NEAR IR CAVITY RINGDOWN SPECTROSCOPY OF PEROXY RADICALS

DISSERTATION

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By

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* * * * *

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Abstract

A sensitive Cavity Ringdown Spectroscopy (CRDS) apparatus has been successfully developed to study reactive intermediates in the near IR region. Many interesting species can be observed in this chemical fingerprint spectral region. Peroxy radicals (RO₂), a class of important intermediates in atmospheric chemistry and low temperature combustion, have been investigated via IR $\tilde{A} - \tilde{X}$ electronic transition.

Moderate resolution (0.2 cm⁻¹) absorption spectra of the near IR electronic transition have been obtained for several members of the alkyl peroxy radical family: methyl (CH₃O₂), ethyl (C₂H₅O₂) and isopropyl (2-C₃H₇O₂) peroxy. CRDS spectra of the acetyl peroxy radical (CH₃C(O)O₂), a key irritant in smog, has been investigated. A sharp, structured electronic spectrum of $\tilde{A} - \tilde{X}$ electronic transition for the fluorinated methyl peroxy (CF₃O₂) radical has been observed. Extensive ab initio calculations have been carried out to help assign spectral carrier, predict and analyze observed spectroscopic features such as rotational contours, vibrational hot bands and frequencies for the $\tilde{A}$ state fundamental vibrations. Structured spectral signatures of the transition contain information sufficient to distinguish the detailed nature of the R group, even when they are quite similar, providing an opportunity to easily identify different peroxy radicals and develop species specific diagnostics.
The absorption cross sections for several peroxy radicals has been determined using CRDS observations and radical recombination kinetic measurements.
To: My father, Joseph Zalyubovsky
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CHAPTER 1

Introduction

Peroxy radicals, RO₂, form a class of important intermediates in the homogeneous oxidation of hydrocarbons. Peroxies have been claimed to play an absolutely key role in atmospheric chemistry¹ and also to be the most important reactive intermediates in low temperature combustion.¹⁰

The role of peroxy radicals in the atmospheric chemistry is well studied and a schematic diagram of the atmospheric hydrocarbon oxidation¹ is shown in Fig. 1.1. Oxidation of hydrocarbons in the atmosphere is initiated primarily by hydroxyl radical, OH, which reacts by hydrogen abstraction forming a hydrocarbon radical:

\[ RH + OH \rightarrow R + H₂O \] \hspace{1cm} (1.1)

In the presence of atmospheric oxygen peroxy radicals are formed from the radical R produced in the initiation step:

\[ R + O₂ + M \rightarrow RO₂ + M \] \hspace{1cm} (1.2)
Figure 1.1: Schematic diagram of atmospheric hydrocarbon oxidation from Ref. 1
Peroxy radicals are involved in what is believed to be the most important cycle of tropospheric ozone production:\textsuperscript{11}

\begin{equation}
NO_2 + h\nu (\lambda < 430 \text{nm}) \rightarrow NO + O(^3P) \tag{1.3}
\end{equation}

\begin{equation}
O(^3P) + O_2 + M \rightarrow O_3 + M \tag{1.4}
\end{equation}

\begin{equation}
O_3 + NO \rightarrow NO_2 + O_2 \tag{1.5}
\end{equation}

\begin{equation}
RO_2 + NO \rightarrow RO + NO_2 \tag{1.6}
\end{equation}

In the absence of peroxy radicals the net reaction of the cycle (1.3)-(1.5) is zero. NO is oxidized to NO\textsubscript{2} by ozone via reaction (1.5) and both ozone and nitric oxide will be present in small equilibrium concentrations. Under steady state approximation for the [O] and [NO], the ozone equilibrium concentration is given by Leighton\textsuperscript{12} photostationary state relationship:

\begin{equation}
[O_3] = \frac{F_{NO_2} \cdot [NO_2]}{k_{1,5} \cdot [NO]} \tag{1.7}
\end{equation}

where $F_{NO_2}$ is NO\textsubscript{2} atmospheric photolysis rate. However in the presence of peroxy radicals, NO can be converted to NO\textsubscript{2} via reaction (1.6). Under atmospheric conditions $k_{1,5}=1.8\cdot10^{-14}$ cm\textsuperscript{3}s\textsuperscript{-1} and $k_{1,6}=(7-9)\cdot10^{-12}$ cm\textsuperscript{3}s\textsuperscript{-1} depending on the nature of the R group.\textsuperscript{1,13} Typical atmospheric concentrations of ozone and peroxy radicals are $7\cdot10^{11}$ cm\textsuperscript{-3} and $1\cdot10^{9}$ cm\textsuperscript{-3} respectively.\textsuperscript{14} Therefore branching ratio between channels (1.5) and (1.6) is 1:0.6 and channel (1.6) represents significant competition to the ozone destruction channel (1.5).
NO₂ and NO equilibrium is shifted towards NO₂ and, according to Eq. (1.7), ozone concentration is elevated. In the absence of the reaction (1.5) the net reaction of the above presented cycle can be written as:

\[ RO_2 + O_2 \rightarrow RO + O_3 \] (1.8)

Alkoxy radicals (RO) generated in reaction (1.6) can further react with molecular oxygen and form hydroperoxy radicals, HO₂ and carbonyl compound R’C=O. Similar to other peroxies, HO₂ will react with NO to produce OH radical:

\[ RO + O_2 \rightarrow R'C = O + HO_2 \] (1.9)
\[ HO_2 + NO \rightarrow NO_2 + OH \] (1.10)

This mechanism of OH regeneration is shown on Fig. 1.1 and represents a major propagation step in the tropospheric ozone formation. Overall it is estimated that the atmospheric chemistry of peroxy radicals is responsible for ca. 90% of the ozone present in the troposphere.

Peroxy cross reactions with hydroperoxy can result in formation of peroxides and may lead to the acid rain deposition, another important form of atmospheric pollution:

\[ RO_2 + HO_2 \rightarrow ROOH + O_2 \] (1.11)
\[ H_2O + SO_2 \rightarrow H^+ + HSO_3^- \] (1.12)
\[ HSO_3^- + ROOH \rightarrow HSO_4^- + ROH \] (1.13)
\[ HSO_4^- + H^+ \rightarrow H_2SO_4 \] (1.14)

Oxidation of various volatile, oxygen containing organic compounds (R’CHO on Fig. 1.1) may result in formation of the acetyl peroxy radical, R’C(O)O₂, a very important
member of peroxy radical family for atmospheric pollution. Acetyl peroxy radical reacts with NO$_2$ and forms thermally stable peroxy acetyl nitrates (PAN), an important component in photochemical smog:

$$RC(O)O_2 + NO_2 + M \rightarrow RC(O)O_2NO_2 + M$$ (1.15)

PAN’s are lachrymators and mutagens and the nitrates can be produced from, and serve as reservoirs, for the corresponding peroxy radical. Reaction (1.15) along with reaction (1.6) provides a linkage between RO$_x$ and NO$_x$ cycles.

In the stratosphere peroxy radicals, predominantly, but not exclusively hydroperoxy, can be involved in catalytic chain reactions leading to ozone destruction:

$$RO_2 + O \rightarrow RO + O_2$$ (1.16)

$$RO + O_3 \rightarrow RO_2 + O_2$$ (1.17)

$$O + O_3 \rightarrow O_2 + O_2$$ (1.18)

with net reaction (1.18). Recently considerable interest has been generated towards CF$_3$O$_x$ radicals that can react with stratospheric ozone directly:\textsuperscript{17–20}

$$CF_3O_2 + O_3 \rightarrow CF_3O + 2O_2$$ (1.19)

$$CF_3O + O_3 \rightarrow CF_3O_2 + O_2$$ (1.20)

$$2O_3 \rightarrow 3O_2$$ (1.21)

These cycles are especially important for stratospheric ozone balance when the RO radical in the chain is substituted with Cl or F atom. Investigation of the stratospheric sources of Cl or F atoms brings a very important issue of atmospheric fate
of hydrofluorocarbons (HFC) and chlorofluorocarbons (CFC) and their role in
the stratospheric ozone destruction.\textsuperscript{17,19} Upon photolysis or oxidation of HFC’s or
CFC’s the resulting fragments will form peroxy radicals with a fluorinated, or chlo-
rinated, R group. Therefore, understanding spectroscopy and kinetics of fluorinated
and chlorinated peroxy radicals is a very important topic.

Analogous to the homogeneous oxidation described above, heterogeneous pro-
cesses may occur on organic aerosols. Collisions of hydroxy radicals with particulate
matter coated with hydrocarbon film may result in H atom abstraction.\textsuperscript{21} Subse-
quent collisions with O\textsubscript{2} may lead to formation of surface bound peroxy radicals. The
kinetics and mechanisms of these heterogeneous reactions will determine influence of
peroxy radicals on atmospheric chemistry.

In addition to their crucial role in the atmospheric chemistry, peroxy radicals are
essential intermediates in the low temperature combustion of hydrocarbons. Schematic
diagram of hydrocarbon oxidation mechanism for the temperatures below 1000K is
shown on Fig. 1.2.\textsuperscript{22} Arguably the most important reaction\textsuperscript{23} for low temperature
oxidation is the production of peroxy radicals (RO\textsubscript{2}) from alkyl radicals (R).

Probably the most intriguing stage in the depicted combustion mechanism is the
peroxy isomerization reaction via internal hydrogen abstraction and formation of a
new radical denoted as \textbullet\textsuperscript{O\textsubscript{2}}QOOH. This isomerization reaction controls both propa-
gation and branching steps. Rearrangement of \textbullet\textsuperscript{O\textsubscript{2}}QOOH produces ROOH, a non-
radical hydroperoxide. Thermal decomposition of latter species can produce two
reactive intermediates RO and OH which results in a runaway radical multiplication.
Therefore, in favorable conditions, peroxy isomerization can lead to the autoignition and engine knock which is critical to the efficiency and fuel economy of internal combustion engines.\textsuperscript{23–25}

Because of the significance of the peroxy radicals, much effort\textsuperscript{1} has been expended studying the mechanisms and kinetics of peroxy radical production and subsequent reactions. This work has largely been based upon monitoring radical concentration via the UV absorption on their $\tilde{B}^2A'' - \tilde{X}^2A''$ transition.\textsuperscript{26} This is a strong transition, common to all the peroxies, that is centered around 240 nm. Unfortunately, this transition is broad and unstructured with a half-width of $\approx 40$nm. The quasi-continuum nature of this transition has at least two clear disadvantages. Firstly, it is unsuitable for obtaining rotational or vibrational information about the radical.
Secondly, overlapping of the UV spectra of different RO₂ radicals makes the identification of a specific alkyl peroxy radical, particularly from a mixture, a significant problem. Then it is difficult to determine the contribution of different peroxy radicals to a given reaction and measure their individual reaction rate.

The infrared \( \tilde{A}^2 A' - \tilde{X}^2 A'' \) transition has been identified as an ideal candidate to overcome these aforementioned difficulties. However, experiments involving the peroxy \( \tilde{A}^2 A' - \tilde{X}^2 A'' \) transition in the IR are sparse. There was an early report, using low resolution modulated absorption spectroscopy, of the observation of the \( \tilde{A} - \tilde{X} \) IR transition of several RO₂ radicals and more recently a report of the observation of fragmentary spectra of ethyl peroxy radical (C₂H₅O₂) using a cw absorption technique. There was also a report of the detection of the \( \tilde{A} - \tilde{X} \) transition of CH₃O₂ by intra-cavity laser absorption spectroscopy, but few spectroscopic details were given.

Based upon the recent observation and analysis of a well resolved spectrum of the hydroperoxy radical, HO₂, it is expected that the \( \tilde{A} - \tilde{X} \) IR transitions of the alkyl peroxy radicals will be well structured and observable with sensitive spectroscopic technique. Historically this IR transition has been viewed as difficult to study because of its small oscillator strength (the cross-section \( \sigma \) is \( \approx 2 \cdot 10^{-21} \text{cm}^2 \) for the corresponding transition in HO₂) and the near IR spectral region (5000-8000 cm⁻¹) in which the transition is located.

Taking into account the significance and importance of peroxy radicals, a sensitive spectroscopic technique to investigate peroxy radicals via their \( \tilde{A}^2 A' - \tilde{X}^2 A'' \) infrared electronic transition have been developed. Cavity ringdown spectroscopy (CRDS), a
powerful tool for spectroscopic observations of weakly absorbing transient species,\textsuperscript{32–34} was chosen as a probing technique. The expected sharp IR transitions should yield resolved vibrational and rotational structure to characterize the peroxy radicals. Additionally, the $\tilde{A}^2A'$ - $\tilde{X}^2A''$ spectra should easily distinguish between different RO\textsubscript{2} radicals even in a mixture. Finally the transient nature of CRDS experiments are readily adaptable for rapidly monitoring RO\textsubscript{2} concentrations and measuring the reaction kinetics of the radicals.

Both development of IR cavity ringdown spectrometer and spectroscopic observations and analysis of $\tilde{A}^2A'$ - $\tilde{X}^2A''$ electronic transition of various peroxy radicals constitute the scope of this dissertation. Alkyl peroxy radicals, fluorinated methyl peroxy radical and acetyl peroxy radical have been investigated.

Peroxy radical pervasive roles in both nature and technology and hence motivation for the study are outlined in the current chapter. The principles of the cavity ringdown technique and detailed description of the experimental apparatus are presented in Chapter II. General methods of \textit{in situ} production of peroxy radicals and sensitivity limits of the build CRDS apparatus are discussed.

Peroxy radicals spectroscopic background and nature of the excited electronic states are presented in Chapter III. Various \textit{ab initio} calculations have been carried out for the $\tilde{A}$ and $\tilde{X}$ states of the peroxy radicals. Several different computational methods have been used to accurately predict frequency of the $\tilde{A}$ - $\tilde{X}$ transition, rotational constants and vibrational frequencies for the $\tilde{A}$ and $\tilde{X}$ states. The results of these \textit{ab initio} calculations are also present in Chapter III. Following three
chapters provide specific details on production, detection and analysis of observed spectroscopic features for each investigated peroxy radical.

CRDS spectra for the methyl (CH$_3$O$_2$) and ethyl (C$_2$H$_5$O$_2$) and isopropyl (2-C$_3$H$_7$O$_2$) peroxy radicals and are presented in Chapter IV. These results demonstrate the ability of CRDS to sensitively detect the $\tilde{A}^2A'$ - $\tilde{X}^2A''$ IR transition, and the spectra show the expected sharp and resolvable vibrational and rotational structure. Analysis of the rotational structure of CH$_3$O$_2$ and CD$_3$O$_2$ provides improved rotational constants compared to those available from high level \textit{ab initio} calculations. Finally the easy adaptability of CRDS technique to the measurement of the reaction kinetics of RO$_2$ radicals it demonstrated.

Chapter V presents the first observation of the sharp, structured spectra of $\tilde{A}^2A'$ - $\tilde{X}^2A''$ transition of the fluorinated methyl peroxy radical (CF$_3$O$_2$). The frequency of the electronic origin for the transition and a couple of vibrational frequencies in the $\tilde{A}$ state are deduced. In addition, the recombination kinetics of CF$_3$O$_2$ has been studied using CRDS as a monitor of its concentration, and estimated absorption cross section for the CF$_3$O$_2$ $\tilde{A}^2A'$ - $\tilde{X}^2A''$ transition.

In Chapter VI observations and analysis of $\tilde{A}^2A'$ - $\tilde{X}^2A''$ transition of acetyl peroxy (CH$_3$C(O)O$_2$) radical and its per-deutero analogue are presented and the issue of conformational identity of the observed spectra is extensively investigated.
CHAPTER 2

Experimental

2.1 IR Cavity Ringdown Absorption Spectrometer

2.1.1 Introduction

Spectroscopy of transient species in the near IR region (3000-10000 cm$^{-1}$) has been a relatively unexplored area due to the absence of efficient, wide range tunable radiation sources and high sensitivity absorption techniques in the near IR region.

Several spectroscopic techniques are routinely used in the IR region, but have their specific reservations and limitations. Sensitivity and tunability of direct absorption methods are limited by availability of the sources of IR radiation, their power and combination of their tunability and the frequency range. As an example, generation of IR light by difference frequency mixing has low power output ($\sim$1 mW) and a 2000 cm$^{-1}$ red cut-off due to the lack of optical transmittance in non-linear crystals. Cryogenically cooled lead salt lasers and color center lasers are extensively used for mid-IR spectroscopic applications with low (1-5 mW) output power being the major drawback. High power ($\sim$100 mW) quantum cascade lasers are still in the development stage, but some prototypes have been successfully used in the spectroscopic applications.\textsuperscript{35} Frequency modulation diode laser techniques possess the required sensitivity,
but are rather complex and have low tunability. Fourier transform IR spectroscopy has relatively low sensitivity and resolution, although it was shown\textsuperscript{36} that it can be coupled to the production of transient species and used as a survey method to provide positions of spectroscopic features for future exploration with sensitive high resolution techniques.

Development of the cavity-ringdown laser absorption spectroscopy (CRDS) technique has opened new horizons for the absorption-based spectroscopic studies in the near IR. The basic idea of measuring the lifetime of a laser pulse trapped within high finesse cavity was first used in mirror reflectivity measurements for military applications (so called ”mirror reflectometers”).\textsuperscript{37,38} In 1988 O’Keefe and Deacon implemented this method to observe weak $b^1\Sigma_g^+ - X^3\Sigma_g^+$ transition in molecular oxygen,\textsuperscript{39} thus demonstrating its spectroscopic applicability and sensitivity.

Since its advent CRDS has been executed in many experimental arrangements and instrumental versions. It has been applied to study various molecular systems in various spectral regions. It has been used for trace gas analysis and probing transparent solid samples,\textsuperscript{40,41} overtone spectroscopy\textsuperscript{42} and cluster studies,\textsuperscript{43} experiments in molecular beams and supersonic jet expansions.\textsuperscript{44,45} CRDS has been applied to probe flames and discharges,\textsuperscript{46–49} investigate molecular dynamics and chemical kinetics.\textsuperscript{50–53}

Though application of CRDS technique has no fundamental limitations to the specific spectral region, the vast majority of CRDS experiments have been done in the visible and near UV region primarily due to availability of convenient tunable sources of laser radiation, high reflective mirrors in this spectral region and fast time-response
detectors. Versatility of CRDS technique has been demonstrated in various experiments combining it with various light sources and complementing it with different spectroscopic methods. It has been coupled with CW and free electron lasers. CRDS has been used with Fourier transform spectroscopy and heterodyne detection. Polarization dependents cavity ringdown experiments and setups based on total internal reflection cavities have been realized.

Recent advances in dielectric coating technology extended range of high reflective ringdown mirrors towards IR and currently 99.99% reflectivity mirrors with center frequency as low as 1000 cm$^{-1}$ can be manufactured. As a demonstration the 10-11 µm vibrational band of ethylene has been detected using free electron laser. Flames in the 1.6 µm and the 3.3 µm region, water clusters in 3.0 µm region and carbon clusters in 5.0 µm region have been explored, but still IR CRDS of transient species are relatively sparse.

Hence only a brief summary of CRDS applications is presented here, additional information on CRDS history and applications can be found in several excellent extensive reviews published recently.

2.1.2 IR Light Sources

To build a spectroscopic apparatus capable of studying transient species in the near IR region one needs to carefully select tunable radiation source that can be efficiently coupled with production of transient species. Operational range of a conventional dye laser is restricted to ~970nm in the red which leaves several limited options for the IR laser sources. Semiconductor lasers and a few other solid state lasers cover
some relatively narrow ranges but necessary requirement to cover the complete spectrum or search desired frequency range might not be always satisfied. In recent years progress in nonlinear technology brought the types of radiation sources in the near IR such as optical parametric oscillator (OPO) and difference frequency mixing (DFM) technique. Narrow bandwidth OPOs are an attractive but rather costly alternative which demands extensive expertise from operating personal. For DFM light generation expensive nonlinear crystals are necessary. Difference frequency mixing also requires injection seeding to produce narrow bandwidth light and wavelength tracking and separation schemes. In using both OPO and DFM care in alignment should be taken to avoid irreversible crystal surface damage. Frequencies around 2.85 µm are not accessible with efficient non linear crystals due to absorption of water molecules embedded into crystal. An elegant and very general solution to aforementioned limitations is down-shifting via stimulated Raman scattering (SRS) in high density gases.

IR Stokes light can be produced by focusing a laser beam into a pressurized vessel filled with a Raman active medium. With pump frequency $\omega_p$ (in cm$^{-1}$), the frequency of the first Stokes component is expressed as $\omega_{1S}=\omega_p-\omega_v$, where $\omega_v$ is the frequency of the Raman active fundamental vibration of the molecules present in the cell. To achieve maximum frequency down-conversion, the H$_2$ molecule is typically used. Being the lightest, H$_2$ molecule has the largest vibrational fundamental frequency equal to$^6$ 4155.24(0.02) cm$^{-1}$. Higher order Stokes ($2^{nd}$ or $3^{rd}$) can be used to obtain radiation further in the infrared. With sufficient energy pumped into 1$^{st}$ Stokes, it can act as a pump for the second Stokes with the frequency $\omega_{2S}=\omega_p-2\cdot\omega_v$. 
Another approach is to combine two Raman cells sequentially and use 1st Stokes from the first cell to drive 1st Stokes in the second cell. In this method Raman cells can be filled with different media to extend or fill the gaps in the spectral coverage.

The efficiency of SRS process has been subject to numerous experimental and theoretical studies. It depends on various factors such as pump laser power and frequency, pressure and composition of the gas used in the Raman cell and pump laser focusing conditions. Typical power conversion efficiency of 5-15% is reported for the 1st Stokes generation using single pass Raman cell. It was also demonstrated that generation of the SRS light exhibits threshold behavior with respect to the pressure in the shifter and the input laser: Stokes generation starts when pump laser power and pressure in the shifter are above certain level. Multipass and capillary waveguide arrangements for the Raman cell have been used to increase Raman gain and, hence, reduce threshold constrains on the pump power and the pressure. For such systems conversion efficiencies of up to 27% and 12.5% have been observed for the 1st and 2nd Stokes respectively. It has been shown that 1-12 µm region can be continuously covered by generation of sequential Raman Stokes components. Upon increase of the laser power, generated 1st Stokes acts as pump for the 2nd Stokes etc. effectively shifting conversion maximum toward higher Stokes.

