#### REACTIVE COLLISIONS IN HELIUM NANODROPLETS STUDIED WITH HIGH RESOLUTION INFRARED SPECTROSCOPY

by

#### ALEXANDER MICHAEL MORRISON

(Under the direction of Professor Gary E. Douberly)

The work presented in this thesis is centered around the use of infrared lasers to characterize molecular clusters, hydrocarbon radicals and products of combustion reactions embedded in liquid helium droplets. Much of the work involves the development and automation of a high power, infrared optical parametric oscillator (OPO). The OPO is capable of producing >1 Watt of continuously tunable idler output between 2.2 and 4.6  $\mu$ m. The developed hardware and software allows for several hundred wavenumbers of efficient, automatic, continuous tuning of the idler wave with an absolute frequency resolution of ±20 MHz.

The rotational and vibrational relaxation dynamics of the  $CH_3$  radical are studied by probing the  $\nu_3$  asymmetric stretch, where five transitions are observed. The linewidths of these transitions in the ro-vibrational spectrum vary considerably and are rationalized in terms of the anisotropy in the He-CH<sub>3</sub> potential energy surface. This anisotropy couples the molecular rotation to the collective modes of the droplet with some rotational states being coupled more efficiently, leading to reduced lifetimes and broadened linewidths.

Highly exothermic reactions (~100-150 kcal/mol) have been observed to take place in the cold, dissipative environment of the helium droplet. However, it was not entirely clear whether the reaction products remain in the droplets or are expelled. In this thesis, the exothermic reaction,  $CH_3 + O_2$ , was studied. This exothermic reaction is known to lead barrierlessly to the methyl peroxy radical,  $CH_3OO$ , releasing ~30 kcal/mol of bond energy that is dissipated by the evaporation of helium atoms. In this study, the infrared spectroscopy shows that the reaction products are still present in the droplet and are cooled to the droplet temperature of 0.37 K.

INDEX WORDS: Helium Nanodroplet, Infrared Spectroscopy, Combustion Intermediates, Automation of Lockheed Martin Aculight OPO

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by

Alexander Michael Morrison

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by

Alexander Michael Morrison

Approved:

Major Professors: Gary E. Douberly

Committee: N

Michael A. Duncan Geoffrey D. Smith

Electronic Version Approved:

Maureen Grasso Dean of the Graduate School The University of Georgia December 2012

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### Chapter 1

### Introduction

Helium nanodroplet isolation (HENDI) has recently emerged as the ideal matrix isolation technique to study embedded molecules and molecular clusters with infrared spectroscopy.<sup>1–3</sup> Liquid helium is a weakly perturbing solvent which allows the rotational transitions of embedded molecules to be described using only a slightly modified gas-phase Hamiltonian and the vibrational transitions to be compared directly with theory. The high spectroscopic resolution is comparable to that achieved in the gas phase and evaporative cooling of the droplets to 0.4 Kelvin maintains an environment colder than other solid matrices. Thus, the benefits of both traditional matrix isolation and gas phase techniques are combined in HENDI.

The first spectroscopic studies of molecules in helium nanodroplets occurred in 1992 by Goyal et al.<sup>4</sup> In a continuation of experiments exploring molecules solvated in and on the surface of rare gas complexes,<sup>5–8</sup> they probed the  $\nu_3$  vibrational mode of SF<sub>6</sub> in helium. The vibrational bands were much narrower than what they had obtained for the heavier rare gas complexes and it was immediately apparent that helium was different. A few years later, Fröchtenicht et al. used a diode laser and obtained the first rotationally resolved spectrum of a helium solvated molecule.<sup>9,10</sup> In agreement with theoretical predictions, it was determined that  $SF_6$  is solvated near the center of the helium droplet.<sup>11,12</sup> Furthermore, the *B* rotational constant of  $SF_6$  was found to be a factor of approximately three smaller than in the gas phase. This reduction was found to be caused by the adiabatic following of eight helium atoms that essentially rotate with the molecule, adding to its effective moment of inertia. The work by Fröchtenicht et al.<sup>10</sup> also provided the first experimental measurement of the temperature of a helium droplet at 0.37 K, a value that is near the theoretical estimate of 0.32 K.<sup>13</sup>

Subsequent studies by the group of Toennies on the OCS molecule in <sup>3</sup>He and <sup>4</sup>He droplets revealed a spectrum that was not rotationally resolved in <sup>3</sup>He.<sup>14</sup> This suggested that the superfluid character of <sup>4</sup>He permits the molecules to rotate with longer coherence times, which provides a spectrum with rotational structure. A gap in the phonon density of states at low energies (below  $5 \text{ cm}^{-1}$ ) in <sup>4</sup>He droplets makes the coupling between molecular rotation and the elementary excitations of the droplet weak. This weak coupling gives rise to the long rotational lifetimes. For the case of <sup>3</sup>He, there is no phonon gap, which results in stronger coupling and gives rise to shorter lifetimes. In the experiments by Toennies et al.,<sup>14</sup> it was discovered that droplets larger than approximately 60 <sup>4</sup>He atoms were required for the onset of superfluidity.

#### 1.1 Infrared Spectroscopy

Helium is completely transparent to photons below  $\sim 160,000 \text{ cm}^{-1}$  which allows embedded impurities to be probed using infrared spectroscopy. Using both continuous wave  $(\text{cw})^{3,4}$  and pulsed lasers,<sup>15</sup> infrared spectra of molecules and clusters embedded in helium nanodroplets have been obtained. In the case of cw lasers, phase sensitive detection is used, which requires the laser beam to be amplitude modulated resulting in a large duty cycle. Up until now, low-power lasers were the only source of continuously tunable infrared light but are only useful for observing transitions with very strong oscillator strengths, such as the 10  $\mu$ m absorption of SF<sub>6</sub>.<sup>16</sup> With the introduction of the Lockheed Martin Aculight Argos Model 2400 periodically-poled Lithium Niobate (PPLN) singly-resonant cw optical parametric oscillator (OPO), there is now a high power (>1 Watt) infrared laser source that can tune continuously from 2.0 to 3.9  $\mu$ m. In Chapters 3 and 4, the theory detailing the laser is discussed, as well as the automation process and a user's guide is provided for the developed software.

#### 1.2 Aggregation-Induced Dissociation

Apart from the ability to obtain rotationally resolved spectra of embedded impurities in helium droplets, HENDI provides the optimal matrix for step-by-step aggregation of molecular clusters where exotic complexes can be formed, stabilized, and interrogated. A controllable pickup process that is dictated by Poisson statistics allows for the formation of desired cluster sizes. In this work, water-solvated HCl is studied in an attempt to determine how many water molecules it takes to to form a solvent-separated ion pair,  $H^+(H_2O)_nCl^-$ . A previous study of HCl and  $H_2O$  clusters in helium droplets determined that four water molecules were required to completely dissociate HCl.<sup>17</sup> Although this study produced astonishing results and resulted in a paper in *Science* magazine, the results were incorrectly interpreted. Chapter 5 discusses these results and provides the correct assignment to the infrared transition thought to arise from the dissociated  $H_3O^+(H_2O)_3Cl^-$  cluster.

#### **1.3** Rotational Dynamics

As mentioned above, there exists a gap in the phonon density of states at low energies (below 5 cm<sup>-1</sup>) in <sup>4</sup>He droplets which makes the coupling between molecular rotation and the elementary excitations of the droplet weak. This allows molecules in the "heavy" rotor

limit  $(B < 1 \text{ cm}^{-1})$  that fall within the phonon gap to have long rotational coherence times and provides the associated spectrum with narrow linewidths. The energy difference between rotational states for "lighter" molecules exceeds this so called phonon gap and transitions to these states couple to the bulk excitations of the helium droplet efficiently and reduce the natural lifetime of the excited state. The resulting transition in the spectrum is much broader than the states that cannot efficiently couple their energy to the droplet indicative of a reduced rotational lifetime. Examples of this effect have been observed in methane  $^{18}$ where the R(1) transition ( $\nu=1$ , J=2) can cool to  $\nu=1$ , J=0; an energy gap of approximately  $30 \text{ cm}^{-1}$  which is enough to couple to the bulk excitations of the helium. Much effort has been put forward to understand how embedded molecules transfer energy to the droplet and have now begun to plot the rotational energy spacing of certain transitions versus the linewidth in an attempt to map out the excitations of the droplet.<sup>1</sup> Although the increasing linewidth with increasing rotational energy spacing shows a distinct relationship with the energy of the roton band in bulk helium,<sup>1</sup> it is difficult to compare results obtained from different molecules. Many factors contribute to the coupling of molecular rotation to the liquid helium environment and are different for different molecules. In this work, the  $\nu_3$ transition of a "light" rotor, CH<sub>3</sub>, is investigated because it has excited rotational states of the same symmetry with energy spacings of  $\sim 20 \text{ cm}^{-1}$ . In Chapter 6, the ro-vibrational spectrum of the  $\nu_3$  band of the methyl radical is presented and the possible relaxation pathways that result in varying linewidths in the spectrum are discussed.

#### 1.4 Reactions in <sup>4</sup>He Droplets

Helium droplets are useful in stabilizing pre-reactive species as well as products of reactions. The earliest studies involving reactions in helium nanodroplets were mass spectrometer experiments that employed electron-beam ionization.<sup>19,20</sup> Observation of bare ionic fragments of the embedded neutral species,  $SF_6$  in this case, reveal that many ion-molecule reactions are occurring. In a more recent study of ion-molecule reactions in helium droplets, ion products from the reaction of He<sup>+</sup> with embedded D<sub>2</sub>, N<sub>2</sub>, and CH<sub>4</sub> were observed in a mass spectrometer equipped with an electron impact ionizer.<sup>21</sup> These experiments showed that the rapid quenching of the internal degrees of freedom due to the very low (0.37 K) temperatures provided by helium droplets has a profound effect on the secondary reactions and can even stabilize intermediate transient complexes. This trapping of intermediate complexes allows for the study of these elusive compounds and in future experiments, energy can be pumped into the system to initiate the reaction and then the products could be studied downstream spectroscopically.

In the pioneering work by Vilesov et al.<sup>22</sup> the reaction  $Ba + N_2O \rightarrow BaO^* + N_2$  was observed to take place inside the helium droplet as well as on the surface. This exothermic reaction (~95 kcal·mol<sup>-1</sup>) has a large chemiluminescent yield making the detection of the reaction products rather straightforward. The surface channel reaction displays a broad feature in the spectrum from  $\lambda$ =400-600 nm and corresponds to hot products ejected from the droplet and radiating in the gas phase. Structure in the spectrum beyond 550 nm corresponds to the chemiluminescence of BaO\* after being cooled by the surrounding helium. Interestingly, upon the addition of Xe atoms, the surface reaction channel vanishes and the emission spectrum shows only the vibrational progression of sharp lines indicative of the vibrationally cooled BaO\* molecule prior to laser excitation.

