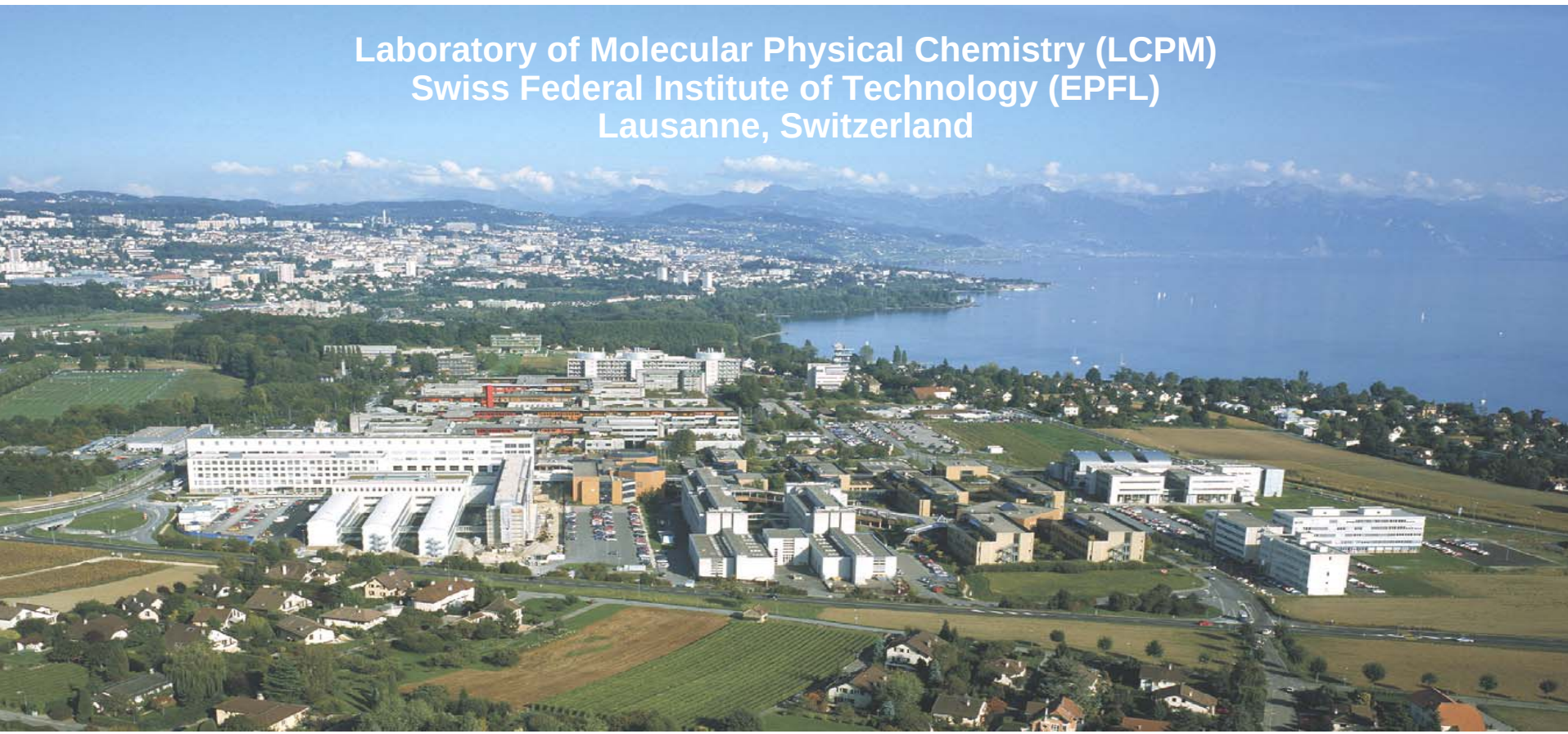
XH_4 molecules dissociation on Si, Ni, Pt surfaces: dynamics of excited vibrational modes and relation to transition state structures

Régis Bisson



06 may 2009

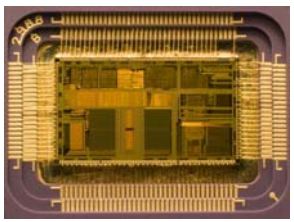
Motivations

applied

$$CH_4 + H_2O \xrightarrow[\text{Ni-catalyst}]{} CO + 3H_2$$

"syngas"

SiH_4/Si(100):*Semiconductor industry*



$$SiH_4\ (gas) + \text{-Si-Si-}\ (s) \xrightarrow[\text{Si(100)-2x1}]{} SiH_3\text{-Si-Si-H}\ (s)$$

Dynamics of XH_4 dissociative chemisorption ?

outline

1. Motivation: XH_4 dissociative chemisorption dynamics?

- CH_4 on Ni surfaces

2. XH_4 vibrations and the relation to transition state structures

- CH_4 on Ni
- SiH_4 on Si
- CH_4 on Pt

3. Survival of excited vibrations in physisorbed precursor

- SiH_4 on Si

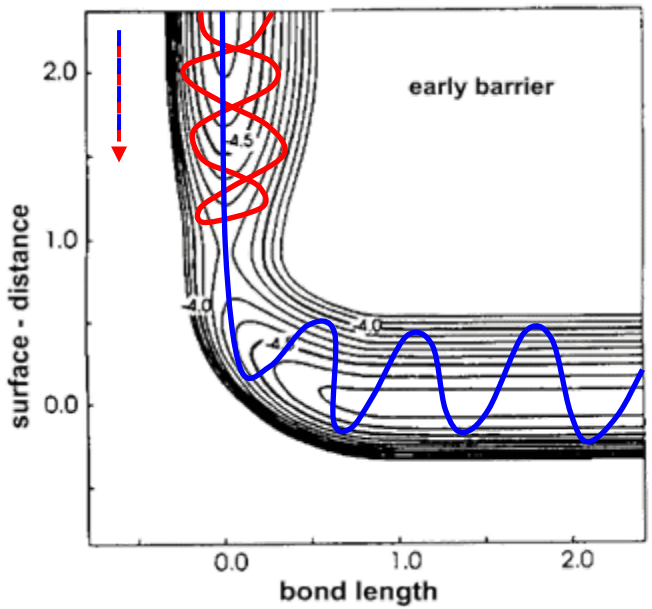
Motivations

fundamental

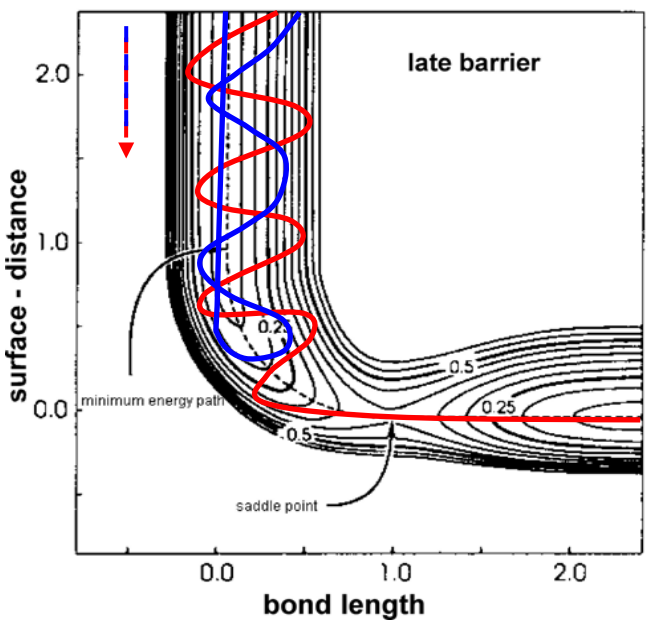
Multidimensionality of potential energy surface (PES)

“Polanyi rules”

barrier location on PES ⇔ energy consumption



more easily overcome with translational energy



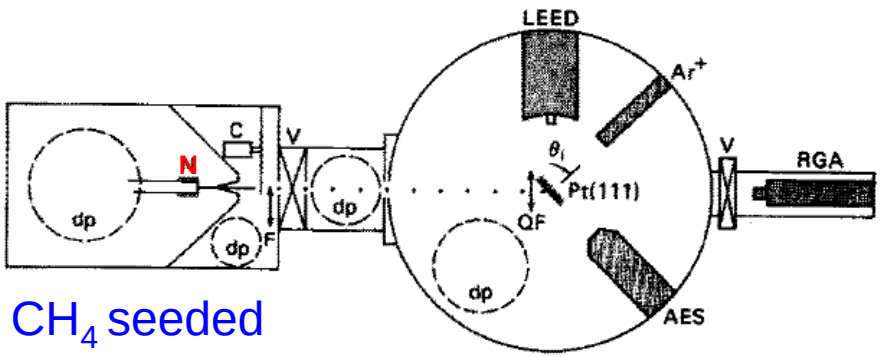
more easily overcome with vibrational energy

diatomic case

Traditional setup

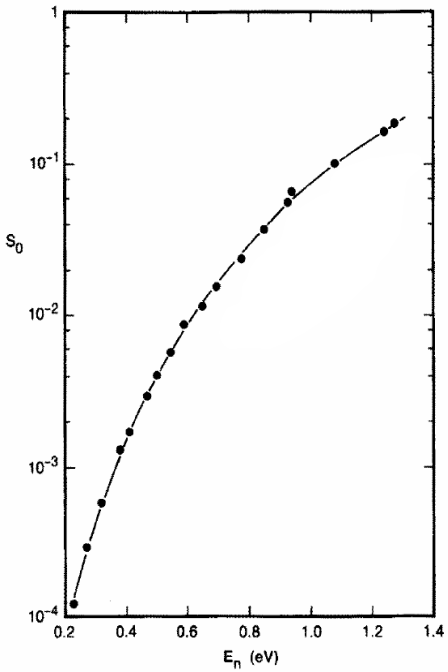
surface science – molecular beam

Luntz and Bethune, JCP **90**, 1274 (1989)

