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SMR. 628 - 19

Research Workshop in Condensed Matter, Atomic and Molecular Physics (22 June - 11 September 1992)

Working Party on: "Energy Transfer in Interactions with Surfaces and Adsorbates" (31 August - 11 September 1992)

"Vibrational Interactions at Surfaces"

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Vibrational Interactions at Surfaces

David Langreth

Collaborators:

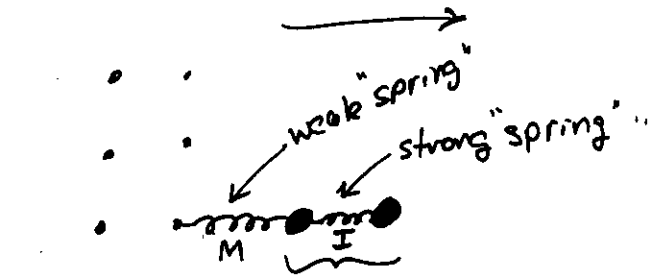
Kieron Burke

Mats Persson

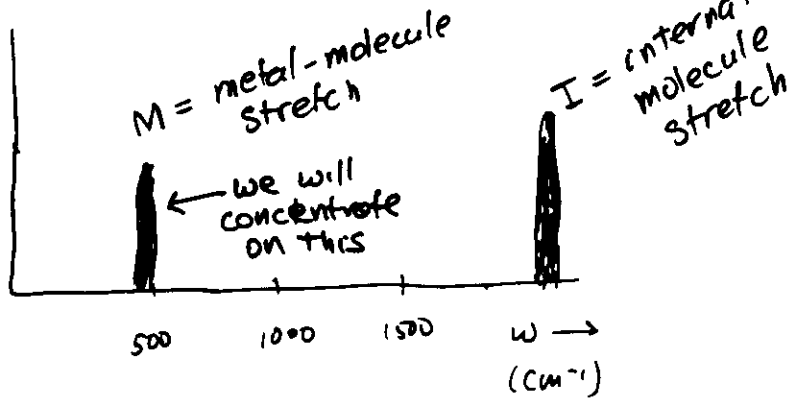
Zhenyu Zhang

More specific title:

Adsorbate vibrational line shapes due to vibrational interactions at Surfaces

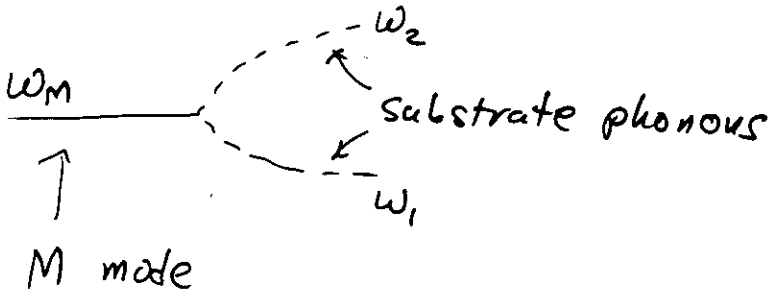


Measure dipole response to E:



Lineshape of metal-molecule (M) mode

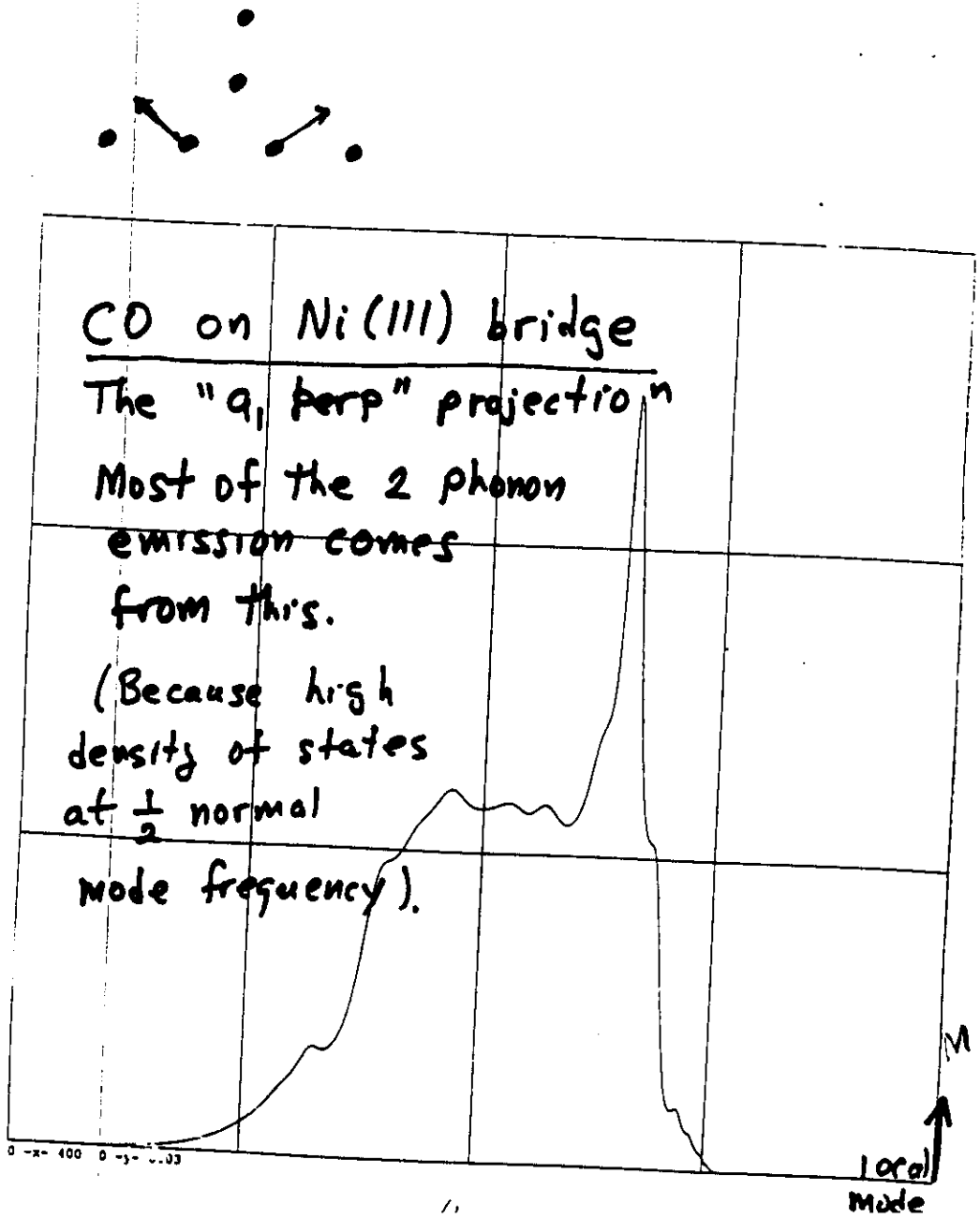
1. Why multi phonon emission + adsorption typically doesn't give much contribution



