High Resolution Cavity Ringdown Spectroscopy of the A – X Electronic Transition of Alkyl Peroxy Radicals

Dissertation

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

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2009

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Abstract

Alkyl peroxy radicals (RO$_2^·$) are examples of reactive intermediates involved in the oxidation of organic molecules. This chemistry plays a key role in combustion as well as in tropospheric chemistry. These reactions are typically very complex involving thousands of elementary steps with a corresponding number of chemical intermediates. Hence, spectroscopic diagnostic based upon fully understood spectra is a key to monitor such reactions and understand their mechanism. Over the last few years, our laboratory has investigated these peroxy radicals via their $\tilde{A} - \tilde{X}$ electronic transition which lies in the near infrared. Due to the relative weakness of this transition, we use cavity ringdown spectroscopy (CRDS) to detect these radicals which is known to be a very sensitive technique. We have obtain high resolution jet-cooled CRDS spectra of several of these alkyl peroxy radical at a rotational temperature of 15 K. This dissertation will focus on the numerous species that we observed and analyzed using our high resolution setup and an Evolutionary Algorithm as well as the analysis of the methyl tunneling splitting of the methyl peroxy radical observed at room temperature and at 15 K.
In memory of my grandparents
   To my parents
   To Samuel and Cecile
   To my grandmother
   To Yvette
ACKNOWLEDGMENTS

When I was younger, I wanted to be a medical doctor, but obviously, this didn’t really worked out for me. I then turned my attention to chemistry and physics and I then discover a real passion for these fields of Science. First of all. I would like to thank my advisor Terry Miller without whom I wouldn’t be where I am right now. Your outstanding guidance and knowledge in any field of science made working in your laboratory such a pleasure and an honor. My philosophy is that, if you don’t have fun in what you are doing, then you are not doing the right thing. Thank you so much for stimulating my way of approaching any new scientific problems and teaching me how to think on my own. Thank you for the weekly group meeting where I was playing a game on my own which was ”What kind of question will Dr Miller ask me and do I have the slide to answer it”. Thank you for making me know all the ins and outs of my experimental setup an making me take several time the CD$_3$O$_2$ spectrum to make sure that the setup is working the way it is supposed to. I now understand the reason of it, it is easier to take new data if you know that you instrument is optimum. Finally, thank you for putting up with me when I was doubting myself and thought that I will never be able to make it that far. For all the above and more, THANK YOU.
I need to also acknowledge my candidacy exam and dissertation defense committee members, Anne McCoy and Frank De Lucia, Heather Allen and Walter Lempert. Thanks for being there in the key moment of my graduate school career.

I would also like to thanks all my present and past labmates from the Miller group. First of all, I would like to thank Sergey Zalyubovsky and Brent Glover who basically introduced me in the world of cavity ringdown spectroscopy the so called, hard way, by making me clean the mirrors and align the cavity over and over again until they were satisfied with it. I would also like to thank some of the other Miller group members that I had the chance to meet during my time at OSU, György Tarczay, Vadim Stakhursky, Shenghai Wu, Jinjun Liu, Patrick Dupré, Phillip Thomas, Rabi Chhantyal Pun, Neal Kline, Terrance Codd and Melissa Marino. Especially thanks to Jinjun for being such a good friend and outstanding scientist. Your jokes made mine look funny. So from a freak to a another, thank you.

I don’t know where to start now to thank the person that are not only my labmates but also my friends, Dmitry Melnik, Patrick Rupper, Ming-Wei Chen and especially Erin Sharp-Williams. I think that I will remember my whole life our trip to the Free Radical Meeting in BigSky, MT. I think that this were the "test" took place for our friendship, will we be able to spend all our time together everyday for a week without killing each other at the end? And the answer is yes. Dmitry, you know so much about anything that it is a real pleasure to come to you office to ask for help even if your taste in terms of music a re quite strange, and yes in BigSky, steak was good. Ming-Wei, I will always remember the long discussion we had about the ring laser
and about the so called "magic Taiwanese screw" also called the ICA tilt angle screw and just after that talking about Chien-Ming Wang and the fact that he is again injured and then go to the chemistry department softball games and then see you hurt yourself by I don’t even understand what process and keep playing even though you are limping like somebody needs to cut your leg. Erin, I don’t even know where to start to express how important of a part you are taking in my life. When I left France to start my graduate study here at OSU, I never thought that I would meet such an amazing friend and scientist. Thank you for cheering me up all these years and to listen to all my jokes that I am the only one to find them funny. Our days at OSU are such an important part of my life that I cannot wait to be able to welcome you in California for the weekend or to fly to Colorado. And Patrick, I do not think anyone besides Dr. Miller that has been so influential during my graduate school times and taught me so many things, and not only the swearing in Swiss German. I will remember for ever the times when we worked together, the good ones on the high-res ringdown and the not so good ones on the time of flight. I only hope that I could be as good of of postdoc as you have been in the Miller group.

I would also like to personally thank Becky Gregory. Thanks for always taking care of everything, even with a somewhat strange filling system, and for always taking care of me. You make it an absolute pleasure to come to work every day.

I would also to particularly thanks Dr. Anne B. McCoy for all the long night that we spent on the methyl peroxy project and for teaching me how to tackle a project from a theoretician point of view. A person that takes the most important part in
my life and that I need to thank is Yvette. Thank you for always being here and to be so comprehensible when I have to stay late in the lab because an experiment has to be done or when I need to finish a paper. Words cannot express how lucky I feel to live with such an amazing person.

Finally, I would like to thanks my parents, my brother Samuel, my future sister-in-law Cecile, my grandmother and my missing grandparents for all the support they have given me and for all the love they have shown me during the dark times.

This work is dedicated to all of you.
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Peroxy radicals (RO$_2^\cdot$) play a crucial role in atmospheric chemistry as well as in low temperature combustion. This chemistry has been discussed in several overview articles.$^{1,6-8}$ A fundamental key to the understanding of these gas phase reactions is the ability to monitor the presence and concentrations of reactive intermediates in these reactions.$^{9-11}$

It has been estimated by Guenther$^{12}$ that the total emission into the troposphere of volatile organic compounds (VOCs), mainly hydrocarbons, is about 1300 Tg/year. Out of these 1300 Tg, 1200 Tg are biogenic from natural sources, such as marine life, forests etc. The remaining 100 Tg are anthropogenically emitted from transportation, stationary urban sources, power plants and other man-made sources. The oxidation of these VOCs in the atmosphere is initiated by the most abundant radical in the troposphere, OH-. For unsaturated hydrocarbons this reaction leads to the formation of an alkyl radical which can react with O$_2$ via a three body process to form an alkyl peroxy radical according to the following mechanism.
RH + OH· → R· + H₂O \hspace{1cm} (1.1)

R· + O₂ + M ↔ RO₂· + M \hspace{1cm} (1.2)

Figure 1.1: Schematic diagram of atmospheric hydrocarbon oxidation from Ref.1
The production of peroxy radicals in the atmosphere has several consequences. Typically, peroxy radicals go on to participate in reactions that re-generate OH· radicals as shown in Fig. 1.1 thereby forming a chain reaction. For example, the peroxy radical, can react with NO· to form NO₂· and alkoxy radical (RO·).

\[
\text{NO} \cdot + \text{RO}_2 \cdot \rightarrow \text{NO}_2 \cdot + \text{RO} \cdot 
\]

(1.3)

This later radical can further react with molecular oxygen and form hydroxyperoxy radicals, HO₂·, and carbonyl compounds R'C=O. The HO₂· radical can react with NO· to produce OH· radical,

\[
\text{RO} \cdot + \text{O}_2 \rightarrow \text{R'C} = \text{O} + \text{HO}_2 \cdot
\]

(1.4)

\[
\text{HO}_2 \cdot + \text{NO} \cdot \rightarrow \text{NO}_2 \cdot + \text{OH} \cdot
\]

(1.5)

The OH· radicals produced can migrate to the stratosphere where they will then reduce the amount of ozone (O₃),

\[
\cdot \text{OH} + \text{O}_3 \rightarrow \text{HO}_2 \cdot + \text{O}_2
\]

(1.6)

Ozone is known to absorb strongly in the wavelength region from 240 to 290 nm; hence its presence in the stratosphere acts as a filter for UV radiation thereby preventing damage to the biosphere. It is obvious that the reduction of the O₃ layer in the stratosphere would significantly increase the amount of UV radiation which could endanger the quality of life on Earth as we know it.

A second major effect of the peroxy radicals is that they upset the NO·/NO₂· balance in the troposphere leading to the formation of ozone, O₃, where it acts as a pollutant, via the reactions,
\[ \text{NO}_2 \cdot + h\nu (\lambda = 430\ \text{nm}) \rightarrow \text{NO} \cdot + \text{O}^3\text{P} \] 

\[ \text{O}^3\text{P} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} \] 

\[ \text{O}_3 + \text{NO} \cdot \rightarrow \text{NO}_2 \cdot + \text{O}_2 \]  

In the absence of peroxy radicals the net reaction of the cycle (1.7)-(1.9) is zero. \( \text{NO} \cdot \) is oxidized to \( \text{NO}_2 \cdot \) by ozone via reaction 1.9 and both ozone and nitric oxide will be present in small equilibrium concentrations. However in the presence of peroxy radicals, \( \text{NO} \cdot \) can be converted to \( \text{NO}_2 \cdot \) via reaction 1.3 leading to the formation of \( \text{O}_3 \) in the troposphere. Also, the reaction rate constant of reaction 1.9 is two orders of magnitude slower\(^\text{13}\) that reaction 1.3. Hence we can then summarize the production of ozone in the troposphere by the following mechanism,

\[ \text{NO} \cdot + \text{RO}_2 \cdot \rightarrow \text{NO}_2 \cdot + \text{RO} \cdot \]

\[ \text{NO}_2 \cdot + (\lambda = 430\ \text{nm}) \rightarrow \text{NO} \cdot + \text{O}^3\text{P} \]

\[ \text{O}_2 + \text{O}^3\text{P} + \text{M} \rightarrow \text{O}_3 + \text{M} \]

This overall mechanism then has a net production of \( \text{O}_3 \) and can me written as,

\[ \text{RO}_2 \cdot + \text{O}_2 \rightarrow \text{RO} \cdot + \text{O}_3 \]

Finally, \( \text{RO}_2 \cdot \) can react with \( \text{NO}_2 \cdot \) in order to form the alkyl peroxy nitrate (\( \text{RO}_2\text{NO}_2 \)) which is a key irritant in of smog and is responsible for the overall degradation of
the atmosphere surrounding urban areas. While these RO$_2$NO$_2$ compounds are only weakly bound, they can act as significant reservoirs for RO$_2^\cdot$ and NO$_x$ in the colder regions of the troposphere. Additionally, they can serve as transporters of NO$_x$ from polluted urban environments into rural ones.

Peroxy radicals are not only key components in atmospheric chemistry but also are of extreme relevance in the low-temperature combustion of fossil fuels$^{14-18}$ which are typically consumed in transportation and are comprised of large hydrocarbons like $n$-heptane or isooctane. The low-temperature ($T<700$ K) oxidation of hydrocarbons is a critically important process that affects the efficiency of our automobiles. The reaction of these hydrocarbons with oxygen, which inevitably occurs in combustion, should be well understood.

One of the key intermediates in the low-temperature oxidation mechanism is the alkyl peroxy radical (RO$_2$), which results from the reaction of molecular oxygen with an alkyl radical as shown in Eq. 1.2.
Figure 1.2: Outline of low temperature alkane oxidation from Ref. 2
The production of the peroxy radicals, (see Eq. 1.2) maintains and accelerates the forward rate of combustion as it is involved in a chain-branching sequence of reactions leading to the production of OH· radicals. This sequence of reactions involves an isomerization of RO₂· via a cyclic transition state, as shown in Fig. 1.2, that allows a hydrogen transfer from one of the carbons to the O₂ moiety forming a compound referred as -QOOH, ie.

\[ \text{RO}_2 \cdot \rightleftharpoons \cdot \text{QOOH} \quad (1.10) \]

The formed -QOOH radical can then react with molecular oxygen to form a new radical denoted -O₂QOOH,

\[ \text{O}_2 + \text{QOOH} + \text{M} \rightleftharpoons \cdot \text{O}_2\text{QOOH} + \text{M} \quad (1.11) \]

The -O₂QOOH can then further decompose to produce R-O-O-H, a non-radical hydroperoxide, and the HO₂ radical. Thermal decomposition of the latter species can produce two reactive intermediates RO· and OH· which results in a runaway radical multiplication.

\[ \text{ROOH} \rightarrow \text{RO} \cdot + \cdot \text{OH} \quad (1.12) \]

Therefore, the subsequent reactions of the QOOH species leads to chain branching and acceleration of ignition via the production of OH· radical leading to the autoignition and engine knock. These two later effect being critical to the efficiency and fuel economy of internal combustion engine.\(^{14,15,19}\) The rate of H-atom transfer depends not only upon the size of the cyclic transition state and the nature of
the H atom transfered (primary, secondary or tertiary) but also upon the number of H atom available.\textsuperscript{19} Hydrogen transfer is inhibited when the atom is bound to a primary group (like methyl). Also, the ring strain energy barrier to these internal intramolecular hydrogen transfers inhibit for small rings transition states. Hence, for long straight-chain hydrocarbon, the supply of secondary hydrogen is abundant, located at distances that are not inhibited by the ring strain energy barrier. However, for highly branched fuel molecules many hydrogen are bound to a primary site and the available transition state ring structure will hence have a high ring strain energy barrier.

These two effects can then explain the dependance that exists between the engine "knock" and the molecular structure of the used fuel.\textsuperscript{20} It becomes obvious that a control of the isomerisation of the alkyl peroxy radical via the nature of the engine fuel used is a critical step in engine efficiency. The isomerisation of the RO\textsubscript{2}. radicals and other reaction of the ·QOOH product determine the overall reaction rate and product distributions. Hence using fuel containing mainly secondary of tertiary hydrogen will lead to the formation of more RO· and OH· as end product than a hydrocarbon containing more primary hydrogens facilitating autoignition and engine "knock". A correct balance between primary/secondary and tertiary hydrogen is then one of the keys for a well running engine.

It has been observed that from 550-700 K, a negative temperature coefficient (NTC) has been observed\textsuperscript{21} in the rate of combustion of hydrocarbons, which is largely attributed to the RO\textsubscript{2} formation step.\textsuperscript{17} As temperature increases in this
NTC regime, the equilibrium of Eq. 1.2 lies towards the reactants, and with increased concentrations of R and O\textsubscript{2} as well as slightly higher temperatures, higher activation energy reaction pathways of R + O\textsubscript{2}, can compete with the formation of RO\textsubscript{2}.\textsuperscript{18} The most typical of these competitive processes is the abstraction of a hydrogen atom from R to form an alkene + HO\textsubscript{2}. When this alternate reaction becomes competitive, the supply of alkyl peroxy radicals, necessary for chain-branching and -OH production to occur, is depleted and the forward rate of combustion slows. Hence, with increasing temperature between 550 and 700 K, the rate of combustion decreases, giving rise to this NTC behavior.

The competition between the alkyl radical’s reaction with O\textsubscript{2} to form a peroxy radical (Eq. 1.2) and its self-reaction, or reaction with other hydrocarbon-containing species to form larger hydrocarbons is critical to the amount of soot produced from combustion.\textsuperscript{22} The presence of large unsaturated hydrocarbons in fuel compounds and their reaction with acetylene (C\textsubscript{2}H\textsubscript{2}) are speculated to be the elementary step in the formation of phenyl radical (C\textsubscript{6}H\textsubscript{5·}) and larger polycyclic aromatic hydrocarbons (PAHs), which are known precursors to soot formation.

The electronic structure and properties of the peroxy radical have been the subject of many theoretical studies.\textsuperscript{23–30} The correlation diagram in Fig. 1.3 illustrates the different positions of the lone electron in the ground \(\tilde{X}\), first excited \(\tilde{A}\), and second excited \(\tilde{B}\) electronic states. This diagram uses as an example the methyl peroxy radical, CH\textsubscript{3}O\textsubscript{2}. For a molecule like methyl peroxy with a point group symmetry of C\textsubscript{s}, the ground state electronic state will have A\textsuperscript{″} symmetry as well as the \(\tilde{B}\) state.
On the other hand, the first excited electronic state has $A'$ symmetry (obviously, for peroxy radicals with $C_1$ point group symmetry, the symmetry of all the electronic states is $A$).

The oxygen molecule in the $X^3\Sigma_g^-$ electronic state has two electrons located in degenerate $\pi_x^*$ and $\pi_y^*$ orbitals. Upon addition of a methyl group, the oxygen $\pi_y^*$ orbital overlaps with the methyl $\pi^*$ orbital to form a C-O bond.
Figure 1.3: Correlation diagram of the methyl peroxy radical. The blue arrows illustrate the $\tilde{B} - \tilde{X}$ electronic excitation as well as the movement of the electrons on the $O_2$ chromophore. The pink arrows represent the $\tilde{A} - \tilde{X}$ electronic excitation as well as the movement of the electrons on the $O_2$ chromophore.
The $\tilde{B} - \tilde{X}$ electronic transition of the peroxy radical, indicated by blue arrows in Fig. 1.3, involves the promotion of one electron in a bonding orbital to an antibonding orbital leading to the repulsive nature of the $\tilde{B}$ electronic state. This excitation is referred as an excitation for the second highest occupied molecular orbital (HOMO-1) to the singly-occupied molecular orbital (SOMO).

The pink arrows in Fig. 1.3 show that the $\tilde{A} - \tilde{X}$ electronic excitation correspond to a one-electron hop from an out-of-plane to an in-plane molecular orbital localized on the terminal oxygen atom. Weisman and Head-Gordon\textsuperscript{30} referred to this as an excitation of an electron from HOMO to the SOMO. This transition is only weakly allowed due to the fact that it corresponds to the triply forbidden $a^1 \Delta_g - X^3 \Sigma_g^-$ transition of the O$_2$ chromophore which is only slightly perturbed by the methyl group.

Due to the relevance of peroxy radicals in atmospheric and combustion chemistry, the ability to monitor their presence and concentration in these reactions\textsuperscript{9–11} is of fundamental importance. Historically, the peroxy radicals have been studied via their strong $\tilde{B} - \tilde{X}$ electronic transition located in the UV around 240 nm which has proven to be a good diagnostic method for kinetics measurement.\textsuperscript{1,8} However the broad nature and overlap of the $\tilde{B} - \tilde{X}$ transition\textsuperscript{31} for different alkyl peroxy radicals render impossible the identification of a particular peroxy. Additionally, due to the repulsive nature of the $\tilde{B}$ state,\textsuperscript{28} no spectroscopically relevant information for the radical electronic and geometric structure can be obtained.

Therefore, the $\tilde{A} - \tilde{X}$ electronic transition, located in the near infrared (NIR),
appears to be the transition of choice both for spectroscopically characterizing peroxies and for monitoring their reactions. However, since this transition is based on the highly forbidden $a^1\Delta_g - X^3\Sigma_g^-$ transition on the $\text{O}_2$ chromophore, its absorption cross-section is estimated to be four to five orders of magnitude weaker than the $\tilde{B} - \tilde{X}$ transition in the UV.

The first experimental observation of the $\tilde{A} - \tilde{X}$ transition in the NIR was by Hunziker and Wendt several years ago. In order to be able to compensate the weak absorption cross-section of the $\tilde{A} - \tilde{X}$, cavity ringdown spectroscopy (CRDS) has been the method of choice in the Miller group to study alkyl peroxy radicals under ambient temperature conditions in a cell. This method offers a long effective pathlength for the light passing through an absorbing medium (≈6 km for a typical experiment). Experiments performed under room temperature conditions demonstrated the suitability of the NIR transition as a species specific, as well as an isomer and even conformer specific, diagnostic technique. However, congestion due to the population of many rotational levels as well as overlap of conformers at room temperature prevents the extraction of spectroscopic parameters, such as rotational and spin-rotational constants, which are highly useful for characterizing the radical and benchmarking electronic structure calculations.

Other groups have used low to moderate resolution laser sources to study gas-phase methyl and ethyl peroxy by a variety of techniques, including negative-ion photoelectron spectroscopy, photoionization, cw-CRDS in the NIR and NIR absorption detected by time-of-flight mass spectroscopy, but have similarly failed to
obtain high precision molecular parameters, characterizing the rotational and spin-rotational structure.

This dissertation will mainly focus on the spectroscopic characterization of peroxy radicals by demonstrating the capability of obtaining high resolution jet-cooled CRDS of several peroxy radicals including ethyl, propyl and phenyl peroxy radicals. It details the analysis of these complicated spectra using an evolutionary algorithm (EA) approach and compares it to the traditional least square fitting (LSF) method. It then utilizes the experimental results to benchmark quantum chemistry calculations for the same radicals. In addition, this dissertation describes some unexpected spectral features of methyl peroxy radical that were observed at room temperature.
CHAPTER 2
EXPERIMENTAL

2.1 Cavity Ringdown Theory

2.1.1 Basic Theory

Traditional absorption experiments are based on the Beer-Lambert law,

\[ I = I_0 \cdot \exp(-\sigma NL) \]  

(2.1)

where \( I_0 \) describes the incident light intensity and \( I \) the measured light intensity after passing through an absorbing medium. The absorption cross-section at a given wavelength is expressed by \( \sigma \) and \( N \) represents concentration of the species of interest. Finally, \( L \) defines the absorption pathlength. In a typical absorption experiment, \( \sigma NL \) is usually small. Traditional absorption experiment consist of monitoring the light intensity \( I \) as a function of wavelength \( I \) is a large number and \( I_0 \) is intrinsically large as well, leading to the conclusion that to be successful in doing a direct absorption experiment, one must be able to detect a small change in a large number. Hence, most absorption methods lack the sensitivity needed to investigate weak absorption cross-sections and for low concentrations of the absorbing molecule.

Cavity ringdown spectroscopy, is based on the trapping of a short laser pulse in a high finesse cavity formed by two high reflectivity mirrors with a typical reflectivity
greater than 99.99%. Most of a short laser pulse injected into the optical cavity through one of the high reflectors (typically the front mirror), reflects back and forth between cavity mirrors for many round trips ($\approx 13 \times 10^4$ for a typical experiment) while a very small portion of the trapped photons leaks through the each mirrors on each round trip, see Fig. 2.1. The losses that are leaking out of the cavity decrease exponentially with consecutive round trips. This increase of pathlength ($L$) traveling through the absorbing medium improves significantly the sensitivity of the absorption experiment without any need to increase sample concentration.

![Figure 2.1: Basic illustration of the principal of cavity ringdown spectroscopy (CRDS). The leak through only one mirror is represented for practical purposes.](image)

By adapting the Beer-Lambert law in order to include the different parameters of
a CRDS experiment,\textsuperscript{45}

\[ I_t = I_0 \cdot \exp \left[ - \left( \frac{\text{number of reflections}}{\text{round trip}} \right) \left( \frac{\text{loss}}{\text{reflection}} \right) \text{(number of round trips)} \right] \]  

(2.2)

where \( I_0 \) is define as in Eq. 2.1 as the light intensity of the initial pulse of light and \( I_t \) is the intensity of the light leaking through the optical cavity after a time \( t \). The number of round trips after a time \( t \), \( n_t \), can simply be calculated according to the following expression,

\[ n_t = \frac{tc}{2L} \]  

(2.3)

where \( c \) is the speed of light and \( L \) is the distance in between both high reflectors. If one assume that the loss per reflection can be approximated by \( 1-R \), with \( R \) the reflectivity of the high reflector, then by doing the appropriate substitutions, one can express Eq. 2.2 as,

\[ I_t = I_0 \cdot \exp \left[ - \frac{tc(1-R)}{L} \right] \]  

(2.4)

One can then define the empty cavity ringdown time \( (\tau_{\text{empty}}) \) as the time constant for the exponential decay of the intensity of the losses and write it as,

\[ \tau_{\text{empty}} = \frac{t_r}{2(1-R)} \]  

(2.5)

Where \( t_r \) is here define as the time it takes for a round trip to occur,

\[ t_r = \frac{2L}{c} \]  

(2.6)
We can now write the empty cavity ringdown time by substituting $t_r$ in Eq. 2.5 as,

$$\tau_{\text{empty}} = \frac{L}{c (1 - R)}$$  \hspace{1cm} (2.7)

Hence, one can now easily calculate a empty cavity ringdown time for a given apparatus. In our case, the distance between both high reflector is 67 cm and the reflectivity of our ringdown mirrors can be as great as 99.999 % giving rise to a empty ringdown time of $\tau_{\text{empty}}=300 \ \mu s$.

Now, let’s turn our attention to the case of a ringdown cavity containing a species absorbing at the wavelength of one of the pulses of light injected inside the cavity. The loss of light intensity due to only the absorbing medium can be written as,

$$\text{absorption loss} = \left( \frac{\text{loss round trip}}{\text{number of round trips}} \right)$$  \hspace{1cm} (2.8)

$$= (2\sigma N) \left( \frac{tc}{2L} \right)$$  \hspace{1cm} (2.9)

where $l$ correspond the the sample effective pathlength instead of the pathlength defined by the distance (L) between both high reflectors.

Hence, the total cavity loss due to the absorbing medium and the optical cavity loss can be express as,

$$\text{total loss} = (1 - R)\frac{tc}{L} + (\sigma Nl)\frac{tc}{L}$$  \hspace{1cm} (2.10)

$$= [(1 - R) + \sigma Nl] \frac{tc}{L}$$  \hspace{1cm} (2.11)
Then, we can write Eq. 2.4 as,

\[ I_t = I_0 \times \exp(-[(1 - R) + \sigma N l] \frac{t_c}{L}) \] (2.12)

We can now express the ringdown time for a cavity containing an absorbing medium as,

\[ \tau_{\text{abs}} = \frac{t_r}{2[(1 - R) + \sigma N l]} \]
\[ \tau_{\text{abs}} = \frac{L}{c[(1 - R) + \sigma N l]} \] (2.13)

It is more convenient to plot absorption per pass defined as \( L/c\tau \). Combining Eq. 2.7 and 2.13, species peak absorption \( S_p = \sigma_p N l \) can be expressed as,

\[ S_p = \sigma_p N l = \frac{L}{c} \left( \frac{1}{\tau_{\text{abs}}} - \frac{1}{\tau_{\text{empty}}} \right) \] (2.14)

and species related absolute absorption measurements can be obtained if baseline of an empty cavity are determined.

The development of the cavity ringdown absorption spectroscopy technique has opened new horizons for the absorption based spectroscopic studies. The fundamental principle of measuring the lifetime of a pulse of light trapped inside a high finesse cavity was first used for military purposes in mirror reflectivity measurements.\(^{46,47}\) In 1988, Okeefe and Deacon implemented this method in order to observe the weak \( b^1\Sigma_g - X^3\Sigma_g \) transition of molecular oxygen.\(^{48}\) This spectroscopic achievement was the
starting point of many experiments which would demonstrate the incredible sensitivity of the cavity ringdown spectroscopy technique. A lot of CRDS studies have been done since then with a wavelength range going from the UV to the microwave region. For example, Saykally et al.\textsuperscript{49} measured vibronic spectra of a variety of transition metals; the kinetic of the phenyl radical performed by Yu and Lin\textsuperscript{50} was the first use of the cavity ringdown spectroscopy for kinetic purposes, Romanini and Lehmann\textsuperscript{51} measured overtone spectra of HCN; Zalicki et al.\textsuperscript{52} detected the methyl radical in a hot filament flow reactor via the 216 nm band and the list can go on.

### 2.1.2 Cavity Ringdown Sensitivity

CRDS is based on the measurement of the decay rate of the light trapped in a high finesse optical cavity. Therefore ability to accurately measure the ringdown time $\tau$ will limit the CRDS sensitivity. Upon introduction of a small absorption per pass, $S_p^{\text{min}}$, into a cavity, the empty cavity ringdown time $\tau_{\text{empty}}$ will decrease by $\Delta \tau_{\text{min}}$, with:

$$\Delta \tau = \tau_{\text{obs}} - \tau_{\text{empty}}$$

(2.15)
According to Eq. 2.14:

\[(\sigma_p Nl)_{\text{min}} = S_{\text{min}}^p = \frac{L}{ct_{\text{abs}}} - \frac{L}{ct_{\text{empty}}}\]

\[= \frac{L}{c(\tau_{\text{empty}} - \Delta \tau_{\text{min}})} - \frac{L}{ct_{\text{empty}}}\]

\[= \frac{L}{c\tau_{\text{empty}}(\tau_{\text{empty}} - \Delta \tau_{\text{min}})}\]

\[= \frac{L}{ct_{\text{empty}}\tau_{\text{abs}}}\]

\[= (1 - R)\frac{\Delta \tau_{\text{min}}}{\tau_{\text{abs}}}\] (2.16)

Several conclusions on CRDS sensitivity can be drawn from the Eq. 2.16. Strong absorption will result in small ring-down time \(\tau_{\text{abs}}\) leading to the decrease in accuracy of the absorption measurements. Increase in mirrors reflectivity \(R\) will result in longer ringdown times and higher sensitivity. It is also evident that sensitivity depends on relative measurement error, \(\frac{\Delta \tau}{\tau}\). It was demonstrated that for pulsed ringdown experiments it is possible to determine \(\frac{\Delta \tau}{\tau}\) with 0.25% accuracy.\(^{51}\) More typically \(\frac{\Delta \tau}{\tau}\) accuracy of 1% is reported predominantly due to multimode excitation.\(^{53,54}\) Taking mirrors with 99.999% reflectivity and using 1% as accuracy of \(\frac{\Delta \tau}{\tau}\) will result in minimum detectable fractional absorption \(S_{\text{min}}^p\) of \(0.1 \times 10^{-6}\) or 0.1 part per million (ppm). The sensitivity of pulsed CRDS apparatus can be substantially increased by ensuring a single mode excitation in the cavity and matching laser to TEM\(_{00}\) mode. With such precautions, accuracy of 0.03% in \(\frac{\Delta \tau}{\tau}\) has been reported.\(^{55}\) Cavity ringdown spectroscopy has a major advantage over traditional spectroscopic techniques. Measurement of decay rate in time domain is intrinsically more accurate than observing small intensity changes on top of the strong laser pulse background. Therefore,
unlike most pulsed, direct-absorption methods, cavity ringdown is insensitive to the fluctuation of probe pulse intensity which can be as much as several per cent. In our current high-resolution experimental setup, we have reached noise level for and empty 67 cm optical cavity of 0.02 ppm per pass. In a typical experiment, we observe, when introducing and absorbing medium via our slit jet and discharge expansion an increase of noise up to 0.05 ppm per pass. This increase can be rationalize by the fact that the jet and discharge initiate the chemistry that produces our radical of interest and hence can create unexpected noise in our optical cavity.

