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ADRIATICO RESEARCH CONFERENCE on

LASERS IN SURFACE SCIENCE

11–15 September 2000

Miramare – Trieste, Italy

Vibrational Energy Transfer and Reactivity of Highly Vibrationally Excited Molecules at Solid Surfaces

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Vibrational Energy Transfer and Reactivity of Highly Vibrationally Excited Molecules at Solid Surfaces

IBM

Coworkers:

IBM Research: H. Hou, C.T. Rettner

UCSB: Y. Huang, S.J. Gulding, A.M. Wodtke

Themes

- Interactions of highly vibrationally excited molecules at surfaces are largely unknown
  - ✓ **how will vibrational relaxation change as we go to very high vibrational states?**
  - ✓ **novel surface chemistry?**
- Energy requirements / energy disposal for surface chemical reactions
  - ✓ **experimentally, put vibrational and translational energy on an equal footing**
  - ✓ **probe the terrain of the PES -- Polanyi rules**
  - ✓ **Effects that are beyond the Polanyi rules**

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Outline

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- Introduction
  - role of vibrational energy in chemical reactions
  - Polanyi rules and beyond
  - preparing vibrationally excited molecules
- Vibrational energy transfer at Metals
  - some history
    - ✓ electronically mediated
  - new data for NO(v=2)
- Studies at high levels of vibrational excitation
  - NO(v=12,15) scattering from Au(111) and O/Cu(111)
    - ✓ vibrational enhancement of electron transfer
    - ✓ vibrational enhancement of dissociative adsorption

Potential Energy Surface for a Chemical Reaction

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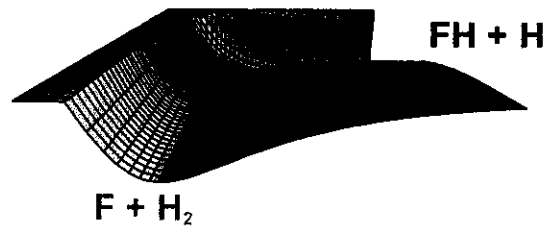
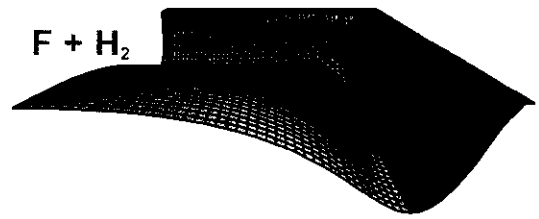
Goal: Determine the Interatomic Interactions / Motions that are a Chemical Reaction

- ✓ **Molecular Beam Experiments**
  Nobel Prize in Chemistry 1986
- ✓ **Theoretical Methods**
  Nobel Prize in Chemistry 1998
- ✓ **Femto Chemistry**
  Nobel Prize in Chemistry 1999



$F + H_2$



FH + H

Early or Late?

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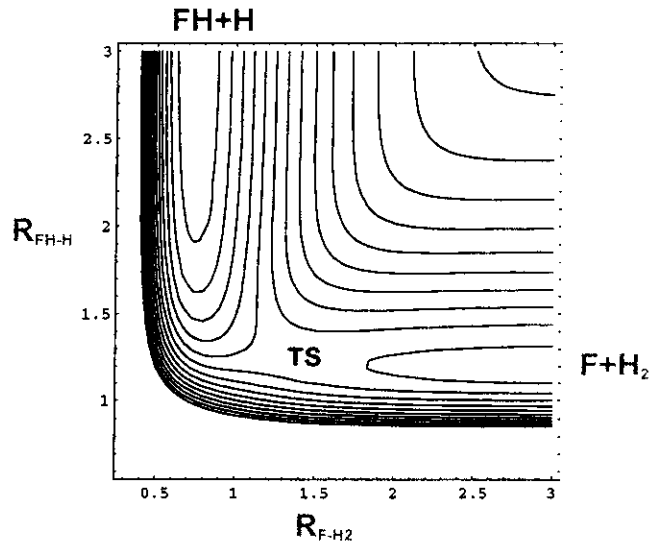
Transition State has similar structure to $F + H_2$

- ✓ **Early Barrier for $F + H_2$**
- ✓ **Late Barrier for H + HF**



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The "Polanyi Rules"

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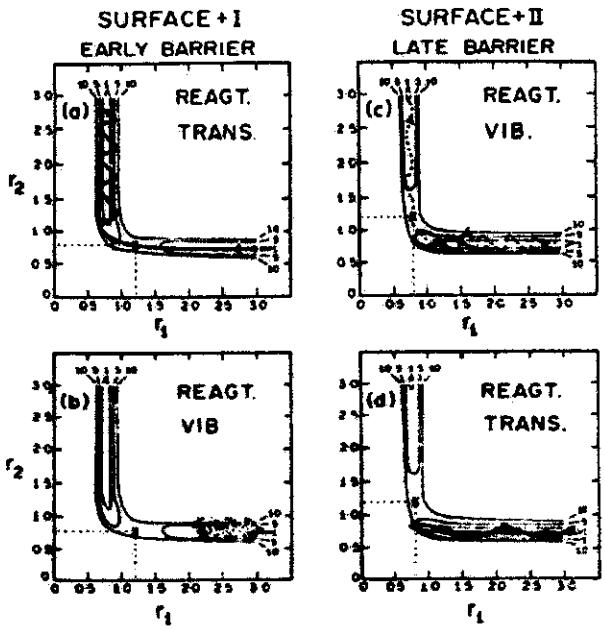
- Translational energy is most effective at overcoming an early barrier
- Vibrational energy is most effective at overcoming a late barrier

"Some concepts in reaction dynamics", John C. Polanyi, *Accounts of Chemical Research, 5 (1972)*



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Preparation of Vibrationally Excited Molecules

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- Thermal
  - ✓ seeded supersonic beams
  - ✓ non specific
- Overtone Pumping
  - ✓ good for hydrides, NO, ...
  - ✓ low lying vibrational levels
- Chemical Activation
  - ✓ non specific
- Stimulated emission pumping (SEP)
  - ✓ more about this later

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Vibrational Excitation of NO in Surface Collisions

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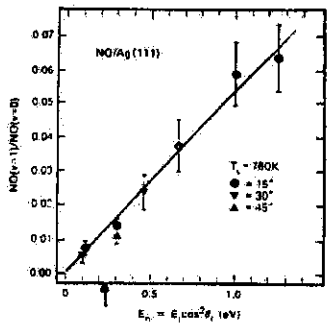
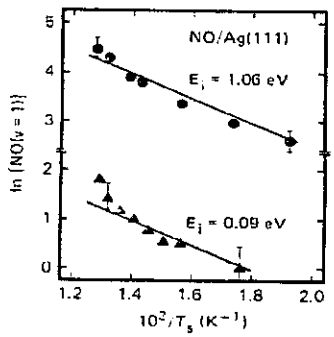
- *Observations for NO(v=0) +*
  - ✓ Ag(111) Rettner, Fabre, Kimman, Auerbach, PRL 55, 1904, (1985)
  - ✓ Cu(111) Watts, Siders, Sitz, Surf. Sci. 374, 191 (197x)
- *excitation probability increases rapidly with*
  - ✓ *kinetic energy*
  - ✓ *surface temperature*
- *scattering similar for 0->0 and 0->1 channels*
  - ✓ *angular distributions*
  - ✓ *velocity distributions*
- *energy required for excitation comes from the surface*





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Previous work on electron mediated surface interactions

IBM

-1. D.M. Newns, "Electron-Hole Pair Mechanism for Excitation of Intramolecular Vibrations in Molecule Surface Scattering" Surf. Sci. (Netherlands), 1986. 171(3): p. 600-614.

