# Development of a Cavity Ring-Down Spectroscopy Setup and Validation with Carbon-Hydrogen Radical Measurements in an Argon and Acetylene Direct Current Low-Pressure Glow Discharge Plasma

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March 2006

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements of the degree of Masters of Engineering

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Bill Clinton, (American 42<sup>nd</sup> US President (1993-2001), b.1946)

# Abstract

Cavity ring-down spectroscopy (CRDS) is a novel, accurate, sensitive and nonintrusive laser-based technique using multiple-paths molecular absorption to measure weak absolute concentrations of atoms or molecules (ppm range or better). In CRDS, a laser pulse is coupled into an optical cavity equipped of highly reflective mirrors mounted at both ends and containing the absorbing medium. The laser pulse experiences numerous round trips inside the cavity thus considerably increasing the absorption path. The decay of the laser pulse intensity leaking out of one of the cavity mirrors is monitored in real-time and the concentration of the species is obtained by fitting a Beer-Lambert's decay to the measured signal. The resulting signal is an exponentially decaying function with a 1/e cavity ring-down time ( $\tau$ ), proportional to the absolute concentration of the absorbing species.

The main objective of this Master's project was to develop a CRDS system to be used for the study of plasma-surface interactions. The CRDS cavity measures 92 cm in length and has a spatial resolution of 1 mm<sup>2</sup>, and is flexible enough in its design to accommodate a low-pressure glow discharge or a miniature atmospheric pressure plasma torch at the centre of the cavity. In this study, the low-pressure glow discharge plasma is used to produce CH radicals from a 95% Ar - 5% C<sub>2</sub>H<sub>2</sub> gas mixture. Preliminary optical emission spectroscopy (OES) measurements near 431 nm indicated the presence of CH radicals in the plasma. For the CRDS experiments, the electronic transition  $A^2\Delta \leftarrow X^2\Pi$  of the CH radical was probed using a tunable dye laser (10Hz, 5 ns pulse, 0.8 cm<sup>-1</sup> linewidth) tuned to 431.131 nm, and at a pulse energy of approximately 30-40 µJ. The CRDS system was able to measure CH radical concentrations ranging from 1.78x10<sup>12</sup>cm<sup>-3</sup> to 2.18 x10<sup>12</sup> cm<sup>-1</sup>

# Résumé

La technique *cavity ring-down spectroscopy* (CRDS) est une approche relativement nouvelle de spectroscopie d'absorption laser multi-passes utilisée pour la mesure de la densité absolue d'espèces présentes en faibles concentrations (ppm ou mieux) et ce, sans perturbation du milieu mesuré. La technique CRDS utilise une cavité optique équipée de miroirs de grande réflectivité pour mesurer le coefficient d'absorption du gaz, liquide ou solide placé entre les miroirs. Une impulsion laser injectée dans la cavité est réfléchie à maintes reprises à l'intérieur de la cavité ce qui augmente sa longueur optique effective. Une mesure de la décroissance de l'intensité lumineuse de l'impulsion laser avec l'aide d'un tube photomultiplicateur placé à l'endos du miroir de sortie de la cavité permet de déterminer le coefficient d'absorption du milieu absorbant. La décroissance exponentielle observée est alors comparée à un modèle de décroissance d'intensité suivant la loi de Beer-Lambert dans le but d'obtenir la densité moyennée d'espèces absorbants présents dans le milieu.

Le but de ce projet de maîtrise était de développer un système CRDS pouvant être utilisé pour l'étude des interactions entre un plasma et une surface. La cavité CRDS qui a été construite mesure 92 cm de longueur et a une résolution spatiale d'environ 1 mm<sup>2</sup>. La cavité peut accommoder à son centre une torche à plasma non-thermique ou une décharge électroluminescente à basse-pression. Dans ce projet, des radicaux CH produits dans la décharge à basse-pression utilisant un mélange 95% Ar - 5%  $C_2H_2$  sont utilisés pour vérifier le bon fonctionnement du système. Des mesures préliminaires réalisées par spectroscopie d'émission optique indiquent la présence de CH (bande d'émission moléculaire aux alentours de 431 nm). La transition électronique  $A^2\Delta \leftarrow X^2\Pi$  du radical de CH fut sondé avec l'aide des impulsions d'un laser à colorant (10Hz, durée d'impulsion de 5 ns, largeur de raie de 0.8 cm<sup>-1</sup>), accordé à 431.131 nm et à une énergie par impulsion 30-40 µJ. Les densités mesurées par le système CRDS varient entre 1.78 x10<sup>12</sup> et 2.18 x10<sup>12</sup> cm<sup>-3</sup>.

# Acknowledgments

This Master's project was a challenging experience both academically and personally. I have a great appreciation for many people who helped me in the conception and assembly of my project. I would like to thank the following people for their help in making this project a success.

First and foremost, Professor Sylvain Coulombe, who supervised me throughout my project and helped me grow into the person I am now. Having the opportunity to work with someone that has valuable technical knowledge, strong personal values, an excellent work ethic and high standards has made me a better person. Thank you very much for believing in me.

Secondly, I would like to thank Lou, Frank, Ed and Melanie for all their help in debugging my experimental setup and for all the great chats. Thanks to the Machine Shop staff for all their hard work in making the parts used in my experimental setup.

Also, to Dr. Richard Engeln from the Eindhoven Technical University for his advice during my CH radical concentration measurements using CRDS.

I would also like to acknowledge the financial support provided by the Natural Sciences and Engineering Research Council of Canada (NSERC), the Canadian Foundation for Innovation (CFI) and les Fonds québecois de la recherche sur la nature et les technologies (FQRNT). Furthermore, I would like to show gratitude to the Eugenie Ulmer Lamothe (EUL) fund for my scholarship and to McGill University.

. I would like to express gratitude to the McGill Plasma Group for their help in my research and also for making work in the lab fun.

I am also grateful to my friends and family for all their support and encouragement. First, to my parents, Renee and Andrew, who helped me throughout my education with their moral support and enthusiasm for my studies. Also to my sister, Sabina, who was always there to make me laugh. To my cousins Peter and Jacquie, who were more like second siblings to me during my time in Montréal. Thanks for all the dinners, football and hockey tickets, laughs and late nights. Finally to my uncle and aunt, Paule and Hugh, who were also very present in my life during my time in Montréal. This thesis was not possible without them!

Finally, I am truly thankful to my girlfriend Laura. Even though I met her during the last year of my Masters, I got to meet a great person who challenges me on all fronts of life.

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# **Chapter 1 - General Introduction**

Since September 2002, a low-power atmospheric pressure cold plasma torch has been under development in Dr. Coulombe's laboratory for use in the biomedical engineering field. The torch produces a micro-scale ( $<500 \ \mu$ m) plasma in mixtures of helium and any source of reactive species (e.g. O<sub>2</sub>, NH<sub>3</sub>, C<sub>2</sub>H<sub>6</sub> ...). The reactive species produced by the torch are transported to a surface under treatment for etching, deposition and/or functionalization purposes. In the etching process for instance, the torch uses a mixture of He and O<sub>2</sub> to produce ozone (O<sub>3</sub>) and oxygen radicals. One potential application of this etching gas is the removal of organic films from surfaces. The "etching" of the surface is done when ions impact the surface with enough energy to either modify its chemistry or remove materials from the surface<sup>1</sup>. Excited helium atoms are used to transfer energy to O<sub>2</sub> in order to produce O<sub>3</sub> according to the following reaction:

$$O + O_2 + He \rightarrow O_3 + He (ozone formation)^2$$
 (1.1)

The ozone then dissociates to produce molecular oxygen and oxygen radicals:

$$O_3 \rightarrow O_2 + O \bullet$$
 (oxygen radical formation)<sup>3</sup>

Oxygen radicals are also formed from the dissociation of oxygen, where the electrons catalyze the reaction.

$$O_2 + e \rightarrow O \bullet + O \bullet + e \text{ (oxygen radical formation)}^4$$
 (1.2)

CH radicals are one of the expected surface erosion products from plasma torch etching<sup>5</sup>. By measuring the concentration of oxygen radicals and CH molecules in the plasma-surface boundary layer, one could better understand the relation between the rate of oxygen transport to the surface and the CH production. This will help produce an online monitoring strategy for various etching applications, and in particular, in the biomedical engineering field.

20/04/2006

In order to monitor the rate at which the torch etches CH radicals from an organic or biological surface, an *in-situ*, non-intrusive measurement has to be performed. For the context of this research project, a Cavity Ring-Down Spectroscopy (CRDS) system will be designed and built as to enable future monitoring of CH release from such surfaces.

# Chapter 2 - Literature Review

#### 2.1 – Plasmas

Plasmas are generally seen as the fourth state of matter. They consist of ionized gases though they are globally electrically neutral (positive and negative charged species are balanced at the macroscopic scale). Plasmas can be found in nature (ex: sun, stars, aurora borealis) and can be man made (ex: arc lamps, fluorescent tubes, plasma torches). Plasmas are attractive to industrial interests because they are sources of reactive species and can operate at high temperatures and energy densities.

Such conditions within the plasma medium favour physical changes to compounds injected in it and/or induce chemical reactions between species present in the plasma. Another advantage to commercial plasma use is that the "active species are more numerous, different in kind, and/or more energetic than those produced in chemical reactors."<sup>6</sup> The active species in the plasma include charged particles such as ions and electrons, excited neutrals (reactive), atoms and reactive radicals<sup>7</sup>.

The electrons and other charged species present in the plasma gain energy from the external electric field and collide with molecules, atoms and ions. They transfer part of their kinetic energy to uncharged particles or ions in the plasma through inelastic collisions. These collisions lead to the excitation and ionization of atoms and molecules, and for molecules, to their fragmentation leading to the production of active radicals.

There are essentially two general families of processing plasmas: thermal and nonthermal plasmas. The main difference between thermal and non-thermal plasmas is that thermal plasmas are assumed to be at local thermodynamic equilibrium (LTE) and that nonthermal plasmas are in a state of non-equilibrium. LTE implies that the heavy species present in the plasma have approximately the same temperature as that of the electrons. Meanwhile, for non-thermal plasmas, the electron temperature is much higher than that of the heavy species. Thermal plasmas offers higher gas temperatures and have higher energy densities than non-thermal plasmas. On the other hand, non-thermal plasmas are more selective chemically and represent a small thermal load to substrate, making them particularly useful for the surface treatment of temperature-sensitive materials.

Processing plasmas are generated by the application of an electric field (E-field) through the help of electrodes on an initially neutral gas. Above a certain threshold electric field which corresponds to the breakdown electric field of the gas, a conducting path, a plasma channel, is created and maintained in the inter-electrode gap hosting the gas. The breakdown E-field depends strongly on the electrode geometry, inter-electrode distance, nature of the gas and pressure. Lowering the pressure to the minimum of the Paschen's<sup>8</sup> curve is a well-down means to favour breakdown. The lower pressure also leads to a reduction of the rate of collisions amongst particles and thus, to the establishment of nonequilibrium conditions. In fact, the electrons gain kinetic energy from the E-field faster than the heavy ions since collisions become important due to their small mass. Correspondingly, they acquire a higher kinetic temperature more quickly than the heavy species. The lower rate of collisions implies a higher mean distance between collisions and thus, to the formation of larger and more uniform plasmas, which are particularly well-suited for the treatment of large surface areas and for diagnostic purposes. In this study, we take benefits of the lower pressure and use a low-pressure (~1 Torr (133.3 Pa)) direct-current (DC) glow discharge plasma to produce CH radicals from an  $Ar/C_2H_2$  gas mixture. Those radicals are important in the study of plasma-surface interactions, and can be detected by laserabsorption (or even by optical emission spectroscopy) from their molecular absorption (and emission) band around 430 nm.

## 2.2 – Production of CH Radicals by a Low-Pressure DC Glow Discharge<sup>9</sup>

For the context of this research, a known reaction producing CH radicals in the plasma phase was used in order to verify the validity of CRDS absorption measurements. A process for CH radical production in an  $\operatorname{argon/C_2H_2}$  gas mixture was suggested by *Engeln et al*<sup>40</sup>. CH radical concentrations ranging between  $5 \times 10^{19} \text{ cm}^{-3}$  and  $8 \times 10^{20} \text{ cm}^{-3}$  were observed. Cavity Ring-Down Spectroscopy (CRDS) was used for the measurement of CH radical concentrations at an absorption wavelength of 431.131 nm. The electronic transition probed by laser absorption was in the  $A^2\Delta \leftarrow X^2\Pi$  system, whose transition involves the CH radical ground state, which state hosts the vast majority of the CH molecules in a non-thermal plasma.

