

PERIODIC DFT STUDY OF THE EFFECT OF UNIFORM ELECTRIC FIELD ON CHEMISORPTION OF MOLECULES ON METAL SURFACES

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Summary

Periodic DFT calculations are used to study the effect of an homogeneous electric field applied perpendicular to a Pt(111) and other metal surfaces on the bond distances, binding energies and vibrational frequencies of adsorbed molecules at different adsorption sites (Figures 1 and 2). The observed structural and energetic modifications can be understood in terms of modest field-induced charge transfer between charged metal surface and adsorbate and are well-described by classical first and second-order Stark models. Zero-field dipole moment and polarizability of the molecule in chemisorbed state are the two parameters affecting the field dependence of chemisorption energy.

Keywords

Computational catalysis

Introduction

Imposed or intrinsic electrostatic fields can have a significant effect on the chemisorption of molecules at metal surfaces and thus are important in a number of physical systems related to electrochemistry and catalysis. For example, electrochemical double layer at metal solution interface imposes a uniform electric field on the molecules adsorbed on the electrode surface in the electrochemical systems¹. In heterogeneous catalysis chemisorbed molecules can experience strong local electric fields due to co-adsorbed ions and molecules² or metal support charge transfer³. In the present study periodic DFT calculations are used to study the effect of an homogeneous electric field applied perpendicular to a Pt(111) and other metal surfaces on the bond distances, binding energies and vibrational frequencies of adsorbed molecules at different adsorption sites.

Results and Discussion

The different molecules studied include CO, NO, ethylene, oxygen and other molecules of interest to heterogeneous catalysis. Particularly, the effect of electric field on adsorption energetics and vibrational properties of CO has been studied in detail⁴. Electronic differences between atop and fcc adsorption cause CO in these sites to respond differently to applied fields. After correcting for the GGA site preference error⁵, CO adsorption on Pt(111) is predicted to shift from atop to fcc at potentials < -0.19 V \AA^{-1} [Figure 2(left)]. The results are in qualitative agreement with previously reported cluster-based DFT models⁶, but differ quantitatively due to difference in modeled coverage, surface relaxation, and finite size

effects. The calculated $44.4 \text{ cm}^{-1} \text{ V}^{-1} \text{ \AA}$ shift in C-O stretch frequency with electric field (Stark tuning rate) [Figure 2 (bottom)] compares favorably with UHV experiments⁷ but is significantly lower than the value obtained in electrochemical measurements⁶, highlighting the importance of adsorbate environment on the magnitude of the tuning rate. The calculated coverage dependence of the tuning rate is in good agreement with previous UHV experiments⁷. Effect of correction of DFT-GGA errors on adsorption energetic and vibrational properties for different metals and adsorbates has also been analyzed. Experimental work is underway using nanofabricated nanowires and a new sensitivity enhanced IR spectroscopy method to verify some of the theoretical predictions on supported catalysts.

References

- (1) Koper, M. T. M.; van Santen, R. A.; Wasileski, S. A.; Weaver, M. J. *The Journal of Chemical Physics* **2000**, *113*, 4392.
- (2) Pacchioni, G.; Lomas, J. R.; Illas, F. *Journal of Molecular Catalysis. A, Chemical* **1997**, *119*, 263.
- (3) Jochum, W.; Eder, D.; Kaltenhauser, G.; Kramer, R. *Topics in Catalysis* **2007**, *46*, 49-55.
- (4) Deshlahra, P.; Wolf, E. E.; Schneider, W. F. *Journal of Physical Chemistry A* **2009**, *113*, 4125-4133.
- (5) Mason, S. E.; Grinberg, I.; Rappe, A. M. *Phys. Rev. B* **2004**, *69*, 161401.
- (6) Wasileski, S. A.; Koper, M. T. M.; Weaver, M. J. *Journal of Physical Chemistry B* **2001**, *105*, 3518-3530.

(7) Luo, J. S.; Tobin, R. G.; Lambert, D. K. *Chemical Physics Letters* **1993**, *204*, 445.

