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ADRIATICO RESEARCH CONFERENCE on

LASERS IN SURFACE SCIENCE

11-15 September 2000

Miramare - Trieste, Italy

Non-linear and femtosecond time-resolved vibrational spectroscopy on surfaces

Mischa Bonn
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Leiden, the Netherlands

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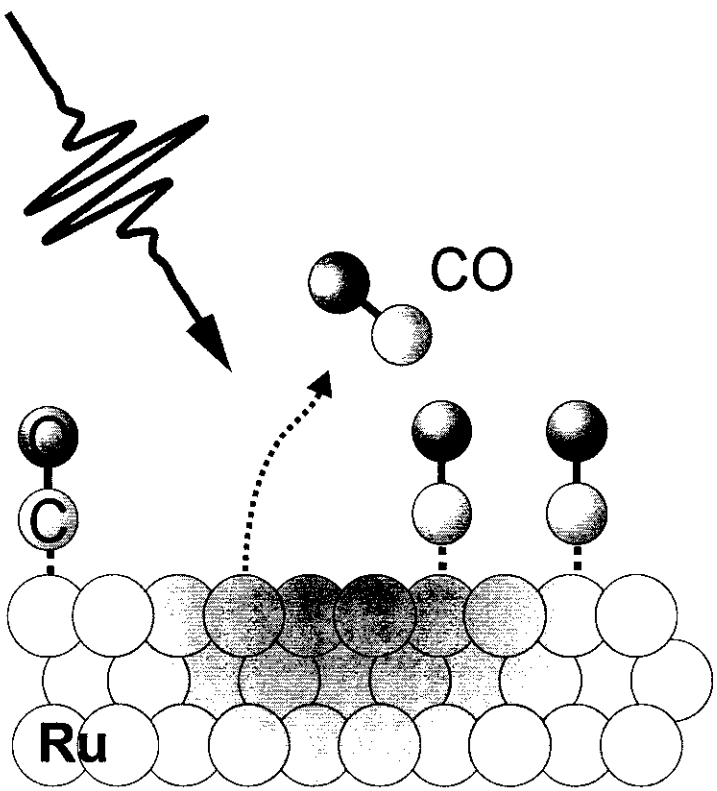
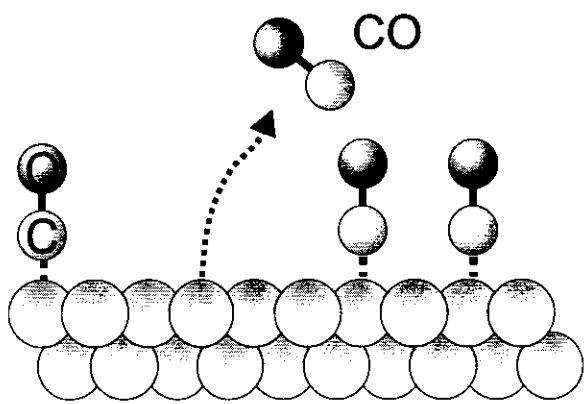


Motivation

- Goal: understanding of ultrafast dynamics of surface reactions and energy transfer

  → Mechanims and timescales of energy flow between substrate and reactants

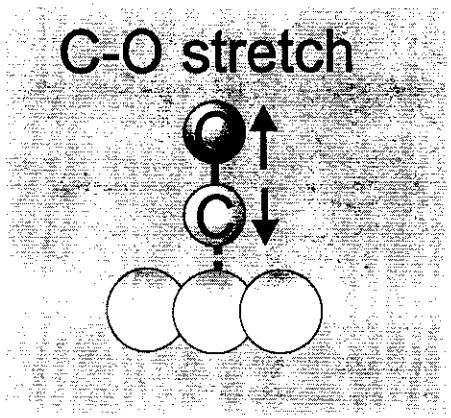


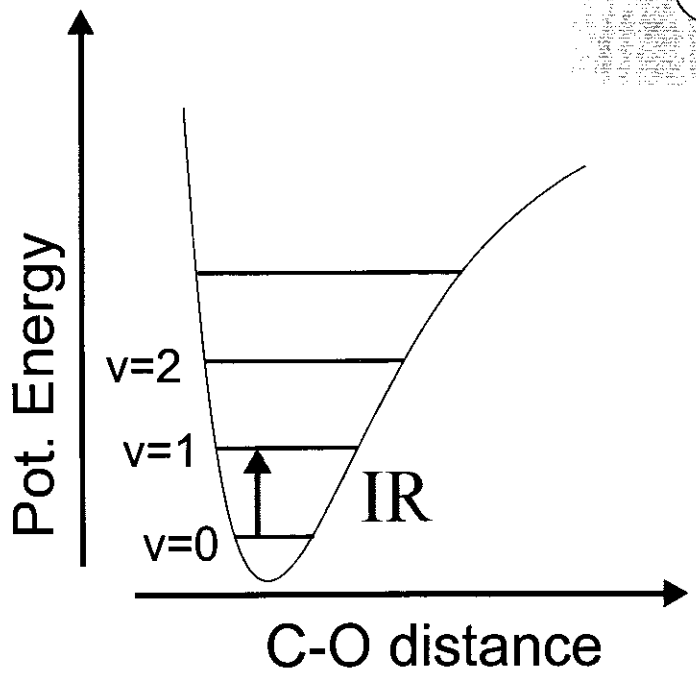
  → Reaction timescales, mechanisms & intermediates (transition states)

- Technique: Look 'inside' molecule during reaction: time-resolved sum-frequency generation

IR vs. Sum-Frequency Generation

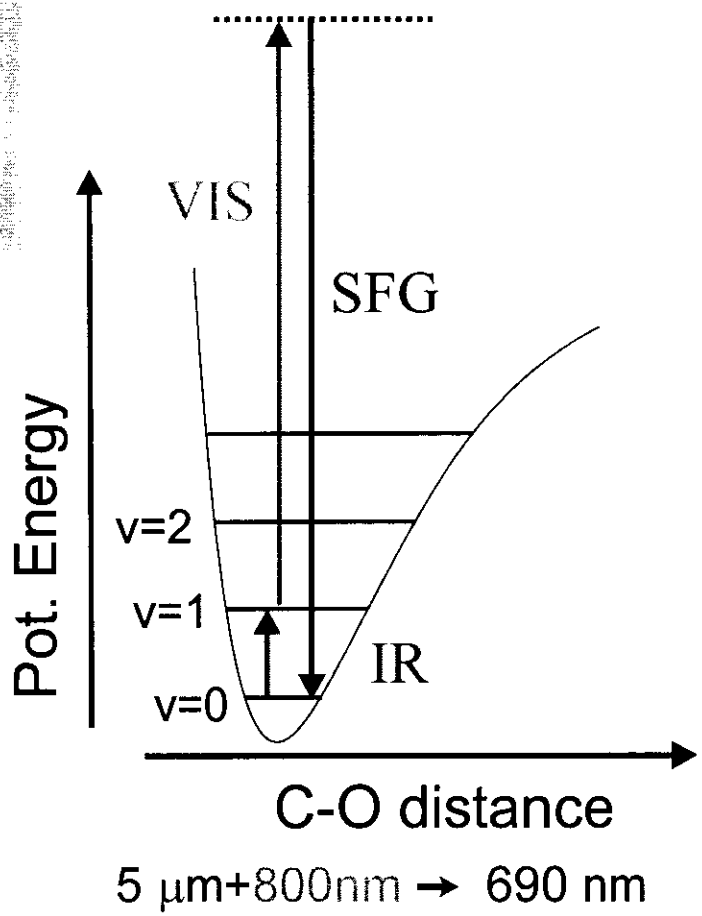
IR





With background, IR detection

SFG



5 μm+800nm → 690 nm

Background-free, visible detection

Sum-Frequency Generation (SFG)

