



# Solutions to selected exercise problems in quantum chemistry and spectroscopy

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# Solutions to selected exercise problems in quantum chemistry and spectroscopy

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# Solutions to selected problems from the previously published collection –



Jens Spanget-Larsen, RUC September 2016 Problem 1 (with suggested solution)

In a classical experiment carried out by the American physicist R. A. Millikan i 1916 (*Phys. Rev.* 7, 355), a sodium surface was irradiated with monochromatic light of different wavelengths  $\lambda$  and the emitted photoelectrons were analyzed according to their kinetic energy.



Millikan used an experimental setup where the photoelectrons hit an electrically conducting screen (collector). The energy of the emitted electrons was determined by measuring the voltage V that should be applied to the screen relative to the sodium surface in order just to stop the photoelectron current ("the stopping voltage"). The kinetic energy of the photoelectrons  $\frac{1}{2}mv^2$  (Joule) is equal to  $e \cdot V$ , where e is the elementary charge in Coulomb and V is the stopping voltage (note that 1 Joule = 1 Coulomb Volt). The following values of wavelength  $\lambda$  and voltage V were measured (1 nm =  $10^{-9}$  m):

$\lambda$ (nm)	V (Volt)
312.5	2.128
365.0	1.595
404.7	1.215
433.9	1.025

Photoelectron data like these lead to the first precise determination of Planck's constant h (± 0.5%). Derive a value of Planck's constant from Millikan's data..

# ANSWER:

Millikan, data for sodium (1916):

$\lambda$ (nm)	$v = c/\lambda (s^{-1})$	V(Volt)	$E_{kin} = \boldsymbol{e} \cdot \boldsymbol{V} \left( \mathbf{J} \right)$
312.5	$9.5934 \cdot 10^{14}$	2.128	$3.409 \cdot 10^{-19}$
365.0	$8.2135 \cdot 10^{14}$	1.595	$2.555 \cdot 10^{-19}$
404.7	$7.4078 \cdot 10^{14}$	1.215	$1.947 \cdot 10^{-19}$
433.9	$6.9093 \cdot 10^{14}$	1.025	$1.642 \cdot 10^{-19}$

Einsteins equation for the photoelectric effect (1905):

 $h \nu = I + E_{kin} \Leftrightarrow E_{kin} = h \nu - I$ 

A plot of  $E_{kin}$  as a function of frequency  $\nu$  should thus yield a straight line with slope equal to Planck's constant, h.

Plot of data points for  $E_{kin}$  (J) against frequency  $v(s^{-1})$ :



The slope of the LS regression line is  $h = 6.644 \cdot 10^{-34} \text{ J s}$ , yielding an estimate of Planck's constant close to the table value:  $h = 6.62608 \cdot 10^{-34} \text{ J s}$ .

# Problem 3 (suggested solution)

In this problem we consider electronic transitions in linear, conjugated polyenes. It is assumed that the so-called  $\pi$ -electrons associated with the double bonds move freely within the length of the conjugated system ("Free-Electron Molecular Orbital" model), and energy levels and wavefunctions are approximated by using the particle in a one-dimensional box-model.



Assume that the length *L* of the box is given by L = (2n + 1)d, where d = 1.4 Å is the average CC bond length in a linear polyene and *n* is the number of formal double bonds. In the electronic ground state, the  $2n \pi$ -electrons (2 per double bond) occupy the *n* lowest energy levels, since each level can contain no more than two electrons (Pauli principle).

Show that the energy difference between the lowest unoccupied level  $\varepsilon_{n+1}$  and the highest occupied level  $\varepsilon_n$  is equal to

$$\varepsilon_{n+1} - \varepsilon_n = \frac{\hbar^2 \pi^2}{2m_e d^2} (2n+1)^{-1}$$

ANSWER:

Particle in a box:  

$$\varepsilon_{n} = \frac{\hbar^{2} \pi^{2}}{2m_{e}L^{2}} \cdot n^{2}, \qquad \varepsilon_{n+1} = \frac{\hbar^{2} \pi^{2}}{2m_{e}L^{2}} \cdot (n+1)^{2}$$

$$\varepsilon_{n+1} - \varepsilon_{n} = \frac{\hbar^{2} \pi^{2}}{2m_{e}L^{2}} \cdot \left[ (n+1)^{2} - n^{2} \right] = \frac{\hbar^{2} \pi^{2}}{2m_{e}L^{2}} \cdot (2n+1)$$

$$L = (2n+1)d \implies \qquad \qquad \varepsilon_{n+1} - \varepsilon_n = \frac{\hbar^2 \pi^2}{2m_e d^2} \cdot (2n+1)^{-1} \qquad (q.e.d)$$

The energy difference corresponds to the transition energy  $\Delta E$  for the most longwave absorption band in the UV-VIS region. Compute the theoretical transition energies  $\Delta E$  [J, eV] and the corresponding wavenumbers  $\tilde{\nu}$  [cm<sup>-1</sup>] and wavelengths  $\lambda$  [nm] for n = 1, 2, 3, and 4 (ethene, butadiene, hexatriene, and octatetraene). Compare with the experimental wavelengths: 163, 210, 247, and 286 nm, respectively.

ANSWER:

$$\frac{\hbar^2 \pi^2}{2m_e d^2} = \frac{(1.05457 \cdot 10^{-34} \,\mathrm{J\,s})^2 \pi^2}{2 \cdot (9.10939 \cdot 10^{-31} \,\mathrm{kg})(1.4 \cdot 10^{-10} \,\mathrm{m})^2} = 3.0737971 \cdot 10^{-18} \,\mathrm{J}$$
$$= \frac{3.0737971 \cdot 10^{-18} \,\mathrm{J}}{1.602177 \cdot 10^{-19} \,\mathrm{C}} = 19.185 \,\mathrm{eV}$$
$$\hat{=} \frac{3.0737971 \cdot 10^{-18} \,\mathrm{J}}{1.98645 \cdot 10^{-23} \,\mathrm{J} \,\mathrm{cm}} = 154740 \,\mathrm{cm^{-1}} \quad \Rightarrow$$

п	$(2n+1)^{-1}$	$\Delta \varepsilon$ [J]	$\Delta \varepsilon [eV]$	$\Delta \varepsilon [\text{cm}^{-1}]$	λ [nm]	Obsd. $[cm^{-1}]$	Obsd. [nm]
1	1/3	$1.03 \cdot 10^{-18}$	6.40	51600	194	61000	163
2	1/5	$6.15 \cdot 10^{-19}$	3.84	30900	323	48000	210
3	1/7	$4.39 \cdot 10^{-19}$	2.74	22100	452	40000	247
4	1/9	$3.42 \cdot 10^{-19}$	2.13	17200	582	35000	286

Order of magnitude and the decrease of transition energy (increase of wavelength) on extension of the length of the polyene are quite well reproduced, considering the simplicity of the model!

# Problem 5 (with suggested solution)

Let us consider a description of the energy levels in the hydrogen atom by using a threedimensional "particle in a box"-model. The eigenfunctions and eigenvalues for a particle in a rectangular box with side lengths I, J, and K are given by

$$\Psi_{ijk}(x, y, z) = \sqrt{\frac{8}{IJK}} \sin \frac{i\pi x}{I} \sin \frac{j\pi y}{J} \sin \frac{k\pi z}{K}$$
$$\varepsilon_{ijk} = \frac{\hbar^2 \pi^2}{2m_e} \left[ \left(\frac{i}{I}\right)^2 + \left(\frac{j}{J}\right)^2 + \left(\frac{k}{K}\right)^2 \right]$$

where *i*, *j*, and *k* are quantum numbers that independently may adopt any positive integer value.

a. Assume that the box has the shape of a cube. Indicate the approximate shape of the wavefunctions for the two lowest energy levels and express the energy difference between them as a function of the side length L of the cube.

ANSWER:

$$\psi_{ijk}(x, y, z) = \sqrt{\frac{8}{L^3}} \sin \frac{i\pi x}{L} \sin \frac{j\pi y}{L} \sin \frac{k\pi z}{L}$$

$$\varepsilon_{ijk} = \frac{\hbar^2 \pi^2}{2m_e L^2} \left[ i^2 + j^2 + k^2 \right]$$

Ζ







$$\varepsilon_{111} = \frac{\hbar^2 \pi^2}{2m_e L^2} \cdot 3$$
  $\varepsilon_{211} = \varepsilon_{121} = \varepsilon_{112} = \frac{\hbar^2 \pi^2}{2m_e L^2} \cdot 6$ 

$$\Delta E^{\text{model}} = \Delta \varepsilon = \frac{\hbar^2 \pi^2}{2m_e L^2} \cdot (6-3) = \underline{1.8 \cdot 10^{-37} \cdot L^{-2}} \quad [J]$$

b. The corresponding spectroscopic transition in atomic hydrogen has a wavelength of 122 nm (the first line in the *Lyman* series). Which volume  $V = L^3$  should our simple cube model have in order to reproduce this wavelength? Compare V with experimental estimates of the volume of the hydrogen atom (*e.g.*, the van der Waals radius  $r_w$  of hydrogen is estimated to be 1.2 Å, corresponding to a volume  $4\pi r_w^3/3 = 7.2 Å^3$ ).

ANSWER:

$$\lambda^{\text{obsd}} = 122 \text{ nm} \implies \Delta E^{\text{obsd}} = \frac{hc}{\lambda^{\text{obsd}}} = \frac{(1.98645 \cdot 10^{-25} \text{ J m})}{(122 \cdot 10^{-9} \text{ m})} = 1.63 \cdot 10^{-18} \text{ J}$$
$$\Delta E^{\text{model}} = \Delta E^{\text{obsd}} \implies 1.8 \cdot 10^{-37} \cdot L^{-2} = 1.63 \cdot 10^{-18} \text{ [J]}$$
$$\implies L = \sqrt{\frac{1.8 \cdot 10^{-37}}{1.63 \cdot 10^{-18}}} = 3.3 \cdot 10^{-10} \text{ m} = 3.3 \text{ Å}, \text{ cube volume } \underline{V} = 37 \text{ Å}^{3}$$

*c*. The "particle in a box"-model for hydrogen is less successful than the FEMO-model for linear polyenes (Problem 3). Why?

