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13. ABSTRACT (Maximum 200 words) The goal of this project was to develop laser-based diagnostics employing the cavity ring-down spectroscopy (CRDS) technique for the investigation of trace quantities of molecular species in hostile environments such as atmospheric pressure air plasmas. As part of a continuing collaboration with the nonequilibrium plasma chemistry program of Prof. Charles Kruger at the Stanford High Temperature Gasdynamics Laboratory, we have successfully applied CRDS in determination of temperature and ground state population gradients of transient species such as ions and radicals generated in plasma environments. This noninvasive absorption diagnostic provided information on ground-state populations that complemented information on excited state populations provided by emission spectroscopy. A prototype CRDS setup was implemented to examine N ₂ ⁺ concentration profiles in a 50 kW air plasma source. Ongoing work that extends the CRDS technique into the infrared "fingerprint" region for many of the hydrocarbon free radicals (CH ₃ , CH ₂ , CH, C ₂ H, etc.) generated in an arc jet plasma-deposition reactor has provided interesting results on the temperature of species present in this hostile environment. These investigations have also identified technical obstacles that limit the sensitivity and spatial resolution of the CRDS technique in such harsh environments.				
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1. INTRODUCTION

Energy-related phenomena such as flames, discharges, and plasmas continue to find application in the synthesis of materials with novel characteristics. Such environments are exploited in the deposition of materials ranging from polymers to diamond as well as in the controlled removal of material as found in the fabrication of semiconductor devices. Despite recent advances in the application of such hostile environments in materials synthesis and processing, little is known of the gas-phase chemistry that leads to the desired processes. This lack of understanding is perhaps not surprising, given the extreme conditions that characterize such phenomena. Indeed, plasmas, discharges, and flames all involve high temperatures and, consequently, strong luminous backgrounds, sharp gradients in both temperature and density, and high concentrations of reactive species generated by such extreme conditions. A need therefore exists for a noninvasive, species specific remote diagnostic capable of providing spatially resolved concentration profiles of relevant gas-phase species.

Cavity ring-down spectroscopy (CRDS) is a sensitive laser-based spectroscopic technique capable of providing spatially resolved concentration profiles of gas-phase species in hostile environments. CRDS was first demonstrated by O'Keefe and Deacon in 1988¹ who employed a pulsed laser source. Figure 1 shows a schematic of the basic CRDS setup. In CRDS, a laser pulse is injected into an external ring-down cavity formed by two or more high reflectivity mirrors. The intensity of the pulse of light trapped within the ring-down cavity decays exponentially from losses within the cavity which include transmission and scattering by the cavity mirrors as well as absorption by gas-phase species present within the cavity. The decrease in the intensity of the trapped laser pulse is monitored by detecting the small fraction of light transmitted by the output cavity mirror. By measuring this decay rate as a function of laser frequency, the absorption spectrum of species present within the cavity is obtained.

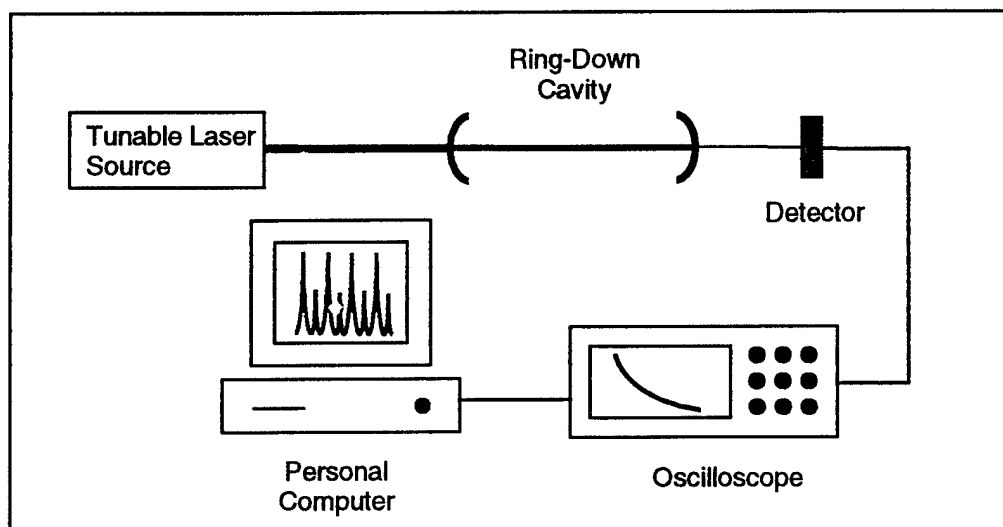


Figure 1. Schematic of pulse laser-based CRDS instrument.

The inherent sensitivity of the CRDS technique stems from the fact that the decay rate is insensitive to fluctuations in the intensity of the laser source, fluctuations that limit the sensitivity of other direct absorption techniques. By placing an aperture before the detector and locating the detector a long distance from the cavity, contributions to the detected signal by any luminous background environment may be minimized. Due to the geometry of the CRDS setup, the measured absorption losses are integrated over the path of the laser beam inside the cavity. For samples that do not completely fill the ring-down cavity, a topological method known as an Abel inversion is used to generate absolute concentration profiles from the spatial absorbance profile obtained by translating the sample in and out of the beam path.

