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ADRIATICO RESEARCH CONFERENCE on

LASERS IN SURFACE SCIENCE

11-15 September 2000

Miramare - Trieste, Italy

Vibrationally assisted DIET

or

How to do photochemistry with low energy photons

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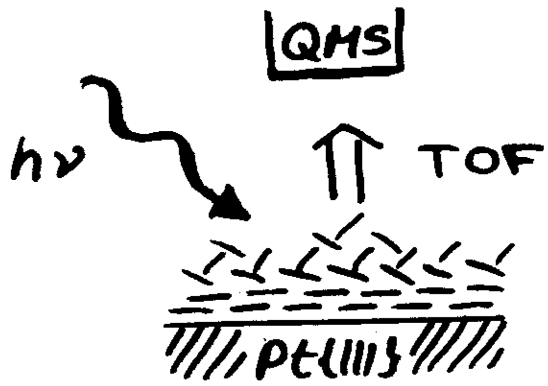
Vibrationally assisted DIET
or
How to do photochemistry with low energy photons

Thanks to: R.J. Levis, D.A. King

System: C_6H_6 / Pt{111}
1-20 ML 100 K

Photons: 800 nm (1.55 eV)
150 fs - 200 ps

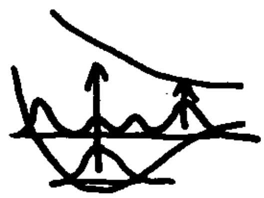


CPL 314 (1999) 389
JPC B 104 (2000) 3375

Examples for thermally assisted DIET/DIMET

- CH_3 / GaAs (100) Xin, Zhu, CPL 265, 259 (1997)

  $P_{des}(v=3) \sim 500 \times P_{des}(v=0)$



- NO / Cr_2O_3 (0001) Thiel et al CP 228, 185 (1998)

  theory + experiment

  T_{surf} : 100K .... 300K factor 2 increase in yield

- NO / Pt (111) Saalfrank, Kosloff JCP 105, 2441 (1996)

  DIET/DIMET theory

  T_{surf} : 0K .... 1000K factor 4 increase in yield

Common theme:

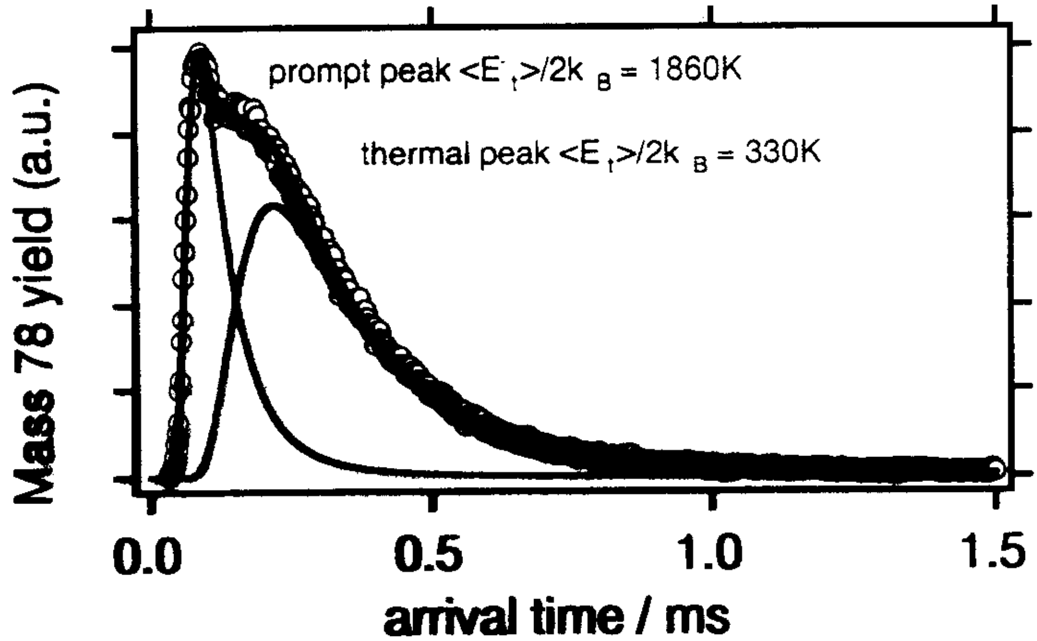
increase in steady state surface temperature leads to increased desorption yield

In our case: C_6H_6 / Pt (111)

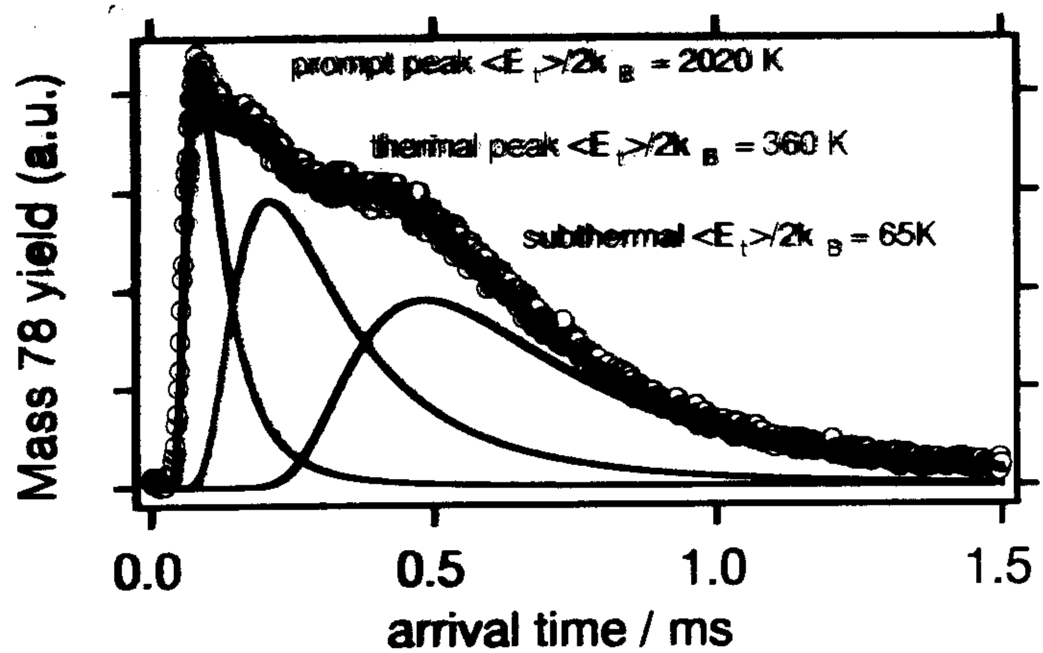
transient temperature rise caused by laser enables DIET process

