Table 3.13
The frequencies and types of the pyrazine normal modes

Species	Measured frequency(cm^{-1})	Measured band type	Calculated frequency(cm^{-1})	Calculated mode character
A_g ∥	(609)	RA p	596	βrg
	1017	RA p	1017	νrg
	1240	RA p	1211	βCH+νrg
	1579	RA p	1593	νrg+βrg
	3063	RA p	3073	νCH
B_{1g} ∥	(641)	RA dp	638	βrg
	(1350)	RA dp	1332	βCH+νrg
	(1523)	RA dp	1566	νrg+βCH
	3053	RA dp	3049	νCH
B_{2g} ⊥	703	RA dp	722	τrg
	(925)	RA dp	938	γCH
B_{3g} ⊥	873	RA dp	886	γCH
A_u ⊥	-	-	400	τrg
	-	-	952	γCH
B_{1u} ⊥	416	IR C	429	τrg
	784	IR C	757	γCH
B_{2u} ∥	1058	IR B	1058	νrg
	1176	IR	1189	νrg
	1413	IR B	1394	βCH
	3072	IR B	3066	νCH
B_{3u} ∥	1018	IR A	1006	βrg
	1145	IR	1126	νrg+βCH
	1495	IR	1478	βCH+νrg
	3060	IR	3053	νCH

The motions in several vibrational modes are determined practically only by one chemical internal coordinate of a chemical group. These modes are called *group modes,* the corresponding bands and frequencies are called *group bands* and *group frequencies,* respectively. The pyrazine molecules has 4 frequencies above 3000 cm^{-1}, these are CH valence (or stretching) frequencies (only CH stretching coordinates move in them). Several other groups have also characteristic frequencies.

Table 3.14 presents the regions of some characteristic valence frequencies. If a group has the form XY_2, the two XY stretchings are coupled. If the stretchings are in phase, this is a *symmetric* (s) vibration, if they are in opposite phase, this is an *antisymmetric* (as) vibration. The frequency of the asymmetric modes is always higher than that of the symmetric ones.

Under the vibrational modes belonging to the same group the valence frequencies are the highest, lower are the in-plane deformation ones, the out-of-plane modes have generally the lowest frequencies.

Table 3.14
Characteristic frequency regions of some group vibrations (cm^{-1})

Group	Environment	Region	
		asymmetric	symmetric
C-H	aliphatic CH_3	2952-2992	2862-2897
	aliphatic CH_2	2916-2948	2843-2878
	$C=CH_2$	3077-3082	
	aromatic CH	3010-3090	
N-H	free NH_2	3350-3580	3220-3450
	free NH	3300-3500	
	NH in H bond	3200-3300	
O-H	alcoholic OH	3600-3650	
	phenolic OH	3600-3650	
	OH in H bond	2500-3300	
S-H		2550-2600	
C=O	carbon acid	1700-1725	
	keton	1680-1725	
	aldehyde	1680-1725	
C-O	carbon acid	1280-1320	
	alcohol	1000-1080	
NO	aliphatic NO_2	1550-1580	1370-1390
	aromatic NO_2	1500-1530	1350-1370
	aliphatic NO	1530-1610	
	aromatic	1480-1520	

3.5.5 Non-linear spectroscopy

The Raman spectrometers use low energy laser light as light sources having frequencies far from the frequencies of electron transitions. Only one laser is applied. Applying other conditions special phenomena are observable.

Applying high energy laser as light source the non-linear terms of Eq. 1.14 become greater and these terms determine the induced dipole moment. The lines $2\nu_o \pm \nu_i$ appear in the scattered light. This is the *hyper Raman effect*.

If the frequency of the high energy laser source fall into an electron transition bond the spectrum changes absolutely. As a result of the interaction some Raman lines disappear, other become more intense and/or shift. This is the *resonance Raman effect*. The strong lines are intense also in diluted solutions and are therefore suitable for quantitative analysis. The so-called *ultraviolet Raman spectroscopy* is recently a version of resonance Raman effect using UV for excitation., applied frequently for quantitative analysis.

If the laser energy is extremely high, as a result of the excitation the population of the excited state is greater than that of the ground state ("inversion" of the population). Some lines become extremely strong, their intensity is comparable to the intensity of the scattered light at the laser frequency. This is the *stimulated laser effect*.

The *coherent anti-Stokes Raman effect* is a multi-photon effect. Two high energy pulse lasers with adequate intensity and frequencies ν_1(fixed) and ν_2 (tuneable) irradiate the sample. If the frequency difference is equal to the frequency of a vibrational transition:

$\nu_i=\nu_2-\nu_1$, then an intense coherent radiation is observable at the frequency $2\nu_1-\nu_2$. In contrary to the Raman effect here the fluorescence does not disturb this effect. This effect is suitable to follow fast processes (ns, ps). It is also applicable in quantitative analysis.

The Raman amplification spectroscopy is an absorption method. The sample is irradiated with two low energy pulse lasers. Their frequencies are ν_1(fixed) and ν_2 (tuneable). If $\nu_i=\nu_2-\nu_1$, the molecule absorbs light at ν_2 frequency and emits at ν_1 one. If the intensity is detected at ν_2 this is the inverse Raman effect, Raman loss spectroscopy. If the intensity at ν_1 frequency is measured, this is the Raman gain spectroscopy.

The light sources of non-linear methods are pulse laser (with ns, ps pulses). These lasers are also suitable for the measurement of short lifetimes of states.

