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# Observation of the $\tilde{A} - \tilde{X}$ electronic transition of C<sub>6</sub>-C<sub>10</sub> peroxy radicals

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# ABSTRACT

The  $\widetilde{A}$ - $\widetilde{X}$  electronic transitions of  $C_6$ - $C_{10}$  peroxy radicals were observed in the near infra red. Spectra have been obtained for straight chain peroxy radicals: hexyl, heptyl, octyl, nonyl, and decyl including one  $C_8$  isomer, *iso*-octyl peroxy. The peroxy radicals were generated using hydrogen abstraction of the corresponding hydrocarbon precursors. Spectra was assigned through spectral/structural relationships established through prior studies of smaller peroxy radicals. The secondary peroxy isomer was determined to be the dominate carrier for the observed *n*-alkyl spectra. However, the *iso*-octyl peroxy radical was found to contain the tertiary and primary isomers in its spectrum.

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#### 1. Introduction

For about a century the spark ignition engine has been a leading choice for personal transportation around the world. As a result combustion reactions have been some of the most heavily investigated chemical processes, but are yet to be fully understood because of the complexity. To comprehend the underlying chemistry of combustion reactions, identification of reactive intermediates that participate in these processes is necessary. The formation of alkyl peroxy radicals (RO<sub>2</sub>) is a fundamental step in the low-temperature combustion to proceed, a hydroxyl radical (OH) abstracts a hydrogen atom from a hydrocarbon fuel (RH) to form an alkyl radical (R). The alkyl radical rapidly undergoes a 3-body reaction in air to form an alkyl peroxy radical (RO<sub>2</sub>), which then participates in one of many reactions leading to chain branching, chain propagation, or chain termination.

Larger hydrocarbons ( $\geq C_6$ ) make up a significant portion of the gasoline mixtures used in spark ignition engines [6–8]. Figure 1 shows that the most prevalent hydrocarbons in regular unleaded fuel contain five carbon atoms and that 73% of the blend is composed of hydrocarbons larger than  $C_5$ . In the premium blend the most prevalent hydrocarbons contain eight carbon atoms with hydrocarbons larger than  $C_5$  making up 75% of the mixture [6]. The disparity in the amount of larger hydrocarbons each fuel mixture correlates with the difference in antiknock rating, or octane rating, of the fuels. The relationship between octane rating and structure of the carbon chain has been well documented [9–12]. As the carbon chain increases in length octane number systematically decreases; however, octane

number will increase by substitution of a methyl group as a side chain. This change in the hydrocarbon chain will also affect the structure of the RO<sub>2</sub> radical that is formed as the combustion process proceeds. The terminal oxygen atom of the peroxy moiety can internally abstract an alkyl hydrogen giving the QOOH species [13–15]. Formation of the QOOH species is the combustion pathway that leads to chain branching and, ultimately, to engine knocking. Miyoshi [16] investigated the unimolecular reaction of alkyl peroxy radicals and found that the 1,3-hydrogen abstraction (using a four membered transition state) is 160(5) kJ/mol high and unimportant. The 1,4-hydrogen abstraction (five membered transition state) is 140(20) kJ/mol, while the 1,5- and 1,6-hydrogen abstractions (6 and 7 membered transition states, respectively) have even lower barriers, with the 1,6-hydrogen abstraction having the lowest barrier to surmount. The barrier for hydrogen atom abstraction then increases slightly for the 1,7- and 1,8-shifts. By using branched hydrocarbons in the gasoline, branched RO2 radicals are formed which have larger barriers to surmount to form the QOOH species than do straight chain peroxy radicals.

In addition to peroxy radicals being important combustion intermediates, they are also relevant in atmospheric oxidation cycles of hydrocarbons [17–19]. When hydrocarbons enter into the atmosphere, they can encounter OH (or depending on the circumstances Cl) which will abstract a hydrogen atom forming an alkyl radical. The alkyl radical reacts with  $O_2$  and a third body, typically N<sub>2</sub>, which collisionally stabilizes the peroxy radical. In a clean atmosphere, RO<sub>2</sub> will undergo self-reaction and cross-reactions with another R'O<sub>2</sub> or HO<sub>2</sub> to form alcohols and other end products. However, in polluted atmospheres organic peroxy radicals will react with NO to produce NO<sub>2</sub> which can be photolyzed by sunlight to produce oxygen atoms that react with O<sub>2</sub> to produce ozone (O<sub>3</sub>) [20–22]. This specific set of reactions has been found to produce





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**Figure 1.** Graph (adapted from data in reference [6]) depicting the typical carbon number distribution of regular unleaded and premium unleaded gasolines based on volume percent.

large amounts of ozone in the troposphere where it is a major pollutant for plants and animals, including humans.

