

Quantum State Resolved Studies of Gas/Surface Reaction Dynamics

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Abstract: Laser light is an invaluable tool for detailed experimental studies of chemical reactions. The ability to prepare reagent molecules in specific quantum states and to resolve the quantum state distribution of reaction products using laser radiation has been key to the field of chemical reaction dynamics, which studies chemistry at a fundamental microscopic level. Today, state-resolved experiments are common for unimolecular and bi-molecular reactions in the gas phase, but equivalent measurements for gas/surface reactions have only recently started to appear. This contribution reviews the methodology developed in our group at the EPFL for the quantum state resolved investigation of molecule/surface reactions and gives representative results on the dissociative chemisorption of methane on single crystal nickel surfaces.

Keywords: Catalysis · Chemical dynamics of gas/surface reactions · Methane chemisorption · Quantum state preparation · State-resolved reactivity

Introduction

Experimental studies of gas/surface reactions have been extensively pursued due to their importance in many areas of science and technology such as catalysis, thin film growth, atmospheric and interstellar chemistry. For example, many useful chemical compounds are produced industrially *via* heterogeneous catalysis, where gas-phase reagents combine on the surface of a catalyst to form gaseous products. The purpose of the catalyst is to increase the reaction rate for the desired product by lowering the reaction's activation barrier, but frequently its microscopic mechanism is unknown and suitable catalysts are found more often by trial and error. A major difficulty in elucidating the mechanism of a molecule/surface reaction is the large number of molecular and surface degrees of freedom involved. Reactivity measurements performed under equilibrium conditions lead to results that are extensively averaged over many initial states, hiding details of the re-

action mechanism. To avoid this problem and obtain data that can be compared with theory without the need for extensive averaging, we perform experiments with incident molecules prepared in specific quantum states and cooled in a supersonic molecular beam. In studying the state-resolved reaction dynamics, we aim to explore how each of the translational, rotational, vibrational, and electronic degrees of freedom of the incident molecule, as well as those of the surface, affect the reaction outcome. This dynamical approach has been applied for several decades to a range of bimolecular reactions in the gas phase principally through crossed molecular beam experiments. The 1986 Nobel prize in Chemistry rewarded the pioneering work by Lee, Herschbach and Polanyi in this area. Similar methodology, combining a molecular beam of state prepared molecules with surface science techniques for preparation and analysis of single crystal surfaces in ultra-high vacuum, has started to be employed during the last five years in order to study technologically important gas/surface reactions at a comparable level of detail.

Methodology

Our experimental setup for the measurement of state-resolved gas/surface reactivity has been described in detail in a recent publication [1]. It combines a tunable, narrow bandwidth, pulsed laser system with a molecular beam/surface science ap-

paratus. Fig. 1 shows a schematic of the overall system with its different components. The main vacuum chamber consists of a triply differentially pumped molecular beam source connected to an ultra-high vacuum surface science chamber (base pressure 6×10^{-11} mbar). The path of the molecular beam inside the vacuum chamber is depicted in Fig. 2. We generate a pulsed molecular beam at 20 Hz by expanding mixtures of a seed molecule such as methane in a carrier gas of He or H₂ through a temperature-controlled solenoid valve with an open time of 300 μ sec. The beam pulses pass through a 1 mm diameter skimmer into the second differential pumping region where their duration is reduced to 30 μ sec by a chopper wheel rotating at 200 Hz. After a third differential pumping stage, the molecular beam enters the UHV chamber through a 1 mm diameter aperture, traverses a laser beam alignment tool and impinges at normal incidence onto a single crystal surface. The alignment tool ensures the overlap of the molecular beam with the laser beam, which is focused to a line by a cylindrical lens and crosses at 90°. The length of the line focus and the duration of the gas pulses are matched, so that depending on the speed of the beam, between 33% and 100% of the seed molecules are exposed to the excitation laser. Fig. 3 shows the layout of the optical system used to generate tunable laser radiation for the quantum state preparation in the molecular beam. We produce infrared laser pulses, tunable in the mid- to near-infrared (3.3–1.4

