
Thesis Title:	**Calculation of vibrational SFG spectra from molecular dynamics simulations**
Study program:	Physical Measurements and Modelling
Year of submission:	2022 (summer term)

Opponent:	RNDr. Zdeněk Futera, Ph.D.
Workplace:	Department of Physics FSci USB (UFY)
Contact e-mail:	zfutera@prf.jcu.cz

Scientific/professional quality:
☑ excellent ❑ very good ❑ average ❑ below average ❑ unsatisfactory

Factual errors:
☑ almost none ❑ a reasonable number ❑ frequent minor errors ❑ serious

Results:
❑ original ☑ original and adopted ❑ non-trivial compilation ❑ cited from the literature
❑ copied

Extent of the work:
❑ large ☑ standard ❑ sufficient ❑ insufficient

Graphic, linguistic, and formal quality:
❑ excellent ☑ very good ❑ average ❑ below average ❑ unsatisfactory

Typographic errors:
❑ almost none ☑ a reasonable number ❑ numerous

Overall quality of the thesis:
☑ excellent ❑ very good ❑ average ❑ below average ❑ unsatisfactory

Verbal evaluation, comments of the opponent:

The reviewed master thesis focuses on the computational approach to sum-frequency generation spectroscopy applied on aqueous metal-oxide interfaces. The work is based on software previously developed by S. Pezzoti in a group of Prof. M.-P. Gaigeot. This code was originally designed for the post-processing of ab-initio molecular-dynamics simulations.

Within his thesis, the candidate analyzed the original program source code, written in a procedural Fortran, refactored it to object-oriented Fortran code, and optimized it for processing relatively long classical molecular-dynamics trajectories. The resulting software is more flexible, easily extensible to various types of input formats, and more efficient in terms of memory usage and computational demand. The code modifications are well documented in the thesis and benchmarked on the relevant reference data. The feasibility of the calculations and performance on classical molecular-dynamics data were demonstrated on the fluorite(111) and quartz (0001) interfaces with liquid water, for which the experimental SFG spectra are available.

Formally, the thesis is well structured, its extent is adequate, and it refers to the relevant original literature. Although the theoretical part is, at some points, confusing, it captures the main ideas and expressions used for the calculations. On the other hand, the technical details of the key program parts are well described, and differences between the original code and the revised version are clearly stated. Also, the performed calculations and all the performed benchmarks are appropriately discussed. Overall, the work fulfills all the criteria required for the master thesis, and I'm happy to recommend it for the defense.

Questions to the defense and suggestions for a discussion:

1) From the thesis, it is not clear whether the SFG technique is limited to the stretching-mode region of the vibrational spectra, or if the other spectral bands can also be probed. For example, bending modes of water should also be affected by the interfacial confinement and hydrogen bonding to metal oxide surfaces like quartz or titania, I suppose. Could you please comment on it?
2) Why is the surface position search done by evaluating the density profile in the direction from the bulk-water region to the surface? Wouldn't it be more efficient to do the search in the opposite direction from the solid-slab surface to the water region regarding the fact that the profile minima are located on the interface?
3) One of the new features of the improved software is the capability to analyze the contributions of the surface hydroxyl groups to the SFG spectra. This analysis was performed on the aqueous quartz(0001) interface. However, I miss the discussion on whether and how the surface OH vibrations differ from the motions of the water molecules hydrogen-bonded to the surface or water molecules from the second hydration shell. Could you please compare the spectra of surface hydroxyls and water molecules from different layers in one plot and comment on it?

☑ **I recommend**
❑ **I do not recommend**
to accept the thesis as a master thesis.

