

17 Spectroscopy 2: electronic transitions

Solutions to exercises

Discussion questions

E17.1(b) The Franck–Condon principle states that because electrons are so much lighter than nuclei an electronic transition occurs so rapidly compared to vibrational motions that the internuclear distance is relatively unchanged as a result of the transition. This implies that the most probable transitions $\nu_f \leftarrow \nu_i$ are vertical. This vertical line will, however, intersect any number of vibrational levels ν_f in the upper electronic state. Hence transitions to many vibrational states of the excited state will occur with transition probabilities proportional to the Frank–Condon factors which are in turn proportional to the overlap integral of the wavefunctions of the initial and final vibrational states. A vibrational progression is observed, the shape of which is determined by the relative horizontal positions of the two electronic potential energy curves. The most probable transitions are those to excited vibrational states with wavefunctions having a large amplitude at the internuclear position R_e .

Question. You might check the validity of the assumption that electronic transitions are so much faster than vibrational transitions by calculating the time scale of the two kinds of transitions. How much faster is the electronic transition, and is the assumption behind the Franck–Condon principle justified?

E17.2(b) Color can arise by emission, absorption, or scattering of electromagnetic radiation by an object. Many molecules have electronic transitions that have wavelengths in the visible portion of the electromagnetic spectrum. When a substance emits radiation the perceived color of the object will be that of the emitted radiation and it may be an additive color resulting from the emission of more than one wavelength of radiation. When a substance absorbs radiation its color is determined by the subtraction of those wavelengths from white light. For example, absorption of red light results in the object being perceived as green. Color may also be formed by scattering, including the diffraction that occurs when light falls on a material with a grid of variation in texture of refractive index having dimensions comparable to the wavelength of light, for example, a bird's plumage.

E17.3(b) The characteristics of fluorescence which are consistent with the accepted mechanism are: (1) it ceases as soon as the source of illumination is removed; (2) the time scale of fluorescence, $\approx 10^{-9}$ s, is typical of a process in which the rate determining step is a spontaneous radiative transition between states of the same multiplicity; slower than a stimulated transition, but faster than phosphorescence; (3) it occurs at longer wavelength (higher frequency) than the inducing radiation; (4) its vibrational structure is characteristic of that of a transition from the ground vibrational level of the excited electronic state to the vibrational levels of the ground electronic state; and (5), the observed shifting and in some instances quenching of the fluorescence spectrum by interactions with the solvent.

E17.4(b) See Table 17.4 for a summary of the characteristics of laser radiation that result in its many advantages for chemical and biochemical investigations. Two important applications of lasers in chemistry have been to Raman spectroscopy and to the development of time resolved spectroscopy. Prior to the invention of lasers the source of intense monochromatic radiation required for Raman spectroscopy was a large spiral discharge tube with liquid mercury electrodes. The intense heat generated by the large current required to produce the radiation had to be dissipated by clumsy water cooled jackets and exposures of several weeks were sometimes necessary to observe the weaker Raman lines. These problems have been eliminated with the introduction of lasers as the source of the required monochromatic radiation. As a consequence, Raman spectroscopy has been revitalized and is now almost as routine as infrared spectroscopy. See Section 17.7(b). Time resolved laser spectroscopy can

be used to study the dynamics of chemical reactions. Laser pulses are used to obtain the absorption, emission, and Raman spectrum of reactants, intermediates, products, and even transition states of reactions. When we want to study the rates at which energy is transferred from one mode to another in a molecule, we need femtosecond and picosecond pulses. These time scales are available from mode-locked lasers and their development has opened up the possibility of examining the details of chemical reactions at a level which would have been unimaginable before.

Numerical exercises

E17.5(b) To obtain the parities of Fig. 14.38 of the text we recognize that what is shown in the figure are the signs (light = positive, dark = negative) of the upper (positive z -direction) lobe of the p_z orbitals. The lower lobes (not shown) have opposite signs. Inversion through the centre changes + to - for the p_z lobes of a_2 and e_2 , but the e_1 and b_2 lobes do not change sign. Therefore a_2 and e_2 are u, e_1 and b_2 are g.

E17.6(b) According to Hund's rule, we expect one $1\pi_u$ electron and one $2\pi_g$ electron to be unpaired. Hence $S = 1$ and the multiplicity of the spectroscopic term is $\boxed{3}$. The overall parity is $u \times g = \boxed{u}$ since (apart from the complete core), one electron occupies a u orbital another occupies a g orbital.

