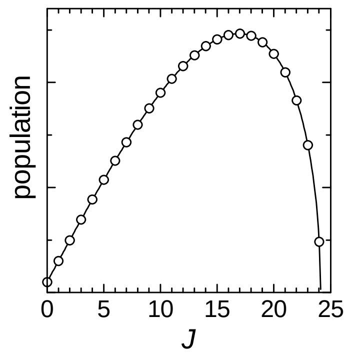
Fig. 3.1 Rotational distribution of CN formed via HCN + $h\nu$ (channel-1)



Rotational sum

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

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

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

product pair	n_r	$C_{rot-sum}$
linear + atom	2	$\frac{\Gamma(1.5)\Gamma(1)}{\Gamma(2.5)} c_{trans} c_{rot}^{2D} = \frac{2}{3}\frac{c_{trans}}{\sigma B}$
non-linear + atom	3	$\frac{\Gamma(1.5)\Gamma(1.5)}{\Gamma(3)} c_{trans} c_{rot}^{3D} = \frac{\pi}{4}\frac{c_{trans}}{\sigma B_{av}^{3/2}}$
linear + linear	2 + 2 = 4	$\frac{\Gamma(1.5)\Gamma(1)\Gamma(1)}{\Gamma(3.5)} c_{trans} c_{rot,1}^{2D} c_{rot,2}^{2D} = \frac{4}{15}\frac{c_{trans}}{\sigma_1 B_1 \sigma_2 B_2}$
linear + non-linear	2 + 3 = 5	$\frac{\Gamma(1.5)\Gamma(1)\Gamma(1.5)}{\Gamma(4)} c_{trans} c_{rot,1}^{2D} c_{rot,2}^{3D} = \frac{\pi}{12}\frac{c_{trans}}{\sigma_1 B_1 \sigma_2 B_{av,2}^{3/2}}$
non-linear + non-linear	3 + 3 = 6	$\frac{\Gamma(1.5)\Gamma(1.5)\Gamma(1.5)}{\Gamma(4.5)} c_{trans} c_{rot,1}^{3D} c_{rot,2}^{3D} = \frac{8\pi}{105}\frac{c_{trans}}{\sigma_1 B_{av,1}^{3/2} \sigma_2 B_{av,2}^{3/2}}$

Vibrational sum

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

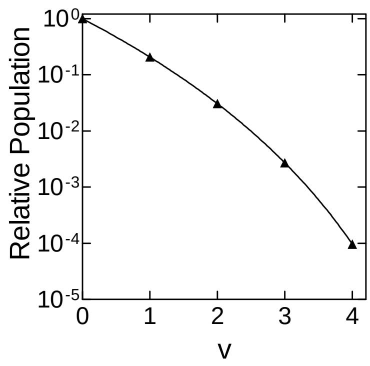


Fig. 3.2 Vibrational distribution of OH formed via O(^{1}D) + CH_4

Problem-3.4

Calculate the *prior* branching fractions for the reaction of O(^1D) with CH_4,

		ΔH°_{0K} / kJ mol^{-1}	
O(^1D) + CH_4	→ CH_3 + OH	–182.7	channel-*a*
	→ CH_3O + H	–129.1	channel-*b*
	→ CH_2OH + H	–173.2	channel-*c*

at room temperature (298 K). Two experimental measurements on H-atom reported the sum of branching fractions for channel-*b* and *c* as 14% and 25%. Compare these with the prior branching fractions.

Molecular constants

chemical species	H	OH	CH_3	CH_3O	CH_2OH
mass / amu	1.008	17.003	15.024	31.019	31.019
symmetry	–	$C_{\infty v}$	D_{3h}	C_{3v}	C_1
rot. sym. num. σ	1	1	6	3	1
num. opt. isom. n_{OPT}	1	1	1	1	2
electronic state	$1^2S_{1/2}$	$X\,^2\Pi$	$\tilde{X}\,^2A_2''$	$\tilde{X}\,^2E$	$\tilde{X}\,^2A$
deg. of electron. state g_e	2	4	2	4	2
rot. deg. of freedom n_r	–	2	3	3	3
rot. consts. / cm^{-1}					
A			(= *B*)	5.169	6.555
B		18.51	9.578	0.9317	1.0061
C			4.742	(= *B*)	0.8879
vib. deg. of freedom n_v	–	1	6	9	9
vib. freqencies* / cm^{-1}					
ν_1		3568	3004	2840	3650
ν_2			606	1362	3019
ν_3			3161 (2)	1047	2915
ν_4			1396 (2)	2774 (2)	1459
ν_5				1487 (2)	1334
ν_6				652 (2)	1183
ν_7					1048
ν_8					607
ν_9					420

* Numbers in parentheses are degeneracy of the vibrational modes.
1 cm^{-1} = 11.96266 J mol^{-1}, R = 8.31451 J K^{-1} mol^{-1}