Quantum state-resolved reactive and inelastic scattering at gas-liquid and gas-solid interfaces

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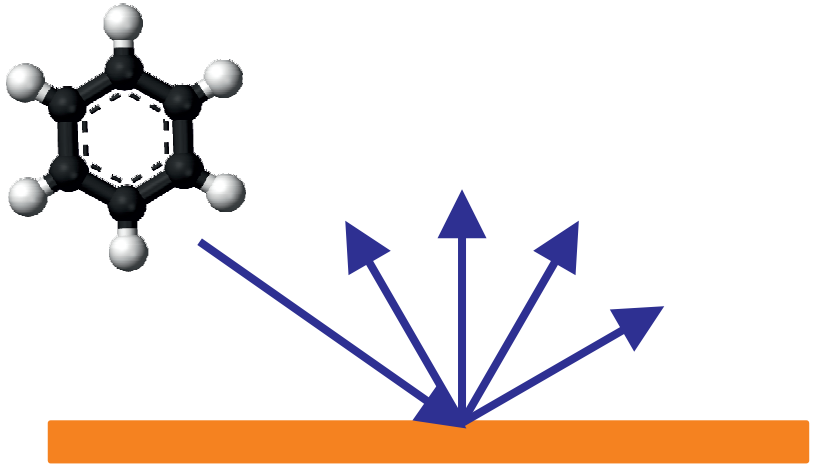
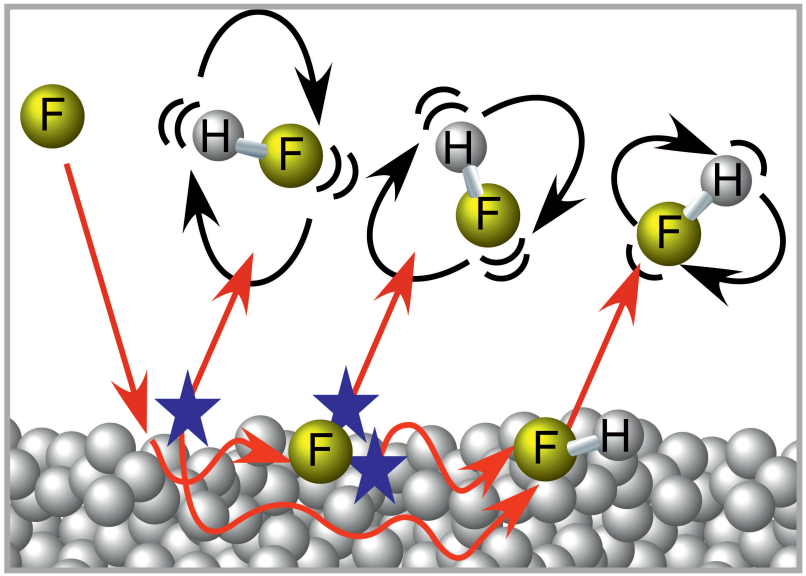
Motivation

Scattering of gas beams from liquid and solid surfaces:

inelastic scattering



reactive scattering



A. M. Zolot *et al.*, *JCP*, **129**, 194705, 2008

➡ heterogeneous chemistry
aerosols
heterogeneous catalysis

➡ dynamics of energy transfer at interfaces

➡ quantum-state resolution: observe all internal degrees of freedom (translational, rotational, vibrational)