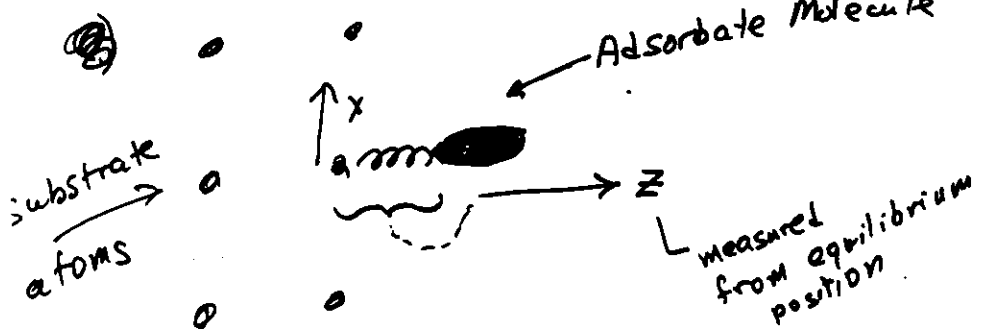
Must conserve energy:

$$\omega_{M1} = \omega_1 + \omega_2$$

But surface phonon projected spectral density dominated by peaks (zone boundary modes), which usually don't come in the right place for energy conservation.



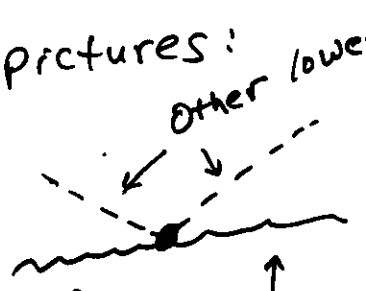
Dephasing



$$H_{int} = K z^2 x^2$$

Two pictures:

a)



$$\text{width} \propto \int \underbrace{n(n+1)}_{\text{Planck distribution}} K^2 \underbrace{\rho^2(\omega)}_{\text{proj. density of states}} d\omega \qquad \text{functions for phonons (here)}$$

$$n = \frac{1}{e^{\beta\omega} - 1}$$

$$\rho(\omega) \sim \frac{\gamma}{(\omega-\omega_0)^2+\gamma^2}$$

$$\Rightarrow \text{width} \propto \frac{n(n+1)K^2}{\gamma}$$

Note: peaky spectrum favors dephasing

This is the weak coupling limit.

b) $$H = \frac{p^2}{2\mu} + \frac{1}{2}\mu\Omega^2 z^2 + K z^2 x^2 + \cdots$$

$$= \frac{p^2}{2\mu} + \left(\frac{1}{2}\mu\Omega^2 + Kx^2\right) z^2 + \cdots$$

So changing x changes frequency of oscillator being measured.