-2. W. Yicheng, "On O⁻ emission from cesium-coated surfaces" J. Chem. Phys., 1995. 102(1): p. 525-8.

-3. N. Chakrabarti, V. Balasubramanian, N. Sathyamurthy, and J.W. Gadzuk, "Photoinduced Desorption in NO/Pt - a Time-Dependent Quantum- Mechanical Study". Chem. Phys. Lett., 1995. 242(4-5): p. 490-498.

-4. J.W. Gadzuk, "Resonance-assisted hot electron femtochemistry at surfaces". Phys. Rev. Lett., 1996. 76(22): p. 4234-4237.

-5. J.W. Gadzuk and S. Holloway, "On the Dissociation of Diatomic-Molecules at Metal-Surfaces". Chem. Phys. Lett., 1985. 114(3): p. 314-317.

-6. S. Holloway and J.W. Gadzuk, "Energy Redistribution and Dissociation in Molecule Surface Collisions Involving Charge-Transfer Surface Hopping". Surf. Sci. (Netherlands), 1985. 152(APR): p. 838-850.

-7. J.W. Gadzuk and S. Holloway, "Charge-Transfer and Vibrational-Excitation in Molecule-Surface Collisions - Trajectorized Quantum-Theory". Phys. Scr., 1985. 32(4): p. 413-422.

-8. J.W. Gadzuk and S. Holloway, "Vibrational excitation in gas-surface collisions". Phys. Rev. B, Condens. Matter (USA), 1986. 33(6): p. 4298-300.

-9. Z. Kirson, R.B. Gerber, A. Nitzan, and M.A. Ratner, "Dynamics of metal electron excitation in molecular dipole-surface collisions". Surf. Sci. (Netherlands), 1985. 151(2-3): p. 531-42.

-10. R.E. Palmer, "Electron-molecule dynamics at surfaces", Progress in Surface Science, vol 41, p51, 1992.

-11. J. Los and J.J.V. Geerlings, "Charge exchange in atom-surface collisions" ,Physics Reports, vol.190, p.133 (1990).

Electronic Mechanism for Vibrational Excitation

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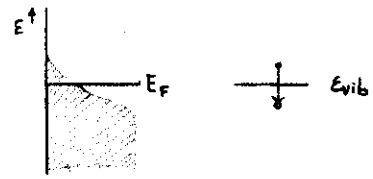
Model

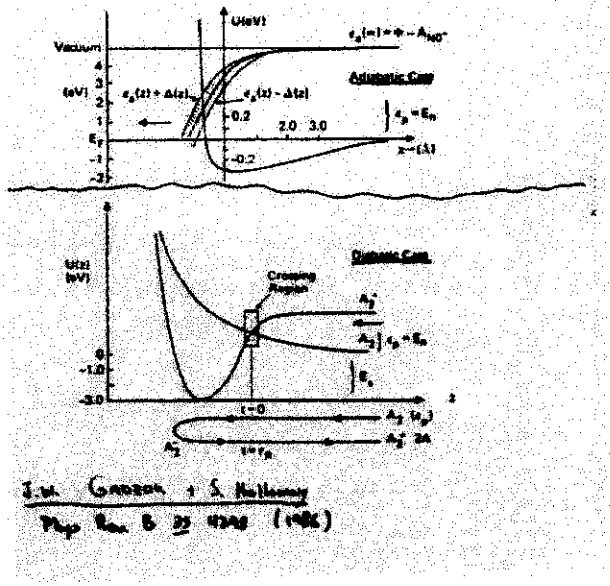


$$P \sim \int \{D(\varepsilon) f(\varepsilon)\} \{D(\varepsilon - \varepsilon_{vib})(1 - f(\varepsilon - \varepsilon_{vib}))\} d\varepsilon$$

Occupied States — Unoccupied States

$$\sim \exp\left[\frac{-\varepsilon_{vib}}{kT_s}\right] \cdot \left[\varepsilon_{vib} - kT_s \ln 2\right]$$

D. NEWNS



T. M. Gadzuk & S. Holloway

Mechanism Controversial

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Various theories reproduce this behavior

- Electron Transfer: non-adiabatic models
  - Holloway and Gadzuk
    - harponing, T->V JCP 82 (1985) 5203
  - Rettner et. al.
    - electron hole pair decay PRL 55 (1985) 1904
  - Gadzuk and Holloway
    - extensive calculation e-h pair PRB 33 (1986) 429
  - Newns
    - e⁻ tranefer to NO π^* Surf. Sci. 171 (1985) 600
- Or Maybe Not: adiabatic models
  - Groes and Brenig
    - T->V Surf. Sci. 289 (1993) 335
  - Gates and Holloway
    - bond softening Surf. Sci. 307 (1994) 132

Incidence energy dependence is probe of mechanism

Gross and Brenig, Surf. Sci 289 (1993) 335

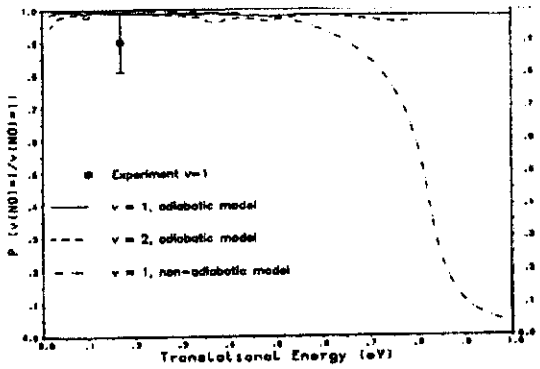

Fig. 3. Survival probability versus incident energy for $T_s = 300$ K of the $v = 1$ and $v = 2$ molecules according to our model and of the $v = 1$ state according to the purely non-adiabatic model. Experimental value from ref. [22].

Observing Survival Probability: Optical Preparation of NO(v=2)

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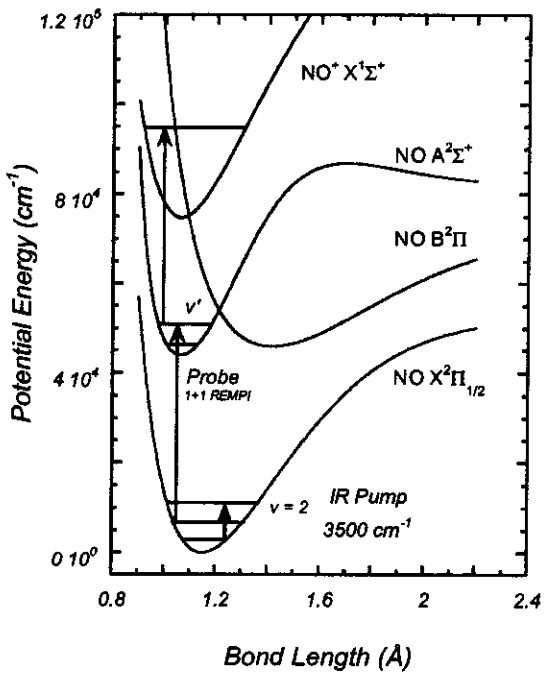
- Problems
  - *Observing Survival of v=1*
    - ✓ Prepare low J-states in beam
    - ✓ v=1 thermal background a big problem
  - *Observing de-excitation of v=1->0*
    - ✓ NO(v=0) background a huge problem
- Solutions
  - *Overtone excitation of NO(v=0->2)*
    - ✓ Difference frequency generation
    - ✓ 5 mJ/pulse
    - ✓ 0.05 cm^{-1}
  - *REMPI Probe*
    - ✓ 1+1 REMPI
  - *Advantages of this experiment*
    - ✓ Probe excitation to v=3
    - ✓ Probe de-excitation to v=1



