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Miramare - Trieste, Italy

Eigenstate-Resolved Measurements of Methane Dissociation on Ni(100)

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Eigenstate-Resolved Measurements of Methane Dissociation on Ni(100)

- Overview
  - Motivation for State-Resolved Studies
  - Methane Surface Chemistry
- Experimental Approach
  - Instrumental Considerations
  - Doppler Mapping Detection
- Experimental Results
  - Efficacy of C-H stretch Excitation (v=1, ν_3)
  - Evidence for Mode Specificity (v=3, ν_4)
  - Rotational Effects
    - Efficacy of Rotational Energy
    - Reactivity of Coriolis-Coupled ν_3 Sublevels
    - Dynamical Effects
- Summary

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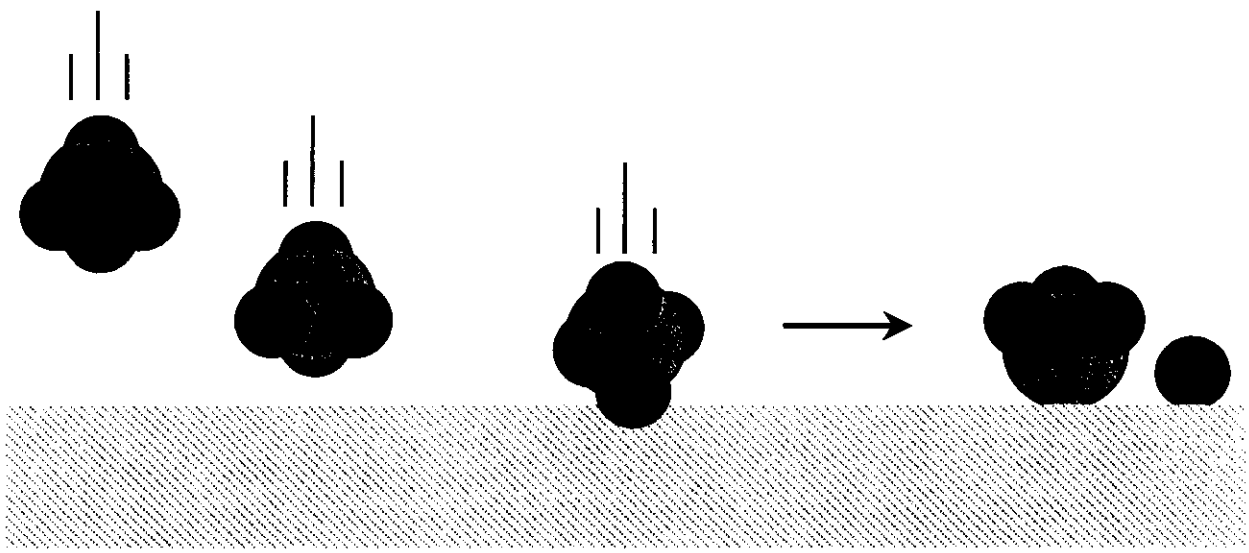
Why study methane dissociation on nickel?

$$CH_4\,(g) \xrightarrow{Ni} CH_3\,(ad) + H\,(ad)$$



- Prototype for C-H bond activation
- Benchmark for theoretical calculations
- Permits comparison of distinct vibrational modes

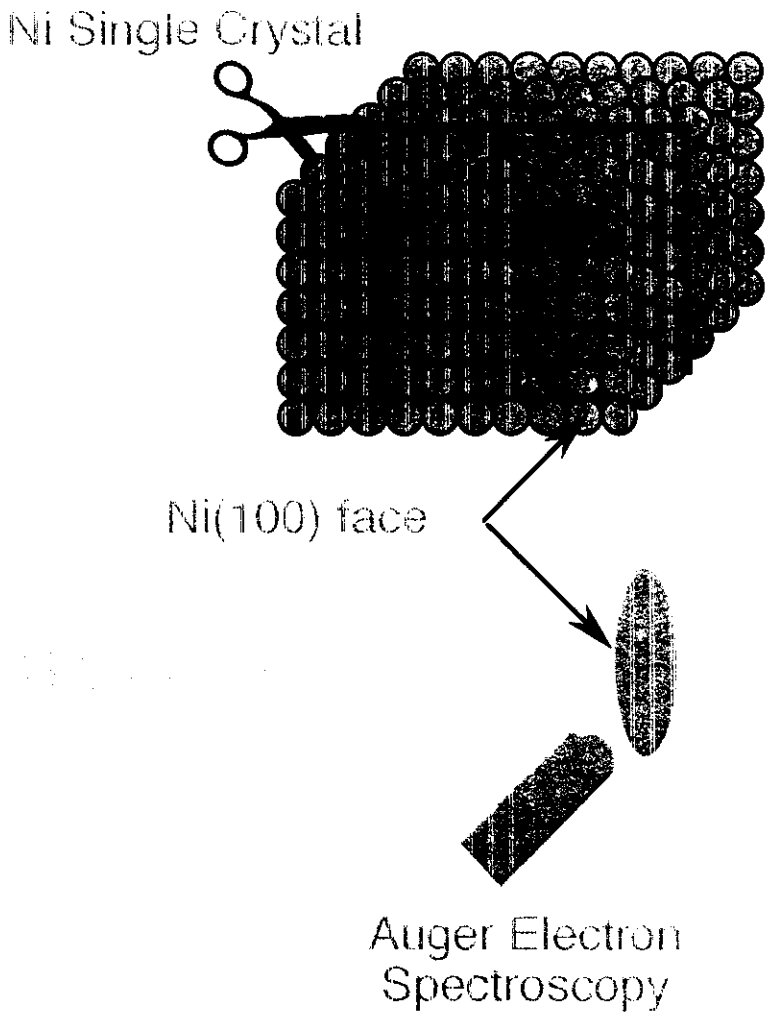
- Methane conversion is important industrial process

Steam Reforming Reaction

$$CH_4 + H_2O \xrightarrow{Ni} CO + 3\,H_2$$

- Chief industrial pathway for H_2 production
- CH_4 dissociation step is rate limiting

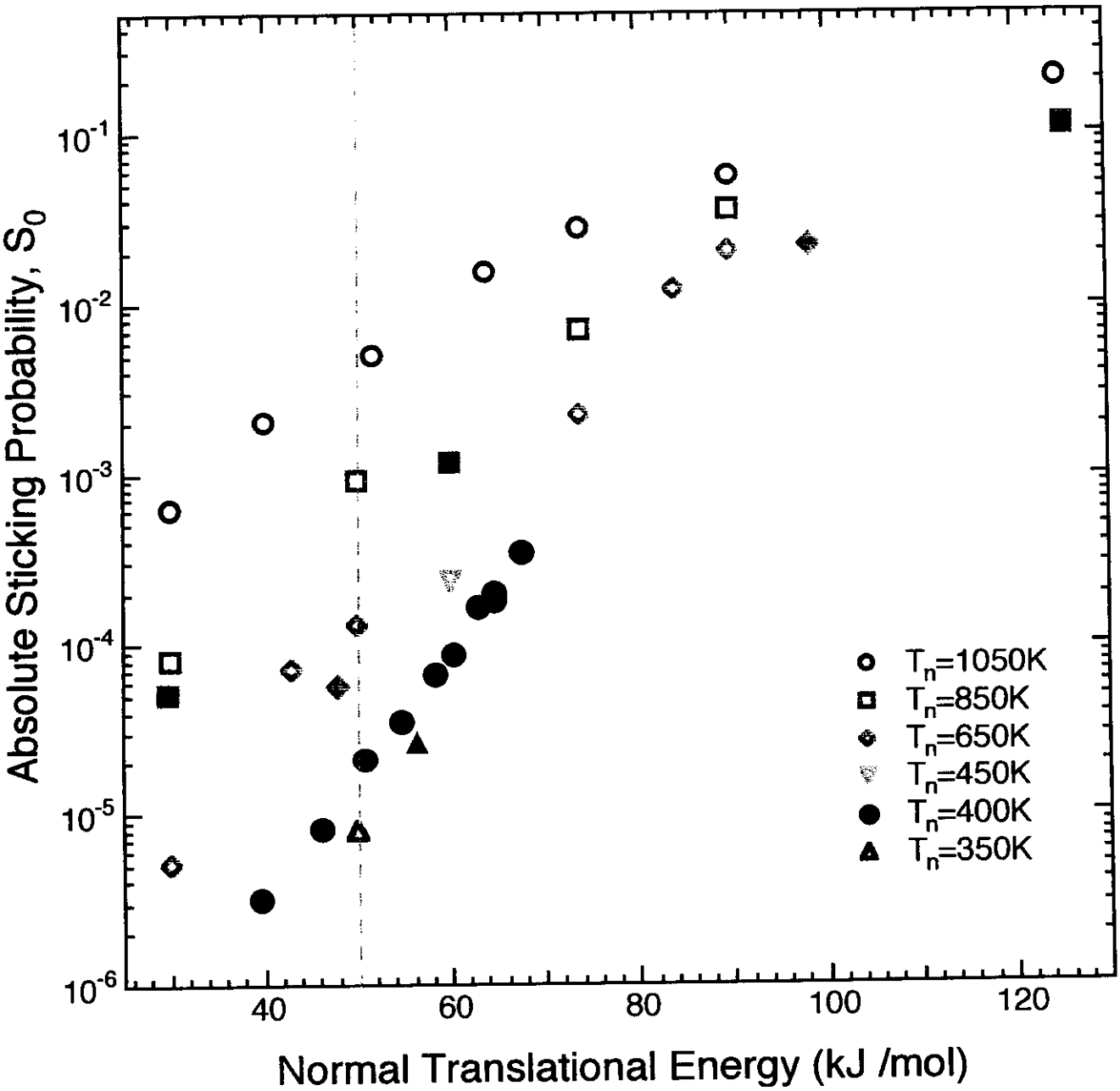
easuring State-Selected ethane Dissociative nemisorption Probabilities



Supersonic Beam
$\Delta E/E \approx 10\%$

$$\frac{\text{Measure C surface coverage Auger Electron Spectroscopy} \} \text{\# of Molecules Dissociated / cm}^2}{\text{Molecular Beam Flux} \times \text{time} \} \text{\# of Incident Molecules / cm}^2} = S_0 \quad \text{Reaction Probability}$$

Some More Experimental Data for CH_4/Ni(100)

