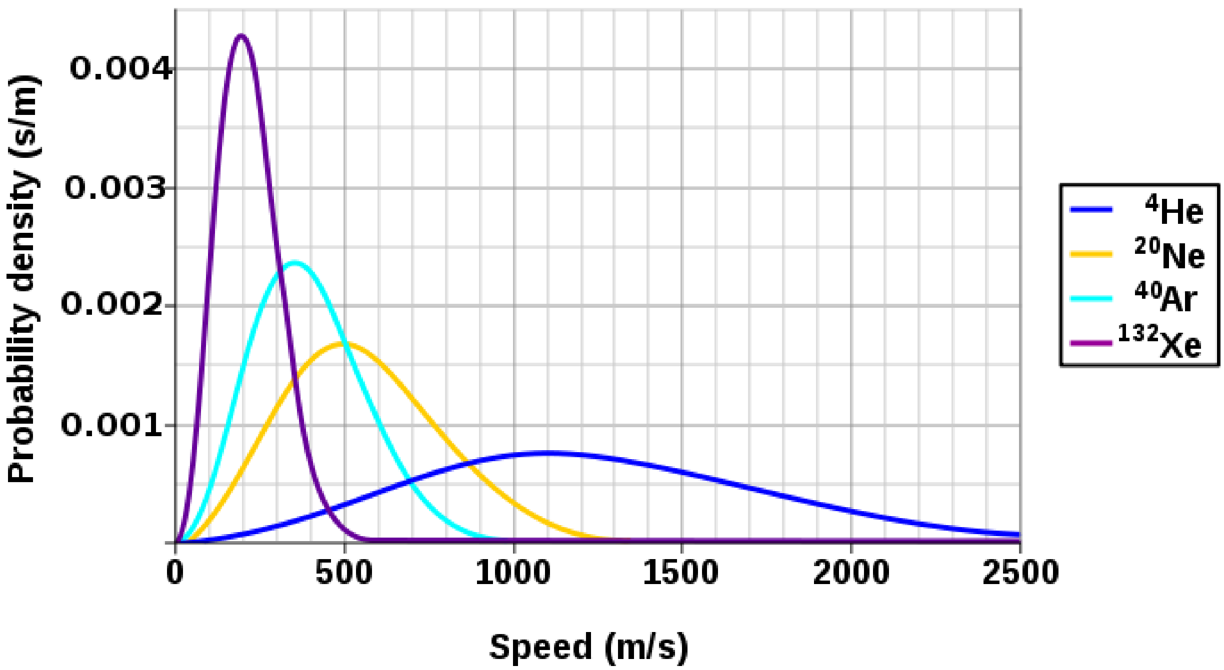
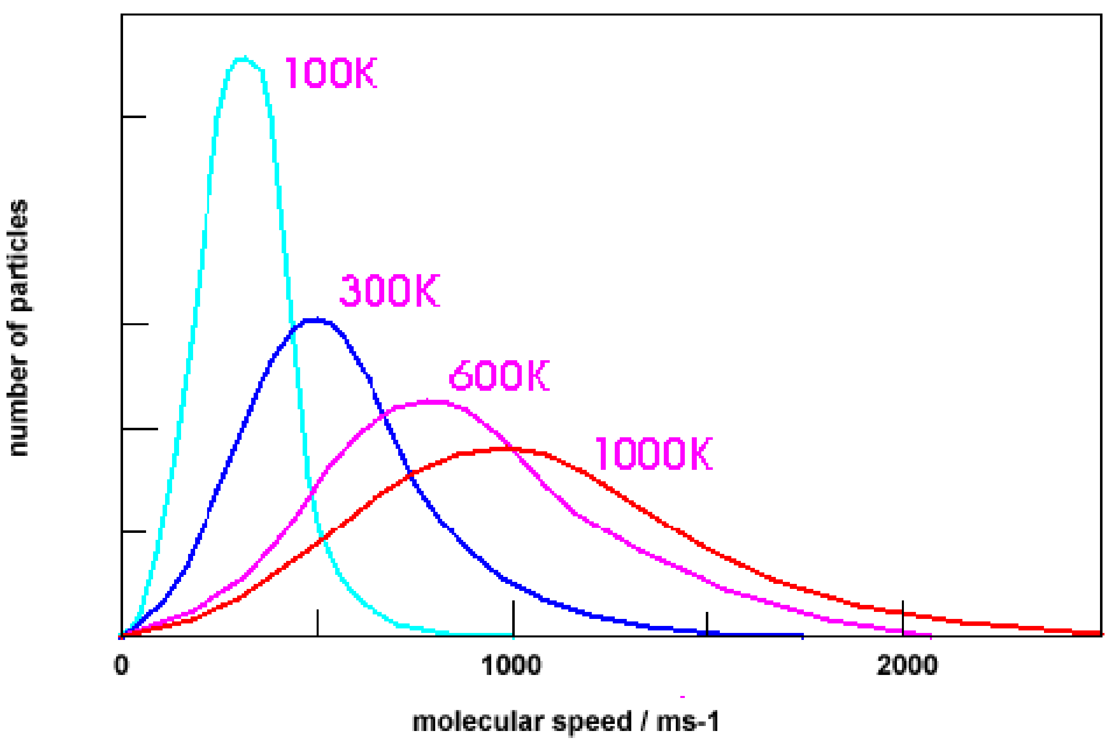
