

Mid-Sem Exam Solution

- In the hard sphere reactive collision model, the collision cross section (b) and the radii of the colliding atoms or molecules (r_1 and r_2) are important in deciding the nature of the reaction. For the reaction to be of the rebound type, we require:
 - $b = r_1 - r_2$, for all r_1 and r_2
 - $b = r_1 + r_2$, for all r_1 and r_2 .
 - $b < r_1 + r_2$, for all r_1 and r_2 .
 - $b = r_1 - r_2$, if $r_1 > r_2$.
- Probability of transition between two states under irradiation of light of suitable frequency depends on
 - excitation light intensity
 - transition moment between the two states
 - monochromaticity of the excitation light
 - difference between the excited state and ground state dipole moment

Note: Fermi's Golden rule

Probability of transition under resonance condition

$$\begin{aligned}\Gamma_{m \rightarrow n} &= \frac{\pi^2}{h} \langle \psi_n | \mu | \psi_m \rangle^2 \rho(h\nu_{mn}) \\ &= \frac{\pi^2}{h} |M_{mn}|^2 \rho(h\nu_{mn})\end{aligned}$$

- Phenomena that came directly out of the Einstein treatment of light-matter interaction is(are)
 - When there is absorption, there will be stimulated emission
 - Rate constant of spontaneous emission decreased with increase in the energy gap between the two states.
 - Rate of stimulated emission depends on the population of the excited state
 - For induced absorption, the Bohr resonance condition must be satisfied.

Remember:

$$B_{mn} = B_{nm}$$

$$\text{Rate of stimulated emission} = \text{Const. } N_n \rho(h\nu_{mn})$$

$$h\nu = \Delta E = E_n - E_m \text{ Bohr resonance condition}$$

- Lifetime of an excited state, after the excitation light is switched off, can be written as (Note: A and B are the Einstein's A, B coefficients)
 - $1/(A+B)$
 - $1/A^2$
 - $1/A$
 - B/A

In absence of excitation light the only possible process is spontaneous emission and is related to the Einstein's A coefficient.

5. Choose the correct option(s) related to the population of energy levels.
 - a. The time required to achieve the saturation of excited state population of a 2-level system decrease with increase in the transition moment integral
 - b. For a 3-level system, a steady-state population inversion may be achieved between the first and third level using direct optical pumping.
 - c. Under suitable condition, it is easy to achieve population inversion between level-3 and level-2 for a 4-level system compared to level-2 and level-1 of a 3-level system.
 - d. When population inversion is achieved, spontaneous emission is dominated over stimulated emission and induced absorption in a ruby crystal in presence of 400 nm light.

For 2-level system

$$\frac{N_2}{N_t} = \frac{B\rho(h\nu_{mn})}{A + 2B\rho(h\nu_{mn})} \{1 - e^{-[A+2B\rho(h\nu_{mn})]t}\}$$

Thus, the time constant is $\frac{1}{[A+2B\rho(h\nu_{mn})]}$. A and B both contains the transition moment integral.

For 3-level system, the ground state is involved, which is highly populated.

6. The ratio of the number of spontaneous emission event to the number of stimulated emission event in a 2-level system is equal to

- a. $\frac{A_{21}}{B_{21}}$
- b. $\frac{A_{21} \rho(h\nu_{21})}{B_{21}}$
- c. $e^{\frac{E_2}{k_B T}}$
- d. $e^{\frac{E_2 - E_1}{k_B T}} - 1$

7. For a laser, the cavity length is 60 cm and the natural band width of the gain medium is 1.5 GHz. The number of longitudinal modes present in the laser is 6

$$dv = \frac{c}{2L} = 0.25 \text{ GHz}$$

$$\frac{1.5 \text{ GHz}}{0.25 \text{ GHz}} = 6$$

8. Stimulated and spontaneous emissions, respectively, are

- a. coherent and incoherent
- b. unpolarized and polarized
- c. polychromatic and monochromatic
- d. unidirectional and omnidirectional

