Fig 3.80c is an example, ^{1}H-NMR 2D-COSY spectrum of o-nitroaniline. H_a and H_b, H_b and H_c, H_c and H_d are correlated, they are in vicinic position to one another. There is not correlation between the amino protons and the ring protons.

3.11 Diffraction methods in the molecular structure elucidation

3.11.1 Introduction to the diffraction methods

We dealt with the collisions of particles with molecules (atoms) in Section 1.2. Not only the inelastic collisions yield information about the molecular structure but also the elastic ones. The incident particle beam scatters on the atoms of the molecule. The overwhelming part of this beam is coherent. In the practice photons, electrons and neutrons are applied. The common is in the scattered radiation of all these particles, they contain some information about the structure of the investigated substance.

The applied *photons* are high energy X-ray beams. Their calculated moving mass is smaller than the mass of the electron. Electric and magnetic fields propagate with the X-ray radiation. This electric field forces the electron on vibration. The vibrating electric charges induce electric fields around them, its frequency and phase are equal to those of the inducing field. Theoretically also the nuclei may be excited but this effect is negligible since their mass is too great. Therefore X-ray diffraction is suitable to determine the electron density distribution. The resulting atomic distances are distances between the mass centers of electron density distributions of the atoms. The method is suitable for the determination of the atomic distances in crystalline phase. Its drawback is the uncertainty in the determination of the hydrogen atom positions. Photons have neither electric charge, nor spin.

The mass of the *electrons* is essentially smaller than that of the nuclei. They have electric charge and spin, the velocity is smaller than the velocity of light. Therefore they can interact with the electron cloud if the atoms and molecules and scatter from them. The intensity of the electron scattering is some million times intense than those of the X-ray. The scattered intensities, however, decrease essentially faster with the scattering angle than that of the X-ray scattering. Owing to the high intensity of the scattered electron beam it is suitable for the determination of the molecular structure in gas phase. The yielded atomic distances are the distances of the average positions of the atoms (e.g. the molecule vibrates).

The *neutrons* are electrically neutral, but they have nuclear spin (its spin quantum number is 1/2), so they have magnetic moments. They interact with magnetic dipoles, scatter both on nuclei and electrons. Their interaction with the nuclei is important above all for the structure determination of the magnetic substances having ordered structure. The scattered intensity of neutrons is smaller than even that of the photon scattering. Therefore the neutron scattering is suitable only for the investigations in condensed matter. The determined atomic distances are essentially the averaged distances between the mass centers of the nucleus density distributions.

3.11.2 Scatterings on isolated molecules

Our scattering model is restricted with the following conditions:

1. the wavelength of the particle does not change during the scattering,
2. each particle scatters only ones,
3. the intensity of the wave does not decrease during the scattering,
4. only coherent elastic scattering is possible.

If a particle with mass m is scattered on a particle with mass M, its direction changes. The situation can follow on Fig. 3.82. The moment of the particle is before the scattering

$$\mathbf{I}_o = h\mathbf{k}_o \tag{3.120}$$

after the scattering

$$\mathbf{I} = h\mathbf{k} \tag{3.121}$$

The vectors **k** are *wavevectors*, their absolute values are

$$|\mathbf{k}| = \tilde{\nu} = \frac{1}{\lambda} \tag{3.122}$$

The difference of the wavevectors is the scattering vector **s**, characterizes the change in moment.

The particles scattering under an angle ϑ scatter along the surface of a cone. The particles detected on a surface perpendicular to the axis of the cone form a ring on the surface (Fig. 3.82). In the coordinate system fixed to the mass center of the molecule the atom j has the position vector $\mathbf{r}_j$, the point of detection has the position vector **R**. Since $|\mathbf{R}| >> |\mathbf{r}_j|$, we assume $|\mathbf{R} - \mathbf{r}_j| >> |\mathbf{r}_j|$ so $|\mathbf{R}| \approx R$. Taking into account the definition of **s**, and assuming $|\mathbf{k}_o| \approx |\mathbf{k}|$, we have (see Fig. 3.82)

