3.4 The rotation of molecules

3.4.1 Introduction

Born and Oppenheimer proved: the energy yielded as solution of the Schrödinger equation of molecules is may be regarded in first approach as the sum of the rotational, vibrational and electron energies. The kinetic energy is not quantified, and therefore the molecule is studied in a system fixed to itself. Therefore inertial forces like Coriolis and centrifugal ones may appear in the system.

Applying a better approach it can be proved, in a good agreement with the experimental results that these three types of motions are in interaction. The change in the vibrational state influences the rotational state, the change in the electron state influences both the vibrational and rotational states of the molecule.

3.4.2 Rotational motion of diatomic molecules

The kinetic energy of the rotating bodies is described by

$$T = \mathrm{E}_r = \frac{1}{2} I\omega^2 = \frac{1}{2}\frac{L^2}{I} \tag{3.28}$$

I is the moment of inertia, L is the angular moment, ω is the angular velocity. The quantum chemical problem is the calculation of the eigenvalues of the operator $\hat{L}^2$. We discussed this problem studying the hydrogen atom (Eq. 2.12). Here, similarly, the eigenvalues of the angular moment are quantized:

$$L = \sqrt{\mathrm{J}(\mathrm{J}+1)}\hbar = \mathrm{J}^*\hbar \qquad \mathrm{J} = 0,1,2,3,... \tag{3.29}$$

J is the rotational quantum number. The length of the L_Z component is determined by the M_J magnetic quantum number

$$L_z = \mathrm{M_J}\hbar \qquad -\mathrm{J} \le \mathrm{M_J} \le \mathrm{J} \tag{3.30}$$

Using the *rigid rotator* approach (the atomic distances do not change with the change of the rotational energy),

$$\mathrm{E_r} = \frac{\hbar^2}{2I}\mathrm{J}(\mathrm{J}+1) = B'\mathrm{J}(\mathrm{J}+1) \tag{3.31}$$

with the rotational constant

$$B' = \frac{\hbar^2}{2I} \tag{3.32}$$

This quantity has the dimension of the energy. Since the experimental data appear in MHz and cm^{-1} units, the rotational constants are used in the forms B'/h (MHz) or B=B'/hc (cm^{-1}).

The relative positions of the energy levels of a rigid rotator are shown in Fig. 3.12. The energy level differences increase with increasing rotational quantum number. The energy levels split if an external magnetic (Zeeman effect, Section 2.3.3) or an electric field (Stark effect, Section 2.3.4) acts on the molecule, i.e. the rotational energy levels are degenerated.

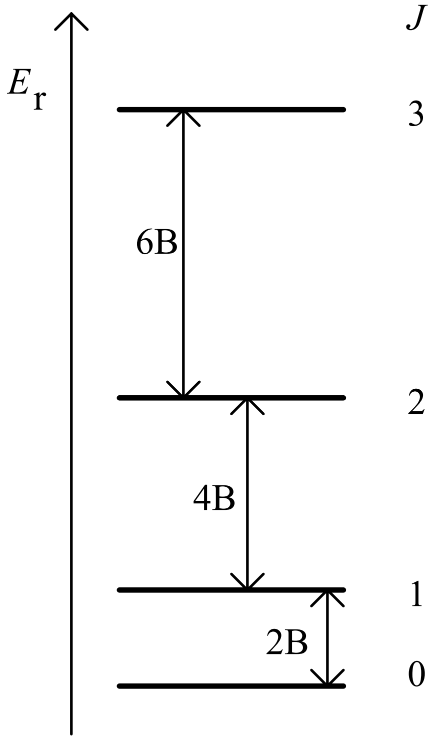


Fig. 3.12

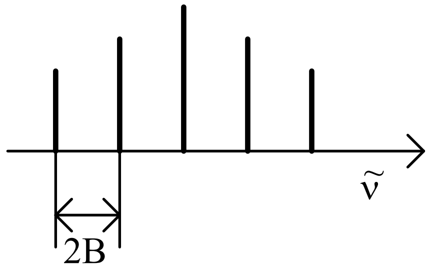


Fig 3.13

According to the definition of the moment of inertia for point systems for a rotational axis

$$I = \sum_{i=1}^{N} m_i r_i^2 \tag{3.33}$$

m is the mass of the atom, r is its perpendicular distance from the axis, N is the number of atoms. The moment of inertia is for a diatomic molecule for an axis that crosses the mass center and is perpendicular to the valence line

$$I = \mu r_o^2 \tag{3.34}$$

r_o is the distance between the two atoms and

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \tag{3.35}$$

is the *reduced mass of the molecule.*

3.4.3 The rotational spectra of the diatomic molecules

Substituting the eigenfunctions of the rotational states into the expression of the transition moment (Eq. 1.46) the following selection rules may be derived:

$$\Delta J = \pm 1 \quad \text{and} \quad M_J = \pm 1 \tag{3.36}$$

Supposing constant atomic distances during the excitation (rigid rotator) the frequencies (as wavenumbers) of the rotational lines are

$$\tilde{\nu} = \frac{E_{r,i} - E_{r,j}}{hc} = B[(J+1)(J+2) - J(J+1)] = 2B(J+1) \qquad (3.37)$$

with

$$B = \frac{B'}{hc} = \frac{h}{8\pi^2 cI} \qquad (3.38)$$

The quantum number J in Eq. 3.37 belongs to the lower energy state. The rotational lines of a rigid rotator are equidistant (see Fig. 3.13).

The rigid rotator model is a good approach. In the reality, however, the atomic distances increase with increasing J. The chemical bonds are elastic, therefore the increasing centrifugal force stretches the bonds. The result is a greater moment of inertia, and so a decreasing rotational constant. For *non-rigid (elastic) rotators* the distances between the energy levels decrease with increasing J. Looking the rotational spectral lines we find their decreasing distance with the rotational quantum number.

The pure rotational spectra appear in the microwave (MW) and in the far infrared (FIR) regions (Fig. 1.12).

The *intensity* of the spectral lines depends on the relative populations of the energy levels. According to Boltzmann's distribution low

$$N_J = N_0(2J+1)\exp\left(-\frac{E_{r,J}}{kT}\right) = N_0(2J+1)\exp\left[-\frac{B'J(J+1))}{kT}\right] \qquad (3.39)$$

N_J is the number of molecules on the J-th level, $2J+1$ is the degree of degeneration according to the magnetic quantum number. According Eq. 3.39 N_J has a maximum (see also Figs. 3.15 and 3.16).

The rotational spectra can be measured recording microwave (MW), far infrared (FIR) or Raman (RA) spectra.

Microwave spectra. Fig. 3.14 presents the flow chart of a microwave spectrometer. Microwave spectra are excited with a tuneable signal source (SS), this is e.g. a reflex-clystron, or a Gunn diode. The waves propagate along tubes having squared cross-sections. A part of the waves crosses the sample (S). The signal is detected by a crystal detector (CD). The CD output is proportional to the intensity of the MW signal. The electronic system (E) elaborates the CD output signal. An other part of the waves is used for the frequency calibration. They are mixed to the frequency standard (FS) by the frequency mixer (FM) and the mixed wave is detected by a radio receiver (RR) that generate the frequency differences. The spectrum will be printed (P) or presented on the screen of a computer.

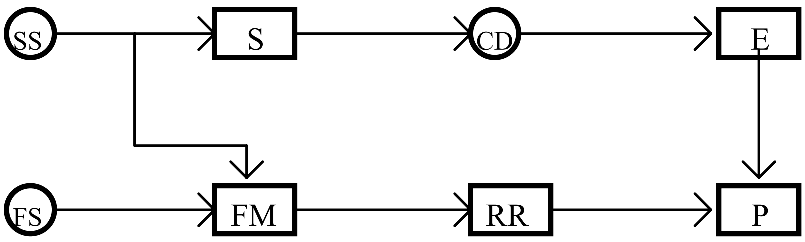


Fig. 3.14

Far infrared spectroscopy. This is a FT spectrometer (see Fig. 1.14). The optical material is polyethylene, the beam splitter is polyethylene-terephtalate foil.

The molecule have to have a permanent dipole moment, since otherwise the transition moment is zero. Therefore the diatomic molecules with two equivalent atoms have not pure rotational MW or IR spectra. Fig. 3.15 presents the rotational IR spectrum of $H^{35}Cl$.

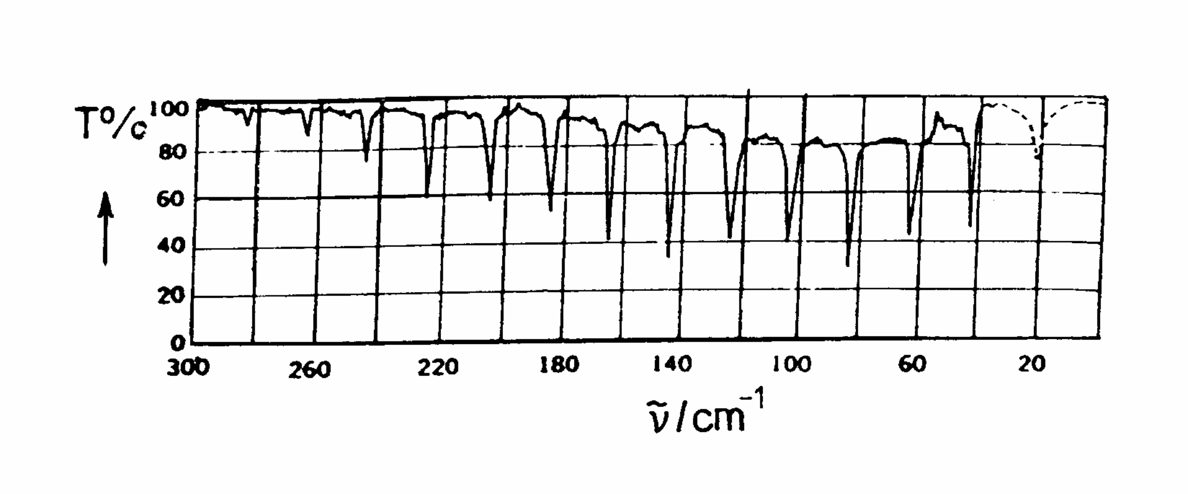


Fig. 3.15

Raman spectroscopy. Raman spectroscopy is a special method of the rotational and the vibrational spectroscopy. This is a scattering spectrum. Spectrum lines are observed in the direction mostly perpendicular to the exciting light (a VIS or NIR laser beam) beside the original signal (Fig. 3.16). The effect is called Raman scattering, the spectral lines are lines of the *Raman spectrum.* The series that appear at lower frequencies than the that of the exciting beam ($\tilde{\nu}_o$) are the *Stokes lines*, the lines having higher frequencies than $\tilde{\nu}_o$ are the *anti-Stokes lines* (Fig 3.16). The intensities of the anti-Stokes lines are lower than that of the Stokes lines, since the populations of their ground states are smaller. Therefore the Stokes lines are detected. The *Raman shifts,* $\Delta\tilde{\nu}_i = \tilde{\nu}_o - \nu_i$ *give the frequencies of the rotational lines.*

