

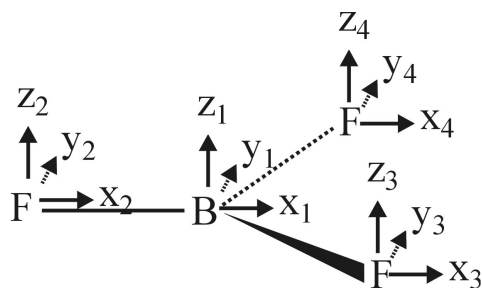
7. Symmetry and Spectroscopy – Molecular Vibrations7.1 Bases for molecular vibrations

We investigate a molecule consisting of N atoms, which has $3N$ degrees of freedom. Taking the translations (3) and rotations (3 for non-linear, 2 for linear molecules) into account, we obtain $3N-6$ (5) vibrational degrees of freedom for the non-linear (linear) case. In order to describe those, we choose an arbitrary set of basis vectors in order to describe the $3N$ displacements from the equilibrium position (the choice is arbitrary, but a choice having simple transformation properties might be advantageous).

Example: BF_3 or CO_3^{2-}

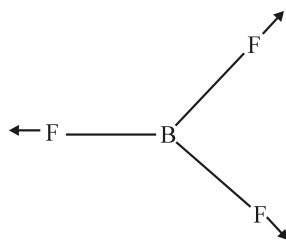
12 degrees of freedom: 3 translations, 3 rotations, 6 vibrations

displacement basis d :

7.2 Normal modes

We are interested in the collective vibrational modes of the molecules. These collective modes Q with identical frequency and phase are denoted as normal modes.

As a pictorial representation of the modes, we indicate the set maximal displacements, e.g.:



As we will see later, normal modes can be classified with respect to the irreps of the point group of the molecule.

In analogy to the strategy followed in chapter 5 for the electronic structure of molecules, we can transform the displacement basis of dimension $3N$ into a symmetry adapted set of displacement coordinates D :

$$\underline{\underline{D}} = \underline{\underline{\alpha}} \underline{\underline{d}} \quad \text{with } \underline{\underline{d}} = \begin{pmatrix} x_1 \\ y_1 \\ z_1 \\ x_2 \\ \vdots \end{pmatrix}$$

In the next step we transform the basis D into the basis of normal modes

$$\underline{\underline{Q}} = \underline{\underline{\beta}} \underline{\underline{D}}.$$

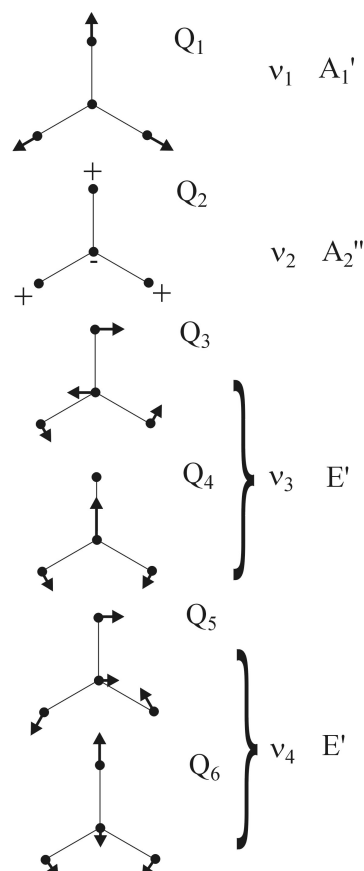
In analogy to chapter 5, the matrix $\underline{\underline{\beta}}$ is blockdiagonal, i.e. the normal coordinates are linear combinations of the SALCs of displacements belonging to one irrep of the point group of the molecule (Wigner's theorem).

As an example we classify the normal vibrations of CO_3^{2-} , BF_3

(D_{3h}):

(7.1 Character table D_{3h}).