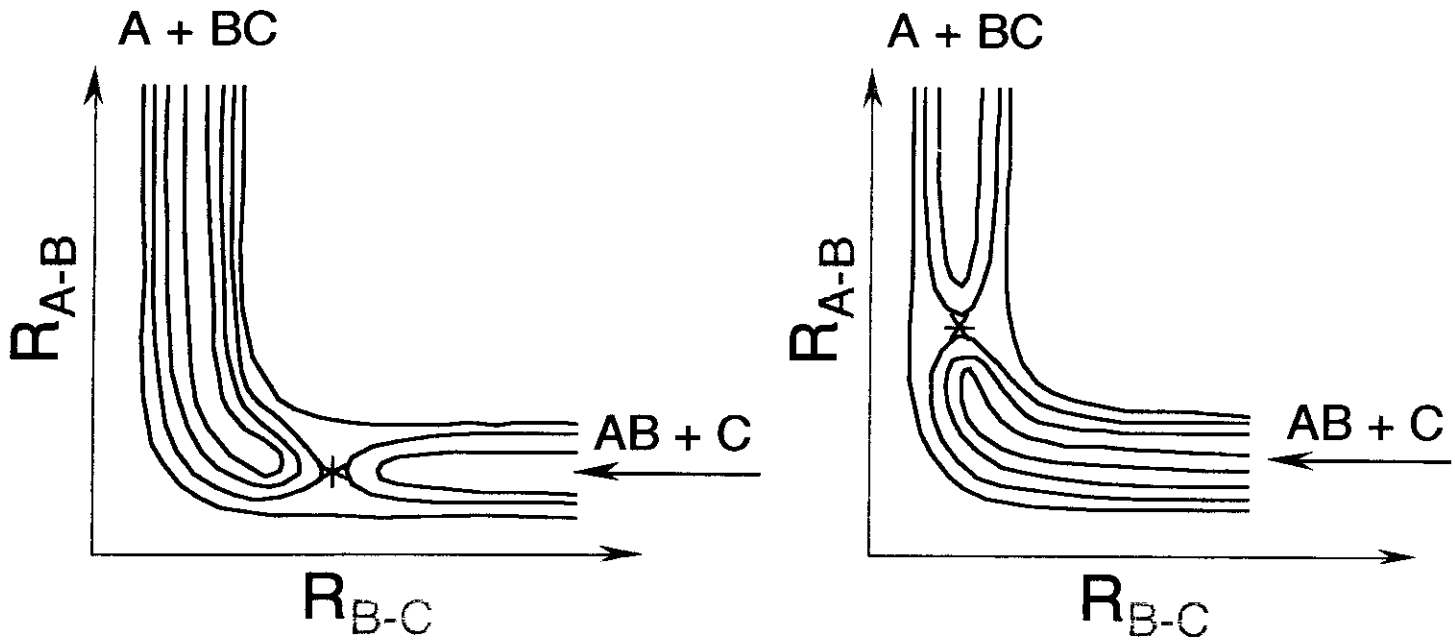


- S_0 increases exponentially with E_{trans}
- Nozzle Temperature (T_n) affects S_0 at fixed E_{trans}
- T_n effect due to enhanced reactivity of thermally populated vibrations in the beam

Open Symbols: Holmblad et al., J. Chem. Phys., **102** , 8255, (1995). Solid Symbols: This Work

2-Dimensional Potential Energy Surface

AB + C ⟶ A + BC (Collinear geometry)



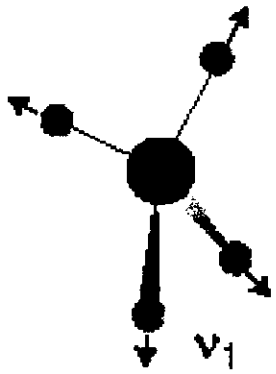
EARLY BARRIER *LATE BARRIER*

- Polanyi's Rules
  - Translational energy for early barrier
  - Vibrational energy for late barrier
- Real PES has many more degrees of freedom
  - Rotations
  - Vibrations (3N-6)
  - Translations …

How do we probe high dimensionality Gas-Surface PES?

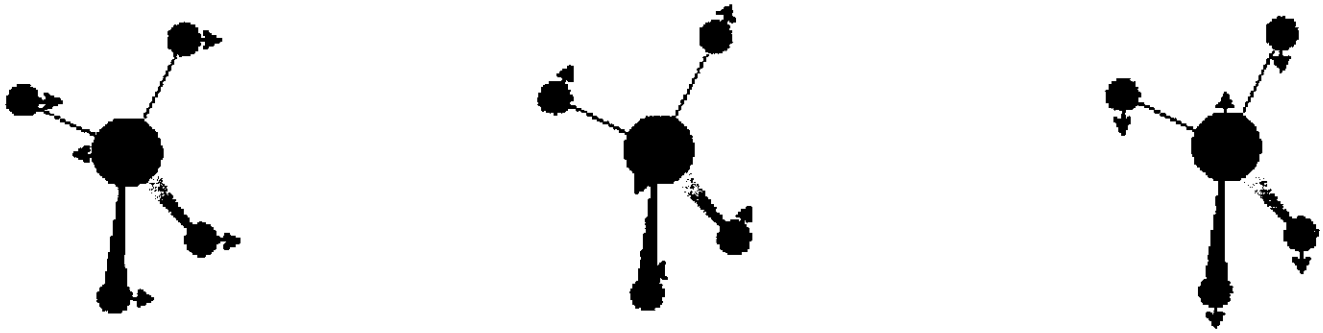
Methane Vibrations

- Methane has four vibrational normal modes

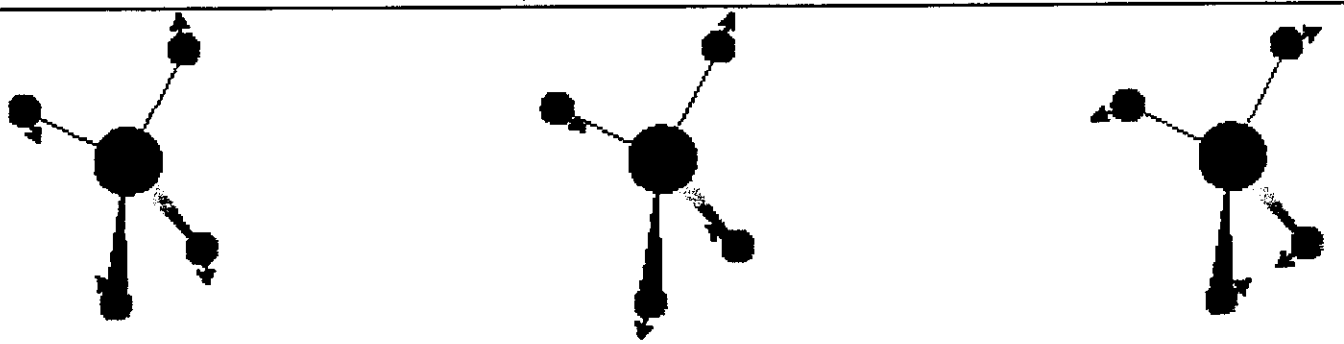


ν_1
Symmetric C-H Stretch
(A_1) 2916 cm^{-1}

ν_2
Doubly Degenerate Bend
(E) 1533 cm^{-1}



ν_3
Triply Degenerate Antisymmetric C-H Stretch
(F_2) 3019 cm^{-1}

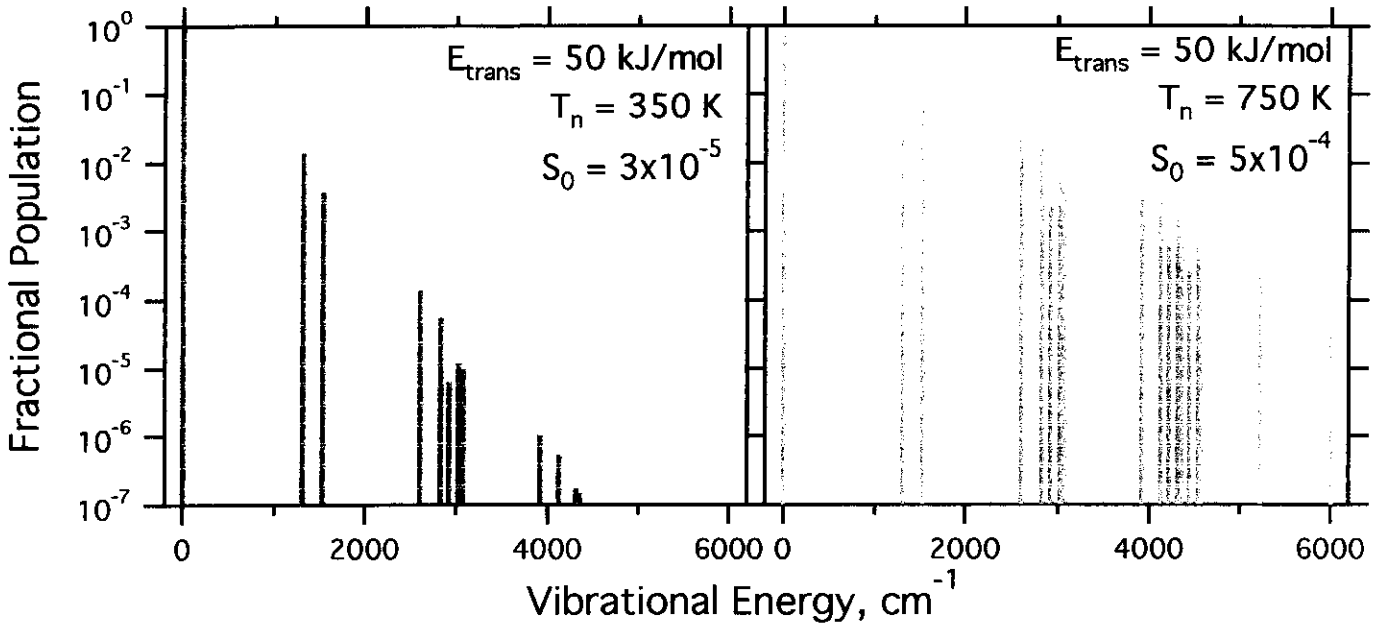


ν_4
Triply Degenerate Bend
(F_2) 1311 cm^{-1}

- These fundamentals, plus their overtones and combination are present in a thermal distribution of vibrational states

The Problem

- "Hot" vibrational distribution is more reactive, but...

