High Resolution Near-Infrared/Visible Intracavity Laser Spectroscopy of Small Molecules

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High Resolution Near-Infrared/Visible Intracavity Laser Spectroscopy of Small Molecules

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Abstract

High Resolution Near-Infrared/Visible Intracavity Laser Spectroscopy
of Small Molecules

by

Jack C. Harms

Chairperson: Professor James J. O'Brien

Intracavity laser spectroscopy has been used to study the electronic structure of several small molecules. The molecules studied as part of this dissertation include germanium hydride (GeH), copper oxide (CuO), nickel chloride (NiCl), platinum fluoride (PtF), platinum chloride (PtCl), and copper hydroxide (CuOH). This work encompasses five peer-reviewed publications and two submitted manuscripts.
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CHAPTER I
AN INTRODUCTION TO MOLECULAR SPECTROSCOPY

1.1 What is Spectroscopy?

Spectroscopy is the study of the interaction between light and matter. High precision measurements of these interactions can provide valuable insight into the physical characteristics of molecules under study. This is possible in part due the discreet energy of light as a function of its frequency (and, therefore, wavelength) as defined by Planck’s equation

\[ E = h\nu = \frac{hc}{\lambda} \]  

(1.1)

where \( E \) is the energy of a photon, \( h \) is Planck’s constant, \( \nu \) is the frequency of the photon, \( c \) is the speed of light, and \( \lambda \) is the wavelength of light. Due to the law of the conservation of energy, light can be absorbed by a molecule only if there exist stable energy states of that molecule separated exactly by the energy of the light. The ability to elucidate physical characteristics of molecules from spectroscopic measurements derives from the application of quantum mechanical models to describe the stable energy levels of the studied molecules.

The need for quantum mechanics arose from attempts to explain the wave-particle duality of nature. Just as light is quantized and has some particle-like characteristics, matter has wave-like characteristics when considered on the smallest scales.\(^1\) Quantum mechanics applies wave-mechanical solutions to classical energy descriptions of material systems through the Schrödinger equation

\[ \hat{H}\psi = (\hat{T} + \hat{V})\psi = E\psi \]  

(1.2)
where $\hat{H}$ is the Hamiltonian operator, $\hat{T}$ is the kinetic energy operator, $\hat{V}$ is the potential energy operator, $\Psi$ is the wavefunction of the system that reflects the wave-particle duality, and $E$ are the stable energy states of the system that are Eigenvalues of the Hamiltonian operator. Because each molecular system will have a unique mass and charge distribution, it will have a correspondingly unique energy landscape. This specificity makes spectroscopy a very powerful tool for investigation of the physical characteristics of molecular species.

1.2 Molecular Rotation

1.2.1 Diatomic Molecules

Rotational energy refers to the angular momentum of the molecule about the center of mass. It is useful to consider the rigid rotor model as an approximate description of this molecular system. This model assumes molecular rotation is similar to the rotation of two masses separated by a fixed distance rotating about an axis perpendicular to the molecular bond. In this model, the rotation has no potential energy, and the Hamiltonian consists only of kinetic energy. The Schrödinger equation, given in equation 1.2, is most useful for this system when represented in spherical coordinates, using the reduced mass, $\mu$, to relate the energy to the internuclear separation, $r$, instead of the separation of each nuclei from the center of mass of the molecule.

$$-\frac{\hbar^2}{2\mu} \left[ \frac{1}{r^2} \left( \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) \right] \Psi = E \Psi$$ \hspace{1cm} (1.3)

Because the internuclear separation is fixed in this model, the partial derivatives with respect to $r$ are zero, producing equation 1.4, where the wavefunctions, $Y_{\ell m}$, are spherical harmonics. Solutions to these equations are analogous to the spherical
harmonic solutions of the hydrogen atom, are quantized, and are given by equation 1.5,\(^2\) where \(J\) is the rotational quantum number and the rotational constant, \(B\), is defined in Joules by equation 1.6.\(^3\) The internuclear separation of the rotational constant is defined as the equilibrium bond length, \(r_e\).

\[
\frac{-\hbar^2}{2\mu r^2} \left( \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right) Y_{JM} = E Y_{JM} \quad (1.4)
\]

\[
E_R = B J(J + 1) \quad (1.5)
\]

\[
B = \frac{\hbar^2}{8\pi^2 \mu r_e^2} \quad (1.6)
\]

In spectroscopy, this equation is more commonly expressed in wavenumbers, cm\(^{-1}\), and has the form seen in equation 1.7,\(^3\) where \(\overline{B}\) is the rotational constant in wavenumbers, defined by equation 1.8.\(^3\)

\[
F(J) = \frac{E_R}{\hbar c} = \overline{B} J(J + 1) \quad (1.7)
\]

\[
\overline{B} = \frac{\hbar}{8\pi^2 \mu c r_e^2} \quad (1.8)
\]

Rotational spectroscopy can be used to determine the equilibrium bond length because of the dependence of the rotational constant on the internuclear separation.

This model fails to describe adequately a molecular system, however. Molecular bonds are not rigid as they result from equilibrium between the Columbic attraction of the positively charged nuclei to the negatively charged electrons and internuclear repulsion. As the velocity of molecular rotation increases, competing centrifugal forces experienced by the nuclei lead to a smaller net attractive force and a larger internuclear separation. This, in turn, leads to an increase in bond length as rotational energy increases, translating to a negative deviation from linearity as rotational quantum number increases. This deviation is incorporated into the rigid
rotor model with the introduction of the centrifugal distortion coefficient, $\bar{D}$, that scales with $J^2(J+1)^2$, as seen in equation 1.93 and defined by the Kratzer relationship in equation 1.10.3

$$F(J) = \bar{B} J(J + 1) - \bar{D} J^2(J + 1)^2$$  \hspace{1cm} (1.9)

$$\bar{D} = \frac{4 \bar{B}^3}{\omega_e^2}$$ \hspace{1cm} (1.10)

The bars over the parameters are included to emphasize that these parameters are in units of cm$^{-1}$ (and not Joules). These bars are omitted in the remainder of the text. The $\omega_e$ term in this expression is the vibrational stretching frequency that will be defined in the next section. This description of rotational energy is adequate for many analytical treatments of rotational spectra.

Selection rules exist for rotational transitions that require $\Delta J=0, \pm 1$. These selection rules lead to different branch shapes, which are known as R, Q, and P branches for $\Delta J=1,0, \mathrm{and} -1$, respectively. Pure rotational transitions are relatively low in energy and fall into the radio, microwave, and far-infrared region of the electromagnetic spectrum.

1.2.2 Polyatomic Molecules

In a polyatomic system, molecular rotation about the principle axes of the molecule is no longer degenerate. As a result, a single rotational constant is no longer adequate to describe the molecular system. Instead, three rotational moments of inertia must be considered, and a unique rotational constant is obtained for each unique moment of inertia. These constants $A$, $B$, and $C$, where $A>B>C$ are defined in equation 1.11.
\[ A, B, C = \frac{\hbar^2}{2I_{A,B,C}} \]  

where \( \hbar \) is the reduced Planck’s constant and \( I_{A,B,C} \) are the moments of inertia about the principle molecular axes.

Only one polyatomic molecule was analyzed as a part of this dissertation (CuOH), and, as such, the remaining discussion of polyatomic systems will regard that specific case. Copper hydride oxide is a triatomic molecule with \( C_3 \) symmetry. It has three unique moments of inertia about the principle axes, so \( A \neq B \neq C \), and the resulting rotational energy levels are complex.\(^4\) The relevant quantum numbers for this system are \( J, K_a, \) and \( K_c \) where \( J \) is the total angular momentum, \( K_a \) is the angular momentum about the \( a \)-axis, and \( K_c \) is the angular momentum about the \( c \)-axis. Selection rules are specific to rotation about each principle axis, and are discussed as applicable in Chapter IX.

1.3 Molecular Vibration

Molecular vibrations may be approximately described using the simple harmonic oscillator model, in which two oscillating masses are connected by a spring. In this system, the potential energy, given by equation 1.12,\(^2\) is equal to half of the product of force constant, \( k \), and the internuclear distance, \( x \), squared.

\[ V(x) = \frac{1}{2}kx^2 \]  

The Schrödinger equation for this system is given by equation 1.13.\(^2\) Because molecular vibration can only occur along the molecular axis, the three-dimensional second derivative of the Hamiltonian is reduced exclusively to the molecular axis. Again, solution of this equation yields quantized energy levels that are, in Joules, of
the form given in equation 1.14, \(^2\) where \(v\) is the vibrational stretching frequency defined in equation 1.15\(^2\) and \(v\) is the vibrational quantum number.

\[
\left( \frac{-\hbar^2}{2\mu} \frac{d^2}{dx^2} + \frac{1}{2} k x^2 \right) \Psi = E \Psi
\]

(1.13)

\[E_v = h \nu (v + \frac{1}{2})\]

(1.14)

\[
v = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}
\]

(1.15)

These equations are more often given in their wavenumber form seen in equations 1.16 and 1.17\(^3\)

\[G(v) = \frac{E_v}{hc} = \omega_e (v + \frac{1}{2})\]

(1.16)

\[\omega_e = \frac{v}{c}\]

(1.17)

Because the force constant is related to the second derivative of the potential energy, the study of vibrational spectra can lead to determination of the shape of the potential energy curve of a molecule.

Again, this model is not a perfect description of the vibration of a molecular system. The model assumes the masses themselves do not interact and that the molecular bond is completely elastic. However, because the nuclei carry positive charges, the potential energy increases rapidly as the internuclear separation decreases because of Columbic repulsion. Also, as the internuclear separation increases, the restoring force of the bond becomes weaker to the point that molecular dissociation occurs and the bond breaks. These deviations make molecular potential energy curves anharmonic, and the vibrational energies are corrected by terms that scale with \(v+\frac{1}{2}\) polynomially, as seen in equation 1.18\(^3\) and
include the anharmonicity constant, $\omega_e x_e$, as well as higher order correctional terms, such as $\omega_e y_e, \omega_e z_e$...

$$G(v) = \omega_e (v + \frac{1}{2}) - \omega_e x_e (v + \frac{1}{2})^2 + \omega_e y_e (v + \frac{1}{2})^3 \ldots$$

(1.18)

While the energy levels of the simple harmonic oscillator model have equal separation between all adjacent levels, these anharmonic corrections result in energy levels that are closer and closer together as $v$ increases. The dissociation energy, $D_e$, of a molecule occurs at the point that an increase in $v$ no longer leads to an increase in the energy of the system and is given by equation 1.19.

$$D_e \approx \frac{\omega_e}{4 \omega_e x_e}$$

(1.19)

Vibrational spectroscopy can be used to estimate bond strength because of the dependence of the dissociation energy on the vibrational stretching frequency and the anharmonicity constant. Vibrational transitions occur in the infrared region of the electromagnetic spectrum.

1.4 Rovibrational Coupling in Electronic States

The anharmonicity of vibrational potential wells leads to a vibrational dependence on the equilibrium bond length of a diatomic molecule. As such, the rotational constants within a given potential well will vary with vibrational level. In 1932, Dunham developed an analytical equation describing of this dependence

$$E(v, J) = \sum_{l,m} Y_{l,m} \left( v + \frac{1}{2} \right)^l [l(l + 1)]^m$$

(1.20)

where the $Y_{l,m}$ parameters describe this vibrational dependence and $Y_{10} \approx \omega_e$, $Y_{20} \approx \omega_e x_e$, $Y_{01} \approx B_e$, $Y_{02} \approx D_e$. The subscript $e$ refers to the equilibrium value of the constant. These $Y_{l,m}$ parameters should not be confused with the $Y_{JM}$ spherical
harmonic wavefunctions, despite their unfortunate similarity in appearance.

Dunham derived this expression with the Born-Oppenheimer approximation, which assumes that nuclear motion can be entirely decoupled from electronic motion because nuclei are much more massive than electrons. Using this approximation, $Y_{l,m}$ parameters can be determined for several isotopologues using the mass scaling

$$Y_{l,m}^\alpha = Y_{l,m}^1 \left(\frac{\mu_1}{\mu_\alpha}\right)^{m+l/2}$$

(1.21)

where $\alpha$ refers to the minor isotopologue and 1 refers to the major (reference) isotopologue. Using equation 1.20 and 1.21, the rotational structure for several vibrational levels of several isototopologues in a given electronic state can be fit to a single expression, and the determined constants can be used to map out the potential energy surface of that electronic state.

In 1974 and 1980, Ross et al.\textsuperscript{6} and Watson\textsuperscript{7} expanded Dunham’s expression to account for the mass-dependent deviations of the $Y_{l,m}$ parameters due to the breakdown of the Born-Oppenheimer approximation that can be observed for light atoms (or for heavy atoms in very high precision measurements). In a series of studies in the 1980s, Tiemann and coworkers further expanded the Dunham expression to include terms that compensate for deviations resulting from finite size differences between nuclei of the isotopes heavy atoms.\textsuperscript{8-12} In 1999, Le Roy combined these expansions into a comprehensive linear equation:\textsuperscript{13}
\[ E^\alpha_{(cm^{-1})}(T_e, v, J) = T_e + \sum_{l,m \neq (00)} Y_{l,m}^1 \left( \frac{\mu_1}{\mu_\alpha} \right)^{m + l/2} \left( v + \frac{1}{2} \right)^l [J(J + 1)]^m + \]

\[
\sum_{l,m \geq (00)} \left\{ \delta < r^2 >^A_{f_{l,m}} + \delta < r^2 >^B_{f_{l,m}} + \frac{\Delta M_A^1}{M_A} \delta_{l,m}^A + \frac{\Delta M_B^1}{M_B} \delta_{l,m}^B \right\} \times 
\left( \frac{\mu_1}{\mu_\alpha} \right)^{m + l/2} \left( v + \frac{1}{2} \right)^l [J(J + 1)]^m \]

where \( E^\alpha \) is the energy of a rovibrational level of an electronic state of isotopologue \( \alpha \), \( T_e \) is the electronic energy of that state, \( l \) and \( m \) refer to the \( l^{th} \)-vibrational and \( m^{th} \)-rotational component in the expansion, \( Y_{l,m}^1 \) are the rovibrational Dunham parameters for the reference isotopologue 1, \( \mu \) is the reduced mass for the reference (i.e., 1) and relative (i.e., \( \alpha \)) isotopologues, \( v \) is the vibrational quantum number, \( J \) is the rotational quantum number, \( \delta < r^2 >^A_{A} \) is the change in mean squared nuclear charge radii between reference and relative isotopes of atom A, \( f_{l,m}^A \) are “field-shift” parameters that depend on the electron density at the nucleus of atom A, \( M_A^\alpha \) is the mass of isotopologue \( \alpha \), \( \Delta M_A^\alpha \) is the difference in mass between the relative and reference isotopologues, and \( \delta_{l,m}^A \) are the mass-dependent Born-Oppenheimer breakdown (BOB) parameters. Equation 1.22 is the form of the Dunham expansion used to analyze spectra of CuO, PtF, and PtCl (Chapters V, VII, and VIII).

### 1.5 Electronic States of Molecules

The last type of energy levels that will be discussed result from the arrangement of electrons in molecular orbitals. The energy of these states depends on the intrinsic spin of the electrons in orbitals that are incompletely filled, the energy of the occupied orbitals, electron-electron repulsion in occupied valence orbitals, and the energy of nucleus-nucleus repulsion as a function of internuclear
separation. These states are notably more complicated than rotational or vibrational levels and cannot be defined by any simple expression. These states are described by a series of quantum numbers that provide information about the angular momentum of the system: the net electron spin, $S$; the projection of $S$ onto the molecular axis, $Σ$; the projection of orbital angular momentum onto the molecular axis, $Λ$; and the projection of total angular momentum onto the molecular axis, $Ω$, given by $Λ+Σ$. The relative projections onto the molecular axis indicate whether components will add to or detract from the total angular momentum of the system.

Hund developed five different cases for electronic structure that relate to the magnitude of various molecular properties and the degree to which individual electronic states interact. Different quantum numbers and selection rules apply for the various cases. The molecular systems considered in this dissertation have electronic states that fall into Hund’s cases (a), (b), and (c). In Hund’s case (a), individual electronic states are well isolated, and the coupling between the orbital angular momentum $Λ$ and the spin angular momentum $Σ$ is large relative to the separation of rotational energy levels. In Hund’s case (a), $Λ$, $S$, $Σ$, $Ω$, and $J$ ($J=Ω+R$ where $R$ is the rotational angular momentum) are good quantum numbers, with selection rules for transitions that require $ΔΛ=ΔΩ=0$, $±1$; $ΔΣ=ΔΩ=0$, and $ΔJ=0$, $±1$. In Hund’s case (b), individual electronic states are again well isolated, but there is little to no coupling of $Λ$ and $Σ$, and $Λ$, $S$, $N$ ($N=Λ+R$), and $J$ ($J=N+S$) are good quantum numbers, with transition selection rules $ΔΛ=0$, $±1$; $ΔS=0$; and $ΔN=ΔJ=0$, $±1$. In Hund’s case (c), spin-orbit ($Λ-Σ$) coupling is so large that individual electronic states
are overlapped and strongly interact. These interactions lead to mixed states that have properties of both “individual” states, and the total angular momentum $\Omega$ and $J$ ($J=\Omega+R$) are the only good quantum numbers, with transition selection rules $\Delta \Omega=0$, $\pm 1$ and $\Delta J=0$, $\pm 1$.

The notation for Hund’s case (a) and (b) and Hund’s case (c) electronic states are slightly different due to the good quantum numbers that describe those states. Hund’s case (a) and (b) states are given the notation $2S+1\Lambda$ (where $2S+1$ is the multiplicity of the state), while Hund’s case (c) states are given the notation $[x.x] \Omega$, where $[x.x]$ is the energy of the electronic state in thousands of wavenumbers. Historically, case (a) and (b) states were assigned letters to indicate their relative energy, with $X$ being the lowest energy state. Capital letters are used to indicate states with the same multiplicity as the ground state, and lower case letters are used to indicate states with a different multiplicity. In this work, the $[x.x]$ notation is also used with these case (a) and (b) states for the convenience of the reader. It is also worth noting that molecular parameters for the upper and lower states of electronic transitions use ′ and ″ notation, respectively, and these symbols are prevalent throughout the text.

1.6 Transition Intensity

Electronic transitions may be induced in molecules by the absorption of a photon if there is an appreciable transition dipole moment between the two electronic configurations involved in the transition. The magnitude of the transition dipole moment is dependent upon the wavefunctions of the electronic states and is a good indicator of expected spectral intensity when it can be accurately predicted.
The intensity of a transition is directly dependent upon the number of molecules that populate the initial state. The population of energy levels in a molecule is directly related to the Boltzmann factor, given by equation 1.23.\(^1\)

\[
N \propto e^{-\frac{E}{kT}}
\]  

(1.23)

This factor indicates that lower energy states have larger populations. Additionally, because rotational energies are small relative to \(kT\) many rotational levels may be populated, even at low temperature. The energies of vibrational and electronic states, however, are large relative to \(kT\) and a significant decrease in population is observed for excited states at low temperature, typically resulting in spectral contributions from only very low-lying states for absorption measurements.

1.7 Why study spectroscopy of small molecules?

There are several incentives to study spectra of small molecules. Periodic trends are not well established in the transition metals, and high resolution spectra provide accurate descriptions of the properties of bonds between transition metals and ligands. By studying the way transition metals in a row or column of the periodic table interact with a specific ligand, a deeper understanding of trends on this frontier could be discovered.

Analysis of diatomic spectra yields well-determined values for molecular constants that can be used as benchmarks for computational chemists. Because the computational complexity of a molecular system increases dramatically with the number of electrons in a molecule, approximations must often be made in calculations so that they may be performed on a feasible time scale. These
determined parameters help to ensure that accuracy is maintained when computational assumptions are applied.

Bond lengths, bond strengths, and electron configurations for molecules can be used to compare the effect of various ligands on transition metals. Examination of relationships can lead to a deeper understanding of ligand effects. These effects may then be used as analogs to help understand more complicated transition metal-ligand systems.

Finally, the study of small molecules has inherent value as fundamental research. The study of free radical species helps to determine the role of $d$-orbital electrons in bonding, a role that is not well understood.
CHAPTER II

DESCRIPTION OF THE INTRACAVITY LASER SYSTEMS

2.1 Theory of the Intracavity Laser Process

Intracavity Laser Spectroscopy (ILS) is a very sensitive technique that utilizes laser action to enhance absorption due to molecular species. To perform an ILS measurement, a sample is introduced between relevant optical components of a tunable laser system. The laser is operated in a cyclical fashion with three critical steps: (1) absorption due to molecular species present in the sample is enhanced by laser evolution over an initial delay period termed the generation time, \( t_g \); (2) the output of the laser is measured by an appropriate detector over a period of time much smaller than \( t_g \) that is termed the viewing window, VW; and (3) the pump laser is diverted, ensuring the gain medium of the tunable laser drops below the lasing threshold and operation of the laser is not continuous. When operated in this fashion, the resonator cavity of the laser is similar to a multi-pass cell, and very long effective pathlengths may be obtained. The absorbance, \( A \), of an ILS process is defined by\(^\text{14}\)

\[
A = \ln \left[ \frac{I_{0}(\nu)}{I_{obs}(\nu)} \right] = k(\nu)\phi(\nu)N \left( \frac{l}{L} \right) c t_g
\]  

(2.1)

where \( \nu \) is the frequency of light, \( I_0(\nu) \) is the intensity of the laser in the absence of the absorber, \( I_{obs}(\nu) \) is the intensity of the laser in the presence of the absorber, \( k(\nu) \) is the intensity of the absorption line, \( \phi(\nu) \) is the normalized absorption lineshape profile, \( N \) is the number density of the intracavity absorber, \( l/L \) is the ratio of the resonator cavity of length \( L \) occupied by the absorber in length \( l \), and \( c \) is the speed of light. Equation 2.1 is related to the traditional Beer-Lambert law\(^1\)}
\[ A = \varepsilon(\nu) bC \]  

(2.2)

where \( \varepsilon(\nu) \) is the molar absorptivity, \( b \) is the pathlength, and \( C \) is the concentration in that the terms \( k(\nu) \) and \( \phi(\nu) \) correlate to \( \varepsilon(\nu) \), \( N \) correlates to \( C \), and \([[(l/L)c t_g]]\) correlates to \( b \) and is the effective pathlength for ILS, \( L_{\text{eff}} \).

The sensitivity of the ILS method derives from the proportionality of the effective pathlength (and, consequently, absorbance) to the speed of light. Effective pathlengths can be optimized for detection by varying \( t_g \), minimizing the length of the resonator cavity, or increasing the portion of the resonator cavity occupied by the absorbing species. While effective pathlengths of up to 70,000 km have been reported using ILS techniques,\(^{15}\) the effective pathlengths used for the various experiments in this dissertation ranged from hundreds of meters to 10 km.

2.2 Dye Laser Intracavity Laser System

Using various laser dyes as gain media, dye laser systems can be used to measure ILS spectra throughout the visible region.\(^{15}\) A schematic of the dye laser-based (DL-ILS) system used for these experiments is provided in Figure 2.1(a). A Verdi\textsuperscript{TM} V-10 Laser operating at 532 nm and set to 0.50-1.50 W is used to pump 3 mM of 4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)4\textsuperscript{H}-pyran (DCM) laser dye in ethyl-phenyl ether (EPH), circulated through a Spectra Physics sapphire nozzle at a pressure of \(~80\) PSI, or 3 mM of rhodamine 6G (Rh6G) laser dye in ethylene glycol circulated at \(~50\) PSI, which together produce a tunable output over the \(14,500 - 17,200\) cm\(^{-1}\) range with a maximum power output of 150 mW. The standing wave 3 mirror dye laser contains a flat output coupler, OC, a curved fold mirror \((f=50\) mm\), FM, and a curved high reflector \((f = 75\) mm\), HR. The
operating wavelength of the dye laser is controlled with a tuning wedge, TW, located in a rotating mount attached to an xyz translation stage. The TW is mounted at Brewster’s angle to minimize power losses. Tuning can be accomplished using three
different approaches: rotation, vertical translation, and horizontal translation. The rotation of the TW through the Brewster’s angle plane of the mount broadly tunes the laser and serves as the coarse adjustment to the operational wavelength range. It was found that rotating the TW so that the thickness gradient of the wedge is at ~45° from vertical produced the broadest spectral output. Vertical translations serve as intermediate adjustment, and fine tuning of the laser is accomplished using horizontal translation of the TW. With this assembly, a single set of optics and two laser dyes (DCM and Rh6G), the dye laser can be tuned from 585-675 nm using less than 2.50 W of pump power.

A hollow cathode is placed within the laser cavity in-line with the optical beam. Molecules are produced in the plasmas formed when a current is applied to the cathode in the presence of reagent and sputter gasses. If these molecules absorb light corresponding to the resonant modes of the laser cavity, those laser modes are not amplified, and a decrease in laser output at that wavelength can be detected. As mentioned above, the effective pathlength depends on portion of the laser cavity occupied by the absorber (which corresponds to the region of the cavity where molecules are produced in the plasma) and the generation time, which is regulated by a process described below.

The dye laser output is passed through an extracavity I₂-cell before being directed through an acousto-optic modulator (AOM) and into a 2 m long Spex 2062 monochromator. The dispersed beam is then imaged onto a 1024-channel EG & G diode array detector. The output from the detector is read using a GPIB board and software program OMA88. The dye laser is operated in an intentionally broadband
ILS fashion using two AOMs with a Pulse-and-Delay Generator. The timing sequence is monitored by directing a portion of the dye-laser output onto a photodiode connected to an oscilloscope. The first AOM is in-line with the pump laser and dictates the total cycle time: at the start of the sequence, AOM1 is switched off and the pump beam is directed into the dye jet. Each sequence ends when AOM1 is switched on and diffracts the pump beam into a beam stop and reducing the pump power below the lasing threshold of the dye. The second AOM is used to set the effective pathlength and detector viewing window for each cycle. The generation time, \( t_g \), corresponds to the time between laser initiation (when AOM1 turns off and the pump beam energizes the dye molecules) and when the viewing window is initiated (AOM2 is turned on). An illustration of the timing sequence used for the ILS process in terms of the AOMs and as observed by the photodiode is provided in Figure 2.1(b).

2.3 Titanium:Sapphire Intracavity Laser System

Titanium doped sapphire crystals have been demonstrated to be excellent gain media for ILS systems operating in the near-infrared (9000-15000 cm\(^{-1}\)).\(^{15}\) The Ti:Sapphire ILS (TS-ILS) system used in this work has been described in detail,\(^{14,16}\) and the description provided here is derived from those reports. A general schematic of the TS-ILS system is provided in Figure 2.2. A Verdi\textsuperscript{TM}-V10 laser is used to pump a Ti:Sapphire crystal. The resonator cavity of this laser includes a high reflector (HR), 2 fold mirrors (FM), an intracavity hollow cathode, 2 Brewster-angle prisms, an adjustable slit, and an output coupler (OC). The Brewster-angle prisms disperse light as a function of wavelength, and the adjustable
slit is translated to select the laser modes of the cavity by selectively allowing transmission of the dispersed light. This optical combination is responsible for tuning the TS-ILS system. All components outside of the resonator cavity are identical to those used for the DL-ILS system.

Figure 2.2: Schematic of the Ti:Sapphire Intracavity Laser (TS-ILS) system.
CHAPTER III

APPLICATIONS FOR DATA PROCESSING

3.1 Initial Data Conversion

Data conversion and derivative calculations are performed with an in house Visual Basic program developed by J. J. O’Brien, SNEW. Three spectra are collected at each monochromator position: a spectrum with the plasma engaged, a spectrum with the plasma turned off and the extracavity I$_2$ cell empty, and a spectrum with the plasma turned off and I$_2$ present in the extracavity cell. The spectral width as each monochromator positions is $\sim$5-7 cm$^{-1}$ wide. To produce a plasma spectrum for a given monochromator position, the baseline current (recorded when the laser was blocked by a beam stop) is subtracted from all data, then the plasma and I$_2$ spectra are divided by the background spectrum for the monochromator position, producing the transmission spectrum that is used for analysis. The 1024-diode array channels are assigned tentative wavenumber positions from an empirically derived polynomial that correlates the order of the diffraction grating, a grating equation for the monochromator position, and detector channel number to the vacuum wavenumber of the detected signal. These initial assignments are typically accurate to $\pm$0.1 cm$^{-1}$. Savitzky-Golay polynomials for the 1$^{\text{st}}$ and 2$^{\text{nd}}$ derivative of the transmission spectrum are then calculated, and text files are produced that contain the 1024 initial wavenumber positions, along with their corresponding transmission, 1$^{\text{st}}$ derivative, and 2$^{\text{nd}}$ derivative values.
3.2 Methods for Data Calibration

In order for accurate molecular constants to be determined from experimentally recorded ILS spectra, absolute wavelength calibration must be performed to ensure that the line positions obtained for observed spectroscopic transitions reflect the accurate frequency, and, therefore, difference in energy levels of the molecular system. To perform absolute wavelength calibration, the iodine spectra are calibrated to reference spectra, and the calibrations are applied to the corresponding plasma spectra. Three methods of data calibration were used in for the analyses performed as part of this dissertation: calibration of the TS-ILS for NiCl data using the program SNEW\textsuperscript{17} and the reference data from Gerstenkorn et al.\textsuperscript{19}, the TS-ILS data for PtCl and DL-ILS data for GeH using the program PGOPHER\textsuperscript{20} developed by C. Western and the predicted I\textsubscript{2} transitions\textsuperscript{21} (TS-ILS) and the reference data from Salami and Ross\textsuperscript{22} (DL-ILS), and the DL-ILS data for CuO, PtF, PtCl, and CuOH using a Visual Basic for Applications (VBA) based macro-enabled Excel workbook (Pseudo-automated Iodine Calibration, i.e., PIC) developed by J. Harms and using the reference data of Salami and Ross.\textsuperscript{22} The measurement accuracy of the reference data from Gerstenkorn et al.\textsuperscript{19} and Salami and Ross\textsuperscript{22} is estimated to be ±0.003 cm\textsuperscript{-1}, and the average deviations between calibrated I\textsubscript{2} lines and reference I\textsubscript{2} lines are frequently within ±0.002 cm\textsuperscript{-1}. Due to a small degree of uncertainty in the application of the external calibration to the experimental plasma spectra, measurement accuracy of the ILS methods for isolated, well-resolved lines is 0.005 cm\textsuperscript{-1}. 
The calibration processes used by SNEW$^{17}$ and PGOPHER$^{20}$ are well documented and are only briefly described here. The process used by PIC is discussed in the following section. SNEW$^{17}$ uses two unblended I$_2$ lines selected by the user with known line positions to determine the position of the diffraction grating in the monochromator. The determined diffraction grating position is used with the empirically determined dispersion equation$^{14}$ to calibrate the I$_2$ spectra, and the calibration is verified by comparing the calibrated positions of unassigned lines to their corresponding reference line positions. Calibration by this method can take anywhere from 5-30 minutes per spectrum depending on the quality of the experimental I$_2$ spectra, number of available reference lines, and skill of the operator in interpreting the I$_2$ atlas. Using the approach in PGOPHER,$^{20}$ the experimental and reference data are displayed together with a vertical offset. Calibration lines are selected from the experimental data and assigned to the corresponding reference lines. The pixel position (corresponding to the diode-array channel) of the experimental line and the reference line positions are fit to a 2$^{nd}$ order polynomial, and the calibration is verified by examining the residuals between the assigned lines and their reference positions. Calibration by this method can take anywhere from 1-10 minutes per spectrum depending on the quality of the experimental and reference I$_2$ spectrum.