The advantage of CRDS over other sensitive absorption techniques, such as photoacoustic spectroscopy and frequency modulation spectroscopy, is the ability of CRDS to measure directly absolute concentrations of gas-phase species. To date, CRDS employing pulsed lasers has been successfully applied when the loss from absorption was as little as $7 \times 10^{-10} \text{ cm}^{-1} \text{ s}^{-1}$ while CRDS systems employing continuous wave (CW) laser sources have detected absorption losses as low as $6 \times 10^{-11} \text{ cm}^{-1} \text{ s}^{-1}$ with a 1 s integration period.³ This technique has been applied to measure the kinetics of phenyl radical reactions^{4,5} and ethyl and ethylperoxy radical reactions,⁶ the temperature of OH radicals in flames,⁷⁻⁹ and linear carbon chain radicals in a pulsed slit discharge.¹⁰

We have found the diamond film reactor to be a particularly suitable system for the study of gas-phase chemistry in hostile environments using CRDS.^{11,12} Two commonly used diamond deposition methods involve chemical vapor deposition (CVD) using either a hot-filament (HFCVD) reactor or an inductively coupled atmospheric plasma torch. Both methods are currently under investigation at the Stanford Gasdynamics Laboratory in an attempt to uncover the elementary growth mechanisms that lead to deposition of diamond films. These studies involve the compilation of information about the numerous radicals generated in high temperature environments (e.g. hydrocarbon radicals like CH_3 , CH_2 , CH , C_2H , C_2 , etc., or atomic hydrogen) for computer modeling and subsequent numerical simulation of the complex high-temperature chemistry.

Temperature and absolute concentration of deposition species are the basic parameters for understanding, modeling, controlling, and optimizing processes such as CVD. To date, we have acquired spatial profiles of several radical and ionic species generated in hot-filament reactors and inductively coupled plasma sources. Initially, CH_3 radical concentration profiles were obtained in a hot-filament reactor during diamond film deposition.^{11,12} These measurements demonstrate submillimeter resolution and a noise-equivalent sensitivity of 25 ppm of CH_3 at a gas temperature of 1600 K. Recently, the acquisition of a new optical parametric oscillator (OPO) laser source has enabled us to acquire preliminary absorption data for CH radicals around 425 nm. A second inductively coupled arc jet plasma source used in deposition of diamond films has also been probed using a narrow-linewidth OPO laser source around $3.28 \mu\text{m}$. Finally, CRDS is being used to examine N_2^+ concentration profiles generated in a 50 kW inductively coupled air plasma as an indirect probe of electron number densities within the plasma source. All of these studies are aimed at developing CRDS as a remote diagnostic for the study of gas-phase plasma chemistry.

2. Probing N_2^+ Concentrations in an Inductively Coupled Atmospheric Pressure Air Plasma

Atmospheric air plasmas have been of interest to researchers in the High Temperature Gasdynamics Laboratory as part of an ongoing study to examine conditions space vehicles encounter upon reentry into the earth's atmosphere. Such nonequilibrium plasmas are also of interest as sources of free electrons. Low-temperature plasmas having high electron number densities could find commercial uses in decontamination of military hardware, and as shields for sensitive electronic equipment from high-energy bursts of electromagnetic radiation. As with the other plasma studies, efforts have been made to model atmospheric pressure nonequilibrium air plasmas in an attempt to identify the chemical reactions responsible for the production and recombination of free electrons. Again, the temperature and absolute concentration of gas-phase species generated in the plasma are the key to modeling, and optimizing free electron production.

Emission spectroscopy provides a powerful tool for probing rotational and vibrational temperatures and relative concentrations of excited-state species within this hostile environment. However, emission spectra do not readily provide information about the absolute concentration of gas-phase species, and such measurements are limited to the investigation of excited-state populations. We have begun to implement CRDS as a remote diagnostic to obtain spatially resolved concentration and temperature profiles of both ground and excited-state populations in nonequilibrium plasma environments.

We have applied CRDS to probe the concentration of N_2^+ in an atmospheric-pressure air plasma at 7000 K. While N_2^+ is only a minor participant in the reaction pathways that govern electron number densities, it serves as an excellent candidate for determining the feasibility of employing CRDS in the hostile environment of an air plasma. Indeed, this represents the first attempt to utilize CRDS to detect trace gasses in a plasma where severe thermal lensing, caused by large temperature gradients, is expected. Figure 2 shows a schematic of the CRDS apparatus. A Nd:YAG pumped dye laser is used to generate light between 387.0 and 392.0 nm. Pulses of light from the dye laser (8-12 mJ/pulse, 8ns duration) are mode matched to the ring-down cavity using a pair of lenses (5.0 cm focal length) and a pinhole (0.25 mm). The ring-down cavity, which is 2.1 m in length, is comprised of two high reflectivity mirrors (Los Gatos Research, $R = 0.9993$) mounted to an aluminum rail 3 m in length. The rail may be translated, allowing the ring-down cavity axis to sample different portions of the air plasma. A turning prism is also mounted to the rail, which deflects the beam into the ring-down cavity. By carefully aligning the beam parallel to the translation axis of the rail before the turning prism, the ring-down cavity may be translated across the plasma orifice (7 cm in diameter) while maintaining alignment between the laser and the ring-down cavity. Baffles (0.6 cm orifice) are mounted in the ring-down cavity to reduce the background light intensity at the detector and to protect the cavity mirrors from the large amount of ultraviolet radiation generated by the air plasma. A mirror (also mounted to the translating rail) deflects light exiting the cavity onto a fast photomultiplier located several meters from the second mirror. Photocurrent generated by the photomultiplier is digitized using a digitizing oscilloscope. A personal computer is used to fit the decay waveforms to an exponential

function and extract $1/\tau$, while stepping the dye laser through a wavelength range of interest. Emission spectroscopy was performed in parallel with the CRDS measurements to provide an independent measurement of plasma temperature.