3.5.6 Other vibrational spectroscopic methods

Neutron molecular spectroscopy (IINS, incoherent inelastic neutron scattering). The region of the wavenumber of thermal neutrons is comparable to that of the molecular vibrations:

$$\tilde{\nu}=\frac{\mathrm{E}}{hc}=\frac{kT}{hc}=\frac{h}{2m_n c\lambda^2} \tag{3.63}$$

k is the Boltzmann constant, T is the absolute temperature, $m_n=1{\cdot}67493\times10^{-27}$ kg, the neutron mass, λ is the wavelength, c is the light velocity in vacuum. The frequency region of the thermal neutrons is 5÷4500 cm^{-1}. the incoherent neutrons interact with the molecules through inelastic scattering (absorption), if their frequency are equal to one of vibrational fundamentals of the molecule. The cross section of the interaction is very high in the case of hydrogen (79.7 barn, 1 barn = 10^{-28} m^2). A lot of elements have cross section between 1 and 10 barn. The cross section of $^{12}\mathrm{C}$ and $^{16}\mathrm{O}$ is zero. This method is very effective in measurement of vibrational spectra of molecules with high hydrogen content. The selection rules differ from that of the optical spectroscopic methods, therefore the transitions that are forbidden in IR and RA may appear.

Tunnel electron spectroscopy. (IETS, inelastic electron tunnelling spectroscopy). It is based on the quantum mechanical *tunnel effect*: particles can cross an energy barrier without an excitation, depending on their mass and the height of the barrier. The molecules are absorbed on an insulator. The insulator layer is placed between two metal plates. Under electric tension the molecules can receive energy from the tunnel electrons with about 1 % probability. This absorption is measurable with a very complicate instrument. The measurement is very sensitive: 2 pg substance can be detected on 20 $\mu\mathrm{m}^2$ surface).

3.5.7 Large amplitude motions

If a molecule has more than one energy minima the motions between these minima are called large amplitude motions. The minima are not always energetically equivalent.

The *internal rotation* is a large amplitude motion with changing torsional coordinate. The rotation of the ethane molecule around its C-C axis is a good example. During a rotation of 360° it has three maxima (eclipsed) and three minima (straggled), see Fig. 3.31. This motion has a periodic potential. The symmetry in the maxima and in the minima are high, in all other positions it is C_3 (see Table 3.15).

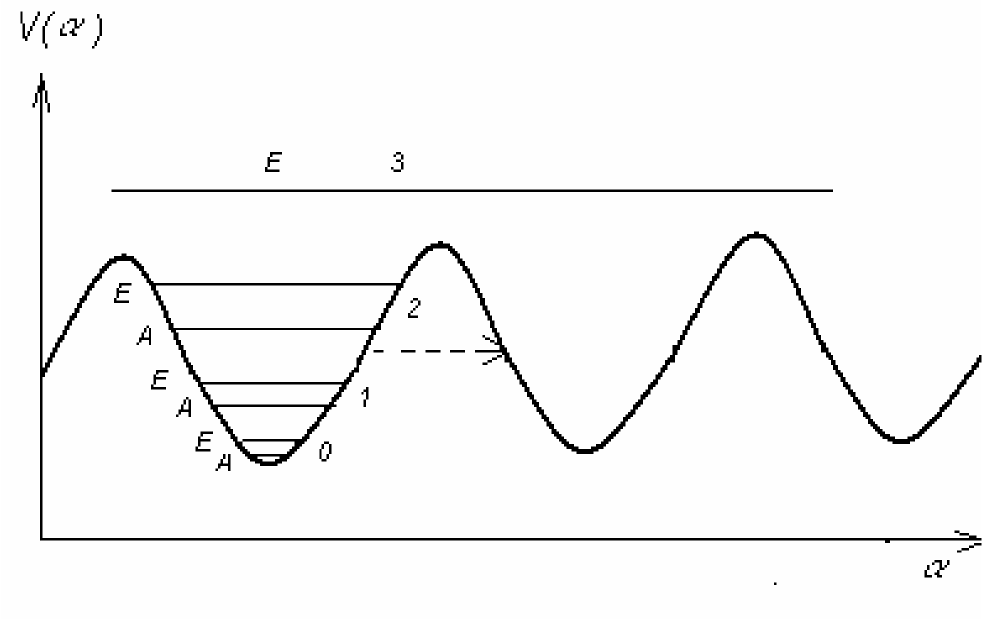

Fig. 3.31

Table 3.15
Character table of the point group C_3

C_3	E	C_3	C_3^2
A	1	1	1
E	1	$\exp\left(i\frac{2\pi}{3}\right)$	$\exp\left(-i\frac{2\pi}{3}\right)$
	1	$\exp\left(-i\frac{2\pi}{3}\right)$	$\exp\left(i\frac{2\pi}{3}\right)$

According to the symmetry two energy level series exist: the A and the E. *The energy barrier is* the difference between the maximal energy and the v=0 level. For the ethane molecule it is 12.25 kJ mol^{-1}. Here it is also possible the quantum mechanical tunnel effect.

The *inversion* is a transition between two energetically equivalent states in the case of non-planar configurations through a planar intermediate state. The ammonia inversion is one of the well known cases. The effect causes a bond doubling in the IR vapour spectrum of ammonia.

The large amplitude motions of the non-planar 4-, 5- and 6-membered *rings* are also known from the organic chemistry.

The existence of more than one energy minima causes splittings in the vibrational spectrum.

3.6 Electronic transitions in molecules

The electronic transitions in molecules are not in connection with any molecular motions. The energy differences are higher, the times of transitions are shorter than in the case of vibrational motions. The electronic transitions may be coupled with vibrational and rotational transitions (vibronic and rovibronic transitions, respectively). Therefore the electronic spectra have vibrational (rovibrational) structure.

The electronic spectra are measured in solutions. Their intensity is recorded in absorbance. According to the Lambert-Beer law

$$A = \alpha \ell c \tag{3.63}$$

α is the *molar absorption coefficient,* ℓ is the layer width, c is the chemical concentration (in concentrated solutions the activity replaces the concentration).

3.6.1 The excitation of the electrons

The molecular energy depends on the molecular geometry. Diatomic molecules have only one parameter, the atomic distance. Therefore the potential energy curve is two-dimensional. For polyatomic molecules the energy function builds a hypersurface. So our model remain the diatomic molecule.