Typically, the  $\tilde{B}-\tilde{X}$  electronic transition in the UV has been used to spectroscopically study peroxy radicals [23,24]. While it is a strong transition and has a large cross-section ( $\sigma \approx 10^{-18}$  cm<sup>2</sup>), the  $\tilde{B}$  state is dissociative giving spectra that are broad, unstructured and cannot be used to characterize or differentiate among organic peroxy radicals. However, over the past decade our group has used cavity ringdown spectroscopy (CRDS) to exploit the much weaker  $\tilde{A}-\tilde{X}$  ( $\sigma \approx 10^{-21}$  cm<sup>2</sup>) transition in the near IR (NIR) to produce spectra that can easily be used to distinguish between different peroxy radicals and even isomers and conformers of the same peroxy radical, for  $C_n$  (n = 1-5) [25]. Due to the significance of the larger  $C_n$  (n = 6-10) hydrocarbons in gasoline and other commercial products we have recently extended those studies to include the  $C_6-C_{10}$  peroxy radicals and present the findings in this Letter.

# 2. Experimental

#### 2.1. Ringdown apparatus

The CRDS apparatus used to observe the NIR peroxy radical transitions has been described in detail previously [26,27]. The 532 nm output of a 20 Hz pulsed Nd:YAG (Spectra Physics, Quanta-Ray Pro 270) was used to pump a dye laser (Sirah, PrecisionScan) to give 50–90 mJ/pulse over the 645–581 nm range. The laser dyes used were DCM, Rhodamine 101, and Rhodamine B (Exciton). Radiation from the dye laser was focused into a 70 cm single-pass Raman cell charged with 325-350 psi of H<sub>2</sub>. The desired second Stokes component (7200–8900 cm<sup>-1</sup>; 1–2 mJ/pulse) of the stimulated Raman scattered radiation was isolated via a long pass filter (Newport, 1000 nm LP) and directed into the ringdown cell. The ringdown cell is 55 cm in length and is terminated by two highly reflective mirrors (Los Gatos Research; 1.3  $\mu$ m,  $\geq$  99.995%; 1.2  $\mu$ m,  $\geq$  99.995%). The inner 20 cm portion of the cell is designed with sample gas inlets on either end, a central vacuum port, and two rectangular UV-grade quartz photolysis windows. The cell has a depth of 15.2 cm along the direction of the photolysis beam so that the quartz windows are spatially removed from the reactant flow zone. The ringdown mirrors and photolysis windows are protected from corrosion and soot deposits by flowing nitrogen over them at 10 and 250 cm<sup>3</sup>/min, respectively. Ringdown decays were detected by an amplified InGaAs photodiode (Thorlabs, PDA400), and the signal is recorded via a 12-bit digitizing card (Measurement Computing). To obtain the CRDS spectra, 20–30 consecutive laser shots were averaged at each dye-laser frequency point. Laser operation and data acquisition were achieved by PC-based Labview software. The scans were recorded with  $\approx$ 1.0 cm<sup>-1</sup> laser step size and spectra were calibrated using a wavemeter (HighFinesse, WS-7).

The chemistry required to create the peroxy radicals was initiated by the 193 nm output from the photolysis excimer laser (LPX120i, LambdaPhysik). The photolysis beam was focused by a cylindrical and spherical lens to a rectangular shape  $(13 \times 0.5 \text{ cm}^2)$  and propagated perpendicular to the NIR radiation. The excimer light passed once through the ringdown cell via UVgrade quartz windows at the central part of the cavity. The laser was typically fired 5 us prior to the NIR probe light entering the ringdown cavity. This is enough time to allow the peroxy radicals to form but not to react further chemically or be pumped out of the cell. The ringdown time (excimer on) determines the absorption within the cavity of the NIR light. To remove spectral artifacts arising from water or precursor absorption, a background ringdown trace (without excimer photolysis) was acquired immediately following the excimer-on trace and subtracted from it leaving only spectral features of molecules produced from photolysis.