The context of Engeln's experiments was for the monitoring of CH radical production using CRDS during the deposition of a-CH (amorphous hydrogenated carbon) films. CH radicals were produced using an expanding Ar thermal plasma, with  $C_2H_2$  being injected downstream the plasma-forming region at flowrates ranging from 30 to 840 sccm. The Ar flowrate inside the reactor was held constant at 6000 sccm, which corresponds to having mole percentages of  $C_2H_2$  ranging between 0.5% and 14%. CH radicals were formed by a charge exchange/dissociation reaction between Ar<sup>+</sup> ions and C<sub>2</sub>H. The reaction mechanism for CH radical formation is depicted below.

$$Ar^{+} + C_{2}H_{2} \rightarrow C_{2}H_{2}^{+} + Ar \quad 2.1$$

$$C_{2}H_{2}^{+} + e^{-} \rightarrow C_{2}H + H \quad 2.2$$

$$C_{2}H + Ar^{+} \rightarrow C_{2}H^{+} + Ar \quad 2.3$$

$$C_{2}H^{+} + e^{-} \rightarrow CH + C \quad 2.4$$

$$C_{2}H^{+} + e^{-} \rightarrow C_{2} + H \quad 2.5$$

The charge exchange reaction occurs after a  $C_2H_2$  molecule is dissociated by  $Ar^+$ , which process leads to the formation of a  $C_2H$  molecule, the principal precursor to CH radical production. Further studies on a-CH film deposition by Engeln *et al.* using mass spectroscopy indicated that  $Ar^+$  is the dominant species contributing to the downstream dissociation of  $C_2H_2$  to produce CH radicals. The  $Ar^+$  ion is very important in CH production since it is responsible for the primary and secondary ionization of  $C_2H_2$  into  $C_2H_2^+$  and  $C_2H^+$ . It is also indicated that there is no further decomposition of CH radicals after the second ionization process. CH concentrations are at their highest values when  $C_2H_2$  is injected downstream from the Ar plasma at concentrations ranging between 1.5% and 8%. It is important to maintain the  $C_2H_2$  concentration within this range since the flux of Ar<sup>+</sup> ions can not be limited, since it is an important reactant for reactions 2.1 and 2.3. Also, there has to be enough  $C_2H_2$  to produce CH radicals. Following Engeln *et al* s work, we adopted a gas mixture containing 5%  $C_2H_2$  (in Ar) that will produce CH radicals in a low-pressure DC glow discharge.

#### 2.3 - Absorption Spectroscopy

Spectroscopy is "the study of how electromagnetic waves interact with matter in order to extract qualitative and quantitative information on the matter"<sup>11</sup>. In plasma applications, spectroscopy is primarily used to determine the particle density, species temperatures and electron temperature. The advantage that spectroscopy has over other measurement methods is that it is highly selective, non-intrusive. Depending on the particular spectroscopy technique used, it can also offer a high spatial resolution.

Optical emission spectroscopy (OES) is a "passive" form of spectroscopy which uses the emission of a particular light source in order to analyze its composition, and determine the particles' density and temperature. "Passive" spectroscopy implies the selfexcitation of the molecules or atoms of interest (i.e. the radiative species are not excited by any component of the system used to perform the spectroscopic measurements). In order to measure light intensity at very specific wavelengths, light is dispersed into its spectral components using a monochromator, where the light intensity is captured using a photomultiplier tube (PMT) (or other fast light conversion devices). Emission spectroscopy is frequently used in the measurement of thermal plasma properties. In fact, due to the high temperature of the plasma, many excited energy states of the atoms, ions and molecules present in the plasma are populated and emit photons through the radiative de-excitation transitions to lower energy states. With OES, a calibration in detected light intensity has to be performed in order to give direct concentration measurements. Due to its simplicity and non-intrusive nature, OES is also commonly used in on-line monitoring and control applications.

Due to the low heavy species temperatures observed in non-thermal plasmas, the excited energy levels of atoms, ions and molecules are weakly populated. Consequently, the intensity of light emitted from the de-excitation of the excited states is much less than what is observed in thermal plasmas. Additionally, the density of species of interest might be low to start with. Emission spectroscopy becomes then of lesser interest when both limitations are combined. When such situation arises, an "active" spectroscopy technique which probes directly the ground energy state, the heavily populated state, is used. Amongst familiar "active" spectroscopy techniques we find Laser-Induced Fluorescence (LIF) and Cavity

Ring-Down Spectroscopy (CRDS). By "active" it is implied that the atoms, ions and molecules of the medium under investigation<sup>12</sup> are intentionally excited from their respective ground states to excited energy states, which may radiate upon de-excitation to the ground states. LIF is thus an "active" optical emission spectroscopy technique whereby a laser is used to populate the upper energy states. CRDS, on the other hand, measures the attenuation of the intensity of a laser beam as its passes through the medium of interest, and selectively promote atoms, ions and molecules to upper energy states. LIF and CRDS thus probe species in their respective ground states.

In laser absorption spectroscopy, a beam of coherent light enters an absorbing medium, where the particles present in the medium absorb or scatter the photons of the beam causing a net attenuation of the beam intensity along the optical path. The losses of electromagnetic energy in the absorbing medium are caused by "atoms, ions, or molecules that absorb radiation at a wavelength  $\lambda$  that excite them from a lower energy state to an upper energy state"<sup>13</sup>. The wavelength associated with this energy transition is expressed as:

$$\lambda_{ik} = \frac{hc}{\Delta E_{ik}}$$
(2.6)<sup>14</sup>

Where  $\lambda$ =wavelength (m), h=Planck's constant=6.626068x10<sup>-34</sup> (J\*s), c=speed of light=3x10<sup>8</sup> (m/s) and  $\Delta$ E=energy difference (J) between the upper (k) and lower states (i).

Energy transitions amongst energy states are quantized and thus the molecules (ions or atoms) can absorb energy only at very specific wavelengths. This spectrally selective "trace" can be used to identify the species that are present in the medium. Specific species can be targeted if the light entering the medium is tuned to the wavelength at which the species can absorb energy. This is achieved by using a tunable laser source or an intense continuous light source which is spectrally-resolved with a monochromator before it enters the probed medium.

In the context of the study of non-thermal plasma-surface interactions, absorption measurements will be performed on a low-temperature plasma gas where a large population of the ground energy state is expected. It is suggested that the absorption of energy by CH radicals be done from the ground electronic state to a low electronic energy level. The absorption to these low levels requires relatively little energy to excite the species at the low plasma temperatures<sup>15</sup>.

### 2.4 - Determination of Concentration from Absorption Measurements

As light enters the absorbing medium, it is both absorbed and scattered by the species present, which process causes the attenuation of the light intensity. The intensity is related to scattering and absorption coefficients ( $S_{\lambda}$  and  $K_{\lambda}$ , respectively) through the following relationship:

$$I_{out}(\lambda) = I_{in}(\lambda) * \exp\left(-\int_{0}^{x} (K_{\lambda} + S_{\lambda}) dx\right)$$
(2.7)<sup>16</sup>

Where  $I_{in}(\lambda)$ =intensity entering the absorbing medium,  $I_{out}(\lambda)$ =intensity exiting the absorbing medium,  $K_{\lambda}$ =spectral absorption coefficient= $\sum_{i=1}^{i} \sigma_{\lambda}^{i} * n_{i}$  (cm<sup>-1</sup>), x=thickness of absorbing medium (cm),  $S_{\lambda}$ =spectral scattering coefficient (cm<sup>-1</sup>),  $n_{i}$ =absorbing species density (cm<sup>-3</sup>),  $\sigma_{\lambda}$ =spectral absorption cross-section (cm<sup>2</sup>), i=absorbing species identifier.

The above equation can be simplified by assuming that there is negligible scattering with respect to absorption (i.e.  $K_{\lambda} >> S_{\lambda}$ )<sup>17</sup>. Thus, the light intensity change after passing through an absorbing medium is proportional to the concentration of absorbing species present in this medium (more molecules absorbing means more photons absorbed and greater attenuation) and distance (longer path implies more photons absorbed)<sup>18</sup>. As the light intensity is attenuated solely by the absorption through the medium, the light exiting the medium follows the Beer-Lambert's law. This law relates the difference in incident and exiting light intensities to population densities, which should be assumed to be uniformly distributed in space.

$$I_{out} (\lambda) = I_{in} (\lambda)^* \exp (-\sigma(\lambda)^* L * n)$$
(2.8)<sup>19</sup>

Where L=length of absorbing path (cm).

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For the context of this research,  $\sigma(\lambda)$  will have a uniform value, independent of the spatial coordinate since it is assumed a uniform plasma will be used over the desired absorption length (L).

### 2.5 – Cavity Ring-Down Spectroscopy

One of the major limitations of the single-pass absorption spectroscopy approach described above lies in the need for long and uniform absorption paths for weakly absorbing species or species present in small concentrations. One particularly interesting approach used to enhance the sensitivity of absorption spectroscopy techniques is the use of a multi-pass cell where the effective absorption path length is increased considerably. Since there might be a low concentration of absorbing species in the medium (concentration in the ppm range<sup>24</sup>), a long absorption path is required so that the small amount of species can have a chance to absorb photons. Such a cell can be made with optical cavities using mirrors facing each other, therefore defining the absorbing volume. Cavity Ring-Down Spectroscopy (CRDS) is one of such techniques making use of multi-passes and is used to detect very low concentrations of species in gas, liquid<sup>21</sup> and solid<sup>22</sup> media. It constitutes one of the numerous multi-pass absorption approaches. It is particularly well-suited to probe small absorption volumes, and has a high spectral resolution.

CRDS uses a laser pulse, a beam of light with high energy density and spectral resolution, which is trapped in a high finesse optical cavity. The absorbing medium placed between the cavity mirrors is probed by the laser pulse over many round trips, which increases the effective path length for the absorption. CRDS has a sensitivity range of 10<sup>12</sup> to 10<sup>17</sup> molecules per cm<sup>3</sup>, with a range that finds suitable application in trace gas analysis<sup>23</sup>. The CRDS optical cavity is comprised of two highly reflective mirrors (reflectivity of 99.99% or better<sup>24</sup>) placed along the same axis, which are enclosed in a controlled-atmosphere vessel (ex. a plasma reactor) used to contain the absorbing species of interest. A block diagram of the CRDS experimental setup (Fig. 1) indicates that there are five main components to the system: a tunable laser source (continuous wave or pulsed laser<sup>25</sup>), the mode matching optics, the optical cavity, a photon detector, followed by a data acquisition system.



Figure 1 - CRDS Technique Block Diagram<sup>26</sup>

A detailed diagram outlining a typical CRDS setup is presented in Figure 2. Once the laser pulse enters the cavity along the centerline, the high reflectivity mirrors cause the laser pulse to become "trapped". Since only a small fraction of the beam incident on the second mirror is transmitted through it, most of the beam is reflected back-and-forth inside the cavity. The light pulse thus makes multiple round trips along the centerline (where the absorbing medium is placed), and during each trip, some of the incident light is absorbed and a small fraction of the light exits the cavity (transmission losses). A high speed photomultiplier tube (PMT) is placed behind the second cavity mirror for the measurement of the intensity of the laser pulses that leak out.

The light source used in CRDS has to provide a beam of light that is short (ns pulse range), collimated, coherent and tuned to the wavelength of absorption. In this research project, a narrow linewidth pulsed tunable laser is used to inject radiation into the cavity, where absorbing species are present. The beam diameter should be equal or less than 1 mm<sup>27</sup> in order to achieve some spatial resolution within the absorbing medium. Thus, before entering the cavity, the laser beam passes through a mode matching optical setup which reduces the size of the laser beam and selects a specific optical mode of the laser. A mode is "the characteristic of the propagation of light through a waveguide that can be designated by a radiation pattern in a plane transverse to the direction of travel"<sup>28</sup>. The most common and

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simple mode matching optical setup used for CRDS consists of a telescope assembly, i.e. two lenses arranged such that their respective focal points coincide. A small aperture pinhole placed at the coincidence point of the lenses is used to remove the unwanted modes of the laser beam and to keep only the Gaussian  $TEM_{00}$  mode<sup>29</sup> (round cross-section profile).

Furthermore, the tunable laser that is used in our application is a mode-locked laser, which means that the cavity longitudinal mode oscillates in a single mode.<sup>30</sup> The single longitudinal mode operation permits the light packets to oscillate in the same phase within the cavity, reducing the random noise and giving rise to a more uniform signal<sup>31</sup>. A narrow bandwidth filter (±5 nm), placed in front of the PMT<sup>32</sup>, and is used in order to filter out the unwanted light (ex. background light from the room and the light emitted by the plasma).



in the medium, D=light exits cavity and its intensity is measured)

#### Figure 2 - CRDS Operation Outline

Having the laser beam perform multiple round trips inside the cavity, the light inside the cavity will cross the absorbing medium many times. By doing so, the effective path length traveled by the beam of light can be increased considerably. O'Keefe and Deacon reported that effective path lengths of 10 km could be attained using a 1 m cavity length equipped with mirrors of reflectivity equal to 99.995%<sup>33</sup>. The number of round-trips performed by the laser beam inside the cavity can be determined using equation 2.9.

$$n = \frac{-1}{2\ln(R)}$$
(2.9)<sup>34</sup>

Where n=number of round trips done by the laser beam inside the cavity and R=mirror reflectivity. The number of round trips in this case only takes into account the losses due to
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transmission through the mirrors. In the context of this research, for a mirror reflectivity of 99.995%, the number of theoretical round trips in an empty cavity is approximately equal to 10,000. For an empty cavity (with no laser beam energy absorption losses) measuring 92 cm, this will give a maximum equivalent absorption path length of 18 km. However, the number of round trips (and subsequently the path length) will decrease with an absorber present; since additional laser beam energy is lost to absorption from the CH radicals in the plasma.