Figures

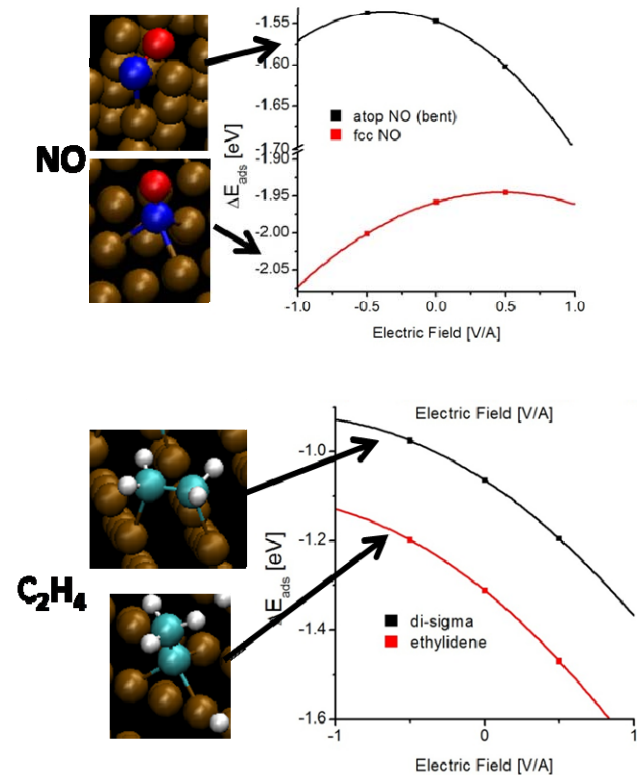


Figure 1: Adsorption energies of NO and C₂H₄ on Pt(111) in the presence of electric fields.

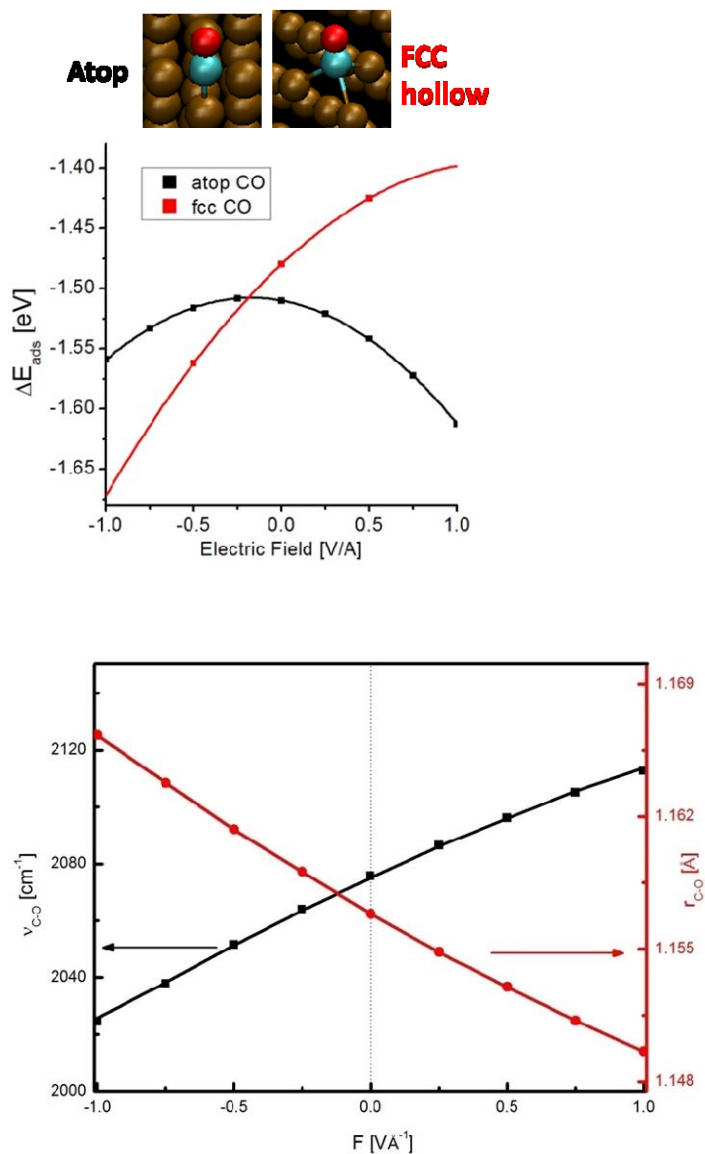


Figure 2: CO adsorption energies (top), and C-O bond lengths and vibrational frequencies (bottom) on Pt(111) in the presence of electric fields.