

Summer Scholar Report

Determination of the Reactivity of the Vibrational Ground State of Methane on Ni(111)

Patrick Kelleher*, Cameron Hill*, Yongli Huang**, Nan Chen**, Dr. Deno Del Sesto*, Dr. Arthur Utz**

*Department of Chemistry, Stonehill College, Easton, MA, **Department of Chemistry, Tufts University, Medford, MA

Introduction:

A great deal of the field of chemistry revolves around the breaking and formation of bonds. The gas-surface dynamics of heterogeneous catalysis are of particular interest due to their pervasiveness in technology and chemical industry. Catalysts contribute towards roughly one third of the material GDP of the US economy¹ and also enable the Earth to sustain an additional 3.2 billion people via the ammonia fertilizer producing Haber-Bosch process.² Understanding exactly how the bonds of a gas molecule break in the presence of a metal catalyst would allow us to better predict and control these reactions in order to develop more efficient processes.

Our work focused on the reaction dynamics of methane on a Ni(111) surface. Methane is the main reagent in the steam reformation process, which is the source of 95% of hydrogen gas produced in the United States.³ Methane is also of great interest from a theoretical standpoint. Its four different vibrational modes can be accessed with sufficiently long excited state lifetimes using infrared radiation, making it ideal for studying the effects of vibrational mode excitation on reactivity. Because methane is the simplest alkane, it is also the most basic gas in which C-H bond activation can be studied. Diatomic gases have only one fundamental vibrational mode and have been well studied. The vibrational modes of more complex polyatomic molecules are often indiscernible from one another and the mathematical tools needed to study them have not yet been developed.

Background:

Statistical models have often been used to describe the scaling of reactivity with total energy. Recent work by the Utz group at Tufts University and others have pointed towards the existence of mode selective chemistry in which the reactivity does not solely depend on how much energy is put into a system but also how this energy is distributed.⁴

A prerequisite condition for mode selective chemistry occurring is that energy redistribution within individual molecules is sufficiently slower than the reaction time. Molecules that are selectively excited must remain excited long enough to react in order to influence reactivity. This condition being met makes mode selective chemistry possible, but does not ensure that it will occur. "Late" barrier reactions with geometrically "tight" transition states provide the best opportunity for vibrational energy to activate the reagent. A "late" transition state more closely resembles the products and requires a great deal of distortion of the reagent's equilibrium geometry. A geometrically "tight" transition state means the activation energy for the reaction increases sharply if the reaction complex varies from the ideal geometry. Vibrational modes that distort the molecule to resemble the transition state will activate the reaction more so than other modes, producing mode selective behavior.

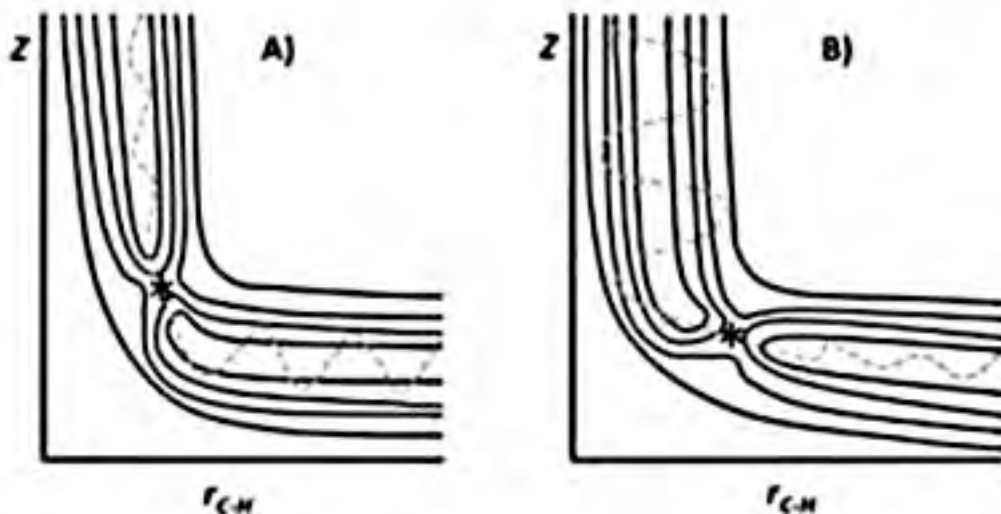


Figure 1. Two-dimensional Polanyi diagrams for methane adsorption.