A constraint exists on the minimum length for the cavity. If the cavity length is too short, there can be interference caused by beams propagating in opposite directions (i.e. if the pulse duration is longer than the round trip time)<sup>35</sup>. Therefore, in order to avoid interference, the round trip time of the beam in the cavity must be superior to the laser pulse duration (ns). Typical commercial Nd:YAG laser-pumped dye lasers have a pulse lengths of the order of 5 ns, which gives rise to minimum optical cavity lengths of the order of 75 cm. A comparative analysis of the round-trip time and pulse time for the proposed CRDS setup will be discussed in section 4.1.2.

By increasing the path length for absorption of a dilute sample, the signal generated by the PMT will decrease faster with higher concentrations of absorbing species<sup>36</sup>. CRDS measurement setups have high sensitivity because they measure the appearance of a small signal and not a small change in a large signal<sup>37</sup>. Figure 3 depicts a schematic of the CRDS signal detected by the PMT. The signal consists of a sinusoidal waveform whose amplitude decays with time. The signal envelope describes the decay, which is due to absorption by the sample and mirror reflection losses.



Figure 3 - Schematic representation of a pulsed laser CRDS signal output<sup>38</sup>

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The data generated by the PMT can be fitted to a modified version of Beer-Lambert's Law, depicted by equation 2.10, where the losses due to the mirror reflectivity are added to the absorption loss term.

$$I_{OUT}(t) = I_{IN}(t) * \exp\left(-((1 - R) + \sigma NL) * (\frac{tc}{L})\right)$$
 (2.10)<sup>39</sup>

Where t=time and c=speed of light in a vacuum

The time constant for the decay, the ring-down time ( $\tau$ ), is the time that it takes for the light intensity to decay by one exponential. The slope of the light intensity signal envelope plot (ln ( $I_{out}/I_{in}$ )) versus time gives the ring-down time, which is defined by equation 2.11, as the time required for the transmission and absorption losses to decrease by a factor of e.

$$\tau = \frac{L}{c(1 - R + \sigma NL)}$$
(2.11)<sup>40</sup>

Where  $\tau$ =ring-down time for absorption.

A ring-down measurement with an empty cavity should be taken first. This measurement is used to filter out background noise and to help correct for scattering losses<sup>41</sup>. The two ring-down times can be compared to one another using equation 2.12 to give the absolutes spectral absorption coefficient (K<sub>λ</sub>), which corresponds to  $\sigma(\lambda)$ \*N.

$$K_{\lambda} = \frac{1}{c} \left( \frac{1}{\tau} - \frac{1}{\tau_{0}} \right)$$
 (2.12)<sup>42</sup>

Where  $\tau_0 =$  ring-down time of the empty cavity.

The signals generated by the PMT for each laser pulse are collected by a fastdigitizing oscilloscope, which automatically calculates the signal envelope. The resulting signal data from the oscilloscope is sent to a PC, where the signal envelopes are averaged using a LabView<sup>TM</sup> VI (Virtual Instrument) in order to improve the signal to noise ratio.

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From the averaged envelope, a ring-down time is extracted using a exponential fitting program, which is embedded within LabView<sup>TM</sup>.

The empty cavity has a longer ring-down time compared to a cavity containing absorbing species because there are less absorption losses. Ring-down times of 2.5  $\mu$ s have been reported for CH molecules ( $\lambda$ =431 nm) present at a concentration of  $1.1 \times 10^{13}$  cm<sup>-3</sup> in a cavity with a length of 80 cm and a mirror reflectivity of over 99.7%<sup>43</sup>. Since the ring-down times are in the  $\mu$ s range, the data acquisition has to take samples in the 100 MHz range (one sample every 10 ns) or higher since there has to be enough sample points in the signal envelope to resolve one ring-down time. In this research project, the signal is acquired by the digital oscilloscope (Tektronix - TDS 3054B) having a 500 MHz sampling frequency capable of direct acquisition of the signal envelope (500 data points per envelope signal).

In addition to pulsed lasers, CRDS can also be performed using continuous wave lasers (cw-lasers). In the past, cw-laser CRDS was limited by the large spectral linewidth of the laser emission line which made it hard to cover the spectral limit of the absorber of interest<sup>44</sup>. Also, the linewidth of the cw-laser was too large to be coupled with the cavity modes. Recent developments in cw-laser technologies have permitted operation at narrower linewidths (~100 MHz)<sup>45</sup>, making cw-CRDS possible. Since these lasers emit coherent light continuously, electro-optical switches are placed in front of the cavity and are used to couple the light into the cavity. These switches operate at MHz repetition rates, either blocking or letting the beam pass, therefore enabling light intensity to build up inside the cavity. The advantages that cw-CRDS has over pulsed laser CRDS is that the lasers are less bulky and are less expensive. Also, cw-CRDS has less shot to shot noise than pulsed CRDS since more light can be coupled inside the cavity, which improves the signal to noise ratio. However, for this research project, a pulsed laser is used for CRDS since it will be used for complimentary applications.

# **Chapter 3 - Objectives**

The main objective of this M. Eng thesis project is to develop a working CRDS unit for the study of non-thermal plasma-organic surface interactions. The specific objectives of the project are:

- 1) The design and construction of the plasma chamber and optical setup for the CRDS unit.
- 2) Incorporate a known reaction mechanism for the production of CH radicals as to validate CRDS operation.
- 3) Prepare the CRDS unit for the integration of an Atmospheric Pressure Glow Discharge torch (APGD-t) and the study of local plasma-surface interactions.

# **Chapter 4 - Experimental Setup Design and Operation**

### 4.1 - Experimental Apparatus

Different variants of CRDS experimental arrangements have been used in conjunction with plasma generation for making gas phase absorption measurements. Each combination differs by: plasma type, molecule or atom being monitored, CRDS cavity length, optical system geometry and data acquisition systems. Most setups also incorporate a tunable dye laser to spectrally target species for absorption measurements. Diagrams of the setup developed for the present study are depicted in Figures 4 and 5. The current CRDS unit was designed to incorporate a low-pressure DC glow discharge in the centre of the cavity. The CRDS experimental setup design was done by focussing on three important sections: **Optical System, CRDS Cavity and Data Acquisition System.** An outline of each part of the experimental apparatus is presented in this section.

#### 4.1.1 – Optical System

The CRDS experimental setup is placed on an optical table (Newport Corporation) measuring 244 cm by 91 cm, with all the optical components placed in the same horizontal plane. The optical table provides evenly spaced holes (2.54 cm apart) that are used to screw in the optical components. The table uses a pneumatic suspension which attenuates vibrations and maintains optical alignment. A pulsed Nd/YAG pumped-tunable dye laser system is placed on the back end of the optical table. A more detailed explanation of laser operating principles and maintenance is presented in section 4.2. Additional accessories such as the oscilloscope, glow discharge power supply and decade box, photomultiplier tube and optical emission setup are also placed on the optical table.



Figure 4 - Diagram of the CRDS Experimental Setup

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Figure 5 - Picture of the actual CRDS unit

The pulsed laser system is comprised of a pump Nd:YAG laser (Quantel Brilliant B10, 800 mJ at 1064 nm) and a tunable dye laser (Quantel TDL 90) operating at 10 Hz pulse rate, with a 5-6 ns pulse length and a  $0.8 \text{ cm}^{-1}$  linewidth. The laser beam that exits the dye laser has a diameter of approximately 9 mm. Literature reports that the criteria for CRDS operation require that the laser beam entering the cavity be of 1 mm in diameter (or less) and in the TEM<sub>00</sub> mode<sup>46</sup>. Also, the total energy of the beam entering the cavity should be approximately 40 µJ per pulse or less<sup>47</sup>. These criteria are attained by using beam profiling and beam alignment optical components placed along the length of the optical table, on the same horizontal axis as the laser beam exit. Figure 6 depicts the optical system used for these experiments.

All the optical components are centered at a height of 19 cm and are held in place using adaptors on pedestal and post systems (Newport Corporation). The beam profiling optics consist of two 5.88 cm diameter fused silica bi-convex lenses (Newport Corporation) held in place by two 5.88 cm lens holders (Newport Corporation), which form a telescope assembly. A high damage threshold tungsten pinhole (Lennox Laser (d=0.5 mm)) is placed at the focal point of each lens ( $f_1$ =25cm and  $f_2$ =20cm). The first lens focuses the beam onto the pinhole for profiling to the desired diameter. The second lens is used to re-collimate the beam.

The beam then hits a highly reflective metallic mirror (Newport Corporation) mounted on a 3-point adjustment holder (Newport Corporation) placed 22.8 cm from the second bi-convex lens. It is then reflected at a ~90 degree angle to a prism (Newport Corporation) placed 16.5 cm from the mirror and mounted on a 3-point adjustment holder (Newport Corporation). The prism reflects the beam by a 90 degree angle, with the mirror and prism reflections totalling a ~180 degree change in the beam direction. The beam then goes through an iris (Newport Corporation) opened to a minimum aperture of 1 mm in diameter which is placed 14 cm from the prism and 10.15 cm from the back end of the front cavity mirror. This iris is used to remove the diffraction rings caused by the pinhole in the telescope system. This optical assembly ensures that the beam is profiled to a uniform Gaussian energy distribution (TEM<sub>400</sub> mode) before entering the first cavity mirror.



Figure 6- Optical System Layout

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The laser beam enters the centerline of the cavity through the back end of first mirror (transmits light), and crosses the absorption volume before being reflected back by the second mirror. A high fraction of the laser beam intensity is reflected back towards the first mirror. The laser pulse thus experiences several round trips in the cavity before its intensity decays to zero due to transmission losses through both mirrors. The decreasing light intensity signal leaking out of the second mirror is captured using a photomultiplier tube (Hamamatsu 6720) placed at the back end of the second mirror. The light intensity exiting the cavity (measured by the PMT) is severally attenuated by the absorption and mirror transmission losses, when compared to the incident light intensity.

A 2.54 cm diameter band pass filter (Thorlabs – 430 nm central wavelength with a  $\pm 5$  nm bandwidth) positioned in a lens holder and post (Newport Corporation) is placed in front of the PMT as to prevent stray light from interfering with the sensitive signal. A piece of 3.81 cm in diameter and 15.25 cm long blackened laser tubing mounted on two posts (Newport Corporation) adapted with optical lens mounts (Newport Corporation) is placed directly at the laser beam exit in order to block the intense stray light emerging from the dye laser. Finally, a black cloth is wrapped around the PMT and back end of the CRDS reactor as to prevent any further stray light from reaching the PMT head.

#### 4.1.2 – CRDS Cavity

The CRDS cavity is placed in parallel to the beam alignment optics, with a horizontal separation of 20.2 cm. The CRDS/Plasma Reactor assembly has the dual task of hosting the CRDS components and the DC glow discharge plasma-generation components. Several design constraints are addressed in Table 1.

The cylindrical cavity measures 92 cm in length and 3.1 cm in diameter, with both highly reflective (R>99.995%) mirrors (Los-Gatos Research Inc. – 430 nm central wavelength with a ±5 nm bandwidth) placed at each end on the CRDS mirror holders (Los-Gatos Research Inc.). A sample mirror reflectivity response curve from Los-Gatos Research Inc. for mirrors (440 nm max reflectivity) similar to the ones used for CH absorption measurements is available in Appendix 3. As discussed in section 2.5, the minimum cavity length for laser pulse durations of 5 ns is 75 cm. With a length of 92 cm, there will be no laser beam interference effects in the cavity. A detailed diagram of the CRDS reactor is illustrated in Figure 7.

C. Statistics and Stat Statistics and Statistics	
Pressure measurement	Incorporation of a pressure gauge port onto the
	reactor
Cavity length	Length of cavity must be long enough to
	accommodate a laser beam with a pulse length of 5 ns.
	This is done to avoid beam interference effects inside
	the cavity.
Vacuum connection	Need to include vacuum pump hose connection to
	reactor design
Easy reactor assembly	Standard flanges (NW) used to facilitate reactor
	assembly
Incorporation of CRDS mirror	CRDS mirror holders need to be placed on MDC Del-
holders	Seal on each end of reactor
Incorporation of electrodes for a	Quartz cross with standard NW40 flange ends is used
DC glow discharge	to place the electrodes inside the reactor.
Maintain a steady vacuum	All parts need to be able to withstand a minimum
	vacuum of 0.01 Torr (1.33 Pa).
Enable flow of gas into reactor	Steady gas flow into the reactor is needed for
	protection of CRDS mirror and to generate the
	plasma.
Integration of reactor on the	Four metal holders designed to be bolted into the
optical table	optical table, while holding the reactor steadily in
	place.

