Scattering of Small Molecules by Surfaces

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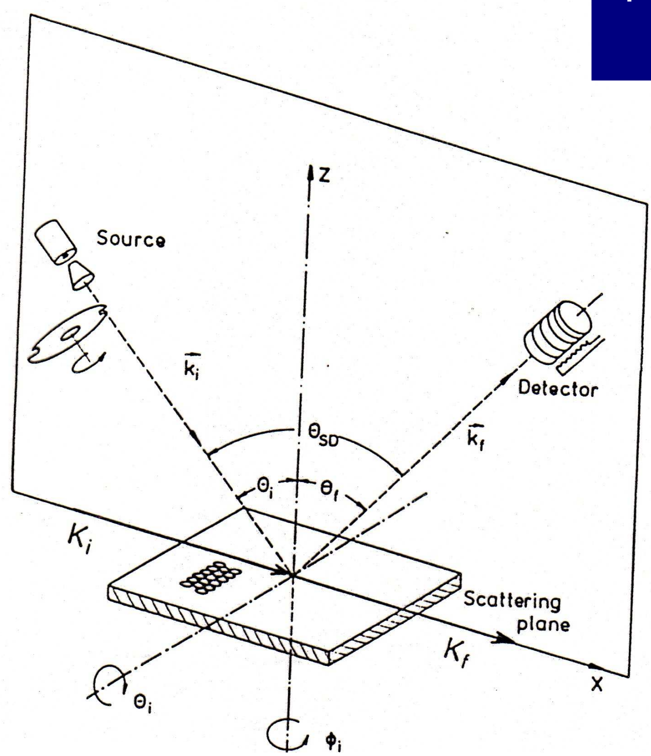
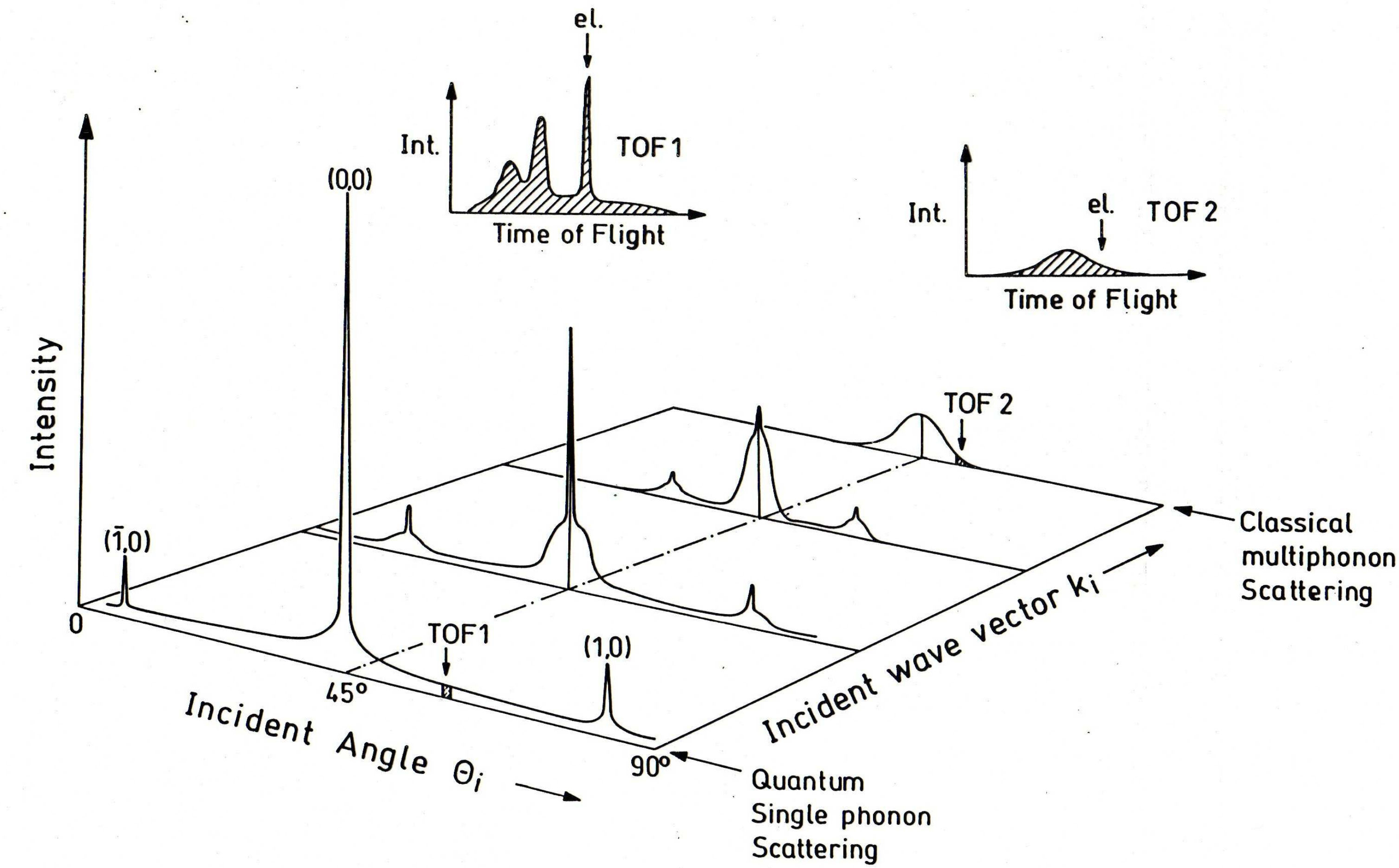
Scattering of Molecules from Surfaces

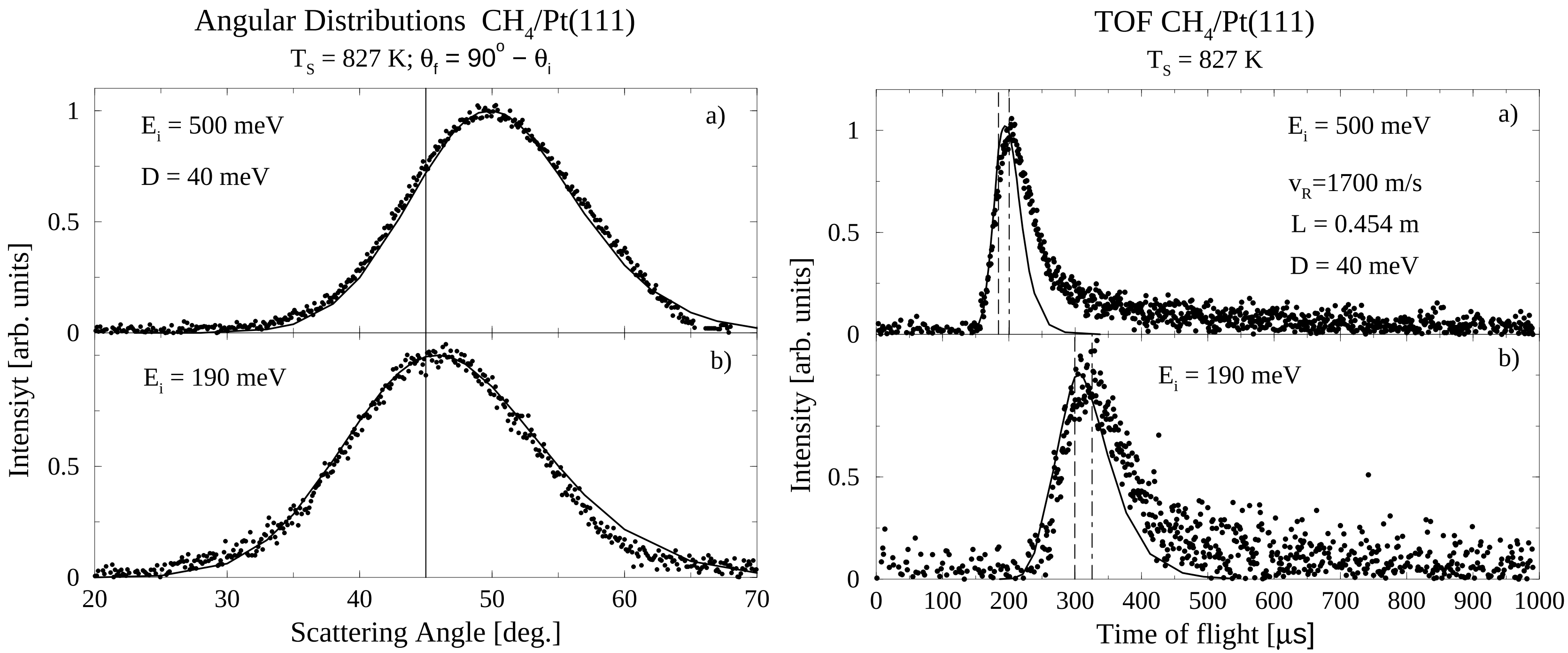
0.1 eV < E_i < 5 eV

4 amu < m < 30 amu




el.
Int.
TOF 1
Time of Flight
Int.
el.
TOF 2
Time of Flight
Intensity
(0,0)
(1̄,0)
TOF 2
Classical
multiphonon
Scattering
0
TOF1
(1,0)
45°
Incident wave vector k_i
Incident Angle Θ_i
90°
Quantum
Single phonon
Scattering

CH_4/Pt(111)



Data: T. Kondo, T. Sasaki, S. Yamamoto, J. Chem. Phys. **116**, 7673 (2002)

Basic Theory

$$w(\mathbf{p}_f, \mathbf{l}_f; \mathbf{p}_i, \mathbf{l}_i) \;=\; \left\langle \frac{2\pi}{\hbar} \sum_{\{n_f\}} |\mathcal{T}_{fi}|^2 \, \delta(\mathcal{E}_f - \mathcal{E}_i) \right\rangle$$

$$\frac{d^3R(\mathbf{p}_f, \mathbf{l}_f; \mathbf{p}_i, \mathbf{l}_i)}{d\Omega_f dE_f^T} = \frac{L^4}{(2\pi\hbar)^3} \frac{m^2|\mathbf{p}_f|}{p_{iz}} \, w(\mathbf{p}_f, \mathbf{l}_f, \mathbf{p}_i, \mathbf{l}_i)$$

$$H = H^c + H^p + V$$

$$H = H^c + H^p + V\Big|_{\{u_j\}=0} + \sum_j \frac{\partial V}{\partial u_j}\Big|_{\{u_j\}=0} u_j \; + \; \ldots$$

Approximations:

- Classically allowed trajectories
- Rapid collision
- Linear coupling with displacement

$$
\begin{aligned}
w(\mathbf{p}_f, \mathbf{p}_i) \;=\; & \frac{1}{\hbar^2\, S_{u.c.}^2} \int_{-\infty}^{+\infty} dt\, e^{-i(E_f - E_i)t/\hbar} \sum_l e^{i\mathbf{P}\cdot\mathbf{R_l}/\hbar} \int_{u.c.} d\mathbf{R} \int_{u.c.} d\mathbf{R}'\, e^{i\mathbf{P}\cdot(\mathbf{R}-\mathbf{R}')/\hbar} \\
& \times\; \tau(\mathbf{R})\, \tau(\mathbf{R}')\, e^{ip_z[z(\mathbf{R}) - z(\mathbf{R}')]}\, e^{-W(\mathbf{R},\mathbf{p}_f,\mathbf{p}_i)}\, e^{-W(\mathbf{R}',\mathbf{p}_f,\mathbf{p}_i)}\, e^{\mathcal{W}_l(\mathbf{R},\mathbf{R}';\mathbf{p}_f,\mathbf{p}_i,t)}
\end{aligned}
$$

$$
\begin{aligned}
\mathcal{W}_l(\mathbf{R};\mathbf{p}_f,\mathbf{p}_i,t) \;&=\; \langle \boldsymbol{\mathcal{F}}\cdot\mathbf{u}_0(\mathbf{0},0)\; \boldsymbol{\mathcal{F}}\cdot\mathbf{u}_l(\mathbf{R},t)\rangle \\
&\longrightarrow\; \frac{1}{\hbar^2}\; \langle \mathbf{p}\cdot\mathbf{u}_0(\mathbf{0},0)\; \mathbf{p}\cdot\mathbf{u}_l(\mathbf{R},t)\rangle
\end{aligned}
$$

$$
2W(\mathbf{R},\mathbf{p}_f,\mathbf{p}_i) \;=\; \mathcal{W}_{l=0}(\mathbf{R}=\mathbf{R}';\mathbf{p}_f,\mathbf{p}_i,t=0)
$$

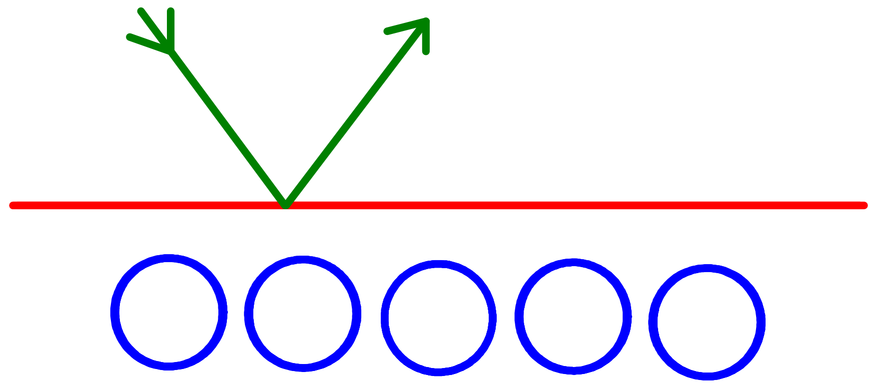
Classical limit: atom-surface scattering (multiphonon transfer)

$$
\frac{dR(\mathbf{p}_f,\mathbf{p}_i)}{d\Omega_f\, dE_f} = \frac{m^2\,|\mathbf{p}_f|}{8\pi^3\hbar^5 p_{iz}}\; |\tau_{fi}|^2 \left(\frac{\pi}{\Delta E_0 k_B T_S}\right)^{1/2} \exp\left\{-\frac{(E_f - E_i + \Delta E_0)^2}{4k_B T_S \Delta E_0}\right\}
$$

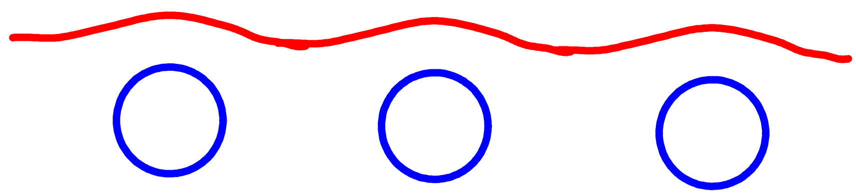
$$
\frac{dR(\mathbf{p}_f,\mathbf{p}_i)}{d\Omega_f\, dE_f} = \frac{m^2\,|\mathbf{p}_f|}{4\pi^3\hbar^5 p_{iz}}\frac{v_R^2}{S_{u.c.}}\; |\tau_{fi}|^2 \left(\frac{\pi}{\Delta E_0 k_B T_S}\right)^{3/2} \exp\left\{-\frac{(E_f - E_i + \Delta E_0)^2 + 2v_R^2\mathbf{P}^2}{4k_B T_S \Delta E_0}\right\}
$$

$$
\Delta E_0 \;=\; \frac{(\mathbf{p}_f - \mathbf{p}_i)^2}{2M}
$$

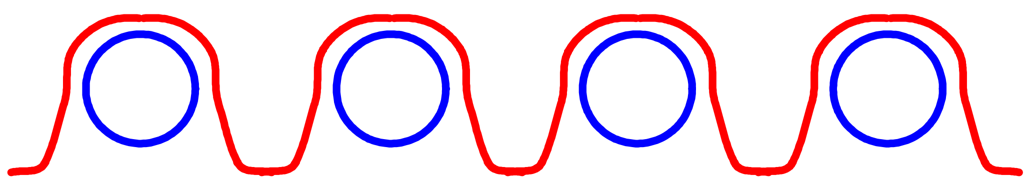
Flat surface potential



Weakly corrugated surface



Strongly corrugated; discrete, isolated atoms



Atom-surface scattering: limiting cases

Elastic diffraction

$$\frac{dR(\mathbf{p}_f,\mathbf{p}_i)}{d\Omega_f\,dE_f} \;=\; \frac{L^4\,m^2}{(2\pi\hbar)^3\,k_{iz}}\,\frac{2\pi}{\hbar}\sum_{\mathbf{G}}\,|\mathbf{k}_f|\;|\tau_{\mathbf{k}_f,\mathbf{k}_i}|^2\,e^{-2W(\mathbf{k})}\;\delta_{\mathbf{K},\mathbf{G}}\;\delta\,(E_f\;-\;E_i)$$