E17.7(b) Use the Beer-Lambert law

$$\begin{aligned}\log \frac{I}{I_0} &= -\varepsilon[J]l = (-327 \text{ L mol}^{-1} \text{ cm}^{-1}) \times (2.22 \times 10^{-3} \text{ mol L}^{-1}) \times (0.15 \text{ cm}) \\ &= -0.10889\end{aligned}$$

$$\frac{I}{I_0} = 10^{-0.10889} = 0.778$$

The reduction in intensity is $\boxed{22.2 \text{ per cent}}$

E17.8(b)

$$\begin{aligned}\varepsilon &= -\frac{1}{[J]l} \log \frac{I}{I_0} [16.9, 16.10] \\ &= \frac{-1}{(6.67 \times 10^{-4} \text{ mol L}^{-1}) \times (0.35 \text{ cm})} \log 0.655 = 787 \text{ L mol}^{-1} \text{ cm}^{-1} \\ &= 787 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1} = 787 \times 10^3 \text{ cm}^3 \text{ mol}^{-1} \text{ cm}^{-1} \quad [1 \text{ dm} = 10 \text{ cm}] \\ &= \boxed{7.9 \times 10^5 \text{ cm}^2 \text{ mol}^{-1}}\end{aligned}$$

E17.9(b) The Beer-Lambert law is

$$\log \frac{I}{I_0} = -\varepsilon[J]l \quad \text{so} \quad [J] = \frac{-1}{\varepsilon l} \log \frac{I}{I_0}$$

$$[J] = \frac{-1}{(323 \text{ L mol}^{-1} \text{ cm}^{-1}) \times (0.750 \text{ cm})} \log(1 - 0.523) = \boxed{1.33 \times 10^{-3} \text{ mol L}^{-1}}$$

E17.10(b) Note. A parabolic lineshape is symmetrical, extending an equal distance on either side of its peak. The given data are not consistent with a parabolic lineshape when plotted as a function of either wavelength or wavenumber, for the peak does not fall at the centre of either the wavelength or the wavenumber range. The exercise will be solved with the given data assuming a triangular lineshape as a function of wavenumber.

The integrated absorption coefficient is the area under an absorption peak

$$A = \int \varepsilon d\tilde{\nu}$$

If the peak is triangular, this area is

$$\begin{aligned} A &= \frac{1}{2}(\text{base}) \times (\text{height}) \\ &= \frac{1}{2}[(199 \times 10^{-9} \text{ m})^{-1} - (275 \times 10^{-9} \text{ m})^{-1}] \times (2.25 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}) \\ &= 1.5\bar{6} \times 10^{10} \text{ L m}^{-1} \text{ mol}^{-1} \text{ cm}^{-1} = \frac{(1.5\bar{6} \times 10^9 \text{ L m}^{-1} \text{ mol}^{-1} \text{ cm}^{-1}) \times (100 \text{ cm m}^{-1})}{10^3 \text{ L m}^{-3}} \\ &= 1.5\bar{6} \times 10^9 \text{ m mol}^{-1} = \boxed{1.5\bar{6} \times 10^8 \text{ L mol}^{-1} \text{ cm}^{-2}} \end{aligned}$$

E17.11(b) Modelling the π electrons of 1,3,5-hexatriene as free electrons in a linear box yields non-degenerate energy levels of

$$E_n = \frac{n^2 h^2}{8m_e L^2}$$

The molecule has six π electrons, so the lowest-energy transition is from $n = 3$ to $n = 4$. The length of the box is 5 times the C—C bond distance R . So

$$\Delta E_{\text{linear}} = \frac{(4^2 - 3^2)h^2}{8m_e(5R)^2}$$

Modelling the π electrons of benzene as free electrons on a ring of radius R yields energy levels of

$$E_{m_l} = \frac{m_l^2 \hbar^2}{2I}$$

where I is the moment of inertia: $I = m_e R^2$. These energy levels are doubly degenerate, except for the non-degenerate $m_l = 0$. The six π electrons fill the $m_l = 0$ and 1 levels, so the lowest-energy transition is from $m_l = 1$ to $m_l = 2$

$$\Delta E_{\text{ring}} = \frac{(2^2 - 1^2)\hbar^2}{2m_e R^2} = \frac{(2^2 - 1^2)h^2}{8\pi^2 m_e R^2}$$

Comparing the two shows

$$\Delta E_{\text{linear}} = \frac{7}{25} \left(\frac{h^2}{8m_e R^2} \right) < \Delta E_{\text{ring}} = \frac{3}{\pi^2} \left(\frac{h^2}{8m_e R^2} \right)$$

Therefore, the lowest-energy absorption will rise in energy.

E17.12(b) The Beer–Lambert law is

$$\log \frac{I}{I_0} = -\varepsilon[J]l = \log T$$

so a plot (Fig. 17.1) of $\log T$ versus $[J]$ should give a straight line through the origin with a slope m of $-\varepsilon l$. So $\varepsilon = -m/l$.

