ChemE 220 - Physical Chemistry II for Engineers – Spring 2025 Solution to Homework Assignment 2

1. A transition is allowed if the following integral is nonzero.

$$\int \psi_{\text{final}}^* \hat{T} \psi_{\text{initial}} d\tau = \int \psi_{2p_z}^* \hat{T} \psi_{1s} d\tau$$

Because the light is z-polarized, the transition operator is

$$\hat{T} = eE_z^0 z = eE_z^0 r\cos\theta$$

Substitute the expressions for the 1s and $2p_z$ orbitals. Because we are interested only whether the integral is zero or nonzero, we drop the constants.

$$\int \Psi_{2p_z}^* \hat{T} \Psi_{1s} d\tau = \int_{0}^{2\pi \pi} \int_{0}^{\infty} e^{-r/a_0} (r \cos \theta) (r e^{-r/2a_0} \cos \theta) r^2 dr \sin \theta d\theta d\phi$$
$$= 2\pi \int_{0}^{\pi} \int_{0}^{\infty} r^4 e^{-3r/2a_0} \cos^2 \theta \sin \theta dr d\theta$$
$$= 2\pi \int_{0}^{\infty} r^4 e^{-3r/2a_0} \left[-\frac{1}{3} \cos^3 \theta \Big|_0^{\pi} \right] dr$$
$$= 2\pi \frac{2}{3} \int_{0}^{\infty} r^4 e^{-3r/2a_0} dr > 0$$

We need not evaluate the integral over r. Because both r^4 and the exponential are positive over the integration range, we know the integral will be nonzero.

2.(A) We seek two orbitals $\psi_{2sp\sigma}$ and $\psi_{2sp\sigma^*}$ that are orthogonal,

$$0 = \int \psi_{2s\sigma}^* \psi_{2s\sigma\sigma} d\tau = \int (\psi_{2s\sigma} - a\psi_{2p_z\sigma})(\psi_{2s\sigma} + a\psi_{2p_z\sigma})d\tau$$
$$= \int \psi_{2s\sigma} \psi_{2s\sigma} d\tau - a \int \psi_{2p_z\sigma} \psi_{2s\sigma} d\tau + a \int \psi_{2s\sigma} \psi_{2p_z\sigma} d\tau - a^2 \int \psi_{2p_z\sigma} \psi_{2p_z\sigma} d\tau$$

The second and third terms integrals cancel. The first and fourth integrals are 1 because $\psi_{2s\sigma}$ and $\psi_{2sp_z\sigma}$ are normalized. Thus the equation simplifies to

$$0 = 1 - a^2$$
$$a = \pm 1$$

We choose arbitrarily a = +1. (The choice is not important. The same hybrid orbitals obtain with a = -1.)

(B) Derive the normalization constant N_{-} such that $\psi_{2sp\sigma^*} = N_{-}(\psi_{2s\sigma} - \psi_{2p_z\sigma})$.

$$1 = \int \psi_{2sp\sigma^{*}}^{*} \psi_{2sp\sigma} d\tau = N_{-}^{2} \int (\psi_{2s\sigma} - \psi_{2p_{z}\sigma})^{2} d\tau$$

= $N_{-}^{2} \left[\int \psi_{2s\sigma} \psi_{2s\sigma} d\tau - 2 \int \psi_{2p_{z}\sigma} \psi_{2s\sigma} d\tau + \int \psi_{2p_{z}\sigma} \psi_{2p_{z}\sigma} d\tau \right]$
= $N_{-}^{2} \left[1 - 2 \int \psi_{2p_{z}\sigma} \psi_{2s\sigma} d\tau + 1 \right] = 2N_{-}^{2} \left[1 - \int \psi_{2p_{z}\sigma} \psi_{2s\sigma} d\tau \right]$
 $N_{-} = \frac{1}{\sqrt{2(1 - \int \psi_{2p_{z}\sigma} \psi_{2s\sigma} d\tau)}}$

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A similar calculation yields N_+ .

$$N_{+} = \frac{1}{\sqrt{2(1+\int \psi_{2p_z\sigma}\psi_{2s\sigma}d\tau)}}$$

2. The ordering of the $2p\sigma$ and $2p\pi$ orbitals is unknown. It is equally valid to put the $2p\sigma$ at a lower energy than the $2p\pi$ orbitals.





- (B) The electrons fill all bonding orbitals. The ground state is a singlet, regardless of whether one places the $2p_z\sigma$ or the $2p_x\pi$ orbital at lower energy.
- (C) The bond order is 3.
- 4. For the $J = 2 \rightarrow 1$ transition, the photon has wavenumber

$$\tilde{\mathbf{v}}_{\text{photon}} = \tilde{\mathbf{v}}_2 - \tilde{\mathbf{v}}_1 = 2 \times 3 \times B - 1 \times 2 \times B = 4B$$

We need to convert from $\tilde{\nu}_{photon}$ (wavenumber units of cm⁻¹) to ν_{photon} (frequency units of cycles/sec).

$$v_{\text{photon}} = \tilde{v}_{\text{photon}}c = 4Bc$$

Now express the moment of inertia in terms of ν_{photon} .

$$B = \frac{\hbar}{4\pi cI}$$
$$I = \frac{\hbar}{4\pi cB} = \frac{\hbar}{\pi (4Bc)} = \frac{\hbar}{\pi v_{\text{photon}}}$$

Compute the moments of inertia for each isotopic combination of OCS.

