A statistical analysis of the rotational structure of the benzyl radical

THESIS

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By

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Abstract

In this work the $6a_0^1$ band of the $\tilde{A} \, ^2A_2 \leftrightarrow \tilde{X} \, ^2B_2$ electronic spectrum of the benzyl radical was analyzed and the rotational constants for both the ground and excited states were accurately determined. This was accomplished by using the rigid rotor asymmetric top Hamiltonian model and minimizing the Chi-squared quantity using the Levenberg-Marquardt nonlinear least squares algorithm. The model fits the experimental data well and there are no systematic errors. Moreover, joint confidence intervals accounting for the correlation between the parameters were accurately determined for each of the parameters using the support plane procedure. This led to a significant increase in the errors reported in earlier work. Finally, error propagation was carried out for ground state combination differences which led to good agreement with the observed combination differences to within experimental error.
Dedication

This document is dedicated to my family.
Acknowledgments

I would like to acknowledge my advisor Dr. Terry Miller for his support and insight. Additionally, I would like to thank Dr. Sherwin Singer for his help and his useful comments. I would also like to thank my friends and family for their unwavering support during this work. Finally, I would like to thank The Ohio State University for allowing me to have this great experience.
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Chapter 1: Introduction

The benzyl radical is a prototype of a class of aromatic molecules known as the odd alternant hydrocarbons and has been the subject of various experimental and theoretical investigations [1-5]. A better accuracy is required for the rotational constants and ultimately the rotational energy levels to enable an accurate prediction of rotational levels within one electronic energy band. The goal of this study is to achieve better accuracy on the rotational constants and energy levels derived previously [6] from the electronic structure and to take the correlation between parameters into account when determining the confidence intervals. This information will be used to predict ground state combination differences which will aid in the analysis of rotationally resolved spectra of the vibrational transitions within the electronic ground state of benzyl which recently observed in the Nesbitt group [7].
The benzyl radical which is shown below in figure 1 had its spectrum first reported by Schuler et al. [8]. Porter et al. observed absorption at the 450 nm band [9] and 305 nm band [10] using the flash photolysis technique. Leach and coworkers studied the excited state symmetry of the 450 nm band via rotational contour analysis of room temperature spectra. Laser-induced fluorescence (LIF) spectra were pioneered by Zare and coworkers [11] and then further studied by Thrush et al. [12]. Miller’s group was the first to report a LIF spectrum in a supersonic jet [3, 13].

Figure 1. The benzyl radical with the molecule-fixed axis system. Carbon atoms are numerically labeled and Greek letters are given to hydrogen atoms. Both (a,b,c), the symmetry-based coordinate system, and (x,y,z), the inertial coordinate system, are shown. Here a coincides with z, b corresponds to x and c corresponds to y.
Experiments in this area have included Eiden’s “zero kinetic energy” photoelectron experiment [14], and an LIF spectral study of excited states [15]. Theoretical investigations have included a number of ab initio studies and attempts to explain the electronic structure for benzyl [16-18]. Some investigators also focused on vibronic coupling in the molecule in their calculations [19, 20].

The benzyl radical possesses planar $C_{2v}$ symmetry and a simple depiction of the molecular orbital (MO) energy level scheme of benzyl has been obtained[16]. From simple Hückel $\pi$-electron theory only the seven $p$-atomic orbitals (AOs) from the carbons should be considered and as a consequence, these give rise to seven MOs. Pairs of bonding and antibonding $\pi$ MOs energies are expressed in units of the overlap integral $\beta$ (which is a semi-empirical quantity). The dominant electron configuration of the ground electronic $\bar{X}^2B_2$ is:

$$(1b_2)^2 (2b_2)^2 (1a_2)^2 (3b_2)^1 (2a_2)^0 (4b_2)^0 (5b_2)^0 2B_2$$

This is shown in the figure below. For excited electronic states there are two iso-energetic ways of promoting an electron involving $a_2$ MOs resulting in two electron configurations of $A_2$ symmetry and these are paths a and b in figure 1. There are also two iso-energetic one-electron promotions (paths c and d in figure 1) involving $b_2$ MOs. These give rise to two electron configurations of $B_2$ symmetry. Hence, and in his one-electron approximation, the lowest excited electronic states would be a degenerate pair of $^2A_2$ states with another degenerate pair of $^2B_2$ states only slightly higher in energy. In configuration interaction (CI), the two degenerate pairs of zeroth order electronic states of the same symmetry repel strongly splitting the initially degenerate pairs. In case of the
$^2B_2$ states the lower frequency state ($\tilde{B}^2B_2$) is the antisymmetric linear combination of mixed state and carries a small oscillator strength due to the cancellation of transition moments calculated from the single configurations [21]. For the same reason, the lower of the $^2A_2$ states ($\tilde{A}^2A_2$) lies in the same region and has a low oscillator strength.

Figure 2. Hückel molecular orbital energy level scheme of benzyl radical. The energies of the Hückel molecular orbitals are given in units of the resonance integral $\beta$. 
Figure 2 shows a LIF excitation spectrum of the visible 450 nm system of benzyl in a supersonic jet. This band arises from transitions between the ground $\tilde{X}^2B_2$ and the lower energy pair of the nearly degenerate $\tilde{A}^2A_2$ and $\tilde{B}^2B_2$ states which interact via the vibrational modes of $b_1$ symmetry\[22, 23].

Figure 3. Low resolution LIF excitation spectrum of the 450 nm band system of benzyl radical

The analysis of the spectrum led to the assignment of three strong bands traditionally labeled as $A^1$, $A^2$ and $A^3$ corresponding to transitions between $\tilde{X}^2B_2$ and three vibronic levels resulting from interactions between the vibrationless level of the $\tilde{B}^2B_2$ state and $\nu = 1$ levels of modes 6b and 18b (both of $b_1$ vibrational symmetry) of the $\tilde{A}^2A_2$ state.
The vibronic transitions $A^1$, $A^2$ and $A^3$ are all $a$-type transitions. The analysis enabled the investigators to place the $\tilde{B}^2B_2$ state $\approx 450$ cm$^{-1}$ above the $\tilde{A}^2A_2$ state. This is summarized in figure 3.
Figure 4. Zero-order levels contributing to observed vibronic levels of benzyl radical. The arrows represent vibronic transitions[5, 14, 20, 22, 24]
From figure 2, the weak feature at 22000 cm\(^{-1}\) in the LIF spectrum corresponds to the origin of the \(\tilde{A}^2A_2 \leftrightarrow \tilde{X}^2B_2\) electronic transition which is a b-type transition and the vibronic transition at 434 cm\(^{-1}\) with respect to the origin has been assigned to the \(6a_0^1\) band of the \(\tilde{A}^2A_2 \leftrightarrow \tilde{X}^2B_2\) electronic transition. The last transition involves the \(\nu = 1\) level of the \(6a\) vibrational mode (\(a_1\) symmetry) of the \(\tilde{A}^2A_2\) state but this is relatively unperturbed because it cannot be mixed vibronically with the \(\nu = 0\) level of the \(\tilde{B}^2B_2\).

