INTERNAL ROTATION IN SYMMETRIC TOP MOLECULES

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Abstract
Internal rotation in symmetric top molecules offers an excellent opportunity to investigate large amplitude motion in a relatively simple intramolecular environment. Due to specific symmetry characteristics of a symmetric top molecular frame, the internal rotation degree of freedom is in the zeroth order approximation separable from the small amplitude vibrations and the overall rotation, thus enabling to characterize the vibrational-torsional-rotational energy structure with a relatively simple Hamiltonian. Lessons from symmetric internal rotor studies may be applied to more complex systems, such as asymmetric internal rotors and macromolecules.

This thesis deals with internal rotation in CH$_3$SiH$_3$, CH$_3$SiD$_3$, CH$_3$CF$_3$ which have become a prototype of symmetric internal rotors. The thesis presents high resolution vibration-torsion-rotation spectra and detailed analysis of these molecules. Particular attention is focused on torsion-mediated interactions, such as Coriolis-type interactions and Fermi-type interactions, coupling the internal rotation and the small amplitude vibrational motion.

The studies show that the expansion of the data to the small amplitude vibrations and inclusion of the torsion-mediated interactions play a crucial role in order to obtain an appropriate characterization of the vibrational-torsional-rotational energy level structure and physically meaningful molecular parameters.

Keywords: high resolution, infrared spectroscopy, internal rotation, symmetric top
To My Family
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This thesis is dedicated to my wife Anne and my children Jaakko, Vappu and Hilla who constantly bring light into my life.

Oulu, October 2004                Jyrki Schroderus
List of Original Papers

The present thesis is based on the following papers which are referred to in the text by their Roman numerals:


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1 Introduction

This thesis deals with internal rotation in polar symmetric top molecules, such as methyl silanes CH$_3$SiH$_3$ and CH$_3$SiD$_3$, and trifluoroethane CH$_3$CF$_3$. Symmetric top molecules with a single internal rotation degree of freedom about the molecular symmetry axis provide an excellent opportunity for studying large amplitude motion in a relatively simple molecular environment. Due to specific symmetry characteristics of the symmetric top molecular frame, the torsional degree of freedom is in the zeroth order approximation separable from the small amplitude vibrational degrees of freedom and the overall rotational degrees of freedom, thus providing a simplification in the overall Hamiltonian and the energy level structure compared to those of more complex molecules, such as asymmetric tops with internal rotation. Thereby, the symmetric top studies may provide important knowledge for studies of large amplitude motion in asymmetric tops.

In molecular rotation-vibration spectroscopy, a gaseous molecular sample is subjected to an oscillating electromagnetic field that interacts with molecular charge distribution and gives rise to transitions from a molecular quantum state to another. In a transition, the molecule either absorbs or emits a part of the radiation spectrum which corresponds to an energy difference between molecular quantum states involved in transitions. The spectrum is recorded by spectroscopic means and analysed by using a molecular model in order to obtain information on molecular properties.

The internal rotation complicates the quantum mechanical treatment and the vibration-rotation energy structure in many respects when compared with semi-rigid symmetric tops. First, the torsional energy typically falls in between rotational and vibrational energy scale, thus generating a dense vibrational-torsional overtone energy level structure. In addition, each vibration-rotation-torsion energy level is split into three torsional sub-levels, labeled by $\sigma = -1, 0, +1$, thus increasing the complexity of the energy level system.

The internal rotation degree of freedom gives rise to a great number of redundant Hamiltonian terms that are difficult to separate into the individual contributions according to their physical origin. The redundant terms primarily arise from two mechanisms.

First, to first order, the electric dipole selection rules ($\Delta v_T = \Delta k - \Delta \ell = \Delta \sigma = 0$) of the vibrational-torsional-rotational transitions forbid direct observations between different $(v_T, k, \sigma)$ states, and therefore, the axial rotational parameters such as $A_0$, $D_{0,k}$, and the leading torsional parameters $F_0$ and $V_{0,3}$ in the ground vibrational state (GS) are difficult
to determine. Here, $v_T$ indicates torsional quanta, $k$ is the eigenvalue of the $z$-component of the total angular momentum, and $\ell$ is the quantum number associated with the vibrational angular momentum.

Second, the molecular Hamiltonian is implicitly subjected to contact transformations by neglecting terms off-diagonal in the Hamiltonian, thus resulting in large model errors on the leading molecular parameters, such as those characterizing the torsional potential. The first mechanism is essentially a technical problem whereas the second mechanism predominantly arises from insufficiency in the vibration-torsion-rotation theory and practical problems in spectrum analyses.

The first result of the selection rules is that the conventional microwave and millimeter-wave spectra are insensitive to the leading terms in the torsional Hamiltonian. However, there are few methods to overcome the complications arising from the electric dipole selection rules. The selection rules ($\Delta k = \Delta \sigma = 0$) can be broken by applying molecular-beam electric-resonance (MBER) spectroscopy [1–3] which is capable of providing dipole moment information and accurate measurements of $(A_0 - B_0)$ quantity and the leading torsional parameters $V_0$ and $\rho$. The MBER measurements form an excellent starting point for molecular studies when no other information is available. Unfortunately, they are confined to the lowest rotational states in the vibrational and torsional ground state, and therefore cannot be used to determine energy levels with a wide range of rotational and torsional quantum numbers.

A second result of the selection rules is that the pure torsional spectra are forbidden in the lowest order. However, the torsional transitions with $(\Delta v_T = 0, \Delta k = 0; \Delta \sigma = 0)$ become weakly allowed by second-order effects, such as intensity capture through torsion-mediated interactions mechanisms and, on the other hand, higher terms of the electric dipole moment expansion [4, 5]. The torsional bands typically fall in the far-infrared region and the line strengths are only 0.1% of those of infrared active fundamental bands. Therefore, experiments on torsional bands require specific experimental conditions, such as high sample pressure, long absorption path length, low sample temperature and long recording time of the spectra.

The large amplitude motion in a periodic potential complicates the quantum mechanical treatment in many respects. The Gaussian basis set is sufficient to characterize small amplitude vibrational motion, thus enabling the use of simple and closed-form expression for eigenenergies, transition frequencies and wave-functions. However, in the case of large amplitude motion in the periodic potential, the Gaussian basis set can no longer be used, and the torsional wave-functions require a plane wave expansion. This leads to computational challenges and poses problems for analytical approach.

One aspect of this thesis is to extend the energy level consideration to the lowest fundamental bands in methyl silanes and to develop the quantum mechanical model to characterize the overall energy levels accurately with a relatively small number of spectroscopic parameters. This involves basic understanding on mechanisms that couple vibrational degrees of freedom with the torsional degree of freedom.

This thesis consists of 6 chapters. Chapter 2 is devoted to the background of the papers and general circumstances affecting this thesis. Chapter 3 gives a brief introduction to the general theory including a formulation of the energy expression and symmetry consideration of the vibration-torsion-rotation states. Chapter 4 deals with the principles of spectrum analysis by accounting for specific aspects due to the internal rotation. Moreover, Chapter
4 contains a summary of the case studies. In Chapter 5, the internal rotor studies and future prospects are discussed.

The aim of this introduction is to provide a brief overview to the background of the energy level characterization of the symmetric tops with internal rotation. Case studies described in Papers I-IV are referred to when appropriate.

Papers I-IV associated with this thesis are self-explanatory and include detailed description of each study. Therefore, the subject matter, especially the theory description, is presented on a general level without going into details of the case studies. Especially, the level of complexity in the description has been limited so that a person familiar with semi-rigid molecular rovibrational spectroscopy may follow the text without overwhelming difficulties.
2 Overview and Background of the Papers

I started my post-graduate studies in early 1994 after finishing my Master’s degree in Oulu University. At that time, my fiance Anne was appointed to a post-doctoral position in the Department of Geography of the University of British Columbia (UBC), Vancouver, starting March 1995. I presented the idea of carrying out a part of my post-graduate studies in Canada to my supervisor Professor Anttila who was compliant to my idea from the beginning and suggested to contact professor Irving Ozier at the Department of Physics and Astronomy at the UBC. After some consultations with professor Ozier and financial arrangements, I started working in professor Ozier’s laboratory on my internal rotation projects.

2.1. Paper I

My first task at the UBC was to modify an analysis program for analyses of symmetric internal rotors to be operable in a UNIX-based system. The analysis program was originally written by professor Leo Meerts from University of Nijmegen for analysing torsional spectra in the GS. The program was later modified to treat coupled two-band systems of the GS and the lowest-lying perpendicular fundamental band $\nu_{12}$ of CH$_3$SiH$_3$ [6].

At that time, unpublished data were available for the lowest fundamental band $\nu_{12}$ of deuterated methyl silane CH$_3$SiD$_3$. The purpose of the $\nu_{12}$ band study was to examine the isotopic dependence of the torsional properties between CH$_3$SiD$_3$ and CH$_3$SiH$_3$. The data set of CH$_3$SiD$_3$ was not as developed as that of CH$_3$SiH$_3$ since the torsional bands $2\nu_6$ and $3\nu_6 - \nu_6$ were not available. However, based on the experience on CH$_3$SiH$_3$ [6], we assumed that the vibrational-torsional-rotational interactions between the $(\nu_{12} = 1)$ state and the torsional dark states $(\nu_6 = 3)$ in the GS would provide information on the torsional dark states so that the correlations between the leading torsional parameters would be avoided, and thus a more reliable torsional Hamiltonian would be determined than was obtained in the previous study [2] based on the MBER measurements. After a thorough investigation, we had to admit that the data were not able to break the correlations between the molecular parameters to the extent that the second torsional potential term $V_6$, for example, could be
obtained with sufficient reliability. Nevertheless, the $\nu_{12}$ band was fit within experimental accuracy and it was analyzed taking into account the torsion-mediated interactions between the GS and the $(\nu_{12} = 1)$ state. The results for CH$_3$SiD$_3$ were published in Paper I in 2000. I carried out the assignment and analysis of the spectra and wrote the first draft of the paper.

2.2. Paper II

The next molecule to be investigated was a quasi-spherical top CH$_3$CF$_3$. This took place in fall 1995. A few years earlier, Irving Ozier had recorded a forbidden rotational Q-branch with $(K + 3 \rightarrow K)$ transitions in the $(v_6 = 0)$ and $(v_6 = 1)$ torsional states in Zurich by using a Fourier transform microwave spectrometer. The forbidden Q-branch data were combined with existing MBER measurements [3] and pure rotational transitions taken from literature [7]. In Paper II, the theoretical questions were addressed in two different areas. The first question concerned the torsion-rotation Hamiltonian and the second question dealt with the $(A_1 - A_2)$ splittings occurring in a near-spherical top exhibiting internal rotation. My contribution to Paper II was focused on the analysis of the $(A_1 - A_2)$ splittings. At that time, the analysis program was not capable of treating Hamiltonians with terms off-diagonal in the $k$ quantum number within one vibrational or torsional state, and the analysis program had to be modified accordingly. To my knowledge, this was the first time that $(A_1 - A_2)$ splittings were examined in a symmetric top with internal rotational degree of freedom by accounting for the torsional effects. One purpose of analyzing the $(A_1 - A_2)$ splittings was to find a physically relevant Hamiltonian that characterizes the $(A_1 - A_2)$ splitting and to test different representations of the interaction Hamiltonian. A careful analysis of the $(A_1 - A_2)$ splittings was made, but unfortunately, a torsional dependence in the $(A_1 - A_2)$ splittings was not observed. In this study, I analyzed the spectra and modified the analysis program to treat the interaction Hamiltonian coupling the rotational $k$ sub-states.

2.3. Paper III

An important step in the internal rotation studies was taken when Irving Ozier and Nasser Moazzen-Ahmadi introduced me high-resolution infrared data on the lowest-frequency parallel fundamental band $\nu_5$ of CH$_3$SiH$_3$ measured a few years earlier in Ottawa. The preliminary analysis of the $\nu_5$ band showed strong torsional anomalies that could not be explained in an isolated $\nu_5$ band scheme. There were assumptions that the anomalies would arise from torsion-mediated anharmonic-type interactions between the GS and the $(\nu_5 = 1)$ state, and the basic form of the interaction Hamiltonian was deduced by symmetry. At that time, the data set of CH$_3$SiH$_3$ included measurements in the lowest vibrational state $(\nu_{12} = 1)$ state and the $(\nu_6 = 0, 1, 2, 3)$ states in the GS. Furthermore, the basics of the interaction mechanisms between the $(\nu_{12} = 1)$ state and the GS were well known.

The analysis program was modified to treat the triad of the GS, the $(\nu_{12} = 1)$ state and the $(\nu_5 = 1)$ state. The analysis of the triad was complicated by several reasons. First, to
my knowledge this was the first time that a torsion-mediated anharmonic-type interaction mechanism was studied in a symmetric top molecule with high resolution, and information on such mechanisms in the literature was limited. Second, the perturbations in the \((\nu_5 = 1)\) state did not allow running a fit for an isolated \(\nu_5\) band so that unperturbed molecular parameters for the \((\nu_5 = 1)\) state would have been obtained. On the other hand, the GS was perturbed by the \((v_{12} = 1)\) state so that it was impossible to analyze separately the dyad of the GS and the \((\nu_5 = 1)\) state. Consequently, the \(\nu_5\) band had to be analyzed with a three-band model from the beginning.

The analysis program at that time treated the quantum mechanical problem in two successive stages. In the first stage, the torsional problem was solved separately for the GS, the \((v_{12} = 1)\) state and the \((\nu_5 = 1)\) state, thus resulting in a first-order effective torsional Hamiltonian. In the second stage, the vibrational-rotational problem including the vibrationally off-diagonal terms was solved by using the first-order effective torsional Hamiltonian obtained from the first stage. However, the second stage neglected second-order terms on the basis of perturbation theory. It should be noted that a corresponding approximation was found relevant in the GS/\(v_{12}\) study of CH$_3$SiH$_3$ [6] and CH$_3$SiD$_3$ of Paper I, and there was no reason to question the relevance of the approximation. We suspected that the approximation might cause a problem, but it was impossible to separate between an approximation problem and unknown details of the possible interaction mechanisms coupling the GS and the \((\nu_5 = 1)\) state. Finally, the analysis program was partly rewritten so that the full Hamiltonian was solved exactly in one step without using the perturbation theory. The exact treatment revealed a severe limitation caused by the perturbation theory in the treatment of the torsion-mediated anharmonic-type coupling between the GS and the \((\nu_5 = 1)\) state in CH$_3$SiH$_3$.

The results from the \(\nu_5\) study were surprising. The analysis showed that the torsional Hamiltonian in the GS is substantially modified when the torsion-mediated anharmonic-type effects between the \((\nu_5 = 1)\) state and the GS are treated explicitly. For example, the second term \(V_6\) in the effective torsional potential in the GS turned out to be an artifact due to the torsion-mediated Fermi-type interaction mechanisms. Second, the strongest coupling between the GS and the \((\nu_5 = 1)\) state can occur even if the perturbing torsional energy level is well above the torsional barrier, the torsional quanta differing by 5 units between the two interacting states. This result reveals that a vibrational-torsional-rotational energy manifold becomes practically chaotic when the higher energy levels systems are considered. In Paper III, I was responsible for the assignment of the \(\nu_5\) spectrum, the analysis of the data, and writing the first draft of the paper.

2.4. Paper IV

Paper I showed that the molecular beam measurements from ref. [2] and the high resolution infrared measurements in the \(v_{12}\) band of CH$_3$SiD$_3$ were not capable of enabling a stringent test to be made for the torsional Hamiltonian. After returning back to Finland from the UBC in spring 1997, a project was launched to record the \(2\nu_6\) and \(3\nu_6 - \nu_6\) torsional bands in CH$_3$SiD$_3$ with high resolution Fourier transform infrared (FTIR) spectroscopy.
Recording pure torsional spectra is a challenging task because the spectral transitions are weak and they fall in the far-infrared region. Our research group had initiated a collaboration with MAX-I electron storage ring in Lund, Sweden, where they have an interferometer coupled to an infrared beam line that acts as a light source for the interferometer. In an ideal case, an electron storage ring light source can provide considerably more intense radiation than the thermal sources traditionally used in infrared spectroscopy, thus reducing time needed for recording the spectra. Furthermore, a coolable multipass absorption cell attached to the spectrometer was available, thus enabling to cool the CH$_3$SiD$_3$ sample in order to increase the intensity of the torsional spectra.

The $2\nu_6$ and $3\nu_6 - \nu_6$ spectra were recorded with 0.002 cm$^{-1}$ resolution by using the electron storage ring during a period of one week in spring 1997. Furthermore, the $\nu_{12}$ spectrum was remeasured in Oulu at an improved resolution of 0.00125 cm$^{-1}$ in order to observe the torsional splittings in the ($\nu_{12} = 1$) state, to increase the rotational quantum number range, and to observe the hot band $\nu_{12} + \nu_6 - \nu_6$.

The primary results of the GS/$\nu_{12}$ study in Paper IV were twofold. First, it was shown that an electron storage ring may be applied for a high resolution far infrared measurements when a relatively long recording time and a long absorption path length are required. Second, the analysis showed that the interaction between the GS and the ($\nu_{12} = 1$) state can be characterized with two models that have different physical interpretation. In Paper IV, I took the initiative to carry out the experiments and recorded the torsional spectra with Dr. Veli-Matti Horneman. Furthermore, I carried out the spectrum analysis and wrote the first draft of Paper IV.

2.5. Remarks on the Studies

The development in understanding the torsional interaction mechanisms dealt in Papers I, II, III and IV is crystallized in the capabilities of the analysis program. To my knowledge, there are no program packages available that are capable of carrying high resolution multi-band analysis of symmetric tops with internal rotation. Therefore, testing of models requires continuous calculational development and implementation of new Hamiltonian terms into the analysis program. Furthermore, a great deal of effort was put to improve the efficiency, flexibility and usability of the analysis program. This is not directly indicated in scientific publications, even though it has a substantial effect on the quality of the studies.

From a personal point of view, internal rotation in symmetric tops provides a wide range of motivating scientific challenges. The torsional motion as such provides an isolated and well-defined problem even in relatively large molecules, and the analyses result in intuitively understandable molecular parameters, such as the torsional barrier height.

Furthermore, the torsional interaction mechanisms of symmetric tops are relatively unknown, and new fundamental information may be generated quite easily from the analyses. Results from Paper III may be taken as an example in this respect.
3 Theoretical Background

This theory chapter deals with relationships between the molecular properties and the energy expression that yield the vibrational-torsional-rotational energies of a symmetric top molecule with internal rotation. The theory discussion is focused on introducing the reader to the field of the vibrational-torsional-rotational states rather than giving definite answers and explicit formulae for the effective molecular parameters.

This chapter is organized as follows. In Section 3.1, Born-Oppenheimer approximation is discussed in order to justify the neglect of the electronic degrees of freedom in the theory discussion. In Section 3.2, a coordinate system for treating a symmetric top with internal rotation is defined. Section 3.3 deals with kinetic energy expressions accounting for vibration, internal rotation and overall rotation. In section 3.4, the Watson form of the vibrational-torsional-rotational Hamiltonian is presented. Section 3.5 is an introduction to an internal rotor in hindering potential. Also, the different coordinate systems in treating torsional motion are discussed, and the quantum mechanical Hamiltonian is presented. Section 3.6 deals with molecular symmetry properties and the use of symmetry in treating the molecular variables, Hamiltonian and wave-functions. In Section 3.7, different approaches including the perturbation methods in solving the Schrödinger equation are represented, and the effective Hamiltonian is defined. Section 3.8 discusses computational aspects when solving the vibrational-torsional-rotational Schrödinger equation.

The approach and notation in this chapter follow that used by Papousek and Aliev [8]. A general theory in internal rotation has been formulated by Lin and Swalen [9], Kirtman [10], Nielsen [11], Bunker and Jensen [12], and Duan and co-authors [13]. Another excellent presentation on the vibration-torsion-rotation theory is given by Wang [14].

One aspect of this thesis is to consider a physically relevant Hamiltonian operator that characterizes the molecular vibrational-torsional-rotational states. This chapter deals with the derivation of the Hamiltonian operator for a symmetric top exhibiting internal rotation and follows the conventional procedure including the following steps:

1. Apply the Born-Oppenheimer approximation to separate electronic and nuclear motion from each other.
2. Define a co-ordinate system providing separation between the translational, vibrational and rotational degrees of freedom.
3. Derive a classical Hamiltonian, which involves further specification of the molecular coordinate system.
4. Obtain a Hamiltonian operator from the classical Hamiltonian.
5. Expand the Hamiltonian operator in respect to vibrational and torsional variables.
6. Define the zeroth order Hamiltonian operators for the vibrational, torsional and rotational degrees of freedom. Solve a Schrödinger equation for each one to obtain basis functions for the full Hamiltonian operator.
7. Apply symmetry properties of the molecule to simplify the Hamiltonian operator and the basis set.
8. Obtain an effective Hamiltonian by solving the Schrödinger equations for the vibrational-torsional-rotational Hamiltonian.

3.1. Born-Oppenheimer Approximation

The spin-free rovibronic Schrödinger equation including the nuclei and electrons is [12]
\[
\left\{ -\frac{\hbar^2}{2} \sum_{r=1}^{l} \frac{\nabla_r^2}{m_r} + \frac{\hbar^2}{2M} \sum_{r,s=1}^{l} \nabla_r \cdot \nabla_s + \sum_{r<s=1}^{l} \frac{C_r C_s e^2}{4\pi\varepsilon_0 R_{rs}} - E_{rve} \right\} \Phi_{rve}(X_1, ..., Z_l) = 0,
\]
(1)
where \( m_r, (X_r, Y_r, Z_r) \) and \( C_r \) present the mass, the position vector, the charge, respectively, of each particle \( r \). The total mass including electron and nuclei is represented by \( M \).
The distance between the particles \( s \) and \( r \) is represented by \( R_{rs} \). The quantities \( E_{rve} \) and \( \Phi_{rve} \) are the rovibronic eigenvalues and eigenfunctions, respectively. In a general case, the electron-nuclear Schrödinger equation (1) cannot be solved exactly and therefore, the solution has to be broken up in separate stages [12]. The stages involve: (a) setting up coordinates that facilitate separation of the variables, (b) making approximations so that there is some separation of the variables, (c) solving the approximate and separate Schrödinger equations obtained, and (d) correcting the approximations by using variational techniques or perturbation theory.

The choice of the coordinate system as applied in the rovibrational theory will be discussed in Section 3.2. The most important assumption used for the purpose of solving the rovibrational Schrödinger equation is the Born-Oppenheimer approximation [15], which allows the rovibronic Schrödinger equation to be solved in a two-step procedure. In the first step, the electronic Schrödinger equation is solved with the nuclei held at fixed positions in space. Then, the vibrational-torsional-rotational Schrödinger equation is solved using the electrostatic potential from the first step to describe the motion of the nuclei. In the context of vibrating and rotating polyatomic molecules, the Born-Oppenheimer approximation is carried out implicitly: the part that involves electronic coordinates in Eq. (1) are simply neglected, and the electrostatic potential experienced by the nuclei in the step of solving the rotational-vibrational Schrödinger equation is an implicit function of the electronic wave-functions. Physically, the Born-Oppenheimer approximation assumes that the motion of the electrons are unaffected by the motion of the nuclei, and during their periodic
time scale, only depend on the nuclear positions. In terms of perturbation theory, the Born-Oppenheimer approximation can be applied, when a separation of two electronic states that are coupled by a vibrational-torsional-rotational-electronic mechanism is large compared to the coupling matrix element, and the effects from the approximation are smaller than the accuracy of the measurements. This assumption is easily fulfilled as the electronic ground state is well below the excited electronic states, and the rovibrational consideration is confined to the lowest vibrational states.

The original form of the Born-Oppenheimer approximation involved separation of the nuclear and electronic motions only. With a similar analog, the molecular wave-function can be separated into an electronic part, a vibrational part, a torsional part and a rotational part [16]. The coordinates yielding such a separation are referred to as Born-Oppenheimer variables. In the following discussion, the electronic variables are neglected and the consideration is confined to the ground electronic state.

3.2. Coordinate system for a Symmetric Top with Two Three-Fold Coaxial Rotors

In the expression of the Born-Oppenheimer variables in a symmetric top molecule with two three-fold coaxial rotors, five Cartesian coordinate systems are needed. They are as follows:

1. Space-fixed axis system \((X', Y', Z')\). Laboratory coordinate system.
2. Center-of-mass-fixed axis system \((X, Y, Z)\). Parallel to the \((X', Y', Z')\) system. Origin \(R_0 = (X_0, Y_0, Z_0)\) fixed to the center of mass of the molecule.
3. Molecule-fixed axis system \((x, y, z)\). Origin \((x_0, y_0, z_0)\) coincides with \(R_0\). The z-axis coincides with the molecular symmetry axis in the reference configuration. Related to the \((X, Y, Z)\) system by the Euler angles \(\theta, \phi\) and \(\chi\). See Fig. 1 for illustration.
4. Top-fixed axis system \((x_T, y_T, z_T)\). The z-axis is parallel to the molecular symmetry axis. The top-fixed axis system is fixed to one of the coaxial rotors.
5. Frame-fixed axis system \((x_F, y_F, z_F)\). The z-axis is parallel to the molecular symmetry axis. The frame-fixed axis system is fixed to the other coaxial rotor.

An instantaneous position vector of the nucleus \(i\) of a molecule in the space-fixed axis system is given by a vector

\[
R_i = R_0 + S^{-1}(\theta, \phi, \chi) t_i, \tag{2}
\]

where

\[
S^{-1}(\theta, \phi, \chi) = \begin{pmatrix}
\cos \chi & \sin \chi & 0 \\
-\sin \chi & \cos \chi & 0 \\
0 & 0 & 1
\end{pmatrix}
\begin{pmatrix}
\cos \theta & 0 & -\sin \theta \\
0 & 1 & 0 \\
\sin \theta & 0 & \cos \theta
\end{pmatrix}
\begin{pmatrix}
\cos \phi & \sin \phi & 0 \\
-\sin \phi & \cos \phi & 0 \\
0 & 0 & 1
\end{pmatrix} \tag{3}
\]
Fig. 1. (a) Definition of the Euler angles. The successive rotations of the Euler angles $\phi$, $\theta$ and $\chi$ generate the following coordinate transformation: $(X, Y, Z) \rightarrow (x', N, Z) \rightarrow (x'', N, z) \rightarrow (x, y, z)$. (b) Definition of the frame-fixed and the top-fixed coordinate systems and the numbering scheme of nuclei in a methyl silane-like molecule. The $z$-axis points from the frame to the top. (c) Definition of the torsional angle $\gamma$. The frame is displaced by $\rho \gamma$ from the reference configuration (solid lines) whereas the top is displaced by $(1 - \rho) \gamma$ to the opposite direction. The total torsional displacement between the top and the frame is $\gamma$.

is the inverse of the direction cosine matrix [17]. It relates the $(x, y, z)$ axis system to the $(X, Y', Z)$ axis system. The instantaneous position of nucleus $i$ in the $(x, y, z)$ system is given by the vector

$$t_i = S_i^{-1}(0, 0, r\gamma)(a_i + d_i),$$  \hspace{1cm} (4)

where $a_i$ and $d_i$ represent reference positions and the vibrational displacements, respectively, of the top and the frame nuclei in the top and frame-fixed axis systems (T/F system). The transformation from the T/F system to the $(x, y, z)$ system is given by

$$S_i^{-1}(0, 0, r\gamma) = \begin{pmatrix} \cos r\gamma & \sin r\gamma & 0 \\ -\sin r\gamma & \cos r\gamma & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{cases} i \subset \text{frame}; r = -\rho \\ i \subset \text{top}; r = 1 - \rho \end{cases}$$  \hspace{1cm} (5)

which rotates the top by angle $\gamma$ relative to the frame and then the entire molecule by $-\rho \gamma$ about the $z$-axis in the $(x, y, z)$ axis system, see Fig. 1 (b) for illustration.