3.3 Pseudo-automated Iodine Calibration (PIC)

Both methods for data calibration described in the previous section can be quite tedious. The VBA-based Pseudo-automated Iodine Calibration (PIC) routine was developed to expedite the calibration process by automating the selection and
assignment of experimental I₂ peaks to be used for calibration. Once selected and assigned, the calibration of the experimental I₂ spectrum proceeds in much the same way as the PGOHPER\textsuperscript{20} calibration process described above, fitting the channel number and reference line positions to a 2\textsuperscript{nd} order polynomial using the LINEST function of Excel and plotting the residuals from the calibration for visual analysis.

The calibration routine used by PIC requires the initial plasma and iodine text files produced by SNEW.\textsuperscript{17} Three operations are performed using the I₂ file: the Savitzky-Golay 3\textsuperscript{rd} derivative is calculated from the provided 2\textsuperscript{nd} derivative, peak positions are determined from zero-crossings in the Savitzky-Golay 1\textsuperscript{st} and 3\textsuperscript{rd} derivatives, and appropriate peaks (defined below) are selected for data calibration.

Ideal peaks for calibration should be isolated, well-resolved, and of adequate signal-to-noise. Significant differences are observed between zero-crossings of the 1\textsuperscript{st} and 3\textsuperscript{rd} derivatives of a spectrum when transitions are not fully resolved. When peaks are overlapped, there can be multiple zero-crossings in the 3\textsuperscript{rd} derivative for each zero-crossing in the 1\textsuperscript{st} derivative. The signal-to-noise of a weak or partially resolved peak can be approximated by the magnitude of the 2\textsuperscript{nd} derivative at a given zero-crossing in the first derivative. As such, three criteria are used for peak selection: agreement between the 1\textsuperscript{st} and 3\textsuperscript{rd} derivative must be within ±0.003 cm\textsuperscript{-1}; there cannot be a 3\textsuperscript{rd} derivative zero-crossing between two zero-crossings in the 1\textsuperscript{st} derivative (i.e., a maximum and minimum); and the magnitude of the 2\textsuperscript{nd} derivative for a given peak must be greater than 40\% of the 2\textsuperscript{nd} derivative of the most intense unblended peak. All experimental I₂ peaks that meet these criteria are passed on to the automated calibration routine.
The transmission spectrum collected by Salami and Ross\textsuperscript{22} was provided in ASCII format in the Supplementary Materials of their publication. The Savitzky-Golay 1\textsuperscript{st} derivatives were calculated from that data using PGOPHER,\textsuperscript{20} and are included as a companion file to PIC because the relatively large size of the file (>25 MB) limits the operational speed of Excel. Portions of that data set pertinent to the experimental data are loaded into PIC, and peak positions are determined from zero-crossings in the 1\textsuperscript{st} derivative. As mentioned above, the initial channel/wavenumber assignments provided by SNEW\textsuperscript{17} are accurate to ±0.1 cm\textsuperscript{-1}, and the primary deviation is a simple offset in energy. The automated calibration routine compares the peak positions determined from the Savitzky-Golay 1\textsuperscript{st} derivatives and chosen by the selection routine to the peak positions from reference data from Salami and Ross.\textsuperscript{22} An offset is applied to the experimental positions in steps of 0.005 cm\textsuperscript{-1} from -2.5 cm\textsuperscript{-1} to +2.5 cm\textsuperscript{-1}, and the experimental peaks are assigned to the closest match from the reference line list. The validity of the assignment at each step is evaluated by multiplying the summed squares of the deviations between the experimental and reference line positions by the summed squares of the deviations between the normalized absorbances of the experimental and reference spectra (i.e., against both position and relative intensity). The lowest-multiplied summed-square value is taken to be the optimal offset, and the experimental data is calibrated by fitting the experimental channel position and reference peak position to a 2\textsuperscript{nd} order polynomial using the LINEST function. Calibrated peak positions are calculated from the determined polynomial, and residuals are calculated between the calibrated and reference line positions.
Misassigned lines are eliminated from the calibration set by application of the Grubb’s test, and the experimental data is refit until all outliers are eliminated. At this point, the calibrated experimental I\(_2\) spectrum and corresponding selection from the data of Salami and Ross\(^{22}\) are overlaid, and a plot of the residuals is provided (in addition to an root mean squared value for those residuals). The user visually inspects the calibration and can add additional peaks or remove misassigned peaks and recalibrate. Once a satisfactory calibration is obtained, the calibration is applied to the corresponding plasma spectrum and the next file in the series is automatically loaded into the program. The entire process takes \(~3\) seconds from when the experimental I\(_2\) file is loaded until the calibrated data is displayed.

In most cases when there are an adequate number of calibration lines, the signal-to-noise of the experimental I\(_2\) spectrum is adequate, and the reference data is of high quality, calibration of an individual spectrum can be accomplishes in \(<10\) seconds, marking a significant improvement over the other calibration methods. Additionally, agreement between the experimental and reference spectra is typically better than \(\pm 0.001\) cm\(^{-1}\), ensuring that the absolute calibration accuracy of the experimental data is entirely limited by the accuracy of the reference spectra (\(\pm 0.003\) cm\(^{-1}\)).

3.4 Concatenation of Spectral Data (ConSpect)

As mentioned previously, individual plasma spectra collected with the TS-ILS and DL-ILS systems are \(~5-7\) cm\(^{-1}\) wide. However, molecular transitions often span 50-200 cm\(^{-1}\). As such, a VBA routine was developed to concatenate the individually
calibrated plasma spectra. This routine plots each plasma spectrum with its overlapping neighbors. The overlapping regions are visually inspected, and a position is selected where overlap of spectral features is optimal and the text files of those spectra are concatenated at the position. If there are significant changes in intensity between spectra, or baseline curvature of the plasma spectrum is observed, corrections can be applied to ensure a smooth baseline, retaining qualitatively accurate relative intensities between the adjacent spectral regions. The output from ConSpect is a single absorption spectrum from a series of ILS spectra with an associated linelist calculated from the zero-crossings in the Savitzky-Golay 1st derivatives. This absorption spectrum may be loaded into PGOPHER\textsuperscript{20} where rotational branches can be identified and the experimental data can be fit to simulated transitions.
CHAPTER IV

GERMANIUM HYDRIDE

4.1 Introduction and Previous Studies of GeH

Germanium hydride is of interest because of its role in the production of germanium thin films produced from the dissociation of Germane, GeH$_4$\textsuperscript{23} The electronic structure of GeH has remained interesting to computational chemists because the comparison between experimentally determined values and theoretical predictions has shown the need for inclusion of several interactions to adequately model this simple molecular system.\textsuperscript{23,27} The incorporation of correlation between the 3$d^{10}$ electrons of Ge and spin-orbit coupling is necessary to accurately estimate the experimental transition energy and interpret the observations.\textsuperscript{23} With added computational sophistication, the deviation of the estimated energy for the experimental $B~^2\Sigma^+ - X^2\Pi_r$ transition from the observed value was from -6%\textsuperscript{24} to 0.6%.\textsuperscript{23} In light of these most recent calculations, Li \textit{et al.}\textsuperscript{23} suggest that disagreements between the computational predictions and the previous experimental observations of the $a~^4\Sigma^- - X^2\Pi_r$ transition merited further experimental measurements.

The spin-forbidden $a~^4\Sigma^- - X^2\Pi_r$ transition was weakly observed by Kleman and Werhagen in 1953 in emission from a King furnace using a Germanium containing graphite boat and 0.5 atm of H$_2$.\textsuperscript{28} The experimental photographs were not reproduced in the publication because "...[the transition's] weakness and the overlapping continuum do not permit of an acceptable reproduction." Budo and
Kovacs\textsuperscript{29} theoretically discussed $^4\Sigma - ^2\Pi$ transitions in a 1940 paper, and predicted that the relative intensities of 8 of the 12 possible branches for a $^4\Sigma$ - Hund’s Case (a) $^2\Pi_{1/2}$ transition will be non-zero, while 10 of the 12 possible transitions would have a non-zero relative intensity for a $^4\Sigma$ – Hund’s Case (a) $^2\Pi_{3/2}$ transition. In their experimental study, Kleman and Werhagen were able only to identify 4 branches connecting to the $X^2\Pi_{1/2}$ component and 5 branches connecting to the $X^2\Pi_{3/2}$ component, and no isotopically resolved features were observed (natural abundances are $^{70}\text{Ge}$ 20.84\%, $^{72}\text{Ge}$ 27.54\%, $^{73}\text{Ge}$ 7.73\%, $^{74}\text{Ge}$ 36.28\%, and $^{76}\text{Ge}$ 7.61\%). The identified branches were fit to obtain molecular constants for the $a$ $^4\Sigma$ state using a non-standard Hamiltonian developed by Budo. In 1966, Klynning\textsuperscript{30} attempted to record the $a$-$X$ transition in absorption, but was unsuccessful and instead reanalyzed the data of Kleman and Werhagen, fitting the term energies to Hougen’s energy expressions.\textsuperscript{31} No other studies have reported experimental observations of this spin-forbidden transition.

In contrast to the $a$ $^4\Sigma$ state, the $X^2\Pi_r$ ground state of GeH has been extensively studied experimentally, using Laser Magnetic Resonance (LMR) and diode laser spectroscopy techniques to examine pure rotational, fine-structure, and vibrational transitions of GeH and GeD in the IR.\textsuperscript{32-37} As an aside on notation, the $X$ state is a $^2\Pi_r$ state ($r$ as in regular) because the molecular orbital configuration for this state results in 1 unpaired electron in a $\pi$-orbital. Following Hund’s rules, the $\Omega=1/2$ component is, therefore, lower in energy than the $\Omega=3/2$ component. This energy ordering of the $\Omega$ components is inverted in a $^2\Pi$ state that results from 3 electrons in a $\pi$-orbital, and is referred to as a $^2\Pi_i$ state.
In 1993, Towle and Brown\textsuperscript{38} performed a comprehensive fit including all available experimental data for the $X^2\Pi_r$ ground state, which included transitions from all GeH isotopologues, excluding those involving tritium. The result is a set of molecular constants that effectively describe the ground state of the all isotopologues of the GeH molecule, not just the most abundant $^{74}\text{Ge}^1\text{H}$.

In this study, the $a\ ^4\Sigma^- - X^2\Pi_{1/2}$ transition was observed in absorption for the first time. All eight expected branches for this transition have been identified and the data is in reasonable agreement with the theoretical predictions of Li \textit{et al.}\textsuperscript{23} Results of this study have been published in the Journal of Chemical Physics.\textsuperscript{39}

\subsection*{4.2 Production of GeH}

The GeH molecules were produced in a plasma formed when a discharge current of 0.40-0.60 A DC was applied to a 150 mm long aluminum cathode located in the 1.1 m long resonator cavity of the DL-ILS system. The reaction chamber was maintained at a total pressure of 800 mtorr with a gas mixture of 62.5\% Ar, 25.0\% GeH\textsubscript{4}, and 12.5\% H\textsubscript{2}. Generation times used ranged from 50 to 200 \textmu s, resulting in effective pathlengths of 1.8-7.5 km for these measurements. It was found that spectral features due to GeH were very strong when the plasma was initially engaged but faded quickly, while features due to GeH\textsubscript{2} became more intense as the discharge continued. Consequently, to maximize the GeH signal, it was necessary to record spectra as single scans synchronized with plasma initiation, resulting in a relatively noisy background.

The $a\ ^4\Sigma^- - X^2\Pi_{1/2}$ transition of GeH was identified in the spectra between 16,000-16,600 cm\textsuperscript{-1}. The 15,000 - 15,550 cm\textsuperscript{-1} region was also investigated, but the
a \, ^4\Sigma - X^2\Pi_{3/2} \) transition reported in that region\textsuperscript{28} was not identified in the observed data.

4.3 Appearance of the Transition and Assignment of Rotational Branches

A portion of the electronic spectrum of GeH is displayed in Figure 4.1. The four branches for the \( a \, ^4\Sigma - X^2\Pi_{1/2} \) transition reported by Kleman and Werhagen,\textsuperscript{28} the \( ^PQ_1, QR_1, ^P\!^P_{21}, \) and \( ^R\!^P_{41} \) branches, were readily identifiable in the experimental data. The blue-degraded \( ^RP_{41} \) branch was somewhat difficult to identify because this branch overlaps the \( 0_0^0 \) band of the \( \tilde{A}^1B_1 - \tilde{X}^1A_1 \) transition of GeH\textsubscript{2}.\textsuperscript{40} The molecular constants from Smith \textit{et al}.\textsuperscript{40} for \( ^{70}\text{GeH}_2, \, ^{72}\text{GeH}_2, \, ^{74}\text{GeH}_2, \) and \( ^{76}\text{GeH}_2 \) were used to produce a simulated spectrum for the transition to prevent possible assignment of GeH\textsubscript{2} features to GeH. Isotopologue structure was partially resolved in the \( ^PQ_1 \) and \( ^P\!^P_{21} \) branches for 4 germanium isotopes: \( ^{70}\text{Ge}, \, ^{72}\text{Ge}, ^{74}\text{Ge} \) and \( ^{76}\text{Ge} \), as can be seen in Figure 7.2. Once these four branches were identified and assigned, a preliminary fit

![Figure 4.1: Excerpt of the ILS spectrum of GeH observed in the dissociation of GeH\textsubscript{4} in a plasma. This image is a compilation of \(~10\) individually collected spectra. The \( R_1, Q_1, \) and \( P_{21} \) branches of the \( a \, ^4\Sigma - X^2\Pi_{1/2} \) transition of \( ^{74}\text{GeH} \) are indicated for clarity. Many of the unassigned features have been attributed to GeH\textsubscript{2} upon comparison with the work of Smith \textit{et al}.\textsuperscript{40}](image)
of the data was performed using PGOPHER. Using the predicted branch structure from PGOPHER based on the initial fit, the four additional branches predicted to have appreciable intensity by Budo and Kovacs, the $^6Q_{21}, ^8Q_{21}, ^7R_{31}$, and $^5Q_{41}$ branches, were identified and assigned in the experimental data. In total, 79 transitions were assigned to $^{70}\text{GeH}$, $^{72}\text{GeH}$ and $^{74}\text{GeH}$. In all cases at low $J$ ($J'' < 5.5$), the isotopologue splitting in the branches is too small to be fully resolved at Doppler-limited resolution. However, in 5 of the 8 identified branches, at least 2 features are isotopically resolved. In total, 26 of the 79 assigned rotational transitions are isotopically resolved. The less abundant $^{76}\text{GeH}$ did not provide enough unique spectral features to justify a rotational analysis.

![Figure 4.2: Experimental plasma spectrum (converted to absorbance) of the $Q_1(8.5)$ and $P_{21}(9.5)$ lines of the $a\,^4\Sigma^+ - X\,^2\Pi_{1/2}$ transition of GeH. Peaks due to $^{70}\text{GeH}$, $^{72}\text{GeH}$, and $^{74}\text{GeH}$ are clearly identifiable and have been highlighted in blue with simulated line positions from the PGOPHER fit. There are weak shoulders due to $^{76}\text{GeH}$ to the blue of the main peak that are insufficiently resolved to justify analysis.](image-url)
4.4 Determination of Molecular Constants

Once branch assignments were obtained, the experimental data were fit to the Hamiltonian for a $^4\Sigma^- - {^2}\Pi_r$ transition using PGOPHER.\textsuperscript{20} The $X^2\Pi_r$ ground state constants were held fixed to the values provided by Towle and Brown\textsuperscript{38} from their comprehensive fit of IR spectra for all isotopologues of GeH. The spin-dependent interaction terms for $\Sigma$ states of quartet and higher multiplicity used by PGOPHER\textsuperscript{20} were developed by Brown and Milton\textsuperscript{41} and based on the initial work of Hougen.\textsuperscript{42} Hougen proposed that a $\Sigma$ state with even multiplicity has $S-\frac{1}{2}$ spin-spin parameters and $S+\frac{1}{2}$ spin-rotation parameters. A $^4\Sigma$ state would then have one spin-spin parameter, $\lambda_{SS}$, and two spin-rotation parameters, namely a first-order parameter, $\gamma$, and a third-order parameter, $\gamma_S$.

For spectral features that were unblended and fully resolved, line positions were assigned using the 1\textsuperscript{st} derivative zero crossings and were assigned an expected uncertainty of 0.005 cm\textsuperscript{-1} in the fit. Spectral features that were degraded but not fully resolved were assigned line positions manually and assigned an uncertainty of 0.01 cm\textsuperscript{-1}. Spectral features that were obscured or partially overlapped by GeH\textsubscript{2} features were assigned line positions as “best guesses” and given a statistical weight of 0.03 cm\textsuperscript{-1}. Of the 237 individual transitions included in the fit, 71 transitions were held to 0.005 cm\textsuperscript{-1}, 132 transitions were held to 0.01 cm\textsuperscript{-1}, and 34 were held to 0.03 cm\textsuperscript{-1}. For $^{74}$GeH, 45 of the 79 transitions were held to 0.005 cm\textsuperscript{-1}, however, only 18 transitions were fully resolved for $^{72}$GeH and 8 transitions were fully resolved for $^{70}$GeH.
To fit the line positions of the \(^{74}\text{GeH}\) \(a\,^4\Sigma^- - X\,^2\Pi_{1/2}\) transition, it was necessary to include \(\lambda_{SS}\), \(\gamma\), and \(\gamma_S\), as well as a term energy \((T)\), a rotational constant \((B)\), a centrifugal distortion term \((D)\), and a centrifugal spin-spin term \((\gamma_D)\) in the PGOPHER\(^{20}\) \(a\,^4\Sigma^-\) Hamiltonian. In the fit of \(^{70}\text{GeH}\) and of \(^{72}\text{GeH}\), \(\gamma_S\) was not determined within experimental uncertainty due to the more limited number of resolved lines available for the less abundant isotopologues and, as a consequence, was held fixed to the value determined for \(^{74}\text{GeH}\). The results of the fit are shown in Table 4.1; our results for \(^{74}\text{GeH}\) are compared with results from the work of Kleman and Werhagen\(^{28}\) and Klynning.\(^{30}\) The line positions, assignments, and residuals can be found in the Supplementary Materials of the published results, along with the correlation matrix for the fit.\(^{39}\)

### 4.5 Evaluation of Experimental Results

Results from the fit are in reasonable agreement with those from the work of Kleman and Werhagen\(^{28}\) and Klynning,\(^{30}\) however, the values obtained in this study

<table>
<thead>
<tr>
<th>(a,^4\Sigma^-) State</th>
<th>(T_0)</th>
<th>(B_0)</th>
<th>(D_0 \times 10^3)</th>
<th>(\lambda_{SS})</th>
<th>(\lambda_D \times 10^3)</th>
<th>(\gamma)</th>
<th>(\gamma_S \times 10^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{70}\text{GeH})</td>
<td>16751.9133(20)</td>
<td>6.769116(50)</td>
<td>0.45604(26)</td>
<td>9.7533(17)</td>
<td>0.373(29)</td>
<td>0.08063(12)</td>
<td>-0.378</td>
</tr>
<tr>
<td>(^{72}\text{GeH})</td>
<td>16751.7314(16)</td>
<td>6.767009(44)</td>
<td>0.45845(24)</td>
<td>9.7515(14)</td>
<td>0.387(23)</td>
<td>0.07924(11)</td>
<td>-0.378</td>
</tr>
<tr>
<td>(^{74}\text{GeH})</td>
<td>16751.5529(13)</td>
<td>6.764917(32)</td>
<td>0.45966(16)</td>
<td>9.7448(11)</td>
<td>0.471(17)</td>
<td>0.077934(81)</td>
<td>-0.378</td>
</tr>
</tbody>
</table>

\(^{74}\text{GeH}^b\) \(^{74}\text{GeH}^c\)

| \(^{74}\text{GeH}^b\) | 16758.0 | 6.775 | 0.472 | 6.4 | 0.04 |
| \(^{74}\text{GeH}^c\) | 16746.50(4) | 6.7554(5) | 0.460(1) | 6.51(2) | 0.041(1) | -2.8(1) |

| RMS\(^d\) | 0.0101 | 0.0078 | 0.0060 | 0.1059 |
| \(N^e\) | 67\(^c\) | 69\(^c\) | 67\(^c\) | 79 |

\(^d\) Held fixed to the value determined for \(^{74}\text{GeH}\).

\(^e\) Line positions for obscured features that were bracketed by identified transitions were roughly approximated and held to 0.03 \(\text{cm}^{-1}\) in the fit. The deviations between the fit and these approximate values were omitted from the RMS calculation due to their somewhat arbitrary nature.

\(^a\) Values from Kleman and Wehagen;\(^{28}\) the zero-point energy of the \(X\,^2\Pi_{1/2}\) state has been added to the term value provided in this reference.

\(^b\) Values from Klynning;\(^{30}\) the term energy from this reference has been modified so that the energy of the \(X\,^2\Pi_{1/2}\) state is set to zero.

\(^c\) RMS \(\sqrt{\sum (\text{Obs} - \text{Calc})^2 / N}\).
are determined to a much higher level of precision. Deviations between the values for parameters obtained in this study and the previously reported values that exceed the estimated standard deviations from the fit (reported in parentheses in Table 4.1) are not only due to the quality of the experimental apparatus available in 1953 in comparison to present instrumentation, but are also affected by slight differences in the Hamiltonian models used in the previous analyses.

The quality of the fit of the partially resolved isotope structure can be evaluated by comparing the ratios of the rotationally dependent parameters determined by the fit to the expected mass dependence of the parameter. The relationships between rotational constants and the reduced masses of the isotopologues were outlined by Dunham and summarized by Herzberg

\begin{align*}
B_{e}^{i} &= \frac{\mu}{\mu^{i}} B_{e} \quad (4.1) \\
D_{e}^{i} &= \left(\frac{\mu}{\mu^{i}}\right)^{2} D_{e} \quad (4.2)
\end{align*}

where the $i$-superscript denotes the less abundant isotopologue, $B_{e}$ values are equilibrium rotational constants, $D_{e}$ values are equilibrium centrifugal distortion constants, and $\mu$ values are reduced masses of the isotopologues. Using these equations, the molecular constants for less abundant isotopologues can be calculated from corresponding constants for the more abundant isotopologue. Because $^{74}$GeH is 1.32 times more abundant than $^{72}$GeH and 1.75 times more abundant than $^{70}$GeH, more transitions can be assigned to $^{74}$GeH than to the less abundant isotopes and many line positions assigned to these weaker features will be skewed slightly by the close-lying more abundant transition. To assess the quality of the fit determined for $^{70}$GeH and $^{72}$GeH, the values determined from the fit
for $B$ and $D$ are compared to the values calculated using equations 4.1 and 4.2 in Table 4.2. One standard deviation for the parameter from the fit is given in parentheses and the deviation between the determined and calculated value have been scaled to match these values. As is to be expected, the magnitude of deviations from the calculated values for $^{70}$GeH are larger than those for $^{72}$GeH. While both determined $B$ and $D$ values agree moderately with the expected isotopologue shift, the deviations are larger in scale than the reported uncertainties from the fit. This could be because the comparison values are specific to $v=0$ and equations 4.1 and 4.2 are only rigidly descriptive for equilibrium values, or the deviations could be due to the limited data for the lighter isotopologues. In most cases, isotopologue splitting was not observed below $J'' = 5.5$, which is already 237 cm$^{-1}$ above the ground state. The observed transition with the highest ground state rotational momentum was the $^q R_1(16.5)$, excited from a state 1915 cm$^{-1}$ higher than the ground state and only intense enough to be observed because the isotopologues have yet to separate in this branch. An experimental barrier was reached where

Table 4.2: The $B_0$ and $D_0$ values for $^{70}$GeH and $^{72}$GeH obtained from the PGOPHER$^{20}$ fit of the $^a \Sigma - X^2 \Pi_{1/2}$ transition of GeH are compared to values predicted from the Dunham equations and the experimental constants for $^{74}$GeH. In the third column, deviations between the determined and predicted values given in terms of $1\sigma$.

<table>
<thead>
<tr>
<th>$^a \Sigma$ State</th>
<th>$B_0$ from Fit$^a$</th>
<th>Calculated $B_0$ from $^{74}$GeH Value</th>
<th>(Fit-Calc)/($\sigma_{Fit}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{74}$GeH</td>
<td>6.764917 (32)</td>
<td>6.767446</td>
<td>-9.93</td>
</tr>
<tr>
<td>$^{72}$GeH</td>
<td>6.767009 (44)</td>
<td>6.770118</td>
<td>-20.04</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$D_0 \times 10^3$ from Fit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{74}$GeH</td>
</tr>
<tr>
<td>$^{72}$GeH</td>
</tr>
<tr>
<td>$^{70}$GeH</td>
</tr>
</tbody>
</table>

$^a$ All values in cm$^{-1}$. 


gentle discharge conditions enhanced the GeH signal but more intense discharge conditions favored formation of GeH₂. As a consequence, a more energetic discharge did not result in a more intense absorption signal from high $J''$ transitions. This experimental barrier is likely the reason no transitions were observed involving the $X^2\Pi_{3/2}$ state, which is 893 cm⁻¹ higher in energy than the $X^2\Pi_{1/2}$ state.

A recent computational paper suggested that discrepancies between experimental constants for the $a^4\Sigma^-$ state and their computational counterparts required more precise experimental data to adequately evaluate the quality of the different computational approaches used to model the lowest $4\Sigma^-$ state of GeH. The experimental $T_0, B_0, D_0$, and $r_0$ values are compared to the reported computational values from Refs. 23, 24, 25, & 27 in Table 4.3. When $\alpha_e$ values were not determined, $B_0, D_0$, and $r_e$ values were used instead of $v=0$ values. The $T_0$ values evaluate the combined accuracy of the excitation energy and vibrational frequency. The $B_0$ and $r_0$ values evaluate the accuracy of the calculated bond length, and the $D_0$ values evaluate the combined accuracy of the bond length and vibrational frequency. The term energy is best predicted by the CCSD(T)/CBS method from Li et al. and the MRCI+Q method without the Core-Valence Effect from Li et al., both accurate within 60 cm⁻¹ of the observed value. The inclusion of the Core-Valence Effect actually resulted in a comparable but slightly worse description of the system. The level of agreement between the predicted $T_0$ and determined excited state energy supports the excited state vibrational assignment as $v'=0$. Differences between predicted bond lengths and the derived value from the experimental $B_0$ values were
all in reasonable agreement, the worst being the CCSD(T)/CBS method of Li et al.\textsuperscript{27} with a percent difference of -1.52% from the determined value. No method predicted the centrifugal distortion constant particularly well, but the best case was the MRCI+Q & Core-Valence Effect method of Li et al.\textsuperscript{23} with a percent difference of 6.6% from the determined value. This is likely due to the reliance of the computational values provided in Table 4.3 upon the Kratzer Relationship\textsuperscript{3} and reported $B_e$ and $\omega_e$ values, rather than a direct computational determination of the centrifugal distortion effects.

The spin-spin parameter, $\lambda_{ss}$, is expected to have a direct contribution from spin-spin dipolar interactions and a second order spin-orbit contribution that results from interactions with nearby states with the same electron configuration.\textsuperscript{43} The $a^4\Sigma^-$, $A^2\Delta$, and $1^2\Sigma^+$ states arise from the $8\sigma^29\sigma^14\pi^2$ configuration.\textsuperscript{23} The isoconfigurational second order contribution to $\lambda_{ss}$, $\lambda_{so}$, can be estimated using the relationship for a $\sigma\pi^2$ configuration from Lefebvre-Brion and Field,\textsuperscript{44}

\[ \lambda_{so} = \frac{1}{6} \left[ \frac{[A(2\Pi,\sigma^2\pi)]^2}{E(2\Sigma^+)-E(4\Sigma^-)} \right] \]  \hspace{1cm} (4.3)

where, for GeH, $A(2\Pi,\sigma^2\pi)$ is the spin-orbit splitting of the $8\sigma^29\sigma^14\pi^1 X^2\Pi$ ground state, reported to be 893 cm$^{-1}$ by Towle and Brown,\textsuperscript{38} $E(2\Sigma^+)$ is computed to be 32,293 cm$^{-1}$ by Li et al.,\textsuperscript{23} and $E(4\Sigma^-)$ is determined to be 15,810 cm$^{-1}$ in this work. The resulting $\lambda_{so}$ of 8.05 cm$^{-1}$ is of similar magnitude to the determined $\lambda_{so}$ value of 9.75 cm$^{-1}$ and indicates that the direct spin-spin interaction in the $a^4\Sigma^-$ state is quite small.
4.6 Conclusions

An intracavity dye-laser absorption spectrometer has been used to record the absorption spectrum of the spin-forbidden \(a^4\Sigma^+ - X^2\Pi_{1/2}\) transition of GeH. Isotopologue structure was observed, and a rotational analysis was performed on transitions of the three most abundant isotopologues: \(^{70}\)GeH, \(^{72}\)GeH, and \(^{74}\)GeH. The obtained rotational constants for the less abundant isotopes are found to be in reasonable agreement with the values predicted from the Dunham equations. The vibrational assignment of this transition, which was ambiguous in the initial report, has been assigned as the (0-0) band due to the strong agreement between theory and experiment. The results of this work have been published in the Journal of Chemical Physics.\(^{39}\)

<table>
<thead>
<tr>
<th>(a^4\Sigma^+) State of (^{74})GeH</th>
<th>(T_0)</th>
<th>(B_0)</th>
<th>(D_0 \times 10^3)</th>
<th>(r_0 (\text{Å}))</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Experiment</strong></td>
<td>16751.5524</td>
<td>6.764912</td>
<td>0.45960</td>
<td>1.5831</td>
</tr>
<tr>
<td><strong>Li et al. 2015(^{23})</strong></td>
<td>16644.98</td>
<td>6.8744</td>
<td>0.48995</td>
<td>1.570</td>
</tr>
<tr>
<td>(\text{MRCI + Q &amp; Core-Valence Effect})</td>
<td>16696.77</td>
<td>6.8519(^c)</td>
<td>0.3406(^c)</td>
<td>1.573(^c)</td>
</tr>
<tr>
<td>(\text{MRCI + Q, No Core-Valence Effect})</td>
<td>16800.65</td>
<td>6.976(^c)</td>
<td>0.3901(^c)</td>
<td>1.559(^c)</td>
</tr>
<tr>
<td><strong>Li et al. 2013(^{27, b})</strong></td>
<td>15069.5</td>
<td>6.806(^c)</td>
<td>0.3980(^c)</td>
<td>1.578(^c)</td>
</tr>
<tr>
<td><strong>Bruna and Grein 2001(^{25})</strong></td>
<td>(\text{CCSD(T)/CBS})</td>
<td>15069.5</td>
<td>6.806(^c)</td>
<td>0.3980(^c)</td>
</tr>
<tr>
<td><strong>Balasubramanian and Li 1988(^{24})</strong></td>
<td>(\text{MRCDI/Full CI})</td>
<td>14732.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>MCSCF (CAS SCF)+CI</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)Calculated using the Kratzer Relationship \(D=4B\omega^2\).

\(^b\)Excitation Energy and Bond Length from the CCSD(T)/CBS, Harmonic frequency from the CCSD(T)/cc-pV5Z level of theory.

\(^c\)Values represent equilibrium constants.

