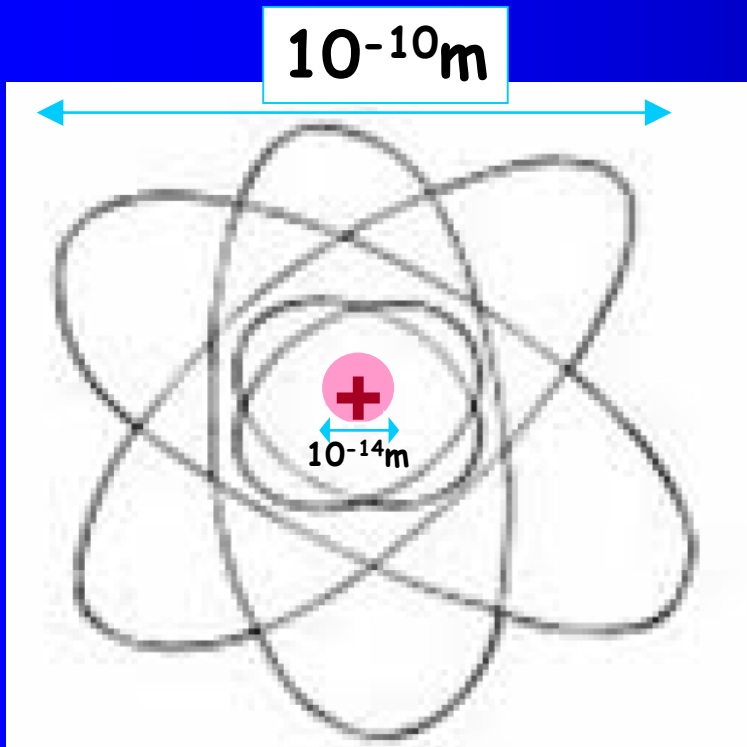
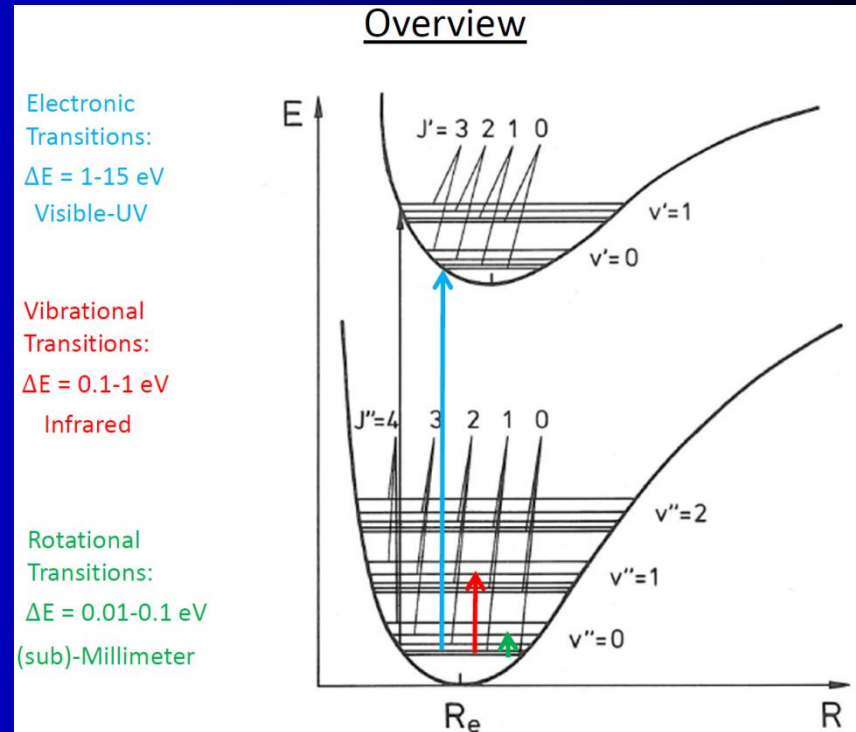


## Rotational and vibrational excitation

## Rutherford atom

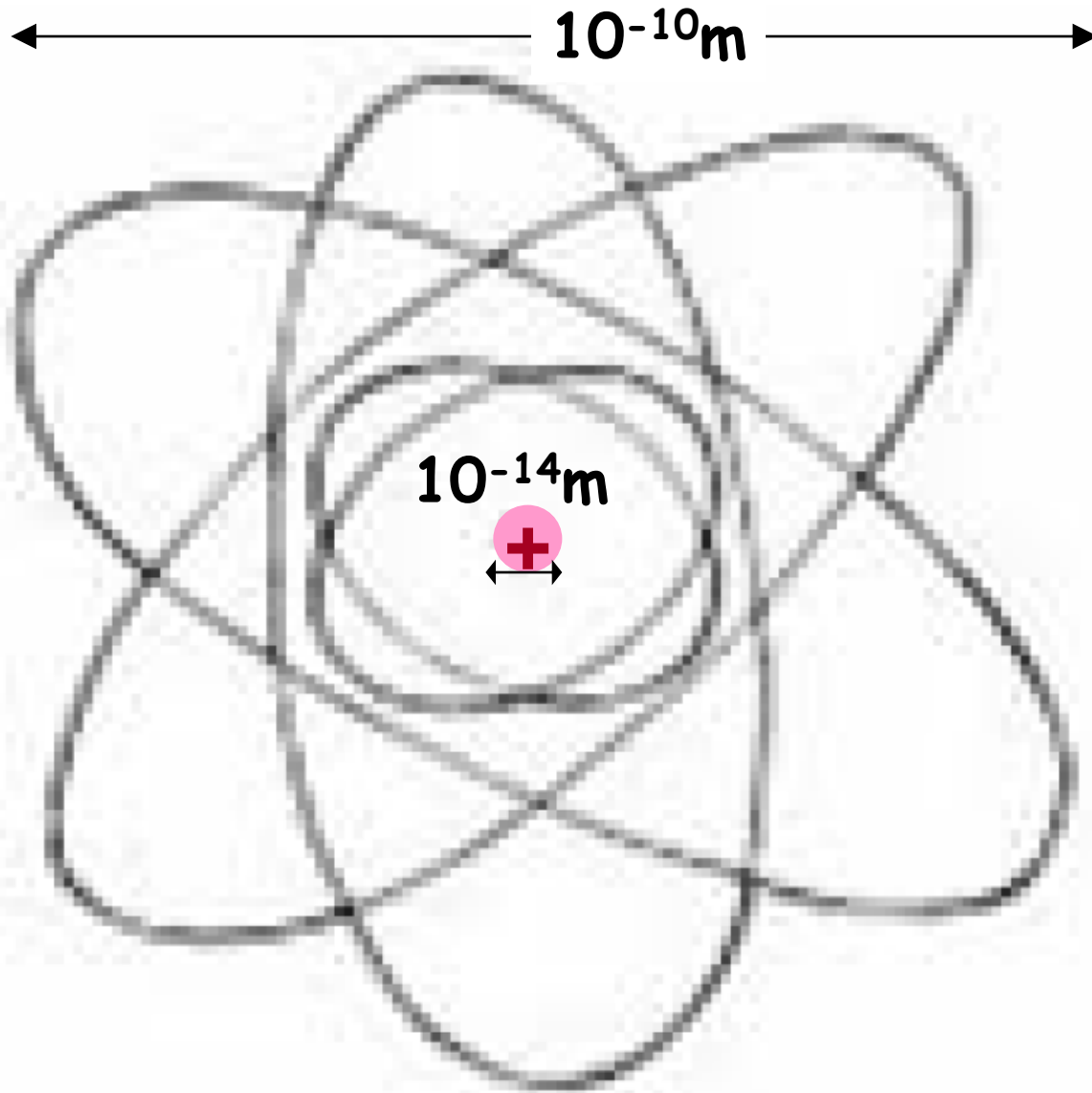


## Excitation energies



A **shape resonance** is a metastable state in which an electron is trapped due to the shape of a potential barrier.