The $S_i^{-1}(0, 0, r\gamma)$ matrix can explicitly be included in the $S^{-1}(\theta, \phi, \chi)$ matrix by re-defining the Euler angles for the top and the frame separately. It is easy to show that the
Euler angles transform to

\[ \theta_F = \theta_T = \theta \]  \hspace{1cm} (6)
\[ \phi_F = \phi_T = \phi \]  \hspace{1cm} (7)
\[ \chi_F = \chi - \rho \gamma \]  \hspace{1cm} (8)
\[ \chi_T = \chi + (1 - \rho) \gamma \]  \hspace{1cm} (9)
\[ \chi_T - \chi_F = \gamma, \]  \hspace{1cm} (10)

where subscript \( T \) refers to the top and \( F \) to the frame, respectively. Parameter \( \rho \) can be an arbitrary number assuming values between 0 and \( \frac{1}{2} \). Specific values of parameter \( \rho \) will be discussed in Section 3.5.

### 3.3. Classical Kinetic Energy of a Rotating and Vibrating Molecule

In the adopted coordinate system, the total kinetic energy of \( N \) mass points of a molecule can be written as

\[
2T_{TOT} = \sum_{i=1}^{N} m_i \mathbf{\ddot{R}}_i \mathbf{\ddot{R}}_i \\
= \mathbf{\ddot{R}}_0 \mathbf{\ddot{R}}_0 \sum_{i=1}^{N} m_i \text{ trans} \\
+ 2 \mathbf{S} \mathbf{S}^{-1} \left( \mathbf{S} \mathbf{S}^{-1} \sum_{i=1}^{N} m_i \mathbf{t}_i + \sum_{i=1}^{N} m_i \mathbf{i}_i \right) \text{ trans-rot-tor} \\
+ \sum_{i=1}^{N} m_i \left( \mathbf{S} \mathbf{S}^{-1} \mathbf{t}_i \right) \left( \mathbf{S} \mathbf{S}^{-1} \mathbf{t}_i \right) \text{ rot, rot-tor} \\
+ 2 \sum_{i=1}^{N} m_i \left( \mathbf{S} \mathbf{S}^{-1} \mathbf{t}_i \right) \mathbf{i}_i \text{ vib-tor-rot} \\
+ \sum_{i=1}^{N} m_i \mathbf{\ddot{t}}_i \mathbf{\ddot{t}}_i \text{ vib, tor, vib-tor} \tag{11a}
\]

where the matrix notation involving factor \( \mathbf{S} \mathbf{S}^{-1} \) can be replaced with

\[
\mathbf{S} \mathbf{S}^{-1} \mathbf{v} = \mathbf{\omega} \times \mathbf{v}, \tag{12}
\]

where \( \mathbf{v} = (v_x, v_y, v_z) \) is an arbitrary vector. Especially,

\[
\mathbf{S}_i (0, 0, r\gamma) \mathbf{S}^{-1} (0, 0, r\gamma) \mathbf{v} = r\mathbf{\omega}, \mathbf{k} \times \mathbf{v}, \tag{13}
\]
where \( k \) is a unit vector along the molecular \( z \)-axis. The components of the angular velocity vector \( \omega \) in the \((x, y, z)\) system can be obtained from the associated angles and can be written as

\[
\begin{align*}
\omega_x &= \dot{\theta} \sin \chi - \dot{\phi} \sin \theta \cos \chi \\
\omega_y &= \dot{\theta} \cos \chi + \dot{\phi} \sin \theta \sin \chi \\
\omega_z &= \dot{\phi} \cos \theta + \dot{\chi} \\
\omega_\gamma &= \dot{\gamma}
\end{align*}
\]

Quantity \( \omega_\gamma \) defines the relative angular velocity of the top and the frame about the molecular \( z \)-axis.

The left hand side of coordinate transformation (2) contains 3 translational, 3 rotational, 1 torsional, and \( 3N - 7 \) vibrational degrees of freedom and therefore, \( 3N \) independent coordinates are required to express the total kinetic energy. However, on the right hand side of the kinetic energy expression (11a) there are \( 3N + 7 \) coordinates in total: there are 3 translational coordinates \((X_0, Y_0, Z_0)\), 3 angular coordinates \((\theta, \phi, \chi)\), 1 torsional coordinate \( \gamma \) and \( 3N \) vibrational displacement coordinates. Therefore, 7 constraint equations are required to orthogonalize the Born-Oppenheimer variables. They can be obtained from equations

\[
\begin{align*}
\sum_{i=1}^{N} m_i S^{-1} (0,0,r_\gamma) \mathbf{d}_i &= 0 & (18) \\
\sum_{i}^{N} m_i S^{-1} (0,0,r_\gamma) (\mathbf{a}_i \times \mathbf{d}_i) &= 0 & (19) \\
\mathbf{k} \cdot \left[ \sum_{T \subset F} m_i (\mathbf{a}_i \times \mathbf{d}_i) \right] &= 0. & (20)
\end{align*}
\]

Eq. (18), also called the first Eckart condition \([18]\), provides 3 constraint equations and conserves the center of mass during a simultaneous vibrational and torsional displacement.

Eq. (19) is called the second Eckart condition and provides 3 more constraint equations that remove the redundancy between the vibrational displacement coordinates and the Euler angles. Furthermore, the molecule-fixed coordinate system is redefined so that the angular momentum arising from the vibrational motion is minimized. The term (20) called a Sayvetz condition \([19]\), is a large amplitude analog to the second Eckart condition and provides one constraint equation that removes the redundancy between the torsional angle and the vibrational displacements. It also redefines the frame-fixed and top-fixed axis systems so as to minimize the interaction between the vibrational angular momentum and torsion.

In Eq. (20), the abbreviation \( \sum_{T \subset F} \) in summation is

\[
\sum_{T \subset F} D_i = (1 - \rho) \sum_{i \subset T} D_i - \rho \sum_{i \subset F} D_i,
\]

where \( T \) and \( F \) correspond to summation over top and frame atoms, respectively.
The constraint equations (18)–(20) along with omission of the first term in Eq. (11a) eliminate the translational contribution from kinetic energy. After applying Eq. (12) and the constraint equations (18)–(19), the kinetic energy expression becomes

\[ 2T_{VTR} = \sum_{i=1}^{3N-7} m_i \mathbf{d}_i \cdot \mathbf{\dot{d}}_i \]  

\[ + \sum_{\alpha,\beta=x,y,z} I_{\alpha\beta} \omega_\alpha \omega_\beta \]  

\[ + \omega_\gamma^2 \left( (1 - \rho)^2 I_{zz}^T + \rho^2 I_{zz}^F \right) \]  

\[ + 2\omega_\gamma N \sum_{i=1}^{N} m_i S_i^{-1} (0,0,r\gamma) \left[ \mathbf{d}_i \times \mathbf{\dot{d}}_i \right] \]  

\[ + 2\omega_\gamma \sum_{\beta=x,y,z} \omega_\beta \left[ (1 - \rho) I_{\beta z}^T - \rho I_{\beta z}^F \right] \]  

\[ + 2\omega_\gamma k \cdot \left[ \sum_{T-F} m_i \left[ \mathbf{d}_i \times \mathbf{\dot{d}}_i \right] \right] \]  

\[ + 2\omega_\gamma (k \times \omega) \sum_{T-F} m_i \left[ S_i^{-1} (0,0,r\gamma) \left( \mathbf{a}_i \times \mathbf{d}_i \right) \right], \]  

where \( I_{\alpha\beta}^T \) and \( I_{\alpha\beta}^F \) are inertial tensor components of the top and the frame, respectively, and \( I_{\alpha\beta}^e \) is an inertial tensor component of the entire molecule in such a way that \( I_{\alpha\beta} = I_{\alpha\beta}^T + I_{\alpha\beta}^F \). Furthermore, for the reference configuration,

\[ I_{\alpha\beta}^{T,e} = I_{\alpha\beta}^{F,e} = I_{\alpha\beta}^e = 0 \]  

\[ \alpha \neq \beta = x, y, z \]  

at any torsional angle \( \gamma \). A kinetic energy expression similar to (21a)–(21g) has also been given in Ref. [10].

Let us assume that the torsional motion is frozen i.e., \( \gamma = \omega_\gamma = 0 \). Then, terms (21a), (21b) and (21d) retain, and the kinetic energy expression (21a)–(21g) reduces to that of a semi-rigid symmetric rotor molecule: term (21a) arises from the small amplitude vibrational motion, term (21b) represents the overall rotation of the molecule, and term (21d) represents the coupling of the overall rotation and the small amplitude vibration. The additional terms are due to internal rotation. Term (21c) represents the pure torsional kinetic energy due to relative angular motion of the two coaxial rotors about the molecular \( z \)-axis. Term (21e) represents the Coriolis interaction energy between overall rotation and torsion. Term (21f) is similar to (21d); it arises from the coupling between the vibrational and torsional angular momenta.
Term (21g) arises from the fact that the time derivative of the second Eckart equation (19) is not simply 

\[ \frac{d}{dt} \left( \sum m_i S_i^{-1} \left( (0, 0, r) \right) \left( a_i \times d_i \right) \right) \]

but

\[ + \omega_k \times \sum_{T-F} m_i \left[ S_i^{-1} \left( (0, 0, r) \right) \left( a_i \times d_i \right) \right] = 0, \tag{23} \]

which implies that the Eckart conditions cannot perfectly be fulfilled in the case of large amplitude motion. Term (23) would vanish if the second Eckart condition (19) held for both the top and the frame separately.

The components \( d_i, \alpha (\alpha = x, y, z) \) and their time derivatives \( \dot{d}_i, \alpha \) of the cartesian displacement coordinates \( d_i \) occurring in the kinetic energy expression (21a)-(21g) can be written in terms of vibrational normal coordinates \( Q_k \) as

\[ d_i,\alpha, k = \sum_{k=1}^{N} m_i^{-1/2} i_{i,\alpha, k} Q_k \tag{24} \]

\[ \dot{d}_i,\alpha, k = \sum_{k=1}^{N} m_i^{-1/2} \left[ \omega \omega_l i_{i,\alpha, k} Q_k + l_{i,\alpha, k} \dot{Q}_k \right], \tag{25} \]

where \( l_{i,\alpha, k} = l_{i,\alpha, k} (r_\gamma) \) is in general a function of the torsional angle implying the torsional dependence of the vibrational motion of a molecule. Furthermore,

\[ l'_{i,\alpha, k} = \frac{\partial l_{i,\alpha, k} (r_\gamma)}{\partial \gamma}. \tag{26} \]

Note, that the \( l_{i,\alpha, k} \) constants are defined in the T/F systems for the top nuclei and the frame nuclei, respectively. By treating the torsion formally as a fourth rotational degree of freedom and adopting the normal coordinate presentation for the vibrational variables, the kinetic energy can be written in the conventional form [8] as

\[ 2T_{TR} = \sum_{k=1}^{3N-7} \left( \dot{Q}_k + \sum_{\alpha=x,y,z} \sum_{i,l} \omega_{i\alpha} \omega_{i\alpha}^2 Q_i \right)^2 + \sum_{\alpha,\beta=x,y,z} \sum_{i,j} \omega_{\alpha} \omega_{\beta} I_{i,j}. \tag{27a} \]

The form of classical kinetic energy (27a) is identical to that of a semi-rigid rotor with additional summation over \( \gamma \) in the rotational part. However, the components of the inertial
The definitions of the components of the inertial tensor are tabulated in Table 1. Furthermore, the vibrational-torsional-rotational interaction constants are given in Tables 2–4.

The momenta conjugate to the molecular coordinates in (27a) are simply

\[
P_{k} \equiv \frac{\partial T}{\partial Q_{k}} = \dot{Q}_{k} + \sum_{\alpha=x,y,z,\gamma} \omega_{\alpha} \sum_{l} \xi_{kl} \zeta_{\alpha l} Q_{l};
\]

\[
J_{\alpha} \equiv \frac{\partial T}{\partial \omega_{\alpha}} \bigg|_{\alpha=x,y,z,\gamma} = \sum_{\beta=x,y,z,\gamma} \mu_{\alpha\beta} \omega_{\beta} + p_{\alpha},
\]

where

\[
p_{\alpha} = \sum_{kl} \xi_{kl} Q_{k} P_{l}
\]

is the vibrational angular momentum. The kinetic energy can be written in terms of the momenta and angular momenta as

\[
2T = \sum_{k=1}^{3N-7} P_{k}^2 + \sum_{\alpha,\beta=x,y,z,\gamma} \mu_{\alpha\beta} (J_{\alpha} - p_{\alpha}) (J_{\beta} - p_{\beta}),
\]

where \( \mu_{\alpha\beta} = \left[ I_{\alpha\beta} \right]^{-1} \).
Table 2. Definitions of the ζ-constants

<table>
<thead>
<tr>
<th>ζ_α^{kl}</th>
<th>ζ_γ^{kl}</th>
<th>ζ_α^{M}</th>
<th>ζ_β^{M}</th>
<th>ζ_α</th>
<th>ζ_β</th>
</tr>
</thead>
<tbody>
<tr>
<td>ζ_α^{kl} = ζ_α^{T,kl} + ζ_α^{F,kl}</td>
<td>ζ_γ^{kl} = ζ_γ^{T,kl} + (1 - ρ) ζ_γ^{T,kl} - ρ ζ_γ^{F,kl}</td>
<td>ζ_α^{M} = \sum_{β=x,y,z} S^{-1}(0,0,ργ)_{αβ} ζ_α^{M}</td>
<td>ζ_β^{M} = \sum_{β=x,y,z} S^{-1}(0,0,ργ)_{αβ} ζ_β^{M}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ζ_α = x, y, z</td>
<td>ζ_β = x, y, z</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[ r = -ρ \text{ for } M = F \text{ and } r = 1 - ρ \text{ for } M = T. \]

\[ S^{-1}(0,0,ργ)_{αβ} \text{ is the } αβ \text{ matrix element of the } S^{-1}(0,0,ργ) \text{ matrix.} \]

\[ \text{Summation over the frame (M=F) or the top (M=T) atoms, respectively.} \]

\[ \text{Index } i \text{ runs over all the nuclear coordinates if not otherwise specified.} \]

3.4. Watson Hamiltonian

When the vibrational amplitudes are small compared to the interatomic distances, the Taylor expansions of the inverse of the tensor \( μ_{αβ} \) and that of the potential energy \( V(γ, q) \) usually converge with a rapidity justifying the use of the perturbation methods. Furthermore, James Watson [20] has shown that terms in the expansion of \( μ_{αβ} \) tensor can be presented with the components of the inertial tensor \( I_{e_{αβ}} \) at the equilibrium and with its first derivatives with respect to normal coordinates. This leads to a relatively simple form of the vibrational-torsional-rotational Hamiltonian, also called the Watson Hamiltonian, that can be expressed in wavenumber units as

\[
H = \frac{1}{2} \sum_{α,β=x,y,z} B_{αβ} (J_α - p_α) (J_β - p_β) + \frac{1}{2} \sum_{k=1}^{3N-7} ω_k p_k^2 + V(γ, q) + U, \tag{32}
\]

where \( B_{αβ} = \hbar c μ_{αβ} \) and \( ω_k \) is a harmonic wavenumber of normal mode \( k \). The units are \([B_{αβ}] = [ω_k] = \text{cm}^{-1}, [c] = \text{cm/s}, \text{and } [V(γ, q)] = \text{cm}^{-1}. \) The term \( U \) acts as a mass dependent contribution to the potential energy \( V(γ, q) \). The dimensionless normal coordinates \( q_k \), their conjugate momenta \( p_k \), and the vibrational angular momentum are defined as

\[
q_k = \left( \frac{λ_k}{h^2} \right)^{1/4} Q_k = \frac{1}{\sqrt{γ}} Q_k, \tag{33}
\]

\[
p_k = -i \frac{∂}{∂q_k} \tag{34}
\]

\[
p_α = \sum_{kl} \zeta_α^{kl} \left( \frac{ω_l}{ω_k} \right) q_k p_l, \tag{35}
\]

where \( λ_k = 4πν_k^2 \) where \( ν_k \) is a harmonic frequency of a normal mode \( k \) in frequency units. When a molecule exhibits a large amplitude motion, the commutation relations between the \( B_{αβ} \) tensor and the molecular variables required by the Watson Hamiltonian are not
Table 3: Definitions of the $\xi$ - constants

<table>
<thead>
<tr>
<th>$\xi_k^{\alpha \gamma}$</th>
<th>$\xi_k^{\gamma \alpha}$</th>
<th>$\sum_{M=0}^{J} \sum_{l=x,y,z} r S^{-1} (0,0,r \gamma)_{\alpha \delta} \tilde{\xi}_k^{\alpha,M}$</th>
<th>$\alpha = x, y$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tilde{\xi}_k^{\alpha \beta}$</td>
<td>$\xi_k^{\alpha \beta}$</td>
<td>$\xi_k^{\beta \alpha}$</td>
<td>$\xi_k^{\gamma \gamma}$</td>
</tr>
<tr>
<td>$\breve{\xi}_k^{\alpha, M}$</td>
<td>$\sum_{i \subseteq M} \frac{m_i}{2} (a_{i \delta} l_{i, \beta k} - a_{i \beta} l_{i, \delta k})$</td>
<td>$\alpha \neq \beta \neq \delta$</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ See footnotes $^a$ and $^b$ in Table 2.

$^b$ See footnote $^c$ in Table 2.

necessarily fulfilled. This is due to the $\gamma$ - dependence of the $B_{\alpha \beta}$ tensor. Furthermore, the commutation relations depend on the choice of the internal coordinate system i.e., on the value of the parameter $\rho$ which is not yet specified. For the simplicity of the following consideration, the Watson form of the Hamiltonian will be used as a starting point. An anticommutator form of the operators is used when required.

### 3.4.1. Expansion of the Watson Hamiltonian

The separation of the normal vibrations and internal rotation may be considered from a viewpoint similar to that adopted in the Born-Oppenheimer separation of electronic and nuclear motions: the time period of the internal rotation is much larger than that of the normal vibrations, and the vibrational constants depend parametrically on the torsional angle. As a consequence, the $B_{\alpha \beta}$ tensor may be written as

$$B_{\alpha \beta} (\gamma) = B_{0}^{\alpha \beta} (\gamma) + \sum_{k} B_{k}^{\alpha \beta} (\gamma) q_k + \frac{1}{2} \sum_{kl} B_{kl}^{\alpha \beta} (\gamma) q_k q_l,$$

(36)

where the coefficients in the Taylor expansion are

$$B_{0}^{\alpha \beta} = \left( \frac{\hbar^2}{2 \hbar c} \right) \left( \frac{1}{T_{\alpha \beta}} \right)$$

(37)

$$B_{k}^{\alpha \beta} = \left( \frac{\hbar^2}{2 \hbar c} \right) \left( \frac{\partial \mu_{\alpha \beta}}{\partial q_k} \right)_{0}$$

(38)

$$B_{kl}^{\alpha \beta} = \left( \frac{\hbar^2}{2 \hbar c} \right) \left( \frac{\partial^2 \mu_{\alpha \beta}}{\partial q_k \partial q_l} \right)_{0}.$$

(39)
Table 4. Definitions of the $\eta^\alpha_{kl}$ constants

\[
\eta^\alpha_{kl} = \eta^\alpha_{kl} = \sum_{M=\ell}^r \sum_{\beta=x,y,z} r S_{1}^{-1} (0,0,r\gamma)_{\alpha\beta} \eta^\beta_{kl} \quad \alpha = x, y, z
\]
\[
\eta^\alpha_{kl} = \eta^z_{kl} + \frac{1}{2} k^z_{kl}
\]
\[
\eta^\alpha_{kl} = \eta^\alpha_{kl} = 0
\]
\[
\eta^\alpha_{kl} = \sum_{i,M} \left[ l_{i,\beta,k}(\gamma) l_{i,\delta,l}(\gamma) - l_{i,\delta,k}(\gamma) l_{i,\beta,l}(\gamma) \right] \quad \alpha, \beta, \delta = x, y, z
\]
\[
k^0_{kl} = \sum_{i,\alpha} l_{i,\alpha,k}(\gamma) l_{i,\alpha,l}(\gamma) \quad \beta \neq \delta \neq \alpha
\]

\[a\] See footnotes $^a$ and $^b$ in Table 2.

\[b\] Index $i$ runs over nuclear coordinates if not otherwise specified.

The coefficients $B^\alpha_{kl}$, $B^\alpha_k$ and $B^\alpha_{kl}$ can be expanded in Fourier series as

\[
B^\alpha_{0,k} (\gamma) = B^\alpha_{0,k} + \sum_{n=1}^\infty B^\alpha_{0,k,n} (1 - \cos 3n\gamma) + B^\alpha_{0,k,n} \sin 3n\gamma \quad (40)
\]

\[
B^\alpha_k (\gamma) = B^\alpha_{0,k} + \sum_{n=1}^\infty B_{0,k,n} (1 - \cos 3n\gamma) + B_{0,k,n} \sin 3n\gamma \quad (41)
\]

\[
B^\alpha_{kl} (\gamma) = B^\alpha_{0,kl} + \sum_{n=1}^\infty B_{0,kl,n} (1 - \cos 3n\gamma) + B_{0,kl,n} \sin 3n\gamma. \quad (42)
\]

In the $B^\alpha_{0,kl}$ notation, indices $\alpha$ and $\beta$ run over coordinates $x, y, z$ and $\gamma$. The superscripts $c$ and $s$ indicate cosine and sine series expansion, respectively. The subscript $l$ indicates the normal coordinate, and subscript $n$ indicates an order in the Fourier series expansion. In the case $\gamma = 0$, the expansion of the quantity $B^\alpha_{0,kl}$ reduces similar to that of a semi-rigid rotor: $B^\alpha_{0,kl}$ are the rotational and torsional constants in equilibrium, while $B^\alpha_k$ and $B^\alpha_{kl}$ are the rotational and torsional derivatives.

### 3.4.2. Potential Function

A normal coordinate analysis of a molecule exhibiting small amplitude vibrations about a single equilibrium configuration can be performed according to the standard GF matrix method [17]. However, for molecules with a large amplitude torsional motion, the standard treatment cannot be applied. In the GF matrix formalism, provided that the Born-Oppenheimer approximation is valid, the kinematic matrix is independent on the torsional angle. However, the elements of the force constant matrix possess torsional dependence and therefore, the vibrational problem of the molecule has to be solved separately for each
torsional angle [21]. On the other hand, the geometry of the molecule is a function of the normal coordinates, and hence the barrier to internal rotation depends on the vibrational state. Therefore, in a general case, the Born-Oppenheimer potential function cannot be fully separated into the vibrational and torsional part. Let us assume that the classical force field calculation in an arbitrary coordinate system has been carried out by taking into account the torsional effects on the initial force constant matrix. In such a case, the potential function can be expressed as

\[
V(\gamma, q) = \sum_k \kappa_k (\gamma) q_k + \frac{1}{2} \sum_k \omega (\gamma) q_k^2 + \frac{1}{6} \sum_{klm} k_{klm} (\gamma) q_k q_l q_m \tag{43a}
\]

\[
+ \sum_i \frac{1}{2} V_{3i} (q) (1 - \cos 3i\gamma) \tag{43b}
\]

The first three terms make up the small amplitude vibrational potential having an implicit

![Fourier components of the torsional potential of CH₃SiD₃. See Eq. (43b) for the formula. The torsional parameters are obtained from Paper IV. The values are: V₃ = 583.9403 cm⁻¹, V₆ = 2.7858 cm⁻¹ and V₉ = 0.1878 cm⁻¹.](image)
torsional dependence. The torsional potential (43b) is given in Fourier series with constants $V_3, V_6, V_9, \ldots$. The formation of the total torsional potential from its Fourier components in CH$_3$SiD$_3$ is exemplified in Fig. 2.

The small amplitude force constants $\kappa_k (\gamma), \omega_k (\gamma), \text{ and } k_{klm} (\gamma)$ can be expanded in Fourier series as

$$\kappa_k (\gamma) = \kappa_{k,0} + \sum_{n=1}^{\infty} \kappa_{k,n}^c (1 - \cos 3n\gamma) + \sum_{n=1}^{\infty} \kappa_{k,n}^s \sin 3n\gamma \quad (44)$$

$$\omega_k (\gamma) = \omega_{k,0} + \sum_{n=1}^{\infty} \omega_{k,n}^c (1 - \cos 3n\gamma) + \sum_{n=1}^{\infty} \omega_{k,n}^s \sin 3n\gamma \quad (45)$$

$$k_{klm} (\gamma) = k_{klm,0} + \sum_{n=1}^{\infty} k_{klm,n}^c (1 - \cos 3n\gamma) + \sum_{n=1}^{\infty} k_{klm,n}^s \sin 3n\gamma, \quad (46)$$

where the cosine and sine terms are indicated with superscripts as before. When $\gamma \to 0$, the vibrational potential converges to that of a semi-rigid rotor. Therefore, it is required that $\kappa_{k,0} = 0$, and constants $\omega_{k,0}$ and $k_{klm,0}$ are the force constants of a semi-rigid molecule.

The torsional potential $V_3 (q)$ can be expanded in Taylor series in terms of the normal coordinates as

$$V_3 (q) = V_{3e}^c + \frac{3N-7}{2} \sum_{k} V_{3k}^k q_k + \frac{3N-7}{2} \sum_{kl} V_{3kl}^{kl} q_k q_l + \ldots, \quad (47)$$

where $V_{3e}^c$ is the torsional potential expansion coefficient in the equilibrium configuration, and $V_{3k}^k$ and $V_{3kl}^{kl}$ are derivatives of the components of the torsional barrier expansion with respect to normal coordinates.

When terms (44)–(46) are substituted to the potential function (43a)–(43b), and terms with identical torsional and vibrational operators are collected together, the following inseparable coefficients are obtained:

$$\tilde{V}_{3k}^k = V_{3k}^k + 2\kappa_{k,i}^c \quad (48)$$

$$\tilde{V}_{3k}^{kk} = V_{3kl}^{kk} + \omega_{k,i}^c \quad (49)$$

It is obvious that components $V_{3k}^k$ and $2\kappa_{k,i}^c$ and components $V_{3k}^{kk} + \omega_{k,i}^c$, respectively, cannot be separated from each other by spectroscopic methods.

The torsional dependence of the GF problem leads to torsional dependent $\zeta, \xi$ and $\eta$ constants given in Tables 2–4. It is customary to express them as Fourier series

$$\zeta_{kl}^\alpha = \zeta_{kl,0} + \sum_{n=1}^{\infty} \left[ \zeta_{kl,n}^{\alpha,c} (1 - \cos 3n\gamma) + \zeta_{kl,n}^{\alpha,s} \sin 3n\gamma \right]; \quad (50)$$

$$\xi_k^\alpha = \xi_{k,0} + \sum_{n=1}^{\infty} \left[ \xi_{k,n}^{\alpha,c} (1 - \cos 3n\gamma) + \xi_{k,n}^{\alpha,s} \sin 3n\gamma \right]; \quad (51)$$

$$\eta_{kl}^{\alpha\beta} = \eta_{kl,0}^{\alpha\beta} + \sum_{n=1}^{\infty} \left[ \eta_{kl,n}^{\alpha\beta,c} (1 - \cos 3n\gamma) + \eta_{kl,n}^{\alpha\beta,s} \sin 3n\gamma \right]. \quad (52)$$
At the infinite barrier limit $\gamma \to 0$, $\zeta_{kl}^\gamma \to \zeta_{kl}^\alpha (\alpha = x, y, z)$, which corresponds to the case of a semi-rigid molecule. From the definition of $\zeta_{kl}^\gamma$ given in Table 2 one can deduce that $\zeta_{kl}^\gamma \to (1 - \rho) \zeta_{kl}^\gamma - \rho \zeta_{kl}^\rho$ by assuming that $l_{\alpha, l} (\gamma = 0) = 0$. Also $\nu_{kl}^\alpha \to 0$. The consideration of the $\nu_{kl}^\alpha$ constants is more complicated as they arise from the specific Eckart condition given by Eq. (23).