The data follow

[dye]/(mol L ⁻¹)	T	$\log T$
0.0010	0.73	-0.1367
0.0050	0.21	-0.6778
0.0100	0.042	-1.3768
0.0500	1.33×10^{-7}	-6.8761

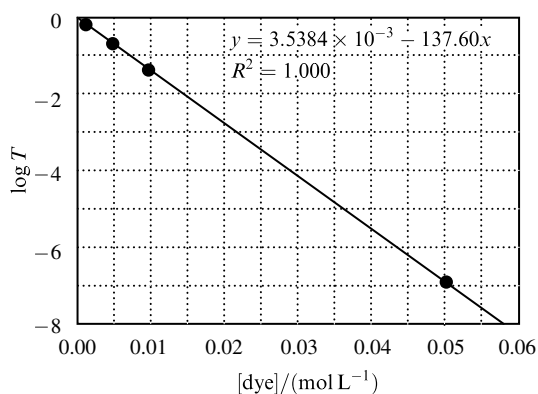


Figure 17.1

The molar absorptivity is

$$\varepsilon = -\frac{-138 \text{ L mol}^{-1}}{0.250 \text{ cm}} = \boxed{552 \text{ L mol}^{-1} \text{ cm}^{-1}}$$

E17.13(b) The Beer-Lambert law is

$$\log T = -\varepsilon[J]l \quad \text{so} \quad \varepsilon = \frac{-1}{[J]l} \log T$$

$$\varepsilon = \frac{-1}{(0.0155 \text{ mol L}^{-1}) \times (0.250 \text{ cm})} \log 0.32 = \boxed{128 \text{ L mol}^{-1} \text{ cm}^{-1}}$$

Now that we have ε , we can compute T of this solution with any size of cell

$$T = 10^{-\varepsilon[J]l} = 10^{-\{(128 \text{ L mol}^{-1} \text{ cm}^{-1}) \times (0.0155 \text{ mol L}^{-1}) \times (0.450 \text{ cm})\}} = \boxed{0.13}$$

E17.14(b) The Beer-Lambert law is

$$\log \frac{I}{I_0} = -\varepsilon[J]l \quad \text{so} \quad l = -\frac{1}{\varepsilon[J]} \log \frac{I}{I_0}$$

$$\text{(a)} \quad l = -\frac{1}{(30 \text{ L mol}^{-1} \text{ cm}^{-1}) \times (1.0 \text{ mol L}^{-1})} \times \log \frac{1}{2} = \boxed{0.020 \text{ cm}}$$

$$\text{(b)} \quad l = -\frac{1}{(30 \text{ L mol}^{-1} \text{ cm}^{-1}) \times (1.0 \text{ mol L}^{-1})} \times \log 0.10 = \boxed{0.033 \text{ cm}}$$

E17.15(b) The integrated absorption coefficient is the area under an absorption peak

$$A = \int \varepsilon \, d\tilde{\nu}$$

We are told that ε is a Gaussian function, i.e. a function of the form

$$\varepsilon = \varepsilon_{\max} \exp\left(\frac{-x^2}{a^2}\right)$$

where $x = \tilde{\nu} - \tilde{\nu}_{\max}$ and a is a parameter related to the width of the peak. The integrated absorption coefficient, then, is

$$A = \int_{-\infty}^{\infty} \varepsilon_{\max} \exp\left(\frac{-x^2}{a^2}\right) dx = \varepsilon_{\max} a \sqrt{\pi}$$

We must relate a to the half-width at half-height, $x_{1/2}$

$$\frac{1}{2}\varepsilon_{\max} = \varepsilon_{\max} \exp\left(\frac{-x_{1/2}^2}{a^2}\right) \quad \text{so} \quad \ln \frac{1}{2} = \frac{-x_{1/2}^2}{a^2} \quad \text{and} \quad a = \frac{x_{1/2}}{\sqrt{\ln 2}}$$

$$\begin{aligned} \text{So } A &= \varepsilon_{\max} x_{1/2} \left(\frac{\pi}{\ln 2}\right)^{1/2} = (1.54 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}) \times (4233 \text{ cm}^{-1}) \times \left(\frac{\pi}{\ln 2}\right)^{1/2} \\ &= \boxed{1.39 \times 10^8 \text{ L mol}^{-1} \text{ cm}^{-2}} \end{aligned}$$

In SI base units

$$\begin{aligned} A &= \frac{(1.39 \times 10^8 \text{ L mol}^{-1} \text{ cm}^{-2}) \times (1000 \text{ cm}^3 \text{ L}^{-1})}{100 \text{ cm m}^{-1}} \\ &= \boxed{1.39 \times 10^9 \text{ m mol}^{-1}} \end{aligned}$$

E17.16(b) F_2^+ is formed when F_2 loses an antibonding electron, so we would expect F_2^+ to have a shorter bond than F_2 . The difference in equilibrium bond length between the ground state (F_2) and excited state ($\text{F}_2^+ + e^-$) of the photoionization experiment leads us to expect some vibrational excitation in the upper state. The vertical transition of the photoionization will leave the molecular ion with a stretched bond relative to its equilibrium bond length. A stretched bond means a vibrationally excited molecular ion, hence a **stronger** transition to a vibrationally excited state than to the vibrational ground state of the cation.