#### Table 1 - CRDS Reactor Design Considerations

The CRDS reactor is comprised of 5 parts that are highlighted in Figure 7. The first part (1) is the CRDS mirror holder, which is placed at both ends of the reactor. This part is made of stainless steel 304 and has a standard mirror holder (Los Gatos Research Inc.) mounted on a Del Seal CF Flanges (MDC Vacuum - 2.75 inch (7 cm) OD). The other side has a NW40 flange (MDC Vacuum), which connects the mirror holder to the rest of the reactor. Duplicate parts are made since mirrors need to be mounted on both ends. Also, two <sup>1</sup>/<sub>4</sub> inch (0.6 cm) diameter stainless tubes, deformed to form a nozzle are welded to the end of the Del Seal flange tubing. The other end of the tube has a standard <sup>1</sup>/<sub>4</sub> inch (0.6 cm) tube Swagelok fitting that is connected to the gas distribution system. These tubes enable the flow of gas to the CRDS mirrors, as to protect them from any volatile compounds or soot formed during  $Ar/C_2H_2$  plasma operation. The mirrors are highly reflective and any impurity

on the surface will deteriorate their reflectivity, which will subsequently decrease the CRDS sensitivity.

The second part (2) is a stainless steel (304) 1.5 inch (3.8 cm) diameter tee (MDC Vacuum) with two NW40 flanges on each end. It is connected on the left hand side to the mirror holder and on the right hand to the quartz cross. This tee adapts a vacuum pump (Alcatel Pascal 2005-SD) connection, where the middle flange is connected to a vacuum pump hose, with a NW25 flange connection. The middle piece of the reactor (3) is a 1.5 inch (3.8 cm) diameter four-way quartz cross (EVAC Vacuum) measuring 5.12 inches (13 cm) in length. Special Teflon adapters (EVAC Vacuum) are used to seal the NW40 stainless steel flanges to the quartz flanges without cracking the piece. The top of the cross incorporates the live electrode for plasma generation via a vacuum tight stainless steel adapter.



Figure 7 - CRDS Reactor Diagram

The flat circular electrodes, each being 1.5 inches (3.8 cm) in diameter, are made of a NW25 flange cap (MDC Vacuum) that is welded to a 6 inch (15.2 cm) long stainless steel tube. The adapter used to feed the electrode is comprised of a NW40 stainless steel flange

(MDC Vacuum) welded to a stainless steel rod 2.5 cm in diameter and 2.5 cm in height, with a 1.3 cm hole bored in the middle of the rod. Two o-rings placed 1.3 cm apart in the tube ensure a vacuum seal. The bottom NW40 cross flange is connected to the ground electrode, which is a NW40 electrical feedthrough piece (MDC Vacuum). The two electrodes are 3.8 cm apart and are mounted along the vertical centerline of the quartz cross (**3**).

The fourth piece (4) is almost identical to the second reactor piece (2), except that the top port ends with a NW16 flange. The 1.5 inch (3.8 cm) diameter tube is connected on the left side with an NW40 connection to the quartz cross and on the right side to the mirror holder. The top tube is connected to a pressure transducer (MKS Corporation-925 series) at the NW16 flange connection. The reactor pressure is monitored via the LabView<sup>TM</sup> interface connected to the pressure transducer via a RS232 connection.

The reactor is integrated to the optical setup by 4 sturdy holders (22.9 cm in height by 5.1 cm in width) bolted into the optical table. The holders have 5.1 cm diameter holes placed at a height of 14.0 cm with screws that hold the reactor steadily in place. The centerline of the reactor is the plane of the laser beam.

A high-voltage power supply (FLUKE 412B, 0-3 kV) placed on a rack above the optical table is used for the generation of the low-pressure glow discharge inside the quartz cross area. The live terminal of the power supply is connected to the top electrode through a decade box set to a resistance value of 5 k $\Omega$ . The lower electrode is connected to the ground terminal of the power supply. Figure 8 depicts a picture of the experimental setup during an experiment with a low-pressure DC glow discharge in Ar.



Figure 8 - Picture of a DC Low-Pressure Glow Discharge in Ar during CRDS Operation

The gas used to generate the CH radicals is a mixture of 95% argon and 5% acetylene ( $C_2H_2$ ). The gas is fed via a tank at a maximum pressure of 180 psig (1241 Pa) with a regulator (MEGS) that is set to a gas line pressure of 10 psig (68.9 Pa). The gas line is connected to a rotameter (Matheson Gas – Cube Series (1-200 sccm)), with flowrates calibrated to the regulator pressure using a Gilianmeter. The rotameter feeds the gas to a stainless steel manifold (McMaster-Carr) and valve (Swagelok), which splits the gas into four 1/4 inch (0.6 cm) tubes that flow the gas to both extremities of the CRDS reactor assembly. All tube connection use Swagelok fittings.

The reactor was set up to operate for a plasma pressure range of 0.2 to 1 Torr (26.7 to 133.3 Pa). Under nominal conditions, the gas flow rate is set to 50 sccm, which value leads to an approximate chamber pressure of  $0.5 \pm 0.05$  Torr (66.7  $\pm$  6.7 Pa). The vacuum pump connected to the CRDS reactor is used to vent the contents of the reactor to the building ventilation system. It also maintains the reactor pressure at the required level. A molecular sieve trap is used to absorb the organic molecules generated by the glow discharge, protecting the pump oil from contamination. The pump is left on continuously as to maintain the reactor as clean as possible. The base pressure of the reactor is 10 mTorr
(1.33 Pa). As depicted by the arrows in Figure 7, the gas flow direction is from the front flange to the back flange, passing though the middle of the reactor, where the plasma is generated.

### 4.1.3 – Data Acquisition System

The purpose of the data acquisition (DAQ) system is to capture ring-down signals from the photomultiplier tube (PMT) measuring the transmitted light intensity at the CRDS unit exit. The acquired signal is used to extract a ring-down time. From literature, traditional CRDS data acquisition systems (DAQ) are comprised of a highly-sensitive PMT, that is connected via a BNC connection to a high speed digital oscilloscope (with an impedance of  $50\Omega$ ) and then to a personal computer (PC).

Engeln et al.48, recommends that 64 ring-down time values be averaged for one concentration measurement, as to eliminate the shot-to-shot noise from the laser energy fluctuations. Most CRDS data acquisition systems are designed to send the data (in ASCII text format) to a PC equipped with a GPIB acquisition card. Often too, LabView<sup>TM</sup> software (National Instruments) is used for the control of the instruments and to perform calculations<sup>48</sup>.

The data acquisition system is comprised of the pressure reading from the pressure transducer and of the CRDS signal acquired with a digital oscilloscope (Tektronix -TDS3054B (9 bit resolution, 4 channels, 500 MHz acquisition rate)). In order to capture each laser beam round trip (approximately every 6 ns) in the CRDS cavity, the oscilloscope needs to acquire the signal data at a minimum DAQ rate of 160 MHz. This is achieved since the oscilloscope used for these experiments acquires data at 500 MHz. The oscilloscope is linked to a GPIB Data Acquisition Card (National Instruments) mounted in a PCI slot of a PC. The oscilloscope acquires the data in equivalent real-time and sends the signal to the GPIB card at a rate of 8 MB/s. The LabView<sup>TM</sup> interface is also used to operate the oscilloscope remotely as well as to apply mathematical operations to extract the ring-down times from the PMT signal.

The following settings are used on the oscilloscope and are set either automatically in the LabView<sup>TM</sup> rear panel diagram or by the experimenter through the interface front panel. 34

The design of the LabView<sup>TM</sup> front and rear panels for the treatment of the CRDS signal is presented is section 4.3. A summary of the important oscilloscope and DAQ settings are presented in Table 2.

	Value	Lint	
Sample Rate	500	MHz	Takes 2500 9 bit points in one sample (per ring-down
			time)
Acquisition Mode	Envelope		Takes the envelope of the CRDS signal sent from the
			PMT. There are 500 samples points (250 min and 250
			max) taken from the boundary of the <i>y(t)</i> modulated
			signal.
Sample Type	Min/Max		Setting that takes minima and maxima for envelope mode
Sample Channel	4		Oscilloscope channel that is used to acquire data
Trigger Channel	4		Sample from which the laser trigger input signal begins
			data sampling.
Trigger Type	Edge		Triggers at when the signal voltage first exceeds the
			voltage threshold set by the user.
Trigger Slope	Positive		Triggers data acquisition when the signal voltage exceeds
			the voltage threshold on the positive edge of the signal
Signal Coupling	DC		Couples AC and DC part of signal for y(t)
Input Impedance	50	Ω	So as to maintain the measurement time constant to the
			lowest possible value.
Vertical Range	200	mV	The voltage range set in the LabView <sup>TM</sup> VI for PMT light
			intensity signal.
Minimum Record	500	Pts	Minimum sample population size acquired by the
Length			oscilloscope
Number of	64		Number of ring-down times taken for the calculation of
Samples per Ring-			one concentration measurement.
Down Time			
Trigger Level	0.85*V <sub>max</sub>	V	The maximum voltage (V <sub>max</sub> ) is displayed on the Front
			Panel. This value corresponds to the voltage threshold
			used to trigger the data acquisition.
Probe	1.0	<u> </u>	No voltage probe needed since signal is in the 0.1-1.0 $ m V$
Attenuation			range.

## Table 2 - DAQ and Oscilloscope Settings for CRDS Operation

## 4.2 – Laser and Maintenance Considerations

The laser system is comprised of two parts: the pump laser and dye laser systems. The pump laser (Quantel Brilliant B10) is used to excite the liquid dye solution; meanwhile the dye laser (Quantel TDL90) provides the tuning range for the laser wavelength. Both are described below.

#### Pump Laser - Quantel Brilliant B

For the Brilliant B pump laser, the active medium used in pumping is a solid crystal of Nd/YAG (Neodymium: Yttrium – Aluminium – Garnet) excited with a Xe flash lamp. The laser pulses at 10 Hz, with a linewidth of  $0.8 \text{ cm}^{-1}$  and a pulse length of 5-6 ns. The light emitted from the pump laser is available at three different harmonic levels: 1064 nm (1<sup>st</sup> harmonic), 532 nm (2<sup>nd</sup> harmonic) and 355 nm (3<sup>rd</sup> harmonic). The corresponding maximum laser beam energies per pulse for each harmonic are the following: 800 mJ for the 1<sup>st</sup> harmonic (6ns pulse duration), 450 mJ for the 2<sup>nd</sup> harmonic (5 ns pulse duration) and 200 mJ for the 3<sup>rd</sup> harmonic (5ns pulse duration). The optical components used for these experiments are able to withstand such laser beam energies.

The actual harmonic used to excite a dye in the TDL90 depends on the tuning range of interest, which makes the dye fluoresce over a given wavelength range. The harmonics can be varied by shifting the direction of the beam inside the laser casing to the different harmonic crystals prior to experiments. The laser beam energy can be varied by manipulating the delay on the Q-Switch that triggers the Xe flashlamp between 465  $\mu$ s (lowest energy setting) and 265  $\mu$ s (highest energy setting).

### Dye Laser - Quantel TDL 90

The laser beam exiting the pump laser enters the second part of the laser system (Quantel TDL 90) which tunes the light to the desired wavelength for absorption (431.131 nm in the present study). The Brilliant B10/TDL 90 lasing system used for these experiments can be used over the 217–760 nm tuning range. With various additional attachments, the TDL90 could cover a range of 200 to 4500 nm.

The cell is placed in the middle of an optical cavity, with a partially reflective mirror on one side and a diffraction grating on the other<sup>49</sup>. The diffraction grating's angle is varied, as to enable the light to be diffracted to the desired wavelength for lasing. The actual wavelength is selected by rotating the diffraction grating with a step motor. The finest spectral displacement that can be used with the TDL90 is 0.001 nm.

The wavelength of the pumping source is selected such that it is smaller that the lower wavelength of the dye's emission range. The dye absorbs the pump laser beam energy, causing a population inversion, where electrons move to excited energy states. Once the pumping is complete, vibrational energy from the dye is lost and the dye molecules move from higher excited states to lower ones<sup>50</sup>, which cause the emission of light at the desired lasing wavelength. This process is repeated for every light pulse. A diagram depicting the absorption and emission of photons from the dye molecules is depicted below.



Figure 9 - Dye Excitation Process<sup>51</sup>

Figure 10 shows a series of tuning ranges for the Nd:YAG pumped TDL90 dye laser. Each tuning range is produced using a different dye. Coumarin 440 (Exciton Corporation) is the dye used for tuning at 431.131nm, since the dye emits in the 423 to 462 nm wavelength range and has its peak in energy output near the desired wavelength. The dye is diluted in an organic solvent (ethanol for Coumarin 440), and fluoresces when excited by light pulses generated at the third harmonic (355 nm) of the Brilliant B pump laser. The light pulses from the Brilliant B are split into two parts, the oscillator and amplifier dye circuits, using a beam-splitter in the TDL 90. Each circuit uses a specific dye concentration that is specified by Quantel for maximum dye operating life.

