Focus 18: Reaction Dynamics

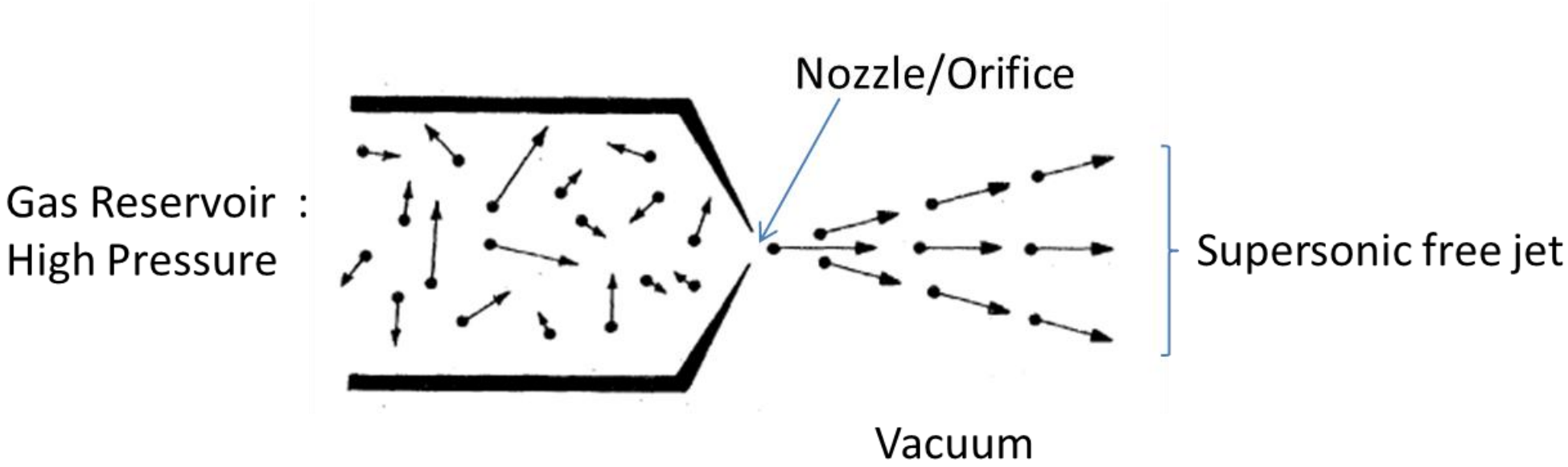
Collision theory

Diffusion-controlled reactions and transition-state

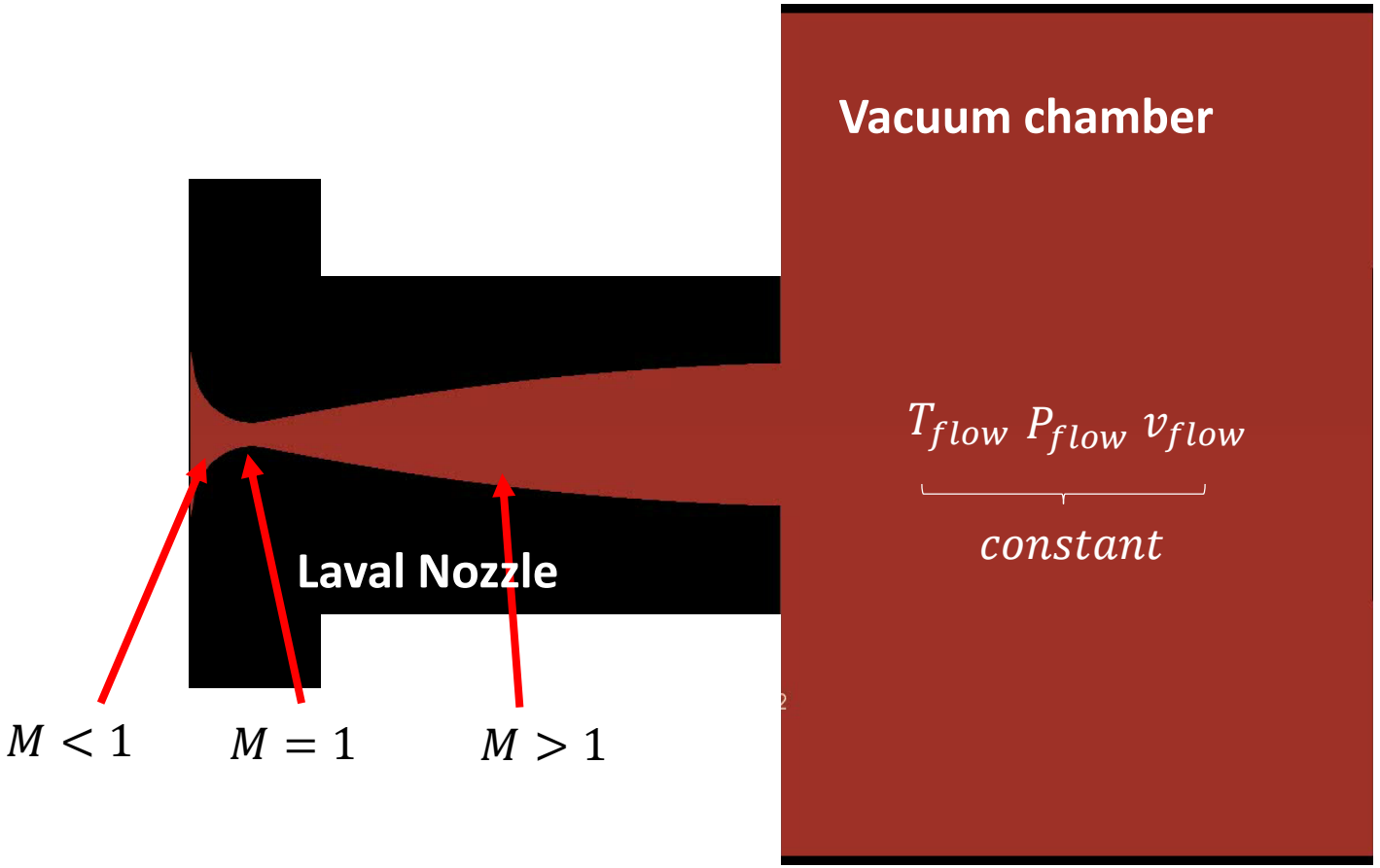
The dynamics of molecular collisions

Electron transfer in homogeneous systems

Molecular beams



Uniform Supersonic Molecular Beams



B. Rowe et al., The Journal of chemical physics 80 (1984) 4915.

Reference:

