

**HIGH-RESOLUTION INFRARED  
STUDIES ON DEUTERATED  
MONOIODOACETYLENE**

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MONOiodoacetylene**

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***Abstract***

This thesis deals with infrared spectroscopy investigations on the linear DCCI molecule. The high resolution spectra between 200–5200  $\text{cm}^{-1}$  were measured with the Fourier transform spectrometer at the University of Oulu. The spectra were analyzed taking into account various types of resonances between rovibrational energy levels. As a result, a set of molecular constants and resonance parameters describing the rotational and vibrational energy states of the molecule were obtained. From the resulting molecular constants, together with previous results from literature for HCCI, the structure of monoiodoacetylene was calculated. In addition, eight harmonic force constants with estimated uncertainties for monoiodoacetylene were determined.

*Keywords:* Fermi resonance, harmonic force field, infrared spectroscopy, linear molecule, molecular constants



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Oulu, November 2004      Hannu Sarkkinen





## Original publications

The present thesis consists of an introductory part and the following papers, which are referred to in the text by their Roman numerals:

- I Sarkkinen H, Tolonen A-M & Alanko S (1997) High-Resolution Infrared Study of the Fundamental Bands of Deuteriodoacetylene. *Journal of Molecular Spectroscopy* 185:15-20.
- II Sarkkinen H, Tolonen A-M & Alanko S (1999) Lowest Overtone and Combination Levels of DCCI: The Fermi Resonance  $v_3 = 1/v_5 = 2$ . *Journal of Molecular Spectroscopy* 193:396-402.
- III Sarkkinen H (2001) Simultaneous Analysis of the Rovibrational Levels  $v_4 = 1, 2$ , and 3 of HCCI and DCCI Based on Infrared Spectra. *Journal of Molecular Spectroscopy* 207:136-142.
- IV Sarkkinen H (2004) High-Resolution Infrared Study on DCCI: Harmonic Force Field of Monoiodoacetylene. *Journal of Molecular Spectroscopy* 226:45-56.



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# 1 Introduction

Spectroscopy is a widely used experimental method applied in the investigation of small particles such as molecules, atoms, and nuclei. It is based on the interaction between electromagnetic radiation and a particle with an always quantized internal energy. When the particle undergoes a transition between two states with different energies, it absorbs or emits a radiation quantum. By measuring the energy of this quantum one can obtain information about the structure and the internal forces of the particle. Depending on the energy of the quantum, it can originate from a nuclear, atomic or molecular process. The research field related to the molecular phenomena is called molecular spectroscopy.

In this thesis molecular energy transitions between quantized rovibrational states have been studied experimentally. Rovibrational state is a combination of rotational and vibrational states. Their energies, as well as the difference between two states, correspond to the quanta of infrared radiation. From an experimental point of view the field is accordingly called infrared spectroscopy. When studying transitions between rotational states within a single vibrational state, the radiation is within the microwave or millimeter-wave region.

The rotational and vibrational motions of a molecule, as well as their energies, are not independent of each other. In addition, according to classical mechanics, the separate intermolecular motions can be connected to each other. In other words, one motion in a molecule can excite the other and vice versa. The connection leads to the transfer of energy between energy states. As a consequence of this, the energy and intensity distribution of lines in the spectrum can be seriously perturbed. Both quantitative and qualitative analyses of the coupling of rovibrational states are among the main points of this thesis.

The deuterated monoiodoacetylene molecule (DCCI) was chosen as the subject of this work. DCCI is a small linear semirigid molecule with five fundamental vibrations (three stretching and two doubly degenerate bending modes). This results in a reasonable amount of lines in the high-resolution infrared spectrum for the analysis. With the increase of the atoms in a molecule, the number of degrees of vibrational freedom will rise rapidly and the spectrum will become too crowded for a detailed analysis. As a semirigid molecule DCCI has a well defined structure. This is an important requirement when applying the perturbation theory to the

treatment of resonances between rovibrational states.

When our infrared studies on DCCI commenced in 1996, there were practically no infrared analyses on DCCI. Only one publication has reported on the observation of the infrared spectrum of DCCI [1]. On the other hand, a few microwave investigations had been published when our study began. Heineking *et al.* [2–4] had observed two rotational transitions and determined the  $B$  and  $D$  rotational constants of the ground vibrational state of the molecule.

The present studies on DCCI are a natural continuation of previous studies on the normal isotopic species (HCCI) of monoiodoacetylene [5–9]. In addition, in order to determine the structure and harmonic force field of monoiodoacetylene with a high degree of accuracy, the appropriate rotational and vibrational constants in various vibrational levels for at least two isotopic species are needed.

Presently, high-resolution measurements play an essential role in infrared spectroscopy. The resulting infrared spectrum of the molecule consists of a number of rovibrational bands, each of which is associated with a particular allowed vibrational transition. Moreover, every band includes tens or hundreds of separate spectral lines. During the course of this work a total of 9694 lines were assigned from the measured spectra. The interpretation of the spectra was one of the most time-consuming parts in this work. Statistical accuracy of the measurements has been estimated from the standard deviations of the polynomial fits. A more detailed description of the experimental arrangements is given in chapter 2, as well as in the experimental portions of the original papers.

The theoretical introduction to the spectral analysis is given in chapter 3. The expression for the rovibrational energy of a semirigid linear molecule in terms of the molecular constants is derived using quantum mechanics. An overview of perturbation theory is included in the treatment for resonance consideration. The nuclear hyperfine interaction conspicuously perturbs the spectral lines in certain bands when the rotational quantum number  $J$  is small. The theoretical background of this phenomenon is described in chapter 4. The effect was studied by conducting simulations. The description of harmonic force field calculations of small molecules is at the end of chapter 5. Specific attention is directed to the determination of the force constants of monoiodoacetylene using the experimental data.

In the original papers detailed spectrum analyses have been reported. In the first paper [I] the ground state rotational constants have been determined from the previous microwave [3] and present infrared measurements simultaneously. Furthermore, the upper states of the fundamental vibrations have been studied in paper [I]. The second paper [II] deals with the various  $l$ -type resonances and the Fermi resonance  $v_3 = 1/v_5 = 2$  at the energy levels of 500 and 750  $\text{cm}^{-1}$ . In paper [III] the simultaneous analysis of the rovibrational states in the levels  $v_4 = 1, 2$ , and 3 of HCCI and DCCI have been conducted. This analysis includes the Coriolis resonance treatment between the levels  $v_3 = 1$  and  $v_4 = 1$  and between the levels  $v_3 = v_4 = 1, k = \pm 1$  and  $v_4 = 2, k = 0, \pm 2$  of DCCI. Paper [IV] consists of the analysis of a large number of combination and overtone infrared bands perturbed by various resonances. In paper [IV] the eight harmonic force constants of monoiodoacetylene have been calculated, as well.

In addition to the structure and harmonic force field of monoiodoacetylene, the most important numerical results of this thesis are the numerous experimental molecular constants and resonance parameters which were determined with a high degree of accuracy. These values are presented in tables included in the original papers.

## 2 Experimental

The gaseous DCCI sample was produced in our laboratory at the University of Oulu. The synthesization process is based on the method of Brown and Tyler [10]. The final sample included acetylene and water as impurities. The spectrum [1] shows that the HCCI species was present in the sample also. The pressure in a 20 liter sample cell varied case by case from 40 to 160 Pa.

The measurements were performed with a Bruker IFS 120 HR FTIR spectrometer at the University of Oulu. The first spectra were measured in 1996 and the latest measurements were carried out using the renovated spectrometer in 2001. In the measurement arrangements, the infrared radiation from a continuous source was directed through the gaseous DCCI sample and a multiple pass White-type cell was used. A discussion of the technical details of the measurements is passed over here.

In the spectroscopical measurements, in general, the two main quantities we are interested in are spectral line intensity and frequency. Considering the present recordings of the infrared spectra, the systematic quantitative studies of the line intensities were ignored. Instead, the main aim was to maximize the frequency information on the rovibrational transitions. In other words the goal was to measure the frequency as accurately as possible for as many transitions as possible. This requires the careful optimization of instrumental parameters in every frequency region separately. The experimental resolution of the measurement, i.e. the spectral linewidth determined as the full width at half height, is a contribution of several factors. The linewidth which arises from the instrumentation is called the instrumental resolution. On the other hand, nature sets the theoretical upper limit to the resolution of the measurements. In addition to the instrumental contribution to the linewidth, the natural line broadening, pressure broadening, and Doppler broadening are present in every spectroscopical recording of a gaseous sample. The Doppler broadening originates from the conventional Doppler effect. In the infrared region it is often the most significant individual factor in line broadening. For example, at room temperature, in the case of fundamental vibration  $\nu_1$  ( $2600\text{ cm}^{-1}$ ) of DCCI, the Doppler linewidth is about  $0.0026\text{ cm}^{-1}$ , whereas the attained experimental linewidth was  $0.0045\text{ cm}^{-1}$ . The smallest experimental linewidth  $0.0020\text{ cm}^{-1}$  was achieved in the case of the lowest fundamental vibration



$\nu_5$  at  $250\text{ cm}^{-1}$ .

The infrared spectrum includes lines with various intensities. Regardless of the line intensities, all the lines arise with approximately equal linewidths. In order to observe very weak transitions, it is important to maximize the signal to noise ratio. Owing to this, the instrumental linewidth and consequently the inaccuracy of the recorded transition frequency will increase. In consideration of this, the compromises between the desired spectral linewidth and signal to noise ratio are unavoidable in usual infrared measurements.

The temperature of the gaseous sample significantly affects the intensity and width of a spectral line. The higher temperature of the sample, the higher intensity of the spectral lines, except those starting from the ground state. This results from the fact that free molecules obey the familiar Boltzmann Distribution Law. On the other hand, the increase of the temperature leads to the broadening of all lines. Information about the accurate temperatures of the sample are only needed for special purposes. In this work all the measurements were carried out at room temperature.

When using a Fourier transform spectrometer, the spectrum is calculated using a registered interferogram with the Fourier technics. The transition wavenumbers are calculated from the spectrum. Before the final calculation of the transition wavenumbers the spectrum has to be calibrated. This is usually carried out using a linear calibration factor in an appropriate spectral region. In this work the calibration was made according to wavenumber standards from the literature [11–13].

### 3 Rotational and vibrational energies of a molecule

When considering rotational and vibrational energies, the molecule is regarded as a point mass system consisting of nuclei held together by interatomic forces. This is, in short, the conventional conception of a molecule, as well as the starting point of the subsequent discussion.

A free molecule rotates about its axes and nuclei vibrate with small amplitudes about their equilibrium positions. As a special case, in a linear molecule the rotation about the axis along the molecule vanishes. The masses and motions of electrons can be conveniently neglected because of the great energy difference between the electronic and nuclear motions. This kind of omission of electrons is in accordance with the Born-Oppenheimer approximation to simplify the treatment of molecular rovibrational energies.

Molecular vibrational and rotational states, as well as their energies, are quantized. The quantified states are identified, for convenience, by a set of quantum numbers. In the absence of resonances between energy states, every rovibrational state consists of both a single rotational and vibrational state. The corresponding energy is a sum of the rotational and vibrational energies. The rovibrational states may often be perturbed by various types of resonances. In this case every observable state is obtained as a linear combination of two or more rovibrational states.

As a result of quantization, the energies of molecular rovibrational states have to be calculated quantum mechanically instead of using classical mechanics which is applicable for macroscopic phenomena. In the quantum mechanical treatment energy is expressed by the Hamiltonian operator and wavefunctions describing the rovibrational states are introduced. In the first approximation, the model of a harmonic oscillator-rigid rotor is serviceable. The anharmonicity of the vibrations, together with the various resonances, can be taken into account by applying the perturbation theory. The rovibrational energy will be written down in terms of molecular constants and resonance parameters.

### 3.1 Classical Hamiltonian

The derivation of the quantum mechanical energy for a rotating and vibrating molecule starts from the classical potential and kinetic energy treatment, which has been written down in great detail by Wilson [14]. Let us first consider kinetic energy. Following Wilson we introduce the moving Cartesian axes  $x$ ,  $y$ , and  $z$ , whose origin in the space fixed axis system  $(X, Y, Z)$  is given by the vector  $\mathbf{R}$ . The vector  $\mathbf{r}_\alpha$  describes the position of the  $\alpha$ th nucleus in the moving coordinate system. The angular velocity of the rotating axis system  $(x, y, z)$  is denoted with  $\boldsymbol{\omega}$  and the velocity of the  $\alpha$ th nucleus with respect to the axis system  $(x, y, z)$  is denoted as  $\mathbf{v}_\alpha$ . Using these variables we can express the kinetic energy of the whole molecule in the form [14]

$$\begin{aligned}
 2T &= \dot{\mathbf{R}}^2 \sum_{\alpha} m_{\alpha} + \sum_{\alpha} m_{\alpha} (\boldsymbol{\omega} \times \mathbf{r}_{\alpha}) \cdot (\boldsymbol{\omega} \times \mathbf{r}_{\alpha}) + \sum_{\alpha} m_{\alpha} \mathbf{v}_{\alpha}^2 \\
 &+ 2\dot{\mathbf{R}} \cdot \boldsymbol{\omega} \times \sum_{\alpha} m_{\alpha} \mathbf{r}_{\alpha} + 2\dot{\mathbf{R}} \cdot \sum_{\alpha} m_{\alpha} \mathbf{v}_{\alpha} + 2\boldsymbol{\omega} \cdot \sum_{\alpha} (m_{\alpha} \mathbf{r}_{\alpha} \times \mathbf{v}_{\alpha}), \quad (3.1)
 \end{aligned}$$

where  $m_{\alpha}$  is the mass of  $\alpha$ th nucleus.

For the complete separation of the translational motion of the molecule we fix the origin of the moving axis system  $(x, y, z)$  to the center of the mass of the molecule. Hence, regardless of vibrations, it can be assumed that

$$\sum_{\alpha} m_{\alpha} \mathbf{r}_{\alpha} = 0, \quad (3.2)$$

which is called the translational Eckart condition [15]. For an adequate separation of the rotational and vibrational motions of the molecule in the forthcoming energy expressions, we introduce the rotational Eckart condition in the form [15]

$$\sum_{\alpha} m_{\alpha} \mathbf{r}_{\alpha}^e \times \mathbf{v}_{\alpha} = 0, \quad (3.3)$$

where  $e$  refers to the equilibrium configuration of the molecule. Eq. (3.3) defines a particular rotation of the axis system  $(x, y, z)$  during molecular vibrations, i.e. the vibration-rotation coupling originating from the last term of Eq. (3.1) is minimized [16]. Similarly, there must be no resultant angular momentum with respect to the rotating axis system  $(x, y, z)$ . The  $x$ ,  $y$ , and  $z$  axes are now said to be so-called Eckart axes, which coincide with the principle axes in equilibrium. For a linear reference configuration along the  $z$  axis, the  $z$  component of Eq. (3.3) is an identity, and there are only two conditions that arise from Eq. (3.3). Altogether, the separation between the translational, vibrational, and rotational motions has been attained, with the exception of the Coriolis interaction originating from the last term in Eq. (3.1). Hereafter the translational energy is ignored, because it is of no interest in the absence of external fields.

