Course on:
Chemical Dynamics at Surface

Boundary Conditions

- Thirteen three-hour lectures
- For a class of students who are nearly finished with their undergraduate studies, with a knowledge of introductory kinetics, quantum mechanics and thermodynamics and statistical mechanics.
- Text book – none. There isn't one. Maybe this will become the first.

Reading List

- See internet site.

Outline of the course

Powerpoints available via googledrive at this link

Audio

of lectures from 2012 available at this link

Outline

Introductory Section (3 Lectures)

Lecture I: A Little History

- Ammonia Synthesis [1, 2]
- Langmuir's first paper: Thermal Equilibrium of Reactions at High Temperatures [3, 4]
- Hydrogen Clean up in a Tungsten Lamp [5, 6]
- Clean-up of Oxygen in a Tungsten Lamp [7]
- Clean-up of Nitrogen in Tungsten Lamp [8]

Lecture II: Framing the Problem: Formulation of the Modern Approach

- Improving the World's greatest microscope
- Born and Oppenheimer make an Approximation [9, 10]
- The 'Standard Model' of Chemical Reactivity: The Electronically Adiabatic Potential Energy Surface
- Interpreting Chemistry through the Potential Energy Surface
- Extracting to the Potential energy surface from experiment
    - The Polanyi Rules: Promoting chemical reactivity and Product Energy Deposition [11].
    - The Hammond Postulate [12].
    - IR chemiluminescence
        - F+H_2 and F + Chlorobenzene[13]
        - JD McDonalds Instrument [14]
        - Extra credit [15]
        - The Chemical Laser [16-18]
    - Typical reaction mechanisms obtained from scattering experiments
        - Stripping
        - Direct rebound
        - Complex forming reactions
    - LIF and REMPI probes of product state distributions
    - Steric effects in chemical reactions [19]
- Properties of Molecular beams
    - Rotational Cooling [20]
    - Cluster formation: He_2 production [21]
- The F+H_2 crossed beam reactive scattering experiment: An instructive example [22, 23]

Lecture III: Dynamics in the Gas Phase – Advanced Topics

- The H + H_2 $\rightarrow$$H_2$+H reaction testing the standard model of chemical reactivity
    - Early attempts: Crossed beam reactive scattering of D + H_2 $\rightarrow$DH+H [24]
    - H-atom Rydberg tagging studies of the simplest Hydrogen exchange reaction [25-28]

        - Testbed for comparison with high level theory
            - Quantum bottleneck states [29]
            -
    - Vibrationally Adiabatic Potential Energy Surfaces: F+H_2 reaction as studied with Rydberg atom tagging [30] Hyperspherical coordinate representation [31]
    - O-atom Rydberg tagging [32]
    - Principles of differential pumping
        - Brink Ionizer [33]
    - Revealing Interstellar Chemistry [34]

What makes Dynamics at Surfaces different than Gas-phase dynamics (3 Lectures)

Lecture IV: The potential surface

- Overview:
    - The multidimensional aspect – i.e. it matters where on the surface you hit and
    - energy transfer to and from the reaction center that is an essential part of the reaction
    - The short answer is incomplete. A third very intriguing and unique aspect of surface dynamics is the ability of surfaces to line up reactants. So, steric effects in surface chemistry can maybe be controlled.
- PES must be treated differently
    - Theoretical methods for calculating the BO PES are different. In general Density functional theory must be used and it has problems.
    - Primer on Solid state physics: Miller indices
    - Surface reconstructions and site specific surface chemistry
    - 6D PES for H_2 dissociation on Cu [35]: The surface has structure, which is in general more complex than anything we have seen in gas phase dynamics. So, more degrees of freedom have to be considered and employed?
    - Phonons

Lecture V: Coupling to the solid through phonons and single molecule extinction of a laser beam

- Radiative Lifetimes, Einstein Coefficients, Cross-sections and all that stuff
- The Heterogeneous Linewidth: Single molecule spectroscopy [36]
- Energy transfer to Insulators [37]
    - Desorption
    - Radiation
    - Vibrational coupling to solid phonons: [38]
        - CPS model [39]
    - Dephasing
        - Single mode coupling model of dephasing [40]
    - Energy Pooling in weakly coupled adsorbate layers

        - Experiment [41]
        - Theory [42, 43]
    - Calculating excitation probabilities and single molecule absorption
        - H atom Lyman-α excitation probability with a laser beam (Hilborn)
        - Single molecule extinction[36]

Lecture VI: Coupling to the Electronic degrees of freedom of metals, IR line-width measurements

- Atomic sticking: Mechanical Model of translational inelasticity based on Ar Pt scattering [44]
- A simple picture of the electronic structure of a Metal:
    - The Fermi Function
    - Particle in a Box Density of states
    - Calculation of the Fermi Energy
    - Population of electronic states at a specific Temperature
    - Population of Holes
    - Extending this picture to Semiconductors
- IR absorption spectroscopy and linewidth measurements: [45, 46]
    - CO on Ni[47] compared to CO on NaCl [48]
    - compared to H on W[49], Assymetric Lineshapes indicate EHP coupling [50]
    - SiH IR Spectrosocpy [51]
- IR Emission Spectroscopy: Instrumental [52] examples [53, 54]

Experimental Probes of elementary steps in surface reactions (5 lectures)

