Enclosure 1b. Category 1 Application form – English version

APPLICATIONS ARE PREFERABLY DRAWN UP IN ENGLISH. AN ENGLISH TRANSLATION HAS TO BE ENCLOSED WITH APPLICATIONS SUBMITTED IN DUTCH.

The application form is available in English on the website
https://www.vscentrum.be/en/access-and-infrastructure/project-access-tier1

Title of the application:

DFT study of reaction paths in zeolite-catalyzed 2-hexene cracking

Name and first name of the applicant:

Cnudde Pieter

Institution:

Ghent University

Research group / department:

EA17 / Center for Molecular Modeling

Title / position:

Ir. / PhD fellow

e-mail address:

Pieter.Cnudde@ugent.be

Total computing time that is needed, in node days:

4536 node days

Total disk storage that is applied for:

~ 1 TB long-term storage (provided by UGent)

1. Title of the research project (with IWETO or FRIS link if available) within the framework of which computing time is applied for:

"Functional Supramolecular Systems (FS2)" – IUAPVII/138 –
prof. dr. ir. Veronique Van Speybroeck

2. Describe your research project in short. Explicitly mention the scientific questions that you are planning to address and the overall scientific goals of the project. (max. 1 A4 in Arial 12):

Cracking of alkenes has recently gained interest as an on-purpose production process for light olefins (ethylene and propylene). In this process, low-value product streams are upgraded by increasing the light olefin yield, which is extremely interesting since it can be coupled to existing (petro)chemical units, like fluid catalytic cracking or methanol-to-olefins. H-ZSM-5 is a widely applied catalyst in industry for hydrocarbon conversion and will therefore be used in this work to model the cracking of 2-hexene. Alkene cracking processes consist of several reaction pathways. To date, the precise mechanism to form the light olefins is still debated. Obtaining experimental information about the olefin cracking reactions is difficult due to the high reactivity of alkenes, even at low temperatures. Furthermore, side reactions like alkylation, isomerization and hydride transfer result in a complex reaction network. Quantum chemical modelling can assist in unravelling the governing reaction mechanism and identifying the key reaction intermediates.

In this study, DFT calculations will be performed on isomerization and cracking reactions of 2-hexene and other C_6 isomers to identify the lowest activated reaction pathways and the most important intermediates. Cracking is generally accepted to occur through a β-scission mechanism of carbenium ions. However, the latter can quickly isomerize to other C_6 species before cracking into smaller alkenes. Therefore, both isomerization and cracking will be studied. A reaction network consisting of 11 elementary steps (5 isomerization and 6 cracking reactions) is proposed to connect the possible intermediates (Figure 1). For each elementary reaction, the transition state and corresponding reactant and product state must be localized. Frequency calculations are required to verify the nature of the optimized geometries and to evaluate entropies and free energies at typical operating temperatures for all the stationary

points. To ensure the quality of the obtained results, an extensive level of theory study will be performed using 4 state-of-the-art DFT functionals.

