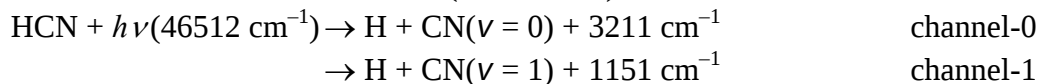


### 3. Prior Distribution

- statistically equal distribution in *final* states

#### 3.1 Rotational distribution and rotational sum

ex.) Photodissociation of HCN at 215 nm ( $46512 \text{ cm}^{-1}$ ):



$E^* \rightarrow \text{rel. translation} + \text{CN rotation}$

· Probability of finding CN in a specific rovibrational state  $\propto$

$$\rho(v, J) = g(J) \rho_{\text{trans}}^{\circ} [E^* - \varepsilon_{\text{vib}}(v) - \varepsilon_{\text{rot}}(J)] \quad (3.1.1)$$

ex.) Rotational distribution of CN via channel-1  $\propto$

$$(2J+1) \rho_{\text{trans}}^{\circ} [1151 - BJ(J+1)] \propto (2J+1) [1151 - 1.8996J(J+1)]^{1/2} \quad (J_{\text{max}} = 24, \text{ fig. 3.1})$$

· Probability of finding CN in a *vibrational* state (indistinctive of rot. states)  $\propto$  Rotational sum:

$$\rho(v) = \sum_J g(J) \rho_{\text{trans}}^{\circ} [E^* - \varepsilon_{\text{vib}}(v) - \varepsilon_{\text{rot}}(J)], \quad [\varepsilon_{\text{rot}}(J) \leq E^* - \varepsilon_{\text{vib}}(v)] \quad (3.1.2)$$

(summation  $\rightarrow$  integration)

$$\begin{aligned} \rho(v) &= \int_0^{E^* - \varepsilon_{\text{vib}}(v)} \rho_{\text{rot}}^{(2D)} [\varepsilon_{\text{rot}}] \rho_{\text{trans}}^{\circ} [E^* - \varepsilon_{\text{vib}}(v) - \varepsilon_{\text{rot}}] d\varepsilon_{\text{rot}} \\ &= \int_0^{E^* - \varepsilon_{\text{vib}}(v)} c_{\text{rot}}^{(2D)} c_{\text{trans}} [E^* - \varepsilon_{\text{vib}}(v) - \varepsilon_{\text{rot}}]^{1/2} d\varepsilon_{\text{rot}} = \frac{2}{3} c_{\text{rot}}^{(2D)} c_{\text{trans}} [E^* - \varepsilon_{\text{vib}}(v)]^{3/2} \quad (3.1.3) \end{aligned}$$

ex.) Branching ratio of channel-0 : channel-1 =  $(3211)^{3/2} : (1151)^{3/2} \sim 4.66 : 1$

#### Problem-3.1 [OPTION] \_\_\_\_\_

Derive an equation similar to 3.1.3 for the formation of an atom and a non-linear molecule.

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#### [Rotational sum]

Rotational sum for two fragments formation:

$$\rho_{\text{rot-sum}} = C_{\text{rot-sum}} E^{\frac{n_r+1}{2}} \quad (3.1.4)$$

$$C_{\text{rot-sum}} = \frac{\Gamma\left(\frac{n_t}{2}\right) \prod_{i=1}^{m_r} \Gamma\left(\frac{n_{r,i}}{2}\right)}{\Gamma\left(\frac{n_t + n_r}{2}\right)} c_{\text{trans}} \prod_{i=1}^{m_r} c_{\text{rot}}^{(n_{r,i})} \quad (3.1.5)$$

$E^{\frac{n_r+1}{2}} = E^* - \sum_i \varepsilon(v_i)$  : Energy in translation and rotation ( $E^*$ : Total excess energy)

$n_t$  : Translational degree of freedom (= 3),  $m_r$  : Number of rotators,  $n_r$  : Total rotational degree

of freedom (=  $\sum_{i=1}^{m_r} n_{r,i}$ )

for integer  $n$  :  $\Gamma(n) = (n-1)!$ ,  $\Gamma(1) = \Gamma(2) = 1$

for half integer  $n$  :  $\Gamma(1/2) = \pi^{1/2}$ ,  $\Gamma(3/2) = \Gamma(1/2) \times (1/2) = \pi^{1/2} / 2$ , ...