High density (1-30 atm) of the Raman medium is required for efficient Stokes generation due to small cross section of SRS process. Under such conditions several processes affect linewidth of the Raman shifted light. For H2 pressures below 2 atm the resulting Raman linewidth is determined by the Doppler broadening while
at densities above 5 atm it is dominated by the pressure broadening mechanism. Competition between Dicke narrowing and pressure broadening results in a minimum of 250 MHz Stokes linewidth\textsuperscript{72} for 2.5 atm pressure of H\textsubscript{2} at room temperature. In some experiments linewidths as narrow as 90 MHz has been reported\textsuperscript{69} in Dicke narrowing regime. For the Raman cell with pressures around 20 atm broadening contribution of \sim1000 MHz is expected\textsuperscript{72} to the pump linewidth. Therefore for high resolution applications high gain multipass Raman cells are used to reduce pressure to the narrowing regime while keeping sufficient conversion efficiency. For the pump laser linewidth of several tens of a wavenumber pressure broadening contribution to the downconverted light linewidth is insignificant.

2.1.3 Cavity Ringdown Theory
"Bouncing Pulses" Model

Cavity ringdown spectroscopy is based on the trapping a short laser pulse in the high finesse cavity formed by the two high reflectivity mirrors ($R >99.9\%$). Most of a short laser pulse injected into the cavity through the front mirror reflects back and forth between cavity mirrors for many round trips while a very small portion of the trapped photons is leaking through back cavity mirror on each round trip. Thus a train of decreasing intensity photon bunches, separated by cavity round trip time, will constitute the temporal profile of the radiation leaving the cavity. The photons "ring down" from the cavity. For a 1 meter length ringdown cavity round trip time $t_r$ is equal to:

$$t_r = \frac{2L}{c} = 6.6\text{ns}$$

(2.1)
Typical Nd:YAG pumped dye laser has a 6-10 ns pulse duration. With 10 MHz bandwidth detector (16 ns response time), individual photon bunches spaced by the cavity round trip time can not be resolved and the observed cavity decay is a convolution of individual laser pulses with detector response function.

If incident light has intensity $I'$ and the cavity is formed by two identical mirrors with reflectivity $R$ and transmission $T$, the first pulse will have an intensity $I_o = T^2 I'$. Diffraction losses and Rayleigh scattering are included in the mirror losses. After the first roundtrip the detected intensity, $I$, will be attenuated by $R^2$ and after $n$ round trips it will be given by: 

$$ I = I' T^2 R^{2n} = I_o R^{2n} = I_o exp\left(2n \ell n R\right)$$

(2.2)

Ringdown mirrors reflectivity $R$ is $\sim 99.99\%$ and $\ell n R = \ell n [1 - (1 - R)]$ can be approximated as $-(1 - R)$. Next term in the $\ell n$ expansion series will be $(1-R)^2/2 \sim 10^{-8}$ which is several orders of magnitude less than pulsed ringdown detection limit discussed later. With Eq. 2.1, number of round trips $n$ can be expressed as:

$$ n = \frac{t}{t_r} = \frac{tc}{2L}$$

(2.3)

where $c$ is the speed of light, $L$ is the length of the cavity and $t$ is a continuous time variable. Now substituting expansion of $\ell n R$ and Eq. 2.3 into Eq. 2.2 one can obtain:

$$ I = I_o exp\left(2n \ell n R\right)$$

(2.4)

$$ = I_o exp\left(-(1 - R)\frac{ct}{L}\right)$$

(2.5)

$$ = I_o exp\left(-\frac{t}{\tau}\right)$$

(2.6)
Time constant for the intensity decay $\tau$ is called a ringdown time and for the empty cavity is equal to:

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

where $(1-R)$ is a mirror absorption per pass. Since time dependence of the intensity envelope can be presented as a single exponential function, $\tau$ can be determined by a simple fitting procedure. Ringdown time $\tau$ is dependent on the mirror absorption $(1-R)$ and for the 1 meter ringdown cavity and 0.9999 mirror reflectivity the ringdown time will be equal to 34 $\mu$s. If the cavity contains a media with an absorption transition in resonance with the frequency of the light inside the cavity, an additional losses will be introduced to the cavity which will result in the shorter ringdown time. If absorber has a path length $l$ and concentration $N$ inside the cavity and transition peak absorption cross section $\sigma_p$, it will contribute $N\sigma_pl$ absorption to the overall cavity losses per pass. Therefore the ringdown time $\tau_{\text{abs}}$ in the presence of absorption will be given by:

$$\tau_{\text{abs}} = \frac{L}{c} \frac{1}{(1-R) + N\sigma_pl}$$  \hspace{1cm} (2.8)

and absorption spectrum of the media can be obtained by recording ringdown time $\tau_{\text{abs}}$ vs. laser frequency. It is more convenient to plot absorption per pass defined as $L/c\tau$. Combining Eq. 2.7 and Eq. 2.8, species peak absorption $S^p = N\sigma_pl$ can be expressed as:

$$S^p = N\sigma_pl = \frac{L}{c\tau_{\text{abs}}} - \frac{L}{c\tau_{\text{empty}}}$$  \hspace{1cm} (2.9)

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

The critical limitation to the above model of pulsed light propagation inside the optical cavity is various interference effects. For CW light the ringdown cavity will act as a Fabry-Perot etalon with discrete transmission on cavity modes. To avoid such an interference the injected pulse has to be short enough so the laser pulse is not overlapping with itself. This photon bouncing model is suitable when ∼15 ns laser pulses are used. In CW ringdown experiment interference effects are avoided by various methods of locking laser to a particular cavity mode and initiating intensity buildup in the ringdown cavity. The condition for such buildup is standing wave formation inside the cavity. Then the laser is turned off and photons stored in the single cavity mode are decaying from the cavity.\textsuperscript{54,74}

More complicated and more general approach in describing laser pulse propagation inside optical cavity is to consider cavity as an optical device with transmission response function in the frequency domain.\textsuperscript{75} For Fabry-Perot cavity this function is known as formula Airy and it is not dependent on input beam characteristics such as duration, bandwidth and central frequency. The time dependent output intensity decay can then be obtain by Fourier transformation of the squared product of the cavity response function and the spectrum of incident pulse.

In majority of CRDS experiments relatively low resolution lasers have beam employed. Conventional pulsed dye laser has a 0.2 cm\(^{-1}\) (6 GHz) linewidth. For the 1 meter cavity the spacing between two adjacent longitudinal cavity modes is equal to:

\[
\Delta \nu_t = \frac{c}{2L} = 150 MHz
\]  

(2.10)
Thus single laser pulse will excite up to 40 cavity modes. Each cavity mode can have slightly different time constant and each laser pulse can be coupled to a different combination of modes. Hence multi-exponential transient decay will be recorded as an output. In addition, coexistence of several modes inside the cavity may result in mode beating. It can lead to excessive noise or appearance of sinusoidal modulation on top of the exponential decay.\textsuperscript{73}

The resolution of the pulsed ringdown experiments is limited by the fact that probe laser pulse should cover at least one cavity mode as the laser is scanned in frequency. Otherwise no light will be transmitted if the laser frequency is not in resonance with cavity modes. For continuous coupling and transmission the linewidth of the laser should contain at least several cavity modes so the ring-down decay can be observed for all frequencies. The condition on the laser bandwidth is actually a different view of the short pulse requirement discussed earlier. When the separation between cavity modes is smaller then $\Delta \nu$ of the laser, the coherence length of the laser, defined as $c/\Delta \nu$, is smaller then the cavity length and interference effects can be neglected.

In addition to longitudinal modes various types of transverse modes can exist in the cavity. Being perpendicular to the propagation direction, these modes form a beam profile inside the cavity and the lowest order (TEM\textsubscript{00}) transverse mode has Gaussian shape determined by cavity geometry. For each longitudinal mode there are number of adjacent transverse modes. For the stable symmetrical resonator the separation between adjacent transverse modes is given by:\textsuperscript{75}

$$\Delta \nu_t = \frac{c}{2L} \cos^{-1}(\pm (1 - \frac{L}{r})) \pi$$ \hspace{1cm} (2.11)
where \( r \) is mirror radius of curvature and \( L \) is the cavity length. For the resonator with \( r=6\text{m} \) and \( L=1\text{m} \), \( \Delta \nu_t \) is equal to 28 MHz which is substantially smaller than \( \Delta \nu_l \). Therefore the frequency space between longitudinal modes will be filled with allowed transverse modes. It was demonstrated that quasi-continuous (longitudinal and transverse) cavity mode structure can be obtained by detuning cavity from initial confocal geometry. Hence higher resolution, pulsed CRDS experiments can be performed with a carefully design cavity that will ensure continuous transmission of a narrow band laser light.

Quantitative Measurements

The ability to establish unambiguous correlation between the observed signal and the absolute concentration of species under investigation is a desirable feature of any spectroscopic technique. According to Eq. 2.9 the determination of cavity exponential decay constant can lead to the absolute concentration measurements if absorption cross section is known. This property of CRDS is considered to be one of the most attractive features of the technique for applications related to chemistry. Therefore it is essential to recognize all effects that can cause deviation from expected behavior and influence quantitative ringdown measurements.

Firstly, Beer-Lambert law has to be valid so species related linear absorption can be introduced in Eq. 2.9. Beer-Lambert law is valid only for monochromatic light. This condition is almost always satisfied when lasers are used and species absorption cross section \( \sigma(\nu) \) is constant within laser linewidth \( \Delta \nu \). Another condition when Beer-Lambert law fails is when absorption is not proportional to the incident light
intensity. It may occur in limited cases of saturation which are not expected for $10^{-3}$ - $10^{-2}$ fractional absorption typical for CRDS. As was mentioned in section 2.1.3, multimode cavity excitation is considered to be a major sources of non single exponential decay in pulsed ringdown experiments. The fitting multiexponential curve with single exponential function may result in absorption spectrum with distorted intensities, or it may introduce an extra noise and limit the sensitivity.

The requirement on the width of laser pulse to overlap with several cavity modes for a successful ringdown event also applies to the width of any molecular absorption feature originated within the cavity. If not, species absorption line might fall between cavity modes and absorption will not be detected or some spectral features will be missing. Therefore it is necessary for the linewidth of the absorbing species to be greater than the spacing between cavity modes.

Another scenario that results in multiexponential ringdown decay is realized when aforementioned condition is satisfied but absorption linewidth is less than the laser linewidth. In this case, only cavity modes that are in resonance with absorption line will have shorter lifetime in the cavity. Modes that are excited by the laser pulse but do not overlap with the absorption line will decay with empty cavity ringdown time. Therefore output intensity will be a weighted sum of waveforms with different time constants.

In principal, observed nonexponential transient can be analyzed if absorption line-shape and laser pulse characteristics are known. In most cases it is not practical to perform such modeling. However it has been shown that for a small absorption
signals simple single exponential model should still yield acceptable absolute absorption measurement even in case of mismatch between laser and absorption linewidth. The exact criteria is depended on the molecular and laser linewidth ratio but generally if species absorption is substantially smaller then losses on the mirrors the single exponential model can be applied.

Cavity ringdown mirrors may also introduce multiexponentiality to the ringdown decay. Surface effects such as variations in the dielectric layers or surface irregularities may result in different reflectivity for different frequency components of the same pulse and therefore variation in the decay time for the laser pulse may be observed. However, for good quantitative measurements these effects are negligible.

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 $S^{p}_{min}$ into a cavity, the empty cavity ringdown time $\tau_{empty}$ will decrease by $\Delta\tau_{min}$. According to Eq. 2.9:

\[
S^{p}_{min} = \frac{L}{c(\tau_{empty} - \Delta\tau_{min})} - \frac{L}{c\tau_{empty}} \quad (2.12)
\]

\[
= \frac{L}{c\tau_{empty}} \frac{\Delta\tau_{min}}{\tau_{empty} - \Delta\tau_{min}} \quad (2.13)
\]

\[
= \frac{L}{c\tau_{empty}} \frac{\Delta\tau_{min}}{\tau_{abs}} \quad (2.14)
\]

\[
= (1 - R) \frac{\Delta\tau_{min}}{\tau_{abs}} \quad (2.15)
\]
Several conclusions on CRDS sensitivity can be drawn from the Eq. 2.15. 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. More typically $\frac{\Delta \tau}{\tau}$ accuracy of 1% is reported predominantly due to multimode excitation.

Taking mirrors with 99.99% reflectivity and using 1% as accuracy of $\frac{\Delta \tau}{\tau}$ will result in minimum detectable fractional absorption $S_{\text{min}}^0$ of $10^{-6}$. In CRDS community fractional absorption is usually expressed in parts per million (ppm) and hence losses within the cavity can be determined to a 1 ppm per pass. 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. Shot noise, systematic effects and instrumental noise that eventually contribute to $\frac{\Delta \tau}{\tau}$ will be considered later in connection with instrumental implementation of cavity ringdown apparatus.

CRDS has several major advantages over traditional spectroscopic techniques. Measurement of decay rate in time domain is intrinsically more accurate then 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 addition, light inside 1 meter cavity equipped with 99.99% reflectivity mirrors will have
34 $\mu$s ringdown time which corresponds to effective absorption pathlength of $\sim$10 km. Multipass cell are frequently used to increase the sensitivity of direct absorption methods, but to approach ringdown ppm sensitivity level light source with sub-1% intensity stability and multipass cell with several kilometers pathlength have to be used.

CRDS is suitable for measuring absorption values from sub-ppm to several percent. The upper limit of the dynamic range is determined by ability of the data acquisition system to record and fit short transient decays. 1% absorption per pass will result in 0.34 $\mu$s ringdown time in the standard cavity and only 7 points will be available on the decay curve for further fitting if 20 MHz digitizer is used.

2.2 Production of Peroxy Radicals Under Ambient Cell Conditions

2.2.1 RO$_2$ Generation

Production of radicals in sufficient quantities for detection is a crucial step in any experiment on the spectroscopy of transient species. Several methods have been successfully developed over the years for production of a variety of organic peroxy radicals. The brief review of the most common conventional production mechanisms will be presented before detailed kinetic considerations are discussed in individual chapters for of the each investigated peroxy radical. The initiation step in peroxy formation is production of the corresponding organic radical R from a stable precursor. In the presence of molecular oxygen R rapidly reacts with O$_2$:

$$R + O_2 + M \rightarrow RO_2 + M$$  \hspace{1cm} (2.16)
to form peroxy radical RO₂. The addition reaction requires presence of a third body M during the collision to conserve energy. For total pressures above 10-100 Torr (depending on the R group) chemically activated peroxy adduct can be stabilized and reaction (2.16) is in the high pressure limit with the typical bimolecular rate constant value of $10^{-12} \text{ cm}^3\text{s}^{-1}$ at room temperature.\textsuperscript{13,79} Having 10 Torr of O₂ in the reaction vessel will result in fast (µs time-scale) conversion of R to RO₂. Formation of peroxy radical via reaction (2.16) is the major channel of the R radical losses at low temperatures. Reaction (2.16) exhibit a negative temperature dependance and at the temperature above $\sim 1000K$ alkoxy radicals (RO) can be formed. Additional channels in reaction (2.16) are known to exist for ethyl\textsuperscript{80,81} or vinyl radicals\textsuperscript{82,83} at low pressures and elevated temperatures.

Irradiation of a suitable precursor with a UV laser is considered to be a clean and selective source of radicals R. However, the precursor should have relatively large UV absorption cross section to decompose with a reasonable photofragmentation yield and have a well established photochemistry to yield only species of interest. Using high precursor concentrations to compensate its low UV absorption cross section may introduce strong precursor absorption in the spectra. This background can reduce overall sensitivity of the experiment and also interfere with the species of interest. Precursors with several decomposition channels will produce mixture of reactive species and may significantly complicate peroxy production mechanism and further analysis of the observed spectra.
Photolysis of azoalkane has been used to produce alkyl radicals in many peroxy experiments\textsuperscript{84,85} via reaction:

\[
RN = NR + hv \rightarrow 2R + N_2 \tag{2.17}
\]

with \(N_2\) as an inert byproduct. Azoalkanes have a large absorption cross section (\(\sim 10^{-17} \text{ cm}^2\) at 193 nm for azomethane), but they are potentially explosive and have to be synthesized in-house. Photolysis of commercially available organic halides \(RX\) (X=I, Cl, Br) can also yield R radicals\textsuperscript{86,87} via:

\[
RX + hv \rightarrow R + X \tag{2.18}
\]

Halides have somewhat smaller UV cross section (8·10\(^{-19}\) cm\(^2\) at 248 nm for CH\(_3\)I\textsuperscript{88}) compare to azoalkanes. Subsequent kinetics in the reaction vessel may be complicated due to formation of photofragment \(X\) which can react with organic compounds in case of \(X=\text{Cl}\). Iodine crystals can be deposited on the walls and windows of the reaction vessel in case of \(X=\text{I}\). Photolysis of ketones\textsuperscript{87,89} or anhydrides\textsuperscript{90} can also be employed to initiate production of peroxy radicals:

\[
R_2C(O) + hv \rightarrow 2R + CO \tag{2.19}
\]

\[
(RC(O))_2O + hv \rightarrow R + CO + CO_2 \tag{2.20}
\]

Photolysis of aldehydes, RCHO at \(\lambda > 250\) nm produces both R and HCO.\textsuperscript{91} In the presence of oxygen both RO\(_2\) and HO\(_2\) are formed via following mechanism:

\[
RCHO + hv \rightarrow R + CHO \tag{2.21}
\]

\[
R + O_2 + M \rightarrow RO_2 + M \tag{2.22}
\]

\[
HCO + O_2 \rightarrow HO_2 + CO \tag{2.23}
\]
which makes this production mechanism an ideal system to study RO\textsubscript{2} and HO\textsubscript{2} cross reaction.\textsuperscript{92} Peroxy radicals can also be generated by hydrogen abstraction from stable hydrocarbon RH by Cl or F atoms in the presence of molecular oxygen. This mechanism is similar to the production of the peroxy radicals in the atmosphere where hydrocarbon RH is attacked by hydroxy radical, OH:

\[
RH + X \rightarrow R + HX \tag{2.24}
\]

\[
R + O_2 + M \rightarrow RO_2 + M \tag{2.25}
\]

where chlorine or fluorine atoms can be produced by UV photolysis or microwave discharge from various stable compounds like Cl\textsubscript{2}, (CClO)\textsubscript{2}, SF\textsubscript{6}, CF\textsubscript{4} or F\textsubscript{2}. The efficiency of this method is limited by the production of the halogen atoms and by rate constant for the reaction (2.24). The rate constant for the halogen atoms reaction with peroxy radicals is very fast\textsuperscript{93} (k\sim10^{-10} \text{ cm}^3\text{s}^{-1}) and therefore if reaction (2.24) is not fast enough, halogen atoms may attack produced peroxy radicals instead of the precursor molecules. Extra care should be taken in handling chemically aggressive precursors for the Cl and F atom production and in protecting optical components of the reactor from harsh byproducts of reaction (2.24) such as HF or HCl.

Both UV photolysis and hydrogen abstraction mechanisms are very general and may be used to produce a variety of peroxy radicals. For each particular RO\textsubscript{2} the choice of production method is dictated by precursor photochemistry, chemical properties and commercial availability. It should be mentioned that some peroxy radicals can be formed directly without oxygen association reaction (2.16). It can be done by
halogen abstraction from peroxides or thermal decomposition of peroxy nitrates:

\[ \text{ROOH} + X \rightarrow \text{RO}_2 + HX \]  
\[ \text{RO}_2\text{NO}_2 \rightarrow \text{RO}_2 + \text{NO}_2 \]

This approach is not widely implemented because reaction (2.26) may exhibit several pathways and produce undesirable reactive intermediates. Compounds like peroxy nitrates are usually not stable enough (except for peroxy acetyl nitrates) to be stored and transported to the reaction vessel.\(^{94}\)

Initial concentration of the peroxy radicals may be estimated from the fragmentation yield of precursors used in \(R\) radical production. Fragmentation yield depends on precursor photolysis cross section, photon flux and quantum yield. In principle, 100\% of precursor molecules may be decomposed by applying sufficient power, but it is desirable to decrease the fragmentation yield to as low as 1\% to avoid possible two photon processes leading to other fragmentation channels. With a couple of Torr of the precursor introduced in the ambient cell \(\sim 6 \cdot 10^{14} \text{ cm}^{-3}\) can be produced assuming 1\% fragmentation yield.

### 2.2.2 \(\text{RO}_2\) Kinetics

In the straight-forward application of CRDS technique, the species of interest have to be present in the ambient cell for at least the duration of the ringdown decay, which is typically on the order of 30 \(\mu\text{s}\). Therefore it is necessary to understand radical chemical kinetics in the reaction vessel and estimate peroxy lifetime under the cell conditions.
In most cases the peroxy self-reaction represents the major loss channel for rapidly produced peroxy radicals. The self-reaction proceeds along the following three pathways:

\[
\text{RO}_2 + \text{RO}_2 \rightarrow \begin{cases} 
\text{RO} + \text{RO} + \text{O}_2 & \text{(a)} \\
\text{ROOR} + \text{O}_2 & \text{(b)} \\
\text{ROH} + \text{R'O} + \text{O}_2 & \text{(c)} 
\end{cases}
\] (2.28)

Channel (b) is believed to be negligible due to rapid ROOR dissociation to RO. Reaction pathway (c) is considered to be a termination channel as it results in production of stable species (carbonyl and alcohol compounds). Propagation channel (a) introduces alkoxy radicals. With an excess of O\(_2\) subsequent secondary reactions will contribute to peroxy losses:

\[
\text{RO} + \text{O}_2 \rightarrow \text{R''O} + \text{HO}_2
\] (2.29)

\[
\text{RO}_2 + \text{HO}_2 \rightarrow \text{products}
\] (2.30)

In principal this system of kinetic equations can be solved numerically yielding concentration vs. time profile. However in many cases this rather complicated peroxy radicals self-reaction mechanism may be simplified by introduction of one effective reaction constants \(k_{\text{eff}}\) representing overall reaction \((\text{RO}_2 + \text{RO}_2 \rightarrow \text{products})\).\(^1\) Thus peroxy self-reaction can be viewed as a second order kinetic process with peroxy concentration half lifetime \(t_{\frac{1}{2}}\) given by:

\[
t_{\frac{1}{2}} = \frac{1}{2k_{\text{eff}}N_0}
\] (2.31)

where \(N_0\) is the initial concentration of peroxy radicals. Reported effective self-reaction rate constants for different peroxy radicals\(^{26}\) have large variations from
$4.7 \cdot 10^{-13}$ cm$^3$s$^{-1}$ for methyl peroxy$^{90}$ to $1.6 \cdot 10^{-11}$ cm$^3$s$^{-1}$ for acetyl peroxy$^{13}$ Taking the initial peroxy concentration of $6 \cdot 10^{14}$ cm$^{-3}$ estimated early in the section 2.2.1 will result in the peroxy half lifetime range from 50 µs to 1.7 ms using the latter and former rate constants respectively. Clearly peroxy radicals are present in the reaction cell on the timescale sufficient to probe them with ringdown technique.

