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HIGH RESOLUTION, ROTATIONALLY RESOLVED, ELECTRONIC SPECTROSCOPY OF FREE RADICALS: MgCH₃, MgNC AND HCCS.

DISSERTATION

Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of The Ohio State University

By

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* * * * *

The Ohio State University

1998

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The rotationally resolved (~ 0.005 cm\(^{-1}\)), laser induced fluorescence spectra of the magnesium monomethyl (MgCH\(_3\)), magnesium isocyanide (MgNC), and thioketenyl (HCCS) radicals were recorded. The HCCS radicals were produced by laser photolysis of thiophene, while the Mg-containing radicals (MgCH\(_3\) and MgNC) were synthesized by laser ablation of a Mg rod and simultaneous photolysis of an appropriate organic precursor. All spectra were acquired in a supersonic free jet expansion, to reduce spectral congestion.

For the magnesium monomethyl radical, both spin-orbit components of the 0\(^0\) vibrational band of the \(\tilde{A} \leftarrow \tilde{X}\) electronic transition were recorded and analyzed to yield the spectroscopic molecular parameters for the main isotopomer, \(^{24}\text{MgCH}_3\), and for \(^{26}\text{MgCH}_3\). From the molecular constants obtained, the geometrical structures of these radicals were determined. All the spectroscopic parameters and the radical structures obtained from the rotational analysis were compared with other metal monomethyl radicals previously studied.

For the MgNC and the HCCS radicals, a number of vibrational bands of the \(\tilde{A} \leftarrow \tilde{X}\) electronic transition were acquired. The rotational analysis of the high resolution spectra provided the molecular constants of the levels involved in the vibronic transitions studied. Since both radicals have a linear \(\tilde{A} \, ^2\Pi\) electronic state, the combined
effects of the spin-orbit coupling and the Renner-Teller interaction were present, and their effects were considered to explain the energy level diagram of the vibronic levels in the bending vibrational modes. This, in addition to the information obtained from the rotational analysis, was taken into account in order to propose vibronic assignments for the transitions studied.
ACKNOWLEDGMENTS

First, I would like to thank my research advisor, Professor Terry A. Miller, for his continuous support, encouragement and guidance during the course of my Ph.D.

Secondly I would like to thank former and present group members for their help in many different areas, for useful discussions, and for keeping life amusing in the lab through these years. I would especially like to thank the "hires people"; Tim Cerny, Chris Carter and Jamie Williamson, who taught me how to run the high resolution apparatus. I am also deeply grateful to the "computer guru" of our group, Sergey Panov, who helped me to solve many computer problems, and for -finally- fixing his program SpecSim -making it "crash-free" under Windows95. Also many thanks to his two successors, Brian Applegate and Dmitry Melnik, who have been there to deal with everyday computer problems since Sergey left. I want to express my deepest gratitude to Becky Gregory, for her great patience and her constant help with administrative matters.

I have had the pleasure of making many friends during the course of my stay here in the USA, and to all of them I would like to express my sincere gratitude for their support and friendship. In particular I want to thank Elaine, Mike, DocZibs, Maggie, Brian, Scott and "the European guys", for keeping life definitely amusing during these four years at Ohio State. Special thanks to Elaine and Mike for suffering
with me through the first year of PChem classes. To Elaine and her family I can only say that their love and support at all times has been greatly appreciated. Thank you for making me feel at home.

I wish to thank my family and friends from Uruguay, for their constant support, love and encouragement whenever it was needed. To my parents, and to Raquel, Silvana, Wes, Camilla, Marcelo, Serenella and Andrés: thank you very much for helping me through these four years.

Lastly, my deepest thanks are offered to my husband Tim, for many helpful discussions, but especially for his understanding, love and support through these past five months, and for always being there to cheer me up in the difficult and stressful moments. I would like to dedicate this dissertation to him.
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PUBLICATIONS


**FIELDS OF STUDY**

Major Field: Chemistry
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CHAPTER 1

INTRODUCTION

In this dissertation the high resolution, rotationally resolved, laser induced fluorescence (LIF) spectra of a number of vibrational bands of the $\tilde{A} \leftarrow \tilde{X}$ electronic transition of three free radicals, MgCH$_3$, MgNC, and HCCS, are presented. The free radicals were obtained by laser photolysis (or by laser ablation/photolysis) of a supersonic jet expansion of an appropriate precursor. The analysis of the high resolution spectra provided the molecular constants of the levels involved in the vibronic transitions studied. In most cases the molecular constants were determined for the first time. With this information, insight into the electronic structure and bonding characteristics of the radicals was obtained.

1.1 Supersonic jet expansions

Supersonic jet expansions in combination with high resolution laser spectroscopy has been successfully applied to the study of the structure of free radicals, since the method was first applied by Smalley et al. to the NO$_2$ radical [1].

The main problem in the study of free radicals is the difficulty of obtaining these highly reactive species in an environment where they will survive long enough to be
studied. The almost collision-free environment of a supersonic jet expansion provides an ideal medium to obtain and study these transient species. Additionally, molecules in a supersonic jet expansion have extremely low temperatures, thus only a few quantum levels are populated. This results in a much less congested spectrum, so that analysis of molecular spectra is greatly simplified. This is what makes the supersonic jet expansion such an excellent environment to study the spectroscopy of highly reactive species.

The key feature of the free jet expansion is a small nozzle orifice, which separates a reservoir with the gas sample at very high pressures from a very low pressure region, usually a vacuum chamber. Once the gas sample expands through the nozzle into the vacuum chamber, the random motion of the particles becomes highly directional. Not only do the molecules travel in nearly the same direction, but also the range of speeds is greatly reduced. Since the width of the velocity distribution of the molecules is a measure of the translational temperature of the molecules, very low temperatures are achieved in a supersonic jet expansion. Under extreme conditions, the temperature can approach 0.01 K [2]. In a supersonic jet expansion the sample, usually a polyatomic molecule, is seeded into an inert, monoatomic carrier gas. In the course of the expansion the translational temperature of the carrier gas falls to a very low value. The cooling of the sample molecules occurs through collisions with the carrier gas molecules. As the sample expands it suffers fewer and fewer collisions, and after a certain distance from the nozzle, it becomes virtually a collision-free expansion, allowing molecular species that otherwise would be highly unstable, to survive. The
molecules can then be probed by laser spectroscopy.

1.2 Motivation for this study

Two Mg-containing radicals, MgCH$_3$ and MgNC, were spectroscopically studied in the work reported in this dissertation. The interest in Mg-bearing molecules is mainly due to its high natural abundance: Mg is the most abundant metal, and the seventh most common element. It is because of this that it is expected that Mg-bearing species play an important role in many different environments. There are at least three areas in which Mg-containing species are of great interest: in astrophysics, in organic and inorganic synthesis, and in biochemical systems. Owing to the high abundance of this metal, Mg-containing species are expected to be very common in interstellar space. However, up to date only two Mg radicals have been identified: MgNC was the first Mg radical detected in the circumstellar envelope of the IRC +10216 star [3, 4], and its metastable isomer, MgCN, was also identified in the same star a few years later [5]. In the area of organic and inorganic synthesis, Grignard reagents (MgCH$_3$Br, for example), are among the most useful and versatile known, making MgCH$_3$ in particular, a very interesting object of study. In biological systems numerous Mg-containing molecules such as chlorophyll play very important roles, so the study of the structure of free radicals related to those molecules is of intense interest.

In this work, the high resolution LIF spectrum of the $0^0 \tilde{A} \,^2E \leftarrow \tilde{X} \,^2A_1$ electronic transition of the MgCH$_3$ radical was obtained and rotationally analyzed. The molecular constants calculated from the simulated spectra were used to obtain the
geometrical structure of the radical $^{24}\text{MgCH}_3$ as well as for one of its isotopomers, $^{26}\text{MgCH}_3$, in both electronic states. A comparison of the obtained spectroscopic parameters and geometry of $\text{MgCH}_3$ with previously studied alkyl organometallic radicals such as $\text{CaCH}_3$, $\text{ZnCH}_3$ and $\text{CdCH}_3$, is also included.

The $\text{MgNC}$ radical presented additional interest: the $\tilde{\text{A}}$ electronic state of this radical is a linear $^2\Pi$ state, and thus it is susceptible to the combined effects of Renner-Teller and spin-orbit interactions. As will be discussed in more detail in Chapter 4, the energy level diagram of molecules with both Renner-Teller and spin-orbit interactions can deviate considerably from the simple harmonic, equally spaced energy levels. Depending on the relative magnitudes of these two interactions with respect to the bending frequency, the vibronic assignment of the transitions involving the bending mode may turn into a very difficult task.

Similarly, the motivation to study the $\text{HCCS}$ radical was based in the interest of studying the combined interactions of the vibronic and spin-orbit couplings. For $\text{HCCS}$, both electronic states, the $\tilde{\text{X}}$ and the $\tilde{\text{A}}$ state are linear $^2\Pi$ states. In this case, there is an additional interest since $\text{HCCS}$ is a tetratomic radical, and although the Renner-Teller effect alone has been studied in tetratomic molecules [6], there is not a study that takes into account both vibronic and spin-orbit interactions simultaneously for tetratomic molecules.
1.3 Outline of the dissertation

The material discussed in this dissertation is organized into five chapters. In this chapter a brief overview of the techniques used to study the radicals was presented, as well as the motivation to study those particular radicals.

In the next chapter, the experimental apparatus where all the data was acquired is described in detail. Also, a brief description of the software used to analyze the data is included. The experimental details that were different for each radical are included in the individual chapters for each of those radicals.

Chapter 3 contains the experimental work carried out on the MgCH$_3$ radical, along with its rotational analysis and a comparison with the other alkyl organometallic radicals studied up to date, MCH$_3$ (M= Ca, Cd, and Zn).

In Chapter 4 the LIF spectra of several vibrational bands of the $\tilde{A} \leftarrow \tilde{X}$ transition of MgNC are included. In addition to the rotational analysis and discussion for each of those bands, a vibronic analysis discussing the combined effects of the Renner-Teller and spin-orbit interactions is presented.

In the last chapter, the LIF electronic spectra of the HCCS radical are presented and rotationally analyzed. Similarly to MgNC, possible vibronic assignments for all the obtained bands are discussed.

An Appendix with a detailed description of the Renner-Teller effect in linear molecules, and of the combined interaction of the Renner-Teller effect and the spin-orbit coupling is presented, along with the formulae to calculate the energy of the vibronic levels in the presence of both interactions.
CHAPTER 2

EXPERIMENTAL APPARATUS

2.1 Introduction

High resolution, rotationally resolved LIF spectroscopy was employed to study the structure of free radicals, which were produced in a supersonic jet expansion. All the spectra included in this dissertation were acquired on the same experimental apparatus. Only the general characteristics of the experimental setup will be discussed here. Particular experimental details for the different species are included in the respective chapters for each radical.

2.2 Radical production

One of the most common techniques used to obtain free radicals in a supersonic jet expansion is by laser photolysis of a suitable compound, known as the precursor. When the desired radical contains a metal atom, a slight variation of this technique can be used instead, known as the laser ablation/photolysis technique. In this method an excimer laser photolyzes the precursor molecules and at the same time it ablates a metal rod. The radicals are created by the reaction between the metal atoms and the photolysis products. In all the experiments described in this dissertation one of these
two techniques was used to generate the free radicals studied. Since these techniques are widely employed, only a brief description of them will be included.

The organic precursor must be chosen carefully. First of all, the precursor must produce the desired radical when photolyzed. Usually an excimer laser is used to photolyze the precursor molecule; therefore, its photolysis must occur at typical excimer laser frequencies. The most commonly used excimer frequencies in the production of radicals are ArF (193 nm), and KrF (248 nm). Another requirement for the organic precursor is that it must have the appropriate physical properties such that vapor pressures of a few Torr can be obtained, particularly at temperatures easily achieved in the laboratory, preferably in the range of 77–373 K.

In the experiments of this work, the precursor was held in a stainless steel reservoir and maintained at an appropriate constant temperature (different in each case), such that its vapor pressure was of the order of a few Torr (5-10 Torr). The carrier gas, a rare gas or N₂, at high backing pressure (from 50-300 psi, depending on the radical), was flowed through the stainless steel reservoir where the precursor was contained. This gas mixture was then expanded through a small nozzle orifice, into a vacuum chamber, generating a supersonic jet expansion. Nozzles with different diameters were available, but for most experiments a diameter of 0.5 mm was used. The nozzle was attached to a pulsed valve (General Valve, Series 9), so that the gas mixture, entered the vacuum chamber in pulses. The duration of the pulses was typically 1–5 msec, at a repetition rate of 10–30 Hz.

The free radicals were produced by laser photolysis of the precursor molecules.
Figure 1: Diagram showing the production of the free radicals.
The excimer laser used for the generation of the MgCH$_3$ radical (Lumonics, model 500), was changed for the other experiments (Lambda Physik, model 120ICC).

As shown in Figure 1, the excimer laser beam was directed into the supersonic jet expansion, to the area just above the nozzle. The excimer beam entered the vacuum chamber through a quartz window (at Brewster's angle) mounted at the end of a side arm, as indicated in Figure 1. A series of baffles were placed inside this arm, in order to reduced scattered laser light inside the chamber. Generally the excimer laser beam was focused with a 50 cm focal length lens. The power of the excimer laser radiation was in some cases adjusted by placing attenuators (metal screens), in the path of the excimer beam. The power and the focusing conditions were experimentally adjusted to obtain the strongest radical production possible.

As mentioned before, the other technique employed to obtain radicals involves the use of the laser ablation/photolysis method. In this method, metal atoms are generated by ablating a metal rod with the excimer pulse, which occurs simultaneously with the photolysis of the precursor molecules.

In this technique, a fixture (referred as the ablation fixture) is attached to the top of the pulsed valve, as shown in Figure 2. There is a channel through the middle of the fixture, where the gas mixture flows and finally expands into the vacuum chamber. The channel is centered with respect to the nozzle orifice, as shown in the diagram of Figure 2. The gas mixture (the precursor diluted in a carrier gas) flows through this central channel. A metal rod is inserted in the middle part of the ablation fixture, as shown in the diagram. The excimer beam enters the ablation fixture through a small
Figure 2: Schematic diagram showing the fixture used to obtain radicals in the laser ablation/photolysis technique.
side aperture, and photolyzes the precursor molecules flowing through the central channel. The same excimer pulse then hits the rod, and ablates metal atoms, which react with the photolysis products in the central channel, producing the desired free radicals. The free radicals created in this way continue traveling through the central channel, and finally expand into the vacuum region, forming a supersonic jet.

The ablation fixture was made from aluminum, and it was found experimentally by Cerny [7], that the best dimensions for this fixture are: 15 mm length and a 2 mm channel diameter. This channel diameter is larger than the nozzle of the pulsed valve, which means that the temperature of the jet expansion is a little higher than in the simple photolysis technique. However, this does not create a problem since still very low temperatures can be achieved with the ablation fixture (~ 3 K at a distance of 25 mm downstream, as reported by Cerny [7]).

2.3 High resolution experimental apparatus

Once the radicals were generated in a supersonic jet expansion, they were probed by LIF spectroscopy. The block diagram of Figure 3 shows the experimental setup of the apparatus used to acquire the high resolution spectra.

The probe laser beam used was the output of a continuous-wave (cw) ring laser, pumped by an Ar+ ion laser. For one of the radicals studied, MgCH₃, the probe laser was a (Coherent, 699-29) cw ring dye-laser, and was pumped by a (Coherent, Innova 200) Ar⁺ laser. Later, the high resolution apparatus was changed: the probe laser was upgraded to the (Coherent, 899-29) cw ring laser, which can be used with dyes
as the 699 model, but can also be used with a Ti:Sapphire crystal. The Ar\textsuperscript{+} laser was also upgraded (Coherent Innova Sabre, model DBW 25/7).

The output of the cw ring laser has a linewidth of \( \sim 1 \) MHz. Typical powers of 100–300 mW were achieved with laser dyes, and powers up to 3 W can be obtained with the Ti:Sapphire crystal and SW optics (710–825 nm tunable region). Detailed information about the operation of the cw ring laser can be found in the Coherent manuals [8].

For the MgNC and HCCS radicals it was necessary to double the frequency of the output of the cw ring laser. Thus the cw laser beam was seeded into a pulse amplifier system (Lambda Physik, FL 2003 model), pumped by an excimer laser (MSC 103 Lambda Physik), operated with a XeCl fill. This pulse amplifier system amplifies the cw output to obtain the high power pulses needed to frequency double using non-linear crystals. The laser linewidth after pulse amplification was \( \sim 120 \) MHz. The pulse amplified beam was then sent to a KDP crystal (Quanta Ray) to double the frequency of the beam into the UV region. The KDP crystal was manually angle-tuned for maximum UV production.

As shown in Figure 3, the probe beam enters the vacuum chamber through a side arm, opposite to the one through which the photolysis beam is brought into the chamber. This side arm also contains baffles to reduce scattered laser light, and a quartz window at Brewster's angle at the open end.

The PC Coherent Autoscan System, version 2.051, is a computer program that was used not only to operate the cw ring laser, but also for averaging and recording of
Figure 3: Block diagram showing the experimental setup of the high resolution apparatus.
all data acquisition. A detailed description of this software can be obtained elsewhere [9].

2.3.1 LIF detection system

The schematic diagram displayed in Figure 4 shows the LIF collection system of the apparatus.

![LIF detection system diagram]

Figure 4: Laser Induced Fluorescence collection system.

The LIF signal is collected at right angles to the probe laser beam, with a 2.5 cm f/1 lens. The collimated LIF signal is then focussed with a 15 cm f/3 lens through an adjustable optical slit, into a photomultiplier tube (PMT) (EMI 9659QB). When
necessary, a filter was placed between the f/3 lens and the PMT, in order to reject scattered laser light.

The optical slit can be carefully adjusted in order to allow only the small central portion of the fluorescence from the jet to be imaged onto the PMT. The use of this slit provides a reduction of the Doppler width of the resulting signal by limiting the fluorescence viewed from the off-axis velocity components in the jet expansion.

The signal from the PMT is pre-amplified and sent to a boxcar averager (Stanford Research, SR250 boxcar) for integration and then the amplified signal is sent to the Coherent Autoscan system for signal averaging and recording.

2.3.2 Frequency calibration

As seen in Figure 3, a small fraction of the probe laser was sent into a home-built, low-finesse plane parallel étalon, with a 475 MHz free spectral range (FSR). Before directing the probe beam into the étalon, the beam was square-wave modulated by a mechanical chopper, at 200 Hz. The signal from the étalon was recorded by a photodiode and sent to a lock-in amplifier (Stanford Research, model SR510), and then it was recorded by the Coherent Autoscan program. The étalon signal was recorded simultaneously with the LIF spectrum of the radical, and was used for relative calibration, since constant frequency steps can be determined by the recorded fringes of this étalon. As demonstrated by Cerny [7], the performance of the Coherent Autoscan System in determining frequency intervals can be slightly improved when checked against the étalon fringes.
The other use of the étalon fringes was to put together the final data files, since the Coherent Autoscan program scans only 0.34 cm\(^{-1}\) at a time. Therefore, the étalon plots were used to combine the individual scan files to form the final spectrum, over the total frequency region scanned. This was done electronically by the Makedat computer program, described in the next section.

Absolute calibration was achieved simply by recording the spectrum of a standard molecule, when a spectrum was available in the region where the LIF spectrum of the radical was recorded. Two molecules have been used for absolute calibration: Te\(_2\) and I\(_2\). The frequencies of the absorption spectrum of Te\(_2\) have been recorded and tabulated by Cariou and Luc in the frequency range of 18,500-21,200 cm\(^{-1}\) [10]. The I\(_2\) atlas with the emission spectrum of this molecule in the 14,000-15,600 cm\(^{-1}\) and in the 14,800-20,000 cm\(^{-1}\) ranges is also available [11, 12]. The uncertainty quoted for the absolute line positions of these standards is ± 0.002 cm\(^{-1}\) for I\(_2\), and ± 0.006 cm\(^{-1}\) for Te\(_2\).

For the MgCH\(_3\) radical, a cell containing Te\(_2\) was heated up to 650 °C, and the absorption spectrum of Te\(_2\) molecule was simultaneously recorded with the LIF spectrum of this radical. For MgNC and HCCS, the region scanned was outside the Te\(_2\) and I\(_2\) spectral atlases. In those two cases the absolute frequencies were obtained from the Autoscan wavemeter of the 899-29 ring laser, with an uncertainty of ± 0.07 cm\(^{-1}\)[8]. The Autoscan wavemeter was calibrated versus the I\(_2\) at the red edge of the atlas, before moving the laser to the desired frequency region.
2.3.3 Experimental linewidth (FWHM)

The *full width at half maximum* (FWHM), or linewidth of the high resolution spectral lines is the resultant of various contributions: laser linewidth; natural lifetime broadened linewidth; power broadened linewidth; and Doppler linewidth.

The laser linewidth of the cw ring laser is only \( \sim 1-2 \text{ MHz} \), and thus its contribution to the total linewidth can be disregarded. However, in cases where the pulse amplifier system was used, the laser linewidth was considerably higher (\( \sim 120 \text{ MHz} \)).

The natural linewidth is expressed by the following expression:

\[
\Delta \nu = \frac{1}{2 \pi \tau}
\]  

(2.1)

where \( \tau \) is the half-lifetime of the excited state, in this case. Only for species with transitions with lifetimes less than 5 ns does the natural broadening contribute significantly to the total linewidth. Since all the radicals studied in this dissertation have lifetimes much longer than this, the natural broadening contribution to the total linewidth can be ignored.

The power broadened linewidth (saturation) can be expressed as:

\[
\Delta \nu = \Delta \nu_o \sqrt{1 + \frac{B \rho}{R}}
\]  

(2.2)

where \( \Delta \nu_o \) is the unsaturated linewidth, \( B \) is the Einstein coefficient, \( R \) is the total relaxation rate for the emitting state, and \( \rho \) is the electromagnetic energy density [13].
The Doppler width is one of the major contributions to the spectral linewidth in gases at low pressures, and is due to the thermal motion of the emitting molecules. It can be expressed as [13]:

$$\Delta \nu_D = 2\sqrt{\ln 2} \, \nu_0 \frac{v_p}{c}$$

(2.3)

where $\nu_0$ is the transition frequency, and $v_p$ is the velocity component of the molecule in the direction of the beam.

Figure 5: Schematic diagram showing the Doppler broadening effect due to the geometrical nature of the jet expansion.

However, the radicals are probed in a supersonic jet expansion where there is a reduction of the Doppler broadening linewidth due to the highly directional flow.
and velocity range reduction of the jet expansions. The velocity of the radicals in the supersonic jet expansion has a perpendicular \( (v_x) \) and a parallel \( (v_y) \) component. The perpendicular component, \( v_x \), will cause a Doppler shift for the radical absorption.

As illustrated in Figure 5, if the LIF of a region of width \( b \) is probed at a distance \( d \) from the nozzle, the maximum Doppler width experienced by the radicals would be from the radicals traveling along the direction marked as A in Figure 5. The perpendicular component of the velocity in direction A, is \( v_x = v \sin \theta \), and thus equation 2.3 becomes:

\[
\Delta \nu_D' = 2\sqrt{\ln 2} \frac{v}{c} \sin \theta = \Delta \nu_D \sin \theta \tag{2.4}
\]

where \( \Delta \nu_D \) was defined in equation 2.3.

2.4 Computer software: Makedat and SpecSim programs

2.4.1 Makedat

As mentioned before, the Coherent Autoscan system scans over a range of only 0.34 cm\(^{-1}\) at a time. To combine these separate scan files into just one data file which contains the whole frequency region scanned, a calibration and merge computer program, Makedat, was used. This program was designed by a former Ph.D. student of Prof. T. A. Miller, Dr. Timothy M. Cerny. A thorough description of this program can be found in Cerny’s Ph.D. dissertation [7]. Makedat is able to import the data files generated by the Coherent Autoscan software, and combine them, two at a time. Four traces are recorded by the Autoscan system: the LIF spectrum of the
radical, the spectrum of a standard molecule (Te$_2$ or I$_2$), the signal from the home-built étalon, and a trace from a vernier étalon (VET), from the Coherent wavemeter. This VET is a temperature-controlled étalon with FSR of 0.2 cm$^{-1}$, which is used to monitor possible mode hops in the cavity of the ring laser, but it can also be used for overlapping individual scans.

**Makedat** allows the handling of those four traces independently, and it is possible to shift them with respect to each other: an option that is used in the calibration process. Consequently, the absolute and relative calibration of the experimental spectra is done electronically using this computer program.

### 2.4.2 SpecSim

The analyses of the rotationally resolved spectra contained in this work have been performed using another computer program, SpecSim, designed by another former Ph.D. student of Prof. T. A. Miller, Dr. Sergey I. Panov. A detailed description of this program can be found in his Ph.D. dissertation [14].

SpecSim simulates transitions between two states, the upper and lower states, which are either electronic or vibronic states, with their own rotational structure. The level structure of these states is determined by the appropriate Hamiltonians for those states, which can be chosen within the program. The most important features of SpecSim will follow. The experimental spectrum can be imported into SpecSim, and the user can choose an appropriate model to study the transition of interest (e.g. diatomic or linear model, symmetric rotor, asymmetric rotor, etc.). Then the symmetry of the upper and lower states should be selected, and the values of the
molecular constants for the model chosen can be edited. Other parameters such as the rotational temperature, linewidth of the experimental lines (Lorentzian or Gaussian lineshapes) must be entered. With the values given for the molecular constants and for the parameters, SpecSim simulates the spectral profiles. It is possible to display the experimental and simulated profiles simultaneously. The simulation contains not only the frequency position, but also the intensity for each transition, calculated assuming a Boltzmann distribution. Once SpecSim has generated the simulated spectrum, it is possible to assign the frequency of lines in the experimental spectrum to selected transitions in the simulated trace. The quantum numbers for the upper and lower states for each transition are displayed when the assign option is being used. The user can then select the molecular constants that he/she wants to be fitted. For the fitting procedure, a non-linear least squares test is run and its results can be displayed.