Reduction factor for perpendicular modes + top. site adsorbate

1. B. Persson - discovery + estimate for light adsorbate

2. Langreth + M. Persson - generalization to arbitrary mass ratio. Exact inequality.

f sum rules a wave-function renormalization of substrate phonon intensity. Multiply by Z_s where

$$Z_s \leq \frac{M_{adsorbate}}{M_{adsorbate} + M_{substrate}} \frac{\omega_{max}^4}{\omega_m^4}$$

(ω_{max}: max substrate phonon frequency)

$<<1$ ← because of frequency ratio

For CO / Pt

$$Z_s \sim 10^{-3}$$

⟹ Can neglect effect of ⊥ modes

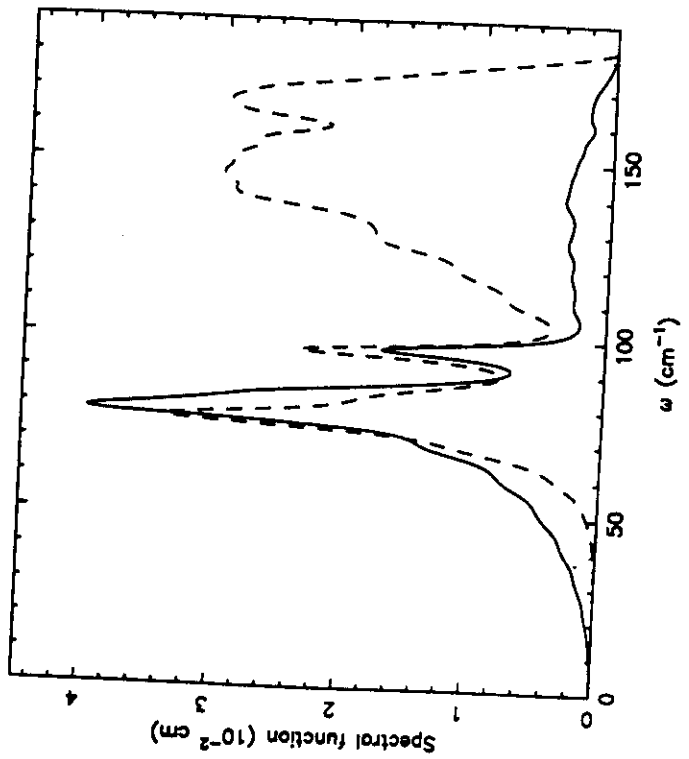


FIG. 2. The bare spectral function $(M_s\omega/\pi)I_{22}^{A_1\text{bare}}(\omega)$ vs. ω for Pt(111) (solid line) and this spectral function times the reduction factor $P(\omega)$ (dashed line) for CO/Pt(111). The dashed line has been multiplied by 1000.

Spectrum of ∥ modes for CO/Pt(111)

frustrated "translation"

ω_T

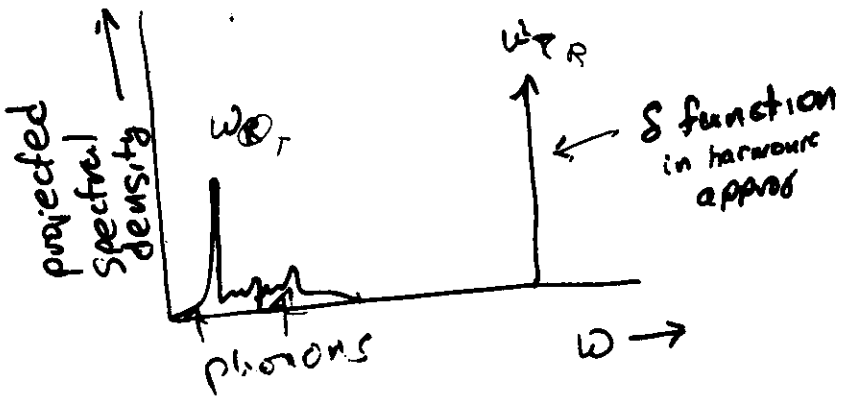
+

frustrated "rotation"

ω_R

+

phonons



CO / Pt(111)

Parallel vibrational projected on mode to be measured

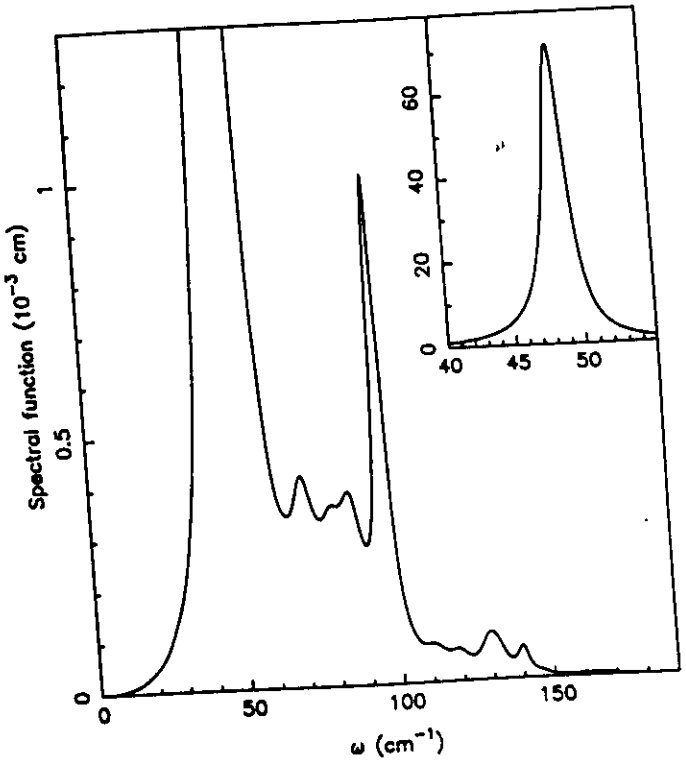
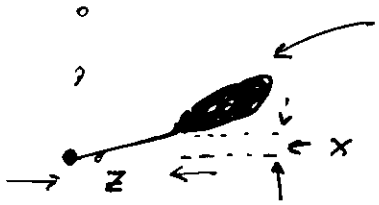


FIG. 5. The spectral function $(M,\omega/\pi)I_{\parallel}^{h}(\omega)$ vs. ω for CO/Pt(111). The inset shows the quasimode at about 49 cm^{-1}.