The Hamiltonian resulting from substituting the expansions of $R^{\alpha\beta}$ and $V(\gamma, q)$ into the Watson Hamiltonian (32) consists of terms of type $M(V,T,R) \times V^k T^m R^l$, where $V^k$, $T^m$, and $R^l$ are the vibrational, torsional, and rotational operators, respectively, and $M(V,T,R)$ is the associated molecular constant. Indices $k$, $m$, and $l$ are the degrees of the operators. In this thesis, we follow the approach introduced by Aliev and Watson [22] and later modified for the internal rotor problem by Duan and co-authors [13]. In an $H_{lm}$ notation, $l$ represents the degree of the vibrational operators $q_k$ and $p_k$, whereas $m$ represents the degree of the torsional and rotational operators. In this case, the notation of the torsional angular momentum follows that conventionally applied to the overall angular momenta. However, terms with $(1 - \cos 3n\gamma)$ and $\sin 3n\gamma$ are classified according to $m = 2n$. For example, the degree of term with $\cos 3\gamma$ is 2.

In this notation, the lowest order molecular Hamiltonian can be expressed as

$$H = H_{20} + H_{30} + H_{40} + .. \quad \text{vib} \quad (53a)$$
$$+ H_{12} + H_{21} + H_{22} + .. \quad \text{vib-tor-rot} \quad (53b)$$
$$+ H_{02} + H_{04} + H_{06} + .. \quad \text{tor+tor} \quad (53c)$$

The lowest order terms of the Hamiltonian $H$ are tabulated in Tables 5 and 6. The operators are not written in the Hermitian form since the commutation relationships between the angular momentum operators are yet not known due to the unspecified parameter $\rho$. Furthermore, the torsional angular momentum operator $J_\gamma$ does not commute with $\cos 3n\gamma$ and $\sin 3n\gamma$. When the operators are written explicitly, an anticommutator form has to be used.

Terms $H_{20}$, $H_{30}$, and $H_{40}$ constitute the pure vibrational terms, the $H_{20}$ representing an isolated harmonic oscillator, and $H_{30}$ and $H_{40}$ being the cubic and quartic anharmonic potential terms, respectively. Term $H_{12}$ contains the conventional centrifugal distortion terms of a semi-rigid rotor with additional torsional contribution. Furthermore, $H_{12}$ contains an anharmonic-type term with $q_k (1 - \cos 3\gamma)$ arising from the linear vibrational dependence of the torsional barrier height plus the linear dependence of the linear potential term. Term $H_{21}$ contains the conventional rigid rotor-harmonic oscillator Coriolis terms with additional torsional contribution. Term $H_{22}$ describes the quadratic stretching of the inertial tensor and the quadratic change of the torsional barrier as a function of the vibrational coordinate. Terms $H_{31}$ and $H_{14}$ are higher order corrections to $H_{21}$ and $H_{12}$, respectively.

Terms in $H_{02}$ make up the rigid rotor Hamiltonian including the zeroth order kinetic torsional term and the cross terms between the torsion and overall rotation. Furthermore, the first Fourier term in the torsional potential expansion is included. The quartic term $H_{04}$ and the sextic term $H_{06}$ are characteristic to an internal rotor molecule only: they characterize the torsional dependence of the rotational constants and also include higher terms in the torsional potential expansion.
Table 5. Terms in the vibrational-torsional-rotation Hamiltonian\textsuperscript{a,b}

<table>
<thead>
<tr>
<th>Vibrational terms</th>
<th>Vibrational-Torsional-Rotational terms</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_{20} = \sum_k \omega_k (q_k^2 + p_k^2)$</td>
<td>$H_{12} = \sum_{kl} R_{kl} q_k$</td>
</tr>
<tr>
<td>$H_{30} = \frac{1}{6} \sum_{klim} k_{klm} q_k q_l q_m$</td>
<td>$H_{21} = \sum_{kl} R_{kl} q_k p_l$</td>
</tr>
<tr>
<td>$H_{40} = \frac{1}{24} \sum_{klimm} k_{klmm} q_k q_l q_m q_n + \sum_{\alpha} B_{0,\alpha}^0 p_\alpha^2$</td>
<td>$H_{22} = \sum_{kl} R_{kl} q_k q_l$</td>
</tr>
<tr>
<td></td>
<td>$H_{31} = \sum_{klim} R_{klm} q_k q_l p_m$</td>
</tr>
<tr>
<td></td>
<td>$H_{14} = \sum_{kl} T_{kl} q_k$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Torsional-Rotational terms</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_{02} = \sum_{\alpha \beta} B_{0,0}^{0,\alpha} J_\alpha J_\beta + \frac{1}{2} V_e^\gamma (1 - \cos 3\gamma)$</td>
</tr>
<tr>
<td>$H_{04} = \sum_{\alpha \beta} \left[ B_{0,1}^{0,\alpha} (1 - \cos 3\gamma) + B_{0,1}^{0,\alpha,\beta} \sin 3\gamma \right] J_\alpha J_\beta + \frac{V_e^\gamma}{2} (1 - \cos 6\gamma)$</td>
</tr>
<tr>
<td>$H_{06} = \sum_{\alpha \beta} \left[ B_{0,2}^{0,\alpha} (1 - \cos 6\gamma) + B_{0,2}^{0,\alpha,\beta} \sin 6\gamma \right] J_\alpha J_\beta + \frac{V_e^\gamma}{2} (1 - \cos 6\gamma)$</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Only terms relevant to this context are considered.
\textsuperscript{b} For a general consideration, a Hermitian form of operators is required.

3.4.3. Rigid Rotor-Symmetric Top

In the treatment of the rotational problem of a polyatomic molecule, the rigid rotor-symmetric top model is most commonly used as a zeroth order of approximation. The rigid rotor-symmetric top Hamiltonian arises from operator $H_{02}$ given in Table 5 and can be written as

$$H_{02,r} = B_{0,0}^{xx} J_x^2 + (B_{0,0}^{zz} - B_{0,0}^{xx}) J_z^2.$$ \hspace{1cm} (54)

The rotational constants have been defined in Eq. (37) and $J^2 = J_x^2 + J_y^2 + J_z^2$. The dimensionless angular momentum operators can be expressed as functions of Euler angles...
Table 6: Torsion-rotation operators

\[
R_k = \sum_{\alpha \beta} B^{\alpha \beta}_{k,0} J_\alpha J_\beta + \frac{1}{2} V^k_{3i} (1 - \cos 3\gamma) \]

\[
R_k^l = -2 \sqrt{\frac{2}{2e}} \sum_{\alpha \beta} B^{\alpha \beta}_{0,\beta} \tilde{B}^{\alpha \beta}_{k,0} J_\alpha \]

\[
R_{kl} = \frac{1}{2} \left[ \sum_{\alpha \beta} B^{\alpha \beta}_{k,0} J_\alpha J_\beta + \frac{1}{2} \tilde{V}_{kl}^k (1 - \cos 3\gamma) \right] \]

\[
R_{kl}^m = -2 \sqrt{\frac{2}{2e}} \sum_{\alpha \beta} B^{\alpha \beta}_{k,0} \tilde{B}^{\alpha \beta}_{k,0} J_\alpha \]

\[
T_k = \sum_{\alpha \beta} \left[ B^{\alpha \beta}_{1,0} (1 - \cos 3\gamma) + B^{\alpha \beta}_{1,1} \sin \gamma \right] J_\alpha J_\beta + \frac{V^k}{2} (1 - \cos 6\gamma) \]

\[a\] For a general consideration, an anticommutator form of operators is required

\[
\tilde{V}_k^3 = V_k^3 + 2\kappa_k^0; \quad \tilde{V}_{kl}^k = \left( V_{kl}^k + \delta_{kl}^0 \right) \]

as

\[
J_x = -i \left[ -\frac{1}{\sin \theta} \cos \chi \frac{\partial}{\partial \varphi} + \sin \chi \frac{\partial}{\partial \theta} + \cot \theta \cos \chi \frac{\partial}{\partial \chi} \right] \]

\[
J_y = -i \left[ \frac{1}{\sin \theta} \sin \chi \frac{\partial}{\partial \varphi} + \cos \chi \frac{\partial}{\partial \theta} - \cot \theta \sin \chi \frac{\partial}{\partial \chi} \right] \]

\[
J_z = -i \frac{\partial}{\partial \chi} \]

which satisfy the commutation relations

\[
[J_x, J_y] = -i J_z; \quad [J_y, J_z] = -i J_x; \quad [J_z, J_x] = -i J_y. \]

The molecular z-axis is chosen as a projection axis by requiring

\[
[J^2, J_z] = 0. \]

The Schrödinger equation of a symmetric top can be obtained by substituting the angular momentum operators (55)–(57) to the symmetric top equation (54). We obtain the Schrödinger equation

\[
\left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \varphi} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} + \frac{\cos^2 \theta}{\sin^2 \theta} + \frac{B_{00}^{zz}}{B_{00}^{zz}} \frac{\partial^2}{\partial \chi^2} - \frac{2 \cos \theta}{\sin^2 \theta} \frac{\partial}{\partial \theta \partial \varphi} + \frac{E_0^0}{B_{00}^{zz}} \right] \Psi_0 = 0, \]

where

\[
E_0^0 (J, k, m) = B_{00}^{zz} J (J + 1) + (B_{00}^{zz} - B_{00}^{zz}) k^2 \]
is the symmetric top eigenvalue. The rotational eigenfunctions are

$$\Psi^0_{jk}(\theta, \phi, \chi) = S_{Jkm}(\theta, \phi) e^{ik\chi}, \quad (60)$$

where $S_{Jkm}(\theta, \phi) = \Theta_{Jkm}(\theta) e^{im\phi}$, where $\Theta_{Jkm}(\theta)$ is the Legendre polynomial. The rotational eigenfunctions are fully characterized by the three rotational quantum numbers $J$, $k$ and $m$. The quantum number $J$ is associated with the total angular momentum operator obeying a relation

$$J^2 |J, k, m\rangle = J (J + 1) |J, k, m\rangle, \quad (61)$$

where Dirac’s notation is used and $J$ assumes values $J = 0, 1, 2, \ldots, \infty$. The quantum number $k$ assumes values $k = -J, -J + 1, \ldots, 0, 1, \ldots, J$ being associated with the component of the total angular momentum along the molecular axis and satisfying a Schrödinger equation

$$J^z |J, k, m\rangle = k |J, k, m\rangle. \quad (62)$$

The magnetic quantum number $m$ assumes values $m = -J, -J + 1, 0, 1, \ldots, J$ obeying the Schrödinger equation

$$J^z |J, k, m\rangle = m |J, k, m\rangle, \quad (63)$$

where $J^z$ is the $z$-component of the total angular momentum in the space fixed coordinate system. Since no external fields exist and hence the orientation of the $(X, Y, Z)$ coordinate system is arbitrary with respect to the molecule, the $m$ quantum number will be dropped from the notation in the following consideration.

The matrix elements of the angular momentum operators are fully defined by the commutation relations (58). Let us define a ladder operator $J^\pm$ following:

$$J^\pm = J_x \pm iJ_y. \quad (64)$$

The matrix elements of the operator $J^\pm$ are

$$\langle J, k | J^\pm | J, k \rangle = \sqrt{J (J + 1) - k (k \mp 1)}, \quad (65)$$

which can be used to calculate matrix elements for any $(J^\pm)^m$ type operator.

### 3.4.4. Harmonic Oscillator

The harmonic oscillator approximation is the most commonly used method to treat the small amplitude vibrational problem as it enables a full separation of the vibrational modes and a simple procedure to obtain the matrix elements. The harmonic oscillator Hamiltonian
is given by operator $H_{20}$ in Table 5 and yields the Schrödinger equation

$$
\frac{1}{2} \sum_{k} ^{3N-7} \omega_k \left( p_k^2 + q_k^2 \right) \Psi^0_{v_k}(q_k) = \sum_{k} ^{3N-7} E^0_{v_k} \Psi^0_{v_k}(q_k). \tag{66}
$$

As a result of solving Eq. (66), we obtain the wave-functions and eigenvalues

$$
\Psi^0_v(q_1, q_2, \ldots q_{3N-7}) = \prod_{k=1} ^{3N-7} \Psi^0_{v_k}(q_k), \tag{67}
$$

$$
E^0_v = E_v = \sum_{k=1} ^{3N-7} \omega_k \left( v_k + \frac{d_k}{2} \right), \tag{68}
$$

where $v_k (= 0, 1, 2, \ldots, \infty)$ is the vibrational quantum number and $d_k$ is the degeneracy, respectively, of normal mode $k$. The vibrational ladder operator $R_k^\pm$ is defined as

$$
R_k^\pm = \frac{1}{\sqrt{2}} (p_k \pm i q_k), \tag{69}
$$

which operates on the Dirac’s ket-vector $|v_k\rangle$ as follows:

$$
R_k^\pm |v_k\rangle = \pm i \sqrt{v_k + \frac{1}{2} \pm \frac{1}{2}} |v_k \pm 1\rangle. \tag{70}
$$

The vibrational variables satisfy their usual commutation relations

$$
[p_k, q_k] = -[q_k, p_k] = -i \tag{71}
$$

$$
[p_k^m, p_k^n] = [q_k^m, q_k^n] = 0 \quad m, n = 0, 1, 2, 3, \ldots \tag{72}
$$

The analytical form of the one-dimensional oscillator wave-function is of no interest here. However, the two-dimensional oscillator wave-function is

$$
\Psi_{v, l} (\rho, \phi) = N_{v_l} e^{-\rho^2/2} L_{m}^{(l)} (\rho) e^{i l \phi}, \tag{73}
$$

where $N_{v_l}$ is the normalization factor and functions $L_{m}^{(l)} (\rho)$ are the associated Laguerre polynomials. The polar coordinates $\rho$ and $\phi$ are defined in terms of the degenerate pair of normal coordinates as

$$
\rho^2 = q_a^2 + q_b^2 \tag{74}
$$

$$
\phi = \arctan \left( \frac{q_a}{q_b} \right). \tag{75}
$$

In Eq. (73), index $l_l (= -v_l, -v_l + 2, \ldots, v_l - 2, v_l)$ is the quantum number which determines the eigenvalue of the vibrational angular momentum about the molecular $z$-axis. In the first excited state $v_l = 1$, there are two states $|v_l = 1, l_l = +1\rangle$ and $|v_l = 1, l_l = -1\rangle$.
that are associated with degenerate zeroth order energies. However, the degeneracy is broken by a vibrational angular momentum operator defined as
\[ \hat{\mathbf{l}} = -i \frac{\partial}{\partial \varphi} = \hat{q}_{tb} \hat{p}_{ta} - \hat{q}_{ta} \hat{p}_{tb}, \]  
(76)
giving rise to Schrödinger equation
\[ \hat{\mathbf{l}} |v_{\ell_{1}} \ell_{1}\rangle = -l_{\ell} |v_{\ell_{1}} \ell_{1}\rangle. \]  
(77)
The ladder operators in the two-dimensional case are
\[ q_{t, \pm} = q_{ta} \pm i q_{tb} \]  
(78)
\[ p_{t, \pm} = p_{ta} \pm i p_{tb}, \]  
(79)
where the phase convention is chosen so that the matrix elements of \( q_{t, \pm} \) are real, and those of \( p_{t, \pm} \) are imaginary. The matrix elements of \( q_{t, \pm} \) and \( p_{t, \pm} \) can be found from Ref. [8].

In the case of a symmetric top molecule with internal rotation, the definition of the normal coordinates in terms of internal displacement coordinates, Cartesian displacement coordinates or symmetric coordinates is problematic because the vibrational force field depends on the torsional angle. To simplify the treatment of the vibrations, the degenerate vibrations have to be localized either in the top or in the frame. Therefore, the polar angle \( \varphi \) characterizing the angular motion of a two-dimensional oscillator measured in an arbitrary \((x, y, z)\) coordinate system is
\[ \varphi_{m} = \varphi_{M} + r \gamma, \]  
(80)
where \( M = F \) for the frame and \( M = T \) for the top. Furthermore, the components of the normal coordinates and the conjugate momenta transform as
\[ q_{ta, m, M} = q_{ta, M} \cos r \gamma - q_{tb, M} \sin r \gamma \]  
(81)
\[ p_{ta, m, M} = p_{ta, M} \cos r \gamma - p_{tb, M} \sin r \gamma \]  
(82)
\[ q_{tb, m, M} = q_{tb, M} \cos r \gamma + q_{ta, M} \sin r \gamma \]  
(83)
\[ p_{tb, m, M} = p_{tb, M} \cos r \gamma + p_{ta, M} \sin r \gamma, \]  
(84)
where \( r = -\rho \) for the frame and \( r = (1 - \rho) \) for the top. It is easy to show that the vibrational angular momentum (76) is invariant in the transformation (81)–(84). Furthermore, the ladder operators (78) and (79) transform to
\[ q_{k, \pm, m} = q_{k, \pm} e^{\pm i r \gamma} \]  
(85)
\[ p_{k, \pm, m} = p_{k, \pm} e^{\pm i r \gamma}. \]  
(86)
In PAM \((\rho = 0)\), the treatment of a vibration localized in the frame is similar to that of a semi-rigid rotor.
3.5. Internal Rotor in Hindering Potential

In the discussion of the classical kinetic energy, the molecular variables are defined in the \((x, y, z)\) system with an arbitrary orientation and angular velocity with respect to the molecule. The angular velocities in the floating \((x, y, z)\) system are related to those presented in the molecule-fixed axis system with transformation

\[
\begin{pmatrix}
\omega_{x,m} \\
\omega_{y,m} \\
\omega_{z,m} \\
\omega_{\gamma,m}
\end{pmatrix} =
\begin{pmatrix}
\cos r\gamma & -\sin r\gamma & 0 & 0 \\
\sin r\gamma & \cos r\gamma & 0 & 0 \\
0 & 0 & 1 & -r \\
0 & 0 & 0 & 1
\end{pmatrix}
\begin{pmatrix}
\omega_{x} \\
\omega_{y} \\
\omega_{z} \\
\omega_{\gamma}
\end{pmatrix},
\]  

(87)

where the subscript \(m\) indicates a molecule-fixed variable. The molecular frame of reference is fixed to the frame when \(r = -\rho\) and to the top, respectively, when \(r = (1 - \rho)\).

It is customary to choose the frame-fixed axis system as a molecular frame of reference i.e., \(r = -\rho\) [9]. The Euler angles \(\theta\) and \(\phi\) are insensitive to the coordinate transformation. However, the nodal Euler angles \(\chi_F\), \(\chi_T\), and \(\chi_m\) for the frame, top and for the entire molecule, respectively, transform according to relations

\[
\chi_F = \chi_m - \rho \gamma
\]  

(88)

\[
\chi_T = \chi_m + (1 - \rho) \gamma
\]  

(89)

\[
\chi_m = (1 - \rho) \chi_F + \rho \chi_T
\]  

(90)

By neglecting the vibrational contribution to the inertial tensor, Eqs. (30) and (87) yield the components of the angular momenta

\[
J_{x,m} = I_{xx,m}^{e,m} \omega_{x,m} = I_{xx}^{e} (\omega_x \cos \rho \gamma + \omega_y \sin \rho \gamma)
\]  

(91)

\[
J_{y,m} = I_{yy,m}^{e,m} \omega_{y,m} = I_{yy}^{e} (\omega_x \cos \rho \gamma - \omega_y \sin \rho \gamma)
\]  

(92)

\[
J_{z,m} = I_{zz,m}^{e,m} \omega_{z,m} + I_{z\gamma}^{e,m} \omega_{\gamma,m}
\]

\[
= I_{zz}^{e} (\omega_z + \rho \omega_{\gamma}) + [(1 - \rho) \lambda - (1 - \lambda) \rho] I_{z\gamma}^{e} \omega_{\gamma}
\]  

(93)

\[
J_{\gamma,m} = I_{z\gamma}^{e,m} \omega_{\gamma,m} + I_{zz,m}^{e,m} \omega_{z,m}
\]

\[
= [\lambda - 2 \rho \lambda + \rho^2] I_{zz}^{e} \omega_{\gamma} + [(1 - \rho) \lambda - (1 - \lambda) \rho] I_{z\gamma}^{e} (\omega_z + \rho \omega_{\gamma})
\]  

(94)

In Eqs. (93) and (94), the constant \(\lambda\) is defined as a ratio of the inertial moment of the top and that of the entire molecule, that is

\[
\lambda \equiv \frac{I_{zz}^{e,T}}{I_{zz}^{e}}.
\]  

(95)
The $\rho$-dependent rotational-torsional Hamiltonian can be written as

$$
H_{02} = B_{0,0}^{xx} J_{x,m}^2 + B_{0,0}^{yy} J_{y,m}^2 + B_{0,0}^{zz} \left[ \frac{\lambda - 2 \rho \lambda + \rho^2}{\lambda (1 - \lambda)} \right] J_{z,m}^2 \tag{96a}
$$

$$
-2B_{0,0}^{zz} \left[ \frac{\lambda - \rho}{\lambda (1 - \lambda)} \right] J_{z,m} J_{\gamma,m} \tag{96b}
$$

$$
+ B_{0,0}^{zz} \left[ \frac{1}{\lambda (1 - \lambda)} \right] J_{\gamma,m}^2 \tag{96c}
$$

$$
+ V_{3} \frac{1}{2} (1 - \cos 3 \gamma_m), \tag{96d}
$$

where the angular momentum operators are defined through Eqs. (55)–(57) with substitution $\chi = \chi_m$, and the torsional angular momentum is defined as

$$
J_{\gamma,m} = -i \frac{\partial}{\partial \gamma_m}. \tag{97}
$$

Eqs. (93)–(94) and (96a)–(96d) show that the choice of parameter $\rho$ has a substantial impact on the form of the angular momenta and the rotational-torsional Hamiltonian. This is because the torsional angular velocity is defined in the molecule-fixed axis system by definition whereas the Euler angles are defined in the floating $(x, y, z)$ system which somehow has to be attached to the molecule. Ultimately, the choice of $\rho$ determines how the torsional angular velocity contributes to the $z$-component of the overall angular momentum and vice versa.

### 3.5.1. Principal Axis Method (PAM): $\rho = 0$

In a PAM (Principal Axis Method) axis system, the $(x, y, z)$ system is fixed to the $(x_F, y_F, z_F)$ system, and the top-fixed axis system $(x_T, y_T, z_T)$ rotates at angular velocity $\omega_\gamma$ relative to the frame about the molecular symmetry axis. The transformation matrix (87) reduces to a unit matrix and the variables (88)-(94) transform to

$$
\chi_F = \chi_P \tag{98}
$$

$$
\chi_T = \gamma + \chi_P \tag{99}
$$

$$
J_{x,P} = I_{xx}^e \omega_{x,P} = J_x \tag{100}
$$

$$
J_{y,P} = I_{xy}^e \omega_{y,P} = J_y \tag{101}
$$

$$
J_{z,P} = I_{xz}^e \omega_{z,P} + \lambda I_{xx}^e \omega_\gamma, P = I_{zz}^e \omega_z + \lambda I_{xx}^e \omega_\gamma = J_z \tag{102}
$$

$$
J_{\gamma,P} = \lambda I_{zz}^e (\omega_\gamma, P + \omega_z, P) = \lambda I_{zz}^e (\omega_\gamma + \omega_z) = J_\gamma, \tag{103}
$$

where subscript P indicates the PAM, $J_{x,P}$, $J_{y,P}$, and $J_{z,P}$ are the components of the total angular momentum and $J_{\gamma,P}$ is the angular momentum of the top including both external and internal rotation. In this coordinate system, the Hamiltonian (96a)–(96c) transforms
to

$$H^P_{02} = B_{00}^{zz,F} J^2 + \left( B_{00}^{zz,F} - B_{00}^{xx} \right) J_z^2$$  \hspace{1cm} (104a)

$$-2B_{00}^{zz,F} J_z J_{z,P}$$  \hspace{1cm} (104b)

$$+ B_{00}^{zz,F} J_z^2, + V_{1}^P \left( 1 - \cos 3\gamma \right)$$,  \hspace{1cm} (104c)

where $B_{00}^{zz,F}$ is the rotational constant of the frame and $B_{00}^{zz,F}$ is the effective rotational constant defined as

$$B_{00}^{zz,F} = \frac{B_{00}^{zz}}{1 - \lambda}$$  \hspace{1cm} (105)

$$B_{00}^{\gamma\gamma} = \frac{B_{00}^{zz}}{\lambda (1 - \lambda)}.$$  \hspace{1cm} (106)

The energy expression (104a)–(104c) looks similar to that of a rigid symmetric top molecule: the first term (104a) presents the energy of the overall rotation of the frame and the top and the second term presents the energy associated with the $z$-component of the total angular momentum of the frame. However, there are additional terms due to internal rotation. The cross term (104b) arises from coupling between the overall rotation and the torsion. The first term in (104c) presents the kinetic energy of the top including both and external rotation while the second term arises from the torsional potential.

### 3.5.2. Internal Axis Method (IAM): $\rho = \lambda$

In an IAM (Internal Axis Method) axis system [11], the frame and the top rotate at angular velocities $-\lambda \omega_{\gamma}$ and $(1 - \lambda) \omega_{\gamma}$, respectively, about the IAM $z$-axis. No external angular momentum is generated since $-I_{z,F}^{e,T} \omega_{\gamma} + I_{z,F}^{e,F} (1 - \lambda) \omega_{\gamma} = 0$. The nodal Euler angles $\chi_F$ and $\chi_T$ of the two coaxial rotors and that of the entire molecule $\chi_I$ are

$$\chi_F = \chi_I - \lambda \gamma$$  \hspace{1cm} (107)

$$\chi_T = \chi_I + (1 - \lambda) \gamma$$  \hspace{1cm} (108)

$$\chi_I = (1 - \lambda) \chi_F + \lambda \chi_T,$$  \hspace{1cm} (109)

where subscript I indicates the IAM. For the sake of simplicity, the components of the angular momenta are presented in terms of the PAM operators (100)–(103). We obtain

$$J_{x,I} = (\cos \lambda \gamma) J_{x,F} + (\sin \lambda \gamma) J_{y,F}$$ \hspace{1cm} (110)

$$J_{y,I} = (-\sin \lambda \gamma) J_{x,F} + (\cos \lambda \gamma) J_{y,F}$$ \hspace{1cm} (111)

$$J_{z,I} = \lambda I_{z,F}^{e,F}, = \lambda I_{z,F}^{e,F} \omega_{z,F} + \lambda I_{z,F}^{e,F} \omega_{\gamma} = J_{z,F}$$ \hspace{1cm} (112)

$$J_{\gamma,I} = \lambda (1 - \lambda) I_{z,F}^{e,F} \omega_{z,F} = J_{\gamma,F} - \lambda J_z.$$  \hspace{1cm} (113)
Again, \( J_{x,I} \), \( J_{y,I} \), and \( J_{z,I} \) are the components of the total angular momenta whose quantum mechanical operators satisfy the commutation relations (58). Furthermore, \( J_{x,I} \), \( J_{y,I} \), and \( J_{z,I} \) all commute with \( J_{y,I} \). However, \( J_{x,I} \) given by Eq. (113) does not represent the pure torsional angular momentum, but possesses additional contribution from the overall rotation. However, when used in the energy expression, \( J_{x,I}^2 \) produces the torsional kinetic energy, and \( J_{y,I} \) is called torsional angular momentum for the ease of discussion.

In the IAM, the cross term in the inertial tensor \( I_{z,I} \) in Eq. (94) vanishes, and the Hamiltonian (96a)–(96c) simplifies to

\[
\begin{align*}
H_{02}^{I} &= B_{0,0}^{zz} J_{z}^2 + (B_{0,0}^{zz} - B_{0,0}^{xx}) J_{x}^2 \
&+ B_{0,0}^{yy} J_{y}^2 + V_{yz} \frac{1}{2} (1 - \cos 3\gamma). 
\end{align*}
\]

(114a)

(114b)

The term (114a) presents the pure rotation of a symmetric top while term (114b) gives the energy of an isolated internal rotor in a hindering potential.