The rotational structure of the 450 nm spectrum was examined by Cossart-Magos \([5, 24]\) via rotational contour analyses of emission and absorption spectra of benzyl at room temperature. Selco and coworkers \([25]\) studied the emission spectrum of benzyl in a supersonic jet using Fourier transform spectroscopy. Fukushima et al. \([15]\) studied rotationally resolved LIF spectra of benzyl in a supersonic jet \((T_{rot} = 1 K)\). Miller’s group also reported a study of the LIF excitation spectra of the \(A'\) and \(6a_0^1\) baof the jet-cooled benzyl radical in the 450 nm region\([26]\). In that study, the authors fit the spectra using the rigid rotor Hamiltonian and obtained good rotational constants for benzyl. The experimental details for how the spectrum was recorded are contained in Lin’s dissertation \([6]\) and included in appendix A for easy reference.
Consider two reference frames for describing \( n \) particles of a rigid body, a coordinate frame located in the laboratory (space-fixed frame) and a coordinate frame located at the center of mass of the rigid body. The position vectors \( \mathbf{r}_i \) and \( \mathbf{r}_i \) to the \( i \)th particle (with mass \( m_i \)) originate from the center of mass and the laboratory origin:

\[
\mathbf{r}_i = \mathbf{R} + \mathbf{r}_i
\]

The angular momentum of the \( i \)th particle about the origin of the lab-fixed coordinate system is:

\[
\mathbf{J} = \sum_i \mathbf{r}_i \times \mathbf{p}_i = \mathbf{R} \times \mathbf{MV} + \mathbf{J}
\]

where \( \mathbf{p}_i = m_i \mathbf{v}_i \) and \( \mathbf{v}_i = \mathbf{V} + \mathbf{v}_i \) and \( \mathbf{V} \) is the velocity of the center of mass origin with respect to the lab-fixed reference system. If we choose a coordinate system with the origin at the center of mass, then:

\[
\mathbf{J} = \mathbf{J} = \sum_i m_i (\mathbf{r}_i \times \mathbf{v}_i)
\]

Since all the particles have the same angular velocity \( \mathbf{\omega} \) about an instantaneous axis of rotation passing through the center of mass for a rigid body, then we may write:

\[
\mathbf{v}_i = \mathbf{\omega} \times \mathbf{r}_i
\]
Hence we arrive at:

\[
J = \sum_i m_i [\omega r_i^2 - \mathbf{r}_i(\mathbf{r}_i, \omega)]
\]  

(4)

The k-th Cartesian component is given by:

\[
J_k = \left[ \sum_i m_i(r_i^2 - r_{ik}^2) \right] \omega_k - \left[ \sum_i m_i r_{ik} r_{iq} \right] \omega_q - \left[ \sum_i m_i r_{ik} r_{is} \right] \omega_s
\]  

(5)

Here, k,q,r take on values x,y,z

In matrix notation this expression may be recast as:

\[
J = I \omega
\]  

(6)

\( I \) is the moment of inertia tensor (a second rank tensor) whose elements are:

\[
I_{jj} = \sum_i m_i (r_i^2 - r_{jj}^2)
\]  

(7)

\[
I_{jk} = I_{kj} = -\sum_i m_i r_{ij} r_{ik}
\]  

(8)

The diagonal elements \( I_{jj} \) are known as the moments of inertia and the off-diagonal elements are the products of inertia. The moment of inertia tensor is symmetric and has real elements and is therefore self-adjoint or Hermitian. Consequently, there exists a particular transformation of coordinates which would diagonalize the moment of inertia tensor. The diagonal elements of the diagonalized matrix (the eigenvalues), are known as the principal moments of inertia and the axis system is termed the principal axis system.

The three principal moments of inertia are designated as \( I_{aa}, I_{bb}, \) and \( I_{cc} \) which are the eigenvalues of the moment of inertia matrix. By convention, \( I_{aa} \) is the smallest moment while \( I_{cc} \) is the largest:

\[
I_{aa} \leq I_{bb} \leq I_{cc}
\]
The components of the angular momentum $\mathbf{J}$ along the principal axes are:

$$J_a = I_{aa}\omega_a \quad ; \quad J_b = I_{bb}\omega_b \quad ; \quad J_c = I_{cc}\omega_c$$ (9)

Molecules and rigid rotors are classified in terms of their three principal moments as linear ($I_{aa} > I_{bb} = I_{cc}$), prolate symmetric top ($I_{aa} < I_{bb} = I_{cc}$), oblate symmetric top ($I_{aa} = I_{bb} < I_{cc}$), spherical top ($I_{aa} = I_{bb} = I_{cc}$), and asymmetric top ($I_{aa} \leq I_{bb} \leq I_{cc}$).

In the center of mass reference frame, the rotational kinetic energy is:

$$T = \frac{1}{2} \sum_i m_i v_i^2 = \frac{1}{2} \mathbf{\omega} \cdot \mathbf{J}$$ (10)

In the principal-axis system, this may be written as:

$$T = A J_a^2 + B J_b^2 + C J_c^2$$ (11)

where $A$, $B$, and $C$ are rotational constants which are in units of Hertz:

$$A = \frac{\hbar}{4\pi I_{aa}} \quad ; \quad B = \frac{\hbar}{4\pi I_{bb}} \quad ; \quad C = \frac{\hbar}{4\pi I_{bb}}$$ (12)

The benzyl radical has three unequal moments of inertia and is thus considered to be an asymmetric top molecule.

*Wave functions of the rigid body rotational Hamiltonian*

If $\Psi_{JM}(\phi, \theta, \chi)$ is an eigenfunction of the rigid body rotational Hamiltonian with the eigenvalue $E_{JM}$, then if we apply a rotation $R_1(\phi_1, \theta_1, \chi_1)$ to the system then the eigenfunctions are transformed as:

$$R_1 \Psi_{JM}(\phi, \theta, \chi) = \sum_M D^J_{JM}(\phi_1, \theta_1, \chi_1)\Psi_{JM}(\phi, \theta, \chi)$$
This equation may also be recast as:

$$\Psi_{JM}(\phi', \theta', \chi') = \sum_{M'} D_{M'M}^J(\phi_1, \theta_1, \chi_1) \Psi_{JM}(\phi, \theta, \chi)$$  \hspace{1cm} (13)

If we use $\phi_1 = \phi, \theta_1 = \theta, \chi_1 = \chi$ then we arrive at:

$$\Psi_{JM}(0,0,0) = \sum_{M'} D_{M'M}^J(\phi, \theta, \chi) \Psi_{JM}(\phi, \theta, \chi)$$  \hspace{1cm} (14)

If we multiply this equation by $D_{M'M}^{J*}(\phi, \theta, \chi)$ and sum over $M$ to show that:

$$\sum_M D_{M'M}^{J*}(\phi, \theta, \chi) \Psi_{JM}(0,0,0) = \Psi_{JM}(\phi, \theta, \chi)$$  \hspace{1cm} (15)

Finally, writing $M$ for $M'$ and $K$ for $M$ we attain the following equation:

$$\Psi_{J'M}(\phi, \theta, \chi) = \sum_K D_{MK}^{J*}(\phi, \theta, \chi) \Psi_{JK}(0,0,0)$$  \hspace{1cm} (16)

Therefore, it may be concluded that the general wave function for an asymmetric top is a linear combination of rotation matrices.

Considering the form of rotation matrices, $D_{MK}^{J*}(\phi, \theta, \chi) = e^{iM\phi} d_{MK}^J(\theta)e^{iK\chi}$. If the rigid body possesses an axis of symmetry, then it is required that $\Psi_{JM}(\phi, \theta, \chi)$ be the same up to some phase factor for a rotation about $z$ through an angle $\chi$. This condition can be satisfied if $\Psi_{JM}(\phi, \theta, \chi)$ is proportional to one matrix element in the sum over $K$. Hence, we conclude that for a symmetric top, the normalized states assume the form[27]:

$$|J K M\rangle = \left[\frac{2J + 1}{8\pi^2}\right]^{1/2} D_{MK}^{J*}(\phi, \theta, \chi) = (-1)^{M-K} \left[\frac{2J + 1}{8\pi^2}\right]^{1/2} D_{M-K}^J(\phi, \theta, \chi)$$  \hspace{1cm} (17)

Therefore, we conclude that the eigenfunctions for an asymmetric top are linear combinations of symmetric top eigenfunctions.

As shown in the table below, there are three possible ways in which $a, b, c$ may be identified with $x, y, z$. For a near-oblate top representation III is used and for a near-prolate top representation I is used.
Table 1. Possible Identifications of Principal Axes a, b, c with body-fixed axes x, y, z

<table>
<thead>
<tr>
<th>Body-fixed coordinates</th>
<th>Representation I</th>
<th>Representation II</th>
<th>Representation III</th>
</tr>
</thead>
<tbody>
<tr>
<td>x</td>
<td>b</td>
<td>c</td>
<td>a</td>
</tr>
<tr>
<td>y</td>
<td>c</td>
<td>a</td>
<td>b</td>
</tr>
<tr>
<td>z</td>
<td>a</td>
<td>b</td>
<td>c</td>
</tr>
</tbody>
</table>

Energy Levels

In the oblate top limit (representation III), the Hamiltonian may be recast as:

$$\mathcal{H}_R = AJ^2 + (C - A)J_z^2$$  \hspace{1cm} (18)

Eigenfunctions of this Hamiltonian are $| J K M \rangle$ and the eigenvalues are given by:

$$E(J, K) = AJ(J + 1) + (C - A)K^2$$  \hspace{1cm} (19)

Similarly and for a prolate top (using representation I) we arrive at the eigenvalues:

$$E(J, K) = AJ(J + 1) + (A - C)K^2$$  \hspace{1cm} (20)

In both cases we notice that for each $J$ level there are $2J+1$ different $K$ levels but those with $K \neq 0$ are doubly degenerate. This phenomenon is known as $K$-type doubling.
Furthermore, it can be seen that the term multiplying $K^2$ has opposite signs in oblate and prolate tops.

