Measurements of Radical and Metastable Species in Nonequilibrium Plasmas
by Cavity Ring-Down Spectroscopy

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In the present work, number densities of HO₂ radical, H₂O and metastable excited electronic state of nitrogen, N₂(A³Σ_u⁺), have been measured in two different Cavity Ring-Down Spectroscopy (CRDS) experiments. In the first experiment, an injection-seeded Optical Parametric Oscillator (OPO) is used to generate a narrowband laser output used in the CRDS spectrometer (spectral linewidth of 0.03 cm⁻¹). Water number density is measured in the effluent of a microwave discharge sustained in an H₂-O₂-Ar mixture. Hydroperoxyl radical number density is measured in two environments, a chemically reacting Cl₂-O₂-CH₃OH-Ar mixture initiated by laser-induced photolysis, and a repetitive ns pulse discharge in a H₂-O₂-Ar mixture. The results demonstrate that HO₂ number density on the order of 1×10¹⁰ cm⁻³ and H₂O number density of 1×10¹⁶ cm⁻³ can be measured, using single laser-shot cavity ring-down traces. The injection-seeded OPO pumped CRDS spectrometer has been shown to have sufficient bandwidth for simultaneous measurements of water vapor and hydroperoxyl radical in reacting flows. In the second experiment, time-resolved absolute number density of N₂(A³Σ_u⁺,v=2) molecules generated in a repetitive ns pulse discharge in nitrogen has been measured by a CRDS spectrometer using a Nd:YAG pumped narrowband dye laser and a high-pressure Raman cell. This spectrometer has a much broader tuning range (up to 50 nm), but a slightly larger spectral linewidth, ≈ 0.07 cm⁻¹. Peak number density measured at the present conditions is [N₂(A³Σ_u⁺,v=2)] ≈ 0.9×10¹⁰ cm⁻³. Measurements of other vibrational states of N₂(A³Σ_u⁺) molecules in different gas mixtures excited by a ns pulse discharge are underway.

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1. Introduction

Measurements of absolute number densities of radical species and metastable excited species in nonequilibrium reactive flows are critical for insight into kinetics of chemical reactions and molecular energy transfer in combustion [1], low-temperature plasmas [2], and strong shock waves [3,4]. Some of these species are extremely difficult to quantify, due to their low number densities or due to low absorption cross sections and long radiative life times. One of these species, hydroperoxy radical (HO₂), plays an essential role in kinetics of oxidation and ignition of hydrogen and hydrocarbon fuels [1]. Another example is a metastable excited electronic state of nitrogen, N₂(A³Σ_u^+), generated in electric discharges in air and fuel-air mixtures, which strongly affects dissociation of O₂, H₂, and hydrocarbon molecules in plasma assisted combustion chemistry [2]. Metastable N₂(A³Σ_u^+) is also an important species affecting UV emission behind strong shock waves, such as occur in nonequilibrium atmospheric reentry flows (specifically, NO β and γ bands) [3,4]. Recently, HO₂ concentration in a mixture of dimethyl ether, oxygen, and helium in a flow reactor was measured by Faraday rotation spectroscopy [5,6]. Another HO₂ measurement during oxidation of n-butane in a jet-stirred reactor used the fluorescence assay by gas expansion technique [7]. Although there are a number of N₂(A³Σ_u^+) measurements in electric discharge plasmas [8], only one of them has been done in a nanosecond pulse discharge in nitrogen and air [9,10], such as used for plasma assisted combustion applications.

In the present work, we report preliminary results of HO₂ and N₂(A³Σ_u^+) measurements by Cavity Ring-Down Spectroscopy (CRDS), in two different CRDS experiments. The focus of the first experiment is on simultaneous measurements of HO₂ (one of the key radical species in low-temperature combustion kinetics) and H₂O (one of the dominant combustion product species), for applications in combustion diagnostics. The goal of the second experiment is measurement of N₂(A³Σ_u^+) in electric discharges in fuel-air mixtures and in nonequilibrium high-speed flows. The measurement techniques used in these two experiments are quite different, as discussed in Section 2. Both techniques are also readily amenable for measurements of another excited metastable species that may be generated efficiently in electric discharges, singlet delta oxygen, O₂(a'Δ) [11].