### 3.5.3. Remarks on the Coordinate Conventions. The Hybrid Method

The concepts of the PAM and IAM were originally associated with coordinate systems of asymmetric rotors, whose rotational-torsional problem is more complex than that of symmetric tops. The choice of the PAM axis system corresponds to fixing the \( (x, y, z) \) system to the principal axes of the molecule, thus leading to the elimination of the \( xy, xz, \) and \( yz \) terms of the inertial tensor. However, cross terms with \( \gamma \alpha \ (\alpha = x, y, z) \) are preserved, and after inverting the inertial tensor to the \( \mu \) tensor, every possible cross term with \( J_{\alpha}J_{\beta} \ (\alpha = x, y, z) \) can appear in the energy expression. The Coriolis-coupling cross terms with \( J_{\gamma}J_{\alpha} \ (\alpha = x, y, z) \) can be eliminated by an appropriate rotation of the \( (x, y, z) \) axis system, which results in so called Rho Axis Method (RAM) system [23]. The remaining terms with \( J_{\gamma}J_{z} \) can then be eliminated by transforming the RAM to PAM.

In the symmetric top case, terms with \( xy, xz, \) and \( yz \) of the inertial tensor vanish both in the PAM and IAM, and the torsional axis coincides with the \( z \)-axes in both of the axis systems. Therefore, terms "PAM" and "IAM" might appear misleading since both the PAM and IAM are in fact based on the principal axes presentations of the molecule. However, in the IAM, the cross term \( I_{zz}^{\gamma z} \) vanishes and the associated energy term does not occur in the angular momentum expression of the rotational-torsional energy.

The primary advantage of the PAM is simplicity: the components of the total angular momentum \( J_{x,P} \), \( J_{y,P} \), and \( J_{z,P} \) are defined in a straightforward manner, and thus the symmetry treatment of the molecular variables is simple. However, in a practical spectrum analysis, the molecular parameters occurring in Eq. (104a)–(104c) are treated as independent fitting parameters, and the large cross term (104b) between the torsion and overall rotation is usually highly correlated with the pure torsional and rotational parameters. Furthermore, at the high barrier limit, the rotational-torsional Hamiltonian does not reduce to that of a symmetric semi-rigid rotor.
The advantage of the IAM is the complete separation of the zeroth order rotational and torsional Hamiltonian, and the rapid convergence of the effective Hamiltonian. However, the explicit expressions of the angular momenta are complex and a complicated theory is needed to carry out the symmetry consideration of the molecular variables.

The physical difference between the PAM and IAM is the way how the conservation of the total angular momentum is being treated. In PAM, the torsion generates external angular momentum whose effect on the rotational energy is then compensated by the cross term (104b). In the IAM, no torsional angular momentum is generated due to suitable choice of the coordinate system.

The simplicity of the IAM form of the Hamiltonian (114a)–(114b) and on the other hand, the straightforward PAM presentation (98)–(103) of the molecular variables can be combined in a Hybrid Method (HM) presented in Ref. [14], where the effective torsional angular momentum is defined as

\[ \tilde{J}_\gamma = J_\gamma - \lambda J_z. \]  

In the HM, the angular momenta are defined as

\[ J_\gamma = -i \frac{\partial}{\partial \gamma_P}, \]  

\[ J_z = -i \frac{\partial}{\partial \chi_P}. \]

In the HM, the angular momentum components \( J_x, J_y \) and \( J_z \), retain their usual commutation relations. However, the effective torsional angular momentum \( \tilde{J}_\gamma \) (115) does not commute with \( J_x \) and \( J_y \) as is the case both in the PAM and the IAM. Therefore, the Hamiltonian terms involving \( \tilde{J}_\gamma \) simultaneously with \( J_x \) and/or \( J_y \) have to be symmetrized i.e., their anticommutator forms have to be considered.

### 3.5.4. Schrödinger Equation of a Hindered Internal Rotor

In the following discussion, the \((x, y, z)\) molecule-fixed coordinate system is not specified, and the torsional angle and the nodal torsional angle \( \chi_m \) are expressed as

\[ \gamma = \chi_T - \chi_F \]  

\[ \chi_m = (1 - \rho) \chi_F + \rho \chi_T. \]

Since the coordinate system is unknown, the product of the rotational and torsional eigenfunctions has to be considered. That is

\[ \Psi_{tr}^0 (\theta, \phi, \chi_m, \gamma) = \Psi_r^0 \Psi_t^0 = S_{jk} (\theta, \phi) e^{jk\chi_m} M (\gamma). \]
The Schrödinger equation of an isolated internal rotor in a threefold hindering potential can be written as

\[
\left[ -B_{00}^{\gamma} \frac{\partial^2}{\partial \gamma^2} + V_3 \frac{1}{2} (1 - \cos 3\gamma) \right] M(\gamma) = E_t M(\gamma). \tag{121}
\]

With substitutions [9]

\[
2x = 3\gamma + \pi \tag{122}
\]

\[
b = \frac{4E_t}{9B_{00}^{\gamma}} \tag{123}
\]

\[
s = \frac{4V_3}{9B_{00}^{\gamma}} \tag{124}
\]

\[
\Psi^0_t\left([3\gamma + \pi]/2\right) = M(x), \tag{125}
\]

eq (121) can be written in the form of the Mathieu equation [9, 11]

\[
\left[ \frac{d}{dx^2} M(x) + \left( b - \frac{1}{2} s \right) - \frac{1}{2} s \cos 2x \right] M(x) = 0. \tag{126}
\]

The periodicity of the variables in the Mathieu equation (126) is not yet known since we assume that the internal coordinate system is not yet selected. A non-periodic solution for the Mathieu equation can be written as

\[
M(\gamma) = e^{i\gamma f} P(\gamma), \tag{127}
\]

where \( P(\gamma) \) is periodic in \( 2\pi \), and the parameter \( f \) is a real constant chosen so that \( M(\gamma) \) has the periodicity according to the physical situation. Equation (127) shows that the internal and overall rotation are separable in as much as the rotational-torsional wave-function can be expressed as a product of a function of the three Eulerian angles and a function of \( \gamma \) alone.

Obviously, the wave-function \( \Psi^0_t(\theta, \phi, \chi_m, \gamma) \) must be periodic in \( 2\pi \) with respect to \( \chi_m \), which requires that

\[
k \left[ (1 - \rho) n_1 + \rho n_2 + f(n_2 - n_1) \right] = n, \tag{128}
\]

where \( n_1, n_2, \) and \( n \) are integers. Eq. (128) can be satisfied by taking \( f = -\rho k \), thus resulting in wave-function

\[
\Psi^0_t(\theta, \phi, \chi_m, \gamma) = S_{jk}(\theta, \phi) e^{ik\chi_m} e^{-i\gamma k \rho} P(\gamma). \tag{129}
\]

Function \( P(\gamma) \) has periodicity of \( 2\pi \) and can be determined by substituting \( e^{-ik\rho} P(\gamma) \) into Eq. (121). It can be shown [9, 11] that the torsional functions \( M_{k\nu\sigma}(\gamma) \) can be expressed in terms of the free rotor functions

\[
|k, k_f, \sigma\rangle = \frac{1}{\sqrt{2\pi}} e^{-i\rho k \gamma} e^{i\gamma (3k_f + \sigma)}, \tag{130}
\]
where \( k_f \) is the free rotor quantum number, \( \sigma \) is the quantum number characterizing the torsional tunnelling states assuming values \( \sigma = -1, 0, 1 \).

Let us fix the \((x, y, z)\) coordinate system to the molecule. In the PAM, \( \rho = 0 \) and consequently, \( \chi_F = \chi_P \) which is periodic in \( 2\pi \) by definition. Therefore, the solution of Eq. (121) in the PAM case can be returned to solving the Mathieu equation (126) which yields free rotor functions

\[
|k_f, \sigma\rangle = \frac{1}{\sqrt{2\pi}} e^{i\gamma(3k_f + \sigma)}
\]

as solutions. In the IAM case, \( \rho = \lambda \) and we obtain

\[
|k, k_f, \sigma\rangle = \frac{1}{\sqrt{2\pi}} e^{i\gamma(3k_f + \sigma - \lambda k)}.
\]

The basis set (130) satisfies the orthonormality relation

\[
\frac{1}{2\pi} \int_0^{2\pi} \left( e^{-i\rho k'\gamma} e^{i\nu(3k'_f + \sigma')} \right)^* \left( e^{-i\rho k\gamma} e^{i\nu(3k_f + \sigma)} \right) d\gamma = \delta_{k', k} \delta_{k'_f, k_f} \delta_{\sigma', \sigma}
\]

for any \( \lambda \). The matrix elements are

\[
\langle k', k_f, \sigma' | J^0_{\gamma,m} | k, k_f, \sigma \rangle = \langle 3k_f + \sigma - \lambda k \rangle^n \delta_{k', k} \delta_{k'_f, k_f} \delta_{\sigma', \sigma}
\]

\[
\langle k', k'_f, \sigma' \rangle \frac{1}{2} (1 - \cos 3n\gamma) | k, k_f, \sigma \rangle = \frac{1}{2} \left( \delta_{k', k_f} - \frac{1}{2} \delta_{k'_f, k_f+n} - \frac{1}{2} \delta_{k'_f, k_f-n} \right)
\]

\[
\times \delta_{k', k} \delta_{\sigma', \sigma},
\]

where \( \delta \) is the Kronecker delta and \( n = 1, 2, .. \).

In practice, the Schrödinger equation is solved numerically both in the PAM and the IAM by setting up a Hamiltonian matrix in the free rotor basis. The diagonalization produces the torsional eigenfunctions

\[
M_{k,v_T,\sigma}(\gamma) = \sum_{k_f=-\infty}^{\infty} A_{3k_f+\sigma}^{v_T,k} |k, k_f, \sigma\rangle,
\]

where \( A_{3k_f+\sigma}^{v_T,k} \) are the eigenvector components of the torsional wave-functions. In the final state (136), the label \( v_T \) has been adopted to represent the principal torsional quantum number. The quantum number \( v_T \) corresponds to a small amplitude labelling of the torsional states and assumes values \( v_T = 0, 1, 2, .. \) in the ascending order of energies.

Neither the effective rotational constant \( B_0^\gamma \) nor the first term \( V_3 \) of the torsional barrier expansion can as such provide an easy classification tool to classify molecules according to their torsional characteristics. However, the Mathieu equation (126) suggests that parameter \( s \) given in Eq. (124) can do so. Therefore, parameter \( s \) is also referred to as an **effective barrier height**.

Figures 3, 4, and 5 illustrate torsional energy level structure and probability densities with \( s = 7, s = 38, \) and \( s = 94 \), respectively. Value \( s = 7 \) illustrates an imaginary case,
while values $s = 38$ and $s = 94$ correspond to CH$_3$SiD$_3$ (Papers I and IV) and CH$_3$CF$_3$ (Paper II), respectively.

In Figures 3, 4 and 5, the torsional potentials are shown with dark solid sinusoidal curves. Energy levels labelled with $v_T = 0, \ldots, 6$ are illustrated with thick dashed/dotted horizontal lines, whereas the probability density curves are plotted with thin dashed/dotted lines. The probability density is obtained by taking a square of the torsional wave-function at each torsional angle and presents the probability of finding the torsional oscillator at a specific torsional angle.

Case $s = 7$ illustrated in Figure 3 represents a low barrier case. The kinetic term in the torsional Hamiltonian (121) dominates, and the energy level structure is similar to that of a free rotor. Furthermore, the $\sigma$-splittings are large due to high torsional tunnelling rate. The free rotor expansion (136) representing the torsional wave-function converges rapidly: in this case 7 terms are required to obtain the accuracy of $10^{-6}$ cm$^{-1}$ in eigenenergy. The energy corresponding to the lowest state with $v_T = 0$ is well below the top of the barrier, and the probability density is similar to that of the harmonic oscillator. At $v_T = 1$, the probability density shows two maxima characteristic to the harmonic oscillator but the curve shape is flattened, and the $\sigma$-splittings are of the order of 10 cm$^{-1}$ indicating the torsional tunnelling. At $v_T > 1$, the quadratic separation of the energy levels typical to free rotor dominates, and the probability density is not well localized in torsional angle. Now, the $\sigma$-splittings are more than 100 cm$^{-1}$.

Case $s = 38$ illustrated in Fig. 4 falls to an intermediate barrier category. The lowest torsional states $v_T = 0, 1, 2$ are almost equally separated, and the probability distribution plot is very similar to that of a harmonic oscillator. Now, $\sim 15$ terms in the wave-function expansion (136) are needed. The $\sigma$-splittings for $v_T = 0, 1, 2$ are $\sim 0.1$ cm$^{-1}$, $\sim 0.7$ cm$^{-1}$ and $\sim 10$ cm$^{-1}$, respectively. For $v > 2 - 6$, the $\sigma$-splittings are more than 40 cm$^{-1}$, and the probability of finding the oscillator inside the barrier i.e., at angles 60, 180, and 240, is now substantially larger.

Case $s = 94$ exemplified in Fig. 5 shows a high barrier case. The $\sigma$-splittings for levels $v_T = 0 - 4$ are $\sim 0.0001$ cm$^{-1}$, $\sim 0.001$ cm$^{-1}$, $\sim 0.01$ cm$^{-1}$, $\sim 0.5$ cm$^{-1}$, and 5 cm$^{-1}$, respectively. The levels with successive values of $v_T$ are virtually evenly spaced indicating the harmonic oscillator nature, and the probability distributions are similar to those of the harmonic oscillator. In this case, $\sim 21$ terms are required in the wave-function expansion (136) to obtain the sufficient accuracy. For $v_T = 5$ and $v_T = 6$, the $\sigma$-splittings increase rapidly to 50 cm$^{-1}$ and the free rotor nature of the probability density takes over.

The classification of the torsional characteristics into the three cases according to the effective barrier height $s$ is given only for discussion purposes and does not follow any known classification given in literature. The main purpose of the classification is to illustrate the cases between a virtual free internal rotor and a virtual harmonic oscillator. It should be pointed out that the free rotor functions (130) provide an efficient basis set for characterizing motion in a periodic potential from the free rotor limit to the harmonic oscillator limit.

The energy level systems exemplified in Figs. 3, 4 and 5 represent the simplest case where no small amplitude vibrational quanta are excited. However, when vibrational states are excited, each vibrational excited state holds a stack of torsional levels with $v_T = 0, 1, 2, \ldots$, whose details primarily depend on the effective rotational constant $B^{\gamma\gamma}$.
Fig. 3. Torsional energy level diagram and the probability density plots in the low barrier case for $K = 1$, $\sigma = -1, 0, +1$. The torsional energies are indicated with thick lines, which also define the baseline for the probability density curve. The $v_T$ quantum number is given for each energy level.

and the torsional potential $V_3$ in the specific vibrational state. As a result, a complex and perturbed energy level system is generated.

### 3.6. Molecular Symmetry

Symmetry properties of molecules together with the mathematical machinery of the group theory make up an efficient tool in studying molecular systems. In molecular spectroscopy, group theory can be used to simplify considerably the theory of the quantum states and the expressions of the Hamiltonian and transition moments.
Fundamentally, the symmetry properties of functions $\Psi_k(\alpha)$, $\Psi_m(\alpha)$, and $P(\alpha)$ discriminate whether a matrix element associated with functions $\Psi_k(\alpha)$, $\Psi_m(\alpha)$, and $P(\alpha)$ given by integral

$$\int_\alpha \Psi_k(\alpha)^* P(\alpha) \Psi_m(\alpha) \, d\alpha$$

vanishes. In the case of a vibrating and rotating molecule, functions $\Psi_k(\alpha)$ represent the vibration-torsion-rotation wave-functions that depend on a set of coordinates $\alpha$ and a set of quantum numbers $k$ and $m$. Function $P(\alpha)$ is a general vibration-torsion-rotation operator. In group theory language, integral (137) may have non-vanishing values, when the direct product of representations spanned by $\Psi_k(\alpha)$, $\Psi_m(\alpha)$ and $P(\alpha)$ contains a totally symmetric representation. Furthermore, the Hamiltonian has to be invariant to time reversal and Hermitian conjugation.
A symmetry group consists of a set of operations to which the energy of the system is invariant: these operations are called elements. The elements of a Complete Nuclear Permutation Inversion (CNPI) group consist of all permutations of the identical nuclei and spins, and inversion. The number of elements in a molecule is

\[ N = 2 \times \prod \ Limit_{k} \ N_k! \]

where \( N_k \) is the number of identical nuclei of type \( k \), and factor 2 arises from the inversion element. For example, methyl silane CH\(_3\)SiH\(_3\) has \( 2 \times 2! \times 6! = 2880 \) elements. However, not all the symmetry elements are feasible. An unfeasible element is one that interconverts a version of an equilibrium configuration to another, when these versions are separated by insuperable potential barrier. An insuperable barrier is one that does not allow observable tunneling to occur through it on an experimental time scale. The feasible elements of a CNPI group compose the elements of a Molecular Symmetry (MS) group [24]. Therefore,
the set of elements and hence the properties of the MS group required are defined to large extent by the experimental resolution and sensitivity.

The invariance of energy to the symmetry operations is based on transformation properties of the space-fixed coordinates \( R_i \) of the nuclei defined in Eq. (2). When the right hand side of equation (2) is subjected to symmetry operations, the symmetry operations operate separately on the Euler angles, the torsional angle and the vibrational displacement coordinates. When the overall translation is neglected, the symmetry operations can be represented by rotational operations rotating the entire molecule (point groups) or specific parts of molecules (PI groups) depending on the feasibility of the elements. For instance, in a molecule with two coaxial symmetric rotors, the two moieties are subjected separately to some of the symmetry operations. The transformation of the vibrational, torsional, and rotational wave-functions can be deduced from the changes in the coordinates by which they are defined.

The point groups compose a special case of symmetry groups. In a point group approximation, the invariance of energy to the symmetry operations is based on invariance of the macroscopic shape of the molecule, and therefore, the point groups cannot characterize molecules with torsional or inversion tunneling.

In practise, the symmetry operations are presented with matrix representations which obey the arithmetic rules of the abstract group. The matrix presentations are given in a basis formed by the molecular variables or wave-functions. The structure of the reducible representation i.e., the number of irreducible representations spanned by an arbitrary basis can be obtained from the little orthogonality theorem (LOT)

\[
  n_a = \frac{1}{h} \sum g_i \chi'^\alpha_i \chi_i,
\]

where \( h \) is the number of elements in the group, \( g_i \) is the number of elements in each class, \( \chi'^\alpha_i \) and \( \chi_i \) are the characters of the irreducible representation and reducible representation, respectively, in each class. The characters can be obtained from the trace of matrices that represent the elements in each class.

### 3.6.1. \( G_{18} \) Permutation Inversion Group

In the frozen torsional equilibrium configuration given in Fig. 1b, methyl silane-like molecules transform according to \( C_{3v} \) point group symmetry. In this case, there are 6 symmetry operations: identity \( E \), 2 bodily rotations \( C_3 \) through \( \pm 2\pi/3 \) and \( -2\pi/3 \) radians about the \( z \)-axis, and 3 reflections \( \sigma_v \) through planes defined by the \( z \)-axis and the lines connecting atoms 1 and 5, 2 and 4, and 3 and 6, respectively. When the torsional tunneling is included, the three equilibrium versions of the molecule cannot transform from one to another with the \( C_{3v} \) operations as only bodily rotations are allowed. However, when the top and the frame are separately allowed to be subjected to rotations about the symmetry
The character table of the $G_{18}$ group is given in Table 7. The correlation table between the $G_{18}$ and $C_{3v}$ groups is given in Table 8. Both groups possess two one-dimensional irreducible representations of $A_1$ and $A_2$ symmetry.

The correlation table suggests that each species in the high barrier limit ($C_{3v}$) splits into two or three components on the decrease of the barrier height, which corresponds to three equivalent minima in the potential function. For example, a non-degenerate state characterized with label $A$ in $C_{3v}$ group is extended to three-fold degenerate state with
Table 8: Correlation table of a methyl silane-like molecule$^a$.

<table>
<thead>
<tr>
<th>$C_{3v}$</th>
<th>$G_{18}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>$A_1 + E_4$</td>
</tr>
<tr>
<td>$A_2$</td>
<td>$A_2 + E_4$</td>
</tr>
<tr>
<td>$E$</td>
<td>$E_1 + E_2 + E_3$</td>
</tr>
</tbody>
</table>

$^a$ Taken from Ref. [12].

reduced representation $A_1 + E_4$. The multiplication table in the $G_{18}$ symmetry is given in Table 9.

### 3.6.2. Symmetry of the Vibrational-Torsional-Rotational States

In a spectroscopic problem, especially at an early stage of the study, the form of the Hamiltonian characterizing the molecular spectrum to be analyzed is unknown. Usually, derivation of the Hamiltonian from scratch is not feasible, and a more straightforward approach should be taken. In such a situation, symmetry properties of the molecule provide a substantial simplification, since appropriate Hamiltonian terms can be deduced from their symmetry properties. The basis set can also be categorized by symmetry so that the quantum mechanical problem can be divided into sub-problems which can be solved separately from each other. In fact, the easy approach to solve the spectroscopic problem with a symmetry tools may appeal to a lazy spectroscopist: it happens too often that the structure of the Hamiltonian is derived with a symmetry consideration only, and attempts to consider the physical interpretation and relevance of the Hamiltonian are neglected.

#### 3.6.2.1. Transformation Properties of the Torsional and Rotational Variables

The transformation properties of the molecular variables and those of the wave-functions are given in Table 10. The transformation properties of the Euler angles, rotational angular momenta and rotational wave-functions are well known [12]. The transformation of the torsional angle can be deduced from the transformation of the nodal Euler angles $\chi_F$ and $\chi_T$ by using definition $\gamma = \chi_T - \chi_F$ of the torsional angle. The angular transformation of the torsional angular momentum is easy to deduce and we obtain the rotational and torsional variables symmetry species

\[
\Gamma (J_x, J_y) = E_1
\]
\[
\Gamma (J_z) = \Gamma (J_\gamma) = A_2.
\]
Table 9. Multiplication table of the $G_{18}$ group.

<table>
<thead>
<tr>
<th>Product $A_i \times E_i$</th>
<th>Result $E_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1 \times E_i$</td>
<td>$E_i$</td>
</tr>
<tr>
<td>$A_2 \times E_i$</td>
<td>$E_i$</td>
</tr>
<tr>
<td>$E_i \times E_i = A_1 + A_2 + E_i$</td>
<td>$E_i$</td>
</tr>
<tr>
<td>$E_i \times E_j = E_k + E_l$</td>
<td>$E_i, j, k, l = 1, 2, 3, 4$, $i \neq j \neq k \neq l$</td>
</tr>
</tbody>
</table>

The torsional Hamiltonian involves operators with $\cos (3n\gamma)$ and $\sin (3n\gamma)$. Both functions are invariant in $\frac{2\pi}{3}$ rotations but operator $\cos (3n\gamma)$ preserves parity in the permutation-inversion, while the operator $\sin (3n\gamma)$ does not. Therefore, we obtain symmetry species

$$\Gamma (\cos (3n\gamma)) = A_1$$

$$\Gamma (\sin (3n\gamma)) = A_2.$$  

3.6.2.2. Transformation Properties of the Vibrational Variables

The structure of the reducible representation spanned by the vibrational coordinates is based on the transformation properties of the cartesian or internal displacement coordinates in symmetry operations. The normal coordinates themselves span the irreducible representations, which substantially simplifies the symmetry consideration. The symmetry classification of the vibrational wave-functions in the case of internal rotor molecule is complicated by the fact that the vibrational frequencies are $\gamma$ dependent, and this makes the determination of the normal coordinates and hence the vibrational wave-functions more involved than in the case of semi-rigid molecules. As the torsional coordinate is allowed to vary over a wide range, the point group symmetry of an instantaneous nuclear configuration may change. As an example, ethane $\text{CH}_3\text{CH}_3$ has $D_{3d}$ symmetry in staggered configuration whereas in the eclipsed configuration, the point group is $D_{3h}$.

To carry out the symmetry consideration for vibrational coordinates in the $G_{18}$ group, the vibrational displacements in the frame half and those in the top half have to be subjected separately to the symmetry operations [26]. This is a clear limitation in the formalism since no end-to-end force constants are allowed to exist between two degenerate symmetry coordinates.

In this case, we consider only degenerate pair of coordinates ($q_{Fa}, q_{Fb}$) of the frame and ($q_{Ta}, q_{Tb}$) of the top, respectively. The normal coordinates located in the frame transform according to Bunker [12], that is

$$C_F \left( \begin{array}{c} q_{Fa} \\ q_{Fb} \end{array} \right) = S_F \left( \begin{array}{c} 0 \\ 0, \frac{2\pi}{3} \end{array} \right) q_F,$$  

(152)

where the $S$ matrix is defined in Eq. (5) and $q_F$ forms a column vector with $q_{Fa}$ and $q_{Fb}$. The transformation of the top coordinates ($q_{Ta}, q_{Tb}$) follows Eq. (152) when carried out
in the frame-fixed axis system. Therefore, we can write

\[ C_T \mathbf{q}_T = C_T (S^{-1} (0, 0, \gamma) \mathbf{q}_T) = C_T S^{-1} (0, 0, \gamma) C_T \mathbf{q}_T \]

\[ = S \left( 0, 0, -\frac{2\pi}{3} \right) S^{-1} (0, 0, \gamma) S \left( 0, 0, \frac{2\pi}{3} \right) \mathbf{q}_T \]

\[ = S^{-1} (0, 0, \gamma) \mathbf{q}_T \]

\[ C_F \mathbf{q}_T = C_F (S^{-1} (0, 0, \gamma) \mathbf{q}_T) \]

\[ = S \left( 0, 0, \frac{2\pi}{3} \right) S^{-1} (0, 0, \gamma) S \mathbf{q}_T. \]

The conclusion is that both \( \mathbf{q}_F \) and \( \mathbf{q}_T \) transform identically and we can write

\[ \Gamma (\mathbf{q}_{Fa}, \mathbf{q}_{Fb}) = \Gamma (\mathbf{q}_{Ta}, \mathbf{q}_{Tb}) = E_1. \]

### 3.6.2.3. Symmetry of the Basis Set Wave-Functions

It is obvious from the transformation properties of the vibrational, torsional and rotational basis functions that the vibrational-torsional-rotational basis functions \(|v, l; J, k; k_f, \sigma_i\) and \(|v, -l; J, -k; -k_f, -\sigma_i\) form a basis for a two-dimensional irreducible representation. As the vibrational wave-functions transform similarly to symmetric tops \([27,28]\) we can adopt the convenient quantum number \(G\) originally introduced by Hougen \([27]\) for semi-rigid molecules defined as

\[ G = k - l, \]

where \(l\) in general represents the sum of quantum numbers associated with the vibrational angular momentum. For the non-degenerate vibrations \(l = 0\), and the overall symmetry can be obtained from direct product \(\Gamma (|J, k; k_f, \sigma_i|) \times \Gamma (|v|)\). The characters of the two-dimensional representation spanned by the basis functions \(|v, l; J, k; k_f, \sigma_i\) and \(|v, l; J, -k; -k_f, -\sigma_i\) are given in Table 10.

The structure of the representations spanned by the vibrational-torsional-rotational basis functions can in general be determined by applying the characters of the irreducible representation given in Table 10 and the LOT given in Eq. (139). The symmetry species of the basis functions are given in Table 11.