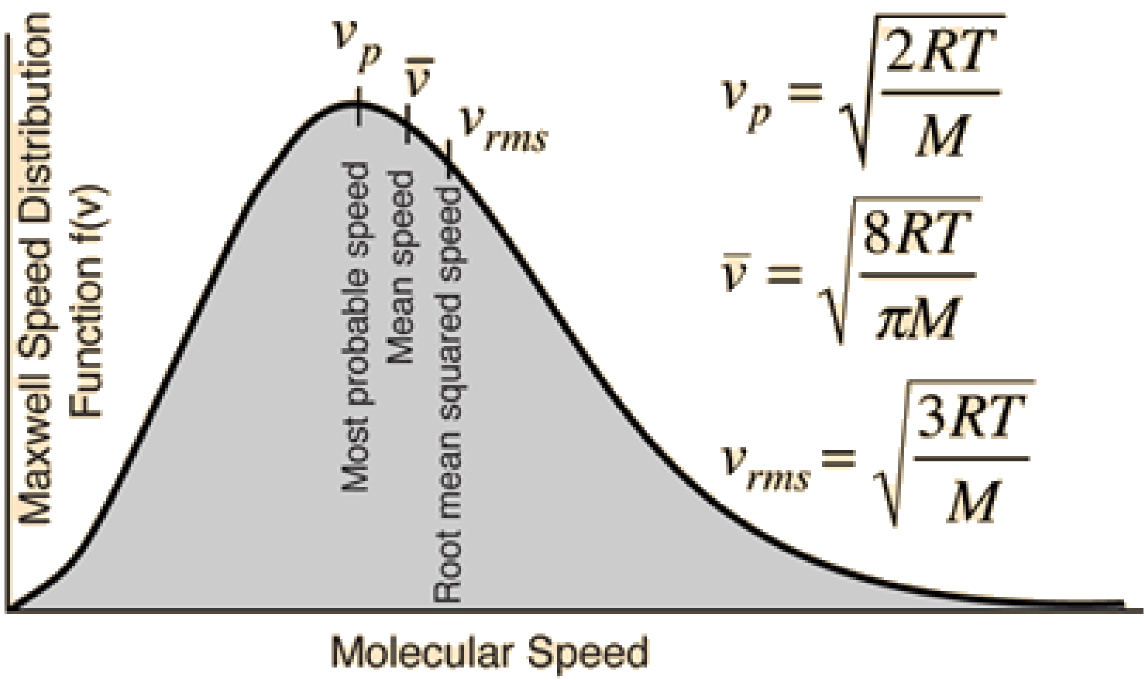
Maxwell-Boltzmann Molecular Speed Distribution for Noble Gases