Typical time-of-arrival spectra

3.8 ML



6.6 ML

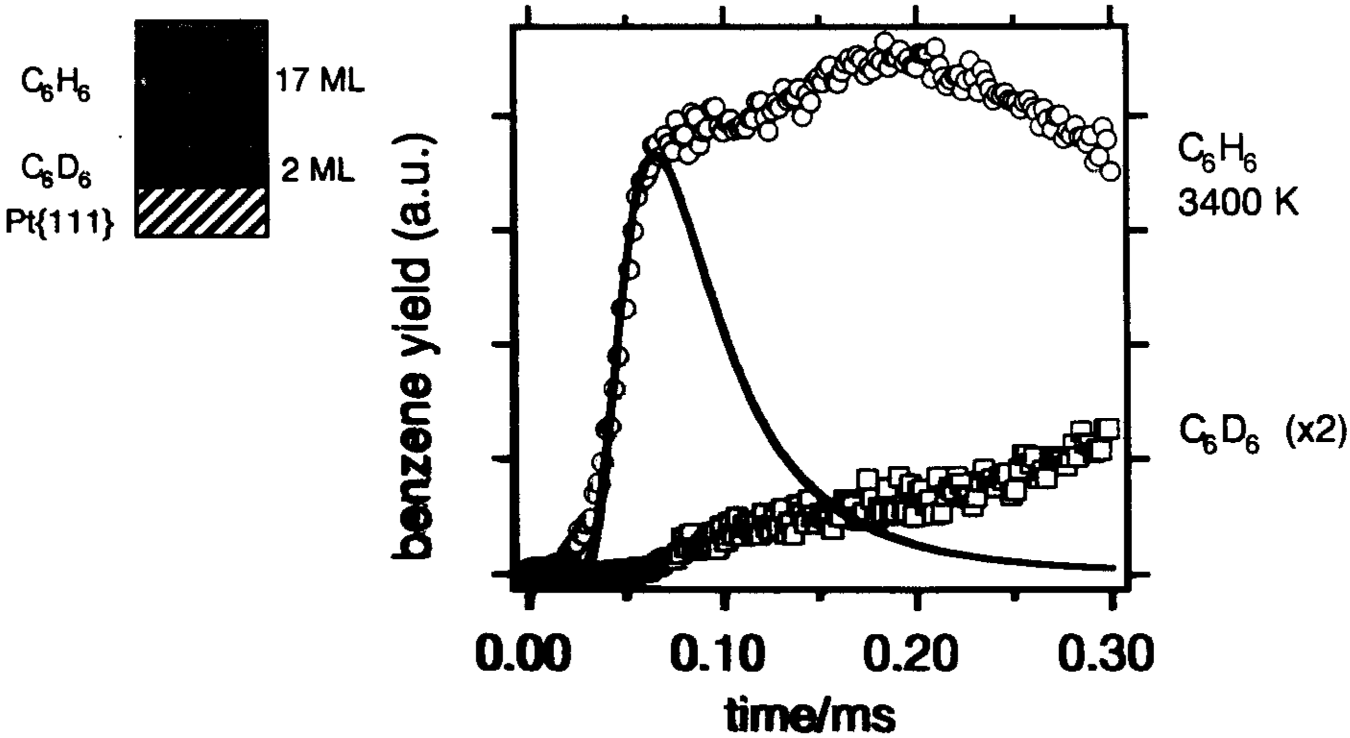


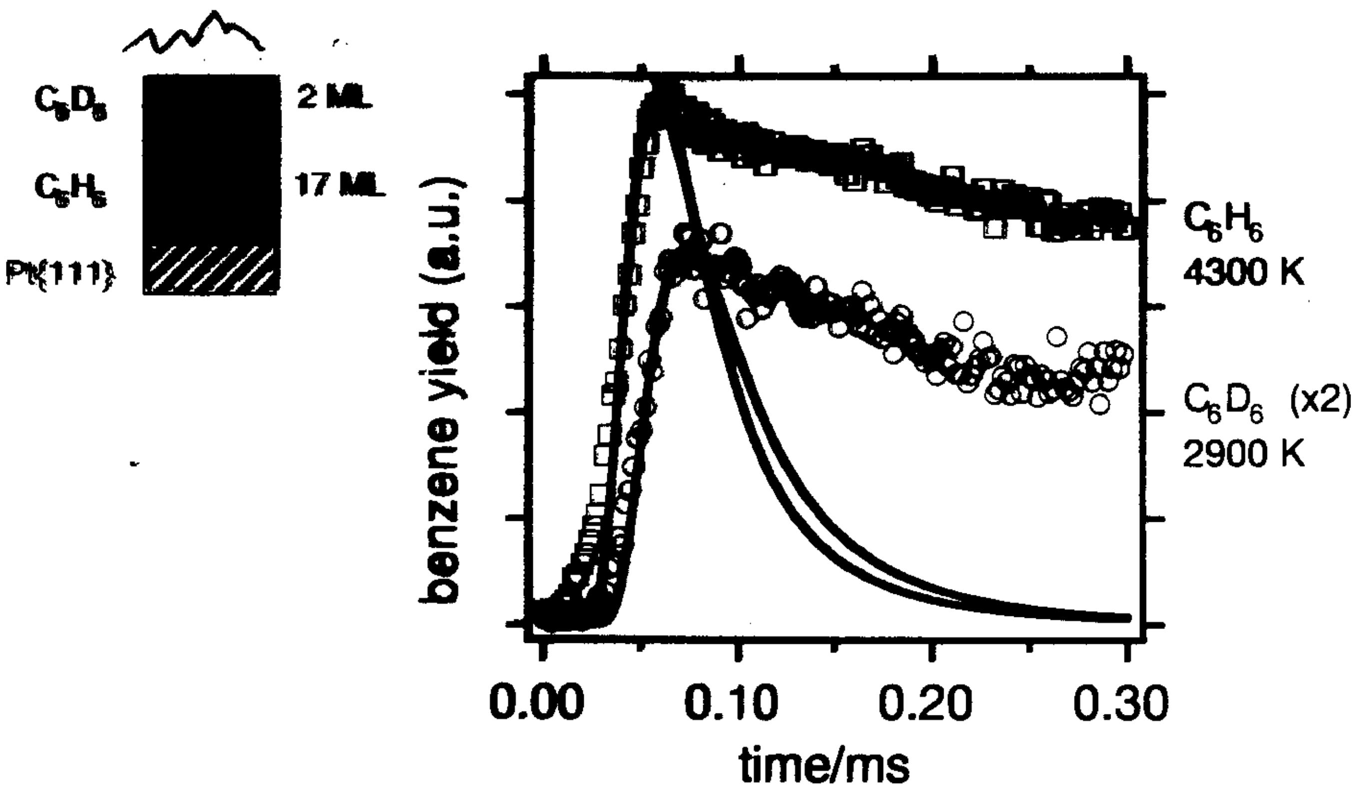
Maxwell-Boltzmann $f(t) = \frac{a}{t^4} \exp\left(\frac{-m}{2kT}\left(\frac{d}{t} - u\right)^2\right)$

