Detection of Shock-Heated Hydrogen Peroxide (H₂O₂) by Off-axis Cavity Enhanced Absorption Spectroscopy (OA-CEAS)

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Abstract: Cavity enhanced absorption spectroscopy (CEAS) is a promising technique for studying chemical reactions due to its desirable characteristics of high sensitivity and fast time response by virtue of the increased path length and relatively short photon residence time inside the cavity. Off-axis CEAS (OA-CEAS) is particularly suited for the shock tube applications as it is insensitive to slight misalignments, and cavity noise is suppressed due to non-overlapping multiple reflections of the probe beam inside the cavity. Here, OA-CEAS is demonstrated in the mid-IR region at 1310.068 cm⁻¹ to monitor trace concentrations of hydrogen peroxide (H₂O₂). This particular probe frequency was chosen to minimize interference from other species prevalent in combustion systems and in the atmosphere. The noise-equivalent detection limit is found to be 3.25 x 10⁻⁵ cm⁻¹, and the gain factor of the cavity is 131. This corresponds to a detection limit of 74 ppm of H₂O₂ at typical high-temperature combustion conditions (1200 K and 1 atm) and 12 ppm of H₂O₂ at ambient conditions (296 K and 1 atm). To our knowledge, this is the first successful application of the OA-CEAS technique to detect H₂O₂ which is vital species in combustion and atmospheric science.

1. Introduction

Despite the growing contribution of alternate sources of energy to the total energy mix, combustion of hydrocarbon fuels continues to remain the most dominant mode of energy generation worldwide [1]. Although the share of biofuels continues to increase, the conversion of these biofuels to useful forms of energy will predominantly be through combustion based systems. Future engine technologies offering better fuel efficiency and lower emissions, such as homogeneous compression charge ignition (HCCI) and reactivity controlled compression ignition (RCCI), operate at low temperature and high pressure conditions. Under these combustion conditions, hydrogen peroxide (H₂O₂) is a key intermediate species that controls the autoignition chemistry for hydrocarbon fuels [2]. Therefore, time-history measurements of the H₂O₂ in reactive environments will lead to a better understanding of reactions affecting its formation and consumption and will subsequently aid the development and validation of chemical kinetic mechanisms, which are crucial to the optimization of new combustion-based energy conversion devices. Furthermore, hydrogen peroxide plays critical role in the atmospheric chemistry where it is primarily formed from the hydroperoxyl radical [3]

Shock tubes are considered ideal chemical reactors to study chemical reactions at high temperatures and pressures. The reaction times at these high temperatures/pressures are typically

of the order of milliseconds. For example, hydrogen peroxide typically exists in trace amounts for a few hundred microseconds during the hydrocarbon oxidation process. This necessitates the use of fast and highly sensitive measurement techniques for diagnostics in shock tubes. In fact, hydrogen peroxide despite being among the key combustion intermediates has hitherto not been directly measured in shock tube oxidation experiments. The conventional single-pass direct absorption method lacks the sensitivity required to detect H_2O_2 produced in low concentrations [4]. Therefore, accurate identification and quantification of hydrogen peroxide requires a sensitive diagnostic with a fast time-response.

Cavity based techniques offer the best avenue to improve the sensitivity of laser absorption spectroscopy while preserving its strong attributes of non-intrusiveness and fast time-response by making the laser light undergo multiple passes through the absorbing medium. The first demonstrations of the off-axis cavity enhanced absorption spectroscopy (OA-CEAS) [5] and pulsed cavity ringdown spectroscopy (CRDS) [6] techniques in the shock tubes were followed by their additional variations and applications. The OA-CEAS has been applied successfully in shock tubes to detect C_2H_2 [5], CO [7], O^* [8], O_2 [9] and CH_3 [10]. In an off-axis alignment, there are multiple configurations in which the laser beam can reflect between the mirrors of the cavity. This makes an OA-CEAS setup robust to slight misalignments and functional over many shock events which lead to discernible vibrations of the absorbing cavity.