# ANSWER:

Consider the potential energy assumptions in the two cases!

# **Problem 6** (with suggested solution)

In the *harmonic approximation*, the stationary vibrational energy levels for a diatomic molecule A–B are given by

$$E_{v} = (v + \frac{1}{2})\hbar\omega = (v + \frac{1}{2})\hbar\sqrt{\frac{k}{\mu}}, \quad v = 0, 1, 2, \cdots$$

where k is the "force constant" for the chemical bond between the atoms A and B (the force constant is a measure of the rigidity of the bond, typically in the order of 500 N m<sup>-1</sup>),  $\mu$  is the reduced mass,  $\mu = m_A m_B/(m_A + m_B)$ , and v is the vibrational quantum number. The parameter  $\omega$  is equal to the classical angular frequency,  $\omega = 2\pi v$  [radian s<sup>-1</sup>], where v is the classical frequency [s<sup>-1</sup> (Hz)]. The corresponding vibrational period is given by  $\tau = v^{-1}$  [s].

The energy of the vibrational ground state,  $E_0$ , is called the "zero-point energy" (ZPE). The lowest excited vibrational level,  $E_1$ , is called the "fundamental level", and the following levels,  $E_2$ ,  $E_3$ , *etc.*, are called "overtone levels". In the harmonic approximation, the energy difference  $\Delta E = E_{v+1} - E_v$  between two neigbouring levels is constant, corresponding to the vibrational energy quantum  $\Delta E = \hbar \omega$ .

a) What is the zero-point energy  $E_0$  and the vibrational energy quantum  $\hbar\omega$  for hydrogen iodide (<sup>1</sup>H<sup>127</sup>I), when the force constant *k* is equal to 314 N m<sup>-1</sup>? Give the results in J, eV, and cm<sup>-1</sup>. In which spectral region does transition from the zero-point level to the fundamental level occur? What is the classical vibrational period?

# ANSWER:

Hydrogen iodide, <sup>1</sup>H<sup>127</sup>I:

$$\mu = \frac{m_{\rm H}m_{\rm I}}{m_{\rm H} + m_{\rm I}} = \frac{1.0078 \cdot 126.9045}{1.0078 + 126.9045} = 0.99986 \,\,\mathrm{u} = 0.99986 \cdot 1.6606 \cdot 10^{-27} \,\rm{kg} = 1.6604 \cdot 10^{-27} \,\rm{kg}$$

Angular frequency (radians per second):  $\omega = \sqrt{\frac{k}{\mu}} = \sqrt{\frac{314 \text{ Nm}^{-1}}{1.6604 \cdot 10^{-27} \text{ kg}}} = 4.349 \cdot 10^{14} \text{ s}^{-1}$ 

Frequency (periods per second):  $v = \frac{\omega}{2\pi} = 6.922 \cdot 10^{13} \text{ s}^{-1} \text{ [Hz]}$ 

Period:  $\tau = v^{-1} = \underline{1.44 \cdot 10^{-14} \text{ s}}$ 

Vibrational energy quantum:  $\hbar \omega = (1.0546 \cdot 10^{-34} \text{ J s})(4.349 \cdot 10^{14} \text{ s}^{-1}) = 4.586 \cdot 10^{-20} \text{ J}$ 

$$= \frac{4.586 \cdot 10^{-20} \text{ J}}{1.602 \cdot 10^{-19} \text{ C}} = \underbrace{0.29 \text{ eV}}_{=}$$
  
$$= \frac{4.586 \cdot 10^{-20} \text{ J}}{1.986 \cdot 10^{-23} \text{ J cm}} = \underbrace{2309 \text{ cm}^{-1}}_{=} (= 0.29 \text{ eV} \cdot 8065.5 \text{ eV}^{-1} \text{ cm}^{-1}); \qquad \underbrace{\text{Mid - IR region}}_{=}$$

Zero point energy (ZPE) =  $E_0 = \frac{1}{2}\hbar\omega = \frac{2.293 \cdot 10^{-20} \text{ J}}{10^{-20} \text{ J}} = 0.14 \text{ eV} \doteq 1155 \text{ cm}^{-1}$ 

b) Compute the ratio between the vibrational energy quanta for hydrogen iodide  $({}^{1}H^{127}I)$  and deuterium iodide  $({}^{2}H^{127}I)$ , when it is assumed that the force constant is the same in the two molecules.

# ANSWER:

$$\text{Ratio} = \frac{\hbar\omega_{\text{HI}}}{\hbar\omega_{\text{DI}}} = \frac{\hbar\sqrt{k/\mu_{\text{HI}}}}{\hbar\sqrt{k/\mu_{\text{DI}}}} = \sqrt{\frac{\mu_{\text{DI}}}{\mu_{\text{HI}}}} = \sqrt{\frac{m_{\text{D}}m_{\text{I}}}{m_{\text{D}} + m_{\text{I}}}} / \frac{m_{\text{H}}m_{\text{I}}}{m_{\text{H}} + m_{\text{I}}} = \sqrt{\frac{m_{\text{D}}}{m_{\text{H}}} \cdot \frac{m_{\text{H}} + m_{\text{I}}}{m_{\text{D}} + m_{\text{I}}}} \approx \sqrt{\frac{m_{\text{D}}}{m_{\text{H}}}} \approx \sqrt{2} = \underline{1.41} \quad \text{*}$$

Hence, the predicted energy quantum, and thus the corresponding vibrational wavenumber, is reduced to ca.  $100\%/\sqrt{2} \approx 71\%$  as a result of the isotope effect!  $(2309 \rightarrow 1640 \text{ cm}^{-1})$ 

More accurately:  $\sqrt{\frac{m_{\rm D}}{m_{\rm H}} \cdot \frac{m_{\rm H} + m_{\rm I}}{m_{\rm D} + m_{\rm I}}} = \sqrt{\frac{2.0141}{1.0078} \cdot \frac{1.0078 + 126.9045}{2.0141 + 126.9045}} = \sqrt{1.9985 \cdot 0.99221} = \sqrt{1.9829} = 1.4082$ 

c) Compute the relative population  $n_1/n_0$  of the fundamental level of hydrogen iodide at T = 298 K and T = 1000 K. It is assumed that at thermal equilibrium, the population is determined by the Bolzmann distribution:  $n_1/n_0 = \exp[-(E_1 - E_0)/k_BT]$ .

# **ANSWER**:

$$\frac{n_1}{n_0} = \exp\left(-\frac{E_1 - E_0}{k_B T}\right) = \exp\left(-\frac{\hbar\omega}{k_B T}\right) = \exp\left(-\frac{2309 \text{ cm}^{-1}}{\tilde{k}_B T}\right)$$
where  $\tilde{k}_B = \frac{k_B}{hc} = \frac{1.38065 \cdot 10^{-23} \text{ J K}^{-1}}{1.98645 \cdot 10^{-23} \text{ J cm}} = 0.69503 \text{ cm}^{-1} \text{ K}^{-1}$ 
 $T = 298K$ :  $\tilde{k}_B T = 0.6950 \text{ cm}^{-1} \text{ K}^{-1} \cdot 298 \text{ K} = 207 \text{ cm}^{-1}$ 
 $\frac{n_1}{n_0} = \exp\left(-\frac{2309 \text{ cm}^{-1}}{207 \text{ cm}^{-1}}\right) = \exp(-11.15) = \underline{10}^{-5}$ 
 $T = 1000K$ :  $\tilde{k}_B T = 0.6950 \text{ cm}^{-1} \text{ K}^{-1} \cdot 1000 \text{ K} = 695 \text{ cm}^{-1}$ 
 $\frac{n_1}{n_0} = \exp\left(-\frac{2309 \text{ cm}^{-1}}{695 \text{ cm}^{-1}}\right) = \exp(-3.32) = \underline{0.036}$  ( $\approx 4\%$ )

# Problem 7 (with suggested solution)

The vibrational energies for a diatomic molecule in the harmonic approximation are, as mentioned in Problem 6, given by  $E_v = (v + \frac{1}{2})\hbar\omega$ . A more accurate model based on the "Morse potential" where anharmonic effects are taken into account yields the vibrational energies  $E_v = [(v + \frac{1}{2}) - (v + \frac{1}{2})^2 x_e] \hbar\omega$ , or in units of wavenumber [cm<sup>-1</sup>]:

$$\widetilde{G}(v) = [(v + \frac{1}{2}) - (v + \frac{1}{2})^2 x_e]\widetilde{V}_e$$

The quantities  $\tilde{G}(v)$  are known as the "vibrational terms" of the molecule. The parameters  $x_e$  and  $\tilde{V}_e$  are called the "anharmonicity constant" and the "vibrational wavenumber", respectively. The wavenumbers of vibrational transitions are obtained as differences between terms; transitions from the ground state are thus obtained as  $\tilde{G}(v) - \tilde{G}(0)$ . Note that  $\tilde{V}_e$  is merely a *parameter*, it does not correspond to the wavenumber of a vibrational transition! The relation between  $\tilde{V}_e$  and the "force constant" k is given by  $\tilde{V}_e = \omega/2\pi c = (2\pi c)^{-1} (k/\mu)^{1/2}$ , where  $\mu$  is the reduced mass.

a) Show that  $\widetilde{G}(v) - \widetilde{G}(0) = v[1 - (v+1)x_e]\widetilde{V}_e$ .