2.5 Moderate resolution system

All the moderate resolution LIF spectra included in this work were obtained in the same basic experimental setup, with the exception of the probe laser, which was of lower resolution. Also, the electronics and optics used for the data acquisition were the same as described for the high resolution system, except that a personal computer was used for digitization and storage of the LIF signal (done by the Coherent Autoscan system in the previous case). To obtain the moderate resolution spectra, the probe laser was a dye laser (Questek, model 5200B), pumped by an excimer laser (Lambda Physik, model MSC 103). The laser linewidth of this dye laser is $\sim 0.06$ cm$^{-1}$. Such
linewidth allowed the partial resolution of the rotational contours of the electronic transitions studied, which was useful for assigning the carrier of the transitions. This laser system was also used as a survey system, since it is not practicable to scan wide ranges of frequencies with the cw ring laser.
CHAPTER 3

HIGH RESOLUTION ELECTRONIC SPECTROSCOPY OF MgCH₃.

3.1 Introduction

The knowledge of organometallic radicals has increased considerably in the last few years by the application of laser induced fluorescence (LIF) spectroscopy to supersonic free jet expansions of these species. In particular, the study of methyl derivatives of the alkaline earth metals has attracted some interest in recent years and a number of reports regarding the spectroscopy of MCH₃ radicals (M=Zn and Cd [15, 16], Ca [17, 18, 19]) have been published.

As was mentioned in Chapter 1, there is great interest in studying Mg-containing radicals, especially in the astrophysical field. MgCH₃ specifically has been suggested to play an important role in the atmosphere of Jupiter and perhaps other large gaseous planets [20], although experimental evidence of this has not been reported yet. Laboratory spectra of species which are believed to be present in interstellar space are indispensable in order to be able to identify them in this environment.

An additional motivation for the study of MgCH₃ was to complete the series of moderate and high resolution LIF studies of MCH₃ (M= Cd and Zn) radicals and their
ions, using ZEKE spectroscopy, performed in Professor T. A. Miller's group [15, 16, 21, 22, 23]. Another methyl organometallic radical that has attracted some attention is the CaCH₃ radical. The first report was done by Bernath and coworkers [17], who obtained the LIF spectrum of the A ← X transition. More recently, Anderson and Ziurys recorded the millimeter-wave spectrum of the X₂A₁ state [18]; and finally, Marr et al. obtained the optical and optical Stark spectra of the origin band of CaCH₃ [19].

It is possible then to compare the spectroscopic parameters obtained from the MgCH₃ spectra, and therefore its structure, with the results obtained for the other methyl radicals.

The work presented in this chapter on MgCH₃ was published in 1995 [24]. Later that same year, Anderson and Ziurys obtained the millimeter and sub-millimeter spectrum of MgCH₃ in its ground electronic state [25]. Last year, an ab initio study of the X and A electronic states of MgCH₃ was reported by Woon [26].

3.2 Experimental Details

The MgCH₃ radicals were obtained by the laser ablation/photolysis technique discussed in detail in the previous chapter. Therefore only a brief description of the particular experimental details for the production of this radical will be presented in this section.

The organic precursor used to generate the methyl moiety of MgCH₃ was acetone
was placed in a stainless steel reservoir and maintained at a constant temperature in a dry ice-acetone bath, at -78 °C. Helium was passed through the reservoir at a pressure of 200-300 psig, and the gas mixture (acetone vapor/He) was introduced into the ablation fixture (see Figure 2) through the pulsed valve. A magnesium rod was mounted inside the ablation fixture, next to the 2 mm central channel through which the gas mixture was flowing. A KrF excimer (248 nm) was used as the ablation/photolysis source, with an attenuated output power of ~ 30 mJ/pulse.

The MgCH$_3$ radicals created in this way expanded into the vacuum region and were then probed by LIF spectroscopy. The continuous wave ring laser (Coherent, 699-29 model) was pumped by an Ar$^+$ laser (Coherent, Innova 200). The laser dye used was Coumarin 102 (Exciton), with an output power of about 100-200 mW. The Te$_2$ spectrum, which was used for absolute frequency calibration [10], was taken simultaneously with the MgCH$_3$ spectrum.

### 3.3 Theory

MgCH$_3$ belongs to the C$_{3u}$ point group, and thus has $^2A_1$ and $^2E$ ground and first excited electronic states, respectively. Expressions for the rotational energy levels for a symmetric top molecule in $^2E$ and $^2A$ states have been derived in detail previously [27, 28, 29], and therefore, only a brief description of the Hamiltonians and basis set used to analyze the data will follow.

The rotational Hamiltonian for the ground electronic state ($^2A_1$) can be expressed
\[ \mathcal{H}(^2 A) = A N_z^2 + B \left( N_x^2 + N_y^2 \right) + \epsilon_{aa} N_z S_z + \frac{1}{2} \epsilon_{bc} (N_+ S_- + N_- S_+) + \mathcal{H}_{CD} \] (3.1)

where \( A \) and \( B \) are the rotational constants of the molecule, and \( \epsilon_{aa} \) and \( \epsilon_{bc} = (\epsilon_{bb} + \epsilon_{cc}/2) \) are the spin-rotation coupling constants. \( N \) is the total angular momentum operator excluding the electronic and the nuclear spin angular momenta, i.e. \( N = J - S \), with \( J \) being the total angular momentum operator excluding nuclear spin, and \( S \) being the electron spin angular momentum operator. The term labelled \( \mathcal{H}_{CD} \) corresponds to the terms for rotational centrifugal distortion,

\[ \mathcal{H}_{CD} = - \left( D_N N_4 + D_{NK} N^2 N_z^2 + D_K N_z^4 \right) \] (3.2)

where \( D_N, D_{NK} \) and \( D_K \) denote the usual centrifugal distortion constants.

The rotational Hamiltonian for the excited state \( (^2 E) \) is much more complicated and can be written as a summation of several terms:

\[ \mathcal{H}(^2 E) = \mathcal{H}_{\text{ROT}} + \mathcal{H}_{\text{SO}} + \mathcal{H}_{\text{COR}} + \mathcal{H}_{\text{SR}} + \mathcal{H}_{\text{JT}} + T_{00} \] (3.3)

where \( \mathcal{H}_{\text{ROT}}, \mathcal{H}_{\text{SO}}, \mathcal{H}_{\text{COR}}, \mathcal{H}_{\text{SR}} \) and \( \mathcal{H}_{\text{JT}} \) correspond to the rotational, spin-orbit, Coriolis, spin-rotation and Jahn-Teller Hamiltonians, respectively, and \( T_{00} \) is the transition energy between the vibrationless levels of the \( \tilde{X} \) and the \( \tilde{A} \) electronic states.

The definition for each term is as follows:

\[ \mathcal{H}_{\text{ROT}} = A N_z^2 + B \left( N_x^2 + N_y^2 \right) + \mathcal{H}_{CD} \] (3.4)
where $\mathcal{H}_{CD}$ is the same as in equation 3.2.

$$\mathcal{H}_{SO} = aL_zS_z + a_D N_z^2 L_zS_z$$  \hspace{1cm} (3.5)$$

where $a$ is the spin-orbit coupling constant, $a_D$ is its centrifugal distortion correction, and $L$ is the total electronic orbital angular momentum operator.

$$\mathcal{H}_{COR} = -2AN_zL_z + \eta_e N^2 N_zL_z + \eta_k N_z^3 L_z$$  \hspace{1cm} (3.6)$$

where $\eta_e$ and $\eta_k$ are centrifugal distortion corrections for the Coriolis interaction.

$$\mathcal{H}_{SR} = \epsilon_{aa} N_z S_z + \frac{1}{2} \epsilon_{bc} (N_+ S_+ + N_- S_-) + \epsilon_1 (L_-^2 N_+ + L_+^2 N_-) + \epsilon_2 \left[ L_-^2 (N_+ S_+ + S_+ N_z) \right]$$

$$+ \epsilon_{2b} \left[ L_-^2 (N_- S_+ + S_+ N_z) \right]$$

$$+ \epsilon_{2b} \left[ L_+^2 (N_+ S_- + S_- N_z) \right]$$

$$+ \epsilon_{2b} \left[ L_+^2 (N_- S_- + S_- N_z) \right]$$  \hspace{1cm} (3.7)$$

where $L_+$ and $L_-$ are artificial ladder operators introduced by Hougen [29], which convert one component of the vibronic state $E$ into the other. $\epsilon_{aa}$ and $\epsilon_{bc}$ are the spin-rotation coupling constants, defined as before. The last three terms in $\mathcal{H}_{SR}$ are higher order contributions to the spin-rotation interaction.

$$\mathcal{H}_{JT} = h_1 \left( L_-^2 N_+^2 + L_+^2 N_-^2 \right) + h_2 \left[ L_-^2 (N_z N_+ + N_- N_z) + L_+^2 (N_z N_+ + N_+ N_z) \right]$$  \hspace{1cm} (3.8)$$

where $h_1$ and $h_2$ are parameters to describe the Jahn-Teller interaction.

The basis set used to diagonalize both $\mathcal{H}(^2A)$ and $\mathcal{H}(^2E)$, is the Hund’s case (a) basis set.
\[ |JPS\Sigma\Lambda; \pm\rangle = \frac{1}{\sqrt{2}} \left[ |+\rangle |JP M_J\rangle |S\Sigma\rangle \pm (-1)^{J-P+S-S} |-\rangle \right] \] (3.9)

Here \( P \) is the projection of \( J \) on the top axis and \( M_J \) is the projection of \( J \) on the space fixed axis. The \(|+\rangle\) and \(|-\rangle\) kets correspond to electronic eigenfunctions with opposite projections of the electronic orbital angular momentum, \( \Lambda \), on the molecule fixed axis. For the \( ^2A \) state, \( \Lambda \) is set to 0, and the linear combination reduces to a single term. The \( \pm \) sign denotes the parity of the basis functions in the basis set \(|JPS\Sigma\Lambda; \pm\rangle\), where \( P \) can take either a positive or negative value.

The selection rules for a \( ^2E \leftarrow ^2A \) electronic transition are [30]:

(i) \( \Delta J = J'-J'' = 0, \pm 1 \);
(ii) \( \Delta K = K' - K'' = 1 \);
(iii) \( p = \pm \leftrightarrow p = \mp \), where \( p \) is the parity.

The parity of the eigenfunctions is \((-1)^N\), where \( N = J - 1/2 \) for the lower energy state (the \( F_1 \) component) and \( N = J + 1/2 \) for the upper energy state (the \( F_2 \) component). Thus, the even parity states only exist for \( N = \) even integer and the odd parity states exist for \( N = \) odd integer.

### 3.4 Results

High resolution, rotationally resolved spectra were taken for both spin-orbit components of the origin band, the \( ^2E_{1/2} \leftarrow ^2A_1 \) (also called \( F_1 \) band), and the \( ^2E_{3/2} \leftarrow ^2A_1 \) (or \( F_2 \) band) of the \( 0^+_0 \) transition of the MgCH₃ radical.

The experimental and the simulated spectra for the \( F_1 \) band are shown in Figure 6, and the corresponding spectra for the \( F_2 \) band are given in Figure 7.
Figure 6: Experimental and simulated spectra for the $0^6_0, ^2E_{1/2} \leftarrow ^2A_1$ (F$_1$ band) of MgCH$_3$. The rotational temperature of the simulated spectrum is 3K. The peak marked with an asterisk corresponds to a (0,0) rotational transition of MgO. The variation between the predicted and observed intensities observed in some of the rotational lines is due to both long and short term variation in the MgCH$_3$ production.
For each band three sub-bands corresponding to the $2 \leftrightarrow 1, 1 \leftrightarrow 0$ and $0 \leftrightarrow -1 (K' \leftrightarrow K'')$ transitions were observed, following the $\Delta K = +1$ selection rule. Given the $\Delta J = 0, \pm 1$ selection rule, P, Q and R branches are present in each subband. The branches with $F_1$ upper levels are designated $P_{1,F''}, Q_{1,F''}$ and $R_{1,F''}$, where $F''$ is either 1 or 2 depending on whether $J''$ is equal to $(N+1/2)$ or $(N-1/2)$, respectively. Similarly, the notation for the $F_2$ band is $P_{2,F''}, Q_{2,F''}$ and $R_{2,F''}$, and $F''$ is defined as above. A stick spectrum for the $F_1'$ band, illustrating the branch structure observed in each $(K' \leftrightarrow K'')$ sub-band, is shown in Figure 8.

Mg has three isotopes, $^{24}$Mg, $^{25}$Mg and $^{26}$Mg, with natural isotopic abundances of 78.99%, 10.00% and 11.01% respectively. However, only transitions for the main isotope ($^{24}$Mg) and for the $^{26}$MgCH$_3$ radical were observed, i.e. it was not possible to assign any experimental lines to $^{25}$MgCH$_3$. This result can be ascribed to the hyperfine splitting of $^{25}$Mg ($I = 5/2$) which causes a splitting of each transition into multiple components with a corresponding decrease in the intensities of the transitions. In Figure 9 an enlargement of the experimental spectrum clearly shows the observed isotopic structure for the $^{24}$MgCH$_3$ and $^{26}$MgCH$_3$ isotopomers.

SpecSim [14], was used to model and fit the experimental spectra, as described in the previous chapter. The simulated plots shown in Figures 6-8 were generated by this program.

A few lines that could not be assigned to either $^{24}$MgCH$_3$ or $^{26}$MgCH$_3$ belong to MgO. The band origins for the (0,0) and (1,1) MgO transitions are at 20,003.57 cm$^{-1}$ and 20,043.43 cm$^{-1}$ respectively, overlapping the regions where the $F_1$ and $F_2$ bands
Figure 7: Experimental and simulated spectra for the $0_0^1, \ ^2E_{3/2} \leftarrow \ ^2A_1$ (or $F_2$ band) of MgCH$_3$. The rotational temperature of the simulated spectrum is 3K. Peaks marked with an asterisk correspond to the (1,1) rotational transitions of MgO. As noted before, variation between the predicted and observed intensities observed in some of the rotational lines is due to both long and short term variation in the MgCH$_3$ production.
Figure 8: Experimental spectrum of the $0^0, {^2}E_{1/2} \leftarrow {^2}A_1$ ($F_1$ band) of MgCH$_3$. Below the experimental spectrum, a stick spectrum with the observed $K' \leftarrow K''$ subbands is displayed. For the $1 \leftarrow 0$ subband the $\Delta J_{F',F''}$ structure is shown.
For the $^{24}\text{MgCH}_3$ radical a total of 71 rotational transitions were fit for the F$_1$ and F$_2$ bands. The standard deviation, calculated from the linear least squares fitting, was $2.7 \times 10^{-3}$ cm$^{-1}$, which shows the good agreement of the simulated and experimental spectra when compared with the experimental linewidth of $\sim 5 \times 10^{-3}$ cm$^{-1}$. Due to the lower intensity of the $^{26}\text{MgCH}_3$ lines with respect to the ones for the main isotope, only 54 lines were observed and fit, with a standard deviation of $3.2 \times 10^{-3}$ cm$^{-1}$.

It was not possible to determine the $A$ rotational constants for both the ground and the excited states independently, because of the limited number of $K' \leftrightarrow K''$ sub-bands observed, as was the case for ZnCH$_3$ and CdCH$_3$ radicals [16]. However, since it is possible to determine $\Delta A$ from the fit, fixing one of the $A$ constants (either $A''$ or $A'$) will allow the other to be determined. Therefore the $A''$ constant was thus fixed at the value of 5.2217 cm$^{-1}$, generated in an ab initio calculation [32]. All the molecular constants determined for both isotopes are summarized in Table 1.

A number of small terms contained in the Hamiltonian (Eqs. 1-8), were found to affect the spectrum less than experimental error. These include rotational distortion terms ($D_N$, $D_NK$ and $D_K$), the Coriolis centrifugal distortion terms ($\eta_c$ and $\eta_k$), the high order spin-rotation parameters ($\epsilon_1$, $\epsilon_2a$ and $\epsilon_{2b}$) as well as the Jahn-Teller parameters ($h_1$ and $h_2$). For the final fits, these were all set equal to zero and are omitted from Table 1. The omission of all these terms probably leaves the theoretical model slightly less accurate than the experimental data. However, owing to the limitation of the observed spectrum to fairly low $J$ values due to its low temperature...
Figure 9: An enlargement of a region of the $0^0, {}^2E_{3/2} \leftarrow {}^2A_1 (F_2 \text{ band})$ showing transitions observed for both isotopomers: $^{24}\text{MgCH}_3$ and $^{26}\text{MgCH}_3$. 
(3K), it would be imprudent to include these parameters in the fit.

3.5 Discussion

The first general issue to be dealt with is the identity of the carrier of the spectrum. The assignment to MgCH₃ radical was made on several grounds: (i) the method of preparation was similar to ones successfully used to prepare the other MCH₃ (M=Ca, Zn, Cd) radicals; (ii) all the other MCH₃ Ā ← Ā spectra were very close in absolute frequency to the corresponding MH spectra, and this is likewise the case for MgCH₃. (iii) While not extensive, the vibrational frequencies seen [33] in the lower resolution spectrum are consistent with those expected for MgCH₃; (iii) finally, and most importantly, the detailed rotational analysis, in terms of ²⁴MgCH₃ and ²⁶MgCH₃ isotopomers, of well over 100 transitions would seem to remove any residual doubt as to the carrier’s identity.

As mentioned earlier, subsequent to the publication of work reported here, ab initio calculations [26] were published by Woon, which are in reasonable good agreement with the experimental values. The best computed value [RCCSD(T)/cc-pVTZ] for the Ā ²E ← Ā ²A₁ excitation energy is 19,999 cm⁻¹ (the experimental value obtained is 20,030.30 cm⁻¹), although the calculated value does not include the zero-point vibrational contribution. The ab initio values of the B rotational constant for both electronic states are within ~ 5 ×10⁻⁴ cm⁻¹ of the experimental value, while for the A rotational constant the agreement is of the order of 0.13-0.17 cm⁻¹, numerically
large but relatively small percentage (2.5-3%). These results give additional support to the assignment of the spectra to the MgCH₃ radical. The \textit{ab initio} values of Woon\cite{26} are included in Table 1 for comparison with the experimental values.

In Table 2 all the molecular constants determined from the simulated spectra, as well as the structural parameters estimated for MgCH₃, are presented. This table also contains the information for the other MCH₃ radicals previously studied. Thus, the results obtained for MgCH₃ will be discussed and compared with the values determined for the other alkyl organometallic radicals.

\subsection*{3.5.1 Coriolis coupling, spin-orbit and spin-rotation interactions.}

From fitting the spectra, the Coriolis coupling constant, $A\zeta$, for the $\tilde{A}$ state can be determined. Since the value of the rotational constant $A$ is also known, it is possible to calculate the $z$ component of the vibronic angular momentum, $\zeta$. The value calculated in this way was 0.86, as shown in Table 2.

Another constant determined from the fitting is the spin-orbit splitting, $\alpha \zeta_d$. Assuming that $\alpha$, the spin-orbit coupling constant of MgCH₃, is similar to that of MgH, it is possible to determine $\zeta_d$, the $z$ projection of the electronic orbital angular momentum. Using $\alpha = 35.3$ cm$^{-1}$, the spin-orbit coupling constant of the $\tilde{A}$ $^2\Pi$ state of MgH\cite{34}, then $\zeta_d$ is calculated as 0.81, very close to the value of $\zeta = 0.86$.

The following expression has been derived for an $X_3$ molecule\cite{35}:

$$\zeta = \zeta_d + \frac{1}{2}d \zeta_2$$

(3.10)
<table>
<thead>
<tr>
<th></th>
<th>( ^{24}\text{MgCH}_3 )</th>
<th>( ^{24}\text{MgCH}_3 )</th>
<th>( ^{26}\text{MgCH}_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A )</td>
<td>5.2217 (^b)</td>
<td>5.3509</td>
<td>5.2217 (^b)</td>
</tr>
<tr>
<td>( \tilde{X}^{2}A_1 ) ( B )</td>
<td>0.36710(8)</td>
<td>0.3664</td>
<td>0.3566 (1)</td>
</tr>
<tr>
<td>( \epsilon_{bc} )</td>
<td>0.0017 (2)</td>
<td>0.0014 (3)</td>
<td>0.0017 (2)</td>
</tr>
<tr>
<td>( A )</td>
<td>4.9923 (6)</td>
<td>5.1580</td>
<td>4.9915 (8)</td>
</tr>
<tr>
<td>( B )</td>
<td>0.36467 (7)</td>
<td>0.3652</td>
<td>0.3544 (1)</td>
</tr>
<tr>
<td>( a\zeta d )</td>
<td>28.591 (1)</td>
<td>28.591 (2)</td>
<td>28.591 (2)</td>
</tr>
<tr>
<td>( \tilde{A}^{2}E ) ( a_{D\zeta d} )</td>
<td>- 0.005 (1)</td>
<td>- 0.006 (2)</td>
<td>- 0.006 (2)</td>
</tr>
<tr>
<td>( A\zeta )</td>
<td>4.3117 (6)</td>
<td>4.3113 (8)</td>
<td>4.3113 (8)</td>
</tr>
<tr>
<td>( \epsilon_{aa} )</td>
<td>0.202 (2)</td>
<td>0.201 (3)</td>
<td>0.201 (3)</td>
</tr>
<tr>
<td>( \epsilon_{bc} )</td>
<td>- 0.004 (2)</td>
<td>- 0.004 (7)</td>
<td>- 0.004 (7)</td>
</tr>
<tr>
<td>( T_{00} )</td>
<td>20,030.296 (2)</td>
<td>19,999 (^c)</td>
<td>20,030.477 (4)</td>
</tr>
</tbody>
</table>

\(^a\) From reference [26].
\(^b\) Fixed at a theoretical value [32].
\(^c\) This value does not include zero-point vibrational contribution.

Table 1: Molecular constants of MgCH\(_3\) in cm\(^{-1}\). Numbers in parentheses indicate one standard deviation.
where $\zeta_2$ is the vibrational Coriolis coupling coefficient for the Jahn-Teller active degenerate vibration mode. This expression can be used to estimate the value of $d$, the Jahn-Teller quenching coefficient. If $\zeta_2d \sim \zeta_t$, as was found for MgCH$_3$ (see above), the second term of equation 3.10 vanishes, and thus $d$ is $\sim 1$. The same result ($\zeta_2 \sim \zeta_t, d \sim 1$) was obtained for the other MCH$_3$ radicals, with the exception of CdCH$_3$, for which a discrepancy between these two values was encountered. As was indicated by Cerny et al. [16], a possible explanation for this would be that the Coriolis coupling constant of CdCH$_3$ has contributions from the spin-orbit interaction.

The spin-rotation interaction in MgCH$_3$ is accounted for by the $\epsilon_{aa}$ and $\epsilon_{bc}$ parameters, i.e. the components of the spin-rotation tensor. The magnitude of $\epsilon_{aa}$ in the $\tilde{X}$ state for any of the radicals is very small, below the precision of the measurements, and thus there are no entries for this constant in Table 2. On the other hand, $\epsilon_{bc}$ was measured for all the radicals. In the IIA metal methyl radicals (MgCH$_3$ and CaCH$_3$), $\epsilon_{bc}$ is approximately $1.7 \times 10^{-3}$ cm$^{-1}$, while for the IIB metals it is about an order of magnitude larger (see Table 2). For either the $\tilde{X}$ or $\tilde{A}$ electronic states, the components of the spin-rotation tensor are expected to be dominated by second order cross terms involving L-uncoupling and spin-orbit coupling. Indeed a comparison among the radicals shows that $\epsilon_{bc}$ qualitatively correlates with the product $B \times a\zeta_e$, but a quantitative relationship cannot be established. In the $\tilde{A}$ state, $\epsilon_{bc}$ is still relatively small but again appears to increase significantly for the radicals which have larger spin-orbit coupling.

$\epsilon_{aa}$ in the $\tilde{A}$ state is, by far, the largest spin-rotation parameter for all the radicals.
It also correlates qualitatively with the magnitude of the spin-orbit coupling but is anomalously large for the IIB metals presumably, as previously noted [16], owing to the interaction of the \( \tilde{A} \) state with another nearby electronic state.

As mentioned in the introduction, several spectroscopic studies have been carried out for the CaCH\(_3\) radical. In the study of Brazier and Bernath, a value of \( \epsilon_{aa} \) of -0.40 cm\(^{-1}\) was reported for CaCH\(_3\) [17]. Assuming that the sign conventions in their work are consistent, a negative \( \epsilon_{aa} \) is quite strange and difficult to explain physically. Electronic states with \( E \) symmetry with a positive spin-orbit coupling (\( a > 0 \)) should have \( \epsilon_{aa} > 0 \), as was the case for MgCH\(_3\), CdCH\(_3\), ZnCH\(_3\) and CaC\(_5\)H\(_5\) [24, 16, 36]. An \( \epsilon_{aa} < 0 \) is obtained for an inverted spin-orbit case (\( a < 0 \)), as was found for the CH\(_3\)O radical [30], for example. In all cases, this assumes that the coupling is only to higher-lying \( ^2E \) states. The \( \epsilon_{aa} \) reported by Brazier and Bernath, implies that a \( ^2E \) perturbing state lies between the \( \tilde{A} \) and \( \tilde{X} \) states for CaCH\(_3\). This inconsistency was reported in the publication of the present work, in 1995 [24]. Marr and coworkers mentioned this apparent inconsistency as one of the reasons to study the spectrum of the \( 0^0 \tilde{A} \rightarrow \tilde{X} ^2A_1 \) transition again [19]. In this work, the spectrum of CaCH\(_3\) was obtained under much cooler conditions than before, which revealed the low-J transitions, unidentified in the work of Brazier and Bernath [17], and possibly causing some misassignments. Marr \textit{et al.} [19], were able to reassign the CaCH\(_3\) spectrum, and found a new set of spectroscopic parameters. As suggested in the MgCH\(_3\) publication, the new value of \( \epsilon_{aa} \) obtained for CaCH\(_3\) was a small \textit{positive} number. The values included in Table 2 for CaCH\(_3\) are the constants obtained in the latter work of Marr.
et al. [19], unless otherwise indicated.