Exciting an electron of the molecule it comes to a new state. This is either an antibonding or a dissociative level. If the electron comes to a lower state it may emit photon(s).

The probability of the transitions is determined above all by the transition moment (Eq. 1.46). Therefore the change in the dipole moment and the symmetry of the ground and excited states are important. The ΔS=0 selection rule is here valid, the group spin quantum number must not change during the transition. This is strictly valid only for *ls* coupling (Section 2.3.2).

The following viewpoints are also acceptable for both absorption and emission:

1. If the molecule is excited, it preserves its ground state structure also in the excited state. This is a state in largest elongation of a vibrational mode.

2. The electronic transition is faster than the motion of the atomic core. The atomic cores do not change their positions during the excitation (Franck-Condon principle).

If the equilibrium nuclear distance do not change during the excitation ($r_g=r_0$), according to the Franck-Condon principle the 0←0 transition is the most probable (Fig. 3.32). If the nuclear distance increases during the excitation ($r_g>r_0$), the 1←0 transitions are favoured. In the first case the positions of the maximal displacements belong to the same nuclear distance. In the second case these positions are shifted and same position belongs to other vibrational levels. Other electronic transitions have lower transitional probability. Here r_g is the equilibrium position in the excited state, r_0 is the same in the ground state.

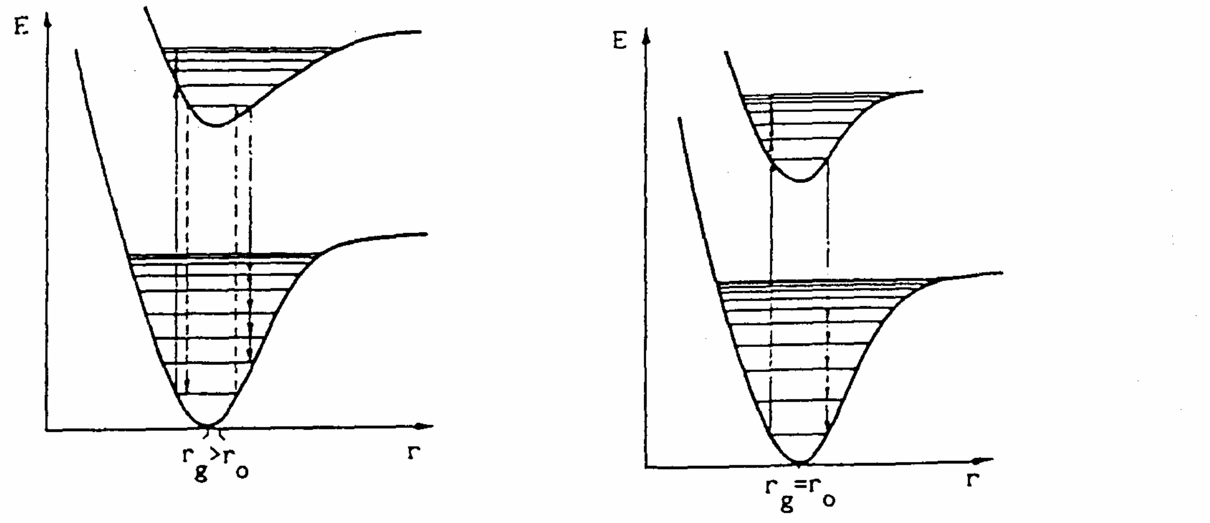

Fig. 3.32

3.6.2 The types of electronic transitions

The principal types of electronic transitions are

- transitions between bonding and antibonding levels,
- d←d transitions,
- charge transfer transitions.

Bonding to antibonding transitions that are observable in the UV (or in the VIS) region and they are possible between levels (orbitals) of π electrons and non-bonded (n) electrons: π*← π and π*←n transitions. Fig. 3.33 is a simplified diagram.

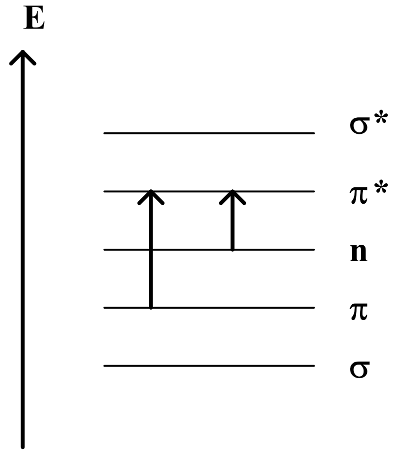

Fig. 3.33

The two transition types are distinguishable in solution with the aid of the solvent effect. The increasing polarity of the solvent decreases the energy levels. The energy of the more polar level decreases more. In the π*←n transitions the ground state is more polar (Fig.

3.34). The π*← π bands shift to the visible (bathochromic shift), the π*←n ultraviolet (hypsochromic shift). With increasing acidity of the solvent the intensity of the π*←n bands decreases (hydrogen bond formation) and at a given pH value the band disappears.

