Ab-initio Molecular Dynamics of CH_3OH at the H_2O/Pt interface

T. R. Mattsson* and S. J. Paddison**

*Surface and Interface Science Department
Sandia National Laboratories, Albuquerque, NM 87105-1415
** Theoretical Chemistry and Molecular Physics Group,
Los Alamos National Laboratory, Los Alamos, New Mexico 87545

ABSTRACT

Improved catalysts are among the engineering achievements, including a reduction in the overall cost of the system, necessary for Direct Methanol Fuel Cells (DMFC) to become a competitive alternative for both portable and stationary power applications. An important step towards improving existing solutions, in turn, is a fundamental, molecular based, understanding of the catalytic processes.

Computer simulations, in particular calculations from first principles, have proven to provide key insights into gas-phase catalytic reactions. Density Functional Theory (DFT) [1,2] stands out as the method of choice for this type of problems. With DFT, it is possible to describe molecular reactions as well as an extended metallic surface without assumptions about the atomic interaction. DFT has therefore been used extensively, and successfully, for explaining properties of gas-phase reactions at surfaces. The situation in a DMFC is, on the other hand, more complex since the water solution and the water/ Platinum interface will influence the reaction kinetics. In this paper we describe first-principles simulations of methanol in the water-Pt interface.

Keywords: ab-initio, molecular dynamics, CH3OH at H2O/Pt interface

1 INTRODUCTION

Improved catalysts are among the engineering achievements, including a reduction in the overall cost of the system, necessary for Direct Methanol Fuel Cells (DMFC) to become a competitive alternative for both portable and stationary power applications. An important step towards improving existing solutions, in turn, is a fundamental, molecular based, understanding of the catalytic processes.

Computer simulations, in particular calculations from first principles, have proven to provide key insights into gas-phase catalytic reactions. Density Functional Theory (DFT) [1,2] stands out as the method of choice for this type of problems. With DFT, it is possible to describe molecular reactions as well as an extended metallic surface without assumptions about the atomic interaction. DFT has therefore been used extensively, and successfully, for explaining properties of gas-phase reactions at surfaces. The situation in a DMFC is, on the other hand, more complex since the water solution and the water/ Platinum interface will influence the reaction kinetics. In this paper we describe first-principles simulations of methanol in the water-Pt interface.

2 METHOD AND SYSTEM

As mentioned in the introduction, DFT is the method of choice for studying large and complex systems from first principles. For the problem at hand, a mixed system consisting of a liquid/ metal interface, it is necessary to use periodic boundary conditions. A periodic calculation will correctly describe the extended surface states of the metal surface in a way a cluster calculation cannot. A Pt cluster will not show metallic character until being very large.

DFT is formally exact, however, the simplification compared to wave-function based method comes with a price, the unknown form of the exchange-correlation (XC) functional. The functional is approximated in calculations and the choice of functional a most important one. Traditionally, the choice has been between local density approximation [2] (LDA) and Generalized Gradient Approximation [3] (GGA). Today, hybrid functionals [4], where Kohn-Sham exchange is mixed with exact exchange, is increasingly common in chemistry. Hybrid functionals give excellent results for many properties of small molecule, like water, and would be a preferred choice for water/methanol interaction. However, it is not at present possible to use hybrid functionals for metallic systems, so we will use the traditional functional PW-91 [3]. The parameters of PW-91 are not found by fitting to experimental data, PW-91 is non-empirical. PW-91 still describes the atomization energy of water well [5].

We use the plane-wave pseudo-potential code VASP [7]. We use the hardest versions of the ultra-soft pseudopotentials [8] with a plane-wave cutoff energy of 400 eV as well as the more advanced PAW potentials [9]. The number of k-points necessary was determined for both geometries used (2×2 and 2×3 Pt atoms). In the 2×2 case we find that a 3×3×1 and 6×6×1 k-point mesh give similar results and for the 2×3 cell we used a 4×2×1 grid. The Molecular Dynamics (MD) simulations were done in a canonical ensemble, using the Nose algorithm [10], as implemented in VASP, with 0.4 fs time step.

Next, we will describe the setup of the system. Each Pt atom has 10 electrons and reducing the number of electrons

is instrumental in being able to get a reasonable calculational time. We confirm the finding that already three Pt layers give a good description of the surface [11]. H adsorption energies for 3, 4, and 5 layer thick slabs, using both LDA and GGA, are given in Table I.