Single phonon transfer

$$\frac{dR(\mathbf{p}_f,\mathbf{p}_i)}{d\Omega_f\,dE_f} \;=\; \frac{L^4\,m^2}{(2\pi\hbar)^3\,k_{iz}}\,\frac{2\pi}{\hbar}\sum_{\mathbf{G}}\,|\mathbf{k}_f|\;|\tau_{\mathbf{k}_f,\mathbf{k}_i}|^2\,e^{-2W(\mathbf{k})}\;n(\omega)\;\mathbf{k}\cdot\underline{\underline{\rho(\mathbf{K}+\mathbf{G},\omega)}}\cdot\mathbf{k}$$

Multiphonon scattering

$$\frac{dR(\mathbf{p}_f,\mathbf{p}_i)}{d\Omega_f\,dE_f} = \frac{m^2\,|\mathbf{p}_f|}{8\pi^3\hbar^5 p_{iz}}\;|\tau_{fi}|^2\;\left(\frac{\pi}{\Delta E_0 k_B T_S}\right)^{1/2}\;\exp\left\{-\frac{(E_f-E_i+\Delta E_0)^2}{4k_B T_S\Delta E_0}\right\}$$

$$\frac{dR(\mathbf{p}_f,\mathbf{p}_i)}{d\Omega_f\,dE_f} = \frac{m^2\,|\mathbf{p}_f|}{4\pi^3\hbar^5 p_{iz}}\frac{v_R^2}{S_{u.c.}}\;|\tau_{fi}|^2\;\left(\frac{\pi}{\Delta E_0 k_B T_S}\right)^{3/2}\;\exp\left\{-\frac{(E_f-E_i+\Delta E_0)^2+2v_R^2\mathbf{P}^2}{4k_B T_S\Delta E_0}\right\}$$

$$\Delta E_0 \;=\; \frac{(\mathbf{p}_f-\mathbf{p}_i)^2}{2M}$$

Molecule-surface scattering: Classical translational and rotational motion

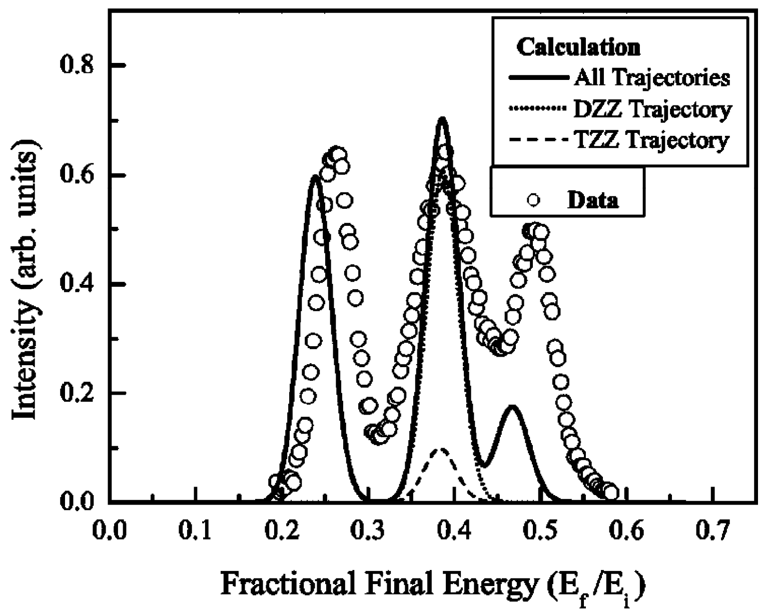
$$
\begin{aligned}
\frac{dR(\mathbf{p}_f,\mathbf{l}_f;\mathbf{p}_i,\mathbf{l}_i)}{d\Omega_f\ dE_f} \quad &= \quad \frac{L^4}{S_{u.c}}\,\frac{1}{\hbar}|\tau_{fi}|^2\frac{|\mathbf{p}_f|}{p_{iz}}\,m^2\,\frac{2\pi v_R^2}{\Delta E_0 k_B T_s}\,\left(\frac{2\pi\omega_R^2}{\Delta E_0^R k_B T_s}\right)^{\frac{1}{2}} \\
&\times \quad \left[\frac{\pi}{k_B T_s(\Delta E_0+\Delta E_0^R)}\right]^{\frac{1}{2}}\exp\left(-\frac{2\mathbf{P^2}v_R^2}{4k_B T_s\Delta E_0}\right)\exp\left(-\frac{2l_z^2\omega_R^2}{4k_B T_s\Delta E_0^R}\right) \\
&\times \quad \exp\left\{-\frac{\left(E_f-E_i+E_f^R-E_i^R+\Delta E_0+\Delta E_0^R\right)^2}{4k_B T_s(\Delta E_0+\Delta E_O^R)}\right\}
\end{aligned}
$$

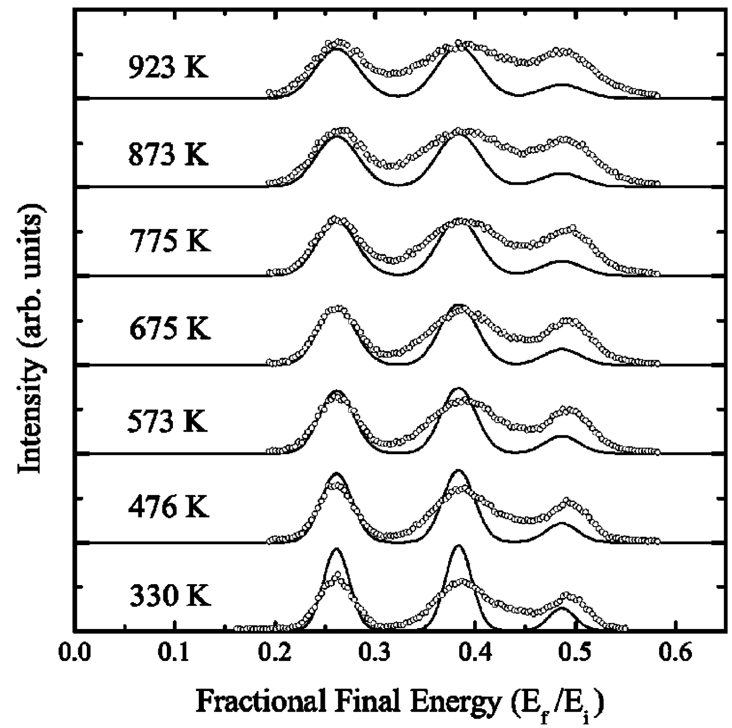
Molecule-surface scattering:
Classical translation and rotation, semiclassical internal mode excitation

$$w(\mathbf{p}_f,\mathbf{l}_f,\mathbf{p}_i,\mathbf{l}_i) = \frac{\hbar^2}{S_{u.c}}\ |\tau_{fi}|^2\ \left(\frac{2\pi v_R^2}{\Delta E_0 k_B T_S}\right)\left(\frac{2\pi \omega_R^2}{\Delta E_0^R k_B T_S}\right)^{1/2}$$
$$\times\ \left(\frac{\pi}{(\Delta E_0+\Delta E_0^R) k_B T_S}\right)^{1/2} \exp\left[-\frac{2\mathbf{P}^2 v_R^2}{4\Delta E_0 k_B T_S}\right]\ \exp\left[-\frac{2 l_z^2 \omega_R^2}{4\Delta E_0^R k_B T_S}\right]$$
$$\times\ \sum_{\kappa,\kappa'=1}^{N_A} \left\{ e^{i(\mathbf{p}_f\cdot\Delta\mathbf{r}^f_{\kappa,\kappa'} - \mathbf{p}_i\cdot\Delta\mathbf{r}^i_{\kappa,\kappa'})/\hbar}\ e^{-W_\kappa(\mathbf{p}_f,\mathbf{p}_i)}\ e^{-W_{\kappa'}(\mathbf{p}_f,\mathbf{p}_i)}\right.$$
$$\times\ \prod_{j=1}^{N_\nu} \sum_{\alpha_j=-\infty}^{\infty} I_{|\alpha_j|}(b_{\kappa,\kappa'}(\omega_j))\ \left[\frac{n(\omega_j)+1}{n(\omega_j)}\right]^{\alpha_j/2}$$
$$\left.\times\ \exp\left[-\frac{(E_f^T - E_i^T + E_f^R - E_i^R + \Delta E_0 + \Delta E_0^R + \hbar\sum_{s=1}^{N_\nu}\alpha_s\omega_s)^2}{4(\Delta E_0+\Delta E_0^R) k_B T_S}\right]\right\}\ ,$$

$$b_{\kappa,\kappa'}(\omega_j)\ =\ \sum_{\beta,\beta'=1}^{3} p_\beta p_{\beta'}\ \frac{1}{N_\nu \hbar\sqrt{m_\kappa m_{\kappa'}}\,\omega_j}\ e\left({\kappa \atop \nu_j}\middle|\beta\right)\ e^*\left({\kappa' \atop \nu_j}\middle|\beta'\right)\ \sqrt{n(\omega_j)[n(\omega_j)+1]}$$

Low energy ion-surface scattering





$$I_{\mathrm{MAX}} \propto \frac{1}{(k_{\mathrm{B}} T_S \Delta E_0)^{1/2}}$$

K^+/Cu(001)<100>

E_i = 154 eV ; $\theta_i = \theta_f = 45^0$; T_S = 675 K

$$\langle \Delta E^2 \rangle \approx 2g(\theta) E_i k_B T_S$$

J. Powers, J. R. Manson, C. E. Sosolik, J. R. Hampton, A. C. Lavery and B. H. Cooper, Phys. Rev. B**70**, 115413 (2004)

General properties of the classical scattering intensity

$$\frac{dR^{(1)}(\mathbf{p}_f,\mathbf{p}_i)}{d\Omega_f dE_f} = \frac{m^2|\mathbf{p}_f|}{8\pi^3\hbar^4 p_{iz}}|\tau_{fi}|^2\left(\frac{\pi}{\Delta E_0 k_B T_S}\right)^{1/2} \exp\left\{-\frac{(\Delta E+\Delta E_0)^2}{4k_\mathrm{B}T_\mathrm{S}\Delta E_0}\right\}$$

$$\bar{E}_f = f(\theta)E_i$$

$$\theta = \pi - \theta_f - \theta_i$$

$$f(\theta) = \left(\frac{\sqrt{1-\mu^2\sin^2\theta}+\mu\cos\theta}{1+\mu}\right)^2 \qquad \mu = m/M_c$$

$$\langle \Delta E^2\rangle \approx 2g(\theta)E_i k_B T_S$$

$$g(\theta) = \frac{g_{TA}(\theta)}{(1+\mu-\mu\cos\theta/\sqrt{f(\theta)})}$$

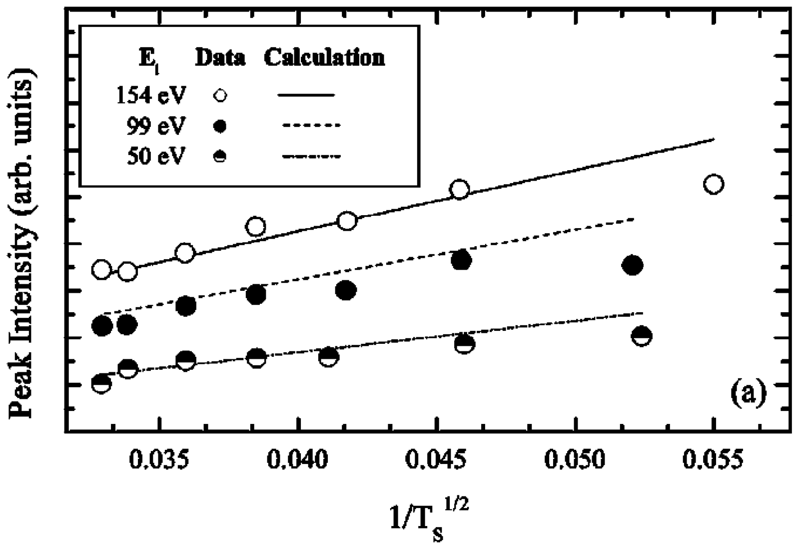
$$g_{TA}(\theta) = \mu(1+f(\theta)-2\sqrt{f(\theta)}\cos\theta)$$

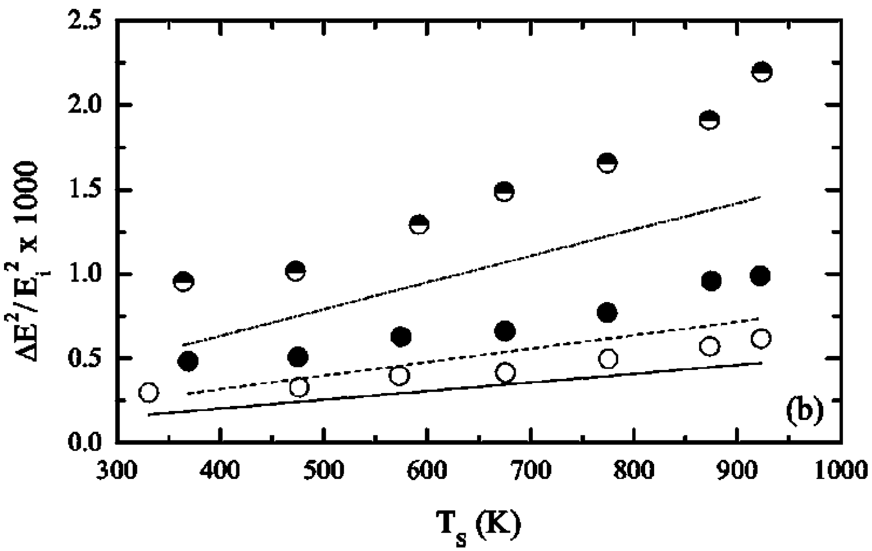
$$I_\mathrm{MAX} \propto \frac{1}{(k_\mathrm{B}T_S\Delta E_0)^{1/2}}$$

$$\Delta E_0 = (\mathbf{p}_f-\mathbf{p}_i)^2/2M_c$$

$$\approx g_\mathrm{TA}(\theta)E_i$$

Single scattering trajectory,
three different incident energies



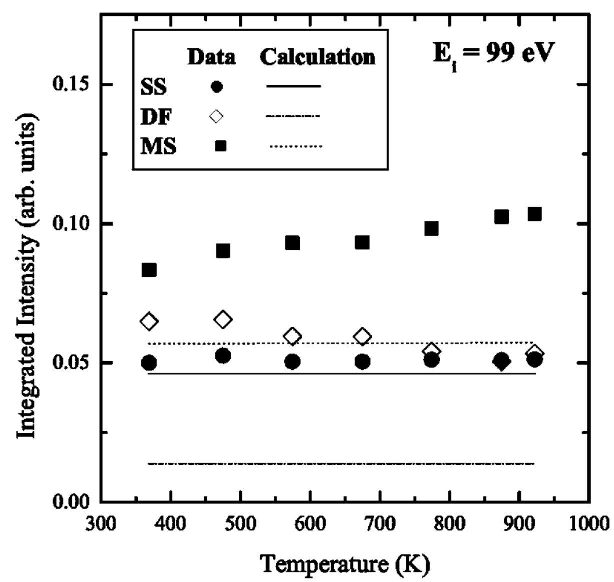


$$\frac{dR^{(1)}(\mathbf{p}_f,\mathbf{p}_i)}{d\Omega_f dE_f} = \frac{m^2|\mathbf{p}_f|}{8\pi^3\hbar^4 p_{iz}}|\tau_{fi}|^2\left(\frac{\pi}{\Delta E_0 k_B T_S}\right)^{1/2} \times \exp\left\{-\frac{(\Delta E + \Delta E_0)^2}{4k_B T_S \Delta E_0}\right\},$$

$$I_{\mathrm{MAX}} \propto \frac{1}{(k_B T_S \Delta E_0)^{1/2}}$$

$$\langle \Delta E^2 \rangle \approx 2g(\theta) E_i k_B T_S$$

Single and multiple scattering
trajectories at 99 meV.