#### 2.2. Production of radicals

To produce the peroxy radicals, hydrogen atom abstraction of the hydrocarbon precursors was used. Hydrogen atoms were abstracted by chlorine atoms that were formed from the 193 nm photolysis of oxalyl chloride, (COCl)<sub>2</sub>. Oxalyl chloride has a large absorption cross section at 193 nm ( $\sigma$  = 3.8 × 10<sup>-18</sup> cm<sup>2</sup>) and has been shown to be a clean source of chlorine atoms [28,29]. When the chlorine atoms abstract a hydrogen atom, they can do it from either a primary, secondary, or a tertiary site which will produce a mixture of isomers. The newly formed alkyl radicals then add O<sub>2</sub> to give the peroxy radical. For this production method a stream of N<sub>2</sub>, with a backing pressure  $\approx$ 4.0 psi, was bubbled through the liquid hydrocarbon precursors with 4.0-10.0 torr of this gas mixture delivered to the ringdown cell. Typical partial pressures in the cell for this method were  $[N_2] \approx 30.0-33.0$  torr,  $[O_2] \approx 20.0$  torr,  $[(COCl)_2] \approx 0.3-0.5$  torr, and hydrocarbon precrsors = 0.2 - 0.4 torr.

### 3. Results and discussion

#### 3.1. Spectral/structural relationships of peroxy radicals

Historically ab initio calculations were done to aid in the assignment of peroxy radical spectra. Our group has successfully used the G2 method of calculation to accurately predict origin frequencies (within 100 cm<sup>-1</sup>) and used DFT methods to calculate vibrational frequencies for both the X and A states [30,31]. However, due to the large size of the peroxy radicals in this Letter it was not feasible to do the kind of calculations that have been done previously. Therefore, to assign the spectra obtained we will use the spectral/structural relationships that have been derived through the prior work done on the  $\tilde{A} - \tilde{X}$  transition of smaller peroxy radicals [25]. Figure 2 shows the dependence of the origin frequency on substitution and specific conformer of the peroxy radical. Origin frequencies for the peroxy radicals appear in the 7300-7800 cm<sup>-1</sup> range and highly depend on the substitution of the radical and its geometrical conformation. In addition to the origin band, other characteristic transitions of peroxy radicals include



**Figure 2.** Graph showing the dependence of  $\widetilde{A} - \widetilde{X}$  origin frequency on peroxy radical species and its structure, based on data presented in reference [25] and results from the present Letter.

an OO stretch band and sometimes a COO bend band that appear  $\sim$ 900 cm<sup>-1</sup> and 400–500 cm<sup>-1</sup> to the blue of the origin, respectively. These relationships between substitution/conformer of the peroxy radical and origin values and the typical shifts from the origin of COO bending and OO stretching will be applied to assign the current spectra.

#### 3.2. Peroxy radical spectra and assignments

Figure 3 shows the CRDS spectra resulting from the straight chain hydrocarbon precursors that were studied (hexane-decane). For each hydrocarbon precursor, oxygen dependent and time dependent tests were performed to provide chemical evidence that a peroxy radical was indeed the carrier of the observed spectrum. In each trace there is a very intense band ~7590 cm<sup>-1</sup> and another almost as intense band about 900 cm<sup>-1</sup> to the blue. The very intense bands ~7590 cm<sup>-1</sup> can be assigned to the origin bands of the corresponding alkyl peroxy radical. The aforementioned transitions ≈900 cm<sup>-1</sup> to the blue of the origin bands in all the spectra are the OO stretch bands of the peroxy radicals. In the hexyl peroxy (red) trace there also appears to be another transition ≈450 cm<sup>-1</sup>

to the blue of the origin which is most likely the COO bend transition of the peroxy radical. The best experimentally determined frequencies for the observed transitions are given in Table 1 and have an estimated error of  $\pm 10$  cm<sup>-1</sup> due to there being several isomers/ conformers that may overlap under a single peak and a limited signal-to-noise ratio.

