

1. Molecules with a permanent dipole moment show pure rotational microwave spectra:

a) H₂, No b) HCl, Yes c) CH₄, No d) CH₃Cl, Yes f) H₂O, Yes
g) H₂O₂, Yes h) NH₃, Yes

2. Molecules with anisotropic polarizability show pure rotational Raman spectra:

(Note: as a general rule, spherical molecules are Raman and microwave inactive.)

a) H₂, Yes b) HCl, Yes c) CH₄, No d) CH₃Cl, Yes e) CH₂Cl₂, Yes
f) CH₃CH₃, Yes g) SF₆, No

3. For a linear diatomic the selection rule is $\Delta J = \pm 2$. This means the separation between the Stokes lines becomes:

$$\Delta \bar{\nu}_{J,J\pm 2} = \bar{\nu}_i - \bar{B}(2J+3) - \bar{\nu}_i + \bar{B}(2(J\pm 2)+3) = -2\bar{B}J - 3\bar{B} + 2\bar{B}J + 4\bar{B} + 3\bar{B} = 4\bar{B}$$

$$\Rightarrow \Delta \bar{\nu} = 4\bar{B} = 4 \left(\frac{h}{8\pi^2 \bar{c} I} \right) = \frac{h}{2\pi^2 \bar{c} \mu r^2} \Rightarrow r_{\text{Cl-Cl}} = \sqrt{\frac{h}{2\pi^2 \bar{c} \mu \Delta \bar{\nu}}}$$

$$\mu = \frac{m_{\text{Cl}}^2}{(m_{\text{Cl}} + m_{\text{Cl}})} = \frac{m_{\text{Cl}}}{2} = \frac{34.9688}{2} \div 1000 \div 6.022 \times 10^{23} = 2.903 \times 10^{-26} \text{ kg}$$

$$\Rightarrow r_{\text{Cl-Cl}} = \sqrt{\frac{(6.626 \times 10^{-34} \text{ J}\cdot\text{s})}{2\pi^2 (2.9979 \times 10^{10} \text{ cm}\cdot\text{s}^{-1})(2.903 \times 10^{-26} \text{ kg})(0.9752 \text{ cm}^{-1})}} = 1.989 \text{ \AA}$$

4. $\bar{\nu}_{J \rightarrow J+1} = \frac{h(J+1)}{4\pi^2 \bar{c} I} \Rightarrow \bar{\nu}_{0 \rightarrow 1} = \frac{h(1)}{4\pi^2 \bar{c} I} \Rightarrow r_{\text{H-Cl}} = \sqrt{\frac{h}{4\pi^2 \bar{c} \mu \bar{\nu}_{0 \rightarrow 1}}}$

$$\mu = \frac{m_{^{35}\text{Cl}} \times m_{\text{H}}}{(m_{^{35}\text{Cl}} + m_{\text{H}})} = \frac{(34.9688)(1.007825)}{(34.9688 + 1.007825)} \div 1000 \div 6.022 \times 10^{23} = 1.6267 \times 10^{-27} \text{ kg}$$

$$\Rightarrow r_{\text{H-Cl}} = \sqrt{\frac{(6.626 \times 10^{-34} \text{ J}\cdot\text{s})}{4\pi^2 (2.9979 \times 10^{10} \text{ cm}\cdot\text{s}^{-1})(1.6267 \times 10^{-27} \text{ kg})(20.8784 \text{ cm}^{-1})}} = 1.2839 \text{ \AA}$$

Similarly, $\mu' = 3.1623 \times 10^{-27} \text{ kg}$ and $r_{\text{D-Cl}} = 1.2813 \text{ \AA}$. This is a difference of $\sim 0.2\%$.

5. a) CH_4 , spherical b) CH_3F , symmetric top c) CH_3D , symmetric top

d) SF_6 , spherical

e) SF_5Br , symmetric top

f) HCN , linear

g) H_2S_2 , asymmetric top (similar to H_2O_2)

h) $\text{CH}_2=\text{CH}_2$, asymmetric top