## Nd: YAG PUMPED LASER DYES (Continuum)<sup>53</sup>



Figure 10 - Dye Tuning Curve for Nd:YAG Laser<sup>52</sup>

A pump system circulates the dye for each circuit to cuvettes that expose the dye to the pumping light pulses. Both the amplifier and oscillator optical paths should produce a laser beam with a uniform cross section. This can be determined using a photothermal Kodak paper placed at the output of the laser. A sample of the desired laser beam cross section is available in Figure 11.



Figure 11 - Sample Beam Profiles

The aging of the dye/solvent solution leads to a loss of the optical emission from the TDL90. In fact, Quantel recommends replacing the dye solution once the energy of the beam leaving the TDL has gone under 40  $\mu$ J for a Q-switch delay of 265  $\mu$ s, which value corresponds to the maximum pump energy. The used solution is discarded in the chemical waste disposal receptacle in the lab. The dye laser circulation system must be cleaned before

a new batch of dye is introduced. The laser cleaning and dye preparation procedures are outlined in section 4.5.

### Absorption Wavelength Scan

Before CRDS experiments are done, it is important to find the optimal wavelength for absorption measurements. The scanning was done over the 429-432 nm range, since it is known that a peak in the molecular absorption spectrum of the CH molecule is located around 431 nm. The procedure for the scan is available in section 4.5.8.

### CRDS Mirror Maintenance

The CRDS mirrors need to be cleaned approximately every 10 days during steady operation. The mirrors may also need to be cleaned when there is a decrease in empty cavity ring-down times to 2.0  $\mu$ s from 2.8  $\mu$ s (approximate value when mirrors are clean). The low-pressure Ar/C<sub>2</sub>H<sub>2</sub> DC glow discharge system produces many organic bi-products that can coat the mirrors and reduce the reflectivity. The experimental procedure in section 4.5.4 should be followed in order to avoid damaging the mirrors or system. After cleaning the mirrors, a complete re-alignment of the CRDS cavity is required.

### <u>Class IV Laser Safety<sup>53</sup></u>

A Class IV laser (high power) is used for these experiments. Safety precautions need to be taken in the laboratory setting since the direct exposure to the laser beam or even to diffuse reflections of the laser beam can cause serious damage to the eyes and skin. All laser operation was done using protective glasses as well as protective shielding around the optical table and work area, which prevent stray reflections from exiting the setup. Once all safety precautions are taken, it is important to measure the energy at the output of the pump laser (entry of dye laser optical system) once every 6 months as to ensure that the lasing conditions remain the same. The energy at the output of the pump laser should read 200 mJ at a Q-Switch delay of 265  $\mu$ s for the third harmonic. The energy level reading is done using a Joulemeter (Gentec Corporation-Solo with QE25 head) The Joulemeter should also be placed at a 5 degree angle to the beam as to prevent backscattering of the light into the

pump laser. Once this is done, the pump laser is ready for use in conjunction with the TDL90. More detailed laser safety considerations are presented in Appendix 2.

## 4.3 – Treatment of the CRDS Signals

The LabView<sup>TM</sup> front-panel interface was designed to accommodate user friendly operation by letting the experimenter set certain oscilloscope parameters for DAQ on the interface front-panel, while some parameters are automatically set in the diagram. A diagram of the interface front-panel is depicted in Figure 12, which breaks down the interface into 6 important sections.



Figure 12 - LabView<sup>TM</sup> Front-Panel Interface for the CRDS System

Each important section of the CRDS Front-Panel Interface is outlined with a dashed line and is described as follows:

## (1) Oscilloscope DAQ Settings

- <u>VISA Session</u>: Identifies the instrument used to acquire the data, should be set to the GPIB2 setting.
- <u>dup VISA Session</u>: Identifies the duplicate VISA session, should be set to the GPIB setting.
- <u>Acquisition Channel Source</u>: Sets the channel on the oscilloscope at which the experimental points are acquired, set to Channel 4.
- <u>Trigger Source</u>: Sets the channel to which the signal acquisition is triggered. This value should be the same as the Acquisition Channel Source (Channel 4).
- <u>Number of Ring-Down Values per Sample</u>: Total number of ring-down curve time constants that are averaged per sample. Set to 64 to minimize the laser shot to shot noise.
- <u>Number of Samples</u>: The number of average ring-down time values that are needed to calculate one concentration value, with a default value is 16.
- <u>Trigger Level</u>: The voltage level on the oscilloscope at which the signal is acquired. It is important to set this to 85% of the maximum value on the oscilloscope. This value can be determined by taking a "max voltage" measurement on the oscilloscope of a ring-down signal before data is acquired.
- <u>Time per Record</u>: This value corresponds to the time span displayed on the oscilloscope display. It is usually set to 4 µs or 10 µs. It is also important to look at the signal prior to the acquisition of data to determine best the time frame needed for full exponential decay.

### (2) Oscilloscope Screen Output

This screen displays the signal being acquired from the oscilloscope in equivalent time. It is important to monitor this signal to ensure that there are no signal discrepancies due to power supply noises (glitches).

### (3) DAQ Signal Information and Error Reporting

This part of the interface outputs important information that will let the user know if the experimental data is being acquired properly and if there are any errors in the model or averaging.

- <u>Actual Record Length</u>: Displays the number of points taken per signal envelope for a ring-down time calculation.
- <u>Sample Mode</u>: Indicates the mode at which the oscilloscope acquires the data. It can do so in two ways:
  - (1) Real Time sampling (value of 0 on the interface)
  - (2) Equivalent Time sampling (value of 1 on the interface), which sends the information in packets to the computer with real-time equivalency.
- <u>Sample Rate</u>: The rate at which the oscilloscope samples data points, with units in MS (million of samples per second).
- <u>Averaging Error</u>: Returns an error message code if there is an error during the averaging of ring-down times. The default value for error free operation is 0.
- <u>Fitting Error</u>: Returns an error message code if there is an error during the fitting on the signal envelope. It is also important for the experimenter to look at the "Positive Damping?" indicator below the scope output. The light will turn on if there is an error in the model fitting.

- <u>Max Voltage</u>: Displays the maximum voltage of the envelope of the ring-down curve. This is useful when determining a trigger value for the next set of ring-down times.
- <u>Ring-Down Time</u>: Displays ring-down times during data acquisition. Lets the user monitor ring-down time values during operation.

## (4) Error Debugging Window

When an error message appears in the Fitting Error or Averaging Error indicators, this control lets the user determine the error type and source. The error debugging window has three components:

- <u>Status</u>: If a checkmark is displayed, then the VI is error free. If an X is displayed, an error has occurred and the VI must be repaired.
- <u>Code</u>: This input identifies the error.
- <u>Source</u>: Describes the origin of the error, use the Error Explain window to get more details about the error type and how to debug it.

## (5) <u>Pressure Gauge Output</u>

This section of the interface lets the user monitor the reactor pressure during data acquisition. The units used during pressure readings are in Torrs.

## (6) File Saving and DAQ Alert

This section enables the user to save the experimental data in a variety of forms. It is important to indicate where the data is to be saved before operation. Also, this part of the interface displays LED error indicators if an error in the model has occurred as well as when the interface is done acquiring data.

• <u>Ring-Down Time</u>: Saves the averaged ring-down times calculated by the model in a format compatible with MS-Excel<sup>TM</sup>.

- <u>All Ring-Down Times</u>: Saves all the ring-down times (before averaging is done) calculated by the model.
- <u>Raw Data</u>: Saves all the experimental data points acquired by the oscilloscope for each ring-down curve.
- <u>Positive Damping</u>: This indicator is used to let the experimenter know if there is a model error. When the LED turns on, the user knows that the curve was not fit to an exponential decay and operation should be terminated.
- <u>DAQ Complete</u>: This indicator lets the experimenter know when the data acquisition is complete.

The signal is treated using a series of operations in a programming diagram interface that is linked to the front-panel, which is where the virtual programming is done. The virtual interface (VI) converts the signal to digital form and the data is treated mathematically to extract a value for the ring-down time ( $\tau$ ). A picture of the CRDS programming diagram is presented in Figure 13.



Figure 13 - CRDS Interface Design Diagram

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The CRDS LabView<sup>TM</sup> interface is comprised of the 5 main sections outlined and numbered in Figure 13. These sections all have an important role in determining how the data is acquired and treated. A description the functionality of each section is described in the section below.

### (1) Pressure Measurement and Data Treatment



Figure 14 - Pressure Measurement Interface Section

- The Interface delay sub-VI waits until the millisecond timer is a multiple of the delay to execute the While Loop.
- The A In sub-VI is used to set the acquisition parameters for the pressure measurements. The DAQ board should be set to 1, with a board channel of 12 and an acquisition voltage range of ±10 V. This sub-VI acquires analog data points and sends these values to the To Eng sub-VI.
- The To Eng sub-VI converts the analog units to engineering units.
- The signal is fitted using the manufacturer's calibration curve to output the correct pressure measurement.
- The pressure measurement is dynamically outputted to the interface where its value can be monitored.

(2) DAQ Settings on Interface for Oscilloscope and Data Treatment



Figure 15 - DAQ User Defined Settings Interface Section Diagram

Pre-determined settings that experimenter sets on interface to run a measurement. These data values help determine how the oscilloscope acquires the data for mathematical treatment. Settings on the interface also permit to determine how many sample and averages are done to calculate the ring-down time  $(\tau)$ .

## (3) <u>LabView<sup>TM</sup> VIs for Oscilloscope Data Handling</u>

Oscilloscope VIs were added in from a virtual interface built by Tektronix that allows the TDS 3054B to connect to LabView. The interface can output commands set by the user to the oscilloscope. A diagram of the section and a description of each sub-VI is available below:



Figure 16 - LabView<sup>TM</sup> VIs Used for Oscilloscope Data Handling Interface Section

The Configure Acquisition Type sub-VI determines whether the oscilloscope acquires data in Sample, Peak Detect, Envelope or Average acquisition modes. This sub-VI is set to Envelope mode, which takes 250 minimum and maximum data points used to determine the envelope of the ring-down signal.

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waveform. A value of 16 is set in the interface diagram as to take 16 sets of minimum and maximum points per waveform.

The Configure Channel sub-VI establishes the channel and properties for data acquisition. These features include:

- Probe Attenuation of 1.00 (no voltage or current probe required for signal acquisition).
- Vertical Range (y axis range of waveform set in volts) set in the diagram to 200 mV, which covers the range needed for signal acquisition from the PMT.
- Vertical Offset is set to 0 V in the interface since there is no bias from the PMT signal acquired.
- *Channel Name* appears as *Acquisition Channel* on the interface and is set by the user to Channel 4. This sends acquisition parameters to the oscilloscope so that the signal can be acquired properly.
- Vertical Coupling is set to the DC setting since the signal being acquired is in DC form.

• The *Channel Enabled* sub-VI parameter is set by the user on the interface. A value of "true", indicated by a green light on the LED control on the interface, should be set if data acquisition is desired.

The Trigger Modifier sub-VI configures the trigger to a value of either Auto or No Modifier. The No Modifier is selected in the interface as to have the user determine the trigger level and settings for signal acquisition.

The Configure Channel Characteristics sub-VI is used to set the oscilloscope electrical characteristics. Since the acquisition signal is in mV and is weak, the Input Impedance is set to a resistance  $50\Omega$  as to match the impedance of the signal to that of the circuit. Also, the Max Input Frequency is set to 300E+6/500E+6, which is the maximum value for data acquisition by the oscilloscope.

This sub-VI, *Configure Acquisition Record*, enables the user to configure basic acquisition parameters. These parameters include:

- Minimum Record Length is set to 500 samples in the diagram, since the acquisition mode is envelope.
- Acquisition Start Time is set to a value of 0 in the diagram, since acquisition must start once the interface run button is pressed.
- *Time per Record* is set by the user on the interface, which is dependant on the oscilloscope signal prior to turning on the interface. It is important that the user look at the time frame in which a full decay occurs.

The Sample Mode sub-VI lets the user know whether the oscilloscope is sampling in Real-Time or in Real-Time Equivalent. This value is presented on the interface front-panel.

This sub-VI, *Sample Rate*, calculates the time frame ( $\mu$ s) at which data points are acquired and this value is used to determine the x-axis (time) boundary conditions for the decaying exponential curve fitting. Its value is outputted to an indicator on the front-panel interface as to enable the user to monitor the proper acquisition rate. The value for the acquisition time frame is sent to the mathematical curve fitting segment of the interface, where it is used to extract the ring-down time from the signal envelope.

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TNYDSA

RTDS3

TKTDSBK



TXTDS3K

THTOSER

The Configure Trigger sub-VI sets the parameters for the trigger used in signal acquisition. The trigger type set is Edge in the diagram since the acquisition will be triggered when the trigger value surpasses the voltage threshold specified by the user.

Configure Trigger Coupling is a sub-VI used to couple the trigger with the same value (DC setting) as the Vertical Coupling in the Configure Channel sub-VI. This ensures that the vertical component (y-axis) of the signal is acquired when the trigger passes the set vertical DC voltage threshold.

