# 3. Electronic Spectroscopy of Molecules I - Absorption Spectroscopy

## 3.1. Vibrational coarse structure of electronic spectra.

The Born Oppenheimer Approximation introduced in the last chapter can be extended to include changes in the energy of a molecule caused by changes in the energy levels of the electrons of the molecule:

$$E_{total} = E_{electronic} + E_{vibration} + E_{rotation}$$

In this approximation the electronic, vibrational and rotational energies are considered to be independent of each other, i.e. transitions between the different energy levels can occur independently. A change in the total energy of a molecule could then be written as

$$\Delta E_{total} = \Delta E_{electronic} + \Delta E_{vibration} + \Delta E_{rotation}$$

The approximate orders of magnitude of these changes are:

$$\Delta E_{electronic} \approx 1000 * \Delta E_{vibration} \approx 1\,000\,000 * \Delta E_{rotation}$$

While rotational spectra are observed only on molecules that have a permanent dipole moment and vibrational spectra are only observed when the dipole moment of the molecule changes during the vibration, electronic spectra can be obtained from all molecules, since changes in the electron distribution in a molecule are always causing a change in the dipole moment of the molecule. This means that homonuclear molecules like $H_2$ or $O_2$ that do not show rotation or rotation-vibration spectra, do give an electronic spectrum and show vibrational and rotational in their spectra that can be used to derive rotational constants and bond vibration frequencies. For now, we will not consider the rotational fine structure and restrict spectral transitions to the vibrational coarse structure of the spectrum.

The Born Oppenheimer approximation can thus be simplified to:

$$E_{total} = E_{electronic} + E_{vibration}$$

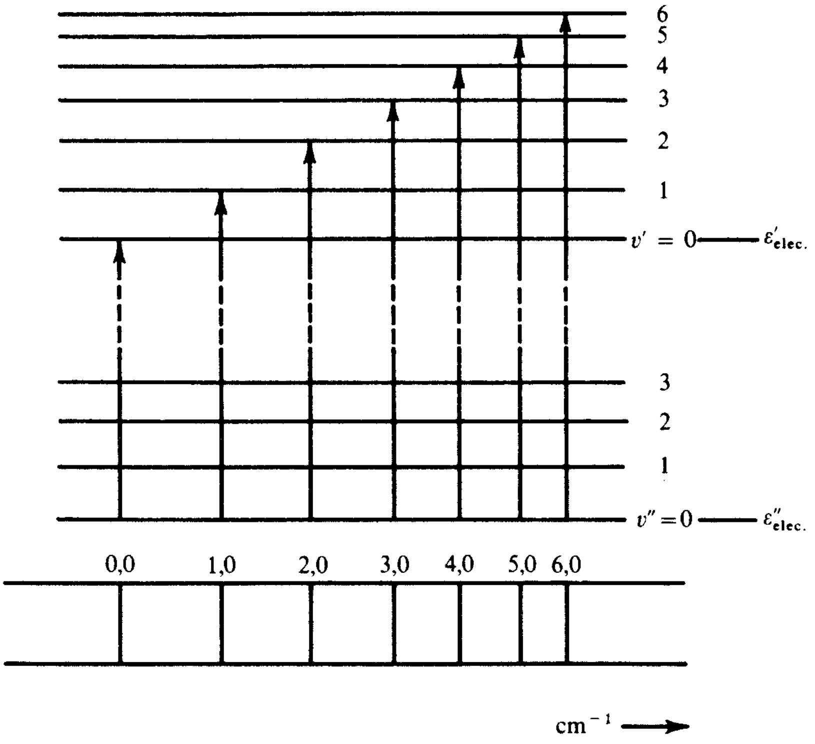
or in terms of wavenumbers:

$$\varepsilon_{total} = \varepsilon_{electronic} + \varepsilon_{vibration}$$

This can be rewritten to

$$\varepsilon_{total} = \varepsilon_{elec.} + \left(v+\frac{1}{2}\right)\tilde{\nu}_e - x_e\left(v+\frac{1}{2}\right)^2\tilde{\nu}_e, \qquad (v = 0,1,2\ldots)$$

The energy levels of this equation are shown in Figure 3.1 below.



**Vibrational 'coarse' structure of the band formed during electronic absorption from the ground ($v''$=0) state to a higher state.**

Figure 3.1 Vibrational coarse structure of electronic absorptions.

Figure 3.1 does not show correctly the relative separations between the different levels of electronic energy ($\varepsilon_{elec}$), on the one hand and those with different ν‘ and ν” on the other. However the spacing between the upper vibrational levels is deliberately shown to be smaller than the spacing between the lower vibrational levels. This is normally true since an excited electronic state usually corresponds to a weaker bond in the molecule and therefore to a smaller vibrational wavenumber $\tilde{\nu}_e$.

There is essentially no selection rule for $v$ when a molecule undergoes an electronic transition., i.e. every transition $v$” to $v$‘ has some probability and a great many spectral lines would be expected. The situation is considerably simplified if the absorption spectrum is considered from the electronic ground state. All molecules shall further exist in the lowest vibrational state ($v$”=0). So all the transitions that may occur are depicted in the Figure above. The transitions are labeled according to their $v$‘ and $v$” numbers (0,0; 0,1; 0,2;...) Such a set of transitions is called a band, since, under low resolution, each line of the set appears somewhat broad and diffuse, and is more particularly called a *‘v‘ -progression*, since the value of $v$‘ increases by unity for each line in the set. The diagram shows that the lines in a band are more closely together at high frequencies, which is a direct consequence of the anharmonicity of the upper state vibration, which causes the excited vibrational levels to converge.

The spectrum can be described by an analytical expression:

$$\Delta\varepsilon_{total} = \Delta\varepsilon_{elec} + \Delta\varepsilon_{vib.}$$

$$\tilde{\nu}_{Spec} = (\varepsilon' - \varepsilon'') + \left\{\left(v' + \frac{1}{2}\right)\tilde{\nu}'_e - x'_e\left(v' + \frac{1}{2}\right)^2 \tilde{\nu}'_e\right\} - \left\{\left(v'' + \frac{1}{2}\right)\tilde{\nu}''_e - x''_e\left(v'' + \frac{1}{2}\right)^2 \tilde{\nu}''_e\right\}$$

Provided that the spectrum can be resolved well and 6 or more lines are observed, the parameters for the energy levels of the vibrational states as well as the separation between the electronic states can be calculated.

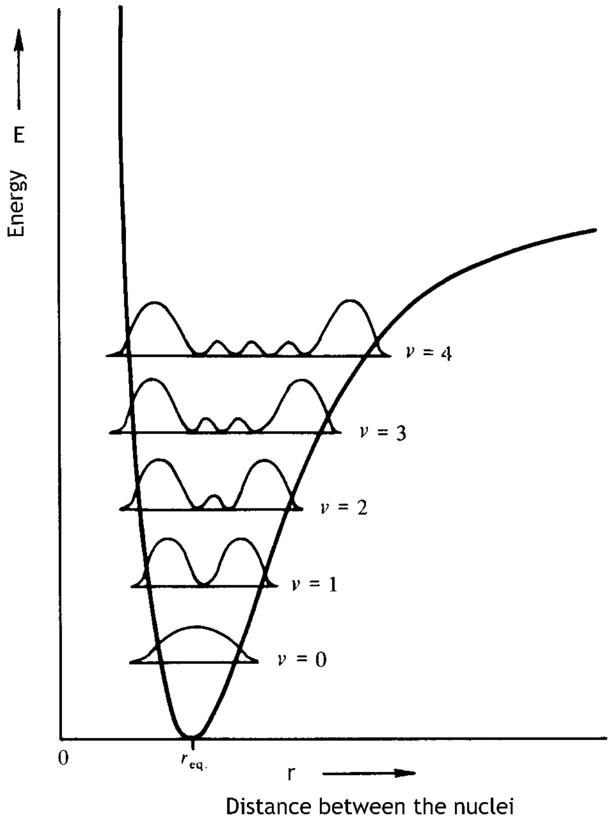
Thus, the observation of a band spectrum not only leads to values of the vibrational frequency and anharmonicity constant in the ground state ($\tilde{\nu}''_e,\ x''_e$), but also to these parameters in the excited electronic state ($\tilde{\nu}'_e,\ x'_e$). This latter information is particularly valuable since such excited states may be extremely unstable and the molecule may exist in them only for very short times. Nonetheless, the band spectrum can tell us a great deal about the bond strength of such species.