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Schematic of Experimental Apparatus

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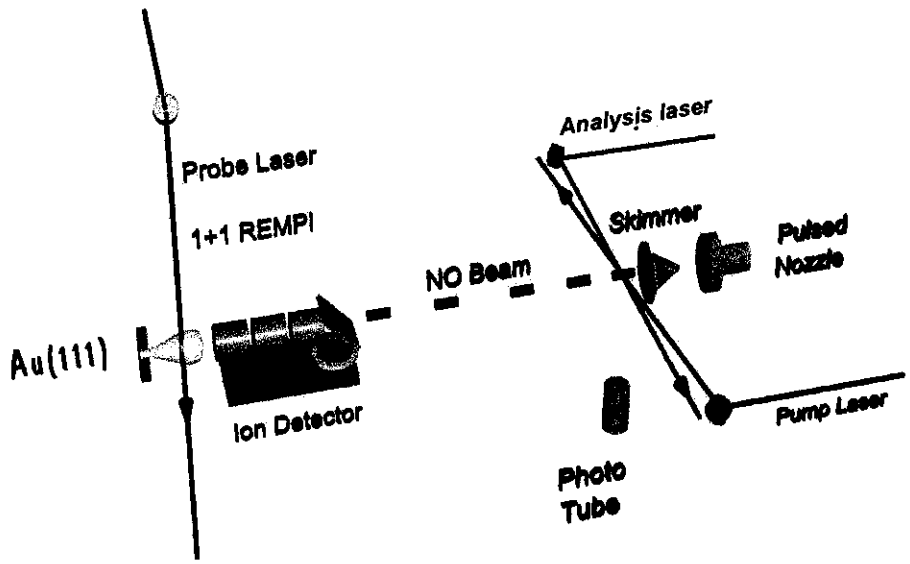

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Scattering of NO(v=2) from Au(111)

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Principle Observations

De-excitation

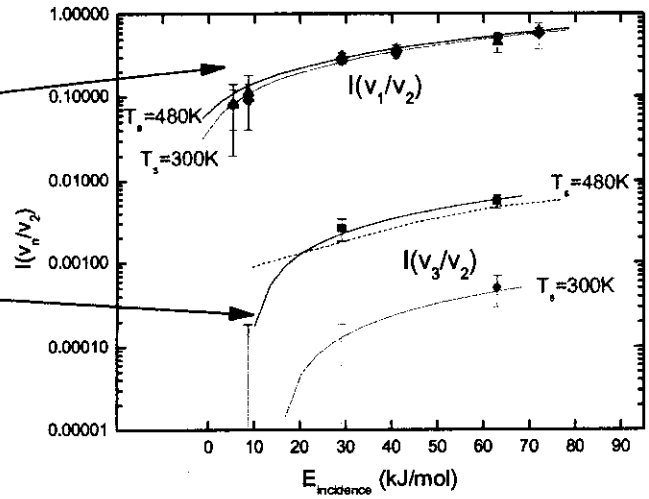
- ✓ **Strong E_i dependence**
- ✓ Weak T_s dependence

Excitation

- ✓ **Strong E_i dependence**
- ✓ **Strong T_s dependence**

At lowest kinetic energy

- ✓ apparently vibrationally elastic
- ✓ what about trapping?



Phys. Rev. Lett. **84** 2985-8 (2000)

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Two vibrational relaxation mechanisms: trapping and direct

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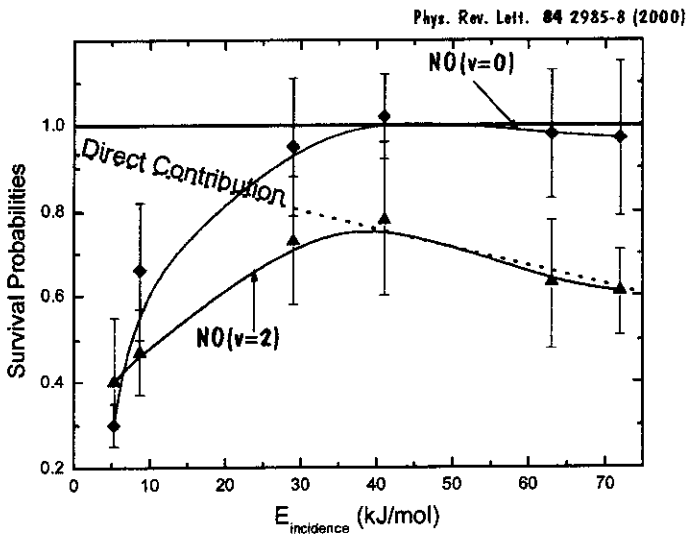
- ✓ both v=0 and v=2 trap at low incidence energy
- ✓ direct mechanism removes v=2 at higher incidence energies



Why such a large influence of translational energy?

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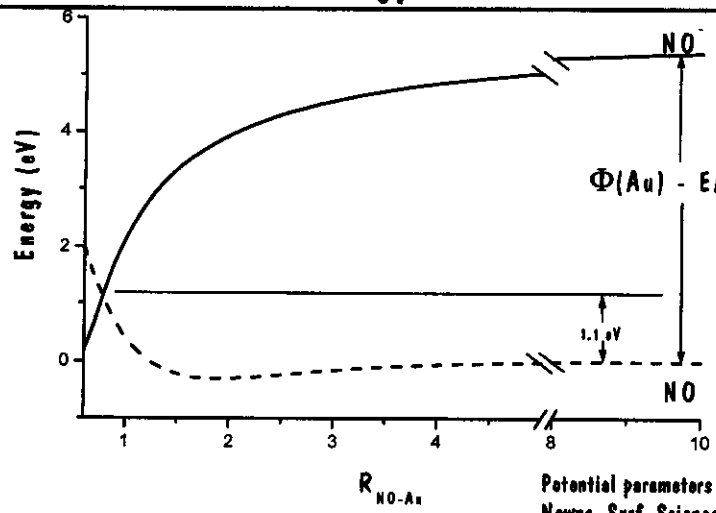

Potential parameters adapted from Newns, Surf. Science 171, 600 (1986)

Neutral Anion Curve Crossing

- Neutral physisorption interaction is repulsive
- Anion/Image Charge Coulombic interaction is attractive
- $\Phi(Au) >> EA(NO)$ leads to barrier

Making Stretched Molecules: Preparation of high vibrational states

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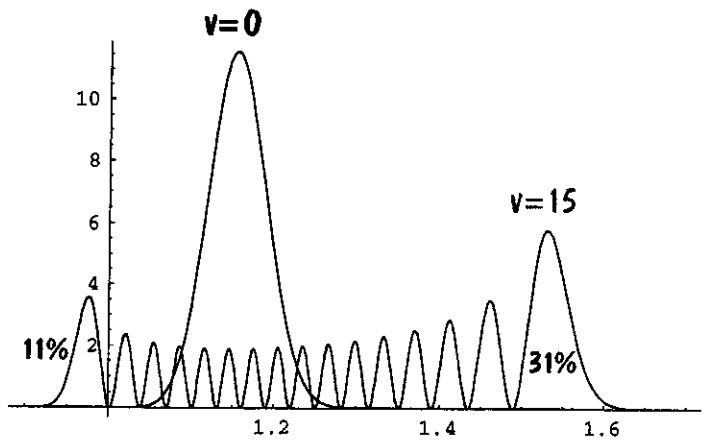

