Q13.3

Calculate the rotational constant and bond length of CO from a rotational band line spacing of 3.86 cm$^{-1}$.

S13.3

The rotational constant is easily obtained from the rotational line spacing for a rigid rotor:

\[ \Delta \tilde{\nu} = 2\tilde{B}(J+1), \] so \[ \Delta \tilde{\nu} = 2\tilde{B}(J=0) \] and \[ \tilde{B} = 1.93 \text{ cm}^{-1} \]

The rotational constant is related to the bond length $R$ by the equation:

\[ \tilde{B} = \frac{\hbar}{8\pi^2 c \mu R^2} \]

with the reduced mass \[ \mu = \frac{m_C m_O}{m_C + m_O} = 1.14 \times 10^{-26} \text{ kg} \]

Therefore, the bond length $R$ is:

\[ R^2 = \frac{\hbar}{8\pi^2 c \mu \tilde{B}} = 1.27 \times 10^{-20} \text{ m}^2 \]

\[ R = 1.13 \text{ Å} \]

P13.4

The rotational constant of NH$_3$ is equivalent to 298 GHz. Compute the separation of the pure rotational spectrum lines in GHz, cm$^{-1}$, and mm, and show that the value of $B$ is consistent with an N-H bond length of 101.4 pm and a bond angle of 106.78$^\circ$.

S13.4

Rotational line separations are $2B$(in wavenumbers), $2Bc$ (in wavenumber units), $2Bc$(in frequency units), and $(2B)^{-1}$ in wavelength units. The transitions are separated by 596 GHz, 19.9 cm$^{-1}$ and 0.503 mm.

For symmetric rotor of NH$_3$, rotational constant is given by:
\[ B = \frac{\hbar}{4\pi c I_{\perp}} \]
\[ I_{\perp} = m_\perp dispos(1 - \cos(\theta)) + \frac{m_\perp m_A}{m} R^2 (1 + 2 \cos(\theta)) \]
\[ I_{\perp} = 1.6735 \times 10^{-27} \times (101.4 \times 10^{-12})^2 (1 - \cos(106)) + \frac{(1.6735 \times 10^{-27}) \times (101.4 \times 10^{-12})^2}{2.8273 \times 10^{-26}} (1 + 2 \cos(106^o)) \]
\[ = 2.8158 \times 10^{-47} \text{kgm}^2 \]

Therefore,
\[ B = \frac{1.05457 \times 10^{-34}}{(4\pi)(2.9979 \times 10^8)(2.8158 \times 10^{-47})} = 994.1 \text{m}^{-1} = 9.941 \text{cm}^{-1} \]

**Q13.5**

The rotational constant for CO is 1.9314 cm\(^{-1}\) and 1.6116 cm\(^{-1}\) in the ground and first excited vibrational states, respectively. By how much does the internuclear distance change as a result of this transition.

**S13.5**

The rotational constant is related to the bond length R by the equation:
\[ \tilde{B} = \frac{\hbar}{8\pi^2 c \mu R^2} \]
with the reduced mass \( \mu = \frac{m_C m_O}{m_C + m_O} = 1.14 \times 10^{-26} \text{ kg} \)

Therefore, the bond lengths \( R_0 \) and \( R_1 \) are:
\[ \{R_0^2\} = \frac{\hbar}{8\pi^2 c \mu \tilde{B}_0} = 1.27 \times 10^{-20} \text{ m}^2 \]
\[ \langle R_0 \rangle = 1.13 \text{Å} \]
\[ \{R_1^2\} = \frac{\hbar}{8\pi^2 c \mu \tilde{B}_1} = 1.52 \times 10^{-20} \text{ m}^2 \]
\[ \langle R_1 \rangle = 1.23 \text{Å} \]

The internuclear distance change as a result of this transition is:
\[ \langle R_1 - R_0 \rangle = 0.1 \text{Å} \]
Q12.8

Is the bond length in HBr the same as that in DBr? The wavenumbers of the \(J=1 \leftarrow 0\) rotational transitions for \(\text{H}^{79}\text{Br}\) and \(\text{D}^{79}\text{Br}\) are 16.68467 and 8.48572 cm\(^{-1}\), respectively. Atomic masses are 1.007825 u and 2.0140 u for \(^{1}\text{H}\) and \(^{2}\text{H}\), respectively. The mass of \(^{79}\text{Br}\) is 78.91833 u. Is there a difference in bond lengths between these two molecules?