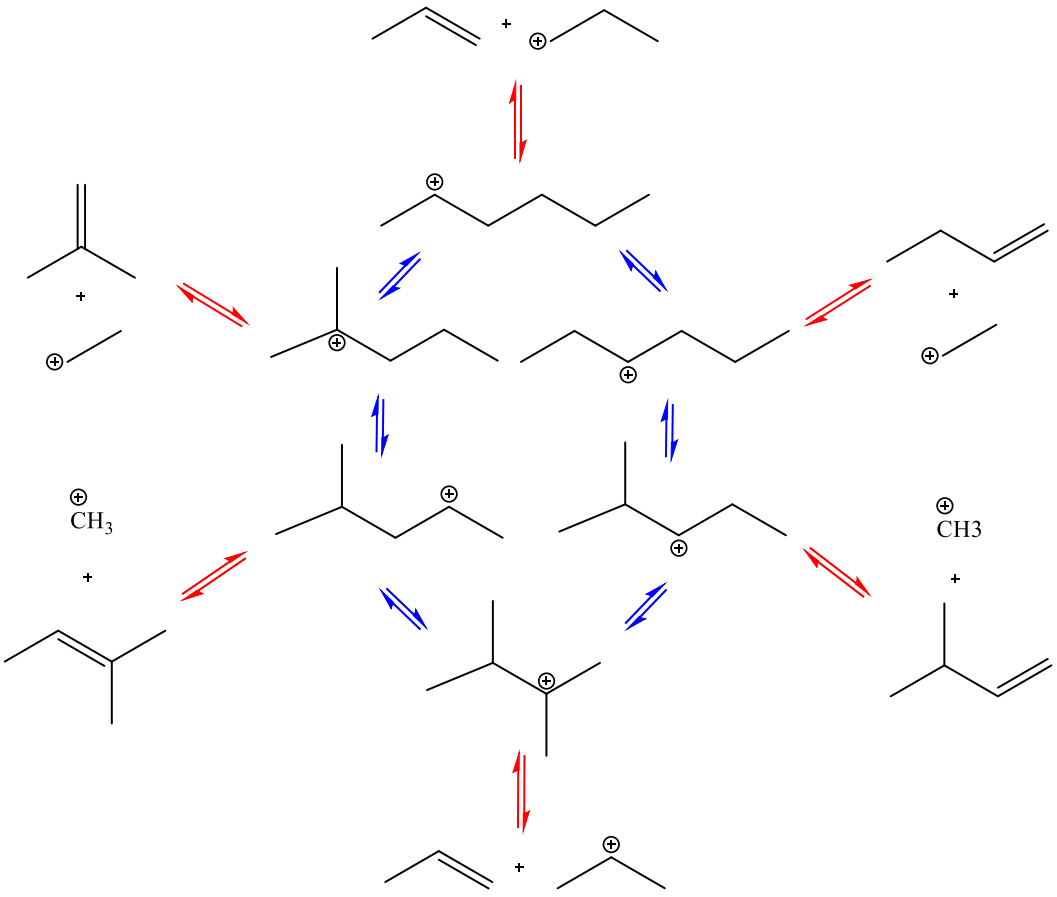

Figure 1. Schematic representation of the proposed reaction network comprising isomerization reactions (blue arrows) and cracking reactions (red arrows) for the 2-hexene system.

3. Provide an abstract (10 lines) for scientific communication on the website in layman's terms. See also item 12 of this application form.

<u>No abstract of this work may be published on the website. (see item 12)</u>

Catalytic cracking of 2-hexene over acidic zeolites plays a crucial role in the on-purpose production of light olefins, ethylene and propylene. A profound insight in the reaction mechanism and the nature and stability of the reaction intermediates is prerequisite to determine accurate reaction kinetics, to optimize the catalyst and to improve the selectivity of the

process. For example, it is still an open question how propylene is formed and which reaction paths will have the highest contribution to the light olefin yield. In this work, a series of possible reaction pathways, including isomerization and cracking of the intermediates, are investigated to clarify the reaction mechanism and to identify the prevailing intermediates.

4. Financing institution or channel, financing the research project in full or in part (FWO, BOF, IWT, EU, …): Please attach the confirmation letter as enclosure (see instructions in enclosure 3 "EasyChair proposals submission procedure").

"Functional Supramolecular Systems (FS2)" - IUAPVII/138 –
prof. dr. ir. Veronique Van Speybroeck (see attachment)

5. Name and email address of the promoter(s) of the research project:

Prof. Dr. Ir. Veronique Van Speybroeck (Veronique.VanSpeybroeck@UGent.be)

6. Persons mandated by the Applicant to compute on the Tier-1 within the framework of the present project: Please provide for every person:
   - name and first name
   - institution
   - research group / department
   - title / position
   - experience of using HPC resources in the past (Tier-0/Tier-1/Tier-2 infrastructure in Belgium and abroad)

Pieter Cnudde - vsc40920
Ghent University, Center for Molecular Modeling
PhD Fellow
1½ year of experience with TIER1 at Ghent University
3 years of experience with TIER2 at Ghent University

Following researchers are actively involved in this project.