No radical diffusion or heterogeneous losses on the walls of the reaction vessel were taken into account in the considered in the mechanisms of peroxy formation and destruction. If radicals are produced by a $0.5 \times 13$ cm excimer photolysis beam the shape of the photolysis volume can be approximated as a cylinder with 0.5cm diameter. First order diffusion rate constant $k_D$ from a cylindrical volume is given by$^{97}$

$$
 k_D = \frac{23.2}{d^2} D_0 \left( \frac{P}{760} \right)
$$

(2.32)

where $d$ is the diameter of the cylinder in cm, $D_0$ is the diffusion coefficient in cm$^2$/s at the atmospheric pressure and $P$ is the pressure in the reactor in Torr. While there is no information about diffusion coefficients of peroxy radicals is available one can accept for a rough estimate a diffusion coefficient of a comparably sized molecule in air. For a pressure $P=760$ Torr and room temperature the diffusion coefficient of CO$_2$ in the air is equal to 0.14 cm$^2$/s. For the 200 Torr pressure in the reactor and 0.5cm diameter of the cylinder $k_D$ is equal to 3.4 s$^{-1}$. Any substantial diffusion losses occur on $1/k_D$ time scale and therefore are negligible compare to radical-radical recombination reactions on 100 µs scale.
2.3 Near IR Cavity Ringdown Apparatus

2.3.1 Experimental Implementation

In presented further experiments the CRDS technique is combined with the laser photolysis initiated production of peroxy radicals. The radiation in the region of 2.1-1.2 μm was generated by stimulated Raman scattering of the output of a dye laser in molecular hydrogen. A diagram of experimental apparatus used in the experiments is shown on Fig 2.1. A dye laser was pumped by the second harmonic (532 nm) of a Nd:YAG laser. Several Nd:YAG models have been used during the course of experiments - DCR2A (Quanta Ray), GCR and PRO-270 (Spectra Physics).

Dye laser system (PDL-2, Quanta Ray) was operated at ether 10 or a 20 Hz repetition rate. In the far red region of the dye laser operation, Exciton LDS 925, LDS 867 and LDS 821 laser dyes were used. To maximize dye laser output in specific spectral regions, mixtures of the dyes with optimized concentrations or dye solvents with different polarity have been used. Additional plano-concave cylindrical lens was inserted in the amplifier stage of the PDL-2 to implement side-pumping scheme and increase pumping efficiency. A pump delay line was set up between oscillator and amplifier stage of the dye laser to minimize broadband amplified spontaneous emission (ASE) which can contaminate laser output. With those modifications, dye laser system was capable of producing 20-30 mJ/pulse of tunable radiation in the region of 830-940 nm with a diameter ~3 mm. Operating in the visible region with the set of LDS765, LDS750, LDS721, LDS698 and DCM laser dyes this system was tuned over 775-670 nm region with pulse energies of 30-50 mJ.
Nd⁺²:YAG: 532nm → Dye Laser → Raman Cell

Figure 2.1: Schematic diagram of the experimental apparatus
Initial frequency calibration was performed with Burleigh Wavemeter and was typically within a 1 cm$^{-1}$ from the dye laser dial reading. Dye laser resolution is limited by the resolution of the dye laser grating and, in agreement with PDL-2 specifications, 0.3 cm$^{-1}$(FWHM) laser linewidth was measured with Burleigh fine etalon. This observation was later confirmed by observing H$_2$O and HCl single rotational lines with a linewidth limited by laser resolution.

The output of dye laser was focused by a f=50 cm lens into a 70cm long single pass Raman cell, filled with 200-400 psi of H$_2$. The body of the Raman cell was constructed in-house of stainless steel material. 1/4 inch diameter and 1/2 inch thick quarts fused silica windows were mounted on screw-in flanges and sealed to the tube with O-rings to contain the pressurized gas. The windows infrared transmission curve was recorded with an FTIR spectrometer and more than 80% transmission was observed for the wavelengths $\leq 2.2$ $\mu$m. The cell was equipped with two 1/4 inch Swagelock ports. One port was connected through high pressure gas line to the H$_2$ (99.99%, Liquid Carbonic Specialty Gases) cylinder with a high pressure regulator. This port was also used to monitor the pressure with high pressure gauge (Matheson 0-1000 psi). The other port was attached to the vacuum pump (Edwards E2M5) for evacuating and back-filling the cell. The emission leaving the Raman cell was analyzed using a Pellin Broca prism. After the prism, the light was focused in the far field with a long focal length lens such that individual Stokes and anti Stokes components are clearly separated. Two Lumitek IR detection cards, Q-11-R for 1.2 $\mu$m and Q-12-R for 1.5 $\mu$m, were used to locate 1$^{st}$ or 2$^{nd}$ Stokes beam and assist with further alignment.
Typically 1 mJ of the 1st Stokes in the 1.5 - 1.2 µm region was measured when the PDL-2 laser system was operating in 830-940nm region. For the 2.1 - 1.5 µm experiments 0.5-1 mJ of 2nd Stokes light was produced using 775-670 nm radiation. Observed similarity in 1st and 2nd Stokes energies is most probably due to increase in dye laser power in the visible region and more efficient Raman conversion for a shorter pump wavelength. Increase in the pump energy may also result in shifting of the Raman gain towards higher Stokes frequencies. It was necessary to keep the pressure in the Raman above 150 psi and the energy of the dye laser above 20 mJ in order to observe any SRS light which is consistent with the threshold type behavior observed previously.68,71 Raman generation was optimized by adjusting the pump beam focusing conditions inside the Raman shifter. It was done by tuning the dye laser beam divergence using a variable beam expanding telescope inside the amplification stage of the dye laser.

It was also noted that stable generation of the anti Stokes SRS components correlate with efficient production of the corresponding order Stokes light. It can be explained as follows. In order to generate anti-Stokes radiation the v=1 vibrational level in the Raman media should be populated. For the H₂ molecule, one vibrational quanta is equal to 4155 cm⁻¹ and it is too high to be populated at room temperature. But it can be populated via efficient Stokes processes connecting v=0 and v=1 levels. This process is similar to four wave mixing and is also responsible for conical shape of the anti Stokes radiation. It was found useful to optimize Raman generation by monitoring visible anti Stokes before proceeding further.
While most of the reported peroxy spectral observations were taken with PDL-2 dye laser, a recently acquired Sirah dye laser (Sirah GmbH) was extensively tested as a pump source for a Raman downconversion. This system is capable of producing \( \sim 100 \) mJ of pulsed light in the visible region with 0.03 cm\(^{-1}\) (FWHM) resolution. Using Sirah laser operating at 594 nm, several observations were made on efficiency of the Raman conversion. With 25 mJ in pump power 3 mJ in the 1\(^{st}\) Stokes and 1.5 mJ in the 2\(^{nd}\) Stokes were measured. Increase in fundamental power to 80 mJ resulted in 9 mJ and 4 mJ in the 1\(^{st}\) and 2\(^{nd}\) Stokes respectively. Conversion efficiencies of 12\% and 5\% for the 1\(^{st}\) and 2\(^{nd}\) Stokes are close to the values reported in the literature for a similar pump frequency and power.\(^9\)

The IR radiation (1\(^{st}\) or 2\(^{nd}\) Stokes) leaving the Raman cell has to be spectrally filtered to separate the fundamental, anti Stokes and Stokes frequencies to avoid detector saturation and damage to optical components. If wavelength separation is done by a dispersive element, such as a prism or diffraction grating, it has to be tuned with the laser frequency to maintain optical alignment, critical in ringdown spectroscopy. With several meters optical path necessary for effective frequency separation, it is possible to scan up to 10 cm\(^{-1}\) without losing ringdown in the cavity. After that cavity has to be realigned which is not practical for a long range scans. Although it is possible to arrange several prisms in optical system with compensated dispersion, a significant fraction of the IR light will be lost due to absorption and reflection on multiple optical surfaces.
The simplest solution for the frequency separation is to employ color filters. The emission leaving the Raman cell was collimated and then both the fundamental, anti-stokes and 1\textsuperscript{st} Stokes (if 2\textsuperscript{nd} Stokes is used) were suppressed using several 1, 1.3 or 1.4 \(\mu\text{m}\) cut-off longwave pass filters (Corion LL-1000, CVI, Spectrogon) to yield tunable radiation in the region of interest.

The efficiency of this method can be demonstrated by following example. According to specifications, Corion LL-1000 filter has transmittance of 0.1\% for wavelengths shorter than 850nm. Raman shifting of 30 mJ dye laser beam at 800nm will produce 1mJ of the IR radiation in 1.2 \(\mu\text{m}\) region. Three LL-1000 filters filters will attenuate pump beam by \(10^{-9}\). Ringdown mirrors with 100 ppm reflectivity will transmit only \(10^{-8}\) of incident IR radiation. Therefore energy of the residual pump beam is comparable to the energy of the IR Stokes light after the ringdown cavity. The light directly transmitted trough the ringdown mirrors is detected as a short spike in the very beginning of the ringdown decay and usually does not constitute a problem. Insufficient attenuation of the pump beam may lead to the detector saturation and distortion of the ringdown curve. In worse case, it can result in damage of ringdown mirrors and IR detector.

The ringdown cavity was formed by two plano-concave mirrors (Los Gatos Research) with radius of curvature \(r\) equal to 6m separated by cavity length \(L\) equal to 55cm to insure a stable resonator configuration. Ringdown mirrors were aligned using a HeNe laser mounted behind the cavity. The IR Stokes radiation in the 2.2-1.2 \(\mu\text{m}\) region was delivered to the ringdown cell using silver coated IR mirrors (ER.2,
Newport). Two 1m focal length lenses were used to approximate TEM\textsubscript{00} cavity mode. For a symmetrical cavity the diameter $w_m$ of the TEM\textsubscript{00} cavity mode on the mirror and the waist of the mode $w_o$ inside the cavity are given by:

$$w_m = 2 \left( \frac{\lambda}{\pi} \right)^{\frac{1}{2}} \left( |2r - L| \frac{L}{4} \right)^{\frac{1}{4}}$$

$$w_o = 2 \left( \frac{\lambda L}{2\pi} \right)^{\frac{1}{2}} \left( \frac{2r^2}{L|r - \frac{L}{2}|} \right)^{\frac{1}{4}}$$

(2.33) (2.34)

where $\lambda$ is the wavelength of the light coupled to the cavity. For $\lambda$ equal to 1.6 \(\mu\)m the $w_m$ and $w_o$ are equal to 1.64 and 1.60 mm respectively. Mirrors were attached to the arms of a stainless steel cell using fine adjustment mounts. The cell was manufactured with various ports for precursor gas inlets, purges, pressure gauge (Baratron) and exhaust for a mechanical vacuum pump. The ringdown mirrors were constantly purged during the course of experiments with a positive nitrogen flow to protect the mirror surfaces from any harsh chemical environment present in the cell. Two rectangular (2×18cm) apertures separated by 2.3cm were made in the center of the cell for UV grade quartz photolysis windows.

The radiation leaving the ringdown cavity was focused by a 2.5cm focal length lens on a fast photodiode. A ThorLabs InGaAs (PDA 255) was used in the 1.2-1.7 \(\mu\)m region. For the experiments in the 1.6-2.2 \(\mu\)m region it was substituted with Judson Technologies InAs (J12) photodiode. PDA 255 was supplied by manufacturer with build-in transimpedance amplifier. Separate amplifier was design by Perry Amplifier to match specifications of J12 unit. The Perry amplifier was equipped with set-0 adjustment to compensate drift in output DC level due thermal instability of InAs
photodiode. The photodiode was incorporated into 3-D optical translational stage. Due to photodiodes small active area (1×1 mm) fine adjustment of the photodiodes position is required to collect all photons leaving the cavity.

The detector output was recorded by a 12 bit 20 MS/s digitizing card (Measurement Computing, PCI-DAS4020/12) or by the 8 bit digital oscilloscope (Tektronix 2430) for further analysis. Typically, 16 or 20 laser shots per frequency point were averaged then the sum was transferred to the computer. The transient decay was fitted to a single exponential for decay time, initial amplitude and baseline using the non-linear Levenberg-Marquardt algorithm. The decay constant was converted to the cavity absorption per pass (in ppm) and saved as a point in the spectrum. It has been found that the high frequency noise, probably produced by mode beats in the ring-down decay waveform, affects the quality of the fit. Consequently the high frequency components of the waveform were filtered by setting the bandwidth limit of the scope to 20 MHz.

The photolysis excimer laser (LPX300, Lambda Physik) was operated either at 248 nm (200 mJ/pulse) to photolyze iodoalkanes, or at 193 nm (150 mJ/pulse) to photolyze ketones or oxalyl chloride. The beam was shaped by 25.4 cm focal length cylindrical lens and 70 cm focal length spherical lens to a 13×0.5 cm rectangle and sent through the photolysis windows into the central part of the flow cell, thereby determining the volume wherein radicals are created. According to the Eq. 2.34 the diameter of the TEM$_{00}$ mode is 0.16 cm inside the ringdown cavity and therefore the probe beam is well contained within the width of the excimer beam. Under this
condition all infrared photons will interact with produced radicals and radicals will be distributed uniformly within the probe beam. The outlet of the flow cell was connected through the needle valve to the vacuum pump (United Vacuum, E2M5). The following procedure was used to determine the pumping speed. Pure nitrogen was introduced into the cell through a calibrated mass flow controller (MKS) and the pressure in the cell was measured against several readings of the flow controller. The slope of the obtained pressure vs. gas flow dependence will represent pumping speed. A throttle valve was adjusted to set the pump speed to 100 cm$^3$/sec. With photolysis a volume of 15 cm$^3$ and laser system repetition rate of 20Hz the photolysis mixture was replaced every third laser pulse.

A significant problem in the acquisition of peroxy radicals spectra is the absorption of the precursors and residual water, which have vibrational overtone and combination bands in the region of interest. In order to eliminate these absorptions from the spectrum, background subtraction with the photolysis laser on and off was implemented. With the probe laser fixed at a given frequency, the ring-down decay is recorded once after the photolysis laser fires and again with the photolysis laser off. This technique is effective in eliminating both broad features, e.g., absorptions of precursor, and sharp rotationally resolved lines of water. Background subtraction is useful for “cleaning up” the spectrum for the rotational analysis described below. However the strong peroxy peaks are clearly visible in the spectrum even without background subtraction. All data was calibrated with 0.25 cm$^{-1}$ accuracy using H$_2$O and HCl overtones with the frequencies taken from HITRAN$^{100}$ database. Control
of the lasers and fitting procedure were performed by a PC-based Labview data acquisition software. The experimental time sequence was controlled by a multichannel pulse generator (BNC 500). The accusation cycle was initiated by the TTL pulse from channel (1) triggering the lamps of the Nd:YAG laser. The TTL pulse from channel (2) was delayed by 200-250 $\mu$s and sent to trigger Nd:YAG Q-switch. This delay was adjusted to maximize Nd:YAG laser output and was used to reduce Nd:YAG laser power if necessary. The data collection on the oscilloscope or digitizing card was triggered with the same pulse from channel (2). The TTL pulse from channel (3) was used to fire the excimer laser 10-20 $\mu$s before Q-switch. This delay between channel (2) and (3) was to used to separate production excimer laser pulse and probe dye laser pulse in time and observe peroxy radicals decay kinetics. After collection of a preset number of pulses, the TTL pulse from channel (3) was interrupted and the same number of shots was collected with excimer laser off. Excimer pulse interruption was performed using an external analog gate. The output of the gate was equal to the input when control level was set to low or was equal to zero when control level was set to high. The setting of the control level was incorporated into data accusation software and was sent to the gate through computer parallel port. After completing the data accusation the dye laser frequency was stepped and cycle was repeated.

2.3.2 Sensitivity and Detection Limits

To estimate the sensitivity and limitations of the experimental apparatus various noise sources should be considered. In CRDS the accuracy of determining ringdown time $\tau$ can be affected by following noise categories:
(I) Technical noise in the detection system

**Data processing noise:**

Data processing noise associated with digitization of the analog signal from the detector depends on digitizer vertical resolution. When a 12-bit digitizing card is employed and vertical resolution of the card is set to ±1 V, digital noise is equal to \( \rho_{\text{digit}} = \frac{2V}{2^{12}} = 0.5 \text{ mV} \). For the 8-bit scope set to 200 mV scale the \( \rho_{\text{digit}} \) is equal to 0.8 mV. Fig. 2.2(A) shows digital noise distribution on the accusation card for a single waveform and for the 20 averaged waveforms.

**Electronics:**

Detector characteristics combined with preamplified noise sources determine electrical noise in the system. ThorLabs PDA255 amplified photodiode system was used in the 1.2-1.7 µm region. It includes InGaAs detector with \( 3\times10^{-11} \text{ W}/\sqrt{\text{Hz}} \) NEP and 0.95 A/W(@1.65 µm) responsivity and build-in amplifier with \( 1\times10^4 \) V/A transimpedance gain. This system has DC-50MHz bandwidth assuming 50 Ω load. According to the specifications the rms broadband voltage noise of the system is 2mV and the value of 1.2 mV was measured experimentally.

Judson Technologies InAs photodiode (J12) was used in 1.6-2.2 µm region. The photodiode has \( 3\times10^{-11} \text{ W}/\sqrt{\text{Hz}} \) NEP and 0.75 A/W(@2.0 µm) responsivity. Coupled with \( 1\times10^4 \) V/A transimpedance gain amplifier the system has DC-5MHz frequency response. Using photodiode parameters such as amplifier voltage and current noise values provided in the specifications the broadband voltage noise of 1.5 mV was estimated. This noise is predominately due to the amplifier voltage noise and detector
thermal noise is several times smaller. Measured statistical distribution of the detection noise is shown on Fig. 2.2(B). The noise histogram shows normal Gaussian distribution and the observed voltage noise for J12 amplified photodiode is 1.3 mV (standard deviation) with no averaging. For the practical purposes the detection noise $\sigma_{det}$ of 2mV can be taken for both ThorLabs and Judson Technologies detector/amplifier packages.

Number of points available for the fitting procedure is determined by the time resolution of the digitizer. For the ringdown time $\tau$ of 30 $\mu$s the waveform of $\sim$100 $\mu$s ($3-4\tau$) long should be recorded for the accurate fitting. The sampling rate $\Delta t$ of the digitizing card was set to its maximum value of 50ns and 2000 points were collected for the 100 $\mu$s time window. Tektronix horizontal resolution is 1024 points per scope time window and therefore 100 $\mu$s long waveform was digitized with sampling rate $\Delta t$ of 100ns. Total technical noise $\rho_{tech}$ can be calculated by adding $\rho_{digit}$ and $\rho_{det}$ in quadratures. The relative standard deviation of the ringdown time due to technical noise is given by:

$$\sigma_{tech} = \frac{\rho_{\tau}}{\tau} = \frac{2\rho_{tech}}{V} \left( \frac{2\Delta t}{\tau} \right)^{\frac{1}{2}}$$

(2.35)

where $V$ is initial ringdown intensity in volts. Taking 100mV as a typical initial ringdown intensity will result in ringdown time relative deviation of $3.5 \cdot 10^{-3}$ and $2.3 \cdot 10^{-3}$ due to the technical noise when data accusation is performed with the digitizing card and the oscilloscope respectively. These calculated values are in good agreement with $4 \cdot 10^{-3}$ and $2 \cdot 10^{-3}$ relative standard errors in the ringdown time determination given by the fitting algorithm when data taken with digitizing card and the oscilloscope.
Figure 2.2: Noise distribution on the digitizing card (A) and J12 amplified photodiode (B). The horizontal axis on all histograms is the bit number and for 12-bit card 1 bit corresponds to 0.5 mV.
Averaging will have a different effect on the $\rho_{tech}$ when data is recorded with digitizing card and oscilloscope. The accusation card is averaging already digitized waveforms while oscilloscope is averaging analog signals and then digitize and transfer single waveform to the computer through GPIB interface. Therefore only electrical noise can be averaged out with the oscilloscope because digital noise is introduced on the final transfer stage. With this reservation $\rho_{tech}$ should be scaled accordingly and for 20 waveforms averaged $\sigma_{tech}$ is calculated to be $1.5 \cdot 10^{-3}$ when oscilloscope is used and $0.5 \cdot 10^{-3}$ for data accusation with the digitizing card.