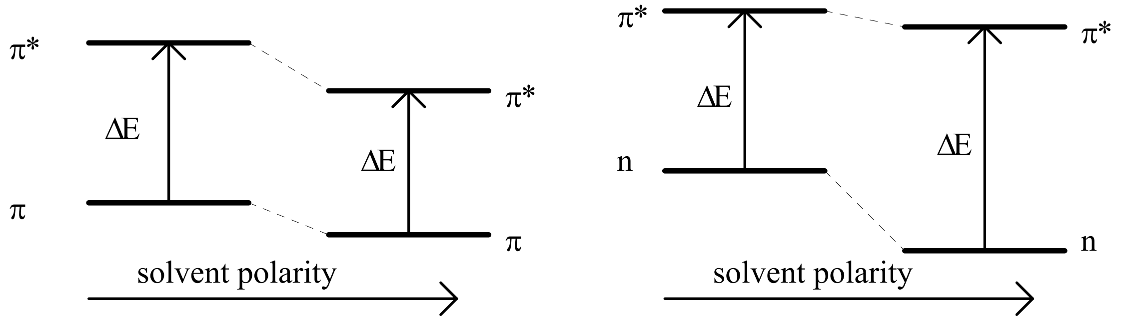

Fig. 3.34

The *d←d transitions* are in case of the transition metal complexes important. The transitions are possible between the splitted d levels (Section 3.3.5). The corresponding bands appear in the VIS or in the NIR regions. This kind complexes give the colours of the solutions of the transition metal complexes. Fig. 3.35 is the electronic spectrum the $Ti[H_2O]_6^{3+}$ ion in the aqueous solution of $TiCl_3$. The Ti^{3+} ion has only one 3d electron and builds its hexaaquo ion in octahedral complex form. (Ti: $Ar3d^24s^2$, Ti^{3+}: $Ar1d^1$). The spectrum has an intense band at 20300 cm^{-1} and a weak shoulder at 17400 cm^{-1}. Since Δ=20300 cm^{-1}, Dq=2030 cm^{-1}.

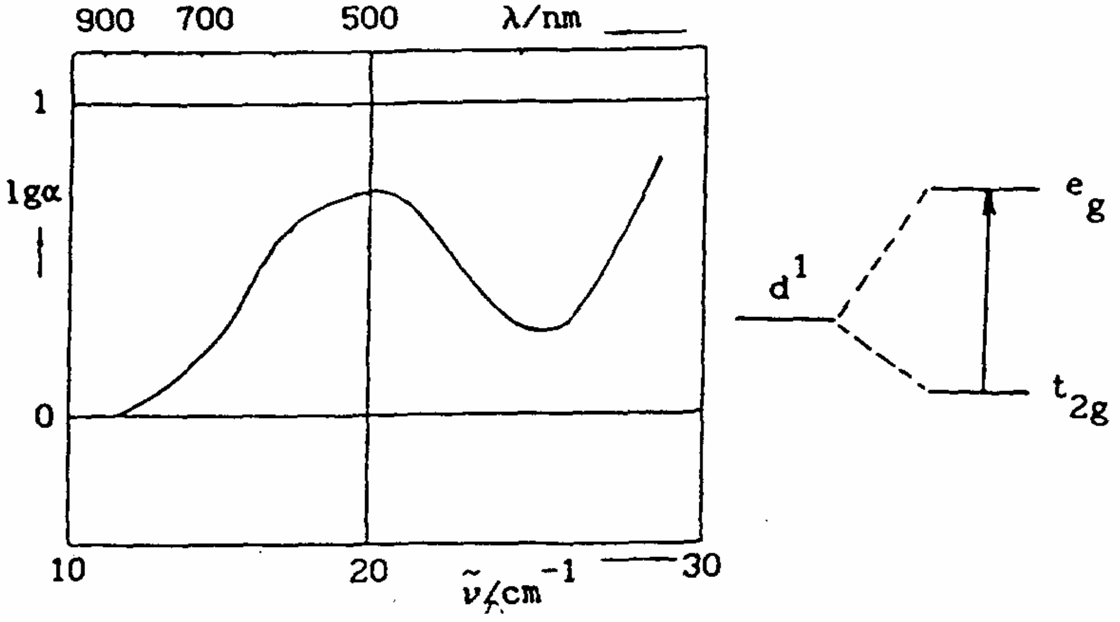

Fig. 3.35

The *charge transfer (CT) transitions* are possible if the polarity of the molecule increases extremely during the transition. The bond is very intense. This is a result of an inter- or intramolecular electron jump. The CT is frequent in excitation of metal complexes (ion-ligand transfer) and also in simple molecule, e.g. nitrobenzene. Fig. 3.36 shows the electron excitation spectrum of nitrobenzene. The intense band at 39.800 cm^{-1} (251 nm) is a CT band.

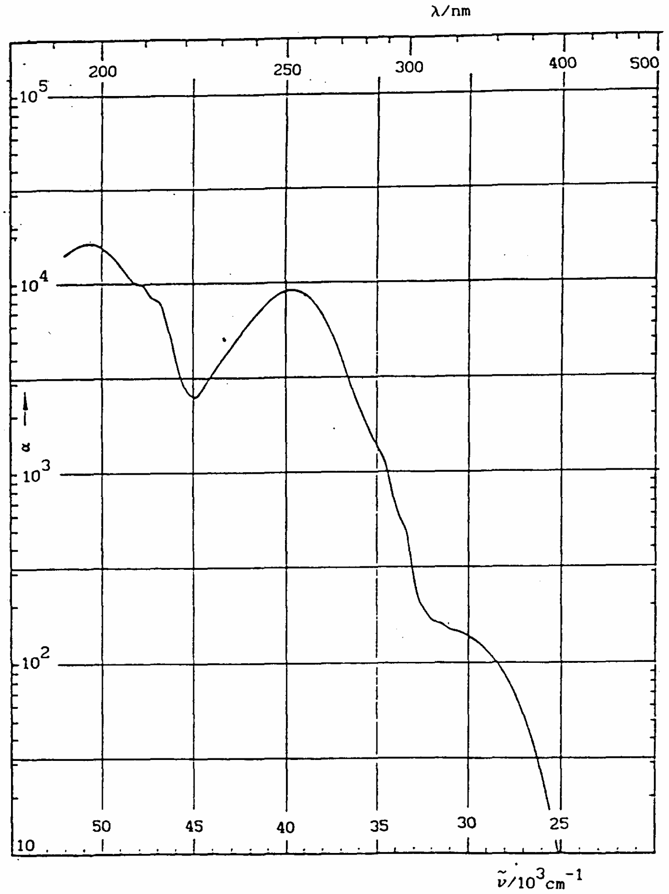

Fig. 3.36

The vibronic transitions are mostly in the vapour spectra observable. Fig. 3.37 is electron excitation spectrum of the benzene vapour. Beside the vibronic bands also combinations and overtones appear. The 0←0 transition is forbidden, but with low intensity appears.

