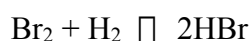**Report from the lecture presented by Richard Zare**

Report written by Ingmar Grenthe, Department of Chemistry, Royal Institute of

Technology, Stockholm

The topography of the energy landscape was discussed in the presentation of Professor Ahmed Zewail. This theme was also taken up in the presentation "Energy Requirements and Energy Release in Elementary Chemical Reactions" by professor Richard N. Zare, Stanford University.

The energy of a molecule is distributed as electronic, vibration, rotation and translation energy and this distribution might affect the course of the chemical reaction. Zare and his coworkers have used the elementary reaction

$Br_2 + H_2 \rightarrow 2HBr$

to investigate how the distribution of the available energy over the internal states might affect the outcome of the chemical reaction. The key question posed is given in Fig. 1 and is related to the location of the transition state as outlined in Fig. 2. Zare and his group have probed the problem by using a combination of molecular beam and laser technique, where a stream of HBr and H_2 with well-defined translation and internal energy are reacted according to the protocol outlined in Fig. 3.
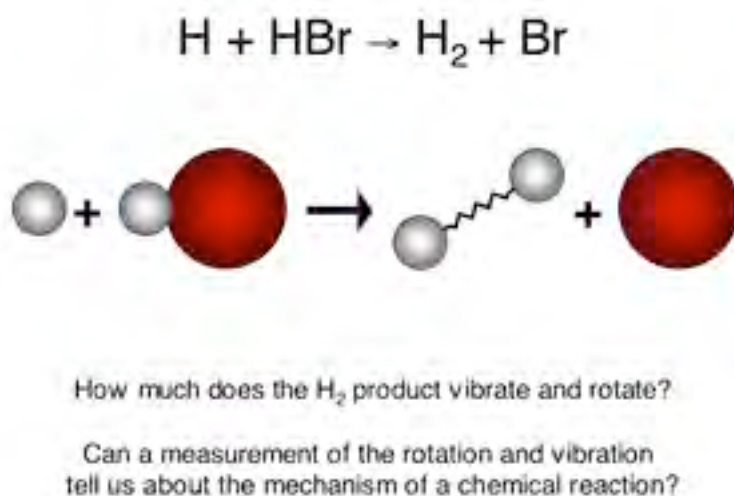

Fig 1. (Fig. 9 in Zare´s PowerPoint presentation).

Asymptotic Approach

The product vibrational energy can be related to the location of the transition state.
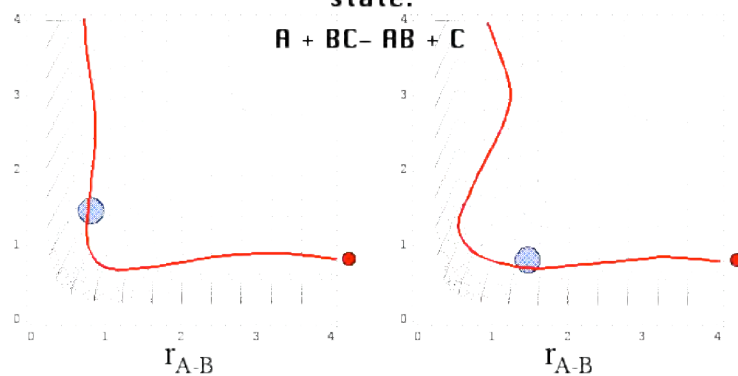
$$A + BC \rightarrow AB + C$$
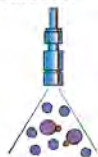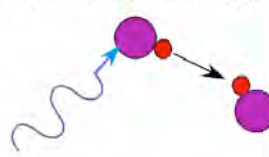
$r_{A\text{-}B}$ $r_{A\text{-}B}$

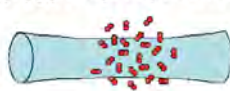**Fig 2. (Fig 12 in PowerPoint presentation).**

Experimental Protocol

1) A gas jet expansion produces translationally and internally cold precursors.

2) A tunable laser photolyzes HBr to produce fast H atoms with a well defined translational energy.