\(^d\)All values reported in cm\(^{-1}\).
CHAPTER V
COPPER OXIDE

5.1 Introduction and Previous Studies of CuO

The electronic spectrum of CuO has been studied extensively, with more than 25 publications over the past 50 years. In a 1989 review on the spectroscopy of 3d transition metal oxides,\textsuperscript{45} Anthony Merer summarized the experimental studies on CuO that were available at the time. The initial studies indicate that the ground state of CuO is $^{2}\Pi_{i}$ in character, resulting primarily from the $(8\sigma)^2(9\sigma)^2(4\pi)^3$ configuration, with some CuO 3$d$ and 4$p$ character in the 4$\pi$ orbital.\textsuperscript{45} The Kronig symmetry of the excited $^{2}\Sigma$ states is ambiguous in the early literature, but identification of the lowest lying [7.7] $Y^{2}\Sigma^{+}$ state from low resolution work, and the assumption that this state is in pure precession with the ground state removed this ambiguity.\textsuperscript{45}

There have been four additional experimental studies of CuO since that review: high resolution Fourier-Transform emission spectroscopy (FTS) of the [7.7] $Y^{2}\Sigma^{+} - X^{2}\Pi_{i}$ transition of CuO in the infrared by O’Brien et al.\textsuperscript{46} in 1996, mm- and sub-mm microwave absorption spectroscopy of the pure rotational spectrum of CuO by Steimle et al.\textsuperscript{47} in 1997, moderate resolution laser induced fluorescence (LIF) spectroscopy of the (0,0), (1,0), (2,0), and (3,0) bands of the [16.3] $X^{2}\Sigma^{-} - X^{2}\Pi_{i}$ transition of CuO by Jin et al.\textsuperscript{48} in 2002, and field-free and optical Stark molecular-beam laser induced fluorescence (MB-LIF) spectroscopy of the (0,0) band of the [16.3] $A^{2}\Sigma^{-} - X^{2}\Pi_{3/2}$ transition of CuO by Zhuang et al.\textsuperscript{49} in 2010. O’Brien et al.\textsuperscript{46} showed that the $Y^{2}\Sigma^{+}$ state must be interacting with excited $^{2}\Pi$ states due to a large
negative spin rotation parameter, $\gamma$. This large $-\gamma$ precludes the $[7.7] \, Y^2\Sigma^+$ state from forming a unique perturber pair with the $X^2\Pi_i$ state, indicating that the pure precession assumption does not strictly apply.\textsuperscript{46} Steimle et al.\textsuperscript{47} determined a complete set of magnetic hyperfine, electric quadrupole, and nuclear spin-rotation parameters for the $^{63}\text{Cu}$ nucleus from their pure rotational data. Jin et al.\textsuperscript{48} determined vibrational constants for the $[16.3] \, A^2\Sigma^-$ state and measured fluorescence lifetimes for $v'=0$-3. However, due to their limited measurement accuracy of $\sim 0.07 \text{ cm}^{-1}$, the determined rotational constants for the $A$ state did not mark a significant improvement from the original rotational analysis of the $[16.3] \, A^2\Sigma^- - X^2\Pi_i$ transition observed in emission by Appelblad and Lagerqvist in 1974.\textsuperscript{50} Finally, Zhuang et al.\textsuperscript{49} determined improved rotational constants for the $[16.3] \, A^2\Sigma^-$ state in the analysis of their field-free spectra, and determined dipole moments for the $[16.3] \, A^2\Sigma^-$ state and $X^2\Pi_{3/2}$ states of CuO in the analysis of their Stark spectra. The early literature on CuO extensively debated the sign of the $\Lambda$-doubling parameter $p$ of the $X^2\Pi_i$ state. Unfortunately, the ambiguity of $\Lambda$-doubling has persisted into these recent publications concerning the sign of the $\Lambda$-doubling parameter $q$ of the ground state of CuO. O’Brien et al.\textsuperscript{46} determined $q$ to be negative, but Steimle et al.\textsuperscript{47} and Zhuang et al.\textsuperscript{49} reported $q$ as a positive value.

Despite the extensive experimental study of CuO, analyses have been restricted to $^{63}\text{CuO}$, despite of the fact that $^{63}\text{Cu}$ and $^{65}\text{Cu}$ have natural abundances of 69\% and 31\%, respectively. In this work, high resolution absorption spectra of the $[16.3] \, A^2\Sigma^- - X^2\Pi_i$ transition of CuO have been recorded using intracavity laser spectroscopy (ILS). Transitions due to (0,0) band of $^{65}\text{CuO}$ are clearly identifiable in
the spectra. The FTS data\textsuperscript{46} were been retrieved from the archive for the McMath-Pierce Solar Telescope associated with Kitt Peak National Observatory.\textsuperscript{51} Several additional vibrational bands of the $[7.7] \ Y^2\Sigma^+ - X^2\Pi_i$ transition were identified in the FTS data, including the (1,0), (0,0), and (0,1) bands of $^{65}$CuO. The ILS, FTS\textsuperscript{46}, microwave\textsuperscript{47}, and MB-LIF\textsuperscript{49} data were fit simultaneously to a mass-independent Dunham type Hamiltonian with PGOPHER.\textsuperscript{20} The results of this analysis indicate a Cu-isotope dependent shift in the electronic energy for the $[7.7] \ Y^2\Sigma^+ - X^2\Pi_i$ transition. The results also indicate that the $q$ parameter of the ground state is negative. The results of this study have been submitted for publication in the Journal of Molecular Spectroscopy.\textsuperscript{52}

5.2 Production of CuO

For the ILS measurements, the CuO molecules were produced in RF discharges formed when 0.30-0.40 A was applied to a Cu hollow cathode in ~500 mTorr H\textsubscript{2} with a trace of O\textsubscript{2} as the oxide source. The hollow cathode was located within the resonator cavity of the DL-ILS system. Effective pathlengths from 0.5 to 1.0 km were utilized for these measurements. The concatenated ILS spectra for the $[16.3] \ A^2\Sigma^+ - X^2\Pi_{3/2}$ and $[16.3] \ A^2\Sigma^+ - X^2\Pi_{1/2}$ subbands are provided in Figure 5.2.

The FTS data was described in its initial publication.\textsuperscript{46} The data was retrieved from the FTP archive for the McMath-Pierce Telescope.\textsuperscript{51} A processed XY date file for the FTS spectrum was extracted using the Gremlin program from J. Brault. The calibration of the FTS data was verified to ±0.001 cm\textsuperscript{-1} using the Ne emission lines in the FTS spectrum and the Ne line positions reported by Sansonetti \textit{et al.}\textsuperscript{53}
5.3 Mass-Independent Dunham-Type Hamiltonian for CuO

The ILS, FTS\textsuperscript{46}, MB-LIF\textsuperscript{49}, and microwave\textsuperscript{47} data for CuO were fit to a mass-independent Dunham-type Hamiltonian using the variable/constraint method for PGOPHER\textsuperscript{20} outlined by Breier et al.\textsuperscript{54,55} With this approach, custom Variables objects are added to the .pgo file for the fitting process, and a series of constraints are incorporated into the PGOPHER input file to define the default band-by-band constants used by PGOPHER in terms of a comprehensive equation. The

Figure 5.1: Intracavity laser absorption spectra of the [16.3] $A^3\Sigma - X^3\Pi_i$ transition of CuO.
The comprehensive equation used in this study is the expression derived by Le Roy\textsuperscript{13} from the initial expressions of Dunham\textsuperscript{5}, Ross \textit{et al.}\textsuperscript{6}, and Watson\textsuperscript{7}:

\[
E(v, j) = \sum_{l,m}[v_{l,m}^1 + \left(\frac{\Delta M_A}{M_A} \delta_{l,m}\right)_A + \left(\frac{\Delta M_B}{M_B} \delta_{l,m}\right)_B] \left(\frac{\mu_1}{\mu_a}\right)^{m+l} \left(v + \frac{1}{2}\right)^l (N^2)^m 
\]

(5.1)

where \(E\) is the energy of a rovibrational level, \(v\) is the vibrational quantum number, \(J\) is the rotational quantum number, \(l\) and \(m\) refer to the degree of vibrational and rotational dependence of a given \(Y_{l,m}\) parameter, \(1\) and \(\alpha\) refer to the reference (\(^{63}\text{CuO}\)) and minor (\(^{65}\text{CuO}\)) isotopologues of the molecule, \(A\) and \(B\) refer to the different atoms of the molecule, \(\Delta M\) is the difference in mass between the reference and minor isotope of the substituted atom, \(M\) is the isotopic mass, \(\delta_{l,m}\) are mass dependent Born-Oppenheimer breakdown parameters, \(\mu\) refers to the reduced mass, and \(N^2\) is the rotational operator of the effective Hamiltonian. This equation was expanded to include parameters, \(P_{l,m}\), to describe spin-orbit, \(\Lambda\)-doubling, and spin-rotation interactions:

\[
A^\alpha_v = A^\alpha_{00} + A^\alpha_{10} \left( v + \frac{1}{2} \right) + A^\alpha_{20} \left( v + \frac{1}{2} \right)^2 
\]

(5.2)

\[
A^\alpha_B v = A^\alpha_{01} + A^\alpha_{11} \left( v + \frac{1}{2} \right) + A^\alpha_{21} \left( v + \frac{1}{2} \right)^2 
\]

(5.3)

\[
p^\alpha_v = p^\alpha_{01} + p^\alpha_{11} \left( v + \frac{1}{2} \right) + p^\alpha_{21} \left( v + \frac{1}{2} \right)^2 
\]

(5.4)

\[
p^\alpha_B v = p^\alpha_{02} + p^\alpha_{12} \left( v + \frac{1}{2} \right) + p^\alpha_{22} \left( v + \frac{1}{2} \right)^2 
\]

(5.5)

\[
q^\alpha_v = q^\alpha_{01} + q^\alpha_{11} \left( v + \frac{1}{2} \right) + q^\alpha_{21} \left( v + \frac{1}{2} \right)^2 
\]

(5.6)

\[
\gamma^\alpha_v = \gamma^\alpha_{01} + \gamma^\alpha_{11} \left( v + \frac{1}{2} \right) + \gamma^\alpha_{21} \left( v + \frac{1}{2} \right)^2 
\]

(5.7)

\[
\gamma^\alpha_B v = \gamma^\alpha_{02} + \gamma^\alpha_{12} \left( v + \frac{1}{2} \right) + \gamma^\alpha_{22} \left( v + \frac{1}{2} \right)^2 
\]

(5.8)
where the $P_{l,m}$ parameters follow the mass scaling of equation 5.1, and the $P_v$ parameters correspond to the default band-by-band parameters used by PGOPHER. In addition to mass scaling, the magnetic hyperfine parameters and the electric quadrupole coupling constant $eQq_0$ were isotopically scaled according the ratio of their nuclear moments ($\mu_{\text{Nuc}}$) and nuclear quadrupole moment $Q$, respectively. For example, the hyperfine coupling parameter $b$ is expressed as

$$b^\alpha = \frac{\mu_{\text{Nuc}}}{\mu_{\text{Nuc}}} [b_0^1 + b_1^1 \left( \frac{\mu_1}{\mu_0} \right)^{0+\frac{1}{2}} (v + \frac{1}{2})]$$

and $eQq_0$ is expressed as

$$eQq_0^\alpha = \frac{Q_1}{Q_0} eQq_0^1$$

The values for $\mu_{\text{Nuc}}$ were taken to be 2.22329 and 2.38167 $\mu_N$ for $^{63}$Cu and $^{65}$Cu, and the values for $Q$ were taken to be -21.1 and -19.5 e fm$^2$.

When fitting the hyperfine structure of the $X^2\Pi$ ground state, a high degree of correlation was observed when simultaneously floating the Frosch and Foley $a_{00}, b_{00}, c_{00},$ and $d_{00}$ parameters, which are the default hyperfine parameters used by PGOPHER. To combat this issue (and to conform more closely to the previous work from Steimle et al.), the on diagonal $h_\Omega$ terms were incorporated as variables in the .pgo file, where

$$h_\Omega = a_{00}\Lambda + (b_{00} + c_{00})\Sigma$$

where $\Omega$ refers to the substate of the $^2\Pi$ electronic state, $\Lambda$ is the orbital angular momentum (i.e., 1), and $\Sigma$ is the projection of the spin-momentum (i.e., -1/2 for $\Omega=1/2$ and +1/2 for $\Omega=3/2$). In the fit, $h_{1/2}, h_{3/2}, b_{00},$ and $d_{00}$ were floated, while $a_{00}$ and $c_{00}$ were constrained to the expressions.
\[ a_{00} = \left( h_{1/2} + h_{3/2} \right) / 2 \]  
\[ c_{00} = 2 \left( a_{00} - \frac{1}{2} b_{00} - h_{1/2} \right) \]

The floated \( b_{00} \) and \( d_{00} \) parameters and constrained \( a_{00} \) and \( c_{00} \) parameters were used to derive the vibrationally dependent Frosch and Foley parameters \( a_v, b_v, c_v, \) and \( d_v \) for each vibrational level of the \( X^2\Pi_i \) state. Only \( b \) was determined for the \( Y \) and \( A \) states, so the additional parameters and constraints were not necessary to treat the hyperfine interactions of those states.

5.4 Fitting the Experimental Data

The various data sets included in the simultaneous Dunham-type fit of CuO were weighted according to their estimated measurement accuracies. An estimated measurement accuracy was not explicitly provided by Steimle et al.\(^{47}\) The fully resolved, unblended lines from the mm- and sub-mm microwave absorption transitions were fit with a root mean squared (RMS) of 22 kHz in the original analysis,\(^{47}\) so these line positions were assigned an uncertainty of 25 kHz (61 transitions). The transitions that were marked as blended or omitted in the initial analysis were assigned an uncertainty of 500 kHz to avoid undue influence in the fitting process (55 transitions). The MB-LIF data were assigned an uncertainty equal to the estimated measurement accuracy of 0.001 cm\(^{-1}\) (77 transitions).\(^{49}\) Unblended lines in the ILS data were assigned an uncertainty of 0.005 cm\(^{-1}\), blended lines were assigned an uncertainty of 0.01 cm\(^{-1}\), and line positions for obscured transitions within a branch were estimated and assigned an uncertainty of 0.03 cm\(^{-1}\). There were 504 transitions identified for the (0,0) band of the [16.3] \( A^2\Sigma - X^2\Pi_i \) transition of \(^{63}\)CuO, 354 transitions for the (1,1) band of \(^{63}\)CuO,
and 354 transitions for the (0,0) band of $^{65}$CuO. The FTS data were assigned uncertainties based on the signal-to-noise of individual vibrational bands of the [7.7] $Y^2\Sigma^+ - X^2\Pi_i$ transition. The (0,0) and (0,1) bands were observed with significant transition intensity in the emission spectra and were assigned an uncertainty of 0.003 cm$^{-1}$. The (0,2), (1,1), (1,2), (1,3), (2,1), and (2,3) bands were observed much more weakly and had significant overlap with more intense transitions and were assigned an uncertainty of 0.0045 cm$^{-1}$ to reflect the larger relative uncertainty in determination of line positions for these bands. Only the intense Q-branches were identified for the (0,2), (1,0), (2,1), and (2,3) bands for both isotopologues, as well as the (0,1) band of the $^{65}$CuO. In total, 11,612 transitions were identified for the [7.7] $Y^2\Sigma^+ - X^2\Pi_i$ transition of CuO, and the global data set included 12,994 observations.

As mentioned in the introduction, the sign of the $\Lambda$-doubling parameter $q$ for the $X^2\Pi_i$ state of CuO is ambiguous in the literature. The available experimental data was examined in order to find a set of combination differences that could remove the ambiguity and definitively assign the sign of $q$. The $^rR_2$ and $^pP_2$ branches from the (0,0) band of the [16.3] $A^2\Sigma^- - X^2\Pi_i$ transition were well resolved and extended from $^rR_2(4.5)$ to $^rR_2(55.5)$ and $^pP_2(2.5)$ to $^pP_2(51.5)$. Ground state combination differences were calculated from the $^rR_2(J''$) and $^pP_2(J''+2)$ lines and are in agreement (RMS=0.007 cm$^{-1}; N=7$) with the $\Delta_2F''$ levels obtained from the pure rotational transitions between e-levels of the $X^2\Pi_{1/2}$ substate, for which the sign of $p$ (and, therefore, the e/f parity) has been firmly established. The differences between the $^rR_2(J''+1)$ and $^pP_2(J''+1)$
lines were then calculated and found to be in agreement with the differences between the $^{9}R_{21}(J''+1)$ and $^{9}P_{21}(J''+1)$ lines (RMS=0.006 cm$^{-1}$; N=40).

This agreement definitively assigns $e$-parity to the $^{9}R_{21}$ and $^{9}P_{21}$ branches of the [16.3] $A^2\Sigma^+ - X^2\Pi_i$ transition, and, as a result, the sign of $q$ for the $X^2\Pi_i$ ground state must be negative. Consequently, the $e/f$ assignments in the microwave and MB-LIF data for transitions involving the $X^2\Pi_{3/2}$ state have been reversed from their original assignments.

A limited preliminary fit was performed to evaluate how the representation of the experimental data was affected by reversing the sign of $q$. The limited data set included the microwave and MB-LIF data (initially fit with a positive $q$), FTS data for the (0,0) band of the [7.7] $Y^2\Sigma^+ - X^2\Pi_i$ transition of $^{63}$CuO (initially fit with a negative $q$), and the ILS data for the (0,0) band of the [16.3] $A^2\Sigma^- - X^2\Pi_i$ transition of $^{63}$CuO.

### Table 5.1: Results from the fit of the mm- and sub-mm data with the experimental data for the (0,0) bands of the $Y-X$ and $A-X$ transitions of CuO. The microwave data was initially fit with $q$ as a positive value, but combination differences between branches of the $A-X$ transition confirm $q$ to be negative. The parameters from the original analysis of the mm- and sub-mm wave spectra are provided for comparison. All values reported in cm$^{-1}$ unless otherwise indicated.

<table>
<thead>
<tr>
<th>X$^2\Pi_i$ State (v=0)</th>
<th>Preliminary Fit</th>
<th>Steimle et al.$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_0$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$B$</td>
<td>0.442070085 (18)</td>
<td>0.44206832 (3)</td>
</tr>
<tr>
<td>$D \times 10^6$</td>
<td>0.860884 (67)</td>
<td>0.861 (1)</td>
</tr>
<tr>
<td>$A$</td>
<td>-276.15972 (13)</td>
<td>-276.15743</td>
</tr>
<tr>
<td>$A_0$</td>
<td>0.001713197 (17)</td>
<td>0.00171313 (2)</td>
</tr>
<tr>
<td>$p$</td>
<td>0.01394615 (84)</td>
<td>0.013652 (3)</td>
</tr>
<tr>
<td>$p_0 \times 10^6$</td>
<td>-0.06380 (18)</td>
<td>0.0863 (5)</td>
</tr>
<tr>
<td>$q \times 10^3$</td>
<td>-0.01726 (22)</td>
<td>-0.01694 (29)$^b$</td>
</tr>
<tr>
<td>$b$</td>
<td>0.004544 (39)</td>
<td>0.00449 (11)</td>
</tr>
<tr>
<td>$eQq$</td>
<td>-0.00038 (10)</td>
<td>-0.00056 (18)</td>
</tr>
<tr>
<td>$h_{1/2}$</td>
<td>0.014369 (61)</td>
<td>0.0144 (11)</td>
</tr>
<tr>
<td>$h_{3/2}$</td>
<td>-0.000181 (41)</td>
<td>-0.000121 (42)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Y$^2\Sigma^*$ State (v=0)</th>
<th>Preliminary Fit</th>
<th>Steimle et al.$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{00}$</td>
<td>7715.47017 (19)</td>
<td></td>
</tr>
<tr>
<td>$B$</td>
<td>0.47360632 (26)</td>
<td></td>
</tr>
<tr>
<td>$D \times 10^6$</td>
<td>0.811143 (95)</td>
<td></td>
</tr>
<tr>
<td>$\gamma$</td>
<td>-0.0887323 (84)</td>
<td></td>
</tr>
<tr>
<td>$\gamma_0 \times 10^6$</td>
<td>0.3985 (38)</td>
<td></td>
</tr>
<tr>
<td>$b$</td>
<td>0.12004 (12)</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>A$^2\Sigma$ State (v=0)</th>
<th>Preliminary Fit</th>
<th>Steimle et al.$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{00}$</td>
<td>16353.95386 (11)</td>
<td></td>
</tr>
<tr>
<td>$B$</td>
<td>0.43144831 (56)</td>
<td></td>
</tr>
<tr>
<td>$D \times 10^6$</td>
<td>0.80049 (26)</td>
<td></td>
</tr>
<tr>
<td>$\gamma$</td>
<td>-0.195376 (14)</td>
<td></td>
</tr>
<tr>
<td>$b$</td>
<td>-0.02892 (14)</td>
<td></td>
</tr>
</tbody>
</table>

### RMS Values

<table>
<thead>
<tr>
<th>mm-/sub-mm</th>
<th>28 kHz</th>
<th>25 kHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>MB-LIF A-X</td>
<td>0.00097</td>
<td></td>
</tr>
<tr>
<td>ILS A-X</td>
<td>0.00573</td>
<td></td>
</tr>
<tr>
<td>FTS Y-X</td>
<td>0.00288</td>
<td></td>
</tr>
</tbody>
</table>

| Fit Error | 0.9417 |

$a$Ref. 47.

$^b$Fitted parameter was $b_f = b + 2/3 c$. 

The e/f assignments for the data subsets were assigned appropriately for both a positive and negative q value, and a “best fit” was performed using the band constants in PGOPHER\textsuperscript{20} (i.e., not Dunham parameters). The results of these fits with ±q indicate that while a moderate fit can be obtained with +q, centrifugal distortion terms $p_D$, $p_H$, and $q_D$ are absolutely necessary to fit the high J” lines of the A-X transition. In contrast, when the data is fit with −q, the Λ-doubling of the ground state is so well described that no centrifugal distortion corrections to Λ-doubling are required to describe the limited data set. The results of the preliminary fit are provided in Table 5.1 with the constants from Steimle et al.\textsuperscript{47} for comparison.

With the sign of q firmly established, microwave, MB-LIF, FTS, and ILS data were fit to a mass-independent Dunham-type Hamiltonian. In total 46 parameters were required to fit the 12,994 observations. While determined reasonably in the preliminary fit, the nuclear quadrupole coupling constant $eQq_0$ was not determined in the simultaneous fit. This is likely due to the fact that this parameter is related only to the low J” transitions well determined in the microwave data, and its contribution is diluted by the large number of transitions in the FTS and ILS data sets. Consequently, $eQq_0$ was held fixed to the value from the preliminary fit. The vibrational mass dependence of the [16.3] $A^{2}\Sigma^-$ state could not be determined adequately in the fit because included transitions only involved $v=0$ and 1. As a result, independent $T_0$ values were fit for $^{63}\text{CuO}$ and $^{65}\text{CuO}$, and Δ$G_{1/2}$ was fit for $^{63}\text{CuO}$. The 45 floated parameters and 1 fixed parameter from the simultaneous fit are summarized in Table 5.2. The weighted fit error for the simultaneous fit was 1.087.
5.5 Comparison to Literature

In general the parameters determined in this fitting process agree quite well with the corresponding constants available in the literature. The notable exceptions are \( q \) for the \( X^2\Pi_i \) state for which the sign has been reversed, and \( c \) and \( H \) for the \([7.7]\)^2\Sigma^+ \) state were not required/adequately determined in the simultaneous fit. A comparison of the parameters determined in this work and their corresponding

<table>
<thead>
<tr>
<th>( X^2\Pi_i ) State</th>
<th>( Y^2\Sigma^+ ) State</th>
<th>( A^2\Sigma ) State</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Y_{00} )</td>
<td>( 0^b )</td>
<td>( \Delta\delta_{00}(\text{Cu}) )</td>
</tr>
<tr>
<td>( Y_{10} )</td>
<td>638.21663(69)</td>
<td>( Y_{10} )</td>
</tr>
<tr>
<td>( Y_{20} )</td>
<td>-4.47211(41)</td>
<td>( Y_{20} )</td>
</tr>
<tr>
<td>( Y_{30} )</td>
<td>0.023675(71)</td>
<td>( Y_{30} )</td>
</tr>
</tbody>
</table>

| \( A_{00} \) | 0.0443590(15) | \( A_{01} \) | 0.007095(38)c | \( A_{01} \) | 0.0906336(64) | \( A_{01} \) | 0.109837(16) | \( A_{01} \) | 0.119837(16) | \( A_{01} \) | 0.128837(16) |
| \( A_{10} \) | 4.03745(32) | \( A_{11} \) | 1.739563(52) | \( A_{11} \) | -0.052690(93) | \( A_{11} \) | 0.004797(32) | \( A_{11} \) | 0.007095(38)c | \( A_{11} \) | 0.007095(38)c |
| \( A_{20} \) | 0.004797(32) | \( A_{21} \) | 0.004797(32) | \( A_{21} \) | 0.014444(16) | \( A_{21} \) | 0.0906336(64) | \( A_{21} \) | 0.109837(16) | \( A_{21} \) | 0.119837(16) |
| \( A_{01} \times 10^3 \) | 1.739563(52) | \( A_{11} \times 10^3 \) | -0.052690(93) | \( A_{11} \times 10^3 \) | 0.004797(32) | \( A_{11} \times 10^3 \) | 0.007095(38)c | \( A_{11} \times 10^3 \) | 0.007095(38)c | \( A_{11} \times 10^3 \) | 0.007095(38)c |
| \( Y_{11} \times 10^3 \) | -4.90981(32) | \( Y_{11} \times 10^3 \) | -5.109837(16) | \( Y_{11} \times 10^3 \) | -0.052690(93) | \( Y_{11} \times 10^3 \) | 0.004797(32) | \( Y_{11} \times 10^3 \) | 0.007095(38)c | \( Y_{11} \times 10^3 \) | 0.007095(38)c |
| \( Y_{21} \times 10^3 \) | 0.026052(63) | \( Y_{21} \times 10^3 \) | -0.01393(22) | \( Y_{21} \times 10^3 \) | 0.004797(32) | \( Y_{21} \times 10^3 \) | 0.007095(38)c | \( Y_{21} \times 10^3 \) | 0.007095(38)c | \( Y_{21} \times 10^3 \) | 0.007095(38)c |
| \( Y_{02} \times 10^6 \) | -0.861570(89) | \( Y_{02} \times 10^6 \) | -0.80477(13) | \( Y_{02} \times 10^6 \) | -0.01393(22) | \( Y_{02} \times 10^6 \) | 0.004797(32) | \( Y_{02} \times 10^6 \) | 0.007095(38)c | \( Y_{02} \times 10^6 \) | 0.007095(38)c |
| \( Y_{12} \times 10^6 \) | 0.001169(88) | \( Y_{12} \times 10^6 \) | -0.01284(16) | \( Y_{12} \times 10^6 \) | 0.004797(32) | \( Y_{12} \times 10^6 \) | 0.007095(38)c | \( Y_{12} \times 10^6 \) | 0.007095(38)c | \( Y_{12} \times 10^6 \) | 0.007095(38)c |

| \( A_{00} \times 10^3 \) | -278.15452(22) | \( A_{10} \times 10^3 \) | 4.03745(32) | \( A_{20} \times 10^3 \) | 0.004797(32) | \( A_{30} \times 10^3 \) | 0.007095(38)c | \( A_{40} \times 10^3 \) | 0.007095(38)c | \( A_{50} \times 10^3 \) | 0.007095(38)c |

**Hyperfine Parameters**

| \( a_{00} \) | 0.007095(38)c | \( b_{00} \) | 0.12095(12) | \( b_{00} \) | -0.02892(17) |
| \( b_{00} \) | -0.01722(23) | \( b_{10} \) | -0.00146(12) | \( b_{10} \) | -0.02892(17) |

---

*a* All values reported in cm⁻¹.

*b* Defined as zero in the fit.

*c* These values are determined from fitted \( h_{1/2} \), \( h_{3/2} \), and \( b_{00} \) parameters and equations (12) and (13). The values in parentheses represent the propagated error from the fitted parameters.

*d* Held fixed to the value determined in the fit of the pure rotational and (0,0) bands of the \( Y-X \) and \( A-X \) transitions of \(^{63}\text{CuO}\). See Table 5.1.
literature values is provided in Table 5.3.

5.6 Potential Energy Surfaces for CuO

The equilibrium parameters from the Dunham fit for the $[7.7] Y^2 Σ^+$ and $X^2 Π_i$ states of $^{63}\text{CuO}$ were used to produce potential energy curves with the Rydberg-Klein-Rees (RKR) method, implemented in a program provided to the authors by J. Tellinghuisen. These potential energy curves provide further evidence that the $[7.7] Y^2 Σ^+$ and $X^2 Π_i$ states cannot form a unique perturber pair. In the pure precession model, the paired Σ-Π states have identical potential energy curves displaced in energy. The potential energy curves presented in Figure 5.2 show significant differences, most notably that the $[7.7] Y^2 Σ^+$ state has a shorter equilibrium bond length and narrower width that the $X^2 Π_i$ state.

Table 5.3: Molecular constants determined in this work compared with the values determined in previous analyses for $^{63}\text{CuO}$. All values reported in cm$^{-1}$.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>This Work</th>
<th>Literature Value</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_0$</td>
<td>$7715.47152(64)$</td>
<td>$7715.47765(54)$</td>
<td>Ref. 46.</td>
</tr>
<tr>
<td>$B_0$</td>
<td>$0.4736054(53)$</td>
<td>$0.473578(28)$</td>
<td>Ref. 46.</td>
</tr>
<tr>
<td>$D_0 \times 10^6$</td>
<td>$8.1118(15)$</td>
<td>$8.22(12)$</td>
<td>Ref. 46.</td>
</tr>
<tr>
<td>$H_0 \times 10^{12}$</td>
<td>$46(10)$</td>
<td>$46(10)$</td>
<td>Ref. 46.</td>
</tr>
<tr>
<td>$\gamma_0$</td>
<td>$-0.0887476(67)$</td>
<td>$-0.089587(42)$</td>
<td>Ref. 46.</td>
</tr>
<tr>
<td>$\gamma_D \times 10^6$</td>
<td>$0.4034(26)$</td>
<td>$0.1272(79)$</td>
<td>Ref. 46.</td>
</tr>
<tr>
<td>$b_0$</td>
<td>$0.12022(13)$</td>
<td>$0.12347(22)$</td>
<td>Ref. 46.</td>
</tr>
<tr>
<td>$c$</td>
<td>$0.0550(74)$</td>
<td></td>
<td>Ref. 46.</td>
</tr>
</tbody>
</table>

Table 5.1: Comparison of molecular constants determined in this work compared with the values determined in previous analyses for $^{63}\text{CuO}$. All values reported in cm$^{-1}$.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>This Work</th>
<th>Literature Value</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_0$</td>
<td>$16353.95401(45)$</td>
<td>$16353.95137(2)$</td>
<td>Ref. 49.</td>
</tr>
<tr>
<td>$\Delta G_{1/2}$</td>
<td>$630.96208(97)$</td>
<td>$631.18(3)$</td>
<td>Ref. 48.</td>
</tr>
<tr>
<td>$B_0$</td>
<td>$0.431445(11)$</td>
<td>$0.431445(11)$</td>
<td>Ref. 49.</td>
</tr>
<tr>
<td>$D_0 \times 10^6$</td>
<td>$0.79991(52)$</td>
<td>$0.793(2)$</td>
<td>Ref. 50.</td>
</tr>
<tr>
<td>$\gamma_0$</td>
<td>$-0.195381(29)$</td>
<td>$-0.195536(73)$</td>
<td>Ref. 49.</td>
</tr>
<tr>
<td>$b_1$</td>
<td>$-0.02892(17)$</td>
<td>$-0.02899(24)$</td>
<td>Ref. 49.</td>
</tr>
</tbody>
</table>

$^a$The $e/f$ symmetry of the $X^2 Π_{1/2}$ state was misassigned in Ref. 47, leading to positive sign for $q$. See Table 5.1.

$^b$This value was determined in the limited preliminary fit (see text and Table 5.1).
Significant deviations were observed in the fit of the (0,0), (0,1), and (1,0) bands of the [7.7] \( ^2\Sigma^+ - X^2\Pi_i \) transition between \( ^{63}\text{CuO} \) and \( ^{65}\text{CuO} \). To determine the appropriate way to treat these deviations in the fit, plots were constructed comparing the residuals of the two isotopologues for each vibrational band. These
plots show that the deviations are approximately constant across vibrational level and $J''$ (+0.003 cm$^{-1}$ for $^{65}$CuO; -0.003 cm$^{-1}$ for $^{63}$CuO). Consequently, these deviations are treated as a breakdown of the Born-Oppenheimer approximation that leads to a difference in electronic energy between the isotopologues (i.e., $\delta_{00}^{\text{Cu}}$). When this parameter was incorporated into the simultaneous fit, the weighted fit error was reduced from 1.223 to 1.087, a significant contribution when one considers the number of observations included in the fit. No additional Born-Oppenheimer breakdown parameters had a significant impact on the quality of the fit, which is understandable when one considers that the magnitude of the shift implicated by the determined $\delta_{00}^{\text{Cu}}$ value is only 0.0056 cm$^{-1}$, i.e., in the 7th digit of $Y_{00}$.

