

MOLECULAR REACTION DYNAMICS

Prof C. Vallance and Prof M. Brouard

8 Lectures

SUMMARY

1. *Introduction*

Types of collisions

Definitions: impact parameter, cross sections, differential cross sections, state-to-state processes

Conservation of energy and momentum

2. *Potential energy surfaces and trajectories*

Introduction to potential energy surfaces

Types of potential energy surface

Quasiclassical trajectory and quantum scattering calculations as a link between experiment and theory

Centrifugal barriers

3. *Experimental techniques for control of initial states*

Spatial/temporal isolation

Laser photolysis and pump and probe methods

Molecular beam methods (including brief examples of state-selection, deceleration and orientation)

4. *Experimental techniques for probing product states*

Crossed molecular beams with mass spectrometric detection

Chemiluminescence and laser induced fluorescence

Resonantly enhanced multiphoton ionization and Rydberg tagging

Velocity map ion-imaging

The lab to centre-of-mass frame transformation

5. *Elastic and Inelastic scattering*

Total (integral) and differential cross sections: examples of molecular beam inelastic scattering experiments

Types of energy transfer and their relationship to intermolecular forces

6. *Reactive scattering*

Examples of crossed molecular beam reactive scattering experiments

Reaction mechanisms: Stripping mechanism and the harpoon model, rebound reactions, complex formation

7. *Controlling reagents and characterizing products*

Effect of translational energy on the reaction cross-section: reactions with and without a barrier

Effect of initial vibrational state on the reaction cross-section: Polanyi's rules

Selective disposal of energy: Microscopic reversibility and the potential energy surfaces for attractive and repulsive energy release

Examples of mass effects and angular momentum conservation effects

Statistical reactions

8. *Probing the transition state.*

Examples of control of molecular orientation, stereochemistry and cone of acceptance, angular momentum polarization

Photodissociation dynamics and femtochemistry

Photoelectron detachment spectroscopy

RECOMMENDED TEXTS

1. *Modern Gas Kinetics*. Eds. M.J. Pilling and I.W.M. Smith, Blackwell. [Straight-forward ideas are found in chapters A3 and B2.]
2. *Chemical Dynamics via Molecular Beam and Laser Techniques*. R.B. Bernstein, Oxford Science Publications, OUP (1982).
3. *Molecular Reaction Dynamics and Chemical Reactivity*. R.D. Levine and R.B. Bernstein, OUP (1987),
4. *Chemical Kinetics and Dynamics*. J.L. Steinfeld, J.S. Francisco, and W.L. Hase, Prentice Hall (1989).
5. *Molecular Reaction Dynamics*. R.D. Levine, Cambridge University Press, (2005).
6. *Reaction Dynamics*. M. Brouard, Oxford Chemistry Primer 61 (1998).
7. *Tutorials in Molecular Reaction Dynamics*, M. Brouard and C. Vallance, Eds., Royal Society of Chemistry, ISBN: 978-0-85404-158-9 (2010).

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PROBLEMS

1. Energy and angular momentum in chemical reactions

The reaction



was studied at a mean relative velocity of 800 ms^{-1} , with I_2 in thermal equilibrium at 300 K. The reaction cross-section was found to be 170 \AA^2 .

Use the data in the table below to estimate

- the total energy available to the products,
- the maximum orbital angular momentum quantum number, L_{max} , and
- the rotational energy of the KI product if $J' = L_{\text{max}}$, where J' is the rotational angular momentum quantum number for KI.

Identify any assumptions made in obtaining the estimate in (b).

	I_2	KI
$D_0/\text{kJ mol}^{-1}$	149	319
ω_e/cm^{-1}	214.5	186.5
B_e/cm^{-1}	0.037	0.061

[The mean vibrational energy of the I_2 reactants may be calculated assuming $E_v = hc\omega_e/(e^{\theta_v/T} - 1)$ with $\theta_v = hc\omega_e/k_B$.]