9. A mode-locked laser

- a. is inherently polychromatic
- b. has a broad spectrum

- c. provides pulsed operation
d. has more than 1 longitudinal mode inside the optical cavity
10. The total Kinetic Energy (K) of two colliding particles with masses (m_1 and m_2) and corresponding velocities (v_1 and v_2) can be expressed as
- $K = \frac{1}{2}m_1v_1^2 + \frac{1}{2}m_2v_2^2$
 - $K = \frac{1}{2}(m_1 + m_2)v_{rel}^2 + \frac{1}{2}\left(\frac{m_1m_2}{m_1+m_2}\right)v_{CM}^2$ where v_{CM} is the velocity of the center of mass of the particles and v_{rel} is their relative velocity
 - $K = \frac{1}{2}Mv_{CM}^2 + \frac{1}{2}\mu v_{rel}^2$, where M is the total mass and μ is the reduced mass of the two particles, v_{CM} is the velocity of the center of mass of the particles and v_{rel} is their relative velocity
 - $K = \frac{1}{2}(m_1 + m_2)v_{CM}^2 + \frac{1}{2}\left(\frac{m_1m_2}{m_1+m_2}\right)v_{rel}^2$ where v_{CM} is the velocity of the center of mass of the particles and v_{rel} is their relative velocity
11. Choose the correct statements that are a consequence of conservation of kinetic energy and linear momentum in a bimolecular collision reaction.
- The kinetic energy associated with the motion of the center of mass is available to overcome the energetic barrier to the reaction.
 - The kinetic energy arising from the relative velocity of the two colliding reactants is available to overcome the energetic barrier to the reaction.
 - The kinetic energy contribution arising from the center of mass motion of the two reactants is known as the collisional energy.
 - The kinetic energy contribution arising from the relative velocity of the two colliding reactants is known as the collisional energy.
12. On which of the following factors do the outcome of a collision in a cross-molecular beam experiment depend?
- Shape of the potential energy surface
 - Initial velocity of the two beams before collision.
 - Internal state of the reactants.
 - Kinetic energy of the products.
13. The threshold energy, E_0 , for the reaction: $H_2^+(g) + He(g) \longrightarrow HeH^+(g) + H(g)$ is 90.0 kJ.mol^{-1} . The spectroscopic constants for H_2^+ are $\tilde{\nu}_e = 2321.7 \text{ cm}^{-1}$ and $\tilde{\nu}_e\tilde{x}_e = 66.2 \text{ cm}^{-1}$. The lowest vibrational level of $H_2^+(g)$ where the internal vibrational energy of the reactants exceeds E_0 is 4
(answer should be given as an integer number only and NOT in words):

The vibrational energy of a molecule can be expressed by:

$$G(v) = \tilde{\nu}_e \left(v + \frac{1}{2} \right) - \tilde{x}_e \tilde{\nu}_e \left(v + \frac{1}{2} \right)^2$$

We want to determine the lowest vibrational level such that the vibrational energy is greater than 90.0 kJ.mol^{-1} . Converting this value into cm^{-1} gives:

$$90 \text{ kJ.mol}^{-1} \left(\frac{83.60 \text{ cm}^{-1}}{\text{kJ.mol}^{-1}} \right) = 7524 \text{ cm}^{-1}$$

Now, we want:

$$7524 \text{ cm}^{-1} < (2321.7 \text{ cm}^{-1}) \left(v + \frac{1}{2} \right) - (66.2 \text{ cm}^{-1}) \left(v + \frac{1}{2} \right)^2$$

Solving this quadratic equation for v gives $v > 3.1$, so the lowest value of v such that the internal vibrational energy of the reactants is greater than E_0 is 4.

14. Consider the reaction, $\text{Cl}(g) + \text{H}_2(v=0) \rightarrow \text{HCl}(v) + \text{H}(g)$, where $(D_e(\text{H}_2) - D_e(\text{HCl})) = 12.4 \text{ kJ.mol}^{-1}$. Assuming there is no activation barrier to this reaction, and considering the reactants as hard spheres, the minimum value of the relative speed (in m.s^{-1}) required for the reaction to occur is **3606** (answer should be given as an integer number only and NOT in words).

From the energy conservation principle, we have:

$$E_{\text{react, int}} + \frac{1}{2} \mu u_{\text{rel}}^2 = E_{\text{prod, int}} + \frac{1}{2} \mu' u_{\text{rel}}'^2 \quad (1)$$

where $E_{\text{react, int}}$ and $E_{\text{prod, int}}$ are the total internal energies, μ and μ' are the reduced masses, and u_{rel} and u_{rel}' are the relative speeds of the reactants and products, respectively. Now, the minimum relative speed of the reactants that would result in product formation would end up producing products that would have no residual energy left for motion, i.e., $u_{\text{rel}}' = 0$ condition.