2. Experimental

2.1. CRDS experiment 1

The laser source used for this experiment consists of an injection-seeded Nd:YAG laser operated at 10 Hz, with the second harmonic output at 532 nm pumping a custom-built, injection-seeded optical parametric oscillator (OPO). A schematic diagram of the OPO is shown in Fig. 1(a). The single-resonance OPO cavity is approximately 105 mm long and is comprised of two plane mirrors reflecting at the signal wavelength (≈ 822 nm, output coupler reflectivity of 30%). The pump laser beam is double-passed through the cavity using two intracavity mirrors and a retro-reflecting, high reflectivity mirror at 532 nm, as shown in Fig. 1(a). Two 7 mm x 7 mm x 12 mm Type I BBO crystals are placed in the cavity at opposing angles to compensate for beam walk-off. The crystals can be angle tuned using high-precision rotation stages. The pump laser pulse energy is ≈ 110-120 mJ/pulse at 532 nm, and the pump beam is collimated to approximately 3-4 mm diameter prior to passing through the BBO crystals. The OPO seed source is an external cavity, cw diode laser, which can be paired with a tapered amplifier, with
the output injected through the output coupler of the OPO cavity at the signal wavelength. A partial reflector (reflectivity of 10%) is used to sample the seed beam and monitor its wavelength and linewidth with a wavemeter (HighFinesse WS6). The injected seed laser power is 40-300 mW. Typical OPO output energies are 0.5-1.0 ml/pulse at the idler wavelength of ≈ 1505 nm. A long-pass filter with cutoff at ≈ 570 nm is used to filter residual pump energy from the idler beam. The idler beam is sampled using a partial reflector (reflectivity of 10%) and characterized by a 0.25 m spectrometer and liquid nitrogen cooled, linear InGaAs array detector, to monitor the quality of the OPO injection seeding and to coarsely tune the idler wavelength. The rest of the idler beam is sent to the CRDS spectrometer, shown schematically in Fig. 1(b). The spectrometer consists of a cavity ring-down cell 90 cm long, made of stainless steel or quartz, with high reflectivity mirrors at both ends (1 m radius of curvature, reflectivity 99.998% at 1505 nm, determined from the empty cell ring-down time). The idler (probe) beam is focused in the center of the cell by a 750 mm focal distance lens. The transmitted beam is focused by a 100 mm focal distance lens and detected by an InGaAs amplified photodiode, with gain set to 30-40 dB. The photodiode signal is recorded by an oscilloscope (Tektronix TDS-2048B). Fine tuning of the probe beam is done by adjusting the wavelength of the OPO seed beam. For this, a stepwise voltage signal is applied to a piezoelectric transducer within the grating mount of the diode seed laser, external to the OPO cavity. The spectral range of the OPO scan is sufficiently narrow (< 1 cm⁻¹) and the bandwidth of the BBO crystals is sufficiently large, such that no angle tuning of the crystals is required during the CRDS spectrum acquisition. The diode laser controller, wavemeter, and the oscilloscope are operated by a computer. The computer software sets the voltage of the piezoelectric transducer controlling the seed laser output wavelength, records the wavelength and the linewidth of the seed beam measured by the wavemeter, records ring-down waveforms measured by the detector and the oscilloscope for each laser shot, fits each waveform to a single exponential decay to determine the ring-down time, and plots the ring-down spectrum. Each data point in the spectrum is proportional to absorbance measured for a single laser shot (determined by the difference between actual and empty cavity ring-down rates). A typical spectrum includes 100-200 data points.

In the present work, three different measurements of H₂O and HO₂ number densities have been performed, to benchmark and characterize the performance of the OPO-based ring-down apparatus. In the first and second measurements, a stainless steel CRDS cell (a 1.5 inch diameter tube) have been used, while in the third measurement it was replaced by a quartz CRDS cell (a 10 mm x 22 mm rectangular cross section quartz channel fused to two 0.5 inch diameter quartz tubes at both ends). In the first measurement, a 2.45 GHz, 70 W microwave discharge sustained in a 0.5 inch diameter quartz tube was used to generate water vapor in a H₂-O₂-Ar mixture (flow rates of 20 SCCM H₂, 20 SCCM O₂, 300 SCCM Ar) at a total pressure of ≈ 50 Torr. The effluent of the discharge entered the CRDS spectrometer cell through a port near its center, and exits through an exhaust port located approximately 5 cm from the end of the discharge tube.

