The Absorption Spectrum and Absolute Absorption Cross Sections of Acetylperoxy Radicals, $CH_3C(O)O_2$ in the near IR

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Revised version

submitted to

Journal of Quantitative Spectroscopy & Radiative Transfer

ABSTRACT

The $\tilde{A}$-$\tilde{X}$ electronic transition of acetylperoxy radicals ($CH_3C(O)O_2$) in the near-infrared was measured at 67hPa synthetic air in the spectral ranges from 6094 cm^{-1} to 6180 cm^{-1} and 6420 cm^{-1} to 6600 cm^{-1}. $CH_3C(O)O_2$ radicals were generated by the pulsed photolysis of a acetaldehyde/Cl_2/O_2 mixture at 351 nm and subsequently measured by time-resolved continuous-wave cavity ring-down spectroscopy (cw-CRDS). The absorption cross sections of eight discrete absorption lines were determined relative to the absorption cross section of HO_2, which has previously been reported. The strongest absorption cross section was found at 6510.73 cm^{-1} and was determined to be $(4.9\pm2.5) \times 10^{-20}$ cm^2.

INTRODUCTION

In the troposphere, the oxidation of volatile organic compounds (VOCs) is mainly driven by hydroxyl (OH) radicals and leads to the formation of organic peroxy radicals (RO_2). The fate of these RO_2 radicals depends on the chemical composition of the environment. In a polluted atmosphere they react mainly with nitric oxide (NO) to form alkoxy radicals or react with nitrogen dioxide (NO_2) to form peroxynitrates (RO_2NO_2). Subsequent to the reaction with NO, alkoxy radicals react with O_2 to form hydroperoxy (HO_2) radicals. HO_2 radicals further oxidise NO to NO_2 and regenerate OH closing the quasi-catalytic cycle. The photolysis of produced NO_2 is the only relevant chemical source of tropospheric ozone. In clean environments with low NO_x (NO_x = NO + NO_2) concentrations, the dominant loss of RO_2 is due to its reaction with HO_2 forming hydroperoxides ROOH and terminating the radical reaction chain. In addition, RO_2 radicals can react either with other RO_2 as self- (RO_2 + RO_2) or cross-reaction (RO_2 + R'O_2) or with OH radicals (RO_2 + OH) [1-3].

The majority of emitted biogenic non methane hydrocarbons are isoprene (53 %) and monoterpene species (16 %) [4]. The photooxidation of these highly abundant compounds and their oxidation products form among other products also significant amounts of acetylperoxy radicals ($CH_3C(O)O_2$). In the reaction with NO_2, $CH_3C(O)O_2$ form peroxyacetyl nitrate (PAN) which is a toxic secondary air pollutant. In addition, PAN acts as the principal tropospheric reservoir species for NO_x [5]. The only relevant source in the troposphere is this photochemical

process, so that PAN is an indicator for photochemical oxidation. Its relatively long atmospheric lifetime of approximately two weeks allows for transport over long distances.

Model calculations of measured radical concentrations in different field studies underestimate HO_x (HO_x = OH + HO_2) radical concentrations in remote regions with high emissions of VOCs from biogenic sources [6-9]. Because acetylperoxy radicals are formed from biogenic precursors and serve as source for HO_2, understanding of its properties is of importance.

Recent studies show that the $CH_3C(O)O_2$ + HO_2 reaction, which is the most important tropospheric reaction in regions that are dominated by biogenic emissions (low NO emissions), does not only lead to radical chain terminating products (R1, R2), but can also regenerate OH (R3) [10-12]:

$$CH_3C(O)O_2 + HO_2 \rightarrow CH_3C(O)OOH + O_2 \quad (R1)$$

$$\rightarrow CH_3C(O)OH + O_3 \quad (R2)$$

$$\rightarrow CH_3C(O)O + OH + O_2 \quad (R3)$$

This additional OH radical regeneration could improve the model-measurement agreement in low NO_x environments with high VOC emission rates.

