

## CSO202A—Atoms, Molecules & Photons

### Homework – 3

#### Vibrational and Rotational Energy of a Diatomic Molecule

For a diatomic rigid rotor, the rotational energy is given by

$$E_J = \frac{\hbar^2}{2I} J(J+1), \quad J = 0, 1, \dots$$

where  $I = \mu R_e^2$ , where  $R_e$  is the equilibrium bond length.

Assuming diatomic molecule as a harmonic oscillator, its vibrational energy is given by

$$E_v = \left(v + \frac{1}{2}\right) h\nu, \quad v = 0, 1, \dots$$

where

$$\nu = \frac{1}{2\pi} \left(\frac{k}{\mu}\right)^{1/2}.$$

Here  $k$  is the force-constant.

Within the rigid rotor-harmonic oscillator approximation, the rotational and vibrational energy of a diatomic molecule is given by

$$E_{v,J} = \frac{\hbar^2}{2I} J(J+1) + \left(v + \frac{1}{2}\right) h\nu$$

The above energy is usually represented in  $\text{cm}^{-1}$  ( $\bar{E}_{v,J}$ ):

$$\bar{E}_{v,J} = \bar{B}J(J+1) + \left(v + \frac{1}{2}\right) \bar{\nu}$$

where

$$\bar{\nu} = \frac{1}{2\pi c} \left(\frac{k}{\mu}\right)^{1/2}$$

and

$$\bar{B} = \frac{h}{8\pi^2 c I}$$

Here  $\bar{\nu}$  and  $\bar{B}$  are in  $\text{cm}^{-1}$  (See Chapter 13, Sections 13.1 and 13.2 of McQuarrie & Simon). Note that all the quantities here with an over-line indicates energy quantities in  $\text{cm}^{-1}$ .

For a better prediction of energy levels, we need to go beyond the simple rigid rotor / harmonic oscillator approximations. The rotational energy levels need to be corrected, as for rotational levels corresponding to higher vibrational levels, can have different values of  $R_e$ , and thus different  $\bar{B}$ . Usually,  $R_e$  increases with the vibrational level. This effect is corrected by rewriting  $\bar{B}$  for a given vibrational level  $v$  as,

$$\bar{B}_v = \bar{B}_e - \bar{\alpha}_e \left( v + \frac{1}{2} \right)$$

$\bar{B}_e$  and  $\bar{\alpha}_e$  are parameters (with units  $\text{cm}^{-1}$ ). Anharmonicity of vibrational levels can be included (to some extent by)

$$\bar{E}_v = \bar{\nu}_e \left( v + \frac{1}{2} \right) - \bar{x}_e \bar{\nu}_e \left( v + \frac{1}{2} \right)^2$$

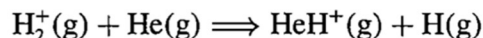
Here  $\bar{\nu}_e$ , and  $\bar{x}_e$  are parameters.

The (corrected) total vibrational-rotational energy (in  $\text{cm}^{-1}$ ) is given by

$$\bar{E}_{v,J} = \bar{B}_v J(J+1) + \bar{\nu}_e \left( v + \frac{1}{2} \right) - \bar{x}_e \bar{\nu}_e \left( v + \frac{1}{2} \right)^2 \quad (1)$$

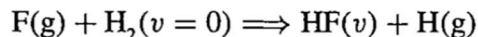
Given the above background, solve the following:

1. The threshold energy,  $E_0$ , for the reaction



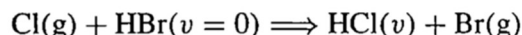
is  $70.0 \text{ kJ} \cdot \text{mol}^{-1}$ . Determine the lowest vibrational level of  $\text{H}_2^+(\text{g})$  such that the internal vibrational energy of the reactants exceeds  $E_0$ . The spectroscopic constants for  $\text{H}_2^+$  are  $\bar{\nu}_e = 2321.7 \text{ cm}^{-1}$  and  $\bar{\nu}_e \bar{x}_e = 66.2 \text{ cm}^{-1}$ .

2. Consider the energetics of the reaction



where the relative translational energy of the reactants is  $7.62 \text{ kJ} \cdot \text{mol}^{-1}$ , and  $D_e(\text{H}_2) - D_e(\text{HF}) = -140 \text{ kJ} \cdot \text{mol}^{-1}$ . Determine the range of possible vibrational states of the product  $\text{HF(g)}$  molecule. Assume the vibrational motion of both  $\text{H}_2(\text{g})$  and  $\text{HF(g)}$  is harmonic with  $\tilde{\nu}_{\text{H}_2} = 4159 \text{ cm}^{-1}$  and  $\tilde{\nu}_{\text{HF}} = 3959 \text{ cm}^{-1}$ .

*For the following four problems, consider the reaction*



*where the relative translational energy of the reactants is  $9.21 \text{ kJ} \cdot \text{mol}^{-1}$ , the difference  $D_e(\text{HBr}) - D_e(\text{HCl}) = -67.2 \text{ kJ} \cdot \text{mol}^{-1}$ , and the activation energy for this reaction is  $\approx 6 \text{ kJ} \cdot \text{mol}^{-1}$ .*

3. Determine the range of possible vibrational states of the product molecule,  $\text{HCl(g)}$ . The spectroscopic constants for  $\text{HBr(g)}$  and  $\text{HCl(g)}$  are

	$\tilde{\nu}_e/\text{cm}^{-1}$	$\tilde{\nu}_e\tilde{x}_e/\text{cm}^{-1}$
HBr	2648.98	45.22
HCl	2990.95	52.82

Draw a reaction coordinate energy diagram, which is like the energy diagram for the  $\text{F(g)} + \text{D}_2(\text{g})$  reaction.

4. Calculate the value of  $|\mathbf{u}_{\text{HCl}} - \mathbf{u}_{\text{cm}}|$ , the speed of the  $\text{HCl(g)}$  molecule relative to the center of mass, for each of the possible vibrational states of  $\text{HCl(g)}$  in Problem 3 above.
5. Determine the speeds for a  $\text{HCl(g)}$  molecule relative to the center of mass  $|\mathbf{u}_{\text{HCl}} - \mathbf{u}_{\text{cm}}|$  in the  $v = 0, J = 0$  and  $v = 0, J = 1$  states. The rotational constants for  $\text{HCl(g)}$  are  $\tilde{B}_e = 10.59 \text{ cm}^{-1}$  and  $\tilde{\alpha}_e = 0.307 \text{ cm}^{-1}$ .
6. Using the data in Problem 5, determine the value of  $J_{\text{min}}$ , the minimum value of  $J$ , such that the kinetic energy of a  $\text{HCl}(v = 0, J = J_{\text{min}})$  molecule is greater than the kinetic energy of an  $\text{HCl}(v = 1, J = 0)$  molecule. [Note that if this reaction produces  $\text{HCl}(v = 0, J \geq J_{\text{min}})$ , then these molecules have relative speeds characteristic of an  $\text{HCl}(v = 1)$  molecule, affecting the analysis of the product velocity contour plots.]