3.5.2 Jahn-Teller effect.

Attempts to fit the spectrum varying the Jahn-Teller constants ($h_1$ and $h_2$) were made, but their values were zero within experimental error. This, in addition to the previous discussion on the values of $\zeta$ and $\zeta_e (d \sim 1)$, leads to the conclusion that the Jahn-Teller interaction is negligibly small in the v=0 level of the $\tilde{A}$ state of MgCH$_3$. The same result was found for the other three MCH$_3$ radicals.

3.5.3 Geometry

From the observed rotational constants, information about the geometry of the molecule can be obtained. For a MCH$_3$ symmetric-top molecule, three structural parameters are needed to define the geometry; the carbon-hydrogen bond length ($R_{CH}$), the metal-carbon bond length ($R_{MC}$) and the hydrogen-carbon-hydrogen angle of the methyl group ($\theta_{HCH}$). The rotational constant $A$ is a function of $R_{CH}$ and $\theta_{HCH}$ only, whereas the $B$ constant depends on all three parameters. Since not enough independent data was obtained for MgCH$_3$, determination of the three parameters was not possible. Attempts to use the $^{24}$MgCH$_3$ and $^{26}$MgCH$_3$ data to determine the structural parameters independently proved unsuccessful, as was the case for the isotopomers of ZnCH$_3$ and CdCH$_3$ [16], owing to lack of experimental precision. Consequently, one of these parameters (the carbon-hydrogen bond length) was fixed at a theoretical value [32], and then the other two structural parameters were evaluated. Following the same procedure that Cerny et al. [16] applied to ZnCH$_3$ and CdCH$_3$
(which has also been applied in some other cases [28, 30, 37]), the $\theta_{HCH}$ value was determined from the $A$ constant, and then $R_{MC}$ was calculated from the $B$ rotational constant. The calculated bond lengths and angles obtained by this method for the ground and excited electronic states of MgCH$_3$, are presented in Table 2.

The change in $R_{MC}$ value, going from the ground to the excited state has some significance. For MgCH$_3$ as well as for CaCH$_3$, the metal-carbon bond length in the $\tilde{A}$ state is longer than that in the ground state. On the other hand, a change in the opposite direction was found for ZnCH$_3$ and CdCH$_3$ as is shown in Table 2. For all these methyl radicals, an increase of about 3-4° was determined for the $\theta_{HCH}$ angle in the $\tilde{A} \leftarrow \tilde{X}$ transition, indicating an opening of the methyl hydrogen umbrella upon excitation.

These structural changes should be viewed in terms of the expected bonding in the radicals. It is useful to consider the radicals as being derived from the corresponding dihydride or dimethyl molecules. The bonding in the ground state of these species is generally thought to consist of promotion of the two metal $s$ electrons to oppositely-directed, hybrid $sp$ orbitals, each of which gives rise to a single $\sigma$ bond with a H or methyl group. The ground state of the radical is formed by "clipping off" one H or methyl group leaving the unpaired electron in the formerly bonding $\sigma$ orbital. The excited $\tilde{A}$ state results from excitation of this electron to a $p\pi$ orbital, mainly localized on the metal, giving rise to the $^2E$ electronic state. Using this picture, the behavior of the IIB metal mono-methyls is easily understood. The excitation of the electron allows a partial $\pi$ bond to form via hyperconjugation, an idea introduced
Table 2: Molecular constants and structural parameters of MCH₃ radicals, in cm⁻¹. Numbers in parentheses indicate one standard deviation. For $R_{MC}$ and $\theta_{HCH}$ the uncertainty was calculated by propagation of errors.

<table>
<thead>
<tr>
<th></th>
<th>$^{24}$MgCH₃</th>
<th>CaCH₃</th>
<th>$^{64}$ZnCH₃</th>
<th>$^{114}$CdCH₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>5.2217</td>
<td>5.44831 (63)</td>
<td>5.15357</td>
<td>5.1568 (16)</td>
</tr>
<tr>
<td>$B$</td>
<td>0.36710 (8)</td>
<td>0.25238487 (7)</td>
<td>0.30976 (20)</td>
<td>0.23405 (17)</td>
</tr>
<tr>
<td>$\epsilon_{bc}$</td>
<td>0.0017 (2)</td>
<td>0.00185 (1)</td>
<td>0.01191 (70)</td>
<td>0.0251 (57)</td>
</tr>
<tr>
<td>$R_{CH}$ (Å)</td>
<td>1.105</td>
<td>1.100 (20)</td>
<td>1.105</td>
<td>1.105</td>
</tr>
<tr>
<td>$R_{CM}$ (Å)</td>
<td>2.102 (2)</td>
<td>2.369 (13)</td>
<td>2.001 (7)</td>
<td>2.221 (7)</td>
</tr>
<tr>
<td>$\theta_{HCH}$ (degrees)</td>
<td>108.16 (1)</td>
<td>105.6 (26)</td>
<td>109.21</td>
<td>109.18 (150)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>$^{2}$A₁</th>
<th>$^{1}$E</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>4.9923 (6)</td>
<td>5.3855 (6)</td>
</tr>
<tr>
<td>$B$</td>
<td>0.36467 (7)</td>
<td>0.254270 (7)</td>
</tr>
<tr>
<td>$c_{d}$</td>
<td>28.591 (1)</td>
<td>72.7092 (18)</td>
</tr>
<tr>
<td>$c_{d}d$</td>
<td>-0.005 (1)</td>
<td>-0.000886</td>
</tr>
<tr>
<td>$R_{CH}$ (Å)</td>
<td>1.105</td>
<td>1.100 (20)</td>
</tr>
<tr>
<td>$R_{CM}$ (Å)</td>
<td>2.124 (6)</td>
<td>2.353 (14)</td>
</tr>
<tr>
<td>$\theta_{HCH}$ (degrees)</td>
<td>111.8 (5)</td>
<td>109.2 (30)</td>
</tr>
<tr>
<td>$\Delta R_{CM}$</td>
<td>0.022 (6)</td>
<td>0.004 (19)</td>
</tr>
<tr>
<td>$\Delta \theta_{HCH}$</td>
<td>3.7 (5)</td>
<td>3.6 (41)</td>
</tr>
<tr>
<td>$T_{00}$</td>
<td>20030.296 (2)</td>
<td>14743.3822 (11)</td>
</tr>
</tbody>
</table>

* From reference [19], unless otherwise indicated.
* From reference [16].
* Fixed at a theoretical value [32].
* From reference [17].
* From reference [18].
by Mulliken which involves the interaction of orbitals of \( \pi \) symmetry [38]. In the case of the MCH\(_3\) radicals a partial \( \pi \) bond could be formed between the \( \pi \) methyl group orbital, and the metal localized \( \pi \) orbital. This explains both the decrease in M—CH\(_3\) bond length and the “opening” of the methyl umbrella to facilitate the hyperconjugation.

While the essential elements of this picture are believed to be correct for the MCH\(_3\) radicals, it cannot be the whole story. Clearly, the lengthening of the M—CH\(_3\) bond in the \( \bar{A} \) state of MgCH\(_3\), and essentially no change for CaCH\(_3\), require an additional explanation. It may be that in the smaller IIA metals electronic repulsion is simply too great to tolerate significant shortening of the bond due to hyperconjugation. Correspondingly the reorganization of the hybrid orbitals upon electron excitation may sufficiently weaken the existing \( \sigma \) bond to result in a net lengthening of the bond, despite the effect of hyperconjugation, which still appears the best explanation for the opening of the HCH angle.

It would be useful to see if detailed \textit{ab initio} calculations can reproduce the observed effects. If so, the resulting eigenfunctions can be studied to provide a chemically intuitive picture of the variation of the bonding in these radicals. Further spectroscopic studies involving deuteration may also be useful to eliminate the necessity of assuming the C—H bond length in the determination of the experimental structures. Asymmetric deuteration could also be used to break the degeneracy to the excited \(^2E\) electronic state.
3.5.4 Isotopic shift

The isotopic shift observed in the origin band is particularly interesting. It was found that the origin of $^{26}$MgCH$_3$ was to the blue of $^{24}$MgCH$_3$ (0.18 cm$^{-1}$), while a red shift for the heavier mass isotopomer is expected. The contribution to the isotopic shift is given by the following formula:

$$
\Delta \nu = \Delta \nu_e + \Delta \nu_v
$$

where $\Delta \nu_e$ and $\Delta \nu_v$ correspond to the electronic and vibrational isotopic shifts, respectively. The vibrational isotope shift arises from the difference in the zero-point energies of the Mg-dependent modes, as can be seen in the following expression:

$$
\Delta \nu_v = (4\pi)^{-1} \sum_i \left\{ \left[ (\mu_{24}^i)^{-1/2} \left( (k'_i)^{1/2} - (k''_i)^{1/2} \right) \right] - \left[ (\mu_{26}^i)^{-1/2} \left( (k''_i)^{1/2} - (k''_i)^{1/2} \right) \right] \right\}
$$

$$
= (4\pi)^{-1} \sum_i \left\{ \left[ (\mu_{26}^i)^{1/2} - (\mu_{24}^i)^{1/2} \right] \left[ (k'_i)^{1/2} - (k''_i)^{1/2} \right] \right\}
$$

where $\mu_{24}^i$ and $\mu_{26}^i$ are the appropriate reduced masses for the $i^{th}$ mode of the $^{24}$Mg and $^{26}$Mg containing species, and $k'_i$ and $k''_i$ are the excited and ground state force constants. The quantity containing the reduced masses is clearly positive. Typically the ground state force constant exceeds that of the excited state causing $\Delta \nu_v$ to be negative. As can be seen from Table 2 the increased Mg—CH$_3$ bond length in the $\tilde{A}$ state is consistent with $k''_i > k'_i$, hence $\Delta \nu_v$ is expected to be negative for MgCH$_3$.

Usually the contribution of the electronic term in equation 3.11 is negligible [39]. However, a small electronic isotope shift has been found in some molecules, which can be either to the red or to the blue for the lighter isotope [40]. Thus, in view of
this argument, for MgCH$_3$ either the electronic contribution, $\Delta\nu_e$, dominates $\Delta\nu$, or the force constants describing the Mg motion are quite unusual.

3.6 Conclusions

The rotationally resolved spectra of the two spin-orbit components of the $0_0^0 \tilde{A}^2E \leftarrow \tilde{X}^2A_1$ electronic transition of the MgCH$_3$ radical have been analyzed. The molecular constants of the ground and excited states were obtained. These molecular parameters were used to propose a geometrical structure for the MgCH$_3$ radical in both states. A comparison with other MCH$_3$ radicals ($M = \text{Ca, Cd and Zn}$) was also made, both in terms of the spectroscopic constants and the geometrical structures.
CHAPTER 4

HIGH RESOLUTION ELECTRONIC SPECTROSCOPY OF MgNC.

4.1 Introduction

The relevance of Mg-containing species was discussed in detail in Chapter 3. The MgNC radical, in particular, has attracted great interest in the recent years since this radical was the first Mg-containing radical identified in interstellar space. Guélin et al. [3] published the millimeter spectrum from the circumstellar envelope of the star IRC+10216 in 1986, although the authors were unable, at that time, to identify the carrier of the spectrum. It was not until 1993, when Kawaguchi et al. [41] obtained the laboratory microwave spectrum of MgNC, that the unidentified lines of the spectrum from IRC+10216 were assigned to that radical. That same year Guélin and coworkers took the interstellar spectrum again [4], and now with the spectroscopic constants obtained by Kawaguchi et al., they were able to assign the emission lines from MgNC in this new spectrum.

The identification of the carrier of Kawaguchi’s spectrum was supported by ab initio studies on MgNC: Ishii and coworkers [42, 43] carried out CISD/TZ2P calculations
on MgNC to predict the spectroscopic constants of the ground electronic state, which helped in the assignment of Kawaguchi’s microwave spectrum.

MgCN, the metastable isomer of MgNC, has also been detected in the star IRC +10216 [5] in 1995, one year after its laboratory identification by Anderson et al. [44].

Recently, there has been some interest in the structure of the metal cyanide /isocyanide (MCN/MNC) molecules, which can be either linear or T-shaped, depending on the nature of the interaction between the metal and the CN/NC moiety. Several studies carried out on these molecules have shown that ionic bonding results in a T-shaped molecule, while for covalent bonding a linear structure is preferred. This was first identified by Bauschlicher, Langhoff and Partridge in their ab initio study [45] on MCN (M= Be, Mg, Ca, Ba). All of these molecules were predicted to be linear, and the isocyanide structure was more stable by 0.3-0.5 eV than the cyanide molecules. Experimental work on some of these radicals (e.g. NaCN [46], KCN [47], SrNC [48], and CaNC [49, 50, 51]) corroborated the ab initio predictions. Two very recent studies on AlNC have been reported, in which the rotational spectrum of the v=0 level of the ground electronic state has been studied, by millimeter-wave spectroscopy [52], and by Fourier transform microwave spectroscopy [53]. These experiments showed that AlNC has a linear structure in the $\tilde{X}$ state.

For MgNC, the linear structure predicted in reference [45] and in subsequent theoretical studies [42, 43, 54], was first confirmed by Kawaguchi’s spectrum [41], which determined that indeed the $\tilde{X}$ state was a linear $^2\Sigma^+$ state. Experimental evidence that the isocyanide structure was more stable than the cyanide molecule
was found by Ziurys et al. from the MgNC/MgCN ratio of ~ 22/1 derived from the interstellar spectral data from IRC+10216 [5]. Additional support of this was given by Anderson et al., who obtained the laboratory Mg-cyanide millimeter-wave spectrum [44]. The authors reported that in addition to the MgCN spectra, much stronger absorption lines from MgNC were always present.

*Ab initio* studies on MgNC and MgCN have given some insight into the isomerization process of this radical. The isomerization barrier between these two molecules is fairly small: Ishii and coworkers [43] reported it to be only 510 cm$^{-1}$. They also found that the transition state lies only at 2171 cm$^{-1}$ above the MgNC energy, which implies that high order bending excitation can cause isomerization.

Another peculiarity about the MgNC radical is its very low bending frequency, whose value is available from *ab initio* methods only, since no direct experimental values are known to date (although Kagi and coworkers [55] estimated it to be 86 cm$^{-1}$ in the $\tilde{X}$ state, from their $l$-type doubling constant of the $v_2=1$ state, obtained from their microwave spectrum.) The value of the ground state bending frequency, $\omega_2$, reported by Ishii et al. is 83 cm$^{-1}$, in agreement with other author's calculations within 20 cm$^{-1}$[56, 54]. Such a small value for the bending frequency, in addition to the low isomerization barrier, make MgNC a very "floppy" molecule.

More recent experimental work performed on this radical was reported by Anderson et al. [57] who observed the millimeter-wave spectra of the MgNC isotopomers $^{25}$MgNC and $^{26}$MgNC, and obtained their molecular constants for the $v=0$ level of the $\tilde{X}$ state. Kagi and coworkers [55] obtained rotational spectra of MgNC in the $\nu_2$
vibrationally excited states, reporting molecular constants for several vibronic levels in the electronic ground state. However, these authors also found anomalous features in some of the obtained constants, which they were unable to explain with their data.

Even though information about the ground electronic state of MgNC has been obtained from the studies mentioned above, no information about the excited states of MgNC has yet been reported. Additionally, there has been no direct observation of the vibrational frequencies, neither in the ground nor in the excited electronic states. The experimental determination of vibrational frequencies could aid in understanding the structure of MgNC and perhaps could lead to some explanation for the anomalous features observed in the microwave spectrum of Kagi et al. [55]. The experimental determination of the bending frequency, in particular, is of interest, in order to confirm, or not, the unusually low value predicted by the ab initio calculations, and since it is expected [43] that $\nu_2$ will show large anharmonic effects, due to the floppy character of the MgNC molecule.

In addition to this, the $\tilde{A}$ state of MgNC is particularly interesting because being a linear $^2\Pi$ electronic state it is susceptible to the Renner-Teller effect, as well as spin-orbit coupling. As it will be discussed later in this chapter, the energy level diagram of molecules with Renner-Teller and spin-orbit interactions deviates considerably from a simple harmonic, equally-spaced, picture. Indeed, depending on the relative magnitudes of these two interactions, the vibronic energy levels may have a very complicated pattern, and therefore it can make the vibronic assignment of the spectrum a very difficult task.
4.2 Experimental Details

The MgNC radicals were produced by the laser ablation/photodissociation technique described in detail in Chapter 2. The organic precursor used in this case was acetonitrile (CH$_3$CN). It was placed in a stainless steel reservoir and maintained at a constant temperature of 0 °C in a bath of ethylene glycol. Helium was used as the carrier gas, with a backing pressure of 200 psig. The ablation of the magnesium rod and the photolysis of the acetonitrile was achieved with a focused KrF pulse (248 nm). Tight focusing conditions increased the MgNC signal, but unfortunately it also increased the concentration of by-products of the photolysis, some of which also fluoresce in the same region as MgNC (e.g. C$_2$, C$_3$). Thus, the focusing conditions were optimized to decrease significantly the presence of other species, whilst still maintaining a very good signal intensity, as it can be seen from the experimental spectra shown later.

A small fraction of the Ti:Sapphire ring laser output was directed into a low finesse étalon (FSR ~ 475 MHz) for relative calibration of the LIF spectrum. As mentioned in the experimental chapter, either Te$_2$ or I$_2$ was used to calibrate the absolute frequencies of the high resolution LIF spectra. In this case the region scanned was outside the range covered in the Te$_2$ or I$_2$ spectral atlases. Therefore, the absolute frequencies were obtained from the Autoscan wavemeter. The wavemeter was calibrated versus I$_2$ at the red edge of the atlas [11], before moving the laser to the MgNC frequency region.
4.3 Theory

As predicted by the ab initio calculations [42, 54, 56], and confirmed experimentally [41, 55], the $\tilde{X}$ electronic state of MgNC is a $^2\Sigma^+$ state, and has a linear structure. It has been predicted that the first excited electronic state of MgNC is also linear, and has $^2\Pi$ symmetry [55].

Therefore, standard linear Hamiltonians were used for both states, in order to analyze and simulate the experimental high resolution spectra presented in this work. These Hamiltonians have been described in detail elsewhere [58], and thus only a brief description will be given here.

$\tilde{X}$ state:

$$\mathcal{H}(^2\Sigma^+) = \mathcal{H}_0 + \mathcal{H}_{\text{ROT}} + \mathcal{H}_{\text{SR}}$$

(4.1)

where $\mathcal{H}_0$ is the non-relativistic Hamiltonian of the non-rotating molecule, $\mathcal{H}_{\text{ROT}}$ and $\mathcal{H}_{\text{SR}}$ correspond to the rotational and spin-rotation Hamiltonians, respectively. The definition for these terms is as follows:

$$\mathcal{H}_{\text{ROT}} = B_\nu \mathbf{R}^2 - D_\nu \mathbf{R}^4$$

(4.2)

where $B_\nu$ is the rotational constant, $D_\nu$ is the centrifugal distortion constant and $\mathbf{R}$ is the rotational angular momentum, defined by $\mathbf{R} = \mathbf{J} - \mathbf{L} - \mathbf{S}$, where $\mathbf{J}$, $\mathbf{L}$ and $\mathbf{S}$ are the total, electronic orbital and electronic spin angular momentum operators respectively. In this case, since $\mathbf{L} = 0$, $\mathbf{R} = \mathbf{J} - \mathbf{S}$. 

51
\[ \mathcal{H}_{SR} = \gamma_v (\mathbf{J} - \mathbf{S}) \cdot \mathbf{S} \]  

(4.3)

where \( \gamma_v \) is the spin-rotation constant, and \( \mathbf{J} \) and \( \mathbf{S} \) are as defined above. Spin-rotation interaction is usually caused by spin-orbit interaction that couples \( ^2\Sigma \) and \( ^2\Pi \) states. When this interaction is present, the rotational levels of a \( ^2\Sigma \) state will be split by:

\[ F(^2\Sigma; vJp^+) - F(^2\Sigma; vJp^-) = \gamma_v \cdot J \]  

(4.4)

where \( p^\pm \) indicates the parity of the rotational energy levels. The magnitude of the spin-rotation splitting increases linearly with \( J \). The spin-rotation constant \( \gamma_v \) may be positive or negative.

\( ^\tilde{A} \) state:

\[ \mathcal{H}(^2\Pi) = \mathcal{H}_0 + \mathcal{H}_{ROT} + \mathcal{H}_{SO} \]  

(4.5)

where \( \mathcal{H}_0 \) and \( \mathcal{H}_{ROT} \) are the same as for the \( ^2\Sigma^+ \) state, and \( \mathcal{H}_{SO} \), the spin-orbit Hamiltonian, is defined as:

\[ \mathcal{H}_{SO} = A_{so} \mathbf{L} \cdot \mathbf{S} \]  

(4.6)

where \( A_{so} \) is the spin-orbit interaction constant.

Linear combinations of Hund’s case(a) wavefunctions were used, which can be written as:
\[ |n^{2S+1} \Lambda \nu J M p^\pm\rangle = \sum_{\Omega} a_{n\Omega} (p^\pm) |n^{2S+1} \Lambda \Omega\rangle |\nu\rangle |J \Omega M\rangle \]  

(4.7)

where \( |n^{2S+1} \Lambda \Omega\rangle \) describes the electronic effect, \( |\nu\rangle \) describes vibration, and \( |J \Omega M\rangle \) describes rotation.

The rotational line strength factor, \( S \), for a \( ^2S^+ \Lambda^t_{\nu J'} \leftarrow ^2S^+ \Lambda \Omega J \) transition, is given by:

\[ S(J' \leftarrow J) = (2J'+1)(2J+1) \times \left| \sum_{\Omega'} \sum_{\Omega} a_{n\Omega'\Omega} (p^\pm) a_{n\Omega} (p^\pm) \times \left( \begin{array}{c} J \\ \Omega \\ (\Omega' - \Omega) \end{array} \right) \right|^2 \]  

(4.8)

4.4 Results

4.4.1 Moderate resolution LIF spectrum

In Figure 10 the LIF spectrum of the MgNC radical in the 25,900-26,900 cm\(^{-1}\) region is shown. This region has been recorded under different experimental conditions, in order to observe the changes in the relative intensities of all the bands. As a result, it was possible to identify which of those bands are "vibronically cold", i.e. which bands originate at the zero-point level of the \( \tilde{X} \) state. The spectrum shown in Figure 10 is vibronically cold: all the bands observed therein are believed to have originated in the vibrationless level of the ground electronic state. The analysis of the rotationally resolved spectra of each of these transitions, presented in the next section, will give additional support to this, since the rotational constants of the ground state can be determined unambiguously from that analysis.
Figure 10: Moderate resolution (~0.1 cm$^{-1}$) LIF spectrum of the MgNC radical in the 25,900 - 26,800 cm$^{-1}$. 
Owing to the spin-orbit splitting in the $\tilde{A}$ state of MgNC, the $0^0$ transition is expected to consist of two lines, corresponding to the $\tilde{A} \ ^2\Pi_{1/2} \leftarrow \tilde{X} \ ^2\Sigma^+$ and the $\tilde{A} \ ^2\Pi_{3/2} \leftarrow \tilde{X} \ ^2\Sigma^+$ transitions. *Ab initio* calculations predicted the $\tilde{A}$ electronic state to be at $\sim 25,000 \text{ cm}^{-1}$ above the $\tilde{X} \ ^2\Sigma^+$ state [55]. Therefore, the two strong peaks centered around 26,080 cm$^{-1}$ in Figure 10, are assigned as the two spin-orbit components of the $0^0 \tilde{A} \ ^2\Pi \leftarrow \tilde{X} \ ^2\Sigma^+$ transition. This vibronic assignment will be supported by the analysis of the high resolution spectra of the two lines, which will be discussed in the next section.

MgNC has four normal vibrational modes, two stretches and a double degenerate bend mode. Following the common practice in triatomic molecules, the two stretches will be called $\nu_1$ and $\nu_3$, corresponding to the MgN–C and the Mg–NC stretch, respectively, and the bending mode will be called $\nu_2$. The two strong lines centered at about 26,660 cm$^{-1}$ are assigned to the transition to one quanta of the Mg–NC stretch ($\nu_3$). Although no vibrational frequencies have been calculated or measured for the $\tilde{A}$ state of MgNC, the $\omega_3$ stretching frequency for the ground state has been calculated by *ab initio* methods to be (in cm$^{-1}$): 538.9 [42], 493.0 [54] and 524 [56]. The value of 580 cm$^{-1}$ for the $\omega_3$ frequency in the excited state seems reasonable, very close to that of the ground state. In addition to this, the separation between the two spin-orbit components for this band are very close to that of the origin band. Again, the rotationally analysis will give additional support to this assignment, in the next section.
The vibronic assignment of the remaining bands is not that straightforward. However, since they occur at lower frequency than the $3^1\Omega$ transition, they can only be fundamentals or overtones of $\nu_2$, the bending mode. As it was discussed in the theory section, the bending mode of MgNC is expected to show vibronic coupling in addition to spin-orbit interaction. As displayed in Figure 31 in Appendix A, when both interactions are present the vibronic levels will be shifted away from the harmonic values. The positions of the levels can be determined \textit{a priori} only if all the following parameters are known: the spin-orbit constant $A_{so}$, the harmonic value of $\omega_2$, and $\epsilon_2$, the Renner-Teller parameter. The value of $A_{so}$ can be obtained from the $0^0$ transition, but unfortunately the values of $\omega_2$ and $\epsilon_2$ are not known. However, knowing the vibronic symmetry of the excited states of those transitions will help to determine in which level of the bending mode (e.g. $\nu=1$, $\nu=2$, etc) those transitions terminate. From the rotationally resolved spectra of these bands it is possible to identify the vibronic symmetry of the levels involved in the transition. Consequently, the vibronic assignment of the bands involving the bending mode will be considered later, once their rotational analysis has been discussed in the next section.

