Vibrational and Rotational Energy of a Diatomic Molecule

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

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

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

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

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 cm^{-1} ($\overline{E}_{v,J}$):

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

where

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

and

$$\overline{B} = \frac{h}{8\pi^2 cI}$$

Here $\overline{\nu}$ and $\overline{B}$ are in 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 quantitates in 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 $\overline{B}$. Usually, R_e increases with the vibrational level. This effect is corrected by rewriting $\overline{B}$ for a given vibrational level v as,

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

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

$$\overline{E}_v = \overline{\nu}_e \left(v + \frac{1}{2} \right) - \overline{x}_e \overline{\nu}_e \left(v + \frac{1}{2} \right)^2$$
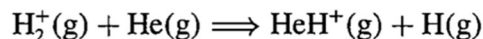
Here $\overline{\nu}_e$, and $\overline{x}_e$ are parameters.

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

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

Given the above background, solve the following:

1. The threshold energy, E_0, for the reaction

$$H_2^+(g) + He(g) \Longrightarrow HeH^+(g) + H(g)$$

is 70.0 kJ·mol^{-1}. Determine the lowest vibrational level of $H_2^+(g)$ such that the internal vibrational energy of the reactants exceeds E_0. The spectroscopic constants for H_2^+ are $\tilde{\nu}_e = 2321.7$ cm^{-1} and $\tilde{\nu}_e\tilde{x}_e = 66.2$ cm^{-1}.

Solution As in the discussion above, the vibrational energy of a molecule is:

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

We want to determine the lowest vibrational quantum number such that the vibrational energy is greater than 70.0 kJ·mol^{-1}. Converting this value to cm^{-1} gives
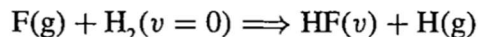
$$(70.0 \text{ kJ·mol}^{-1}) \left(\frac{83.60 \text{ cm}^{-1}}{\text{kJ·mol}^{-1}}\right) = 5850 \text{ cm}^{-1}$$

Now

$$5850 \text{ cm}^{-1} < (2321.7 \text{ cm}^{-1})(v + \tfrac{1}{2}) - (66.2 \text{ cm}^{-1})(v + \tfrac{1}{2})^2$$

Solving this quadratic equation for v gives $v > 2.2$, so the lowest value of v such that the internal vibrational energy of the reactants is greater than E_0 is 3.

2. Consider the energetics of the reaction

$$F(g) + H_2(v = 0) \Longrightarrow HF(v) + H(g)$$

where the relative translational energy of the reactants is 7.62 kJ·mol^{-1}, and $D_e(H_2) - D_e(HF) = -140 \text{ kJ·mol}^{-1}$. Determine the range of possible vibrational states of the product HF(g) molecule. Assume the vibrational motion of both $H_2(g)$ and HF(g) is harmonic with $\tilde{v}_{H_2} = 4159 \text{ cm}^{-1}$ and $\tilde{v}_{HF} = 3959 \text{ cm}^{-1}$.

Solution Assuming that the reactants and products are in the ground electronic and rotational states

$$E_{trans} + E_{vib} - D_e(H_2) = E'_{trans} + E'_{vib} - D_e(HF)$$

Because $E_{vib} = \frac{1}{2}hv_{H_2} = 24.88 \text{ kJ·mol}^{-1}$, we can write the above equation as

$$E'_{trans} = 7.62 \text{ kJ·mol}^{-1} + 24.88 \text{ kJ·mol}^{-1} + 140 \text{ kJ·mol}^{-1} - E'_{vib}$$
$$= 170 \text{ kJ·mol}^{-1} - E'_{vib}$$

Translational energy is an intrinsically positive quantity, so for the reaction to occur, $E'_{vib} < 170 \text{ kJ·mol}^{-1}$. Using the harmonic oscillator approximation, we obtain

$$E'_{vib} = \left(v + \tfrac{1}{2}\right) hv_{HF} < 170 \text{ kJ·mol}^{-1}$$
$$\left(v + \tfrac{1}{2}\right) < \frac{170 \text{ kJ·mol}^{-1}}{47.35 \text{ kJ·mol}^{-1}}$$
$$v \leq 3.6$$

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

For the following four problems, consider the reaction

$$Cl(g) + HBr(v = 0) \Longrightarrow HCl(v) + Br(g)$$
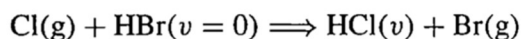
where the relative translational energy of the reactants is 9.21 kJ·mol^{-1}, the difference $D_e(HBr) - D_e(HCl) = -67.2 \text{ kJ·mol}^{-1}$, and the activation energy for this reaction is $\approx 6 \text{ kJ·mol}^{-1}$.

3. Determine the range of possible vibrational states of the product molecule, HCl(g). The spectroscopic constants for HBr(g) and 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 that is similar to that for the F(g) + D$_2$ (g) reaction done in class.