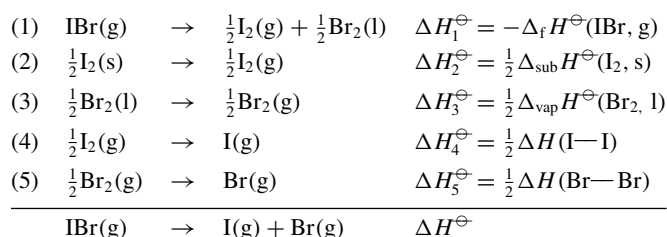
Solutions to problems

Solutions to numerical problems

P17.3 Initially we cannot decide whether the dissociation products are produced in their ground atomic states or excited states. But we note that the two convergence limits are separated by an amount of energy exactly equal to the excitation energy of the bromine atom: $18\,345 \text{ cm}^{-1} - 14\,660 \text{ cm}^{-1} = 3\,685 \text{ cm}^{-1}$. Consequently, dissociation at $14\,660 \text{ cm}^{-1}$ must yield bromine atoms in their ground state. Therefore, the possibilities for the dissociation energy are $14\,660 \text{ cm}^{-1}$ or

$14\,660\text{ cm}^{-1} - 7598\text{ cm}^{-1} = 7062\text{ cm}^{-1}$ depending upon whether the iodine atoms produced are in their ground or excited electronic state.

In order to decide which of these two possibilities is correct we can set up the following Born–Haber cycle



$$\begin{aligned} \Delta H^\ominus &= -\Delta_f H^\ominus(\text{IBr, g}) + \frac{1}{2}\Delta_{\text{sub}} H^\ominus(\text{I}_2, \text{s}) + \frac{1}{2}\Delta_{\text{vap}} H^\ominus(\text{Br}_2, \text{l}) \\ &\quad + \frac{1}{2}\Delta H(\text{I—I}) + \frac{1}{2}\Delta H(\text{Br—Br}) \\ &= \left\{ -40.79 + \frac{1}{2} \times 62.44 + \frac{1}{2} \times 30.907 + \frac{1}{2} \times 151.24 + \frac{1}{2} \times 192.85 \right\} \text{kJ mol}^{-1} \\ &\quad \text{[Table 2.6 and data provided]} \\ &= 177.93 \text{ kJ mol}^{-1} = \boxed{14\,874 \text{ cm}^{-1}} \end{aligned}$$

Comparison to the possibilities $\boxed{14\,660 \text{ cm}^{-1}}$ and 7062 cm^{-1} shows that it is the former that is the correct dissociation energy.

P17.5 We write $\varepsilon = \varepsilon_{\text{max}} e^{-x^2} = \varepsilon_{\text{max}} e^{-\tilde{\nu}^2/2\Gamma}$ the variable being $\tilde{\nu}$ and Γ being a constant. $\tilde{\nu}$ is measured from the band centre, at which $\tilde{\nu} = 0$. $\varepsilon = \frac{1}{2}\varepsilon_{\text{max}}$ when $\tilde{\nu}^2 = 2\Gamma \ln 2$. Therefore, the width at half-height is

$$\Delta\tilde{\nu}_{1/2} = 2 \times (2\Gamma \ln 2)^{1/2}, \quad \text{implying that } \Gamma = \frac{\Delta\tilde{\nu}_{1/2}^2}{8 \ln 2}$$

Now we carry out the integration

$$\begin{aligned} \mathcal{A} &= \int \varepsilon d\tilde{\nu} = \varepsilon_{\text{max}} \int_{-\infty}^{\infty} e^{-\tilde{\nu}^2/2\Gamma} d\tilde{\nu} = \varepsilon_{\text{max}} (2\Gamma\pi)^{1/2} \left[\int_{-\infty}^{\infty} e^{-x^2} dx = \pi^{1/2} \right] \\ &= \varepsilon_{\text{max}} \left(\frac{2\pi \Delta\tilde{\nu}_{1/2}^2}{8 \ln 2} \right)^{1/2} = \left(\frac{\pi}{4 \ln 2} \right)^{1/2} \varepsilon_{\text{max}} \Delta\tilde{\nu}_{1/2} = 1.0645 \varepsilon_{\text{max}} \Delta\tilde{\nu}_{1/2} \end{aligned}$$