2.2 Cavity Ringdown Experimental Apparatus

2.2.1 Room Temperature Experimental Setup

The apparatus for the room temperature experiment is represented is Figure 2.2. The required NIR radiation, around 1.3\( \mu \)m, was generated by a Raman shifting of the output of a dye laser in molecular hydrogen. The second harmonic of Nd:YAG (PRO-270, Spectra Physics) is pumping a Sirah dye laser system with a 20 Hz repetition rate. Operated with DCM and Rhodamine B laser dye (Exiton), the system produced 90-130 mJ/pulse of tunable radiation in the region of 605-640 nm with a linewidth of 0.06 cm\(^{-1}\). The output of the dye laser was focused by a lens (f=50 cm) into a 70 cm long single Raman cell filled with 200-300 psi of H\(_2\). The output radiation from the Raman cell was spectrally filtered using several 1.0 \( \mu \)m cut-off longwave filters (Corion LL-1000-F) to eliminate antiStokes and first Stokes radiation. The resulting 1-2 mJ of the second Stokes radiation in the 1.2-1.3 \( \mu \)m region was delivered to the
ringdown cell through two 1 m focal length lenses. The ringdown cavity was fabricated

![Diagram of experiment apparatus](image)

Figure 2.2: Overview illustration of the room temperature experimental apparatus.

of stainless steel and consists of a 20 cm long central part with two rectangular UV
grade quartz photolysis windows and two 15 cm long arms. The cavity ringdown
mirrors (purchased from Los Gatos Research Inc.) were positioned at the ends of the
arms on adjustable mounts. A Thorlabs InGaAs (PDA400) photodiode was used to
detect the outcoming radiation, and its output was recorded by a 12 bit digitizing card (Measurement Computing) for further analysis.

The photolysis excimer laser (LPX120icc, Lambda Physics) was operated at 193 nm, and the beam was shaped by cylindrical and spherical lenses to form a rectangle (0.5×13 cm). The excimer laser was sent through the photolysis quartz windows into the central part of the flow cell. Background absorption of the precursors and residual water vapor were eliminated by the subtraction of data points taken with the excimer beam on and off for each laser step. The energy of the excimer laser pulse that entered the ringdown cell after it passed through the lenses and windows was approximately 150 mJ.

To produce the normal and deuterated methyl peroxy radical (CH$_3$O$_2$/CD$_3$O$_2$) acetone and $d_6$-acetone was photolyzed to produce the CH$_3$ and CD$_3$ radicals. After the two latter were produced by photolysis, they can react with molecular oxygen to form the normal or deuterated methyl peroxy radicals. Typically, the room temperature ringdown cell was filled with a gas mixture of 60 Torr of O$_2$, 90 Torr of N$_2$ and ~ 2-3 Torr of acetone (or $d_6$-acetone). Typically, the photolysis pulse is fired approximately 100$\mu$s before the dye laser, allowing enough time for the peroxy radical to form, but not too much time to allow for radical-radical recombination or other secondary reactions. Finally, the near infrared Raman-shifted frequencied were calibrated using the HITRAN$^{56}$ database for water absorption.
2.2.2 High-Resolution Experimental Setup

The experimental setup, illustrated in Fig. 2.3, consists of a high resolution (Fourier transform limited), high energy, pulsed laser sources, a Raman shifter or a BBO crystal, a pulsed slit-jet discharge expansion and an optical cavity.

![Figure 2.3: Overview illustration of the high-resolution experimental apparatus.](image)

The laser source is based on a homemade Ti:Sa pulse amplifier, which is seeded by a cw-Ti:Sa ring laser (Coherent 899-29, tunable from 730 nm to 930 nm) pumped
(\approx 10.4 \text{ W}) by a cw (single-mode) injection seeded Nd:YAG laser with a bandwidth \lesssim 1 \text{ MHz}. The pulse amplification is accomplished in two Ti:Sa crystals pumped by a nanosecond Nd:YAG laser (Spectra Physics 170) operated at 20 Hz.\textsuperscript{57} The pumped power is adjusted by a half wave-plate and is typically in the range of 200-250 mJ. The amplifier can produce 40-100 mJ pulse energies with a linewidth of 40-60 MHz (FWHM) Fourier transform limited.\textsuperscript{57} In order to shift the fundamental frequency coming out of the Ti:Sa amplifier to the NIR region, the amplified laser source is focused (by a 1m focal length lens) into the middle of the (1 m long, single pass) Raman cell pressurized with 150 PSI (10.2 atm) of gaseous H\textsubscript{2} generating 1-4 mJ of first Stokes radiation in the NIR with a bandwidth of the output radiation limited by pressure broadening in H\textsubscript{2},\textsuperscript{58,59} resulting in an \approx 200 MHz bandwidth. Also, the same amplified radiation can be mixed with the second harmonic of a seeded Nd-YAG laser (Spectra Physics 270) operating at a repetition rate of 20 Hz into a BBO crystal generating NIR radiation via difference frequency mixing (DFM) with a bandwidth of then 60 MHz. The output radiation from both experimental techniques are first collimated (by a 50 cm focal length lens) for the SRS, then sent to two CaF\textsubscript{2} Pellin-Broca prisms in order to separate various wavelengths.

The ring-down cavity itself is formed by a pair of homemade cavity ring-down mounts and commercially available mirrors (Advanced Thin Films, 1 m radius of curvature with a reflectivity R of 99.999 \%) attached to the ends of two arms of a vacuum chamber evacuated by a mechanical booster pump (1200 m\textsuperscript{3}/h). The mirrors are kept clean by continually flushing with N\textsubscript{2} or inert gas. The cavity length \( L \) is
67 cm, which corresponds to a 224 MHz longitudinal mode spacing. Problems can arise from the fact that the mode spacing is $\geq$ to the bandwidth of the radiation. The efficient coupling of the radiation to a specific TEM mode of cavity is almost impossible due to the mismatch in the source and cavity mode bandwidth as well as a varying spatial shape of the NIR beams. However problems of this nature are largely avoided by utilizing both longitudinal and transverse modes to form a pattern dense compared to the $\approx$200 MHz IR radiation bandwidth. To achieve this result, no mode matching optics are used to couple the light into the cavity. A slightly off-axis geometry in the alignment is used to minimize the interferences between the two faces of the mirrors.

At the end, collection of the transmitted radiation is accomplished by using a 30 cm focal length in front of InGaAs (Thorlabs PDA400) detector.

Ringdown times of up to 300 $\mu$s (corresponding to an absorption equivalent length of $\sim$6 km with a sample absorption length of 5 cm from our slit jet) and an experimental sensitivity of 0.02 ppm/pass can be achieved fairly straightforwardly.

The data acquisition is performed by a PC, running a Labview program, and an acquisition card (Measurements Computing PCI-DAS4020/12, 12 bit). The frequency steps when scanning are in the 35-50 MHz range and controlled by the Coherent Autoscan unit through a handshake triggering process.

Typically, the ring-down time is extracted from an averaged (typically 4 shot) transient decay curve. This means that for every laser shot, a ringdown time is derived and then average 4 time for a given frequency point. The extraction of
ringdown times is based on an algorithm (compiled by C compiler, and embedded in the Labview program) allowing the shot to shot (at rates of 20 Hz) analysis of up to 10000 data points. The program also allows fitting the transient decay in several (typically 3) sections, offering the possibility of extracting multiple ring-down times thereby dealing with non-exponential behavior.

In order to produce jet-cooled radicals, a slit-jet expansion combined with an electric discharge is implemented inside the ringdown cavity, see Fig. 2.4.

Figure 2.4: Illustration of the slit-jet expansion combined with a DC electric discharge.\textsuperscript{3}
The slit-jet discharge expansion is an adaptation from that used in the Nesbitt and Saykallay groups.\textsuperscript{62–64} The slit body and the solenoid mount, were made from aluminum. The opening of the slit (1 mm $\times$ 5 cm) is accomplished by two modified General Valve devices (Parker, series 9) activated by General Valve drivers (Iota), with an opening time of $\approx$ 1 ms. The plasma channel length ($\approx$ 9 mm) and the spacing ($\approx$1 mm) between the two stainless steel electrodes are not critical parameters, but the electrode surface finishing is a key point for the stability of the plasma.

The plasma is produced by applying a time controlled electric field (typically 300 $\mu$s) between the two electrodes during the opening time of the slit. In the DC discharge, the current is delivered to the electrodes from two 50 $\mu$F capacitors, charged by an adjustable high voltage power supply ($\leq$ 3 kV, Spellman). The connection is via a fast switch (DEI) through a ballast resistor which can be varied from 0.5 to 5 k$\Omega$ giving a typical plasma voltage drop of $\approx$ 500 V. The maximum current obtain is of the order of 1 A, but 300-400 mA is typically used.

In order to produce the required alkyl radical to form the alkyl peroxy radicals, a iodo-alkane is used as a precursor. Good control of the mole fractions of these species is required to optimize the discharge expansion. Important adjustable parameters are the backing pressure ($\approx$ 600 Torr) and the rates of seeding of both species. These are optimized to obtain a high radical density and efficient cooling. We found that a precursor concentration of 1% and $\approx$10% O$_2$ in “first run” neon (75% of Ne and 25% of He from Airgas) was the optimum conditions in order to obtain the best S/N ratio. Finally, the radicals of interest were usually probed 10 mm downstream distance from
the jet throat.

The spectra were recorded using frequency scans of of ∼10 GHz segments with a frequency step size of 50 MHz with 4 laser shots averaged at each frequency point. Each segment is linearized using a simultaneously recorded Fabry-Perot etalon trace (FSR ≈1 GHz). Calibration of the absolute frequency is achieved by using absorption from residual water in our CRDS spectrometer and matching the observed frequencies with those provided in the HITRAN database.$^{56}$
CHAPTER 3

THEORY

3.1 Quantum Mechanical Representation of the Spectrum

All our high resolution jet-cooled recorded spectra of peroxy radicals only involve the $0^0_0$ band of the $\tilde{A} - \tilde{X}$ electronic transition. Since the radical is in a doublet state we expect both rotational structure and an observable spin-rotation interaction as has been seen with the alkoxy radicals.\textsuperscript{65} Hence, the structure of each vibronic level should be described by a Hamiltonian of the from,

$$H_T = H_{\text{Rot}} + H_{\text{SR}} + T_0(i)$$

(3.1)

where $T_0(i)$ is the energy of the vibronic state (vibrationless level of $\tilde{A}$ or $\tilde{X}$ electronic state) with $i = \tilde{A}$ or $\tilde{X}$ and $T_0(\tilde{X})$ is taken as zero. We expect any hyperfine splittings to be well below our experimental resolution and neglect them in $H_T$. Differences in the eigenvalues of $H_T$ for the $\tilde{A}$ and $\tilde{X}$ states produces the frequencies of the observed transitions. The intensities of these transitions are determined but the square of the matrix elements of the transition dipole between the eigenfunctions of $H_T$. 

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3.1.1 Rotational and Fine Structure Hamiltonian

Due to the fact that the spin-rotation coupling is expected to be fairly small, we use a case (b) like basis, with the prolate symmetric top representation, $|J N K S M_J \rangle$, in which the rotational angular momentum, $N$, and the spin-angular momentum, $S$, are coupled to generate the resultant total angular momentum $J$. The $M_J$ quantum number represents the projection of $J$ on the space fixed $Z$ axis and $K$ denotes the projection of $N$ on the $a$ principal axis. For a rigid molecule, we can now simply write the rotational Hamiltonian, $\mathcal{H}_{\text{Rot}}$, in the principal axis system,

$$\mathcal{H}_{\text{Rot}} = AN_a^2 + BN_b^2 + CN_c^2$$  \hspace{1cm} (3.2)

where $A$, $B$ and $C$ denote, by convention, the rotational constants of the radical. The matrix elements of the rotational Hamiltonian, $\mathcal{H}_{\text{Rot}}$, are well-known.$^{66,67}$

The spin-rotation Hamiltonian has been examined by many authors$^{66,68-72}$ and can be written as:

$$\mathcal{H}_{SR} = \frac{1}{2} \sum_{\alpha, \beta} \epsilon_{\alpha \beta} (N_\alpha S_\beta + S_\beta N_\alpha)$$  \hspace{1cm} (3.3)

where $\epsilon_{\alpha \beta}$ represent the different components of the spin-rotation tensor expressed in the same principal axis system.

It is well known that the components of the spin rotation tensor, $\epsilon_{\alpha \beta}$, have two contributions,$^{68,73,74}$ which can be expressed as,

$$\epsilon_{\alpha \beta} = \epsilon_{\alpha \beta}^{(1)} + \epsilon_{\alpha \beta}^{(2)}$$  \hspace{1cm} (3.4)
where $\epsilon^{(1)}_{\alpha\beta}$ is defined as the first-order contribution from the direct coupling between the electron spin and the magnetic field raising from the rotation of the molecule. Typically, this first order contribution to the spin-rotation tensor component is considered to be negligible with respect to the second order contribution, $\epsilon^{(2)}_{\alpha\beta}$, which arises from the interaction of the spin-orbit coupling and the Coriolis interaction. One can write the second order contribution to the tensor components, $\epsilon^{(2)}_{\alpha\beta}$, as:

$$\epsilon_{\alpha\beta} \approx \epsilon^{(2)}_{\alpha\beta} = -2 \sum_{j \neq i} \frac{\langle i|\xi \hat{L}_\alpha|j\rangle\langle j|X_\beta \hat{L}_\beta|i\rangle + c.c.}{E_i - E_j}$$

In the above expression for $\epsilon^{(2)}_{\alpha\beta}$, $\xi$ represent the spin-orbit coupling operator, $\hat{L}$ describes the electronic orbital angular momentum and $X_\beta$ represents the rotational constant for the $\beta$ principal axis. Finally, $i$ denotes the state of interest and the sum extends over all states $j$.

In principle the spin-rotation tensor contains nine parameters (three diagonal and six off-diagonal). On the other hand, Brown and Sears have shown\textsuperscript{73} that, in the most general case, i.e., $C_1$ symmetry, that only six out of nine parameters could be independently determined from an experimental spectrum. For a molecule with $C_s$ symmetry, only four spin-rotation parameters are determined. In the case of a molecule with $C_1$ symmetry, a convenient way to express the tensor components is via their irreducible tensor combinations,

$$T_0^0(\hat{\epsilon}) = \frac{-1}{\sqrt{3}}(\hat{\epsilon}_{aa} + \hat{\epsilon}_{bb} + \hat{\epsilon}_{cc}) = \sqrt{3}a_0$$

$$T_0^2(\hat{\epsilon}) = \frac{1}{\sqrt{6}}(2\hat{\epsilon}_{aa} - \hat{\epsilon}_{bb} - \hat{\epsilon}_{cc}) = -\sqrt{6}a$$
\[ T_{\pm 1}(\tilde{\epsilon}) = \pm \frac{1}{2} [(\tilde{\epsilon}_{ba} + \tilde{\epsilon}_{ab}) \pm i(\tilde{\epsilon}_{ca} + \tilde{\epsilon}_{ac})] = \pm (d \pm ie) \] (3.8)

\[ T_{\pm 2}(\tilde{\epsilon}) = \frac{1}{2} [(\tilde{\epsilon}_{bb} - \tilde{\epsilon}_{cc}) \pm i(\tilde{\epsilon}_{bc} + \tilde{\epsilon}_{cb})] = b \pm ic \] (3.9)

where the \( \tilde{\epsilon}_{\alpha\beta} \) are the reduced tensor components of Bowater et al.\textsuperscript{75} and Brown and Sears\textsuperscript{73} and where the spin rotation parameters, \( a_0, a, b, c, d \) and \( e \), were introduced by Raynes\textsuperscript{69} and are used in our numerical analysis. While in principle (but not in practice – see below) all six Raynes parameters are necessary for molecules with \( \text{C}_1 \) symmetry, \( c \) and \( e \) vanish by symmetry molecules that have \( \text{C}_s \) point group symmetry.

### 3.1.2 Transitions Intensities

Zare\textsuperscript{67} has derived a formula for the linestrength \( S \) of an asymmetric top transition for a singlet state. Ref. 66 modified it for a doublet state and Bunker and Jensen\textsuperscript{76} have derived a general formula (Eq. 14.48) for the linestrength of an asymmetric top in an arbitrary spin state. We can use and simplify that formula to obtain

\[
S(J'f'T'; J''f''T'') = g_{ns}(2J'' + 1)(2J' + 1)
\]

\[
| \sum_{N''} \sum_{K''} \sum_{K''} \sum_{q} (-1)^{N''+N''+K''} [(2N'' + 1)(2J'' + 1)]^{1/2} \left( \begin{array}{ccc}
N'' & 1 & N' \\
K'' & q & -K''
\end{array} \right) \left( \begin{array}{ccc}
N'' & J'' & S \\
J' & N' & 0
\end{array} \right) a_{N''}^{K''} a_{N''}^{K''} \langle A, 0 | T_{q}^{1}(\mu) | X, 0 \rangle |^{2}
\]

In the above vibronic mixing is neglected and \( S \) is assumed to be a good quantum number. The nuclear spin degeneracy of the final and initial state is denoted \( g_{ns} \) and the mixing coefficients \( a_{N''}^{J''} \) are assumed real and \( T_{q}^{1}(\mu), q = 0, \pm 1, \) is a component of the dipole moment tensor in the molecule fixed axis system.
The mixing coefficients of the basis functions in the eigenfunctions of $H_T$ have
been defined in a somewhat more general and simplified manner than before:

$$|Jf\tau(NK)SM_J\rangle = \sum_{N''=J+S} \sum_{K''=-N''} a^{Jf\tau}_{N''K''}|JN''K''SM_J\rangle$$ (3.11)

In the eigenket $|Jf\tau(NK)SM_J\rangle$, the quantum numbers not in parenthesis are
assumed to be rigorously good while $N$ and $K$ are not but are still useful since $H_{SR}$ is
generally small compared to $H_{Rot}$. The “new” quantum numbers, $f$ and $\tau$, denote for
a given $J$ respectively the spin components and the asymmetric rotor level (standardly
designated by $K_a$, $K_c$).

### 3.1.3 The Torsional Hamiltonian

We have recorded the room temperature cavity ringdown spectrum of the methyl
peroxy radical which is going to be discuss in Chapter 4. Our experimental observation
suggested that the CH$_3$ torsional mode play a key role in the understanding of
this radical. Hence, we need to implement a torsional Hamiltonian into our existing
model described above.

Following Lin and Swalen, the rotation-vibration Hamiltonian can be written as

$$\hat{H} = F (p_{\alpha} - \rho \cdot N)^2 + V(\alpha) + H_{Rot}$$ (3.12)

$H_{Rot}$ has been defined previously in Eq 3.2. We can now write,

$$\hat{H} = F (p_{\alpha} - \rho \cdot N)^2 + V(\alpha) + A N_a^2 + B N_b^2 + C N_c^2$$ (3.13)
In the above equation, \((a, b, c)\) refer to the principal (inertial) axis (PAM system) and Eq (3.13) assumes that the torsional motion about \(\alpha\) is decoupled from any other vibrational degree of freedom. The rotational angular momentum is \(N\), and the definitions of the rotational constants, as well as \(F\) and \(\rho\), are given in Table 3.1.

\[
\begin{align*}
A &= \frac{\hbar^2}{2I_a} & \rho_a &= \frac{\lambda_a I_\alpha}{I_a} \\
B &= \frac{\hbar^2}{2I_b} & \rho_b &= \frac{\lambda_b I_\alpha}{I_b} \\
C &= \frac{\hbar^2}{2I_c} & \rho_c &= \frac{\lambda_c I_\alpha}{I_c} \\
\theta &= \tan^{-1}(\rho_b/\rho_a) \\
F &= \frac{\hbar^2}{2rI_\alpha} & r &= 1 - I_\alpha(\frac{\lambda_a^2}{I_a} + \frac{\lambda_b^2}{I_b} + \frac{\lambda_c^2}{I_c})
\end{align*}
\]

Table 3.1: Definitions\(^5\) of constants in molecular Hamiltonian that are dependent on molecular geometry. \(I_a, I_b, I_c\) are the moments of inertia in the PAM system and \(I_\alpha\) is the corresponding quantity for methyl group rotation about the CO axis. The components, \(\rho_i\), of \(\rho\) are defined in terms of \(\lambda_i\), where the \(\lambda_i\) are direction cosines relating the principal axes and the CO axis. Physically \(\theta\) is the angle \(\rho\) makes with the \(a\) axis.

When the axis of internal motion lies in the \(a, b\) plane as is the case with the methyl peroxy radical, the \(c\) component of \(\rho\) vanishes. We can further simplify \(\hat{H}\) by following the procedure (\(\rho\) axis method - RAM) of Hougen \textit{et al.}\(^5,\text{78}\) and Herbst, De Lucia, and co-workers\(^79-81\) by rotating to the \(\rho\) axis system, i.e. \((a, b, c) \rightarrow (z, x, y)\), which causes \(\rho_x = \rho_y = 0\) by definition. Since \(\rho_c = 0\) by symmetry, the transformation corresponds to a simple rotation about the \(c\)–axis through an angle \(\theta\) which is defined.
in Table 3.1 in terms of the geometric parameters of the molecule.

Hougen et al. have shown that in the RAM system,

\[ \hat{H} = \hat{H}_1 + \hat{H}_2 \]

\[ \hat{H}_1 = F(p_\alpha - \rho N_z)^2 + V(\alpha) \] (3.15)

and

\[ \hat{H}_2 = A_R N_z^2 + B_R N_x^2 + C_R N_y^2 + D_R (N_z N_x + N_x N_z) \] (3.16)

Hougen et al. have pointed out that \( \hat{H}_1 \) is diagonal in the primitive rotational basis, \( |N, K\rangle \) where \( K \) is the projection of \( N \) along \( \rho \). Due to the fact that we tend to analyze a room temperature spectrum, this basis set is adequate and one does not need to consider the \( M_J \) quantum number. \( \hat{H}_2 \) is the “normal” asymmetric top \( \hat{H} \) expressed in the RAM system, which of course can have matrix elements off-diagonal in \( K \). In transforming from the PAM to the RAM system, we have decoupled \( \hat{H}_1 \) and \( \hat{H}_2 \) but introduced the rotational term with the coefficient \( D_R \). The relationship between the rotational constants, \( A_R \), etc, in the RAM and those in the PAM system are given in Table 3.2.

Since for the most part rotational structure is not resolved due to the congestion for room temperature spectra, we will concentrate on \( \hat{H}_1 \) and the terms in \( \hat{H}_2 \) that are diagonal in \( K \). Jet-cooled higher resolution experiments are presently under analysis. For those experiments, the eigenvalues of \( \hat{H}_1 \) must be added to the entire \( \hat{H}_2 \) matrix, which also must be supplemented by the spin-rotation interaction since the electronic states involved are doublets.
A_R = A \cos^2 \theta + B \sin^2 \theta

B_R = A \sin^2 \theta + B \cos^2 \theta

C_R = C

D_R = (B-A) \cos \theta \sin \theta

\rho = (\rho_a^2 + \rho_b^2)^{1/2} = \rho_z

Table 3.2: Relationship between molecular constants (see Table 3.1) in the PAM and those (subscripted R) in the RAM system. The components of the vector $\rho$ in the two systems are also related.

3.2 Analyzing the Spectrum

Historically, our group has used the approach of a least square fitting (LSF) procedure, employing the SpecView software package,\textsuperscript{82} in order to obtain molecular parameters from a high resolution spectrum. This approach is traditional and completely appropriate if one has a well resolved spectrum for which individual line assignments are possible. However the applicability of such an approach is limited when one only has partially resolved spectra. To resolve this issue, we employed a different approach to simulate partially rotationally resolved spectra by using an Evolutionary Algorithm (EA). The EA is a semi-automated fitting procedure which mimic the mutation processes present in nature. It also has the advantage to consider both the line position as well as the line intensity to fit an experimental spectra. This allows us to obtain as much as possible all possible spectroscopic information present in an experimental
The EA is a method based on a Darwinian approach. In nature, natural selection occurs by reproduction with mutation of genes leading to only the best adapted individuals surviving. From a spectroscopic point of view, the EA approach reproduces this behavior to fit an experimental spectrum with a model based upon the differences of the eigenvalues of a given Hamiltonian.

Each of the molecular parameters can be thought of as a gene. Typically, for high-resolution $\tilde{A} - \tilde{X}$ electronic spectra of peroxy radicals 15 molecular parameters are considered and are mutated like genes, to select a set, corresponding to the chromosome, which ultimately best reproduces the experimental spectra. The evolution to this “best fit” chromosome is determined by how well a spectral simulation based on a given chromosome resembles the experimental result. In this work, a chromosome is formed from 18 genes corresponding to the parameters that are fitted. These include the 15 total molecular parameters, i.e., 3 rotational and 4 spin-rotational constants for each the ground and first electronic state and the band origin ($T_{00}$) that are best appropriate to describe the radical under our experimental conditions, as well as the rotational temperature, and the two angles $\theta$ and $\phi$ describing the orientation of the electric dipole moment with respect to the principal axis system. During the initial step of the fit, values for all the parameters, i.e., genes, are randomly set between the upper and lower limits input by the user. (See below the process for choosing these limits.) Typically a total of 567 chromosomes are generated.
The next generation of chromosomes is generated from the selected best parent(s) (highest fitness) using an Evolution Strategy (ES) with mutative step size control. Mutative step size control adapts the speed at which the parameter space is explored with each optimization step. It tends to work well for the adaptation of a global step size but tends to fail when it comes to the step size of each individual parameter due to several disruptive effects. The derandomized algorithm DR2 used here is aiming at the accumulation of information about the correlation or anticorrelation of past mutation vectors that connect trial solutions in order to tackle this problem. The high effectiveness of this approach for spectral analysis has been demonstrated recently.

As mentioned previously, the quality of the match between the experimental spectrum and a given simulation is evaluated by a fitness function, \( F_{fg} \). It has been shown by Hageman that \( F_{fg} \) can be defined as:

\[
F_{fg} = \frac{\sum_{r=-l}^{l} w(r) \sum_{i=1}^{N} f(i)g(i + r)}{\sqrt{\sum_{r=-l}^{l} w(r) \sum_{i=1}^{N} f(i)f(i + r)} \sqrt{\sum_{r=-l}^{l} w(r) \sum_{i=1}^{N} g(i)g(i + r)}}
\]

(3.17)

In the above \( f \) represent the experimental spectrum while \( g \) represents the simulated spectrum. The function \( w(r) \) is called the overlap function and controls the sensitivity of the fitness function for a shift of the experimental and simulated spectra relative to each other.

If both the experimental and simulated spectra are viewed as vectors with \( N \) dimensions (frequency points), then the numerator of \( F_{fg} \) is a weighted dot product.
of these vectors and the denominator is simply a normalization factor, i.e.,

\[ F_{fg} = \frac{(f \cdot g)}{\|f\| \|g\|} \]  \hspace{1cm} (3.18)

where the dot product \((f \cdot g)\) includes the weighting function \(W_{ij}\) and the norms of \(f\) and \(g\) are defined as:

\[ \|f\| = \sqrt{(f \cdot f)} \]  \hspace{1cm} (3.19)

and

\[ \|g\| = \sqrt{(g \cdot g)} \]  \hspace{1cm} (3.20)

It has been found\(^{87}\) that \(w(r)\) can be equated to a simple triangular function with a basewidth of \(2\ell\) points:

\[ w(r) = \begin{cases} 
1 - |r|/\ell & \text{for } |r| < \ell \\
0 & \text{otherwise}
\end{cases} \]  \hspace{1cm} (3.21)

The EA is a very suitable for parallel computation. Hence a quick convergence or the molecular parameters can be achieve fairly straight forwardly. A detailed description of the EA input and output parameters can be found in Appendix A.

### 3.3 Quantum Chemistry Calculations

In order for the fitting procedure to be effective, one need to define a priori a range within which each parameter value may lie. Electronic structure calculations
are very useful in setting these ranges. After the spectrum has been fit by the EA approach, the fit parameter values can in turn be used to benchmark the quality of particular electronic structure methods.

Using the Gaussian 03 software package,\textsuperscript{88} we computed the global minima for each alkyl peroxy of interest for both ground, $\tilde{X}$ and first excited, $\tilde{A}$, electronic states using different methods and basis sets.

### 3.3.1 Details of the Performed Calculations

These calculations included a density functional theory (DFT) method (B3LYP) with a 6-31+g(d) basis set which represents a fairly inexpensive calculation. We also used a full second order Møller-Plesset perturbation calculation (MP2 (FULL)) with a 6-31g(d) basis set. The latter set of calculation has been chosen since it has been shown that, in the case of the alkyl peroxy radicals, the G2 composite method yields very accurate $T_{00}$ values.\textsuperscript{39} Hence, the optimized geometry from the G2 method, which is MP2(FULL)/6-31g(d),\textsuperscript{89} ought to be fairly representative of the electronic eigenenergies and corresponding geometries of the molecule, which are necessary for calculations of, respectively, the $T_{00}$ values and rotational constants. The final method used was the coupled cluster singlet and doublet, CCSD [6-31g(d)]. This is a somewhat more computationally expensive method and would be of considerable interest to benchmark. For the components of the dipole moments, we turned to a configuration interaction, singles, CIS, method with a 6-31g+(d) basis. We performed the calculation at the $\tilde{X}$ state geometries found by each the CCSD, B3LYP, and MP2 methods.
In order to predict the $T_{00}$ electronic transition by the CCSD and B3LYP methods, we computed the vibrational frequencies for each method and made the zero point energy (ZPE) correction. The $T_{00}$ value from the MP2 method is actually from the G2 method and hence it already contains extra correction terms including the ZPE. It also should be noted that all the corresponding rotational constants have been calculated for the equilibrium geometry and not for the experimentally observed vibrationless level. However since zero-point corrections for rotational constants are typically less than a few tenths of a percent, this only mildly affects comparison between the calculated and observed values.