In this study, we have developed a highly sensitive fast-time response diagnostic for H_2O_2 . The OA-CEAS based sensor was utilized to measure H_2O_2 mole fraction time-histories in H_2O_2 pyrolysis experiment. The derived rate coefficients of hydrogen peroxide decomposition provide an excellent target to validate the diagnostic over a wide range of conditions. In what follows, we present a detailed description of the experimental apparatus and the design of our sensitive and fast time-response diagnostic. We then characterize its gain by measuring known amounts of dilute acetylene mixtures in a static cell. Lastly, we demonstrate its capability to measure time-histories of H_2O_2 decomposition in high-temperature shock tube pyrolysis experiments. To our knowledge, this is the first successful application of the OA-CEAS technique to measure trace amounts of H_2O_2 in shock tube kinetics experiments.

2. Theory of Off-axis Cavity Enhanced Absorption Spectroscopy

A cavity enhanced absorption spectroscopy (CEAS) technique enhances the absorption signal by increasing the path length of the interaction between the probe beam and the target species. This is accomplished by reflecting the probe beam multiple times between the cavity mirrors which enclose the test sample comprising of the target species. The increase in path length inside a cavity comes at the cost of increased optical noise as the resonance between cavity modes and laser modes occurs only at discrete wavelengths while other wavelengths are suppressed by the cavity. There are several strategies to reduce the cavity noise. These strategies may include off-axis alignment, laser frequency scanning and adjustments of the response time of the detector, as explained in this section.

First, the effective free spectral range (FSR_{eff}) is estimated and then it is compared with the linewidth of the cw-laser. The FSR_{eff} of a multiple pass cavity is given by

$$FSR_{eff} = \frac{c}{2nL} \quad (1)$$

where n is the number of non-overlapping passes before the re-entrant condition is met and L is the length of the cavity [11]. For our work, L is the inner diameter of the shock tube (14.2 cm). The value of n can be approximated as follows. The FWHM of the mirror spot size in a mode-matched cavity is estimated by [11]

$$s = \sqrt{\frac{2\lambda L}{\pi \ln 2} \sqrt{\frac{2R_m^2}{L \left(R_m - \frac{L}{2}\right)}}} \quad (2)$$

Here, λ (7.63 μm) is the wavelength of light and R_m (1 m) is the magnitude of the radius of curvature. According to Eq. (2), the mirror spot size in this study is estimated to be 2 mm. The spot pattern on the mirror surface is assumed to be circular for estimation. The circumference of a 2 cm diameter mirror is 6.3 cm, but the number of non-overlapping spots is limited by the separation between the spots. According to the equation given below, the circular pattern is traced by successively shifting the spot by 31 degrees on the mirror according to the equation [11]:

$$\theta = \arccos\left(1 - \frac{L}{R_m}\right). \quad (3)$$

This means there are less than 12 non-overlapping passes, and so the value of FSR_{eff} is approximately $3.2 \times 10^{-3} \text{ cm}^{-1}$.

If the mirror reflectivity, R is 99.24%, the cavity finesse is 411.8 from $F = \pi\sqrt{R}/(1 - R)$; the width of the cavity resonance is $7.7 \times 10^{-6} \text{ cm}^{-1}$ using $\delta\nu = FSR/F$ [12,13], and the ratio of the maximum to the minimum intensity of the resonance profile is calculated to be 68700 [13]. The laser linewidth of a cw-QCL at a given frequency is approximately $5 \times 10^{-5} \text{ cm}^{-1}$ [14]; the laser linewidth is still narrow in comparison to the FSR_{eff} by 2 orders of magnitude. Furthermore, the resonance width of the cavity modes is small, and the ratio of maximum to minimum intensity of the resonance profile is not negligible. Because of these 3 factors, the off-axis alignment alone is not sufficient to mitigate the optical noise for the cavity used in this work.

