

Quantum Chemical Calculations Applied to Surface Science

A comparison of density
functional theory, Hartree-
Fock, and semiempirical
methods

Acknowledgements

- STM experiments

Fred Leibsle
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- FTIR experiments

Fred Leibsle
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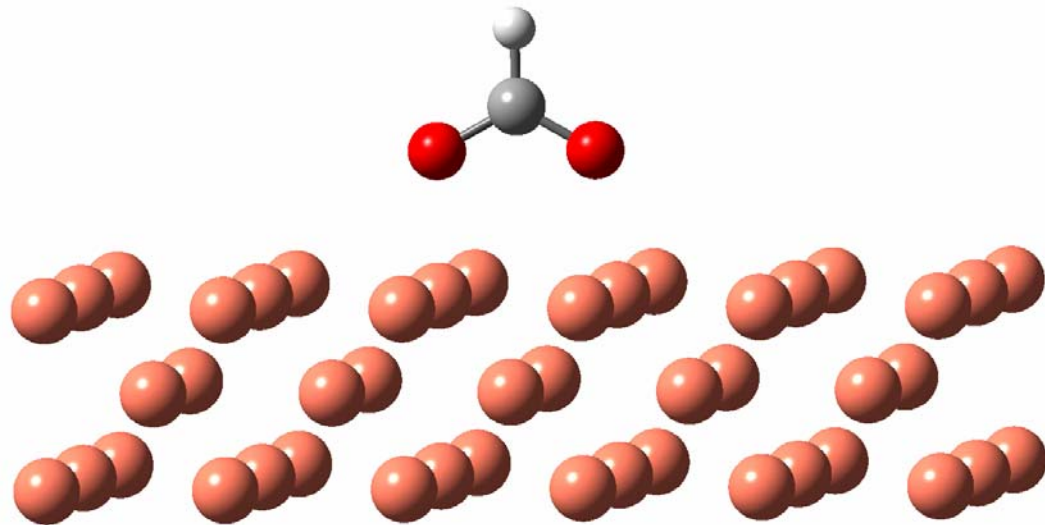
- Computation Chemistry and Semichem

Shizhong Yang
Andy Holder
Todd Keith

Requirements of a computational method in Surface Science

- Predict the correct adsorption site
- Give the structure of the chemisorbed molecule
- Produce the observable vibrational frequencies
- A method of estimating the adsorption energy
- Sufficient computational speed for large substrate models
- A graphics user interface to model and animate
- Map surface potentials and orbital structure

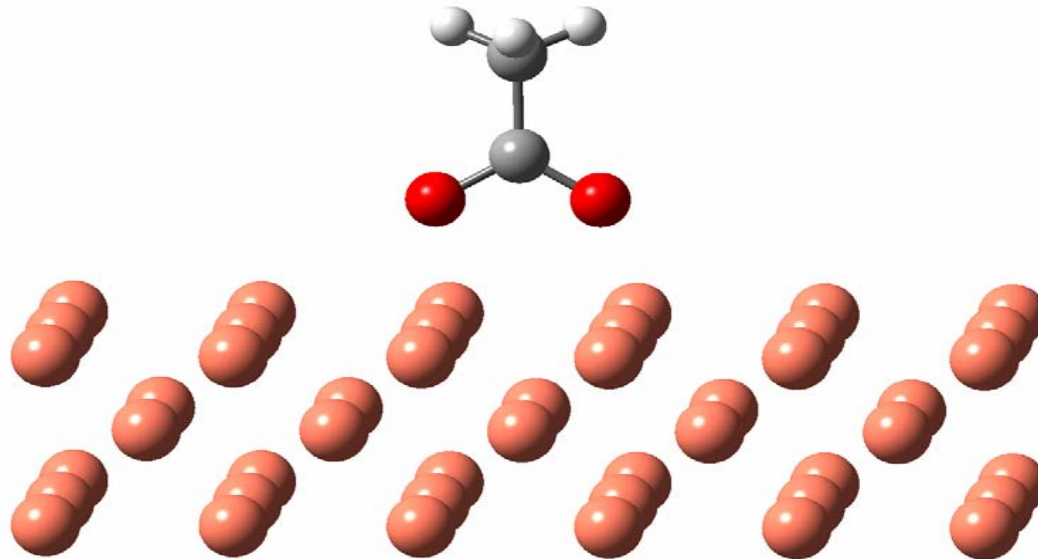
Formate/Cu(110)



A comparison of the structure and frequencies of a formate ion bonded to a Cu(110) surface. The frequencies are in cm^{-1} , the Cu O bond distance is in Angstroms, and the bond angle of the $\angle\text{O-C-O}$ is given.