SPECIAL ISSUE ARTICLE

The Spectroscopy of Very Cold Gases

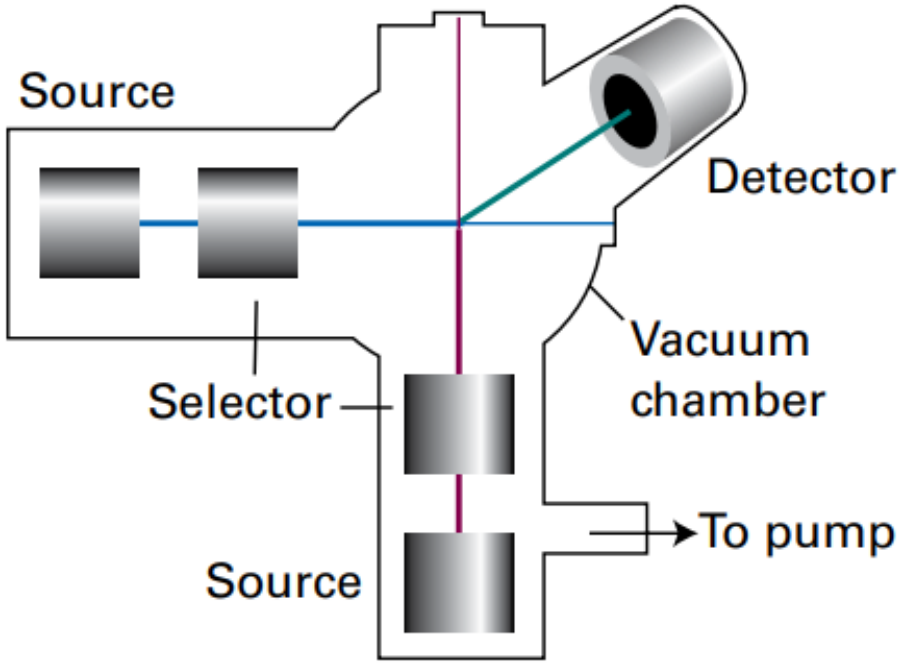
DONALD H. LEVY Authors Info & Affiliations

SCIENCE • 16 Oct 1981 • Vol 214, Issue 4518 • pp. 263-269 • DOI: 10.1126/science.214.4518.263

Abstract

The technique of supersonic free jet spectroscopy can be used to study the structure and dynamics of molecules which have been cooled to far below their boiling points but which remain in the gas phase. Cooling of the internal degrees of freedom, the molecular rotations and vibrations, produces a highly resolved and greatly simplified molecular spectrum. The principles of the technique are discussed and its utility is demonstrated by two examples: the spectroscopy of porphyrins in the gas phase and the photochemistry of van der Waals molecules.

Molecular beams in reaction dynamics



- Two beams of molecules are crossed, allowing controlled collisions between the beams.

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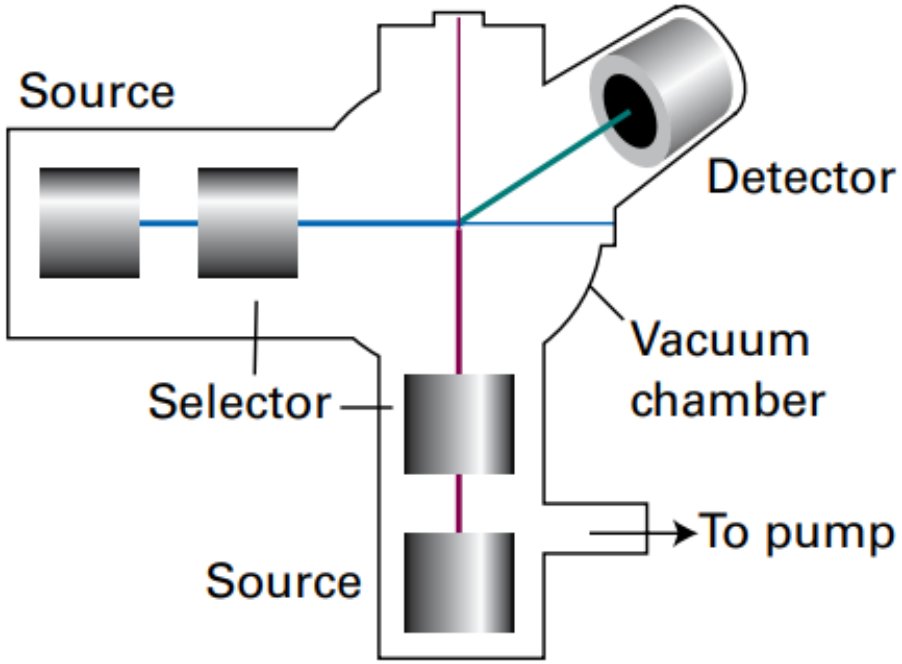

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- The setup maps the angular dependence of product distribution