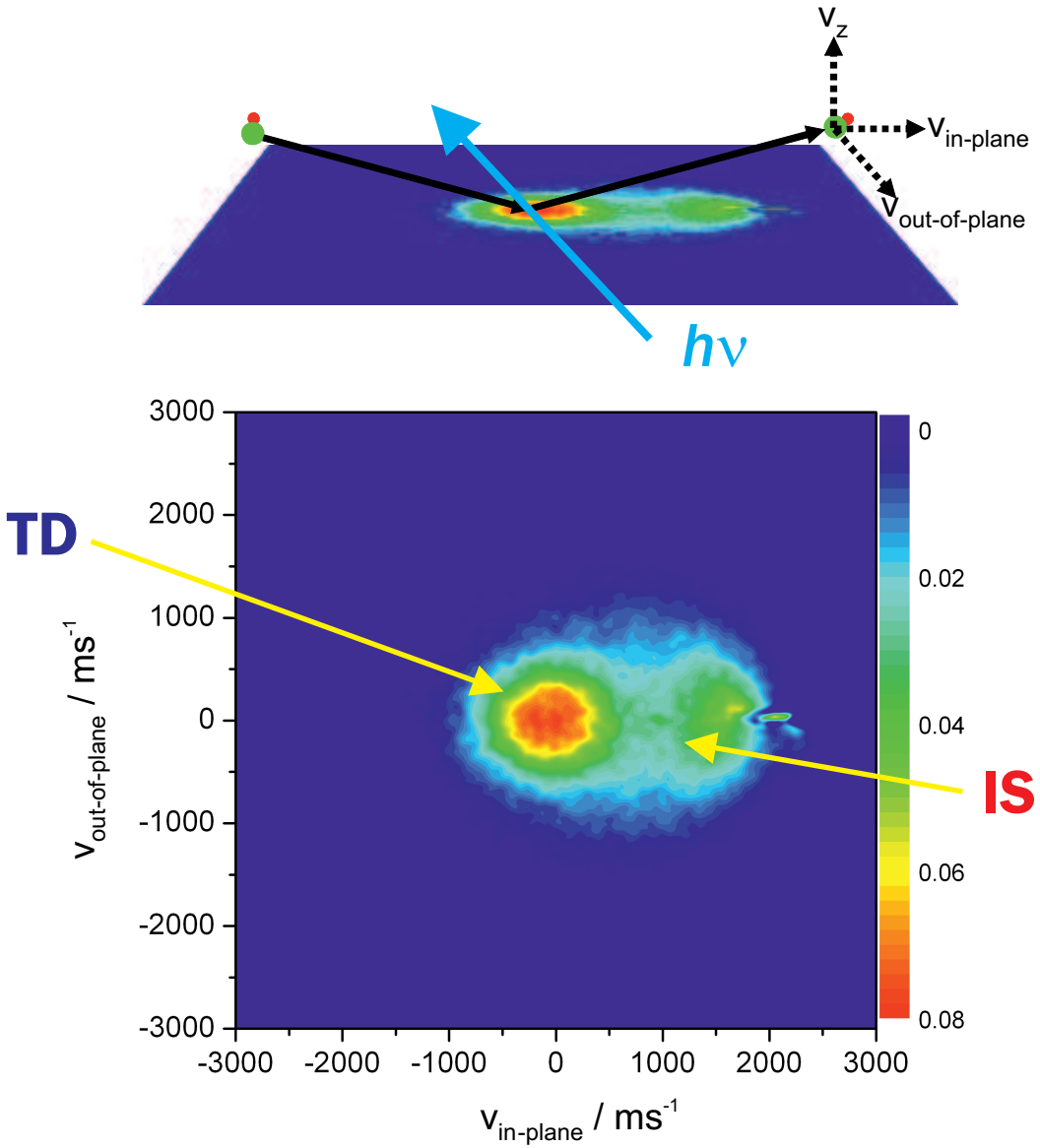
Experimental overview

How to obtain quantum-state resolution in a scattering process:

- gas: supersonic expansion, skimmed
  - ➡ cooling of internal degrees of freedom
  - ➡ control over collision energy
- heated gold surface (500 K): locally atomically flat (111) surface
  - ➡ no reaction dynamics
- Resonance-enhance multi-photon ionization (REMPI)
  - ➡ vibrational and rotational resolution
- Velocity-map imaging (VMI)
  - ➡ translational degree of freedom

Two main channels in a scattering process

Former work: HCl inelastically scattered from a heated gold surface [1]:



Velocity map image integrated over all rotational states of HCl:

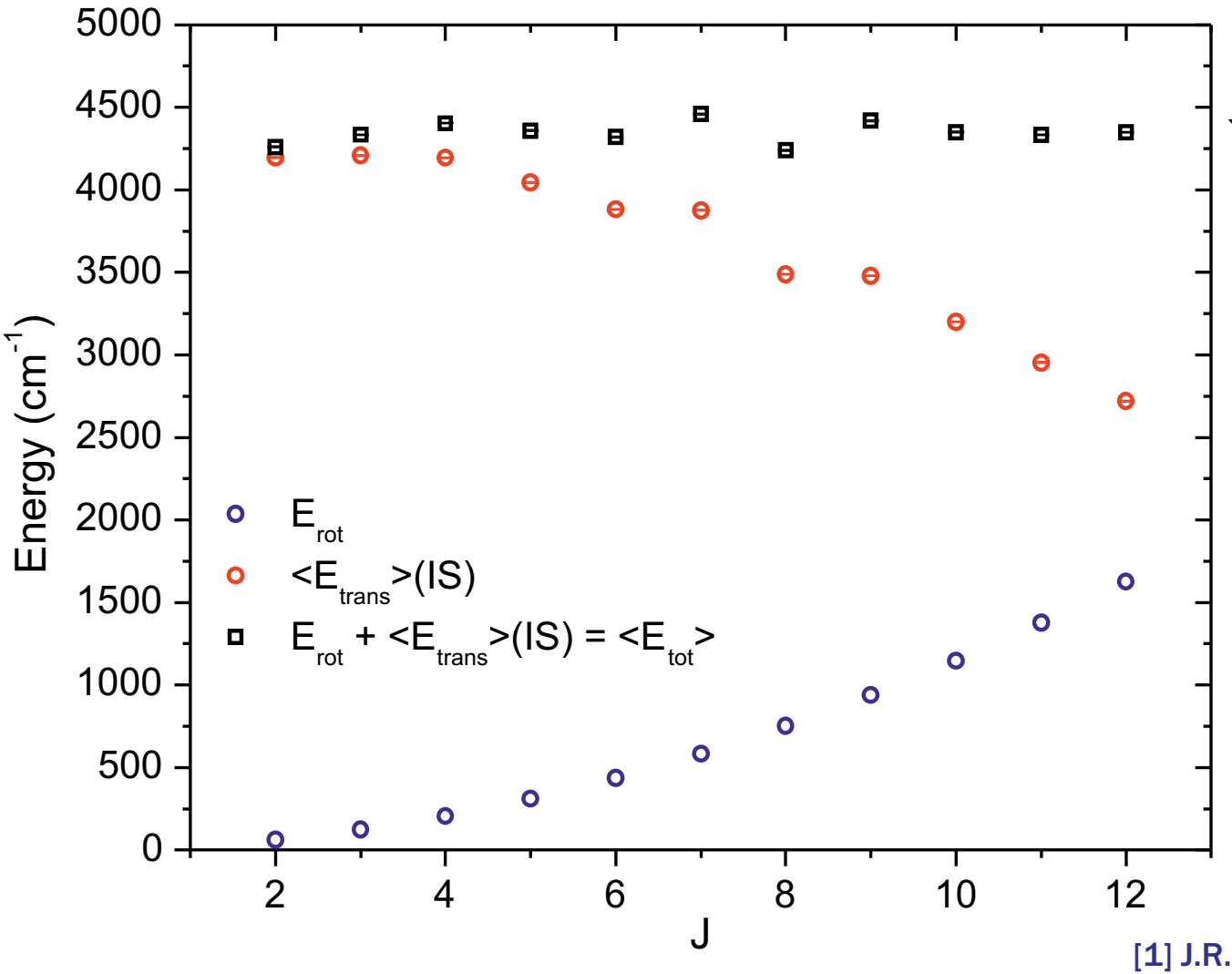
TD: Trapping-desorption
- ➡ equilibrium with surface
- ➡ isotropic velocity distribution

IS: Impulsive scattering
- ➡ hyperthermal
- ➡ forward-scattered

[1] J.R.Roscioli, D.J.Bell, D.J.Nelson and D.J.Nesbitt, *PhysChemChemPhys*, **14**, 4070, 2012

