Chapter II: Experimental apparatus

2.1 Laser Induced Fluorescence (LIF) detection and analysis

In all of the studies presented in this dissertation, LIF spectroscopy is used to obtain quantum state distributions for NO or OH molecules which result from various dynamical processes. Since the line intensities of the LIF spectra are the main experimental result and are used to make inferences about the nature of the chemical dynamics under study, a good deal of effort must be expended in order to ensure that these results are both meaningful and reproducible. The detection scheme begins with a tunable ultraviolet (UV) laser which brings molecules to an excited electronic state ($^{2}\Sigma$ in the case of both NO and OH). Over the course of the spontaneous emission lifetime (~ 200 ns for NO and $\sim 1 \,\mu s$ for OH), fluorescence photons are detected over a range of solid angle chosen to omit the incident laser beam. This separation between the directions of wavevectors for excitation versus signal photons results in a very high detection sensitivity (~ 10^4 molecules per cubic centimeter per quantum state). However, in order to achieve these levels of signal to noise, it is very important to reduce the number of incident photons which are able to find their way to the detector by reflections from various parts of the experimental apparatus. Since our photosensitive device is capable of observing a single photon and the incident beam may contain $\sim 10^{12}$ photons, even very unlikely paths from laser to detector may result in unacceptably high nonresonant background. This is prevented by a variety of geometrical and optical techniques designed to limit the freedom for scattered photons to be recorded. Once

selected in this way, the fluorescence light encounters a photomultiplier tube (PMT) which converts them into an electrical signal. The resulting voltage is amplified and recorded over a range of UV excitation frequency, producing a spectrum which is then analyzed using a least squares fitting program in order to extract the population distribution from the areas below the different peaks. The raw populations are afterwards subjected to more analysis in order to understand the data in terms of various theoretical pictures.

Fig. 2.1 shows the general scheme for detecting NO or OH by LIF. Briefly, a UV laser excites from nonvibrating (v=0) levels in the electronic ground state $(^{2}\Pi)$ up to the first excited doublet level ($^{2}\Sigma$). Due to the large difference in equilibrium bond length for the two electronic manifolds, fluorescence tends to be much redder than the excitation frequency since Franck-Condon overlaps are most efficient for ${}^{2}\Sigma(v=0) \rightarrow {}^{2}\Pi(v \sim 5)$. For this reason, a Schott Glass UG11 absorption filter will effectively block scattered light from the probe laser while passing the majority ($\sim 60 \%$) of fluorescent light. This effect is not present in OH, meaning that ${}^{2}\Sigma(v=0) \leftarrow {}^{2}\Pi(v=0)$ excitation light can not be substantially reduced by filtering. Fig. 2.2 shows the basic energy level structure of NO in both the electronic ground $(^{2}\Pi)$ and excited $(^{2}\Sigma)$ states relevant for LIF detection. Each ${}^{2}\Pi(v)$ ground state is split into four electronic sublevels $({}^{2}\Pi_{1/2}{}^{e}, {}^{2}\Pi_{1/2}{}^{f}, {}^{2}\Pi_{3/2}{}^{e}$, and ${}^{2}\Pi_{3/2}{}^{f}$), each of which can exist in a manifold of different N-O tumbling states as denoted by the total angular momentum, J. The spin-orbit $({}^{2}\Pi_{3/2} \text{ vs. }{}^{2}\Pi_{1/2})$ splitting of 125 cm⁻¹ in NO reflects the mean relative orientation of the spin projection along the internuclear axis (also called Σ) vs. the unpaired electron angular momentum projection (known as Λ). The much smaller lambda doublet $(^{2}\Pi^{e} \text{ vs. }^{2}\Pi^{f})$ splitting of 0.1 cm⁻¹ for $^{2}\Pi_{1/2}(J = 10.5)$,



Figure 2.1 Electronic and vibrational levels involved in LIF detection of NO. Excitation is done on the transition ${}^{2}\Sigma(v = 0) \leftarrow {}^{2}\Pi(v = 0)$ with a tunable ultraviolet laser. When this is resonant with a transition from an occupied ground state, flourescentce preferentially involves relaxation vibrationally excited ${}^{2}\Pi$ levels due to more favorable Franck-Condon overlaps. For this reason, probe laser beam scatter can be largely removed using a UG11 low-pass optical filter.

on the other hand, arises from weak terms in the Hamiltonian sensitive to the relative direction of molecular tumbling angular momentum and internal angular momentum of the electron about the internuclear axis. These Λ -doublet levels are labeled *e* and *f* according to their inversion symmetry, i.e. an *e* state with angular momentum J has inversion symmetry of $(-1)^{J-1/2}$ while an *f* state would have $(-1) \times (-1)^{J-1/2}$. Note the need to remove the contribution of spin by adding (or equivalently subtracting) 1/2 from J in the exponent. The energy level structure of the ${}^{2}\Sigma$ upper state is simpler than that of



Figure 2.2 Absorption spectroscopy of NO $({}^{2}\Sigma \leftarrow {}^{2}\Pi)$. The 12 branches which originate from J = 3/2 levels are labeled to show which ground states they address. Each level is also labeled in terms of its parity in both (+/-) and (e/f) format.

the ground electronic state, but nevertheless, a similar naming convention is employed. However, due to the lack of any orbital angular momentum about the internuclear axis in a Σ state, the energy level structure is essentially that of a closed shell diatomic rotor with a small spin-rotation splitting built on top of each molecular tumbling state (labeled with approximate quantum number N). Also shown in Fig. 2.2 is the naming system for the various dipole-allowed transitions in this molecule, which appear as peaks in the LIF spectrum. Taking the transition $R_{11}(3/2)$ as an example, the "R" refers to the increase in J by one quantum from the ${}^{2}\Pi$ (J" = 3/2) state to the ${}^{2}\Sigma$ (J' = 5/2) level, while "P" corresponds to transitions with J'=J"-1, and "Q" means that J'=J". The first and second subscripts refer to which spin-splitting level is addressed in ${}^{2}\Sigma$ and ${}^{2}\Pi$ respectively with "1" referring to the lower splitting state and "2" referring to the more energetic one in each case. Note, however, that "spin-splitting" in the ${}^{2}\Sigma$ level actually refers to the energy difference between each two levels with the same total angular momentum (J), which actually correspond to rotational energy differences in this species. Finally, the number in parenthesis is the total angular momentum in the ${}^{2}\Pi$ starting level. Each ground state rotational and electronic level is accessed by three transitions with the following correspondence between branch and electronic manifold probed:

$${}^{2}\Pi_{1/2}^{e} \rightarrow P_{11}, R_{11}, Q_{21}$$

$${}^{2}\Pi_{1/2}^{f} \rightarrow P_{21}, R_{21}, Q_{11}$$

$${}^{2}\Pi_{3/2}^{e} \rightarrow P_{22}, R_{22}, Q_{12}$$

$${}^{2}\Pi_{3/2}^{f} \rightarrow P_{12}, R_{12}, Q_{22}$$

Fig. 2.3 shows a sample NO LIF spectrum to give a rough idea of where the various branches appear in frequency. In this molecule, the following transitions are not resolvable within the 0.25 cm⁻¹ frequency resolution of the dye laser, so together they each appear as one peak: $Q_{11} \& P_{21}, Q_{21} \& R_{11}, Q_{22} \& R_{12}$, and $P_{22} \& Q_{12}$. In OH, on the other hand, sufficient spin-rotation excitation exists in the ² Σ manifold to separate these pairs, causing these peaks to separate beyond the laser linewidth.