In the second measurement, laser-induced photolysis chemistry was used to generate HO₂ in a mixture of chlorine, oxygen, and methanol vapor, using the third harmonic output of a Nd:YAG laser operated at 50 mL/pulse. The flow rates of the mixture components are 1 SCCM CH₃OH, 15 SCCM O₂, ≈ 0.2 SCCM Cl₂, and 650 SCCM Ar buffer at a total pressure of 65 Torr. The 355 nm output of the laser was expanded using a pair of cylindrical lenses with focal lengths of –25 mm and +150 mm, and a rectangular cross section mask was used to limit the beam cross section to 2 cm x 1 cm before irradiating the central part of the CRDS cell orthogonal to the
probe beam, through a quartz optical access window. The delay time between the photolysis laser pulse and the CRDS probe pulse was 200 μs.

In the third measurement, a mixture of 5% H₂, 5% O₂, and 90% Ar flowing through the cell, at a total flow rate of ≈ 500 SCCM and total pressure of approximately 50 Torr, was excited by a plane-to-plane, nanosecond pulse, double dielectric barrier discharge. The discharge electrodes, 1 cm x 10 cm rectangular copper plates, are attached to the top and bottom walls of the quartz channel in the middle of the cell, using silicone rubber adhesive. The electrodes are powered by a custom-built high-voltage pulse generator producing alternating polarity pulses with peak voltage up to 15 kV and pulse duration of approximately 100 ns FWHM [12]. In the present work, the pulser is operated in burst mode, with burst repetition rate of 10 Hz, pulse repetition rate of 10 kHz, and 50 pulses per burst. The probe laser pulse delay after the end of the discharge burst is approximately 100 microseconds after the end of the last pulse in the burst.

2.2. CRDS experiment 2

The schematic of the experimental apparatus is shown in Fig. 2. Briefly, a 10 Hz Nd:YAG laser (Continuum PowerLite Precision II) pumps a narrowband tunable dye laser (Continuum Vista) using a Rhodamine 590 dye. The dye laser output is frequency shifted using a Raman cell filled with 15 bar of hydrogen. The output beams from the Raman cell (first Stokes, second Stokes, and anti-Stokes) are dispersed by a Pellin-Broca prism, isolating the first Stokes beam from the fundamental, second Stokes, and the anti-Stokes beams, as shown schematically in Fig. 2. The wavelength and the linewidth of the ≈ 745 nm first Stokes beam are measured by a wavemeter (High Finesse WS6), using scattering off the prism, for each laser shot. The collimated beam is passed through the ring-down spectrometer, using a 90 cm long optical cavity formed by two 1 m radius of curvature plano-concave mirrors (Layertec). The ring-down cell is a 10 mm x 22 mm rectangular cross section quartz channel 55 cm long, fused to two 0.5 inch diameter quartz tubes at both ends, identical to the one used in CRDS experiment 1. The ring-down mirrors are attached to the ends of the ring-down cell by stainless steel adjustable mounts, for precision alignment. Two electrodes, 12 mm x 60 mm rectangular copper plates, encapsulated in acrylic plastic blocks, are attached to the top and bottom walls of the quartz channel in the middle of the cell, using silicone rubber adhesive. Gaps between the electrodes and the quartz channel are also filled by silicone rubber, to avoid corona discharge formation.

