united nations educational, scientific and cultural organization

international atomic energy agency

the **abdus salam** international centre for theoretical physics

SMR/1238-14

ADRIATICO RESEARCH CONFERENCE on

LASERS IN SURFACE SCIENCE

11-15 September 2000

Miramare - Trieste, Italy

State-to-state scattering at a reactive surface: H_2 ($v=1$, $J=1$) from Cu(100) and Pd(111)

Greg O. Sitz
University of Texas at Austin
Austin - TX, United States of America

State-to-state scattering at a reactive surface: H_2 (v=1,J=1) from Cu(100) and Pd(111)

Greg O. Sitz

Micheal Gostein, Elizabeth Watts, Leah Shackman, Marcia Isakson

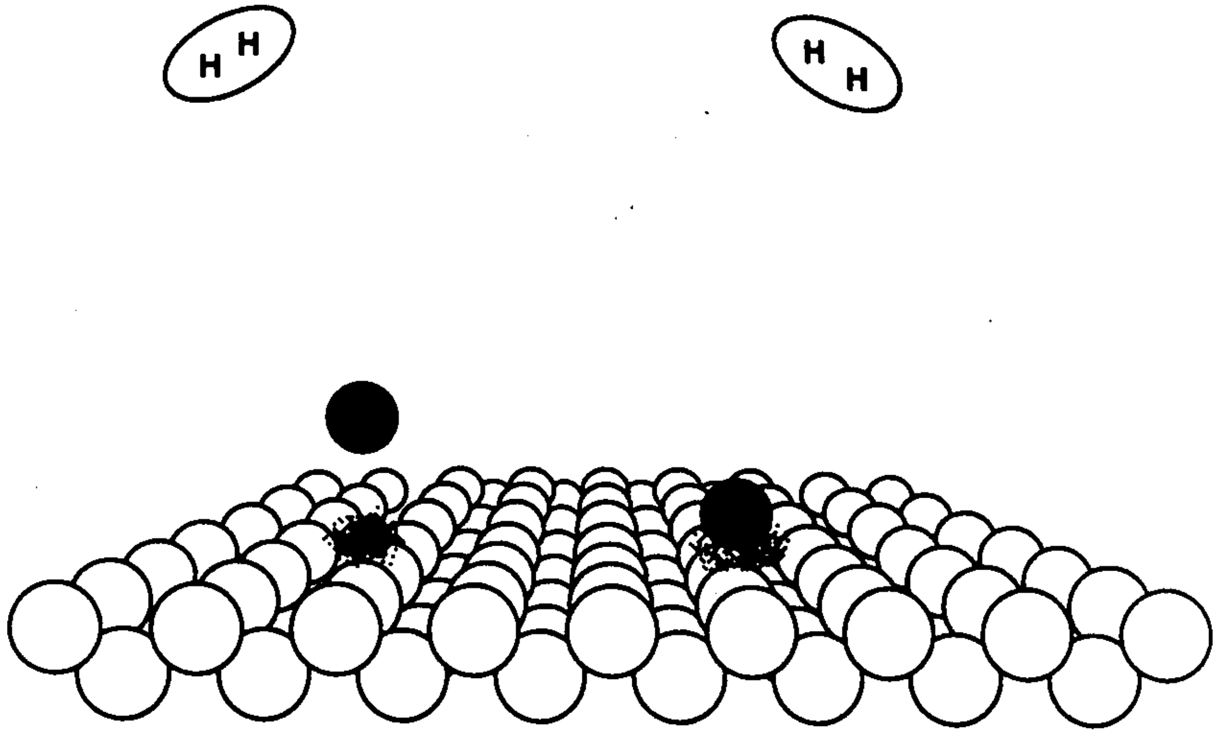
Physics Department, The University of Texas at Austin

- Surface dynamics and degrees-of-freedom
- Experimental techniques
- (In)elastic scattering
- Comparison to theory

Support:

National Science Foundation

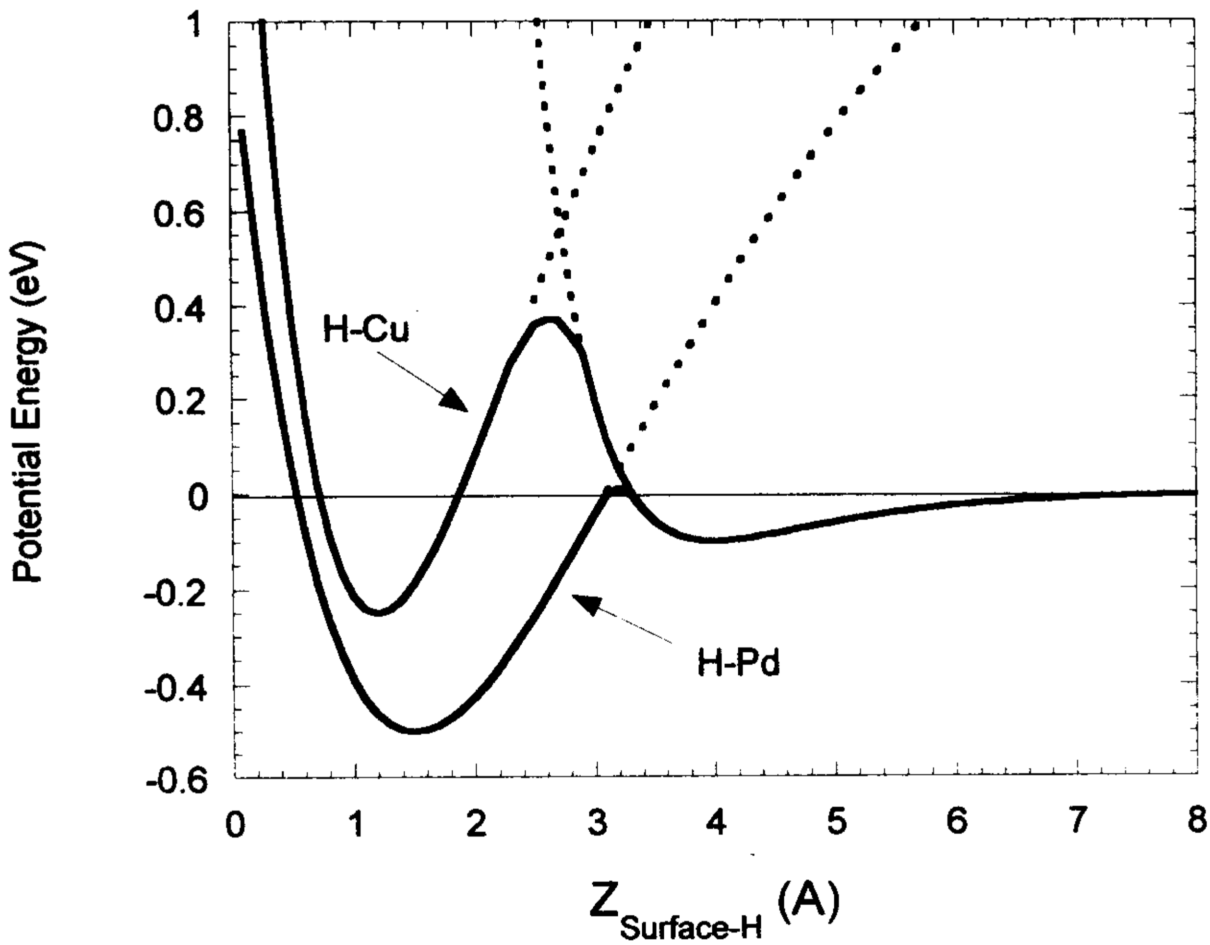
CHE-9512232, CHE-9815282

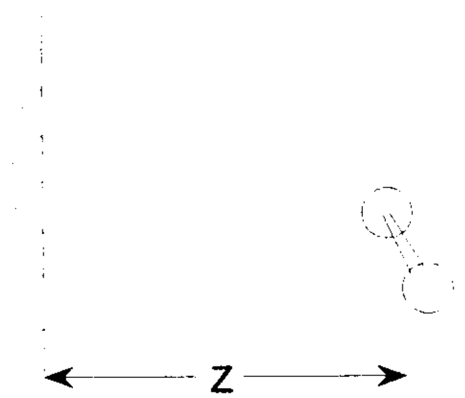


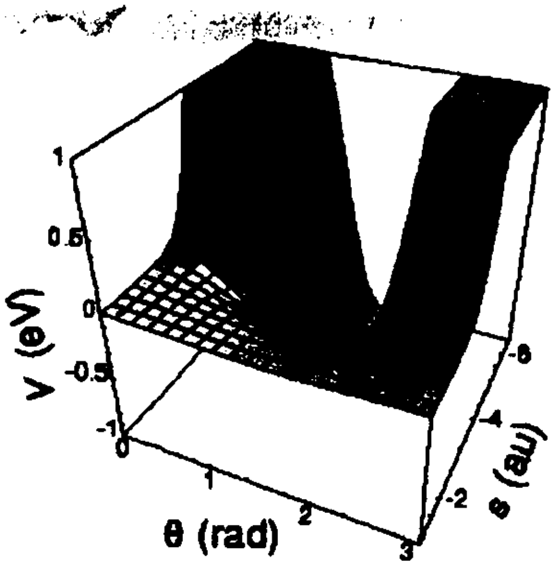
Potential:

$$V(r, z, \theta, \phi, x, y, \vec{r}_{surf})$$

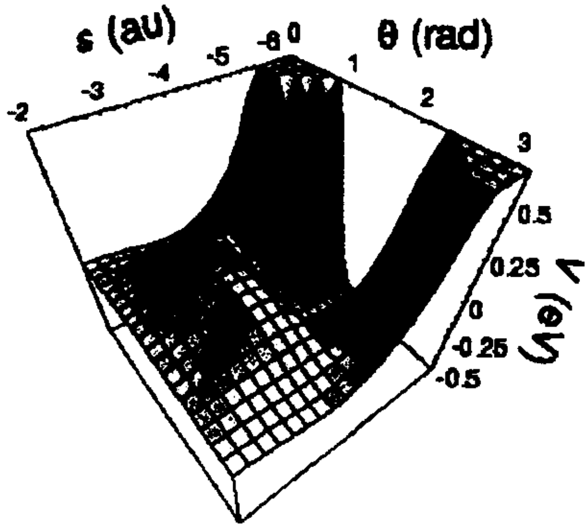
Schematic 1-D Potential Energy Curves







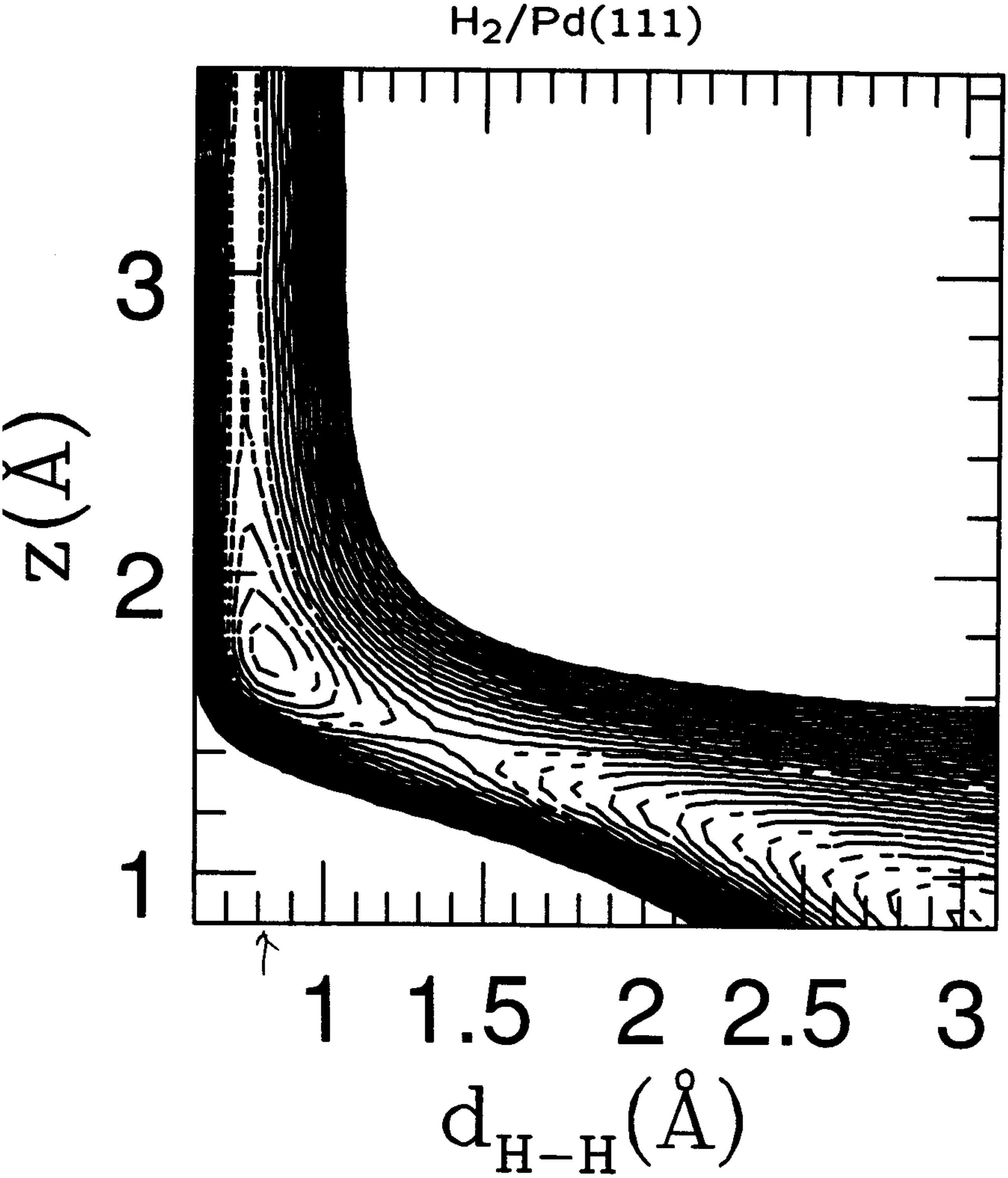
1
0.5
0
-0.5
-1
V (eV)
0
1
2
3
θ (rad)
-6
-4
-2
s (au)



s (au)
-2
-3
-4
-5
-6
0
θ (rad)
1
2
3
0.5
0.25
0
-0.25
-0.5
V (eV)

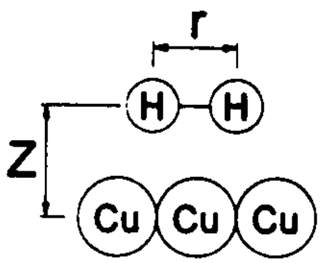
Potential Energy Surface

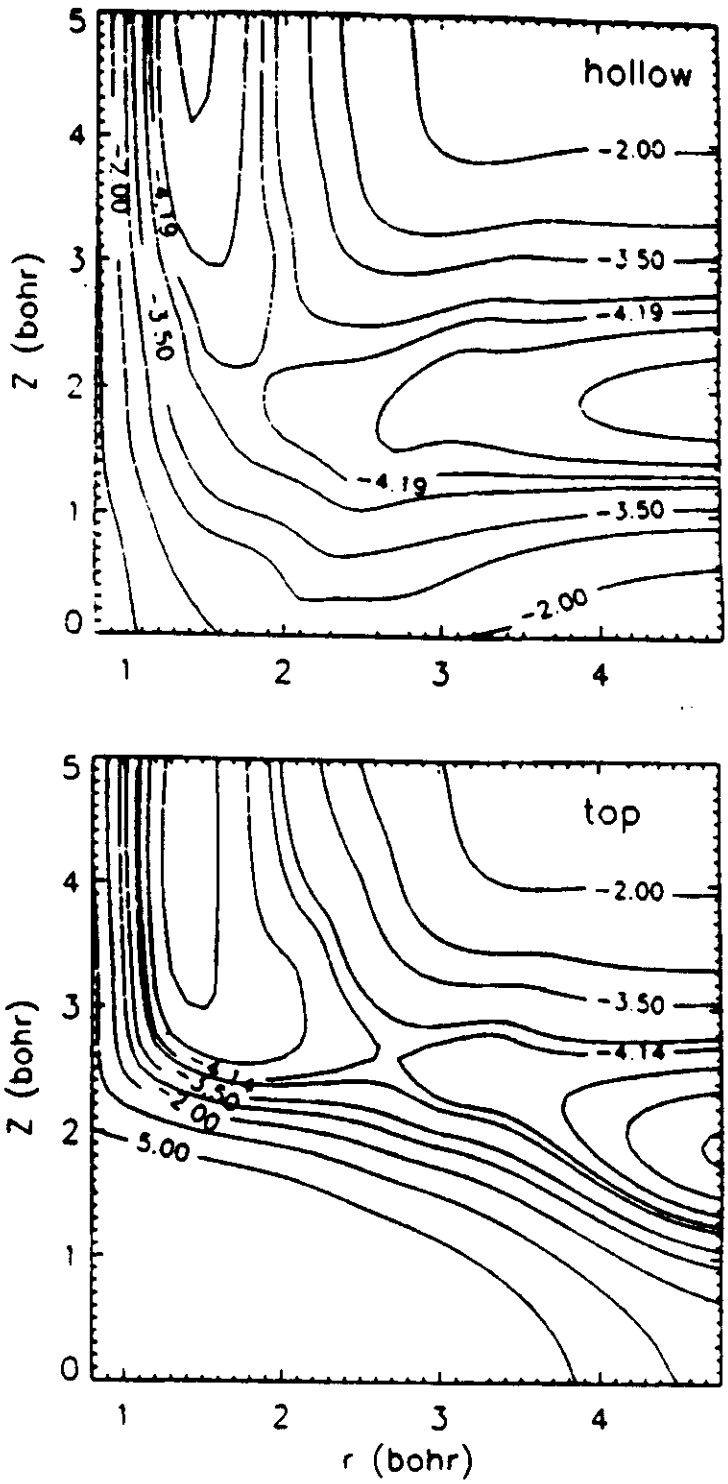
H_2/Pd(111)



W. Dong & J. Hafner, PRB **56** 15396 (1998)

H_2 / Cu(100) Potential Energy Surface





G. J. Kroes, G. Wiesenekker, E. J. Baerends, R. C. Mowrey,
Phys. Rev. B. 53, p. 10397 (1996).

State of the art theory

DFT-GGA potential energy surface

+

six-dimensional Quantum dynamics

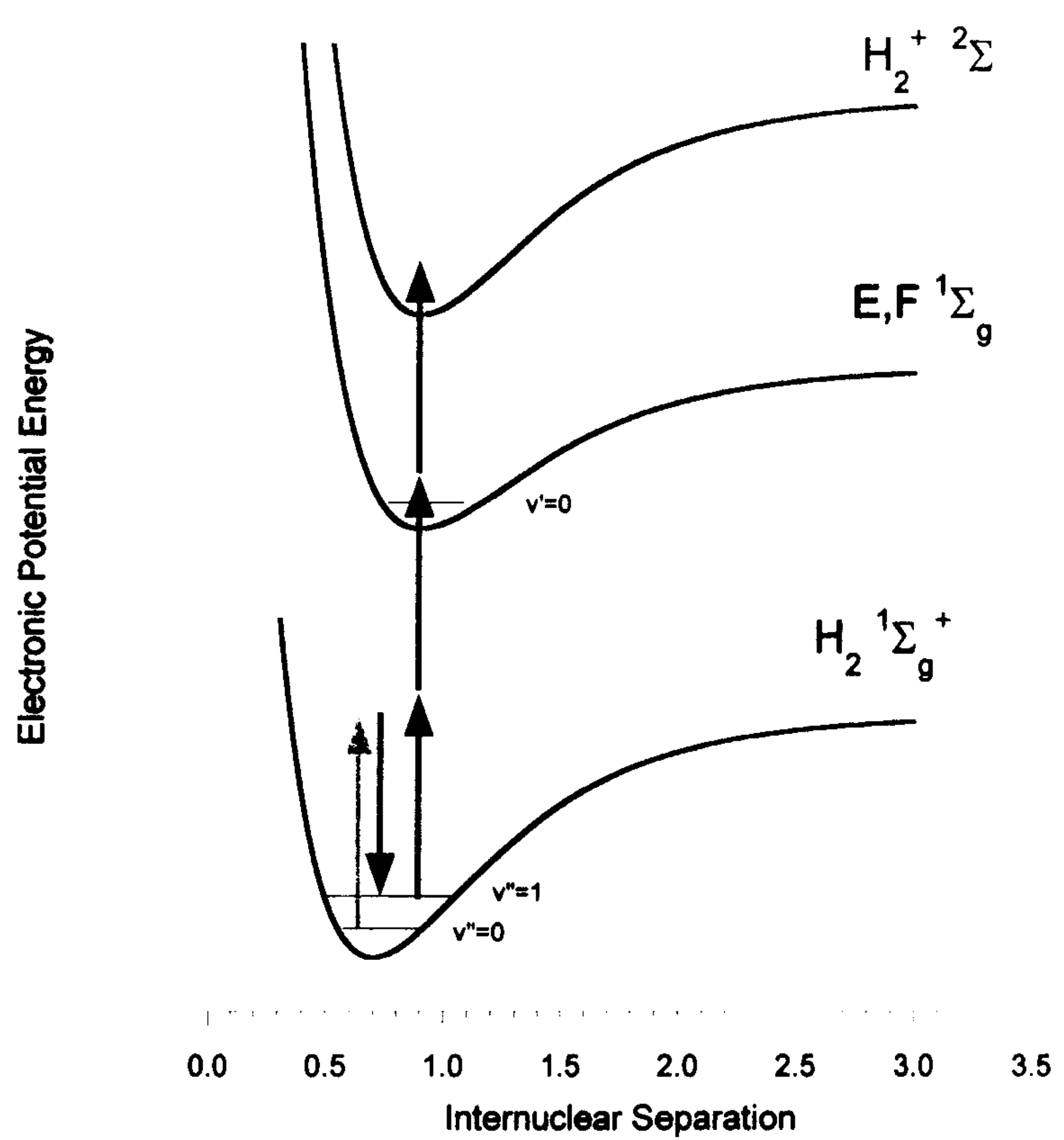
=

the answer

A.Gross, S. Wilke, and M. Scheffler, Phys. Rev. Lett. **78** 2718 (1997)