# Rutherford atom

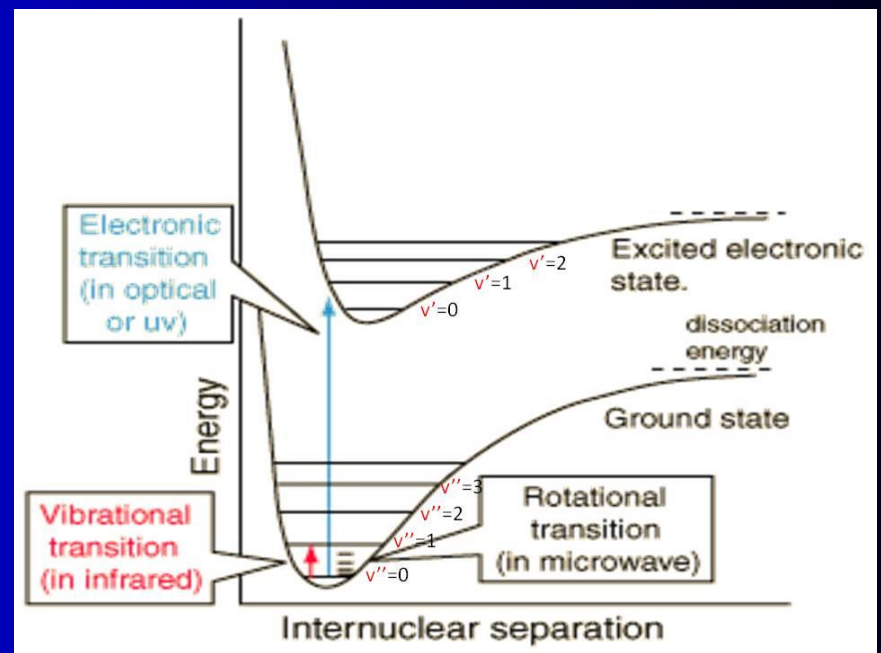
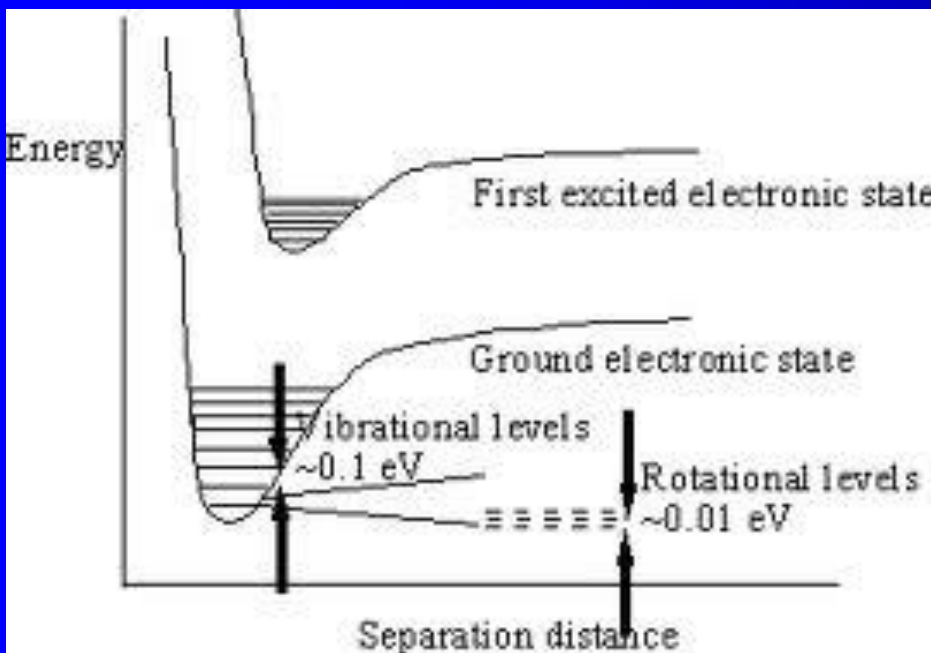
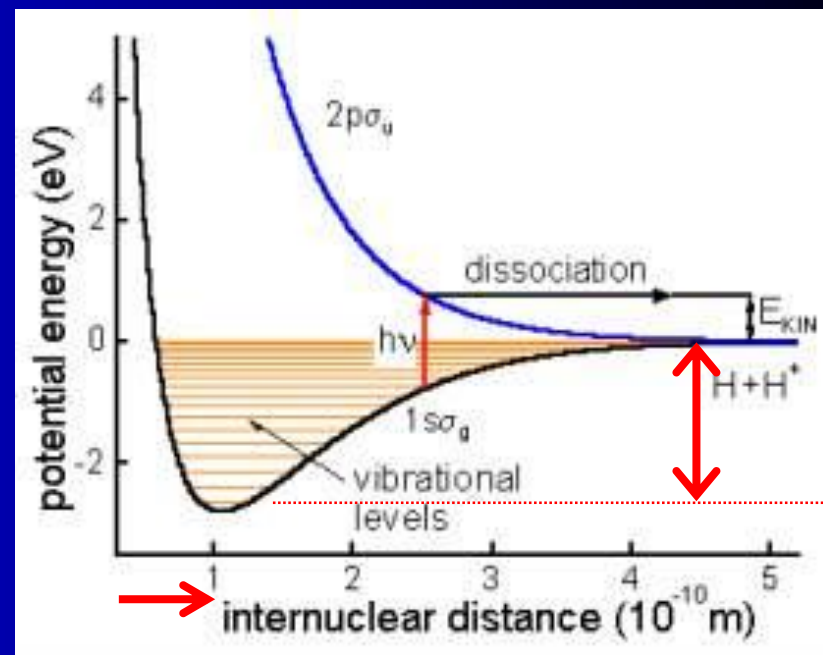
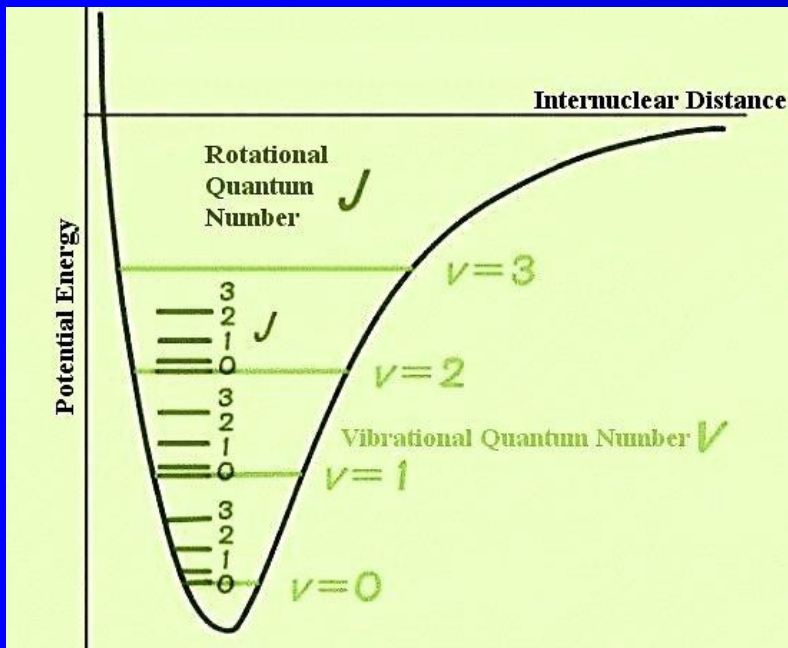


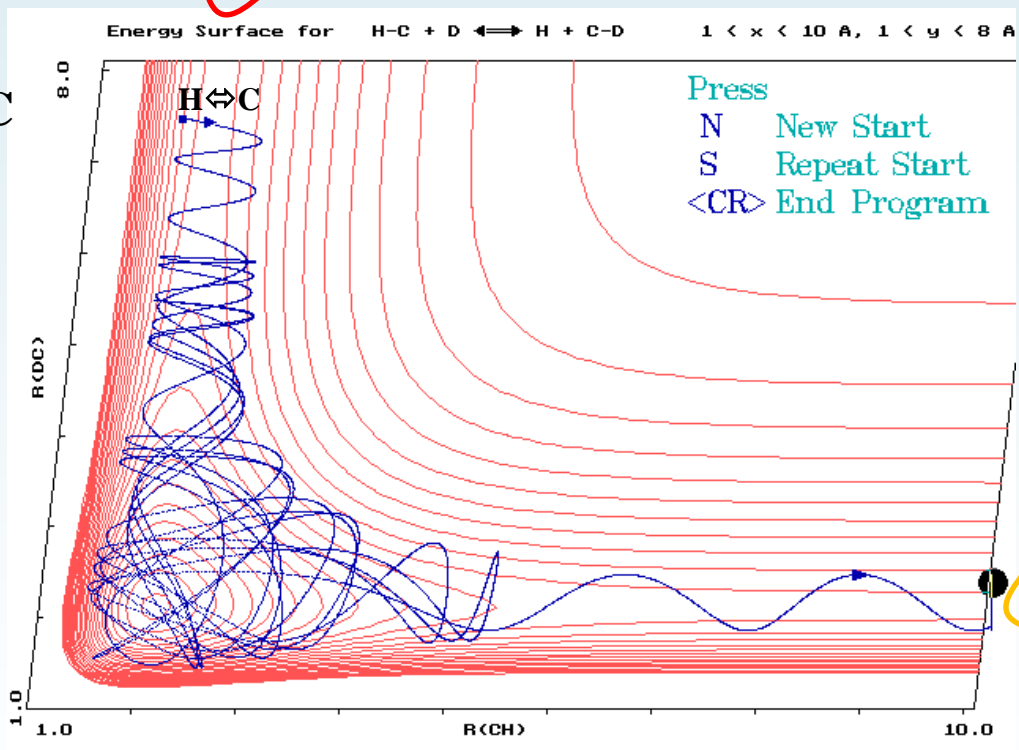
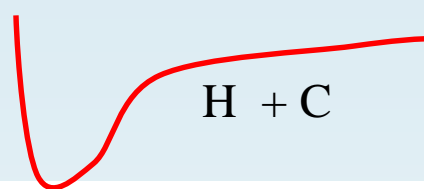
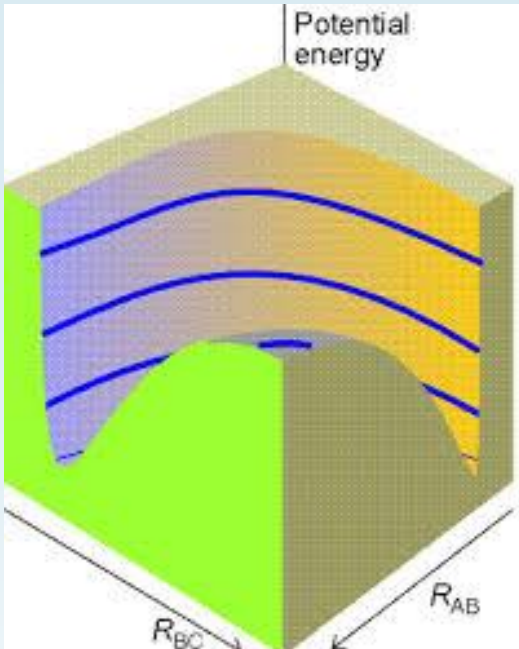
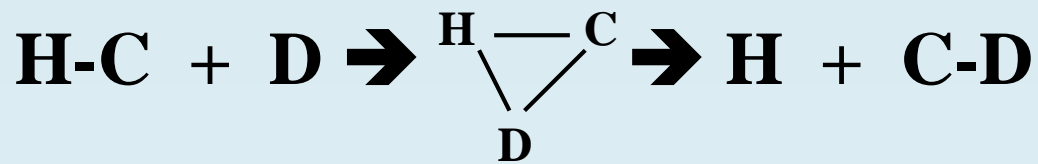
**Not to scale!!**