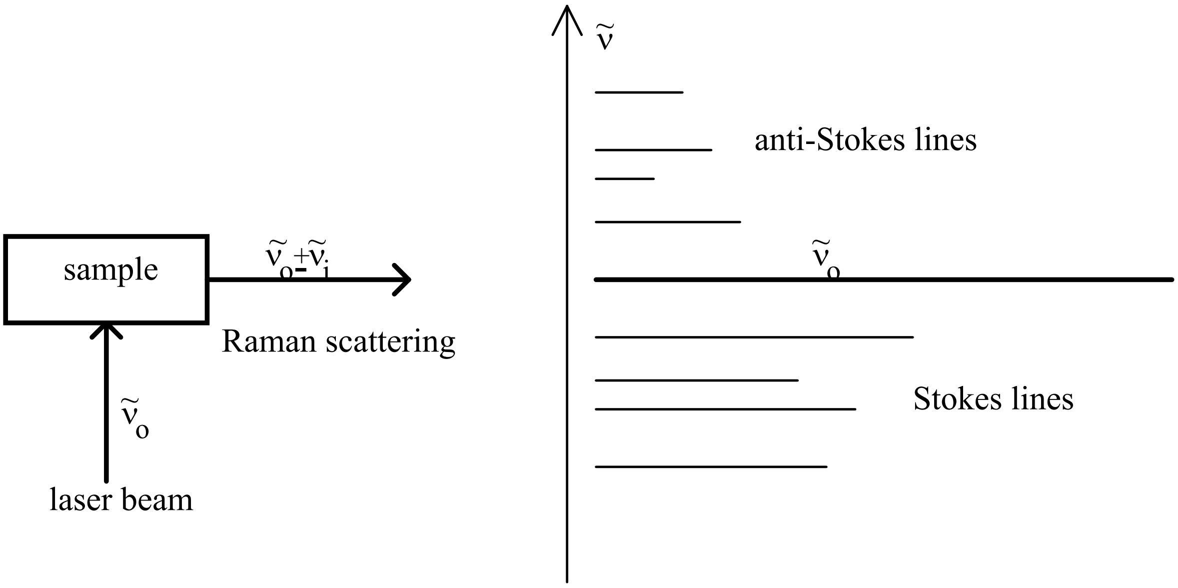


Fig. 3.16

The Raman lines appear if the polarizability (Section 1.3) of the molecule changes during the transition,

$$\Delta\mathbf{p} = \Delta\alpha * \mathbf{E} \tag{3.40}$$

The selection rules are

$$\Delta J = \pm 2 \qquad \text{for identical atoms} \tag{3.41}$$

This is a difference in comparison with the MW and IR spectra.

$$\Delta J = \pm 1, \pm 2 \qquad \text{for different atoms} \tag{3.42}$$

Each second line is very weak in the rotational Raman spectrum of the oxygen molecule (Fig. 3.17), therefore they are not observable in the spectrum (this is an exclusion).

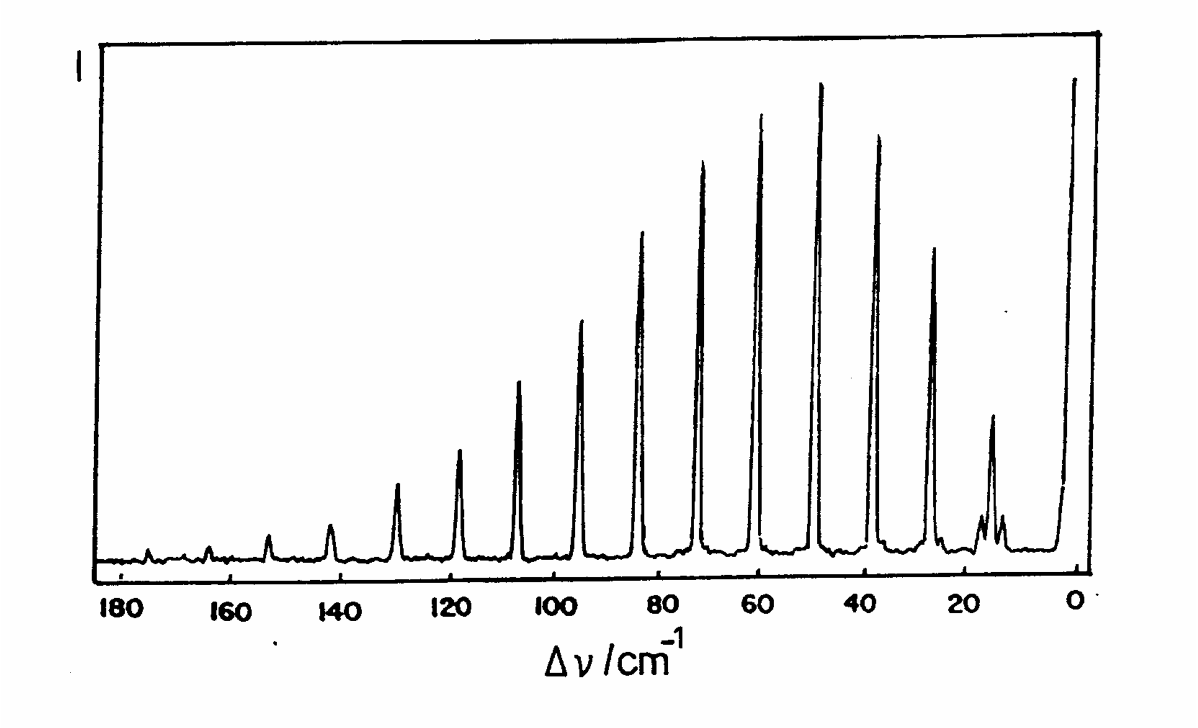


Fig. 3.17

The *bond length* of a diatomic molecule is easily calculable from the rotational spectrum. According to Eq. 3.37 the distance between the rotational lines is 2B. The distances of the lines (Fig. 3.15) are 20.7 $\mathrm{cm^{-1}}$. Using Eq. 3.38, $I = 2.703 \times 10^{-27}$ kg $\mathrm{m^2}$. Therefore the bond length is 129 pm. Similarly, taking into account the line distance in the Raman spectrum of oxygen (11.5 $\mathrm{cm^{-1}}$) and it is equivalent with 4B, the bond length in the oxygen molecule is 121 pm.

3.3.4 The rotational spectra of polyatomic molecules

It is suitable to calculate the rotational motion of the polyatomic molecules in a coordinate system fixed to the molecule. Its origin is the mass center, the axes coincide with the principal inertial axis of the molecule. The value of the moment of inertia depends on the direction of the rotational axis. There exists an axis with maximal (C) and an other with minimal (A) moment of inertia. These axes are perpendicular each to the other. The third axis (B) is perpendicular to both the C and the A axes.

From the viewpoint of rotation the molecules are rotating tops (rotators). Four top types exist:

Top type	Relation	Examples
Spherical	$I_A = I_B = I_C$	CH_4, SF_6
Symmetric, prolate	$I_A < I_B = I_C$	CH_3Cl, NH_3
Symmetric, oblate	$I_A = I_B < I_C$	$CHCl_3$, benzene
Asymmetric	$I_A \neq I_B \neq I_C$	H_2O, C_2H_4

The simplest is the expression for *spherical top molecules* since the Equ. 3.37 is valid.

The quantum chemistry yields for the energy levels of the non-linear *symmetric top molecules* the following equation:

$$E_r = hc\left[BJ(J+1) + (A-B)K^2\right] \tag{3.43}$$

for proplate molecules, and

$$E_r = hc\left[BJ(J+1) + (C-B)K^2\right] \tag{3.44}$$

for oblate molecules. Beside the rotational quantum number the *nutational quantum number K* plays important role in these equations. It quantifies the component of the angular moment to highest order the symmetry axis of the molecule (e.g. C_6 for the benzene molecule).

For *linear* symmetric top molecules see Equ. 3.37.

Selection rules

for non-linear symmetric top molecules: $-J \le K \le +J$

$\Delta J = \pm 1$ $\Delta K = 0$ (IR) (3.45)

$\Delta J = \pm 1, \pm 2$ $\Delta K = 0$ (RA) (3.46)

for linear symmetric top molecules: $K = 0$

$\Delta J = \pm 1$ (IR) (3.47)

$\Delta J = \pm 2$ (RA) (3.48)

Fig. 3.18 is the rotational IR, Fig. 3.19 is the rotational Raman spectrum of a non-linear triatomic molecule the N_2O (r_{NO}=118 pm, $\angle NON = 140°$). Pay attention on the double density of the RA spectral lines comparing to the IR ones (in the RA spectrum only the ΔJ=-2 transitions appear) and the maxima of the line intensities.

The description of the energy levels of the *asymmetric top* molecules is very complicate. There do not exist solutions for these rotators in closed mathematical form.