Classical Scattering Intensity: General Properties

$$\frac{dR^{(1)}(\mathbf{p}_f,\mathbf{p}_i)}{d\Omega_f dE_f} = \frac{m^2|\mathbf{p}_f|}{8\pi^3\hbar^4 p_{iz}}|\tau_{fi}|^2\left(\frac{\pi}{\Delta E_0 k_B T_S}\right)^{1/2} \exp\left\{-\frac{(\Delta E + \Delta E_0)^2}{4k_{\mathrm{B}}T_{\mathrm{S}}\Delta E_0}\right\}$$

$$\frac{dR(\mathbf{p}_f,\mathbf{p}_i)}{d\Omega_f\, dE_f} = \frac{m^2\,|\mathbf{p}_f|}{4\pi^3\hbar^5 p_{iz}}\frac{v_R^2}{S_{u.c.}}\ |\tau_{fi}|^2\ \left(\frac{\pi}{\Delta E_0 k_B T_S}\right)^{3/2} \exp\left\{-\frac{(E_f - E_i + \Delta E_0)^2 + 2v_R^2\mathbf{P}^2}{4k_B T_S \Delta E_0}\right\}$$

$$\bar{E}_f = f(\theta)E_i \qquad \theta = \pi - \theta_f - \theta_i$$

$$f(\theta) = \left(\frac{\sqrt{1-\mu^2\sin^2\theta} + \mu\cos\theta}{1+\mu}\right)^2 \qquad \mu = m/M_c$$

$$\langle \Delta E^2\rangle \approx 2g(\theta)E_i k_B T_S \qquad g(\theta) = \frac{g_{TA}(\theta)}{(1+\mu-\mu\cos\theta/\sqrt{f(\theta)})}$$

$$g_{TA}(\theta) = \mu(1+f(\theta) - 2\sqrt{f(\theta)}\cos\theta)$$

$$I_{\mathrm{MAX}} \propto \frac{1}{(k_{\mathrm{B}}T_S\Delta E_0)^{1/2}} \qquad \Delta E_0 = (\mathbf{p}_f - \mathbf{p}_i)^2/2M_c \approx g_{\mathrm{TA}}(\theta)E_i$$

$$I_{\mathrm{MAX}} \propto \frac{1}{(k_B T_s \Delta E_0)^{3/2}}$$

“High?” energy He scattering: He/Cu(001), E_i > 100 meV

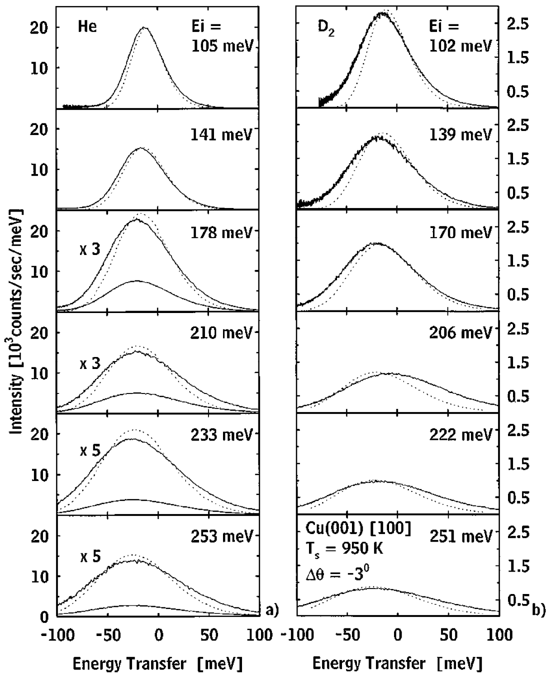


FIG. 1. Time-of-flight spectra of He (a) and D_2 (b) scattered from the [100] direction of Cu(001) at a temperature $T_s = 950$ K and a deviation angle $\Delta\theta = -3°$. The incident energy was increased from $E_i \sim 100$ meV to $E_i \sim 250$ meV for both He and D_2 scattering. The D_2 TOF spectra at energies $E_i = 206$ meV and $E_i = 222$ meV are anomalous because of the proximity of a RID peak. The dotted lines indicate the best fit of Eq. (2) to the TOF spectra with the parameters reported in Table II.

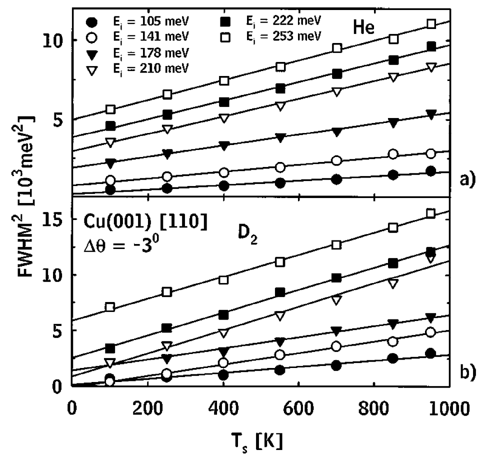


FIG. 6. The FWHM^2 of time-of-flight spectra of He (a) and D_2 (b) beams incident along the [100] direction of Cu(001). In each data set the incident energy is constant and the surface temperature T_s increases. The deviation angle was $\Delta\theta = -3°$. The solid lines are linear fits to the experimental data. The slope of the best-fit lines to the D_2 data taken at $E_i = 210$ meV and $E_i = 222$ meV are anomalous due to the proximity of RID peaks.

M. Bertino,
W. Silvestri
and
J. R. Manson,
J. Chem. Phys.
108,
10239 (1998).

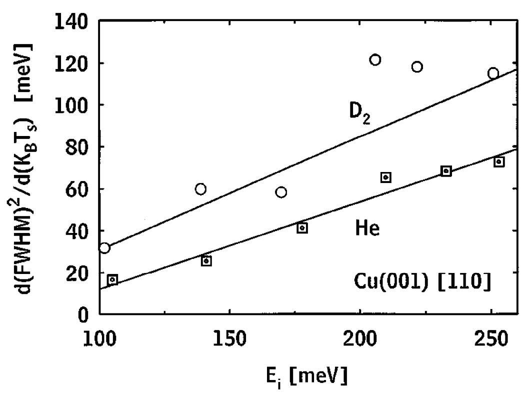


FIG. 7. The slope of the squared widths $d(\mathrm{FWHM})^2/d(k_BT_s)$ as a function of incident energy. Dotted squares: He. Circles: D_2. The lines are linear fits to the data. The D_2 data taken at an energy $E_i = 206$ meV and $E_i = 222$ meV are anomalous because of the proximity of RID peaks and were not considered in the linear fit.

$$(\mathrm{FWHM})^2 \approx 16 \ln(2) g(\theta) E_i k_\mathrm{B} T_s$$

"High?" energy He scattering: He/Cu(001), Ei > 100 meV

Both energy and temperature dependence of
intensity agree with the "flat surface model"

$$I_{\mathrm{MAX}} \propto \frac{1}{(k_B T_s \Delta E_0)^{3/2}} \qquad \Delta E_0 \approx g_{\mathrm{TA}}(\theta) E_i$$

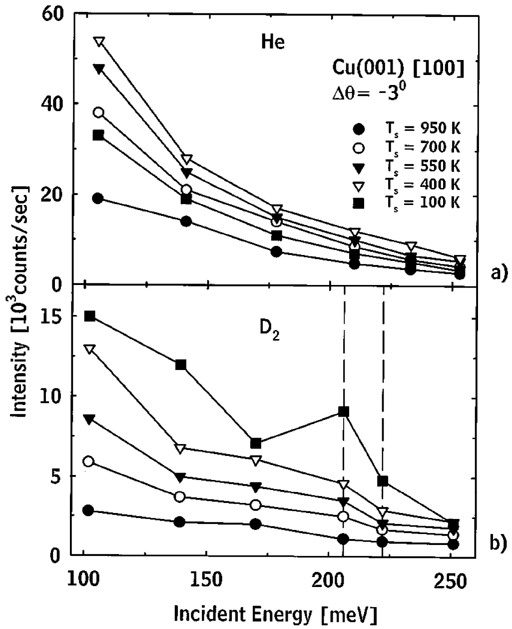


FIG. 5. Maximum peak intensities of time-of-flight spectra of He (a) and D_2 (b) beams incident along the [100] direction of Cu(001). In each data set the surface temperature T_s is constant and the incident energy E_i increases. The deviation angle was $\Delta\theta = -3°$. The lines are a guide to the eye. The vertical dashed lines in (b) indicate the energies where a RID peak is in the immediate neighborhood of $\Delta\theta = -3°$.

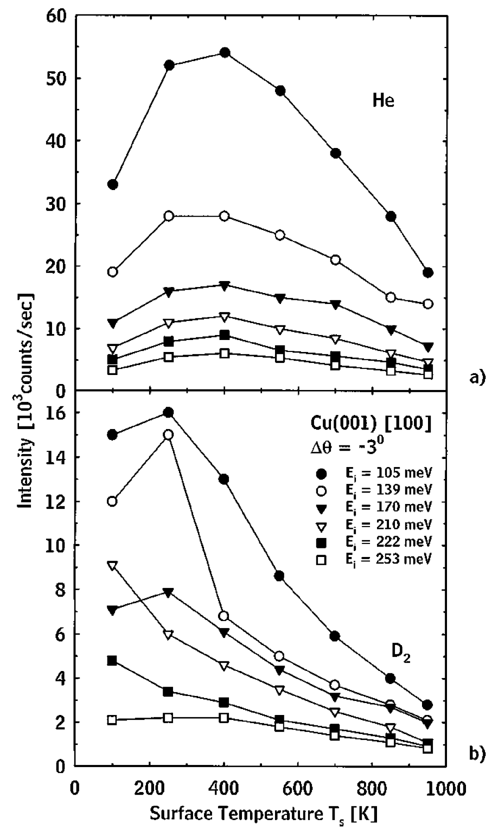


FIG. 4. Maximum peak intensities of time-of-flight spectra of He (a) and D_2 (b) beams incident along the [100] direction of Cu(001). In each data set the incident energy E_i is constant and the surface temperature T_s increases. The deviation angle was $\Delta\theta = -3°$. The lines are a guide to the eye.

Molecule-surface scattering:
Classical translation and rotation,
semiclassical internal mode excitation

$$
\begin{aligned}
w(\mathbf{p}_f, \mathbf{l}_f, \mathbf{p}_i, \mathbf{l}_i) = {} & \frac{\hbar^2}{S_{u.c}} \; |\tau_{fi}|^2 \; \left(\frac{2\pi v_R^2}{\Delta E_0 k_B T_S}\right) \left(\frac{2\pi \omega_R^2}{\Delta E_0^R k_B T_S}\right)^{1/2} \\
\times & \left(\frac{\pi}{(\Delta E_0 + \Delta E_0^R) k_B T_S}\right)^{1/2} \exp\left[-\frac{2\mathbf{P}^2 v_R^2}{4\Delta E_0 k_B T_S}\right] \exp\left[-\frac{2 l_z^2 \omega_R^2}{4\Delta E_0^R k_B T_S}\right] \\
\times & \sum_{\kappa,\kappa'=1}^{N_A} \left\{ e^{i(\mathbf{p}_f \cdot \Delta \mathbf{r}^f_{\kappa,\kappa'} - \mathbf{p}_i \cdot \Delta \mathbf{r}^i_{\kappa,\kappa'})/\hbar} \; e^{-W_\kappa(\mathbf{p}_f,\mathbf{p}_i)} \; e^{-W_{\kappa'}(\mathbf{p}_f,\mathbf{p}_i)} \right. \\
\times & \prod_{j=1}^{N_\nu} \sum_{\alpha_j=-\infty}^{\infty} I_{|\alpha_j|}(b_{\kappa,\kappa'}(\omega_j)) \; \left[\frac{n(\omega_j)+1}{n(\omega_j)}\right]^{\alpha_j/2} \\
\times & \left. \exp\left[-\frac{(E_f^T - E_i^T + E_f^R - E_i^R + \Delta E_0 + \Delta E_0^R + \hbar \sum_{s=1}^{N_\nu} \alpha_s \omega_s)^2}{4(\Delta E_0 + \Delta E_0^R) k_B T_S}\right] \right\} ,
\end{aligned}
$$

$$
b_{\kappa,\kappa'}(\omega_j) \; = \; \sum_{\beta,\beta'=1}^{3} p_\beta p_{\beta'} \; \frac{1}{N_\nu \hbar \sqrt{m_\kappa m_{\kappa'}} \, \omega_j} \; e\left(\begin{smallmatrix}\kappa \\ \nu_j\end{smallmatrix}\Big|\beta\right) e^*\left(\begin{smallmatrix}\kappa' \\ \nu_j\end{smallmatrix}\Big|\beta'\right) \sqrt{n(\omega_j)[n(\omega_j)+1]}
$$

Discussion

Form factor

$$\left|\tau_{fi}\right|^2 = \left|V_{J-M}\right|^2 \rightarrow \left(\frac{2\hbar^2 k_{iz} k_{fz}}{m}\right)^2$$

Parameters

$$v_R \sim c_R \qquad 1000m/s < v_R < 2000m/s$$

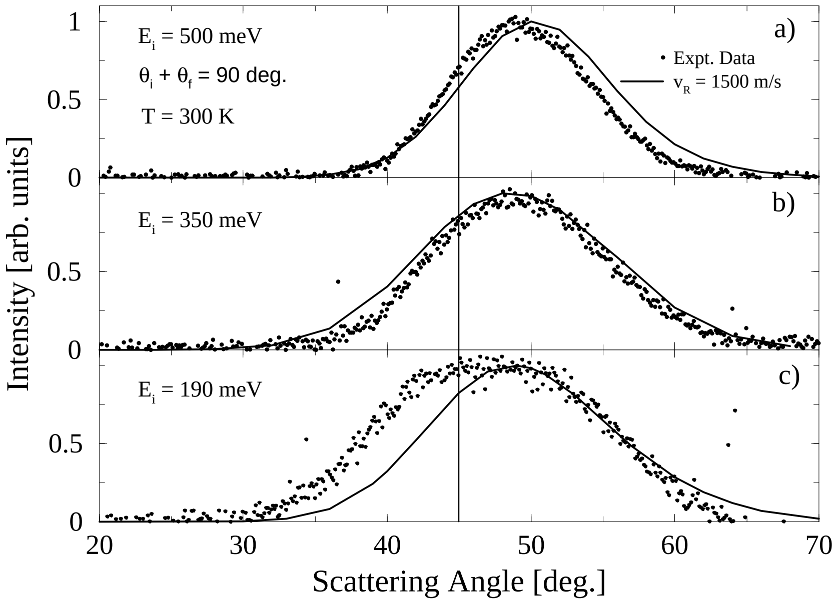
$$\omega_R \approx 10^{10}\, s^{-1}$$ Value is unimportant