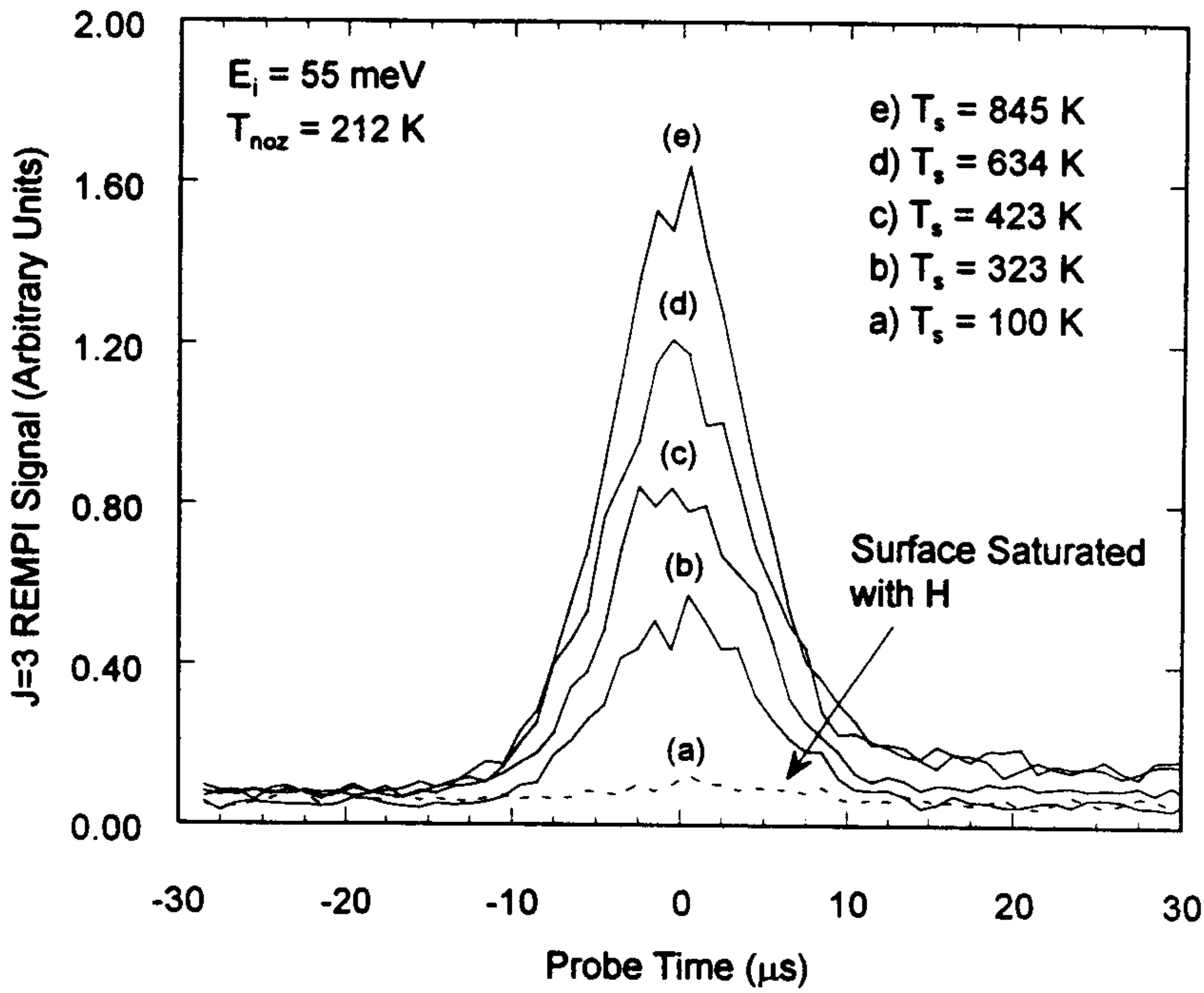
G.J.Kroes, E.J.Baerends, R.C.Mowrey, Phys. Rev. Lett. **78** 3583 (1997)

J.Dai and J.C.Light, J. Chem. Phys. **107** 1676 (1997)



2+1 Resonance Enhanced Ionization and Stimulated Raman Pumping in H_2

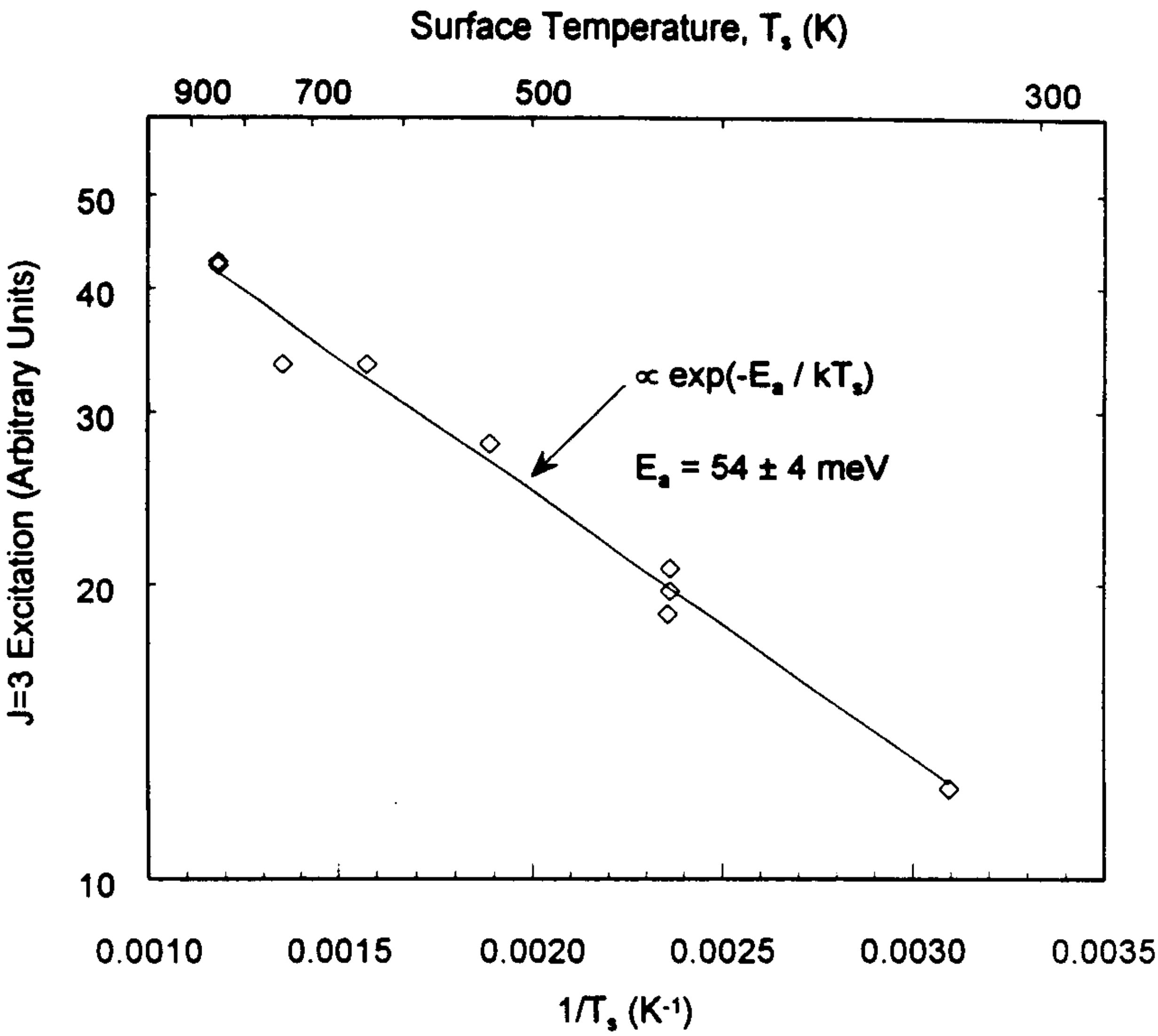
Rotational Excitation vs. Surface Temperature (Time-of-flight Data)



- Incident rotational distribution has negligible J=3 population, as shown by curve (a) for saturated, reflective surface.

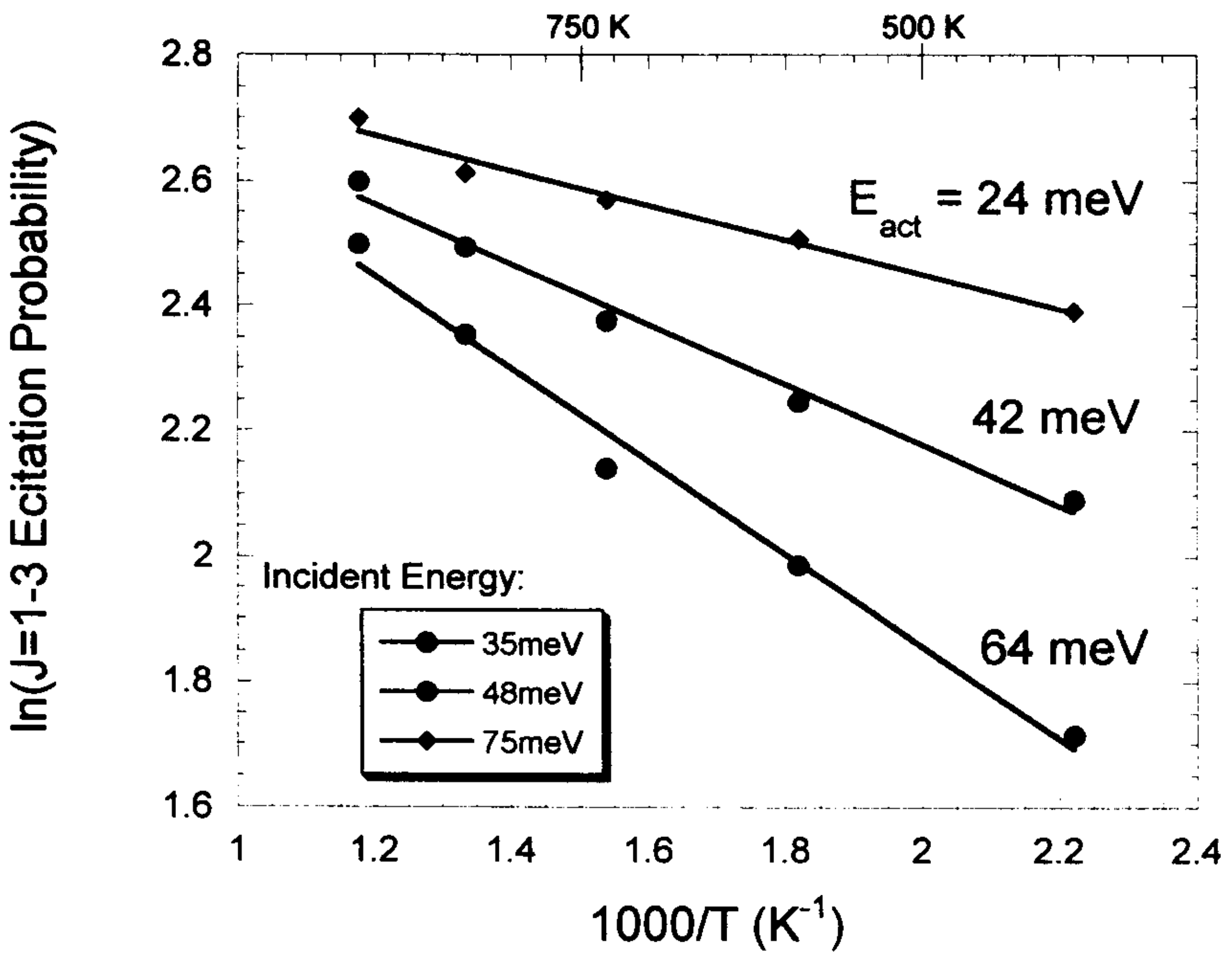
- Scattered J=3 population goes up dramatically with surface temperature.