$\mathcal{A} = 1.0645 \varepsilon_{\text{max}} \Delta\tilde{\nu}_{1/2}$, with $\tilde{\nu}$ centred on $\tilde{\nu}_0$

Since $\tilde{\nu} = \frac{1}{\lambda}$, $\Delta\tilde{\nu}_{1/2} \approx \frac{\Delta\lambda_{1/2}}{\lambda_0^2}$ [$\lambda \approx \lambda_0$]

$$\mathcal{A} = 1.0645 \varepsilon_{\text{max}} \left(\frac{\Delta\lambda_{1/2}}{\lambda_0^2} \right)$$

From Fig. 17.52 of the text, we find $\Delta\lambda_{1/2} = 38 \text{ nm}$ with $\lambda_0 = 290 \text{ nm}$ and $\varepsilon_{\text{max}} \approx 235 \text{ L mol}^{-1} \text{ cm}^{-1}$; hence

$$A = \frac{1.0645 \times (235 \text{ L mol}^{-1} \text{ cm}^{-1}) \times (38 \times 10^{-7} \text{ cm})}{(290 \times 10^{-7} \text{ cm})^2} = \boxed{1.1 \times 10^6 \text{ L mol}^{-1} \text{ cm}^{-2}}$$

Since the dipole moment components transform as $A_1(z)$, $B_1(x)$, and $B_2(y)$, excitations from A_1 to A_1 , B_1 , and B_2 terms are allowed.

P17.8

Draw up a table like the following:

Hydrocarbon	$h\nu_{\text{max}}/\text{eV}$	$E_{\text{HOMO}}/\text{eV}^*$
Benzene	4.184	-9.7506
Biphenyl	3.654	-8.9169
Naphthalene	3.452	-8.8352
Phenanthrene	3.288	-8.7397
Pyrene	2.989	-8.2489
Anthracene	2.890	-8.2477

*Semi-empirical, PM3 level, PC Spartan Pro™

Figure 17.2 shows a good correlation: $r^2 = 0.972$.

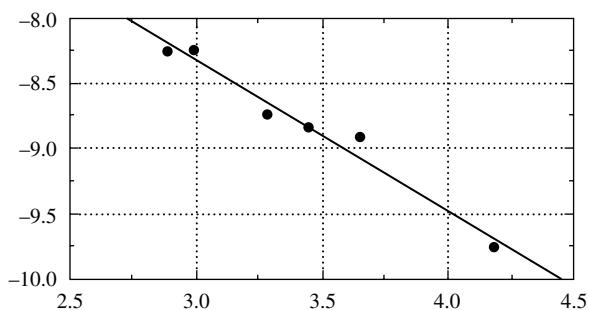


Figure 17.2

P17.11

Refer to Fig. 14.30 of the text. The lowest binding energy corresponds to the highest occupied orbital, the next lowest to next highest orbital, and so on.

We draw up the following table

	Line E_K/eV	Binding energy/eV	Assignment
N_2	5.6	15.6	3σ
	4.5	16.7	1π
CO	2.4	18.8	$2\sigma^*$
	7.2	14.0	3σ
	4.9	16.3	1π
	1.7	19.5	$2\sigma^*$

The spacing of the 4.5 eV lines in N_2 is 0.24 eV, or about 1940 cm^{-1} . The spacing of the 4.9 eV lines in CO is 0.23 eV, or about 1860 cm^{-1} . These are estimates from the illustrations of the separation of the vibrational levels of the N_2^+ and CO^+ ions in their excited states.

P17.13

0.125 eV corresponds to 1010 cm^{-1} , markedly less than the 1596 cm^{-1} of the bending mode. This suggests that the ejected electron tended to bond between the two hydrogens of the water molecule.

Solutions to theoretical problems

P17.14 We need to establish whether the transition dipole moments

$$\mu_{fi} = \int \Psi_f^* \mu \Psi_i d\tau \quad [16.20]$$

connecting the states 1 and 2 and the states 1 and 3 are zero or nonzero. The particle in a box wavefunctions are $\Psi_n = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right)$ [12.8]

$$\text{Thus } \mu_{2,1} \propto \int \sin\left(\frac{2\pi x}{L}\right) x \sin\left(\frac{\pi x}{L}\right) dx \propto \int x \left[\cos\left(\frac{\pi x}{L}\right) - \cos\left(\frac{3\pi x}{L}\right) \right] dx$$