# ANSWER:

$$\widetilde{G}(\mathbf{v}) - \widetilde{G}(0) = [(\mathbf{v} + \frac{1}{2}) - (\mathbf{v} + \frac{1}{2})^2 x_e] \widetilde{V}_e - [\frac{1}{2} - \frac{1}{2}^2 x_e] \widetilde{V}_e = [\mathbf{v} - (\mathbf{v}^2 + \frac{1}{2}^2 + \mathbf{v}) x_e + \frac{1}{2}^2 x_e] \widetilde{V}_e = \mathbf{v} [1 - (\mathbf{v} + 1) x_e] \widetilde{V}_e$$

b) Show that 
$$x_e = \frac{2-R}{6-2R}$$
, where  $R = \frac{\tilde{G}(2) - \tilde{G}(0)}{\tilde{G}(1) - \tilde{G}(0)}$ .

# ANSWER:

$$R = \frac{\tilde{G}(2) - \tilde{G}(0)}{\tilde{G}(1) - \tilde{G}(0)} = \frac{2[1 - 3x_e]\tilde{V}}{1[1 - 2x_e]\tilde{V}} = \frac{2 - 6x_e}{1 - 2x_e} \implies x_e = \frac{2 - R}{6 - 2R}$$

c) For the molecule <sup>14</sup>N<sup>16</sup>O, the fundamental band is observed at 1876.06 cm<sup>-1</sup> and the first overtone band at 3724.20 cm<sup>-1</sup>. Estimate the vibrational wavenumber  $\tilde{\nu}_e$ , the anharmonicity constant  $x_e$ , and the force constant k for <sup>14</sup>N<sup>16</sup>O.

# ANSWER:

$$R = \frac{\tilde{G}(2) - \tilde{G}(0)}{\tilde{G}(1) - \tilde{G}(0)} = \frac{3724.20 \text{ cm}^{-1}}{1876.06 \text{ cm}^{-1}} = 1.98512 \implies x_e = \frac{2 - R}{6 - 2R} = \underline{0.0073320}$$

$$\tilde{G}(1) - \tilde{G}(0) = (1 - 2x_e)\tilde{v}_e \implies \tilde{v}_e = \frac{\tilde{G}(1) - \tilde{G}(0)}{1 - 2x_e} = \frac{1876.06 \text{ cm}^{-1}}{1 - 2 \cdot 0.007332} = \underline{1903.98 \text{ cm}^{-1}} \quad (x_e \tilde{v}_e = 13.96 \text{ cm}^{-1})$$

$$\mu = \frac{14.0031 \cdot 15.9949}{14.0031 + 15.9949} 1.66054 \cdot 10^{-27} \text{ kg} = 7.4664 \cdot 1.66054 \cdot 10^{-27} \text{ kg} = 1.23983 \cdot 10^{-26} \text{ kg}$$

$$\tilde{v}_e = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \implies k = 4\pi^2 c^2 \mu \tilde{v}_e^2 : \qquad (N \equiv \text{ kg m s}^{-2})$$

$$\underline{k} = 4\pi^2 (2.9979 \cdot 10^{10} \text{ cm s}^{-1})^2 (1.23983 \cdot 10^{-26} \text{ kg})(1903.98 \text{ cm}^{-1})^2 = \underline{1594.7 \text{ kg s}^{-2}} = \underline{1594.7 \text{ kg}}^{-2} = \underline{1594.7 \text{ kg}}^{-2}$$

# Problem 8 (with suggested solution)

For a classical rotating body, the magnitude of the angular momentum is given by  $J = I\omega$ , where *I* is the moment of inertia with respect to the axis of rotation and  $\omega$  is the angular frequency. In the vector representation, the angular momentum is represented by a vector  $\vec{J}$  in the direction of the rotation axis and with length  $|\vec{J}| = J$ . The sign convention for  $\vec{J}$  is given by a right-hand rule. The rotational energy is given by  $E = I\omega^2/2 = J/2I$ .

The quantum mechanical description of a *rigid linear rotor* that may rotate freely in the three dimensions of space leads to quantization of the length J of the angular momentum vector, and of the projection  $J_z$  of the vector on an external axis of reference:

$$J = \sqrt{j(j+1)} \cdot \hbar, \qquad j = 0, 1, 2, 3, \cdots$$
$$J_z = m_j \cdot \hbar, \qquad \qquad m_j = \underbrace{0, \pm 1, \pm 2, \cdots, \pm j}_{2j+1 \text{ possible values}}$$

For a moment vector  $\vec{J}$  corresponding to the quantum number *j* there are 2j + 1 possible projections  $J_z$ , corresponding to the possible  $m_j$  quantum numbers. This amounts to a quantization of space! But in the absence of external fields, the rotation energy is independent of  $m_j$ :

$$E_{j} = \frac{J^{2}}{2I} = j(j+1) \cdot \frac{\hbar^{2}}{2I}$$

The constant quantity  $\hbar^2/2I$  is often expressed in wavenumbers  $[\text{cm}^{-1}]$  and is then called the rotational constant,  $\tilde{B} = (\hbar^2/2I)/hc = \hbar/4\pi cI$ . The multiplicity (degeneracy)  $g_j$  of the *j*'th energy level is the number of rotational states with the same energy  $E_j$ , *i.e.*,  $g_j = 2j + 1$ . At thermal equilibrium, the relative population  $n_j/n_0$  of the *j*'th and the 0'th energy level is determined by the Boltzmann distribution:

$$\frac{n_j}{n_0} = \frac{g_j}{g_0} \exp\left(-\frac{E_j - E_0}{k_B T}\right) = (2j+1) \exp\left(-j(j+1)\frac{hc\widetilde{B}}{k_B T}\right)$$
(1)

where  $k_B$  is the Boltzmann constant [J/K] and T the thermodynamical temperature [K].

- *a*. Compute the five lowest rotational energies  $E_j$  [kJ/mol, cm<sup>-1</sup>] for hydrogen iodide, HI, and the corresponding relative populations  $n_j/n_0$  at 100 K, 298 K, and 1000 K. The molecule is considered as a rigid rotor. The moment of inertia for a rigid diatomic molecule A-B rotating around an axis through its centre of gravity perpendicular to its bond axis is  $I = \mu R^2$ , where  $\mu = m_A m_B/(m_A + m_B)$  and *R* is the bond length (R = 1.6 Å for HI).
- b. Show by differentiation of (1) that the quantum number  $j_{\text{max}}$  corresponding to the most populated level is given by

$$j_{\text{max}} = \sqrt{\frac{k_B T}{2hc\tilde{B}}} - \frac{1}{2} = \sqrt{\frac{\tilde{k}_B T}{2\tilde{B}}} - \frac{1}{2}$$
 (rounded off to nearest integer value),

and determine  $j_{\text{max}}$  for HI at 100 K, 298 K, and 1000 K.

# ANSWERS:

Hydrogen iodide: H—I  $R = 1.6 \text{ Å} = 1.6 \cdot 10^{-10} \text{ m}$   $m_{\text{H}} = 1.0078 \text{ u}$   $m_{\text{I}} = 126.9 \text{ u}$ 1 u = 1.6606 \cdot 10^{-27} kg

а.

$$E_{j} = j(j+1)\frac{\hbar^{2}}{2I}, I = \mu R^{2}$$

$$\mu = \frac{m_{\rm H}m_{\rm I}}{m_{\rm H} + m_{\rm I}} = \frac{1.0078\,\mathrm{u}\cdot126.9\,\mathrm{u}}{1.0078\,\mathrm{u}+126.9\,\mathrm{u}} = 0.99986\,\mathrm{u} = 0.99986\cdot1.6606\cdot10^{-27} = 1.6604\cdot10^{-27}\,\mathrm{kg}$$

$$I = \mu R^2 = (1.6604\cdot10^{-27}\,\mathrm{kg})(1.6\cdot10^{-10}\,\mathrm{m})^2 = 4.2505\cdot10^{-47}\,\mathrm{kg}\,\mathrm{m}^2$$

$$\frac{\hbar^2}{2I} = \frac{(1.0546\cdot10^{-34}\,\mathrm{J}\,\mathrm{s})^2}{2\cdot4.2505\cdot10^{-47}\,\mathrm{kg}\,\mathrm{m}^2} = 1.30826\cdot10^{-22}\,\mathrm{J}$$

$$= (1.30826\cdot10^{-25}\,\mathrm{kJ})\cdot(6.022\cdot10^{23}\,\mathrm{mol}^{-1}) = 0.07878\,\mathrm{kJ}\,\mathrm{mol}^{-1}$$

$$\frac{\hbar^2}{2I} = hc\tilde{B} \implies \tilde{B} = \frac{\hbar^2}{2I}\frac{1}{hc} = \frac{1.30826\cdot10^{-22}\,\mathrm{J}}{1.98645\cdot10^{-23}\,\mathrm{J}\,\mathrm{cm}} = 6.585\,\mathrm{cm}^{-1} \text{ (rotational constant)}$$

$$\frac{j}{[j(j+1)]} = \frac{0}{0} \frac{1}{2.2} \frac{3}{6} \frac{4}{1.2} \frac{20}{0}$$

$$\frac{1}{(3.17)} \frac{2}{39.51} \frac{3}{79.03} \frac{4}{131.71}$$

$$\frac{n_j}{n_0} = (2j+1) \exp\left(-j(j+1)\frac{hc\tilde{B}}{k_BT}\right) = (2j+1) \exp\left(-j(j+1)\frac{\tilde{B}}{\tilde{k}_BT}\right)$$

