Spectroscopy

Corrections Chapter 3B

1. *For the $^{12}C^{32}S$ molecule the following millimeter wave pure rotational transitions have been observed (in MHz):*

Transition	*v=0*	*v=1*
J=1←0	*48'990.978*	*48'635.977*
J=2←1	*97'980.950*	*97'270.980*
J=3←2	*146'969.033*	*145'904.167*
J=4←3	*195'954.226*	*194'534.321*

a. *For each vibrational level, determine the corresponding rotational constant, B.*

b. *From your answers in (a), determine the vibrational-rotation interaction constant, α and determine B_e.*

c. *From B_e calculate r_e.*

a. As a first approximation, we can neglect the centrifugal distortion constants. The frequencies of purely rotational transitions for a linear molecule are therefore given by the expression: $\Delta\nu_{v,J+1\leftarrow J} = 2B_v\left(J+1\right)$.

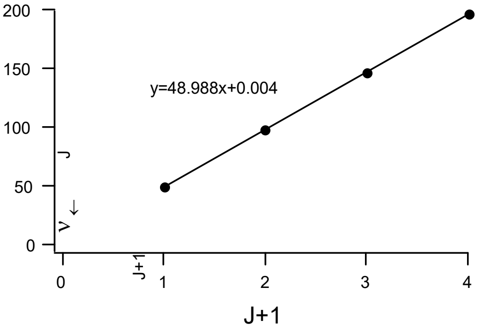
J+1 ← J	**B_0 [MHz]**	**B_1 [MHz]**
1 ← 0	24495.49	24317.99
2 ← 1	24495.24	24317.75
3 ← 2	24494.84	24317.36
4 ← 3	24494.28	24316.79

By representing the experimental frequencies as a function of J+1 and by performing a linear regression, we can determine the rotational constant, B= slope/2

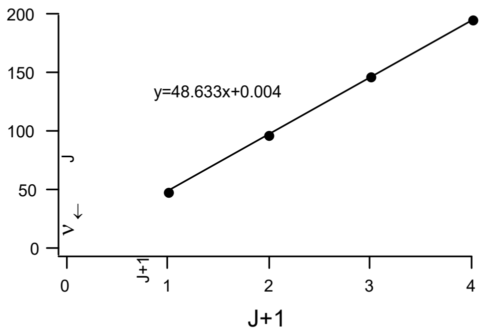
The following results are obtained for the first two vibrational levels of $^{12}C\,^{32}S$.

$\underline{v=0}$:

B_0=24494.62 MHz



$\underline{v=1}$:



B_1=24317.13 MHz

If we want to take into account the centrifugal distortion, that is to say the fact that the bond lengthens when the molecule rotates, then B decreases when J increases (which we observe on the values of the transitions).

By using the equation :

$$\nu_{J+1\leftarrow J} = 2B_{\mathrm{v}}\left(J+1\right) - 4D_{\mathrm{v}}\left(J+1\right)^3,$$

and by adjusting the experimental results, we obtain the following values,

v	B_{v} [MHz]	D_{v} [MHz]
0	24495.56	0.04
1	24318.07	0.04

b.

If we neglect the centrifugal distortion, we can assimilate the vibrational constants calculated in (a) to $B_v = B_e - \alpha\left(v+\tfrac{1}{2}\right)$. The values of B_0 and B_1 allow us to determine the vibration-rotation interaction constant α and the rotational constant of the rigid rotator B_e.

$$B_0 - B_1 = \left(B_e - \tfrac{1}{2}\alpha\right) - \left(B_e - \tfrac{3}{2}\alpha\right) = \alpha$$

$$\alpha = 24\,494 - 24\,316 = 178\ \text{MHz}$$

$$3B_0 - B_1 = 3\left(B_e - \tfrac{1}{2}\alpha\right) - \left(B_e - \tfrac{3}{2}\alpha\right) = 2B_e$$

$$B_e = \frac{3B_0 - B_1}{2} = 24.583\ \text{GHz}$$

c. Given that $B_e = \dfrac{h}{8\pi^2 I} = \dfrac{h}{8\pi^2 \mu r_e^2}$ (in frequency units), the value of r_e from that of B_e calculated in point (b).