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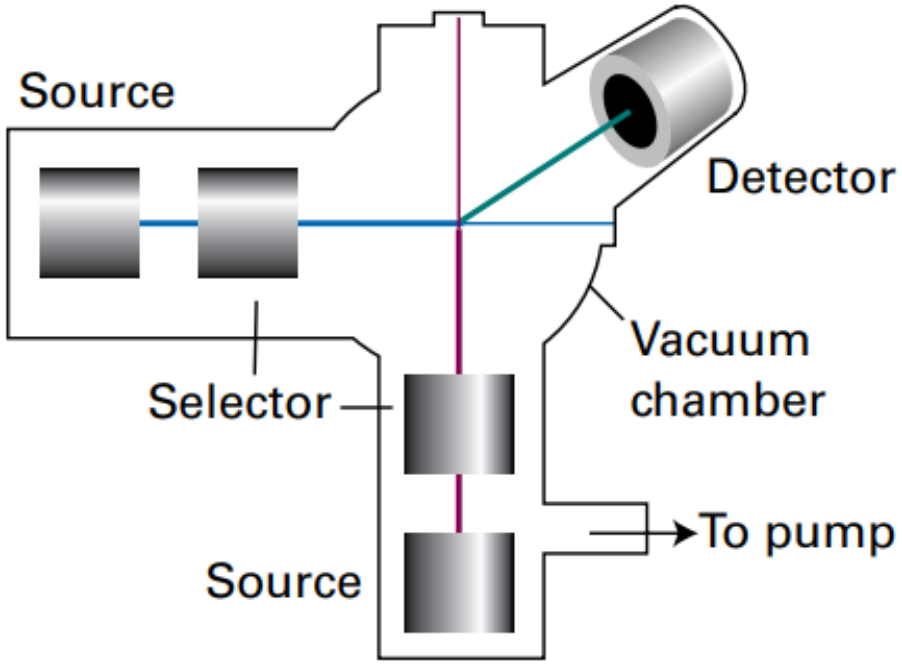
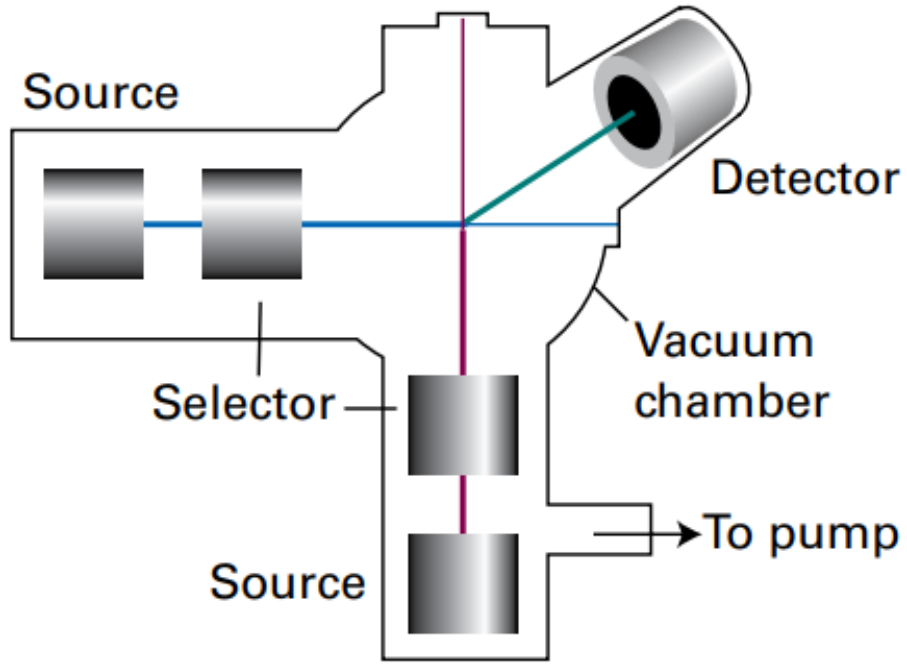


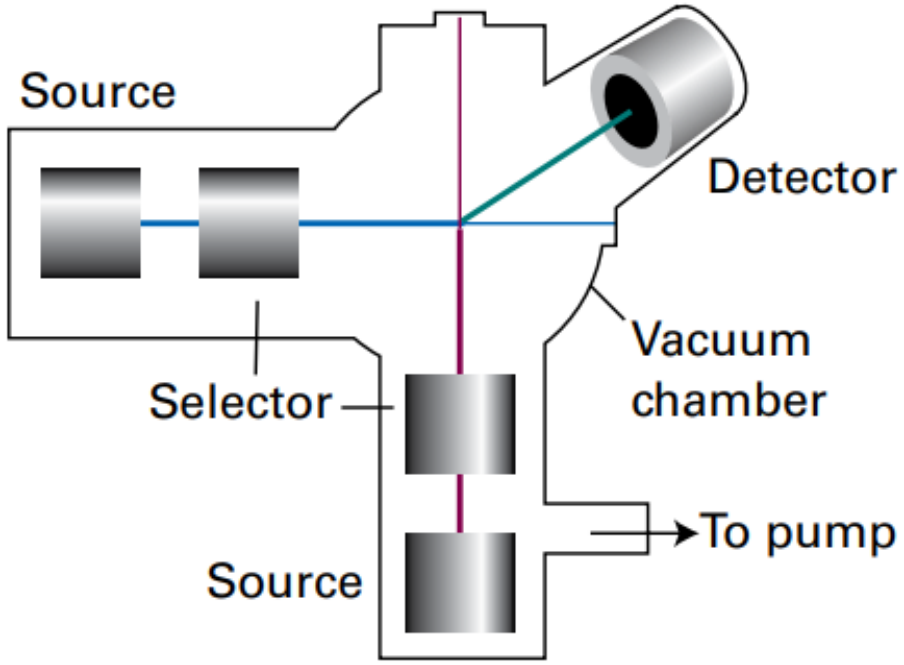
- Two beams of molecules are crossed, allowing controlled collisions between the beams.
- The setup maps the angular dependence of product distribution
- Different reactions produce different angular "fingerprints," which reveal the mechanism, energy flow, and stereodynamics (how orientation matters)