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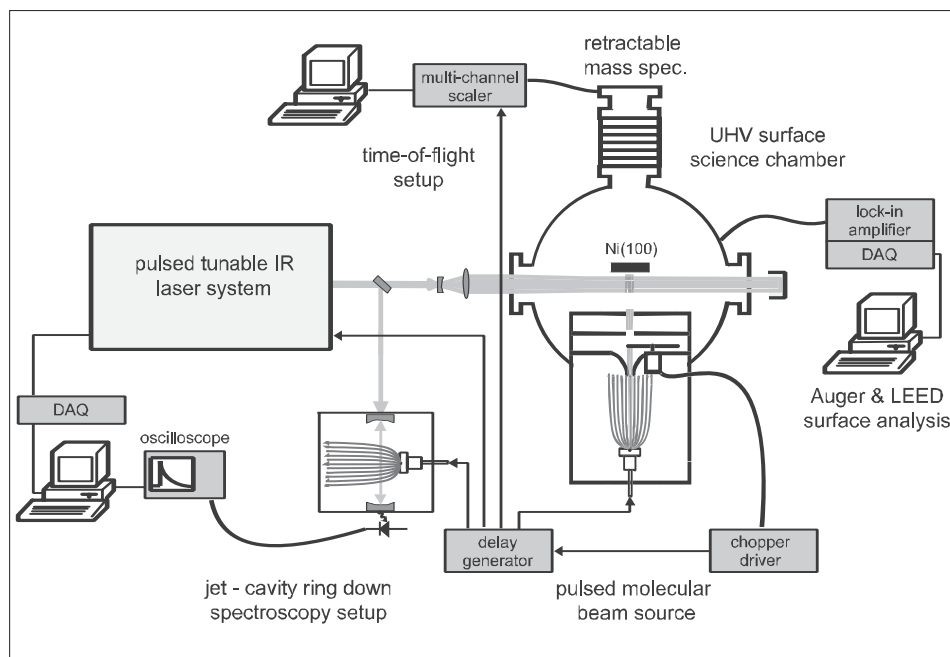


Fig. 1. Overall schematic of the experimental apparatus. The apparatus includes a molecular beam source for producing microsecond gas pulses, an ultra-high vacuum chamber equipped for surface analysis and product detection, a time-of-flight setup for molecular beam speed measurements, a pulsed laser system for generating intense laser pulses tunable in the range 3.3–1.4 μm , and a cavity ring-down spectrometer for measuring laser absorption in a jet expansion.