For an accurate understanding of the $CH_3C(O)O_2$ + HO_2 reaction, it is necessary to understand the secondary chemistry. For example, the $CH_3C(O)O_2$ self-reaction (R4) competes with the reaction with HO_2, forming the same product $CH_3C(O)O$ as (R3) making it hard to distinguish between both reactions.

$$2\ CH_3C(O)O_2 \rightarrow 2\ CH_3C(O)O + O_2 \quad (R4)$$

In addition, reaction rate constants of the self-reaction ($k_4 = 2.9 \times 10^{-12}$ exp(500/T) cm^3 $molecule^{-1}$ s^{-1} [13]) and of the reaction with HO_2 ($k_{1\text{-}3} = 3.14 \times 10^{-12}$ exp(580/T) cm^3 $molecule^{-1}$ s^{-1} [13]) are in the same order of magnitude which makes it complicated to study those reaction kinetics.

The detection of RO_2 in previous kinetic laboratory studies was mainly done in the UV region. The spectral overlap of different peroxy species in this region is prone to systematic errors in the quantitative detection [14-18]. Therefore, experiments analysing different RO_2 are difficult to evaluate, if they are detected by UV absorption.

Here, we use absorption of $CH_3C(O)O_2$ in the $\tilde{A}$-$\tilde{X}$ electronic transition located in the near infrared region. This results in absorption cross sections that are up to several orders of magnitude smaller compared to values in the UV, but the detection is more selective due to less spectral overlap with formed products. In order to measure these small absorption cross sections, very sensitive detection methods need to be used, in our case continuous wave-Cavity Ring Down Spectroscopy (cw-CRDS). While the relative spectrum has already been measured by Zalyubovsky *et al*. [19] in a large wavelength range and the absolute absorption cross section of the strongest band at 5582 cm^{-1} has been estimated, we present here the determination of absolute absorption cross sections in two ranges from 6094 cm^{-1} - 6180 cm^{-1} and from 6420 cm^{-1} - 6600 cm^{-1}, corresponding to the COO bend and to the OO stretch transition, respectively, relative to the absorption cross section of HO_2. These cross sections can be used in future works for the quantitative detection of this radical.

EXPERIMENTAL

Experimental setup

The setup has been described in detail before [20-23] and is briefly discussed here (**Figure 1)**.

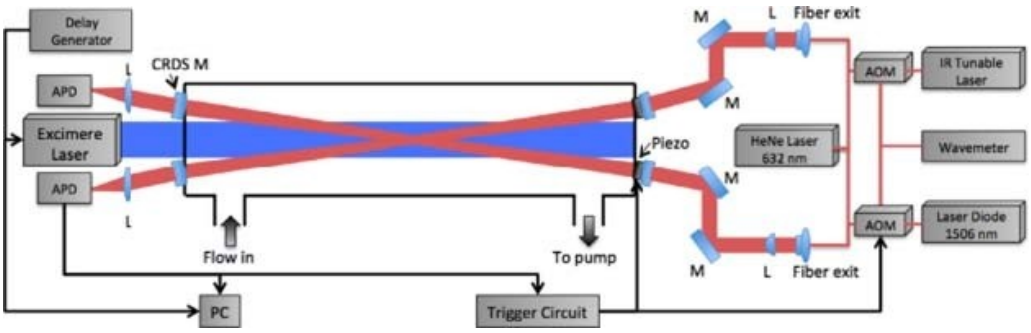

Figure 1. Schematic view of the used experimental setup: AOM, Acousto-Optic Modulator; APD, Avalanche Photo Diode; M, Mirror; L, Lens. Both cw-CRDS systems are equipped with identical trigger circuits and data acquisition systems.

The setup consisted of a 0.79 m long flow reactor made of stainless steel. The beam of a pulsed excimer laser (Lambda Physik LPX 202i) passed the reactor longitudinally. The flow reactor contained two identical continuous wave cavity ring-down spectroscopy (cw-CRDS) absorption paths, which were installed in a small angle with respect to the photolysis path. An overlap with the photolysis beam of 0.377 m is achieved. Both beam paths were tested for a uniform overlap