Numerical Solution to the Vibrational Schroedinger Equation for NO

Large Amplitude Motion: Electronic Coupling to Nuclear Motion

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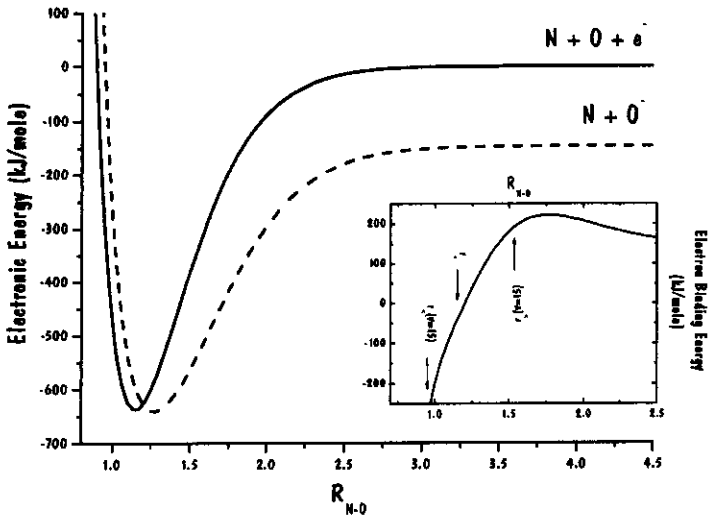

Can we vibrationally activate electron transfer Chemistry?

Effect of Vibrational Enhancement of electron Affinity on Charge Transfer

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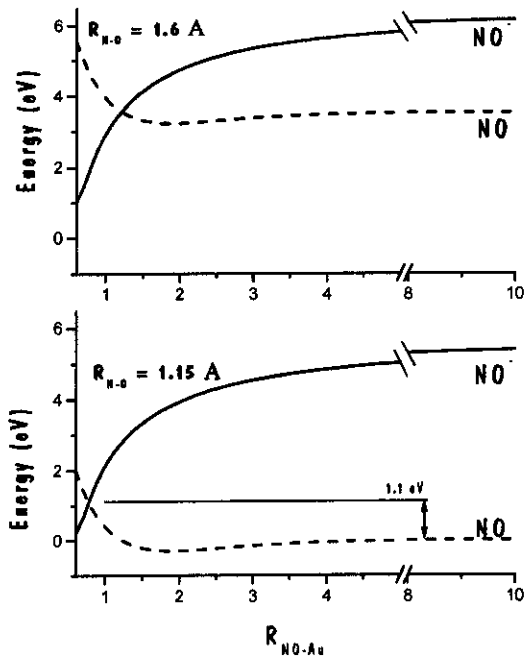
Neutral Anion Curve Crossing

- Neutral physisorption interaction is repulsive
- Anion/Image Charge interaction is attractive
- Enhanced EA of "stretched" NO causes barrier to curve crossing to disappear and to move out.



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Stimulated Emission Pumping

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Pump Step

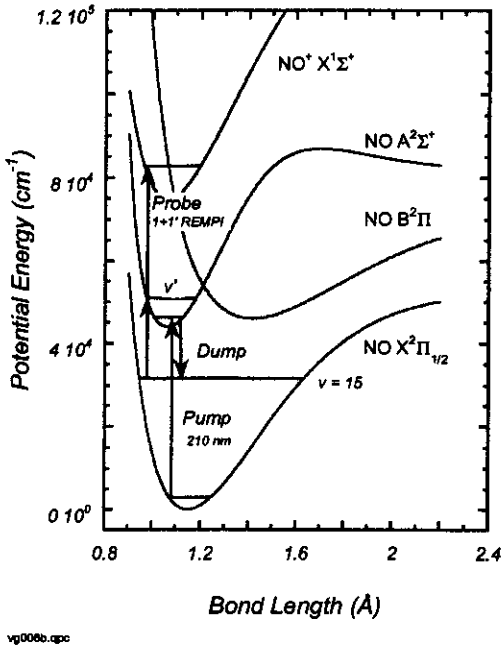
- ✓allows transition to excited electronic state

Dump Step

- ✓allows transition back to the ground state

Probe Step

- ✓detects outcome



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Schematic of Experimental Apparatus

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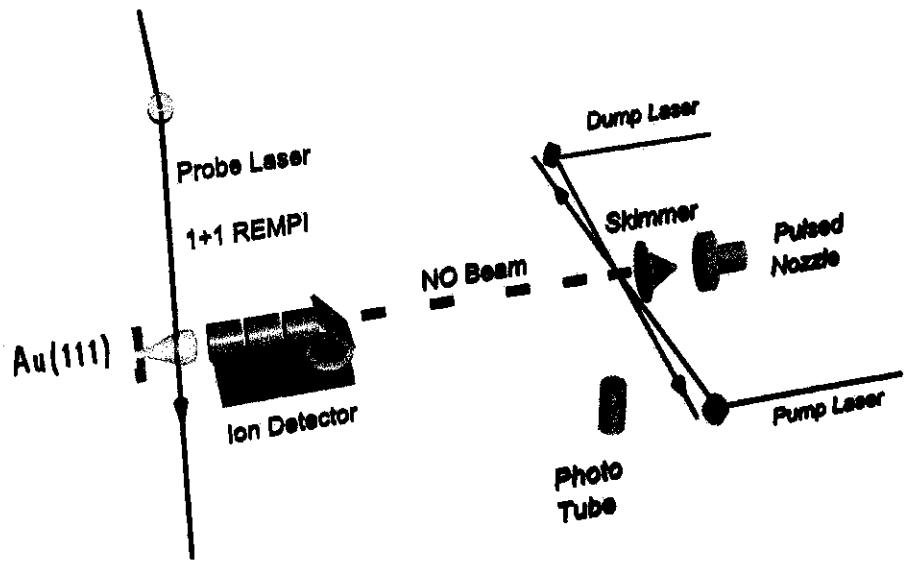

Vibration to electronic coupling possible over 2 eV energy range

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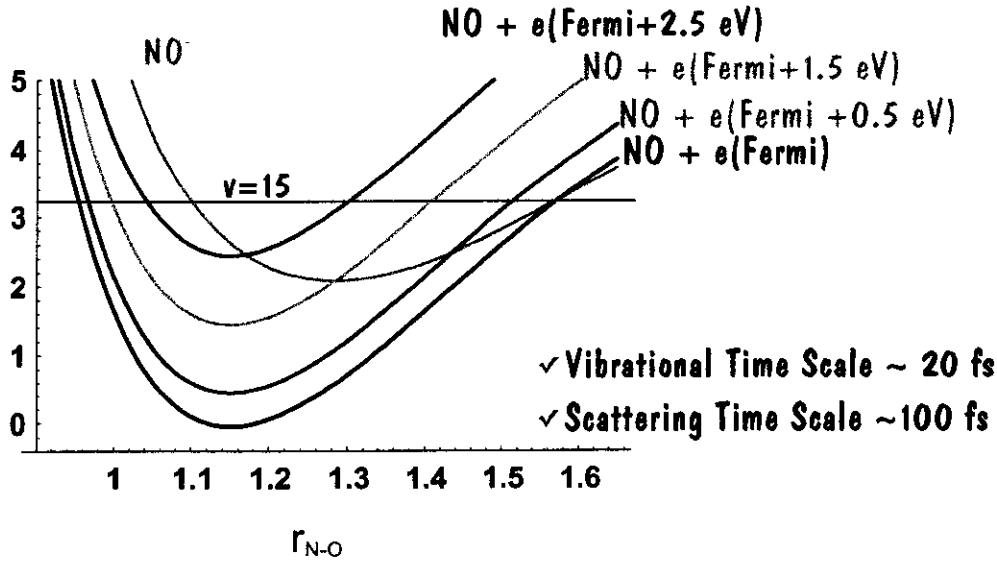
R_{NO-Au}= 1.5 Angstroms



