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Femtosecond Laser Desorption of Molecules from Surfaces

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Distinctive Features of Molecular Desorption from metal surfaces using femtosecond laser excitation

1. *Higher desorption yield*
2. *Nonlinear yield dependence on laser fluence*
3. *High vibrational energy content*

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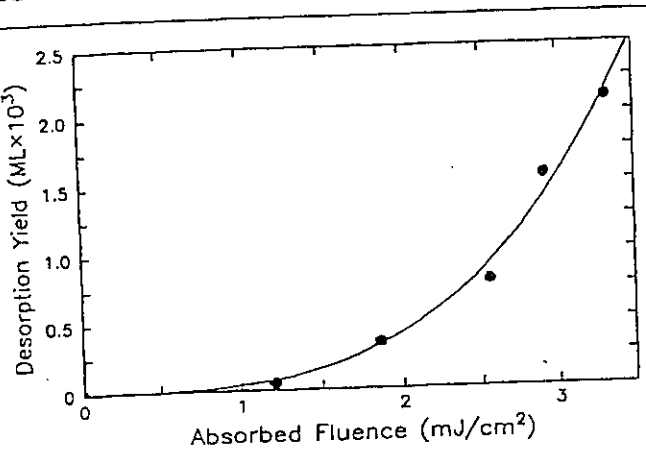

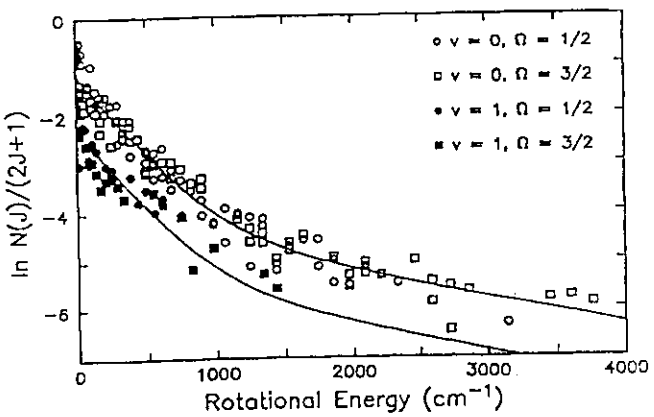

4. *Picosecond response time for the desorption process.*

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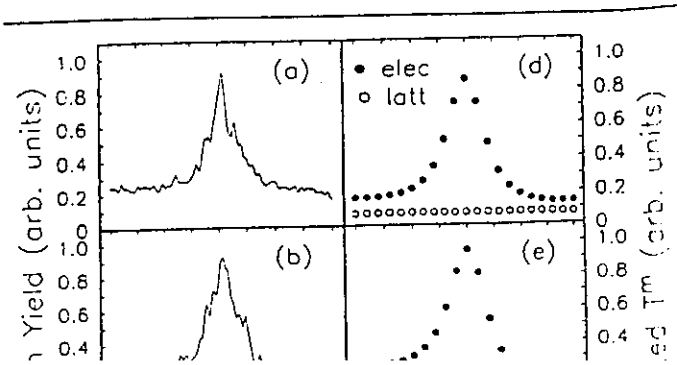

of the total adsorbed laser intensity $I(t)$ raised to the appropriate power to reproduce the fluence dependence, namely, $[I(t)]^{3.3}$. This results in a feature with a width (FWHM) of 450 fs. Since this width falls below the experimental value, it is clear that a finite response time for desorption is present.[21]

In Figs 1(b) and 1(c) data are presented for excitation with pulse pairs with unequal adsorbed fluences. For such conditions, the correlation trace exhibits a strongly asymmetric form. The desorption yield is observed to be higher when the weak pulse precedes the strong one

Methods of Measurement of (picosecond) Response Time

Two- pulse Correlation

- *Simple in concept*

- *Complex in real experiment, particularly involving samples in UHV systems*
- *With two pulses, further complicates avoiding unwanted effects due to beam profile variations (from alignment) and self-focusing from optical elements*

Methods of Measurement of (picosecond) Response Time

Changing width of excitation pulse

- *Very simple with regenerative amplifier system*
- *No additional optical elements*
- *Can monitor pulse width using FROG (and beam profile with CCD Camera.)*