$$f(v) = 4\pi \left[\frac{M}{2\pi RT}\right]^{\frac{3}{2}} v^2 \exp\left[\frac{-Mv^2}{2RT}\right]$$



For discrete energy levels, the distribution of population follows:

$$f_i = \frac{g_i \exp(E_i/kT)}{\sum_j g_j \exp(E_j/kT)} = \frac{g_i \exp(E_i/kT)}{Z}$$

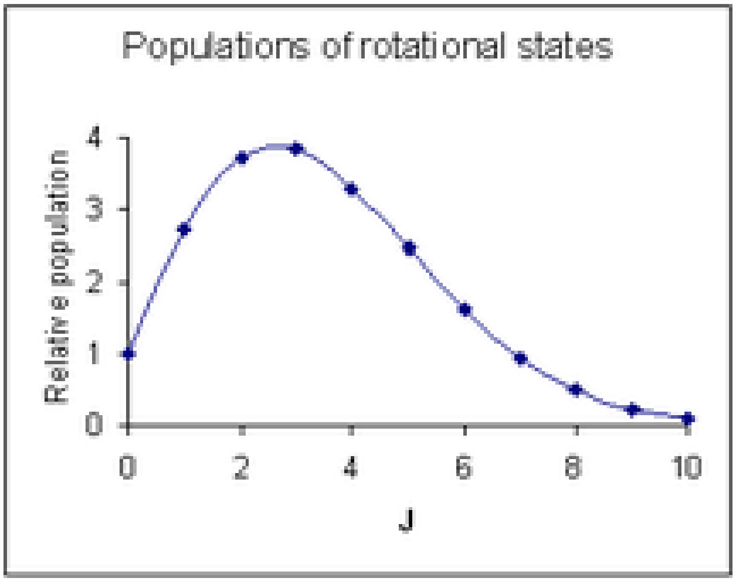
Where f_i is the fraction of population in the "i" level. The term in the denominator is the partition function.

For rotation in a diatomic, $E_{rot} = B_e J(J+1)$ – to first approximation. Degeneracy is 2J+1. To first approximation $Z_{rot} = kT/B_e$ for a heteronuclear diatomic and $kT/2B_e$ for a homonuclear.

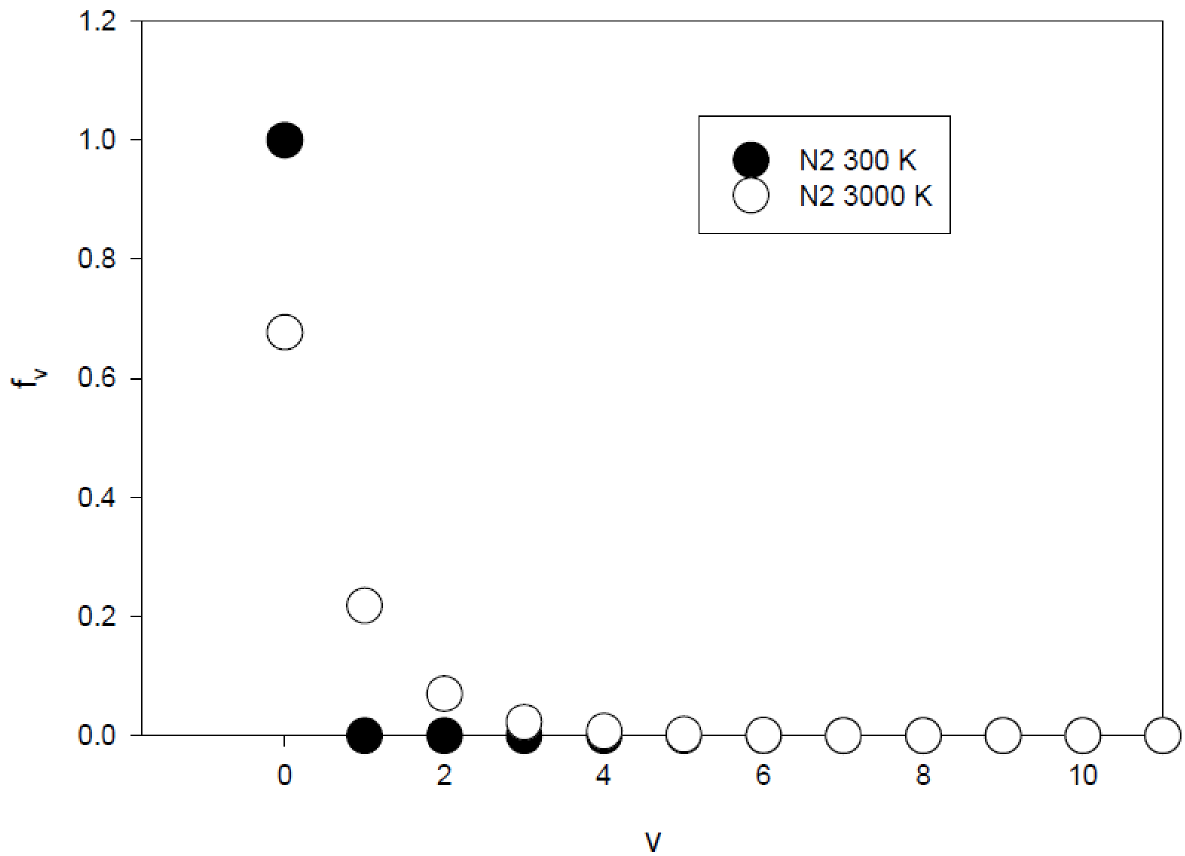
For vibration, $E_{vib} = \omega(v+1/2)$, degeneracy is 1, and

