

# PTPC2019

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## Quantum State-Resolved Studies of Gas/Surface Reaction Dynamics by Vibrational Spectroscopies

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Methane dissociation is the rate limiting step in the steam reforming process used by the chemical industry to convert natural gas into a mixture of H<sub>2</sub> and CO known as synthesis gas. To better understand the microscopic mechanism and reaction dynamics of methane chemisorption, we use vibrational spectroscopies and infrared lasers for quantum state-resolved studies of methane dissociation and state-to-state scattering on Ni and Pt surfaces [1]. Our experiments prepare surface incident methane molecules in specific ro-vibrational quantum states by state-selective infrared laser excitation via rapid adiabatic passage in a molecular beam. The state prepared molecules then collide with a clean single crystal transition metal surface in ultrahigh vacuum and both reactive and non-reactive processes are monitored by infrared spectroscopic techniques.

Surface bound methyl species as products of the dissociative chemisorption of methane are detected on the platinum surface by Reflection Absorption Infrared Spectroscopy (RAIRS). RAIRS allows for real-time and in-situ monitoring of the uptake of chemisorbed methyl species enabling quantum state-resolved measurements of reactive sticking coefficients. RAIRS is also used to study the vibrationally bond selective dissociation of partially deuterated methanes demonstrating that a single quantum of C-H stretch excitation of the incident methane is sufficient to achieve bond-selective chemisorption. Furthermore, RAIRS allows for site specific detection of reaction products used to measure separately the dissociation probability of methane on steps and terraces sites on Pt(211) [2-3].

Non-reactive, inelastic energy transfer is probed by combining infrared laser tagging of scattered molecules with bolometric detection. These first methane state-to-state scattering experiments yield state-resolved information about rotation and vibrational energy transfer between the incident molecule and the solid surface [4].

Our state-resolved experiments provide clear evidence for mode- and bond-specificity as well as steric effects in chemisorption reactions and show that methane dissociation cannot be described by statistical rate theory but requires a dynamical treatment including all internal vibrational and rotational degrees of freedom of the dissociating molecule. The detailed reactivity and state-to-state scattering data from our measurements are used as stringent tests in the development of a predictive understanding by first principles theory [5-6] of these industrially important gas/surface reactions.

### References

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### Summary

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