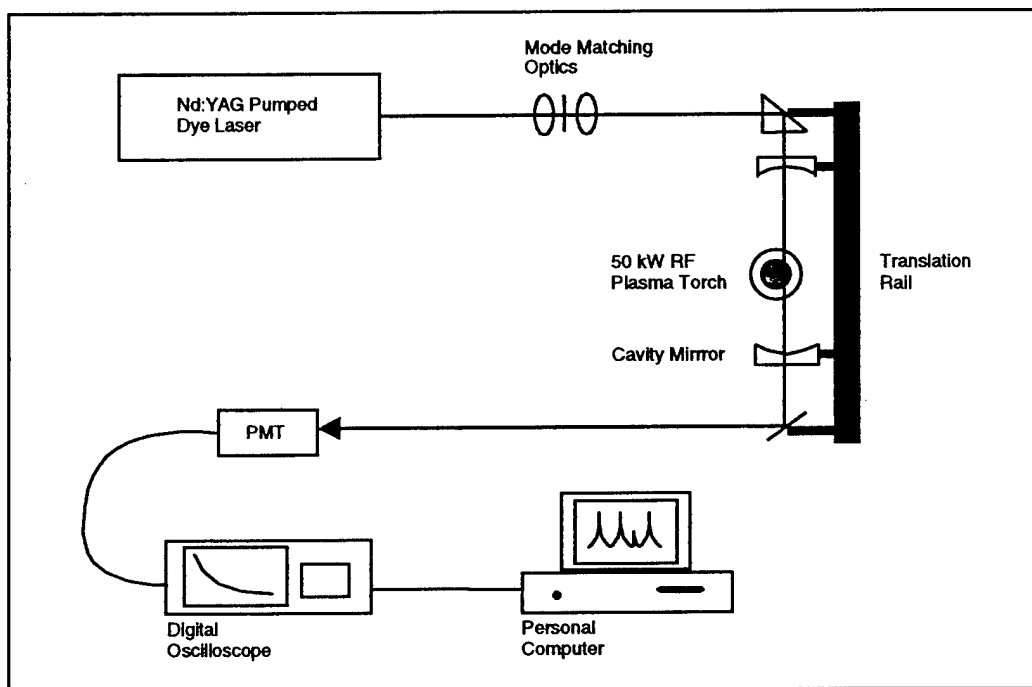


Figure 2. Schematic diagram of CRDS setup used to probe N_2^+ in an equilibrium air plasma.

Figure 3 shows the absorption spectrum of N_2^+ , obtained with the ring-down cavity aligned through the center of the air plasma, 1.0 cm above the plasma torch head, along with the predicted absorption spectrum generated with NEQAIR.¹⁶ The temperature of the air plasma, determined independently via emission spectroscopy, was approximately 7000 K. Each spectral element represents an average of 10 decay rates, each obtained by fitting a waveform that was itself an average of 25 single-shot waveforms.

With the RF plasma torch off, the empty cavity decay lifetime, τ , was typically 10 μ s. With the RF plasma on, however, τ decreased to 0.65 μ s, even with the cavity translated 2.5 cm beyond the edge of the plasma torch orifice. This decrease in τ was attributed to two loss mechanisms within the RDC. First, there exists a long-lived gas-phase species generated by the plasma torch, possibly O_3 or NO_2 , which possesses a broad featureless absorption feature in the wavelength region of interest. The concentration of this background absorber fluctuates in the turbulent air surrounding the plasma causing shot-to-shot fluctuations in τ . These fluctuations decrease the sensitivity of the absorption measurement and increase in severity as the cavity is translated toward the edge of the plasma where the laser beam samples more of the surrounding air. Currently, we are exploring methods to purge the turbulent region surrounding the plasma without perturbing the plasma itself. The second source of noise is caused by irradiation of the dielectric mirrors by UV radiation from the air plasma. UV-induced