In the general case of an asymmetric top, the eigenfunctions are linear combinations of symmetric top wavefunctions and we write:

$$|J \ K_a \ K_c\rangle = \sum_{K=-J}^{J} A_K |J \ K \ M\rangle$$

In an asymmetric top, the projection of $J$ along any molecule-fixed axis is not consistent along any direction. This leads to $K$ no longer being a good quantum number.

Nonetheless, $J$ and $M$ are still good quantum numbers and hold the same meaning as they do for symmetric tops. In the absence of external fields, one need not consider $M$ any further. The parameter $K$ is kept to label the energy levels. $K_a (K_{-1})$ is the value $K$ would have in the case of a prolate symmetric top ($\kappa=-1$) while $K_c (K_{+1})$ is the value of $K$ for the limiting case of oblate symmetric top ($\kappa=+1$). The parameter $\kappa$ is the Ray’s asymmetry parameter which runs from -1 for a symmetric top to +1 for an oblate top. It is defined as:

$$\kappa = \frac{2B - A - C}{A - C}$$

The notation $J_{K_pK_o}$ allows the three energy levels associated with $J=1$ to be labeled as

$$E(1_{10}); \ E(1_{11}); \ and \ E(1_{01})$$

The labeling of the energy levels is carried out by considering the correlation diagram that connects the energy of a prolate top with those of an oblate top and the requirement that $I_A \leq I_B \leq I_C$. 

14
The asymmetric top Hamiltonian takes the form:

\[
\hat{H} = \frac{J_a^2}{2I_A} + \frac{J_b^2}{2I_B} + \frac{J_c^2}{2I_C}
\]  \hspace{1cm} (23)

This operator can be recast in the form as raising and lowering operators as follows:

\[
\hat{H} = A\hat{J}_a^2 + B\hat{J}_b^2 + C\hat{J}_c^2
\]  \hspace{1cm} (24)

\[
\hat{H} = \left(\frac{A + B}{2}\right)\hat{J}^2 + \left(C - \frac{A + B}{2}\right)\hat{J}_c^2 + \left(\frac{A - B}{4}\right)\left(\hat{J}_+^2 - \hat{J}_-^2\right)
\]  \hspace{1cm} (25)

If we apply the rotational Hamiltonian to the equation we arrive at:

\[
\sum_K A_K \mathcal{H}_R |J K M\rangle = E \sum_K A_K |J K M\rangle
\]  \hspace{1cm} (26)

The summation over J and M is unnecessary because they are good quantum numbers for an asymmetric top. After multiplying both sides of the equation by \langle J K^* M | and integration we arrive at:
\[ \sum_k A_k (\mathcal{H}_{K'K} - E \delta_{K'K}) = 0 \]  \hspace{1cm} (27)

where \( \mathcal{H}_{K'K} = \langle K' M | \mathcal{H} | K M \rangle \). Therefore and in order to find nontrivial solutions to the above equation we require that the determinant:

\[ |\mathcal{H}_{K'K} - E \delta_{K'K}| = 0 \]  \hspace{1cm} (28)

Therefore, the roots of this \( 2J+1 \) by \( 2J+1 \) secular determinant allow us to find the energies. These energies will correspond to the diagonal elements of the Hamiltonian matrix after it has been diagonalized.

The rigid rotor Hamiltonian has the property it is invariant under a rotation by 180° about a, b, c. Therefore, the asymmetric top Hamiltonian belongs to the point group D\(_2\) whose characters are included in the table below:

<table>
<thead>
<tr>
<th></th>
<th>E</th>
<th>( C_2 ) (z)</th>
<th>( C_2 ) (y)</th>
<th>( C_2 ) (x)</th>
<th>Linear, rotations</th>
<th>Quadratic</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>( x^2, y^2, z^2 )</td>
<td></td>
</tr>
<tr>
<td>B(_1)</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>( z, R_z )</td>
<td>( xy )</td>
</tr>
<tr>
<td>B(_2)</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>( y, R_y )</td>
<td>( xz )</td>
</tr>
<tr>
<td>B(_3)</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>( x, R_x )</td>
<td>( yz )</td>
</tr>
</tbody>
</table>

Table 2. Character table for D\(_2\) point group. Here \( z \) corresponds to a, \( y \) corresponds to c and \( x \) corresponds to b.
Next, we examine how the $|J K M\rangle$ functions transform under the operations of $D_2$. This entails making a connection between the effect of these operations on the Cartesian components and the Euler angles by utilizing the direction cosine matrix elements that relate the Cartesian components in the lab-fixed reference frame to the Cartesian components in the body-fixed reference frame. This analysis results in:

$$C_2(z)|J K M\rangle = (-1)^K |J K M\rangle \quad (29a)$$

$$C_2(y)|J K M\rangle = (-1)^{J-K} |J - K M\rangle \quad (29b)$$

$$C_2(x)|J K M\rangle = (-1)^{-J} |J - K M\rangle \quad (29c)$$

Hence, these equations suggest that a symmetry basis set constructed from linear combinations of $|J K M\rangle$ and $|J - K M\rangle$ transform the same way under the operations of the $D_2$ group. If we define for $K \neq 0$:

$$|J K M s\rangle = \frac{1}{\sqrt{2}} [ |J K M\rangle + (-1)^s |J - K M\rangle] \quad (30)$$

Here, ($s$) may take on the values (0 or 1) and for $K = 0$, $s=0$:

$$E |J K M s\rangle = |J K M s\rangle \quad (31a)$$

$$C_2(z)|J K M s\rangle = (-1)^K |J K M s\rangle \quad (31b)$$

$$C_2(y)|J K M s\rangle = (-1)^{J-K+s} |J K M s\rangle \quad (31c)$$

$$C_2(x)|J K M s\rangle = (-1)^{-J+s} |J K M s\rangle \quad (31d)$$

Therefore, the $(2J+1) \times (2J+1)$ secular determinant factors are divided into four blocks (because the group contains four irreducible representations). Then the eigenvalues and eigenfunctions of each block belong to one of the symmetry species of the $D_2$ group. From the commutation relations of $\mathbf{J}$ we can calculate the matrix elements of $\mathcal{H}_R$ as:
\begin{align}
\langle J K M | J^2 | J K M \rangle &= \langle J K M | J^2 | J K M \rangle = \frac{1}{2} \left[ J (J + 1) - K^2 \right] \\
\langle J K M | J^2 | J K M \rangle &= K^2 \\
\langle J K M | J^2 | J K \pm 2 M \rangle &= -(J K M | J^2 | J K \pm 2 M) \\
&= \frac{1}{4} \left[ J (J + 1) - K (K \pm 1) \right]^2 \left[ J (J + 1) - (K \pm 1) (K \pm 2) \right]^2 
\end{align}

In the prolate top basis set (representation I) we arrive at:

\begin{align}
\mathcal{H}_{KK} &= \frac{1}{2} (B + C) \left[ J (J + 1) - K^2 \right] + AK^2 \\
\mathcal{H}_{K,K\pm 2} &= \frac{1}{4} (B - C) \left[ J (J + 1) - K (K \pm 1) \right]^2 \left[ J (J + 1) - (K \pm 1) (K \pm 2) \right]^2 
\end{align}

With the symmetric top basis functions, the asymmetric top Hamiltonian operator has matrix elements with \( \Delta K = 0 \) and \( \Delta K = \pm 2 \). Since the Hamiltonian matrix is diagonal in quantum number \( J \), each \( J \) defines a matrix sub-block which can be solved independently.