The electrodes are powered by the same high-voltage pulse generator as used in CRDS experiment 1. The pulser is operated in burst mode, with burst repetition rate of 10 Hz, pulse repetition rate of 0 kHz, and 10 pulses per burst, with coupled pulse energy of approximately 0.3 mJ/pulse. The pulse voltage and current are measured by a high-voltage probe (Tektronix P6015) and a current probe (Pearson 2877). Figure 3 plots typical pulse voltage, current, and coupled energy waveforms measured during a single discharge pulse. Two Stanford Research Systems delay generators are used to control the timing of the high-voltage pulse generator and the Nd:YAG laser. The first delay generator, acting as the master clock, triggered the high-voltage generator at a burst repetition rate of 10 Hz and pulse repetition rate of 10 kHz, with 10 pulses in each burst. The second delay generator controlled the delay between the discharge burst and the laser pulse. The ns pulse discharge and the laser pulse probe timing is shown schematically in Figure 3.
The cavity ring-down trace is recorded by a Si-amplified detector (PDA36A Thorlabs) with gain set to 30 dB. A bandpass filter centered around 780 nm is placed in front of the detector to block plasma emission and stray laser output at 1064 nm. The data is acquired by a PC running Labview software, which also controls the wavelength of the tunable dye laser, fits ring-down trace for each laser shot to measure the ring-down time, and plots the ring-down spectrum.

3. Results and Discussion

3.1. CRDS experiment 1

Figure 4 plots a full bandwidth CRDS scan (approximately 1 cm$^{-1}$) of the effluent products of a 2.45 GHz, 70 W microwave discharge sustained in a H$_2$-O$_2$-Ar mixture. An H$_2$O absorption line at 6638.91 cm$^{-1}$ is clearly evident. An additional, much weaker, water vapor absorption line at 6638.57 cm$^{-1}$, may also be detected near the sensitivity limit of the present diagnostics. Although the bandwidth of this scan included a strong HO$_2$ absorption transition (at 6638.20 cm$^{-1}$), no measureable absorption at this wavelength was detected at these conditions, suggesting that HO$_2$ radical, even if its generated in sufficient quantities in the microwave discharge, decays before it reaches the CRDS cavity. For absolute calibration of CRDS absorption data, a single-pass absorption path of 5 cm was assumed (same as the distance between the flow inlet and exit lines), resulting in peak absorption of approximately 1.3 ppm/pass.

The CRDS spectrum shown in Figure 5(a) is measured during the laser-induced photolysis experiment, with absolute calibration assuming a single-pass absorption path of 2 cm (the same as the width of the mask limiting the size of the laser beam used for photolysis). This corresponds to peak absorption of approximately 0.2 ppm/pass.

These results demonstrate the capability of the OPO-based CRDS apparatus for simultaneous measurements of H$_2$O and HO$_2$ number densities. They also provide an estimate of the probe laser spectral linewidth, approximately 0.03 cm$^{-1}$, inferred from the FWHM of the H$_2$O spectral line in Figure 4. The absorption line positions and line strengths for H$_2$O are taken from the HITRAN database [13]. The absorption line positions and absorption cross sections for HO$_2$ are reported by Thiebaud et al [14]. Using these data, the estimated H$_2$O number density in the effluent of the microwave discharge is $\approx 1.0\cdot10^{16}$ cm$^{-3}$. The estimated HO$_2$ number density produced by laser-induced photolysis is $\approx 1.0\cdot10^{10}$ cm$^{-3}$. Note that the sensitivity of HO$_2$ measurements using this absorption line is much higher compared to that of H$_2$O, due to much higher absorption cross section.

The CRDS spectrum shown in Figure 5(b) is measured in the afterglow of a repetitive ns pulse discharge in an H$_2$-O$_2$-Ar mixture, sustained directly in the CRDS cell. Although the observed absorption peak center deviates slightly from the tabulated value for HO$_2$ (by $\approx 0.03$ cm$^{-1}$) the absorption feature is assigned to the same overtone band absorption line of HO$_2$ as shown in Fig. 5(a), at 6638.20 cm$^{-1}$. The FWHM of this absorption line is approximately the same as the HO$_2$ absorption line in Fig. 4, $\approx 0.03$ cm$^{-1}$, and the estimated HO$_2$ number density is $\approx 1.0\cdot10^{10}$ cm$^{-3}$. To the best of our knowledge, this is the first detection of HO$_2$ radical in a nanosecond pulse discharge.
3.2. CRDS experiment 2