- ✓Vibrational Time Scale ~ 20 fs
- ✓Scattering Time Scale ~100 fs

NO(v=15) +Au(111): Overview spectrum and vibrational Assignments

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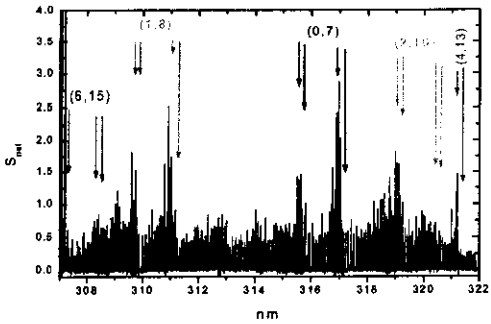
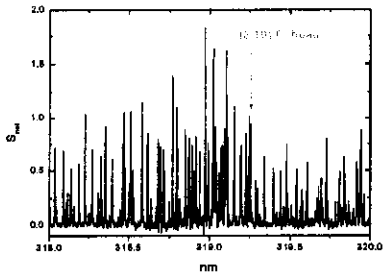
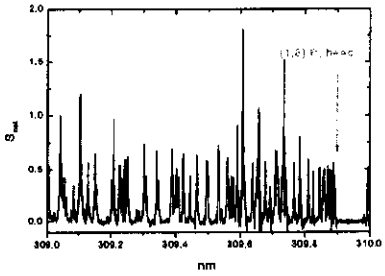
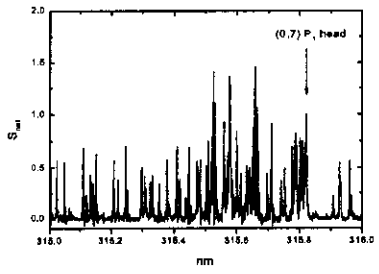
E_i=0.05 eV, T_s = 300K









Vibrational Distribution for NO(v=15) + Au(111) at E_i=0.05 eV

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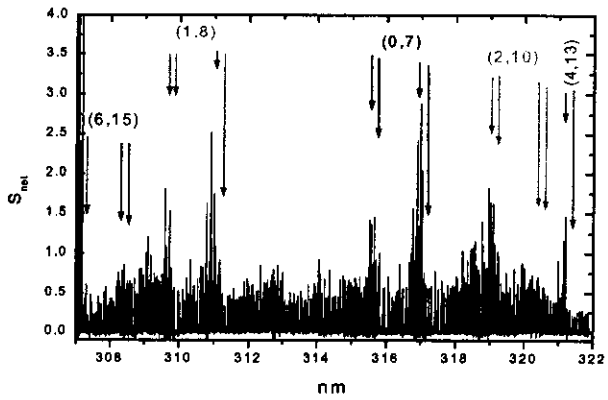
- Converting signals to vibrational populations
  - *Assign lines...*
  - *Measure vibrational state specific detectivity using FCP*
    - ✓ All lines are saturated
    - ✓ Power dependence is linear
  - *Measure*
    - ✓ Rotational Temperatures
    - ✓ Angular Distributions
    - ✓ Translational Energy Distributions
- Vibration Induced electron transfer Reaction?
  - *should be a direct reaction*
  - *vibrational energy results in electronic excitation*



Rotational Excitation is Low: NO(v=15) + Au(111)

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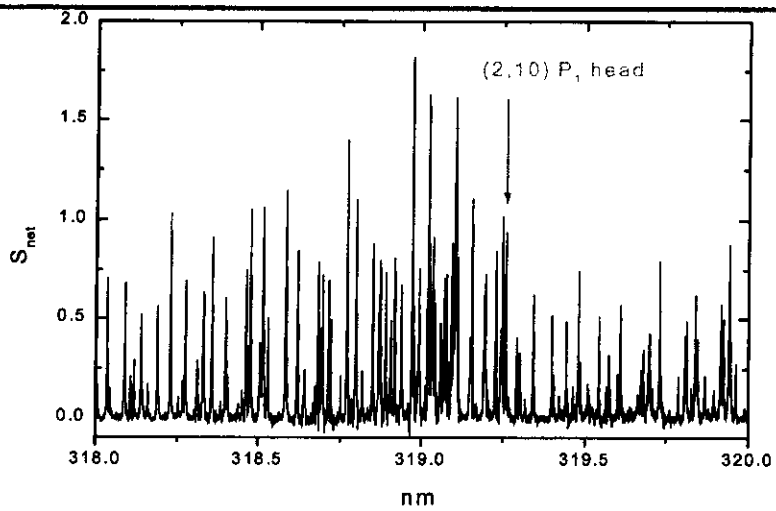

preliminary analysis

- ✓ rotational temperatures of ~275-300K
- ✓ independent of Δv

TOF spectra vs. Δv: NO(v=15) + Au(111)

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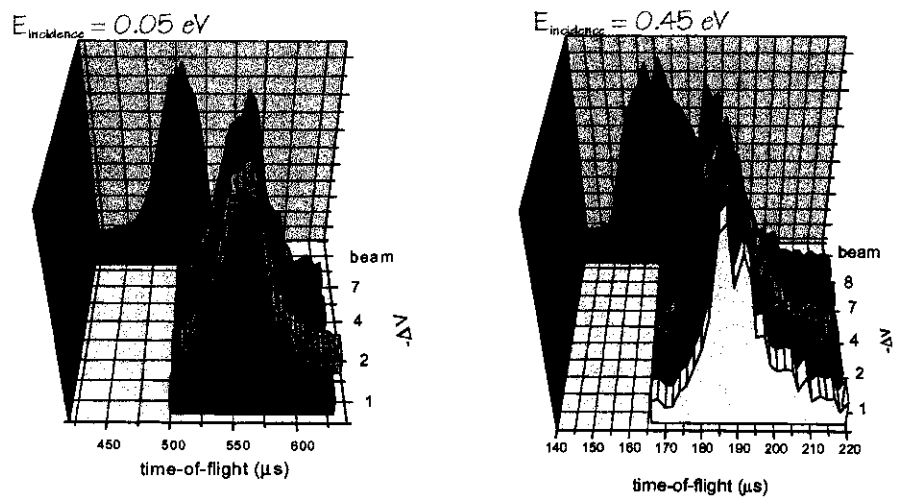

- Translation is a Spectator!
  - ✓ Shift from beam TOF due to difference in Flight Path
  - ✓ Translational energy transfer small
  - ✓ Approximately independent of Δv

Angular Distributions: More Evidence for Direct Scattering

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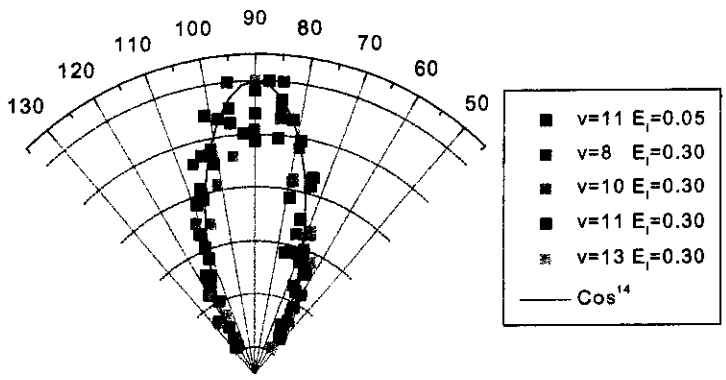

Important Points

- ✓ highly peaked angular distributions
- ✓ independent of $E_{incidence}$
- ✓ Independent of Δv
- ✓ classical scattering on 100 fs time scale