Pt layers	E_{Ads}^{GGA} (eV)	E_{Ads}^{LDA} (eV)
3	3.05	3.36
4	3.07	3.33
5	3.03	3.28

Table 1: Hydrogen adsorption energy as a function of slab thickness for LDA and GGA. A three layer thick slab allows a good description of hydrogen adsorption.

Hydrogen is chemisorbed to the surface and thus much more strongly bound to it than physisorbed water or methanol molecules. The slab thickness is arguably even less important in the weakly bound cases.

The next factor limiting the computational time is the number of water molecules. There is evidence of a first solvation shell around the methanol molecule consisting of 12-15 water molecules [12,13]. This sets a lowest limit on the number for water molecules required for approaching a realistically solvated system. We used 19 water molecules, which enable a first shell to be formed. In total, the system studied in the Molecular Dynamics simulations has 18 Pt atoms (six atoms in each of the three layers of the slab), 19 water molecules, and one Methanol molecule. The system is shown in Figure 1.

In order to have a well-defined pressure in the calculation we minimize the energy with respect to the periodicity in the Z direction, looking for minimum volume. This corresponds to zero pressure. In a standard liquid calculation zero pressure is achieved by changing, uniformly, the volume of the periodic cell. In the case of a periodic cell including a metal slab we must proceed differently. The slab geometry allows only for volume optimization by changing the difference between the slabs since the distances in the metal planes is set by the Pt lattice constant. First, we assumed that the initial layer towards the metal is of the typical bi-layer form of ice. We then found the optimum distance by freezing the water bilayer and changing the slab distance until a minimum in energy was found after optimization. This optimal slab-slab distance was then kept .

To quantify the surface-methanol interaction we looked at different geometries with the methanol at different distances from the surfaces, as illustrated in Figure 1.

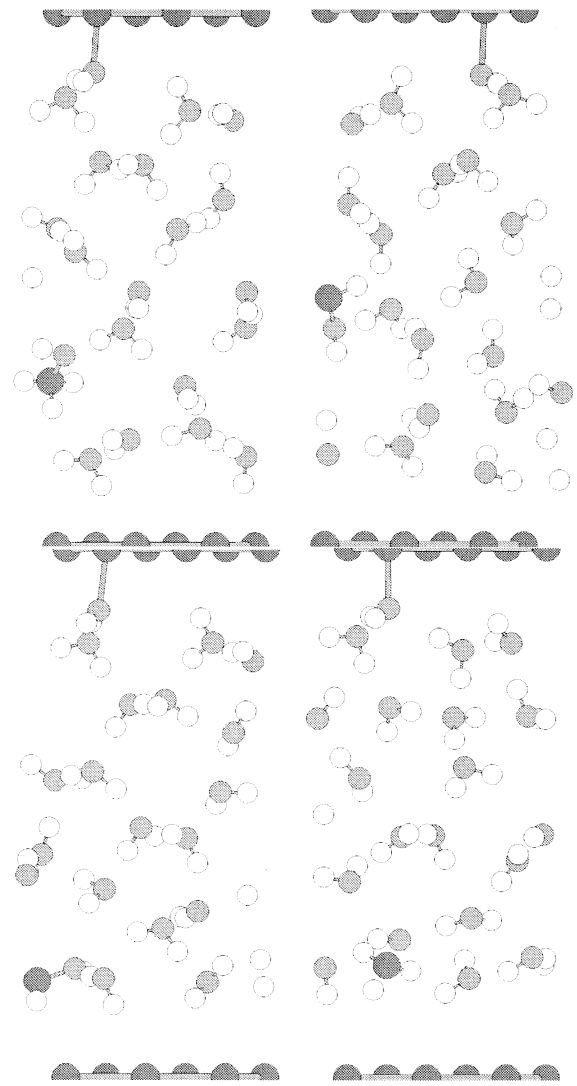

Fig. 1: The four primary structures compared in this study, a) CH3OH just outside the water bilayer; b) CH3OH in bulk water, represented by being in the center of the simulation cell; c) CH3OH replacing a water molecule in the bilayer; d) CH3OH replacing a water molecule in the bilayer, initially with a different orientation than c). The periodic boundary conditions cause atoms in the same molecule to appear disconnected.

3 ANALYSIS OF THE MD RUNS

A molecular dynamics run results in a wealth of data, all providing details of the system under study. We primarily monitor energies, bond-lengths, bond-angles, radial distribution functions, and correlation functions. In this paper we will focus solely on the vibrational spectrum obtained from he velocity-velocity correlation function [14]. The vibrational spectra are based on 7-10 ps long MD simulations; the resolution is 80 cm^{-1}.