The spin-orbit splitting in OH is ~ 120 cm⁻¹, similar to NO, but the ordering of the two levels is reversed, with ${}^{2}\Pi_{3/2}$ being the lower state of the hydroxyl radical. Additionally, unlike NO which remains in Hund's case A up to high J, OH rather quickly transitions to Hund's case B before J = 5, often resulting in a different naming convention for levels and transitions for this species. Because N, the tumbling angular



Figure 2.3 Sample LIF spectrum for NO scattered from liquid Ga. The branches corresponding to the four prominent bandheads are roughly labeled. Also shown is a blowup of a smaller section to show the average density of peaks. The negative-going red peaks show the best-fit simulation used to extract populations from the peak heights.

momentum of the molecule, becomes a useful quantum number in this limit, states are labeled, for example, as ${}^{2}\Pi_{1/2}(N = 1)$, where N = J + 1/2 for ${}^{2}\Pi_{1/2}$ and N = J - 1/2 for ${}^{2}\Pi_{3/2}$. Transitions are also now referenced to the lower N level, rather than the lower J, and the two subscripts in the transition symbol continue the convention of 1 referring to the ground (now $\Omega = 3/2$) spin-orbit level while 2 refers to the excited spin-orbit state (Ω = 1/2) — note that the symbol $\Omega = \Lambda + \Sigma$ represents the total angular momentum about the internuclear axis. As an example, the transition O₂₁(N = 2) corresponds to an excitation originating from ${}^{2}\Pi_{1/2}(N = 2)$ which changes N by +2 to N = 4 in the upper state. Note that, unlike in the case of closed shell molecules, this "o-branch" corresponds to a change in N by + 2, but total angular momentum J changes by only + 1. Therefore, this is still an electric dipole allowed transition despite its strange naming scheme, and in fact, an s-branch can also be found in the OH excitation spectrum.

As a first step to produce spectra as shown in Fig. 2.3, ultraviolet laser light is created in a chain of devices starting with a Nd-YAG oscillator/amplifier which produces an ~ 8 ns pulse of green light at 532 nm. Fig. 2.4 shows the components of this device.



Figure 2.4 Internal workings of the YAG laser. In addition to some of the most important optical elements, the beam path of fundamental and doubled light are also shown.

The oscillator cavity, which is capable of producing 200 mJ of infrared (IR) light at 1064 nm, is bounded by two coated mirrors both of which sit in adjustable mounts. If a hotspot (as seen on a highly filtered CCD camera) forms in the output laser beam, a slight cavity alignment may be necessary. However, it is not advised to make more significant changes to the mirror angles unless lasing has been lost. If this is the case, shine a helium-neon (HeNe) laser through the center of the output coupler and all internal cavity

elements so that it strikes the centers of the back mirror. Irises should be mounted before and after the cavity to define a beam path. Adjust the back mirror to retroreflect the red beam through the first iris. Then, using a series of steering mirrors, send the HeNe into the cavity through the back mirror, through the same irises, and retroreflect from the output coupler. Now that the cavity is set, the output coupler must be translated so that the HeNe beam strikes it in its center (which can be identified by a series of faint concentric colored rings on the surface of the glass). Two set screws, on the side of the mount, should be used to move the mirror in plane until the red beam coincides with the colored rings. This entire process may need to be iterated several times to obtain a good alignment. The YAG active gain medium is a 15 cm long crystal rod with a diameter of 7.5 mm which sits in the middle of the cylindrical laser head. The head also contains a discharge flashlamp whose lifetime is somewhat limited and therefore must be replaced whenever laser power drops to unacceptably low levels. See the laser manual for information on how to replace the flashlamps. The manual also contains instructions on how to refresh the deionized water supply which cools the laser head, a task which must be carried out every few months. Before exiting the laser, the beam passes through a Nd-YAG amplifier crystal mounted in a similar head (but with two flashlamps) and a Beta barium borate (BBO) doubling crystal which produces 532 nm green light. The laser control box contains two buttons for adjusting the angle of this crystal to obtain maximum output power at 532 nm.

YAG laser timing, as well as all other synchronization in this experiment, is controlled by a Stanford Research Systems (SRS) digital delay generator (DDG), which presents rising edge triggers with delay specified by entering numbers in the front panel for each of the four output channels. Each YAG laser requires two separate triggers to produce a laser pulse. The first activates the three flashlamps which bathe the crystals in light, leading to a population inversion. The second trigger controls a high voltage pulse in the Pockels cell, an electro-optical component in the oscillator beam path which "opens" the cavity. In short, the oscillator cavity contains a window oriented at Brewster's angle for 1064 nm, which results in lasing only for p-polarized light due to rejection of $\sim 10\%$ of s-polarized radiation on each pass. Normally, the combination of the Pockels cell and a 1/4-wave plate in the cavity results in a change from s to p polarization for each round trip in the cavity, meaning that lasing will not occur. However, when the Pockels cell is transiently activated, s and p components are no longer interconverted on a round trip, resulting in a cavity which is "open" for p-polarized light. Therefore, while the first DGG timing pulse creates a population inversion, the second pulse opens the cavity so that lasing can actually occur. Varying the delay between these two channels is one means of adjusting the 1064 nm output power as the opening of the cavity becomes more or less synchronized with the flashlamp firing. However, IR power can also be adjusted by simply turning down the flashlamp voltage as controlled by a dial on the laser power supply. This is the preferred method since lower voltages result in longer flashlamp lifetime, and furthermore, the flashlamp - Pockels cell delay can be directly accessed by a dial on the front of the power supply. Nevertheless, the design of the YAG laser electronics requires one rising edge flashlamp trigger and a second trigger for the Pockels cell. Furthermore, the latter trigger pulse must have negative polarity (i.e. held at +5 V when not triggering) and a short duration to avoid damage to the Marx bank, a set of transistors that then delivers the high voltage pulse to

the Pockels cell. The instruction manual contains information on how to arrange triggers to produce the necessary timing inputs for the YAG electronics.

The 532 nm beam is used to pump a dye laser filled with one of two dyes: DCM for detecting OH, or LDS 698 for detecting NO molecules. Best results for tuning over the entire ${}^{2}\Sigma(v = 0) \leftarrow {}^{2}\Pi(v = 0)$ bands are obtained at a (oscillator, amplifier) DCM concentration of ~ (3.6x10⁻⁴ M, 1.9x10⁻⁴ M) in methanol for OH detection and an LDS 698 concentration of ~ (3.0x10⁻⁴ M, 5.0x10⁻⁵ M) in methanol for NO. Fig. 2.5 shows the internal



Figure 2.5 Photograph of the dye laser, which converts green laser light into a beam of lower energy photons. Paths are shown for both the 532 nm pump laser and the red output.

workings of this stage of light generation. A green beam from the previous YAG laser

"side pumps" three liquid-containing dye cells, one of which is in the dye oscillator

cavity and two of which function as amplifier stages. The front mirror of the cavity is the edge a fully silvered mirror, from which output coupling achieved by having a small amount of radiation miss the it and travel through the amplification stages. Instead of a back mirror, the cavity is bounded on the other side by a diffraction grating which retroreflects a specific color of light depending on its angular position. The laser is managed by a dedicated DOS computer which is in turn controlled by Labview acquisition software on a modern computer (see appendix B.1). This tunable laser is able to cover both the $0 \leftarrow 0$ and $1 \leftarrow 1$ bands of the ${}^{2}\Sigma \leftarrow {}^{2}\Pi$ transitions¹ in both OH and NO. It converts 100 mJ of 532 nm light into 20 mJ at 616 nm when filled with DCM dye. The output energy varies by ~ 10% from pulse to pulse, the frequency resolution is about 0.25 cm⁻¹, and the polarization is vertical.