Simon Bailleul – vsc41224
Ghent University, Center for Molecular Modeling
PhD fellow
1 year of experience with TIER1 at Ghent University
2 years of experience with TIER2 at Ghent University

Jeroen Van der Mynsbrugge – vsc40163
Ghent University, Center for Molecular Modeling
BOF Post-doc
2 ½ year of experience with TIER1 at Ghent University
7 years of experience with TIER2 at Ghent University

Kristof De Wispelaere – vsc40490
Ghent University, Center for Molecular Modeling
ERC Post-doc
2 ½ year of experience with TIER1 at Ghent University
½ year of experience with TIER1 and TIER2 in The Netherlands
5 ½ years of experience with TIER2 at Ghent University

Veronique Van Speybroeck – vsc40021
Ghent University, Center for Molecular Modeling
Full Professor
2 ½ year of experience with TIER1 at Ghent University
7 years of experience with TIER2 at Ghent University

7. Explain why this project needs to run on a Tier-1 system, why the machine you have requested is suitable for the project and how the use of the system will enable the science proposed (max. ½ A4 in Arial 12).

This project is part of a large study on catalytic cracking in zeolites in collaboration with experimental partners. A computing time of over 4000 node days is needed to converge all calculations required for this study within the necessary limits and to obtain accurate results that can be compared with experimental data. Running several multi-node jobs in parallel is imperative to complete this project in an acceptable timeframe. The ability to run a large amount of jobs simultaneously on the TIER1 infrastructure is therefore essential for the success of this research.

Furthermore, during the past years the Center for Molecular Modeling has made several high-impact contributions (see item 11) in this highly competitive field. To maintain this prominent position, access to the TIER1 infrastructure with fast nodes and efficient inter-nodal communications is indispensable.

8. Justify the number of node days requested. This should include information such as: number and nature of computing tasks, software used, and the sequence in which they will be performed.
   Indicate for each typical computing task the required resources:

   - wall clock time (note that 3 days is the maximal wall clock time for any job; checkpointing should be used for longer run times)
   - memory (maximum 64 GiB/node)
   - number of nodes
   - number of CPU cores
   - disk space (estimated volume in GiB and the total number of files); make a clear distinction between usage of Tier-2 DATA/HOME partitions and the Tier-1 SCRATCH partition
   - number of tasks, and an indication of how many such tasks would be submitted concurrently.

   This information should take the form of a table (an example is provided as Table 2 in the appendix). Provide additional descriptions of the computing tasks and comments as needed. Resource estimates should be preferably based on the results of actual calculations on Tier-1 (via, e.g., a Starting Grant) for system/problem sizes that are on par with those of the intended computing tasks (e.g., same mesh sizes, actual molecular system, …). If not, provide the name, architecture, #cores, memory, etc. of the machine that was used to obtain these results and explain how you have calculated/rescaled the wall clock times, number of cores, etc.
   (max. 1 A4 Arial 12).

During this study, four types of calculations will be performed using the VASP software package on a periodic model of H-ZSM-5 consisting of approximately 300 atoms. The computational requirements for this study have been carefully considered based on test simulations on similar

systems, performed on both TIER2 (delcatty cluster) and TIER1 infrastructure. Based on these scaling tests (see item 10), optimal efficiency is reached when these calculations are run as multi-node jobs on **2 nodes**.

