Chapter 2: Overview, energy levels, and the electromagnetic spectrum

2.1. Combining Equations 2.2 and 2.5 and rearranging to make *r* the subject yields

$$r = \sqrt{\frac{h}{8\pi^2 B\mu c}}$$

The reduced mass of H^{35}Cl is $\mu = \frac{1\times 34.97}{1+34.97}\times\frac{1}{1000\times N_A} = 1.6144\times 10^{-27}\ \text{kg}$

With B = 10.4 cm^{-1}, we obtain a value for the bond length

$$r = \sqrt{\frac{6.626\times 10^{-34}\ \text{J s}}{8\pi^2\times 10.4\ \text{cm}^{-1}\times 1.6144\times 10^{-27}\ \text{kg}\times 2.997\times 10^{10}\ \text{cm s}^{-1}}} = 1.291\times 10^{-10}\ \text{m} = 1.291\ \text{Å}.$$

2.2. Lines appear in the rotational spectrum of a linear molecule at wavenumber positions according to $\tilde{\nu} = 2B(J+1)$ for J=0, 1, 2,… Thus, with B = 10.4 cm^{-1} for H^{35}Cl, the first four lines will appear at 20.8, 41.6, 62.4 and 83.2 cm^{-1}. The relationship between $\tilde{\nu}$ (cm^{-1}) and ν (s^{-1}) is given by $\nu = c\times\tilde{\nu}$ where c is the speed of light in cm s^{-1}. Thus the first four lines in the rotational spectrum in frequency terms appear at 623.4, 1246.8, 1870.1 and 2493.5 GHz. These frequencies lie within the 0.6 to 2.5 THz region which falls into the far infrared part of the electromagnetic spectrum.

2.3. Our initial assumption is that the separation between adjacent lines in the rotational spectrum is constant. However, as we explore further up the rotational energy level ladder, the molecule acquires greater amounts of rotational energy and as a consequence the bond will extend through the centrifugal effect. Increasing bond length results in an increase in the moment of inertia and a decrease in the rotational constant, with the separation between adjacent lines decreasing. Thus, although inclusion of a greater number of lines will improve the statistical significance of the measurement, in doing so, we will obtain a slightly smaller rotational constant and a slightly larger value for the bond length.

2.4. The weak features between 20 and 60 cm^{-1} in the rotational spectrum of CO are due to the ^{13}C^{16}O and ^{12}C^{18}O isotopomers. The former will account for about 1% of the CO and the latter about 0.2%. They appear separately from the ^{12}C^{16}O lines because the moments of inertia will be slightly different, leading to slightly different rotational constants.

2.5. The most intense line in the spectrum is the 6th line which corresponds to the J=5-6 transition and so $J_{\max}$ = 5. Rearranging $J_{\max} = \left(\frac{kT}{2B}\right)^{1/2} - \frac{1}{2}$ in terms of the temperature gives

$$T = \frac{2B}{k}\left(J_{\max} + \frac{1}{2}\right)^2$$

and so the temperature at the coldest place on Earth is obtained as

$$T = \frac{2\times 1.917\ \text{cm}^{-1}}{0.695\ \text{cm}^{-1}\ \text{K}^{-1}}\left(5+\frac{1}{2}\right)^2 = 166.9\ \text{K}.$$

The precision with which we can determine this certainly does not extend to 1 decimal place and so we might reasonably say the temperature is approximately 165 K or about −110 °C.

2.6. Multiplying Equation 2.17 by a factor of m_D/m_H yields

$$22.6487 = \frac{1}{29.02}\left(24.168\times r_{12}{}^2 + 32.224(r_{12}+r_{23})^2 + 383.68 r_{23}{}^2\right)\ \text{u.Å}^2$$

In comparing this to Equation 2.18

$$14.0306 = \frac{1}{30.014}\left(24.168\times r_{12}{}^2 + 32.224(r_{12}+r_{23})^2 + 192 r_{23}{}^2\right)$$

we see that the second and third terms on the right hand side are now the same in each. The obvious strategy is to multiply each equation by the respective total mass, M, (29.008 u for HCO^+ and 30.014 u for DCO^+) and then to subtract the smaller valued equation from the larger. If we do this we obtain

$$657.2653 - 421.1144 = 383.71 r_{23}{}^2 - 192 r_{23}{}^2$$

which upon rearrangement yields

$$r_{23} = r_{\mathrm{CO}} = \sqrt{\frac{236.151}{191.682}} = 1.110 \text{ Å}.$$

With r_{23} known, we can now substitute its value back into either of Equations 2.17 or 2.19 and then solve for r_{12}.

