



# Molecular spectroscopy

Answers to the Questions 6,8,10,12,14,15,16



6. Using your answers to question 5, calculate the relative populations of the vibrational levels  $\nu = 0$  and  $\nu = 1$  for carbon monoxide at room temperature and 600 K. How would the rotation-vibration of carbon monoxide change at higher temperatures?

A:  $\varepsilon_{0-1} = 2143.26 \text{ cm}^{-1} = \tilde{\omega} - 2\tilde{\omega}x_e = 4.2575 \times 10^{-20} \text{ J}$

$$\frac{N_1}{N_0} = \exp\left(\frac{-\varepsilon_{0-1}}{kT}\right)$$

$$298\text{K}, N_1/N_0 = \exp[-4.2575 \times 10^{-20} / (298 \times 1.38066 \times 10^{-23})] = 3.21 \times 10^{-5}$$

$$600\text{K}, N_1/N_0 = 5.86 \times 10^{-3}$$

温度升高，更多转动能级占据数升高，振转光谱精细结构中峰数更多且信号更强， $\nu_0-\nu_2$ 、 $\nu_1-\nu_2$ 等吸收带强度升高



## MS Ex.8



8. Which of the following molecules will show a rotational spectrum?

$\text{CH}_4$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{HCl}$ ,  $\text{C}_2\text{H}_2$ ,  $\text{O}_3$ ,  $\text{CO}_2$ ,  $\text{SO}_2$ ,  $\text{N}_2\text{O}$ , *cis* and *trans*  $\text{ClHC=CHCl}$ ?

Molecules can be promoted from one rotational energy level to the next with the absorption of a photon but there are certain restrictions. For the rigid diatomic rotor the *selection rules* are:

1. The molecule must possess *a permanent dipole moment* to absorb EM radiation.
  2. During the transition  $J$  must change by  $\pm 1$  only (*i.e.*  $\Delta J = \pm 1$ ).
  3. There are also restrictions on  $\Delta M_J$  but these are less important.
- **Yes:**  $\text{CH}_2\text{Cl}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{HCl}$ ,  $\text{O}_3$ (V-shaped),  $\text{SO}_2$ ,  $\text{N}_2\text{O}$ , *cis*- $\text{ClHC=CHCl}$
  - **No:**  $\text{CH}_4$ ,  $\text{C}_2\text{H}_2$ ,  $\text{CO}_2$ , *trans*- $\text{ClHC=CHCl}$



10. Calculate the value of the rotational constants for  $^{12}\text{C}^{16}\text{O}$  and  $^{13}\text{C}^{16}\text{O}$  assuming a bond length of  $1.128 \text{ \AA}$ . Express your answers in J, Hz and  $\text{cm}^{-1}$ .

$$\text{A: } B = \frac{\hbar^2}{2I} = \frac{\hbar^2}{2\mu r^2} \quad \mu(^{12}\text{C}^{16}\text{O}) = \frac{12 \times 16}{28} \times 1.6605 \times 10^{-27} \text{ kg}$$

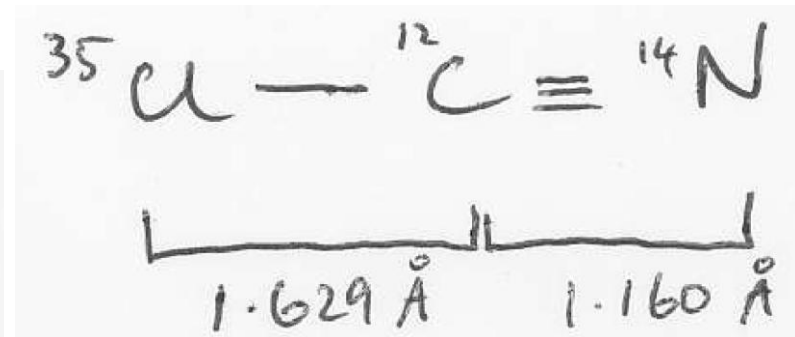
$$\begin{aligned} B(^{12}\text{C}^{16}\text{O}) &= \frac{\hbar^2}{2\mu r^2} = \frac{(1.05457 \times 10^{-34})^2}{2 \left( \frac{12 \times 16}{28} \times 1.6605 \times 10^{-27} \right) (1.128 \times 10^{-10})^2} = 3.838 \times 10^{-23} \text{ J} \\ &= (B \text{ in J/h}) = 5.7925 \times 10^{10} \text{ Hz} = (B \text{ in Hz}/\tilde{c}) = 1.9322 \text{ cm}^{-1} \end{aligned}$$

$$\begin{aligned} B(^{13}\text{C}^{16}\text{O}) &= \frac{\hbar^2}{2\mu r^2} = \frac{(1.05457 \times 10^{-34})^2}{2 \left( \frac{13 \times 16}{29} \times 1.6605 \times 10^{-27} \right) (1.128 \times 10^{-10})^2} = 3.6694 \times 10^{-23} \text{ J} \\ &= (B \text{ in J/h}) = 5.5378 \times 10^{10} \text{ Hz} = (B \text{ in Hz}/\tilde{c}) = 1.8472 \text{ cm}^{-1} \end{aligned}$$