If it were to scale,  
the nucleus would  
be too small to see

Even though it has  
more than 99.9%  
of the atom's mass

# Energy levels





H ⇌ C

D

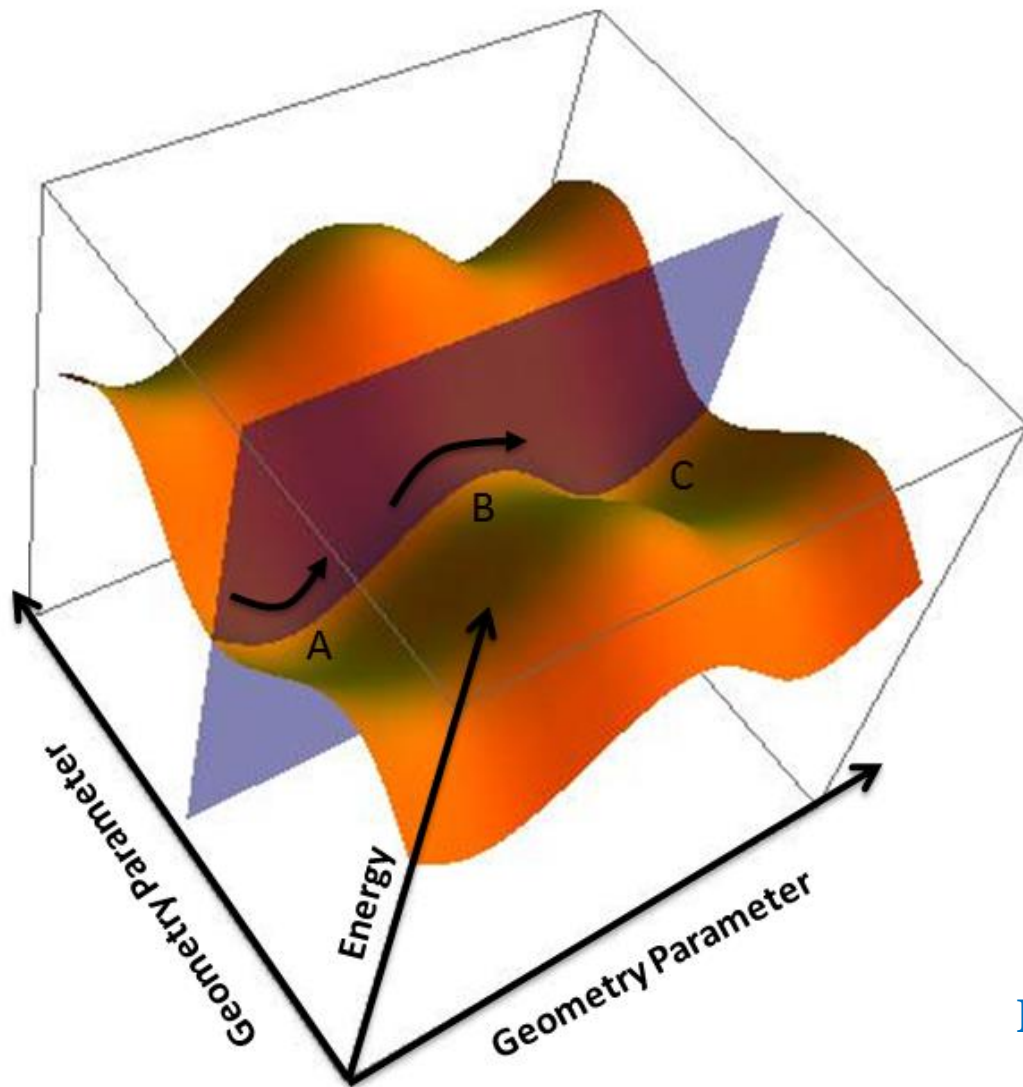
A blue arrow points from the 'H ⇌ C' label to the 'D' label.

H

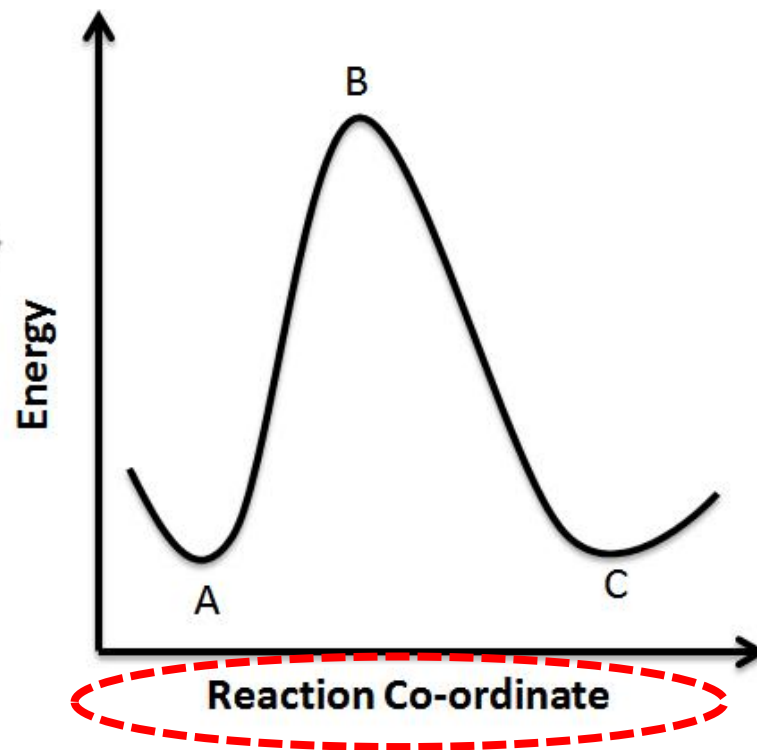
C ⇌ D

A blue arrow points from the 'C ⇌ D' label to the 'H' label.





## Reaction coordinate



## Reaction Coordinate

“.....In chemistry, a **reaction coordinate**<sup>[1]</sup> is an abstract one-dimensional coordinate which represents progress along a reaction pathway. It is usually a geometric parameter that changes during the conversion of one or more molecular entities. In molecular dynamics simulations, a reaction coordinate is called **collective variable**.<sup>[2]</sup> .....”



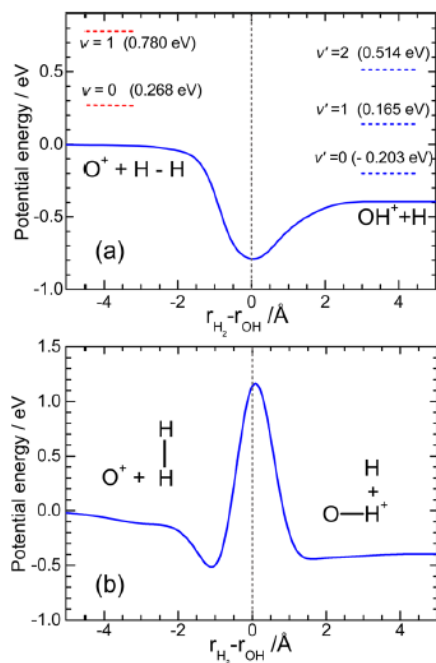
Accurate Time-Dependent Wave Packet Calculations for the  
 $\text{O}^+ + \text{H}_2 \rightarrow \text{OH}^+ + \text{H}$  Ion-Molecule ReactionN. Bulut,<sup>†</sup> J.F. Castillo,<sup>‡</sup> P. G. Jambrina,<sup>‡</sup> J. Klos,<sup>§</sup> O. Roncero,<sup>||</sup> F. J. Aoiz,<sup>‡</sup> and L. Bañares<sup>\*,‡</sup>*J. Phys. Chem. A* 2015, 119, 11951–11962

Figure 1. Minimum energy path for the  $\text{O}^+ + \text{H}_2 \rightarrow \text{OH}^+ + \text{H}$  reaction calculated on the MMG PES<sup>10</sup> as a function of  $r_{\text{H}_2} - r_{\text{OH}}$ . (a) Collinear configuration,  $\overline{\text{OHH}}$  angle  $\alpha = 180^\circ$ . The dashed horizontal lines indicate the energy of the initial  $\text{H}_2$   $v=0$  and  $v=1$ , and final  $\text{OH}^+$   $v'=0$ ,  $v'=1$ , and  $v'=2$  vibrational states. (b) Perpendicular configuration  $\overline{\text{OHH}}$  angle  $\alpha = 90^\circ$ .

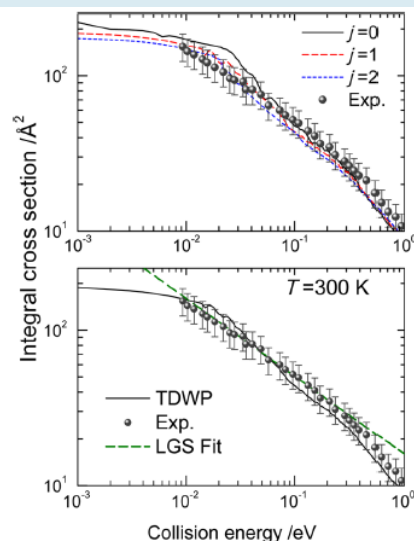


Figure 8. Top: total reaction cross section as a function of collision energy for the  $\text{O}^+ + \text{H}_2(v=0, j)$  reactions. Solid black line:  $j=0$ . Red dashed line:  $j=1$ . Blue short-dashed line:  $j=2$ . Solid circles: experimental results from ref 7. Bottom: Total reaction cross section as a function of collision energy for the  $\text{O}^+ + \text{H}_2(v=0, j)$  reaction averaged over the thermal rotational population at 300 K. Black solid line: TDWP. Solid circles: experimental results from ref 7. Green dashed line: Langevin model,  $\sigma_r(E_c) = AE_c^{-1/2}$ ;  $A = 16 \text{ \AA}^2 \text{ eV}^{1/2}$ .