Rotational Excitation vs. Surface Temperature (Arrhenius Plot)



Excitation increases with surface temperature.

H_2/Pd(111)
Rotational Excitation
Arrhenius Plot vs. Incident Energy

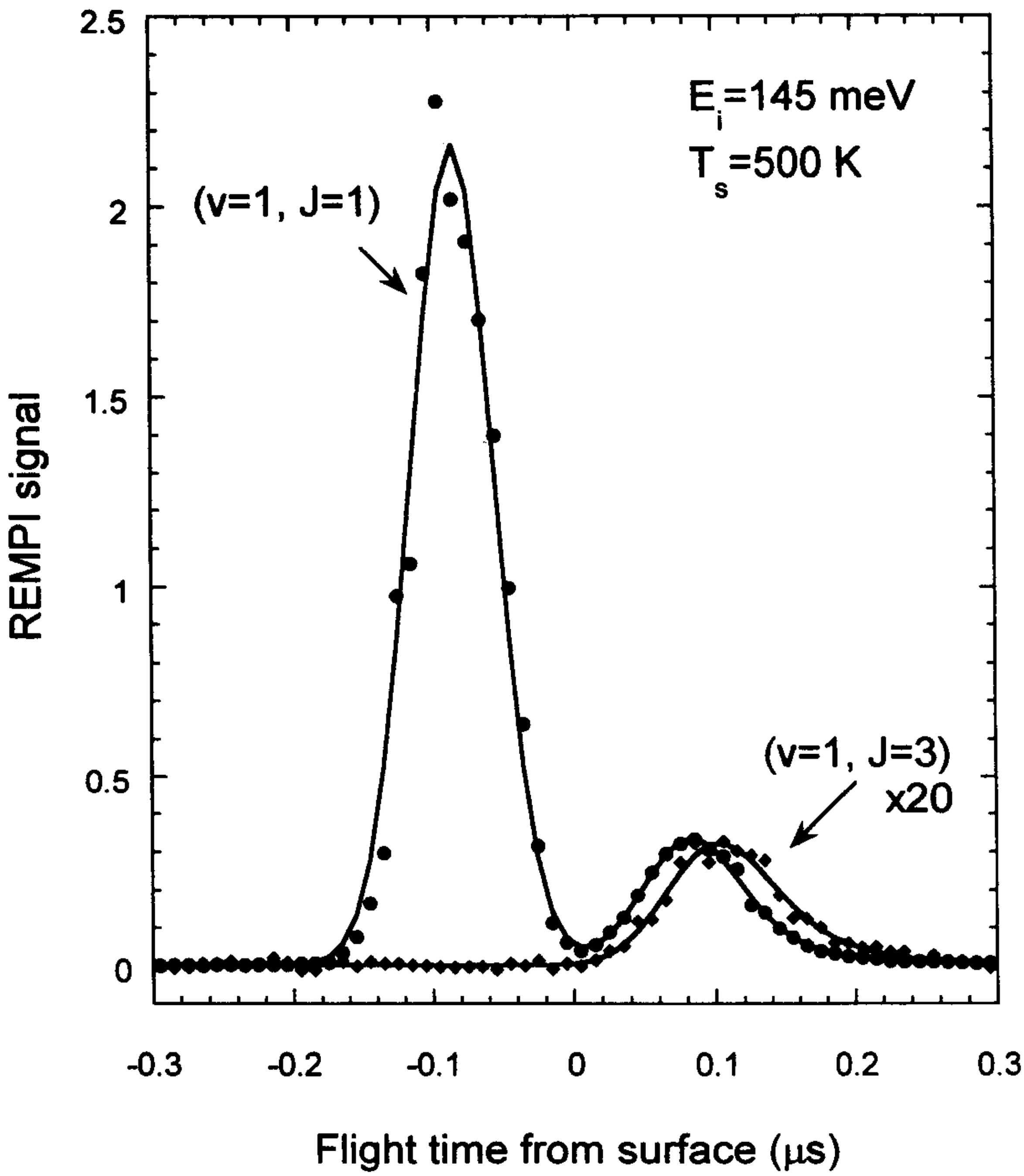


H_2- copper selected papers

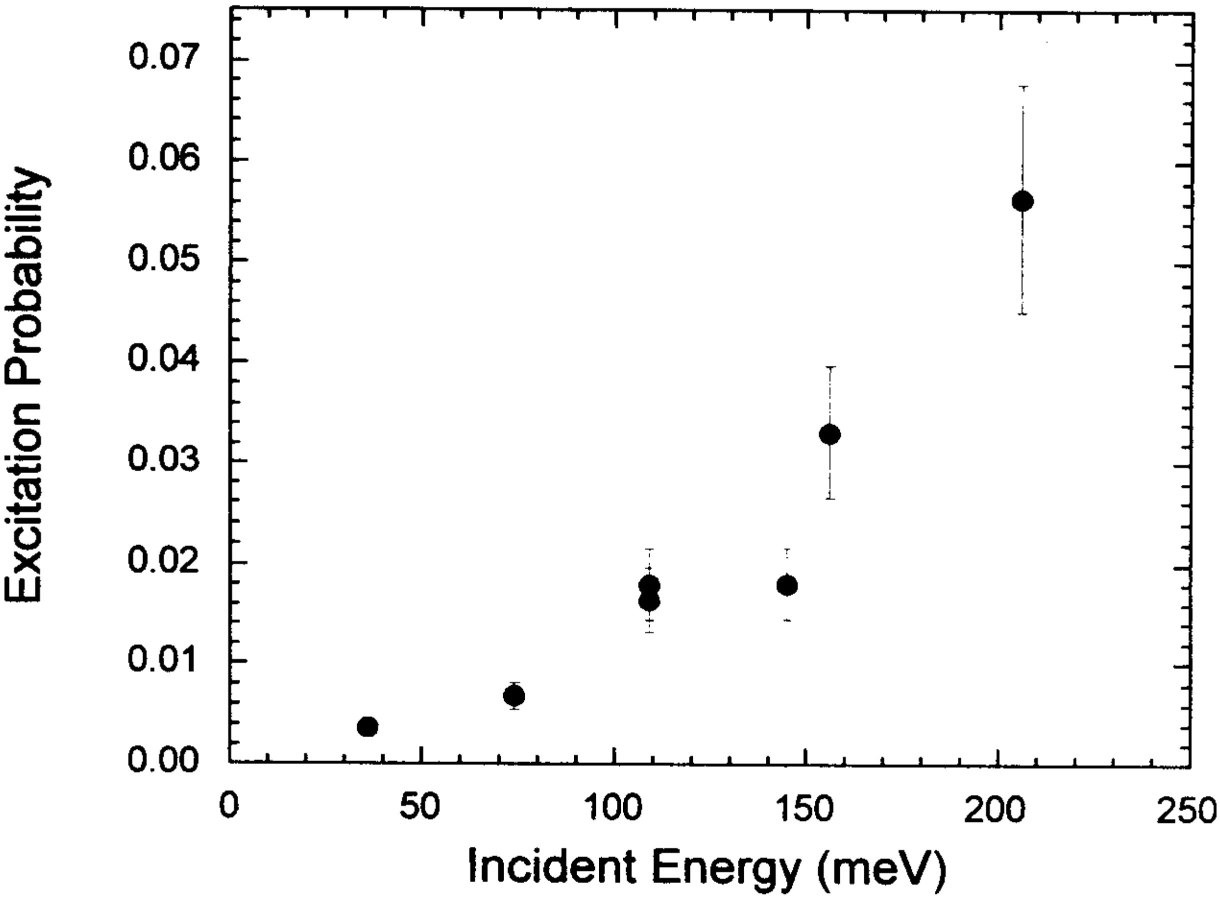
1). J.E.Lennard-Jones, Trans. Faraday Soc. **84**, 333 (1932).
2). J.Pritchard and F.C.Tomkins, Trans. Faraday Soc. **56**, 540 (1960).
3). J.Pritchard, Trans. Faraday Soc. **59**, 437 (1963).
4). C.S.Alexander and J.Pritchard, J. Chem. Soc. Faraday Trans. 68, 202 (1972).
5). J.Pritchard, T.Catterick, and R.K.Gupta, Surf. Sci. **53**, 1 (1975).
6). T.L.Bradley and R.E.Stickney, Surf. Sci. **38**, 313 (1973).
7). M.Balooch and R.E.Stickney, Surf. Sci. **44**, 310 (1974).
8). M.J.Cardillo, M.Balooch, D.R.Miller, and R.E.Stickney, Surf. Sci. **46**, 358 (1974).
9). M.J.Cardillo, M.Balooch, and R.E.Stickney, Surf. Sci. **50**, 263 (1975).
10). A.Gelb and M.J.Cardillo, Surf.Sci. **59**, 128 (1975).
11). A.Gelb and M.J.Cardillo, **64**, 197 (1977).
12). A.Gelb and M.J.Cardillo, **75**, 199 (1978).
13). G.Comsa, R.David, and B.J.Schumacher, Surf. Sci. **95**, L210 (1980).
14). G.Comsa and R.David, Surf. Sci. **117**, 77 (1982).
15). J.Lapujoulade, U. le Cruer, M.Lefort, Y. Lejay, and G.Maurel, Surf. Sci. **103**, L85 (1981).
16). P.Madhavan and J.L.Whitten, J. Chem. Phys. **77**, 2673 (1982).
17). J.Perreau and J.Lapujoulade, Surf. Sci. **122**, 341 (1982).
18). J.Lapujoulade and J.Perreau, Phys. Scr. **T4**, 138 (1983).
19). G.D.Kubiak, **G.O.Sitz**, and R.N.Zare, J. Chem. Phys. **81**, 6397 (1984); J. Vac. Sci. Tech. **A 3**, 1649 (1985); J. Chem. Phys. **83**, 2538 (1985).
20). J.E.Miller, Phys. Rev. Lett. **59**, 2943 (1987).
21). S.Holloway, A.Hodgson, and D.Halstead, J. Electon. Spectrosc. **45**, 207 (1987).
22). J.Harris, Apply. Phys. A **47**, 63 (1988).
23). S.Holloway, A.Hodgson, and D.Halstead, Chem. Phys. Lett. **147**, 425 (1988).
24). B.E.Hayden and C.L.A.Lamont, Chem. Phys. Lett. **160**, 331 (1989).
25). B.E.Hayden and C.L.A.Lamont, Phys. Rev. Lett. **63**, 1823 (1989).
26). M.Hand and S.Holloway, Surf. Sci. **221**, 940 (1989); J. Chem. Phys. **91**, 7209 (1989).
28). G.Anger, A.Winkler, and K.D.Rendulic, Surf. Sci. **220**, 1 (1989).
29). D.Halstead adn S.Holloway, J. Chem. Phys. 93, 2859 (1990).
30). M. Cacciatore and G.D.Billing, Surf. Sci. **232**, 35 (1990).
31). H.F.Berger and K.D.Rendulic, Surf. Sci. **253**, 325 (1991).
32). H.A.Michelsen and D.J.Auerbach, J. Chem. Phys. **94**, 7502 (1991).
33). A.Hodgson, J.Morly, and H.Zhao, Chem. Phys. Lett. **182**, 152 (1991).
34). J.M.Campbell and C.T.Campbell, Surf. Sci. **259**, 1 (1991).
35). C.T.Rettner, D.J.Auerbach, and H.A.Michelsen, Phys. Rev. Lett. **68**, 1164 (1992).
36). G.R.Darling and S.Holloway, J. Chem. Phys. **97**, 734 (1992); Surf. Sci. **268**, L305 (1992).
37). C.T.Rettner, D.J.Auerbach, and H.A.Michelsen, Phys. Rev. Lett. **68**, 2547 (1992).
38). H.A.Michelsen, C.T.Rettner, and D.J.Auerbach, Phys. Rev. Lett. **69**, 2678 (1992).
39). C. Engdahl and U.Nielsen, J. Chem. Phys. **98**, 4223 (1993).
(40). Lichang Wang, Qingfeng Ge, and Gert D. Billing, Surf. Sci. 301, 353 (1994).
(41). Greg Mills and Hannes Jonsson, Phys.Rev.Lett. 72, 1124 (1994).
(42). Christer Engdahl and Ulrik Nielsen, J.Chem.Phys. 98 4223 (1993).
(43). Bjork Hammer,Matthias Scheffler, Karsten W.Jacobsen and Jens K.Norskov, Phys.Rev.Lett. **73** 1400 (1994).
(44). J.A.White, D.M.Bird, M.C.Payne and I.Stich, Phys.Rev.Lett.73 1404 (1994).