The Cartesian displacements  $\Delta r_{\alpha\sigma}$  ( $\sigma = x, y, z$ ) of the  $\alpha$ th atom with respect to the equilibrium configuration can be expressed in terms of the normal coordinates

$Q_k$ , which describe the vibrational normal modes. We have in general [17]

$$\Delta r_{\alpha\sigma} = m_{\alpha}^{-1/2} \sum_k \ell_{\alpha k}^{\sigma} Q_k. \quad (3.4)$$

In addition we introduce the Coriolis coupling constants in the form

$$\zeta_{kl}^{\sigma} = -\zeta_{lk}^{\sigma} = \sum_{\alpha} (\ell_{\alpha k}^{\tau} \ell_{\alpha l}^{\rho} - \ell_{\alpha k}^{\rho} \ell_{\alpha l}^{\tau}), \quad \sigma, \tau, \rho = x, y, z, \quad (3.5)$$

where  $\sigma \neq \tau \neq \rho$ . The indexes  $k, l$ , and  $m$  refer to normal vibrational modes. Now the classical kinetic energy can be expressed as [18]

$$\begin{aligned} 2T &= \sum_{\sigma, \tau} I_{\sigma\tau} \omega_{\sigma} \omega_{\tau} + \sum_k \dot{Q}_k^2 + 2 \sum_{\sigma} \omega_{\sigma} \sum_{k, l} \zeta_{kl}^{\sigma} Q_k \dot{Q}_l \\ &= \sum_{\sigma, \tau} I'_{\sigma\tau} \omega_{\sigma} \omega_{\tau} + \sum_k \left( \dot{Q}_k + \sum_{\sigma, l} \omega_{\sigma} \zeta_{lk}^{\sigma} Q_l \right)^2, \end{aligned} \quad (3.6)$$

where

$$I'_{\sigma\tau} = I_{\sigma\tau} - \sum_{k, l, m} \zeta_{km}^{\sigma} \zeta_{lm}^{\tau} Q_k Q_l. \quad (3.7)$$

The parameter  $\omega_{\sigma}$  is the angular velocity of the  $\sigma$  axis, and  $I_{\sigma\tau}$  is the element of the instantaneous inertia tensor of the molecule.

For the operator expression the kinetic energy is formulated in terms of linear vibrational and angular momenta. From Eq. (3.6) the linear vibrational momentum  $P_k$  conjugate to  $Q_k$  becomes

$$\begin{aligned} P_k &= \frac{\partial T}{\partial \dot{Q}_k} \\ &= \dot{Q}_k + \sum_{\sigma, l} \omega_{\sigma} \zeta_{lk}^{\sigma} Q_l, \end{aligned} \quad (3.8)$$

The components of the total angular momentum are obtained from the expression (3.6) by taking the derivative

$$\begin{aligned} J_{\sigma} &= \frac{\partial T}{\partial \omega_{\sigma}} \\ &= \sum_{\tau} I_{\sigma\tau} \omega_{\tau} + \sum_{k, l} \zeta_{kl}^{\sigma} Q_k \dot{Q}_l \\ &= \sum_{\tau} I'_{\sigma\tau} \omega_{\tau} + \pi_{\sigma}, \end{aligned} \quad (3.9)$$

where so called vibrational angular momentum  $\pi_{\sigma}$  is of the form

$$\pi_{\sigma} = \sum_{k, l} \zeta_{kl}^{\sigma} Q_k P_l. \quad (3.10)$$

Substituting Eqs. (3.8) and (3.9) into (3.6) the kinetic energy for a non-linear molecule is obtained in the Hamiltonian form

$$H = \sum_{\sigma,\tau} \mu_{\sigma\tau} (J_{\sigma} - \pi_{\sigma})(J_{\tau} - \pi_{\tau}) + \sum_k^{3N-6} P_k^2, \quad (3.11)$$

where the inverse of  $I'_{\sigma\tau}$  has been denoted by  $\mu_{\sigma\tau}$  and  $N$  is the number of atoms.

Next, let us consider a linear molecule. We direct attention to the Euler angles  $(\theta, \phi, \chi)$ , which define the orientation of the molecule fixed axis system  $(x, y, z)$  relative to the space fixed axis system  $(X, Y, Z)$  (the angles are defined in [14]). With the  $z$  axis along the molecule in equilibrium, only  $\theta$  and  $\phi$  are determined by Eq. (3.3), whereas the third angle  $\chi$  can be equal to zero or more generally a chosen function of  $\theta$  and  $\phi$ . Accordingly, the number of rotational degrees of freedom is reduced by one, and there will be  $3N-5$  vibrational degrees of freedom instead of the usual  $3N-6$ . Furthermore, the determinant of  $I'_{\sigma\tau}$  derived in Eq. (3.11) is cancelled out identically, which means that the expression in Eq. (3.11) is incorrect for a linear molecule. Introducing the non-zero derivatives of the inertia tensor as [19]

$$\left( \frac{\partial I_{\sigma\tau}}{\partial Q_k} \right)_e = a_k^{xx} = a_k^{yy} = a_k = 2 \sum_{\alpha} m_{\alpha}^{1/2} r_{\alpha z}^e \ell_{\alpha k}^z, \quad (3.12)$$

the total classical Hamiltonian for a linear molecule becomes

$$H = \boldsymbol{\mu} \{ (J_x - \pi_x)^2 + (J_y - \pi_y)^2 \} + \sum_k^{3N-5} P_k^2 + V, \quad (3.13)$$

where,

$$\boldsymbol{\mu} = (\mathbf{I}')^{-1} = \mathbf{I}^e (\mathbf{I}'')^{-2} \quad (3.14)$$

and further,

$$\mathbf{I}'' = \mathbf{I}^e + \frac{1}{2} \sum_k a_k Q_k. \quad (3.15)$$

Above  $V$  is the vibration potential.

### 3.2 Hamiltonian operator

The quantized rotational and vibrational energies of a molecule are calculated from the quantum mechanical Schrödinger wave equation, for which a correctly constructed Hamiltonian operator is needed. In this section we consider the transformation from the classical Hamiltonian to the quantum mechanical one.

Let us write the classical kinetic energy in terms of the momenta  $p_i$  conjugate to the generalized coordinates  $q_i$  in the form

$$2T = \sum_{i,j} g^{ij} p_i p_j, \quad (3.16)$$

where  $g^{ij}$  is the inverse of the matrix  $g_{ij}$ , which is in turn the function of the generalized coordinates.

Podolsky [20] has pointed out that by normalizing the wavefunctions  $\psi$  with the volume element  $d\tau = dq_1 dq_2 \dots dq_N$ , the momenta  $p_i$  can be chosen as

$$p_i = -i\hbar\partial/\partial q_i. \quad (3.17)$$

Instead of using  $q_i$  our application uses the Euler angles and normal coordinates. For this reason the volume element is multiplied by a weight-function  $\rho_q$ , which is a function of the coordinates  $q_i$ . Consequently, the wavefunctions and the momentum operators will be of the forms  $(\rho_q)^{-1/2}\psi$  and  $(\rho_q)^{-1/2}(-i\hbar\partial/\partial q_i)(\rho_q)^{1/2}$ . The commutation relations are still unaffected by the transformation. Now the quantum kinetic energy operator can be derived in the form [18]

$$2T = \sum_{ij} g^{1/4} p_i g_{ij} g^{-1/2} p_j g^{1/4}. \quad (3.18)$$

In order to obtain the correct quantum kinetic energy, one can apply this general expression to momenta conjugate to true coordinates. Since for any molecule the total angular momentum components  $J_\sigma$  are quasi-momenta, a slight extension is needed. Let us introduce the quasi-momenta  $M_m$  and the coefficient matrix  $G_{mn}$  with the relations

$$p_i = \sum_m s_{im} M_m, \quad (3.19)$$

$$G_{mn} = \sum_{i,j} g_{ij} s_{im} s_{jn}, \quad (3.20)$$

where  $s_{im}$  are the elements of a real non-singular matrix. With these notations the kinetic energy expression can be given in the form

$$2T = \sum_{mn} G^{1/4} (M_m - 1/2i\hbar \sum_r \gamma_{mr,r}) G_{mn} G^{-1/2} (M_m + 1/2i\hbar \sum_s \gamma_{ms,s}) G^{1/4}, \quad (3.21)$$

where  $G$  is the determinant of  $G_{mn}$ . Only for true momenta the coefficients  $\gamma_{mn,r}$  determined by Watson [18] all vanish. However, it can be shown that  $\sum \gamma_{mr,r}$  equals zero for all  $m$  in the case of a non-linear molecule. This is equivalent to the familiar Wilson and Howard condition [21]. This is not true for a linear molecule and thus, the subsequent derivation of the final quantum energy differs from the expression used for non-linear molecules.

Let us apply the general energy expression in Eq. (3.21) to a linear molecule. First, the commutation relations between the conjugate momenta  $J_x - \pi_x$ ,  $J_y - \pi_y$ , and  $P_k$  appearing in the Hamiltonian in Eq. (3.13) are required [18, 19]. Second, we introduce the  $\xi_x$ ,  $\xi_y$ , and  $\xi_z$  quantities as scalar components of a vector  $\boldsymbol{\xi}$  for which

$$\sum_\sigma \xi_\sigma \omega_\sigma = 0. \quad (3.22)$$

Physically this means that  $\boldsymbol{\xi} \perp \boldsymbol{\omega}$ . Actually, the  $\xi_x$  and  $\xi_y$  components, as well as  $\omega_\sigma$ , are functions of the Euler angles. Third, following Watson, the relations for

the non-vanishing coefficients  $\gamma_{mn,r}$  are written in the form

$$\gamma_{xy,y} = -\xi_y, \quad \gamma_{yx,x} = \xi_x. \quad (3.23)$$

Substituting the determinant  $G = \boldsymbol{\mu}^2$  and the relations in Eq. (3.23) into Eq. (3.21), the correct kinetic energy in the quantum Hamiltonian form becomes [18]

$$\begin{aligned} H = & \frac{1}{2}\boldsymbol{\mu}\left\{(J_x - \pi_x + \frac{1}{2}i\hbar\xi_y)(J_x - \pi_x - \frac{1}{2}i\hbar\xi_y) + \right. \\ & \left. (J_y - \pi_y + \frac{1}{2}i\hbar\xi_x)(J_y - \pi_y - \frac{1}{2}i\hbar\xi_x)\right\} + \frac{1}{2}\sum_k P_k^2. \end{aligned} \quad (3.24)$$

Furthermore, the  $J_\sigma$  components can be expressed in terms of conjugate momenta. First we define the momenta conjugate to  $\phi$  and  $\theta$  in the form

$$p_\phi = \frac{\partial T}{\partial \dot{\phi}} = \sum_\sigma J_\sigma \left( \frac{\partial \omega_\sigma}{\partial \dot{\phi}} \right), \quad p_\theta = \frac{\partial T}{\partial \dot{\theta}} = \sum_\sigma J_\sigma \left( \frac{\partial \omega_\sigma}{\partial \dot{\theta}} \right). \quad (3.25)$$

Then calculating the derivatives  $\partial\omega_\alpha \backslash \partial\dot{\phi}$  and  $\partial\omega_\alpha \backslash \partial\dot{\theta}$ , the expressions for  $J_x$  and  $J_y$  are obtained in terms of the Euler angles and the momenta conjugate to them. The  $J_z$  component reduces to  $\pi_z$ . We have

$$\begin{aligned} J_x &= -\csc \theta \cos \chi p_\phi + \sin \chi p_\theta + \xi_x \pi_z, \\ J_y &= \csc \theta \sin \chi p_\phi + \cos \chi p_\theta + \xi_y \pi_z, \\ J_z &= \pi_z = \sum_{k,l} \zeta_{kl}^\sigma Q_k P_l. \end{aligned} \quad (3.26)$$

Analogous to Eq. (3.17) the momentum operators  $P_k$  and  $\pi_\sigma$  are of the form

$$P_k = -i\hbar \frac{\partial}{\partial Q_k}, \quad (3.27)$$

$$\pi_\sigma = -i\hbar \sum_{k,l} \zeta_{kl}^\sigma Q_k \frac{\partial}{\partial Q_l}. \quad (3.28)$$

### 3.2.1 Isomorphic Hamiltonian

The given commutation relations and the kinetic energy operators for linear molecules can be reduced using of Hougen's isomorphic Hamiltonian ( $H_{iso}$ ) [22]. This means that a linear molecule is treated in much the same way as a non-linear molecule. For example, the matrix elements can be calculated from the same integrals which are used for non-linear molecules.

Let us introduce a new molecule fixed axis system ( $x',y',z'$ ) having the Euler angles  $(\theta,\phi,\chi)$  in the axis system  $(X,Y,Z)$ . The coordinates of the atoms in the molecule are referred to  $(x',y',z')$ , and the components of the angular momenta are denoted with  $J'_x, \pi'_x$ , etc. Let be  $\chi = 0$  initially in the true Hamiltonian. Now

we introduce  $\chi$  as an independent variable describing the rotation of the  $(x', y', z')$  axes from the  $(x, y, z)$  axes about  $z(= z')$ . Since the vibrational coordinates are unaffected by the transformation, the vibrational kinetic energy operator is also unchanged. Instead, the number of rotational degrees of freedom increases in the transformation. Hence, the Hamiltonian ( $H_{iso}$ ) has additional eigenvalues that are not eigenvalues of the true Hamiltonian. The eigenvalues of ( $H_{iso}$ ) of interest for the linear configuration are those relating to the eigenvalue zero of  $(J'_z - \pi'_z)$ . Correspondingly, the wavefunctions are obtained by adopting only those products of the rotational and vibrational factors that belong to the same eigenvalue of  $J'_z$  and  $\pi'_z$ . In other words, we choose only those wavefunctions for which  $k = l$  ( $k$  and  $l$  will be determined in the next subsection) and [23]

$$J'_z \psi_{rot} = \hbar k \psi_{rot}, \quad (3.29)$$

$$\pi'_z \psi_{vib} = \hbar l \psi_{vib}. \quad (3.30)$$

### 3.3 Harmonic oscillator - rigid rotor approximation

So far only the Born-Oppenheimer approximation has been adopted when considering a molecule and its motions. The Schrödinger equation for the determination of the eigenvalues of molecular energy can be written shortly

$$(H - E)\psi = 0. \quad (3.31)$$

Certain approximations are needed to solve the rovibrational energies from Eq. (3.31). When treating the molecule as a semirigid one vibrating with small amplitudes, the dependence of  $\boldsymbol{\mu}$  and  $\mu_{\alpha\beta}$  on the normal coordinates can be neglected. With an appropriate selection of the  $x$ ,  $y$ , and  $z$  coordinates the products of inertia will cancel out. Also, the matrix  $\boldsymbol{\mu}$  reduces to three diagonal elements, which are the reciprocals of rigid moments of inertia  $I_x$ ,  $I_y$ , and  $I_z$ . In addition, the vibrational momenta are often vanishing small. Within these statements the rovibrational energy operator takes the form

$$H_{VR} = \frac{1}{2} \left( \frac{J_x^2}{I_x^e} + \frac{J_y^2}{I_y^e} + \frac{J_z^2}{I_z^e} \right) + \frac{1}{2} \sum_k P_k^2 + V. \quad (3.32)$$

The first term in Eq. (3.32) describes the energy of a rigid rotor and the last two terms describe the energy of a harmonic oscillator. The Schrödinger equation for the rigid rotor and the harmonic oscillator can be solved separately.