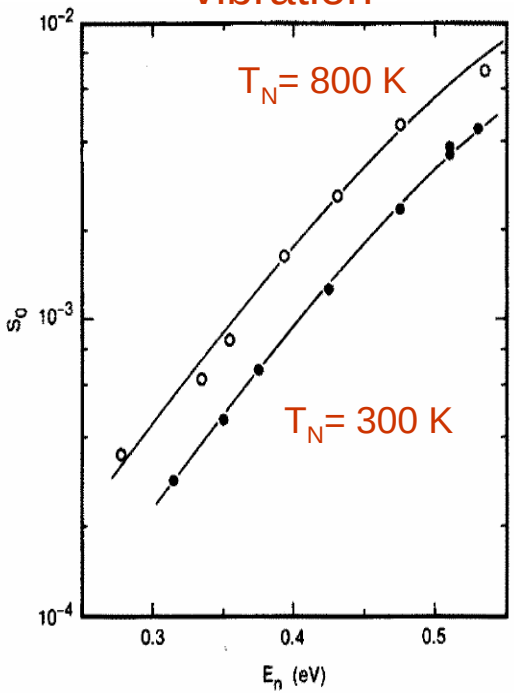


CH_4 seeded

translation



vibration



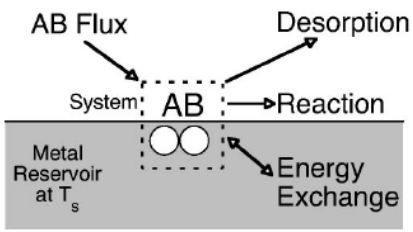
sub-ps time scale

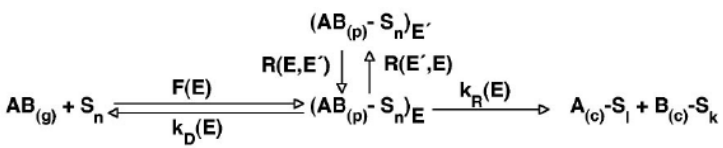
Translation activation ~ Vibrational activation

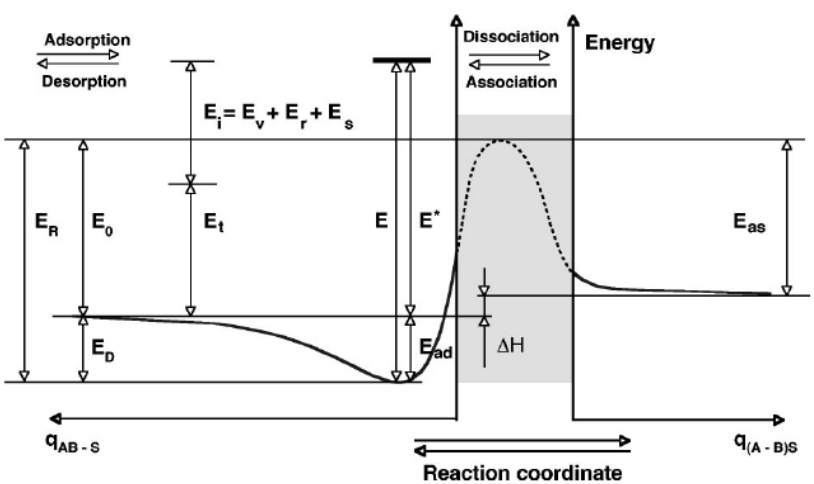
Motivations

fundamental

Statistical model *Bukoski and Harrison JCP 118, 9762 (2003)*







CH_4 – surface collision complex:

short-lived (10^{-13}s)
<u>but</u>
surface-induced IVR faster
due to high-density of states

complete microscopic randomization

of E_t, E_v, E_r

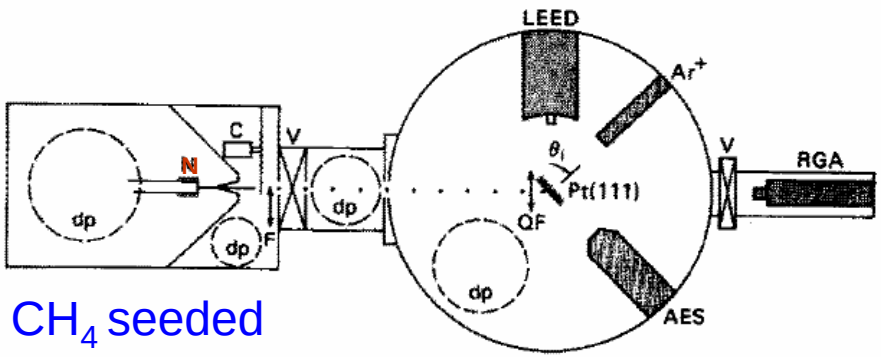
quantitative agreement with "traditional" experimental data

▷ one-dimensional picture of the barrier to reaction is sufficient ! ?

Traditional setup

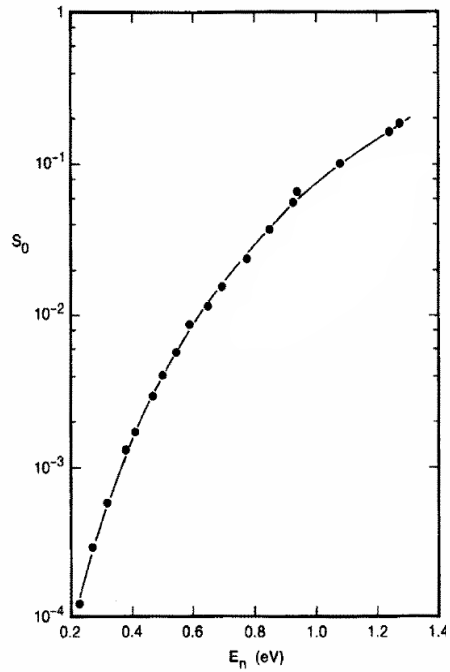
surface science – molecular beam

Luntz and Bethune, JCP **90**, 1274 (1989)

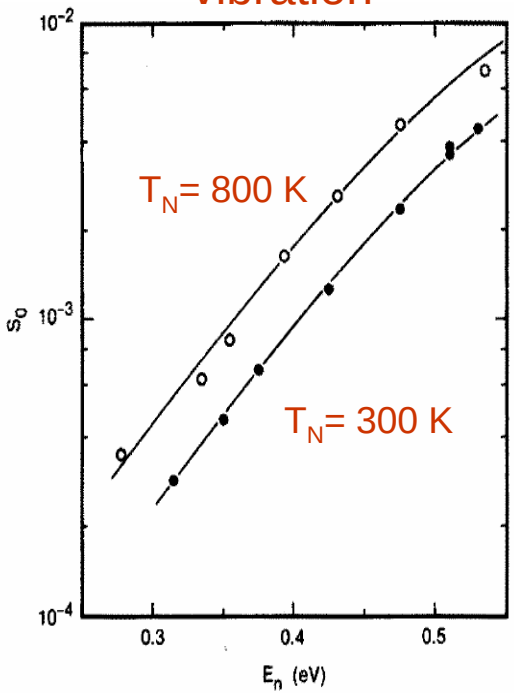


CH_4 seeded

translation



vibration

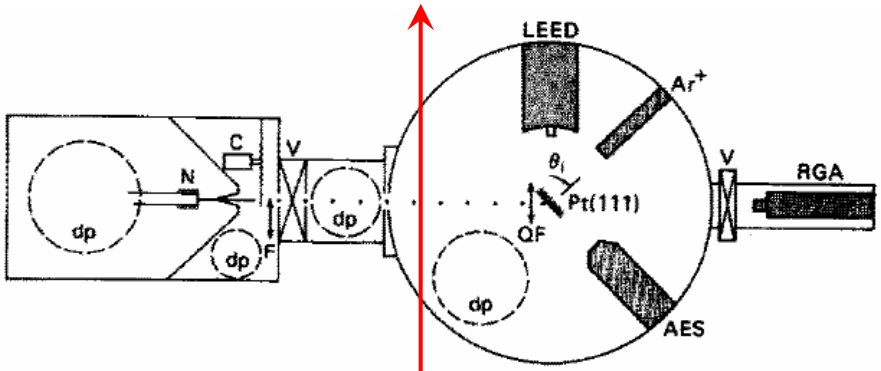


Translation activation ~ Vibrational activation

here the extent of vibrational activation is obtained from a thermally populated ensemble of excited vibrational modes

State-resolved setup

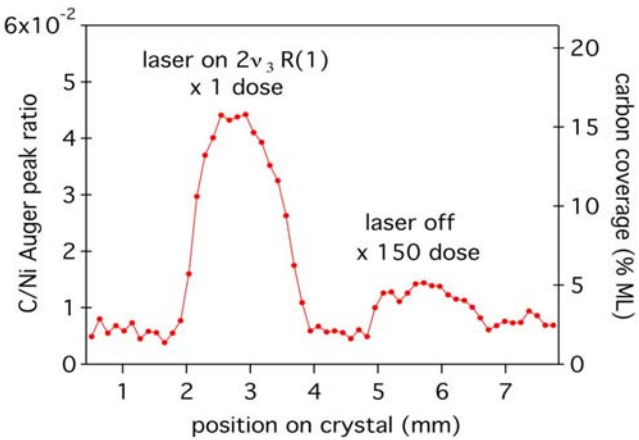
general approach



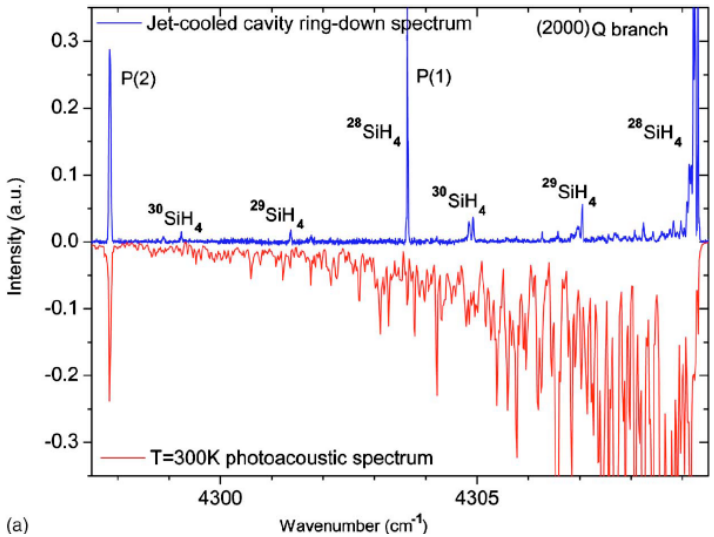
laser-assisted
state-selective
vibrational excitation

$$S_0^{\nu_i} = \frac{S_0^{laser-on} - S_0^{laser-off}}{f_{exc}} + S_0^{GS}$$

need to know and to measure:



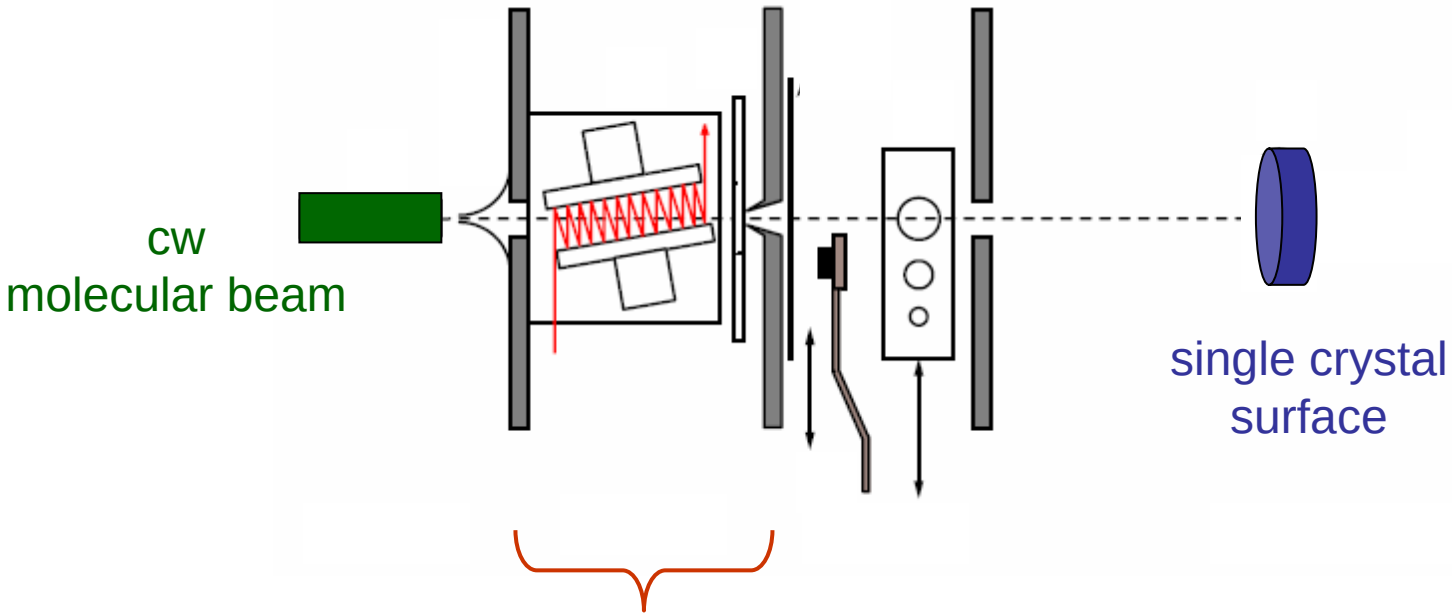
Compare molecular beam reactivity
with/without laser excitation



Rotationally cooled temperature
thanks to jet expansion

State-resolved setup

Utz's group approach

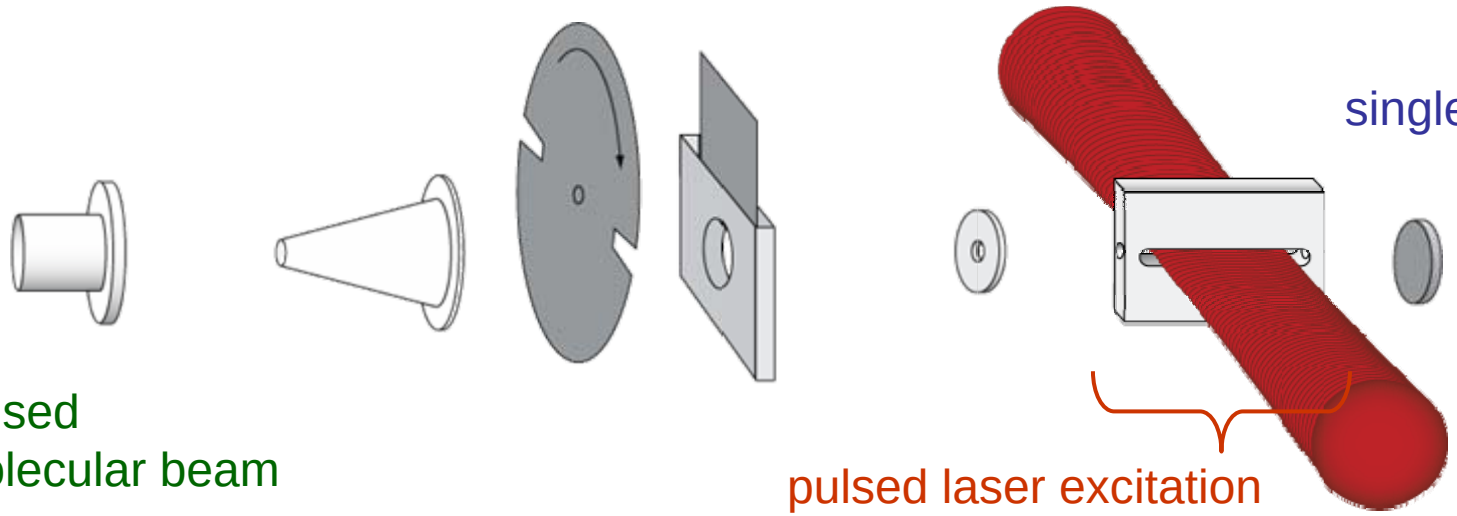


IR (3000-4000 cm^{-1})

CH_4 : ν_3 - $3\nu_4$

State-resolved setup

Beck's group approach



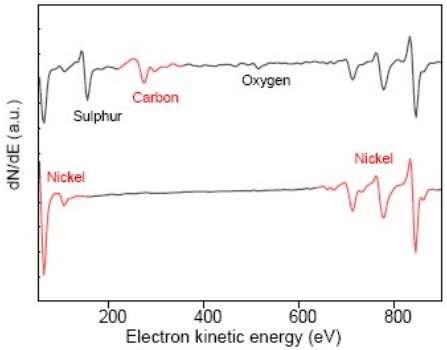
IR (4000-6000 cm^{-1}) CH_4 : $\nu_1+\nu_4$ - $2\nu_3$ - … SiH_4 :|*1100*>, |*2000*>

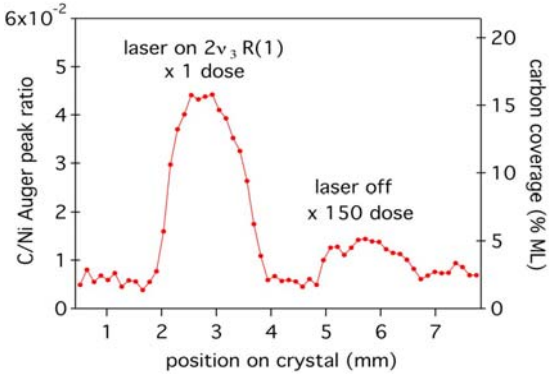
RAMAN CH_4 : ν_1

State-resolved setup

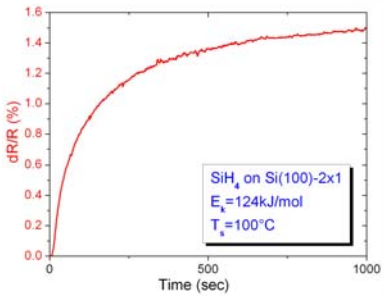
Reactivity measurement: product quantification

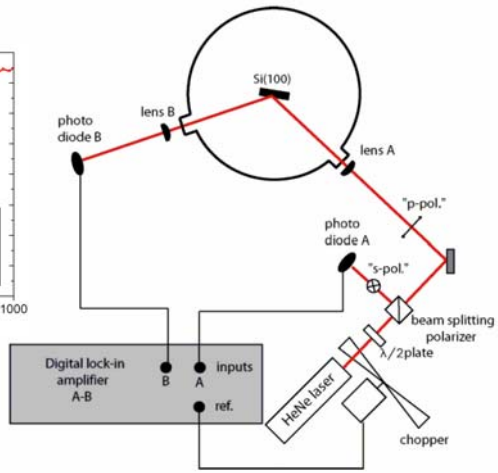
"Heterogeneous" system (CH_4/metals): Auger Electron Spectroscopy