$$Z_{\text{vib}} = \exp(-\hbar\omega/2kT)[1 - \exp(-\hbar\omega/kT)]^{-1}$$

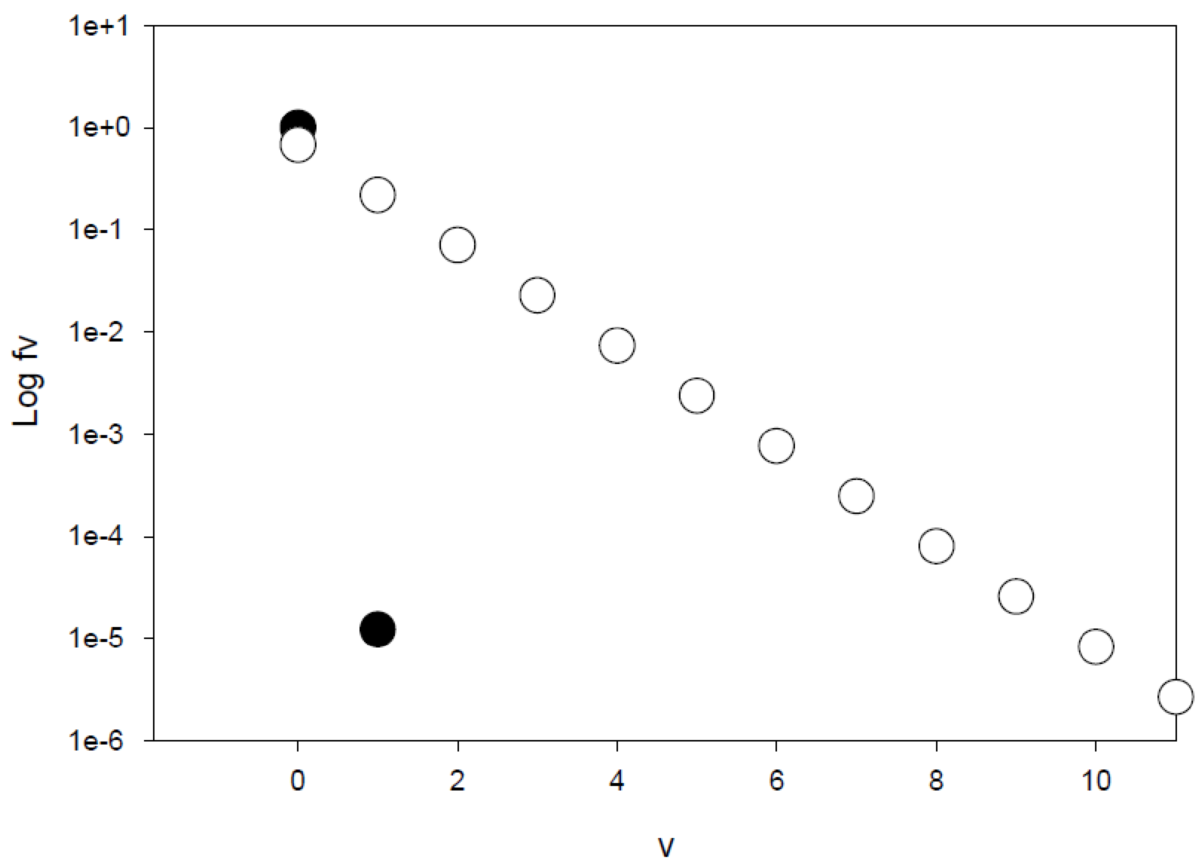
For electronic states, there's no reduced formula, so you have to use the full expression above and sum over all known electronic states. In some cases, where the E/kT value for the first excited state is suitably large such that the first term in the sum is so much larger than all the other terms, then the first term with E = 0 dominates, and $Z = g_o$ where g_o is the degeneracy of the ground state.



