Recherche d'une méthodologie pour la simulation des spectroscopies vibrationnelles exaltées par effet de surface de systèmes adsorbés

Matatu Mbengo, Christ

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Recherche d'une méthodologie pour la simulation des spectroscopies vibrationnelles exaltée par effet de surface de systèmes adsorbés

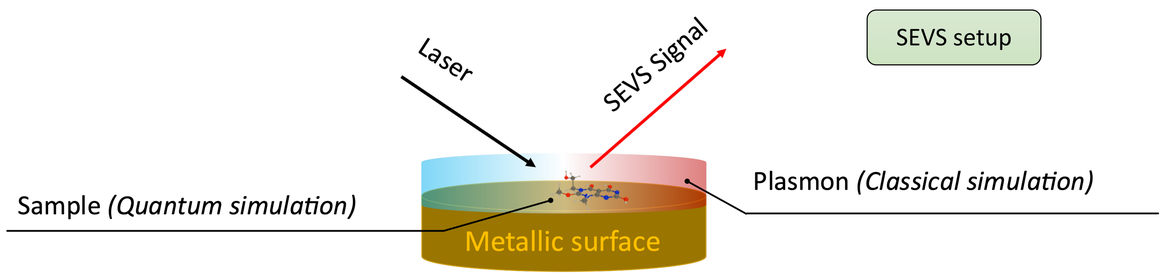
MATATU MBENGO Christ Daniel;[A] LIÉGEOIS Vincent[A]

A) Namur Institute of structured Matter (NISM), Unité de Chimie Physique Théorique et Structurale (UCPTS), LCT, University of Namur, 61 rue de Bruxelles, B-5000 Namur, Belgium

Introduction

Vibrational spectroscopies are of great interest for the study of materials and molecules. Their simulation allows to have some insight about their structures. Several materials can be studied: nanoparticles, crystals or 2D materials. The spectroscopic signal of the sample can be enhanced by placing it near a nanostructured surface (Au or Ag) during the analysis. These are surface enhanced vibrational spectroscopies (SEVS). Their mechanisms are complex because of the coupling between the sample and the surface. A unified numerical approach would be useful for the simulation of SEVS. The SURFASCOPE (Surface Enhanced Spectroscopy by Second-Principles Calculations) project aims at designing and implementing a second-principles (2ndP) numerical approach to interpret and guide SEVS. 2ndP methods rely on access to 1stP data that can be used as parameters to study system responses, with a fixed topology. My methodological research is part of the current challenge of inhomogeneous systems treatment in a 2ndP approach. This treatment involves 1stP simulations on sufficiently small systems or those that benefit from a certain periodicity to deduce transposable parameters to larger structures.