## Reaction Coordinate Diagrams

“ ..... We can follow the progress of a reaction on its way from reactants to products by graphing the energy of the species versus the reaction coordinate. We will be vague in describing the reaction coordinate because its definition is a mess of other variables composed to best make sense of the progress of the reaction. The value of the reaction coordinate is between zero and one. Understanding the meaning of the reaction coordinate is not important, just know that small values of reaction coordinate (0-0.2) mean little reaction has taken place and large values (0.8-1.0) mean that the reaction is almost over. It is a kind of scale of the progress of a reaction. A typical reaction coordinate diagram for a mechanism with a single step is shown below: .....“

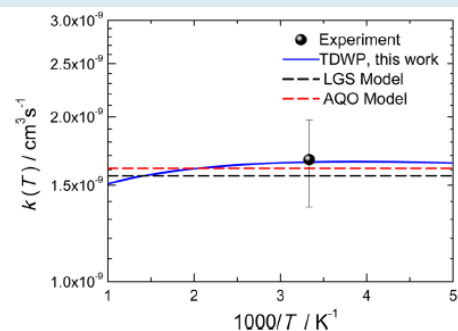


Figure 9. Thermal rate constants for the  $\text{O}^+ + \text{H}_2$  reaction. Blue solid line: TDWP. Solid circle: experimental result from ref 7. Black dashed line: Langevin model. Red dashed line: AQO model.

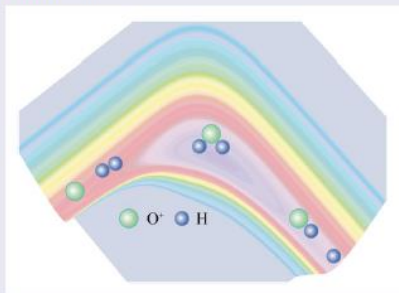
# Dynamics studies of $O^+ + D_2$ reaction using the time-dependent wave packet method

Ziliang Zhu<sup>a,b</sup>, Li Li<sup>b</sup>, Qiju Li<sup>b</sup> and Bing Teng<sup>a</sup>

<sup>a</sup>College of Physics, Qingdao University, Qingdao, People's Republic of China; <sup>b</sup>Shandong Peninsula Engineering Research Center of Comprehensive Brine Utilization, Weifang University of Science and Technology, Shouguang, People's Republic of China

## ABSTRACT

Based on the potential energy surface (PES) reported by Li *et al.* (Phys. Chem. Chem. Phys. **20**, 1039 (2018)), the initial state dynamics calculation of  $O^+ + D_2$  ( $v = 0, j = 0$ ) reaction was conducted using the time-dependent wave packet method with a second order split operator. Dynamics properties such as reaction probability, integral cross section, differential cross section, and distribution of products were calculated and compared with available experimental and theoretical results. The present integral cross section values were in good agreement with experimental results. In addition, the differential cross section indicates that the mechanism of the complex-formation reaction plays a dominant role during the reaction.



## ARTICLE HISTORY

Received 15 November 2018  
Accepted 7 May 2019

## KEYWORDS

Reaction probability;  
 $O^+ + D_2$  reaction; integral cross section;  
time-dependent wave packet

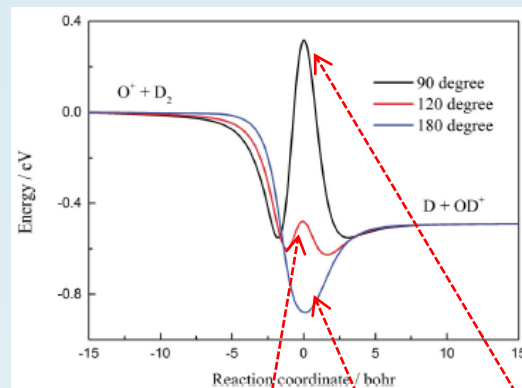


Figure 1. Minimum energy path of  $O^+ + D_2$  PES for 90, 120, and 180 degrees.

“....In chemistry, a reaction coordinate<sup>[1]</sup> is an abstract one-dimensional coordinate which represents progress along a reaction pathway. It is usually a geometric parameter that changes during the conversion of one or more molecular entities. In molecular dynamics simulations, a reaction coordinate is called collective variable.<sup>[2]</sup> .....

## Reaction Coordinate

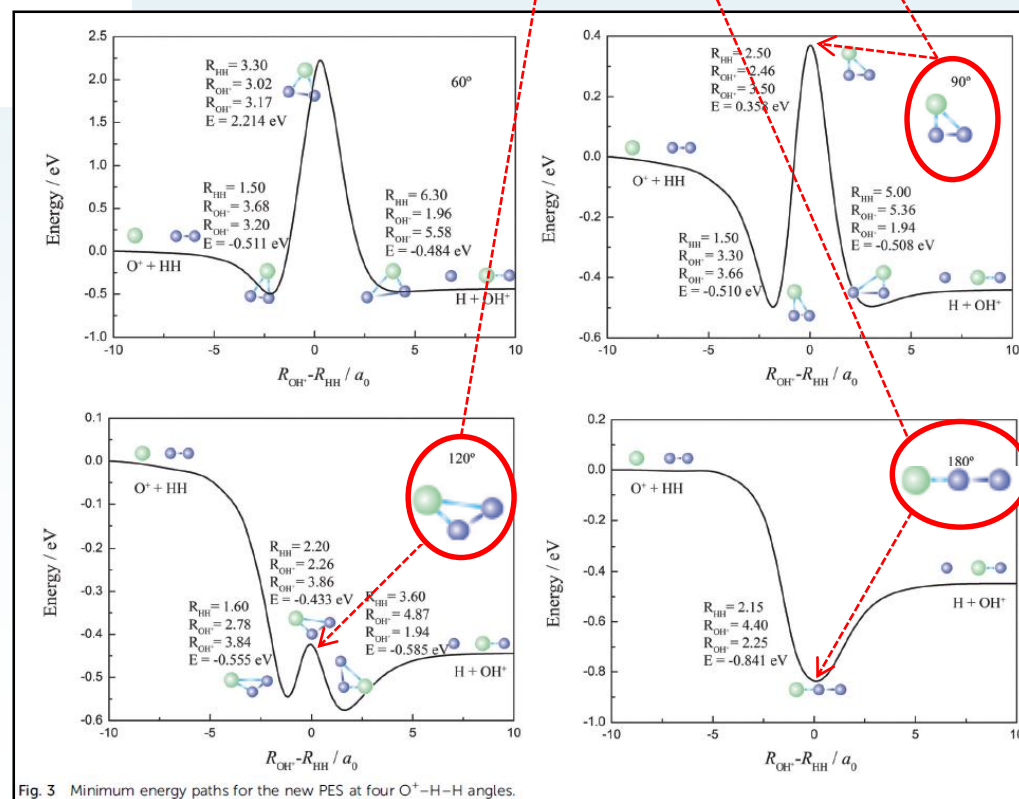


Fig. 3 Minimum energy paths for the new PES at four  $O^+-H-H$  angles.



# A new potential energy surface of the $\text{OH}_2^+$ system and state-to-state quantum dynamics studies of the $\text{O}^+ + \text{H}_2$ reaction†

Wentao Li,<sup>a,b</sup> Jiuchang Yuan,<sup>b</sup> Meiling Yuan,<sup>c</sup> Yong Zhang,<sup>d</sup> Minghai Yao<sup>a</sup> and Zhigang Sun<sup>a,b</sup>

Cite this: *Phys. Chem. Chem. Phys.*, 2018, 20, 1039

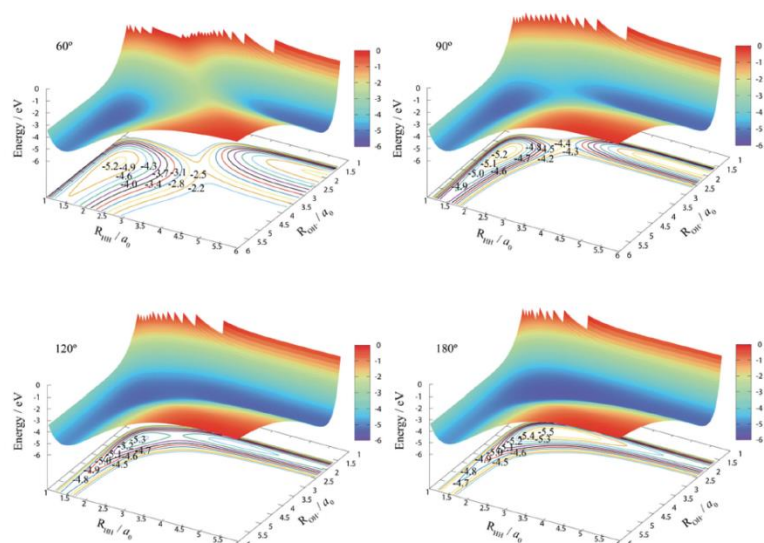


Fig. 2 Potential energy surfaces for  $\text{O}^+ - \text{H} - \text{H}$  angles of  $60^\circ$ ,  $90^\circ$ ,  $120^\circ$ , and  $180^\circ$ .