Let us consider the harmonic oscillator first. The vibrational potential function  $V$  can be written as a power series in the normal coordinates  $Q_k$ . Taking into account only the quadratic terms, the harmonic vibrational Hamiltonian becomes

$$H_V^0 = \frac{1}{2} \sum_k P_k^2 + \lambda_k Q_k^2, \quad (3.33)$$



where the coefficients  $\lambda_k$  are related to normal frequencies. Especially in the case of a linear  $N$  atomic molecule, the operator  $H_V^0$  above separates into  $3N-5$  independent equations corresponding to the  $3N-5$  normal vibrational modes. For non-degenerate vibrations the harmonic vibrational energies are

$$E_V^0 = h\nu_n\left(v_n + \frac{1}{2}\right), \quad v_n = 0, 1, 2, \dots \quad (3.34)$$

where  $v_n$  is the vibrational quantum number and  $\nu_n$  is the classical frequency of the  $n$ th vibration. The corresponding eigenfunctions are the Hermite orthogonal functions [14].

A linear molecule with the exception of two atomic one can possess two normal coordinates, let us say  $Q_{ta}$  and  $Q_{tb}$ , involving motions parallel to the  $x$  and  $y$  axes. The energies of these motions are degenerate with each other. This means that there exist two independent normal vibrations with the same frequency. The atoms do not move along straight lines but describe ellipses around the equilibrium positions. Therefore, there is a vibrational angular momentum associated with the degenerate vibrations. This is described by the vibrational angular momentum quantum number  $l_t$  restricted to the integer values

$$l_t = v_t, v_t - 2, \dots, -v_t + 2, -v_t, \quad (3.35)$$

where the subscript  $t$  denotes a bending vibration. Each vibrational energy level has  $v_t + 1$  fold degeneracy, which disappears as a consequence of rotational resonances, as will be seen later. The solutions of the Schrödinger equation are given by Laguerre polynomials and the vibrational energies independent of  $l_t$  are [24]

$$E_V^0 = h\nu_t(v_t + 1), \quad v_t = 0, 1, 2, \dots \quad (3.36)$$

Next we will consider the energies of the rigid rotor. A set of the independent angular momenta of a molecule consist of  $\mathbf{J}^2$ ,  $J'_z$ , and  $J_Z$ . Here  $J'_z$  is the component of  $\mathbf{J}$  along the molecule's fixed axis  $z'$  and  $J_Z$  is the component along the space fixed axis  $Z$ . The corresponding operators are Hermitian and the eigenvalues are real. These operators have simultaneous eigenfunctions which are represented for convenience by the quantum numbers  $J$ ,  $k$ , and  $m$ , respectively. The eigenvalue equations with bracket notations are [18, 25]

$$\mathbf{J}^2 |J, k, m\rangle = \hbar^2 J(J+1) |J, k, m\rangle, \quad (3.37)$$

$$J'_z |J, k, m\rangle = \hbar k |J, k, m\rangle, \quad (3.38)$$

$$J_Z |J, k, m\rangle = \hbar m |J, k, m\rangle. \quad (3.39)$$

All the eigenfunctions associated with the operators  $\mathbf{J}^2$ ,  $J'_z$ , and  $J_Z$  are orthogonal in relation to each other. This requires that they have only the diagonal non-vanishing matrix elements

$$\langle J, k, m | \mathbf{J}^2 | J, k, m \rangle = \hbar^2 J(J+1), \quad (3.40)$$

$$\langle J, k, m | J'_z | J, k, m \rangle = \hbar k, \quad (3.41)$$

$$\langle J, k, m | J_Z | J, k, m \rangle = \hbar m, \quad (3.42)$$

and for the stationary states the allowed values for the quantum numbers are

$$J = 0, 1, 2, \dots, \quad (3.43)$$

$$k = -J, -J + 1, \dots, J - 1, J, \quad (3.44)$$

$$m = -J, -J + 1, \dots, J - 1, J. \quad (3.45)$$

For derivation the rotational energies of a rigid linear molecule in an external field free case, we write the Schrödinger equation with the introduced Hermitian operators in the form

$$\frac{1}{2I} (\mathbf{J}^2 - J_z^2) |J, k, m\rangle = E_R^0 |J, k, m\rangle. \quad (3.46)$$

The energies are thus expressed by the equation

$$E_R^0 = \frac{\hbar^2}{2I} (J(J+1) - k^2). \quad (3.47)$$

Since the inertia moment along the  $z'$  axis of a linear molecule vanishes,  $J'_z = \pi'_z$  (see Eq. (3.24)) is purely a vibrational operator. Thus, the eigenvalues of  $\pi'_z$  are expressed as  $\hbar k$ , where  $k = \sum l_t$ .

### 3.4 Expanded Hamiltonian

In practise, the anharmonicity of molecular vibrations, the centrifugal distortion by rotation, and rotational-vibrational interactions must always be taken into account during high-resolution rovibrational studies of molecules. For the consideration of these effects by conventional perturbation methods some restrictions must be set. For example, the vibrational amplitudes have to be small compared to the interatomic distances, as a consequence of the clearly defined potential well around the equilibrium structure of the molecule.

For the perturbation calculations the potential function  $V$  is written as Taylor series in terms of the dimensionless normal coordinates

$$V = \frac{1}{2} \hbar c \sum_i \omega_i q_i^2 + \frac{1}{6} \sum_{i,j,k} k_{ijk} q_i q_j q_k + \frac{1}{24} \sum_{i,j,k,l} k_{ijkl} q_i q_j q_k q_l + \dots, \quad (3.48)$$

where  $\omega_k$  are harmonic vibrational frequencies and  $k_{ijk}$ ,  $k_{ijkl}$  are the cubic and quartic potential derivatives. The inertia tensor  $\boldsymbol{\mu}$  can be expanded as [17, 19]

$$\mu_{\alpha\beta} = \frac{1}{I^e} - \frac{1}{(I^e)^2} \sum_k a_k q_k + \frac{3}{4} \frac{1}{(I^e)^3} \sum_{k,l} a_k a_l q_k q_l - \dots, \quad (3.49)$$

where  $a_k = (\partial I_{\alpha\beta} / \partial q_k)_e$ . For small displacements of the nuclei, the higher order parts of  $V$  and  $\boldsymbol{\mu}$  are very small compared to the zeroth order ones. On this basis the rovibrational Hamiltonian may be divided into orders of magnitude. For the various terms of the expanded Hamiltonian it is given the notation

$$H = \sum_{m,n} H_{mn}, \quad (3.50)$$

where the subscripts  $m$  and  $n$  are the degrees in the vibrational operators and components of the total angular momentum operator, respectively.

Perturbation theory can be effectively utilized to calculate the corrections to the energies due to the various  $H_{mn}$  terms. In the case of non-degenerate energy levels, standard perturbation theory can be applied with little difficulty to the first and second-order corrections. A modified form of perturbation theory involving a transformation of the Hamiltonian can also be applied. This is convenient when considering not only the non-degenerate, but also degenerated or nearly degenerated levels which do not accidentally possess the same energy.

### 3.5 Contact transformation

The total rovibrational Hamiltonian in the rigid rotor-harmonic oscillator basis can be given as a convergent series

$$H = H_0 + \lambda H_1 + \lambda^2 H_2 + \dots, \quad (3.51)$$

where  $H_0$  is diagonal. The higher-order terms  $H_1, H_2$  etc. may have diagonal as well as off-diagonal elements, and  $0 < \lambda < 1$ . The operator  $H$  can be transformed into a desired diagonal form  $H^{(')}$  for the Schrödinger equation by a similarity transformation with an unitary operator  $U$  [17]

$$H^{(')} = U H U^{-1} = e^{i\lambda S} H e^{-i\lambda S}, \quad (3.52)$$

where  $S$  is a Hermitian operator. The eigenvalue spectrum and the normalization of the wavefunctions are preserved in the transformation. The vibrational contact transformation, specifically, diagonalizes  $H$  only with respect to the vibrational quantum numbers  $\nu$ , not the rotational quantum numbers or even  $l$ . Instead, the rotational contact transformation leads to  $H^{(')}$  diagonal in rotational quantum numbers.

The diagonalization of the Hamiltonian operator is carried out in steps in the form

$$H^{(1)} = U_1 H U_1^{-1} = e^{i\lambda S_1} H e^{-i\lambda S_1}, \quad (3.53)$$

$$\dots \\ H^{(n)} = U_n H^{(n-1)} U_n^{-1} = e^{i\lambda S_n} H^{(n-1)} e^{-i\lambda S_n}. \quad (3.54)$$

After the first contact transformation, the operator  $H^{(1)}$  can be expanded in  $\lambda$  as

$$H^{(1)} = H_0^{(1)} + \lambda H_1^{(1)} + \lambda^2 H_2^{(1)} + \dots \quad (3.55)$$

By developing  $U$  in powers of  $\lambda$  one obtains

$$U = 1 + i\lambda S + \frac{(i\lambda S)^2}{2!} + \dots, \quad (3.56)$$

$$U^{-1} = 1 - i\lambda S + \frac{(-i\lambda S)^2}{2!} + \dots, \quad (3.57)$$

and by collecting terms together with the same power of  $\lambda$

$$H_0^{(1)} = H_0, \quad (3.58)$$

$$H_1^{(1)} = H_1 + i[S_1, H_0], \quad (3.59)$$

$$H_2^{(1)} = H_2 + i[S_1, H_1] - \frac{1}{2}[S_1 [S_1, H_0]], \quad (3.60)$$

...

Now  $H_1^{(1)}$  becomes diagonal with the properly chosen  $S_1$  in the representation which diagonalizes  $H_0$ . Similarly the Hamiltonian obtained by a first contact transformation can be subjected to a second contact transformation and the procedure can be repeated.

The transformation functions  $S$  consist of combinations of  $m$  vibrational and  $n$  rotational operators and can be expressed as

$$S = \sum_{m,n} S_{mn}. \quad (3.61)$$

Some detailed forms of  $S$  are given, for example, in Ref. [24]. In the cases of accidental resonances, the functions  $S$  contain terms with denominators which may accidentally be very small. The contribution to the energy of the corresponding terms of the Hamiltonian will become very large. As a consequence, the contact transformation method, as well as the usual methods of perturbation theory, fail. The consideration of resonances are contained in their own subsection.

For example, let us apply the vibrational contact transformation in greater detail for the vibrational operator involving the cubic and quartic anharmonicities

$$H_V = H_{20} + H_{30} + H_{40}. \quad (3.62)$$

The term  $H_{30}$  has only off-diagonal matrix elements in the representation  $\psi_{20}$  which diagonalizes  $H_{20}$ . Thus, the first order correction operator  $H_{30}^{(1)}$  vanishes, and  $S_{30}$  can be determined from the relation (see Eq. (3.59))

$$0 = H_{30} + i[S_{30}, H_{20}]. \quad (3.63)$$

From Eq. (3.60) the second order correction operator becomes

$$H_{40}^{(1)} = H_{40} + i[S_{30}, H_{30}] - \frac{1}{2}[S_{30} [S_{30}, H_{20}]] \quad (3.64)$$

$$= H_{40} + (i/2)[S_{30}, H_{30}], \quad (3.65)$$

which can be evaluated with aid of  $S_{30}$ . Altogether, the diagonal matrix elements of the operator  $H_V^{(1)} = H_{20} + H_{40}^{(1)}$  in the harmonic oscillator representation give

the harmonic vibrational energies, as well as the most important anharmonic contribution to the vibrational energy. The operator  $H_V^{(1)}$  is not diagonal in  $l$  and therefore the energy correction from the vibrational angular momentum is taken into account with non-diagonal matrix elements, as will be seen later.

### 3.6 Energy expressions

The diagonal matrix elements of  $H_V^{(1)} = H_{20} + H_{40}^{(1)}$  in the harmonic oscillator basis yield the vibrational energy term values (usually in  $\text{cm}^{-1}$ ) for a linear molecule in the form [26]

$$G(v, l_t) = \sum_s \omega_s^e (v_s + \frac{d_s}{2}) + \sum_{s \leq s'} x_{ss'}^e (v_s + \frac{d_s}{2})(v_{s'} + \frac{d_{s'}}{2}) + \sum_{t \leq t'} g_{tt'} l_t l_{t'}, \quad (3.66)$$

where  $\omega_s^e$  are the harmonic frequencies, whereas  $x_{ss'}^e$  and  $g_{tt'}$  are the anharmonicity constants. The symbol  $d_s$  denotes the degree of degeneracy of the vibration  $s$ . The index  $s$  denotes any vibration and  $t$  double degenerated normal vibrational modes. To fully utilize the information involved in the typical high-resolution experimental data, a sextic order transformation of the Hamiltonian is needed. This yields small correction terms to Eq. (3.66). Since the vibrational ground state works as a reference state for spectral observations, the vibrational ground state constants  $\omega_s^0$  and  $x_{ss'}^0$  are used instead of  $\omega_s^e$  and  $x_{ss'}^e$ . Hence we write

$$G(v, l_t) = \sum_s \omega_s^0 v_s + \sum_{s \leq s'} x_{ss'}^0 v_s v_{s'} + \sum_{t \leq t'} g_{tt'} l_t l_{t'}. \quad (3.67)$$

The pure rotational operator becomes  $H_R = H_{02} + H_{04}^{(2)} + H_{06}^{(4)}$ , of which diagonal matrix elements give the term values [27]

$$F(J, k) = B_v [J(J+1) - k^2] - D_v [J(J+1) - k^2]^2 + H_v [J(J+1) - k^2]^3, \quad (3.68)$$

where  $B_v$  is the rotational constant and  $D_v$  and  $H_v$  are the centrifugal distortion constants. The vibrational dependence of the rotational constants is obtained from the matrix elements of  $H_{22}$ ,  $H_{24}$ , ... diagonal in  $v_s$  and  $l_t$ . We have the expressions of the form

$$B_v = B_e - \sum_s \alpha_s (v_s + \frac{d_s}{2}) + \sum_{s \leq s'} \gamma_{ss'} (v_s + \frac{d_s}{2})(v_{s'} + \frac{d_{s'}}{2}) + \dots, \quad (3.69)$$

$$D_v = D_e + \sum_s \beta_s (v_s + \frac{d_s}{2}) + \sum_{s \leq s'} \beta_{ss'} (v_s + \frac{d_s}{2})(v_{s'} + \frac{d_{s'}}{2}) + \dots, \quad (3.70)$$

$$H_v = H_e + \sum_s \delta_s (v_s + \frac{d_s}{2}), \quad (3.71)$$

where  $\alpha_s$ ,  $\beta_s$ ,  $\beta_{ss'}$ ,  $\gamma_{ss'}$ , and  $\delta_s$  are so-called rovibrational interaction constants. The appropriate higher order terms in a rovibrational term value expression are examined case by case in the original papers. In general, more accurate data demand higher order terms.