The cavity noise can be reduced further by scanning the laser wavelength such that the time taken to scan over multiple cavity modes is of the same order as the cavity time constant (or the photon residence time in the cavity). The photon residence time is given by [15]:

$$\tau = \frac{L}{c(1 - R + \alpha L)}. \quad (4)$$

When the absorbance αL is 0.01 and reflectivity R is 0.9924, the cavity time constant is approximately 30 ns. Scanning rate of 50 kHz is selected as it provides an optimum balance between rapid scanning needed to reduce optical noise and the time resolution constraint set by the width of the beam pattern ($< 5\text{mm}$). At 50 kHz, the linear laser scan range is 0.6 cm^{-1} , which includes both the up and the down scan, so a single scan covers 1.2 cm^{-1} in 20 μs . At this rate, the laser scans $1.8 \times 10^{-3} \text{ cm}^{-1}$ during 30 ns. However, for a sinusoidal injection current, the scan rate is not uniform. The scan rate in the region with the steepest gradient in the sinusoidal waveform is faster than the average scan rate. If the scanning is centered at the probe wavelength, then the laser can sweep multiple FSR's in the spectral region of interest during one cavity time constant. Additional suppression of noise is achieved by implementing a low pass FFT filter *in situ* during

data acquisition. The cavity noise suppression is also aided by the relatively slow response time of the photo-detector. The bandwidth of the detector used in this work is 10 MHz, so that the rise time is 35 ns. During this time interval, the laser scans over $2.1 \times 10^{-3} \text{ cm}^{-1}$, which is approximately 66% of the successive cavity mode separation (or the *FSR*). This indicates the bandwidth of the detector is not adequate to fully resolve the cavity mode structure at 50 kHz scan rate, and it leads to partial smoothening of the high frequency noise profile in the recorded signal.

The cavity gain is calculated using [7,16]

$$G = \frac{e^{A_{CEAS}(\nu)} - 1}{1 - e^{-A_{SP}(\nu)}}, \quad (5)$$

where $A_{CEAS}(\nu)$ is the cavity-enhanced absorbance at frequency ν , and it is given by $-\ln(I_t/I_o)$, where I_t is the output intensity from the cavity in the presence of the absorber, and I_o is the intensity in the absence of the absorber. Both I_t and I_o are measured experimentally. The $A_{SP}(\nu) = XP S(T) \phi(\nu) L$ is the single-pass absorbance. It is calculated using the known values of the partial pressure XP of the absorber, the transition strength $S(T)$ at temperature T , the line shape function $\phi(\nu)$, and the cavity length L . The value of reflectivity is obtained from the gain factor, G using [7,16]

$$R = \frac{G}{1 + G}. \quad (6)$$

After the cavity gain is determined, the single-pass absorbance is inferred from the measured value of the CEAS absorbance:

$$A_{SP} = \frac{1}{G} \left(\frac{I_t}{I_o} - 1 \right). \quad (7)$$

The mole fraction of target species (H_2O_2) can be calculated from the single-pass absorbance as [17]:

$$X = \frac{A_{SP} k T}{\sigma(P, T) P L}. \quad (8)$$

The absorption cross section, $\sigma(P, T)$, is computed using the line parameters available from the HITRAN database [18]; k is the Boltzmann constant, $1.3806488 \times 10^{-23} \text{ JK}^{-1}$. The HITRAN values of the absorption cross section were verified experimentally for the conditions shown in Table 1. For these measurements, relatively high concentration of H_2O_2 was used, and the mole fraction of H_2O_2 was determined at a previously used probe frequency of $1302.5119 \text{ cm}^{-1}$ [4].

Table I: Verification of the H_2O_2 absorption cross section at 1310.068 cm^{-1}

T [K]	P [bar]	Measured cross section [cm^2]	HITRAN cross section [cm^2]
1055	3.8	9.7×10^{-20}	8.8×10^{-20}
1126	3.7	7.5×10^{-20}	7.7×10^{-20}
1241	2.1	6×10^{-20}	6.3×10^{-20}