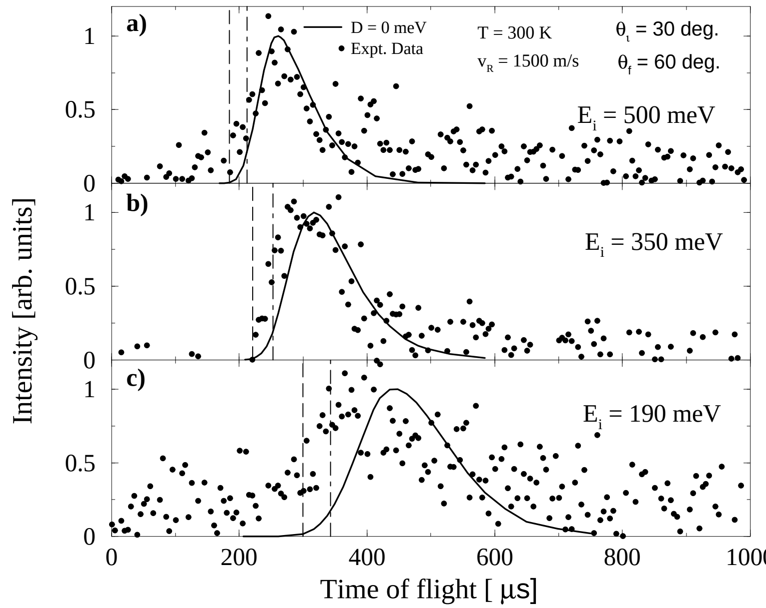
Physisorption potential well:

Square well of depth *D*

Averaging over molecular orientation

CH_4/LiF(001)



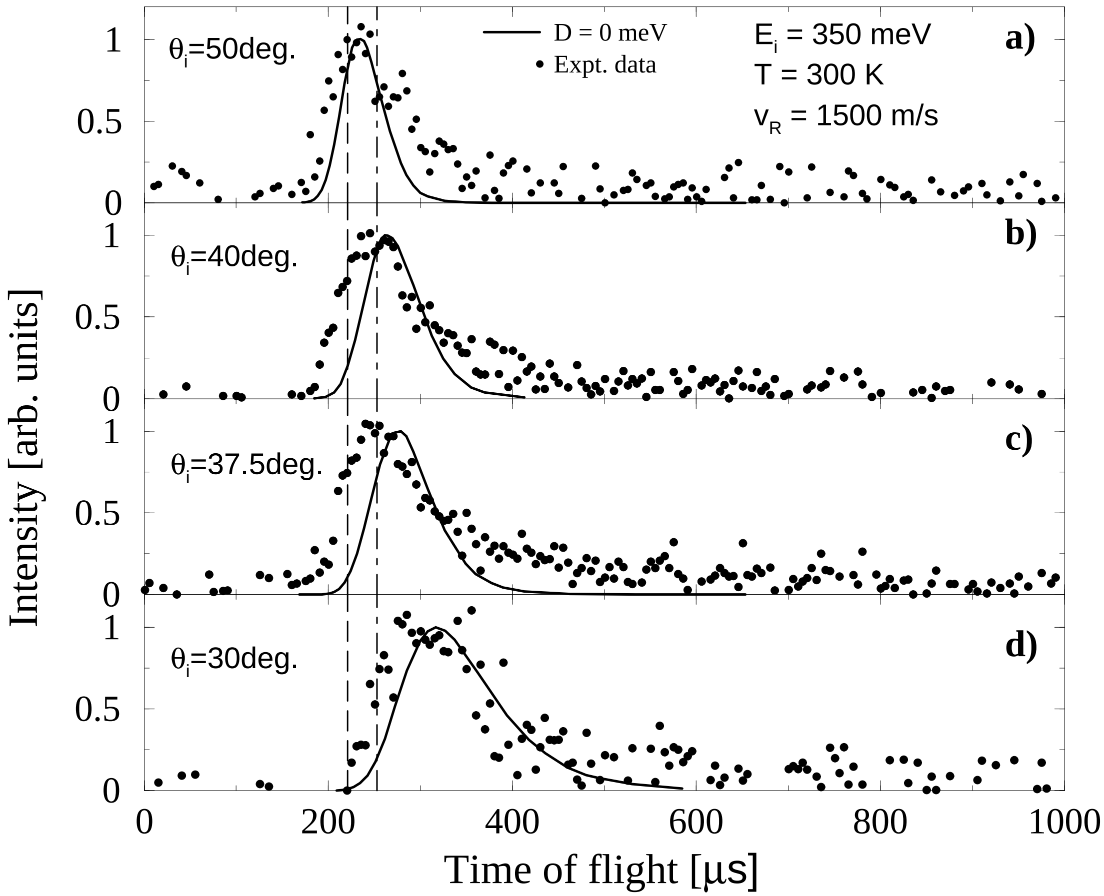


T. Kondo, T. Tomii, T. Hiraoka, T. Ikeuchi, S. Yagyu and S. Yamamoto, J. Chem. Phys. **112**, 9940 (2000).

T. Tomii, T. Kondo, T. Hiraoka, T. Ikeuchi, S. Yagyu and S. Yamamoto, J. Chem. Phys. **112**, 9052 (2000)

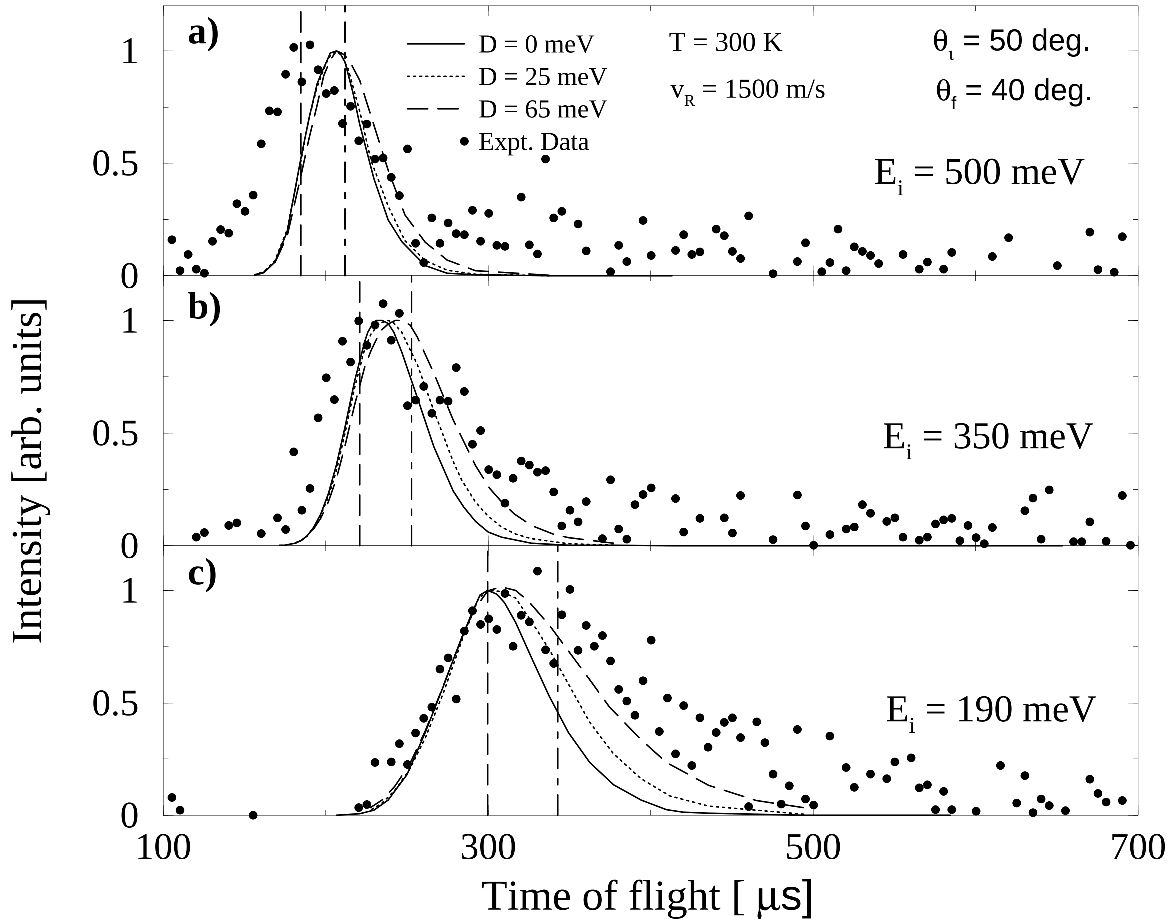
Calcs.: I. Moroz and J. R. Manson, PRB **69**, 205406 (2004).

CH_4/LiF(001)
Incident angle dependence



T. Tomii, T. Kondo, T. Hiraoka, T. Ikeuchi, S. Yagyu and S. Yamamoto, J. Chem. Phys. **112**, 9052 (2000)

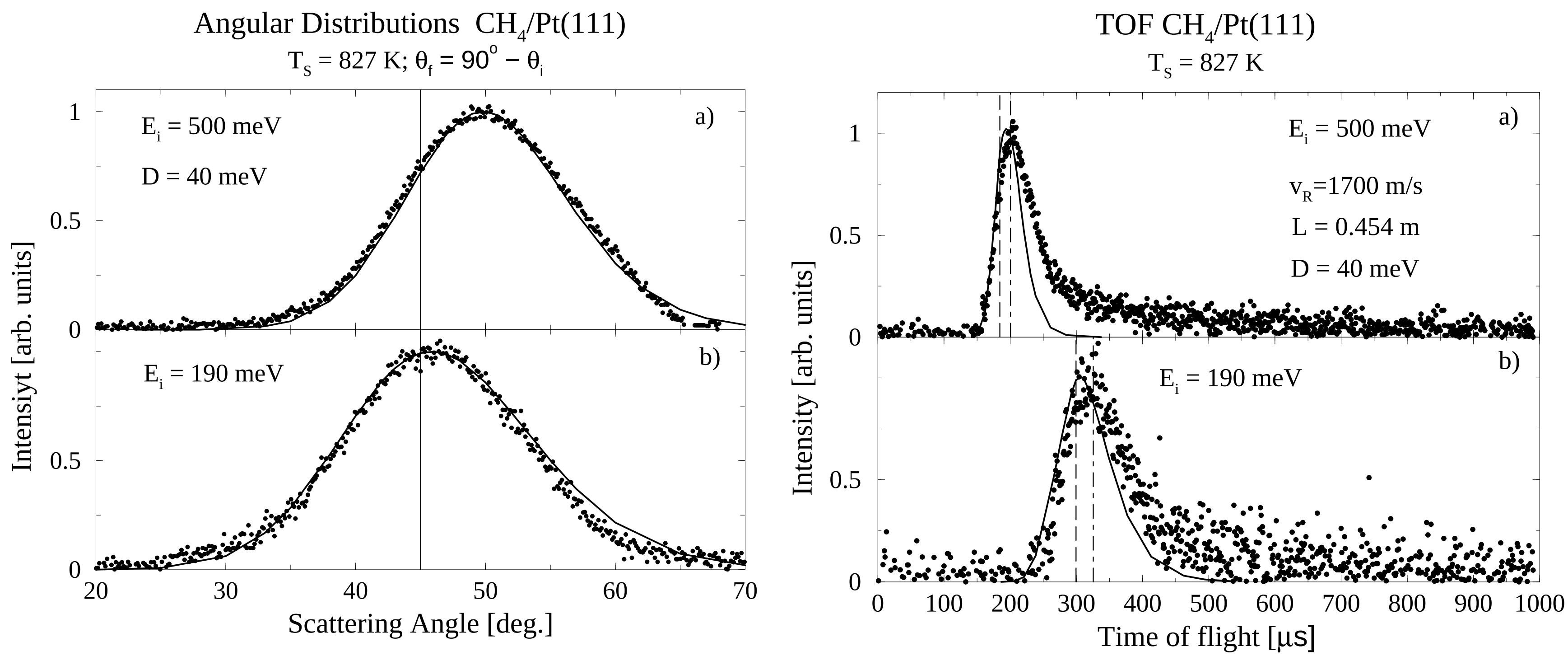
CH_4/LiF(001)
Physisorption potential well



T. Tomii, T. Kondo, T. Hiraoka, T. Ikeuchi, S. Yagyu and S. Yamamoto, J. Chem. Phys. **112**, 9052 (2000)

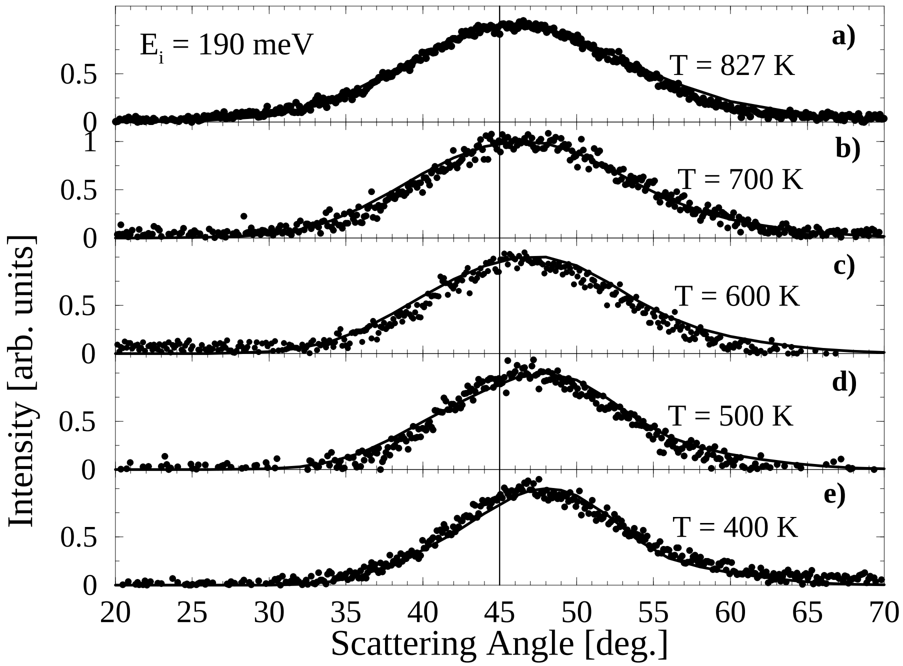
CH_4/Pt(111)
T_S = 827 K; E_i = 190 and 500 meV