$$s = 2|\mathbf{k}_o| \sin\frac{\vartheta}{2} \tag{3.123}$$

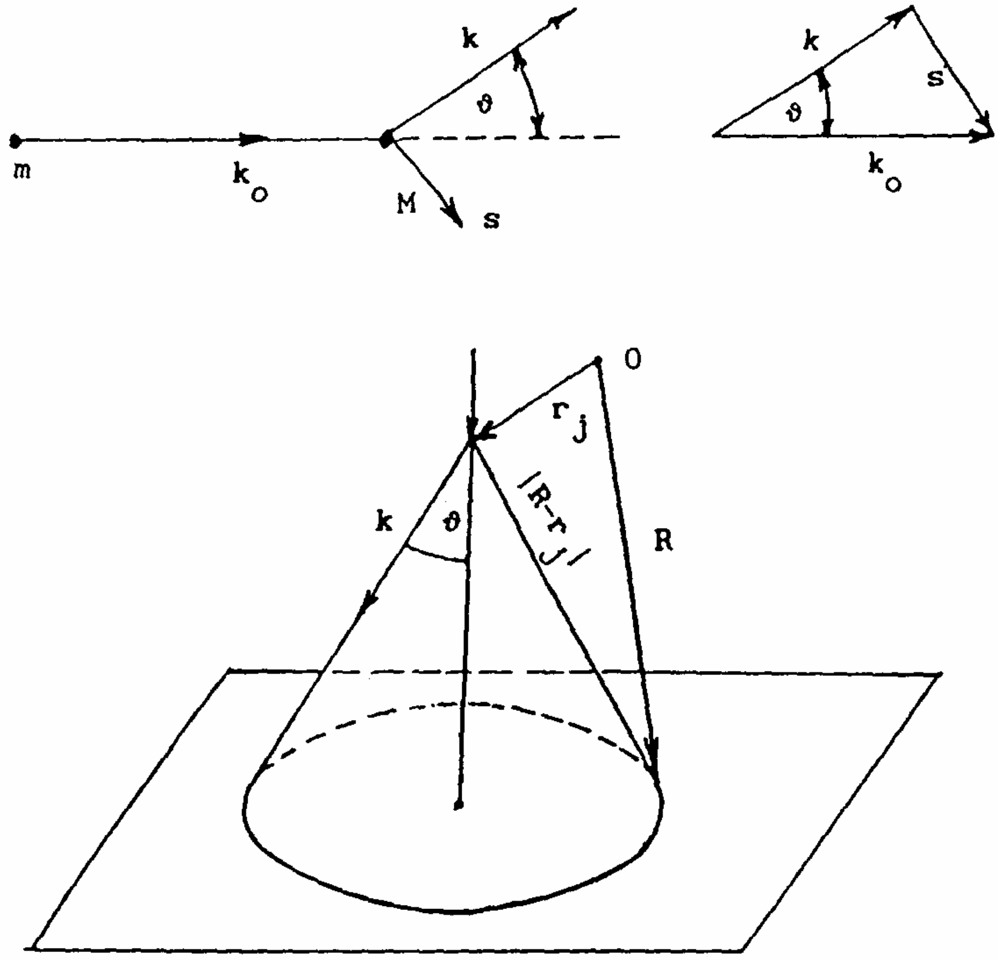

Fig. 3.82

The amplitude of the scattered radiation depends on the type and the scattering vector of the atom. It is, however, practically independent of the chemical environment of the atom. The wavefunction of the j-th atom depends on the atomic scattering function f(s) depending only on the type of atom:

$$\psi_j = A\frac{\exp(i\mathbf{k}_o\mathbf{R})}{R} f_j(s)\exp(i\mathbf{s}\mathbf{r}_j) \tag{3.124}$$

A is a constant. The further approach is the independent atom model, the scatterings of the individual atoms do no affect the scatterings of other atoms. According to this the wavefunction of the molecule is

$$\Psi = \sum_{j=1}^{N} \psi_j \tag{3.125}$$

N is the number of the atoms in the molecule.