3. Experimental Details

3.1 Optical Configuration

The experimental setup used in this work is shown in Fig. 1. A continuous wave distributed feedback quantum cascade laser (Alpes Lasers, sbcw5721 DN) with a tuning range of 1302.2-1314.2 cm^{-1} was used as the radiation source. A function generator (Stanford Research Systems, DS345) modulated the input current of the laser with a sinusoidal wave of 50 kHz frequency which resulted in a tuning range of about 0.6 cm^{-1} in the output wavelength. The tuning range was characterized by recording transmission through a 7.62 cm long Germanium etalon with free spectral range (FSR) of 0.0163 cm^{-1} . The central wavelength emitted by the laser was controlled by adjusting the temperature or the injection current on the laser controller. A 10 mW He-Ne laser was co-propagated with the QCL beam to initiate the alignment process. A ZnSe plano-convex lens (100 mm focal length) was used to focus the beam coming out of the optical cavity into a thermoelectrically-cooled photovoltaic detector (Vigo PVM 2TE-10.6; 10 MHz bandwidth). A stable optical cavity was formed by plano-concave mirrors with 1 m radius of curvature, 20 mm diameter and 5 mm thickness. Relatively small diameter mirrors were utilized due to the limited optical access available on the shock tube. As described previously [6], the mirrors were glued to custom-designed plugs which were mounted on the shock tube ports at an axial distance of 2 cm from the end-wall of the shock tube. The orientation of the cavity mirrors was controlled using three fine adjustment screws (Thorlabs FAS100) which allowed three-axis rotation of the custom-designed plugs. To begin the alignment procedure, the cavity was aligned on-axis. The on-axis alignment was confirmed by observing the maximum optical noise in the signal displayed on the digital oscilloscope (PicoScope 5444B; 15 bits, 200 MHz bandwidth, 125 MS/s). The off-axis alignment was achieved by adjusting the tilt of the input plane mirror (IPM) and the cavity mirrors. This was evidenced by a drastic decrease in the optical noise in the signal. The HeNe laser spot pattern was not visible on the mirror surfaces because ZnSe, the mirror substrate, has a relatively small transmittance of 50% at 632.8 nm.

Fig. 1. Schematic of the experimental set up: mid-IR laser (QCL), flipper mirror (FM), alignment laser (HeNe), neutral density filter (NDF), plane mirror (PM), ZnSe window (ZW), germanium etalon (GE), detector (D), input plane mirror (IPM), ZnSe focusing lens (ZFL) and oscilloscope (O).

3.2 Shock Tube Facility

All measurements reported here were carried out in the chemical kinetics shock tube facility at King Abdullah University of Science and Technology (KAUST). The stainless steel shock tube has an inner diameter of 14.2 cm and consists of 9-meter long driven section. The length of the driver section can be varied up to a maximum of 9 meters depending on the required test time. The driven section is vacuumed with a turbomolecular pump to achieve an ultimate pressure on the order of 10^{-5} Torr. The pre-shock mixture pressure was measured via a high accuracy Baratron manometer (MKS Instruments). Five piezoelectric pressure transducers (PCB 113B26) placed axially along the last 1.3 m of the driven section were used to obtain the incident shock speed. One-dimensional shock-jump relations were used to calculate the temperature and pressure behind reflected shock waves. The uncertainty in the calculated end-wall shock speed ranges between 0.02 – 0.16 % which translates to negligible uncertainties in the temperature ($< 0.5\%$) and pressure ($< 1\%$) behind reflected shock waves. Side-wall pressure history was measured at an axial distance of 2 cm from the shock tube end-wall using a piezoelectric pressure transducer (Kistler 603B1). Further details on this shock tube are available in the literature [19, 20].

3.3 H_2O_2 Source and Loading

The hydrogen peroxide molecule is known to decompose upon contact with any surface [21]. Due to its unstable nature, high concentrations of H_2O_2 solutions are hazardous and are not available commercially. Commercial grades consisting of 30% to 50% aqueous solutions of hydrogen peroxide can be used as a source of hydrogen peroxide. However, it is challenging and time-consuming to extract pure H_2O_2 from the diluted aqueous solutions because of the significantly lower vapor pressure of H_2O_2 compared to water. Urea- H_2O_2 adduct offers an alternate way of obtaining relatively pure H_2O_2 vapor and is available as powder commercially [22]. It releases relatively pure H_2O_2 when heated to about 60 °C. This makes the urea- H_2O_2 adduct safer and an easier-to-handle substitute to obtain pure hydrogen peroxide. In this study, hydrogen peroxide-urea adduct powder (97% purity, Sigma Aldrich) was used as the source of H_2O_2 . The adduct powder was mixed with an almost equal amount of diatomaceous earth powder (SiO_2 , Sigma Aldrich) in a polycarbonate flask to avoid agglomeration on heating. The flask was then placed in a water bath maintained at 60 °C. Research grade argon was passed through the adduct mixture at a flow rate of about 50 sccm. To avoid accidental back flow of hydrogen peroxide towards the mass flow controller for argon, an empty flask was placed between the argon mass flow controller and the flask containing the adduct mixture [4]. As H_2O_2 decomposes quickly upon contact with the stainless steel surfaces, it was decided to minimize the time needed to fill the shock tube driven section to the desired pre-shock pressure by further diluting the $\text{H}_2\text{O}_2/\text{Ar}$ mixture with pure argon stream. Therefore, the $\text{H}_2\text{O}_2/\text{Ar}$ mixture exiting the flask was diluted by mixing with a pure argon stream at flow rates of 1000 sccm, resulting in H_2O_2 concentrations of ~ 500 ppm in the pre-shock mixture. The final $\text{H}_2\text{O}_2/\text{Ar}$ mixture was introduced in the driven section of the shock tube through a filling port at a distance of 2 cm from the shock tube end-wall.