Changing pulsewidth comes with frequency chirping, and the theoretical work of D.A. Micha and Z. Yi (Chem Phys Letts, 1998) predicts that …

Optical Control of desorption yields using frequency chirped light pulses

Optical control of yields of CO photodesorbed from Cu(001) by chirped light pulses: density matrix theory and calculations

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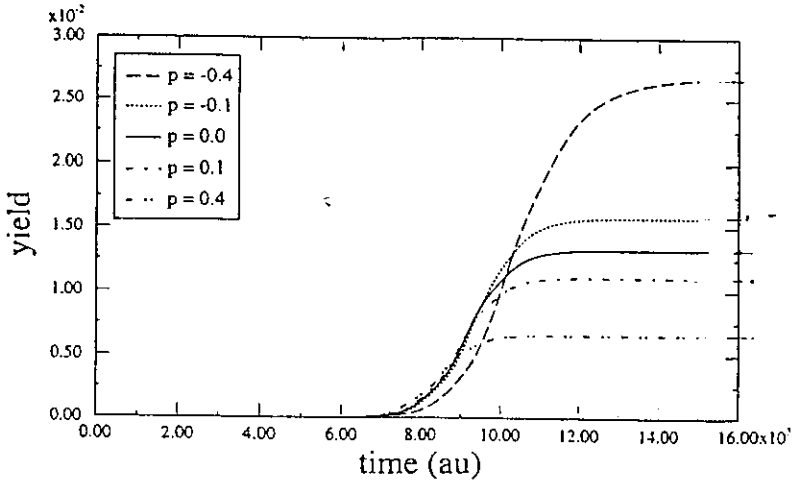
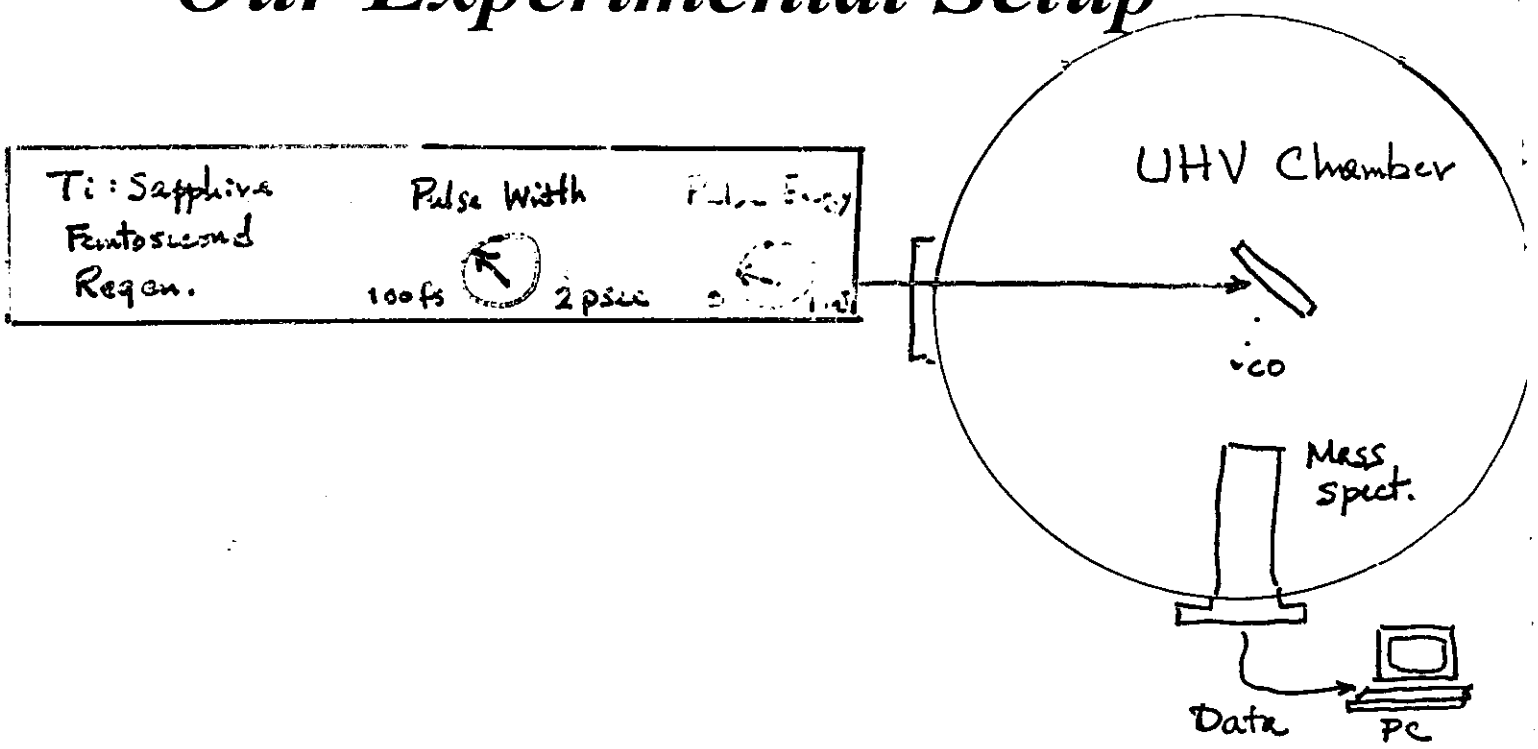


