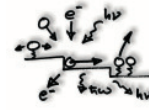


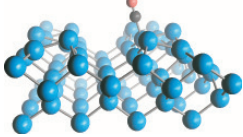
Vibrational dynamics of the CO internal stretch mode of CO/Si(100)

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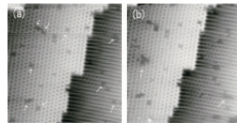
Structure and properties of the CO/Si(100) surface



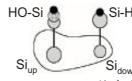
M. Gruber, P. Entel, unpublished results

- One CO molecule is adsorbed per Si dimer.
- Saturation coverage is 0.5 ML.
- CO is adsorbed at the lower Si atom of the dimer.
- The bond to the surface is very weak: The thermal desorption peak maximum is at about 180 K.
- Translationally energetic CO molecules can produce a structure with bridge-bonded CO.

- C-O internal stretch vibration at 2081 cm^{-1} .
- C-Si vibration at 407 cm^{-1} .
- CO adsorbs as islands around type C defects:



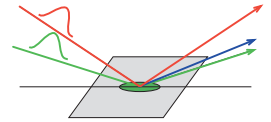
Type C defects originate from dissociative adsorption of water on adjacent dimers:



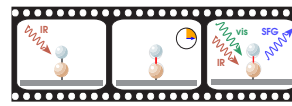
[1] Bu Li, Lin, Surf. Sci. 298 (1993), 94
[2] Kubo et al., Surf. Sci. 385 (1998), L248
[3] Hu et al., PRB 76 (1997), 1178
[4] Yamashita et al., PRB 58 (2003), 033314
[5] Hossain et al., PRB 67 (2003), 153307

Principle of sum frequency generation (SFG) spectroscopy ...

- Superposition of two laser pulses on a surface
- Second-order nonlinear optical process: Two photons are combined into one new photon.
- Takes place only in non-centrosymmetric media: Specifically sensitive for surfaces!
- Becomes more efficient, when one of the incident photons is resonant with a transition on the surface.
-> vibrational spectroscopy using tunable IR light.

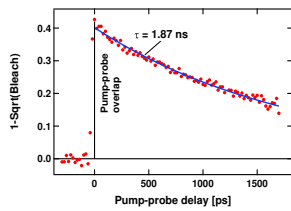


... for measuring vibrational lifetimes



- Population of the first excited vibrational state by an intense IR laser pulse.
- Probe of the population by means of an SFG pulse pair.
- The SFG signal intensity is proportional to the square of the population difference between vibrational ground

Vibrational lifetime of CO/Si(100)



- Vibrational lifetime on differently doped silicon samples: No correlation with the carrier density.

No.	1	2	3	Overall
Doping type	p	n	n	
Dopant	B	P	As	
Dopant density [cm^{-3}]	$5 \cdot 10^{15}$	$5 \cdot 10^{12}$	$5 \cdot 10^{19}$	
τ [ps] (average)	2080	2550	2100	2300
σ_c [ps] (std. dev.)	330	650	280	500

- Vibrational lifetime: $\tau = 2.3 \pm 0.5 \text{ ns}$ (Assumption: purely statistical scatter).

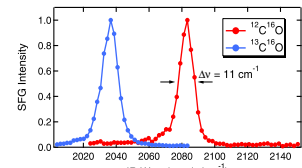
- C-O vibrational quantum is about 260 meV. The bandgap is 1,17 eV and 3,4 eV, respectively. This precludes vibrational relaxation via electron-hole pairs.
- Scatter of the observed lifetimes > Imperfections of the surface structure? > Defect density, sample preparation?
- Role of defects for the vibrational relaxation: CO on defect sites as energy drain (in analogy to H on steps in the system H/Si(100))?
- If the measured lifetime is dominated by defects, our measured value represents the lower limit of the "true" vibrational lifetime.
- The signal decay is described well by a single-exponential fit.
- Observed vibrational lifetime: 1.8 to 4 ns.
- Vibrational lifetime is the same for ^{13}C .

- Maximum excitation density: about 40%.
 τ found to be independent of the excitation density.

[8] Laß et al., JCP 123 (2005), 051102

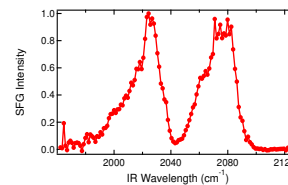
Vibrational resonance of CO/Si(100)

- C-O internal stretch vibration is resonant at
 - * 2081 cm^{-1} for $^{12}\text{C}^{16}\text{O}$.
 - * 2036 cm^{-1} for $^{13}\text{C}^{16}\text{O}$.
- $\Delta\nu_{\text{resonance}} \approx 11-13 \text{ cm}^{-1} > \Delta\nu_{\text{Laser linewidth}}$
Possible Reasons:
 - * interadsorbate dipole coupling > energy delocalisation > more rapid dephasing.
 - * power broadening.

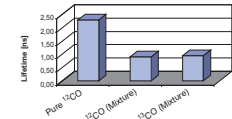


Isotopic mixtures

- C-O mixtures of about 50 % each show an isotopic shift, compared to the pure adsorbates:



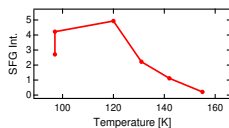
- When mixed, vibrational lifetime of both isotopic species shortens down to about 900 ps.



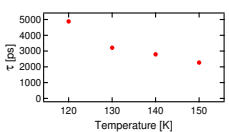
No explanation yet.
> Indicator for interadsorbate dipole coupling taking part in decay mechanism?

Effects of surface coverage changes

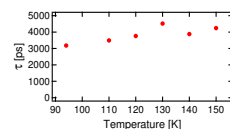
- The equilibrium surface coverage can be changed by varying the sample temperature while keeping the CO background pressure constant at $2 \cdot 10^{-7}$ mbar:



- Variation of the observed lifetime with sample temperature:



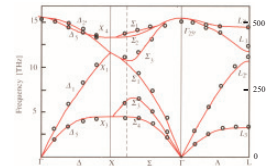
- At a higher background pressure ($1.5 \cdot 10^{-8}$ mbar), the lifetime change seems to be merely statistical:



- > These results indicate: There is rather an influence from the surface coverage than from the sample temperature!
- > Together with the lifetime results from the isotopic mixtures: Lifetime shortens down, if CO molecules (islands?) of the same species are isolated.
- > Role of interadsorbate dipole coupling in energy dissipation? Energy delocalisation?

Possible decay mechanisms

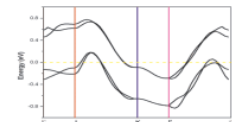
- Coupling to phonons?
 - * In the system H/Si vibrational relaxation takes place by multiphonon emission. Also for CO/Si?
 - * The weak and soft C-Si bond decouples the C-O internal vibration from the crystal lattice, but $\mu(\text{C-Si}) \approx \mu(\text{H-Si})!$
 - * Four LO phonons with an energy of 520 cm^{-1} have exactly the same energy as one C-O vibrational quantum of 2081 cm^{-1} .



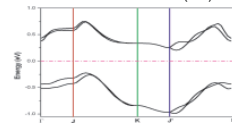
Phonon dispersion curves along the axes of high symmetry (taken from Yu, Cardona: Fundamentals of Semiconductors, Springer, Berlin 2001)

- Can the CO/Si(100) surface be metallic?

- * DFT calculations by Zhang et al. show that at low temperatures the clean symmetric Si(100) surface can become metallic:



- * A similar calculation for CO/Si(100) shows:



The band gap is even wider > The terminally adsorbed surface is not metallic. Z. Zhang et al., unpublished results