Magnesium,<sup>23</sup> aluminum,<sup>24</sup> and silicon atoms<sup>25</sup> have been collided with molecular oxygen in helium nanodroplets and have shown strong evidence that the reaction occurred. Unlike the work by Vilesov et al.,<sup>22</sup> the products for the reactions with aluminum and silicon were not detected spectroscopically. Instead, the exothermic reaction ( $\sim$ 100-150 kcal·mol<sup>-1</sup>) leads to an evaporation of a significant number of helium atoms (7000-10000) from the droplet and the pressure of atomic helium is monitored in the reaction chamber to signify that the reaction occurred. Also, the products of the reaction were observed in a mass spectrometer. However, for these experiments, the product molecules, MgO<sub>2</sub> and SiO<sub>2</sub>, were not observed in the mass spectrometer. It was concluded from these experiments that the product molecules were expelled from the helium droplets upon reaction, thus making future spectroscopic investigations impossible. Alkali metal (Na, Cs) clusters have been shown to react with water molecules in helium droplets, as well.<sup>26</sup> These experiments revealed that Cs clusters react chemically with water while Na clusters form van der Waals complexes. In Chapter 7, the oxidative addition reaction of CH<sub>3</sub> with O<sub>2</sub> is investigated. We observe the stable trapping of the CH<sub>3</sub>OO radical even though the product molecule ion, CH<sub>3</sub>OO<sup>+</sup> was not observed in the mass spectrometer.

### Chapter 2

### Methodology

Liquid helium droplets are formed in a cryogenic nozzle expansion of high purity helium gas into vacuum through a small orifice. There are three distinct regimes for helium droplet production; subcritical, critical, and supercritical. Subcritical expansions occur when droplets condense in the high pressure region of the expansion and cool via evaporation as the pressure in the expansion falls below the droplet's equilibrium vapor pressure. These expansions correspond to nozzle temperatures of  $\sim 10-20$  K for a stagnation pressure of 20 bar and result in droplets with sizes up to 10<sup>4</sup> helium atoms. Supercritical expansions are produced when the nozzle temperature is sufficiently cold (<10 K) to allow for the formation of liquid helium in the nozzle. The droplets are then produced by the breaking of the liquid helium jet and results in droplets made of up to 10<sup>7</sup> helium atoms. Critical expansions occur between these two regimes, resulting in a droplet beam that is hard to characterize. All experiments described in this dissertation utilize a helium droplet beam that was formed by a supersonic, subcritical expansion of <sup>4</sup>He atoms.

Droplets made of <sup>4</sup>He atoms evaporatively cool to  $\sim 0.37$  K and the rate of evaporation below this temperature is negligible on the time-scale of the droplet flight time through the apparatus.<sup>13</sup> For droplets composed of <sup>3</sup>He atoms, the higher zero-point energy character



Figure 2.1: Schematic diagram of the helium nanodroplet spectrometer instrument illustrating the four stages of the experiment.

allows the droplets to cool to ~0.15 K.<sup>13,27</sup> In our spectrometer, shown schematically in Figure 2.1, droplets are formed by the continuous free jet expansion of 99.9995% high purity <sup>4</sup>He gas through a 5  $\mu$ m diameter pin-hole nozzle. Therefore, droplets and the subsequent spectroscopy involving <sup>3</sup>He atoms will not be discussed further. Both cw<sup>1,3</sup> and pulsed<sup>15</sup> nozzles can be used in the expansion. However, all experiments described in this work utilize cw droplet beams. Typically, the backing pressure of the helium gas is held between 20 and 30 bar with the temperature of the nozzle ranging between 14 and 24 K. With these nozzle conditions, droplets with an average size between 1000 and 10000 helium atoms are produced.<sup>28,29</sup> The droplet sizes follow a log-normal distribution, and the sizes can be obtained from published scaling laws.<sup>28</sup> As an example, Figure 2.2 shows a mean droplet size of 8200±1100 obtained for conditions 26.5 bar, 14 K and 5  $\mu$ m, assuming ±0.5  $\mu$ m uncertainty in the nozzle diameter. The droplet size distribution is fairly broad and at a given mean droplet size there is a range of droplet sizes present in the beam.<sup>1</sup> Having



Figure 2.2: The droplet size uncertainty associated with a  $\pm 0.5 \ \mu m$  uncertainty in the nozzle diameter is a constant 27.5 % of the mean value for all nozzle temperatures in this range. It is 55.8 % of the mean droplet size for a  $\pm 1.0 \ \mu m$  nozzle diameter uncertainty.

the ability to vary the droplet size is an extremely useful tool. For example, two or more molecules or atoms can react exothermically inside of the droplet, however, the droplets must be large enough to accommodate the heat of reaction of the complexes without losing all of the helium to evaporation. The complex must still be solvated in helium for spectroscopic interrogation.

About 1 cm downstream from the nozzle, the expansion is skimmed by a 0.4 mm diameter conical skimmer to form a well-collimated droplet beam that passes into a differential pumping chamber. In this chamber, droplets are doped with the species of interest using the "pick-up" technique.<sup>30,31</sup> First shown as a successful method for doping rare-gas clusters,<sup>5–7</sup> the "pick-up" technique involves passing the helium droplet beam through a "pick-up" chamber where the pressure of gas-phase atoms or molecules is controlled so only the desired number are captured. By simply varying the pick-up cell pressure, the average number of molecules or atoms picked up per droplet changes. This pick-up process obeys Poisson statistics and has been discussed in detail previously.<sup>2,32</sup>

For the experiments presented in this dissertation, the pick-up cells, shown in Figure 2.1, take on two different forms. A simple gas cell is used when doping droplets with molecules that are stable at room temperature. With a pick-up cell length of 10 cm and droplets in the size range of 1000-5000 atoms, a pressure of approximately  $10^{-6}$  torr will permit the pick-up of only one molecule or atom per droplet, on average.<sup>20</sup> For the production of methyl radicals, a homemade pyrolysis source is used and is shown in Figure 2.3. This source is built using the standardised vacuum load-lock system<sup>1,33</sup> which allows it to be easily introduced into and removed from the instrument. It consists of a 72 cm long quartz tube with an outer diameter of 6 mm. The tip of the quartz tube is wrapped with 0.25 mm thick tantalum wire that is connected to two copper electrodes for resistive heating. The copper electrodes are water cooled and the tip of the quartz tube can reach temperatures of up to 1800 K.<sup>33</sup> The heated quartz tube is separated from a precursor reservoir by a fine metering valve. The precursor used to generate methyl radicals is di-tert-butyl peroxide (DTBP). When the tip of the quartz tube is heated to near 700 K, DTBP fragments into two CH<sub>3</sub> radicals and two (CH<sub>3</sub>)<sub>2</sub>CO molecules.

The idler beam output from a continuous wave Infrared Optical Parametric Oscillator (OPO) (Lockheed-Martin Aculight) is used as the vibrational excitation source. The tuning and calibration of this IR-OPO system is described in the following chapter. The OPO output is amplitude modulated with a mechanical chopper, and the ion signal is processed with a lock-in amplifier, which is referenced to the chopper frequency. There exists two



Figure 2.3: A schematic diagram of the pyrolysis source used to generate methyl radicals from the precursor molecule, di-tert-butyl peroxide (DTBP).

methods of overlapping the IR laser beam with the helium droplet beam and can be seen in Figure 2.1. The infrared laser can either be introduced through a window in the mass spectrometer and overlapped coaxially with the helium droplet beam or a multipass cell can be used to cross the droplet beam with approximately 50 laser passes. In the latter case, two parallel, stainless steel electrodes are positioned orthogonal to the multipass cell such that a static dc electric field can be applied to the laser/droplet beam interaction region.<sup>1</sup>

The vibrational excitation of helium solvated molecular dopants followed by vibrational energy relaxation leads to a laser induced depletion of the droplet beam intensity. This reduction of the average geometric droplet cross section results in a reduction in the ionization cross section as measured by a quadrupole mass spectrometer equipped with an electron impact ionizer. Upon electron impact, a He<sup>+</sup> ion is produced in the droplet, which rapidly leads to the formation of  $(He)_n^+$  cluster ions and the fragmentation of the droplet.<sup>34</sup> Figure 2.4 shows an example of a mass spectrum of droplets doped with HCl and H<sub>2</sub>O molecules. In this spectrum, we can see a series of peaks separated by 4 amu which correspond to the  $(He)_n^+$  ions. Alternatively, charge transfer<sup>35</sup> from He<sup>+</sup> to the solvated molecular cluster leads to the formation of  $(HCl)_n^+$ , H<sup>+</sup>(HCl)<sub>n</sub>, H<sup>+</sup>(H<sub>2</sub>O)<sub>n</sub>, and H<sup>+</sup>(HCl)<sub>m</sub>(H<sub>2</sub>O)<sub>n</sub> ions. These can be seen as the more intense features in the mass spectrum in Figure 2.4.

Two different schemes for detecting the ion signal attenuation exist; either the mass spectrometer is operated in the so-called "rf-only" mode, in which all masses greater than 6 u are allowed to pass to the detector, or the dc voltage on the quadrupole is fixed to allow the transmission of a single mass/charge ratio. The latter detection scheme is used to discriminate between the spectral signatures of different isotopomers or cluster sizes. An IR spectrum is obtained as a depletion signal in specific mass channels by fixing the quadrupole mass spectrometer to a particular mass to charge ratio or operating in "rf-only" mode while scanning the IR-OPO. Additionally, Optically Selective Mass Spectra (OSMS) are obtained by scanning the quadrupole while the OPO frequency is fixed to the peak of a particular transition in the infrared spectrum.<sup>36,37</sup> Since the OPO is amplitude modulated, the OSMS corresponds to the difference in the mass spectrum with and without the OPO present. In other words, the OSMS represents the mass spectrum of only those droplets that contain clusters that have been resonantly excited by the OPO.



Figure 2.4: Mass spectrum of helium droplet beam (chopping beam and processing ion signal with lock-in amplifier) shows peaks at every mass, with the protonated water series (19,37,55,73,91) dominating; but, there are clearly peaks at masses that must contain chlorine, for example mass 72 is most likely  $(\text{HCl}^{35})_2^+$ . This mass spectrum illustrates the diversity of cluster species that must be present in the droplet beam.

