Prediction of heterodyne-detected VSFG spectra from classical molecular dynamics simulations

Patrik Musil[1], Milan Předota[1], Marie-Pierre Gaigeot[2]

[1]Department of Physics, Faculty of Science, University of South Bohemia, České Budějovice, Czech Republic

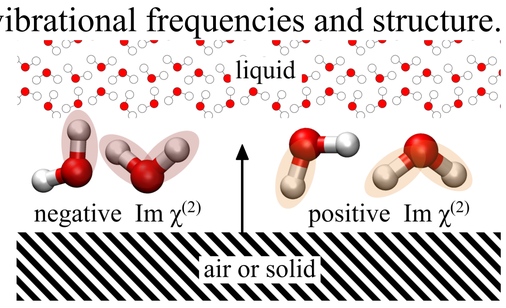
[2]Laboratoire Analyse et Modélisation pour la Biologie et l'Environnement (LAMBE), CNRS, Université d'Evry val d'Essonne, Evry, France

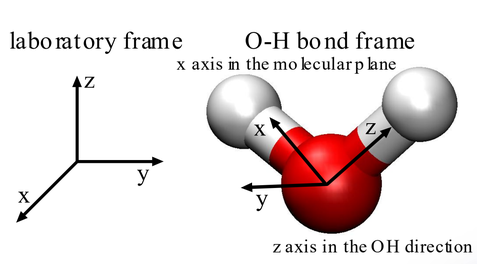
University of South Bohemia in České Budějovice
Faculty of Science

musilp01@prf.jcu.cz

SFG SPECTROSCOPY

- **Sum Frequency Generation (SFG)** is one of second order nonlinear optical processes, allowed only in media where inversion symmetry is broken which makes it an excellent method for investigation of surfaces and interfaces.
- In vibrational SFG experiment, a pulsed polarized broadband IR (ω_{IR}) laser beam is mixed with a tunable polarized VIS (ω_{VIS}) beam to produce an output at the **sum frequency** ($\omega_{SFG}=\omega_{IR}+\omega_{VIS}$).
- **Sign** of Im $\chi^{(2)}(\omega_{SFG})$ ⇒ OH orientation with respect to the surface normal **Position** of peaks of Im $\chi^{(2)}(\omega_{SFG})$ ⇒ strength of interactions **Intensity** of Im $\chi^{(2)}(\omega_{SFG})$ ⇒ abundance of water molecules with spec. orientation.
- **Our goal** is to develop a computational software with ability to process MD trajectories (both CMD and AIMD), produce SFG spectra, and interpret them.
- AIMD is more accurate and versatile but limited by system size and sampling.
- CMD requires FFs with flexible water and hydroxyl groups with accurate vibrational frequencies and structure. [1]





THEORETICAL BACKGROUND OF THE METHOD USED

- The second order susceptibility $\chi^{(2)}(\omega)$ is calculated as Fourier-Laplace transform of the time-correlation function of polarizability A_{PQ} and dipole moment M_R of the medium. [2]

$$\chi^{(2)}_{PQR} = \frac{i\omega}{k_B T}\int_0^\infty e^{i\omega t}\langle A_{PQ}(t)M_R(0)\rangle dt = \frac{-i}{k_B T\omega}\int_0^\infty e^{i\omega t}\langle \dot{A}_{PQ}(t)\dot{M}_R(0)\rangle dt$$

$$\dot{A}_{PQ}(t)\dot{M}_R(0) = \left\{\sum_{m=1}^{M}\left[\sum_{n=1}^{N_m}\dot{\alpha}_{mn,PQ}(t)\right]\right\}\left\{\sum_{m=1}^{M}\left[\sum_{n=1}^{N_m}\dot{\mu}_{mn,R}(0)\right]\right\}$$

- Computationally it is convenient to work with their time derivatives. Considering only the dominant OH vibration terms ($\dot{D}_{Ri} \approx 0$ and $\frac{dr_z}{dt} \gg \frac{dr_x}{dt} \approx \frac{dr_y}{dt}$) yields