The Configure Edge Trigger sub-VI is used in conjunction with the Edge trigger setting in the Configure Trigger sub-VI. The settings used are as follows:

- *Trigger Source* is the channel specified by the user on the front-panel for triggering data acquisition.
- Trigger Slope is set to Positive on the diagram since the trigger should be done on the initial segment of the signal that is increasing as to ensure that the interface acquires the initial light intensity change.
- Trigger Level is set the trigger voltage value by the user on the front-panel.



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This sub-VI, Record Length, takes a measurement of the waveform length and its value is outputted on the front-panel as Actual Record Length. Its value is also used in the curve fitting section of the interface diagram to determine the time increments used in the exponential decay model.

The *Read Min Max Waveform* is used to extract the maximum points, initial X values and increments of X of the signal envelope that is then sent to a bundling array sub-VI. The parameters used to operate this sub-VI are the following:

- Source is the channel set by the user for acquiring the signal envelope.
- Waveform Size is set to the waveform value calculated in the Record Length sub-VI.

### (4) Storage of Data and Mathematical Data Treatment



Figure 17 - Mathematical Operation Diagram Section

Figure 17 depicts the Mathematical Operations Section of the interface. The signal envelope is sent to a series of LabView<sup>TM</sup> VIs that perform a decaying exponential curve fitting that extracts the ring-down time from the signal. The ring-down time is measured by performing the following mathematical operations:

- a) Extract maximum value of the sample population (250 points).
- b) Normalize the signal  $(I(t)/I_{max})$ , since the data will be fit according to Beer-Lambert's Law.
- c) Data is sent to a VI that performs a decaying exponential curve fitting to the signal envelope  $(y(t)=A^*exp(-t/\tau))$ , where A=Amplitude and

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 $\tau = \text{decay time} = -1/\tau$ ). <sup>54</sup>

- d) After the curve fitting, the absolute value of the decay time is taken and is then inverted to give the ring-down time for the set of data points.
- e) The ring-down times are recorded in array form, which are then averaged using a matrix multiplication sub-VI in the interface.
- f) Once the ring-down times are averaged, they are indexed and put in an array form.
- g) The array is then transposed and saved in MS-Excel<sup>TM</sup> form. The user can determine the path for saving the ring-down times on the front-panel interface.

A detailed description of the mathematical operations performed on the ring-down signal is depicted below.

- (1) From the  $\frac{1}{1}$  array bundling sub-VI, the data points are split along two paths:
  - The first path takes the data to be used for normalizing the transmitted light intensity  $(I_t(t))$  to the initial light intensity  $(I_0)$ .

• The second path takes the data to a sub-VI, the Array Max/Min Array  $(\square)$  that extracts the minimum and maximum points from a set of data. The maximum value is used as the  $I_{max}$  value for the  $I(t)/I_{max}$ . Meanwhile, the minimum value is used to give a baseline point measurement.

- Since the baseline point might have a negative value, absolute value is taken and added to all data points. This adds a bias to the data so that they have a positive value, which is a requirement for error free curve fitting.
- The biased points are then multiplied by 0.01 as to ensure a non-zero value before normalizing, which is another requirement for curve fitting. The non-zero and positive bias points are added to the maximum point  $(I_0)$  as well as all other data points  $(I_1(t))$  prior to normalization.
- The data points are then normalized using the maximum voltage point on the signal envelope.
- The normalized data points are sent to an exponential decay curve fitting sub-VI (

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exponential coefficients, amplitude and damping, that fits the experimental data  $(I_t(t) \text{ vs. } t)$  to a y(x) vs. x curve.

- In order to fit data properly, the array used for time values (x axis values) has to be of the same size as the I<sub>i</sub>(t) (y axis values).
- Termination of the array formation takes place when the array size is equal to that of the number of y(x) data points.
- Once the data set is fit, the curve fitting sub-VI outputs a time constant (τ=large negative value), who's absolute value is taken is then split into two paths:
  - The first path, then inverts the time constant to give the ringdown time, which is outputted to an indicator on the front-panel.
  - The second path sends the time constants to be indexed into an array, and then the array of ring-down times is sent to be averaged. This produces one averaged ring-down time per 64 samples taken.
  - An error message appears if there is positive damping, which is a value indicating an error in the signal acquisition (when signal envelope does not follow decaying exponential trend). A LED indicator will be lit and the experimenter should stop CRDS operation.
- Once the ring-down times have been indexed in array format, the data enters the second *while* loop and is further indexed to include all ring-down times.
- Another *while* loop is indexed in the second *while* loop. This loop produces a unity matrix (1 x number of samples) used for averaging all the ring-down times sampled.
- The data exiting the mathematical treatment to the Data Averaging and Saving in MS-Excel<sup>TM</sup> diagram section is a 64 x 16 (64 ring-down times x 16 samples) matrix.

### (5) Averaging of Ring-Down Time and Storage of Data

The outer loop array of ring-down times (set to 16 sets of averages on the front panel interface) is averaged into one set of sample values. The signal envelope raw data, all ring-down and averaged ring-down times are stored in an MS-Excel<sup>TM</sup> spreadsheet.

- The A x Vector sub-VI performs the multiplication of an input matrix to an input vector. In this case, the "all sample ring-down times" array is multiplied to a 1 x 64 unity matrix (vector). This sums up all the ring-down times (set on the front panel interface to 64 values per average) before averaging.
- This produces a 1 x 16 matrix that is then divided by the number of ringdown times per concentration measurement, which completes the averaging of ring-down times.
- The Write to Spreadsheet sub-VI is used three times to save the averaged ring-down time, signal envelope raw data and all ring-down time samples matrices in MS-Excel<sup>TM</sup> format. The user defines the location for saving the data.

## 4.4– Process Parameters

In the previous parts of this chapter, several parameters for the operation of the CRDS experimental setup were discussed. In order to make CH radical concentration measurements, several parameters and practices need to be applied when operating the LabView<sup>TM</sup> interface, the laser remote control, CRDS reactor and the high-voltage power supply. A description of experimental and equipment maintenance procedures is presented in section 4.5 and in the Appendix. The values used for the operating parameters are resumed in Table 3.

Oscilloscope Sampling Rate	500	MHz
Oscilloscope Acquisition Mode	Envelope	250 max pts per sample
Number of Ring-Down Times per Sample	64	
Total Sample Count	16	
Time per Measurement	5	min
Total Experiment Time	10	min
Reactor Pressure	0.5 (66.7)	Torr (Pa)
Power Supply Voltage	700	V
Decade Box Resistance	5000	Ohms
Gas Flowrate	75-85	sccm
Composition of Gas	95% Ar and 5% C <sub>2</sub> H <sub>2</sub>	Mole Percent
Laser Pulse Duration	5	Ns
Laser Beam Energy at Cavity Entry	30-40	μJ
Laser Linewidth	0.8	cm <sup>-1</sup>
Laser Pulse Frequency	10	Hz
Laser Dye Used	Coumarin 440	420 nm to 440 nm

Table 3 - CRDS Experimental Setup Operating Parameters

## 4.5 – Experimental Procedures

## 4.5.1 - Laser Cleaning

- Remove the oscillator and amplifier dye bottles from the pump of the laser and replace them with empty bottles (ensure that both intake and flushing hoses do not touch any surfaces and are placed in empty bottles).
- (2) Pour out the used dyes in the laboratory liquid waste receptacles.
- (3) Fill the oscillator and amplifier dye bottles half way with ethanol (solvent), rinse out into waste receptacle.

- (4) Fill up both bottles <sup>3</sup>/<sub>4</sub> of the way with ethanol and remove the empty bottles, with the intake hose (left hand side) in the bottle and the flushing hose in the empty bottle.
- (5) Turn on the oscillator pump and flush out the old dye. It is important to wait until all the old dye is completely removed (the dye line will go from a dull yellow to a clear fluid once it is all out). Turn off TDL 90 pump. Repeat above procedure for the amplifier circuit.
- (6) Empty all dye bottles of ethanol or old dye and replace them on the oscillator and amplifier dye cells. Once this is done, the laser will be ready for new dye.

### 4.5.2 - Dye Preparation<sup>55</sup>

- Decant 0.5 L 100% anhydrous ethanol into a 2L glass container with a lid covered in aluminium foil as to prevent contamination from glues or plastic in solvent.
- (2) Remove dye and oxygen quencher from the fridge and weigh 0.219<sup>56</sup> g of each compound using a high precision scale.
- (3) Place the beaker and solvent on a hot plate (do not heat the solution at all) and add place a stir bar in the beaker. Make sure to do this in a fumehood.
- (4) Turn on the stirring mechanism on the hot plate at medium stir; slowly begin placing dye and oxygen quencher into solvent.
- (5) Once all the solids are in the solution, place the lid on the container and stir for 24 hrs. It is important that all solids are dissolved.
- (6) Once the mother solution is diluted,
- (7) Place 200 mL of mother solution in the oscillator dye bottle and another 70 mL into the amplifier dye bottle. Followed by 600 mL of ethanol in the oscillator bottle and 730 mL of ethanol in the amplifier bottle.
- (8) Place bottles in the pump casing and turn on the pump. Let the pump run for an hour as to ensure that all solids are dissolved. Tests using the laser can now begin.

### 4.5.3 - Laser Preliminary Tests

- 1) Turn on the TDL 90 and Brilliant B laser systems, while ensuring that the dye pumps are on and that the dye is flowing in the TDL 90 (listening for flowing noises or air bubbles in the tubing).
- 2) The lasers should take approximately 30 min to warm up. Once the green light is activated on the TDL90, turn on the Q-Switch delay to 465 µs and turn on the Q-Switch and Flashlamp using the remote control.
- 3) Using the "single shot" feature on the laser remote control, place a piece of Kodak paper at the laser beam exit and perform a laser shot on the paper surface.
- 4) Then increase the laser beam energy by decreasing the Q-Switch delay by 10 μs increments from 465 μs until the Kodak paper begins to burn.
- Continue to decrease the Q-Switch delay but by 5 μs until there is a uniform beam profile on the Kodak paper.
- 6) Then measure the laser beam energy using the Joulemeter and take note of the energy measurement.
- 7) Also measure the laser beam energy at the entry of the CRDS cavity and take a note.
- 8) The laser is now ready for CRDS measurements.

### 4.5.4 - Cleaning Procedure for CRDS Mirrors

- Release pressure in CRDS reactor by closing the vacuum pump valve and slowly unscrewing the nut for the gas intake on the manifold (gradually letting air leak in to the reactor).
- (2) Remove gas line connections from both flanges that connect the mirrors to the reactor.
- (3) Disconnect the NW40 connections from reactor to the flange from the part holding the mirror. Place both parts on a clean and dust free workbench.
- (4) Remove the flange screws from the Del-Seal 1.5 inch (3.8 cm) diameter flange connecting the mirror holder to the NW40 flange (connection to main reactor apparatus).

- (5) Remove the screws holding the mirror holder in place and then remove the part which holds the mirror onto the flange.
- (6) Put on dust-free gloves.
- (7) Remove the mirror from the flange with care and place it on the lens Teflon cleaning mount (Los Gatos Research Inc.).
- (8) Remove all dust on the mirror surface by blowing air on it using the rubber cleaning bulb.
- (9) Place a piece of optical tissue on the surface of the mirror.
- (10) Add 4 drops of spectroscopy grade methanol to the surface.
- (11) Let the drops sit on the surface for approximately 30 seconds.Wipe mirrors in a clockwise fashion until all the methanol has been evaporated or wiped off.
- (12) Repeat steps (8) through (10). If there is any remaining dirt on the mirror surface, you may need to add more methanol and wipe the mirror down for a longer period of time.
- (13) Make sure there are no streaks from the methanol, if so wipe down the mirror thoroughly until all marks are removed.
- (14) Place the mirror back on the flange with the protective ring in place. It is important to place the mirror with the arrow (on the side of mirror which indicates the reflective side) facing the interior of the reactor.
- (15) It is important to re-connect only the back end mirror holder to the reactor, while connecting the quartz NW40 flange window on the front end side of the reactor.
- (16) Re-screw the holder and window reactor to the NW40 flange attachments on both ends of the reactor.
- Reconnect the gas line intakes to the mirror holder assembly.
   Turn on argon gas to a setting of 20 with the black ball on the rotameter, which corresponds to a flowrate of approximately 50 sccm.
- (18) Slowly turn on the vacuum pump on the reactor.
- (19) You must now re-align the CRDS for operation.