The symmetry properties of the Hamiltonian matrix (which belongs to the \( D_2 \) symmetry discussed above) facilitate the factoring of each \( J \) block into four independent sub-matrices by means of a Wang transformation. Each of these sub-matrices may be diagonalized independently to give rotational energies. The order of each Wang sub-matrix is approximately \( J/2 \) which is computationally convenient for the diagonalization process of large \( J \).

**Selection rules**

For an electric dipole transition the fundamental interaction is \( \mu \cdot E \) where \( \mu \) is the electric dipole moment of the molecule and \( E \) is the electric field vector of the radiation. The line strength \( S(J';J) \) refers is known as natural excitation where the excitation is isotropic.
In this case and since each lab-fixed component of the dipole moment contributes equally
to the line strength factor we can write[27]:

$$S(J';J'') = 3 \sum_{M',M''} |\langle J' M' | \mu_z | J'' M'' \rangle|^2$$

(37)

It is more convenient to work in the molecule-fixed coordinates system. Therefore, we
use the rotation matrices to transform this rank (1) tensor via the equation:

$$\mu(1,p) = \sum_q D_{pq}^{1*}(\phi, \theta, \chi) \mu(1,q)$$

(38)

For $\mu_Z$:

$$\mu(1,0) = \sum_q D_{0q}^{1*}(\phi, \theta, \chi) \mu(1,q)$$

(39)

And the line strength factor can be expressed as:

$$S(J';J'') = 3 \sum_{M',M''} \left| \sum_q D_{0q}^{1*}(\phi, \theta, \chi) \mu(1,q) \right|^2$$

(40)

Now we examine the transition $J'K' \leftrightarrow J''K''$ for a symmetric top. The only component of
the dipole moment which makes a contribution is the component $q = K' - K''$

An evaluation of the line strength factor yields[27]:

$$S(J' K';J'' K'') = (2J' + 1)(2J'' + 1) \left( \frac{J'}{K'} - \frac{1}{K' - K''} - \frac{J''}{K''} \right)^2$$

(41)

From the general properties of the 3-j symbol, we conclude that the line strength will
vanish unless:

$$\Delta J = 0, \pm 1 \quad (J' + J'' \geq 1)$$

Transitions with $\Delta J = -1, 0, +1$ are said to belong to the P-branch, Q-branch, and R-
branch respectively.
For an asymmetric top there are in general three non-vanishing components of the transition dipole \( \mu_a, \mu_b, \) and \( \mu_c \) which transform as \( B_1, B_3, \) and \( B_2 \) respectively under the symmetry operations of the \( D_2 \) group. For an asymmetric top molecule we can derive general selection rules on the \( K_aK_c \) quantum numbers by means of the rotation group \( D_2 \).

To do this we write the components of the electric dipole moment in principal axes (which should be identified with the molecule-fixed axis according to a convention in table 1):

\[
\begin{align*}
\mu_A &= \lambda_{aA}\mu_a + \lambda_{bA}\mu_b + \lambda_{cA}\mu_c \quad ; \quad A = X, Y, Z
\end{align*}
\]

The functions \( \lambda_{\beta A} ; \beta = a, b, c \) are the elements of the direction cosine matrix used for transforming from lab fixed coordinates \((X, Y, Z)\) to molecule-fixed coordinates \((a, b, c)\). These functions have \( B_\beta \) symmetry in the \( D_2 \) group.

In order to calculate the line strength we need the matrix element:

\[
\left\langle f_{K_aK_c}^{K_a'K_c'} |\mu_A| f_{K_aK_c}^{K_a'K_c'} \right\rangle = \sum_{\beta=a,b,c} \left\langle f_{K_aK_c}^{K_a'K_c'} |\lambda_{\beta A}| f_{K_aK_c}^{K_a'K_c'} \right\rangle
\]

If we apply the vanishing integral rule to each rotational element i.e. for the matrix element not to vanish, it is necessary that the product of the three factors be symmetric (belong to \( A \)) under all group operations. This analysis leads to the following results[29]:
<table>
<thead>
<tr>
<th>$\mu_a \neq 0$</th>
<th>$\Delta K_a = \text{even}$</th>
<th>$\Delta K_c = \text{odd}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_b \neq 0$</td>
<td>$\Delta K_a = \text{odd}$</td>
<td>$\Delta K_c = \text{odd}$</td>
</tr>
<tr>
<td>$\mu_c \neq 0$</td>
<td>$\Delta K_a = \text{odd}$</td>
<td>$\Delta K_c = \text{even}$</td>
</tr>
</tbody>
</table>

Table 3. Electric dipole transition rules on $K_a K_c$
To achieve higher accuracy on the rotational constants, the simulated transition frequency must be fitted against the experimental values and accurate confidence intervals taking the correlation of the parameters into account should be reported. In this chapter we will review fundamental ideas from statistics in regards to fitting, and the determination of joint confidence intervals.

Introduction to least squares methods

When the curve being fitted to the data is a straight line, the term linear regression is used. For the general case in which a plane based upon several independent variables is used instead of a simple straight line, the term multiple linear regression is used. For the simplest problem, the assumed relationship between the dependent variable $y$ and the independent variable $x$ is:

$$ y = a_1 + a_2 x \quad (1) $$

In order to fit a straight line to a plot of points $(x_i, y_i)$ where $i=1,\ldots,m$, the slope and intercept of the line $y = a_1 + a_2 x$ must be found from the data. In order to fit a $p$-th order polynomial, $p+1$ coefficients need to be determined.
The most common method for determining the parameters in curve fitting problems is the method of least squares. The main idea behind this method is to minimize the sum of the squared deviations of the fitted values from the curve from the actual observations. If a straight line is to be fit to points \((x_i, y_i)\) \(y\) is called the dependent variable and \(x\) is called the independent variable. We attempt to minimize the quantity\[30\]:

\[ S(a_1, a_2) = \sum_{i=1}^{m} (y_i - a_1 - a_2 x_i)^2 \] (2)

To find \(a_1\) and \(a_2\) that minimize this quantity we evaluate the derivatives:

\[ \frac{\partial S}{\partial a_1} = -2 \sum_{i=1}^{m} (y_i - a_1 - a_2 x_i) \] (3)

\[ \frac{\partial S}{\partial a_2} = -2 \sum_{i=1}^{m} x_i (y_i - a_1 - a_2 x_i) \] (4)

When we set these two partial derivatives to zero and solve the system of equations we arrive at\[30\]:

\[ \hat{a}_1 = \frac{(\sum_{i=1}^{m} x_i^2)(\sum_{i=1}^{m} y_i) - (\sum_{i=1}^{m} x_i)(\sum_{i=1}^{m} x_i y_i)}{n \sum_{i=1}^{m} x_i^2 - (\sum_{i=1}^{m} x_i)^2} \] (5)

\[ \hat{a}_2 = \frac{m(\sum_{i=1}^{m} x_i y_i) - (\sum_{i=1}^{m} x_i)(\sum_{i=1}^{m} x_i y_i)}{m \sum_{i=1}^{m} x_i^2 - (\sum_{i=1}^{m} x_i)^2} \] (6)

Functional forms more complicated than straight lines are often used to fit the data. When the function to be fit is linear in the unknown parameters, the minimization is straightforward because calculating partial derivatives and setting them equal to zero results in a set of simultaneous linear equations that can be solved in closed form and using standard methods of linear algebra. This case is known as linear least squares.
If the function to be fit is not linear in the unknown parameters, a system of nonlinear equations must be solved to find the parameters and iterative procedures are typically used. This case is known as nonlinear least squares.

Once a function has been fitted to the data by the least squares method, it may be necessary to consider the stability of the fit and the estimated parameters.

Generally, the objective function to be minimized can be written as:

\[ S = \sum_{i=1}^{m} w_i (y_i - y(x_i))^2 \]  

(7)

In this equation \( m \) is the number of data points, \( y_i \) is the \( i \)-th input value of the dependent variable and \( y(x_i) \) is the \( i \)-th computed value of the dependent variable. The variable \( w_i \) is called the weight associated with data point \( i \). It will be proportional to the inverse of the variance (proportional to \( 1/\sigma_i^2 \)). If \( w_i \) are taken to be equal to \( \frac{1}{\sigma_i^2} \) where \( \sigma_i^2 \) is independently estimated for each point, the quantity \( S \) becomes equal to \( \chi^2 \). For this reason, the least squares fit is sometimes called a chi-square fit. In the case of unit weighting, then \( w_i = 1 \) for all \( i \).