$\langle T_{trans} \rangle = \langle E_{trans} \rangle / 2k$

Spatial origin of prompt peak

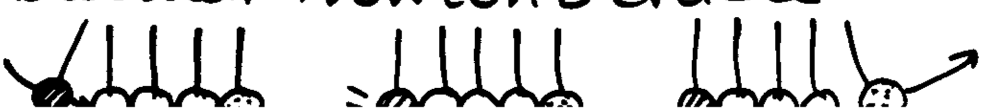
→ isotopic labelling



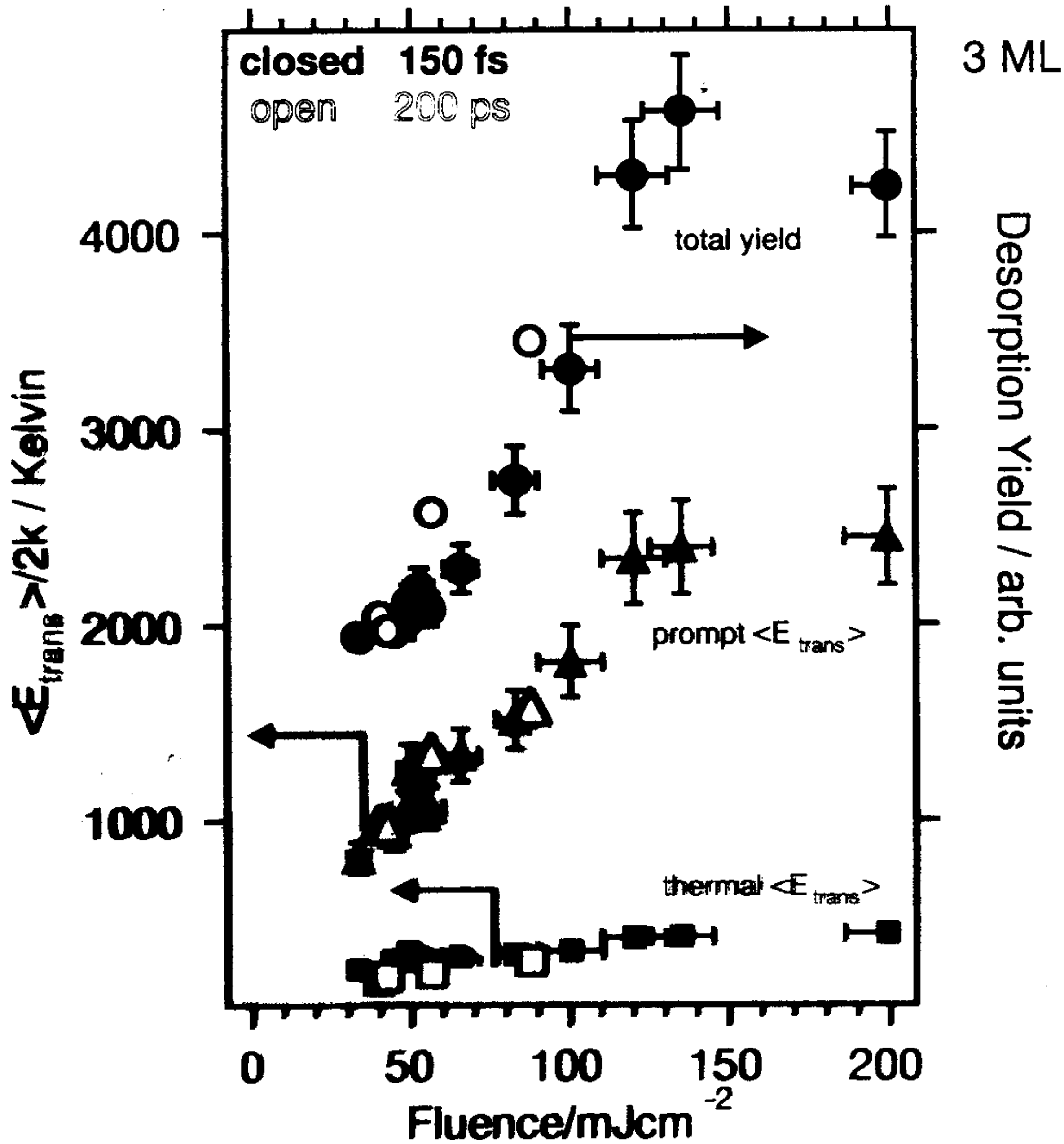


⇒ prompt molecules desorb from top of layer

⇒ molecular Newton's cradle