Remarkable multiquantum vibrational relaxation on Au(111)

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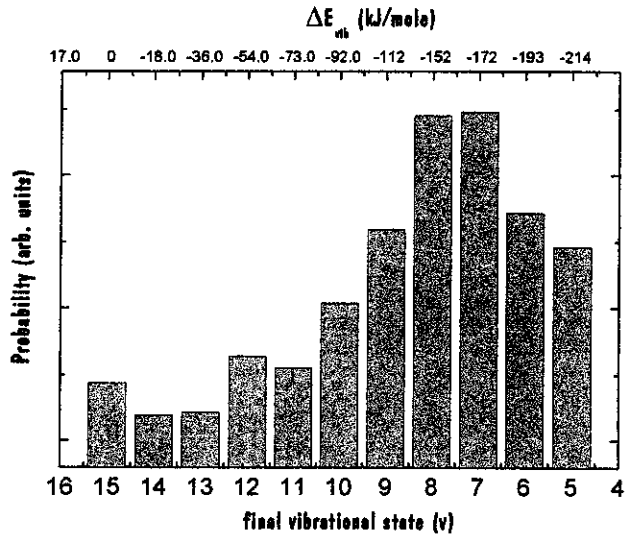
– Conditions

- Prepare NO(v=15) with SEP
- E_i= 0.05 eV
- T_s = 300K
- Clean Au(111)



Important Points

✓ **<1% survival in v=15**

✓ **Δv=-8 likely vibrational exchange**

Electron transfer induced vibrational relaxation

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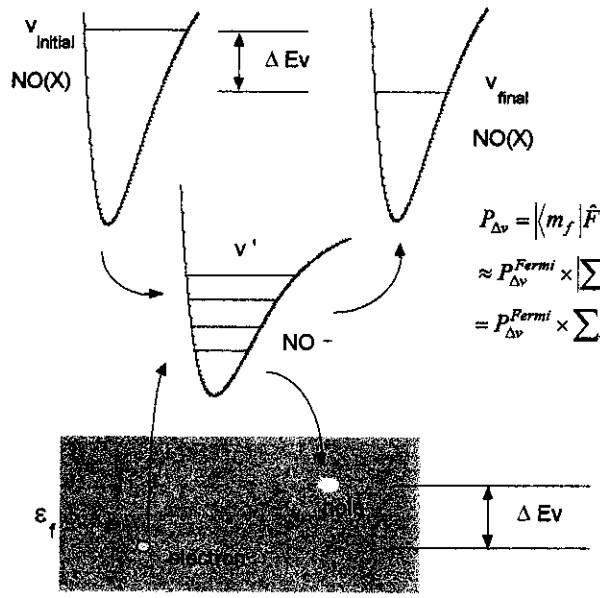

$$P_{\Delta v} = \left|\langle m_f|\hat{F}|m_i\rangle\sum_{v'}\langle v_f|\hat{L}|v'\rangle\langle v'|\hat{L}|v_i\rangle\right|^2$$

$$\approx P_{\Delta v}^{Fermi} \times \left|\sum_{v'} L(v_f,v')L(v',v_i)\langle v_f|v'\rangle\langle v'|v_i\rangle\right|^2$$

$$= P_{\Delta v}^{Fermi} \times \sum_{v'} L^2(v_f,v')L^2(v',v_i) f_{v_f\leftarrow v'} f_{v'\leftarrow v_i}$$

$$P_{\Delta v}^{Fermi} = \int_0^\infty g(E)f(E)g(E+\Delta E_{vib})[1-f(E+\Delta E_{vib})]\sigma(E)dE$$

Remarkable multiquantum vibrational relaxation on Au(111)

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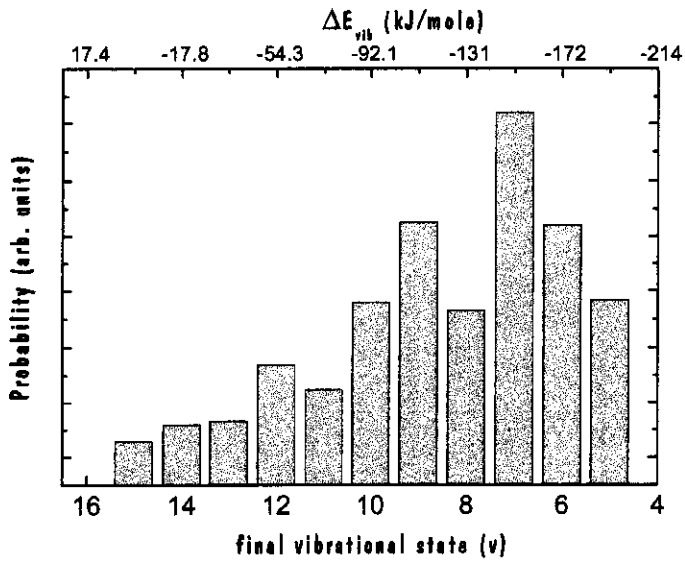
- Conditions
  - Prepare NO(v=15) with SEP
  - E_i= 0.05 eV
  - T_s = 300K
  - Clean Au(111)



Important Points

✓ **<1% survival in v=15**

✓ **150 kJ/mol most likely vibrational exchange**

Electron transfer induced vibrational relaxation

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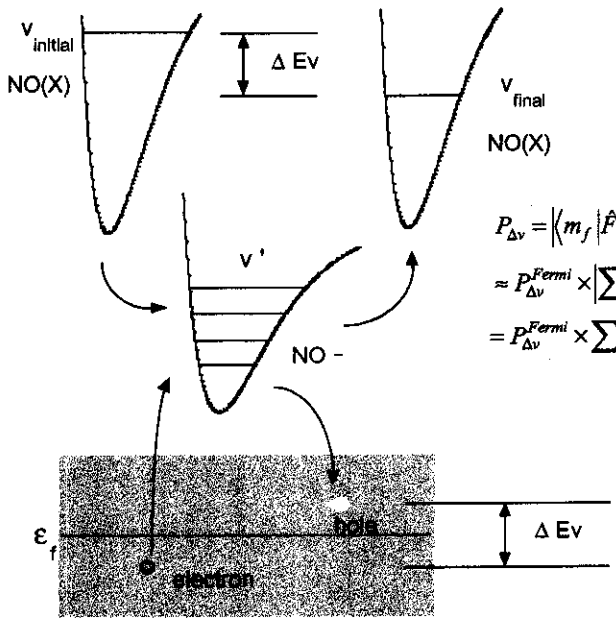

$$P_{\Delta v} = \left|\langle m_f|\hat{F}|m_i\rangle \sum_{v'}\langle v_f|\hat{L}|v'\rangle\langle v'|\hat{L}|v_i\rangle\right|^2$$

$$\approx P_{\Delta v}^{Fermi} \times \left|\sum_{v'} L(v_f,v')L(v',v_i)\langle v_f|v'\rangle\langle v'|v_i\rangle\right|^2$$

$$= P_{\Delta v}^{Fermi} \times \sum_{v'} L^2(v_f,v')L^2(v',v_i) f_{v_f \leftarrow v'} f_{v' \leftarrow v_i}$$

$$P_{\Delta v}^{Fermi} = \int_0^\infty g(E)f(E)g(E+\Delta E_{vib})[1-f(E+\Delta E_{vib})]\sigma(E)dE$$

Comparison: Scattering of NO(v=2) from Au(111)