Method	Model	$d_{\text{Cu-O}}$	$\angle\text{OCO}$	$\nu(\text{OCu})$	$\delta(\text{OCO})$	$\nu_s(\text{OCO})$	$\nu_a(\text{OCO})$	$\nu(\text{CH})$
RHF	$\text{Cu}_{10}(110)$	2.06	128°	274	759	1367	1622	2789
DFT	$\text{Cu}_{10}(110)$	1.98	128.9°	337	771	1378	1653	2924
SAM1	$\text{Cu}_{22}(110)$	1.98	132°	349	752	1452	1615	2842
Exp	$\text{Cu}(110)$	1.98	na	390	780	1360	1560	2920

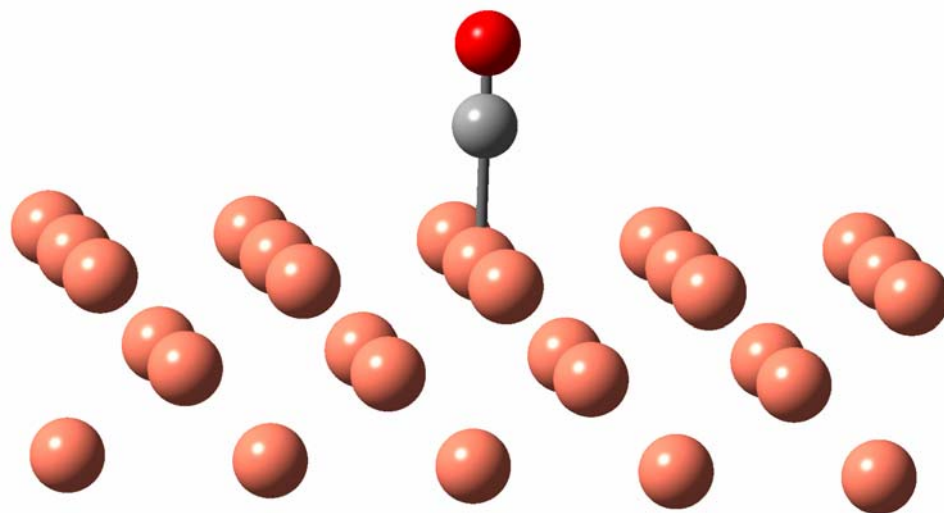
Acetate/Cu(110)



Experimental and calculated vibrational frequencies for acetate on Cu(110) surfaces.

Mode	Expt cm-1	RHF		B3LYP	SAM1
		6-31G(d) cm-1	6-311G(d) cm-1	6-311G(d) cm-1	cm-1
$\nu_s(\text{CH}_3)$	2932	2872	2850	3036	2957
$\nu_s(\text{OCO})$	1434	1459	1446	1434	1616
$\delta_a(\text{CH}_3)$	1391	1433	1423	1423	1370
$\delta_s(\text{CH}_3)$	1335	1352	1338	1338	1364
$\delta_s(\text{OCO})$	678	647	645	675	706

CO/Cu(110)



A comparison of the structure and frequencies of a **carbon monoxide molecule bonded to a Cu(110) surface**. The energy levels are given in eV.

Method	Model	$d_{\text{Cu-C}}$	$d_{\text{C-O}}$	HOMO	LUMO	$\nu(\text{CO})$	$\nu(\text{COCu})$
DFT	$\text{Cu}_8(110)$	1.82	1.16(1.13)	-3.86(-10.36)	-2.56(-0.79)	2143	
RHF	$\text{Cu}_8(110)$	1.77	1.13(1.11)	-4.34(-14.86)	0.10(4.57)	2441	
SAM1	$\text{Cu}_{28}(110)$	1.82	1.15(1.16)	-6.46(-14.17)	-2.70(1.08)	2374	448.82
Exp	$\text{Cu}(110)$	na	na (1.13)	na (-14.1)		2090 (2170)	345