Visible red light from the dye laser is then passed through more BBO crystals, each of which resides in its own "autotracker" box (Fig. 2.6) featuring rotating stages for a crystal and a refractive compensator block as well as an active feedback system for maximizing production of UV laser light. Type II sum frequency generation (SFG) is employed, meaning that the output polarization is rotated by 90° from that of the input photons. A motor continuously adjusts the BBO angle for optimal SFG output energy, employing the principle that best phase matching is achieved when the input and output laser beams are coaxial. To this end, a small amount of output UV light is picked off, and sent through a series of color and neutral density filters before striking a split photodiode which is sensitive to changes in UV laser direction. At a fixed dye laser frequency, the BBO angular position is first chosen for maximum production of output UV light. Next, the position of the split photodiode must be adjusted so that equal



Figure 2.6 Elements of the autotracker, which doubles input visible light in a BBO crystal. A small amount of the output radiation is picked off and sent to a split photodiode which feeds back on the crystal position for maximum UV generation.

radiation lands on each side. Finally, putting the device in "auto" mode will allow it to continuously adjust the phasematching condition over the course of a spectral scan. In order to detect OH, only a single BBO stage is needed to double the \sim 616 nm dye laser output to produce a 308 nm tunable UV beam. To detect NO, two BBO stages are needed. The first converts some of the 690 nm incident beam into 345 nm light; next, the combination of fundamental and doubled radiation are both passed through a polarization

rotator to bring the 345 nm radiation back to the proper polarization. Finally, the two frequencies enter a second BBO crystal where sum frequency generation takes one photon from each beam to produce radiation at three times the frequency of the original light (230 nm). While these doubling and tripling stages do not broaden the output laser frequency distribution, they do tend to increase shot-to-shot energy noise due to the nonlinear nature of SFG. For example, for an input red beam of 20 mJ \pm 10%, a typical doubled output energy would be ~ 2 mJ \pm 20%, while a tripled beam would come out at $0.2 \text{ mJ} \pm 30\%$. The efficiency of UV light generation is sufficient for high sensitivity detection of these species, and in fact the flashlamp voltage often must be turned down to avoid saturation of the LIF transitions. For NO, a laser pulse of 5 μ J and a beam diameter of 2.5 mm was found to put the measurement in a safely non-saturating regime. The 30% pulse to pulse variation, on the other hand, represents a significant amount of on-peak noise, so it is important to record laser energy for each shot so that each data point can be normalized to this value. After passing through all necessary UV generation stages, the beam passes through a harmonic separator where two prisms mounted on a translatable stage shift the spatial positions of the various frequency components with respect to each other so that only the desired color is allowed to exit the device.

Since the resulting UV laser beam has poor spatial quality, a very small (~ 750 μ m) portion is selected by placing an iris at the brightest part of the intensity distribution. This results in some diffraction which takes the form of a series of circular rings around the central bright spot which can be seen by fluorescence with the naked eye when a normal piece white paper is placed in the UV beam path. These diffracted photons cannot be allowed to enter the chamber because they come in at an off-axis angle, making

them more likely to scatter off of a surface inside the experiment. They are removed by sending the spatially-selected UV light down a long (2.7 m) path before it passes through a second aperture whose diameter is chosen to be large compared to the final beam size but small compared to the diameter of the brightest diffracted rings which do not pass on to the chamber. This beam path requires two turning mirrors as well as a periscope to raise the beam to the level of the chamber. In order to avoid scattered light contributions from multiple reflections from the two faces of a typical dichroic reflector, right angle fused silica prisms are employed instead. Ultraviolet light enters normally through one face, totally internally reflecting off the long face and leaving the reflected beam free of any ghosting. After being raised by a periscope, the UV beam enters the chamber through a thin (2 mm) calcium fluoride window which is tilted near Brewster's angle to minimize multiple reflections from its two planar surfaces which can be another source of stray photons inside the chamber. Once inside the vacuum, the beam passes through a series thin metal baffles (Fig. 2.7), four aluminum rings with increasing diameter ranging



Figure 2.7 Aluminum baffles used to minimize scattered light produced as the ultraviolet laser beam enters the chamber. These stacked rings are slid into the 24" baffle arms on either side of the chamber.

from 5 mm to 11 mm. These apertures are chosen to be large compared to the 3 mm incident laser beam size but small enough to block light scattered from the entrance window. The beam then passes through the center of the cubical vacuum chamber, where it produces fluorescent light when resonant with a transition from a populated ground state of OH or NO. Afterwards, it again passes through an identical series of baffles with steadily decreasing size before passing through another fused silica Brewster window. After the exit window, the UV beam enters a solid state (J5) power meter which measures the energy of each laser pulse.

After NO or OH molecules are excited by the laser beam in the center of the vacuum chamber, fluorescence is collected by a pair of plano-convex fused silica lenses with diameter of 5 cm. These optics sit at the end of a welded stainless steel imaging tube (Fig. 2.8), and the first of them is pressed against an o-ring which forms a chamber seal. Therefore, there is no need for a window between the vacuum and the first collection optic, which results in reduced losses due to reflection from these surfaces. The two imaging lenses each are characterized by a focal length of 5 cm, and they are placed at a distance of 5 cm from the UV laser beam path, meaning that a 1 to 1 image is produced approximately 5 cm from the back of the second lens. A flat metal ring with inner diameter of 4 mm is placed in the imaging plane so that only a segment of the laser induced fluorescence is allowed to pass. This spatial filtering scheme serves to minimize



Figure 2.8 Schematic of the imaging tube. Fluorescence enters through a pair of plano-convex lenses (blue), the first of which must form a vacuum seal with an o-ring whose groove is machined into the endpiece. A second lens tube (aqua) contains a spatial filter (black) which limits the in-chamber detection region to a 4 mm segment of the UV excitation laser. Only light passing through this circular aperture is then allowed to reach the photomultiplier tube (red).

contributions from fluorescing NO molecules which are located far away from the collision geometry of interest. For example, in the absence of this mask, a very large and cold background signal is observed which occurs at the intersection of the incident supersonic molecular beam with the LIF laser beam. After the spatial filter, fluorescent light generally passes through a low pass glass filter chosen to further minimize background contributions from scattered photons in the chamber. This step is often not employed for detecting OH, but NO exhibits very favorable Franck-Condon overlaps for fluorescence from ${}^{2}\Sigma(v = 0)$ into a wide range of vibrationally excited ground state levels.

Fluorescent light is detected using a photomultiplier tube (PMT) which has been wired in the manufacturer-suggested configuration for maximum linearity (see Fig. 2.9) but is still capable of observing single photons striking its surface. In fact, the baseline noise from this device is so low that output noise is instead dominated by the arrival of the occasional stray photon on the detector. These background photons are inevitably



Figure 2.9 PMT wiring scheme. The resistor chain is chosen for maximum linearity to avoid saturation for large numbers of LIF photons per pulse. Current flows from the anode through a 50 Ω resistor over which signal voltage is measured.

related to direct scatter from the UV probe pulse or from fluorescence in, for example, the entrance and exit fused silica chamber windows, which is the reason that great effort is expended in reducing stray photons as discussed above. The PMT photocathode voltage is generally set somewhere between -2000 V and -1600 V relative to the anode stage where photocurrents are collected. Over this range of voltage, PMT sensitivity varies by about a factor of 13, which is sometimes needed in order to avoid charge saturation in the final few dynodes in cases where OH or NO LIF signals are large. At -2000 V, the device (Electron Tubes model 9813QB) is characterized by a gain g = 2.2(9)x 10⁷ electrons per detected photon and a quantum yield of approximately 30%. For studies on reactive scattering of F with H₂O, it is necessary to transiently turn off² the PMT while the discharge fluorine source is firing in order to avoid saturation by resulting photons. This was done with a home made high voltage switch (see appendix A.1) which transiently sets the relative voltage from the cathode to the first dynode to -200 V, which is sufficient to repel photoelectrons and thus avoid PMT saturation. The switch effectively turns off the PMT throughout the duration of a TTL positive pulse from a sum combination of two channels on the DDG. After the collection anode, the device is wired through a 50 Ω readout resistor to the ground of the high voltage power supply.

