# Calorimetric Benchmark Energies of Adsorbed Intermediates, Solvent Effects and Solvent / Catalyst Bonding

Overview:
Better catalysts and electrocatalysts are essential for the efficient production and use of clean fuels, for energy efficient chemical synthesis with less environmental impact, for energy storage, for pollution abatement and for many other future technologies needed to achieve environmentally friendlier energy supply and chemical industry. Crucial for rational design of better catalyst and electrocatalyst materials is the knowledge of the energies of elementary chemical reactions on late transition metal surfaces. Experiments are proposed to measure the energetics of selected elementary chemical reactions occurring on late transition metal surfaces, carefully chosen to enable development of new theoretical methods for more accurately predicting such energies, to improve basic understanding of catalytic action and the effect of liquid solvents on these, and to facilitate the design of better catalysts and electrocatalysts. The main goal of this research is to broaden the database of reliable experimental energies of adsorbed catalytic intermediates (and effects of liquid solvents on these) that can be used by theoreticians as benchmarks to guide development of computational methods with improved accuracy for calculating the energetics of chemical reactions at late transition metal surfaces in both liquid and gas phase.
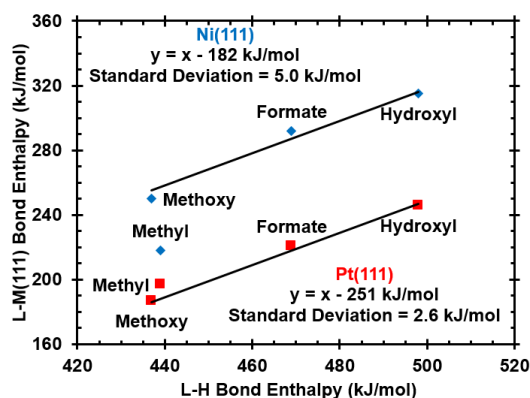
Figure 1: Calorimetrically measured bond enthalpies of four molecular fragments to Ni(111) and Pt(111) versus their corresponding gas-phase hydrogen-ligand bond dissociation enthalpies, from [P10]. The two lines shown, one for each metal and each with a slope of 1, fit the three oxygen-bound adsorbed species well.

Intellectual Merit:
Fast computational methods like density functional theory (DFT) offer our greatest promise for designing new catalysts, electrocatalysts, and batteries and new processes for energy and environmental technologies. However, their power at achieving this would be multiplied many fold if these methods could be improved to achieve higher accuracy in calculating the energies of adsorbed reaction intermediates and the effects of liquid solvents on these energies. This would be transformative for catalysis research, enabling greater reliability in computational prediction of reaction rates and mechanisms. Such improvement requires an accurate experimental database of adsorbate energies on a range of well-defined model catalyst surfaces, the effects of solvents on these energies, and the strengths of solvent bonding to well-defined catalyst surfaces. Developing such a database is the main goal of the proposed research. In addition to guiding improvements in DFT, it will also help clarify the energetic basis for structure-reactivity correlations and solvent effects in transition metal catalysis and electrocatalysis. Specifically, the adsorption energies of several common adsorbed catalytic reaction intermediates will be measured by calorimetry on Cu(111) in gas phase, for comparison to earlier results for these same adsorbates on Pt(111) and Ni(111). The adhesion energies of several liquid solvents to these metal surfaces will also be measured. According to a theoretical model recently developed by the PI, these can be combined with gas-phase adsorption energies to estimate solvent effects on adsorption energies of reaction intermediates. This model will be validated by direct calorimetric measurements of the effects of thin solvent layers on adsorption energies. The proposed measurements cannot be performed anywhere else in the world, yet they will provide crucial input to improve accuracy of

computational methods and enable substantial progress in understanding and computationally predicting the differences in activity and selectivity between different catalyst materials and different solvents.