4.4.2 Rotationally-resolved spectra

Origin band

In Figure 11 both the moderate resolution and the rotationally-resolved spectra of the $\bar{A}^2\Pi_{1/2} \leftarrow \bar{X}^2\Sigma^+$ spin-orbit component are shown, in order to illustrate the degree of resolution that can be obtained in the rotationally-resolved LIF experiment.
Figure 11: In the upper trace, a portion of the moderate resolution spectrum from Figure 10 is shown. Below, the high resolution, rotationally-resolved spectrum of the feature indicated in the moderate spectrum.
As was performed in the previous chapter, for the MgCH₃ spectra, all the rotationally resolved spectra of MgNC were analyzed, simulated and fit with the computer program SpecSim.

The two spin-orbit components of the origin band were fit simultaneously, using the Hamiltonians described in the theory section. A total of 116 lines were observed and fit, with a standard deviation of \(3.7 \times 10^{-3}\) cm\(^{-1}\), which shows the quality of the fit when compared to the experimental linewidth of \(8.3 \times 10^{-3}\) cm\(^{-1}\). In Figure 12 the experimental and simulation traces for the \(\tilde{\text{A}}^2\Pi_{1/2} \leftarrow \tilde{\text{X}}^2\Sigma^+\) spin-orbit component are shown, and the corresponding plots for the upper spin-orbit component are presented in Figure 13. As may be seen in those figures, in addition to the excellent agreement between the experimental and predicted frequencies, there is also good correspondence among the intensities in the overall spectrum. A few exceptions can be attributed mainly to the non-regularity of the radical production, and to saturation of some of the strongest rotational lines in the Q branch. The rotational temperature (determined by assuming a Boltzmann distribution in the simulation) was found to be 12 K.

The spectroscopic constants obtained from the linear least squares fitting are presented in Table 3, which may be found at the end of this section. The rotational constants of the vibrationless ground state level are in excellent agreement with the reported values of Kawaguchi et al. [41], within experimental error. The centrifugal distortion constant for the \(\tilde{\text{X}}\) state, also reported by Kawaguchi et al. [41], is \(1.44 \times 10^{-7}\) cm\(^{-1}\), well below the experimental resolution of the present experiments. Thus the \(D''\) and \(D'\) constants were not included in the fit. The spin-orbit constant
Figure 12: Experimental spectrum of the $\tilde{A}^{2} \Pi \leftarrow \tilde{X}^{2} \Sigma^{+}$ spin-orbit component of the origin band of MgNC. The lower trace shows the simulated plot, with a rotational temperature of 12K. The weaker lines that do not appear in the simulated plot are due to $^{25}$MgNC and $^{26}$MgNC isotopomers (see text for a discussion).
Figure 13: Rotationally resolved LIF spectrum of the $0^3 \Pi_{3/2} \leftarrow \tilde{X} \Sigma^+$ MgNC band. The experimental spectrum is shown in the upper trace, and the simulated spectrum is displayed in the lower trace. The weaker lines that do not appear in the simulated plot are due to $^{25}$MgNC and $^{26}$MgNC isotopomers (see text for a discussion).
for the $\tilde{A}$ state has been measured for the first time in the present work, and it was determined to be $36.926 \text{ cm}^{-1}$.

![Diagram of MgNC isotopomers](image)

Figure 14: Expanded region of Figure 13 showing the observed isotopomers of MgNC. The splitting of the $^{25}\text{MgNC}$ lines is due to hyperfine interactions (see text).

Weak lines that can be seen in the experimental spectrum, which do not appear in the simulated plot are due to isotopomers of MgNC. As mentioned in Chapter 3, Mg has three isotopes with a natural abundance of: 78.99% $^{24}\text{Mg}$, 10.00% $^{25}\text{Mg}$ and 11.01% $^{26}\text{Mg}$. In Figure 14 an enlargement of a small region of the spectrum is shown, where the isotopic structure can be seen more clearly. As expected, the relative
intensities of the peaks agree well with the relative abundances of the isotopes. Unlike MgCH₃ for which the S/N ratio was much smaller than for MgNC, the three isotopes of magnesium can be seen in this case. The splitting observed in some of the isotopic lines can be ascribed to hyperfine interaction between the nucleus of $^{25}$Mg (with $I = 5/2$) and electron spin. Anderson and Ziurys [57], who obtained the millimeter-wave spectrum of $^{25}$MgNC and $^{26}$MgNC, also observed a splitting of each rotational transition for the $^{25}$MgNC radical.

Unfortunately, a considerable number of the lines of $^{25}$MgNC and $^{26}$MgNC lie underneath the strong features of the main isotope, which makes it impossible to determine the frequency of those transitions. In spite of this, simulations were obtained by fitting only the observed lines, and very good agreement with the experimental spectra was obtained. The rotational constants determined for the $^\tilde{X}$ state were in excellent agreement (to within experimental error) with the millimeter spectroscopy values of Anderson and Ziurys [57], which gives additional support to the assignment.

**Mg–NC stretching mode**

Experimental and simulated plots for both spin-orbit components of this transition are shown in Figures 15 and 16. The simulations include a total number of 113 rotational transitions. As for the previous band, the vibronic symmetry of the levels used for the simulations were $^2\Sigma^+$ and $^2\Pi$ for the ground and excited states, respectively, with a spin-orbit splitting of 37.193 cm$^{-1}$. The standard deviation of the linear least squares fitting was $3.2\times10^{-3}$ cm$^{-1}$, which clearly indicates the excellent agreement between the simulation and the experimental lines. Not only were the frequencies of
the rotational lines well simulated, but also the intensities of the observed bands with a Boltzmann distribution with a temperature of $\sim 12K$. The rotational constant of the ground state for this transition, verify that this transition originates in the $v=0$ level of the $\tilde{X}$ electronic state as well. All the molecular parameters obtained are presented in Table 3.

Isotopic structure was not observed in this region, probably owing to the poorer S/N ratio of this band in comparison with the $0_0^0$ transition. Nevertheless, a number of weak lines can be seen underneath the P branch in both spin-orbit components. Since only a few lines are seen, it is difficult to tell if they are due to either MgNC isotopomers or, more likely, to another transition, perhaps a weak hot band of MgNC. It could also be possible that those few lines correspond to another species.
Figure 15: Experimental (upper) and simulated (lower) plots of the $\tilde{A} \; ^2\Pi_{1/2} \leftarrow \tilde{X} \; ^2\Sigma^+$ spin-orbit component of the $3^0_1$ transition of MgNC ($\nu_3$ is the stretching mode). A few weak lines underneath the P branch that are not included in the simulated plot do not belong to the $3^0_1$ transition (see text).
Figure 16: Rotationally-resolved LIF spectrum of the $3\Pi_0 \leftarrow \tilde{X}^2\Sigma^+$ transition of the MgNC radical. The lower trace shows the simulated plot. The weaker transitions at the red end of the spectrum that do not appear in the simulation, do not belong to this transition (see text).
Transitions involving the bending mode

Band at 26,291 cm\(^{-1}\) (Band A).

The high resolution spectrum of this transition is shown in Figure 17. Even though the S/N ratio of this band is not as good as for the other transitions because of its weaker intensity (see the moderate resolution spectrum of Figure 10), the S/N ratio is still very good, and thus this did not affect the rotational analysis. The most obvious feature of this band is that its appearance is very different from the \(0_0^0\) and the \(3_1^0\) transitions. A closer look reveals the presence of one band, for which the simulation is shown in the lower plot of Figure 17. The absence of a Q branch is indicative of a \(^2\Sigma \leftarrow ^2\Sigma\) transition. A splitting of each rotational line was observed, increasing with the \(J\) value, which is typical of \(\Sigma\) states that show spin-rotation coupling. In Figure 17 the spin-rotation splitting for each pair of levels in the \(R\) branch is indicated. Indeed this band was fit with a \(^2\Sigma \leftarrow ^2\Sigma\) model, and all the molecular constants can be found in Table 3, at the end of this section. For this transition, 51 experimental lines were fit, with a standard deviation of \(3.9\times10^{-3}\) cm\(^{-1}\). The rotational temperature of the fit was 15K. Rotational constants of the ground electronic state coincide with the ones determined before for the \(v=0\) level, which indicates that this is another vibronically cold transition.

The remaining unassigned lines in this experimental trace belong to another species, since their intensity changed dramatically with different experimental conditions. Additionally, the much smaller spacing between some of those lines (especially the ones towards the blue end of the spectrum) also indicates that they are not due
Figure 17: Two bands overlap in this region. The simulated plot for Band A, a MgNC transition, is shown in the bottom trace. For the R branch the spin-rotation splitting for each rotational transitions is indicated. The lines in the experimental spectrum which are not in the simulated plot are due to another species (see text).
Band at 26,452 cm$^{-1}$ (Band B).

The high resolution spectrum of this band can be found in Figure 18. It is possible to distinguish two distinct bands in this region. The overall rotational pattern appears fairly complicated because the two bands overlap, especially in the center where it is very difficult to distinguish between them. Both bands have the general appearance of the $0^0_0$ and $3^1_0$ transitions, with the one to the blue having a more congested Q branch. The simulated plot contains two contributions: from a $^2\Pi_{3/2} \leftarrow ^2\Sigma^+$ and a $^2\Pi_{1/2} \leftarrow ^2\Sigma^+$ transition, and it is shown in the lower trace of Figure 18. The band centered to lower frequency corresponds to the upper spin-orbit component ($^2\Pi_{3/2} \leftarrow ^2\Sigma^+$). The value of $\Omega$ for each transition can be determined unequivocally from the $J$ quantum number of the first lines of the P and Q branches.

Since the $^2\Pi_{3/2}$ level is at lower energy than the $^2\Pi_{1/2}$ component, the value of the spin-orbit constant obtained from the fit was negative. Additionally, since the two components are within 14 cm$^{-1}$, the value of $A_{so}$ is also very small ($A_{so} = -8.138$ cm$^{-1}$). It seems that the $A_{so}$ constant is quenched considerably for these levels, when compared to the values obtained from $0^0_0$ and $3^1_0$. An explanation for this observation will be discussed in the next section.

These two spin-orbit components were fit with the same Hamiltonian for the excited state, with $A_{so} = -8.138$ cm$^{-1}$. The fit of 68 rotational transitions was not as good as for the previously discussed bands, since the standard deviation was slightly
Figure 18: Experimental spectrum and simulated plot for Band B. Two features are seen in this region, corresponding to a $\tilde{A} \ ^2\Pi \leftarrow \tilde{X} \ ^2\Sigma^+$ transition. The feature observed at lower frequencies is a $\tilde{A} \ ^2\Pi_{3/2} \leftarrow \tilde{X} \ ^2\Sigma^+$ transition, and the other feature corresponds to the lower spin-orbit component, a $\tilde{A} \ ^2\Pi_{1/2} \leftarrow \tilde{X} \ ^2\Sigma^+$ transition.
higher, \(8.0 \times 10^{-3}\), but it is still comparable to the experimental linewidth.

The rotational constants of the ground state of this transition also compared well with the values obtained for the \(v=0\) of the \(\tilde{X}\) state, as can be seen in Table 3, where all the spectroscopic parameters determined for this transition can be found.

\[
\begin{array}{cccccc}
 & 0^0 & 3^0 & \text{Band A} & \text{Band B} \\
\hline
X \quad B'' & 0.19901(4) & 0.19907(4) & 0.19908(7) & 0.1991(1) \\
B' & 0.20426(4) & 0.20314(4) & 0.20509(6) & 0.2071(1) \\
\tilde{A} \quad A_{40} & 36.926(1) & 37.193(1) & \text{N/A} & -8.138(4) \\
\gamma' & \text{N/A} & \text{N/A} & 0.0496(2) & \text{N/A} \\
\hline
T_e & 26,084.01(1) & 26,665.74(1) & 26,290.59(1) & 26,451.57(1) \\
\hline
\text{Vibronic Symmetry} & 2^2 \Pi \leftarrow 2^2 \Sigma & 2^2 \Pi \leftarrow 2^2 \Sigma & 2^2 \Sigma \leftarrow 2^2 \Sigma & 2^2 \Pi \leftarrow 2^2 \Sigma \\
\hline
\text{Standard deviation} & 0.0037 & 0.0032 & 0.0039 & 0.0080 \\
\hline
\text{Number of lines fit} & 116 & 113 & 51 & 68 \\
\end{array}
\]

\(^a\)This value compares with the value determined by Kawaguchi et al. \([41]\) using microwave spectroscopy, \(B'' = 0.1990342(8) \text{ cm}^{-1}\).

Table 3: Molecular parameters obtained from the rotational analysis of the observed transitions of MgNC (in \(\text{cm}^{-1}\)).
4.5 Discussion of the vibronic assignments

**Band A (at 26,291 cm⁻¹).**

From the rotational analysis, it was determined that the upper level of this transition has ²Σ vibronic symmetry. Only levels with odd quanta of bending excitation can have such symmetry. Since this is the lowest feature observed above the origin, the most reasonable vibronic assignment seems to be a transition to one quantum of the bending mode. For linear molecules, only transitions with Δν = 0, 2, 4, ... of the bending mode are allowed; however, by virtue of vibronic interaction, transitions to odd quanta of the bending mode may become allowed. In NCS, where Renner-Teller and spin-orbit effects are present, transitions to the ²Σ⁺ and ²Σ⁻ states of the 2⁰ level were observed and it is notable that the transition to the ²Σ⁺ level was stronger than the transition to the ²Σ⁻ level, as indicated by the observed intensities of these bands [59]. For SrOH, another radical for which Renner-Teller and spin-orbit effects are present, transitions to the ν=1 vibronic levels were observed, but again, the transition to the ²Σ⁺ state was three to four times stronger than the transition to the ²Σ⁻ state [60]. For MgNC, the intensity of Band A is very weak, when compared to the origin and the other vibronic bands. If this band is due to the transition to the ²Σ⁺ state of ν=1, and if, as in the previous cited works, transition to the ²Σ⁻ state is much weaker, it is unsurprising that the transition to the ²Σ⁻ state is not observed.

**Band B (at 26,454 cm⁻¹).**

The upper state of this band has ²Π vibronic symmetry. Only levels with even
quanta of bending vibration will have states with that symmetry. Thus, this band may be assigned as a transition to two quanta of the bending mode. Another interesting feature of this band was the determination of the negative and apparently quenched spin-orbit splitting constant \( A_{so} = -8.138 \text{ cm}^{-1} \), when compared to the \( A_{so} \) coupling constant obtained for the \( v=0 \) level \( (A_{so} = 36.926 \text{ cm}^{-1}) \). This is expected when Renner-Teller and spin-orbit interactions are present. The \( v=2 \) level will have four states with \( ^2\Pi \) symmetry: two \( ^2\Pi_{1/2} \) and two \( ^2\Pi_{3/2} \) states (see Figure 31 in Appendix A). As suggested by Hougen [61], there are three possible ways to group these levels, as shown in Figure 19. When \( |\varepsilon \omega| \gg |A_{so}| \), is more convenient to consider the four spin-orbit components to be grouped into two separate \( ^2\Pi \) states as shown in part (b) in Figure 19. When \( |A_{so}| \gg |\varepsilon \omega| \), it is convenient to consider the levels grouped as indicated in part (c). When both interactions are comparable, it is not recommended to group them in any way, but to consider the four levels together as suggested in Figure 19(a).

Usually, the lower pair of \( ^2\Pi \) states is referred to as the "\( \mu \)" \( ^2\Pi_{1/2} \) and the "\( \mu \)" \( ^2\Pi_{3/2} \) states, and are upper pair of states are referred to as the "\( \kappa \)" \( ^2\Pi_{1/2} \) and the "\( \kappa \)" \( ^2\Pi_{3/2} \) states. When the Renner-Teller effect is present, the separation between these levels is no longer \( A_{so} \). As can be derived from Pople's equations, the separation between the \( \mu \) and \( \kappa \) pair is determined by an "effective" spin-orbit coupling constant, \( A_{eff} \), which is related to the real \( A_{so} \) by the following expression:

\[
A_{eff} = \sqrt{A_{so}^2 + [(v + 1)^2 - K^2] \varepsilon^2 \omega^2}
\]

(4.9)
Figure 19: Three ways of grouping the $^2\Pi$ vibronic states of the $v=2$ level of the bending mode, when Renner-Teller and spin-orbit effects are present: (a) the levels are not grouped in any way; (b) $||\epsilon|\omega| >> |A_{so}|$, the pairs are grouped as two separate $^2\Pi$ states; and (c) $|A_{so}| >> ||\epsilon|\omega|$, the other pairs are grouped as two separate $^2\Pi$ states.

The separation between the two $^2\Pi$ states of the $\mu$ pair (which is equal to the separation between the two $^2\Pi$ states of the $\kappa$ pair), is determined by the following expression:

$$
\Delta \nu = \frac{A_{so}K(v + 1)\epsilon^2\omega}{4\sqrt{A_{so}^2 + [(v + 1)^2 - K^2]\epsilon^2\omega^2}}
$$

(4.10)

The small separation observed between the two $^2\Pi$ states of Band B (-8.138 cm$^{-1}$) seems to indicate that these states correspond to either the $\mu$ or to the $\kappa$ pair of $^2\Pi$ states, and thus separated by $\Delta \nu$ of equation 4.10. The negative value of the splitting might seem to indicate that these are the transitions to the $\kappa$ pair of $^2\Pi$ states which are expected to be inverted (i.e. the $^2\Pi_{3/2}$ state is lower in energy than the $^2\Pi_{1/2}$ state), as seen in Figure 19.
An additional support to the assignment of these two bands, Band A and B, to transitions to the bending mode of MgNC comes from a closer look at the rotational constants in the A excited state, $B'$. The value of the rotational constant of the $v=1$ level of the $\nu_3$ stretching mode is smaller than the value of $B'$ of $v=0$, as expected. However, the $B'$ for Band A and B are larger than the $B'$ of the vibrationless level. Excitation of the bending vibration can be thought as a displacement of the N atom from the linear configuration, as shown in Figure 20. The value of the rotational constants for small displacements (δ in Figure 20) of the N atom were calculated and compared with the experimental values of $B'$ of $v=1$ and $v=2$. If the N atom is moved 0.105 Å from the linear axis, the $B'$ constant agrees with the value obtained for Band A, and a displacement of 0.200 Å reproduces the value of the $B'$ constant of Band B, as summarized in Figure 20. This is consistent with the vibronic assignment proposed for these bands.

For the $\tilde{X}$ $^2\Sigma^+$ state of MgNC, the molecular constants for several bending vibrational states were obtained by Kagi and coworkers [55]. Thus it would be interesting to compare the values of the $B''$ rotational constants obtained for the vibrational states of the $\tilde{X}$ state with the ones obtained for Band A and B. The value of the rotational constant $B''$ was 0.20124 cm$^{-1}$ for the $^2\Pi_{1/2}$ state, and 0.20216 cm$^{-1}$ for the $^2\Pi_{3/2}$ state of the $v=1$ level. In the $v=2$ level, the constant $B''$ was 0.20477 cm$^{-1}$ for the $^2\Sigma$ state, and 0.20456 cm$^{-1}$ for the $^2\Delta$ ($\Omega = \frac{3}{2}, \frac{5}{2}$) states [55]. A comparison of the $\Delta B$ ($\Delta B = B_v - B_{v=0}$) in the $\tilde{X}$ and A electronic states shows that the $\Delta B$ is much bigger in $\tilde{X}$ state: $\Delta B_1 = B_{v=1} - B_{v=0} = 2.2$ and $3.1 \times 10^{-3}$ cm$^{-1}$ (for
\( v = 0 \)

\[
\text{Mg} \quad \text{N} \quad \text{C}
\]

\[
\begin{array}{c}
v = 0 \\
B = 0.20426 \text{ cm}^{-1}
\end{array}
\]

\( v = 1 \)

\[
\text{Mg} \quad \theta \quad \text{N} \quad \text{C} \quad \delta 
\]

\[
\begin{array}{c}
\delta = 0.105 \text{ Å} \\
\theta = 172^\circ
\end{array}
\]

\( v = 2 \)

\[
\text{Mg} \quad \theta \quad \text{N} \quad \text{C} \quad \delta 
\]

\[
\begin{array}{c}
\delta = 0.200 \text{ Å} \\
\theta = 164^\circ
\end{array}
\]

Figure 20: Geometric structures of the MgNC radical. In part (a), the structure of MgNC for the \( v=0 \) level of the \( \tilde{A} \) state is shown. In parts (b) and (c) the radical is bent by small displacements of the N atom from the linear configuration (\( \delta \)). The values of \( \delta = 0.105 \text{ Å} \) and \( \delta = 0.200 \text{ Å} \) reproduced the values of the experimental \( B' \) constant for Bands A and B, respectively. This gives additional support to the assignment of those Bands as transitions to \( v=1 \) and \( v=2 \) of the bending mode (see text).
the $^2\Pi_{1/2}$ and the $^2\Pi_{3/2}$ states, respectively), and $\Delta B_2 = B_{v=2} - B_{v=0} = 5.7$ and $5.5 \times 10^{-3}$ cm$^{-1}$ (for the $^2\Sigma$ and for the $^2\Delta_{\Omega}$ states, respectively). In the $^\bar{A}$ state the change in the rotational constants was $\Delta B_1 = B_{v=1} - B_{v=0} = 0.8 \times 10^{-3}$ cm$^{-1}$, and $\Delta B_2 = B_{v=2} - B_{v=0} = 2.8 \times 10^{-3}$ cm$^{-1}$. These results imply that the bending potential in the ground state is more shallow than the potential in the $^\bar{A}$ state, which is consistent with the expected bigger bending frequency for the excited state. In conclusion, the values of the rotational constants obtained for Bands A and B are consistent with the assignment of those bands as bending vibronic transitions.

Another way to confirm these vibronic assignments for Band A and Band B, is to apply the equations derived by Pople (discussed in detail in Appendix A), to see if values for $|\epsilon|$ and $\omega$ can be obtained, and determine if those values are consistent with these assignments.

The frequencies (measured from the $v=0$ level of the $^\bar{A}$ state) of the three vibronic levels from the bending mode are:

206.58 cm$^{-1}$ $^2\Sigma$ vibronic symmetry
363.49 cm$^{-1}$ $^2\Pi_{3/2}$ vibronic symmetry
371.63 cm$^{-1}$ $^2\Pi_{1/2}$ vibronic symmetry

As pointed out previously, the assignments for these three levels are:

206.58 cm$^{-1}$ $^2\Sigma$ vibronic symmetry $\rightarrow$ $^2\Sigma^+$ vibronic level of $v=1$
363.49 cm$^{-1}$ $^2\Pi_{3/2}$ vibronic symmetry $\rightarrow$ upper($\kappa$) $^2\Pi_{3/2}$ vibronic level of $v=2$
371.63 cm$^{-1}$ $^2\Pi_{1/2}$ vibronic symmetry $\rightarrow$ upper($\kappa$) $^2\Pi_{1/2}$ vibronic level of $v=2$
The frequency of these vibronic levels are given by the following expressions (see Appendix A), after the appropriate substitution of the values for \( v \) and \( K \) have been made:

\[
E(2\Sigma^+) = \omega\left(1 - \frac{1}{8} \epsilon^2\right) + \frac{1}{2} \sqrt{A^2 + 4 \epsilon^2 \omega^2} \tag{4.11}
\]

\[
E(\kappa, 2\Pi_{3/2}) = 2 \omega \left(1 - \frac{1}{8} \epsilon^2\right) + \frac{1}{2} \sqrt{A^2 + 8 \epsilon^2 \omega^2} - \frac{3 A \epsilon^2 \omega}{8 \sqrt{A^2 + 8 \epsilon^2 \omega^2}} \tag{4.12}
\]

\[
E(\kappa, 2\Pi_{1/2}) = 2 \omega \left(1 - \frac{1}{8} \epsilon^2\right) + \frac{1}{2} \sqrt{A^2 + 8 \epsilon^2 \omega^2} + \frac{3 A \epsilon^2 \omega}{8 \sqrt{A^2 + 8 \epsilon^2 \omega^2}} \tag{4.13}
\]

After substituting the experimental value of the spin-orbit coupling constant into the above equations, they were solved for \(|\epsilon|\) and \(\omega\). The values obtained are: \(|\epsilon| = 0.53\) and \(\omega = 136.4\). The value of \(\omega\) does not seem unreasonable since the \textit{ab initio} value calculated for the ground state bending frequency is 83 cm\(^{-1}\) [42]. The value obtained for the Renner-Teller parameter, \(|\epsilon| = 0.53\), would indicate a strong Renner-Teller effect for this radical. However, there is a problem with this assignment: if transitions to the \(\kappa\ 2\Pi\) states are observed, the transitions to the \(\mu\ 2\Pi\) states should also be seen, in between the \(2\Sigma\ v=1\) state, Band A, and the \(\kappa\ 2\Pi\) states, Band B. One possible explanation for not observing the \(\mu\ 2\Pi\) states could be due to a low intensity. The
relative intensities for all the bending transitions were calculated [62], and they indicated that the transitions to the $\kappa^2\Pi$ states are much weaker than transitions to the $\mu^2\Pi$ states. Consequently this poor agreement of the calculated and experimental intensities, indicates that this assignment of the observed vibronic features might not be correct.

Attempts to solve Pople's equations assuming that the level from $v=1$ was the $^2\Sigma^-$ state (instead of the $^2\Sigma^+$) were made, but the solutions obtained did not make "physical" sense, since imaginary values for $|\epsilon|$ and $\omega$ were obtained. Similarly, assuming that the pair of levels from $v=2$ were the $\mu^2\Pi$ states, in combination with either $^2\Sigma^+$ or $^2\Sigma^-$ for the $v=1$ state, gave no meaningful solutions for $|\epsilon|$ and $\omega$.