Calculation flow:

1. First, the geometry of the transition states (TS) is sought. Transition state searches for similar systems have shown that approximately 12 node days on TIER1 are required to obtain a converged transition state geometry. This is the most difficult part which will require on average 4 iterations (see item 4) to find a proper transition state. Therefore, it is expected that for each of the reactions about **48 node days** are needed. Since there are 11 reactions and 4 functionals, **44** transition state searches will be performed.
2. Intrinsic reaction coordinate (IRC) calculations scan the motion alongside a negative frequency. This type of calculation is necessary to verify if the motion alongside the negative frequency corresponds to the actual transition state. Furthermore, this calculation yields initial guesses for the corresponding reactant and product geometries. Each IRC calculation requires about **8 node days**.
3. Next, geometry optimizations are performed to localize the reactant and product states (GEO). Convergence is obtained after approximately 6 node days. To find a true local minimum on the potential energy surface, 4 iterations are typically required (see item 4). Each reactant/product search is thus expected to take up to **24 node days**. In total, 12 reactants and products need to be identified. Since each state will be evaluated with 4 functionals, a total number of **48 geometry optimizations** will be carried out.
4. To verify the nature of the optimized reactant/product states and transition states and to calculate entropies and free energies at operating temperatures, frequency calculations (FREQ) will be performed. Transition states should have precisely 1 negative frequency. Reactant/product minima should have all positive frequencies. Frequency calculations requiring about **2.5 node days each** are performed after each iteration in the transition state searches and geometry optimizations until convergence is reached. Based on the estimates in items 1 and 2, about **92 frequency calculations** will be required.

Table 1 summarizes the estimated node and core days required for each simulation type:

Table 1. Estimated core and node days required for the project.

Job type	# of simulations	Node days per simulation	Total node days	Total core days
TS	44	48 (=12 * 4 iterations)	2112	33792
IRC	44	8	352	72576
GEO	48	24 (= 6 * 4 iterations)	1152	18432
FREQ	92	10 (=2.5 * 4 iterations)	920	14720
			4536	72576

Table 2 summarizes the requirements for long-term storage for each calculation type.

Table 2. Estimated long-term storage requirements for the project.

Job type	Long-term storage [GB/simulation]	Total long-term storage [GB]
TS	1	44 x 1 = 44
IRC	16	44 x 16 = 704
GEO	1	48 x 1 = 48
FREQ	2	92 x 2 = 184
		980

9. Describe the software required to perform the computing task(s). Please clearly provide the following per item in this regard:

   - a reference to the software's web page
   - the software license system (open source, GPL, etc.)
   - if there is no free academic use of the software, state which license makes the installation and the use valid on the Tier-1 by the Applicant (+ add a copy of the signed license)

- whether the software is already available on the Tier-1 (see https://www.vscentrum.be/cluster-doc/software/tier1-muk) and, if this is not the case, compilation and installation instructions (possibly with reference to existing Tier-2 installation)

The VASP software package (http://www.vasp.at/) will be used to perform the static DFT calculations. This package (version VASP/5.3) is already available on Tier1 under a non-exclusive academic license (see attachment).

Provide the results of scaling tests that were conducted with this software, preferably on Tier-1 (using, e.g., a Starting Grant) for system/problem sizes that are on par with those of the intended computing tasks (e.g., same mesh sizes, actual molecular system, …). If not, provide the name, architecture, #cores, memory, etc. of the machine that was used to obtain these results.
Provide both a table and scaling plot such as table 1 and plot 1 in the appendix (max. 2 A4 in Arial 12).

A scaling test for the VASP software package on TIER1 has been conducted using a model system similar to the ones that will be studied, namely an isobutene molecule adsorbed in H-ZSM-5. Table 3 summarizes the results for the average length of a single electronic step (SCF) during a geometry optimization. For a regular geometry optimization, the number of electronic steps will be in the range of 150 – 200. Table 4 shows the results for a frequency calculation. In Figure 2 the speedup normalized to the 16 core simulation is plotted for both types of calculations. This graph indicates that using more than 2 nodes does not efficiently speed up the simulation.

Table 3. Summary of the scaling test of a single step in a geometry optimization with the VASP software package using an isobutene molecule adsorbed in H-ZSM-5 as a model system.

#nodes	# cores	Absolute timing (s)	Speedup
1	16	2641	1
2	32	1471.9	1.79
4	64	1063.5	2.48
8	128	613.7	4.30

Table 4. Summary of the scaling test of a frequency calculation with the VASP software package using an isobutene molecule adsorbed in H-ZSM-5 as a model system.