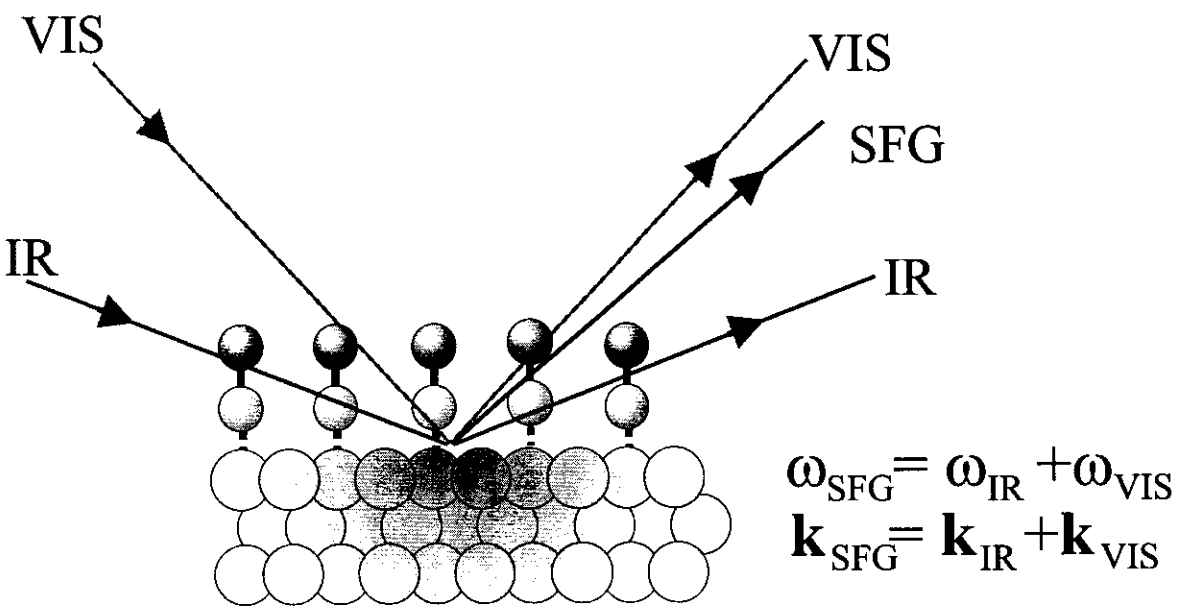
SFG: second order non-linear optical process

$$\mathbf{P}^{SFG} = \chi^{(2)}(\omega_{SFG} = \omega_{IR} + \omega_{VIS}) : \mathbf{E}^{IR}\,\mathbf{E}^{VIS} \quad \textit{met} \quad \chi^{(2)} = \chi^{(2)}_{ijk}$$

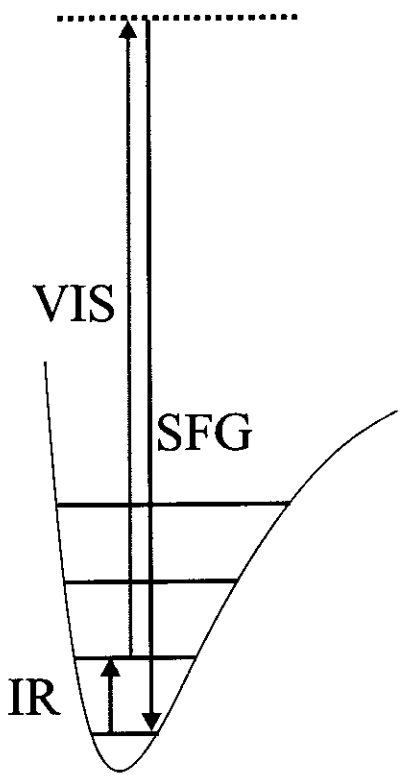
For system with inversion symmetry (centro-symmetric medium):

$$\chi^{(2)} = -\chi^{(2)} \rightarrow \chi^{(2)} = 0 \quad \longrightarrow \textit{Surface specific}$$

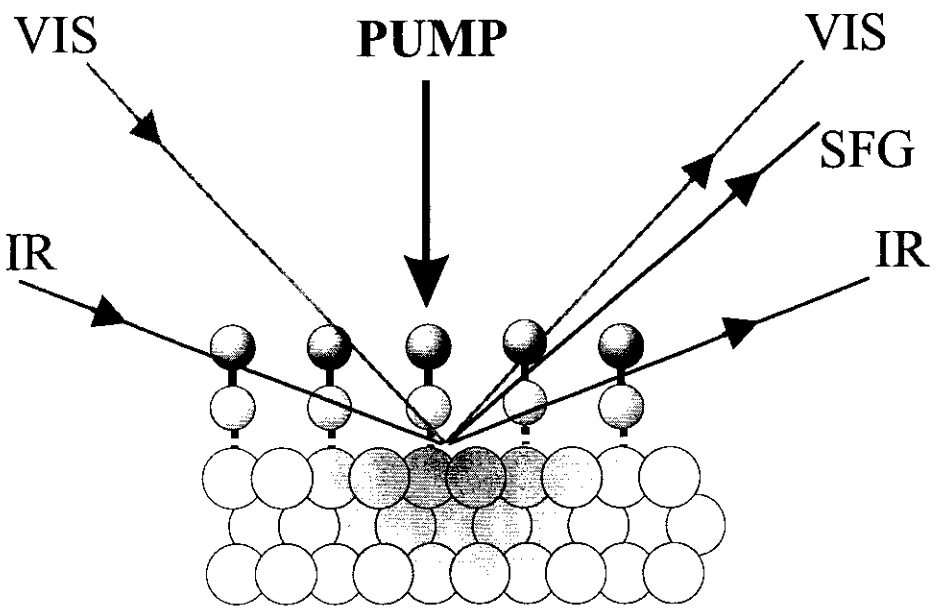
$$\chi^{(2)} = \chi^{(2)}_{RES} + \chi^{(2)}_{NON\text{-}RES} \qquad [\chi^{(2)}_{RES}]_{ijk} = \frac{NM_{ij}A_k}{\hbar(\omega_{IR} - \omega_{ab} + i\Gamma_{ab})}$$

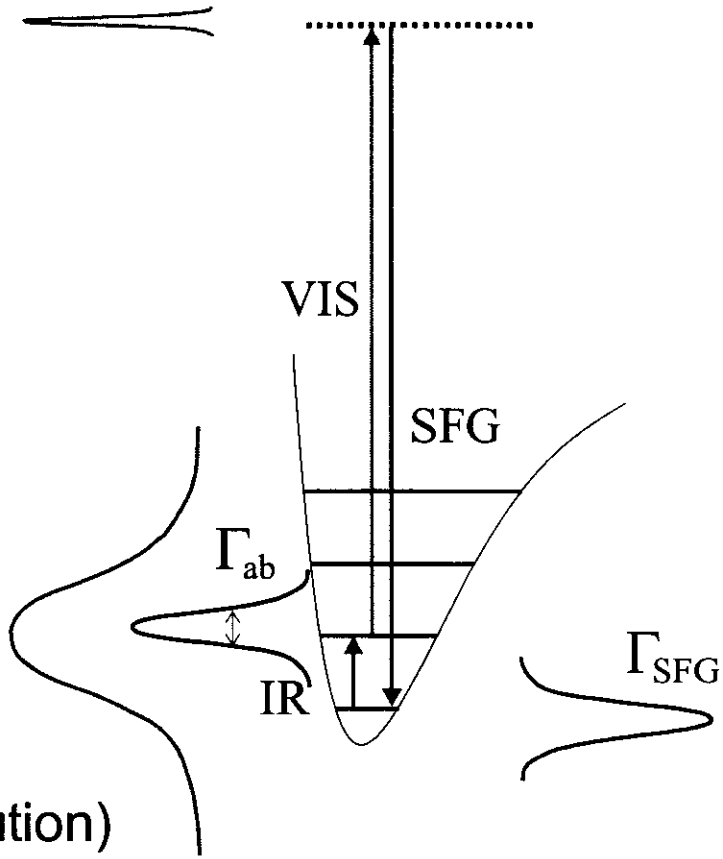


$$\omega_{SFG} = \omega_{IR} + \omega_{VIS}$$
$$\mathbf{k}_{SFG} = \mathbf{k}_{IR} + \mathbf{k}_{VIS}$$