Fig. 4. Positive and negative chirping effects on photodesorption yields.

Predictions:

- *Negatively chirped (frequency decreasing) pulses more effective in desorption than positively chirped pulses*
- *~ 40% effect for 10% chirp*

Our Experimental Setup



- Must maintain the same beam profile while changing pulsewidth and pulse energy

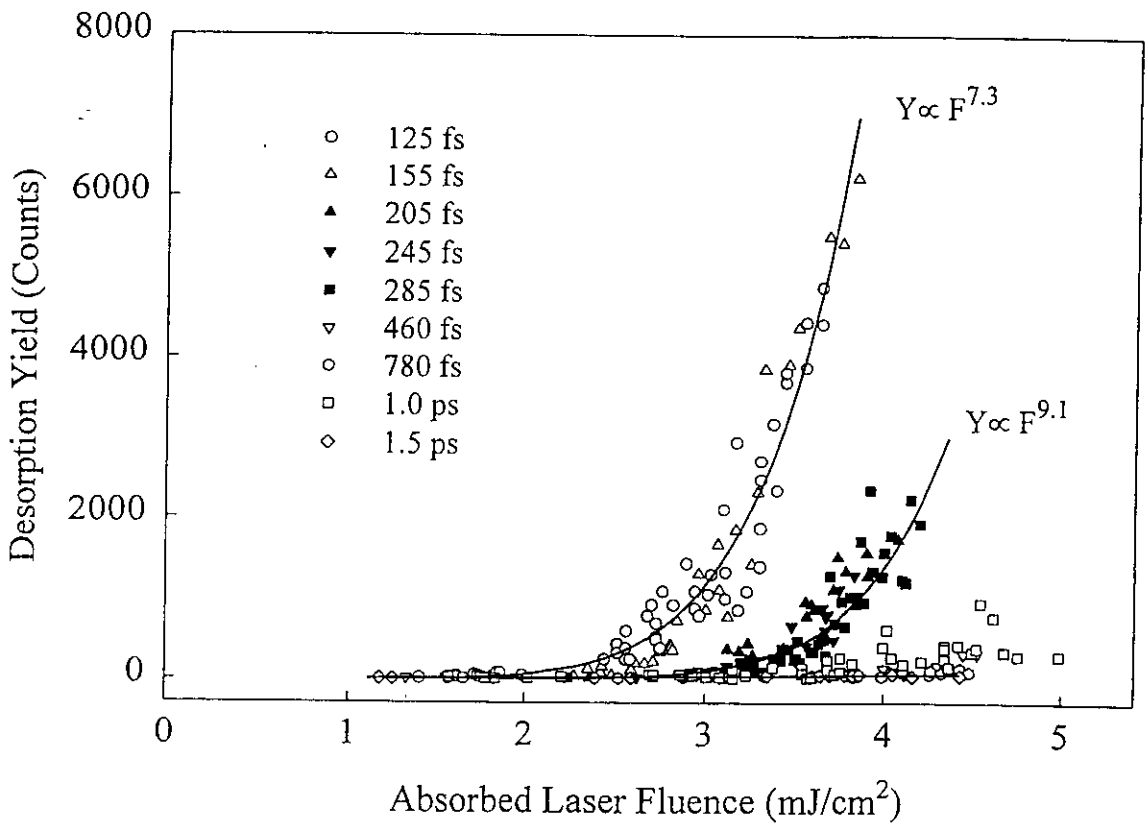
- Given the expected power dependence, must avoid self-focusing in optical elements
  → reflective optics used whenever possible