#nodes	# cores	Absolute timing (s)	Speedup
1	16	142903	1
2	32	76411	1.87
4	64	58585	2.44
8	128	47368	3.02

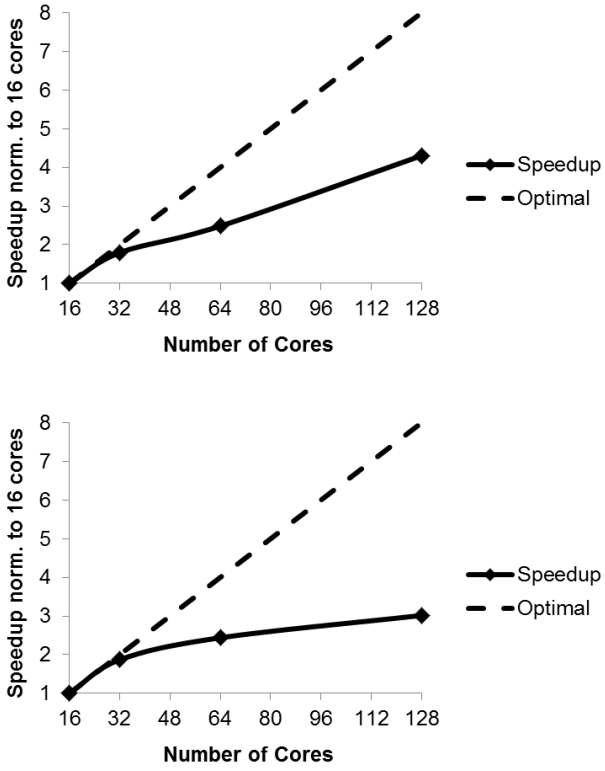

Figure 2. Speedup normalized to 16 cores for a geometry calculation (top) and a frequency calculation (bottom) of an isobutene molecule adsorbed in H-ZSM-5 as a model system using the VASP software package.

10. Describe how you will manage the resources requested in the period during which the task is to be performed. What usage

pattern do you anticipate (similar usage on monthly basis, bursts, …)?

We estimate the proposed simulations can be completed over a time period of approximately **6 months**, preferably starting in **September 2016**. Similar usage on a monthly basis is expected.

This estimated timeframe takes into account the actual runtime of the simulations, as well as intermediate data analysis tasks and job restarts.

11. List the granted computing time allocations to the promoter(s) of this research project, on the Flemish Tier-1 system, as well as other Tier-1 and Tier-0 systems. Also, describe the scientific output obtained within the framework of computing time that was granted during the past two years on the Flemish Tier-1 or on other Tier-1 or Tier-0 supercomputers. DOI links are sufficient.

List of granted research projects of the Flemisch TIER1 system:

- Molecular dynamics study of pentene in H-ZSM-5: towards a better estimate of adsorption enthalpies (J. Van der Mynsbrugge – 1824 node days – 07/03/2014 – 06/07/2014)
- Dynamical kinetic study of zeolite catalyzed reactions (K. De Wispelaere, 4371 node days, 07/07/2014 – 31/12/2014)
- Exploring the kinetics and selectivity of butene cracking using molecular dynamics simulations (J. Van der Mynsbrugge, 4864 node days, 01/01/2015 – 30/06/2015)
- Characterizing adsorption properties of C4 – C6 alkenes on H-ZSM-5 using molecular dynamics simulations (P. Cnudde, 4260 node days, 13/07/2015 – 31/12/2015)
- Dynamical first principle benchmark studies on alkene methylation in H-ZSM-5 (K. De Wispelaere, 1400 node days, 01/12/2015 – 30/06/2016)
- Ab initio molecular dynamics study on the role of water in the reaction mechanism during methanol conversion in H-SAPO-34 (S. Bailleul, 4880 node days, 01/03/2016 – 30/08/2016

List of scientific output within the framework of granted computing time:

- On the stability and nature of adsorbed pentene in Brønsted acid zeolite H-ZSM-5 at 323K, J. Hajek, J. Van der Mynsbrugge, K. De Wispelaere, P. Cnudde, L. Vanduyfhuys, M. Waroquier, V. Van Speybroeck, Journal of Catalysis, in press, 2016

- Suppression of Aromatic Cycle in Methanol-to-Olefins Reaction over ZSM-5 by post-synthetic modification using Calcium, I. Prokopyeva, S. Bailleul, A. Pustovarenko, J. Ruiz-Martínez, K. De Wispelaere, J. Hajek, B.M. Weckhuysen, K. Houben, M. Baldus, V. Van Speybroeck, F. Kapteijn, J. Gascon, ACS Catalysis, Submitted 2016
- http://dx.doi.org/10/1039/C5CY02073E
- http://dx.doi.org/10.1021/acscatal.5b02139
- http://dx.doi.org/10.1002/chem.201500473
- http://dx.doi.org/10.1016/j.jcat.2015.01.013
- http://dx.doi.org/10.1002/cctc.201402146
- http://dx.doi.org/10.1021/cs400706e
- http://dx.doi.org/10.1039/c4mh00127c
- http://dx.doi.org/10.1039/C3CP54132K

12. Are the applicants of this application bound by a confidentiality agreement? If so, the title and the abstract of this application will not be published on the website of the FWO / Flemish Supercomputer Center.

    Yes

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Interuniversity Attraction Poles (IAP)
Phase VII

2012 - 2017

CONTRACT P7/05

ANNEX I - Section II

Information on the partner

To be completed by each network partner including the international partner(s)

Name of the partner: **Van Speybroeck Veronique** Institution: **Universiteit Gent**
Title of the project : Functional Supramolecular Systems
Acronym of the project : FS2

II. 8. BUDGET (per partner) *

(in EURO without decimals)

P7/05 - P11 (V.Van Speybroeck)	2012-2017
Personnel	399,533
Operating costs	59,334
Equipment	18,190
Overheads (max 5% P+O)	22,943
Subcontracting	
Subtotal	**500,000**
Int partner 1 [name A]	
Int partner 2 [name B]	
Int partner 3 [name C]	
Int partner 4 [name D]	
Total	**500,000**

* This table should not be completed by the International partner(s) as their budget is mentioned in the budgetary table of the Belgian partner of the network responsible for the follow-up of the partnership

Double click to complete the table.

- Personnel: indexed gross remunerations; employer's social contributions; statutory insurance costs as well as any other compensation or allocation legally due in addition to the salary; the reimbursements for PhD and postdoctoral grant holders (exempt from tax and benefiting from social security). Personnel costs must account for minimum 60% of the total budget attributed to each partner of the network. The costs for the tax-free PhD grants and postdoctoral grants may not account for more than 60% of the total personnel costs. The partners with a total budget of less than 600.000 euros can exceed this limit.

- Operating costs: basic supplies and products for laboratory, workshop or office; documentation, travel and accommodation; use of computing facilities; software; telecommunications; maintenance and operation of equipment and, more generally, consumables; hosting of visiting foreign researchers.

- Equipment: acquisition and installation of scientific and technical appliances and instruments, including IT equipment placed with a unit price higher than 500 euros.

- Overheads: general expenses of the institutions covering, on an inclusive basis, administrative, telephone, postal, maintenance, heating, lighting, electricity, rental, material depreciation and insurance costs (the total amount for this heading may not exceed 5% of total personnel and operating costs).

- Subcontracting: costs incurred by a third party in order to perform tasks or provide services necessitating specific scientific or technical skills outside the normal framework of the institution's activities (the amount may not exceed 25% of the total budget). Each request for subcontracting needs an approval from the programme manager.

II. 9. EQUIPMENT

Indicate the equipment (with an estimation of the cost) that will be purchased from the IAP-budget for the coming years (2012-2016) and justify.

A small budget of 18190 Euro is foreseen for purchase of small workstations.

II. 10. SUBCONTRACTING

To be completed only if subcontracting is foreseen.