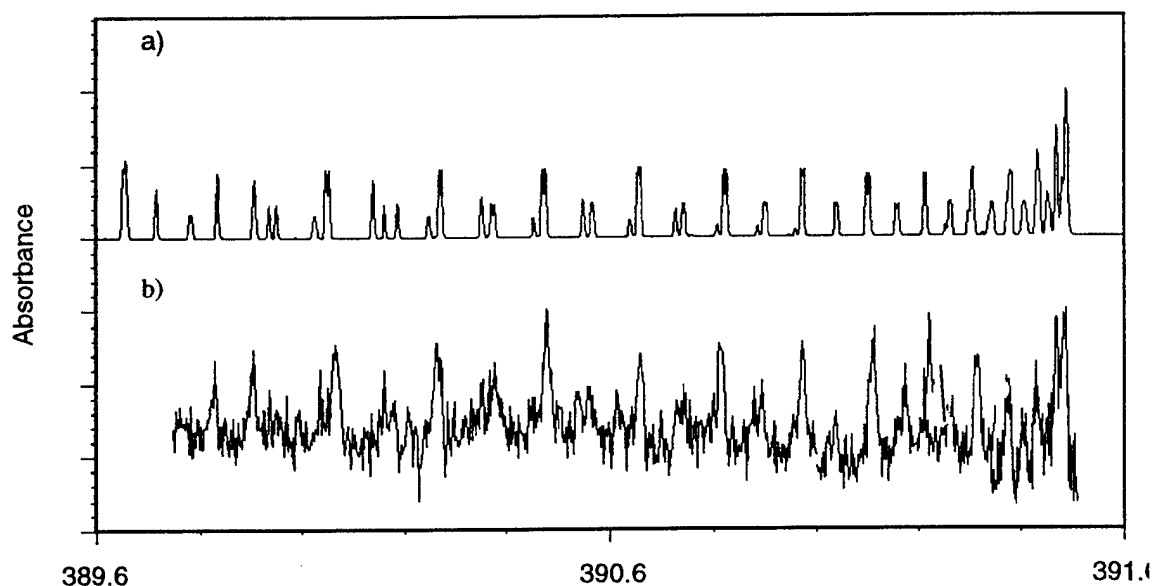


Figure 3. (a) Predicted and (b) experimental absorbance spectra of N_2^+ in a 7000 K air plasma obtained using CRDS.

reduction in the reflectivity of dielectric mirrors has been observed previously,¹³ and was attributed to deformation of the top dielectric layer after absorption of UV photons with energies of a few eV. The effect of UV radiation on the reflectivity of the dielectric mirrors used in the study outlined here was examined by translating the ring-down cavity well outside of the air plasma and shielding the mirrors from radiation from the plasma. A 50% increase in τ was observed when the mirrors were shielded from the plasma torch. Rapid recovery of mirror reflectivity is observed when the RF torch is extinguished. Therefore, fluctuations in the intensity of UV radiation from the RF torch produce fluctuations in τ . This second source of noise is most acute when probing the center of the air plasma and decreases as the cavity is translated toward the edge of the plasma.

Figure 4 is an expanded view of the N_2^+ absorption spectrum showing the rotational bandhead obtained experimentally and the predicted absorption spectrum generated with the nonequilibrium air plasma model NEQAIR. The width of the absorption feature generated by NEQAIR was broadened to fit the width of the observed absorption feature. After broadening, the intensity of the predicted transition is in excellent agreement with that obtained experimentally.

A spatial profile of the concentration of N_2^+ was obtained by measuring the absorption by N_2^+ at 391.6 nm as the ring-down cavity was translated from the center of the plasma torch to the edge of the plasma orifice. Optical losses caused by absorption of N_2^+ as a function of distance from the center of the plasma are shown in Fig. 5a. The losses from N_2^+ were probed

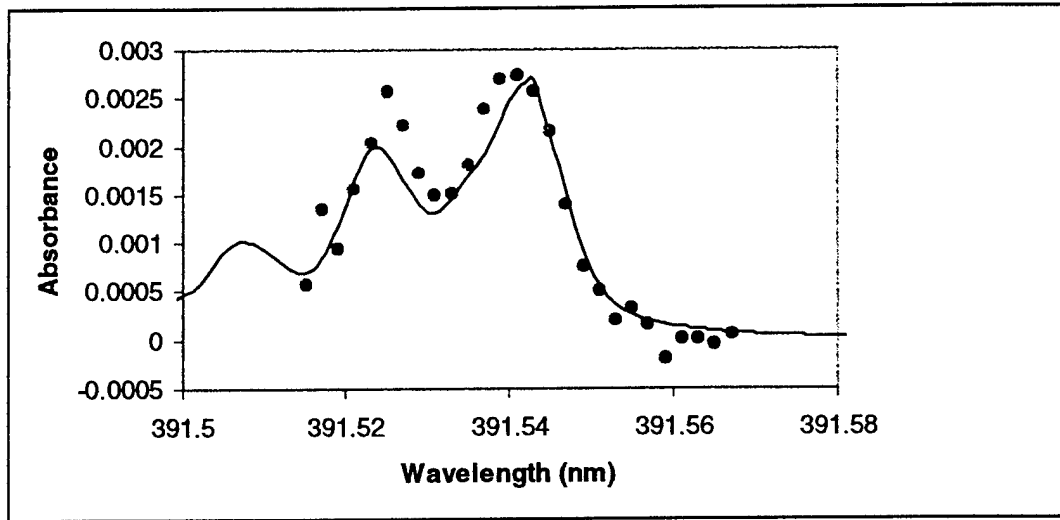


Figure 4. Experimental (points) and Simulated (line) absorption spectrum of the N_2^+ bandhead.

at 0.2 cm intervals with a spatial resolution of 0.5 mm, the average laser beam diameter over the plasma orifice. The absorbing background gasses in the turbulent air surrounding the plasma cause an increase in the uncertainty in the determination of the optical losses near the edge of the plasma. The CRDS technique measures line-of-sight integrated losses within the air plasma. An Abel transform¹¹ was employed to extract absorption losses of N_2^+ as a function of radial distance from the center of the plasma from the optical loss data. Using the absorption cross section obtained from NEQAIR, these losses were used to calculate the absolute concentration of N_2^+ as a function of radial distance (see Fig. 5b). These N_2^+ concentrations are in excellent agreement with the N_2^+ concentrations calculated from the plasma temperature profile, which was obtained by measuring the integrated absolute intensity of the O triplet at 777.3 nm.

We have demonstrated the ability of CRDS to probe the concentration of a trace species present within an equilibrium air plasma at 7000 K. A preliminary spatially resolved concentration profile of N_2^+ within an air plasma at 7000 K was obtained, and noise sources limiting the sensitivity of the measurement have been identified. We are currently exploring methods to increase sensitivity. Future investigations involving N_2^+ include probing both rotational and vibrational temperature profiles of N_2^+ , as well as N_2^+ concentration as a function of plasma temperature. As yet, thermal lensing of the laser beam by the plasma has not been identified as a major source of loss within the ring-down cavity. Future experiments employing significantly smaller plasma nozzles (1 - 5 cm diameters) that may result in a stronger lensing effect are planned.