In this experiment, metastable excited electronic state of nitrogen, \( N_2(A^3\Sigma_u^+) \), generated in a repetitive ns pulse discharge in nitrogen, was detected by measuring CRDS absorption on the \( N_2(B^3\Pi_g, v'=4 \rightarrow A^3\Sigma_u^+, v''=2) \) band. Figure 6 plots typical time-resolved ring-down signals measured in the evacuated (“empty”) CRDS cell and in a ns pulse discharge in nitrogen at \( P=20 \) Torr, on one of \( N_2(B^3\Pi_g \leftarrow A^3\Sigma_u^+) \) absorption line centers. It is readily apparent that absorption of the probe laser beam by \( N_2(A^3\Sigma_u^+) \) results in significant reduction of the ring-down time. In the present work, every ring-down signal is fit to a single-exponential decay, yielding the ring-down time. Although this effect was detected in previous work [10], when the ring-down time was comparable with the \( N_2(A^3\Sigma_u^+) \) decay time in the afterglow, the origin of this behavior at the present conditions, when the \( N_2(A^3\Sigma_u^+) \) decay time is very long, remains not completely understood.

Discharge pulse voltage, current, and coupled energy waveforms at these conditions are plotted in Figure 3. A typical CRDS spectrum acquired at these conditions is shown in Figure 7. The scan covers approximately \( 10 \) cm\(^{-1} \), incorporating nearly 20 ro-vibrational lines in the \( (4\rightarrow2) \) vibrational band of the first positive system of \( N_2 \), all of which have been identified. Each data point in the spectrum is an average of ten single-laser-shot ring-down times. Absorption line assignments are obtained from line positions reported by Dieke and Heath [15].

By varying the time delay between the discharge burst and the laser pulse (as shown in Fig. 3), time-resolved absorption coefficient on one of the isolated absorption line centers has been measured, providing measurement of the relative concentration of \( N_2(A^3\Sigma_u^+, v=2) \) vibrational state. Absolute number density of molecules in this state have been inferred from the data following the data reduction procedure discussed in greater detail in Ref. [10], assuming the single-pass absorption path of 6 cm and the temperature in the afterglow of \( T=300 \) K. For these measurements, shown in Figure 8, the probe laser beam was tuned to 13413.77 cm\(^{-1} \), which corresponds to the peak of the R\(_{327}\) transition in the \( N_2(B^3\Pi_g, v'=4 \rightarrow A^3\Sigma_u^+, v''=2) \) vibrational band (see Fig. 7). During the measurements, the laser beam wavelength was monitored continuously by the wavemeter. The nitrogen was flown through the CRDS cell at a flowrate of 0.60 SLM, at a pressure of 21.3 Torr. The time delay between the end of the discharge burst and the laser pulse was varied from \( 25 \) µs to \( 1.8 \) ms. It can be seen that the characteristic time for the \( N_2(A^3\Sigma_u^+, v=2) \) number density decay in the afterglow is very long, much greater than \( 1 \) ms.

Peak absolute population of \( N_2(A^3\Sigma_u^+, v=2) \) state, inferred from the data plotted in Figs. 7 & 8, is \([N_2(A^3\Sigma_u^+, v=2)] \approx 0.9 \cdot 10^{10} \) cm\(^{-3} \). Assuming the vibrational population distribution of \( N_2(A^3\Sigma_u^+, v) \) molecules to be the same as in Ref. [16], the estimated \( N_2(A^3\Sigma_u^+) \) number density at the present conditions is \([N_2(A^3\Sigma_u^+) \sim 10^{11} \) cm\(^{-3} \). Absolute populations of other vibrational states of \( N_2(A^3\Sigma_u^+) \), \( v=0-3 \), can be measured by changing the dye in the narrowband dye laser, which would give a more accurate result for the total \( N_2(A^3\Sigma_u^+) \) number density. At the present conditions, the decay of \( N_2(A^3\Sigma_u^+) \) in the afterglow is likely due to pooling reactions, \( N_2(A^3\Sigma_u^+) + N_2(A^3\Sigma_u^+) \rightarrow N_2(B^3\Pi) + N_2(X^1\Sigma), N_2(C^3\Pi) + N_2(X^1\Sigma), \) with the characteristic time of \( \tau \sim (k_{pool} \cdot [N_2(A^3\Sigma_u^+)])^{-1} \sim 25 \) ms, where \( k_{pool} = 4 \cdot 10^{-10} \) cm\(^3\)/s [8]. These results demonstrate the capability of the present CRDS apparatus to measured temporal evolution of excited metastable species of interest, such as \( N_2(A^3\Sigma_u^+) \) and \( O_2(a^1\Delta) \), in nonequilibrium plasmas and nonequilibrium high-speed flows.
4. Summary