3.4 Predicting the Spin-Rotation Tensor Components

There is no electronic structure package that directly calculates spin-rotational coupling constants so we use a semi-empirical approach. We have recently, simulated the high resolution, jet cooled CRDS spectrum of the CD$_3$O$_2$ radical. We experimentally determined$^{13}$ for CD$_3$O$_2$ the rotational constants in both the $\tilde{X}$ and the $\tilde{A}$ states and four components of the spin rotation tensor for this C$_s$ symmetry molecule, i.e., $\epsilon_{aa}$, $\epsilon_{bb}$, $\epsilon_{cc}$ and $\frac{1}{2}(\epsilon_{ab}+\epsilon_{ba})$. Brown, Sears and Watson showed that, in the inertial axis system, one could relate the reduced spin-rotation tensor component of two isotopologues via the following transformation:

$$I_R \tilde{\epsilon}_R = I_S \tilde{\epsilon}_S$$  \hspace{1cm} (3.22)

where $I$ represent the moment of inertia tensor and $\tilde{\epsilon}$ the reduced spin-rotation tensor in the respective principal axis systems, with R denoting the reference molecule and
S the isotopologue of interest. Tarczay et al.\textsuperscript{90} extended this procedure to relate the components of the spin-rotation tensor for any molecule in the same family. The basic physical requirement for the Tarczay extension is that the electronic transition be localized on a given chromophore with common electronic structure for all the family members. Under these circumstances, structural modifications to the rest of the molecule will re-orient the principal inertial axes and change the values of tensor components expressed along them but leave unchanged the spin-rotational tensor components expressed in a local axis system tied to the chromophore. Radicals like methyl, ethyl and propyl peroxy seem likely to be well described by this physical picture since for all the open-chain primary peroxy radicals the electronic transition is localized on the $O_2$ chromophore. A convenient local frame for the peroxy radicals has the $z$ axis along the $O_2$ bond with $x$ and $y$ coinciding with the $p$ orbitals perpendicular to it. We therefore conclude that in the local frame:

\[(I_s \tilde{\epsilon}_s)^{loc} = (I_R \tilde{\epsilon}_R)^{loc}\] (3.23)

If $U$ is the unitary transformation relating the local and principal axes system then

\[U_S I_S \tilde{\epsilon}_S U_S^{-1} = U_R I_R \tilde{\epsilon}_R U_R^{-1}\] (3.24)

or

\[\tilde{\epsilon}_S = I_S^{-1} U_S^{-1} U_R \tilde{\epsilon}_R U_R^{-1} U_S\] (3.25)

where $\tilde{\epsilon}_S$ is expressed in the principal axis system. Both the $I$ and the $U$ matrices are solely dependent upon the geometry of the molecule and hence can be calculated.
from the optimized geometry of the electronic structure calculation. We use the spin-
rotation tensor $\epsilon_R$, experimentally determined for CD$_3$O$_2$, as the reference molecule
to calculate $\epsilon_S$ for other peroxy radicals of the same family.
CHAPTER 4

THE METHYL PEROXY RADICAL, CH$_3$O$_2$

4.1 Introduction

The simplest organic peroxy radical, methyl peroxy, CH$_3$O$_2$, is obviously the starting point for spectroscopic detection and analysis. Recently there has been considerable activity surrounding its $\tilde{A}^2A' - \tilde{X}^2A''$ near infrared (NIR) transition. Its potentially richly structured spectrum offers an unambiguous means for the radical’s detection, as well as a starting point for the spectral analyses of all the organic peroxy radicals. These analyses can provide highly accurate benchmarks for quantum chemistry computations on both the structure and dynamics of organic peroxy radicals.

The $\tilde{A} - \tilde{X}$ NIR transition was first observed$^{32}$ by a modulated absorption technique in 1976. The observation lay relatively fallow for a number of years as the strong $\tilde{B} - \tilde{X}$ UV absorption was used to monitor$^{31}$ CH$_3$O$_2$ and other peroxy radicals because its much greater oscillator strength made the detection of the radicals much more sensitive.

However the $\tilde{B} - \tilde{X}$ transition is intrinsically unstructured due to the dissociative nature$^{28}$ of the $\tilde{B}$ state. Hence it is nearly impossible to distinguish one organic peroxy radical from another based upon the $\tilde{B} - \tilde{X}$ transition. This has led to renewed
interest in the study of the $\tilde{A} - \tilde{X}$ electronic transition. Fortunately the relatively new
technique of cavity ringdown spectroscopy (CRDS), due to its inherent multi-passing
capability, provides a highly sensitive technique\textsuperscript{33,65} for detection of organic peroxy
radicals in spite of the low oscillator strength of the NIR $\tilde{A} - \tilde{X}$ transition.

The room temperature CRDS spectra of CH$_3$O$_2$ and CD$_3$O$_2$ were first reported\textsuperscript{33}
in 2000. Thereafter Atkinson and Spillman\textsuperscript{42} used cw (continuous wave) CRDS on
the $\tilde{A} - \tilde{X}$ transition to follow the kinetics of methyl peroxy radicals. Bernstein
and co-workers\textsuperscript{43} have observed the $\tilde{A} - \tilde{X}$ transition using mass spectroscopic de-
tection. A much more detailed study\textsuperscript{37} of the ambient temperature CRDS spectrum
is described in the preceding paper. Recently we have obtained\textsuperscript{3} the first jet-cooled
CRDS spectrum of CH$_3$O$_2$ and CD$_3$O$_2$ and analysis of these spectra is on-going.

Recently, the Miller group studied\textsuperscript{3,37} of the methyl peroxy NIR $\tilde{A}^2A' - \tilde{X}^2A''$
transition, they have detected unusual spectral features. After some investigation we
attribute them to large amplitude motion between the methyl group and the peroxy
group. For simplicity we shall henceforth refer to this motion as methyl torsion since
methyl torsional studies have a rich history and even though the difference in mass
is not that great, the methyl group is lighter than that of the peroxy group.

To more fully understand this wide amplitude motion and its spectral ramifica-
tions we have performed a series of theoretical computations. First we carried out
quantum chemistry calculations for both the $\tilde{X}$ and $\tilde{A}$ states to determine the nature
of the potential energy surface (PES) along a cut in the direction of the wide ampli-
tude motion. Using this PES, the eigenvalues and eigenfunctions were calculated for
the torsional motion along this surface for both states. From the eigenvalues, predictions for the frequencies of the observed torsional transitions could be made. The eigenfunctions also allow for the evaluation of Franck-Condon factors for the various torsional transitions. These are then used to determine which transitions ought to be observable experimentally in the $\tilde{\text{A}} - \tilde{\text{X}}$ spectrum and their relative intensities. Finally the PES for the $\tilde{\text{A}}$ and $\tilde{\text{X}}$ states were scaled to achieve the best match between the predicted and observed ambient temperature spectra. In this way “experimental” barrier heights in both the $\tilde{\text{X}}$ and $\tilde{\text{A}}$ states are determined.

4.2 Electronic Structure Calculation

The description of the electronic structure calculation for methyl peroxy falls into two parts. First we need to determine the electronic structure and energies at the stationary points (global minima and saddle points) on the $\tilde{\text{X}}$ and $\tilde{\text{A}}$ state potentials respectively. Once these have been characterized, we calculate a cut through each of these twelve-dimensional potential surfaces along the methyl torsion coordinate. These one-dimensional cuts are then fit to an expansion in $\cos(3n\alpha)$. This provides an analytical expression for the potential, which is then used to solve the Schrödinger equation for the nuclear motion. The resulting eigenenergies and eigenfunctions allow the prediction of the positions and intensities of transitions involving the wide amplitude torsional motion.

By optimizing the geometry to minimize the energy for both $C_s$ configurations, staggered and eclipsed, we are able to calculate the energies of the stationary points
<table>
<thead>
<tr>
<th>Method/Basis Set</th>
<th>Barrier height in the $\tilde{X}$ state</th>
<th>Barrier height in the $\tilde{A}$ state</th>
<th>$T_e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ROHF/6-31+G(d)</td>
<td>534</td>
<td>1111</td>
<td>4321</td>
</tr>
<tr>
<td>UHF/6-31+G(d)</td>
<td>474</td>
<td>1108</td>
<td>4601</td>
</tr>
<tr>
<td>CCSD/6-31+G(d)</td>
<td>394</td>
<td>1119</td>
<td>7019</td>
</tr>
<tr>
<td>QCISD(T)/6-311G(d,p)</td>
<td>417</td>
<td>1211</td>
<td>7304</td>
</tr>
<tr>
<td>MP2/6-311G(d,p)</td>
<td>306</td>
<td>1250</td>
<td>7116</td>
</tr>
<tr>
<td>MP2/6-311+G(d,p)</td>
<td>283</td>
<td>1173</td>
<td>7145</td>
</tr>
<tr>
<td>MP2/6-311G(2df,p)</td>
<td>252</td>
<td>1189</td>
<td>7151</td>
</tr>
<tr>
<td>MP2/6-311+G(3df,2p)</td>
<td>253</td>
<td>1164</td>
<td>7298</td>
</tr>
<tr>
<td>MP4/6-311G(d,p)</td>
<td>343</td>
<td>1222</td>
<td>7022</td>
</tr>
<tr>
<td>MP4/6-311+G(d,p)</td>
<td>318</td>
<td>1138</td>
<td>7037</td>
</tr>
<tr>
<td>MP4/6-311G(2df,p)</td>
<td>284</td>
<td>1160</td>
<td>7036</td>
</tr>
<tr>
<td>G1</td>
<td>267</td>
<td>945</td>
<td>7334$^a$</td>
</tr>
<tr>
<td>G2</td>
<td>291</td>
<td>996</td>
<td>7451$^a$</td>
</tr>
<tr>
<td>B3LYP/6-31+G(d)</td>
<td>292</td>
<td>1131</td>
<td>7614</td>
</tr>
</tbody>
</table>

Table 4.1: Calculated torsional barriers of methyl peroxy for the $\tilde{X}$ and $\tilde{A}$ electronic states (in cm$^{-1}$).

$^a$ The $T_e$ values have been obtained by correcting $T_{00}$ from the G1 calculation by the $\tilde{A} - \tilde{X}$ difference in ZPE, found to be 76 cm$^{-1}$ using the standard scaling factor of 0.8929.
and hence the torsional barrier heights in both the \( \tilde{X} \) and \( \tilde{A} \) states of CH\(_2\)O\(_2\) at various levels of electronic structure theory using Gaussian 03.\(^{88}\) These results along with the energy difference between the \( \tilde{X} \) and \( \tilde{A} \) states, \( T_e \), are summarized in Table 4.1. As the numbers indicate, the barrier height for the \( \tilde{X} \) state is consistently around 300 cm\(^{-1}\) with a corresponding barrier of between 900 and 1200 cm\(^{-1}\) for the \( \tilde{A} \) state. Calculations including the zero-point energies (ZPE) at both the minimum and maximum energy along the path gave roughly the same barrier height as those without ZPE.

With the exception of the uncorrelated Hartree-Fock calculations, \( T_e \) is predicted to be between 7200 and 7400 cm\(^{-1}\). To compare this with experiment, we must take into account ZPE. When this is done using the G2 method, we obtain a value for the band origin of 7375 cm\(^{-1}\), which is in excellent agreement with the experimental value of 7382 cm\(^{-1}\), as has been previously reported.\(^{33}\)

An interesting feature of the calculated barrier heights is that the barrier on the \( \tilde{A} \) state is three to four times larger than the barrier on the \( \tilde{X} \) state potential surface. In order to understand the origin of this increase, we investigated the molecular orbitals that are involved in the electronic transition. The lower energy orbital has \( A' \) symmetry while the higher energy orbital has \( A'' \) symmetry. Comparing the orbitals with the same symmetry in the staggered and eclipsed configurations for the \( \tilde{X} \) and \( \tilde{A} \) states, we note that the orbitals do not change significantly between the two states. In addition, the shape and extent of the orbitals with \( A' \) symmetry also do not change significantly between the staggered and eclipsed configurations. The orbitals with \( A'' \)
symmetry contain three lobes, separated by nodes. Two are localized on the oxygen atoms and the third is near the hydrogen atoms that are above and below the plane of symmetry. In the staggered configuration, there is some overlap between the parts of the orbital that are on the terminal oxygen and the hydrogen atoms. The larger distance between these atoms in the eclipsed configuration leads to a loss of this overlap and an increase in the energy of this orbital. Since the \( A'' \) orbital is doubly occupied in the \( \tilde{A} \) state, the higher energy of this orbital in the eclipsed configuration leads to a significantly larger barrier for methyl rotation in the \( \tilde{A} \) state compared to the \( \tilde{X} \) state.

After the extrema were examined, the remainder of the potential energy surfaces for both the states were calculated. We could not map out the methyl torsional mode PES using the G2 method since motion along this coordinate reduces the symmetry from \( C_s \) to \( C_1 \) so that in these lowered symmetry configurations the \( \tilde{X} \) and \( \tilde{A} \) states no longer have different symmetry. We therefore mapped the PES of the \( \text{CH}_3 \) torsional mode using a DFT method (i.e. B3LYP) with the 6-31+g(d) basis set.

Figures 4.1 and 4.2 show the resulting PES for these two states of the methyl peroxy radical as functions of the angle, \( \alpha \), defined as the OOCH dihedral angle for one of the three hydrogen atoms in the methyl torsion. The other two OOCH dihedral angles were allowed to relax along with the remaining nine internal coordinates. This angle was varied from 180 to 120 degrees and the remaining angular dependence is determined by symmetry. In constructing these cuts, \( \alpha \), was changed in increments of 5°. The circles in Figures 4.1 and 4.2 represent the points at which electronic
structure calculations were performed. There are other possible definitions for this coordinate, for example the average value of the three OOCH dihedral angles. For methyl peroxy, these two definitions deviate from each other by at most 0.8° for the $\tilde{X}$—state potential and 1.8° for the $\tilde{A}$—state potential.
Figure 4.1: Calculated B3LYP/6-31+g(d) energies are plotted as a function of the methyl torsional angle ($\alpha$) of the methyl peroxy radical in the ground and the first excited electronic state. The points result from the DFT calculation described in the text and the curve represents the analytical potential function $V(\alpha)$. The horizontal lines represent the calculated CH$_3$O$_2$ eigenvalues. The dashed vertical arrows represent the typical sequence bands involving the CH$_3$ torsional mode while the solid ones represent examples of atypical transitions involving the free rotor regime.
Figure 4.2: Calculated B3LYP/6-31+g(d) energies are plotted as a function of the deuterated methyl torsional angle ($\alpha$) of the methyl peroxy radical in the ground and the first excited electronic state. The points result from the DFT calculation described in the text and the curve represents the analytical potential function $V(\alpha)$. The horizontal lines represent the calculated CD$_3$O$_2$ eigenvalues. The dashed vertical arrows represent the typical sequence bands involving the CD$_3$ torsional mode while the solid ones represent examples of atypical transitions involving the free rotor regime.
4.3 Torsional Eigenfunction and Eigenvalue Calculation

To calculate the eigenvalues and eigenfunctions of the torsional Hamiltonian described in Section 3.1.3, Eq. 3.13, we employ an analytical form, $V(\alpha)$, for the cut through the PES. We choose

$$V^y(\alpha) = \frac{1}{2} \sum_{n=0}^{N} S^y V_{3n}^y \cos(3n\alpha)$$

(4.1)

where $y = A$ or $X$ to denote the PES of the $\tilde{A}$ and $\tilde{X}$ states. We fit the $V_{3n}^y$ coefficients using the ab initio points. The analytical fits along the ab initio points are shown with thick, solid lines in Figs. 4.1 and 4.2. As these curves demonstrate, the potential function displays three equivalent wells at $\pm 60^\circ$ and $180^\circ$, the staggered configurations; and the saddle points at $0^\circ$ and $\pm 120^\circ$, the eclipsed configurations. For both the $\tilde{X}$ and $\tilde{A}$ state cuts, we find that a value of $N = 2$ suffices to fit the thirteen computed points with RMS errors of 0.45 cm$^{-1}$ and 2.2 cm$^{-1}$, respectively. Including more terms in the fit will decrease this error, but it does not alter the calculated energies by more than the RMS error of the fits. The resulting values for the $V_{3n}^y$ from the fit are reported in Table 4.2. Table 4.3 reports numerical values of the parameters in $\hat{H}$ that are determined by the ab initio geometry of the molecule.

For purposes of comparing to experiment, we modify the calculated parameters in Tables 4.2 and 4.3 in two ways.

Rather than use the ab initio $F$ value obtained from the structures calculated at the B3LYP/6-31+G(d) level of theory/basis we multiply it by 0.97. This value was chosen based on the fact that when we compared the values of $F$ that are obtained when the geometry of methyl peroxy was evaluated at different levels of theory we
Table 4.2: Values of $F^y$ and the parameters used to analytically fit the potential.

<table>
<thead>
<tr>
<th>Function</th>
<th>$n = 0$</th>
<th>$n = 1$</th>
<th>$n = 2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V^X$</td>
<td>300.220152</td>
<td>294.61972</td>
<td>-5.311006</td>
</tr>
<tr>
<td>$F^X_{\text{CH}_3\text{O}_2}$</td>
<td>6.84669359</td>
<td>0.03417795</td>
<td>-0.0011931</td>
</tr>
<tr>
<td>$F^X_{\text{CD}_3\text{O}_2}$</td>
<td>4.2626301</td>
<td>0.036006</td>
<td>-0.000765</td>
</tr>
<tr>
<td>$V^A$</td>
<td>1085.652582</td>
<td>1126.468376</td>
<td>46.320494</td>
</tr>
<tr>
<td>$F^A_{\text{CH}_3\text{O}_2}$</td>
<td>6.545783</td>
<td>0.025874</td>
<td>0.004023</td>
</tr>
<tr>
<td>$F^A_{\text{CD}_3\text{O}_2}$</td>
<td>3.961716</td>
<td>0.0218658</td>
<td>0.003759</td>
</tr>
</tbody>
</table>

Table 4.3: Values of the parameters in Table 3.1 from the DFT calculation. $1/2I_\alpha$, $A$, $B$ and $C$ are all reported in cm$^{-1}$; the direction cosines, $\lambda_a$ and $\lambda_b$, are both dimensionless and $\lambda_c = 0$. The reported values are the isotropic terms from an expansion of these parameters in $\cos(3n\theta)$ with $n \leq 2$.

<table>
<thead>
<tr>
<th>$y$</th>
<th>molecule</th>
<th>$1/2I_\alpha$</th>
<th>$A$</th>
<th>$B$</th>
<th>$C$</th>
<th>$\lambda_a$</th>
<th>$\lambda_b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X$</td>
<td>CH$_3$O$_2$</td>
<td>4.994454</td>
<td>1.770583</td>
<td>0.371262</td>
<td>0.326303</td>
<td>0.854423</td>
<td>0.519566</td>
</tr>
<tr>
<td></td>
<td>CD$_3$O$_2$</td>
<td>2.499147</td>
<td>1.315576</td>
<td>0.314316</td>
<td>0.281333</td>
<td>0.866334</td>
<td>0.499453</td>
</tr>
<tr>
<td>$A$</td>
<td>CH$_3$O$_2$</td>
<td>5.030221</td>
<td>1.597203</td>
<td>0.372793</td>
<td>0.321352</td>
<td>0.822266</td>
<td>0.569085</td>
</tr>
<tr>
<td></td>
<td>CD$_3$O$_2$</td>
<td>2.517043</td>
<td>1.212843</td>
<td>0.315868</td>
<td>0.277986</td>
<td>0.838299</td>
<td>0.545190</td>
</tr>
</tbody>
</table>
noticed variations. The 0.97 value allowed us to scale the B3LYP value to a value close to that obtained at the CCSD level of theory. This value is also consistent with the expectation that F should be lowered by a couple of percent due to coupling of the torsional motion with other vibrational modes.

We include in \( V^y(\alpha) \) a scalar, \( S^y \), to compensate for errors in the quantum chemistry calculation of the PES. The values of \( S^y \) for the \( \tilde{X} \) and \( \tilde{A} \) states are ultimately chosen to obtain the best agreement between the experimental and calculated spectra.

To calculate numerical eigenvalues and eigenfunctions of \( \hat{H} \), we use a Fourier basis. The eigenfunctions can then generally be written as

\[
|j, \sigma, K\rangle = \sum_n C_{3n,\sigma}(K)e^{i(3n+\sigma)\alpha}
\]

where \( n \) takes on all positive and negative integer values, \( \sigma = 0 \) and \( \pm 1 \). The integer index \( j \) labels eigenvalues of the same value of \( |\sigma| \) in increasing order of energy.

A convenient way to consistently label the torsional eigenvalues and corresponding eigenfunctions is to invoke the \( G_6 \) molecular symmetry group, which is isomorphic to the \( C_{3v} \) point group. The eigenfunctions of methyl peroxy transform as either \( A_1 \), \( A_2 \), or \( E \) under \( G_6 \). For \( K=0 \), the states for which \( \sigma=0 \) transform as \( A_1 \) or \( A_2 \). The states that transform as \( A_1 \) have linear combinations of exponentials with \( C_{3n,0}^j(0) = C_{-3n,0}^j(0) \) for a given \( 3n \), while \( C_{3n,0}^j(0) = -C_{-3n,0}^j(0) \) for the states that transform as \( A_2 \). For \( \sigma=\pm 1 \), the two components transform as \( E \) and have \( C_{3n,1}^j(0) = \pm C_{-3n,-1}^j(0) \). It has long been known that the corresponding eigenvalues can be expressed by
\[ E(j, \sigma, K) = F \sum_n a_n^j \cos \left[ \frac{2\pi n}{3} (\rho K - \sigma) \right] \] (4.3)

By fitting the numerical eigenvalues to the above expression for \( E(j, \sigma, K) \) we can determined numerical values for all \( a_n \) that contribute significantly to the energy.

### 4.4 Spin Statistical Weight

In order to determine the statistical weight of a given molecule (ie in this case CH\(_3\)O\(_2\) and CD\(_3\)O\(_2\)), we need to obtain the symmetry of the rovibronic wavefunction \( \Gamma_{RVE} \) and the symmetry of the total nuclear spin wavefunction \( \Gamma_{NS}^{Tot} \). The rovibronic wavefunction can be obtain by direct product of the rotational wavefunction \( \Gamma_R \), with the vibrational wavefunction \( \Gamma_V \) and the electronic wavefunction \( \Gamma_{El} \).

\[ \Gamma_{RVE} = \Gamma_R \otimes \Gamma_V \otimes \Gamma_{El} \]

Let examine point per point the derivation of the symmetry of all these wavefunctions.

#### 4.4.1 Symmetry of the Nuclear Spin Wavefunction \( \Gamma_{NS}^{Tot} \) for CH\(_3\)O\(_2\)

In the case of CH\(_3\)O\(_2\), we are dealing with fermions (ie hydrogen) with \( I=1/2 \).

Let’s first recall the character table for the \( G_6 \) group which is the appropriate one for methyl peroxy.

<table>
<thead>
<tr>
<th>( G_6 )</th>
<th>( E )</th>
<th>( 2(123) )</th>
<th>( 3(23)^* )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equiv Rot</td>
<td>( R^0 )</td>
<td>( R^0 )</td>
<td>( R^c )</td>
</tr>
<tr>
<td>( A_1 )</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>( A_2 )</td>
<td>1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>( E )</td>
<td>2</td>
<td>-1</td>
<td>0</td>
</tr>
</tbody>
</table>

58
As mentioned previously, for Hydrogen atoms, \( I = 1/2 \). So, we can easily calculate the number of spin functions we will have to deal with for \( \text{CH}_3\text{O}_2 \).

\[
\# \text{ of spin functions} = \prod (2I_i + 1)
\]

Here, we have 3 Hydrogen atoms with a nuclear spin of 1/2 for each of them. So, the number of spin functions will be:

\[
\# \text{ of spin functions} = (2I_i + 1)^3
\]
\[
\# \text{ of spin functions} = (2 \times 1/2 + 1)^3
\]
\[
\# \text{ of spin functions} = 8
\]

Let’s now write the 8 possible spin functions for \( \text{CH}_3\text{O}_2 \)

\( m_J = 3/2 \)

\[
\psi_{ns}^{(1)} = |1/2, 1/2, 1/2\rangle
\]

\( m_J = 1/2 \)

\[
\psi_{ns}^{(2)} = |1/2, 1/2, -1/2\rangle \quad \psi_{ns}^{(3)} = |1/2, -1/2, 1/2\rangle \quad \psi_{ns}^{(4)} = |-1/2, 1/2, 1/2\rangle
\]

\( m_J = -1/2 \)

\[
\psi_{ns}^{(5)} = |1/2, -1/2, -1/2\rangle \quad \psi_{ns}^{(6)} = |-1/2, 1/2, -1/2\rangle \quad \psi_{ns}^{(7)} = |-1/2, -1/2, 1/2\rangle
\]

\( m_J = -3/2 \)

\[
\psi_{ns}^{(8)} = |-1/2, -1/2, -1/2\rangle
\]
Obviously, $\psi^{(1)}_{ns}$ and $\psi^{(8)}_{ns}$ are invariant to any operations of the group and hence have $A_1$ symmetry.

In the case of $m_I = 1/2$, there is 3 spin functions which transform amongst themselves by the elements of the group. The $(23)^*$ operation leaves $\psi^{(4)}_{ns}$ (ie $|-1/2, 1/2, 1/2\rangle$) alone and interchange $\psi^{(2)}_{ns}$ and $\psi^{(3)}_{ns}$ (ie $|1/2, 1/2, -1/2\rangle$ and $|1/2, -1/2, 1/2\rangle$). The $(123)$ operation permutes all the 3 functions.

So, for $m_I = 1/2$

<table>
<thead>
<tr>
<th>$\Gamma_{ns}$</th>
<th>E</th>
<th>2(123)</th>
<th>3(23)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

We can then conclude that for $m_I = 1/2$

$$\Gamma_{ns} = A_1 \oplus E$$

It is obvious that the result for $m_I = -1/2$ will be the same as the one for $m_I = 1/2$.

We can now determine the overall symmetry of the spin wavefunction for CH$_3$O$_2$.

$$\Gamma_{NS}^{Tot} = A_1 \oplus A_1 \oplus A_1 \oplus E \oplus A_1 \oplus E$$

$$\Gamma_{NS}^{Tot} = 4A_1 \oplus 2E$$

We can correlate the above results as a function of $I_T$ and express it for all it possible values as function of irreducible representations.

We can define the total spin function $|I_T,M_I\rangle$. $I_T$ is defined by,

$$\tilde{I}_T = \tilde{I}_1 + \tilde{I}_2 + \tilde{I}_3$$

(4.4)
where 1, 2, 3 denote the 3 H (or D) nuclei. Now, let’s write,

\[ \tilde{I}_T = \tilde{I}_1 + \tilde{I}_3 \]  
\[ \tilde{I}_T = \tilde{I}_1 + \tilde{I}_2 \]  

(4.5)

For CH$_3$O$_2$, the possible values of $I_T$ are: $I_T = 1, 0$ and $I_T = 3/2, 1/2, 1/2$. We now need to find out the symmetry of the nuclear spin functions. For this, we will use the G$_6$ character table expressed previously. A straightforward way to do this would be to express each function $|I_T, M_I\rangle$ in terms of linear combination of the basis $|I_T, M_1\rangle |I_T, M_2\rangle |I_T, M_3\rangle$ using the Clebsch-Gordon coefficients. We would then examine the transformation properties of each $|I_T, M_I\rangle$ under the elements of G$_6$. This is straightforward but for one at least too laborious. Hence, we will try to assign the correct irreducible representation to the $|I_T, M_I\rangle$. To do this, we will consider the symmetry by product function $|I_T, M_1\rangle |I_T, M_2\rangle |I_T, M_3\rangle$ and their general relation to $|I_T, M_I\rangle$. We can then find that,

\[ |I_T = 3/2, M_I = \pm 3/2\rangle = |I_T = 3/2, M_I = \pm 1/2\rangle |I_T = 1/2, M_I = \pm 1/2\rangle \]  
\[ |I_T = 1/2, M_I = \pm 1/2\rangle \]  

(4.6)

The RHS is obviously invariant under any exchange of H nuclei, so $|I_T, M_I\rangle$ must be A$_1$ for $T'=3/2$ for all 4 $M_I$ values. Now, we can consider the two $|I_T=1/2, M_I\rangle$ functions. For all startes, $M_I=m_1+m_2+m_3 = \pm 1/2$ and the 3 decoupled functions pr $|m_I\rangle$ are,

$|1/2, 1/2, -1/2\rangle$, $|1/2, -1/2, 1/2\rangle$ and $|-1/2, 1/2, 1/2\rangle$
We now see which function are invariant or not with respect of the $G_6$ character table.

We generally see that

\[
\begin{array}{ccc}
E & (123) & (23) \\
3 & 0 & 1
\end{array}
\]

In the $G_6$ character table, we see that this correspond to $A_1 + E$. The $A_1$ irrep is already assign to $|I_T=3/2, M_I=1/2\rangle$ state. The two remaining $I_T=1/2$ functions must then transform as $E$. We can now summarize the $I_T$ symmetry as:

<table>
<thead>
<tr>
<th>$I_T$</th>
<th>Irreducible representation</th>
</tr>
</thead>
<tbody>
<tr>
<td>3/2</td>
<td>$A_1$</td>
</tr>
<tr>
<td>1/2</td>
<td>$E$</td>
</tr>
<tr>
<td>1/2</td>
<td>$E$</td>
</tr>
</tbody>
</table>

4.4.2 Symmetry of the Nuclear Spin Wavefunction $\Gamma_{NS}^{Tot}$ for CD$_3$O$_2$

Let’s now try to figure out the symmetry of the spin wavefunction for CD$_3$O$_2$. This derivation becomes a little bit more tricky since D has a nuclear spin of $I = 1$ and so that the total number of spin function will be:

\[
\# \text{ of spin functions} = (2 \times 1 + 1)^3
\]

\[
\# \text{ of spin functions} = 27
\]

Let’s now try to write all the 27 spin functions for CD$_3$O$_2$.