12. Calculate the value of the rotational constant for  $^{35}\text{ClCN}$ . ( $r_{\text{ClC}} = 1.629 \text{ \AA}$ ;  $r_{\text{CN}} = 1.160 \text{ \AA}$ ).

$$I = m_{\text{Cl}} r_{\text{Cl}}^2 + m_{\text{N}} r_{\text{CN}}^2 - \frac{(m_{\text{Cl}} r_{\text{Cl}} - m_{\text{N}} r_{\text{CN}})^2}{m_{\text{Cl}} + m_{\text{C}} + m_{\text{N}}}$$



$$= \left[ 35 \times 1.629^2 + 14 \times 1.160^2 - \frac{(35 \times 1.629 - 14 \times 1.160)^2}{35 + 12 + 14} \right] \times 1.6605 \times 10^{-27} \times 10^{-10 \times 2}$$

$$= 1.4025 \times 10^{-45} \text{ kg} \cdot \text{m}^2$$

$$B = \frac{\hbar^2}{2I} (\text{J}) = \frac{h}{8\pi^2 c I} (\text{cm}^{-1})$$

$$= 3.9648 \times 10^{-24} \text{ J}$$

$$= 0.19959 \text{ cm}^{-1}$$



14.

A 476.5 nm argon ion laser was used to record the rotational Raman spectrum of  $^{14}\text{N}_2$ . The spectrum shows a series of regularly spaced lines, the first of which are  $11.937\text{ cm}^{-1}$  either side of the peak due to the Rayleigh scattering of the laser. What is the separation of the remaining lines from these first ones? At what frequencies do the  $S_{10}$  peaks occur in the Stokes and anti-Stokes branches? Calculate the bond length  $\text{N}_2$ .

A: 转动拉曼光谱中, 光谱谱线在入射光信号两侧依序出现, 信号线与入射光的能量(频率)差满足下式:

$$S_J = \Delta\varepsilon_J = \varepsilon_{J+2} - \varepsilon_J = \tilde{B}(J+2)(J+3) - \tilde{B}J(J+1) = \tilde{B}(4J+6)$$

依题意有:  $S_0 = 6\tilde{B} = 11.937\text{ cm}^{-1}$        $\tilde{B} = 1.9895\text{ cm}^{-1}$

则其它相邻信号线的间距当为:  $S_{J+1} - S_J = 4\tilde{B} = 7.958\text{ cm}^{-1}$

$$S_{10} = 46\tilde{B} = 91.517\text{ cm}^{-1} \quad \text{入射线频率 } \omega_0 = \frac{1}{\lambda} = \frac{1}{476.5 \times 10^{-7}}\text{ cm}^{-1} = 20986.4\text{ cm}^{-1}$$

*Stoke line at  $20986.4 - 91.5 = 20894.9\text{ cm}^{-1}$       anti-Stoke line at  $20986.4 + 91.5 = 21077.9\text{ cm}^{-1}$*

$$I = \frac{h}{8\pi^2 \tilde{c} \tilde{B}} = \mu r^2 \quad r = \sqrt{\frac{h}{8\pi^2 \tilde{c} \tilde{B} \mu}} = \sqrt{\frac{6.626 \times 10^{-34} \times 2}{8\pi^2 \times 3 \times 10^{10} \times 1.9895 \times 14 \times 1.66054 \times 10^{-27}}} \text{ (m)} = 1.10\text{Å}$$



15. The rotational spectrum of  $^{79}\text{Br}^{19}\text{F}$  shows a series of equidistant lines  $0.71433 \text{ cm}^{-1}$  apart. Calculate the rotational constant,  $B$ , and hence the moment of inertia and the bond length of the molecule. Determine the wavenumber of the  $J = 9 \rightarrow J = 10$  transition and find the transition which gives rise to the most intense spectral line at room temperature (say 300 K). State any assumptions you make. Calculate the number of revolutions per second which the BrF molecule undergoes when in (a) the  $J = 0$  state, (b) the  $J = 1$  state, and (c) the  $J = 10$  state.