with the photolysis beam before experiments were done. For this purpose, both cw-CRDS instruments were operated to simultaneously measure HO_2 concentrations. Deviations between HO_2 concentrations were less than 5 % demonstrating that the photolysis laser was very well aligned, *i.e.* both light paths probed a very similar photolysed volume in the reactor. A small helium purge flow prevented the mirrors from being contaminated. For measuring the $CH_3C(O)O_2$ spectrum, a tunable laser source (Agilent 81680A) was coupled into one of the cavities by systems of lenses and mirrors. On the other path, a DFB laser was coupled into the cavity for the detection of HO_2 radicals during the calibration measurements. The calibration of the acetyl peroxy absorption cross section at 6497.94 and 6638.30 cm^{-1} in 67hPa helium has also been carried out using a DFB laser instead of the Agilent module. Each probe beam passed an acousto-optic modulator (AOM, AAoptoelectronic) to rapidly turn off the 1st order beam once a threshold for light intensity in the cavity was reached, in order to measure the ring-down event. Then, the decay of light intensity was recorded and an exponential fit is applied to retrieve the ring-down time. The absorption coefficient α is derived from Equation (1).

$$\alpha = [A] * \sigma_A = \frac{R_L}{c}\left(\frac{1}{\tau} - \frac{1}{\tau_0}\right) \quad \text{(Eq. 1)}$$

where τ is the ring-down time with an absorber present; τ_0 is the ring-down time with no absorber present; σ_A is the absorption cross section of the absorbing species A; R_L is the ratio between cavity length (79 cm) and effective absorption path (37.7 cm); c is the speed of light. To calculate the absorption cross section it is necessary to know the absorber concentration.

Acetylperoxy radicals were generated by pulsed 351 nm photolysis of acetaldehyde (CH_3CHO) / Cl_2 / O_2 mixtures:

$$Cl_2 + h\nu \rightarrow 2\ Cl \quad \text{(R5)}$$

$$CH_3CHO + Cl \rightarrow CH_3CO + HCl \quad \text{(R6)}$$

$$CH_3CO + O_2 + M \rightarrow CH_3C(O)O_2 + M \quad \text{(R7)}$$

The Cl radical concentration for the measurement of the spectrum was around 1.7×10^{12} cm^{-3} and was varied for the calibration measurements between (1 and 8) $\times 10^{12}$ cm^{-3}. Acetaldehyde was prepared as a diluted mixture in a glass bulb. A small flow was added to the mixture through a calibrated flow meter giving a concentration of 2.5×10^{14} cm^{-3}. Nearly all experiments were performed in synthetic air, at 298 K and 67hPa total pressure, the absorption cross sections at 6697.94 and 6638.30 cm^{-1} were also determined at 67hPa helium. N_2 (Praxair, 4.5), He (Praxair

4.5) and O_2 (Praxair, 4.5) were used without further purification. All gas flows were controlled by calibrated mass flow controllers (Bronkhorst, Tylan).

Absorption spectra measurements

The procedure to measure absorption spectra has been described before [24, 25] and is only briefly discussed here. The spectrum was measured with a point spacing of 0.1 cm^{-1} for the wavelength range from 6094 - 6180 cm^{-1} and 0.2 cm^{-1} for the wavelength range from 6420 - 6600 cm^{-1}, corresponding to the COO bend and the OO stretch, respectively [19]. Both wavelength regions have been sampled by changing incrementally the wavelength of the laser while a constant amount of $CH_3C(O)O_2$ was generated in the reactor.

For each wavelength, a time series of ring-down measurements testing the acetyperoxy radical absorption was recorded. After the data acquisition was triggered ring-down events were usually recorded 0.5 s each before and after the photolysis laser shot which led to the formation of acetylperoxy radicals. A typical trace is shown in **Figure 2,** where ring-down times from ring-down events occurring before the photolysis pulse are shown in black, and those after the photolysis pulse are shown in green. The loss of $CH_3C(O)O_2$ radicals is for the first tens of ms mostly due to self-reaction and to the reaction with the radical products of this self-reaction (CH_3O_2 and HO_2). With decreasing radical concentrations on the longer time scale, diffusion out of the photolysis volume becomes the major loss process. To derive the absorbance of the initially produced acetylperoxy radicals, the time-resolved series of ring-down events was extrapolated to the moment of the photolysis pulse (t = 0 s). Different fitting procedures were tested, and it turned out that a bi-exponentiel fit over the first 50 ms following the photolysis pulse reproduced the data very well and allowed a reliable extrapolation to t = 0 s. However, it has to be kept in mind that the decay of the $CH_3C(O)O_2$ concentration is due to a complex reaction scheme, and the decay constants from the fit have no physical meaning. The quality of the fit is shown as a black line in the insert of **Figure 2.** τ_0, that is required to calculate the absorbance (Eq. 1), was derived from the average of all detected ring-down events that occurred before the photolysis pulse when no $CH_3C(O)O_2$ was present. The ring-down events are randomly distributed in time at each photolysis shot because of the random nature of when exactly an efficient coupling of the laser into the cavity was achieved. Ring-down events were therefore accumulated over several laser pulses (10 – 20 generally) to get a better coverage of the whole time range.