Solution of Biquadratic

dephasing model – Langreth + M. Persson
Phys. Rev. B 43, 1353 (1991)

Related model – Volokitin, Surf. Sci. 224, 355 (1989)



neglect stretching of internal bond

$k_I >> k_M$

or

$M_c \omega_M^2 << \mu \omega_I^2$

Fit spectral density of parallel modes to Lorentzian (for ω_T) + δ function (for ω_R)

$$\propto \frac{\gamma}{(\omega - \omega_T)^2 + (\gamma/2)^2} + 2\pi\delta(\omega - \omega_R)$$

For CO / Pt(111):

$\omega_T = 49\ cm^{-1}$

$\omega_R = 410\ cm^{-1}$

$\omega_M = 480\ cm^{-1}$

$\gamma = 1.9\ cm^{-1}$

$H_{int} = K x^2 z^2$

Assumption: $\omega_T << \omega_M$ then solution for all K

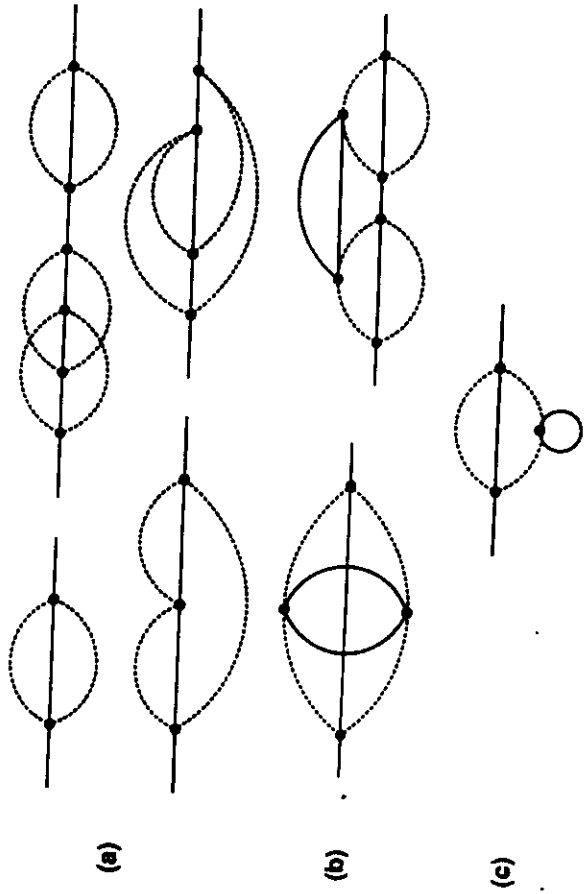
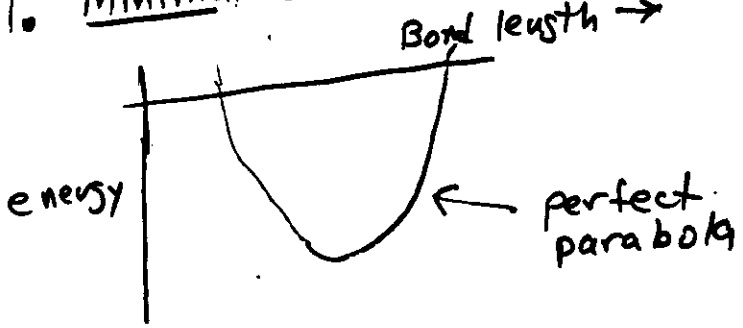


FIG. 4. Typical diagrams for the correlation function $L_\perp$. As in Fig. 1, the solid lines represent the correlation function $L_\perp^h$ while the dashed lines represent the correlation function $L_\parallel^h$. Diagrams of the type (a) must always be kept, while those of type (b) can be neglected if $\Omega > \omega_0$. For $\Omega > \omega_0$ diagrams of the type (c) do nothing more than give a shift in the phonon energies.

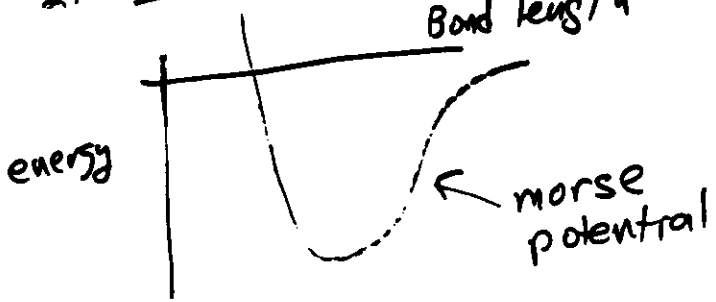
Models of anharmonic constant k:

Assume principle anharmonicity is in stretching the metal adsorbate bond, since the angle bending forces are much weaker.