5.8 Conclusions

A comprehensive mass-independent Dunham-type fit has been applied to the high resolution microwave, MB-LIF, FTS, and ILS spectroscopic data for CuO. This work is the first to incorporate transitions due to the minor isotopologue $^{65}$CuO in the fit. This study indicates that the sign of the $\Lambda$-doubling parameter $q$ is negative and reverses the e/f assignments for the transitions involving the $X^{2}\Pi_{3/2}$ substate reported by Steimle et al.$^{47}$ and Zhuang et al.$^{49}$ Breakdown of the Born-Oppenheimer approximation was observed as a 0.0056 cm$^{-1}$ shift in transition energy of the [7.7] $Y^{2}\Sigma^{+} - X^{2}\Pi_{i}$ transition between $^{63}$CuO and $^{65}$CuO. Determination of additional Born-Oppenheimer breakdown parameters were precluded by the precision of the measurements involving $^{65}$CuO and the limited vibrational information on the [16.3] $A^{3}\Sigma^{-} - X^{2}\Pi_{i}$ transition. However, in the event future
analyses involving higher precision measurements of $^{65}$CuO or Cu$^{18}$O are conducted, the experimental data used in this work is provided in the Supplementary Materials of the submitted manuscript$^{52}$ along with the .pgo file and constraints used for the fit, hence these data could easily be incorporated to better determine the mass-independent constants.
CHAPTER VI

NICKEL CHLORIDE

6.1 Introduction and Previous Studies of NiCl

There have been several prior investigations into the electronic spectrum of NiCl. Many of the observed states are best classified as Hund’s case (c), but the case (a) notation has prevailed in the literature and is used here for consistency. Experimentally, the visible region was examined at high resolution using Laser Induced Fluorescence (LIF) and Fourier-Transform Emission Spectroscopy (FTS), definitively identifying 5 excited electronic states 20,000-25,000 cm\(^{-1}\) above the ground state and the 3 expected low-lying electronic states predicted from the \(3d^9\) configuration of Ni\(^+\), all within 2000 cm\(^{-1}\) of the ground state. Yamazaki et al. investigated the millimeter- and submillimeter-region and were able to obtain ground state constants for 6 isotopologues of NiCl. The near-infrared region has been studied using ILS and FTS. Thirty-two transitions were observed in the 9,000-15,000 cm\(^{-1}\) region, and 13 of those transitions were rotationally analyzed. O’Brien et al. identified several vibrational components of System G, the \([13.0]\) \(^2\Pi_{3/2} - \chi ^2\Pi_{3/2}\) transition, and System H, as \([12.3]\) \(^2\Sigma^+ - \chi ^2\Pi_{3/2}\) transition. However, the King Furnace emission method employed in those emission studies led to broad features, and only the (0,0) bands of Systems G and H, also recorded using ILS, were rotationally analyzed. Figure 6.1 provides an energy level diagram of the previous experimentally observed transitions.

Theoretical studies for NiCl also have been reported. Zou and Liu presented a theoretical investigation of the low-lying states of NiX molecules (X = F,
Cl, Br, I), including relativistic effects. Additionally, Jon Hougen\textsuperscript{71} developed an effective Hamiltonian describing the electronic states of Ni\textsuperscript{+}X\textsuperscript{−} molecules and the 5 spin-orbit states resulting from the distortion of the 3d\textsuperscript{9} configuration of Ni\textsuperscript{+} by the bonded, closed-shelled X\textsuperscript{−} ion. Both of these studies suggested that the [12.3] \textsuperscript{2}\Sigma \textsuperscript{−} state reported by O’Brien \textit{et al.}\textsuperscript{16} was \textsuperscript{2}\Sigma \textsuperscript{−} in character. In light of these theoretical studies, Dahms \textit{et al.}\textsuperscript{72} reassigned the \textit{e}/\textit{f} levels of the [12.3] \textsuperscript{2}\Sigma \textsuperscript{−} - \textit{X'} \textsuperscript{2}\Pi\textsubscript{3/2}, [12.3] \textsuperscript{2}\Sigma \textsuperscript{+} - \textit{X'} \textsuperscript{2}\Pi\textsubscript{1/2}, and [12.3] \textsuperscript{2}\Sigma \textsuperscript{+} - [1.7] \textit{B} \textsuperscript{2}\Sigma \textsuperscript{+} transitions, resulting in conversion of the [12.3] \textsuperscript{2}\Sigma \textsuperscript{+} state to the [12.3] \textsuperscript{2}\Sigma \textsuperscript{−} state and inversion of the Λ-doubling parameters of the \textit{X'} \textsuperscript{2}\Pi states and the spin-rotation parameters of the \textit{B} \textsuperscript{2}\Sigma \textsuperscript{+} state.

In this study, several of the observed vibrational bands assigned\textsuperscript{16,64} as the (3,1), (2,1), (2,0), (1,0), and (0,1) bands of System G and the (1,0) band of System H, the [13.0] \textsuperscript{2}\Pi\textsubscript{3/2} - \textit{X'} \textsuperscript{2}\Pi\textsubscript{3/2} and [12.3] \textsuperscript{2}\Sigma \textsuperscript{−} - \textit{X'} \textsuperscript{2}\Pi\textsubscript{3/2} transitions, respectively, have been
observed in high resolution and analyzed. Additionally, a previously unreported transition with a bandhead at 13,480 cm\(^{-1}\) was rotationally analyzed and found to involve a previously unobserved state. The transition was identified as a component of the \([13.8]^{2}\Pi_{1/2} - [0.38]^{2}\Pi_{1/2}\) transition. Rotational analysis of the (2,0), (1,0), and (0,1) bands of System G and the (1,0) band of System H proceeded without issue. However, rotational analysis revealed that the bands originally assigned\(^{16}\) as the (3,1) and (2,1) vibrational components of System G are actually a vibrational progression of a different system involving the previously unknown \([13.5]^{2}\Phi_{7/2}\) state. Molecular constants have been obtained via simultaneous fit of these transitions using PGOPHER.\(^{20}\) In addition, a potential energy curve has been constructed for the \([13.0]^{2}\Pi_{3/2}\) state with the RKR-method using a program from J. Tellinghuisen\(^{59}\) and the \(T_{e}, B_{e}, \alpha_{e}, \omega_{e}\) and \(\omega_{e}\alpha_{e}\) values obtained from the constants for the (2,0), (1,0) and (0,0) bands of System G. Finally, a comparison is made between the known electronic states of NiCl and those predicted by Zou and Liu.\(^{70}\) The results of this study have been published in the Journal of Molecular Spectroscopy.\(^{73,74}\)

6.2 Production of the NiCl Molecules

The near-IR spectrum of NiCl was collected in the 12,400-12,600 cm\(^{-1}\), 13,200-13,500 cm\(^{-1}\), and 13,600-13,750 cm\(^{-1}\) regions using the TS-ILS system. The NiCl molecules were produced in the plasma discharge of a nickel-lined copper hollow cathode in the presence of 0.3-0.6 torr of Ar as sputter gas, and a trace amount of CCl\(_4\). In spectral regions where intense Ar plasma lines occur, \(~1.8\) torr of He was used as a sputter gas in place of Ar. It was found that a flow of CCl\(_4\)
suppressed the observed transitions, but a chamber “seeded” by small, intermittent additions of \( \text{CCl}_4 \) greatly enhanced the absorption intensity of the transitions. A portion of the plasma spectrum overlaid with the experimental \( \text{I}_2 \) spectrum is shown in Figure 6.2.

### 6.3 Analysis Vibrational Bands of System G and H

O’Brien et al.\(^ {16,64} \) reported several vibrational bandheads associated with System G and System H between 12,000 cm\(^{-1} \) and 14,000 cm\(^{-1} \). For this work, the reported (2,0), (1,0), (3,1), (2,1), and (0,1) bands of System G and the (1,0) band of System H were observed at high resolution using ILS, and the transitions were rotationally resolved. The spectra confirmed the red-degraded bandheads near the positions reported by O’Brien et al.\(^ {16,64} \) The primary focus of this section is the (2,0),
(1,0), and (0,1) bands of System G and the (1,0) band of System H because rotational analysis revealed that the transitions near the (2,1) and (3,1) bands of System G belong to a different electronic transition. Those bands are discussed in following sections of this chapter.

Vibrational assignments were confirmed via comparison of bandhead positions for $^{58}\text{Ni}^{35}\text{Cl}$ (52\%) and $^{60}\text{Ni}^{35}\text{Cl}$ (20\%). The relationship between the vibrational energies of different isotopologues is given by equation 6.1

$$\frac{v_1}{v_2} = \sqrt{\frac{\mu_2}{\mu_1}}$$

where $v_{1,2}$ refer to the vibrational constants and $\mu_{1,2}$ refer to the reduced masses of the isotopologues. For the typical NiCl vibrational frequency for the involved electronic states of $\sim 400 \text{ cm}^{-1}$, the expected isotope shift in origin is $\sim 2.5 \text{ cm}^{-1}$ from $^{60}\text{Ni}^{35}\text{Cl}$ to $^{58}\text{Ni}^{35}\text{Cl}$ for each change in vibrational level. The bandhead shift from

![Figure 6.3: (2, 0) band of [13.0] 2Π_{3/2}–X 2Π_{3/2} transition. Isotopologue peaks consistent with (2, 0) transition (top) and PGOPHER simulation from fit (bottom).](image-url)
$^{58}\text{Ni}^{35}\text{Cl}$ to $^{60}\text{Ni}^{35}\text{Cl}$ for the (2,0) band of System G was -4.89 cm$^{-1}$; for the (1,0) band of System G, it was -2.41 cm$^{-1}$; for the (1,0) band of System H, it was -2.50 cm$^{-1}$; and for the (0,1) band of System G, it was +2.66 cm$^{-1}$. The labeled isotopologue bandheads for the (1,0) band of System H are shown in Figure 6.2 and for the (2,0) band of System G in Figure 6.3. The $^{58}\text{Ni}^{37}\text{Cl}$ (16%) peaks were also observed shifted ~6 cm$^{-1}$ for each change in vibrational level, but were much less apparent amongst the dense clusters of lines present in the NiCl spectrum. However, the $^{58}\text{Ni}^{37}\text{Cl}$ peak for the (2,0) band of System G can be seen clearly in Figure 6.3, when the experimental data is overlaid with the simulation for $^{58}\text{Ni}^{35}\text{Cl}$ using PGOPHER, an open-source, spectral simulation program.

The transitions belonging to System G of NiCl had 4 clear branches, 2 P-type and 2 R-type. The (1,0) band of System H of NiCl showed clear P- & Q-bandheads and a total of 6 branches, consistent with a $^2\Sigma$ - $^2\Pi$ transition. The R-bandhead was obstructed by interfering species in the plasma that remained under various discharge conditions. Assignments for the (2,0) and (1,0) bands of System G and the (1,0) band of System H of NiCl were confirmed using combination differences and $\Delta_2F''$ values calculated from parameters of the $X^2\Pi_{3/2}$ ground state reported by Hirao et al.$^{60}$ Assignment for the (0,1) band of System G of NiCl was confirmed using combination differences and $\Delta_2F'$ values calculated from parameters of the [13.0] $^2\Pi_{3/2}$ state reported by O'Brien et al.$^{16}$ All transitions were fit simultaneously using PGOPHER.$^{20}$ The line positions$^{16,64}$ for the (0,0) bands of Systems G and H also were included in the fit to avoid the confusion over the sign of fine splitting.
parameters present in the NiCl literature. In total, over 1500 lines were fit to 30 molecular parameters.

Obtained molecular constants for $^{58}\text{Ni}^{35}\text{Cl}$ are shown in Table 6.1. It should be noted that the matrix element of the $\Lambda$-doubling parameter for a $^2\Pi_{3/2}$ state in PGOPHER, $q_D$, has the reverse sign of the matrix element of the $q_J$ $\Lambda$-doubling parameter used by Hirao et al.,$^{60}$ accounting for the positive value of $q_D$ after treating the (0,0) bands of Systems G and H in the manner suggested by Hougen.$^{71}$ Equilibrium constants obtained from the fit are provided in Table 6.2, and vibrational intervals of the states are provided in Table 6.3.

Our work reports the first high resolution analysis of the $v=1$ level of the $X^2\Pi_{3/2}$ ground state. It is interesting to note that the sign of $q_D$ in $v=1$ has changed from that in $v=0$. This is understandable when looking at the energy of the low-lying $X^2\Pi_{1/2}$ state with term value $T_0 = 382$ cm$^{-1}$, which lies between $v=0$ and $v=1$ levels of the $X^2\Pi_{3/2}$ state. Remembering that the Hougen model and previous experimental

| Table 6.1: Molecular constants and bond lengths for $^{58}\text{Ni}^{35}\text{Cl}$.$^a$ |
|-----------------|-----------------|------------------|---------------------|-----------------|-----------------|
| $^2\Pi_{3/2}$   | $^2\Sigma$      | $^2\Pi_{1/2}$    | $^2\Delta$         | $^2\Pi_{3/2}$    | $^2\Sigma$      |
| $T_v$           | $B_v$           | $D_v \times 10^6$| $H_v \times 10^{12}$| $q_D \times 10^5$| $r_v$ (Å)       |
| $v'=2$          | 13740.0965(12)  | 0.1659064(68)    | -0.11964(68)        | -0.1095(10)      | 2.1586          |
| $v'=1$          | 13351.1462(13)  | 0.1667857(61)    | -0.11873(76)        | -0.0915(11)      | 2.1529          |
| $v'=0$          | 12959.2518(13)  | 0.1676705(59)    | 0.11910(64)         | 0.30604(84)      | 2.1472          |
| $v'=0$          | 12959.2556(13)  | 0.16769720(74)   | 0.11977(74)         | 0.08135(71)      | 2.1472          |
| $v''=1$         | 12647.2249(14)  | 0.1695539(62)    | 0.11857(82)         | -0.746539(39)    | 0.04590(58)     | 2.1297          |
| $v''=0$         | 12252.0495(19)  | 0.1704462(60)    | 0.12694(64)         | -0.746539(24)    | 0.04758(27)     | 2.1297          |
| $v''=0$         | 12252.1867(13)  | 0.17045427(87)   | 0.127910(96)        | -0.746635(24)    | 0.04758(27)     | 2.1297          |
| $v''=0$         | 422.5856(28)    | 0.1806398(83)    | 0.0978(28)          | -0.2404(45)      | 2.0687          |
| $v''=0$         | 0.00            | 0.18149280(59)   | 0.12549(70)         | -0.133(24)       | 0.11519(23)     | 2.0638          |
| $v''=0$         | 0.00            | 0.18150389(12)   | 0.16704(41)         | -0.1004(45)      | 0.115225(14)    |

$^a$ All values in cm$^{-1}$ unless otherwise noted; one standard deviation given in parenthesis
$^b$ Values in italics are from Ref. 72.
$^c$ Literature values converted to $qD$, where $qJ = -qD$
$^d$ This value was determined from a PGOPHER$^{20}$ fit of the previously reported line positions. The difference in origin is due to variations between fitting programs, not transition assignment.
work have shown considerable mixing between the low-lying \( X^2\Pi_{1/2} \) and \( B^2\Sigma^+ \) states, the negative sign of \( q_D \) for the \( v=1 \) level of the \( X^2\Pi_{3/2} \) ground state, which is less than 40 cm\(^{-1}\) higher in energy than the \( X^2\Pi_{1/2} \) state, further supports interactions between this level and \( v=0 \) of the \( X^2\Pi_{1/2} \) state.

<table>
<thead>
<tr>
<th>State</th>
<th>( T_e )</th>
<th>( B_e )</th>
<th>( \alpha_e \times 10^3 )</th>
<th>( r_e ) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>([13.0] \ 2\Pi_{3/2})</td>
<td>12762.201</td>
<td>0.1681106(27)</td>
<td>0.8820(16)</td>
<td>2.1444</td>
</tr>
<tr>
<td>([12.3] \ 2\Sigma^-)</td>
<td>12054.462</td>
<td>0.1708924(86)</td>
<td>0.892(86)</td>
<td>2.1269</td>
</tr>
<tr>
<td>(X^2\Pi_{3/2})</td>
<td>0.1819193(59)</td>
<td>0.8530(83)</td>
<td>2.0614</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) All units in cm\(^{-1}\) unless otherwise noted, one standard deviation given in parenthesis

The equilibrium constants shown in Tables 6.2 and 6.3 were used to construct a potential energy curve for the \([13.0] \ 2\Pi_{3/2}\) state of NiCl with the RKR-method using a program supplied by Joel Tellinghuisen.\(^59\) The constructed curve is shown in Figure 6.4. While this curve is accurate for \( v=0 \)-2 levels, there may be

![Figure 6.4: Potential energy curve for the [13.0] \ 2\Pi_{3/2} state of NiCl. The experimentally observed states from Leung et al.\(^9\) nearly overlap the predicted \( v=5 \) and \( v=5 \) levels.](image-url)
some irregularities in the potential energy surface at \( v=3 \) and \( v=5 \), which nearly overlap the \([14.2] \ ^2\Delta_5/2\) state near 14,165 cm\(^{-1}\) and the \([15.0] \ ^2\Pi_3/2\) and \([15.0] \ ^2\Delta_5/2\) states at 14,782 cm\(^{-1}\) and 14,792 cm\(^{-1}\).\(^68\) As both the excited vibrations of the \([13.0] \ ^2\Pi_3/2\) state and their near overlapping states can be reached from both the \(X \ ^2\Pi_3/2\) and \([0.16] \ ^2\Delta_5/2\) states, future investigation into the spectrum of NiCl in the 13,750-15,000 cm\(^{-1}\) region could yield more interesting information from this spectrally dense species. These results have been published in the Journal of Molecular Spectroscopy.\(^73\)

<table>
<thead>
<tr>
<th>State</th>
<th>(\Delta G_{1/2})</th>
<th>(\omega_e)</th>
<th>(\omega_{xc})</th>
</tr>
</thead>
<tbody>
<tr>
<td>([13.0] \ ^2\Pi_3/2)</td>
<td>391.8944(18)</td>
<td>394.84</td>
<td>1.47</td>
</tr>
<tr>
<td>([12.3] \ ^2\Sigma\cdot)</td>
<td>395.1754(24)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(X \ ^2\Pi_3/2)</td>
<td>422.5856(28)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) All units in cm\(^{-1}\) unless otherwise noted, one standard deviation given in parenthesis

6.4 The \([13.5] \ ^2\Phi_7/2 - [0.16] \ ^2\Delta_5/2\) Transition of NiCl

The rotational analysis of the bands originally reported\(^16\) as the (2,1) and (3,1) vibrational components of System G proved to be a bit problematic. Spectra of the (3,1) bandhead can be seen in Figures 6.5. The simulated spectra of the (2,1) and (3,1) bands of System G, with bandheads predicted at 13,319.56 cm\(^{-1}\) and 13,710.34 cm\(^{-1}\) from the analysis described in the previous section, were inconsistent with the experimentally observed bandheads at 13,317.96 cm\(^{-1}\) and 13,709.22 cm\(^{-1}\). Additionally, only 3 branches were found in these transitions, not the 4 branches expected for a \(^2\Pi_3/2 - ^2\Pi_3/2\) transition with large \(\Lambda\)-doubling constants. The presence of three branches suggested that the transitions are \(\Delta \Lambda \neq 0\) with no resolved fine structure, i.e. not a transition of System G. Thus we believed
the experimentally observed bandheads at 13,317.96 cm\(^{-1}\) and 13,709.22 cm\(^{-1}\) were a vibrational progression of a different electronic system.

The molecular source for these experiments is relatively high in energy, and the NiCl molecules inhabit many low-lying energy levels. The low-lying excited electronic states likely to be populated and readily observable in absorption experiments are the \(A^{2}\Delta_{5/2}\) and the \(X^{2}\Pi_{1/2}\) states, both of which are located less than 500 cm\(^{-1}\) above the ground state. It is less likely that the \(A^{2}\Delta_{3/2}\) and \(B^{2}\Sigma^{+}\) states at 1645 cm\(^{-1}\) and 1768 cm\(^{-1}\) would have the population necessary to produce the observed absorption intensities of the distinct rotational progressions observed in the experimental spectra. Indeed, the ground state of these two bands was confirmed to be the \(v = 0\) level of the \(A^{2}\Delta_{5/2}\) state based on the constants reported by Hirao \textit{et al.}\(^{60}\)

Figure 6.5: Overlay of the experimental spectrum (black) and PGOPHER\(^{20}\) simulation (blue) of the (1,0) band of the [13.5] \(^{2}\Phi_{7/2} - [0.16] A^{2}\Delta_{5/3}\) transition of NiCl. The (2,0) band of System G for NiCl overlaps this transition, as can be seen from the PGOPHER\(^{20}\) simulation for \(^{58}\)Ni\(^{35}\)Cl included in the figure (red).
There are 4 Ω-states predicted by Zou and Liu\(^7\) between 13,000 and 15,000 cm\(^{-1}\), namely the (II)\(^2\)\(\Pi_{3/2}\), (I)\(^2\)\(\Phi_{7/2}\), (II)\(^2\)\(\Pi_{1/2}\), and (II)\(^2\)\(\Delta_{5/2}\) states, and only 1 experimentally observed electronic state located between 13,000 and 14,000 cm\(^{-1}\), the [13.0] \(^2\)\(\Pi_{3/2}\) state [the (II)\(^2\)\(\Pi_{3/2}\) state]. Absorption from the low-lying \(A\) \(^2\)\(\Delta_{5/2}\) state could connect to the (II)\(^2\)\(\Pi_{3/2}\) state or the (I)\(^2\)\(\Phi_{7/2}\) state. The vibrational constants for the (II)\(^2\)\(\Pi_{3/2}\) state are known, and the nearest [13.0] \(^2\)\(\Pi_{3/2}\) - [0.16] \(A\) \(^2\)\(\Delta_{5/2}\) transitions deviate from the observed transitions by several hundred wavenumbers. However, treatment of the transitions as the (1,0) and (0,0) bands of the [13.5] \(^2\)\(\Phi_{7/2}\) - [0.16] \(A\) \(^2\)\(\Delta_{5/2}\) transitions was very promising.

The experimentally determined \(T_e\) values were consistent with the theoretical predictions, and the experimental \(\Delta G_{1/2}\) value of 391 cm\(^{-1}\) was very close to the predicted \(\omega_e\) value of 403 cm\(^{-1}\) for the (I)\(^2\)\(\Phi_{7/2}\) state. Thus the transitions observed near 13,709 cm\(^{-1}\) and 13,318 cm\(^{-1}\), respectively, are newly reassigned as the (0,0) and (1,0) bands of the [13.5] \(^2\)\(\Phi_{7/2}\) - [0.16] \(A\) \(^2\)\(\Delta_{5/2}\) transition. Secure vibrational assignments for the excited state could not be confirmed using isotopologue shifts because no clear isotopologue bandheads were observed; the (2,0) and (1,0) bands of System G overlap the transitions resulting in spectra that are quite clustered.

For the final fit, the reported line positions of the (1,0) and (0,0) bands of the [21.9] \(^2\)\(\Delta_{5/2}\) - [0.16] \(A\) \(^2\)\(\Delta_{5/2}\) transition\(^6\) were included with the line positions for the (1,0) and (0,0) bands of the [13.5] \(^2\)\(\Phi_{7/2}\) - [0.16] \(^2\)\(\Delta_{5/2}\) transition. The obtained molecular constants are displayed in Table 6.4, with the values from Hirao \textit{et al.}\(^6\)
shown in italics. These results have been published in the Journal of Molecular spectroscopy.74

Table 6.4: Molecular Constants for (1,0) and (0,0) bands the [13.5] $^2\Phi_{7/2} - [0.16] A^2\Delta_{5/2}$ transition of $^{58}\text{Ni}^{35}\text{Cl}$.a

<table>
<thead>
<tr>
<th></th>
<th>$T_v$</th>
<th>$B_v$</th>
<th>$D_v \times 10^6$</th>
<th>$r_v$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[13.5] $^2\Phi_{7/2}$</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>$v' = 1$</td>
<td>13869.042(15)</td>
<td>0.167633(13)</td>
<td>0.1461(20)</td>
<td>2.1474</td>
</tr>
<tr>
<td>$v' = 0$</td>
<td>13477.6790(21)</td>
<td>0.168305(13)</td>
<td>0.1375(21)</td>
<td>2.1432</td>
</tr>
<tr>
<td>[0.16] $^2\Delta_{5/2}$</td>
<td></td>
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<tr>
<td>$v'' = 0$</td>
<td>161.550a</td>
<td>0.183891(13)</td>
<td>0.1507(20)</td>
<td>2.0503</td>
</tr>
<tr>
<td>$v'' = 0b$</td>
<td>161.550(4)b</td>
<td>0.183752(46)b</td>
<td>0.1311(10)b</td>
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</tr>
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</table>

a All units in cm$^{-1}$ unless otherwise noted
b Values reported by Hirao et al. 60

6.5 The [13.8] $^2\Pi_{1/2} - [0.38] X^2\Pi_{1/2}$ Transition

While scanning in the 13,000 – 14,000 cm$^{-1}$ region, an additional transition was observed with an apparent bandhead near 13,480 cm$^{-1}$. The exact position of the bandhead was obscured by the presence of a strong Cl atomic line and a weak Ni atomic line, but red-degraded branches were clearly visible. A sample spectrum is provided in Figure 6.6. Upon inspection, 4 branches were identified; 2 R-branches and 2 P-branches. No Q-branch was observed, and the overall branch pattern is consistent with a $\Delta \Lambda = 0$ transition. As stated above, only the $X^2\Pi_{3/2}$ state and the relatively low-lying $[0.16] A^2\Delta_{5/2}$ the $[0.38] X^2\Pi_{1/2}$ states are expected to be populated for our absorption studies. The appearance of large $\Lambda$-doubling constants excluded the possibility of a $^2\Delta_{5/2} - ^2\Delta_{5/2}$ transition. Additionally, a $^2\Pi_{3/2} - ^2\Pi_{3/2}$ transition was also excluded since the other predicted $^2\Pi_{3/2}$ states are known and are not in this spectral region.70 Thus, we suspected a $^2\Pi_{1/2} - ^2\Pi_{1/2}$ transitions. Combination differences between the 4 branches of the observed transition were compared to the $\Delta F$ levels calculated from the constants for the $[0.38] X^2\Pi_{1/2}$ state.
reported by Rice et al.\textsuperscript{67} and a secure rotational assignment for the transition was obtained. The transition was fit using PGOPHER\textsuperscript{20}. Line positions for the\[12.3] 2\Sigma^- - X^2\Pi_{3/2} \] transition reported by O’Brien et al.\textsuperscript{16} and for the Table 6.5: Molecular constants for the [13.8] 2\Pi_{1/2} - [0.38] X^2\Pi_{1/2} transition of $^{58}$Ni$^{35}$Cl. The line positions from Rice et al.\textsuperscript{67} were included in the fit, and the parameters for the $X^2\Pi_{1/2}$ state were allowed to float. Deviations arise from differences in the polynomial used by Rice et al.\textsuperscript{67} and the matrix elements utilized by PGOPHER.\textsuperscript{20}

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<th>B</th>
<th>D x 10^{16}</th>
<th>H x 10^{12}</th>
<th>r_0 (Å)</th>
</tr>
</thead>
<tbody>
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<td>0.11781 (21)</td>
<td>-1.317 (85)</td>
<td>2.0680</td>
</tr>
<tr>
<td>[0.38] X^2\Pi_{1/2}</td>
<td>384.8747 (14)</td>
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<td></td>
</tr>
<tr>
<td>[0.38] X^2\Pi_{1/2}</td>
<td>0.837914 (94)</td>
<td>-2.549 (60)</td>
<td>-7.117 (86)</td>
</tr>
</tbody>
</table>

a All values reported in cm\(^{-1}\) unless otherwise noted
b Values reported by Rice et al.\textsuperscript{67}
c Sign convention in PGOPHER\textsuperscript{20} is inverted relative to polynomial used for this fit.
[12.3] \( ^2\Sigma^- - [0.38] \ X^2\Pi_{1/2} \) transition reported by Rice et al.\(^{67} \) were included in the fit in order to eliminate the ambiguity in the reported constants due to the inversion of the \( \Lambda \)-doubling parameters that was described in the introduction. The obtained constants for the fit of the newly assigned [13.8] \( ^2\Pi_{1/2} - [0.38] \ X^2\Pi_{1/2} \) transition are provided in Table 6.5. These results have been published in the Journal of Molecular Spectroscopy.\(^{74} \)

6.6 The Experimentally Observed and Theoretically Predicted States of NiCl

With the observation of these two new electronic states, the \( v=0 \) vibrational level for 11 of the 12 predicted\(^{70} \) doublet spin-orbit components for NiCl below 15,000 \( \text{cm}^{-1} \) have been rotationally analyzed. In general, the experimental data shows an excellent agreement with the predictions of this theoretical study, predicting the energy of the observed state within 500 \( \text{cm}^{-1} \) in all but 2 observed cases. Additionally, in all but 1 case, the predicted energy was higher than the observed energy, showing a clear trend. A comparison of the observed and calculated spin-orbit components of \(^{58}\text{Ni}^{35}\text{Cl} \) is shown in Figure 6.7. It should be noted that only the \( v = 2 \) level of the [14.2] \( ^2\Delta_{5/2} \) state has been observed and analyzed.\(^{68} \) The analysis performed in this work was greatly assisted by these valuable calculations.

6.7 Conclusions

Several new NiCl electronic transitions have been identified in the near-infrared and rotationally analyzed. A simultaneous fit of the (2,0), (1,0), (0,0), & (0,1) bands of System G and the (1,0) & (0,0) bands of System H has been performed, fitting 1500 lines to 30 parameters. The reported constants have fine
splitting parameters adjusted in accordance with the suggestion from Jon Hougen.

A potential energy curve has been produced for the \([13.0] 2\Pi_{3/2}\) state based on the equilibrium constants obtained from the rotational constants for the \(v=0-2\) levels.

Two new electronic states for \(^{58}\text{Ni}^{35}\text{Cl}\) have been identified and a misassignment in the previous literature have been corrected: the \((3,1)\) and \((2,1)\) bands of System G have been reassigned as the \((1,0)\) and \((0,0)\) bands of the \([13.5] 2\Phi_{7/2}\) - \([0.16] A 2\Delta_{5/2}\) transition and the \([13.8] 2\Pi_{1/2}\) - \([0.38] X^2\Pi_{1/2}\) transition has been observed and rotationally analyzed. Molecular constants have been obtained for the new \([13.5] 2\Phi_{7/2}\) and \([13.8] 2\Pi_{1/2}\) states. The good agreement

Figure 6.7: A comparison of the experimentally observed electronic states [Right: (a) O’Brien et al.\(^{16}\), (b) O’Brien et al.\(^{64}\), (c) Rice & O’Brien\(^{65}\), (d) Tumturk et al.\(^{66}\), (e) Rice et al.\(^{67}\), (f) Leung et al.\(^{68}\), (g) Gibbs et al.\(^{69}\) and (h) this work.] and the doublet states of NiCl predicted by Zou and Liu.\(^{70}\)
between the experimental data and the theoretical predictions of Zou and Liu\textsuperscript{70} underscores how valuable contributions from computational investigations can be in experimental analysis. The work presented in this chapter has been published in the Journal of Molecular Spectroscopy.\textsuperscript{73,74}
CHAPTER VII

PLATINUM FLUORIDE

7.1 Introduction and Previous Studies of PtF

The electronic landscapes of platinum containing molecules are of scientific interest not only due to the broad catalytic utility of Pt containing compounds,\textsuperscript{75-76} but also because of the difficulty in accurately describing this electronic structure theoretically due to complications from electronic correlations and relativistic effects.\textsuperscript{77} The electronic structure of the first row main group diatomics PtB,\textsuperscript{78} PtC,\textsuperscript{79-86} PtN,\textsuperscript{83,87-89} PtO,\textsuperscript{83,90-100} and PtF\textsuperscript{101-104} have been investigated spectroscopically, but the coverage provided by these studies is far from complete.