 $k_B = 1.38066 \cdot 10^{-23} \text{ J K}^{-1}; \ \tilde{k}_B = k_B/hc = 0.69503 \text{ cm}^{-1} \text{ K}^{-1}$ 

$$T = 100 \text{K}: \quad \tilde{k}_B T = (0.6950 \text{ cm}^{-1} \text{ K}^{-1})(100 \text{ K}) = 69.50 \text{ cm}^{-1}; \quad \tilde{B} / \tilde{k}_B T = 0.0947$$
$$T = 298 \text{K}: \quad \tilde{k}_B T = (0.6950 \text{ cm}^{-1} \text{ K}^{-1})(298 \text{ K}) = 207.3 \text{ cm}^{-1}; \quad \tilde{B} / \tilde{k}_B T = 0.0318$$
$$T = 1000 \text{K}: \quad \tilde{k}_B T = (0.6950 \text{ cm}^{-1} \text{ K}^{-1})(1000 \text{ K}) = 695.0 \text{ cm}^{-1}; \quad \tilde{B} / \tilde{k}_B T = 9.47 \cdot 10^{-3}$$

j	0	1	2	3	4
2j + 1	1	3	5	7	9
j(j + 1)	0	2	6	12	20
<mark>n<sub>j</sub>/n<sub>0</sub> Т = 100 К</mark>	(1)	<mark>2.48</mark>	<mark>2.83</mark>	<mark>2.25</mark>	<mark>1.35</mark>
T = 298  K	(1)	<mark>2.83</mark>	<mark>4.13</mark>	<mark>4.78</mark>	<mark>4.77</mark>
T = 1000 K	(1)	<mark>2.94</mark>	<mark>4.72</mark>	<mark>6.25</mark>	<mark>7.45</mark>



$$\frac{n_j}{n_0} = (2j+1) \exp\left(-j(j+1)\frac{\tilde{B}}{\tilde{k}_B T}\right):$$

$$\frac{d}{dj}\left(\frac{n_j}{n_0}\right) = 2 \cdot \exp\left(-j(j+1)\frac{\tilde{B}}{\tilde{k}_B T}\right) - (2j+1)^2 \frac{\tilde{B}}{\tilde{k}_B T} \exp\left(-j(j+1)\frac{\tilde{B}}{\tilde{k}_B T}\right) = 0$$

$$\Rightarrow 2 - (2j+1)^2 \frac{\tilde{B}}{\tilde{k}_B T} = 0$$

$$\Rightarrow j^2 + j + \left(\frac{1}{4} - \frac{\tilde{k}_B T}{2\tilde{B}}\right) = 0$$

$$\Rightarrow j = \frac{1}{2}\left(-1 \pm \sqrt{1 - 1 + \frac{2\tilde{k}_B T}{\tilde{B}}}\right)$$

*j* must be positive, select plus-sign:

$$\underline{j_{\max}} = \frac{1}{2} \left( -1 + \sqrt{\frac{2\tilde{k}_B T}{\tilde{B}}} \right) = \underline{\sqrt{\frac{\tilde{k}_B T}{2\tilde{B}}}} - \frac{1}{2} \quad q.e.d.$$

$$T = 100 \text{ K:} \quad j_{\text{max}} = 1.80 \rightarrow 2$$
  

$$T = 298 \text{ K:} \quad j_{\text{max}} = 3.47 \rightarrow 3$$
  

$$T = 1000 \text{ K:} \quad j_{\text{max}} = 6.76 \rightarrow 7$$

# Problem 9 (with suggested solution)

For a linear molecule considered as a rigid rotor, the magnitude of the angular momentum is given by  $J = \sqrt{j(j+1)} \cdot \hbar$  and the rotational energy by  $E_j = J^2 / 2I = j(j+1) \cdot \hbar^2 / 2I$ , where *j* is the angular momentum quantum number and *I* is the moment of inertia. If the molecule has a permanent electric dipole moment, transitions between different rotational states can be observed by optical spectroscopy (in the far IR and microwave regions). However, not all rotational transitions are spectroscopically allowed; the selection rule is  $\Delta j = 1$ . Hence, absorption of electromagnetic radiation can occur only for transitions corresponding to  $j \rightarrow j + 1$ .

a. Show that the wavenumber  $\tilde{v}$  for an allowed rotational transition  $j \rightarrow j + 1$  is given by  $\tilde{v} = 2\tilde{B}(j+1)$ , where  $\tilde{B}$  is the rotational constant ( $\tilde{B} = \hbar^2 / 2Ihc = \hbar / 4\pi cI$ ). The interval  $\Delta \tilde{v}$  between two neighbouring lines in the rotational spectrum is thus constant,  $\Delta \tilde{v} = 2\tilde{B}$ .

# ANSWER:

$$\Delta E = E_{j+1} - E_j = \left[ (j+1)(j+2) - j(j+1) \right] \frac{\hbar^2}{2I} = 2(j+1)\frac{\hbar^2}{2I}$$
$$\underbrace{\widetilde{V}}_{II} = \frac{\Delta E}{hc} = 2(j+1)\frac{\hbar^2}{2Ihc} = 2(j+1)\widetilde{B} = \underbrace{2\widetilde{B}(j+1)}_{III}; \quad \Delta \widetilde{V} = 2\widetilde{B}$$

b. For hydrogen chloride <sup>1</sup>H<sup>35</sup>Cl in the gas phase the following absorption lines have been measured: 83.32, 104.13, 124.73, 145.37, 165.89, 186.23, 206.60 and 226.86 cm<sup>-1</sup> (R. L. Hausler & R. A. Oetjen: *J. Chem. Phys.* 21, 1340 (1953)). Compute the bond length *R* for hydrogen chloride.

# ANSWER:

The 7 intervals between the 8 wavenumbers are approximately equal:

$$\begin{split} \Delta \widetilde{v} &= 20.81, 20.60, 20.64, 20.52, 20.34, 20.37, 20.26 \text{ cm}^{-1} \\ \text{Average:} \quad \Delta \widetilde{v} &= (226.86 - 83.32) / 7 = 20.51 \text{ cm}^{-1} = 2\widetilde{B} \\ \Rightarrow \quad \widetilde{B} &= 20.51 / 2 = 10.26 \text{ cm}^{-1} \\ \widetilde{B} &= \frac{\hbar}{4\pi cI} \Rightarrow I = \frac{\hbar}{4\pi c\widetilde{B}} = \frac{1.05457 \cdot 10^{-34} \text{ J s}}{4\pi \cdot 2.998 \cdot 10^{10} \text{ cm s}^{-1} \cdot 10.26 \text{ cm}^{-1}} = 2.728 \cdot 10^{-47} \text{ kg m}^2 \\ I &= \mu R^2 \Rightarrow R = \sqrt{\frac{I}{\mu}} \\ \mu &= \frac{m_{\text{H}} m_{\text{Cl}}}{m_{\text{H}} + m_{\text{Cl}}} = \frac{1.0078 \cdot 34.9688}{1.0078 + 34.9688} = 0.97957 \text{ u} = 0.97957 \cdot 1.66054 \cdot 10^{-27} = 1.6266 \cdot 10^{-27} \text{ kg} \\ \widetilde{R} &= \sqrt{\frac{I}{\mu}} = \sqrt{\frac{2.728 \cdot 10^{-47} \text{ kg m}^2}{1.6226 \cdot 10^{-27} \text{ kg}}} = \frac{1.295 \cdot 10^{-10} \text{ m}}{1.295 \cdot 10^{-10} \text{ m}} = \frac{129.5 \text{ pm}}{1.295 \text{ km}} = \frac{1.295 \text{ km}}{1.295 \text{ km}} \end{split}$$

<u>Additional question</u>: What are the *j*-values for the transition with  $\tilde{v} = 83.32 \text{ cm}^{-1}$ ?  $\tilde{v}_{(j \to j+1)} = 2\tilde{B}(j+1) \Rightarrow j = \frac{\tilde{v}}{2\tilde{B}} - 1 = \frac{83.32}{20.51} - 1 = 3.06 \cong 3$ ; the transition is  $3 \to 4$ . *c*. Predict the wavenumbers for the corresponding lines in the spectrum of deuterium chloride  ${}^{2}\text{H}^{35}\text{Cl}$ , when it is assumed that deuterium chloride has the same bond length *R* as hydrogen chloride.

# ANSWER:

$$\mu_{\rm HCl} = 1.6266 \cdot 10^{-27} \,\text{kg}$$

$$\mu_{\rm DCl} = \frac{m_{\rm D} m_{\rm Cl}}{m_{\rm D} + m_{\rm Cl}} = \frac{2.0141 \cdot 34.9688}{2.0141 + 34.9688} = 1.90441 \,\text{u} = 1.90441 \cdot 1.66054 \cdot 10^{-27} = 3.1624 \cdot 10^{-27} \,\text{kg}$$

$$\frac{\tilde{v}_{\rm DCl}}{\tilde{v}_{\rm HCl}} = \frac{2\tilde{B}_{\rm DCl}(j+1)}{2\tilde{B}_{\rm HCl}(j+1)} = \frac{\tilde{B}_{\rm DCl}}{\tilde{B}_{\rm HCl}} = \frac{I_{\rm HCl}}{I_{\rm DCl}} = \frac{\mu_{\rm HCl}}{\mu_{\rm DCl}} = \frac{1.6266}{3.1624} = 0.5144$$

$$\Rightarrow \quad \tilde{v}_{\rm DCl} = 0.5144 \, \tilde{v}_{\rm HCl}$$

$$\tilde{v}_{\rm HCl} = 83.32 \, \text{cm}^{-1}, 104.13 \, \text{cm}^{-1}, \dots$$

$$\tilde{v}_{\rm DCl} = 42.86 \, \text{cm}^{-1}, 53.56 \, \text{cm}^{-1}, \dots$$

Problem 11 (with suggested solution)