A possible explanation for the observed transitions is that the bending vibronic transitions have been perturbed. As stated in section A.3 in Appendix A, it was demonstrated by Northrup and Sears that when the $\mathcal{H}_{RT}$ operator is combined with the spin-orbit operator, the $\mathcal{H}_{SO} \times \mathcal{H}_{RT}$ operator will mix levels with $\Delta v = \pm 1$, $\Delta \Lambda = 0, \pm 2$, $\Delta l = \pm 1$ $\Delta \Sigma = \pm 1$ [59]. This interaction could mix the $^2\Pi_{1/2}$ vibronic state of the $v=2$ level and the $^2\Sigma^+$ state from $v=1$, since these levels differ in $v, l$ and $\Sigma$ by one. In Figure 21, a diagram showing this probable interaction is presented.

As shown in the diagram, the $^2\Sigma^+$ state and the $\mu^2\Pi_{1/2}$ state could interact with each other and be perturbed from their original frequencies, by a magnitude "d". The magnitude of this interaction could be such that the perturbed $\mu^2\Pi_{1/2}$ state ends up higher in energy than the $\mu^2\Pi_{3/2}$ state, as shown in Figure 21. This vibronic interaction could then explain the observed transitions, because then the $\mu^2\Pi_{1/2}$ state
Figure 21: Diagram showing the interaction between the $^2\Sigma^+$ (from $v=1$) and the $\mu^2\Pi$ (from $v=2$) states, which causes a shift of those levels from the expected positions (see text).
will be above the $\mu^2\Pi_{3/2}$ state, as is observed experimentally. Additionally, with the assignment of Band B as the transition to the $\mu^2\Pi$ states in $v=2$, the assignment is then consistent with the prediction of the intensity calculations of MgNC mentioned earlier [62].

Under this assumption, the values obtained were: $|e| = 0.05$, $\omega = 193$ cm$^{-1}$, and $d = 8$ cm$^{-1}$. The value obtained for $\omega$ is approximately twice the value of calculated for the bending frequency of the $\tilde{X}$ state, $\omega_2 = 83$ cm$^{-1}$ [42]. A similar result has been predicted for the CaNC radical, for which bending frequencies have been calculated, and the bending frequency in the $\tilde{A}$ state is almost twice its ground state value ($\omega_2' = 26.9$ and $\omega_2' = 52.6$ cm$^{-1}$, [63]).

It would be desirable to determine if the value obtained for "d" (8 cm$^{-1}$) is reasonable for MgNC. The expression for "d" has been derived in Appendix A in equation A.37. For the $^2\Sigma$ state of $v=1$ we have $|1, -1; 1, 1/2\rangle$ ([v, l; $\Lambda$, $\Sigma$]) and for the $^2\Pi_{1/2}$ state, $|2, 0; 1, -1/2\rangle$. Applying equation A.37 to these two states, the value of $d$ is:

$$d = 2^{-1/2} \left(v + 2 + l\right)^{1/2} \frac{AL_+ VL_-}{4\Delta E} = 2^{-1/2} \left(v + 2 + l\right)^{1/2} F$$

substituting $v$ and $l$ ($v = 1$ and $l = -1$), $d = F = 8$ cm$^{-1}$ is obtained.

In NCS the value of $F$ was obtained fitting several vibronic levels of the $\tilde{X}$ state, and it was determined as 7.03 cm$^{-1}$ [59], comparable with the value determined here for MgNC of 8 cm$^{-1}$. The parameter $F$ is $F = \frac{A_{so} L_+ V L_+}{4\Delta E}$, where $\Delta E$ is the difference between the electronic state $\tilde{A}$ and another electronic state (either $\Sigma$ or $\Delta$), through which the coupling occurs. If the value of $A_{so}$ is used as an estimate of

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the quantity $A_{so}L_{\pm}$ (as was done for NCS [59]), the ratio $\frac{VL_{\pm}}{4\Delta E}$ is $\sim 0.22$. For NCS the corresponding value of $\frac{VL_{\pm}}{4\Delta E}$ was estimated as $\sim 0.02$, an order of magnitude smaller.

Since the spin-orbit coupling constant of MgNC is an order of magnitude smaller than $A_{so}$ of NCS ($A_{so}=36.9 \text{ cm}^{-1}$ for MgNC and $-327.59 \text{ cm}^{-1}$ for NCS), it might be expected that the $\Delta E$ in MgNC would be much smaller too. In NCS the $\Delta E$ of 27,000 cm$^{-1}$ corresponds to the difference in energy between the $\tilde{X}$ and the $\tilde{B}$ states. For MgNC, the perturbing $^2\Sigma$ electronic state through which this coupling occurs is assumed to be the $\tilde{B} \Sigma$ state, and so the $\Delta E$ would correspond to the difference between the $\tilde{A}$ and the $\tilde{B}$ states in this case. Unfortunately, the position of the $\tilde{B}$ state of MgNC has not been determined up to date. However, the difference between the $\tilde{A}$ and $\tilde{B}$ states in MgNC is most likely much smaller than the $\Delta E$ between the $\tilde{X}$ and $\tilde{B}$ states in NCS, which would explain the larger value of $\frac{VL_{\pm}}{4\Delta E}$ obtained for MgNC.

4.6 Conclusions

The high resolution LIF spectra of the $0_0^0$ (origin), $3_0^1$ ($\nu_3$ NC stretch), and three vibrational transitions of $\nu_2$ (bending mode) of the $\tilde{A}^2\Pi \leftarrow \tilde{X}^2\Sigma^+$ electronic transition of the MgNC radical have been recorded and rotationally analyzed. The rotational constant obtained for the vibrationless level of the ground electronic state, agreed with the reported value of Kawaguchi and coworkers [41]. The spectroscopic parameters of the $\tilde{A}$ state, such as the spin-orbit coupling constant, and the rotational constants for the vibronic levels have been obtained for the first time, as well as the
value of the excited stretching frequency.

The assignments of the bending vibronic levels have been discussed taking into account the combined interactions of the Renner-Teller effect and the spin-orbit coupling, which are present in the MgNC radical. Owing to the Renner-Teller vibronic coupling, a very weak transition to the \( v=1 \) level of the bending mode has been observed. The vibronic symmetry of this level was determined to be \( \Sigma^+ \). Two \(^2\Pi\) vibronic states of the \( v=2 \) level were also observed, and were assigned as the \( \mu \) pair of \(^2\Pi\) states of the \( v=2 \) level. The \( \mu \)^{2\Pi}_{1/2} \) state is observed at 8 cm\(^{-1}\) higher in energy than the \( \mu \)^{2\Pi}_{3/2} \) state, owing to an interaction with the \( \Sigma \) state from \( v=1 \). This interaction has been seen before [59], and is caused by a product of the Renner-Teller and spin-orbit operators, which mix vibronic states differing in \( v \) by one.
CHAPTER 5

HIGH RESOLUTION ELECTRONIC SPECTROSCOPY OF HCCS.

5.1 Introduction

A considerable number of sulfur-containing molecules have been detected in interstellar space in the recent years, and as a consequence there has been an increased interest in the laboratory spectra of such species. The HCCS radical was considered as a candidate to be detected in interstellar space [64, 65, 66], which promoted the study of this radical in particular. A number of experimental and theoretical studies have been published since the first experimental identification of this radical, by Krishnamachari and Venkitachalam in 1978 [67], who performed flash photolysis experiments on thiophene (C$_4$H$_4$S). The observed spectrum, however, was tentatively assigned to the C$_4$H$_3$ radical. In 1980 Krishnamachari and Ramsay [68] repeated the experiment with thiophene and its deuterated analogue, with the resulting radicals being probed by absorption spectroscopy. From the analysis of the spectra and the isotopic shifts observed, they concluded that the carriers of the spectra were HCCS and DCCS, although only a preliminary report on the rotational and vibrational analysis of the spectra was given. A complete rotational analysis could not be performed.
because they were not able to observe the Q branches in any of the bands, and thus it was not possible to determine the rotational numbering of the branches unambiguously. Vibrational assignments were proposed only for the strongest bands in their spectrum, which were assigned as the origin band and transitions to the fundamental and up to v=3 quanta of the $\nu_3$ mode, the CS stretch.

In 1985, Coquart [69] investigated the emission spectroscopy of the HCCS radical, obtained by a radio-frequency discharge in thiophene. A rotational analysis was carried out on the strongest bands, and vibrational assignments were discussed. As in the absorption experiment [68], Coquart did not detect Q branches for any of the bands observed, which made the rotational analysis very difficult. The author proposed that further studies would be useful to confirm his preliminary assignments.

A few years later, Dunlop et al. [70] applied a new flash vacuum pyrolysis technique to several organic precursors. Pyrolysis of 1,2,3-thiadiazole and its deuterated compound produced HCCS and DCCS and they obtained the first low-resolution laser induced fluorescence spectra of these radicals, although no spectral analysis was performed on the data.

The first microwave spectrum of HCCS was reported by Vrtilek and coworkers [64] in 1992. They were able to detect the two spin orbit components of the vibrationless level of the electronic ground state, and as a result of the rotational analysis of this spectrum, the molecular constants for these levels were obtained.

Tang and Saito [71] recently investigated rotational transitions in several vibronic levels of the $\tilde{X}$ state of HCCS and DCCS by microwave spectroscopy. Their main
interest was to study the Renner-Teller interaction within these vibronic states.

While the experiments presented here were in progress, Kohguchi et al. [72] published the laser induced fluorescence spectrum of the $\tilde{A} ^2\Pi \leftarrow \tilde{X} ^2\Pi$ electronic transition. Since the experiment was performed in a supersonic jet expansion, only transitions from very low J values were detected. Vibronic assignments for only some of the bands observed were proposed, and they concluded that a previous vibrational assignment for one of the bands was incorrect (see a more detailed discussion below). Due to the resolution of their system ($\sim 0.1 \text{ cm}^{-1}$), their assignments were based only on the rotational contours of the transitions.

Several theoretical studies have been published for HCCS. The first ab initio study of the ground state of the radical was done by Cooper [73] in 1981. His results were discussed in relation with the absorption work of Krishnamachari and Ramsay. The HF studies done by Cooper indicated a linear structure for the ground state of HCCS, and the calculated $B''$ constant was in agreement with the one obtained from the absorption spectrum [68]. Later, Goddard reported ab initio HF and Møller-Plesset perturbation theory calculations on the ground state of HCCS and HCCO [74]. These calculations also predicted a linear structure for the ground state and the $B''$ rotational constant agreed with the experimental value. In 1989 Largo-Cabrérizo and Barrientos [75] performed ab initio studies of the low-lying states of CICC and HCCS. The motivation for this work was an attempt to identify a new spectrum observed in the envelope of a carbon star by Guélin et al. [3]. Last year, Szalay [76] reported new ab initio calculations for HCCS using coupled-cluster methods for its ground and first
excited electronic states. This work included a Renner-Teller analysis for the bending modes in both electronic states. Very recently, Li and Iwata [77] using CASSCF \textit{ab initio} methods, calculated the equilibrium geometries and potential energy curves of the low-lying electronic states of HCCS and NCS.

In the emission work of Coquart, several vibronic features of the $\tilde{A} \leftarrow \tilde{X}$ transition were observed and their assignments were discussed [69], but in more recent studies carried out on HCCS a reassignment of some of those bands have been proposed. Based on his \textit{ab initio} values, Szalay discussed a new assignment of Coquart’s spectrum [76]. Using the predicted harmonic frequencies from the \textit{ab initio} calculations, vibronic bands assigned by Coquart to the CC and CH stretching modes, were reassigned by Szalay. The values obtained in this new assignment were in agreement with the theoretical predictions. Although several lines in Coquart’s spectrum were assigned to the overtones of the bending modes of HCCS, Szalay considered that these assignments were not correct, since it was assumed by Coquart that these states would have the same spin-orbit splitting difference as the $v=0$ vibronic states. This assumption is only valid if Renner-Teller effect is negligible, and according to Szalay this is not the case for HCCS, as his \textit{ab initio} calculations showed large Renner-Teller splitting. Although no new assignments were proposed by Szalay for these transitions, he mentioned that he planned to include spin-orbit interaction into his Renner-Teller treatment in the near future.

Kohguchi \textit{et al.} also disagreed with some of Coquart’s assignments. A feature at 24,660 cm$^{-1}$, assigned by Coquart to the $4_{1}^{1} 2\Delta_{5/2} \leftarrow 2\Delta_{5/2}$ transition, was also
observed in the jet-cooled LIF spectrum of Kohguchi et al.. It was indicated by Kohguchi and coworkers, however, that this transition cannot be a hot band since according to their data it originates in the $0_0$ state. Nonetheless, a new vibrational assignment for this band was not proposed by these authors. In fact, six out of the twelve vibronic features recorded in their LIF spectrum were not assigned. According to Kohguchi et al., more experimental work was needed in order to establish the vibrational structure of the HCCS radical [72].

Due to the controversy in the vibronic assignment on some of the HCCS transitions, the aim of the present work was twofold: (i) to obtain the spectroscopic rotational parameters of these transitions, and from those, to determine the structure of the HCCS radical; (ii) and to attempt to clarify the vibronic assignments of these transitions, once the vibronic symmetry is known. The vibronic symmetry of the two levels involved in a transition can be determined by analyzing its rotational structure, since different vibronic bands have very different rotational branch structure. The rotational appearance of a $\Sigma \leftarrow \Sigma$ transition, for example, is very different from the rotational structure of a $\Pi \leftarrow \Pi$ transition. Additionally, by examining the rotational structure of vibronic bands it is possible to differentiate between a $^2\Pi_{1/2} \leftarrow ^2\Pi_{1/2}$ from a $^2\Pi_{3/2} \leftarrow ^2\Pi_{3/2}$ transition, for example, by the different spacing between the various branches which is determined by the $J$ value of the lowest rotational lines in the P and R branches. All this information, obtained from the rotational analysis of the high resolution spectra, might make the assignment of vibronic transitions a somewhat easier task.

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In the present study, the HCCS radical was studied by LIF spectroscopy in a supersonic jet expansion. Six $^1A \leftarrow ^1X$ vibronic transitions in the 24,200–24,700 cm$^{-1}$ region were probed under high resolution spectroscopy.

5.2 Experimental Details

The experimental method used to obtain the jet-cooled LIF spectra of the HCCS radical will only be briefly outlined, as the details have been given previously in Chapter 2. The HCCS radical was produced by photolyzing thiophene ($C_4H_4S$), with the 248 nm output of a KrF excimer laser. The photolysis laser output was unfocussed and attenuated to roughly 6 mJ-pulse$^{-1}$, since increasing the photolysis power only produced photolysis by-products such as $C_3$. The thiophene was obtained from Aldrich (99 %) and was used without further purification. It was held in a stainless steel reservoir at room temperature, seeded into a high pressure carrier gas: either He (300 psig) or $N_2$ (80 psig), depending upon the degree of vibrational and rotational cooling that was desired. The gas mixture was then introduced into the vacuum chamber through a pulsed valve, forming a supersonic jet expansion.

The probe laser was the pulse-amplified output of a Coherent 899-29 Ti:Sapphire cw ring laser. The pulse-amplified laser output was frequency doubled in a KDP crystal, which was angle-tuned for maximum UV production. The jet stream was probed approximately 20 mm downstream of the photolysis region. The fluorescence was collected at right angles to the probe laser beam and focused onto a photomultiplier tube. A cut-off filter (Hoya L39), was used to reject scattered laser light. The
UV probe laser power was attenuated with neutral density filters, to decrease power broadening of the spectral lines.

Similarly to MgNC, the LIF spectrum of HCCS was outside the range covered in the Te$_2$ or I$_2$ spectral atlases. Therefore, the absolute frequencies were obtained from the Autoscan wavemeter. The preamplified PMT signal was integrated and amplified and then sent to the Coherent Autoscan system for signal averaging. The HCCS signal was very strong and only five laser shots were averaged for the excellent S/N ratios of the recorded spectra.

The moderate resolution HCCS spectra, spanning a larger frequency range, as the one included in Figure 22, were obtained with the moderate resolution probe laser described previously in Chapter 2.

5.3 Theory

As in the previous cases, SpecSim [14] was used to analyze and fit all the rotationally resolved spectra presented in this chapter. A description of this computer program has been included in Chapter 2.

The HCCS radical has a linear configuration and $^3\Pi$ symmetry in both the $\tilde{X}$ and the $\tilde{A}$ electronic states. This was predicted by ab initio calculations performed on HCCS and confirmed by previous experimental work on HCCS. Thus, the linear molecule model was used to analyze the HCCS spectra, which can be described, in the absence of external fields and disregarding hyperfine interactions, as [58]:

\begin{equation}
\end{equation}
\[ \mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{\text{ROT}} + \mathcal{H}_{\text{SO}} + \mathcal{H}_{\text{LD}} \]  

(5.1)

where \( \mathcal{H}_0 \) is the non-relativistic Hamiltonian of the non-rotating molecule, \( \mathcal{H}_{\text{ROT}}, \mathcal{H}_{\text{SO}} \)

and \( \mathcal{H}_{\text{LD}} \) correspond to the rotational, spin-orbit and lambda doubling Hamiltonians, respectively. The definition for each of these terms is as follows:

\[ \mathcal{H}_{\text{ROT}} = B_v \mathbf{R}^2 - D_v \mathbf{R}^4 \]  

(5.2)

\( B_v \) is the rotational constant, \( D_v \) is the centrifugal distortion constant and \( \mathbf{R} \) is the rotational angular momentum operator, defined by \( \mathbf{R} = \mathbf{J} - \mathbf{L} - \mathbf{S} \), where \( \mathbf{J}, \mathbf{L} \) and \( \mathbf{S} \) are the total, electronic orbital and electronic spin angular momentum operators, respectively.

The next term in the Hamiltonian corresponds to the spin-orbit coupling interaction, and can be expressed as:

\[ \mathcal{H}_{\text{SO}} = A_{so} \mathbf{L} \cdot \mathbf{S} \]  

(5.3)

where \( A_{so} \) is the spin-orbit coupling constant, and \( \mathbf{L} \) and \( \mathbf{S} \) are defined as before. Although for HCCS \( A_{so} \) has not been directly measured, neither in the \( \tilde{X} \) nor in the \( \tilde{A} \) state, their values have been predicted by ab initio methods, and \( A''_{so} \) has been estimated from experimental data. The four \( A''_{so} \) values reported up to date, however, are not consistent: -185 cm\(^{-1}\) [64]; -270 cm\(^{-1}\) [71]; -360 cm\(^{-1}\) [73]; and -347 cm\(^{-1}\) [76]. The first two are estimations from experimental data, and the other two are ab initio calculations. Except for the value of -185 cm\(^{-1}\) reported by Vrtilek et al. [64],
the other values are $-315 \pm 45$ cm$^{-1}$, a value close to the $A''_{so}$ of NCS ($-323.43$ cm$^{-1}$, [78]). NCS is isoelectronic with HCCS, and many similarities have been noted between the absorption spectra of these two radicals [68]. NCS is also a $^2\Pi$ linear molecule in both the $\tilde{X}$ and $\tilde{A}$ electronic states, and both states are inverted, i.e. the $A_{so}$ coupling constant is negative. Consequently, the large negative $A_{so}$ coupling constant predicted (or estimated) for the $\tilde{X}$ state of HCCS (and close to the value of the $A_{so}$ of NCS) is not unexpected.

Owing to the rather large $A''_{so}$ constant predicted for HCCS, and to the low temperatures of the supersonic jet expansion, the HCCS radicals produced in the experiment reported here only populated the lower spin-orbit level of HCCS, the $^2\Pi_{3/2}$ state. Since the $\Delta\Omega = 0$ selection rule holds, only transitions between the $\Omega = \frac{3}{2}$ spin-orbit components were observed. Consequently, it is not possible to determine neither the $A''_{so}$ nor the $A'_{so}$ from the experimental data observed in this work. Therefore, the calculated spectroscopic constants obtained in this work are effective rotational constants.

The final term in the Hamiltonian corresponds to the $\Lambda$-doubling interaction. Electronic states of the same multiplicity and with $\Delta\Lambda = \pm 1$ may perturb each other. To first order, only $\Sigma$ states interact with $\Pi$ states, and this interaction is described by $\mathcal{H}_{LD}$. This interaction removes the degeneracy of the $\Lambda$ components and causes a splitting between them. This $\Lambda$-type splitting in $^2\Pi$ states can be described in terms of the so-called $\Lambda$-doubling parameters: $p_\nu$ and $q_\nu$. The $\mathcal{H}_{LD}$ can be defined in terms of these parameters as follows [58]:
\[ \mathcal{H}_{LD} = \frac{q_v}{2} (J_+ + J_-)^2 - \left( \frac{q_v}{2} + \frac{p_v}{4} \right) \left( (J_+ + J_-)(S_+ + S_-) + (S_+ + S_-)(J_+ + J_-) \right) \]
\[ + \left( \frac{q_v}{2} + \frac{p_v}{2} \right) (S_+ + S_-)^2 \]  
(5.4)

where the \( \Lambda \)-doubling parameters can be defined as [58]:

\[ p_v = 4 \sum_{n'v'} \left| \langle \frac{1}{2} A_{so} \quad B_v \quad L_+ \mid n' \quad 2\Sigma^\pm \quad v' \rangle \right| \left| \langle n \quad 2\Pi \quad v \mid B_v \quad L_+ \mid n' \quad 2\Sigma^\pm \quad v' \rangle \right| \frac{E_{nv} - E_{n'v'}}{E_{nv} - E_{n'v'}} \]
(5.5)

\[ q_v = 2 \sum_{n'v'} \left| \langle n \quad 2\Pi \quad v \mid B_v \quad L_+ \mid n' \quad 2\Sigma^\pm \quad v' \rangle \right|^2 \frac{E_{nv} - E_{n'v'}}{E_{nv} - E_{n'v'}} \]
(5.6)

The \( \Lambda \)-doubling parameter \( p_v \) connects off-diagonal terms, for which it is necessary to observe transitions of both spin-orbit components in order to determine its value. Since only transitions from the \( ^2\Pi_{3/2} \) level were recorded, only the \( q_v \) parameter can be determined from the present data. Consequently, the \( \Lambda \)-doubling parameter \( p_v \) was not included in the fitting of the HCCS rotationally spectra discussed in this chapter.

The basis functions for the calculation of the Hamiltonian matrix were linear combinations of Hund's case(a) functions.

5.4 Results

In Figure 22 the moderate resolution LIF spectrum of the HCCS radical in the 24,200 - 24,700 cm\(^{-1} \) region is shown. As can be seen in that figure from the excellent signal
Figure 22: Moderate resolution (~0.1 cm⁻¹) LIF spectrum of HCCS. Features indicated with the letters A-F are vibrationally cold bands, whereas $H_A$ and $H_B$ are hot bands. The weaker lines, marked with asterisks, are not due to the HCCS radical, but to by-products of the laser photolysis (see text).
to noise ratios, the HCCS signal was very strong. By changing the experimental conditions it is possible to alter the vibrational temperature of the jet expansion, and thus to control the presence (or absence) of vibrationally hot bands. The rotational temperature of the vibrationally cold transitions was also very low (2-3K), and only three to four rotational lines were recorded for each branch under those conditions. On the other hand, when a vibrationally warmer spectrum was recorded, the rotational temperature obtained was higher (12-15K), which provided spectra richer in rotational transitions. With such spectra it is often possible to obtain a more accurate set of molecular parameters, since more lines can be included in the fitting procedure. Thus, even though hot bands are superimposed on the HCCS transitions of interest, the vibrationally warmer spectra were used for the final fittings, and are the ones displayed in the figures presented in this chapter. Therefore, it was experimentally determined that the features marked with the letters A to F in Figure 22 were vibrationally cold HCCS transitions, i.e. they originated in the vibrationless level of the \( \tilde{X} \) electronic state. Bands indicated with the letters \( H_A \) and \( H_B \) were hot bands. The weaker lines marked with asterisks in Figure 22 are not due to HCCS, but to by-products of the photolysis of thiophene, most likely the \( C_3 \) radical, which has been reported to fluoresce in this region [72]. All the vibrationally cold HCCS transitions, bands A to F, were probed by high resolution LIF. These high resolution spectra and their rotational analyses are presented in the following sections.
Band A

Figure 23: High resolution LIF spectrum of Band A, a $^2\Pi_{3/2} \leftarrow ^2\Pi_{3/2}$ transition. The lower trace shows the simulated spectrum generated with SpecSim, with a rotational temperature of 14K.
5.4.1 Band A

The high resolution, rotationally resolved LIF spectrum of band A is shown in Figure 23. The rotational structure of this feature was analyzed with SpecSim, and the simulation, shown in the bottom part of Figure 23, was generated assuming a $^2\Pi \leftarrow ^2\Pi$ transition, which reproduces the structure of this band very well, as can be seen in that figure. $^2\Pi_{3/2} \leftarrow ^2\Pi_{3/2}$ and $^2\Pi_{1/2} \leftarrow ^2\Pi_{1/2}$ simulations were compared to the experimental data, and it was determined that band A is a $^2\Pi_{3/2} \leftarrow ^2\Pi_{3/2}$ transition. This can be deduced from the lowest J value of the rotational lines in each branch. Therefore, the ground state is $^2\Pi_{3/2}$, which confirms that the $A''_{so}$ is negative, as predicted in previous studies [64, 71, 73, 76].

Thirty-six lines were observed and fit for this band. The standard deviation obtained from the least squares fitting procedure was $2.3 \times 10^{-3}$ cm$^{-1}$, which when compared with the experimental linewidth of the HCCS rotational lines, $\sim 8 \times 10^{-3}$ cm$^{-1}$, shows the excellent agreement between the predicted lines in the simulation and the experimental rotational transitions. The rotational temperature determined from the simulation was 14K.