The intensity is proportional to $\Psi^*\Psi$. The atoms of the molecule are regarded as fixed but it must be considered the different orientations of the molecules in the gas phase. The calculations resulted for the intensity of the scattered radiation

$$I(s) = K\sum_{j=1}^{N}\sum_{k=1}^{N} f_j(s) f_k(s)\frac{\sin(\mathbf{s}\mathbf{r}_{jk})}{\mathbf{s}\mathbf{r}_{jk}} \tag{3.126}$$

$\mathbf{r}_{jk}$ is the difference of the two position vectors, K is a constant. The distribution of the intensities in directions is characterized by the scalar products $\mathbf{s}\mathbf{r}_{jk}$. This distribution depends on the atomic distances. Omitting from Eq. 3.126 the terms j=k that characterize the atoms, all other terms form the molecular scattering:

$$I_m(s) = K\sum_{j=1}^{N}\sum_{k=1}^{N} f_j(s) f_k(s)\frac{\sin(\mathbf{s}\mathbf{r}_{jk})}{\mathbf{s}\mathbf{r}_{jk}} \qquad j \neq k \tag{3.127}$$

The atomic scattering function for X-ray photons is approached by

$$f_j^{\varphi}(s) = \int \rho_j(\mathbf{r}')\exp(-i\mathbf{s}\mathbf{r}')d\mathbf{r}' \tag{3.128}$$

ρ_j is the electron density around the atom j, r' is the position vector centered on the nucleus. These functions decrease with s, that of the hydrogen atom decreases drastically (Fig. 3.83).

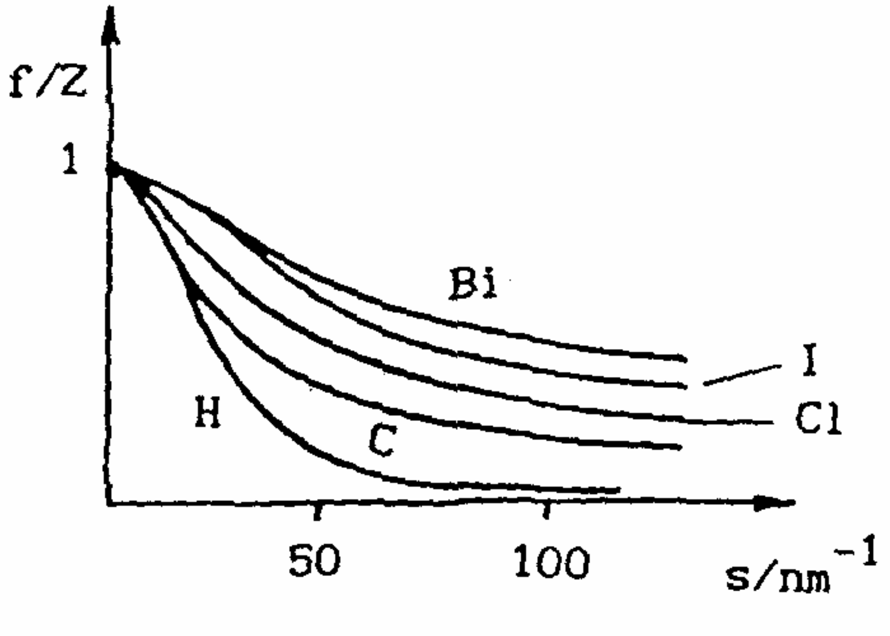

Fig. 3.83

The atomic scattering functions for the scattered electrons are more complicate. Taking into account the scattering of both the nucleus and the electrons we have

$$f_j^{e}(s) = \frac{C}{s^2}\left[Z_j - f_j^{\varphi}(s)\right] \tag{3.129}$$

C is a constant, Z is the atomic number.

The atomic scattering functions of the neutrons consist of two parts. The first term describes the scattering on the nucleus, the second one characterizes the magnetic interaction with the electron cloud. The first term is important for magnetic systems.

3.11.3 Electron diffraction in gas phase (ED)

As it was mentioned a regularity was observed in the scattering of disordered molecules in gas phase that approach the isolated molecule model. The electron diffraction is applied for the determination of the geometric parameters of molecules since the scattered electron beam has high intensity. The ED is suitable also for the determination of intramolecular motions and charge densities.