The hydrocarbon methylenecyclopropene (C<sub>4</sub>H<sub>4</sub>) is a very reactive species, but in 1984 Staley and Norden (*J. Am. Chem. Soc.* **106**, 3699 (1984)) succeeded in isolation of the compound by trapping it in a cryogenic matrix. In this problem we perform a population analysis of the  $\pi$ -electron system of methylenecyclopropene within the Hückel model. The computed molecular orbitals (MOs)  $\psi_i = \sum_i c_{ui} p_u$  and their energies  $\varepsilon_i$  are given below:

$$\begin{split} \varepsilon_{2} &= \alpha - 1.48\beta, & \psi_{2} &= 0.30 \ p_{1} + 0.30 \ p_{2} - 0.75 \ p_{3} + 0.51 \ p_{4} \\ \varepsilon_{1} &= \alpha - 1.00\beta, & \psi_{1} &= 0.71 \ p_{1} - 0.71 \ p_{2} \\ \varepsilon_{1} &= \alpha + 0.31\beta, & \psi_{1} &= 0.37 \ p_{1} + 0.37 \ p_{2} - 0.25 \ p_{3} - 0.82 \ p_{4} \\ \varepsilon_{2} &= \alpha + 2.17\beta, & \psi_{2} &= 0.52 \ p_{1} + 0.52 \ p_{2} + 0.61 \ p_{3} + 0.28 \ p_{4} \end{split}$$

a) The  $\pi$ -electron population  $P_{\mu} = \sum_{i} n_i c_{\mu i}^2$  is a measure of the  $\pi$ -electron density on the atomic centre  $\mu$ . The summation is over all MOs *i*, and  $n_i$  is the occupation number of the *i*'th MO (we have  $\sum_{\mu} P_{\mu} = \sum_{i} n_i = N$ , where *N* is the total number of electrons in the  $\pi$ -system). Compute the four  $\pi$ -electron populations  $P_{\mu}$  for the ground configuration of methylene-cyclobutene, and for the lowest excited configuration  $|1 \rightarrow -1\rangle$ .

# ANSWER:

# **Ground configuration**

For the ground configuration,  $n_2 = n_1 = 2$ ,  $n_{-1} = n_{-2} = 0$ . Hence, we have for position 1:  $P_1 = \sum_i n_i c_{1,i}^2 = 2 \cdot c_{1,2}^2 + 2 \cdot c_{1,1}^2 + 0 \cdot c_{1,-1}^2 + 0 \cdot c_{1,-2}^2$ , and so forth!  $\Rightarrow$ 

 $P_1 = 2 \cdot 0.52^2 + 2 \cdot 0.37^2 = 0.82 \qquad P_2 = 2 \cdot 0.52^2 + 2 \cdot 0.37^2 = 0.82$  $P_3 = 2 \cdot 0.61^2 + 2 \cdot (-0.25)^2 = 0.88 \qquad P_4 = 2 \cdot 0.28^2 + 2 \cdot (-0.82)^2 = 1.49$ 



Dipole:  $+ \rightarrow -$ 

# **Excited configuration**

For the excited configuration,  $n_2 = 2$ ,  $n_1 = 1$ ,  $n_{-1} = 1$ ,  $n_{-2} = 0$ .  $\Rightarrow$   $P_1^* = 2 \cdot 0.52^2 + 1 \cdot 0.37^2 + 1 \cdot 0.71^2 = 1.18$   $P_2^* = 2 \cdot 0.52^2 + 1 \cdot 0.37^2 + 1 \cdot (-0.71)^2 = 1.18$  $P_3^* = 2 \cdot 0.61^2 + 1 \cdot (-0.25)^2 = 0.81$   $P_4^* = 2 \cdot 0.28^2 + 1 \cdot (-0.82)^2 = 0.82$ 



Discuss in qualitative terms how the transition energy is expected to be influenced by a shift from non-polar to polar solvent. Experimentally, an extremely large solvent effect is observed:  $\lambda_{max} = 309$  nm in *n*-pentane and  $\lambda_{max} = 210$  nm in methanol.

# ANSWER:

The computed charge distributions indicate reversal of the molecular dipole moment on excitation. Relative to the situation in a non-polar solvent, the ground state will be stabilized and the (vertically) excited state destabilized in a polar solvent, leading to the prediction of a shift towards higher transition energy = lower wavelength ("blue shift") in polar solvents.

b) The  $\pi$ -electron bond order  $P_{\mu\nu} = \sum_i n_i c_{\mu i} c_{\nu i}$  is a measure of the  $\pi$ -electron density in the bond between the centres  $\mu$  and  $\nu$ . There is an approximate, empirical correlation between experimentally determined bond lengths  $R_{\mu\nu}(\text{\AA})$  and Hückel bond orders  $P_{\mu\nu}$  for conjugated hydrocarbons:

$$R_{\mu\nu}(\text{Å}) \cong 1.52 - 0.18 P_{\mu\nu}$$

Compute the bond orders  $P_{\mu\nu}$  for the ground configuration and for the lowest excited configuration of methylenecyclopropene. Is the usual constitutional formula for the compound consistent with the computed bond orders? What change in bond lengths is predicted by excitation from the ground configuration to the excited configuration?

ANSWER:

# **Ground configuration**

$$P_{12} = 2 \cdot 0.52 \cdot 0.52 + 2 \cdot 0.37 \cdot 0.37 = 0.82$$
  

$$P_{13} = 2 \cdot 0.52 \cdot 0.61 + 2 \cdot 0.37 \cdot (-0.25) = 0.45$$
  

$$P_{23} = 2 \cdot 0.52 \cdot 0.61 + 2 \cdot 0.37 \cdot (-0.25) = 0.45$$
  

$$P_{34} = 2 \cdot 0.61 \cdot 0.28 + 2 \cdot (-0.25) \cdot (-0.82) = 0.76$$



The computed bond orders indicate high double bond character in the 1-2 and 3-4 positions, consistent with the usual constitutional formula.

# **Excited configuration**

$$P_{12}^{*} = 2 \cdot 0.52 \cdot 0.52 + 1 \cdot 0.37 \cdot 0.37 + 1 \cdot 0.71 \cdot (-0.71) = 0.18$$

$$P_{13}^{*} = 2 \cdot 0.52 \cdot 0.61 + 1 \cdot 0.37 \cdot (-0.25) = 0.55$$

$$P_{23}^{*} = 2 \cdot 0.52 \cdot 0.61 + 1 \cdot 0.37 \cdot (-0.25) = 0.55$$

$$P_{34}^{*} = 2 \cdot 0.61 \cdot 0.28 + 1 \cdot (-0.25) \cdot (-0.82) = 0.55$$



Predicted bond lengths



The bond orders indicate a significant weakening of the 1-2 bond in the excited configuration, corresponding to lengthening in the order of one tenth of an Å.

Problem 12 (with suggested solution)



In this problem we perform population analyses of the  $\pi$ -electron systems in *1,3-butadiene* and *acroleïn* within the Hückel model.

a) Write the secular equations and the secular determinant for the  $\pi$ -electron system of butadiene (the equations must not be solved).

ANSWER:

$$\begin{pmatrix} \alpha - \varepsilon & \beta & 0 & 0 \\ \beta & \alpha - \varepsilon & \beta & 0 \\ 0 & \beta & \alpha - \varepsilon & \beta \\ 0 & 0 & \beta & \alpha - \varepsilon \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \end{pmatrix}$$

Or, with  $\chi = \frac{\alpha - \varepsilon}{\beta}$ :

(X	1	0	0)	$\left(c_{1}\right)$		(0)	
1	χ	1	0	$c_2$		0	
0	1	χ	1	<i>c</i> <sub>3</sub>	=	0	
(0	0	1	χ)	$\left(c_{4}\right)$		(0)	

Secular determinant:

$\alpha - \varepsilon$	$\beta$	0	0		χ	1	0	0
β	$\alpha - \varepsilon$	$\beta$	0	or	1	χ	1	0
0	β	$\alpha - \varepsilon$	β	01	0	1	χ	1
0	0	$\beta$	$\alpha - \varepsilon$		0	0	1	χ

b) Below are given the molecular orbitals (MOs)  $\psi_i = \sum_i c_{\mu i} p_{\mu}$  and their energies  $\varepsilon_i$  determined by solution of the secular problem defined in question a).

$\varepsilon_{-2} = \alpha - 1.618\beta,$	$\psi_{2} = 0.372 \ p_1 - 0.602 \ p_2 + 0.602 \ p_3 - 0.372 \ p_4$
$\varepsilon_{-1} = \alpha - 0.618\beta,$	$\psi_{-1} = 0.602 \ p_1 - 0.372 \ p_2 - 0.372 \ p_3 + 0.602 \ p_3$
$\varepsilon_1 = \alpha + 0.618\beta,$	$\psi_1 = 0.602 \ p_1 + 0.372 \ p_2 - 0.372 \ p_3 - 0.602 \ p_4$
$\varepsilon_2 = \alpha + 1.618\beta,$	$\psi_2 = 0.372 \ p_1 + 0.602 \ p_2 + 0.602 \ p_3 + 0.372 \ p_4$

Show that the  $\pi$ -electron populations  $P_{\mu} = \sum_{i} n_i c_{\mu i}^2$  for the ground electronic configuration of butadiene all are equal to unity,  $P_1 = P_2 = P_3 = P_4 = 1$ . This is a general result for neutral alternant hydrocarbons, *i.e.*, conjugated hydrocarbons with no odd-membered rings. The Hückel model thus predicts that these compounds are distinctly "non-polar" (in contrast, *e.g.*, to the results for methylenecyclopropene, se Problem 11). Is this prediction in agreement with experimental evidence?

# ANSWER:

$$P_1 = 2 \cdot 0.372^2 + 2 \cdot 0.602^2 = 1.00 \qquad P_2 = 2 \cdot 0.602^2 + 2 \cdot 0.372^2 = 1.00$$
$$P_3 = 2 \cdot 0.602^2 + 2 \cdot (-0.372)^2 = 1.00 \qquad P_4 = 2 \cdot 0.372^2 + 2 \cdot (-0.602)^2 = 1.00$$

c) Determine the  $\pi$ -bond orders  $P_{\mu\nu} = \sum_i n_i c_{\mu i} c_{\nu i}$  for butadiene, and compare them with the experimentally determined bond lengths  $R_{12} = R_{34} = 1.34$  Å and  $R_{23} = 1.48$ .