Molecular beams in reaction dynamics



differential scattering cross-section

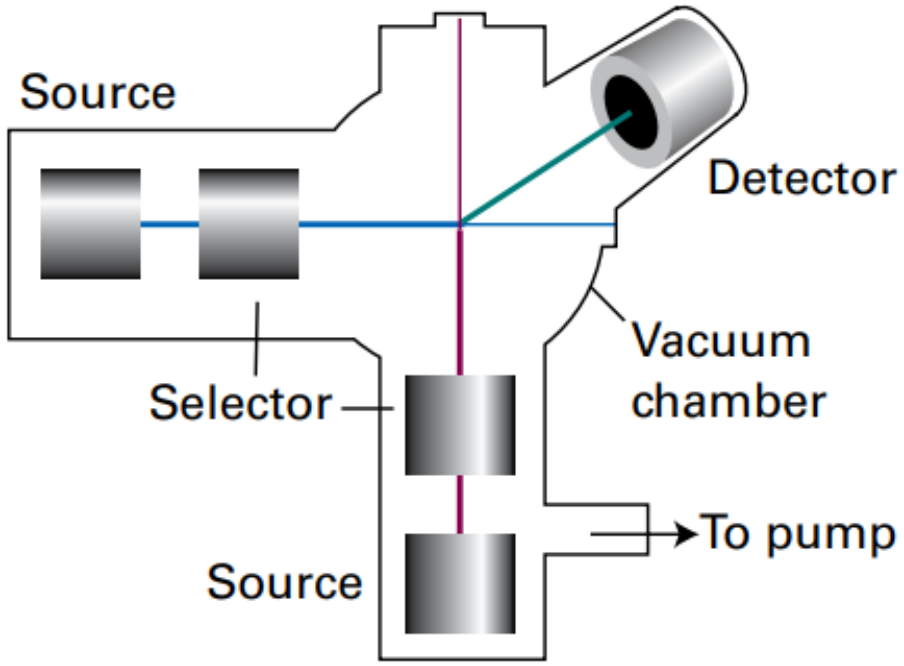
Molecular beams in reaction dynamics



differential scattering cross-section

Quantifies how many particles are scattered into a specific solid angle dΩ

Molecular beams in reaction dynamics

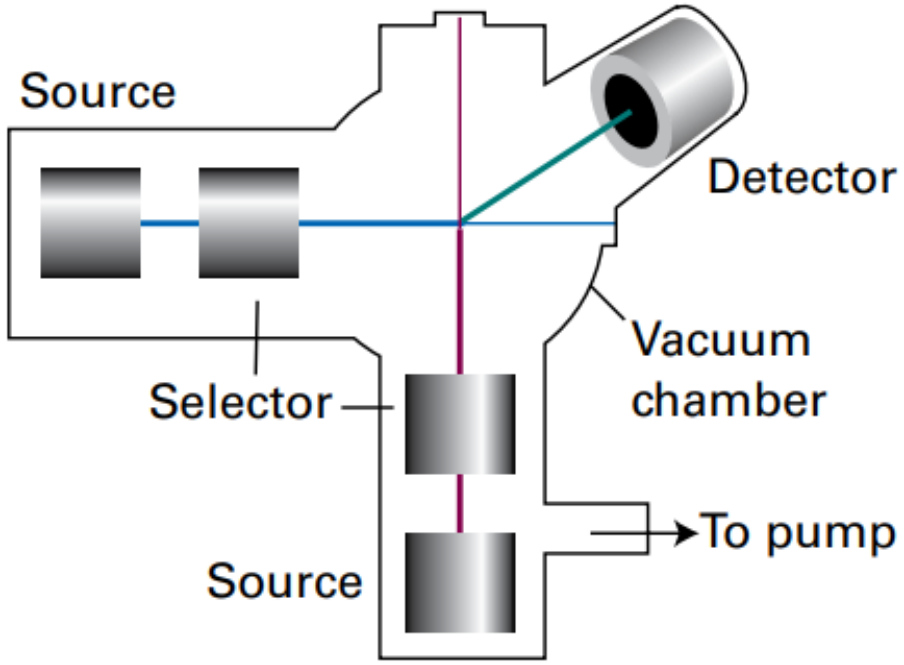


differential scattering cross-section

Quantifies how many particles are scattered into a specific solid angle dΩ and depends on:

- Impact parameter (How far to the side the incoming particle is aimed from hitting the center of the target particle)
- Collision energy
- Molecular orientation
- Scattering angle

Molecular beams in reaction dynamics



- Different reaction pathways can lead to distinct angular distributions of the scattered products
- Reaction pathways identification
- How energy is transferred during the collision (translational=> rot/vib)
- Reactants' orientation-dependent effects

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Nobel Prize in Chemistry 1986

Photo from the Nobel Foundation archive.

Dudley R. Herschbach

Prize share: 1/3

Photo from the Nobel Foundation archive.

Yuan T. Lee

Prize share: 1/3

Photo from the Nobel Foundation archive.

John C. Polanyi

Prize share: 1/3

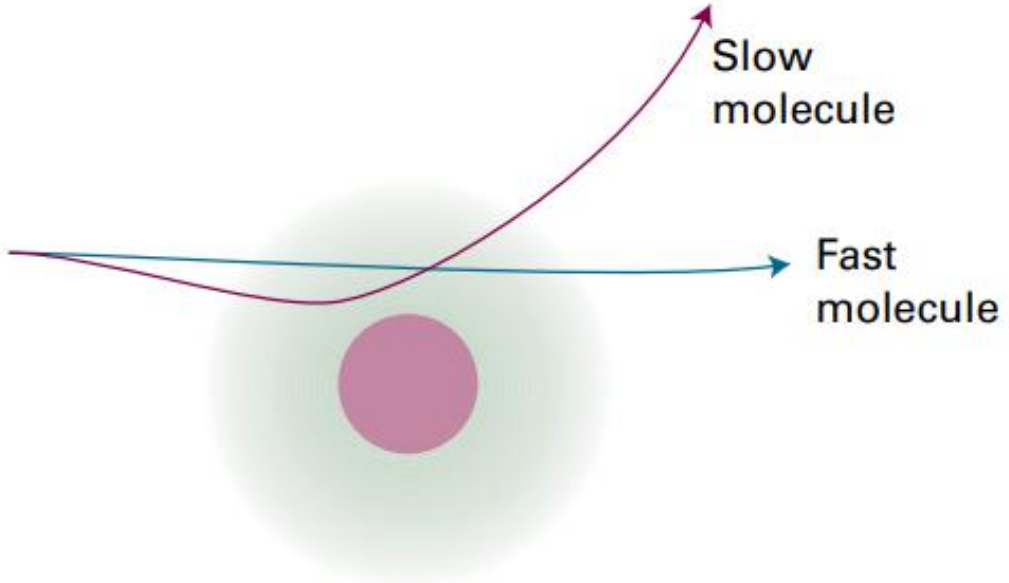
The Nobel Prize in Chemistry 1986 was awarded jointly to Dudley R. Herschbach, Yuan T. Lee and John C. Polanyi "for their contributions concerning the dynamics of chemical elementary processes"