1. Minimal anharmonicity model:



2. Morse model



Note:

$K_{morse} >> K_{minimal}$ (factor of 10)

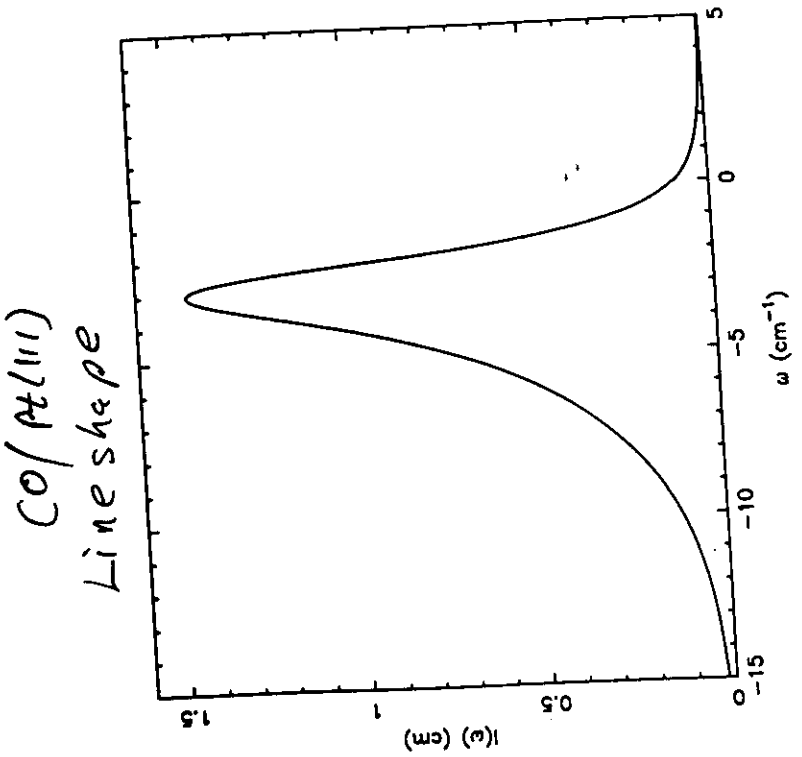
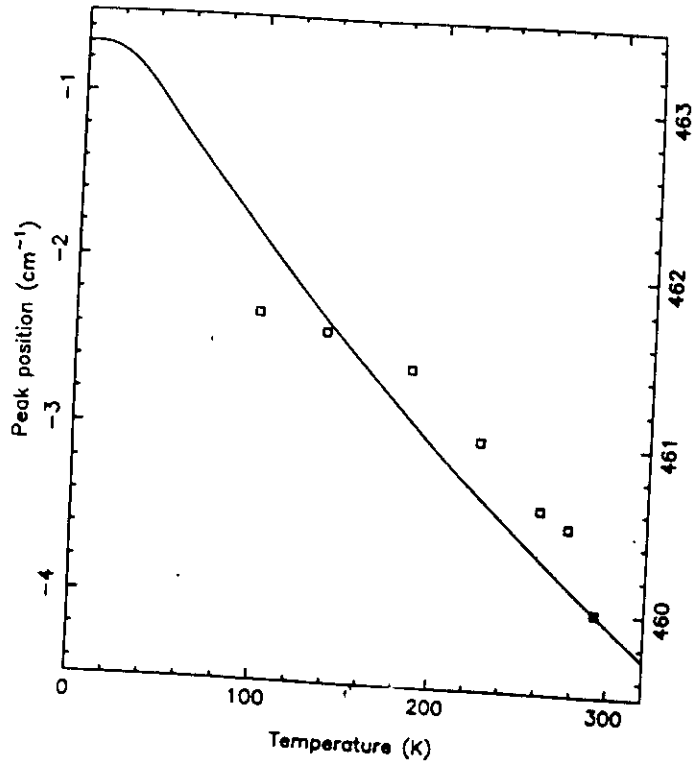


FIG. 8. Our prediction in the minimal anharmonicity model for the line shape $I(\omega)$ [see Eq. (4.15)] for CO/Pt(111) at 225 K.