3) About 20 ns later, a focused, polarized laser ionizes $H_2(v', j')$ via (2+1) REMPI.

4) H_2^+ is propelled down the TOF by electric fields. A microchannel plate detector is used to count the ions.
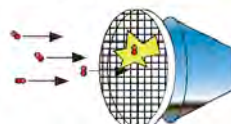
Fig 3. (Fig 14 in PowerPoint presentation).

By using jet-cooling the distribution of rotation energy levels is different from that at room temperature, Fig 4.
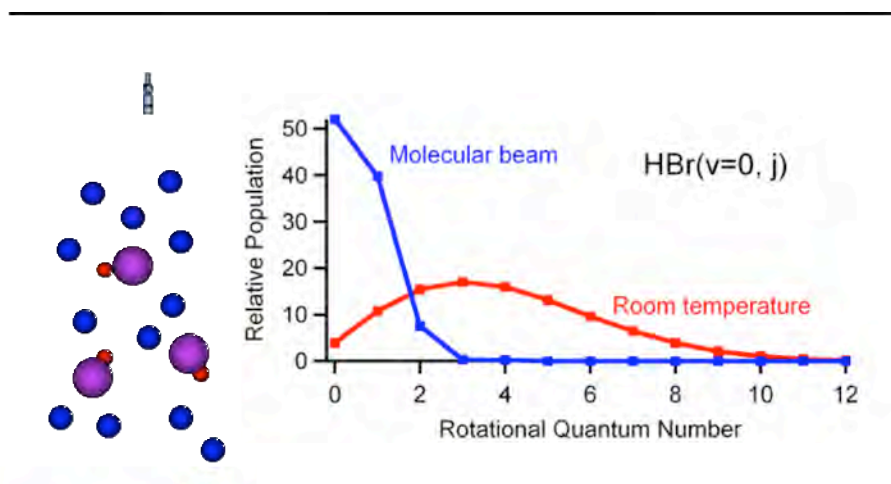
Jet Cooling

Fig. 4. *Construct high vacuum chamber: 10^{-6} Torr. *Single collision conditions: (mean free path = 50 m). *Expand HBr/Ar into vacuum. *Translational and internal cooling occurs. *Rotational Temperature = 25 K. (Fig. 63 in PowerPoint presentation)

If there are no favored directions for the reaction trajectories, the available reaction energy is distributed "democratically" over the internal states. If not, e. g. collinear H-H-Br head-on collision trajectories are favored on chemical grounds, the activation energy and the internal energy distribution will be different (Fig 5 and Figs. 1 and 2 in the Abstract). The reaction is then kinematically constrained.
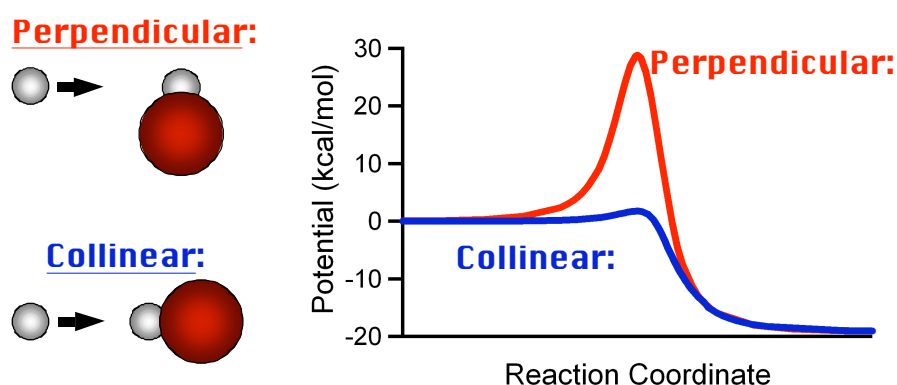
Different Approach Geometries

Fig. 5. (Fig. 17 in PowerPoint presentation)

A pictorial representation of how the vibration and rotation energy states of H_2 can be used to obtain information of the course of the reaction is shown in the following two videos:

