



## Frontiers article

# Hydrogen peroxide vapor cross sections: A flow cell study using laser absorption in the near infrared

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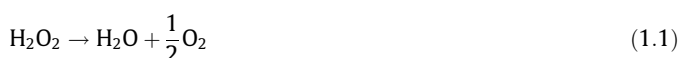
## ABSTRACT

The absorption spectra of vapors of concentrated hydrogen peroxide/water mixtures (without a carrier gas) were characterized at wavelengths from 1390 to 1470 nm utilizing a near-infrared diode laser. Low pressures were employed to examine these spectral features near the Doppler-broadened limit. An advantageous portion of the spectra near 1420 nm containing several distinct H<sub>2</sub>O<sub>2</sub> peaks and one well-known H<sub>2</sub>O peak (for calibration) was identified and the cross-sections of these peaks determined. These cross section values can be employed to measure vapor-phase concentrations of H<sub>2</sub>O<sub>2</sub> in propulsion, atmospheric chemistry, and sterilization applications.

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## 1. Introduction

Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) is typically known for its household and medical uses in dilute solutions as a disinfectant or bleaching agent [1,2] and is a known product of photochemical reactions in urban atmospheres [3]. At higher concentrations it can be used as a rocket propellant [4]; in the presence of a catalyst, H<sub>2</sub>O<sub>2</sub> will decompose exothermically into water (H<sub>2</sub>O) and oxygen (O<sub>2</sub>):



Typical H<sub>2</sub>O<sub>2</sub> thrusters pump-feed or pressure-feed liquid H<sub>2</sub>O<sub>2</sub> to a catalyst chamber where the liquid reacts with the catalyst creating a high pressure, high temperature gas. This gas is then expanded through a nozzle to generate thrust. Another option is to use H<sub>2</sub>O<sub>2</sub> in the vapor state. For very low thrust in-space applications, H<sub>2</sub>O<sub>2</sub> liquid can be vacuum-boiled to generate a low-pressure reactive vapor which may provide finer control at lower thrust levels than liquid H<sub>2</sub>O<sub>2</sub> systems can. To characterize H<sub>2</sub>O<sub>2</sub> vapor thruster performance, it is important to quantify the concentration of H<sub>2</sub>O<sub>2</sub> vapor in the vicinity of the catalyst bed and the amount of unreacted vapor present in the exhaust. From this information the thruster efficiency can be determined and chemical kinetics of the catalytic reaction can be inferred.

For relevance to propulsion applications, a traditional spectroscopic approach using highly diluted samples at relatively high total pressures contained in a stagnant vessel is not appropriate because (1) the H<sub>2</sub>O<sub>2</sub> vapor may decompose on a time scale shorter than the measurement duration; (2) individual absorption lines cannot be determined in higher-pressure systems due to collisional broadening and (3) such conditions would not provide spectra that are representative of those present in low-pressure vapor-phase propulsion applications. Additional considerations for measuring H<sub>2</sub>O<sub>2</sub> spectra are (1) the diagnostic must be able to differentiate between H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>O, a difficult task because the molecules have similar O-H bond characteristics and therefore some similar spectral features and (2) the diagnostic must not cause decomposition of H<sub>2</sub>O<sub>2</sub>.

Using absorption spectroscopy to measure concentrations of H<sub>2</sub>O<sub>2</sub> has been employed previously, however, the focus of most of these studies has been in the ultraviolet (UV) or far infrared regions. The UV region has been of particular interest due to the impact of H<sub>2</sub>O<sub>2</sub> photolysis in the atmosphere at UV wavelengths. As early as the 1930s, Fergusson et al. [5] measured broadband absorption cross sections from 200 to 500 nm. Recently Kahan et al. compared cross section measurements from six different studies spanning 40 years [6]. The mid to far infrared, including the fundamental ν<sub>3</sub> and ν<sub>6</sub> bands, have also been explored and these data are available in the HITRAN2012 database [7].