Time-resolved broad-band Sum-Frequency Generation





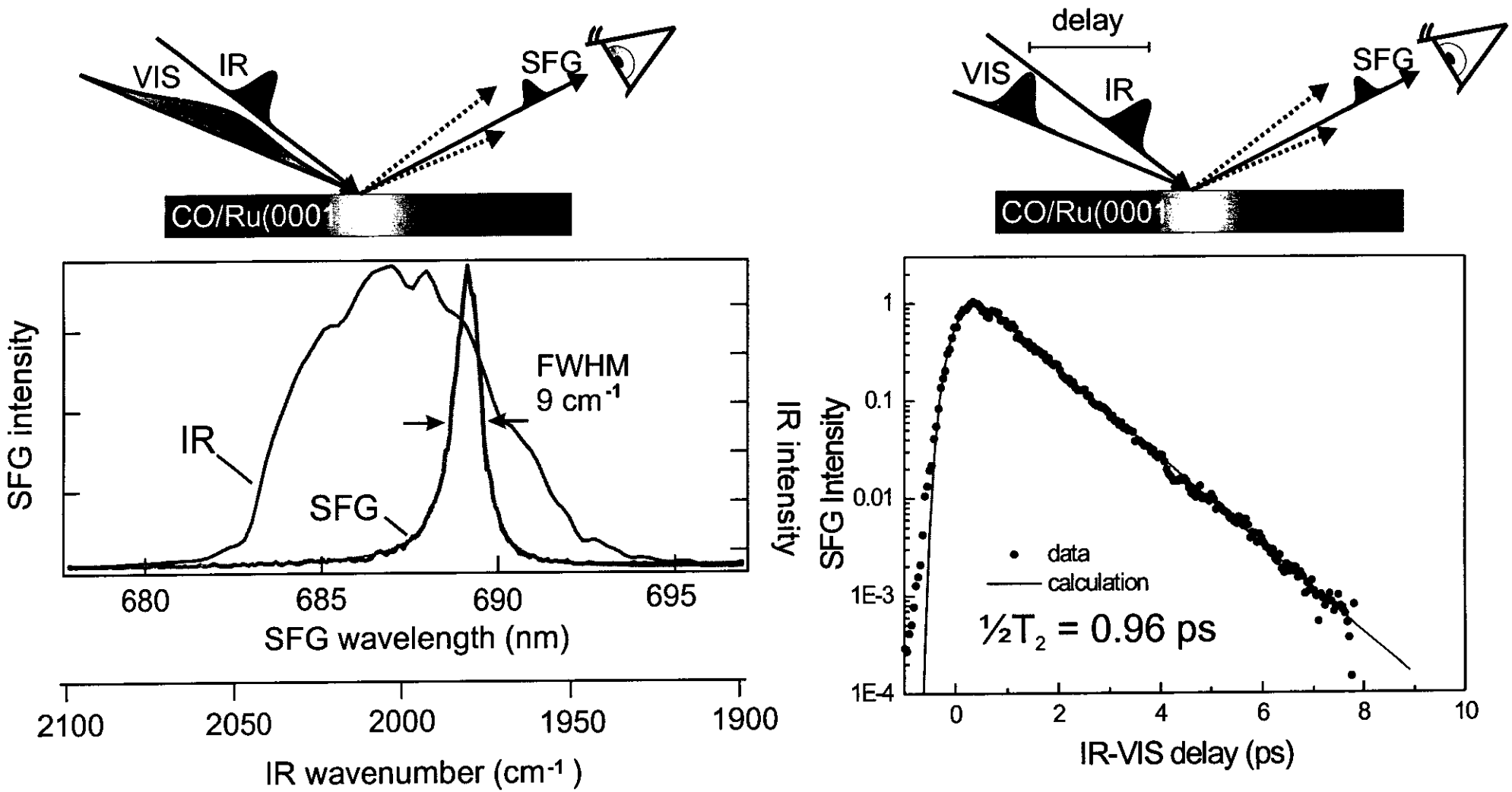
→ Spectrally broad (temporally short - time resolution) IR pulse with spectrally narrow (temporally long) VIS pulse, so that $\Gamma_{SFG} = \Gamma_{ab}$

→ SFG with dispersive optics onto ICCD-camera: 'single-shot' spectrum

SPECTRAL* *AND* TIME RESOLUTION

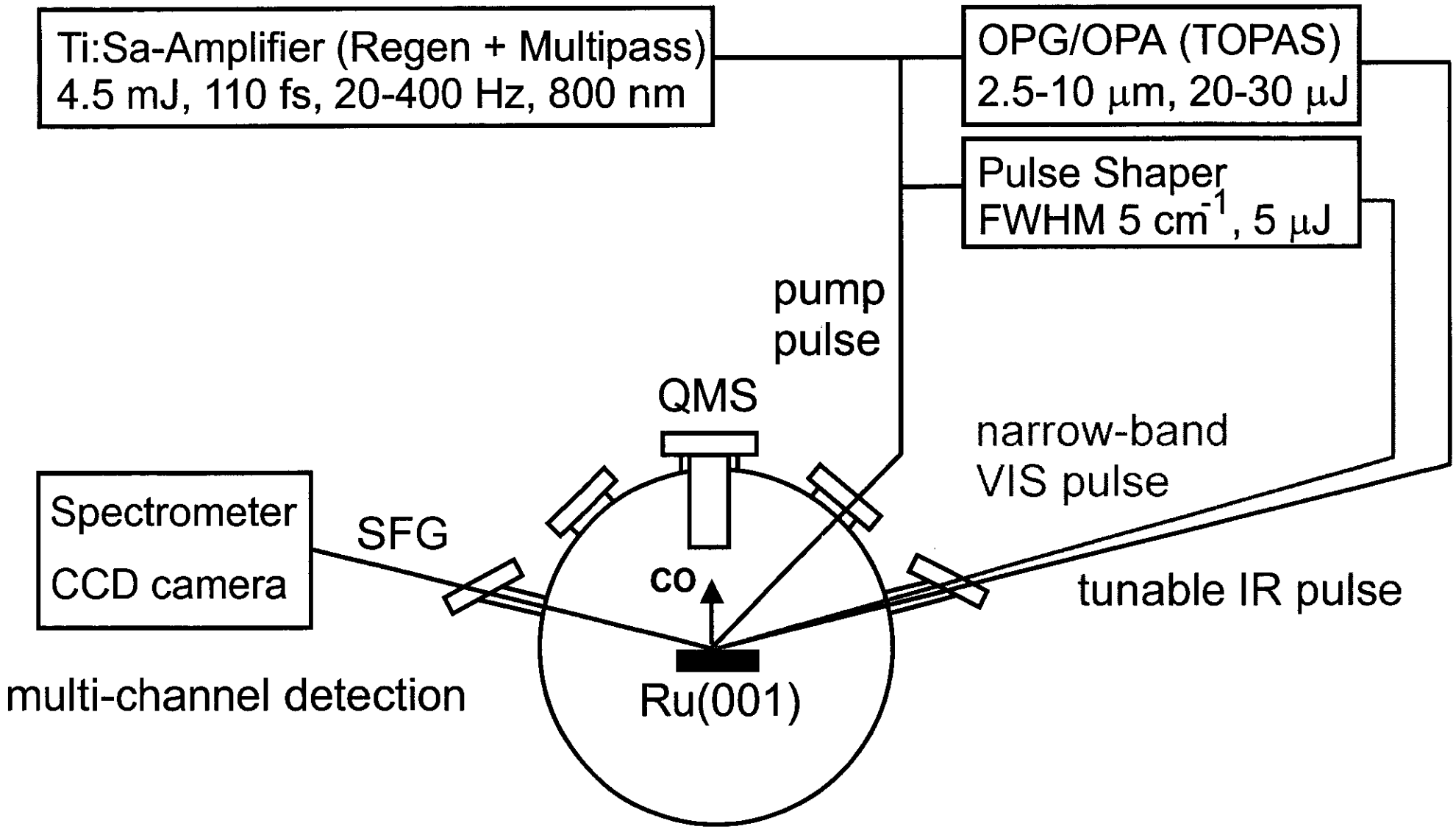
* L.J. Richter et al. Opt. Lett. **23**, 1594 (1998).

Broad-band SFG: Spectral AND time-resolution



- Experimental time resolution: better than 500 fs
- Experimental frequency resolution: better than 4.5 cm^{-1}

Experimental set-up



What's to come...?