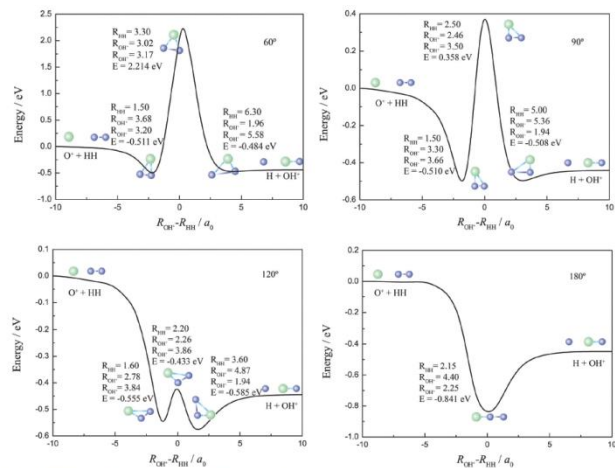


Fig. 3 Minimum energy paths for the new PES at four  $\text{O}^+ - \text{H} - \text{H}$  angles.

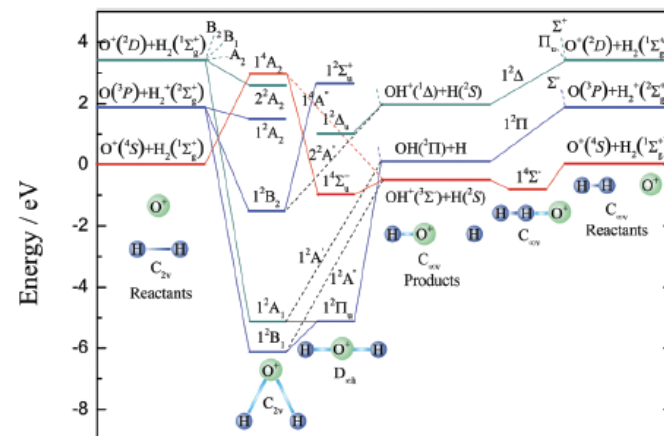


Fig. 1 Electronic correlation diagram for reactant, intermediate, and product arrangements of the  $\text{H}_2\text{O}^+$  system under  $C_{2v}$ ,  $C_{\infty v}$ , and  $D_{\infty h}$  symmetries. The PESs of the title reaction are plotted by the red lines. This diagram is an adaptation of that reported in ref. 24.

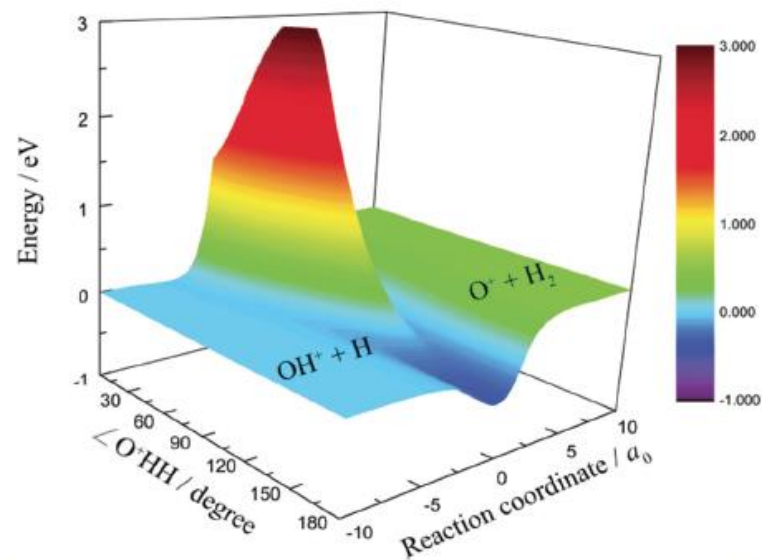


Fig. 4 Minimum energy paths of the new PES as a function of the bond-bond angle.

## Reaction Coordinate



# Princip akce a reakce



Henri Louis Le  
Chatelier   
(1850-1936)



Karl Ferdinand  
Braun   
(1850-1918)



Při ovlivňování rovnováhy se uplatňuje princip akce a reakce aplikovaný na chemické děje, známý pod názvem ***Le Chatelierův-Braunův princip***.

*Porušení rovnováhy vnějším zásahem (akcí) vyvolá děj (reakci), který směřuje ke zrušení účinku vnějšího zásahu (akce).*

$$P \sim \langle \Psi_{\text{initial}} | \Psi_{\text{final}} \rangle^2.$$

# Franck Condon principle



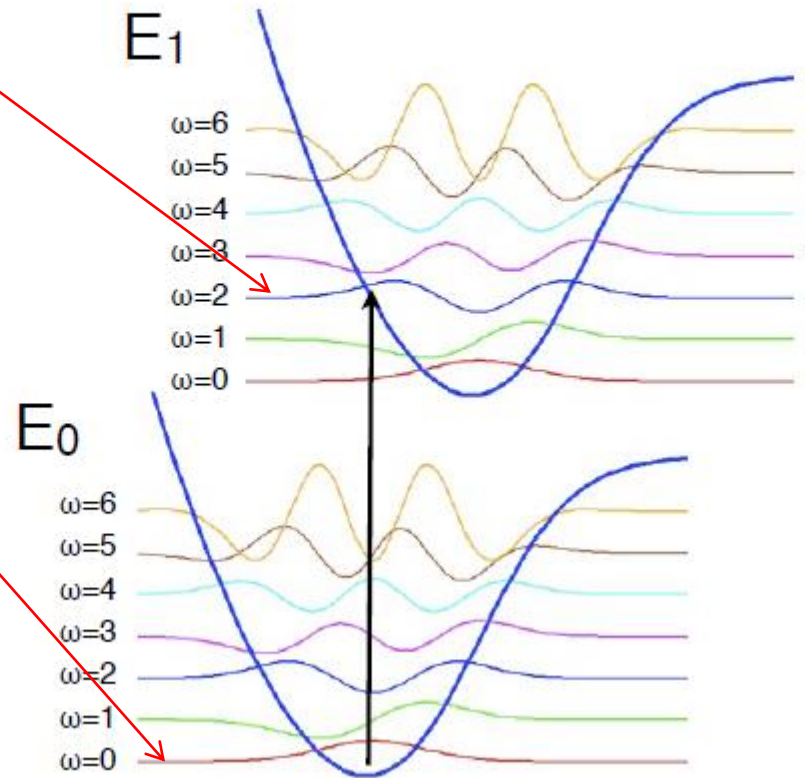
James Franck  
1882-1964  
1925 Nobel prize



Edward Condon  
1902-1974

The probability (or amplitude) of a simultaneous electronic and vibrational transition to a new “vibronic” state depends on the overlap between the wavefunctions of the ground and excited states.

Or:  
Electrons move much faster than nuclei. For an electronic excitation to occur, the nucleic configuration should be optimal (the same).



# Transitions between molecular potential energy surfaces

During an electronic transition  
the complex absorbs energy  
electrons change orbital  
the complex changes energy state

electron transitions  
higher energy  
visible and UV radiation

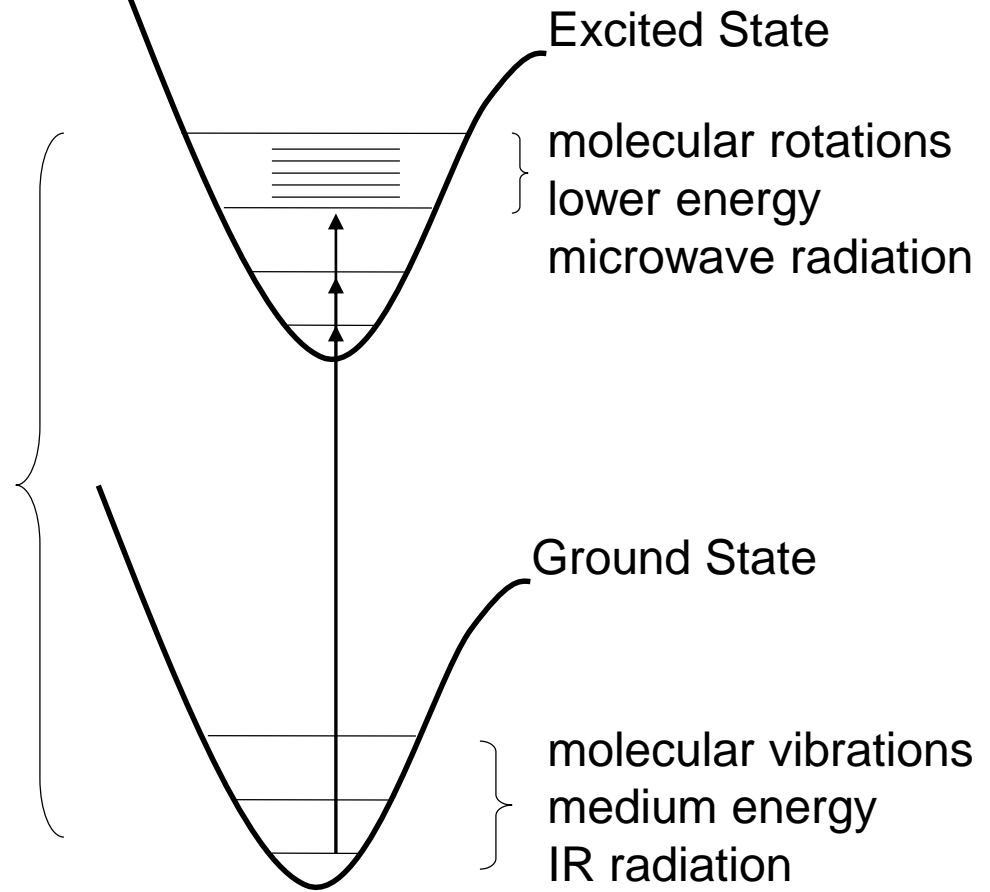
$$\text{Electron: } 1\text{eV} \rightarrow \nu = 5.9 \times 10^7 \text{ cm s}^{-1}$$
$$\tau \sim a_0 / \nu \sim 10^{-8} / 5.9 \times 10^7 = 2 \times 10^{-16} \text{ s}$$