Under this condition (minimum relative speed of the reactants generating products), equation (1) becomes:

$$E_{\text{prod, int}} - E_{\text{react, int}} = \frac{1}{2} \mu u_{\text{rel}}^2 \quad (2)$$

Treating the reactants and products of this reaction as hard spheres gives:

$E_{\text{HCl, int}} - E_{\text{H}_2, \text{int}} = D_e(\text{H}_2) - D_e(\text{HCl})$, so we can solve equation (2) for u_{rel} to get:

$$u_{\text{rel}} = \sqrt{\frac{2(D_e(\text{H}_2) - D_e(\text{HCl}))}{\mu}}$$

$$= \sqrt{\frac{2(12400 \text{ J.mol}^{-1})}{\left[\frac{(35.453 \text{ g.mol}^{-1})(2.016 \text{ g.mol}^{-1})}{(37.469 \text{ g.mol}^{-1})} \right] (10^{-3} \text{ kg.g}^{-1})}} = 3606 \text{ m.s}^{-1}$$

15. Consider the reaction, $\text{F}(g) + \text{H}_2(v=0) \rightarrow \text{HF}(v) + \text{H}(g)$, where the relative energy of the reactants is $40.12 \text{ kJ.mol}^{-1}$, and $D_e(\text{H}_2) - D_e(\text{HF}) = -140 \text{ kJ.mol}^{-1}$. Treat the vibrational motion of both $\text{H}_2(g)$ and $\text{HF}(g)$ as harmonic with $\tilde{\nu}_{\text{H}_2} = 4159 \text{ cm}^{-1}$ and $\tilde{\nu}_{\text{HF}} = 3959 \text{ cm}^{-1}$. Choose the possible vibrational states of the product $\text{HF}(g)$ from the choices given.
- 5
 - 4
 - 3
 - 2

Assuming that the reactant and products are in the ground electronic and rotational states and using the energy conservation principle, we get:

$$E_{trans} + E_{vib} - D_e(\text{H}_2) = E'_{trans} + E'_{vib} - D_e(\text{HF})$$

Since $E_{vib} = \frac{1}{2} h\nu_{\text{H}_2} = 24.88 \text{ kJ} \cdot \text{mol}^{-1}$, we can write the above equation as:

$$E'_{trans} = 40.12 \text{ kJ} \cdot \text{mol}^{-1} + 24.88 \text{ kJ} \cdot \text{mol}^{-1} + 140 \text{ kJ} \cdot \text{mol}^{-1} - E'_{vib}$$

$$= 205 \text{ kJ} \cdot \text{mol}^{-1} - E'_{vib}$$

Translational energy is an intrinsically positive quantity, so for the reaction to occur, $E'_{vib} < 205 \text{ kJ} \cdot \text{mol}^{-1}$. Using the harmonic oscillator approximation, we obtain:

$$E'_{vib} = \left(v + \frac{1}{2}\right) h\nu_{\text{HF}} < 205 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\left(v + \frac{1}{2}\right) < \frac{205 \text{ kJ} \cdot \text{mol}^{-1} \left(\frac{83.60 \text{ cm}^{-1}}{\text{kJ} \cdot \text{mol}^{-1}}\right)}{3959 \text{ cm}^{-1}}$$

$$\left(v + \frac{1}{2}\right) < 4.3$$

$$v < 3.8$$

The possible vibrational states of the product are thus, $v = 0, 1, 2$, and 3 .