The first experimental observation of PtF was reported by Handler \textit{et al.} in 2011.\textsuperscript{101} The \((1,0)\) and \((0,0)\) bands of the \([11.9] \Omega = 3/2 - X^2\Pi_{3/2}\) transition were recorded using Intracavity Laser Spectroscopy (ILS) with a Ti:Sapphire laser. Two additional bands were observed that were believed to connect to the low-lying \(A^2\Sigma^+\) state of PtF, but a conclusive rotational assignment of these bands remained elusive due to extensive overlap with the much stronger \(\Omega' = \Omega'' = 3/2\) transition.\textsuperscript{105} In 2012, Qin \textit{et al.}\textsuperscript{103} determined the dipole moments of the \([11.9] \Omega = 3/2\) and \(X^2\Pi_{3/2}\) states to be 2.47\,(11) D and 3.42\,(6) D, respectively, through the analysis of Stark spectra from the same electronic transition. Concurrently, Okabayashi \textit{et al.}\textsuperscript{102} reported analyses of the pure rotational spectra of PtF and PtCl in their \(X^2\Pi_{3/2}\) ground states.

The most recent experimental spectroscopic observation of PtF was reported by Ng \textit{et al.},\textsuperscript{104} who used a molecular beam Laser Induced Fluorescence (LIF) approach to study
the electronic spectrum of PtF between 431 and 560 nm. Eight vibrational bands were identified in the LIF data, and six were rotationally analyzed and assigned to four electronic transitions, identifying four new electronic states: the [0.4] \( ^2\Delta_{5/2} \), [18.9] \( ^2\Pi_{3/2} \), [19.9] \( ^2\Delta_{5/2} \), and [23.2] \( ^2\Delta_{5/2} \) states. The [18.9] \( ^2\Pi_{3/2} \) - [0.4] \( ^2\Delta_{5/2} \) transition was observed weakly, and spectral congestion inhibited identification of first lines, thereby preventing conclusive assignment of the lower state. Their tentative assignment of the lower state as a \( ^2\Delta_{5/2} \) state was rationalized by the relative intensities of the P-, Q-, and R-branches and the disagreement between the rotational constant for their [0.4] state (0.2750 cm\(^{-1}\)), the rotational constant for the \( X \ ^2\Pi_{3/2} \) state (0.27719 cm\(^{-1}\)),\(^{102}\) and a preliminary rotational constant for the \( A \ ^2\Sigma^+ \) (\( \sim 0.2690 \) cm\(^{-1}\)).\(^{105}\) The results of their analysis were summarized with all PtF work to date, and an energy level diagram of the known electronic states of PtF was included in their paper.

The first theoretical investigation into the electronic structure of PtF was performed by Liu ad Franke in 2002,\(^{106}\) who used relativistic \textit{ab initio} and Density Functional Theory (DFT) methods to study PtH, PtF, PtCl, and Pt(NH\(_3\))\(_2\)Cl\(_2\). Zou \textit{et al}.\(^{107}\) used relativistic \textit{ab initio} methods to study the three lowest-lying electronic states of PtF and linear HePtF in 2010. The electronic structure of PtX molecules (X=F, Cl, Br, and I) was examined by Zou and Suo\(^{77}\) in 2016 using relativistic \textit{ab initio} methods, applying a perturbative approach to treat spin-orbit coupling. All \( \Omega \) states below 35,000 cm\(^{-1}\) were included in the calculations, and spectroscopic constants were predicted. In general, the agreement between their predictions and experimental observations is reasonable. The most recent theoretical investigation of PtF was reported by Deng \textit{et al}.\(^{108}\) in which the permanent electric dipole
moment and equilibrium geometries were predicted for PtX molecules in their ground states using the Feller-Peterson-Dixon (FPD) composite approach.

The aim of this study was to use the DL-ILS system to expand the spectral coverage of the experimentally examined electronic spectrum of PtF. Several transitions due to PtF have been observed in this region, including 6 band systems that have been assigned as the (2,1), (1,0), (0,0), (0,1), (1,2), and (0,2) bands of the [15.8+x] Ω = 5/2 – B 2Δ5/2 transition of PtF. Transitions due to 194PtF, 195PtF, 196PtF, and 198PtF have been identified, and a simultaneous fit of all isotopologues and vibrational bands has been performed with PGOPHER\textsuperscript{20} using the variable-constraint method outlined by Breier \textit{et al.}\textsuperscript{54,55} and the mass-independent Dunham expressions of Le Roy.\textsuperscript{13} Interestingly, an isotopologue-dependent shift in electronic excitation energy was identified in the fitting process and has been treated as a field-shift effect resulting from the difference in nuclear charge radius between Pt isotopes.\textsuperscript{9-12} The determined molecular constants correspond well with the constants for the (4) Ω = 5/2 and (1) Ω = 5/2 states predicted by Zou and Suo.\textsuperscript{77} However, the constants for the lower state do not agree with the values reported by Ng \textit{et al.}\textsuperscript{104} for the [0.4] 2Δ5/2 state: we suggest that this [0.4] state be reassigned as the A 2Σ* state of PtF.

The results of this study have been published in the Journal of Molecular Spectroscopy.\textsuperscript{109}

7.2 Production of the PtF Molecules

The PtF molecules were produced in the plasma discharge formed by applying RF current to a 50 mm long Pt-lined Cu hollow cathode. A variety of conditions were used to optimize signals due to the different band systems of PtF. Discharge currents ranged from 0.30-0.80 A, and the gas composition consisted of 1-5% SF\textsubscript{6} in either a mixture of Ar/He or
just Ar, with total pressures ranging from 0.50-1.25 Torr. The cathode was located within the DL-ILS system. Generation times spanning 30-150 μsec were used, resulting in effective pathlengths of 0.4 – 2.0 km for the 50 mm cathode and 1.1 m long resonator cavity. The absorption spectrum for the (0,0) band of the $[15.8+x] \Omega = 5/2 - B^{2}\Delta_{5/2}$ transition is provided in Figure 7.1.

7.3 Observed Transitions in the ILS Data

Molecular transitions due to platinum containing species were observed in the ILS data throughout the investigated 14,500-16,500 cm$^{-1}$ region, including the previously analyzed (0,0) band of the $[15.9] B\Omega=0 - X\Omega=0$ transition of Pt$^{110}$ and (0,1) band of the $[16.9] A\Omega = 0 - X\Omega = 0$ transition of PtO. Many additional bands were observed that have not been rotationally analyzed: these bands were assigned a molecular identity through a

![Figure 7.1: PGOPHER display of ILS absorption spectrum of the (0,0) band of the $[15.8+x] \Omega = 5/2 - B^{2}\Delta_{5/2}$ transition of PtF. Spectral features due to $^{194}$PtF, $^{195}$PtF, and $^{196}$PtF are not resolved for transitions with $j'' < 40.5$, resulting in a simple appearance for this band dominated by a single R- and single P-branch. The weak appearance of the Q-branch is consistent with a $\Delta\Omega = 0$ transition. The data for this figure were produced from the concatenation of ~15 individual spectral segments using a macro-enabled Excel workbook.](image)
preliminary rotational analysis, using the large difference in rotational constant as a
diagnostic tool ($B''_{PtO} \approx 0.38 \text{ cm}^{-1}$, $B''_{PtF} \approx 0.27 \text{ cm}^{-1}$, $B''_{PtS} \approx 0.15 \text{ cm}^{-1}$). A summary of the
observed band systems in this region is provided in Table 7.1. The focus of this
dissertation is restricted to the rotational analysis of the observed vibrational bands
assigned to the $[15.8+x] \Omega=5/2 - B^2 \Delta_5/2$ transition of PtF. Rotational analyses of several
newly observed bands in Table 7.1 are ongoing.

Conditions for the preferential production of PtF were optimized by monitoring
absorption features of the overlapping $(1,0)$ bands of the $[15.8+x] \Omega=5/2 - B^2 \Delta_5/2$
transition of PtF and $B \Omega=0 - X \Omega=0$ transition of PtS as plasma conditions were modified. It
was discovered that the PtF transition appeared very strongly upon the onset of plasma
formation, but diminished rapidly as the discharge continued. However, the PtS signals
grew

<table>
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<tr>
<th>Bandhead Position (cm$^{-1}$)</th>
<th>Molecular Species</th>
<th>Vibrational Assignment</th>
<th>Electronic Transition</th>
<th>Rotational Analysis</th>
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<td>14,567</td>
<td>PtF</td>
<td>$a(1,3)$ band</td>
<td>[15.8+x] $\Omega=5/2 - B^2 \Delta_5/2$</td>
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<tr>
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<td>This Study</td>
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<td>This Study</td>
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<td>[16.9] $A \Omega=0 - X \Omega=0$</td>
<td>Nilsson et al.$^c$</td>
</tr>
</tbody>
</table>

*a Bandhead observed.

References:

$b$ Reference (110).

c Reference (90).
intensity over time. In accordance with this observation, the detection window for the ILS data was manually synchronized to the onset of the plasma discharge to minimize interference effects from PtS for this PtF analysis.

7.4 Assignment and Identification of the PtF Band Systems

A strong transition was observed with a red-degraded bandhead near 15,791 cm\(^{-1}\) (Figure 7.1). This transition was identified as a Pt-containing molecule due to clear isotopologue splitting observed at high \(J''\), as illustrated in Figure 7.2(a). The overlap of isotopologues at low \(J''\) is consistent with a (0,0) vibrational band. The transition is dominated by a single R- and single P-branch, indicating a \(\Delta \Omega=0\) electronic transition. A preliminary rotational analysis of the transition resulted in \(B''\) and \(B'\) values of 0.2693 cm\(^{-1}\) and 0.2512 cm\(^{-1}\), consistent with the known rotational constants for electronic states of PtF\(^{101-104}\). Branch doubling was not observed at the experimental resolution (~0.01 cm\(^{-1}\)), despite the observation of lines originating from \(J''>90.5\). This lack of observable spin-rotation coupling or \(\Lambda\)-doubling at such high \(J''\) suggests that \(\Omega>3/2\) for the involved electronic states. Weak features due to the (0,0) band of the [15.9] \(B \Omega=0 - X \Omega=0\) transition of PtS with intensities just above baseline preclude definitive \(\Omega\) assignment through assignment of first lines, but lines in the ILS data originating from \(J''=2.5\) were clearly observed well above baseline, eliminating an electronic assignment with \(\Omega>5/2\). Therefore, this band is assigned as the (0,0) band of the [15.8+x] \(\Omega=5/2 - B^2 \Delta 5/2\) transition of PtF, where \(x\equiv T_e(B^2 \Delta 5/2)\).

The known \(\Delta G_{1/2}\) values for PtF are 594 cm\(^{-1}\) for the \(X^2 \Pi_{3/2}\) ground state\(^{104}\), 556 cm\(^{-1}\) for the [11.9] \(\Omega=3/2\) state\(^{101}\), and 538 cm\(^{-1}\) for the [18.9] \(\Omega=3/2\) state\(^{104}\). These values make
the initial assignment of the 16,327 cm\(^{-1}\) (\(+536\) cm\(^{-1}\)) and 15,198 cm\(^{-1}\) (\(-593\) cm\(^{-1}\)) bands as the (1,0) and (0,1) bands of the \([15.8+x]\) \(\Omega = 5/2 - B^2\Delta_{5/2}\) transition of PtF reasonable, and combination differences between rotational branches of the observed bands confirmed these assignments. While the features due to \(^{194}\)PtF, \(^{195}\)PtF, and \(^{196}\)PtF were not resolved for the (0,0) band except at very high \(J''\) [Figure 7.2(a)], isotopologue separation for the off-diagonal vibrational bands was well resolved, as can be seen in a portion of the (0,1) band provided in Figure 7.2(b).

The effective molecular constants obtained for \(v'\) and \(v''=0\) and 1 were used to predict the constants for both \(v'\) and \(v''=2\). These constants were used with PGOPHER\(^{20}\) to simulate the (2,1), (1,2), and (0,2) vibrational bands of the PtF transition, and rotational branches of these bands were easily identified in the experimental spectra. In total, 476 transitions were assigned to \(^{194}\)PtF (32.97% abundant), 612 to \(^{195}\)PtF (33.83%), 471 to \(^{196}\)PtF (25.24%), and 134 to \(^{198}\)PtF (7.16%) for the (2,1), (1,0), (0,0), (0,1), (1,2), and (0,2) vibrational bands of the \([15.8+x]\) \(\Omega = 5/2 - B^2\Delta_{5/2}\) transition.

7.5 Fitting the Data

Rotational assignments for the observed transitions of \(^{194}\)PtF, \(^{195}\)PtF, and \(^{196}\)PtF were obtained by fitting the identified P- and R-branches to Fortrat polynomials using the LINEST function in Excel. The rotational assignments were adjusted until the \(R^2\) value of the Fortrat polynomial was maximized and the effective \(B', D', B'',\) and \(D''\) constants determined from the coefficients of the 4\(^{th}\) order Fortrat polynomial were in reasonable agreement with the known rotational constants for PtF.\(^{101-104}\) Once the rotational assignments were obtained, the data were fit using PGOPHER.\(^{20}\) Initially, the data were fit
Figure 7.2: Platinum fluoride isotopologue structure of the (a) (0,0) and (b) (0,1) bands of the [15.8+x] $\Omega = 5/2 - B \ ^2\Delta_{5/2}$ transition. The natural abundances of $^{194}$PtF (Red: 32.97%), $^{195}$PtF (Blue: 33.83%), $^{196}$PtF (Green: 25.24%), and $^{198}$PtF (Purple: 7.16%) are reflected in the relative intensities of features in the isotopologue clusters, which are only partially resolved for the (0,0) band but well resolved for the off-diagonal vibrational bands. The stick spectrum in the figure are the simulated line positions for the transitions from the PGOPHER$^{20}$ fit. Peaks indicated with an asterisk are due to the (a) (1,0) and (b) (0,0) bands of the [15.3] $\Omega = 3/2 - X \ ^2\Pi_{3/2}$ transition of PtF.

The abundance of high quality vibrational level- and isotopologue-specific data for this relatively simple system motivated investigation through a Dunham analysis. In a Dunham analysis, spectroscopic data from multiple vibrational levels and isotopologues are fit to a single set of parameters that account for the mass-dependence of rotational and vibrational energy. The comprehensive equation incorporating this single set of parameters was derived by Dunham in 1932,$^5$ modified to include mass-dependent Born-Oppenheimer breakdown (BOB) parameters by Ross et al. in 1974$^6$ and Watson in 1980.$^7$
further modified to treat BOB resulting from differences in the finite nuclear charge
distribution between isotopes by Tieman et al. in the mid-1980s. This equation was
converted to a convenient linear form by Le Roy in 1999:

\[ E_\alpha^{(cm^{-1})}(T_e, v, J) = T_e + \sum_{l,m \neq (00)} Y_{l,m}^1 \left( \frac{\mu_\alpha}{\mu_{\text{ref}}} \right)^{m+\frac{l}{2}} \left( v + \frac{1}{2} \right)^l [J(J+1)]^m + \]

\[ \sum_{l,m \neq (00)} \left\{ \delta < r^2 >^A \right. \left. f_{l,m}^A + \delta < r^2 >^B f_{l,m}^B + \frac{\Delta M_A^{\alpha}}{M_A^\alpha} \delta_{l,m}^A + \frac{\Delta M_B^{\alpha}}{M_B^\alpha} \delta_{l,m}^B \right\} \times \]

\[ \left( \frac{\mu_\alpha}{\mu_{\text{ref}}} \right)^{m+\frac{l}{2}} \left( v + \frac{1}{2} \right)^l [J(J+1)]^m \]

(7.1)

where \( E_\alpha \) is the energy of a rovibrational level of an electronic state of isotopologue \( \alpha \), \( T_e \) is the electronic energy of that state, \( l \) and \( m \) refer to the \( l \)-th vibrational and \( m \)-th rotational component in the expansion, \( Y_{l,m}^1 \) are the rovibrational Dunham parameters for the reference isotopologue 1, \( \mu \) is the reduced mass for the reference (i.e., 1) and relative (i.e., \( \alpha \)) isotopologues, \( v \) is the vibrational quantum number, \( J \) is the rotational quantum number, \( \delta < r^2 >^A \) is the change in mean squared nuclear charge radii between reference and relative isotopes of atom A, \( f_{l,m}^A \) are “field-shift” parameters that depend on the electron density at the nucleus of atom A, \( M_A^\alpha \) is the mass of isotopologue \( \alpha \), \( \Delta M_A^\alpha \) is the difference in mass between the relative and reference isotopologues, and \( \delta_{l,m}^A \) are the mass-dependent BOB parameters.

Breier et al. demonstrated that PGOPHER could be used to fit spectroscopic data to a Dunham expression by defining custom \( Y_{l,m}^1 \) and BOB parameters. In the following description of PGOPHER custom variables, quotation marks indicate nomenclature used in PGOPHER. To generate a .pgo file appropriate for the Dunham analysis, the
isotopologues are incorporated as individual “Linear Molecules” within the same “Species” manifold. Each “Linear Molecule” contains a “Linear Manifold” for each electronic state included in the PGOPHER\textsuperscript{20} model, and each “Linear Manifold” contains a “Linear” component for each vibrational level included in the model. Isotopic masses\textsuperscript{111} and $\delta<r^2>$ values\textsuperscript{112} from reference data, equation 7.1, and the custom $Y_{l,m}^1$ and BOB parameters are used with “Expressions” and “Constraints” to calculate the Hamiltonian components of each “Linear” state and fit to spectroscopic data from multiple vibrational levels and isotopologues.

This constrained-variable approach was used to fit the ILS PtF data to equation 7.1. Using this approach, the 1559 observations were fit to 16 parameters, 15 of which correspond to parameters from Herzberg\textsuperscript{3}: $\Delta T_e$, $\omega_e'$, $\omega[e]_e'$, $B_{e'}$, $\alpha[e]_e'$, $\gamma[e]_e'$, $D_{e'}$, $\beta[e]_e'$, $\omega[e]_e''$, $\omega[e]_e''$, $B_{e''}$, $\alpha[e]_e''$, $\gamma[e]_e''$, $D_{e''}$, $\beta[e]_e''$. The constraints that define the custom variables were built parameter by parameter, and the fit quality was monitored as the custom Dunham parameters replaced isotopologue- and vibrational level- dependent parameters. All the rovibrational Dunham parameters ($l\geq0$, $m\geq0$) were incorporated without any detriment to the fit quality. However, the independently determined $\Delta T_e$ (where $\Delta T_e=T_{e'}-T_{e''}$) values for the PtF isotopologues were not exactly equal. This evidence of BOB in the electronic energy of a Pt containing molecule was quite surprising. Tieman \textit{et al.}\textsuperscript{8-12} were able to treat similar anomalous appearances of BOB in Pb and Tl containing molecules by incorporating parameters that scaled with the change in nuclear charge radii between isotopes, $\delta<r^2>$, and it was discovered that the shift in $\Delta T_e$ was indeed proportional to the $\delta<r^2>$ values. The parameter describing this proportionality, $\Delta f_{00}$, is derived in equation 7.2.
\[ \Delta T_e^\alpha = T_e^{\alpha'} - T_e^{\alpha''} = T_e^{1'} + \delta<r^2>_\text{Pt} f_{00} - T_e^{1''} - \delta<r^2>_\text{Pt} f_{00}'' = \Delta T_e^1 + \delta<r^2>_\text{Pt} \Delta f_{00} \] (7.2)

where \( \alpha \) indicates the relative isotopologue to the reference isotopologue, \( 1 \equiv ^{195}\text{Pt} \text{F} \) and where \( \Delta f_{00} \) is defined as

\[ \Delta f_{00} = f_{00}' - f_{00}'' \] (7.3)

The shift in \( \Delta T_e \) is analogous to the optical isotope shifts observed in atomic spectra that were analyzed to generate many of the \( \delta<r^2> \) values in the nuclear data reference tables.\(^\text{112}\)

Once the data for the three most abundant isotopologues were adequately described by the Dunham fit, transitions of the less abundant \( ^{198}\text{Pt} \text{F} \) were predicted, leading to the identification of 134 unique spectral features due to this isotopologue. In total, 1693 observations were fit to 16 parameters.

The sixteen determined Dunham parameters are presented in Table 7.2 with 1\sigma for the last two digits provided in parentheses. Table 7.2 also contains: the parameters for the (1) and (4) \( \Omega = 5/2 \) states predicted by Zou and Suo;\(^\text{77}\) the parameters for the [0.4] state determined by Ng \textit{et al.};\(^\text{104}\) and the isotopologue shift in \( \Delta T_e^\alpha (\Delta \Delta T_e^\alpha) \) calculated from the \( \delta<r^2> \) values from Angeli and Marinova,\(^\text{112}\) the determined \( \Delta f_{00} \) parameter, and equation 7.2. The calculated uncertainty in the \( \Delta \Delta T_e^\alpha \) values results from the propagation of the uncertainty in the reference \( \delta<r^2> \) values and the fit uncertainty in \( \Delta f_{00} \).
Table 7.2: Determined molecular Constants for \(^{195}\text{PtF}\) from the simultaneous multi-isotopologue PGOPHER\(^{20}\) fit. The molecular constants for the other PtF isotopologues were calculated using the parameters in this table and isotopologue relationships outlined by Watson.\(^{7}\) The determined parameters agree well with the predicted parameters for the calculated \((1) \Omega = 5/2\) and \((4) \Omega = 5/2\) states of Zou and Suo,\(^{7}\) however, the determined parameters for the ground state are not consistent with the parameters for the \([0.4]\) state of Ng et al.\(^{104}\) The isotopologue shift in \(\Delta T_e\) was treated using the \(\Delta f_{00}\) parameter of equation (2) and reference \(\delta<r^2>\) values from Angeli and Marinova.\(^{112}\) This shift has been calculated from these values and is shown at the bottom of the table. The uncertainty of these shifts is on par with the uncertainty of the reference \(\delta<r^2>\) values.\(^{111}\) The values in parentheses indicate 1\(\sigma\) relative to the last reported digits of the parameter.

<table>
<thead>
<tr>
<th>State</th>
<th>Parameter</th>
<th>Value</th>
<th>Predicted Value from Zou and Suo(^{(a)})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(Y_{00}(T_e))</td>
<td>(T_{e}')</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(Y_{10}(\omega_e))</td>
<td>(\omega_e)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(Y_{20}(-\omega_e \chi_e))</td>
<td>(B_e)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(Y_{01}(B_e))</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(Y_{11}(-\alpha_e))</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(Y_{21}(Y_e) \times 10^3)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(Y_{02}(-D_e \chi_e) \times 10^6)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(Y_{12}(-\beta_e) \times 10^9)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(r_e(\text{Å}))</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(T_e'')</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(x)</td>
<td></td>
</tr>
<tr>
<td>(B^2\Delta_{5/2})</td>
<td>(1) (5/2)</td>
<td>(599.6181(23))</td>
<td>(1105)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(-3.14381(75))</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.27024469(39))</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(-0.00182453(100))</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(-0.01024(30))</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(-0.21131(58))</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(-1.163(90))</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(1.8983)</td>
<td></td>
</tr>
<tr>
<td>([15.8+x] \Omega' = 5/2)</td>
<td>(4) (5/2) ([T_e' = 17,946 \text{ cm}^{-1}])</td>
<td>(15815.8416(21)+x)</td>
<td>(16,841)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(540.0104(22))</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(-3.14824(78))</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.25194999(39))</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(-0.00155287(117))</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(-0.10167(34))</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(-0.21591(60))</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(-0.398(128))</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(1.9660)</td>
<td></td>
</tr>
<tr>
<td>Adiabatic Energy Correction</td>
<td>(\Delta f_{00}) ((\text{cm}^{-1} \text{fm}^{-2}))</td>
<td>(0.2910(36))</td>
<td>(0.2548)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Isotopologue Shift</th>
<th>(\Delta T_e)</th>
<th>(T_0)</th>
<th>(\Delta G_{1/2})</th>
<th>(B_0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{194}\text{PtF}(\Delta T_e)) - (^{195}\text{PtF}(\Delta T_e))</td>
<td>-0.01049(60)</td>
<td>373.31(1)</td>
<td>590(10)</td>
<td>0.27504(5)</td>
</tr>
<tr>
<td>(^{195}\text{PtF}(\Delta T_e)) - (^{195}\text{PtF}(\Delta T_e))</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(^{196}\text{PtF}(\Delta T_e)) - (^{195}\text{PtF}(\Delta T_e))</td>
<td>0.01137(64)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(^{198}\text{PtF}(\Delta T_e)) - (^{195}\text{PtF}(\Delta T_e))</td>
<td>0.03439(80)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^{(a)}\) Reference (77).
\(^{(b)}\) Held to zero in the fit.
\(^{(c)}\) Reference (78).
\(^{(d)}\) Parameter that produces a linear isotopic shift in \(\Delta T_e\) proportional to the change in nuclear radii \(\delta<r^2>\) between isotopes, formally identical to the \(f_{00}\) parameter of Le Roy.\(^{13}\) \(\delta<r^2>\) values were taken from the tables provided by Angeli and Marinova.\(^{112}\) [See equation (7.2)]

\(^{(e)}\) All values reported in \(\text{cm}^{-1}\) unless otherwise noted.
7.6 Electronic Assignment and Correspondence with Computational Predictions

The lowest lying Λ-S states of PtF are derived from the $^2D$ ground state of the Pt$^+$ 5$d^9$ configuration: $^2\Sigma^*$, $^2\Pi$, and $^2\Delta$. The large spin-orbit coupling constant of Pt$^+$ leads to a significant separation between the Ω-components of these Λ-S states. As a result, only 3 Ω states are predicted to have energies <6500 cm$^{-1}$ for PtF: the $^2\Sigma^*$, $^2\Pi_{3/2}$ and $^2\Delta_{5/2}$ states. The ground state of PtF has been established as the $X^2\Pi_{3/2}$ state, and the $T_e$ values of the $^2\Sigma^*$ and $^2\Delta_{5/2}$ states are predicted to be 79 cm$^{-1}$ and 1105 cm$^{-1}$, respectively. As such, these low-lying states will be referred to as $A^2\Sigma^*$ and $B^2\Delta_{5/2}$ states in the following discussion.

Due to the nature of the absorption technique, any electronic transition of PtF observed via ILS likely originates from either the $X^2\Pi_{3/2}$, $A^2\Sigma^*$, or $B^2\Delta_{5/2}$ state. The spectroscopic evidence outlined vide supra, i.e., the observed $J''=2.5$ lines and overall rotational structure of the transition, indicates that the lower state of the observed electronic transition must be the $B^2\Delta_{5/2}$ state. For reasons outlined vide infra, the separation between the $X^2\Pi_{3/2}$ state and $B^2\Delta_{5/2}$ state is unknown, and, therefore, the $T_e$ of the exited state of the observed transition cannot be exactly determined. As a result, this excited state is assigned as the $[15.8+x] \Omega=5/2$ state, where $x$ is $T_e$ of the $B^2\Delta_{5/2}$ state.

Comparison of these experimental findings to computational predictions for PtF provides valuable insight in two regards: first, the Hund’s case (c) character of the electronic states of PtF limits the information that can be derived directly from spectroscopic analysis, and the electronic origin of observed states can be inferred from
theoretically predicted states; and, second, high precision spectroscopic measurements and their analyses can be to evaluate the accuracy of the theoretical model. As such, it is useful to identify predicted electronic states that correspond to the observed electronic transition to infer the origin of the [15.8+x] \( \Omega = 5/2 \) state and to evaluate the accuracy of predicted spectroscopic constants.

The molecular constants obtained from the PGOPHER\textsuperscript{20} Dunham fit of the [15.8+x] \( \Omega = 5/2 \) - \( B^2 \Delta_{5/2} \) transition were compared to the states of PtF predicted by Zou and Suo\textsuperscript{77} to identify the corresponding electronic transition. The transition dipole moments (TDM), transition energies, \( \omega_e' \) and \( B_e' \) values of PtF predicted by Zou and Suo\textsuperscript{77} for the three \( \Omega' = \Omega'' = 5/2 \) transitions closest in energy to the observed transition can be found in Table 7.3, with the transition energy, \( \omega_e' \) and \( B_e' \) values determined in this analysis provided for comparison. The predicted vibrational and rotational constants between the three excited states are too similar to be diagnostic, but these predicted values are in reasonable agreement with the determined parameters. The large TDM for the (4) \( 5/2 \) - (1) \( 5/2 \) transition, and the reasonable agreement between the observed and predicted transition energies strongly support the assignment of this predicted transition to the observed [15.8+x] \( \Omega = 5/2 \) - \( B^2 \Delta_{5/2} \) transition of PtF. The predicted transition energy is 6.4\% larger than the experimental transition energy, the predicted \( \omega_e' \) and \( \omega_e'' \) values deviate from the experimental values by +2.3\% and -0.7\%, and the predicted \( B_e' \) and \( B_e'' \) values deviate from the experimental values by +1.1\% and -0.2\%.

The (1) \( 5/2 \) state is almost exclusively derived from the lowest lying (1) \( ^2 \Delta \) state (93\%). The electronic configuration giving rise to this \( ^2 \Delta \) state is \( 1\sigma^21\pi^41\delta^32\pi^42\sigma^23\sigma^0 \)
using the molecular orbital notation of Zou and Suo. In contrast, the (4) 5/2 state is highly mixed and primarily comprised of (1) 4Φ state (43%) and the (2) 4Π state (36%). The primary electronic configuration leading to these Λ-S states is 1σ^21π^41δ^32π^22σ^23σ^1 (4Φ: 99%; 4Π: 75%), which can be obtained from the (1) 2Δ configuration by promoting an electron from the 2π orbital to the 3σ. This fully allowed electronic transition helps rationalize the large transition dipole moment for the predicted transition and is consistent with the intensity of the observed electronic transition.

Table 7.3: Predicted transition dipole moments (R^2tot), transition energies (ΔT_e), vibrational frequencies (ω_e) and rotational constants (B_e) from Zou and Suo. The R^2tot values provide support for the proposed electronic assignment. Units in cm\(^{-1}\) unless otherwise noted.

<table>
<thead>
<tr>
<th>Transition</th>
<th>R^2tot (au)</th>
<th>ΔT_e (cm(^{-1}))</th>
<th>ω_e'' (cm(^{-1}))</th>
<th>B_e'' (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(7) 3/2 - (1) 1/2</td>
<td>0.038</td>
<td>20,094</td>
<td>610.6</td>
<td>0.2735</td>
</tr>
<tr>
<td>(7) 3/2 - (1) 5/2</td>
<td>0.015</td>
<td>19,068</td>
<td>595.5</td>
<td>0.2696</td>
</tr>
<tr>
<td>[18.8] Ω = 3/2 - [0.4] (ΔΩ = ± 1)</td>
<td>18,861</td>
<td>*590(10)</td>
<td>0.27504</td>
<td></td>
</tr>
<tr>
<td>(3) 5/2 - (1) 5/2</td>
<td>0.064</td>
<td>10,814</td>
<td>569.1</td>
<td>0.2501</td>
</tr>
<tr>
<td>(4) 5/2 - (1) 5/2</td>
<td>0.261</td>
<td>16,841</td>
<td>555.7</td>
<td>0.2548</td>
</tr>
<tr>
<td>(5) 5/2 - (1) 5/2</td>
<td>0.046</td>
<td>18,871</td>
<td>553.0</td>
<td>0.2548</td>
</tr>
<tr>
<td>[15.8+x] - [x] (Ω' = Ω'' = 5/2)</td>
<td>15,816</td>
<td>543.0177(24)</td>
<td>0.25195</td>
<td></td>
</tr>
</tbody>
</table>

* Estimated ΔG\(_{1/2}\) from Ng et al.