It is noteworthy that the free rotor quantuk number \(k_f\) does not enter in the expression of the characters of the irreducible representation spanned by the basis functions and therefore does not contribute to the symmetry. However, the symmetry of the pure torsional wave-functions (136) labelled by the quantum number \(v_T\) are

\[ A_1 \text{ for } v_T \text{ even} \]

\[ A_2 \text{ for } v_T \text{ odd}. \]
Table 10. The transformation properties of molecular variables and of the basis functions in the \(G_{18}\) group

<table>
<thead>
<tr>
<th>(E)</th>
<th>(C_F)</th>
<th>(C_T)</th>
<th>(C_T C_F)</th>
<th>(C_T C_F^*)</th>
<th>(\sigma)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R)</td>
<td>(+R)</td>
<td>(+R)</td>
<td>(+R)</td>
<td>(+R)</td>
<td>(-R)</td>
</tr>
<tr>
<td>(\theta^a)</td>
<td>(\theta)</td>
<td>(\theta)</td>
<td>(\theta)</td>
<td>(\theta)</td>
<td>(\pi - \theta)</td>
</tr>
<tr>
<td>(\phi^a)</td>
<td>(\phi)</td>
<td>(\phi)</td>
<td>(\phi)</td>
<td>(\phi + \pi)</td>
<td></td>
</tr>
<tr>
<td>(\chi_F^{a,b})</td>
<td>(\chi_F^p + p)</td>
<td>(\chi_F^p)</td>
<td>(\chi_F^p + p)</td>
<td>(\chi_F^p - p)</td>
<td>(\pi - \chi_F^p)</td>
</tr>
<tr>
<td>(\gamma)</td>
<td>(\gamma - p)</td>
<td>(\gamma - p)</td>
<td>(\gamma + p)</td>
<td>(\gamma)</td>
<td>(\gamma)</td>
</tr>
</tbody>
</table>

\(q_{Fa}^{a,b}\) | \(cq_{Fa} + sq_{Fb}\) | \(q_{Fa} \) | \(cq_{Fa} + sq_{Fb}\) | \(cq_{Fa} - sq_{Fb}\) | \(q_{Fa}\) |
| \(q_{Fb}^{a,b}\) | \(-sq_{Fb} + cq_{Fb}\) | \(q_{Fb} \) | \(-sq_{Fb} + cq_{Fb}\) | \(sq_{Fb} + cq_{Fb}\) | \(-q_{Fb}\) |
| \(q_{Ta}^{a,b}\) | \(cq_{Ta} + sq_{Tb}\) | \(q_{Ta} \) | \(cq_{Ta} + sq_{Tb}\) | \(cq_{Ta} - sq_{Tb}\) | \(q_{Ta}\) |
| \(q_{Tb}^{a,b}\) | \(-sq_{Tb} + cq_{Tb}\) | \(q_{Tb} \) | \(-sq_{Tb} + cq_{Tb}\) | \(sq_{Tb} + cq_{Tb}\) | \(-q_{Tb}\) |

| \(J_{x,y}^{a,b}\) | \(cJ_{x} + sJ_{y}\) | \(J_{x}\) | \(cJ_{x} + sJ_{y}\) | \(cJ_{x} - sJ_{y}\) | \(-J_{x}\) |
| \(J_{y}\) | \(-sJ_{x} + cJ_{y}\) | \(J_{y}\) | \(-sJ_{x} + cJ_{y}\) | \(sJ_{x} + cJ_{y}\) | \(+J_{y}\) |
| \(J_{z}\) | \(J_{z}\) | \(J_{z}\) | \(J_{z}\) | \(-J_{z}\) | |
| \(J_{\gamma}\) | \(J_{\gamma}\) | \(J_{\gamma}\) | \(J_{\gamma}\) | \(-J_{\gamma}\) | |
| \(\cos(3\pi\gamma)\) | \(\cos(3\pi\gamma)\) | \(\cos(3\pi\gamma)\) | \(\cos(3\pi\gamma)\) | \(\cos(3\pi\gamma)\) | |
| \(\sin(3\pi\gamma)\) | \(\sin(3\pi\gamma)\) | \(\sin(3\pi\gamma)\) | \(\sin(3\pi\gamma)\) | \(-\sin(3\pi\gamma)\) | |

| \(e^{ikp}\) | \(|J, k\rangle\) | \(e^{ikp}\) | \(|J, k\rangle\) | \(e^{-ikp}\) | \(|J, k\rangle\) | \((-1)^{f-k}\) | \(|J, -k\rangle\) |
| \(e^{-i\sigma p}\) | \(|k_f, \sigma\rangle\) | \(e^{-i\sigma p}\) | \(|k_f, \sigma\rangle\) | \(e^{i\sigma p}\) | \(|k_f, \sigma\rangle\) | \(|k_f, -\sigma\rangle\) | |
| \(e^{-i\gamma p}\) | \(|v, l\rangle\) | \(e^{-i\gamma p}\) | \(|v, l\rangle\) | \(e^{-i\gamma p}\) | \(|v, l\rangle\) | \(|v, -l\rangle\) | |
| \(e^{-i\phi p}\) | \(|v, l\rangle\) | \(e^{-i\phi p}\) | \(|v, l\rangle\) | \(e^{-i\phi p}\) | \(|v, l\rangle\) | \(|v, -l\rangle\) | |

Characteris of the reducible representation spanned by

\[
\begin{array}{c}
|v, l; J, k; k_f, \sigma\rangle \\
|v, -l; J, -k; -k_f, -\sigma\rangle
\end{array}
\]

\(2\cos[(G - \sigma)p] 2\cos|\sigma|p 2\cos[(G + \sigma)p] 2\cos[Gp] 0\)

\(a\) Transformation properties taken from Ref. [12].
\(b\) \(c = \cos(p)\); \(s = \sin(p)\); \(p = \frac{2\pi}{3}\)
\(c\) Transformation properties taken from Refs. [27] and [28].

From Table 11, it is evident that the case \(\sigma = 0\) simplifies the symmetry consideration to the \(C_{3v}\) case: the symmetry species \(A_1, A_2,\) and \(E_1\) are characterized by the \(G\) quantum number, and the symmetry species \(E_2, E_3,\) and \(E_4\) vanish. The two torsional \(\sigma\)-substates for each \(G \neq 3n\) possess different \(E\) symmetry, whereas for \(G = 3n\) they transform identically.

In the case of the \((G = 3n, \sigma = 0)\) states, any orthogonal pair of the linear combination of the basis functions spans the representations \(A_1 + A_2\). The representation can be factorized into two one-dimensional representations by introducing a symmetry adapted basis, which can be written as

\[
|v, G; J; k_f, \sigma = 0, A_1\rangle = \frac{1}{\sqrt{2}} \left(|v, G; J, k_f, 0\rangle + (-1)^J |v, G; J, -k_f, -0\rangle\right),
\]

(159)
Table 11. The symmetry species spanned by the basis functions $|v, l, J, k, k_f, \sigma\rangle$ and $|v, l, J, -k, -k_f, -\sigma\rangle$ in the $G_{18}$ group $^{a,b}$

<table>
<thead>
<tr>
<th>$G = k - l$</th>
<th>$\sigma$</th>
<th>$\Gamma_{vtr}$</th>
<th>Statistical Weights</th>
</tr>
</thead>
<tbody>
<tr>
<td>3$n$ - 1</td>
<td>-1</td>
<td>$E_2$</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>$E_1$</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>$E_3$</td>
<td>4</td>
</tr>
<tr>
<td>3$n$</td>
<td>-1</td>
<td>$E_4$</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>$A_1 + A_2$</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>$E_4$</td>
<td>4</td>
</tr>
<tr>
<td>(3$n$ + 1)</td>
<td>-1</td>
<td>$E_3$</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>$E_1$</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>$E_2$</td>
<td>8</td>
</tr>
</tbody>
</table>

$^a$ In case $G=0$, $\Gamma = A_1$ for even $J$ and $\Gamma = A_1$ for odd $J$.

where $i = 1$ for even $J$ and $i = 2$ for odd $J$. Obviously, the $G$ quantum number can be obtained with various combinations of $l$ and $k$ quantum numbers.

### 3.6.2.4. Spin Statistical Weights of the Overall States

The effect of nuclear spin in vibration-torsion-rotation spectroscopy becomes observable through the coupling of the spin angular momentum with the rotational angular momentum. The effect of coupling on the transition spectrum is often far beyond the experimental line width, and therefore can be neglected in the Hamiltonian. However, the effect of nuclear spin plays an important role in the line intensities through its contribution to the symmetry of the total wave-function.

Based on the Pauli exclusion principle, the total wave-function changes in sign in an odd permutation of nuclei that possess half integer spins (fermions) and is invariant to any permutation of identical nuclei that have integer spins (bosons). The dimension of the reducible representation spanned by the spin functions $|I, m_I, \sigma\rangle$, where $I$ is the spin, and $m_I$ is the spin projection quantum number, is

$$n = \prod_{\alpha}^N (2I_{\alpha} + 1).$$  \hspace{1cm} (160)

For example, in methyl silanes CH$_3$SiH$_3$ and CH$_3$SiD$_3$, the dimensions of the reducible representations are 64 and 216, respectively. The structure of the reducible representation can be obtained by subjecting the total spin function $|I_1, m_{I_1}, \ldots, m_{I_N}\rangle$ to the symmetry operations of the group, and by applying the LOT given by Eq. (139). For
methyl silanes, we obtain spin representations [47]

\[
\begin{align*}
\text{CH}_3\text{SiH}_3 & : \quad \Gamma_S = 16A + 8E_1 + 8E_2 + 4E_3 + 4E_4 \\
\text{CH}_3\text{SiD}_3 & : \quad \Gamma_S = 44\text{A} + 32E_1 + 22E_2 + 16E_3 + 16E_4.
\end{align*}
\]

(161) (162)

The symmetry of the overall wave-function can be obtained from direct product

\[
\Gamma_{\text{trans}} = \Gamma_{\text{utr}} \times \Gamma_s.
\]

(163)

The multiplication table 9 suggests that the \(A\) symmetry species is obtained only when the symmetry species is multiplied by itself. Therefore, the spin statistical weights of each symmetry species can be directly obtained from their coefficients in (161) and (162). The spin statistical weights of states \(|v, G; J, k_f, \sigma\rangle\) are summarized in Table 11.

### 3.6.2.5. Symmetry of the Hamiltonian

The symmetry properties of the molecular variables play an important role when simplifying the Hamiltonian. The symmetry consideration serves two main purposes: a) filter out terms that give vanishing matrix elements, and b) establish the algebraic relationship between the molecular parameters.

In order to have non-vanishing matrix elements, the Hamiltonian operator or parts of it have to preserve total symmetry in all the symmetry operations of the group. If the Hamiltonian is written as a product of operators \(P_i\) as \(P_1P_2\ldots P_N\), then it is required that

\[
\Gamma(H) = \Gamma(P_1) \times \Gamma(P_2) \times \ldots \times \Gamma(P_N) \supset A_1.
\]

(164)

**Example 1** Let us take a special case of the Coriolis operator \(H_{21}\) from Table 5 as an example. In this case, both \(k\) and \(l\) are associated with the same two-dimensional normal mode \(t\) and therefore \(\Gamma(q_i) = \Gamma(p_i) = E_1\) and \(J_a = J_\gamma\), i.e. \(\Gamma(J_a) = A_2\). The operator is

\[
H_{21}^{2,1} = -2 \left( B_{0,0}^{2,1} + B_{0,0}^{1,2} \right) B_{0,0}^{2,3} \gamma \left( \tilde{\zeta}_{a,b}^t \sigma_p a \sigma_q p_a + \tilde{\zeta}_{a,b}^t \sigma_p b + \tilde{\zeta}_{b,a}^t \sigma_q a \sigma_p a + \tilde{\zeta}_{b,a}^t \sigma_q b + \tilde{\zeta}_{a,b}^t \sigma_q a \sigma_p b + \tilde{\zeta}_{a,b}^t \sigma_q b \right),
\]

(165)

where the index \(t\) is dropped and the indices \(a\) and \(b\) refer to the two degenerate components of \(t\). Obviously, the reducible representation of operator (165) is \(E_1 \times E_1 \times A_2 = A_1 + A_2 + E_2\), and hence (165) contains one totally symmetric linear combination of product of operators \(q, p, \) and \(J_\gamma\). Let us transform (165) with \(\sigma\). We obtain

\[
\sigma H_{21}^{2,1} = -2 \left( B_{0,0}^{2,1} + B_{0,0}^{1,2} \right) \left( \sigma_p \gamma \right) \left[ \tilde{\zeta}_{a,b}^t \left( \sigma_p a \right) \left( \sigma_q a \right) + \tilde{\zeta}_{b,a}^t \left( \sigma_p b \right) \left( \sigma_q a \right) \left( \sigma_p b \right) \right] + \tilde{\zeta}_{b,a}^t \left( \sigma_p a \right) \left( \sigma_q b \right) \left( \sigma_p b \right) + \tilde{\zeta}_{a,b}^t \left( \sigma_q b \right) \left( \sigma_p a \right) \left( \sigma_p b \right) + \tilde{\zeta}_{b,a}^t \left( \sigma_q b \right) \left( \sigma_p b \right) + \tilde{\zeta}_{a,b}^t \left( \sigma_q b \right) \left( \sigma_p b \right)
\]

\[
= -2 \left( B_{0,0}^{2,1} + B_{0,0}^{1,2} \right) \left( -\gamma \right) \left[ \tilde{\zeta}_{a,b}^t \left( \sigma_p a \right) \left( \sigma_q b \right) + \tilde{\zeta}_{a,b}^t \left( \sigma_p a \right) \left( \sigma_q b \right) \left( \sigma_p b \right) \right] + \tilde{\zeta}_{b,a}^t \left( -\sigma_q b \right) + \tilde{\zeta}_{b,a}^t \left( -\sigma_q b \right) \left( -\sigma_p b \right)
\]

(166)
Obviously, terms with $\zeta_{ab}^\gamma$ and $\zeta_{ba}^\gamma$ retain, and $\zeta_{aa}^\gamma = \zeta_{bb}^\gamma = 0$. In the next step, the remaining terms are subjected to the $C_F$ operation as

$$C_F H_{21}^{\gamma,t} = C_F \left( -2 \left( B_{0,0}^{\gamma \gamma} + B_{0,0}^{zz} \right) J_\gamma \left( \zeta_{ab}^\gamma q_a p_b + \zeta_{ba}^\gamma q_b p_a \right) \right)$$

$$- 2 \left( B_{0,0}^{\gamma \gamma} + B_{0,0}^{zz} \right) J_\gamma \left( \zeta_{ab}^\gamma (cq_a + sq_b) \right) (cp_a - sp_b)$$

$$+ \zeta_{ba}^\gamma (cq_b - sq_a) (cp_a + sp_b)$$

$$= - 2 \left( B_{0,0}^{\gamma \gamma} + B_{0,0}^{zz} \right) J_\gamma \left( \zeta_{ab}^\gamma \left( c^2 q_a p_b - s c q_b p_a + s c q_b p_b - s^2 q_b p_a \right) \right)$$

$$+ \zeta_{ba}^\gamma \left( c^2 q_b p_a + sc q_b p_a - sc q_a p_a - s^2 q_a p_b \right)$$

where $c = \cos \left( \frac{2\pi}{3} \right) = \frac{1}{2}$ and $s = \sin \left( \frac{2\pi}{3} \right) = \frac{\sqrt{3}}{2}$. In order to cancel terms $q_a p_a$ and $q_b p_b$ that do not occur in the untransformed Hamiltonian, we must have $\zeta_{ba}^\gamma = - \zeta_{ab}^\gamma$. Finally we get

$$H_{21}^{\gamma,t} = - 2 \left( B_{0,0}^{\gamma \gamma} + B_{0,0}^{zz} \right) \zeta_{ab}^\gamma J_\gamma \left( q_a p_b - q_b p_a \right).$$

The operator $H_{21}^{\gamma,t}$ is invariant to $C_T$ and furthermore,

$$C_T C_F H_{21}^{\gamma,t} = C_T C_F^2 H_{21}^{\gamma,t} = C_F H_{21}^{\gamma,t}.$$

The vibrational operator in (170) can be interpreted as the vibrational angular momentum according to Eq. (77) and we can write

$$H_{21}^{\gamma,t} = - 2 \left( B_{0,0}^{\gamma \gamma} + B_{0,0}^{zz} \right) \zeta_{ab}^\gamma J_\gamma \hat{\ell}.$$ 

Since $\Gamma(J_\gamma) = \Gamma(J_z)$, the symmetry treatment of term $H_{21}^{\gamma,t}$ similar to (165) with $J_2$ can be carried out. As a result we obtain

$$H_{21}^{\gamma,t} = - 2 \left( B_{0,0}^{\gamma \gamma} + B_{0,0}^{zz} \right) \zeta_{ab}^\gamma J_z \hat{\ell}.$$

Term (172) characterizes a coupling between the torsional angular momentum and the vibrational angular momentum about the molecular symmetry axis. Term (173) yields a $z$–Coriolis term that characterizes the coupling between the $z$-component of the overall angular momentum and the vibrational momentum about the molecular symmetry axis.

The procedure described above can be applied to any term in the Hamiltonian. Non-vanishing constants and their algebraic relationships in the Hamiltonians $H_{12}$, $H_{21}$, $H_{22}$, $H_{04}$ and $H_{06}$ have been tabulated in Tables 12 and 13.

The properties of the inertial derivatives and of the Coriolis constants are similar to those of a $C_{3v}$, case with additional terms due to torsional angular momentum and the torsional potential terms. The relationships for the cubic and quartic anharmonicity constants are given in Refs. [29, 30].
The Schrödinger equation of a vibrating and rotating molecule with internal rotation in the Born-Oppenheimer approximation can be written as

\[ H_{VTR} |\Psi_k\rangle = E_k |\Psi_k\rangle, \tag{174} \]

where \( H_{VTR} \) is the complete vibrational-torsional-rotational Hamiltonian given in Eq. ??, \( E_k \) is the vibration-torsion-rotation energy, and \( |\Psi_k\rangle \) represents the corresponding wavefunction. In general, (174) cannot be solved in a closed form and various approximative methods, such as variational methods and perturbation theory must be used. In both methods, the wave-function \( |\Psi_k\rangle \) is expressed as an expansion

\[ |\Psi_k\rangle = \sum_i u_{ik} |\phi_i\rangle, \tag{175} \]

where \( |\phi_i\rangle = |v, \ell; J, k; k_f, \sigma\rangle \) is the vibration-torsion-rotation basis function, and the coefficients \( u_{ik} \) are normalized components of an eigenvector. By multiplying Eq. (174) from left by \( |\Psi_k\rangle \) we obtain eigen-equation

\[ E_k = \sum_{j,i} u_{jk} \langle \phi_j | H | \phi_i \rangle u_{ik} = \sum_{j,i} u_{jk} H_{ji} u_{ik}, \tag{176} \]

where \( H_{ji} = \langle \phi_j | H | \phi_i \rangle \) are the matrix elements of \( H \) between states \( j \) and \( i \). Eq. (176) can be written as a matrix equation

\[ U H U^{-1} = E, \tag{177} \]

where components of \( E_k \) form a diagonal matrix \( E \), and \( U \) is a unitary transformation matrix.
The explicit form of (177) can be written in a matrix form as

\[ \begin{pmatrix}
  u_{11} & u_{12} & \cdots & u_{1n} \\
  u_{21} & u_{22} & \cdots & u_{2n} \\
  \vdots & \vdots & \ddots & \vdots \\
  u_{n1} & u_{n2} & \cdots & u_{nn}
\end{pmatrix}
\begin{pmatrix}
  H_{11} & H_{12} & \cdots & H_{1n} \\
  H_{21} & H_{22} & \cdots & H_{2n} \\
  \vdots & \vdots & \ddots & \vdots \\
  H_{n1} & H_{n2} & \cdots & H_{nn}
\end{pmatrix}
\begin{pmatrix}
  u_{11} & u_{21} & \cdots & u_{n1} \\
  u_{12} & u_{22} & \cdots & u_{n2} \\
  \vdots & \vdots & \ddots & \vdots \\
  u_{n1} & u_{2n} & \cdots & u_{nn}
\end{pmatrix}
= \begin{pmatrix}
  E_1 \\
  E_2 \\
  \vdots \\
  E_n
\end{pmatrix}.
\] (178)

The Hamiltonian matrix \( \mathbf{H} \) can be transformed to a block-diagonal form by introducing a symmetry adapted basis set. This means that the basis functions \( |\phi_i\rangle \) in the trial wave-function \( |\Psi_i\rangle \) are replaced by their linear combination that transform according to the irreducible representation in the symmetry group in question. See Eq. (159) for an example of symmetrized basis functions. Each block in the Hamiltonian matrix can then be
diagonalized separately as no coupling matrix elements exist between the basis functions spanning two different symmetry species, see Eq. (137).

The energies $E_k$ and the components of the transformation matrix $u_{ij}$ can be obtained by diagonalizing the matrix of $H$. When $n \leq 4$, the eigenvalues and eigenvectors can be obtained by analytic algebra, whereas with $n > 4$, the Hamiltonian has to be set up explicitly, and then diagonalized with a numerical procedure. The diagonal elements of the Hamiltonian matrix $H$ are often referred to as unperturbed energies and the associated states unperturbed states. The off-diagonal elements or operators are referred to as perturbations. The corresponding quantities after diagonalization are perturbed energies and perturbed states, respectively.

The dimension $n$ of the Hamiltonian matrix $H$ i.e., the vibrational, torsional and rotational states that have to be included in the basis set, depends to large extent on the case. In the case $n > 4$, the parameters that define the molecular Hamiltonian have to be known a priori, and the numerical diagonalization produces exact energies provided that the Hamiltonian characterizes the physical problem with sufficient precision. The accuracy of the eigenvalues is limited by the numerical accuracy of the diagonalization and the truncation limit of the basis set. In practice, the accuracy is limited by the Hamiltonian, and by the accuracy requirement itself.

3.7.2. Time-Independent Perturbation Methods

The use of the direct method requires large computational power and numerical values for the molecular parameter that are seldom available a priori. In spectroscopy, we usually deal with an inversion problem: the form of the Hamiltonian is known at some accuracy, but the explicit values of the molecular parameters of the Hamiltonian are to be determined from spectroscopic data. Furthermore, the exact form of the Hamiltonian is often to be investigated and hence the analytical expressions of the eigenvalues in terms of the molecular parameters are required. As a consequence it is necessary to find a method to diagonalize the Hamiltonian matrix in a closed form. As the roots of a polynomial of more than degree of four cannot be obtained analytically, approximative methods have to be employed and therefore, the Hamiltonian matrix has to be diagonalized with a perturbation method.

Rayleigh-Schrödinger (RS) perturbation theory [31] is a conventional method to determine the eigenvalues and eigenvectors in quantum mechanics. The first order wavefunction $|\Psi_k\rangle$ and the second order correction $\Delta_k$ to the energy $E_k$ are given by

$$|\Psi_k\rangle = \sum_{i \neq k} \frac{H_{ki}}{E_k^0 - E_i^0} |\phi_i\rangle$$

$$\Delta_k = \sum_i \Delta_{ki} = \sum_{i \neq k} \frac{H^2_{ki}}{E_k^0 - E_i^0}$$

where $E_k^0$ is the unperturbed energy of the perturbing state $i$, and $H_{ki}$ is the coupling matrix element. Another state denoted $j$, shifts energy $E_k^0$ of state $k$ by $\Delta_{kj}$, and the total shift to
$E^0_k$ is $\sum_i \Delta_{ki}$. In Eq. (180), the denominator $E^0_k - E^0_i$ does not account for the shift of the perturber $E^0_i$, nor the shift of the level $E^0_k$ due to other perturbers. In other words, the total second order correction to energy $E^0_k$ is the sum of perturbations in independent two-level systems.

### 3.7.2.1. Contact Transformation Equations

The RS perturbation theory provides a rule-of-thumb approach in practical spectroscopic work. However, it is not practical for systematic derivation of the high order expressions of the eigenvalues and eigenvectors of a vibration-torsion-rotation Hamiltonian. This is due to tedious summations over a large number of intermediate states in the higher order correction formulae and due to large degree of cancellation of terms in the final algebraic expressions.

It is significantly easier to use the contact transformation method, where the perturbation formulas are expressed in commutator form and thus the explicit matrix elements are not required. The original form of contact transformation was applied to a rotation-spin coupling problem in diatomic molecules by Van Vleck [32] and later to polyatomic molecules by Shaffer and co-authors [33]. From the early 1950’s, contact transformation has been the standard perturbation theory treatment for vibration-rotation problems in polyatomic molecules [8, 34].

In the following, we consider the general theory of contact transformation, and apply it to the vibration-torsion-rotation problem. A detailed recipe for carrying out a contact transformation in a special case of a semi-rigid molecules is given in Ref. [34].

In contact transformation, the unitary transformation $U$ occurring in Eq. (177) is given in an operator form as

$$\tilde{\mathbf{H}} = \mathbf{U} \mathbf{H} \mathbf{U}^{-1},$$

(181)

where $\tilde{\mathbf{H}}$ is the transformed Hamiltonian. The essence in contact transformation is to find an operator $\mathbf{U}$ that produces diagonal matrix representation for $\tilde{\mathbf{H}}$ i.e., the commutator $[\tilde{\mathbf{H}}, \mathbf{H}_0] = 0$, where $\mathbf{H}_0$ is a zeroth order Hamiltonian.

Let us suppose that the original and transformed Hamiltonian $\mathbf{H}$ and $\tilde{\mathbf{H}}$, respectively, can be expressed as converging series as

$$\mathbf{H} = \mathbf{H}_0 + \lambda \mathbf{H}_1 + \lambda^2 \mathbf{H}_2 + \ldots + \lambda^k \mathbf{H}_k + \ldots \lambda^n \mathbf{H}_n,$$

(182)

$$\tilde{\mathbf{H}} = \tilde{\mathbf{H}}_0 + \tilde{\lambda} \tilde{\mathbf{H}}_1 + \tilde{\lambda}^2 \tilde{\mathbf{H}}_2 + \ldots + \tilde{\lambda}^k \tilde{\mathbf{H}}_k + \ldots \tilde{\lambda}^n \tilde{\mathbf{H}}_n,$$

(183)

where $\lambda$ is a bookkeeping parameter that defines the orders of magnitude of terms $\mathbf{H}_k$ and $\tilde{\mathbf{H}}_k$ in expansions (182) and (183). The subscript $i$ associates the term $\mathbf{H}_i$ with the appropriate order of magnitude. In a general case, the contact transformation is carried out sequentially for operators $\mathbf{H}_1, \mathbf{H}_2, \ldots, \mathbf{H}_n$. The total transformation operator $\mathbf{U}$ can be
expressed with elementary operators \( U_k \) as

\[
U = U_n U_{n-1} \ldots U_k U_{k-1} U_1,
\]

(184)

where each \( U_i \) eliminates term \( H_i \) in (182) or in (183). Each \( U_k \) represents a unitary transformation defined by a Hermitian operator \( S_k \) as

\[
U_k = \exp \left( i \lambda S_k \right) = 1 + i \lambda S_k - \frac{1}{2} \lambda^2 S_k^2 + \ldots,
\]

(185)

where \( U_k \) has been expanded in Taylor series.

Let us carry out the first contact transformation with \( S_1 \). From Eq. (181) we get

\[
\tilde{H}^{(1)} = \left[ 1 + i \lambda S_1 - \frac{1}{2} \lambda^2 S_1^2 + \ldots \right] H \left[ 1 - i \lambda S_1 - \frac{1}{2} \lambda^2 S_1^2 + \ldots \right].
\]

(186)

where superscript \((1)\) refers to the first contact transformation, and \( n \) is the length of the commutator. By ordering the terms in (186) according to \( \lambda \) and then fixing \( \lambda = 1 \), we obtain terms of the effective Hamiltonian

\[
\tilde{H}_0^{(1)} = H_0
\]

(187)

\[
\tilde{H}_1^{(1)} = H_1 + i [S_1, H_0]
\]

(188)

\[
\tilde{H}_2^{(1)} = H_2 + i [S_1, H_1] - \frac{1}{2} [S_1, [S_1, H_0]]
\]

(189)

\[
\tilde{H}_3^{(1)} = H_3 + i [S_1, H_2] - \frac{1}{2} [S_1, [S_1, H_1]] - \frac{i}{6} [S_1, [S_1, [S_1, H_0]]].
\]

(190)

The same procedure can be applied to the once-transformed Hamiltonian \( \tilde{H}^{(1)} \) to eliminate further terms required.