16. The concentric circles in the Newton Diagram correspond to the maximum expected speeds for the product molecule in the specific vibrational state (e.g., $v = 0, 1$, etc.) when the rotational quantum number, $J = 0$. Pick the correct choice(s) from the options given below on the change in the radius (r) of the product distribution for any specific concentric circle (consider the $v = 0$ case), when the relative translational energy of the reactants is doubled.
- Radius (r) will increase
 - Radius (r) will increase by $\sqrt{2}$
 - For the $v = 0$ case, no change in the Radius (r) will occur but it will increase for the $v = 1$ case.
 - Radius (r) will decrease

The concentric circles in the Newton Diagram correspond to the maximum relative speeds a product molecule can have. Because speed and translational energy are related, and because the translational energy of the product is directly related to the translational energy of reactants (energy conservation principle), the radii of the circles will increase as the translational energy of the reactants is increased. If the relative translational energy were doubled, then the relative speed of the reactants u_{rel} would increase by $\sqrt{2}$. Because the radius of the circle is proportional to u_{rel} , the radius would also increase by $\sqrt{2}$.

17. Consider the reaction, $\text{F}(g) + \text{D}_2(v=0) \longrightarrow \text{DF}(v) + \text{D}(g)$, where the relative translational energy of the reactants is $7.62 \text{ kJ} \cdot \text{mol}^{-1}$ and $(D_e(\text{D}_2) - D_e(\text{DF})) = -140 \text{ kJ} \cdot \text{mol}^{-1}$. Assume that the reactants and products are in their ground electronic and rotational states, and the vibrational motion of both D_2 and DF is harmonic with $\tilde{\nu}_{\text{D}_2} = 2990 \text{ cm}^{-1}$ and $\tilde{\nu}_{\text{DF}} = 2907 \text{ cm}^{-1}$. Remember, under the supersonic beam experimental conditions, the reactant $\text{D}_2(g)$ is in the ground vibrational state. The spectroscopic constants for $\text{DF}(g)$ are: $\tilde{\nu}_e = 2998.3 \text{ cm}^{-1}$, $\tilde{\nu}_e \tilde{x}_e = 45.71 \text{ cm}^{-1}$, $\tilde{B}_e = 11.007 \text{ cm}^{-1}$, and $\tilde{\alpha}_e =$

0.293 cm^{-1} . The minimum value for J such that a $\text{DF}(v=2, J)$ molecule has a relative speed same as that of a $\text{DF}(v=3, J=0)$ molecule is **16**
(answer should be given as an integer number only and NOT in words)

Energy must be conserved by the reaction. Also, since the reactant and products are to be considered in their ground electronic states, we have:

$$E_{\text{trans}} + E_{\text{vib}} - D_e(\text{D}_2) = E'_{\text{trans}} + E'_{\text{vib}} - D_e(\text{DF})$$

Solving for E'_{trans} , we get:

$$E'_{\text{trans}} = E_{\text{trans}} + E_{\text{vib}} - E'_{\text{vib}} - [D_e(\text{D}_2) - D_e(\text{DF})] \quad (1)$$

The reactant $\text{D}_2(\text{g})$ is in its ground vibrational state, so

$$E_{\text{vib}} = \frac{1}{2} h \nu_{\text{D}_2} = \frac{\tilde{\nu}_{\text{D}_2}}{2} = 17.9 \text{ kJ} \cdot \text{mol}^{-1}$$

Thus, equation (1) gives:

$$\begin{aligned} E'_{\text{trans}} &= 7.62 \text{ kJ} \cdot \text{mol}^{-1} + 17.9 \text{ kJ} \cdot \text{mol}^{-1} - E'_{\text{vib}} + 140 \text{ kJ} \cdot \text{mol}^{-1} \\ &= 166 \text{ kJ} \cdot \text{mol}^{-1} - E'_{\text{vib}} = 13877.6 \text{ cm}^{-1} - E'_{\text{vib}} \end{aligned}$$

From here, given the fact that the translational energy is an intrinsically positive quantity, we find that the reaction will only occur if $E'_{\text{vib}} < 166 \text{ kJ} \cdot \text{mol}^{-1}$. Assuming vibrational motion of $\text{DF}(\text{g})$ is harmonic, we find:

$$E'_{\text{vib}} = \left(v + \frac{1}{2}\right) h \nu_{\text{DF}} = \left(v + \frac{1}{2}\right) \tilde{\nu}_{\text{DF}} = \left(v + \frac{1}{2}\right) (34.8 \text{ kJ} \cdot \text{mol}^{-1}) < 166 \text{ kJ} \cdot \text{mol}^{-1}$$

Thus, $v \leq 4$.