3.4 Selection of Probe Wavelength

Figure 2 shows simulated absorption coefficient of hydrogen peroxide at representative temperature/pressure conditions used in this study. Commercial lasers are generally not available at small wavenumbers (730 cm^{-1} and lower) [17], which makes the absorption features near 1310 cm^{-1} the most viable option in the $1000 - 1500\text{ cm}^{-1}$ spectral window. Since it is desired to utilize

the current diagnostic for measuring the formation and consumption of hydrogen peroxide in combustion experiments, detailed simulations were carried out in the spectral window of 1295 – 1315 cm^{-1} to investigate spectral overlap from potential interfering species formed during fuel oxidation (CH_4 , C_2H_2 , H_2O , HO_2). The comparison between the H_2O_2 absorbance and the combined absorbance of the major interference species is shown in Fig. 3. Hydroperoxyl radical (HO_2) has negligible absorbance in the selected wavenumber region and is, therefore, not included in Fig. 3. All selected interfering species have relatively strong absorption lines in the selected spectral window and a thorough analysis indicated that the contribution of interfering species to the total absorbance is the minimum at 1310.068 cm^{-1} , which makes it the most promising probe wavelength to measure H_2O_2 by direct absorption spectroscopy in combustion experiments. Therefore, 1310.068 cm^{-1} was selected as the probe wavelength in this study. In the current work, as a proof-of-concept, we have applied the developed diagnostic to measure H_2O_2 decomposition reaction. In future, we plan to investigate and implement a multi-wavelength strategy to measure H_2O_2 in fuel oxidation experiments. Such an approach will be necessary to overcome potential broadband interference from large hydrocarbon fuel molecules.

Fig. 2. Simulated absorption coefficients of 1% H_2O_2 at typical reflected shock conditions of 1200 K and 1 atm. Spectral data are taken from HITRAN database [18].

Fig. 3. Simulated absorption coefficient of H_2O_2 and expected interfering species (H_2O , CH_4 and C_2H_2) at 1200 K, 1 atm. Mole fraction of each species is taken as 1%. Spectral data are taken from HITRAN and HITEMP databases[18,23].

4. Results & Discussion

The gain factor (G) of the CEAS cavity is needed to infer the species mole fractions from the intensity measurements. The gain can be estimated from the value of reflectivity available from the mirror manufacturer (98.8% for the mirrors used here). However, the manufacturer specified reflectivity usually has relatively high uncertainty limits which can lead to substantial errors in measurement. It is, therefore, very important to measure the reflectivity (or gain) of the cavity to be able to accurately measure species mole fraction. In this work, the gain of the OA-CEAS cavity was characterized at 1309.459 cm^{-1} by measuring the absorbance of an acetylene/nitrogen mixture of known concentration in a static cell. Acetylene was chosen over H_2O_2 because the concentration of H_2O_2 in a mixture cannot be known *a priori*. The H_2O_2 concentration estimated from the flow rates is not accurate as the H_2O_2 adsorbs to the inner surfaces of the tubes and the static cell. Among the candidate acetylene transitions at 1309.459 , 1309.649 and 1309.704 cm^{-1} , the transition at 1309.459 cm^{-1} is selected for gain characterization as the uncertainty in line strength at this transition is $\sim 2\%$ in contrast with the uncertainty of 5 – 10% at other neighboring transitions. A representative measured absorbance signal of acetylene is shown in Fig. 4.