Saalfrank, Peter JCP ...
Surf Sci

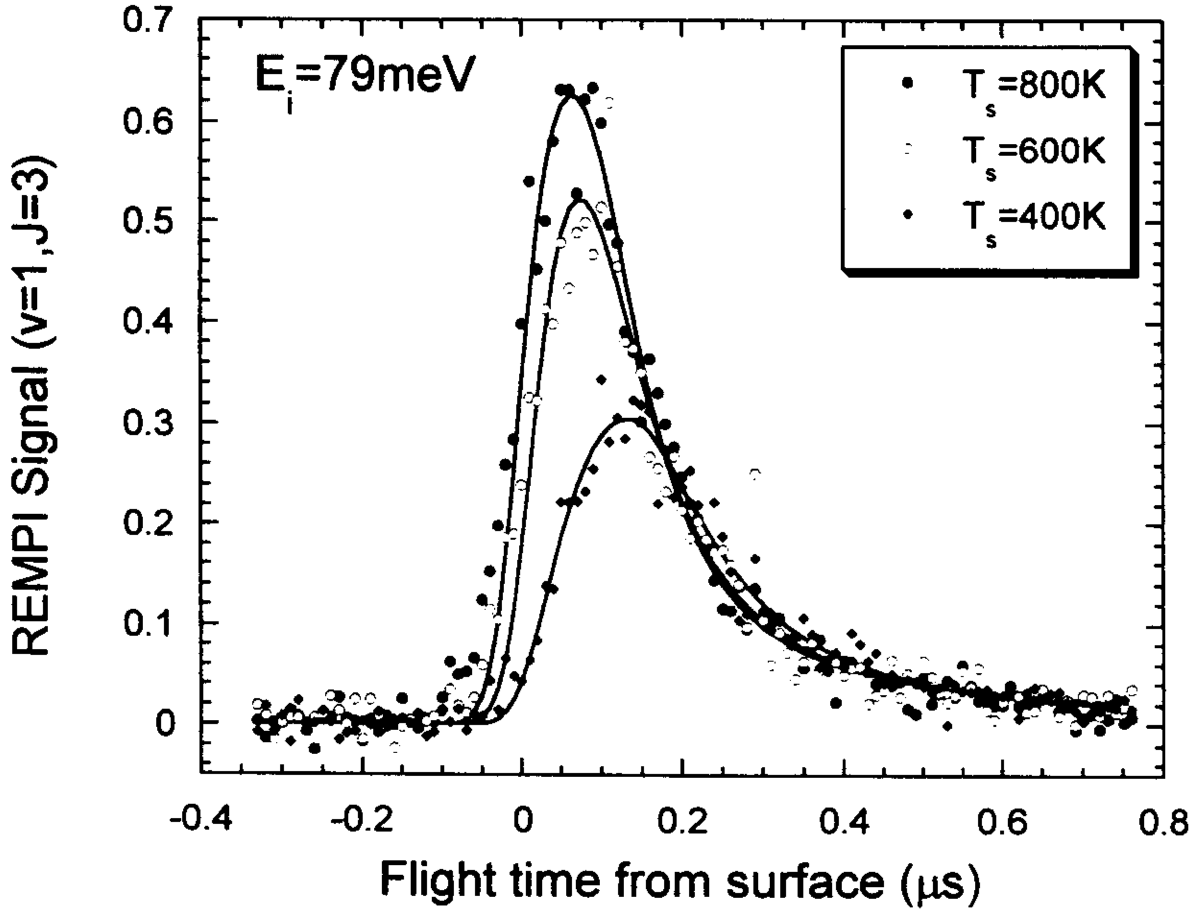
Rotationally Inelastic Scattering of H_2(v=1, J=1)/Cu(100)



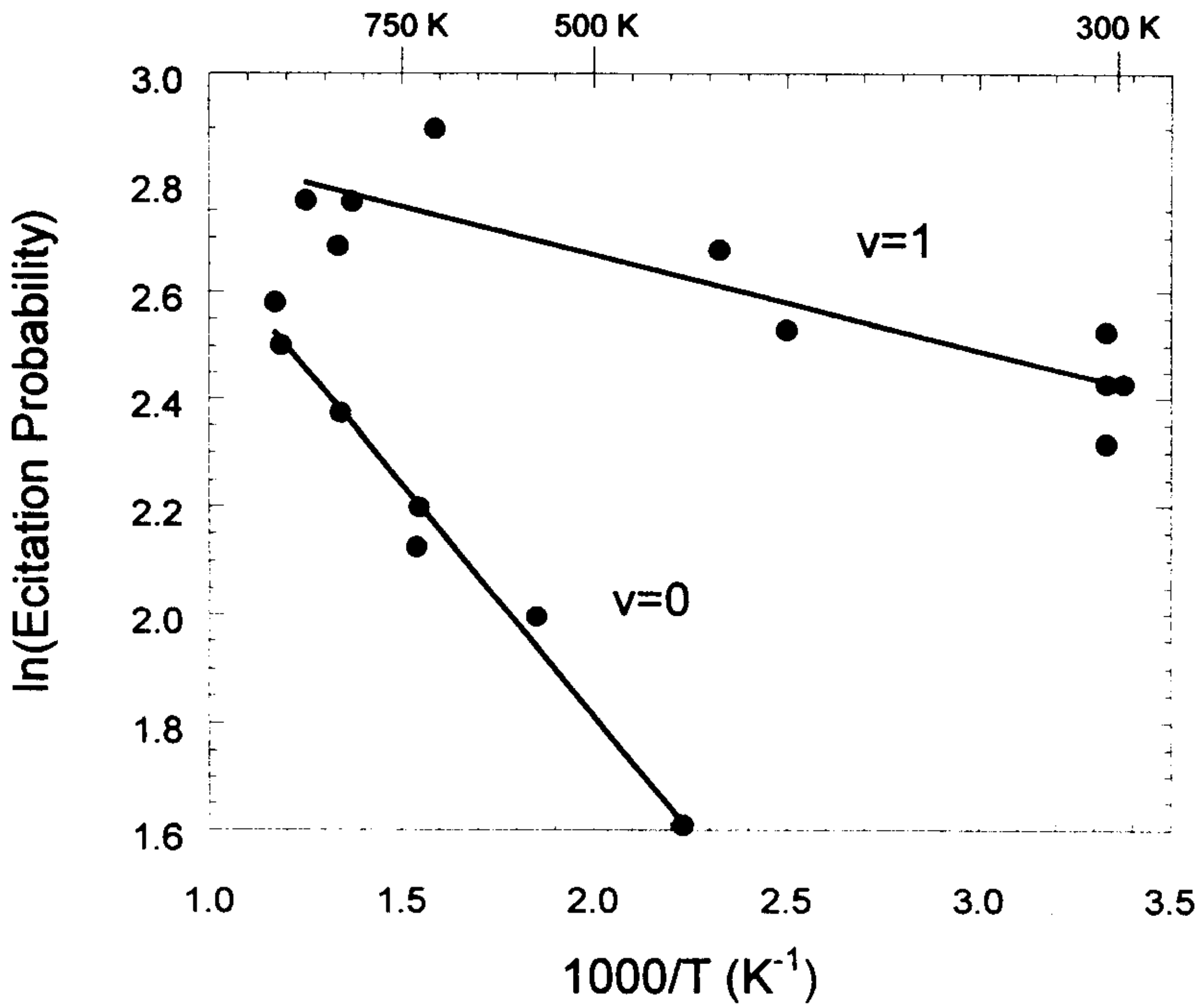
H_2/Cu(100)
Rotational Excitation (v=1,J=1 to J=3) vs E_i