Molecules normally have many electronically excited states so that the whole absorption spectrum of a diatomic molecule will be more complicated than depicted in the Figure 1 above. The ground state can usually undergo a transition to several excited states, and each such transition will be accompanied by a band spectrum shown in Figure 1 above.
Further, in emission spectra, the previously excited molecule may be in one of a large number of available $\tilde{\nu}'_e,\ \varepsilon'_e$ states, and has a similar order of magnitude of $\tilde{\nu}''_e,\ \varepsilon''_e$ states to which it may revert. Thus, emission spectra are usually extremely complicated.

## 3.2. Intensity of Vibrational-Electronic Spectra: The Franck-Condon Principle.

Although quantum mechanics imposes no restrictions on the change in the vibrational quantum number during an electronic transition, the vibrational lines in a progression are not observed to be of the same intensity. In some spectra, the (0,0) transition is the strongest, in others, the intensity of the spectrum increases to a maximum at some value of v', while yet in others, only a few vibrational lines with high v' are seen, followed by a continuum. All these types of spectra are readily explainable in terms of the **Franck-Condon principle** which states that **an electronic transition takes place so rapidly that a vibrating molecule does not change its internuclear distance appreciably during the transition**.

We have already learned on the example of the description of a vibrating molecule with the anharmonic oscillator that the energy of a diatomic molecule varies with internuclear distance. This Morse potential represents the energy when one atom is fixed in place at r=0 and the other is allowed to oscillate between the limits of the curve. Classical theory would suggest that the molecule spends most of its time on the curve at the turning point of its motion, since it is moving most slowly there. Quantum theory, while agreeing this view for high values of the vibrational quantum number, shows that for v=0 the atom is most likely found at the center of this motion, i.e. at the equilibrium internuclear distance $r_{eq}$. For v=1, 2, 3, the most



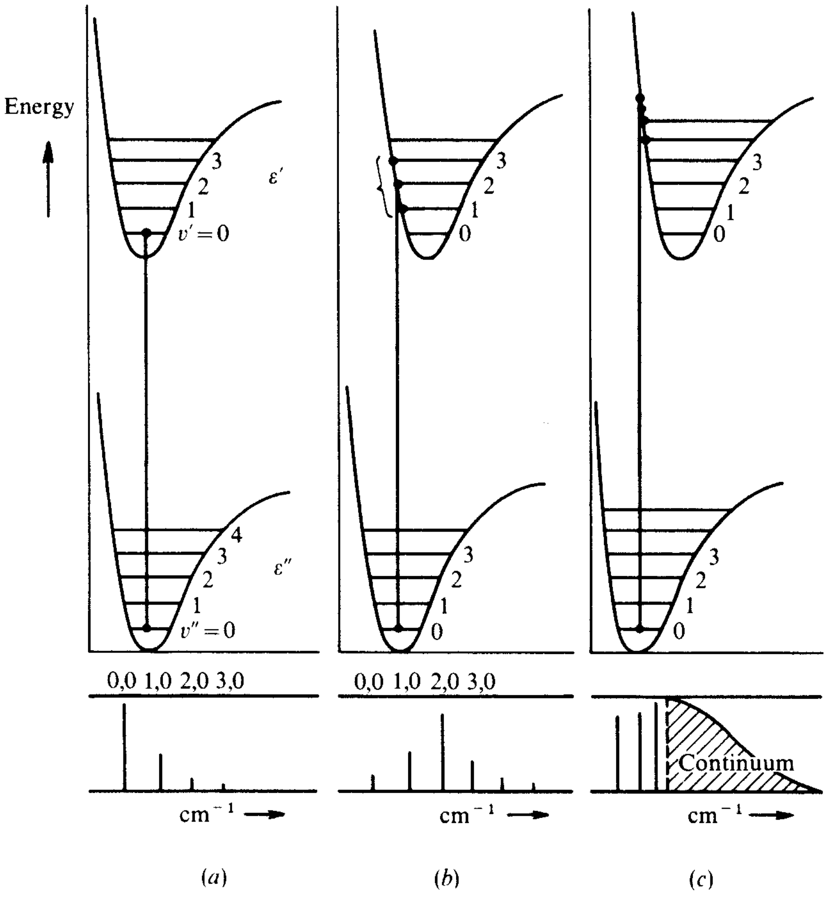
The probability distribution for a diatomic molecule depicted after the quantum theory. The nuclei are most likely found at distances apart that are given by the maxima of the curve for each vibrational state.

Figure 3.2 Probability distribution of the internuclear distance of a diatomic molecule.

probable positions steadily approach the extremities until, for high v, the quantum and classical pictures merge (see figure below) where we plot the probability distribution in each vibrational state against internuclear distance.

If a diatomic molecule undergoes a transition into an upper electronic state in which the excited molecule is stable with respect to dissociation into its atoms, then we can represent the upper state by a Morse curve similar in outline to that of the ground state. There will probably (but not necessarily) be differences in such parameters as vibrational frequency, internuclear distance, or dissociation energy between the two states, but this simply means that we should consider each excited molecule as a new, but rather similar molecule with a different, but also rather similar Morse Potential.

Figure 3.3 below shows three possibilities: In (a) we show the upper electronic state having the same equilibrium internuclear distance as the lower. Now the Franck-Condon principle suggests that a transition occurs vertically on this diagram, since the internuclear distance



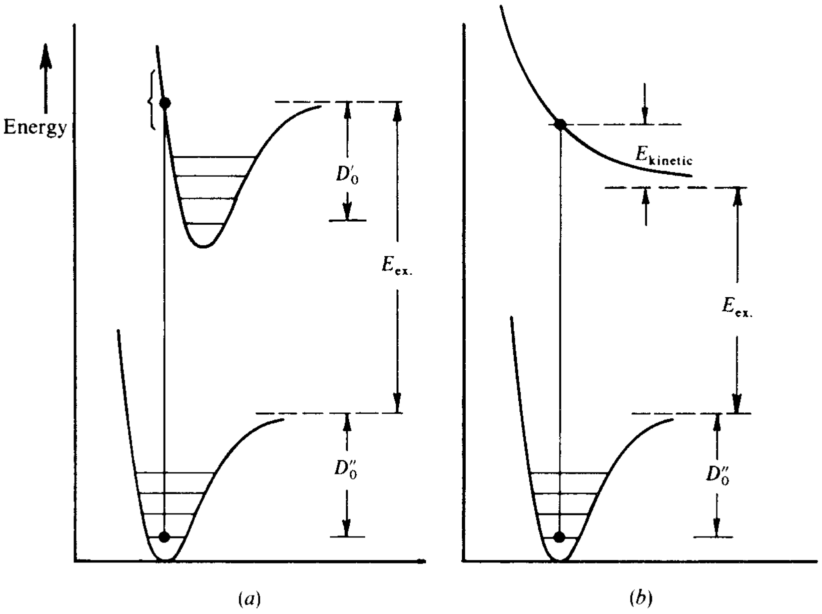
Franck-Condon principle for
(a) internuclear distances equal in upper and lower states,
(b) upper state internuclear distance a little greater than lower state internuclear distance,
(c) upper state internuclear distance considerably greater.

Figure 3.3 Franck-Condon principle for electronic transitions does not change, and so, if we consider the molecule to be initially in the ground state both electronically and vibrationally, then the most probable transition is that indicated by the vertical line in (a). Thus, the strongest spectral line of the v” = 0 progression will be the (0,0). However, the quantum theory only says that the probability of finding the oscillating atom is greatest at the equilibrium distance in the v=0 state, it allows some, although small, chance of the atom being near the extremities of its vibrational motion. Hence there is some chance of the transition starting from the ends of the v”=0 and finishing in the v=1, 2, etc. states. The (1,0), (2,0), etc. lines diminish rapidly in intensity, however as shown in the foot of the figure above.

In part b of Figure 3.3 above, it is shown a case where the excited electronic state has a slightly greater internuclear separation than the ground state. Now a vertical transition from the v=0 level will most likely occur into the upper vibrational state v’=2. Transitions to lower or higher v’ states are less likely. In fact, the upper state most probably reached will depend on the difference between the equilibrium distances of the atoms in the lower and upper electronic states. In part c of the Figure above, the equilibrium distance of the upper state is drawn considerably greater than that of the lower state and we see that, firstly, the vibrational energy level to which the transition most probably takes place has a high v’ vibrational quantum number. Further transitions can occur where the vibrational energy of the excited state is larger than the dissociation energy. From such a state, the molecule will dissociate without vibrations, since the atoms that are formed may take up any kind of value for kinetic energy. Such transitions are not quantized and a continuum results. This is again shown at the foot of the Figure.