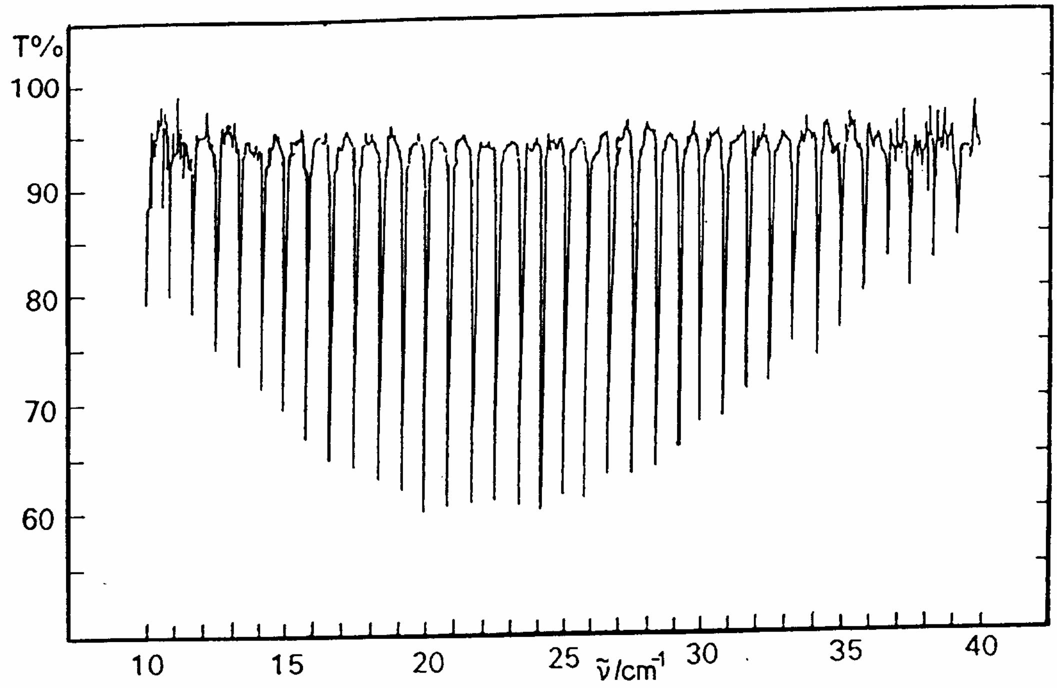


Fig. 3.18

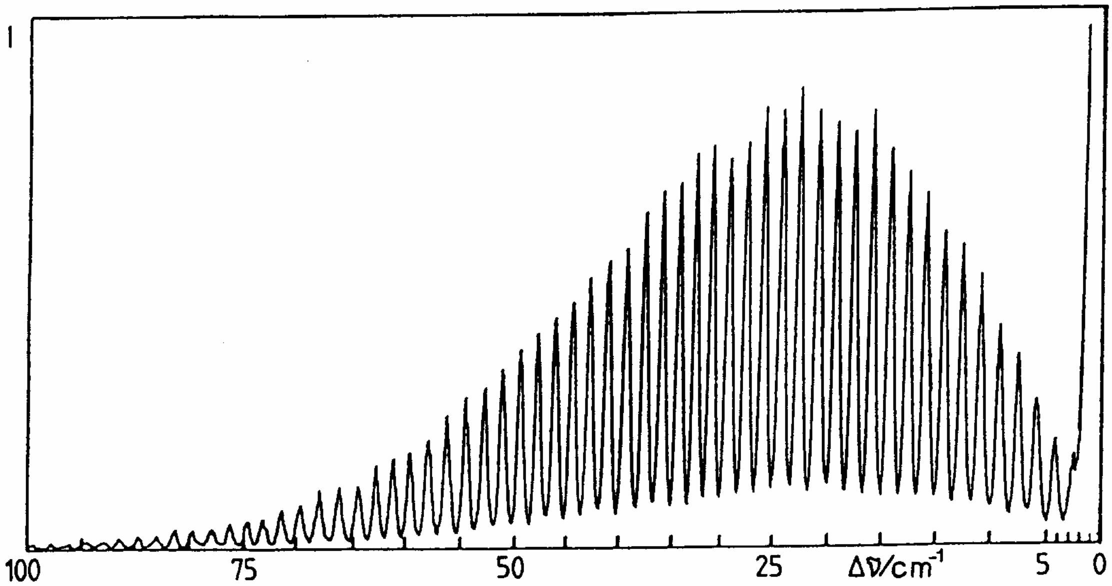


Fig. 3.19

3.5 The vibration of molecules

3.5.1 Vibrational motion of diatomic molecules

We regard the vibration of the molecule in first approach independent of its rotation. As a further approach we apply the *harmonic oscillator model*, i.e. harmonic vibrations are assumed.

The Hamilton operator of a diatomic molecule with a reduced mass μ (Eq. 3.35) is

$$\hat{H} = -\frac{\hbar^2}{2\mu}\frac{d^2}{dq^2} + \frac{1}{2}kq^2 \qquad (3.49)$$

q is the displacement coordinate (in vibrational equilibrium its value is zero), k is the force constant of the harmonic vibration; the first term is the operator of the kinetic, the second term is the operator of the potential energy of the oscillator.

The solution of the Schrödinger equation with the operator in Eq. 3.49 is

$$\mathrm{E_v} = \mathrm{h}\nu\left(\mathrm{v} + \frac{1}{2}\right) \qquad \mathrm{v} =,1,2,... \qquad (3.50)$$

v is the *vibrational quantum number*, ν is the oscillator frequency. Since the oscillator energy is not zero even if v=0, the molecule has vibrational zero point energy.

Fig. 3.20 presents the vibrational wavefunctions (dotted lines) and the probability density distributions (full lines). Fig. 3.20 presents the vibrational wavefunctions (dotted lines) and the probability density distributions (full lines). Fig. 3.21 introduces the equidistant energy levels (full lines) and the potential energy curve of the harmonic oscillator (dashed line).

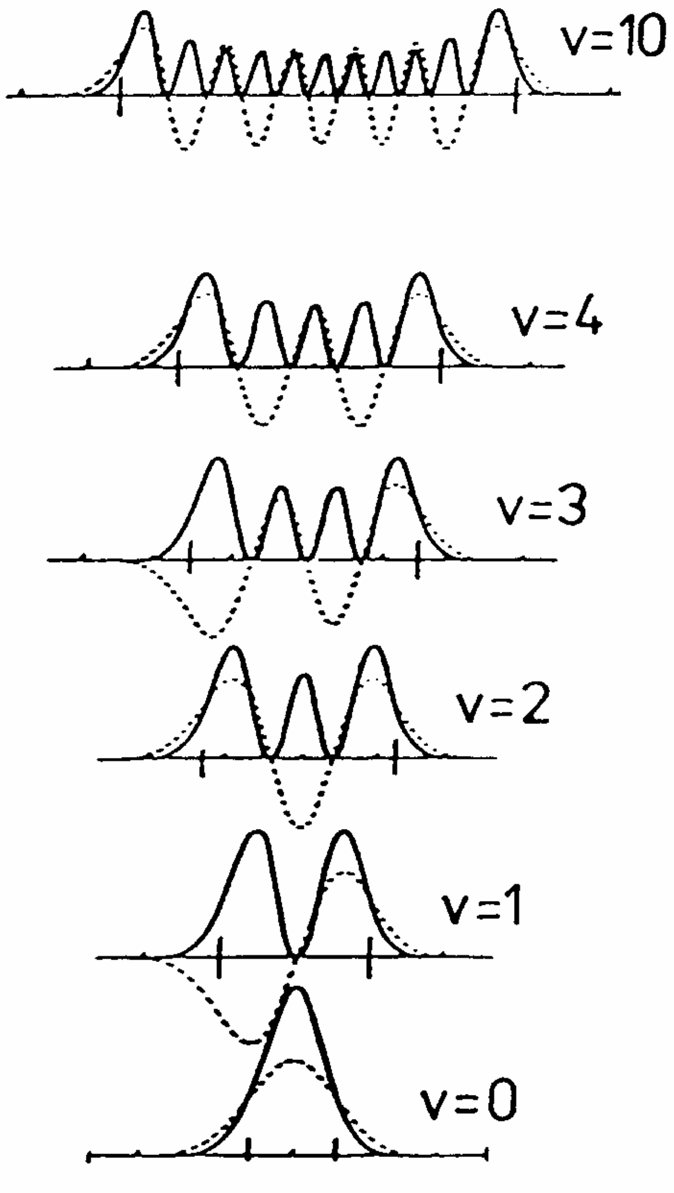


Fig. 3.20

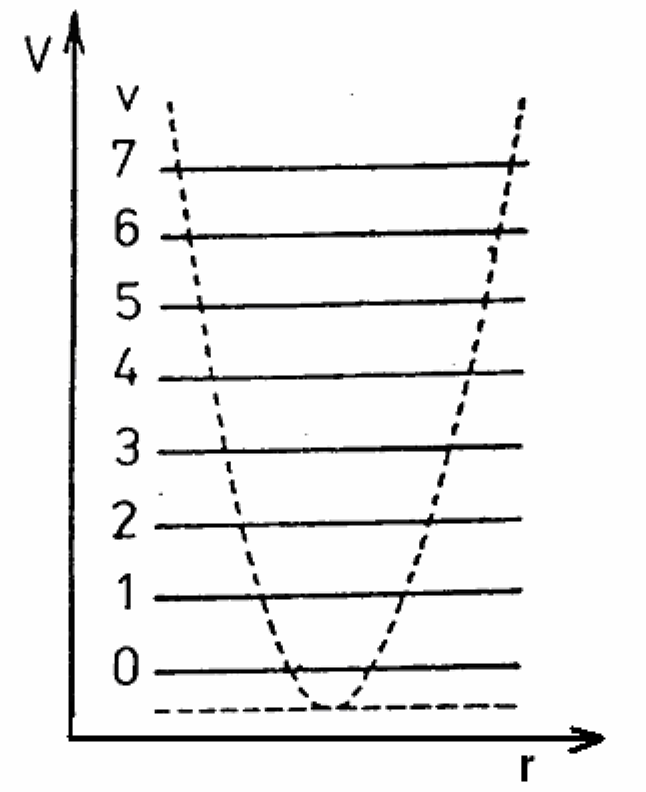


Fig. 3.21

The probability density distribution of the v=1 state is very similar to the classical mechanical model of the vibrations. According to the classical model the system has also two points with maximal staying time. Since the most important transition is v=0 → v=1, the mechanical model is a good approach.