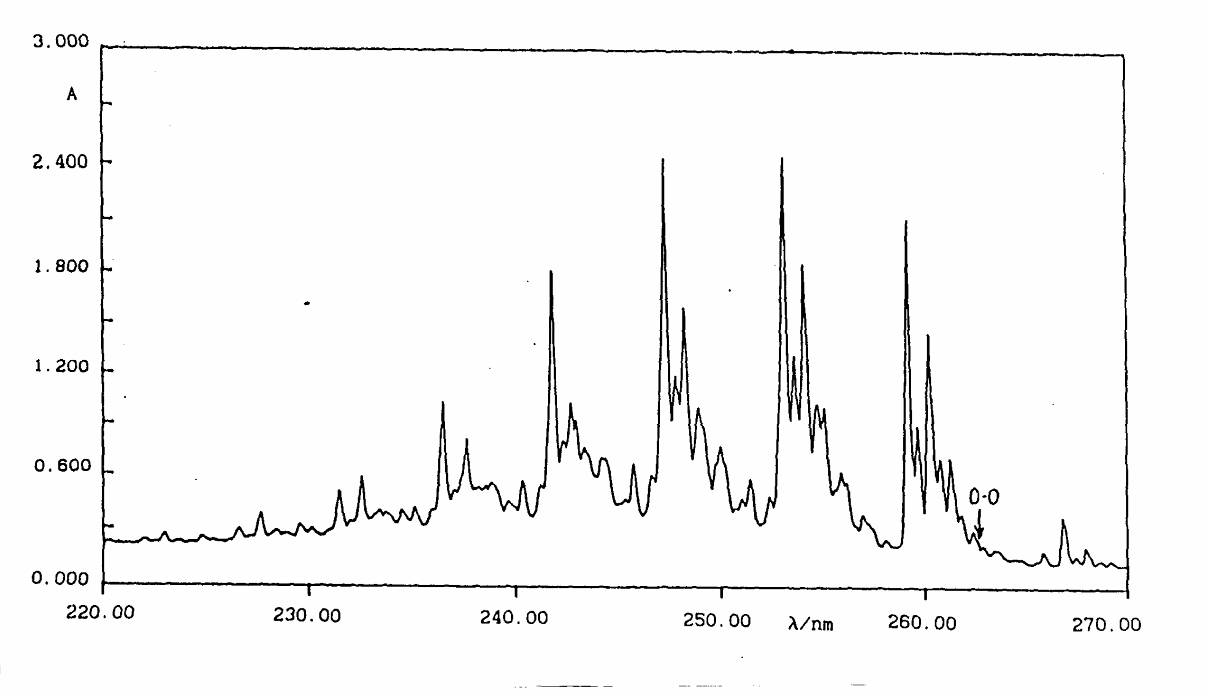

Fig. 3.37

The solvent spectrum of benzene contains less vibronic bands (Fig. 3.38).

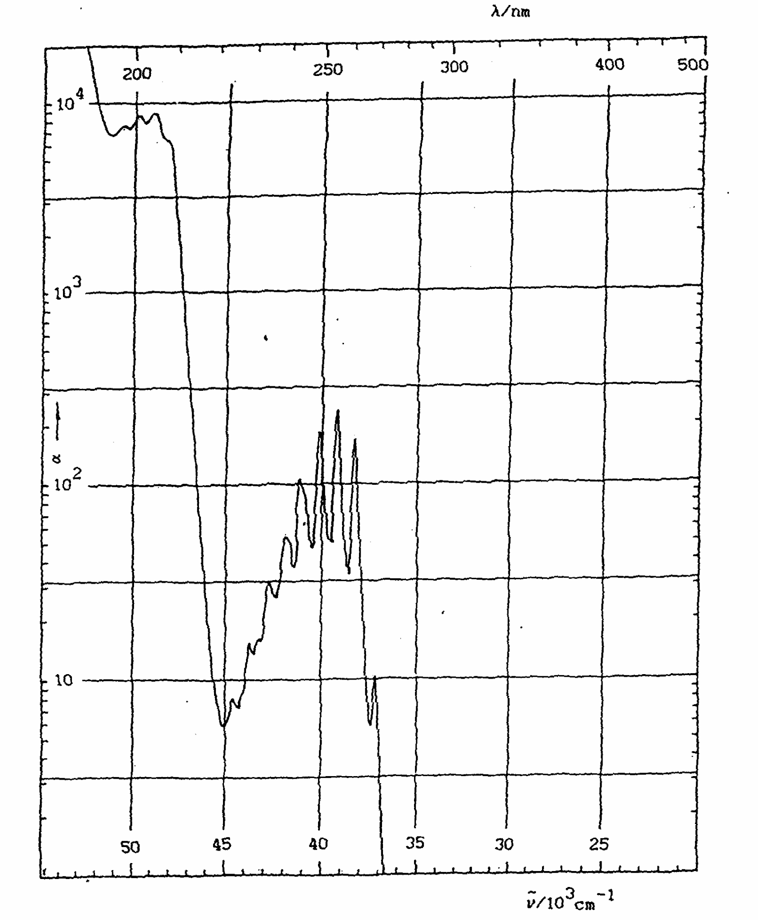

Fig. 3.38

Hot bands appear with increasing temperature: the populations of the higher energy levels increase and they may be also ground states of excitation.

The electron excitation spectrum of the iodine vapour contains also several overtones and combinations (Fig.3.39). In high resolution also the rovibronic lines are observable (Fig. 3.40).