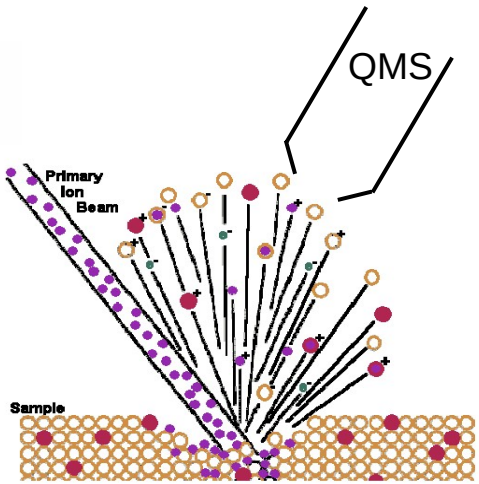


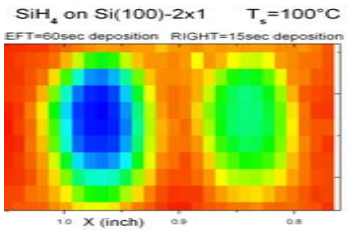


"Homogeneous" system (SiH_4/Si): optical reflectivity & SIMS





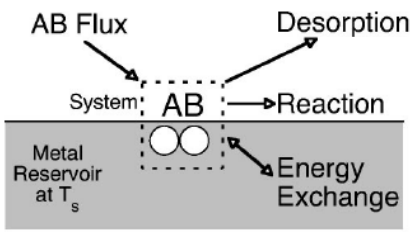


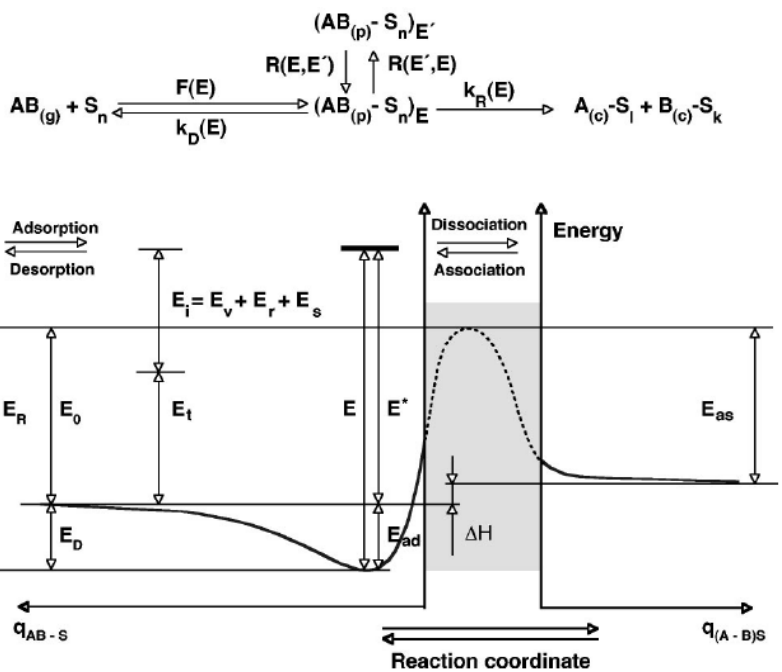


Motivations

fundamental

Statistical model *Bukoski and Harrison JCP 118, 9762 (2003)*





complete microscopic randomization of E_{trans}, E_{vib}, E_{rot}

one-dimensional picture of the barrier to reaction is sufficient ! ?

predictions

?

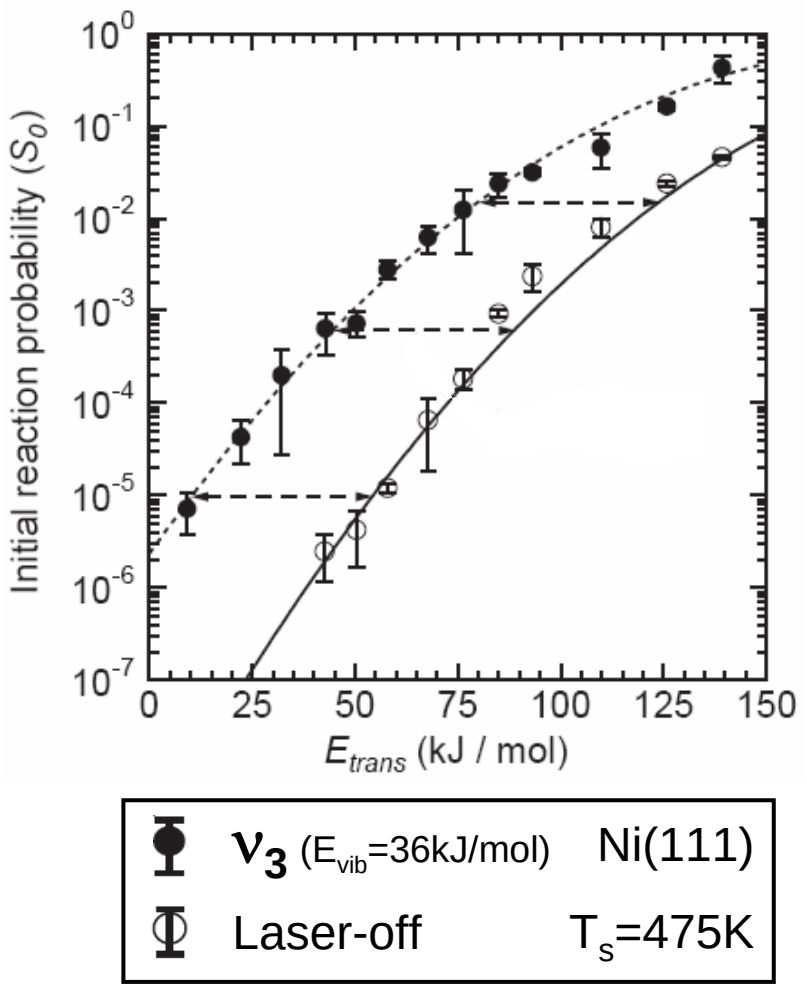
E_{vib} and E_{trans} are equivalent
i.e. lead to same reactivity

+

$E_{vib}(\nu_x) = E_{vib}(\nu_y)$ are equivalent

vibration vs. translation

Smith .... Utz, Science **304** (5673), 992 (2004)



If one remove 36 kJ/mol of E_{vib}

one nee to add 45 kJ/mol of E_{trans}

to keep S_0 identical

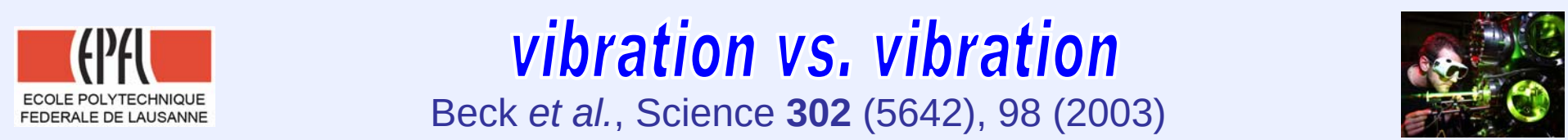
vibration and translation

are not equivalent:

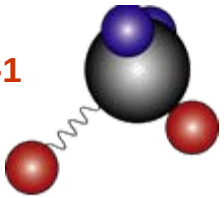
NON-STATISTICAL

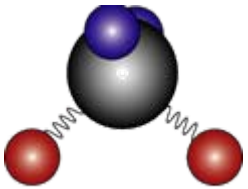
vibration vs. vibration

Beck *et al.*, Science **302** (5642), 98 (2003)



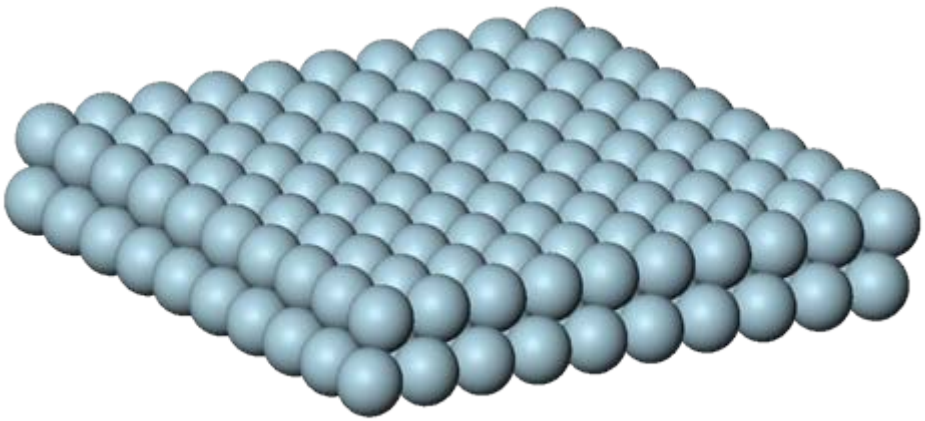
$\nu_1 + \nu_6 \Leftrightarrow$ **|2000>** **5879 cm^{-1}**





6000 cm^{-1} $2\nu_6 \Leftrightarrow$ **|1100>**

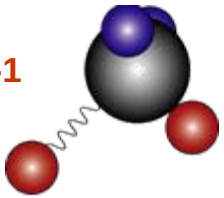
CD_2H_2
Ni(100)

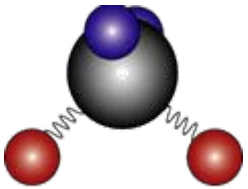


vibration vs. vibration

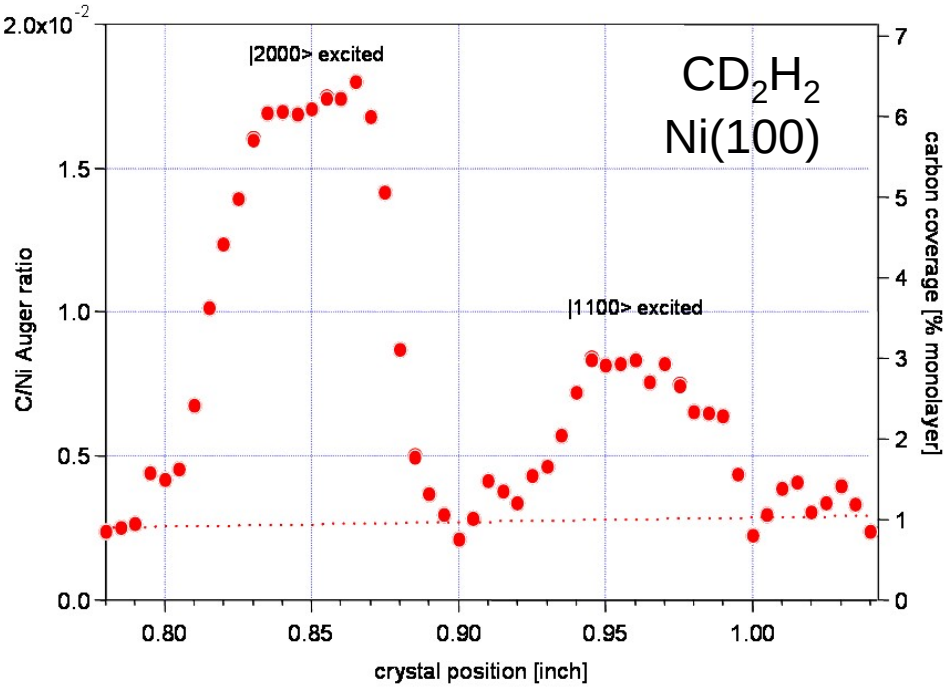
Beck *et al.*, Science **302** (5642), 98 (2003)