### Chapter 3

# Automation of an Aculight cw-Optical Parametric Oscillator

We report the automation of a continuous wave, singly resonant optical parametric oscillator (Lockheed-Martin Aculight ARGOS 2400-SF-15). This commercially available OPO is capable of producing >1 Watt of continuously tunable idler output between 2.2 and 4.6  $\mu$ m. An algorithm based on the feedback from a high accuracy wavemeter is implemented to synchronize three separate OPO tuning elements; the translation of a fan-out type PPLN crystal, the rotation of an intracavity etalon, and the continuous tuning of the pump and idler wavelengths via piezoelectric strain of the tunable fiber pump laser. This allows for several hundred wavenumbers of efficient, automatic, continuous tuning of the idler wave. Continuous feedback from the wavemeter limits the absolute frequency resolution to ±20 MHz. The broad, automatic tuning of the OPO is demonstrated via its implementation as a probe laser for the infrared action spectroscopy of methanol solvated in helium nanodroplets.

#### 3.1 Introduction

Lockheed Martin Aculight has made commercially available a singly resonant (SR), continuous-wave (cw), optical parametric oscillator (OPO) that is capable of producing >1 Watt of continuously tunable idler output between 2.2 and 4.6  $\mu$ m.<sup>38,39</sup> This OPO is turnkey in virtually all regards, except that it cannot be continuously tuned over a frequency range greater than ~100 GHz without user intervention. We present in this report a simple algorithm for hands-free, broad wavelength tuning of the Aculight OPO, along with the hardware and software necessary for its implementation, which we have independently developed.

These mid-infrared (IR) coherent light sources are now being applied in a broad range of applications,<sup>39–42</sup> including high-resolution laser spectroscopic methods that benefit from high output power, such as photo-acoustic spectroscopy for trace gas detection<sup>43–45</sup> or any technique classified as an "action" or photo-dissociation spectroscopy.<sup>3</sup> The sensitivity associated with gas phase molecular beam "action" spectroscopic methodologies that aim to probe the vibrational spectra and dynamics of molecular clusters have in the past been limited by the low fluences associated with the available lasers in this wavelength region, such as lead salt diode lasers or color-center lasers. The commercial cw-SR-OPO system discussed here is capable of producing greater than 100 times the output power of a color-center laser at 3  $\mu$ m, which vastly expands the range of molecular systems that can be probed with these methods in this wavelength region.

Despite the fact that cw-SR-OPOs based on non-linear frequency conversion in quasiphase-matched periodically poled lithium niobate (PPLN) were demonstrated nearly two decades ago,<sup>46,47</sup> the feasibility of providing such a system commercially has until recently been limited by the availability of a robust and turnkey multi-Watt, cw, tunable pump laser operating near 1064 nm. With an output coupler in an SR-OPO bow-tie cavity,<sup>48</sup> it is now well established that multi-Watt output in the mid-IR can be achieved from PPLN. The drawback of this approach is that the high oscillation threshold associated with this configuration demands a cw pump laser capable of producing 10-15 Watts. Provided a suitable multi-Watt cw pump source can be implemented, a singly resonant OPO (where only the signal wave is resonated) can be realized that provides several advantages over doubly or triply resonant designs, such as much higher output powers, better stability, and ease of alignment and tuning. Moreover, SR-OPOs do not require the expensive cavity locking electronics associated with resonating both the pump and signal waves. Nevertheless, the first commercial cw IR OPOs were based on these multiply resonant configurations due to the lack of a stable yet tunable pump source suitable for a cw-SR-OPO.

The development of all-in-fiber based multi-Watt pump lasers vastly improved the prospects for a commercial cw-SR-OPO system.<sup>38</sup> Indeed, coupling an all-in-fiber pump laser into a PPLN based cw-SR-OPO cavity is much simpler than and eliminates many of the problems associated with the through-space coupling of a high power solid-state pump laser.<sup>49</sup> An all-in-fiber pump laser coupled to a cw-SR-OPO provides a simple and robust system that provides broadly tunable wavelength coverage in the mid-IR without having to resort to the more complicated doubly or triply resonant OPO configurations. In this report, we describe the implementation of an automatic tuning algorithm developed for an all-in-fiber laser pumped cw-SR-OPO. Specifically, a Lockheed Martin Aculight (ARGOS Model 2400-SF-15) PPLN based cw-SR-OPO is used in conjunction with a helium nanodroplet isolation (HENDI) spectrometer to measure with high resolution the IR spectra of methanol between 2800 and 3200 cm<sup>-1</sup>.

#### 3.2 Experimental Set-up

A detailed description of the Aculight OPO (ARGOS 2400-SF-15) has been described elsewhere.<sup>38</sup> The OPO is pumped by an all-in-fiber based laser system in a master-oscillator power-amplifier configuration. The pump laser system consists of a cw Yb-doped fiber seed laser (1064 nm, 15 mW, <100 kHz bandwidth) (Koheras AdjustiK, Y10 PM PztM, NKT Photonics) coupled to a diode-pumped fiber amplifier (IPG Photonics, YAR-15K-1064-LP-SF) capable of generating 15 W at 1064 nm. The pump seed laser can be tuned either by temperature tuning or by strain variation of the fiber length, which is achieved by modulating the voltage applied to a piezoelectric transducer (PZT) element.

Figure 3.1 shows a schematic of this cw-SR-OPO system, in which a polarization maintaining fiber couples the pump laser emission directly into the OPO cavity. The 15 W, 1064 nm emission from the fiber reflects off two steering mirrors and into a bow-tie cavity. As the pump beam travels through a MgO doped PPLN crystal (maintained at  $\sim 60^{\circ}$ C), pump photons are converted into signal and the idler photons via optical parametric generation. The PPLN crystal is fabricated with a "fan-out" polling periodicity, resulting in an essentially linearly varying poling period along its width.<sup>50</sup> The signal wave is resonant, and the pump and idler beams make a single pass through the PPLN crystal before exiting the cavity. The presence of the output coupler (OC) in the cavity results in an oscillation threshold of approximately 6 W. Moreover, the OC allows as high as 3 W of idler and 5 W of signal to be extracted from the cavity when pumping with 15 W.<sup>48</sup> An intracavity etalon (ICE) mounted to a galvanometer acts as a loss mechanism for longitudinal cavity modes non-coincident with an etalon transmission fringe, which helps to maintain the single mode operation of the OPO. As discussed in detail below, the idler output can in principle be tuned continuously over several hundred wavenumbers by synchronizing three separate tuning elements: the translation of the fan-out PPLN crystal, the rotation of the ICE, and the continuous tuning of the pump seed laser wavelength via piezoelectric strain.

Figure 3.2 is a schematic of the OPO coupled to the HENDI spectrometer. The signal and pump beam are dumped immediately upon exiting the OPO module. The idler beam passes through a set of  $CaF_2$  windows, reflection ~20 mW from each surface for diagnostic



Figure 3.1: Schematic of the cw-SR-OPO pumped by an all-in-fiber laser in a MOPA configuration.

detection via a power meter, a Bristol Instruments Model 621A-IR wavemeter, and a 750 MHz free-spectral-range (FSR), Burleigh, Fabry-Perot (FP) interferometer. The wavemeter employs a Michelson interferometer-based design to measure the wavelength to an absolute accuracy of  $\pm 0.2$  ppm (e.g.  $\pm 0.0002$  nm at 1000 nm) with a repeatability of  $\pm 6$  MHz at 3  $\mu$ m. The main portion of the idler beam passes through a Glan-Taylor polarizer, which can be used to attenuate the power prior to it entering the spectrometer.

The HENDI apparatus shown in Figure 3.2 has been described in detail elsewhere,<sup>3</sup> and only a brief overview is given here. Helium droplets are formed by the continuous expansion of 99.9995% pure <sup>4</sup>He into vacuum through a 5  $\mu$ m diameter cryogenically cooled nozzle (15-25 K) with a stagnation pressure of 20 bar. This results in the formation of liquid helium nanodroplets (~ 10<sup>12</sup>s<sup>-1</sup>) consisting of ~ 4000 He atoms on average. The droplets cool by evaporation to 0.4 K as they leave the high-pressure region of the expansion.<sup>51</sup> The expansion is skimmed 1 cm downstream by a 400  $\mu$ m diameter conical skimmer. A few cm downstream from the skimmer, the droplet beam passes through a differentially pumped gas pick-up cell that contains methanol (CH<sub>3</sub>OH) vapor at ~ 3 × 10<sup>-6</sup> Torr. The pick-up process obeys Poisson statistics and varying the pick-up cell pressure changes the average number of methanol molecules picked up by the droplets.<sup>20</sup> For the spectrum presented here, the CH<sub>3</sub>OH pressure is kept low to suppress the pick-up of multiple molecules and the formation of methanol clusters within the helium droplets.

A quadrupole mass spectrometer (Extrel CMS) is used to measure the ion signal resulting from the electron impact ionization of the droplet beam. Vibrational excitation of the helium solvated CH<sub>3</sub>OH molecules followed by vibrational energy transfer to the solvent results in the evaporation of several hundred helium atoms per droplet (1 He atom per 5 cm<sup>-1</sup>). Therefore, vibrational excitation reduces the average geometric cross section of the droplets and hence the average droplet ionization cross section, which is detected as an attenuation of the integrated ion signal in the mass spectrometer. The idler beam is amplitude modulated



Figure 3.2: Experimental set-up of the cw-SR-OPO coupled to the HENDI spectrometer. (1) Seed laser. (2) Diode-pumped fiber amplifier. (3) cw-SR-OPO. (4) Beam dumps for the pump and signal beams. (5) CaF<sub>2</sub> beam splitters. (6) Power meter. (7) Wavemeter. (8) Fabry Perot scanning etalon. (9) Glan Taylor polarizer. (10) Optical chopper. (11). HENDI spectrometer. The asterisks indicate gold steering mirrors.

with an optical chopper at  $\sim 100$  Hz, allowing for lock-in detection of the laser induced depletion of the ion signal as the OPO idler wavelength is tuned.

The continuous measurement of the output from the idler beam diagnostics and mass spectrometer, along with the control of the three OPO tuning elements is achieved with National Instruments hardware and LabView software, the latter of which has been developed in this laboratory. Software has also been developed for the work-up of the experimental data via spectral reconstruction, as discussed below. All of this software is available from the authors upon request.