Non time-resolved, non-linear experiments:

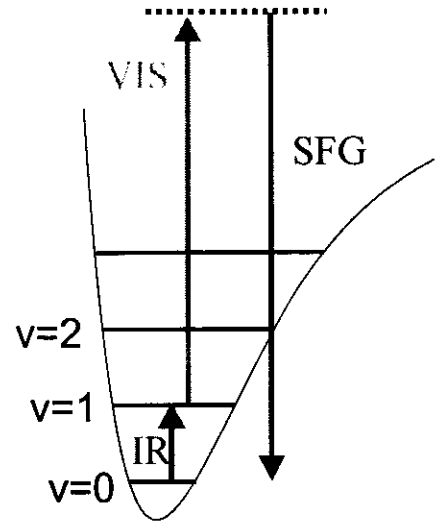
- Population ladder climbing
- Observation of vibrational energy delocalization

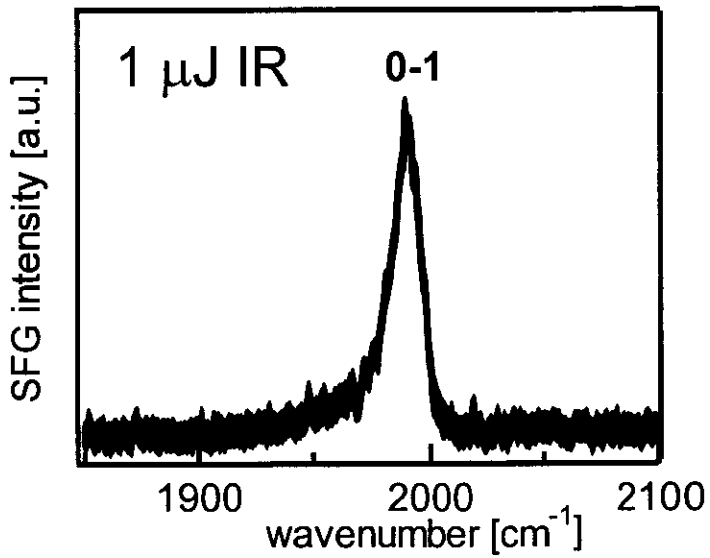
Time-resolved, linear experiments:

- Vibrational spectroscopy during CO desorption

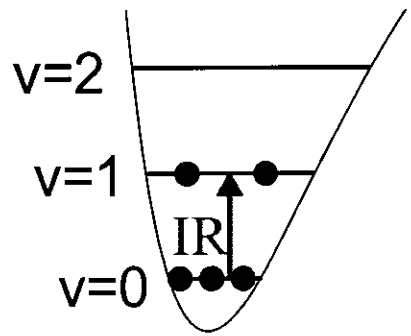
Saturation spectroscopy: population ladder climbing

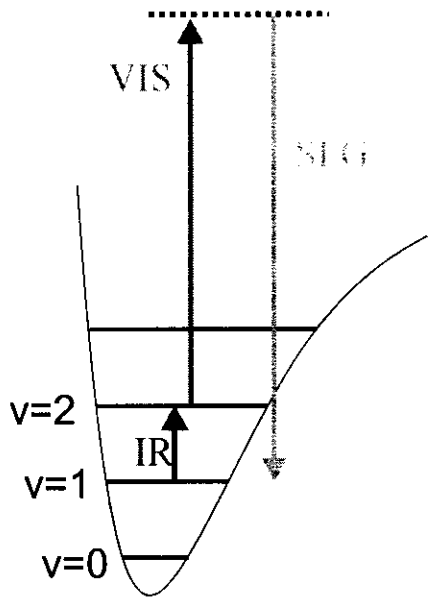
Low IR intensities:

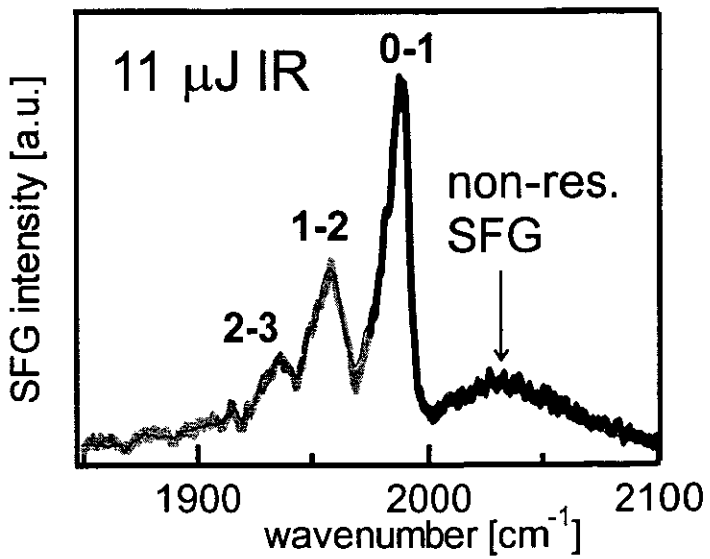




High IR intensities:

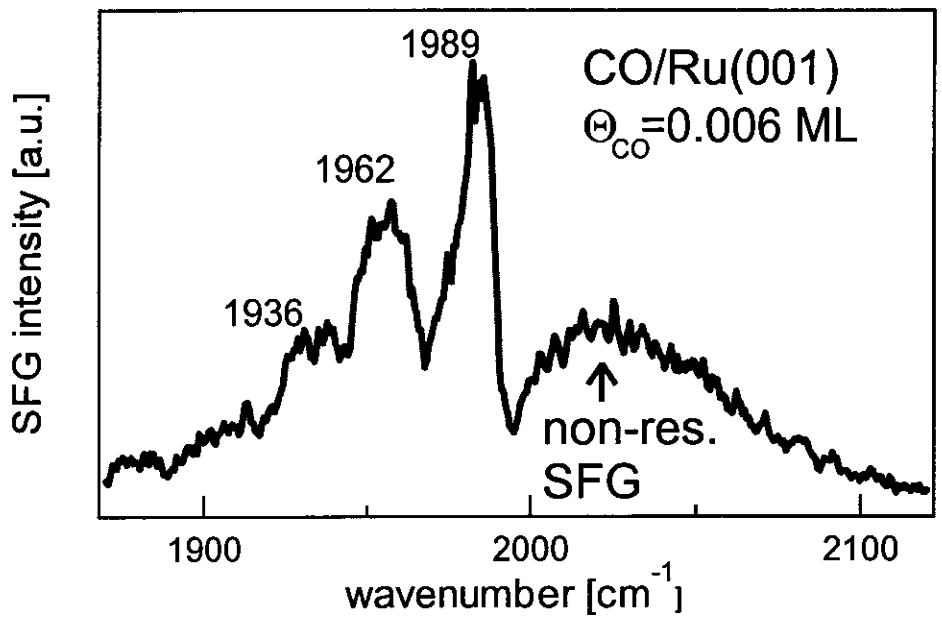


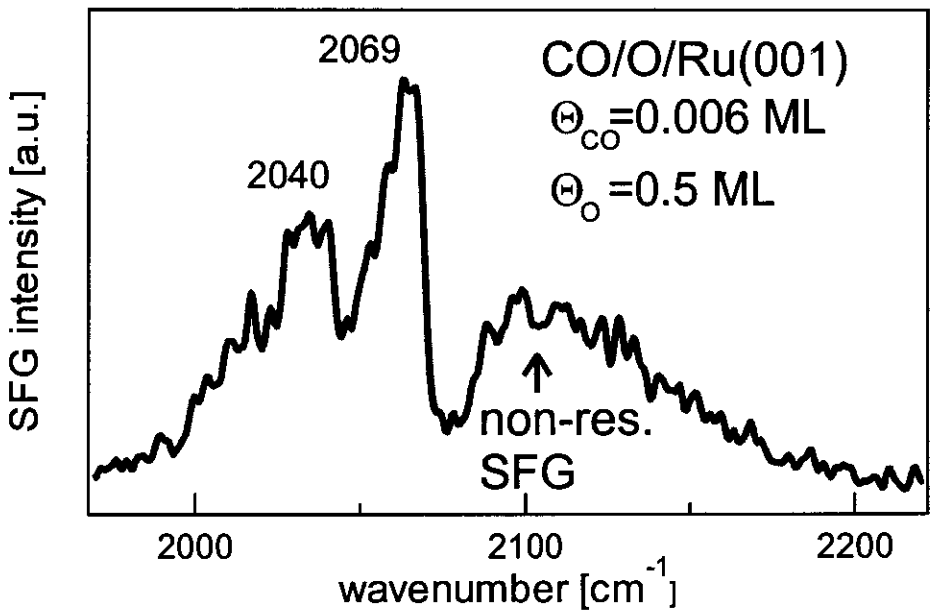




Multi-vibrational excitation by population ladder climbing:
bond-selective surface chemistry?