Herschbach and Lee pioneered crossed molecular beam experiments, which allowed chemists to observe how molecules collide and react at the quantum level. They measured differential cross sections, angular distributions, and energy partitioning

Polanyi used infrared chemiluminescence to study vibrational energy redistribution in reactive collisions

Non-Reactive Scattering - Intermolecular potential

The variation of the scattering cross-section with the relative speed of approach gives information about the strength and range of the intermolecular potential



The dark central zone represents the repulsive core; the fuzzy outer zone represents the long-range attractive potential

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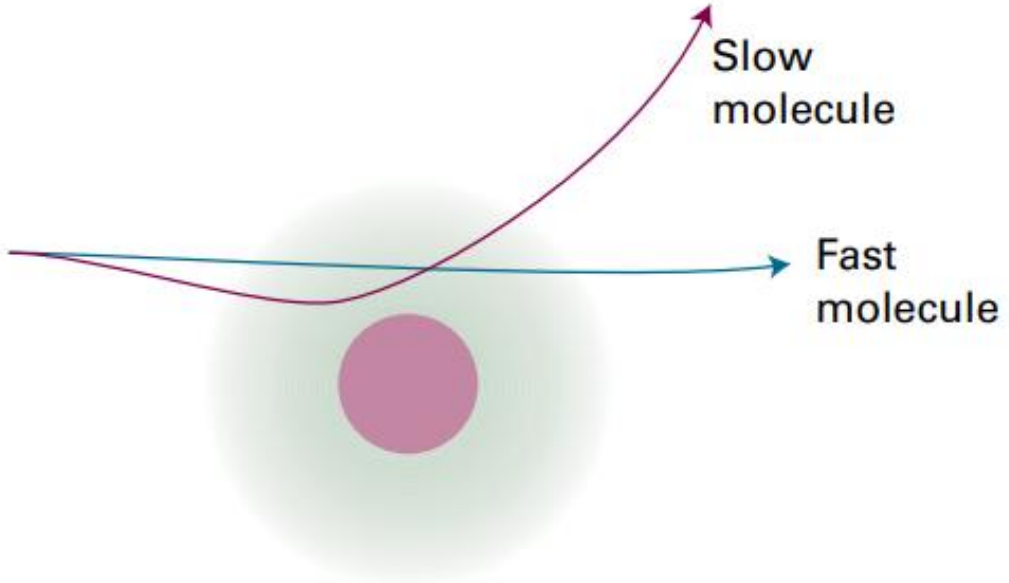

Gives us precise, reaction-free insights into how molecules interact, transfer energy, and move through space.

The dark central zone represents the repulsive core; the fuzzy outer zone represents the long-range attractive potential

Reactive Collisions Detection

Technique	
Infrared chemiluminescence (IRCL)	Vibrationally excited products emit radiation

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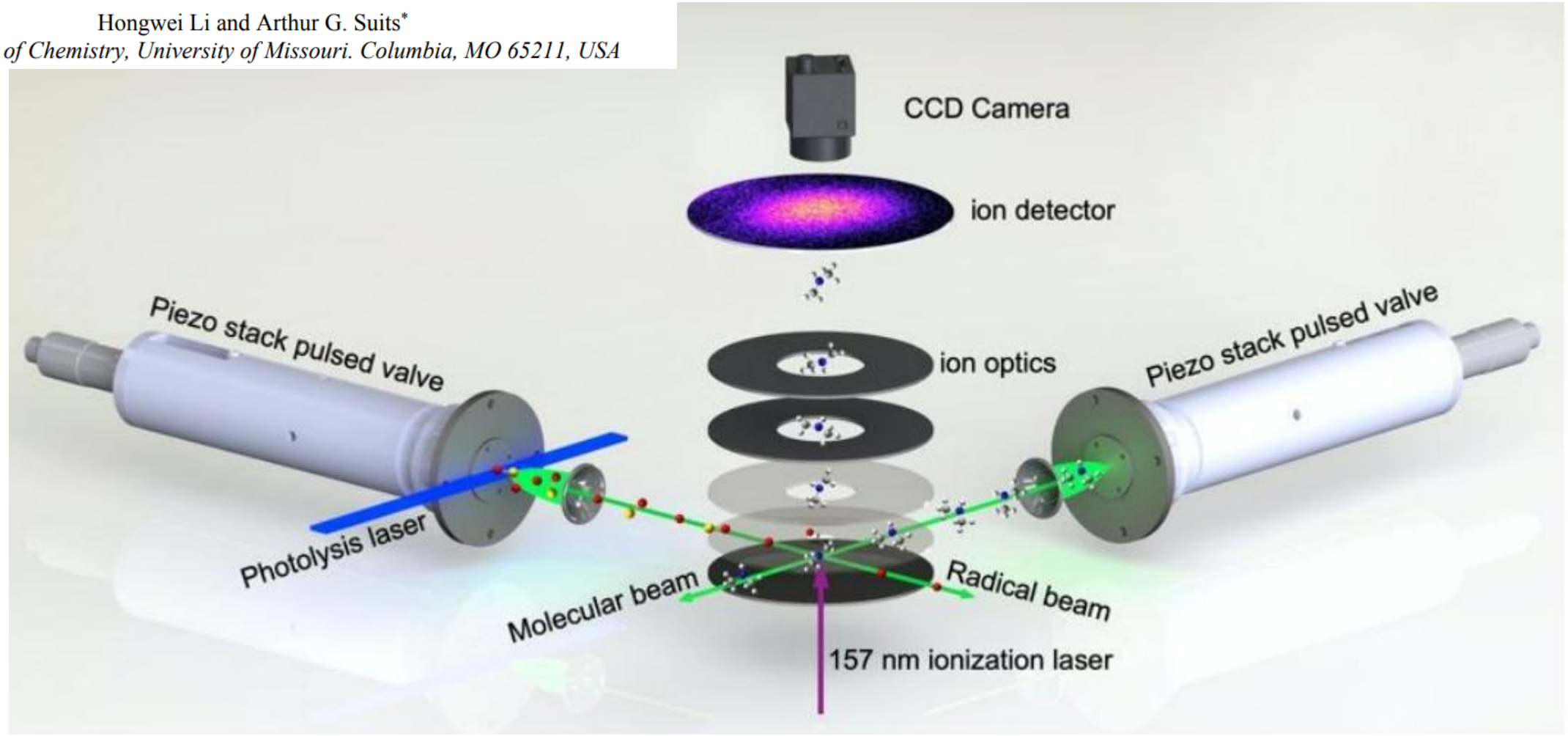
Multiphoton ionization techniques, (MPI, REMPI)	Ionization by consecutive absorption of photons from one or more pulsed lasers
Reaction product imaging	Record the angular distribution of ions using a phosphorescent screen