## 3.3. Dissociation Energy and Dissociation Products.

Figure 3.4 shows two of the ways in which electronic excitation can lead to dissociation. Part a presents the case that we just discussed, where the equilibrium nuclear separation in the upper state is considerably greater than in the lower. The dashed line limits of the Morse curves represent the dissociation of the normal and excited molecule into atoms, the dissociation energies being D0” and D0’ from the v=0 state in each case. We see that the total energy of the dissociation products (i.e.) atoms form the upper state is greater by an amount $E_{ex}$ than that of the products of dissociation in the lower state. This energy is called the excitation energy of one (or rarely both) of the atoms produced on dissociation. We saw in the previous section that the spectrum of this system consists of some vibrational transitions (quantized) followed by a continuum (non-quantized transitions) representing dissociation. The lower



Dissociation

A: Excitation into a stable upper state
B: Excitation into a continous upper state

Figure 3.4 Dissociation upon electronic excitation of a diatomic molecule.

wave number limit of this continuum must represent just sufficient energy to cause dissociation and no more (i.e. the dissociation products separate with virtually zero kinetic energy) and thus we have:

$$\bar{\nu}_{c.l.} = D_0'' + E_{ex} \qquad (\text{cm}^{-1})$$

and we see that we can measure the dissociation energy, if we know $E_{ex}$., the excitation energy of the products. This excitation energy is readily measurable by atomic spectroscopy the precise state of dissociation products is not always obvious. There are several ways in which the total energy D0”+$E_{ex}$ may be separated into its two components, and one example shall be given. Thermochemical studies often lead to an approximate value of D0” and hence, since D0”+$E_{ex}$ is accurately measurable spectroscopically, a rough value for $E_{ex}$ is obtained. When the spectrum of the atomic products is studied, it usually happens that only one value of excitation energy corresponds at all well with $E_{ex}$. Thus the state of the products is known, $E_{ex}$ measured accurately and a precise value of D0” is deduced.

In many electronic spectra, no continua appear at all — the internuclear distances in the upper and lower states are such that transitions near to dissociation limit are of negligible probability — but still it is possible to derive a value for the dissociation energy by noting how the vibrational lines converge. We have already seen that the vibrational levels may be written:

$$\varepsilon_v = \left(v+\frac{1}{2}\right)\tilde{\nu}_e - x\left(v+\frac{1}{2}\right)^2\tilde{\nu}_e \qquad (\mathrm{cm}^{-1})$$

and so the separation between neighboring levels is

$$\Delta\varepsilon = \varepsilon_{v+1} - \varepsilon_v = \tilde{\nu}_e\{1-2x_e(v+1)\} \qquad (\mathrm{cm}^{-1})$$

This separation obviously decreases linearly with increasing v and the dissociation limit is reached when Δε -> 0. Thus the maximum value of v is given by $v_{max}$,where:

$$\tilde{\nu}_e\{1-2x_e(v_{\max}+1)\} = 0,$$

i.e.

$$v_{\max} = \frac{1}{2x_e} - 1$$

since the anharmonicity constant is of the order of $10^{-2}$, $v_{max}$ is about 50.

Two vibrational transitions are sufficient to determine the $x_e$ and $\tilde{\nu}_e$. Thus, an example given here for HCl yielded $\tilde{\nu}_e$=2990 cm$^{-1}$ and $x_e$ = 0.0174. From the last equation we can calculate $v_{max}$ = 27.74 and the next lowest integer is v =27.

## 3.4. Rotational Fine Structure of Electronic-Vibration Spectra

Until now we have only considered the vibrational coarse structure of electronic spectra, which consist of one or more series of convergent lines. Usually the lines are broad and diffuse. If the resolution is sufficiently good, each line appears as a cluster of many very close lines. This is the rotational fine structure.

To a very good approximation, we can ignore centrifugal distortion and we have the energy levels of a rotating diatomic molecule:

$$\varepsilon_{rot} = \frac{h}{8\pi^2 Ic}J(J+1) = BJ(J+1) \qquad (\mathrm{cm}^{-1})$$

where I is the moment of inertia, B the rotational constant and J the rotational quantum number. Thus by the Born-Oppenheimer approximation, we can express the total energy as

$$\varepsilon_{total} = \varepsilon_{elec} + \varepsilon_{vib} + BJ(J+1) \qquad (\text{cm}^{-1})$$

Changes in the total energy may be written

$$\Delta\varepsilon_{total} = \Delta\{\varepsilon_{elec} + \varepsilon_{vib}\} + \Delta\{BJ(J+1)\} \qquad (\text{cm}^{-1})$$

The wavenumber is then given by

$$\tilde{\nu}_{Spectrum} = \tilde{\nu}_{(v',v'')} + \Delta\{BJ(J+1)\} \qquad (\text{cm}^{-1})$$

This plainly corresponds to any one of the transitions, for example, (0,0) or (0,1) between the electronic vibrational states. Here we are interested to analyze the rotational fine structure Δ{BJ(J+1)}

The selection rule for J depends on the type of electronic transition undergone by the molecule. If the electron is in a state where it does not have an angular momentum (we will describe the angular momentum of electrons in a future chapter) the selection rule for a transition is

$$\Delta J = \pm 1$$

only. For all other transitions, (i.e. provided either the upper or the lower state of the electron contains a contribution from the angular momentum of the electron), the selection is

$$\Delta J = 0, \text{ or } \pm 1$$

In this latter case, there is one added restriction that a state with J=0 cannot undergo a transition to another state with J=0.

Spectra of electronic transitions between state of no electronic angular momentum thus are characterized by P and R branches only, while other transitions include Q branches.

The equation for the wavenumber can be reshaped to

$$\tilde{\nu}_{Spectrum} = \tilde{\nu}_{(v',v'')} + B'J'(J'+1) - B''J''(J''+1) \qquad (\text{cm}^{-1})$$

where B’ and J’ refer to the upper electronic state and B” and J” refer to the lower electronic state.

When we considered vibration-rotational spectra, we saw that the difference in the B values in different vibrational states was very small and could be ignored, except in explaining finer details of the spectra. However this is not the case for electronic spectra, where we discussed in context with the Franck-Condon principle that equilibrium internuclear distances in the lower and in the upper electronic state may differ considerably, a case in which the moment of inertia, and hence the rotational constant B will also differ considerably. Quite often, the electron excited is one of those forming the bond between the nuclei. In this case, the bond in the upper state will be weaker and probably longer, so that the equilibrium moment of inertia increases during the transition and B decreases.

The rotational fine structure can be discussed by applying the selection rules discussed above to the expression for the spectral lines:

$$\tilde{\nu}_{Spectrum} = \tilde{\nu}_{(v',v'')} + B'J'(J'+1) - B''J''(J''+1) \qquad (\mathrm{cm}^{-1})$$

In analogy to the treatment of the vibration-rotational spectra we can define again different rotational branches in the different vibrational states. In vibration-rotational spectra we were concerned with B0 and B1-B values in lower and upper vibrational states. Here, our concern is with B values in lower and upper electronic states, B" and B', and we also consider the formation of a Q-branch.

Taking the P, Q and R branches in turn:

1. P-branch: ΔJ = –1, J" = J'+1

$$\Delta\varepsilon = \tilde{\nu}_P = \tilde{\nu}_{(v',v'')} - (B'+B'')(J'+1) + (B'-B'')(J'+1)^2 \qquad \mathrm{cm}^{-1}, \text{ where } J'=0,\ 1,\ 2,\ \ldots$$

2. R-branch: ΔJ = +1, J' = J"+1

$$\Delta\varepsilon = \tilde{\nu}_R = \tilde{\nu}_{(v',v'')} + (B'+B'')(J''+1) + (B'-B'')(J''+1)^2 \qquad \mathrm{cm}^{-1}, \text{ where } J''=0,\ 1,\ 2,\ \ldots$$