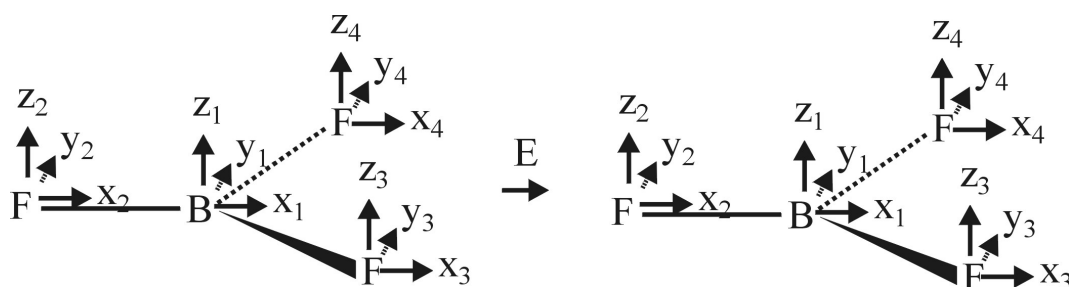
Note: $Q_{3,4}$ and $Q_{5,6}$ are transformed into linear combinations of each other by symmetry operations of the group. They belong to 2 dimensional irreps.



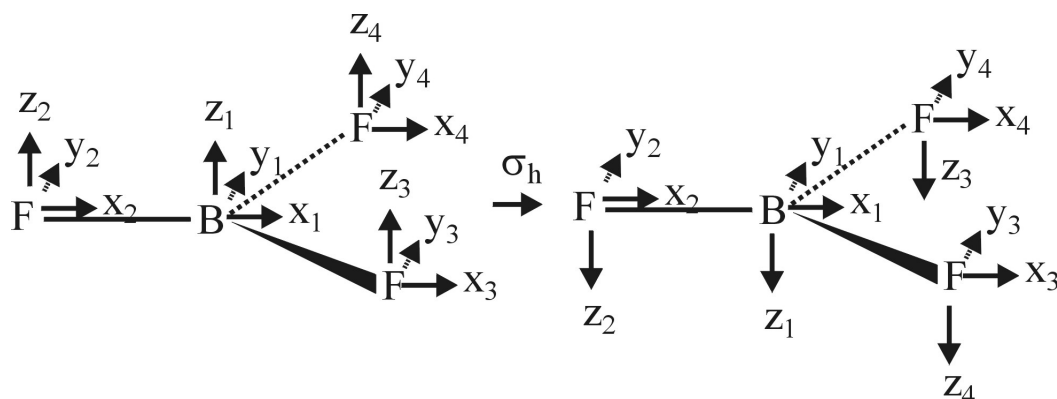
7.3 Symmetry of normal modes

We would like to classify the normal modes Q_i of the molecules with respect to the irreps which they belong to. For this purpose, we analyse the $3N$ dimensional representation of the displacements with respect to the irreps of the group.

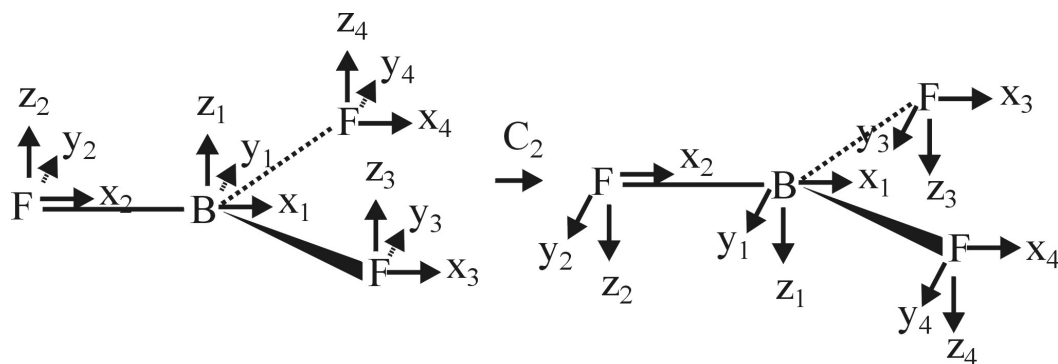
Example: BF_3 (C_{3v}), 12 dimensional displacement basis