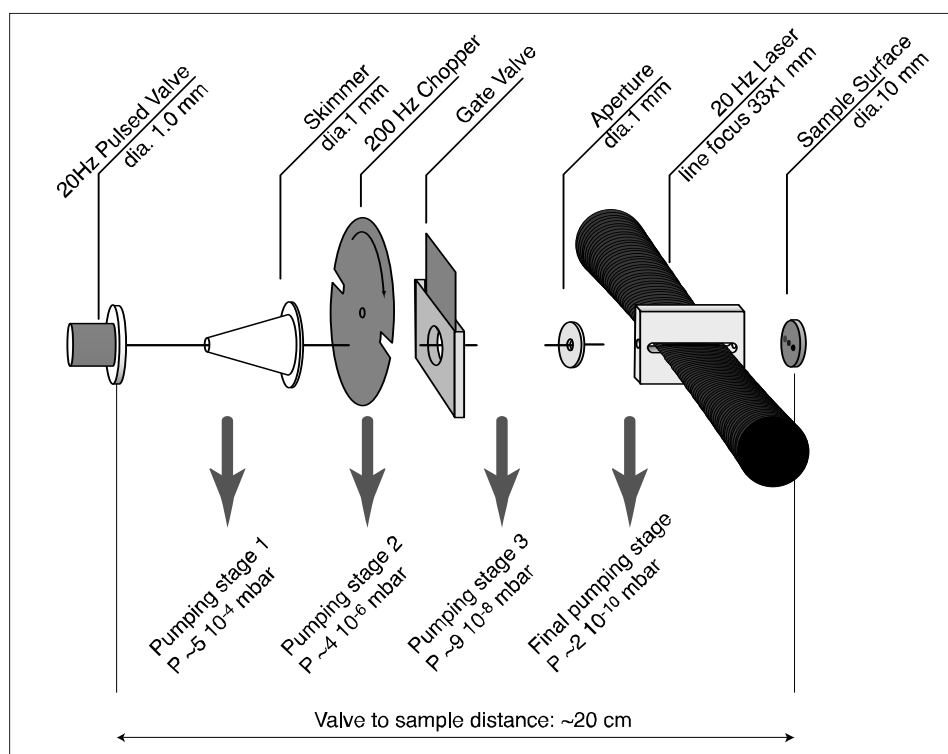


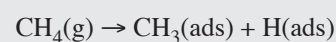
Fig. 2. Schematic view of the molecular beam path. Short molecular pulses formed by a pulsed valve and fast chopper wheel pass through three differential pumping stages before entering the UHV deposition chamber. A pulsed infrared laser beam is focused in one dimension by a cylindrical lens and overlapped with the molecular beam in an alignment tool.

μm), by generating the difference frequency between the fundamental output of an injection-seeded, single-mode Nd-YAG laser and a narrow band dye laser in a lithium niobate crystal followed by amplification in a two-stage optical parametric amplifier using KTP crystals. To ensure that the infrared

laser is tuned into resonance with the selected rovibrational transition of the incident molecules, we split off a small portion of the IR beam and do cavity ring-down spectroscopy (CRDS) in a separate expansion chamber. We also use the rotationally resolved CRDS spectra of the seed molecules

in the jet expansion to obtain information on the rotational level population needed for the sticking coefficient determination.

For the methane reactivity measurements described in this review, we use a 10 mm diameter Ni(100) single crystal surface oriented to within 0.1° . The surface is cleaned in the UHV chamber by Ar^+ sputtering/annealing cycles followed by oxidation and reduction treatments until impurities can no longer be detected by Auger electron spectroscopy (AES). We measure the translational energy, E_t , of the methane molecules in the beam by time-of-flight using the chopper wheel and an on-axis quadrupole mass spectrometer. We adjust E_t by varying the seed ratio and by small changes in the nozzle temperature. To determine absolute sticking coefficients for methane, we perform a timed exposure of the clean Ni(100) crystal to the molecular beam, measuring both the incident dose of CH_4 molecules per unit area as well as the resulting surface density of carbon reaction products. Initial sticking coefficients S_0 are calculated as the ratio between the surface density of carbon and the incident dose per unit area in the limit of low coverage (5–10% ML). We determine the flux of methane [$\text{molecules sec}^{-1} \text{cm}^{-2}$] incident on the surface from the methane partial pressure rise due to the molecular beam measured by a calibrated quadrupole mass spectrometer together with the beam cross section at the surface, which is measured by AES to be 0.03 cm^2 . The primary reaction products of the direct methane chemisorption on Ni(100) are adsorbed methyl and hydrogen according to [2]:



At the surface temperature of 475K at which we perform the deposition, the methyl radicals quickly dehydrogenate, and the hydrogen leaves the surface by recombinative desorption of H_2 . The carbon atoms remain on the nickel surface and are detected by AES. We repeat the deposition several times at different positions on the Ni(100) surface for improved statistics of the sticking coefficient measurements. After the depositions are completed, we move the surface in front of the Auger system and quantify the C coverage, recording C and Ni Auger signals at typically 80 points across the surface in an automated computer-controlled scan.

Fig. 4 shows an example of such an Auger line scan across the Ni(100) surface on which two depositions were performed with (left) and without (right) laser excitation. For the laser-on deposition, ~14% of the incident CH_4 molecules were excited with two quanta of asymmetric C-H stretch excitation *via* the $2\nu_3 \text{ R}(1)$ transition at 6026.21 cm^{-1} . The two ‘carbon spots’ pro-