$$r_e = \sqrt{\frac{h}{8\pi^2 \mu B_e}}$$

where

$$\mu = \frac{m\left(^{12}C\right)m\left(^{32}S\right)}{m\left(^{12}C\right)+m\left(^{32}S\right)} = \frac{12.000\cdot 31.972}{12.000+31.972} = 8.725\ \text{uma}$$

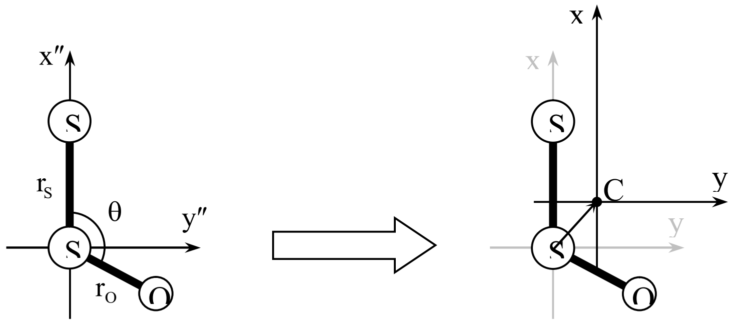
$$r_e = 1.53\ \text{Å}$$

2. *The S_2O molecule is a bent triatomic molecule. The S-S bond is 1.884 Å long, the S-O bond is 1.465 Å long, and the SSO angle is 118.0°.*

a. *Locate the center of mass and set up the moment of inertia tensor. Pick the z-axis out of the plane and the x-axis parallel to the S-S bond.*
b. *Diagonalize the moment of inertia tensor to find I_A, I_B, and I_C.*
c. *Determine the value of the asymmetry parameter κ.*

a. There are two ways to locate the center of mass of the molecule:

- Either we define a system of axes $O''x''y''z''$ temporarily (according to the data of the problem) and we calculate the coordinates $\vec{r}''_{CM} = \frac{\sum_i m_i \vec{r}''_i}{\sum_i m_i}$ of the centre of mass of the system. We then translate $O''x''y''z''$ to find the system of axes centred at the centre of mass $Oxyz$ in which we will calculate the tensor of inertia.



The procedure is as follows: for example, we place the central atom S on the origin O'' and the other S on the axis $O''x''$. Thanks to r_S, r_O and θ, we determine the coordinates of the three atoms (let $\vec{r}''_0$ for *O*, $\vec{r}''_1$ for the central *S* and $\vec{r}''_2$ for the other *S*):

$$\vec{r}_0'' = \begin{pmatrix} -0.688 \\ 1.294 \\ 0 \end{pmatrix} [\text{Å}] \qquad \vec{r}_1'' = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix} [\text{Å}] \qquad \vec{r}_2'' = \begin{pmatrix} 1.884 \\ 0 \\ 0 \end{pmatrix} [\text{Å}]$$

Using $m_O = m\left({}^{16}O\right) = 15.9949$ $[\text{uma}]$ and $m_S = m\left({}^{32}S\right) = 31.9721$ $[\text{uma}]$ in the formula given above, we calculate:

$$\vec{r}_{CM}'' = \frac{\left(m_O\vec{r}_0'' + m_S\vec{r}_1'' + m_S\vec{r}_2''\right)}{m_O + 2m_S} = \begin{pmatrix} 0.616 \\ 0.259 \\ 0 \end{pmatrix} [\text{Å}]$$