(II) Shot noise:

As was mentioned in section 2.3.1 approximately 0.5-1 mJ of infrared radiation was produced via stimulated Raman shifting process. For the following estimation one can assume that 0.5 mJ of 1.5 $\mu$m radiation is reaching the cavity after all optical elements. Such a laser pulse will consist of $3.8 \cdot 10^{15}$ photons. After first pass through ringdown cavity with 99.99% mirror reflectivity only $N_{ph}=3.8 \cdot 10^7$ photons will be transmitted. Quantum efficiency $Q$ of the both InAs and InGaAs photodiodes is $\sim 0.8$ and this value can be converted into number of electrons generated per incident photon:

$$Q = 0.8 \frac{A}{W} = 0.8 \frac{e}{L} = 0.8 \frac{6.25 \cdot 10^{18} \text{e} \text{coul}}{7.6 \cdot 10^{18} \text{photon}} \approx 0.7 \frac{\text{electron}}{\text{photon}}$$

Fluctuation in number of electrons on the detector will represent the shot noise. Accordingly, shot noise in this case is equal to $\sigma_{shot} = 1/\sqrt{N_{ph} \cdot Q} = 2 \cdot 10^{-4}$. Alternatively, shot noise can be estimated as a fluctuation of the detected signal level $V$.
(in volts):

\[ \sigma_{\text{shot}}^2 = \frac{\hbar \omega Q G V}{\Delta t} \]  

(2.37)

where \( \hbar \omega \) is the photon energy, \( Q \) is the detector responsivity in \( \frac{A}{W} \), \( G \) is the amplifier gain in \( \frac{V}{A} \) and \( \Delta t \) is the sampling rate. Using values for \( V \), \( \Delta t \), \( Q \) and \( G \) given previously one can calculate \( \sigma_{\text{shot}} \) equal to \( 4.5 \cdot 10^{-4} \). The values of \( \sigma_{\text{shot}} \) are similar to estimated \( 3 \cdot 10^{-4} \) shot noise limit for a generic pulsed CRDS apparatus\(^3\) and an order of magnitude smaller than technical noise \( \sigma_{\text{tech}} \) for a single laser shot.

(III) Multimode cavity excitation

In practice uncertainties in the repeated measurements of the ringdown time represent actual sensitivity of the CRDS method. To check distribution of the ringdown time measurements 600 single shot ringdown curves were recorded for a fixed laser frequency. Each curve was fitted to a single exponential decay and histogram of the obtained ringdown times is presented on insert (A) of Fig. 2.3. The histogram can be fitted with Gaussian distribution yielding relative ringdown time standard deviation \( \sigma_{\text{tau}}/\langle \tau \rangle \) of \( 2 \cdot 10^{-2} \). When 20 laser shots per waveform were averaged and same 600 waveforms were collected, much narrow time distribution with \( \sigma_{\text{tau}}/\langle \tau \rangle \) of \( 5 \cdot 10^{-3} \) was observed. The distribution of the ringdown times assessed from averaged waveforms is shown on insert (B) of Fig. 2.3. In both cases observed time uncertainty is following normal distribution with standard deviation scaled as square root of number of averaged laser shots.

Similar ringdown time relative uncertainties of \( (1 - 0.2) \cdot 10^{-2} \) are reported\(^3\,\,6\,\,5\,\,101\) in most pulsed ringdown experiments where laser pulse is covering many cavity modes.
Figure 2.3: Histogram of the ringdown times: (A)—single laser shot per waveform, (B)—20 laser shots per waveform. Data was taken with 12-bit accusation card. Solid line represents a fit to Gaussian distribution.
As was mentioned earlier multimode cavity excitation may result in multiexponential ringdown decay, shot-to-shot variation in laser pulse coupling, longitudinal and transverse mode beating hence affecting accurate determination of the decay time. For a pulsed single mode CRDS these various contributions of multimode excitation to the ringdown noise are eliminated and the sensitivity $\sigma_{\tau \langle \tau \rangle}$ of $3 \times 10^{-4}$ has been achieved, ultimately approaching instrumental and shot noise limits.\textsuperscript{78}

As evident from the noise analysis, the multimode cavity excitation noise is an order of magnitude bigger than technical or shot noise therefore introducing the major limiting factor in the sensitivity of presented cavity ringdown spectrometer. According to the histogram, the mean empty cavity ringdown time is equal to $34.29 \mu s$ which corresponds to a loss of $53.64$ ppm per pass for a 55cm long cavity. According to Eq. 2.15 it corresponds to a minimum detectable fractional absorption of:

$$S_{\text{min}}^{p} = (1 - R)\frac{\sigma_{\tau \langle \tau \rangle}}{\langle \tau \rangle} = 53.64 \times 5 \cdot 10^{-3} = 0.27 \text{ppm} \quad (2.38)$$
A fundamental understanding of the nature of peroxy electronic states and, hence, the origin of the peroxy radical electronic absorption spectra is a key to the interpretation and assignment of observed peroxy spectra and absolutely necessary for predicting spectra of yet to be detected peroxies. Therefore the electronic structure of various peroxy radicals has been investigated in numerous *ab initio* studies.\textsuperscript{102–107}

The structure of the electronic energy levels in peroxy radicals can be illustrated by example of the methyl peroxy radical, the simplest alkyl peroxy. Geometry optimization calculations revealed that methyl peroxy, as well as all peroxy radicals of $C_3$ symmetry,\textsuperscript{102,105} has a $^2A''$ ground electronic state. *Ab initio* results can also be used to visualize molecular orbitals and obtain orbital eigenvalues. A diagram of the molecular orbitals and the eigenvalues for two lowest occupied molecular orbitals of CH$_3$O$_2$ radical is presented on Fig. 3.1. The relative energies and shapes of the CH$_3$O$_2$ orbitals can be rationalized by constructing correlation diagram between energy levels and molecular orbitals of the two building blocks of methyl peroxy radical, methyl radical and oxygen molecule. This correlation diagram is also shown on Fig. 3.1.
The oxygen molecule in the $X^3\Sigma_g^-$ electronic state has two electrons located on degenerate $\pi^*_x$ and $\pi^*_y$ orbitals. Upon addition of the methyl radical, the oxygen $\pi^*_y$ orbital and methyl $\pi^*$ orbital overlap and C–O bond is formed. The diagram for CH$_3$O$_2$ highest doubly occupied orbital (HOMO) clearly shows $\pi^*$ character on the oxygen moiety and $\sigma$ bonding along C–O bond. Stabilization energy introduced by formation of the C–O bond results in lower HOMO energy relatively to the CH$_3$ and O$_2$ orbitals bearing unpaired electrons. It should be noted that oxygen $\pi^*_y$ orbital and methyl $\pi^*$ orbital have $A'$ symmetry in methyl peroxy $C_S$ framework and hence methyl peroxy HOMO is totally symmetric.

The remaining oxygen $\pi^*_x$ orbital is correlated to the methyl peroxy singly occupied molecular orbital (SOMO). Therefore the unpaired electron in CH$_3$O$_2$ is primarily localized in the $\pi^*$ orbital of the O$_2$ group. Mixing of the oxygen $\pi^*_x$ orbital with methyl radical antisymmetric HOMO orbital results in some electron density allocation on the peroxy hydrogen atoms. The $\pi^*_x$ orbital is antisymmetric in $C_S$ framework giving rise to the methyl peroxy $^2A''$ ground electronic state. The above molecular orbital mixing scheme demonstrates that one can consider peroxy HOMO as a $\sigma$ and peroxy SOMO as a $\pi^*$ in character. Promotion of an electron from the highest doubly occupied orbital to the half filled $\pi^*$ orbital constitutes the nature of the $\tilde{A}^2A' – \tilde{X}^2A''$ electronic transition in peroxy radicals.

To calculate the splitting between the $\tilde{A}$ and $\tilde{X}$ states the $\tilde{X}$ state was first examined on HF/6-31G(d) level. Using $\tilde{X}$ state orbitals as a reference the electron was promoted from the HOMO $A'$ to the SOMO $A''$ orbital and geometry optimization
Figure 3.1: Diagram of the two lowest occupied molecular orbitals in CH$_3$O$_2$ calculated at the BLYP/6-31+G* level and correlation diagram between energy levels and molecular orbitals of methyl radical, oxygen and methyl peroxy radical. The dashed line in methyl peroxy lies in the $C_S$ symmetry plane.
<table>
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Table 3.1: Ab initio calculations of the $\tilde{A} - \tilde{X}$ origin frequency for a number of peroxy radicals. Both G2 and HF values were corrected for zero point energy.

and energy calculations were performed. The unpaired election was fixed on the $\tilde{A}'$ orbital to prevent convergence to the $\tilde{X}^2A''$ state. $\tilde{A}$ state vibrational frequencies were calculated as well to make sure that calculated geometry and energy represent a true minimum on the excited state potential energy surface. Using HF optimized geometries and orbital configurations as starting points both $\tilde{A}$ and $\tilde{X}$ energies at G2 level were calculated. Resulting frequencies for the $\tilde{A} - \tilde{X}$ origin transition of various alkyl peroxy radicals calculated at the HF/6-31G(d) and G2 levels are listed in Table 3.1.

Hybrid G2 method was design to compute accurate energies using a set of built in calculations taken with various corrections.$^{108}$ The standard error for G2 energy calculations$^9$ is $\sim$350cm$^{-1}$ which is extremely good for the ab initio method. The G2 accuracy was estimated by comparing calculated and experimental values of electron affinities, ionization energies and heats of formation for the set of test molecules. As one can notice from Table 3.1, HF calculations systematically underestimate $\tilde{A} - \tilde{X}$ separation compare to values from G2 method probably due to neglecting effects of electron correlation.
Table 3.2: $R-O_2$ bond dissociation energies (BDE) in various peroxy radicals. Values of $\Delta H_{298}^0$ for reaction $RO_2 \rightleftharpoons R+O_2$ are listed for alkyl peroxies.\(^5\) BDE’s for $HO_2$ and $CF_3O_2$ are taken from ref. [6] and [7] respectively. All values are in cm\(^{-1}\).

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<tr>
<th>$RO_2$</th>
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<th>$C_2H_5O_2$</th>
<th>i-$C_3H_7O_2$</th>
<th>t-$C_4H_9O_2$</th>
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<td>12990±802</td>
<td>12773±619</td>
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</table>

According to G2 calculations the $\tilde{A} - \tilde{X}$ electronic transition for all the peroxy radicals should reside in the near IR region (approximately 7500 cm\(^{-1}\)). As was described earlier, the $\tilde{A} - \tilde{X}$ transition can be characterized as an electron excitation from the $\sigma$ HOMO orbital to the $\pi^*$ SOMO orbital on the O$_2$ group. With $\pi^*$ orbital being well localized, the $\tilde{A}$ and $\tilde{X}$ separation should depend primarily on the strength of the $R-O$ $\sigma$ bond. Table 3.2 shows that in the first approximation it should be similar in all alkyl peroxy radicals.

However, Table 3.1 shows that the origin of the $\tilde{A} - \tilde{X}$ transition shifts slightly to the blue with the size of the alkyl group. This blue shift is apparently small ($\sim$300 cm\(^{-1}\)) yet can be clearly observed experimentally which will be demonstrated latter in the Chapter 4.

The similarity in $\tilde{A} - \tilde{X}$ transition frequency can also be explained qualitatively by considering effects of alkyl group substitution on peroxy SOMO and HOMO orbitals. Fig. 3.2(A) shows orbital eigenvalues for the SOMO, HOMO and 2HOMO (second highest occupied orbital) in various peroxy radicals. The energy difference between ground state SOMO and HOMO orbitals is $\sim$1.38 eV (11130 cm\(^{-1}\)) for all peroxies and comparable to the $\sim$0.93 eV (7500 cm\(^{-1}\)) calculated by G2 method treating
optimization of the $\tilde{X}$ and $\tilde{A}$ states separately. Such simplistic approach of taking SOMO/HOMO energy difference expectedly produces overestimated value for the transition energy yet suggesting that considering SOMO and HOMO separation is a reasonable approximation for $\tilde{A} - \tilde{X}$ transition frequency. As evident from Fig. 3.2(A) both SOMO and HOMO orbitals involved in the $\tilde{A} - \tilde{X}$ transition are shifting simultaneously with R group substitution. The maximum variation of SOMO/HOMO separations shown on Fig. 3.2(B) is $\sim 0.03$ eV (220 cm\(^{-1}\)) which is even smaller than error bars for highly accurate G2 calculations. Fig. 3.2(B) also shows no clear trend in the SOMO/HOMO separations with respect to peroxy radicals which makes it difficult to establish qualitative correlation between nature of the R group and frequency of the $\tilde{A} - \tilde{X}$ transition.

The simultaneous increase of both SOMO and HOMO orbital energies with alkyl ($\text{CH}_3\text{O}_2 \rightarrow \text{tC}_4\text{H}_9\text{O}_2$) group substitution can be rationalized in the following way. As was mentioned early, the SOMO orbital localized on the terminal oxygen atom is $\pi^*$ in character. HOMO orbital is bonding along the C–O bond but has a significant $\pi^*$ character on the oxygen moiety. Alkyl groups are known to exhibit inductive effect - a shifting of electrons toward radical center. Therefore electron density can be donated from the alkyl group to the antibonding SOMO orbital and non-bonding along O–O HOMO orbital. Hence the energy for the both SOMO and HOMO is increasing with respect to the numbers of carbons in the alkyl group. Shift of the peroxy SOMO and HOMO orbitals can be considered from somewhat different prospective. Increase in the peroxy SOMO energy with respect to the size of the alkyl group is consistent
Figure 3.2: (A) Orbital eigenvalues for the (▲)SOMO, (●)HOMO and (■)2HOMO ground state molecular orbitals in peroxy radicals calculated at the BLYP/6-31+G* level. (B) Difference between SOMO and HOMO eigenvalues(▼).
with decrease of the ionization energy for alkyl peroxy radicals shown in Table 3.3. In the assumption that the radical does not relax upon ionization, the energy of the radical SOMO orbital is equal to the negative of its ionization energy (Koopman’s theorem\textsuperscript{109}). According to the IP energies for alkyl radicals listed in Table 3.3 and Koopman’s theorem, the energy of the alkyl radical SOMO orbital should also increase with the numbers of carbons in the alkyl chain. \textit{Ab initio} calculations\textsuperscript{8} support this approximation and show increase in both SOMO and HOMO orbital energies in the alkyl radicals.

By comparison, substitution of the methyl group by the ethyl group will make separation between alkyl HOMO orbital and oxygen $\pi^*$ orbital smaller (see Fig. 3.1), leading to the stronger interaction between aforementioned orbitals and therefore formed peroxy SOMO orbital will have higher energy in ethyl peroxy radical. Interaction between alkyl $\pi^*$ SOMO orbital and oxygen $\pi^*_y$ orbital will be weaker in case of ethyl peroxy and hence ethyl peroxy HOMO should reside higher in energy having the energy of the oxygen $\pi^*_y$ orbital as an upper limit. Therefore it is reasonable to assume that peroxy SOMO orbital will be affected stronger upon alkyl group substitution than HOMO orbital. In other words, SOMO orbital goes up in energy faster

<table>
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</table>

Table 3.3: Ionization energies (eV) for different peroxy radicals and their parent fragments.
than HOMO orbital and the net effect of alkyl group substitution is an increase of
the HOMO and SOMO energy gap and hence blue shifting of the alkyl peroxy $\tilde{A} -
\tilde{X}$ electronic transition predicated in Table 3.1.

Calculations provided in Fig. 3.2(A) also show that SOMO and HOMO orbitals
for the fluorinated methyl peroxy are significantly lower in energy compared to the
protonated alkyl peroxies. One can rationalize this \textit{ab initio} prediction using MO
diagram for the CH$_3$O$_2$ and CF$_3$O$_2$ and considering similar electron density donation
arguments. As evident from the MO plots provided on Fig. 3.3, fluorination of the
methyl group does affect significantly the character of the singly occupied molecular
orbital and highest doubly occupied molecular orbital.

Interaction of the electrons on both SOMO and SOMO orbitals with the CX$_3$
group is distinctively different in the CH$_3$O$_2$ and CF$_3$O$_2$. As clearly seen from Mul-
liken charges depicted on Fig. 3.4, the strong electronegativity of the fluorine atoms
results in electron density withdrawal by the trifluoromethyl group compare to methyl
group. This is similar to the known inductive effect in the halogenated hydrocarbons,
where charge withdrawal towards halogen atom is propagated through sigma bond
framework in the hydrocarbon chain. Indeed comparison of the SOMO/HOMO dia-
grams for the CH$_3$O$_2$ and CF$_3$O$_2$ provided on Fig. 3.3 shows substantial increase of
the electron density on the CF$_3$ group. The delocalization of the electron density on
the SOMO and HOMO orbitals leads to a decrease in orbitals antibonding or non-
bonding character. Such stabilization of the orbitals in the CF$_3$O$_2$ radical results in
lowering of the SOMO and HOMO orbital energies. Highly accurate G2 calculations
Figure 3.3: Single and highest doubly occupied orbitals in CH$_3$O$_2$ and CF$_3$O$_2$ calculated at the BLYP/6-31+G* level.
provided in Table 3.1 predict that the net effect of such simultaneous SOMO/HOMO energy decrease upon methyl peroxy fluorination will result in shifting of the $\tilde{A} - \tilde{X}$ transition to the red in CF$_3$O$_2$ compare to CH$_3$O$_2$.

The red shift of the $\tilde{A} - \tilde{X}$ transition predicted in Table 3.1 for hydroperoxy with respect to the methyl peroxy is rather difficult to rationalize. As evident from hydroperoxy and methyl peroxy MO diagram shown on Fig. 3.5, there is no electron density sharing between hydrogen atom and the orbital on terminal oxygen because hydrogen 1s$\sigma$ orbital is involved completely in formation of the H–OO bond. Therefore $\pi^*$ SOMO orbital in hydroperoxy should have lower energy compare to methyl peroxy.

Hydroperoxy H–OO bond is formed by hydrogen $\sigma$ orbital and therefore completely different in nature from the alkyl peroxy C–O bond formed by carbon $\pi^*$ orbital. The experimentally determined peroxy bond energies listed in Table 3.2 show that H–OO bond is 5200 cm$^{-1}$ (62 kJ/mol) stronger than CH$_3$-OO bond. Therefore, in the first approximation, the HOMO in hydroperoxy should reside lower in energy than HOMO in methyl peroxy.

The above arguments for the SOMO/HOMO behavior are supported by theoretical calculations shown on Fig. 3.2. Ab initio results predict that both HOMO and SOMO orbitals in hydroperoxy will have lower energies with respect to their counterparts in methyl peroxy. Therefore it is difficult to estimate relative contribution of the HOMO and SOMO stabilization to the net orbital separation in hydroperoxy and draw a correlation with methyl peroxy orbital splitting. Experimentally observed and
Figure 3.4: Mulliken charges (in parenthesis) on corresponding atoms for CH$_3$O$_2$ and CF$_3$O$_2$. 
theoretically calculated red shift of the hydroperoxy $\tilde{A} - \tilde{X}$ transition is apparent indication that substitution of the H atom for the methyl group contributes more to the destabilization of the $\pi^*$ SOMO.

The second excited electronic state in the peroxy radicals is formed by electron promotion from the second lowest occupied (2HOMO) orbital to the half-filled (SOMO) orbital resulting in $^2A''$ electronic state. Fig. 3.5 shows that 2HOMO orbital is clearly $\pi$ in character, therefore withdrawal of the electron from the bonding orbital to the anti-bonding orbital will form dissociative $\tilde{B}$ state. $\tilde{B}^2A'' - \tilde{X}^2A''$ transition is common for all alkyl peroxies and resides in the UV region around 200-240 nm. Previously established correlation between peroxy SOMO/HOMO energy gap and $\tilde{A} - \tilde{X}$ transition frequency can be cross checked comparing the energy difference between SOMO and 2HOMO orbitals and experimental values for the $\tilde{B}^2A'' - \tilde{X}^2A''$ transition in various peroxy radical. Such a comparison is presented on Fig. 3.6 demonstrating that MO energy gap is a valid approximation for the frequency of electronic transition. *Ab initio* analysis predicts significant delocalization of the $\pi$ 2HOMO orbital density distribution for unsaturated peroxy radicals (compared to saturated ones) shifting the $\tilde{B} - \tilde{X}$ transition in vinyl peroxy to the near UV and phenyl peroxy to the visible region.

The potential energy surface for the ground state and the lowest excited electronic states of CH$_3$O$_2$ was examined in an early *ab initio* study. Cuts trough the potential energy surface for R(O–O) and R(C–O) internal coordinates are presented on Fig. 3.7. One can see that the $\tilde{A}^2A'$ state is non-dissociative along both R(O–O)
Figure 3.5: Molecular orbitals for the HO$_2$ and CH$_3$O$_2$ calculated at the BLYP/6-31+G* level.
Figure 3.6: (■) Difference in SOMO and HOMO eigenvalues in various peroxy radicals. (▲) Experimental values for the peroxy $B^2A'' - X^2A''$ transition: HO$_2$-210 nm (5.90 eV),$^1$ CH$_3$O$_2$-237 nm (5.23 eV),$^2$ C$_2$H$_5$O$_2$-240 nm (5.17 eV),$^2$ i-C$_3$H$_7$O$_2$-240 nm (5.17 eV),$^2$ t-C$_4$H$_9$O$_2$-240 nm (5.17 eV),$^2$ CF$_3$O$_2$-208 nm (5.96 eV)$^2$
and R(C−O) coordinates. Hence $\tilde{A}^2A' - \tilde{X}^2A''$ transition can be used to obtain rotationally and vibrationally resolved spectra. The equilibrium O–O bond length is somewhat longer in the $\tilde{A}$ state than that of in the $\tilde{X}$ state which is consistent with promotion of an electron from a slightly bonding to a antibonding orbital discussed earlier. The $\tilde{B}^2A''$ state is slightly bonded along R(C−O) coordinate and dissociative along O−O bond indicating methoxy radical and oxygen atom as primary dissociation products. The Gaussian width of the $\tilde{B} - \tilde{X}$ peroxy transition is $\sim 40$ nm with corresponding lifetime of $\sim 5$ fs. The $\tilde{B} - \tilde{X}$ transition can be used for peroxy detection but it is not suitable for spectroscopic studies due to the repulsive nature of the $\tilde{B}^2A''$ state.

Significant changes in the dipole moment functions calculated for the $\tilde{X}^2A''$ and $\tilde{A}^2A'$ states suggest that $\tilde{B} - \tilde{X}$ transition should be relatively strong. To the contrary, the dependence of the dipole moments on the changes in coordinates and dipole moments absolute values are similar for both $\tilde{X}^2A''$ and $\tilde{A}^2A'$ states indicating a weak $\tilde{A} - \tilde{X}$ transition moment. The latter transition can be viewed as a perturbed $a^1\Delta_g - X^3\Sigma_g^-$ transition in molecular oxygen. In O$_2$ this transition is extremely weak with a radiative lifetime of 76 min. Even thought interaction with alkyl group should result in a stronger transition, the $\tilde{A} - \tilde{X}$ transition moment in peroxy radicals is still expected to be quite small.
Figure 3.7: Potential energy slices along $R(C-O)$ and $R(O-O)$ internal coordinates in methyl peroxy$^3$
CHAPTER 4

Alkyl Peroxy Radicals

4.1 Introduction

There are a number of alkyl peroxy radicals defined by the nature of the R group, ranging from the simplest species, methyl (R=CH₃) peroxy to complex species with R containing at least 8-10 carbon atoms with correspondingly many structural isomers and conformers.