I suggest that the thesis be graded:
☑ excellent ❑ very good ❑ good ❑ failed

Place, date, and signature of the opponent:

V Cáchách, 16. 5. 2022

Zdenek Futera
Digitally signed by Zdenek Futera
Date: 2022.05.16 00:07:40 +02'00'

Report of a thesis

submitted at the Faculty of Science, University of South Bohemia

☐ supervisor's report ☑ opponent's report
☐ bachelor thesis ☑ master thesis

Author: **Bc. Patrik Musil**
Thesis Title: **Calculation of vibrational SFG spectra from molecular dynamics simulations**
Study program: Physical Measurements and Modelling
Year of submission: 2022 (summer term)

Opponent: Prof Marie-Pierre GAIGEOT
Workplace: University Paris-Saclay, Univ Evry, Paris, France
Contact e-mail: mgaigeot@univ-evry.fr

Scientific/professional quality:
☒ excellent ☐ very good ☐ average ☐ below average ☐ unsatisfactory

Factual errors:
☒ almost none ☐ a reasonable number ☐ frequent minor errors ☐ serious

Results:
☐ original ☒ original and adopted ☐ non-trivial compilation ☐ cited from the literature
☐ copied

Extent of the work:
☒ large ☐ standard ☐ sufficient ☐ insufficient

Graphic, linguistic and formal quality:
☐ excellent ☒ very good ☐ average ☐ below average ☐ unsatisfactory

Typographic errors:
☐ almost none ☒ a reasonable number ☐ numerous

Overall quality of the thesis:
☒ excellent ☐ very good ☐ average ☐ below average ☐ unsatisfactory

Verbal evaluation, comments of the opponent:

Patrik Musil presents a very well written master thesis manuscript written in English.
His manuscript is well organized with the basics of Sum Frequency Generation calculation from theory and from molecular dynamics (MD) simulations, followed by the numerous coding implementations that he has done in order to largely improve and transfer a software that was initially developed in the Gaigeot group for short time scale and small system size simulations boxes coming from ab initio MD trajectories to long time-scale and large simulation boxes generated in classical MD simulations. The manuscript then reports and discusses results. All these sections are extremely well documented in the manuscript.
I congratulate Patrik for such achievement.
The whole manuscript shows that Patrik Musil has well understood the theory together with the implementations to be done and the limitations inherent to these numerical implementations. Patrik discusses several aspects of the SFG calculation that require a certain number of parameters for e.g. the filter, length of trajectory and length-time of the window over which to calculate the SFG signal, influence of the thermostat into the SFG spectrum, etc. The presentations and associated discussions are convincing and show an excellent comprehension. Several aspects of the new software implementations and improvements from the initial software are very well described, very well documented, and very well tested.
In this manuscript, Patrik Musil is successfully showing that he can discuss fundamental science/research and software implementation on the same foot, which is indeed required for numerical theoreticians.
The work reported in the manuscript has also developed one new feature that was not accounted for in the initial implementation in the Gaigeot group: inclusion of cross-correlation terms into the SFG signal calculation (which requires convergence over long time-scales that only classical MD simulations can provide). Patrik shows preliminary data at the end of his manuscript that open the path to such novelty into theoretical SFG.
I also believe the current version of the software developed by Patrik Musil could be soon freely distributed to the community through github for instance. That would be helpful for the theory community.

Questions to the defense and suggestions for a discussion:

I would suggest a few discussions along the following lines:

- technical points on the implementation: it could be good to have a practical demonstration of how the code works in practice for one given system (the one reported in the manuscript), to see how the software works in practice, so that I can ask a few questions on the pre-requisite input files, order of running and how is the order controlled in practice with error/warning messages, what has to be changed in the software whenever we change the MD-software (for instance we are currently running the LAMMPS software instead of GROMACS).
- another technical point concerns the self- and cross-correlation terms for the SFG signal calculation: can we have their separate contributions to the SFG signal ? this is important in order to check convergence of this term in the SFG response.
- between technical and requirement for the SFG signal: I am not sure I have understood how the water molecules are associated to a given water layer.
- scientific comments: I would like to rediscuss eq 25, I am not entirely convinced that all indices are correct ; I would like to rediscuss the test made on the increase of the simulation box size as there is a change in the frequency of the band together with a change in the surface charge ; I would

like to discuss the (non)influence of the thermostat, that I find very interesting (at least for the system tested in the manuscript) ; if time allows, I would also like to discuss the cross-terms to the SFG signal ;

☒ **I recommend**
❑ **I do not recommend**
to accept the thesis as a master thesis.

I suggest that the thesis be graded:
☒ excellent ❑ very good ❑ good ❑ failed

Place, date and signature of the opponent:

Paris, France,
Monday 16 May 2022

M.-P. Gaigeot