The origin frequencies for the straight chain peroxy radicals show a slight upward trend for  $C_6-C_9$  and then there is a decrease for  $C_{10}$ . It was somewhat surprising to see the decrease at  $C_{10}$ , however, there may be additional chemical processes occurring as there is evidence of  $HO_2$  (sharp structure from  $\sim 7800-$ 8100 cm<sup>-1</sup>) which is not present in any other spectra obtained. Observing the spectrum at longer delay times gives some insight to what is occurring. The upper right inset in Figure 3 shows the 7300–7800 cm<sup>-1</sup> region of the decyl peroxy spectrum at different delay times. At the 5 µs delay time (black trace) there is some unidentifiable structure  $\approx$ 7385 cm<sup>-1</sup>; as we increase the delay time it becomes obvious that this is the origin of methyl peroxy [32]. The appearance of methyl peroxy in this situation is quite curious as now both it and HO<sub>2</sub> appear in the decyl peroxy spectrum while not appearing in any others. As a check of the chemistry, a photolysis experiment was performed in the absence of the oxalyl chloride to see if the methyl peroxy or HO<sub>2</sub> formation could be due to photolysis of the decane precursor itself. When oxalyl chloride was not present none of the above spectra (decyl peroxy, HO<sub>2</sub>, nor methyl peroxy) are observed. This means that the initial hydrogen atom abstraction of the alkane precursor is required. We also believe it suggests the formation of HO<sub>2</sub> and methyl peroxy is related and could be part of additional chemistry that the decyl peroxy radical is undergoing. The exact mechanism to produce HO<sub>2</sub> and methyl peroxy from decyl peroxy is unclear but there are a number of chemical pathways that are available to decyl peroxy once it is formed including direct elimination of HO<sub>2</sub> to give an alkene (as stated in the introduction), and the terminal oxygen atom of the peroxy moiety internally abstracting an alkyl hydrogen to give the QOOH species which can also eliminate HO<sub>2</sub> to give an alkene. One could easily imagine methyl peroxy, and possibly larger alkyl peroxy, radicals being formed as part of a reaction pathway including the QOOH species.

Given that  $HO_2$  and methyl peroxy are formed, the effect their presence can have on the spectrum should be addressed. The  $HO_2$  signals are far enough from any decyl peroxy signal that they probably have very little influence on the decyl peroxy spectrum itself. However, methyl peroxy absorbs at lower energies than decyl peroxy and its spectrum partially overlaps with decyl peroxy. Larger alkyl peroxy radicals will still absorb to the red of decyl, but closer in frequency so that their bands are even more overlapped. This may be enough to give the appearance that the decyl peroxy band center has been red shifted when in actuality there are other peroxy radical absorbers present that are influencing the band. This could explain why the decyl peroxy origin and OO stretch bands do not seem to follow the upward trend in frequency of the C<sub>6</sub>-C<sub>9</sub> peroxy radicals. However, while the argument is suggestive it is not definitive.

Comparing with the values presented in Figure 2, the positions of the  $\hat{A}-\hat{X}$  origin bands demonstrate that the predominant carriers are the secondary peroxy radical isomers in the G<sub>1</sub>... conformation. This result is primarily an outcome of the chemistry used to generate the peroxy radicals. Each straight chain hydrocarbon used as a precursor has six primary sites from which a hydrogen atom can be abstracted. However, in each precursor there are more secondary sites than primary sites with ratios (secondary:primary) of 1.33:1 for hexane, 1.67:1 for heptane, 2:1 for octane, 2.33:1 for nonane, and 2.67:1 for decane giving more secondary sites to abstract a hydrogen from. In addition the reported, relative reactivities [26,33] of hydrogen atoms to abstraction, 2:9:18



**Figure 3.** Main figure is  $\tilde{A} - \tilde{X}$  spectra of peroxy radicals from hexane-decane (straight chain) precursors. Red (top) trace is hexyl peroxy, blue trace is heptyl peroxy, green trace is octyl peroxy, pink trace is nonyl peroxy, and black (bottom) trace is decyl peroxy. In the hexyl peroxy trace there is some interference that appears in the spectrum from 8230–8489 cm<sup>-1</sup> caused by incomplete subtraction from precursor absorption in that region. The sharp line structure in the *n* = 8 likely arises from HO<sub>2</sub>. Upper right inset is 7300–8000 cm<sup>-1</sup> region of decyl peroxy  $\tilde{A} - \tilde{X}$  spectrum at different time delays. Black (top) trace is 5 µs time delay, blue trace is 100 µs, pink trace is 500 µs time delay, and red trace is 1 ms delay. Structure near 7383 cm<sup>-1</sup> and 7488 cm<sup>-1</sup> are the origin and 12<sup>1</sup><sub>1</sub> bands, respectively, of methyl peroxy [32]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this Letter.)

Table 1										
Experimental	origin	frequencies,	C00	bend	vibrations,	and	00	stretch	bands	of
hexyl-decyl p	eroxy i	adicals.								