Fig. 4. Measured OA-CEAS absorbance, Voigt fit and residuals for static cell measurements of 0.06% C_2H_2/N_2 mixture at 121 Torr and 295 K. Residual is normalized with the peak absorbance.

The single-pass absorbance was obtained from the spectral simulations based on the line parameters listed in the HITRAN database [18]. This was compared with the experimental measurements of the CEAS absorbance to obtain the gain factor and mirror-reflectivity using Eqs. (5) and (6), respectively. The gain factor varied slightly between the experimental runs and during the up-scan and down-scan of the injection current frequency, possibly because of the residual optical noise and some noise in the laser injection current. The gain factor and reflectivity used in the data analysis is the mean of the values shown in Fig. 5. Note that Fig. 5 does not intend to suggest that the gain factor is a function of gas pressure. The only purpose of the pressure variation was to increase the number of data samples in the process of filling the static cell to a specific target pressure. According to the data in Fig. 5, the gain is 130.6 ± 6.7 and the corresponding mirror reflectivity is 99.24 ± 0.04 %.

Fig. 5. Cavity gain of the OA-CEAS cavity characterized by measuring the absorbance of a 0.06% C_2H_2/N_2 mixture near 1309.459 cm^{-1} at various pressures in a static cell at 295 K.

It is imperative to maintain the alignment of the OA-CEAS cavity to carry out reliable and repeatable absorption measurements. The passage of incident and reflected shock waves are accompanied by sudden changes in temperature, pressure and refractive indices of the shock-heated gases. These effects along with the mechanical vibrations that accompany a shock wave can potentially disturb the alignment of the OA-CEAS cavity and thereby make it challenging to implement such multi-pass techniques in a shock tube. Consequently, these effects were considered carefully during the design of the OA-CEAS diagnostic discussed here. The alignment of the OA-CEAS cavity was tested by measuring the photo-detector signals before and after the arrival of incident and reflected shock waves for non-reactive (pure argon) shocks. Figure 6 shows the detector signal (black) and the pressure trace (blue) for a representative non-reactive argon shock. In this experiment, neither any absorption nor any change of laser intensity is expected. The pre-shock conditions (temperature, pressure) and the conditions behind the reflected shock wave are shown in green and red color, respectively. The instantaneous jumps in the pressure trace indicating the arrival of incident and reflected shock waves do not cause any obvious reduction in the transmitted laser intensity implying that the alignment of the OA-CEAS cavity remained unperturbed throughout the measurement.

Fig. 6. Measured pressure (blue) and detector signal (black) for a non-reactive (pure argon) shock tube experiment.

The OA-CEAS H_2O_2 diagnostic developed here is significantly more sensitive than the competing direct absorption sensors and thereby enables the utilization of highly dilute mixtures for carrying out reaction kinetic studies. The use of dilute mixtures leads to negligible temperature and pressure changes during the reaction and enables the operation of the shock tube close to ideal conditions of constant volume and energy (constant UV). Dilute mixtures also minimize the effect of secondary reactions which otherwise may obscure the determination of a specific target reaction rate constant.

The diagnostic was subsequently applied to measure trace amounts of hydrogen peroxide in reactive experiments of hydrogen peroxide pyrolysis. The decomposition rate of hydrogen peroxide has been measured previously at high temperatures [4,21,24] and is, therefore, a good target to validate the sensitive diagnostic over wide range of conditions. Table 2 shows the conditions (temperature, pressure) behind reflected shock waves and the corresponding

decomposition rates inferred from the concentration time-histories of hydrogen peroxide. The decomposition of hydrogen peroxide results in two hydroxyl (OH) radicals. The reaction can be written as follows (M is a third-body collision partner, argon for this study):

Table 2. Experimental conditions and measured reaction rates

T (K)	P (atm)	Initial H ₂ O ₂ loading (ppm)	k ₁ (cm ³ mol ⁻¹ s ⁻¹)
925	1.55	240	1.02 x 10 ⁶
1007	1.56	305	8.55 x 10 ⁶
1044	1.12	460	1.38 x 10 ⁷
1066	0.87	830	2.74 x 10 ⁷
1074	1.64	564	2.45 x 10 ⁷
1127	1.48	470	6.21 x 10 ⁷
1200	1.32	780	1.95 x 10 ⁸