### Problem-3.2

- 1) Calculate the *prior* vibrational energy distribution of OH formed from  $O(^1D) + H_2 \rightarrow OH + H$  ( $\Delta H_{0K}^\circ = -182.2 \text{ kJ mol}^{-1}$ ) at 298 K. (total excess energy)  $E^* = -\Delta H_{0K}^\circ + 2.5RT$ , (vib. freq.)  $\tilde{\nu}(\text{OH}) = 3568 \text{ cm}^{-1}$ .
- 2) [OPTION] Calculate the *prior* rotational distribution OH in its  $v = 0$  state formed in the above reaction. (rot. const.)  $B(\text{OH}) = 18.51 \text{ cm}^{-1}$ .

### 3.2 Vibrational sum

Branching probability for a reaction channel  $\propto \rho_{\text{vib-sum}} = \sum_v \rho_{\text{rot-sum}}(v)$  (vibrational sum)



$$\Delta H_{0K}^\circ [O(^1D) + H_2 \rightarrow OH + H] = -182.2 \text{ kJ mol}^{-1}$$

Vibrational frequencies ( $\text{cm}^{-1}$ ) - OH: 3568, OD: 2632,  $H_2$ : 4162, HD: 3633

Rotational constants ( $\text{cm}^{-1}$ ) - OH: 18.51, OD: 9.87

(after ZPE & thermal corr. @ 298 K)  $E^*(a) = 15952$ ,  $E^*(b) = 15484 \text{ (cm}^{-1}\text{)}$

$$C_{\text{rot-sum}}(a) : C_{\text{rot-sum}}(b) = \frac{\mu_{H+OD}^{3/2}}{B_{OD}} : \frac{\mu_{D+OH}^{3/2}}{B_{OH}} \sim 1 : 1.382$$

$$v_{\text{max}}(a) = 6 [15792 \text{ cm}^{-1}], \quad v_{\text{max}}(b) = 4 [14272 \text{ cm}^{-1}]$$

$$\text{Branching ratio} = \rho_{\text{vib-sum}}(a) : \rho_{\text{vib-sum}}(b) = \sum_v \rho_{\text{rot-sum}}(a, v) : \sum_v \rho_{\text{rot-sum}}(b, v)$$

$$= C_{\text{rot-sum}}(a) \sum_{v=0}^6 [E^*(a) - 2632v]^{3/2} : C_{\text{rot-sum}}(b) \sum_{v=0}^4 [E^*(b) - 3568v]^{3/2} = 1 : 1.017$$

cf.) summation  $\rightarrow$  integration

$$\rho_{\text{vib-sum-cl}}(a) = \frac{C_{\text{rot-sum}}(a)}{h\nu(\text{OD})} \int_0^{E_{cl}^*(a)} [E_{cl}^*(a) - \varepsilon_{\text{vib}}]^{3/2} d\varepsilon_{\text{vib}} = \frac{2}{5} \frac{C_{\text{rot-sum}}(a)}{h\nu(\text{OD})} [E_{cl}^*(a)]^{5/2} \quad (3.2.1)$$

$$\text{note) } E_{cl}^*(a) = E^*(a) + \text{ZPE}(\text{OD}) = 17268 = E^*(b) + \text{ZPE}(\text{OH}) = E_{cl}^*(b)$$

$$\rho_{\text{vib-sum-cl}}(a) : \rho_{\text{vib-sum-cl}}(b) = \frac{C_{\text{rot-sum}}(a)}{h\nu(\text{OD})} : \frac{C_{\text{rot-sum}}(b)}{h\nu(\text{OH})} = 1 : 1.019$$

