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

The rotational constant is easily obtained from the rotational line spacing for a rigid rotor:
\[ \tilde{\nu} = 2\tilde{B}(J+1), \text{ so } \Delta \tilde{\nu} = 2\tilde{B} \text{ and } \tilde{B} = 1.93\text{cm}^{-1} \]

The rotational constant is related to the bond length \(R\) by the equation:
\[ \tilde{B} = \frac{h}{8\pi^2 c \mu R^2} \]

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:
\[ R^2 = \frac{h}{8\pi^2 c \mu \tilde{B}} = 1.27 \times 10^{-20} \text{m}^2 \]
\[ R = 1.13\text{Å} \]

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°.

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.
\[ B = \frac{\hbar}{4\pi c I_{\perp}} \]

\[ I_{\perp} = m_A R^2 (1 - \cos(\theta)) + \frac{m_A m_B}{m} R^2 (1 + 2 \cos(\theta)) \]

\[ I_{\perp} = 2.8158 \times 10^{-47} \text{kgm}^2 \]

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:

\[ \tilde{B}_0 = \frac{h}{8\pi^2 c \mu R_0^2} = 1.27 \times 10^{-20} \text{m}^2 \]

\( R_0 = 1.13 \text{Å} \)

\[ \tilde{B}_1 = \frac{h}{8\pi^2 c \mu R_1^2} = 1.52 \times 10^{-20} \text{m}^2 \]

\( R_1 = 1.23 \text{Å} \)

The internuclear distance change as a result of this transition is:

\( R_1 - R_0 = 0.1 \text{Å} \)
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 \(H^{79}Br\) and \(D^{79}Br\) are 16.68467 and 8.48572 cm\(^{-1}\), respectively. Atomic masses are 1.007825 u and 2.0140 u for \(^1\)H and \(^2\)H, respectively. The mass of \(^{79}\)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:

\[
\mu(HBr) = \left(\frac{1.007825 \text{ u} \times 78.91833 \text{ u}}{1.007825 \text{ u} + 78.91833 \text{ u}}\right) \times (1.66054 \times 10^{-27} \text{ kg} \cdot \text{u}^{-1}) = 0.995117 \times 10^{-27} \text{ kg}
\]
\[
\mu(DBr) = \left(\frac{2.0140 \text{ u} \times 78.91833 \text{ u}}{2.0140 \text{ u} + 78.91833 \text{ u}}\right) \times (1.66054 \times 10^{-27} \text{ kg} \cdot \text{u}^{-1}) = 1.96388 \times 10^{-27} \text{ kg}
\]

We then solve for the bond lengths:

\[
R^2(HBr) = \frac{(2.79927 \times 10^{-44} \text{ kg} \cdot \text{m})}{(0.995117 \times 10^{-27} \text{ kg} \times 1.6860 \times 10^3 \text{ m}^{-1})} = 1.6860 \times 10^{-20} \text{ pm}^2
\]
\[
R(HBr) = 129.85 \text{ pm}
\]
\[
R^2(DBr) = \frac{(2.79927 \times 10^{-44} \text{ kg} \cdot \text{m})}{(1.96388 \times 10^{-27} \text{ kg} \times 8.48572 \times 10^2 \text{ m}^{-1})} = 1.6797 \times 10^{-20} \text{ pm}^2
\]
\[
R(DBr) = 129.60 \text{ pm}
\]

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

P13.10

The microwave spectrum of \(^{16}O^{12}CS\) 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.

\[
\begin{align*}
I(^{16}O^{12}C^{32}S) &= (16 u \cdot 31.9721 u) \cdot (R + R')^2 + (16 u \cdot 12 u) \cdot R^2 + (16 u \cdot 31.9721 u) \cdot R'^2 \\
I(^{16}O^{12}C^{34}S) &= (16 u \cdot 33.96) \cdot (R + R')^2 + (16 u \cdot 12 u) \cdot R^2 + (16 u \cdot 33.96) \cdot R'^2
\end{align*}
\]

After converting atomic mass to kg, the equation is:

\[
\begin{align*}
1.37998 \cdot 10^{-45} \text{kgm}^2 &= (1.4161 \cdot 10^{-26}) \cdot (R + R')^2 + (5.3150 \cdot 10^{-27}) \cdot R^2 + (1.0624 \cdot 10^{-26}) \cdot R'^2 \\
1.41460 \cdot 10^{-45} \text{kgm}^2 &= (1.4560 \cdot 10^{-26}) \cdot (R + R')^2 + (5.1437 \cdot 10^{-27}) \cdot R^2 + (1.0923 \cdot 10^{-26}) \cdot R'^2
\end{align*}
\]

The outcome is \( R = 116.28 \text{pm} \) and \( R' = 155.97 \text{pm} \).

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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.