Describe and justify the tasks and/or services that will be provided by a third party from outside the institution.

SOFTWARE LICENSE AGREEMENT FOR THE USE OF VASP5.2 BY ACADEMIC INSTITUTIONS

The Universität Wien, Austria (UW in the following) and
Ghent University, Belgium (UG in the following) [1]
conclude the following agreement:

(1) The UG acquires a non-exclusive academic license for the use of the software-package VASP (Vienna ab-initio simulationprogram) for ab-initio local-density-functional total-energy and molecular-dynamics calculations, versions VASP5.2 and VASP4.6, by the research group Functional Nanomaterials (FUNNANO)[2]. Under this licence the use of the software is restricted to a maximum of six researchers or students, all belonging to this research group and to the same organisatorial unit and working at the same location. The licence does not cover the use of VASP by external collaborators working at other institutions.

(2) The license covers access to the source-code, the program documentation and to the data-base for ultrasoft pseudopotentials and PAW-potentials. UW reserves the exclusive property of the software. It declines any liability for the software and any responsibility for the results of calculations produced with the program. The license does not cover any maintenance service for the software or support for its implementation.

(3) The license is not transferable to another research group of UG without the written agreement of UW. UW reserves the right to refuse authorization of such a transfer. A transfer to a research group not belonging to UG is excluded.

(4)The UG guarantees that the software or parts thereof shall not be made accessible to third parties without the explicit written consent of UW. Access to the code and to the data-base shall be made available through an account of the UW. The UG guarantees that the password for this account will be known only to one contact-person and shall not be communicated to temporary co-workers or guests. All installations of the source code, the executable or the data-base must be copy-protected and accessible only to the authorized users.

[1] Please insert here the name of the institution concluding this agreement with UW. This institution must be a legal person and the agreement must be signed by an authorized representative of this institution. Define the acronym (replacing .....) under which this institution is referred to in the text of the agreement.

[2] Please insert here the name and affiliation research group for which the license is acquired

SOFTWARE LICENSE AGREEMENT FOR THE USE OF VASP5.2 BY ACADEMIC INSTITUTIONS

(5) If VASP is used as the basis of further methodological or software-development, UG agrees to make these additions available to UW. UW will also be entitled to include these additions in further releases of VASP.

(6) In future publications of work performed using VASP, the use of the software shall be properly acknowledged, e.g. in the form
"The calculations have been performed using the ab-initio total-energy and molecular-dynamics program VASP (Vienna ab-initio simulation program) developed at the Institut für Materialphysik of the Universität Wien [1-3]."
[1] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11 169 (1996).
If the PAW-version is used, reference will be made to
[2] G. Kresse and D. Joubert, Phys. Rev. **59**, 1758 (1999).
If special features implemented in VASP will have been used, reference should be made to the relevant publications as listed on the VASP home-page.

(7) The UG accepts to pay to UW a licence fee Euro 4.000,- (fourthousand Euro). The licence fee is strongly discounted and applies only to academic institutions with undergraduate teaching.

(8) The licensee will use VASP exclusively for non-profit research. If VASP is used in contractual research in cooperation with or for industry or for military institutions, the financial conditions will have to be re-negotiated.

(9) UW declares that it has the full power and authority to grant the rights granted in this agreement without the consent of any other person, and that the license and use of the software by the licensee will not in any way constitute an infringement or other violation of any copyright, proprietory right or any other rights of any third party.

(10) Any disputes arising from the license agreement are subject to the laws of the Republic of Austria.

(11) The terms of this agreement shall prevail any terms or conditions of the licensee.

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For the Universität Wien:

Jürgen Hafner
Fakultät für Physik, Universität Wien
Sensengasse 8/12, A-1090 Wien, Austria

Date

For the UG

Name (in print): Michel Waroquier
Institution: Faculty of Sciences, Ghent University

Address: Technologiepark 903, BE-9052 Zwijnaarde, Belgium

Date: 26 January 2010

For the research group entitled to use VASP5.2:

Name (in print): Veronique Van Speybroeck (FUNNANO)