One of the spectral regions of H<sub>2</sub>O<sub>2</sub> notably lacking in the literature is the near infrared (NIR), which is an ideal wavelength region for *in-situ* measurements because H<sub>2</sub>O<sub>2</sub> is a strong absorber

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in this region and because of the availability and robustness of commercially-available NIR diode lasers with optical fiber couplings. Using a high-resolution diode laser and low total pressures, individual  $\text{H}_2\text{O}_2$  absorption lines can be resolved near their Doppler-broadened limit, which eliminates issues that arise with broadband measurements, primarily the need to account for  $\text{H}_2\text{O}$  vapor in the sample. Parker et al. [8] investigated two NIR lines near 1506 nm of the vapor from a 50/50  $\text{H}_2\text{O}_2$  solution bubbled with helium at a total pressure of 50 Torr. They were able to identify the individual absorption lines without  $\text{H}_2\text{O}$  interference, but for only four different  $\text{H}_2\text{O}_2$  concentrations, thus limiting the statistical confidence in these data. Other studies in the NIR investigated broadband spectra and discrete transitions [1,2,9–11] but cross sections were not measured. Johnson et al. [9] published quantitative broadband spectra for the  $\nu_1 + \nu_5$  combination band, which covers 1390–1450 nm. This combination band has also been observed by Giguère [10] at low resolution in the gas phase and the spectra was partially assigned. Corveleyn et al. [1] also made broadband NIR measurements, particularly for a strong  $\text{H}_2\text{O}_2$  peak near 1420 nm previously observed by Giguère.

Based on the aforementioned broadband studies, we conducted a preliminary spectral survey in the 1390–1470 nm range. We noted that the spectrum near 1420 nm contains several distinct  $\text{H}_2\text{O}_2$  peaks and one well-known  $\text{H}_2\text{O}$  peak, making this region particularly advantageous for measurements of  $\text{H}_2\text{O}_2$  vapor concentration in the presence of  $\text{H}_2\text{O}$  vapor. Consequently, the objective of this work is to investigate the spectrum of  $\text{H}_2\text{O}_2$  vapor near 1420 nm at high resolution.

## 2. Experiment

### 2.1. $\text{H}_2\text{O}_2$ flow cell

A diagram of the apparatus is shown in Fig. 1. A Newport tunable diode laser, TLB-6725, capable of spanning 1390–1470 nm was used for this study due its high power of 45 mW, excellent 0.01 nm tuning resolution and narrow, stable linewidths (<200 kHz).

The laser beam was split into two beams using a  $\text{CaF}_2$  flat with one beam directed to a wavemeter to record the wavelength and the other beam into a Herriott-type multipass cell [12] of 10 cm length and radius 2 cm. The multipass cell was configured to provide 17 passes, yielding a total beam path length within the cell of 170 cm. After the beam exited the cell, it was directed through a short-focus lens and onto an infrared detector. Liquid  $\text{H}_2\text{O}_2$  was placed under vacuum and the vapor passed through this multipass flow cell. To minimize  $\text{H}_2\text{O}_2$  decomposition, the only materials within the flow path were passivated borosilicate glass, Teflon™,

and stainless steel. The concentration of  $\text{H}_2\text{O}_2$  was varied by changing the  $\text{H}_2\text{O}_2$  liquid temperature, the  $\text{H}_2\text{O}_2$  liquid concentration, and the downstream orifice size. Operating total pressures inside the flow cell were 0.5–1.75 Torr at ambient temperatures ( $22 \pm 2$  °C).

The liquid  $\text{H}_2\text{O}_2/\text{H}_2\text{O}$  mixture was provided by PeroxyChem. As delivered, the concentration of  $\text{H}_2\text{O}_2$  was 84% by mass. This solution was further purified up to 90%  $\text{H}_2\text{O}_2$  by mass prior to testing. The liquid  $\text{H}_2\text{O}_2$  reservoir was placed in a temperature-controlled water bath to maintain a steady liquid temperature during vacuum evaporation. The pressure was measured both upstream and downstream of the flow cell. Any pressure differential would imply  $\text{H}_2\text{O}_2$  decomposition inside the flow cell, e.g. via Eq. (1.1) which would lead to an increase in pressure within the cell. Only conditions resulting in a pressure difference of less than 5% of the total pressure were employed in this study.