7.7 Reassignment of the [0.4] State

The electronic assignment outlined vide supra requires reassignment of the [0.4] state of Ng et al. The B_0'' value determined in this analysis (0.2693 cm\(^{-1}\)) does not agree with B_0=0.2750 cm\(^{-1}\) for the [0.4] state. Therefore, as the [0.4] state can be neither the \(X^2\Pi_{3/2}\) nor the \(B^2\Delta_{5/2}\) state, it stands to reason that it is the \(A^2\Sigma^+\) state. This proposed reassignment is supported by the predicted TDM for PtF from Zou and Suo (Table 7.3),
which indicates that the \((7) \ 3/2 - (1) \ 1/2\) transition would be roughly twice as intense as the \((7) \ 3/2 - (1) \ 5/2\) transition.

As a result of this reassignment, \(T_0\) of the \(A \ 2^\Sigma^+\) state is assigned as 374 cm\(^{-1}\) and the energetic separation between the \(X^2\Pi_{3/2}\) state and the \(B^2\Delta_{5/2}\) state is unknown. An energy level diagram including the results of this analysis with the known electronic states of PtF and those predicted by Zou and Suo\(^77\) is provided in Figure 7.3.

7.8 Born-Oppenheimer Breakdown

The observed isotopologue shift in \(\Delta T_e\) was somewhat surprising. The electronic potential energy arises from Coulombic interactions between the electrons and nuclei of a molecule. The Born-Oppenheimer approximation states that if nuclear motion occurs at a rate much slower than that of electronic rearrangement, a “clamped” nuclei approach may be used to describe the energetics, and internuclear Coulombic repulsion becomes constant. A result of this approximation is degeneracy in electronic energy between isotopologues. In the case of the Pt nucleus, the mass of \(^{195}\text{Pt}\) is 3.5 \times 10^5 times greater than \(m_e\), so the Born-Oppenheimer approximation should rigidly hold upon Pt isotope substitution. As mentioned above, Tiemann \textit{et al.}\(^8\)\(^{-12}\) demonstrated that anomalous BOB for Pb- and Tl-containing molecules could be treated using parameters that scale proportionally to \(\delta<r^2>\). This approach is rationalized by considering the small changes in nuclear charge radii between isotopes as small differences in internuclear distance between the isotopologues. This slight change in distance would result in a slightly different Coulombic potential between the isotopologues, and a corresponding shift in
electronic energy. This shift is analogous to the atomic optical isotope shifts that were analyzed to generate the reference $\delta<r^2>$ values reported by Angeli and Marinova.\textsuperscript{112}

Field-shift effects have been used by Cooke and Gerry to describe BOB observed in rotational constants determined from the multi-isotopologue analysis of pure rotational spectra of PtO,\textsuperscript{113} PtS,\textsuperscript{114} and PtSi\textsuperscript{115} collected using Fourier-Transform Microwave Spectroscopy. Reported isotopologue shifts in electronic excitation energy are less prevalent in the literature. Only two examples of a shift in electronic energy for a molecule containing no light atoms (H or Li). The first was observed by Tiemann and coworkers\textsuperscript{9,12} for transitions of PbS in the initial works outlining the appearance of field-shift effects. The second resulted from a direct potential fit of electronic, vibrational, and rotational spectra of Br$_2$ performed by Yukiya et al.\textsuperscript{116} That study showed that there was an isotopologue dependent variance in the well depth of the $X^1\Sigma^+_g$ state.

It should be noted that the quality of the PGOPHER\textsuperscript{20} fit was improved slightly when four independent $\Delta T_e$ values were allowed to float instead of using one $\Delta T_e$ value and one $\Delta f_{00}$ parameter. However, the precision of the determined $\Delta f_{00}$ parameter is limited by the precision of the reference $\delta<r^2>$ values,\textsuperscript{112} suggesting that this slight decrease in fit quality is possibly due to the uncertainty in determined changes in nuclear charge radii.

7.9 Conclusions

The [15.8 + x] $\Omega = 5/2 - B^2 \Delta s_{5/2}$ transition of PtF has been observed in absorption using Intracavity Laser Spectroscopy. Six vibrational bands were identified and rotationally analyzed, including transitions of $^{194}$PtF, $^{195}$PtF, $^{196}$PtF, and $^{198}$PtF. The observed transitions for the vibrational bands were simultaneously fit to 16 mass-
independent Dunham parameters, using the analytical expression of Le Roy.\textsuperscript{13} The determined molecular parameters are consistent with the (4) and (1) $\Omega = 5/2$ states of Zou and Suo,\textsuperscript{77} and support reassignment of the [0.4] state of Ng \textit{et al.}\textsuperscript{104} as the $A^2\Sigma^+$ of PtF. Born-Oppenheimer breakdown in the electronic transition energy was treated as a manifestation of the difference in nuclear charge radii between Pt isotopes. Isotopologue shifts in electronic excitation energy ranged from $-0.010$ cm$^{-1}$ to $0.034$ cm$^{-1}$ relative to the reference isotopologue, $^{195}$PtF. The results of this study have been published in the Journal of Molecular Spectroscopy.\textsuperscript{109}
Figure 7.3: Energy level diagram for the known and predicted states of PtF. The blue arrow corresponds to the work of Handler et al., the red arrows correspond to the work of Ng et al., the solid green arrows correspond to observed transitions with ongoing rotational analysis, and the dashed green arrow corresponds to this study.
CHAPTER VIII
PLATINUM CHLORIDE

8.1 Introduction and Previous Studies of PtCl

Platinum containing diatomic molecules are valuable gas-phase spectroscopic targets because the electronic structures of these molecules, which are found to be highly sensitive to electron correlation and relativistic effects, are difficult to describe by theoretical modeling.\(^{77}\) The platinum chloride (PtCl) bond is of particular interest for several reasons. A PtCl bond can be found in cisplatin, \([\text{cis-PtCl}_2(\text{NH}_3)_2]\). Cisplatin has been a powerful chemotherapy agent for almost 50 years\(^{117}\) and the development of new Pt-containing anti-cancer drugs is a prominent field of research.\(^{118}\) PtCl bonds also appear in quasi-linear MX and MMX (M=Ni, Pd, Pt; X=Cl, Br, I) type compounds, which have drawn a great deal of scientific interest due to their dichroic and mixed valence properties,\(^{119}\) chemical tunability,\(^{120}\) charge-density- and spin-density-wave states,\(^{120}\) and high electrical conductivity and negative differential resistance.\(^{121}\) Additionally, catalytic complexes containing PtCl bonds, like Speier’s catalyst \((\text{H}_2\text{PtCl}_6)\), are used in industry to accelerate hydrosilylation reactions.\(^{122}\)

Despite the interesting properties of molecules containing Pt-Cl bonds, spectroscopic investigation into the electronic structure of diatomic PtCl has been quite limited. The first spectroscopic observation of PtCl was reported in 2002 by Bridgeman \textit{et al.}\(^{123}\) In that study, molecules produced in the plasma discharge of a Pt-lined hollow cathode with 1-5% Cl\(_2\) in Ar were matrix isolated in solid Ar. The resulting matrices were characterized using IR, UV-visible, and X-ray spectroscopies. Vibrational transitions in the
IR spectrum at 399.1 cm\(^{-1}\) and 390.2 cm\(^{-1}\) were attributed to Pt\(^{35}\)Cl and Pt\(^{37}\)Cl with the aid of DFT calculations. In 2012, Okabayashi et al.\(^{102}\) measured the pure rotational spectrum of PtF and PtCl in the 150-313 GHz region. The ground state of PtCl was discovered to be \(^2\Pi_{3/2}\) in character via rotational analysis of 7 isotopologues: \(^{194}\)Pt\(^{35}\)Cl (24.98 % abundant), \(^{195}\)Pt\(^{35}\)Cl (25.64 %), \(^{196}\)Pt\(^{35}\)Cl (19.13 %), \(^{198}\)Pt\(^{35}\)Cl (5.43 %), \(^{194}\)Pt\(^{37}\)Cl (7.98 %), \(^{195}\)Pt\(^{37}\)Cl (8.19 %), and \(^{196}\)Pt\(^{37}\)Cl (6.11 %). There have been no other spectroscopic observations of PtCl to the best knowledge of the authors.

The theoretical description of the electronic structure of PtCl is more comprehensive. In 2002, Liu and Franke\(^{122}\) used \textit{ab initio} and DFT approaches including various relativistic and electron correlation treatments to investigate the three \(\Lambda\)-\(S\) states derived from the \(^2\)D ground state from the \(5d^9\) configuration of Pt\(^{+}\): \(^2\Sigma^+, ^2\Pi\), and \(^2\Delta\). Their results predict the ground state of PtCl to be \(^2\Pi_{3/2}\), consistent with the conclusions of Okabayashi et al.\(^{102}\) recorded 10 years after these calculations were reported. In 2016, Zou and Suo\(^{77}\) used the multi-reference interaction method with relativistic core potentials to investigate the electronic states of PtX species (X=F, Cl, Br, and I) at energies below 35,000 cm\(^{-1}\). Spin-orbit coupling was treated using a perturbative state-interaction approach. Due to the large atomic spin-orbit coupling of Pt, only the \(^2\Sigma^+_{1/2}\) and \(^2\Delta_{5/2}\ \Omega\) states from the \(^2\)D ground state of Pt\(^{+}\) are predicted to lie within 9000 cm\(^{-1}\) of the \(X\ ^2\Pi_{3/2}\) ground state of PtCl. These three low-lying states of PtCl are \(>60\%\) \(^2\Sigma^+\), \(>70\%\) \(^2\Pi\), and \(>95\%\) \(^2\Delta\) for the \(1/2, 3/2\), and \(5/2\ \Omega\) states, so Hund’s case (a) notation is used for these states even though they are somewhat mixed by spin-orbit interactions. The most recent theoretical investigation of PtCl was reported by Deng et al.\(^{108}\) in 2017. In that study, the
permanent electric dipole moment and equilibrium geometries were predicted for PtX molecules in their ground states using the Feller-Peterson-Dixon (FPD) composite approach.

In this study, intracavity laser spectroscopy (ILS) was used to identify electronic transitions of diatomic PtCl in the 12890-12990 cm\(^{-1}\), 13,255-13,365 cm\(^{-1}\), and 14,500-16,500 cm\(^{-1}\) regions. Eight band systems due to PtCl are observed in the ILS spectra, with bandheads at 12,955 cm\(^{-1}\), 13,349 cm\(^{-1}\), 14,751 cm\(^{-1}\), 15,081 cm\(^{-1}\), 15,339 cm\(^{-1}\), 15,410 cm\(^{-1}\), 15,662 cm\(^{-1}\), and 15,736 cm\(^{-1}\). These bands are assigned respectively as the (0,2), (0,1), (3,0), (4,0), (6,1), (5,0), (7,1), and (6,0) vibrational bands of the [13.8] \(\Omega=3/2-X^2\Pi_{3/2}\) transition of PtCl. Rotational assignments for the bands with \(v''=0\) are confirmed by the agreement between branch combination differences and calculated \(\Delta_2 F''\) levels from the constants reported by Okabayashi et al.\(^{102}\) Vibrational assignments are confirmed via analysis of isotopologue dependent shifts in band origins. The line positions from the microwave data of Okabayashi et al.\(^{102}\) were incorporated with the ILS data in a mass-independent Dunham type fit using PGOPHER.\(^{20}\) The centrifugal distortion constants of the excited state were not well described by the Dunham expansion and were independently determined for each vibrational level. Additionally, small but significant deviations from the Dunham expression were observed for the \(v'=7\) vibrational level of the [13.8] state. These deviations from the Dunham model suggest that the [13.8] state interacts with a nearby electronic state, a reasonable assumption given that Zou and Suo\(^{77}\) predict 5 \(\Omega\) states of PtCl between 13,000 and 16,500 cm\(^{-1}\). Correction terms were incorporated into the Dunham fit to compensate for these deviations *in lieu of* experimental data.
characterizing the unknown interacting state(s). Electronic transitions of NiF, NiCl, and PtF analogous to the \([13.8] \Omega=3/2 - X^2\Pi_{3/2}\) transition of PtCl have been studied both by theory\(^{70,77}\) and by experiment.\(^{60,63,66,102,103,124,125}\) Analysis of the data for these MX (M=Ni, Pt; X=F, Cl) molecules indicates similar bonding between NiX and PtX species, with NiX bonds slightly stronger, and a significant halogen effect, with the force constants \((k)\) of the MF species more than twice the corresponding MCl \(k\) values. The results of this study are published in the Journal of Molecular Spectroscopy.\(^{126}\)

### 8.2 Production of the PtCl Molecules

The PtCl molecules were produced in the plasma discharge formed by applying RF current to a 50 mm long Pt-lined Cu hollow cathode. Discharge currents of 0.30 A and 0.60 A were used with ~1 Torr of a sputter gas mixture of Ar/He containing 2% CCl\(_4\). Similar to recent experience with PtF described in the previous chapter, it was discovered that features due to PtCl appeared strongly upon initiation of the plasma discharge, but those signals depleted rapidly as the plasma reached stable operating conditions. For the bands with \(v''=0\), the hollow cathode was located within the resonator cavity of the DL-ILS system. For the bands with \(v'=0\), the hollow cathode was located within the cavity of a TS-ILS system. For this study, generation times \((t_g)\) ranging from 50 to 150 μsec were utilized, resulting in effective pathlengths of 0.6-2.0 km via the ILS method. A sample spectrum of the \((6,0)\) band of the \([13.8] \Omega=3/2 - X^2\Pi_{3/2}\) transition is provided in Figure 8.1 along with a simulation produced from the final PGOPHER\(^{20}\) fit.
Figure 8.1: A selection of the ILS absorption spectrum (top) for the (6,0) band of the \([13.8] \Omega=3/2 - X^2\Pi_{3/2}\) transition of PtCl. The PGOPHER\textsuperscript{20} simulation (bottom) corresponds to \(^{194}\text{Pt}\text{Cl}, \(^{195}\text{Pt}\text{Cl},\) and \(^{196}\text{Pt}\text{Cl},\) generated using a rotational temperature of 600 K with Gaussian and Lorentzian linewidths of 0.035 cm\(^{-1}\).

8.3 Assignment of the Band Systems

Six band systems are observed in the ILS data over the 14,500-16,500 cm\(^{-1}\) region. The strongest four bands are separated by \(~330\) cm\(^{-1}\), with bandheads located near 14,751 cm\(^{-1}\), 15,081 cm\(^{-1}\), 15,410 cm\(^{-1}\), and 15,736 cm\(^{-1}\). Other band systems were observed weakly \(~70\) cm\(^{-1}\) to the red of two of the major bands, with bandheads occurring near 15,339 cm\(^{-1}\) and 15,662 cm\(^{-1}\).

All bands have very similar rotational structure, with 6 predominant rotational branches for each band: 3 P-type and 3 R-type. Splitting observed in the identified P- and R-branches branches for \(J''>30.5\) and the lack of a strong Q-branch are consistent with a \(\Omega'=\Omega''=3/2\) transition. Agreement between combination differences of the identified
branches and calculated $\Delta_2 F''$ values from the rotational constants reported by Okabayashi et al.\textsuperscript{102} for the $X^2\Pi_{3/2}$ state of $^{194}$Pt$^{35}$Cl, $^{195}$Pt$^{35}$Cl, and $^{196}$Pt$^{35}$Cl confirm the molecular identity, electronic and vibrational ground state, and rotational assignment for the four strong bands. The branch splitting in the R-lines ($J''>37.5$) can be seen in the portion of the (6,0) band of the $[13.8] \Omega=3/2 - X^2\Pi_{3/2}$ transition provided in Figure 8.2, but the $e$- and $f$- lines of the P-branch ($J''<27.5$) are overlapped at the experimental resolution used.

The excited state vibrational levels for the observed bands were initially assigned via analysis of isotopologue bandhead shifts. The ground state vibrational frequency, $\omega_o$, of $^{195}$Pt$^{35}$Cl was estimated to be 394 cm$^{-1}$ from the rotational constants determined by Okabayashi et al.\textsuperscript{102} The observed band separation of 330 cm$^{-1}$ was used as an estimate of
\( \omega_e \) for the excited state of \(^{195}\text{Pt}^{35}\text{Cl} \). The corresponding vibrational frequencies for \(^{194}\text{Pt}^{35}\text{Cl} \) and \(^{196}\text{Pt}^{35}\text{Cl} \) were calculated using the relationship:

\[
\omega_e^\alpha = \omega_e^1 \sqrt{\frac{\mu_1}{\mu_\alpha}} \tag{8.1}
\]

where \( \alpha \) refers to the minor isotopologue, \( 1 \equiv ^{195}\text{Pt}^{35}\text{Cl} \), \( \omega_e \) is the harmonic frequency, \( \mu \) is the reduced mass, and \( \mu_1/\mu_\alpha \) is the reduced mass ratio, \( \rho \). The theoretical vibrationally dependent isotopologue shift, \( \Delta G_{v'v''} \), was then calculated using the expression:

\[
\Delta G_{v'v''} = \left[ \omega_e^{194} (v' + \frac{1}{2}) - \omega_e^{194} \left( 0 + \frac{1}{2} \right) \right]_{\text{194}\text{Pt}^{35}\text{Cl}} - \left[ \omega_e^{196} (v' + \frac{1}{2}) - \omega_e^{196} \left( 0 + \frac{1}{2} \right) \right]_{\text{196}\text{Pt}^{35}\text{Cl}} \tag{8.2}
\]

These calculated \( \Delta G_{v'v''} \) values (see Table 8.1) were then compared to the experimentally observed bandhead shifts, as shown in Figure 8.3, resulting in the assignment of the four strong transitions as the vibrational progression of the (3,0), (4,0), (5,0), and (6,0) bands and a predicted excitation energy, \( T_e \), of 13,775 cm\(^{-1} \). Thus, the observed electronic transition is assigned as the \([13.8] \Omega=3/2 - X^{2}\Pi_{3/2} \) transition of PtCl.

The corresponding isotopologue shifts for \(^{195}\text{Pt}^{37}\text{Cl} \) for the (5,0) and (6,0) bands are predicted to be 37 cm\(^{-1} \) and 45 cm\(^{-1} \), respectively, supporting the assignment of the weak transitions 70 cm\(^{-1} \) to the red of the (5,0) and (6,0) bands as the (6,1) and (7,1) bands. The preliminary assignment of the \( v''=1 \) bands are confirmed through analysis of combination differences with the (6,0) and (6,1) bands.

The vibrational analysis led to a targeted search in the near-infrared for bands involving \( v'=0 \) with the TS-ILS system. Detection of the (0,0) band was impractical using the ILS method due to strong absorption features of atmospheric water. However, the (0,1) and (0,2) bands were readily observed near their expected transition energies, and
the assignment of these bands was confirmed through combination differences initially with the (6,1) and (0,1) bands, and subsequently with the (0,1) and (0,2) bands.

8.4 Fitting the Isolated Bands

With a secure rotational and vibrational assignment, the ILS data were fit using PGOPHER. In the fit, the 3974 ILS line positions for the (0,2), (0,1), (3,0), (4,0), (5,0), (6,0), (6,1), and (7,1) bands of \( ^{194}\text{Pt}^{35}\text{Cl} \), \( ^{195}\text{Pt}^{35}\text{Cl} \), and \( ^{196}\text{Pt}^{35}\text{Cl} \) from this work were supplemented with the 194 line positions for \( ^{194}\text{Pt}^{35}\text{Cl} \), \( ^{195}\text{Pt}^{35}\text{Cl} \), \( ^{196}\text{Pt}^{35}\text{Cl} \), \( ^{198}\text{Pt}^{35}\text{Cl} \), \( ^{194}\text{Pt}^{37}\text{Cl} \), \( ^{195}\text{Pt}^{37}\text{Cl} \), and \( ^{196}\text{Pt}^{37}\text{Cl} \) from the pure rotational spectrum recorded by Okabayashi \textit{et al.} A statistical weight of 10 kHz was assigned to the microwave line positions that were fully resolved, and a weight of 25 kHz was assigned to the 24 transitions of \( ^{195}\text{PtCl} \) without resolved hyperfine structure. Statistical weights of 0.005 and 0.0075 cm\(^{-1}\) were assigned to the ILS data calibrated with the data provided by Salami and Ross (DL-ILS), and calculated by PGOPHER (TS-ILS), respectively.

In the initial fitting process, each vibrational level and each isotopologue were treated independently and fit using standard PGOPHER Hamiltonian elements. Using this approach for a Hund’s case (c) \( ^2\Pi_{3/2} \) state, “S” is set to 0.5, “Lambda” is set to “Pi”, and “OmegaSelect” is set to 1.5. The Λ-doubling parameters of the Hund’s case (c) \( ^2\Pi_{3/2} \) state are restricted to the parameters with diagonal matrix elements, i.e., “q_D”, “q_H” and “q_L”. As discussed by Okabayashi \textit{et al.}, the magnitude of \( q \) can be roughly estimated using the pure precession assumption.
Figure 8.3: Vibrationally dependent isotopologue bandhead shifts between $^{194}\text{Pt}^{35}\text{Cl}$ and $^{196}\text{Pt}^{35}\text{Cl}$ ($\Delta E$) for the observed bands is consistent with the expected splitting (3,0), (4,0), (5,0), and (6,0) bands. See Table 8.1.

\[
q = \frac{8B_v^3}{\Delta E}
\]  

(8.3)

where $B_v$ is the vibrationally dependent rotational constant, $A$ is the spin-orbit constant, and $\Delta E$ is the separation between the $^2\Pi$ ground state and the first $^2\Sigma^+$ state.

As $A$ is negative for a $^2\Pi_i$ state and all other terms in equation 8.3 must be positive, $q$ is expected to have a negative value.

However, the $\Lambda$-doubling parameters used by Okabayashi et al.,\textsuperscript{102} namely $q$ and $q_J$ (which correspond to the “$q_D$” and “$q_H$”

<table>
<thead>
<tr>
<th>$v'$</th>
<th>$v''$</th>
<th>Predicted $\Delta G(v'-v'')^b$</th>
<th>Measured Bandhead Shift$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>-0.03</td>
<td>0.719</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>0.23</td>
<td>0.981</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>0.48</td>
<td>1.097</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>0.74</td>
<td>1.480</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>0.99</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>1.25</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>0</td>
<td>1.50</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0</td>
<td>1.76</td>
<td></td>
</tr>
</tbody>
</table>

$^a$All values reported in cm$^{-1}$.

$^b$ Vibrationally dependent isotopologue origin shift calculated with eqn. 8.2.

$^c$Measured separation between $^{194}\text{Pt}^{35}\text{Cl}$ and $^{196}\text{Pt}^{35}\text{Cl}$ bandhead positions.
parameters in PGOPHER\textsuperscript{20} do not follow the standard sign convention for \( \Lambda \)-doubling parameters outlined by Yamada\textsuperscript{128} and utilized in PGOPHER,\textsuperscript{20} i.e., "\( q_D \equiv -q \) and "\( q_H \equiv q \). Therefore, the sign of the \( \Lambda \)-doubling parameters in this work is consistent (though of opposite sign) with those of the initial microwave analysis.\textsuperscript{102}

In total, 139 parameters were fit to 4168 observations with a root mean square (RMS) deviation of 12 kHz for the resolved microwave data, 0.0039 cm\(^{-1}\) for the DL-ILS data, and 0.0067 cm\(^{-1}\) for the TS-ILS data. It should be noted that use of the higher order centrifugal distortion constant, \( H \), was necessary to adequately fit the excited state vibrational levels with \( v' > 0 \). The determined \( H \)-values are roughly two orders of magnitude larger than is expected based on the theoretical relationship\textsuperscript{129}

\[
H_v \approx H_e = \frac{2}{3} D_e \left[ 12 \left( \frac{\beta_1}{\omega_e} \right)^2 + \frac{\alpha_1}{\omega_e} \right]
\]  

\textbf{8.5 Linear Model for Mass-Independent Dunham Analysis}

The large spin-orbit coupling constant for Pt\( \textsuperscript{0,+} \) is expected to lead to widely spaced spin-orbit components for the electronic states of PtX (X=F, Cl, Br, I) molecules, resulting in an electronic structure containing several interacting states.\textsuperscript{77} In Hund’s case (c), near-degenerate \( \Lambda \)-\( S \) states mix to produce \( \Omega \)-states whose properties relate only to total angular momentum and not to orbital- or spin-angular- momenta individually, i.e., \( \Lambda \) and \( S \) are no longer good quantum numbers.\textsuperscript{3} In this case, much of the fine structure that can be used to distinguish a specific \( \Lambda \)-\( S \) state is difficult to observe and identify spectroscopically. To better understand the underlying characteristics of the electronic states involved in this transition of PtCl, which indeed appear to follow Hund’s case (c), a mass-independent Dunham analysis was performed using the constrained variable method utilized in the
previous chapters with PGOHPER. The Dunham analysis can be used to interpret

differences between isotopologues and rovibrational levels, helping to make sense of
spectroscopic observations even when electronic fine structure cannot be identified
unambiguously.

The constrained variable method uses the approach outlined by Breier and

cauthors to simulate and fit spectroscopic data with PGOHPER using a mass-

independent Dunham model. The Dunham expression derived by Le Roy was utilized in

this study. The expression included terms that account for deviations from the Born-

Oppenheimer Approximation as outlined by Watson and from the assumption that atomic

nuclei are point charges as outlined by Tiemann et al. Le Roy’s method was selected

based on the several advantages over the traditional Watson expression originally

outlined by Le Roy in the work containing his derivation. The fitted parameters are specific
to the most abundant isotopologue, for which the greatest number of observations is
expected. The electronic and rovibrational constants for minor isotopologues are generated
using the relationships originally outlined by Dunham. Deviations from Dunham’s model are treated as linear perturbations resulting from isotope-specific differences in mass or
nuclear-charge-radius.

The form of Le Roy’s Dunham expression used for this analysis contained elements

outlined by the following expression

\[ H_{\Omega-\text{State}} = H_{\text{Elec}} + H_{\text{Rovib}} + H_\Omega + H_{\text{BOB}} + H_{\text{field-shift}} + H_{HF} \]  

(8.5)

where \( H_{\Omega-\text{State}} \) is specific to a single Hund’s case (c) \( \Omega \)-state, \( H_{\text{Elec}} \) is the contribution from
electronic energy, \( H_{\text{Rovib}} \) is the rovibrational energy expression outlined by Dunham, \( H_\Omega \) is
the expression that addresses the coupling between total orbital-spin angular momentum and rotational angular momentum, $H_{BOB}$ addresses the breakdown of the Born-Oppenheimer approximation first derived from theory by Watson,7 $H_{field-shift}$ addresses breakdown of the Dunham model due to changes in the nuclear-charge-radius of isotopes as first derived from theory by Tiemann et al., 8-12 and $H_{HF}$ addresses spectroscopic structure due to hyperfine interactions with the $^{195}$Pt nucleus (I=1/2). No hyperfine structure due to the Cl nuclei $[I(^{35}Cl, ^{37}Cl)=3/2]$ was observed in either the microwave102 or the ILS data.

The components of equation 8.5 can be expanded to the following expressions:13,130

$$H_{Elec} = Y_{00}^1$$  \hspace{1cm} (8.6)

$$H_{Rovib} = \sum_{l,m} Y_{l,m}^1 \left( \frac{\mu_1}{\mu_\alpha} \right)^{m+\frac{l}{2}} (v+\frac{1}{2})^m [l(J+1)^m]$$  \hspace{1cm} (8.7)

$$H_{\Omega=3/2} = \frac{1}{2} (J - \frac{1}{2}) (J + \frac{3}{2}) \sum_{m \geq 0} \sum_{l \geq 0} q_{l,m}^1 \left( \frac{\mu_1}{\mu_\alpha} \right)^{m+\frac{l}{2}} (v+\frac{1}{2})^m [l(J+1)^m-1]$$  \hspace{1cm} (8.8)

$$H_{BOB} = \sum_{m \geq 0} \sum_{l \geq 0} \left[ \left( \frac{4M_A^1}{M_\alpha^2} s_{l,m}^A + \frac{4M_B^1}{M_\alpha^2} s_{l,m}^B \right) \sum_{m \geq 0} \sum_{l \geq 0} q_{l,m}^1 \left( \frac{\mu_1}{\mu_\alpha} \right)^{m+\frac{l}{2}} (v+\frac{1}{2})^m [l(J+1)^m] \right]$$

$$\times \left( \frac{\mu_1}{\mu_\alpha} \right)^{m+\frac{l}{2}} (v+\frac{1}{2})^m [l(J+1)^m]$$  \hspace{1cm} (8.9)

$$H_{field-effect} = \sum_{m \geq 0} \sum_{l \geq 0} \left( \delta < r^2 > A f_{l,m}^A + \delta < r^2 > B f_{l,m}^B \right) \left( \frac{\mu_1}{\mu_\alpha} \right)^{m+\frac{l}{2}} (v+\frac{1}{2})^m [l(J+1)^m]$$  \hspace{1cm} (8.10)

where A and B refer to the two atoms of the diatomic molecule; 1 and $\alpha$ refer to the reference and relative isotopologues, respectively; $Y_{00}^1$ is the independent variable for the electronic energy of the reference isotopologue for a given $\Omega$-state; $l$ and $m$ refer to the $l$th-vibrational and $m$th-rotational component in the expansion; $Y_{l,m}^1$ are the independent rovibrational Dunham parameters for the reference isotopologue 1; $\mu$ is the reduced mass.
for the reference (1) and relative (α) isotopologues, \( v \) is the vibrational quantum number; \( J \) is the rotational quantum number; \( \delta\langle r^2\rangle_{\alpha}^{A1} \) is the change in mean squared nuclear charge radii between reference (1) and relative (α) isotopes of atom \( A \); \( M_{\alpha}^{A} \) is the mass of isotopologue \( \alpha \); \( \Delta M_{\alpha}^{A1} \) is the difference in mass between the relative (α) and reference (1) isotopologues; \( \delta_{\text{lm}}^{A} \) are the independent variables that treat mass-dependent Born-Oppenheimer breakdown (BOB), closely related to the \( \Delta_{\text{lm}} \) parameters derived by Watson;\(^7\) and \( f_{\text{lm}}^{A} \) are “field-shift” parameters introduced by Tiemann \textit{et al.}\(^8\text{-}12\) that depend on the electron density at the nucleus of atom \( A \) \( (\delta\langle r^2\rangle_{\alpha}^{A1}) \).\(^112\) The second set of terms in brackets in equation 8.9 treat mass-dependent Born-Oppenheimer breakdown in the \( \Omega \)-doubling parameters \( q_{\text{lm}} \) in the method outlined by Le Roy.\(^130\) The - and + in equations 8.8 and 8.9 refer to the e- and f-levels, respectively.

