Chapter 15
Overview of Molecular Basics

1. **(a)** For $T = 273$ K and pressure 1 atmosphere, that is 10^6 dyne cm^{-2} (760 mm of Hg), find the density, n, of an ideal gas in cm^{-3}. Repeat for conditions in a molecular cloud, that is $T = 10$ K, pressure 10^{-12} mm of Hg.
(b) For both sets of conditions, find the mean free path, λ, which is defined as $1/(\sigma\, n)$, and the mean time between collisions, τ, which is $1/(\sigma\, n\, v)$, where v is the average velocity. In both cases, take $\sigma = 10^{-16}$ cm^{-3}. For the laboratory, take the average velocity to be 300 m s^{-1}; for the molecular cloud, take the average velocity of H_2 as 0.2 km s^{-1}.
(c) Suppose that the population of the upper level of a molecule decays in 10^5 s. How many collisions in both cases occur before a decay?
(d) For extinction we define the penetration depth, λ_v, in analogy with the mean free path. When $\lambda_v = 1$ the light from a background star is reduced by a factor 0.3678. For a density of atoms n, λ_v, in cm, is $2 \times 10^{21}/n$. Calculate the value of λ_v for a molecular cloud and for standard laboratory conditions. The parameters for both are given in part **(a)** of this problem.

2. **(a)** The result of problem 2(c) of chapter 13 gives $T_{\rm k} = 21.2\,(m/m_{\rm H})\,(\Delta V_{\rm t})^2$ where $\Delta V_{\rm t}$ is the FWHP thermal width, i.e. there is no turbulence and the gas has a Maxwell–Boltzmann distribution. Apply this formula to the CO molecule (mass $28\,m_{\rm H}$) for a gas of temperature T. What is $\Delta V_{\rm t}$ for $T = 10$ K, $T = 100$ K, $T = 200$ K?
(b) The observed linewidth is 3 km s^{-1} in a dark cloud for which $T = 10$ K. What is the turbulent velocity width in such a cloud if the relation between the observed FWHP linewidth, $\Delta V_{1/2}$, the thermal linewidth, $\Delta V_{\rm t}$ and the turbulent linewidth $\Delta V_{\rm turb}$ is

$$\Delta V_{1/2}^2 = \Delta V_{\rm t}^2 + \Delta V_{\rm turb}^2\,?$$

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3. The following expression is appropriate for the spontaneous decay between two rotational levels, (u, l) of a linear molecule: $A_{\rm ul} = 1.165 \times 10^{-11}\, \mu_0^2 \nu^3\, (J+1)/(2J+3)$ where ν is in GHz, μ_0 is in Debyes and J is the lower level in the transition from $J+1 \rightarrow J$. Use this to estimate the Einstein A coefficient for a system with a dipole moment of 0.1 Debye for a transition from the $J = 1$ level to the $J = 0$ level at 115.271 GHz.

4. To determine whether a given level is populated, one frequently makes use of the concept of the "critical density", n^*, defined as:

$$A_{\rm ul} = n^*\ \langle \sigma v \rangle\ .$$

where u is the quantum number of the upper rotational level, and l is that for the lower level. If we take $\langle \sigma v \rangle$ to be $10^{-10}\,{\rm cm}^3\,{\rm s}^{-1}$, determine n^* from the following $A_{\rm ul}$ coefficients

$${\rm CS} : A_{10} = 1.8 \times 10^{-6}\,{\rm s}^{-1}$$

$${\rm CS} : A_{21} = 2.2 \times 10^{-5}\,{\rm s}^{-1}$$

$${\rm CO} : A_{10} = 7.4 \times 10^{-8}\,{\rm s}^{-1}.$$

5. Suppose the effective radius $r_{\rm e} = 1.1 \times 10^{-8}$ cm and the reduced mass, $m_{\rm r}$, of a perfectly rigid molecule is 10 atomic mass units, AMU (an AMU is 1/16 of the mass of a 16-oxygen atom; 1 AMU= 1.660×10^{-24} g), where $\Theta = m_{\rm r} r_{\rm e}^2$.
(a) Calculate the lowest four rotational frequencies and energies of the levels above the ground state. One needs a simplified version of Eq. 15.11 to 15.13 from 'Tools' for the rotational constant is

$$B_{\rm e} = \frac{\hbar}{4\pi\, \Theta_{\rm e}} \tag{15.1}$$

The energy of level J is:

$$E_{\rm rot} = W(J) = \frac{\hbar^2}{2\, \Theta_{\rm e}}\, J(J+1) - hD\,[J(J+1)]^2\ . \tag{15.2}$$

and the frequency is the difference between the energy of level $J+1$ and J divided by the Planck constant:

$$\nu(J) = \frac{1}{h}\,[W(J+1) - W(J)] = 2\, B_{\rm e} \left[(J+1) - 4D(J+1)^3\right] \tag{15.3}$$

(b) Repeat if the reduced mass is (2/3) AMU with a separation of 0.75×10^{-8} cm; this is appropriate for the HD molecule. The HD molecule has a dipole moment $\mu_0 = 10^{-4}$ Debye, caused by the fact that the center of mass is not coincident with

Table 15.1 Parameters of the more commonly observed carbon monoxide lines (problem 6)