The predominant parts of the molecules are at room temperature in ground state (v=0).

3.5.2 Vibrational spectra of diatomic molecules

The spectra are recorded applying infrared or Raman spectroscopy.

Infrared spectra are measured with dispersive (mostly in the past) (Fig. 1.13) or Fourier transform (Fig. 1.14) spectrometers (recently).

The *selection rules* are for IR spectra from the definition of the transition moment (Eq. 1.46)

$$\Delta v = \pm 1 \qquad \text{(+: absorption, -: emission)} \qquad (3.51)$$

Mostly absorption spectra are recorded, the measurement of the emission spectra is difficult. According Eq. 1.49 the vibrational transition is *infrared active* if the molecule has permanent dipole moment (necessary condition, as for the rotational spectra). Therefore the X_2 type molecules have not IR spectra.

Raman spectra are measured classically with perpendicularly incident laser light applying a monochromator, or with the introduction of the laser light in a FT spectrometer (in Fig. 1.14 the light source is replaced with the scattered light beam). The *selection rules are* as Eq. 3.51. Since the Raman activity depends on the change in the components of the probability tensor the X_2 molecules are *Raman active*.

The real vibrations are *anharmonic* (Fig. 3.22). Therefore the selection rule (Eq. 3.51) is not severe. Overtones ($\Delta v = v_i - v_j \quad j = 0, i = 2,3,...$) appear with low intensity. The density of the overtone bands increases with increasing v_i. The energy of the anharmonic oscillator is (approach):

$$E_v = h\nu\left[\left(v + \frac{1}{2}\right) - x\left(v + \frac{1}{2}\right)^2\right] \tag{3.52}$$

x is the anharmonicity factor.

Increasing the ambient temperature the population of the higher levels increase and the bands belonging to the excitations from these levels also appear in the spectrum ("hot bands"). A considerably excitation leads to the dissociation of the molecule (Fig. 3.22). The energy difference of the v=∞ and the v=0 states is the *dissociation energy* (D) of the molecule, r is the bond length.

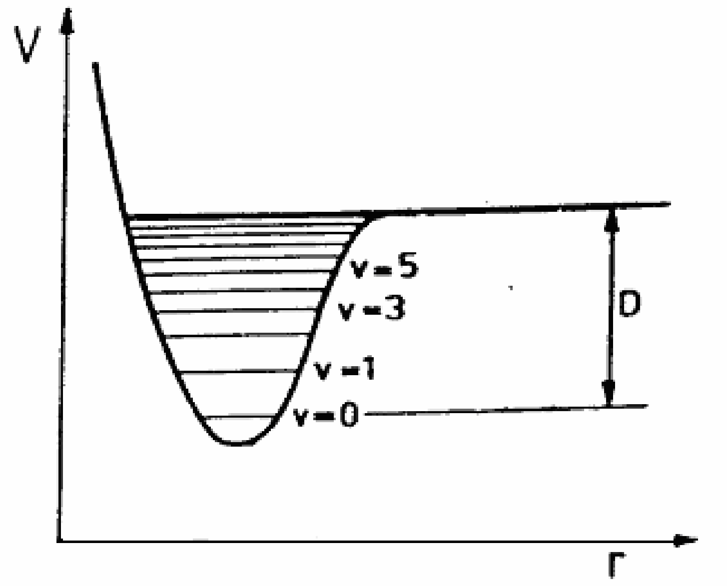


Fig. 3.22

3.5.3 Vibrations of polyatomic molecules

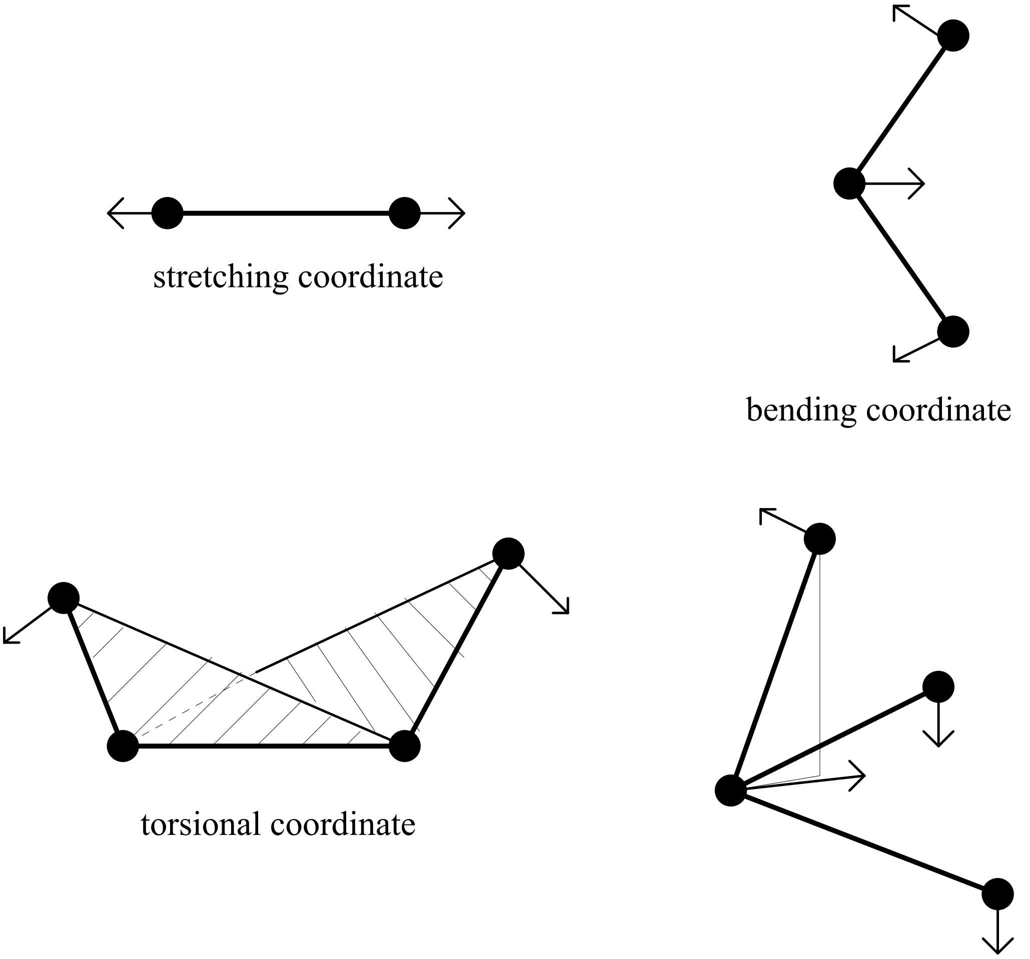
An N-atomic molecule has 3N degrees of freedom. Three of them are translations, three of them are rotations (for linear molecules only two), the other 3N-6 (for linear molecules 3N-5) are vibrational degrees of freedom.

For the description of the vibrational motions of polyatomic molecules three coordinate types are used. Each is fixed to the molecule, i.e. they are internal coordinates.

1. *Cartesian displacement coordinates* (r). They are zero in the equilibrium position. An N-atomic molecule has 3N Cartesian displacement coordinates. Instead of these coordinates sometimes the so-called *mass weighted coordinates* (q) are applied. The Cartesian displacement coordinates are multiplied with the square root of the mass of the corresponding atoms.

2. *Chemical internal coordinates* (S). These are the changes in the geometric parameters of the molecule. Four types of chemical internal coordinates exist (see Fig. 3.23):

- stretching coordinate, i.e. change in bond length;
- bending coordinate , i.e. change in the valence angle (in-plane deformation);
- dihedral angle coordinate, i.e. change in the dihedral angle (out-of-plane deformation);
- torsional coordinate, i.e. change in the torsion.



stretching coordinate

bending coordinate

torsional coordinate

dihedral coordinate

Fig. 3.23

3. *Normal coordinates* (Q). Applying these are coordinates the Schrödinger equation of the vibrational motion of molecules separates into 3N-6 (3N-5) independent equations. Each depends only on one normal coordinate and is therefore relatively easily solvable.

It seems, the application of the normal coordinates is the most reasonable for the solution of the vibrational problems. Using normal coordinates the equations of the kinetic and potential energies have the form in the framework of the classical mechanical harmonic model:

$$2V = 4\pi^2 c^2 \sum_{i=1}^{3N-6} \tilde{\nu}_i^2 Q_i^2 \qquad 2T = \sum_{i=1}^{3N-6} \dot{Q}_i^2 \tag{3.53}$$

Since the spectra contain information only about the vibrational frequencies we have not information about the normal coordinates. This coordinates can be determinated only by further calculations.

The S and the q (or r) coordinates are applied in the real calculations. The potential and kinetic energies that correspond the Eqs. 3.53 have the form (in vector-matrix formulations):

$$2V = \mathbf{q}'\mathbf{f}\mathbf{q} \qquad 2T = \dot{\mathbf{q}}'\mathbf{g}^{-1}\dot{\mathbf{q}} \tag{3.54}$$

$$2V = \mathbf{S}'\mathbf{F}\mathbf{S} \qquad 2T = \dot{\mathbf{S}}'\mathbf{G}^{-1}\dot{\mathbf{S}} \tag{3.55}$$

q and **S** are column vectors of dimension 3N-6, **f** and **F** are the force constant matrices(they are the unknown quantities), **g** and **G** are the inverse kinetic energy matrices, they depend only on the atomic masses and geometric parameters of the molecule. The solution of the equation of motion (applying Eq. 3.55) lead to the eigenvalue equation

$$|\mathbf{GF} - \lambda\mathbf{E}| = 0 \tag{3.56}$$

the λ's are the eigenvalues containing the vibrational frequencies, **E** is a unit matrix. The solutions are

$$\lambda_i = 4\pi^2 c^2 \tilde{\nu}^2 \qquad i = 1,2,\ldots,3N-6 \tag{3.57}$$

The eigenvectors are columns vectors. Fitting these column vectors each beside the other we have the eigenvector matrix **L**. Wit the help of this matrix we can calculate the normal coordinates:

$$\mathbf{Q} = \mathbf{L}^{-1}\mathbf{S} \tag{3.58}$$

Since the S coordinates are known Eq. 3.58 give us the possibility to calculate the largeness and the direction of the atomic displacements in the normal coordinates. The movements belonging to the individual normal coordinates are the *vibrational modes* (or *normal modes*) of the molecule, the corresponding frequencies are the *fundamental or normal frequencies*.