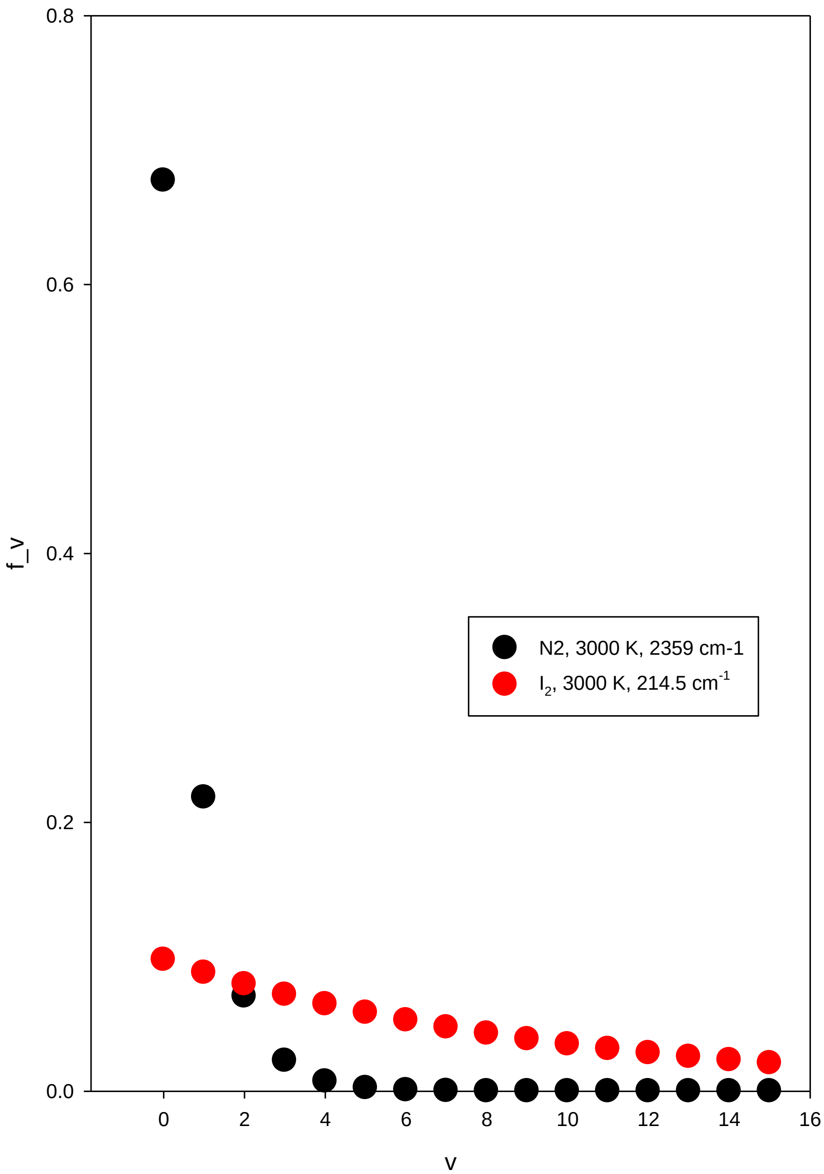
Populations of rotational states
Relative population
J
0
1
2
3
4
0
2
4
6
8
10