Assuming that the model, the data and the uncertainty estimates are correct, the value of \( S \) will be distributed according to a \( \chi^2 \) distribution with \( n-p \) degrees of freedom.
Nonlinear least squares methods

All nonlinear least-squares parameter estimation procedures have six inherent basic assumptions and they are:

1. All the experimental uncertainties of the data must be attributable to the dependent variables.
2. The experimental uncertainties of the dependent variables must follow a Gaussian distribution.
3. No systematic uncertainties can either exist in either the dependent or independent variables.
4. The fitting function for fitting the vector of parameters must have the correct mathematical description of the data.
5. There must be a sufficient number of data points to yield a good random sampling of the parent population of residuals.
6. The data points must be independent observations.

The nonlinear least squares procedure involves the minimization of the scalar-valued goodness-of-fit measure which is called the Chi-square function [31]:

$$
\chi^2(p) = \sum_i \left( \frac{\hat{y}(x_i; p) - y(x_i)}{\sigma_i} \right)^2
$$

(8)

where $x$ is the independent variable and $y(x_i)$ is the measured data value for a given point $i$ and $\hat{y}(x_i, p)$ is the fitted value for the point and $\sigma_i$ is an estimate of the standard deviation.
deviation for the measurement of $y(x_i)$. In our case, the experimental uncertainty $\sigma_i$ will be the same for all measurements and the Chi squared reduces to the residual norm. The function $\hat{y}$ is a function of an independent variable $t$ and a vector of $n$ parameters $p$ to a set of $m$ data points. The Chi-squared function can also be written in matrix form as:

$$\chi^2(p) = (y - \hat{y}(p))^T W (y - \hat{y}(p))$$  \hspace{1cm} (9)

where the weighting matrix $W$ is diagonal with $W_{ii} = (1/\sigma_i)^2$.

The best values for the vector parameters $p$ are the ones that minimize the value of the Chi-squared.

When the function $\hat{y}$ is nonlinear in the model parameters, then the minimization of $\chi^2$ with respect to the parameters must be carried out iteratively. A perturbation $h$ is introduced to the parameter vector $(p)$ during every iteration in such a way that it reduces the value of $\chi^2$. There are various methods to carry out this minimization and we will briefly review some of these methods below.

**The Gauss-Newton Method**

This method can only be used to minimize a sum of squared function values. Here second derivatives which are sometimes challenging to compute are not required.

The function evaluated with perturbed model parameters may be expanded through a Taylor series:

$$\hat{y}(p + h) \approx \hat{y}(p) + Jh + O(h^2)$$  \hspace{1cm} (10)

Since $\hat{y}(p)$ is an $m \times 1$ vector evaluated at each of the $m$ data points $x_i$ and the derivative is taken for each of the $n$ components of the parameter vector $p$, and $J$ is the Jacobian $m \times n$
matrix $J_{lk} = \frac{\partial \hat{y}(x_l,p_1,\ldots,p_n)}{\partial p_k}$ If we substitute this equation into the equation for Chi-squared we obtain:

$$\chi^2(p + h) = (y - \hat{y}(p + h))^TW(y - \hat{y}(p + h))$$  \hspace{1cm} (11)

If we expand the above equation we arrive at:

$$\chi^2(p + h) = y^TWy - 2y^TW\hat{y}(p + h) + \hat{y}^T(p + h)W\hat{y}(p + h)$$  \hspace{1cm} (12)

Then we substitute the Taylor series expansion for the perturbed function to obtain:

$$\chi^2(p + h) \approx y^TWy - 2y^TW\hat{y}(p) + \hat{y}^T(p)W\hat{y}(p) - 2(y - \hat{y}(p))^TWJh + h^TJ^TWJh$$

To find the perturbation $h$ that minimizes the Chi-squared function we set the first derivative to zero:

$$\frac{\partial}{\partial h} \chi^2(p + h) = 0$$

This yields:

$$-2(y - \hat{y}(p))^TWJ + 2h^TJ^TWJ = 0$$  \hspace{1cm} (13)

The resulting equations for the Gauss-Newton perturbation are found by taking the transpose of each term in the preceding equation to arrive at:

$$(J^TWJ)h = J^TW(y - \hat{y}(p))$$  \hspace{1cm} (14)

This algorithm may not converge if the initial guess is far from the minimum or if the matrix $J^TJ$ is not ill conditioned.

**The Gradient Descent Method**

From equation (1) it can be shown that the right hand side of the last equation is equal to half the negative gradient of the Chi squared: $-\frac{1}{2} \nabla_p \chi^2(p)$

In this method, one takes steps along a vector whose components are proportional to the components of the negative gradient vector:

$$h = -\alpha J^TW(\hat{y}(p) - y)$$  \hspace{1cm} (15)
where $\alpha$ is a constant of proportionality. In this expression, the positive scalar $\alpha$ corresponds to the size of the step in the steepest-descent direction. There are different methods for determining the optimal size of this step. The gradient method works well when we are far away from the minimum but converges very slowly near the function minimum.

**The Levenberg-Marquadt Algorithm**

This algorithm interpolates between the gradient descent algorithm and the Gauss-Newton algorithm. This is done by adding a term to the Gauss-Newton equation from the previous section to arrive at:

$$ (J^TWJ + \lambda I) h = J^TW(y - \hat{y}(p)) $$

The added term contains a damping parameter $\lambda$ multiplying the identity matrix. Small values for the parameter $\lambda$ result in a Gauss-Newton update and large values of the parameter $\lambda$ result in a gradient descent update. When we are far away from the function minimum the gradient descent method is used. However, as the solution approaches the minimum, the parameter is decreased and the Levenberg-Marquardt method approaches the Gauss-Newton method [32]. The Levenberg-Marquardt method may be viewed as Gauss-Newton using a trust region approach and $\lambda$ can be viewed as the parameter controlling the trust region size. Trust region methods choose a step size then a step direction.

In the MATLAB code used for implementing the Levenberg-Marquardt algorithm, Marquardt’s updating relationship:

$$ (J^TWJ + \lambda\text{diag}(J^TWJ)) h = J^TW(y - \hat{y}(p)) $$

(17)
is utilized.

Once the optimal fit parameters are determined, parameter statistics are computed for the converged solution. The parameter covariance matrix is computed via:

\[ Cov = [J^T W J]^{-1} \] (18)

In nonlinear regression, the least squares estimates for the parameters have important properties:

1. They are asymptotically unbiased: The expectation value for the estimator yields the true value for the parameter vector in the limit of a large number of data points. i.e. \( \lim_{n \to \infty} E[\hat{y}] = y \)

2. They are consistent: \( \lim_{n \to \infty} \hat{y} = y \)

3. They are efficient: The variance of least squares estimates is less than that of other types of parameter estimates.

**Simplex Method**

The Nedler-Mead algorithm [33] is used for unconstrained optimization. The method attempts to minimize a scalar-valued nonlinear function of \( n \) real variables (the Chi-squared function in our case) using only function values without any derivative information. Hence, this method is classified as a direct search method. A large subclass of direct search methods, including the Nedler-Mead method, maintains a non-degenerate
simplex at each step. The “simplex” is a geometric figure of n-dimensions of nonzero volume that is the convex hull of \( n+1 \) vertices.

Each iteration of a simplex-based direct search method begins with a simplex specified by its \( n+1 \) vertices and the associated function values. One or more test points are computed along with their function values and the iteration terminates with a new simplex such that the function values at its vertices satisfy some form of descent condition compared with the previous simplex. The Nedler-Mead algorithm is a popular simplex-based direct search method because it requires few function evaluations to construct a new simplex compared to other methods and is hence computationally efficient.

The Nelder-Mead algorithm iteratively generates a sequence of simplices that eventually shrink towards an optimal point for minimizing a function. In each iteration, the function values are calculated at the vertices of the simplex and then sorted in order of the value of the function at that point. The worst point is then replaced through reflection and then stretching or shrinking. A more comprehensive description of the algorithm is given below.