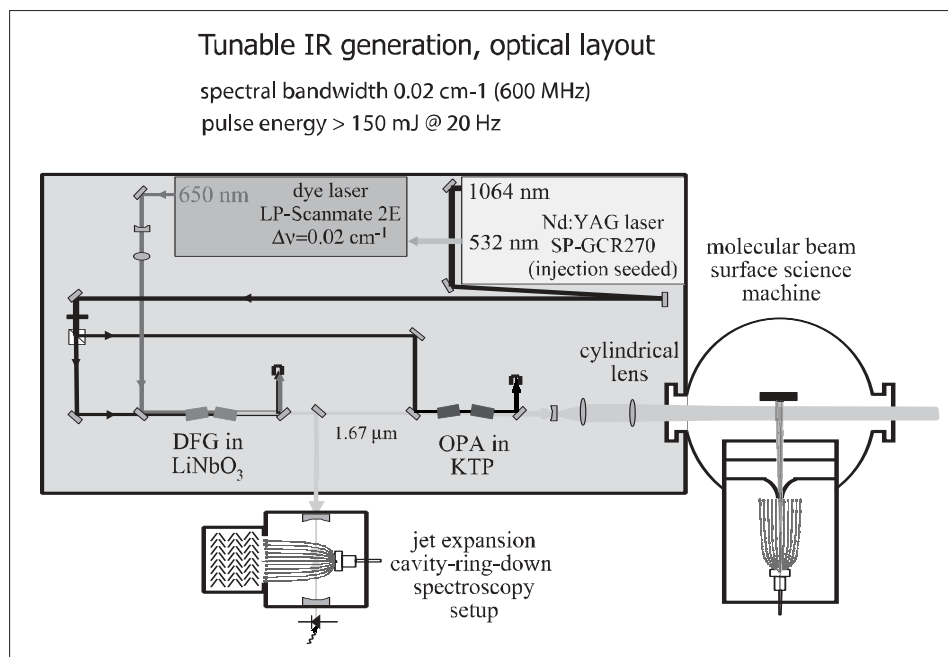


Fig. 3. Schematic of the laser system used for state preparation of the molecular beam. Tunable, narrowband infrared radiation is produced by difference frequency generation (DFG) between a single mode Nd-YAG and a narrow bandwidth dye laser. The output of the DFG stage is amplified in an optical parametric amplifier (OPA) to 150 mJ/pulse (20 Hz) of infrared energy.

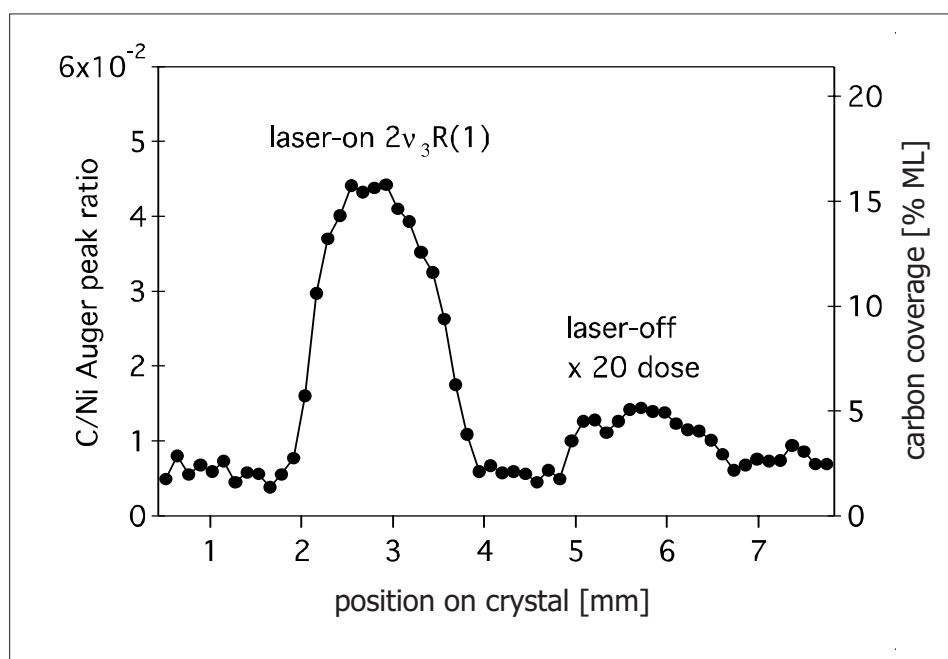


Fig. 4. Auger analysis of two carbon spots on the Ni(100) surface, resulting from local carbon deposition due to chemisorption of CH₄ in a molecular beam with 52 kJ/mol of incident kinetic energy. For the laser-on spot (left) 14% of the incident CH₄ molecules were prepared with 6004.69 cm⁻¹ of vibrational energy by pulsed laser excitation via the 2ν₃ R(1) transition. For the laser-off spot (right), a 20-time higher incident dose of methane was deposited to produce a detectable carbon spot.