Solution. Assuming that the molecules are in their ground rotational and electronic states, we write

$$E'_{\text{trans}} = E_{\text{trans}} + E_{\text{vib}} - E'_{\text{vib}} - \left[D_e(\text{HBr}) - D_e(\text{HCl}) \right]$$

the ground vibrational state of HBr:

$$E_{\text{vib}} = \tilde{\nu}_e(v + \tfrac{1}{2}) - \tilde{x}_e\tilde{\nu}_e(v + \tfrac{1}{2})^2$$
$$= (2648.98 \text{ cm}^{-1})(\tfrac{1}{2}) - (45.22 \text{ cm}^{-1})(\tfrac{1}{2})^2$$
$$= 1313.2 \text{ cm}^{-1} = 15.71 \text{ kJ}\cdot\text{mol}^{-1}$$
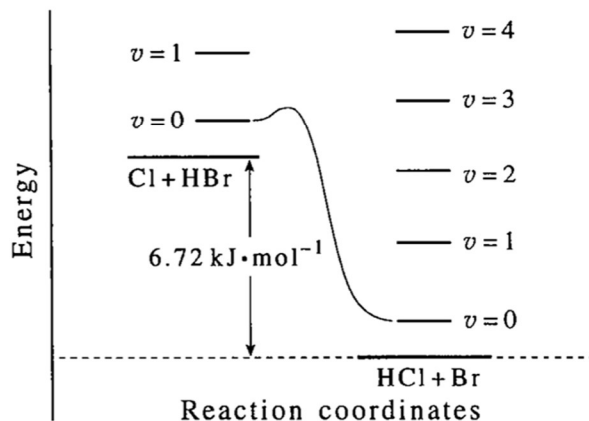
Then

$$E'_{\text{trans}} = 9.21 \text{ kJ}\cdot\text{mol}^{-1} + 15.71 \text{ kJ}\cdot\text{mol}^{-1} - E'_{\text{vib}} + 67.2 \text{ kJ}\cdot\text{mol}^{-1}$$
$$= 92.12 \text{ kJ}\cdot\text{mol}^{-1} - E'_{\text{vib}}$$

For the reaction to occur, $E'_{\text{trans}} > 0$, so $E'_{\text{vib}} < 92.12 \text{ kJ}\cdot\text{mol}^{-1}$:

$$E'_{\text{vib}} = \tilde{\nu}_e(v + \tfrac{1}{2}) - \tilde{x}_e\tilde{\nu}_e(v + \tfrac{1}{2})^2 < 92.12 \text{ kJ}\cdot\text{mol}^{-1}$$
$$(2990.95 \text{ cm}^{-1})(v + \tfrac{1}{2}) - (52.82 \text{ cm}^{-1})(v + \tfrac{1}{2})^2 < 92.12 \text{ kJ}\cdot\text{mol}^{-1}$$

Because v must be an integer, we find that $v \leq 2$. Therefore, $v = 0$, $v = 1$, and $v = 2$ are the possible vibrational states of the product.

4. Calculate the value of $|\mathbf{u}_{HCl} - \mathbf{u}_{cm}|$, the speed of the HCl(g) molecule relative to the center of mass, for each of the possible vibrational states of HCl(g) in Problem 3 above.

Solution.   From Problem 3 above, we have:

$$E'_{trans} + E'_{vib} = 92.12 \text{ kJ} \cdot \text{mol}^{-1}$$

Now substitute for E'_{trans} and E'_{vib} to find u'_r in terms of v:

$$E'_{trans} + E'_{vib} = \tfrac{1}{2}\mu' u'^2_r + \tilde{v}_e(v + \tfrac{1}{2}) - \tilde{v}_e \tilde{x}_e(v + \tfrac{1}{2})^2$$

or

$$92.12 \text{ kJ} \cdot \text{mol}^{-1} = \tfrac{1}{2}(2.504 \times 10^{-2} \text{ kg} \cdot \text{mol}^{-1})u'^2_r + (35.772 \text{ kJ} \cdot \text{mol}^{-1})(v + \tfrac{1}{2})$$
$$-(0.6317 \text{ kJ} \cdot \text{mol}^{-1})(v + \tfrac{1}{2})^2 \qquad (1)$$

where the reduced mass of the products is given by

$$\mu' = \left[\frac{(36.461 \text{ g} \cdot \text{mol}^{-1})(79.904 \text{ g} \cdot \text{mol}^{-1})}{(116.365 \text{ g} \cdot \text{mol}^{-1})}\right](1 \times 10^{-3} \text{ kg} \cdot \text{g}^{-1}) = 2.504 \times 10^{-2} \text{ kg} \cdot \text{mol}^{-1}$$

Solving Equation 1 for u'_r gives

$$u'_r = \left\{\left(\frac{2}{2.504 \times 10^{-2}}\right)[92\,120 - 35\,772(v + \tfrac{1}{2}) - (631.7)(v + \tfrac{1}{2})^2]\right\}^{1/2} \text{ m} \cdot \text{s}^{-1} \qquad (2)$$

the speed of the HCl(g) molecule relative to the center of mass is given by

$$|\mathbf{u}_{HCl} - \mathbf{u}_{cm}| = \frac{m_{Br}}{M}u'_r = \frac{79.904 \text{ amu}}{116.365 \text{ amu}}u'_r \qquad (3)$$