- Beam profile monitored by CCD camera
  Beam pulse width and frequency chirp monitored by FROG

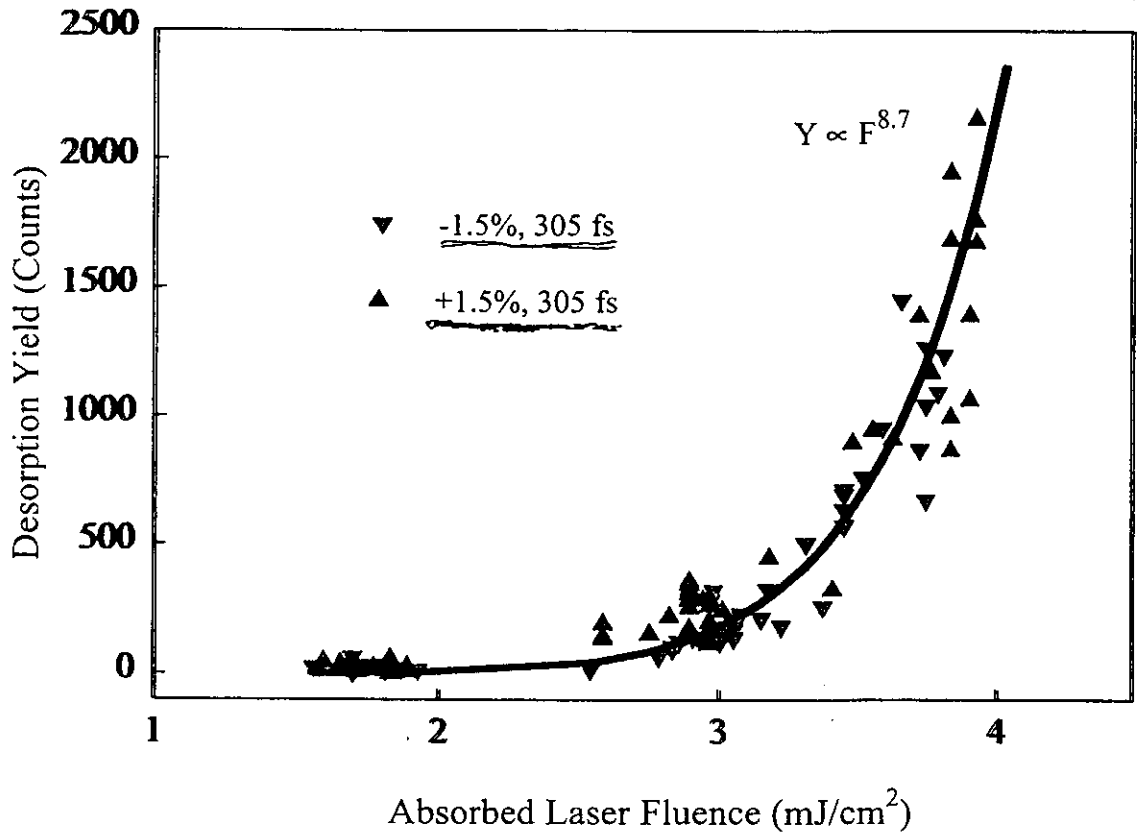
Our data for CO/Pt(111)

(100 counts ~ a few times 10^{-5} ML)

Signal vanishes at pulse width > 500 fsec



Chirped pulse excitation: Negative chirp and Positive Chirp



Expected enhancement (negative over positive chirp at 1.5% chirp): 5 – 8 %

Our Results on CO Desorption from Pt(111) compared with previous studies

- *high desorption yields? Yes*
- *nonlinear dependence on fluence? Yes*
- *subpicosecond response time? Yes*
  - *predicted effects due to frequency chirping not observed.*

Experimentally, our CO/Pt results are very similar to the CO/Cu results (PRL 96, NIST)

(In fact, all the (diatomic) systems studied so far behave rather similarly.)