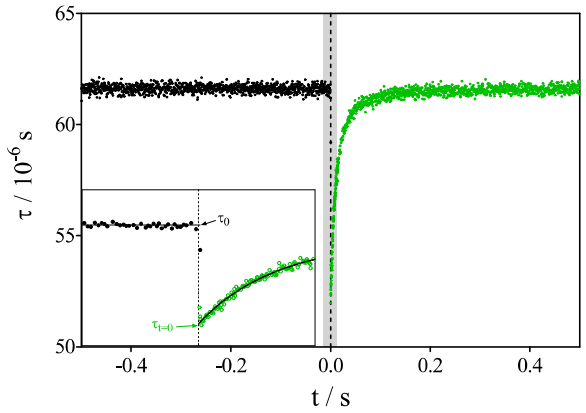

Figure 2. Typical series of ring-down times for $CH_3C(O)O_2$, the insert shows the zoom of the grey-shaded area (+/-15 ms). The dashed line represents the time of the photolysis pulse (t = 0 s). Ring-down events before the photolysis pulse (black) are used to determine τ_0, extrapolation to t=0s of a bi-exponential fit of the ring-down times occurring during the first 50 ms after the photolysis pulse (black line in the insert) are used to determine τ.

RESULTS AND DISCUSSION

A portion of the relative absorption spectrum of the OO stretch region is shown in **Figure 3**. For each wavenumber, measurements were evaluated as shown in **Figure 2.** Ring-down times extrapolated to t = 0 s (green) and τ_0 as the average of all ring-down times before the photolysis pulse (black) are shown for each wavenumber in **Figure 3**. The absorption coefficients (blue) are calculated by applying equation (Eq. 1) to each data pair τ and τ_0.

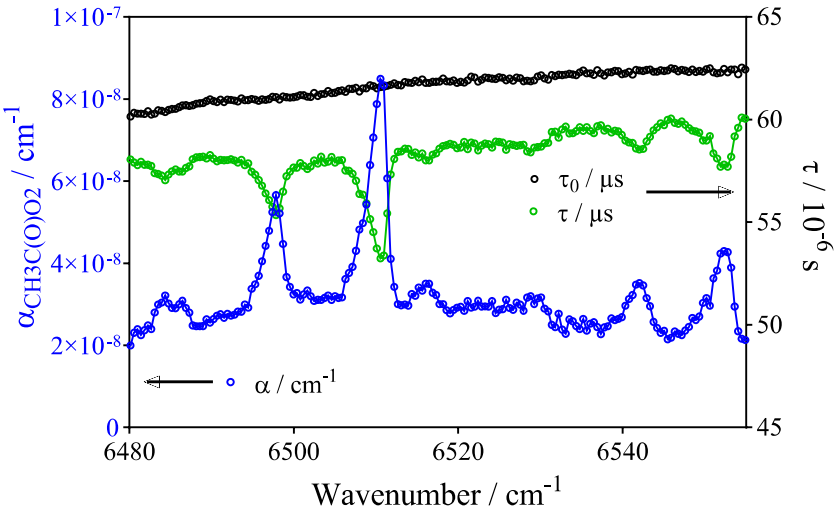

Figure 3: Portion of the relative absorption spectrum: each dot, corresponding to one wavelength, is extracted from a kinetic decay such as shown in **Figure 2**. Black dots represent baseline (τ_0), green dots obtained from extrapolation of bi-exponential fitting such as shown in **Figure 2** ($\tau_{t=0}$), blue dots (α) obtained by applying equation (Eq. 1).

