Ultra-cold chemistry

Prof. Dr. Viatcheslav Kokoouline

Department of Physics

University of Central Florida

Wednesday, 11:00-12:45

October 5, 2016 – February 1, 2017

Books

P.R. Bunker, P. Jensen *Molecular Symmetry and Spectroscopy,*

H. Friedrich, *Theoretical Atomic Physics.*

Quantum Mechanics textbooks:

L.D. Landau and E.M. Lifshitz *Quantum Mechanics: Non-Relativistic Theory, Vol.3,*

J.J. Sakurai *Modern Quantum Mechanics,*

A.S. Davydov *Quantum Mechanics,*

research articles.

Main topics (modules)

1) Quantum-mechanical description of molecules

2) Elements of the scattering theory at low energies

3) Formation of ultracold molecules in degenerate gases

4) Low-energy collisions in plasma

Introduction

✳Cold < 10K, ultracold: <1mK. This separation is very approximate.

✳Cold and thermal chemistry is dominated by an averaging over a large number of quantum states and a large number of impact parameters, statistical approach is applicable. At 300K, $\lambda(O_2) \sim 0.3\text{Å}$.

✳Little is known about chemistry at ultra-cold regime.

✳Ultracold chemistry is dominated by quantum effects. At 3mK, $\lambda(O_2) \sim 100\text{Å}$.

✳Weak interactions between colliding molecules become important in the ultracold regime. Experiments with ultracold molecules help to reveal fundamental details of intermolecular forces.

✳External EMs field can be used to influence chemical reactions at ultracold temperatures.

Introduction

* Sensitivity to a external electric or/and magnetic field allows trapping the ultracold molecules using EM fields.

* Trapping ultracold molecules allows much longer observation time compared to such "traditional" techniques as molecular beams.

* Long observation time and small Doppler broadening (uncertainty in the observed energies of quantum states) allows highly-accurate spectroscopy.

* This offers several opportunities for testing fundamental physics.

* Among applications of ultracold molecules in fundamental physics: the search for an electric dipole moment of the electron, parity-violation in chiral molecules, the time variation of fundamental constants.

* Different tests in many-body theories in condensed matter physics.

* Ultracold molecules are used as qubits in research on quantum information.

Potential barrier in the reaction path

* Reactions at thermal energies often proceed through a potential barrier.

* Such reactions are very slow at low T.

* The rate of such reactions is given by Arrhenius' law:

$$k(T) = k_0 e^{-\Delta G / k_B T}$$

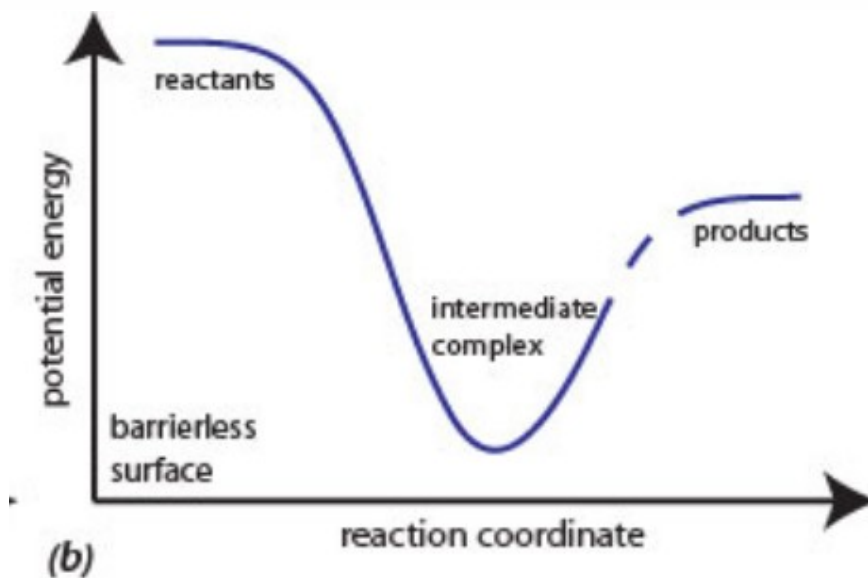* Transition state theory describes the process in more detail.