CO/Pt(111)

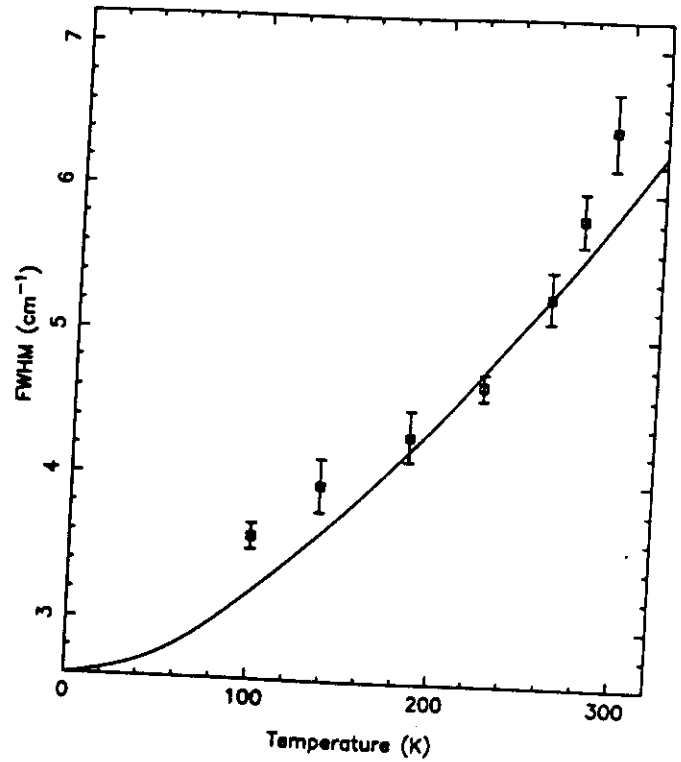


Peak Position

FIG. 7. Our prediction in the minimal anharmonicity model for the shift in peak position (solid line—left scale) vs. temperature for CO/Pt(111). The points are Ryberg's data for peak position (right scale) for the c(4×2) structure ($\theta = 0.5$).

CO/Pt(111)

Min Anharm model



Linewidth

FIG. 6. Our prediction in the minimal anharmonicity model for the linewidth (FWHM) for CO/Pt(111) vs. temperature (solid line). Our prediction has been convoluted with a 2.6 cm^{-1} gaussian to represent the experimental resolution. The points are Ryberg's raw data for the c(4×2) structure ($\theta = 0.5$).

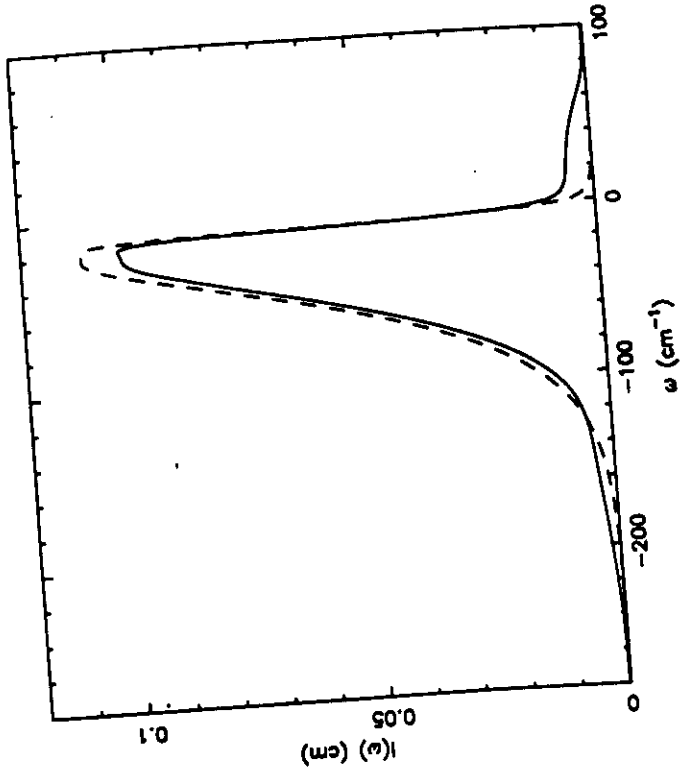


FIG. 9. The line shape for CO/Pt(111) at 225 K (solid line) in the Morse model. The result of the weak fluctuation approximation is also shown (dashed line).

CO /Ni (100)

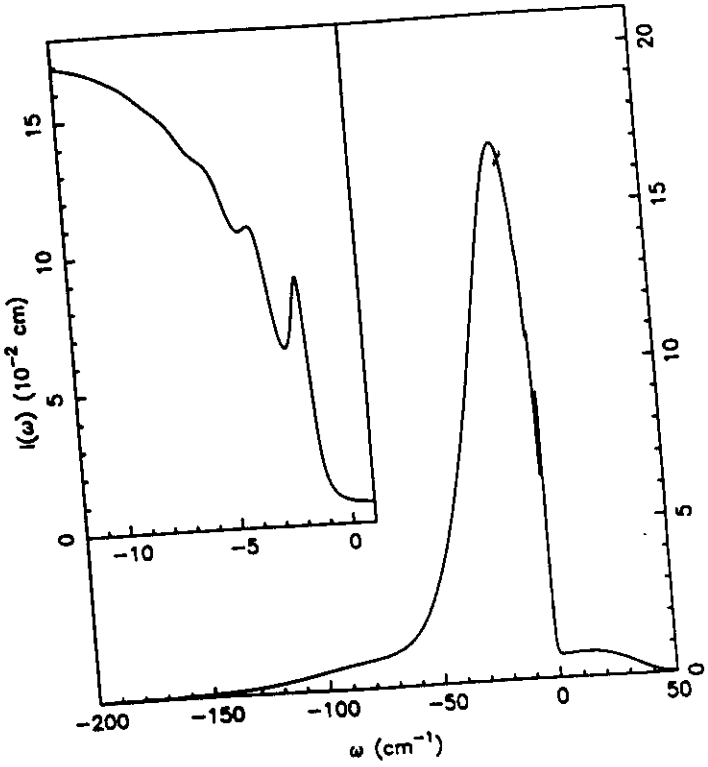


FIG. 10. Our prediction of the line shape in the minimal anharmonicity model for CO/Ni(100) at 310 K. The inset shows an expanded view of the quantum oscillations on the right edge of the line.