$\theta_I = 45^0$

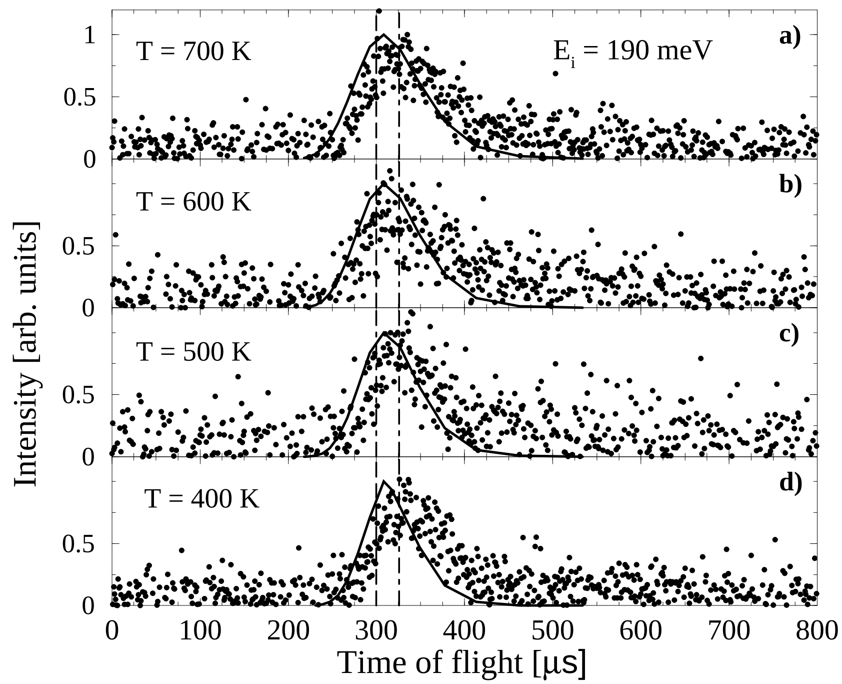


T. Kondo, T. Sasaki, S. Yamamoto, J. Chem. Phys. **116**, 7673 (2002)

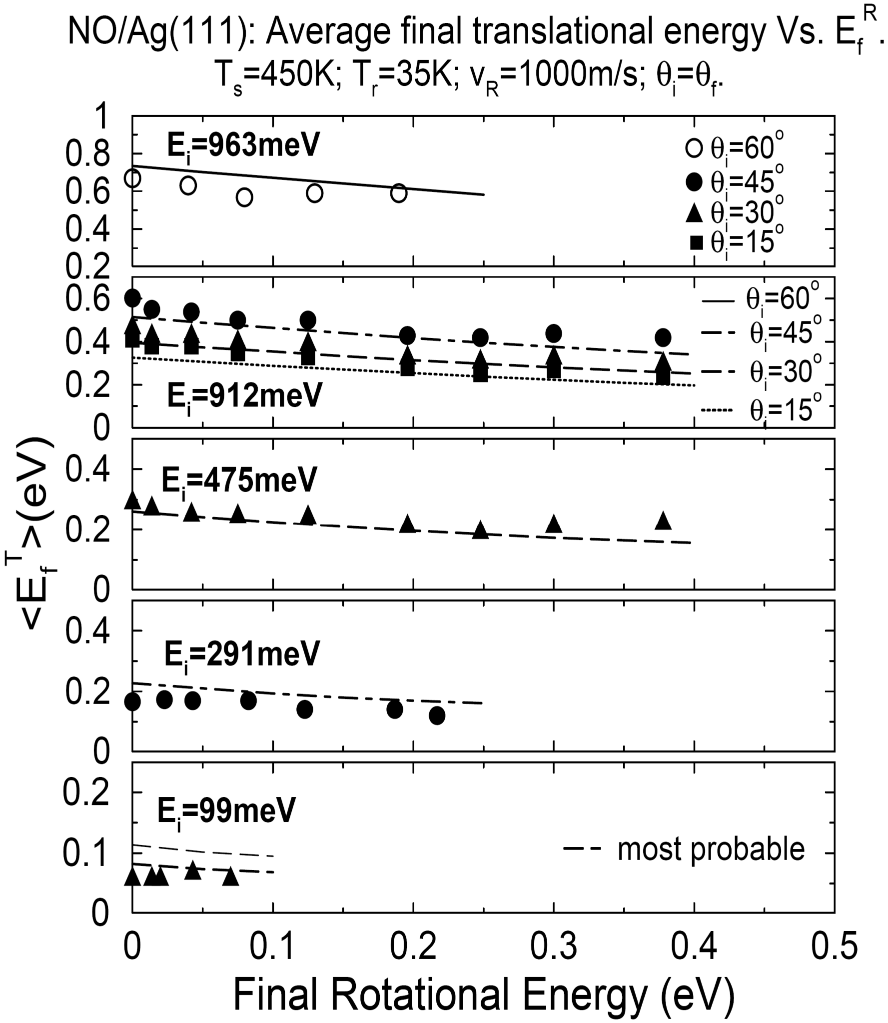
CH_4/Pt(111)

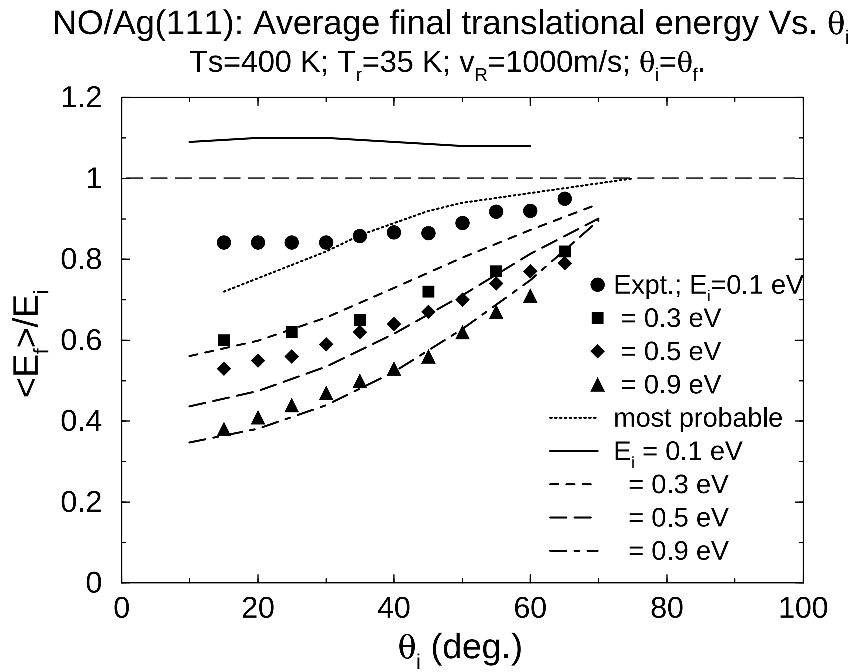


$\theta_i = 45^0$



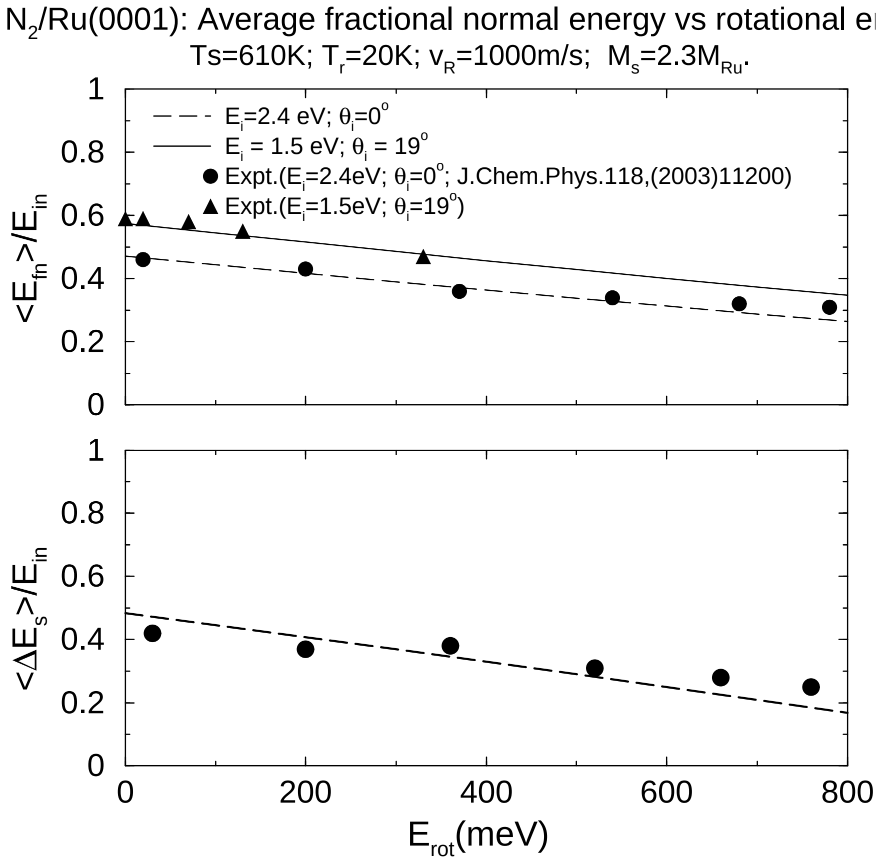
NO/Ag(111)

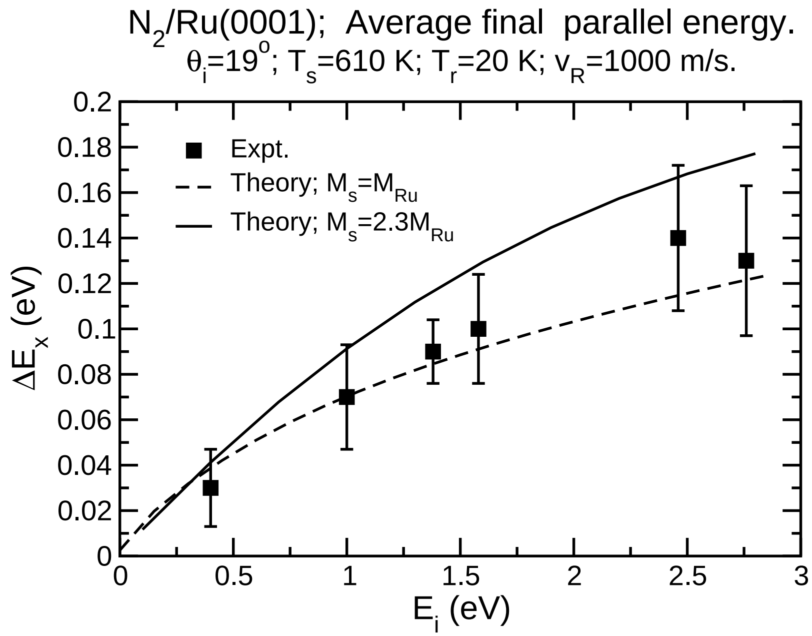




Data: C.T. Rettner, J. Kimman, and D.J. Auerbach, J.Chem.Phys. **94**,734(1991)

N_2/Ru(0001)



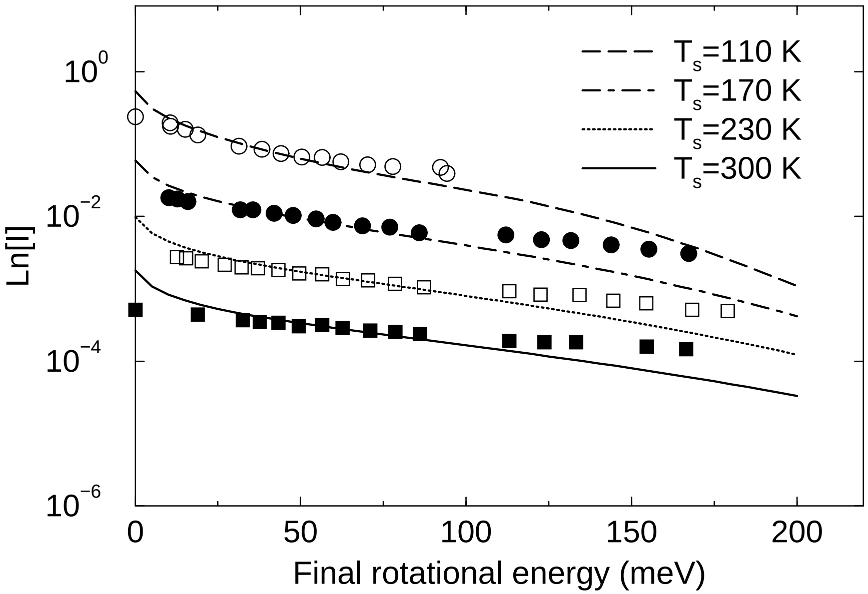


Expt.: H.Mortensen, E. Jensen, L. Diekhoener, A. Baurichter,
A. C. Luntz, and V. V. Petrunin, J. Chem. Phys. 118, 11200 (2003).

Data: H. Mortensen, E. Jensen, L. Diekhöner, A. Baurichter, A. C. Luntz and V. V. Petrunin, J. Chem. Phys. **118**, 11200 (2003).

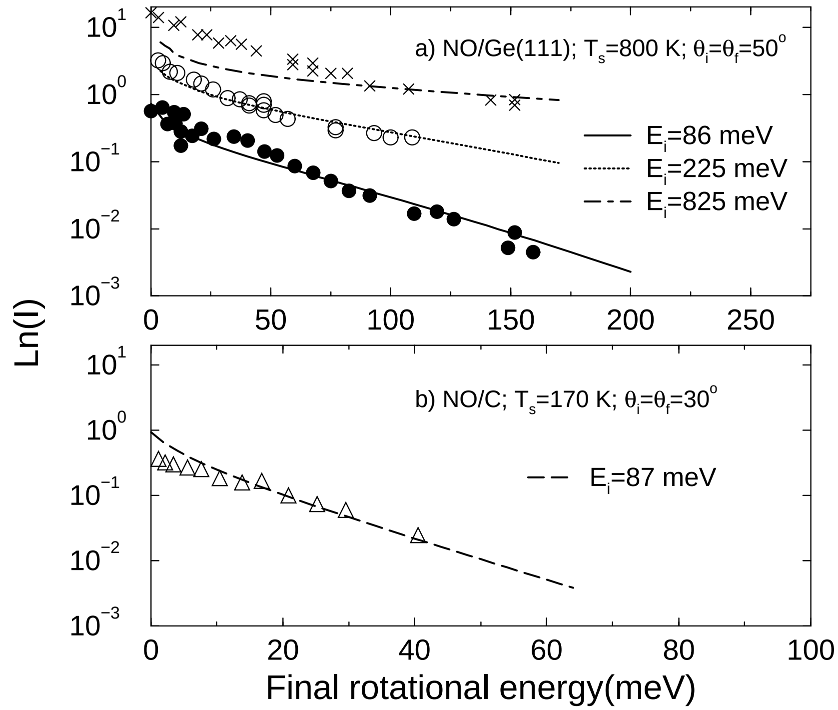
Molecular Rotational Excitation

NO/Pt: Rotational energy resolved intensity.
E_i = 352 meV; v_R = 1000 m/s; $\theta_i = \theta_f = 20^o$; T_r = 9 K.