H_2/Cu(100)
Rotational Excitation vs T_s

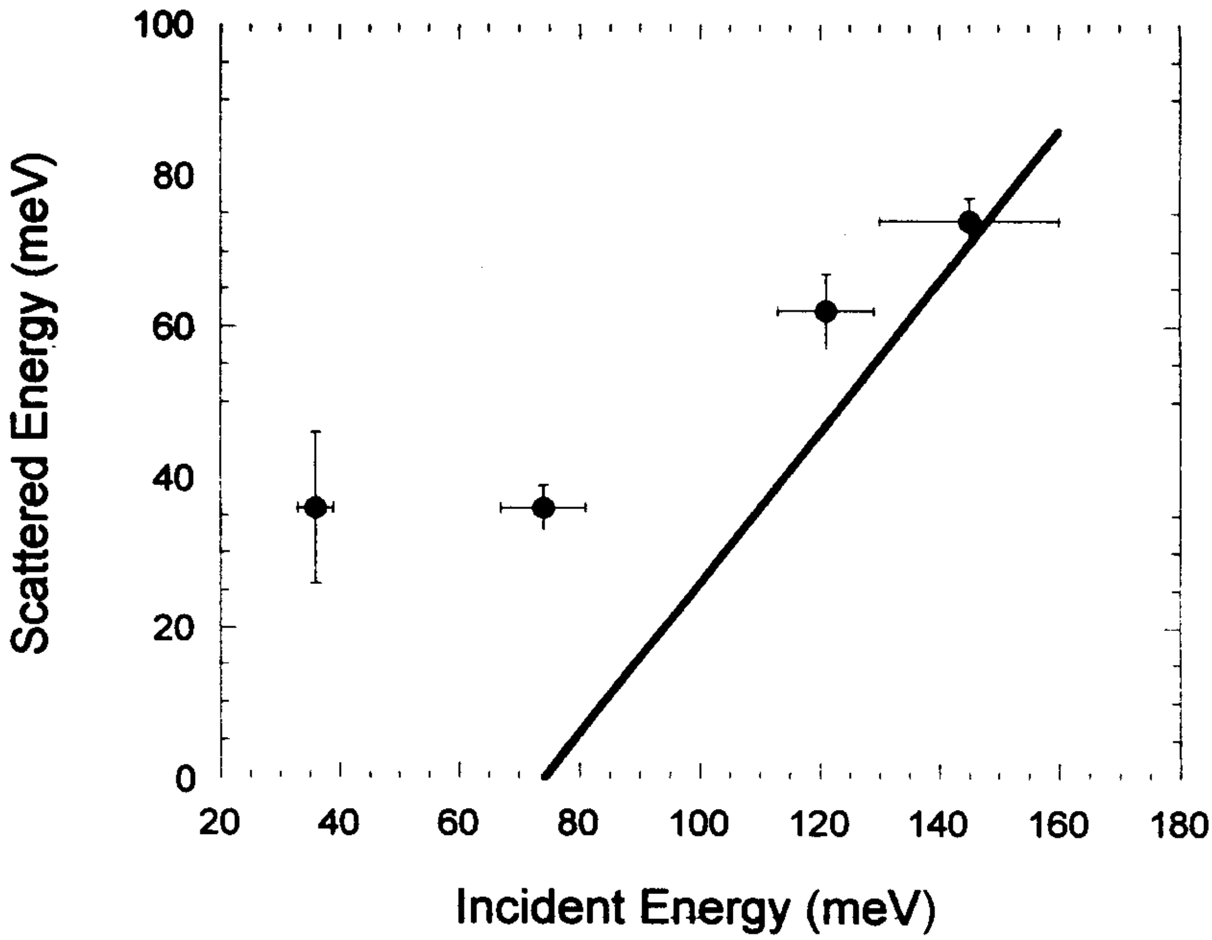


H_2/Cu(100)
J=1 to 3 Rotational Excitation
Arrhenius Plots E_i = 75 meV

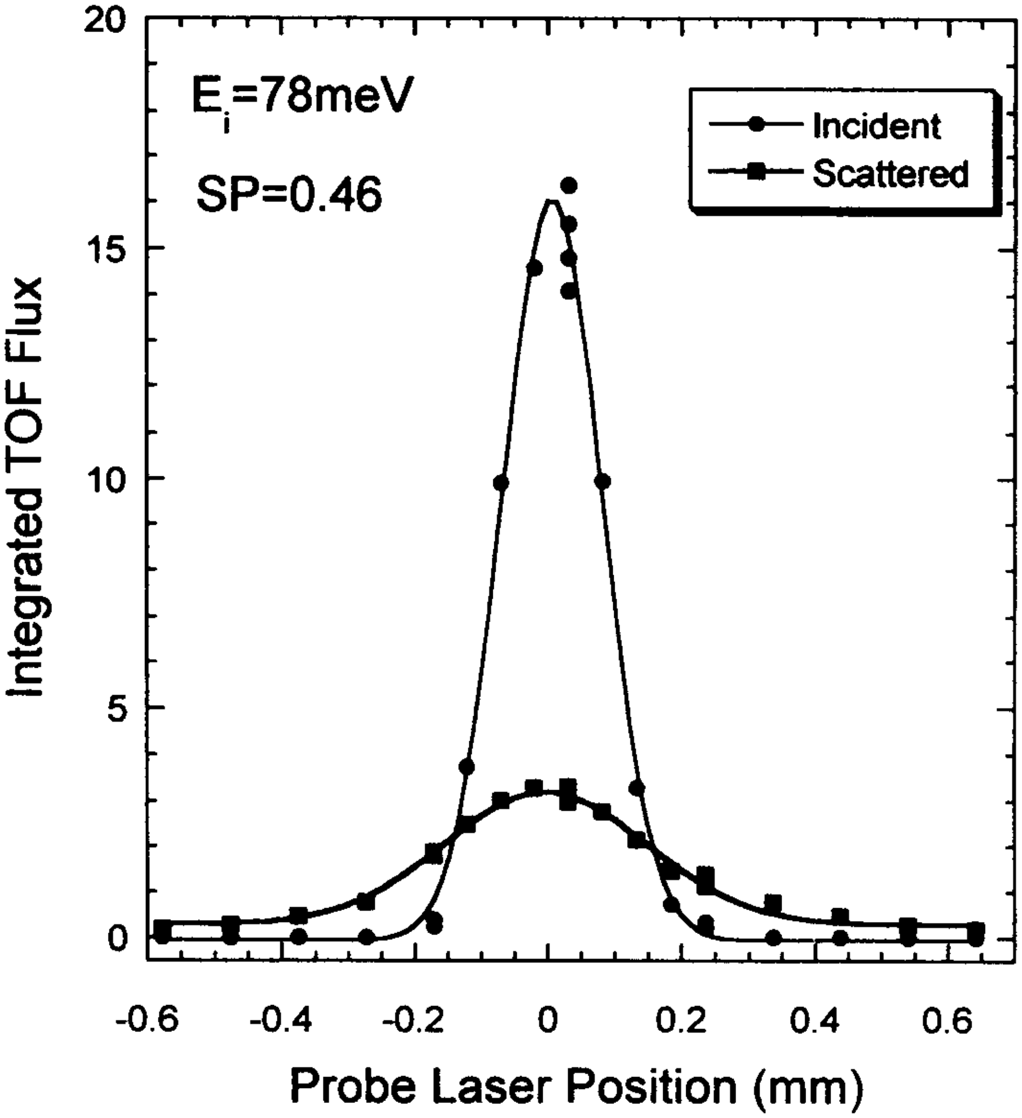


n

H_2(v=1,J=1->3)/Cu(100) Translational Energies

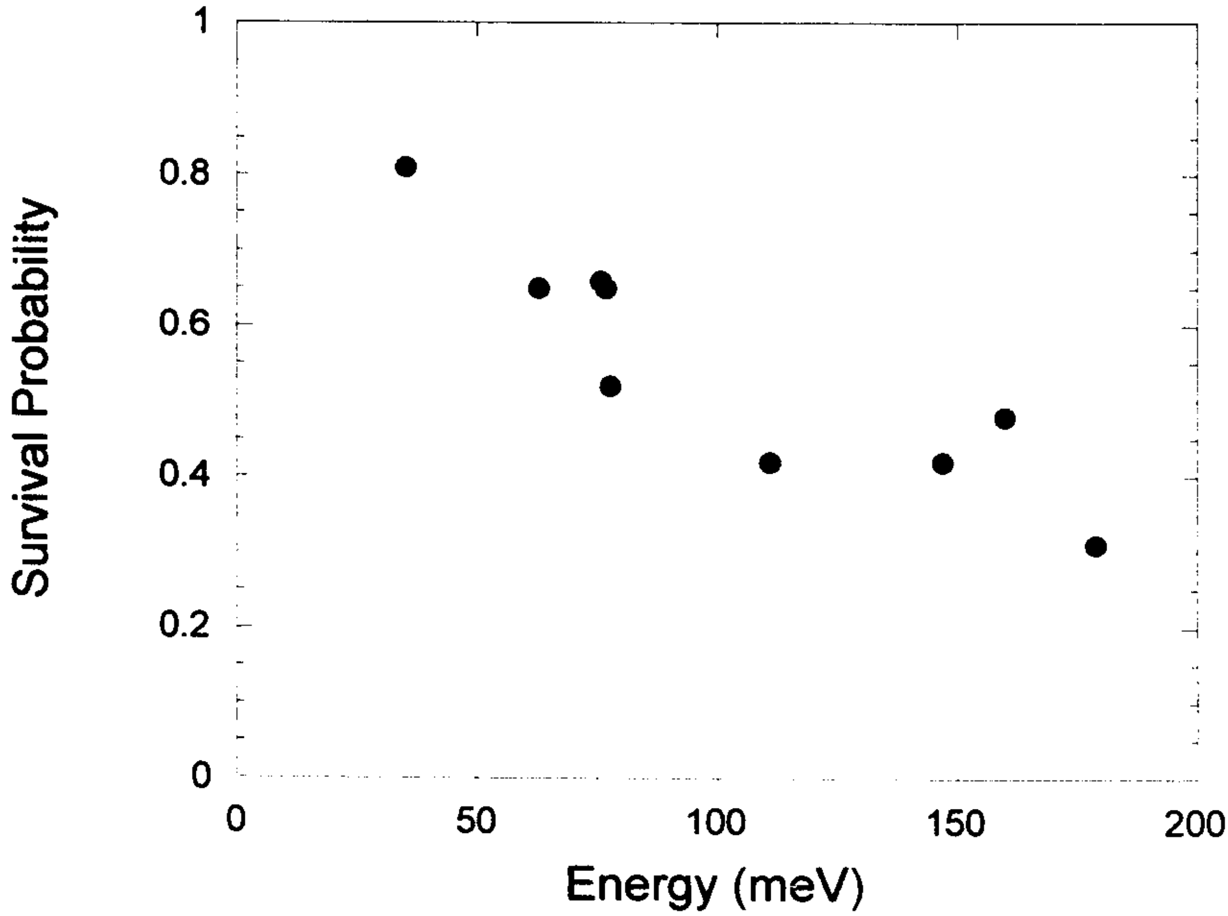


Spatial Profile of Incident and Scattered H_2(v=1, J=1)