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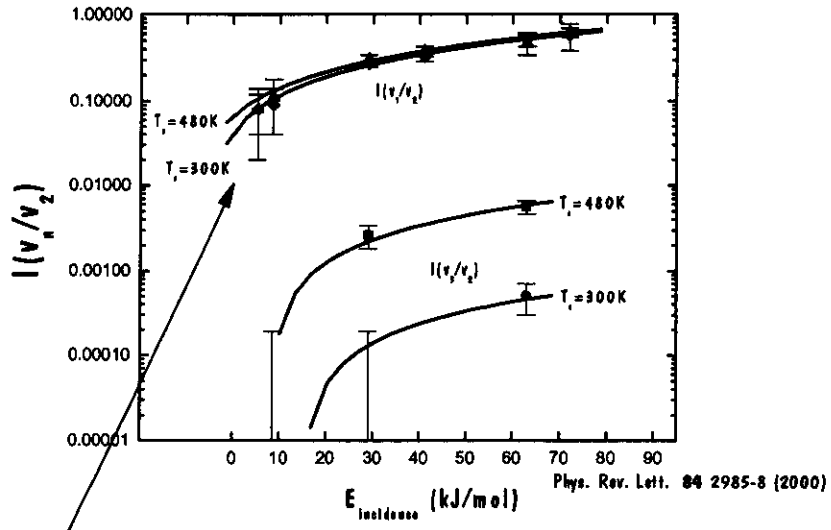

E_i = 50 meV

- >95% survives in v=2

This is not a Franck-Condon Effect

- $Q[NO(2)|NO^-(O)]$ ~0.5

Comparison: Scatering of NO(v=12) from LiF

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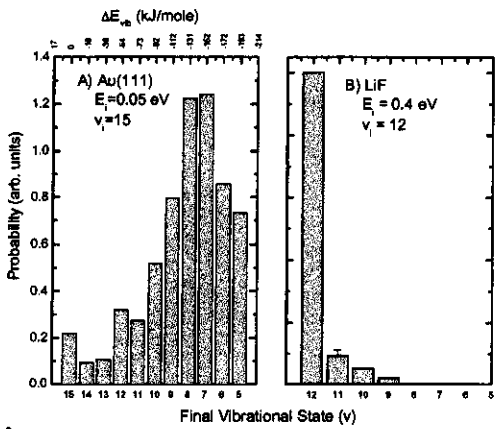
Principle Observation

- Relaxation Inefficient
- Vibrational relaxation inversely related to E_i



Data Consistent with:

- Little relaxation unless trapping occurs
- NO(v=12) can survive trapping/desorption

Scattering from LiF: Angular Distribution depends on E_i

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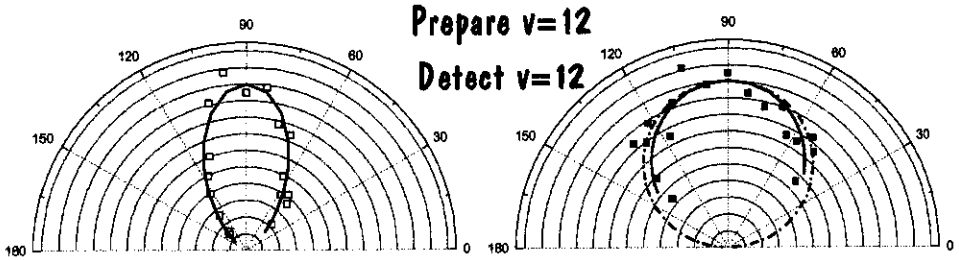
E_i=700 meV, $Cos^{5.2+/-0.4}(\theta)$ | E_i=50 meV, $Cos^{1.2+/-0.2}(\theta)$



Principal Observation

- Angular distribution narrows with increasing incidence energy

Data Consistent with:

- Little relaxation unless trapping occurs
- NO(v=12) can survive trapping/desorption

Trapping as a function incidence energy

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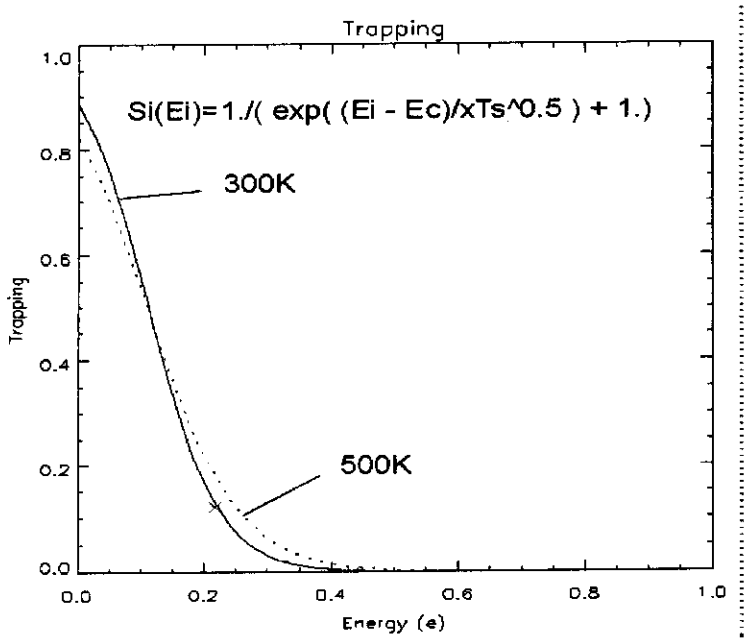

Vibrational Promotion of Electron Transfer Chemistry

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- Observation of Multiquantum Vibrational relaxation on Au(111)
  - ✓ <1% survival probability at 0.05 eV incidence energy
  - ✓ 150 kJ/mol most probable exchange
  - ✓ Direct Scattering, narrow angular distribution
  - ✓ circa 100 fs time scale
  - ✓ rotational energy spectator
  - ✓ translation energy spectator
- Vibrational Energy Transferred to Surface Electronic Excitation
  - ✓ NO(v=12) LiF scattering is "vibrationally elastic"
  - ✓ NO(v=2) from Au(111) at E_i = 50 meV is vibrationally elastic in direct channel; energy transfer increases with incidence energy.

Conclusions

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- For high vibrational excitation, the fundamental change in the electronic nature and the resulting influence on Chemistry cannot be ignored
  - ✓ e.g. triggering electron transfer reactions
- At Metal Surfaces there can be a strong coupling between molecular vibration and surface bound electrons
  - ✓ Is this true for semiconductors?
  - ✓ vibrational excitation from valence to conduction band?

Future Work: Shottky Barrier Diode detection of hot electrons

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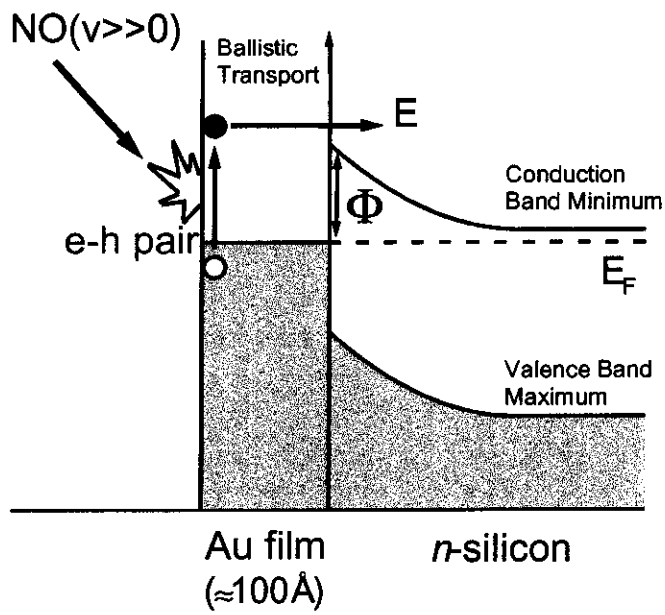