#### 3.3 Tuning Algorithm

The OPO tuning algorithm relies on the feedback from a high accuracy wavemeter, which measures the wavelength of the mid-IR idler beam. The continuous feedback from this wavemeter (Bristol Instruments 621A) limits the absolute frequency accuracy to  $\pm 20$ MHz, while the relative frequency calibration depends on the scan rate, but in principle is limited only by the wavemeter repeatability, which is advertised as  $\pm 6$  MHz at 3  $\mu$ m. If desired, a high finesse cavity, such as a 150 MHz FP etalon, can also be implemented for high precision relative frequency calibration, although this is not found to be necessary. The basis of the tuning algorithm is discussed with reference to Figure 3.3, which shows schematically the phase matching (PM) gain curve associated with the intracavity etalon (ICE), and the cavity resonator modes associated with the resonant signal wave within the bow-tie cavity. In principle, oscillation will occur only for the cavity mode that lies underneath both the ICE transmission and PM gain curves. As shown schematically in Figure 3.3, the FSR of the ICE is chosen to be broader than the PM gain curve such that only one cavity mode is ever above the oscillation threshold.


Figure 3.3: Schematic of the overlap of the PPLN phase matching (PM) gain curve (red), the intracavity etalon (ICE) transmission curve (black), and the cavity modes of the signal wave (blue). In general, only the central cavity mode would oscillate in this configuration of the PM and ICE curves.

The ICE consists of a 250  $\mu$ m thick piece of fused silica, which is anti-reflection coated for the signal wave. As the ICE is tilted, the signal wave hops to a non-adjacent longitudinal cavity mode. Each "cluster" hop corresponds to a change in idler frequency of ~30 GHz (Figure 3.4), which can be compared to the cavity FSR of ~500 MHz. The inability to hop to an adjacent cavity mode has been described to us a being due to some sort of "OPO inertia", which is almost certainly due to the low finesse of the ICE.<sup>43</sup> The FSR of the ICE is ~350 GHz, which is broader than the PPLN PM gain curve, ensuring single mode oscillation. For the purpose of broad wavelength scanning, the ICE tilt angle is varied over approximately two degrees, corresponding to the ~350 GHz FSR of the etalon. Furthermore, the range of angles is chosen such that the wavelength changes linearly with ICE tilt angle.

A homemade linear actuator system is used to translate the PPLN crystal. This linear actuator is shown in Figure 3.5, and the detailed design aspects and parts list for its construction is given in the following chapter. The actuator is designed to reside entirely outside the OPO tuning module so as to preserve the temperature stability built into the Aculight design, which is critically important for maintaining stable single-mode operation. The PPLN crystal has a linearly varying poling period (in a so-called "fan out" design).<sup>50</sup> Tuning the PPLN position results in discrete hops of the signal wavelength equal to one FSR of the etalon ( $\sim$ 11 cm<sup>-1</sup> for the idler). The mechanism for this is illustrated schematically in Figure 3.6. As the PPLN crystal is translated, the PM curve shifts with respect to the optimally phase-matched signal wavelength. If the ICE tilt angle is fixed as the PM curve is shifted, then eventually the gain associated with the oscillating cavity mode (the one under the middle ICE transmission fringe in Figure 3.6a) is below threshold, and the signal wavelength will hop by one FSR of the ICE. Oscillation now occurs on the cavity mode with the largest gain, which corresponds to the one residing under the ICE transmission fringe on the right hand side of Figure 3.6c.

As shown experimentally in Figure 3.7, as the PPLN crystal is vertically translated while



Figure 3.4: Wavemeter reading of the idler frequency versus intracavity etalon tilt angle. Continuous tilting of the etalon over an  $2^{\circ}$  range results in mode-hop tuning (~30 GHz) over the full ~350 GHz FSR of the etalon.



Figure 3.5: Linear actuator attached to OPO tuning module. The exploded view illustrates the basic mechanism of linear actuation, in which a 1/4-80 fine pitched screw is both rotated and translated through a brass 1/4-80 bushing sealed to the bottom of the metal housing.



Figure 3.6: Cartoon showing the outcome of vertically translating the fan-out PPLN crystal while keeping the ICE tilt angle fixed. The PM gain curve systematically shifts with respect to the optimally phase-matched signal wavelength. a) The peak of the PM curve is overlapped with a peak in the ICE transmission curve, and the cavity mode that oscillates is the one with the largest gain, i.e. the one indicated by the left most blue arrow. b) The peak of the PM curve has been shifted to the right such that it is between two adjacent ICE transmission fringes, and the cavity modes indicated by the two blue arrows can both potentially oscillate, as they are both above threshold (dotted horizontal line). c) The peak of the PM curve is shifted such that it now overlaps the ICE transmission curve on the right side of the figure. At this point the signal wavelength has hopped by on FSR of the ICE and the mode indicated by the right most blue arrow oscillates.



Figure 3.7: The laser power (left axis, black) and wavemeter reading of the idler frequency (right axis, red) are plotted versus stepper motor encoder position as the PPLN crystal is vertically translated. The ICE angle is held constant at a relative angle of 0.0 degrees throughout. The power oscillates as the PM gain curve is translated across the ICE transmission fringes. At the minimum of each oscillation the signal and idler waves hop by on FSR of the ICE ( $\sim 11 \text{ cm}^{-1}$ ). The vertical blue dashed lines indicate that the peak in each power oscillation corresponds to the center of each step in the idler wavenumber.

holding the ICE angle fixed, the power oscillates ( $\sim 25\%$  change) and the idler wavelength hops by one FSR of the ICE at the minimum of each oscillation. The peak of each power oscillation corresponds almost exactly to the middle of each "stair-step" associated with the wavemeter reading of the idler (vertical dashed lines in Figure 3.7). Therefore, our strategy is to map out an analytical expression (motor curve) that accurately predicts the stepper motor positions associated with the peaks in these power oscillations. Thereby, given a wavemeter reading, the PPLN crystal can be translated to maximize the idler output power. This process corresponds to a shift in the PM curve such that the peak of the PM gain and ICE curves remain overlapped, as shown schematically in Figure 3.3. As shown in Figure 3.8, a fourth order polynomial fit to a collection of motor scans at different fixed ICE angles results in a motor curve that runs through the regions of maximum power for a given wavenumber. We find that a fourth order polynomial fit is sufficient to generate a suitable motor curve for broad wavelength tuning. It is interesting to note that if the ICE is removed, the signal and idler waves will usually remain single mode, and the tuning of the PPLN crystal position will lead to mode hops of  $\sim 30$  GHz, due to the "OPO inertia" discussed above. This can be seen in Figure 3.9, where the PPLN crystal position is translated with and without the intracavity etalon included. We find that it is much simpler to build motor curves without the ICE in place, but we do caution that with the ICE removed, as the idler frequency increases (high idler frequency side of the "B-module" and "A-module" offered by Aculight), the tendency for the OPO to oscillate multi-mode increases significantly. This is a result of the systematic increase in phase-matching bandwidth with increasing signal wavelength (increasing idler frequency).

After the generation of the stepper motor curve (motor encoder versus wavemeter reading), mode hop scans ( $\sim$ 60-80 GHz hops) are obtained by synchronizing the tuning of the ICE and the PPLN position. The data shown in Figure 3.10 was generated as the ICE angle was adjusted from 1.0° to -1.0° in 0.5° increments. Each time the etalon angle changes, the



Figure 3.8: A plot of the motor encoder position versus idler wavemeter reading while the ICE tilt angle is held constant at  $1.0^{\circ}$  (relative). The inset shows the summation of a collection of motor scans with different fixed ICE tilt angles. A  $4^{th}$  order polynomial fit through the data (red line) runs almost exactly through the regions of maximum power for a given wavenumber, i.e. the central part of each wavenumber step. Therefore, the coefficients from the fit can be used to keep the PPLN PM gain curve overlapped with a maximum in the ICE transmission curve.



Figure 3.9: Two separate scans of the fan-out PPLN crystal. The red data corresponds to a scan in which the ICE is held constant at  $0.0^{\circ}$ , and the black data corresponds to a scan with the ICE removed. The scan with the etalon angle at  $0.0^{\circ}$  results in hops equal to one FSR of the ICE, while the scan with the etalon removed consists of hops equal to ~30 GHz, with each hop ("cluster" hop, see text) corresponding to a hop to a non-adjacent cavity mode.



Figure 3.10: Motor encoder position (black) and relative ICE tilt angle (red) versus time for a monotonically increasing mode hop scan over multiple FSRs of the etalon. The ICE angle was changed from  $1.0^{\circ}$  to  $-1.0^{\circ}$  in  $0.5^{\circ}$  increments, leading to ~60-80 GHz mode hops.

wavemeter is read, and the motor is sent to the encoder position that corresponds to that wavenumber (from the previously obtained motor curve), thereby tracking the etalon and PPLN gain curves. As shown in Figure 3.10, this continuous tracking of the gain curves via wavemeter feedback allows for smooth monotonically increasing mode hop scans over multiple FSRs of the etalon. Figure 3.11 shows the motor encoder position and wavemeter reading versus time with this scanning method covering  $\sim 200 \text{ cm}^{-1}$ .

Continuous, automatic tuning is achieved by ramping (sine wave or triangle wave) the PZT voltage, which stretches the seed fiber laser, leading to  $\sim 100$  GHz of continuous pump



Figure 3.11: Motor encoder position (red) and wavemeter reading of the idler frequency (black) versus time. This mode hop scan was carried out with the same scan parameters as in Figure 3.10, and it covers  $\sim 20$  FSRs of the ICE.

frequency tuning. Because the signal frequency is fixed by the optical resonator for a given set of ICE and PPLN positions, a change in the pump laser frequency results in an identical change in the idler frequency. At each peak and trough of the sine (or triangle) wave, the scanning is briefly paused, the ICE angle is stepped by 0.5°, the wavemeter is read, and the motor updates its position based on the established motor curve. The wavenumber input into the motor curve equals the wavemeter reading minus 100 GHz when the PZT voltage is at a peak, otherwise the wavemeter reading is used directly. Figure 3.12 shows the wavemeter reading and motor encoder position versus time for a scan that incorporates all three of the tuning mechanisms. In principle, the PZT voltage could be rapidly returned to its starting voltage (0 Volts) at the end of each ramp and prior to each ICE adjustment (i.e. a sawtooth ramp), which would produce a more linear frequency scan. Nevertheless, we caution against this as there is some empirical evidence that suggests scanning in this mode can lead to the damage of the fiber amplifier.

Figure 3.13 shows a zoom in of the raw wavemeter reading during continuous tuning at two different scan rates. The update rate of the wavemeter is reported to be 2 Hz, but we observe a rate equal to 5 Hz, and this leads to the discrete steps in the raw wavemeter reading as the idler frequency is continuously tuned. Post data collection work-up begins with a linear interpolation of the wavemeter reading, as shown in Figure 3.13. The work-up of the data proceeds by chopping regions containing mode hops, interpolating the data such that an evenly spaced grid of points are obtained (0.001 cm<sup>-1</sup> for survey scans and 0.0001 cm<sup>-1</sup> for higher resolution scans), averaging data at each grid point, sorting data, and then normalizing to laser power. The software associated with this data work-up is provided in the electronic supplemental material.