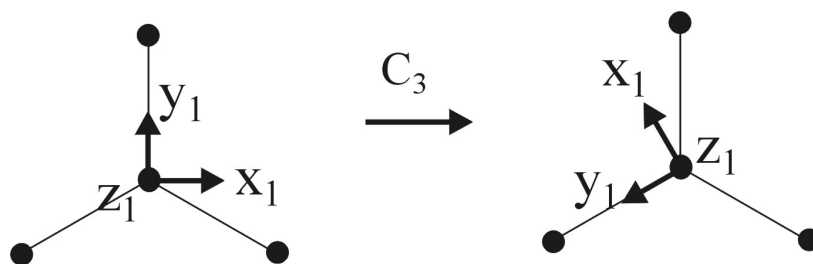
E : all diagonal elements $\Gamma_{ii}(E)=1 \Rightarrow \chi(E) = 12$



σ_h : x, y , displacements are retained, z displacement changes sign $\Rightarrow \chi(\sigma_h) = 4$



C_2 : displacements of atoms, which change position do not contribute to Γ_{ii} (off diagonal elements) $\Rightarrow \chi(C_2) = -2$

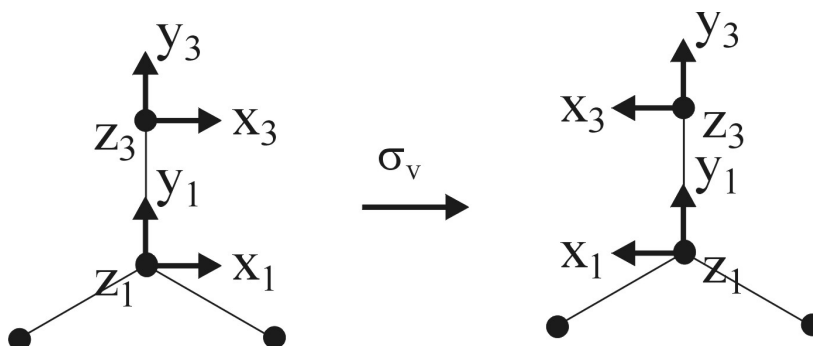


$$C_3: z_1 \text{ is invariant } (\chi = 1), \text{ for } x_1, y_1: \begin{pmatrix} x'_1 \\ y'_2 \end{pmatrix} = \begin{pmatrix} \cos 120^\circ & \sin 120^\circ \\ -\sin 120^\circ & \cos 120^\circ \end{pmatrix} \begin{pmatrix} x_1 \\ y_2 \end{pmatrix} (\chi = -1)$$

$$\Rightarrow \chi(C_3) = 0$$

S_3 : analogous to C_3 , but $z_1' = -z_1$ ($\chi = -1$)

$$\Rightarrow \chi(C_3) = -2$$



σ_v : y, z , displacements at two positions are invariant, x displacement changes sign

$$\Rightarrow \chi(\sigma_v) = 2$$

$$D_{3h} \quad E \quad 2C_3 \quad 3C_2 \quad \sigma_h \quad 2S_3 \quad 3\sigma_v$$

$$\chi \quad 12 \quad 0 \quad -2 \quad 4 \quad -2 \quad 2$$

$$\Rightarrow \Gamma = A_1' + A_2' + 3E' + 2A_2'' + E''$$

Symmetry of translations and rotations from character table:

$$\Gamma_{Tx, Ty} = E'; \quad \Gamma_{Tz} = A_2''$$

$$\Gamma_{Rx, Ry} = E''; \quad \Gamma_{Rz} = A_2'$$

(7.2 Classify translations and rotations in D_{3h}).

The remaining vibrational normal modes are: $\Gamma_{vib} = A_1' + 2E' + A_2''$

(7.3 Exercise: classify the vibrational modes of SF₆ with respect to their symmetry, substitute one F by Cl).