These two equations can be combined into

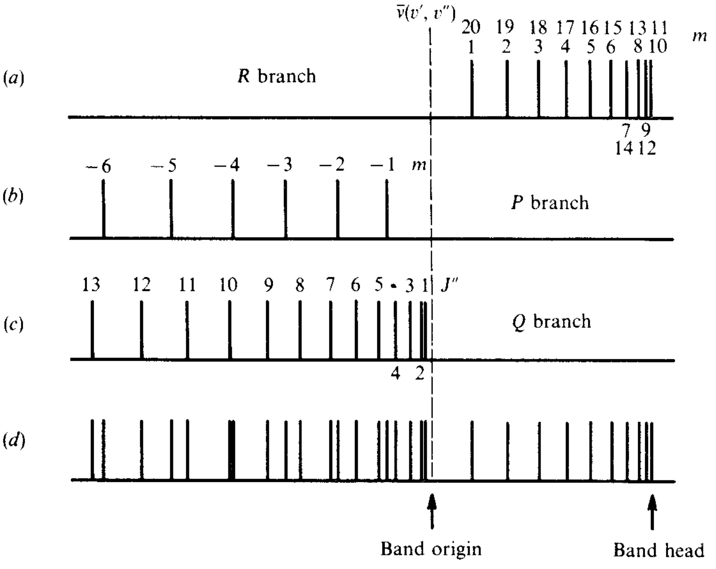
$$\tilde{\nu}_{P,R} = \tilde{\nu}_{(v',v'')} + (B'+B'')m + (B'-B'')m^2 \qquad \mathrm{cm}^{-1}, \text{ where } m=\pm1,\ \pm2,\ \ldots$$

Positive m values comprising the R branch (i.e. corresponding to ΔJ = +1) and negative values comprising the P branch (ΔJ = –1). m cannot be zero, since e.g. J' cannot be –1 in the P-branch. We draw the appearance of the R and the P branches separately (see Figure 3.5 , a and b), taking a 10% difference in B for the upper and lower B values and choosing B' < B". With this choice, P branches occur on the low wavenumber side of the band origin and the spacing between the lines increases with m. On the other hand the R branch appears on the wavenumber of the origin and the line spacing decreases rapidly with m, so rapidly that the lines eventually reach a maximum wavenumber and then begin to return to low wavenumbers with increasing spacing. It will be remembered that a similar decrease was observed in the R-branch but this was much to slow for a convergence limit to be reached; the rapid convergence here is simply due to the magnitude B’-B”. The point at which the R-branch separation reaches decreases to zero is termed the band head.

3. Q-branch: ΔJ=0, J’=J”

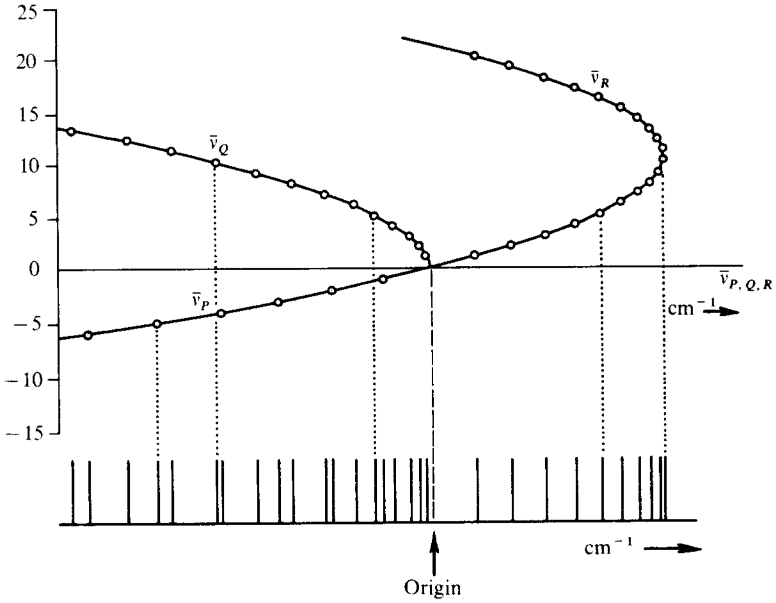
$$\Delta\varepsilon = \tilde{\nu}_Q = \tilde{\nu}_{(v',v'')} + (B'-B'')J'' + (B'-B'')J''^2 \qquad \text{cm}^{-1}\text{, where } J''= 1,\ 2,\ \ldots$$

Note that here J”=J’≠0 since we have the restriction mentioned above. Thus, again no line will appear at the band origin. We sketch the Q-branch again for B’ < B” and a 10% difference between the two. We see that the lines are at low wavenumbers towards the band origin and their spacing increases. The first few lines of this branch are usually not resolved.



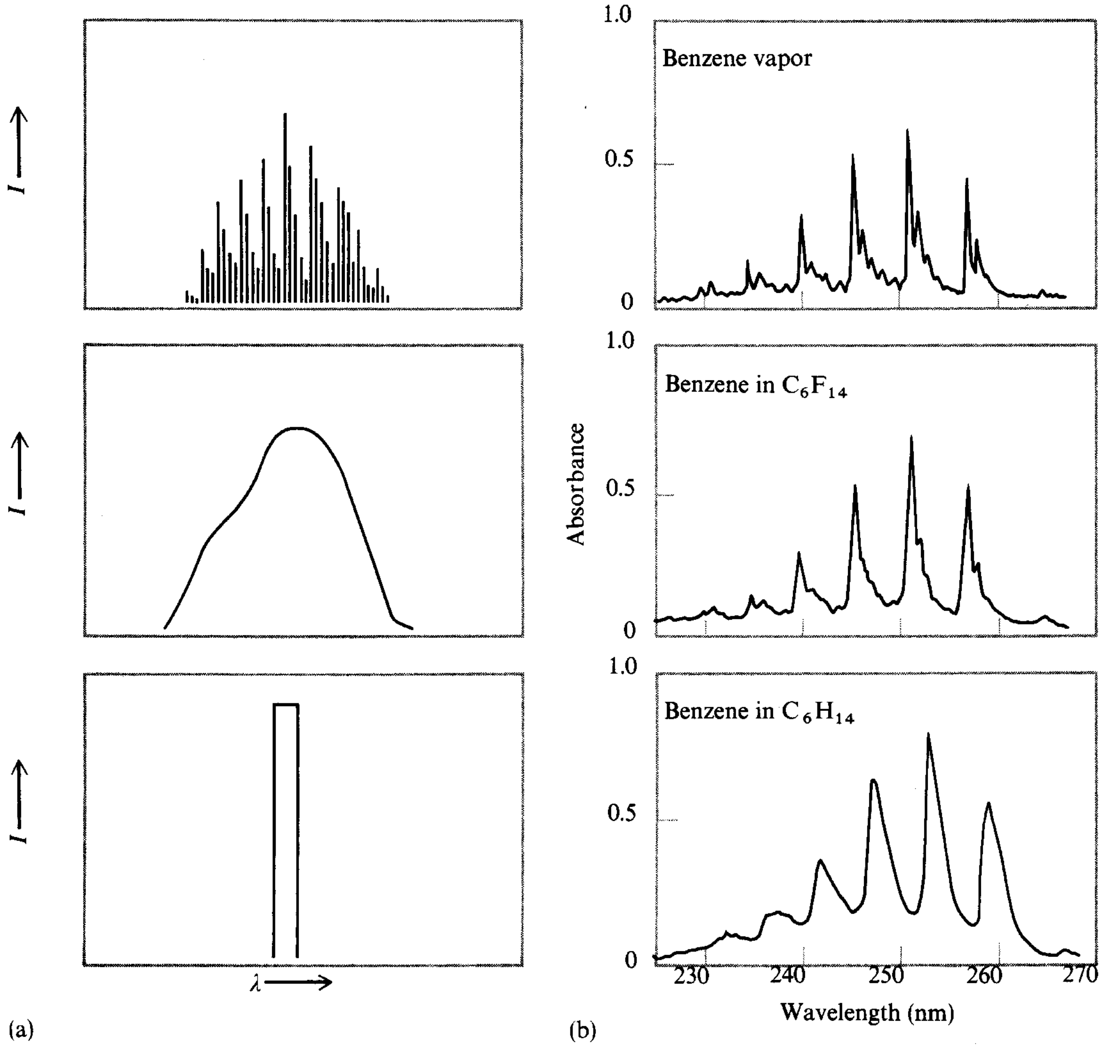
The rotational fine structure of a particular vibrational-electronic transition for a diatomic molecule. The R, P, Q, branches are shown separately in (a), (b), and (c), respectively, with the complete spectrum at (d).

Figure 3.5 Rotational fine structure of the vibrational coarse structure of an electronic transition.