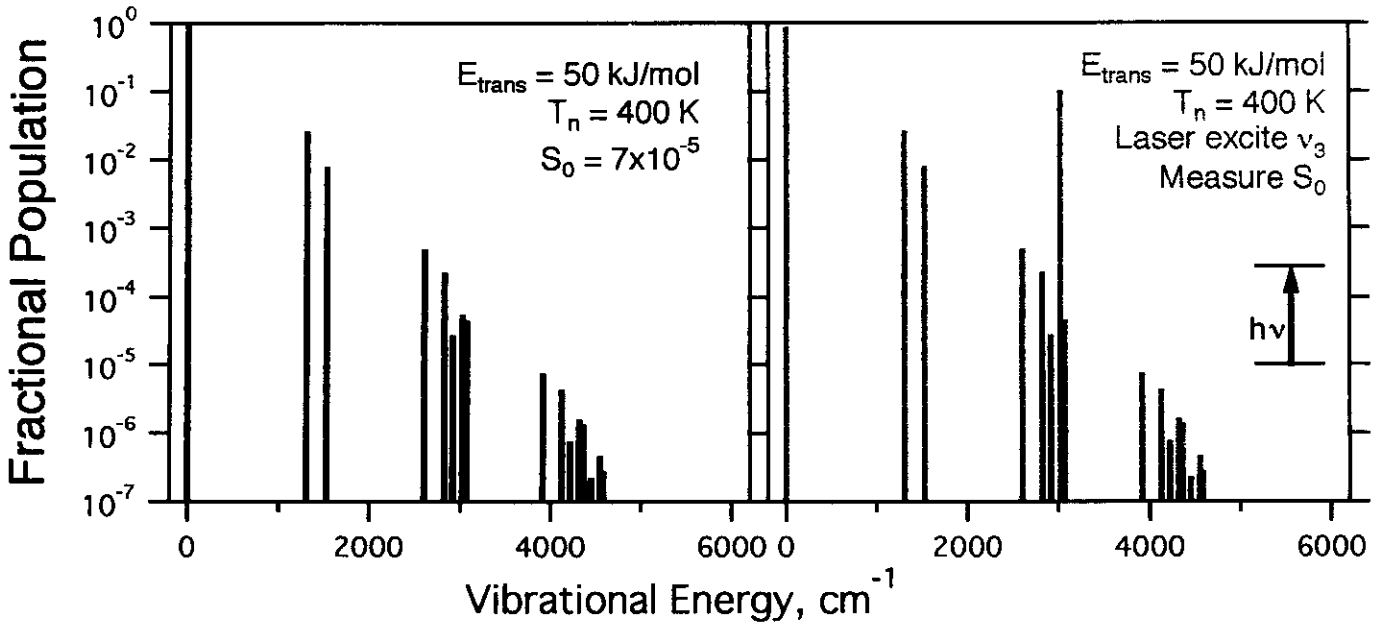


- Many vibrations populated in thermal distribution
  - Different modes
  - Different levels of excitation
- Thermal averaging obscures identity of most reactive mode
- Absolute number of highly excited molecules remains small

Fractional populations calculated.
Dissociation probabilities from P. M. Holmblad, J. Wambach, and I. Chorkendorff, *J. Chem. Phys.*, **102**, 8255 (1995) (Tn = 350 and 750K) and this work (Tn = 400K).

A Solution

- Infrared laser excites single rovibrational eigenstates (e.g. ν_3)



Laser Off: Average S_0 has contributions from v=0 and v>0

$$S_0^{LaserOff} = f_{v=0}\, S_0^{v=0} + (1 - f_{v=0})\, S_0^{v>0}$$

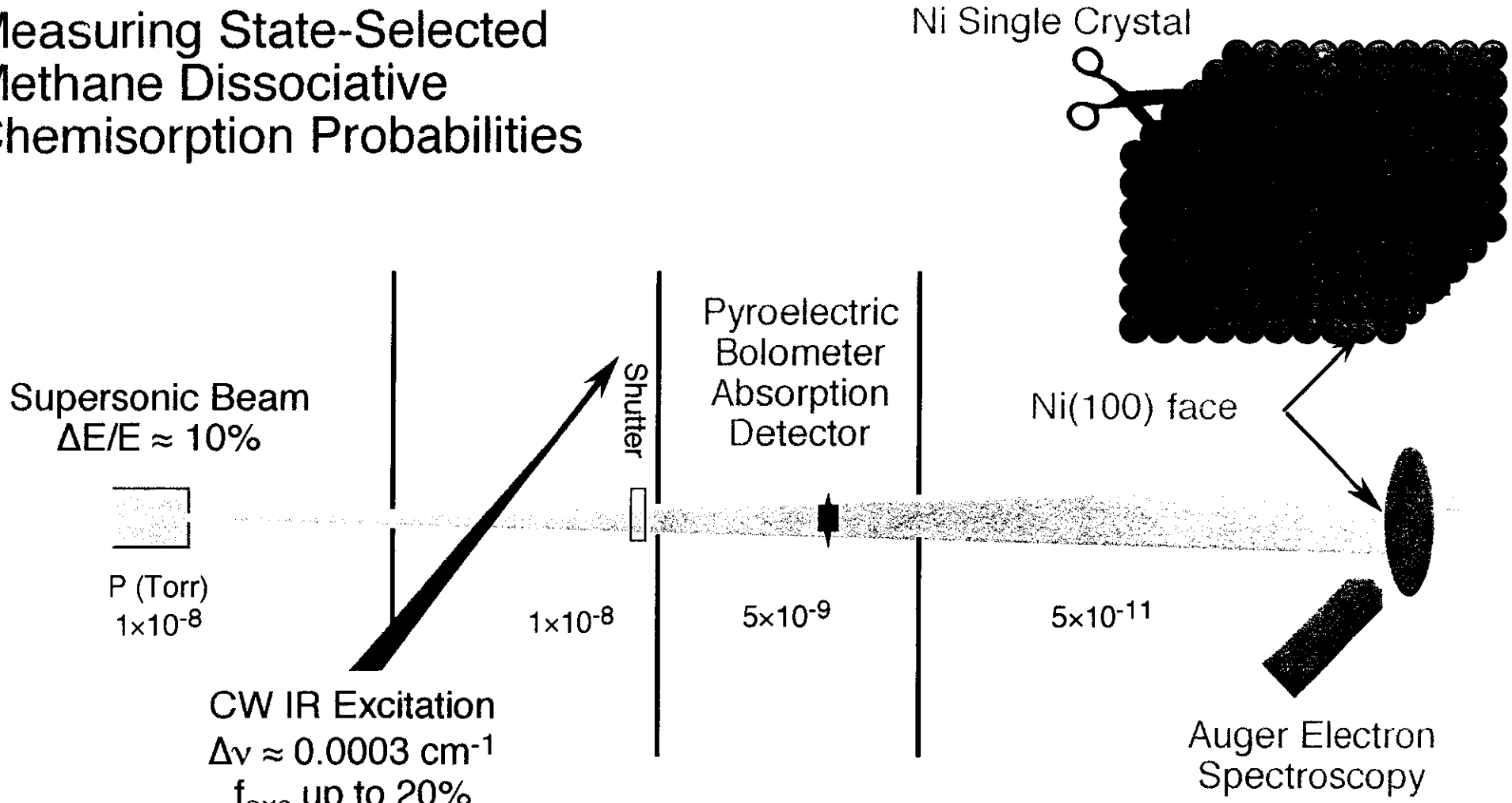
Laser on: Average S_0 has contributions from v=0, v>0, and ν_3

$$S_0^{LaserOn} = (f_{v=0} - f_{exc})S_0^{v=0} + (1 - f_{v=0})S_0^{v>0} + f_{exc}S_0^{\nu_3}$$

$$S_0^{\nu_3} = \frac{S_0^{Laser\ On} - S_0^{Laser\ Off}}{f_{exc}} + S_0^{v=0}$$

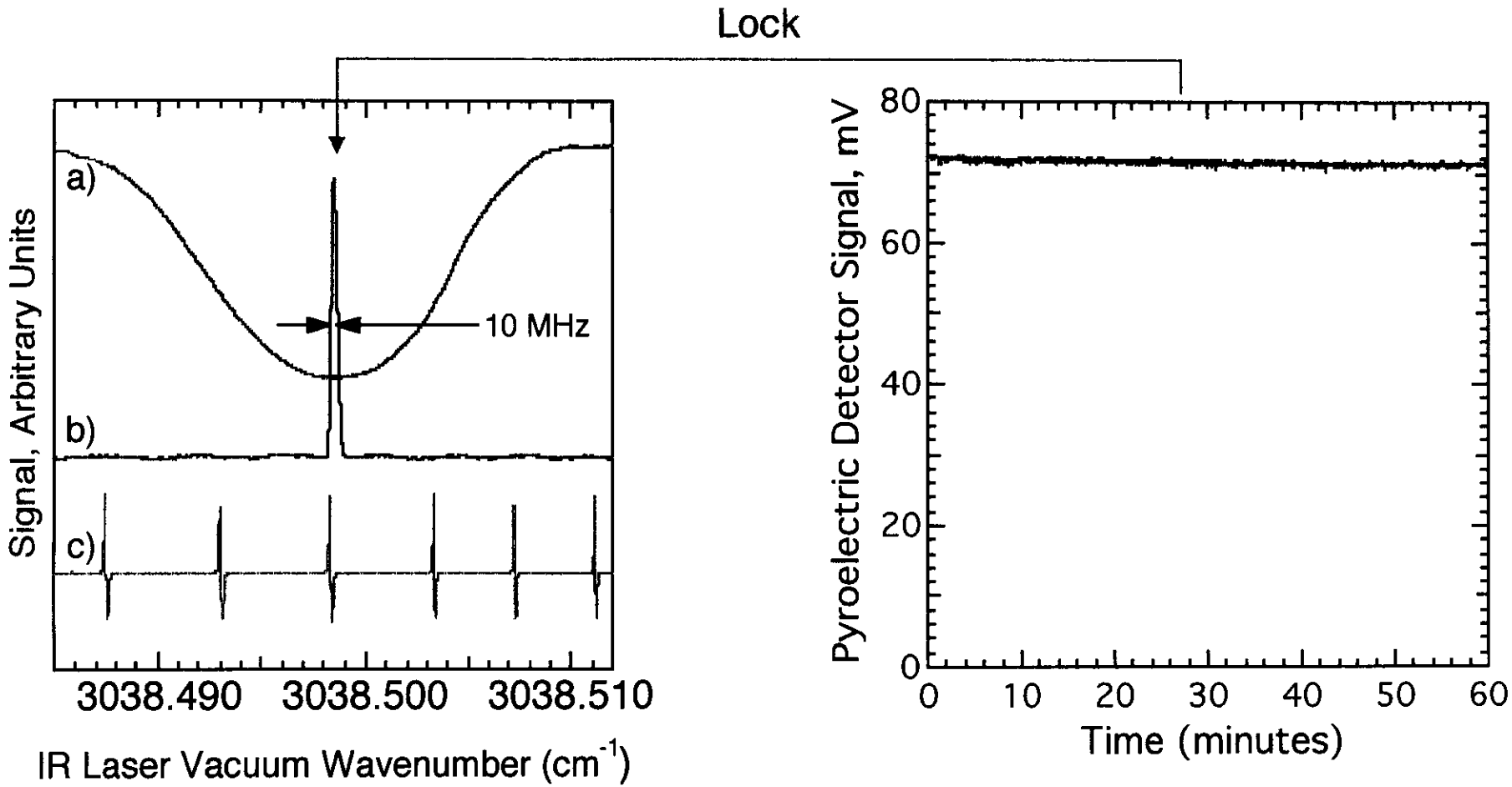
- Measure $S_0^{LaserOff}$ and $S_0^{LaserOn}$
- Optical Saturation Measurement yields f_{exc} (12 - 16%)
- $S_0^{v=0} \ll S_0^{\nu_3}$
- Extracted S_0 independent of vib. state distribution in beam

Measuring State-Selected Methane Dissociative Chemisorption Probabilities



$$\frac{\text{Measure C surface coverage Auger Electron Spectroscopy} \} \text{\# of Molecules Dissociated / cm}^2}{\text{Molecular Beam Flux} \times \text{time} \times \text{IR Excitation Fraction} \} \text{\# of Incident Molecules / cm}^2} = S_0 \quad \text{Reaction Probability}$$