With this background, the largest value of E'_{trans} expected for a $\text{DF}(v=3)$ molecule corresponding to its $J=0$, would be:

$$\begin{aligned} E'_{\text{trans}} &= 13877.6 \text{ cm}^{-1} - \tilde{\nu}_e \left(\frac{7}{2}\right) + \tilde{\nu}_e \tilde{x}_e \left(\frac{7}{2}\right)^2 \\ &= 13877.6 \text{ cm}^{-1} - (3.5)(2998.3 \text{ cm}^{-1}) + (3.5)^2(45.71 \text{ cm}^{-1}) \\ &= 3943.7 \text{ cm}^{-1} \end{aligned}$$

Now, consider a $\text{DF}(v=2)$ molecule in the rotational state J . We want to determine the smallest value of J , such that $E'_{\text{trans}} = 3943.7 \text{ cm}^{-1}$. Because energy is conserved, this requires that

$$\begin{aligned} E'_{\text{rot}} &= 13877.6 \text{ cm}^{-1} - 3943.7 \text{ cm}^{-1} - \tilde{\nu}_e \left(\frac{5}{2}\right) + \tilde{\nu}_e \tilde{x}_e \left(\frac{5}{2}\right)^2 \\ &= 9933.9 \text{ cm}^{-1} - (2.5)(2998.27 \text{ cm}^{-1}) + (2.5)^2(45.72 \text{ cm}^{-1}) \\ &= 2723.96 \text{ cm}^{-1} \end{aligned}$$

The general mathematical form of the rotational energy $E_{\text{rot}}(J, v)$ is expressed as:

$$E_{\text{rot}}(J, v) = \left[\tilde{B}_e - \tilde{\alpha}_e \left(v + \frac{1}{2}\right)\right] J(J+1)$$

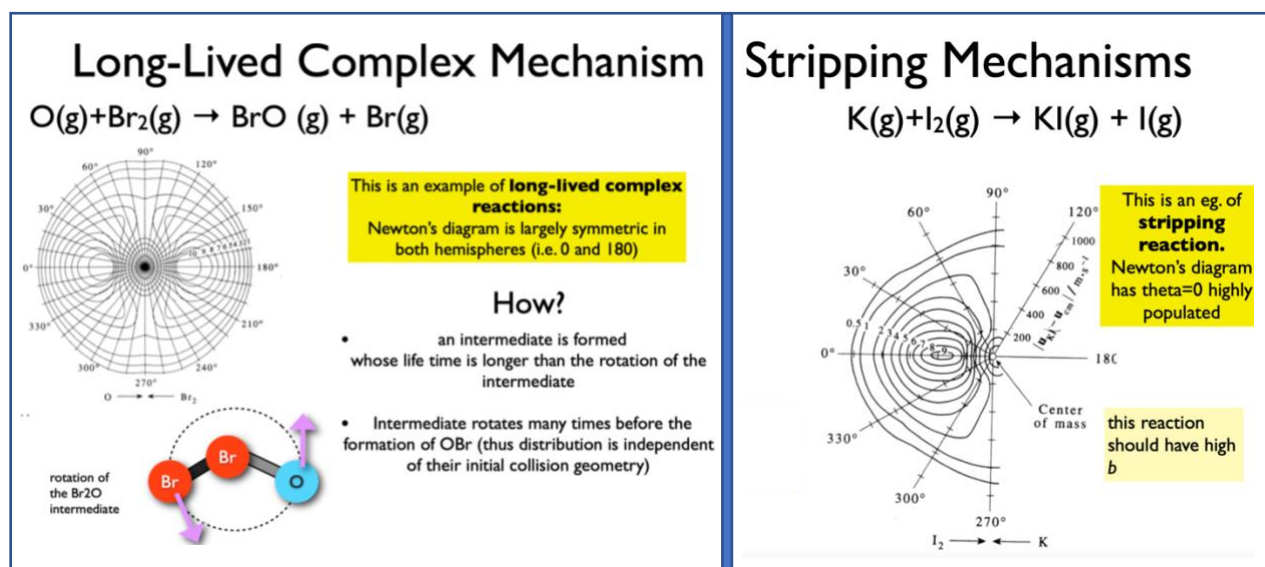
So, from above two equations, we can find the minimum value for J as follows:

$$\begin{aligned} 2723.96 \text{ cm}^{-1} &= \left[\tilde{B}_e - \tilde{\alpha}_e \left(v + \frac{1}{2}\right)\right] J(J+1) \\ &= \left[11.007 \text{ cm}^{-1} - (0.293 \text{ cm}^{-1}) \left(\frac{5}{2}\right)\right] J(J+1) \end{aligned}$$

and since J is an integer, we get $J = 16$.