Hexapole Focusing of NO

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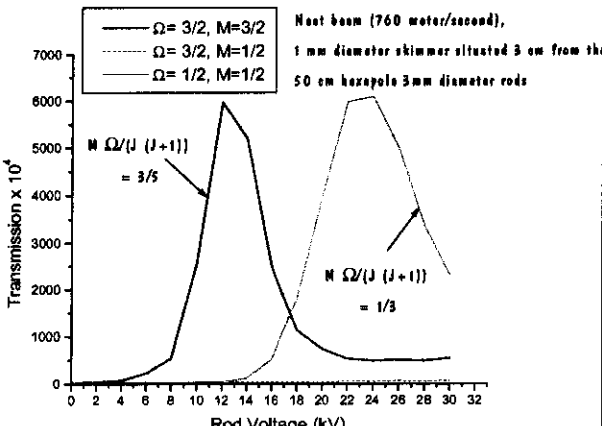

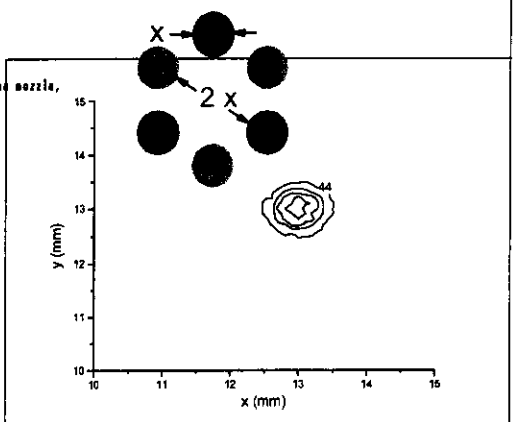

- The "trick"
  - ►NO(v=0) all Ω = 1/2
  - ►Pump NO(v>>0) to Ω = 3/2
  - ►Stark shift ~ M Ω /(J (J+1))
- Key features to note
  - ► 60% transmission
  - ►Neat NO beam
  - ►Tight focus possible

Classical Trajectory Calculations: Roger W. Anderson (Modifications by Marcel Drabbels), J. Phys. Chem. A 101, 7671 (1997)]

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Chemical Reaction of NO(v=13) + Cu(111)

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Question

- Given that vibrational relaxation occurs with unprecedented efficiency, Is it reasonable to expect vibrational promotion of chemical reactivity?

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Increase in REMPI signal from vibrationally inelastic scattering with NO exposure

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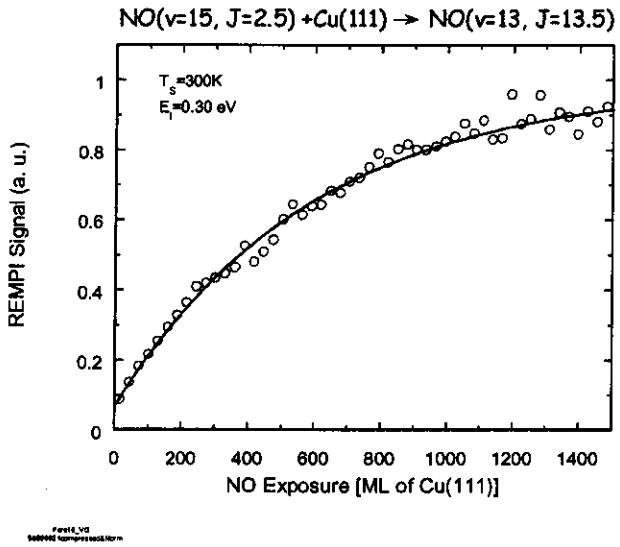
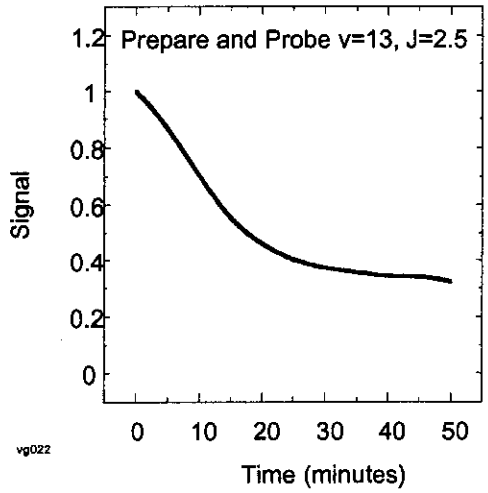


Prediction for Vibrationally Elastic Scattering

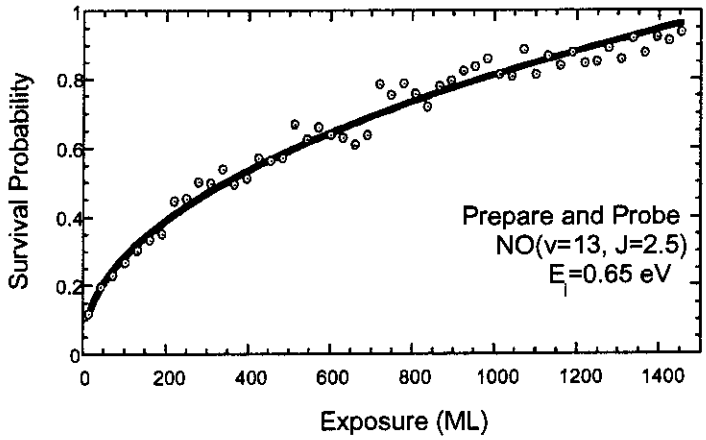
- Hypothesis:
  - ✓ vibrational relaxation strong only for oxygen covered surface
- Prediction
  - ✓ vibrationally elastic scattering should be large on clean surface
  - ✓ decrease as surface becomes covered
  - ✓ total loss should calibrate absolute fraction of vibrational relaxation !



Results: Vibrationally Elastic Scattering

Survival Probabilitry vs Exposure

NO(v=13, J=2.5) + Cu(111)



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Results: Vibrationally Elastic Scattering

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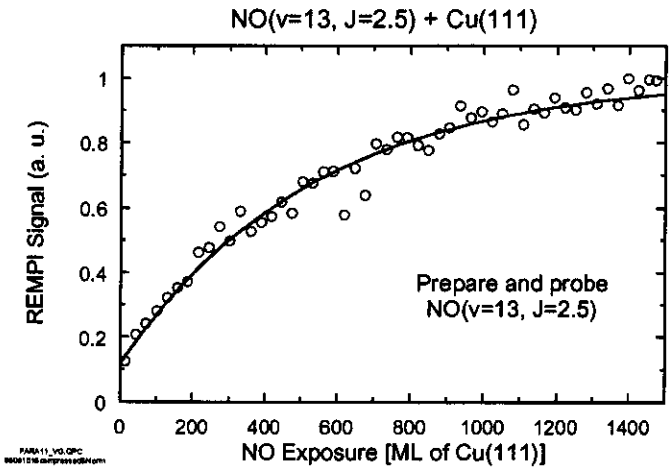

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Summary

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- The translational and vibrational energy dependence of surface reactions provides an effective probe of PES topography and reaction mechanisms
  - *Translation promotes activated reactions*
  - *Vibration can also be effective -- generally less*
    - early and late barriers
- Electronic effects are important in vibrational energy transfer for NO at metal surfaces
- High degrees of vibrational excitation produce new phenomena
  - fundamental change in the electronic nature and resulting influence on chemistry
    - surprisingly efficient vibrational relaxation
    - indirect evidence for dramatic enhancement of dissociative adsorption.
    - triggering electron transfer reactions

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