As was discussed in the introduction, Chapter I, peroxy radicals are key intermediates in both atmospheric chemistry and low temperature combustion. For example, the methyl peroxy radical CH₃O₂, one of the simplest members in the alkyl peroxy family, plays a critical role in the atmospheric oxidation of methane and cycles involving methane oxidation can produce up to four molecules of tropospheric ozone per one methane molecule.¹⁶ Larger alkyl peroxies formed in oxidation of longer chain alkanes are extremely important in combustion because they are prone to isomerization and can produce branching and propagation reaction routes.¹¹⁶

Investigation of simplest alkyl peroxy radicals may provide significant information for scientific community. From a theoretical point of view CH₃O₂ is a prototype for the whole peroxy family, and quality spectroscopic data may serve as a benchmark
for theoretical studies of other peroxies. For practical applications the well estab-
lished spectroscopy of the bound excited electronic state of the alkyl peroxies may be
extremely useful for monitoring their concentrations in complex systems containing
more than one type of peroxy radical. From pure spectroscopic point of view the
spectroscopy of the \( \tilde{A} \) state of the peroxy radicals is a very interesting yet practi-
cally untouched subject. The analysis of the vibrational structure will provide the
frequencies of the vibrational modes. The analysis of the rotational structure will
yield the geometry of the \( \tilde{A} \) and \( \tilde{X} \) states. Detailed spectroscopic investigations may
reveal a number of interesting spectroscopic features such as magnetic dipole induced
transitions and vibronic coupling between the \( \tilde{A} \) and \( \tilde{X} \) states.

Alkyl peroxy radicals kinetics and reaction mechanisms have been extensively
investigated using their strong \( \tilde{B}^2A'' - \tilde{X}^2A'' \) UV electronic transition.\(^1\) Previous
observations of the \( \tilde{A}^2A' - \tilde{X}^2A'' \) IR electronic transition of alkyl peroxy radicals
are limited to low resolution modulated absorption studies\(^2\)\(^7\) and experiments using
intra-cavity laser absorption spectroscopy.\(^2\)\(^9\) The emphasis of both studies was on
the observation of the spectra that can be attributed to the peroxy radical \( \tilde{A} - \tilde{X} \)
electronic transition and contain essentially no spectroscopic information. The
assignment of the observed bands was based on the production mechanism favoring
peroxy formation and transient nature of the detected signal.

The thermochemistry of methyl and ethyl peroxy radicals was investigated using
negative-ion photoelectron spectroscopy.\(^1\)\(^1\)\(^7\) Adiabatic electron affinities and values
for the \( \tilde{A} - \tilde{X} \) term energies were measured with 40 cm\(^{-1}\) accuracy. Also several
localized vibrational modes in the $\tilde{X}$ state were reported for both methyl and ethyl peroxy radicals. More systematic study of the CH$_3$O$_2$ ground state vibrational modes was reported recently using polarized infrared absorption spectroscopy combined with matrix isolation technique.$^{118}$ Ethyl peroxy radical gas phase spectrum in the region of 800 - 4000 cm$^{-1}$ was investigated using FTIR technique and several $\tilde{X}$ vibrational frequencies were assigned.$^{119}$ Finally, proof-of-principal report on measuring alkyl peroxy radical kinetics via their $\tilde{A} - \tilde{X}$ transition using CW cavity ring down spectroscopy was published recently$^{120}$ following the spectroscopic assignments reported earlier.$^{121}$

Infrared cavity ringdown spectra of the $\tilde{A}^2A' - \tilde{X}^2A''$ electronic transition for the methyl (CH$_3$O$_2$), ethyl (C$_2$H$_5$O$_2$) and isopropyl (2-C$_3$H$_7$O$_2$) peroxy radicals are presented in the following sections. Partially rotationally resolved spectra of CH$_3$O$_2$ and CD$_3$O$_2$ will be analyzed. Extensive spectroscopic and chemical arguments will be presented in support the assignment of the spectral carrier. Finally the CRDS technique will be used to observe methyl peroxy self reaction kinetics and determine methyl peroxy absorption cross section for the $\tilde{A}^2A' - \tilde{X}^2A''$ electronic transition.

4.2 Methyl and Ethyl Peroxy Radicals

4.2.1 Production

Excimer laser photolysis of ketones (acetone or 3-pentanone) at 193 nm was used as a primary source of corresponding alkyl radicals. As alternative precursors, methyl and
ethyl iodides were photolyzed at 248 nm. Perdeuterated isotopomers of acetone, 3-pentanone and methyl iodide were used to observe isotopically substituted methyl and ethyl peroxy radicals. All further presented spectroscopic features were observed with both photolysis of ketones and halides therefore supporting spectroscopic assignment of the observed features to the particular peroxy radical.

Experimentally, ketones appear to be much cleaner precursors. Photolysis of iodides results in formation of iodine crystals in the ringdown cell and photolysis of bromides tends to leave a brown deposit on photolysis windows. Therefore after several hours of operation the cell has to be taken apart and both photolysis windows and cell have to be cleaned. The photolysis pulse was fired approximately 100 $\mu$s before the dye laser, allowing time for peroxy radicals to be formed, but not enough time for them to recombine. The flow cell was filled with a mixture of 200 Torr Ne and 50 Torr $O_2$ plus 1-10 Torr of a precursor. The precursor was introduced into the cell by flowing pure Ne over the surface of the liquid precursor contained in the glass sample bomb. It was noticed that under present flow conditions equilibrium between flowing carrier gas and precursor molecules is not reached. Acetone has a vapor pressure of 180 Torr at room temperature, but only few Torr of the acetone was propagated to the cell. This estimate was made by comparing infrared acetone absorption under slow flow conditions and acetone absorption in the static cell. Therefore, for the low vapor pressure precursors, the sample bomb was emerged in the heated water bath. For example, the sample bomb with 3-pentanone was kept at 30 $^0$C to increase 3-pentanone vapor pressure from 90 Torr at room temperature to 270 Torr at 30 $^0$C.
4.2.2 CH$_3$O$_2$: Ab Initio Calculations

Methyl peroxy radical structure, vibrational modes and frequencies were investigated using ab initio methods. Geometry optimization on UHF/6-31+G(d) level has yielded geometrical structure and rotational constants for both $\tilde{A}^2A'$ and $\tilde{X}^2A''$ electronic states of the radical.

Figure 4.1: Geometry and orientation of the inertial axis for the methyl peroxy radical. Dashed lines represent the $C_S$ plane of symmetry.

Optimized geometrical parameters for the CH$_3$O$_2$ are provided in Table 4.1. Structures and inertial axis of the methyl peroxy radical and are shown on Fig. 4.1. The radical is near prolate top and $\tilde{A}$ and $\tilde{X}$ rotational constants for both CH$_3$O$_2$ and CD$_3$O$_2$ are given in Table 4.2. Methyl peroxy radical has only one minimum energy conformer. Calculations on the structure where one of the hydrogens is eclipsed with terminal oxygen resulted in a saddle point effectively representing barrier to the
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Table 4.1: Optimized geometrical parameters for the \( \tilde{X} \) and \( \tilde{A} \) states of CH\(_3\)O\(_2\). The labeling of the atoms is adapted from the radical structure provided on Fig. 4.1.

methyl group free rotation. The calculated value for the methyl torsion barrier in CH\(_3\)O\(_2\) is 292 cm\(^{-1}\) at B3LYP/6-31+G(d) level. Vibrational frequencies were calculated for both \( \tilde{A} \) and \( \tilde{X} \) states of CH\(_3\)O\(_2\) and CD\(_3\)O\(_2\). Resulted scaled values along with approximate mode descriptions based upon viewing the motion of the atoms with the gOpenMol software are listed in Table 4.3.

4.2.3 CH\(_3\)O\(_2\): Experimental Results

The experimental traces in the 7300 - 7700 cm\(^{-1}\) region taken when acetone was used as a precursor are shown in Fig. 4.2. The trace (A) on Fig. 4.2 was recorded with photolysis laser on and trace B on Fig. 4.2 was taken with photolysis laser off. Broad features on trace (B) are attributed to the acetone vibrational overtones and
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<th>CH$_3$O$_2$</th>
<th>CD$_3$O$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tilde{X}$</td>
<td>A</td>
<td>1.799</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>0.390</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>0.341</td>
</tr>
<tr>
<td>$\tilde{A}$</td>
<td>A</td>
<td>1.637</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>0.392</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>0.337</td>
</tr>
</tbody>
</table>

Table 4.2: UHF/6-31+G(d) rotational constants for the $\tilde{X}$ and $\tilde{A}$ states of CH$_3$O$_2$ and CD$_3$O$_2$ in cm$^{-1}$.

<table>
<thead>
<tr>
<th>CH$_3$O$_2$</th>
<th>$\tilde{X}$</th>
<th>$\tilde{A}$</th>
<th>CD$_3$O$_2$</th>
<th>$\tilde{X}$</th>
<th>$\tilde{A}$</th>
<th>Vib. mode and description</th>
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<tr>
<td>162</td>
<td>232</td>
<td>130</td>
<td>182</td>
<td>$A''$ CH$_3$ torsion</td>
<td></td>
<td></td>
</tr>
<tr>
<td>476</td>
<td>401</td>
<td>434</td>
<td>369</td>
<td>$A'$ C-O-O bend</td>
<td></td>
<td></td>
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<tr>
<td>947</td>
<td>914</td>
<td>839</td>
<td>823</td>
<td>$A'$ C-O stretch</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1138</td>
<td>1147</td>
<td>874</td>
<td>879</td>
<td>$A''$ CH$_3$ asym. deformation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1139</td>
<td>1058</td>
<td>991</td>
<td>964</td>
<td>$A'$ O-O stretch</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1196</td>
<td>1180</td>
<td>1046</td>
<td>1037</td>
<td>$A'$ H1-C-O bend</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1435</td>
<td>1434</td>
<td>1055</td>
<td>1047</td>
<td>$A'$ CH$_3$ umbrella motion</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1452</td>
<td>1450</td>
<td>1119</td>
<td>1065</td>
<td>$A''$ CH$_3$ asym. deformation</td>
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<td></td>
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<tr>
<td>1466</td>
<td>1478</td>
<td>1149</td>
<td>1116</td>
<td>$A'$ H2-C-H3 bend</td>
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<td>2886</td>
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<td>2066</td>
<td>2056</td>
<td>$A'$ CH$_3$ sym. stretch</td>
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<td>2183</td>
<td>$A''$ CH2+CH3 asym. stretch</td>
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<td>2977</td>
<td>2213</td>
<td>2210</td>
<td>$A'$ CH1 sym. stretch</td>
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<td></td>
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<td>ZPE$<em>{\tilde{A}}$ - ZPE$</em>{\tilde{X}}$</td>
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<td>-101</td>
<td>Difference in ZPE</td>
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<td></td>
</tr>
</tbody>
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Table 4.3: Scaled UHF/6-31+G(d) vibrational frequencies (in cm$^{-1}$) for the ground $\tilde{X}$ and excited $\tilde{A}$ states of CH$_3$O$_2$ and CD$_3$O$_2$. Scaling factor is 0.8953$^8$
combination bands and sharp features on trace (B) are ascribed to the rovibrational transitions of the residual water. Using deuterated methyl iodide as a precursor results in survey scans shown on Fig. 4.3. Traces (A) and (B) on Fig. 4.3 represent experimental conditions with photolysis on and photolysis off respectively. As one can notice there are no broad absorption features on trace (B) of Fig. 4.3 probably due to the red shift upon deuteration of precursor overtones and combination bands involving CH stretch vibration. The monotonic decrease of the broad background absorption from red to the blue region on trace (B) of Fig. 4.3 is attributed to the absorption profile of the cavity ringdown mirrors. Precursor absorption bands, water absorption lines and mirrors absorption are eliminated by applying the background subtraction procedure described earlier and the resulting spectra are shown on Fig. 4.4.

For the trace A of Fig. 4.4, acetone was photolyzed, and the lower frequency band therein is attributed to the $0_0^0$ origin band of the $\tilde{A}^2A' - \tilde{X}^2A''$ transition of methyl peroxy radical. This strong band is centered around 7382(1) cm$^{-1}$ which is in excellent agreement with 7375 cm$^{-1}$ value predicted for the $\tilde{A} - \tilde{X}$ electronic origin by high level G2 calculations.

The weaker transition to higher frequency is attributed to the transition involving the methyl torsion in the radical. According to the $ab\ inicial$ calculations presented in Table 4.3 the frequency of the $\nu_1$ torsional vibration of CH$_3$O$_2$ in the $\tilde{A}$ and $\tilde{X}$ electronic states is 232 cm$^{-1}$ and 162 cm$^{-1}$ respectively consistent with $\tilde{A}$ and $\tilde{X}$ bonds. Therefore $1^1$ vibronic transition from the ground electronic state to the first
Figure 4.2: Survey scan taken with photolysis of acetone. Traces (A) and (B) represent traces with photolysis on and photolysis off respectively.
Figure 4.3: Survey scans taken with photolysis of CD$_3$I
Figure 4.4: Spectra of CH$_3$O$_2$ (A) and CD$_3$O$_2$ (B) obtained after background subtraction procedure. The extra noise on the trace of protonated methyl peroxy is introduced by subtraction of a strong background absorption (see Fig. 4.2). For the sake of presentation the CH$_3$O$_2$ spectrum is shifted up by 800 ppm with respect to the zero baseline.
excited electronic state should be shifted by 70 cm\(^{-1}\) to the blue from the position of \(\tilde{A} - \tilde{X}\) electronic origin. The observed position of the weaker transition on trace A of Fig. 4.4 is 106(2) cm\(^{-1}\) to the blue with respect to the strong 0\(_0^0\) band which is in a good agreement with predicted value.

The \(1_1^1\) transition is allowed and its intensity depends on thermal population of the \(1_1\) level in the \(\tilde{X}\) state. According to the Boltzmann distribution the population of this level with respect to the vibrationless level is equal to \(\exp(-\nu_1/kT)\). Taking \textit{ab initio} value for \(\nu_1\) (162 cm\(^{-1}\)) results in 0.46 value for the Boltzmann factor at room temperature. Therefore \(1_1^1\) transition should be factor of 2 weaker than the origin transition. Indeed observed peak intensity of the torsional hot band is factor 2 to 3 weaker than that of the origin. \textit{Ab initio} frequency of the \(\nu_2\) vibration in the \(\tilde{X}\) state of methyl peroxy is almost 500 cm\(^{-1}\). With the Boltzmann factor of 0.1, the transitions originated from \(\nu_2\) level should be relatively weak.

For the trace B of Fig. 4.4, \(d6\) -acetone was used as a precursor. The strong feature centered around 7372(1) cm\(^{-1}\) is assigned to the origin transition of the CD\(_3\)O\(_2\). The strongest peak in this band is shifted to the red by 10(2) cm\(^{-1}\) with respect to the origin of protonated methyl peroxy. Table 4.3 shows that the difference between zero point energy levels in \(\tilde{A}\) and \(\tilde{X}\) states is -96 cm\(^{-1}\) for protonated methyl peroxy and -101 cm\(^{-1}\) for deuterated methyl peroxy. This change in zero point energies should result in 5 cm\(^{-1}\) red shift of methyl peroxy electronic origin upon deuteration. Observed 10(2) cm\(^{-1}\) red shift is in qualitative and acceptable quantitative agreement with \textit{ab initio} prediction.
The weaker band on trace B of Fig. 4.4 centered at 7451(1) cm\(^{-1}\) is the counterpart of the \(1^1\) torsional hot band observed in the protonated methyl peroxy spectrum. Based on the \textit{ab initio} calculations (Table 4.3), the frequency of the methyl torsion vibration in \(\tilde{A}\) and \(\tilde{X}\) states of CD\(_3\)O\(_2\) is equal to 182 cm\(^{-1}\) and 130 cm\(^{-1}\) respectively, predicting 52 cm\(^{-1}\) blue shift of the \(1^1\) transition with respect to the origin. The observed blue shift of the torsional hot band in deuterated methyl peroxy is 79(2) cm\(^{-1}\). As expected, the frequency of the methyl torsion vibration is lower for the CD\(_3\)O\(_2\) than that of for the CH\(_3\)O\(_2\) in both \(\tilde{A}\) and \(\tilde{X}\) states, resulting in smaller separation between origin and \(1^1\) transition.

Fig. 4.5 shows on an expanded scale a portion of the CH\(_3\)O\(_2\) spectrum. The experimental trace (A) clearly shows rotational structure. Unfortunately this structure is not completely resolved so that a line-by-line rotational assignment and analysis cannot be performed. It is well known that the analysis of rotational contours can provide rather detailed information about the rotational constants and ultimately the geometric structure of molecules. However a danger of such analysis lies in their lack of uniqueness. On occasion a contour analysis will produce a set of constants that will reproduce the spectrum, but are actually quite different from a second, correct set that also reproduces the spectrum well.

The simulation of the rotational structure was performed using SpecView\(^4\) spectral analysis program. Observed spectra were modelled with simple asymmetric rotor Hamiltonian and neglecting any centrifugal terms and any spin-rotation effects due to the doublet nature of the electronic state.
Figure 4.5: Spectra of CH$_3$O$_2$ radical from (A) the CRDS experiment, (C) a simulation using the *ab initio* rotational constants, and (B) a simulation designed to best reproduce the experimental spectrum by refining the *ab initio* rotational constants to best fit values. The best fit and the *ab initio* values for the rotational constants used in simulations are given in the Table 4.4.
Simulation of the observed $\tilde{A}^2A' - \tilde{X}^2A''$ rotational structure with the ab initio rotational constants is shown in trace C of Fig. 4.5. As traces A and C of Fig. 4.5 show, there is a good qualitative resemblance between the experimental spectrum and that predicted by the ab initio constants. However there are also clear discrepancies between the two. Now one can refine the ab initio rotational constants of both the $\tilde{A}$ and $\tilde{X}$ states to match the experimental spectrum. As shown in Fig. 4.5, traces A and B (simulated with the refined constants) are effectively indistinguishable within experimental variation. Analogous analysis of the partially rotationally resolved spectrum of $\tilde{A}^2A' - \tilde{X}^2A''$ electronic transition of CD$_3$O$_2$ is presented on Fig. 4.6. The values of the experimentally fit rotational constants used to simulate spectra in Fig. 4.5 and Fig. 4.6 are given in Table 4.4.

As with the ab initio values no error limits are indicated for the experimental values. Notwithstanding the fact that considerable analysis has been done to insure the “unique correctness” of the refined rotational constants, there is no absolute proof

<table>
<thead>
<tr>
<th>state</th>
<th>CH$_3$O$_2$</th>
<th>CD$_3$O$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tilde{X}$</td>
<td>A 1.716 (1.799)</td>
<td>1.296 (1.338)</td>
</tr>
<tr>
<td></td>
<td>B 0.384 (0.390)</td>
<td>0.332 (0.328)</td>
</tr>
<tr>
<td></td>
<td>C 0.348 (0.341)</td>
<td>0.290 (0.293)</td>
</tr>
<tr>
<td>$\tilde{A}$</td>
<td>A 1.528 (1.637)</td>
<td>1.182 (1.249)</td>
</tr>
<tr>
<td></td>
<td>B 0.391 (0.392)</td>
<td>0.340 (0.331)</td>
</tr>
<tr>
<td></td>
<td>C 0.345 (0.337)</td>
<td>0.288 (0.291)</td>
</tr>
</tbody>
</table>

Table 4.4: Experimentally fit rotational constants for the $\tilde{X}$ and $\tilde{A}$ states of CH$_3$O$_2$ and CD$_3$O$_2$ in cm$^{-1}$. Ab initio values for the rotational constants are given in parenthesis.
Figure 4.6: Spectra of CD$_3$O$_2$ radical from (A) the CRDS experiment, (C) a simulation using the \textit{ab initio} rotational constants, and (B) a simulation with refined rotation constants.
that these values represent the only set of rotational constants that reproduce the spectrum. However, probably more to the point the correlation among the constants, and the effects of neglecting spin-rotation interactions, are difficult to estimate. Nevertheless, the present experimental rotational constants will prove an excellent starting point for the analysis of the fully resolved rotational spectrum. Finally from the rotational analysis come accurate values for $T_{00}$ for CH$_3$O$_2$ and CD$_3$O$_2$ which are respectively 7382.8±0.5 and 7372.6±0.5 cm$^{-1}$. These values are in good agreement with the work of Hunziker et al.$^{27}$ (7375(6) cm$^{-1}$ for CH$_3$O$_2$) and with work of S. J. Blanksby et al.$^{117}$ (7372(40) cm$^{-1}$ for CH$_3$O$_2$ and 7364(32) cm$^{-1}$ for CD$_3$O$_2$), but of much higher precision.

Peroxy $\tilde{A}^2A' - \tilde{X}^2A''$ electronic transition involves promotion of the electron to the $\pi^*$ orbital on terminal oxygen thus resulting to the O–O stretching progression in the $\tilde{A}$ state. The frequency of the transition from the vibrationless level in the $\tilde{X}$ state to one quanta of O–O stretch excitation in the $\tilde{A}$ state is similar in all peroxies$^{27}$ ($\sim$900 cm$^{-1}$) and experimental observation of the O–O stretching band provides additional grounds for the assignment of peroxy spectra.

Using experimental conditions optimized for the methyl peroxy production, frequency region around 8300 cm$^{-1}$ has been searched and observed absorption band is shown in trace A of Fig. 4.7. The band is centered at 8270(1) cm$^{-1}$ which is in good agreement with the previously reported 8271(7) cm$^{-1}$ value for the position of the $\tilde{A}$ state O–O stretching vibration.$^{27}$ The separation between this band and the origin represents frequency of the O–O stretch in the $\tilde{A}$ state and is equal to 887(1) cm$^{-1}$. 