SEVS setup



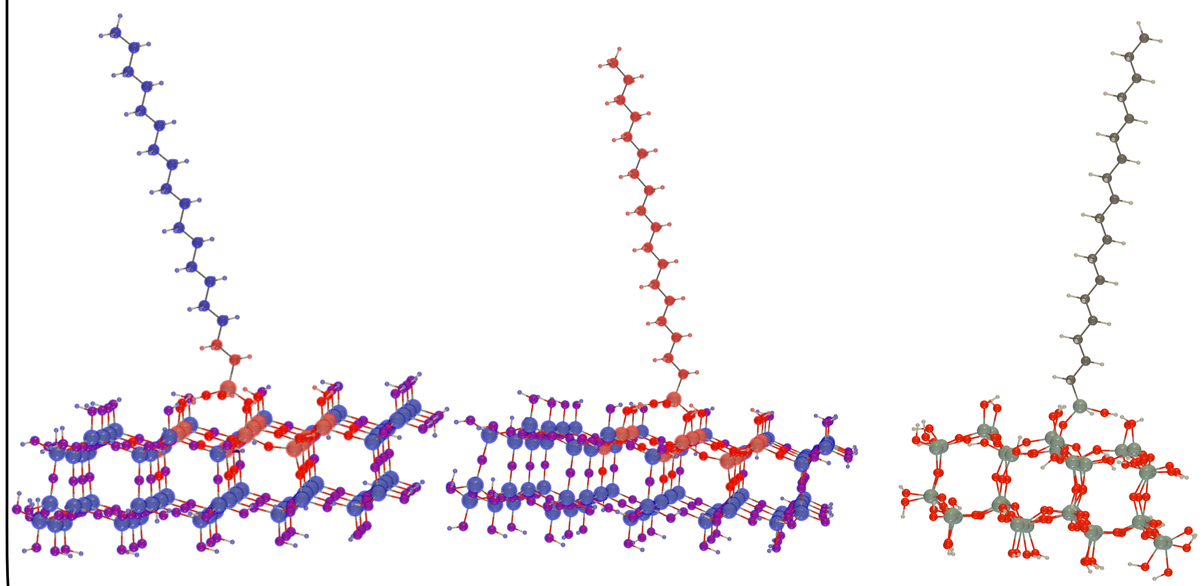
Strategy

Study the adsorption of an alkyl chain on a surface using ONIOM QM/QM method as implemented in Gaussian. Previous results on the adsorption of n-octadecyl-trichlorosilane (OTS) adsorbed on a SiO_2 surface[1] are used as a reference.

Optimization

Level of theory : ONIOM(wB97XD/6-311++G(2d,p):wB97XD/STO-3G

- The idea behind this strategy is to focus on a specific part of the structure. In this study, it is the interface between the surface and the molecule. The benefit is to diversify the data sources and focus on the most accurate way to describe each part of the large structure.
- The ONIOM models are designed to fulfill this objective. To deal with this 395 atoms structure, other options are needed. These options concern the choice of the SCF algorithm, convergence thresholds, and atom freezing.
- 2 model systems, with most of the surface in the low layer (blue) and the most relevant part of the surface and OTS in the high layer (red), are evaluated against the reference.
- For vibrational spectroscopy simulation, tight convergence criteria, which are the most difficult and challenging to achieve, are required.
- The default Gaussian optimization parameters and the short-chain ONIOM model consume fewer resources.

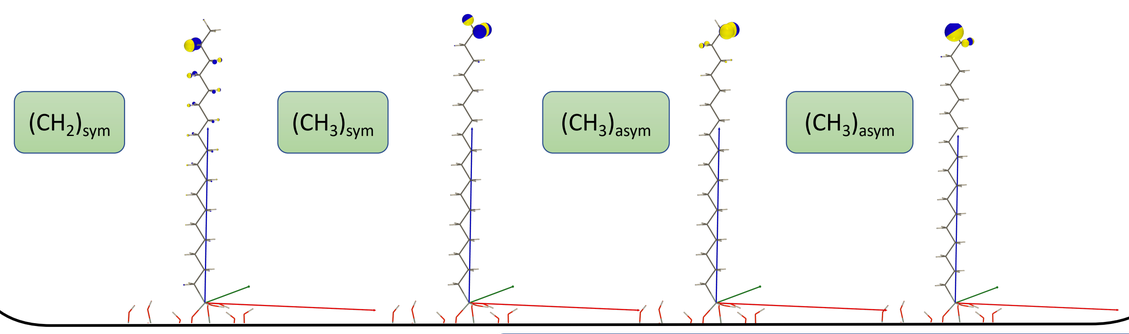


Short chain model (SCM) | Long chain model (same as reference)(LCM) | Reference Structure (RF)