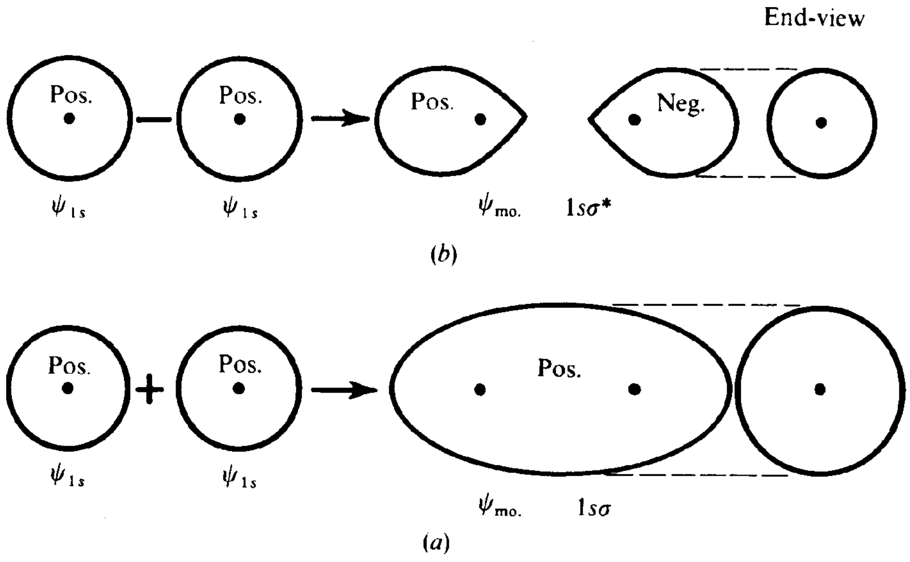


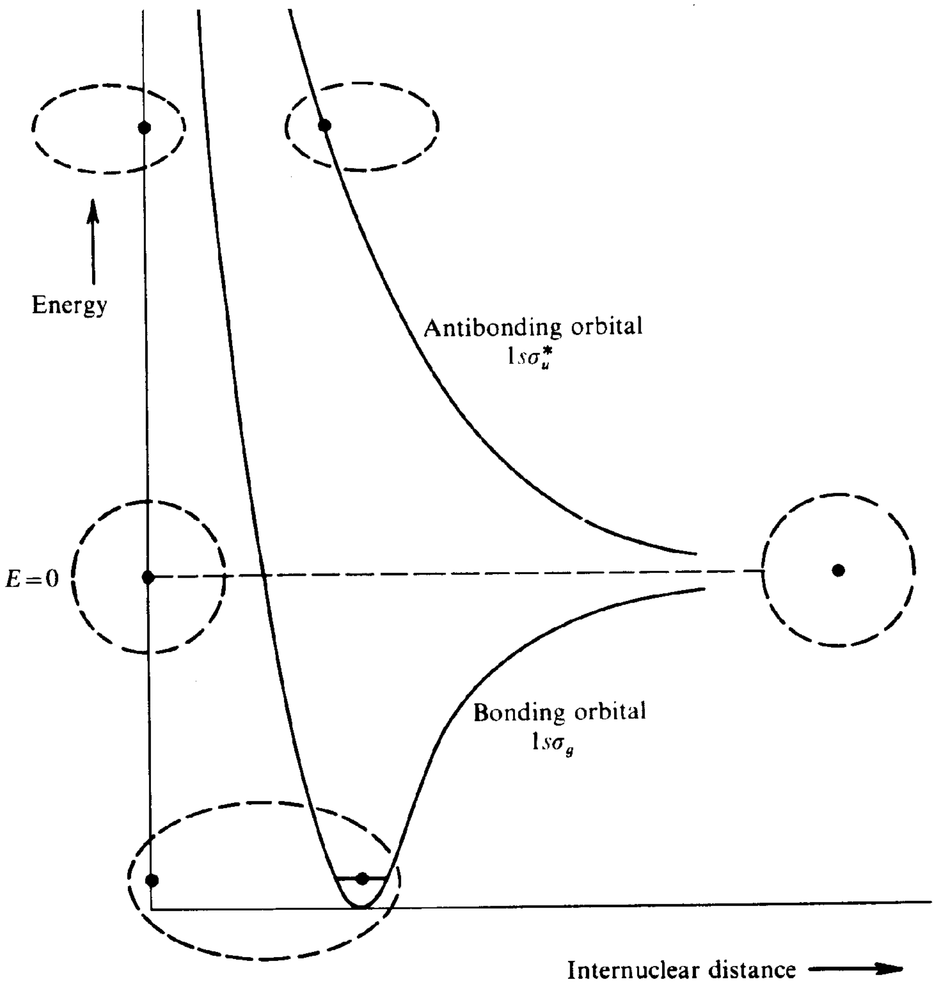
Fortrat Diagram scetched for a 10 % difference between B' and B" (with B' < B").

Figure 3.6 Fortrat diagram for the rotational fine structure of vibrational electronic spectra.

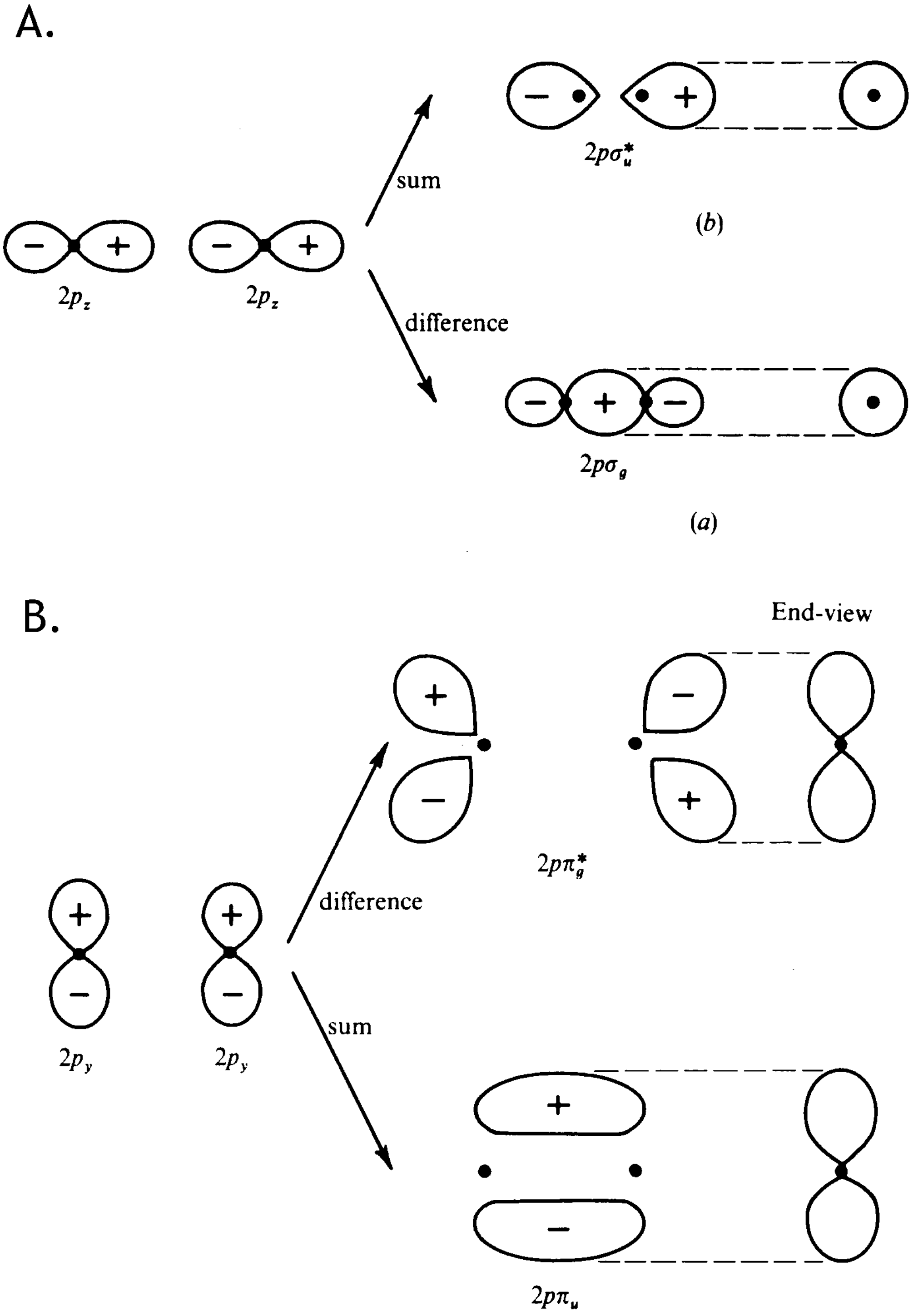


*Electronic absorption spectra of small molecules.* **(a)** Spectra of a typical small molecule. Shown, from top to bottom, are the gas-phase spectrum, the solution spectrum, and the theoretical spectrum usually dealt with in calculations. **(b)** Absorption spectra of benzene, showing solvent-induced broadening. [After J. B. Birks, *Photophysics of Aromatic Molecules* (New York: Wiley, 1970), p. 117.]