In order to convert the absorption coefficient α into absolute cross sections σ, the knowledge of the exact $CH_3C(O)O_2$ concentration is necessary. Therefore, a series of experiments was conducted to quantify the initial amount of radicals. This was achieved by quantitatively converting all Cl-atoms to HO_2 radicals, which can be reliably measured by cw-CRDS on a strong absorption line at 6638.205 cm^{-1} [23, 26-29]. The measurement of the HO_2 absorption cross section is based on the measurement of HO_2 decays during self-reaction, which allows for retrieval of the initial concentration, and thus the absorption cross section, if the rate constant is known. While the uncertainty of the measured HO_2 decays itself is small (<10%), the uncertainty of the rate constant is currently recommended by the IUPAC committee to ±40%. This same uncertainty has to be considered for the absorption cross sections obtained in this work, as they are measured relative to the HO_2 absorption cross section. The quantitative conversion of Cl-atoms to HO_2 is done by photolysing a Cl_2 / methanol (CH_3OH) mixture:

$$Cl + CH_3OH \rightarrow HCl + CH_2OH \quad \text{(R9)}$$

$$CH_2OH + O_2 \rightarrow CH_2O + HO_2 \quad \text{(R10)}$$

Then, CH_3OH is substituted by CH_3CHO to form $CH_3C(O)O_2$ following reactions (R11) and (R12), while keeping conditions for the generation of Cl radicals constant.

$$Cl + CH_3CHO \rightarrow HCl + CH_3CO \quad \text{(R11)}$$

$$CH_3CO + O_2 \rightarrow CH_3C(O)O_2 \quad \text{(R12a)}$$

Assuming that the concentration of HO_2 radicals corresponds to the concentration of Cl atoms, the ratio of absorbance measured for $CH_3C(O)O_2$ and HO_2 can be used to calculate the $CH_3C(O)O_2$ absorption cross section relative to the well known HO_2 absorption cross section according to:

$$\sigma_{CH_3C(O)O_2} = \alpha_{CH_3C(O)O_2}\frac{\sigma_{HO2}}{\alpha_{HO2}} \quad \text{(Eq. 2)}$$

However, the assumption does not entirely apply, because the reaction of $CH_3CO + O_2$ leads also to the formation of some OH radicals, the yield depending on pressure and nature of the CH_3CO precursor [30-32]. An OH yield of 0.25 is expected in nitrogen at 67hPa [30].

$$CH_3CO + O_2 \rightarrow OH + \text{products} \quad \text{(R12b)}$$

OH radical concentrations can in principle be measured by cw-CRDS in the experimental set-up

[33]. However, concentrations in these experiments were below the limit of detection likely due to the fast reaction with acetaldehyde [13]:

$$CH_3CHO + OH \rightarrow CH_3CO + H_2O \quad \text{(R13)}$$

Because under our experimental conditions ([CH_3CHO] = 2.5×10^{14} cm^{-3}), (R13) is leading with $k_{13} = 1.5 \times 10^{-11}$ cm^3 s^{-1} to an OH lifetime of 250 µs, and can thus, in absence of other potential reaction partners, be considered as the nearly exclusive fate of OH radicals. And because (R13) leads to formation of another CH_3CO radical, this reaction does not introduce an error in the calculation of the absorption cross section using equation (Eq. 2).

However, it was observed in our experiments that small amounts of HO_2 radicals are formed immediately from the initial reaction of CH_3CHO + Cl. Radical concentrations measured in a typical experiment are shown in **Figure 4**: the left graph shows the HO_2 signal obtained from photolysis of Cl_2 / CH_3CHO / O_2 mixture. Because $CH_3C(O)O_2$ has a broad absorption spectrum [19], it still absorbs in the wavelength range where HO_2 is detected (6638.2 cm^{-1}). Therefore, absolute HO_2 concentrations (blue symbols) are obtained from the difference of the online (6638.2 cm^{-1}) and the offline (6638.3 cm^{-1}) absorption signal. It can be seen that the HO_2 concentration immediately after the photolysis pulse is not zero. The blue symbols on the right graph show the HO_2 concentration time profile under the same conditions, but with CH_3OH instead of CH_3CHO. Comparing the HO_2 concentrations measured from methanol mixtures ($[HO_2]_{CH3OH}$) and acetaldehyde mixtures ($[HO_2]_{CH3C(H)O}$) shows that around 3 % of the Cl-atoms are converted to HO_2 (δ_{HO2}) in the presence of CH_3CHO.