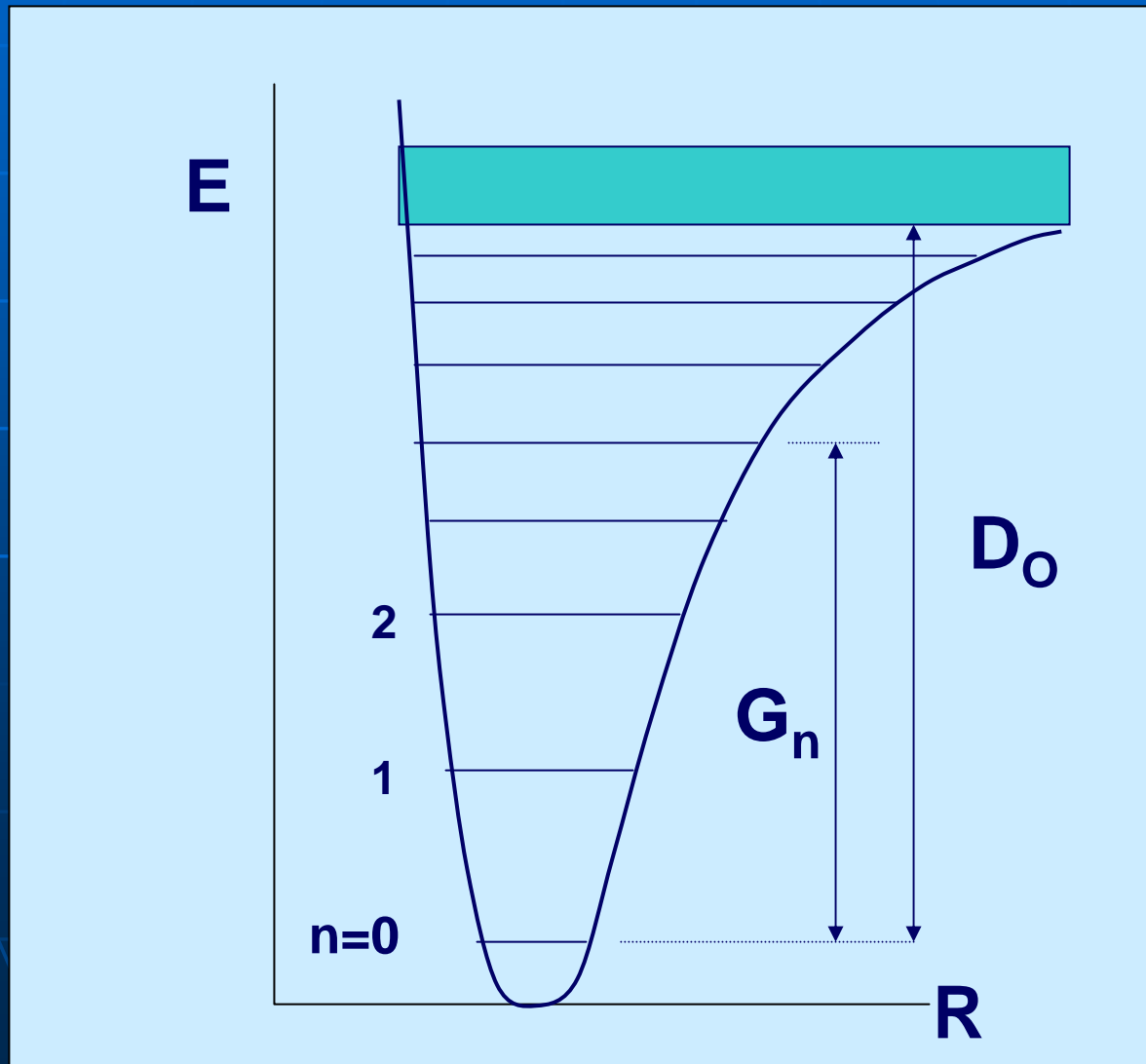
Estimates of the **adsorption energy** using an anharmonic model with the frequencies found by **SAM1**.