7.4 Analysis of normal modes

We assume that we have determined the complete potential energy surface of an N atom molecule $V(r_1, r_2, \dots, r_{3N})$ and expand V into a Taylor series at the equilibrium geometry:

$$V = \underbrace{V_0}_{\text{equilibrium energy}} + \sum_i \underbrace{\left(\frac{\partial V}{\partial r_i} \right)_0}_{=0 \text{ for expansion at equilibrium position}} r_i + \frac{1}{2} \sum_{i,j} \underbrace{\left(\frac{\partial^2 V}{\partial r_i \partial r_j} \right)_0}_{\text{force constants } k_{ij} \text{ (harmonic)}} r_i r_j + \frac{1}{6} \sum_{i,j,k} \underbrace{\left(\frac{\partial^3 V}{\partial r_i \partial r_j \partial r_k} \right)_0}_{\text{anharmonicities}} r_i r_j r_k + \dots$$

We start from the equation of motion for the molecule

$$m_i \ddot{r}_i = -\sum_j k_{ij} r_j$$

and use the ansatz $r_i = r_{i0} e^{i\omega t}$ which yields

$$m_i r_{i0} \omega^2 = \sum_j k_{ij} r_{j0}.$$

Introducing mass weighted coordinates $R_i = m_i^{1/2} r_i$ this equation is simplified to

$$R_{i0} \omega^2 = \sum_j \underbrace{\frac{k_{ij}}{m_i^{1/2} m_j^{1/2}}}_{K_{ij}} R_{j0} \quad \text{or} \quad \bar{R} \omega^2 = \underline{\underline{K}} \bar{R}.$$

As usual we solve the set of 3N linear equations by determining the eigenvalues ω_i^2 and eigenvectors $\bar{\Omega}_i$. By transforming to a new basis $\bar{Q} = \underline{\underline{\Omega}} \bar{R}$ with $\underline{\underline{\Omega}} = (\bar{\Omega}_1, \bar{\Omega}_2, \dots, \bar{\Omega}_{3N})$, i.e. the basis of normal coordinates, the matrix of force constant $\underline{\underline{k}} = \underline{\underline{\Omega}} \underline{\underline{K}} \underline{\underline{\Omega}}^{-1}$ becomes diagonal:

$$\bar{Q} \omega^2 = \underline{\underline{k}} \bar{Q} \quad \text{or} \quad Q_{i0} \omega^2 = \sum_j k_{ij} Q_{j0} = k_{ii} Q_{i0}.$$

Thus we obtain a set of 3N decoupled degrees of motion (vibrations, rotations, translations). If we express the total energy

$$E = T + V = \frac{1}{2} \sum_i m_i \dot{r}_i^2 + \frac{1}{2} \sum_{i,j} k_{ij} r_i r_j$$

in terms of the new coordinates, we obtain

$$E = \frac{1}{2} \sum_i \dot{Q}_i^2 + \frac{1}{2} \sum_{ij} k_{ij} Q_i Q_j = \frac{1}{2} \sum_i \dot{Q}_i^2 + \frac{1}{2} \sum_i k_{ii} Q_i^2 = \frac{1}{2} \sum_i \dot{Q}_i^2 + k_{ii} Q_i^2$$

In a quantum mechanical description we can describe the Hamiltonian as a simple sum over harmonic oscillators

$$\hat{H} = \frac{1}{2} \sum_i \hat{H}_i \quad \text{with} \quad \hat{H}_i = -\frac{\hbar^2}{2} \frac{\partial^2}{\partial Q_i^2} + \frac{1}{2} k_{ii} Q_i^2$$

with the well known solutions

$$f_{v_i}(Q_i) = N_{v_i} H_{v_i} \left(\frac{W_i^{1/2}}{\hbar^{1/2}} Q_i \right) e^{-\frac{1}{2} \frac{W_i}{\hbar} Q_i^2}; \quad E_{v_i} = \left(v_i + \frac{1}{2} \right) \hbar W_i; \quad W_i = k_i^{1/2}; \quad v_i = 1, 2, 3, \dots;$$