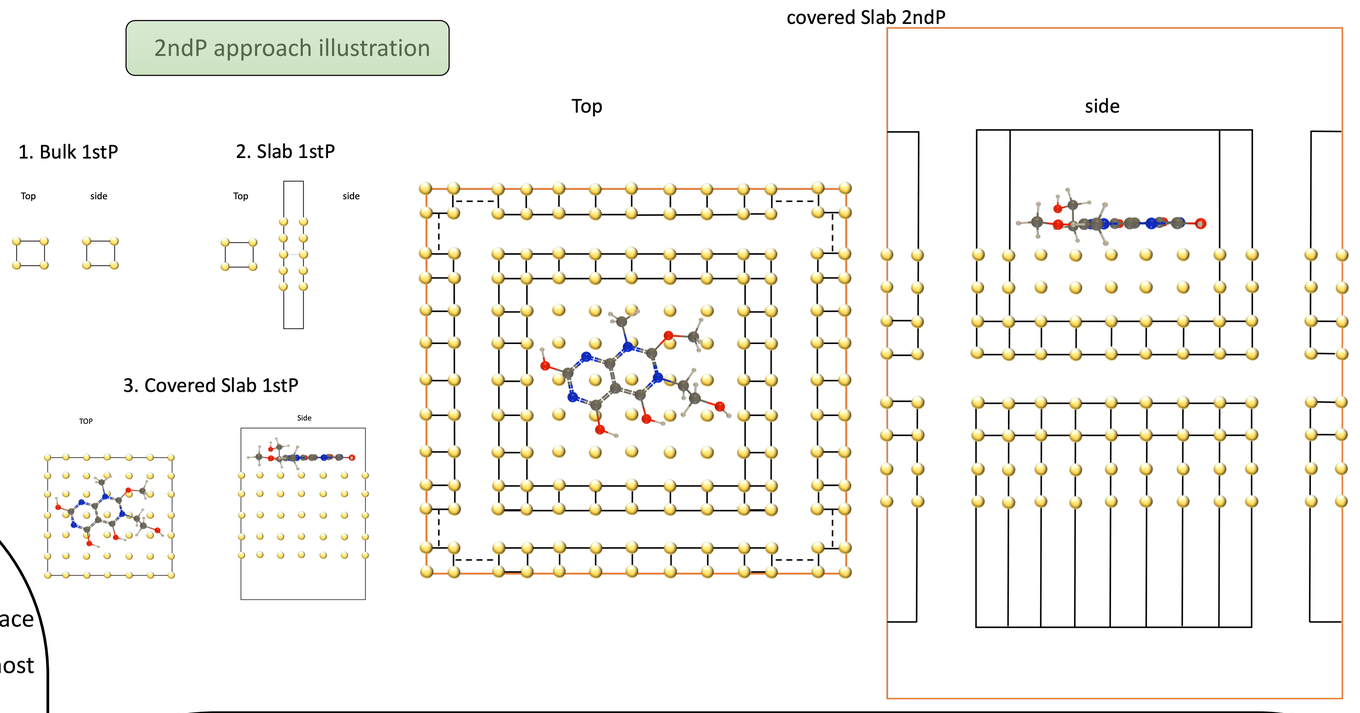
Vibrational frequencies

- Harmonic vibrational frequencies and normal modes are calculated analytically by setting atomic masses of 1000 amu to the atoms of the low layer and the H atoms saturating the dangling oxygen bonds.
- Frequencies are scaled (0.95) to account for missing anharmonicity effects as well as for the limitations of the XC functional.

	RF			LCM		
vibration	FREQ (cm^{-1})	IR (Km/mol)	Raman (A^4/AMU)	FREQ (cm^{-1})	IR (Km/mol)	Raman (A^4/AMU)
$(CH_2)_{sym}$	2884	271	30	2883	279	36
$(CH_3)_{sym}$	2888	45	169	2886	43	224
$(CH_3)_{asym}$	2955	87	31	2954	85	24
$(CH_3)_{asym}$	2960	50	107	2959	49	105



2ndP approach illustration



Geometrical parameters

- The Z-axis(in dark blue) is defined as normal to the surface. The molecular z-axis (in light blue) is fitted using the least-squares approach as the best vector through the C atoms of the silane molecule.

✓ θ : Tilt angle of the alkyl chain . The angle between the molecular *z*-axis and the laboratory *Z*-axis

$$\theta = \cos^{-1}(Z.z)$$

✓ α : Tilt angle of the terminal (CH2 –CH3) bond with respect to the *Z*-axis.