The effective rotational constants, $B''_v$ and $B'_v$, for the ground and excited states, respectively, were determined from the fit and their values are presented in Table 4. The centrifugal distortion constant, $D_v$ and the $\Lambda$-doubling parameter $q_v$ were found to affect the spectrum less than the experimental error. When these constants were allowed to vary in the fitting process, their value was practically zero (two orders of magnitude smaller than the experimental uncertainty). This result is not surprising.
since the values of $D_v$ and $q_v$ for several vibrational levels of the $\bar{X}$ state, determined from the microwave spectra of Tang and Saito [71], are of the order of $10^{-8}$ cm$^{-1}$, well below the experimental resolution of the present experiments.

5.4.2 Band B

The next strong features shown in the LIF spectrum of Figure 22 are three overlapping bands: B, C and H$_A$, although it is difficult to discern these at the scale shown in that figure. When a vibrationally cold spectrum was recorded, only two HCCS transitions were observed in this region (at 355 cm$^{-1}$ from band A), the features called B and C. Kohguchi et al. [72], who also obtained the LIF spectrum of HCCS in this region, observed only two transitions at this frequency, which confirms that H$_A$ is a hot band.

The high resolution spectrum of band B was analyzed with the SpecSim program, and also simulated by a $^2\Pi_{3/2} \leftrightarrow ^2\Pi_{3/2}$ transition. The experimental and simulated spectra of this band are shown in Figure 24. In this band a splitting of the rotational lines can be observed, which increases with the $J$ value. The splitting can be better seen in the P branch in Figure 24, since the presence of a band head in the R branch makes the observation of the splitting in transitions with high $J$ value difficult. In the simulation the splitting was reproduced by the introduction of the A-doubling parameter, $q_v$ in the $\bar{A}$ state. For this transition the value of the centrifugal distortion constant in the excited state, $D'_v$, was found to be different from zero. All the molecular constants obtained for this transition are presented in Table 4.
Figure 24: High resolution LIF spectrum of the group of transitions near 24655 cm\(^{-1}\). In the lower trace the simulated plot for band B is shown. The experimental lines that are not reproduced in the simulation belong to the other bands (bands C and H\(_A\)) that occur in this region. The simulation corresponds to a \(^2\Pi_{3/2} \leftrightarrow ^2\Pi_{3/2}\) transition.
Figure 25: High resolution LIF spectrum of the group of transitions near 24655 cm\(^{-1}\). In the lower trace the simulated plot for band C only is shown. The experimental transitions that are not seen in the simulation belong to the other bands that occur in this region, bands B and H\(_A\). Band C is a \(^2\Pi_{3/2} \leftarrow ^2\Pi_{3/2}\) transition.
5.4.3 Band C

The other HCCS transition recorded in this region, band C, is shown in Figure 25. The simulation of this band is also shown in that figure, in the bottom trace. At first sight, band C looks almost identical to band A. This band was also well simulated by a $^2\Pi_{3/2} \leftrightarrow ^2\Pi_{3/2}$ transition, as can be seen in Figure 25 by the good agreement between the experimental and simulated plots. Forty rotational lines were fit for this band, with a standard deviation of $4.9 \times 10^{-3}$ cm$^{-1}$, also smaller than the experimental linewidth. The rotational temperature of the simulation was 16K. In Table 4 the rotational constants obtained for band C are presented.

5.4.4 Bands D, E and F

The rotationally resolved spectra for bands D, E and F are shown in Figure 26. Since all three bands have the same general appearance and look very similar to the HCCS bands shown before, the simulated plots obtained for them are not included here, to avoid repetition. Indeed, the three transitions were very well simulated by a $^2\Pi_{3/2} \leftrightarrow ^2\Pi_{3/2}$ transition, also. A few lines in the experimental spectra of bands E and F, marked with asterisks in Figure 26, are not due to HCCS but to other species, by-products of the photolysis process, as mentioned in the experimental section. All the observed rotational lines for these three transitions (34 lines each for bands D and E, and 33 transitions in band F) were modeled and fit with SpecSim, with excellent standard deviation: $3.0, 2.2$ and $2.6 \times 10^{-3}$ cm$^{-1}$ for bands D, E and F, respectively. The rotational constants obtained for the levels involved in these three
$\tilde{A} \leftarrow \tilde{X}$ transitions are also listed in Table 4.
Figure 26: High resolution LIF spectra of bands D, E and F. The three bands correspond to $\tilde{A} \ ^2\Pi_{3/2} \leftarrow \tilde{X} \ ^2\Pi_{3/2}$ transitions. The lines marked with asterisks in bands E and F are not due to HCCS, but to by-products of the photolysis of thiophene (see text).
<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tilde{X}$</td>
<td>$B''_{eff}$</td>
<td>0.19579(8)</td>
<td>0.1959(2)</td>
<td>0.1957(1)</td>
<td>0.19574(7)</td>
<td>0.19565(6)</td>
</tr>
<tr>
<td></td>
<td>$B'_{eff}$</td>
<td>0.18141(6)</td>
<td>0.1651(9)</td>
<td>0.1855(1)</td>
<td>0.1815(1)</td>
<td>0.18383(6)</td>
</tr>
<tr>
<td>$\tilde{A}$</td>
<td>$D'_{eff}$</td>
<td>3.6(2)x10^{-6}</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$(g'<em>{0})</em>{eff}$</td>
<td>9(2)x10^{-3}</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Frequency$^a$</th>
<th>0</th>
<th>354</th>
<th>359</th>
<th>657</th>
<th>712</th>
<th>740</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard deviation of the fit</td>
<td>0.0023</td>
<td>0.0057</td>
<td>0.0049</td>
<td>0.0030</td>
<td>0.0022</td>
<td>0.0026</td>
</tr>
<tr>
<td>Rotational Temperature (K)</td>
<td>14</td>
<td>16</td>
<td>16</td>
<td>12</td>
<td>11</td>
<td>12</td>
</tr>
<tr>
<td>Number of lines fit</td>
<td>36</td>
<td>42</td>
<td>40</td>
<td>34</td>
<td>34</td>
<td>33</td>
</tr>
</tbody>
</table>

$^a$Relative to band A, at 24,300 cm$^{-1}$.

Table 4: Molecular constants, in cm$^{-1}$, of the ground and first excited electronic states of the observed HCCS transitions (bands A-F). Numbers in parentheses indicate two standard deviations.
5.5 Discussion

5.5.1 Rotational Analysis

From the rotational analysis performed on the six vibronic bands analyzed (bands A to F) it was determined that all six bands are $^{2}\Pi_{3/2} \leftarrow ^{2}\Pi_{3/2}$ transitions. The rotational spectra of these bands were very similar, except for band B. For this band only, the $\Lambda$-doubling splitting constant ($q_v$) and the centrifugal distortion constant ($D_v$) in the excited state were large enough to be experimentally observed. These two constants were ca. two orders of magnitude larger than the values of the corresponding constants in the ground state (determined by Tang and Saito [71]). For all the other observed bands, $D'_v$ and $q'_v$ were equal to zero. Not only were the magnitudes of $D'_v$ and $q'_v$ of band B much larger than for the other HCCS bands, but also the change in the rotational constant, $\Delta B$, was unusually large when compared with the $\Delta B$ of the other transitions. All these unexpected values suggest that the upper state of band B is being perturbed by a nearby state. The presence of $\Lambda$-doubling splitting seems to indicate that the perturbing state is a $\Sigma$ vibronic state. If this perturbing state were from the $\tilde{A}$ electronic state, a transition from the $0_0$ state to this $\Sigma$ state would have been observed in the LIF spectrum, but this was not the case. It could be possible that the transition dipole moment was not large enough to be observed. The other possibility is that the $\Sigma$ state does not belong to the $\tilde{A}$ state but to another electronic state, perhaps a high vibrationally excited level from the $\tilde{X}$ state, or a vibrational level from another low-lying excited electronic state.

Krishnamachari and Ramsay, the first to obtain the HCCS spectrum, were also
the first to assign the band at 24,300 cm\(^{-1}\) (band A), as the \(0^0_0 \: \tilde{A} \: ^2 \Pi_{3/2} \leftarrow \tilde{X} \: ^2 \Pi_{3/2}\) transition. The \(B''\) constant determined by those authors was 0.19568(8) cm\(^{-1}\) (see note added in proof in their work [67]), which agrees with the \(B''\) obtained in this work (\(B'' = 0.19579(8)\) cm\(^{-1}\)). Since the work of Krishnamachari and Ramsay, more accurate determinations of the \(B''\) constant have been obtained, in particular by microwave spectroscopy. The value determined in the present work for \(B''\) agrees well with the two microwave spectroscopic determinations of this constant: \(B'' = 0.1958000(3)\) cm\(^{-1}\) from Vrtilek et al. [64], and \(B'' = 0.19574695(7)\) cm\(^{-1}\) of Tang and Saito [71].

The \(B'\) constant of the \(0^0_0\) has only been reported by Coquart [69]. However, due to the problem in assigning rotational numbering in his spectrum, his rotational analysis was not definitive. Three possible rotational numbering (X, Y and Z in [69]) were determined from combination differences, and listed in Table 2 of his work. The rotational constants for the Y numbering are \(B'' = 0.19563\) and \(B' = 0.18118\) cm\(^{-1}\), which are very close to the values obtained in the present analysis (see Table 4).

As mentioned before, it was experimentally determined that bands A to F were vibrationally cold, i.e. that they originate in the vibrationless level of the ground electronic state. In Table 4, the rotational constants \(B''\) obtained independently from the rotational analysis performed on each of those transitions are listed. The value of \(B''\) of these bands agree well with each other and with the values previously reported for the \(B''\) of the vibrationless level of the ground electronic state, which confirms that indeed all of these bands originate in the \(v'' = 0\) level of the \(\tilde{X}\) state.
The band observed at 740 cm$^{-1}$ from the origin band (band F), has been previously assigned as the transition to one quantum of the CS stretch, the $\nu_3$ mode. The value of 740 cm$^{-1}$ agrees well with the $ab\ initio$ estimated value of the harmonic frequency $\omega_3 = 730$ cm$^{-1}$, reported by Szalay [76]. As was the case for the origin band, the rotational constants obtained for this transition, $B''=0.19570(7)$ and $B'=0.18098(6)$ cm$^{-1}$, agree well with the rotational constants of Coquart's Y rotational numbering: $B''=0.19575$ and $B'=0.18100$ cm$^{-1}$ (see Table 2 in Coquart [69]).

Since the other four bands observed between the $0_0^0$ and $3_0^0$ transitions have originated at $v=0$ in the $\tilde{X}$ state, they can only belong to the $\nu_4$ and $\nu_5$ bending modes, the CCS and the CCH bends. A detailed discussion of the possible vibronic assignment of these four bands is presented in the next section.

### 5.5.2 Vibronic Analysis

As mentioned before, HCCS is a $^2\Pi$ linear molecule in both $\tilde{X}$ and $\tilde{A}$ electronic states. Thus, as discussed in Appendix A, the Renner-Teller effect is expected to be present in HCCS, as well as spin-orbit coupling. In order to be able to assign the vibronic transitions involving the bending modes of HCCS, it is necessary to calculate the energy diagram of the vibronic levels of the $\tilde{A}$ excited electronic state, taking into account vibronic and spin-orbit couplings, as was done for the MgNC radical. HCCS is a tetra-atomic molecule, therefore the formulas applied to MgNC, which were derived for triatomic molecules, will not be strictly appropriate for this radical.

The Renner-Teller effect for tetra-atomic molecules has been studied by Petelin and Kiselev [6], who derived analogous formulas to those for triatomic molecules.
However, these authors did not include the spin-orbit interaction in their treatment. Unfortunately, there is no theory yet that includes vibronic and spin-orbit coupling for tetra-atomic molecules. As stated in Appendix A, if it is assumed that there is no interaction between the two bending modes of the tetra-atomic molecule, then the formulas derived for triatomic molecules could be applied to each bending mode separately. Pople’s equations [79] will then be applied to HCCS, to obtain at least an approximate picture of the combined effects of Renner-Teller and spin-orbit interactions in the $\tilde{A}$ state of HCCS.

In order to calculate the energy of the bending vibronic levels with Pople’s equations, the following parameters need to be known: the spin-orbit coupling constant $A_{so}'$, the harmonic vibrational frequencies $\omega_4'$ and $\omega_5'$, and the Renner-Teller parameters $\epsilon_4'$ and $\epsilon_5'$. The only value reported up to date for $A_{so}'$ is -113 cm$^{-1}$, which was calculated with ab initio methods by Szalay and Blaudeau [80]. The values of the harmonic vibrational frequencies of HCCS in the $\tilde{A}$ state have been calculated by Szalay, using CCSD(T) methods [76]. More recently, Li and Iwata have determined the vibrational frequencies of HCCS using very accurate ab initio methods (CASSCF), but only the $\tilde{X}$ state frequencies were calculated [77].

The bending frequencies calculated by Szalay were the “perturbed” Renner-Teller frequencies, not the harmonic bending frequencies. At the distorted geometry, the upper ($\Sigma^+$) and the lower ($\Sigma^-$) Renner-Teller surfaces correspond to the $^2A'$ and $^2A''$ states of the $C_2$ symmetry, and these were the ones calculated by Szalay and Li &
Iwata [76, 77]. From these two surfaces, the vibrational contribution to the energy of the \( \Sigma^+ \) and \( \Sigma^- \) states, \( \omega^+ \) and \( \omega^- \), are obtained and from the Renner-Teller equations [81] the following relation can be derived:

\[
\omega = \frac{\omega^+}{\sqrt{1 + \epsilon}} = \frac{\omega^-}{\sqrt{1 - \epsilon}} \tag{5.7}
\]

With the calculated values of \( \omega^+ \) and \( \omega^- \), and using equation 5.7, the unperturbed harmonic frequency \( \omega \), and the Renner-Teller parameter \( \epsilon \), can be obtained.

<table>
<thead>
<tr>
<th>bending mode</th>
<th>bending frequency ( (\omega'_i \text{, in cm}^{-1}) )</th>
<th>Renner-Teller parameter ( (\epsilon'_i) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCS bend</td>
<td>423</td>
<td>0.085</td>
</tr>
<tr>
<td>CCH bend</td>
<td>367</td>
<td>-0.46</td>
</tr>
<tr>
<td>( \tilde{A}'_e )</td>
<td>-113</td>
<td></td>
</tr>
</tbody>
</table>

Table 5: Szalay's \textit{ab initio} values for the bending frequencies, Renner-Teller parameters and spin-orbit coupling constant of the \( \tilde{A} \) electronic state of HCCS.

In Table 6 the calculated energies of the bending vibronic levels, up to \( v=2 \), are shown. These vibronic energies were calculated using Pople's equations, and Szalay's \textit{ab initio} values for the bending frequencies, Renner-Teller parameters and spin-orbit coupling constant of the \( \tilde{A} \) electronic state, presented in Table 5. The column labeled "Equation" in Table 6 contains references to the equations from Appendix A that were used in each case. The experimental energies of the observed bending transitions are: 354, 359, 657, and 712 cm\(^{-1}\). However those frequencies were determined from the \( 0^0_0 \) transition, while the energies calculated with equations from
section A.2.1, in Appendix A, are the energies from the v=0 level of the \( \tilde{A} \) state. The frequency of the experimental bands, with respect to v=0, are: 297.5, 302.5, 600.5, and 655.5 cm\(^{-1}\), when \( A_{\text{vo}} \) is set equal to -113 cm\(^{-1}\)(the same value used in the calculations). The vibronic symmetry of all these levels is \( ^2\Pi_{3/2} \).

<table>
<thead>
<tr>
<th>( \nu )</th>
<th>( K )</th>
<th>Equation( ^a )</th>
<th>Vibronic level</th>
<th>CCS bend</th>
<th>CCH bend</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1</td>
<td>A.23</td>
<td>( \kappa \Pi_{3/2} )</td>
<td>923</td>
<td>973</td>
</tr>
<tr>
<td></td>
<td></td>
<td>A.23</td>
<td>( \kappa \Pi_{1/2} )</td>
<td>919</td>
<td>947</td>
</tr>
<tr>
<td></td>
<td></td>
<td>A.24</td>
<td>( \mu \Pi_{1/2} )</td>
<td>771</td>
<td>483</td>
</tr>
<tr>
<td></td>
<td></td>
<td>A.24</td>
<td>( \mu \Pi_{3/2} )</td>
<td>767</td>
<td>457</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>A.22</td>
<td>( \Phi_{5/2} )</td>
<td>897</td>
<td>656</td>
</tr>
<tr>
<td></td>
<td></td>
<td>A.22</td>
<td>( \Phi_{7/2} )</td>
<td>785</td>
<td>579</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>A.21</td>
<td>( \Sigma^+ )</td>
<td>490</td>
<td>535</td>
</tr>
<tr>
<td></td>
<td></td>
<td>A.21</td>
<td>( \Sigma^- )</td>
<td>356</td>
<td>179</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>A.22</td>
<td>( \Delta_{3/2} )</td>
<td>477</td>
<td>356</td>
</tr>
<tr>
<td></td>
<td></td>
<td>A.22</td>
<td>( \Delta_{5/2} )</td>
<td>365</td>
<td>261</td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>A.22</td>
<td>( \Pi_{1/2} )</td>
<td>56.5</td>
<td>56.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>A.22</td>
<td>( \Pi_{3/2} )</td>
<td>-56.5</td>
<td>-56.6</td>
</tr>
</tbody>
</table>

\( ^a \)Equations from section A.2.1, in Appendix A.

Table 6: Energy (in cm\(^{-1}\)) of the bending vibronic levels of the \( \tilde{A} \) electronic state of HCCS, calculated using Pople's equations, and Szalay's \textit{ab initio} values for the bending frequencies, Renner-Teller parameters and spin-orbit coupling constant.

As can be seen in Table 6, there are two \( ^2\Pi_{3/2} \) states in the v=2 level of each bending mode, the so-called \( \kappa \) and \( \mu \) \( ^2\Pi_{3/2} \) states. A comparison between the calculated and experimental energies shows that they are in very poor agreement. Since the discrepancy between the experimental and the calculated values is so large, it suggests that either some of the \textit{ab initio} values are not a good estimate of the HCCS
parameters, or the assumption of non-interacting bending modes is not valid for the
HCCS radical.

In Szalay's calculation, UHF based methods were used. According to Szalay, this
was possible since no significant spin contamination was present for HCCS [76]. This
is in contrast to the recent paper by Li & Iwata, who reported that $< S^2 >$ was
0.943 for HCCS, as opposed to the ideal 0.75, and they concluded that this spin
contamination showed the necessity of studying the electronic structure of HCCS
with multi-reference wavefunctions [77]. Such a large value of $< S^2 >$ indicates
that a single-reference method such as CCSD(T) (as used by Szalay) may not be
appropriate for HCCS [77].

Using Szalay's \textit{ab initio} values the observed transitions could not be explained,
consequently another procedure was applied. Possible assignments were assumed
for the observed transitions, and the values of $|\epsilon|$ and $\omega$ were calculated using the
appropriate equations. If the values obtained in this way for $|\epsilon|$ and $\omega$ for a particular
assignment, are in some way unreasonable for HCCS, then that assignment can be
discarded.

The observed transitions have frequencies of 354, 359, 657, and 712 cm$^{-1}$, mea-
sured from the $0^0_0$ transition. Since all of these transitions originate in the $v=0$
level of the $\bar{X}$ state, these frequencies correspond to the energy difference between the up-
per state of each transition and the vibrationless level of the $\bar{A}$ state, the $^2\Pi_{3/2, v=0}$
level. The frequency of this state, with respect to the $v=0$ level, is $-\frac{|A|}{2}$ ($A$ being

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the spin-orbit coupling constant of the $\tilde{A}$ state, $A_{s0}'$), and the frequencies of the observed states (with respect to the $v=0$ level) are: $354-\frac{|\Delta l|}{2}$, $359-\frac{|\Delta l|}{2}$, $657-\frac{|\Delta l|}{2}$, and $712-\frac{|\Delta l|}{2}$ cm$^{-1}$. Since the vibronic symmetry of all the observed states is $^{2}\Pi_{3/2}$, they must be states with even quanta of bending frequency (see Figure 31, in Appendix A). For each of these levels with even quanta of bending frequency, there are only two states with $^{2}\Pi_{3/2}$ vibronic symmetry: the so-called $^\mu\,^{2}\Pi_{3/2}$, at $-\frac{A_{e\,LL}}{2}$ from the harmonic frequency, where $A_{e\,LL}$ represents the spin-orbit coupling constant which has been quenched by the Renner-Teller effect; and the $^\kappa\,^{2}\Pi_{3/2}$ state, at $+\frac{A_{e\,LL}}{2}$ from the harmonic frequency. The following possible assignments for these four vibronic transitions will be considered:

(1) Two of the four observed $^{2}\Pi_{3/2}$ states correspond to the $^\mu$ and $^\kappa$ pair of $^{2}\Pi_{3/2}$ states of the $v=2$ level for one of the bending modes, and the other two observed $^{2}\Pi_{3/2}$ states correspond to the $^\mu$ and $^\kappa$ pair of $^{2}\Pi_{3/2}$ states of the $v=2$ level of the other bending mode.

(2) Two $^{2}\Pi_{3/2}$ states are the $^\mu\,^{2}\Pi_{3/2}$ state of $v=2$ and the $^\mu\,^{2}\Pi_{3/2}$ state of $v=4$ of $\nu_4$, and the other two levels are the $^\mu\,^{2}\Pi_{3/2}$ state of $v=2$ and $^\mu\,^{2}\Pi_{3/2}$ state of $v=4$ of $\nu_5$.

(3) Two $^{2}\Pi_{3/2}$ states are the $^\mu,^\kappa\,^{2}\Pi_{3/2}$ states of $v=2$ of $\nu_4$, and the other two levels are the $^\mu\,^{2}\Pi_{3/2}$ state of $v=2$ and $^\mu\,^{2}\Pi_{3/2}$ state of $v=4$ of $\nu_5$.

(4) There is no Renner-Teller effect in the $\tilde{A}$ electronic state of HCCS, or at least the parameters are so small that the splitting due to the Renner-Teller interaction is too small to be observed experimentally. The four observed transitions correspond to
transitions to \( v=1 \) and \( v=2 \) levels of each bending mode.

**CASE 1**

Of the four observed \( ^2\Pi_{3/2} \) levels, two are the \( \mu, \kappa \) pair of \( ^2\Pi_{3/2} \) levels from \( v=2 \) of the CCH bend, for example, and the other two states are the \( \mu, \kappa \) pair of \( ^2\Pi_{3/2} \) levels from \( v=2 \) of the CCS bend, or vice versa, as represented in the following figure:

![Diagram of bending mode levels](image)

**Figure 27:** CASE 1- Of the four \( ^2\Pi_{3/2} \) states experimentally observed for the bending modes, two are the \( \mu, \kappa \) pair of states from the \( v=2 \) level of the CCH bending mode, and the other two states are the \( \mu, \kappa \) pair of \( ^2\Pi_{3/2} \) levels from \( v=2 \) of the CCS bend.

For this possible assignment there are two different ways of grouping the levels:

(i) the \( 354-\frac{|A|}{2} \) and \( 657-\frac{|A|}{2} \) states are one pair (i.e. the \( \mu \) and \( \kappa \) \( ^2\Pi_{3/2} \) states for one of the bending modes); and the \( 359-\frac{|A|}{2} \) and \( 712-\frac{|A|}{2} \) correspond to the other pair.

(ii) \( 354-\frac{|A|}{2} \) and \( 712-\frac{|A|}{2} \) are the \( \mu \) and \( \kappa \) \( ^2\Pi_{3/2} \) states for one of the bending modes, and \( 359-\frac{|A|}{2} \) and \( 657-\frac{|A|}{2} \) are the other.
Pople's equations that correspond to the energy of these vibronic levels are:

\[
E(\mu^2\Pi_{3/2}) = 2\omega \left(1 - \frac{1}{8} \epsilon^2\right) - \frac{1}{2} \sqrt{A^2 + 8\epsilon^2\omega^2} + \frac{3}{8} \frac{A\epsilon^2 \omega}{\sqrt{A^2 + 8\epsilon^2\omega^2}} \tag{5.8}
\]

\[
E(\kappa^2\Pi_{3/2}) = 2\omega \left(1 - \frac{1}{8} \epsilon^2\right) + \frac{1}{2} \sqrt{A^2 + 8\epsilon^2\omega^2} - \frac{3}{8} \frac{A\epsilon^2 \omega}{\sqrt{A^2 + 8\epsilon^2\omega^2}} \tag{5.9}
\]

These equations should be applied separately for each bending mode, to the two cases discussed above. However, since in each case there are two equations and three unknowns: \(A, |\epsilon|, \omega\), one of these parameters must be substituted for a known value. Szalay’s \textit{ab initio} value for \(A'_{so}\) (-113 cm\(^{-1}\)) was substituted, and the equations were solved for \(|\epsilon|\) and \(\omega\). Then the value of \(A'_{so}\) was changed and the equations solved again for \(|\epsilon|\) and \(\omega\), and this procedure was repeated for five different values of \(A'_{so}\). This was done in order to establish the dependence of the solutions on the \(A'_{so}\) value, since only an \textit{ab initio} estimate of \(A'_{so}\) is known.

For case (i), equation 5.8 was set equal to \(354 - \frac{1}{2} |A|\) and equation 5.9 was set equal to \(657 - \frac{1}{2} |A|\), for one of the bending modes. The next table summarizes the obtained solutions for this case. Exactly the same was done for the other pair of \(^2\Pi_{3/2}\) states: equation 5.8 was set equal to \(359 - \frac{1}{2} |A|\) and equation 5.9 was set equal to \(712 - \frac{1}{2} |A|\), for the other bending mode. The solutions obtained in this case are also summarized in the next table.
The same procedure was performed for possibility (ii), as discussed above:

\[ E(\mu \Pi_{3/2}) = 354 - \frac{|A|}{2}, \quad \text{and} \quad E(\eta \Pi_{3/2}) = 712 - \frac{|A|}{2} \]

for one of the bending modes; and

\[ E(\mu \Pi_{3/2}) = 359 - \frac{|A|}{2}, \quad \text{and} \quad E(\eta \Pi_{3/2}) = 657 - \frac{|A|}{2} \]

for the other bend.