Internal degrees of freedom

Information on rotational and translational energy distributions [1]:



$\langle E_{inc} \rangle \sim 21(5)$ kcal/mol

$\langle E_{tot} \rangle \sim 12.4$ kcal/mol

substantial energy transfer into the surface

[1] J.R.Roscioli, D.J.Bell, D.J.Nelson and D.J.Nesbitt, *PhysChemChemPhys*, **14**, 4070, 2012

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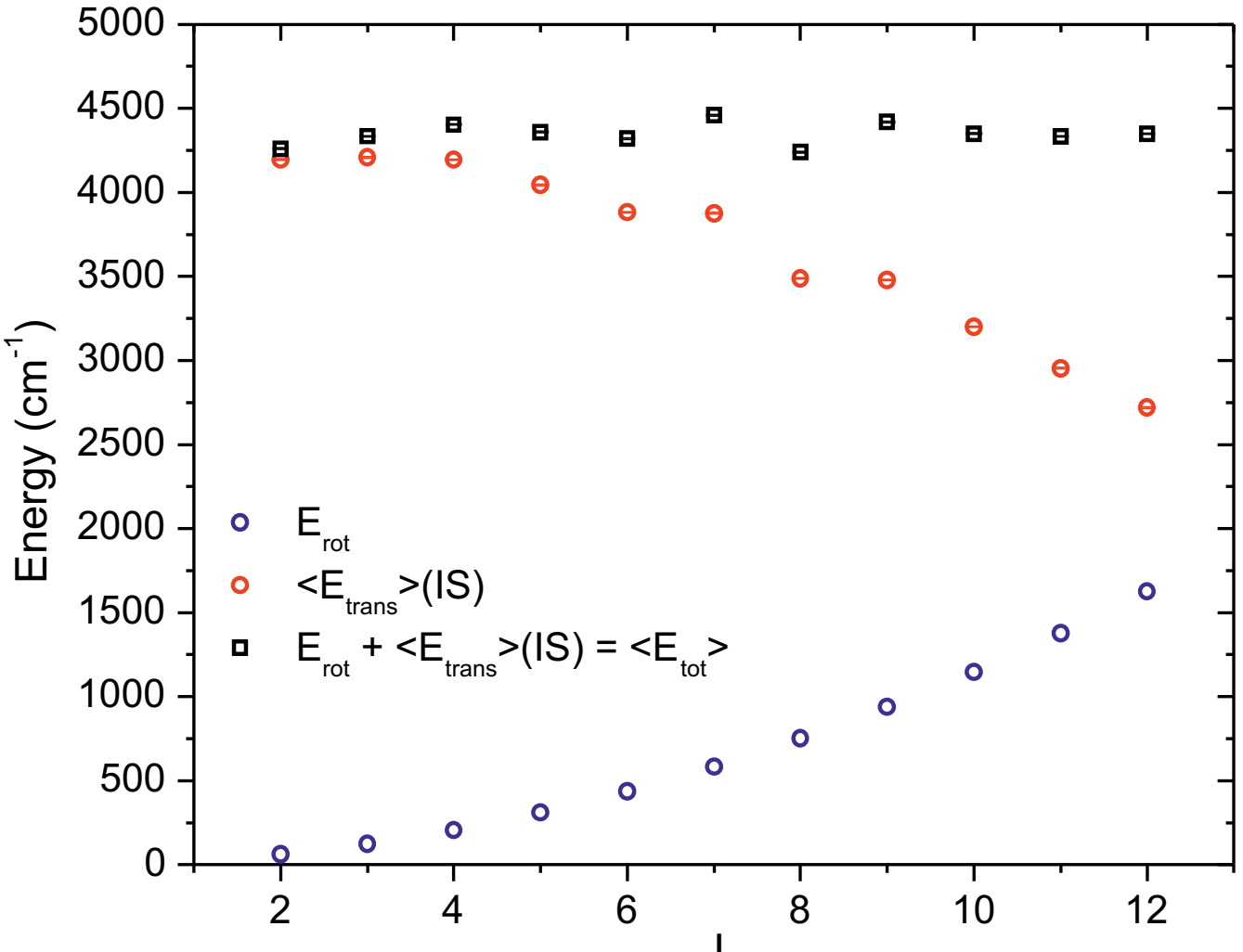

<E$_{inc}$>~21(5) kcal/mol

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➡ Where is the vibrational degree of freedom?

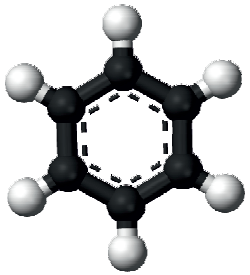
[1] J.R.Roscioli, D.J.Bell, D.J.Nelson and D.J.Nesbitt, *PhysChemChemPhys*, **14**, 4070, 2012

Vibrational excitation in inelastic scattering

HCl:
diatomic molecule

ω_e ~ 2890 cm^{-1}

No observable collision
energy transfer into vibration



Benzene:
symmetric top of D_{6h} symmetry
20 normal modes
prototype hydrocarbons

ω_{20} ~ 405 cm^{-1} C-C-C bend
ω_{19} ~ 970 cm^{-1} C-H bend
ω_{11} ~ 845 cm^{-1} C-H bend
ω_{8} ~ 703 cm^{-1} C-C-C bend
ω_{7} ~ 992 cm^{-1} C-H bend
ω_{6} ~ 608 cm^{-1} C-C-C bend
ω_{4} ~ 673 cm^{-1} C-H bend
ω_{2} ~ 993 cm^{-1} C-C stretch

[2] G. Herzberg, *Mol. Spectra & Mol. Structure, Volume III*, Krieger, 1991
[3] E. Riedle *et al.*, *JCP*, **91**, 4555, 1989
[4] M. Okruss *et al.*, *JMS*, **193**, 293, 1999

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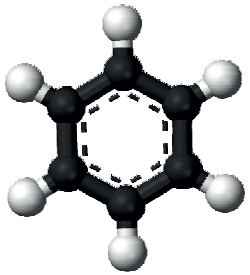

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«hard» ⟷ «soft»

➡ Collisional-vibrational excitation?