If the **F** matrix is known the frequencies become calculable using Eq. 3.57. The **F** matrix was calculated earlier with the help of the frequencies and isotopomer frequencies of the molecule. Today, with the development of the quantum chemistry and the computer technology the calculation of **F** matrices is already possible. The basis of these calculations if the equation

$$\mathrm{F_{ij}} = \left(\frac{\partial^2 \mathrm{E}}{\partial \mathrm{S_i} \partial \mathrm{S_j}}\right)_0 \quad \text{or} \quad \mathrm{f_{ij}} = \left(\frac{\partial^2 \mathrm{E}}{\partial \mathrm{q_i} \partial \mathrm{q_j}}\right)_0 \tag{3.59}$$

the 0 subscript refers to the equilibrium position. The differentiation is either once analytical and one numerical or twice analytical. The result is the **f** matrix that is to be transformed into the **F** matrix.

The values of the calculated force constants depend on the chemical quality of the atoms belonging to the S coordinate, the type of the chemical bonds and the applied quantum chemical method. Since the greatest part of the errors is systematic the calculated force constants are fitted to the measured frequencies by multiplication with scale factors. Chemically similar compounds have transferable scale factors. The calculation of force constants is a very good tool for the interpretation of vibrational spectra.

The change of the diagonal elements of the force constant matrix with the quality of the atoms and the strength of the bonds is well observable on the data of Table 3.9 (average values).

Table 3.9
Force constants of some stretching coordinates (F_{ii} /100 N m^2)

Bond	F_{ii}	Bond	F_{ii}
Hydrides			
H-F	9.7	H-S	4.3
H-Cl	5.2	H-Se	3.3
H-Br	4.1	H-N	6.5
H-I	3.2	H-P	3.1
H-O	7.8	H-As	2.6
Organic compounds			
C-H	4.9-5.9	C-Cl	3.0-3.5
C-C	4.5-5.6	C-N	4.9-5.6
$C=C_{Ar}$	6.6-7.6	$C=N_{Ar}$	6.7-7.8
C=C	9.5-9.9	C=N	10.0-11.0
C≡C	15.6-17.0	C≡N	16.2-18.2
C-O	5.0-5.8	N-N	3.5-5.5
C=O	11.8-13.8	N=N	13.0-13.5

3.5.4 Vibrational spectra of polyatomic molecules

The vibrational spectra of polyatomic molecules are recorded as IR or RA ones. The spectra consist of bands. This has several reasons:

1. the interaction of the vibration with the rotation;
2. intra- and intermolecular interactions;
3. the translational energy of the molecules;
4. the Fermi resonance.

The vibrational spectra contain three types of information: the frequencies, the intensities and the shapes of the bands.

The vibration-rotation interaction. The change in the vibrational state of the molecule may go together with the change in the rotational state. Therefore *rovibrational lines* appear shifted from the vibrational frequency both left and right with the frequencies of the rotational term differences. This is in the gas (vapour) phase observable. Fig 3.24 is a part of the IR vapour spectrum of acetonitrile. The vibrational frequency is 920 cm^{-1}. The line belonging to ΔJ=-1 build the P branch. The Q branch belongs to the ΔJ=0 transitions. TheΔJ=+1 lines build the R branch. If J increases, the moment of inertia also increases, therefore the rotational constant decreases: the lines of the R branch are more dense than that of the P branch. Since the population of the higher rotational levels is smaller the intensities in the R branch are smaller than in the P branch. Band contours appear in the vapour spectra of large molecules at medium resolution instead of the individual lines (the spectrometer builds average).

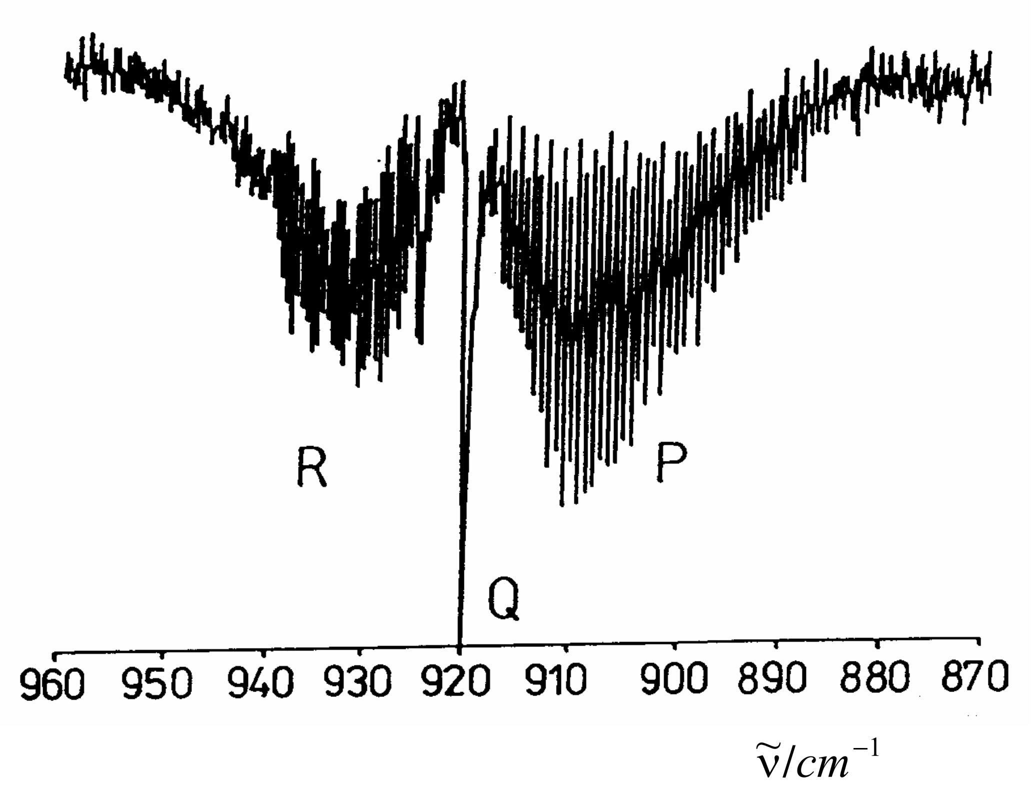


Fig. 3.24

The rotational structure is complicated through the Coriolis vibrational - rotational interaction (one of the inertial forces in non-inertial coordinate systems).

The *inter- and intramolecular interactions* discussed in Section 4.3. The interactions change the energy levels and since the environments of the individual molecules are not the same their frequencies shift individually from the frequency of the separated molecule (in condensed phases).

Doppler effect appear as a result of the velocity distribution of the molecules in gas phase.

Fermi resonance bands appear in the case of the accidental coincidence of two bands with the same symmetry. Their intensities equilize and the bands move away from one another.

Infrared spectra.

The selection rules are the same as for the diatomic molecules (Eq. 3.51). If the molecule has symmetry elements, this selection rules become more sever. Thos vibrational modes are infrared active that have the same symmetry as the translations of the molecule. Table 3.10 completes Table 3.5, T labels the translations, R stands for the rotations and the elements of the polarizability tensor are denoted by α.

Table 3.10
Character table of the point group C_{2v}

C_{2v}	E	$C_2(z)$	σ_{xz}	σ_{yz}		
A_1	1	1	1	1	T_z	$\alpha_{xx}, \alpha_{yy}, \alpha_{zz}$
A_2	1	1	-1	-1	R_z	α_{xy}
B_1	1	-1	1	-1	$T_x;R_y$	α_{xz}

B_2	1	-1	-1	1	$T_y;R_x$	α_{yz}

The IR spectra are measured in gas, liquid (also in solution) and solid state. The spectra are measured generally in solid state, using 0.1-0.2 % of the substance in KBr. This mixture is pressed to transparent KBr discs. The substances have strong absorption in liquid phase, therefore very thin layers are necessary. The same problem arises in solution: the solvents have also strong absorption in some regions of the IR.

Raman spectra.

The *selection rule* is like Eq. 3.51. If the molecule has symmetry, the selection rule becomes more sever. Only those vibrational modes are Raman active that belongs to symmetry species common with at least one of the elements of the α polarizability tensor (see Table 3.10). If a molecule has a symmetry center, the IR and Raman activities mutually exclude one another.

There is a special possibility of the Raman spectroscopy for more information. Supplementing a Raman spectrometer with a polarizer (Fig. 3.25) the detected intensities of the spectral bands depend on the on the direction of the polarizer.