Reaction: $HO^- + CH_3Br \rightarrow [HO\text{---}CH_3\text{---}Br]^{\ddagger} \rightarrow CH_3OH + Br^-$
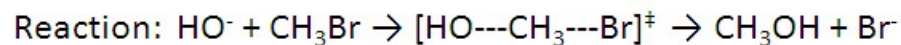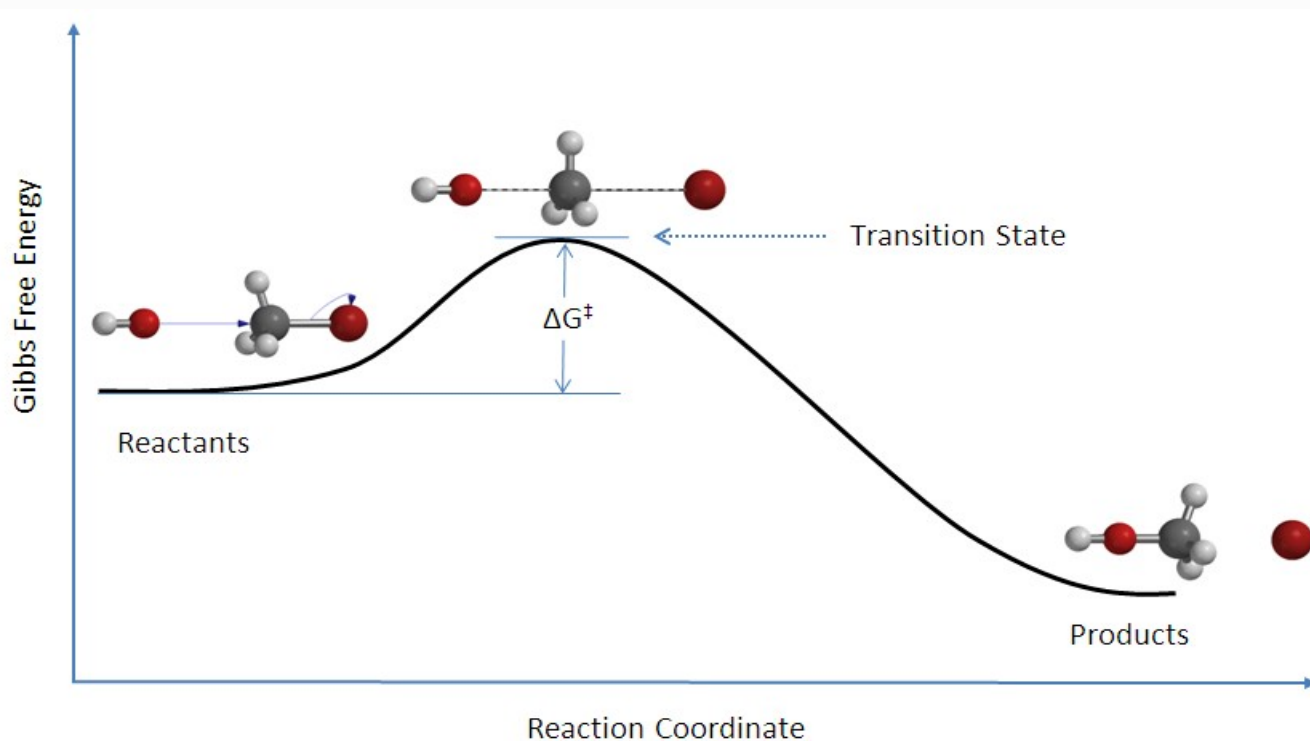
Barrierless reactions

* At ultracold temperature, only barrierless reactions are possible.

* With an exception for reactions involving quantum tunneling.

* Arrhenius' law is not applicable.

* Examples:

$H_2 + H_2^+ \rightarrow H_3^+ + H,$

$O + OH \rightarrow O_2 + H,$

$CN + O_2 \rightarrow NCO + O.$

Qualitative classical approach

At large distances the interaction between two molecules is $\sim 1/R^s$.
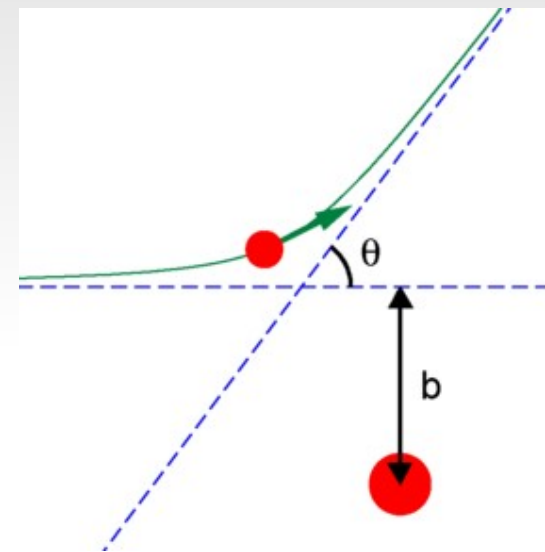
If centrifugal barrier is included

$$V_{eff}(R) = \frac{bE_c}{R^2} - \frac{C_s}{R^s}$$

b is the impact parameter.

In terms of the angular momentum L :

$$L = b\,\mu_c\,v_c$$

For a given E_c, only small b, such that $b < b_m$ contribute to the reaction probability.