Benzene scattering: Key questions

- Translational energy:

  ➡ TD vs. IS: Do the molecules equilibrate with the surface?

- Rotational excitation:

  ➡ Is there transfer from translational to rotational energy?

- Vibrational excitation:

  ➡ Can we observe collisional-vibrational excitation?

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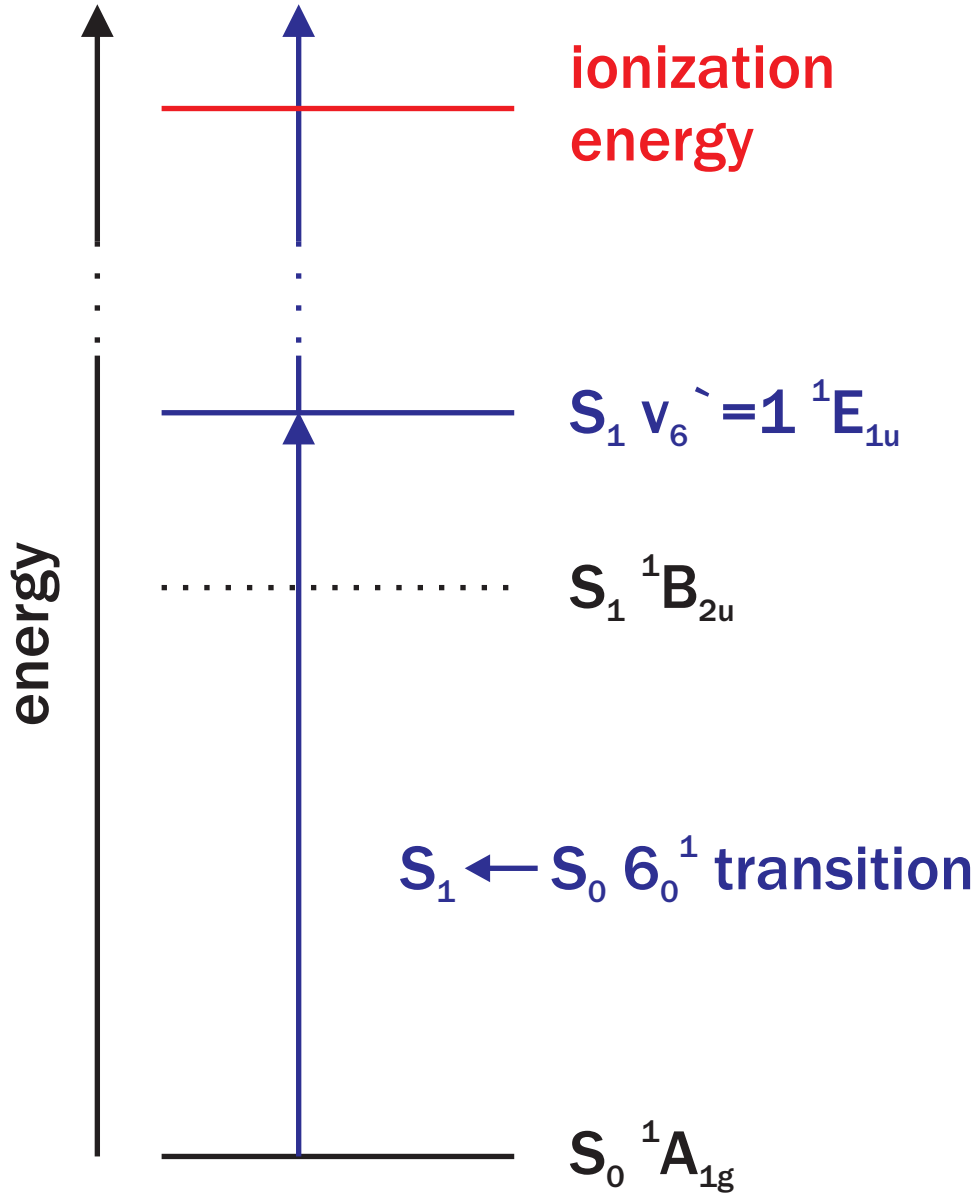
Dynamics of inelastic collision