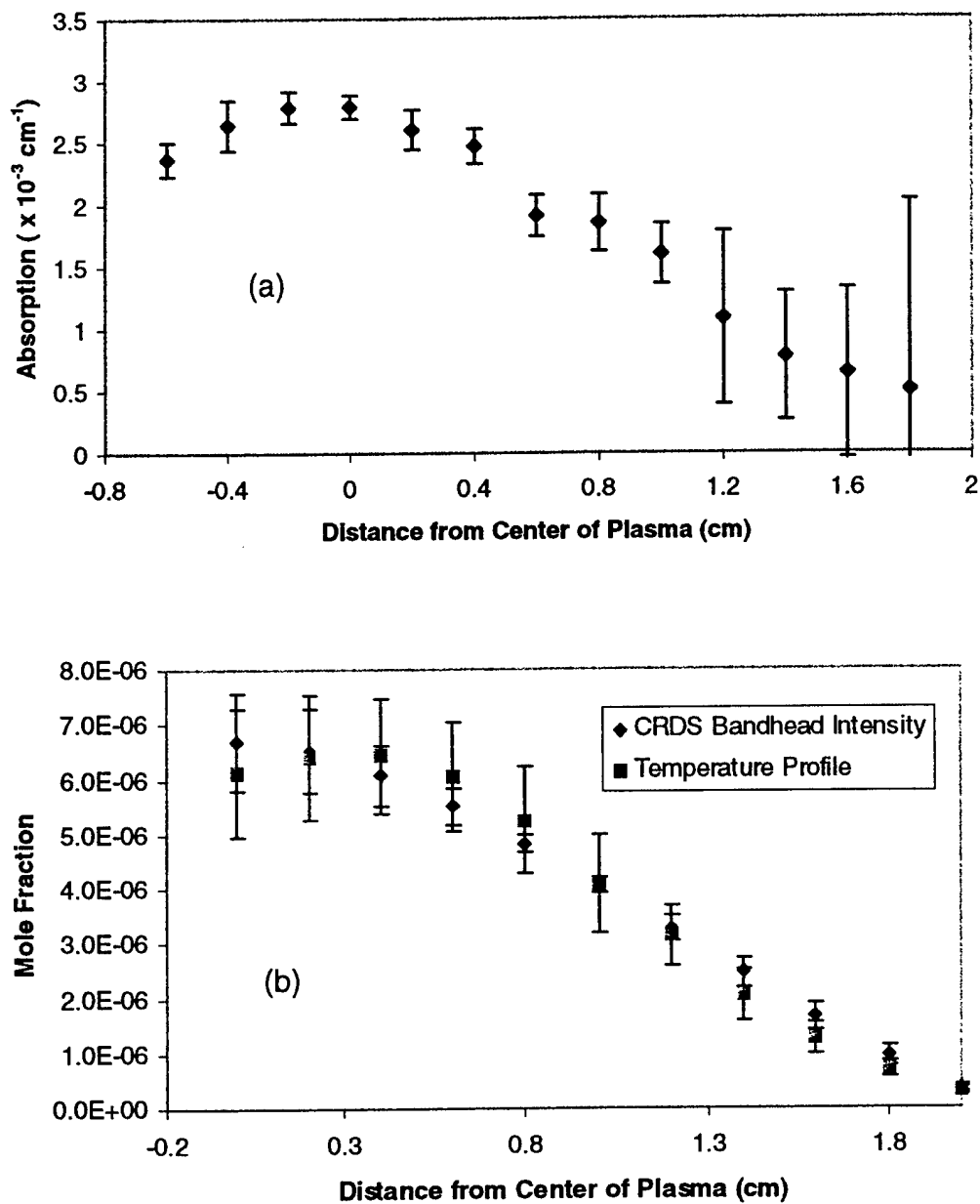


Figure 5. a) Spatially resolved absorbance profile of N_2^+ in an equilibrium air plasma at 7000 K. b) Concentration profile of N_2^+ obtained by Abel inversion of absorbance profile and calculated from temperature profile.

3. Infrared Measurements by CRDS

The infrared region of the electromagnetic spectrum is rich in rovibrational transitions forming molecular "fingerprints" that are well known as a means for identifying and characterizing specific gas-phase species. This region is therefore rather ideal for mapping species concentration or temperature gradients in hot-filament reactors and plasma sources. This statement is especially true given the fact that the fundamental C-H stretching mode (ν_3) that occurs around 3.17 μm for methyl radical species. For use as a diagnostic, however, the success of IR spectroscopy depends on overcoming three obstacles: (1) obtaining sufficient resolution to resolve spectral features, (2) obtaining sufficient sensitivity to detect dilute species, and (3) minimizing the effect of background radiation. In recent preliminary experiments, cavity ring-down spectroscopy has been explored as a tool for probing gas-phase species generated in an atmospheric pressure arc jet used in the deposition of diamond films.