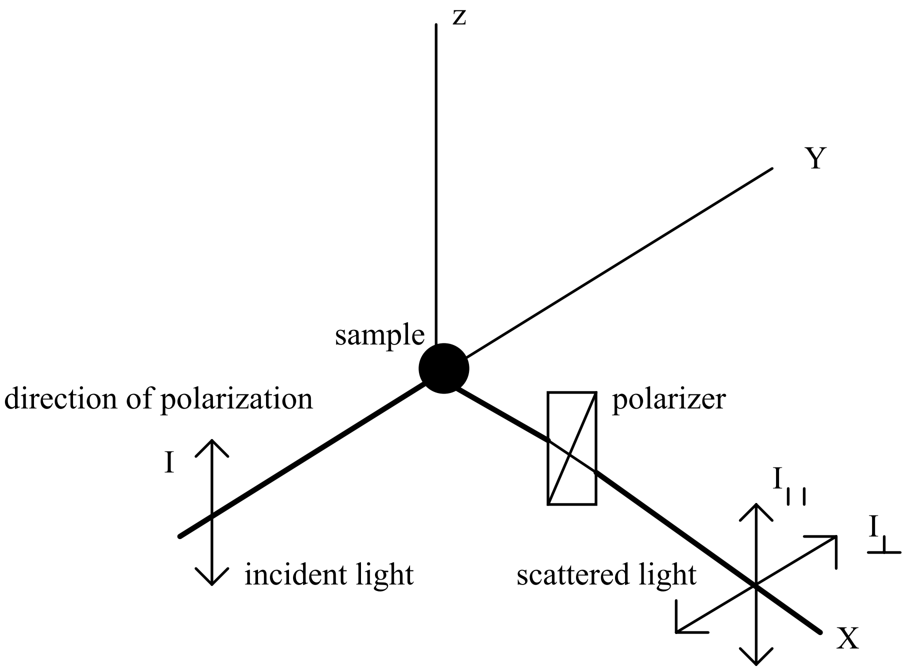


Fig. 3.25

The incident light is polarized in the xz plane. The scattered light is analyzed in parallel and in perpendicular polarizer direction. The *depolarization ratio* of a spectral band is

$$\rho = \frac{I_{\perp}}{I_{\parallel}} \qquad (3.60)$$

The maximal value of ρ is 0.75. The bands belonging to the vibrational modes of the most symmetric species are polarized, i.e. their depolarization ratio is smaller than 0.75. This is a good information for the assignment of these bands (assignment, i.e. the interpretation of the band).

Example

The formaldehyde molecule (4 atoms) has 3×4-6=6 vibrational modes. Their approximate forms are presented in Fig. 3.26.

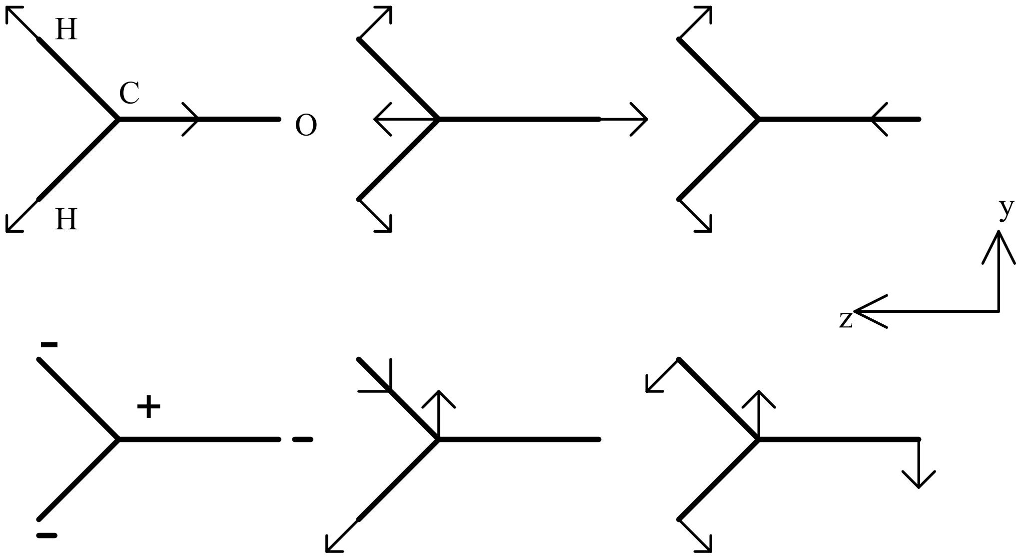


Fig. 3.26

Table 3.11
Character table of the formaldehyde molecule

C_{2v}	E	C_{2z}	σ_{zx}	σ_{yz}	r_i	m_i
A_1	1	1	1	1	T_z	3
A_2	1	1	-1	-1	R_z	0
B_1	1	-1	1	-1	T_x,R_y	1
B_2	1	-1	-1	1	T_y,R_x	2
χ_j	3	-1	1	1		
n_j	4	2	2	4		

Table 3.11 contains the character table of the formaldehyde molecule, the rotation (R) and the translation (T) are also given, m_i give the number of the vibrational miodes. This table will be applied also for the calculation of the number of vibrational mode belonging to the individual symmetry species. This is possible using the χ_j characters of the R symmetry operations:

$$\chi_j = \pm 1 + 2\cos\left(2\pi \frac{p}{n}\right) \qquad p = 1,2,...,n-1 \tag{3.61}$$

The number of the vibrational modes in the i-th symmetry species is

$$m_i = \frac{1}{h}\sum_j n_j \chi_j(R)\chi_{ij} - r_i \qquad (3.62)$$

h is the total number of the symmetry operations, n_j is the number of atoms that are not moved under the effect of the R_j operation, r_i is the number of non-vibrational degrees of freedom belonging to the i-th species (rotations and translations), the χ_{ij} values are elements of the character table.

As it is clear from Fig. 3.26 the formaldehyde molecule is planar, its plane is the zy one. Applying Eq. 3.62 to the species B_1 we have

$$m_i = \frac{1}{4}[4*3*1+2*(-1)*(-1)+2*1*1+4*1*(-1)]-2=1$$

The full representation of the formaldehyde molecule is this like

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

Now let us see Fig. 3.26!

The vibrational modes belonging to A_1 preserve the symmetry of the molecule. The first three formations are of this kind.

The modes belonging to A_2 must be antisymmetric to the molecular plane (zy) since $\chi_{A_2}(\sigma_{yz}) = -1$, and must be similarly also antisymmetric to the perpendicular plane since $\chi_{A_2}(\sigma_{zx}) = -1$. This is possible if only the molecule rotates around the z axis. Therefore $m_{A_2} = 0$.

In species B_1 σ_{yz} has also a character -1, the other mirror plane, however, has a +1 character. Only one mode, the fourth belongs to here. Since a planar molecule with N atoms has N-3 out-of-plane vibrational modes, this is the only out-of-plane mode of the formaldehyde molecule.

The vibrational modes of the B_2 species move again in the molecular plane. They are, however, antisymmetric to the perpendicular mirror plane. The fifth and sixth formations in Fig. 3.26 belong to this species. A planar molecule has 2N-3 in-plane vibrational modes and we found under the 6 formations 5 in-plane modes (A_1 + B_2).

Table 3.11 presents the χ_j characters and the m_i values. According to the mentioned conditions the modes of the species A_1, B_1 and B_2 are IR active and all vibrational modes are RA active.

Example

The pyrazine molecule (1,4-diazine) belongs to the D_{2h} point group. The molecule is planar in the xy plane. The character table of this group is presented in Table 3.12.

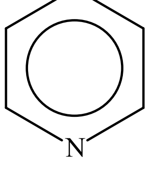


Table 3.12
The character table of the point group D_{2h}

D_{2h}	E	C_{2z}	C_{2y}	C_{2x}	i	σ_{xy}	σ_{xz}	σ_{yz}	
A_g	1	1	1	1	1	1	1	1	$\alpha_{xx},\alpha_{yy},\alpha_{zz}$
B_{1g}	1	1	−1	−1	1	1	−1	−1	R_z,α_{xy}
B_{2g}	1	−1	1	−1	1	−1	1	−1	R_y,α_{xz}
B_{3g}	1	−1	−1	1	1	−1	−1	1	R_x,α_{yz}
A_u	1	1	1	1	−1	−1	−1	−1	
B_{1u}	1	1	−1	−1	−1	−1	1	1	T_z
B_{2u}	1	−1	1	−1	−1	1	−1	1	T_y
B_{3u}	1	−1	−1	1	−1	1	1	−1	T_x

According to Eq. 3.62 the full representation of the pyrazine molecule is

$$\Gamma = 5A_g + 4B_{1g} + 2B_{2g} + B_{3g} + 2A_u + 2B_{1u} + 4B_{2u} + 4B_{3u}$$

10 vibrational modes are IR active, 12 modes are RA active, 2 do not appear in the spectra. Since the molecule has a symmetry center, the IR active modes do not appear in the RA and vice versa.

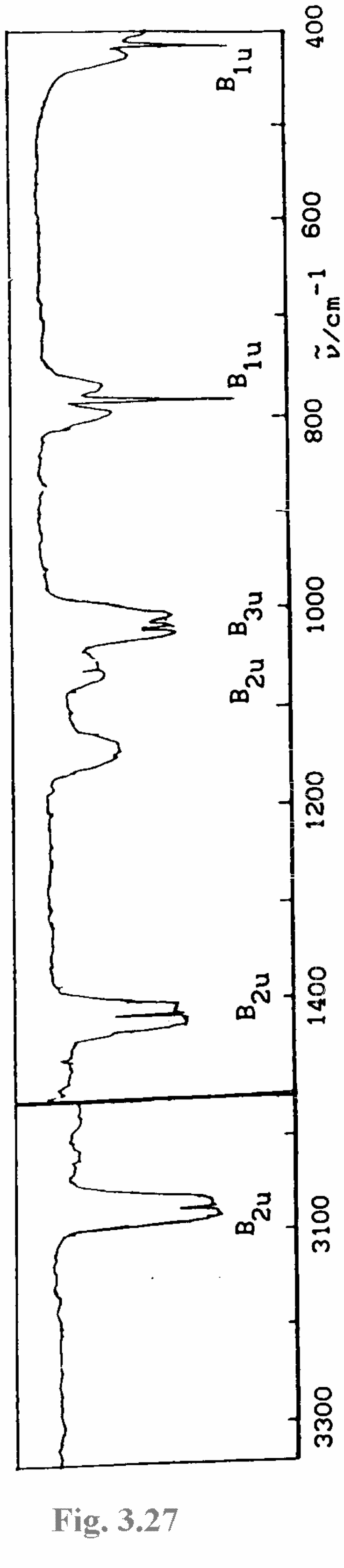
The IR vapour spectrum is Fig. 3.27. The molecule is an asymmetric top. The shape of the band in characteristic to the direction of the transition.