M. K. Ainsworth, V. Fiorin, M. R. S. McCoustra and M. A. Chesters, Surf. Sci. **433-435**, 790 (1999).

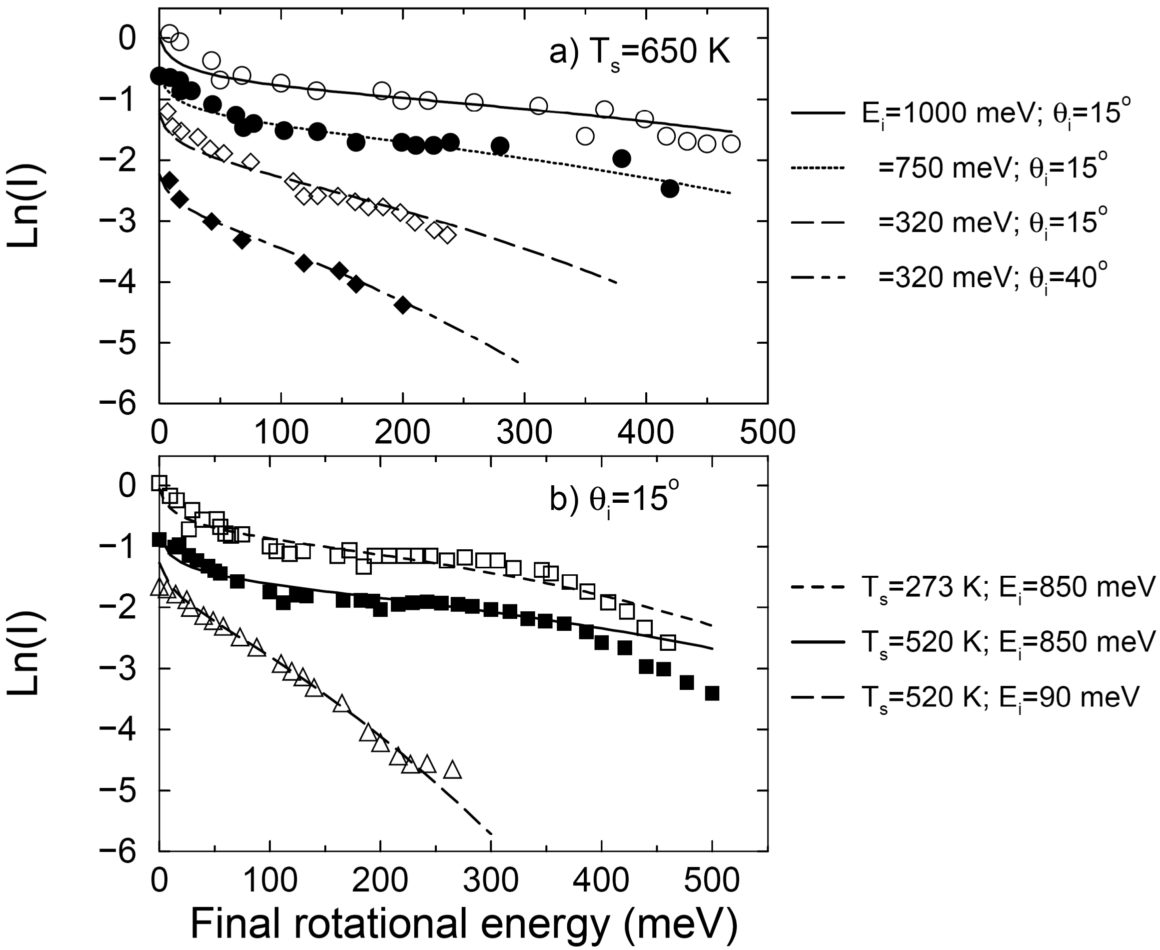
NO/Ge(111)/C: Rotational energy resolved intensity.
T_r=49 K; v_R=1000m/s.



A. Mödl, H. Robota, J. Segner, W. Vielhaber, M. C. Lin and G. Ertl, J. Chem. Phys. **83**, 4800 (1985); Ertl et al., Chem. Phys. Lett. **90**, 225 (1982).

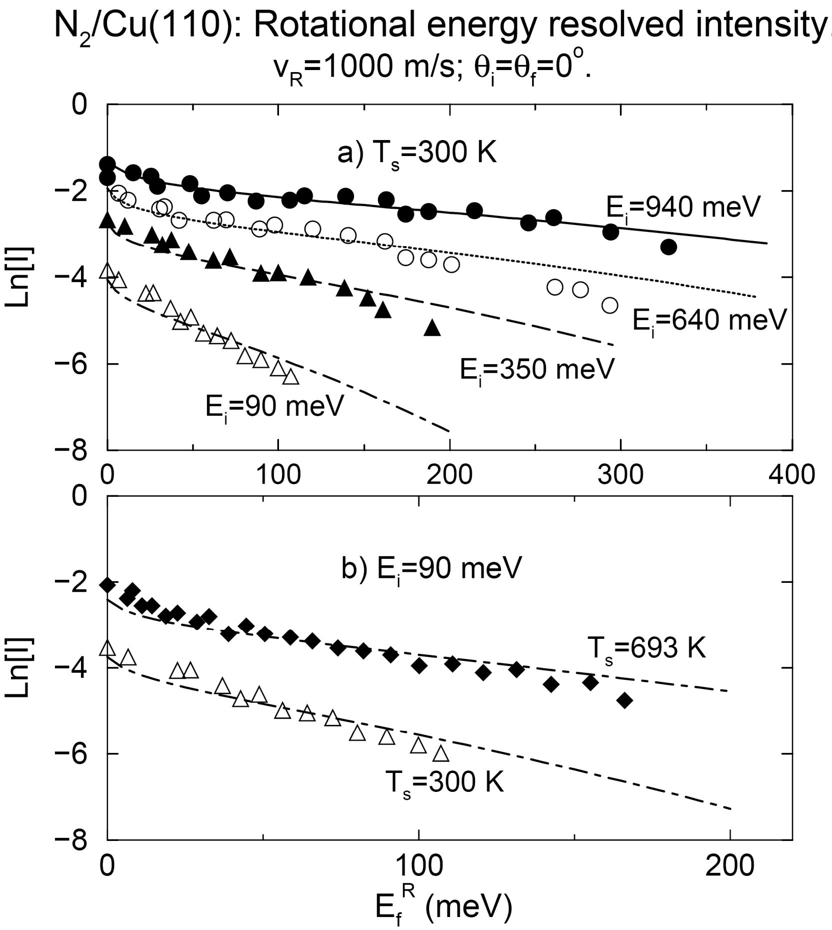
Molecular Rotational Excitation

NO/Ag(111): Final rotational energy resolved intensity.
T_r=35K; $\theta_i=\theta_f$; v_R=1000m/s.

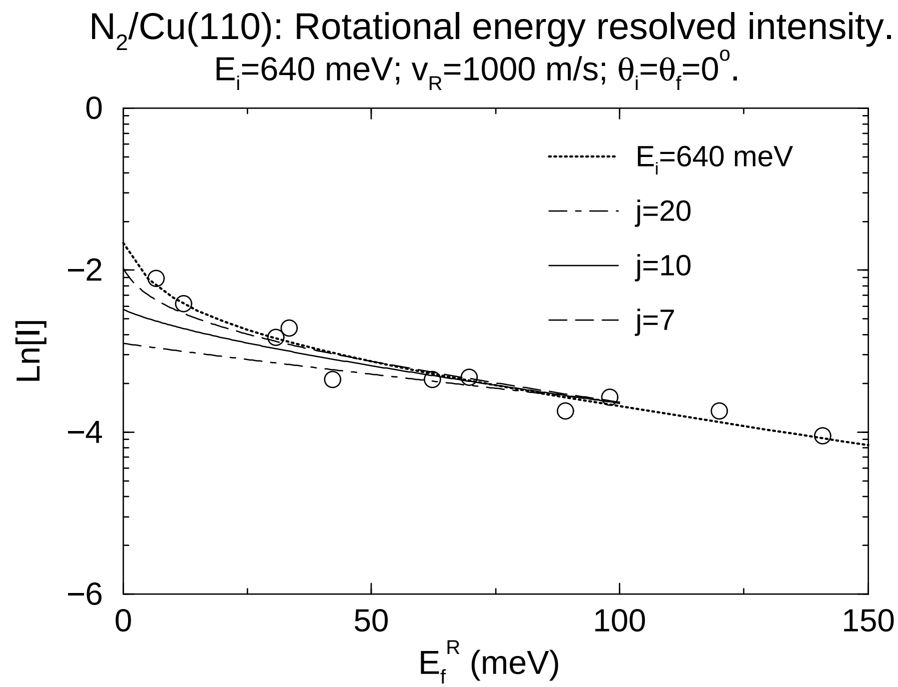


A. W. Kleyn,
B. A. C. Luntz and
D. J. Auerbach,
Phys. Rev. Lett. **47**, 1169 (1981).

C. T. Rettner,
J. Kimman and
D. J. Auerbach,
J. Chem. Phys. **94**, 734 (1991).

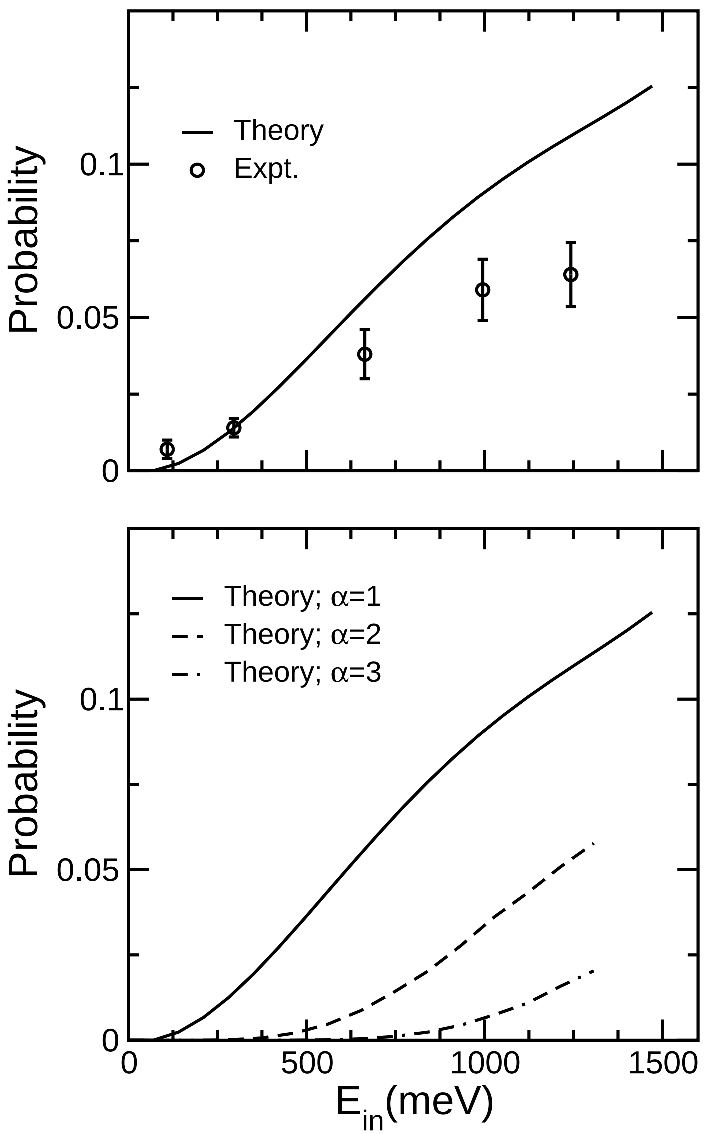


Effect of initial state rotational distribution on observed scattered rotational spectrum.



Jennifer L. Siders and G. O. Sitz, J. Chem. Phys. **101**, 6264 (1994).

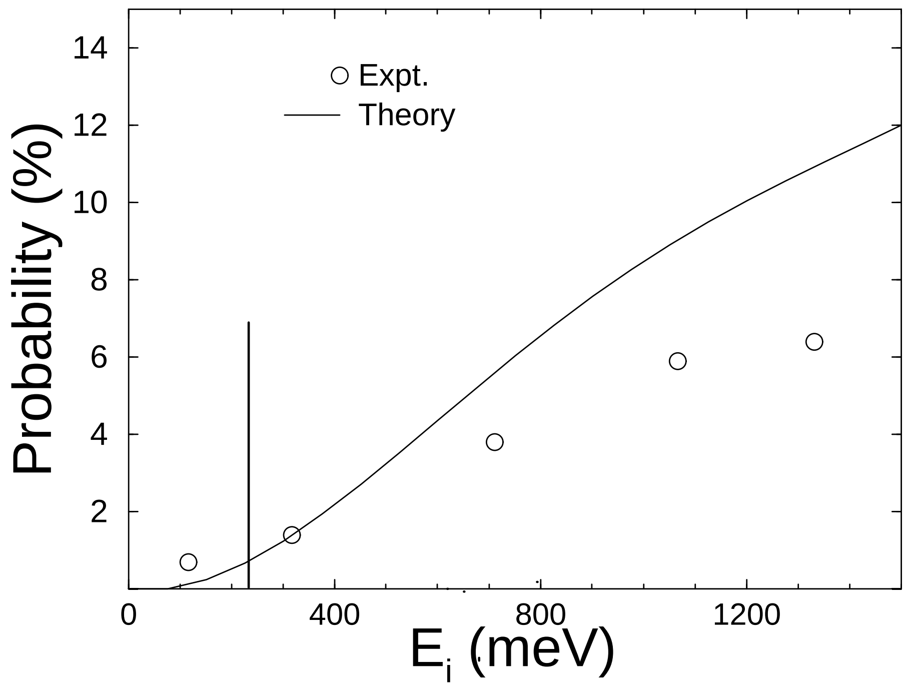
NO/Ag(111): Excitation probability vs E_{in}.
Ts=760K; T_r=35K; v_R=1000m/s; $\theta_i=\theta_f=15^o$



Molecular Internal Vibrational State Excitation

N-O *Stretch Mode*

NO/Ag(111): Excitation probability vs E_i.



Data: C. T. Rettner, F. Fabre, J. Kimman and D. J. Auerbach, Phys. Rev. Lett. **55**, 1904 (1985).
D. M. Newns, Surf. Sci. 171, 600 (1986).