duced by localized carbon deposition from the incident molecular beam show the footprint of the molecular beam on the Ni(100) crystal surface. The observed C/Ni Auger signal ratio (left-hand scale) is calibrated in terms of C coverage (right-hand scale) using ethylene exposures, which lead to a known saturation coverage of 0.5 ML carbon on the Ni(100) surface.

A comparison of the carbon spots, normalized to the incident dose of methane, shows the increase in the sticking coefficient averaged over all states populated with and without laser excitation, $S_0^{\text{laser-on}}$ and $S_0^{\text{laser-off}}$ respectively. As Juurlink *et al.* have shown [3], the state-resolved sticking coefficient can be calculated from the difference between laser-on and laser-off

measurements, taking into account the fractional population f_{exc} of the laser-excited state and adding the sticking coefficient for the vibrational ground state $v = 0$:

$$S_0^{2\nu_3} = \frac{S_0^{\text{laser-on}} - S_0^{\text{laser-off}}}{f_{\text{exc}}} + S_0^{v=0}$$

We determine f_{exc} experimentally from the laser power dependence of the carbon coverage. The power dependence is fitted to the functional form describing the saturation of the selected transition and the excited fraction is determined as a fitting parameter. Both the fit of the experimental data and calculations using the known Einstein coefficient confirm that we can completely saturate the methane overtone transition, transferring close to 50% of the irradiated molecules from $v' = 0, J' = 1$ to the excited state with $v_3 = 2$ and $J = 2$.

Dissociative Chemisorption of Methane

The reaction of methane on a nickel catalyst to form surface-bound methyl and hydrogen is the rate-limiting step in steam reforming, which is the principal process for industrial hydrogen production as well as the starting point for the large-scale synthesis of many important chemicals such as ammonia, methanol and higher hydrocarbons [4]. Because of its importance, the dissociation of methane on nickel has been considered a prototype for chemical bond formation between a polyatomic molecule and a solid surface, with many experimental and theoretical studies directed at elucidating its mechanism [3][5–9]. Despite intense effort, there is still no atomic scale picture of the dynamics of this important gas/surface reaction. Molecular beam experiments [6] have firmly established that methane chemisorption is a direct process that can be activated with about equal efficiency by both incident kinetic energy normal to the surface and thermal vibrational energy of the incident methane. Our group [7][10] and others [3][11] have recently performed state-resolved reactivity measurements for the dissociative chemisorption of CH₄ and its isotopomers on nickel in order to obtain detailed information on the role of vibrational excitation in the reaction.

The first set of experiments was designed to compare the effect of translational energy of the incident methane with vibrational energy contained in the antisymmetric stretching vibration [7]. It is apparent from Fig. 5 that the excitation of the antisymmetric stretch vibration has a dramatic effect on the reaction probability, increasing it as much as four orders of magnitude. For a quantitative comparison of the