$m_I = 3$

\[
\psi_{1s}^{(1)} = |1, 1, 1\rangle
\]

$m_I = 2$
\begin{align*}
\psi_{ns}^{(2)} &= |1, 1, 0\rangle \quad \psi_{ns}^{(3)} = |1, 0, 1\rangle \quad \psi_{ns}^{(4)} = |0, 1, 1\rangle \\
\psi_{ns}^{(5)} &= |1, 0, 0\rangle \quad \psi_{ns}^{(6)} = |0, 1, 0\rangle \quad \psi_{ns}^{(7)} = |0, 0, 1\rangle \\
\psi_{ns}^{(8)} &= |1, 1, -1\rangle \quad \psi_{ns}^{(9)} = |1, -1, 1\rangle \quad \psi_{ns}^{(10)} = |-1, 1, 1\rangle \\
\psi_{ns}^{(11)} &= |0, 0, 0\rangle \quad \psi_{ns}^{(12)} = |1, -1, 0\rangle \quad \psi_{ns}^{(13)} = |1, 0, -1\rangle \\
\psi_{ns}^{(14)} &= |0, 1, -1\rangle \quad \psi_{ns}^{(15)} = |0, -1, 1\rangle \quad \psi_{ns}^{(16)} = |-1, 1, 0\rangle \\
\psi_{ns}^{(17)} &= |-1, 0, 1\rangle \\
\psi_{ns}^{(18)} &= |-1, 0, 0\rangle \quad \psi_{ns}^{(19)} = |0, -1, 0\rangle \quad \psi_{ns}^{(20)} = |0, 0, -1\rangle \\
\psi_{ns}^{(21)} &= |-1, -1, 1\rangle \quad \psi_{ns}^{(22)} = |-1, 1, -1\rangle \quad \psi_{ns}^{(23)} = |1, -1, -1\rangle \\
\psi_{ns}^{(24)} &= |-1, -1, 0\rangle \quad \psi_{ns}^{(25)} = |-1, 0, -1\rangle \quad \psi_{ns}^{(26)} = |0, -1, -1\rangle \\
\psi_{ns}^{(27)} &= |-1, -1, -1\rangle
\end{align*}

When we are looking carefully at the spin functions, we can see that it is obvious that \(\psi_{ns}^{(1)}\), \(\psi_{ns}^{(11)}\) and \(\psi_{ns}^{(27)}\) have \(A_1\) symmetry.

Let’s now try to figure out the symmetry for different values of \(m_I\).

For \(m_I = 2\)
None of the spin functions are conserved with respect of (123). Concerning (23)*, only $\psi_{ns}^{(4)}$ is conserved.

So,

<table>
<thead>
<tr>
<th></th>
<th>E</th>
<th>2(123)</th>
<th>3(23)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_{ns}$</td>
<td>3</td>
<td>0</td>
<td>1</td>
</tr>
</tbody>
</table>

Obviously, the result for $m_I = -2$ will be the same as the one for $m_I = 2$

$$\Gamma_{ns} = A_1 \oplus E$$

For $m_I = 1$

None of the spin functions are conserved with respect of (123). Concerning (23)*, only $\psi_{ns}^{(5)}$ and $\psi_{ns}^{(10)}$ are conserved.

So,

<table>
<thead>
<tr>
<th></th>
<th>E</th>
<th>2(123)</th>
<th>3(23)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_{ns}$</td>
<td>6</td>
<td>0</td>
<td>2</td>
</tr>
</tbody>
</table>

This imply that :

$\chi(A_1) = 1/6 \times (6+0+6) = 2$

$\chi(A_2) = 1/6 \times (6+0-6) = 0$

$\chi(E) = 1/6 \times (12+0+0) = 2$

Obviously, the result for $m_I = -1$ will be the same as the one for $m_I = 1$

$$\Gamma_{ns} = 2A_1 \oplus 2E$$

Let finally deal with $m_I = 0$

$m_I = 0$
\( \psi_{ns}^{(11)} \) has obviously \( A_1 \) symmetry.

None of the other spin functions are conserved with respect to (123) as well as (23)*.

So,

\[
\begin{array}{c|ccc}
\Gamma_{ns} & E & 2(123) & 3(23)^* \\
\hline
6 & 0 & 0
\end{array}
\]

This imply that:

\[
\chi(A_1) = \frac{1}{6} \times (6+0+0) = 1
\]

\[
\chi(A_2) = \frac{1}{6} \times (6+0+0) = 1
\]

\[
\chi(E) = \frac{1}{6} \times (12+0+0) = 2
\]

So,

\[
\Gamma_{ns} = A_1 \oplus A_2 \oplus 2E
\]

Now, we can easily determine the symmetry of \( \Gamma_{NS}^{\text{Tot}} \) for CD_3O_2.

\[
\Gamma_{NS}^{\text{Tot}} = A_1 \oplus A_1 \oplus A_1 \oplus 2(A_1 \oplus E) \oplus 2(2A_1 \oplus 2E) \oplus A_1 \oplus A_2 \oplus 2E
\]

\[
\Gamma_{NS}^{\text{Tot}} = 10 \ A_1 \oplus A_2 \oplus 8E
\]

We can express the total spin function as described previously and find that:

<table>
<thead>
<tr>
<th>( I_T )</th>
<th>Irreducible representation</th>
</tr>
</thead>
<tbody>
<tr>
<td>(</td>
<td>I_T=3,M_I\rangle )</td>
</tr>
<tr>
<td>(</td>
<td>I_T=1,M_I\rangle )</td>
</tr>
<tr>
<td>(</td>
<td>I_T=0,M_I=0\rangle )</td>
</tr>
<tr>
<td>( 2</td>
<td>I_T=2,M_I\rangle )</td>
</tr>
</tbody>
</table>

Now that we have the symmetry of the total nuclear spin wavefunction, we need to work the symmetry of the rotational, vibrational and electronic wavefunction.
4.4.3  Symmetry of the Rotational wavefunction $\Gamma_R$

Let’s see how the symmetry of the rotational wavefunction changes with respect of $K$ and $J$.

4.4.4  Case where $K = 0$

Let first treat the case where $K = 0$ and recall the $G_6$ character table.

<table>
<thead>
<tr>
<th>$G_6$</th>
<th>E</th>
<th>2(123)</th>
<th>3(23)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equiv Rot</td>
<td>R$^0$</td>
<td>R$^0$</td>
<td>R$^\pi_z$</td>
</tr>
<tr>
<td>$A_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$A_2$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>E</td>
<td>2</td>
<td>-1</td>
<td>0</td>
</tr>
</tbody>
</table>

From Bunker and Jensen$^{76}$ on page 279, for a symmetric top wavefunction $|J,0\rangle$ using the transformation properties of the Euler angle given in Table 12-2 (page 266), that we can deduce that

$$R_\beta^z |J,0\rangle = |J,0\rangle$$

and

$$R_\alpha^\beta |J,0\rangle = (-1)^J|J,0\rangle$$

where $z$ represent the principal axis of the molecule of interest and $\beta$ the rotation angle along the z-axis and where $\alpha$ represent a plan of symmetry of the molecule corresponding to a rotation of and angle $\pi$. So, from this 2 relations, we can deduce that for $K = 0$ and $J$ even, the rotational wavefunction will have $A_1$ symmetry and that for $K = 0$ and $J$ odd, the rotational wavefunction will have $A_2$ symmetry.
Now that we have the symmetry of the rotational wavefunction for $K = 0$, let’s work out the symmetry for $K > 0$.

### 4.4.5 Case where $K > 0$

In that case, we need to use the following formulae (Bunker and Jensen\textsuperscript{76} page 279).

$$R^\beta_\pi |J, K\rangle = e^{iK\beta} |J, K\rangle$$

and

$$R^\pi_\alpha |J, K\rangle = (-1)^Je^{-2iK\alpha} |J, -K\rangle$$

$$R^\pi_c \equiv R^\pi_{\pi/2}$$

So,

$$R^\pi_\alpha |J, K\rangle = (-1)^Je^{-2iK\pi/2} |J, -K\rangle$$

$$R^\pi_\alpha |J, K\rangle = (-1)^{J-K}|J, -K\rangle$$

We can now derive the symmetry of the rotational wavefunction for $K > 0$

$$R^\pi_c \{|J, K\rangle \pm (-1)^{J-K}|J, -K\rangle\} = \{(-1)^{J-K}|J, -K\rangle \pm |J, K\rangle\}$$

$$\{|J, K\rangle \pm (-1)^{J-K}|J, -K\rangle\} = |J, K\rangle_{\pm}$$

$$R^\pi_c \{|J, K\rangle \pm (-1)^{J-K}|J, -K\rangle\} = \pm |J, K\rangle_{\pm}$$

This imply that for + we will have $A_1$ symmetry and for - we will have $A_2$ symmetry.

So, for $K > 0$ $\Gamma_R$ transform as:
\[ \Gamma_R = A_1 \oplus A_2 \]

<table>
<thead>
<tr>
<th>( K &gt; 0 )</th>
<th>( \Gamma_R )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( A_1 \oplus A_2 )</td>
</tr>
</tbody>
</table>

### 4.4.6 Symmetry of the Vibrational and the Electronic Wavefunctions \( \Gamma_V \) and \( \Gamma_{EI} \)

Now that we have have the symmetry of the rotational wavefunction for any \( K \) or \( J \), we can work out the symmetry of the vibrational and the electronic wavefunctions.

First of all let’s work on the vibrational wavefunction’s symmetry. Since we are only dealing with the torsional eigenvalues of methyl peroxy, the vibrational wavefunction will have either \( A_1 \), or \( A_2 \) or \( E \) symmetry.

\[ \Gamma_V = A_1 \oplus A_2 \oplus E \]

Now, concerning the symmetry of the electronic wavefunction, we know the the \( \tilde{X} \) electronic state of CH\(_3\)O\(_2\) has \( A'' \) symmetry in the \( C_s \) group. This correspond to a symmetry of \( A_2 \) under \( G_6 \).

So,

\[ \Gamma_{EI} = A_2 \]

The last small remaining point we have to deal with before summarizing everything is the way to count the weighting for a given level.
4.4.7 Counting

It is known that for fermions, the total wavefunction has to be antisymmetric with respect of interchange of the 2 other protons, and that for bosons, the total wavefunction has to be symmetric with respect of interchange of the 2 other protons.

So, one would think that for CH$_3$O$_2$, the total wavefunction has to contain $A_2$ and that for CD$_3$O$_2$, the total wavefunction has to contain $A_1$.

The "problem" here is that we are working under $G_6$ which means that we don’t have the (23) operation but the (23)*. So, for fermions if we are looking to the CNPI group associated to $G_6$ (ie $D_{3h}$) which contains the operation (23), we can easily see that $A'_2$ under $D_{3h}$ will correspond to $A_2$ under $G_6$ and that $A''_2$ under $D_{3h}$ will correspond to $A_1$ under $G_6$.

For bosons, the same principle is applied. The total wavefunction has to be totally symmetric with respect of interchange of the 2 other protons. So, for bosons if we are looking to the CNPI group associated to $G_6$ (ie $D_{3h}$) which contains the operation (23), we can easily see that $A'_1$ under $D_{3h}$ will correspond to $A_1$ under $G_6$ and that $A''_1$ under $D_{3h}$ will correspond to $A_2$ under $G_6$.

So, we can conclude that for both, fermions and bosons, the total wavefunction has to contain either $A_1$ or $A_2$.

We can now determine the weight associated to any transition for methyl peroxy.

4.4.8 Statistical Weight for CH$_3$O$_2$ and CD$_3$O$_2$
Table 4.4: Statistical Weight for the CH$_3$O$_2$ radical for $K = 0$

<table>
<thead>
<tr>
<th>$K=0, J$ even</th>
<th>$A_1$</th>
<th>$A_2$</th>
<th>$E$</th>
<th>$A_2$</th>
<th>$4A_2$</th>
<th>2E</th>
<th>4</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K=0, J$ odd</td>
<td>$A_2$</td>
<td>$A_1$</td>
<td>$A_2$</td>
<td>$E$</td>
<td>$4A_1$</td>
<td>$2A_1 \oplus 2A_2 \oplus 2E$</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>CH$_3$O$_2$</td>
<td>$\Gamma_R$</td>
<td>$\Gamma_V$</td>
<td>$\Gamma_{V'\Gamma}$</td>
<td>$\Gamma_{RVE} \otimes \Gamma_{tot}^{NS}$</td>
<td>$\Gamma_{RVE} \otimes \Gamma_{tot}^{NS}$</td>
<td>SW ($\uparrow A_1 + \uparrow A_2$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-----------</td>
<td>----------</td>
<td>----------</td>
<td>----------------</td>
<td>--------------------------------</td>
<td>--------------------------------</td>
<td>-----------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>A$_1$</td>
<td>A$_2$</td>
<td>4A$_2$</td>
<td>2E</td>
<td>+</td>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>+</td>
<td>A$_1$</td>
<td>+</td>
<td>+</td>
<td>2E</td>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>A$_2$</td>
<td></td>
<td>4A$_1$</td>
<td>2E</td>
<td>+</td>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>+</td>
<td>A$_2$</td>
<td>+</td>
<td>+</td>
<td>2E</td>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>E$_+$</td>
<td>E</td>
<td>4E</td>
<td>2A$_1$\oplus 2A$_2$\oplus 2E</td>
<td>+</td>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>+</td>
<td>E$_-$</td>
<td>4E</td>
<td>2A$_1$\oplus 2A$_2$\oplus 2E</td>
<td>+</td>
<td>4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4.5: Statistical Weight for the CH$_3$O$_2$ radical for $K > 0$
<table>
<thead>
<tr>
<th>CD$_3$O$_2$</th>
<th>$\Gamma_R$</th>
<th>$\Gamma_V$</th>
<th>$\Gamma_{E'l}$</th>
<th>$\Gamma_{RVE} \otimes \Gamma_{Tot}^{10A_1}$</th>
<th>$\Gamma_{RVE} \otimes \Gamma_{Tot}^{10A_1}$</th>
<th>$\Gamma_{RVE} \otimes \Gamma_{Tot}^{10A_1}$</th>
<th>SW ($\sharp A_1 + \sharp A_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K=0, J$ even</td>
<td>$A_1$</td>
<td>$A_1$</td>
<td>$A_2$</td>
<td>$A_2$</td>
<td>$A_1$</td>
<td>$A_1$</td>
<td>$8E$</td>
</tr>
<tr>
<td></td>
<td>$A_2$</td>
<td>$A_2$</td>
<td>$A_1$</td>
<td>$A_1$</td>
<td>$A_2$</td>
<td>$A_2$</td>
<td>$8E$</td>
</tr>
<tr>
<td></td>
<td>$E$</td>
<td>$E$</td>
<td>$10A_2$</td>
<td>$10A_1$</td>
<td>$10E$</td>
<td>$10E$</td>
<td>$8A_1 \oplus 8A_2 \oplus 8E$</td>
</tr>
<tr>
<td>$K=0, J$ odd</td>
<td>$A_2$</td>
<td>$A_1$</td>
<td>$A_1$</td>
<td>$A_1$</td>
<td>$A_2$</td>
<td>$A_2$</td>
<td>$8E$</td>
</tr>
<tr>
<td></td>
<td>$A_2$</td>
<td>$A_2$</td>
<td>$A_1$</td>
<td>$A_1$</td>
<td>$A_2$</td>
<td>$A_2$</td>
<td>$8E$</td>
</tr>
<tr>
<td></td>
<td>$E$</td>
<td>$E$</td>
<td>$10A_2$</td>
<td>$10A_1$</td>
<td>$10E$</td>
<td>$10E$</td>
<td>$8A_1 \oplus 8A_2 \oplus 8E$</td>
</tr>
</tbody>
</table>

Table 4.6: Statistical Weight for the CD$_3$O$_2$ radical for $K = 0$
<table>
<thead>
<tr>
<th>CD$_3$O$_2$</th>
<th>$\Gamma_R$</th>
<th>$\Gamma_V$</th>
<th>$\Gamma_{ET}$</th>
<th>$\Gamma_{RVE}\otimes\Gamma_{NS}^{10A_1}$</th>
<th>$\Gamma_{RVE}\otimes\Gamma_{NS}^{A_2}$</th>
<th>$\Gamma_{RVE}\otimes\Gamma_{NS}^{8E}$</th>
<th>SW ($\sharp A_1 + \sharp A_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$A_1$</td>
<td>A$_2$</td>
<td>10A$_2$</td>
<td>A$_1$</td>
<td>8E</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$+$</td>
<td>$+$</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>8E</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>$A_1$</td>
<td>10A$_1$</td>
<td>A$_2$</td>
<td>8E</td>
<td>11</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$+$</td>
<td>+</td>
<td>+</td>
<td>A$_1$</td>
<td>8E</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>$K &gt; 0$</td>
<td>(A$_1$ $\oplus$ A$_2$)</td>
<td>A$_2$</td>
<td>A$_2$</td>
<td>8A$_1$ $\oplus$ 8A$_2$ $\oplus$ 8E</td>
<td>16</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$E$</td>
<td>E$_+$</td>
<td>10E</td>
<td>E</td>
<td>8A$_1$ $\oplus$ 8A$_2$ $\oplus$ 8E</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$+$</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>8A$_1$ $\oplus$ 8A$_2$ $\oplus$ 8E</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$E_-$</td>
<td>10E</td>
<td>E</td>
<td>8A$_1$ $\oplus$ 8A$_2$ $\oplus$ 8E</td>
<td>16</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4.7: Statistical Weight for the CD$_3$O$_2$ radical for $K > 0$
We can finally conclude that the statistical weight for CH₃O₂ is

<table>
<thead>
<tr>
<th>CH₃O₂</th>
<th>A₁</th>
<th>A₂</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Statistical Weight</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
</tbody>
</table>

And that the one associated with CD₃O₂ is

<table>
<thead>
<tr>
<th>CD₃O₂</th>
<th>A₁</th>
<th>A₂</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Statistical Weight</td>
<td>11</td>
<td>11</td>
<td>16</td>
</tr>
</tbody>
</table>

4.5 Results

In order to calculate the eigenenergies and eigenfunctions, we used the values given in Tables 4.2 and 4.3 for the parameters in Eqs. (3.15) and (3.16). With the exception of $1/2I_\alpha$ and $F$, the reported values came directly from the geometries obtained from the DFT calculations. In the case of $1/2I_\alpha$ and $F$ we multiplied the calculated values by 0.97, as discussed above.

Using these parameters, and with $S^X$ and $S^A$ both equal to one, we obtain the energies and wave functions for CH₃O₂ and CD₃O₂. Graphical representations of the lower eigenvalues of the relevant vibrational levels of CH₃O₂ are shown in Fig. 4.1, with corresponding results for CD₃O₂ plotted in Fig. 4.2. Near the bottom of the well, the A₁ and A₂ states alternately combine with an E state to form the nearly 3-fold degenerate eigenstates, which can be labeled by a single torsional vibration quantum number $\nu_{12}$. Well above the barrier, the eigenstates are free-rotor in character and A₁ and A₂ become nearly degenerate and, along with the E eigenfunction, correspond approximately to the doubly degenerate free rotor functions, which are labeled by the 2-dimensional rotor quantum number, $m$. Eigenvalue and function labels of $k_1A_1$, $k_2A_2$, and $lE$ are therefore appropriate throughout, where $k_1$, $k_2$, and $l$ are the even,
odd and all values of $j$ respectively, increasing with the corresponding energy of the eigenvalue. Near the barrier top, we label states using only the rigorous $G_6$ notation, while far above and below the barrier, we indicate as appropriate in Tables 4.8 and 4.9 the $\nu_{12}$ and $m$ notation.
| State  | $\nu_{12}$ / $m$ | CH$_3$O$_2$ E$^X$ | $|\langle p_\alpha \rangle|$ | CD$_3$O$_2$ E$^X$ | $|\langle p_\alpha \rangle|$ |
|--------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 0A     | $\nu_{12}= 0$   | 0.000           | 0.0000          | $\nu_{12}= 0$   | 0.000           | 0.0000          |
| 0E     | $\nu_{12}= 0$   | 0.092           | 0.0081          | $\nu_{12}= 0$   | 0.007           | 0.0010          |
| 1E     | $\nu_{12}= 1$   | 124.576         | 0.2066          | $\nu_{12}= 1$   | 102.580         | 0.0375          |
| 1A     | $\nu_{12}= 1$   | 127.060         | 0.0000          | $\nu_{12}= 1$   | 102.847         | 0.0000          |
| 2A     | $\nu_{12}= 2$   | 213.628         | 0.0000          | $\nu_{12}= 2$   | 188.369         | 0.0000          |
| 2E     | $\nu_{12}= 2$   | 230.160         | 1.9899          | $\nu_{12}= 2$   | 191.939         | 0.5624          |
| 3E     | ...             | 292.358         | 3.6668          | $\nu_{12}= 3$   | 253.718         | 2.0922          |
| 3A     | ...             | 354.159         | 0.0000          | $\nu_{12}= 3$   | 275.994         | 0.0000          |
| 4A     | ...             | 361.394         | 0.0000          | ...             | 297.567         | 0.0000          |
| 4E     | $m = 7$         | 442.487         | 6.7558          | ...             | 336.423         | 6.2168          |
| 5E     | $m = 8$         | 542.551         | 7.8477          | ...             | 395.667         | 7.5634          |
| 5A     | $m = 9$         | 657.211         | 0.0000          | ...             | 465.019         | 0.0000          |
| 6A     | $m = 9$         | 657.235         | 0.0000          | ...             | 465.331         | 0.0000          |
| 6E     | $m = 10$        | 786.110         | 9.9261          | $m = 10$        | 544.174         | 9.8047          |
| 7E     | $m = 11$        | 929.016         | 10.9452         | $m = 11$        | 632.257         | 10.8564         |
| 7A     | $m = 12$        | 1085.831        | 0.0000          | $m = 12$        | 729.227         | 0.0000          |
| 8A     | $m = 12$        | 1085.831        | 0.0000          | $m = 12$        | 729.227         | 0.0000          |
| 8E     | $m = 13$        | 1256.489        | 12.9673         | $m = 13$        | 834.968         | 12.9150         |
| 9E     | $m = 14$        | 1440.947        | 13.9739         | $m = 14$        | 949.408         | 13.9325         |
| 9A     | $m = 15$        | 1639.178        | 0.0000          | $m = 15$        | 1072.502        | 0.0000          |
| 10A    | $m = 15$        | 1639.178        | 0.0000          | $m = 15$        | 1072.502        | 0.0000          |
| 10E    | $m = 16$        | 1851.160        | 15.9827         | $m = 16$        | 1204.217        | 15.9552         |
| 11E    | $m = 17$        | 2076.882        | 16.9856         | $m = 17$        | 1344.531        | 16.9628         |
| 11A    | $m = 18$        | 2316.332        | 0.0000          | $m = 18$        | 1493.426        | 0.0000          |
| 12A    | $m = 18$        | 2316.332        | 0.0000          | $m = 18$        | 1493.426        | 0.0000          |
| 12E    | $m = 19$        | 2569.504        | 18.9897         | $m = 19$        | 1650.893        | 18.9735         |

Table 4.8: The $K=0$ eigenenergies\(^a\) in cm$^{-1}$ and $|\langle p_\alpha \rangle|$ in units of $\hbar$ for the ground electronic states of both CH$_3$O$_2$ and CD$_3$O$_2$. The $X$ state has been scaled by a factor of 1.10.

\(^a\) Torsional mode ZPE for CH$_3$O$_2$ is 59.8 cm$^{-1}$ and 46.3 cm$^{-1}$ for CD$_3$O$_2$

\(^b\) The $jA$ levels with even $j$ have $A_1$ symmetry, for $j$ odd $A_2$ symmetry
| State\(^b\) | \(\nu_{12}/m\) | \(E_A\) | \(|\langle p_\alpha \rangle|\) | \(\nu_{12}/m\) | \(E_A\) | \(|\langle p_\alpha \rangle|\) |
|---|---|---|---|---|---|---|
| 0A | \(\nu_{12}=0\) | 0.000 | 0.0000 | \(\nu_{12}=0\) | 0.000 | 0.0000 |
| 0E | \(\nu_{12}=0\) | 0.000 | 0.0000 | \(\nu_{12}=0\) | 0.000 | 0.0000 |
| 1E | \(\nu_{12}=1\) | 227.060 | 0.0004 | \(\nu_{12}=1\) | 178.217 | 0.0000 |
| 1A | \(\nu_{12}=1\) | 227.064 | 0.0000 | \(\nu_{12}=1\) | 178.217 | 0.0000 |
| 2A | \(\nu_{12}=2\) | 443.655 | 0.0000 | \(\nu_{12}=2\) | 350.815 | 0.0000 |
| 2E | \(\nu_{12}=2\) | 443.748 | 0.0086 | \(\nu_{12}=2\) | 350.816 | 0.0002 |
| 3E | \(\nu_{12}=3\) | 645.759 | 0.1135 | \(\nu_{12}=3\) | 516.258 | 0.0034 |
| 3A | \(\nu_{12}=3\) | 647.006 | 0.0000 | \(\nu_{12}=3\) | 516.280 | 0.0000 |
| 4A | \(\nu_{12}=4\) | 821.916 | 0.0000 | \(\nu_{12}=4\) | 672.466 | 0.0000 |
| 4E | \(\nu_{12}=4\) | 831.555 | 0.9935 | \(\nu_{12}=4\) | 672.749 | 0.0435 |
| 5E | \(\nu_{12}=5\) | 967.244 | 3.0656 | \(\nu_{12}=5\) | 816.299 | 0.3782 |
| 5A | \(\nu_{12}=5\) | 1014.651 | 0.0000 | \(\nu_{12}=5\) | 818.874 | 0.0000 |
| 6A | \(\nu_{12}=6\) | 1068.713 | 0.0000 | \(\nu_{12}=6\) | 935.561 | 0.0000 |
| 6E | \(\nu_{12}=6\) | 1148.697 | 8.4108 | \(\nu_{12}=6\) | 949.109 | 2.4836 |
| 7E | \(\nu_{12}=7\) | 1271.466 | 10.0256 | \(\nu_{12}=7\) | 1037.800 | 5.3033 |
| 7A | \(\nu_{12}=7\) | 1410.756 | 0.0000 | \(\nu_{12}=7\) | 1088.115 | 0.0000 |
| 8A | \(\nu_{12}=8\) | 1412.623 | 0.0000 | \(\nu_{12}=8\) | 1114.690 | 0.0000 |
| 8E | \(\nu_{12}=8\) | 1567.952 | 12.5129 | \(\nu_{12}=8\) | 1185.838 | 11.2301 |
| 9E | \(\nu_{12}=9\) | 1739.077 | 13.6231 | \(\nu_{12}=9\) | 1281.579 | 12.7785 |
| 9A | \(\nu_{12}=9\) | 1924.494 | 0.0000 | \(\nu_{12}=9\) | 1387.751 | 0.0000 |
| 10A | \(\nu_{12}=10\) | 1924.510 | 0.0000 | \(\nu_{12}=10\) | 1388.545 | 0.0000 |
| 10E | \(m=16\) | 2123.887 | 15.7571 | \(\nu_{12}=10\) | 1504.560 | 15.2829 |
| 11E | \(m=17\) | 2337.010 | 16.7999 | \(\nu_{12}=11\) | 1630.185 | 16.4202 |
| 11A | \(m=18\) | 2563.716 | 0.0000 | \(\nu_{12}=11\) | 1764.668 | 0.0000 |
| 12A | \(n=18\) | 2563.716 | 0.0000 | \(\nu_{12}=12\) | 1764.676 | 0.0000 |
| 12E | \(m=19\) | 2803.899 | 18.8590 | \(\nu_{12}=12\) | 1907.789 | 18.6002 |

Table 4.9: The \(K=0\) eigenenergies\(^a\) in cm\(^{-1}\) and \(|\langle p_\alpha \rangle|\) in units of \(\hbar\) for the first excited electronic states of both CH\(_3\)O\(_2\) and CD\(_3\)O\(_2\). The \(\tilde{A}\) state has been scaled by a factor 1.00.

\(^a\) Torsional mode ZPE for CH\(_3\)O\(_2\) is 112.6 cm\(^{-1}\) and 87.0 cm\(^{-1}\) for CD\(_3\)O\(_2\).

\(^b\) The \(jA\) levels with even \(j\) have \(A_1\) symmetry, for \(j\) odd \(A_2\) symmetry.
While such behavior is well-known, in interpreting the spectra, it is useful to consider how the energy spacings evolve from the low to high barrier limit. The plot in Fig. 4.3 illustrates the correlation between the two limiting behaviors.

For this plot, we truncate the potential and include only the first two terms. In order to remove dependence on the value of $F_y$, we replace $V_0^y$ and $V_3^y$ by $bF_y$. Making these substitutions,

$$\hat{H}_{\text{model}} = F_y \left[ \frac{p_\alpha^2}{\alpha} + \frac{b}{2} \left[ 1 + \cos (3\alpha) \right] \right]$$ (4.7)

With $\hat{H}_{\text{model}}$ the barrier to free rotation is just $bF_y$. We define a reduced energy, $e_j$, by dividing the resulting eigenvalues by $F_y$ and plot the $e_j$ as a function of $b$ in Fig. 4.3. When $b = 0$ we are in the free-rotor limit and the energies are proportional to $m^2$, with $m \geq 0$. For larger values of $b$ the lower energy levels are nearly evenly spaced and are triply degenerate, as expected in the high barrier limit. In this limit $\nu_{12}$ becomes the good quantum number. As the barrier height increases, there is a build up of states with vibrational energies nearly equal to $b$. This is the energy at which the transition between having primarily bound and free rotor character also takes place. In this energy range, assignment of the states to specific $m$ or $\nu_{12}$ quantum numbers is not particularly appropriate.