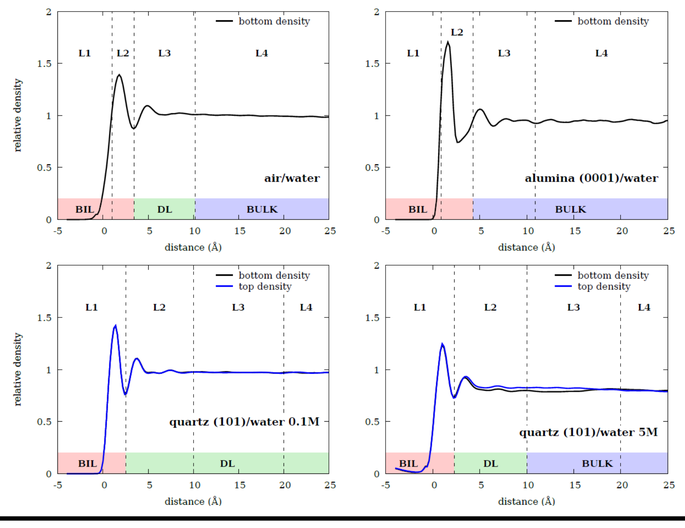
$$\dot{\alpha}_{PQ}(t) \approx \sum_i^{x,y,z}\left[D_{Pi}(t)\sum_j^{x,y,z}\left(\frac{\partial \alpha_{ij}}{\partial r_z}D_{Qj}(t)\right)\right]v_z(t)\,;\dot{\mu}_R(t) \approx \sum_i^{x,y,z} D_{Ri}(t)\frac{\partial \mu_i}{\partial r_z}v_z(t)$$

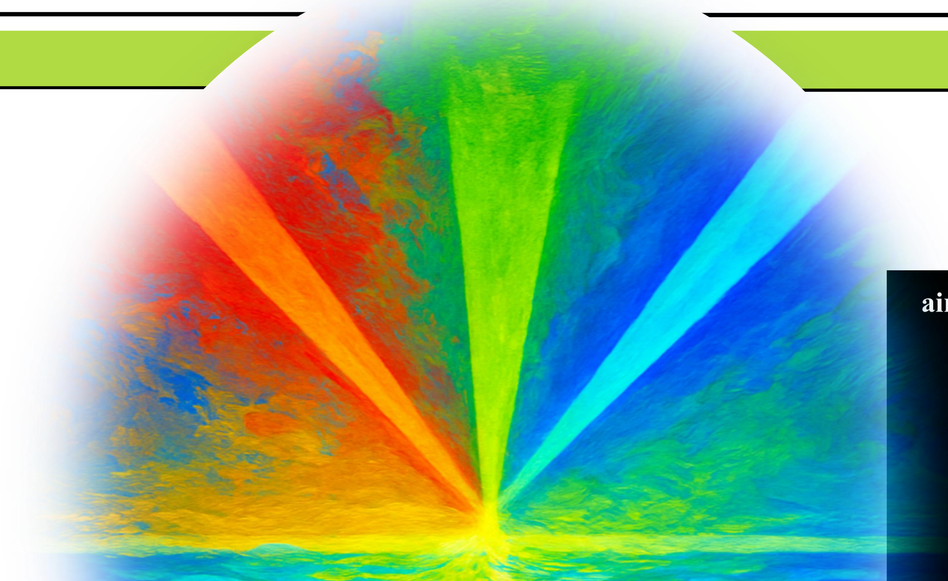
Ab-initio parametrized — From MD trajectory

COMPUTATIONAL SOFTWARE FEATURES

Computational features:

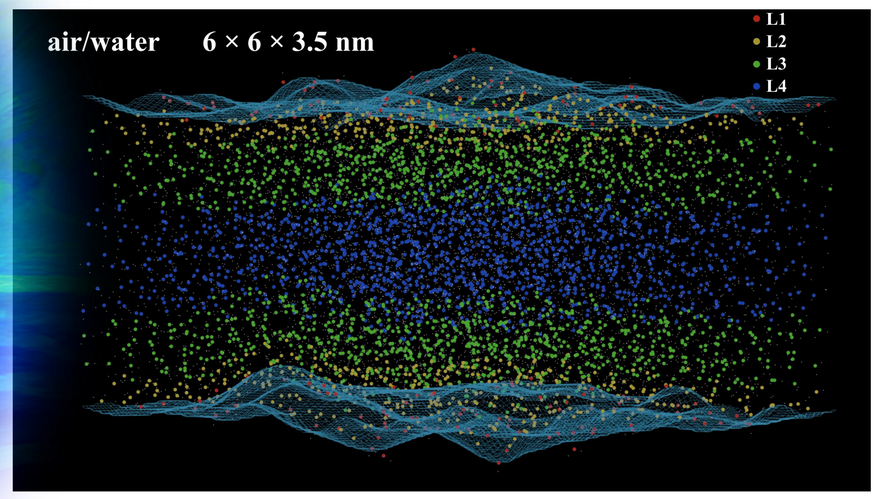
- Calculation of the instantaneous surface, evaluation of water density as a function of distance from the instantaneous surface allows analyzing contributions from specific layers.





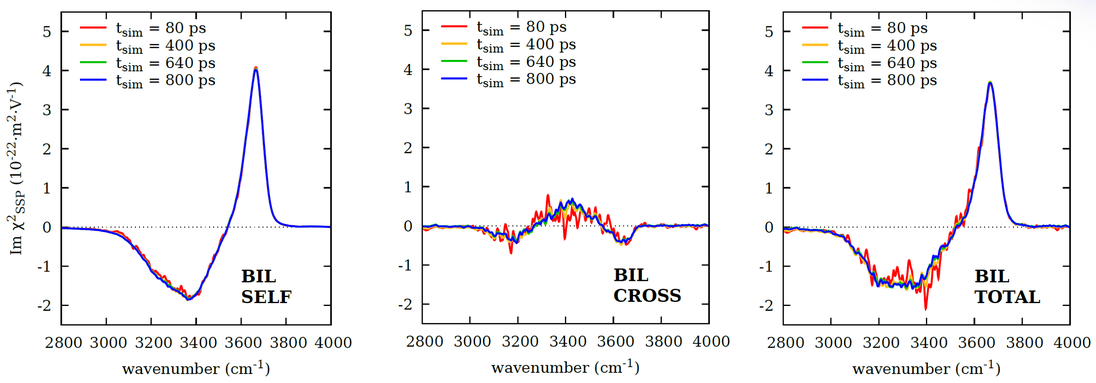
Technical features:

- Detailed documentation, **parallelization**, and tweakable input/output/calculation parameters.

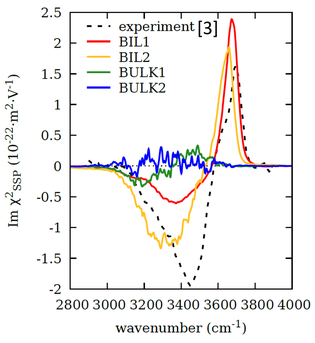


COMPUTED SPECTRA

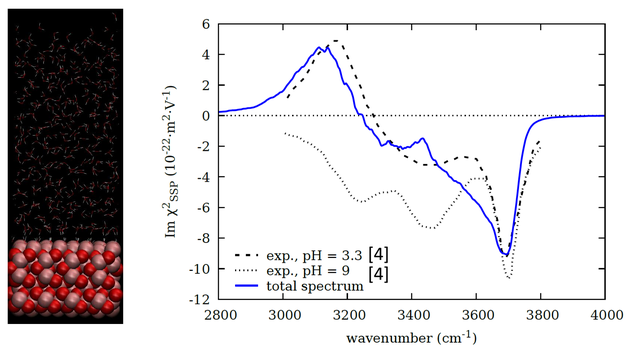
Air/water interface 6 × 6 × 3.5 nm



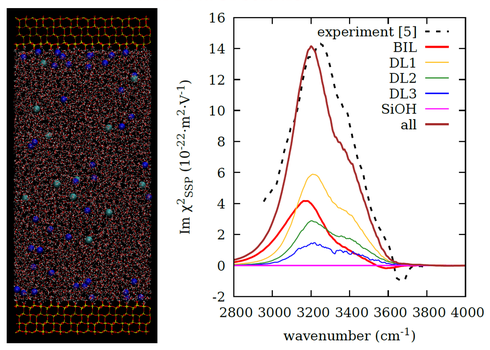
Air/water interface 3 × 3 × 3.5 nm, 400 ps