2.7. For $^{16}O^{12}C^{32}S$, the moment of inertia is

$$I = \frac{1}{M_{^{16}\mathrm{O}^{12}\mathrm{C}^{32}\mathrm{S}}}\left(m_{^{16}\mathrm{O}} m_{^{12}\mathrm{C}} r_{\mathrm{CO}}{}^2 + m_{^{16}\mathrm{O}} m_{^{32}\mathrm{S}} r_{\mathrm{OS}}{}^2 + m_{^{12}\mathrm{C}} m_{^{32}\mathrm{S}} r_{\mathrm{CS}}{}^2\right)$$

$$= \frac{1}{59.972}\left(16 \times 12 \times 1.16^2 + 16 \times 31.972 \times 2.72^2 + 12 \times 31.972 \times 1.56^2\right)$$

$$= \frac{1}{59.972}\left(258.3552 + 3784.6663 + 933.6847\right)$$

$$= 82.9838 \text{ u.Å}^2$$

The rotational constant, given by $B/\mathrm{MHz} = \dfrac{505379.006}{I/\mathrm{uÅ}^2}$ is thus 6090.1 MHz.

The J=1→2 transition occurs at $4B$ according to Equation 2.9 and Figure 2.5 and so the approximate position in MHz of the J=1→2 rotational transition in $^{16}O^{12}C^{32}S$ is 24360 MHz or 24.35 GHz. Repeating this process for $^{16}O^{12}C^{34}S$ yields a value for the J=1→2 rotational transition of 23.76 GHz.

2.8 Ammonia, phenol, tryptophan and C_{60} are all non-linear molecules and so have $3N$-6 vibrational modes. With 4 nuclei, ammonia has 6 vibrational modes; with 13 nuclei, phenol has 33 modes; with 27 nuclei, tryptophan has 76 vibrational modes and with 60 nuclei, C_{60} has 174 modes. The only linear molecule in the list is ethyne and so although it has the same number of nuclei as ammonia, it has 7 vibrational modes, one more than ammonia.

2.9. The reduced mass, μ, of a C–H bond is

$$\frac{m_\mathrm{C} m_\mathrm{H}}{m_\mathrm{C} + m_\mathrm{H}} = \frac{12 \times 1.0078}{12 + 1.0078} = \frac{12.0936}{13.0078} = 0.9297 \text{ u.}$$

Dividing through by Avogadro's number, N_A×1000, yields the reduced mass in kg of

$$1.5438 \times 10^{-27} \text{ kg.}$$

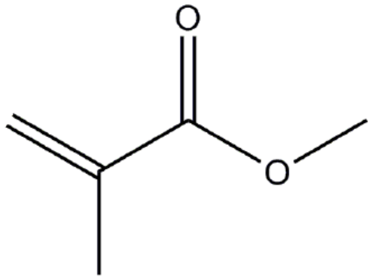
Inserting our value for μ into Equation 2.21 yields a vibrational frequency of

$$\nu_i = \frac{1}{2\pi}\sqrt{\frac{4.8 \times 10^2 \text{ N m}^{-1}}{1.5438 \times 10^{-27} \text{ kg}}} = 8.875 \times 10^{13} \text{ s}^{-1}.$$

2.10. Using $B_v = B_\mathrm{e} - \alpha_e(v + \frac{1}{2})$ and values for B_e of 1.923 cm^{-1} and for α_e of 0.018 cm^{-1} we can readily calculate B_{10} , B_{20} and B_{30} as 1.734, 1.554 and 1.374 cm^{-1}, respectively. The three corresponding bond lengths are calculated in the same way as in Exercise 2.1 as 1.191, 1.258 and 1.338 Å. With r_0 having been determined as 1.133 Å in Worked Example 2.7, these three bond lengths represent increases of 5.1%, 11.0% and 18.1%, respectively.

2.11. The reduced mass of the C-D bond in C_6D_6 is 1.724 u which is nearly twice as large as the value of 0.930 u in C_6H_6. Given that the vibrational frequency scales in inverse proportion to the square root of the reduced mass, we might expect the vibrational frequency of the C-D stretch to be a factor of 0.734 smaller than the C-H stretch in undeuterated benzene.

2.12. The bands at 2950 and 1450 cm^{-1} suggest the presence of alkyl groups whilst those at 1730 and 1200 cm^{-1} are consistent with an alkanoate ester group. The constituent monomer in Perspex is methyl methacrylate whose structure is shown below.



2.14. The higher of the two carbonyl stretches is consistent with a terminal carbonyl group whose force constant might be expected to be closer to that of free CO. The lower wavenumber band is consistent with a bridging carbonyl group, for which we might expect both the effective mass to be higher and the force constant associated with the weaker C=O bond to be smaller.