### 3.7.2.2. Transformation Operators

The transformation operator \( S_i \) has to be chosen so that the term \( \tilde{H}_1 \) defining the off-diagonal matrix elements vanishes i.e.,

\[
\tilde{H}_1 = H_1 + i [S_1, H_0] = 0.
\]

(191)

For the ease of discussion, we assume that term \( H_1 \) defines only off-diagonal elements since the grouping of the terms in (182) and (183) is to large extent a matter of choice. Usually, operator \( H_1 \) consists of group of operators with the same order of magnitude and
similarity in the operator form. Therefore, we can write
\[ H_1 = \sum_i h_{1i}, \tag{192} \]
where the general form of \( h_{1i} \) can be expressed with general rotational and vibrational operators \( R_{1i}^n \) and \( V_{1i}^m \) as
\[ h_{1i} = R_{1i}^n V_{1i}^m. \tag{193} \]
In (193), indices \( m \) and \( n \) follow the notation of the Watson Hamiltonian discussed in Section 3.1.

Now, Eq. (191) returns to similar equations of individual \( h_{1i} \) as
\[ \tilde{h}_{1i} = h_{1i} + i [s_{1i}, H_0] = 0, \tag{194} \]
where \( s_{1i} \) are the elementary transformation functions.

In the vibrational contact transformation i.e., in a transformation eliminating the Hamiltonian terms that include off-diagonal matrix elements in vibrational quantum numbers, the transformation functions can be written in terms of the Hamiltonian \( H_1 \) and the harmonic oscillator Hamiltonian \( H_{20} \). As a result, a trial function for component \( s_{1i} \) can be written as
\[ s_{1i} = X_{1i} [H_0, h_{1i}], \tag{195} \]
where \( X_{1i} \) is a reduction coefficient. The determination of the total transformation function \( S_1 \) returns to the determination of the reduction coefficients \( X_{1i} \), which can be determined by substituting the trial function (195) into Eq. (194).

3.7.2.3. Corrections to the Hamiltonian

The next step in the contact transformation is to transfer the contribution of the operator \( H_1 \) to be eliminated to the parts of the Hamiltonian that are diagonal in the representation of \( H_0 \). Since the \( S_1 \) function carries a unitary transformation, the eigenvalues of the transformed Hamiltonian \( \tilde{H} \) have to be identical with those of the original Hamiltonian \( H \). This is done by substituting \( S_1 \) function to Eqs. (189)-190) transforming the higher order terms \( \tilde{H}_2, \tilde{H}_3, \tilde{H}_4 \), such that the eigenvalues remain. For example, the second order corrections to the untransformed Hamiltonian generate the once-transformed second order term
\[ \tilde{H}_2 = H_2 + \frac{i}{2} [S_1, H_1] \\
= H_2 + \frac{i}{2} \sum_{i,j} [s_{1i}, h_{1j}] \\
= H_2 + \frac{i}{2} \sum_{i,j} [R_{1i}^n V_{1i}^m, R_{1j}^n V_{1j}^m]. \tag{196} \]
It is easy to show that the last commutator in Eq. (196) can be expressed as a sum of two commutators as

$$
\left[ R^n_{ij} V^m_{ii}, R^n_{ij} V^m_{jj} \right] = \left[ V^m_{ij}, V^m_{ii} \right] R^n_{ij} R^n_{ii} + V^m_{ij} V^m_{ii} \left[ R^n_{ij}, R^n_{ii} \right].
$$

(197)

In a general case, the first term in commutator (197) results in diagonal and off-diagonal terms in vibrational quantum numbers, which are to be eliminated in the second contact transformation, and hence create correction terms in the higher order. Furthermore, when the vibrational commutator in the first term in Eq. (197) is non-zero, the degree of the rotational operators becomes $2n$. This generates rotational terms with a degree higher than 2. It can be shown [8] that the second term in (197) is approximately two orders of magnitude smaller than the first term, and therefore can be neglected in the non-degenerate case.

It should be noted that the contact transformation is a version of perturbation theory having the same limitations as the standard RS perturbation theory. This is easily deduced by deriving matrix elements of the $S$ operator. That is

$$
\langle k | S_1 | i \rangle = -i \frac{\langle k | H_1 | i \rangle}{E^0_k - E^0_i},
$$

which is identical to the coefficient occurring in the first order wave-function in Eq. (179). In the case of resonance, ie. when $E^0_b - E^0_a \leq \langle a | H_1 | b \rangle$, the normalization of the wave-function fails, and the second order correction in energy (180) becomes physically irrelevant. The usability and the confidential limit of the perturbation theory largely depend on the accuracy of the energy levels that can be determined from an experiment and on the transition selection rules that occur in the data set.

The sequential contact transformations lead finally to an effective Hamiltonian that leads to a block-diagonal matrix. The $1 \times 1$ blocks form a polynomial representation of the energy levels which is desirable for simple analysis of the energy levels. The off-diagonal elements of the blocks are due to degeneracy or near-degeneracy of states that cannot be treated with perturbation methods. Those blocks of the Hamiltonian matrix have to be treated with the direct method described in Section 3.1. In an inversion problem, the definition of near-degeneracy and judgement between the perturbation theory and direct method depends on various aspects. In a spectral analysis, the Hamiltonian terms have to be sensitive enough to the spectral transitions, and terms having a mutual relationship through a contact transformation become redundant.

### 3.7.3. Contact Transformation of the Vibration-Torsion-Rotation Operator

The contact transformation procedure was described in general terms in the previous section. To implement this method, the sequence of the sequential transformation must be assessed to arrange the terms $H_{mn}$ in expansions (182) and (183) according to the order of the bookkeeping parameters $\lambda$. The magnitude of each Hamiltonian term $H_{mn}$ depends...
on its contribution to the energy and therefore, the degrees $m$ and $n$ of the vibrational and rotational operators and the range of relevant quantum numbers have to be taken into account. The vibrational and rotational energies are transformed to the same scale of magnitude with the Born-Oppenheimer ratio \[ \kappa = (m_e/m_n)^{1/4} \sim 1/10, \] where $m_e$ and $m_n$ are the mass of an electron and that of a nucleus, respectively, so that

\[ E_v \approx \kappa^{-2} E_r. \]  

(198)

In Eq. (198), $E_v$ and $E_r$ are typical vibrational and rotational ground state energies indicating the magnitude of the vibrational and rotational constants in the zeroth order. The power of $\kappa$ in general indicates the order of magnitude of the coefficient relative to a typical harmonic vibrational frequency. It can be shown \[22, 35, 36\] that the order of the sequential contact transformations can be chosen according to calculational convenience without affecting neither the expression of the transformation functions $S$ nor the final effective Hamiltonian $H$.

In this context, we follow the ordering of Duan \[13\] originally introduced by Aliev and Watson \[22\]. The appropriate Hamiltonian terms to be considered here are

\[ H^{(0)} = H_{20} \]

(199)

\[ H^{(1)} = H_{12} + H_{21} + H_{30} + H_{30} \]

(200)

\[ H^{(2)} = H_{22} + H_{04} + H_{13} + H_{40} \]

(201)

\[ H^{(3)} = H_{14}. \]

(202)

The sequence of the $S$ operators is represented by a two-dimensional array as

\[ S_{12}, S_{13}, S_{14}, S_{14}, \ldots \]

\[ S_{21}, S_{22}, S_{23}, S_{24}, \ldots \]

\[ S_{30}, S_{31}, S_{32}, S_{33}, \ldots \]

\[ S_{40}, S_{41}, S_{42}, S_{43}, \ldots, \]

(203)

where each column or row can be truncated according to the particular problem.

### 3.7.3.1. Vibrational Contact Transformation

Usually, the first step in the contact transformation is to eliminate the lowest order terms that generate off-diagonal matrix elements in vibrational quantum numbers. The procedure and the equations are similar to those in the treatment of a semi-rigid molecule \[34\] since the torsional operators are embedded in the $R$ operators given in Table 6. However, additional terms $H_{04}$ and $H_{14}$ are due to internal rotation since they do not exist in the Hamiltonian of semi-rigid molecules in the rotational zeroth order.

In the first sequential vibrational contact transformation, the first column in (203) is used to transform the first order operators $H_{30}, H_{21},$ and $H_{12}$. According to Eq. (194), the
Table 14: Contact transformation functions

<table>
<thead>
<tr>
<th>Vibrational Contact Transformation Functions</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_{12} = -\sum_k \omega_k^{-1} R_k p_k$</td>
</tr>
<tr>
<td>$S_{21} = \sum_{k \neq l} R_k^l \left( \Theta^{kl} p_k p_l + \Theta^{kl} q_k q_l \right)$</td>
</tr>
<tr>
<td>$S_{30} = -\frac{1}{6} \sum_{klm} k_{klm} \Omega^{-1}_{klm} [2\omega_k \omega_l \omega_m p_k p_l p_m$</td>
</tr>
<tr>
<td>$+ 3\omega_l \left( \omega_l^2 - \omega_k^2 + \omega_m^2 \right) q_k p_l q_m]$</td>
</tr>
<tr>
<td>$\Theta^{kl} = \Theta_{lk} = \omega_k^{l^2} - \omega_l^{k^2}$</td>
</tr>
<tr>
<td>$\Omega^{-1}_{klm} = (\omega_k + \omega_l + \omega_m)(-\omega_k + \omega_l + \omega_m)$</td>
</tr>
<tr>
<td>$\times (\omega_k - \omega_l + \omega_m)(\omega_k + \omega_l - \omega_m)$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Torsional-Rotational Contact Transformation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_{01} = \sum_{\alpha} \Phi_{\alpha} J_{\alpha}$</td>
</tr>
<tr>
<td>$S_{03} = \sum_{\alpha\beta\delta} \Phi_{\alpha\beta\delta} J_{\alpha} J_{\beta} J_{\delta} + \sum_{\alpha} [\Theta^{1,2}<em>\alpha (1 - \cos 3\gamma) + \Omega^{1,2}</em>\alpha \sin 3\gamma] J_{\alpha}$</td>
</tr>
</tbody>
</table>

---

\(^a\) Taken from Ref. [13]. See also Ref. [22].

\(^b\) Only terms relevant to this thesis are considered.

defining equations of $S$ are

\[
\begin{align*}
[S_{12}, H_{20}] &= iH_{12} \quad (204) \\
[S_{21}, H_{20}] &= iH_{21} \quad (205) \\
[S_{30}, H_{20}] &= iH_{30}. \quad (206)
\end{align*}
\]

The resulting transformation functions are shown in Table 14. The terms in the second order once-transformed Hamiltonian $\tilde{H}_1$ are

\[
\tilde{H}^{(0)}_{20} = H_{20}
\]

\[
\tilde{H}^{(1)}_{02} = H_{02}
\]

\[
\tilde{H}^{(2)}_{40} = H_{40} + \frac{1}{2} i [S_{30}, H_{30}]
\]

\[
\tilde{H}^{(2)}_{22} = H_{22} + \frac{1}{2} i ([S_{21}, H_{21}] + 2 [S_{12}, H_{30}] + 2 [S_{21}, H_{02}])
\]

\[
\tilde{H}^{(2)}_{04} = H_{04} + \frac{1}{2} i [S_{12}, H_{12}]
\]
\[
\tilde{H}_{31}^{(2)} = H_{31} + i [S_{21}, H_{30}] 
\]

\[
\tilde{H}_{13}^{(2)} = i ([S_{12}, H_{02}] + [S_{12}, H_{21}]),
\]

where the commutators can be either vibrational or rotational commutators.

Even though the explicit formulae for the correction terms (209)-(213) are not shown, the implications of the near-degeneracy and the applicability of the first contact transformation can be deduced from the structure of the transformation operators \(S\) that occur in each correction term. Terms involving \(S_{12}\) operator, for example, are safe as far as the near-degeneracy is concerned. The perturbation denominator in \(S_{12}\) consists of a single harmonic frequency, which does not lead to singularity in any circumstances.

Terms that involve \(S_{21}\) may encounter problems in the case of Coriolis resonance i.e., when \(\omega_l \approx \omega_k\) and vibrational states \(\langle v_l = 1 \rangle\) and \(\langle v_k = 1 \rangle\) are coupled by a Coriolis matrix element of \(H_{21}\) operator. In this case, the portion of an \(H_{12}\) that couples the near-degenerate state has to be treated with the direct method described in Section 3.7.1. At the same time, the contribution of \(S_{12}\) to \(\tilde{H}_{22}^{(2)}, \tilde{H}_{31}^{(2)}\), and \(\tilde{H}_{13}^{(2)}\) operators has to be removed.

Terms that contain \(S_{30}\) cannot be applied as transformation functions in the case of an anharmonic resonance. The cases are \(2\omega_k \approx \omega_l\) and \(\omega_k + \omega_l \approx \omega_m\), where the former corresponds to a case when the states \(\langle v_k = 2 \rangle\) and \(\langle v_l = 1 \rangle\) in a near degeneracy are coupled by anharmonic term \(k_{klm}q_k^2q_lq_m\), and the latter when the states \(\langle v_k = v_l = 1 \rangle\) and \(\langle v_m = 1 \rangle\) are coupled by term \(k_{klm}q_kq_lq_m\).

Terms in \(\tilde{H}_1\) resulting in off-diagonal matrix elements are eliminated in the second contact transformation with transformation functions \(S_{40}, S_{22}, S_{31},\) and \(S_{13}\) in a similar manner as in the first contact transformation. The second vibrational contact transformation will not be discussed here.

### 3.7.4. Effective Hamiltonian

The contact transformation procedure described above results in an effective Hamiltonian that is observed in spectroscopic studies. The effective Hamiltonian is related to the original Hamiltonian, i.e. the Hamiltonian constructed from the internal molecular parameters, by the unitary transformation represented by the contact transformation functions.

#### 3.7.4.1. Effective Vibrational Operator

The perturbation treatment of the pure vibrational operator \(H_V = H_{20} + H_{30} + H_{40}\) follows that of a semi-rigid molecule and is well documented in literature [8, 34].
vibrational contact transformation produces an effective vibrational operator of form

\[
\tilde{H}_V = \tilde{H}_{20} + \tilde{H}_{40} \\
= \sum_k \frac{1}{2} \omega_k (p_k^2 + q_k^2) + \frac{1}{24} \sum_{k,l,m,n} k_{klmn} q_k q_l q_m q_n \\
- \frac{1}{8} \sum_{k,l,m,n,r} k_{klmr} k_{klm} \Omega_{klm}^{-1} \left[2 \omega_k \omega_l \omega_m, q_n, q_{l'}, p_{l'}, p_m\right] \\
+ \omega_k \left(\omega_k^2 + \omega_k^2 - \omega_k^2\right) q_k q_{l'} q_{m'} q_{n'} + \sum_\alpha B_\alpha p_\alpha^2,
\]

where \(\Omega_{lmn}\) is given in Table 14. The last term in (214) arises from the original Watson Hamiltonian representing the energy associated with the pure vibrational angular momentum. It should be noted that only terms with operators \(q_k^2 q_{l'}^2\) and \(q_k^2 p_{l'}^2\) in Eq. (214) result in diagonal matrix elements. In the symmetric top case, the diagonal terms result in the linear expression of the pure vibrational energy given by

\[
G(v, \ell) = \sum_s \omega_s \left(\frac{v_s + \frac{1}{2}}{2}\right) + \sum_t \omega_t \left(\frac{v_t + 1}{2}\right) \\
+ \sum_{s \geq s'} x_{ss'} \left(\frac{v_s + \frac{1}{2}}{2}\right) \left(\frac{v_s' + \frac{1}{2}}{2}\right) + \sum_{t \geq t'} x_{tt'} \left(\frac{v_t + 1}{2}\right) \left(\frac{v_t' + 1}{2}\right) \\
+ \sum_{s,t} \omega_t \left(\frac{v_t + \frac{1}{2}}{2}\right) \left(\frac{v_t + 1}{2}\right) + \sum g_{tt'} \ell_t \ell_t',
\]

where \(x_{kl}\) and \(g_{tt'}\) are anharmonic constants, and indices \(s\) and \(t\) refer to a non-degenerate and a degenerate vibration, respectively. The explicit formulae of the anharmonic constants \(x\) and \(g\) can be found in Ref. [8].

3.7.4.2. Effective Torsion-Rotation Operator: Torsion-mediated Interactions

In this thesis, the primary interest regarding the perturbation treatment of the vibration-torsion-rotation Hamiltonian lies in the reduction of the centrifugal distortion operator \(H_{12}\). A systematic approach for treating the quartic centrifugal distortion Hamiltonian in an internal rotor molecule was introduced by Duan and Takagi [37] whose approach is followed here. By solving the commutator \(\frac{1}{2} i \left[ S_{12}, H_{12}\right]\) and sorting the resulting corrections ac-
cording to \( nm \) notation adopted, we obtain once-transformed Hamiltonian

\[
\begin{align*}
\tilde{H}_{00}^{(2)} &= \Theta_{0}^{0,0} \\
\tilde{H}_{02} &= H_{02} + \Theta_{0}^{0,2} \frac{1}{2} (1 - \cos 3\gamma) \\
\tilde{H}_{04} &= H_{04} \\
&+ \Theta_{0}^{0,4} \frac{1}{2} (1 - \cos 6\gamma) \\
&+ \frac{1}{4} \sum_{\alpha\beta\gamma\epsilon=x,y,z,\gamma} \tau_{\alpha\beta\epsilon\zeta} J_{\alpha} J_{\beta} J_{\gamma} J_{\epsilon} \\
&+ \sum_{\alpha\beta=x,y,z,\gamma} \Theta_{0}^{2,2} \frac{1}{2} (1 - \cos 3\gamma) J_{\alpha} J_{\beta} \\
&+ \sum_{\alpha=x,y,z,\gamma} \Omega_{0}^{1,2} \sin 3\gamma J_{\alpha}, 
\end{align*}
\]

where coefficients are

\[
\begin{align*}
\Theta_{0}^{0,0} &= \frac{9}{8} \sum_{k \subset A_1} \frac{1}{\omega_k} B_{k,0}^{\gamma\gamma} V_k^3 \\
\Theta_{0}^{0,2} &= -\frac{1}{2} \sum_{k \subset A_1} \frac{1}{\omega_k} \left( V_k^3 \right)^2 + \frac{9}{2} B_{k,0}^{\gamma\gamma} V_k^3 \\
\Theta_{0}^{0,4} &= \frac{1}{8} \sum_{k \subset A_1} \frac{1}{\omega_k} \left( V_k^3 \right)^2 \\
\tau_{\alpha\beta\epsilon\zeta} &= -2 \sum_{k} \frac{1}{\omega_k} B_{k,0}^{\alpha\beta} B_{\beta,0}^{\epsilon\zeta} \\
\Theta_{0}^{2,2} &= -\frac{1}{2} \sum_{k \subset A_1} \frac{1}{\omega_k} B_{k,0}^{\alpha\beta} V_k^3 \\
\Omega_{0}^{1,2} &= \frac{3}{8} \sum_{k \subset A_1} \frac{1}{\omega_k} B_{k,0}^{\gamma\epsilon} V_k^3.
\end{align*}
\]

In Eq. (216), the term \( \Theta_{0}^{0,0} \) introduces a constant shift in the zero-point energy of the molecule, and therefore does not introduce spectroscopic interest. In Eqs. (217) and (218), terms with \( \Theta_{0}^{0,2} \) and \( \Theta_{0}^{0,4} \), respectively, modify the torsional potential constants, thus resulting in effective potential constants

\[
\begin{align*}
\tilde{V}_3 &= V_3^e + \Theta_{0}^{0,2} \\
\tilde{V}_6 &= V_6^e + \Theta_{0}^{0,4}. 
\end{align*}
\]

In Eq. (218), the term with the centrifugal distortion constants \( \tau_{\alpha\beta\epsilon\zeta} \) represent the conventional quartic centrifugal distortion terms of a semi-rigid molecule plus additional terms due to internal rotation. Terms with \( \Theta_{0}^{2,2} \) represent a combined effect on the torsional-
rotational energy due to distortion of the inertial tensor and the potential barrier. In Eq. (218), terms that involve $J_\gamma$ and $\sin^3\gamma$ or $\cos^3\gamma$ have been symmetrized.

The symmetry properties of the rotational derivatives $B_{\alpha\beta}^{\gamma} k$ and the derivatives of the torsional potential $V_k^\gamma$ given in Table 13 limit substantially the number of possible $\Theta$ and $\tau$ terms given in Eqs. (216)-(218). Still, the derivation of the remaining terms is a cumbersome task, and will not be presented here.

An example of applying contact transformation to the centrifugal distortion Hamiltonian in a real spectroscopic problem is given in Section II D in Paper III. Specifically, the example deals with centrifugal distortion operators of type

$$H_{12}^{\gamma} = \left[ M_{\gamma}^{\gamma \gamma} J_\gamma^2 + M_{\gamma}^{\gamma z} J_\gamma J_z + M_{\gamma}^{zz} J_z^2 + C_{\gamma}^3 \frac{1}{2} (1 - \cos 3\gamma) \right] q_5,$$

(227)

where $M_{\gamma}^{\gamma \gamma}$, $M_{\gamma}^{\gamma z}$, $M_{\gamma}^{zz}$, $C_{\gamma}^3$, and $C_{\gamma}^6$ are fitting parameters whose relation with the internal molecular parameters can be deduced by comparing the terms of (227) with those given in Tables 5 and 6. It should be noted that Eq. (227) has been expressed in the Hybrid Model discussed in Section 3.3. The operator (227) couples the C-Si stretching mode $\nu_5$ and the torsional motion.

In Paper III, operator (227) is also referred to as a "Fermi-type" operator, since it includes an anharmonic type component $\frac{1}{2} (1 - \cos 3\gamma) q_5$. The reference to anharmonicity is justified on the basis of high barrier approximation, where term $\cos 3\gamma$ is proportional to $\gamma^2$, and thus results in a third power operator in the displacement coordinates $q_5$ and $\gamma$.

The contact transformation of term (227) leads to effective molecular parameters shown in Table II in Paper III. The numeric values are also given.

Another application of the centrifugal distortion terms to a real spectroscopic study is given in Section II in Paper IV. In this case, the centrifugal distortion operator is

$$H_{12}^{\gamma y} = M_{\gamma}^{\gamma \gamma} J_\gamma^2 + M_{\gamma}^{\gamma z} J_\gamma J_z + M_{\gamma}^{zz} J_z^2 + C_{\gamma}^3 \frac{1}{2} (1 - \cos 3\gamma) q_5,$$

(228)

where $\gamma = J_\gamma - \rho J_z$. The centrifugal distortion operator (228) couples the torsional states with the lowest degenerate vibrational state $\nu_{12}$. In Paper IV, the operator (228) is also referred to as "an $xy$-Coriolis-type" operator, since in the high barrier approximation, $\gamma$ may be interpreted as vibrational momentum associated with a small amplitude vibration, and thus operator (228) has a similar structure to the classical $xy$-Coriolis between $\Lambda_1$ and $E$ vibrations of a semi-rigid symmetric top.

In symmetric tops with internal rotation, the Hamiltonian term with constants $\tau_{\alpha\beta\delta\epsilon} J_{\alpha} J_{\beta} J_{\gamma} J_{\delta}$ in Eq. (218) generate a rotational operator

$$H_{04}^{\gamma} = \epsilon \left[ J_\gamma, e^{3i\rho\gamma} J_\gamma^3 + e^{-3i\rho\gamma} J_\gamma^3 \right]_+ + \frac{1}{2} \epsilon_\gamma \left[ J_\gamma, e^{3i\rho\gamma} J_\gamma^3 + e^{-3i\rho\gamma} J_\gamma^3 \right]_+,$$

(229)

where $\epsilon$ and $\epsilon_\gamma$ may be expressed as a function of $\tau_{\alpha\beta\delta\epsilon}$ coefficients. The operator (229) couples rotational states with $\Delta k = 3$, and is typically observable in quasi-spherical sym-
metric tops with $A \sim B$. Especially, the effects become dramatic for states where $k$ is multiple of three, and thus the levels are doublets of $A_1$ and $A_2$ energy levels. In such cases, the operator of type (229) breaks the degeneracy and splits up the $A_1$ and $A_2$ energy levels.

An investigation of terms (229) in CH$_3$CF$_3$ is presented in Paper II. Especially, Paper II deals with reduction schemes where terms (229) have been subjected to a rotational contact transformation. Numerical examples of the effect of various elimination schemes are shown in Tables 5 and 6 in Paper II. An energy level diagram illustrating the interaction mechanisms associated with the centrifugal distortion of type (229) is shown in Fig. 4 in Paper II.

In this thesis, another interest lies in an effective Hamiltonian of form

$$H_{eff}^v = H_V^v + H_T^v + H_R^v + H_{TR}^v + H_{VTR}^v,$$  \hspace{1cm} (230)

where

$$H_V^v = \frac{1}{2} \tilde{\nu}_v \left( q_v^2 + p_v^2 \right);$$  \hspace{1cm} (231)

$$H_T^v = \left( \tilde{F}_v + \tilde{F}_{v,m} \right) J_\gamma^2 - D_{v,m} J_\gamma^4 + \tilde{V}_{v,3} \frac{1}{2} (1 - \cos 3\gamma) + \tilde{V}_{v,6} \frac{1}{2} (1 - \cos 6\gamma);$$  \hspace{1cm} (232)

$$H_R^v = \tilde{B}_v J_2^2 + \left( \tilde{A}_v - \tilde{B}_v \right) J_2^2 - D_{v,J} J_4 - \tilde{D}_{v,K} J_2^2 J_2^2 - \tilde{D}_{v,K} J_4^2;$$  \hspace{1cm} (233)

$$H_{TR}^v = -\left( D_{v,J} J_4^2 + D_{v,K} J_2^2 \right) J_\gamma^2 - \left( D_{v,J} J_4^2 + D_{v,K} J_2^2 \right) J_\gamma^2 + \left( F_{v,3} J_2^2 + F_{v,3} J_2^2 \right) \frac{1}{2} (1 - \cos 3\gamma);$$  \hspace{1cm} (234)

$$H_{VTR}^v = -\left[ 2(A\zeta_\gamma^2 - \eta_{t,J} J_2^2 - \eta_{t,K} J_2^2) J_\gamma \ell_\gamma + 2(A\zeta_\gamma^m) J_\gamma \ell_\gamma \right].$$  \hspace{1cm} (235)

Terms from (230) to (235) represent a Hamiltonian for a vibrational state $v$. The harmonic oscillator Hamiltonian $H_V^v$ in Eq. (231) is written in terms of the normal co-ordinate $q_v$ and its conjugate momentum $p_v$. The parameter $\tilde{\nu}_v$ is the effective vibrational quantum. This usually includes implicitly anharmonic and Coriolis effects resulting from interactions of state $v$ with other vibrational states.

The torsional Hamiltonian $H_T^v$ in Eq. (232) is made up of pure torsional terms. The terms in $\tilde{F}_v$ and $\tilde{V}_{v,m}$ form the zeroth-order torsional Hamiltonian. The reduced rotational constant $F_v \equiv A_v / \rho (1 - \rho)$, while $F_{v,m}$ is a quartic distortion correction. In the lowest order, $\tilde{V}_{v,m}$ is the height of the hindering potential $V_v(\gamma)$: the Fourier expansion of $\tilde{V}_v(\alpha)$ is truncated after the second term.

The rotational Hamiltonian $H_R^v$ in Eq. (233) includes terms arising from rigid rotation, and pure rotational distortion terms. The torsion-rotation Hamiltonian $H_{TR}^v$ in Eq. (234) contains the distortion terms that involve both torsional and rotational operators, but not the vibrational angular momentum $\ell_1$. 
Finally, the first three terms in Eq. (235) arise from the Coriolis coupling between $\ell_{12}$ and $J_z$, while the fourth term is the result of the Coriolis-like coupling between $\ell_{12}$ and $J_\alpha$.

It should be noted that the distribution of terms in Eqs. (231)-(235) is done purely for discussion purposes. Another approach would be to order the terms according to their order of magnitude.

3.8. Computational Aspects

The slow convergence of the torsional eigenfunctions (136) complicates the quantum mechanical treatment of internal rotors when compared to the treatment of semi-rigid rotors. The solution of the vibrational-torsional-rotational Schrödinger equation always involves a combination of the effective Hamiltonian and the use of the direct method described in Section 3.1.