($H_j(x)$): Hermite polynomials)

Consequently, the vibrational wavefunction of the molecules is

$$\Phi_{vib} = \prod_i f_{v_i}(Q_i) \quad \text{with} \quad E_{vib} = \sum_i E_{v_i}.$$

(7.4 Example: normal modes of C₂H₂)

7.5 Symmetry of vibrational wavefunctions: fundamental modes

We consider a molecules with N vibrational modes. The excitation from the vibrational ground state ($v_i = 0; i = 1 \dots N$) to a state with a singly excited normal mode

($v_k = 1; v_i = 0; i = 1, \dots, k-1, k+1 \dots N$) is referred to as a fundamental mode of the molecule.

Symmetry of the ground state:

$$\Phi_{vib} = N e^{-\sum_i \frac{1}{2} \frac{W_i}{\hbar} Q_i^2}$$

Effect of symmetry operation \hat{R} on

(a) non degenerate modes:

$$Q_i \rightarrow \pm Q_i$$

$$\hat{R} \Phi_{vib} = N e^{-\sum_i \frac{1}{2} \frac{W_i}{\hbar} (\pm Q_i)^2} = \Phi_{vib}$$

(a) $i = 1 \dots n$ degenerate modes:

$$Q_i \rightarrow \sum_j a_{ij} Q_j \text{ with } \sum_j a_{ij} a_{kj} = d_{ik} \text{ (orthonormalization)}$$

$$\hat{R}\Phi_{vib} = Ne^{-\frac{1}{2} \sum_i \frac{w_i}{\hbar} Q_i^2} = Ne^{-\frac{1}{2} \sum_i \frac{w_i}{\hbar} \left(\sum_j a_{ij} Q_j \right)^2} = Ne^{-\frac{1}{2} \sum_i \frac{w_i}{\hbar} Q_i^2} = \Phi_{vib}$$

Thus, the vibrational ground state is invariant under all symmetry operations, i.e. $\Gamma_{vib,0} = A_1$.

Symmetry of the excited state:

$$\Phi_{vib} = N Q_k e^{-\sum_i \frac{1}{2} \frac{w_i}{\hbar} Q_i^2}$$

Symmetry of wavefunction is equal to symmetry of Q_k , i.e. $\Gamma_{vib,k=1} = \Gamma_{Q_k}$.

7.6 Symmetry of vibrational wavefunctions: combination modes

The excitation from the vibrational ground state ($v_i = 0; i = 1 \dots N$) to a state with several normal modes excited by one vibrational quantum each ($v_k = 1; v_l = 1$) is referred to as a combination mode of the molecule.

Symmetry of the excited state:

$$\Phi_{vib} = N Q_k Q_l e^{-\sum_i \frac{1}{2} \frac{w_i}{\hbar} Q_i^2}$$

Symmetry of wavefunction is equal to the direct product of the representations of Q_k and Q_l , i.e. $\Gamma_{vib,k=1,l=1} = \Gamma_{Q_k} \otimes \Gamma_{Q_l}$.

(7.5 Exercise: symmetry of the combination modes of BF_3).

7.7 Symmetry of vibrational wavefunctions: overtones

The excitation from the vibrational ground state ($v_i = 0; i = 1 \dots N$) to a state with several vibrational quanta in one normal mode ($v_k > 1$) is referred to as an overtone of the mode.

Symmetry of the excited state:

(a) non degenerate case

$$\Phi_{vib} = NUH_{v_k} \left(g_k^{1/2} Q_k \right) \text{ with } U = e^{-\sum_i \frac{1}{2} \frac{w_i}{\hbar} Q_i^2} \text{ and } g_k = \frac{W_k}{\hbar}$$