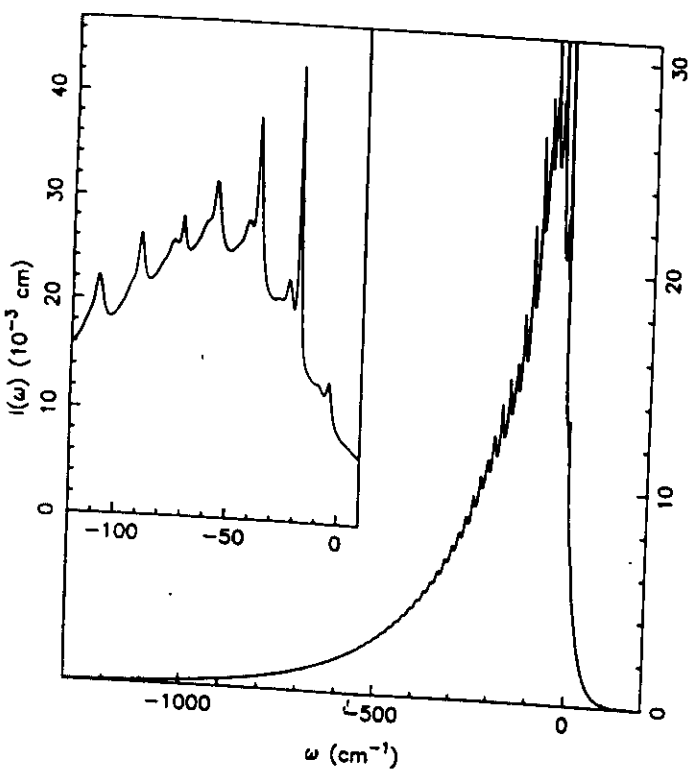


FIG. 12. The line shape in the Morse model for CO/Ni(100) at 310 K. The inset shows an expanded view of the quantum oscillations.

The minimal anharmonicity model fits the data well with no adjustable parameters.

The more physical Morse potential model gives results that are vastly different from experiment.

Why ?

Effect of Cubic terms

(Burke + Zhang)

Note: Also exist cubic terms.

e.g. in minimal harmonicity model

$$H_{int} = \frac{\frac{1}{2} M_c \omega_n^2}{l_0^2} \left[l_0 z x^2 - z^2 x^2 \right]$$

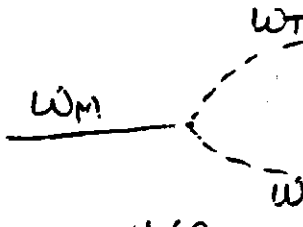
where l_0 is bond length. Also have z^3 terms in addition in Morse model.

1. $z x^2$ terms give emission + absorption of lower frequency excitations —

and

2. Renormalize K, the biquadratic coupling.

1.



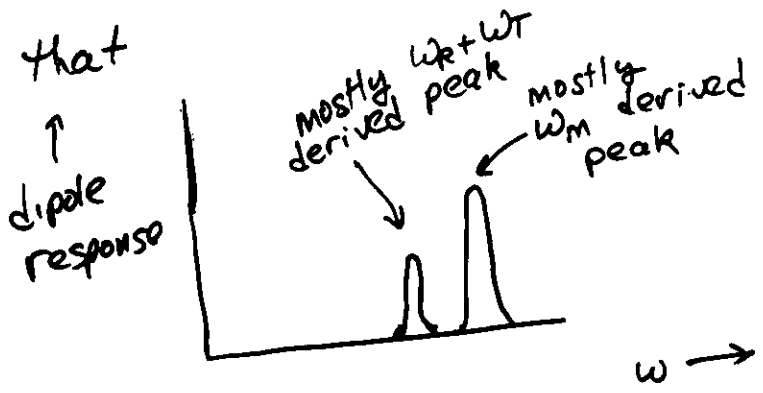
numbers for CO/Pt (cm^{-1})

$\omega_M = 460$; $\omega_R + \omega_T = 410 + 49 = 459$

close - a fermi resonance ?

for minimal anharmonic model

If put in numbers, find that



Relative strengths

$$\frac{Z_{RT}}{Z_M} \sim 0.3$$

!!

Should see two peaks ?!?