The measurement needs high vacuum. The electrons are accelerated with some ten thousand volts. Their narrow, some tenth mm of diameter electron beam crosses the beam of the molecules in investigation (Fig. 3.84). The scattered electrons are detected on a plane photo film or observed on a screen.

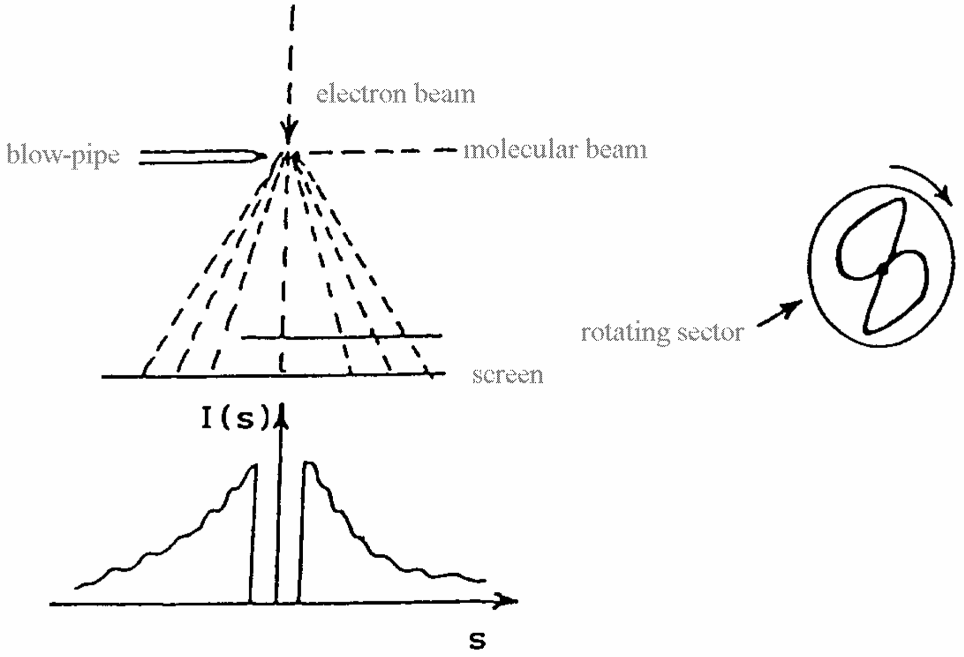

Fig. 3.84

Some problems arise in course of the evaluation of the measurements. The real scattered intensity consists of three parts. The first two, the incoherent scattering and the atomic scattering form the background intensity, I_g, those are not periodic. The molecular scattering, however, is periodic. (Fig. 3.85a).

The I_g is very intense at small scattering angles (small values of s) and therefore a rotating sector is applied at this values for decreasing its intensity (Fig. 3.84).

For the evaluation of the results the periodic part of the function must be separated from the background. This is a bit subjective, difficult iteration process. We can follow it on the example of sulfuryl chloride. Fig 3.85a shows the results of two measurements in different s regions. Passing all the measured values a smooth curve is drawn as background. After them the reduced molecular intensity is calculated:

$$M(s) = \frac{I_m(s)}{I_g(s)} \tag{3.130}$$

Practically the function sM(s) is used (Fig. 3.85b). The experimental values (dots) are compared with the calculated theoretical model (connected curve). The theoretical model is changed up to the difference between the experimental and calculated functions becomes minimal (iteration). The lower curve in Fig. 3.85b shows this difference. For very low s values the experimental function is not determinable. This part is substituted by the theoretical values. The Fourier transform of M(s) is the *radial distribution function,* f(r). Fig. 3.85c presents this result. The dashed curve is the experimental radial distribution function, the connected one is the theoretical curve. The maxima of the f(r) function give the atomic distances.