The Nelder-Mead algorithm was proposed as a method for minimizing a real-valued function \( f(\mathbf{x}) \) for \( \mathbf{x} \in \mathbb{R}^n \). Four scalar parameters are needed for the Nelder-Mead method and these are coefficients for reflection \( \rho \), expansion \( \chi \), contraction \( \gamma \) and shrinkage \( \sigma \). These parameters should satisfy:

\[
\rho > 0 ; \; \chi > 1 ; \; \chi > \rho ; \; 0 < \gamma < 1 \quad \text{and} \quad 0 < \sigma < 1
\]

Typically, in the standard Nelder-Mead algorithm, the coefficients are chosen as:
\[ \rho = 1; \chi = 2; \gamma = \frac{1}{2}; \text{and} \sigma = \frac{1}{2} \]

At the beginning of the \( k \)-th iteration, a non-degenerate simplex \( \Delta_k \) is given along with its \( n + 1 \) vertices each of which is a point in \( \mathcal{R}^n \). The iteration begins by ordering and labeling the vertices as \( x_1^{(k)}, \ldots, x_{n+1}^{(k)} \) such that:

\[ f_1^{(k)} \leq f_2^{(k)} \leq \cdots \leq f_{n+1}^{(k)} \]

Here \( f_i^{(k)} \) denotes \( f(x_i^{(k)}) \). The \( k \)-th iteration generates a set of \( n + 1 \) vertices that define a different simplex for the next iteration so that \( \Delta_{k+1} \neq \Delta_k \). Because we seek to minimize \( f \), we refer to \( x_1^{(k)} \) as the best point or vertex, to \( x_{n+1}^{(k)} \) as the worst point of vertex and to \( f_{n+1}^{(k)} \) as the worst function and so on. A single iteration of the algorithm is specified below[34] with the superscript \( k \) omitted to avoid cluttering.

1. Order the its \( n + 1 \) vertices such that \( f_1^{(k)} \leq f_2^{(k)} \leq \cdots \leq f_{n+1}^{(k)} \) using the tie breaking rules [34].

2. Compute the reflection point \( x_r \):

\[ x_r = \bar{x} + \rho(\bar{x} - x_{n+1}) = (1 + \rho)\bar{x} - \rho x_{n+1} \] \hspace{1cm} (19)

where \( \bar{x} = \sum_{i=1}^{n} x_i / n \) is the centroid of the \( n \) best points (i.e. except \( x_{n+1} \)). If \( f_1 \leq f_r \leq f_n \) accept the reflected point \( x_r \) and terminate the iteration.

3. If \( f_r < f_1 \) calculate the expansion point \( x_e \):

\[ x_e = \bar{x} + \chi(x_r - \bar{x}) = (1 + \rho \chi)\bar{x} - \rho \chi x_{n+1} \] \hspace{1cm} (20)

If \( f_e < f_r \) accept \( x_e \) and terminate the iteration; otherwise accept \( x_r \) and terminate the iteration.
4. If \( f_r \geq f_n \) perform a contraction between \( \bar{x} \) and the better of \( x_{n+1} \) and \( x_r \).

a. If \( f_n \leq f_r < f_{n+1} \) perform an outside contraction:

\[
x_c = \bar{x} + \gamma (\bar{x} - x_{n+1}) = (1 + \rho \gamma) \bar{x} - \gamma x_{n+1}
\]

If \( f_c \leq f_r \) accept \( x_c \) and terminate the iteration otherwise go to step 5.

b. If \( f_r \geq f_{n+1} \) perform an inside contraction:

\[
x_{cc} = \bar{x} - \gamma (\bar{x} - x_{n+1}) = (1 - \gamma) \bar{x} + \gamma x_{n+1}
\]

If \( f_{cc} < f_{n+1} \) accept \( x_{cc} \) and terminate the iteration otherwise go to step 5.

5. Evaluate \( f \) at the \( n \) points \( v_i = x_1 + \sigma (x_i - x_1) \) and the vertices of the simplex at the next iteration consist of \( x_1, v_2, ..., v_{n+1} \).

Confidence Intervals

Asymptotic Standard Errors

The simplest estimates of the precision of the determined parameters are the square roots of the diagonal elements of the covariance matrix. However, this estimation of the asymptotic standard errors is based on the assumptions that the fitting equation is linear and that the determined parameters are orthogonal. When the parameters are orthogonal, the determination of one parameter is independent of the determination of all other parameters and all the off-diagonal elements in the covariance matrix are zero (i.e. the parameters are not correlated). In our case, these assumptions will not be satisfied as the determined rotational constants will be correlated. Therefore, the correlation needs to be taken into account to estimate more accurate confidence intervals of the determined parameters.
Joint confidence intervals

The joint confidence intervals of the determined parameters provide a measure of the overall precision of the parameters and the reliability of the estimated values. These include the effects of variations of all the other parameters.

Linear problems:

Suppose we found a solution $\mathbf{b}$ to the overdetermined problem:

$$ Y = X\mathbf{b} + \mathbf{e} $$

where $Y$ is an n-dimensional column vector containing observed values and $X$ is an $N \times K$ matrix representing a known model and $\mathbf{b}$ is a $K \times 1$ column vector containing the parameters to be determined. The vector $\mathbf{e}$ has $N$ elements and errors which are assumed to be independent and normally distributed, then the joint 100(1-$\alpha$)% confidence region for the elements of the parameter vector are represented by the values of vector $\mathbf{b}$ which satisfy [35, 36]:

$$ (\mathbf{b} - \mathbf{b})^T X^T X (\mathbf{b} - \mathbf{b}) \leq \frac{K}{N - K} F_p(K, N - K) $$

Here $F$ stands for the F-distribution with $N - K$ degrees of freedom and $p$ is the confidence level.

The above inequality leads to an ellipsoidal region as a solution in the parameter space $R^p$. This approximation to the joint confidence interval correctly considers the non-orthogonal nature of the determined parameters but fails to consider the nonlinear nature of the fitting equation and consequently the nonlinearity of the variance space.
Support Plane method

The idea behind support plane analysis is to vary a parameter and study the consequences of this alteration on the $\chi^2$ value. As long as $\chi^2$ is smaller than a given tolerance level of the best fit $\chi^2$, the corresponding parameter set can be regarded as "also acceptable". The range of those "also acceptable" parameter sets defines a confidence interval. In this procedure a series of values for a particular determined parameter are assumed and for each of these assumed values the optimal values of all other determined parameters are re-determined by a nonlinear least squares and the variance at each of the series of assumed values is tabulated. This procedure thus creates a table of values for the optimal variance as a function of assumed values for one of the determined parameters and this series can now be interpolated to determine where a statistically significant increase in the variance occurs. The points at which these statistically significant increases occur mark the ends of the confidence interval for that determined parameter. Finally, the process is repeated for each of the determined parameters.

What the asymptotic standard error and support plane algorithms actually do, is to calculate $\chi^2$ as a function of each single parameter and to estimate the region of this function, which lies below a given tolerance value. This tolerance level is a function of the probability of the true parameter to be located in the confidence interval, the number of freely varying model parameters and the number of data points. It is usually given in units of the best fit $\chi^2$:

$$\frac{\chi^2_{\text{max}}}{\chi^2_{\text{opt}}} = 1 + \frac{K}{N - K} F_p(K, N - K)$$  \hspace{1cm} (25)
where $F_p(K, N - K)$ is the upper p percent point of the F-distribution with K and N-K degrees of freedom. The value of p is the desired confidence level (90 per cent for example)

The support plane analysis correctly treats the nonlinear variance spaces and the non-orthogonal determined parameters. Its major limitation is the large amount of computer time required to evaluate the confidence limits and the optimization solvers being used are efficient and run within seconds on a personal computer.
Chapter 4: Results and discussion

In this chapter the ideas presented in previous chapters will be used to determine the optimal values for the parameters by fitting the resulting model frequencies to the experimentally determined frequencies. Moreover, the correlation between the parameters will be accounted for to determine joint confidence intervals. Finally, combination differences will be reported and compared to the corresponding experimental values to determine their accuracy for future use.