### 4.5.5 - CRDS Mirror Optical Alignment Procedure

- (1) Turn on the lasers and dye pumps 30 minutes prior to operation.
- (2) Once the lasers are warmed up, set the Q-Switch delay to the last recorded value prior to mirror cleaning.
- (3) Turn on the laser and ensure that there is enough light intensity from the laser beam such that a spot of light can be seen when a piece of paper is placed in front of the beam.
- (4) Carefully look onto the Glaxon Pyrex viewport replacing the front-end CRDS mirror holder.
  - i. If there is a second spot of light on the glass, other than the one entering the cavity at the centreline, this is the reflection from the back-end mirror.
  - ii. If there is no second spot, then the back end mirror is reflecting the beam on the cavity walls. Using the three point adjustment screws on the mirror holder, adjust one screw at a time until a second spot can be seen on the viewport.
- (5) Holding a piece of paper along the viewport at the location of the second spot on the glass, adjust the three point mirror holders as to align the second spot with the incident beam of light entering the centreline of the cavity.
- (6) Turn off the laser and close the valve to the vacuum pump.
- (7) Release the Swagelok fitting on the manifold valve and slowly release the pressure till it reaches atmospheric.
- (8) Remove the NW40 quartz viewport from the front end flange and replace it with the second CRDS mirror holder.
- (9) Reconnect the gas lines to the mirror holder and close the valve connecting the manifold to the reactor. Reconnect the Swagelok fitting connecting the manifold valve to the gas tank. Turn on the pump and open the valve. Evacuate the reactor to the base pressure of 0.01 Torr (1.3 Pa).
- (10) Turn on the laser and set the Q-Switch delay such that the laser beam energy is approximately 60 µJ.
- (11) Using the oscilloscope, resolve the vertical and horizontal resolutions in order to see the initial light pulse that enters that cavity.

- (12) Using the three-point adjustment dials on the second CRDS mirror, turn them such that additional pulses appear on the oscilloscope signal. The pulses will form a tail with decreasing pulse amplitude.
- (13) By maintaining a close eye on the oscilloscope signal, continue to turn the dials until the signal reaches an approximate ring-down time value of 2.8 µs.
- (14) Once the desired ring-down time signal is attained, turn off the laser and secure the bolts on the mirror holder as to maintain the current alignment.

## 4.5.6 - Laser Start-Up

Thirty minutes prior to experimentation, the laser dye pumps and TDL 90 and Brilliant B lasers should be turned on so they can warm up. The following steps are to be done prior to CRDS operation:

- (1) Turn on the power to the electrical panel and turn on laser warning light.
- (2) Place all safety laser panels around CRDS unit and laser table.
- (3) Set the Q-Switch delay time to minimum energy (465  $\mu$ s).
- (4) Open the amplifier laser beam dump inside the TDL 90 box.
- (5) Set Q-Switch to "Ready" on the Brilliant B operating pad.Set the Joulemeter to measure the laser energy at the exit of the TDL 90.
- (6) Turn on the Flash Lamp by pressing "Start" on the pad.
- (7) Fire the laser in single shot mode, record energy level.
- Set the laser to operate in the continuous mode to monitor energy over time.
   Repeat at decreasing Q-Switch delays until a beam of desired intensity is found.
- (9) Take energy measurements before and after the irises and pinhole.
- (10) Ensure that beam energy entering the CRDS cavity is approximately  $40 \mu$ J.
- (11) Make sure the CRDS signal is triggering the data acquisition on the oscilloscope.
- (12) Once the desired energy is obtained and that CRDS interface is ready for operation. Set laser to "Ready Mode" and begin the glow discharge start-up.

## 4.5.7 - Ar and Ar/ C2H2 Glow Discharge Start-up

This procedure should be done ten minutes prior to experimentation.

- (1) Open the LabView<sup>TM</sup> interface that controls the CRDS operation.
- (2) Open pump exhaust valve and turn on Ar tank and feed the gas to the reactor. Also adjust all regulator pressures to 10 psig (68.9 Pa).
- (3) Set the mass flow rate to 75 sccm on the rotameter. Monitor the reactor pressure on both the vacuum pressure transducer so that it read between 0.5 and 0.55 Torr (66.7 and 73.3 Pa).
- (4) Ensure that all electrical connections are in place and that the settings on the high voltage power supply are at a null value.
- (5) Turn on the power on the power supply and wait for the standby light to turn off. Ignite the plasma by gradually increasing the voltage level.
- (6) Once the plasma is ignited, verify that all parameters are stable.
- (7) Set desired settings on the LabView<sup>TM</sup> interface for the DAQ.
- (8) Turn on the laser to continuous mode and begin CRDS measurements with pure Ar.
- (9) Do triplicates of each run while monitoring the laser energy and correcting the Q-Switch delay to ensure the light energy entering the cavity remains in the 30-40 μJ range.
- (10) Acquire data as a background for the CRDS ring-down time which will correspond to non-absorption related cavity losses.
- (11) Turn off laser and power to plasma and evacuate the reactor for 10 min.
- (12) Switch the gas line to  $Ar/C_2H_2$  and set to 75 sccm and monitor pressure such that it reads approximately 0.5 Torr (66.7 Pa).
- (13) Turn on laser to continuous and repeat steps (3) to (11).
- (14) Acquire data for the CRDS ring-down time which will correspond to absorption related cavity losses.
- (15) Press "stop" on the LabView<sup>TM</sup> interface.
- (16) Turn off the power on the discharge and turn the laser off.
- (17) Close the gas regulators and wait for them to read a zero pressure value.
- (18) Once the gas regulators reach a zero value, evacuate the reactor and gas lines for 20 min.

### 4.5.8 - Laser Scan to Find Optimal Absorption Wavelength for CH

- (1) Follow steps 1 to 13 of section 4.5.7 for DC glow discharge operation.
- (2) Set the laser energy to 30 μJ and momentarily turn off the laser. Turn on the CRDS LabView<sup>TM</sup> interface. Prepare the interface for data acquisition.
- (3) On the TDL90 RS232 remote control, set the scan rate by going to GOTO on the menu and setting the scan rate to 2 pm/s and the initial wavelength to 429 nm and the final one to 432 nm. The scan will take 1500 seconds and the total number of ring-down times will be 15,000 (10 ring-down times taken per second).
- (4) Turn on the laser and set the trigger on the LabView<sup>TM</sup> interface to 30 mV.
- (5) Press the G button on the laser remote control box, this will begin the scan.
- (6) Once the scan is complete, a set of 10 ring-down times per wavelength (2 pm resolution) will be available. Look for the wavelength with the lowest ring-down times; this will point to the wavelength where the maximum absorption occurs.

# Chapter 5 – Results and Discussion

## 5.1 – Optical Emission Spectroscopy Measurements

Preliminary measurement of CH radicals in the 95% Ar and 5%  $C_2H_2$  low pressure DC glow discharge were done using optical emission spectroscopy (OES). These measurements were performed as to determine the conditions at which there was a maximum concentration of CH radicals produced. This method is a simple and quick way to determine these conditions, while it is not intrusive. The emission spectra of the pure Ar and  $Ar/C_2H_2$  glow discharges were taken using USB-2000 UV-VIS spectrometer (Ocean Optics) using an integration time of 300 ms, while averaging two spectra per sample.

Additionally, the spectra of both plasma mixtures will provide the experimenter with an indication as to what ions, molecules or atoms are present in the glow discharge. This is important in confirming the reaction pathway that is assumed to produce CH radicals in the 95% Ar and 5%  $C_2H_2$  low pressure DC glow discharge plasma. Spectral emission lines or bands associated with ions, atoms or molecules involved in the decomposition reaction of  $C_2H_2$  are identified in Table 4.

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Ar <sup>57</sup>	420	1
Ar	696	2
Ar	706	3
Ar	738	4
Ar	750	5
Ar	763	6
Ar	772	7
Ar	795	8
Ar	800	9
Ar	810	10
Ar	826	11
Ar	840	12
C <sup>58</sup>	505	13
CH <sup>59</sup>	431	14
$C_{2}^{60}$	516	15
H <sup>61</sup>	656	16
Ar <sup>+62</sup>	428	17
Ar <sup>+</sup>	435	18
Ar <sup>+</sup>	458	19
Ar <sup>+</sup>	476	20
Ar <sup>+</sup>	488	21

\*These numbers help identify emission lines outlined in Table 4 with those in Figure 18. Table 4 – Important Emission Lines for Species Participating in the Ar/C<sub>2</sub>H<sub>2</sub> Decomposition Reaction

The emission spectrum of the  $Ar/C_2H_2$  low-pressure DC glow discharge, with important spectral features, is outlined in Figure 18.



Figure 18 - Emission Spectrum of an Ar/C<sub>2</sub>H<sub>2</sub> (95%/5%) Low Pressure DC Glow Discharge

The emission spectrum of the  $Ar/C_2H_2$  low-pressure DC glow discharge was a reference point in confirming the production of CH from the decomposition of acetylene. The emission lines associated with the ionization of Ar into Ar<sup>+</sup> confirm, via lines **17-21** in Figure 18, that the ion responsible for the decomposition of  $C_2H_2$  was present in the plasma. From the reaction pathway for CH formation outlined in section 2.2, the Ar<sup>+</sup> decomposes  $C_2H_2$  into  $C_2H$  and subsequently to CH and C or  $C_2$  and H. The reaction products of the  $C_2H$  breakdown were identified in the OES spectrum (Fig. 18) by emission lines **13** (C), **14** (CH), **15** (C<sub>2</sub>) and **16** (H). The presence of these species in the OES spectrum confirms that there was a net production of CH in the Ar/C<sub>2</sub>H<sub>2</sub> low-pressure DC glow discharge.

The ideal operating conditions for maximum CH emission (production) were determined by doing a comparison of the emission line intensities of Ar and  $Ar/C_2H_2$ 

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plasmas operating at pressures ranging from 0.3 to 0.7 Torr (40 to 93.3 Pa) and discharge voltages ranging from 500 to 700 V. By subtracting the pure Ar and 95% Ar - 5%  $C_2H_2$  glow discharge spectra, one can determine the optimal conditions at which CH was produced. Comparing the intensity of the emission peaks of the plasmas in the spectral region around 431 nm indicates whether there is a net production of CH. A comparison of the pure Ar and the Ar/C<sub>2</sub>H<sub>2</sub> glow discharge emission intensities, between 420 and 440 nm, is depicted below.



Figure 19 - Comparison of the Pure Ar and Ar/C2H2 Low-Pressure DC Glow Discharge Spectra

From the above figure, one can deduce that there was a net production of CH radicals when comparing the pure Ar and  $Ar/C_2H_2$  glow discharge spectra. Maximal CH production occurs at a pressure of 0.5 Torr (66.7 Pa) and at a discharge voltage of 700 V. Table 5 outlines the OES light intensity measurements from the  $Ar/C_2H_2$  glow discharge spectra using various operating parameters.

	Polesee(V)	Light Intensity (A.U.).
0.3 (40.0 Pa)	500.00	119.21
0.3 (40.0 Pa)	600.00	204.50
0.3 (40.0 Pa)	700.00	253.69
0.4 (53.3 Pa)	500.00	197.15
0.4 (53.3 Pa)	600.00	311.07
0.4 (53.3 Pa)	700.00	458.10
0.5 (66.7 Pa)	500.00	268.88
0.5 (66.7 Pa)	600.00	459.99
0.5 (66.7 Pa)	700.00	554.15*
0.6 (80.0 Pa)	500.00	290.38
0.6 (80.0 Pa)	600.00	487.93
0.7 (93.3 Pa)	500.00	316.65
0.7 (93.3 Pa)	600.00	534.32

\* Maximum CH production occurs at these conditions

Table 5 - Comparison of the CH (431.22 nm) emission line intensity at CH emission line

The operating conditions for maximum CH production were selected by choosing the intensity with the highest value. The OES spectrum (Fig. 19) also indicates that CH radical emission around 431 nm is significant. The wavelength  $\lambda = 431.131$  nm was used by Engeln *et al*<sup>63</sup> to probe the CH ground state population density. These conditions were selected for the CRDS study, which is presented in the next section.

### 5.2 – CH Concentration Measurements Using CRDS

After the OES was used to determine the conditions for optimal CH production, CRDS measurements of the CH absorption coefficient were performed at a reactor pressure of 0.5 Torr (66.7 Pa) and a plasma discharge voltage of 700 V. In order to determine the absorption coefficient for CH, two CRDS measurements were performed. The first one was done in pure Ar and the other in 95% Ar and 5%  $C_2H_2$ . A comparison between two typical ring-down curves obtained during experimentation is depicted below.



Figure 20 - Ring-Down Curve Comparison for Ar and Ar/C<sub>2</sub>H<sub>2</sub> at 700 V and 0.5 Torr (66.7 Pa)

Figure 20 illustrates that the 95% Ar and 5%  $C_2H_2$  ring-down curve decays faster than the curve obtained with the pure Ar glow discharge. It can be deduced that there are not only transmission losses in the Ar/ $C_2H_2$  glow discharge but also losses due to the absorption of radiation by CH radicals formed during the decomposition of  $C_2H_2$ . Since the pure Ar glow discharge only takes transmission losses into account, the difference between both ring-down curves determines the optical cavity losses associated with absorption by the CH molecules present in the cavity.
Triplicates of each experiment were performed to ensure reproducibility of the results. For each absorption coefficient measurement, 16 ring-down time samples<sup>64</sup> were averaged, with 64 ring-down times averaged per sample<sup>65</sup>. Sampling 64 ring-down times per sample helps reduce the noise associated with the variations in laser beam energy between each shot. Experimental measurements were taken over approximate 10 min period with 5 min increments per sample population. The experiment was not run for longer periods due to the formation of a deposited organic film on the live electrode surface that inhibited CH production after 15 min of operation. In addition to film formation, soot particles (amorphous carbon) were formed on the electrodes and walls of the reactor. Such soot could lead to a degradation of the mirrors' performance.