How do these electrons, transiently at elevated temperatures, affect the desorption of molecules from surfaces?

Two (related) physical pictures have been proposed:

1. *DIMET (Desorption Induced by MULTIPLE Electronic Transition) : Make connection to the well-known DIET process, enhanced by multiple transitions within a short time due to the high density of hot electrons.*

2. *Electronic Friction Model: Make connection with vibrational lifetime of molecules on surfaces – much shorter on metallic surfaces, attributed to energy exchange by electron-hole pair generation.*

The CO/Pt(111) system compared with the CO/Cu(100) system

- ***One molecule, two metallic surfaces***
- ***The relevant parameters:***

	Desorption kinetic first order?	Prefactor	E_{ads}	$\lambda_{excitation}$
CO/Pt	yes	10^{15}-10^{16} s^{-1}	1.1 eV	800 nm
CO/Cu	yes	10^{15}-10^{16} s^{-1}	0.6 eV	400 nm

	e-h coupling	E_F
Pt	1.6 ps	8 eV
Cu	35 ps	7 eV

Yet, the desorption results are similar:

- ***desorption at a few mJ/cm^2 fluence***
- ***same power dependence (n=8+-1)***

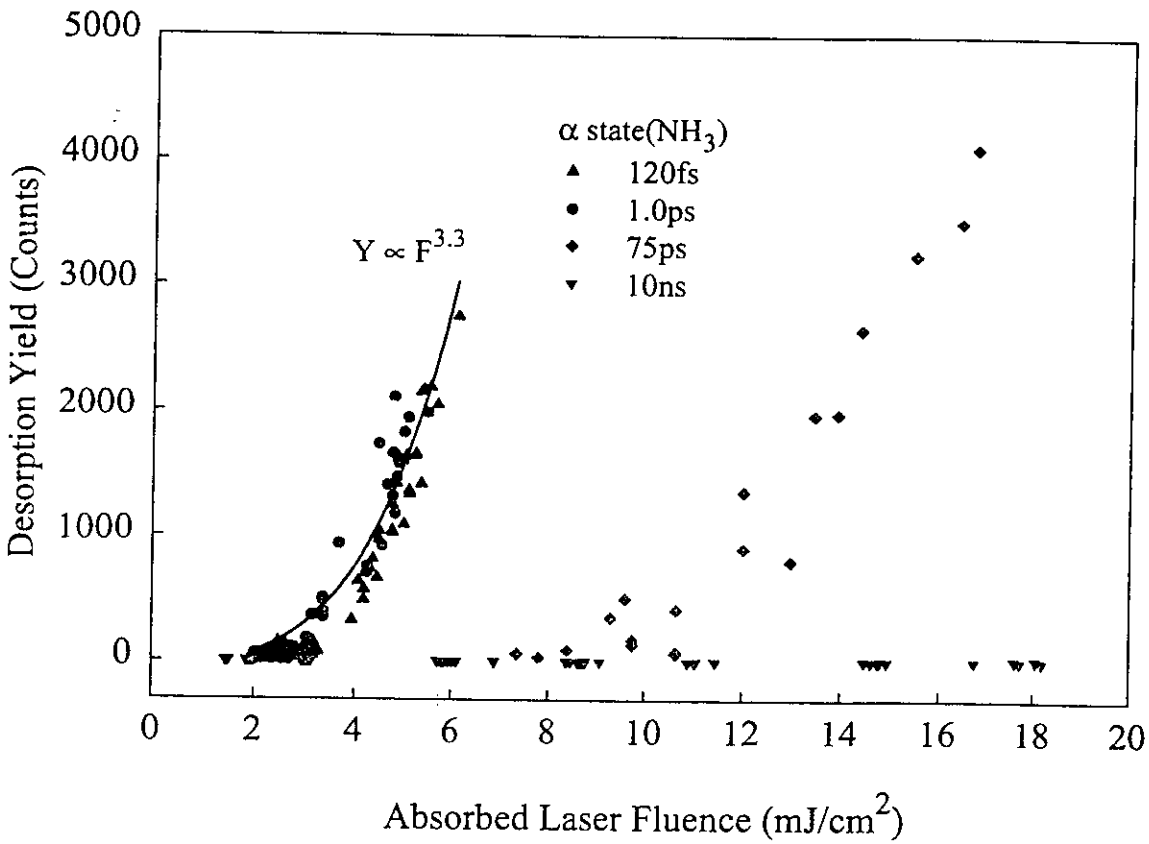
DIMET or Electronic Friction?