Therefore, a single collected photon produces a peak signal of $V_{peak} = \frac{geR}{\Delta t}$. Since the time response (Δt) is on the order of 3.5 ns for this device, peak signal is ~ 50 mV for a PMT cathode-anode bias of -2000 V. PMT signals can be related to NO or OH densities in the detected region by taking into account the major sources of reduction in collection efficiency, starting with the fact that the first imaging lens subtends a solid angle of $\Omega_{det} = 0.66$ steradians. Taking into account the R ~ 5% reflections from the six glass surfaces encountered en route to the PMT, the 60% signal transmission through the UG11 filter, as well as the 30% PMT quantum yield and the capability to saturate the LIF transition of interest (saturation means that $f_{ex} = 50\%$ of molecules from a particular ground state will be excited by the pulse to a level with the same degeneracy), it is possible to predict the number of NO molecules from a particular ground state corresponding to a single

detected photon as
$$N_{\min} = \left(\frac{\Omega_{det}}{4\pi} \times T_{filter} \times (1 - R_{glass})^6 \times QY_{det} \times f_{ex}\right)^{-1} \approx 300$$
. Since the

probed volume is on the order of 0.006 cm^3 , this means that the fundamental detection sensitivity limit is ~ 5 x 10^4 molecules/cm³/quantum state. For NO detection, stray photons arrive with a frequency on the order of 1 photon per 10 laser shots, meaning that this limiting level of sensitivity is readily achievable with minimal time averaging required. Due to the less favorable Franck-Condon overlaps in OH, the minimum detectable density is higher for this system by an order of magnitude. In either case, to preserve maximum sensitivity, it is important to avoid adding noise in subsequent amplification and data processing steps.

Signal level is obtained by measuring the voltage across the 50 Ω resistor on each shot of the 10 Hz UV laser beam. Voltages are next increased by a factor of 10 in a 20 dB preamplifier (1 GHz bandwidth) in order to swamp input voltage noise in the next stage where the fluorescence transient is captured with a boxcar integrator. The boxcar width is set at the radiative lifetime of the molecule (~ 200 ns for NO) and is timed to begin averaging on the order of 20 ns after the firing of the probe laser. The boxcar duration sets the bandwidth of the measurement to ~ 5 MHz and also provides a final, temporal, means of discriminating against scattered photons from the incident laser beam, resulting in a background level of typically less than one photon per pulse. Note that the output from the boxcar is equal to the average voltage during the detection window. Therefore, the 500 mV, 3.5 ns signal after the preamp corresponds to an output of ~

 $500 mV \frac{3.5 ns}{200 ns} = 9 mV$. This signal is typically further boosted by a factor of 20 in a

second amplifier which is built into the input of the boxcar integrator. Finally, this signal

enters an analog to digital converter which sends the digitized boxcar signal level to a data taking computer. Like all elements of the experiment, this digitization step is triggered at 10 Hz by a TTL pulse delivered from one channel of one of the SRS digital delay generators.

In fact, all experimental timing is ultimately controlled by a pair of Stanford Research Systems delay generators, one of which is triggered from the other master clock. In addition to specific devices which will be discussed separately for each experimental setup, the following items each require their own timing pulse: 1) the Nd-YAG flashlamps, 2) the Nd-YAG Q-switch which determines the time when the probe laser pulse fires, 3) the LIF boxcar integrator, 4) a boxcar integrator for the probe laser energy, and 5) the Labview control and readout program (Fig. 2.10 and appendix B.1). Upon receiving a timing pulse, the program records values for both LIF signal and probe laser energy which has its own preamplifier and boxcar integrator. On each laser shot, these values are stored in memory, and upon termination of the spectral scan, they are stored with a set of UV frequency values. These frequencies are calculated based on the assumption that the probe laser wavelength continuously advances at a rate which is determined in the Labview program and fed into the laser control computer at the beginning of the scan.

A typical scan proceeds as follows. Start by using the "go to" button to move the dye laser to the desired starting frequency. For the two channels of importance (LIF signal and Probe energy), enter the gain values selected with the boxcar amplifier stage into the appropriate boxes on the Labview program's front panel. Next, press the button



Figure 2.10 Front panel for the Labview data taking program. This virtual is capable of scanning the dye laser or the infrared OPO. It can also automatically vary laser timing.

called "Monitor", which records data at 10 Hz with the probe laser frequency fixed. Press "stop" after a minute or two, and the program will report both the background and noise for both channels. Write these numbers down for later use. Incidentally, due to low frequency variation in boxcar output, it is necessary to perform this procedure at the beginning and ending of each spectral scan. Once the background has been obtained, choose the desired direction and velocity and press "Start" to initiate a manual UV spectrum. At 0.1 cm⁻¹/s, it takes about 2.5 hours to scan the entire ${}^{2}\Sigma(v = 0) \leftarrow {}^{2}\Pi(v = 0)$ NO band, and no other inputs are required of the user during this time. Once the scan is complete, hit "stop", and an output file will automatically be generated in C:\spectra in a folder and file corresponding to the current date and time. Note that it is often useful to increase the PMT voltage for the last half of the spectrum, where the smaller peaks are less likely to saturate the PMT. This necessitates saving two separate scans (making sure to change the "LIF signal \rightarrow Conversion" variable to reflect the change in PMT sensitivity) which can then be manually combined in a spreadsheet program such as Origin. One final note, the program is also capable of scanning in the time domain, where for example, the firing time of the pulsed jet source (which introduces NO into the chamber) can be varied with respect to the probe laser pulse to observe the gas arrival distribution in the time domain. These scans are done in the "Delay Scan" section by directly controlling the DGG timing on a shot to shot basis with time delays randomly selected between two user-specified limits in order to avoid systematic errors associated with low frequency drift in the system.

During a frequency scan, the actual laser light frequency tends to differ from this value by up to 0.2 cm^{-1} in a random manner over the course of a spectrum. It is likely that this error is caused by some lack of mechanical reproducibility in the scanning mechanism, but given that the output laser linewidth is only about 0.2 cm⁻¹, this frequency error is unacceptable. This is particularly true in the case of NO where a good frequency calibration is necessary in order to extract populations from the congested spectrum. Therefore, the frequencies must be calibrated in a second Labview program (Fig. 2.11 and appendix B.2) which performs a linear calibration to ensure proper line positions in a semi-automated manner. In short, the program displays a segment of the experimental spectrum along with a simulation at some user-defined temperature. Frequency shift and linear correction are automatically chosen via a least squares fit which must be accepted by the program user for each wavelength region, typically set to 50 cm⁻¹ in width. The automatic calibration is generated by comparing the experimental spectrum with a thermal simulation based on a user-defined temperature. While the peak intensities are, of course, not expected to agree with the simulation, the program still does a reasonably good job of choosing a frequency offset and a linear correction term to correct the wavelength error. However, this does not always work, so it is sometimes necessary for the user to vary the limits of the fitted frequency region ("backwalk" and "step") until a visually satisfactory fit is obtained. Press "next segment" when a reasonable frequency calibration has been obtained. Upon pressing the "stop" button at the end of the scan, the output data will be saved as "C-*", where "*" stands for the name of the input data file.



Figure 2.11 Front panel of the Labview frequency calibration program. The abscissa of the raw data (white) is shifted and scaled to obtain agreement with known line positions (shown as a thermal simulation in red).