2. The line-of-centres model (for reactions with a barrier)

The cross-section, $\sigma_r(E_{\text{col}})$, for the endothermic reaction



increases with the collision energy, E_{col} , in the following way:

$E_{\text{col}}/\text{kJ mol}^{-1}$	9	15	30	50
$\sigma_r(E_{\text{col}})/10^{-20} \text{ m}^2$	0.5	1.25	2.0	2.2

- (a) Show that the cross-section data are consistent with the line-of-centres model

$$\sigma_r(E_{\text{col}}) = \pi d^2 \left(1 - \frac{E_0}{E_{\text{col}}}\right) \quad E_{\text{col}} \geq E_0$$

and determine the threshold energy, E_0 , and the limiting, high collision energy cross-section, πd^2 .

- (b) In terms of the reaction cross-section, the thermal rate constant can be written

$$k(T) = \left(\frac{8k_B T}{\pi \mu}\right)^{1/2} \int_{E_0}^{\infty} \frac{E_{\text{col}}}{k_B T} \sigma_r(E_{\text{col}}) e^{-(E_{\text{col}}/k_B T)} \frac{dE_{\text{col}}}{k_B T}$$

Use this equation to obtain a line-of-centres expression for $k(T)$. Comment on the result you obtain. You may use the following integral without proof

$$\int_a^{\infty} (x - a) e^{-x} dx = e^{-a}$$

- (c) Vibrational excitation of HCl from $v = 0$ to $v = 1$ increases the reaction cross-section by a factor ~ 10 . What features of the potential energy surface for the reaction would be likely to give rise to such behaviour.

3. Harpoon reactions (a class of reactions often without barriers)

- (a) When neutral K reacts with Br_2 , the KBr product is scattered in the forward direction relative to the K atom, with a reaction cross-section that is large compared with the gas kinetic cross-section. Explain how the IP of K ($418.8 \text{ kJ mol}^{-1}$) and the electron affinity of Br_2 (245 kJ mol^{-1}) can be incorporated into the harpoon mechanism to account for this. Estimate the reaction cross-section.

[The Coulomb potential between particles of charge q_1 and q_2 is $V = \alpha q_1 q_2 / r$ with $\alpha = 9.0 \times 10^9 \text{ J C}^{-2} \text{ m}^{-1}$.]

- (b) How would you expect the cross-sections for reaction with Br_2 to vary in the series, Na, K, Rb, Cs?
- (c) Describe an experiment that could be used to study the angular dependences of the KBr product in the K + Br_2 reaction.

4. Kinematics and spectator stripping

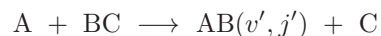
Two reagent molecules A and BC, on collision course with initial velocities \mathbf{w}_A and \mathbf{w}_{BC} with respect to their centre of mass, react to form AB and C. If the final velocities of the two products are \mathbf{w}'_{AB} and \mathbf{w}'_C , show that their final translational energy is

$$E'_{\text{col}} = \frac{m_A m_C}{m_{AB} m_{BC}} \left(\frac{w'_C}{w_{BC}} \right)^2 E_{\text{col}} \quad (1)$$

Discuss the dynamical consequences of Equation (1) if the atom C acts as a 'spectator', so that the relative speed of C and BC are equal, $w'_C = w_{BC}$. Under what conditions would you expect 'spectator' dynamics to convert the initial collision energy, E_{col} , into product translational energy, product internal energy, or to promote collision induced dissociation?

5. Energy disposal and kinematic constraints

- (a) Briefly outline experimental strategies currently available for measuring the partitioning of energy in between vibration, rotational, and translation in the products of an exothermic atom transfer reaction



- (b) How may the properties for vibrational and translational energy disposal be influenced by the topography of the potential energy surface over which the reaction proceeds, and by the masses of the atoms involved? Illustrate your answer by reference to the data, determined at 300 K, for the following reactions

	$\langle f_{\text{vib}} \rangle$	$\langle f_{\text{trans}} \rangle$	Product scattering
$\text{H} + \text{Cl}_2 \longrightarrow \text{HCl}(v', j') + \text{Cl}$	0.39	0.54	backward
$\text{Cl} + \text{HI} \longrightarrow \text{HCl}(v', j') + \text{I}$	0.71	0.16	forward

[$\langle f_{\text{vib}} \rangle$ and $\langle f_{\text{trans}} \rangle$ are the mean fractions of the total energy disposed into vibration and translation, respectively.]