Hermite polynomials:

$$H_0(z) = 1$$

$$H_1(z) = 2z$$

$$H_2(z) = 4z^2 - 1$$

$$H_3(z) = 8z^3 - 12z$$

$$H_4(z) = 16z^4 - 48z^2 + 12$$

Note: even for even v_k , odd for odd v_k . Therefore

$$\hat{R}\Phi_{vib} = \begin{cases} \Phi_{vib} & \text{for } v_k = 2n \\ \Gamma_{Q_k}(R)\Phi_{vib} & \text{for } v_k = 2n+1 \end{cases} \quad \text{or} \quad \Gamma_{vib} = \begin{cases} A_1 & \text{for } v_k = 2n \\ \Gamma_{Q_k} & \text{for } v_k = 2n+1 \end{cases}$$

(a) degenerate case

Similar as for the problem of several electrons occupying the same set of degenerate orbitals (chapter 6), quantum statistics restricts the number of vibrational states if several vibrational quanta occupy the same degenerate mode. Thus the problem becomes significantly more complicated.

We consider the case of a twofold degenerate vibrational mode ($Q_1, v_1; Q_2, v_2$):

1 vibrational quantum: $(v_1=1; v_2=0) (v_1=0; v_2=1)$

2-fold degenerate

2 vibrational quanta: $(v_1=2; v_2=0) (v_1=1; v_2=1) (v_1=0; v_2=2)$

3-fold degenerate

3 vibrational quanta: $(v_1=3; v_2=0) (v_1=2; v_2=1) (v_1=1; v_2=2) (v_1=0; v_2=3)$

4-fold degenerate

n vibrational quanta: n+1 fold degenerate

(analogous: n vibrational quanta in three-fold degenerate mode: $\frac{1}{2}(v+1)(v+2)$ vibrational wavefunctions; see textbooks)

As an example we consider the wavefunctions for $v_1+v_2=3$:

$$\Phi_{3,0} = NU(8g^{3/2}Q_a^3 - 12g^{1/2}Q_a)$$

$$\Phi_{2,1} = NU(4gQ_a^2 - 2)(2g^{1/2}Q_b)$$

$$\Phi_{1,2} = NU(2g^{1/2}Q_a)(4gQ_b^2 - 2)$$

$$\Phi_{0,3} = NU(8g^{3/2}Q_b^3 - 12g^{1/2}Q_b)$$

We consider linear combinations Q_a, Q_b , for which the transformation matrix of a given symmetry operation R is diagonal (this is always possible for single operation, for other symmetry operations the transformation is of course not diagonal because the functions belong to a two dimensional representation):

$$Q_a' = \Gamma_{aa}Q_a$$

$$Q_b' = \Gamma_{bb}Q_b$$

As the cubic and the linear terms of the wavefunctions must transform indetically, we only consider the cubic terms:

$$\Phi_{3,0} : Q_a'^3 = \Gamma_{aa}^3 Q_a^3$$

$$\Phi_{2,1} : Q_a'^2 Q_b' = \Gamma_{aa}^2 \Gamma_{bb} Q_a^2 Q_b$$

$$\Phi_{1,2} : Q_a' Q_b'^2 = \Gamma_{aa} \Gamma_{bb}^2 Q_a Q_b^2$$

$$\Phi_{0,3} : Q_b'^3 = \Gamma_{bb}^3 Q_b^3$$

Therefore, the character of the 4 dimensional representation is

$$c_3(R) = R_a^3 + R_a^2 R_b + R_a R_b^2 + R_b^3$$

Analogous: $c_2(R) = R_a^2 + R_a R_b + R_b^2$ and $c(R) = R_a + R_b^3$

Repeated application of R: $c(R^n) = R_a^n + R_b^n$

In general, one can show that the general recursion formula is valid (see Wilson, Decius, Cross):

$$c_v(R) = \frac{1}{2} (c(R)c_{v-1}(R) + c(R^v)).$$

(analogous for triply degenerate normal coordinates:

$$c_v(R) = \frac{1}{3} \left[2c(R)c_{v-1}(R) + \frac{1}{2} (c(R^2) - [c(R)]^2)c_{v-2}(R) + c(R^v) \right], \text{ see Wilson, Decius, Cross}$$

With this information it is possible to construct the characters of an k-fold excited vibrational states corresponding to a twofold degenerate normal coordinate and analyse the representation (notation $(\Gamma)^n$) which they span in terms of the irreps of the group (similar formulae exist for higher degenerate normal coordinate, see Wilson, Decius, Cross).