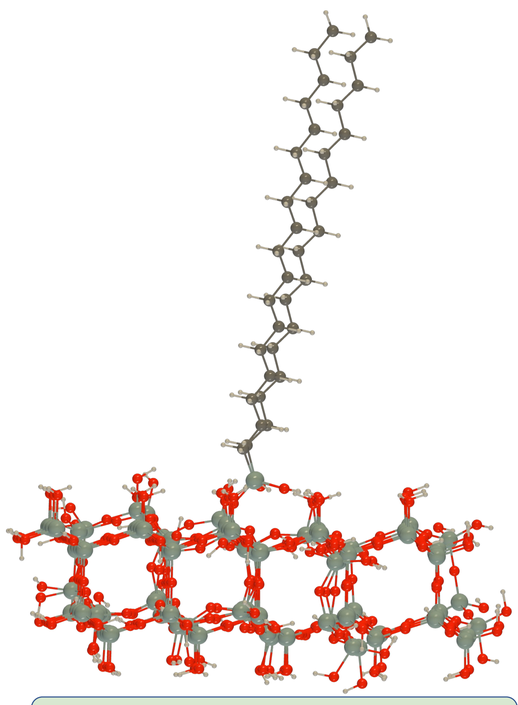
$$\alpha = \cos^{-1}(Z.CH2 - CH3)$$

✓ ξ : The rotation of the plane of the alkyl chain around the molecular *z*-axis.

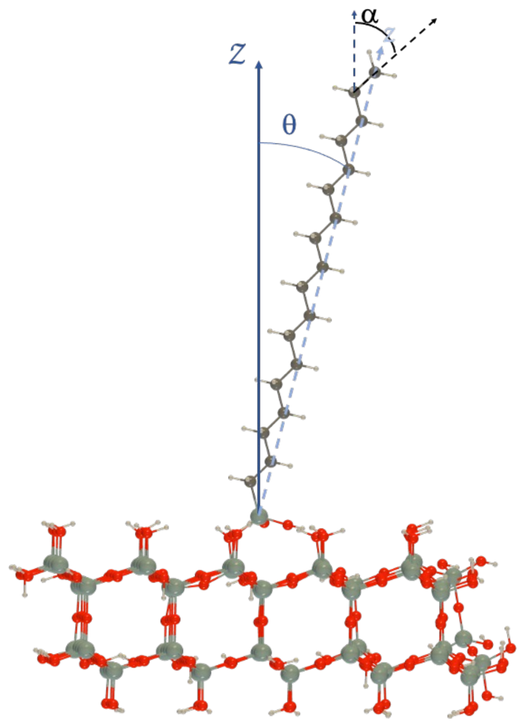
$$\xi = atan2(x.Z, y.Z)$$

- Analytical and experimental scales for those parameters from [1] :

θ< 15◦ 40◦ < α < 50◦



overlap of optimized RF and optimized LCM



Axis illustration for geometrical parameters calculation

	Calculated from RF files	LCM	SCM
θ	11	15	16
ξ	-116	-171	-172
α	39	49	49

Conclusion

Structure reproduced, optimized and analysed

Calculation results are coherent with the reference data

The ONIOM approach is valid for this system

IS this approach reproductible with different systems ?

Perspectives

Is default parameters + Short chain Less resources consuming

Basis set and functional influence

How to handle metallic surface

Options to optimized the methodology

The calculations were performed on computers of the Consortium des Equipements de Calcul Intensif, including those of the Technological Platform of High-Performance Computing, supported by the FNRS-FRFC (Conventions No. 2.4.61707.F and 2.5020.11) and the University of Namur. Thanks to the ARC SURFASCOPE project for the founding and support on this work.

[1]C. G. Tetsassi Feugmo, V. Liégeois, Y. Caudano, F. Cecchet, and B. Champagne, "Probing alkylsilane molecular structure on amorphous silica surfaces by sum frequency generation vibrational spectroscopy: First-principles calculations," *The Journal of Chemical Physics*, vol. 150, no. 7, p. 074703, 2019, doi: 10.1063/1.5080007.