Fluence dependence



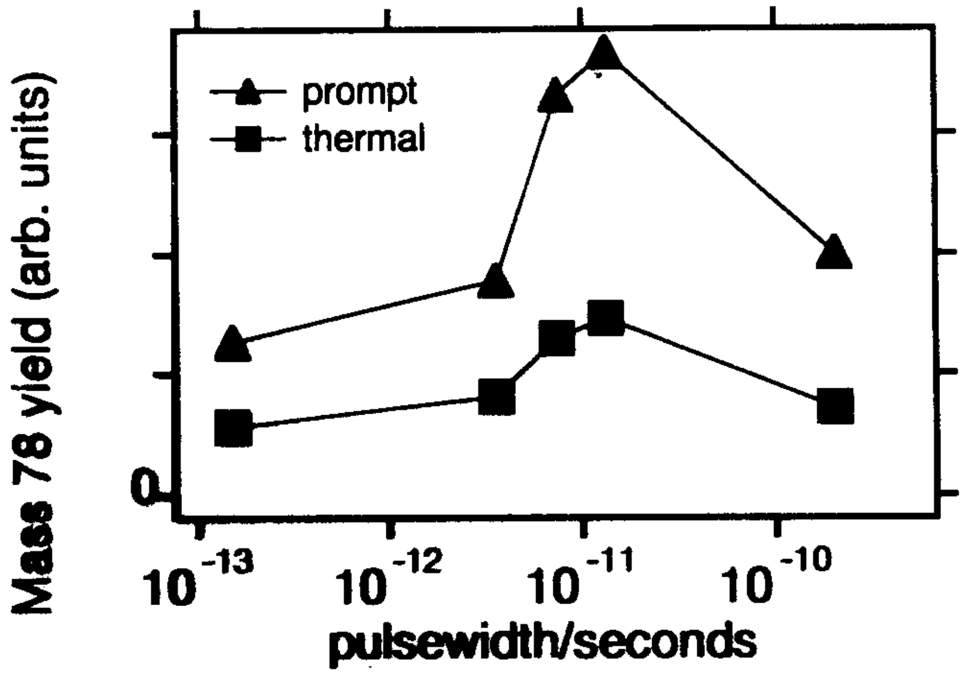
- yield nonlinear } in fluence
- <E_{trans}> linear }

⇝ laser induced thermal desorption?

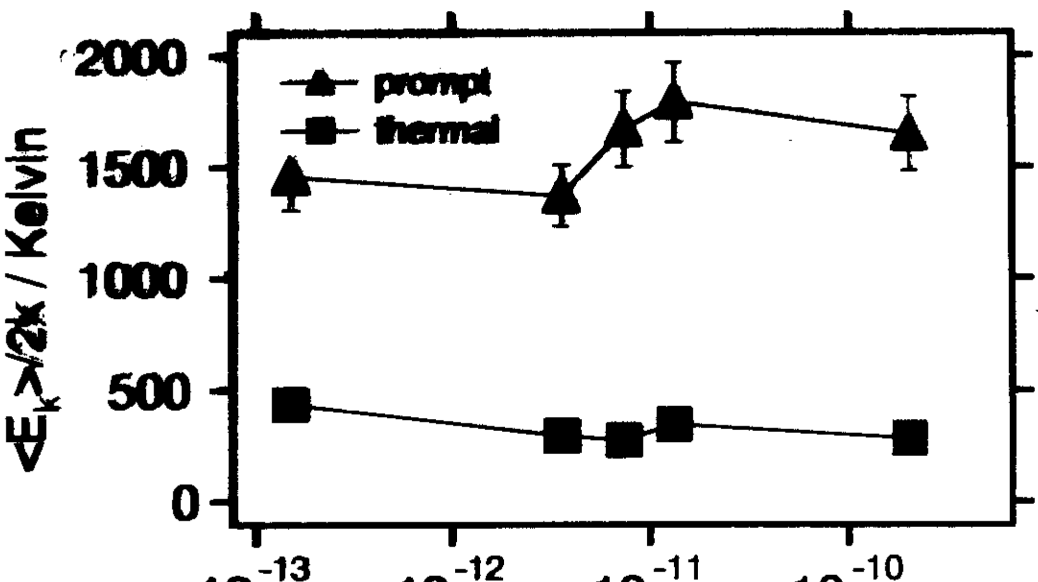
But why bimodal distribution even for 1 ML C_6H_6?