(7.6 Exercise: What is the symmetry of the first and second overtone of an E vibrational mode of CH₄?)

The intensity of overtones and combination bands is relatively low in most cases. In some cases these weak transitions become important. We assume that there is a singly excited state $\Phi_{v_1=1, v_2=0}$ and a 1st overtone $\Phi_{v_1=0, v_2=2}$ with similar vibrational energy. If both states have the same symmetry (or contain a component with identical symmetry), a coupling between both state is possible, i.e. matrix elements $\langle \Phi_{v_1=1, v_2=0} | \hat{H} | \Phi_{v_1=0, v_2=2} \rangle$ can be nonzero. The eigenstates of the coupled modes are mixed vibrational wave functions $\Phi_i' = c_{i1} \Phi_{v_1=1, v_2=0} + c_{i2} \Phi_{v_1=0, v_2=2}$. The effect is denoted as Fermi resonance and leads to an “intensity borrowing” of the weak combination band or overtone from the fundamental as well as to a “repulsion” between both states (compare section 5.6).

(7.7 Example: Fermi resonance in CO₂).

7.8 Symmetry of vibrational wavefunctions: arbitrary excited states

According to sections 7.5 to 7.8 the symmetry of an arbitrary vibrational state with the vibrational quantum numbers $\nu_1, \nu_2, \nu_3, \dots$ corresponding to the normal modes of symmetry $\Gamma_1, \Gamma_2, \Gamma_3, \dots$ is:

$$\Gamma_{vib} = (\Gamma_1)^{\nu_1} \otimes (\Gamma_2)^{\nu_2} \otimes (\Gamma_3)^{\nu_3} \dots$$

Note: We have discussed the symmetry of vibrational wavefunctions in terms of the harmonic approximation. However, the results are not affected, if we take anharmonicities into account, as the different parts of the Taylor expansion of the Hamiltonian (section 7.4) must be totally symmetric (A_1) within the group of the molecule. If we thus express the anharmonic wave function as a sum over harmonic functions $\Phi_{anh} = \sum_i a_i \Phi_i$, only those functions contribute, which have the same symmetry.

7.9 Selection Rules

Electrical dipole transitions are described by matrix elements of the type

$$\langle f | \hat{m}_i | i \rangle$$

where \hat{m}_i are the components of the vector of the dipole operator (with $i=x,y,z$).

We have seen that the integrand must be totally symmetric (A_1) for the integral to be non zero. This immediately leads to the dipole selection rule:

$$A_1 \in \Gamma_{vib,f} \otimes \Gamma_{m_i} \otimes \Gamma_{vib,i}$$

Note:

We consider the components of the dipole moment operator

$$\hat{m}_x = \sum_i q_i x_i; \hat{m}_y = \sum_i q_i y_i; \hat{m}_z = \sum_i q_i z_i$$

- (1) A symmetry operation exchanges equivalent atoms with identical charge.

(2) The operator contains the sums $\sum_i x_i$, $\sum_i y_i$, $\sum_i z_i$ only, which remain unaffected by a change of indices.

Therefore, it is sufficient to investigate the transformation properties of the functions x , y , z , which span the same representation as the components of the dipole operator. Typically, these are tabulated in the character table.