**Timescale :  $\approx 10^{-15}$  sec**

Timescale of geometry changes  
(vibrations):  $\approx 10^{-12}$  sec

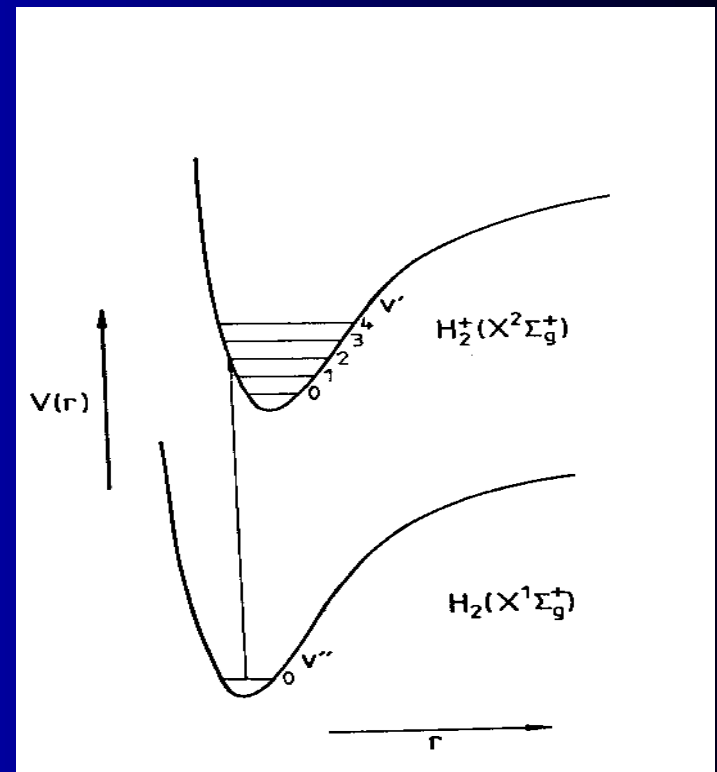
As a result, observe vertical (Franck-Condon) transitions

**In other words, we assume that we only have to consider the electronic portion of the ground- and excited-state wavefunctions to understand these transitions: Born-Oppenheimer approximation**



# The Born-Oppenheimer Approximation

The Born Oppenheimer Approximation assumes that electrons in a molecule move much faster than the nuclei, and adapt instantaneously, finding the lowest potential energy for each nuclear configuration. Therefore, it is possible to calculate an electronic energy for each nuclear configuration, considering the nuclei frozen.



Condon approximation or Franck-Condon principle.

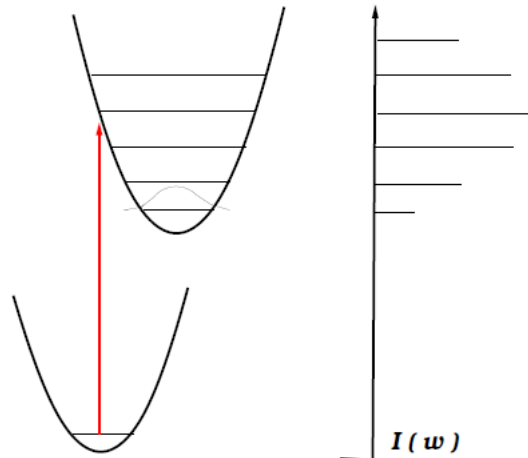
In the Condon approximation:

$$\int \Psi_F^* H_1 \Psi_I dx dQ = T_{fi}(Q=0) S_{v'v}$$

with

$$S_{v'v} = \int \tilde{\chi}_{v'}^*(Q) \chi_v(Q) dQ.$$

$S_{v'v}$  and its square are Franck-Condon overlap integral and Franck-Condon factor, respectively (see also [2]).



The spectrum follows immediately:

$$I(\omega_{ph}) \sim |T_{fi}(Q=0)|^2 \sum_{v'} |S_{v'v}|^2 \delta(\tilde{E}_{v'} - E_v - \hbar\omega_{ph})$$

The relative intensities are determined only through vibrational wave functions, electronic wave functions play almost no role.

Principle of vertical transitions !

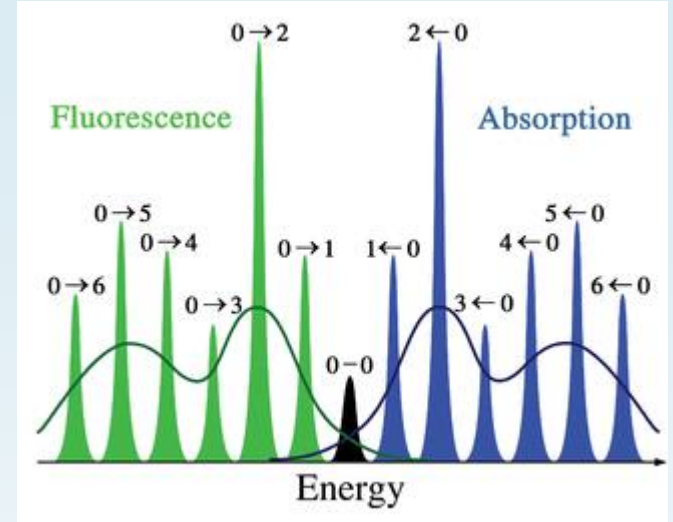
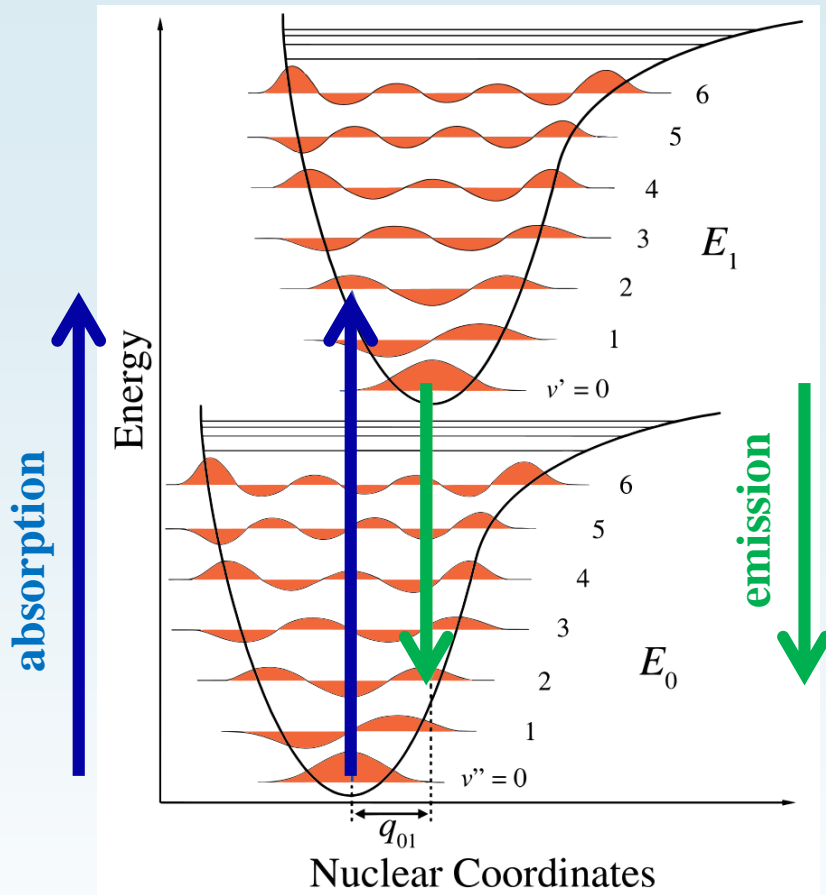
$$P \sim \langle \Psi_{\text{initial}} | \Psi_{\text{final}} \rangle^2.$$

## Absorption or emission of a photon

## Collision with electron

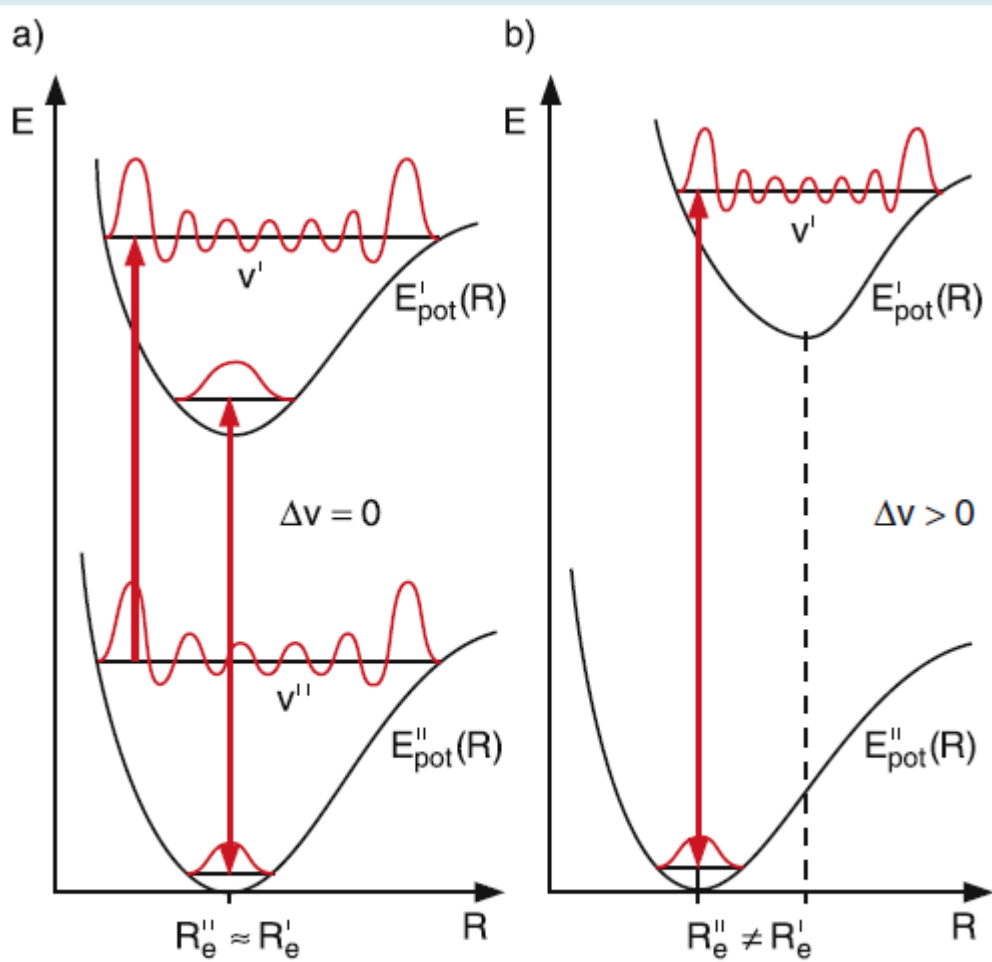
The **Franck–Condon principle** is a rule in spectroscopy and quantum chemistry that explains the intensity of vibronic transitions. Vibronic transitions are the simultaneous changes in electronic and vibrational energy levels of a molecule due to the absorption or emission of a photon of the appropriate energy. The principle states that during an electronic transition, a change from one vibrational energy level to another will be more likely to happen if the two vibrational wave functions overlap more significantly.