In plasma-assisted deposition of diamond films, a high-power plasma is used to decompose a fuel mixture of methane and hydrogen into hydrocarbon-free radicals such as CH_3 , CH_2 , CH , etc. that are believed to be responsible for diamond formation. The clean-burning environment of the plasma provides an excellent opportunity to probe concentration gradients of radical precursors unlike combustion flames where unconsumed hydrocarbon fuel and water vapor contribute large background signals that mask absorption by radical species. To achieve the necessary sensitivity to detect radical species in the plasma source, CRDS has been employed to obtain IR spectra in the region around 3 μm .

High-resolution cavity ring-down spectra were obtained using a linear ring-down cavity with mirrors having 99.7% reflectivity, and a narrow linewidth (0.017 cm^{-1}) IR OPO laser (Mirage 3000, Continuum). This setup was able to deliver a detection limit of 10^{-4} cm^{-1} over a region between 1.4 – 4.5 μm using a single set of mirrors. In this setup the mirrors that formed the ring-down cavity were mounted through bellows to the containment chamber of an atmospheric pressure inductively coupled arc jet plasma source. The mirrors were mounted on translation stages allowing the beam to probe species at different heights above the substrate onto which diamond films were deposited. To obtain optimum spatial resolution, the cavity waist was minimized by increasing the length of the cavity to a nearly confocal geometry, and it was positioned directly over the substrate.

In the preliminary results, we have found the spectral lines of molecules in the arc jet plasma to have narrower linewidths than those found in room temperature air. Figure 6 shows four absorption spectra obtained using the CRDS setup. Traces (a) and (b) show low- and high-resolution scans between 3.280 and 3.293 nm, respectively. These scans were obtained with a 5000 K plasma, and with the methane/hydrogen fuel mixture present. Trace (c) was obtained with the plasma on but with no fuel present, while Trace (d) is a spectrum obtained with the plasma off showing absorption features attributed to H_2O present in the room air.

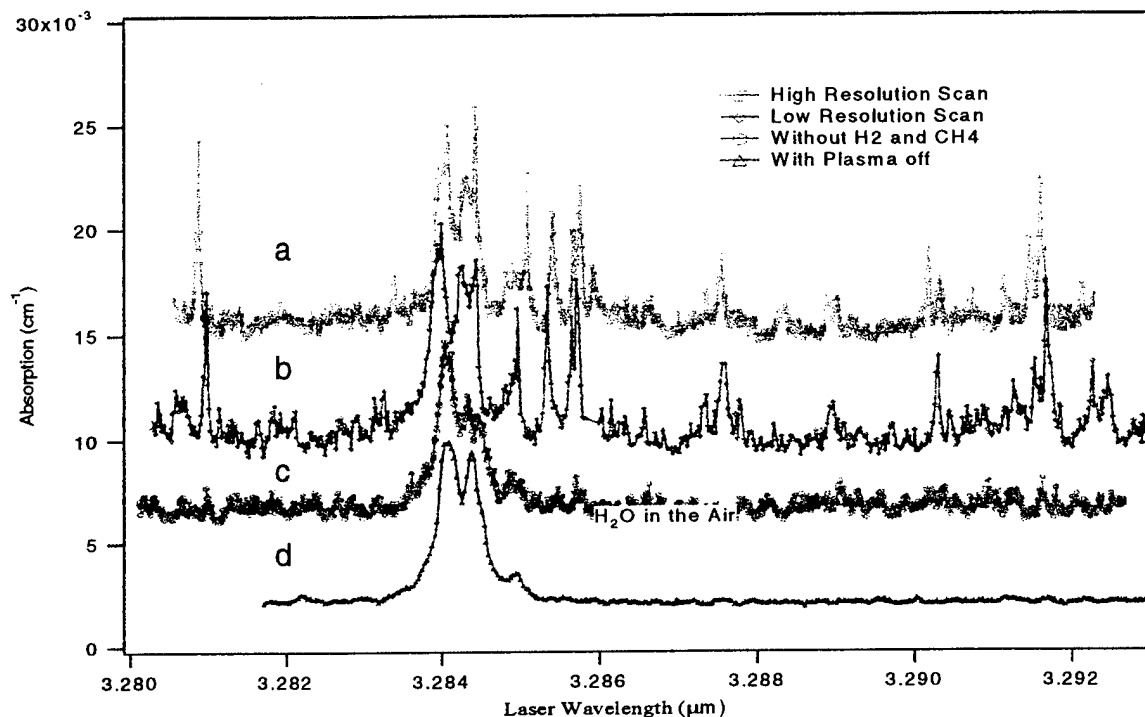


Figure 6. Absorption spectra obtained via CRDS in an arc jet diamond deposition reactor

The presence of these same features in traces (a)-(c) is caused by absorption from room air surrounding the arc jet. Although not yet assigned, the narrow features observed in traces (a) and (b) are attributed to absorption by species generated from the methane/hydrogen fuel mixture in the arc jet plasma.

Interestingly, from these spectra it is evident that the absorption features of species generated in the plasma are significantly narrower than those of H_2O in room-temperature air. Figure 7 shows an expanded view of the high-resolution spectrum and a spectrum of room-temperature air. The linewidth of the room-temperature water absorption feature is 0.26 cm^{-1} while the measured linewidth of features attributed to molecules in the plasma is about 0.022 cm^{-1} . Given a laser linewidth of 0.017 cm^{-1} , the actual linewidth of the absorption feature is no larger than 0.01 cm^{-1} and likely as narrow as 0.006 cm^{-1} . This finding went against our intuitive guess that features attributed to species in the hot plasma should be broader than those of room-temperature species owing to pressure broadening and Doppler broadening.