$$\delta_{HO_2} = \frac{[HO_2]_{CH_3CHO}}{[HO_2]_{CH_3OH}} \quad (3)$$

This small correction of the initial $CH_3C(O)O_2$ concentration was taken into account when converting the absorption coefficient of $CH_3C(O)O_2$ into absorption cross sections:

$$\sigma_{CH_3C(O)O_2} = \alpha_{CH_3C(O)O_2} \frac{\sigma_{HO_2}}{\alpha_{HO_2}} \times \frac{1}{(1 - \delta_{HO_2})} \quad (4)$$

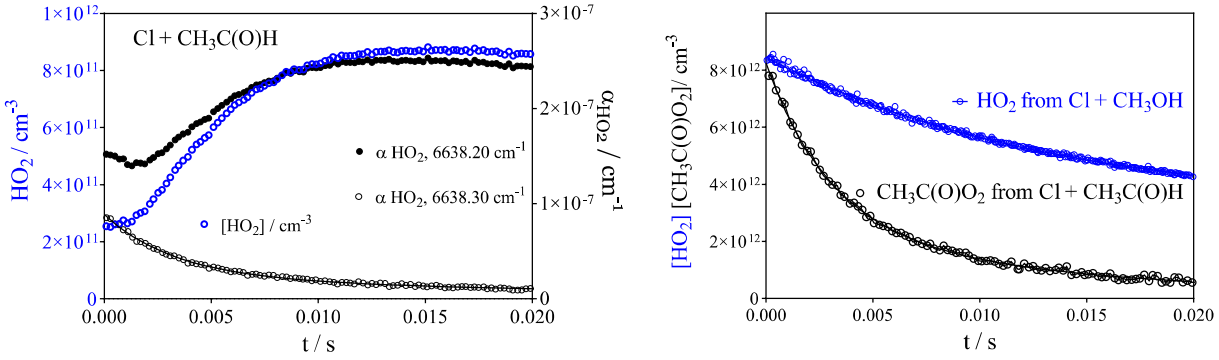

Figure 4: Left plot shows HO_2 absorption coefficient online (6638.20 cm^{-1}, black dots) and offline (6638.30 cm^{-1}, open black symbols, right y-axis apply for both) and HO_2 concentration (blue symbols, left y-axis) measured after photolysing a Cl_2 / CH_3CHO / O_2 mixture. Right graph shows the HO_2 concentration from the photolysis of Cl_2 / CH_3OH / O_2 mixture (blue symbols) and the $CH_3C(O)O_2$ concentration time profile from the photolysis of the Cl_2 / CH_3CHO/ O_2 mixture (black symbols). Both experiments used the same Cl_2 concentration.

The origin of this rapid HO_2 formation is not clear, but is formed possibly through the reaction

$$CH_3CO + O_2 \rightarrow CH_2CO + HO_2 \qquad \text{(R12c)}$$

Such a rapid HO_2 formation with similar yields had already been observed by Morajkar et al.[34] with a yield of around 7%, independent of pressure between 10 and 90 Torr helium, following the 248 nm photolysis of CH_3CHO, and also by Hui et al.[35] with a yield of 2-3% following the reaction of Cl-atoms with CH_3CHO at 100 Torr N_2. HO_2 concentrations at 67 hPa N_2 have been calculated using an absorption cross section of $\sigma_{HO2,6638.20cm-1}=2.01 \times 10^{-19}$ cm^2, obtained from the empirical expression of Assaf *et al.*[27].

This way, absorption cross sections σ were measured for 8 wavenumbers in synthetic air and for 2 wavenumbers in helium, given in **Table 1** together with the absorption coefficients α for the same wavelengths in synthetic air, such as found during the measurement of the full spectrum. Also given in **Table 1** are the absorption cross sections for two wavenumbers, obtained in 67 hPa helium: 6697.94 cm^{-1} corresponds to one peak of the OO-stretch transition band, while 6638.30 cm^{-1} corresponds to the wavenumber that we commonly use for the measurement of the HO_2-offline signal, i.e. the open circles in **Figure 4**. The error bars of the absorption coefficients α are statistical only and are given with ±5%, obtained from the 95% confidence interval of the extrapolation of the bi-exponential fit to t = 0s (black curve in the insert of **Figure 2**, typically below 4%) as well as the τ_0 (average of all ring down events before the photolysis pulse: typically less than 1%). The error bars for the absorption cross sections are given with ±50% and are composed of twice the uncertainty of extrapolating α to t = 0s (once for $\alpha_{CH3C(O)O2}$ and once for

α_{HO2}) and the 40% uncertainty given by the IUPAC committee[36] for the rate constant of the HO_2 self-reaction, that was used to determine the absorption cross section of HO_2.