Once calibrated, spectra are entered into a FORTRAN program called "LIFfits.f" (appendix B.3) which uses STARPAC³ nonlinear least squares fitting to vary NO or OH populations until the experimental spectrum is reproduced as shown in Fig. 2.3. Extensive spectral overlap in both systems is mitigated by the fact that each quantum state is generally represented by several peaks in well separated areas of the spectrum. Therefore, low intensity lines in the uncluttered blue end, for example, are absolutely crucial for disentangling spectral information in the dense central portion, so it is very important to scan over a sufficiently wide range. This is especially true in OH, where the Hund's case B character of the molecule results in low intensity "O" and "S" branches far from the highest peaks.⁴ The program outputs populations tabulated according to ground rotational level as well as electronic manifold of which there are four $({}^{2}\Pi_{1/2}{}^{e}, {}^{2}\Pi_{1/2}{}^{f})$, ${}^{2}\Pi_{3/2}^{e}$, and ${}^{2}\Pi_{3/2}^{f}$) for both NO and OH (see Fig. 2.12). The accuracy of this rather involved analysis can be tested by firing the probe laser well after the supersonic jet so that radical populations are allowed to fully thermally equilibrate with the chamber walls. Fig. 2.12 shows a Boltzmann plot of such a study for NO. Not only is the rotational distribution characteristic of a room temperature sample, but the summed spin-orbit ratio also corresponds to a temperature of 300 K, showing that this degree of freedom has also reached thermal equilibrium and is properly handled by the data analysis procedure. The LIFfits.f program is controlled by an input file called "par.dat" whose inputs include the folder and name of the input file, the wavenumber range to be considered, the maximum J to include in the fit, the peak width, and the names of files containing information on transitions and energy levels.

Once an acceptable fit has been achieved, several output files are generated including mC* (showing the best fit model spectrum), pC* (with the quantum state populations extracted from the raw data), and prawC* (containing a Boltzmann analysis of the population distribution). The file pC* in turn serves as an input for another fortran



Figure 2.12 LIF analysis procedure applied to a 300 K static NO fill ($4x 10^{-8}$ Torr). When plotted on a Boltzmann axis, populations extracted from the spectrum agree well with the expected 300 K distribution. Inset: energy level diagram for NO($X^2\Pi_{\Omega}$) showing the spin-orbit splitting of $E_{\text{Spin-Orbit.}} \approx 125 \text{ cm}^{-1}$ and negligibly small energy difference between lambda doublet levels.

programs for further data analysis. "Double_Exp_fit.f" (appendix B.4), fits the raw data (population(J) for each electronic manifold) to a two temperature distribution according

to
$$P(J) = (2J+1) \left[\frac{\alpha}{Q_1} \exp(-\varepsilon_J / kT_1) + \frac{1-\alpha}{Q_2} \exp(-\varepsilon_J / kT_2) \right]$$
, where T₁ and T₂ are the

temperatures of the two sub-populations and α is the branching between them. Q_1 and Q_2 are normalization factors for each sub-distribution. Yet another file called "par.dat" contains the name of the input file, the energy range to consider, guesses for the parameters T_1 , T_2 , & α , and Boolean variables which determine whether to float or fix these values in the fit.

2.2 State-to-State Scattering at the Gas-Liquid Interface

Several aspects of the nature of liquid surfaces are explored by observing inelastic collisions of ground state NO molecules to form excited rotational and spin-orbit states. LIF detection (section 2.1) is employed to determine the probability to populate various internal motions of the NO molecule after interaction with molten metals and room temperature ionic liquids (RTIL's). In addition to examining rotational excitation of the scattered NO, a good deal of effort is expended in obtaining reproducible electronic distributions showing the probability for incident ground spin-orbit state molecules to undergo a spin-orbit flip to scatter in the excited ${}^{2}\Pi_{3/2}$ manifold. These experiments are performed using a much improved LIF detection scheme compared to that used for examining clusters and gas phase reaction dynamics, but the basic principles are the same. For brevity, the LIF system described in section 2.1 is in fact the one used for these studies on scattering from liquids. These NO scattering studies are somewhat simpler due to the use of only a single laser and the lack of need for an electric discharge to produce reagents. However, considerable care must be taken to ensure purity and

cleanliness of these liquid surfaces so that, for example, the NO molecules are not inadvertently scattered from a gallium oxide surface rather than bare liquid gallium.

A turbomolecular pump is employed so that surfaces under study will not experience contamination from oil molecules. This device features a rated pumping speed of 1800 l/s for N₂ molecules and an 8" entrance. The turbomolecular device is backed by a E2M80 25 l/s foreline pump. Additionally, a residual gas analyzer is installed inside the chamber to observe, in real time, the constituents of the background gas. The vacuum-chamber system is able to reach a base pressure of $\sim 3 \times 10^{-8}$ Torr as measured on a Bayard-Alpert style ionization gauge. Further exmination of the composition of this background gas on the RGA reveals a proportion of more than 90 % of H₂O, and a molecular oxygen partial pressure of less than 10⁻⁹ Torr.

 O_2 concentrations are of particular importance because liquid gallium surfaces are expected to form several monolayers of Ga₂O₃ in the presence of an oxidizing environment. The rate of this process has been measured, by sensitive x-ray reflectivity studies,¹³ to occur on a timescale of several hours at 10⁻⁹ Torr O₂. This means that experiments can be carried out on a clean surface throughout the 2 hour scanning times in this study as long as the oxide layer has been removed prior to scanning. Removal is done with the use of a 2 keV Ar⁺ sputtering source mounted 5 cm away and at 45° from the surface normal. Prior to each spectral scan, this device is run for 15 minutes, which is sufficient to completely clean the surface as observed by reduction in the total intensity of the scattered NO signal (Fig. 2.13). This effect of surface cleaning is thought to be a consequence of increased excitation of thermal capillary waves on the pure metal surface compared with the flatter oxidized interface. As this backfill Ar⁺ source requires a

neutral Ar chamber pressure of 5 x 10^{-5} Torr, a lecture bottle of 99.995 % pure argon is introduced directly into the chamber through a needle valve followed by a small port in the side of the vacuum can.

 Ar^+ cleaning is not possible on the RTIL surfaces because local heating vaporizes the material, resulting in a white coating on the nearby LIF imaging lens, which decreases overall detection sensitivity. However, these liquids will not form a floating oxide layer



Figure 2.13 The effect of Ar^+ cleaning on NO + Ga LIF signal integrated over the P₁₂ branch of NO. Cleaning decreases the overall amount of scattered NO, likely a result of increased roughening of the pure Ga surface relative to the flatter oxide.

in the presence of O_2 as was the case for liquid metals in the chamber. Also, due to their superior ability to dissolve H₂O, the dominant background species in the chamber, these liquids are not expected to form a water film on their surface at the background water pressures used in this experiment. For example, previous studies¹⁴ on the effect of gas phase H₂O on surface properties of RTIL's found no measureable effect below partial

pressures of 10^{-4} Torr, a value which is 4 orders of magnitude greater than what is seen in the vacuum can. Nevertheless, cleanliness can be confirmed by periodically scraping and disposing of the surface every 5 minutes with a steel wire which can be fed through an UltraTorr fitting below the entrance baffle arm. When this is done, scattered NO distributions are in good agreement with those from an unscraped surface, indicating that these liquid surfaces are sufficiently clean. Before being placed in the crucible, ionic liquid samples, even BMIM-Cl, which is a solid at room temperature, must be degassed. Removal of dissolved gases is crucial because it eliminates H₂O contaminant, and it also avoids violent degassing in the experimental vacuum chamber, which can result in a liquid coating on the LIF collection lens. Removal of dissolved N₂ and O₂ is done in a round bottomed glass flask which is heated to 350 K (to additionally boil away dissolved H₂O) and agitated with a teflon-coated stir bar. The top of the flask is evacuated with a mechanical pump whose backstreaming oil is eliminated by pumping through a coil of 14" copper tubing immersed in liquid nitrogen. Typically, liquids are degassed for 4 hours prior to being quickly transferred to the chamber.