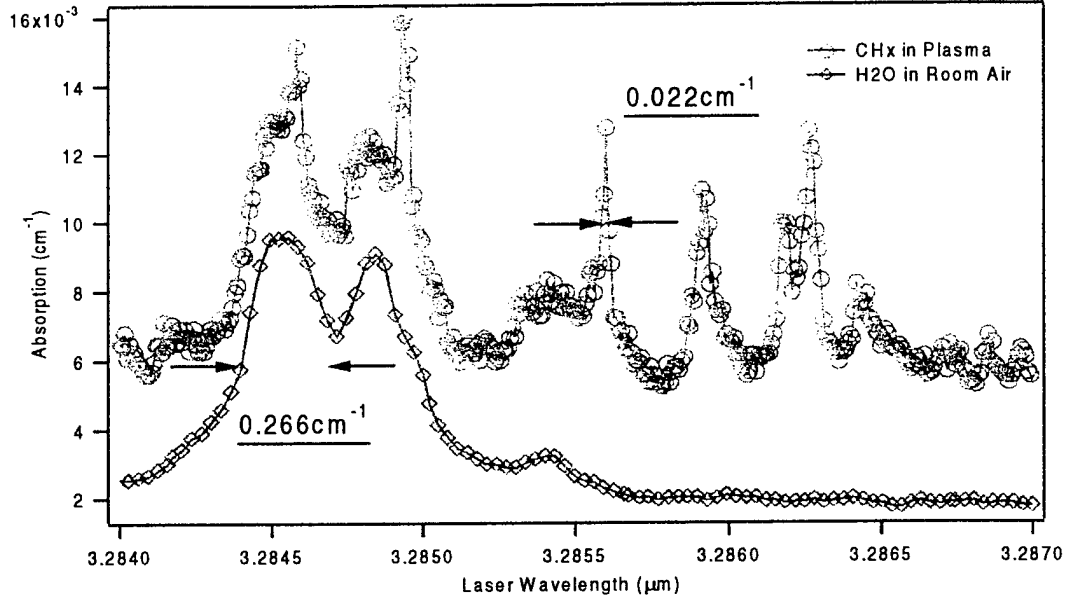


Figure 7. High resolution scan of CH_x species in plasma and H_2O in room air

Pressure broadening of an absorption feature, δv_p , is a function of number density, N , mean velocity, v , and collisional cross section, σ , and is given by¹⁴:

$$\delta v_p = Nv\sigma \quad (1)$$

Both number density and mean velocity are functions of temperature, T ¹⁴:

$$N = p / kT \quad (2)$$

$$v = (8kT / \pi\mu)^{1/2} \quad (3)$$

Where p is the pressure of the gas, k is Boltzmann's constant, and μ is the reduced mass of the collision encounter complex. Combining equations 1-3, δv_p is given by:¹⁴

$$\delta v_p = 2p\sigma(2 / \pi\mu kT)^{1/2}. \quad (4)$$

From Eq. 4 it is apparent that an increase in temperature results in a decrease in collisional broadening. This is due to the fact that the decrease in pressure broadening caused by the expansion of the hot gas is greater than the increase in broadening caused by the increase in mean velocity.

However, the increase in mean velocity also contributes to an increase in Doppler broadening for the gas-phase species. The Doppler limited linewidth for species in a 5000 K plasma is given by:

$$\delta\nu_D = 7.16 \times 10^{-7} v_0 (T/m)^{1/2}. \quad (5)$$

For CH_x species, the Doppler limited linewidth is calculated to be 0.043 cm^{-1} , a value four times larger than the observed linewidth. This discrepancy may be caused by two factors: the plasma may be cooler than 5000 K, or the species giving rise to the observed transitions may be heavier than expected. Furthermore, Dicke narrowing,¹⁴ a narrowing of absorption features that occurs when the excited-state lifetime becomes long compared to the mean collision frequency, may also account for the observed linewidth.

In this preliminary work we have shown that a CRDS setup is capable of detecting dilute gas-phase species in an atmospheric air plasma. Furthermore, the linewidth of spectral features attributed to species within a 5000 K plasma is significantly narrower than expected. We have also established a limitation on the spatial resolution of the CRDS technique near surfaces.

3.1 Novel Data Acquisition Schemes for CRDS

Traditionally, data acquisition electronics in CRDS systems include a digitizing oscilloscope that captures ring-down waveforms and a personal computer which fits the waveforms to an exponential function to determine the ring-down rate. For CW-CRDS systems such as those described in the previous section, often the source of noise which ultimately limits detection sensitivity is that imposed by the digital data acquisition electronics. Furthermore, digital data acquisition schemes are incapable of attaining acquisition rates faster than 20-50 Hz and are therefore incapable of taking full advantage of the increased signal acquisition rates afforded by CW-CRDS systems. For this reason we are beginning to develop fully analog detection electronics that are capable of extracting the ring-down rate from the exponentially decaying signal at kHz repetition rates without imposing excess noise on the ring-down waveform. The noise source that ultimately limits the sensitivity of any cavity ring-down system is that imposed by the statistical fluctuations in the intensity of the light exiting the ring-down cavity, the so called "shot noise." Real-time shot-noise-limited detection sensitivities for CRDS systems could approach $5 \times 10^{-14} \text{ cm}^{-1}$ for photocurrents of 1 mA.³ To achieve such sensitivities with digital electronics would require a digital oscilloscope with better than 20 bits of resolution.