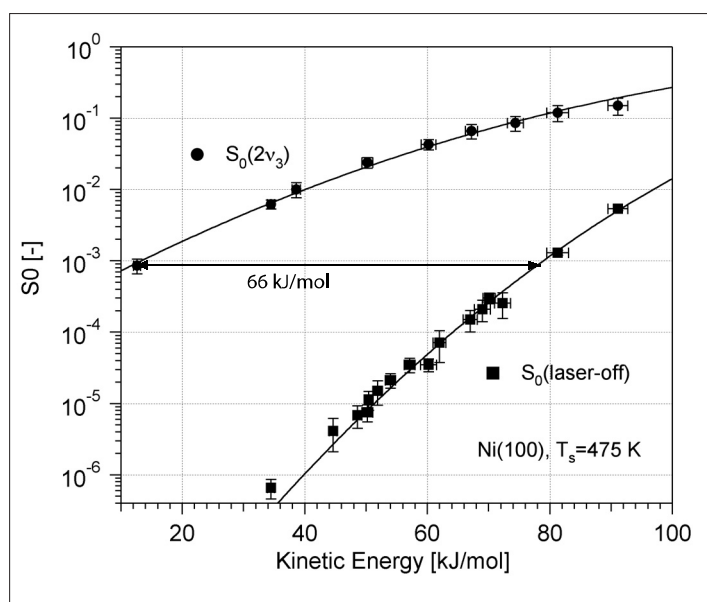


Fig. 5. Sticking coefficients as a function of incident kinetic energy (normal incidence) for dissociative chemisorption of CH_4 on $\text{Ni}(100)$. Squares: laser-off data giving an upper limit for $S_0(v=0)$; circles: state-resolved sticking coefficients for $2\nu_3$, $J=2$. Solid lines show fitted sticking functions using a model described in [7]. Error bars are 95% confidence limits of convoluted uncertainties.

effect of translation and vibration motion on the reaction probability, we mapped out the kinetic energy dependence of the state-resolved sticking coefficient both for the vibrational ground state as well as for the first overtone of the antisymmetric stretch, labeled $2\nu_3$. The horizontal offset of the two state-resolved datasets clearly shows that the relative effect of translational and $2\nu_3$ vibrational energy depends on the kinetic energy. At low incident energy (12 kJ/mol) an offset of 66 kJ/mol in kinetic energy along the surface normally results in the same reactivity increase as 72 kJ/mol of vibrational energy contained in the antisymmetric C–H stretch, indicating that vibration is about 92% as efficient as translation in promoting the dissociation reaction. With increasing kinetic energy the horizontal offset between the datasets decreases, indicating that the effect of $2\nu_3$ vibration relative to translation decreases. This decrease most likely reflects the fact that when the total energy of the incident molecule (translation + vibration) reaches and exceeds the barrier height, the reaction probability cannot exceed a value of one, which will cause the two datasets to merge towards a common asymptote. The state-resolved sticking coefficient for CH_4 on $\text{Ni}(100)$ reported by Juurlink *et al.* [3] show equal (100%) efficiency for a single quantum of ν_3 vibration relative to translation, consistent with this interpretation.

Statistical versus Mode-specific Chemisorption

The result that vibrational energy in the antisymmetric stretch is found to have nearly identical efficiency as translational energy for activating the dissociation reaction might be interpreted as evidence for a sta-

tistical reaction mechanism. In fact, Harrison and coworkers have proposed a microcanonical model for the chemisorption reaction of methane on nickel [12], which assumes the formation of a transient complex consisting of the incident molecule and a few surface atoms prior to the dissociation. In this model, translational energy along the surface normal as well as vibrational energy of the incident molecule are freely and rapidly redistributed within the complex, leading either to desorption or chemisorption, the rates of which are calculated using microcanonical theory. One of the salient features of this model, termed physisorbed complex microcanonical unimolecular rate theory, (PC-MURT) [9], is that translational and vibrational energy of any mode are treated equally as part of the total available internal energy. The model therefore predicts that all vibrational modes of the incident molecule will activate the chemisorption with equal efficiency as translation, excluding the possibility of mode-specificity in the state resolved reaction probability. On the other hand, dynamical calculations, which include the detailed motion in all or in at least a subset of internal degrees of freedom of the incident molecule, have predicted the occurrence of mode specific reactivity for the chemisorption of methane on Ni. For example, wavepacket calculations by Milot and Jansen [8], which included all nine vibrational degrees of freedom of methane, showed clear mode-specific effects in the energy transfer during the collision with the target surface. The simulations found the loss of kinetic energy of the incident molecules to the surface depends on their vibrational state, exhibiting the trend $\nu_1 > \nu_3 > \nu_4 >$ ground state, where ν_1 , ν_3 , and ν_4 designate the symmetric stretch, antisymmetric stretch and umbrella bending modes of CH_4 respectively. Since

a larger inelasticity is thought to lead to higher reactivity, the simulation was interpreted as evidence for decreasing chemisorption probability in the same order, which would be a sign of mode specific reactivity.