Controlling Reagent Internal Energy



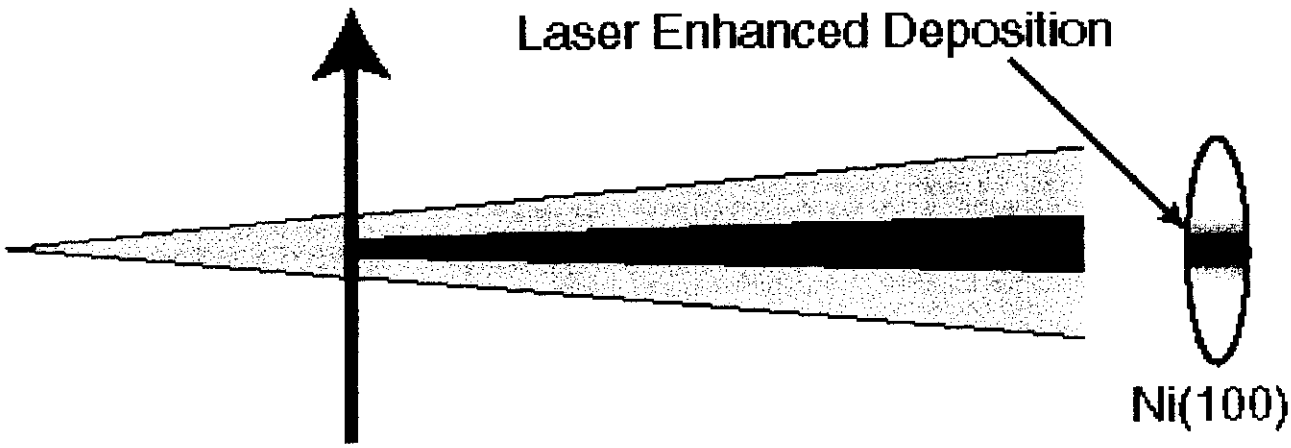
a) CH_4 absorption in room temperature cell. b) CH_4 absorption in molecular beam.

c) Derivative signal of light transmitted through 150 MHz FSR Fabry-Perot etalon.

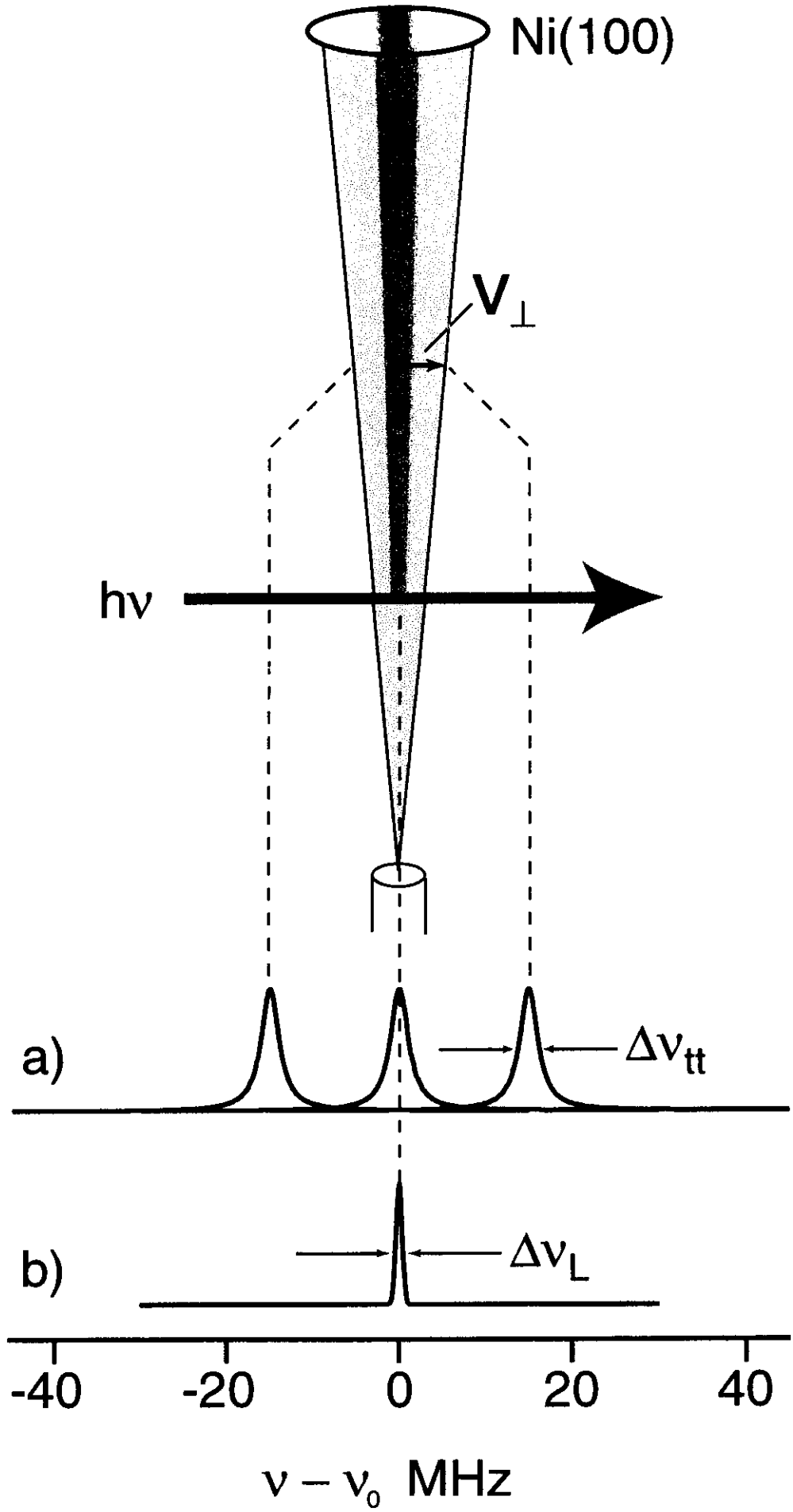
- Transition shown excites J=2 of ν_3, the antisymmetric C-H stretch of $^{12}CH_4$, via R(1).
- Lock laser frequency to zero crossing of Fabry-Perot reference cavity.

Doppler Mapping Detection

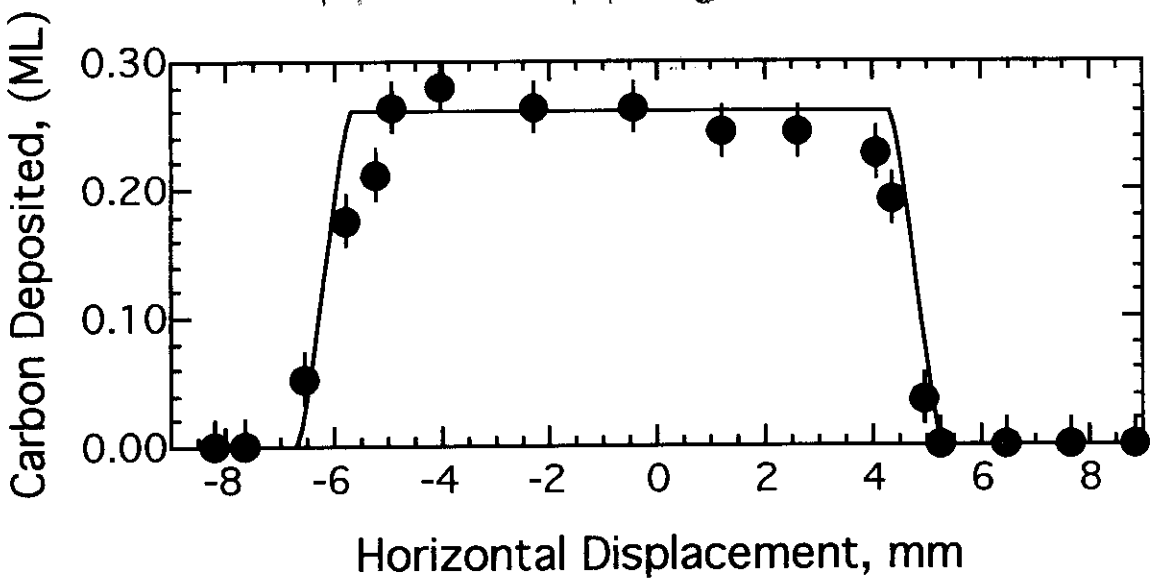
- CW single mode infrared laser linewidth < 1MHz.
- Transit-time broadening dominates lifetime broadening: $\Delta\nu_L \approx 1\text{MHz}$
- Doppler broadening dominates absorption profile due to spread of transverse velocities in diverging molecular beam.
- Narrow bandwidth laser excites subset of the inhomogeneous Doppler profile in the molecular beam.



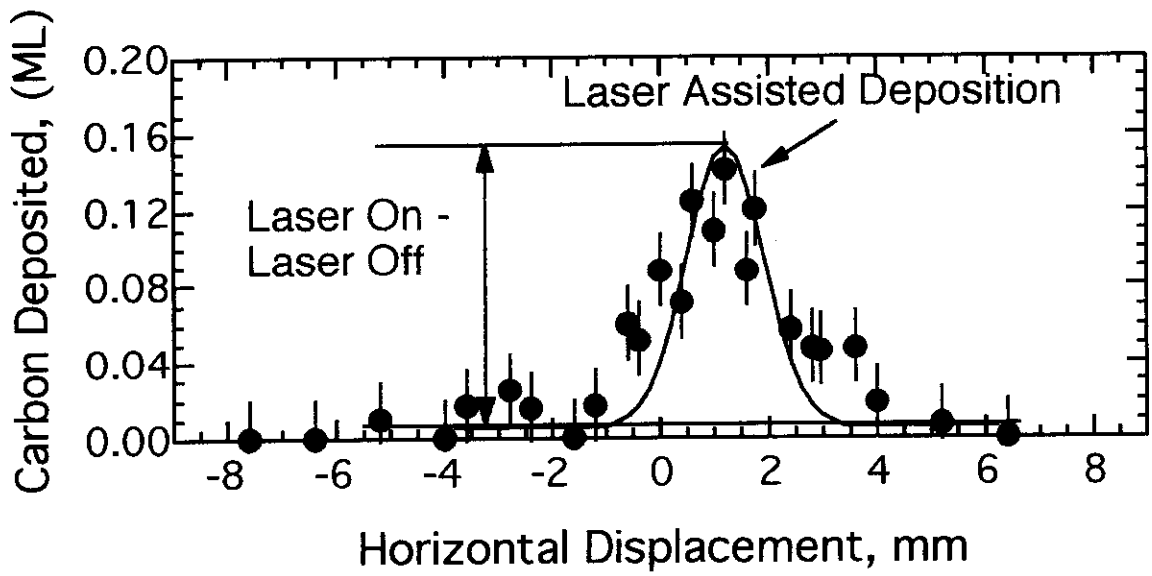
Laser-enhanced deposition is localized on the surface


Ni(100)
$v_\perp$
hν
a)
$\Delta\nu_{tt}$
b)
$\Delta\nu_L$
-40
-20
0
20
40
$\nu - \nu_0$ MHz