For these studies, NO is seeded in a variety of nonreactive ballast gases in order to control the collision energy with which the molecules strike the surface. These gases include argon, neon, helium, and hydrogen, which give collision energies of 1.0, 2.7, 10, and 20 kcal/mol respectively. In each case, 50 Torr of NO gas is mixed with 5000 Torr of ballast in a 1 L stainless steel tank, resulting in a NO concentration of 1%. Mixing pressures are measured on a 10,000 Torr Baratron gauge to ensure accurate NO concentrations which are further confirmed by using the RGA to directly observe chamber NO and ballast concentration while the gas is pulsed through the valve. Before

use, the steel premix tanks are left untouched for at least 24 hours to allow full diffusive mixing of NO with the carrier gas. All gas handling is done in a welded stainless steel manifold featuring o-ring sealed VCO fittings and PTFE tubing connecting to gas cylinders, the premix cylinders, Baratrons, and the pulsed valve, as shown in figure 2.14. It is exceptionally important to ensure that this manifold is leak free because even a very small concentration of O_2 is capable of reacting with NO and reducing observed signal



Figure 2.14 Manifold used for creating gas mixtures and delivering them to the pulsed valve inside the vacuum chamber. Violet circles represent ball valves for flow control. The manifold itself is welded stainless steel tubing with VCO fittings. All tubing is teflon.

levels. Therefore, anytime a change is made to the gas handling system, it is important to use a helium leak checker to ensure leak rates less than 10^{-6} standard cubic centimeters per minute (sccm).

After the premix cylinder, gas flows through a corrosion-resistant stainless steel and monel regulator which determines the backing pressure and is typically operated at its maximum value of 3000 Torr (absolute). Next, a metal mesh filter is encountered which is meant to remove any particulates that might clog the pulsed valve downstream. After the filter, the gas encounters another 10,000 Torr Baratron gauge which serves to accurately measure the backing pressure. Finally, gas flows into the pulsed valve, an Evan Lavie style device which accepts a 1/8" teflon tube through a small swagelok fitting. It is very important to realize that these small swagelok fittings do not require 1 and ¼ turns of initial tightening like normal swagelok nuts, but instead only need ¾ of a turn. These devices are designed to handle very high pressures, up to 76,000 Torr. Since this number is very high compared to the 3000 Torr backing pressure employed in this experiment, it is necessary to input relatively large values for "pulse time" into the control unit in order to ensure full valve opening. In practice, it has been found that a pulse time between 40 and 45 µs is sufficient for all carrier gases used here; larger values are not recommended since they tend to lead to a good deal of afterpulsing as seen when running a "Delay Scan" on the Labview control program (Fig. 2.10). The subsequent molecular beam travels 5.3 cm before passing through a 3 mm skimmer (Fig. 2.15) which collimates the molecular paths well enough to eliminate LIF background from the cold incident beam when looking at specular scattering a distance 1.6 cm above the surface. The pulsed valve is mounted on a rotatable 80/20 structure allowing access to a large

range of incident collision angles from at least 0° to 45° with respect to the surface normal. Additionally, the liquid surface can be translated in both dimensions in the scattering plane in order to control the detected angle over a similar range. In the studies presented below, incidence angles are fixed at 45° and specular detection is employed except for the special case where the incident beam itself is observed by removing the liquid surface completely and placing the detected point (fixed at the center of the chamber) directly in line with the molecular beam. When this is done, incident beam



Figure 2.15 Gas-liquid scattering experimental apparatus. An mixture of NO in a seed gas flows out of an Evan Lavie valve and is collimated in a skimmer to form a small spot on the liquid surface. Specularly scattered molecules are detected using laser induced fluorescence. Also shown is the aluminum and stainless steel crucible assembly for heating, cooling, and containment of the molten sample.

temperatures are found to be exceptionally cold (often below 1 K), attesting to the high cooling power of this valve system.

The liquid surface is contained in a stainless steel crucible which is held near the center of the chamber and attached to the 80/20 mounting structure by four 4-40 threaded stainless steel standoffs with a length of 4 cm. This setup provides a good deal of thermal isolation between crucible and chamber which is expected to be characterized by on the order of 25 W of conductive heat loss when the crucible is heated to 1000 K. This is a result of the standard heat flow equation for heat flow power (P): $P = \kappa \Delta T \frac{A}{I}$. $\kappa = 27.7$

W/mK is the thermal conductivity of stainless steel at 1000 K, ΔT is the 700 K temperature difference across the standoffs, $A = 8 \times 10^{-5} \text{ m}^2$ is the total cross sectional area of the four 4-40 rods, and l = .04 m is the length of the standoffs. In fact, at these temperatures, this conductive loss is very small compared to the expected radiatave power of ~ 150 W. Note that thermally radiated power can be roughly estimated as $P_{rad} = \sigma A T^4$, where $\sigma = 5.67 \times 10^{-8} \text{ W/m}^2/\text{K}^4$ and A ~ 30 cm² is the crucible surface area. 285 K cooling water is flowed through a block of aluminum to which the stainless steel standoffs connect, ensuring that the chamber itself remains cool as the crucible is heated. As shown in Fig. 2.15, the crucible itself is a block of stainless steel with cavity dimensions of 4 cm x 2.4 cm x 0.25 cm (2.4 mL) - a previous version also exists with dimensions 4.4 cm x 2.4 cm x 0.5 cm. Two NiCr cartridge heaters are sandwiched between the bottom of the crucible and a lower plate each of which contains machined grooves for the cylindrical devices. These heaters, each of which is capable of delivering 500 W of power, can easily heat the crucible to 1000 K. However, higher temperatures cannot be achieved due to a rapid loss of mechanical stability of the NiCr wires which

eventually leads to an electrical spark as the wire breaks. 4-40 nuts on the standoff rods hold the whole device together and provide enough pressure to ensure good thermal contact between heaters and crucible. A small blind hole is drilled through the back of the crucible block, and threaded 4-40 set screws come in from the top and bottom of the resulting cavity. A type K thermocouple is inserted into the blind hole and secured by tightening the set screws, a scheme which provides a measurement of liquid temperature with an accuracy of 1 K, as confirmed with a thermocouple placed directly in the liquid under study or in an icewater bath.

In liquid metals at high temperature, the choice of crucible material is very important because of the possibility of amalgamation where metallic crucible atoms are dissolved into the liquid under study. This is particularly serious because of a phenomenon whereby a small bulk concentration of an unwanted species in a liquid metal can lead to a very high proportion of impurities on the surface¹⁵ For gallium in steel, solvation of Fe in Ga is the most important interaction, and previous studies¹⁶ show that the iron concentration will be below 1% at temperatures below 900 K. However, upon further heating, the Fe concentration rises rather rapidly, meaning that a steel crucible is not ideal for a very hot gallium sample. Many other potential materials such as aluminum also amalgamate well with Ga, and even carbon will be dissolved, ruling out the use of a graphite crucible. One promising alternative is to line the steel crucible with a layer of tungsten foil, which does not easily leave the solid phase to amalgamate with a nearby liquid metal at an interface¹⁷.

