3. Prior Distribution

- statistically equal distribution in *final* states

3.1 Rotational distribution and rotational sum

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

HCN + $h\nu$(46512 cm^{-1}) → H + CN(v = 0) + 3211 cm^{-1} channel-0

→ H + CN(v = 1) + 1151 cm^{-1} channel-1

E^* → rel. translation + CN rotation

· Probability of finding CN in a specific rovibrational state ∝

$$\rho(v,J) = g(J)\rho^{\circ}_{trans}\left[E^* - \varepsilon_{vib}(v) - \varepsilon_{rot}(J)\right] \tag{3.1.1}$$

ex.) Rotational distribution of CN via channel-1 ∝

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

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

$$\rho(v) = \sum_J g(J)\rho^{\circ}_{trans}\left[E^* - \varepsilon_{vib}(v) - \varepsilon_{rot}(J)\right], \quad [\,\varepsilon_{rot}(J) \le E^* - \varepsilon_{vib}(v)\,] \tag{3.1.2}$$

(summation → integration)

$$\rho(v) = \int_0^{E^*-\varepsilon_{vib}(v)} \rho^{(2D)}_{rot}[\varepsilon_{rot}]\rho^{\circ}_{trans}\left[E^* - \varepsilon_{vib}(v) - \varepsilon_{rot}\right]d\varepsilon_{rot}$$

$$= \int_0^{E^*-\varepsilon_{vib}(v)} c^{(2D)}_{rot} c_{trans}\left[E^* - \varepsilon_{vib}(v) - \varepsilon_{rot}\right]^{1/2} d\varepsilon_{rot} = \frac{2}{3} c^{(2D)}_{rot} c_{trans}\left[E^* - \varepsilon_{vib}(v)\right]^{3/2} \tag{3.1.3}$$

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

[Rotational sum]

Rotational sum for two fragments formation:

$$\rho_{rot-sum} = C_{rot-sum} E^{\neq \frac{n_r+1}{2}} \tag{3.1.4}$$

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

$E^{\neq} = E^* - \sum_i \varepsilon(v_i)$: 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 → OH + H (ΔH°_{0K} = –182.2 kJ mol^{-1}) at 298 K. (total excess energy) $E^* = -\Delta H^\circ_{0K} + 2.5RT$, (vib. freq.) $\tilde{\nu}$ (OH) = 3568 cm^{-1}.
2) [OPTION] Calculate the *prior* rotational distribution OH in its v = 0 state formed in the above reaction. (rot. const.) B(OH) = 18.51 cm^{-1}.

3.2 Vibrational sum

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

ex.) O(^1D) + HD → H + OD channel-*a*
→ D + OH channel-*b*

ΔH°_{0K} [O(^1D) + H_2 → OH + H] = –182.2 kJ mol^{-1}

Vibrational frequencies (cm^{-1}) - OH: 3568, OD: 2632, H_2: 4162, HD: 3633
Rotational constants (cm^{-1}) - OH: 18.51, OD: 9.87
(after ZPE & thermal corr. @ 298 K) $E^*(a)$ = 15952, $E^*(b)$ = 15484 (cm^{-1})

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

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

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

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

cf.) summation → integration

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

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

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

[Vibrational sum]

General formula by replacement of summation by integration:

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

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

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

ex.) $O(^1D) + CH_4 \rightarrow OH + CH_3$ (ΔH°_{0K} = –182.3 kJ mol^{-1}): *Prior* vibrational distribution of OH (298 K)

Motion other than OH-vibration → (3.2.2), $h\nu_{OH}$ = 3568 cm^{-1}

ZPE(CH_3) = 76.1 kJ mol^{-1} → E_{cl}^* = (182.3 + 76.1) [kJ mol^{-1}] + 3RT = 22222 cm^{-1}

cf. E^* = 182.3 [kJ mol^{-1}] + 3RT = 15860 cm^{-1}

v_{max} = 4 [14272 cm^{-1}], l_r = (3 + 2 + 1) / 2 = 3, n_v = 6, $l_r + n_v$ = 9

Vibrational distribution $\propto \left(E_{cl}^{\neq}\right)^9 = \left(E_{cl}^* - v h\nu_{OH}\right)^9$ (fig. 3.2)

v = 0	1
v = 1	0.207
v = 2	0.0306
v = 3	0.00270
v = 4	9.60×10^{-5}

Problem-3.3

Calculate the *prior* vibrational distribution of OH formed by $O(^1D) + C_2H_6 \rightarrow OH + C_2H_5$ ($\Delta H°_{0K}$ = –210.7 kJ mol^{-1}, ZPE(C_2H_5) = 148.5 kJ mol^{-1}) similarly to above, and compare it with the cases for $O(^1D) + H_2$ and $O(^1D) + CH_4$.

3.3 Degeneracy of the electronic states

[Atoms] (except for the excited states of rare gas atoms)

(spectrum) Term : $^{2S+1}[L]_J$

S : electron spin q. n.

L : electron orbital angular momentum q. n.

J: total angular momentum q. n. $J = |L-S|, |L-S|+1, \ldots, L+S$

[L]: symbolic representation of L - S, P, D, F, G, H, ... (for L = 0, 1, 2, 3, 4, 5, ...)