Doppler Mapping Detection



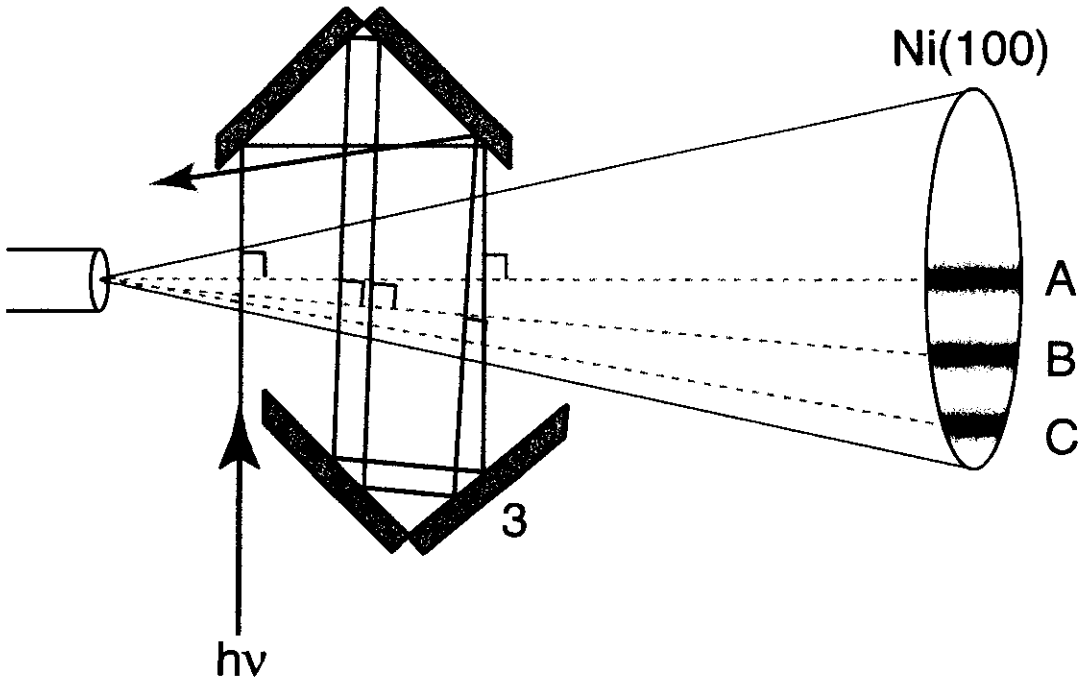
- Dose with Laser OFF. t = 1200 s
- Carbon uniformly deposited across 10 mm diameter crystal

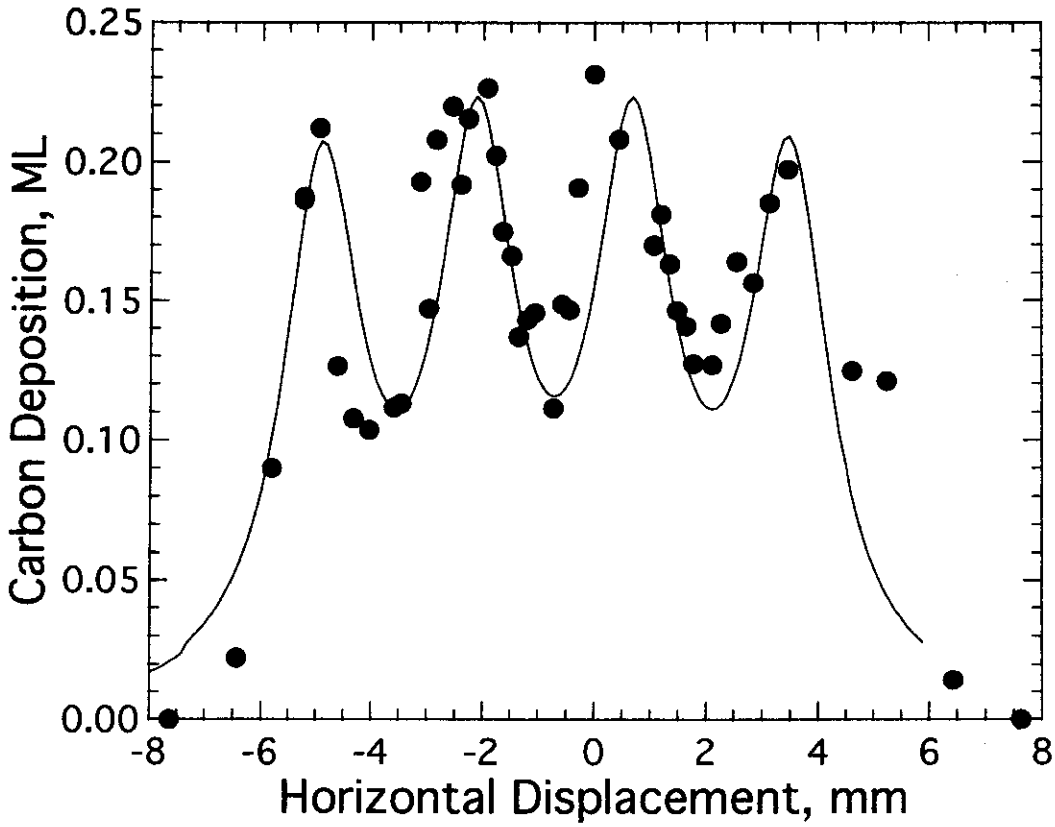


- Dose with Laser ON. t = 50 sec
- Laser-excited molecules localized near crystal center
- Nonzero baseline due to "Laser Off" reactivity

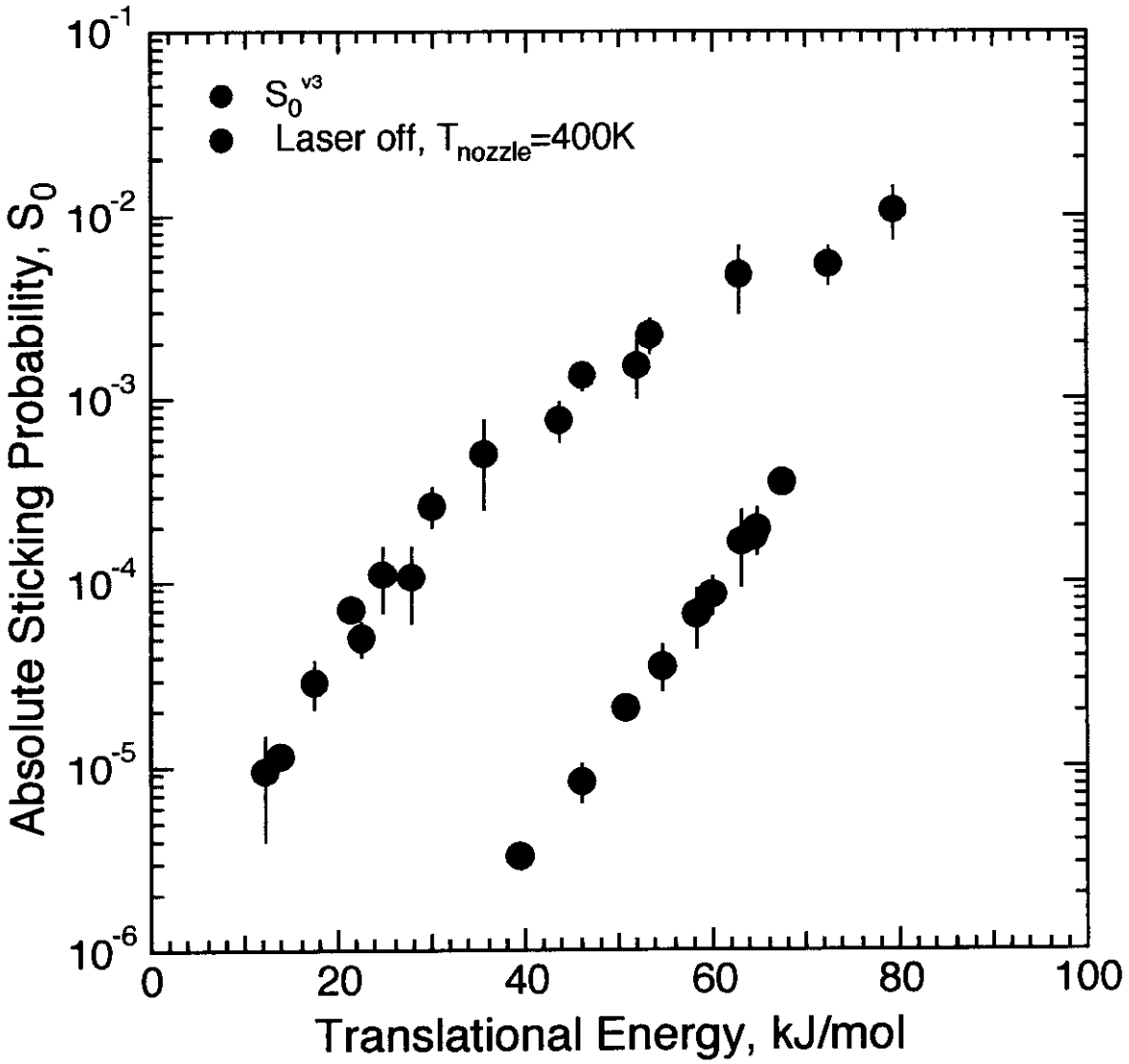
- Simultaneous measurement of signal and background enhances sensitivity.

Effect of Misaligned Mirror





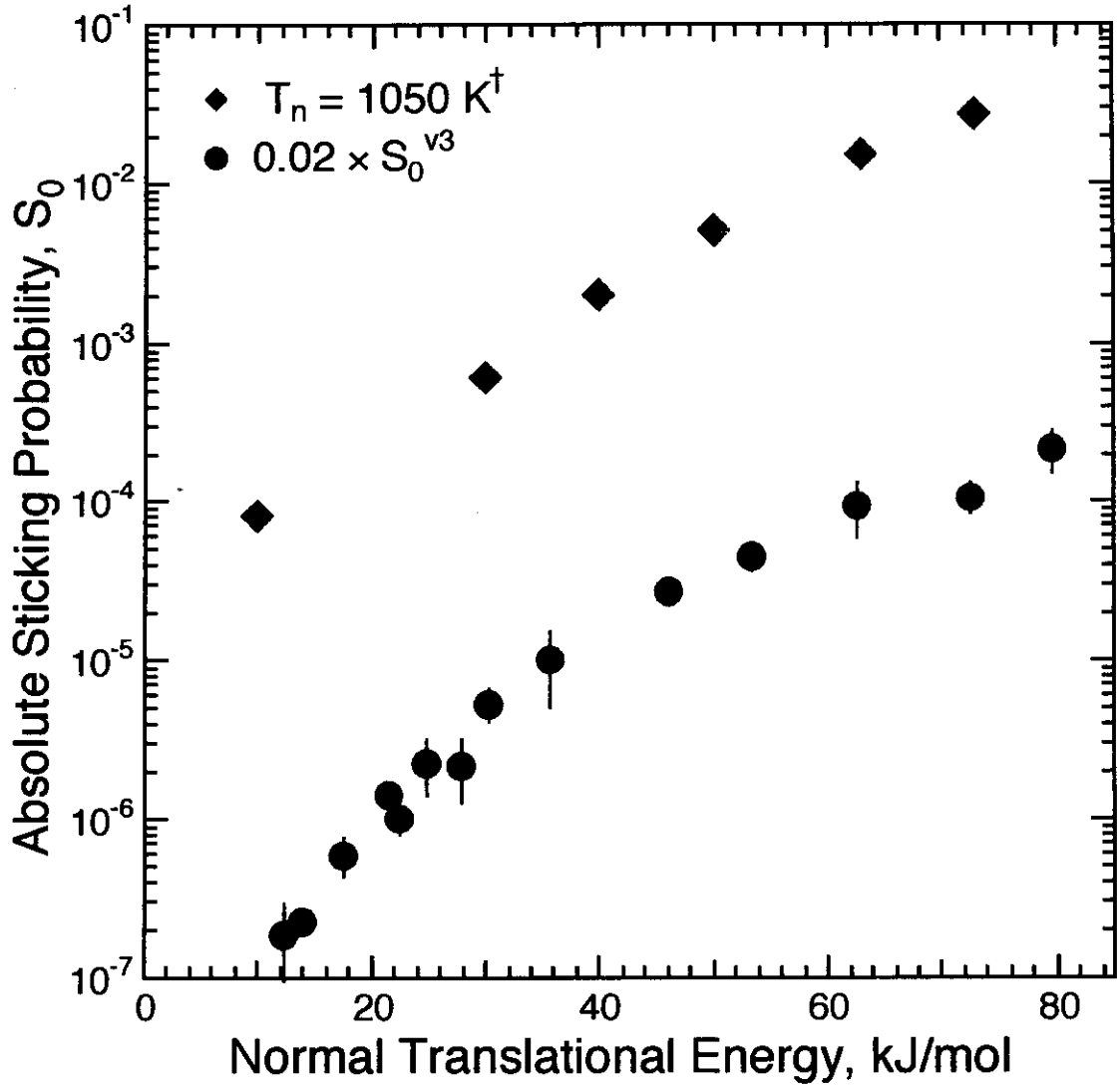
State-Resolved Sticking Probabilities for CH_4 (ν_3, J=2) on Ni(100)