Figure 3.12: Motor encoder position (red) and idler wavemeter reading (black) versus time with the synchronization of all three tuning elements. The PZT element attached to the fiber seed laser is scanned with a sine waveform from 0-200 volts, resulting in  $\sim 100$  GHz of continuous tuning. At every peak and trough of the sine wave, the etalon angle is tilted by 0.5° resulting in a mode hop of  $\sim 60-80$  GHz, and the PPLN crystal is translated to track the PM and ICE gain curves (see text).



Figure 3.13: A plot of the raw wavemeter reading during continuous tuning at two different scan rates. The wavemeter is read at 5 Hz while data collection occurs at 20 Hz. The red and purple data correspond to the interpolated wavemeter reading for the 1.9 and 0.43 GHz/s scan rates, respectively. The wavemeter reading is interpolated in the post data collection work-up software.

## **3.4** Experimental Example

HENDI has recently emerged as an ideal matrix isolation technique for the study of novel molecular systems with infrared laser spectroscopy.<sup>1,2</sup> At the 0.4 K droplet temperature, these liquid helium droplets provide a dissipative yet weakly interacting medium. The rovibrational transitions of embedded molecules or clusters can be modeled using only a slightly modified gas-phase Hamiltonian, and the band origins associated with vibrational transitions can be compared directly to the predictions of quantum chemistry, as a result of essentially negligible solvent frequency shifts. A part of the mid-IR spectrum of helium solvated CH<sub>3</sub>OH is shown in Figure 3.14. At 0.4 K, only the lowest rotational levels associated with each nuclear spin modification are populated, and each vibrational band appears as a pair of resolved peaks, and these are labeled by vibrational mode in Figure 3.14. The peaks labeled by asterisks are associated with transitions of the methanol dimer (CH<sub>3</sub>OH)<sub>2</sub>. Table 3.1 shows a comparison of the line positions for CH<sub>3</sub>OH isolated in helium nanodroplets, solid p-H<sub>2</sub>,<sup>52</sup> solid neon,<sup>53</sup> and in the gas phase.<sup>54–59</sup> A detailed discussion of this helium droplet CH<sub>3</sub>OH spectrum will appear in a future paper.

The methanol C-H stretch spectrum made for a good test case for our OPO tuning algorithm, because all of the C-H stretching fundamentals, along with the various combination and overtone bands, were previously observed in the gas phase and in a solid p-H<sub>2</sub> matrix. Furthermore, these bands lie throughout the idler wavelength range and span several hundred wavenumbers. This spectrum represents a single scan over ~200 cm<sup>-1</sup> (6000 GHz) obtained at a rate of ~0.5 GHz/s, which resulted in a total acquisition time of approximately 4 hours. We note here that this scan required no user intervention, and the idler wave of the OPO appeared to remain single mode throughout the scan. With this scan rate, the time required to obtain this spectrum could be reduced slightly by optimizing the scan range of the PZT element on the seed laser to reduce the degree of wavelength duplication during the scan.



Figure 3.14: The mid-IR C-H stretch spectrum of methanol isolated in helium nanodroplets. Fundamentals, overtones, and combination bands are all observed including transitions that arise from higher order clusters ( $(CH_3OH)_n$  n >1), which are indicated by asterisks. This spectrum represents a single worked up, fully automated scan obtained at a 0.5 GHz/s scan rate, which required a total acquisition time of ~4 hours.

# 3.5 Summary

We have discussed an automation scheme for a Lockheed Martin Aculight cw-SR-OPO that is based on the continuous feedback from a high accuracy wavemeter for the idler wavelength. The tuning algorithm is general and can be applied equally well to any homebuilt OPO system that is pumped by a suitable cw all-in-fiber laser. The synchronization of the three OPO tuning elements, PPLN crystal translation, ICE tilt angle adjustment, and pump laser tuning, has been achieved with the combination of a home-built linear actuator system and LabView software. The details of the design aspects and software implementation of the algorithm is provided in the following chapter. The OPO was coupled to a HENDI spectrometer to obtain high resolution infrared spectra of helium solvated  $CH_3OH$  in the C-H stretching region (2800-3100 cm<sup>-1</sup>). This broad wavelength scan was obtained with the fully automated tuning of the OPO and hands-free in approximately 4 hours (~0.5 GHz/s scan rate). Spectral reconstruction software, also discussed in the following chapter, was employed to work-up the raw data and produce the final spectrum.

ison of line positions between CH <sub>3</sub> OH isolated in helium droplets with previous work of CH <sub>3</sub> OH isolated	lid neon, and in the gaseous phase.
on of line positi	d neon, and in
Table 3.1: Comparise	in solid p-H <sub>2</sub> , in solid

		7	Ga	ş	$p-H_2$	Matrix	Ne M	atrix	He M	atrix
Mode	Description	əym	$\mathrm{cm}^{-1}$	$\Delta(E-A)$	$\mathrm{cm}^{-1}$	$\Delta(E-A)$	$\mathrm{cm}^{-1}$	$\Delta(E-A)$	$\mathrm{cm}^{-1}$	$\Delta(E-A)$
$\nu_2$	C-H asym stretch	Э	2994.6	-12.39	2995.61	-7.62	2990.6	-10.6	3000.69	-9.27
		$\mathrm{A}_1$	3006.99		3003.23		3001.2		3009.96	
$ u_3 $	C-H sym stretch	Э	2844.66	-0.06	2840.66	0	2840.8	0	2845.01	-0.92
		$\mathrm{A}_1$	2844.72		2840.66		2840.8		2845.93	
$\nu_7$	$CH_3 rock$	Э	1070.31	-4.574	1073.69	-1.33	1071.3	-6.7	N/A	N/A
		$\mathrm{A}_1$	1074.884		1075.02		1078.0			
$ u_8 $	C-O stretch	Э	1033.707	-0.189	1031.12	-0.19	1032.12	-0.38	N/A	N/A
		$\mathrm{A}_1$	1033.896		1031.31		1032.50			
$\nu_9$	C-H asym stretch	Э	2952.04	-14.61	2951.72	-14.14	2948.6	-10.9	2957.65	-14.78
		$\mathrm{A}_2$	2966.65		2965.86		2959.5		2972.43	
$2\nu_4$	overtone	E	2957.57	-0.79	2956.5	-0.54	N/A	N/A	2958.96	-3.8
		$\mathbf{A}_{1}$	2958.36		2957.04				2962.76	

# Chapter 4

# Automation of an Aculight Argos 2400 cw-OPO: A User's Manual

This chapter discusses the hardware and software package designed by the Gary Douberly research group for the automatic tuning of an Argos<sup>TM</sup> Model 2400 CW OPO system (Lockheed Martin Aculight). The software is compatible only with both a Bristol Instruments 621A high precision wavemeter and a suitable piezo driver (e.g. Thorlabs MDT694A or Piezo Systems EPA104). As long as the user has the appropriate hardware, this chapter can be considered as a user's manual. It should be noted, however, that user manuals for the OPO module and controller as well as the OPO pump source were included with the system when you purchased it. Therefore, those manuals have the supreme authority over whatever is suggested in this manual, and the user uses this manual and the included software/hardware package at their own risk.

The  $\operatorname{Argos}^{TM}$  Model 2400 is a periodically-poled Lithium Niobate (PPLN) optical parametric oscillator (OPO). The OPO consists of the OPO controller and the OPO module. The OPO is pumped by an IPG Photonics YL Series high power fiber laser. The top picture in Figure 4.1 shows the OPO pump source as well as the OPO controller, and the bottom



Figure 4.1: Top: OPO Pump Source and OPO Control Unit. Bottom: OPO Module

picture shows the OPO module.

Figure 4.2 shows a cartoon of the inside of the OPO module. The black fiber optic cable extends from the pump source and is inserted into the OPO module. The collimator on the end of the fiber optic cable maintains the proper polarization alignment when switching the pump source between different OPO tuning modules. The 1064 nm emission from the fiber reflects off two steering mirrors and into the bow-tie cavity. The OPO is singly resonant, and the only beam that is resonant inside the cavity is the signal beam. The pump and idler beams make a single pass through the MgO:PPLN crystal and exit the cavity. The MgO:PPLN crystal is in a "fan out" design so translating the crystal vertically with respect to the pump beam (whose position is fixed) changes the poling periodicity and provides coarse tuning of the idler and signal frequencies. Tilting the intracavity etalon changes the signal frequency of maximum gain, leading to mode hops of both the idler and the signal frequency. The pump frequency can be tuned continuously over a range of 50-100 GHz (depending on the exact fiber laser used) by piezo strain of the fiber seed laser. Tuning the pump frequency translates directly into idler tuning due to conservation of energy and the fact that the signal wave is fixed by the presence of the cavity and the intracavity etalon.

Continuous tuning of the OPO idler frequency over a broad range is achieved by synchronizing three separate tuning mechanisms. These mechanisms provide course (PPLN crystal translation), intermediate (intracavity etalon angle tilting), and fine (piezo control of pump frequency) tuning of the idler frequency. Computer control of these three tuning elements leads to continuous tuning of the OPO idler frequency over the entire tuning range with 30 MHz resolution (limited by the wavemeter absolute accuracy). Course tuning is computer controlled by interfacing the UGA built linear actuator to the OPO. The linear actuator turns a fine-pitch screw that results in the vertical translation of the PPLN crystal, leading to hops of the idler frequency equal to one free spectral range (FSR) of the etalon ( $\sim$ 800 GHz). If the etalon is removed, the idler wave will usually remain single mode, and the



Figure 4.2: Schematic of OPO module

tuning of the PPLN crystal position will lead to mode hops of  $\sim 10-30$  GHz, due to "OPO inertia". Intermediate tuning is achieved by the synchronous computer control of the etalon tilt angle and the PPLN crystal position, leading to broad "mode-hop" scans of the idler frequency in steps of approximately 10-30 GHz. For these "mode-hop" scans, the etalon tilt angle is varied over approximately two degrees, corresponding to one FSR of the etalon. Subsequently, the etalon "hops" back to the start angle and once again begins to scan the angle over the same two degree range. Upon each etalon angle adjustment, the PPLN crystal position is updated to achieve maximum overlap of the PPLN and etalon gain curves. Etalon and PPLN gain curve overlap is maintained via the feedback from a high-precision wavemeter and pre-determined motor position versus wavenumber curves. Since the overlap of the Etalon and PPLN gain curves is maintained, the OPO idler frequency is unchanged following an etalon hop-back after tuning over one FSR of the etalon, and 10-30 GHz "mode-hop"

scans can be obtained over the entire PPLN tuning range. Stretching the fiber seed laser results in the continuous tuning of the OPO pump frequency by about 50-100 GHz (again depending on the exact fiber seed laser employed). Piezoelectric control of the stretching of the fiber is automated so that the frequency can be varied continuously, filling in the 10-30 GHz gaps associated with the etalon/PPLN crystal tuning. In practice, we find that it is best to scan continuously for 50 GHz, change the etalon tilt angle to hop forward by 100 GHz, and then scan back  $\sim$ 50 GHz continuously. Simultaneous tuning of the PPLN crystal while scanning in this fashion leads to continuous scans with  $\sim$ 30 MHz resolution over several thousand GHz. All of the computer control is achieved using the "SCAN ARGOS" LabView program that has been developed at the University of Georgia.