Qualitative classical approach

$$V_{eff}(R) = \frac{bE_c}{R^2} - \frac{C_s}{R^s}$$

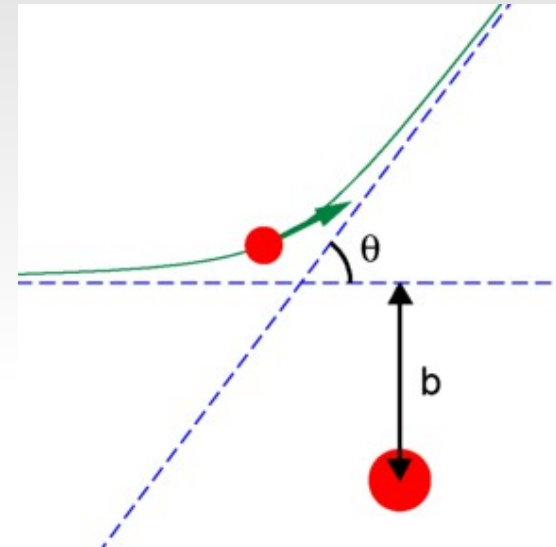$$L = b\,\mu_c\,v_c$$

So the cross section for the reaction is

$$\sigma_L = \pi\, b_m^2(E_c)$$

$$\sigma_L(E_c) = \pi\left(\frac{s}{s-2}\right)^{1-2/s}\left(\frac{sC_s}{2E_c}\right)^{2/s}$$

$$k_L(T) = \langle v_c\, \sigma(E_c)\rangle = \frac{8\pi}{(2\pi k_B T)^{3/2}}\int \sigma_L(E_c)\, e^{E_c/k_B T}\, E\, dE$$
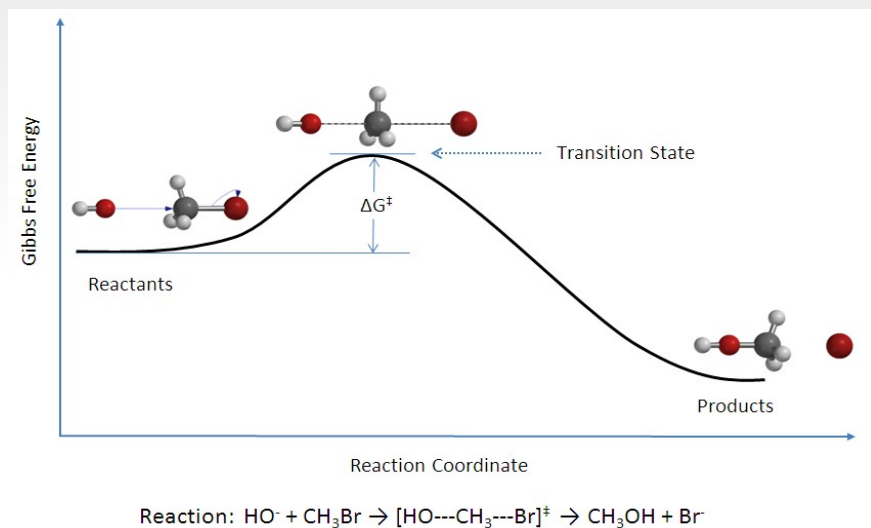
$$k_L(T) \sim T^{1/2-2/s} \quad \text{Langevin rate constant.}$$

Arrhenius' vs Langevin's behavior

Arrhenius' rate constant

Reaction: $HO^- + CH_3Br \rightarrow [HO\text{---}CH_3\text{---}Br]^{\ddagger} \rightarrow CH_3OH + Br^-$
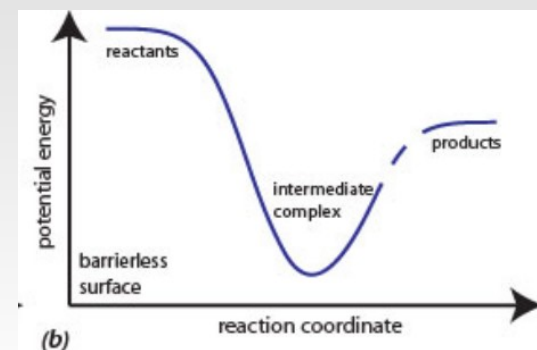
$$k_A(T) = k_0 e^{-\Delta G/k_B T}$$

When T is large

$$k_A(T) = k_0$$

Langevin rate constant

$$k_L(T) \sim T^{1/2 - 2/s}$$

For barrierless collisions between an ion and a non-rotating polar molecule $s=2$.

$$k_L(T) \sim T^{-1/2}$$

For an ion + rotating or non-polar molecule, $s=4$.

$$k_L(T) \sim const$$

Classical vs quantum approach

Quantum approach is needed even if classical Langevin or Arrhenius laws are used.

$$V_{eff}(R) = \frac{bE_c}{R^2} - \frac{C_s}{R^s} \qquad k_A(T) = k_0 e^{-\Delta G/k_B T}$$

$$\sigma_L = \pi b_m^2 (E_c)$$

$$k_L(T) \sim T^{1/2 - 2/s}$$

When collision velocities are small, relative motion of the reactants should be treated using quantum mechanical methods.

A quantum-mechanical approach is needed, especially, if photon emission or absorption is involved (radiative collisional processes).

Experimental techniques to produce ultracold molecules