$$\text{and } \mu_{3,1} \propto \int \sin\left(\frac{3\pi x}{L}\right) x \sin\left(\frac{\pi x}{L}\right) dx \propto \int x \left[\cos\left(\frac{2\pi x}{L}\right) - \cos\left(\frac{4\pi x}{L}\right) \right] dx$$

having used $\sin \alpha \sin \beta = \frac{1}{2} \cos(\alpha - \beta) - \frac{1}{2} \cos(\alpha + \beta)$. Both of these integrals can be evaluated using the standard form

$$\int x(\cos ax) dx = \frac{1}{a^2} \cos ax + \frac{x}{a} \sin ax$$

$$\int_0^L x \cos\left(\frac{\pi x}{L}\right) dx = \frac{1}{\left(\frac{\pi}{L}\right)^2} \cos\left(\frac{\pi x}{L}\right) \Big|_0^L + \frac{x}{\left(\frac{\pi}{L}\right)} \sin\left(\frac{\pi x}{L}\right) \Big|_0^L = -2 \left(\frac{L}{\pi}\right)^2 \neq 0$$

$$\int_L^0 x \cos\left(\frac{3\pi x}{L}\right) dx = \frac{1}{\left(\frac{3\pi}{L}\right)^2} \cos\left(\frac{3\pi x}{L}\right) \Big|_0^L + \frac{x}{\left(\frac{3\pi}{L}\right)} \sin\left(\frac{3\pi x}{L}\right) \Big|_0^L = -2 \left(\frac{L}{3\pi}\right)^2 \neq 0$$

Thus $\mu_{2,1} \neq 0$.

In a similar manner $\mu_{3,1} = 0$.

Comment. A general formula for μ_{fi} applicable to all possible particle in a box transitions may be derived. The result is ($n = f, m = i$)

$$\mu_{nm} = -\frac{eL}{\pi^2} \left[\frac{\cos(n-m)\pi - 1}{(n-m)^2} - \frac{\cos(n+m)\pi - 1}{(n+m)^2} \right]$$

For m and n both even or both odd numbers, $\mu_{nm} = 0$; if one is even and the other odd, $\mu_{nm} \neq 0$. See also Problem 17.18.

Question. Can you establish the general relation for μ_{nm} above?

P17.16 We need to determine how the oscillator strength (Problem 17.17) depends on the length of the chain. We assume that wavefunctions of the conjugated electrons in the linear polyene can be approximated by the wavefunctions of a particle in a one-dimensional box. Then

$$f = \frac{8\pi^2 m_e v}{3he^2} |\mu_{fi}^2| \quad [\text{Problem 17.17}]$$

$$\begin{aligned} \mu_x &= -e \int_0^L \Psi_{n'}(x) x \Psi_n(x) dx, \quad \Psi_n = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right) \\ &= -\frac{2e}{L} \int_0^L x \sin\left(\frac{n'\pi x}{L}\right) \sin\left(\frac{n\pi x}{L}\right) dx \end{aligned}$$

$$= \begin{cases} 0 & \text{if } n' = n + 2 \\ + \left(\frac{8eL}{\pi^2} \right) \frac{n(n+1)}{(2n+1)^2} & \text{if } n' = n + 1 \end{cases}$$

The integral is standard, but may also be evaluated using $2 \sin A \sin B = \cos(A - B) - \cos(A + B)$ as in Problem 17.14

$$h\nu = E_{n+1} - E_n = (2n+1) \frac{h^2}{8m_e L^2}$$

Therefore, for the transition $n+1 \leftarrow n$,

$$f = \left(\frac{8\pi^2}{3} \right) \left(\frac{m_e}{h^2} \right) \left(\frac{h}{8m_e L^2} \right) (2n+1) \left(\frac{8eL}{\pi^2} \right)^2 \frac{n^2(n+1)^2}{(2n+1)^4} = \left(\frac{64}{3\pi^2} \right) \left[\frac{n^2(n+1)^2}{(2n+1)^3} \right]$$

Therefore, $f \propto \frac{n^2(n+1)^2}{(2n+1)^3}$

The value of n depends on the number of bonds: each π bond supplies two π electrons and so n increases by 1. For large n ,

$$f \propto \frac{n^4}{8n^3} \rightarrow \frac{n}{8} \quad \text{and} \quad f \propto n$$

Therefore, for the longest wavelength transitions f increases as the chain length is increased. The energy of the transition is proportional to $\frac{(2n+1)}{L^2}$; but as $n \propto L$, this energy is proportional to $\frac{1}{L}$.