Saturation spectroscopy: determination of anharmonicity





Anharmonicity: 13.6± 0.6 cm^{-1}

Anharmonicity: 14.6± 0.7 cm^{-1}

From anharmonicity and vibrational frequency:

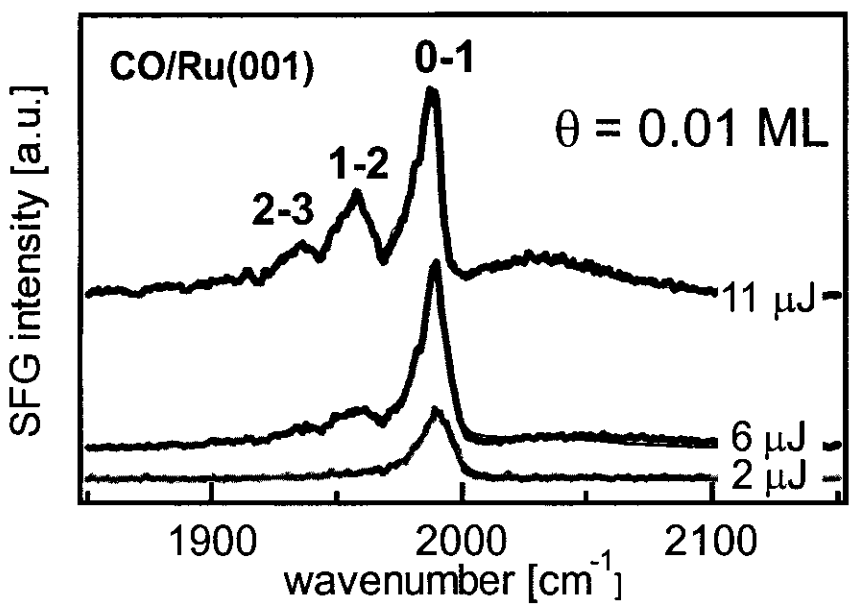
Similar strength of C-O bond for different environment of CO

Saturation spectroscopy: vibrational energy delocalization

IR-energy dependent SFG spectra

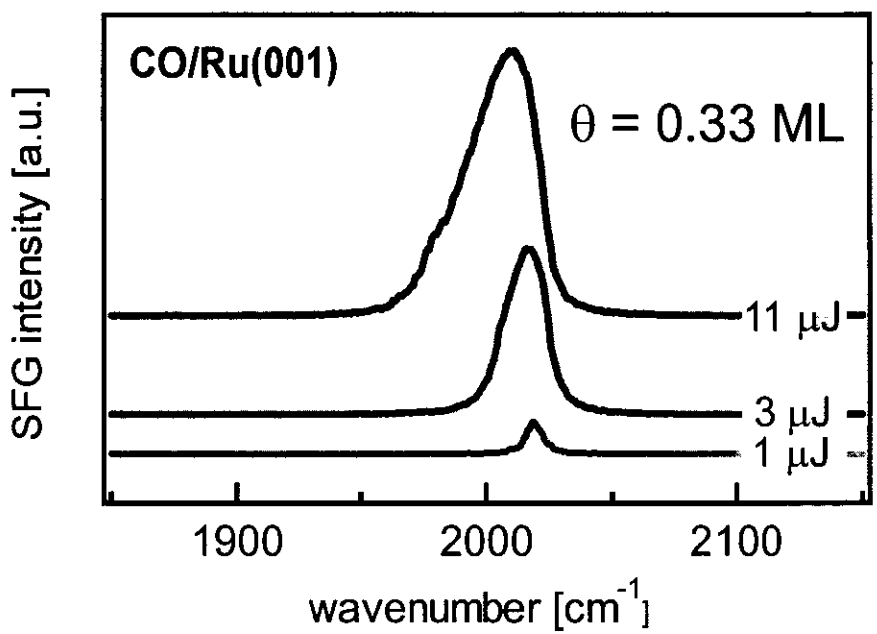
LOW coverage

Localization of excitation



HIGH coverage

Delocalization due to dipole coupling



delocalization of excess vibrational energy through dipole-dipole coupling

Saturation spectroscopy: vibrational energy delocalization

For high coverage, due to strong vibrational dipolar coupling, dispersion W exceeds anharmonicity Γ, and the 1→2 transition becomes delocalized

Shen, PRB 23, 4946 (1981)

3-D observations of phonon-localization transition:

J. H. Eggert, PRL 70 2301(1993) - varying W.

P. Calvani, JCP 101 20 (1994) - varying Γ.

But no theoretical description of spectral changes associated with transition

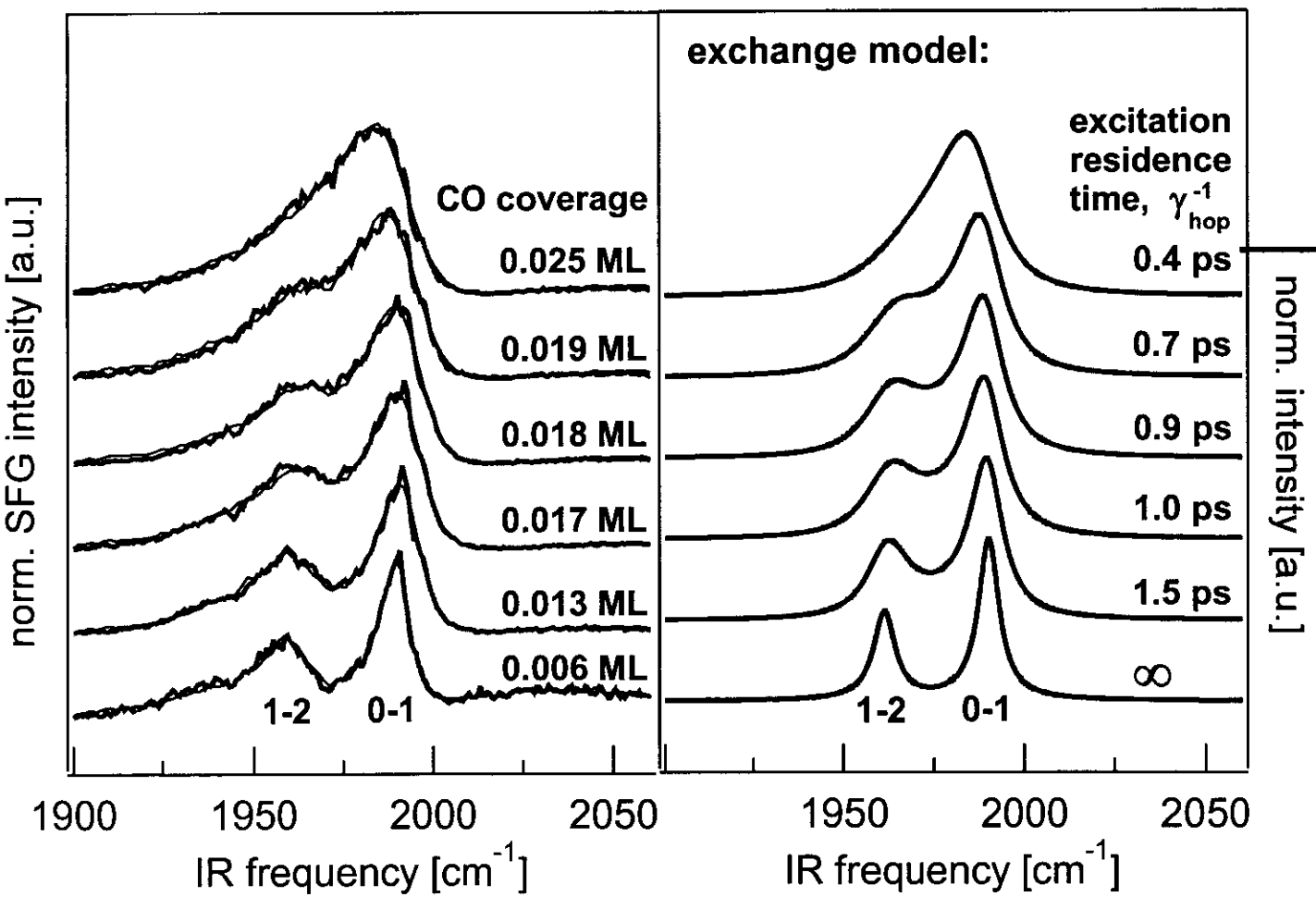
Here: Change W by changing intermolecular coupling strength through surface coverage to observe transition in 2-D.

Model: Coverage dependent residence time of vibrational excitation: excitation resides on oscillator for time $\tau=\gamma_{hop}^{-1}$

$$I(\omega) = \frac{\gamma_{\mathrm{hop}} n_{\mathrm{exc}} (2\Gamma)^2 / (1 + n_{\mathrm{exc}})}{[\omega'^2 - \Gamma^2]^2 + [\gamma_{\mathrm{hop}}(\omega' + \Gamma) + \gamma_{\mathrm{hop}} n_{\mathrm{exc}}(\omega' - \Gamma)]^2}$$

* Shelby et al., JCP 70 (1979) 34.