Table 1: Absorption coefficient α for $CH_3C(O)O_2$ from the measurement of the full spectrum for eight wavenumbers (marked by lines in the full spectrum of **Figure 6**) and absorption cross sections σ for the same lines, determined relative to the HO_2 cross section at 67 hPa N_2 and for two wavenumbers at 67 hPa helium

Wavenumber / cm^{-1}	α / 10^{-8} cm^{-1}	σ / 10^{-20} cm^2
6121.08	5.65±0.28	3.4±1.7
6164.75	2.75±0.14	1.7±0.8
6108.74	4.01±0.20	2.2±1.1
6114.53	1.59±0.08	0.9±0.5
6497.94	5.35±0.27	3.2±1.6
6697.94 (helium)		3.3±1.7
6502.80	3.03±0.15	1.7±0.9
6552.76	4.29±0.21	2.5±1.3
6510.74	8.49±0.42	4.9±2.4
6638.30 (helium)		0.8±0.4

In **Figure 5** the absorption coefficients are plotted for all eight wavenumbers as a function of the absorption cross sections σ. A good linearity is found, assuring that the $CH_3C(O)O_2$ concentration was stable during the measurement of the full spectrum.

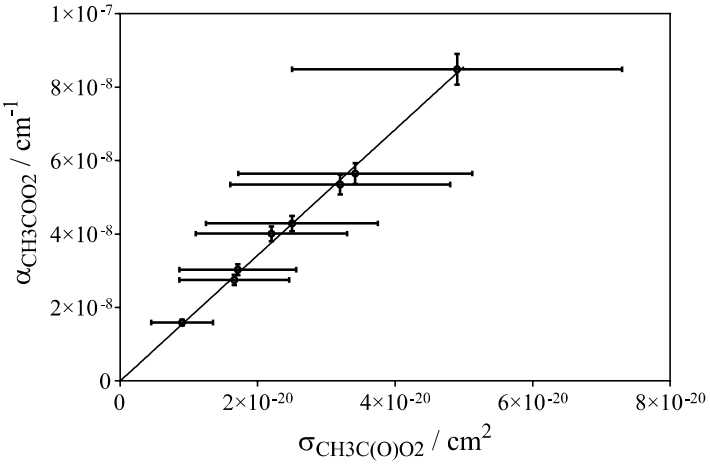

Figure 5: Absorption coefficients α as a function of the absorption cross sections σ from **Table 1**. Error bars are statistical for absorption coefficients α (5%), and an uncertainty of 45% is added for the absorption cross section σ, taking into account the uncertainty in the absorption cross section for HO_2.

The slope from the linear regression of **Figure 5** leads to the concentration of $CH_3C(O)O_2$ radicals that was generated during the measurement of the full spectrum: 1.7×10^{12} cm^{-3}. This value was used for the conversion of the absorption coefficients from the relative spectra (blue line in **Figure 3**) of the two wavelength ranges into absolute absorption cross sections, shown in **Figure 6**. A comparison with a previously published spectrum [19] shows an excellent agreement of the positions and relative intensities of the different absorption maxima.