Since $E_n = \frac{n^2 h^2}{8m_e L^2}$, $\Delta E = \frac{(2n+1)h^2}{8m_e L^2} [\Delta n = +1]$

but $L = 2nd$ is the length of the chain (Exercise 17.11(a)), with d the carbon-carbon interatomic distance. Hence

$$\Delta E = \frac{\left(\frac{L}{2d} + 1 \right) h^2}{8m_e L^2} \approx \frac{h^2}{16m_e d L} \propto \frac{1}{L}$$

Therefore, the transition moves toward the red as L is increased and the apparent color of the dye shifts towards blue.

P17.17
$$\mu = -e \int \Psi_{v',x} \Psi_v dx$$

From Problem 12.15, $\mu_{10} = -e \int \Psi_{1,x} \Psi_0 dx = -e \left[\frac{\hbar}{2(m_e k)^{1/2}} \right]^{1/2}$

Hence, $f = \frac{8\pi^2 m_e \nu}{3he^2} \times \frac{e^2 \hbar}{2(m_e k)^{1/2}} = \left[\frac{1}{3} \right] \left[2\pi \nu = \left(\frac{k}{m_e} \right)^{1/2} \right]$

- P17.19**
- Vibrational energy spacings of the lower state are determined by the spacing of the peaks of A. From the spectrum, $\tilde{\nu} \approx 1800 \text{ cm}^{-1}$.
 - Nothing can be said about the spacing of the upper state levels (without a detailed analysis of the intensities of the lines). For the second part of the question, we note that after some vibrational

decay the benzophenone (which does absorb near 360 nm) can transfer its energy to naphthalene. The latter then emits the energy radiatively.

P17.21 (a) The Beer–Lambert Law is:

$$A = \log \frac{I_0}{I} = \varepsilon[J]l.$$

The absorbed intensity is:

$$I_{\text{abs}} = I_0 - I \quad \text{so} \quad I = I_0 - I_{\text{abs}}.$$

Substitute this expression into the Beer–Lambert law and solve for I_{abs} :

$$\log \frac{I_0}{I_0 - I_{\text{abs}}} = \varepsilon[J]l \quad \text{so} \quad I_0 - I_{\text{abs}} = I_0 \times 10^{-\varepsilon[J]l},$$

$$\text{and} \quad I_{\text{abs}} = \boxed{I_0 \times (1 - 10^{-\varepsilon[J]l})}.$$

(b) The problem states that $I_f(\tilde{\nu}_f)$ is proportional to ϕ_f and to $I_{\text{abs}}(\tilde{\nu})$, so:

$$I_f(\tilde{\nu}_f) \propto \phi_f I_0(\tilde{\nu}) \times (1 - 10^{\varepsilon[J]l}).$$

If the exponent is small, we can expand $1 - 10^{-\varepsilon[J]l}$ in a power series:

$$10^{-\varepsilon[J]l} = (e^{\ln 10})^{-\varepsilon[J]l} \approx 1 - \varepsilon[J]l \ln 10 + \dots,$$

$$\text{and} \quad I_f(\tilde{\nu}_f) \propto \boxed{\phi_f I_0(\tilde{\nu}) \varepsilon[J]l \ln 10}.$$

P17.22 Use the Clebsch–Gordan series [Chapter 13] to compound the two resultant angular momenta, and impose the conservation of angular momentum on the composite system.

(a) O_2 has $S = 1$ [it is a spin triplet]. The configuration of an O atom is $[\text{He}]2s^2 2p^4$, which is equivalent to a Ne atom with two electron-like “holes”. The atom may therefore exist as a spin singlet or as a spin triplet. Since $S_1 = 1$ and $S_2 = 0$ or $S_1 = 1$ and $S_2 = 1$ may each combine to give a resultant with $S = 1$, both may be the products of the reaction. Hence multiplicities $\boxed{3 + 1}$ and $\boxed{3 + 3}$ may be expected.

(b) N_2 , $S = 0$. The configuration of an N atom is $[\text{He}] 2s^2 2p^3$. The atoms may have $S = \frac{3}{2}$ or $\frac{1}{2}$. Then we note that $S_1 = \frac{3}{2}$ and $S_2 = \frac{3}{2}$ can combine to give $S = 0$; $S_1 = \frac{1}{2}$ and $S_2 = \frac{1}{2}$ can also combine to give $S = 0$ (but $S_1 = \frac{3}{2}$ and $S_2 = \frac{1}{2}$ cannot). Hence, the multiplicities $\boxed{4 + 4}$ and $\boxed{2 + 2}$ may be expected.