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. term
^{1}D	2	0	5	5	2	
^{2}S	0	1/2	2	2	1/2	
^{2}P	1	1/2	6	2	1/2	$^2P_{1/2}$
				4	3/2	$^2P_{3/2}$
^{3}P	1	1	9	1	0	$^3P_0$
				3	1	$^3P_1$
				5	2	$^3P_2$

ex.)

			branching ratio
HCl + $h\nu$	$\rightarrow$ H + Cl($^2P_{3/2}$)	(*a*)	$4\times\rho_{\text{trans}}(a)$
	$\rightarrow$ H + Cl($^2P_{1/2}$)	(*b*)	$2\times\rho_{\text{trans}}(b)$

[Linear molecules]

(spectrum) Term : $^{2S+1}[\Lambda]^{(+-)}_{\Lambda+\Sigma}$

Λ: projection of L to the molecular axis

Σ: projection of S to the molecular axis

$[\Lambda]$: symbolic representation of Λ - Σ, Π, Δ, Φ, ... (for Λ = 0, 1, 2, 3, ...)

(+–): parity (+ or –, only for Σ states)

Total degeneracy: $g_{\Lambda S} = (2S+1)g_\Lambda$; $g_\Lambda = 2$ ($\Lambda \neq 0$) or 1 ($\Lambda = 0$)

Degeneracy of the fine-structure state: $g_\Lambda \neq 2(\Lambda+\Sigma)+1$

ex.)

term	Λ	S	$g_{\Lambda S}$	g_Λ	$\Lambda+\Sigma$	fine str. term
$^1\Delta$	2	0	2	2	2	
$^2\Sigma$	0	1/2	2	1	±1/2	
$^2\Pi$	1	1/2	4	2	1/2	$^2\Pi_{1/2}$
				2	3/2	$^2\Pi_{3/2}$
$^3\Pi$	1	1	6	2	0	$^3\Pi_0$
				2	1	$^3\Pi_1$
				2	2	$^3\Pi_2$

ex.)

			branching ratio
NH_3	$\rightarrow H_2$ + NH($X^3\Sigma^-$)	(*X*)	$3\times\rho_{vib-sum}(X)$
	$\rightarrow H_2$ + NH($a^1\Delta$)	(*a*)	$2\times\rho_{vib-sum}(a)$

[Non-linear molecules]

(spectrum) Term : $^{2S+1}\Gamma$

Γ: symmetry species of the electronic state ... A, A', A_2, B_1, E, F, *etc.*

Total degeneracy: $g_{\Gamma S} = (2S+1)g_\Gamma$; $g_\Gamma = 1,2,3,4,5,\ldots$ *for* $\Gamma = [A,B],E,T(F),G,H,\ldots$

non-degenerates (A, B) and E of spherical group: → no angular momentum

E of cylindrical group, T[F], G, H, ... of spherical group: (non-integer) angular momentum

Degeneracy of the fine-structure state: g_Γ

ex.)

term	S	$g_{\Gamma S}$	g_Γ	fine str. term
^1T	0	3	3	
$^2A'$	1/2	2	1	
^2E	1/2	4	2	$^2E_{1/2}$
			2	$^2E_{3/2}$

ex.)

			branching ratio
CH_3OH	$\rightarrow H + CH_3O(\tilde{X}\,^2E)$	(X)	$4\times\rho_{vib-sum}(X)$
	$\rightarrow H + CH_3O(\tilde{A}\,^2A_1)$	(A)	$2\times\rho_{vib-sum}(A)$

3.4 Number of optical isomers and rotational symmetry number

[Number of optical isomers]

ex.)

			branching ratio
$CFCl_2Br + h\nu$	$\rightarrow Cl(^2P_{3/2}) + CFClBr$	(a)	$2\times\rho_{vib-sum}(a)$
	$\rightarrow Br(^2P_{3/2}) + CFCl_2$	(b)	$1\times\rho_{vib-sum}(b)$

channel-a → 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.) H_2 (v = 0) – Rotational state distribution

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

	ortho-H_2		para-H_2
T	1 (↑↑)		0 (↑↓)
$\psi_{n.s}$	Sym.	↔	Asym.
ψ_{rot}	Asym.	↔	Sym.
J	1, 3, ...(odd)	↔	0, 2, ...(even)
$g_T \times g_J$	$3 \times (2J + 1)$		$1 \times (2J + 1)$

ex.) N_2 or D_2 (v = 0) – Rotational state distribution

- N or D nucleus : I = 1 (Bose particle) → ψ_{tot} should be Symmetric

	ortho-N_2/D_2		para-N_2/D_2
T	0(↑↓) or 2 (↑↑)		1 (↑↗)
$\psi_{n.s}$	Sym.	↔	Asym.
ψ_{rot}	Sym.	↔	Asym.
J	0, 2, ...(even)	↔	1, 3, ...(odd)
$g_T \times g_J$	$(1+5) \times (2J + 1)$		$3 \times (2J + 1)$

· σ = 2 ← either in sym. or asym. rotational state, rotational density of states is 1/2

Problem-3.4 ———