# The absorption or emission of a photon



Schematic representation of the absorption and fluorescence spectra corresponding to the energy diagram in Figure 1. The symmetry is due to the equal shape of the ground and excited state potential wells. The narrow lines can usually only be observed in the spectra of dilute gases. The darker curves represent the inhomogeneous broadening of the same transitions as occurs in liquids and solids. Electronic transitions between the lowest vibrational levels of the electronic states (the 0–0 transition) have the same energy in both absorption and fluorescence

Franck–Condon principle energy diagram. Since electronic transitions are very fast compared with nuclear motions, vibrational levels are favoured when they correspond to a minimal change in the nuclear coordinates. The potential wells are shown favouring transitions between  $v = 0$  and  $v = 2$ .

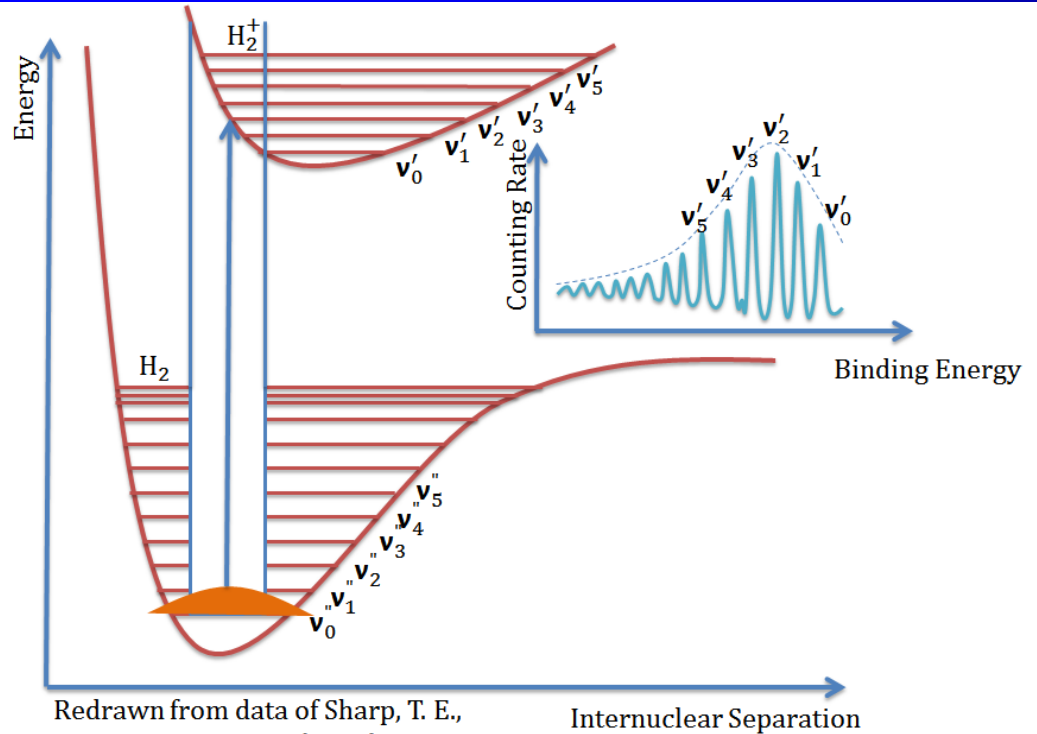


**Fig. 9.62.** Illustration of the Franck-Condon principle for vertical transitions with  $\Delta v = 0$  (a) and  $\Delta v > 0$  in case of potential curves with  $R''_e = R'_e$  and  $R'_e > R''_e$



# Photoelectron spectrum $H_2$

$$P \sim \langle \Psi_{\text{initial}} | \Psi_{\text{final}} \rangle^2.$$

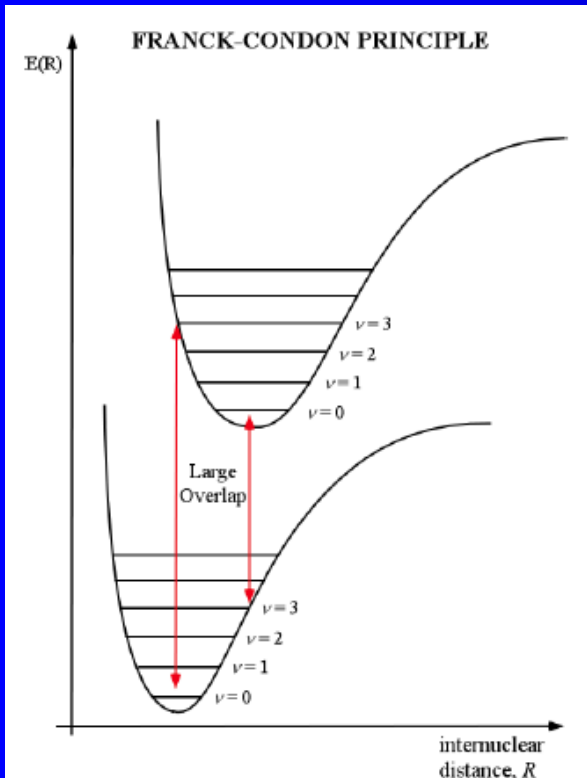


Redrawn from data of Sharp, T. E.,  
*Atomic Data*, **2**, 119 (1971)

Fig. 3 Photoelectron spectrum of the ionization of  $H_2$

## Franck-Condon Principle

- Absorption of light and promotion of an electron from one state to another happens rapidly.
- Because of the short time it takes for the electronic transition, there is little or no geometry change in the molecular system.
- As a result, we say that **electronic transitions occur vertically** on a potential energy diagram.



# Franck-Condon Principle

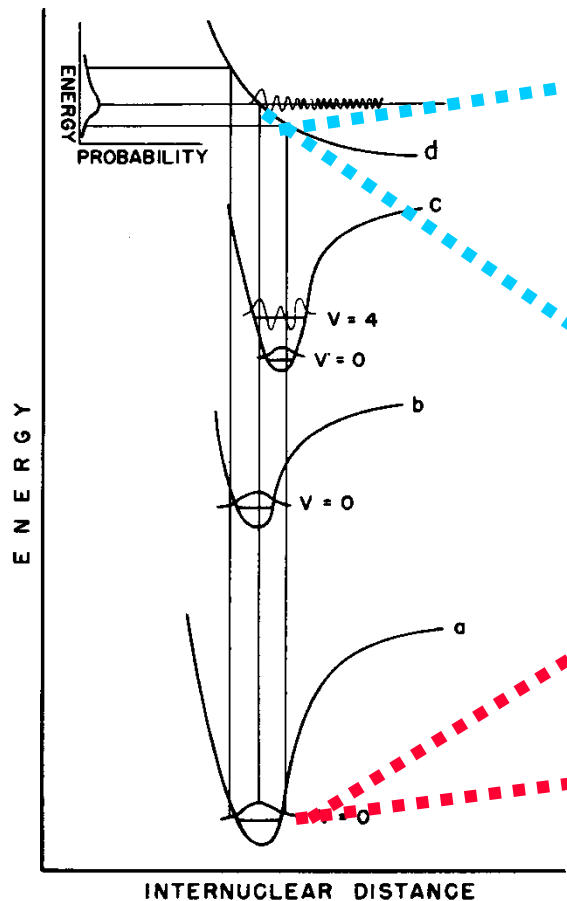
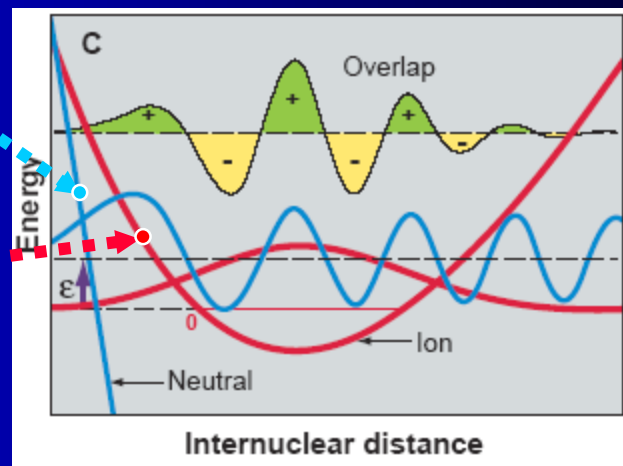
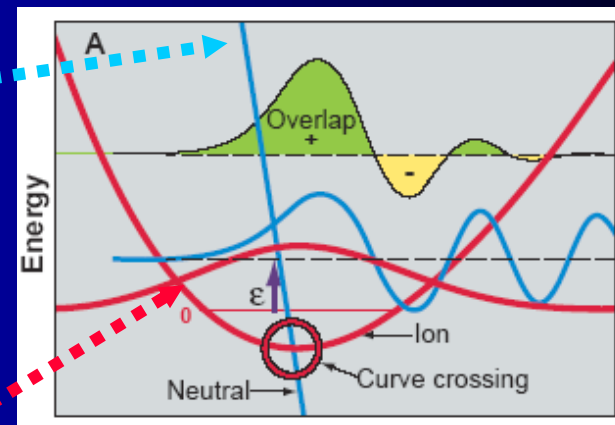


FIG. 21. Illustrative diatomic molecule and molecule-ion potential energy curves. The actual energy difference between curves a and b, c, and d is much greater than represented.