Crossed molecular beams + Velocity map imaging

Universal Crossed Beam Imaging Studies of Polyatomic Reaction Dynamics

Hongwei Li and Arthur G. Suits*
Department of Chemistry, University of Missouri. Columbia, MO 65211, USA



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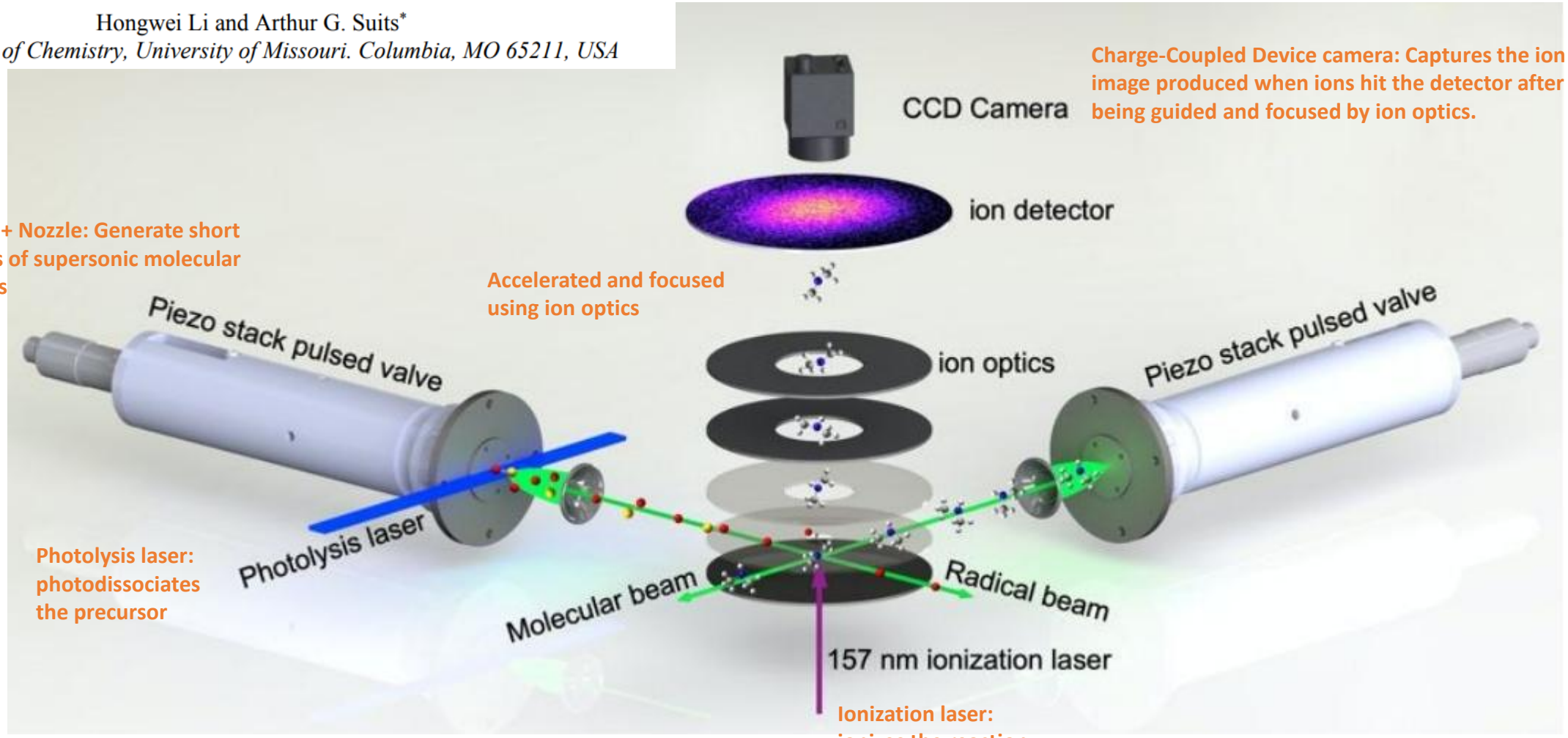

Charge-Coupled Device camera: Captures the ion image produced when ions hit the detector after being guided and focused by ion optics.