Figure 7 shows representative concentration time-histories of hydrogen peroxide measured using the OA-CEAS diagnostic. The mole fraction time-histories are normalized with the initial H₂O₂ mole fraction. The detector signal was averaged over 1310.068 ± 0.005 cm⁻¹ to ensure that the transmitted signal (I_t) captured the H₂O₂ peak. Similarly, detector signal in evacuated shock tube condition was used to obtain I_0 . The I_t and I_0 values were used with the measured gain factor of OA-CEAS diagnostic to calculate single-pass absorbance using Eq. (7). The H₂O₂ absorbance at time zero was used to determine the initial H₂O₂ loading by using the absorption cross-section values available from HITRAN database [18]. The measured concentration time-histories compare well with the kinetic simulations carried out using Hong et al. [21] chemical kinetic model .

Fig. 7. Representative normalized H₂O₂ mole fraction time-histories for various reflected shock conditions in Ar bath gas. Simulations carried out using Hong et al. [21] model compare well with time-history measurements

Figure 8 shows the second-order decomposition rates of hydrogen peroxide plotted as a function of $1000/T$ for the current study and previous experimental works [4,21,24]. The hydrogen peroxide decomposition rates for the current study were extracted from the best-fit of the simulation to the measured H_2O_2 time-history profiles. The decomposition rates of hydrogen peroxide agreed well with previous measurements thereby validating the sensitive H_2O_2 diagnostic over a wide range of conditions. Moreover, the previous work of Sajid et al. [4] used relatively large initial mole fractions of H_2O_2 (~ 5000 ppm) because the detection was based on single-pass absorption of H_2O_2 . The current OA-CEAS diagnostic has much higher sensitivity and the use of small H_2O_2 mole fractions enables more accurate determination of reaction rate constant.

The noise in the measured hydrogen peroxide concentration in the pre-shock region was used to estimate the detection limit of the diagnostic. Small variations were observed in the values of standard deviation (1σ) for different mole fractions of hydrogen peroxide and the maximum standard deviation in absorbance was $3.25 \times 10^{-5} \text{ cm}^{-1}$, which corresponds to a detection limit of 12 ppm at 296 K and 74 ppm at 1200 K, both at atmospheric pressure.

Fig. 8. H_2O_2 decomposition rate coefficients measured as a function of temperature. Previous experimental measurements shown as a reference. Nominal pressures for the current and previous data are noted in the legend.

Utilizing the aforementioned sensitive diagnostic for measuring H_2O_2 , time-histories in fuel oxidation experiments is an exciting possibility. However, before embarking on such an experimental campaign, it is necessary to carry out a detailed analysis to identify all possible interfering species during the fuel oxidation reaction. Water vapor and methane are among the major interfering species but interference from large fuel molecules with broad spectral features should also be considered carefully since these may be present in orders of magnitude larger mole fractions compared to H_2O_2 . Currently, it is not possible to predict the absorbance by the fuel molecules as their absorption cross sections are not available at high temperatures. Future work

will entail detailed characterization of spectral interferences from large hydrocarbons and use of multi-wavelength strategy to measure H₂O₂ in fuel oxidation experiments.

5. Conclusions

A highly sensitive and fast time-response diagnostic based on off-axis cavity enhanced absorption spectroscopy (OA-CEAS) was successfully developed and utilized for measuring trace amounts of hydrogen peroxide. The fast time-response diagnostic achieved a noise-equivalent detection limit better than $3.25 \times 10^{-5} \text{ cm}^{-1}$ and gain of 131, which makes it orders of magnitude more sensitive than the single-pass direct absorption based diagnostics. Hydrogen peroxide mole fraction as low as 74 ppm can be detected at typical high-temperature pyrolytic conditions of 1200 K and 1 atm. At room temperature and pressure, 12 ppm of hydrogen peroxide can be measured. The OA-CEAS diagnostic was used to measure time-histories of H₂O₂ during the high-temperature pyrolysis reaction. These measurements were used to calculate the rate constants of H₂O₂ decomposition over 925 – 1200 K. The ability to measure trace amounts of hydrogen peroxide makes this diagnostic highly valuable for future chemical kinetic studies of fuel oxidation.

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