Z ~ B_{1u} ~ maximal moment of inertia ~ C band (very strong Q branch).

Y ~ B_{2u} ~ medium moment of inertia ~ B band (no Q branch).

X ~ B_{3u} ~ minimal moment of inertia ~ A band (relatively weak Q branch).

The IR spectrum of the solid pyrazine in KBr disc is shown in Fig. 3.28. The sample was a bit wet (strong and broad band at about 3400 cm^{-1}).



B1u
B1u
B3u
B2u
B2u
B2u
400
600
800
1000
1200
1400
3100
3300
ν̃/cm-1

Fig. 3.27

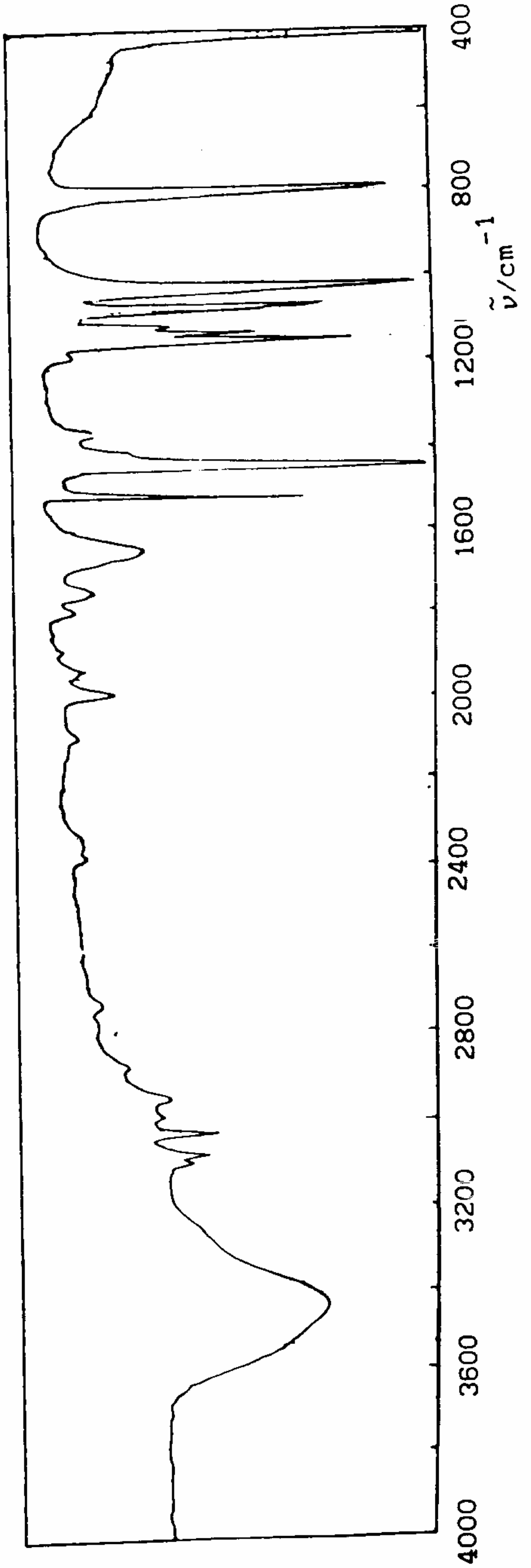


Fig. 3.28

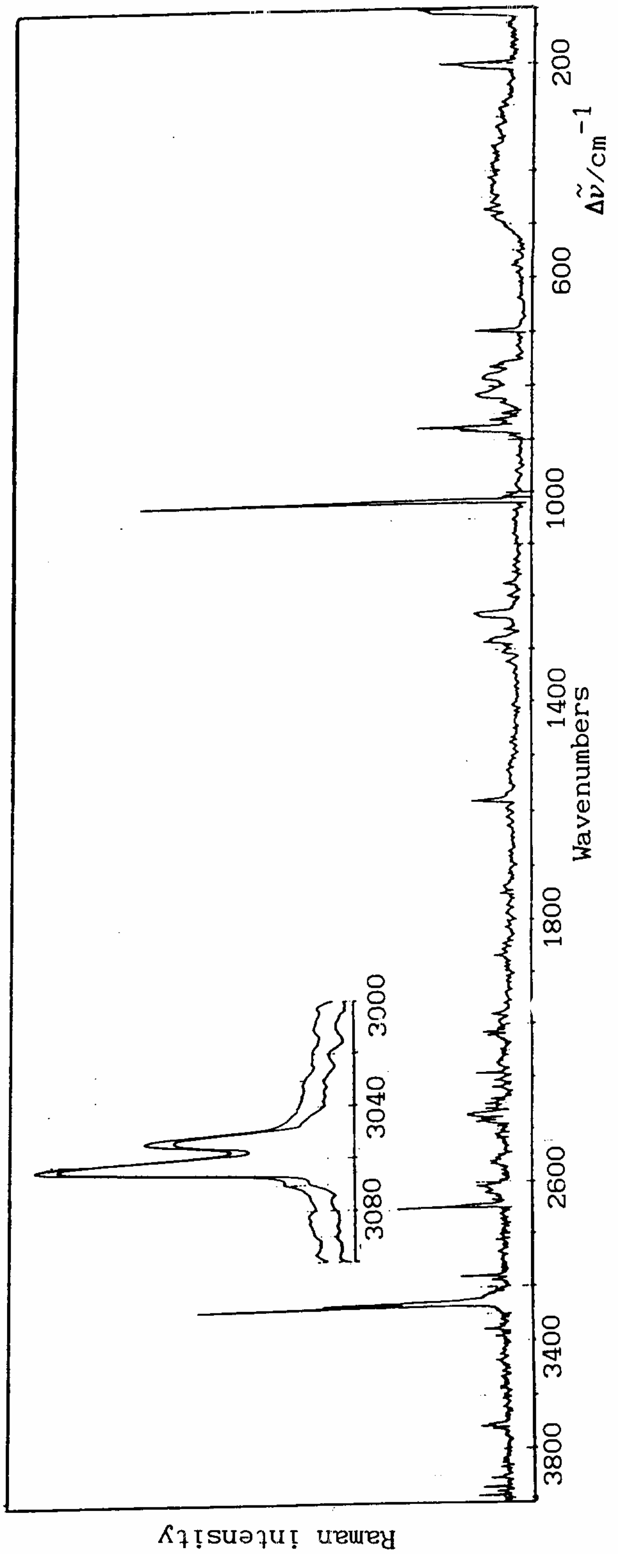

Raman intensity
3800
3400
2600
1800
1400
1000
600
200
Wavenumbers
$\Delta\tilde{\nu}/\mathrm{cm}^{-1}$
3080
3040
3000

Fig. 3.29

The RA spectrum of the solid pyrazine is presented in Fig. 3.29. The bands below 250 cm^{-1} are vibrations of the crystal lattice.

The RA spectrum of the pyrazine melt is the Fig. 3.30. It is a polarized RA spectrum. Curve 1 is recorded with parallel, curve 2 with perpendicular polarizer. Find the polarized bands belonging to the A_{1g} species.

Table 3.13 gives the quantum chemically calculated and measured normal frequencies and the types of the normal modes. The individual vibrational modes have order numbers, the fundamental modes of the parent compounds and of the substituted molecules can be compared in this way. Beside frequencies also the *characters of the vibrational modes* are calculated ab initio. Their character show the weight of the participation of the individual chemical internal coordinates. The ring (rg) and CH motions are distinguished here. The stretching modes are labelled by ν, the in-plane deformations by β, the out-of-plane deformations by γ and the torsions by τ. The labels p and dp denotes the polarized and depolarized bands, respectively. A, B, and C denote the observed IR vapour band types. Values in parentheses are results of other measurements. The molecule has 2N-3=17 in-plane modes ($\|$) and N-3=7 out-of--plane modes ($\perp$).