The variation of energy with internuclear distance in the bonding and antibonding orbitals, $1s\sigma_g$ and $1s\sigma_u^*$.



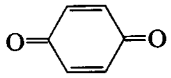
A. Linear combination of $2p_x$-orbitals to bonding and antibonding $2p\sigma$ molecular orbitals.
B. Linear combination of $2p_y$-orbitals to bonding and antibonding $2p\pi$ molecular orbitals

| | $\pi \rightarrow \pi^*$ (strong) (nm) | $n \rightarrow \pi^*$ (weak) (nm) |
|---|---|---|
| $>C=C<$ | 170 | — |
| $-C\equiv C-$ | 170 | — |
| $>C=O$ | 166 | 280 |
| $>C=N\diagdown$ | 190 | 300 |
| $>N=N\diagup$ | ? | 350 |
| $>C=S$ | ? | 500 |

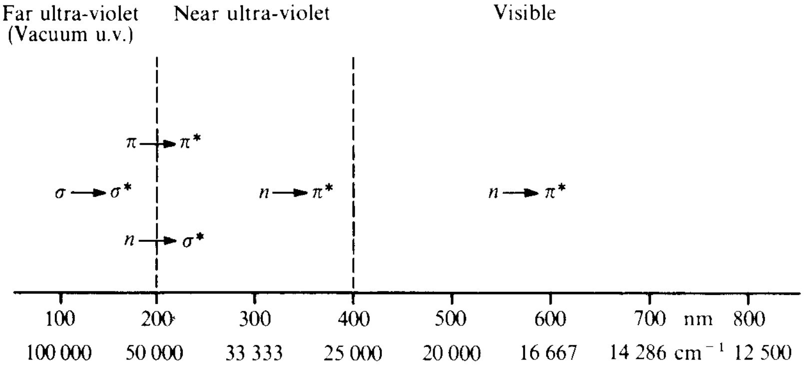
Isolated multiple bonds within a molecule: π to π* transitions are relatively insensitive to the atoms that participate in the bond. In contrast, n to π* transitions are affected more strongly.

| | $\lambda_{max.}$ (nm) | $\varepsilon$ |
|---|---|---|
| $-C=C-$ | 170 | 16 000 |
| $-C=C-C=C-$ | 220 | 21 000 |
| $-C=C-C=C-C=C-$ | 260 | 35 000 |

Effect of conjugation of bonds on the position of the absorbance maximum. The position of the wavelength maximum depends on the number of double bonds that are conjugated.

| | $\pi \rightarrow \pi^*$ (strong) (nm) | $n \rightarrow \pi^*$ (weak) (nm) |
|---|---|---|
| $-C=O$ | 166 | 280 |
| $-C=C-C=O$ | 240 | 320 |
| $-C=C=C-C=O$ | 270 | 350 |
|  | 245 | 435 |

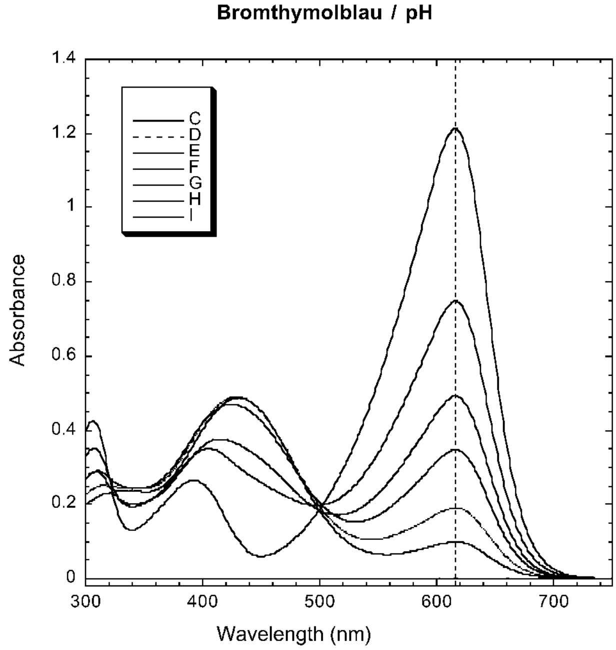
Effect of conjugated bonds on the n to p* transition of non-bonding electrons of keto-oxygene.

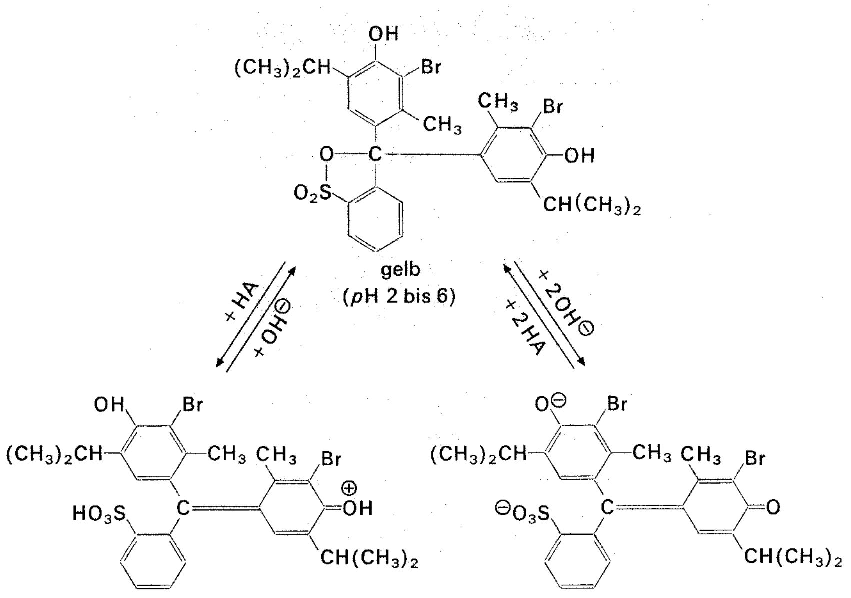


The regions of the electronic spectrum and the types of transitions that occur in each.

Figure 3.7 Types of electronic transitions in molecules absorbing UV/VIS radiation