### 3.7 Symmetry of rovibrational states

In general, small molecules and their internal motions exhibit symmetry which can be exploited in the treatment of the rovibrational states of molecules. The utilization of the molecular symmetry is based on the mathematical group theory. The convenient symmetrical classification of the rovibrational states is introduced in the following.

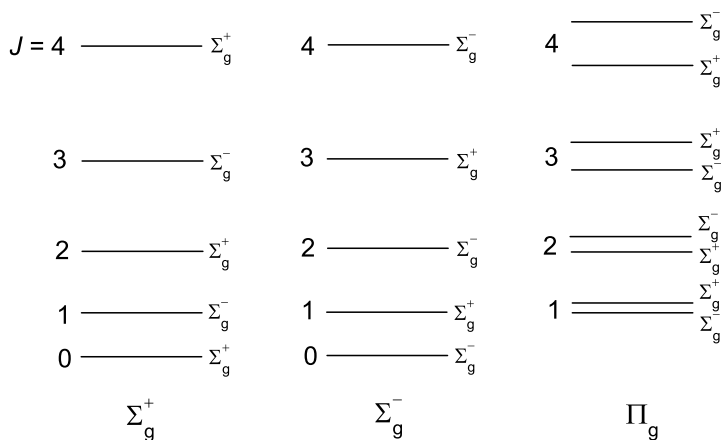
Every small molecule belongs to some specific point group. Point groups make use of the geometrical symmetry of a molecule. They are defined by the symmetry operations which transform a rigid molecule on to itself. The definition of a symmetry operation is, in turn, a procedure which does not change the appearance of the molecule. Symmetry operations rotate and/or reflect the vibrational displacements of the nuclei and the electronic coordinates. (We are dealing with the electronic ground state only and thus, the electronic coordinates can be neglected in the consideration of the rovibrational states [28].) Concerning linear molecules, there are only two different point groups which are denoted as  $C_{\infty v}$  and  $D_{\infty h}$ . The last group is for the molecules with a center of symmetry, and the first one is for other linear molecules.

When classifying the vibrational and rovibrational states of non-linear molecules, the Permutation-Inversion group (PI group) has to be considered [29]. The symmetry operations of the PI group leave the total Hamiltonian (vibrational and rotational) invariant. The correspondence of the PI group for a linear molecule is the Extended Permutation-Inversion group (EPI group) [30]. As a result of the isomorphism between the appropriate PI/EPI and the point groups, the vibrational and rovibrational states can be conveniently classified in the point group of the molecule.

The vibrational wavefunctions (or states) belong to the species  $\Sigma, \Pi, \Delta, \Phi, \dots$ , depending on the eigenvalue of  $\pi'_z$ . Similarly the rotational wavefunctions may possess the species  $\Sigma, \Pi, \Delta, \Phi, \dots$ , depending on the eigenvalue of  $J'_z$ . The basis functions for the isomorphic rovibrational Hamiltonian are obtained as products of these functions, whereas the corresponding symmetry species can be calculated as direct products of the species of the vibrational and rotational wavefunctions. The resulting basis functions may be classified as  $\Sigma, \Pi, \Delta, \Phi, \dots$ , depending on the eigenvalue of  $(J'_z - \pi'_z)$ . The only rovibrational states of interest for linear molecules are those belonging to the  $\Sigma$  species, which corresponds to the zero eigenvalue of  $(J'_z - \pi'_z)$  [18].

For linear molecules, the labelling of the rovibrational states can be continued as follows. What we are interested in is whether the total wavefunction remains unchanged or if it just changes the sign in an inversion of the nuclei in the center

of mass. In the vibrational ground state, the vibrational contribution is always invariant in relation to the inversion. Instead, the rotational wavefunction changes the sign in the inversion for odd  $J$  values but remains unchanged for even  $J$  values [31]. The rovibronic states are designated negative or positive according to the odd and even  $J$  values, respectively. Consequently the rovibronic states of a linear molecule are denoted with the superscripts  $\Sigma^-$  and  $\Sigma^+$ . This negative and positive property is referred to as parity. In the excited vibrational levels the vibrational wavefunction may change sign by inversion. This leads to an opposite manner in response to changes in the signs of rovibrational states. Especially, in the bending vibrational level of a linear molecule there are two rovibrational states with equal energy as a result of degeneration. As a consequence, in every  $J$  level there are two rovibrational states with opposite signs, as can be seen in Fig. 3.1 [30].



**Figure 3.1.** The symmetry properties of rovibrational states in the electric ground state of linear  $D_{\infty h}$  molecules. For the 'u' vibrational levels the  $u$  and  $g$  subscripts have to be exchanged throughout. For  $C_{\infty v}$  molecules, as in this work, the  $u$  and  $g$  subscripts have to be excluded.

In addition to the classifications given above, in the case of linear molecules with a center of symmetry, the rovibrational states are referred to as symmetric ( $s$ ) if the total wavefunction is invariant with respect to changes in identical nuclei. Accordingly, the states are antisymmetric ( $a$ ) if the total wavefunction changes the sign in response to the changes in identical nuclei. This property is taken into account using the subscripts of  $g$  (gerade) and  $u$  (ungerade). Altogether, the symmetry species of rovibrational states for linear molecules are expressed as

$$\begin{aligned}
 C_{\infty v} & : \Sigma^+, \Sigma^- \\
 D_{\infty h} & : \Sigma_g^+, \Sigma_u^+, \Sigma_g^-, \Sigma_u^-
 \end{aligned}$$

In addition to the vibrational wavefunctions, the normal vibrational modes can be classified according to their symmetry species. For example, in the case of DCCI the three stretching modes belong to the totally symmetric  $\Sigma^+$  species and the two bending modes belong to the double degenerated  $\Pi$  species.

When writing out the energy matrix, the Wang symmetrization [32] can be conveniently used. In a symmetrized (Wang) rovibrational basis the energy matrix for a given value of  $J$  splits into two blocks, one containing the  $\Sigma^+$ ,  $\Pi_e$ ,  $\Delta_e$ ,  $\Phi_e$ , etc., vibrational states and the other including the  $\Sigma^-$ ,  $\Pi_f$ ,  $\Delta_f$ ,  $\Phi_f$ , etc., states. These blocks differ in their rovibrational symmetry with respect to the inversion operation. The explicit basis functions depend on the phase convention used in defining the rotational and vibrational states separately [33]. The usual transition selection rules and selection rules for perturbations can be given in terms of the  $e$  and  $f$  parities [34]. The transformation of the energy matrix into the block-diagonalized form for a linear molecule has been discussed in detail in [35, 36].

### 3.8 Resonances

If two or more energy states have equal or almost equal energy and if they possess the same symmetry species, they interact with each other. In other words, there exists a resonance between states. Resonances are an essential and unavoidable part of infrared spectrum analysis. Since the resonances are widely discussed in the original papers, only a short overview is given in the following.

As a consequence of an interaction, the states in question become mixed. The wavefunctions of the perturbed states are then linear combinations of the unperturbed wavefunctions and the corresponding energy levels repel each other. This sometimes results in very peculiar appearances of spectral lines. Due to the resonances non-zero off-diagonal terms arise in the transformed Hamiltonian. Considering the off-diagonal matrix elements, the resonances can be conveniently classified into essential or accidental resonance categories.

#### 3.8.1 *Essential resonances*

Let us now study the essential resonances with the aid of the bending vibration of a linear molecule. As a result of the equal  $x$  and  $y$  directions the bending vibration is doubly degenerate. Therefore, the corresponding energy level splits into two components with all  $J$  values. This rotational  $l$ -doubling is due to molecular symmetry and is said to be an essential resonance. It is clear that the Hamiltonian term, which couples the states given above, is diagonal with respect to vibrational quantum numbers  $\nu_s$ . Instead, there are the changes of  $\Delta k = \pm 2$  and  $\Delta l_t = \pm 2$  between the resonance components. The  $l$ -doubling introduced is a special case of a rotational resonance which is identified with  $\Delta k \neq 0$  and  $\Delta l_t \neq 0$  between interacting levels. This means that various types of rotational resonances may



arise including higher order ones. The coupling matrix elements for the lowest order rotational  $l$  resonances take the form

$$\begin{aligned} \left\langle v_t^{l_t}, k, J \parallel v_t^{l_t \pm 2}, k \pm 2, J \right\rangle &= \frac{q_t^*}{4} \{ (v_t \mp l_t) (v_t \pm l_t + 2) [J(J+1) \\ &\quad - k(k \pm 1)] [J(J+1) - (k \pm 1)(k \pm 2)] \}^{1/2}, \end{aligned} \quad (3.72)$$

where  $q_t^*$  is the effective coupling parameter describing the efficiency of the resonance. In addition to the  $J$  dependence of the matrix element, the  $q_t^*$  parameter may be a function of  $J$ . The shift of the energy levels depends on both the coupling parameter and the energy difference between the unperturbed levels. In general, the determination of  $q_t^*$  numerically is often the main goal of the resonance analysis. On the other hand, the parameters  $q_t^*$  do not depend on the anharmonicity of the vibrations immediately and they can be determined from harmonic frequencies [17]. For DCCI these determinations have been reported in paper [IV].

In addition to the rotational  $l$  resonance, the vibrational  $l$  resonance belongs to essential resonances. The vibrational  $l$  resonance may take place between rovibrational levels including the changes  $\Delta k = 0$  and  $\Delta l_t \neq 0$ . The coupling matrix elements become

$$\begin{aligned} \left\langle v_t^{l_t}, v_{t'}^{l_{t'}}, k, J \parallel v_t^{l_t \pm 2}, v_{t'}^{l_{t'} \mp 2}, k, J \right\rangle &= \frac{1}{4} r_{tt'}^* \{ (v_t \mp l_t) (v_t \pm l_t + 2) \\ &\quad (v_{t'} \pm l_{t'}) (v_{t'} \mp l_{t'} + 2) \}^{1/2}, \end{aligned} \quad (3.73)$$

where  $r_{tt'}^*$  is the effective coupling parameter.

Altogether, in essential resonances the coupling matrix elements are off-diagonal with respect to one or more  $l_t$  quantum numbers only. In the spectrum analysis of DCCI, the different types of  $l$  resonances have been taken into account. The explicit expressions of the coupling matrix elements, together with the coupling parameters, have been shown in the original papers.

### 3.8.2 Accidental resonances

When vibrational levels possess nearly the same energy by chance, the resulting resonance is referred to as accidental. The matrix element between the connected states is off-diagonal with respect to at least two quantum numbers  $v_s$ . The accidental resonances are classified into two groups. First, an anharmonic resonance takes place between vibrational states with the same symmetry species. The coupling matrix elements originate from the off-diagonal Hamiltonian terms containing the vibrational operators only. Although the elements are not functions of  $J$ , the coupling resonance parameter may depend on  $J$  due to the influence of higher order terms in the Hamiltonian. In the present studies of DCCI the strong third and the weak fifth order anharmonic resonances originated from  $H_{30}$ ,  $H_{32}$ , and  $H_{50}$  were analysed. In literature the third order anharmonic resonance especially, is referred to as Fermi resonance [37]. The coupling matrix elements for the Fermi

resonances analysed in DCCI are obtained from the expression

$$\left\langle v_3, v_5^{l_5} \parallel v_3 - 1, (v_5 + 2)^{l_5} \right\rangle = \frac{1}{2} W_{355}^* \{v_3[(v_5 + 2)^2 - l_5^2]\}^{1/2}, \quad (3.74)$$

where  $W_{355}^*$  is the coupling parameter.

Second, in a linear molecule the Coriolis resonance results from the interaction between the non-degenerate and degenerate vibrational modes due to the rotation about the  $x$  and  $y$  axes. According to the Jahn rule [38] Coriolis coupling may occur between the vibrational modes if the direct product of their symmetry species contains a species of a rotation. The coupling matrix element is a function of both vibrational and rotational quantum numbers. The off-diagonal elements take the form [17]

$$\begin{aligned} \left\langle v_n^{l_t}, v_t^{l_t}, k, J \parallel v_n - 1, (v_t + 1)^{l_t \pm 1}, k \pm 1, J \right\rangle = \\ \pm W_C [v_n(v_t \pm l_t + 2)]^{1/2} [J(J + 1) - k(k \pm 1)]^{1/2}, \end{aligned} \quad (3.75)$$

where  $W_C$  is the coupling parameter.

An important feature of the Coriolis coupling is a progressively increasing perturbation of rovibrational states with increasing  $J$ . In other words, the energy shift may be greatest with high  $J$  values in spite of the larger original energy difference between the interacting states. This has been observed in the DCCI studies, as well [III].

## 4 High-resolution infrared spectrum analysis

### 4.1 Rovibrational spectrum

In this section we discuss the spectrum consisting of transition lines as a function of the energy of a radiation quantum. Spectral lines adopted in the following discussion originate from the one-photon transitions between quantized rovibrational energy states, when the molecule is in the electronic ground state. In principle, a molecule can emit or absorb the same quantum, even if absorption is a more useful process in laboratory measurements. The allowed transitions between rovibrational states can be predicted by exploiting both symmetry theory and quantum mechanical selection rules. The accurate treatment of line intensities is a separate branch of spectroscopy and out of the scope of this work.

#### *4.1.1 Selection rules and intensities*

In a molecule the transition between the rovibrational states may happen if there exists at least one non-vanishing matrix element of the type

$$\langle \psi_i | \mu_A | \psi_f \rangle, \quad A = X, Y, Z, \quad (4.1)$$

where  $\mu_A$  is an electric dipole moment component with respect to a space fixed coordinate  $A$ . The eigenfunctions  $\psi_i$  and  $\psi_f$  relate to the initial and final states.