Additional ring-down times were taken for "cold" samples for both the Ar and  $Ar/C_2H_2$  gases. Cold samples were done without igniting the plasma, in an attempt to confirm whether the gas alone absorbs laser radiation. Table 6 summarizes all measurements performed.

Run1				
Time (asio)	t(as) - Ar Only	Standard Deviation (ps)	s(10) - 95% Ar and 5% C2142	Standard Deviation (sa)
0.00	2.51	0.03	1.00	0.02
5.00	2.54	0.03	1.18	0.05
10.00	2.51	0.02	1.27	0.02
Average	2.52	Average	1.15	
Cold	2.58	Cold	2.55	
Run2				
Time (min)	r(ps) - Ar Only	Standard Deviation (µs)	t(ps) - 95% Ar and 5% C2H2	Standard Deviations (m)
0.00	2.73	0.04	1.15	0.10
5.00	2.81	0.03	1.26	0.01
10.00	2.85	0.06	1.28	0.02
	2.80	Average	1.23	
Cold	2.69	Cold	2.54	
Run3				
Time (min)	t(µs) - Ar Only:	Standard Deviation (ps)	r(µs) - 95% Ar and 5% C2H2	, Standard Deviation (pr)
0.00	2.84	0.00	1.09	0.03
5.00	2.95	0.00	1.17	0.03
10.00	2.99	0.00	1.07	0.02
		Average		
Cold	2.87	Cold	2.58	

Table 6 - Experimental Results Obtained with Ar and  $Ar/C_2H_2$  Gas Mixtures With and Without the Glow Discharge Ignited.

As depicted above, the ring-down times for the  $Ar/C_2H_2$  glow discharge conditions decay faster than those obtained in pure Ar. The difference between the two ring-down times confirms that there are optical losses associated with the absorption of radiation by CH radicals. Also, the standard deviation of both the pure Ar and  $Ar/C_2H_2$  glow discharges are approximately two orders of magnitude lower than the measured value, indicating a good repeatability of the measurements.

Furthermore, there was no substantial difference between the ring-down times obtained under the "cold" gas conditions and the pure Ar plasma ring-down times, thus indicating that the background gas does not absorb radiation at 431.131nm. CH concentration measurements can be determined by computing the absorption coefficient using Equation 2.12. After manipulating Equation 2.12, by dividing the absorption coefficient by the absorption cross-section ( $\sigma=4.5e-16$  cm<sup>2</sup> at 431.131 nm)<sup>66</sup>, one can obtain the CH concentration (N=molecules/cm<sup>3</sup>) directly.

$$N = \frac{1}{\sigma(\lambda)c} \left(\frac{1}{\tau} - \frac{1}{\tau_0}\right)$$
 (5.1)

Once species concentrations are calculated, they need to be corrected to compensate for the linewidth of the absorption band which was larger than that of the beam of light used for CRDS. LIFBASE<sup>67</sup>, a database and spectral simulation program for diatomic molecules, was used to model the CH transition system  $(A^2\Delta \leftarrow X^2\Pi)$  in order to determine the linewidth of the absorption band at the experimental conditions. A CH species temperature of 373K was assumed in the model since a non-thermal plasma was used during experimentation. A robust value for temperature can be used in the model since the CH transition used does not have a high dependence on changes in temperature<sup>68</sup>. The results of the LIFBASE simulation, with a resolution of 10 cm<sup>-1</sup> (equivalent to approximately 0.02 nm) and set to a pressure of 0.5 Torr (66.7 Pa), are depicted in Figure 21. The resolution value was selected to a value different to that of the laser linewidth since the absorption lines of the CH transition could be resolved to one band.



Figure 21 - LIFBASE Simulation of the CH Absorption Line Profile at the Experimental Conditions Used for CRDS Measurements

Since the CH absorption linewidth associated with the  $A^2\Delta \leftarrow X^2\Pi$  transition has an approximate width of 42 cm<sup>-1</sup> and the laser beam covers only a linewidth of 0.8 cm<sup>-1</sup>, the CH absorption coefficient measurements would be underestimated by a factor of 53. This correction factor was multiplied by the initial concentration measurement to give a true value for the CH concentration. Results obtained from the CH absorption coefficient measurements are presented in Table 7.

Run1			
linel(ain)	stAr(ps)= rC2H2(ps)	Absorption Coef (cm-I)	Concentration CH (creation)
0	1.52	2.01E-05	2.35E+12
5	1.36	1.50E-05	1.76E+12
10	1.24	1.29E-05	1.51E+12
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Run2			
- Time (min) 💷	r As(µs) - c C2H2 (µs)	Absoption Coef (cm-1)	Concentration CIT (cm.362
0	1.59	1.69E-05	1.97E+12
5	1.54	1.45E-05	1.69E+12
10	1.58	1.44E-05	1.68E+12
	152	Exercise Average	
Run3			
Time (min)	τ <b>Ατ(μ</b> ε) - τ C2H2 (με)	Absoption Coef (cm-1)	Concentration OH (cm 3)
0	1.75	1.89E-05	2.20E+12
5	1.78	1.72E-05	2.01E+12
10	1.91	1.99E-05	2.32E+12
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#### Table 7 - Summary of CH Absorption Coefficient and Concentration Measurements

For CRDS experiments with laser beam energies of 30-40  $\mu$ J, experimental results indicate that during 10 minute experimental runs, averaged CH concentration measurements ranged between  $1.78 \times 10^{12}$  cm<sup>-3</sup> and  $2.18 \times 10^{12}$  cm<sup>-3</sup>.

### **Chapter 6 - Conclusions & Recommendations**

Cavity ring-down spectroscopy (CRDS) is a relatively novel, sensitive and nonintrusive laser-based technique using multiple-paths laser absorption to measure the absorption coefficient of species in gases, liquids and solids. For the context of this research, a CRDS unit was designed and assembled, incorporating four main parts: the laser and CRDS unit, the beam profiling and delivery unit, the gas distribution and vacuum pumping system, and the data acquisition system. Validation of the proper functioning of the experimental setup was performed with a low-pressure DC glow discharge plasma capable of producing detectable radicals. Actual experiments were conducted using a 95% Ar/5%  $C_2H_2$ gas mixture at optimal operating pressure and voltage of 0.5 Torr (66.7 Pa) and 700 V, respectively. CH radicals were monitored at 431.131 nm and species concentrations ranging from 1.78x10<sup>12</sup> cm<sup>-3</sup> to 2.18 x10<sup>12</sup> cm<sup>-3</sup> were obtained.

It was found that the sources of error that contribute to the fluctuations in CH concentration measurements are due to the pressure variations in the reactor during glow discharge operation. Variations in reactor pressure were due to the use of a rotameter that fed the gas used during plasma operation. The rotameter had to be set manually by the experimenter, while monitoring the pressure on the LabView<sup>TM</sup> interface such that it read approximately 0.5 Torr (66.7 Pa). This quick and simple method for gas flow regulation caused the pressure within the reactor to fluctuate by 0.05 Torr (6.7 Pa) or 10%. This was a major source of error since the flow of gas could not be kept at a steady value during operation. In order to reduce the effect of this source of error during future experiments, a mass flow controller interfaced with a control scheme in LabView<sup>TM</sup> should be used to control the flow of gas.

In order to improve on the accuracy of CH concentration measurements, a conversion factor should be used in future experiments as to take into account for the radiative lifetime of the  $A^2\Delta \leftarrow X^2\Pi$  transition. The lifetime of this radical has been reported to be 526 ± 11 ns<sup>69</sup>. Since the ring-down times for CH reported during experiments are within the 1000 ns range, it is possible that a CH radical absorb radiation twice during operation. It is recommended that a conversion factor be used to compensate for the

discrepancy between the relaxation time of the CH radical and the ring-down time for CH concentration measurement.

In conclusion, a CRDS unit capable of hosting a non-thermal plasma source under controlled atmosphere conditions was designed, built and validated. The CRDS unit is now ready for use for etching experiments.

# Appendix 1 - Pump Oil Change and Zeolite Regeneration Procedure

Everyday, prior to experimentation, a pump oil level measurement should be taken. If the oil level is below the bottom line on the oil flow window on the pump, the oil should be removed and replaced with fresh one. The pump oil does not need replacement when the oil level is between the upper and lower level lines on the pump. The pump oil used for the vacuum pump is Alcatel 119 oil. During every pump oil change, the molecular sieve trap zeolite should be regenerated as well. Both procedures are available below.

- (1) Turn off the vacuum pump and let it cool down for 30 minutes.
- (2) Lift the pump and place a pan under it to recover the drained oil.
- (3) Once the pump is cool, release the casing at the front side of the pump, which covers the pump oil level window and oil draining plugs.
- (4) With a screwdriver, slowly unscrew the pump oil draining plug at the bottom of the oil level window.
- (5) Drain the oil in the pan and wait for 2 minutes for all the oil to escape the casing.
- (6) Wipe down the pump casing with a clean paper towel, removing all oil from the pump casing.
- (7) Re-screw the bottom draining cap into the pump casing.
- (8) Unscrew the top cap covering the pump casing oil intake hole.
- (9) Using a funnel, pour in the Alcatel 119 oil into the top hole of the pump casing.
- (10) Fill the oil till the meniscus of the oil line is in between the top and bottom fill lines on the oil window.
- (11) Re-screw the cap on the top oil casing intake hole.
- (12) Remove the oil pan and drain the oil in the laboratory waste receptacle.
- (13) Clean all remaining oil from the pump casing.
- (14) Once the pump oil has been changed, ensure that all plugs to intake and draining holes are tightly sealed.
- (15) Turn on the pump and let it run for 2 hours with the reactor evacuation valve closed.

- (16) During the 2 hours used to circulate the pump oil, the zeolite catalyst can be regenerated.
- (17) Place the cylindrical zeolite heating element into the hole at the top of the molecular sieve trap. The element should fit completely into the hole; none of the element cylindrical heating area should be exposed to the outside.
- (18) Turn on the element and heat the zeolite for 2 hours. This enables catalytic regeneration as to ensure that all volatile compounds produced in the reactor do not contaminate the pump oil.
- (19) After two hours, turn off the element and wait for another hour for the molecular sieve trap to cool down.
- (20) Remove the heating element and open the reactor evacuation valve.
- (21) Let the pump evacuate the reactor for 15 minutes; monitor the pressure as to ensure that the pump is able to establish a minimum vacuum of 0.01 Torr (1.3 Pa).

## Appendix 2 - CRDS Experimental Setup Safety

### Laser Safety Considerations

#### 1) Flammable Gases, Liquids and Solids

- a) Solvents
  - i) <u>Storage</u>: Solvents are stored in a flammable cabinet (vented) in the "storage" hallway outside the lab.

#### b) Dyes

- i) <u>Ventilation</u>: Flexible tube placed over the dye circulation unit, which is connected to building ventilation system.
- ii) <u>Storage</u>: The dye solids are placed in the refrigerator. Once prepared, the dyes will be placed in the refrigerator in sealed containers.
- iii) MSDS sheets for the dyes are available next to the front door of the lab.

#### 2) Toxic and/or Corrosive Gases and Solids

#### a) Solvents and Dyes

- i) <u>Manipulation</u>: The dyes and solvents will be manipulated with Neoprene gloves in fumehood.
- ii) Storage: The same procedure will be used as in the above section

#### 3) <u>Electromagnetic Interference or High Energy Laser</u>

#### a) Laser

- i) <u>Scattering and Reflection</u>: There are three levels of protection for scattering or reflection. Scattering and reflection will be prevented by having the laser beam shoot along a single axis, therefore reducing chances of confining the laser beam to a plane parallel to the optical table. Furthermore, a curtain is placed around the perimeter of the optical table, where the material is suitable to absorb high energy radiation if the beam is scattered or reflected in unwanted places. Also, a protective panel is placed around the workspace as to further absorb any light that might escape from the optical table.
- ii) <u>Security</u>: A warning light is placed outside the lab and is connected to the interlock of the laser as to turn it on once the laser is in operation. Laser safety indicators are also placed inside and outside the lab to indicate a Class 4 laser.

iii) Eye Protection: In order to prevent damage caused by scattering or direct contact with the laser beam, each person who operates the laser wears a pair of protective goggles. Also, beam dumps are used to absorb beams (stop beams) that may be shot or reflected into an unwanted area.

#### 4) Voltages > 115 V

- a) The flash lamp voltage is approximately 1520 V. It is isolated (in a protective housing) from the system and cannot be reached by experimenters. Interlocks are placed around the lamp, with the system shutting down when it is touched or when there is a problem with the system.
- b) Warning lights on the laser also indicate when the flashlamp is on.



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<sup>52</sup> http://www.exciton.com/catalogmain.htm

<sup>53</sup> http://ehs.uky.edu/radiation/laser\_fs.html

<sup>54</sup> LabView<sup>TM</sup> Program Help Menu

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