Conclusions

- Classical Atom and Ion Scattering from Surfaces
- Theory of Molecule-Surface Scattering
  - Classical translation and rotation
  - Semiclassical treatment of internal modes
  - Correct angular and linear momentum conservation
- C_2H_2/LiF(001); CH_4/LiF(001); CH_4/Pt(111); O_2/Al(111); NO/Ge(111); NO/Ag(111); N_2/Ru(0001); N_2/Cu(110)
- Extensions: gas-surface interactions, adsorption-desorption, description of thermal energy transfer
- New Physical Information: Surface corrugation, Physisorption well depths, Rotational temperatures, Effective surface mass and collective effects, Surface segregation, Accommodation and energy transfer, Simple Baule approximations for energy losses are not accurate.
- Useful theory for describing molecule-surface scattering

CLEMSON UNIVERSITY

Judson Powers

Anil Kota

Fan Guoqing

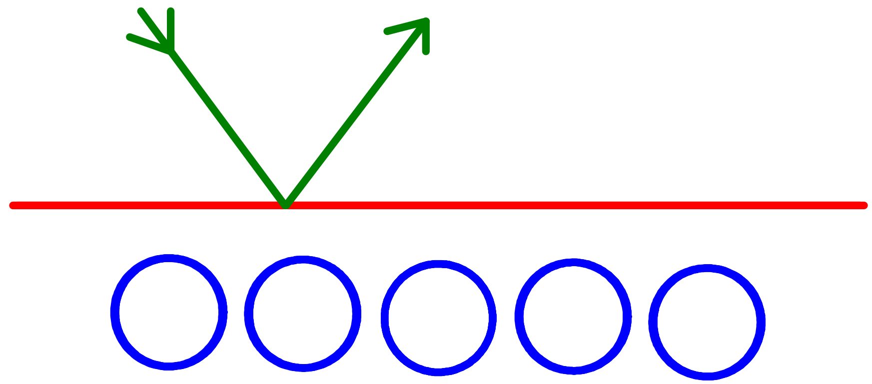
Jason Brown

Wayne Hayes

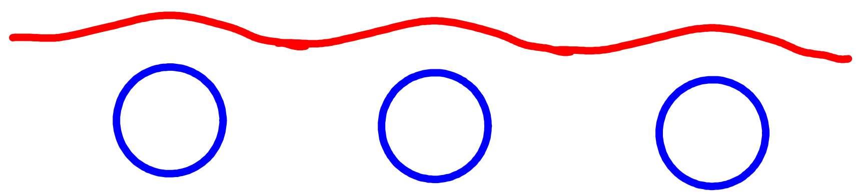
Iryna Moroz

Haile Ambaye

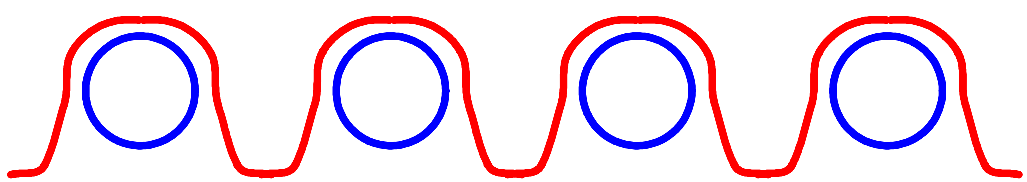
Flat surface potential



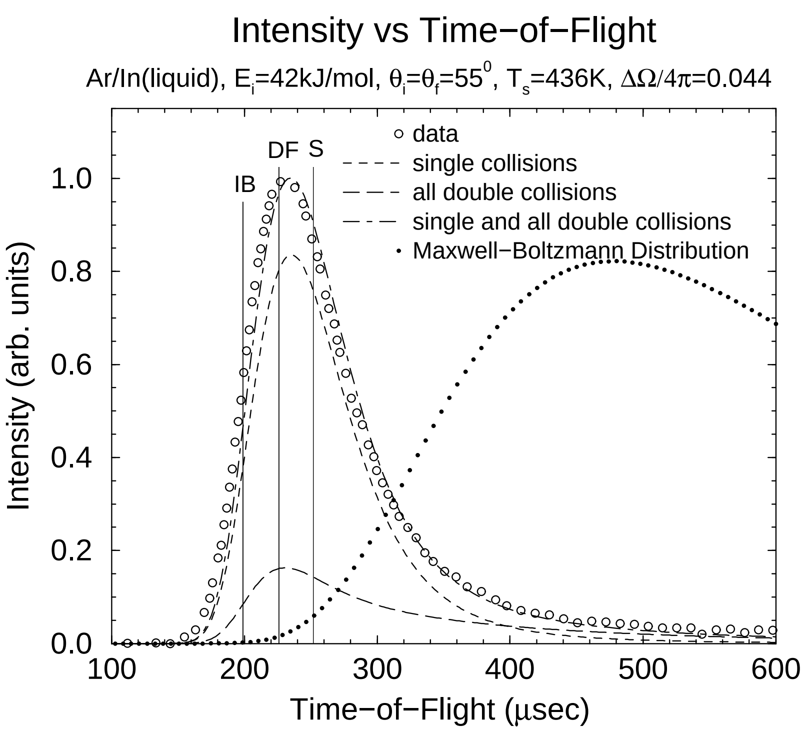
Weakly corrugated surface

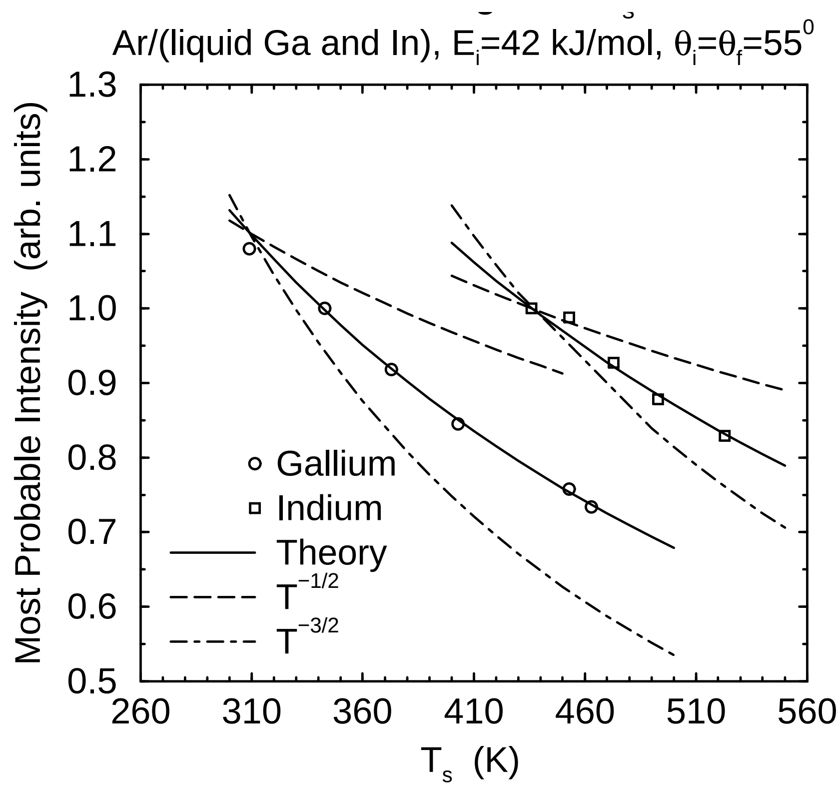


Strongly corrugated; discrete, isolated atoms



Temperature Dependence and Surface Corrugation



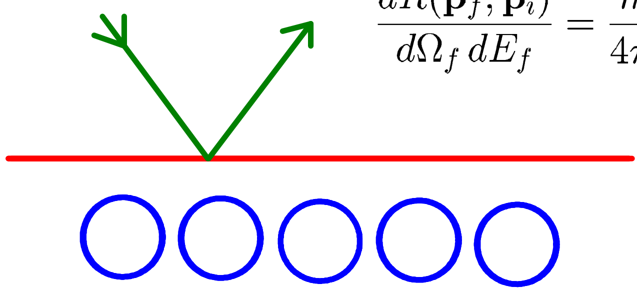


Data: W. Ronk, D. Kowalski, M. Manning, and G. Nathanson, JCP **104**, 4842 (1996).

Determination of Surface Corrugation

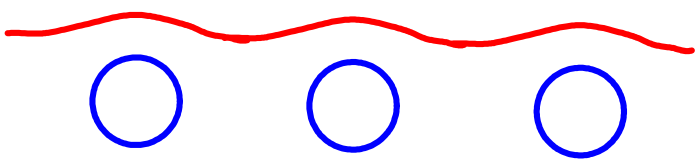
Flat surface potential

$$\frac{dR(\mathbf{p}_f, \mathbf{p}_i)}{d\Omega_f \, dE_f} = \frac{m^2 \, |\mathbf{p}_f|}{4\pi^3 \hbar^5 p_{iz}} \frac{v_R^2}{S_{u.c.}} \, |\tau_{fi}|^2 \left(\frac{\pi}{\Delta E_0 k_B T_S}\right)^{3/2} \exp\left\{-\frac{(E_f - E_i + \Delta E_0)^2 + 2v_R^2 \mathbf{P}^2}{4 k_B T_S \Delta E_0}\right\}$$



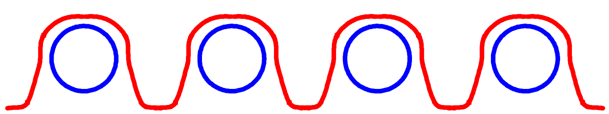
A simple measure of temperature dependence of most-probable intensities, when compared with classical theories, produces mean square corrugation heights.

Weakly corrugated surface



Examples: Ar/Ga, E_i=42 kJ/mol; $h_{RMS} \approx 0.5$ Å
Ar/Ga, E_i=95 kJ/mol; $h_{RMS} \approx 0.8$ Å
Ar/In, Ei=42 kJ/mol; $h_{RMS} \approx 0.3$ Å
Ar/In, Ei=95 kJ/mol; $h_{RMS} \approx 0.5$ Å
$\Theta_f = \theta_i = 55^0$

Strongly corrugated; discrete, isolated atoms



$$\frac{dR^{(1)}(\mathbf{p}_f, \mathbf{p}_i)}{d\Omega_f dE_f} = \frac{m^2 |\mathbf{p}_f|}{8\pi^3 \hbar^4 p_{iz}} |\tau_{fi}|^2 \left(\frac{\pi}{\Delta E_0 k_B T_S}\right)^{1/2} \exp\left\{-\frac{(\Delta E + \Delta E_0)^2}{4 k_B T_S \Delta E_0}\right\}$$

Classical Scattering Intensity: General Properties

$$\frac{dR^{(1)}(\mathbf{p}_f,\mathbf{p}_i)}{d\Omega_f dE_f} = \frac{m^2|\mathbf{p}_f|}{8\pi^3\hbar^4 p_{iz}}|\tau_{fi}|^2\left(\frac{\pi}{\Delta E_0 k_B T_S}\right)^{1/2} \exp\left\{-\frac{(\Delta E+\Delta E_0)^2}{4k_\mathrm{B}T_\mathrm{S}\Delta E_0}\right\}$$

$$\frac{dR(\mathbf{p}_f,\mathbf{p}_i)}{d\Omega_f\, dE_f} = \frac{m^2\,|\mathbf{p}_f|}{4\pi^3\hbar^5 p_{iz}}\frac{v_R^2}{S_{u.c.}}\;|\tau_{fi}|^2\;\left(\frac{\pi}{\Delta E_0 k_B T_S}\right)^{3/2} \exp\left\{-\frac{(E_f-E_i+\Delta E_0)^2+2v_R^2\mathbf{P}^2}{4k_B T_S\Delta E_0}\right\}$$

$$\bar{E}_f = f(\theta)E_i \qquad\qquad \theta = \pi - \theta_f - \theta_i$$

$$f(\theta) = \left(\frac{\sqrt{1-\mu^2\sin^2\theta}+\mu\cos\theta}{1+\mu}\right)^2 \qquad\qquad \mu = m/M_c$$

$$\langle\Delta E^2\rangle \approx 2g(\theta)E_i k_B T_S \qquad\qquad g(\theta) = \frac{g_{TA}(\theta)}{(1+\mu-\mu\cos\theta/\sqrt{f(\theta)})}$$

$$g_{TA}(\theta) = \mu(1+f(\theta)-2\sqrt{f(\theta)}\cos\theta)$$

$$I_\mathrm{MAX} \propto \frac{1}{(k_\mathrm{B}T_S\Delta E_0)^{1/2}} \qquad\qquad \Delta E_0 = (\mathbf{p}_f-\mathbf{p}_i)^2/2M_c$$

$$\approx g_\mathrm{TA}(\theta)E_i$$

$$I_\mathrm{MAX} \propto \frac{1}{(k_B T_s\Delta E_0)^{3/2}}$$

$$\frac{dR^{(1)}(\mathbf{p}_f,\mathbf{p}_i)}{d\Omega_f dE_f} = \frac{m^2|\mathbf{p}_f|}{8\pi^3\hbar^4 p_{iz}}|\tau_{fi}|^2\left(\frac{\pi}{\Delta E_0 k_B T_S}\right)^{1/2} \times \exp\left\{-\frac{(\Delta E+\Delta E_0)^2}{4k_\mathrm{B}T_\mathrm{S}\Delta E_0}\right\},$$

Multiple scattering

$$\frac{dR^{(2)}(\mathbf{p}_f,\mathbf{p}_i)}{d\Omega_f dE_f} = \sum_{n=1}^{N}\int_0^\infty dE_q \int_{\Delta\Omega_n} d\Omega_q \frac{dR^{(1)}(\mathbf{p}_f,\mathbf{p}_q)}{d\Omega_f dE_f}\frac{dR^{(1)}(\mathbf{p}_q,\mathbf{p}_i)}{d\Omega_q dE_q}$$

General properties of the single collision classical scattering intensity

$$\bar{E}_f = f(\theta)E_i \qquad f(\theta) = \left(\frac{\sqrt{1-\mu^2\sin^2\theta}+\mu\cos\theta}{1+\mu}\right)^2 \qquad \mu = m/M_c$$

$$\langle\Delta E^2\rangle \approx 2g(\theta)E_i k_B T_S$$

$$I_{\mathrm{MAX}} \propto \frac{1}{(k_\mathrm{B}T_S\Delta E_0)^{1/2}}$$

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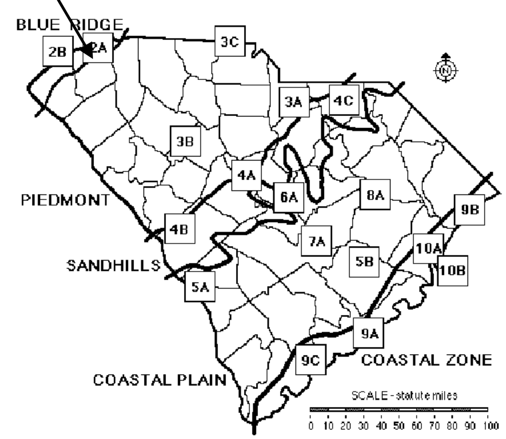
South Carolina




Welcomes You To Death Valley

General properties of the classical scattering intensity

$$\frac{dR^{(1)}(\mathbf{p}_f,\mathbf{p}_i)}{d\Omega_f dE_f} = \frac{m^2|\mathbf{p}_f|}{8\pi^3\hbar^4 p_{iz}}|\tau_{fi}|^2\left(\frac{\pi}{\Delta E_0 k_B T_S}\right)^{1/2}\exp\left\{-\frac{(\Delta E+\Delta E_0)^2}{4k_\mathrm{B}T_\mathrm{S}\Delta E_0}\right\}$$

$$\bar{E}_f = f(\theta)E_i \qquad \theta = \pi - \theta_f - \theta_i$$

$$f(\theta) = \left(\frac{\sqrt{1-\mu^2\sin^2\theta}+\mu\cos\theta}{1+\mu}\right)^2 \qquad \mu = m/M_c$$

$$\langle\Delta E^2\rangle \approx 2g(\theta)E_i k_B T_S \qquad g(\theta) = \frac{g_{TA}(\theta)}{(1+\mu-\mu\cos\theta/\sqrt{f(\theta)})}$$

$$g_{TA}(\theta) = \mu(1+f(\theta)-2\sqrt{f(\theta)}\cos\theta)$$

$$I_\mathrm{MAX} \propto \frac{1}{(k_\mathrm{B}T_S\Delta E_0)^{1/2}} \qquad \Delta E_0 = (\mathbf{p}_f-\mathbf{p}_i)^2/2M_c \approx g_\mathrm{TA}(\theta)E_i$$