1.2
1.0
0.8
0.6
0.4
0.2
0.0
f_v
0
2
4
6
8
10
v
N2 300 K
N2 3000 K



1e+1
1e+0
1e-1
1e-2
1e-3
1e-4
1e-5
1e-6
Log fv
0
2
4
6
8
10
v



0.8
0.6
0.4
0.2
0.0
f_v
N2, 3000 K, 2359 cm-1
I2, 3000 K, 214.5 cm-1
0
2
4
6
8
10
12
14
16
v

Example 1: At 3000 K, find the ground state population fraction of helium and sodium.

Configuration	Term	J	Level (cm^{-1})	Ref.
$1s^2$	^1S	0	0.000	M02
$1s2s$	^3S	1	159855.9745	M02
$1s2s$	^1S	0	166277.4403	M02
$1s2p$	$^3P°$	2	169086.7666	M02
		1	169086.8430	M02
		0	169087.8309	M02
$1s2p$	$^1P°$	1	171134.8970	M02
$1s3s$	^3S	1	183236.7918	M02
$1s3s$	^1S	0	184864.8294	M02
$1s3p$	$^3P°$	2	185564.5620	M02
		1	185564.5840	M02
		0	185564.8547	M02
$1s3d$	^3D	3	186101.5463	M02
		2	186101.5488	M02
		1	186101.5930	M02
$1s3d$	^1D	2	186104.9668	M02
$1s3p$	$^1P°$	1	186209.3651	M02
$1s4p$	$^1P°$	1	191492.7120	M02
He II ($^2S_{1/2}$)	*Limit*		198310.6691	M02

J	E	(2J+1)e^(E/kT)
0	0	1
1	159856	1.51739E-33
0	166277.4	2.32523E-35
2	169086.8	3.02195E-35
1	169086.8	1.8131E-35
0	169087.8	6.04082E-36
1	171134.9	6.78951E-36
1	183236.8	2.04722E-38
0	184864.8	3.12566E-39
2	185564.6	1.11729E-38
1	185564.6	6.70368E-39
0	185564.9	2.23427E-39
3	186101.5	1.20906E-38
2	186101.5	8.63612E-39
1	186101.6	5.18156E-39
2	186105	8.62198E-39
1	186209.4	4.92055E-39
1	191492.7	3.90443E-40
	Z	1
	f_i	1

Configuration	Term	J	Level (cm^{-1})
3s	^2S	1/2	0.000
3p	$^2P°$	1/2	16956.172
		3/2	16973.368
4s	^2S	1/2	25739.991
3d	^2D	5/2	29172.839
		3/2	29172.889
4p	$^2P°$	1/2	30266.99
		3/2	30272.58
4f	$^2F°$	5/2,7/2	34586.92
5p	$^2P°$	1/2	35040.38
		3/2	35042.85
Na II $2s^2$ $2p^6$ ($^1S_0$)	*Limit*		**41449.451**

J	E	(2J+1)e^(E/kT)
0.5	0	2
0.5	16956.172	0.000587853
1.5	16973.368	0.00116605
0.5	25739.991	8.70379E-06
0.5	29172.839	1.6776E-06
1.5	29172.889	3.35512E-06
0.5	30266.99	9.92637E-07
1.5	30272.58	1.97996E-06
2.5	34586.92	3.7508E-07
3.5	34586.92	5.00106E-07
0.5	35040.38	1.00589E-07
1.5	35042.85	2.00941E-07
	Z	2.00177179
	f_i	0.000876176

Example 2: At 3000 K, calculate the fraction of OH in A (1st excited) electronic state with v = 1 and J = 5.