Video (low) >>>
Video (high) >>>

High and low refer to the total energy in the reaction. The theoretical analysis can be made as outlined in Fig. 6 and compared with experiment, Fig. 7.
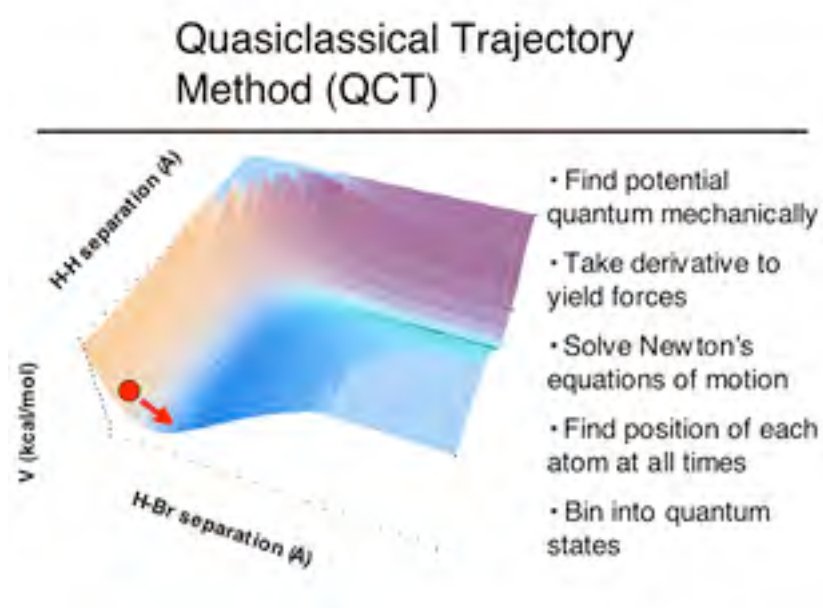

Fig. 6. (Fig. 26 in PowerPoint presentation).

Experimental and Theory
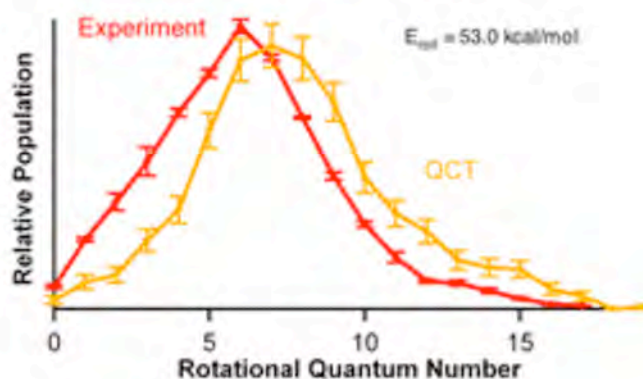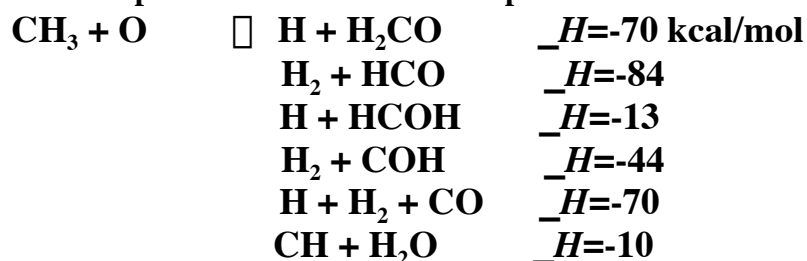H + HBr → H$_2$(v'=2, j') + Br

Fig. 7. (Fig. 27 in PowerPoint presentation).