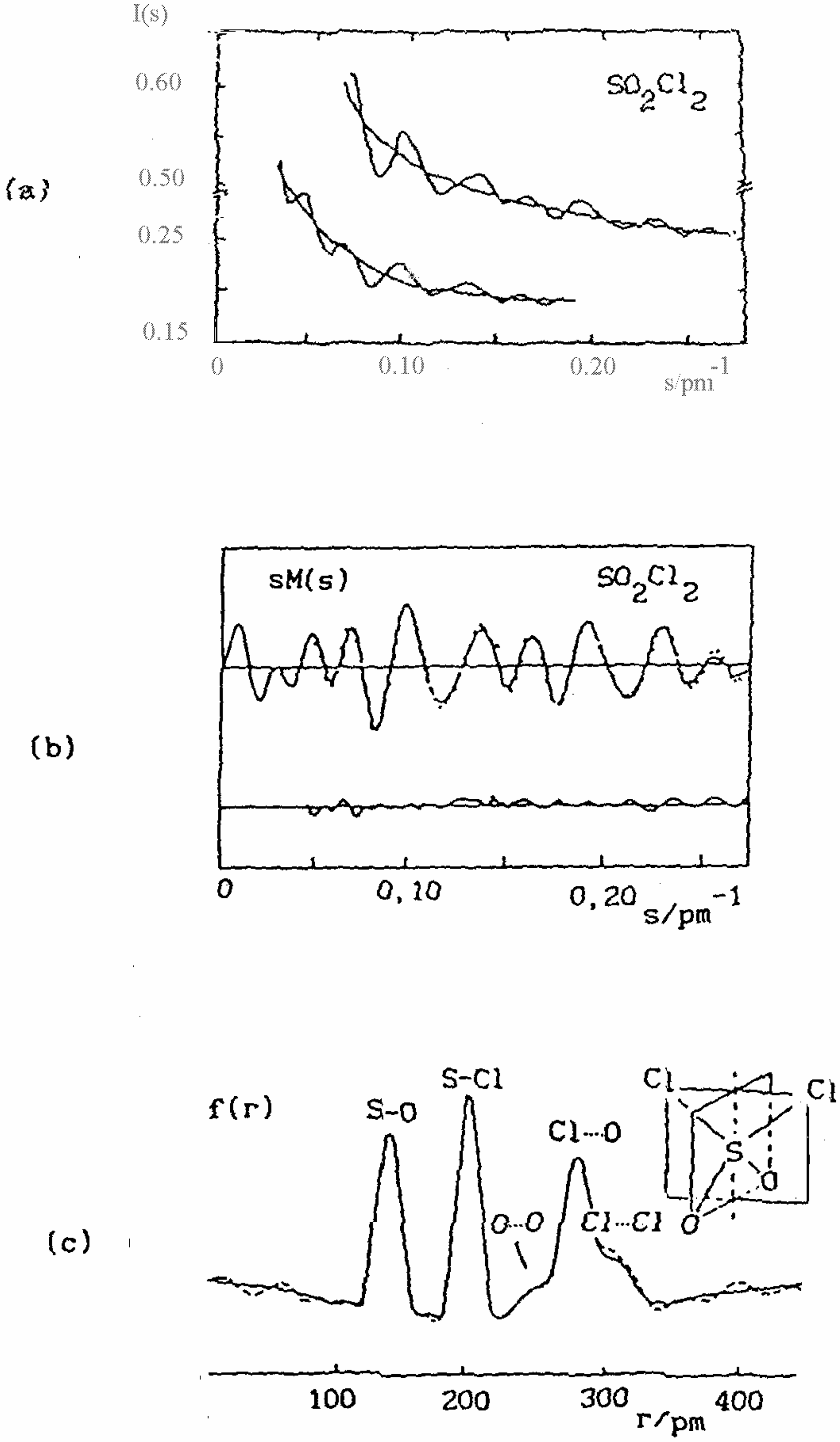
(a)
I(s)
0.60
0.50
0.25
0.15
0
0.10
0.20
s/pm-1
SO2Cl2
(b)
sM(s)
SO2Cl2
0
0,10
0,20
s/pm-1
(c)
f(r)
S-O
S-Cl
Cl···O
O···O
Cl···Cl
Cl
Cl
S
O
O
100
200
300
400
r/pm

Fig. 3.85

3.11.4 The character of the measured and calculated geometric parameters

The structure, i.e. the geometric parameters of the isolated molecules are determinable with spectroscopic methods (rotational spectroscopy, Section 3.4) or with electron diffraction (Section 3.11.3). These data are also calculable using quantum chemical methods. The resulted structures differ fundamentally from one another. The structures of molecules in crystalline phase are determinable with X-ray diffraction. Let us evaluate the different types of geometries of isolated molecules.