Within an assumption of small vibration amplitudes the rotational and vibrational motions, as well as the rotational and vibrational transition selection rules can be treated separately. Since the field free space is isotropic, only one of the  $\mu_A$  components is necessary to take into consideration. Let us make a random choice and write  $\mu_Z$  in terms of  $\mu_\alpha$ . Therefore we have

$$\mu_Z = \Phi_{Zx}\mu_x + \Phi_{Zy}\mu_y + \Phi_{Zz}\mu_z. \quad (4.2)$$

Above  $\Phi_{Z\alpha}$  is a direction cosine which depends on the rotational coordinates that comprise the Euler angles and  $\alpha$  is a molecule fixed axis. The operator  $\mu_\alpha$  is a

function of the vibrational coordinates  $Q_k$  only, and hence  $\mu_\alpha$  can be expanded in a power series

$$\mu_\alpha = (\mu_\alpha)_0 + \sum_k \left( \frac{\partial \mu_\alpha}{\partial Q_k} \right)_0 Q_k + \dots \quad (4.3)$$

Normally, the higher terms are very small and it is customary to only consider the first two terms of Eq. (4.3). Getting back to the matrix elements given in Eq. (4.1) one obtains

$$\begin{aligned} \langle \psi_i | \mu_Z | \psi_f \rangle &= \sum_\alpha (\mu_\alpha)_0 \langle \psi_i(v, l) | \psi_f(v, l) \rangle \langle \psi_i(J, k) | \Phi_{Z\alpha} | \psi_f(J, k) \rangle \\ &+ \sum_{\alpha, j} \left( \frac{\partial \mu_\alpha}{\partial Q_j} \right)_0 \langle \psi_i(v, l) | Q_j | \psi_f(v, l) \rangle \langle \psi_i(J, k) | \Phi_{Z\alpha} | \psi_f(J, k) \rangle. \end{aligned} \quad (4.4)$$

Now it can be seen that the vibrational transition is possible if it associates with a dipole moment change. That is to say vibration  $j$  is infrared active if  $\left( \frac{\partial \mu_\alpha}{\partial Q_j} \right)_0 \neq 0$ . On the other hand, the matrix elements  $\langle \psi_i(v, l) | Q_j | \psi_f(v, l) \rangle$  give rise to the conventional vibrational selection rules for absorptions. For a linear molecule we have [24]

$$\Delta v_n = +1, \quad (\text{non-degenerate mode}) \quad (4.5)$$

$$\Delta v_t = +1, \quad \Delta l_t = \pm 1, \quad (\text{degenerate mode}) \quad (4.6)$$

which are true for a harmonic oscillator only. In practise, the anharmonicity is always present and a transition may occur contradicting these rules. From the statements in Eqs. (4.5) and (4.6) it follows that both fundamental transitions and hot bands between two consecutive levels are allowed. The rotational fine structure in vibrational bands originates from the non-zero matrix elements of  $\langle \psi_i(J, k) | \Phi_{Z\alpha} | \psi_f(J, k) \rangle$  [39]. This will be discussed more in the next subsection. One sees from the first term of Eq. (4.4) that the pure rotational spectrum can appear only if a molecule possesses a permanent dipole moment, that is  $(\mu_\alpha)_0 \neq 0$ . The selection rule for a pure rotational spectrum is [25]

$$\Delta J = \pm 1. \quad (4.7)$$

Considering the symmetry properties of a molecule, the symmetry selection rules for the allowed electric dipole moment transitions can be deduced. Basically, the  $\langle \psi_i | \mu_Z | \psi_f \rangle$  matrix element has to remain unchanged by any symmetry operation. In the case of vibrational transitions this means that the direct product of the symmetry species of the  $\psi_i$  and  $\psi_f$  wavefunctions in the point group has to include the symmetry species of at least one of the  $\mu_\alpha$  components. Hence the symmetry selection rule becomes

$$\Gamma(\psi_i) \otimes \Gamma(\psi_f) \ni \Gamma(\mu_\alpha). \quad (4.8)$$

It is important to notice that none of the approximations of the molecular motions have been made in the derivation of this rigorous rule.

Let us consider transitions involving the ground vibrational state. Since the ground vibrational wavefunction belongs to the totally symmetric  $\Sigma^+$  species of the point group, the transitions in question are infrared active only if the excited state carries the same symmetry species as one of the  $\mu_\alpha$  components.

With the use of the labelling system introduced in section 3.7, the selection rules for the rovibrational transitions can be given as follows. We are interested in the matrix elements of the form  $\langle \psi_f | \mu_x | \psi_i \rangle$ ,  $\langle \psi_f | \mu_y | \psi_i \rangle$ , and  $\langle \psi_f | \mu_z | \psi_i \rangle$ . The  $\mu_\alpha$  components change the sign upon inversion. Therefore, if both wavefunctions  $\psi_i$  and  $\psi_f$  have the same parity, the integrals will also change signs upon inversion. Since the value of a definite integral is independent of any transformation of coordinates, such transitions are forbidden. Altogether, the transitions between a positive and a negative level are allowed [31].

There are many factors contributing to line intensity of an electric dipole transition. First, transition probability plays a role as an intermolecular intensity factor. It depends on, for example, the square of the dipole moment matrix element, as well as the energy difference between the initial and final states. On the other hand, the population in the initial state significantly affects transition intensity. The populations are functions of temperature and they are obtained from the Boltzmann distribution law. In addition, the spin statistics may give rise to noticeable intensity variations in the spectrum. This is the case if a molecule has a symmetry center in an equilibrium state, i.e. there are nuclei in identical positions. The spin statistical effect may appear, for example, in the linear molecules belonging to the  $D_{\infty h}$  point group. DCCI shows  $C_{\infty v}$  point group symmetry and therefore spin statistics have no role in the present spectrum analysis. A more detailed discussion on the intensity factors is provided in [40].

### 4.1.2 Band types

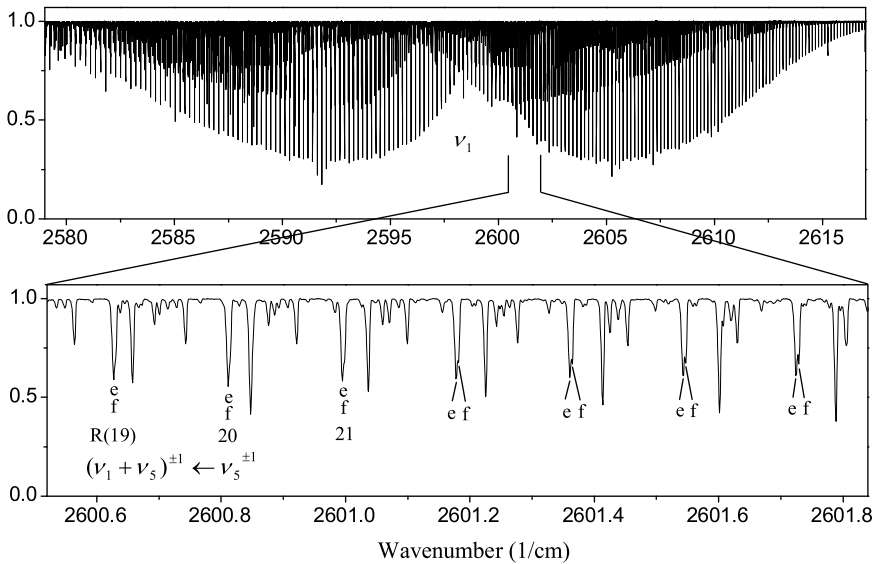
When interpreting infrared spectra, the selection rules based on the harmonic approximation are not adequate. The anharmonicity of vibrations and various interactions render so called forbidden transitions possible leading to overtone and combination bands. Thus there are several types of rovibrational bands in an infrared spectrum. A customary classification of the bands is mainly based on the rotational fine structure. In a linear molecule rotational selection rules have to be considered separately between stretching and bending vibrations. In the stretching mode dipole moment varies along the molecular axis only and  $\Delta k = 0$ . Instead, the change of the perpendicular vibrational state of a molecule changes the vibrational angular momentum along the molecular axis and  $\Delta k = \pm 1$ . A detailed derivation of rotational selection rules is given in [25]. Altogether, the bands can be conveniently classified into the following groups. Below the notations  $k = 0$  and  $k \neq 0$  refer to a lower level.

- 1)  $\Delta k = 0$ ,  $k = 0$ ,  $\Delta J = \pm 1$ .

This is a parallel band including the  $P$  ( $\Delta J = -1$ ) and  $R$  ( $\Delta J = +1$ ) branches. In addition to strong fundamentals difference or combination bands may appear. The symmetry of the upper and lower vibrational levels is  $\Sigma^+$ .

$$2) \Delta k = 0, k \neq 0, \Delta J = 0, \pm 1.$$

This transition takes place between the upper and lower levels with the symmetries of the form  $\Pi - \Pi$ ,  $\Delta - \Delta$ , and so on. Sometimes a weak  $Q$  branch ( $\Delta J = 0$ ) occurs between the  $P$  and  $R$  branches in the spectrum. Because the upper and lower levels are doublets the bands arise as pairs. In spite of different types of doublings the lines of these pairs may often coincide with each other. The coincident lines of the  $(\nu_1 + \nu_5)^{\pm 1} - \nu_5^{\pm 1}$  bands of DCCI are illustrated in Fig. 4.1.



**Figure 4.1.** The experimental spectrum of DCCI in the region of  $\nu_1$ . The lower part presents in detail a short piece of the fundamental  $\nu_1$  and in addition the structure of  $\Pi$ -type hot band  $\nu_1 + \nu_5 - \nu_5$  indicating how the  $e$  and  $f$  components begin to be resolved. The weak  $Q$  branch of the hot band cannot be observed in the overview spectrum.

3)  $\Delta k = \pm 1$ ,  $\Delta J = 0, \pm 1$ .

In this type of band, the symmetries of the upper and lower levels differ from each other. All the bands possess the  $P$ ,  $R$ , and  $Q$  branches. The perpendicular fundamentals and the hot bands  $\Delta k = \pm 1$  belong to this group.

## 4.2 Nuclear hyperfine structure in an infrared spectrum

Nuclear hyperfine structure in a pure rotational, as well as in rovibrational spectra, results from the interactions between the molecular electric field gradient and the quadrupole moments of a nucleus. The effect of the interaction depends strongly on the rotational state of a molecule. Accordingly, the rotational energy levels are split into hyperfine components.

In a rotating molecule the nuclear spin  $\mathbf{I}$  is coupled to the molecular angular momentum  $\mathbf{J}$  resulting in a new angular momentum  $\mathbf{F}$ , which is quantized. If there is only one single nucleus coupling the number of the hyperfine components of a rotational state is the number of the allowed values of the quantum number  $F$  given by

$$F = J + I, J + I - 1, \dots, |J - I|. \quad (4.9)$$

There also may be more than one coupling nucleus leading to a more complicated case [41] which is not reasonable to analyze in the present context. In addition, only the first order treatment has been adopted here. The higher order corrections [42] may be significant in microwave studies, for example.

The transition selection rules and the relative intensities for the hyperfine components originate from the non-zero matrix elements of the molecular dipole moment component along the space fixed axis. The selection rules become

$$\Delta J = 0, \pm 1, \quad \Delta F = 0, \pm 1. \quad (4.10)$$

The relative intensities of the transitions depend on the  $J$  and  $F$  quantum numbers in upper and lower energy states [41, 43].

In general, the interactions are possible for molecules which include non-spherical nuclei with the nuclear spin  $I \geq 1$ . The nuclear spins of iodine and deuterium nuclei are  $\frac{5}{2}$  and 1, respectively. Hence, in principle a two nuclei quadrupole coupling occurs in the DCCI molecule. The quadrupole coupling coefficients for the I and D nuclei are 2254.2 MHz and 209.5 kHz [2, 3]. This means that the coupling effect with the D nucleus will be vanishing small at least in the case of the infrared spectrum. The number of the hyperfine components for each  $J$  value can be calculated from Eqs. (4.9) and (4.10). In DCCI there are six hyperfine levels for each rotational states with  $J > 2$ . This splitting yields 16 hyperfine components into a single rovibrational line with the  $J > 2$  lower level values. For  $J \leq 2$  the number of both the hyperfine levels and sublines is smaller.

As a consequence of quadrupole coupling, the spectral lines of a high resolution infrared spectrum will be asymmetrically broadened or even split into subcomponents. With increasing  $J$  values the separations of subcomponents decrease.

Thus the separate subcomponents are most probably seen for small  $J$  values, and also in far infrared vibration bands where the Doppler effect does not disturb. The vibrational dependence of the interaction is very small and that is why the quadrupole effect is similar between the rovibrational bands of a molecule. In the case of DCCI the infrared lines with  $J \leq 5$  were broadened in all the bands and therefore were excluded from the analyses as discussed in paper I.

### 4.3 Least-squares fit

A least-squares fit method can conveniently be applied in the experimental determination of the molecular and resonance parameters. The ground state rotational constants can be determined from the observed rotational and rovibrational transitions using the standard linear least-squares fit method. On the other hand, the energies derived from the Hamiltonian matrix are typically non-linear in parameters and thus the non-linear least-squares fit has to be introduced. The non-linear fit plays an essential role in an infrared spectrum analysis and it will be discussed in some detail in the following.

In spite of the non-linearity in a rigorous sense, most spectroscopical models are approximately linear in a reasonable region about the appropriate values of the parameters. In other words, the approximately linearized expression of the transition energies with respect to the parameters is justified. Hence, the non-linear fit reduces to an iterative procedure based on the standard least-squares fit. In this application the linear function in the parameters  $p_j$  becomes

$$E_i^{obs} - E_i^{calc} = \sum_j \left( \frac{\partial E_i^{calc}}{\partial p_j} \right) \delta p_j, \quad (4.11)$$

where  $E_i^{obs}$  are the observed transition energies. The calculated transition energies  $E_i^{calc}$  are obtained by diagonalizing the Hamiltonian. The coefficient matrix  $X = \partial E_i^{calc} / \partial p_j$  can be calculated numerically from the Hamiltonian derivatives and the eigenvectors of the Hamiltonian. The  $\delta p_j$  terms actually describe the corrections to the parameters instead of the estimated values of the parameters themselves. The prescription for calculating the  $\delta p$  values from the observations  $E = E^{obs} - E^{calc}$  is the following matrix expression [44]

$$\delta p = (X^T W X)^{-1} X^T W E, \quad (4.12)$$

where  $W$  is a diagonal matrix, which contains the weights of the observed transitions. In the first step of the procedure the appropriate transition energies are calculated with the carefully chosen estimations of the initial parameters. Then the corrections to the parameters are estimated from Eq. (4.12). The initial parameters are corrected with these estimates and the procedure is repeated iteratively, until the fit has converged. The data must be, of course, more numerous than the unknown parameters.