- Excitation of ν_3 J=2 deposits 36 kJ/mole of internal energy and increases S_0 by 500-fold or more at low E_{trans}
- S_0 increases monotonically from E_{trans} = 13-80 kJ/mole
- Despite having $E_{trans} + E_{vib}$ = 116 kJ/mole, S_0 @ E_{trans} = 80kJ/mol is 0.01

The Role of ν_3 in Thermal Processes

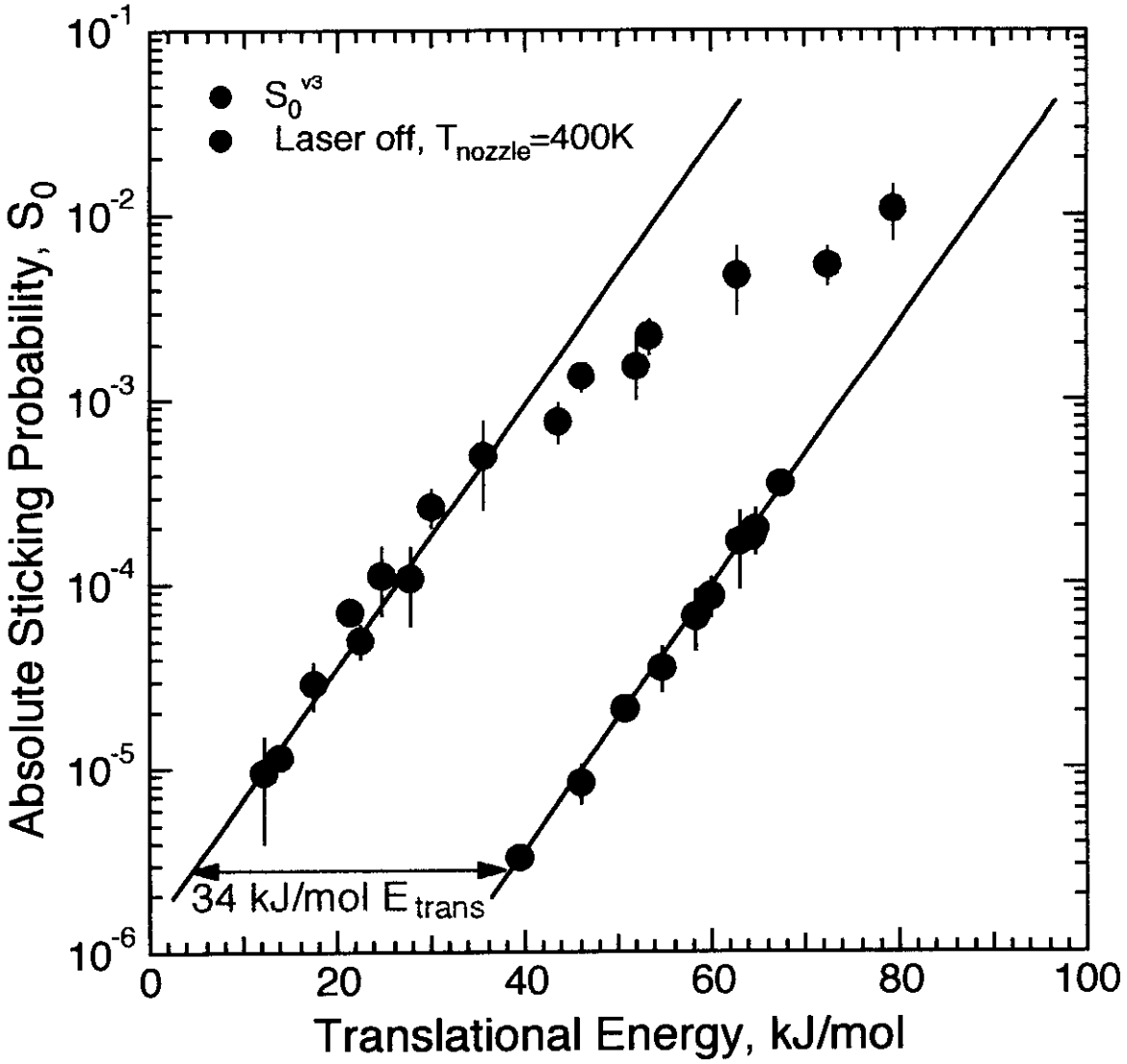
- State-resolved data reveal the contribution of molecules in the ν_3 eigenstate to thermally averaged reaction probabilities.
- Holmblad et al.† report reaction probabilities averaged over a thermal vibrational state distribution at 1050K.



- At 1050K, the fractional population of ν_3, v=1 is $f_{\nu_3} = 0.02$
- $f_{\nu_3} \times S_0^{\nu_3} \approx 0.02 S_0^{T_{vib}=1050K}$
- ν_3, v=1 only accounts for ≈ 2% of S_0 at T_{nozzle} = 1050K.

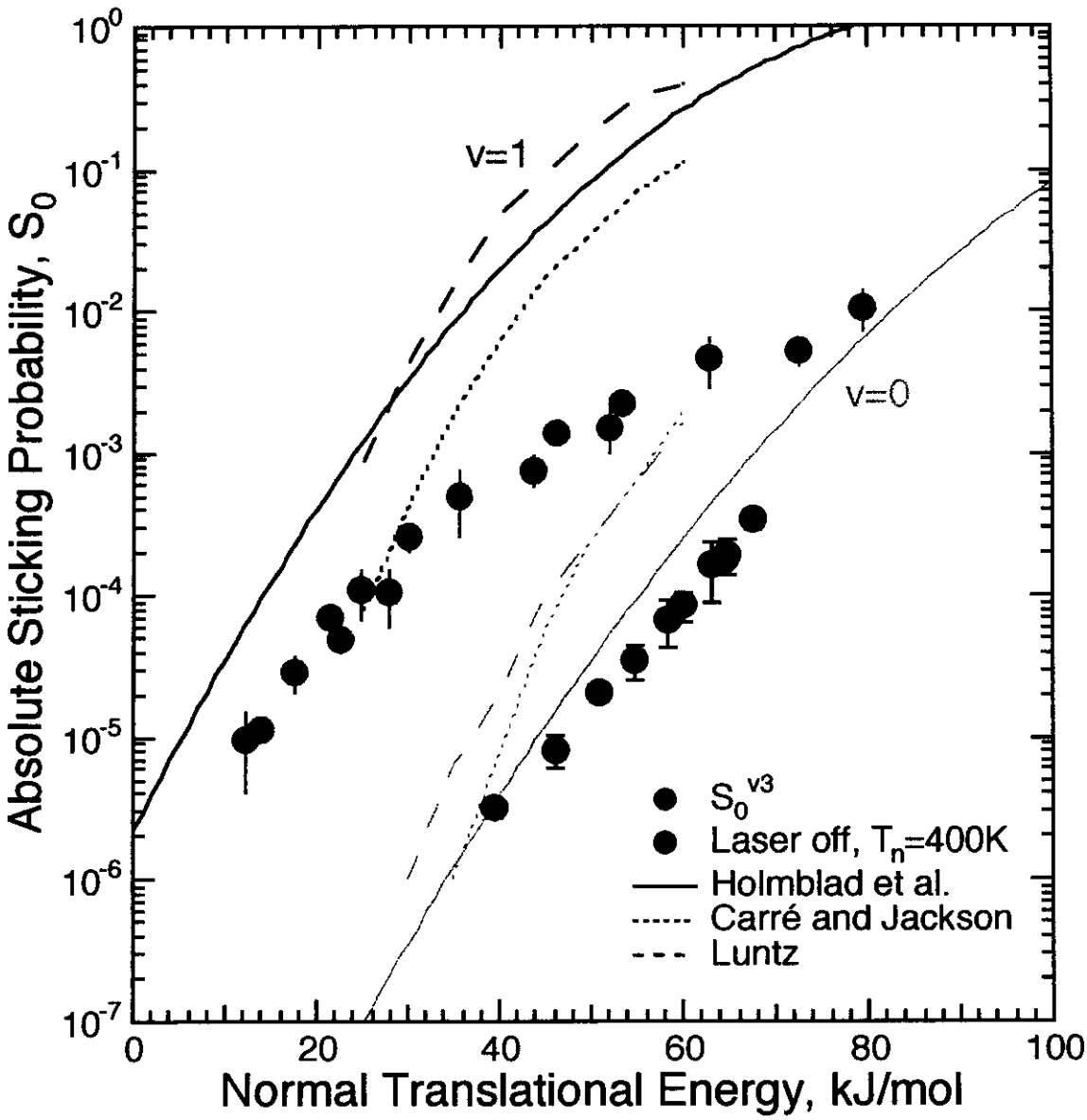
† Data from P. M. Holmblad, J. Wambach, and I. Chorkendorff, *J. Chem. Phys.*, **102**, 8255 (1995).

Testing a Statistical Model of Reactivity



- Excitation of ν_3 deposits 36 kJ/mol of internal energy and increases S_0 by a factor of $\approx$ 200.
- At low S_0, ν_3 excitation shifts the E_{trans} threshold $\approx$ 34 kJ/mol
- These data do not rule out a statistical model of methane dissociation on Ni(100).