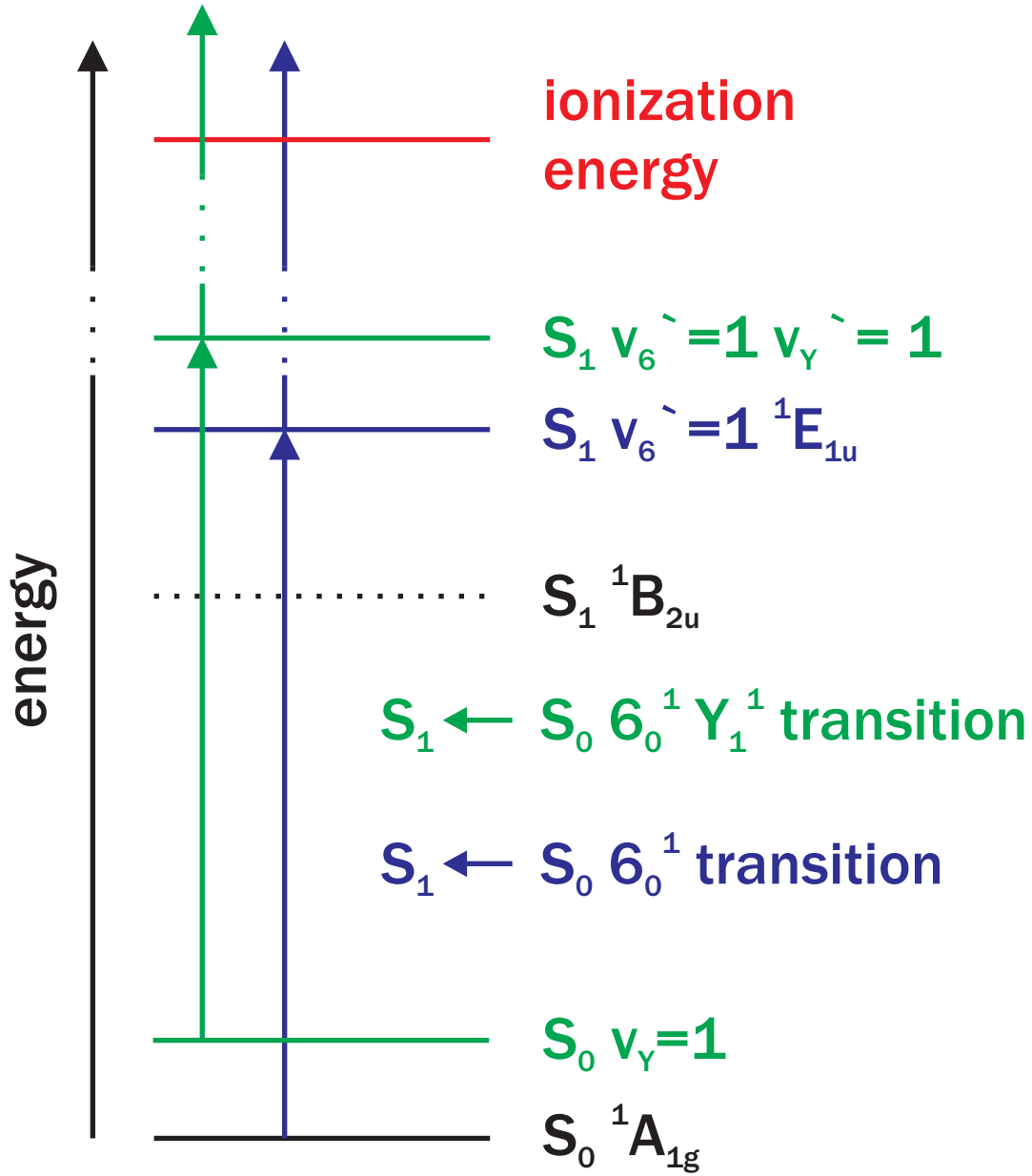
tunable collision energy:
$\langle E_{inc} \rangle$ ~ 8 kcal mol^{-1} ~ 2800 cm^{-1}

Vibronic transitions in benzene (D_{6h})



1 + 1 REMPI scheme to ionize vibrational ground state of benzene

Vibronic transitions in benzene (D_{6h})



➡ Investigate excited vibrational states of ground state benzene after the scattering process

Y: normal mode

[2] G. Herzberg, *Mol. Spectra & Mol. Structure*, *Volume III*, Krieger, 1991
[3] E. Riedle *et al.*, *JCP*, **91**, 4555, 1989
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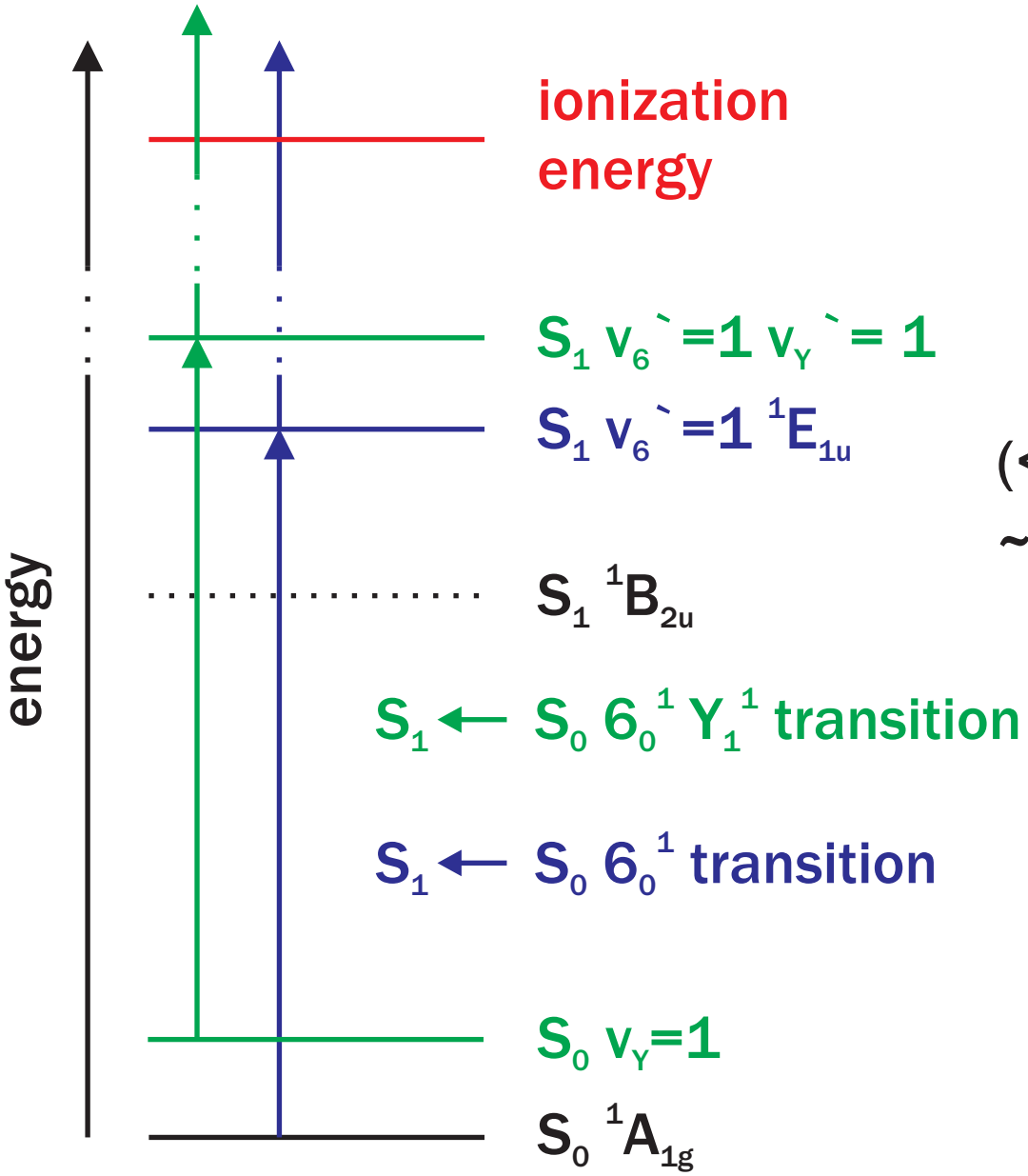