Figure 1 shows two-dimensional Polanyi diagrams for the adsorption of methane on a surface. The contour lines show equal potential energy, and the saddle point is the energy of the transition state. The distance between carbon and hydrogen is denoted r and Z is the distance between hydrogen and the surface. Plot A represents the case where the reaction barrier, or saddle point, occurs in the translational coordinate (change in Z) before the C-H bond stretches. This is an “early” barrier and translational energy would be expected to be the most effective at promoting reaction. Plot B represents the case where the reaction barrier occurs in the vibrational coordinate (change in r) where the C-H bond length

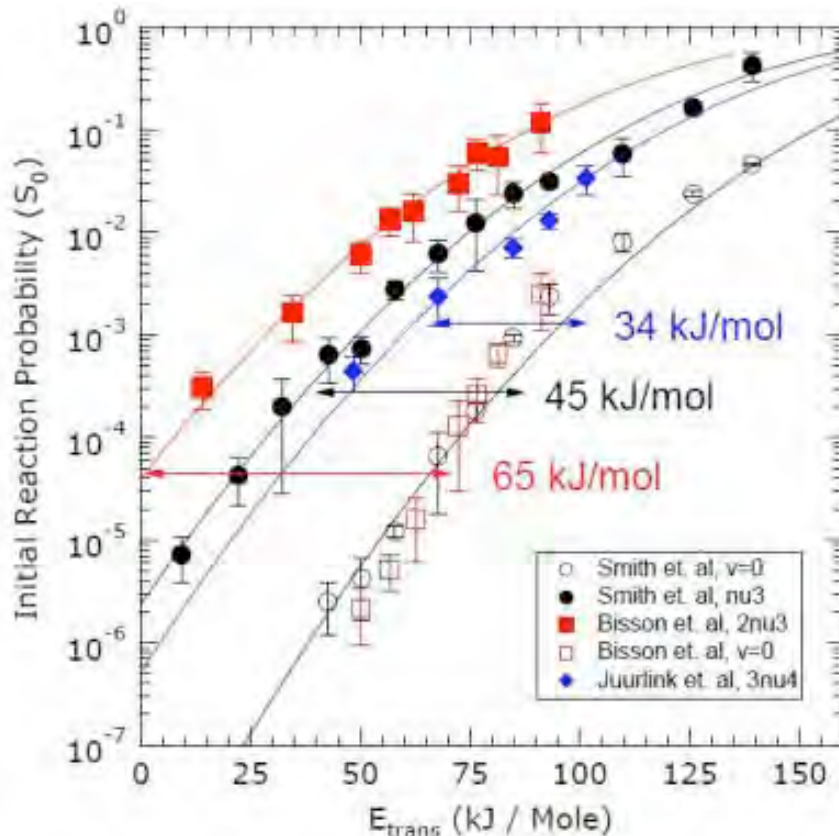


Figure 2. Sticking curves for ground state and activated CH_4 dissociation on Ni(111).⁶

is stretched. This is a “late” barrier and in this case vibrational energy would be expected to be the most effective at promoting reaction.

The Utz group⁴ and Beck group⁵ have performed a number of previous experiments to measure the reaction probability of methane on several surfaces. Differing reactivity for methane with the same total energy but different energetic configurations has been shown, identifying the vibrational modes that best promote transition state access for methane dissociation.

Figure 2 shows state-resolved reaction probabilities for methane dissociation on a Ni(111) surface at a surface temperature of 475 K. The filled in symbols denote reaction probabilities (black circles), (red squares), and (blue diamonds). Elevated nozzle temperatures are required to reach E_{trans} above 75 kJ/mol. Higher nozzle temperatures excite vibrational states in the molecules, which results in enhanced reactivity. This explains the deviation between the measured $S_0^{\text{Laser Off}}$ (open symbols) and the solid curve approximating $S_0^{v=0}$. The thermal excitation of vibrational states at higher E_{trans} makes it difficult to interpret how each state contributes to the sticking probability. The difference in energy between the $v=0$ curve and an excited vibrational state curve at a specific sticking probability is used to determine the vibrational efficacy. Determining an exact value for $S_0^{v=0}$ rather than using a curve to approximate it would enable us to more accurately calculate the sticking probability contribution for each vibrational state using Equation 1.

$$S_0^{v=n} = \frac{S_0^{\text{laser on}} - S_0^{\text{laser off}}}{f_{\text{exc}}} + S_0^{v=0}$$

The goal of our research this summer was to experimentally determine a value for $S_0^{v=0}$. Sticking curves needed to be prepared for gas mixes with the same kinetic energy but different fractions of thermally excited molecules. This can be achieved by mixing methane with lighter or heavier gas to vary the energy of a molecular beam at a given temperature. The relationship between nozzle temperature and the fraction of excited molecules (f_{exc}) follows a Boltzmann distribution. A second plot of sticking probability as a function of f_{exc} can then be made by taking vertical slices of the first plot. Each slice will have a specific kinetic energy and correspond to its own curve on the second plot. $S_0^{v=0}$ is the sticking probability of a beam in which all molecules are in the ground state. By extrapolating to the y-axis ($f_{\text{exc}}=0$) in the second plot, we can infer the ground state sticking probability at different kinetic energies. A final plot of the sticking probability as a function of kinetic energy at $f_{\text{exc}}=0$ will give us reliable values for $S_0^{v=0}$.