$\nu_1 + \nu_6 \Leftrightarrow$ **|2000>** **5879 cm^{-1}**





6000 cm^{-1} $2\nu_6 \Leftrightarrow$ **|1100>**



Isoenergetic vibrations are not equivalent

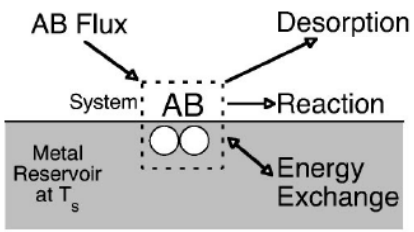
(mode-specificity)

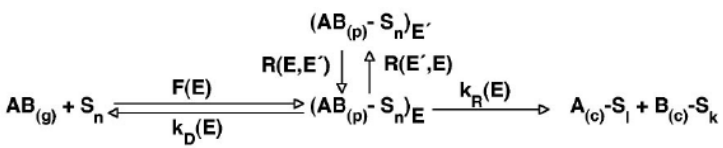
NON-STATISTICAL

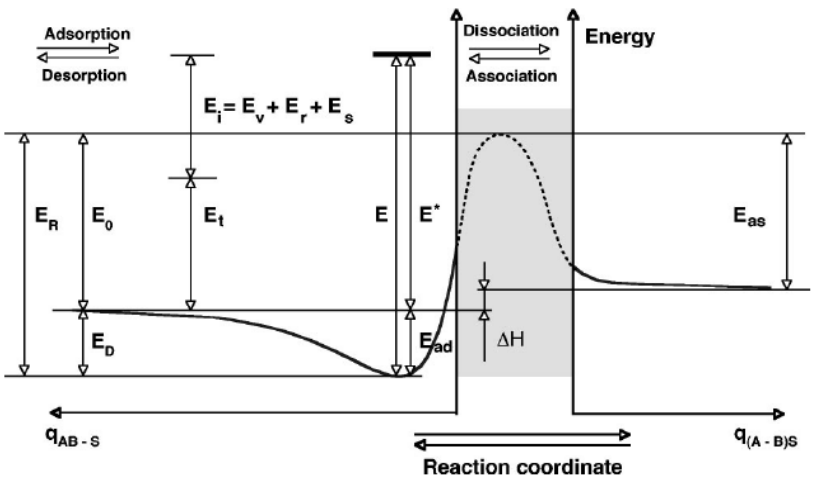
Motivations

fundamental

Statistical model *Bukoski and Harrison JCP 118, 9762 (2003)*







complete microscopic randomization of E_{trans}, E_{vib}, E_{rot}

E_{vib} and E_{trans} are equivalent
i.e. lead to same reactivity
+
$E_{vib}(\nu_x)$ and $E_{vib}(\nu_y)$ are equivalent

Motivations

fundamental

JOURNAL OF CHEMICAL PHYSICS VOLUME 121, NUMBER 8 22 AUGUST 2004

Microcanonical unimolecular rate theory at surfaces. II. Vibrational state resolved dissociative chemisorption of methane on Ni(100)

H. L. Abbott, A. Bukoski, and I. Harrison[a)]
Department of Chemistry, University of Virginia, Charlottesville, Virginia 22904-4319

quanta in each of the two C-H bonds. In this paper, we show by comparison to experiments that the dissociative chemisorption of methane on Ni(100) can be quantitatively treated using the statistical PC-MURT for some methane isotopomers, CH_4 and CD_4, but not for CD_2H_2.

THE JOURNAL OF PHYSICAL CHEMISTRY B LETTERS
2005, *109*, 685–688
Published on Web 12/21/2004

Nonequilibrium Activated Dissociative Chemisorption: SiH_4 on Si(100)

David F. Kavulak, Heather L. Abbott, and Ian Harrison*
Department of Chemistry, University of Virginia, Charlottesville, Virginia 22904-4319

Received: November 10, 2004; In Final Form: December 6, 2004

A three-parameter local hot spot model of gas–surface reactivity is employed to analyze and predict dissociative sticking coefficients for SiH_4 incident on Si(100) under varied nonequilibrium conditions. Two Si surface

the Figure 1c PC-MURT predictions are consistent with energy in all of the molecular vibrational and rotational degrees of freedom being fully exchangeable within the reactive transition state. The influence of rotational energy on dissociative sticking

Motivations

fundamental

XH_4 dissociative chemisorption dynamics
over the time scale of a direct dissociative chemisorption

Vibrational and translational energy are not equivalent

Vibrational modes are not completely scrambled

outline

1. Motivation: XH_4 dissociative chemisorption dynamics

- Vibrational modes are not scrambled over the time scale of a direct dissociative chemisorption

2. XH_4 vibrations and the relation to transition state structures

- CH_4 on Ni
- SiH_4 on Si
- CH_4 on Pt

3. Survival of excited vibrations in physisorbed precursor

- SiH_4 on Si

vibrational modes

a short introduction

NORMAL MODES

strongly coupled harmonic oscillators

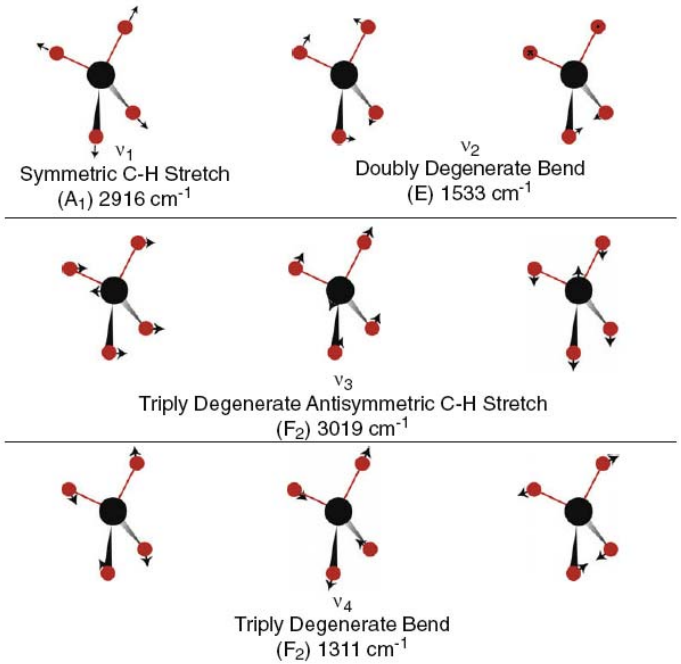


Fig. 6. Methane (CH_4) vibrational normal modes. Adapted from Ref. [119].

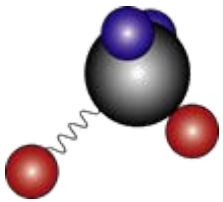
Good descriptor for CH_4 fundamental and overtones