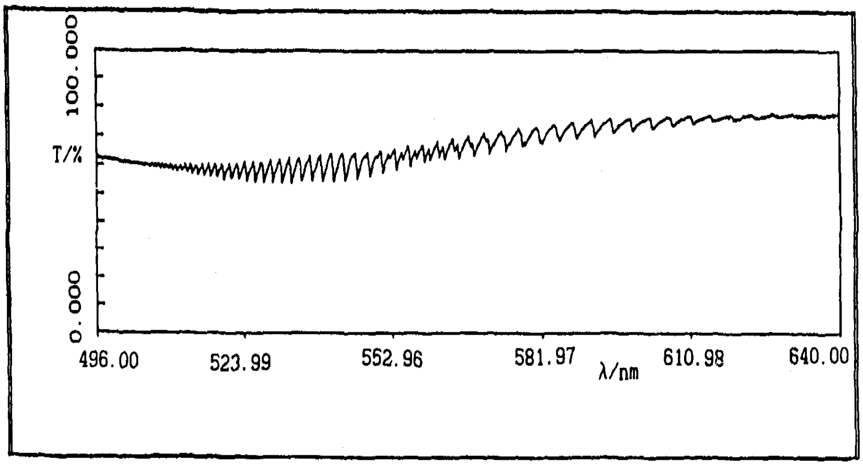

Fig. 3.39

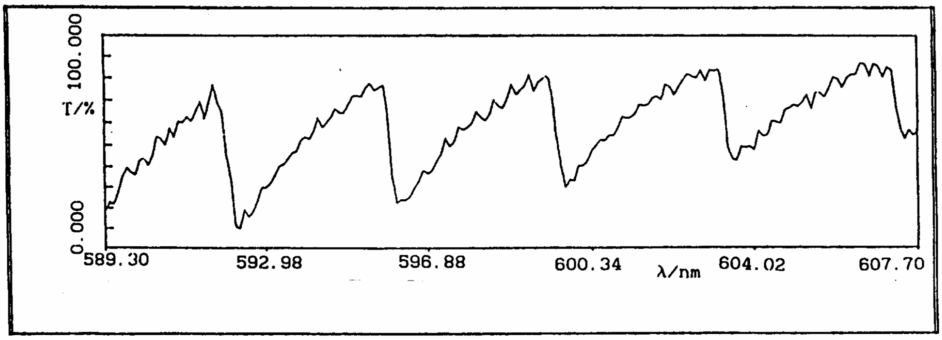

Fig. 3.40

3.6.3 The excited state and its decay

The molecule cannot remain in excited state for a longer time (Subsection 1.5). It loses the received energy either with the emission of a photon (spontaneous emission, *radiative decay*) or with *nonradiative decay.*

The ways of the nonradiative decay may be different:

- energy transfer during collisions (Section 1.2) increasing the internal energy (vibration, rotation) of an other molecule,
- solutes may be interact with the solvent molecule increasing its energy,
- a *photodissociation* process,
- the excited molecule gets reactant in a chemical reaction.

If the molecule emits after the photon absorption a photon immediately, this is the phenomenon of the *fluorescence.* The process illustrated in Fig. 3.41. The molecule absorbs a photon according the Franck-Condon principle, then comes to the v_i=0 level with nonradiative decay and from this level may arrive to the vibrational levels of the ground state with fluorescence. The absorption and the fluorescence spectra are mirror images of one another.

The fluorescence is a spontaneous emission. Its frequency is always lower than that of the absorption. The analytical fluorescence indicators absorb in the UV or in the VIS region near to the UV. The emitted light appears in the VIS. The intensity of the florescence is often very high (e.g. condensed aromatics). The fluorescence is very useful in the detection and quantitative analysis of small quantities of fluorescent substances beside non-fluorescent ones.