Saturation spectroscopy: Phonon-localization transition

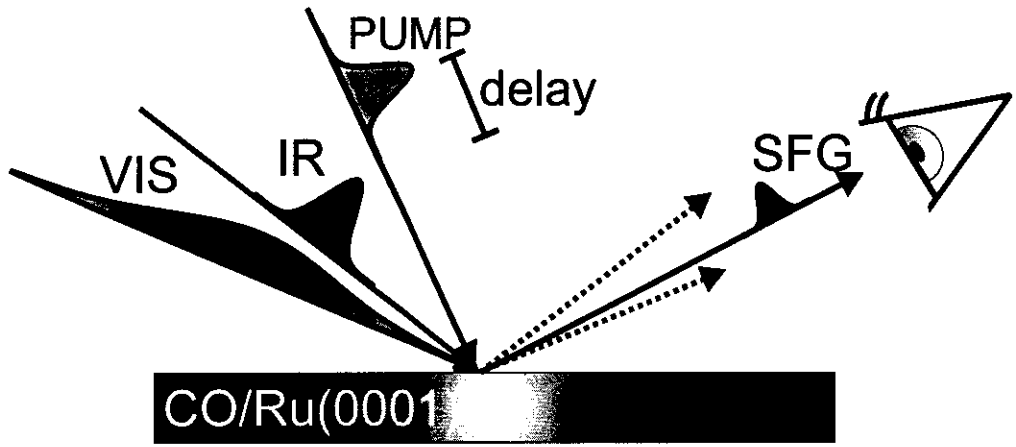


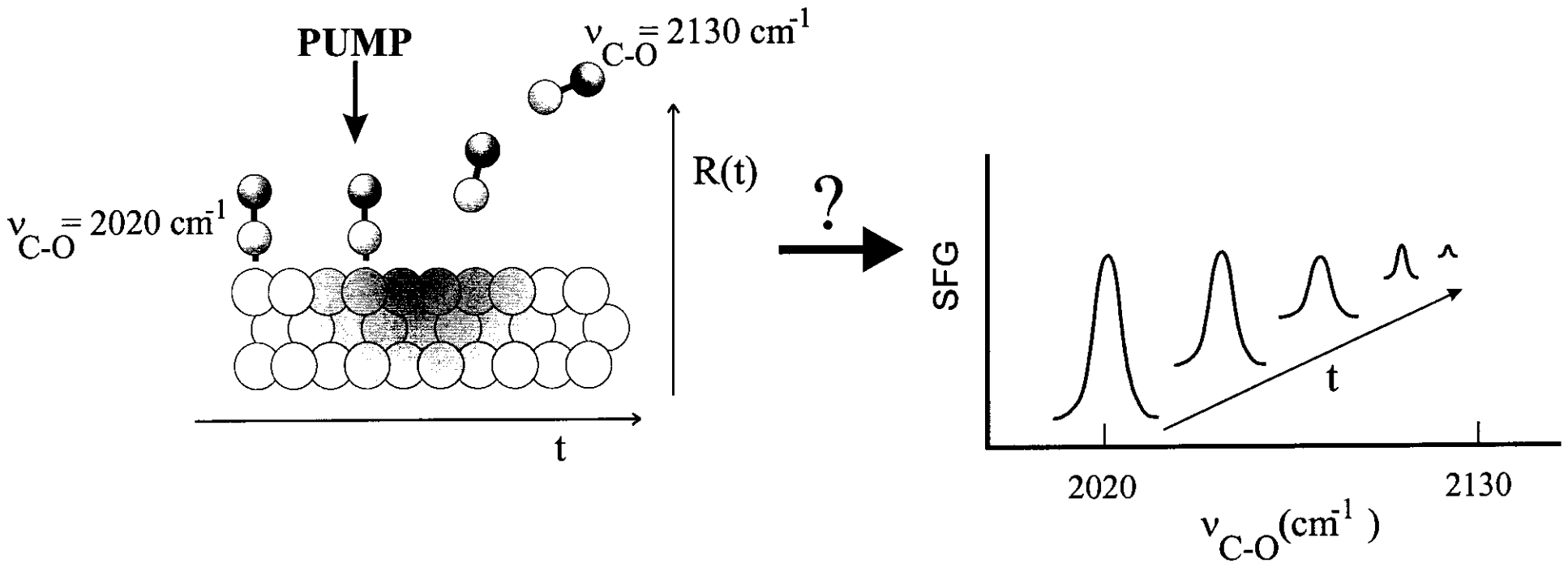
→ Compare to ~2 ps vibrational lifetime of CO/Pt(111)*

$$I(\omega) = \frac{\gamma_{\mathrm{hop}} n_{\mathrm{exc}} (2\Gamma)^2 / (1 + n_{\mathrm{exc}})}{[\omega'^2 - \Gamma^2]^2 + [\gamma_{\mathrm{hop}}(\omega' + \Gamma) + \gamma_{\mathrm{hop}} n_{\mathrm{exc}}(\omega' - \Gamma)]^2}$$

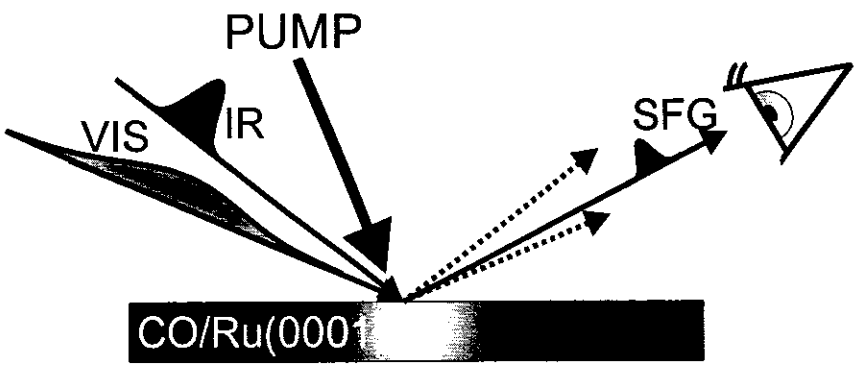
*J.D.Beckerle, et al.JCP95 (1991) 5403.