2.3 Spectroscopy and Dynamics of H₂O-containing Clusters

A variety of water clusters were studied using a slit jet spectroscopy apparatus. The list of species consists of Ar-H₂O, H₂-H₂O, and H₂O-H₂O. With the exception of H_2O dimer⁵, these complexes⁶ are bound by tens to hundreds of cm⁻¹, meaning that samples must be cooled rather aggressively in order to ensure measureable cluster concentrations in the detection region. This is done by co-expanding on the order of 0.1% H₂O in a gas of the desired atomic or molecular partner in a supersonic beam⁷. Gases are typically mixed by bubbling Ar, Ne, or H₂ through a reservoir of purified liquid water which is cooled in an ice bath to maintain a steady water vapor pressure of ~ 5 Torr. The richness of the water mixture is adjusted by varying the carrier gas pressure in the mixing cylinder, and the total backing pressure in the nozzle is dynamically varied with an inline needle valve to control total gas flow and thus pressure behind the expansion. The expansion is produced by a home made pulsed supersonic slit jet source which has been discussed in detail elsewhere⁸. A pair of steel jaws typically limits the slit width to ~ 100 µm, and the length is held fixed at 5 cm. Because of the inherent propensity for three body collisions in a slit expansion as opposed to a pinhole, this is an ideal setup for generating water clusters by cold gas phase collisions. The resulting molecular beam expands into a 96 L cubical vacuum chamber evacuated by a 10" diffusion pump which is backed by a 25 l/s E2M80 mechanical pump. A liquid nitrogen cooled baffle is employed to limit the presence of backstreaming diffusion pump oil in the chamber. The resulting chamber pressure of $\sim 10^{-6}$ Torr exhibits a mean free path ~ 70 m which is more

than sufficient to ensure an absence of collisions with background gases in the chamber before encountering the set of detection laser beams 2 cm downstream.

Gas phase clusters within the 5 cm path length of the molecular beam are detected by three-laser action spectroscopy⁹ as shown schematically in Fig. 2.16. Briefly, each cluster first encounters a tunable infrared laser beam whose frequency is chosen to be near resonance¹⁰ for two quanta of H₂O monomer vibrational excitation. Next comes a 193 nm photolysis pulse whose energy is appropriate to preferentially break apart vibrationally excited water molecules. Finally, resulting OH molecules are state-selectively detected by LIF with a 308 nm probe pulse as discussed in section 2.1. All three laser beams are spatially overlapped inside the chamber, and the fused silica



Figure 2.16 Scheme used to detect $H_2 - H_2O$ clusters: a) Complexes are formed in a ~ 3 K slit supersonic jet. The potential energy minimum structure is shown here. b) An infrared laser pulse excites the 102^{-} overtone stretch vibration of the H2O moiety. c) The H₂O is photolyzed by a laser at 193 nm, a color which efficiently breaks apart vibrationally excited water while minimizing background from photolysis of the ground state. The time delay between the IR and photolysis lasers can be varied to probe predissociation of the metastable cluster state. d) OH photolysis products are detected by laser induced fluorescence following excitation by a tunable 308 nm pulse.

Brewster windows must be replaced with calcium fluoride in order to minimize

absorption of the 193 nm pulse. Due to the mm-scale diameter for these beams, OH

products are expected to fly out of the probed region on a microsecond timescale, meaning that the time delay between photolysis and probe lasers can safely be set to several tens of nanoseconds to allow the PMT to recover from the flash of scattered UV radiation from the excimer beam. Even though photolysis cross sections are at least an order of magnitude greater for vibrationally excited versus ground state water molecules, this still leaves a significant OH background which is observed even in the absence of any infrared laser light. Since these background radicals originate mostly from water monomers, they are not at all specific to the presence of cluster species and therefore must be removed from reported data. This is done by running the infrared laser at 5 Hz while all other experimental components are pulsed at 10 Hz. Then, the Labview data taking program automatically subtracts adjacent data points in order to obtain a background-free spectrum.

Infrared laser light is produced by a Laser Vision optical parametric oscillator (OPO) pumped by a Nd-YAG laser as shown in Fig. 2.17. 1064 nm laser light exits the YAG before entering the OPO where it is immediately doubled to make a 532 nm green beam. This beam enters a grating-containing oscillator cavity in which KTP crystals





Figure 2.17 Optical parametric oscillator (OPO) laser used to produce tunable infrared light. A doubled YAG (532 nm) beam is introduced to a cavity where it is converted into an idler frequency (resonant with a cavity) and a signal beam (which is removed by specular reflection from the diffraction grating.

consume photons at 532 nm (pump) and output two photons (signal and idler) whose energies add up to that of the green pump photon. The grating and output coupler retroreflect the signal beam while the idler exits through the output coupler before leaving the laser. This system is equipped with an amplifier stage where the idler beam and some 1064 nm light is sent through four KTA crystals to produce more idler light by optical parametric amplification. However, at the wavelengths of interest for these studies (~ 1.4 μ m), the amplifier stage tends to actually attenuate the idler, so it is physically removed from the beam path. The device is capable of producing about 15 mJ

of light at 1.4 µm, which is near the resonance for first harmonic excitation of the OH stretch in H₂O. Tuning is done on the accompanying computer which moves the grating and nonlinear crystal angles with stepper motors. The position of the grating ultimately controls the value of the output idler frequency, and the angular positions of the KTP crystals are chosen to ensure phase matching to produce maximum OPO power. The laser must be periodically recalibrated for maximum power by manually tuning through the desired frequency range while recording optimal (maximum idler power) positions for all crystals. This information is then fit to a third order polynomial and entered into the OPO controller software for velocity control of the stepper motors. Frequency calibration of this laser is done using a low pressure H₂O cell containing a microphone for acquiring optoacoustic spectra during each IR scan. While the peak intensities of such a scan are of limited use, the frequencies are compared with expected values in the HITRAN H₂O database.¹⁰ Linear interpretation between such peaks results in an accurate frequency measurement compared to the 0.2 cm⁻¹ linewidth of the laser radiation.

Photolysis at 193 nm is done with a Lambda Physik Lextra 50 excimer laser running on metastable argon fluoride. The laser head is filled with 65 mbar of 10% F_2 in He. 250 mbar of Ar, and 2700 mbar of "Ne-70" (70% Ne, 30% He), and the discharge voltage is typically set to 24 kV. Under these conditions, approximately 100 mJ of UV light is produced at the laser output, but due to significant losses from dichroic mirrors, focusing lenses, and travel through air, only about 10 mJ is actually focused to the inside of the chamber. Under normal operating conditions, the inside surface of the output coupler must be cleaned every few weeks due to the formation of a white residue which seems to originate from the discharge source. To do this, the laser head must be emptied, purged, and opened. The caked-on white residue is removed by hard scrubbing with a fine abrasive powder such as Vienna chalk. Upon replacing the output coupler, the laser head must then be evacuated, repassivated, and refilled before use. Passivation is done by filling first with 2600 mbar of He and running at 16 kV and 15 Hz for 10 minutes. Next, the head is loaded with 100 mbar of 10% F_2 in He and 2000 mbar of He, and the discharge is run at 24 kV, 10 Hz for 15 minutes.