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Figure 4.7: Spectra of the O–O stretching vibration in the $\tilde{A}$ state of CH$_3$O$_2$ radical from (A) the CRDS experiment, (B) a simulation with fitted rotational constants.
Table 4.5: CH$_3$O$_2$ rotational constants used in the simulation of the O–O stretching band and electronic origin.

<table>
<thead>
<tr>
<th>cm$^{-1}$</th>
<th>X</th>
<th>A</th>
<th>A (O–O stretch)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.716</td>
<td>1.528</td>
<td>1.491</td>
</tr>
<tr>
<td>B</td>
<td>0.384</td>
<td>0.391</td>
<td>0.392</td>
</tr>
<tr>
<td>C</td>
<td>0.348</td>
<td>0.345</td>
<td>0.341</td>
</tr>
</tbody>
</table>

Fixing the rotational constants for the $\tilde{X}$ state to the values obtained from the fit of the origin band and adjusting the rotational constants for the excited vibrational state results in the simulation shown in trace B of Fig. 4.7. The simulation reproduces most of the features of the rotational contour reasonably well and rotational constants used in the simulation of the O–O stretching band and the electronic origin are given in Table 4.5.

The differences in the rotational constants shown in Table 4.5 represent geometrical changes in the methyl peroxy radical upon electronic and vibrational excitation. The most evident change is a decrease of the A rotational constant and it can be rationalized as follows. Excitation of the electron to the nonbonding orbital on the oxygen atom in the $\tilde{A} – \tilde{X}$ transition should result in increase of the OO bond length. This simple argument is in agreement with results of ab initio calculations presented in Table 4.1. Geometry optimization performed for the $\tilde{A}$ and $\tilde{X}$ states shows that the most significant change in methyl peroxy geometry occurs in the OO bond length and it is equal to 1.39Å for the $\tilde{A}$ state and 1.30Å for the $\tilde{X}$ state. According to the orientation of the methyl peroxy inertial axis shown on Fig. 4.1, an increase in the
OO bond length should result in a smaller rotational constant A. This effect is even more pronounced for the O–O stretching vibration in the $\tilde{A}$ state where in addition to the electronic excitation the equilibrium O–O bond length is increased due to the vibrational motion.

4.2.4 CH$_3$O$_2$ IR Absorption Cross Section

Besides spectroscopic observations, one experiment has been performed that demonstrates the potential of CRDS for monitoring the reactions of peroxy radicals. The laser frequency was set at the origin of the CH$_3$O$_2$ $\tilde{A}^2A' - \tilde{X}^2A''$ electronic transition. Then the decay of the absorption was measured as a function of time after the CH$_3$O$_2$ is produced by the photolysis of acetone by the excimer laser. This decay should be due almost entirely to radical-radical recombination. Defining the observed rate constant, $k_{obs}$, by:

$$\frac{d[CH_3O_2]}{dt} = -2k_{obs}[CH_3O_2]^2$$

(4.1)

and integrating yields:

$$\frac{[CH_3O_2]_0}{[CH_3O_2]} = 1 + 2k_{obs}[CH_3O_2]_0 t$$

(4.2)

The experimental results are plotted in this form in Fig. 4.8, which shows a good straight line as expected. Traces A and B in Fig. 4.8 correspond to different powers of the photolysis laser and, hence, different initial concentrations of methyl peroxy radicals. Methyl peroxy peak absorption at t=0 time was equal to 515 ppm for trace A and 349 ppm for trace B. From the slope, 2$k_{obs}[CH_3O_2]_0$, and the known$^1$ value of $k_{obs} = 4.9 \times 10^{-13}$ cm$^3$ s$^{-1}$, one can obtain the initial concentration, [CH$_3$O$_2$]$_0$. The
calculated methyl peroxy initial concentration is equal to $1.54 \times 10^{15}$ cm$^{-3}$ for the trace A and $0.96 \times 10^{15}$ cm$^{-3}$ for the trace B in Fig. 4.8. Combination of $[\text{CH}_3\text{O}_2]_0$ with the absolute absorption measurements yields an empirical peak absorption cross-section $\sigma \approx 2.7 \times 10^{-20}$ cm$^2$ for the origin under typical experimental conditions. While the precision of the experiments is considerably better, the estimated overall error in $\sigma$ is $\lesssim 50\%$, considering possible systematic errors such as inhomogeneities in radical production in the cell, etc. Additional experiments with a somewhat re-designed apparatus can significantly reduce these errors. There is always the possibility of other systematic errors, e.g., other radical reactions or peroxy radical diffusion out of the observation region. These possibilities have been considered in some detail and it has been concluded that they either make minor contributions or are ruled out completely by the time scale and the concentration dependence of the plots of Fig. 4.8.

The value for $\sigma$ is about an order of magnitude greater than that expected for the strongest rotational transition of CH$_3$O$_2$ assuming the same oscillator as reported for HO$_2$. However the observed $\sigma$ is very consistent with the rotational simulations which indicate that the strong peak in the origin band corresponds to the superposition of 10-20 rotational transitions. While $\sigma$ is rather small for an allowed electronic transition, the fact that it is about an order of magnitude larger than might have been anticipated is encouraging for the use of CRDS spectroscopy to monitor peroxy radical reactions in applications relevant to both atmospheric and combustion related hydrocarbon oxidation.
Figure 4.8: Methyl peroxy radical decay plots of the form of Eq. 4.2. Relative concentrations of CH$_3$O$_2$ are determined by the ratio of absorption at various times to that at $t = 0$. Plot (A) corresponds to an initial, net absorption of 515 ppm and (B) to 349 ppm.
### 4.2.5 $\text{C}_2\text{H}_5\text{O}_2$: Experimental Results

Photolysis of 3-pentanone and deuterated iodoethane coupled with the background subtraction procedure resulted in the spectra shown in Fig. 4.9. The spectrum in trace A in Fig. 4.9 is assigned to the origin of the $\tilde{A}^2A' - \tilde{X}^2A''$ transition in protonated ethyl peroxy radical and the spectrum in trace B in Fig. 4.9 is attributed to the origin of the $\tilde{A}^2A' - \tilde{X}^2A''$ transition in the deuterated ethyl peroxy radical. Both ethyl peroxy isotopomers have several low lying vibrational modes populated at room temperature which can lead to the multiple hot band transitions overlapping with the electronic origin. Overall both spectra exhibit limited resolved rotational structure preventing further rotational analysis.

The position of the sharpest feature (presumably Q branch) is $7591(1)$ cm$^{-1}$ in the ethyl peroxy spectrum and $7595(1)$ cm$^{-1}$ in the spectrum of deuterated analog of thereof. Previously reported value\textsuperscript{27} for the $\tilde{A} - \tilde{X}$ origin of the $\text{C}_2\text{H}_5\text{O}_2$ is $7593(6)$ cm$^{-1}$ and it agrees well with presented experimental observations.

### 4.3 Summary

A relatively broad spectral scan with three traces illustrating absorptions assigned to methyl peroxy, ethyl peroxy and isopropyl peroxy radicals is shown in Fig. 4.10. Traces B and C show a second, weaker absorption at lower frequency, which one can assign in part to CH$_3$O$_2$ due to its close resemblance to the origin band shown in trace A. The source of CH$_3$O$_2$ in traces B and C is not well determined, but the simplest explanation is that it is produced as a by-product of the reaction yielding mainly
Figure 4.9: Absorption spectra of the $\tilde{A}^2A' - \tilde{X}^2A''$ electronic transition in $\text{C}_2\text{H}_5\text{O}_2$ (A) and $\text{C}_2\text{D}_5\text{O}_2$ (B) peroxy radicals.
Figure 4.10: Experimental CRDS spectra following photolysis of acetone (A), 3-pentanone (B) and 2-bromo-2-methylpropane (C). In the top trace the origin band of methyl peroxy radical is indicated; the feature to higher frequency arises from a “hot” methyl torsional transition. In the traces (B) and (C) the origins of the ethyl and isopropyl peroxy radicals are indicated. At the low frequency end of those traces there are several weaker absorptions that have been determined experimentally to arise from the reaction of the photolysis products of 3-pentanone or 2-bromo-2-methylpropane with O₂. Almost certainly part of these absorptions is due to CH₃O₂ but there appears as well to be other lines not attributable to CH₃O₂.
C$_2$H$_5$O$_2$, with the most probable source of the by-product arising from production of methyl radical in the initial photolysis step. In any case trace B demonstrates the importance of having a spectroscopic technique that is capable of distinguishing between the various alkyl peroxy radicals.
CHAPTER 5

Fluorinated Methyl Peroxy Radical

5.1 Introduction

Great interest has been generated over the atmospheric destruction mechanisms for chlorofluorohydrocarbons (CFCs) because of their role in the stratospheric reduction of ozone.\textsuperscript{17–19} Indeed alternate hydrofluorocarbons (HFCs) have now been introduced to replace many of the now banned chlorofluorocarbons (CFCs). The initial steps in degradation\textsuperscript{122–124} of either a CFC or an HFC will involve the production of an alkyl radical that will react with O\textsubscript{2} via a 3-body process to form the corresponding alkyl peroxy radical, R′O\textsubscript{2}, where R′ denotes a partially or fully fluorinated alkyl group. The resulting peroxy radicals are in turn involved\textsuperscript{1,125} in a variety of chemistry with other atmospheric molecules including O\textsubscript{3}, NO, and NO\textsubscript{2}.

Almost all the spectroscopic and diagnostic work involving the fluorinated or non-fluorinated alkyl peroxy radicals has involved their UV $\tilde{B} - \tilde{X}$ electronic transition. This transition is quite broad ($\approx$40nm) and centered about 240 and 220 nm for the alkyl and fluorinated alkyl radicals respectively.\textsuperscript{26} Generally speaking, it is possible to distinguish between the UV absorption of an alkyl compare to a fluorinated alkyl peroxy radical, but it is nearly impossible to distinguish the nature of the R′ group.
among the R′O2 radicals on the basis of their UV absorption spectra. For HO2 itself\textsuperscript{30,126} and the alkyl peroxy radicals,\textsuperscript{27,29} there were limited gas phase observations of the $\tilde{A} - \tilde{X}$ transition prior to the CRDS experiments. However for the fluorinated analogues there appears to have been no such observations. Indeed the known spectroscopy, other than the aforementioned broad UV transition of the R′O2 radicals, appears limited to vibrational studies\textsuperscript{127–131} in the $\tilde{X}$ state using matrix isolation techniques and to EPR studies of the radicals in solution.\textsuperscript{132}

Because of the importance of the fluorinated alkyl peroxy radicals, it was decided to search for the IR $\tilde{A} - \tilde{X}$ transition of CF$_3$O$_2$ using the CRDS technique. To narrow the region of this search \textit{ab initio} calculations for the $\tilde{A}$ and $\tilde{X}$ states of the CF$_3$O$_2$ radical have been carried out and results are presented in Chapter 5.3.

The following sections describe the first observation of the $\tilde{A} - \tilde{X}$ spectrum of the simplest R′O2 radical, CF$_3$O$_2$. T$_{00}$ for the transition and a couple of vibrational frequencies in the $\tilde{A}$ state have been deduced. In addition the recombination kinetics of CF$_3$O$_2$ has been briefly studied using CRDS as a monitor of CF$_3$O$_2$ concentration.

### 5.2 Production of the CF$_3$O$_2$ Radical

In the experiments CF$_3$O$_2$ radicals were produced via KrF excimer laser photolysis of the trifluoroacetic anhydride (or in a few cases CF$_3$I) in the presence of O$_2$. Both (CF$_3$CO)$_2$O and CF$_3$I are known precursors for the photolytical production of trifluoromethyl radical,\textsuperscript{88,90,133} though (CF$_3$CO)$_2$O appears to be much cleaner source and more convenient to work with. (CF$_3$CO)$_2$O was introduced into the cell by seeding it
into the nitrogen in a glass bulb. The concentration of the trifloromethyl iodide was controlled by the needle valve. There are several steps involved in the production of a detectable concentration of CF$_3$O$_2$. The initiation step for peroxy radical production is to first generate the CF$_3$ radical by photolysis of trifluoroacetic anhydride,

$$(CF_3CO)_2O \xrightarrow{248\text{nm}} 2CF_3 + CO + CO_2$$ (5.1)

The photolytic production of CF$_3$ takes place in the presence of O$_2$ and N$_2$, followed by the 3-body CF$_3$O$_2$ formation reaction and radical − radical recombination reactions occurred simultaneously:

$$CF_3 + O_2 + N_2 \xrightarrow{k_p} CF_3O_2 + N_2, \quad k_p = 8.5 \cdot 10^{-12}\text{cm}^3/\text{mol} \cdot \text{s}$$ (5.2)

$$CF_3 + CF_3 \xrightarrow{k_{r1}} C_2F_6, \quad k_{r1} = 2.5 \cdot 10^{-11}\text{cm}^3/\text{mol} \cdot \text{s}$$ (5.3)

$$CF_3 + CF_3O_2 \xrightarrow{k_{r2}} CF_3O + CF_3O, \quad k_{r2} = 1.1 \cdot 10^{-11}\text{cm}^3/\text{mol} \cdot \text{s}$$ (5.4)

$$CF_3O_2 + CF_3O_2 \xrightarrow{k_d} \text{products}, \quad k_d = 3.1 \cdot 10^{-12}\text{cm}^3/\text{mol} \cdot \text{s}$$ (5.5)

The O$_2$ partial pressure in the cell is 50 Torr and that of N$_2$ 300 Torr. The partial pressure of (CF$_3$CO)$_2$O is 1 Torr. The reported absorption cross section for the trifluoroacetic anhydride is 2.5 · 10$^{-19}$ cm$^2$ at 248 nm. With a photon flux of 4 · 10$^{16}$ cm$^{-2}$ about 1% of the (CF$_3$CO)$_2$O is photolyzed to produce CF$_3$ radicals. Using the above kinetic model and reported values for the rate constants one can compute the expected evolution of CF$_3$O$_2$ in the cell. As plot A of Fig. 5.1 shows, a nearly steady concentration of $\approx 7 \times 10^{14}$ radicals/cm$^3$ should be achieved in less than 1µsec after the photolysis laser pulse.
Figure 5.1: Simulated concentration profiles for the CF$_3$O$_2$ generation (A) and recombination (B). For the simulations the following initial concentration are chosen: [O$_2$]=50 Torr, [(CF$_3$CO)$_2$O]=1 Torr with photolysis fragmentation yield of 1%. No first order losses on the walls were taken into account.
At presented experimental conditions the dominant decay mode of CF$_3$O$_2$ radicals should occur via reaction Eq. 5.5. Products of this self-reaction may initiate rather complex reaction mechanism,\textsuperscript{20} however an effective value for the apparent second order recombination $k_d$ has been reported.\textsuperscript{134} Using this value for $k_d$ leads to the expected decay profile shown on plot B of Fig. 5.1.

The most important point to be gleaned from plots A and B on Fig. 5.1 is that one would expect a nearly constant concentration of CF$_3$O$_2$ radicals in photolysis cell between 1-100 $\mu$s after the photolysis pulse. During this time cavity ringdown spectroscopy can easily be carried out on CF$_3$O$_2$. Once a spectral feature has been identified the relative concentration of CF$_3$O$_2$ as a function of time can easily be followed by varying the delay between firing the photolysis and spectroscopic lasers on the millisecond time scale. Such results are illustrated in Fig. 5.6 and will be discussed in more detail below.

5.3 \textit{Ab Initio} Calculations

As mentioned in the introduction, there have been no experimental observation involving the $\tilde{A}^2A' - \tilde{X}^2A''$ transition of CF$_3$O$_2$ or any other of the fluorinated alkyl peroxy radicals. Therefore one has to turn to \textit{ab initio} calculations for guidance concerning this transition.
Alkyl peroxy radicals have been the subject of a number\textsuperscript{103,104,106,107,135} of \textit{ab initio} studies. However theoretical calculations on structure and vibrational frequencies of halogenated peroxy radicals are limited to a few \textit{ab initio} studies.\textsuperscript{136–139} Therefore, geometry optimization and vibrational frequency calculations for both the $\tilde{A}^2A'$ and $\tilde{X}^2A''$ states of CF$_3$O$_2$ have been performed on UHF/6-31+G(d) level. Optimized geometries and rotational constants for both $\tilde{A}$ and $\tilde{X}$ states are given in Table 5.3 and Table 5.2 respectively. Calculated vibrational frequencies are provided in Table 5.3. The qualitative mode descriptions are based upon viewing the motion of the atoms with the gOpenMol software and structure of the trifluoromethyl radical is shown on Fig. 5.2. The results of the calculations are consistent with the $C_s$ symmetry assumed for the state symbols.

Figure 5.2: Structure of the trifluoromethyl radical
Table 5.1: UHF/6-31+G(d) optimized geometrical parameters and relative energy for the \( \tilde{X} \) and \( \tilde{A} \) states of CF\(_3\)O\(_2\). Atom labeling is consistent with radical structure provided on Fig. 5.2

<table>
<thead>
<tr>
<th>UHF/6-31+G(d)</th>
<th>Coordinate</th>
<th>( \tilde{X} )</th>
<th>( \tilde{A} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>bond length (Å)</td>
<td>OO</td>
<td>1.314</td>
<td>1.368</td>
</tr>
<tr>
<td></td>
<td>CO</td>
<td>1.373</td>
<td>1.357</td>
</tr>
<tr>
<td></td>
<td>CF(_1)</td>
<td>1.302</td>
<td>1.301</td>
</tr>
<tr>
<td></td>
<td>CF(_2)</td>
<td>1.306</td>
<td>1.310</td>
</tr>
<tr>
<td></td>
<td>CF(_3)</td>
<td>1.306</td>
<td>1.310</td>
</tr>
<tr>
<td>bond angles (deg.)</td>
<td>COO</td>
<td>110.8</td>
<td>110.4</td>
</tr>
<tr>
<td></td>
<td>F(_1)CO</td>
<td>106.0</td>
<td>106.2</td>
</tr>
<tr>
<td></td>
<td>F(_2)CO</td>
<td>111.2</td>
<td>111.7</td>
</tr>
<tr>
<td></td>
<td>F(_3)CO</td>
<td>111.2</td>
<td>111.7</td>
</tr>
<tr>
<td>dihedral angles (deg.)</td>
<td>F(_1)COO</td>
<td>180</td>
<td>180</td>
</tr>
<tr>
<td></td>
<td>F(_2)COO</td>
<td>60.7</td>
<td>60.5</td>
</tr>
<tr>
<td></td>
<td>F(_3)COO</td>
<td>-60.7</td>
<td>-60.5</td>
</tr>
</tbody>
</table>

Table 5.2: UHF/6-31+G(d) rotational constants for the \( \tilde{X} \) and \( \tilde{A} \) states of CF\(_3\)O\(_2\).

<table>
<thead>
<tr>
<th>cm(^{-1})</th>
<th>( \tilde{X} )</th>
<th>( \tilde{A} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.1931</td>
<td>0.1929</td>
</tr>
<tr>
<td>B</td>
<td>0.1122</td>
<td>0.1110</td>
</tr>
<tr>
<td>C</td>
<td>0.1109</td>
<td>0.1096</td>
</tr>
</tbody>
</table>

Table 5.1: UHF/6-31+G(d) optimized geometrical parameters and relative energy for the \( \tilde{X} \) and \( \tilde{A} \) states of CF\(_3\)O\(_2\). Atom labeling is consistent with radical structure provided on Fig. 5.2

Table 5.2: UHF/6-31+G(d) rotational constants for the \( \tilde{X} \) and \( \tilde{A} \) states of CF\(_3\)O\(_2\).
<table>
<thead>
<tr>
<th>Symmetry</th>
<th>$\tilde{X}$</th>
<th>$\tilde{A}$</th>
<th>Vib. mode and description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A'$</td>
<td>1320</td>
<td>1311</td>
<td>1 CF$_3$ sym. stretch</td>
</tr>
<tr>
<td>$A'$</td>
<td>1240</td>
<td>1248</td>
<td>2 C-O stretch</td>
</tr>
<tr>
<td>$A'$</td>
<td>1128</td>
<td>1048</td>
<td>3 O-O stretch</td>
</tr>
<tr>
<td>$A'$</td>
<td>876</td>
<td>865</td>
<td>4 CF$_3$ sym. stretch</td>
</tr>
<tr>
<td>$A'$</td>
<td>686</td>
<td>667</td>
<td>5 CF$_3$ sym. deformation</td>
</tr>
<tr>
<td>$A'$</td>
<td>570</td>
<td>572</td>
<td>6 CF$_3$ umbrella motion</td>
</tr>
<tr>
<td>$A'$ ($\nu_7 \sim 3%$)</td>
<td>442</td>
<td>432</td>
<td>7 CF$_3$ rock(in plane)</td>
</tr>
<tr>
<td>$A'$ ($\nu_8 \sim 5%; 2\nu_8 \sim 1%$)</td>
<td>278</td>
<td>256</td>
<td>8 COO bend</td>
</tr>
<tr>
<td>$A''$</td>
<td>1266</td>
<td>1254</td>
<td>9 CF$_3$ asym. stretch</td>
</tr>
<tr>
<td>$A''$</td>
<td>592</td>
<td>599</td>
<td>10 CF$_3$ asym. deformation</td>
</tr>
<tr>
<td>$A''$ ($\nu_{11} \sim 3%$)</td>
<td>421</td>
<td>426</td>
<td>11 CF$_3$ rock(out of plane)</td>
</tr>
<tr>
<td>$A''$ ($\nu_{12} \sim 12%; 2\nu_{12} \sim 6%$)</td>
<td>126</td>
<td>116</td>
<td>12 CF$_3$ torsion</td>
</tr>
</tbody>
</table>

Table 5.3: Scaled (by factor 0.8953)$^8$ vibrational frequencies (in cm$^{-1}$) for ground $\tilde{X}$ and excited $\tilde{A}$ states of CF$_3$O$_2$. Boltzmann populations at 300K for the four lowest lying vibronic levels for the $\tilde{X}$ state are provided in parenthesis. Population of the vibrationless level is 20%.
Accurate prediction of the excited electronic energy levels has always been a challenge for the \textit{ab initio} calculations. However, the origin frequencies of the $\tilde{A} - \tilde{X}$ electronic transition calculated at the G2 level of theory for various alkyl peroxy radicals are in excellent agreement with experimentally observed values (see Chapter IV). Encouraged by the success of the G2 level of theory on alkyl peroxy radicals, \textit{ab initio} energy calculations have been performed using GAUSSIAN98 for the trifluoromethyl peroxy radical. The calculated frequencies for the $T_{00}$ transitions are listed in Table 5.4, along with the experimental results for several alkyl peroxy radicals.