	HCOO-/Cu₄₆(110)	H3CCOO-/Cu₄₆(110)	CO/Cu₂₈(110)
k_e (millidynes/Å)	0.03693	0.029 79	0.05934
ω_e (cm-1)	342.7	318.0	448.82
ω_0x_0 (cm-1)	6.65 ^a	6.65 ^a	10.0 ^b
D_0 (eV)	1.14	0.99	0.65
D_0 (kcal/mole)	-26.3	-22.7	-15.0

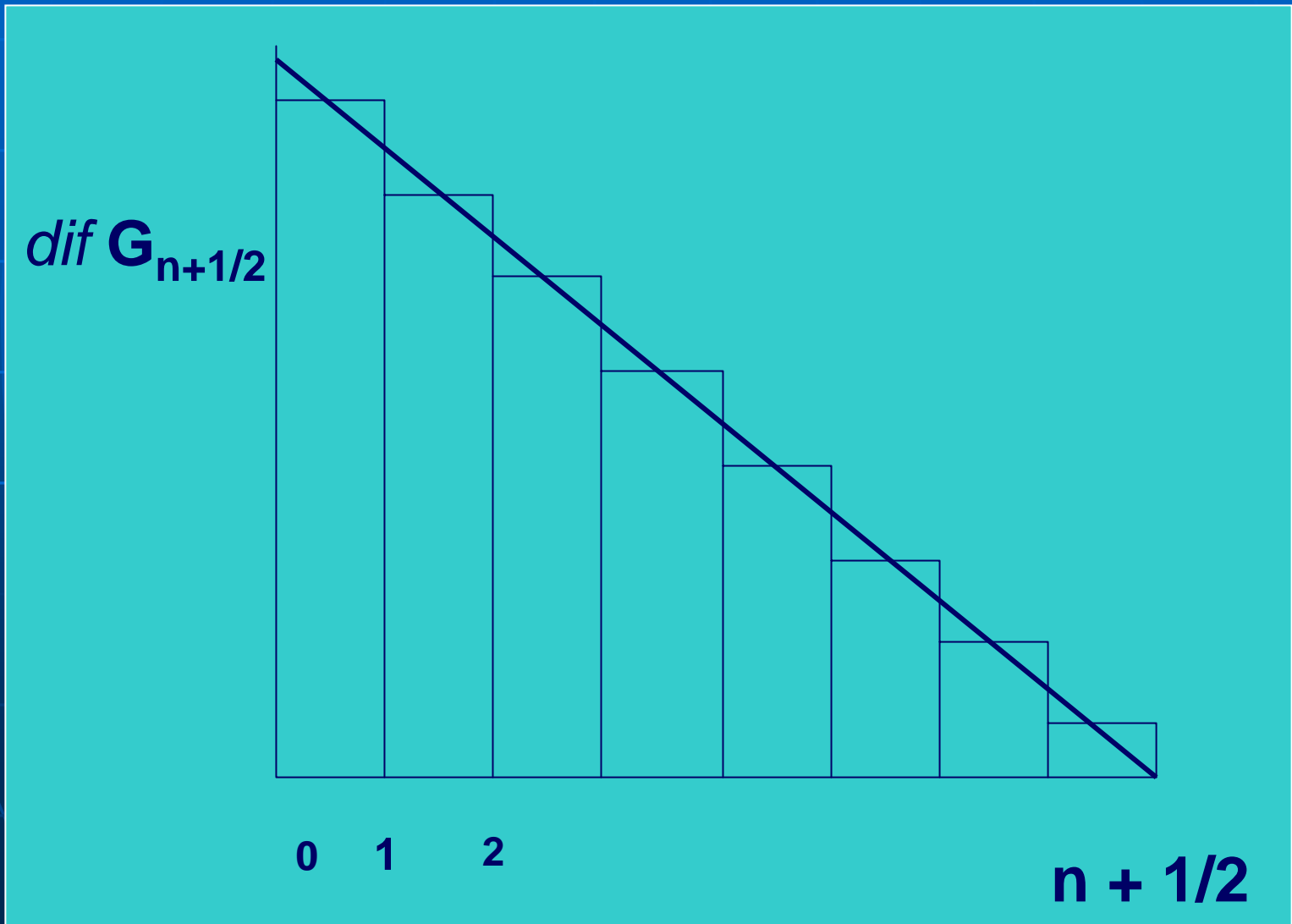
a) Note there are two Cu O bonds.

b) Base on the work of C. W. Bauschlicher, Jr. He used MP2 perturbation theory on the Cu CO molecule.