State	T_e	ω_e	$\omega_e x_e$	$\omega_e y_e$	B_e	α_e	γ_e	D_e	β_e	r_e	Trans.	ν_{00}
Theoretical potential functions for 48 states Easson and Pryce, 1973; for X $^2\Pi$ and A $^2\Sigma^+$ see Stevens, Das, et al., 1974 Chu, Yoshimine, et al., 1974 Meyer and Rosmus, 1975.												
C $^2\Sigma^+$	$89459._1$	1232.9 Z	19.1		4.247 1 2	0.078		2E-4		2.046_1	C → A 3 4 R	55820.7 Z
	↳Michel, 1957; Felenbok, 1963; *missing citation*											
C $^2\Sigma^+$ 5											(C → X) 3	(88223)
	↳Michel, 1957; *missing citation*											
D $^2\Sigma^-$	(82130)	(2954)			[15.2179] 6			[16.16E-4]		[1.0809_3]	D ← X 7 R	81759.7_8 8 Z
	↳Douglas, 1974											
State	T_e	ω_e	$\omega_e x_e$	$\omega_e y_e$	B_e	α_e	γ_e	D_e	β_e	r_e	Trans.	ν_{00}
B $^2\Sigma^+$	69774	[660.0] Z	9		[5.086] 10 2	11		[9.29E-4] 12		[1.869_8]	B → A 4 R	35965.5 Z
	↳Barrow, 1956; Michel, 1957; Herman, Felenbok, et al., 1961; *missing citation*; *missing citation*; *missing citation*; Czarny, Felenbok, et al., 1971											
A $^2\Sigma^+$	32684.1	3178.8_6 Z	92.91_7 13		17.358 14 15 16 2	0.786_8 17	-0.016	[20.39E-4] 18		1.0121	A ↔ X 19 20 R	32402.3_9 8 Z
	↳Dieke and Crosswhite, 1948; Stoebner and Delbourgo, 1967; *missing citation*											
	0 21	3737.76_1 Z	84.881_3 22		18.910_8 23 2	0.7242 24		19.38E-4 25		0.96966	1/2 ← 3/2 26	126.23

Ground state is $^2\Pi$, so degeneracy of 4. The *A* state has a degeneracy of 2. At 3000 K, the A state term in Z_{elec} is ~10^{-7}, so Z_{elec} = 4 to great approximation.

For rotation, J = 5 gives us energy of 17.358*5*6 = 520.74 wavenumbers. Numerator is then: 8.57, and Z_{rot} = kT/B_e = 120.1, so $f_{J=5}$ is .071, about 7%.

For vibration, using v = 1 and the equations above with ω = 3178.8, we get a fraction of 0.170.

So we've got 7% in the J = 5 level, 17% in the v = 1 level. For electronic, f_A = 3.11e-7. Populations are, to first order, independent, so the fraction in the listed levels is:.071*.17*3.11e-7 = 3.8e-9, or about 4 parts per billion.

Example 3: In the ground state electronic and vibrational state, the ratio of population in the J = 5 state to that in the J = 1 state is 0.75. What is the gas temperature?

$$f_{J=5} = \frac{(2 \cdot 5 + 1)\exp(-18.910 \cdot 5(5+1)1.4388/T)}{Z(T)}$$

$$f_{J=4} = \frac{(2 \cdot 4 + 1)\exp(-18.910 \cdot 4(4+1)1.4388/T)}{Z(T)}$$

$$\frac{f_{J=5}}{f_{J=4}} = \frac{11\exp(-18.910(30)1.4388/T)}{9\exp(-18.910(20)1.4388/T)} = 1.222\exp(-272.08/T)$$

Solve for T. T = 557 K