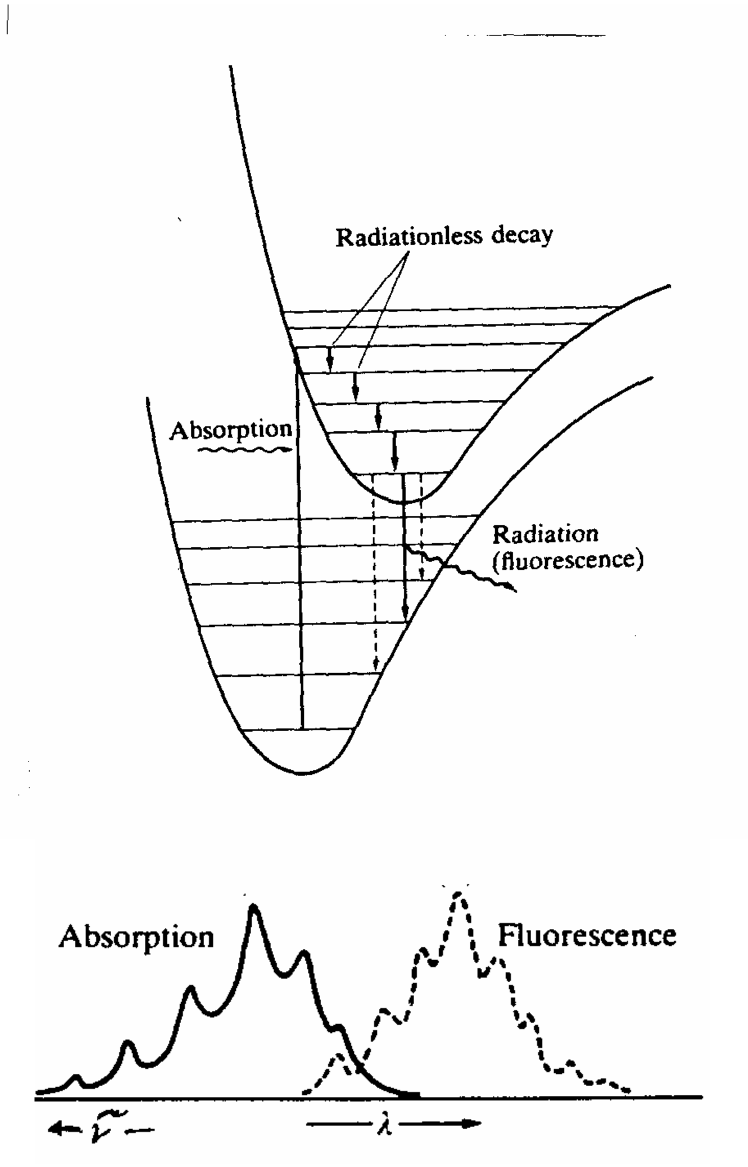

Fig. 3.41

The *phosphorescence* is a spontaneous light emission with a delay of some seconds or minutes. It occurs if the spin-orbital (*jj)* coupling is strong (Section 2.3.2). The multiplicity of the ground state is *singlet* (*S*), the excited state is *triplet* (*T*). The potential energy curves may cross one another in excited states (Fig. 3.42). The molecule arrives the excited state during absorption. From this state it loses its energy in non-radiative decay until the cross-point of the two curves. Here is the geometry of the two states the same. From this point the molecule is in triplet state since this has the lower energy. Continuing the non-radiative decay the molecule arrives the $v_i=0$ level on this curve. Since the ground state is singlet, the excited state is triplet and the ΔS=0 selection rule is valid, the molecule is in an energy hole. Since this rule is valid strictly for *ls* coupling and here is also the *jj* coupling important, the validity of the rule is not so strong, the *S*←*T* transition has a finite probability. Electron spin resonance (Section 3.9.2) measurements found such kind molecules paramagnetic. The phosphorescence of solid substances may be very strong, see e.g. the computer and television screens.

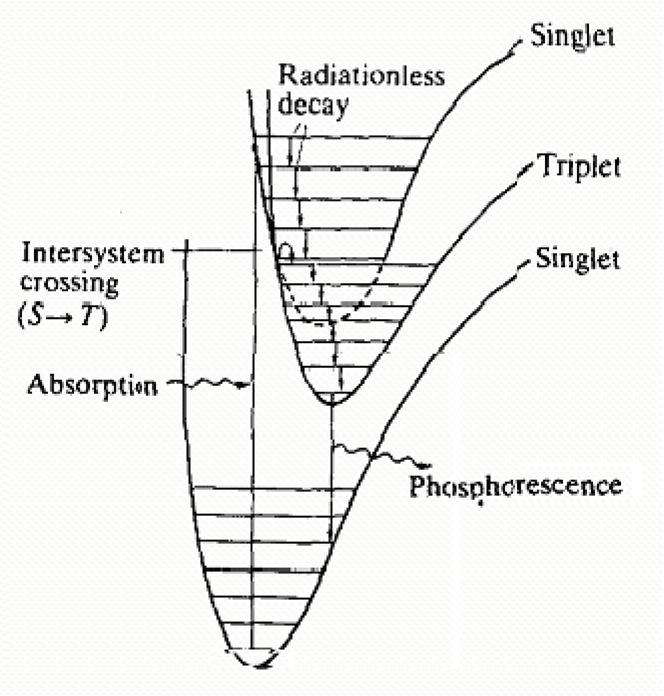

Fig. 3.42

The excitation of the molecule may lead to its *dissociation*. Fig. 3.43 shows us the process of dissociation. The vibrational levels pile up in the region of the long bondlength. There are two possibilities: either the molecule arrives the horizontal part of the potential curve (Fig. 3.43) or its excited state is dissociative (e.g. in the case of diatomic molecules, Fig. 3.44). A continuum is observed in the spectrum in both cases since the molecular energy over the level of dissociation is kinetic energy. The kinetic energy, however, is not quantified. The compounds of the noble gas elements have a dissociative state as ground state and a bonding state as excited one (Fig. 3.45).