**[Vibrational sum]**

General formula by replacement of summation by integration:

$$\rho_{\text{vib-sum-cl}} = \frac{\Gamma(l_r + 1)}{\Gamma(l_r + n_v + 1)} \frac{C_{\text{rot-sum}}}{n_v} E_{cl}^{\neq(l_r + n_v)} \prod_{i=1}^{n_v} h\nu_i \quad (3.2.2)$$

 $l_r = (n_r + 1)/2$ ,  $n_v$ : vibrational degree of freedom,  $\nu_i$ : vibrational frequency

 $E_{cl}^{\neq}$ : excess energy measured from the classical origin

*ex.)*  $\text{O}(^1D) + \text{CH}_4 \rightarrow \text{OH} + \text{CH}_3$  ( $\Delta H_{0K}^\circ = -182.3 \text{ kJ mol}^{-1}$ ): *Prior* vibrational distribution

of OH (298 K)

Motion other than OH-vibration  $\rightarrow$  (3.2.2),  $h\nu_{\text{OH}} = 3568 \text{ cm}^{-1}$ 
 $\text{ZPE}(\text{CH}_3) = 76.1 \text{ kJ mol}^{-1} \rightarrow E_{cl}^* = (182.3 + 76.1) [\text{kJ mol}^{-1}] + 3RT = 22222 \text{ cm}^{-1}$ 
*cf.*  $E^* = 182.3 [\text{kJ mol}^{-1}] + 3RT = 15860 \text{ cm}^{-1}$ 
 $\nu_{\text{max}} = 4 [14272 \text{ cm}^{-1}]$ ,  $l_r = (3 + 2 + 1) / 2 = 3$ ,  $n_v = 6$ ,  $l_r + n_v = 9$ 

 Vibrational distribution  $\propto (E_{cl}^{\neq})^9 = (E_{cl}^* - \nu h\nu_{\text{OH}})^9$  (fig. 3.2)
 $\nu = 0$  1 $\nu = 1$  0.207 $\nu = 2$  0.0306 $\nu = 3$  0.00270 $\nu = 4$   $9.60 \times 10^{-5}$ **Problem-3.3** \_\_\_\_\_

Calculate the *prior* vibrational distribution of OH formed by  $\text{O}(^1D) + \text{C}_2\text{H}_6 \rightarrow \text{OH} + \text{C}_2\text{H}_5$  ( $\Delta H_{0K}^\circ = -210.7 \text{ kJ mol}^{-1}$ ,  $\text{ZPE}(\text{C}_2\text{H}_5) = 148.5 \text{ kJ mol}^{-1}$ ) similarly to above, and compare it with the cases for  $\text{O}(^1D) + \text{H}_2$  and  $\text{O}(^1D) + \text{CH}_4$ .

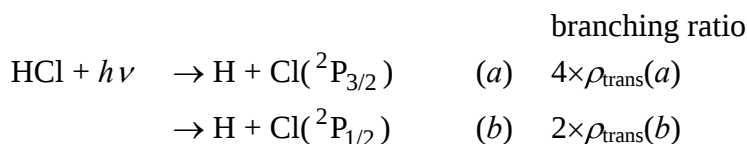
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**3.3 Degeneracy of the electronic states****[Atoms]** (except for the excited states of rare gas atoms)(spectrum) Term :  $2^{S+1}[L]_J$  $S$ : electron spin q. n. $L$ : electron orbital angular momentum q. n. $J$ : total angular momentum q. n.  $J = |L - S|, |L - S| + 1, \dots, L + S$  $[L]$ : symbolic representation of  $L$  - S, P, D, F, G, H, ... (for  $L = 0, 1, 2, 3, 4, 5, \dots$ )Total degeneracy:  $g_{LS} = (2S + 1)(2L + 1)$ Degeneracy of the fine-structure state:  $g_J = 2J + 1$

ex.)