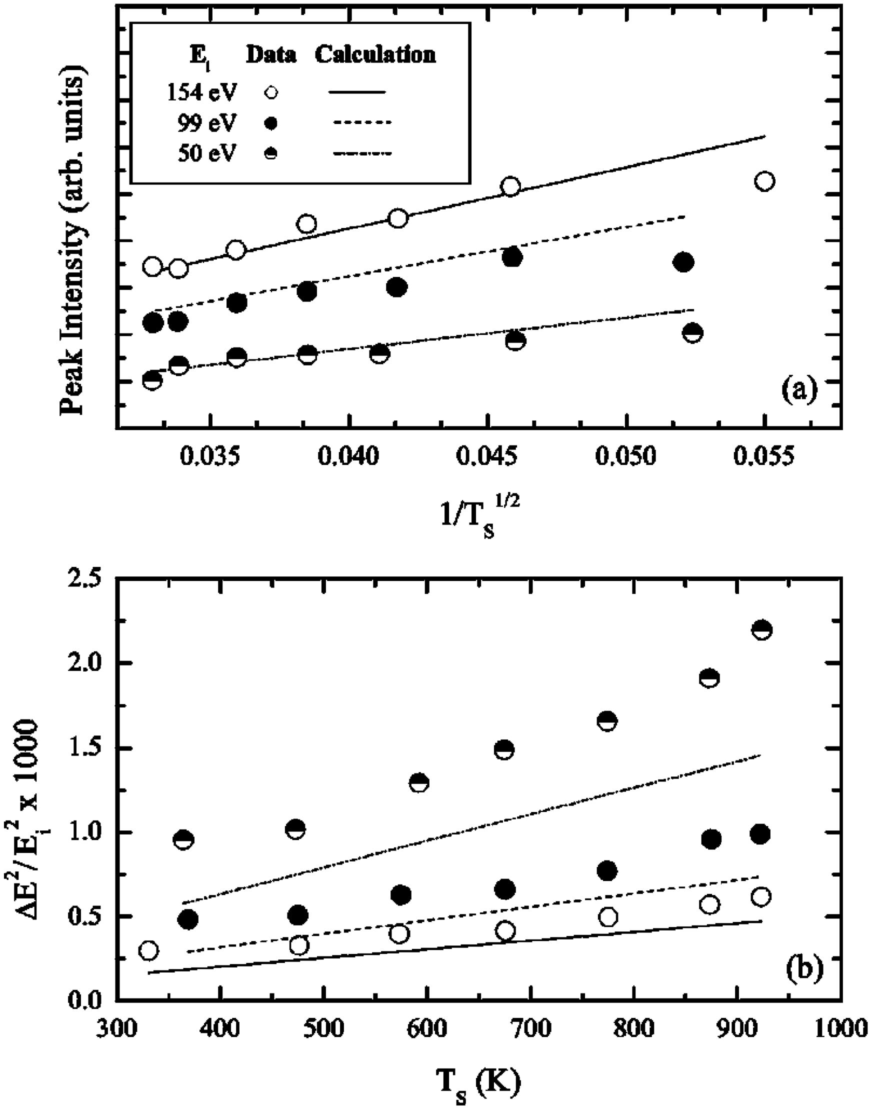
$$I_\mathrm{MAX} \propto \frac{1}{(k_B T_s\Delta E_0)^{3/2}}$$

Single scattering trajectory

$$\frac{dR^{(1)}(\mathbf{p}_f,\mathbf{p}_i)}{d\Omega_f dE_f} = \frac{m^2|\mathbf{p}_f|}{8\pi^3\hbar^4 p_{iz}}|\tau_{fi}|^2\left(\frac{\pi}{\Delta E_0 k_B T_S}\right)^{1/2} \times\exp\left\{-\frac{(\Delta E+\Delta E_0)^2}{4k_\mathrm{B}T_\mathrm{S}\Delta E_0}\right\},$$

$$I_\mathrm{MAX} \propto \frac{1}{(k_\mathrm{B}T_S\Delta E_0)^{1/2}}$$

$$\langle\Delta E^2\rangle \approx 2g(\theta)E_i k_B T_S$$



Correlation speed v_R

$$\frac{1}{v_R^2} = \frac{1}{k_B T_S} \sum_{\alpha=1}^{3} \sum_{\beta=1}^{3} \hat{k}_\alpha \hat{k}_\beta \sum_{\vec{Q},\nu} \frac{\hbar}{N\,\omega_\nu(\vec{Q})} e_\alpha(\vec{Q},\nu)\, e_\beta(\vec{Q},\nu)[2n(\omega_\nu(\vec{Q}))+1](\vec{Q}\cdot\hat{\vec{R}})^2$$

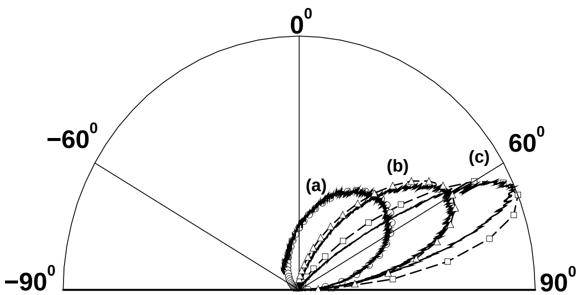
$e_\beta(\vec{Q},\nu)$ Phonon mode polarization vector

$\vec{k} = \vec{k}_f - \vec{k}_i$ Momentum transfer

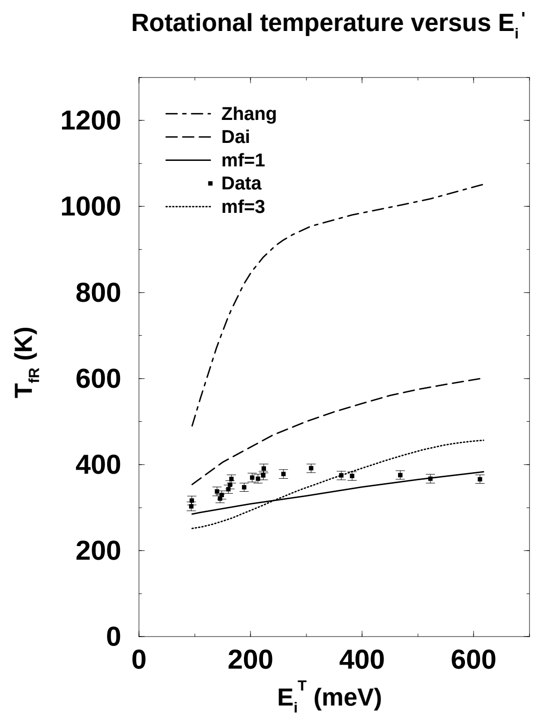
$$n(\omega) = \frac{1}{e^{\hbar\omega/k_B T_S} - 1}$$

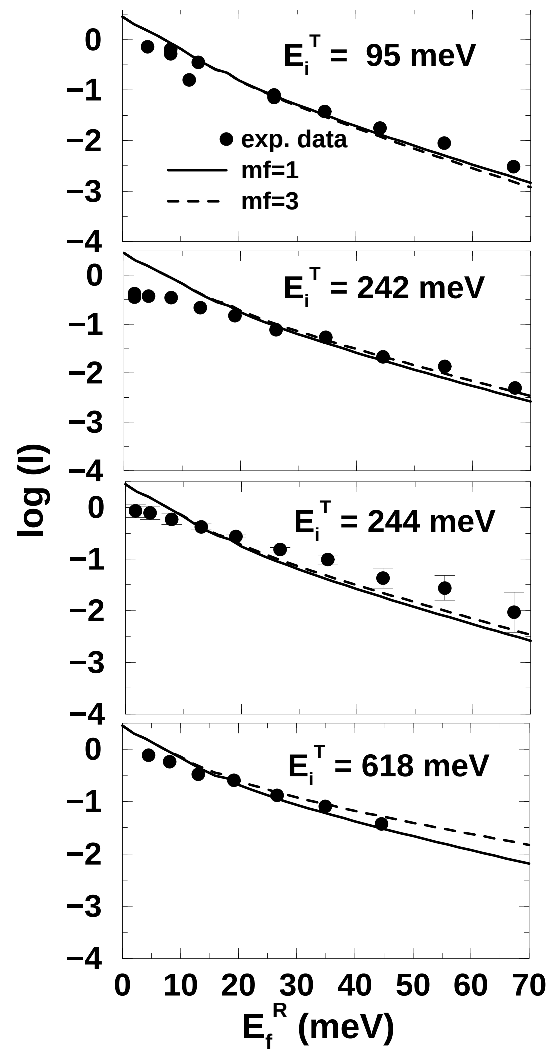
$$\hat{R} = \frac{\vec{R}}{R}$$

C_2H_2/LiF(001)



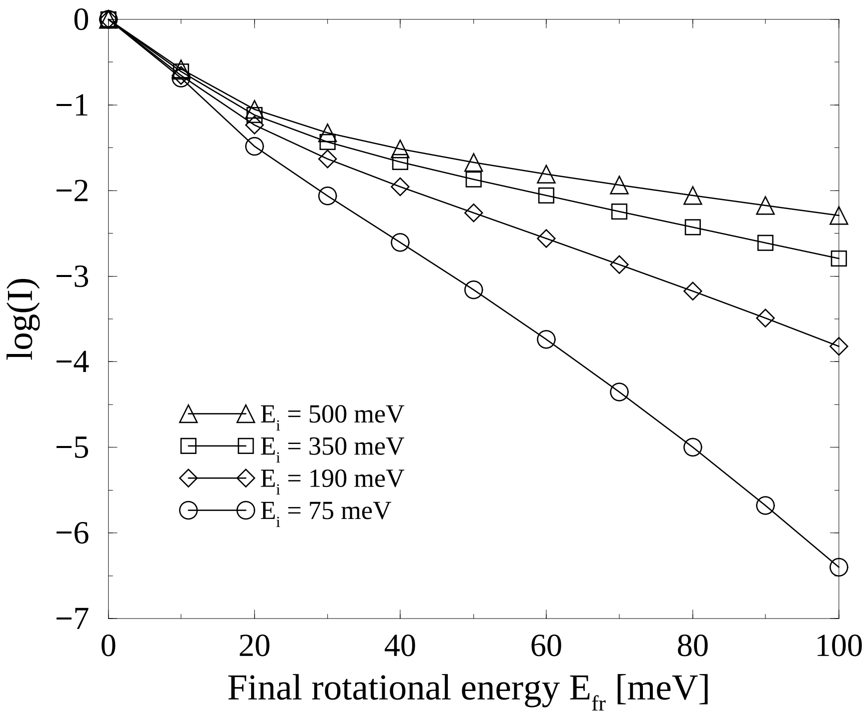
Ei=110 (a), 275 (b) and 618 meV (c).

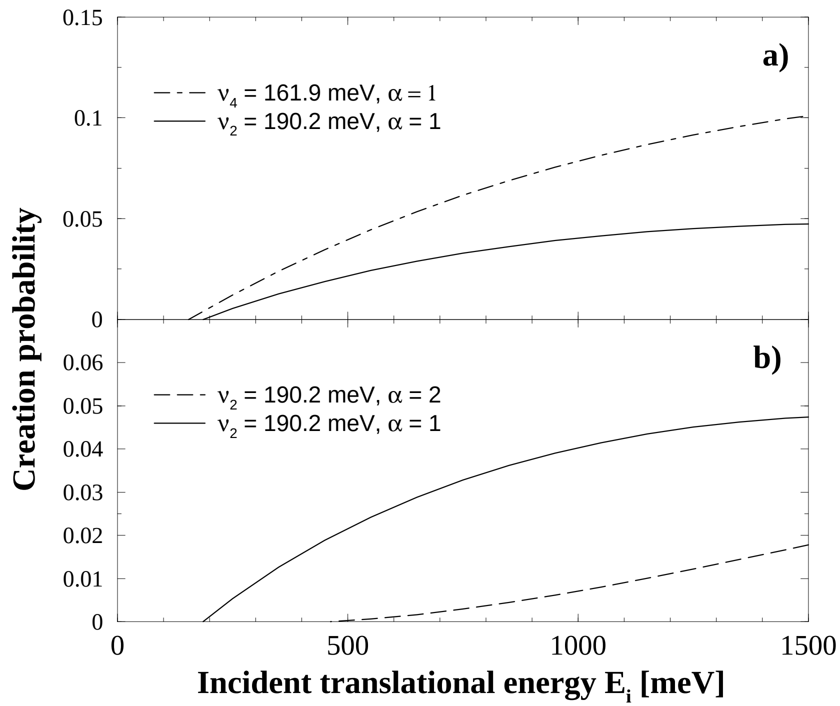




Expt.: T. W. Francisco, N. Camilone and R. E. Miller, Phys. Rev. Lett. **77**, 1402 (1996).
Theory: Ileana Iftimia and J. R. Manson, Phys. Rev. Lett. **87**, 093201 (2001).

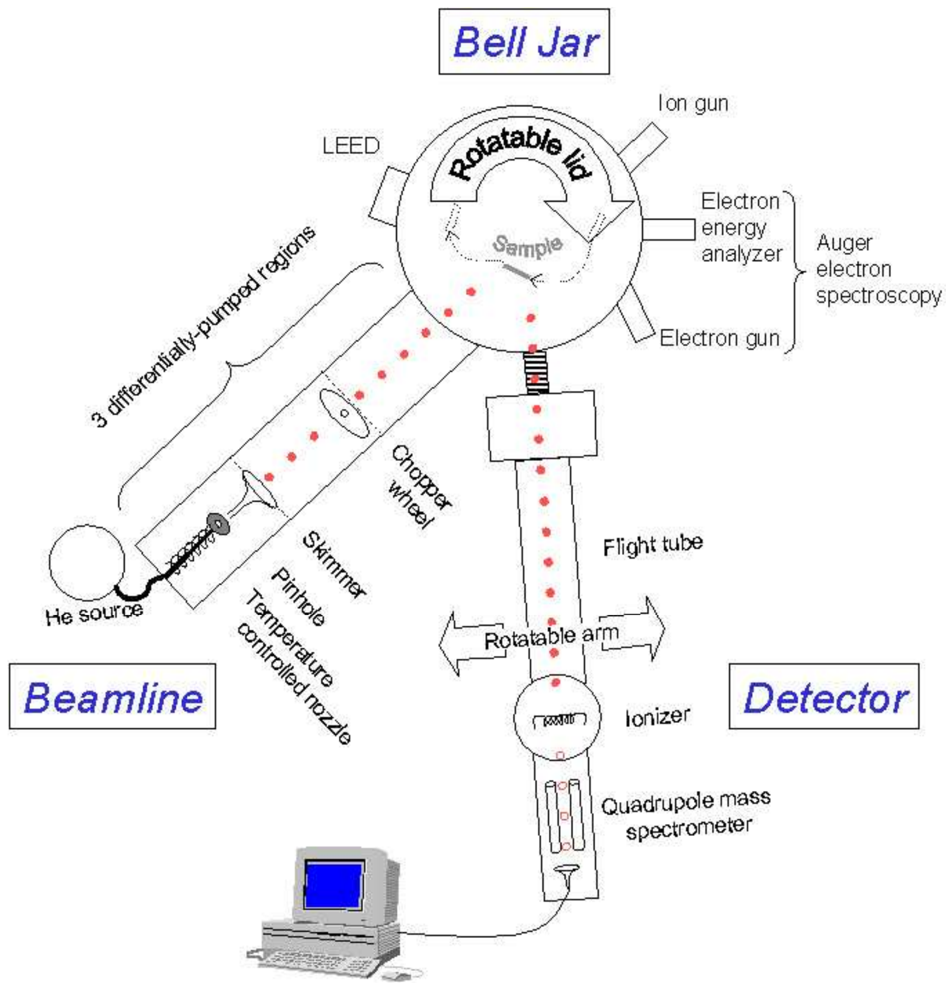
CH_4/LiF(001)
Rotation and Internal Mode Excitation





Effective Rotational Temperature

E_i = 75 meV, $T_{R\text{-effective}}$ = 212 K (Miller et al. $T_{R\text{-expt}}$ = 240 K)



Molecular Beam-Surface Scattering Apparatus
Steve Sibener, University of Chicago