The coordinates of the atoms in the Oxyz system translated to the center of mass are simply obtained by subtracting this vector from the coordinates in $O''x''y''z''$:

$$\vec{r}_i = \vec{r}_i'' - \vec{r}_{CM}''$$

- The other method is to directly work in the Oxyz system whose origin is at the centre of mass. In this case, we set the condition of the centre of mass as : $\left(\sum_i m_i\right) \cdot \vec{r}_{CM} = \sum_i m_i \vec{r}_i = \vec{0}$. We then try to identify the 9 unknown coordinates (3 for each atom). For this, we use the fact that the molecule is in the Oxy plane with the SS bond parallel to Ox, as well as r_S, r_O and θ :

$$\begin{cases} z_0 = z_1 = z_2 = 0 \\ x_2 = x_1 + r_S \\ y_2 = y_1 \\ x_0 = x_1 + r_O\cos\theta \\ y_0 = y_1 + r_O\sin\theta \end{cases} \overset{\sum_i m_i\vec{r}_i = \vec{0}}{\Rightarrow\Rightarrow\Rightarrow} \begin{cases} x_1 = -\dfrac{m_S r_S + m_O r_O \cos\theta}{2m_S + m_O} \\ y_1 = -\dfrac{m_O r_O \sin\theta}{2m_S + m_O} \end{cases}$$

$$\Rightarrow \qquad \vec{r}_0 = \begin{pmatrix} -1.304 \\ 1.035 \\ 0 \end{pmatrix} [\text{Å}] \qquad \vec{r}_1 = \begin{pmatrix} -0.616 \\ -0.259 \\ 0 \end{pmatrix} [\text{Å}] \qquad \vec{r}_2 = \begin{pmatrix} 1.268 \\ -0.259 \\ 0 \end{pmatrix} [\text{Å}]$$

These coordinates allow us to calculate the tensor of the moment of inertia with respect to the Oxyz system according to its definition:

$$I=\begin{pmatrix} \sum_i m_i\left(y_i^2+z_i^2\right) & -\sum_i m_i x_i y_i & -\sum_i m_i x_i z_i \\ -\sum_i m_i x_i y_i & \sum_i m_i\left(x_i^2+z_i^2\right) & -\sum_i m_i y_i z_i \\ -\sum_i m_i x_i z_i & -\sum_i m_i y_i z_i & \sum_i m_i\left(x_i^2+y_i^2\right) \end{pmatrix} = \begin{pmatrix} 21.41 & 26.97 & 0 \\ 26.97 & 90.73 & 0 \\ 0 & 0 & 112.13 \end{pmatrix} \left[\text{uma Å}^2\right]$$

b. To diagonalize this matrix, it is necessary for us to calculate its eigenvalues which will happen to be the diagonal elements of the tensor in the system of principal axes. We solve this with its characteristic equation:

$$\left|I-\lambda\right|=0$$

$$\left[(21.41-\lambda)(90.73-\lambda)-(26.97)^2\right](112.13-\lambda)=0$$

$$\left(\lambda^2-112.13\lambda+1214.67\right)(112.13-\lambda)=0$$

$$\begin{cases} \lambda_A = 12.15 & \left[\text{uma Å}^2\right] \\ \lambda_B = 99.99 & \left[\text{uma Å}^2\right] \\ \lambda_C = 112.13 & \left[\text{uma Å}^2\right] \end{cases}$$

$$I'=\begin{pmatrix} I_A & & \\ & I_B & \\ & & I_C \end{pmatrix} = \begin{pmatrix} 12.15 & & \\ & 99.99 & \\ & & 112.13 \end{pmatrix} \left[\text{uma Å}^2\right]$$

c. The asymmetric parameter is defined from rotational constants *A*, *B* and *C*:

$$\kappa=\frac{2B-A-C}{A-C}.$$

Given the definition of *A*, *B* and *C*, we could get directly κ in terms of I_A, I_B and I_C, by using:

$$\kappa=\frac{\frac{2}{I_B}-\frac{1}{I_A}-\frac{1}{I_C}}{\frac{1}{I_A}-\frac{1}{I_C}}.$$

But let’s calculate A, B and C to get an idea of their values:

$$A=\frac{\hbar^2}{2I_A}[J]=\frac{h}{8\pi^2 c I_A}\left[\text{cm}^{-1}\right]$$

And the same for *B* and *C*

$$\begin{cases} A = 1.386\ \left[\mathrm{cm}^{-1}\right] \\ B = 0.168\ \left[\mathrm{cm}^{-1}\right] \\ C = 0.150\ \left[\mathrm{cm}^{-1}\right] \end{cases}$$

We calculated $\kappa = -0.97$. This result being relatively close to, we deduce that the molecule is not very different from a symmetrical elongated top (prolate).

d. <u>For question b) for those who are curious of what the main axis looks like</u>

By determining the normalised eigenvector $\vec{v}_A$, $\vec{v}_B$ and $\vec{v}_C$ associated with the eigenvalues λ_A, λ_B and λ_C, we will obtain the rotation matrix R which transforms the system of axes *Oxyz* to the principal axis system *Oabc* for which the moment of inertia tensor is diagonal.