We use the Birge-Sponer extrapolation to estimate the dissociation energies.
Consider a Morse type potential,



A graphical representation of the Birge-Sponer extrapolation.



Assume an anharmonic oscillator

$$V(R) = \frac{1}{2}\kappa x^2 - ax^3 - bx^4 + \dots$$

where $x = R - R_{\min}$

Let $G(n) = \omega_e(n + \frac{1}{2}) - \omega_e x_e(n + \frac{1}{2})^2 + \omega_e y_e(n + \frac{1}{2})^3 + \dots$

$$G(n) - G(0) = \omega_0 n - \omega_0 x_0 n^2 + \omega_0 y_0 n^3 \dots$$

$$\text{dif } G_{n+1/2} = G_{n+1} - G_n$$

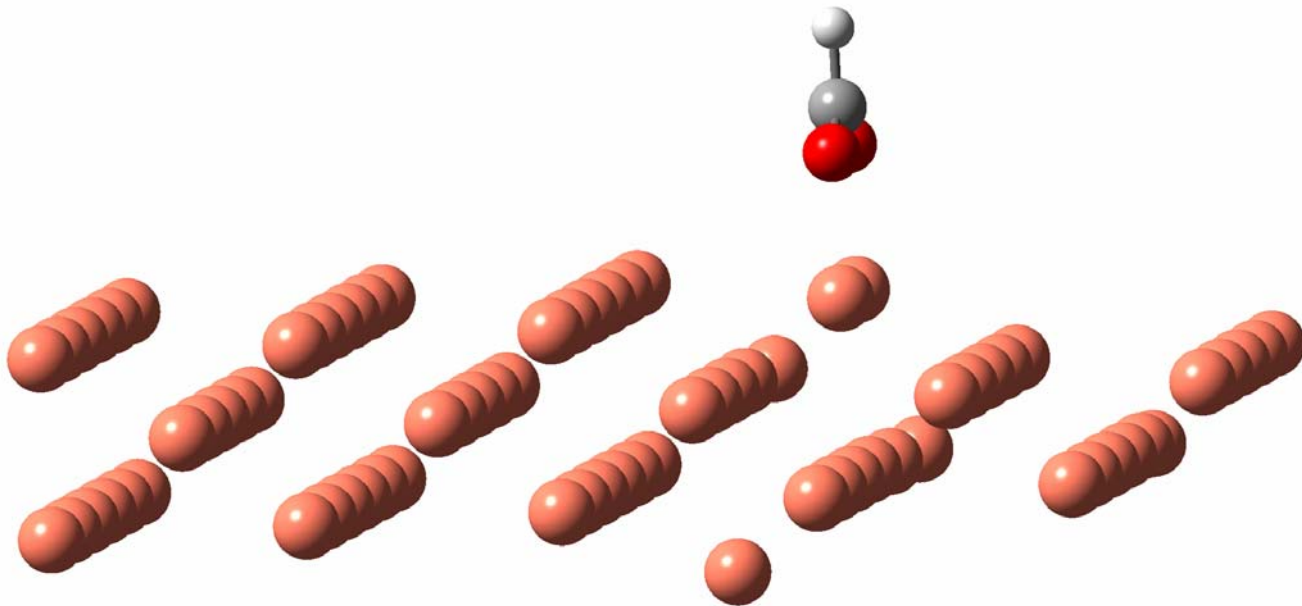
$$n_{\text{last}} = \frac{\omega_0}{2\omega_0 x_0} - \frac{1}{2}$$

$$D_0 = \sum_{n=0}^{n_{\text{last}}} \text{dif } G_n + \frac{1}{2} \approx \frac{1}{2} \omega_0 (n_{\text{last}} + \frac{1}{2}) = \frac{(\omega_e + x_0 \omega_0)^2}{4\omega_0 x_0}$$

Applications

- Step edge instabilities
- Coupled oscillators
- Replacement reactions
- Limits to cluster models and semiempirical methods.