This chapter will explain how to use the three tuning mechanisms (PZT strain, etalon angle, and crystal position) along with the provided LabVIEW programs to acquire signals and collect data. Instructions on how to assemble and use the laser system will also be given followed by a description of the software.

## 4.1 Measurement and Automation Explorer Set-up

Before the system can be scanned automatically, all hardware components need to be plugged in and communicating with the computer. This includes the OPO controller and the Bristol wavelength meter which communicate via RS232 and USB, respectively. Also, BNC cables need to be attached from the National Instruments breakout board to the appropriate piece of hardware. Using Measurement and Automation Explorer, tasks need to be created for each analog input or output. Table 4.1 shows what values to use when creating the tasks. Labview calls upon these tasks when it is operating to receive or send voltage signals.

Analog input 0 (AI0) is the signal from the lock-in amplifier. This is just a simple BNC to BNC connection from the output of the lock-in amplifier to AI0. Analog input 1 (AI1)

				I			
AI7	PiezoIn	0	0	10	"	n/a	n/a
AO0	PiezoOut	0	-0.001	10	1 Sample on demand	n/a	n/a
AI2	Detector	2	0	10	"	2	10
AI1	Detector	Ţ	0	10	"	2	10
AI0	Detector	0	-10	10	Cont. Samples	2	10
input/output	Task	Channels	Minimum Voltage	Maximum Voltage	Acquisition Mode	Samples to Read	Rate (Hz)

Table 4.1: Measurement and Automation Explore Cheat-Sheat

is the voltage reading from the Thorlabs power meter. This is a SMA to BNC connection where the SMA end is connected to the power meter and the BNC end is connected to AI1. Analog input 2 (AI2) is the voltage reading from an optional component such as a pick-up cell ion gauge controller or another chamber pressure gauge. Analog output 0 (AO0) is an output voltage sent to the external input of the Thorlabs piezo driver. This output is split using a tee connector and also attached to analog input 7 (AI7). This is for feedback that the scanning program will use, so a task will need to be created for it as well.

# 4.2 Stepper Motor Set-up

In this section, a brief description is given for the hardware required to build the stepper motor assembly. Also, an example of how to generate a wavenumber versus motor encoder position curve is described.

See the Appendix for a list of parts required to set-up the stepper motor assembly from scratch. Figure 4.3 is a schematic of the hardware for the stepper motor construction. (Not shown is the stepper motor wired to the power supply and the programmable controller.) The flexible couplings, stepper motor, power supply and programmable controller are all purchased from Anaheim Automation. The 1/4-80 bushing can be purchased from Thorlabs. The 3" long, 1" diameter cylindrical housing is a custom piece that was made in the UGA instrument shop. Also made in the UGA instrument shop is the rotatable shaft and the 1/4-80 screw with the drive-bar welded to the top (see the Appendix for engineering drawings of these custom components). A stand (not shown) holds the stepper motor above the OPO module, and the cylindrical housing is screwed onto the bottom of this custom stand (see engineering drawings for the full assembled view). Within the cylindrical housing, the flexible coupling, the rotatable shaft and the 1/4-80 screw with drive-bar are assembled as shown. The 1/4-80 screw threads through the 1/4-80 bushing, which is Torr sealed into the hole at



Figure 4.3: Schematic of Stepper Motor Assembly

the bottom of the cylindrical housing. Finally, the second flexible coupling shown outside the cylindrical housing is attached to the end of the 1/4-80 screw, and an appropriately sized hex key is attached to this flexible coupling. A small cylindrical adaptor may be necessary to rigidly link the hex key to the flexible coupling.

Once everything in Figure 4.3 is assembled, the stepper motor is wired to the power supply and the programmable controller. The cables required for wiring can also be purchased from Anaheim Automation. The programmable controller is connected to the computer via USB. Software is provided from Anaheim Automation and is used for the initial set-up of the motor. With the software installed and successful communication with the computer established, the stepper motor is ready for initialization. In practice, this only needs to be done once. Switching between modules won't interfere with the stepper motor communication to the computer.

#### 4.2.1 Initializing the Motor

1) Make sure the stepper motor assembly is built correctly and that the Anaheim Automation software is installed on the computer.

2) Open the Anaheim Automation software and make sure a connection is established between the computer and the hardware. (pick the correct COM port!)

3) Familiarize yourself with the Anaheim Automation software.

4) Slowly move the stepper motor clockwise (cw) using the software and watch the 1/4-80 screw move through the bushing. Keep turning the the screw cw until the stepper motor no longer turns the screw through the cylindrical housing. When the screw no longer turns, stop the stepper motor (MOTOR HARD-STOP). With your hand, turn the 1/4-80 screw in the opposite direction that the stepper motor was turning it. It won't turn much. Now, using the software, move the stepper motor counter clockwise (ccw) until the 1/4"-80 screw

turns about 2 complete revolutions. This is going to be the starting point for the stepper motor.

5) Select the tab in the software that's titled "Encoder Options and Registration Inputs". Click on the button titled "Reset position to 0". The motor is now ready to be connected to the OPO module.

#### 4.2.2 Connecting the Motor

1) Remove the hex key and flexible coupling that is attached to the 1/4-80 screw of the stepper motor assembly.

2) Take the hex key and flexible coupling and insert it into the top of the OPO module, fitting the hex key in the screw that vertically translates the PPLN crystal.

3) Turn the hex key cw (translate the crystal down) until it cannot turn any more. Now, turn the crystal ccw for 2 complete revolutions. This is the crystal position that corresponds to an encoder position of 0.

4) With the hex key and flexible coupling connected to the OPO module, carefully take the rest of the stepper motor assembly and straddle it about the OPO module with the 1/4-80 screw centered above the hole in the flexible coupling. Adjust the position of the stepper motor assembly such that the 1/4-80 screw fits perfectly into the hole of the flexible coupling. Make sure that the hex key is not tilted. If attached properly, hex key rotation will not put directional strain on the crystal housing. Tighten the screw on the flexible coupling such that it is again attached to the 1/4-80 screw.

#### 4.2.3 Generating Motor Curves

Now, the stepper motor is assembled with the encoder position 0 representing the bottommost crystal position. Scanning the motor from encoder position 0 to about 55,000 will translate the crystal completely from the bottommost position to the topmost position. The next steps will discuss collecting the wavenumber data for each encoder position to generate a curve that the master program will eventually use when automatically scanning.

1) The best way to generate a motor curve for this OPO is to remove the intracavity etalon. This is easily achieved by opening the OPO Module and removing the 4 screws that mount the galvanometer that has the etalon attached. Then, the galvanometer can be lifted out of the cavity and placed safely inside the bottom of the OPO module. This is important because without the etalon in the cavity and translating the crystal vertically, the OPO will hop between modes of about 30 GHz instead of about 800 GHz (or whatever the value is for the FSR of the currently used etalon) when the etalon is inside the cavity and kept at a fixed angle. The user can also choose to generate the motor curve by keeping the etalon in place. This requires motor curves to be generated for multiple etalon angles spanning one FSR of the etalon. For example, if the etalon scans one FSR between -1 and +1 degree tilt angles, then the user needs to obtain a motor curve for angles in this range with an increment of 0.2 degrees.

2) Now, with the intracavity etalon removed and the stepper motor assembly attached to the OPO module, the laser can be powered up following the procedure in the manual provided with the laser.

3) Open the LabView VI titled "motoring\_for\_curve\_make".

4) The front panel of motoring\_for\_curve\_make.vi has a few options. The first allows you to choose where you want to save the data. The maximum speed that the motor turns can also be controlled. (We found that a speed of about 20 seems to work well for this procedure) There is also a boolean switch that allows the user to choose the direction the motor turns. For this application, we want it to turn ccw. And the last option is the number of steps the motor will turn. 53,000 is set as the default and should work just fine.

5) Push play and the vi starts. The user needs to keep an eye on it to push stop when



Figure 4.4: Example Motor Curve

the stepper motor has stopped turning to quit collecting data.

6) Now a file with wavenumber vs. encoder position has been generated and saved to the location of the user's choice. (Note: if you choose to keep the etalon in place and generate multiple motor curves, then now you will need to combine all of those files into one ascii file, sorted by wavenumber)

7) Open the file in a program like Microsoft Excel!

8) Plot the wavenumber on the x-axis and the encoder on the y-axis. Delete the outlier points. The plot should look something like the plot in Figure 4.4.

9) Fit a  $4^{th}$  order polynomial through the data and record the coefficients to the highest precision possible. We refer to this  $4^{th}$  order polynomial fit as the motor curve for the OPO module.

The scanning software is written to allow the user to make three separate motor curves for both the B and C modules. These three curves should be generated with the PPLN crystal temperature set to three different temperatures:  $55^{\circ}$ C,  $60^{\circ}$ C, and  $65^{\circ}$ C. The values of the coefficients from the 4<sup>th</sup> order polynomials (a, b, c, d, and e) of each motor curve is inserted into the controls on the front panel of the scanning software, as described below. Generating these motor curves only needs to be done once. Once the coefficients from the 4<sup>th</sup> order polynomials are obtained, they are input and saved into the scanning software and used forever.