overtone/combination states have a “purity” >90% in a normal mode description

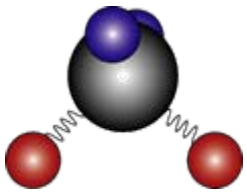
LOCAL MODES

uncoupled anharmonic oscillators

|2000>



|1100>



Good descriptor for CD_2H_2 and SiH_4 stretch overtones

overtone states have a “purity” of 50-70% in a normal mode description

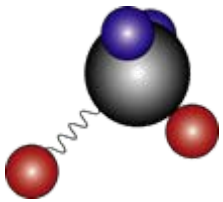
vibrational modes

a short introduction

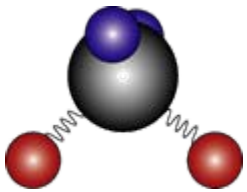
LOCAL MODES

uncoupled anharmonic oscillators

|2000>



|1100>

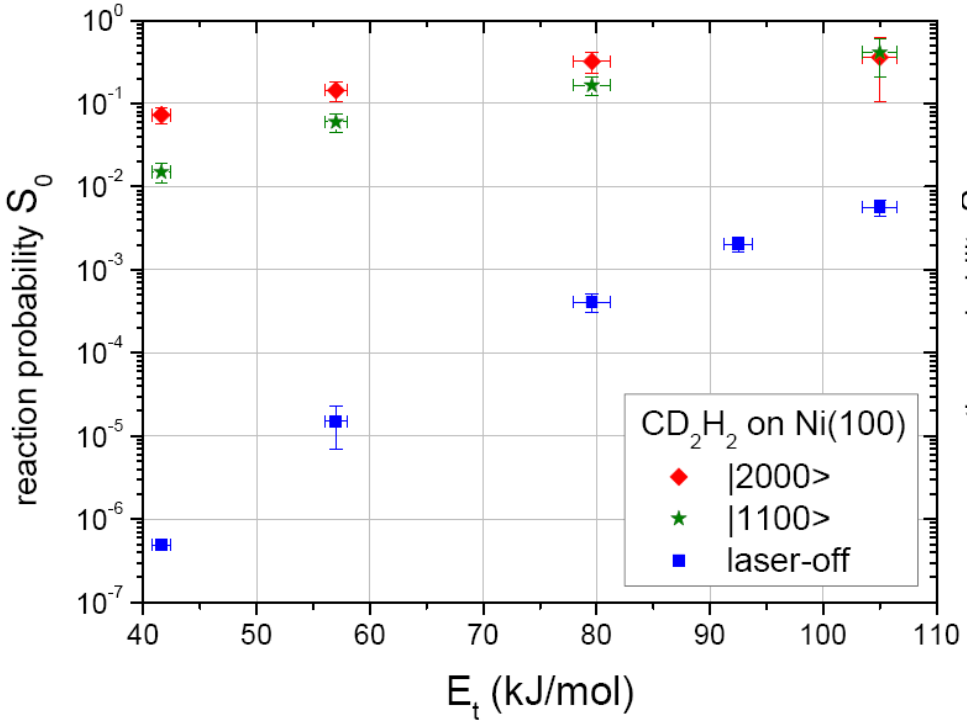


Good descriptor for CD_2H_2 and SiH_4 stretch overtones

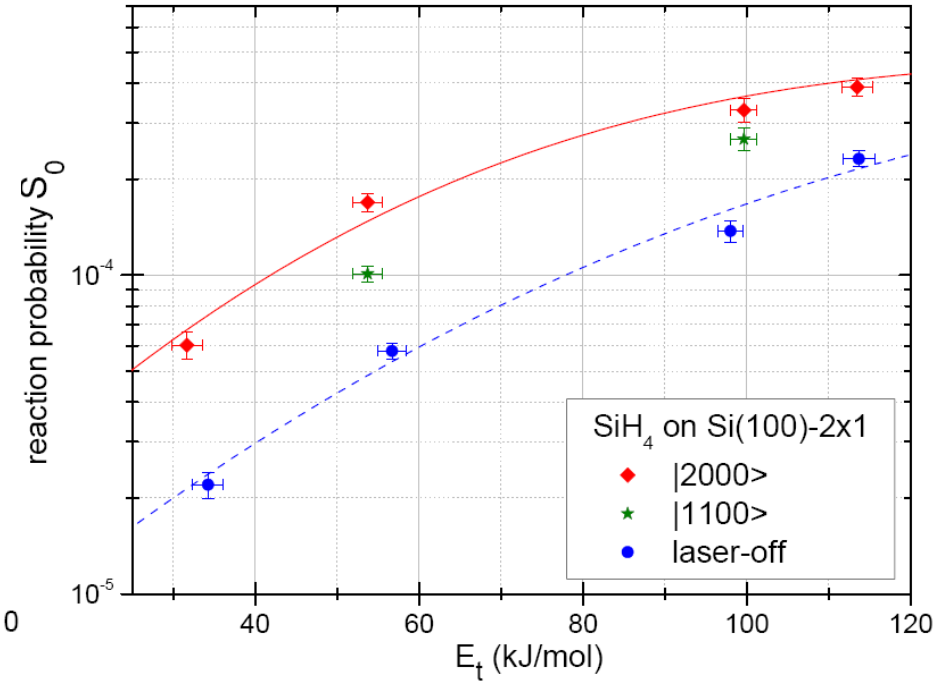
overtone states have a “purity” of 50-70% in a normal mode description

state-resolved results vs. transition state structures

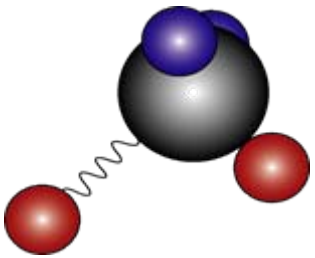
Local modes



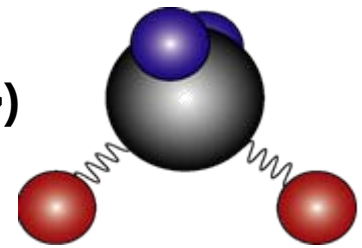
Beck *et al.*, Science **302** (5642), 98 (2003)



Bisson ... Beck, J. Chem. Phys. **129** (8), 081103 (2008)



S_0 (|2000>) > S_0 (|1100>)



state-resolved results vs. transition state structures

Local modes: the spectator model

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Bond and mode selectivity in the reaction of atomic chlorine with vibrationally excited CH_2D_2

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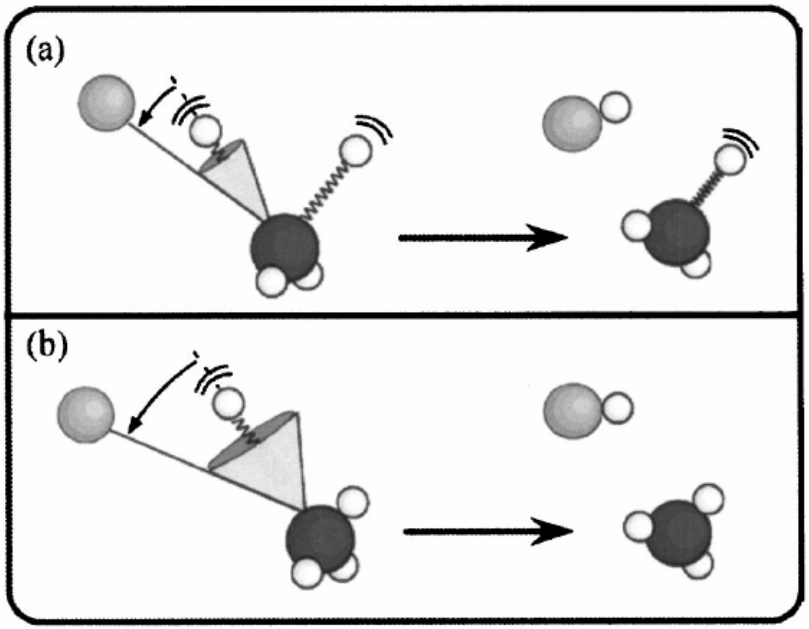


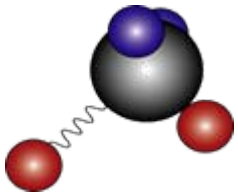
FIG. 8. Spectator model and cone of acceptance diagram. (a) The Cl $+CH_2D_2|1100\rangle$ reaction produces C–H excited methyl radical and has a narrower cone of acceptance than (b) the $Cl+CH_2D_2|2000\rangle^-$ reaction, which produces ground state methyl radical.

On the time scale of reaction

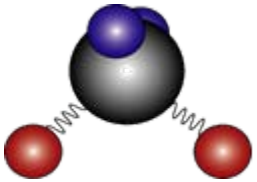
- limited energy flow between C-H bonds
- reaction partner interacts with a single C-H oscillator
- (excited) methyl group acts as spectator

state-resolved results vs. transition state structures

Local modes: the spectator model

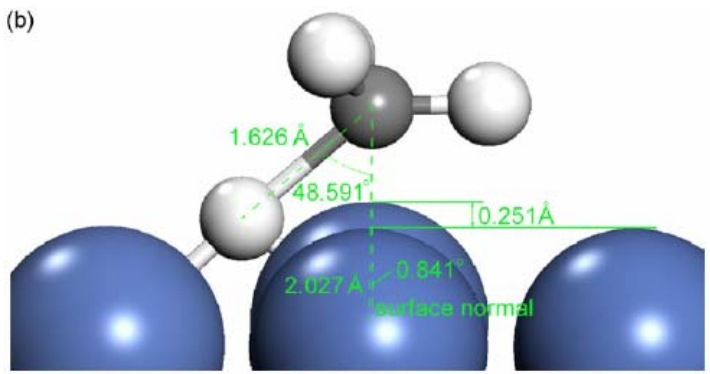


S_0 (|2000>) > S_0 (|1100>)



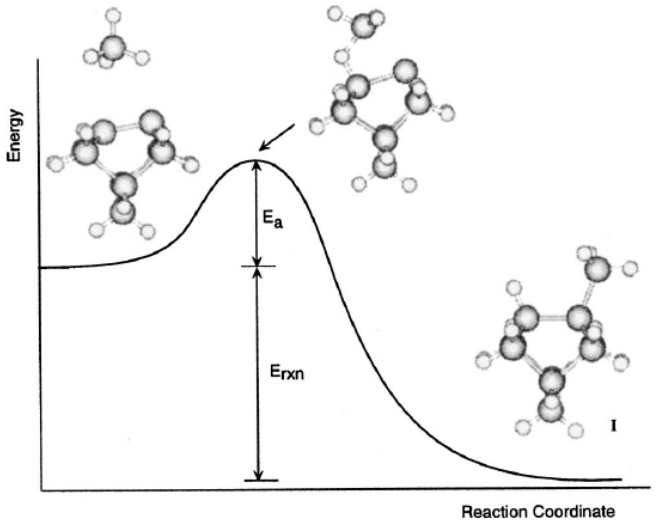
- |2000> as a greater extension of the active X-H bond compared to |1100>
- |2000> better access the transition state structure

CH_4 on Ni(100)



Zhu *et al.*, J. Mol. Cat. A **264** (1-2), 299 (2007)

SiH_4 on Si(100)-2x1



Brown and Doren, J. Chem. Phys. **110** (5), 2643 (1999)

vibrational modes

NORMAL MODES
strongly coupled harmonic oscillators

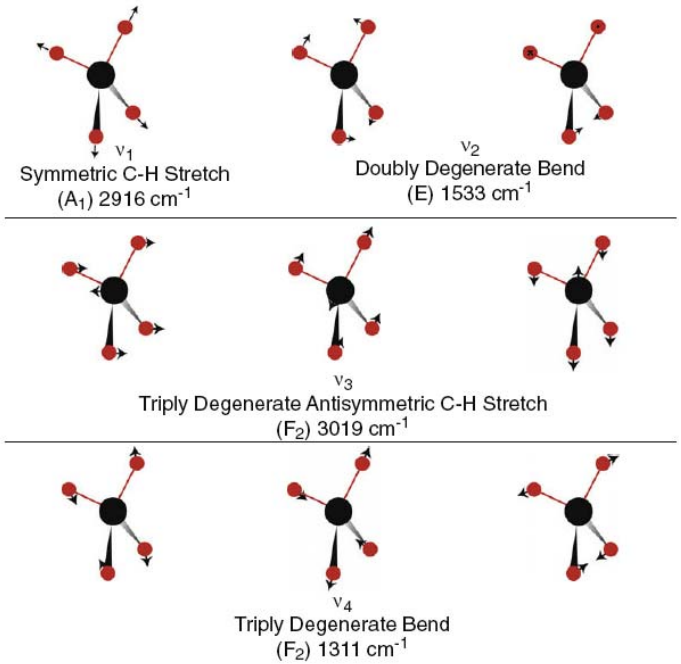


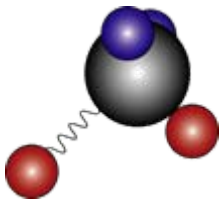
Fig. 6. Methane (CH_4) vibrational normal modes. Adapted from Ref. [119].