Parameter determination

First we set up the rigid Hamiltonian matrix elements and calculated the eigenvalues using the relations given in section 2. To determine different energies and make the appropriate assignments we used the same parameter values reported in Lin’s thesis[6]. Furthermore, and to obtain the optimum parameter values, the Chi squared quantity must be minimized.
In this case and due to the fact that the experimental errors are all the same, then minimizing the Chi-squared reduces to minimizing the residual norm:

\[ f(p) = \sum_i \left( \hat{y}_i(p) - y_{exp,i} \right)^2 \]  

(1)

where \( \hat{y} \) is the vector of theoretically predicted transition frequencies and is a function of the parameter vector \( p \) (which contains six elements in this case), and \( y_{exp} \) is the vector of experimentally determined transition frequencies. The minimization was carried out using the Nedler-Mead Simplex method which does not require the evaluation of gradients and also using the Levenberg-Marquardt nonlinear least squares algorithm [37]. The work described in this thesis was carried out in MATLAB and the simplex method was implemented using the built-in “fminsearch” and “lsqnonlin” commands.

Moreover, the transition frequencies corresponding to the best-fit rotational constants are reported in table 4 below along with the experimentally observed transition frequencies and the difference between the theoretically-predicted and experimentally observed frequencies.
<table>
<thead>
<tr>
<th>Transition number</th>
<th>Predicted Transition Frequency (GHz)</th>
<th>Observed Transition Frequency (GHz)</th>
<th>$\nu_{\text{pred}} - \nu_{\text{observ}}$ (GHz)</th>
</tr>
</thead>
<tbody>
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<td>0.879</td>
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Table 4. Predicted and observed transition frequencies. These values are based on the best fit obtained by using the Levenberg-Marquardt algorithm. The transition frequencies obtained from using the parameter values of the simplex method led to comparable errors.
Table 4 continued

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Table 4 continued

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<td>90</td>
<td>94.94323</td>
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Continued
From Table 4 we see that the model with the optimum parameter values agrees well with the experimental data. The values of the six parameters are reported in Table 5 below. The values in the column labeled “This work (1)” were obtained using the Nedler-Mead algorithm and the results in the column labeled “This work (2)” were obtained using the Levenberg-Marquardt algorithm. As can be seen from the table, both sets of parameters produced in this work lead to a smaller residual norm than the values reported by Lin [6]. The parameters produced from the Levenberg-Marquardt nonlinear least squares lead to
the best fit and those were the parameters used to produce the transition frequencies in table 4. This set of parameters which corresponds to the best fit will be used for the remainder of this work.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>This work (1)</th>
<th>This work (2)</th>
<th>Lin’s work</th>
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</thead>
<tbody>
<tr>
<td>A'' (GHz)</td>
<td>5.524235</td>
<td>5.524198</td>
<td>5.520978</td>
</tr>
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<td>B'' (GHz)</td>
<td>2.708103</td>
<td>2.708132</td>
<td>2.702029</td>
</tr>
<tr>
<td>C'' (GHz)</td>
<td>1.816842</td>
<td>1.816844</td>
<td>1.814044</td>
</tr>
<tr>
<td>A' (GHz)</td>
<td>5.410611</td>
<td>5.410583</td>
<td>5.409155</td>
</tr>
<tr>
<td>B' (GHz)</td>
<td>2.657628</td>
<td>2.657652</td>
<td>2.651065</td>
</tr>
<tr>
<td>C' (GHz)</td>
<td>1.783675</td>
<td>1.783859</td>
<td>1.781067</td>
</tr>
<tr>
<td>Residual Norm</td>
<td>1.012092</td>
<td>1.012089</td>
<td>1.940170</td>
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</tbody>
</table>

Table 5. Optimal values of the rotational constants in GHz; (1) minimizing the residual norm using Nedler-Mead (“fminsearch”); 2) minimizing the residual norm using the nonlinear least squares Levenberg-Marquardt algorithm.

The difference between the theoretically-predicted and experimentally observed transition frequencies are plotted in figure 6 below. From the figure it may be concluded that there were no systematic errors and only random errors.
Figure 6. Frequency transition number plotted against the difference between the theoretically-predicted and experimentally observed transition frequencies.

A histogram of the differences was also prepared using MATLAB and a Gaussian distribution was fit to the histogram. This resulted in a mean of (-0.00017) and a standard deviation of (0.04) GHz. This standard deviation compares well against the experimental uncertainty of (0.05) GHz. The histogram and the fit Gaussian function are shown in figure 7 and confirm the random nature of the errors.
Figure 7. A histogram of the difference between the theoretically-predicted and experimentally observed transition frequencies.

Estimate of errors

The six rotational constants are correlated with each other. This can be seen from the correlation matrix which is found from the covariance matrix (defined in chapter 3) in the Levenberg-Marquardt nonlinear least squares. This $6 \times 6$ correlation matrix is shown in table 6 below and it is seen that all the off-diagonal elements are non-zero and a few of
these off-diagonal elements even approach unity. For instance, it can be seen from the table that A' and A`` are highly correlated and so are C' and C``. Therefore and due to the strong correlation between the parameters, it is essential that this correlation is taken into account when assigning confidence intervals.

Table 6. The correlation matrix between the six parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>A``</th>
<th>B``</th>
<th>C``</th>
<th>A`</th>
<th>B`</th>
<th>C`</th>
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<tr>
<td>A``</td>
<td>1</td>
<td>-0.1794</td>
<td>-0.1097</td>
<td>0.865985</td>
<td>-0.08506</td>
<td>-0.12111</td>
</tr>
<tr>
<td>B``</td>
<td>-0.1794</td>
<td>1</td>
<td>-0.01234</td>
<td>-0.15185</td>
<td>0.889805</td>
<td>0.03455</td>
</tr>
<tr>
<td>C``</td>
<td>-0.1097</td>
<td>-0.01234</td>
<td>1</td>
<td>-0.1466</td>
<td>0.064919</td>
<td>0.942274</td>
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<tr>
<td>A`</td>
<td>0.865985</td>
<td>-0.15185</td>
<td>-0.1466</td>
<td>1</td>
<td>-0.18835</td>
<td>-0.12813</td>
</tr>
<tr>
<td>B`</td>
<td>-0.08506</td>
<td>0.889805</td>
<td>0.064919</td>
<td>-0.18835</td>
<td>1</td>
<td>0.016502</td>
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<tr>
<td>C`</td>
<td>-0.12111</td>
<td>0.03455</td>
<td>0.942274</td>
<td>-0.12813</td>
<td>0.016502</td>
<td>1</td>
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</tbody>
</table>

To obtain the confidence intervals for the parameters and in order to accurately take into account the correlation between the parameters, the support plane procedure was implemented in MATLAB. For each parameter a set of values was chosen about the optimum value and for each of these values the residual norm was minimized as a function of the five other parameters. For each parameter, this procedure yielded a convex parabola when the parameter was plotted against the residual norm with the minimum located at the optimum value for that particular parameter as reported in table 5. Therefore, a parabola was fit to each of these figures and its intersection with the line representing the critical ratio for a particular confidence level allowed us to determine the...
confidence intervals. The 68% and 90% confidence intervals along with the optimum values of the rotational constants are reported in table 7 below. Moreover, the parameter variation vs. the residual norm was plotted for each parameter and these are included in figures 9 through 14.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Optimum value [GHz]</th>
<th>68% Confidence interval (CI)</th>
<th>90% CI</th>
<th>Lin’s values</th>
<th>Lin’s 68% CI</th>
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<tr>
<td>A``</td>
<td>5.524198 ± ±0.00732</td>
<td>± ±0.00909</td>
<td>± ±0.0015</td>
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<td></td>
</tr>
<tr>
<td>B``</td>
<td>2.708132 ± ±0.00678</td>
<td>± ±0.00863</td>
<td>± ±0.0009</td>
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<tr>
<td>C``</td>
<td>1.816844 ± ±0.00337</td>
<td>± ±0.00418</td>
<td>± ±0.0006</td>
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<tr>
<td>A`</td>
<td>5.410583 ± ±0.00581</td>
<td>± ±0.0072</td>
<td>± ±0.0009</td>
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</tr>
<tr>
<td>B`</td>
<td>2.657652 ± ±0.00761</td>
<td>± ±0.00944</td>
<td>± ±0.0009</td>
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<tr>
<td>C`</td>
<td>1.783859 ± ±0.00318</td>
<td>± ±0.00394</td>
<td>± ±0.0006</td>
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</table>

Table 7. The optimal values of the rotational constants (in GHz) and the joint confidence intervals.