### 4.3 ScanArgos.vi

The ScanArgos vi incorporates the three tuning elements of the OPO to obtain a continuous spectrum. First, the piezo element of the pump laser is scanned from 0 volts to about 200 volts (90 volts if using the Thorlabs MDT694A piezo driver). This will change the frequency of the idler beam from lower energy to higher energy by about 3 cm<sup>-1</sup> (1.5 cm<sup>-1</sup> if using Thorlabs MDT694A). Once 200 volts is applied, the intracavity etalon angle is changed. The angle is changed by a value that corresponds to the change in frequency from scanning the piezo. Now, the PPLN crystal is translated to achieve the best phase matching to maximize output power. The piezo can now be scanned down from 200 volts back to 0 volts. Once the applied voltage on the piezo is 0 volts, the intracavity etalon angle is changed just like before and the PPLN crystal is translated again. Figure 4.5 shows what the raw wavenumber obtained with time looks like when the sine waveform scan option is selected (can also be scanned with a triangle waveform). The scan isn't continuous but it



Figure 4.5: A schematic showing how the laser is scanned with time.

does cover all the wavenumbers. It just needs to be sorted in order to obtain a spectrum that is linear with respect to the frequency.

We can now open ScanArgos.vi and get familiar with the front panel. Figure 4.6 shows what the front panel of the ScanArgos vi looks like. At the very top of the front panel is the tab selector where the coefficients from the  $4^{th}$  order polynomial motor curves are input. The other tab selector to the right has various control variables that set up the scan conditions. Below that is the ABORT! button. To the left of the tab selector and ABORT! button are controls that tell the vi which OPO module is in use and controls that tell the vi to scan the etalon, piezo, and/or motor. Below that are 3 indicators; absolute frequency from the

		Enter Coefficients for D	ifferent Crystal Tempe	ratures	
	B Mod C Mod	Enter coefficients for E	interent crystal rempe		
	55	c	60 C	65 C	
	-1.68494720293	303200000000E+6	1727668900000000E+6	1.28474091847365000000000E+6	
	<b>b</b> 1.385141487745	52200000000E+3	88710840000000000E+3	3219127847320800000000E+2	
	6 4 4 3 3 5 3 8 0 0 3 6 9	-3 729536	52129287400000000E-1	2.41556415224273000000000F-1	
Stepper Motor	-4.52558092885	9214000000000E-1 () 5/12555			
KCOM2	d - 6.314457569898	317000000000E-5 - 5.205006-	463/165800000000E-5		
OPO Controller	e -3.63392414026	5224000000000E-9	365552965000000000E-9	1.13942543350910000000000E-9	
g C:\scandata\temp.dat	-	C Mod	B Mod	Piezo Etalon Motor Crystal Loops	
wavelength from arr				Triangle	
		Etalon Hop? Piezo	Scan? Scan Motor?	piezo analog out channel 3	
old wavelength from 0	array		- J	% PiezoOut	
Steps motor moves		]		StartVoltage Increment 0.1 0.005	
encoder position new	v	Freque	ncy cm-1	EndVoltage milliseconds to wait	
0		0		195 0	
initial voltage	Piezo Voltage	Country	Loren Derrore	Manual Crystal Tweak	
0	0	Counter	Laser Power		
		0	0	ABORT!	
meter Piezo Voltage Las	er Power				
3307 -					

Figure 4.6: ScanArgos.vi front panel

wavelength meter, the laser power, and counter (ensures that data is being recorded). To the left of that is a control for the file name and 6 various indicators. To the top of that are comport options for the stepper motor and the OPO controller. Below all of this is a tab selector with 3 options that show various waveform charts. More detail on each section is described below.



Figure 4.7: Tab selector to input coefficients from  $4^{th}$  order polynomial motor curves. The user can choose between the B Module or the C Module and must input the coefficients (a, b, c, d, and e) for the three different temperatures shown for each module.

#### 4.3.1 Inputting Motor Curve Coefficients

Figure 4.7 shows what the input control panel looks like for the 4<sup>th</sup> order polynomial coefficients that are collected for each module (see section "Generating Motor Curves" above). There are two tabs to choose from corresponding to OPO module B or C. The different OPO modules will not follow the same curve so the procedure in the "Generating Motor Curves" section above needs to be followed for each module. In addition, the software will read the temperature of the OPO crystal and choose the appropriate motor curve (corresponding to  $55^{\circ}$ C,  $60^{\circ}$ C, or  $65^{\circ}$ C). If the PPLN crystal is not set to one of these three temperatures, the software will, by default, scan the crystal using the  $65^{\circ}$ C motor curve. It is important to record the coefficients to as high of a precision as shown in Figure 4.7. Once the coefficient values are typed in, the user can right click on the value then Data Operations  $\rightarrow$  Make Current Value Default. Now when the vi is opened and closed, the coefficient values are saved.



Figure 4.8: Section of the front panel that allows the user to choose a file path and name and set the comport for the OPO controller and stepper motor. The indicators refer to the stepper motor and the piezo driver.

# 4.3.2 File Name, Comports, Stepper Motor Indicators, and Piezo Voltage Indicators

The left side of the front panel is shown in Figure 4.8. In the middle is a control for the file path. The path can either be typed in or the button with the picture of the folder on it can be clicked to browse for a path. The two control options to the top select the comports that are communicating with the stepper motor and the OPO controller.

There are two sets of boxed in indicators also shown in Figure 4.8. The box with 4 indicators deals with the stepper motor. The "wavelength from array" and "old wavelength from array" are two variables that the program uses to calculate the stepper motor position. The next indicator, "steps motor moves", shows the number of steps the motor moved from the most recent calculation. The last indicator in this box is "encoder position new" and it just displays the current encoder position for the given wavelength. These indicators are only updated at each peak and trough of the piezo scan waveform.



Figure 4.9: Options to choose which OPO Module is in use; On/Off Switches for hopping the etalon, scanning the piezo, and scanning the motor; indicators for laser frequency, Counter, and laser power.

The bottom set of boxed in indicators shown in Figure 4.8 display the "initial voltage" and "piezo voltage". The initial voltage is important when starting the ScanArgos vi. If the computer is still outputting a voltage from a previous scan, the ScanArgos vi will slowly rewind the piezo voltage back to zero. This value is only updated on start up of the ScanArgos vi. The other indicator updates continuously and shows the current voltage being applied to the piezo element.

# 4.3.3 OPO Module Selection and Scanning Elements; Frequency, Counter, and Laser Power Indicators

The central portion of the ScanArgos vi front panel is shown in Figure 4.9. At the top are two radio buttons that allow the user to choose which OPO module is in use. These radio buttons are important because they tell the stepper motor which motor curve to follow.
BristolExample.vi Front Panel *	
File Edit View Project Operate Tools Wind	low Help Brist
Port	RxMsgCnt
Open Close	0
Units	Error Code
Get Lambda nm 🤝 999.99999	0
AutoScan 9.9900000 nm Stop	
Example Application Ver.	1.1 Exit
Frequency cm-1	
0 0000000	
0.0000000	

Figure 4.10: BristolExample.vi Front Panel

Below the three radio buttons are three on/off switches: "Etalon Hop?", "Piezo Scan?", and "Scan Motor?". This allows the user to turn on and off the three different elements that scan the laser since some applications may not require all three tuning mechanisms. When the switch is up, it is on. When it is down, it is off.

Below the radio buttons and on/off switches are three indicators. The first shows the absolute laser frequency from the Bristol wavelength meter. This value will only read when BristolExample.vi is open and running in the background. Figure 4.10 shows what the front panel of the BristolExample vi looks like. This is a vi that was provided when the wavemeter was purchased. The correct comport needs to be selected from the option at the top. Then when the green light indicates that the computer is communicating with the wavelength meter, the "AutoScan" button can be pushed. The indicator at the bottom of the front panel is a global variable that ScanArgos.vi is able to access.

The bottom two indicators in Figure 4.9 are called "Counter" and "Laser Power". The laser power is monitored by sending a voltage from a Thorlabs power meter into one of the National Instruments breakout board's analog inputs. The other indicator, "Counter", is an important one. If it stops slowly counting up during data acquisition, it means that the subvi in the background that is collecting all the data has failed. The solution to this is to stop the ScanArgos vi and start over. This rarely happens, however, it is helpful to know that the data being collected during an experiment is being recorded.

### 4.3.4 The Piezo, Etalon, Motor, Crystal, and Loops Tab Selector

The next stop on our tour of the ScanArgos front panel is the piezo, etalon, motor, crystal and loops tab selector located on the right side. Figure 4.11 shows the options contained in each tab.

### The Piezo Tab

A waveform is generated in LabView that controls the piezo driver that applies strain to the PZT element of the seed laser. Figure 4.11A shows the different controls that will determine the type of waveform, the amplitude, and the frequency of the waveform selected. Pressing the blue button in Figure 4.11A will change the waveform from a triangle wave to a sine wave and turn the button green. Pressing it again changes it back to a triangle wave. These are the two waveform options available. Below the button is an option that lets the user select the task that applies the voltage to the piezo driver. The button, "Scan Piezo", can be viewed as a pause button. The piezo will only scan when it is on. It can be turned on and off during scans to pause the piezo scanning. The four controls at the bottom of the tab control the amplitude and frequency of the piezo scan waveform. There is an option for the start voltage and the end voltage. Then there is an option, "Increment", that controls the voltage steps from the start to end voltage. The last control is "milliseconds to wait".



Figure 4.11: Pictures of the controls and indicators contained in the piezo, etalon, motor, crystal and loops tabs.

This controls the frequency of the waveform by waiting the number of specified milliseconds between adding voltage increments from the start to end voltage. The "Manual Crystal Tweak" button becomes important when the user chooses to scan the piezo and etalon, but does not wish to scan the motor (This is the current configuration of the software shown in Figure 4.9. In this scenario, when the piezo voltage reaches a peak or a trough in its waveform, the etalon will hop and the user is prompted to manually rotate the crystal to maximize the idler power. The user will then click to continue the scan.

### The Etalon Tab

The etalon tab is shown in Figure 4.11B. There are two controls titled "Etalon Now" and "etalon end" These values correspond to the beginning angle and end angle of the etalon's free spectral range. See the section below to see how to determine an OPO module's intracavity etalon's free spectral range. Once this range of angles is determined for an OPO module, the start angle and end angle should be typed into the correct box. Each module has a different range and the values should be saved somewhere and typed into the control when that particular module is being used. The "Etalon Now" control is to input the current etalon angle before starting a scan. Note that this value must fall between the etalon start and etalon end angles for a given OPO module. This is helpful because the user may not want to start at the same etalon angle for every scan. The "etalon hop wait" control is set with a default value of 0 seconds. This control becomes important when generating the etalon curves to determine the intracavity etalon's free spectral range.