“Plot” der Absorptionsspektren von Bromthymolblau in Abhängigkeit vom pH



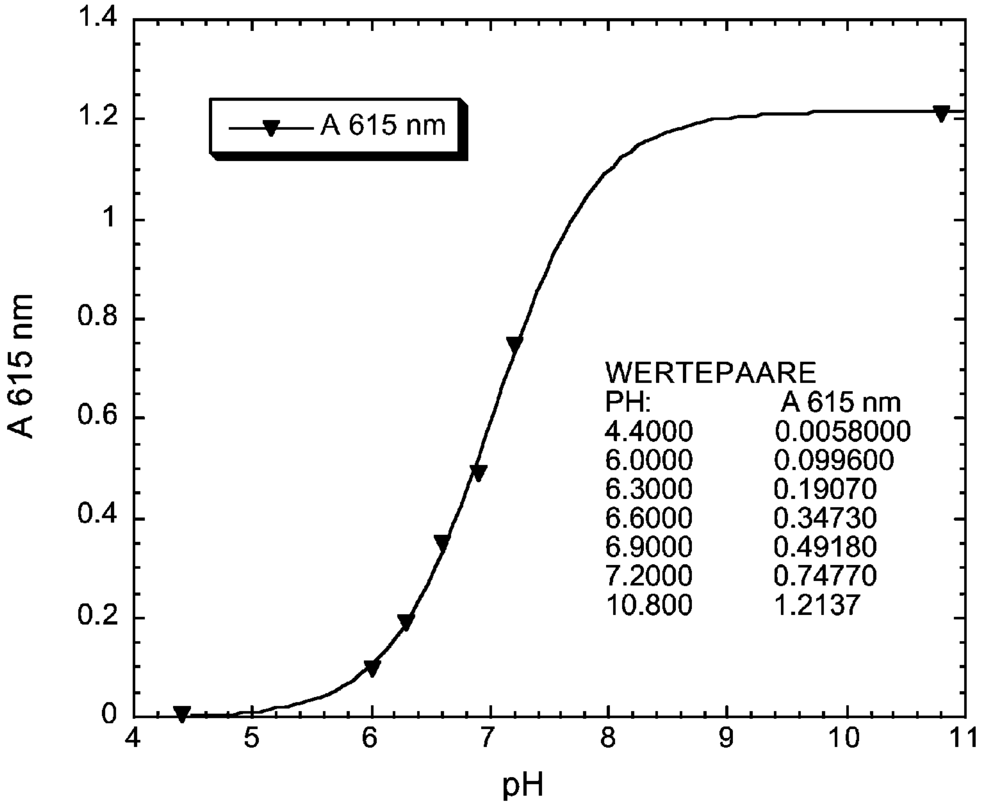


(4)
rot
(unterhalb pH 1 bis 2)
mesomer

Bromthymolblau

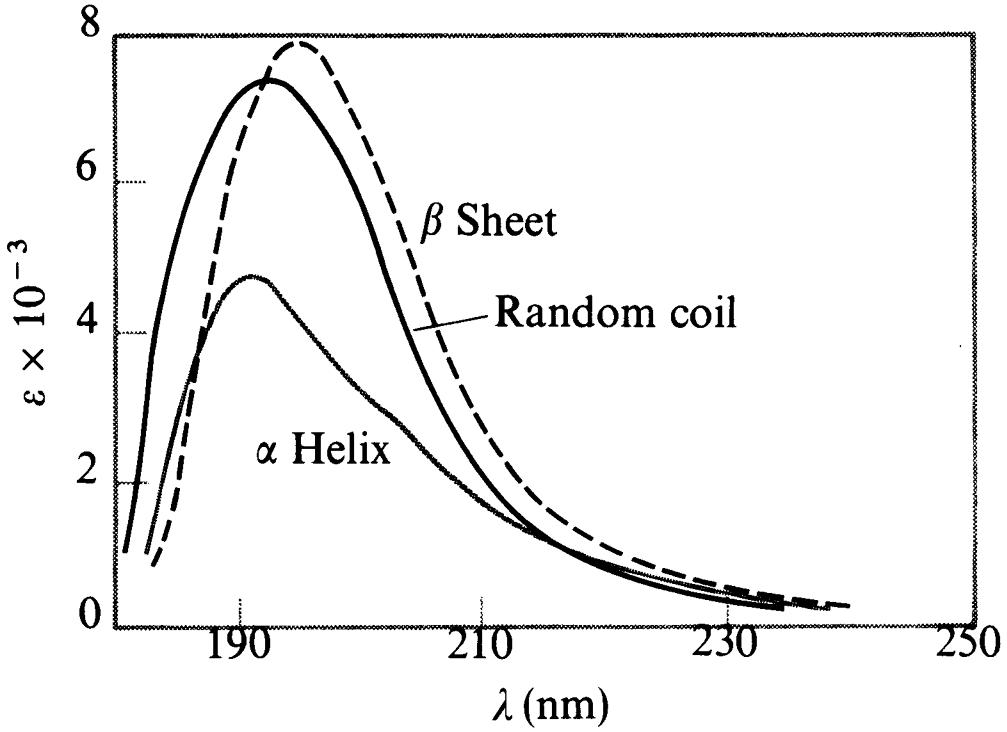
(5)
blau
(oberhalb pH 7,5)
mesomer

**Plot Bromthymolblau, A615/pH**

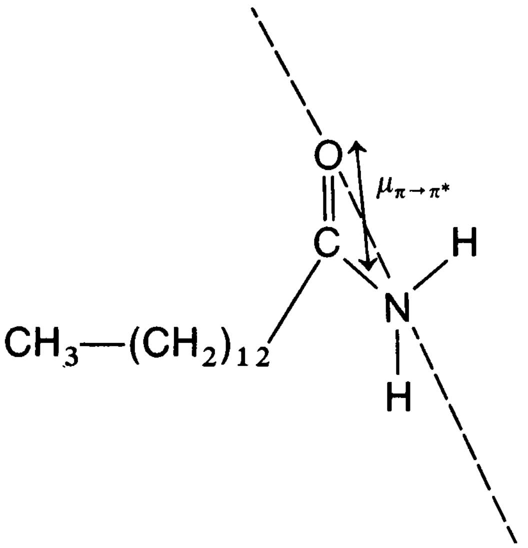


WERTEPAARE

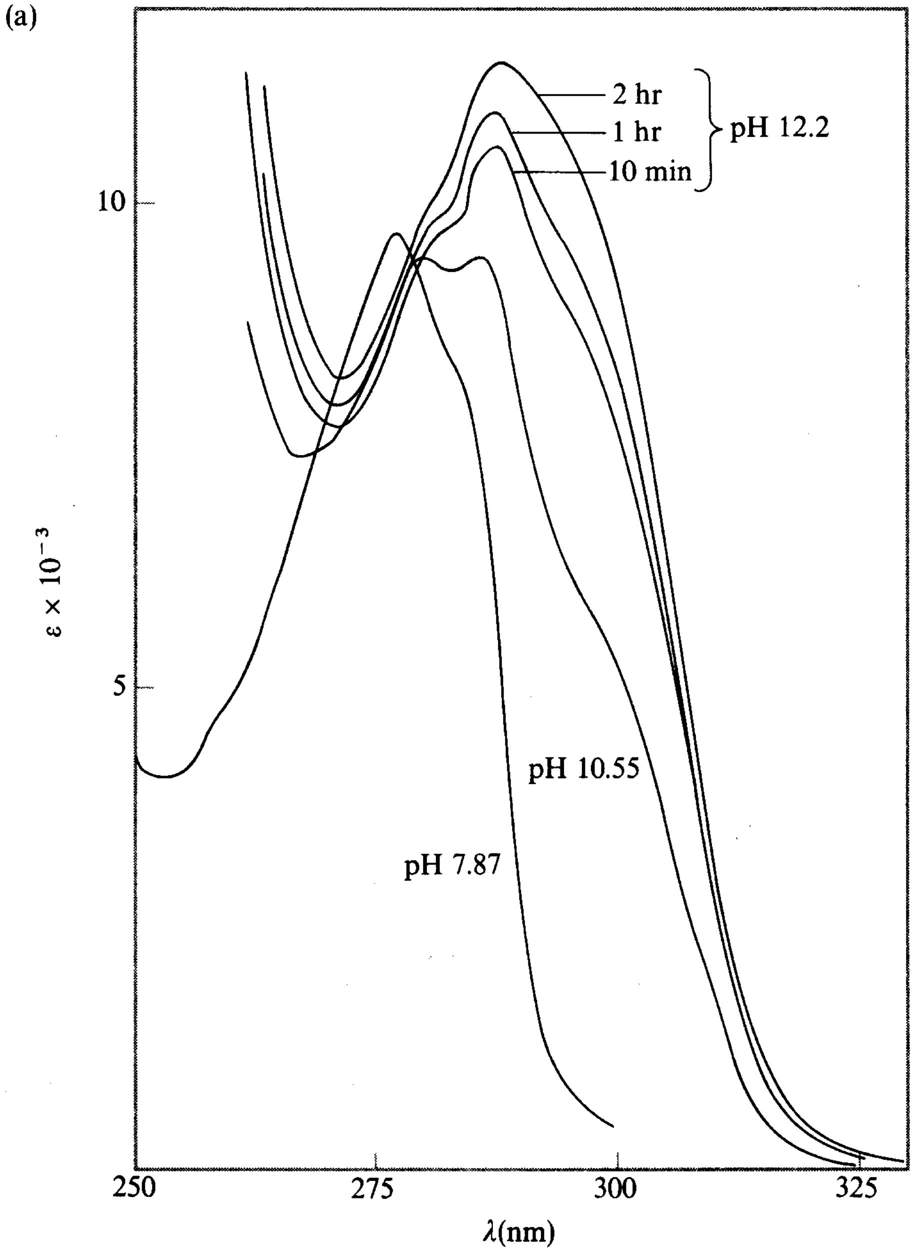
| PH: | A 615 nm |
|---|---|
| 4.4000 | 0.0058000 |
| 6.0000 | 0.099600 |
| 6.3000 | 0.19070 |
| 6.6000 | 0.34730 |
| 6.9000 | 0.49180 |
| 7.2000 | 0.74770 |
| 10.800 | 1.2137 |