We can calculate u'_r for $v = 0$, 1, and 2 using Equation 2, and then use Equation 3 to obtain $|\mathbf{u}_{HCl} - \mathbf{u}_{cm}|$. The results are tabulated below.

v	$u'_r/10^3 \text{m} \cdot \text{s}^{-1}$	$|\mathbf{u}_{HCl} - \mathbf{u}_{cm}|/10^3 \text{m} \cdot \text{s}^{-1}$
0	2.438	1.674
1	1.785	1.225
2	0.7275	0.500

5.   Determine the speeds for a HCl(g) molecule relative to the center of mass $|\mathbf{u}_{HCl} - \mathbf{u}_{cm}|$ in the $v = 0, J = 0$ and $v = 0, J = 1$ states. The rotational constants for HCl(g) are $\tilde{B}_e = 10.59$ cm^{-1} and $\tilde{\alpha}_e = 0.307$ cm^{-1}.

Solution.   The rotational energy is $\tilde{B}_v J(J + 1)$, where $\tilde{B}_v = \tilde{B}_e - \tilde{\alpha}_e \left(v + \frac{1}{2} \right)$. Given the energy conservation, we have:

$$E'_{trans} + E'_{vib} + E'_{rot} = E_{trans} + E_{vib} - \left[D_e(HBr) - D_e(HCl) \right]$$
$$= 9.21 \text{ kJ·mol}^{-1} + 15.71 \text{ kJ·mol}^{-1} + 67.2 \text{ kJ·mol}^{-1}$$
$$= 92.1 \text{ kJ·mol}^{-1}$$

The reduced mass of the products is, as in Problem 4, 2.504×10^{-2} kg·mol^{-1}. We now express the energy of the products as

$$E'_{trans} + E'_{vib} + E'_{rot} = \tfrac{1}{2}\mu' u_r'^2 + \tilde{v}'_e(v + \tfrac{1}{2}) - \tilde{v}'_e \tilde{x}'_e(v + \tfrac{1}{2})^2 + \left[\tilde{B}'_e - \tilde{\alpha}'_e(v + \tfrac{1}{2}) \right] J(J + 1)$$

For $v = 0$, this becomes

$$92.12 \text{ kJ·mol}^{-1} = \tfrac{1}{2}(2.504 \times 10^{-2} \text{ kg·mol}^{-1})u_r'^2 + (35.772 \text{ kJ·mol}^{-1})(\tfrac{1}{2})$$
$$- (0.6317 \text{ kJ·mol}^{-1})(\tfrac{1}{2})^2 + (0.1249 \text{ kJ·mol}^{-1})J(J + 1)$$

or

$$u_r^2 = 5.942 \times 10^6 \text{ m}^2\text{·s}^{-2} - 9973 J(J + 1) \text{ m}^2\text{·s}^{-2}$$

As in Problem 4,   the speed of the HCl(g) molecule relative to the center of mass is given by

$$|\mathbf{u}_{HCl} - \mathbf{u}_{cm}| = \frac{79.904 \text{ amu}}{116.365 \text{ amu}} u_r'$$

For $v = 0, J = 0$, $|\mathbf{u}_{HCl} - \mathbf{u}_{cm}| = 1674$ m·s^{-1}; for $v = 0, J = 1$, $|\mathbf{u}_{HCl} - \mathbf{u}_{cm}| = 1671$ m·s^{-1}.

6.   Using the data in Problem 5,   determine the value of J_{min}, the minimum value of J, such that the kinetic energy of a $HCl(v = 0, J = J_{min})$ molecule is greater than the kinetic energy of an $HCl(v = 1, J = 0)$ molecule. [Note that if this reaction produces $HCl(v = 0, J \geq J_{min})$, then these molecules have relative speeds characteristic of an $HCl(v = 1)$ molecule, affecting the analysis of the product velocity contour plots.]

Solution.   From Problem 5 above, we have:

$$92.12 \text{ kJ} \cdot \text{mol}^{-1} = E'_{trans} + (35.772 \text{ kJ} \cdot \text{mol}^{-1})(\tfrac{1}{2} + v)$$
$$-(0.6317 \text{ kJ} \cdot \text{mol}^{-1})(\tfrac{1}{2} + v)^2$$
$$+(0.1249 \text{ kJ} \cdot \text{mol}^{-1})J(J + 1)$$

For $v = 1$, $J = 0$, E'_{trans} (the kinetic energy of the HCl molecule) is $39.87 \text{ kJ} \cdot \text{mol}^{-1}$. For a molecule in the $v = 0$, $J = J_{min}$ state to have a greater kinetic energy,

$$39.87 \text{ kJ} \cdot \text{mol}^{-1} < 92.12 \text{ kJ} \cdot \text{mol}^{-1} - (35.772 \text{ kJ} \cdot \text{mol}^{-1})(\tfrac{1}{2})$$
$$+(0.6317 \text{ kJ} \cdot \text{mol}^{-1})(\tfrac{1}{2})^2$$
$$-(0.1249 \text{ kJ} \cdot \text{mol}^{-1})J_{min}(J_{min} + 1)$$

Because J must be an integer, $J \geq 17$.