The components of \( H_{\text{HF}} \) utilized in this study \((h_{3/2}, c_I)\) are identical to those used in the original analysis of the microwave spectrum by Okabayashi \textit{et al.}\(^102\) The effective hyperfine parameter \( h_{3/2} \) scales proportionally with the Frosch and Foley\(^58\) \( a \), \( b \), and \( c \) parameters and is defined in the Hund’s case (a) limit as\(^102\)

\[
h_{3/2} = a + \frac{1}{2} (b + c) \quad (8.11)
\]

Hyperfine splitting due to the chlorine nucleus was not observed in either data set, so the effective \( h_{3/2} \) parameter refers only to hyperfine structure due to the \(^{195}\)Pt nucleus. Therefore, \( h_{3/2} \) for \(^{195}\)Pt\(^{35}\)Cl and \(^{195}\)Pt\(^{37}\)Cl were constrained to be equal in the fit. The nuclear spin-rotation coupling constant \( c_I \) is proportional to the rotational constant, so\(^102\)

\[
c_I^\alpha = c_I^1 \left( \frac{\mu_1}{\mu_\alpha} \right) \quad (8.12)
\]
where \( \alpha \) refers to the relative isotopologue \(^{195}\text{Pt}^{37}\text{Cl} \) and \( 1 \) refers to the reference isotopologue \(^{195}\text{Pt}^{35}\text{Cl} \).

### 8.6 Mass-Independent Analysis of the \( X \, \Pi_{3/2} \) Ground State of \( \text{PtCl} \)

The \( X \, \Pi_{3/2} \) ground electronic state of \( \text{PtCl} \) was fit to a Dunham expression that included 16 independent variables. The spectroscopic data set included transitions specific to 3 vibrational levels \( (v''=0, 1, 2) \), 7 \( \text{PtCl} \) isotopologues, and rotational levels ranging from \( J''_{\text{min}}(2.5) \) to \( J''_{\text{max}}(84.5) \). The electronic energy of the ground state was set to zero by definition (i.e., \( H_{\text{Elec}}=0 \)). The rovibrational structure of the ground state was well described by 8 parameters \( (Y_{10}, Y_{20}, Y_{01}, Y_{11}, Y_{21}, Y_{02}, Y_{12}, Y_{30}) \), the \( \Omega \)-doubling structure by 2 parameters \((q_{01}, q_{02})\), mass-dependent Born-Oppenheimer breakdown by 2 parameters \((\delta_{01}^{\text{Cl}}, \delta_{01}^{\text{Pt}})\), isotope specific field-shift effects by 2 independent parameters \((f_{01}^{\text{Pt}}, f_{01}^{\text{Pt}})\), and hyperfine structure with 2 independent parameters \((h_{3/2}, c_{1})\). The mass-dependent Born-Oppenheimer breakdown of \( Y_{01} \) due to Pt-isotope substitution \((\delta_{01}^{\text{Pt}})\) was highly correlated to \( f_{01}^{\text{Pt}} \) and could not be reliably determined when treated independently. To overcome this issue, it was assumed that the mass-dependent Born-Oppenheimer correctional terms for Pt- and Cl-isotope substitution were approximately equal when expressed in terms of Watson’s dimensionless \( \Delta_{lm} \) parameters. The \( \delta_{l,m}^{\text{Pt,Cl}} \) parameters of equation 8.9 are related to the \( \Delta_{lm} \) parameters by the following expressions:\(^{13}\)

\[
\Delta_{01}^{\text{Cl}} = -\frac{\delta_{01}^{\text{Cl}} M_{1}^{\text{Cl}}}{m_{e}(Y_{01} + \delta_{01}^{\text{Cl}} + \delta_{01}^{\text{Pt}})}
\]

\[
\Delta_{01}^{\text{Pt}} = -\frac{\delta_{01}^{\text{Pt}} M_{1}^{\text{Pt}}}{m_{e}(Y_{01} + \delta_{01}^{\text{Cl}} + \delta_{01}^{\text{Pt}})} \approx \Delta_{01}^{\text{Cl}}
\]
where $m_e$ is the mass of an electron and all other terms are defined above. This assumption was used by Cooke and Gerry to perform mass-independent Dunham analyses of PtSi$^{115}$ PtS$^{114}$ and PtO$^{113}$ when similar problems were encountered. In order to maintain the advantages of Le Roy’s linear Dunham expression,$^{13}$ this assumption was incorporated into the fitting model by solving for the approximate equality of equation 8.14:

$$
\delta_{01}^{Pt} = \delta_{01}^{Cl} \frac{m_{Cl}}{m_{Pt}}
$$

(8.15)

In the fit, the value for $\delta_{01}^{Pt}$ was constrained to equation 8.15.

8.7 Mass-Independent Analysis of the [13.8] $\Omega=3/2$ State of PtCl

The spectroscopic transitions observed with ILS in this study correspond to 6 vibrational levels ($\nu^\prime=0,3,4,5,6,7$) and rotational levels ranging from $J'_{min}(1.5)$ to $J'_{max}(85.5)$ in the [13.8] $\Omega=3/2$ state of 3 isotopologues of PtCl ($^{194}$Pt$^{35}$Cl, $^{195}$Pt$^{35}$Cl, $^{196}$Pt$^{35}$Cl). The data were fit to a Dunham expression with 13 Dunham parameters from equations 8.6 through 8.10 and 16 vibrationally dependent parameters discussed in detail at the end of this section. The Dunham parameters that were reasonably determined included: 1 parameter ($Y_{00}$) for the electronic energy; 3 parameters ($Y_{10}$, $Y_{20}$, $Y_{30}$) for the vibrational structure; 3 parameters ($Y_{01}$, $Y_{11}$, $Y_{21}$) for the rotational structure absent centrifugal distortion; 4 parameters ($q_{01}$, $q_{11}$, $q_{02}$, $q_{03}$) for the $\Omega$-doubling structure; and 2 parameters ($\Delta f_{00}^{Pt}$, $f_{01}^{Pt}$) for Pt-isotope dependent deviations from the Dunham model that are currently treated as field-effects due to the change in nuclear charge radius between Pt isotopes. The field-shift parameters $\Delta f_{00}$ is defined as

$$
\Delta f_{00} = f_{00}^\prime - f_{00}^\prime
$$

(8.16)
where the (′) and (″) indicate the excited and ground states, respectively, and \( f_{00} \) is the field-shift in electronic energy. Only the difference term can be determined due to the same arguments outlined by Le Roy\(^{130} \) regarding the mass-dependent \( \delta_{00} \). The choice to treat the isotope dependent deviations as field-shift effects and not mass-dependent Born-Oppenehiemer breakdown is explained in the following sections.

An empirically derived Dunham expression should not be used to infer any real physical properties of a molecule unless the parameters determined for that expression satisfy certain conditions and theoretical relationships.\(^{44} \) One such condition is that the expansion terms of the Dunham expression should eventually converge to zero. When the terms that compensate for centrifugal distortion (\( Y_{l,m}; l=0,1,2; m=2,3 \)) were included in the Dunham expression for the fit, the determined values for the expansion terms (\( l>0 \)) were of opposite sign and of equal magnitude with those for the lowest order terms (\( Y_{02} \approx D_e \), \( Y_{03} \approx H_e \)). As mentioned above, the rotational structure of the ILS transitions exhibits a dramatic \( J \)-dependence with the values for \( H_v \) from the band-by-band fit roughly two orders of magnitude larger than the value expected using equation 8.4 for \( v'=3-7 \). Additionally, the RMS values for \( v'=7 \) were significantly larger for the Dunham fit than for the band-by-band fit even when additional expansion terms were included. These observations would seem to indicate that an additional electronic state of PtCl is slightly higher in energy than and interacting with the [13.8] \( \Omega=3/2 \) state. Because the Dunham model applies only to isolated electronic states, the effective Hamiltonian used to describe the rovibrational levels of the [13.8] \( \Omega=3/2 \) state serves to reduce the number of parameters necessary to reproduce the known spectroscopic data on PtCl within measurement accuracy, and not as
an absolute characterization of the electronic structure of the state. If the interacting state is identified experimentally, a deperturbation analysis could be performed, but such an approach is not currently possible given the lack of data on the electronic structure of PtCl.

To ensure that the above mentioned issues did not affect the Dunham fit of the \(X^2\Pi_{3/2}\) ground state, additional parameters were incorporated into the Dunham model to separate individual rovibrational parameters \((P_v)\) from the Dunham expression. These correctional parameters \((\Delta P_v)\) determine the difference between the individual parameter and the calculated value expected from the Dunham expression:

\[
T_v^{\alpha} = T_e + Y_{10}^{\alpha}(v + \frac{1}{2}) + Y_{20}^{\alpha}(v + \frac{1}{2})^2 + Y_{30}^{\alpha}(v + \frac{1}{2})^3 + \Delta T_v^{\alpha} \tag{8.17}
\]

\[
B_v^{\alpha} = Y_{01}^{\alpha} + Y_{11}^{\alpha}(v + \frac{1}{2}) + Y_{21}^{\alpha}(v + \frac{1}{2})^2 + \Delta B_v \left(\frac{\mu_1}{\mu}\right) \tag{8.18}
\]

\[
D_v^{\alpha} = Y_{02}^{\alpha} + Y_{12}^{\alpha}(v + \frac{1}{2}) + \Delta D_v \left(\frac{\mu_1}{\mu}\right)^2 \tag{8.19}
\]

\[
H_v^{\alpha} = Y_{03}^{\alpha} + \Delta H_v \left(\frac{\mu_1}{\mu}\right)^2 \tag{8.20}
\]

where the \(Y\) parameters, \(\alpha\), and \(\mu\) follow the same definitions from equations 8.6 and 8.7, \(\Delta T_v^{\alpha}\) was unique for each isotopologue, \(\Delta B_v\) was assigned the same mass dependence as \(Y_{01}\), \(\Delta D_v\) was assigned the same mass dependence as \(Y_{02}\), and \(\Delta H_v\) was assigned the same mass dependence as \(Y_{03}\). In the final fit, the \(Y_{12}\) and \(Y_{13}\) terms for the [13.8] \(\Omega=3/2\) state were set to zero and 16 parameters from equations 8.17 through 8.20 were included in the fit: 12 mass-independent but vibrationally-dependent centrifugal distortion parameters \((\Delta D_v, \Delta H_v: v'=0,3-7)\), 1 mass-independent rotational parameter for \(v'=7\) \((\Delta B_7)\), and three isotope-dependent electronic parameters \((\Delta T_7^{194}, \Delta T_7^{195}, \Delta T_7^{196})\).
In total, 4168 observations were fit to 45 parameters. The Dunham parameters determined for the $X^2\Pi_{3/2}$ ground state and [13.8] $\Omega=3/2$ state are provided in Table 8.2.

The vibrationally dependent centrifugal distortion parameters for the [13.8] $\Omega=3/2$ state are provided in Table 8.3. These results are published in the Journal of Molecular Spectroscopy.\(^{126}\)

### 8.8 Identity of the [13.8] $\Omega=3/2$ State and Comparison of Experiment to Theory

The [13.8] $\Omega=3/2$ state was relatively straightforward to identify as the (4) 3/2 state of PtCl predicted by Zou and Suo.\(^{77}\)

The (4) 3/2 notation corresponds the 4\(^{th}\) $\Omega=3/2$ state once spin-orbit effects have been incorporated into the calculated energies. In most cases, Zou and Liu\(^{70}\) (NiX) and Zou and Suo\(^{77}\) (PtX) predicted transition energies for MX molecules (M=Ni, Pt, X=F,Cl) that were accurate within 1000 cm\(^{-1}\). For PtCl, only three $\Omega=3/2$ states have $T_e$ values predicted within 4500 cm\(^{-1}\) of the determined

---

**Table 8.2: Determined parameters for $^{195}$Pt$^{35}$Cl from the PGOPHER\(^{20}\) mass-independent Dunham type fit of the [13.8] $\Omega=3/2$ - $X^2\Pi_{3/2}$ transition. The spectroscopic parameters for the (1) and (4) 3/2 states predicted by Zou and Suo\(^{77}\) and the ground state hyperfine constants from Okabayashi et al.\(^{102}\) are provided for comparison. All values are provided in cm\(^{-1}\) unless otherwise indicated.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>This Study</th>
<th>Zou and Suo(^{a})</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\omega_e$</td>
<td>399.50026 (138)</td>
<td>393.9</td>
</tr>
<tr>
<td>$f_{10}$ (Pt)</td>
<td>0.1090 (46)</td>
<td></td>
</tr>
<tr>
<td>$-\omega_e x_e$</td>
<td>-1.33508 (48)</td>
<td></td>
</tr>
<tr>
<td>$Y_{01}(B_e)$</td>
<td>0.12299909 (49)</td>
<td>0.1203</td>
</tr>
<tr>
<td>$f_{01}$ (Pt) $\times 10^3$</td>
<td>-0.0011812 (85)(^b)</td>
<td></td>
</tr>
<tr>
<td>$\delta_{01}$ (Pt) $\times 10^3$</td>
<td>0.02190218(^c)</td>
<td></td>
</tr>
<tr>
<td>$\delta_{01}$ (Cl) $\times 10^3$</td>
<td>0.11870 (18)</td>
<td></td>
</tr>
<tr>
<td>$Y_{11}(-\alpha_e) \times 10^3$</td>
<td>-0.63463 (114)</td>
<td></td>
</tr>
<tr>
<td>$Y_{11}(\gamma_e) \times 10^3$</td>
<td>0.01705 (33)</td>
<td></td>
</tr>
<tr>
<td>$Y_{02}$ (-$D_e$) $\times 10^6$</td>
<td>-0.046199 (45)</td>
<td></td>
</tr>
<tr>
<td>$Y_{12}$ ($\beta_e$) $\times 10^6$</td>
<td>0.002818 (87)</td>
<td></td>
</tr>
<tr>
<td>$Y_{03}$ ($H_e$) $\times 10^14$</td>
<td>-0.0828 (102)</td>
<td></td>
</tr>
<tr>
<td>$q_{00} \times 10^6$</td>
<td>-0.026136 (58)</td>
<td></td>
</tr>
<tr>
<td>$\delta_{00}$ (Cl) $\times 10^6$</td>
<td>-0.04569 (52)</td>
<td></td>
</tr>
<tr>
<td>$q_{02} \times 10^{12}$</td>
<td>-0.1099 (114)</td>
<td></td>
</tr>
<tr>
<td>$h_{3/2}$ /MHz</td>
<td>622.8 (48)</td>
<td>631.3 (98)(^a)</td>
</tr>
<tr>
<td>$c_0$(Pt$^{35}$Cl)/MHz</td>
<td>1.2438 (64)</td>
<td>1.259 (15)(^d)</td>
</tr>
<tr>
<td>$c_0$(Pt$^{37}$Cl)/MHz</td>
<td>1.1868(^e)</td>
<td>1.213 (11)(^d)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Transition</th>
<th>$X^2\Pi_{3/2}$ $(1) 3/2$</th>
<th>$X^2\Pi_{3/2}$ $(4) 3/2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Y_{00}$ ($T_e$)</td>
<td>13774.30424 (169)</td>
<td>13847</td>
</tr>
<tr>
<td>$\Delta T_7$ ($^{194}$Pt$^{35}$Cl)</td>
<td>0.5577 (59)(^b)</td>
<td></td>
</tr>
<tr>
<td>$\Delta T_7$ ($^{195}$Pt$^{35}$Cl)</td>
<td>0.1406 (18)(^f)</td>
<td></td>
</tr>
<tr>
<td>$\Delta T_7$ ($^{198}$Pt$^{35}$Cl)</td>
<td>0.1339 (17)(^f)</td>
<td></td>
</tr>
<tr>
<td>$\Delta T_7$ ($^{194}$Pt$^{37}$Cl)</td>
<td>0.1302 (17)(^f)</td>
<td></td>
</tr>
<tr>
<td>$Y_{10}$ ($\omega_e$)</td>
<td>339.7009 (19)</td>
<td>326.1</td>
</tr>
<tr>
<td>$Y_{20}$ (-$\alpha_e$)</td>
<td>-1.16472 (57)</td>
<td></td>
</tr>
<tr>
<td>$Y_{30}$ ($\omega_e \gamma_e$)</td>
<td>0.01115 (15)</td>
<td></td>
</tr>
<tr>
<td>$Y_{01}(B_e)$</td>
<td>0.1141111 (17)</td>
<td>0.1081</td>
</tr>
<tr>
<td>$\Delta B_7$</td>
<td>-0.0001017 (50)(^f)</td>
<td></td>
</tr>
<tr>
<td>$Y_{11}(-\alpha_e) \times 10^3$</td>
<td>-0.4420 (19)</td>
<td></td>
</tr>
<tr>
<td>$Y_{21}(\gamma_e) \times 10^6$</td>
<td>-2.32 (29)</td>
<td></td>
</tr>
<tr>
<td>$q_{01} \times 10^6$</td>
<td>0.1083 (131)</td>
<td></td>
</tr>
<tr>
<td>$q_{02} \times 10^9$</td>
<td>0.1631 (33)</td>
<td></td>
</tr>
<tr>
<td>$q_{12} \times 10^{12}$</td>
<td>-3.43 (24)</td>
<td></td>
</tr>
<tr>
<td>$q_{03} \times 10^{15}$</td>
<td>-12.40 (27)</td>
<td></td>
</tr>
</tbody>
</table>

*Ref. 77.*

* Born-Oppenheimer Breakdown parameter.
* Constrained to eqn. 8.15 in the fit.
* Constrained to eqn. 8.12 in the fit.
* Ref. 102.
* Correction to $v' = 7$. See eqns. 8.17 and 8.18.

\(^{a}\) Ref. 77.

\(^{b}\) Ref. 102.

\(^{c}\) Constrained to eqn. 8.15 in the fit.

\(^{d}\) Ref. 102.

\(^{e}\) Constrained to eqn. 8.12 in the fit.

\(^{f}\) Correction to $v' = 7$. See eqns. 8.17 and 8.18.
for the [13.8] state. The surprisingly accurate $T_e$, only 72 cm$^{-1}$ larger than the determined value, and large transition dipole moment ($R^2_{Tot}$), more than 4 times larger than either energetic neighbor, make the (4) 3/2 state of Zou and Suo$^{77}$ a convincing candidate for the [13.8] $\Omega=3/2$ state of PtCl. The predicted harmonic frequency, $\omega_e$, for this assignment is accurate within 15 cm$^{-1}$ and the predicted equilibrium bond length, $r_e$, is only 0.030 Å larger than the value determined by this study. The equilibrium parameters determined for the [13.8] $\Omega=3/2$ of $^{195}$PtCl are presented in Table 8.6 with the corresponding values for the (4) 3/2 state predicted by Zou and Sou.$^{77}$

The predicted ground state $\omega_e$ value was accurate within 10 cm$^{-1}$ and the predicted $r_e$ was 0.028 Å longer than the determined value. The excellent agreement between the predicted$^{77}$ and determined spectroscopic parameters for the observed electronic states of PtCl provides a compelling motivation for further spectroscopic study of the electronic structure of PtCl to discover whether the source of this outstanding computational accomplishment is anomalous in origin or from a truly predictive theoretical model.

The difficulties encountered when attempting to produce a Dunham model of the [13.8] $\Omega=3/2$ state can be rationalized by examining the electronic states of PtCl predicted by Zou and Suo$^{77}$ The vibrational levels known for the [13.8] $\Omega=3/2$ state span more than 2300 cm$^{-1}$ ($T_0=13,944$ cm$^{-1}$; $T_7=16,257$ cm$^{-1}$). Zou and Sou$^{77}$ predict 3 $\Omega=1/2$ states and 1 $\Omega=5/2$ within 2500 cm$^{-1}$ of the (4) 3/2 state, and all but one of these states is predicted to

<table>
<thead>
<tr>
<th>$v'$</th>
<th>$D_v \times 10^6$</th>
<th>$H_v \times 10^{12}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.05528(41)</td>
<td>0.747(41)</td>
</tr>
<tr>
<td>3</td>
<td>0.16376(148)</td>
<td>15.69(31)</td>
</tr>
<tr>
<td>4</td>
<td>0.15596(142)</td>
<td>10.71(33)</td>
</tr>
<tr>
<td>5</td>
<td>0.17201(129)</td>
<td>12.47(35)</td>
</tr>
<tr>
<td>6</td>
<td>0.20670(19)</td>
<td>19.44(51)</td>
</tr>
<tr>
<td>7</td>
<td>0.18390(28)</td>
<td>15.26(75)</td>
</tr>
</tbody>
</table>

$T_e$ for the [13.8] state. The surprisingly accurate $T_e$, only 72 cm$^{-1}$ larger than the determined value, and large transition dipole moment ($R^2_{Tot}$), more than 4 times larger than either energetic neighbor, make the (4) 3/2 state of Zou and Suo$^{77}$ a convincing candidate for the [13.8] $\Omega=3/2$ state of PtCl. The predicted harmonic frequency, $\omega_e$, for this assignment is accurate within 15 cm$^{-1}$ and the predicted equilibrium bond length, $r_e$, is only 0.030 Å larger than the value determined by this study. The equilibrium parameters determined for the [13.8] $\Omega=3/2$ of $^{195}$PtCl are presented in Table 8.6 with the corresponding values for the (4) 3/2 state predicted by Zou and Sou.$^{77}$

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The difficulties encountered when attempting to produce a Dunham model of the [13.8] $\Omega=3/2$ state can be rationalized by examining the electronic states of PtCl predicted by Zou and Suo$^{77}$ The vibrational levels known for the [13.8] $\Omega=3/2$ state span more than 2300 cm$^{-1}$ ($T_0=13,944$ cm$^{-1}$; $T_7=16,257$ cm$^{-1}$). Zou and Sou$^{77}$ predict 3 $\Omega=1/2$ states and 1 $\Omega=5/2$ within 2500 cm$^{-1}$ of the (4) 3/2 state, and all but one of these states is predicted to
have a reasonable transition dipole moment with one of the three low-lying 5d⁹ states of PtCl. If the interacting state is one of these visible states, spectroscopic observation and characterization is possible and could lead to a more precise understanding of the [13.8] Ω=3/2 state.

8.9 Rotational Born-Oppenheimer Breakdown and Field-Shift Effects

Several diatomic molecules containing 5d transition metals have been characterized using mass-independent Dunham models: HfO, HfS, WO, PtO, TlCl, PtSi, PtS, PbO, PbS, PbSe, and PbTe. The rotational structure of these molecules exhibited field-shift effects in addition to mass-dependent Born-Oppenheimer breakdown (BOB) in all cases but for Hf. The determined δ₀₁ and f₀₁ values for PtCl have been converted into the more commonly used Watson Δ₀₁ parameter with equations 8.13 and 8.14 and the Tiemann V₀₁ parameter with

\[ V₀₁^{Pt} = \frac{r₀₁^{Pt}}{Y₀₁^{Pt} + δ₀₁^{Pt} + δ₀₁^{Cl}} \]  (8.21)

which is derived by equating the two different expressions for Y₀₁ from Schlembach and Tiemann and from Le Roy. These converted values for PtCl are presented with the reported BOB and field-shift parameters for known 5d transition metal diatomics in Table 8.4.

The determined Δ₀₁ parameters for the \( X^2\Pi_{3/2} \) state of PtCl are almost equal to the determined parameters for PtO and PtS, while the BOB parameters for PtSi are smaller by over an order of magnitude and resemble the determined BOB parameters for the other 5d diatomics. The determined ground state \( V₀₁ \) parameters for all studied Pt-containing molecules are reasonably consistent in magnitude, as is the case with the studied Pb
species. The $V_{01}$ parameter determined for the $[13.8] \Omega=3/2$ state of PtCl, however, is of opposite sign and more than 20 times larger than the value of the $X^2\Pi_{3/2}$ state (or any other Pt-containing molecule), providing further evidence that the excited state is strongly interacting with a nearby state(s). It is again worth mentioning that the effective Hamiltonian applied to the $[13.8] \Omega=3/2$ state of PtCl is useful for parameter reduction, but insight into the physical characteristics of the state is speculative absent additional observations of electronic transitions of PtCl.

Table 8.4: A comparison of the known Born-Oppenheimer breakdown parameters of molecules for which field-shift effects have been observed. The anomalously large effective $V_{01}$ parameter for the $[13.8] \Omega=3/2$ state of PtCl is highly suggestive of interactions with nearby electronic states.

<table>
<thead>
<tr>
<th>Molecule (MX)</th>
<th>State</th>
<th>$\Delta_{01}^M$</th>
<th>$\Delta_{01}^X$</th>
<th>$V_{01}^M \times 10^7$ fm$^{-2}$</th>
<th>$R_M$ (fm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HfO$^a$</td>
<td>$X \Omega=0^+$</td>
<td>-3.40(57)</td>
<td>-5.656(23)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HfS$^b$</td>
<td>$X \Omega=0^+$</td>
<td>-4.18(53)</td>
<td>-5.820(49)</td>
<td>5.3470(32)</td>
<td></td>
</tr>
<tr>
<td>WO$^d$</td>
<td>$X \Omega=0^+$</td>
<td>-19.084$^d$</td>
<td>-19.084(12)</td>
<td>-13.6(13)</td>
<td>5.3658(23)</td>
</tr>
<tr>
<td>PtO$^e$</td>
<td>$X \Omega=0^+$</td>
<td>-70.5(10)$^f$</td>
<td>-70.46(2)</td>
<td>-145(5)</td>
<td></td>
</tr>
<tr>
<td>PtSi$^g$</td>
<td>$X \Omega=0^+$</td>
<td>-3(1)$^f$</td>
<td>-2.99(4)</td>
<td>-72(12)</td>
<td></td>
</tr>
<tr>
<td>PtS$^h$</td>
<td>$X \Omega=0^+$</td>
<td>-62.5(10)$^f$</td>
<td>-62.46(5)</td>
<td>-104(9)</td>
<td>5.4270(26)</td>
</tr>
<tr>
<td>PtCl$^i$</td>
<td>$X^2\Pi_{3/2}$</td>
<td>-61.462$^d$</td>
<td>-61.462(94)</td>
<td>-95.92 (69)</td>
<td></td>
</tr>
<tr>
<td>PtCl$^j$</td>
<td>$[13.8] \Omega=3/2$</td>
<td></td>
<td>2340(25)$^j$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TlCl$^k$</td>
<td>$X \Omega=0^+$</td>
<td>-0.500$^i$</td>
<td>-1.257(73)</td>
<td>40.9(55)</td>
<td>5.4759(26)</td>
</tr>
<tr>
<td>PbO$^m$</td>
<td>$X \Omega=0^+$</td>
<td>-1.545$^l$</td>
<td>-2.400(20)</td>
<td>26.4(36)</td>
<td></td>
</tr>
<tr>
<td>PbS$^n$</td>
<td>$X \Omega=0^+$</td>
<td>-1.333$^l$</td>
<td>-1.988(70)</td>
<td>26.38(51)</td>
<td></td>
</tr>
<tr>
<td>PbSe$^o$</td>
<td>$X \Omega=0^+$</td>
<td>-1.9(10)$^l$</td>
<td>-1.916(15)</td>
<td>22.5(20)</td>
<td>5.5012(13)</td>
</tr>
<tr>
<td>PbTe$^n$</td>
<td>$X \Omega=0^+$</td>
<td>-1.8(10)$^l$</td>
<td>-1.859(25)</td>
<td>20.7(21)</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Ref. 131.$^b$Ref. 132.$^c$Ref. 133.$^d$Value constrained to $\Delta_{01}^X$ in fit.$^e$Insufficient data for Pt$^{37}$Cl prevented determination of $\Delta_{01}$ parameters.$^f$Ref. 113.$^g$Ref. 115.$^h$Ref. 114.$^i$Held fixed to theoretical value in fit.$^j$Ref. 134.$^k$Ref. 135.

8.10 Electronic Field-Shift Effects

Optical isotope-shifts in electronic energy have been widely observed and well established for electronic transitions of atomic species. This shift in electronic energy results from effects due to both differences in mass and nuclear size between isotopes of a
given element, with nuclear size contributions (termed “field-shifts”) dominating for large atoms ($Z \geq 58$).\textsuperscript{136} Knöckel and Tiemann\textsuperscript{9} discovered an analogous electronic isotope-shift in the mass-independent Dunham analysis of the $[18.9] A0^+ - X^1\Sigma^+$ transition of PbS, and the theoretical justification for this observation was provided by Schlembach and Tiemann.\textsuperscript{10} The results of their analysis indicated that field-shift effects were an order of magnitude larger than mass-dependent effects. A similar shift in electronic energy was observed in the mass-independent Dunham analysis of PtF described in the previous chapter and in this work on PtCl. Table 8.5 provides a comparison of the electronic field-shift reported for the $[18.9] A0^+ - X^1\Sigma^+$ and $[21.8] B1 - X^1\Sigma^+$ transitions of PbS, the $[15.8+x] \Omega=5/2 - B^2 \Delta_{5/2}$ transition of PtF (previous chapter), and the $[13.8] \Omega=3/2 - X^2\Pi_{3/2}$ transition of PtCl. It should be noted that the mass-dependent and nuclear size dependent effects could not be determined independently for the Pt-containing molecules due to a high degree of correlation in the fit. The field-shift parameters were selected over the mass-dependent parameters as these contributions are expected to be larger for Pt with $Z=78$. However, the fitted $\Delta f_{00}$ parameters for these molecules contain mass-dependent contributions that were treated separately for PbS, for which a wider range of vibrational transitions and a greater number of isotopologues were observed.

<table>
<thead>
<tr>
<th>MX</th>
<th>Transition</th>
<th>$\Delta f_{00}$ (cm$^{-1}$ fm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PtF$^a$</td>
<td>$[15.8+x] \Omega=5/2 - B^2 \Delta_{5/2}$</td>
<td>0.2910(36)</td>
</tr>
<tr>
<td>PtCl$^b$</td>
<td>$[13.8] \Omega=3/2 - X^2\Pi_{3/2}$</td>
<td>0.5556(59)</td>
</tr>
<tr>
<td>PbS$^c$</td>
<td>$[18.9] A0^+ - X^1\Sigma^+$</td>
<td>0.1004(15)</td>
</tr>
<tr>
<td>PbS$^d$</td>
<td>$[21.8] B1 - X^1\Sigma^+$</td>
<td>0.0848(16)</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Chapter VII. \textsuperscript{b}This work. \textsuperscript{c}Ref. 9. \textsuperscript{d}Ref. 12.
8.11 Low-Lying States of the M’X: Bonding Model (M=Ni, Pt; X=F, Cl)

While this study represents the first experimental observation of an electronic transition of PtCl at rotational resolution, similar electronic transitions have been observed experimentally for the related MX diatomics PtF, NiF, and NiCl, and all 4 of the MX (M=Ni, Pt; X=F, Cl) molecules have been investigated theoretically.\textsuperscript{70,77} To understand the differences between the spectroscopic constants of the MX molecules, it helps to first understand the electronic structure of these molecules at the ionic bonding limit. If the MX molecules are truly ionic, M will donate an electron to X leading to many possible low-lying states of M’ ion resulting from the distribution of 9 electrons throughout the 6 nd (n+1)s valence orbitals of the M’ ion, and a single low-lying 1S state for the closed shell X’ ion. These electronic states for the M’ and X’ ions mix upon bond formation, producing a variety of possible Λ-S states for the MX molecules. The resulting Λ-S states are separated due to spin-orbit splitting from electronic coupling to the M’ nucleus, and the resulting Ω-states often comprise of multiple Λ-S state configurations. The ground electronic states of Ni’ and Pt’ are 2D in character, and result primarily from the [Ar]3d\textsuperscript{9} and [Xe]5d\textsuperscript{9} configurations of the ions. In agreement with Hund’s rules, spin-orbit coupling leads to the stabilization of the larger J component of an L-S state from an orbital that is more than half filled, and the 2D\textsubscript{5/2} component is the true ground state for the M’ ions. The lowest-lying excited states are the Ω-components of the lowest energy quartet state, 4F.
The [13.8] $\Omega=3/2$ state is now assigned as the (4) 3/2 state predicted by Zou and Suo. This predicted state is highly mixed with similar contributions from the lowest-lying $^4\Sigma^-$ and $^4\Delta$ and second lowest-lying $^2\Pi$ and $^2\Delta \Lambda$-$S$ states. A molecular orbital (MO) diagram for $M^+X$ molecules is provided in Figure 8.4 and the primary MO configurations for the contributing $\Lambda$-$S$ states were provided by Zou and Suo. For almost all of these excited states, the bonding $\sigma_a$ and $\pi_a$ orbitals are fully occupied, the $\sigma_c$ orbital is singly occupied, and 2 electron holes are distributed through the remaining $\delta_a$, $\pi_b$, and $\sigma_b$ orbitals. Both electron holes are in the $\pi_b$ orbital in the primary configuration leading to the (1) $^4\Sigma^-$ state. The (1) $^4\Delta$ and (2) $^2\Delta$ differ only in a spin flip for their primary configurations that have electron holes in the $\delta_a$ and $\sigma_b$ orbitals. These contributing configurations and $\Lambda$-$S$ states were used to identify electronic transitions in NiF, NiCl, and PtF that are analogous to the [13.8] $\Omega=3/2 - X^2\Pi_{3/2}$ transition of PtCl. The predicted and experimentally determined molecular constants for the rotation, vibration, and electronic energy of the analogous transitions are provided in Table 8.6.