$$\text{A: } 2\tilde{B} = 0.71433 \text{ cm}^{-1} \rightarrow \tilde{B} = 0.357165 \text{ cm}^{-1}$$

$$\tilde{B} = \frac{h}{8\pi^2 \tilde{c} I} (\text{cm}^{-1}) \rightarrow I = \frac{h}{8\pi^2 \tilde{c} \tilde{B}} = \frac{6.626 \times 10^{-34}}{8\pi^2 \times 3 \times 10^{10} \times 0.357165} = 7.8375 \times 10^{-46} \text{ kg m}^2$$

$$\mu = \frac{M_{\text{Br}} \times M_{\text{F}}}{(M_{\text{Br}} + M_{\text{F}}) N_0} = \frac{79 \times 19}{(79 + 19)} \times 1.66054 \times 10^{-27} = 2.543337 \times 10^{-26} \text{ kg}$$

$$r = \sqrt{I/\mu} = \sqrt{7.8375 \times 10^{-46} / 2.543337 \times 10^{-26}} \text{ m} = 1.755 \text{ \AA}$$

$$(\varepsilon_J - \varepsilon_{J-1})_{J=10} = 2J\tilde{B} = 20\tilde{B} = 7.1433 \text{ cm}^{-1}$$

$$J_{\text{max}, T=300\text{K}} = \sqrt{\frac{kT}{2h\tilde{c}\tilde{B}}} - \frac{1}{2} = \sqrt{\frac{1.380856 \times 10^{-23} \times 300}{2 \times 6.26076 \times 10^{-34} \times 3 \times 10^{10} \times 0.357165}} - \frac{1}{2} = 17(.08) \quad J=18 \leftarrow 17 \text{ 最强}$$





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$$\text{A: } \varepsilon_J = J(J+1)\tilde{B}(\text{cm}^{-1}) = J(J+1)h\tilde{c}\tilde{B}(J) = I\omega^2/2 \quad I = \frac{h}{8\pi^2\tilde{c}\tilde{B}}$$

$$\omega_J = \sqrt{2J(J+1)h\tilde{c}\tilde{B}/I} = 4\pi\tilde{c}\tilde{B}\sqrt{J(J+1)}(\text{rad s}^{-1}) = 2\tilde{c}\tilde{B}\sqrt{J(J+1)}(\text{s}^{-1}) = 2.14299 \times 10^{10}\sqrt{J(J+1)} \text{ s}^{-1}$$

$$\omega_0=0 \quad \omega_1= 3.03 \times 10^{10} \text{ s}^{-1}$$

$$\omega_{10}= 2.246 \times 10^{11} \text{ s}^{-1}$$





16. The following data are obtained from the vibration-rotation spectrum of  $\text{H}^{79}\text{Br}$ . Determine  $B_0$ ,  $B_1$ , and  $B_e$  from these data and their corresponding bond lengths.

Line      Frequency /cm-1

$R_0$       2642.60

$R_1$       2658.36

$P_1$       2609.67

$P_2$       2592.51

A: 
$$\tilde{B}_1 = (\tilde{R}_J - \tilde{P}_J) / [2(2J + 1)] = (\tilde{R}_1 - \tilde{P}_1) / 6$$
$$= 8.115 \text{ cm}^{-1}$$

$$\tilde{B}_0 = (\tilde{R}_{J-1} - \tilde{P}_{J+1}) / [2(2J + 1)] = (\tilde{R}_0 - \tilde{P}_2) / 6$$
$$= 8.3483 \text{ cm}^{-1}$$

$$\tilde{B}_v = \tilde{B}_e - \tilde{\alpha} \left( v + \frac{1}{2} \right) = \tilde{B}_e - (\tilde{B}_0 - \tilde{B}_1) \left( v + \frac{1}{2} \right)$$

$$\tilde{B}_e = \frac{3\tilde{B}_0 - \tilde{B}_1}{2} = 8.465 \text{ cm}^{-1} \quad \tilde{B}_v = \frac{h}{8\pi^2 \tilde{c} (\mu r_v^2)}$$

$$\tilde{r}_v = \sqrt{\frac{h}{8\pi^2 \mu \tilde{c} \tilde{B}_v}} = \sqrt{\frac{h}{8\pi^2 m_u \left( \frac{79 \times 1}{79 + 1} \right) \tilde{c} \tilde{B}_v}} = \sqrt{\frac{6.6260693 \times 10^{-34}}{8\pi^2 \times 1.6605 \times 10^{-27} \left( \frac{79 \times 1}{79 + 1} \right) \times 3 \times 10^{10} \times \tilde{B}_v}} = 0.41295 \times 10^{-9} / \sqrt{\tilde{B}_v} (\text{m})$$

$$\tilde{r}_1 = 0.41295 \times \frac{10^{-9}}{\sqrt{\tilde{B}_1}} (\text{m}) = 1.450 (\text{\AA}) \quad \tilde{r}_0 = 0.53223 \times \frac{10^{-9}}{\sqrt{\tilde{B}_0}} (\text{m}) = 1.429 (\text{\AA})$$

$$\tilde{r}_e = 0.41295 \times \frac{10^{-9}}{\sqrt{\tilde{B}_e}} (\text{m}) = 1.419 (\text{\AA})$$