Broader Impacts:
This research will aid in designing more efficient and environmentally-clean catalysts, electrocatalysts and processes for energy technologies and chemical industry, and for storing solar and wind energy, all crucial for sustainable living. It will provide strong interdisciplinary, research-integrated education for numerous graduate and undergraduate students. These students will get hands-on experience with state-of-the-art measurement instrumentation and will learn to apply these to solve intellectually-challenging research problems on topics of great national interest. The students will interact with outstanding visiting scientists and will be offered opportunities for research in national labs or labs of international collaborators. They will be mentored in scientific leadership, public speaking and responsible conduct of research. This research will be integrated into the PI's classes. It will also provide new research opportunities for a young female Associate Professor. The PI will continue his extensive outreach to the broader community, through his frequent public lectures, numerous editorships and advisory board memberships, and service to university and external science and education initiatives.
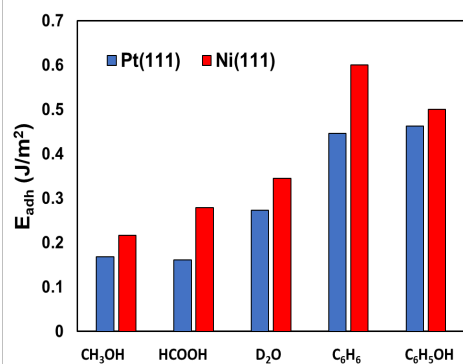
Figure 2: Adhesion energies for five liquid solvents on clean Pt(111) and Ni(111) surfaces estimated using their calorimetric heats of adsorption. From [P14].
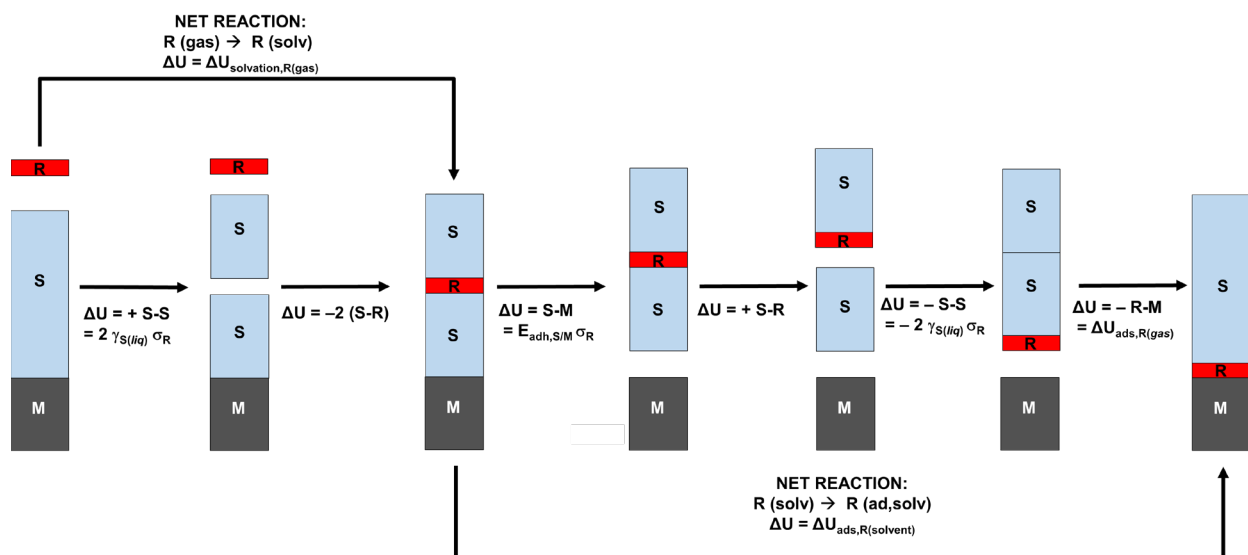
Figure 3. Thermodynamic cycle using pairwise bond additivity to relate the energy of adsorption of a flat reactant molecule (R) onto a clean metal surface (M) in gas phase (– R-M) with that measured in a solvent (S). Here we show each step's change in internal energy (ΔU) at the temperature of interest. The surface energy ($\gamma_{S(liq)}$) and adhesion energy (E_{adh}) are energies per unit area, so these are multiplied by the area per adsorbed R molecule (σ_R). From [P14], adapted from ref. [43].
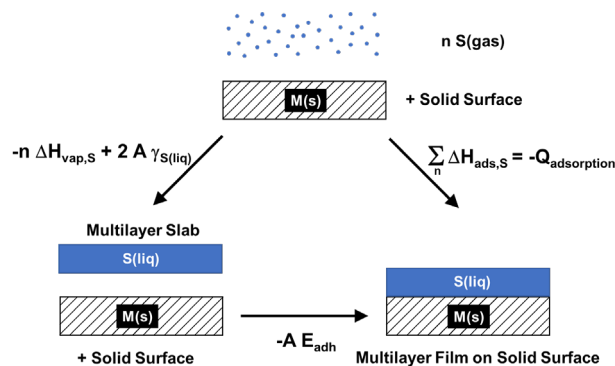
Figure 4. Thermodynamic cycle connecting the integrated heat of adsorption of gas phase solvent molecules (S) to its adhesion energy (E_{adh}) for a thick multilayer film of S(liq) on a surface of some solid material (M) covering some surface area (A). From [P14].

Recent publications from this NSF-funded project:

P1. Energies of Formation Reactions Measured for Adsorbates on Late Transition Metal Surfaces, T. L. Silbaugh and C. T. Campbell, *J. Physical Chemistry C* (Invited Review) 120, 25161–25172 (2016). http://dx.doi.org/10.1021/acs.jpcc.6b06154

P2. A DFT-Based Method for More Accurate Adsorption Energies: An Adaptive Sum of Energies from RPBE and vdW Density Functionals, A. J. R. Hensley, K. Ghale, C. Rieg, T. Dang, E. Anderst, F. Studt, C. T. Campbell, J-S. McEwen and Y Xu, *J. Physical Chemistry C* 121, 4937−4945 (2017). http://dx.doi.org/10.1021/acs.jpcc.6b10187

P3. The Energetics of Adsorbed Methyl and Methyl Iodide on Ni(111) by Calorimetry: Comparison to Pt(111) and Implications for Catalysis, S. J. Carey, Wei Zhao, A. Frehner and C. T. Campbell, *ACS Catalysis* 7, 1286−1294 (2017). http://dx.doi.org/10.1021/acscatal.6b02457

P4. Energetics of Adsorbed Formate and Formic Acid on Ni(111) by Calorimetry" Wei Zhao, Spencer J. Carey, Sawyer E. Morgan and Charles T. Campbell, *Journal of Catalysis* 352, 300–304 (2017). http://dx.doi.org/10.1016/j.jcat.2017.05.023 .