# ANSWER:

- $P_{12} = 2 \cdot 0.372 \cdot 0.602 + 2 \cdot 0.602 \cdot 0.372 = 0.89$ high double bond character  $P_{23} = 2 \cdot 0.602 \cdot 0.602 + 2 \cdot 0.372 \cdot (-0.372) = 0.45$ low double bond character  $P_{34} = 2 \cdot 0.602 \cdot 0.372 + 2 \cdot (-0.372) \cdot (-0.602) = 0.89$ high double bond character
- d) The  $\pi$ -system of acrolein is isoelectronic with that of butadiene, but deviates by containing a heteroatom, namely the oxygen atom in the carbonyl group. It is well known that oxygen has a much larger electronegativity than carbon. Within the Hückel model, differences in electronegativity may be taken into account by adjustment of the parameters involving the hetero centre: The Coulomb integral for the O-atom is taken as  $\alpha_0 = \alpha_C + h_0 \beta_{CC}$  and the resonance integral for the C-O bond is taken as  $\beta_{CO} = k_{CO}\beta_{CC}$ . Here  $\alpha_{C}$  and  $\beta_{CC}$  are the standard parameters ( $\alpha$  and  $\beta$ ) used for hydrocarbons. In the literature, several suggestions of adequate numerical values of  $h_0$  and  $k_{CO}$  may be found (as well as corresponding values  $h_X$  and  $k_{CX}$  for other heteroatoms X). The most frequently applied values for carbonyl type oxygen are  $h_0 = 2$ and  $k_{\rm CO} = \sqrt{2}$ . Write the secular equations and the secular determinant for acrolein with these values for  $h_0$  and  $k_{CO}$ .

()

$$\begin{pmatrix} \alpha - \varepsilon & \beta & 0 & 0 \\ \beta & \alpha - \varepsilon & \beta & 0 \\ 0 & \beta & \alpha - \varepsilon & \sqrt{2}\beta \\ 0 & 0 & \sqrt{2}\beta & \alpha + 2\beta - \varepsilon \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix}$$
  
Or, with  $\chi = (\alpha - \varepsilon)/\beta$ :  
$$\begin{pmatrix} \chi & 1 & 0 & 0 \\ 1 & \chi & 1 & 0 \\ 0 & 1 & \chi & \sqrt{2} \\ 0 & 0 & \sqrt{2} & \chi + 2 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix}$$
  
Secular determinant:

1

$$\begin{vmatrix} \alpha - \varepsilon & \beta & 0 & 0 \\ \beta & \alpha - \varepsilon & \beta & 0 \\ 0 & \beta & \alpha - \varepsilon & \sqrt{2}\beta \\ 0 & 0 & \sqrt{2}\beta & \alpha + 2\beta - \varepsilon \end{vmatrix}$$
 or 
$$\begin{vmatrix} \chi & 1 & 0 & 0 \\ 1 & \chi & 1 & 0 \\ 0 & 1 & \chi & \sqrt{2} \\ 0 & 0 & \sqrt{2} & \chi + 2 \end{vmatrix}$$

e) Below are given the molecular orbitals (MOs)  $\psi_i = \sum_i c_{\mu i} p_{\mu}$  and their energies  $\varepsilon_i$  determined by solution of the secular problem defined in question d).

$\varepsilon_{-2} = \alpha - 1.593\beta,$	$\psi_{-2} = 0.400 \ p_1 - 0.636 \ p_2 + 0.614 \ p_3 - 0.242 \ p_4$
$\varepsilon_{-1} = \alpha - 0.386\beta,$	$\psi_{-1} = 0.686 \ p_1 - 0.264 \ p_2 - 0.584 \ p_3 + 0.346 \ p_3$
$\varepsilon_1 = \alpha + 1.152\beta,$	$\psi_1 = 0.605 \ p_1 + 0.696 \ p_2 + 0.198 \ p_3 - 0.331 \ p_4$
$\varepsilon_2 = \alpha + 2.826\beta,$	$\psi_2 = 0.071 \ p_1 + 0.199 \ p_2 + 0.493 \ p_3 + 0.844 \ p_4$

Compute the  $\pi$ -electron populations for acrolein in the ground configuration, and compare with the corresponding results for butadiene. How is acrolein polarized, compared with butadiene? Are the predictions in agreement with chemical intuition?

# ANSWER:

$$P_1 = 2 \cdot 0.071^2 + 2 \cdot 0.605^2 = 0.74 \qquad P_2 = 2 \cdot 0.199^2 + 2 \cdot 0.696^2 = 1.05$$
  

$$P_3 = 2 \cdot 0.493^2 + 2 \cdot 0.198^2 = 0.56 \qquad P_4 = 2 \cdot 0.844^2 + 2 \cdot (-0.331)^2 = 1.64$$



The results predict the expected polarization with increased electron density on the electronegative oxygen center. Notice also the prediction of a positive charge on the  $\beta$ -carbon center (position 1 in the molecular graph), which is in agreement with "chemical intuition". Compare with the prediction based on simple organic chemical resonance theory:



f) In general, an *electrophilic* reagent has a deficit of electrons, and a *nucleophilic* reagent has a surplus of electrons. On the basis of the predicted electronic distribution, how would you expect acroleïn to react with an electrophilic and a nucleophilic reagent? Compare with characteristic chemical reactions for  $\alpha$ , $\beta$ -unsaturated carbonyl compounds.

# ANSWER:

*Electrophilic attack* preferably on the negatively charged oxygen position, f.inst. protonation. *Nucleophilic attack* preferably on the positively charged carbons in positions 1 and 3. There are numerous examples of nucleophilic attack on a carbonyl carbon position (here position 3): Formation of hydrates, acetals, imines, etc. An example of attack on position 1 would be the addition of a carbonion in the  $\beta$ -position (here position 1) of an  $\alpha$ , $\beta$ -unsaturated carbonyl compound ("Michael addition").

# 1,3-Butadiene:



Hückel secular equations for the  $\pi$ -electron system:

$$\begin{pmatrix} \alpha - \varepsilon & \beta & 0 & 0 \\ \beta & \alpha - \varepsilon & \beta & 0 \\ 0 & \beta & \alpha - \varepsilon & \beta \\ 0 & 0 & \beta & \alpha - \varepsilon \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix}$$
Or with  $\chi = \frac{\alpha - \varepsilon}{\beta}$ :  
$$\begin{pmatrix} \chi & 1 & 0 & 0 \\ 1 & \chi & 1 & 0 \\ 0 & 1 & \chi & 1 \\ 0 & 0 & 1 & \chi \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix}$$

Molecular orbitals (MOs)  $\psi_i = \sum_i c_{i\mu} p_{\mu}$  and energies  $\varepsilon_i$ :

# Heteroatoms in the Hückel MO model (HMO):

In the standard version for planar, conjugated hydrocarbons, a common "coulomb" parameter  $\alpha$  is adopted for all carbon centers and a common "resonance" parameter  $\beta$  for all linkages in the  $\pi$  system. This leads to the classical Hückel secular equations

$$(\alpha - \varepsilon)c_{\mu} + \sum_{\nu \to \mu} \beta c_{\nu} = 0$$
  
With  $\varepsilon = \alpha - \chi \beta \iff \chi = \frac{\alpha - \varepsilon}{\beta}$ :  $\chi c_{\mu} + \sum_{\nu \to \mu} c_{\nu} = 0$ 

In systems where one or more carbon atoms are replaced by "heteroatoms" X (e.g., X = O or N), the Hückel parameters for these centers may be modified to reflect the difference in electronegativity of the heterocenter relative to that of carbon. In general, the parameters  $\alpha_X$  and  $\beta_{CX}$  for the centers affected by the hetero-substitution may be written:

$$\alpha_{\rm X} = \alpha + h_{\rm X}\beta$$
$$\beta_{\rm CX} = k_{\rm CX}\beta$$

Here  $\alpha$  and  $\beta$  are the standard parameters for hydrocarbons, and  $h_X$  and  $k_{CX}$  are empirical parameters adjusted to reflect the nature of the heteroatom X (several parameter suggestions can be found in the literature). This leads to the secular equations and HMO matrix:

$$(\alpha + h_{\mu}\beta - \varepsilon)c_{\mu} + \sum_{\nu \to \mu} k_{\mu\nu}\beta c_{\nu} = 0, \qquad \begin{pmatrix} \alpha + h_{1}\beta - \varepsilon & k_{12}\beta & k_{13}\beta & \cdots \\ k_{21}\beta & \alpha + h_{2}\beta - \varepsilon & k_{23}\beta & \cdots \\ k_{31}\beta & k_{32}\beta & \alpha + h_{3}\beta - \varepsilon & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}$$

Or with  $\frac{\alpha + h_{\mu}\beta - \varepsilon}{\beta} = \frac{\alpha - \varepsilon}{\beta} + h_{\mu} = \chi + h_{\mu}$ :

$$(\chi + h_{\mu})c_{\mu} + \sum_{\nu \to \mu} k_{\mu\nu}c_{\nu} = 0, \qquad \begin{pmatrix} \chi + h_{1} & k_{12} & k_{13} & \cdots \\ k_{21} & \chi + h_{2} & k_{23} & \cdots \\ k_{31} & k_{32} & \chi + h_{3} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}$$

The parameters  $h_{\mu}$  are taken as  $h_{\mu} = 0$  for carbon and  $h_{\mu} = h_X$  for hetero-centers X, and for the parameters  $k_{\mu\nu}$  we have  $k_{\mu\nu} = 1$  for bonds between carbon centers and  $k_{\mu\nu} = k_{CX}$  for bonds between carbon and X (parameters may of course also be defined for bonds between two hetero-centers, if necessary).