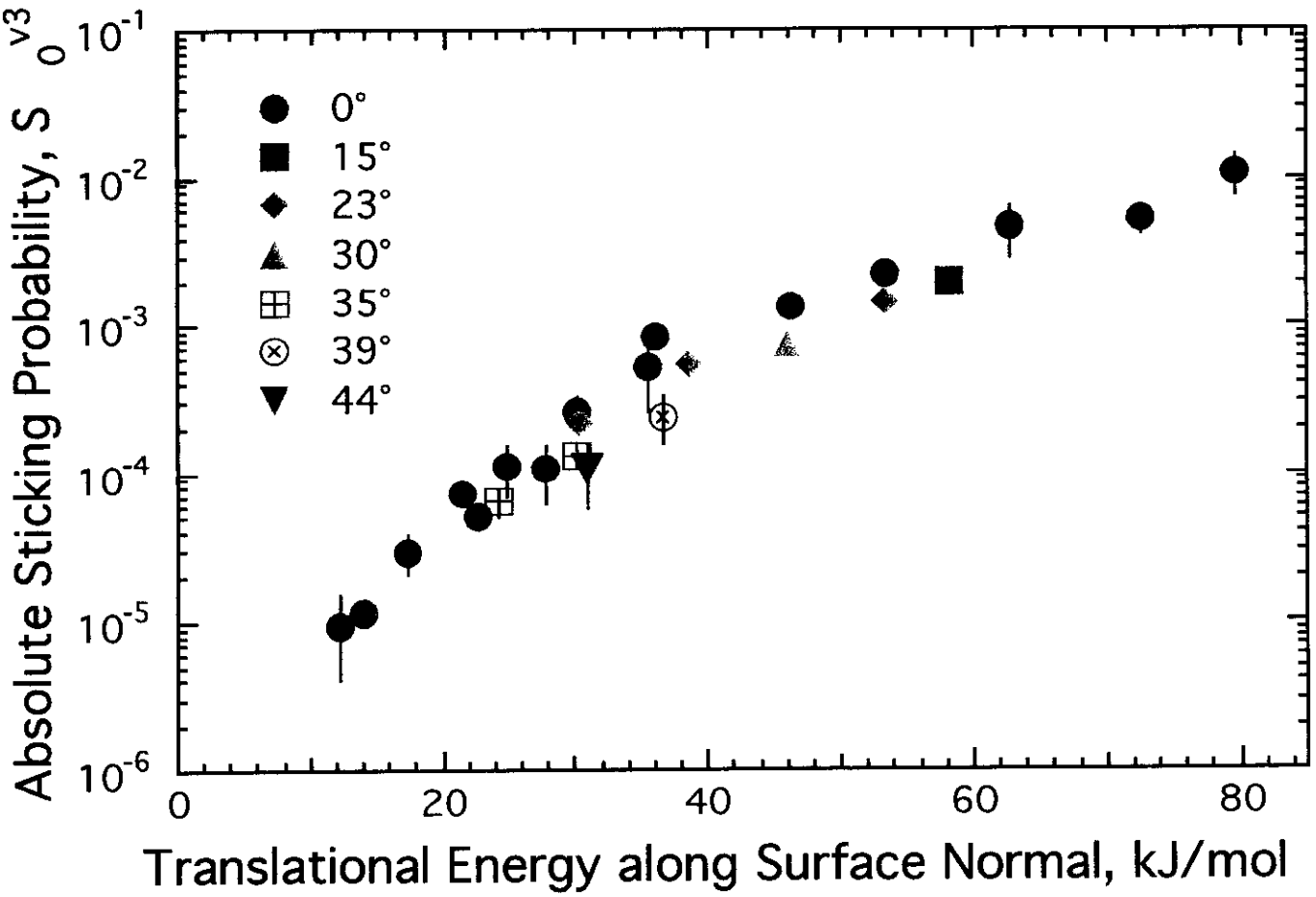
Comparison with Current Theories & Models



- Carré & Jackson: Quantum Dynamics on *ab initio* PES
- Luntz: Quantum Calculation on Empirical PES.
- Holmblad et al.: Empirical model of data assuming only active vibration is C-H stretch.
- Models and calculations overestimate S_0 at high E_{trans}

Normal Energy Scaling

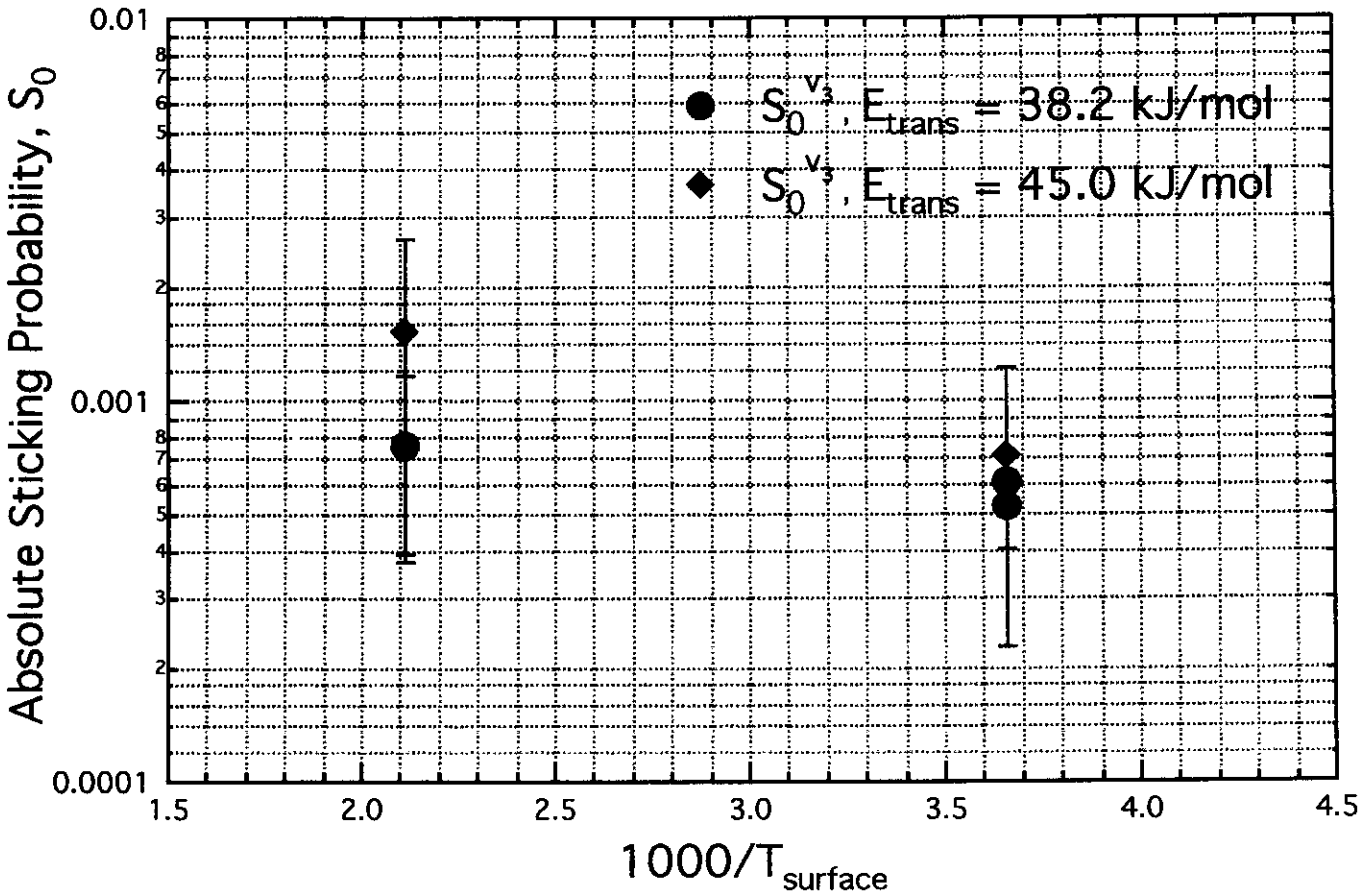
- Methane dissociation on many surfaces, including Ni(100), exhibits normal energy scaling in which only kinetic energy directed along the surface normal promotes reactivity.
- Adherence to normal energy scaling implies that translational motion along the surface normal is coupled to the reaction coordinate while translation parallel to the surface is not.
- We have measured $S_0^{v_3}$ for several translational energies and incident angles. Values are plotted vs. the normal kinetic energy, E_{trans} $(\cos^2\theta)$.



- The data show that CH_4 (ν_3) nearly follows normal energy scaling over the kinetic energy range investigated.
- Excitation of ν_3 does not eliminate the need for translational energy directed along the surface normal.

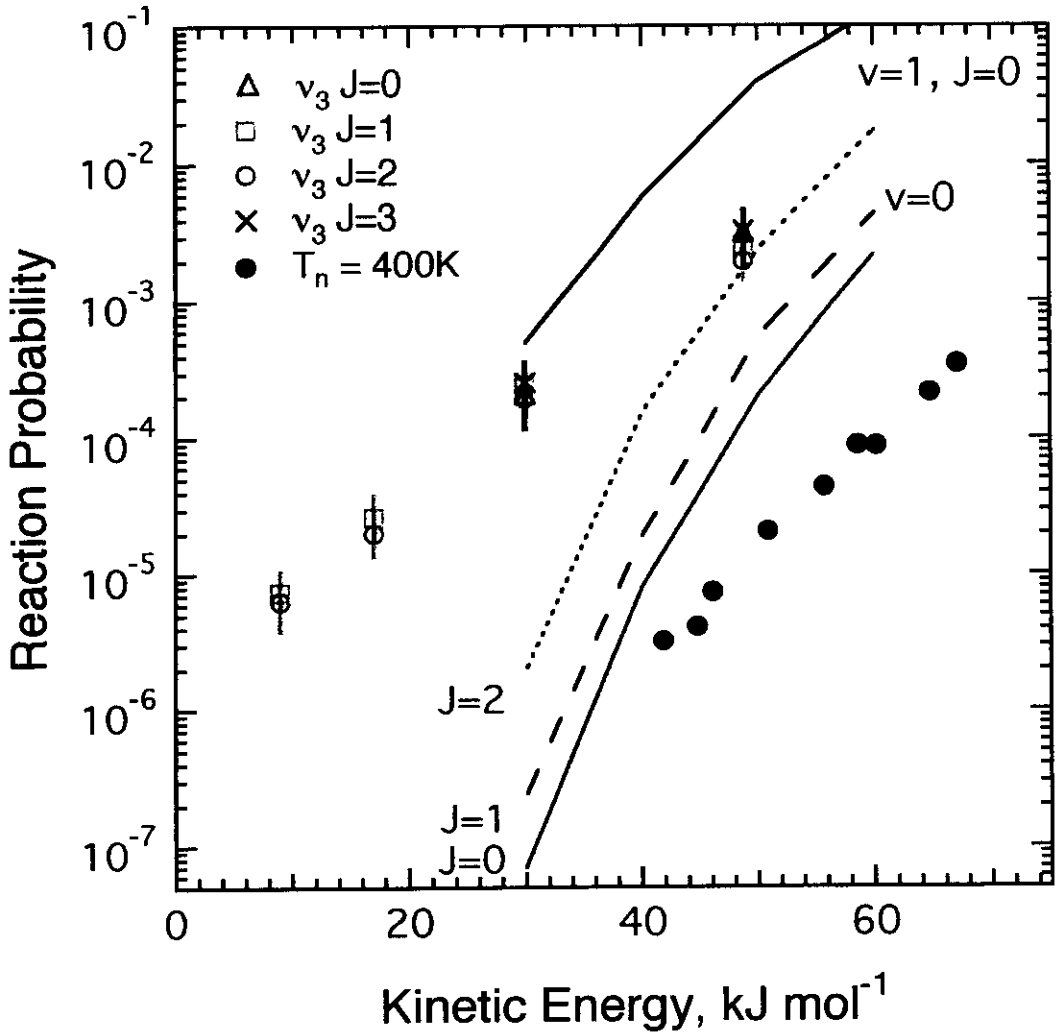
Surface Temperature Dependence

- Methane dissociation on some transition metal surfaces is strongly influenced by surface temperature.
- Such dependence suggests that degrees of freedom associated with the surface are coupled to the reaction coordinate.
- We have measured S_0 for CH_4 in ν_3, v=1, J=2 at different surface temperatures and incident translational energies.