Experimental Procedure:

The Ni(111) crystal was cleaned each day by flashing above 1000K to bring impurities to the surface, followed by 5 minutes of argon ion sputtering to remove impurities, and finally annealing for 15 minutes

at 1075K to recover a (111) ordered surface. Auger electron spectroscopy was used to confirm the surface was clean. Once cleanliness was verified, the Ni(111) was dosed with a molecular beam. The schematic of the molecular beam apparatus is shown in Figure 3. The IR laser is used in mode-selective experiments to excite vibrational modes of methane. Our experiment deals only with molecules in the ground state, so the laser was not used. The main chamber has a base pressure of approximately 8×10^{-11} torr and a pressure with the beam on of approximately 1.7×10^{-7} torr.⁷ After each dose concluded all remaining gas was pumped from the chamber and the QMS was warmed up for analysis. The Ni(111) surface was exposed to a molecular oxygen beam created by the nozzle. Oxygen dissociates on the surface, reacting with adsorbed carbon to form CO which then desorbs. By monitoring the $m/z=28$ signal, the amount of carbon on the surface can be determined. The total amount of carbon in each dose is dependent on the dose time, flux, and composition of the gas mix used.

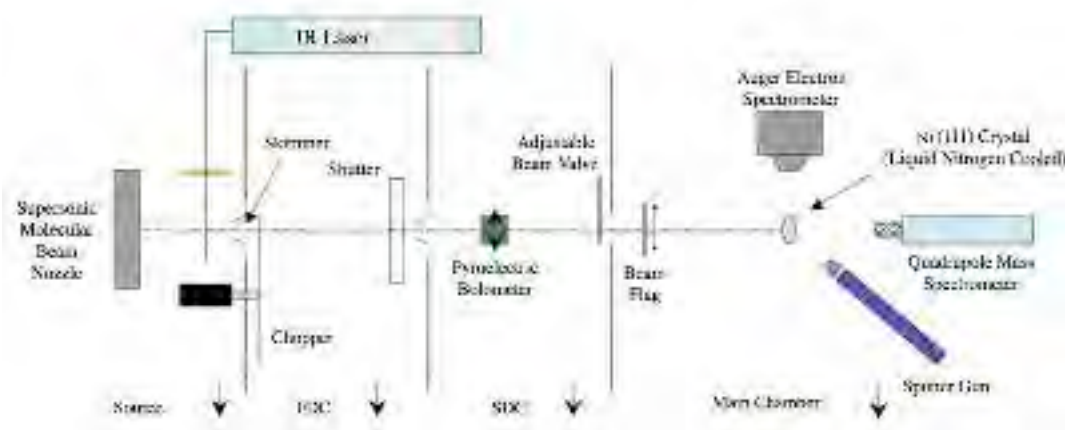


Figure 3. Molecular beam apparatus diagram.

Results and Discussion:

Several data points were gathered for a nozzle temperature of 900K. A curve to model the data was created using IGOR Pro 5.03 software. The data follows a trend that was expected based on past studies. Sticking probability data needs to be gathered at several different nozzle temperatures (f_{exc}) before further analysis can be carried out as discussed earlier.

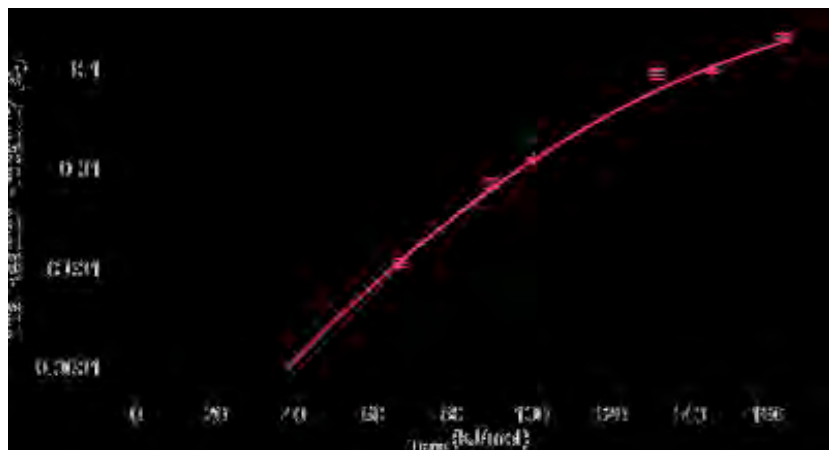


Figure 4. Sticking probabilities for $T_N=900K$.

Future Work:

Due to time constraints and setbacks with the molecular beam apparatus during the summer we were only able to construct a curve for one temperature. Future work needs to be done to gather data for a range of other nozzle temperatures. Once sufficient data is collected it can be analyzed as discussed earlier and a curve for $S_0^{v=0}$ as a function of kinetic energy constructed.

Acknowledgments:

I would like to thank the Norris/ Richards Undergraduate Summer Research Scholarship, my advisor, Dr. Deno Del Sesto (Stonehill College), our collaborator Dr. Arthur Utz, Stonehill SURE Scholar Cameron Hill, and the Utz Research Group at Tufts University including: Eric Dombrowski, Eric Peterson, Nan Chen, and Yongli Huang.

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