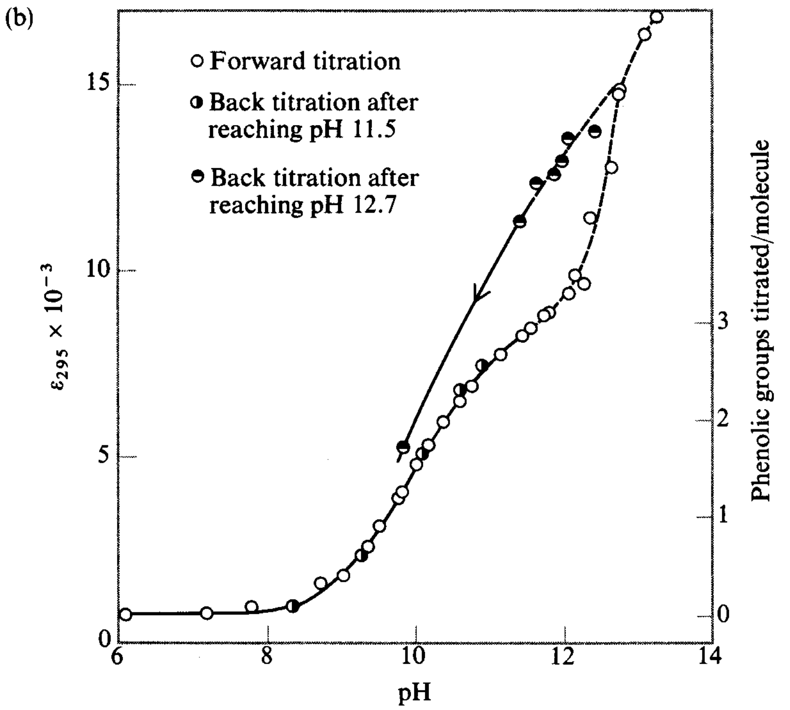
*Ultraviolet absorption spectrum of poly-*L*-lysine in aqueous solution:* random coil, pH 6.0, 25°C; α helix, pH 10.8, 25°C; β sheet pH 10.8, 52°C. [After K. Rosenheck and P. Doty, *Proc. Natl. Acad. Sci. USA* 47:1775 (1961).]



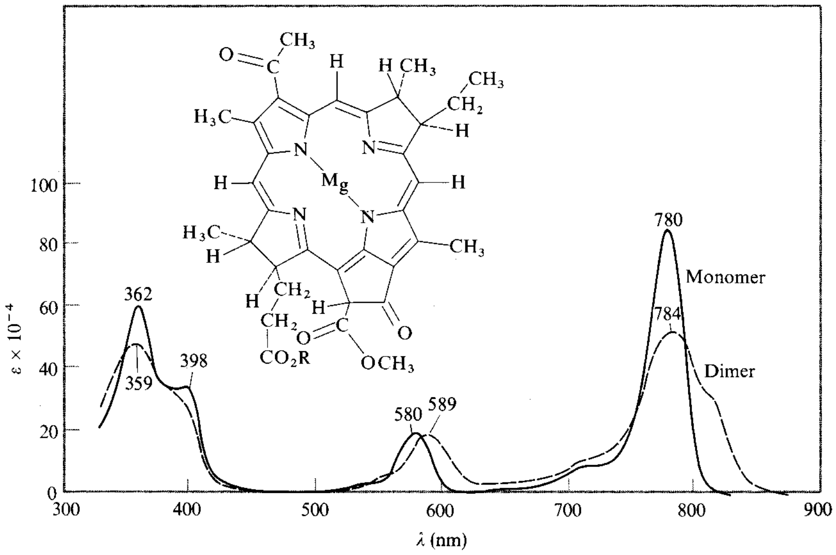
direction of the transition dipole moment for a π —> π* transition in an amide.



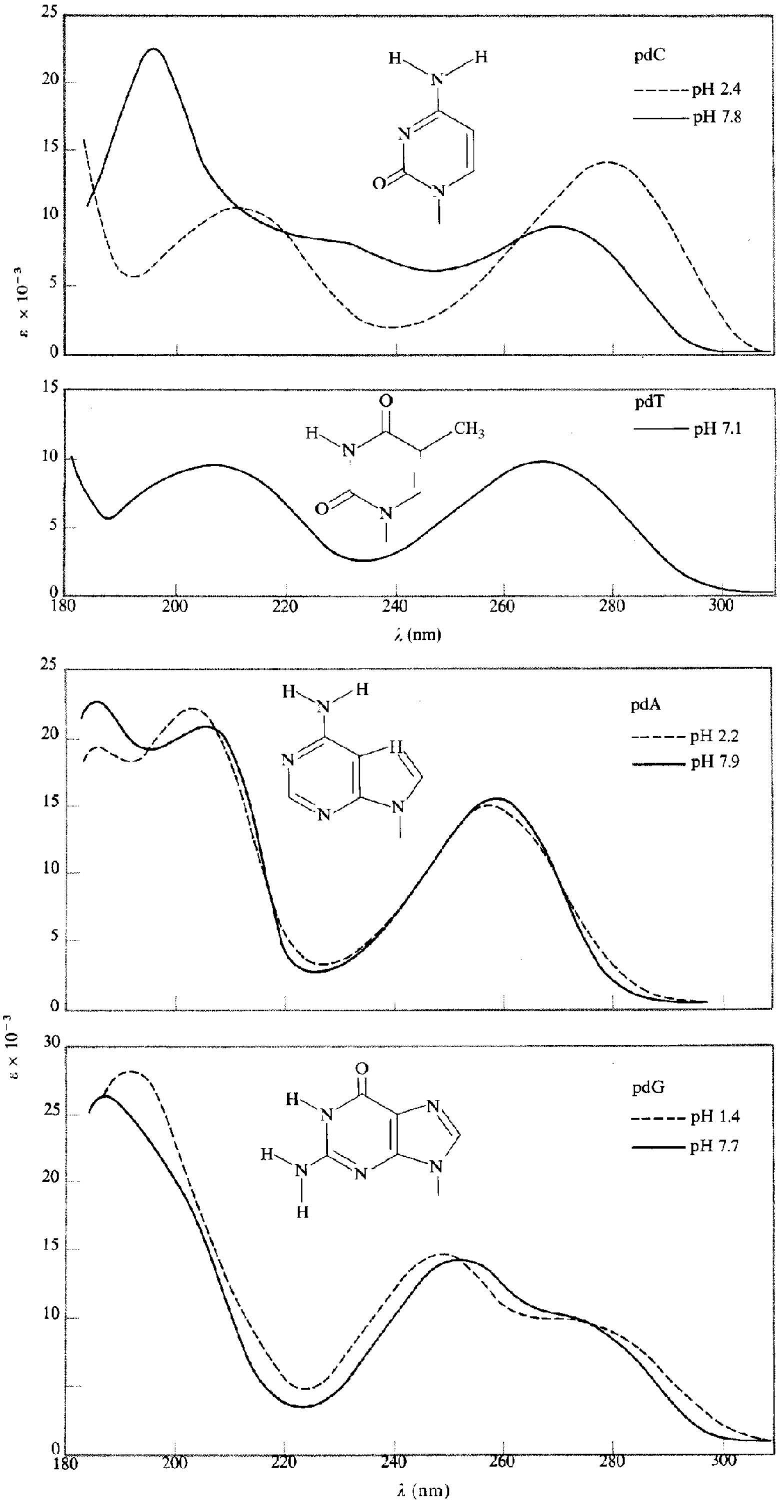
Spectrophotometric titration of bovine pancreatic RNase. (a) The ultraviolett spectrum as a function of pH and, at pH 12.2, as a function of time. There is no time dependence at the lower pH values.



Extinction coefficient at 295 nm as a function of increasing pH. RNase has six tyrosines. The results show that roughly three of the tyrosines titrate reversibly with a pKa near 10.2 (normal for isolated tyrosine residues). The other three tyrosines do not titrate until the higher pH values, and this titration is accompanied by denaturation of the protein that causes the histeresis seen when back titration is attempted. (After Tanford, C., Hauenstein, J.D., and Rands, D.G., J. Am. Chem. Soc., 1955, 77, 6409)



*Monomer and dimer spectra for solutions of bacteriochlorophyll.* A pronounced splitting of the longest-wavelength band in the dimer is visible. [After K. Sauer, J. R. L. Smith, and A. J. Schultz, *J. Am. Chem. Soc.* 88:2681 (1966).]



Absorption spectra of four deoxynucleotides as a function of pH. Spectra of the corresponding ribo-compounds are extremely similar, except that uridine has a near UV maximum at 260 nm rather than the 268 nm maximum of thymidine.