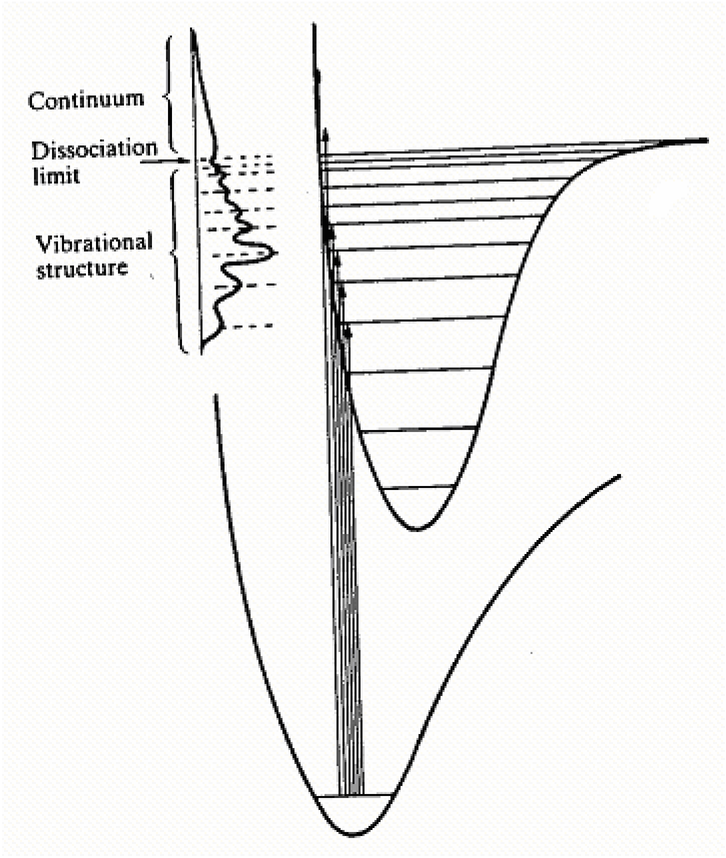

Fig. 3.43

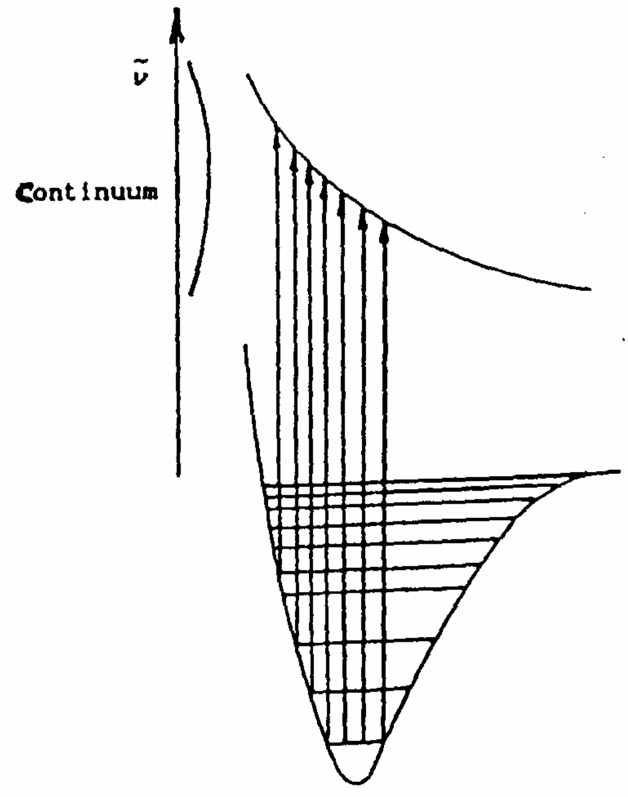

Fig. 3.44

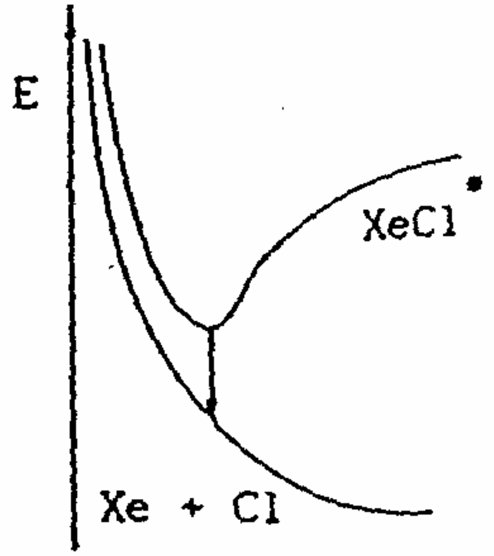

Fig. 3.45

The *dissociation energy* (D) is the energy that is necessary to bring the molecule from its electronic ground state into dissociate state.

If the molecule comes during the excitation into a state where the potential curve of a dissociative state crosses the potential curve of the excited bonding state we find in the spectrum a diffuse region before the dissociation but at higher energies again a vibrational structure. This phenomenon is called *predissociation* (see. Fig. 3.46). If the crossing point energy is equal to the energy of a vibrational level of the bonding state the molecule may change its bonding state to the dissociative state.

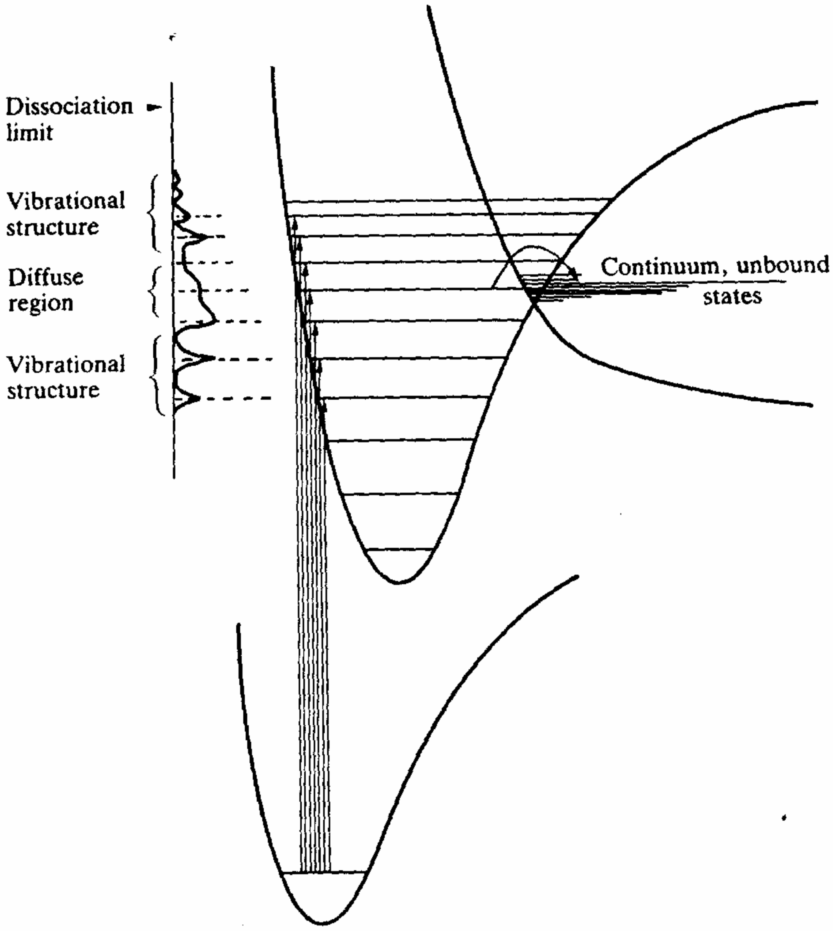
Dissociation limit
Vibrational structure
Diffuse region
Vibrational structure
Continuum, unbound states

Fig. 3.46