Valve + Nozzle: Generate short bursts of supersonic molecular beams

Accelerated and focused using ion optics

Photolysis laser: photodissociates the precursor

Ionization laser: ionizes the reaction products at the collision point

Ion optics are usually made of conductive metals like stainless steel, shaped into electrodes and separated by insulating materials, to control ion motion with high precision using electric fields.

doi.org/10.1039/D0CP00522C

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From the journal:
Physical Chemistry Chemical Physics

Universal crossed beam imaging studies of polyatomic reaction dynamics

Hongwei Li [a] and Arthur G. Suits [*a]

Author affiliations

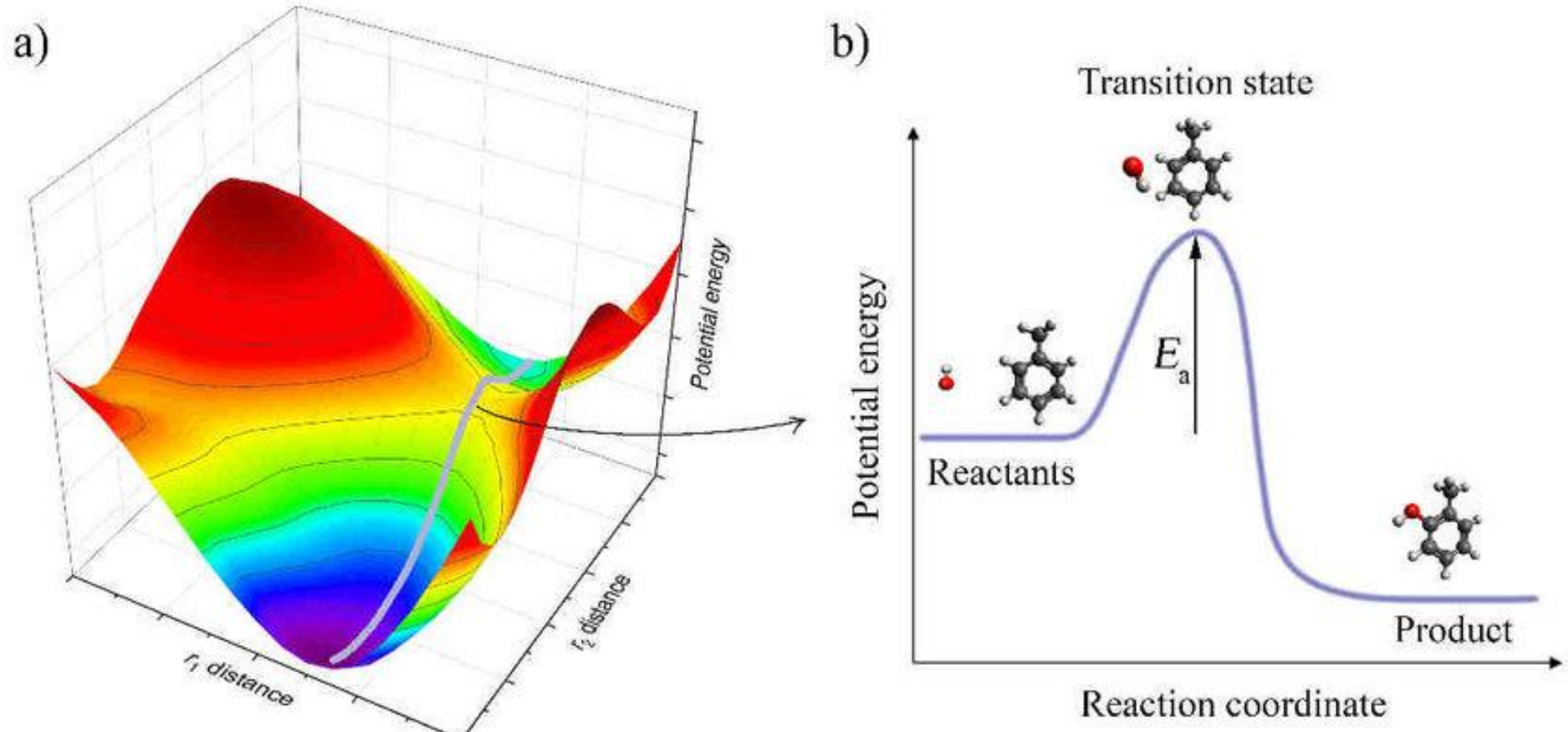
* Corresponding authors

[a] Department of Chemistry, University of Missouri, Columbia, MO 65211, USA
E-mail: suitsa@missouri.edu