In Tables 4.8 and 4.9, we report the energies obtained by solving the Schrödinger equation, using $\hat{H}_1$ in Eq. (3.15) with $K=0$. The eigenfunctions are labeled by $j$ and symmetry, and where possible by the appropriate value of $\nu_{12}$ or $m$. To aid in comparison of the curves in Fig. 4.3 and the energies reported in Tables 4.8 and
Figure 4.3: Correlation diagram representing the correlation of the eigenfunctions and eigenenergies for the methyl peroxy radical as a function of the barrier height of the torsional mode. The stars represent the E levels. The A levels are represented by open circles. The appearance of solid circles arises when the A and E levels become degenerate within the resolution of the figure.
4.9, four vertical lines were added in Fig. 4.3 at the values of \( b \) for each \( \text{CH}_3\text{O}_2 \) and \( \text{CD}_3\text{O}_2 \) that correspond to the barriers on the \( \tilde{X} \) and \( \tilde{A} \) states. An interesting feature of systems like the \( \tilde{X} \) state of methyl peroxy which contain low barriers to free methyl rotation, is the potential for coupling between the methyl rotor motion and the overall rotation of the molecule. Within the Hamiltonian in Eq. (3.15) this coupling is represented by the \( 2F\rho p_\alpha N_z \) term, which scales as \( \langle p_\alpha \rangle \), or the net torsional angular momentum. For states with \( A_1 \) or \( A_2 \) symmetry with \( K=0 \), since \( C_{3n,0}^j = \pm C_{-3n,0}^j \), \( \langle p_\alpha \rangle = 0 \), by symmetry. In contrast, for states with \( E \) symmetry, there are no symmetry constraints on \( \langle p_\alpha \rangle \) except that the values for the components of the doubly degenerate states be equal in magnitude and opposite in sign. In the high barrier limit, for example the ground vibrational level in the \( \tilde{A} \) electronic state of methyl peroxy, the splitting is \( 4 \times 10^{-5} \) cm\(^{-1}\) and the corresponding \( \langle p_\alpha \rangle \) is \( < 0.0001\hbar \).

On the other hand for the ground vibrational state of the \( \tilde{X} \) state of methyl peroxy, \( \langle p_\alpha \rangle = 0.0081\hbar \) for \( \text{CH}_3\text{O}_2 \) and \( 0.0010\hbar \) for \( \text{CD}_3\text{O}_2 \). As seen in Tables 4.8 and 4.9, for the states with \( E \) symmetry the value of \( \langle p_\alpha \rangle \) increases with increasing quanta in the torsion and is roughly proportional to the energy difference between the nearly degenerate levels with \( A \) and \( E \) symmetry.

The fact that \( \langle p_\alpha \rangle \neq 0 \) leads to a splitting of the otherwise nearly degenerate \( K \) levels for this near prolate asymmetric rotor. We can analyze this further by calculating the energies using \( \hat{H}_1 \) plus only the first term of \( \hat{H}_2 \), i.e. with \( B_R, C_R \) and \( D_R \) set to zero. These energies are plotted against \( K \) in Fig. 4.4b for \( j = 0 - 2 \) and \( \sigma = 0, \pm 1 \).
Based on Eq. (4.3), one would expect that the energy levels should be doubly degenerate with $E(j, 0, K) = E(j, 0, -K)$ and $E(j, \pm 1, K) = E(j, \mp 1, -K)$. Further, taking the difference between levels with the same value of $|K|$, one finds that\(^5\)

$$E(j, +1, +K) - E(j, +1, -K) = \sqrt{3} F \sum_{n=0} a_{3n+1}^j \sin \left[ \frac{2\pi (3n + 1) \rho K}{3} \right] - a_{3n+2}^j \sin \left[ \frac{2\pi (3n + 2) \rho K}{3} \right]$$

(4.8)

This equation represents the energy difference between levels with $\sigma = \pm 1$ and opposite signs of $K$. As such, we refer to this as the $K$ splitting in the discussion that follows. The resulting energies are plotted with black circles in Fig. 4.4a. Likewise, one can look at the energy difference between the levels with $\sigma = 0$ and $\pm 1$. Here one finds that

$$E(j, \pm 1, K) - E(j, 0, K) = \mp \sqrt{3} F \sum_{n=0} a_{3n+1}^j \sin \left[ \frac{2\pi (3n + 1) (\rho K \pm 1)}{3} \right] - a_{3n+2}^j \sin \left[ \frac{2\pi (3n + 2) (\rho K \mp 1)}{3} \right]$$

(4.9)

Since this energy difference is between levels with $A_{1/2}$ and $E$ symmetry, it will be referred to as the $A/E$ splitting and the resulting points are plotted with white and black squares in Fig. 4.4a.
Figure 4.4: Diagram (b) representing the K dependence of the torsional energy levels for the CH₃O₂ radical in the RAM system for different levels of excitation of the CH₃ torsional mode in the ground electronic state. Panel (a) presents the evolution of the splittings for \( j = 2 \) of the torsional mode in the ground state of CH₃O₂. The circles represents the K splitting while the white and black squares represent the A/E splitting for positive and negative values of K respectively.
When we fit the calculated eigenvalues to these functional forms, we find that only the first two terms in the expansion contribute significantly to the summation. The values of $a_1$ and $a_2$ are given in Table 4.10 for the $j = 0 - 3$ levels of CH$_3$O$_2$ and CD$_3$O$_2$ for the $\tilde{X}$ state. The corresponding values for the $\tilde{A}$ state are a factor of $\approx 10^2$ smaller and make a negligible contribution to the spectra. In this sense, the $\tilde{A} - \tilde{X}$ spectrum “reads out” directly the $\tilde{X}$ state torsional structure. Further, if we compare the fit values of $\rho$ obtained from the $K$ splitting fits to the expected values, they differ by less 1%. Statistically identical parameters are obtained when we fit the A/E splittings, as is also expected.

More important from the perspective of the present study, the results plotted in Fig 4.4 show that the amplitude of the oscillations of the $K$ splittings is the same as the amplitude of the oscillations in the A/E splittings. In addition, we find that the amplitude of these oscillations in the $K$ splittings is directly proportional to the A/E

<table>
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<tr>
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<th>3</th>
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<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a_1$</td>
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<td>0.24</td>
<td>$-1.84$</td>
<td>4.98</td>
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<td>$4.7 \times 10^{-3}$</td>
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</tr>
<tr>
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<td>0.09</td>
<td>-2.48</td>
<td>16.53</td>
<td>-61.80</td>
</tr>
<tr>
<td>CD$_3$O$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a_1$</td>
<td>$-1.1 \times 10^{-3}$</td>
<td>$4.2 \times 10^{-2}$</td>
<td>$-0.58$</td>
<td>3.02</td>
</tr>
<tr>
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<td>$1.2 \times 10^{-4}$</td>
<td>$2.1 \times 10^{-2}$</td>
<td>0.41</td>
</tr>
<tr>
<td>$A/E$</td>
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<td>$-0.27$</td>
<td>3.57</td>
<td>$-22.28$</td>
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</table>

Table 4.10: Coefficients, $a_n$, of the Fourier expansion (Eq 4.3) of the torsional values. Values in cm$^{-1}$ of the A/E splitting (see text for definition) for $K=0$ are also included.
splittings at $K = 0$ with $\sqrt{3}F(a_1 + a_2) = -1.16(E(j, 1, 0) - E(j, 0, 0))$ for $j = 0 - 3$ in CH$_3$O$_2$. This relationship holds for states above and below the barrier and the coefficient is in excellent agreement with the expected value of $2/\sqrt{3}$. This will have important implications in the interpretation of the low-resolution electronic spectrum spectrum, reported in Ref. 37, as this result implies that it will be challenging to deconvolute the vibrational and rotational dependence of observed structure splittings in the band contours of transitions for which there is a non-negligible tunnelling splitting between the levels with A and E symmetry. Conversely this should lead to rich structure observable in the high-resolution spectrum.

4.5.1 Spectral Simulation

Once we have the computed eigenfunctions and eigenvalues, it is straightforward to calculate all possible transition frequencies involving the methyl torsion by taking the possible differences in the calculated eigenvalues and adding a value of $T_{00}$ for the origin of the electronic transition. The relative intensity of the transitions is determined by a Franck-Condon factor for the torsional levels involved in this transition, since the electronic transition moment and Franck-Condon factors for the other vibrational modes can be assumed constant. For electronically allowed transitions a rigorous selection rule of no change in the $G_6$ irreducible representation applies. However for the transitions of interest, propensity rules involving either $\nu_{12}$ or $m$ are of very limited value due to the extensive mixing of these zero order states. This fact plus the very different barrier heights (and hence different mixing for a given level) in the $\tilde{X}$ and $\tilde{A}$ states, combine to give rise to rather unusual patterns in the torsional transitions.
Fortunately we can calculate numerically the relative intensities of any transition by squaring the overlap integral of the corresponding torsional eigenfunctions from Eq. 4.2.

### 4.5.2 Simulation of Overall Spectrum

We can now simulate a version of the $\tilde{A} - \tilde{X}$ electronic spectrum for both CH$_3$O$_2$ and CD$_3$O$_2$ (involving only the methyl torsional levels). Here we consider only the $Q$–branch of each transition, as most of the intensity results from the $Q$ branch and hence it dominates the spectral simulation. The R and P branches mainly contribute broad, partially overlapping contours to the background. For these calculations, we solved for the eigenfunctions and eigenvalues of the Hamiltonian in Eq. (3.14), but with $B_R$, $C_R$ and $D_R$ set to zero to provide the transition frequencies. Without these smaller terms, the energy is independent of $J$ and $K$ is a good quantum number. The intensities were evaluated using the calculated Franck-Condon factors at $K = 0$ and by assuming a $\tilde{X}$ state Boltzman population distribution at 300 K. As we discussed above, the A/E splitting depends on the value of $K$. Consequently, we included all thermally populated $K$–levels in our calculation of the intensity of the $Q$–branch transitions, e.g. $\Delta J = 0$, $\Delta K = \pm 1$. This provides a stick plot of the overall spectrum and a full simulation is generated by convoluting each of the sticks with a rotational contour (assumed Lorentzian with a 5 cm$^{-1}$ FWHM to accommodate the unresolved $J$ structure). The nuclear spin weightings$^{77}$ of 1:1:1 for transitions originating from vibrational levels with $A_1$:$A_2$:$E$ symmetry in CH$_3$O$_2$, see Tables 4.4 and 4.5, are included in the simulation. For CD$_3$O$_2$, the corresponding nuclear spin
weightings are 11:11:16, see Tables 4.6 and 4.7. As described, this analysis neglects any $K$—dependence of the Franck-Condon factors or any explicit $J$—dependence on the Hönl London or Boltzmann factors. We have performed simulations that include these two factors and found the spectra to be nearly identical to the ones plotted in Figs. 4.5 and 4.6.
Figure 4.5: Overview of experimental (top) $\tilde{A}-\tilde{X}$ CH$_3$O$_2$ spectrum and a simulation (below) involving only the torsional motion. The convoluted spectrum has a FWHM of 20 cm$^{-1}$ with a Lorentzian line profile at a temperature of 300 K. The calculated potential for the simulation was scaled by $S_X=1.10$ and $S_A=1.00$. The star denotes a transition which has been assigned as $8_0^1$ while † denotes the $8_0^1 12_1^1$ electronic transition. These latter transitions are not included in the simulation.
Figure 4.6: Overview of experimental (top) $\tilde{A}-\tilde{X}$ CD$_3$O$_2$ spectrum and a simulation involving only the torsional motion. The convoluted spectrum has a FWHM of 20 cm$^{-1}$ with a Lorentzian line profile at a temperature of 300 K. The calculated potential for the simulation was scaled by $S^X=1.10$ and $S^A=1.00$. The star denotes a transition which has been assigned as $8^1_0$, the † denotes the $8^1_0$ 12$^1_1$ transition, the ‡ the $8^1_0$ 12$^2_2$ and the # denotes the $8^1_0$ 12$^3_3$ electronic transition. These latter transitions are not included in the simulation.
As indicated above, the PES can be systematically scaled by varying $S^y$. The resulting simulations of the low resolution spectrum were then compared with experiment. A value of $S^X=1.10$ for the $\tilde{X}$ state potential and $S^A=1.00$ were found to provide the best match to the experimental spectra. The resulting simulations are plotted in Figs. 4.5 and 4.6. For comparison, we also plot the experimental spectrum above the corresponding calculated spectrum. Comparing the two overall band contours we observe that the simulation does a good job of reproducing the observed spectrum.

Tables 4.11 and 4.12 summarize the calculated transition frequencies and intensities for both normal and deuterated methyl peroxy. These tables include all transitions whose intensity is greater than 3% of the $0^0_0$ band. We report the energy at which the intensity of the calculated $Q$–branch is largest as well as the width (FWHM) of the band. For the lowest energy transitions, the shapes of the contours are roughly what one would expect for a typical $Q$–branch of a near symmetric top molecule and the width reflects the rotational temperature of the molecules. The contours associated with the higher energy transitions lose this characteristic appearance due to the strong coupling between rotation and torsion in methyl peroxy.

It should be noted in Fig. 4.5 that the region between 7700 cm$^{-1}$ and 7900 cm$^{-1}$ does not match the simulation as well as in other regions. In this region part of the experimental spectrum has been assigned to the COO bend band, $8^1_0$ in Herzberg notation, and combinations between it and the torsional transitions (1E$\leftrightarrow$1E, 1A$_2$ $\leftrightarrow$ 1A$_2$ and 2E$\leftrightarrow$2E, 2A$_1$ $\leftrightarrow$2A$_1$). These combinations are not included in the simulation.
Table 4.11: Calculated positions and intensities of torsional mode transitions for the CH$_3$O$_2$ radical.

<table>
<thead>
<tr>
<th>$j^A$</th>
<th>$j^X$</th>
<th>Position$^a$ (cm$^{-1}$)</th>
<th>FWHM (cm$^{-1}$)</th>
<th>Intensity$^b$</th>
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$^a$ The calculated transitions represent the position of the maximum in the band contour and are all relative to the peak of the 0$_0^0$ band, which is 13 cm$^{-1}$ higher than the K$' = 0 \rightarrow$K$'' = 0$ transition.

$^b$ All the intensities are normalized to the intensity of the 0$_0^0$ transition and contain the spin statistical weights.
<table>
<thead>
<tr>
<th>$j^A$</th>
<th>$j^X$</th>
<th>Position$^a$ (cm$^{-1}$)</th>
<th>FWHM (cm$^{-1}$)</th>
<th>Intensity$^b$</th>
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<td>827</td>
<td>82</td>
<td>0.033</td>
</tr>
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</table>

Table 4.12: Calculated positions and intensities of torsional mode for the CD$_3$O$_2$ radical.

$^a$ The calculated transitions represent the position of the maximum in the band contour and are all relative to the peak of the 0$^0_0$ band, which is 13 cm$^{-1}$ higher than the K$^\prime$ = 0 $\rightarrow$ K$^\prime\prime$ = 0 transition.

$^b$ All the intensities are normalized to the intensity of the 0$^0_0$ transition and contains the spin statistical weights.
The corresponding situation exists for the region 7700 - 7900 cm\(^{-1}\) for the deuterated methyl peroxy spectrum shown in Fig. 4.6. Another feature in the experimental spectrum worth attention is the region around 8000 cm\(^{-1}\). From our simulated spectrum, we were able to assign several bands as transitions between high-lying states that become fully allowed only in the free rotor limit. Such transitions are relatively atypical. These transitions result from the low barrier height in the \(\tilde{X}\) state causing levels at or above it to be populated at room temperature. Corresponding features have also been observed for CD\(_3\)O\(_2\) in the region of 7900-8000 cm\(^{-1}\).

### 4.5.3 Simulation of the Band Contours

The sequence band structure in the room temperature spectrum allows us to probe how the band contour changes as one goes from well below the barrier where the torsional structure is small compared to the overall rotational structure reflected in \(\hat{H}_2\), to a situation where the torsional splitting can be readily observed on this scale. This is easily seen from Tables 4.8 and 4.9 where the values of the A/E splitting for \(K = 0\) goes from negligibly small to 16 cm\(^{-1}\) for \(j = 2\) CH\(_3\)O\(_2\) and 22 cm\(^{-1}\) for \(j = 3\) CD\(_3\)O\(_2\). The origin bands and the \(12^1_i\) bands in both isotopologues as well as the \(12^2_2\) band in CD\(_3\)O\(_2\) all have the same shape with sharp Q–branch structure. In contrast, the contours associated with the bands arising from the \(12^2_2\) transition in CH\(_3\)O\(_2\) and \(12^3_3\) transition in CD\(_3\)O\(_2\) appear broadened. The broadening is shown clearly in Fig. 4.7 where the experimental and calculated spectral band structures are compared for several bands. The complexity of the torsion/rotation coupling and the fact that the \(K\) and A/E splittings have the same order of magnitude broadens
the Q-branch structure in these bands and lead to the loss of the simple Q-branch structure observed for the lower energy transitions.

It would be tempting to try to assign tunneling parameters based on this structure, but as the results shown in Fig. 4.4 indicate as one increases $K$ from 0, the splittings oscillate and, in fact, the splitting is near its maximum value at $K = 0$. As is seen in Fig. 4.7, the simulations reproduce not only the width of the contour but the overall shape. As a point of comparison, we also plot the experimental contour for the origin band, which has been previously simulated by a simple asymmetric top rotational Hamiltonian, and note that it looks nothing like the other two. In a calculation we can separate contributions from transitions between states with $A$ and $E$ symmetry. We find that the width of the contours associated with the two subsets of the transitions in this spectral range are roughly equal. As such, the broadening cannot be directly ascribed to a change in the tunneling splitting. Rather it reflects the strong dependence of the $K$ splittings, shown in Fig. 4.4. As mentioned above, these two effects are correlated. The fact that the contours reflect A/E and $K$ splitting as well as rotational structure means that one cannot directly extract a tunneling splitting from the experimental low-resolution contour spectra. On the other hand, the overall good agreement between the experimental and calculated band contours lead us to believe that the simulation not only captures the overview of the spectrum but also the contours of bands with significant torsional splitting.
Figure 4.7: Plots (experimental and calculated) showing the variation of the band structure as different levels of excitation are present in the torsional mode. The top 2 traces represent the $12^3_3$ band of CD$_3$O$_2$. The lower trace is the experimental spectrum while the top trace is a simulation (see text for details) at 300 K of this sequence band. The middle two traces show the corresponding result for the $12^2_2$ band of CH$_3$O$_2$. Both simulated traces are convoluted with a FWHM of 5 cm$^{-1}$ to account for the unresolved $J$ structure in the spectrum. In order to compare the overall band contour of the sequence bands with the $0^0_0$ band (equivalent to the $12^0_0$ sequence band) of CH$_3$O$_2$, we also plot its experimental trace at the bottom.
Similar behavior is also observed for the transitions that carry intensity in the 8000 cm\(^{-1}\) region of the calculated and experimental spectrum. Consequently, while we can make reasonable quantum number assignments for these transitions, it is difficult, if not impossible, to deconvolute the contributions to the spectrum that come from transitions from the \(A\) or \(E\) levels. As a result, in Tables 4.11 and 4.12, we report the position of the maximum in the calculated \(Q\)–branch and the width (FWHM) of the feature. In the calculations we can separate the contributions to the bands from transitions between levels with \(A\) or \(E\) symmetry. When we compare the positions of the maximum in the \(A\) and \(E\) band contours as well as the associated widths we find, in all cases, that while there is a difference in the peak positions, the widths are at least a factor of two larger than this difference.

### 4.6 Discussion and Conclusions

A combination of quantum chemistry calculations of the PES of methyl peroxy plus numerical solutions of the Schrödinger equation for nuclear motion along the torsional coordinate has promoted an understanding of the structure found in the room temperature CRDS spectrum of methyl peroxy. The quantum chemistry calculations find a factor of \(\approx 4\) difference in torsional barrier heights in the \(\tilde{X}\) and \(\tilde{A}\) states. Furthermore the \(\tilde{X}\) state barrier is sufficiently low that substantial population exists in states near the top or above the barrier.

Use of the quantum chemistry PES allows a simulation and assignment of numerous atypical torsional transitions, including a number which would be strongly
forbidden in the highly hindered rotor model. Scaling \((S^X = 1.10 \text{ and } S^A = 1.00)\) of the PES to best reproduce the observed spectra of both CH₃O₂ and CD₃O₂ results in “experimental” barrier heights of 322 \(\text{cm}^{-1}\) in the \(\tilde{X}\) state and 1131 \(\text{cm}^{-1}\) in the \(\tilde{A}\) state. The simulations degrade significantly for barriers differing from these values by more than \(\approx 3\%\). However it is very difficult to establish what systematic errors the model may have introduced in these values.

Tunneling splittings have been calculated for all the torsional levels and are of course significantly greater for the \(\tilde{X}\) state than for the corresponding \(\tilde{A}\) state levels. Lack of resolution of sharp Q branch features in the partially resolved rotational structure in transitions involving higher \(\tilde{X}\) state torsional levels is expected and observed.

No tunneling splittings are observed as predicted for the \(0_0^0\) band in the room temperature spectrum. However recently we have recorded a jet-cooled spectrum of CH₃O₂ and CD₃O₂ with instrumental resolution \(\lesssim 250\text{MHz}\). At this resolution predicted tunneling splittings of 2-3 GHz should be observable in CH₃O₂ while for CD₃O₂, the predicted values of 0.1 - 0.2 GHz are likely within the experimental linewidth. While the analyses of the low temperatures spectra are still in progress, there is evidence that these predictions are consistent with the observations.
CHAPTER 5

THE ETHYL PEROXY RADICAL, $\text{C}_2\text{H}_5\text{O}_2$

5.1 Introduction

We have shown in the previous chapter than in the case of the methyl peroxy radical $\text{CH}_3\text{O}_2$ that the presence of a tunneling splitting was observed in the room temperature experimental spectrum. However, no high-precision molecular parameters, such as rotational constants or spin-rotation tensor components, describing both the ground and the first excited electronic state could be deduced from the experimental spectrum. Hence, it appears obvious than obtaining such parameters would be of great interest to benchmark quantum chemistry calculation. Hence, using our high resolution experimental apparatus would eliminate this lack of accuracy and allow us to perform a deep analysis of peroxy radicals. In 2007, Wu et. al. obtained the first high resolution jet-cooled cavity ringdown spectrum of the $\text{CD}_3\text{O}_2$ radical as shown in Fig 5.1.
Figure 5.1: High resolution jet-cooled experimental CRDS spectrum of the CD$_3$O$_2$ radical obtained by Wu et al.$^3$ The vertical axis gives the absolute absorption in parts per million per pass (PPMP) as a function of laser frequency along the horizontal axis.
This result is critical for the analysis of the different peroxy radicals presented in this and the following chapters. This spectrum has been analyzed using a least square fitting procedure and high-precision molecular parameters were obtained. One of the key results that one can obtain from this result are the spin-rotation tensor component that will allow us to derive them for radical of a same family using the method described in Section 3.4. Also, this result unambiguously shows the capability of obtaining high-resolution jet-cooled spectra of alkyl peroxy radicals. Recent CRDS studies of the C$_2$H$_5$O$_2$ and C$_2$D$_5$O$_2$, under room-temperature conditions,\textsuperscript{36} identified the G and the T conformers of the radicals. However, due to the rotational congestion of these spectra, no accurate values of the rotational constants nor the spin-rotation constants were reported. This chapter extends our previous work on CD$_3$O$_2$\textsuperscript{3} to obtain and analyze the $\tilde{A} - \tilde{X}$ spectra for the ethyl peroxy radical under jet-cooled conditions with a narrowband laser source. We have found it of use to analyze and fit these spectra using an evolutionary algorithm approach thereby obtaining a set of high precision molecular parameters characterizing the $\tilde{A}$ and $\tilde{X}$ of both ethyl peroxy conformers.

We have recorded high resolution, partially rotationally resolved, jet-cooled cavity ringdown spectra of the origin band of the $\tilde{A} - \tilde{X}$ electronic transition of both the G and T conformers of the perproteo and perdeutero isotopologues of the ethyl peroxy radical, C$_2$H$_5$O$_2$. This transition, located in the near infrared, was studied using a narrow band laser source ($\lesssim 250$ MHz) and a supersonic slit-jet expansion coupled with an electric discharge allowing us to obtain rotational temperatures of about 15
5.2 Spectral Analysis and Simulation.

Historically, our group has used the approach of a least square fitting (LSF) procedure, employing the SpecView software package, in order to obtain molecular parameters from a high resolution spectrum. This approach is traditional and completely appropriate if one has a well resolved spectrum for which individual line assignments are possible.

However the applicability of such an approach is limited when one only has partially resolved spectra such as are shown in Fig. 5.2 for the G conformers of C$_2$H$_5$O$_2$ and C$_2$D$_5$O$_2$. Under these conditions, unique transition assignments are nearly impossible as most features in the spectra correspond to multiple (~2-5) overlapping transitions. In order to fit such complicated spectrum, we decided to use the evolutionary algorithm (EA) which has been proven to provide reliable results for semi-automated fits of both fully and partially resolved spectra. (see Section 3.2.1 for details). The Hamiltonian employed in order to fit such spectra has been described in details on Section 3.1.1 (Eq. 3.1).
Figure 5.2: The top green trace is the high resolution jet-cooled experimental CRDS spectrum of the G conformer of the $\text{C}_2\text{H}_5\text{O}_2$ radical. The bottom blue trace represents the high resolution jet-cooled experimental CRDS spectrum of the G conformer of the $\text{C}_2\text{D}_5\text{O}_2$ radical. The vertical axis gives the absolute absorption in parts per million per pass (PPMP) as a function of laser frequency along the horizontal axis.
5.3 Experimental Results

5.3.1 The G Conformer of the Ethyl Peroxy Radical

Ethyl peroxy is the simplest alkyl peroxy radical that has more than one conformer. As noted previously its conformers can be labeled as G (CCOO dihedral angle $\pm 60^\circ$) which has a $C_1$ symmetry and T (CCOO dihedral angle of $\pm 180^\circ$) which has $C_s$ symmetry. In 2007, Rupper *et. al.* observed and analyzed the room temperature CRDS spectra of both conformers of this radical.\textsuperscript{36} Based upon high level quantum chemistry calculations, they determined that the G conformer was about 80 cm$^{-1}$ lower in energy than the T conformer in the $\tilde{X}$ state. Therefore, we decided to first investigate the G conformer $0_0^0$ band with our high resolution jet-cooled apparatus, since the T conformer would have negligible population if the conformers were in equilibrium at the 15 K rotational temperature typical of the apparatus.\textsuperscript{95}

We were able to record the spectra of both the normal and deuterated species of the G conformer with a good signal to noise ratio ($S/N \approx 60 - 100$ for the strongest features). Figure 5.2, a scan over about 20 cm$^{-1}$ of the two isotopologues, shows that the spectra are highly congested, primarily due to the population of many rotational and spin-rotational levels even at a temperature of $\approx 15$ K. Because of this congestion, assignments of spectral features to individual transitions is mostly impossible.

Due to the inability to assign individual lines, use of the traditional least square fit (LSF) method to simulate the spectrum and obtain the best values of the molecular parameters is counter-indicated. We therefore have employed the EA approach
described in Section 3.2.1 to simulate the spectra and determine the molecular parameters contained in the $\mathcal{H}_T$ (Eq. 3.1) for each the $\tilde{A}$ and $\tilde{X}$ states.

Because it is somewhat more resolved (see below for details) we first analyzed the spectrum of the C$_2$D$_5$O$_2$ G radical using the EA approach. The fitted constants are summarized in Table 5.1. The converged result of the EA not only produces the best values for the fit constants but at the same time the quantum numbers of the individual transitions are assigned. This allows a classical least-squares fit using the assigned frequencies. In Meerts and Schmitt$^{91}$ this is called an assigned fit, and the definitions of the statistical errors and correlation coefficients are discussed in Appendix B of that paper. The errors reported in Table I are based on a 0.01 cm$^{-1}$ uncertainty in the experimental line positions.

