Spectroscopy Exercises

Solutions to Exercise 3A

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Classify each of the following molecules as spherical, symmetric, or asymmetric top.:

a. CH_4
b. CH_3F
c. CH_3D
d. SF_6
e. SF_5Br
f. trans-SF_4Br_2
g. cis-SF_4Br_2
h. HCN
i. H_2S

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a. spherical top
b. symmetric top
c. symmetric top
d. spherical top
e. symmetric top
f. symmetric top
g. asymmetric top
h. symmetric top (linear)
i. asymmetric top

2) The moment of inertia for a linear triatomic molecule is given by:

$$I = \frac{1}{M}\left(m_1 m_2 r_{12}^2 + m_2 m_3 r_{23}^2 + m_1 m_3 r_{13}^2\right)$$

The lowest frequency microwave transitions of $^1H^{12}C^{14}N$ and $^2H^{12}C^{14}N$ occur at 88'631 MHz and 72'415 MHz, respectively (these are for the ground vibrational state). **Calculate the bond distances in HCN.**

Firstly, one should note that since the bond length is primarily determined by the electronic environment and not by the nuclear properties, the bond lengths may be considered to be the same for HCN and DCN (independently on the isotope).
For a linear molecule, the rotational selection rule state that only excitations from J to J+1 are allowed, which are given by the following formula:

$$\Delta\nu_{J\to J+1} = 2B(J+1)$$

For ground state excitations (J = 0) the moment of inertia is then expressed as follows:

$$\nu_0 := \Delta\nu_{0\to 1} = 2B$$
$$\Longrightarrow I = \frac{h}{4\pi\Delta\nu_{0\to 1}}$$

Naming Convention:
Without loss of generality, assign the indices 1,2 and 3 to the atoms H/D, C and N respectively. Furthermore, introduce an index $\xi \in \{H, D\}$ in order to distinguish the two substances HCN and DCN for the following work.

Note, that for the considered linear molecules $r_{\xi N} = r_{\xi C} + r_{CN}$. With this, the problem reduces to two unknowns, for which the following 2 equations can be solved:

$$\frac{hM_{\xi CN}}{4\pi^2\nu_0^{\xi}} = m_C(m_\xi + m_N)r_{\xi C}^2 + m_N(m_\xi + m_C)r_{\xi N}^2 - 2m_C m_N r_{\xi C} r_{\xi N} \qquad \text{for } \xi \in \{H, D\}$$

When solving this system of equations without electronic help, the brute-force way of substitution is accompanied with significant work. Therefore the following transformation

and introduction of variables is suggested, thereby reducing the workload by orders of magnitude:

Transformations & new variables:

• Subtract the two equations from each other to yield 1 new equation (the purpose being that the mixed term vanishes) replacing an old one. The second equation remains untouched.

- $\tilde{r}_{\xi j} := \sqrt{m_j} r_{\xi j}$
- $\Delta m := m_D - m_H$
- $\Delta\alpha := \frac{h}{4\pi^2}\left(\frac{M_{DCN}}{\nu_0^D} - \frac{M^H}{\nu_0^H}\right)$

With this, the following set of 2 equations are obtained:

$$\frac{\Delta\alpha}{\Delta m} = \tilde{r}_{\xi 2}^2 + \tilde{r}_{\xi 3}^2 \tag{1}$$

$$\alpha_\xi = (m_\xi + m_C)\tilde{r}_{\xi N}^2 + (m_\xi + m_N)\tilde{r}_{\xi C}^2 - 2\sqrt{m_N m_C}\tilde{r}_{\xi C}\tilde{r}_{\xi N} \tag{2}$$

Substituting equation 1 for $\tilde{r}_{\xi C}$ into equation 2 and solving this equation for $\tilde{r}_{\xi N}^2$, gives:

$$\tilde{r}_{\xi N}^2 = \frac{(M_{DCN}m_N - m_D m_C)\frac{\Delta\alpha}{\Delta m} + \alpha_D(m_C - m_N)}{(m_C + m_N)^2} \pm$$

$$\pm\sqrt{\left[\frac{(M_{DCN}m_N - m_D m_C)\frac{\Delta\alpha}{\Delta m} + \alpha_D(m_C - m_N)}{(m_C + m_N)^2}\right]^2 - \left[\frac{(m_D + m_N)\frac{\Delta\alpha}{\Delta m} - \alpha_D}{(m_C + m_N)}\right]^2}$$

Having solved for $\tilde{r}_{\xi N}^2$ (and choosing the appropriate solution), one back-substitutes in order to solve for $\tilde{r}_{\xi C}^2$. In a last step, after plugging in, the following bond distances are obtained:

$$r_{\xi C} = r_{HC} = r_{DC} = 1.063\,\text{Å}$$
$$r_{CN} = 1.153\,\text{Å}$$

3) A triatomic molecule has the formula A_2B. Its microwave spectrum shows a progression of strong lines at 15 MHz, 30 MHz, 45 MHz, 60 MHz,. . . and no other lines. **Which of the following structures are compatible with this spectrum:**
a. linear AAB
b. linear ABA
c. bent AAB
d. bent ABA

Firstly, the molecule needs to possess a permanent dipole moment in order to be IR active, which excludes structure b). Since the difference between two consecutive peaks is constant throughout the spectrum, the molecule can only be linear, or symmetric top, which excludes c) and d). In that sense, only structure a) is compatible with the described spectrum.