# Formaldehyde

Let us consider a simple example, the  $\pi$  system of formaldehyde, H<sub>2</sub>C=O. The  $\pi$  system comprises just the two centers of the carbonyl group. For carbonyl-type oxygen, the parameters  $h_0 = 2$  and  $k_{CO} = \sqrt{2}$  have been suggested:

$$\alpha_{\rm o} = \alpha + h_{\rm o}\beta = \alpha + 2\beta$$
$$\beta_{\rm co} = k_{\rm co}\beta = \sqrt{2}\beta$$

The HMO equations are

$$\begin{pmatrix} \chi & \sqrt{2} \\ \sqrt{2} & \chi + 2 \end{pmatrix} \begin{pmatrix} c_{\rm C} \\ c_{\rm O} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

Expansion of the secular determinant yields

$$\begin{vmatrix} \chi & \sqrt{2} \\ \sqrt{2} & \chi + 2 \end{vmatrix} = \chi(\chi + 2) - \sqrt{2}\sqrt{2} = \chi^2 + 2\chi - 2 = 0 \implies \chi = -1 \pm \frac{\sqrt{12}}{2} = \begin{cases} +0.732 \\ -2.732 \end{cases}$$

and we obtain the MO energies and wavefunctions:

$$\pi^*: \qquad \varepsilon_{-1} = \alpha - 0.732\beta, \qquad \psi_{-1} = 0.888 \ p_{\rm C} - 0.460 \ p_{\rm O} \\ \pi: \qquad \varepsilon_1 = \alpha + 2.732\beta, \qquad \psi_1 = 0.460 \ p_{\rm C} + 0.888 \ p_{\rm O}$$

We see that the bonding  $\pi$  MO of the carbonyl group is strongly polarized, with high amplitude on the oxygen center. This is a result of increasing the effective electronegativity of oxygen relative to carbon in our model. On the other hand, the antibonding  $\pi^*$  MO has large amplitude on carbon. These results lead to the predictions that electrophilic reagents will attack the carbonyl oxygen, and nucleophilic reagents will attack the carbonyl carbon. This is of course consistent with common chemical experience. – We can also see that transfer of an electron from the  $\pi$  to the  $\pi^*$  MO, resulting in an excited electronic configuration, is predicted to lead to a transfer of electron density from the oxygen to the carbon atom, and this will affect the reactivity pattern.

For comparison, illustration of the results of a more sophisticated MO procedure; the MO contour diagrams are viewed in a plane containing the C=O bond axis, perpendicular to the molecular plane:



# Problem 13 (with suggested solution)

Determine the symmetry operations of the following molecules. What are their symmetry point groups? Which compounds may have a permanent dipole moment? Which compounds are chiral?

- a) Formaldehyde, CH<sub>2</sub>O  $\rightarrow \hat{E}, \hat{C}_2, \hat{\sigma}_{\nu}, \hat{\sigma}'_{\nu} \Rightarrow C_{2\nu}$
- b) Ammonia, NH<sub>3</sub>  $\rightarrow \hat{E}, 2\hat{C}_3, 3\hat{\sigma}_{\nu} \Rightarrow C_{3\nu}$
- c) Ethylene, H<sub>2</sub>C=CH<sub>2</sub>  $\rightarrow \hat{E}, \hat{C}_2(z), \hat{C}_2(y), \hat{C}_2(x), \hat{i}, \hat{\sigma}(xy), \hat{\sigma}(xz), \hat{\sigma}(yz) \Rightarrow D_{2h}$
- d) Hydrogen peroxide, HO–OH  $\rightarrow \hat{E}, \hat{C}_2 \Rightarrow C_2$
- e) Bromobenzene, C<sub>6</sub>H<sub>5</sub>Br  $\rightarrow \hat{E}, \hat{C}_2, \hat{\sigma}_{\nu}, \hat{\sigma}'_{\nu} \Rightarrow C_{2\nu}$
- f) 1,4-Dibromobenzene,  $C_6H_4Br_2 \rightarrow \hat{E}, \hat{C}_2(z), \hat{C}_2(y), \hat{C}_2(x), \hat{i}, \hat{\sigma}(xy), \hat{\sigma}(xz), \hat{\sigma}(yz) \Rightarrow D_{2h}$
- g) 1,4-Dibromo-2,5-dichlorobenzene,  $C_6H_2Br_2Cl_2 \rightarrow \hat{E}, \hat{C}_2, \hat{i}, \hat{\sigma}_h \Rightarrow C_{2h}$

Only molecules with  $C_n$ ,  $C_{nv}$ , or  $C_s$  symmetry may have a permanent dipole moment, *i.e.*, a), b), d), and e). – A molecule may be chiral if it neither has a centre of inversion nor a mirror plane. Here, d) is the only chiral molecule (see *Atkins*', 11.3).



Problem 14 (with suggested solution)

In its electronic groundstate, formaldehyde (H<sub>2</sub>CO) is a planar molecule with C<sub>2v</sub> symmetry:



a) What are the symmetries (irreducible representations) of the 10 molecular orbitals (MOs) that can be constructed on the basis of the 10 valence atomic orbitals H(1s), H'(1s), C(2s,  $2p_x$ ,  $2p_y$ ,  $2p_z$ ) and O(2s,  $2p_x$ ,  $2p_y$ ,  $2p_z$ )? Hint: Determine the characters of the reducible representation  $\Gamma$ based on the 10 atomic orbitals, and decompose  $\Gamma$  to irreducible representations.

$C_{2v}$	Ê	$\hat{C}_2$	$\hat{\sigma}_v(xz)$	$\hat{\sigma}'_{v}(yz)$	<i>h</i> = 4
$A_1$	1	1	1	1	Z.
$A_2$	1	1	-1	-1	$R_z$
$B_1$	1	-1	1	-1	$x, R_y$
$B_2$	1	-1	-1	1	$y, R_x$
Γ	10	0	4	6	$n_i$ :
$\Gamma \times A_1$	10	0	4	6	20/4 = 5
$\Gamma  imes A_2$	10	0	-4	-6	0
$\Gamma \times B_1$	10	0	4	-6	8/4 = 2
$\Gamma \times B_2$	10	0	_4	6	12/4 = 3

Check: 
$$\sum_{i} n_i = 5 + 0 + 2 + 3 =$$

$$\Rightarrow \Gamma = 5A_1 + 2B_1 + 3B_2$$

b) The highest occupied MO in the groundstate (HOMO) can be characterized as a "lone pair" orbital, largely localized in the  $2p_y$  orbital of the oxygen atom. This MO contributes very little to the chemical bonding in the molecule; such an orbital is often called an *n* orbital ("*n*" for "non-bonding"). What is the symmetry  $\Gamma_n$  of formaldehydes *n* orbital?

ANSWER:



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c) The second highest MO (SHOMO) and the lowest unoccupied MO (LUMO) are the  $\pi$  and  $\pi$ \* MOs, respectively, of the C=O double bond. Indicate the shape of these orbitals (you may compute them with the Hückel model, see Problem 12). What are their symmetries?

ANSWER:



d) The lowest electronic transition of formaldehyde corresponds to the HOMO  $\rightarrow$  LUMO transition,  $n \rightarrow \pi^*$ . What is the symmetry of the excited state?

ANSWER:



The symmetry of the *n*- $\pi^*$  excited configuration is  $B_2 \times B_1 = A_2$ 

e) This transition is observed as an extremely weak absorption band near 30000 cm<sup>-1</sup>. Why is the transition so weak?

ANSWER: Transition from the ground state,  $A_1 \rightarrow A_2$ , is forbidden by symmetry!

Supplementary material is given below!

Symmetrie: C<sub>2V</sub>



Drawings of some of the MOs of formaldehyde computed with ab initio Hartree-Fock theory (W.L. Jorgensen & L. Salem: "The Organic Chemist's Book of Orbitals"). - Note that relative to the usage in Problem 14, the symmetry labels  $B_1$  and  $B_2$  are reversed. This is because the authors have reversed the labeling of the coordinate axes x and y. It is important that the definition of the coordinate system is given; otherwise the designation of symmetry labels may become ambiguous. - The numbers in front of the symmetry labels indicate the energy ordering of MOs with the same symmetry:  $1A_1$ ,  $2A_1$ ,  $3A_1$ , etc. The numbering starts with the inner orbitals, *i.e.*, the MOs based on C(1s) and O(1s), which are not considered in Problem 14.



Fig. 10.21. Localized MO's and electronic transitions for the carbonyl group. The symmetry species on the far right apply to the formaldehyde molecule.

Qualitative representation of some of the MOs of formaldehyde (G. W. King: "Spectroscopy and Molecular Structure"). AO basis orbitals are indicated to the left, and the resulting MOs are given to the right. – Note that "small letters" are used in the MO symmetry labels, like  $a_1$ ,  $b_1$ , etc. It is common practice in the spectroscopic literature to use "small letters" in the symmetry designation of one-electron functions like MOs, while capital letters ( $A_1$ ,  $B_1$ , etc.) are used for the wavefunctions of many-electronic states.

Problem 15 (with suggested solution)



a) How many normal vibrations has the formaldehyde molecule?

ANSWER: Formaldehyde is a non-linear molecule, *i.e.*,  $N_{\text{VIB}} = 3N_{\text{ATOMS}} - 6 = 3 \cdot 4 - 6 = 6$ 

- b) What is the symmetry point group of the molecule? ANSWER:  $C_{2v}$
- c) Define a set of  $3N_{\text{ATOMS}} = 12$  cartesian displacement coordinates for the four nuclei and determine the characters for the reducible representation  $\Gamma_{3N}$  based on these coordinates.  $\rightarrow \rightarrow$
- d) Decompose  $\Gamma_{3N}$  to irreducible representations ("symmetry species") and determine which of those that correspond to the normal vibrations of the molecule, i.e., determine  $\Gamma_{VIB} = \Gamma_{3N} \Gamma_{ROT} \Gamma_{TRANS}$ .