The least-squares method cannot provide the true values of the spectroscopical parameters. In addition to the estimates for the parameters, the standard



deviation of the measurement errors as well as the standard errors (or standard deviations) of the estimated parameters are obtained from the fit. It is worthwhile to emphasize that the standard errors are not absolute uncertainties but together, with the standard deviation of the measurement errors, describe the internal accuracy of the model. The estimation of the absolute accuracy of the parameters is an essential part of the spectroscopical analysis. However, at the same time the estimation is very troublesome when starting from the measurement arrangements. On the other hand, one criterion for a correct physical model is the random distribution of residuals, which are comparable to the inaccuracy of the experimental lines. In this work only those fits are accepted which have satisfied the criterion given above.

## 5 Harmonic force field calculations

In this chapter the procedure for the evaluation of the harmonic force constants of monoiodoacetylene will be introduced, even if the consideration is partially valid for small molecules in general. The treatment of the force constants is based on the classical ball-and-spring molecular model which assumes that the atoms are point masses and weightless springs hold them together obeying Hooke's Law. The force constants determine the linear dependence between the displacement of atoms and the restoring forces acting on the atoms.

### 5.1 Harmonic potential approximation

According to the Born-Oppenheimer approximation the internal potential energy  $V$  of a molecule can be written as a Taylor series in Cartesian displacement coordinates  $x_i$  of the nuclei. For  $N$  nuclei we have

$$2V = V_e + 2 \sum_i^{3N} \left( \frac{\partial V}{\partial x_i} \right)_e x_i + \sum_{i,j}^{3N} \left( \frac{\partial^2 V}{\partial x_i \partial x_j} \right)_e x_i x_j \quad (5.1)$$

$$+ \frac{1}{3} \sum_{i,j,k}^{3N} \left( \frac{\partial^3 V}{\partial x_i \partial x_j \partial x_k} \right)_e x_i x_j x_k + \dots \quad (5.2)$$

The zero of the energy scale is conveniently chosen so that  $V_e = 0$ . Considering the potential with respect to the equilibrium state of the molecule, the second term vanishes. The cubic and higher terms provide the anharmonic contributions to the potential and are neglected here. The remaining second derivatives are the harmonic force constants  $f_{ij}$ , even if they are useless physically in the Cartesian coordinates. Therefore, let us choose the coordinate basis consisting of bond lengths, angles between chemical bonds, and torsional angles which are characteristic of intermolecular motions, i.e. molecular vibrations. These coordinates, being unaffected by translations and rotations of the molecule as a whole, are called

internal coordinates  $s_k$ . When approximating that the variation in one internal coordinate causes no redistribution of the electrons in the molecule, the coordinates are called valence coordinates and the corresponding force field is the valence force field (VFF). Such a model is obtained by setting the terms  $F_{ij}$ ,  $i \neq j$  equal to zero in the potential function written in the basis of internal coordinates. When using the non-zero  $F_{ij}$  terms related to next-neighbouring  $i$  and  $j$  internal coordinates, the force field is said to be the simplified general valence force field (SGVFF). For example, in DCCI the coordinates  $\Delta R_1$  and  $\Delta R_2$  are the next-neighbouring ones, but  $\Delta R_1$  and  $\Delta R_3$  are not (see Fig. 5.1). Without restrictions of the off-diagonal  $F_{ij}$  terms, we have the general valence force field (GVFF) [24].

The general relation between  $s_k$  and  $x_i$  is written in the form

$$s_k = \sum_i b_{ki} x_i + \sum_{i,j} b_{kij} x_i x_j + \sum_{i,j,h} b_{kijh} x_i x_j x_h + \dots, \quad (5.3)$$

where the coefficients  $b_{ki}$ ,  $b_{kij}$ , etc. are determined by the molecular geometry. Within the restriction of the infinitesimal amplitudes of vibrations, the nuclei move along straight lines. This leads to the linear relation between  $s_k$  and  $x_i$ , and in the matrix notation Eq. (5.3) becomes

$$\mathbf{s} = \mathbf{B}\mathbf{x}. \quad (5.4)$$

## 5.2 Secular equation for molecular vibrations

The kinetic and potential energy in the internal coordinates can be written in the forms [24]

$$2T = \tilde{\mathbf{x}}\mathbf{M}\dot{\mathbf{x}} = \tilde{\mathbf{s}}\tilde{\mathbf{B}}^{-1}\mathbf{M}\mathbf{B}^{-1}\dot{\mathbf{s}} = \tilde{\mathbf{s}}\mathbf{G}^{-1}\dot{\mathbf{s}}, \quad (5.5)$$

$$2V = \tilde{\mathbf{x}}\mathbf{f}_x\mathbf{x} = \tilde{\mathbf{s}}\tilde{\mathbf{B}}^{-1}\mathbf{f}_x\mathbf{B}^{-1}\mathbf{s} = \tilde{\mathbf{s}}\mathbf{F}\mathbf{s}, \quad (5.6)$$

where  $\mathbf{M}$  is a mass matrix and  $\tilde{\phantom{x}}$  denotes a transpose matrix. The matrices  $\mathbf{f}_x$  and  $\mathbf{F}$  are the force constant matrices in the Cartesian and internal coordinates, respectively. One can formulate from these energy expressions the conventional secular equation in the general form [24]

$$\mathbf{GFL} = \mathbf{L}\mathbf{\Lambda}, \quad (5.7)$$

where  $\mathbf{\Lambda}$  is a diagonal matrix whose elements are the normal wavenumber parameters  $\lambda_k = 4\pi^2 c^2 \bar{\nu}_k^2$  and  $\bar{\nu}_k$  is the wavenumber of the vibration  $k$  in  $\text{cm}^{-1}$ . The structure of the molecule and the masses of the nuclei are usually known for the construction of the  $\mathbf{G}$  matrix. The normal wavenumbers can be evaluated if the force constants are known, and vice versa, though unambiguousness of the solution depends on the number of the wavenumbers with respect to that of the force constants. The normal wavenumber parameters are obtained by diagonalizing the  $\mathbf{GF}$  matrix, which is rarely symmetric. For convenience,  $\mathbf{GF}$  is symmetrized before diagonalization with a matrix mechanical method given by Miyazawa [45].

The  $\mathbf{L}$  matrix introduced above is composed of the eigenvectors of  $\mathbf{GF}$ . The  $\mathbf{L}$  matrix determines the transformation between the internal coordinates  $\mathbf{s}$  and the normal coordinates  $\mathbf{Q}$ , which are characteristic of the normal vibrational modes of a molecule. In the matrix form we have

$$\mathbf{s} = \mathbf{LQ}. \quad (5.8)$$

In a symmetry adapted basis the  $\mathbf{GF}$  matrix breaks up into blocks which can be diagonalized separately. The separate  $\mathbf{G}$  and  $\mathbf{F}$  matrices are broken up in the same way. In a linear molecule there exists one block associated with the stretching modes and two identical blocks related to the double degenerate bending modes. In a linear molecule the block form is obtained immediately by using the appropriately ordered internal coordinates. The factorization is based on the fact that a linear molecule and its potential function are symmetric along the axis of the molecule [14].

### 5.3 Experimental data and harmonic force field

The experimental harmonic force constants are mainly based on observed vibrational frequencies. However, the number of the vibrational frequencies is only comparable to the number of the force constants when considering small molecules with high symmetry. A useful way to obtain additional data is to utilize different isotopomers whose force fields are equal within the Born-Oppenheimer approximation. In addition, the Coriolis coupling constants and the centrifugal distortion constants provide information about the harmonic force field. Mean square amplitudes are one source of information for the determination of the force constants, but they will not be discussed here. Next an iterative method, developed by I. M. Mills [46] will be introduced, by which a trial set of force constants is refined to fit the experimental vibrational frequencies as well as the supplementary spectroscopical data.

#### 5.3.1 Normal vibrational frequencies

Suppose  $\mathbf{F}_0$  is the initial trial force constant matrix. The corresponding eigenvalues and eigenvectors are  $\mathbf{\Lambda}_0$  and  $\mathbf{L}_0$ . Mills has applied a first order perturbation theory to refine  $\mathbf{F}_0$  so that the difference between observed and calculated frequencies is minimized [46]. First a small change  $\mathbf{F}_1$  in the  $\mathbf{F}$  matrix is considered producing a corresponding change in the eigenvalues and eigenvectors of the secular equation

$$\mathbf{F} = \mathbf{F}_0 + \mathbf{F}_1, \quad (5.9)$$

$$\mathbf{\Lambda} = \mathbf{\Lambda}_0 + \mathbf{\Lambda}_1, \quad (5.10)$$

$$\mathbf{L} = \mathbf{L}_0 + \mathbf{L}_1 = \mathbf{L}_0(\mathbf{E} + \mathbf{L}_0^{-1}\mathbf{L}_1) = \mathbf{L}_0\mathbf{A}. \quad (5.11)$$

The secular equation for the perturbed system in the original eigenvectors  $\mathbf{L}_0$  becomes

$$\mathbf{GFL}_0\mathbf{A} = \mathbf{L}_0\mathbf{A}\mathbf{\Lambda}. \quad (5.12)$$

Since  $\tilde{\mathbf{L}}\mathbf{F}\mathbf{L} = \mathbf{\Lambda}$  and  $\mathbf{G} = \mathbf{L}_0\tilde{\mathbf{L}}_0$ , we obtain

$$\mathbf{L}_0^{-1}\mathbf{GFL}_0 = \mathbf{L}_0^{-1}\mathbf{GF}_0\mathbf{L}_0 + \mathbf{L}_0^{-1}\mathbf{GF}_1\mathbf{L}_0 \quad (5.13)$$

$$= \mathbf{\Lambda}_0 + \tilde{\mathbf{L}}_0\mathbf{F}_1\mathbf{L}_0 \quad (5.14)$$

$$= \mathbf{H}_0 + \mathbf{H}_1. \quad (5.15)$$

Now the secular determinant is of the form [14]

$$\begin{vmatrix} (\lambda_0)_1 + (H_1)_{11} - \lambda & (H_1)_{12} & \\ (H_1)_{21} & (\lambda_0)_2 + (H_1)_{22} - \lambda & etc. \\ & & etc. \end{vmatrix} = 0, \quad (5.16)$$

from which the eigenvalues in the first order approximation become

$$\lambda_i = (\lambda_0)_i + (\tilde{\mathbf{L}}_0\mathbf{F}_1\mathbf{L}_0)_{ii}. \quad (5.17)$$

Further, the first order frequency correction to the normal vibration  $i$  can be written

$$(\lambda_1)_i = \sum_{u,w} (L_0)_{ui} (L_0)_{wi} (F_1)_{uw}, \quad (5.18)$$

where  $u$  and  $w$  denote the internal coordinates used as basis of the potential function. By letting  $\mathbf{\Lambda}_1 \rightarrow 0$  and  $\mathbf{F}_1 \rightarrow 0$  the elements of the so called Jakobian matrix  $\mathbf{J}$  of  $\mathbf{\Lambda}$  with respect to  $\mathbf{F}$  become

$$J_i^{uw} = \frac{\partial \lambda_i}{\partial F_{uw}} = 2 (L_0)_{ui} (L_0)_{wi}, \quad (5.19)$$

$$J_i^{uu} = \frac{\partial \lambda_i}{\partial F_{uu}} = (L_0)_{ui} (L_0)_{ui}. \quad (5.20)$$

Now Eq. (5.18) can be written as

$$\mathbf{JF}_1 = \boldsymbol{\lambda}_1, \quad (5.21)$$

where  $\boldsymbol{\lambda}_1$  is a column vector with elements  $(\lambda^{obs} - \lambda^{calc})$ . If there are more data than the unknown force constants, it is convenient to solve Eq. (5.21) by least-square fitting. Using the weighting matrix  $\mathbf{P}$  Eq. (5.21) becomes

$$\left(\tilde{\mathbf{J}}\mathbf{P}\mathbf{J}\right)\mathbf{F}_1 = \left(\tilde{\mathbf{J}}\mathbf{P}\right)\boldsymbol{\lambda}_1. \quad (5.22)$$

The first order corrections to the original eigenvectors  $\mathbf{L}_0$  can be determined using the elements of matrix  $\mathbf{A}$  (see Eq. (5.11)). They are easily derived to the expanded form [46]

$$A_{ij} = \frac{\sum_{u,w} (L_0)_{ui} (L_0)_{wj} (F_1)_{uw}}{(\lambda_0)_j - (\lambda_0)_i}, i \neq j, \quad (5.23)$$

$$A_{ii} = 1. \quad (5.24)$$

### 5.3.2 Coriolis coupling constants

In a free molecule the rotational and vibrational motions may interact through Coriolis coupling. The strength of Coriolis coupling depends on the Coriolis coupling constants  $\zeta_{ij}^\sigma$  ( $\sigma = x, y, z$  and the indexes  $i$  and  $j$  denote the normal vibrations). The effect of Coriolis coupling on molecular vibrational frequencies is usually weak and may sometimes be observed from high-resolution spectral bands with high  $J$  values. The coupling constants  $\zeta_{ij}^\sigma$  depend upon the normal modes of vibration of a molecule and provide useful information about force constants. The  $\zeta_{ij}^\sigma$  constants are obtained experimentally from rovibrational or rotational spectra, and they can only be determined for relatively small molecules. Meal and Polo [47, 48] have developed a theory about the relationship between the Coriolis coupling constants and the normal vibrations of a molecule. Let us derive next the corresponding expression with Eqs. (5.19) and (5.20) for the Coriolis coupling constants in terms of the theory proposed by Meal and Polo.

The normal coordinates  $Q_i$  and mass-weighted Cartesian displacement coordinates  $q_\alpha^x, q_\alpha^y, q_\alpha^z$  for each atom  $\alpha$  of the molecule are given as column vectors

$$\mathbf{Q} = (Q_1 Q_2 Q_3 \dots Q_n R_x R_y R_z T_x T_y T_z)^T, \quad (5.25)$$

$$\mathbf{q} = (q_1^x q_1^y q_1^z \dots q_N^x q_N^y q_N^z)^T, \quad (5.26)$$

where  $N$  is the number of the atoms in the molecule and  $n = 3N-6$  ( $3N-5$  for linear molecules) is the number of the normal modes. The last six (five for linear molecules) coordinates relate to the rotational and translational motions of the molecule. These coordinates disappear according to the Eckart conditions [15, 49] in the consideration of molecular vibrations.