For λ_A :
$$I \cdot \begin{pmatrix} x_A \\ y_A \\ z_A \end{pmatrix} = \lambda_A \begin{pmatrix} x_A \\ y_A \\ z_A \end{pmatrix} \Rightarrow \begin{cases} 9.259 x_A + 26.973 y_A = 0 \\ z_A = 0 \end{cases} \Rightarrow \vec{v}_A = \begin{pmatrix} 0.946 \\ -0.325 \\ 0 \end{pmatrix} \left[\text{Å}\right]$$

For λ_B :
$$I \cdot \begin{pmatrix} x_B \\ y_B \\ z_B \end{pmatrix} = \lambda_B \begin{pmatrix} x_B \\ y_B \\ z_B \end{pmatrix} \Rightarrow \begin{cases} 26.973 x_B - 9.259 y_B = 0 \\ z_B = 0 \end{cases} \Rightarrow \vec{v}_B = \begin{pmatrix} 0.325 \\ 0.946 \\ 0 \end{pmatrix} \left[\text{Å}\right]$$

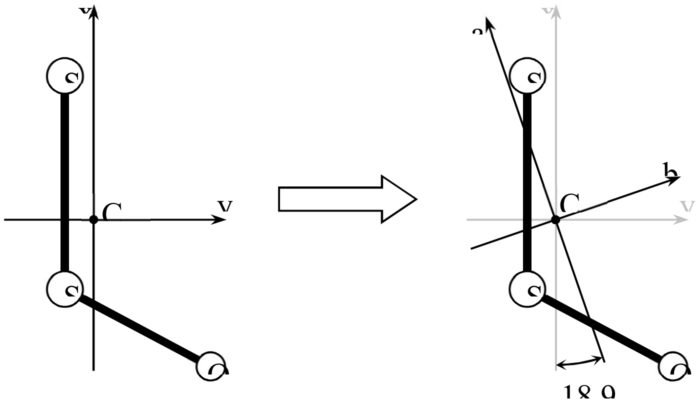
For λ_C :
$$I \cdot \begin{pmatrix} x_C \\ y_C \\ z_C \end{pmatrix} = \lambda_C \begin{pmatrix} x_C \\ y_C \\ z_C \end{pmatrix} \Rightarrow \begin{cases} -90.727 x_C + 26.973 y_C = 0 \\ 26.973 x_C - 21.407 y_C = 0 \end{cases} \Rightarrow \vec{v}_C = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \left[\text{Å}\right]$$

These vectors are the basic vectors of the new coordinate system (Oabc) expressed in the old coordinate system (*Oxyz*).

The rotation matrix *R* is therefore:

$$R = \begin{pmatrix} 0.946 & 0.325 & 0 \\ -0.325 & 0.946 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} \cos\phi & -\sin\phi & 0 \\ \sin\phi & \cos\phi & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

where $\phi = -18.95°$ is the angle whose old axis system had to be rotated around the Oz axis to obtain the main axis system (Oz axis remains fixed, i.e. Oc=Oz).



The coordinate of the atoms in this new axes of system are given by:

$$\vec{r}_i' = R^{-1} \cdot \vec{r}_i$$

We obtain:

$$\vec{r}_0' = \begin{pmatrix} -1.569 \\ 0.555 \\ 0 \end{pmatrix} \left[\text{Å}\right] \qquad \vec{r}_1' = \begin{pmatrix} -0.498 \\ -0.445 \\ 0 \end{pmatrix} \left[\text{Å}\right] \qquad \vec{r}_2' = \begin{pmatrix} 1.283 \\ 0.167 \\ 0 \end{pmatrix} \left[\text{Å}\right]$$