Define the moment of inertia of ${}^{16}O^{12}C^{32}S = I_1$.

$$I_1 = \frac{1.0546 \times 10^{-34} \text{ joule} \cdot \text{sec}}{\pi (24.326 \times 10^9 \text{ sec}^{-1})} = 1.3800 \times 10^{-45} \text{ kg} \cdot \text{m}^2$$

Define the moment of inertia of ${}^{16}\text{O}{}^{12}\text{C}{}^{34}\text{S} = I_2$.

$$I_2 = \frac{1.0546 \times 10^{-34} \text{ joule} \cdot \text{sec}}{\pi (23.731 \times 10^9 \text{ sec}^{-1})} = 1.4145 \times 10^{-45} \text{ kg} \cdot \text{m}^2$$

Define the moment of inertia of ${}^{16}O^{13}C^{32}S = I_3$.

$$I_3 = \frac{1.0546 \times 10^{-34} \text{ joule} \cdot \text{sec}}{\pi (24.248 \times 10^9 \text{ sec}^{-1})} = 1.3844 \times 10^{-45} \text{ kg} \cdot \text{m}^2$$

As given in the Hint, define distances to the center of mass, which is assumed to lie between C and S.

$$O \longrightarrow C \xrightarrow{r_{C}} S$$

The general equation for the moment of inertia about the center of mass is thus,

$$I_{\rm OCS} = m_{\rm O} r_{\rm O}^2 + m_{\rm C} r_{\rm C}^2 + m_{\rm S} r_{\rm S}^2$$

Define $m_{\rm p}$ as the proton mass.

$$I_{1} = 16m_{p}r_{O}^{2} + 12m_{p}r_{C}^{2} + 32m_{p}r_{S}^{2}$$

$$I_{2} = 16m_{p}r_{O}^{2} + 12m_{p}r_{C}^{2} + 34m_{p}r_{S}^{2}$$

$$I_{3} = 16m_{p}r_{O}^{2} + 13m_{p}r_{C}^{2} + 32m_{p}r_{S}^{2}$$

There are many methods to solve this set of simultaneous equations. I will use successive substitution. Subtract the expression for I_1 from the expression for I_2 .

$$I_2 - I_1 = 2m_{\rm p}r_{\rm S}^2$$

Solve for $r_{\rm S}$.

$$r_{\rm S} = \left(\frac{I_2 - I_1}{2m_{\rm p}}\right)^{1/2} = \left(\frac{(1.4145 - 1.3800) \times 10^{-45} \,\rm kg \cdot m^2}{2 \times 1.6726 \times 10^{-27} \,\rm kg}\right)^{1/2} = 1.02 \times 10^{-10} \,\rm m$$

Subtract the expression for I_1 from the expression for I_3 .

$$I_3 - I_1 = m_{\rm p} r_{\rm C}^2$$

Solve for $r_{\rm S}$.

$$r_{\rm C} = \left(\frac{I_3 - I_1}{m_{\rm p}}\right)^{1/2} = \left(\frac{(1.3844 - 1.3800) \times 10^{-45} \,\mathrm{kg} \cdot \mathrm{m}^2}{1.6726 \times 10^{-27} \,\mathrm{kg}}\right)^{1/2} = 5.1 \times 10^{-11} \,\mathrm{m}$$

Solve the expression for I_1 for r_0 .

$$r_{\rm O} = \left(\frac{I_1}{16m_{\rm p}} - \frac{12}{16}r_{\rm C}^2 - \frac{32}{16}r_{\rm S}^2\right)^{1/2} = 1.70 \times 10^{-10}\,{\rm m}$$

C–S bond length = $r_{\rm C} + r_{\rm S} = 1.53 \times 10^{-10} \,{\rm m} = 1.53 \,{\rm \AA}.$

O–C bond length =
$$r_{\rm O} - r_{\rm C} = 1.19 \times 10^{-10} \,\text{m} = 1.19 \,\text{\AA}$$

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5.(A) This is a rotational spectrum, in the microwave band. The spacing between the peaks is 2*B*, where *B* is the rotational constant. The nine peaks span a range of $452.6 - 150.9 \text{ cm}^{-1} = 301.7 \text{ cm}^{-1}$. There are 8 uniform gaps between the 9 peaks, so a single gap is $301.7 \text{ cm}^{-1}/8 = 37.71 \text{ cm}^{-1}$.