When both IR and probe lasers are fixed on particular transitions of an H₂Ocontaining cluster and OH respectively, the time delay between vibrational excitation and photolysis can be varied in order to obtain a predissociation spectrum. Given the approximately 8 ns time duration of these pulses, this procedure allows measurement of LIF signal versus time delay with a resolution of about 5 ns. Such a process can be used to discover the rate for predissociation of a cluster from a metastable initial state where ~ 7250 cm⁻¹ of internal energy is present in the water monomer inside a cluster which is only bound by an energy on the order of 30 cm⁻¹. Photolysis of a free, predissociated water molecule leads to a very different OH distribution than does photolysis of H₂O bound in a cluster. Therefore, variation of IR-excimer time delay tends to show an exponential change in LIF intensity between that observed for photolysis of bound water and that of free H₂O, as shown in Fig. 2.18. For short-lived complexes, analysis of these



Figure 2.18 Direct observation of predissociation lifetime in oH_2-oH_2O . This is obtained by varying the time delay between the infrared excitation and the photolysis pulse while examining a specific cluster transition and a particular OH level. The measured lifetime of 15(2) ns is large compared to the instrument response function of 8 ns as determined by observing H₂O monomer lines (inset).

results is somewhat complicated by the finite temporal resolution associated with the nanosecond laser pulses in use. However, this can be mitigated by deconvoluting the observed signal from a Gaussian which is used to describe the overlap between the two beam. The following function is employed:

$$f(t) = S_0 + \left(\frac{s_f - s_0}{2}\right) \left\{ 1 + erf\left(\frac{t - t_0}{\sigma}\right) - e^{\frac{(\tau^2/4\tau^2)^2}{4\tau^2}} e^{-(t - t_0)/\tau} \left[1 - erf\left(\frac{\sigma}{2\tau} - \frac{t - t_0}{\sigma}\right) \right] \right\}$$
(2.1)

where S_0 is the background signal level, which is seen when the photolysis laser fires before vibrational excitation, S_f is the signal after predissociation, and t_0 is the time delay resulting in a signal halfway between these extremes. σ is a parameter describing the instrument response function arising from the ~ 8 ns duration of both pulsed laser beams; it is found by looking at photolysis of water monomer, a system which does not predissociate. Finally, τ is the predissociation lifetime, which is extracted from the data by a least squares fit. Note that this fitting procedure is only appropriate in the case where the LIF laser is parked on a transition from an OH level whose production is enhanced after predissociation. In the clusters studied here, $N_{OH} = 8$ levels meet that criterion.

2.4 Crossed Jet Reactive Scattering

As shown schematically in Fig. 2.19, LIF detection of OH (or OD) molecules (see section 2.1) is also used as a method to observe the result of reactive scattering collisions between fluorine atoms and water molecules to produce HF + OH(D). In short, F_2 molecules, seeded in helium, are converted to F atoms in a pulsed discharge supersonic beam source. At the same time, a water-containing helium molecular beam is crossed with the fluorine one at 90° and 5 cm from each valve, leading to a collision energy of 6(2) kcal/mol. After



Figure 2.19 Reactions between F and H_2O are carried out in a crossed molecular beam experiment. F2 is converted into its atomic form with a -1 kV pulsed electrical discharge at the throat of the expansion. Product OH molecules are detected by laser induced fluorescence at the intersection of the two jets. Also shown is the dynode control which shuts off the PMT during the discharge pulse.

the fluorine atom has abstracted a hydrogen from the water molecule, OH is produced in some rotational and electronic state which is then detected by LIF. This experiment is carried out in the same 96 L cubical chamber as that used for water cluster studies. The vacuum system is also essentially the same as that used in the cluster experiments with typical base pressure of 10^{-6} Torr.

Molecular fluorine is purchased in cylinders where it is already mixed with He at a ratio of 10% F_2 to 90% He. This tank is connected to the stagnation region of a general valve with a stainless steel needle valve in between in order to adjust pressure by controlling flow. Choice of tubing is crucial since sintered teflon tends to trap H₂O

which degases and produces an OH background after the discharge. Extruded PTFE tubing was found to be much freer of background moisture. The backing pressure is typically set to 50 Torr $(1.6 \times 10^{16} \text{ molecules/cm}^3)$, and the value is opened for approximately 1 ms. As the hydrogen-fluorine mix expands through a 400 μ m oriface into the vacuum chamber, it travels through an electrical discharge driven by a transient high voltage pulse. This pulse is created by a home made push-pull circuit (appendix A.2) which supplies ~ 800 V and 200 mA through a 1 k Ω ballast resistor in line with the discharge gap. The electronics are wired as shown in Fig. 2.19 so that the cathode is formed by a pair of knife edges spaced to produce a miniature slit expansion with a spacing of ~ 1 mm. The body of the steel general valve forms the anode so that electrons flow upstream through the exiting gas, leading to a more stable discharge than can be obtained by wiring in the opposite direction with respect to gas flow. This is likely due to the relative ease cations to flow in the direction of gas motion while the negatively charged electrons flow upstream relative to the opposite situation where cations attempt to move against the direction of mass transport. In between cathode and anode lies a glass insulator with 1.5 mm thickness. These insulators can be produced by drilling a 1 mm hole through a microscope slide, but they must be periodically replaced because the discharge will slowly damage and blacken the edges of the hole.

Water-helium mixtures are produced in an ice-cooled bubbler similar to that used in the water cluster experiments in section 2.2. The resulting H_2O / He gas flows through a separate manifold and a needle valve before entering a piezoelectric actuated valve¹¹ with total backing pressure of 200 Torr (6x10¹⁸ molecules/cm3). Care must be taken to avoid electrical breakdown to the piezoelectric drum since a single discharge event is

capable of ruining it. Therefore, it is important to always turn off the high voltage source when the valve is being pumped down. Internal metal surfaces are painted with Corona Dope high voltage insulation in order to further suppress breakdown through the watercontaining backing gas. Experiments on $F + D_2O$ are performed with the same setup after extensive passivation with respect to $H \rightarrow D$ exchange, where a D₂O-containing mixture is contained the valve and manifold over the course of several days. The degree of passivation can be immediately seen in the small OH / OD background which can be seen in the absence of flourine collision partners and originates from background H₂O / D₂O in the discharge.

Care is taken to ensure that single collision conditions are obtained so that each fluorine atom is likely to collide with at most one atom or molecule during its flight through the detected region of the experiment. At the same time, it is important to ensure that background gas pressures are low enough that there is a low probability for OH products to collide with anything before being interrogated by the probe laser beam. Both of these criteria are met by ensuring that gas pressures are sufficiently low in this crossed-beam experiment. For example, as the H₂O / He jet travels x = 5 cm from the stagnation region, its density drops from its stagnation region value of $n_0 = 6x 10^{16} \text{ #/cm}^3$

(where "#" stands for "molecules") down to $n(x) \approx 0.24 n_0 \left(\frac{d}{x}\right)^2$. Given that d, the

aperture diameter, is equal to ~ 500 μ m for the jet source valve, a density of n(5 cm) ~ 1.4×10^{12} #/cc of mostly He atoms is expected in the collision region as potential targets for the incident F atoms. For a hard sphere collision cross section of $\sigma \sim 5 \times 10^{-15} \text{ cm}^2$, the

fluorine collision probability is $P_{coll} \sim \sigma_{H.S.} n_{He/H_2O} l_{ravel}$, which comes out to $P_{coll} \sim 4 \%$, i.e. safely in the single-collision regime.

A collision of F seeded in He with H₂O also seeded in He at an angle of 90° is characterized by a center of mass kinetic energy (E_{COM}) of 6 kcal/mol. However, these unskimmed molecular beams collide with a rather wide range of E_{COM}, and therefore OH products from high E_{COM} geometries (i.e. places where the two molecules have more of a head on collision) feature some finite probability of arriving in the LIF detection region which lies at the 90° collision point between the centerlines of the two beams. To gain a higher order understanding of the range of collision geometries under consideration, Monte Carlo simulations¹² are employed in which incident beam angular distributions are modeled by $\cos^{n}(\theta)$ functions. From this analysis, the likelihood that an OH product is the result of a collision at a certain E_{COM} can be found from the probability for collision at a specific point in space times the probability that the resulting OH molecule will be found within the 0.16 cm³ detection region at the time of laser pulse firing. Such an analysis depends on some assumptions about the angular distribution of reactively scattered OH molecules, but it was found to be insensitive over a rather large range of possibilities. For example, less than a 10% change in both the average and the standard deviation of the collision energy distribution is observed when the molecular frame scattering distribution is changed from isotropic to $cos(\theta)$. On the basis of this Monte Carlo analysis, the effective collision energy is found to have an average of 6 kcal/mol with a standard deviation of 2 kcal/mol.

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