Indian Institute of Science Education and Research Kolkata

End - Semester Examination

Course Name: Molecular Reaction Dynamics

Course No:CH4209 Time: 2.5 Hours Max. Marks: 50

1. (a) Write the generalized form of Gaussian Wave Packet (GWP) for 1-d dynamical process and define its parameters; (b) Find its normalization in terms of width parameter; (c) Derive the "Classical" equation of motion for the parameters of GWP to obtain its' time dependence.

   1+2+4

2. Derive the algorithms for (a) Fourier transformation to evaluate kinetic energy operator; (b) The Lanczos iteration technique for time propagation of Schrödinger Equation;

   2+3

3. Write down the assumptions of RRK theory. Derive the expression of composite rate constant (k^1) and predict the form of k^1 at high pressure limit.

   2+4+1

4. F + p-$H_2(v = 0, j = 0) \rightarrow FH(v_f, j_f)$ + H reaction was studied by crossed molecular beam experimental studies. Figure 1 depicts the lab angular distribution of various FH vibrational products, whereas Figure 2 shows the time-of-flight mass spectra at various lab angles (Θ).

   (a) Expain and assign the forward/backward peaks at $\Theta = 8^o$, 24^o and 45^o from the Newton circle of Figure 1.

   (b) Expain the forward/backward peaks at $\Theta = 8^o$ and 18^o from Figure 2 in terms of conservartion of energy.

   (c) Could you expain the gradual increase in the number of the peaks in Figure 2 ?

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(d) Approximately around which Θ do you expect to appear $v_f = 1$ products?

(e) What would you expect at Θ below 8^o and why ?

(f) Compare the size of the Newton circle corrseponding to $j = 1$ rotational state of H_2 with respect to that of $j = 0$ state.

2+2+2+1+2+2

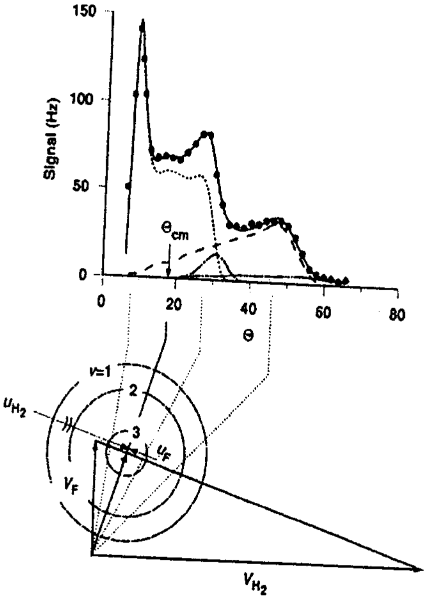

Figure 1: Laboratory angular distribution for F+p-H_2 reaction.

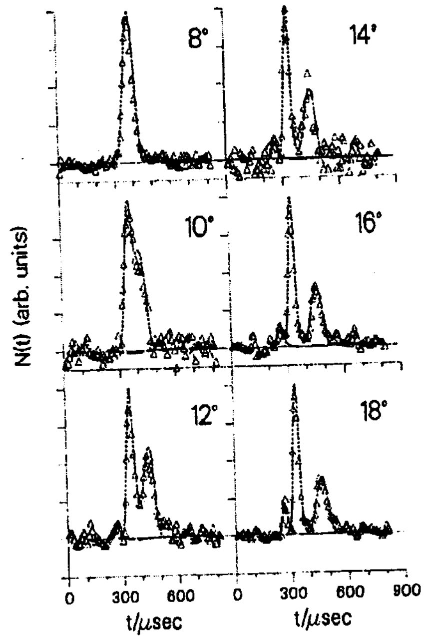

Figure 2: Time-of-flight mass spectra for F+p-H_2 reaction.

5. (a) A Lennard-Jones potential is given by

$$V(r) = 4\epsilon\left[\left(\frac{r_0}{r}\right)^{12} - \left(\frac{r_0}{r}\right)^{6}\right]$$

is often used to describe an intermolecular interaction that does not involve the formation of a covalent bond (for example, between noble gas atoms).

(a) Determine the internuclear distance at the potential energy minimum.

(b) Using this value, derive an expression for the (quadratic) force constant.

2+3

6. (a) For a reaction without an energy threshold, it was found that the total reaction cross-section could be represented as $\sigma_R(E_{tr}) = A/\sqrt{E_{tr}}$, where A is a constant. Calculate the thermal rate consant $k(T)$ for the reaction.

(b) For a reaction with an energy threshold, it was found that the total reaction cross-section

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could be represented as

$$\sigma_R(E_{tr}) = \begin{cases} 0 & \text{for } E_{tr} < E_0 \\ f(E_{tr} - E_0) & \text{for } E_{tr} \geq E_0 \end{cases}$$

Show that the thermal rate constant $k(T)$ for the reaction can be written in the form $k(T) = A(T)e^{-E_0/k_BT}$, and specify the connection between $A(T)$ and $f(E_{tr} - E_0)$.

2+3

7. A simple expression for rate constant is given by $k(T) = \pi d^2 \left(\frac{8k_BT}{\pi\mu}\right)^{1/2} e^{-E*/k_BT}$, where $E*$ is the threshold energy value for reaction to occur, evaluate $exp(-E*/k_BT)$ and $k(T)$ for $T = 1000K, 1500K, 2000K$ for a system where $\mu = 10g/mol, d = 0.1nm, E* = 100kJ/mol$.

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8. For the case of classical scattering of two particles with a repulsive Coulomb potential given by $U(r) = +B/r$, the deflection angle is given by

$$\chi(E, b) = 2cosec^{-1}\left[1 + \left(\frac{2bE}{B}\right)^2\right]^{1/2}$$

Show that the differential cross section is given by

$$\left(\frac{d\sigma}{d\Omega}\right)(\chi, E) = \left(\frac{B}{4E}\right)^2 cosec^4(\chi/2)$$

$$dcosec^{-1}[u(x)]/dx \text{ is given by } -(|u|\sqrt{u^2-1})^{-1}\frac{du}{dx}.$$

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