A linear transformation between the normal vibrational coordinates  $\mathbf{Q}$  and mass-weighted Cartesian displacement coordinates  $\mathbf{q}$  can be written in the form

$$\mathbf{Q} = \boldsymbol{\ell}^{-1} \mathbf{q}, \quad (5.27)$$

where  $\boldsymbol{\ell}$  consists of the elements of the form  $\ell_{\alpha i}^\sigma$ . The coupling constants  $\zeta_{ij}^\sigma$  can be given as

$$\zeta_{ij}^\sigma = \sum_{\alpha} (\ell_{\alpha i}^\tau \ell_{\alpha j}^\rho - \ell_{\alpha i}^\rho \ell_{\alpha j}^\tau), \quad \sigma, \tau, \rho = x, y, z, \quad (5.28)$$

where the sum applies to all atoms of the molecule. The expression (5.28) shows that the Coriolis coupling constants  $\zeta_{ij}^\sigma$  depend on the atomic displacements in the two vibrations  $i$  and  $j$ . Actually, this equation was already introduced in the construction of the classical Hamiltonian. Since the secular equation is usually solved in internal coordinates, it is convenient to calculate  $\zeta_{ij}^\sigma$  in this basis. The reformulation of  $\zeta_{ij}^\sigma$  is based on the eigenvector matrix  $\mathbf{L}$  obtained as a solution of the secular equation. We have

$$\zeta_{ij}^\sigma = \sum_{u,w} L_{ui}^{-1} L_{wj}^{-1} C_{uw}^\sigma, \quad (5.29)$$

where the indices  $u$  and  $w$  label the internal coordinates and  $C_{uw}^\sigma$  is obtained from the atomic masses and geometry of the molecule. The  $\zeta^\sigma$  matrices are independent

of the force field. However, the  $\zeta_{ij}^\sigma$  elements depend upon small variations in the  $\mathbf{L}$  matrix elements produced by small changes in the force constants. This is the basis for the refinement of the force constants by applying perturbation theory.

Following Mills [46], we consider a small change in the  $\zeta^\sigma$  matrix given by

$$\zeta^\sigma = \zeta_0^\sigma + \zeta_1^\sigma. \quad (5.30)$$

Mills has derived the relation between the elements of  $\zeta_1^\sigma$  and the correction term  $\mathbf{F}_1$  in the form

$$(\zeta_1^\sigma)_{ij} = \frac{\sum_{k \neq i} (\zeta_0^\sigma)_{jk} \sum_{u,w} (L_0)_{ui} (L_0)_{wi} (F_1)_{uw}}{\sum_{k \neq i} (\lambda_i - \lambda_k)} \quad (5.31)$$

$$+ \frac{\sum_{k \neq j} (\zeta_0^\sigma)_{ik} \sum_{u,w} (L_0)_{uj} (L_0)_{wk} (F_1)_{uw}}{\sum_{k \neq j} (\lambda_j - \lambda_k)}. \quad (5.32)$$

Further, letting  $\zeta_1^\sigma \rightarrow 0$  and  $\mathbf{F}_1 \rightarrow 0$  the elements of the Jakobian  $\mathbf{J}$  become

$$\frac{\partial \zeta_{ij}^\sigma}{\partial F_{uw}} = \sum_{k \neq i} \zeta_{jk}^\sigma \frac{L_{ui} L_{wk} + L_{wi} L_{uk}}{(\lambda_k - \lambda_i)} - \sum_{k \neq j} \zeta_{ik}^\sigma \frac{L_{uj} L_{wk} + L_{wj} L_{uk}}{(\lambda_k - \lambda_j)}, \quad u \neq w \quad (5.33)$$

$$\frac{\partial \zeta_{ij}^\sigma}{\partial F_{uu}} = \sum_{k \neq i} \zeta_{jk}^\sigma \frac{L_{ui} L_{uk}}{(\lambda_k - \lambda_i)} - \sum_{k \neq j} \zeta_{ik}^\sigma \frac{L_{uj} L_{uk}}{(\lambda_k - \lambda_j)}. \quad (5.34)$$

The non-zero Jakobian elements given above can be deduced from the structures of the  $\mathbf{L}$  and  $\zeta^\sigma$  matrices. The so-called Jahn rule [38], originating from the symmetry theory, states that the elements  $\zeta_{ij}^\sigma \neq 0$  only if the direct product of the irreducible representations  $\Gamma(Q_i) \otimes \Gamma(Q_j)$  contains the representation  $\Gamma(R_\sigma)$ . It should be noted, however, that the Jahn rule is not a sufficient condition for the  $\zeta_{ij}^\sigma$  elements to be different from zero. If we consider the elements  $\ell_{\alpha i}^\sigma$ ,  $\ell_{\alpha i}^\tau$ , and  $\ell_{\alpha i}^\rho$  as the components of a vector  $\mathbf{l}_{\alpha i}$ , we can rewrite Eq. (5.28) in the form

$$\zeta_{ij}^\sigma = \sum_{\alpha} (\mathbf{l}_{\alpha i} \times \mathbf{l}_{\alpha j}) \cdot \mathbf{e}_\sigma, \quad (5.35)$$

where  $\mathbf{e}_\sigma$  is a unit vector. One sees that  $\zeta_{ij}^\sigma = 0$  if either  $\mathbf{l}_{\alpha i}$  and  $\mathbf{l}_{\alpha j}$  are parallel or one of them is parallel to the  $\sigma$  axis.

In general case the  $\zeta^\sigma$  matrices are skew-symmetric and thus

$$\tilde{\zeta}^\sigma = -\zeta^\sigma. \quad (5.36)$$

Especially for linear molecules, we can write out the next properties of the  $\zeta^\sigma$  matrices. We divide the normal coordinates, according to symmetry, into three different types  $Q_{tx}$ ,  $Q_{ty}$ , and  $Q_s$  involving motions parallel to the  $x$ ,  $y$ , and  $z$  axes (the molecular axis coincides with the  $z$  axis). Now the non-zero elements of  $\zeta^\sigma$  are [16, 25]

$$\zeta_{st_y}^x = -\zeta_{st_x}^y, \quad (5.37)$$

$$\zeta_{t_x t'_y}^z = -\zeta_{t'_y t_x}^z = \delta_{tt'}, \quad (5.38)$$

where  $\delta_{tt'}$  is the Kronecker delta. In addition the Coriolis coupling constants obey certain relations among themselves [47] and are not independent of each other.

### 5.3.3 Centrifugal distortion constants

In a rotating molecule the interatomic distances and the bond angles will vary slightly as a function of the speed of rotation. This gives rise to centrifugal distortion of the molecule. On the other hand, the distortion depends on the vibrational state of the molecule. Neglecting terms, higher than the fourth order with respect to angular momentum, the Hamiltonian for the rotational energy is of the form [50]

$$H_R = \frac{1}{2} \sum_{\alpha} \sigma_{\alpha\alpha} P_{\alpha}^2 + \frac{1}{4} \sum_{\alpha, \beta, \gamma, \delta} \tau_{\alpha\beta\gamma\delta} P_{\alpha} P_{\beta} P_{\gamma} P_{\delta}, \quad (5.39)$$

where  $\alpha, \beta, \gamma,$  and  $\delta$  are summed over the molecule fixed Cartesian coordinates  $x, y,$  and  $z$ . The constant  $\sigma_{\alpha\alpha}$  relates to the  $\alpha\alpha$  component of the inverse of the effective principal inertia tensor and  $P_{\alpha}$  is the component of the angular momentum along the  $\alpha$  axis. A detailed evaluation of Eq. (5.39) is given by Allen and Cross [25]. When applying a perturbation calculation the centrifugal distortion constant  $\tau_{\alpha\beta\gamma\delta}$  becomes

$$\tau_{\alpha\beta\gamma\delta} = \sum_{v'} \frac{\langle v | \mu_{\alpha\beta} | v' \rangle \langle v' | \mu_{\gamma\delta} | v \rangle}{h\nu_{vv'}}, \quad (5.40)$$

where the sum applies to the vibrational states  $v'$ , excluding state  $v$  under consideration. The nominator  $h\nu_{vv'}$  is the energy difference between the  $v$  and  $v'$  states, and  $\mu$ 's are the components of the inverse instantaneous inertia tensor. The above expression shows that  $\tau_{\alpha\beta\gamma\delta}$  is independent of the rotational quantum numbers.

A simplified expression for  $\tau_{\alpha\beta\gamma\delta}$  using rectilinear internal coordinates shows that  $\tau_{\alpha\beta\gamma\delta}$  can be expressed in terms of the geometry and harmonic force constants of the molecule. According to Kivelson [51]  $\tau_{\alpha\beta\gamma\delta}$  can be derived by using the form

$$\tau_{\alpha\beta\gamma\delta} = -\frac{1}{2} \sum_{u,w} \mu_{\alpha\beta}^u (F^{-1})_{uw} \mu_{\gamma\delta}^w, \quad \alpha, \beta, \gamma, \delta = x, y, z, \quad (5.41)$$

where the linear dependence between  $\mu_{\alpha\beta}^u$  and the internal coordinate  $s_u$  has been used, that is

$$\mu_{\alpha\beta}^u = \frac{\partial \mu_{\alpha\beta}}{\partial s_u}. \quad (5.42)$$

In terms of an inertia tensor and displacement internal coordinates the approximation above corresponds to the expression

$$I_{\alpha\beta} = I_{\alpha\beta}^e + \sum_u \frac{\partial I_{\alpha\beta}}{\partial s_u} \Delta s_u, \quad (5.43)$$



where the index  $e$  refers to the equilibrium state of the molecule. Further we can write

$$\mu_{\alpha\beta}^u = -\frac{J_{\alpha\beta}^u}{I_{\alpha\alpha}^e I_{\beta\beta}^e} \quad (5.44)$$

and

$$J_{\alpha\beta}^u = \frac{\partial I_{\alpha\beta}}{\partial s_u}. \quad (5.45)$$

Now the  $\tau_{\alpha\beta\gamma\delta}$  constant becomes

$$\tau_{\alpha\beta\gamma\delta} = -\frac{1}{2I_{\alpha\alpha}^e I_{\beta\beta}^e I_{\gamma\gamma}^e I_{\delta\delta}^e} \sum_{u,w} J_{\alpha\beta}^u (F^{-1})_{uw} J_{\gamma\delta}^w. \quad (5.46)$$

Again, according to Mills' treatment [46] we introduce a small change  $\mathbf{F}_1$  to the initial trial force field matrix  $\mathbf{F}_0$  and apply the first order perturbation theory. Hence we obtain the Jacobian elements of  $\tau_{\alpha\beta\gamma\delta}$  with respect to  $\mathbf{F}$  in the form

$$\begin{aligned} \frac{\partial \tau_{\alpha\beta\gamma\delta}}{\partial F_{rt}} &= \frac{1}{2I_{\alpha\alpha}^e I_{\beta\beta}^e I_{\gamma\gamma}^e I_{\delta\delta}^e} \sum_{u,w} J_{\alpha\beta}^u J_{\gamma\delta}^w [(F_0^{-1})_{ur} (F_0^{-1})_{tw} \\ &\quad + (F_0^{-1})_{ut} (F_0^{-1})_{rw}], \end{aligned} \quad (5.47)$$

$$\frac{\partial \tau_{\alpha\beta\gamma\delta}}{\partial F_{rr}} = \frac{1}{2I_{\alpha\alpha}^e I_{\beta\beta}^e I_{\gamma\gamma}^e I_{\delta\delta}^e} \sum_{u,w} J_{\alpha\beta}^u J_{\gamma\delta}^w (F_0^{-1})_{ur} (F_0^{-1})_{rw}. \quad (5.48)$$

These equations, together with Eqs. (5.19, 5.20, 5.33, 5.34), can be utilized simultaneously in the refinement of the harmonic force field.

It is notable that many of the  $\tau_{\alpha\beta\gamma\delta}$  constants vanish. The nonvanishing ones can be determined for each molecule from symmetry considerations [50]. Especially for a linear molecule there is only one non-zero constant  $\tau_{\alpha\alpha\alpha\alpha}$  corresponding to the equilibrium structure of the molecule. The relation between the  $\tau_{\alpha\alpha\alpha\alpha}$  and spectroscopical  $D_e$  constants is [17]

$$D_e = -\frac{\tau_{\alpha\alpha\alpha\alpha}}{4}. \quad (5.49)$$

In the harmonic approximation with the straight line motions of the atoms the experimental  $D_e$  constant of a linear molecule provides information about the stretching force constants only.

### 5.3.4 Isotopic substitution

The force constants depend on the electronic structure of the molecule but not on the masses of atoms. Hence, the force fields of the isotopically substituted molecules are equal within the limits of the Born-Oppenheimer approximation.

This is the basis for the utilization of the different data measured for the isotopically substituted molecules.

The treatment of the vibrational frequencies depends on the substituted atoms. Apart from deuterium-hydrogen substitution in a molecule, isotopic substitutions involve small differences in atomic mass and thus small vibrational frequency shifts. It has been pointed out that the small, accurate experimental frequency shifts are even more significant than the supplementary frequencies from other isotopomers in the determination of the force field [24, 52, 53]. In the case of small, shifted frequencies the use of a simple first order perturbation treatment is convenient when refining force constants [54]. Instead, for the hydrogen substituted molecules one has to use another method which will be adopted in the case of monoiodoacetylene. Let us write out for  $m$  different isotopic species  $m$  different secular equations in the form

$$\begin{aligned} \mathbf{G}_1 \mathbf{F} \mathbf{L}_1 &= \mathbf{L}_1 \mathbf{\Lambda}_1, \\ \mathbf{G}_2 \mathbf{F} \mathbf{L}_2 &= \mathbf{L}_2 \mathbf{\Lambda}_2, \\ &\dots \\ \mathbf{G}_m \mathbf{F} \mathbf{L}_m &= \mathbf{L}_m \mathbf{\Lambda}_m. \end{aligned} \tag{5.50}$$

If the frequencies for every isotopomer would be independent of each other, the number of frequencies would be  $m \times (3N-5)$  for a linear molecule. However, the frequencies of isotopomers are related by, so-called, isotopic rules and are thus not independent. The number of the independent frequencies can be deduced from the Teller-Redlich product rule [55], according to which the relation of  $n$  frequencies belonging to each symmetry block is

$$\frac{\omega_1 \omega_2 \dots \omega_n}{\omega'_1 \omega'_2 \dots \omega'_n} = \left( \frac{|\mathbf{G}|}{|\mathbf{G}'|} \right)^{1/2}, \tag{5.51}$$

where the prime relates to an isotopically substituted molecule. If the  $\mathbf{G}$  matrix has been written in symmetry coordinates, the expression above relates the frequencies of two isotopically substituted molecules in each symmetry block. In a linear molecule the number of the independent frequencies is thus equal to [24]

$$2 \times (3N - 5) - h, \tag{5.52}$$

where  $h$  is the number of symmetry blocks.

## 5.4 Harmonic force field for monoiodoacetylene

The harmonic force field determination for monoiodoacetylene is based on the five experimental unperturbed normal vibrational frequencies  $\omega_s^e$  and equilibrium quartic centrifugal distortion constant  $D_e$  for both the HCCI and DCCI isotopic species. The experimental data is seen in Table 5.1, and a detailed description of the determination of the data is given in paper [IV].