| term  | $L$ | $S$ | $g_{LS}$ | $g_J$       | $J$         | fine str.<br>term             |
|-------|-----|-----|----------|-------------|-------------|-------------------------------|
| $^1D$ | 2   | 0   | 5        | 5           | 2           |                               |
| $^2S$ | 0   | 1/2 | 2        | 2           | 1/2         |                               |
| $^2P$ | 1   | 1/2 | 6        | 2<br>4      | 1/2<br>3/2  | $^2P_{1/2}$<br>$^2P_{3/2}$    |
| $^3P$ | 1   | 1   | 9        | 1<br>3<br>5 | 0<br>1<br>2 | $^3P_0$<br>$^3P_1$<br>$^3P_2$ |

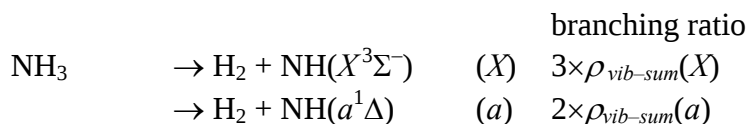
ex.)

**[Linear molecules]**(spectrum) Term :  $^{2S+1}[\Lambda]_{\Lambda+\Sigma}^{(+-)}$  $\Lambda$ : projection of  $L$  to the molecular axis $\Sigma$ : projection of  $S$  to the molecular axis $[\Lambda]$ : symbolic representation of  $\Lambda$  -  $\Sigma, \Pi, \Delta, \Phi, \dots$  (for  $\Lambda = 0, 1, 2, 3, \dots$ ) $(+-)$ : parity (+ or -, only for  $\Sigma$  states)Total degeneracy:  $g_{\Lambda\Sigma} = (2S+1)g_{\Lambda}$ ;  $g_{\Lambda} = 2$  ( $\Lambda \neq 0$ ) or 1 ( $\Lambda = 0$ )Degeneracy of the fine-structure state:  $g_{\Lambda} \neq 2(\Lambda + \Sigma) + 1$ 

ex.)

| term       | $\Lambda$ | $S$ | $g_{\Lambda\Sigma}$ | $g_{\Lambda}$ | $\Lambda+\Sigma$ | fine str.<br>term                   |
|------------|-----------|-----|---------------------|---------------|------------------|-------------------------------------|
| $^1\Delta$ | 2         | 0   | 2                   | 2             | 2                |                                     |
| $^2\Sigma$ | 0         | 1/2 | 2                   | 1             | $\pm 1/2$        |                                     |
| $^2\Pi$    | 1         | 1/2 | 4                   | 2<br>2        | 1/2<br>3/2       | $^2\Pi_{1/2}$<br>$^2\Pi_{3/2}$      |
| $^3\Pi$    | 1         | 1   | 6                   | 2<br>2<br>2   | 0<br>1<br>2      | $^3\Pi_0$<br>$^3\Pi_1$<br>$^3\Pi_2$ |

ex.)

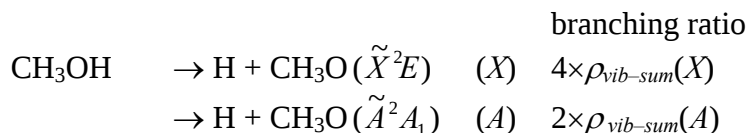


**[Non-linear molecules]**(spectrum) Term :  $^{2S+1}\Gamma$  $\Gamma$ : symmetry species of the electronic state ...  $A, A', A_2, B_1, E, F$ , etc.Total degeneracy:  $g_{\Gamma S} = (2S+1)g_{\Gamma}$ ;  $g_{\Gamma} = 1, 2, 3, 4, 5, \dots$  for  $\Gamma = [A, B], E, T(F), G, H, \dots$ non-degenerates ( $A, B$ ) and  $E$  of spherical group:  $\rightarrow$  no angular momentum $E$  of cylindrical group,  $T(F), G, H, \dots$  of spherical group: (non-integer) angular momentumDegeneracy of the fine-structure state:  $g_{\Gamma}$ 