- (c) Explain how the constraints imposed by the conservation of angular momentum influence the disposal of rotational energy in the reaction

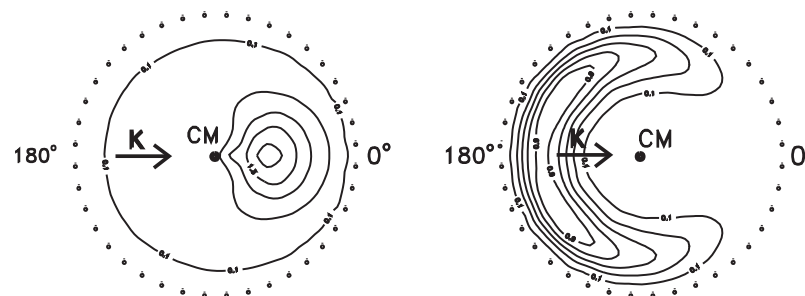


This reaction has been studied under crossed molecular beam conditions, at a reagent relative velocity, $v_{\text{rel}} = 976 \text{ ms}^{-1}$; the rotational state distribution in the product, BaI, was found to peak at the value $J' = 420$. Given the orbital angular momentum of the reagents in this reaction can be written $L = \mu v_{\text{rel}} b$, estimate the most probable impact parameter, b , and the reaction cross-section.

[Take the masses to be $m_{\text{Ba}} = 137.3 u$, $m_{\text{H}} = 1.0 u$, and $m_{\text{I}} = 126.9 u$.]

6. Differential cross-sections

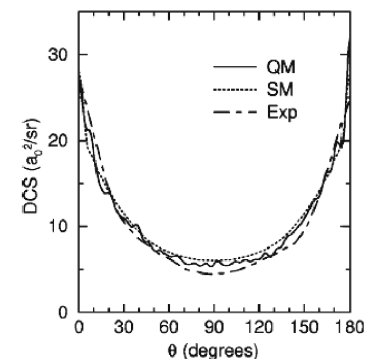
The figures below show the KI product flux contour plots in the centre-of-mass (CM) frame for the K + I₂ (left) and K + CH₃I (right) reactions.



Explain how data like these might be obtained.

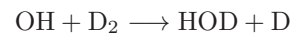
What can be learnt about the dynamics of the two reactions from these figures? (The outer rings of dots show the maximum CM velocities of KI in the two reactions.)

Contrast the scattering behaviour observed for the above two reactions with that found for the reaction $\text{S}(^1\text{D}) + \text{H}_2 \longrightarrow \text{SH} + \text{H}$, the differential cross-section for which is shown below.

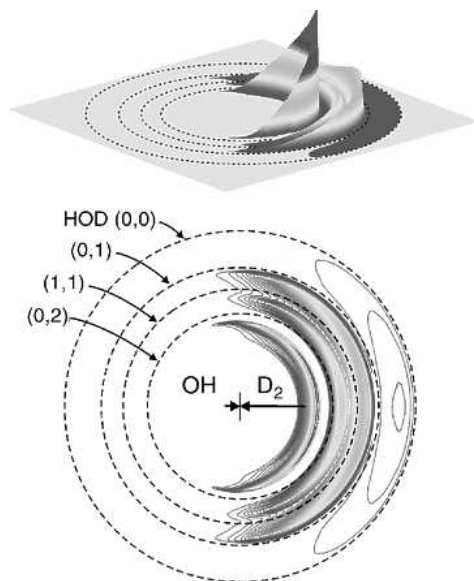


7. *Differential cross-sections and transition state spectroscopy*

OH in its ground electronic state undergoes the reaction



which is isoelectronic with the $\text{F} + \text{H}_2$ reaction. The figures below show plots of the D-atom product flux in the centre-of-mass frame for the above reaction. The experiments were performed under molecular beam conditions, with the D-atom products detected by a laser ionization technique.



The dashed rings are labelled according to the number of quanta m in the bending mode, and n in the OD stretching mode of $\text{HOD}(m, n)$.

- What does the above figure suggest about the mechanism of the reaction?
- What spectroscopic experiments might be performed to probe the transition state region of this reaction (or a similar reaction) more directly?

The following past paper questions might also be worth looking at. The old Option II paper questions are of the same length as the new Option course questions.

Year	Old General Paper	Old Option II
2011	3	–
2010	3	6
2009	3	6
2008	3	5
2007	3	6
2006	3	–
2005	3	–