Pulsewidth dependence

Yield



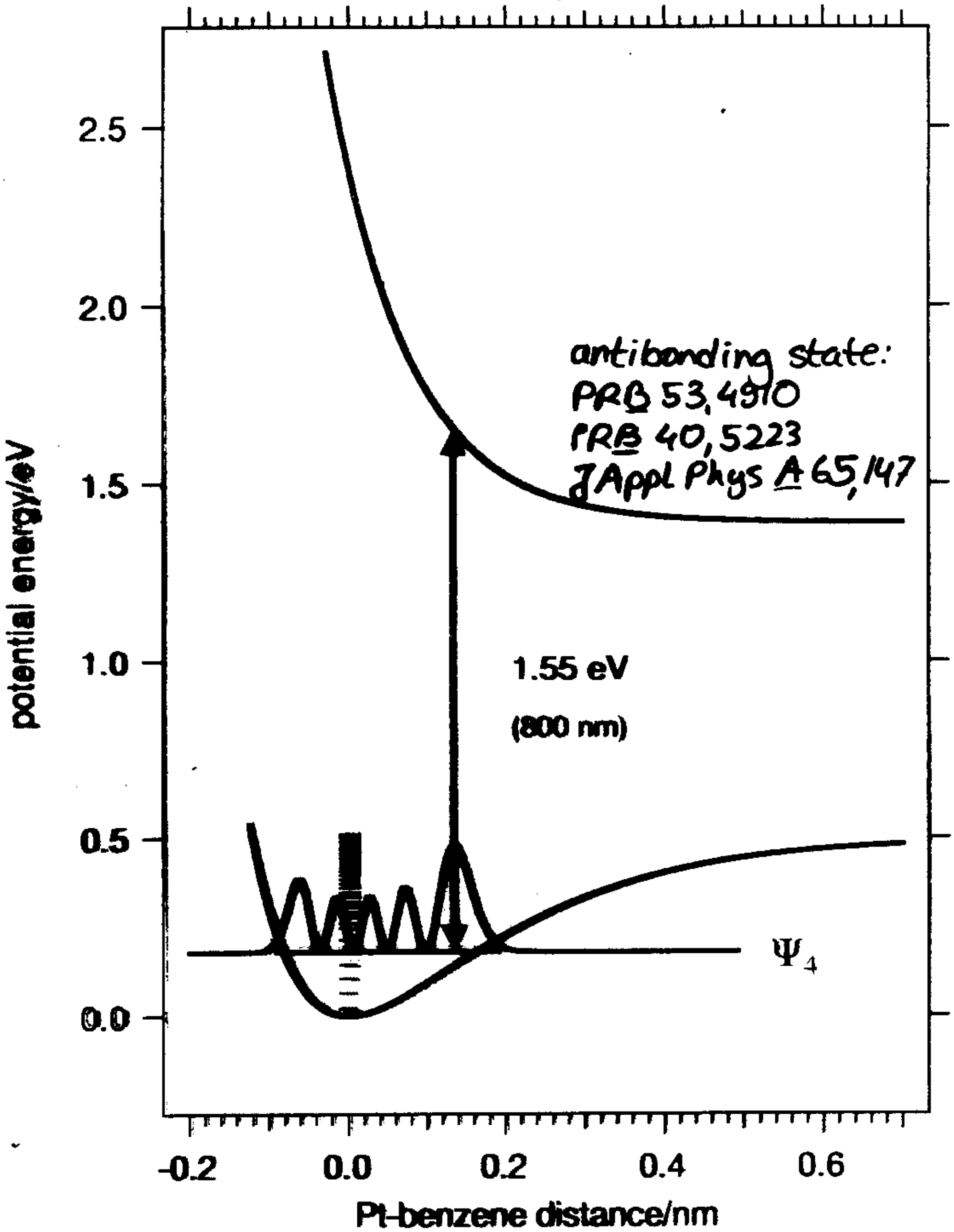
E_{trans}



→ optimal pulsewidth for desorption

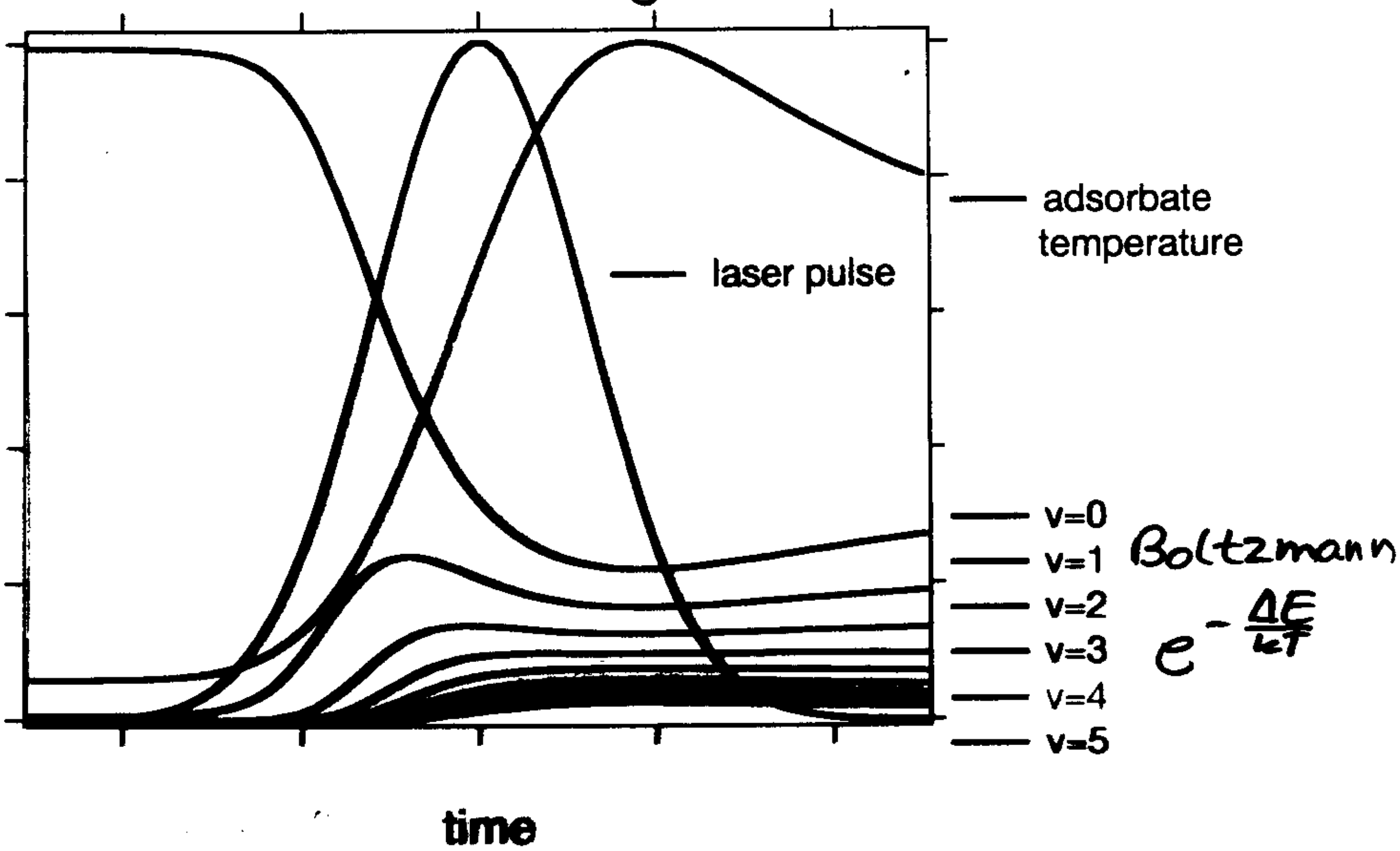
→ non-thermal

Vibrationally assisted DIET with near-IR photons



incident laser pulse acts as
- heat source first