Figure 5.3 shows portions of the resulting simulation and parameters. The best agreement between the experimental spectrum and the fit was obtain with a rotational temperature of 15 K and with a fixed Gaussian component of 250 MHz$^3$ and 450 MHz for the Lorentzian component of a Voigt profile for individual transitions.
<table>
<thead>
<tr>
<th>Const. (cm(^{-1}))</th>
<th>Fit</th>
<th>MP2(FULL)(\text{6-31g(d)})</th>
<th>CCSD(\text{6-31+g(d)})</th>
<th>B3LYP(\text{6-31+g(d)})</th>
</tr>
</thead>
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<td>(A'')</td>
<td>0.44963 (3)</td>
<td>0.45106 [-0.318 (7)]</td>
<td>0.4458 [1.123 (7)]</td>
<td>0.45608 [-1.435 (7)]</td>
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<td>(B'')</td>
<td>0.16298 (2)</td>
<td>0.16387 [-0.55 (1)]</td>
<td>0.16211 [0.53 (1)]</td>
<td>0.15784 [3.15 (1)]</td>
</tr>
<tr>
<td>(C'')</td>
<td>0.14083 (2)</td>
<td>0.14182 [-0.70 (1)]</td>
<td>0.13995 [0.62 (1)]</td>
<td>0.13805 [1.97 (1)]</td>
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<td>(\tilde{\epsilon}_{aa}'' = -(a_0 + 2a)'')</td>
<td>-0.0115 (5)</td>
<td>-0.0114 (15) [0.9 (43)]</td>
<td>-0.0113 (15) [1.7 (43)]</td>
<td>-0.0122 (15) [-6.1 (43)]</td>
</tr>
<tr>
<td>(\tilde{\epsilon}_{bb}'' = (a + b - a_0)'')</td>
<td>-0.0064 (4)</td>
<td>-0.0062 (14) [3.6 (6)]</td>
<td>-0.0062 (14) [3.6 (6)]</td>
<td>-0.0056 (14) [12.6 (6)]</td>
</tr>
<tr>
<td>(\tilde{\epsilon}_{cc}'' = (a - b - a_0)'')</td>
<td>-0.0023 (5)</td>
<td>-0.0031 (15) [-3.4 (21)]</td>
<td>-0.0030 (15) [-3.0 (21)]</td>
<td>-0.0032 (15) [-3.9 (21)]</td>
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<tr>
<td>((1/2)(\tilde{\epsilon}<em>{ab} + \tilde{\epsilon}</em>{ba})'' = d'')</td>
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<td>-0.0061 (22) [27.1 (13)]</td>
<td>-0.0060 (22) [28.1 (13)]</td>
<td>-0.0063 (22) [25.1 (13)]</td>
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<tr>
<td>((1/2)(\tilde{\epsilon}<em>{bc} + \tilde{\epsilon}</em>{cb})'' = e'')</td>
<td>0.0036 [-]</td>
<td>0.0035 [-]</td>
<td>0.0034 [-]</td>
<td>0.0044 [-]</td>
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<tr>
<td>((1/2)(\tilde{\epsilon}<em>{ac} + \tilde{\epsilon}</em>{ca})'' = e'')</td>
<td>-0.0011 [-]</td>
<td>0.0010 [-]</td>
<td>0.0014 [-]</td>
<td>0.0014 [-]</td>
</tr>
<tr>
<td>(A')</td>
<td>0.42660 (3)</td>
<td>0.42703 [-0.101 (7)]</td>
<td>0.42102 [1.308 (7)]</td>
<td>0.43081 [-0.987 (7)]</td>
</tr>
<tr>
<td>(B')</td>
<td>0.16560 (2)</td>
<td>0.16638 [-0.47 (1)]</td>
<td>0.16542 [0.65 (1)]</td>
<td>0.16099 [2.78 (1)]</td>
</tr>
<tr>
<td>(C')</td>
<td>0.14046 (2)</td>
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<td>0.13710 [2.39 (1)]</td>
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<td>(\tilde{\epsilon}_{aa}' = -(a_0 + 2a)')</td>
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<td>0.0135 (15) [-25.5 (5)]</td>
<td>0.0136 (15) [-26.5 (5)]</td>
<td>0.0147 (15) [-36.5 (5)]</td>
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<td>(\tilde{\epsilon}_{bb}' = (a + b - a_0)')</td>
<td>0.0084 (10)</td>
<td>0.0071 (14) [11.5 (5)]</td>
<td>0.0070 (14) [13.5 (5)]</td>
<td>0.0065 (14) [18.5 (5)]</td>
</tr>
<tr>
<td>(\tilde{\epsilon}_{cc}' = (a - b - a_0)')</td>
<td>0.0006 (4)</td>
<td>0.0009 (15) [-50.66 (66)]</td>
<td>0.0008 (15) [-33.66 (66)]</td>
<td>0.0008 (15) [-33.66 (66)]</td>
</tr>
<tr>
<td>((1/2)(\tilde{\epsilon}<em>{ab} + \tilde{\epsilon}</em>{ba})' = d')</td>
<td>0.0098 (6)</td>
<td>0.0100 (22) [-2.6 (6)]</td>
<td>0.0099 (22) [-1.6 (6)]</td>
<td>0.0101 (22) [-3.6 (6)]</td>
</tr>
<tr>
<td>((1/2)(\tilde{\epsilon}<em>{bc} + \tilde{\epsilon}</em>{cb})' = e')</td>
<td>-0.0035 [-]</td>
<td>-0.0034 [-]</td>
<td>-0.0033 [-]</td>
<td>-0.0007 [-]</td>
</tr>
<tr>
<td>((1/2)(\tilde{\epsilon}<em>{ac} + \tilde{\epsilon}</em>{ca})' = e')</td>
<td>-0.0006 [-]</td>
<td>-0.0006 [-]</td>
<td>-0.0006 [-]</td>
<td>-0.0007 [-]</td>
</tr>
<tr>
<td>(T_{00})</td>
<td>7595.1855 (4)</td>
<td>7582.3000 [0.17]</td>
<td>7094.7782 [6.59]</td>
<td>7668.0560 [-0.96]</td>
</tr>
<tr>
<td>(</td>
<td>\mu_a/\mu_b</td>
<td>)</td>
<td>0.569</td>
<td>0.263</td>
</tr>
<tr>
<td>(</td>
<td>\mu_c/\mu_b</td>
<td>)</td>
<td>0.639</td>
<td>0.438</td>
</tr>
</tbody>
</table>

Table 5.1: Molecular parameters of G conformer of \(\text{C}_2\text{D}_5\text{O}_2\) radical from the experimental spectrum and from the indicated electronic structure calculations (see text for details). The calculated \(T_{00}\) have corrected by the scaled ZPE correction. The rotational temperature was fitted to be 14.8K. The numbers in square brackets represent the percentage of error of the predicted constant with respect to the fitted results. The calculated and predicted constants are for the equilibrium geometry. The components of the transition moment are computed using the CIS method using the optimized geometries indicated from the normalize dipole moment. The values of \(\theta\) and \(\phi\) where found to be: \(\theta = 60.0^\circ\), \(\phi = 60.7^\circ\).
Figure 5.3: Expanded scale for the C$_2$D$_5$O$_2$ radical G conformer. The top blue traces are the experimental spectrum shifted upward by 0.5 PPMP while the bottom red traces are the simulations based upon the fit constants in Table 5.1. Axis conventions are the same as Fig. 5.2.
Fig. 5.3 shows the simulation and observed spectra are virtually indistinguishable, which clearly shows the ability of the EA approach to successfully fit the molecular parameters and simulate the spectrum. Furthermore Table 5.1 shows that all 15 molecular parameters involved in $H_T$ for the $\tilde{A}$ and $\tilde{X}$ states are well determined. Indeed the rotational constants are determined to $\approx 10$ ppm and the smaller spin-rotational constants, while having larger percentage errors, have similar absolute precision.

The components of the transition dipole along the principal axes given in Tables 5.1 and 5.2 are determined from the fit values of $\theta$ and $\phi$ using the relationships,

$$\mu_a = \mu \sin \phi \cos \theta \quad (5.1)$$
$$\mu_b = \mu \sin \phi \sin \theta \quad (5.2)$$
$$\mu_c = \mu \cos \phi \quad (5.3)$$

Perhaps even more remarkable is that the experimental precision of the parameters for ethyl peroxy is very comparable to that which we previously reported for CD$_3$O$_2$, although in the former case individual transitions were mostly resolved and the parameters were determined from the transition frequencies by an LSF approach. While this result is counterintuitive, we expect the high precision obtained in the present G C$_2$D$_3$O$_2$ spectrum fit is attributable to the fact that the EA approach uses both the (somewhat less precise) frequencies for the ethyl peroxy transitions and the intensity information contained in the C$_2$H$_5$O$_2$ spectrum while the LSF method used
only the transition frequency information for CD$_3$O$_2$. Since CRDS is an absorption-based technique even absolute intensities are reliable, and the EA approach is ideal for fitting even highly congested CRDS spectra.

As with any fitting procedure, there is always a question as to whether the final parameters set (chromosome) is unique. One way of answering that question is to look at the fit molecular parameters and compare them to those resulting from quantum chemistry calculations. Since we expect all the quantum chemistry methods described in Section 3.3 to be relatively accurate, significant discrepancies between calculated and experimental results are neither expected nor are they found as is shown in Table 5.1. Therefore we accept the fit parameters to be valid and in turn use them to judge the relatively adequacy of the computational methods. It appears obvious that the MP2(FULL) method with a 6-31g(d) basis set reproduces quite well the experimental constants (within 0.3% for the rotational constants). The CCSD method also reproduces the experimental constants rather well but does not do as good as a job as MP2(FULL), the geometry optimization step of the G2 compound method. (However it should be remembered that these comparisons are between the values of the rotational constants calculated at the equilibrium position and the experimental values averaged over the vibrationless level.) Finally, the DFT method provides rotational constants that are within $\approx 3\%$ of the fitted constants.

Turning our attention to the components of the spin-rotation tensor, we can easily see from Table 5.1 that these constants are well determined and that they are in generally good agreement with the predictions, thereby validating the method of Section
3.2.1. It appears evident that, as for the rotational constants, the MP2(FULL) calculation best predicts the spin-rotation constants while the B3LYP predictions deviate fairly significantly from the fitted results. The explanation of the difference in accuracy is actually fairly simple. To derive the components of the spin-rotation tensors for a given molecule one needs a good optimized geometry. The rotational constants are best predicted by the MP2(FULL) method compared to the DFT method implying the optimized geometry of this method is most accurate, so MP2(FULL) should also be best at predicting the spin-rotation parameters, which again depend upon this geometry.

As Table 5.1 shows we actually only used the real part of the spin-rotation tensor to fit our spectrum. This result is partially predicated upon practicality. The EA program has not been adapted to diagonalize a complex $\mathcal{H}_T$ (Eq. 3.1) matrix. However, this approximation was justified by using our SpecView program\textsuperscript{82} which can handle complex matrices. By adding the estimated values for c and e from the MP2(FULL) prediction into $\mathcal{H}_T$ and by examining the resulting predicted spectrum from SpecView the largest shift in frequency is found to be $\approx 16.5$ MHz, which, at our resolution, is not significant. This approximation is further confirmed by comparing simulations including or not the two extra imaginary component of the spin-rotation tensor.

Table 5.1 also summarizes the calculated excitation energy $T_{00}$ for all three electronic structure methods. The MP2(FULL) energy separation has been obtained by calculating both electronic states with the G2 compound method which contains not
only the ZPE correction but also several higher order energy correction terms. The CCSD and B3LYP energies are corrected by the ZPE correction under the harmonic oscillator approximation. It is no surprise that the MP2(FULL) energy calculation is the most accurate one as has been pointed out previously by Sharp et al.\textsuperscript{39} On the other hand, it is more surprising that the CCSD calculation is less accurate than the B3LYP calculation since its global minimum structure of the radical appears to be more accurate than the B3LYP one. The explanation for this inadequacy could lie in the fact that the ZPE correction comes, obviously, from the calculation of the normal mode frequencies of the molecule and it is well known that’s the result of a frequency calculation using a CCSD method will be less accurate than the one coming from a B3LYP calculation.

Since the G conformer of the ethyl peroxy radical has $C_1$ symmetry, non-vanishing components of the transition dipole moment lie along all three axes, $a$, $b$ and $c$. The calculated and experimental results are again summarized in Table 5.1. Somewhat larger errors are present between experiment and calculations for the relative components of the transition dipole than for the $\tilde{A}$ and $\tilde{X}$ state parameters. However transition dipoles are notoriously difficult to calculate and likely the nearby forbidden nature of the $\tilde{A} - \tilde{X}$ transition makes it even a greater challenge. The fairly significant variation of the calculated dipoles using the three different optimized geometries, which are really quite similar, supports this supposition.

We have performed a similar analysis for the $C_2H_5O_2$ isotopologue. These results are summarized in Table 5.2 and in Fig. 5.4. This experimental spectrum has been
simulated at a rotational temperature of 16 K with a Voigt profile with a Gaussian component of 250 MHz and a Lorentzian component of 1400 MHz. It is clear that the simulated spectra are again in near perfect agreement with the experimental trace. Comparing the experimental and calculated parameters in Table 5.1 we came to the same conclusion, i.e., MP2(FULL) makes the best predictions for molecular parameters while, of the three, the B3LYP method predicts most poorly. However, the agreement between the predicted and the fitted molecular parameters is poorer by a factor of ≈2 for C$_2$H$_5$O$_2$ compared to C$_2$D$_5$O$_2$. This can be explained by the fact that the C$_2$H$_5$O$_2$ spectrum is not as resolved as its isotopologue.
<table>
<thead>
<tr>
<th>C2H5O2</th>
<th>Const. (cm^{-1})</th>
<th>Fit</th>
<th>MP2(FULL) (6-31\text{g}(d))</th>
<th>CCSD(6-31+\text{g}(d))</th>
<th>B3LYP(6-31+\text{g}(d))</th>
</tr>
</thead>
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<td>0.58427 [1.14 (1)]</td>
<td>0.60182 [1.83 (1)]</td>
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Table 5.2: Molecular parameters of G conformer of C\(_2\)H\(_5\)O\(_2\) radical. The calculated \(T_{00}\) have corrected by the scaled ZPE correction. The rotational temperature was fitted to be 16.2K. The numbers in square brackets represent the percentage of error of the predicted constant with respect to the fitted results. The calculated and predicted constants are for the equilibrium geometry. The components of the transition moment are computed using the CIS method using the optimized geometries indicated from the normalize dipole moment. The values of \(\theta\) and \(\phi\) where found to be: \(\theta = 55.7^\circ, \phi = 58.8^\circ\)
Figure 5.4: Expanded scale for the C$_2$H$_5$O$_2$ radical G conformer. The top green traces are the experimental spectrum shifted upward by 0.5 PPMP while the bottom red traces are the fitted spectra using the constants in Table 5.2. Axis conventions are the same as Fig. 5.2.
We have also obtained the spectra for the C$_2$H$_5$O$_2$ and C$_2$D$_5$O$_2$ radicals under somewhat warmer conditions obtained by reducing the backing pressure upstream of our slit jet. Fig. 5.5 confirms the parameters from the 15 K spectra well simulate the warmer C$_2$H$_5$O$_2$ spectrum (fit at 32 K) and that of C$_2$D$_5$O$_2$ (fit at 28 K).
Figure 5.5: Experimental and simulation of the warmer spectra of the normal and deuterated ethyl peroxy radical G conformer. The top panel represents the normal isotopologue with the top green trace the experimental spectrum and the bottom red trace the simulation using the fitted constants in Tables 5.3 and 5.4. The bottom panel represents the deuterated isotopologue with the experimental spectrum on top and its simulation at the bottom. For both sets of traces, the experimental spectrum has been shifted upward by 2.0 PPMP. Axis conventions are the same as Fig. 5.2.
5.3.2  The T Conformer of the Ethyl Peroxy Radical

Since the T conformer of the ethyl peroxy radical has $C_s$ symmetry, its electronic transition dipole moment lies along the $c$-axis and the spin-rotation tensor components $c$ and $e$ are equal to zero by symmetry. Normally, this would give the T conformer a simpler and somewhat stronger spectrum. However, Rupper et al. have calculated that in the ground electronic state, the T conformer lies about 80 cm$^{-1}$ above the G conformer.\textsuperscript{36} Under equilibrium conditions at $T \approx 15$ K, we could expect the ratio of populations between the T and the G conformer would be of

$$\frac{N_T}{N_G} = \frac{1}{2} e^{-7.7} = 4.7 \times 10^{-4} \quad (5.4)$$

where the factor of 1/2 results from the mirror image enantiomers of the G conformer. Nonetheless, we decided to search for the T conformer, albeit at somewhat higher temperatures using lower backing pressures. We were able to record warmer spectra for both $\text{C}_2\text{H}_5\text{O}_2$ and $\text{C}_2\text{D}_5\text{O}_2$, which are shown with their simulations, in Figs. 5.6 and 5.7 respectively. The rotational temperatures were found to be 99 K for the normal species and 73 K for the deuterated one. These observations allows us to reach the conclusion that, in our slit jet expansion, the radicals are not at thermal equilibrium. Thereafter we also observed T conformer spectra under the 15 K rotational temperature conditions, although with relatively low signal/noise ($\lesssim 5$).
Figure 5.6: Experimental and simulated spectra of the T conformer of the C$_2$H$_5$O$_2$ radical. The upper panel shows an enlargement of a 5 cm$^{-1}$ section of the lower panel. In each panel, the top trace is the experimental spectrum shifted upward by 0.5 PPMP while the bottom trace is the simulated spectrum, using the fitted constants in Table 5.3. Axis conventions are the same as Fig. 5.2.
Table 5.3: Molecular parameters of T conformer of C$_2$H$_5$O$_2$ radical. The calculated T$_{00}$ have corrected by the scaled ZPE correction. The rotational temperature was fitted to be 99.3K. The numbers in square brackets represent the percentage of error of the predicted constant with respect to the fitted results. The calculated and predicted constants are for the equilibrium geometry. By symmetry only the c component of the dipole moment is non-zero.
Figure 5.7: Experimental and simulated spectra of the T conformer of the C$_2$D$_5$O$_2$ radical. The upper panel shows an enlargement of a 5 cm$^{-1}$ section of the lower panel. In each panel, the top trace is the experimental spectrum shifted upward by 0.5 PPMP while the bottom trace is the simulated spectrum using the fitted constants in Table 5.4. The star represents the CD$_3$O$_2$ radical that was also observed in the experiment. The constants used to simulate it are the one published by Wu et al.$^3$
<table>
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<tr>
<th>Const. (cm⁻¹)</th>
<th>Fit</th>
<th>MP2 (FULL)\6-31g(d)</th>
<th>CCSD\6-31+g(d)</th>
<th>B3LYP\6-31+g(d)</th>
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<tr>
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<tr>
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<td>0.72511 [0.015 (12)]</td>
<td>0.72220 [0.416 (12)]</td>
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<tr>
<td>(B')</td>
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<td>0.12953 [-0.676 (52)]</td>
<td>0.12747 [0.925 (62)]</td>
<td>0.12657 [1.624 (62)]</td>
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<td>0.11752 [1.434 (67)]</td>
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<tr>
<td>(\frac{1}{2}(\tilde{\bar{\epsilon}}<em>{ac} + \tilde{\bar{\epsilon}}</em>{ca})')' = (e')</td>
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<td>(T_{00})</td>
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<td>6916.2306 [5.96]</td>
<td>7501.4582 [2.00]</td>
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Table 5.4: Molecular parameters of T conformer of C₂D₅O₂ radical. The calculated \(T_{00}\) have corrected by the scaled ZPE correction. The rotational temperature was fitted to be 73.2 K. The numbers in square brackets represent the percentage of error of the predicted constant with respect to the fitted results. The calculated and predicted constants are for the equilibrium geometry. By symmetry only the c component of the dipole moment is non-zero.
Looking carefully at Fig. 5.7, one can see on the blue end of the spectrum a broad feature which was found and fitted to be the $0^0_0$ band of the CD$_3$O$_2$ radical. The constants used to fit this unexpected band have been fixed to the one published by Wu et al.\textsuperscript{3} and only the rotational temperature was fitted in this simulation and was found to be 83 K. The individual lineshapes employed in the simulations for the T conformer were similar to the ones used for the G conformer, i.e., Voigt profiles with a Gaussian component of 445 MHz due to the increased Doppler broadening at higher temperature and a Lorentzian component of 1400 MHz for the normal species and 450 MHz for the deuterated one.

Tables 5.3 and 5.4 show the calculated and predicted rotational and spin-rotational constant for the normal and the deuterated isotopes of the T conformer of the ethyl peroxy radical. Looking at these results it appears for the $\tilde{X}$ state of the T conformer the CCSD method is equal or perhaps even better than the MP2(FULL) method. However, the DFT method still lags these two techniques and gives more qualitative predictions. When looking at the first excited state calculated and predicted constants, the same trend as for the G conformer can be found, i.e., the MP2(FULL) predictions are closer to the fitted values than the CCSD.

5.4 Conclusion

We have successfully recorded the partially rotationally resolved spectra for both conformers (G and T) of the ethyl peroxy radical, C$_2$H$_5$O$_2$ and its perdeutero analogue, C$_2$D$_5$O$_2$. We have used an EA approach to analyze the observed spectra. This
approach has yielded simulated spectra virtually indistinguishable from the experimental traces and produced a set of molecular parameters characterizing the $\tilde{X}$ and $\tilde{A}$ states of the radicals.

In earlier room temperature work on ethyl peroxy it was recognized that the spectra of two conformers clearly existed. The assignment of the two origin bands to given conformers was initially based upon an \textit{ab initio} prediction that the T conformer origin was at lower frequency. Support for this assignment was given by an analysis\textsuperscript{36} of the rotational contours of the band. Obtaining a complete set of rotational constants characterizing the respective bands and comparing them to those expected based upon the conformers’ geometries removes any remaining doubt about the conformer assignment.

Furthermore, comparison (see Tables 5.1-5.4) of the experimental parameters with those from electronic structure calculation allows us to benchmark the latter. We have further demonstrated that we were able to predict the observed spin-rotation constants using the isotopic substitution approach proposed by Brown, Sears and Watson\textsuperscript{74} and extended by Tarczay \textit{et al.}\textsuperscript{90}

The fact that we were able to obtain and analyze spectra from the higher energy T conformer leads to the conclusion that in our jet expansion, the conformers are not produced in thermal equilibrium. This work shows that observing \textit{and} analyzing the spectra of even larger radicals is quite feasible.
CHAPTER 6

THE PROPYL PEROXY RADICAL, C$_3$H$_7$O$_2$

6.1 Introduction

As shown in the previous chapter, recently developed an experimental apparatus that allows us to combine a high-resolution laser source\textsuperscript{57} with a slit-jet-cooled CRDS setup,\textsuperscript{95} and have successfully used it to record the rotationally resolved $\tilde{A} \rightarrow \tilde{X}$ spectrum near 1.35 $\mu$m transition of the perdeuterated methyl peroxy radical, CD$_3$O$_2$\textsuperscript{3} as well as the two conformers of the proteo and deutero isotopologues of the G and T conformers of the ethyl peroxy radical.\textsuperscript{96} The experimental spectra have been modeled using a Hamiltonian that includes the rigid body rotation of an asymmetric top and the spin-rotation interaction. In the case of the CD$_3$O$_2$ spectrum, a least squares fitting procedure was used to simulate the well resolved spectrum. On the other hand, due to the incompletely resolved structure, an evolutionary algorithm (EA) approach was used to analyze and simulate the C$_2$H$_5$O$_2$ spectra. For both methyl and ethyl peroxy, the studies resulted in the high precision determination of 15 molecular parameters characterizing the $\tilde{A}$ and $\tilde{X}$ electronic states.

Recently, cavity ringdown studies of the C$_3$H$_7$O$_2$ radical under room-temperature conditions\textsuperscript{34} directly identified 5 conformers of the n-propyl peroxy radical(G$_1$G$_2$,G$_1$T$_2$,}
$T_1G_2, T_1T_2$ and $G'_1G_2$) and both conformers of the iso-propyl peroxy radical, (G and T). However, the conformer assignments were based only upon high level electronic structure calculations $^4$ and spectral congestion caused significant overlap between conformer bands and prevented resolving rotational constants or spin-rotation structure in the spectra.

This chapter extends our previous work to obtain and analyze the $\tilde{A} - \tilde{X}$ spectra for several conformers and isomers of the propyl peroxy radical under jet-cooled conditions (rotational temperatures of about 15 K) with a narrow band laser source ($\lesssim 250$ MHz), see Section 5.1 for details. As in the ethyl peroxy study, we have found it of use to analyze and fit these spectra using the EA approach due to the partially resolved nature of the experimental spectra. Our analysis produces a set of high precision molecular parameters characterizing the $\tilde{A}$ and $\tilde{X}$ states which we compare with the results of electronic structure calculations for these radicals.

6.2 Spectral Analysis and Simulation.

All the spectra of the propyl peroxy radical that have been recorded involve the $0_0^0$ band of the $\tilde{A} - \tilde{X}$ electronic transition. Due to the fact that the radical is in a doublet state we expect both an observable rotational and spin-rotation structure in the spectra, but we expect hyperfine splittings to be unresolvable. Hence, the structure of each vibronic level is described by a Hamiltonian, see Section 3.1.1 for details, $\mathcal{H}_T$, Eq. 3.1.

In the previous chapter we have found that for partially resolved experimental
spectra such as the ethyl peroxy radical, the LSF approach is not suitable due to the nearly impossible task of assigning spectral features to given transitions. Under such circumstances the use of an EA approach has been found preferable for spectral analysis and we adopt this approach for the present analysis.

The EA method is based upon the Darwinian theory of a natural selection process occurring by reproduction and mutation of genes in a chromosome leading to only best adapted individuals. From a spectroscopic point of view, the EA approach reproduces this behavior to fit an experimental spectrum with a model based upon the differences of the eigenvalues of the Hamiltonian such as $\mathcal{H}_T$ given by Eq. 3.1. The use of the EA approach to analyze the spectra of RO$_2$ has been discussed previously in Section 3.2.1 with more details.

6.3 Experimental Results

The propyl peroxy radical is the smallest alkyl peroxy that not only possesses multiple conformers, but also two different isomers. We first consider 1-propyl peroxy and then 2-propyl peroxy.

6.3.1 The 1-Propyl Peroxy Radical

As mentioned previously, 1-propyl peroxy radical has 5 different conformers, see Figure 6.1, that are expected to be populated under room temperature conditions; however, under jet cooled conditions ($T_R \approx 15K$), this would not be the case assuming equilibrium exists between the rotational and conformer, i.e., degrees of freedom.
Figure 6.1: Representations of the different isomers and conformers of the propyl peroxy radical. The numbers in parenthesis represent the relative energy of the conformers in the ground electronic state.\textsuperscript{4}
Tarczay et al.⁴ calculated the ground state relative energy of all these conformers and assuming equilibrium only two conformers would be significantly populated, i.e., the most stable G₁G₂ conformers and the G₁T₂ conformer which lies only 27 cm⁻¹ above the G₁G₂. The other 3 conformers are located more than ≥100 cm⁻¹ above G₁G₂ and hence are not expected to be observed. There is evidence from other works on jet-cooled radicals that equilibrium in the conformer degree of freedom is probably not completely reached. Nonetheless conformations with energies well above kT_R are usually not observed.⁹⁷ Indeed we have been able to record resolved spectra for two sub-bands of the ˜A – ˜X transition. The strongest band lies quite close to the unresolved contour assigned to the G₁G₂ conformer in the room-temperature spectrum, while the other band is close to the putative G₁T₂ assignment. We therefore take these assignments as our starting point recognizing that their confirmation or not will depend upon the qualitative agreement or disagreement between the rotation consistently determined experimentally and those from electronic structure calculations.

6.3.1.1 The G₁G₂ Conformer of n-C₃H₇O₂

We were able to record the spectra of the putative G₁G₂ conformer with a good signal to noise ratio (S/N≈ 25 for the strongest spectral features). As Figure 6.2 shows, the band spread over about 10 cm⁻¹ and appears to be relatively highly congested due to the population of many rotational as well as spin rotational level even at 15K.
Figure 6.2: Experimental and simulated spectra of the G$_1$G$_2$ conformer of the n-C$_3$H$_7$O$_2$ radical. The upper panel shows an enlargement of a 4 cm$^{-1}$ section of the lower panel. In each panel, the top red trace is the simulated spectrum, using the fitted constants in Table 6.1, shifted upward by 0.2 PPMP while the bottom trace is the experimental spectrum. The vertical axis gives the absolute absorption in parts per million per pass (PPMP) as a function of laser frequency along the horizontal axis.
This congestion renders assignments of individual spectral features to unique quantum-state defined transitions nearly impossible. Due to this inability to assign individual lines, the use of the LSF method to simulate the experimental spectrum is inappropriate. We therefore used the EA approach, whose description can be found in Section 3.2.1, to simulate the spectrum and determine the most accurate values for the molecular parameters contained in $\mathcal{H}_T$ (Eq. 3.1) for both ground and first excited electronic states.

The resulting constants are summarized in Table 6.1. The converged result of the EA not only produces the best values for the fitted constants but at the same time assigns quantum numbers for individual transitions. This allows a classical least-squares fit using the assigned frequencies. In Meerts and Schmitt this is called an assigned fit, and the definitions of the statistical errors and correlation coefficients are discussed in Appendix B of that paper. The errors reported in Table 6.1 are based on a 0.01 cm$^{-1}$ uncertainty in the experimental line positions. The best agreement between the experimental spectrum and the fit was obtained with a rotational temperature of 15 K and a Voigt profile with a fixed Gaussian component of 250 MHz and 1450 MHz Lorentzian width.
Table 6.1: Molecular parameters of G1G2 conformer of n-C₃H₇O₂ radical from the experimental spectrum and from the indicated electronic structure calculations (see text for details). The calculated T₀₀ have corrected by the scaled ZPE correction. The rotational temperature was fitted to be 15.0K. The numbers in square brackets represent the percentage of error of the predicted constant with respect to the fitted results. The calculated and predicted constants are for the equilibrium geometry. The components of the transition moment are computed using the CIS method using the optimized geometries indicated from the normalize dipole moment. The values of θ and φ where found to be: θ = 68.2°, φ = 49.7°.
The components of the transition dipole along the principal axes given in Table 6.1 are determined from the fit values of $\theta$ and $\phi$ using the relationships,

\begin{align*}
\mu_a &= \mu \sin \phi \cos \theta \\
\mu_b &= \mu \sin \phi \sin \theta \\
\mu_c &= \mu \cos \phi
\end{align*}

Figure 6.2 shows both the overall spectrum (bottom) as well as a portion (top) of the resulting simulation and experimental trace. It appears obvious that the simulation and the experimental spectra are virtually identical. Table 6.1 shows all 15 molecular parameters incorporated in $\mathcal{H}_T$ for the $\tilde{A}$ and $\tilde{X}$ states are well determined.

Rather striking is the fact that the experimental precision of the parameters for the $G_1G_2$ conformer of propyl peroxy is very comparable to that which we previously reported for $\text{CD}_3\text{O}_2$ and $\text{C}_2\text{H}_5\text{O}_2$. While this result is counterintuitive, we expect the high precision obtained in this spectral fit to be attributable to the fact that the EA approach uses both the (somewhat less precise) frequencies for the propyl peroxy transitions and the intensity information contained in the $\text{C}_3\text{H}_7\text{O}_2$ spectrum while the LSF method used only the transition frequency information for $\text{CD}_3\text{O}_2$. Since CRDS is an absorption-based technique even absolute intensities are reliable, and the EA approach is ideal for fitting even highly congested CRDS spectra.