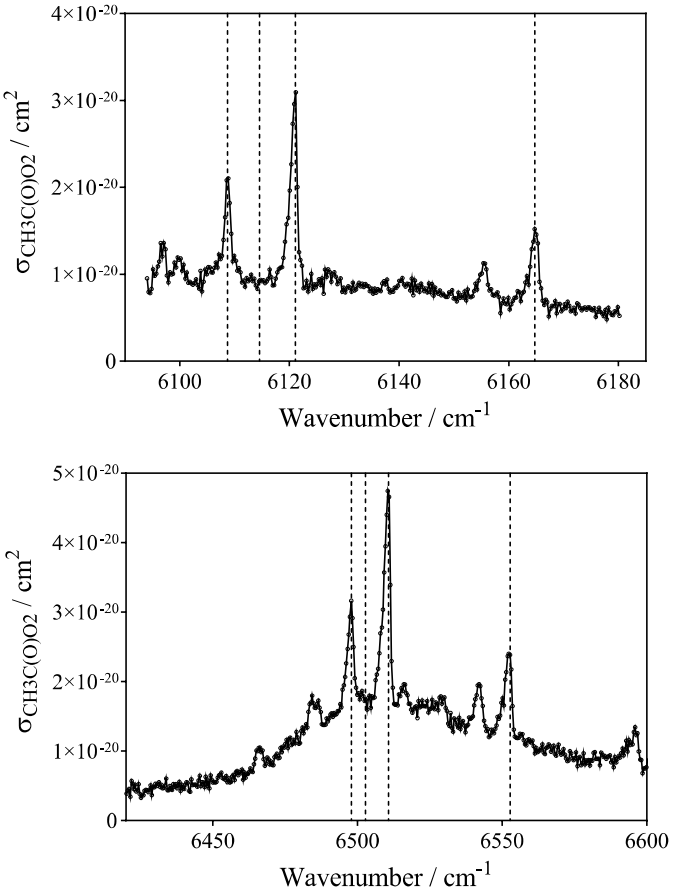

Figure 6: Absolute absorption spectrum of $CH_3C(O)O_2$. Vertical lines indicate the wavelengths where absolute absorption cross sections have been determined relative to the absorption cross section of HO_2 (see **Table 1**). The data can be downloaded as supplementary data.

Zalyubovsky *et al.* [19] determined an absorption cross section of $\sigma = (1 \pm 0.5) \times 10^{-19}$ cm^2 at 5582.5 cm^{-1}. This is consistent with our absorption cross section of $(4.9 \pm 2.4) \times 10^{-20}$ cm^2 at the absorption maximum 6510.71 cm^{-1}, which has in the spectrum of Zalyubovsky *et al.* a relative intensity of approximately a factor 2 less than the absorption maximum at 5582.5 cm^{-1}.

The results obtained in this work will be used in future studies on the reaction kinetics of $CH_3C(O)O_2$ radicals. Depending on the quality of alignment, cleanliness of mirrors, etc. a decrease of the ring-down time of $\Delta\tau = 0.5$ µs on a typical $\tau_0 = 50$ µs can be achieved in time-resolved experiments, leading to a limit of detection below $[CH_3C(O)O_2] = 4 \times 10^{11}$ cm^{-3}, making this technique more sensitive than typical UV-absorption measurements. And even though the spectrum features a rather broad background, *i.e.* lacks the high selectivity that can be achieved for HO_2 or OH measurements, its main absorption peaks are red-shifted compared to other small peroxy radicals such as HO_2, CH_3O_2 [24, 37, 38], $C_2H_5O_2$ [37] and should thus allow a selective detection for measuring the rate constants and branching ratios of self- and cross-reactions.

CONCLUSION

We measured the $CH_3C(O)O_2$ absorption spectrum in the ranges from 6094 cm^{-1} - 6180 cm^{-1} and 6420 cm^{-1} - 6600 cm^{-1}. Measurements were performed in 67hPa synthetic air or helium total pressure. Radicals were generated by the pulsed photolysis of acetaldehyde / Cl_2 / O_2 mixtures at 351 nm.

Some large peaks on top of a broad absorption spectrum were obtained, in good agreement with an earlier measurement by Zalyubovsky *et al.* [19]. Absolute absorption cross sections were measured for eight different wavelengths and are in good agreement relative to the only available measurement by Zalyubovsky *et al.* [19] performed at a lower wavenumber.

Acknowledgements

This project was supported by the French ANR agency under contract No. ANR-11-Labx-0005-01 CaPPA (Chemical and Physical Properties of the Atmosphere), the Région Hauts-de-France, the Ministère de l'Enseignement Supérieur et de la Recherche (CPER Climibio) and the European Fund for Regional Economic Development. This project has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (SARLEP grant agreement No. 681529) and from the exchange program of the Deutscher Akademischer Austauschdienst (DAAD) (project number 57316518) and PHC Procope project no. 37666WA.

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