Appear to favor electronic friction because:

- ***Desorption result similar even though the hot electron energy distribution likely to be very different for Cu and Pt.***

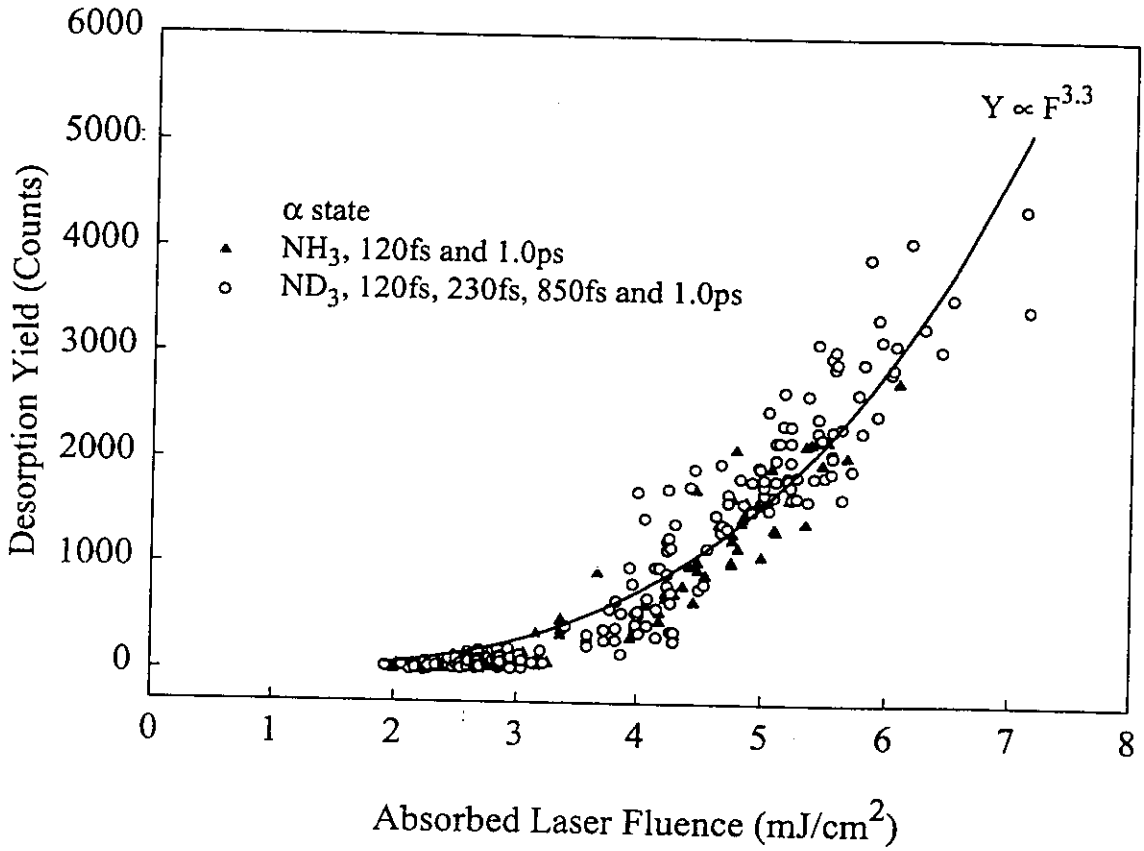
- ***Experimentally, the vibrational lifetimes of CO on Pt and CO on Cu are the same (about 2 ps).***

Femtosecond desorption of NH_3/ND_3 from Pt (111)



- **No subpicosecond time dependence**
- **No isotope effects**

Femtosecond desorption of NH_3/ND_3 from Pt (111)



- No subpicosecond time dependence
- No isotope effects

Conclusions

- **CO/Pt similar to CO/Cu (but not to CO/Ru!)**
- **NH_3 (ND_3)/ Pt - 'mostly thermal'**
- **Electronic Frictional Model is a good description of the process**

Questions for future:

Why only diatomics?

Can desorption process be controlled by chirped pulses with much higher chirp rate?