Peroxy radical	Origin (cm <sup>-1</sup> )	$COO bend$ $(cm^{-1})$	OO stretch (cm <sup>-1</sup> )	
Hexyl	7584(10)	8053(10)	8511(10)	
Heptyl	7587(10)	-	8515(10)	
Octyl	7591(10)	-	8520(10)	
Nonyl	7592(10)	-	8526(10)	
Decyl	7576(10)	-	8523(10)	

(primary:secondary:tertiary), indicate that secondary hydrogens are 4.5 times more reactive to abstraction than primary hydrogens. Moreover, the origin frequencies (see Figure 2) of the primary peroxy radicals and secondary peroxy radicals (T<sub>1</sub>... conformation) are not consistent with our experimental data. Origin positions for primary peroxy radicals in the  $T_1$ ... and  $G_1G_2$ ... conformation are noticeably red shifted from our experimental data, while origin values for primary and secondary peroxy radicals in the G<sub>1</sub>T<sub>2</sub>...  $G'_1G_2...$  and  $T_1...$  conformation, respectively, are much more scattered and do not correlate well with our data. (One exception is the  $T_1$ ... conformer of 2-propyl peroxy which has an origin of 7692 cm<sup>-1</sup>.) Taking into account the relative abundances and reactivities of primary to secondary hydrogen atoms as well as origin frequencies support assigning the carriers of the spectra in Figure 3 to the corresponding straight chain peroxy radicals, secondary isomers in the  $G_1$ ... conformation.

Figure 4 shows the spectrum when *iso*-octane is the precursor and it is compared to the *n*-octyl peroxy spectrum. The same chemical tests were performed on the *iso*-octane trace and it again displayed behavior consistent with that of a peroxy radical. The *iso*-octyl peroxy spectrum appears more complex than the straight chain peroxy radicals studied presumably due to the fact that it has primary, secondary, and tertiary sites for hydrogen atom abstraction. In the origin region the *iso*-octyl peroxy trace has two intense bands ( $\approx$ 7500 and  $\approx$ 7800 cm<sup>-1</sup>) compared to the one intense band of the straight chain peroxy radicals. The  $\approx$ 7800 cm<sup>-1</sup> band is significantly blue shifted from the other origin bands that have been observed in this Letter. In Figure 2, there is a data point at 7757 cm<sup>-1</sup> representing the origin of *t*-butyl peroxy, a tertiary peroxy radical. We therefore assign the  $\approx$ 7800 band of the *iso*-octyl peroxy spectrum as the likely origin of the tertiary isomer.

However, the band near 7500 cm<sup>-1</sup> has more than one possible assignment. In Figure 2, the primary peroxy radicals in the  $G_1G_2$ ... conformation have origin frequencies from 7480 to 7592 cm<sup>-1</sup>, with all but one origin falling into the  $7480-7551 \text{ cm}^{-1}$  range. One could easily argue that an origin value of 7503 cm<sup>-1</sup> falls well within this range and make the assignment that this band belongs to a primary isomer of iso-octyl peroxy in the G<sub>1</sub>G<sub>2</sub>... conformation. But if a rough calculation is made to predict band intensities of the different isomers using the relative abundances of primary:secondary:tertiary (p:s:t) abstraction sites (15:2:1) along with relative reactivities of Cl atoms to p:s:t H atoms (2:9:18) we obtain relative intensities for the p:s:t isomer bands of 30:18:18. This predicts that the primary isomer origin will be 2/3 stronger than either the secondary or tertiary origin bands while the transitions we observe in our spectrum are the same intensity. This argument would be consistent with the band at 7503 cm<sup>-1</sup> belonging to the secondary isomer even though it is red shifted nearly 60 cm<sup>-1</sup> from any other secondary isomer origin band. Moreover this latter assignment would also leave unanswered the lack of any observation of a band attributable to the primarily isomer despite predictions that it should be most abundant. Furthermore we searched for spectra to the red of 7300 cm<sup>-1</sup> and could not see any structure we could attribute to any peroxy radical, whereas assignment of



**Figure 4.**  $\tilde{A} - \tilde{X}$  spectra of *iso*-octyl peroxy blue (bottom) trace produced from *iso*-octane precursor (structure in upper right corner of Figure) and *n*-octyl peroxy red (top) trace. Primary hydrogen abstraction sites on *iso*-octane are labeled with an "a", secondary sites with a "b", and tertiary sites with a "c". (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this Letter.)

the 7503 cm<sup>-1</sup> band to a secondary isomer would lead to the expectation of a primary isomer origin in this region. Regardless of the assignment it is surprising that we do not observe origin bands from each the p:s:t conformer.