Lecture VII: Real-time measurements of surface dynamics

- Isotope selective IR photodesorption of H_2 from H-terminated Si(111) [55]
- H on Si using IR-PUMP SFG-PROBE ultrafast spectroscopy
    - Experiment [56],
    - phonon dephasing model [47]
- CO on Cu using IR-PUMP SFG-PROBE ultrafast spectroscopy [57, 58]
- Polyatomic behavior: CH_3S [57]
- Transient IR absorption PUMP Probe: CO on Pt(111) [59]
- Intra-adsorbate Vibrational energy flow on vicinal Hydrogen terminated Si(111) [60]

Lecture VIII: Trapping dynamics and Surface Scattering as a probe of Energy transfer

- Measuring Sticking probability – The King and Wells Method [61].
- Precursor Mediated Chemisorption [62, 63]
- Dynamics of trapping: Direct Observation of Trapping-Desorption: Ar on H terminated W [64]
- Principle of Detailed Balance

- Cosθ distribution

Lecture IX: State-to-state scattering as a probe of reaction dynamics at surfaces

- A theoretical picture of sticking: H atom trapping to Cu(111) [65]
  - Evidence for the Hot atom effect
- Production of Subsurface H
  - Subsurface reactivity of H with methyl on Ni(111) [66, 67]
- Eley-Rideal Chemistry – One reaction partner is trapped already, but dynamics are very much like a gas phase reaction.
  - DABCO proton transfer from H-Pt [68, 69]
  - H on $Cl_{(ad)}$ [70, 71]
  - REMPI detection [72]
  - H/D on H-covered Copper [73] [74]
  - $CD_{3(ad)}$+D->CD_4 [75]
  - Hot atom variant of the Eley-Rideal reaction [76]. Collision Induced LH desorption [77]
- Vibrationally and Translationally promoted dissociative adsorption
  - CH_4 on Ni[78, 79]
  - SiH_4 on Si [80]

Lecture X: State-to-state beam scattering methods as a probe of electronically non-adiabatic energy transfer at surfaces

- Electron mediated proton transfer in molecular collisions at surfaces [68, 69]
- Rotationally Inelastic Scattering Zare N_2 on something. Rettner, Auerbach NO on Ag.
  - When you move to molecules, you need state-to-state methods.
- Adiabatic (mechanical) Energy transfer [81]
- Vibrational Excitation in a single bounce mediated by hot electron hole pair energy transfer: NO on Ag, [82]
- Vibrational excitation and Surface Temperature Dependence: NO scattering from Silver [82, 83]
- Scattering of highly vibrationally excited molecules
  - Stimulated emission Pumping [84, 85]
  - NO on Au(111) [86].
  - NO on Cs covered Gold [87] [88]
- Electronically Nonadiabatic Sticking [89, 90]
- Vibrational relaxation of CO on Cu [91] [58]
- NO vibrational energy transfer on Au(111) [86]
- Vibrationally promoted electron emission [87]
- Molecular Dynamics with Friction [92]
- Independent Electron Surface Hopping [93]
- Scattering oriented NO from Au(111) [94]

Lecture XI: The STM as a means of probing Surface Dynamics

- Elementary Background on how an STM works [95]
- Imaging electronic states [96]

- AFM can be better: CO functionalized tips [97]
- O_2 dissociation on Aluminum [98-100] O2 on Pt [101] Ertl; Hasselbrink did some REMPI (O_2-> $O_{(ad)}$ + $O_{(g)}$)
- Acetylene Vibrational spectroscopy Wilson Ho [102]
- Manipulating Atoms with an STM tip [103]
- Initiating reactions by bringing reactants together [104]
- Tunnel Electron induced Rotation of molecules on surfaces [105]
- State selective dissociation of H_2O on MgO covered Ag(100) [106]
- Laser heating for thermal desorption: Seeing the reaction mechanism with STM [107]
- Diffusion and its influence on reaction mechanism. [107-112]
- A comment about combining ultrafast fs lasers with STM's – a challenge for the future.

Interpreting Experiments with Theory (2 lectures)

Lecture XII: Quantum state dependence on reactivity: Comparison to the standard model of chemical reactivity

- Motivation
  - Activated dissociative adsorption, one of the important reaction mechanism paradigms for surface reactions [113]
  - Why is the study of activated adsorption interesting? Why H_2 / Cu in particular?
  - Need for benchmark systems
- 150 Years of Confusion – a little history [114]
- Experimental methods
- Main experimental results
  - Adsorption probabilities – state resolved results without state resolved measurements [115]
  - State resolved associative desorption – detailed balance [116, 117]
  - State resolved reflection [118]
- Low dimensional theory
  - Explains some of the puzzling results from the measurements
  - Gives a clear qualitative picture of the main physical phenomena [119]
- 6D Ab Initio Quantum Theory
  - Good agreement with adsorption probability as a function of translational energy, vibrational and rotational states [120]
  - Not quite there: still don't have agreement on vibrational excitation and orientational effects [121]
- Value of benchmarks and next steps

Lecture XIII: Applying Theory to heterogeneous catalysis

- Tools are limited but should not be underestimated.
- Strengths of DFT
  - DFT describes trends well [122]
  - DFT describes relative energies well [123]

- Application of DFT energetic Analysis to Heterogeneous catalysis: Kinetic Monte Carlo bridges time scales.
    - CO Oxidation on Ru [124]
    - NH_3 synthesis on Ru particles [125]
- The concept of Meta-data [126]
    - Scaling all the important kinetic parameters to a few calculable quantities
    - Calculating the reaction energetic for many metals, based on only knowing one. [127]
- The Volcano Plot [128]
- Computational Catalyst Design: Screening with software.
    - Using simple DFT calculations and scaling ideas in combination with kinetic understanding to screen for new candidate catalysts. [129]
    - Hydrogen evolution catalysts [130, 131]

READING LIST

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