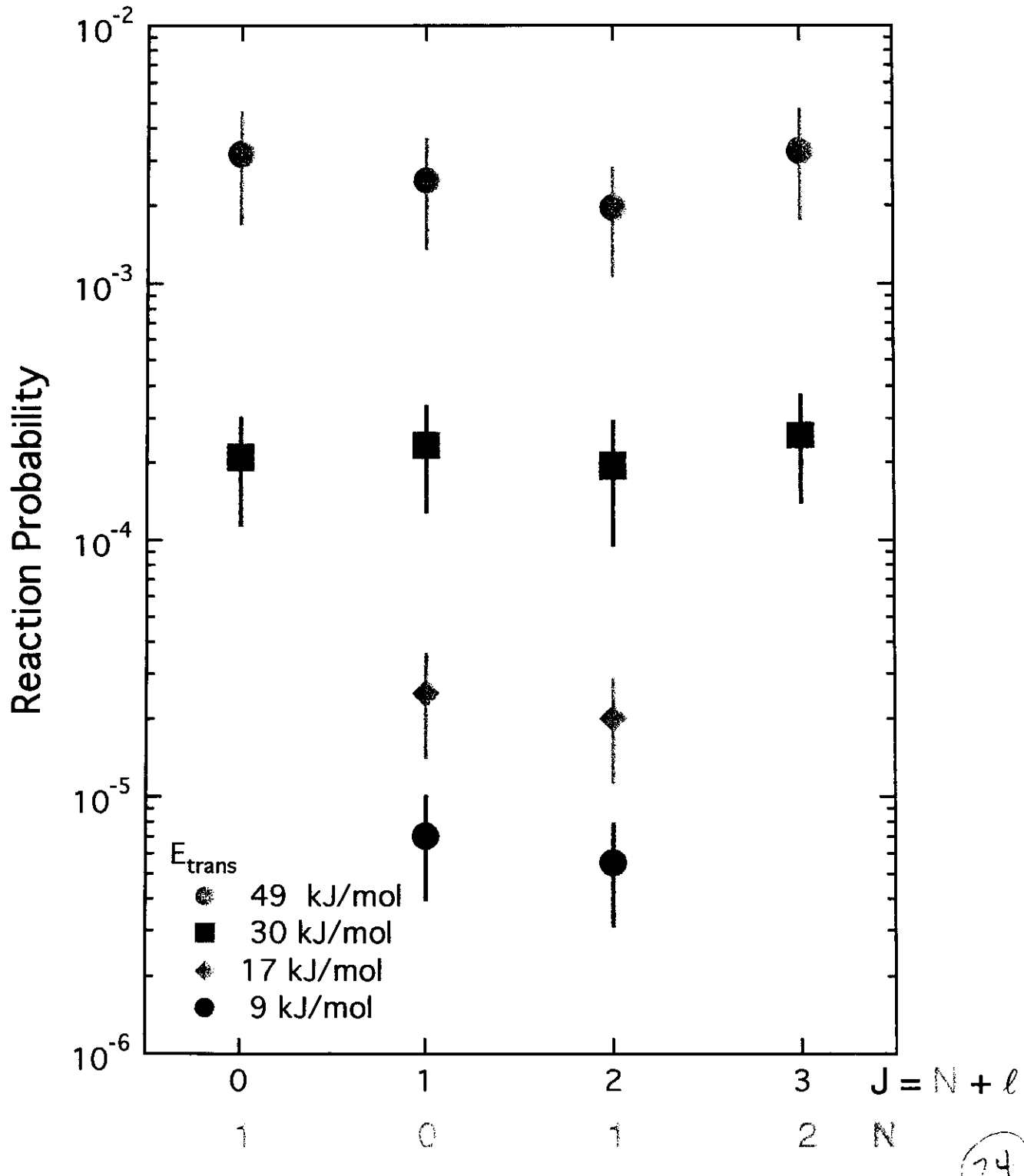
- The data show that $S_0^{\nu_3}$ depends only weakly on $T_{surface}$.

Rotational-State Resolved Sticking Probabilities for CH_4, ν_3 (v=1)

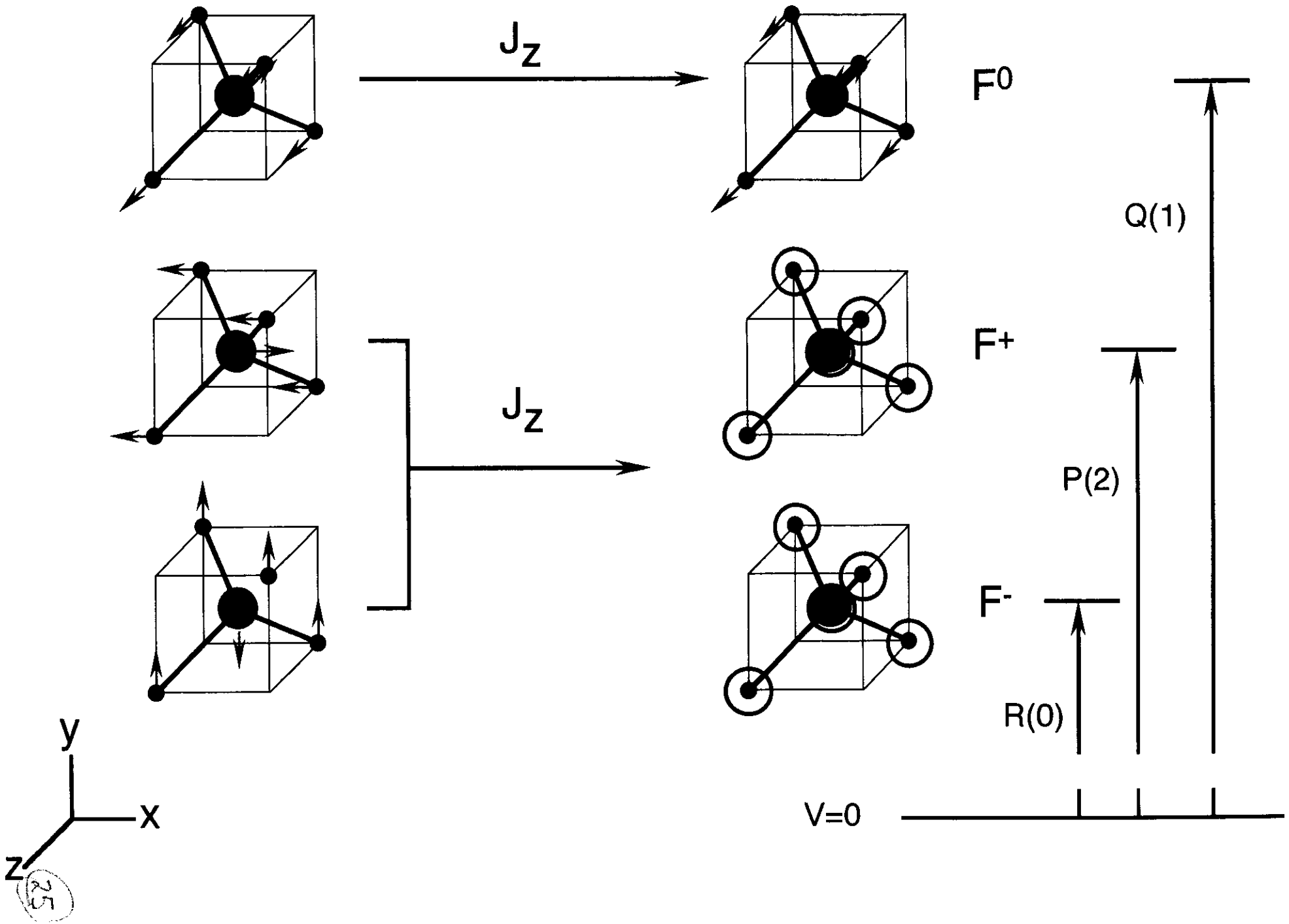


- Excitation of the P(1), R(0), R(1) and R(2) transitions prepares CH_4 in selected rotational levels of ν_3, v=1.
- Rotational excitation does not dramatically alter CH_4 reactivity over the range of J = 0 to 3.
- Results of Carré and Jackson's quantum dynamics calculation appear for comparison.

Rotational-State Resolved Sticking Probabilities for CH_4, ν_3 (v=1)



Coriolis Mixing in ν_3



Reactivity of the ν_3 Vibrational Sublevels

	v = 0					v = 1					fractional excitation	total internal energy (cm^{-1})	Sticking probability
T	N"	ℓ"	J"	RS	population	N'	ℓ'	J'	RS	VS			
R(0)	0	0	0	A_1	0.313	0	1	1	A_2	F^-	0.154	3028.7522	0.0025 ± 0.0012
Q(1)	1	0	1	F_1	0.563	1	0	1	F_2	F^0	0.110	3029.3058	0.0021 ± 0.0010
P(2)	2	0	2	E	0.125	2	-1	1	E	F^+	0.016	3030.5024	0.0019 ± 0.0013

- Vibrational Sublevels share similar reactivity
- Nuclear motions differ in the phase of the C-H motions
- Reactivity appears to depend on the excitation of a single C-H oscillator and not its phase relative to the other C-H oscillators in the molecule
- Detailed results for ν_3, J=2, F^- state are representative of all three vibrational sublevels.

Conclusions

- Supersonic Beam + IR Excitation + UHV Techniques
  - Experiments are feasible and widely applicable
  - State resolved data reveal efficacy of energy in different coordinates

- Mechanistic Insights
  - C-H stretch enhances reactivity
  - Efficacy of C-H stretch and $E_{trans,\perp}$ comparable
  - $3\nu_4$ bend less effective than ν_3 C-H stretch
  - Other modes contribute to thermal reactivity
  - Stretch + Bend combination vibrations likely resemble reaction coordinate most

- Comparison with theory
  - Current models overestimate the reactivity of the C-H stretching state.
  - Experimental data point to the importance of both stretching and bending excitation.
  - Statistical model inconsistent with 3 ν_4 reactivity

- Future work
  - Investigate reactivity of combination modes
  - "Tuning" molecular eigenstates

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