Chemical[a] formula	Molecule name	Transition	ν/GHz[b]	E_u/K[c]	A_{ij}/s^{-1}[d]
$C^{18}O$	Carbon monoxide	$J = 1 - 0$	109.782182	5.3	6.5×10^{-8}
^{13}CO	Carbon monoxide	$J = 1 - 0$	110.201370	5.3	6.5×10^{-8}
CO	Carbon monoxide	$J = 1 - 0$	115.271203	5.5	7.4×10^{-8}
$C^{18}O$	Carbon monoxide	$J = 2 - 1$	219.560319	15.9	6.2×10^{-7}
^{13}CO	Carbon monoxide	$J = 2 - 1$	220.398714	15.9	6.2×10^{-7}
CO	Carbon monoxide	$J = 2 - 1$	230.538001	16.6	7.1×10^{-7}

[a] If isotope not explicitly given, this is the most abundant variety, i.e., ^{12}C is C, ^{16}O is O, ^{14}N is N
[b] From Lovas (1992, J. Chem. Phys. Ref. Data 21, 18)
[c] Energy above the ground state in Kelvins
[d] Spontaneous transition rate, i.e., the Einstein A coefficient

the center of charge. Take the expression for $A(ul)$ from Problem 3 and apply to the $J = 1 - 0$ and $J = 2 - 1$ transitions of the HD molecule.
(c) Find the "critical density", $n^* \approx 10^{10}\,A(ul)$.

6. The $^{12}C^{16}O$ molecule has $B_e = 57.6360\,\text{GHz}$ and $D_e = 0.185\,\text{MHz}$. Calculate the energies for the $J = 1, 2, 3, 4, 5$ levels and line frequencies for the $J = 1 - 0$, $2 - 1$, $3 - 2$, $4 - 3$ and $5 - 4$ transitions. Use the expression energy $E(J)/h \approx B_e\,J(J+1) - D_e\,J^2(J+1)^2$ for the energy calculation. Check the results against the relevant parts of Table 16.1 in 'Tools', given here as Table 15.1.

7. Apply for $J = 0, 1$ the analysis in problem 6 to the linear molecule $HC_{11}N$, which has $B_e = 169.06295\,\text{MHz}$ and $D_e = 0.24\,\text{Hz}$. Estimate J for a transition near 20 GHz. What is the error if one neglects the distortion term?

8. In the following, we neglect the distortion term D_e and assume that the population is in LTE. The population in a given J level for a linear molecule is given by Eq. (15.33):

$$n(J)/n(\text{total}) = (2J+1)\mathrm{e}^{B_0 J(J+1)/kT}/Z$$

where Z, the partition function, does not depend on J. Differentiate $n(J)$ with respect to J to find the state which has the largest population for a fixed value of temperature, T. Calculate this for CO if $T = 10\,\text{K}$ and $T = 100\,\text{K}$. Repeat for CS ($B_0 = 24.584\,\text{GHz}$) and $HC_{11}N$, for $T = 10\,\text{K}$.

9. Extend Eq. (15.33 in 'Tools'), which is:

$$N(J)/N(\text{total}) = \frac{(2J+1)}{Z}\exp\left[-\frac{h\,B_e J(J+1)}{kT}\right]$$

to include the optical depth relation Eq. (15.26), which is:

$$N_l = 1.95 \times 10^3 \frac{g_l\,\nu^2}{g_u\,A_{ul}} \int T_B\,\mathrm{d}V$$

to obtain an estimate of which J level has the largest optical depth, τ, in the case of emission for a linear molecule.

(a) Show that when the expression for the A coefficient for a linear molecule is inserted into Eq. (15.26 of 'Tools'), we have

$$N_l = \frac{1.67 \times 10^{14}}{\mu_0^2\ \nu[\mathrm{GHz}]} \times \frac{2J+1}{J+1}\, T_{\mathrm{ex}}\, \tau \Delta v \ ,$$

where μ is in Debyes and v is in km s^{-1}.

(b) Use the above expression to estimate whether the J for the maximum $T_{\mathrm{MB}} = T_{\mathrm{ex}}\,\tau$ is larger or smaller than the J obtained in Problem 8.

10. Find the ratio of the intensities of the $J = 2-1$ to $J = 1-0$ transitions for a linear molecule if the excitation temperature of the system, T, is very large compared to the energy of the $J = 2$ level above the ground state, and both lines are optically thin. What is the ratio if both are optically thick? Use the last equation in the statement of Problem 9 of this Chapter.

11. The ammonia molecule, NH_3, is an oblate symmetric top. For ammonia, $B = 298\,\mathrm{GHz}$, $C = 189\,\mathrm{GHz}$. If $T \gg B, C$, the value of Z, the partition function, with C and B in GHz, is $Z = 168.7\sqrt{(T^3)/(B^2 A)}$.

(a) Evaluate Z for NH_3 for $T = 50\,\mathrm{K}, 100\,\mathrm{K}, 200\,\mathrm{K}, 300\,\mathrm{K}$. For this approximation to be valid, what is a lower limit to the value of T?

(b) The (3,3) levels are 120 K above ground. Use the partition function and

$$n(J)/n(\mathrm{total}) = (2J+1)\mathrm{e}^{120/T}/Z$$

to calculate the ratio of the total population to that in the (3,3) levels.

(c) If only metastable ($J = K$) levels are populated, use the definition of Z as a sum over all populated states, and

$$n(J)/n(\mathrm{total}) = (2J+1)\mathrm{e}^{(BJ(J+1)+K^2(C-B))/kT}/Z$$

and the B and C values for NH_3 to obtain the ratio between the population of the (3,3) levels and all metastable levels.

12. The selection rules for dipole transitions of the doubly deuterated isotopomer D_2CO differ from that of H_2CO since D_2CO has two Bosons, so the symmetry of the total wavefunction must be symmetric. Determine these rules following the procedure in Sect. 15.6.2.