Solutions to applications

P17.24 The integrated absorption coefficient is

$$\mathcal{A} = \int \varepsilon(\tilde{\nu}) d\tilde{\nu} \quad [16.12]$$

If we can express ε as an analytical function of $\tilde{\nu}$, we can carry out the integration analytically. Following the hint in the problem, we seek to fit ε to an exponential function, which means that a

plot of $\ln \varepsilon$ versus $\tilde{\nu}$ ought to be a straight line (Fig. 17.3). So if

$$\ln \varepsilon = m\tilde{\nu} + b \quad \text{then} \quad \varepsilon = \exp(m\tilde{\nu}) \exp(b)$$

and $\mathcal{A} = \frac{e^b}{m} \exp(m\tilde{\nu})$ (evaluated at the limits integration). We draw up the following table and find the best-fit line

λ/nm	$\varepsilon/(\text{L mol}^{-1} \text{cm}^{-1})$	$\tilde{\nu}/\text{cm}^{-1}$	$\ln \varepsilon/(\text{L mol}^{-1} \text{cm}^{-1})$
292.0	1512	34248	4.69
296.3	865	33748	4.13
300.8	477	33248	3.54
305.4	257	32748	2.92
310.1	135.9	32248	2.28
315.0	69.5	31746	1.61
320.0	34.5	31250	0.912

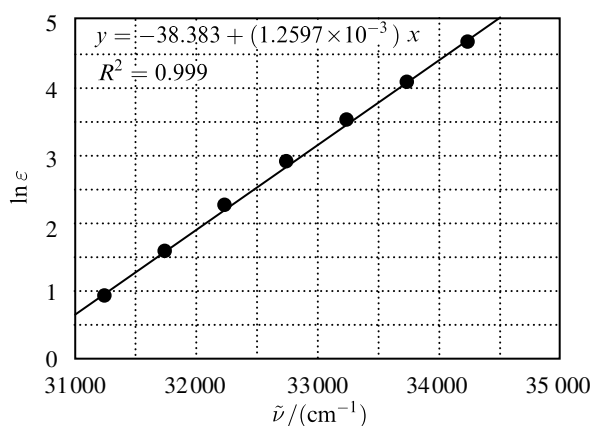


Figure 17.3

$$\begin{aligned} \text{So } \mathcal{A} &= \frac{e^{-38.383}}{1.26 \times 10^{-3} \text{ cm}} \left[\exp\left(\frac{1.26 \times 10^{-3} \text{ cm}}{290 \times 10^{-7} \text{ cm}}\right) - \exp\left(\frac{1.26 \times 10^{-3} \text{ cm}}{320 \times 10^{-7} \text{ cm}}\right) \right] \text{ L mol}^{-1} \text{ cm}^{-1} \\ &= \boxed{1.24 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-2}} \end{aligned}$$

P17.25 The concentration of the hypothetical pure layer is

$$[\text{O}_3] = \frac{n}{V} = \frac{p}{RT} = \frac{1 \text{ atm}}{(0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}) \times (273 \text{ K})} = 4.46 \times 10^{-2} \text{ mol L}^{-1}$$

So for 300 DU

$$A = \varepsilon cl = (476 \text{ L mol}^{-1} \text{ cm}^{-1}) \times (0.300 \text{ cm}) \times (4.46 \times 10^{-2} \text{ mol L}^{-1}) = \boxed{6.37}$$

and for 100 DU

$$A = \varepsilon cl = (476 \text{ L mol}^{-1} \text{ cm}^{-1}) \times (0.100 \text{ cm}) \times (4.46 \times 10^{-2} \text{ mol L}^{-1}) = \boxed{2.12}$$

P17.27 The reaction enthalpy for process (2) is

$$\Delta_r H^\ominus = \Delta_f H^\ominus(\text{Cl}) + \Delta_f H^\ominus(\text{OCIO}^+) + \Delta_f H^\ominus(\text{e}^-) - \Delta_f H^\ominus(\text{Cl}_2\text{O}_2)$$

$$\text{so } \Delta_f H^\ominus(\text{Cl}_2\text{O}_2) = \Delta_f H^\ominus(\text{Cl}) + \Delta_f H^\ominus(\text{OCIO}^+) + \Delta_f H^\ominus(\text{e}^-) - \Delta_r H^\ominus$$

$$\begin{aligned}\Delta_f H^\ominus(\text{Cl}_2\text{O}_2) &= (121.68 + 1096 + 0) \text{ kJ mol}^{-1} - (10.95 \text{ eV}) \times (96.485 \text{ kJ eV}^{-1}) \\ &= 161 \text{ kJ mol}^{-1}\end{aligned}$$

We see that the Cl_2O_2 in process (2) is different from that in process (1), for its heat of formation is $\boxed{28 \text{ kJ mol}^{-1}}$ greater. This is consistent with the computations, which say that ClOOC is likely to be the lowest-energy isomer. Experimentally we see that the Cl_2O_2 of process (2), which is not ClOOC , is not very much greater in energy than the lowest-energy isomer.