- photon source next

A simple view of vibrationally assisted DIET



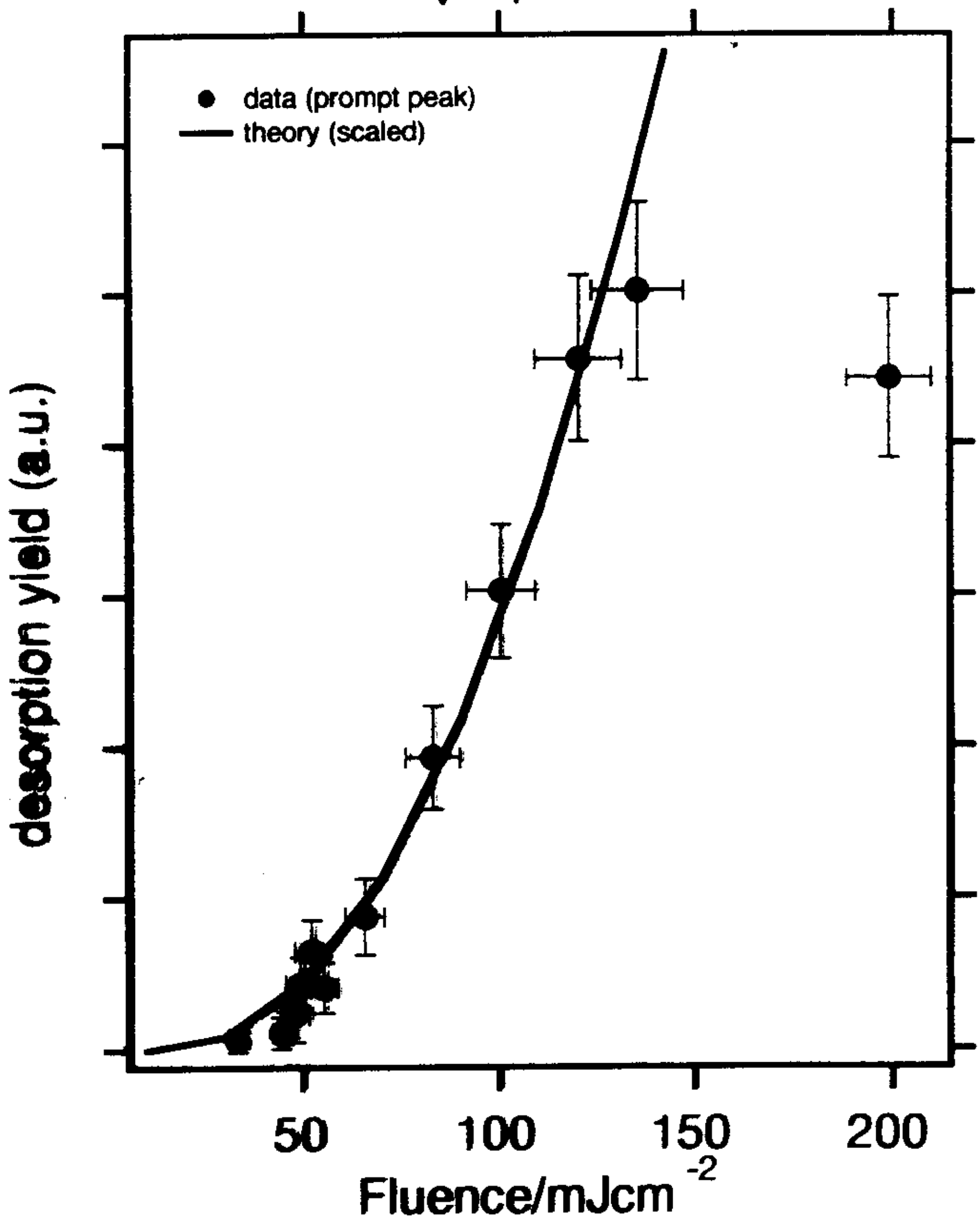
Prompt Yield

Σ occupation of v-states 4...18 × number of photons = yield

Thermal Yield

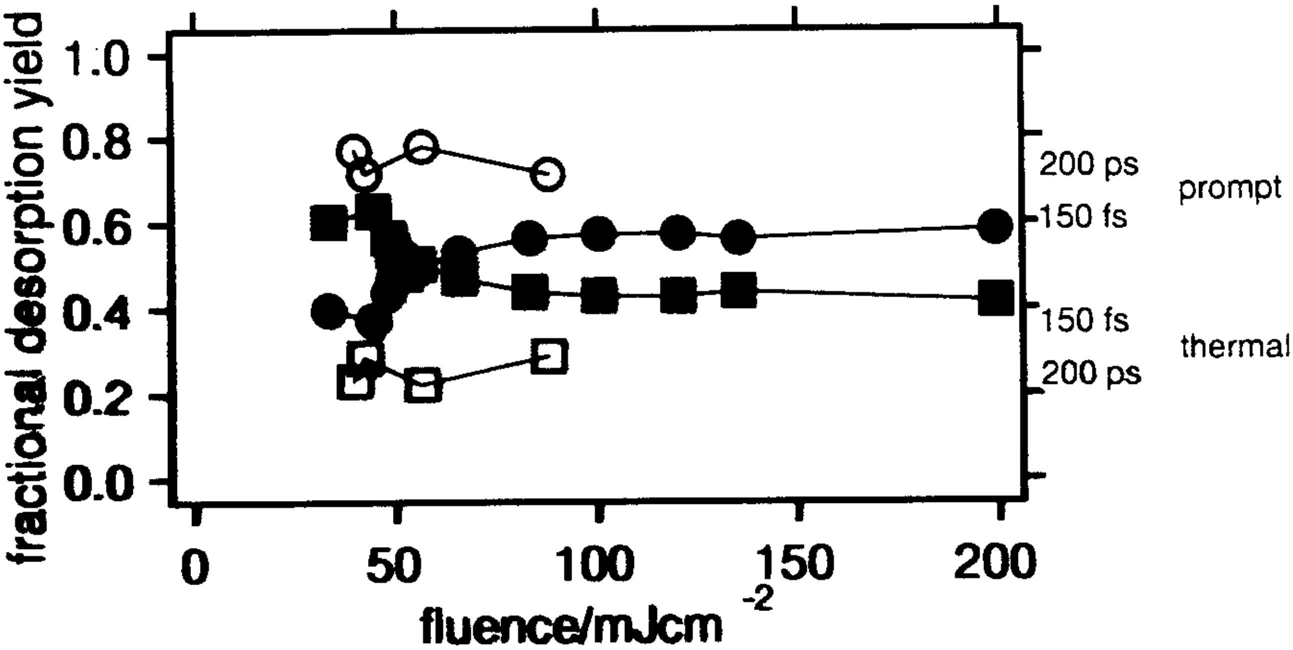
$$rate(t) \sim e^{-E_{des}/kT_{ads}(t)}$$