Time-resolved SFG spectroscopy

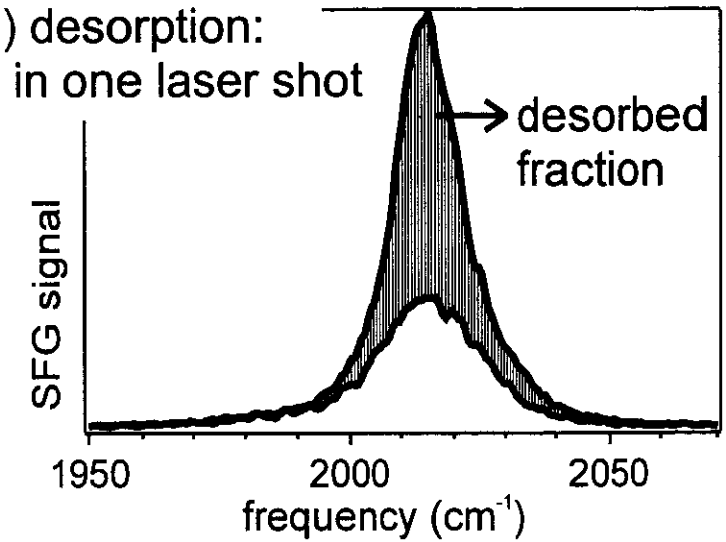




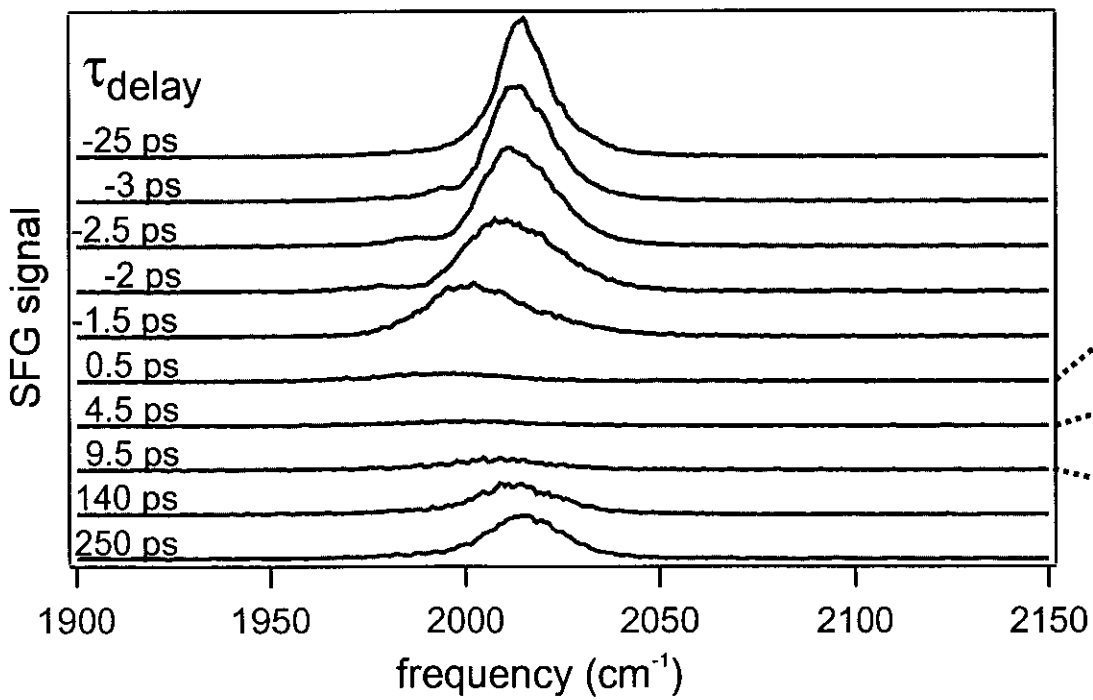
Time-resolved desorption of CO from (√3x√3)CO/ Ru(0001)

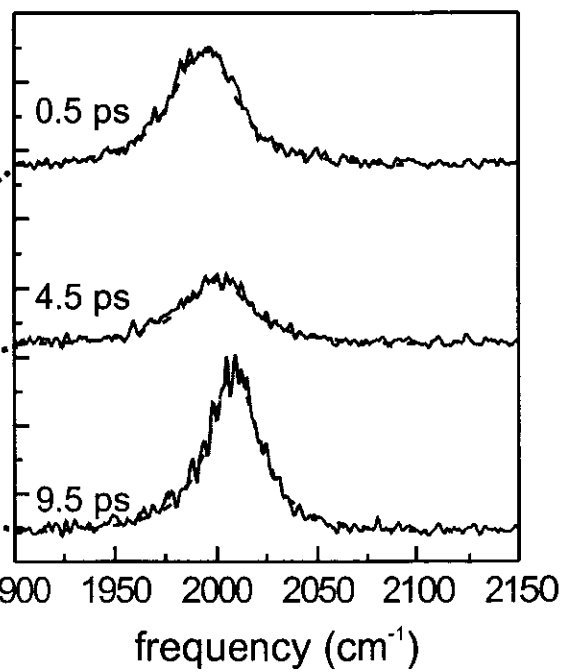


SFG spectra before (-25 ps)
and after (250 ps) desorption:
~30% desorption in one laser shot

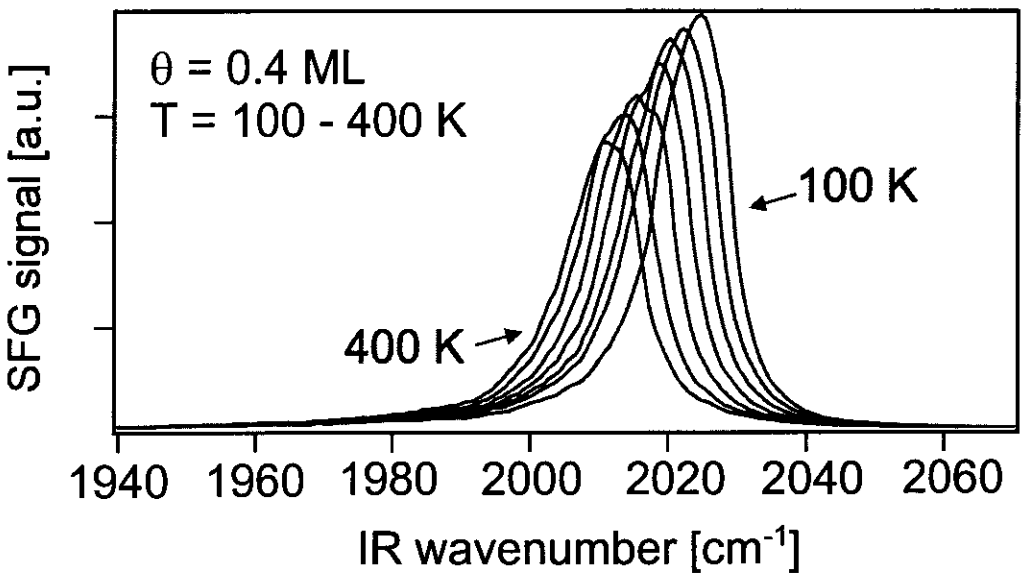


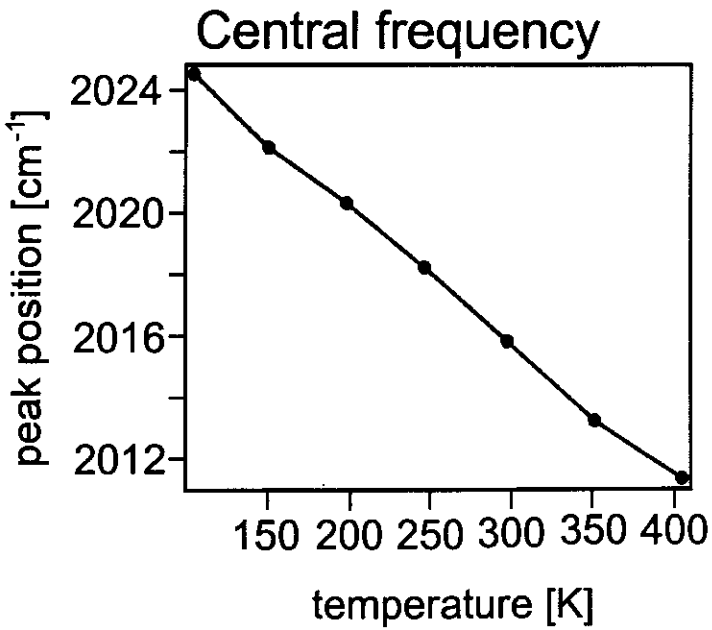
spectroscopic 'snapshots' during desorption process:





Temperature dependence CO absorption

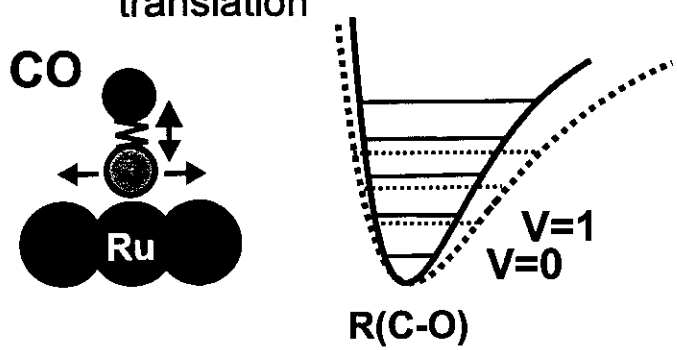




→ Under ambient conditions, temperature dependence of C-O stretch vibration can be accounted for by anharmonic coupling to thermally populated frustrated translation mode (47 cm^{-1})*