Remark concerning IR reflection absorption spectroscopy (IRAS) at metallic surfaces: For metallic surfaces the parallel component of the electric field is efficiently screened by the conduction electron. Thus the electric field vector must be nearly perpendicular to the surface, and only the electric field component perpendicular to the surface contributes to the field strength at the surface. Similarly, dipole fields of the oscillating molecules are screened by the conduction electrons. This resulting field is normally constructed by assuming an (imaginary) image charge inside the metal. The image charge leads to the effect that perpendicular dipole moments are amplified, whereas parallel dipoles are extinguished. Thus the relevant matrix element for IR absorption at metallic surfaces is:

$$\langle f | \hat{m}_z | i \rangle.$$

If we assume excitation from the ground state ($\Gamma_i = A_1$) and take into account that \hat{m}_z or z is symmetric with respect to any possible symmetry operation of a surface, i.e. $\Gamma_{m_z} = A_1$, we obtain the so called metal surface selection rule (MSSR) as:

$$\Gamma_f = A_1.$$

Raman transitions are described by matrix elements of the type

$\langle f | \hat{\alpha}_{ij} | i \rangle$ where $\hat{\alpha}_{ij}$ are the components of the tensor of the dielectric polarizability (with $i, j = x, y, z$). Analogous to the previous case, we obtain the selection rule:

$$A_1 \in \Gamma_{vib,f} \otimes \Gamma_{a_i} \otimes \Gamma_{vib,i}$$

As we will discuss in the next section, the polarizability is a symmetric tensor of rank 2 connecting the electric field and the induced dipole moment:

$$\vec{m} = \begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{12} & a_{22} & a_{23} \\ a_{13} & a_{23} & \chi_{33} \end{pmatrix} \vec{E}$$

We will see that upon a symmetry operation described by the transformation matrix R_{ij} this type of tensor transforms according to

$$a'_{ij} = \sum_{kl} R_{ik} R_{jl} a_{kl}$$

e.g.

$$a'_{xx} = R_{xx}^2 a_{xx} + R_{xy}^2 a_{yy} + R_{xz}^2 a_{zz} + 2R_{xx} R_{xy} a_{xy} + 2R_{xx} R_{xz} a_{xz} + 2R_{xy} R_{xz} a_{yz}$$

Transformation of function x^2 for comparison:

$$(x')^2 = (R_{xx}x + R_{xy}y + R_{xz}z)^2 = R_{xx}^2 xx + R_{xy}^2 yy + R_{xz}^2 zz + 2R_{xx} R_{xy} xy + 2R_{xx} R_{xz} xz + 2R_{xy} R_{xz} yz$$

Thus, the components of the tensor show the same transformation behaviour as the quadratic forms x^2 , y^2 , z^2 , xy , xz , yz .

Typically, these functions are tabulated in the character table. But how are they determined?

In principle there are two methods:

- (1) Application of the symmetry operation to the basis (x^2 , y^2 , z^2 , xy , xz , yz), determination of the representation matrices and of their characters, analysis in terms of the irreps of the symmetry group.
- (2) Analogous to the method applied in the symmetry analysis of overtones (section 7.7)

wavefunctions of 1st overtone of 3fold deg. mode: $Q_a^2, Q_b^2, Q_c^2, Q_a Q_b, Q_a Q_c, Q_b Q_c$

quadratic functions of three coordinates: $x^2, y^2, z^2, xy, xz, yz$

Example:

Symmetry of the quadratic forms in T_d :

$$\Gamma_{xyz} = T_2$$

R	E	8C ₃	3C ₂	6S ₄	6σ _d	
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R ²	E	C ₃	E	C ₂	E	
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χ(R)	3	0	-1	-1	1	(E)
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χ(R ²)	3	0	3	-1	3	
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Recursion formula for triply degenerate modes (see section 7.7):

$$c_2(R) = \frac{1}{3} \left[2c(R)c(R) + \frac{1}{2} (c(R^2) - [c(R)]^2) c_0(R) + c(R^2) \right]$$

$$= \frac{1}{2} [(c(R))^2 + c(R^2)]$$

c ₂ (R)	6	0	2	0	2	⇒	A ₁ + E + T ₂
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(7.8 Exercise: CO₃²⁻: Symmetry of normal modes, IR / Raman activity of fundamentals and 1st overtones).

Note: from the IR and Raman selection rules it is immediately evident that if the inversion i is element of the symmetry group of the molecule, a IR active transition is Raman inactive and vice versa (exclusion principle). Moreover all 1st overtones of centrosymmetric molecules are IR inactive.