The ability of our experimental setup to measure quantum state-specific sticking coefficients allows us to test for the presence or absence of mode-specific behavior in the chemisorption of methane. For a first test [10], we chose the doubly deuterated isotopomer of methane, CD_2H_2 , because of its spectroscopic properties. While the symmetric stretch vibration of CH_4 (ν_1) is infrared inactive due to its symmetry and can only be excited by stimulated Raman pumping, both the symmetric (ν_1) and antisymmetric (ν_6) C–H stretch modes of CD_2H_2 are infrared active and can be excited by our pulsed infrared laser. For comparison, we prepared different nearly isoenergetic vibrational eigenstates corresponding to $2\nu_6$ and $\nu_1 + \nu_6$ in normal mode notation. In a local mode C–H stretch basis for the vibrational states of CD_2H_2 , these two states correspond to $|11\rangle$ and $|20\rangle$ with energies of 5999 and 5829 cm^{-1} respectively [13]. Fig. 6 shows the results of a direct comparison of the reactivity of CD_2H_2 prepared in these two states. For this experiment, a molecular beam containing 18% CD_2H_2 in H_2 was directed at two different locations of the clean $\text{Ni}(100)$ crystal. During the first deposition, labeled $|20\rangle$, a fraction of the incident CD_2H_2 was prepared in the $|20\rangle$ state by our pulsed laser system. For the second deposition, shown on the right hand side of Fig. 6, laser pulses of the same energy promoted the incident molecules to the $|11\rangle$ state. From the absorption spectra measured by cavity ring down spectroscopy in the jet expansion, we determined the strength of the transition to the $|11\rangle$ level to be a factor 1.5 times higher than of the equivalent transition leading to $|20\rangle$. Despite being weaker, excitation of CD_2H_2 to the $|20\rangle$ state leads to a three-times larger amount of carbon product, indicating a higher sticking coefficient compared to CD_2H_2 in the $|11\rangle$ state. For a quantitative comparison of the sticking coefficients for the two vibrational states, we determine the degree of saturation of the optical excitation from the measured fluence dependence and correct the observed carbon peak intensities. The results shown in Fig. 7, together with the much lower ground state reactivity, constitute the first experimental observation of mode-specific reactivity in a chemisorption reaction. At the lowest kinetic energy, we observe a factor of five difference in sticking coefficients between the two local mode state $|20\rangle$ and $|11\rangle$. The higher reactivity of the $|20\rangle$ state can be rationalized in terms of a larger projection onto the reaction coordinate consis-

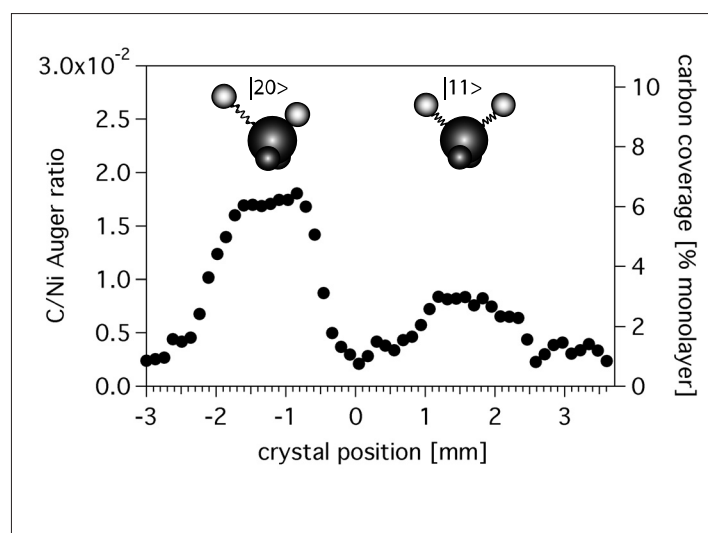


Fig. 6. Surface carbon Auger signal for identical doses of CD_2H_2 excited to the $|20\rangle$ and $|11\rangle$ vibrational states incident on a Ni(100) surface at 41 kJ/mol of kinetic energy. The cartoon visualizes the vibrational amplitudes for the two local mode states.