Formate/Cu(110) Kink Site



Formate/Cu(110)

ω_e (cm^{-1})	k_e (millidyne / Angstroms)	D_0
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Top site	342.7	0.03488	1.14eV (26.24 kcal/mole)
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Edge site	330.5	0.03219	1.06eV (22.4 kcal/mole)
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Kink site	372.6	0.04090	1.34eV (30.9 kcal/mole)
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Terrace site	171.9	0.00871	0.30eV (6.86 kcal/mole)
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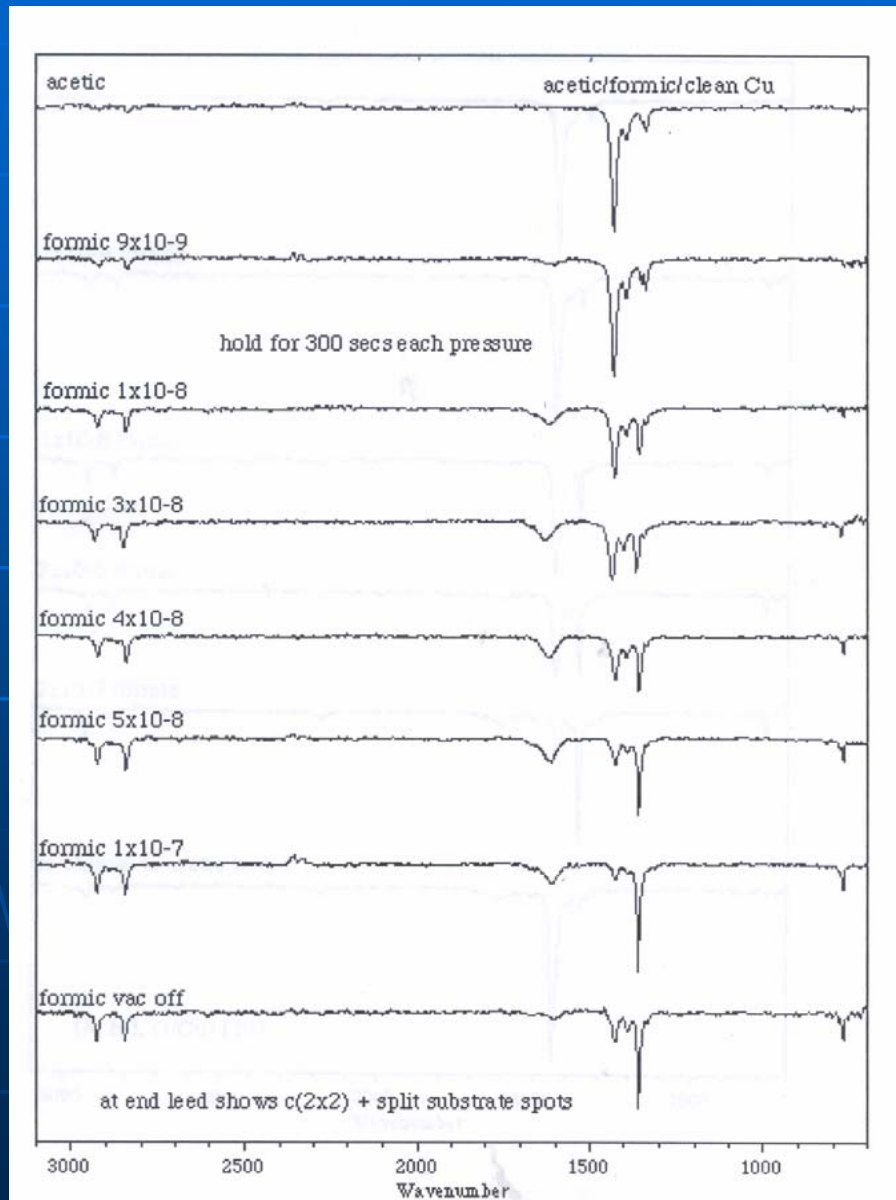
Coupled Oscillators

- Dipole coupling CO/Cu(110)
- Mechanical coupling O/diamond

Replacement Reactions

- Acetate replacement by Formate

Acetate replaced by Formate



Limitations

- SAM1 has a limited list of wave functions (C, Cu, Fe, Si)
- No back bonding of CO/Metal
- Cluster model and surface polarization