Use the rotational constant to calculate the bond length.

$$B = \frac{\hbar}{4\pi cI} = \frac{\hbar}{4\pi c\mu R^2}$$
$$R = \left(\frac{\hbar}{2\pi c\mu (2B)}\right)^{1/2}$$

Calculate the reduced mass.

$$\mu = \frac{m_{\rm H}m_{\rm O}}{m_{\rm H} + m_{\rm O}} = \frac{1 \times 16}{1 + 16} 1.67 \times 10^{-27} \,\rm kg = 1.56 \times 10^{-27} \,\rm kg$$

Substitute into the equation for *R*.

$$R = \left(\frac{\hbar}{2\pi c\mu(2B)}\right)^{1/2} = \left(\frac{1.05 \times 10^{-34} \text{ joule} \cdot \text{sec}}{2\pi (3.0 \times 10^8 \text{ m/s}) (1.56 \times 10^{-27} \text{ kg}) (37.71 \text{ cm}^{-1})} \left(\frac{1 \text{ m}}{100 \text{ cm}}\right)\right)^{1/2}$$

$$R = 9.7 \times 10^{-11} \text{ m} = 0.97 \text{ Å}$$

(B) The first peak in a rotational spectrum is at 2*B*, which is at 37.71 cm⁻¹ in this case. But because the spectrometer malfunctioned, this peak was not detected. The complete set of peaks is thus

position	transition	intensity
37.7 cm ⁻¹	$J = 0 \rightarrow 1$	(not detected)
75.4 cm^{-1}	$J = 1 \rightarrow 2$	(not detected)
113.1 cm ⁻¹	$J = 2 \rightarrow 3$	(not detected)
150.9 cm^{-1}	$J = 3 \rightarrow 4$	3.530
188.6 cm ⁻¹	$J = 4 \rightarrow 5$	2.876

Now that we have determined the transitions associated with the observed peaks we can use the relative intensities to calculate the temperature. The intensity of a rotational transition is proportional $(2J+1)\exp(-E_J/kT)$, where *J* is the initial state and $E_J = -BJ(J+1)hc$.

The ratio of intensities is thus

$$\frac{\text{intensity of } J \to J+1 \text{ peak}}{\text{intensity of } J+1 \to J+2 \text{ peak}} = \left(\frac{2J+1}{2(J+1)+1}\right) \frac{\exp(-BJ(J+1)hc/kT)}{\exp(-B(J+1)(J+2)hc/kT)}$$
$$= \left(\frac{2J+1}{2J+3}\right) \exp\left[-\frac{Bhc}{kT}[J(J+1)-(J+1)(J+2)]\right]$$
$$= \left(\frac{2J+1}{2J+3}\right) \exp\left[\frac{2Bhc}{kT}(J+1)\right]$$

Substitute the particulars.

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$$\frac{-5}{100} - 5 - \frac{1}{100} = \frac{2(3) + 1}{2(3) + 3} \exp\left[\frac{2Bhc}{kT}(3 + 1)\right]$$

$$\frac{3.530}{2.876} = \frac{7}{9} \exp\left[\frac{4(2B)hc}{kT}\right]$$

$$1.578 = \exp\left[\frac{4(2B)hc}{kT}\right]$$

$$\ln(1.578) = \frac{4(2B)hc}{kT}$$

$$T = \frac{4(2B)hc}{k\ln(1.578)} = \frac{4 \times (37.71 \text{ cm}^{-1})(6.63 \times 10^{-34} \text{ J} \cdot \text{sec})(3.0 \times 10^8 \text{ m/s})}{(1.38 \times 10^{-23} \text{ J/K}) \ln(1.578)} \left(\frac{100 \text{ cm}}{1 \text{ m}}\right)$$

$$T = 476 \text{ K}$$

Note that although the peak at 150.9 cm⁻¹ is the first peak in the spectrum, it does not correspond to the $J = 0 \rightarrow 1$ transition. The first peak must be at 2B.

6. For a rotational transition from J to J+1 the intensity of the spectra peak is proportional to the number of states at quantum number J times the Boltzmann population of the states,

intensity
$$\propto (2J+1)\exp\left[-\frac{E_J}{kT}\right] = (2J+1)\exp\left[-\frac{BJ(J+1)hc}{kT}\right]$$

To find the maximum, set the derivative with respect to J equal to 0.

$$0 = \frac{d}{dJ} \text{ intensity } \propto 2 \exp\left[-\frac{BJ(J+1)hc}{kT}\right] - (2J+1)\left[\frac{B(2J+1)hc}{kT}\right] \exp\left[-\frac{BJ(J+1)hc}{kT}\right]$$
$$0 = 2 - (2J+1)^2 \frac{Bhc}{kT}$$
$$\frac{2kT}{Bhc} = (2J+1)^2$$
$$J_{\text{max}} = \left(\frac{kT}{2Bhc}\right)^{1/2} - \frac{1}{2}$$

Of course, this derivation assumes that the intensity is a continuous function of J. That is, to take the derivative with respect to J we assumed implicitly that J was continuous. To calculate the largest peak, one must use the formula above and round to the nearest integer.

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