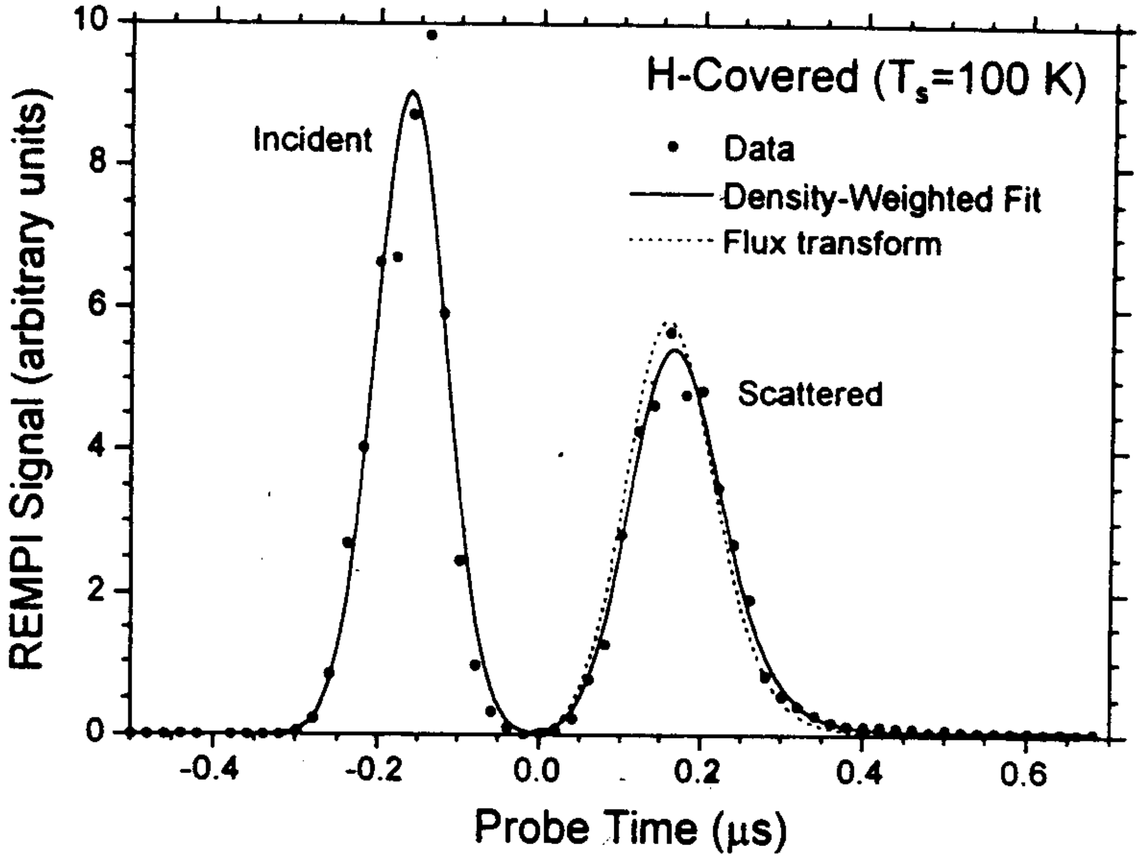


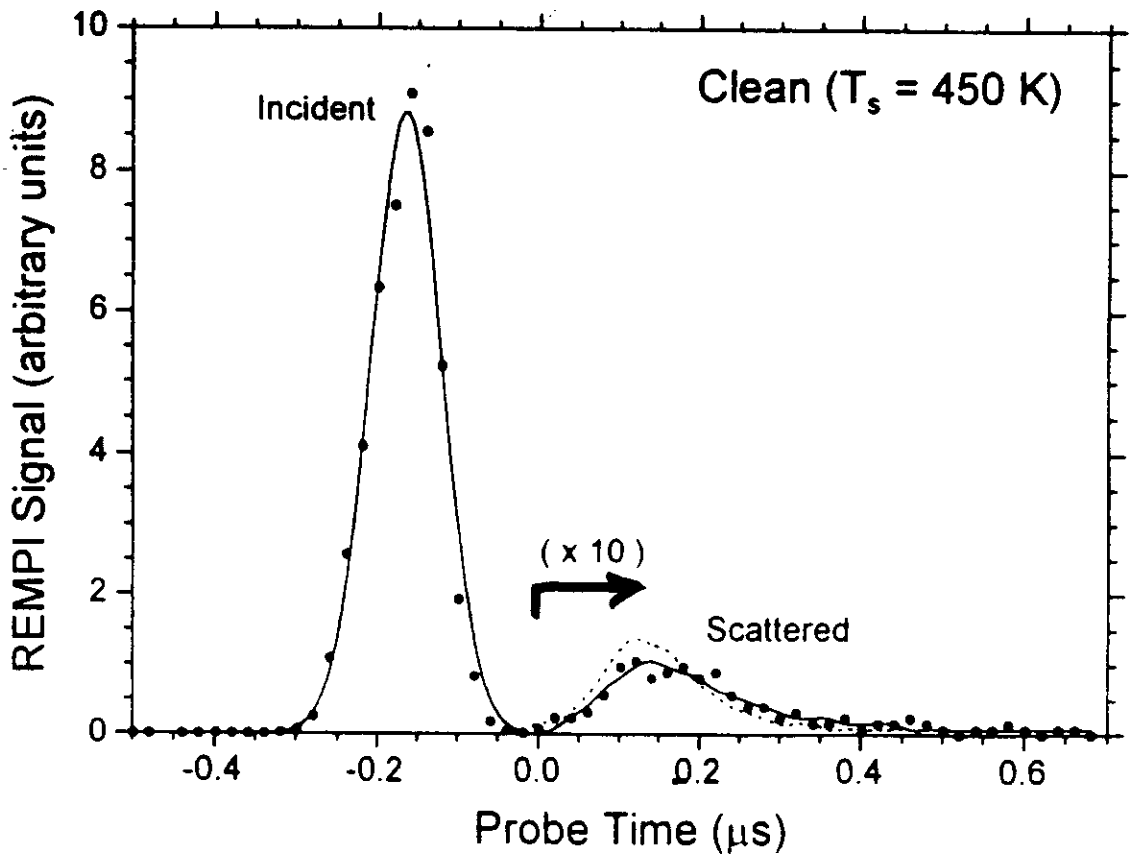
Absolute survival probability: Ratio of area under scattered profile to area under incident profile

H_2(v=1,J=1)/Cu(100)
Survival Probabilty vs E_i

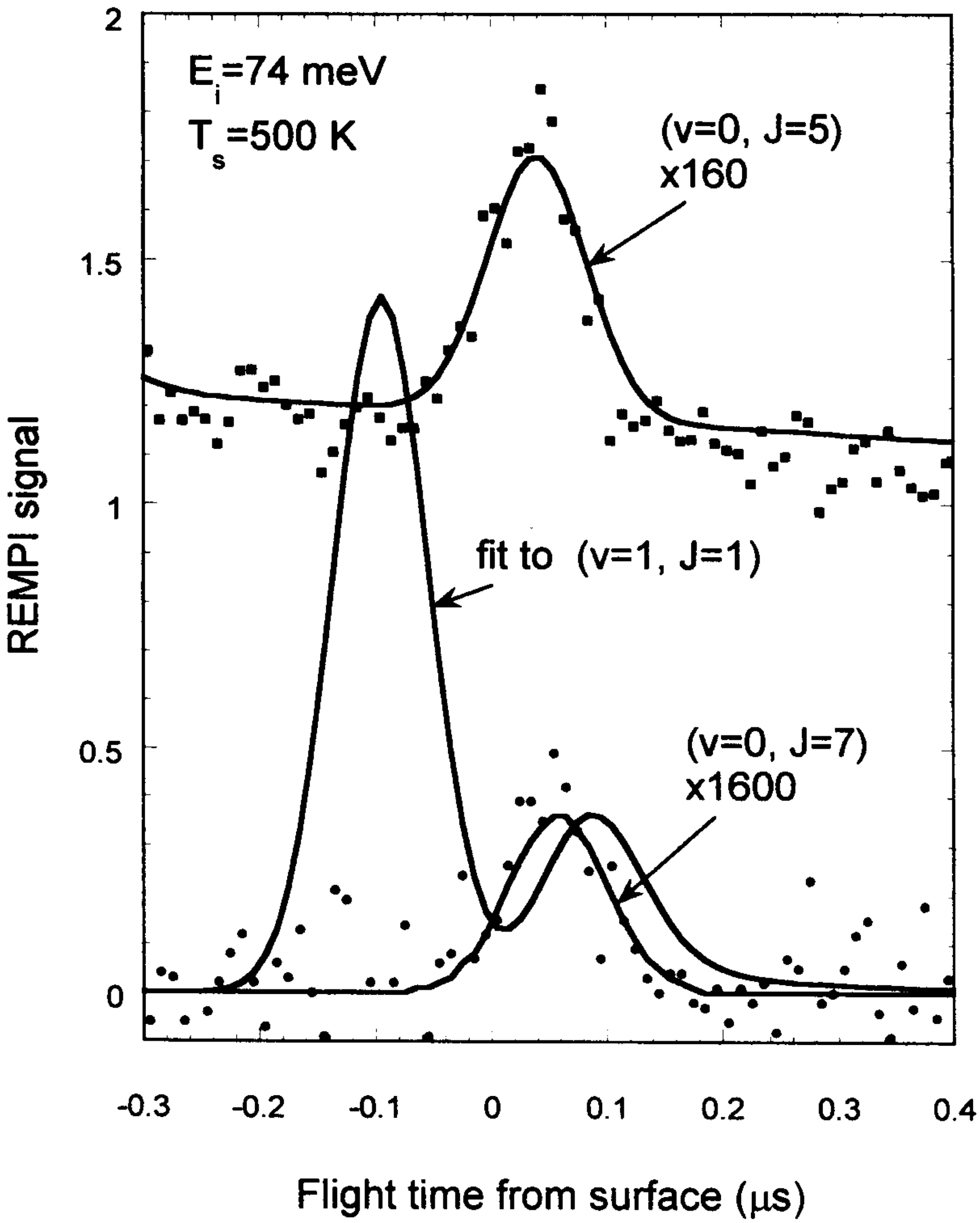


TOF Data for Clean vs. H-Covered Pd





Vibrationally Inelastic Scattering of H_2(v=1, J=1)/Cu(100)



Energy Transfer

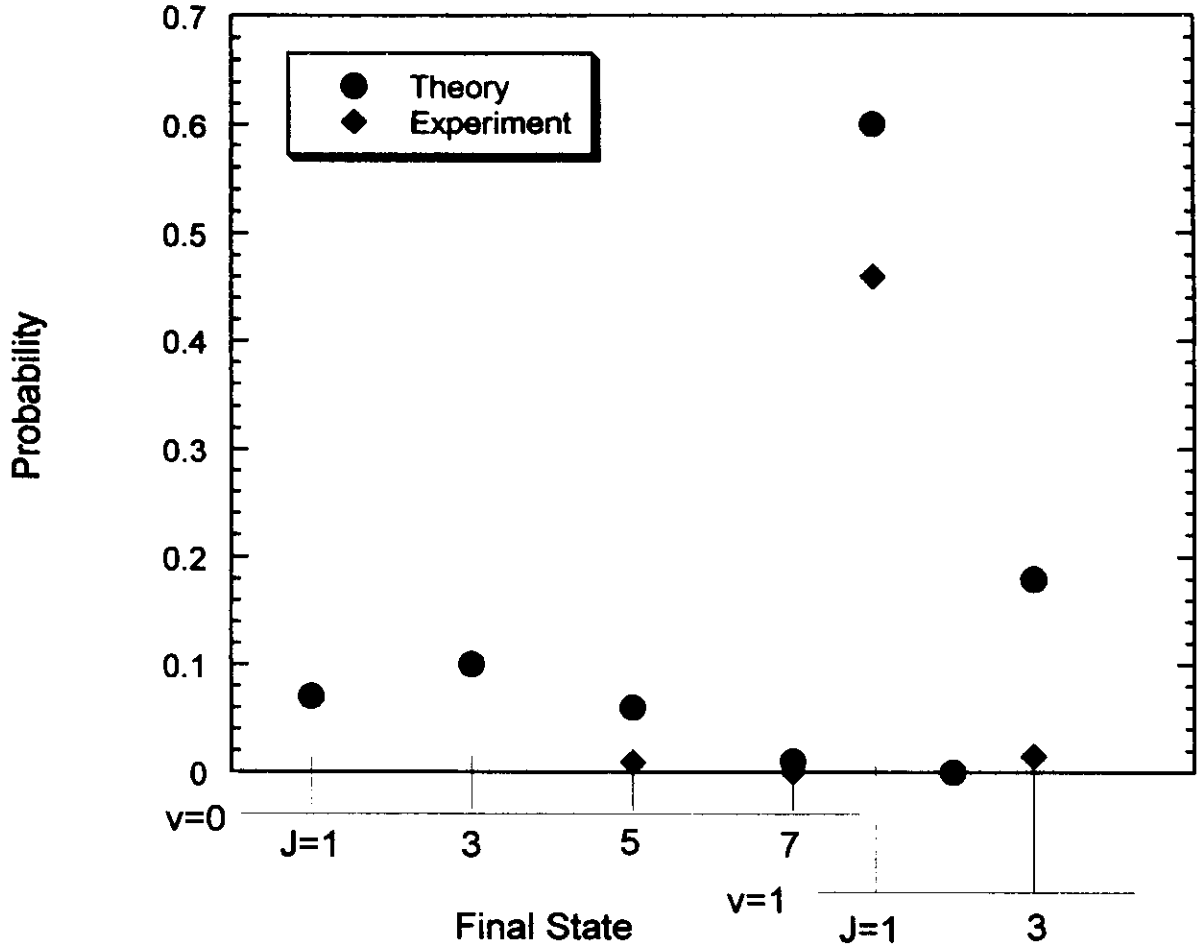
Vibrational relaxation releases about 516 meV of energy

state	E_i	E_f	ΔE_{tr}	ΔE_r	Net loss
v-0,J=5	74±7	258±35	211	207	98±36
v-0,J=7	74±7	151±23	77	400	39±24