Once we have the experimental results of Table 6.1 we can use them to benchmark the results of various electronic structure calculations that are also given in Table 6.1. It appears that the MP2(FULL) method with a 6-31g(d) basis set reproduces
extremely well the rotational constants for both the $\tilde{A}$ and $\tilde{X}$ states (within 0.4%) which is consistent with the observations made in our study of the ethyl peroxy radical.\textsuperscript{96} As expected, the CCSD method also reproduces the rotational constants well but does not make as good a job as the MP2(FULL) method, the geometry optimization step of the G2 compound method.\textsuperscript{89} Finally, the DFT method provides the least precise rotational constants.

Having found that MP2(Full) provides an economical method to calculate accurate rotational constants, we have used it to calculate them for all 7 conformers of the two propyl peroxy isomers. These results are shown in Table 6.2. Comparison of these values with the experimental rotational constants of Table 6.1 confirms unambiguously the assignment of the analyzed sub-band to the $G_1 G_2$ conformer of 1-propyl peroxy.

<table>
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<th>$G_1' G_2$</th>
<th>$T_1 T_2$</th>
<th>$T_1 G_2$</th>
<th>$G_1 T_2$</th>
<th>$G_1 G_2$</th>
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</tbody>
</table>

Table 6.2: Calculated rotational constants of the optimized equilibrium geometry for all conformers of the propyl peroxy radical for both the ground and first excited electronic state. The calculations were performed at the MP2(FULL) level with a 6-31g(d) basis set.

If one looks at the different components of the spin-rotation tensor, we can easily
see from Table 6.1 that these constants are generally in good agreement with the predictions made using the semi-empirical method described in Section 3.3. As for the rotational constants, the MP2(FULL) method provides the most accurate estimate. The discrepancy among the calculated values is fairly easy to understand. Since the prediction of the spin-rotation tensor depends upon the optimized geometry of the molecule, it becomes obvious that the MP2(FULL) geometry would provide the best estimate of the spin-rotation constants while the B3LYP will do a least good job, just as we found for the rotational constants.

As Table 6.1 shows we actually only used the real part of the spin-rotation tensor to fit our spectrum. This result is partially predicated upon practicality. The EA program has not been adapted to diagonalize a complex $H_T$ matrix. However, this approximation was justified by using our SpecView program which can handle complex matrices. By adding the estimated values for $c$ and $e$ from the MP2(FULL) prediction into $H_T$ and by examining the resulting predicted spectrum from SpecView the largest shift in frequency is found to be $\approx 4.0$ MHz, which, at our resolution, is not significant. This approximation is further confirmed by comparing simulations including, or not, the two extra imaginary components of the spin-rotation tensor.

Since the $G_1G_2$ conformer of the propyl peroxy radical has $C_1$ symmetry, non-vanishing components of the transition dipole moment lie along all three axes, $a$, $b$ and $c$. The calculated and experimental results can be found in Table 6.1. One can observe a somewhat larger discrepancy between experiment and calculations for the relative components of the transition dipole than for the $\tilde{A}$ and $\tilde{X}$ state parameters.
However it is well known that transition dipoles are difficult to calculate and even more so for nearly forbidden $\tilde{A} - \tilde{X}$ transition. The fairly significant variation of the calculated dipoles using the three different optimized geometries supports this supposition.

6.3.1.2 The $G_{1}T_{2}$ Conformer of $n$-$C_{3}H_{7}O_{2}$

As mentioned previously, the $G_{1}T_{2}$ conformer of the n-propyl peroxy is estimated to be located about $27 \text{ cm}^{-1}$ above the $G_{1}G_{2}$ conformer and a sub-band is observed near to the location of the unresolved band in the room-temperature spectra that is assigned to the $G_{1}T_{2}$ conformer (as shown in Fig. 6.3). The spectrum spreads over $\approx 10 \text{ cm}^{-1}$ with a signal to noise ratio of about 20:1 for the strongest bands.
Figure 6.3: Experimental and simulated spectra of the G\textsubscript{1}T\textsubscript{2} conformer of the n-C\textsubscript{3}H\textsubscript{7}O\textsubscript{2} radical. The upper panel shows an enlargement of a 4 cm\textsuperscript{-1} section of the lower panel. In each panel, the top ref trace is the simulated spectrum, using the fitted constants in Table 6.3, shifted upward by 0.2 PPMP while the bottom trace is the experimental spectrum. Axis conventions are the same as Fig. 6.2.
We have performed a similar analysis on this band as the one for the band of the $G_1G_2$ conformer. The parameters resulting from the EA analysis of this sub-band are given in Table 6.3. The rotational temperature has been fitted to be $\approx 18K$. 
Table 6.3: Molecular parameters of G\textsubscript{1}T\textsubscript{2} conformer of n-C\textsubscript{3}H\textsubscript{7}O\textsubscript{2} radical from the experimental spectrum and from the indicated electronic structure calculations (see text for details). The calculated T\textsubscript{00} have corrected by the scaled ZPE correction. The rotational temperature was fitted to be 17.9K. The numbers in square brackets represent the percentage of error of the predicted constant with respect to the fitted results. The calculated and predicted constants are for the equilibrium geometry. The components of the transition moment are computed using the CIS method using the optimized geometries indicated from the normalize dipole moment. The values of θ and φ where found to be: θ = 36.3°, φ = 60.2°.

<table>
<thead>
<tr>
<th>Const. (cm\textsuperscript{-1})</th>
<th>Fit</th>
<th>MP2(FULL)\textbackslash{}6-31g(d)</th>
<th>CCSD\textbackslash{}6-31+g(d)</th>
<th>B3LYP\textbackslash{}6-31+g(d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A\textquoteright\prime \prime</td>
<td>0.50544 (4)</td>
<td>0.50935 [-0.774 (8)]</td>
<td>0.50192 [0.696 (8)]</td>
<td>0.51277 [-1.450 (8)]</td>
</tr>
<tr>
<td>B\textquoteright\prime \prime</td>
<td>0.08389 (2)</td>
<td>0.08420 [-0.370 (24)]</td>
<td>0.08345 [0.524 (24)]</td>
<td>0.08185 [2.432 (24)]</td>
</tr>
<tr>
<td>C\textquoteright\prime \prime</td>
<td>0.07905 (2)</td>
<td>0.07925 [-0.253 (25)]</td>
<td>0.07843 [0.784 (25)]</td>
<td>0.07745 [2.024 (25)]</td>
</tr>
<tr>
<td>\tilde{\epsilon}_{aa} \prime \prime = -(a\textsubscript{0}+2a)\prime \prime</td>
<td>-0.0106 (7)</td>
<td>-0.0118 (15) [-11. (7)]</td>
<td>-0.0117 (15) [-10. (7)]</td>
<td>-0.0125 (15) [-18. (7)]</td>
</tr>
<tr>
<td>\tilde{\epsilon}_{bb} \prime \prime = (a+b-a\textsubscript{0})\prime \prime</td>
<td>-0.0037 (3)</td>
<td>-0.0035 (14) [5. (8)]</td>
<td>-0.0035 (14) [5. (8)]</td>
<td>-0.0032 (14) [14. (8)]</td>
</tr>
<tr>
<td>\tilde{\epsilon}_{cc} \prime \prime = (a-b-a\textsubscript{0})\prime \prime</td>
<td>-0.0025 (3)</td>
<td>-0.0016 (15) [36. (12)]</td>
<td>-0.0016 (15) [36. (12)]</td>
<td>-0.0017 (15) [36. (12)]</td>
</tr>
<tr>
<td>(1/2)(\tilde{\epsilon}<em>{ab} + \tilde{\epsilon}</em>{ba})'' = d''</td>
<td>-0.0021 (33)</td>
<td>-0.0049 (22) [-133. (157)]</td>
<td>-0.0049 (22) [-133. (157)]</td>
<td>-0.0053 (22) [-152. (157)]</td>
</tr>
<tr>
<td>(1/2)(\tilde{\epsilon}<em>{ac} + \tilde{\epsilon}</em>{ca})'' = c''</td>
<td>-</td>
<td>0.0020</td>
<td>0.0020</td>
<td>0.0020</td>
</tr>
<tr>
<td>(1/2)(\tilde{\epsilon}<em>{bc} + \tilde{\epsilon}</em>{cb})'' = c''</td>
<td>-</td>
<td>0.0006</td>
<td>0.0006</td>
<td>0.0010</td>
</tr>
<tr>
<td>A\textquoteright\prime \prime</td>
<td>0.47968 (4)</td>
<td>0.48144 [-0.367 (8)]</td>
<td>0.47526 [0.921 (8)]</td>
<td>0.48692 [-1.509 (8)]</td>
</tr>
<tr>
<td>B\textquoteright\prime \prime</td>
<td>0.08518 (2)</td>
<td>0.08538 [-0.235 (23)]</td>
<td>0.08453 [0.763 (23)]</td>
<td>0.08306 [2.489 (23)]</td>
</tr>
<tr>
<td>C\textquoteright\prime \prime</td>
<td>0.07899 (2)</td>
<td>0.07931 [-0.405 (25)]</td>
<td>0.07838 [0.772 (25)]</td>
<td>0.07723 [2.228 (25)]</td>
</tr>
<tr>
<td>\tilde{\epsilon}_{aa} \prime = -(a\textsubscript{0}+2a)\prime</td>
<td>0.0104 (7)</td>
<td>0.0135 (15) [-30. (7)]</td>
<td>0.0137 (15) [-32. (7)]</td>
<td>0.0149 (15) [-43. (7)]</td>
</tr>
<tr>
<td>\tilde{\epsilon}_{bb} \prime = (a+b-a\textsubscript{0})\prime</td>
<td>0.0037 (3)</td>
<td>0.0041 (14) [-11. (8)]</td>
<td>0.0040 (14) [-8. (8)]</td>
<td>0.0037 (14) [0. (8)]</td>
</tr>
<tr>
<td>\tilde{\epsilon}_{cc} \prime = (a-b-a\textsubscript{0})\prime</td>
<td>0.0005 (3)</td>
<td>0.0004 (15) [20. (60)]</td>
<td>0.0003 (15) [40. (60)]</td>
<td>0.0004 (15) [20. (60)]</td>
</tr>
<tr>
<td>(1/2)(\tilde{\epsilon}<em>{ab} + \tilde{\epsilon}</em>{ba})' = d'</td>
<td>0.0092 (4)</td>
<td>0.0086 (22) [2. (4)]</td>
<td>0.0086 (22) [7. (4)]</td>
<td>0.0090 (22) [2. (4)]</td>
</tr>
<tr>
<td>(1/2)(\tilde{\epsilon}<em>{ac} + \tilde{\epsilon}</em>{ca})' = c'</td>
<td>-</td>
<td>-0.0020</td>
<td>-0.0020</td>
<td>-0.0019</td>
</tr>
<tr>
<td>(1/2)(\tilde{\epsilon}<em>{bc} + \tilde{\epsilon}</em>{cb})' = c'</td>
<td>-</td>
<td>-0.0007</td>
<td>-0.0007</td>
<td>-0.0009</td>
</tr>
<tr>
<td></td>
<td>\mu_{b}/</td>
<td>\mu_{a}</td>
<td></td>
<td>0.747</td>
</tr>
<tr>
<td></td>
<td>\mu_{c}/</td>
<td>\mu_{a}</td>
<td></td>
<td>0.699</td>
</tr>
<tr>
<td>T\textsubscript{00}</td>
<td>7576.2469 (4)</td>
<td>7566.8709 [0.12]</td>
<td>7099.6110 [6.29]</td>
<td>7655.9997 [1.05]</td>
</tr>
</tbody>
</table>

| µ\textsubscript{b}/µ\textsubscript{a} | 0.747 | 0.495 | 0.540 | 0.554 |
| µ\textsubscript{c}/µ\textsubscript{a} | 0.699 | 0.462 | 0.460 | 0.386 |
| T\textsubscript{00} | 7576.2469 (4) | 7566.8709 [0.12] | 7099.6110 [6.29] | 7655.9997 [1.05] |
It is clear that the simulation is in perfect agreement with the experimental spectrum. By comparing the experimental molecular parameters with the calculated and predicted ones in Table 6.3, we came to the same conclusion as for the $G_1G_2$ conformer, i.e., that the MP2(FULL) is suitable to make the best predictions for molecular parameters and that the B3LYP method gives the poorest agreement of the three methods employed. By comparing the calculated rotational constants in Table 6.2 with the experimental values in Table 6.3, it is clear that the assignment of this band to the $G_1T_2$ conformer is correct.

It is of interest to compare the present highly accurate values of $T_{00} = 7501.2532(3)$ and $7576.2469(4)$ cm$^{-1}$ for the $G_1G_2$ and $GT_2$ conformers respectively with the values of $7508(2)$ and $7569(2)$ cm$^{-1}$ from the room-temperature spectra.$^{34,39}$ It is somewhat surprising to see discrepancies significantly beyond the estimated experimental measurement error in the room-temperature experiments. This result is particularly striking since our recently reported $T_{00}$ values from jet-cooled spectra agreed too well within the room-temperature experimental error for $CD_3O_2$, and both the G and T conformers of ethyl peroxy.$^{96}$ However, in these cases, the room-temperature bands while unresolved were isolated. In the case of the $G_1G_2$ and $GT_2$ conformers of 1-propyl peroxy the room-temperature bands are significantly overlapped and this may well explain the discrepancies.

It also is interesting to compare the present experimental results with the calculated excitation energy $T_{00}$ for the electronic structure methods which are summarized in Tables 6.1 and 6.3. The energy separation for the MP2(FULL) was obtained by
calculating both electronic states using the G2 compound method which already con-
tains the ZPE correction as well as several higher order energy correction terms. The
energies obtained for the CCSD and B3LYP energies have been corrected by the ZPE
correction under the harmonic oscillator approximation. In the former case an aver-
age of the B3LYP and G2 ZPE (which differ by \( \approx 10 \text{ cm}^{-1} \)) was used. It is no surprise
that the MP2(FULL) calculation is the most accurate one as pointed out by Sharp
et.al.\textsuperscript{39} On the other hand, it is surprising that the CCSD calculation is less accurate
than the DFT one since its global minimum structure of the radical appears to be
more accurate that the B3LYP one.

6.3.2 The G Conformer of the 2-Propyl Peroxy Radical Iso-
mer

The 2-propyl peroxy isomer is known to have only 2 conformers, as show in Fig.
6.1. It has been calculated\textsuperscript{4} that the G conformer is the most stable and that the T
conformer lies about 147 cm\(^{-1}\) higher. So it is likely that under jet-cooled conditions
one should only observe the G conformer. The only hand observed for isopropyl
peroxy is illustrated in Fig. 6.4. The signal to noise ratio appears to be excellent on
this spectrum (more than 120:1 for the strongest feature) and the spectrum spreads
over \( \approx 10 \text{ cm}^{-1} \). However, the experimental spectrum exhibits less resolved rotational
or spin-rotational structure than with the n-propyl peroxy isomer, which makes the
EA approach even more important for analyzing the spectra.

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Figure 6.4: Experimental and simulated spectra of the G conformer of the iso-$\text{C}_3\text{H}_7\text{O}_2$ radical. The upper panel shows an enlargement of a 4 cm$^{-1}$ section of the lower panel. In each panel, the top ref trace is the simulated spectrum, using the fitted constants in Table 6.4, shifted upward by 2. PPMP while the bottom trace is the experimental spectrum. Axis conventions are the same as Fig. 6.2.
We have employed the same approach as described above for the analysis of 1-propyl isomer. The results are summarized in Table 6.4 and Fig. 6.4. The rotational temperature was found to be 13.3 K. When looking at the top insert of Fig. 6.4, one can see that discrepancies between the simulation and the experimental spectrum are essentially non-existent. Moreover there is extremely good agreement between the fitted molecular parameters and the calculated and predicted ones using the MP2(FULL) method.
Table 6.4: Molecular parameters of the G conformer of iso-C$_3$H$_7$O$_2$ radical from the experimental spectrum and from the indicated electronic structure calculations (see text for details). The calculated $T_{00}$ have corrected by the scaled ZPE correction. The rotational temperature was fitted to be 13.3K. The numbers in square brackets represent the percentage of error of the predicted constant with respect to the fitted results. The calculated and predicted constants are for the equilibrium geometry. The components of the transition moment are computed using the CIS method using the optimized geometries indicated from the normalize dipole moment. The values of $\theta$ and $\phi$ where found to be: $\theta = 1.4^\circ$, $\phi = 48.8^\circ$.

<table>
<thead>
<tr>
<th>Const. (cm$^{-1}$)</th>
<th>Fit</th>
<th>MP2(FULL)\6-31g(d)</th>
<th>CCSD\6-31+g(d)</th>
<th>B3LYP\6-31+g(d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A''$</td>
<td>0.26527 (4)</td>
<td>0.26572 [-0.170 (15)]</td>
<td>0.26340 [0.705 (15)]</td>
<td>0.26162 [1.376 (15)]</td>
</tr>
<tr>
<td>$B''$</td>
<td>0.13692 (3)</td>
<td>0.13718 [-0.190 (22)]</td>
<td>0.13530 [1.183 (22)]</td>
<td>0.13408 [2.074 (22)]</td>
</tr>
<tr>
<td>$C''$</td>
<td>0.09916 (4)</td>
<td>0.09979 [-0.635 (40)]</td>
<td>0.09860 [0.565 (40)]</td>
<td>0.09772 [1.452 (40)]</td>
</tr>
<tr>
<td>$\tilde{\epsilon}_{aa''} = -(a_0+2a)'$</td>
<td>-0.0139 (7)</td>
<td>-0.0135 (15) [-3. (5)]</td>
<td>-0.0134 (15) [4. (5)]</td>
<td>-0.0133 (15) [4.317 (5)]</td>
</tr>
<tr>
<td>$\tilde{\epsilon}_{bb''} = (a+b-a_0)''$</td>
<td>-0.0013 (5)</td>
<td>-0.0024 (14) [-84. (38)]</td>
<td>-0.0023 (14) [-77. (38)]</td>
<td>-0.0021 (14) [-62. (38)]</td>
</tr>
<tr>
<td>$\tilde{\epsilon}_{cc''} = (a-b-a_0)''$</td>
<td>-0.0012 (7)</td>
<td>-0.0017 (15) [-42. (58)]</td>
<td>-0.0017 (15) [-42. (58)]</td>
<td>-0.0018 (15) [-50. (58)]</td>
</tr>
<tr>
<td>$(1/2)(\tilde{\epsilon}<em>{ab} + \tilde{\epsilon}</em>{ba})'' = d''$</td>
<td>0.0128 (19)</td>
<td>0.0029 (22) [77. (15)]</td>
<td>0.0028 (22) [78. (15)]</td>
<td>0.0027 (22) [79. (15)]</td>
</tr>
<tr>
<td>$(1/2)(\tilde{\epsilon}<em>{bc} + \tilde{\epsilon}</em>{cb})'' = e''$</td>
<td>-</td>
<td>-0.0019</td>
<td>-0.0019</td>
<td>-0.0019</td>
</tr>
<tr>
<td>$A' = 0.26406 (4)$</td>
<td>0.26403 [0.011 (15)]</td>
<td>0.26241 [0.625 (15)]</td>
<td>0.26142 [1.000 (15)]</td>
<td>0.26142 [1.000 (15)]</td>
</tr>
<tr>
<td>$B' = 0.13710 (3)$</td>
<td>0.13729 [-0.139 (22)]</td>
<td>0.13519 [1.393 (22)]</td>
<td>0.13399 [2.268 (22)]</td>
<td>0.13399 [2.268 (22)]</td>
</tr>
<tr>
<td>$C' = 0.09912 (4)$</td>
<td>0.09961 [-0.494 (40)]</td>
<td>0.09827 [0.858 (40)]</td>
<td>0.09723 [1.907 (40)]</td>
<td>0.09723 [1.907 (40)]</td>
</tr>
<tr>
<td>$\tilde{\epsilon}_{aa'} = -(a_0+2a)'$</td>
<td>0.0172 (7)</td>
<td>0.0184 (15) [-7. (4)]</td>
<td>0.0184 (15) [-7. (4)]</td>
<td>0.0185 (15) [-8. (4)]</td>
</tr>
<tr>
<td>$\tilde{\epsilon}_{bb'} = (a+b-a_0)'$</td>
<td>0.0013 (5)</td>
<td>0.0010 (14) [23. (38)]</td>
<td>0.0010 (14) [23. (38)]</td>
<td>0.0010 (14) [23. (38)]</td>
</tr>
<tr>
<td>$\tilde{\epsilon}_{cc'} = (a-b-a_0)'$</td>
<td>0.0004 (7)</td>
<td>0.0003 (15) [25. (175)]</td>
<td>0.0003 (15) [25. (175)]</td>
<td>0.0002 (15) [50. (175)]</td>
</tr>
<tr>
<td>$(1/2)(\tilde{\epsilon}<em>{ab} + \tilde{\epsilon}</em>{ba})' = d'$</td>
<td>-0.0018 (50)</td>
<td>-0.0031 (22) [-72. (276)]</td>
<td>-0.0030 (22) [-67. (276)]</td>
<td>-0.0030 (22) [267 (276)]</td>
</tr>
<tr>
<td>$(1/2)(\tilde{\epsilon}<em>{bc} + \tilde{\epsilon}</em>{cb})' = e'$</td>
<td>-</td>
<td>-0.0018</td>
<td>-0.0018</td>
<td>0.0017</td>
</tr>
<tr>
<td>$</td>
<td>\mu_b/\mu_a</td>
<td>$</td>
<td>0.023</td>
<td>0.515</td>
</tr>
<tr>
<td>$</td>
<td>\mu_c/\mu_a</td>
<td>$</td>
<td>0.883</td>
<td>0.697</td>
</tr>
<tr>
<td>$T_{00} = 7568.0950 (4)$</td>
<td>7566.2345 [0.02]</td>
<td>7124.1834 [5.87]</td>
<td>7662.2373 [1.24]</td>
<td></td>
</tr>
</tbody>
</table>
Comparison between the experimental rotational constants in Table 6.4 and the calculated ones in Table 6.2 confirm the room-temperature assignment of this band to the G conformer of isopropyl peroxy. The highly accurate value of \( T_{00} = 7568.0950(2) \) agrees well with the room-temperature value\textsuperscript{34,39} of 7567(2) given the latter’s experimental error. The good agreement here, compared to the poorer agreement for the n-propyl peroxy conformers, likely reflects the fact that while the room-temperature band is unresolved it is isolated for the isopropyl peroxy isomer. Referring to Table 6.4, we see that the G2 calculation using the MP2(Full) result, is by far the closest to experiment.

6.4 Conclusion

We have successfully recorded the partially rotationally resolved spectra of several isomers and conformers of the propyl peroxy radical, \( \text{C}_3\text{H}_7\text{O}_2 \), i.e., the \( G_1G_2 \) and \( G_1T_2 \) conformers of the n-propyl peroxy and the G conformer of iso-propyl peroxy. We have used an EA approach to analyze the observed spectra. This approach allowed us to obtain an excellent match between the simulated and the experimental spectra producing a set of molecular parameters characterizing the \( \tilde{X} \) and \( \tilde{A} \) states of the radicals.

We have confirmed the conformer room-temperature assignments previously made by Tarczay \textit{et al.}\textsuperscript{4} which were made entirely based upon electronic structure calculations. Obtaining molecular parameters characterizing these radicals in both electronic states allowed us to benchmark quantum chemistry calculations by several different
methods and basis sets. We also demonstrated that by following the formalism of Brown, Sears and Watson\textsuperscript{74} and extended by Tarczay \textit{et al.},\textsuperscript{90} one is able to predict the different components of the spin-rotation tensors rather well. Finally, this work confirm the effectiveness of using an EA approach to simulate spectra varying degrees of resolution.
CHAPTER 7

THE PHENYL PEROXY RADICAL, C₆H₅O₂

7.1 Introduction

The previous two chapters have shown the capabilities of our high-resolution jet-cooled experimental setup for obtaining and analyzing the spectra of the ethyl and propyl peroxy radicals and hence confirming the previous assignments of room temperature cavity ringdown spectra which were based upon high level quantum chemistry calculations.

We are now going to focus on a somewhat larger unsaturated cyclic peroxy radical, the phenyl peroxy radical, C₆H₅O₂. We were able to record high-resolution spectra of the later radical with our narrow band laser source (≈250 MHz), and with rotational temperature of about 15K, see Section 5.1 for details.

As in the former two chapters, we have found it of use to analyze and fit these spectra using the EA approach due to the partially resolved nature of the experimental spectra. Our analysis produces a set of high-precision molecular parameters characterizing the Š and Š states which we compare with the results of electronic structure calculations for this radical.
The reaction of phenyl radical (C₆H₅) with oxygen is of critical importance, in that it is believed to impede the formation of soot, which is inherent in hydrocarbon combustion reactions. If phenyl radical is not further oxidized, then its recombination reactions can lead to larger unsaturated hydrocarbons that are precursors to soot.

Even if the oxidation reaction occurs, its product distribution differs with temperature and pressure, e.g.,

\[ C_6H_5 + O_2 \leftrightarrow C_6H_5OO^* \] \hspace{1cm} (7.1)

\[ C_6H_5OO^* \rightarrow C_6H_5OO + M \] \hspace{1cm} (7.2)

\[ C_6H_5OO^* \rightarrow C_6H_4OO + H \] \hspace{1cm} (7.3)

\[ C_6H_5OO^* \rightarrow C_6H_5O + O \] \hspace{1cm} (7.4)

Clearly Eqs. 7.2-7.4 provide an important branching mechanism for combustion chain reaction. A theoretical study using RRKM methods found that at relatively low temperatures (T<1000 K), the formation and stabilization of phenyl peroxy radicals dominates the reaction, while at higher temperatures, the production of phenoxy radical becomes competitive (Eq. 7.4). Indeed, the appearance of phenyl peroxy at lower oxidation temperatures (297-500 K) has been verified experimentally.
7.2 Spectral Analysis and Simulation.

The recorded spectrum of the phenyl peroxy radical only involve the $0^0_0$ band of the $\tilde{A} - \tilde{X}$ electronic transition. Due to the fact that the radical is in a doublet state we expect both an observable rotational and spin-rotation structure in the spectra, but we expect hyperfine splittings to be unresolvable. Hence, the structure of each vibronic level is described by the Hamiltonian $\mathcal{H}_T$, Eq. 3.1 (see Section 3.1.1 for details).

We have shown in the previous two chapters that in the case of only partially resolved spectra that the LSF approach is not suitable in order to simulate such complicated spectra and that the EA method is more appropriate and provides high precision molecular constants. From a spectroscopic point of view, the EA approach reproduces this behavior to fit an experimental spectrum with a model based upon the differences of the eigenvalues of the Hamiltonian such as $\mathcal{H}_T$ given by Eq. 3.1. The use of the EA approach to analyze the spectra of RO$_2$ has been discussed previously in Section 3.2.1 with more details.

7.3 Experimental results

The room temperature cavity ringdown spectra has shown that the phenyl peroxy radical only has one conformer with $C_s$ symmetry. Fig 7.1 represents the $0^0_0$ band of the phenyl peroxy radical recorded using our high-resolution apparatus described in Section 2.2.2.
Figure 7.1: Experimental and simulated spectra of the C₆H₅O₂ radical. The upper panel shows an enlargement of a 2 cm⁻¹ section of the lower panel. In each panel, the bottom trace is the experimental spectrum while the top trace is the simulated spectrum shifted upward by 2.0 PPMP, using the fitted constants in Table 7.1. The vertical axis gives the absolute absorption in parts per million per pass (PPMP) as a function of laser frequency along the horizontal axis.
The recorded spectrum, which spreads over 10 cm$^{-1}$, has a good signal to noise ratio (S/N $\approx$ 1900 for the strongest feature). This high S/N is rather unexpected considering the size of this radical and the fact that in the previous chapter, the propyl peroxy radical only had a S/N of about 25. By looking more carefully at the spectrum it appears that due to the congested nature of the spectrum, even at 15K, that the LSF method is not appropriate and the an EA approach is suitable in order to simulate such congested spectrum. The fitted constants are summarized in Table 7.1. The best agreement between the experimental spectrum and the fit was obtain with a rotational temperature of 15 K and a Voigt profile with a fixed Gaussian component of 250 MHz$^3$ and 450 MHz Lorentzian width.

Due to the C$_s$ symmetry nature of the phenyl peroxy radical, we only expect to determine 4 spin-rotation tensor components. Also by symmetry, only the c component of the dipole moment is non-zero.

Rather striking is the fact that the experimental precision of the parameters are comparable to the ones obtained in previous studies of the CD$_3$O$_2$, C$_2$H$_5$O$_2$ and C$_3$H$_7$O$_2$, even with such a poorly resolved spectrum.