Figure 2, shows the effect of water solvation and the presence of a Pt surface on the vibrational properties of

methanol. The hydrogen atom on the OH group is strongly influenced by solvation in water: the vibrational peak shifts 500 cm^{-1}. Solvation in water has a far less influence on the hydrogen atoms in the CH_3 group. In this geometry, c in Figure 1, the CH3 group is closest to the Pt surface and it clearly affects the Hydrogen vibration: the peak is broadened and the frequency is lower by about 300 cm^{-1}. A lower vibrational frequency is a signature of a weaker C-H bond. For comparison, a Raman study [15] shows that the methanol concentration affects the C-H vibrational frequency 10 cm^{-1} over the entire range of concentration ($0.0<x<1.0$).

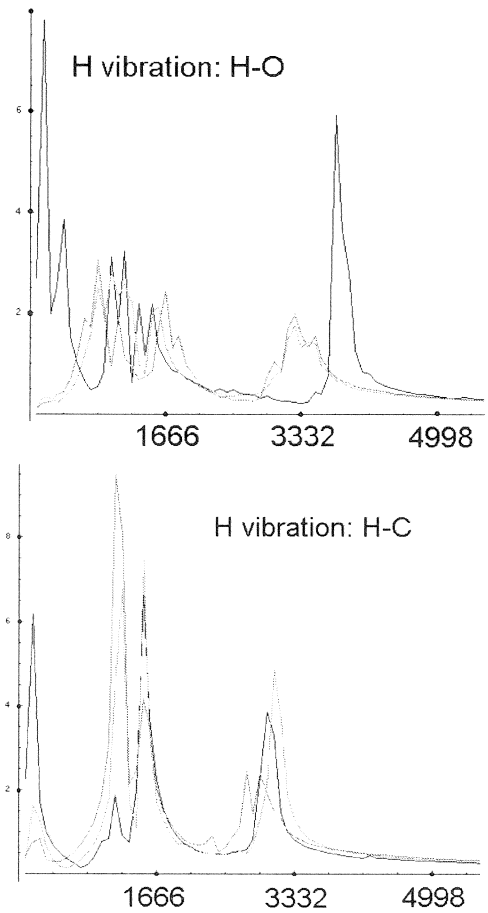

Fig. 2: Hydrogen vibrational spectra plotted as a function of the inverse wavenumber, in cm^{-1}. **Left**: for the H atom in the OH group. **Right**: for one of the H atoms in the CH3 group. Methanol in vacuum (black); Methanol in water - geometry b in Figure 1 (red); Methanol in water close to the Pt surface- geometry c in Figure 1 (blue).

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REFERENCES

[1] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).
[2] W. Kohn and L. J. Sham, Phys. Rev. **140**, 1133 (1965).
[3] A. D. Becke, J. Phys. Chem. **98**, 1372 (1993).
[4] J.P. Perdew, *et. al* Phys. Rev. B **46**, 6671 (1992); Phys. Rev. B **48**, 4978 (1993).
[5] S. Kurth, J.P. Perdew, and P. Blaha, I. J.of Quantum Chemistry 75, 889 (1999).
[6] G. Kresse and J. Hafner, Phys. Rev. B **47**, 558 (1993); **49**, 14251 (1994); G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).
[7] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L.J. Sham, Phys. Rev. **140**, A1133 (1965).
[8] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990); G. Kresse and J. Hafner, J. Phys. Cond. Matt. **6**, 8245 (1994).
[9] P.E. Blöchl, Phys. Rev. B **50**, 17953 (1994); G. Kresse, and J. Joubert, Phys. Rev. B **59**, 1758 (1999).
[10] S. Nosé, J. Chem. Phys. **81**, 511 (1984).
[11] S. K. Desai, M. Neurock, and K. Kourtakis, J. Phys. Chem. **106**, 2559 (2002).
[12] A.K. Soper and J.L. Finney, Phys. Rev. Lett. **71**, 4346 (1993).
[13] T. S. van Erp and E.J. Meijer, Chem. Phys. Lett. 333, 290 (2001).
[14] C. Lee, D. Vanderbilt, K. Laasonen, R. Car, and M. Parrinello, Phys. Rev. B. **47**, 4863 (1993).
[15] S. Dixit, W.C.K. Poon, and J. Crain, J. Phys. Cond. Matt. **12**, L323 (2000).