The vibrational-torsional-rotational Hamiltonian is set up in the basis set

$$\Psi (v; J, k; k_f, \sigma) = |v\rangle |J, k\rangle |k_f, \sigma\rangle,$$  \hspace{1cm} (236)

where $|v\rangle$ represents vibrational basis functions characterizing the overall vibrational state, $|J, k\rangle$ is the rigid rotor wavefunction (60), and $|k_f, \sigma\rangle$ is the free rotor basis function (131). In this case, we assume that the Hybrid Model described earlier is used.

The basis set (236) results in an infinite Hamiltonian matrix. However, in a real spectroscopic case, the quantum number range is limited by the quantum number coverage and the accuracy requirement of the data. Furthermore, the full Hamiltonian matrix can be divided into sub-matrices by introducing the symmetry-adapted basis set given in Eq. (159).

In the torsional problem, the free rotor quantum $k_f$ assumes values $0, \pm 2, \pm 3, .., k_{f,\text{max}}$, thus giving rise to dimension of $2k_{f,\text{max}} + 1$ of the pure torsional matrix. In the case of CH$_3$CF$_3$ of Paper II, the effective barrier height of $s \sim 90$ and the high-accuracy Fourier transform microwave data require $k_{f,\text{max}} = 10$, whereas for methyl silanes CH$_3$SiH$_3$ and CH$_3$SiD$_3$ with $s \sim 40$, $k_{f,\text{max}} = 7$ is sufficient.

In the simplest case, the vibrational and rotational quantum numbers are good quantum labels, and a Hamiltonian matrix can be set up independently for each combination of $v$, $J$, $k$, and $\sigma$ quantum numbers. The diagonal elements originate from operators that exclude terms that are dependent on the torsional angle. Terms having torsional angular dependence i.e., terms with $\cos 3i\gamma$ or $\cos 6i\gamma$ operators containing $(i = 1, 2, ..)$, form off-diagonal bands in the matrix. In this case, the energy levels are obtained by diagonalizing a matrix of dimension of $2k_{f,\text{max}} + 1$ for each combination of $v$, $J$, $k$, and $\sigma$ quantum numbers.
3.8.1. Two-step Procedure

A significant reduction in the computational requirements is achieved by diagonalizing the Hamiltonian matrix in two stages and by using first order perturbation theory. A two-step procedure includes the following steps:

1. Set up a torsional matrix for the torsional Hamiltonian $H_T^v$ (232) for each combination of the $v$, $k$, and $\sigma$ quantum numbers.
2. Obtain torsional eigenvalues $E(v, v_T, k, \sigma)$ and torsional eigenvectors of Eq. (136) by diagonalizing each matrix.
3. Store the torsional eigenvalues $E(v, v_T, k, \sigma)$.
4. Calculate effective torsional operators of type $\langle J^{mT}_\gamma \rangle_{v, v_T, v'_T, k, \sigma}$ and overlap integrals $I_{v,v',v_T,v'_T,k,k',\sigma}$ by using components $A^{mT}_{v k, v'_T, k'}$ of the torsional eigenvectors.
5. Store the effective torsional operators and the overlap integrals.
6. Set up a vibrational-rotational matrix for each $J$ by using the torsional eigenvalues, effective torsional operators and overlap integrals. Include the intervibrational and the interrotational terms in the matrix.
7. Diagonalize the vibrational-rotational matrix, store the eigenvalues, and calculate required transition wavenumbers.

Steps 1 to 5 result in torsional energy levels and eigenvectors similar to those illustrated in Figs. 3-5. The effective torsional operators can be obtained by applying the torsional operators to the torsional eigenvectors $M_{k,v_T,\sigma}(\gamma)$. The overlap integrals account for the rearrangement of the Hamiltonian matrix elements due to the partial diagonalization carried out in Steps 1 to 3. In the rearrangement, a portion of the contribution of the diagonal terms, such as the pure rotational terms, occurs off-diagonal in the $v_T$ quantum number. Furthermore, the overlap integrals account for the modification of the off-diagonal terms characterizing intervibrational and interrotational interactions.

In Step 6, terms with $J$ dependence, such as $H_R^v$, $H_{TR}$ and $H_{VTR}$ given in Eqs. (233), (234) and (235) respectively, and the pure vibrational term $H_V^v$ (231) are included in the matrix. At this stage, the detailed structure of the matrix depends on the intervibrational and interrotational interactions.

In the simplest case, intervibrational and the interrotational interactions are not involved, and Step 6 is simple. Terms off-diagonal in $v_T$ primarily arise from high order torsional centrifugal distortion terms that are small in magnitude, and can be neglected on the basis of the first order perturbation theory. As a result, the rotational-torsional-rotational energy levels can be expressed as a superposition of the torsional energy levels $E(v, v_T, k, \sigma)$ obtained in Step 2, and the polynomial type expression from expectation values of $H_R^v$, $H_{TR}$, $H_{VTR}$.

When intervibrational and interrotational interactions are involved, Step 6 requires an explicit set-up of a matrix. In this thesis, the two-step procedure has been applied in Papers I and II.
In Paper I, the energy level system of CH$_3$SiD$_3$ includes the GS, and the $(v_{12} = 1)$ state having two $\ell$–components. An example of the energy level system in this case is given in Fig. 1 of Paper I. The torsional problem is solved for the GS and the $(v_{12} = 1)$ state separately by using molecular parameters and operators given in Table I of Paper I. In Step 6, the matrix includes torsional stacks with $v_T = 0 - 6$ for each GS, $(v_{12} = 1, \ell_{12} = 1)$ and $(v_{12} = 1, \ell_{12} = -1)$ states, thus resulting in $18 \times 18$ matrix for each $J$.

In Paper II, the energy level system to be treated simultaneously includes rotational $k$ sub-states of the same symmetry, see energy level diagram of Fig. 4 of Paper II. In this case, the torsional Hamiltonian is solved for each $(k, \sigma)$ state in Steps 1 to 5 and overlap integrals given in Eqs. (10) and (11) of Paper II are calculated. In Step 6, the $J$ dependent Hamiltonian and the centrifugal distortion coupling matrix elements are implemented in the matrix. In this case, the diagonalization in Step 6 was eased by truncating the $k$ range even though an exact treatment assumes values of $k$ between 0 and $\pm J$. The energy level to be calculated exactly was located between an appropriate number of bath states that provide perturbations to the energy level to be calculated.

The reduction in the computational effort compared to a full Hamiltonian model is primarily due to two factors. First, the number of matrix diagonalizations is significantly reduced by omitting the $J$ dependent terms from the torsional problem and by treating the $J$ dependent terms in Steps 6 and 7. Second, the preprocessing of the torsional problem in Steps 1 to 5 enables to truncate the Hamiltonian matrix in the free rotor quantum number $k_f$ in an early stage of the calculational procedure. The experimental data is usually confined to the lowest torsional states and thereby, the need to calculate and store torsional energies and eigenvectors for high $v_T$ is not relevant. In a typical case, $v_{T,\text{max}} = 6$ is sufficient. The truncation of the torsional levels at $v_{T,\text{max}}$ reduces significantly the dimension of the matrix set up in Step 6.

### 3.8.2. One-step Procedure

The use of the two-step procedure originates from the early days of the analysis program when the computational resources were not developed. Mathematically, the two-step procedure corresponds to subjecting the Hamiltonian matrix to successive unitary transformations, and thus produces accurate eigenvalues if the first order perturbation theory is not applied and the truncation of the $v_T$ is done correctly.

The use of the perturbation theory in the matrix treatment assumes that the effect of the off-diagonal terms left out is insignificant. However, when there is no a priori information available on the nature of the interaction, it is safer not to use any approximations.

In Paper III, the energy level system of CH$_3$SiH$_3$ includes the GS, the $(v_{12} = 1)$ state and the $(v_5 = 1)$ state. The intervibrational interactions consist of an $xy$– Coriolis-type interaction between the GS and the two $\ell$-components of the $(v_{12} = 1)$ state. Furthermore, the GS and the $(v_5 = 1)$ state are coupled by the Fermi-type interaction mechanism.

In Paper III, the two-step procedures with the first order perturbation approximation was found to be insufficient to reproduce the vibrational-torsional-rotational energies. Therefore, the Hamiltonian matrix was set up with four stacks of 15 free rotor functions, one
stack for the GS, two stacks for the \((v_{12} = 1)\) state, and one stack for the \((v_5 = 1)\) state. One such \(60 \times 60\) matrix was set up and diagonalized for each \(J\).

The two computational procedures have their advantages and drawbacks. Assuming that the first order perturbation is not applied, both procedures provide exact eigenvalues and eigenvectors. The advantages of the two-step procedure are primarily due to computational convenience, while the one-step procedure requires more computational power. From the aspect of the implementation, the implementation of the one-step procedure is straightforward, while the two-step procedure involves algorithms for calculating rather complicated overlap integrals and expectation values of the torsional operators. The programming convenience plays an important role when the Hamiltonian includes plenty of terms that must be tested.

### 3.8.3. Remarks on the Computational Procedure

In a least-squares fitting procedure used in a spectrum analysis, the requirement of great computational power results from the calculation of Hessian matrix with respect to the molecular parameters. However, the Hessian matrix may be obtained from the first derivatives but still, the calculation requires great computational power.

The first derivatives of the energies with respect to the molecular parameters are obtained by first calculating reference energies with the best instantaneous molecular parameters. Then, each molecular parameter is shifted by an appropriate amount in order to produce energy values for a finite difference calculation. The finite difference calculation requires \(N+1\) diagonalizations of each matrix where \(N\) is the number molecular parameters left varying in a fit. A convergent fit usually requires 3 to 5 cycles, where each cycle involves the calculation of the finite differences.

The calculation of the derivatives would be made faster by using a reference eigenvector matrix obtained from the diagonalization of each of the reference Hamiltonian matrices. The reference eigenvector matrix represents a unitary transformation that diagonalizes the reference Hamiltonian matrix, and the reference eigenvector matrix would be used to diagonalize approximatively the matrices constructed with the shifted molecular parameters. As a result, the Hamiltonian matrices with the shifted molecular parameters would be diagonalized by using a matrix multiplication instead of diagonalizing them with a time-consuming iterative process.

The method described above would be easy to apply to the one-step procedure. It could also be applied to Step 7 of the two-step procedure, but the benefit would only be limited to the second step.

Due to the architecture of the fitting procedure, the reference eigenvectors were not used for diagonalizing the Hamiltonian matrices for the shifted molecular parameters, and the Hamiltonian matrices were explicitly diagonalized at every stage of the calculation. However, the fitting program enables to reuse the first derivatives in the successive iteration steps, and the first derivatives are required to be calculated only once at the beginning of the fit. In this case, the most time-consuming step is the first iteration step where the first
derivatives are calculated. This procedure substantially accelerates the fitting procedure and it has been found to produce reliable results.

The computational procedure may further be made more efficient by storing the first derivatives in a file and by reusing the first derivatives in several fits. This method may be applied when the molecular Hamiltonian is well established and the primary aim of the analysis is to test higher order Hamiltonian terms or combination of higher order Hamiltonian terms. This method requires the initial molecular parameters to be the same in the tests.
4 Spectrum Analyses and Case Studies

The purpose of the spectrum analysis is to generate a link between spectroscopic observables of a spectroscopic object and human understanding of the spectroscopic object. The spectroscopic observables are typically measurable quantities, such as transition frequencies and transition intensities. The aim of this section is to discuss specific characteristics of spectrum analyses in an internal rotor case.

4.1. Identification of Spectral Transitions

The purpose of the identification is to associate the spectral transition with correct lower and upper state quantum numbers. The identification process is usually based on a priori knowledge about the selection rules of the transitions and regular structures occurring in the vibrational-torsional-rotational spectra.

The selection rules can be deduced from symmetry consideration by applying fundamental rules described in Section 3.6. In vibrational-torsional-rotational spectra of free molecules, the transition between two states may occur when the overall electric dipole moment is symmetric under all permutations and asymmetric under all permutation inversions of the symmetry group [12]. In practice, the vibrational and rotational selection rules are identical to those of semi-rigid molecules with torsional extension, thus yielding selection rules

\[
\begin{align*}
\Delta v &= 0, 1, 2, 3, \ldots \quad (237) \\
\Delta G &= (\Delta k - \Delta l) = 3n \quad (238) \\
\Delta J &= 0, \pm 1 \quad (239) \\
\Delta v_T &= 0, 2, 4, \ldots \quad (240) \\
\Delta \sigma &= 0 \quad (241)
\end{align*}
\]

where \(n\) is an integer including zero.

The identification of the vibrational bands in methyl silanes and in CH\(_3\)CF\(_3\) is trivial and will no further be discussed in this context. The rotational structure of the lowest lying
fundamental bands in the methyl silanes shows similarities to that of semirigid symmetric
tops, such as methyl cyanide [38] and propyne [39]. The infrared spectra show easily
detectable \((k, \sigma)\) sub-bands with varying \(J\) quantum number. The \((k, \sigma)\) sub-bands may be
found by using a Loomis-Wood computer program allowing a visual inspection of the sub-
bands during an identification process. The \((k, \sigma)\) sub-bands may be fit in a polynomial
model against the \(J\) quantum. The \(k\) and \(J\) identification may verified by using lower state
combination differences of type \(\Delta (J,K,\sigma) = R (J-1,K,\sigma) - P (J+1,K,\sigma)\), which
is a commonly used identification method of infrared bands.

Since the \(\sigma\)–quantum number is preserved in infrared transitions, the intrinsic \(\sigma\)–splittings
when \(\Delta v_6 = 0\) depend primarily on the difference of the torsional barrier height in the
lower state and the upper state of the transition. It should be noted that on the basis of the
studies of the \(\nu_{12}\) bands in Papers I, III, and IV, the order of the components of the \(\sigma\)–
triplets are similar for a fixed \(G (= k - \ell)\) quantum number regardless of the vibrational
state. The torsional splittings in the infrared \(\Delta G = 0\) transitions vanish when the torsional
barrier height in the GS and the excited vibrational state converge with each other. This
phenomenon is associated with the coupling between the vibrational angular momentum
and the torsional angular momentum and is discussed in Section VI of paper IV.

The starting point of finding regularities in the torsional bands by the visual inspection
of the Loomis-Wood graph requires some effort which is based on trial and error. How-
ever, when the regularities are found, the identification process can be continued by using
the ground state combination differences (GSCD), line intensities and predictions from
previous identification steps. Furthermore, spectrum simulations may be used to assist
the identification process. The identification process of \(2v_6\) and \(v_6 - 3v_6\) bands has been
described in detail in Section IV of Paper IV.

4.2. Model Testing

In model testing, the correspondence between the model and experimental data is usually
characterized by a value of a merit function. The error bars of data points are usually
assumed to follow a Gaussian distribution, and thus the merit function has a form

\[
\chi^2 = \sum_{i=1}^{N} w_i (f_{\text{exp},i} - f_{\text{calc},i})^2,
\]  

(242)

where \(f_{\text{exp},i}\) is an \(i\)th experimental data element, \(f_{\text{calc},i}\) is a data point predicted from the
model, and \(w_i\) is the weight factor of the experimental data element \(i\). The experimental
data element is typically a transition frequency or difference between transition frequencies.
In the Gaussian distribution, the weight factor \(w_i\) is inversely proportional to the square of
the given error of the data element \(f_{\text{exp},i}\). The spectrum analysis is primarily aimed at
finding a Hamiltonian and molecular parameters that yield minimum value for the merit
function (242).
4.3. Paper I: The Lowest Fundamental Band of CH$_3$SiD$_3$

The data set in Paper I consists of three major data groups. The first group consists of 7 data points from the MBER measurement [2] in the torsional ground state ($\nu_6 = 0$). The second group consists of 15 pure rotational transitions with ($\Delta J = 1$) in the ($\nu_6 = 0, 1, 2$) torsional states from Ref. [47], and the third group consists of 997 infrared transitions with ($\nu_{12} = 1 \leftrightarrow 0, \Delta \nu_6 = 0$) not published earlier.

The MBER measurements include 3 ($A - B$) crossings and 5 barrier crossings, thus proving strong constraints for the ($A - B$) quantity, the parameter $\rho$, and the barrier height $V_{0,3}$ in the ($\nu_6 = 0$) state. The pure rotational transitions include 2 data for the ($\nu_6 = 0$) state, 2 data for the ($\nu_6 = 1$) state, 5 data for the ($\nu_6 = 2$) and 6 data for the ($\nu_{12} = 1$) state. The pure rotational transitions in the ($\nu_6 = 0$) state provide a constraint for the $J$ dependent rotational terms, such as those with parameters $B_0, D_{0,JK}$ and $D_{0,J}$. Furthermore, the pure rotational terms in the ($\nu_6 = 1, 2$) states are sensitive to torsional-rotational terms, such as those with $D_{0,Jm}, F_{0,3J}$, and $F_{0,3K}$. The detailed form of the Hamiltonian and the values of the molecular parameters are listed in Table 1 of Paper I.

The main features of the $\nu_{12}$ band are similar to those of a semirigid rotor of $C_{3v}$. The dominant structure arises from the P, Q and R branches of a perpendicular band where the separation of successive Q branches is close to 1 cm$^{-1}$. Due to the similar effective barrier heights in the GS and the ($\nu_{12} = 1$) state, the intrinsic torsional splittings in the infrared transitions are of the order of 0.002 cm$^{-1}$. Therefore, they were not resolved with the available resolution of 0.004 cm$^{-1}$. A portion of the $\nu_{12}$ spectrum with no $\sigma-$splittings is shown in Fig. 2 of Paper I. However, the torsional splittings become visible due to the $xy-$Coriolis-type interaction between the ($\nu_{12} = 1, \nu_6 = 0$) state and the ($\nu_{12} = 0, \nu_6 = 3$) state. An example of the $\nu_{12}$ spectrum including $\sigma-$splittings is shown in Fig. 3 of Paper I.

4.3.1. Analysis of the GS/$\nu_{12}$ System

The energy level diagram of the GS/$\nu_{12}$ system is shown in Figure 1 of Paper I. The outermost columns show the two $\ell-$components of the ($\nu_{12} = 1$) state while the three columns in the middle show the three $\sigma-$components of the ($\nu_6 = 3$) state.

The $xy$-Coriolis- type coupling may be characterized by a Hamiltonian term

\[ H_{21}^{xy,\nu_{12}} = B_{s_{0,12}} \left\{ \frac{1}{2} \left[ J_+ q_{12-} + J_- q_{12+} \right] + -2\lambda \sin (3\gamma) \left[ J_+ p_{12-} + J_- p_{12+} \right] \right\} \]

(243)

where $q_{12}$ and $p_{12}$ are the HM representations of the dimensionless normal coordinate and the conjugate momentum, respectively, of the normal mode $\nu_{12}$, and $\lambda$ is a weight factor that determines the magnitude of the term in $\sin 3\gamma$ relative to that in $[p + \rho J_3][6]$. The structure of the first term in operator (243) is similar to that of the centrifugal distortion Hamiltonian given in Eq. (228). The starting point of the derivation of the interaction
term of Eq. (243) was the customary $xy$-Coriolis interaction discussed in Ref. [40] in a semi-rigid symmetric top between two small amplitude modes. In this case, the small amplitude mode with the $A$ symmetry represents the torsion whereas the vibrational mode with the $E$ symmetry represents the $\nu_{12}$ mode. This high barrier approximation is then transformed into a large amplitude model for the torsional mode by a procedure introduced by Hougen [41] and discussed with respect to methyl silane CH$_3$SiH$_3$ in Ref. [6]. The resulting operator (243) yields a coupling mechanism which acts in many respects like the classical $xy$-Coriolis interaction.

The interaction obeys the selection rule $(\Delta G = 0, \Delta \sigma = 0)$. The energy level diagram in Fig. 1 of Paper I shows that the $(k, \sigma)$ structure of the $(v_6 = 3)$ state is virtually randomly scattered, thus introducing a great variation in energy levels with respect to the $\sigma$-levels of the $(v_{12} = 1)$ state. Therefore, the $\sigma$-levels of the $(v_{12} = 1)$ state experience different perturbations which result in a separation of the $\sigma$-levels of the $(v_{12} = 1)$ states, and the observable $\sigma$-splittings in the $v_{12}$ spectrum.

In the transitions spectra, the separation of the $(v_{12} = 1 \leftrightarrow 0)$ transitions into $\sigma$ components increases the number of spectrum lines with unambiguous $\sigma$-identification and whose peak accuracy is restricted by the instrumental resolution rather than a blurred line shape of the unresolved $\sigma$-triplet. Thereby, the $\sigma$-splittings in the $(v_{12} = 1)$ state provide a great deal of information on the torsional characteristics of the molecule.

The frequencies of the $\sigma$-components of the $(v_{12} = 1 \leftrightarrow 0)$ transitions are also contributed by the energies of the $\sigma$-states in the lower state i.e., the $(v_6 = 0)$ state, thus providing a constraint for the leading torsional terms and the rotational and torsional-rotational terms, such as those listed above, through implicit GSCD. Furthermore, the $(v_{12} = 1 \leftrightarrow 0)$ transitions and especially the resolved $\sigma$-components reflect the energies of the $(v_{12} = 0, v_6 = 3)$ dark states due to mixing of the wave-functions of the $(v_{12} = 1)$ states and those of the $(v_6 = 3)$ dark states. The mixing contributes virtually all the molecular parameters in the $(v_6 = 0)$ state, and especially those mostly contributing to the $(v_6 = 3)$ states.

In the $(v_{12} = 1)$ state, the observable $\sigma$-splittings bring the intrinsic splittings available and enable the torsional characterization of the $(v_{12} = 1)$ state. In this case, the effect of the $\sigma$-splittings is limited to the determination of the torsional barrier height $V_{12,3}$ in the $(v_{12} = 1)$ state.

The virtually random and sparse $(k, \sigma)$ structure in the $(v_6 = 3)$ state results in several benefits. The coupling matrix elements of the interaction Hamiltonian (243) is practically constant compared to the difference between the interacting $(G, \sigma)$ levels of the $(v_6 = 3)$ and $(v_{12} = 1)$ states. Therefore, the relative order of the $\sigma$-components in the $(v_{12} = 1 \leftrightarrow 0)$ transitions may be deduced from the relative order of the perturbing $(k, \sigma)$ levels in the $(v_6 = 3)$ state by assuming that the dynamics of the push from the perturber is primarily due to the perturbation denominator. From the same reason, the plurality of interacting level pairs with a varying perturbation denominator prevents the interaction being treated with perturbation theory, but instead requires an explicit introduction and determination of the interaction Hamiltonian (243). The analysis of the GS/$v_{12}$ system in CH$_3$SiD$_3$ indicates that this is the case even when the interaction is not strong and no perturbation-induced transitions occur.
4.3.2. Results and Discussion of the GS/ν12 System of CH₃SiD₃

The molecular parameters obtained from the GS/ν₁₂ analysis are listed in Table 1 of Paper I. The original attempt to determine the second terms $V_{0,6}$ of the expansion of the torsional barrier height through the $xy$–Coriolis-type interaction failed because the crossings between the interacting states did not occur. Still, the data were fitted to within the experimental accuracy with 20 molecular parameters left varying and 2 parameters being fixed. The analysis showed that the $xy$–Coriolis-type interaction mechanisms are similar in CH₃SiH₃ and CH₃SiD₃ and may be characterized with the $xy$–Coriolis-type Hamiltonian earlier tested with CH₃SiH₃ [6].
4.4. Paper II: Ground State Rotational Analysis of CH$_3$CF$_3$

The data set and its characteristics used in Paper II are listed in Table 1 of Paper II. The data set can be divided into three groups according to the transition selection rules. The first group (rows MB2 and MB3 in Table 1) consists of 12 Stark anticrossings with $(K = \pm 2 \leftrightarrow \mp 1)$ for $J-$range 2 to 6 in the torsional ground state ($v_6 = 0$). The Stark anticrossings were measured with the MBER technique by Meerts and Ozier and published in Ref. [3]. These data provide stringent constraints for the leading torsional parameters $V_3$ and $\rho$.

The second group (rows MWFT2 and MWFT3 in Table 1) consists of 234 forbidden $(\Delta K = 3, \Delta J = 0)$ microwave lines measured with a Fourier transform microwave spectrometer in the 8 to 18 GHz region. The $K$ and $J$ quantum numbers range from 3 to 8 and from 27 to 75, respectively. The second group determines axial rotational constants, such as $A$ and $D_K$, and the effective rotational constant $F$, thus enabling the Stark anticrossing to determine the leading torsional parameters more accurately. The second group further includes 16 rotational $A_1/A_2$ splittings in the ($v_6 = 0$) state. The magnitude of the splittings ranges from 1 MHz at $J = 37$ to 69 MHz at $J = 74$. Predictions were made to find $A_1/A_2$ splittings in the ($v_0 = 1$) state, but the population in the ($v_0 = 1$) state is too low for producing doublets that are strong enough, and thus no $A_1/A_2$ splittings were observed in the ($v_0 = 1$) state. The off-diagonal centrifugal distortion terms with $\varepsilon$ and $\varepsilon_J$ are determined by the $A_1/A_2$ splittings.

The third group (MB1 to MMW3) includes conventional microwave, millimeterwave and sub-millimeterwave transitions with selection rules $(\Delta K = 0, \Delta J = 1)$. Altogether 6 lines were obtained from the microwave Fourier transform experiment while the rest of the lines were taken from Refs. [3, 7]. The main part of the third group consists of millimeterwave transitions spanning a frequency range between 196 GHz and 470 GHz corresponding to the $J-$range from 18 to 44. The sub-millimeterwave measurements span a frequency range from 620 GHz to 909 GHz corresponding to $J-$range from 56 to 86. The third group provides a constraint to determine $J-$dependent terms, such as the rigid rotor quartic and sextic centrifugal distortion terms and torsional centrifugal distortion terms $D_{J,M}, F_{3,J}$.

4.4.1. Analysis of the Sextic Splittings

One aspect of Paper II was to investigate the $(\Delta k = 3)$ interaction in a symmetric internal rotor molecule. Furthermore, a particular attention was focused on comparing different representations of the interaction Hamiltonian. It is known [42] that the first term in the centrifugal distortion Hamiltonian given in Eq. (229) is related to a sextic Hamiltonian

$$H_0 = \hbar'_3 [e^{+6i\rho\gamma} J^6_+ + e^{-6i\rho\gamma} J^6_-]$$

by contact transformation. The representation provided by the quartic rotational Hamiltonian given in Eq. (229) is referred to as Reduction B, while the representation provided
by Eq. (244) is referred to as Reduction A. The interaction mechanisms in both reduction schemes are shown in an energy level diagram in Fig. 4 of Paper II.

The two reduction schemes represent two extremes between which the "real" reduction scheme is supposed to be located. Fit characteristics and the most appropriate molecular parameters obtained in Reduction A and B are given in columns Model F2 and Model F1, respectively, in Table 5 of Paper II. The stability of the merit function $\chi^2$ indicates that the data are not sensitive to the reduction scheme.

The $(\Delta k = 3)$ transitions are driven by a distortion dipole moment $\mu_D$ that borrows a contribution from the $z$ component $\mu_z$ of the permanent dipole moment via the $(\Delta k = 3)$ interaction. Thereby, the distortion dipole moment $\mu_D$ may be written in terms of $\mu_z$ and the $(\Delta k = 3)$ interaction parameter $\varepsilon$ according to Eq. (19) of Paper II. The distortion dipole moment $\mu_D$ and the permanent dipole moment $\mu_z$ have been determined experimentally in Ref. [3], thus providing a constraint for the interaction parameter $\varepsilon$. Column Model F4 in Table 5 in Paper II shows the fit characteristics when $\varepsilon$ was fixed to the distortion dipole moment constraint while the sextic Hamiltonian (244) was left varying.

4.4.2. Results and Discussion of the Rotational Analysis of the GS in $\text{CH}_3\text{CF}_3$

Results shown in Table 5 of Paper II fail to indicate the best and the most physically relevant model to characterize the $(\Delta k = 3)$ interaction. However, monitoring the merit function $\chi^2$ as such does not provide a sufficient test to verify the relevance of the different reduction schemes. Sarka [42] has introduced a uniform measure to characterize the effect of the contact transformation between two reduction schemes to the molecular parameters, such as the sextic constants. An explicit expression for the uniform measure is given in Eq. (17) in Paper II. The values of the uniform measure in comparison between different reduction schemes are shown in Table 6 of Paper II. In an ideal case, each element in a column in Table 6 would give a constant value. The deviation of the uniform measure from an average value is of the order of 5% indicating that the contact transformation leads smoothly from one reduction scheme to another, and thereby, any model given in Table 5 may freely be chosen to characterize the $(\Delta k = 3)$ interaction.