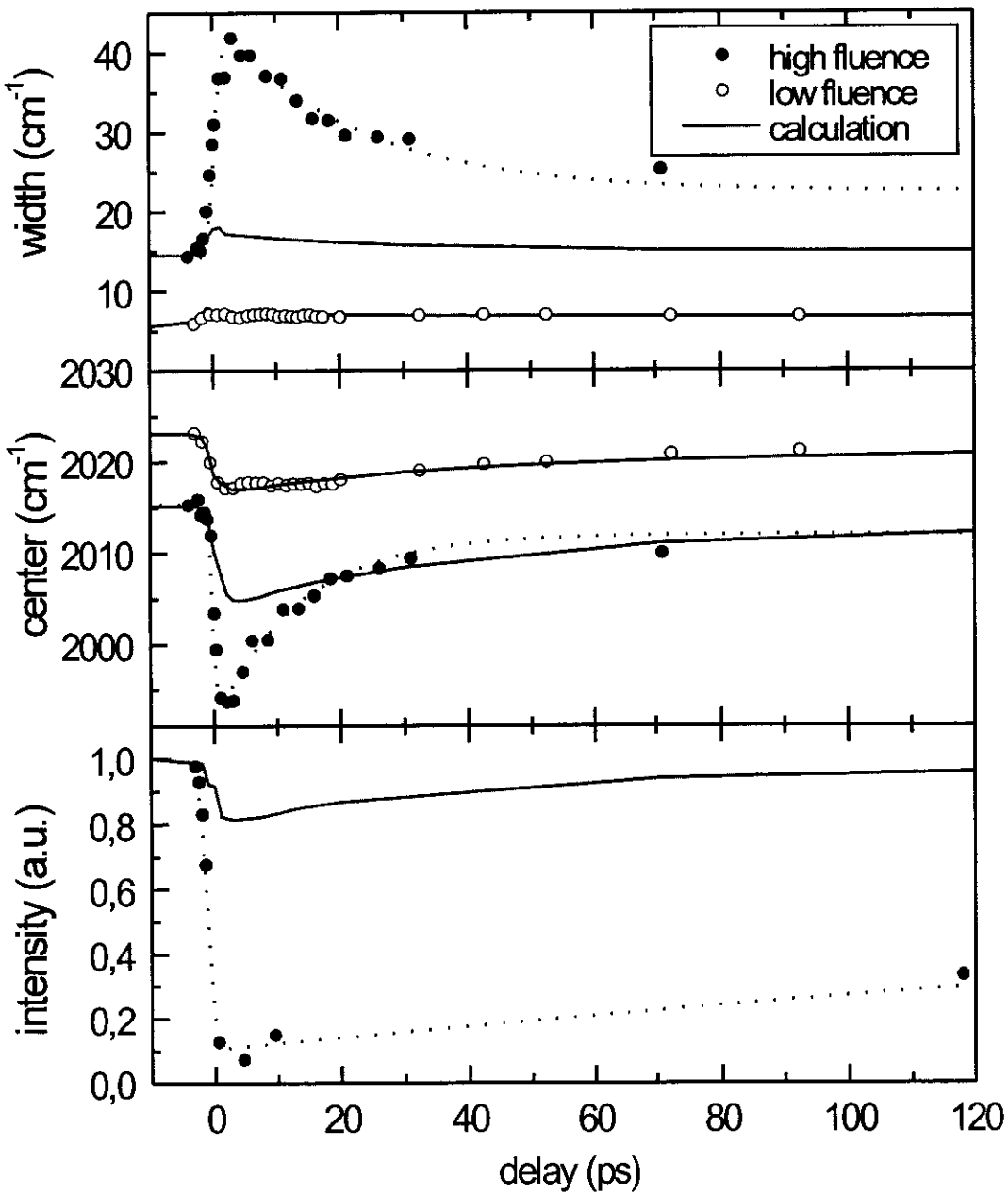
Also for time-resolved experiments?

→ Redshift with increasing amplitude of frustrated translation



* Persson et al., Phys. Rev. B, 56 (1985) 10645

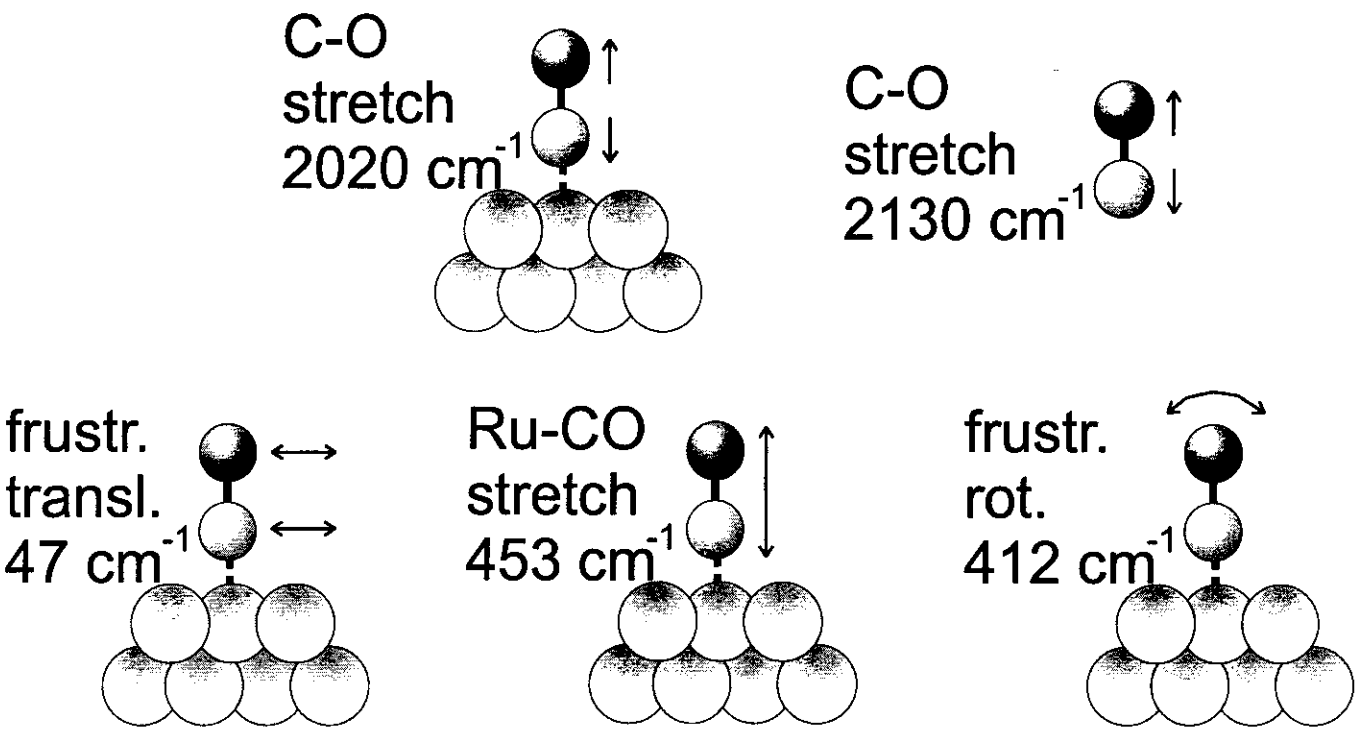
Time-resolved desorption of CO from Ru(0001)



Calculation assuming energy exchange between frustrated translation (47 cm^{-1}) and substrate. Frustr. transl. mode is anharmonically coupled to C-O stretch:

- GOOD description for low fluence
- poor description for high fluence

Interpretation of time-resolved data



effect of thermal excitation on C-O stretch:

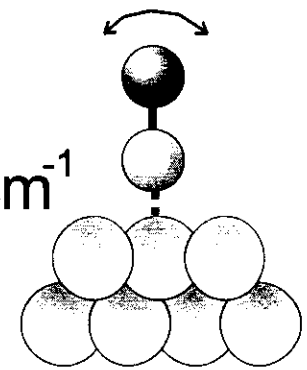
weak redshift blueshift *redshift*

For high fluence: T_{phon} > 1000 K. Hence also thermal excitation of frustrated rotation and Ru-CO stretch vibration.

Strong redshift due to frustrated rotation dominates over blueshift from Ru-CO stretch from desorbing molecules

Interpretation of time-resolved data

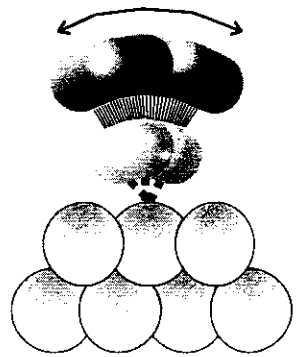
Frustrated rotation is dominant cause for strong redshift and broadening.



High degree of thermal excitation of frustrated rotation then explains large decrease in SFG intensity around zero delay

$$\mathbf{P}^{SFG} = \chi^{(2)}(\omega_{SFG} = \omega_{IR} + \omega_{VIS}) : \mathbf{E}^{IR}\,\mathbf{E}^{VIS}$$

with $\chi^{(2)}_{RES} \sim \mu_{\perp}^{CO}$



The decrease of $\mu_{\perp}^{CO}$ with increasing T accounts for decreased intensity, beside the decrease in T_2.

Conclusions

Broadband IR-VIS SFG spectroscopy allows for:

→ High-resolution- both in time and spectral domain-, very sensitive surface spectroscopy

Non-linear IR data:

→ Direct observation of delocalization of excess vibrational energy through dipole-dipole coupling by disappaerance of hot-band.

Time-resolved data:

→ Spectroscopy of adsorbates under desorption conditions: new information on mode coupling at surfaces

Co-workers: Christian Hess, Stephan Funk, Daniel Denzler, Martin Wolf and Gerhard Ertl

Thanks: Huib Bakker, Tony Heinz