This table outlines the importance of including the correlation between parameters when assigning confidence intervals as there is a significant difference between the asymptotic standard errors which were reported by Lin and the joint standard errors reported in this study. The joint confidence intervals in the above table can be up to nine times as big as the confidence intervals from the asymptotic standard errors. Therefore it is vital to account for the correlation between the parameters in these problems.
Figure 8. The variation of the rotational constant $A''$ plotted against the residual norm.
Figure 9. The variation of the rotational constant $B''$ vs. residual norm
Figure 10. The variation of rotational constant $C''$ vs. the residual norm
Figure 11. The variation of rotational constant $A'$ vs. the residual norm
Figure 12. The variation of rotational constant $B'$ plotted against the residual norm.
Finally, a table of the optimum parameter values along with the joint confidence intervals was prepared and the results of this work were compared against Lin’s results and against Goetz[5]. The results of this work show better agreement with Lin’s results and that is understandable because the parameters were obtained by refitting the simulation to Lin’s experimental data. Moreover, the results obtained in this work show slightly better agreement with Goetz et al. especially when considering the confidence intervals.

Figure 13. The variation of parameter $C''$ plotted against the residual norm.
<table>
<thead>
<tr>
<th>Parameter</th>
<th>This work with 90% CI</th>
<th>Goetz et al.[5]</th>
<th>Lin’s work [6]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A`` (cm⁻¹)</td>
<td>0.184268±0.0003</td>
<td>0.18225</td>
<td>0.18416(5)</td>
</tr>
<tr>
<td>B`` (cm⁻¹)</td>
<td>0.0903325±0.00029</td>
<td>0.09033</td>
<td>0.09013(3)</td>
</tr>
<tr>
<td>C`` (cm⁻¹)</td>
<td>0.0606033±0.00014</td>
<td>0.0604</td>
<td>0.06046(4)</td>
</tr>
<tr>
<td>A´ (cm⁻¹)</td>
<td>0.1804776±0.00024</td>
<td>0.17832(10)</td>
<td>0.18043(3)</td>
</tr>
<tr>
<td>B´ (cm⁻¹)</td>
<td>0.088650±0.00031</td>
<td>0.08868(10)</td>
<td>0.08843(3)</td>
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<tr>
<td>C´ (cm⁻¹)</td>
<td>0.0595031±0.00013</td>
<td>0.05925(5)</td>
<td>0.05941(2)</td>
</tr>
</tbody>
</table>

Table 8. The rotational constants in cm⁻¹

Applications to vibrational spectroscopy

Finally, we attempted to propagate the errors determined from the energy values when taking combination differences. This has an important application in the area of vibrational spectroscopy. For example, an ongoing experiment [7] recording the rotationally-resolved vibrational transition from the ground state vibrational level \( \nu = 0 \) to the excited vibrational state for the benzyl radical will examine the rotational structure of the vibrational ground state through combination differences and these results can be directly analyzed using the outcome of this study.

To accomplish this, we first had to determine the error in the eigen-energies by using:

\[
\Delta E = \frac{\partial E}{\partial A''} \cdot \Delta A'' + \frac{\partial E}{\partial B''} \cdot \Delta B'' + \frac{\partial E}{\partial C''} \cdot \Delta C'' + \frac{\partial E}{\partial A'} \cdot \Delta A' + \frac{\partial E}{\partial B'} \cdot \Delta B' + \frac{\partial E}{\partial C'} \cdot \Delta C' \quad (2)
\]

The partial derivatives were calculated numerically using the formula:

\[
\frac{df(x)}{dx} = \frac{f(x + h) - f(x - h)}{2h} + O(h^2) \quad (3)
\]
This formula is derived from the Taylor series expansions for $f(x + h)$ and $f(x - h)$ and it can be shown that it has error of order $O(h^2)$ for a small step $h$ [38].

After determining the errors in the energy values, then this error $\delta(\Delta v_{CD})$ was propagated when taking combination differences via:

$$\Delta v_{CD} = E_1 - E_2$$

$$\delta(\Delta v_{CD}) = \sqrt{(\Delta E_1 + \Delta E_2)^2} \quad (4)$$

Then these values were compared against the experimental values of these combination differences to determine the accuracy of the confidence intervals.
Table 9. Comparison of experimental and theoretical combination differences: (all frequencies are reported in GHz).

Table 9 shows good agreement between the model and the experiment so the rigid rotor model works well for this problem. The propagated errors in the theoretically derived
combination differences increases with increasing $J$ values and the difference between theory and experiment lies within the theoretically determined confidence interval for most values in the table and all values overlap when taking the experimental uncertainty into account. This shows that the rigid rotor model is good for reproducing the experimentally-observed combination differences. Therefore, it should also correctly predict combination differences not directly observed experimentally. Moreover, this table also underlines the significance of utilizing joint confidence intervals and accounting for the correlation between the parameters. Finally, the results indicate that this analysis can be used with confidence when analyzing the vibrationless ground state rotational structure of benzyl.

The rigid-rotor model is useful for characterizing the energy levels of an asymmetric model. However, molecules are not rigid and a centrifugal force induced by rotation causes the atoms to shift away from the equilibrium positions. Typically, this effect is small (a few MHZ) but under some circumstances the non-rigidity effect can be significant. To accurately account for this effect, higher order terms in the Hamiltonian which arise from the distortion of the molecule under centrifugal forces ($O(J^4)$ and higher) should be included [29]. However, these effects will be small.
Summary and Conclusions

The rotational Hamiltonian used in this study is that of the rigid asymmetric top. The Hamiltonian matrix was diagonalized as a function of the rotational constants A, B, and C for both the ground and the excited electronic states to obtain the rotational energy levels. The energies of the transitions allowed by the selection rules were determined by combining levels of an upper state with the lower state. The calculated transition energies were then fitted to the rigid rotor model by the Levenberg-Marquardt and the Nelder-Mead algorithms and these procedures allowed for an accurate determination of the rotational constants. Furthermore, and using the support plane procedure, the correlation of the parameters was taken into account when assigning confidence intervals. There were six variable parameters in the global fit and they were the A, B and C constants in the ground state, and in the excited states of the 6 a_0^1 band. It was shown that including the correlation between the parameters leads to a significant change in the reported errors. Finally, propagating these errors ultimately leads to better agreement with experiment when taking combination differences.
Appendix A: Experimental details

A block diagram of the experimental apparatus is included in figure 4. The pulsed free jet was furnished by a pulsed valve (General Valve Series 9). The heated pulsed nozzle assembly has an 800 μm orifice. The nozzle and the tubing connecting it to the sample reservoir are maintained at the reservoir temperature or slightly above. The benzyl free radicals were generated in the free jet by photolyzing benzyl chloride (purchased from Aldrich and without further purification) with an ArF excimer laser (Lumonics TE-861T-4). Benzyl chloride was heated in a reservoir and maintained at 60°C and seeded in He with a backing pressure of about 400 psi. After ArF photolysis at the throat of the jet the radicals were probed 9 mm downstream from the excimer laser (typical rotational temperatures were 1-4 K). The probe laser was a 699-29 Autoscan cw ring dye laser (specified linewidth of about 1 MHz) pumped by an Ar+ laser whose output was then seeded into a pulse amplifier (Lambda Physik FL2003) pumped by a 308nm XeCl excimer laser (Lambda Physik EMG 103 MSG).
The linewidth of the resulting pulse amplified beam was \( \leq 100 \text{ MHz} \). The total laser-induced fluorescence was collected by an f/2 62.5 mm planoconvex lens and then imaged by a matching lens through adjustable optical slits onto an EMI 9659QB photomultiplier (PMT) and a submillimeter slit width was used. The observed Doppler and laser limited linewidth of a single rotational line is about 150 MHz for benzyl. Signals from the PMT were averaged by a Stanford Research SR250 gated integrator/boxcar averager. Absolute calibration of the spectra was made by reference to a Te\(_2\) spectrum. Relative frequency calibration was accomplished by simultaneously recording the transmission fringes of a home-built external etalon (with a free spectral range of 474.54 MHz) and the laser-induced fluorescence spectra.

Figure 14. Schematic diagram of the high resolution experimental apparatus[26].
References