In the present work, number densities of HO2 radical, H2O, and metastable excited electronic state of nitrogen, N2(A3Σu+), have been measured in two different Cavity Ring-Down Spectroscopy (CRDS) experiments. In the first experiment, an injection-seeded Optical Parametric Oscillator (OPO) is used to generate a narrowband laser output used in the CRDS spectrometer (spectral linewidth of 0.03 cm⁻¹). The H2O number density is measured in the effluent of a microwave discharge sustained in a H2-O2-Ar mixture. Hydroperoxyl radical number density is measured in two environments, a chemically reacting Cl2-O2-CH3OH-Ar mixture initiated by laser-induced photolysis, and a repetitive ns pulse discharge in a H2-O2-Ar mixture. Hydroperoxyl radical number density on the order of 1×10¹⁰ cm⁻³ and H2O number density on the order of 1×10¹⁶ cm⁻³ can be measured, using single laser-shot cavity ring-down traces. The injection-seeded OPO pumped CRDS spectrometer has been shown to have sufficient bandwidth for simultaneous measurements of water vapor and hydroperoxyl radical. This spectrometer is also amenable to pumping by a high-repetition rate pulse-burst laser, producing time-resolved measurements with high temporal resolution (up to at least tens of kHz).

In the second experiment, time-resolved number density of N2(A₃Σu₊,v=2) molecules generated in a repetitive ns pulse discharge in nitrogen has been measured by a CRDS spectrometer using an Nd:YAG pumped narrowband dye laser and a high-pressure Raman cell. This spectrometer has a much broader tuning range (up to 50 nm), but a slightly larger spectral linewidth, ≈ 0.07 cm⁻¹. Peak number density measured at the present conditions is [N2(A₃Σu₊,v=2)] ≈ 0.9×10¹⁰ cm⁻³. Measurements of other vibrational states of N2(A₃Σu₊) molecules in different gas mixtures excited by a ns pulse discharge are underway.

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Figure 1. Schematic diagram of injection-seeded Optical Parametric Oscillator (a) and Cavity Ring-Down Spectrometer (b) used for CRDS experiment #1 (measurements of HO$_2$ and H$_2$O number densities).
Figure 2. Schematic diagram of Cavity Ring-Down Spectrometer for CRDS experiment #2 (measurements of N₂(A³Σ) number density).

Figure 3. Left: voltage, current, and coupled energy waveforms measured in a nanosecond pulse discharge in nitrogen in CRDS experiment #2 at P=20 Torr; right: timing schematic for a repetitively pulsed ns discharge operated in burst mode and laser pulses.
Figure 4. Typical CRDS spectrum of H₂O vapor generated in a 70 W microwave discharge in a H₂-O₂-Ar mixture at P=50 Torr (CRDS experiment #1). Absolute calibration assumes single-pass absorption path of 5 cm.

Figure 5. Typical CRDS spectra of HO₂ generated in CRDS experiment #1: (a) laser-induced photolysis in a Cl₂-O₂-CH₃OH-Ar mixture at P=65 Torr and (b) ns pulse discharge in a H₂-O₂-Ar mixture at P=50 Torr. Absolute calibration assumes single-pass absorption path of 2 cm (a) and 10 cm (b).
Figure 6. Typical time-resolved ring-down signals in CRDS experiment #2, measured in an empty cell and in a ns pulse discharge in nitrogen at P=20 Torr, on a N$_2$(B$^3\Pi_g$ ← A$^3\Sigma_u^+$) absorption line center.

Figure 7. Typical N$_2$ (B$^3\Pi_g$, v=4 ← A$^3\Sigma_u^+$, v=2) band absorption spectrum measured in CRDS experiment #2, in a ns pulse discharge in nitrogen at P=20 Torr.
Figure 8. Time-resolved $N_2 (A^3\Sigma^+_u, v=2)$ number density measured in CRDS experiment #2, in a ns pulse discharge in nitrogen at P=20 Torr, vs. time delay after the discharge burst.