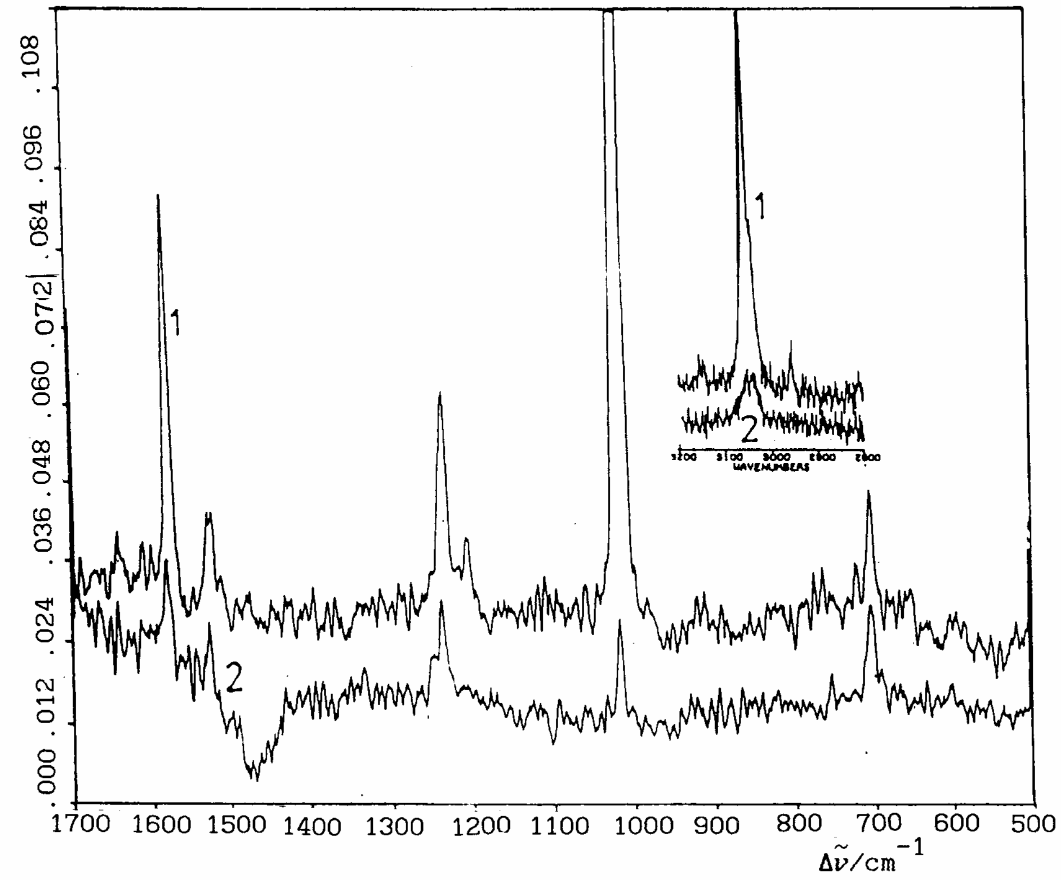


Fig. 3.30

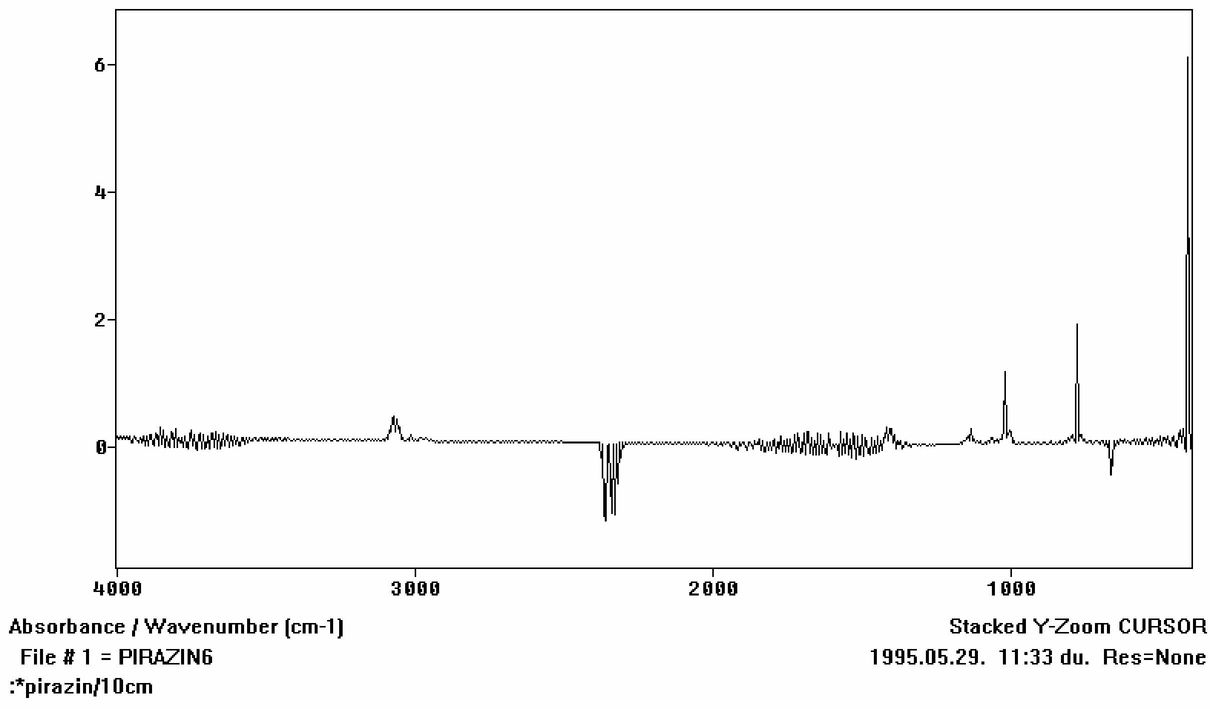


Fig. 27a

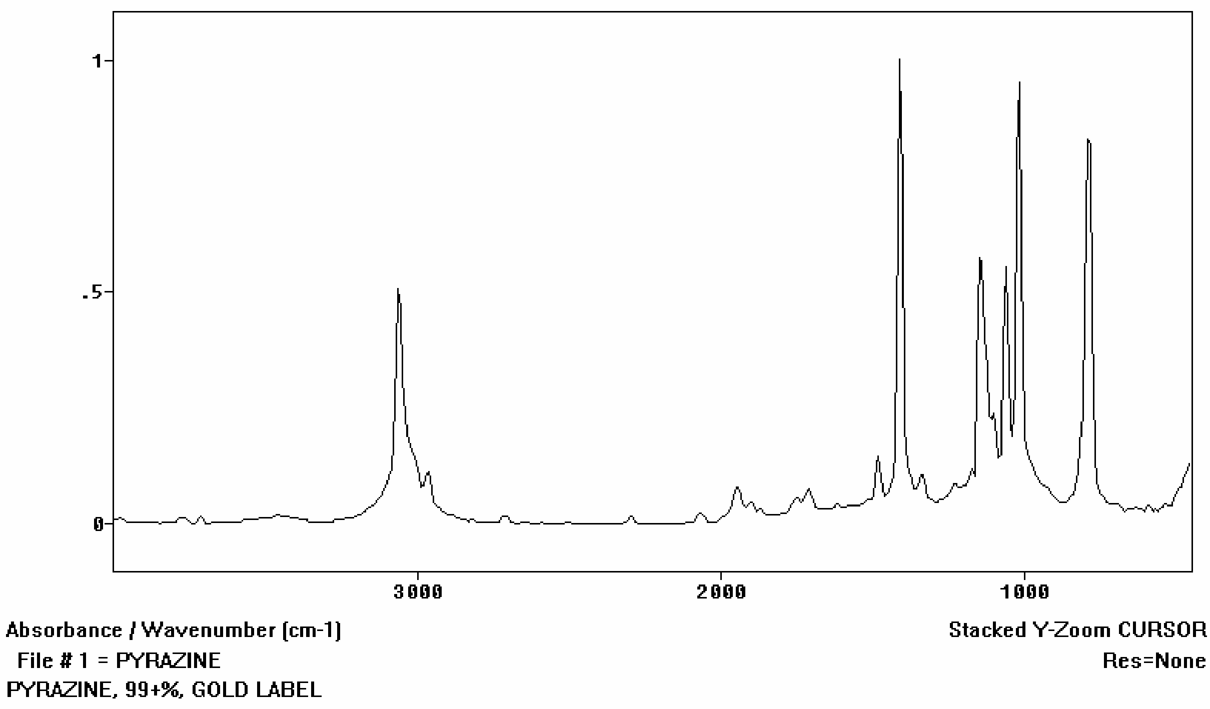


Fig.3.28a

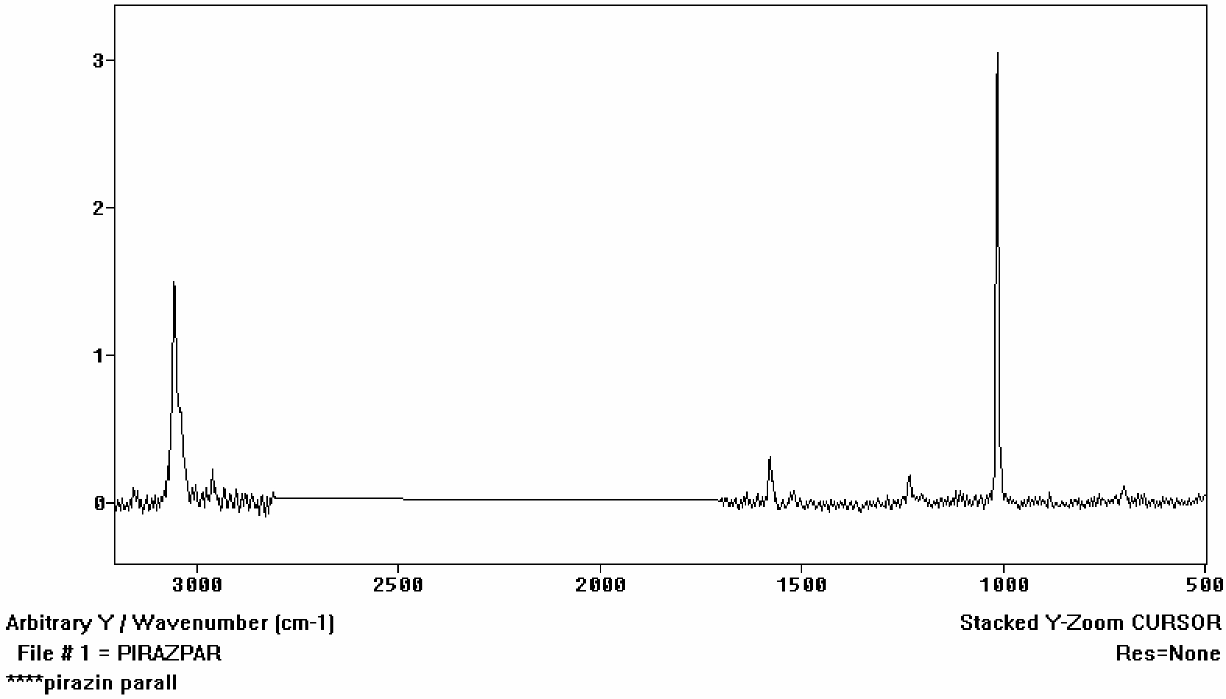


Fig. 3.29a

Fig 27a presents the vapour spectrum of pyrazine in a larger resolution (0.05 cm^{-1}) than Fig. 27. Besides, alo negative bands are observed. The bands about 2400 cm^{-1} builds the rotational structure of the C=O stretching band of CO_2. The other negative band about 700 cm^{-1} is the O=C=O in-plane deformation band of carbon dioxide. The crowded band structure between 3800 and 3400 cm^{-1} is the rotational structure of the two OH strething bands, while the similar structure between 1900 an 1400 cm^{-1} is the HOH in-plane deformation band structure.

Fig. 28a is a successful infrared spectrum of solod pyrazine (it sublimates) without adsorbed water.

Fig. 29a is the Raman spectrum of solid pyrazine. The area were eliminated where the florescence of the compound (see Subsection 3.4) was stronger than the Raman scattering.