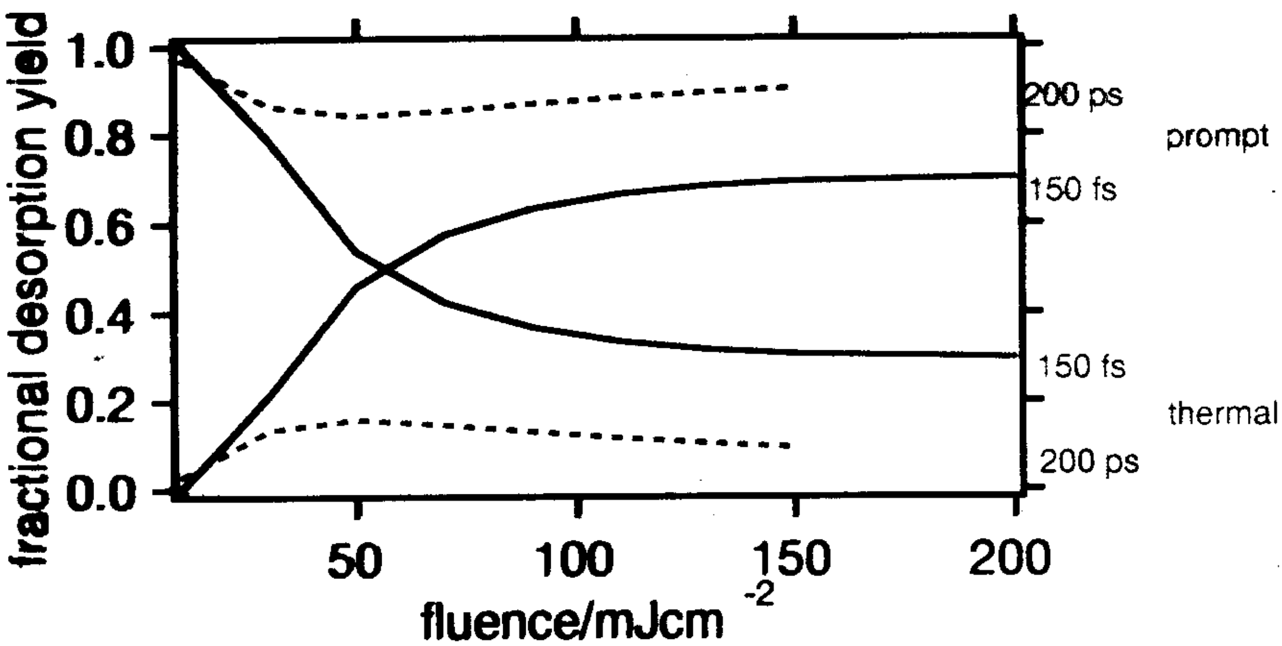
Fluence dependence
150 fs pulses



→ model reproduces nonlinear dependence of yield on fluence

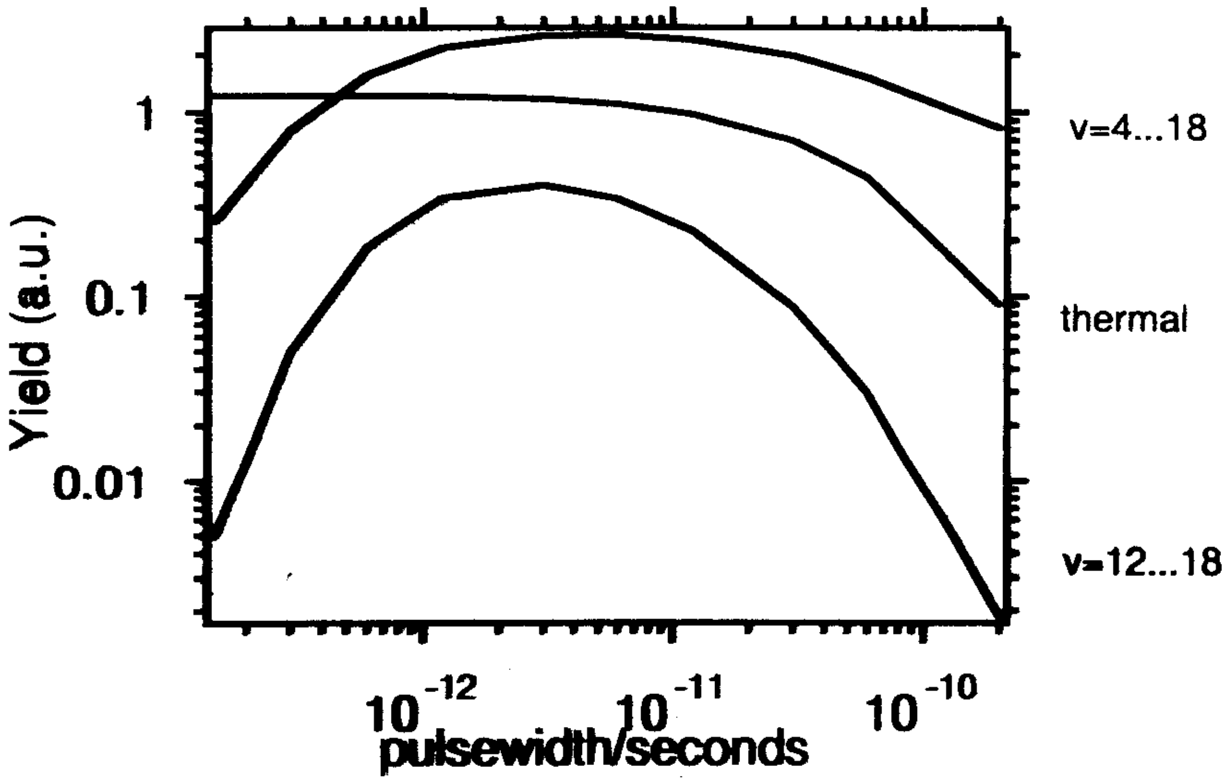
Contribution of prompt and thermal peaks to total yield