The analysis of the entire data set produces 19 molecular parameters in the GS. Especially, the axial constants, such as $A$ and $D_k$, were determined with high accuracy, thus providing a good starting point for analysis of the fundamental bands and the torsional bands. The studies on $\text{CH}_3\text{CF}_3$ have been later continued on the torsional excited states and the lowest-lying fundamental bands in Refs. [43, 44].
4.5. Paper III: Three-Band System of CH$_3$SiH$_3$

Protonated methyl silane CH$_3$SiH$_3$ has become a prototype case possessing perhaps the most extensive high resolution data set of a polar symmetric internal rotor molecule. The data set has been developed over the years both in terms of diversity of transition selection rules and the energy level coverage.

The GS and the ($v_{12} = 1$) state in CH$_3$SiH$_3$ form a GS/$\nu_{12}$ system similar to that in CH$_3$SiD$_3$. In both molecules, the GS and the ($v_{12} = 1$) state are coupled through the $xy$-Coriolis-type Hamiltonian of Eq. (243), and the most dramatic effects take place between the ($v_6 = 3$) and ($v_{12} = 1$) states. However, in CH$_3$SiH$_3$, the interaction shows resonance between the ($v_6 = 3$) and the $-\ell-$ component of the ($v_{12} = 1$) state resulting in perturbation-induced transitions with ($v_6 = 3 \leftrightarrow 0$). The analysis of the two-band system in CH$_3$SiH$_3$ was originally carried out in Ref. [6].

The primary interest in Paper III was to investigate the Fermi-type interaction between the GS and the ($v_5 = 1$) state while the $xy$-Coriolis interaction between the GS and the ($v_{12} = 1$) state is accounted for as to provide correct characterization of the GS energy levels.

4.5.1. Data Set of CH$_3$SiH$_3$

The data set and its characteristics used in Paper III are listed in Table IV of Paper III. The data set can be divided into seven main groups according to the transition selection rules.

The first group (Item 7 in Table IV) includes 15 MBER measurements from Ref. [1]. It includes ($A - B$) crossings and barrier crossings in the ($v_6 = 0$) state, thus providing constraints for the ($A_0 - B_0$) and the leading torsional parameters.

The second group (Items 1 to 3) includes a total of 317 infrared transitions with ($v_6 = 2 \leftrightarrow 0$) from Refs. [?], and 528 infrared transitions with ($v_6 = 3 \leftrightarrow 1$) from Ref. [46]. These infrared transitions determine the torsional energy levels up to the ($v_6 = 3$) state in an absolute energy scale.

The third group (Items 8 to 11) consists of microwave and millimeterwave transitions with ($\Delta J = 1$) in the ($v_6 = 0, 1, 2, 3$) states published in Refs. [47–50]. The microwave and millimeterwave transitions include $\sigma-$splittings and determine the relative positions of the torsional-rotational energy levels in the ($v_6 = 0, 1, 2, 3$) states.

The fourth group (Item 5 in Table IV) consists of 1279 infrared transitions of the lowest-lying $\nu_{12}$ perpendicular fundamental band published in Ref. [6].

The fifth group (Item 12) consists of 34 pure rotational transitions with ($\Delta J = 1$) in the ($v_{12} = 1$) state from Refs. [47,50]. These transitions determine the relative positions of the rotational energy levels in the ($v_{12} = 1$) states. Furthermore, the $A_1$ and $A_2$ components due to $\ell-$doubling are determined.

The sixth group consists of 780 transitions of the lowest-lying parallel $\nu_5$ fundamental band at 700 cm$^{-1}$ region. The $\nu_5$ band was measured with Bomem interferometer at 0.004 cm$^{-1}$ resolution, and later deconvoluted to a line width of 0.0022 cm$^{-1}$.
The infrared measurement in the $\nu_5$ region expands the data coverage to the 800 cm$^{-1}$ region in absolute energy scale, thus extending the spectral observations about 200 cm$^{-1}$ above the torsional barrier $V_{0,3}$ of the GS. Examples of energy level diagrams showing ($\nu_5 = 1$) levels and associated excited torsional energy levels in the GS are illustrated in Figs. 2 and 3 of Paper III.

With reference to Fig. 1 in Paper III, the overall appearance of the $\nu_5$ band is that of a parallel band of a semirigid symmetric rotor with selection rules ($\Delta J = 0, \pm 1, \Delta k = \Delta \sigma = 0$). The main features arise from the strong unresolved Q-branch centered at 703 cm$^{-1}$. The symmetric internal rotor characteristics are demonstrated by the scattered $(k, \sigma)$ structure.

There are two predominant mechanisms that give rise to $\sigma$-splittings in the $\nu_5$ band. First, the difference in the barrier height between the GS and the ($\nu_5 = 1$) state is of the order of 30 cm$^{-1}$, thus giving rise to $\sigma$-splittings of the order of the spectral line width. The second mechanism is due to the Fermi-type interaction resulting in giant torsional splittings that exceed 1.70 cm$^{-1}$ in maximum. Furthermore, 29 perturbation-induced transitions with ($\nu_6 = 5 \leftarrow 0$) forming the seventh data group (Item 5 in Table IV) were detected.

4.5.2. Analysis of the GS/$\nu_{12}/\nu_5$ system

The Fermi-type interaction between the GS and the ($\nu_5 = 1$) state is primarily characterized by the Fermi-type operator given in Eq. (227). The Fermi-type interaction affects the ($\nu_5 = 1$) states through two mechanisms. First, the levels in the ($\nu_6 = 4$) state shown in the left column of the energy level diagram of Fig. 2 of Paper III are systematically lower than the ($\nu_5 = 1$) levels, thus introducing a uniform shift of $\sim 0.75$ cm$^{-1}$ upwards for the levels in ($\nu_5 = 1$). Second, the levels in ($\nu_6 = 5$) are randomly scattered around the levels in the ($\nu_5 = 1$) state. This results in both positive and negative shifts for levels in the ($\nu_5 = 1$) state. The ($K = 1, \sigma = -1$) sub-levels are of special interest. Here, an accidental degeneracy with about 50/50 mixing between the ($\nu_5 = 1$) and ($\nu_6 = 5$) states occurs. This results in the 29 perturbation-induced allowed transitions that differ in the principal torsional quantum number by 5 units i.e., the high torsional overtone ($\nu_6 = 5 \leftarrow 0$) becomes observable.

The seven data groups described above were fit simultaneously to Hamiltonian terms listed in Table I of Paper III by using the one-step procedure described in Section 3.2. The 3316 data were fit within the experimental accuracy by varying a total of 41 parameters, 19 of which belong to the GS, 9 of which belong to the ($\nu_{12} = 1$) state, 5 of which belong to the ($\nu_5 = 1$) state, 4 of which characterize the $xy$-Coriolis-type interaction, and 4 of which characterize the Fermi-type interaction.
4.5.3. Results and Discussion of the GS/$\nu_{12}/\nu_5$ System

The molecular parameters are compared to those obtained from the GS/$\nu_{12}$ analysis published in Ref. [6]. The comparison shows that the leading torsional terms, such as $V_{0,6}$, $V_{0,9}$, and $F_m$, in the two-band analysis are due to an implicit contact transformation rather than an indication of a fundamental cause, such as the molecular charge and mass distribution, of the torsional parameters. This assumption has been tested numerically in Table II of Paper III.

The energy level diagram in Fig. 3 of Paper III illustrates the physical implication of the Fermi-type interaction. The left column shows the torsional potential $V_{0,3}$ in the GS and the energy levels of the $(K = 1, \sigma = -1)$ sub-state in the $(\nu_6 = 4)$ and $(\nu_6 = 5)$ torsional states. Furthermore, the left column shows the probability density curve for the $(\nu_5 = 5, K = 1, \sigma = -1)$ state in the unperturbed case (dashed line) and when the perturbation is turned on (solid line).

The right-hand column shows the torsional potential $V_{5,3}$ in the $(\nu_5 = 1)$ state and the energy level and probability density curves in unperturbed case (dashed line) and in the perturbed case (solid line) in the $(\nu_5 = 1, K = 1, \sigma = -1)$ state.

The Fermi-type mixing has dramatic effects to the wave-function in the $(\nu_5 = 1, K = 1, \sigma = -1)$ state. The unperturbed wave-function follows the sharp Gaussian curve indicating that the probability to find the torsional oscillator inside the torsional barrier vanishes. However, mixing of the wave-functions results in uniform shift of the baseline of the probability density so that the probability to find the torsional oscillator is greater than 10% inside the torsional barrier.

4.6. Paper IV: Torsional Analysis in CH$_3$SiD$_3$

The pure torsional spectra have been observed with high resolution only for few internal symmetric rotors. FTIR spectroscopy has been applied to ethane with an intermediate resolution of 0.015 cm$^{-1}$ [51–53, 56] and with a high resolution of 0.0016 cm$^{-1}$, see Ref. [55]. In protonated methyl silane CH$_3$SiH$_3$, the first torsional overtone $(\nu_6 = 2 \leftarrow 0)$ [58] and its first hot band $(\nu_6 = 3 \leftarrow 1)$ [46] were recorded at resolution of 0.015 cm$^{-1}$ by using FTIR spectroscopy. The torsional overtone $(\nu_6 = 2 \leftarrow 0)$ in CH$_3$SiH$_3$ has also been recorded with a diode laser with 0.0015 cm$^{-1}$ resolution [45].

The GS/$\nu_{12}$ study in Paper I indicates that a full characterization of the torsional Hamiltonian in CH$_3$SiD$_3$ requires direct observations of the excited torsional states and thereby, a project for recording torsional spectra with high resolution was started in 1997. Furthermore, the infrared transitions in the $\nu_{12}$ band in Paper I were recorded with a resolution that could be improved by a factor of three by using advanced FTIR spectrometers.

In Paper IV, the torsional spectra between 230 and 350 cm$^{-1}$ were recorded with a resolution of 0.002 cm$^{-1}$, thus providing a larger quantum number range and improvement of one order of magnitude in the accuracy of the line positions. The torsional spectra were recorded using a synchrotron radiation source coupled to a Bruker high resolution FTIR spectrometer.
4.6.1. Data Set of CH$_2$SiD$_3$

The data set in Paper IV consists of four groups. The data set and its characteristics are given in Table 3 of Paper IV.

The first group (Item 4 in Table 3) consists of the 8 MBER measurements analyzed in Paper I. The second group (Item 3 in Table 3) includes 3263 transitions with ($v'_{12} = 1 \leftrightarrow 0$) replacing the 997 transitions presented in Paper I. In the meantime, the $J$ and the $K$ maximum quantum numbers occurring in the data set increase from 30 to 40 and from 14 to 22, respectively. The third group (Item 1 in Table 3) and the fourth group (Item 2 in Table 3) consist of 783 transitions with ($v_0 = 2 \leftrightarrow 0$) and 630 transitions with ($v_0 = 3 \leftrightarrow 1$), respectively. The experimental conditions of measurements are given in Table 2 of Paper IV.

The torsional bands ($v_0 = 2 \leftrightarrow 0$) and ($v_0 = 3 \leftrightarrow 1$) obey rotational-torsional selection rules ($\Delta J = 0, \pm 1$, $\Delta k = 0, \Delta \sigma = 0$). In the ($v_0 = 2 \leftrightarrow 0$) band, the torsional characteristics arise from the torsional splittings of order of $\sim$ 4 cm$^{-1}$. In the identification, the relative positions of the ($K, \sigma$) sub-bands were predicted with parameters determined by the MBER data [2]. After the positive identification of the strongest ($K, \sigma$) sub-bands, preliminary fits were run and other ($K, \sigma$) sub-bands were predicted.

The energy level diagram in Fig. 3 in Paper IV shows torsional splittings of the order of $\sim$ 25 cm$^{-1}$ in the ($v_0 = 3$) states. As the torsional splittings in the ($v_0 = 1$) state are of the order of 0.25 cm$^{-1}$, the torsional characteristics of the ($v_0 = 3 \leftrightarrow 1$) band are virtually determined by the splittings in the upper state of the transition. The molecular parameters obtained from the preliminary analysis of the ($v_0 = 2 \leftrightarrow 0$) band predict the ($v_0 = 3 \leftrightarrow 1$) transitions about 0.15 cm$^{-1}$ low from their observed position, and they could not be used in the assignment. However, the $\sigma-$splittings in the GSCDs in the ($v_0 = 1$) state are of the order of $2 \times 10^{-4}$ enabling to identify the ($k, \sigma$) sub-bands by using the lower state GSCDs in the ($v_0 = 1$) state.

4.6.2. Analysis of the Torsional Bands in CH$_2$SiD$_3$

The energy level diagrams in Fig. 1 in Paper I and Fig. 3 in Paper IV show the relative positions of the interacting levels coupled by the $xy-$Coriolis-type interaction. The energy separation between the ($v_0 = 3$) and ($v_{12} = 1, l_{12} = -1$) states varies from 16 cm$^{-1}$ to 66 cm$^{-1}$ and the $xy$-Coriolis-type interaction may be absorbed to effective constants if sub-bands with $\Delta K = -1$ are only included in the data set. In the $\Delta K = +1$ sub-band, the energy denominator between the ($v_0 = 3$) and ($v_{12} = 1, l_{12} = +1$) states varies from zero to 49 cm$^{-1}$, and the strength of the interaction is highly dependent on the $G$ and $\sigma$ quantum numbers. The ($v_0 = 3$) levels with $0 \leq G \leq 15$ are systematically higher than their counterparts in the ($v_{12} = 1, l_{12} = +1$) state. At ($G = 15 - 18, \sigma = -1$) and ($G = 19, \sigma = 0$) the energy separation is only $\sim$ 1 cm$^{-1}$ and the difference in the $J$ dependence of the diagonal Hamiltonian of the ($v_0 = 3$) and ($v_{12} = 1$) states brings the two states into degeneracy. Crossings occur at ($G = 15, \sigma = -1, J = 36$), ($G = 18, \sigma = -1, J = 19$), and ($G = 19, \sigma = 0, J = 24$), but the perturbation allowed transitions with ($v_0 = 3 \leftrightarrow 0$) were
only observed for \((G = 19, \sigma = 0)\). Although the forbidden transitions were identified, they were excluded from the data set due to blending either with \(\nu_{12}\) band transitions or the associated hot band \(\nu_{12} + \nu_6 - \nu_6\). However, the allowed transitions through the crossings were identified and analyzed for \((G = 18, \sigma = -1)\) and \((G = 19, \sigma = 0)\). The crossings provide valuable information on the states of high \(K\) since the maximum \(K\) in the \((\nu_6 = 3 \leftarrow 1)\) band is only 12.

The direct information on the torsional states \((\nu_6 = 2, 3)\), the improved accuracy and the expanded quantum number range in the \(\nu_{12}\) band, and the near degeneracy in the high \(k\) states change the nature of the analysis from that carried out in Paper I. The model used in Paper I was adequate to reproduce the data within the quantum number range \(0 \leq k \leq 8\). However, for sub-bands with \(k > 8\), the calculated transitions in the \(\Delta K = +1\) sub-bands deviate by several error bars from the measured values indicating that the \(xy\)-Coriolis-type Hamiltonian must be reconsidered.

Two models were tested to characterize the \(xy\)-Coriolis-type interaction. The \textit{High Barrier Model} is based on the interaction Hamiltonian of Eq. (243) originating from the small amplitude characterization of the torsional motion discussed above. The \textit{High Barrier Model} has proved to be accurate to characterize the \(xy\)-Coriolis-type interactions between the lowest perpendicular vibration and the GS in ethanes, see Refs. [54, 55].

In \textit{Low Barrier Model}, the \(xy\)-Coriolis-type interaction Hamiltonian is obtained by a formal treatment of the torsion as a fourth rotational degree of freedom. This treatment is systematically followed in this thesis. In this case, the \(xy\)-Coriolis-type interaction Hamiltonian arises from the centrifugal distortion Hamiltonian \(H_{12}\). The leading term is given in Eq. (228). See also Eqs. (1) and (2) in Paper IV for comparison.

The interaction Hamiltonians in the two models are similar: the difference in the leading terms \(H_{12}^{xy,\nu_{12}}\) and \(H_{12}^{xy,\nu_{12}}\) arises from the factor \(-2\lambda_\zeta \sin(3\alpha)\) in \(H_{21}^{xy,\nu_{12}}\). The higher order corrections with \(M_{12a,1}^{xy}\) and \(N_{12a,1}^{xy}\) parameters can be obtained in both models. The term with \(M_{12a,1}^{xy}\) is characteristic to the \textit{Low Barrier Model} only.

In total, 4684 transitions were fit to within the experimental error. The two interaction Hamiltonians give almost identical results in terms of the merit function \(\chi^2\). The best model can be obtained with 36 [36] terms, 20 [20] of which characterize the GS, 12 [11] the \(\nu_{12} = 1\) state, and 4 [5] the \(xy\)-Coriolis-type interaction. The numbers quoted are from the \textit{High Barrier Model}, and those in the square brackets from the \textit{Low Barrier Model}.

### 4.6.3. Results and Discussion of the Torsional Analysis of CH$_3$SiD$_3$

The molecular parameters obtained in the two models are given in Table 1 of Paper IV. The leading torsional parameters \(V_{0,3}, V_{0,6}, V_{0,8}, F_m,\) and \(\rho\) in the GS, as well as the leading terms \(\nu_{12}\) and \(V_{12,3}\) in the \((\nu_{12} = 1)\) state were determined with high accuracy.

A comparison of the \textit{High Barrier Model} and the \textit{Low Barrier Model} shows that the differences in the leading diagonal molecular parameters such as those that characterize the torsional potential are of the same magnitude as their statistical errors. The leading \(xy\)-Coriolis-type interaction terms are \((B\zeta_{6,12a}^{xy}) = 374.61\) MHz and \(M_{12a}^{xy} = 1859.4\) MHz.
The higher order terms $Q_{6,12a}^{yz}$ and $M_{6,12a}^{xy,3}$ and are almost identical in the two models, while the term with $M_{6,12a}^{xy,3}$ is required in the Low Barrier Model. The large difference in the leading interaction terms suggests that the contact transformation relation between the leading interactions terms and the GS terms is realized, and the modifications in the interaction terms can partially be absorbed by the effective diagonal Hamiltonian in the GS and in the $(v_{12} = 1)$ state. The difference in the GS and $(v_{12} = 1)$ parameters between the two models supports this conclusion; the $B_0$ and $\Delta B_{12}$ parameters are changed by $\sim 1$ MHz and $\sim 4$ MHz, respectively. In the quartic Hamiltonian, the term with $D_{0,3}^{xy}$ can be replaced by terms with $F_{0,3}^{xy}$ when the Low Barrier Model is applied. Furthermore, the $\ell-$doubling constant changes from $\sim 22$ MHz to $\sim 18$ MHz.

The data set and the parametrization similar to those in Paper IV were applied in the recent two-band analysis of the protonated methyl silane [50]. This allows one to make an analysis of the changes that occur in the molecular parameters when the silyl frame is deuterated. The parameters of CH$_3$SiH$_3$ are given in the column furthest to the right in Table I of Paper III.

In the lowest order, the inertial moment of the methyl top $I_{CH_3}$ is insensitive to the deuteration of the silyl frame, and a theoretical relation $I_{SiD_3} \equiv 2I_{SiH_3}$ for the silyl frame is valid. When using experimental values of $\rho$ parameter from Paper IV and from Ref. [50], we obtain an experimental relation $I_{SiD_3} = 1.9931I_{SiH_3}$ which is close to the theoretical value. The correspondence between the theoretical and the experimental values indicates that the zero-point axial geometry of methyl silane is not sensitive to the isotopic substitution, and the changes that occur in the torsional energy structure primarily arise from the heavier silyl frame in the deuterated species and the difference in the torsional barrier height rather than deformation of the molecule. Furthermore, the $xy$-Coriolis-type interaction term 374.61 MHz in CH$_3$SiD$_3$ agrees with $(B_{6,12a}^{C}) = 432.20$ MHz in CH$_3$SiH$_3$.

The first two barrier height terms $V_{0,3}$ and $V_{0,6}$ in CH$_3$SiD$_3$ and CH$_3$SiH$_3$ are 583.9 cm$^{-1}$ and 2.8 cm$^{-1}$ and 591.4 cm$^{-1}$ and 2.9 cm$^{-1}$, respectively. The difference of $\sim 7.5$ cm$^{-1}$ in $V_{0,3}$ between the two isotopomers is too large to arise entirely from the zero-point vibrational effects. The two lowest-lying parallel harmonic wavenumbers $\nu_5$ and $\nu_4$ in CH$_3$SiH$_3$ are $\sim 702$ cm$^{-1}$ and $\sim 943$ cm$^{-1}$. In CH$_3$SiD$_3$, the corresponding wavenumbers are 653 cm$^{-1}$ and 741 cm$^{-1}$, respectively [57]. The difference in $V_{0,3}$ may be assumed to arise from different Fermi-like mechanisms in the two cases.

The torsional potential in the $(v_{12} = 1)$ state is larger by $\sim 46$ cm$^{-1}$ than that in the GS. As the $\nu_{12}$ vibration is essentially a silyl rocking, the difference in the torsional potential suggests that the C-Si-D-bond angle reduces in the $(v_{12} = 1)$ state from that in the GS, thus resulting in an increased overlap between the electron distribution of the silyl frame and the methyl top.
5 Discussion and Future Prospects

The torsional degree of freedom complicates the vibrational-rotational energy level structure in many respects. First, the low fundamental frequency of the torsion results in a dense stack of overtone torsional levels in each vibrational state. Second, the torsional sub-states split each rotational state split into a triplet, where the separation of the triplet components may vary from the megahertz magnitude to the wavenumber magnitude. As a result, the torsional degree of freedom causes a great density of states with a high probability of accidental degeneracy or near-degeneracy.

The Fermi-type and \( xy^{-} \) Coriolis-type interactions examined in this thesis represent perhaps the simplest cases of torsion-mediated coupling mechanisms. In both cases, the leading interaction terms are due to the lowest order centrifugal distortion terms \( H_{12} \) that couples an excited vibrational state with the vibrational ground state. The interacting states may differ by several torsional quanta \( v_6 \). However, the shifts in the energy levels from their unperturbed positions may reach the wavenumber magnitude. This leads to a prediction that the Fermi-type and \( xy^{-} \) Coriolis-type interactions may have significant effects on the energy spectrum even with \( \Delta v_6 \sim 7 \) or even with \( \Delta v_6 \sim 10 \).

Hamiltonian terms in Tables 5 and 6 generate a great variety of higher order torsion-mediated interaction terms, such as \( H_{21} \) and \( H_{22} \). These terms couple two small amplitude vibrations via a torsional mechanism. It is assumed that their implications are similar to those of the Fermi-type and \( xy^{-} \) Coriolis-type interactions, but in somewhat reduced scale due to higher order expansion of molecular parameters occurring in those terms.

The large number of candidate coupling mechanisms and the high probability of degeneracy of the vibrational-torsional-rotational states produce a complex molecular system where the identification of the states with quantum numbers becomes difficult. In this situation, the existing methods for spectrum analysis will be found insufficient.

The coupling between the torsional and vibrational angular momenta raises interesting and fundamental questions. This phenomenon has previously been discussed in several contexts [6, 59] and characterized by term \( 2 (A_{12}^{m}) \bar{J}_y \ell_{12} \), see Example 1 and Papers I, III and IV for further details. The coupling term is strongly correlated with the band origin, and therefore, it is difficult to determine it experimentally.

In Papers I and III, the \( A_{12}^{m} \) constant was the constrained at the value \( A_{12, \rho} = A_{12}/(1 - \rho) \) on the basis of an earlier experience from Ref. [6]. The relevance of the constraint was
tested by running a series of fits while scanning the value of $A_{12}^\zeta$ over an appropriate range. In Paper IV, the $A_{12}^\zeta$ constant was determined to an accuracy of 1% and is about 86\% of $A_{12,F}$.

The $A_{12,F}$ constraint leads to two equivalent Hamiltonians

$$F_{12}J_2^2 + 2(A\zeta)_{12}^m J_2 \ell_{12} \Leftrightarrow F_{12}J_2^2 + \rho^2 F_{12}.$$ (245)

The left-hand side and right-hand side Hamiltonians yield the same torsional energy when applied to basis functions $|k,k_f,\sigma\rangle$ and $|G = k - l_{12}, k_f, \sigma\rangle$, respectively. The equivalence between the two basis functions $|k,k_f,\sigma\rangle$ and $|G, k_f, \sigma\rangle$ is similar to that between the PAM and IAM basis functions (131) and (132). When transforming the molecular representation from the PAM to the IAM, the coupling between the torsion and the $z-$component of the overall rotation is removed in the zeroth order by introducing factor $-\rho K$ in the PAM wave-function. In this case, the factor $-\rho K$ of the IAM representation is further replaced by $-\rho G$. In terms of the wave-function (73) of the two-dimensional oscillator, the transformation corresponds to transferring factor $e^{il\varphi}$ from the wave-function (73) to the torsional basis function (132).

A question arises whether the constraint has a real physical explanation, or is it solely an accidental phenomenon specific to methyl silane. This question requires a detailed consideration of the explicit form of $\zeta_m$ constants given in Table 2, analysis of spectra with variety in vibrational angular quanta $l$ with variety of molecules, and possibly, force field calculations.

This thesis shows the important role of the IR spectroscopy in the studies of internal rotation. In skilled hands, a commercial FTIR spectrometer is an efficient and accurate tool for providing direct observations between a great variety of vibrational-torsional-rotational states. Although the line position accuracy achieved with IR spectroscopy cannot compete with the accuracy obtained with rotational spectroscopy, the wide energy level coverage and the extensive number of observations with IR spectroscopy increase the effective accuracy of the measurement. This is especially important when the torsion-mediated interactions are characterized. One drawback of the IR measurements is the insensitivity to the axial rotational constants, such as $A_0$ and $D_0$. However, there are specific methods, such as the use of hot bands and perturbation allowed transitions that enable a direct or indirect determination of the axial rotational constants.

The great number of diagonal and interaction terms in the vibrational-torsional-rotational Hamiltonian leads to a situation where the molecular parameters obtained from the analysis include a contribution from a plurality of physical mechanisms, thus complicating their physical interpretation. Thereby, a great variation in the selection rules and high data accuracy are required. These can be obtained by combining data recorded with different experimental techniques. Paper III and Ref. [60] are good examples in this respect.

The future prospects for studies of internal rotation in symmetric tops are numerous. In terms of experiments, more data should be collected in terms of accuracy, selection rules and energy coverage. In terms of theoretical tools, ab initio approach could be taken to generate information on the molecular potential energy surfaces in order to provide internal molecular parameters, such as those occurring in the interaction terms, and to predict spectroscopic parameters and to aid their physical interpretation.
References

42. Sarka K (1989) Reduced Sextic Rotational Hamiltonian for C$_3$v Molecules that are Quasi-Spherical Tops (AsH$_3$, PH$_3$, OPF$_3$). J Mol Spectrosc 133: 461-466.
50. Moazzen-Ahmadi N, Ozier I, McRae GA, & and Cohen EA (1996) Millimeter-Wave Spectra of CH$_3$SiH$_3$ in the Two Interacting Torsional States ($v_{12} = 0, v_6 = 3$) and ($v_{12} = 1, v_6 = 0$). J Mol. Spectrosc 175: 54-61.
60. Ozier I, Bauder A, Meerts WL, Moazzen-Ahmadi N & Schroederus J (2004) Microwave and Sub-Mmwave Study of CH$_3$SiH$_3$ including the Perturbation-Allowed Torsion-Vibration Difference Band ($v_{12} = 0, v_6 = 3$) $\rightarrow$ ($v_{12} = 1, v_6 = 0$). J Mol Spectrosc accepted for publication, available online.