Now that we have the experimental results of Table 7.1, we can compare them to several electronic structure calculations. As for the ethyl and the propyl radical, it appear that the MP2(FULL) method with a 6-31g(d) basis set reproduces extremely well the fitted parameters for both the ground and the first excited electronic states. This is rather surprising considering the size of the radical of interest. The percentage errors of the predicted constants with respect to the fitted results for the latter
<table>
<thead>
<tr>
<th>Const. (cm(^{-1}))</th>
<th>Fit</th>
<th>MP2(FULL)(6-31)g(d)</th>
<th>CCSD(6-31+)g(d)</th>
<th>B3LYP(6-31+)g(d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A'')</td>
<td>0.17228 (4)</td>
<td>0.17232 [-0.02 (2)]</td>
<td>0.17156 [0.42 (2)]</td>
<td>0.17218 [0.06 (2)]</td>
</tr>
<tr>
<td>(B'')</td>
<td>0.05398 (3)</td>
<td>0.05394 [0.07 (6)]</td>
<td>0.05363 [0.65 (6)]</td>
<td>0.05364 [0.63 (6)]</td>
</tr>
<tr>
<td>(C'')</td>
<td>0.04101 (5)</td>
<td>0.04108 [-0.17 (12)]</td>
<td>0.04086 [0.37 (12)]</td>
<td>0.04090 [0.27 (12)]</td>
</tr>
<tr>
<td>(\tilde{\epsilon}_{aa}'')</td>
<td>-((a_0+2a))''</td>
<td>0.0080 (7)</td>
<td>-0.0107 (15) [-34. (9)]</td>
<td>-0.0106 (15) [-33. (9)]</td>
</tr>
<tr>
<td>(\tilde{\epsilon}_{bb}'')</td>
<td>((a+b-a_0))''</td>
<td>0.0013 (5)</td>
<td>-0.0012 (14) [8. (38)]</td>
<td>-0.0012 (14) [8. (38)]</td>
</tr>
<tr>
<td>(\tilde{\epsilon}_{cc}'')</td>
<td>((a-b-a_0))''</td>
<td>0.0</td>
<td>0.0 (15) [-]</td>
<td>0.0 (15) [-]</td>
</tr>
<tr>
<td>((1/2)(\tilde{\epsilon}<em>{ab} + \tilde{\epsilon}</em>{ba})'')</td>
<td>(d'')</td>
<td>0.0015 (10)</td>
<td>0.0009 (22) [40. (67)]</td>
<td>0.0010 (22) [33. (67)]</td>
</tr>
<tr>
<td>((1/2)(\tilde{\epsilon}<em>{bc} + \tilde{\epsilon}</em>{cb})'')</td>
<td>(e'')</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>((1/2)(\tilde{\epsilon}<em>{ac} + \tilde{\epsilon}</em>{ca})'')</td>
<td>(e'')</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>(A')</td>
<td>0.17011 (4)</td>
<td>0.17042 [-0.18 (2)]</td>
<td>0.16932 [0.46 (2)]</td>
<td>0.17087 [-0.45 (2)]</td>
</tr>
<tr>
<td>(B')</td>
<td>0.05443 (3)</td>
<td>0.05439 [0.07 (6)]</td>
<td>0.05399 [0.81 (6)]</td>
<td>0.05369 [1.36 (6)]</td>
</tr>
<tr>
<td>(C')</td>
<td>0.04117 (5)</td>
<td>0.04123 [-0.15 (12)]</td>
<td>0.04094 [0.56 (12)]</td>
<td>0.04085 [0.78 (12)]</td>
</tr>
<tr>
<td>(\tilde{\epsilon}_{aa}')</td>
<td>-((a_0+2a))'</td>
<td>0.0090 (7)</td>
<td>0.0011 (15) [-7. (8)]</td>
<td>0.0014 (15) [-27. (8)]</td>
</tr>
<tr>
<td>(\tilde{\epsilon}_{bb}')</td>
<td>((a+b-a_0))'</td>
<td>0.0010 (5)</td>
<td>0.0013 (14) [-30. (50)]</td>
<td>0.0013 (14) [-30. (50)]</td>
</tr>
<tr>
<td>(\tilde{\epsilon}_{cc}')</td>
<td>((a-b-a_0))'</td>
<td>0.0</td>
<td>0.0 (15) [-]</td>
<td>0.0 (15) [-]</td>
</tr>
<tr>
<td>((1/2)(\tilde{\epsilon}<em>{ab} + \tilde{\epsilon}</em>{ba})')</td>
<td>(d')</td>
<td>-0.0011 (7)</td>
<td>-0.0025 (22) [-127. (64)]</td>
<td>-0.0024 (22) [-118. (64)]</td>
</tr>
<tr>
<td>((1/2)(\tilde{\epsilon}<em>{bc} + \tilde{\epsilon}</em>{cb})')</td>
<td>(e')</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>((1/2)(\tilde{\epsilon}<em>{ac} + \tilde{\epsilon}</em>{ca})')</td>
<td>(e')</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>(T_{00})</td>
<td>7495.3160 (6)</td>
<td>7304.7970 [2.54]</td>
<td>7056.4250 [5.84]</td>
<td>7791.9792 [3.96]</td>
</tr>
</tbody>
</table>

Table 7.1: Molecular parameters of the \(\text{C}_6\text{H}_5\text{O}_2\) radical. The calculated \(T_{00}\) have corrected by the scaled ZPE correction. The rotational temperature was fitted to be 12.6K. The numbers in square brackets represent the percentage of error of the predicted constant with respect to the fitted results. The calculated and predicted constants are for the equilibrium geometry. By symmetry only the c component of the dipole moment is non-zero.
method are also in good agreement with the one obtained previously for the \( \text{C}_2\text{H}_5\text{O}_2 \)
and \( \text{C}_3\text{H}_7\text{O}_2 \) radicals. It is also expected and confirmed that the CCSD method repro-
duces as well the fitted rotational constants but is not doing as good of a job as the
MP2(FULL) method. Finally, the DFT method produces the least precise rotational
constants.

If we are now turning our attention to the spin-rotation tensor components, one
can see from Table 7.1 that the fitted constants are generally in good agreement with
the one predicted using the method described in Section 3.3. As for the rotational
constant, the MP2(FULL) method provides the most accurate prediction.

The discrepancy among the calculated values is fairly easy to understand. Since
the prediction of the spin-rotation tensor depends upon the optimized geometry of
the molecule, it becomes obvious that the MP2(FULL) geometry would provide the
best estimate of the spin-rotation constants while the B3LYP will do a least good
job, just as we found for the rotational constants.

When one is looking carefully at the rotational constants presented in Table
7.1, one can see that it appears that the rotational constants predicted using the
MP2(FULL) method are really close from the fitted values for both the ground and
the first excited electronic state. Figure 7.2 compares this 2 set of rotational constants
and also shows the effect of the addition of the spin-rotation tensor component in the
simulation.
Figure 7.2: Experimental and simulated spectra of the C₆H₅O₂ radical. The upper panel represent a simulation only using the rotational constants predicted using the MP2(FULL) method. The second upper panel represent the same simulation but using the fitted rotational constant from Table 7.1. The second lower panel is a simulation containing both rotational and spin-rotation constants from Table 7.1. Finally, the bottom panel represent the experimental spectrum.
From Figure 7.2 it appears obvious that the simulated spectrum, by only including
the rotational constants, for both fitted and calculated constants are almost identical
at the exception of some small features. Also, it is surprising that, in order to obtain a
perfect match between the experimental and the fitted spectrum, one need to take into
account the spin-rotation tensor component even for such a important size molecule
as shown in Fig 7.2.

Finally, we can turn our attention to the calculated $T_{00}$ and compare them to
the fitted results. First of all, it is of interest to note that the high-resolution $T_{00}$
(7495.3160 (6) cm$^{-1}$) is in good agreement with the value obtained from room temper-
ature (7497 cm$^{-1}$). Even more interesting is the comparison between the calculated
and the fitted $0^3_0$ band. As for the ethyl and propyl peroxy radicals, the energy sep-
aration for the MP2(FULL) was obtained by calculating both electronic states using
the G2 compound method which already contains the ZPE correction, as well as
several higher order energy correction terms. The energies calculated for the CCSD
and B3LYP methods have been corrected by the ZPE under the harmonic oscillator
approximation. In the former case, an average of the B3LYP and G2 ZPE (which
differ by $\approx 15$ cm$^{-1}$) was used. It is not surprising that the MP2(FULL) calculation is
the most accurate one as pointed out by Sharp et.al. However, the percentage error
(2.54%) for this calculation is significantly higher than the one for the ethyl and propyl
peroxy radical (about 0.1%). This discrepancy can be rationalized by both the cyclic
and the unsaturated nature of phenyl peroxy and the inability for the higher order
energy correction terms contained in the G2 method to manage this latter aspect of
the molecule.

On the other hand, it is surprising that the CCSD calculation is less accurate than
the DFT one since its global minimum structure of the radical appears to be more
accurate than the B3LYP one.

7.4 Conclusion

We have successfully obtained partially resolved spectra of the phenyl peroxy radical
C₆H₅O₂. The EA approach appeared to be extremely adequate in order to simulate
such congested spectrum. This method allowed us to obtain an excellent match
between the experimental and the simulated spectrum and produces a set of molecular
parameters that characterize both the $\tilde{X}$ and $\tilde{A}$ states of the radicals.
CHAPTER 8

CONCLUSIONS

High-resolution jet-cooled cavity ringdown spectroscopy in the near-infrared has been applied to measure the $\tilde{A}-\tilde{X}$ electronic transition of several alkyl peroxy radicals, RO$_2$$^\cdot$. This transition, unlike the $\tilde{B}-\tilde{X}$ provides well resolved spectra leading to unambiguous assignment of a given peroxy radical.

We have successfully recorded the partially rotationally resolved spectra of both conformers of the ethyl peroxy radical as well as 2 conformers of the n-propyl peroxy radical isomer and the G conformer of the iso-propyl peroxy radical. Finally we demonstrated the capabilities of our experimental technique to record an aromatic unsaturated peroxy radical, phenyl peroxy.

Due to the inadequacy of the traditional least square fitting procedure, we have used an evolutionary algorithm approach to analyze all the observed spectra. This approach has yielded simulated spectra virtually indistinguishable from the experimental traces and produced a set of molecular parameters characterizing the $\tilde{X}$ and $\tilde{A}$ states of the radicals.

Using this approach, we were able to confirm the previously room temperature conformer assignments which were based upon high level quantum chemistry calculations.
Obtaining molecular parameters characterizing these radicals in both electronic states allowed us to benchmark quantum chemistry calculations by several different methods and basis sets. We could unambiguously conclude that the MP2(FULL) method with a 6-31g(d) basis set is extremely appropriate to predict the rotational constants for both the ground and the first excited state and that the optimized geometry from this calculation allows us to predict accurately the spin-rotation tensor component of a given alkyl peroxy radical. The CCSD method is a more time-consuming method and has been shown to produce good agreement between fitted and calculated molecular constant but with less good of an agreement than the MP2(FULL) method. Finally the B3LYP method only produces qualitative results. We also demonstrated that by following the formalism of Brown, Sears and Watson\textsuperscript{74} and extended by Tarczay \textit{et al.}\textsuperscript{90}, one is able to predict the different components of the spin-rotation tensors rather well using CD$_3$O$_2$ as a reference molecule.

Finally, we analyzed were able to assign and simulate unexpected features present in the room temperature spectrum of the methyl peroxy spectrum using a one-dimensional model of methyl rotation. This work will be of great help in the simulation of the high-resolution cavity ringdown spectral analysis of the latter radical.

To extend the work on the alkyl peroxy radicals and especially to understand the experimental observations that were made on the Lorentzian component of the linewidth observed between normal and deuterated species, obtaining a high-resolution spectrum of the C$_6$D$_5$O$_2$ radical would be of great interest. An observation of a smaller linewidth for the deuterated phenyl peroxy radical would open the door to a better
understanding of the lifetime issues that the alkyl peroxy radical might have. Also, due to its relevance in the night time chemistry, obtaining high-resolution spectra of the NO$_3$ radical would be of great interest to understand and model this Jahn-Teller active radical.
APPENDIX A

Explanation and Definition of the Input Parameters of EA

The EA is a very suitable for parallel computation. The calculations were performed on a Linux cluster in Nijmegen based on SUN Fire X4100 and X4150 machines. Typically 32 CPUs were used. Convergence occurs in approximately 200 generations corresponding to a wall clock time of about 20 minutes.

In order to achieve fast convergence, a wise choice for the initial ranges of the different parameters of a given Hamiltonian is needed. Initially, we chose the predicted rotational constants from a B3LYP calculation and assumed a search range of ±2%. After observing that the fitted results were in significantly better agreement with the values from the MP2(FULL) calculation we used them with a range of ±0.25% as our starting point in the fits. For the spin-rotation constants we used the procedure described in the next section to estimate their values and assumed a search range of predicted value times $10^{±1}$.

The operation of the program is controlled by an input file with a control command on each line. The general structure is as follow:

\[ \text{keyword string} = \text{value(s)} \]  

(A.1)
The value consists of a string or of one or more values; of numerical and/or character type. The order of appearance of the keywordstrings in the file is not important. Blanks or TABs at the beginning of a line are removed. A line starting with ”#”, an unknown keywordstring or in which no ”=” sign is found is considered as comment and its content is ignored. The EA program can read Unix/Linux as well as DOS type of file.\textsuperscript{102} So irrespectively of the editor you use to create the input file, the EA will be able to read it. The list of the different parameters used in our fits can be found in Table A.1

The keyword string parameter is different from the other keyword strings. It is used to communicate to the EA program which parameters are used and what their properties are. The keyword string parameter has the structure:

\begin{equation}
\text{parameter} = n\# \text{name start [lower] [upper]} \tag{A.2}
\end{equation}

Here, \textit{n} is the number of the parameter as used in the EA, \textit{name} are user friendly name to facilitate the recognition of the parameter in the output, \textit{start} defines the start value of the parameter, \textit{lower} and \textit{upper} represent the respectively the lower and upper limits of the parameter in the EA evaluation.

- All lines with the keyword string parameter should be put together in the input file as a single block

- The entries behind the ”=” sign should be separated by at least one blank; a TAB may also be used as separator. The \textit{name}-field main contain no blanks or TABs.
• The minimum input on a line with a keyword parameter is n, name and start. The start-values are used (i) to simulate the spectrum if no EA-fit is done, (ii) as start values before the EA-procedure starts and (iii) for those parameters that are held fixed during the EA-calculation.

• Parameters for which no lines is present in the input are set to zero in the EA, are no fit and are not shown in the output lists.

• The numbering n should be incremental, except to indicate more spectra.

• It is possible to have more spectra calculated in the same frequency interval with different parameter values and ranges, even calculated from different Hamiltonians. In order to indicate this, the program assumes that if during the reading of the parameter list a number n is found smaller or equal to the last read one, the following parameters to be read are from a next spectrum. This is indicated as a different sets.

A.1 Running the Program

The calculations are performed under a unix or linux operating system. To speed up the computing time, the program allows parallel processing with very high efficiency; so the use of cluster machines looks the ideal solution. As mentioned previously the cluster located in Nijmegen consists of a number of Sun Fire X4100 machines with 2 Opteron 280 (2.4 GHz, dual-core) processors, two 73 GB SAS disks and 4 or 8 GB of memory and a number of Sun Fire X4150 machines with 2 Intel Xenon
<table>
<thead>
<tr>
<th>Number</th>
<th>Suggested name</th>
<th>Description of the parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$A''$</td>
<td>A-RC ground state (in MHz/cm$^{-1}$)</td>
</tr>
<tr>
<td>2</td>
<td>$B''$</td>
<td>B-RC (in MHz/cm$^{-1}$)</td>
</tr>
<tr>
<td>3</td>
<td>$C''$</td>
<td>C-RC ground state (in MHz/cm$^{-1}$)</td>
</tr>
<tr>
<td>4</td>
<td>$D''$</td>
<td>D constant ground state (in MHz/cm$^{-1}$)</td>
</tr>
<tr>
<td>5</td>
<td>$\epsilon_{aa}''$</td>
<td>$\epsilon_{aa}$ SRC ground state (in MHz/cm$^{-1}$)</td>
</tr>
<tr>
<td>6</td>
<td>$\epsilon_{bb}''$</td>
<td>$\epsilon_{bb}$ SRC ground state (in MHz/cm$^{-1}$)</td>
</tr>
<tr>
<td>7</td>
<td>$\epsilon_{cc}''$</td>
<td>$\epsilon_{cc}$ SRC ground state (in MHz/cm$^{-1}$)</td>
</tr>
<tr>
<td>8</td>
<td>$1/2 \epsilon_{(ab+ba)}''$</td>
<td>$1/2 \epsilon_{(ab+ba)}$ SRC ground state (in MHz/cm$^{-1}$)</td>
</tr>
<tr>
<td>9</td>
<td>$F_{A_1}''$</td>
<td>$F_{A_1}$ TC ground state (in MHz/cm$^{-1}$)</td>
</tr>
<tr>
<td>10</td>
<td>$F_{A_2}''$</td>
<td>$F_{A_2}$ TC ground state (in MHz/cm$^{-1}$)</td>
</tr>
<tr>
<td>11</td>
<td>$\rho''$</td>
<td>$\rho$ angle ground state (dimensionless)</td>
</tr>
<tr>
<td>12-81</td>
<td></td>
<td>Free</td>
</tr>
<tr>
<td>82</td>
<td>$\phi$</td>
<td>Polar angle $\phi$ (in degrees) of TM</td>
</tr>
<tr>
<td>83</td>
<td>$\theta$</td>
<td>Azimuthal angle $\theta$ (in degrees) TM</td>
</tr>
<tr>
<td>85</td>
<td>Weight E/A</td>
<td>Ratio E and A-levels for 3-fold internal rotation</td>
</tr>
<tr>
<td>86-89</td>
<td></td>
<td>Reserved</td>
</tr>
<tr>
<td>90</td>
<td>$T_1$</td>
<td>Temperature $T_1$ (in K)</td>
</tr>
<tr>
<td>95</td>
<td>$\Delta_{Lorentzian}$</td>
<td>Lorentz contribution, FWHM (in MHz/cm$^{-1}$)</td>
</tr>
<tr>
<td>96</td>
<td>$\Delta_{Gaussian}$</td>
<td>Gauss contribution, FWHM (in MHz/cm$^{-1}$)</td>
</tr>
<tr>
<td>100</td>
<td>$\nu_0$</td>
<td>Frequency of $\nu_0$ (in MHz/cm$^{-1}$)</td>
</tr>
<tr>
<td>101</td>
<td>$A'$</td>
<td>A-RC excited state (in MHz/cm$^{-1}$)</td>
</tr>
<tr>
<td>102</td>
<td>$B'$</td>
<td>B-RC excited state (in MHz/cm$^{-1}$)</td>
</tr>
<tr>
<td>103</td>
<td>$C'$</td>
<td>C-RC excited state (in MHz/cm$^{-1}$)</td>
</tr>
<tr>
<td>104</td>
<td>$D'$</td>
<td>D constant excited state (in MHz/cm$^{-1}$)</td>
</tr>
<tr>
<td>105</td>
<td>$\epsilon_{aa}'$</td>
<td>$\epsilon_{aa}$ SRC excited state (in MHz/cm$^{-1}$)</td>
</tr>
<tr>
<td>106</td>
<td>$\epsilon_{bb}'$</td>
<td>$\epsilon_{bb}$ SRC excited state (in MHz/cm$^{-1}$)</td>
</tr>
<tr>
<td>107</td>
<td>$\epsilon_{cc}'$</td>
<td>$\epsilon_{cc}$ SRC excited state (in MHz/cm$^{-1}$)</td>
</tr>
<tr>
<td>108</td>
<td>$1/2 \epsilon_{(ab+ba)}'$</td>
<td>$1/2 \epsilon_{(ab+ba)}$ SRC excited state (in MHz/cm$^{-1}$)</td>
</tr>
<tr>
<td>109</td>
<td>$F_{A_1}'$</td>
<td>$F_{A_1}$ TC excited state (in MHz/cm$^{-1}$)</td>
</tr>
<tr>
<td>110</td>
<td>$F_{A_2}'$</td>
<td>$F_{A_2}$ tTC excited state (in MHz/cm$^{-1}$)</td>
</tr>
<tr>
<td>111</td>
<td>$\rho'$</td>
<td>$\rho$ angle excited state (dimensionless)</td>
</tr>
<tr>
<td>112-199</td>
<td></td>
<td>Free</td>
</tr>
<tr>
<td>200</td>
<td>Hamiltonian</td>
<td>Reserved to define the type of Hamiltonian</td>
</tr>
</tbody>
</table>

Table A.1: List of parameters of $^2\Sigma\leftarrow^2\Sigma$ rotational spectra used by the EA. For technical reasons, RC denotes Rotational Constants, SRC Spin-Rotation Constants, TC Torsional Constants and TM Transition Moment. The Hamiltonian value is set to be 9 in order to use an asymmetric rotor with spin-rotation model and 10 in order to use an asymmetric rotor with spin-rotation and torsion.
(2.83 GHz, quad-core) processors, four 146 GB SAS disks and 12 GB of memory. They are all running under Feudora9 linux. The cluster can be used by logging on cn16.science.ru.nl but required an IP adress corresponding to the Nijmegen University. Hence a VPN connection through vpn-srv.science.ru.nl is required. For the EA-calculation a total of 48 processors (nodes) is available. If proper environmental parameters are set, the command to start a fit is:

\[ ga - run [-n N[-w H[-b [-h]]]] project.ini \] (A.3)

The file `project.ini` controls the EA-calculation and contains the appropriate keywordstrings as defined in Sect. 3.1.2. Here \( N \) is the number of nodes to be used and \( H \) the maximum of wall clock hours claimed be the program. The default value for \( N \) depends of the cluster system on which the program is started and it is determined by `ga - run`.

A typical example of a project.ini file is:

```
# Settings file for spectrum fitting using a GA.
# Part 1. Spectrum and properties
comment=Doublet sigma spectra CD3O2
experimental spectrum=spectra/CD3O2lin.dat
type of spectrum=abc

# lineshape G(auss) L(orentz) V(oigt)
lineshape=Gauss

# spectrum_assignments 1 - printing out of list of frequencies from the average resulting parameters
```
# 0 - Not

# spectrum assignments=1
# spectrum assignments Kisiel=1
# spectrum assignments Picket=1
maximum J value=15
create Full spectrum file=1
create Ini file=1
create Exel file=1

# output Costfunction values=1
output for assignFit=1
units in cm-1=1
minimum intensity line=0.001

# Part 2. Definition and "start" values of the parameters
# parameterset 1

parameter= 1 A"  1.2932  1.27  1.31
parameter= 2 B"  0.32079  0.30  0.34
parameter= 3 C"  0.28546  0.26  0.30
parameter= 4 D"  0.
parameter= 5 Eaa"  -0.0718  -0.1  0.0
parameter= 6 Ebb"  -0.0091  -0.1  0.0
parameter= 7 Ecc"  -0.0003  -0.1  0.0
parameter= 8 (Eab+Eba)/2"  0.0138  0.0  0.1
parameter= 9 Fa1"  0.
parameter= 10 Fa2"  0.
parameter= 11 rho"  0.
#parameter= 82 Phi    66  40  90
#parameter= 83 Theta  59  40  90
parameter= 90 T1     14.  10.  20.
#parameter= 95 DeltaLorentz  0.032
parameter= 96 DeltaGauss  0.016
parameter= 98 Scaling  200.
parameter= 100 Nu_0  7373.27  7370.  7376.
parameter= 101 A'     1.1781  1.15  1.19
parameter= 102 B'     0.32707  0.30  0.34
parameter= 103 C'     0.28387  0.26  0.30
parameter= 104 D'     0.
parameter= 105 Eaa'   0.0695  0.  0.1
parameter= 106 Ebb'   0.0107  0.  0.1
parameter= 107 Ecc'   -0.0029  -0.1  0.0
parameter= 108 (Eab+Eba)/2'  0.0218  0.  0.1
parameter= 109 Fa1'   0.
parameter= 110 Fa2'   0.
parameter= 111 rho'   0.
parameter= 200 Hamiltonian 9

163
# Part 2. GA requirements.

random seeds=567

number of generations=300

population size=200

#derandomized DR2 algorithm=1

CMA-ES algorithm=1

#Number of parents=1

create CMA-ES output=0

# Part 3. Optimisation details.

# Test calculation = 1: Performs just one call to find the
# value of the evaluation function for the input parameters
# = 0: Normal genetic algorithm calculation

test calculation=0

full width overlap function=0

logfile=logs/CD3O2

A.2 Stopping the Program

To stop a running EA-job and still creating the normal output files, the following command can be given from the directory where the EA-job has started:

\[ ga \text{ -- stopEA -- dateANDtime } \] (A.4)
Here, *dateANDtime* is the date and time stamp of the running EA-job. One can find the latter extensions to *ga − stopEA* by looking to the *logfile name* extension. Usually it will be enough to check the startup directory of the EA-job. In this directory the file *ga − stopEA − dateANDtime* can be found. Additionally, during run time a file is created from its name indicates the progress of the EA calculation: *CurrentRunningXX − ng − dateANDtime*. Here *ng* is the number of the currently calculated generation and *dateANDtime* is defined above. The string *XX* stands for *GA*, *DR2* or *CMA − ES* for a genetic algorithm, a derandomized DR2 or a Covariance Matrix Adaptation Evolution Strategy fit, respectively.

### A.3 Output Generated by the Program

The default output by the program are a number of files showing the progress of the algorithm and the final result. The file names are constructed form the *basename* defines by the *keyword string logfile* followed by a unique identification based on the date and time of the start of the program. This defines the *rootname*. Using this *rootname* several file names are constructed to distinguish the various outputs:

- Test output: *rootmane − T − txt*. The output file is only a testrun has to be carried out. *keyword string*: *test calculation = 1*

- Normal output: *rootname − n − .txt*. The normal output file for the *nth-seed*.  
  *keyword string*: *test calculation = 0 and one or more seed values*:  
  *random seeds = i j k*

- Summarizing text file: *rootname − final − .txt*. 

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• Summarizing Excel type file: rootname − final − .csv.

• New input file based on the final parameter values:

  rootname − n − .ini for the nth seed.

• An output file in the form of a (3 + nset+[1/2/3/4])-column ASCII array with the frequency in the first column, the intensities of the calculated and experimental spectra in the second and third column, while the next nset-columns contains the sole spectrum of the i-th parameter set.

  The file name is: rootname − full_output_spectrum.answ. This file is created if keyword string: create Full spectrum file = 1.
APPENDIX B

Running the Gaussian03 Software Package

All calculations were performed on the Glenn Cluster at the Ohio Supercomputer Center. In order to access the cluster, a SSH connection has to be established between the user computer and the cluster using the following command:

\[
\text{ssh username}@opt \ - \ login01.osc.edu
\]  \hspace{1cm} (B.1)

The cluster hardware configuration consists of the following (http://www.osc.edu/supercomputing/hardware/):

- 877 System x3455 compute nodes
  
  Dual socket, dual core 2.6 GHz Opterons
  
  8 GB RAM
  
  48 GB local disk space in /tmp

- 650 System x3455 compute nodes
  
  Dual socket, dual code 2.5 GHz Opterons
  
  24 GB RAM
  
  393 GB local disk space in /tmp
• 88 System x3755 compute nodes
  Quad socket, dual core 2.6 GHz Opterons
  64 GB (2 nodes), 32 GB (16 nodes), or 16 (70 nodes) RAM
  1.8 TB (10 nodes) or 218 GB (76 nodes) local disk space in /tmp

• 10 System 3755 compute nodes
  Quad socket, quad core 2.4 GHz Opterons
  64 GB RAM
  188 GB local disk space in /tmp

• 1 e Blade Center
  4 Dual Cell based QS20 blades
  Voltaire 10 Gbps PCI Express adapter

• 4 System x3755 login nodes
  Quad socket 2 dual core 2.6 GHz Opterons
  8 GB RAM

• all connected together by 10 Gbps or 20 Gbps Infiniband

In order to be able to start a Gaussian03 job on this kind of cluster, a specific input file has to be made. This file need to contain several information such as the requested Wall time, the number of nodes/CPU requested as well as the invocation of
the program requested (here Gaussian03). The editing of the input file can be done using the \textit{nano} command:

\begin{center}
\texttt{nano filename.inp}
\end{center}

\textbf{B.1 The Gaussian Input}

A typical input file can be found below:

\begin{verbatim}
# walltime=100:00:00
#PBS -l nodes=1:ppn=8
#PBS -N phenyl
#PBS -S /bin/ksh
#PBS -joe
#PBS -o /home/username/output.log

cd TMPDIR

moduleload g03

JOB = phenyl

g03 < EOF
\end{verbatim}
The first 6 lines, which all start with # are treated by the interpreter as comments.

The lines that begins #PBS -l (lowercase "L") defines the resources that your job is requesting (here the requested time in line 1 and the number of nodes/CPU in line 2).

The next line that begins #PBS -N defines the name applied to the job

The next line that begins with #PBS -S defines the language and the interpreter used to interpret the job script

#PBS -o describes where the output file of a given job has to be saved and its name and extension
• module load g03 request the use of the Gaussian03 software package

• JOB=phenyl defines the name of the check file for a Gaussian job

• g03 < EOF tells the software that the input files ends with EOF (End Of File)

Now, the user is ready to create the input of his choice in order to perform electronic structure calculation using the Gaussian 03 software package.

It has to be kept in mind that consistency between labeling of input/check/output files is a necessity in order to be able to perform such calculations.

To calculate optimized geometry for a given species, some informations have to be kept in mind. All calculations for the ground electronic state $\tilde{X}$ can be performed with the keyword opt in order to optimize the geometry and all subsequent calculation to the first one (that contains the $z$-matrix) can use the keyword geom = check in order to use the optimized geometry of the previous calculation as a starting point.

To calculate the optimized geometry of a given species for the excited state (here the first excited electronic state $\tilde{A}$), some ”tips” need to be implemented in the input of the calculation in order to force the software to converge to the excited state and not back to the ground state.

• When all the ground state calculations are performed, the user can use the optimized geometry of the last ground state calculation as a starting point for the excited state calculations using the keyword geom = check.

• In order to calculate optimized geometry for the excited state, the following procedure needs to be used:
The first calculation has to be a \# opt rohf/6−31+g(d) with the keyword geom=check and guess=alter the last keyword guess = alter indicates that 2 molecular orbitals (specified by the user) have to be switch (typically for peroxyl radical the last 2)

The a \# opt uhf/6 − 31 + g(d) geom = check guess = check calculation has to be performed, guess = check specify the program to keep the electronic structure of the previous calculation and has to be carried for all the subsequent excited state calculations

Finally, a \# opt B3LYP/6 − 31 + g(d) geom = check guess = check calculation has to be performed in order to assure the correct electronic state

- The user can then perform any method and basis set of his choice for the electronic state calculation

In order to start a job, the job file has to be named yourjobfile.inp and the command:

\[
qsub yourjobfile.inp
\]  

(B.3)

has to be executed. The status of a calculation can be obtained by executing the following command:

\[
qstat -u yourusername
\]  

(B.4)
Finally, if one desires to stop a running calculation, one can type the following command:

\[ qdel \text{ yourjobid} \]  \hspace{1cm} (B.5)

The job id is obtained using the previously described \textit{qstat} command.
Bibliography