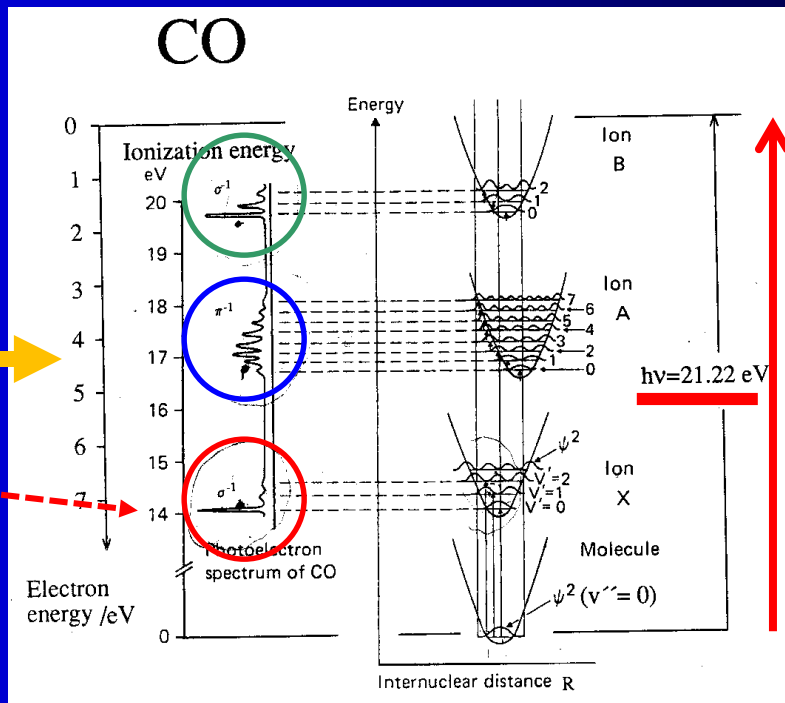
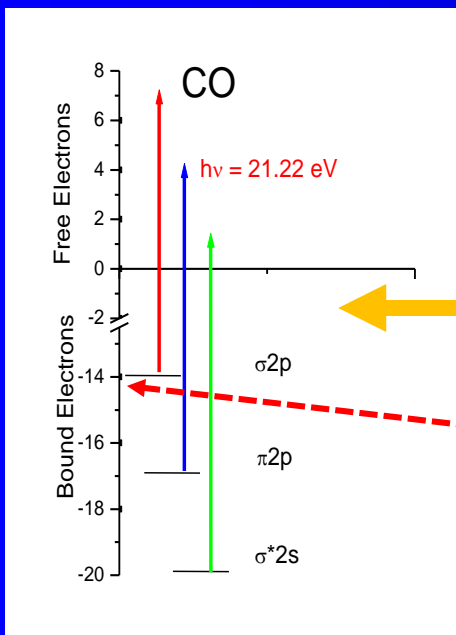


## Franck-Condon Factors

$$P \sim \langle \Psi_{\text{initial}} | \Psi_{\text{final}} \rangle^2$$

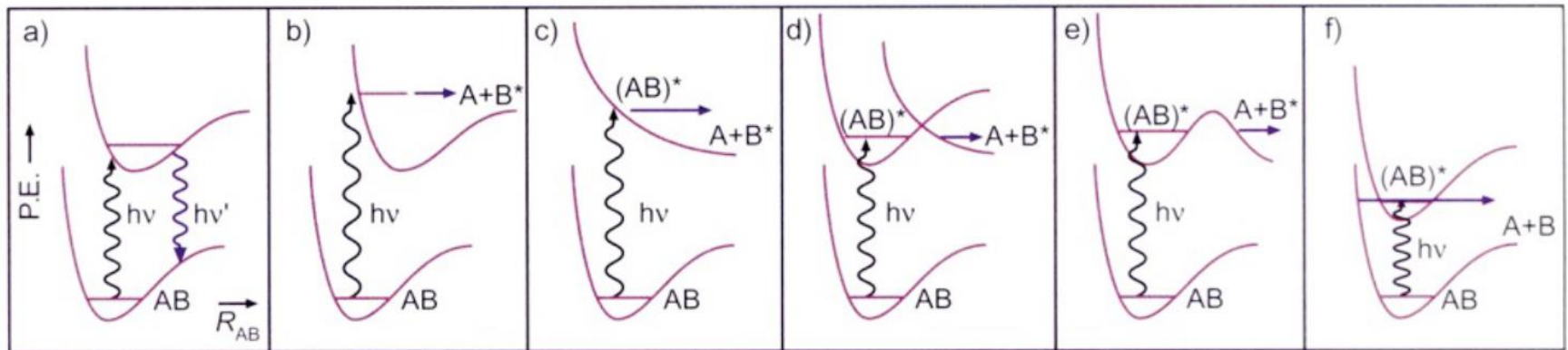
# Franck-Condon principle - FOTOIONIZATION

MO diagram for the three highest occupied MOs in CO accessible by HeI radiation. PES of CO obtained by HeI radiation and potential energy curves for the neutral molecule and the three ionized states.



## 4.5.1 Dynamics of electronically excited states

A molecule which is electronically excited by (laser) radiation can undergo a range of dynamical processes:



a) Laser-induced fluorescence

b) Excitation to the repulsive wall of a bound state, leading to direct dissociation

c) Excitation of a repulsive state, leading to direct dissociation

d) Excitation to a bound state and dissociation by coupling to a repulsive state

e) Excitation to a bound state and dissociation by tunneling through a barrier

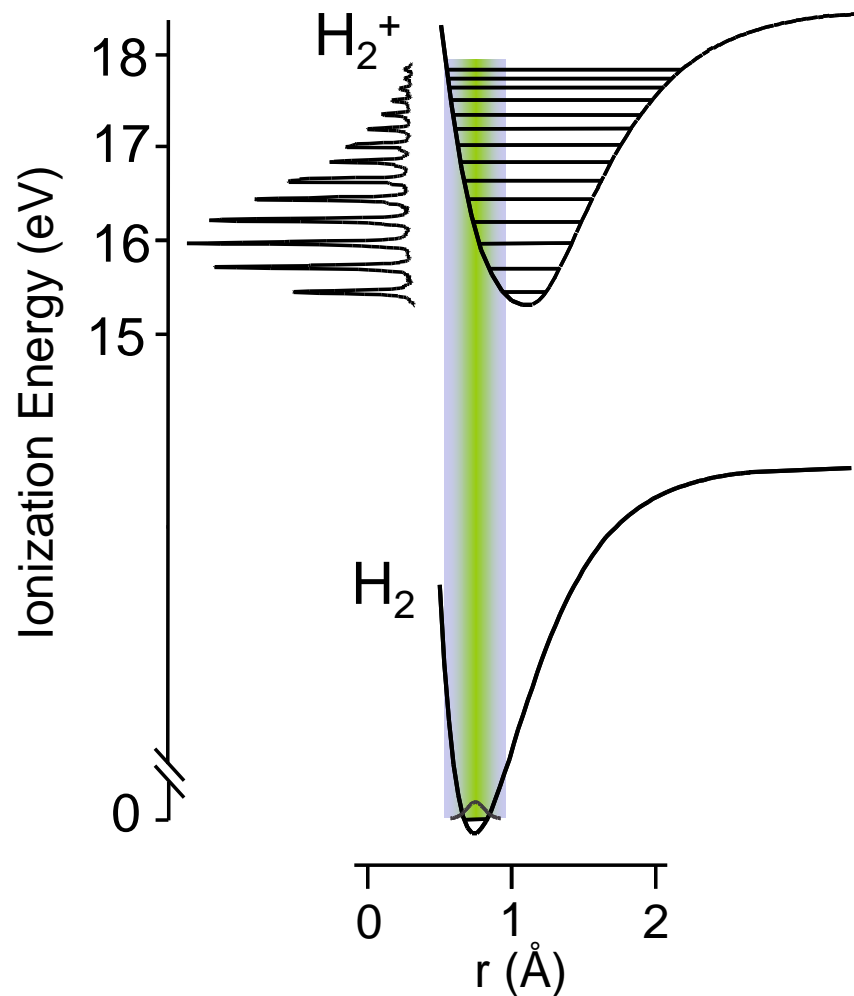
f) Excitation to a bound state and dissociation by internal conversion to the dissociation continuum of the ground state

Processes d)-f) are referred to as **predissociation**.

Details of interaction of electron with molecules

Details of interaction of electron with H<sub>2</sub>

# Potential Energy Surface Description of the Ionization of Dihydrogen



# PES of H<sub>2</sub>