In general, the agreement between the predicted and determined molecular constants for the MX species is remarkably good. All predicted $T_e$ values in Table 8.6 are within 5% of the determined values, as are all but one of the $\omega_e$ values. The $B_e$ values are slightly better predicted with the

Figure 8.4: Molecular orbital diagram for MX species using the ionic bonding model (M=Ni, Pt; X=F, Cl). Low-lying electronic states of MX molecules are derived from ionic states resulting from electron hole configurations in the $M^+ nd(n+1)s$ manifold.
largest discrepancy occurring for the PtCl, leading to a bond length underestimated by 2.6%.

To facilitate the comparison of the spectroscopic data for the MX species provided in Table 6, force constants (k) and equilibrium bond lengths (r_e) were calculated from predicted and experimental molecular constants. Calculated r_e values for the MX species were then divided by the sum of the van der Waals radii\(^{137}\) of the M and X atoms to compensate for differences in elemental size so that the relative stability of the MX bonds can be evaluated.

The MX force constants reported in Table 8.6 indicate that the NiX species are slightly more strongly bound than the PtX species. However, the effect of metal substitution is small compared to halogen substitution effect, which results in k values 2.5 times smaller when Cl replaces F. The PtX molecules have very similar bond lengths to the reference values, but the NiX bond lengths are ~15% shorter suggesting a significantly more favorable NiX bonding interaction as a diatomic species. Equilibrium bond lengths increase by 0.067, 0.076, 0.023, and 0.073 Å upon electronic excitation of PtF, PtCl, NiF, and NiCl from the (1) 3/2 to (4) 3/2 states.

8.12 Conclusions

The first electronic transition of PtCl recorded at rotational resolution has been observed in the visible using Intracavity Laser Spectroscopy (ILS). The (0,2), (0,1), (3,0), (4,0), (5,0), (6,0), (6,1) and (7,1) vibrational bands of the \(\Omega=3/2 - \chi^2\Pi_{3/2}\) transition of\(^{194}\)Pt\(^{35}\)Cl, \(^{195}\)Pt\(^{35}\)Cl, and \(^{196}\)Pt\(^{35}\)Cl have been rotationally analyzed. The 4168 observations have been fit to 45 effective parameters. Equilibrium electronic and vibrational
parameters were determined for the [13.8] $\Omega=3/2$ and $X^2\Pi_{3/2}$ states of PtCl. Isotopic field-shift effects for Pt-isotope substitution are consistent with observations of other 5$d$
transition metal diatomics. In addition, the predicted and experimentally determined
spectroscopic parameters for the (1) $3/2$ and (4) $3/2$ states of MX molecules (M=Ni, Pt;
X=F, Cl) were examined. In general, the electronic states of the MX species are well
described using current computational methods as utilized by Zou and Suo\textsuperscript{77} and Zou and
Liu.\textsuperscript{70} Bond strength decreases slightly when Ni is replaced by Pt and decreases by \~50% when F is replaced by Cl. The results of this study have been published in the Journal of
Molecular Spectroscopy.\textsuperscript{126}
Table 8.6: Equilibrium MX (M=Ni, Pt; X=F,Cl) molecular parameters for the lowest energy $\Omega=3/2$ States derived from the lowest energy quartet ($^4\Psi$) and doublet ground ($^2\Delta$) states of M+X. All theoretical NiX and PtX spectroscopic parameters were taken from the work of Zou and Liu\textsuperscript{70} and Zou and Suo\textsuperscript{77}, respectively.

### Mixed $^4\Sigma$ / $^4\Delta \Omega=3/2$ Excited States

<table>
<thead>
<tr>
<th>M=Pt</th>
<th>( \Omega=3/2 ) States</th>
<th>Molecular Parameters</th>
<th>A-S Components</th>
</tr>
</thead>
<tbody>
<tr>
<td>( ^{195}\text{Pt}^{19F} )</td>
<td>(4) 3/2</td>
<td>T( _e ) ( 11936.161^c )</td>
<td>1.9490</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \omega_e ) 556.43</td>
<td>0.608</td>
</tr>
<tr>
<td></td>
<td></td>
<td>k (N m(^{-1})) 315.7</td>
<td>0.25854(3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B(_e ) 1.942</td>
<td>0.609</td>
</tr>
<tr>
<td></td>
<td></td>
<td>r(<em>e )/ r(</em>{vdW} ) 0.2560</td>
<td>0.7193</td>
</tr>
<tr>
<td></td>
<td>This Study</td>
<td>13774.296 (20)</td>
<td>1.9409</td>
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<tr>
<td></td>
<td></td>
<td>339.8522 (124)</td>
<td>0.608</td>
</tr>
<tr>
<td></td>
<td></td>
<td>117.8</td>
<td>0.25854(3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.1112392 (51)</td>
<td>0.609</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.2609</td>
<td>0.652</td>
</tr>
<tr>
<td>( ^{58}\text{Ni}^{19F} )</td>
<td>(4) 3/2</td>
<td>T( _e ) 6311.177 ( ^c )</td>
<td>1.7621</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \omega_e ) 621</td>
<td>0.568</td>
</tr>
<tr>
<td></td>
<td></td>
<td>k (N m(^{-1})) 393.2</td>
<td>0.3795195(15)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B(_e ) 0.3790</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>r(<em>e )/ r(</em>{vdW} ) 1.865</td>
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</tr>
<tr>
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<td>Experiment( ^d )</td>
<td>8774</td>
<td>1.8743</td>
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<tr>
<td></td>
<td></td>
<td>404</td>
<td>0.27722738(59)</td>
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<tr>
<td></td>
<td></td>
<td>160.6</td>
<td>0.1717728(15)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.134</td>
<td>0.631</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.1081</td>
<td>0.628</td>
</tr>
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<td></td>
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<td>1.764</td>
<td>0.652</td>
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<tr>
<td>( ^{58}\text{Ni}^{35Cl} )</td>
<td>(4) 3/2</td>
<td>T( _e ) 9101.2610 ( ^c )</td>
<td>1.7621</td>
</tr>
<tr>
<td></td>
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<td>( \omega_e ) 396.8</td>
<td>0.568</td>
</tr>
<tr>
<td></td>
<td></td>
<td>k (N m(^{-1})) 160.6</td>
<td>0.3795195(15)</td>
</tr>
<tr>
<td></td>
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<td>B(_e ) 0.1717728(15)</td>
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<td></td>
<td>r(<em>e )/ r(</em>{vdW} ) 1.8743</td>
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<tr>
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<td>Experiment( ^e )</td>
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<td>0.1717728(15)</td>
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<td></td>
<td>2.134</td>
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<td>0.628</td>
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<td></td>
<td></td>
<td>1.764</td>
<td>0.652</td>
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### \( \Omega=3/2 \) Ground States

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<th>( \Omega=3/2 ) States</th>
<th>Molecular Parameters</th>
<th>A-S Components</th>
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<td>( \omega_e ) 599.2</td>
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<td>k (N m(^{-1})) 366.1</td>
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<td>r(<em>e )/ r(</em>{vdW} ) 1.865</td>
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<td>Experiment( ^f )</td>
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</tr>
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<td>594(10)</td>
<td>0.27722738(59)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>359.8</td>
<td>0.1717728(15)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.134</td>
<td>0.631</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.1081</td>
<td>0.628</td>
</tr>
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<td></td>
<td></td>
<td>1.764</td>
<td>0.652</td>
</tr>
<tr>
<td>( ^{58}\text{Ni}^{35Cl} )</td>
<td>(1) 3/2</td>
<td>T( _e ) 0 ( ^c )</td>
<td>2.1502</td>
</tr>
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<td>( \omega_e ) 643</td>
<td>0.620</td>
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<td>k (N m(^{-1})) 421.6</td>
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<td>B(_e ) 0.12203</td>
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<td></td>
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<td>0.18142</td>
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<td>0.606</td>
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<td>0.12298719 (25)</td>
<td>0.558</td>
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<td>163.2</td>
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<tr>
<td></td>
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<td>2.0482</td>
<td>0.606</td>
</tr>
</tbody>
</table>

---

*a\(_{vdW} \) values are the sums of the van der Waals radii reported by Bondi. (Ref. 137)*  
*b Ref. 103.*  
*c Values derived from constants for v=0 (I,e, T\(_e \), \Delta G\(_{1/2} \), B\(_0 \), r\(_0 \) etc.).  
*d Ref. 125.*  
*e Ref. 114.*  
*f Ref. 102.*  
*g Determined using Kratzer relationship: \( \omega_e = \sqrt{4B_e^3/\Delta_e} \)  
*h Refs. 124 (\( \omega_e \)) and 125 (B\(_0 \)).  
*i Refs. 60 (\( \omega_e \)) and 63 (B\(_0 \)).
CHAPTER IX
COPPER HYDROXIDE

9.1 Introduction and Previous Studies of CuOH

Metal hydroxides offer an appealing target for the investigation and understanding of metal-ligand interactions.\textsuperscript{138} In many cases, isoelectronic diatomic fluorides have been studied extensively by experiment, and hydroxides offer challenging computational targets that can be investigated in feasible time-frames. The orientation of the hydroxide ligand can be used to rationalize ionic/covalent bonding descriptions, and it has been shown that the calculated geometry is highly sensitive to the treatment of electron correlation in the computational method.\textsuperscript{138}

There have been several spectroscopic investigations of copper hydroxide.\textsuperscript{139-146} The first rotational analysis of CuOH was performed by Trkula and Harris,\textsuperscript{139} who recorded the (1,0) and (0,1) K-sub-bands of the $B^1A'' - X^1A'$ transition of CuOH with laser induced fluorescence (LIF). Jarman \textit{et al.}\textsuperscript{140} recorded additional LIF spectra of that band system and expanded the rotational analysis up to $K_a'=9$ and 12 for CuOH and CuOD, respectively, determining rotational constants more precisely. The same group reported three additional electronic transitions of CuOH occurring near 19,040 cm$^{-1}$, 15,910 cm$^{-1}$, and 15,150 cm$^{-1}$, and the 15,910 cm$^{-1}$ band system was rotationally analyzed as the $A^1A' - X^1A'$ transition.\textsuperscript{141} However, neither the 19,040 cm$^{-1}$ band system (termed the $C^1A' - X^1A'$ transition) nor the 15,150 cm$^{-1}$ band system were rotationally analyzed. Whitham \textit{et al.}\textsuperscript{142-143} recorded the pure rotational spectrum of $^{63}$CuOH, $^{65}$CuOH, and $^{63}$CuOD, determining more precise molecular constants for the $X^1A'$ ground state. The improved molecular
constants were used to perform a harmonic force field analysis and estimate a vibrationally averaged structure for the $\tilde{X} 1A'$ ground state of CuOH. Tao et al.\textsuperscript{144} used single vibronic level emission spectroscopy of the $\tilde{B} 1A'' - \tilde{X} 1A'$ transition of CuOH and CuOD to determine bending and stretching frequencies for the ground state and to measure the fluorescence lifetime of the $\tilde{B} 1A''$ state. Wang et al.\textsuperscript{145} determined the dipole moment of the $\tilde{X} 1A'$ state to be 3.968(32) D via optical Stark spectroscopy of the $\tilde{B} 1A'' - \tilde{X} 1A'$ transition of CuOH. Most recently, Qin et al.\textsuperscript{146} used electron velocity map imaging to determine the adiabatic detachment energy of CuOH$^-$ and CuSH$^-$. Additionally, their results indicate that neutral CuOH has a Cu-OH bond that is $\sim$20% covalent.

While there have been several theoretical studies of CuOH,\textsuperscript{138,147-152} only two have attempted to describe the electronic structure of CuOH beyond the ground state.\textsuperscript{130,150} Mochizuki et al.\textsuperscript{150} used multi-reference singly and doubly excited configuration interaction (MRSDCI) methods to investigate the excited singlet states of CuOH. Their results predict 7 states with transition energies from the ground state between 18,500 and 45,000 cm$^{-1}$ and demonstrate that electron correlation has a large impact on computational results. Wang et al.\textsuperscript{138} used a variety of computational methods to investigate the three lowest lying singlet states of CuOH. Their 1 $1A''$ and 1 $1A'$ states (where 1 indicates the relative energy of a state of a given symmetry) agree well with the experimentally observed $\tilde{B} 1A''$ and $\tilde{X} 1A'$ states, respectively. However, the energy of the 2 $1A'$ state is more than 3000 cm$^{-1}$ higher than the observed transition energy for the $\tilde{A} 1A' - \tilde{X} 1A'$ transition. As a result, they suggest that the $\tilde{A} 1A'$ is actually a low-lying triplet state, even though
the determined rotational constants for the $\bar{A}^1A'$ state are in poor agreement with 
the predicted constants for the $1^3A'$ and $1^3A''$ states.

In this work, the previously unanalyzed band system of CuOH near 
15,150 cm$^{-1}$ has been observed and recorded at high resolution using Intracavity 
laser Spectroscopy (ILS). The band system has been rotationally analyzed as the 
[15.1] $A''$ - $\bar{X}^1A'$ transition of CuOH and fit to a Watson $S$-reduced Hamiltonian with 
PGOPHER.$^{20}$ Transitions due to $^{63}$CuOH, $^{65}$CuOH, and $^{63}$CuOD were identified and 
included in the analysis. The pure rotational transitions reported by Whitham et 
al.$^{142,143}$ for those isotopologues were incorporated into the fit. The determined 
rotational constants were used to calculate an $r_0$ structure for the [15.1] $A''$ state. A 
global perturbation was observed in for $K_{a}'=1$ for CuOH, but no perturbations were 
observed for CuOD. A correlation diagram comparing the experimental$^{153-158}$ and 
theoretical$^{159,160}$ data for the isoelectronic CuF is used to rationalize the observed 
electronic structure for CuOH. The results of this study have been submitted to the 
Journal of Molecular Spectroscopy.$^{161}$

9.2 Production of the CuOH Molecules

The CuOH molecules were produced in the RF discharges formed when 
0.40 A was applied to a 130 mm long Cu hollow cathode in ~500 mTorr O$_2$ with a 
trace amount of H$_2$. The CuOD molecules were produced under similar conditions, 
using 0.45 A as the discharge current and a gas mixture ~80:20 O$_2$:D$_2$. The Cu 
hollow cathode was located in resonator cavity of the DL-ILS system. By setting a 
generation time, $t_g$, of 300 µsec, effective pathlengths of ~10 km were obtained for
the measurements utilizing the ILS method. The concatenated ILS spectrum for the [15.1] $A'' - \tilde{X} \, 1A'$ transition of CuOD is provided in Figure 9.1.

The CuOH spectra feature two prominent sub-bands with strong P-, Q-, and R-branches, consistent with a $c$-type transition expected for a $A''-A'$ transition of a $C_3$ asymmetric top. The P- and R-branches have clear satellite branches with intensities consistent with the relative abundance of $^{63}$Cu to $^{65}$Cu (69% to 31%). The Q-branches are too congested to resolve any features due to the minor isotopologue $^{65}$CuOH. The separation between the Q-bandheads of the prominent sub-bands is $\sim 60 \text{ cm}^{-1}$. Minor sub-bands are observed to the red of the prominent bands. However, ILS operation to the blue of the prominent bands is prohibited by absorption due to the Balmer H$_\alpha$ line near 15,233 cm$^{-1}$ that saturates the ILS system and prevents laser operation over a region $\sim 20 \text{ cm}^{-1}$ wide when the plasma discharge is engaged. The spectra of CuOD are much more compact with the separation between the prominent sub-bands reduced to $\sim 30 \text{ cm}^{-1}$, and 5 Q-

![Figure 9.1](image)

Figure 9.1: (a) Intracavity laser absorption spectra of the [15.1] $A'' - \tilde{X} \, 1A'$ transition of CuOD and (b) PGOPHER simulation. The labels in the top trace are centered over the Q-bandheads of the $K_a$ sub-bands.
bandheads can be identified (see Figure 9.1).

The rotational constants from Whitham et al.\textsuperscript{142,143} were used to calculate energy levels for the $\tilde{X} 1A'$ state of $^{63}$CuOH, $^{65}$CuOH, and $^{63}$CuOD. Rotational assignments were confirmed through ground state combination differences, and the transition was assigned as the [15.1] $A''$-$\tilde{X} 1A'$ transition of CuOH. The omission of multiplicity from the [15.1] $A''$ state is discussed in the next section. P-, Q-, and R-branches could be identified for the (1,0) and (0,1) $K_a$ sub-bands of $^{63}$CuOH, but only P- and R-branches were identified for the (1,2) sub-band of $^{63}$CuOH and (1,0) and (0,1) sub-bands of $^{65}$CuOH due to spectral congestion in the Q-bandheads. For $^{63}$CuOD, P-, Q-, and R-branches were identified for the (2,1), (1,0), and (0,1) $K_a$ sub-bands, but, again, spectral congestion limited the (1,2) sub-band to only P- and R-branches. A global perturbation was observed for $K_{a}'=1$ for both $^{63}$CuOH and $^{65}$CuOH at $J'>20$, but no perturbations were observed in the branches of $^{63}$CuOD.

Consequently, only transitions with $J'\leq20$ in the (1,0) sub-band of $^{63}$CuOH and $^{65}$CuOH were included in the fit.

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<th>[15.1] $A''$ State</th>
<th>$^{63}$CuOH</th>
<th>$^{65}$CuOH</th>
<th>$^{63}$CuOD</th>
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<tbody>
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<td>15116.2370(12)</td>
<td>15110.6663(13)</td>
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<td>$A$</td>
<td>39.0488(21)</td>
<td>39.0613(24)</td>
<td>18.3714(17)</td>
</tr>
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<td>0.3851567(26)</td>
<td>0.3826469(35)</td>
<td>0.3547780(40)</td>
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<td>$\delta_B$</td>
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<td>0.00359(13)</td>
<td>0.0073419(34)</td>
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<td>$B$</td>
<td>0.3872625(59)$^a$</td>
<td>0.384440(65)$^a$</td>
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<tr>
<td>$\overline{C}$</td>
<td>0.3830509(59)$^b$</td>
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<td>0.0005292(21)</td>
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<td>$D_{NK} \times 10^3$</td>
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<table>
<thead>
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<th>$^\text{r}_0$ Structure$^c$</th>
<th>$^{63}$CuOH</th>
<th>$^{65}$CuOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-O</td>
<td>1.7482(71)Å</td>
<td>1.7482(71)Å</td>
</tr>
<tr>
<td>O-H</td>
<td>138.51(37)dÅ</td>
<td>138.51(37)dÅ</td>
</tr>
<tr>
<td>Cu-O-H</td>
<td>0.9470(65)$^d$</td>
<td>0.9470(65)$^d$</td>
</tr>
</tbody>
</table>

$^a$Calculated from $B = \overline{B} + \frac{1}{2} \delta_B$: Value in parentheses reflects propagated error.

$^b$Calculated from $C = \overline{B} - \frac{1}{2} \delta_B$: Value in parentheses reflects propagated error.

$^c$Isotopologue averaged $^\text{r}_0$ structure. Determined $r_s$ structure resulted in erroneously small O-H bond length. See text.
The identified branches were fit to the Watson $S$-reduced Hamiltonian for a $^1A''-^1A'$ transition of a Cs molecule using PGOPHER. The prominent, well-resolved (1,0) and (0,1) $K_a$ sub-bands for all isotopologues were assigned an uncertainty of 0.005 cm$^{-1}$ in the fit, but the weaker, more congested sub-bands were assigned an uncertainty of 0.0075 cm$^{-1}$. The line positions for the Q-branches of the (1,0) and (0,1) $K_a$ sub-bands of $^{65}$CuOH were approximated as the equivalent transitions of $^{63}$CuOH and assigned an uncertainty of 0.05 cm$^{-1}$. The line positions reported by Whitham et al. for $^{63}$CuOH and $^{65}$CuOH were included with the 695 ILS observations in the fit and were assigned an uncertainty of 25 kHz. However, only the line positions reported for $^{63}$CuOD for $K_a''<3$ were included in the fit because the reported line positions for $K_a''=3$-5 were not consistent with those calculated from their own reported parameters. The $A$, $D_K$, $L_K$, and higher order $K_a$ centrifugal distortion constants for the $\tilde{X}$ $^1A'$ state were held to the values reported by Jarman et al. for each isotopologue due to the limited number of $K_a$ sub-bands included in this analysis.

In total, 846 observations were fit to 15 fixed and 46 floated parameters. The fixed and floated parameters for the $\tilde{X}$ $^1A'$ ground state are summarized and compared to literature values in Table S1 of the Supplementary Materials of these submitted results. The molecular constants determined for the [15.1] $A''$ transition are summarized in Table 9.1, and the root mean squared (RMS) values for individual $K_a$ sub-bands and isotopologues are provided in Table 9.2.
9.3 Perturbation in $K_{a'}=1$

The (1,0) $K_{a}$ sub-band of the 

[15.1] $A'' - \tilde{X} 1A'$ transition of CuOH was well resolved, isolated, and the P-, Q-, and R-branches could be easily identified. However, significant deviations were observed in the residuals of the fit when transitions with $J'>20$ were included in the fit. These deviations were not consistent with effects due to centrifugal distortion and are completely absent in the rotational branches of $^{63}$CuOD. The rotational levels are shifted to lower energy, indicating that the perturbation is due to an interacting state slightly higher in energy than the [15.1] $A''$ state. The $\tilde{A} 1A'$ state of Jarman et al.\textsuperscript{141} is 800 cm$^{-1}$ higher in energy than the [15.1] $A''$ state, and, therefore, cannot be the perturbing state. This would seem to suggest that $K_{a}=1$ of the [15.1] $A''$ state of $^{63/65}$CuOH is interacting with a vibrational mode of an unknown low-lying state of CuOH. The ILS data for the (1,0) sub-band of the [15.1] $A'' - \tilde{X} 1A'$ transition of CuOH is provided in Figure 9.2 along with a plot of the residuals from the fit vs. $J'$ for the (1,0) sub-band of $^{63}$CuOH.

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Table 9.2: Band-by-band root mean squared (RMS) values from the PGOPHER\textsuperscript{20} fit of the [15.1] $A'' - \tilde{X} 1A'$ transition of CuOH. RMS values are in cm$^{-1}$ unless otherwise indicated.

<table>
<thead>
<tr>
<th>Isotopologue</th>
<th>$N$</th>
<th>$\text{RMS (Original)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{63}$CuOH</td>
<td>62</td>
<td>24.6 (19.6) kHz</td>
</tr>
<tr>
<td>$^{65}$CuOH</td>
<td>27</td>
<td>30.4 (23.2) kHz</td>
</tr>
<tr>
<td>$^{62}$CuOD</td>
<td>25</td>
<td>28.3 (37.2) kHz</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$^{63}$CuOH</th>
<th>$N^b$</th>
<th>$\text{RMS (Original)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1,0)</td>
<td>43</td>
<td>0.0043</td>
</tr>
<tr>
<td>(0,1)</td>
<td>105</td>
<td>0.0058</td>
</tr>
<tr>
<td>(1,2)</td>
<td>60</td>
<td>0.0080</td>
</tr>
<tr>
<td>Total</td>
<td>208</td>
<td>0.0061</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$^{65}$CuOH</th>
<th>$N^b$</th>
<th>$\text{RMS (Original)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1,0)</td>
<td>32</td>
<td>0.0072</td>
</tr>
<tr>
<td>(0,1)</td>
<td>73</td>
<td>0.0060</td>
</tr>
<tr>
<td>Total</td>
<td>105</td>
<td>0.0064</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$^{63}$CuOD</th>
<th>$N^b$</th>
<th>$\text{RMS (Original)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1,0)</td>
<td>91</td>
<td>0.0054</td>
</tr>
<tr>
<td>(0,1)</td>
<td>92</td>
<td>0.0046</td>
</tr>
<tr>
<td>(2,1)</td>
<td>130</td>
<td>0.0080</td>
</tr>
<tr>
<td>(1,2)</td>
<td>69</td>
<td>0.0083</td>
</tr>
<tr>
<td>Total</td>
<td>382</td>
<td>0.0066</td>
</tr>
</tbody>
</table>

$^a$For $K_{a}=0-2$

$^b$Unresolved Q-lines assigned an uncertainty of 0.05 cm$^{-1}$ are omitted from these values.
A limited geometric structure for CuOH in the [15.1] $A''$ state can be obtained from the principle rotational constants for the 3 fitted isotopologues: $^{63}$CuOH, $^{65}$CuOH, and $^{63}$CuOD. In principle, the position of an atom relative to the center-of-mass (COM) of a molecule can be obtained if rotational constants are known for a single isotopic substitution of that atom using the Kraitchman equations. As rotational constants were obtained for Cu and H substitution, the positions of these atoms relative to the COM can be determined. Once these positions are known, the
relative position of oxygen can be directly determined because the CuOH is planar by definition and the COM is defined as (0,0,0) in the xyz coordinates of the Kraitchman equations. These relative positions can then be converted to the internal coordinates of the molecule (Cu-O bond length, O-H bond length, and Cu-O-H bond angle).

The Kraitchman equations were solved using the KRA program available on the Programs for Rotational SPEctroscopy (PROSPE) website. However, the determined COM coordinates resulted in unrealistically small O-H bond lengths (0.83 Å). There are several explanations for this result. The limited number of $K_a$ sub-bands observed for $^{63}$CuOH and $^{65}$CuOH prevented the determination of centrifugal distortion corrections to the A rotational parameter for these isotopologues. Additionally, the $K_a=1$ level of the [15.1] $A''$ state for $^{63}$CuOH and $^{65}$CuOH is known to be interacting with a nearby state, and it is entirely possible that the rotational constants determined in this analysis for those isotopologues are contaminated by that interaction.

In lieu of a satisfactory $r_s$ structure, $r_0$ structures for each isotopologue were determined using an Excel routine that varied the internal coordinates of CuOH, diagonalized the resulting inertial matrix, and calculated principle rotational constants $A$, $B$, and $C$ for each isotopologue. The internal coordinates were optimized by subtracting these calculated rotational constants from the experimentally determined values, normalizing these residuals to the uncertainty of each determined parameter, and minimizing the sum of the squares of the normalized residuals. The internal coordinates determined by this method and
averaged across the three isotopologues were: Cu-O bond length of 1.7482(71) Å, O-H bond length of 0.9470(65) Å, and Cu-O-H bond angle of 138.51(37)°. These values reflect a decrease in Cu-O bond length, slight decrease in O-H bond length, and significant increase in Cu-O-H bond angle relative to the \( r_s \) structure of the \( \tilde{X} ^1A' \) state [Cu-O 1.76893(25) Å, O-H 0.9520(50) Å, Cu-O-H 19.245(80)°].

9.5 Comparison to Theory, CuF, and the Multiplicity of the [15.1] \( A'' \) State

The origin of the [15.1] \( A'' \) state poses an interesting question when examining the electronic structure of CuOH. The [15.1] \( A'' \) - \( \tilde{X} ^1A' \) transition is very well described as a \( ^1A'' \) - \( ^1A' \) transition. As mentioned in the Introduction, however, there are no singlet states predicted to lie below 18,500 cm\(^{-1}\) by either computational study that investigated the excited states of CuOH. Wang et al.\(^\text{138} \) briefly mention the \( ^13A' \) and \( ^13A'' \) states in their concluding remarks, whose transition energies of 15,214 cm\(^{-1}\) and 16,508 cm\(^{-1}\), respectively, are reasonably close to the experimental \( T_{00} \) of 15,116 cm\(^{-1}\). However, the predicted \( A \) rotational constants of \(^{63}\)CuOH for these states (\( A \approx 24 \) cm\(^{-1}\)) do not agree with the experimentally determined value [\( A = 39.0488(12) \) cm\(^{-1}\)].

In the absence of a clear assignment for the [15.1] \( A'' \) from the available computational data, the electronic structure of the well-studied isoelectronic CuF can be used as a source of additional insight. Due to the descent in symmetry from \( C_{\infty h} \) to \( C_s \) from linear CuF to bent CuOH, the \( \Pi \) states of CuF result in one \( A' \) and one \( A'' \) state in CuOH, the \( \Sigma^+ \) states result in one \( A' \) state, and the \( \Sigma^- \) states result in one \( A'' \) state.\(^\text{163} \) The \( a ^3\Sigma^+ \) state of CuF is the lowest-lying known state with \( T_e = 14.580 \) cm\(^{-1}\).\(^\text{153,154} \) However, this state cannot correlate to the [15.1] \( A'' \) state of
CuOH because it is of the wrong symmetry. The next lowest state of CuF is the $b \, ^3\Pi$ state with $T_e=17,540 \text{ cm}^{-1}$ and should correlate to $^3A'$ and $^3A''$ states in CuOH.\textsuperscript{154} The lowest-lying known singlet state of CuF is the $A \, ^1\Sigma^+$ state is significantly higher in energy, with $T_e=19,304 \text{ cm}^{-1}$, and the lowest-lying singlet state resulting in a $^1A''$ state in CuOH is the $B \, ^1\Pi$ state of CuF, with $T_e=20,260 \text{ cm}^{-1}$.\textsuperscript{153,154} Based on the known electronic states of CuOH, it is likely that the $B \, ^1\Pi$ state of CuF correlates to the $\tilde{B} \, ^1A''$ and $\tilde{C} \, ^1A'$ states of CuOH and the $b \, ^3\Pi$ state of CuF correlates to the $\tilde{A} \, ^1A'$ and [15.1] $A''$ states, and, consequently, both of these states of CuOH are actually triplet in character. However, it should be emphasized that there is no direct
spectroscopic evidence to indicate that the [15.1] $A''$ state is triplet, so the multiplicity of this state has been omitted in this text to avoid confusion. High level calculations considering both the triplet and singlet states could shed further light on the electronic structure of CuOH and help definitively assign the multiplicity of the [15.1] $A''$ and $\tilde{A}^1A'$ states. A correlation diagram between the predicted and calculated electronic states of CuF and CuOH is provided in Figure 9.3. It is likely that the lowest-lying $^3A'$ state of CuOH is responsible for the observed perturbation in $K_a=1$ of the [15.1] $A''$ state of $^{63/65}$CuOH.

9.6 Conclusions

The 15,150 cm$^{-1}$ band system of CuOH has been observed and recorded at high resolution using ILS. The transition has been fit to a Watson $S$-reduced Hamiltonian using PGOPHER and has been assigned as the [15.1] $A'' - \tilde{X}^1A'$ transition of CuOH. An isotopologue averaged $r_0$ structure for the [15.1] $A''$ state indicates a shortening of the Cu-O bond length and increase in the Cu-O-H bond angle upon electronic excitation. A global perturbation was observed in $K_a=1$ of the [15.1] $A''$ state of $^{63/65}$CuOH and is believed to be due to interactions with excited vibrational levels of an unknown, low-lying triplet state. Correlation to the known states of CuF suggests that the [15.1] $A''$ state is triplet, but the observed transition was well-described as a $^1A'' - ^1A'$ transition. Computational investigation involving both the triplet and singlet excited states of CuOH could provide valuable insight into the underlying nature of the electronic structure of CuOH. The results of this study have been submitted to the Journal of Molecular Spectroscopy.
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