### Table 5.4: Calculated using G2 method and observed frequencies ($T_{00}$) of electronic origins of $\tilde{A} - \tilde{X}$ transitions of various peroxy radicals. (a) This work.

<table>
<thead>
<tr>
<th></th>
<th>$T_{00}$, cm$^{-1}$</th>
<th>CF$_3$O$_2$</th>
<th>HO$_2$</th>
<th>CH$_3$O$_2$</th>
<th>C$_2$H$_5$O$_2$</th>
<th>i-C$_3$H$_7$O$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>\textit{Ab initio}</td>
<td>6703</td>
<td>7061</td>
<td>7372</td>
<td>7355</td>
<td>7771</td>
<td></td>
</tr>
<tr>
<td>Experiment</td>
<td>6656(3)(a)</td>
<td>7029.68(2)</td>
<td>7382.8 (0.5)</td>
<td>7591(1)</td>
<td>7568(1)</td>
<td></td>
</tr>
</tbody>
</table>

Accurate prediction of the excited electronic energy levels has always been a challenge for the \textit{ab initio} calculations. However, the origin frequencies of the $\tilde{A} - \tilde{X}$ electronic transition calculated at the G2 level of theory for various alkyl peroxy radicals are in excellent agreement with experimentally observed values (see Chapter IV). Encouraged by the success of the G2 level of theory on alkyl peroxy radicals, \textit{ab initio} energy calculations have been performed using GAUSSIAN98 for the trifluoromethyl peroxy radical. The calculated frequencies for the $T_{00}$ transitions are listed in Table 5.4, along with the experimental results for several alkyl peroxy radicals.

### 5.4 Experimental Results

#### 5.4.1 Spectral Observations

Guided by the predicted value for the $\tilde{A}^2A' - \tilde{X}^2A''$ electronic transition of CF$_3$O$_2$ the region around 6700 cm$^{-1}$ have been searched. The experimental trace is shown in a trace A of Fig. 5.3. The observed band is centered at 6656 cm$^{-1}$ with an uncertainty of ±3 cm$^{-1}$ which reflects an uncertainty in associating $T_{00}$ with the peak of the contour. There is very good agreement between experimental and calculated 6703 cm$^{-1}$ \textit{ab initio} value for $T_{00}$ listed in Table 5.4. And observed spectral feature appears only
with the simultaneous presence of the excimer photolysis radiation, organic precursor, and oxygen. The \textit{ab initio} calculations for CF$_3$O$_2$ show (see Table 5.1) that upon excitation from the $\tilde{X}$ to the $\tilde{A}$ state the O–O bond distance increases, thus likely leading to an O–O stretch progression. Previously observed non-fluorinated peroxy radicals exhibit this stretching progression with a frequency of approximately 900 cm$^{-1}$ in the $\tilde{A}$ state.$^{27}$ The experimental scan in the region of 7600 cm$^{-1}$ is presented in trace B of Fig 5.3. The close resemblance of the bands in traces A and B in Fig. 5.3 allows us to attribute them to the same molecular species, and lends strong confirmation that the species observed is the CF$_3$O$_2$ radical. Further confirmation is obtained by observing weakly but reproducibly the first overtone of the O–O stretch as shown in trace C of the Fig. 5.3. Using the observed frequencies ($T_{00}+980(5)$ and $T_{00}+1946(5)$ cm$^{-1}$) yield value of $\omega_e = 994(5)$ cm$^{-1}$ and $\omega_e x_e = 7(5)$ cm$^{-1}$ for the O–O stretch.

A simulation of the observed $\tilde{A} - \tilde{X}$ rotational contour generated by SpecView spectral analysis program$^4$ is presented in a trace A of Fig 5.4. The simulation was obtained using the rotational constants from the \textit{ab initio} calculations given in Table 5.2.

As trace C of Fig. 5.4 shows, there are some similarities as well as clear discrepancies between the experimental spectra and the solid line in the Fig 5.4A. The difference between the \textit{actual} and the \textit{ab initio} rotational constants will affect somewhat the shape of the contour and lack of resolved rotation structure prevents precise analysis. However, several important features on the shoulders of the experimental band can
Figure 5.3: Experimental CRDS spectra following photolysis of trifluoroacetic anhydride. (A) Origin of $A^2A' - \tilde{X}^2A''$ electronic transition of CF$_3$O$_2$; (B) The fundamental of the O–O stretch; (C) First overtone of the O–O stretch.
not be explained by any reasonable change in the rotational constants but rather by the population of the low lying vibrational levels. At room temperature (see Table 5.3) several excited vibrational levels of the ground electronic state have a population comparable to that of for the vibrationless level. The change in these low lying ($\nu_7$, $\nu_8$, $\nu_{11}$, $\nu_{12}$) vibrational frequencies between $\tilde{A}$ and $\tilde{X}$ states predicted from \textit{ab initio} calculations is but a few wavenumbers. Thus one has to expect transitions from vibrational hot bands to contribute to the observed contour. As Fig. 5.4B shows, the experimental spectrum is well reproduced when vibrational hot bands (dashed lines in Fig 5.4A) are included.

As Fig. 5.5 shows, a band at 1192(5) cm$^{-1}$ to the blue of the electronic origin is observed and tentatively assigned as the fundamental of the C–O stretch. The basis for this assignment is as follows. Turning to Table 5.3 one can note that the O–O stretch frequency is estimated to be about 7% high by the \textit{ab initio} calculations. Assuming the same error in C–O stretch prediction suggests the actual value the actual value should be near 1160 cm$^{-1}$, which is in a good agreement with the experimental observation. Furthermore, the \textit{ab initio} computations shown in Table 5.3 suggest that the most significant changes in molecular geometry between $\tilde{A}$ and $\tilde{X}$ states take place in the O–O bond length (1.368Å in $\tilde{A}$ and 1.314Å in $\tilde{X}$) and C–O bond lengths (1.357Å in $\tilde{A}$ and 1.373Å in $\tilde{X}$) compared to the C–F bond lengths (1.310Å in $\tilde{A}$ and 1.306Å in $\tilde{X}$) and COO bond angle (110.4$^0$ in $\tilde{A}$ and 110.8$^0$ in $\tilde{X}$). Thus vibrations associated with the O–O and C–O stretching motion are anticipated to be most active ones in the spectrum.
Figure 5.4: Observed and simulated rotational contour of the origin region of the $\tilde{A}^2A'$ – $\tilde{X}^2A''$ electronic transition of CF$_3$O$_2$ radical. (A) Solid line - ambient temperature simulation using \textit{ab initio} rotational constants from Table 5.2. Dashed lines - three vibrational hot bands. The positions and relative peak intensities (in parenthesis) of the hot bands with respect to the origin are 30 cm$^{-1}$ (0.27) to the red, 6 cm$^{-1}$ (0.25) to the blue, 21 cm$^{-1}$ (0.18) to the blue. The relative spectral offsets and intensities of the hot bands were adjusted to optimize spectral simulation. Rotational constants are assumed to be the same for the origin and hot bands. (B) Sum of the origin and vibrational hot bands. (C) Experimental spectra of CF$_3$O$_2$ radical.
Figure 5.5: Spectral scan over the region of O–O stretch. The feature at higher frequency is tentatively assigned to the fundamental of the C–O stretch.
5.4.2 CF$_3$O$_2$ Decay Kinetics

The integrated form of the rate equation for Eq. 5.5 can be written as:

$$\frac{[CF_3O_2]_0}{[CF_3O_2]} = 1 + 2k_d [CF_3O_2]_0 t$$  (5.6)

The quantity on the LHS of Eq. 5.6 is easily obtained by taking the ratio of the CRDS absorption (proportional to $[CF_3O_2]$) at $t = 0$, i.e., $t \leq 10 \mu$sec and the absorption at time $t$ later, where $t$ measures the time between the photolysis laser pulse and the spectroscopic laser pulse.

As Fig. 5.6 shows the experimental data points yield, as expected, a good straight line whose slope is $2k_d [CF_3O_2]_0$. If the reported value of $k_d = 3.1 \times 10^{-12}$ cm$^3$/mol s is used one can deduce an experimental value of $[CF_3O_2]_0 = 6.5 \cdot 10^{14}$ mol/cm$^3$, a value very consistent with the initial estimate as shown on Fig. 5.1.

In principle the derived value of $[CF_3O_2]_0$, along the experimental value of the CRDS absorption, allows the deduction of an empirical peak absorption cross-section ($\sigma_p$) for CF$_3$O$_2$ of $\sigma_p \approx 6 \cdot 10^{-21}$ cm$^2$. However the factor of 2 range in the reported value for $k_d^{20}$ makes the reliability of $\sigma_p$ not particularly high. However it does appear that under the present conditions $\sigma_p$ for CF$_3$O$_2$ is the same order of magnitude, but probably somewhat smaller than $\sigma_p$ ($2.7 \cdot 10^{-20}$ cm$^2$ for CH$_3$O$_2^{121}$).

Taking into account all the above mentioned spectroscopic, computational and kinetic evidence the 6656(3) cm$^{-1}$ band can be confidently assigned to the origin of the $\tilde{A}^2A' - \tilde{X}^2A''$ electronic transition of CF$_3$O$_2$. 

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Figure 5.6: Temporal profile of the CF$_3$O$_2$ degradation with experimental data points from the CRDS experiment.
5.5 Conclusions

It was demonstrated that CRDS spectroscopy can be used to detect the $\tilde{A}^2A' - \tilde{X}^2A''$ electronic transition of the fluorinated alkyl peroxy radicals in the near IR. A sharp structured electronic spectrum for the trifluoromethyl peroxy radical is observed for the first time. The partially resolved rotational contours in the origin region has been well simulated using \textit{ab initio} rotational constants, once hot bands arising from low-lying, thermally populated levels are considered. The spectral analysis yields $T_{00}$ as well as the $\tilde{A}$ state vibrational frequencies for the $O-O$ and $C-O$ stretch.

A series of experiments where the time is varied between photolysis laser initialization and CRDS laser detection, demonstrates the capability of CRDS to monitor CF$_3$O$_2$ for kinetic studies. These observations determine absolute concentration of CF$_3$O$_2$ in the experiments and provide an estimate for its absorption cross-section.
CHAPTER 6

Acetyl Peroxy Radicals

6.1 Introduction

Acetyl peroxy \( \text{CH}_3 \text{C(O)O}_2 \) radical is one of the most abundant and important organic peroxy radicals in the atmosphere.\(^{140}\) Atmospheric oxidation or upper tropospheric photolysis of a variety of oxygen containing organic compounds - acetone, acetaldehyde, methyl glyoxal, etc. can lead to the formation\(^{141,142}\) of the acetyl peroxy radical, \( \text{CH}_3 \text{C(O)O}_2 \). This radical, as well as other peroxy radicals, plays a significant role in many key atmospheric processes.\(^{11,143}\) It can affect ozone destruction in the stratosphere by linking odd O cycles. Peroxy radical participation in tropospheric NO\(_x\) cycles is considered to be a major source of tropospheric ozone production. Acetyl peroxy reaction with HO\(_2\) is believed to be responsible for acid rain formation and can also lead to the production of ozone and atomic oxygen.\(^{92,144}\) Fast acetyl peroxy self-reaction results in the generation of methyl peroxy radical,\(^{145,146}\) another very important intermediate in atmospheric chemistry.

Acetyl peroxy radicals are of particular importance in polluted atmospheres as they react with NO\(_2\) and form peroxy acetyl nitrate (PAN). PAN has been identified as a key component in photochemically generated smog.\(^{147}\) It can irritate eyes and
damage crops.\textsuperscript{148,149} PAN has a relatively high stability to thermal decomposition compared to other peroxy nitrates\textsuperscript{94} and therefore it can serve as an efficient reservoir for both CH\textsubscript{3}C(O)O\textsubscript{2} and NO\textsubscript{2}. PAN can be transported from sources of pollution to remote locations or to the upper troposphere where it decomposes photolytically,\textsuperscript{150} to regenerate the reactive radicals.

Similar to the other members of the peroxy family, the vast majority of the spectroscopic and kinetic research on acetyl peroxy radical has been performed using its UV $\tilde{B}^2A'' - \tilde{X}^2A''$ electronic transition.\textsuperscript{19} This transition is broad and structureless due to the repulsive nature of the $\tilde{B}$ state, which makes it inapplicable for rotational or vibrational spectroscopic analysis. Despite its large absorption cross sections ($\sim 10^{-18}$ cm\textsuperscript{2}), kinetic experiments of a mixture of peroxy radicals become compromised because nearly all peroxies have nearly superimposed $\tilde{B} - \tilde{X}$ UV bands.\textsuperscript{26}

In the following sections observation of $\tilde{A}^2A' - \tilde{X}^2A''$ electronic transition of acetyl peroxy radical using IR CRDS apparatus is presented. A recently suggested source of chlorine atoms is implemented in the acetyl peroxy production scheme. To facilitate spectroscopic assignment, \textit{ab initio} calculations for the $\tilde{A}$ and $\tilde{X}$ states of the \textit{cis} and \textit{trans} conformers of acetyl peroxy radical have been carried out to predict geometry, vibrational frequencies and the transition frequency $T_{00}$ for the electronic origin.
6.2 Acetyl Peroxy Production and Kinetics

Photolysis of $(\text{COCl})_2$ in $\text{CH}_3\text{CHO}/\text{O}_2/\text{N}_2$ mixture has been used to produce acetyl peroxy radicals. The reaction mechanism is likely

\[
(COCl)_2 \xrightarrow{193\,\text{nm}} 2\text{Cl} + 2\text{CO} \tag{6.1}
\]

\[
\text{CH}_3\text{CHO} + \text{Cl} \rightarrow \text{CH}_3\text{CO} + \text{HCl} \tag{6.2}
\]

\[
\text{CH}_3\text{CO} + \text{O}_2 + \text{N}_2 \rightarrow \text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{N}_2 \tag{6.3}
\]

Recently photolysis of oxalyl chloride $(\text{COCl})_2$ has been proposed as a clean source of Cl atoms. It has a large ($\sigma_{\text{OxCl}} = 3.8 \cdot 10^{-18}\,\text{cm}^2$) absorption cross section at 193 nm, and only Cl and CO have been reported as dissociation products in reaction 6.1. Carboxylic hydrogen abstraction in reaction 6.2 has been shown as a predominant (93\%) channel in experimental observations supported by theoretical considerations, and therefore, formation of methyl formyl radical in this reaction is neglected in the kinetic mechanism. Acetyl peroxy formation via reaction 6.3 is followed by radical recombination reactions. Finally, the above peroxy radicals production scheme was successfully tested on the previously observed ethyl peroxy radical. Typical concentrations of the reactants in the experiments (in Torr) are:

\[
[(\text{COCl})_2]=0.5, [\text{CH}_3\text{CHO}]=1, [\text{O}_2]=50, [\text{N}_2]=150. \]

With the $\sim 9 \cdot 10^{15}\,\text{cm}^{-2}$ flux of 193 nm photons about seven percent of the $(\text{COCl})_2$ molecules will be dissociated yielding $1 \cdot 10^{15}\,\text{cm}^{-3}$ of Cl atoms. Using the set of reactions and rate constants presented in Table 6.1 and the above initial concentrations for the reactants, one can simulate acetyl peroxy radicals evolution under ambient cell conditions. Fig.
<table>
<thead>
<tr>
<th>Reaction</th>
<th>$k(298K)$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$CHO + Cl → CH$_3$C(O) + HCl</td>
<td>$7.8 \cdot 10^{-11}$</td>
<td>[155]</td>
</tr>
<tr>
<td>CH$_3$C(O) + CH$_3$C(O) → products</td>
<td>$7.47 \cdot 10^{-11}$</td>
<td>[156]</td>
</tr>
<tr>
<td>CH$_3$C(O) + O$_2$ + N$_2$ → CH$_3$C(O)O$_2$+N$_2$</td>
<td>$5.10^{-12}$</td>
<td>[13]</td>
</tr>
<tr>
<td>CH$_3$C(O)O$_2$+CH$_3$C(O)O$_2$ → 2CH$_3$+2CO +2O$_2$</td>
<td>$1.64 \cdot 10^{-11}$</td>
<td>[13]</td>
</tr>
<tr>
<td>CH$_3$ + O$_2$ + N$_2$ → CH$_3$O$_2$+N$_2$</td>
<td>$2.9 \cdot 10^{-12}$</td>
<td>[96]</td>
</tr>
<tr>
<td>CH$_3$C(O)O$_2$+CH$_3$O$_2$ → products</td>
<td>$1.26 \cdot 10^{-11}$</td>
<td>[13]</td>
</tr>
</tbody>
</table>
| CH$_3$C(O)O$_2$+Cl → products                                          | $1.6 \cdot 10^{-10}$  | [96] *
| CH$_3$C(O)+Cl → CH$_2$CO + HCl                                         | $1.79 \cdot 10^{-10}$ | [157] |
| Cl+O$_2$ → products                                                    | $1.7 \cdot 10^{-14}$  | [96] |

Table 6.1: Kinetic mechanism for the acetyl peroxy radical formation. * Rate constant for the chlorine atom reaction with acetyl peroxy radical is assumed to be the same as for CH$_3$O$_2$+Cl reaction.

6.1 shows that within several microseconds after photolysis pulse, effectively all Cl atoms will be consumed by acetaldehyde and $\sim 1 \cdot 10^{15}$ cm$^{-3}$ acetyl peroxy radicals will be formed. In some experiments, 193 nm photolysis of biacetyl (CH$_3$CO)$_2$ was used as alternative source of acetyl radical to support spectroscopic assignment of the spectral carrier. Both acetyl sources resulted in similar CH$_3$C(O)O$_2$ spectra presented further but acetyl peroxy absorption signal was significantly weaker in case of biacetyl photolysis.

Direct photodissociation$^{142}$ of CH$_3$CHO in the presence of oxygen may introduce other reactive species (HCO, HO$_2$, CH$_3$O$_2$) into the system, but all four components - 193nm excimer light, oxalyl chloride, acetaldehyde and oxygen - are necessary to observe the spectroscopic transitions described below. Additionally, because of the
Figure 6.1: Simulation of the acetyl peroxy temporal profile using the reaction mechanism provided in Table 6.1 and initial concentrations listed in the text. Due to excess concentrations of CH$_3$CHO and O$_2$, chlorine atoms are stoichiometrically converted to CH$_3$C(O)$O_2$. 
small ($\sim 10^{-21} \text{ cm}^2$) acetaldehyde UV absorption cross section$^{91}$ only $\sim 10^{12} \text{ cm}^{-3}$ acetaldehyde photofragments can be produced in the system, which would be negligible compare to the considered kinetic mechanism.

The subsequent fate of the acetyl peroxy radicals is primarily guided by self reaction and reaction with other peroxy radicals (see Table 6.1). The half-life of the acetyl peroxy radicals in the cell is $\sim 50 \mu s$, which is long enough for their probing by the 10-15 $\mu s$ long ringdown decays (due to precursor absorption, typical ringdown times are a factor of two shorter then that of the empty cavity). Under present experimental conditions, the rate of the radical axial diffusion losses is estimated to be a negligible $2.5 \text{ s}^{-1}$. The excimer laser is fired $5 \mu s$ before the probe laser, allowing sufficient time for peroxy formation.

Concentrations of the reactants were controlled by calibrated mass flow controllers (MKS). Additionally, $(\text{COCl})_2$ concentration was monitored by its UV absorption at 193 nm. Pump speed was set to 100 cm$^3$/sec. With photolysis volume of 15 cm$^3$ and laser system repetition rate of 20Hz the photolysis mixture is replaced every third laser pulse. 4.3 UHP grade $\text{O}_2$ and $\text{N}_2$ (6.0 Research grade) were used. Oxalyl chloride (99%), aldehyde (99.5%), $d_4$-aldehyde(98%) and biacetyl (99%) were obtained from Aldrich. Liquid compounds were purified by repeated freeze-pump-thaw cycles at 77K and premixed in $\text{N}_2$ with the following concentrations : 0.5 % $(\text{COCl})_2$, 10% CH$_3$CHO or CD$_3$CDO.
6.3 Results and Discussion

6.3.1 Ab Initio Calculations

To support and predict spectroscopic observations, \textit{ab initio} calculations on the acetyl peroxy radical and its perdeutero analog have been performed using the GAUSSIAN 98 package. Acetyl peroxy radical, similar to other RC(O)O$_2$ peroxy radicals,$^{135,138}$ can exist in \textit{cis} and \textit{trans} stable conformational forms, interconverted by O–O internal rotation around the C-O bond. $C_s$ symmetry for the ground ($A''$) and exited ($A'$) state minima geometry for both conformers was first found using low level UHF calculations. Then, the excitation frequency for the $\tilde{A}^2A' - \tilde{X}^2A''$ electronic transition and the relative energy for both conformers were calculated using the G2 method. The barrier to the O–O internal rotation was calculated at the G2 level following transition state geometry optimization. Results of the G2 calculations, geometries for \textit{cis} and \textit{trans} acetyl conformers of peroxy, as well as the transition state are shown on Fig. 6.2.