An important conclusion of this study is that at sufficiently high energies some significant fraction of reactions do not proceed along or close to the minimum energy path and this might be general and more important than realized before. An example is the reaction between CH$_3$ and O radicals that might result in six possible sets of exothermic products as shown in Fig. 8.
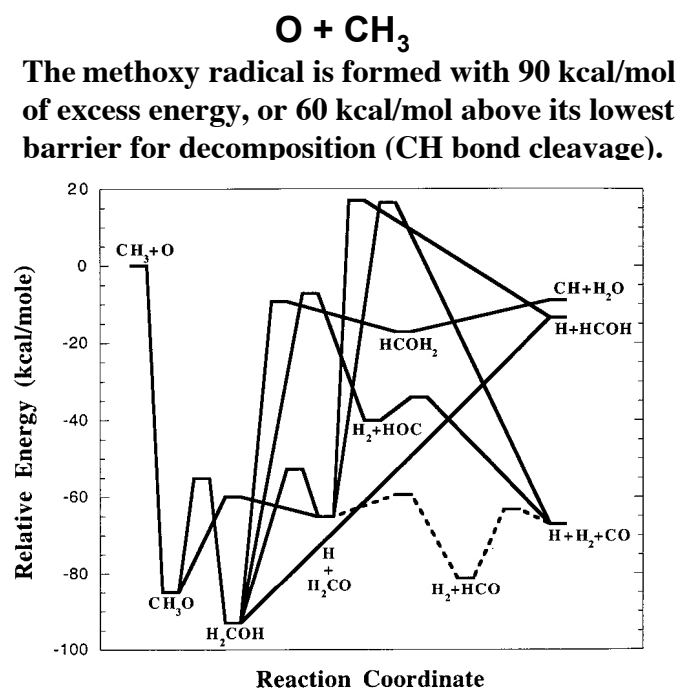
O + CH$_3$
Six possible sets of exothermic products:

CH$_3$ + O   → H + H$_2$CO   _H=-70 kcal/mol

                       H$_2$ + HCO   _H=-84

                       H + HCOH   _H=-13

                       H$_2$ + COH   _H=-44

                       H + H$_2$ + CO   _H=-70

                       CH + H$_2$O   _H=-10

Seakins and Leone (1992) reported the detection of CO (v) from this reaction using FTIR emission spectroscopy. They estimated the CO branching fraction to be 0.40 ± 0.10.
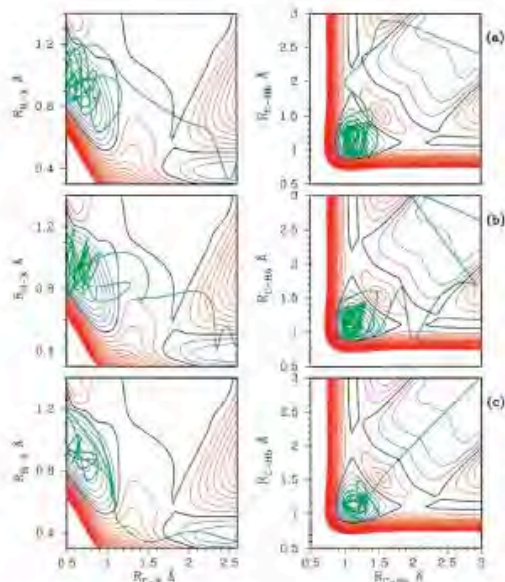
Fig. 8. (Fig. 57 in PowerPoint presentation).

Some details of the possible pathways for the formation of different products are shown in Figs. 9 and 10. An important implication of the phenomena discussed by Zare is that it seems possible to direct the course of chemical reactions by external means.

O + CH₃

The methoxy radical is formed with 90 kcal/mol of excess energy, or 60 kcal/mol above its lowest barrier for decomposition (CH bond cleavage).

Schematic of the stationary point energies on the CH₃O potential surface. The results shown are from CCSD(T)/aug-cc-pvtz// CCSD(T)/cc-pvdz calculations (including zero point).

Fig. 9. (Fig. 59 in PowerPoint presentation).

At these high energies, trajectories are found to stray far from the minimum-energy path, resulting in the production of unexpected products.

Two-dimensional projections of each of the three selected H_2-producing trajectories. The black contours correspond to the saddle point for the reaction $H + H_2CO \rightarrow H_2 + HCO$. Blue contours are lower in energy and red contours are higher in energy.

Fig.10. (Fig. 60 in PowerPoint presentation)