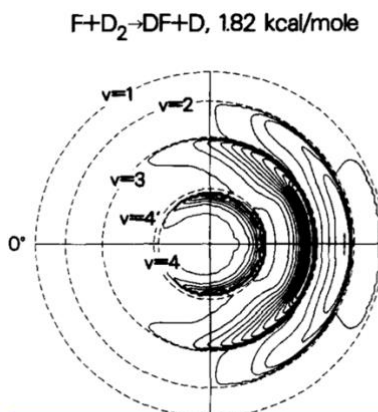
THE Q.17 HAS BEEN CANCELLED AS FOUR NECESSARY INPUTS FOR THE QUESTION WAS MISSED OUT IN THE Q-PAPER.

18. Consider the reaction 1: $\text{O}(g) + \text{Br}_2(g) \longrightarrow \text{BrO}(g) + \text{Br}(g)$. Newton's diagram is largely symmetric in both the hemispheres. This is in contrast to the reaction 2: $\text{K}(g) + \text{I}_2(g) \longrightarrow \text{KI}(g) + \text{I}(g)$, where the Newton's diagram is in the forward direction for the relative translational energy of the reactants is $15.13 \text{ kJ.mol}^{-1}$. Pick the correct statement(s) from the following choice(s).
- Newton's diagram is a product distribution measure and it highlights non-Boltzmann product distribution. Both the reactions thus follow the same mechanism.
 - Reaction 1 is an example of long-lived complex reaction, where the reaction progresses through an intermediate that rotates many times before the product formation and thus the distribution is independent of their initial collision geometry.
 - Reaction 2 is an example of a stripping reaction where the reaction cross section is larger than the collision impact parameter and is dominated by forward scattering.
 - Reaction 2 is an example of rebound reaction where the reactants undergo a head-on collision.



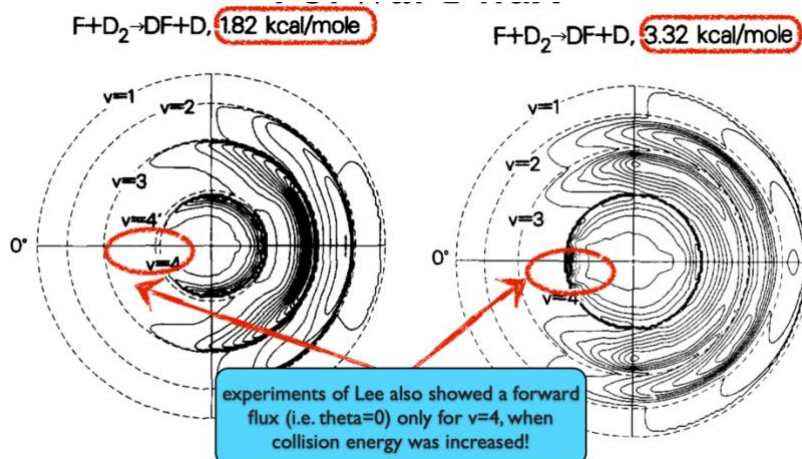
19. When isotope effect on the cross-beam collisional reactions: $\text{F} + \text{D}_2$ and $\text{F} + \text{HD}$ were investigated at several collisional energies the $\text{DF}(g)$ product from both cases $\text{DF}(v=3)$ although some forward scattered $\text{DF}(v=4)$ was observed at highest reactant collisional energy studied. The HF angular distributions from $\text{F} + \text{HD}$ were quite different, showing considerable forward scattered $\text{HF}(v=3)$ and no other identifiable structure. These results (pick all possible correct choice(s) given)
- disagree with classical trajectory studies.
 - agree with the formation of the weakly bound $\text{HF}\cdots\text{H}$ transient complex with a definite lifetime during the reaction.
 - agree with the predicted dependence of dynamical resonance effects on isotopic substitution.

d. support the role of dynamical resonances in the $F + H_2$ reaction.