➡ Quantitative comparison of the population in each vibrational mode:

Line strength:

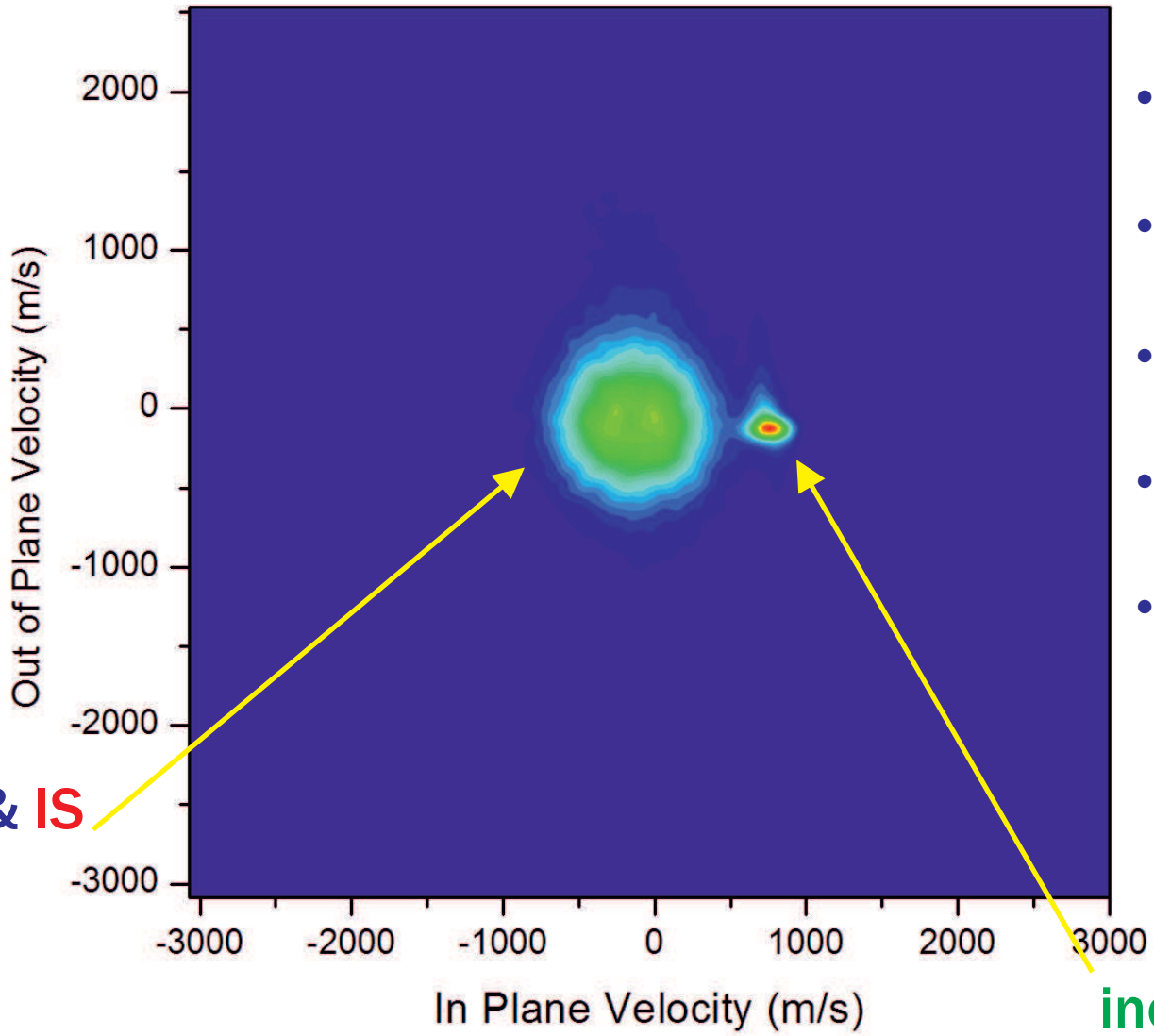
$$(\langle ev(S_1\ v_6`=1\ v_Y`=1)|\mu|ev(S_0\ v_Y=1)\rangle)^2$$
$$\sim (\langle ev(S_1\ v_6`=1)|\mu|ev(S_0)\rangle \times \langle v_Y`=1|v_Y=1\rangle)^2$$

both electronic states very similar in structure

➡ $\langle v_Y`=1|v_Y=1\rangle$ very similar for all Y

Translational energy distribution

Velocity-map image of vibrational ground state of benzene:



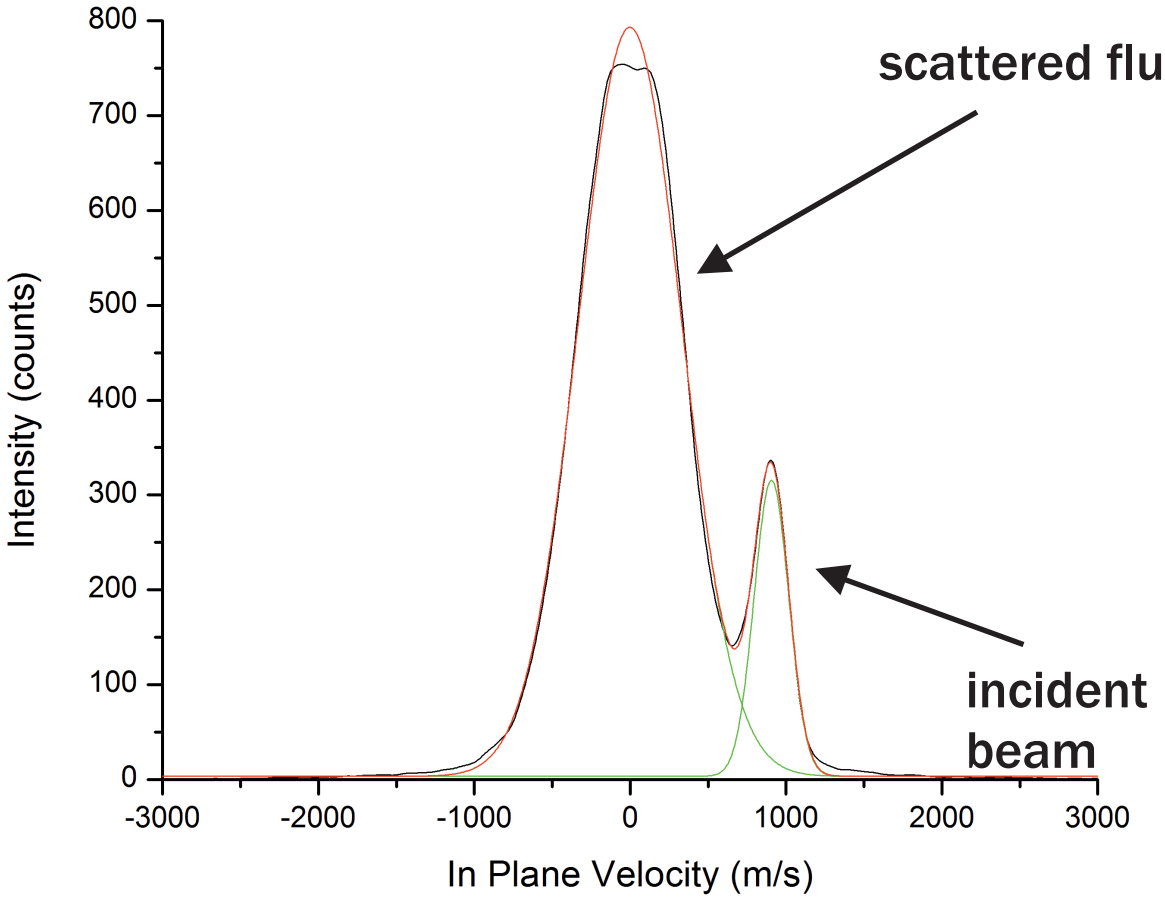
TD & IS

incident beam

- heated Au surface (500 K)
- $S_1 \leftarrow S_0\ 6_0^1$ transition
- 2% benzene in 70% Ne/30% He
- incident beam ~ 8 kcal/mol
- TD and IS overlap strongly

Translational energy distribution

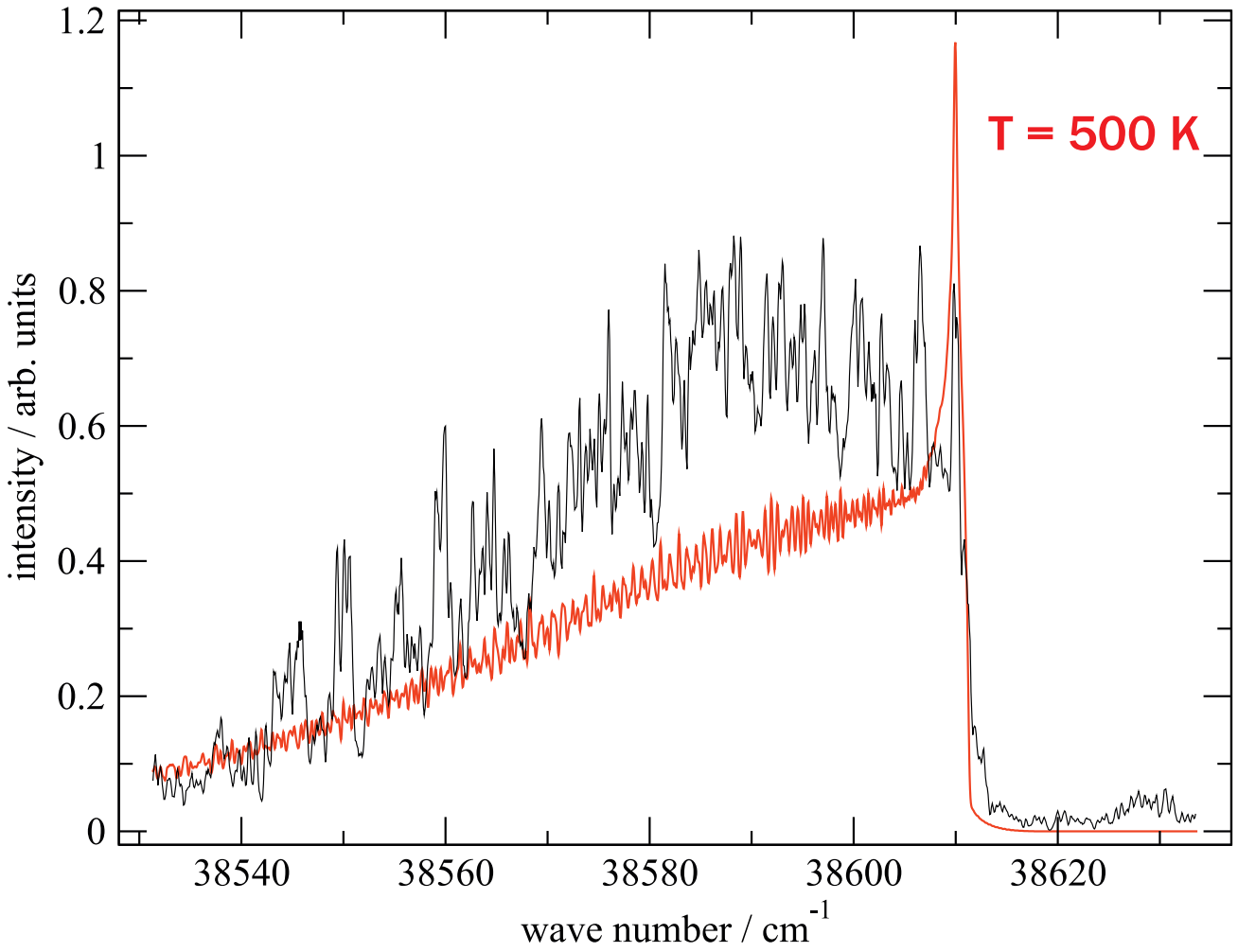
➡ Integrated velocity-map image:



- ➡ T ~ 1000 K
- ➡ significantly hotter than surface
- ➡ IS component dominant
- ➡ almost no forward-scattering
- ➡ ~20% of translational energy retained

Rotational excitation of ground state

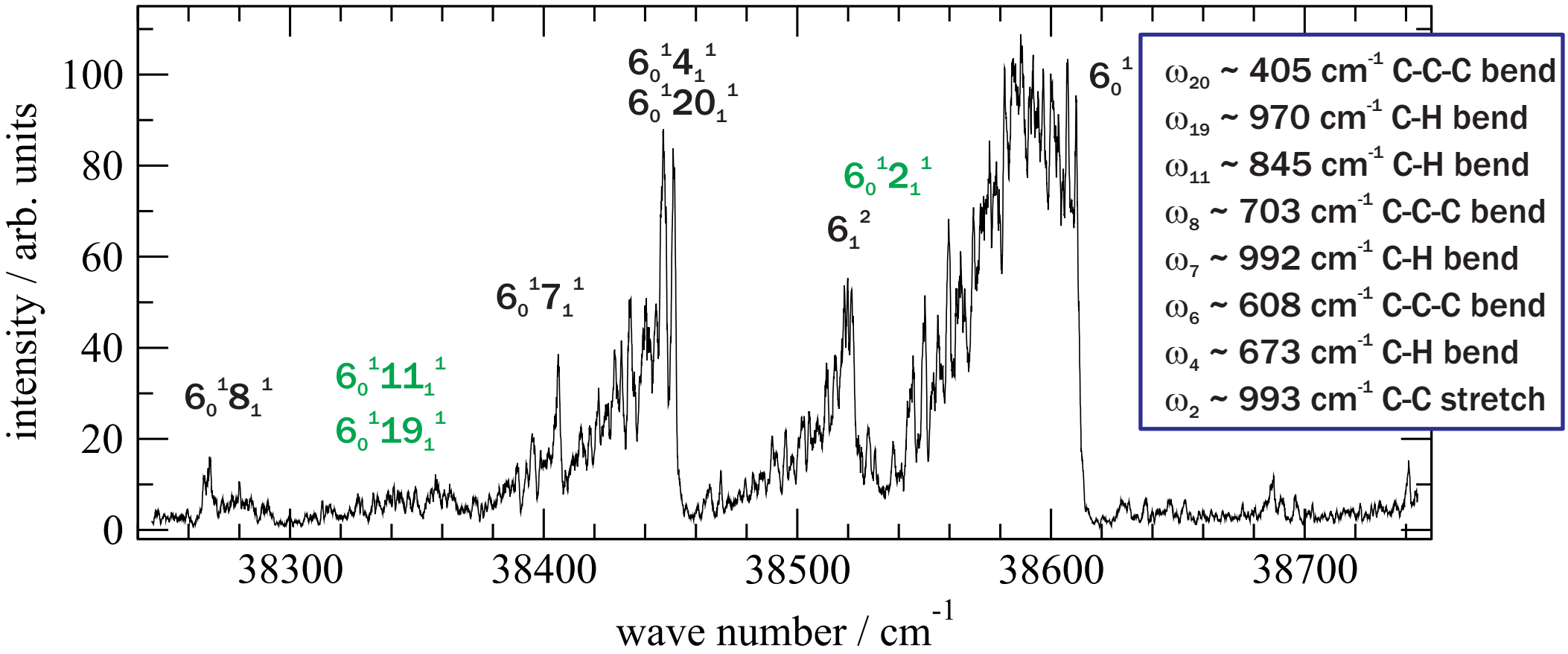
Integrate over translational distribution and scan detection frequency



- rotational distribution hotter than surface
- not a single rotational T
- not equilibrated with surface
- dynamics during scattering process
- 30% of incident beam energy in rotation
- energy transfer with surface

Vibrational excitation in the scattering

REMPI spectrum of the integrated scattered flux:



- significant vibrational excitation
- not all low-energy modes equally excited

Conclusions & Outlook

- benzene is a ‹soft› molecule:
  - ➡ almost no forward-scattering of scattered molecules
  - ➡ impulsively-scattered component is dominant, no equilibrium
  - ➡ efficient transfer from translational to rotational energy
  - ➡ collisional-vibrational energy transfer, complex dynamics

- next steps:
  - ➡ better understanding of rotational and vibrational excitation
  - ➡ increase collision energy

Thank you!

20	E2u	CCC bend perp	405
19	E2u	C-H bend perp	970
18	E2g	CCC bend par	608.13
17	E2g	C-H bend par	1177.78
16	E2g	C-C stretch	1591.33
15	E2g	C-H stretch	3056.7
14	E1u	C-H bend par	1038.27
13	E1u	C-C stretch	1483.98
12	E1u	C-H stretch	3047.91
11	E1g	C-H bend perp	845
10	B2u	C-H bend par	1149.7
9	B2u	C-C stretch	1309.4
8	B2g	CCC bend perp	703
7	B2g	C-H bend perp	992
6	B1u	CCC bend par	1010
5	B1u	C-H stretch	3059
4	A2u	C-H bend perp	673
3	A2g	C-H bend par	1366.6
2	A1g	C-C stretch	993.06
1	A1g	C-H stretch	3073.94