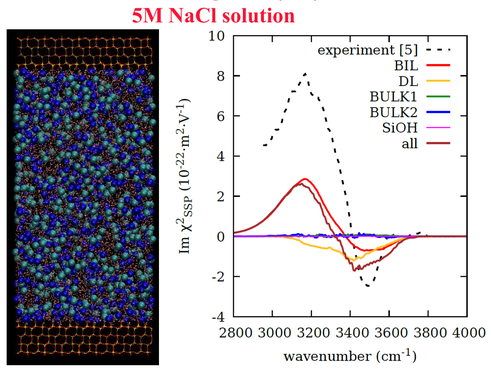
Neutral Alumina (0001)/ water interface



-0.12 C/m² Quartz (101)/ 0.1M NaCl solution

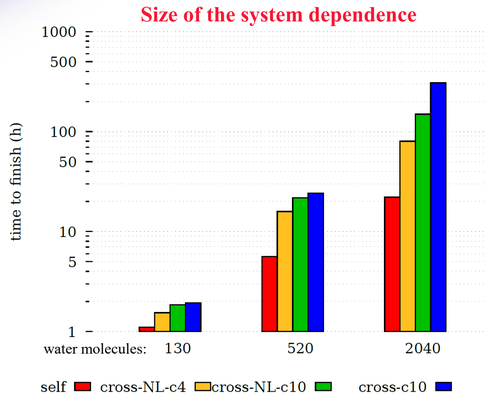


-0.12 C/m² Quartz (101)/ 5M NaCl solution

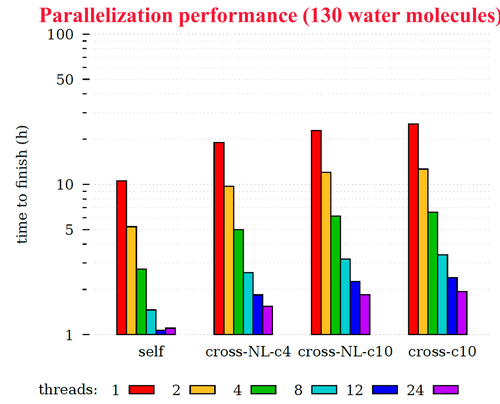


Program performance

Size of the system dependence



Parallelization performance (130 water molecules)



- The benchmark was performed on Ryzen 9 5900X CPU (12 cores, 24 threads)
- RAM used < 32GB

WORK IN PROGRESS

- Providing the software to broad scientific community
- Evaluating the effect of calculation parameters on the calculated spectra
- Further study of surface hydroxyl contributions
- Application of the software on OTS/PEG SAM interfaces with tunable hydrophobicity/hydrophilicity
- The program will be released on GitHub upon article submission or publication.

REFERENCES

[1] Kroutil, O.; Pezzotti, S.; Gaigeot, M.-P.; Předota, M. Phase-Sensitive Vibrational SFG Spectra from Simple Classical Force Field Molecular Dynamics Simulations. *The Journal of Physical Chemistry C* **2020** *124* (28), 15253-15263

[2] Khatib, R.; Backus, E.; Bonn, M. et al. Water orientation and hydrogen-bond structure at the fluorite/water interface. *Sci Rep* **2016** 6, 24287

[3] Nihonyanagi, S.; Kusaka, R.; Inoue, K.; Adhikari, A.; Yamaguchi, S.; Tahara, T. Accurate Determination of Complex $\chi^{(2)}$ Spectrum of the Air/Water Interface. *J. Chem. Phys.* **2015**, 143, 124707

[4] Zhang, L.; Tian, C.; Waychunas, G. A.; Shen, Y. R. Structures and Charging of α-Alumina (0001)/Water Interfaces Studied by SumFrequency Vibrational Spectroscopy. J. Am. Chem. Soc. **2008**, 130, 7686−7694.

[5] Urashima S.; Myalitsin A.; Nihonyanagi S.; Tahara T. The Topmost Water Structure at a Charged Silica/Aqueous Interface Revealed by Heterodyne-Detected Vibrational Sum Frequency Generation Spectroscopy. J. Phys. Chem. Lett. **2018**, 9, 4109-4114.

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