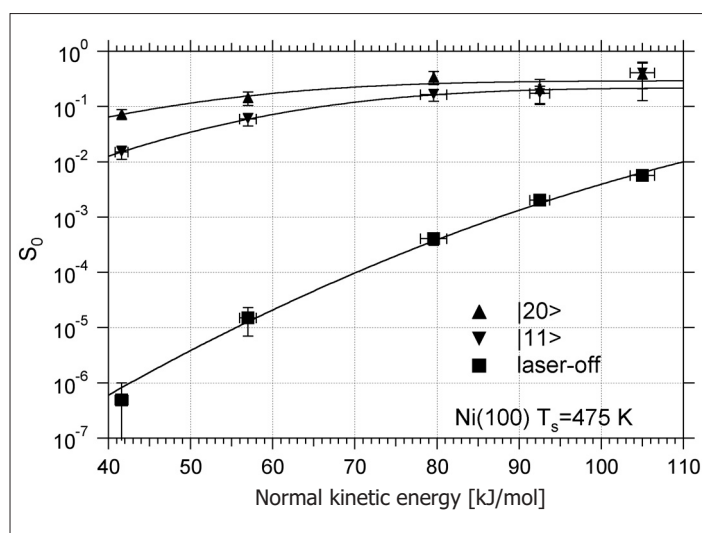


Fig. 7. State-resolved sticking coefficients for CD_2H_2 in the $|20\rangle$ (▲), $|11\rangle$ (▼) and ground (■) vibrational states on Ni(100) as function of incident kinetic energy normal to the surface. The surface temperature is 473 K.

tent with a calculated transition state structure with a single C-bond extended by up to 30% [14]. The observation of a large difference in the reactivity for two nearly isoenergetic vibrational states clearly excludes statistical models such as the PC-MURT from correctly describing the chemisorption reaction. It also provides compelling evidence that intramolecular vibrational redistribution (IVR) does not randomize the vibrational energy during the 10 μs flight time between laser preparation and surface impact. Moreover, the interaction of the incident molecule with the surface is not sufficient to scramble the vibrational energy on the psec approach timescale before the chemisorption reaction occurs.

Summary and Future Directions

Over the last five years we have developed new methodology to study the chemical dynamics of gas/surface reactions with single quantum state resolution. Our experiments use a molecular beam/surface science apparatus together with pulsed laser preparation of the incident molecules in known rovibrational eigenstates for the determination of state-specific sticking coefficients. Efficient excitation of weak overtone and combination band transitions is made possible with a tunable infrared laser system that generates narrow-band laser radiation with energies of up to 150 mJ/pulse at 20 Hz. We have demonstrated the feasibility of the method by performing state-specific measurements of the reactivity of CH_4 excited to the first overtone of the antisymmetric C–H stretch on Ni(100) as a function of incident translational energy. Comparison of the reactivity for two nearly isoenergetic states of CD_2H_2 provides for

the first time unequivocal evidence for mode specific reactivity in a gas/surface reaction and sheds light on the mechanism of methane chemisorption. In future experiments, we will exploit the wide tuning range of our DFG-OPA pulsed infrared source to access a variety of different vibrational states *via* infrared active fundamental transitions as well as overtone and combination bands in order to explore more fully the reactive part of the potential energy surface. Furthermore, pulsed laser excitation can also be used for stimulated Raman pumping of totally symmetric vibrational states, which cannot be populated by single photon absorption. The ability to obtain state-resolved reactivity data for a range of different vibrational states of a given molecule will help our understanding of the chemical dynamics of gas/surface reactions by pinpointing the types of intramolecular motion that best map onto the reaction coordinate. Finally, for molecule/surface systems where vibrational energy strongly increases the sticking coefficient, the method may be used for isotopically selective deposition, since the vibrational excitation in the molecular beam using narrow band laser radiation can usually be done with very high isotope selectivity.

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