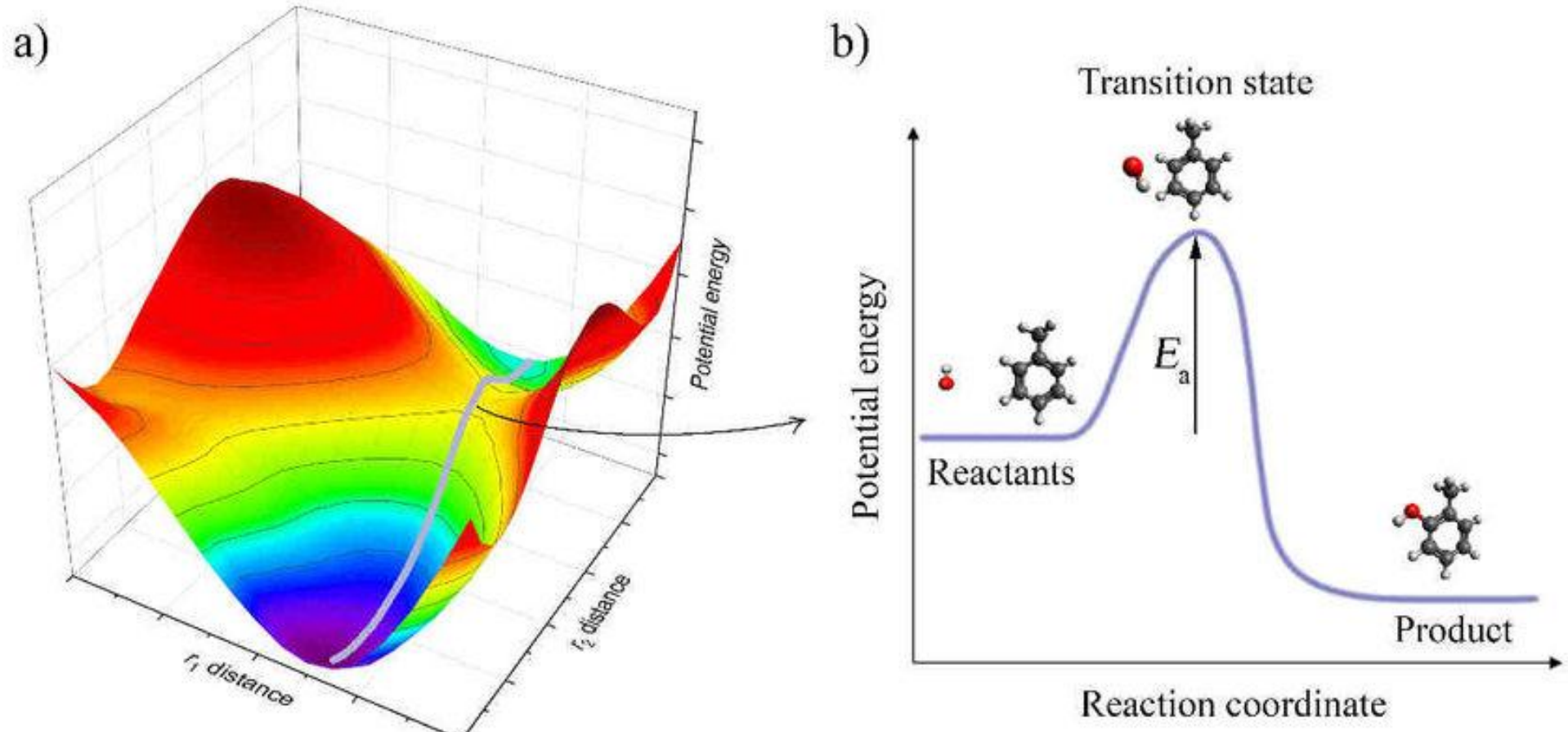
Abstract

The marriage between high level quantum calculations and experimental advances in laser technology, quantum state control, and detection techniques have opened the door to the study of molecular collision dynamics at a new level of detail. However, one current challenge lies in adapting these powerful strategies to address questions beyond the scope of the small ground state systems that have largely been the focus of reaction dynamics investigations to-date. For molecules with intermediate or large size (more than 6 atoms), lack of spectroscopic information and spectral congestion limit quantum state preparation, control and detection for experiment, and the large number of degrees of freedom of the system makes accurate quantum dynamics calculations prohibitively expensive. Nevertheless, studies of the chemical dynamics of such systems can reveal novel aspects of reactivity not anticipated based upon the behavior of smaller model systems. This Perspective will highlight applications of soft vacuum

Potential energy surfaces



Potential energy surfaces



Saddle point: Potential energy surface reaches a maximum along one direction and a minimum along all other directions

Databases

NIST Chemical Kinetics Database

Standard Reference Database 17, Version 7.1 (Web Version), Release 1.6.8
Data Version 2023

A compilation of kinetics data on gas-phase reactions

https://kinetics.nist.gov/kinetics/

NDRL/NIST Solution Kinetics Database on the Web

NIST Standard Reference Database 40

A compilation of kinetics data on solution-phase reactions

https://kinetics.nist.gov/solution/

https://kida.astrochem-tools.org/

Focus 18: Reaction Dynamics

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Electron transfer reactions

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$$D^+A^- \xrightarrow{k_d} D^+ + A^- \qquad \text{break apart and the ions diffuse}$$

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$$\frac{d[D^+A^-]}{dt}$$

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replace the terms in blue by the expression for [DA]

$$[D^+A^-] = \frac{k_a k_{et}}{(k'_{et} + k_d)(k'_a + k_{et}) - k'_{et}k_{et}}[D][A]$$

$$= \frac{k_a k_{et}}{k'_{et}k'_a + k_d k'_a + k_d k_{et}}[D][A]$$

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dividing the numerator and denominator on the right-hand side by $k_d k_{et}$

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$$\frac{1}{k_r} = \frac{1}{k_a} + \frac{k'_a}{k_a k_{et} k_d}(k'_{et} + k_d) \qquad \text{reciprocal}$$

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$$\frac{1}{k_r} = \frac{1}{k_a} + \frac{k'_a}{k_a k_{et}}\left(1 + \frac{k'_{et}}{k_d}\right) \qquad \text{rearrange}$$

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Assume

$$k_d[D^+A^-] >> k'_{et}[D^+A^-] \qquad k_d >> k'_{et}$$

If it's much more likely to dissociate into free ions than to recombine via reverse electron transfer

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$$\frac{1}{k_r} \approx \frac{1}{k_a}\left(1 + \frac{k'_a}{k_{et}}\right)$$

$$k_{et}[DA] >> k'_a[DA]$$

=> Once the encounter pair is formed, electron transfer is faster than dissociating back to reactants

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$$k_{et}[DA] >> k'_a[DA]$$

$$k_r \approx k_a$$

Electron transfer reactions

$$D + A \rightarrow D^+ + A^- \qquad v = k_r[D][A]$$

$$D + A \underset{k'_a}{\overset{k_a}{\rightleftarrows}} DA$$

$$DA \underset{k'_{et}}{\overset{k_{et}}{\rightleftarrows}} D^+A^- \qquad \text{electron transfer}$$

$$D^+A^- \xrightarrow{k_d} D^+ + A^- \qquad \text{break apart and the ions diffuse}$$

$$\frac{1}{k_r} = \frac{1}{k_a} + \frac{k'_a}{k_a k_{et}}\left(1 + \frac{k'_{et}}{k_d}\right) \qquad v = k_d[D^+A^-]$$

Assume

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Diffusion of D and A in solution

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Diffusion of D and A in solution

The rate of product formation is controlled by diffusion of D and A in solution

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rate of product formation is controlled by diffusion of D and A in solution

$$k_{et}[DA] << k'_a[DA]$$

$$k_r \approx (k_a/k'_a)k_{et} = Kk_{et},$$

Rate is controlled by the activation energy of electron transfer in the DA complex