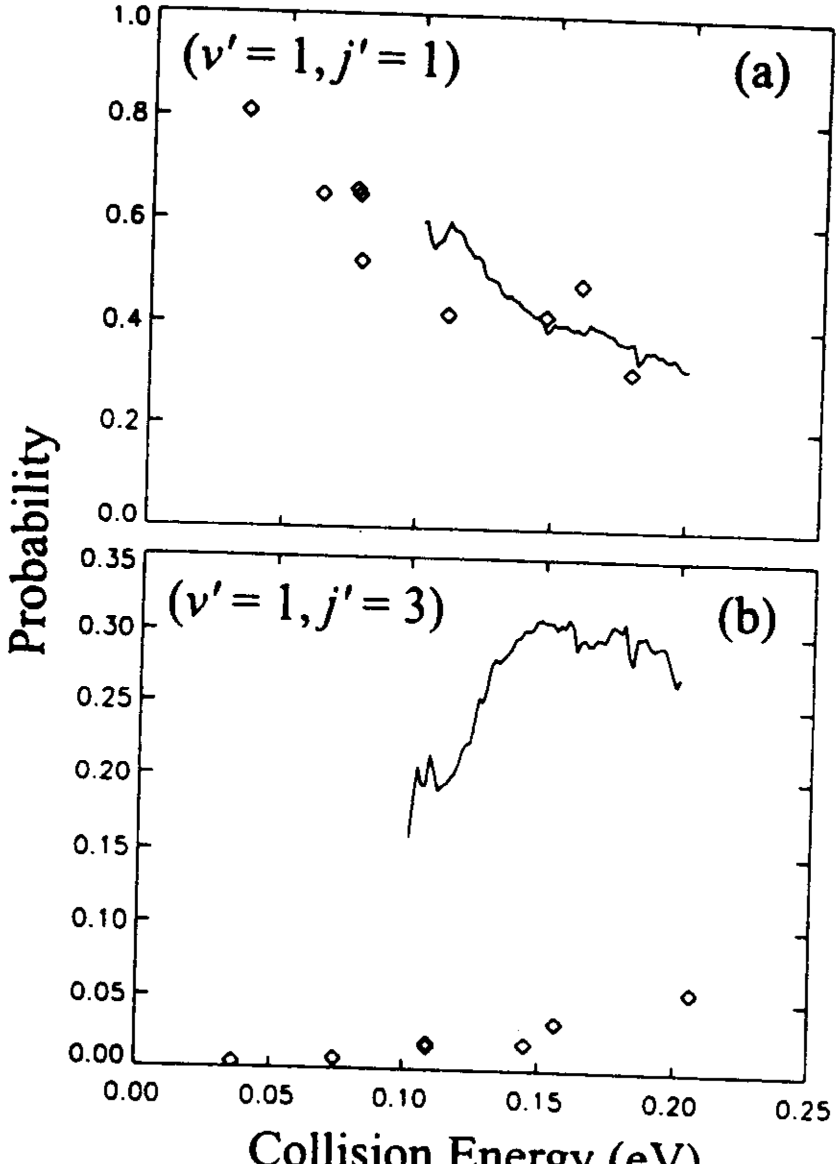
all energies in meV

Experiment-Theory Comparison H_2/Cu(100)

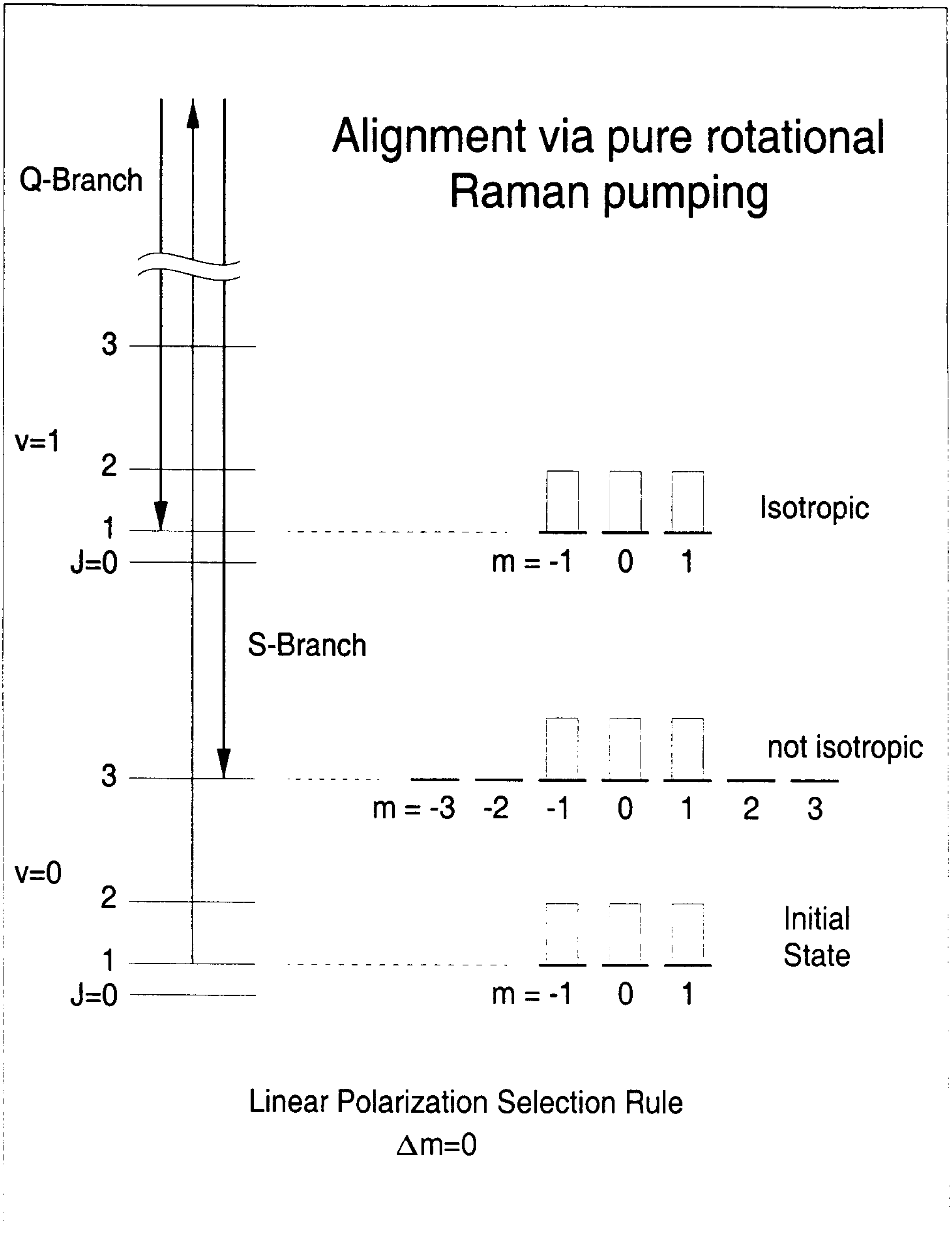
Calculations by Kroes et al.



Final State	Experiment	Theory
v=0, J=1		0.07
J=3		0.10
J=5	0.009	0.06
J=7	0.001	0.01
v=1, J=1	0.46	0.60
J=3	0.015	0.16

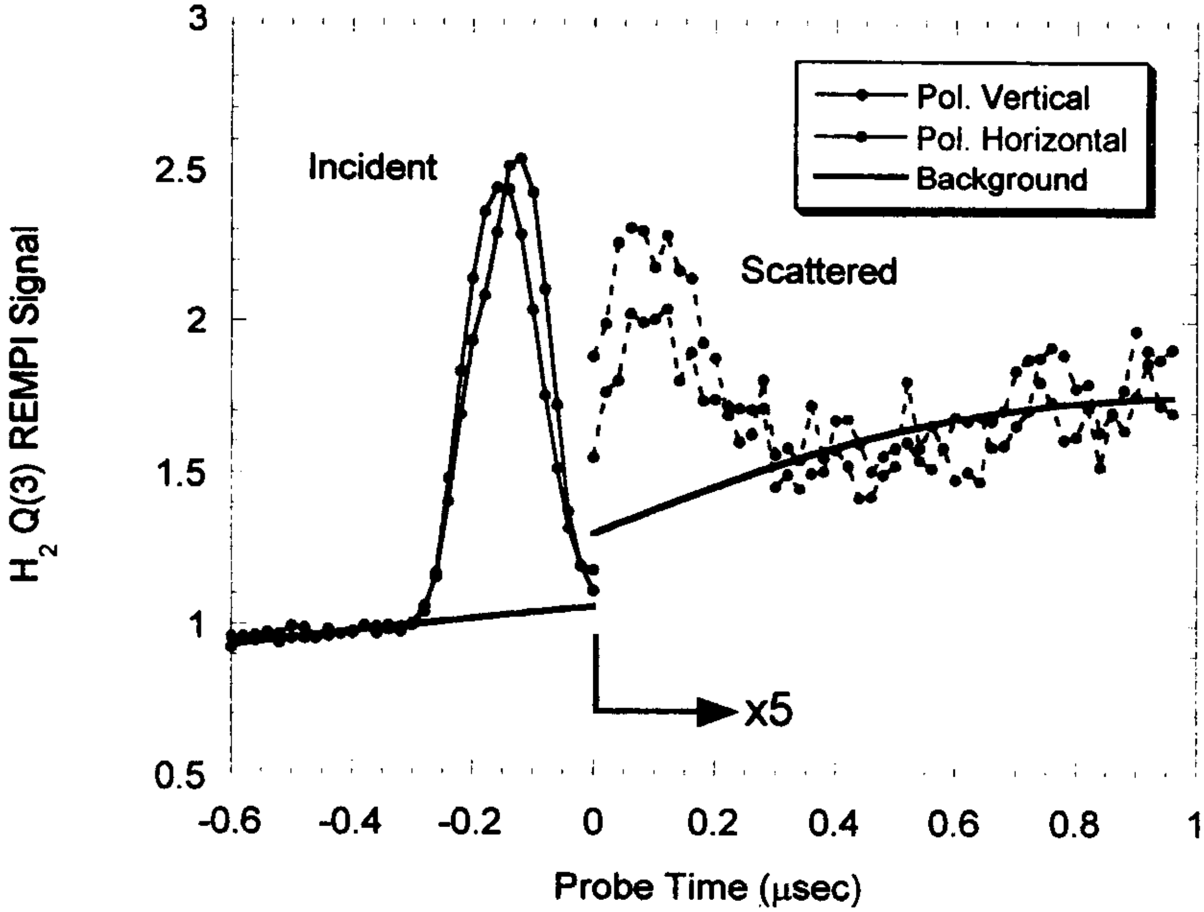


Quantum Dynamical Calculations of
H_2(v=1, J=1)/Cu(100)
Kroes and McCormack



Alignment via pure rotational Raman pumping
Q-Branch
3
v=1
2
1
J=0
m = -1 0 1
Isotropic
S-Branch
3
not isotropic
m = -3 -2 -1 0 1 2 3
v=0
2
1
J=0
Initial State
m = -1 0 1
Linear Polarization Selection Rule
Δm=0

J=3 reflectivity vs. pump polarization



Integrated Signal Ratio, Horizontal:Vertical

Incident 1.05 : 1.00
Scattered 1.33 : 1.00

Horizontal - all cartwheels
Vertical- mixed cartwheels & helicopters

Conclusions:

- State-to-state scattering points to PES anisotropies
- bond softening or peaking around the corner
- rotational excitation is not simple T-to-R
- energy balance in vibrational relaxation on Cu and Pd shows substrate participation
- theory: good news and bad news