ANSWER:

$C_{2v}$	$\hat{E}$	$\hat{C}_2$	$\hat{\sigma}_v(xz)$	$\hat{\sigma}'_{v}(yz)$	<i>h</i> = 4
$A_1$	1	1	1	1	Z.
$A_2$	1	1	-1	-1	$R_z$
$B_1$	1	-1	1	-1	$x, R_y$
$B_2$	1	-1	-1	1	$y, R_x$
$\Gamma_{3N}$	12	-2	2	4	$n_i$ :
$\Gamma_{3N} \times A_1$	12	-2	2	4	16/4 = 4
$\Gamma_{3N} \times A_2$	12	-2	-2	-4	4/4 = 1
$\Gamma_{3N} \times B_1$	12	2	2	-4	12/4 = 3
$\Gamma_{3N} \times B_2$	12	2	-2	4	16/4 = 4

Check:  $\Sigma n_i = 4 + 1 + 3 + 4 = 12$  ③

$\Gamma_{3N}$	=	$4 A_1$	+	$1 A_2$	+	$3 B_1$	+	$4 B_2$
$\Gamma_{\rm ROT}$	=			$1 A_2$	+	$1 B_1$	+	$1 B_2$
$\Gamma_{\text{TRANS}}$	=	$1 A_1$			+	$1 B_1$	+	$1 B_2$
$\Gamma_{\rm VIB} = \Gamma_{3N} - \Gamma_{\rm ROT} - \Gamma_{\rm TRANS}$	=	$3A_1$			+	$B_1$	+	$2 B_2$

e) How many of the normal vibrations are IR active? What are the polarization directions of the corresponding fundamental transitions?

ANSWER: All 6 are IR active. Fundamental transitions to levels of  $A_1$ ,  $B_1$ , and  $B_2$  symmetry are z, x, and y polarized, respectively.

f) The IR spectrum of formaldehyde shows peaks at 1164, 1247, 1500, 1746, 2766, and 2843 cm<sup>-1</sup>. Try to assign these transitions with the help of tables of group frequencies.

ANSWER:



Fig. 10.22. The six normal vibrations of planar formaldehyde [ground state wave numbers (cm<sup>-1</sup>) from H. H. Blau Jr. and H. H. Nielsen, J. Mol. Spectroscopy, 1, 124 (1957)] and the  $-CH_2$  wagging vibration  $\nu'_4$  in the pyramidal excited state.

Picture from G. W. King: "Spectroscopy and Molecular Structure". Note that "small letters" are used in the symmetry labels, like  $a_1$ ,  $b_1$ , etc. It is common practice in the spectroscopic literature to use "small letters" in the symmetry designation of vibrational modes, while capital letters ( $A_1$ ,  $B_1$ , etc.) are used for many-electronic states.

# Problem 17 (with suggested solution)

Below is shown the IR absorption spectrum of gaseous sulphur dioxide, SO<sub>2</sub>. The observed transitions are listed in the ensuing table [R.D. Shelton, A.H. Nielsen, W.H. Fletcher, *J. Chem. Phys.* **21**, 2178 (1953)]:



\*) Temperature dependent.

a) The intense transitions at 518, 1151, and 1362 cm<sup>-1</sup> can be assigned to three IR active fundamental levels ( $v_{1-3}$ ). Decide on the basis of symmetry arguments whether the molecule is linear ( $D_{\infty h}$ ) or angular ( $C_{2v}$ ):



# ANSWER:

*Linear equilibrium geometry*: This situation would correspond to that previously described for the linear molecule carbon dioxide, CO<sub>2</sub>. We would have 4 normal modes of vibration: One symmetric stretching vibration, one anti-symmetric stretching vibration, and two degenerate bending vibrations. However, only the anti-symmetric stretching and the bending vibrations would be IR active, and because of the degeneracy, the two bending vibrations would give rise to only one band in the IR spectrum. We should thus observe only two IR active fundamental levels (as in the case of CO<sub>2</sub>), but three are observed for SO<sub>2</sub>. We thus conclude that the observed IR spectrum is not consistent with the assumption of a linear geometry of the SO<sub>2</sub> molecule.

Angular equilibrium geometry: For  $C_{2v}$  symmetrical SO<sub>2</sub>, three IR active modes are expected: One symmetric stretching vibration, one anti-symmetric stretching vibration, and one bending vibration. This is consistent with the observed IR data. We conclude that the SO<sub>2</sub> molecule has an angular geometry with  $C_{2v}$  symmetry.

b) Suggest an assignment of the three fundamental transitions to stretching and bending vibrations (the stretching frequency of a bond is generally about twice as large as the corresponding bending frequency). What are the symmetries (irreducible representations) of the three vibrations?

# ANSWER:

- v<sub>3</sub>: 1316 cm<sup>-1</sup>, y polarized  $\rightarrow B_2$ , anti-symmetric stretching v<sub>1</sub>: 1151 cm<sup>-1</sup>, z polarized  $\rightarrow A_1$ , symmetric stretching v<sub>2</sub>: 518 cm<sup>-1</sup>, z polarized  $\rightarrow A_1$ , bending
- c) Try to assign the remaining (weak) peaks in the spectrum to *hot*, *overtone*, or *combination* bands, with indication of symmetries and polarization directions.

# ANSWER:

The literature assignment is indicated below.

Table 9.3—Infrared bands and assignments for sulfur dioxide in the gas phase (after R. D. Shelton, A. H. Nielsen, and W. H. Fletcher, J. Chem. Phys., 21, 2178 (1953), who used absorption paths of up to 20 m-atm)

$\sigma_0,  \mathrm{cm}^{-1}$	Absorption Path, m-atm	Relative Intensity	Assignment
517.69	0.0052	455	ν2
844.9 <b>3</b>	20.0	0.55	$\nu_3 - \nu_2$
1151.38	0.012	565	ν <sub>1</sub>
1361.76	0.0008	1000	ν <sub>s</sub>
1535.06	20.0	0.1	322
1665.07	20.0	0.1	$\nu_1 + \nu_2$
1875.55	1.6	6.0	$\nu_2 + \nu_3$
2295.88	2.0	5.5	$2\nu_1$
2499.55	4.8	20.0	$\nu_1 + \nu_3$
2715.46	4.8	0.2	2v3
2808.32	20.0	0.8	$2\nu_1 + \nu_2$
3011.25	20.0	0.02	$\nu_1 + \nu_2 + \nu_3$
3431.19	20.0	0.01	3v1
3629.61	20.0	0.8	$2\nu_1 + \nu_3$
4054.26	6.0	0.03	$3\nu_3$
4751.23	20.0	0.006	$3\nu_1 + \nu_3$
5165.64	20.0	0.020	$\nu_1 + 3\nu_3$

 $v_1$ ,  $v_2$ , and  $v_3$  indicate the three **fundamental** transitions of SO<sub>2</sub>, as discussed above.

 $2v_3$ ,  $3v_3$ ,  $4v_3$ , *etc.*, indicate the first, second, and third **overtone** level of the  $v_3$  mode, and so forth. Their wavenumbers are given approximately by the corresponding multiples of the fundamental wavenumber, *i.e.*,  $2v_3 = 2 \times 1362 = 2724$  cm<sup>-1</sup>,  $3v_3 = 3 \times 1362 = 4086$  cm<sup>-1</sup>, *etc.* The weak transitions observed at 2715 and 4054 cm<sup>-1</sup> are assigned to these levels (because of anharmonic effects, overtone wavenumbers predicted by simple multiples of the fundamental wavenumber are usually slightly overestimated). The symmetries of the overtone vibrations are given by the corresponding multiples of the symmetry of the fundamental:  $\Gamma(v_3) = B_2$ ;  $\Gamma(2v_3) = \Gamma(v_3) \times \Gamma(v_3) = B_2 \times B_2 = A_1$ ;  $\Gamma(3v_3) = \Gamma(v_3) \times \Gamma(v_3) = B_2 \times B_2 = B_2$ , *etc.* 

 $v_1 + v_2$  and  $v_2 + v_3$  are examples of **combination** levels. The notation  $v_1 + v_2$  indicates that one quantum of the mode  $v_1$  and one quantum of the mode  $v_2$  are excited simultaneously. Hence,  $v_1 + v_2 + v_3$  indicates a molecular vibration where one quantum of each of the three normal modes of SO<sub>2</sub> are excited simultaneously.  $2v_1 + v_3$  indicates a vibration where the first overtone of the  $v_1$  mode is excited simultaneously with the  $v_3$  fundamental. Their wavenumbers are given approximately by the corresponding sums of fundamental wavenumbers, and their symmetries are given by the pertinent multiples of the symmetries of the involved modes, just as in the case of the overtones (see above). For example:  $\Gamma(2v_1 + v_3) = \Gamma(v_1) \times \Gamma(v_1) \times \Gamma(v_3) = A_1 \times A_1 \times B_2 = B_2$ . – Overtone and combination bands are referred to as **summation** bands. These bands are forbidden within the harmonic approximation, but because of anharmonic effects, they are frequently observed in the experimental spectra, generally as weak transitions.

Finally, the notation  $v_3 - v_2$  indicates a **hot band**. The transition is from a thermally excited fundamental level of the  $v_2$  mode to a higher energy level, namely the fundamental level of the  $v_3$  mode. The wavenumber of the transition thus corresponds to the difference  $v_3 - v_2$ . The intensity of the transition is proportional to the number of molecules in the thermally excited state, and thus depends on the temperature (according to the Boltzmann distribution).