Figure 8 shows waveforms generated by a prototype analog detection system. Trace (a) shows the output of the system photodetector where single-shot ring-down decay waveforms are generated at a rate of 30 kHz. The logarithm of this waveform (Trace (b)) is acquired using a logarithmic amplification scheme. This waveform is then differentiated to generate a dc potential over the ring-down period that is a direct measure of the decay rate.

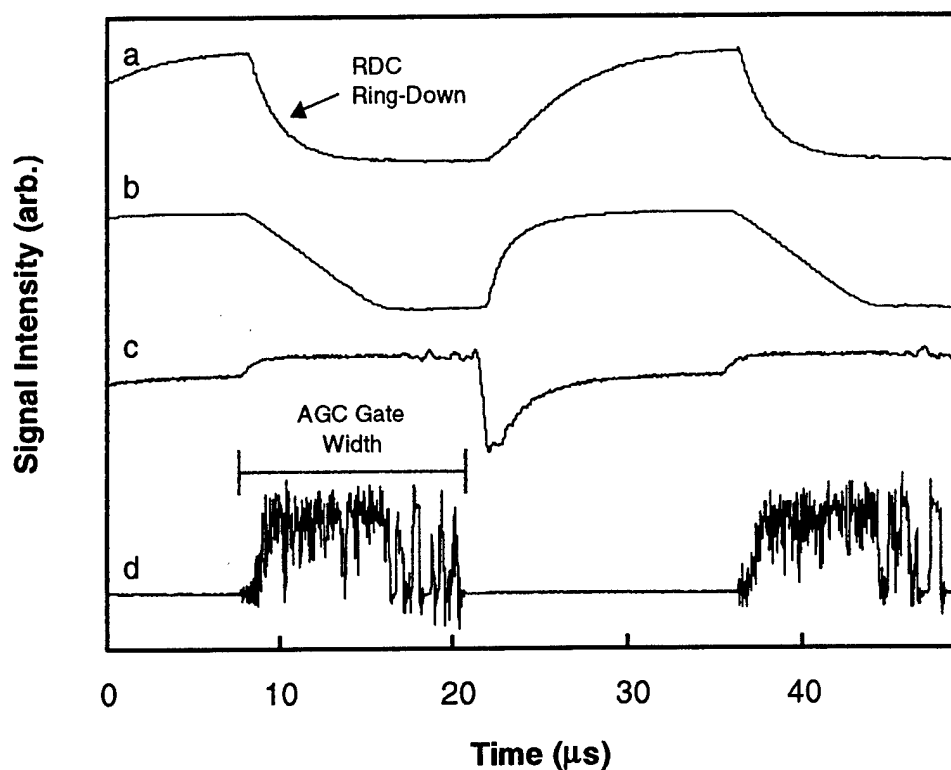


Figure 8. Decay waveforms generated by analog detection system

The unwanted portion of the waveform generated during the “ring-up” of the ring-down cavity is then eliminated and the desired information amplified using an automatic gain control (AGC) amplifier. The portion of the waveform that is preserved is then optimized by varying both the AOM modulation frequency and the width of the pulse used to gate the AGC amplifier. Finally, the amplitude of this modulated waveform may be detected using a lock-in amplifier or a simple sample and hold circuit. We propose to continue development of this scheme as a general-purpose tool for low noise detection of ring-down decay waveforms.

References

- (1) O'Keefe, A.; Deacon, D. A. G. *Rev. Sci. Instr.* **1988**, *59*, 2544.
- (2) Romanini, D. D.; Lehmann, K. K. *J. Chem. Phys.* **1993**, *99*, 6287.
- (3) Spence, T. G.; Harb, C. C.; Paldus, B. A.; Zare, R. N.; Willke, B.; Byer, R. L. *manuscript in preparation* **1999**.
- (4) Yu, T.; Lin, M. C. *J. Am. Chem. Soc.* **1993**, *115*, 4371.
- (5) Yu, T.; Lin, M. C. *J. Phys. Chem.* **1994**, *98*, 9697.
- (6) Atkinson, D. B.; Hudgens, J. W. *J. Phys. Chem.* **1997**, *101*, 3901.
- (7) Meijer, G.; Boogaarts, M. G. H.; Jongma, R. T.; Parker, D. H.; Wodtke, A. M. *Chem. Phys. Lett.* **1994**, *217*, 112.
- (8) Lozovsky, V. A.; Derzy, I.; Cheskis, S. *Chem. Phys. Lett* **1998**, *284*, 407.
- (9) Mercier, X.; Therssen, E.; Pauwels, J. F.; Desgroux, P. *Chem. Phys. Lett* **1999**, *299*, 75.
- (10) Motylewski, T.; Linnartz, H. *Rev. Sci. Instrum.* **1999**, *70*, 1305.
- (11) Zalicki, P.; Ma, Y.; Zare, R. N.; Wahl, E. H.; Dadamio, J. R.; Owano, T. G.; Kruger, C. H. *Chem. Phys. Lett.* **1995**, *234*, 269.
- (12) Zalicki, P.; Ma, Y.; Zare, R. N.; Dadamio, J. R.; Wahl, E. H.; Owano, T. G.; Kruger, C. H. "Proceedings of the 47th Annual Gaseous Electronics Conference"; , 1994, Gaithersburg, Maryland.
- (13) Elleaume, P.; Velghe, M.; Millardon, M.; Ortega, J. M. *App. Opt.* **1985**, *24*, 2762.
- (14) Demtroder, W. *Laser Spectroscopy, Basic Concepts and Instrumentation*, 2 ed.; Springer Verlag: Berlin, 1996.