	Pt(111)	Cu(100)	Ni(100)	IR(100)
trix lement / 2	26	28	42	28
Splitting $\omega_R - \omega_T$	1	23	69	19
	units (cm^{-1})			
λ_{eff}	169	7.5	8.3	11
λ_0	-.73	-1.07	-1.66	-0.77

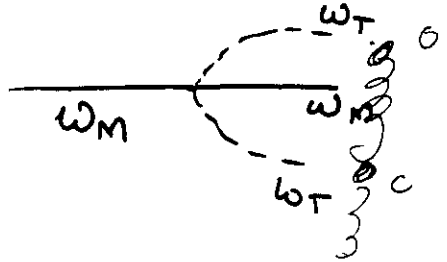
2. Renormalization of K

For ordinary biquadratic dephasing:

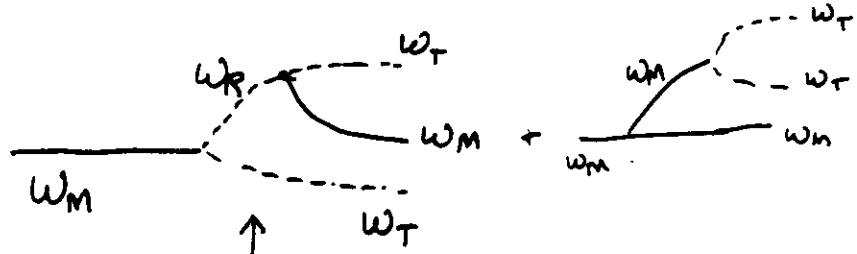
ω_T = frustrated trans. ⊥

ω_R = frustrated rotation

ω_M = metal - molecule stretch



With cubic term, build up second order matrix element:



energy denominator here is very large because of near fermi resonance

$\omega_M \simeq \omega_R + \omega_T$

Result:

$$K_{eff} = K\left(1 - g\frac{\mu_\perp}{\mu_{||}}\right)$$

($\mu_\perp = M_c + M_O$ for CO; $\mu_{||} = M_c$ for CO)

↑ effective cubic coupling constant

$$g = Z_T + Z_R \frac{\omega_M^2}{2}\left[\frac{1}{(\omega_M - \omega_T)^2 - \omega_R^2} + \frac{1}{(\omega_M + \omega_T)^2 - \omega_R^2}\right]$$

Z_T and Z_R are the fractional spectral weights of the R and T modes; for CO/Pt(111)

$$Z_T \simeq .2 \; ; \; Z_R \simeq .8$$

---

for a monatomic adsorbate:

$$\mu_\perp = \mu_{||}$$

$$Z_- = 1 - Z_R = 1 \; ; \; K_{eff} = 0 \; !$$

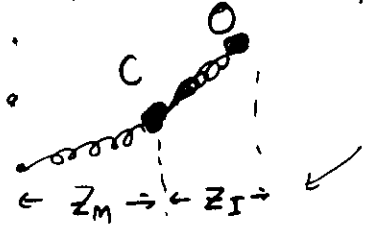
Status at this point:

1. All differences between minimal anharmonicity models and morse (or other) models has <u>cancelled out</u> (Good)

2. If the adsorbate is an <u>atom</u> (e.g. H on Si) there is <u>no</u> dephasing from the central force. All dephasing must come from anharmonicity in the angle bending forces which are much weaker. (surprising)

3. Diatomic adsorbates - near Fermi resonance, huge K_{eff}. (a disaster)

The way out; internal anharmonicity
– Mats Persson



measure z's from equilibrium length.

$z_I \ll z_M$ (why we always neglected it)

in fact

$$\frac{z_I}{z_M} = \frac{M_O k_M}{(M_O + M_C) k_I} \ll 1$$ ← force constants

because $k_M \ll k_I$

But one term in interaction hamiltonian:

$$\frac{k_M}{l_M} z_M x_M^2 + \frac{k_I}{l_I} z_I x_I^2$$

x_M: relative displacement ⊥ to surf; x_I: relative displacement ∥ to surf

l_M: Bond lengths

This term not present in rigid internal bond model. Neglected because $z_I \ll z_M$.

But $k_I z_I \sim k_M z_M$ so term must be kept!!

Principal effect is to greatly weaken the Fermi resonance

in rigid lattice (substrate) model

$$z_R \rightarrow z_R \times \left(\frac{M_C}{M_O + M_C}\right)^2 \left(\frac{l_I}{l_I + l_M}\right)^2$$

$$\sim z_R / 40$$ (similar for full numerical solution)

$$z_I \rightarrow z_r \times \left(1 + \frac{M_O}{M_O + M_C} \frac{l_I}{l_C}\right)^2$$

So where do we stand?

1. No dephasing from central forces for monatomic adsorbate
2. Weak dephasing (minimal anharmonicity) for diatomic adsorbates. True anharmonic constants that are large have no effect!
3. Only weak fermi resonance effects even though $\omega_M \simeq \omega_R + \omega_T$ and strong cubic anharmonicity constants!

CO on

	Pt(111)	Cu(100)	Ni(100)	Ir(100)
eff		4.6	7.0	4.4
matrix element / 2	4.0			
Matrix element / 2	26	28	42	28
Splitting	1	23	69	19
$-\frac{\lambda_{eff}}{\lambda_0}$	1.4	0.15	0.10	0.33

Conclusion:

Dephasing line widths + shapes give information about anharmonicities in non-central forces. anharmonicities in central forces give negligible contributions except in the rare case where one is very close to a Fermi resonance.