Good descriptor for CH_4 fundamental and overtones

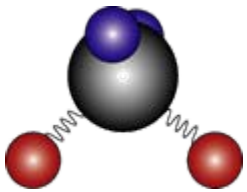
overtone/combination states have a “purity” >90% in a normal mode description

LOCAL MODES
uncoupled anharmonic oscillators

|2000>



|1100>



Good descriptor for CD_2H_2 and SiH_4 stretch overtones

overtone states have a “purity” of 50-70% in a normal mode description

vibrational modes

NORMAL MODES

strongly coupled harmonic oscillators

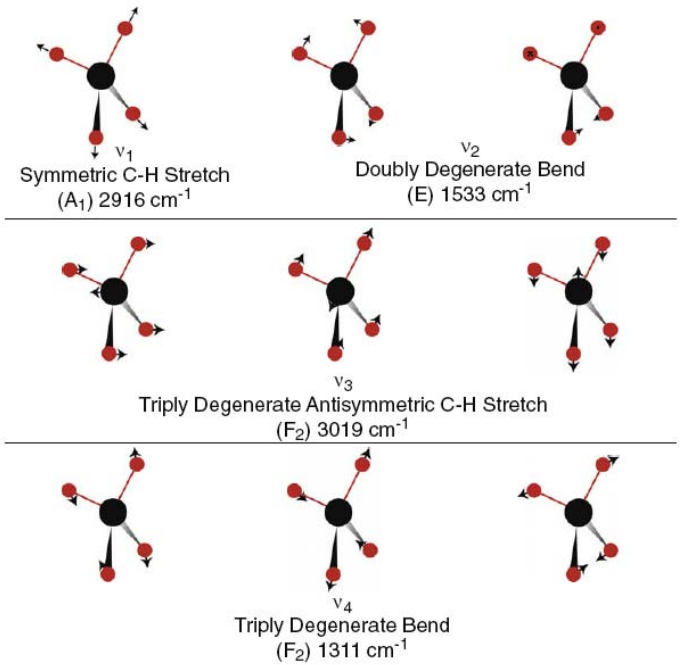


Fig. 6. Methane (CH_4) vibrational normal modes. Adapted from Ref. [119].

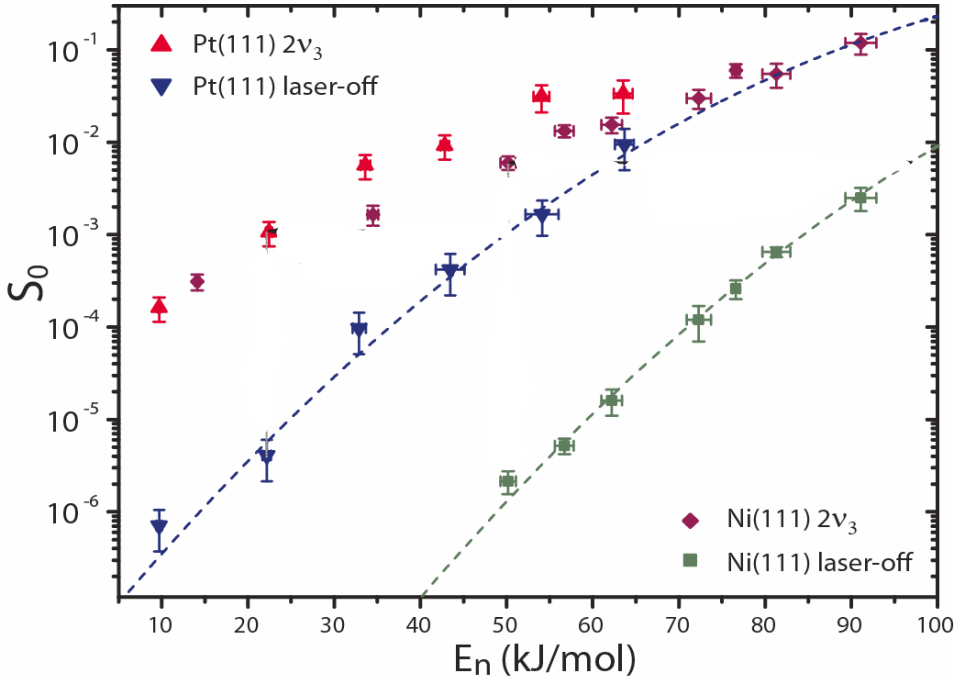
Good descriptor for CH_4 fundamental and overtones

overtone/combination states have a “purity” >90% in a normal mode description

state-resolved results vs. transition state structures

Normal modes: CH_4 on Ni(111) and Pt(111)

Bisson … Beck, J. Phys. Chem. A **111** (49), 12679 (2007)

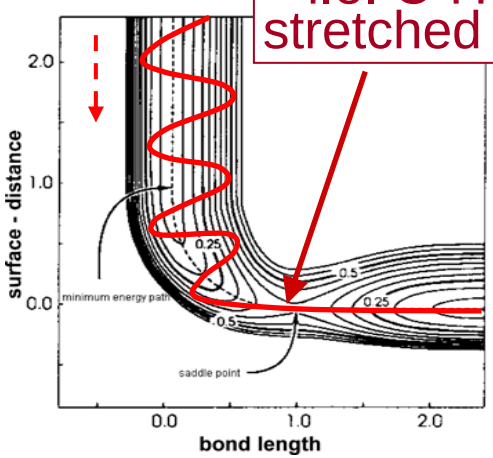


If one remove E_{vib} how much one need to add of E_{trans} to keep the reactivity identical

vibrational efficacy

$$\eta(\nu_3) = \frac{\Delta E_{trans}}{E_{vib}(\nu_3)}$$

Ni(111) has a later barrier i.e. C-H more stretched at TS ?



$2\nu_3$ stretch vibration projects better on reaction coordinates on Ni(111) than on Pt(111)

Nave and Jackson, J. Chem. Phys. 130 (5), 054701 (2009)

state-resolved results vs. transition state structures

Normal modes

A lesson?

one might maximize the projection on reaction coordinates

(i.e. the probability for dissociative chemisorption)

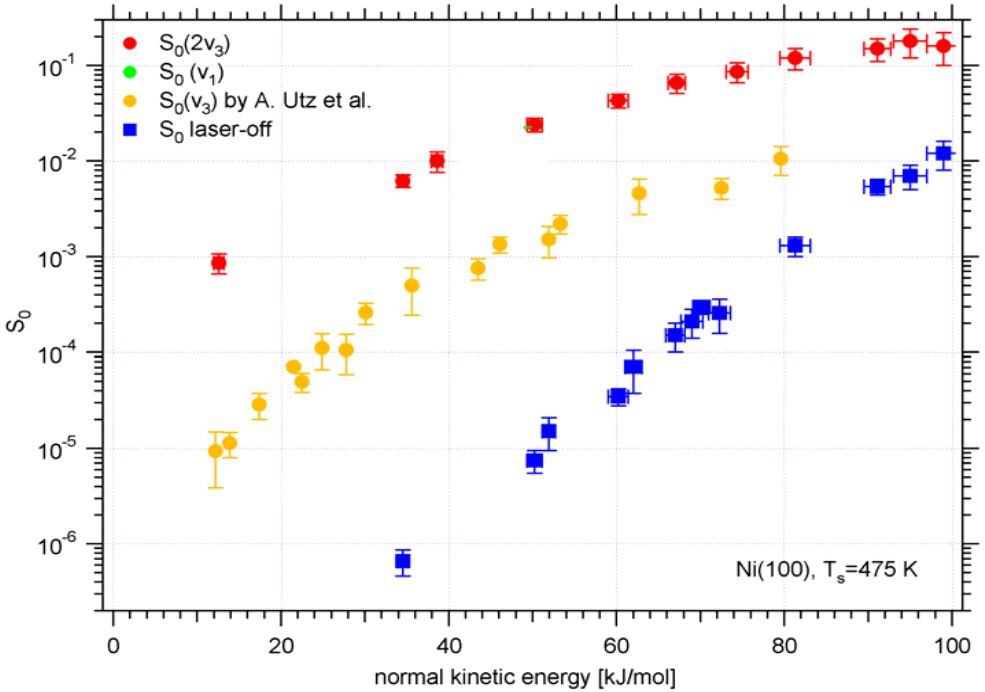
by exciting a vibrational mode resembling the transition state structure

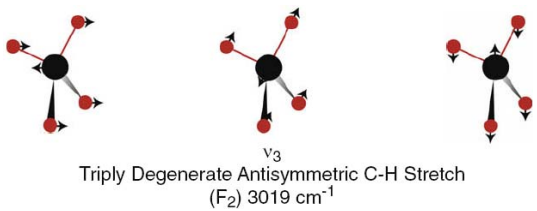
Well… qualitatively… maybe…

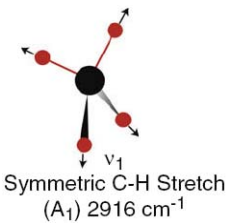
state-resolved results

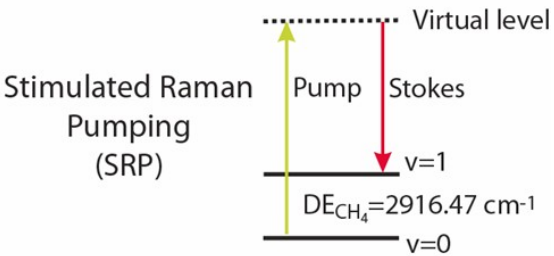
Normal modes: CH_4 on Ni(100)