The solutions in this case are:

| \( A'_{so} \) (cm\(^{-1}\)) | \( |\varepsilon| \) | \( \omega \) (cm\(^{-1}\)) | \( A'_{so} \) (cm\(^{-1}\)) | \( |\varepsilon| \) | \( \omega \) (cm\(^{-1}\)) |
|-----------------|--------|------|-----------------|--------|------|
| -30             | 0.42   | 251  | -30             | 0.46   | 267  |
| -90             | 0.42   | 235  | -90             | 0.46   | 252  |
| -140            | 0.40   | 222  | -140            | 0.45   | 239  |
| -200            | 0.36   | 206  | -200            | 0.43   | 223  |

Summary of CASE 1:

1) This assignment is possible, since it gives reasonable solutions for \( |\varepsilon| \) and \( \omega \), the values obtained for \( |\varepsilon| \) are < 1, and the solutions for \( \omega \) although somewhat smaller than the \textit{ab initio} values, do not seem unreasonable.

2) The solutions for \( |\varepsilon| \) and \( \omega \) are not very sensitive to the value of \( A'_{so} \). When
$A'_{so}$ was changed by 74%, the values of $|e|$ and $\omega$ only change 3-8% and 9-10%, respectively. This small dependence of $|e|$ and $\omega$ on the value of $A'_{so}$ can be regarded as advantageous, given the unproven reliability of the $A'_{so}$ known. Therefore, even if the \textit{ab initio} value of $A'_{so}$ is not very accurate, the calculated $|e|$ and $\omega$ here will not be affected too much by the change in $A'_{so}$.

3) Since the two lower frequency levels, at $354-\frac{|A|}{2}$ and $359-\frac{|A|}{2}$, are so close in energy, the different ways of grouping the levels (case (i) and (ii)) give very similar solutions, as can be seen in the table below. With the present data only, it is not possible to choose among these two possible cases. In other words, it is not possible to determine which pair of $^2\Pi_{3/2}$ states belongs to one bending mode, and which one belongs to the other. However, the different values of $|e|$ and $\omega$ in those two cases are very close (see table below).

A summary of the solutions for CASE 1 is shown in the following table. The range of values of $|e|$ and $\omega$ are non-statistical, they only represent the values that were obtained as solutions when the following values for $A'_{so}$ were substituted into the equations: -30, -90, -113, -140 and -200 cm$^{-1}$.

<table>
<thead>
<tr>
<th>case :</th>
<th>$\nu_4$</th>
<th>$\nu_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i)</td>
<td>0.44 ± 0.01</td>
<td>0.39 ± 0.03</td>
</tr>
<tr>
<td>(ii)</td>
<td>0.45 ± 0.01</td>
<td>0.38 ± 0.03</td>
</tr>
<tr>
<td>$\omega$ (cm$^{-1}$)</td>
<td>245 ± 22</td>
<td>228 ± 22</td>
</tr>
<tr>
<td></td>
<td>244 ± 22</td>
<td>228 ± 22</td>
</tr>
</tbody>
</table>
CASE 2

Another possible assignment is to assume that two $^2\Pi_{3/2}$ states are the $^2\Pi_{3/2}$ from the $v=2$ level and the $^2\Pi_{3/2}$ from $v=4$, for each bending mode, as illustrated in the next figure.

Figure 28: CASE 2- Of the four $^2\Pi_{3/2}$ states experimentally observed for the bending modes, two are the $^2\Pi_{3/2}$ states from the $v=2$ level (one for each bending mode), and the other two states are the $^2\Pi_{3/2}$ states from $v=4$ level.

This possibility was explored since one of the higher energy $^2\Pi_{3/2}$ states is at twice the frequency of the lower energy states: $354 \times 2 = 708$ and $359 \times 2 = 718$, both values very close to the 712 cm$^{-1}$ $^2\Pi_{3/2}$ state. The other high energy $^2\Pi_{3/2}$ state is at 657 cm$^{-1}$, which is 50 cm$^{-1}$ "off" of twice the value of the lower $^2\Pi_{3/2}$ states (708 and 718 cm$^{-1}$). However, when the Renner-Teller effect is present, the splittings of the levels
depend on \( v \) (where \( v \) corresponds to the number of quanta of the bending mode). Thus the overtones to \( v=2 \) and to \( v=4 \), are not necessarily at twice the frequency from each other. Additionally, anharmonicity has not been taken into account, which could be very important, especially in the bending modes of HCCS. Therefore, this CASE 2 seems to be a possible assignment. For this case there are also two ways of assigning the levels:

(i)

\[
E(\mu^2 \Pi_3/2, v=2) = 354 - \frac{|A|}{2}, \quad \text{and} \quad E(\mu^2 \Pi_3/2, v=4) = 657 - \frac{|A|}{2}
\]

for one of the bending modes;

and \( E(\mu^2 \Pi_3/2, v=2) = 359 - \frac{|A|}{2}, \quad \text{and} \quad E(\mu^2 \Pi_3/2, v=4) = 712 - \frac{|A|}{2} \)

for the other mode.

(ii)

\[
E(\mu^2 \Pi_3/2, v=2) = 354 - \frac{|A|}{2}, \quad \text{and} \quad E(\mu^2 \Pi_3/2, v=4) = 712 - \frac{|A|}{2}
\]

for one of the bending modes;

and \( E(\mu^2 \Pi_3/2, v=2) = 359 - \frac{|A|}{2}, \quad \text{and} \quad E(\mu^2 \Pi_3/2, v=4) = 657 - \frac{|A|}{2} \)

for the other mode.

Equation 5.8 is used again to calculate the energy of the \( \mu^2 \Pi_3/2 \) levels of \( v=2 \), and the following equation is applied to the \( \mu^2 \Pi_3/2 \) levels of \( v=4 \):

\[
E(\mu^2 \Pi_3/2) = 4\omega \left( 1 - \frac{1}{8} \epsilon^2 \right) - \frac{1}{2} \sqrt{A^2 + 24\epsilon^2\omega^2} + \frac{5 A \epsilon^2 \omega}{8 \sqrt{A^2 + 24\epsilon^2\omega^2}}
\]

(5.10)

In case (i) and for the 354-\( \frac{|A|}{2} \) & 657-\( \frac{|A|}{2} \) pair, the solutions obtained for \( |\epsilon| \) and \( \omega \) are either imaginary numbers, or real numbers that do not make any physical sense: negative values of \( \omega \), or values of \( |\epsilon| > 1 \). However, for the other pair (359-\( \frac{|A|}{2} \) & 712-\( \frac{|A|}{2} \)), the following solutions were found:
(a) When $A'_{so}$ was put equal to -30 cm$^{-1}$, the solution of the equations gave imaginary numbers for $|\epsilon|$ and $\omega$.

For each value of $A'_{so}$, two possible solutions for $|\epsilon|$ and $\omega$ were found. These solutions can be grouped as two separate sets: in one case $|\epsilon_1| = 0.15 \pm 0.01$ and $\omega_1 = 185 \pm 1$ cm$^{-1}$, and in the other case $|\epsilon_2| = 0.36 \pm 0.13$ and $\omega_2 = 219 \pm 20$ cm$^{-1}$. The latter solution is closer to the values obtained in the previous case, but the change in $|\epsilon|$ with different $A'_{so}$ is much larger: a 74% change in $A'_{so}$ produced a 36% change in $|\epsilon|$.

Similar to case (i), for case (ii), when the equations were set equal to $359 - \frac{|A|}{2}$ & $657 - \frac{|A|}{2}$, the solutions obtained for $|\epsilon|$ and $\omega$ were either imaginary numbers or values which do not make physical sense (see above). For the other pair of $^2\Pi_{3/2}$ states ($354 - \frac{|A|}{2}$ & $712 - \frac{|A|}{2}$), the following solutions were found:
A summary of the solutions for both case(i) and (ii) can be found in the following table (as in the previous case, the range of values of $|\epsilon|$ and $\omega$ listed in this table are non-statistical, they only represent the values that were obtained as solutions when different values of $A'_{so}$ were substituted into the equations).

| $A'_{so}$ (cm$^{-1}$) | $|\epsilon|$ | $\omega$ (cm$^{-1}$) |
|----------------------|-----------|----------------|
| -30                 | 0.20      | 201           |
| -90                 | 0.39      | 228           |
| -113                | 0.44      | 237           |
| -140                | 0.50      | 247           |
| -200                | 0.59      | 269           |

Summary of CASE 2:

1) Although in theory there would be two ways of grouping the four observed levels for CASE 2, it was found that meaningful solutions are obtained only when either of the lower energy $^2\Pi_{3/2}$ states are assigned as the $\mu^2\Pi_{3/2}$ state from $v=2$ and the state at 712$-\frac{|A|}{2}$ is assumed to be the $\mu^2\Pi_{3/2}$ state from $v=4$. The assignment of 657$-\frac{|A|}{2}$ cm$^{-1}$ as a $\mu^2\Pi_{3/2}$ state from $v=4$ does not seem correct, as it gives wrong values (from a physical point of view) of $|\epsilon|$ and $\omega$.

2) The change in $|\epsilon|$ with $A'_{so}$ with $A'_{so}$ is much larger than in the previous case (see table above).
3) There is one problem with this assignment that needs to be addressed. If the transition to the $\mu^2 \Pi_{3/2}$ state of $v=2$ is observed, a transition to the $\kappa^2 \Pi_{3/2}$ state of $v=2$ would be observed in the probed region, so another $^2 \Pi_{3/2}$ state would have been observed in this region. On the other hand, the $\kappa^2 \Pi_{3/2}$ state from $v=4$ would be out of the frequency range probed here.

CASE 3

In view of the results obtained for CASE 2, an alternative assignment would be a mixture of the two previous cases: either the $354-\frac{l_{1}l}{2}$ or the $359-\frac{l_{1}l}{2}$ level is the $\mu^2 \Pi_{3/2}$ state from $v=2$ and the $712-\frac{l_{1}l}{2}$ is the $\mu^2 \Pi_{3/2}$ state from $v=4$ for one bending mode; and either the $354-\frac{l_{1}l}{2}$ or the $359-\frac{l_{1}l}{2}$ level is the $\mu^2 \Pi_{3/2}$ state from $v=2$ and the $657-\frac{l_{1}l}{2}$ is the $\kappa^2 \Pi_{3/2}$ state from $v=2$ for the other bending mode. The appropriate set of equations for this case were already solved previously (in CASE 1 and CASE 2), therefore, only a summary of the combination of those will follow.

(i)

$E(\mu^2 \Pi_{3/2}, v=2) = 354 - \frac{l_{1}l}{2}$, and $E(\mu^2 \Pi_{3/2}, v=4) = 712 - \frac{l_{1}l}{2}$ for one of the bending modes; and $E(\mu^2 \Pi_{3/2}, v=2) = 359 - \frac{l_{1}l}{2}$, and $E(\kappa^2 \Pi_{3/2}, v=2) = 657 - \frac{l_{1}l}{2}$ for the other mode.

(ii)

$E(\mu^2 \Pi_{3/2}, v=2) = 359 - \frac{l_{1}l}{2}$, and $E(\mu^2 \Pi_{3/2}, v=4) = 712 - \frac{l_{1}l}{2}$ for one of the bending modes; and $E(\mu^2 \Pi_{3/2}, v=2) = 354 - \frac{l_{1}l}{2}$, and $E(\kappa^2 \Pi_{3/2}, v=2) = 657 - \frac{l_{1}l}{2}$ for the other mode.
Summary of CASE 3:

1) For $\nu_5$, three different values of $|\varepsilon|$ and $\omega$ were obtained, two of which are very close but the third one is quite different. Unfortunately, there is no way by which one solution could be chosen over the other.

2) The other problem with this assignment (as was pointed in CASE 2), is that the transition to the $\kappa^2 \Pi_{3/2}$ state of $v=2$ has not been observed.

**CASE 4**

There is only one more possible vibronic assignment, and this involves the assumption that there is no Renner-Teller effect in the $\tilde{A}$ state of HCCS, or at least the Renner-Teller parameters are so small, that their effect cannot be experimentally observed. In the absence of a Renner-Teller interaction, since the bending modes are non-totally symmetric vibrations, the selection rule for an electronic transition is: $\Delta v = 0, \pm 2, \pm 4, \ldots$. In this case, the observed transitions to the $354-\frac{|A|}{2}$ and $359-\frac{|A|}{2}$ levels in the $\tilde{A}$ state could be assigned as the transitions to $v=2$ of each bending mode; while the transitions to $657-\frac{|A|}{2}$ and $712-\frac{|A|}{2}$ could be assigned to $v=4$. This is supported by the fact that $712$ cm$^{-1}$ is equal to $356 \times 2$. For the other case, although $657$ is smaller than either $2 \times 354$ or $2 \times 359$, the difference could be attributed to anharmonicity. This assignment, however, would give a vibrational
frequency for the bending modes of: $\omega_4 = 179.5 = \frac{359}{2}$ and $\omega_5 = 177 = \frac{354}{2}$ cm$^{-1}$, which seem quite small for the HCCS radical, if compared with the frequencies predicted by \textit{ab initio} methods ($\omega_4 = 423$ cm$^{-1}$, and $\omega_5 = 367$ cm$^{-1}$, [76]), or with frequencies of similar molecules: for HCCCl, the CCH bend frequency has been measured as 604 cm$^{-1}$, whereas the CCCl bending frequency was 326 cm$^{-1}$ [82], and the frequencies for the HCCO radical have been calculated as follows: CCH bend = 328 cm$^{-1}$, and CCO bend = 525 cm$^{-1}$[83].

If, however, it is assumed that the lower energy observed features are transitions to the $v=1$ level, the bending vibrational frequencies would be 354 and 359 cm$^{-1}$, which are more comparable with the \textit{ab initio} values. If this is the case, there needs to be a mechanism by which these forbidden transitions become allowed. A Herzberg-Teller interaction is a possible means by which non-totally symmetric vibrational transitions may be observed in odd quanta. The Herzberg-Teller effect is another case of vibronic coupling caused by the breakdown of the Born-Oppenheimer approximation. Forbidden vibronic transitions are observed because of intensity "borrowing" from a nearby electronic state.

Unfortunately, very little is known about the $\tilde{B}$ or other electronic states of HCCS. As mentioned before, many similarities have been found between the HCCS and NCS radicals. The $\tilde{A} \ ^2\Pi$ electronic state of HCCS is very close in energy to the corresponding state in NCS: the origin of the $\tilde{A} \leftarrow \tilde{X}$ transition is at 24,300 and 26,054 cm$^{-1}$ for HCCS and NCS, respectively [84]. For NCS, the origin of the $\tilde{B} \leftarrow \tilde{X}$ transition is at 26,809.3 cm$^{-1}$ [78]. Since the difference in energy between
the Ā and the Ń states in NCS is so small, experimental studies showed evidence of strong interaction between these two states [59, 78, 84]. Since the Ā states of NCS and HCCS are so close in energy, it is expected that the same is true for the Ń \(^2\Sigma\) electronic state [64, 68, 69]. If this is the case, the above hypothesis of interactions with other electronic states seems plausible. However, in the recent \textit{ab initio} paper of Li and Iwata, potential curves for the low-lying electronic states (᪠, Ā and Ń states) of NCS and HCCS were presented. According to these calculations, although the calculated energy difference between the two excited states of NCS is very small, in agreement with experiments, the gap between the two excited states of HCCS is not so small [77].

There is some additional experimental data on HCCS, reported by Kohguchi \textit{et al.} [72], which could support this assumption that there is no Renner-Teller interaction in the Ā state of HCCS. It should be noted, however, that the resolution of their system was only \(\sim 0.1 \text{ cm}^{-1}\), so that they were only able to observe the rotational contours of the transitions. Thus, their assignment of the symmetry of the vibronic states was only based on the rotational contours of their LIF spectra, and not on a full rotational analysis as the ones described in this dissertation.

Since in their experiment the HCCS radicals were produced in an electric discharge, the radicals were not only in the lowest energy \(^2\Pi_{3/2}\) state, but also in the other spin-orbit component of the \(v=0\) level, the \(^2\Pi_{1/2}\) state. It was possible then to observe not only the \(^2\Pi_{3/2} \leftarrow ^2\Pi_{3/2}\) transitions, but also the \(^2\Pi_{1/2} \leftarrow ^2\Pi_{1/2}\) transitions in their LIF spectrum. The four \(^2\Pi_{3/2} \leftarrow ^2\Pi_{3/2}\) transitions that were observed
in the present work were also recorded by Kohguchi and coworkers. Three further features, \( ^2\Pi_{1/2} \leftarrow ^2\Pi_{1/2} \) transitions, were observed and assigned as corresponding to the \( \Omega = \frac{1}{2} \) spin-orbit components of three of the \( ^2\Pi_{3/2} \leftarrow ^2\Pi_{3/2} \) transitions mentioned above. These three \( ^2\Pi_{1/2} \leftarrow ^2\Pi_{1/2} \) transitions may be measured from Figure 1 in Kohguchi's paper as \( \sim 356+\frac{4}{2}, 650+\frac{4}{2} \) and \( 690+\frac{4}{2} \) from the \( v=0 \) level of the \( \tilde{A} \) state [72]. These are all almost exactly at \( A_{s0}' \) above the \( ^2\Pi_{3/2} \) levels. This seems to give support to the assignment discussed previously (CASE 4), since Kohguchi's data imply that the energy difference between the \( ^2\Pi_{3/2} \) and the \( ^2\Pi_{1/2} \) states is equal to the spin-orbit constant, \( A_{s0}' \). If there were a Renner-Teller interaction, then the separation between these states would not be \( A_{s0}' \) but an effective spin-orbit splitting constant, modified by the vibronic interaction as follows [81]:

\[
A_{s0,K}' = \sqrt{A_{s0}^2 + [(v + 1)^2 - K^2]e^2\omega^2}
\]

(5.11)

5.6 Conclusions

Rotational constants for the \( 0^0_0 \) and \( 3^0_1 \) bands of the \( \tilde{A} \ ^2\Pi \leftarrow \tilde{X} \ ^2\Pi \) electronic transition of HCCS are obtained (\( \nu_3 \) being the CS stretch mode of HCCS). The ground state rotational constant agreed with previously reported values [64, 71]. The rotational constants for the excited states are reported here for the first time. Rotationally resolved spectra are obtained for the first time for four other vibrational features of the \( \tilde{A} \ ^2\Pi \leftarrow \tilde{X} \ ^2\Pi \) electronic transition of HCCS. These bands are assigned as transitions involving the CCS and CCH bending modes of HCCS (\( \nu_4 \) and \( \nu_5 \)), since
they are vibrationally cold bands observed between the origin and the 30 band. The
analysis of their spectra yield the vibronic symmetries of the states involved in the
transitions, as well as their molecular parameters.

A thorough discussion of possible assignments of these four vibronic transitions
was presented. For each possible case, Pople's equations, derived to estimate the en­
ergy of vibronic levels when Renner-Teller and spin-orbit interactions are present [79],
were applied to each bending mode separately, and solved for |e| and ω. However,
as mentioned earlier, Pople's equations will apply to HCCS only if the interaction
between the bending modes is negligible, and that might not be the case for HCCS.
A summary of the different possible cases follows:

(I) The four 2Π3/2 states correspond to the μ and κ pair of 2Π3/2 states of the
v=2 level, for each bending mode. If A′so is allowed to vary in the range -115±85
cm⁻¹ (A′so = -30, -90, -113, -140 and -200 cm⁻¹), the following values of |e| and ω are
obtained:
ν4: |e| = 0.45±0.01 and ω = 244±22 cm⁻¹
ν5: |e| = 0.38±0.03 and ω = 229±23 cm⁻¹

(II) Two 2Π3/2 states are the μ, κ2Π3/2 pair of v=2 of one of the bending modes,
and the other two states are the μ 2Π3/2 state of v=2 and the μ 2Π3/2 state of v=4 of
the other bend. When A′ so is allowed to vary in the range -115±85 cm⁻¹, the values
obtained for |e| and ω are:
\[ \nu_4: |\epsilon| = 0.39 \pm 0.19 \text{ and } \omega = 232 \pm 34 \text{ cm}^{-1} \]

And for \( \nu_5 \) there are two possibilities:

(i) \( |\epsilon| = 0.37 \pm 0.13 \text{ and } \omega = 224 \pm 22 \text{ cm}^{-1} \);

or (ii) \( |\epsilon| = 0.15 \pm 0.01 \text{ and } \omega = 185 \pm 1 \text{ cm}^{-1} \).

(III) There is no Renner-Teller effect in the \( \tilde{\text{A}} \) electronic state of HCCS, or at least the parameters are so small that the splitting due to the Renner-Teller interaction is too small to be observed experimentally. Forbidden transitions to the \( v=1 \) level are observed, probably due to the Herzberg-Teller effect. The bending frequencies are:

\[ \omega_4 = 359 \text{ cm}^{-1}, \text{ and } \omega_5 = 354 \text{ cm}^{-1}. \]

The last possibility (III) seems the most probable in view of the assignments of Kohguchi et al. and on the bending frequencies obtained. However, with only the present data, it is not possible to determine, unambiguously, which of these different possibilities is the correct vibronic assignment.

For NCS, only the extensive experimental work performed by Sears and Northrup [59, 78] allowed these authors to determine the bending vibronic structure in the \( \tilde{\text{X}} \) electronic state of NCS. The authors were able to analyze many vibronic levels of the ground, first and second electronic states, applying a variety of spectroscopic techniques (laser induced fluorescence, dispersed fluorescence and stimulated emission pumping). The bending structure of HCCS is even more complicated than NCS, since in HCCS there are two bending vibrations instead of one, which according to
*ab initio* predictions, are very close in energy.

More experimental work is needed in order to understand the vibronic structure of the bending modes of HCCS. For example, rotationally resolved spectra of the features observed by Kohguchi *et al.*, presumably $^2\Pi_{1/2} \leftarrow ^2\Pi_{1/2}$ transitions, would determine the vibronic symmetry of those bands.

A detailed rotational study of the DCCS radical would be very helpful in determining the vibrational structure of the bending modes, in terms of the isotopic shifts observed. It would be possible to discriminate between the two bending modes, since they would have different isotopic shifts. Similarly, HCCS radicals with isotopically enriched sulfur could be used with this purpose as well.

An experimental determination of the $A'_{so}$ coupling constant is desirable, since only an *ab initio* estimate is known up to date. Since the $\Delta A = A'_{so} - A''_{so}$ has been measured experimentally [69, 72], determining only one of the two constants, either $A'_{so}$ or $A''_{so}$, is necessary. One way of measuring one of the $A_{so}$ is to obtain transitions from the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ states of one electronic state to a common vibronic level in the other electronic state. For example, if the hot bands $\tilde{A} 0^2 \Pi_{1/2} \leftarrow \tilde{X} 4^1 \mu^2 \Sigma$ and $\tilde{A} 0^2 \Pi_{3/2} \leftarrow \tilde{X} 4^1 \mu^2 \Sigma$ can be obtained, then the difference in energy of these two transitions will give the $A'_{so}$ coupling constant.

More accurate *ab initio* studies on HCCS are necessary in order to be able to estimate an energy level diagram for the bending modes, which would help in assigning the experimental transitions. Also, a detailed study of the low-lying excited electronic states would be helpful to look at the possibility of interactions between the $\tilde{A}$ and
other electronic states.

Certainly an understanding of the vibronic structure of the HCCS radical would be very interesting, since that could be used to develop a theory for explaining the combined effects of Renner-Teller and spin-orbit coupling interactions in tetratomic molecules, which has yet to be done.
APPENDIX A

The Renner-Teller interaction.

The name Renner-Teller effect is used to describe the coupling of electronic orbital momentum with the vibrational angular momentum, and occurs in degenerate electronic states of linear molecules, although the concept has been extended to non-linear molecules that can become linear as a result of vibration. The idea was first developed by Renner in 1934 [85]. Since then this type of interaction has been extensively studied and its theory has been successfully applied to interpret the spectra of a large number of linear molecules. Two thorough reviews on this topic have been published by Jungen and Merer [86] and by Brown and Jørgensen [87].

The Renner-Teller effect causes the splitting of the degenerate electronic states of linear molecules through the coupling of the electronic and vibrational angular momenta. When the nuclei have a linear configuration, their charges do not interact with the motion of the electrons around the molecular axis. However, as soon as the nuclei adopt a non-linear configuration, their charges disturb the cylindrical motion of the electrons, causing coupling between the two angular momenta, and the degeneracy of the electronic motion is lifted. Therefore, there are two electronic potential functions, which cross at the linear configuration only, and they diverge when the
Figure 29: Potential functions \( W_k^+ \) and \( W_k^- \) of the bending mode in a \( ^2\Pi \) electronic state of a linear molecule with vibronic coupling. \( \rho \) is the bending coordinate. In part (a) the potentials are shown when the vibronic interaction is small, while part (b) shows the case when there is large vibronic interaction.
molecule bends. These potentials are normally referred as $W^+$ and $W^-$, where the 
± sign denotes the parity of the defining electronic wavefunction. The magnitude 
of the coupling between the two angular momenta determines the splitting of these 
two potentials, as it can be seen in the diagram of Figure 29. Consequently, when 
the Renner-Teller effect is present, it is no longer possible to separate the electronic 
and vibrational angular momenta, and the Born-Oppenheimer approximation breaks 
down. $\Lambda$ and $l$ (the projections along the axis of the electronic orbital and the vibra­
tional angular momenta, respectively) are no longer good quantum numbers, and so 
$K$ is defined as $K = \Lambda + l$, which is a good quantum number.