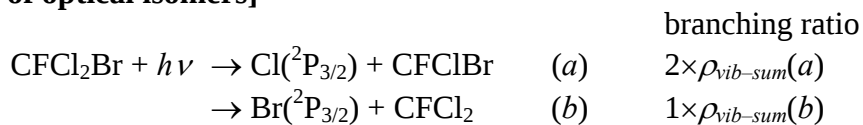
ex.)

| term   | $S$ | $g_{\Gamma S}$ | $g_{\Gamma}$ | fine str.<br>term |
|--------|-----|----------------|--------------|-------------------|
| $^1T$  | 0   | 3              | 3            |                   |
| $^2A'$ | 1/2 | 2              | 1            |                   |
| $^2E$  | 1/2 | 4              | 2            | $^2E_{1/2}$       |
|        |     |                | 2            | $^2E_{3/2}$       |

ex.)

**3.4 Number of optical isomers and rotational symmetry number****[Number of optical isomers]**

ex.)

channel-a  $\rightarrow$  two optical isomers for CFClBr (= two reaction pathway = inversion doubling)

**[Rotational distribution and nuclear spin statistics]**

- Nuclear spin  $I$ :  $g_I = 2I + 1$
- Resultant total nuclear spin of a molecule  $T$ :  $g_T = 2T + 1$
- Bose/Fermi particle obeys Bose/Fermi statistics (symmetric/asymmetric to permutation)

ex.)  $\text{H}_2$  ( $v = 0$ ) – Rotational state distribution

- H nucleus :  $I = 1/2$  (= proton / Fermi particle)  $\rightarrow \psi_{tot}$  should be Asymmetric
- $\psi_{elec}(^1\Sigma_g^+)$  : Sym.,  $\psi_{vib}(v = 0)$  : Sym.

|                  | ortho- $\text{H}_2$      |                   | para- $\text{H}_2$         |
|------------------|--------------------------|-------------------|----------------------------|
| $T$              | 1 ( $\uparrow\uparrow$ ) |                   | 0 ( $\uparrow\downarrow$ ) |
| $\psi_{n.s}$     | Sym.                     | $\leftrightarrow$ | Asym.                      |
| $\psi_{rot}$     | Asym.                    | $\leftrightarrow$ | Sym.                       |
| $J$              | 1, 3, ...(odd)           | $\leftrightarrow$ | 0, 2, ...(even)            |
| $g_T \times g_J$ | $3 \times (2J + 1)$      |                   | $1 \times (2J + 1)$        |

ex.)  $\text{N}_2$  or  $\text{D}_2$  ( $v = 0$ ) – Rotational state distribution

- N or D nucleus :  $I = 1$  (Bose particle)  $\rightarrow \psi_{tot}$  should be Symmetric

|                  | ortho- $\text{N}_2/\text{D}_2$                         |                   | para- $\text{N}_2/\text{D}_2$ |
|------------------|--------------------------------------------------------|-------------------|-------------------------------|
| $T$              | 0 ( $\uparrow\downarrow$ ) or 2 ( $\uparrow\uparrow$ ) |                   | 1 ( $\uparrow\rightarrow$ )   |
| $\psi_{n.s}$     | Sym.                                                   | $\leftrightarrow$ | Asym.                         |
| $\psi_{rot}$     | Sym.                                                   | $\leftrightarrow$ | Asym.                         |
| $J$              | 0, 2, ...(even)                                        | $\leftrightarrow$ | 1, 3, ...(odd)                |
| $g_T \times g_J$ | $(1+5) \times (2J + 1)$                                |                   | $3 \times (2J + 1)$           |

- $\sigma = 2 \leftarrow$  either in sym. or asym. rotational state, rotational density of states is  $1/2$

Problem-3.4 ———