Table 5.1. The experimental data in  $\text{cm}^{-1}$  used in the determination of the harmonic force field of monoiodoacetylene.

	HCCI	$\sigma^a$	o-c	DCCI	$\sigma$	o-c
$\omega_1^e$	3455.223169	3.46	-0.0001	2673.365468	2.67	0.0001
$\omega_2^e$	2103.248000	2.10	-0.0001	1973.153584	8.80	0.0279
$\omega_3^e$	524.195769	3.21	-0.0782	512.706549	3.21	0.0844
$\omega_4^e$	642.140110	0.642	-0.5157	502.529893	0.503	0.3890
$\omega_5^e$	262.816410	0.263	-0.2010	249.826042	0.250	0.2030
$D_e \times 10^8$	1.697351	0.0170	0.0006	1.352856	0.0135	-0.0070

<sup>a</sup> Estimated uncertainty used to calculate the weighting factor.

The intramolecular quadratic potential function in the basis of the rectilinear internal coordinates is of the form [56]

$$V(R_1 R_2 R_3 R_4 R_5) = V_e + \frac{1}{2} \sum_{i,j} F_{ij} \Delta R_i \Delta R_j, \quad (5.53)$$

where  $V_e$  is the equilibrium potential. The coordinates  $\Delta R_1$ ,  $\Delta R_2$ , and  $\Delta R_3$  describe the bond stretchings and the double degenerated coordinates  $\Delta R_4$  and  $\Delta R_5$  are the linear angle bendings illustrated in Fig. 5.1. The coefficients  $F_{ij}$  are the harmonic force constants.

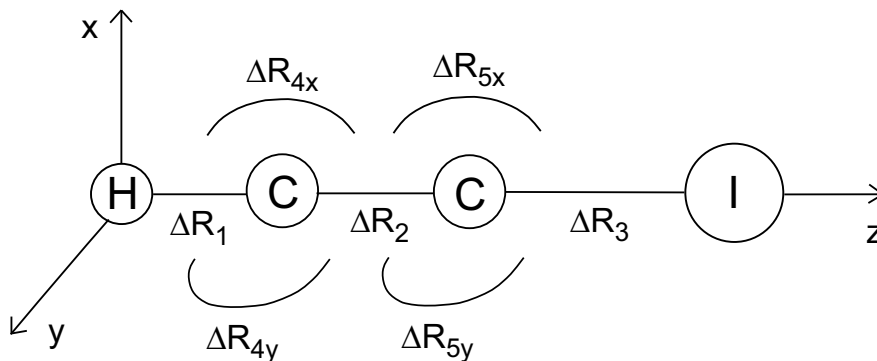


Figure 5.1. The linear monoiodoacetylene molecule. The internal displacement coordinates are denoted with  $\Delta R_i$ . The bond lengths are  $1.0591 \text{ \AA}$  (H-C),  $1.21767 \text{ \AA}$  (C-C), and  $1.97964 \text{ \AA}$  (C-I) [IV].

According to Eq. (5.4) the non-zero elements of the  $\mathbf{B}$  matrix ( $7 \times 12$ ) become [56]

$$b_{13} = b_{26} = b_{39} = 1,$$

$$\begin{aligned}
b_{16} &= b_{29} = b_{3,12} = -1, \\
b_{41} &= b_{62} = \sqrt{\frac{R_2}{R_1}}, \\
b_{44} &= b_{65} = -\sqrt{\frac{R_2}{R_1}} - \sqrt{\frac{R_1}{R_2}}, \\
b_{47} &= b_{68} = \sqrt{\frac{R_1}{R_2}}, \\
b_{54} &= b_{75} = \sqrt{\frac{R_3}{R_2}}, \\
b_{57} &= b_{78} = -\sqrt{\frac{R_3}{R_2}} - \sqrt{\frac{R_2}{R_3}}, \\
b_{5,10} &= b_{7,11} = \sqrt{\frac{R_2}{R_3}}.
\end{aligned}$$

Above, the double degenerated internal coordinates associated with the adjacent  $R_i$  and  $R_j$  coordinates have been scaled with the factor  $\sqrt{R_i R_j}$ . The internal displacement coordinates in the order of  $\Delta R_1, \Delta R_2, \Delta R_3, \Delta R_{4x}, \Delta R_{5x}, \Delta R_{4y}, \Delta R_{5y}$  correspond to the symmetry displacement coordinates. Hence, the transformation  $\mathbf{F} = \widetilde{\mathbf{B}}^{-1} \mathbf{f}_x \mathbf{B}^{-1}$  (see Eq. (5.6)) results in the force constant matrix  $\mathbf{F}$  in the block form. The block structure of the  $\mathbf{G}$  and  $\mathbf{GF}$  matrices coincide with that of  $\mathbf{F}$ . Using the simplified general valence force field (SGVFF) approximation the  $\mathbf{F}$  matrix constitutes a total of eight non-zero independent force constants

$$\mathbf{F} = \begin{vmatrix} F_{11} & F_{12} & & & & & & & \\ F_{12} & F_{22} & F_{23} & & & & & & \\ & F_{23} & F_{33} & & & & & & \\ & & & F_{44} & F_{45} & & & & \\ & & & F_{45} & F_{55} & & & & \end{vmatrix}. \quad (5.54)$$

The  $3 \times 3$  and  $2 \times 2$  blocks are of  $\Sigma^+$  and  $\Pi$  symmetries respectively and can be treated separately.

The eight harmonic force constants with the estimated uncertainties were calculated by a weighted least-squares fit method [44] from the set of 12 experimental data (normal vibrational frequencies and centrifugal distortion constants), as discussed in paper [IV]. The results are seen in Table 5.2.

The  $\mathbf{L}$  matrix is associated with the solution of the secular equation Eq. (5.7). The  $\mathbf{L}$  matrix elements corresponding to the resulted force constant matrix  $\mathbf{F}$  are

$$\mathbf{L} = \begin{vmatrix} 0.6949 & 0.3111 & 0.0124 & & & & & & \\ -0.2600 & 0.3110 & 0.0481 & & & & & & \\ 0.0943 & -0.2180 & 0.1866 & & & & & & \\ & & & 0.9881 & -0.0440 & & & & \\ & & & -0.3504 & 0.6090 & & & & \end{vmatrix}. \quad (5.55)$$

When writing out the Jacobian elements of  $\mathbf{\Lambda}$  and  $D_e$  with respect to  $\mathbf{F}$ , the effect of different data on the separate force constants  $F_{ij}$  can be deduced. Let us

Table 5.2. The resulting harmonic force constants in  $aJ/\text{\AA}^2$  for monoiodoacetylene.

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$F_{11} = 6.340(18)^a$
$F_{22} = 14.1(46)$
$F_{33} = 4.2(20)$
$F_{12} = -0.272(36)$
$F_{23} = -1.3(39)$
$F_{44} = 0.17338(46)$
$F_{55} = 0.10509(22)$
$F_{45} = 0.04856(77)$

---

<sup>a)</sup> The error limits are one standard deviation in the units of the last digit given.

first consider the vibrational frequencies with the aid of the equations of (5.19) and (5.20). One sees that the frequencies always give information about the diagonal force constants. In addition, the frequencies provide information about the off-diagonal force constants depending on the off-diagonal  $\mathbf{L}$  elements, which describe the strength of the mixing of symmetry coordinates. It is remarkable that although the interaction between the  $\Delta R_1$  and  $\Delta R_3$  coordinates in the construction of the potential function was neglected, these coordinates are slightly mixed with each other. This is seen from the off-diagonal elements of the  $\mathbf{L}$  matrix given above.

The centrifugal distortion constant  $D_e$  gives information for both the diagonal and off-diagonal force constants related to stretching vibrations. The derivatives given below describe the relative efficiency in the determination of different force constants. Because of the rectilinear internal coordinate approximation the derivatives associated with the bending force constants are zero. The derivatives, with respect to the non-diagonal force constants  $F_{12}$  and  $F_{23}$ , are precisely equal in both isotopic species (see Table 5.3). This is a numerical result from the computer calculation according to Eq. (5.47). In order to check the result with algebra a tedious calculation is needed due to the complexity of the Jacobian elements  $J_{\alpha\beta}^u = \partial I_{\alpha\beta} / \partial s_u$  [24]. This has been omitted.

Next, let us consider the role that the Coriolis coupling constants play in the refinement of the force field in the case of monoiodoacetylene (point group  $C_{\infty v}$ ), even if there was no experimental  $\zeta_{ij}^\sigma$  constant in the present force field determination. Monoiodoacetylene has three stretching modes ( $Q_1, Q_2, Q_3$ ) of ( $\Sigma^+$ ) symmetry and two bending modes ( $Q_4, Q_5$ ) of ( $\Pi$ ) symmetry. One sees from the character table of  $C_{\infty v}$  that the rotation  $R_y$  (or  $R_x$ ) is of species ( $\Pi$ ). This corresponds to the species from the direct product between the representations of the stretching and bending modes. Now we obtain, from the Jahn rule and Eqs. (5.36, 5.37, 5.38), the  $\zeta^y$  matrix in the form

Table 5.3. The non-zero Jacobian elements of  $D_e$  with respect to the force constants  $F_{ij}$ .

HCCI	DCCI
$\frac{\partial D_e}{\partial F_{11}} = -0.0047 \times 10^{-7}$	$\frac{\partial D_e}{\partial F_{11}} = -0.011 \times 10^{-7}$
$\frac{\partial D_e}{\partial F_{22}} = -0.12 \times 10^{-7}$	$\frac{\partial D_e}{\partial F_{22}} = -0.10 \times 10^{-7}$
$\frac{\partial D_e}{\partial F_{33}} = -1.7 \times 10^{-7}$	$\frac{\partial D_e}{\partial F_{33}} = -1.3 \times 10^{-7}$
$\frac{\partial D_e}{\partial F_{12}} = -0.048 \times 10^{-7}$	$\frac{\partial D_e}{\partial F_{12}} = -0.048 \times 10^{-7}$
$\frac{\partial D_e}{\partial F_{23}} = -0.91 \times 10^{-7}$	$\frac{\partial D_e}{\partial F_{23}} = -0.91 \times 10^{-7}$

$$\zeta^y = \begin{pmatrix} 0 & 0 & 0 & \zeta_{14}^y & \zeta_{15}^y \\ 0 & 0 & 0 & \zeta_{24}^y & \zeta_{25}^y \\ 0 & 0 & 0 & \zeta_{34}^y & \zeta_{35}^y \\ -\zeta_{14}^y - \zeta_{24}^y - \zeta_{34}^y & 0 & 0 & 0 & 0 \\ -\zeta_{15}^y - \zeta_{25}^y - \zeta_{35}^y & 0 & 0 & 0 & 0 \end{pmatrix}. \quad (5.56)$$

One obtains from Eq. (5.33), for example, the expression

$$\frac{\partial \zeta_{14}^y}{\partial F_{12}} = \zeta_{24}^y \frac{L_{11}L_{22} + L_{21}L_{12}}{(\lambda_1 - \lambda_2)} - \zeta_{34}^y \frac{L_{11}L_{23} + L_{21}L_{13}}{(\lambda_1 - \lambda_3)}, \quad (5.57)$$

which is not equal to zero. This is even true when considering the disappearance of mixing among coordinates. This is a consequence of having the term  $L_{11}L_{22}$  in the numerator. Further, one can deduce that the Coriolis coupling constants may furnish useful information about off-diagonal force constants (see Eq. 5.19).

## 6 Conclusions

An experimental infrared study on a small molecule is typically a multi-phased process starting from a sample preparation and ending with a set of numerical results and their interpretation. When considering infrared measurements, the basic idea is to generate an energy transition between two rovibrational energy states and register the corresponding transition wavelength as accurately as possible. The applied theoretical model, the molecule with atomic motions, has to be in accordance with observations. The classical model of a rigid rotor-harmonic oscillator is a suitable starting point for the derivation of the quantum mechanical energy expression. The various anharmonicity corrections and resonance terms are unavoidable in practice and play an essential role in the optimization of the model.

The determination of the ground state rotational constants of DCCI was a straightforward process. The microwave data adopted from previous work by Heineking *et al.* [3] increased the accuracy of the constants significantly. Thus the fixing of the ground state constants used in upper level analyses is well-grounded.

Sometimes the analysis of a desired vibrational level means the simultaneous treatment of a very complex level system in its entirety. The complexity is usually a consequence of a large amount of various resonances acting on the level in question. This is what occurs, for example, in the  $v_2 = v_4 = 1$  level of DCCI. On the other hand, the resonance effects possess a scientific importance of their own. The vibration and rotation dependence of resonance on is one interesting research subject.

In addition to the customary step by step analysis, the simultaneous analysis of vibrational levels is sometimes practical. First, simultaneous analysis may decrease the amount of fitting parameters in proportion to observations. At the same time the parameters may become more characteristic when considering energy distribution between different types of atomic motions. Second, when analyzing the vibrational levels simultaneously, weak resonances may be revealed. This happened in the case of the Coriolis resonance  $v_3 = 1(\Sigma^+)/v_4 = 1(\Pi_e)$  in DCCI. In the step by step analysis this resonance was absorbed by the rovibrational constants, whereas in the simultaneous analysis of the consecutive vibrational levels it was revealed. Third, simultaneous analysis may be helpful in assignment work. This

has been discussed in studies on the HCCNC molecule [57]. Therein Vigouroux *et al.* report about the wide simultaneous analysis of infrared and millimeter-wave transitions, which is referred to as global analysis. Global analyses comprise one of the main trends in the spectroscopy of linear molecules nowadays.

In reviewing one of the goals of this work, the accurate normal vibrational frequencies for DCCI were obtained, even if there are two exceptions. Because there were not observations to the  $v_2 = 2$  and  $v_3 = 2$  levels, the attained  $\omega_2^e$  and  $\omega_3^e$  parameters are still less accurate. This reflects to the relatively large uncertainties of particular force constants.

In considering the calculation of numerical parameters, computer programming is an essential part of the work. All of the fits for the experimental data were carried out by self-made computer programs. The programming language Fortran was used for numerical computing and proved to be efficient for the present purposes.

Altogether, the immediate results of this thesis are the numerous experimental rovibrational and resonance parameters determined mostly with high accuracy. The estimated statistical uncertainties for the parameters have been obtained, also. Furthermore, these results were utilized partly together with previous results for HCCI in the determination of the bond lengths of monoiodoacetylene. The attained accurate structure is in turn necessary for the precise harmonic force field calculation. Finally, the eight harmonic force constants were calculated with their estimated uncertainties. The resulting structure will be useful data when one is carrying out theoretical quantum chemical applications. Again, the present results for the force constants will be the reference values for results from *ab initio* calculations. This could be the next step in studies on monoiodoacetylene.



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