P5. Velocity resolved kinetics reveals the site-specific mechanism of CO oxidation on platinum surfaces, J. Neugebohren, D. Borodin, H. W. Hahn, J. Altschäffel, A. Kandratsenka, D. J. Auerbach, C. T. Campbell, D. Schwarzer, D. J. Harding, A. M. Wodtke and T. N. Kitsopoulos, *Nature* 558, 280-283 (2018). https://doi.org/10.1038/s41586-018-0188-x

P6. Adsorbed Hydroxyl and Water on Ni(111): Heats of Formation by Calorimetry, Wei Zhao, Spencer J. Carey, Zhongtian Mao and Charles T. Campbell, *ACS Catalysis* 8, 1485-1489 (2018). http://dx.doi.org/10.1021/acscatal.7b04041

P7. Energetics of Adsorbed Benzene on Ni(111) and Pt(111) by Calorimetry, Spencer J. Carey, Wei Zhao, and Charles T. Campbell, *Surface Science* (special issue in honor of Peter Norton) 676, 9-16 (2018). http://dx.doi.org/10.1016/j.susc.2018.02.014

P8. Energetics of Adsorbed Phenol on Ni(111) and Pt(111) by Calorimetry," Spencer J. Carey, Wei Zhao, Zhongtian Mao and Charles T. Campbell, *J. Phys. Chem. C* 123, 7627–7632 (2019) (invited). http://dx.doi.org/10.1021/acs.jpcc.8b03155

P9. Energetics of Adsorbed Methanol and Methoxy on Ni(111): Comparisons to Pt(111), Spencer J. Carey, Wei Zhao, Elizabeth Harman, Ann-Katrin Baumann, Zhongtian Mao, Wei Zhang and Charles T. Campbell, *ACS Catalysis* 8, 10089−10095 (2018). http://dx.doi.org/10.1021/acscatal.8b02992

P10. Bond Energies of Adsorbed Intermediates on Metal Surfaces Correlate with H-Ligand and H-Surface Bond Energies and Electronegativities, Spencer J. Carey, Wei Zhao and

Charles T. Campbell, *Angewante Chemie International Edition (Communications)*, 57, 1 – 6 (2018). http://dx.doi.org/10.1002/anie.201811225

P11.   Energies of Adsorbed Catalytic Intermediates on Transition Metal Surfaces: Calorimetric Measurements and Benchmarks for Theory, Charles T. Campbell, *Accts. of Chemical Research* 52, 984–993 (2019). (invited) (Also selected as *ACS Editors' Choice*). http://dx.doi.org/10.1002/anie.201811225

P12.   Origin of thermal and hyperthermal CO_2 from CO oxidation on Pt surfaces: The role of post-transition state dynamics, active sites, and chemisorbed CO_2, Linsen Zhou, Alexander Kandratsenka, Charles T. Campbell, Alec M. Wodtke and Hua Guo, *Angewandte Chemie Int. Ed.* 58, 1 – 6 (2019) http://dx.doi.org/10.1002/anie.201900565

P13.   The kinetics of elementary thermal reactions in heterogeneous catalysis, G. Barratt Park, Theofanis Kitsopoulos, Dmitriy Borodin, Kai Golibrzuch, Jannis Neugebohren, Daniel J. Auerbach, Charles T. Campbell and Alec M. Wodtke, *Nature Reviews: Chemistry* 3, 723-732 (2019). (invited *Perspective*) https://doi.org/10.1038/s41570-019-0138-7).

P14.   Adhesion Energies of Solvent Films to Pt(111) and Ni(111) Surfaces by Adsorption Calorimetry, John R. Rumptz and Charles T. Campbell, *ACS Catalysis* **9**, 11819−11825 (2019). DOI: 10.1021/acscatal.9b03591.

P15.   Enhanced Bonding of Pentagon-Heptagon Defects in Graphene to Metal Surfaces: Insights from the Adsorption of Azulene and Naphthalene to Pt(111), Benedikt P. Klein, S. Elizabeth Harman, Lukas Ruppenthal, Griffin M. Ruehl, Samuel J. Hall, Spencer J. Carey, Jan Herritsch, Martin Schmid, Reinhard J. Maurer, Ralf Tonner, Charles T. Campbell, J. Michael Gottfried, *Chemistry of Materials* **32**, 1041−1053 (2020). DOI: 10.1021/acs.chemmater.9b03744