A dry air purge tent was placed around the entire apparatus to minimize interference from atmospheric  $\text{H}_2\text{O}$  vapor. Thirty minutes prior to any testing the purge was initiated to displace the  $\text{H}_2\text{O}$  vapor within the laser path. Despite this precaution not all of the atmospheric water vapor could be excluded, therefore prior to each test an atmospheric background scan was recorded without any gas in the flow cell to determine the atmospheric water vapor background.

### 2.2. Water line cross section

The cross section of the  $\text{H}_2\text{O}$  line at 1420.015 nm was measured and compared to the Doppler-broadened line strength calculated from the integrated line strength ( $S$ ) in the HITRAN database [7]. The integrated line strength is related to the Doppler-broadened peak cross section  $\sigma_0$  by the following equation:

$$\sigma_0 = \left( \frac{\lambda_0}{\sqrt{\pi}} \right) \left( \frac{c}{\mu} \right) S \quad (2.1)$$

where  $\lambda_0$  is the centerline wavelength,  $c$  is the speed of light, and  $\mu$  is the most probable molecular thermal velocity:

$$\mu = \sqrt{2kT/m} \quad (2.2)$$

where  $k$  is the Boltzmann constant,  $T$  is the temperature, and  $m$  is the molecular mass. The integrated line strength at 1420.015 nm yields a peak cross section  $\sigma_0 = (4.25 \pm 0.02) \times 10^{-20} \text{ cm}^2 \text{ molec}^{-1}$  based on HITRAN data in the temperature range of  $22 \pm 2$  °C.

Using  $\text{H}_2\text{O}$  rather than  $\text{H}_2\text{O}_2$  in the liquid reservoir, absorption at 1420.015 nm was measured for varying concentrations of  $\text{H}_2\text{O}$  vapor in the flow cell (obtained by varying liquid temperature). A simple plot of peak absorption versus concentration multiplied by the path length was used to determine the measured peak cross section by using the Beer-Lambert law:

$$I = I_0 e^{-\sigma n L} \quad (2.3)$$

where  $I$  and  $I_0$  are the transmitted and initial intensity, respectively,  $L$  is the path length and  $n$  is the number density of absorbing molecules.

Fig. 2 shows a plot of the  $\text{H}_2\text{O}$  absorption at 1420.015 nm as a function of  $\text{H}_2\text{O}$  vapor concentration. The slope of the data yields a peak cross section of  $(4.15 \pm 0.20) \times 10^{-20} \text{ cm}^2 \text{ molec}^{-1}$ . This value matches the HITRAN calculated cross section noted above which confirms that the measurements are near the Doppler-broadened limit, i.e., collision broadening is insignificant under these conditions.

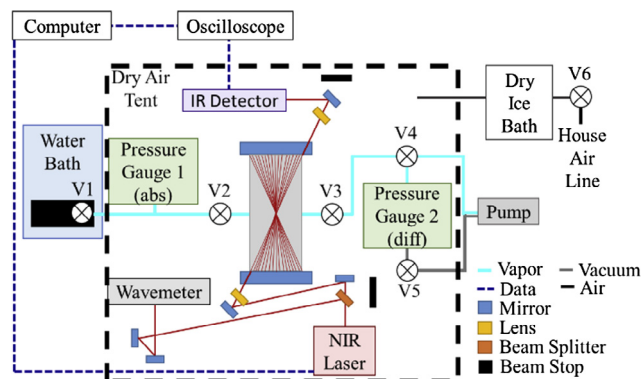


Fig. 1. Experimental set-up including paths for the laser, vapor, dry air, and data.

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