It is probably worth noting that the relative reactivities of Cl atoms to p:s:t H atoms was determined through experimentation on *n*-butane and *iso*-butane. Iso-octane is relatively complex compared to either of those molecules and it is unknown whether the relative reactivities of Cl atoms to p:s:t H atoms will hold quantitatively for *iso*-octane in this situation. We therefore tentatively assign the band near  $7500 \text{ cm}^{-1}$  as the primary isomer based on the spectral/structural relationships that we have derived, but clearly note that we are puzzled by the absence of a third band for *iso*-octane.

In addition to the spectral/structural relationships, one can also utilize self-reaction rate information to determine to which isomer a given band belongs. In our experiments we have the ability to delay the time between the excimer photolysis pulse and the NIR probe pulse. Figure 5 shows the results of these time delay experiments. At long delay times there are three bands, labeled as A', B', and C', that are still clearly visible. Long lived spectral lines were observed in our previous investigation of tertiary radicals [26]. In that study a much slower self-reaction rate constant was found for the *t*-butyl peroxy radical than for its secondary and primary isomer counterparts. These additional observations strongly support the assignment of bands A', B', C' to the tertiary decyl peroxy isomer.

Additional information about the isomers can be obtained by estimating the initial radical concentrations. Melnik et al. [34] found their chlorine atom concentration to be  $2 \times 10^{15}$  molecules/cm<sup>-3</sup>; since we are using similar conditions that should be a good approximation for the concentration of chlorine atoms in our current Letter. Looking at Figure 4, the two bands near 7500 and 7800 cm<sup>-1</sup> have nearly the same intensity. If we assume equal oscillator strengths we can infer the isomers are formed in a 1:1 ratio. Given our initial chlorine atom concentration, this will yield a peroxy radical concentration of  $1 \times 10^{15}$  molecules/cm<sup>3</sup> for each of the species present in our spectrum.

We can estimate the half-life of the peroxy radicals from the data in Figure 5. The bands that we have assigned as the tertiary



**Figure 5.** Time delay tests of  $\tilde{A} - \tilde{X}$  spectrum of *iso*-octyl peroxy. Red (top) trace is taken at a 5  $\mu$ s delay of NIR probe from the excimer photolysis beam, blue trace taken at 500  $\mu$ s delay of NIR probe, and black trace taken at 1 ms delay of NIR probe. Labeling of bands signifies assignment of transition to primary or tertiary isomer. A and B bands are tentatively assigned to primary isomer while A', B', and C' bands belong to tertiary isomer. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this Letter.)

peroxy radicals do not seem to decay at all. This consistent with a reported self-reaction rate constant of  $2 \times 10^{-17}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> [21] for tertiary peroxy radicals, which would make their self reaction not observable on our millisecond timescale, with comparable observations being obtained in similar experiments [26,21]. From Figure 5 we can estimate a half-life of  $\approx$ 500 µs for bands A and B and obtain self reaction rate constants of  $\approx 2 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. Unfortunately this rate constant does not allow us to differentiate between isomers, since it is roughly consistent with either primary or secondary peroxy radicals. Based on a combination of the self-reaction rates and the spectral/structural relationships our conclusion therefore is that

Table 2Spectral assignments for *iso*-octyl peroxy.

Band	Frequency	Assignment
А	7503	Origin of primary isomer
A'	7804	Origin of tertiary isomer
Β′	8230	COO bend of tertiary isomer
В	7597	OO Stretch of primary isomer
C′	8734	OO Stretch of tertiary isomer

we can definitively assign bands A', B', and C' to the tertiary isomer. Using the spectral/structural relationships, we feel it is more likely, but not certain, that bands A and B belong to the primary isomer. These results are summarized in Table 2.

# 4. Conclusion

The  $\widetilde{A} - \widetilde{X}$  absorption spectra of hexyl-decyl (straight chain) peroxy radicals and iso-octyl peroxy have been recorded and assigned. Spectral assignments were made through the spectral/ structural relationships that have been determined through previous work on peroxy radicals. All of the straight chain peroxy radicals studied were found to have origin values between 7550 and  $7600 \text{ cm}^{-1}$  and OO stretch bands about  $900 \text{ cm}^{-1}$  to the blue of the origin, with hexyl peroxy also exhibiting evidence of a COO bending band. The positions of the origin bands of the straight chain peroxy radicals indicate that the main carriers of the spectra are the secondary peroxy isomers. The iso-octyl peroxy spectrum shows evidence that both the primary and tertiary peroxy isomers are formed. Assignments of the iso-octyl peroxy spectrum were further confirmed by examining the temporal behavior of the bands in the spectrum and finding that some of the bands were long lived (>1 ms) which is expected for the tertiary peroxy isomers.

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