S12.8

Given that:

\[ R^2 = \frac{\hbar}{4\pi c \mu B} \]
\[ B = \frac{\hbar}{4\pi c I} \]
\[ I = \mu R^2 \]

We find the following values:

\[ \frac{\hbar}{4\pi c} = 2.79927\times10^{-44}\text{kg}\cdot\text{m} \]
\[ \mu(\text{HBr}) = \left( \frac{1.007825\text{u}\times78.91833\text{u}}{1.007825\text{u}+78.91833\text{u}} \right)\times(1.66054\times10^{-27}\text{kg}\cdot\text{u}^{-1}) = 0.995117\times10^{-27}\text{kg} \]
\[ \mu(DBr) = \left( \frac{2.0140\text{u}\times78.91833\text{u}}{2.0140\text{u}+78.91833\text{u}} \right)\times(1.66054\times10^{-27}\text{kg}\cdot\text{u}^{-1}) = 1.96388\times10^{-27}\text{kg} \]

We then solve for the bond lengths:

\[ R^2(\text{HBr}) = \frac{(2.79927\times10^{-44}\text{kg}\cdot\text{m})}{(0.995117\times10^{-27}\text{kg}) (1.668467\times10^3\text{m}^{-1})} = 1.6860\times10^{-20}\text{pm}^2 \]
\[ R(\text{HBr}) = 129.85\text{pm} \]
\[ R^2(DBr) = \frac{(2.79927\times10^{-44}\text{kg}\cdot\text{m})}{(1.96388\times10^{-27}\text{kg}) (8.48572\times10^2\text{m}^{-1})} = 1.6797\times10^{-20}\text{pm}^2 \]
\[ R(DBr) = 129.60\text{pm} \]

Yes, there exists a small difference between the bond lengths of \((\text{H}^{79}\text{Br})\) and \((\text{D}^{79}\text{Br})\).

P13.10

The microwave spectrum of \(^{16}\text{O}^{12}\text{CS}\) gave absorption lines (in GHz) as follows:
Use the expressions for moments of inertia and assume that the bond lengths are unchanged by substitution; calculate the CO and CS bond lengths in OCS.

S13.10

Equation for a linear rotor is shown as:

\[ I_{m} = m_{a}m_{c}(R + R')^2 + m_{a}m_{b}R^2 + m_{b}m_{c}R'^2 \]

\[ I^{(^{16}O^{12}C^{32}S} = \left( \frac{m(^{16}O)m(^{32}S)}{m(^{16}O^{12}C^{32}S)} \right) (R + R')^2 + \left( \frac{m(^{12}C)(m(^{16}O)R^2}+ {m(^{32}S)R'^2)}{m(^{16}O^{12}C^{32}S)}) \right) \]

\[ I^{(^{16}O^{12}C^{34}S} = \left( \frac{m(^{16}O)m(^{34}S)}{m(^{16}O^{12}C^{34}S)} \right) (R + R')^2 + \left( \frac{m(^{12}C)(m(^{16}O)R^2}+ {m(^{34}S)R'^2)}{m(^{16}O^{12}C^{34}S)}) \right) \]

\[ m(^{16}O) = 16 u, \ m(^{12}C) = 12 u, \ m(^{32}S) = 31.9721u, \ m(^{34}S) = 33.96 \]

\[ I^{(^{16}O^{12}C^{32}S} = (8.5279)*(R + R')^2 + (0.20011)*(16R^2 + 31.972R'^2)\]

\[ I^{(^{16}O^{12}C^{34}S} = (8.7684)*(R + R')^2 + (0.19366)*(16R^2 + 33.9679R'^2)\]

use the relation between \( \tilde{v} = 2cB(J + 1) \) and \( B = \frac{\hbar}{4\pi cI} \) to get moment of inertia I.

\[ I^{(^{16}O^{12}C^{32}S} = 1.37998 * 10^{-45}kgm^2 \]

\[ I^{(^{16}O^{12}C^{34}S} = 1.41460 * 10^{-45}kgm^2 \]

After converting atomic mass to kg, the equation is:

\[ 1.37998 * 10^{-45}m^2 = (1.4161 * 10^{-26})^2 + (5.3150 * 10^{-27}R^2) + (1.0624 * 10^{-26}R'^2) \]

\[ 1.41460 * 10^{-45}m^2 = (1.4560 * 10^{-26})^2 + (5.1437 * 10^{-27}R^2) + (1.0923 * 10^{-26}R'^2) \]

The outcome is \( R = 116.28pm \) and \( R' = 155.97pm \)

E13.12B

Which of the following molecules have a rotational microwave spectrum: (a) O2, (b) HCl, (c) IF, (d) F2?
A pure rotational spectrum will be observed only for those molecules that contain a permanent dipole moment or the ability to create a dipole moment. Therefore, spectra will be observed only for HCl and IF.