This is an example of **rebound reactions**:
Newton's diagram has $\theta = 180^\circ$ highly populated

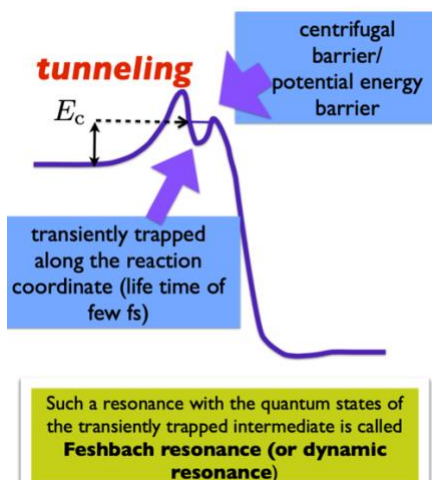
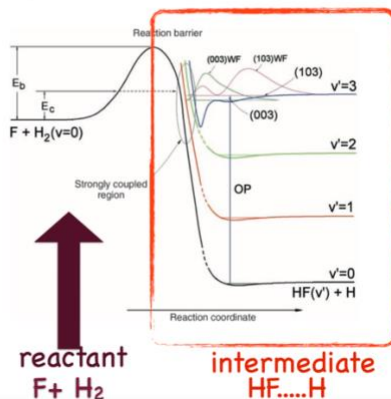
this reaction should have small b



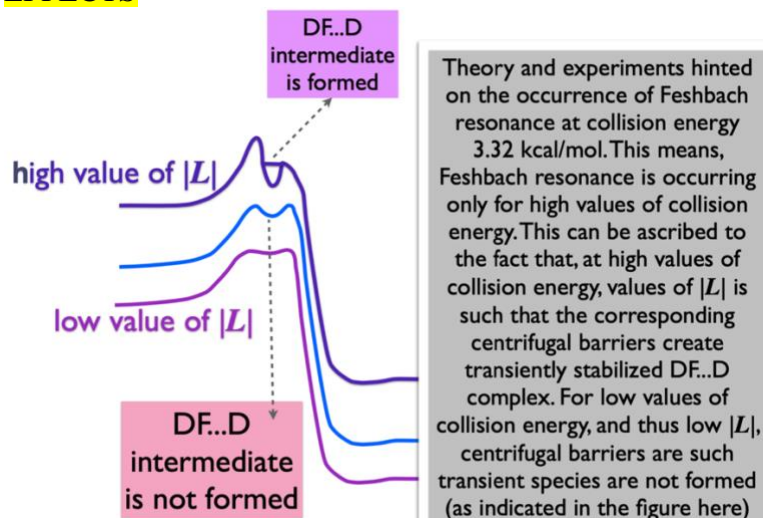
DISAGREE WITH CLASSICAL TRAJECTORY

In the case of $F + H_2$ reaction, it was identified that a weakly bound ($HF \cdots H$) complex form during the reaction, and has a definite life time

This complex has similar behavior of HF , but coordinated weakly to the H atom that will be cleaved from the H_2



QUANTUM EFFECT; WEAKLY BOUND COMPLEX; DYNAMICAL RESONANCE EFFECTS



DYNAMICAL RESONANCE EFFECTS ON ISOTOPIC SUBSTITUTION

20. Consider the cross-molecular reaction, $F(g) + D_2(g) \longrightarrow DF(g) + H(g)$, at different reactant collisional energies that result in the product vibrational state population of $DF(g)$ that is not Boltzmann distributed. For Boltzmann distribution, one expects higher population for the lowest vibrational states and exponentially decreasing population for the higher vibrational states. $DF(g)$ is seen to have maximum population at $v = 3$ or $v = 4$ and minimum population at $v = 0$. Pick all possible correct statement(s) from the choices provided below that are a consequence of this non-Boltzmann distribution.

- $F(g) + D_2(g)$ reaction can be exploited to make a chemical laser between the state $v = 3$ and the states $v = 0, 1$, and 2 .
- DF product molecules formed are in equilibrium.
- There is a population inversion between the state $v = 2$ and the states $v = 0$ and 1 for the DF product molecules formed.
- There could be many possible population inversion transitions in the DF product molecules formed in this reaction, which could be exploited to achieve lasing.

Population of Vibrational States