Maroni ... Beck, Phys. Rev. Lett. **94** (24), 246104 (2005)









even though both modes are stretching mode and have similar vibrational energy

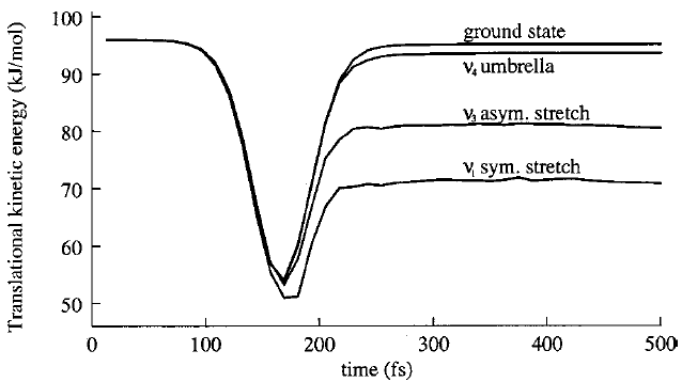
$$S_0(\nu_1) > S_0(\nu_3)$$

state-resolved results vs. theoretical dynamics

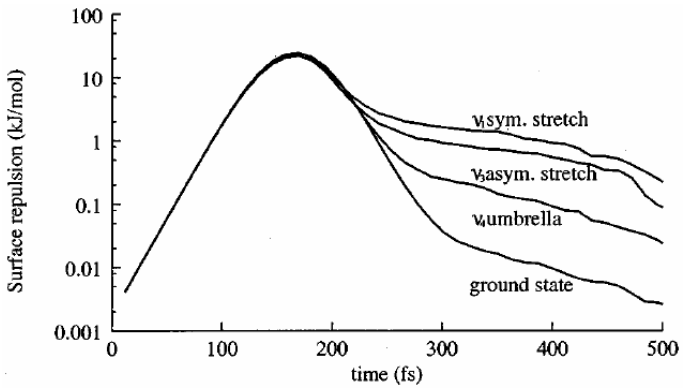
Normal modes

Wave packet simulation Milot and Jansen, Phys. Rev. B **61** (23), 15657 (2000)

PES
- CH_4 / Ni but without exit channel (no dissociation)
- no corrugation



ν_1 scatters more inelastically than ν_3



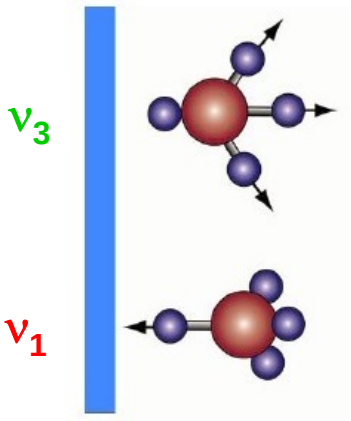
ν_1 spends more time in the entrance channel than ν_3

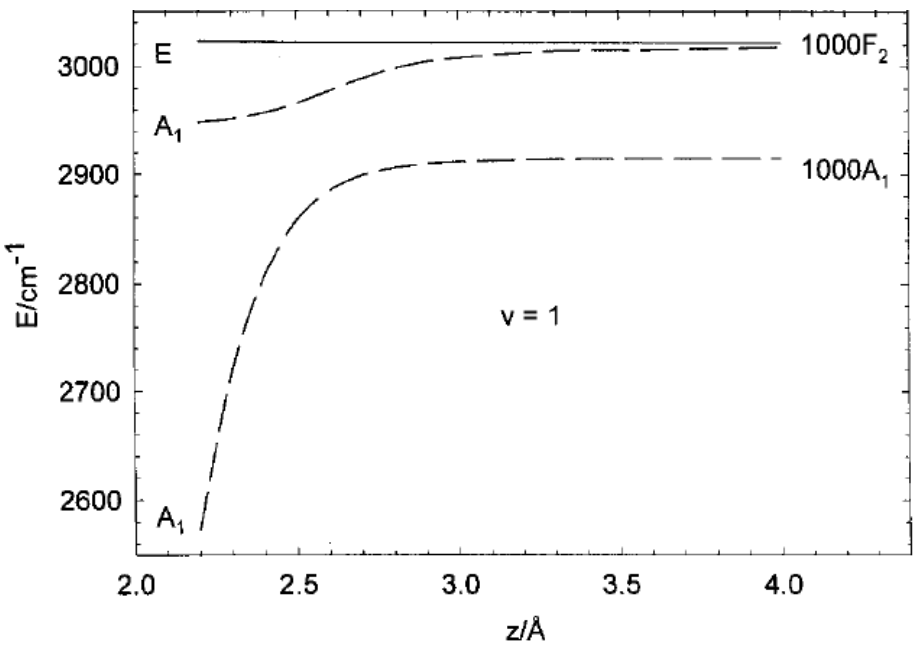
➢ ν_1 should be more reactive than ν_3

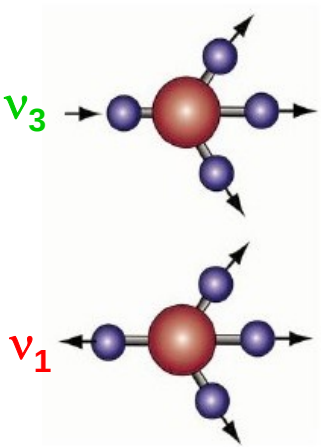
energy flow dynamics during vibrationally adiabatic approach

Halonen … Nesbitt, J. Chem. Phys. **115** (12), 5611 (2001)

PES
- CH_4 / Ni
- no corrugation







➢ ν_1 should be more reactive than ν_3

outline

1. Motivation: XH_4 dissociative chemisorption dynamics

- Vibrational modes are not scrambled over the time scale of a direct dissociative chemisorption

2. XH_4 vibrations and the relation to transition state structures

- Qualitatively, one might maximize the projection on reaction coordinates by exciting a vibrational mode resembling the transition state structure
- Quantitatively, one must be precautious because of dynamics

3. Survival of excited vibrations in physisorbed precursor

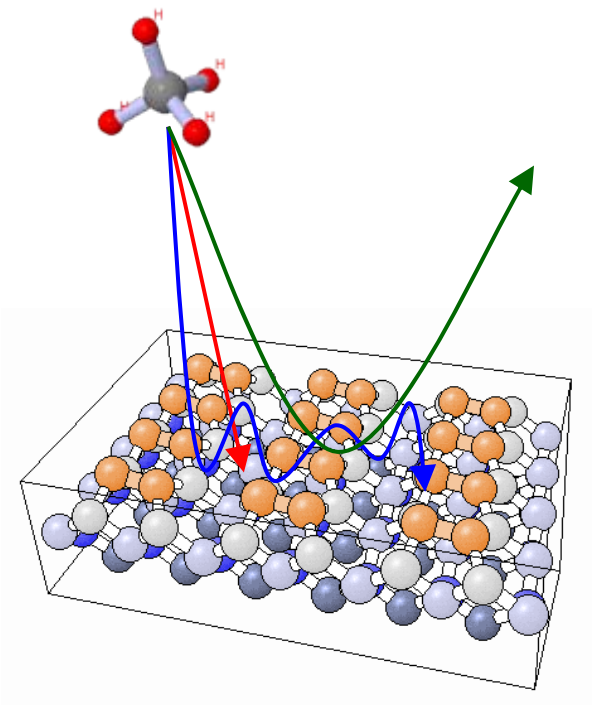
- SiH_4 on Si

direct vs. precursor-mediated adsorption

- Scattering (<ps):

- Direct adsorption (<ps):

  XH_4/Surf: no surface-induced IVR on the sub-ps timescale

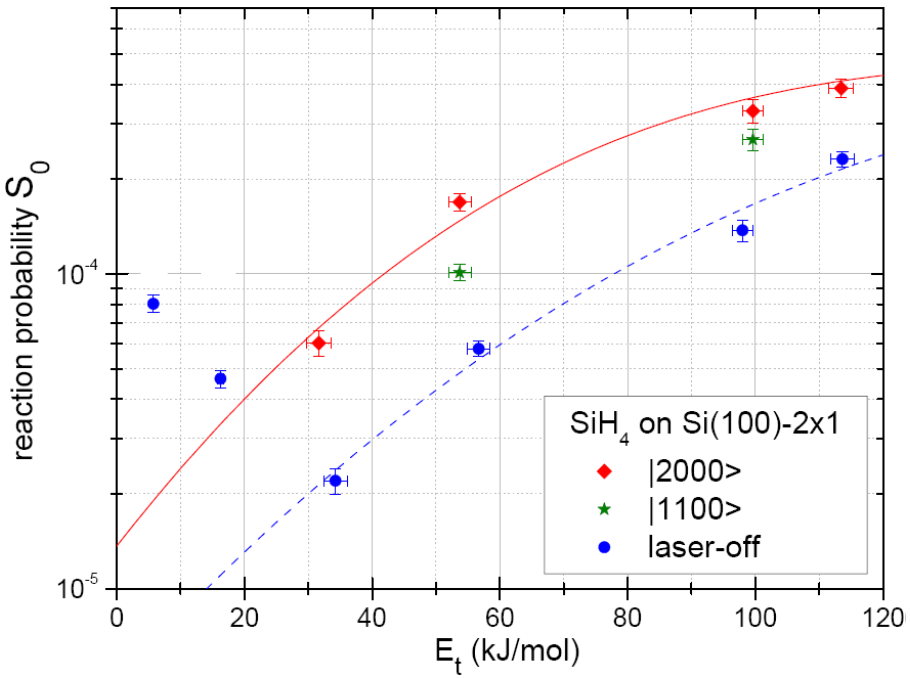


- Precursor-mediated adsorption (>ps):

  What about survival of excited vibrational modes ?

excited vibrations in precursors

Bisson ... Beck, J. Chem. Phys. **129** (8), 081103 (2008)



on the time scale of the precursor <u>no vibrational damping</u> on silicon

Excited Si-H stretch ~4300-4400 cm^{-1}
Band gap ~8950 cm^{-1}
Energy mismatch with 3rd bend overtones

→ multi-phonon process

outline

1. Motivation: XH_4 dissociative chemisorption dynamics

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2. XH_4 vibrations and the relation to transition state structures

- Qualitatively, one can maximize the projection on reaction coordinates by exciting a vibrational mode resembling the transition state structure
- Quantitatively, one must be precautious because of dynamics

3. Survival of excited vibrations in physisorbed precursor

Conclusion

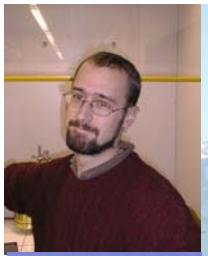
we need more theoretical studies on

dynamics

- Evolution of normal modes upon the approach of a metal surface ?
- Local modes survival in physisorbed precursor (in the spectator approach)?

The group

Dr. Mathieu Schmid / Dr. Plinio Maroni / Dr. Marco Sacchi / Dr. Tung T. Dang
Dr. Régis Bisson / Bruce Yoder / Li Chen / Prof. Rainer D. Beck



funding