A.1 The Renner-Teller Hamiltonian.

In this Appendix the derivation of the Renner-Teller Hamiltonian and of its eigenval­
ues will be presented. The coordinate system that will be used in the derivation of the 
appropriate Hamiltonian is shown in Figure 30. The plane that contains the molecule 
at any moment, the molecular plane, lies at an angle $\chi$ with respect to an arbitrary 
reference plane (see Figure 30). The so-called azimuth angle $\nu$ of the electron is the 
angular distance of the electron with respect to the reference plane. If the dipole of 
the nuclei is $\mu$, and the electron is at a distance $r$ from it, the potential that the 
electron experiences can be written as:

$$V'(r, \nu - \chi) = \mu \cos(\nu - \chi)/r^2 + \text{higher terms in } \cos(\nu - \chi) \quad (A.1)$$

The interaction between the nuclear and electronic motions involves all the electrons, 
thus the Hamiltonian for this interaction is derived by averaging the energy of each
Figure 30: Coordinate system used to describe the Renner-Teller effect.
electron over the range of all its coordinates except $\nu$, and summing over the various
electrons. Here it is assumed that these steps have been carried out, and that $\nu$ no
longer refers to one electron.

In order to calculate the vibronic energy levels of the components of a degenerate
electronic state, the Hamiltonian can be defined as the sum of four terms,
\begin{equation}
H = H_{el}(\rho = 0) + H'_{el} + H_b + H_{rot} \tag{A.2}
\end{equation}
where a new coordinate, $\rho$, has been introduced and it denotes the amplitude of the
bending motion displacement from the linear configuration. The term $H_{el}(\rho = 0)$ is
the fixed-nuclei Hamiltonian for the linear molecule, $H_b$ corresponds to the kinetic
energy of the bending motion, and $H_{rot}$ is the rotation of the nuclei around the linear
axis $z$. The operator $H'_{el} = H_{el}(\rho) - H_{el}(\rho = 0)$ represents the additional interaction
between the nuclei and the electrons, when the nuclei move into a non-linear con­
figuration. Although it depends on all electronic and nuclear coordinates, only the
electronic coordinate $(\nu - \chi)$ and the bending amplitude $\rho$ need appear explicitly in
the Hamiltonian, since the Born-Oppenheimer approximation allows to average over
the other electronic coordinates. In equation A.1 the form of the interacting potential
between the dipole of the nuclei and one electron has been derived. In terms of these
two coordinates, $\nu - \chi$ and $\rho$, the operator $H'_{el}$ is a double power series in $\rho$ and
$\cos(\nu - \chi)$, which can be written as:
\begin{equation}
H'_{el} = V_0(\rho) + j_1 \rho \cos(\nu - \chi) + j_2 \rho^2 \cos 2(\nu - \chi) + ... \tag{A.3}
\end{equation}
where the parameters $j_i$ arise from averaging over the radial wavefunctions of the
electrons. $V_0(\rho)$ is a potential function (the potential for the bending motion), while
the other terms are coupling terms. The eigenvalue of $H_{el}(\rho = 0)$, $E_{el}(\rho = 0)$, is the energy at the linear configuration, and it can be included in $V_0(\rho)$.

The operator $H_{rot}$ has the form:

$$H_{rot} = \left( \frac{\hbar}{8\pi^2 c I} \right) (J_z - L_z)^2$$

(A.4)

where $I$ is the moment of inertia around the $z$ axis. $(J_z - L_z)$ is the vibrational angular momentum, and it is essentially the same as the $z$-axis rotational angular momentum as the bent molecule. Note that the rotation around the $x$ and $y$ axis will not be included in this treatment.

These expressions can be substituted in the Hamiltonian of equation A.2, which has the form:

$$H = H_b + H_{el} + H_{el}(\rho = 0) + H_{rot} = H_b + \left[ V_0(\rho) + j_1 \rho \cos(\nu - \chi) ight. \left. + j_2 \rho^2 \cos 2(\nu - \chi) \right] + \left[ \left( \frac{\hbar}{8\pi^2 c I} \right) (J_z - L_z)^2 \right]$$

(A.5)

Since the eigenvalue of $L_z$ can take the two values, $\pm \Lambda$, the vibronic wavefunction $\Psi(\nu, \chi, \rho)$ can be considered as a superposition of two functions, one for each component of the electronic state, $\Psi^\pm(\nu, \chi, \rho)$, and can be written in general form as:

$$\Psi^\pm(\nu, \chi, \rho) = \psi_{el}^\pm(\nu - \chi) \cdot (2\pi)^{-1/2} e^{-iKx} \psi_{v,K}^\pm(\rho)$$

(A.6)

where the quantum number $K$ has been introduced, the eigenvalue of $J_z$, and the "good" quantum number for labelling vibronic states. If $[H - E]\Psi(\nu, \chi, \rho) \rightarrow 0$ (where $H$ is the Hamiltonian defined above in equation A.5), is premultiplied by $(2\pi)^{-1/2} e^{-iKx} \psi_{el}^\pm$, and integrated over $\nu$ and $\chi$, the result is a differential equation
in the single variable \( \rho \), which involves two vibrational functions \( \psi_{v,K}(\rho) \) and \( \psi_{\bar{v},K}(\rho) \). A similar differential equation is obtained by premultiplying by \( (2\pi)^{-1/2} e^{-iKx} \psi_{el}^* \). Schrödinger equation.

With these definitions, the two coupled differential equations needed can be written into matrix form as:

\[
\begin{pmatrix}
\mathcal{H}_b + W^-_K(\rho) - E & H_K(\rho) \\
H_K(\rho) & \mathcal{H}_b + W^+_K(\rho) - E
\end{pmatrix}
\begin{pmatrix}
\psi_{\bar{v},K}(\rho) \\
\psi_{v,K}(\rho)
\end{pmatrix} = 0 \quad (A.7)
\]

The form of the coupling functions \( H_K(\rho) \) and the potential functions \( W_K^\pm(\rho) \), depends on the choice of suitable basis functions to treat the problem.

An appropriate choice is to choose the “linear molecule” basis functions, which can be written as:

\[
|\Lambda, v, l \rangle = (2\pi)^{-1/2} e^{i\Lambda \nu} \cdot (2\pi)^{-1/2} e^{ilx} \cdot \psi_{v,l}(\rho) \quad (A.8)
\]

where the first two parts are equivalent as treating the electron and nuclear motions as independent circular motions around the axis, and the last part, is a radial vibrational factor. The quantum number \( l \), is the eigenvalue of \( (J_z - L_z) \), so \( l = K - \Lambda \). With this choice of basis set, \( H_K(\rho) \) and \( W_K^\pm(\rho) \) can be written as:

\[
W^K_\pm(\rho) = V_0(\rho) + (\hbar/8\pi^2 c I)(K \pm \Lambda)^2
\]

\[
H_K(\rho) = \frac{1}{2} j_{2\Lambda} \rho^{2\Lambda} + ...
\quad (A.9)
\]

Renner made the following two approximations: (i) he considered the potential \( V_0(\rho) \) as a quadratic function, so that the Hamiltonians \( \mathcal{H}_b + W^-_K(\rho) \) become the well-known two-dimensional harmonic oscillator Hamiltonian; and (ii) he truncated the
function $H_K(\rho)$ after the first term, which is equivalent to keep only the second term in equation A.3, $j_2 \rho^2 \cos 2(\nu - \chi)$. This approximation gives the matrix elements within an electronic state, and Renner made his derivation for a II electronic state. However, the neglected term $(j_1 \rho \cos (\nu - \chi))$, becomes important when considering interactions within different electronic states, as it will be shown later, in section A.3. For convenience, the bending shift operators $\rho_+$ and $\rho_-$ will be introduce, since these have well-know matrix elements between the harmonic oscillator vibrational functions. The relation between $\rho$ and $\rho_+$ and $\rho_-$ is given by:

$$\rho_{\pm} = \rho e^{\pm i\chi} \quad (A.10)$$

Also, the matrix elements of $\rho^2$ are the same as those of $\rho_{\pm}^2$, since the integration over $\chi$ gives unity:

$$\langle l \pm 1 | e^{\pm i\chi} | l \rangle = (2\pi)^{-1} \int e^{-i(l\pm 1)\chi} e^{\pm i\chi} d\chi \rho_{\pm} = \rho e^{\pm i\chi} \quad (A.11)$$

The matrix elements of $\rho_{\pm}^2$ (and $\rho^2$) are:

$$\langle v + 2, l \pm 2 | \rho_{\pm}^2 | v, l \rangle = (h/8\pi^2 \mu \nu)[(v \pm l + 2)(v \pm l + 4)]^{1/2}$$

$$\langle v, l \pm 2 | \rho_{\pm}^2 | v, l \rangle = 2(h/8\pi^2 \mu \nu)[(v \mp l)(v \pm l + 2)]^{1/2} \quad (A.12)$$

$$\langle v - 2, l \pm 2 | \rho_{\pm}^2 | v, l \rangle = (h/8\pi^2 \mu \nu)[(v \mp l)(v \mp l - 2)]^{1/2} \quad (A.13)$$

### A.1.1 Energy of the vibronic levels.

Evaluation of the basis functions of equation A.8 with the Hamiltonians derived in equation A.9 gives the following vibronic energy matrix:
\[ |\Lambda = 1, v, l = K - 1 \rangle \quad |\Lambda = -1, v, l = K + 1 \rangle \]

\[ |\Lambda = 1, v, l = K - 1 \rangle \quad \omega (v + 1)(1 - \frac{1}{8} \epsilon^2) \quad \frac{1}{2} \epsilon \omega [(v + 1)^2 - K^2]^{1/2} \]

\[ |\Lambda = -1, v, l = K + 1 \rangle \quad \frac{1}{2} \epsilon \omega [(v + 1)^2 - K^2]^{1/2} \quad \omega (v + 1)(1 - \frac{1}{8} \epsilon^2) \]

The next step is to take linear combinations of the basis functions, and obtain the same vibronic energy matrix as before, but for the linear combinations of the basis functions. The resulting diagonal matrix gives the expression for the vibronic energy as follows:

\[ E(v, K) = \omega (v + 1)(1 - \frac{1}{8} \epsilon^2) \pm \frac{1}{2} \epsilon \omega [(v + 1)^2 - K^2]^{1/2} \quad (A.14) \]

This expression gives the energy of the vibronic levels. On the derivation of the Renner-Teller equations usually a distinction is made between \( K = 0 \) and \( K \neq 0 \) vibronic states, mainly following Renner’s original treatment. The expressions for the vibronic energies are as follows:

\[ E(v, K = 0) = \omega (v + 1)(1 \pm \epsilon)^{1/2} \quad (A.15) \]

for the \( K = 0 \) levels, and for the other vibronic levels \( (K \neq 0) \), the same expression as the equation derived here \( (K \neq 0) \) is given. When \( K \) is put equal to 0 in equation A.14, the following expression is found:

\[ E(v, K = 0) = \omega (v + 1) \left(1 - \frac{1}{8} \epsilon^2 \right) \pm \frac{1}{2} \epsilon \omega (v + 1) = \omega (v + 1) \left(1 \pm \frac{1}{2} \epsilon - \frac{1}{8} \epsilon^2 \right) \quad (A.16) \]

It can be easily shown that the expansion of the term \( (1 \pm \epsilon)^{1/2} \) (see below) from Renner’s equation gives the same result obtained here for the particular case \( K = 0 \).

\[ (1 \pm \epsilon)^{1/2} = 1 \pm \frac{1}{2} \epsilon - \frac{1}{8} \epsilon^2 + ... \quad (A.17) \]
A.1.2 Tetratomic molecules.

Petelin and Kiselev extended the Renner-Teller theory for tetratomic molecules, and derived similar expressions for the energies of the vibronic states [6]. The difference is that for tetratomic molecules there are two bending modes subject to the vibronic coupling. Petelin and Kiselev derived the energy of the vibronic levels for $X_2Y_2$ and $X_2YZ$ molecules up to the second order, for some specific cases. For an $X_2YZ$ molecule, a new Renner-Teller parameter called $\varepsilon_3$, was needed, which accounts for interaction between the two bending modes, and is expected to be small. The frequencies of the bending modes of the tetratomic molecule are called $\omega_4$ and $\omega_5$, and the corresponding Renner-Teller parameters are defined as $\varepsilon_4$ and $\varepsilon_5$.

The expressions for the vibronic levels for the case when $v_4 \neq 0$ $v_5 = 0$, for example, are given by:

$$E(K = 0) = \omega_4 (v_4 + 1) (1 - \frac{1}{8} \varepsilon_4^2) \pm \frac{1}{2} \varepsilon_4 \omega_4 (v_4 + 1)$$

$$+ \omega_5 (1 - \frac{1}{4} \varepsilon_5^2) - \frac{1}{4} \varepsilon_3^2 \frac{\omega_4 \omega_5}{\omega_4 + \omega_5} (v_4 + 1)$$

(A.18)

$$E(K < v_4 + 1)) = \omega_4 (v_4 + 1) (1 - \frac{1}{8} \varepsilon_4^2) \pm \frac{1}{2} \varepsilon_4 \omega_4 \sqrt{(v_4 + 1)^2 - K^2}$$

$$+ \omega_5 (1 - \frac{1}{4} \varepsilon_5^2) - \frac{1}{4} \varepsilon_3^2 \frac{\omega_4 \omega_5}{\omega_4 + \omega_5} (v_4 + 1)$$

(A.19)
Figure 31: Vibronic energy levels for the bending mode of a $^2\Pi$ electronic state of a linear molecule. The left part of the figure shows the case for only spin-orbit interaction (and zero vibronic interaction), the right part shows the case for only vibronic coupling, and in the center both interactions are present.
In cases when the coupling parameter $\epsilon_3$ is small, or in other words, if the interaction between the two bending modes can be neglected, the formulae derived for triatomic molecules can be applied to each bending mode separately.

A.2 Spin-orbit interaction.

If the molecule in which the Renner-Teller effect occurs contains unpaired electrons, the energy level diagram shown in the right part of Figure 31 is considerably modified by the spin-orbit splitting, as it can be appreciated in the middle part of the same figure. As suggested by Hougen [61], when both interactions are present one can explain the splitting of the levels in two ways. From one point of view, the Renner-Teller effect can be considered as superimposed on the spin-orbit interaction (going from the left to the middle part of the diagram). The states with the same symmetry will repel each other with the addition of vibronic coupling (see for example the two $\Sigma_{1/2}$ levels of $v=1$, the two $^2\Pi_{1/2}$ and the two $^2\Pi_{3/2}$ levels of $v=2$, and so on). On the other hand, the $^2\Delta_{3/2}$ and $^2\Delta_{5/2}$ of $v=1$ remain unaffected, as they are the only ones of their symmetry (as the $^2\Phi_{5/2}$ and $^2\Phi_{7/2}$ of $v=2$, $^2\Gamma_{7/2}$ and $^2\Gamma_{9/2}$ of $v=3$, etc). From the other point of view, when the spin-orbit interaction is considered superimposed to the Renner-Teller interaction, the central vibronic levels in the Renner-Teller picture are now split into two components, while the states with the same symmetry mix and repel each other.

The theory of the Renner-Teller effect in linear triatomic molecules was extended
by Pople, to take account of the spin-orbit coupling [79]. In this case the Renner-Teller effect was considered as a perturbation as before, and in addition the spin-orbit coupling was introduced as a perturbation as well. Therefore, perturbation expressions for the splittings and shifts of the vibronic energy levels were obtained, under the assumption that the Renner-Teller splittings and the spin-orbit coupling were of the same order of magnitude, but much less than the vibrational energy of the bending mode. By adding an extra perturbation $h'$, the new energies can be obtained by repeating the perturbation treatment done before, with the new added perturbation term. Pople's perturbing Hamiltonian for the spin-orbit coupling has the well-known form:

$$h' = A_{so} L_z S_z$$  \hspace{1cm} (A.20)

where $A_{so}$ is the spin-orbit coupling constant.

### A.2.1 Pople's equations

The energy of the vibronic levels can be calculated with the formulae derived first by Pople [79], and corrected later by Hougen [61]. These expressions were derived for linear triatomic molecules in a $^2\Pi$ electronic state, taking into account vibronic and spin-orbit interactions.

**$K = 0$ ($\Sigma$) vibronic states**

$$E^\pm (v, K = 0) = \omega v \left( 1 - \frac{1}{8} \epsilon^2 \right) \pm \frac{1}{2} \sqrt{A_{so}^2 + (v + 1)^2 \epsilon^2 \omega^2}$$ \hspace{1cm} (A.21)
\[ K = v + 1 \text{ vibronic states} \]

\[ E^\pm(v, K, \pm 1/2) = \omega v - \frac{1}{8} \epsilon^2 \omega K(K + 1) \pm \frac{1}{2} A_{so} \left[ 1 - \frac{1}{8} \epsilon^2 K(K + 1) \right] \] (A.22)

\[ K < v + 1 \text{ vibronic states} \]

\[ E^+(v, K, \pm 1/2) = \omega v \left( 1 - \frac{1}{8} \epsilon^2 \right) + \frac{1}{2} r \pm \frac{A_{so} K(v + 1)\epsilon^2 \omega}{8r} \] (A.23)

\[ E^-(v, K, \pm 1/2) = \omega v \left( 1 - \frac{1}{8} \epsilon^2 \right) - \frac{1}{2} r \pm \frac{A_{so} K(v + 1)\epsilon^2 \omega}{8r} \] (A.24)

where \( r = \sqrt{A_{so}^2 + [(v + 1)^2 - K^2] \epsilon^2 \omega^2} \).

In all these expressions, \( E^\pm \) represents the energy of the vibronic levels measured from the \( v=0 \) level. When there are two levels with the same \( K \), \( E^+ \) gives the energy for the upper level (higher energy), and \( E^- \) gives the energy of the lower vibronic level, usually called \( \kappa \) and \( \mu \) levels, respectively. When \( K < v + 1 \) there are four vibronic levels; and again the \( E^+ \) and \( E^- \) give the energy of the two upper and two lower levels, respectively, while the \( \pm 1/2 \) indicates the value of \( \Omega \) for those levels.

### A.3 Further interactions between the Renner-Teller effect and the spin-orbit coupling

In electronic spectra of molecules with Renner-Teller interaction, it often happens that a non-totally symmetric vibration gives rise to forbidden components in an electronic transition (see examples given in section 4.5). The term causing this effect is the term
\[ j_1 \rho \cos(\nu - \chi) \], which has been neglected in the treatment of the Renner-Teller effect so far. When two interacting states are close in energy, and are observed in transitions from a third state, the interaction is found to induce formally forbidden \( \Delta v = \pm 1 \) transitions in the bending vibration, and small energy perturbations may occur. The first in observing this perturbation were Brown and Bolman [88], who applied this idea to explain the occurrence of formally forbidden parallel bands (\( \Delta K = 0 \)) in the \( \tilde{\text{A}}^2\Sigma^+ \leftarrow \tilde{\chi}^2\Pi \) electronic transition of NCO. This was explained by a theoretical model by which the forbidden transitions were attributed to a manifestation of the Renner-Teller interaction [88]. In their model, it was assumed that one of the two electronic states was vibronically perturbed, either the \( \tilde{\text{A}}^2\Sigma^+ \) was mixed with a \( ^2\Pi \) electronic state through the bending vibration coordinate, or the \( \tilde{\chi}^2\Pi \) state was mixed with a \( ^2\Sigma \) electronic state.

Northrup and Sears have studied the combined effects of Renner-Teller and spin-orbit interactions in the NCS radical extensively [78, 59], and applied the same idea of Bolman and Brown of vibronically induced bands, to explain the observation of forbidden transitions in their NCS spectrum. In this case, energy shifts of some vibronic levels were also observed [59]. They discovered that an additional interaction term was necessary to explain the observed vibronic energy level structure of the bending mode and intensities found in NCS. This extra term derives from a product of the Renner-Teller and the spin-orbit operators, and acts on states that differ in \( \nu \) by one, through other electronic state. This term becomes significant when the electronic state through which the Renner-Teller and spin-orbit operators mix is close in energy.
When the Renner-Teller operator is combined with the spin-orbit operator, states differing in \( v \) by one can be mixed in second order, since they have the same value of \( P \), the projection of the total angular momentum on the axis. This interaction was used successfully in NCS to explain the observation of forbidden transitions and especially the energy shifts of some of the vibronic levels [59].

### A.3.1 Matrix elements

In this section the matrix elements for the interaction of the Renner-Teller and spin-orbit operators will be presented, following the discussion of Northrup and Sears [59]. The interaction term was obtained by combining the off-diagonal term of the spin-orbit operator and the term of \( j_1 \rho \cos(\nu - \chi) \) from the Renner-Teller Hamiltonian.

The off-diagonal term of the \( \mathcal{H}_{SO} \) operator can be written as:

\[
\mathcal{H}_{SO} = \frac{1}{2} A_{so} (L_+ S_- + L_- S_+) \tag{A.25}
\]

The term of the Renner-Teller Hamiltonian used by Northrup and Sears, in their notation, has the following form:

\[
\mathcal{H}_{RT} = \frac{1}{2} V (q_+ L_- + q_- L_+) \tag{A.26}
\]

where \( q_+ \) and \( q_- \) are the normal coordinate shift operators for the bending vibrational mode, \( V \) is a function of the electronic and radial coordinates, and \( L_\pm \) are the electronic orbital angular momentum shift operators. (Note that in the present work the variable \( \rho \) has been used to refer to the bending coordinate, instead of \( q \) used by Northrup and Sears). By simple algebra relations, it can be shown that the \( \mathcal{H}_{RT} \) of
equation A.26 is equivalent with the \( j_1 \rho \cos(\nu - \chi) \) term:

\[
\cos(\nu - \chi) = \frac{1}{2} \left( e^{i(\nu - \chi)} + e^{-i(\nu - \chi)} \right)
\]  
(A.27)

\[
\rho = \rho e^{\pm ix}
\]  
(A.28)

then

\[
\rho \cdot \cos(\nu - \chi) = \frac{1}{2} \rho_+ e^{-i\nu} + \rho_- e^{i\nu}
\]  
(A.29)

The azimuthal angle of the electron, \( \nu \), is defined such that [89]:

\[
\langle \Lambda' | e^{\pm i\nu} | \Lambda \rangle = \delta_{\Lambda', \Lambda \pm 1}
\]  
(A.30)

Thus, the term \((q_+ L_+ + q_- L_-)\) from the \( \mathcal{H}_{RT} \) is equivalent with \( \rho \cos(\nu - \chi) \).

The \( q_\pm \) operator can be defined as [87]:

\[
q_\pm |v, l\rangle = 2^{-1/2} \left( (v + 2 \pm l)^{1/2} |v + 1, l \pm 1\rangle + \left( (v \mp l)^{1/2} |v - 1, l \pm 1\rangle \right) \right)
\]  
(A.31)

In the following it will be shown, that when the \( \mathcal{H}_{RT} \) is mixed in second order with the \( \mathcal{H}_{SO} \) operator, this results in coupling vibronic levels of the same electronic state, \( \Lambda \), with \( \Delta v = \pm 1, \Delta l = \pm 1 \) and \( \Delta \Sigma = \pm 1 \).

For example, the vibronic states \(|v, l; \Lambda, \Sigma\rangle\) and \(|v + 1, l + 1; \Lambda, \Sigma - 1\rangle\), will mix via second-order perturbation coupling with the state \(|v + 1, l + 1; \Lambda - 1, \Sigma\rangle\). The effective matrix element that couples these two states can be written as:

\[
d = \frac{1}{\Delta E} \langle v + 1, l + 1, \Lambda, \Sigma - 1 | \mathcal{H}_{SO} | v + 1, l + 1, \Lambda - 1, \Sigma \rangle \times
\]

\[
\langle v + 1, l + 1, \Lambda - 1, \Sigma | \mathcal{H}_{RT} | v, l, \Lambda, \Sigma \rangle
\]  
(A.32)
where $\Delta E = E_\Lambda - E_{\Lambda-1}$, the energy difference of the electronic states. If the following definitions are made:

$$
\langle \Lambda | A_{so} L_\pm | \Lambda \mp 1 \rangle \equiv A_{so} L_\pm \quad (A.33)
$$

$$
\langle \Lambda | V L_\pm | \Lambda \mp 1 \rangle \equiv V L_\pm
$$

then

$$
\langle v + 1, l + 1, \Lambda, \Sigma - 1 | \mathcal{H}_{SO} | v + 1, l + 1, \Lambda - 1, \Sigma \rangle =
\frac{1}{2} A_{so} \langle v + 1, l + 1, \Lambda, \Sigma - 1 | L_+ S_- | v + 1, l + 1, \Lambda - 1, \Sigma \rangle =
\frac{1}{2} A_{so} L_+
$$

$$
\langle v + 1, l + 1, \Lambda - 1, \Sigma | \mathcal{H}_{RT} | v, l, \Lambda, \Sigma \rangle =
\frac{1}{2} V \langle v + 1, l + 1, \Lambda - 1, \Sigma | q_+ L_- | v, l, \Lambda, \Sigma \rangle =
\frac{1}{2} V L_- 2^{-1/2} (v + 2 + l)^{1/2}
$$

and $d$ (equation A.32), can be expressed as:

$$
d = 2^{-1/2} (v + 2 + l)^{1/2} \frac{A L_+ V L_-}{4 \Delta E} \quad (A.37)
$$

In NCS, an effective mixing parameter $F$, was defined as:

$$
F = \frac{A L_+ \cdot V L_-}{4 \Delta E}
$$

was allowed to vary and fitted, with the experimental data. The obtained value was $7.03 \text{ cm}^{-1}$ [59]. When this parameter was set to zero, the authors were unable to fit the data satisfactorily.
In terms of $F$, equation A.37 can be written as:

\[
d = 2^{-1/2} (v + 2 + l)^{1/2} F
\]  \hspace{1cm} (A.39)
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