The *quantum chemical methods* (QCH) are suitable for calculation of molecular energies. Changing the atomic distances in the directions of decreasing interatomic forces and decreasing molecular energy the calculations lead to an energy minimum. This is the process of *geometry optimization*. The energy corresponds the minimum of the potential energy curve, it is under the vibrational zero point energy. The programs apply Born-Oppenheimer approach, and calculate with harmonic forces. The results depend on the applied quantum chemical approach and basic functions. The molecule is regarded as unmoved. This method yields the *r_e geometry* (e: equilibrium).

The molecule rotates and vibrates during the experiments. Therefore the measured parameters differ from the equilibrium values. Above all vibrational effect is important. These differences can be taken into account with the probability density functions of the vibrations and the distribution of the molecules under the vibrational states (Boltzmann distribution). In this way the p(r) probability density functions of the r atomic distances are the results. The *average* (or *estimated*) value of r in thermal equilibrium is the position of the mass center of p(r):

$$r_g = \int_0^\infty r \frac{p(r)}{r} dr \tag{3.131}$$

The mass center of area under p(r)/r is the *effective atomic distance:*

$$r_a = \frac{\int_0^\infty r \frac{p(r)}{r} dr}{\int_0^\infty \frac{p(r)}{r} dr} \tag{3.132}$$

Since the radial distribution function f(r) has maxima exactly at the same points the *ED measurements yield r_a geometry*. These atomic distances must be corrected for the stretchings of the non-rigid rotator.

The rotational constants A_o, B_o and C_o are directly calculable from the *rotational spectra* of the molecule. The geometric parameters calculated from these constants form the r_o geometry. Taking into account the effect of vibrations a harmonic (H) correction is necessary. The corrected rotational constants are A_z, B_z and C_z. Applying these constants we have the *r_z geometry*.

If the geometry of the vibrational ground state is calculated from ED data this is the r_a^o geometry.

From the rotational constants one can have only three independent geometric parameters. If more parameters exist the rotational constants of isotopomers are necessary (isotopic correction, I), and so we get the *r_s geometry*.

Correcting the rotational constants for anharmonicity (AH) the A_e, B_e and C_e constants are resulted and the r_e geometry may be calculated.

The name of the geometry refers always on the model and not on the values of the parameters.

Figs. 3.86 and 3.87 give overview on the connections of the different geometries.

$$\begin{tikzcd}
\text{SP} & & & & & \text{ED} \arrow[dd] \\
& r_o & & & & \\
r_s & A_oB_oC_o \arrow[l, "I"'] \arrow[u] \arrow[r, "H"] \arrow[d, "AH"'] & A_zB_zC_z \arrow[r] & r_z & r_g \arrow[l, "H"'] & r_a \arrow[l] \arrow[dllll, "AH"] \\
& A_eB_eC_e \arrow[r] & r_e & & & \\
& & \text{QCH} \arrow[u] & & &
\end{tikzcd}$$

Fig. 3.86

$$\begin{tikzcd}
\text{thermal equilibrium} & \sum\limits_i w_i r_{v_i} & r_\alpha \arrow[l] \arrow[dd] & r_g \arrow[l] \arrow[dd] & r_a \arrow[l] \\
v > 0 & r_v \arrow[u] & & & \\
v = 0 \quad T = 0\ \text{K} & r_z \arrow[u] \arrow[r, phantom, "\approx"] & r_\alpha^o & r_g^o \arrow[l] &
\end{tikzcd}$$

Fig. 3.87

The state with vibrational zero energy (v=0) is theoretically equal to the state of absolute zero (T=0 K). This is expressed by the zero superscripts of r_α^o and r_g^o. If the molecular vibrations are excited the molecular geometry is denoted with r_v. In thermal equilibrium the different vibrational states have w_i weights.