→ model reproduces increasing contribution of prompt peak at higher fluences

Pulsewidth dependence



- change in yield depends on <u>lower limit</u> of v-state

  ΔY (v=4...18) factor 10

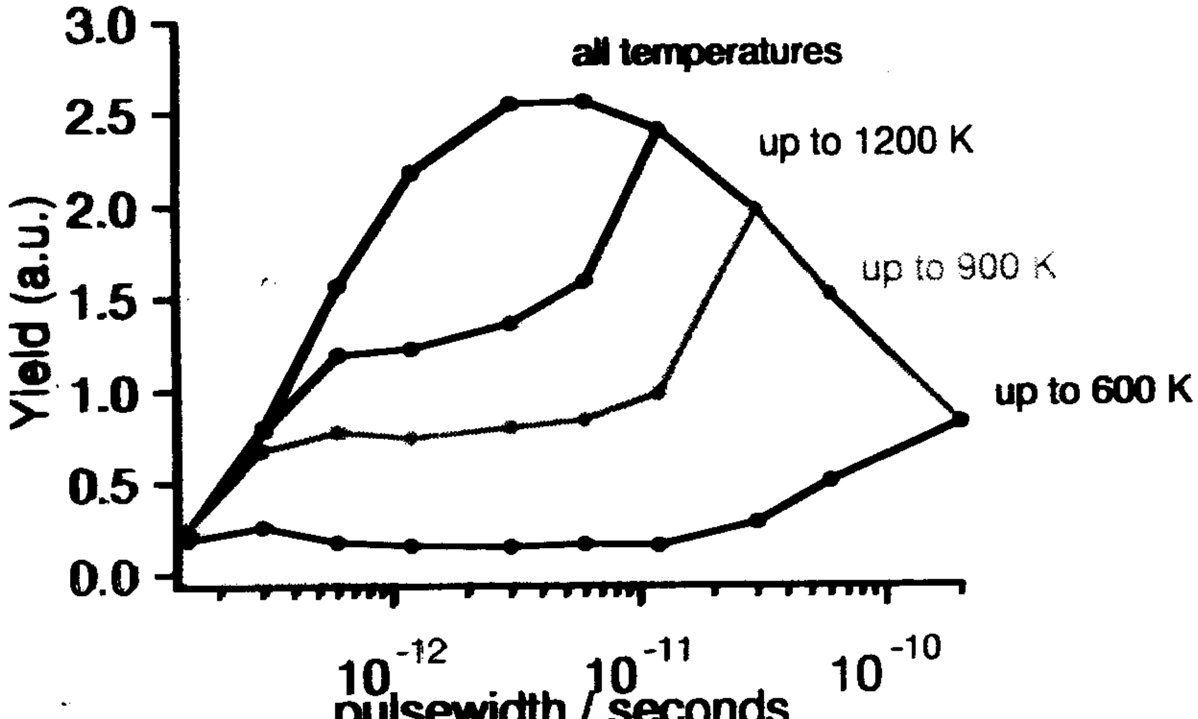
  ΔY (v=12...18) factor 80

→ data give information on relative energetic positions of ground and excited state

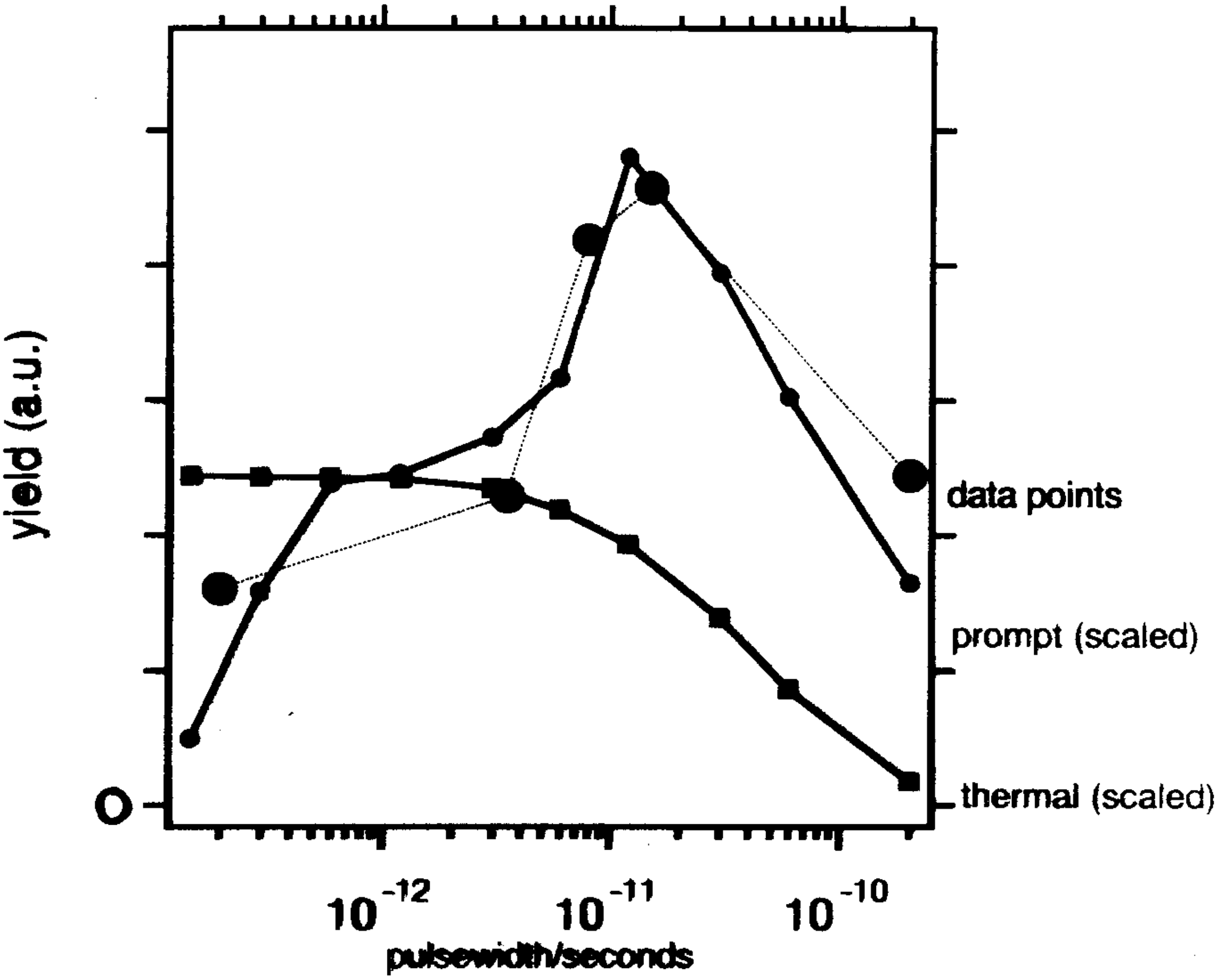
Pulsewidth dependence

To reproduce data, need to introduce upper limit to adsorbate temperature

Idea: explosive boiling at high adsorbate temperatures
→ whole layer lifts off



Pulsewidth dependence: comparison with data



- change in yield determined by number of v-states involved (lower limit to excitation)
- position of maximum determined by
  - Pt-adsorbate coupling
  - existence of maximum temperature before layer "lifts off"

Conclusion

- new spin on thermally assisted DIET
  → transient temperature rise in benzene adlayer enables DIET process with low-energy photons

Outlook

- pump-probe spectroscopy
  - pump pulse of even lower energy photons (e.g. $\lambda = 2\mu m$, $E = 0.62 eV$) heats adlayer
  - probe pulse of higher energy photons initiates DIET process