To check the accuracy of G2 method, G2 calculations for numerous peroxy radicals have been performed, and the results are present in Table 6.2. Maximum disagreement between experimental observations$^{27,121,158}$ and theoretical predications is around 250 cm$^{-1}$, which is well within the error bars reported for the G2 method.$^9$

In the spectrum one should expect transitions to the origin and exited vibrational levels of the $\tilde{A}$ state from the vibrationless level of the $\tilde{X}$ state. One should also expect to observe hot bands originating from low lying vibrations in the ground state populated at room temperature. To predict vibrational features in the spectrum,
Figure 6.2: Results of the G2 calculations for the origin of $\tilde{A} - \tilde{X}$ electronic transition and the barrier between trans and cis acetyl peroxy radicals in cm$^{-1}$. Trans acetyl peroxo conformer is slightly lower in energy, probably due to a slight bonding interaction between the oxygen and the methyl hydrogens.
Table 6.2: G2 calculations and experimental values (in cm$^{-1}$) for the electronic origins of $\tilde{A} - \tilde{X}$ transitions of various peroxy radicals. Standard error for G2 energy calculations$^9$ is 350cm$^{-1}$.

<table>
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<th>$\text{HO}_2$</th>
<th>$\text{CH}_3\text{O}_2$</th>
<th>$\text{C}_2\text{H}_5\text{O}_2$</th>
<th>$\text{i-C}_3\text{H}_7\text{O}_2$</th>
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<td>7375</td>
<td>7355</td>
<td>7771</td>
<td>6703</td>
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<td>7590(3)$^{121}$</td>
<td>7568(3)$^{159}$</td>
<td>6656(3)$^{158}$</td>
</tr>
<tr>
<td>$\text{Exp.-Ab initio}$</td>
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<td>7</td>
<td>235</td>
<td>-203</td>
<td>-47</td>
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</tbody>
</table>

Table 6.3: $\text{Ab initio}$ B3LYP/6+31-G(d) rotational constants for $\text{cis}$ and $\text{trans}$ $\text{CH(D)}_3\text{C(O)}\text{O}_2$ in GHz.

<table>
<thead>
<tr>
<th></th>
<th>$\text{CH}_3\text{C(O)}\text{O}_2$</th>
<th>$\text{CD}_3\text{C(O)}\text{O}_2$</th>
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<td>$\text{Trans}$</td>
<td>$\tilde{A}$</td>
<td>$\tilde{X}$</td>
</tr>
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<td>$\tilde{A}$</td>
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<td>4.68775</td>
</tr>
<tr>
<td>$\tilde{X}$</td>
<td>9.2073</td>
<td>4.78426</td>
</tr>
<tr>
<td>$\text{Cis}$</td>
<td>$\tilde{A}$</td>
<td>$\tilde{X}$</td>
</tr>
<tr>
<td>$\tilde{A}$</td>
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<tr>
<td>$\tilde{X}$</td>
<td>10.3699</td>
<td>4.3789</td>
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</table>

frequency calculations have been done using the UHF/6-31+G(d) method for $\tilde{A}$ and $\tilde{X}$ states for both acetyl peroxy conformers and their per-deutero analogs. Frequencies for several low lying vibrational modes are listed in Table 6.4. Geometry optimization for both acetyl peroxy conformers and their perdeutero analogs on B3LYP/6-31+G(d) level has yielded the rotational constants shown in Table 6.3.
6.3.2 Spectral Observations and Analysis

The key issue to be confronted is whether the carrier of these spectra is the acetylperoxy radical and, if so, whether it is the cis or trans conformer. Certainly as documented in Section 6.2, the chemistry is expected to produce CH$_3$C(O)O$_2$ in relative abundance, and this is one of the most persuasive arguments as to the spectral carrier. However such arguments can never rule out all possible minor channels or be totally conclusive.

Further evidence for CH$_3$C(O)O$_2$ can be derived from the spectrum itself. The only likely transitions for small organic molecules under these conditions in this spectral region are between a ground electronic state and a low-lying one and a vibrational overtone or combination band in the ground state. Considering the chemistry involved the only likely species present with a near IR electronic transition are peroxy radicals. Peroxy radicals other than acetyl peroxy will have transitions in this frequency region, but the chemistry seems overwhelmingly to favor acetyl peroxy radical.

Vibrational overtones or combinations are expected to be quite weak and are likely at or below the level of detectivity. The strongest such transitions likely involve at least one, and more likely two quanta of CH stretch. As one can see below, the observed isotope shifts do not support this hypothesis.

Experimental CRDS spectral traces are shown on Fig. 6.3, traces A and B respectively, using acetaldehyde or $d_4$-acetaldehyde as precursors. The position of the strongest band on trace A of Fig. 6.3 centered at 5582.5(5) cm$^{-1}$ is in a good agreement with both the predicted ab initio $T_{00}$ value for the trans acetyl peroxy conformer.
given in Fig. 6.2 and the acetyl peroxy origin assignment (5562(3) cm$^{-1}$) based on previous low resolution experiments. The strongest band in trace B is positioned at 5589.6(5) cm$^{-1}$.

The observed blue shift of 7 cm$^{-1}$ is consistent with the first order effect of deuteration on the electronic origin due to a change in the zero point energy level. Based upon the \textit{ab initio} calculations, the difference between $\tilde{A}$ and $\tilde{X}$ zero point energies for protonated and deuterated trans acetyl peroxy is -112 cm$^{-1}$ and -104 cm$^{-1}$ respectively, meaning that the origin transition for deuterated trans acetyl peroxy should be shifted to the blue by roughly 8 cm$^{-1}$ with respect to the protonated origin. For the cis conformer, same considerations predict a slightly smaller 2 cm$^{-1}$ blue shift for the deuterated origin. The effect of deuteration on species with CH stretching vibrations with possible overtones residing in this region, would have been significantly more pronounced. For instance, in trans acetyl peroxy calculated frequency for the symmetric CH stretch will decrease from 2979 cm$^{-1}$ to 2212 cm$^{-1}$ upon deuteration, leading to an $\approx$1500 cm$^{-1}$ red shift upon deuteration.

The general appearance of the spectrum can be explained by the presence of vibrational hot bands. \textit{Ab initio} calculations of the effect of an electronic excitation on the frequencies of the low lying vibrational modes are given in Table 6.4. With respect to the $\tilde{X}$ state, excitation to the $\tilde{A}$ state in both cis and trans conformers will result in a decrease of the CH$_3$ torsional and an increase of the C(O)O$_2$ wag vibrational frequencies. Therefore, red-shifted torsional and blue-shifted wag hot band progressions are expected in the spectrum.
Figure 6.3: CRDS spectra of the origin of the $\tilde{A}^2A' - \tilde{X}^2A''$ electronic transition of the acetyl peroxy radical taken with CH$_3$CHO (trace A) and CD$_3$CDO (trace B) as precursors. Hot bands are labeled according $N\nu',\nu''$ notation. Vibration $\nu_1$ is a methyl torsion, $\nu_2$ - COO wag and $\nu_3$ - CCO bend. Insert shows two P(6) lines from the H$^{37}$Cl and H$^{35}$Cl first overtone bands left after background subtraction procedure.
<table>
<thead>
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<th>$\tilde{X}$</th>
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<th>mode</th>
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<td><strong>Trans</strong> CH$_3$C(O)O$_2$</td>
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<td></td>
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<td>143</td>
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<td>266</td>
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<td>-29</td>
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<td>A'</td>
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Table 6.4: Scaled (0.89) UHF/6-31+G(d) frequencies of several low lying vibrations in the *trans* and *cis* acetyl peroxy radicals and their perdeutero analogues. Experimental values are obtained by measuring separation between 0$^0_0$ band and the first member of the hot band progression according to the assignment in Fig. 6.3. At room temperature all the listed vibrational levels will have population comparable (within 1/e) to that of the vibrationless levels and transitions originating from those levels should have intensities similar to the origin transition. The next vibrational frequency for both conformers is $\approx 500$ cm$^{-1}$ with a corresponding level population of 0.1 relative to the vibrationless level, and therefore higher frequency levels were not considered in the hot band analysis.
Based on the aforementioned \textit{ab initio} considerations several members of the methyl torsion ($\nu_1$), COO wag ($\nu_2$) and CCO bend ($\nu_3$) hot band progressions have been assigned. Additionally several hot bands originating from $\nu_1$ and $\nu_2$ combination levels are assigned as well. Positions of the individual hot bands and shifts, relative to the origin, for CH$_3$C(O)O$_2$ are presented in Table 6.5 and depicted on Fig. 6.3, trace (A).

Referring to Table 6.5, one can note red shifted progressions of -12 and -44 cm$^{-1}$ (single line) spacing. Table 6.4 has comparable \textit{ab initio} predictions, which due to the fact that computed differences in vibrational frequencies are semi-quantitative at best. Nonetheless, one can see from Table 6.4 that the CH$_3$ torsion and CCO bend hot bands should be shifted with respect to the origin by -19 and -34 cm$^{-1}$ for the \textit{trans} isomer and -35 and -36 cm$^{-1}$ for \textit{cis} isomer. Thus in Table 6.5 the two red shifted vibrations are assigned to $\nu_1$ (CH$_3$ torsion) and $\nu_3$ (CCO bend). In Table 6.5 there is a blue shifted progression with spacing $\approx$44 cm$^{-1}$, which correlates well with the blue shift predicted for $\nu_2$ (COO wag) of +18 cm$^{-1}$ (\textit{trans}) or 43 cm$^{-1}$ (\textit{cis}). Assignment of $\nu_1$ and $\nu_3$ further allows a couple of combinations band to be assigned as shown in Fig. 6.3 and Table 6.5.

\textit{Ab initio} calculations can also aid in finding $\nu_1$, $\nu_2$ and $\nu_3$ counterparts in the deuterated spectrum. As Table 6.4 shows, upon deuteration, the methyl torsional frequency drops which manifests itself in the experimental spectrum of CD$_3$C(O)O$_2$ shown in Fig. 6.3, trace (B), as smaller separations (see Table 6.5) between members of the torsional ($\nu_1$) hot band progression. Conversely, Table 6.4 shows that the
<table>
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**CH\(_3\)C(O)O\(_2\)**

<table>
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**CD\(_3\)C(O)O\(_2\)**

Table 6.5: Observed origin frequencies, hot band positions and their relative shifts with respect to the origin for CH\(_3\)C(O)O\(_2\) and CD\(_3\)C(O)O\(_2\). Vibrational hot bands are labeled according to \(N\nu''\) notation, where \(\nu''\) and \(\nu'\) are \(\tilde{X}\) and \(\tilde{A}\) vibrational quantum numbers in vibration \(N\). Vibration \(\nu_1\) is a methyl torsion, \(\nu_2\) - C(O)O wag and \(\nu_3\) - CCO bend. Each peak position is measured within \(\pm 0.5\text{cm}^{-1}\), but due to differing rotational contours the precision of the resulting vibrational frequencies is somewhat less.
C(O)O₂ wag and CCO bend modes are almost unaffected by deuteration, leaving the separations in the \( \nu_2 \) and \( \nu_3 \) hot band progressions almost unchanged. Assignments and frequencies for the CD₃C(O)O₂ hot bands are listed in Table 6.5.

Some of the combination hot bands in the deuterated spectrum do not have obvious correlations in the protonated one. The two low frequency vibrations listed in Table 6.4 are \( A'' \) symmetry. For an \( \tilde{A}^2A' - \tilde{X}^2A'' \) electronic transition, all vibronic transitions between modes with the same symmetry are allowed given favorable Frank-Condon factors. In the case of the deuterated acetyl peroxy, especially in the \textit{trans} conformer, the CD₃ torsion and C(O)O₂ wag are almost degenerate. This may result in various effects, such as vibrational resonances, intensity borrowing, enhanced combination bands, etc. leading to a spectrum enriched in hot band combinations.

The individual peaks in Fig. 6.3 correspond to the rotational contours of vibronic transitions. Such rotational contours might allow us to distinguish between \textit{cis} and \textit{trans} conformers. Room temperature simulations of the rotational contour for \( \tilde{A}^2A' - \tilde{X}^2A'' \) transition with \textit{ab initio} rotational constants (Table 6.3) and experimental resolution have revealed similar overall rotational contours for both \textit{trans} and \textit{cis} acetyl peroxy conformers as shown in Fig. 6.4. However, some features in the \textit{trans} conformer simulations are in better agreement with experimental observations. A strong unresolved Q branch in the \textit{trans} simulated rotational contour has a width similar to the width of individual peaks in the observed spectra. Deuteration of the \textit{trans} conformer will result in a rotational contour with a somewhat sharper Q branch, which is consistent with the experimental observations. Rotational simulations for
the cis conformer predict a broader than experimentally observed Q branch and also show that the shape of the Q branch is almost unaffected by deuteration, contrary to the experimental observations. Convolution of individual rotational contours of the origin band and multiple vibrational hot bands gives rise to the spectra shown on Fig. 6.3.

All previously observed RO$_2$ peroxy radicals have a strong OO stretching vibrational progression in the $\tilde{A}$ state due to the unpaired electron on the terminal oxygen. Typical frequencies for this vibration fall around 920 cm$^{-1}$ depending on the nature of the R group$^{27,158}$ In the search for $\tilde{A}$ state vibrational bands of protonated acetyl peroxy, the region between 5470 cm$^{-1}$ and 6650 cm$^{-1}$ has been covered with a small gap between 5790-5890 cm$^{-1}$ due to insufficient overlap of ringdown mirrors. All bands observed in this region are presented in Fig. 6.5. The close resemblance of the bands in Fig. 6.5 allows us to attribute them to the same molecular species. The strongest peak in trace (c) of Fig. 6.5 is positioned at 6511(1) cm$^{-1}$ and separated from the origin, trace (a), by 929(1) cm$^{-1}$, which is in excellent agreement with the OO stretching frequency observed for other peroxy radicals.

Further confirmation is obtained by observing the COO bending vibration specific for acetyl peroxy$^{27}$ and presented in trace (b). This band has its strongest peak at 6121(1) cm$^{-1}$ shifted 539(1) cm$^{-1}$ to the blue from the origin. An additional band has been observed at 6055(1) cm$^{-1}$, shifted 473(1) cm$^{-1}$ to the blue from the origin and assigned to a CCOO backbone vibration based on the ab initio calculations provided in Table 6.6. The frequencies of the observed $\tilde{A}$ state vibrations are in a good
Figure 6.4: Comparison between observed and simulated rotational contours of the *trans* and *cis* acetyl peroxy radicals and their perdeutero analogues. Room temperature rotational contours are simulated using SpecView\textsuperscript{4} spectral analysis program and *ab initio* rotational constants from Table 6.3.
Figure 6.5: Experimental CRDS spectra of the $\text{CH}_3\text{C(O)O}_2$: (a) Origin, (b) COO bend, (c) OO stretch. Weak absorption band at $\approx 6050 \text{ cm}^{-1}$ is attributed to the CCO backbone vibration in the $\tilde{A}$ state (see Table 6.6.)
Table 6.6: Calculated $\tilde{A}$ state UHF/6-31+G(d) scaled frequencies for the $A'$ symmetry modes that have terminal oxygen involved into vibrational motion. Unpaired electron is localized on terminal oxygen and therefore listed modes are expected to be the most active ones. As was mentioned in the text only transitions to the $A'$ symmetry modes in the $\tilde{A}$ state are allowed from the vibrationless level in the $\tilde{X}$ state.

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<td>$A'$</td>
</tr>
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<td></td>
<td>546</td>
<td>539(1)</td>
<td>COO bend</td>
<td>$A'$</td>
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<td></td>
<td>1036</td>
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<td>OO stretch</td>
<td>$A'$</td>
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<td>Cis CH$_3$C(O)O$_2$</td>
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<td>CCO backbone</td>
<td>$A'$</td>
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<tr>
<td></td>
<td>847</td>
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<td>COO bend</td>
<td>$A'$</td>
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<td>$A'$</td>
</tr>
</tbody>
</table>

agreement with *ab initio* calculations especially for the *trans* acetyl peroxy conformer. To confirm the chemical identity of the spectral carrier, some experiments have been carried out with an alternative production scheme. Similar spectral features, but with considerably less signal to noise, have been observed when direct photolysis of biacetyl was used to produce the acetyl radical.

Based on the totality of the observed spectroscopic data, analysis and *ab initio* calculations, the observed spectrum is very likely the $\tilde{A}^2 A'-\tilde{X}^2 A''$ electronic transition of CH$_3$C(O)O$_2$, with an origin at 5582.5(5) cm$^{-1}$ and the other bands represent transitions to the exited $\tilde{A}$ state and vibrational hot bands. Although not as certain, based particularly on the agreement of the observed and predicted band origin, shape of the rotational contour and agreement between predicted and observed vibrational frequencies for the $\tilde{A}$ state, it is most likely that the observed spectrum is due to the *trans* acetyl peroxy conformer.
The region of 4600-5200 cm\(^{-1}\) where the cis conformer origin is predicted by G2 calculations has been searched and no spectra attributable to the cis acetyl peroxy radical have been observed. The cis conformer is predicted to be higher in energy than the trans one by 290 cm\(^{-1}\), and at room temperature its equilibrium population is therefore decreased by a factor of 4 compared to the trans conformer. If the calculated energy difference is underestimated (increasing the separation between cis and trans conformer by a factor of 2 gives a factor of 18 in their relative population) and/or the cis absorption cross section is less favorable then the trans one, the cis absorption signal might well fall below apparatus sensitivity. Alternatively, the G2 prediction might be unusually inaccurate in the specific case of the cis acetyl peroxy radical, and its origin may simply reside outside the searched spectral region. Future high resolution rotational studies of the observed bands are necessary to unambiguously distinguish between cis and trans acetyl peroxy conformers.

### 6.3.3 Absorption Cross Section Estimation

Given the spectroscopic assignment, the absorption cross section for the acetyl peroxy \(\tilde{A}^2A' - \tilde{X}^2A''\) transition can be estimated if one can calibrate the initial concentration of acetyl peroxy radical. Equal amounts of acetyl peroxy radicals and HCl molecules are formed under present experimental conditions due the very rapid reactions 6.2 and 6.3. In addition to spectra assigned to acetyl peroxy, sharp lines which remain after background subtraction have been observed and, therefore, are photolytically produced. Several such lines are shown in the insert to Fig. 6.3. Assisted by the HITRAN\textsuperscript{100} database, sharp lines have been assigned to the first vibrational overtone
of HCl and have been used for frequency and absorption intensity calibration since the line positions and absorption cross sections for HCl overtone lines are well established.

Using the known integrated absorption cross sections and the ringdown absorption signal, one can estimated the concentration of HCl as follows. As an example, the H^{37}Cl P(6) line shown on the insert to Fig. 6.3 has an integrated absorption cross section of $I = 1.2 \cdot 10^{-21}$ cm/mol from HITRAN and a measured peak absorption, $S_{HC\text{Cl}} = 20$ ppm. According to the Beer-Lambert law,

$$S_{HC\text{Cl}} = \sigma_{HC\text{Cl}} \cdot [\text{HCl}] \cdot L \quad (6.4)$$

where $L$ is the sample path length of 13 cm. $\sigma_{HC\text{Cl}}$, peak absorption cross section, can be related to the integrated absorption cross section $I$,

$$\sigma_{HC\text{Cl}} = \alpha \cdot \frac{I}{\Delta \nu} \quad (6.5)$$

The numerical coefficient $\alpha$ is taken to be a unity (0.94 in case of Gaussian lineshape), since the experimental lineshape is Voight due to a convolution of instrumental, Doppler and collisional effects. Under current experimental conditions the laser bandwidth is the dominant contribution. The HCl molecular linewidth (0.03 cm$^{-1}$) is significantly smaller than instrumental laser linewidth (0.3 cm$^{-1}$) and Eq. 6.4 might not be generally valid. However, in the case of small molecular absorption signals, ringdown spectroscopy can still be used as a quantitative tool with ringdown molecular absorption still being related to the concentration of absorbing species using Beer-Lambert law. Combining Eq. 6.4 and 6.5 one can calculate [HCl]
Concentration:

\[
[HCl] = \frac{S_{HCl} \cdot \Delta \nu}{L \cdot I} = 3.8 \cdot 10^{14} \text{cm}^{-3}
\]  \hspace{1cm} (6.6)

Concentration measurements using several observed HCl lines is resulted in an averaged [HCl] concentration of \((6 \pm 3) \cdot 10^{14} \text{ mol/cm}^3\), which is consistent with predictions from the kinetic model (see Fig. 6.1). With the acetyl peroxy origin band peak absorption of \(S^p_{CH_3C(O)O_2} = 805 \text{ ppm}\), the sample path length of \(L=13 \text{ cm}\) and \([HCl]=[CH_3C(O)O_2]_0\) the peak absorption cross section, \(\sigma^p_{CH_3C(O)O_2}\) is given by

\[
\sigma^p_{CH_3C(O)O_2} = \frac{S^p_{CH_3C(O)O_2}}{L \cdot [HCl]} = (1 \pm 0.5) \cdot 10^{-19} \text{cm}^2
\]  \hspace{1cm} (6.7)

This cross section is somewhat bigger but comparable to that of methyl peroxy \(^{121}\)

\(\sigma^p_{CH_3O_2} = 0.3 \times 10^{-19} \text{ cm}^2\). It should be noted that one should consider the value for both radicals as empirical cross sections under present ambient cell conditions and with instrumental laser linewidth. It represents total absorption of many closely spaced, partially overlapping individual rotational lines in the Q branch convoluted with probe laser linewidth.

### 6.3.4 Conclusions

Cavity ringdown spectroscopy has been successfully implemented to study an important member of the peroxy radical family, acetyl peroxy radical. Extensive arguments are presented that the observed ringdown spectra are the \(\tilde{A}^2 A' - \tilde{X}^2 A''\) electronic transitions of the \(CH_3C(O)O_2\) and \(CD_3C(O)O_2\) radicals. \textit{Ab initio} calculations have been carried out to assign spectral carrier and analyze observed spectroscopic features such as vibrational hot bands, \(\tilde{A}\) state fundamental vibrations, and rotational contours. It
is most probable that the observed CH$_3$C(O)O$_2$ origin band at 5582.5(5) cm$^{-1}$ and $\tilde{A}$ state vibrational fundamentals correspond to the trans acetyl peroxy conformer. However high resolution studies are necessary to confirm presented conformer assignment.

It was demonstrated that the newly proposed source of chlorine atoms, (COCl)$_2$, can be efficiently used to produce peroxy radicals under ambient cell conditions. A by-product of the proposed production scheme, HCl, has been used to calibrate acetyl peroxy radical concentration and hence to derive an empirical absorption cross section.
Bibliography


[8] NIST Computational Chemistry Comparison and Benchmark Database .