#### The Motor Tab

Figure 4.11C shows the control options for the stepper motor in the tab selector. The controls "milliseconds to wait to let laser stabilize before building array", "# wavemeter points in array", and "allowable difference between points in array" are options that shouldn't

require a lot of changing. The values of 3000, 100, and 0.5 respectively will work just fine. The fourth control is "curve shift". This allows the user to shift the motor curve slightly. This may be useful if the hex key wasn't attached to the stepper motor at exactly the right position. The fifth control is "motor max speed" and controls the speed at which the motor turns. To reduce the risk of damaging the crystal, it is best to not exceed a value of 200 for this control.

To the right of these five controls are two buttons and one last control. These three options are used in the middle of scans to "tweak" the crystal position if the laser happens to be multi-mode or outputting low laser power. The way it works is to choose the number of steps you want the motor to turn and the direction (ccw or cw). Then, when the "tweak motor" button is pressed, the motor will turn the number of specified steps in the specified direction.

### The Loops Tab

Figure 4.11E shows the control options for the Loops tab. These options become important if the user decides that they want to scan the same wavelength region multiple times for averaging. The user must simply click the "Loops?" control into the ON position (pointing up) and select a "Start Wavlength" and an "End Wavelength". The software will then scan that wavelength range in a loop until the user chooses to stop the vi. While scanning in loops, the user may decide to change the crystal temperature between looping and this is described in the next section. The user must flip the "Change xstal temp" control into the on position to initiate the options in the Crystal tab.

### The Crystal Tab

Figure 4.11D shows the control options for the Crystal tab, as long as the "Change xstal temp" control in the Loops tab is set in the ON position. Here, the user can select two

different crystal temperatures to change between while scanning continuously in a loop. The "Xstal Temp Set (High)" control is to set the high temperature value and the "Xstal Temp Set (Low)" control is to set the low temperature value. The "low or high?" control is to choose the temperature that the crystal is set at for the beginning of the scan. If the initial temperature is the low temperature, then a value of -1 needs to be input into the "low or high?" control. If the initial temperature is the high temperature, then a value of 1 needs to be input into the "low or high?" control. If the initial temperature is the high temperature, then a value of 1 needs to be input into the "low or high?" control. The control "xstal temp wait ms" is the amount of time the software gives the OPO module to change the temperature of the crystal. Since this is an event that takes some time, a value of 300000 ms is sufficient to allow the crystal to come into thermal equilibrium between loops.

### 4.3.5 Waveform Charts and the Abort Button

At the bottom of the ScanArgos vi front panel is a tab selector with three options; "Wavemeter", "Piezo Voltage", and "Laser Power". Each of these tabs selects a different waveform chart that show what each option is doing with time. However, the Wavemeter tab not only shows the wavemeter reading versus time, it also contains a graph that displays the spectroscopy signal versus time. It is helpful to monitor the output of the wavelength meter and laser power using these charts during a scan. They are only there to serve as a visual aid. The "ABORT" button is essentially useless. It is recommended that the user just hit the LabView stop button to stop a scan.

### 4.4 Generating Etalon Curves

In this section, a description on how to develop an etalon curve and input the necessary information into the etalon tab (see above) controls is given. Since each OPO module has it's own intracavity etalon unique to it, etalon curves need to be generated for each module.



Figure 4.12: Example Etalon Curve

The idea is to find a range of angles about  $0^{\circ}$  that will correspond to one free spectral range of the etalon. It is important for the range of angles to fall around  $0^{\circ}$  because if not, the OPO module's block temperature will begin heating up.

1) Open ScanArgos.vi.

2) On the front panel, choose the module that you are using. Turn the "Etalon Hop?" switch up and turn the "Piezo Scan?" and "Scan Motor?" switches down. This enables the vi to only scan the etalon.

3) Select the Etalon tab from the tab selector on the right side of the front panel.

4) Type in a "Start Angle" of -5. Type in an "End Angle" of +5. Type in an "Increment" of 0.01.

5) Set the "etalon hot wait" time to 2000. This is 2000 milliseconds or 2 seconds. This sets it up so the etalon angle is changed by 0.01° every 2 seconds.

6) Make a plot of the etalon angle versus wavenumber reading. It should look like the plot shown in Figure 4.12.

Once the plot has been created, a set of angles can be chosen to use during experiments. In Figure 4.12, the best set of angles to use would fall between -2° and 1°. The entire free spectral range of the etalon is covered in this range and it is about 0° so there are no concerns of over heating the block. The plot in Figure 4.12 was created using the OPO C module. Under the etalon tab in the tab selector on the right side of the ScanArgos vi, the values of -2 and 1 need to be typed into the appropriate "Start Angle" and "End Angle" control options. The best way to determine the proper "Increment" value is to run a couple scans with different values and then choose the value that allows all wavelengths to be covered. We don't want to hop the etalon too much to where wavelengths are skipped and we don't want to hop too little where we're collecting the same wavelength data multiple times.

# 4.5 Output File. What's in it?

The data output file contains 8 columns of ascii data. The data from analog inputs 1-3 are collected at 20 Hz, so 20 rows of data are written to the output file per second. Columns 1-3 correspond to these three analog inputs, which are wired to the lock-in amplifier output (spectroscopy signal), the laser power meter, and an optional component (such as the pick-up cell ion gauge controller or another chamber pressure gauge), respectively. The fourth column of data is the wavemeter reading in wavenumbers (cm<sup>-1</sup>). The wavemeter reading is collected at 5 Hz so for every 20 rows of data, the output file will contain 5 separate

wavemeter readings, each repeated 4 times. Columns 5-8 correspond to the motor encoder position, etalon angle, piezo voltage, and PPLN crystal temperature.

### 4.6 dataworkup.vi

Figure 4.13 shows the front panel of the data worker software written to clean up the data collected using the ScanArgos vi. To the left of the panel, there is a control to specify the location of the output file as well as a column of controls to specify the locations of all the input files. In order for a file to be used as an input, the green LED indicator next to the file path must be turned on (the LED is bright green). This gives the user the advantage of choosing which files are used to produce an averaged spectrum.

There is then a raised box that has a button, 2 indicators, and 5 controls. The boolean button, "Master Plot?", is used to decide whether or not to view the raw data in the plot before the work-up of data begins. This option is visually helpful to ensure the correct data is being input into the software, however, it uses a lot of memory. Therefore, it is up to the user to decide if they want the "Master Plot?" button ON or OFF. To the right of the button is a box with 2 indicators and 2 controls. The "compare range (cm-1)" and "average window" controls are used to get rid of bad data before the work-up begins. Looking at the current state of these controls in Figure 4.13, the software will look at each individual data point in the array, average the wavemeter reading associated with 100 points to the left and to the right of this point in the array, and if the current data point has an associated wavemeter reading within  $0.3 \text{ cm}^{-1}$  of this average value, it is kept; if not, it is deleted.

The two controls to the far right side of the front panel, "chop range" and "cutoff slope (cm-1)", deletes the data associated with "hops". Essentially, when the piezo is scanning, it is scanning linearly with time and has an associated slope. During a "hop" (such as when changing the intracavity etalon angle), the slope between two points will change drastically

and signal from the previous wavelength will linger in the new wavelength reading due to averaging by the lock-in amplifier. To eliminate this, the user simply chooses a "cutoff slope (cm-1)" value (the value depends on the rate of the scan) and a "chop range". Looking at the current state of these controls in Figure 4.13, once the slope exceeds 0.5 between any given data points, 10 points to the left of and 10 points to the right of these slope exceeding data points are deleted. Below these two controls is the last control, "Precision". In its current state in Figure 4.13, the output file has signal vs. wavelength data that is separated by  $0.001 \text{ cm}^{-1}$  (value of 3 in the "Precision" control). If the value is changed to 2 or 4, then the signal vs. wavelength data is spaced by  $0.01 \text{ cm}^{-1}$  or  $0.0001 \text{ cm}^{-1}$ , respectively. Higher "Precision" values result in larger file sizes.



Figure 4.13: dataworker.vi Front Panel

# Chapter 5

# Infrared spectroscopy of $(HCl)_m(H_2O)_n$ clusters in helium nanodroplets: Definitive assignments in the HCl stretch region

Infrared spectra in the HCl stretch region (2600-2900 cm<sup>-1</sup>) are presented for small, mixed  $(HCl)_m(H_2O)_n$  clusters solvated in helium nanodroplets. Sharp bands associated with the Cl-H···Cl stretch vibrations in m:n=1:1, 2:1, 2:2, and 3:1 clusters are superimposed on a broad background that increases in intensity as larger clusters are grown within the droplets. The broad background is determined to be partially due to mixed clusters with m>3 and n>2. The sharp bands are assigned to specific cluster compositions, m:n, *via* pick-up pressure dependence studies and optically selected mass spectrometry. Orientation of the clusters is achieved with the application of a large electric field to the laser/droplet beam interaction region. The intensity of each band is measured as a function of the applied field strength. Simulations of this electric field dependence based on ab initio calculations of permanent dipole moments and vibrational transition moment angles leads to definitive structural assignments for each sharp band. The 2:1 complex is cyclic, and a band associated with the 2:2 cluster is determined to arise from the non-alternating cyclic structure.

# 5.1 Introduction

The dissociation mechanism of HCl in aqueous media is a fundamental problem in chemical physics and remains an active area of research.<sup>60,61</sup> A fundamental question motivating these studies is how many water molecules does it take to pry apart HCl to form a solvent separated ion pair  $H^+(H_2O)_nCl^-$ . This seemingly simple question has proved to be a challenge for both theory and experiment. One approach to this problem is to study the structure of small clusters composed of HCl and water and look for the signatures of dissociation. We report here an infrared spectroscopy study of mixed  $(HCl)_m(H_2O)_n$  clusters that are grown in the low temperature environment of a helium nanodroplet.<sup>1,2,62</sup> A somewhat non-traditional version of Stark spectroscopy is employed to arrive at unambiguous assignments of cluster bands in the HCl stretch region of the spectrum.

There is now a vast literature on the experimental and theoretical characterization of the acid dissociation mechanism. Molecular dynamics simulations employing various methodologies have lead to a better understanding of the acid dissociation process in bulk water<sup>63,64</sup> and on ice surfaces.<sup>65–67</sup> Infrared spectra of HCl on the surface of bulk ice and ice nanoparticles have provided important insights into the temperature dependence of acid ionization in environments relevant to the stratosphere and the chemistry associated with ozone depletion.<sup>65,66,68–71</sup> For the smaller (HCl)<sub>m</sub>(H<sub>2</sub>O)<sub>n</sub> clusters, there are many reports of electronic structure calculations, which aim to determine the onset of acid ionization.<sup>72–82</sup> These ab initio studies generally agree that four water molecules are necessary before the ion pair becomes the minimum energy structure.<sup>73–75,77,83,84</sup> On the experimental front, microwave<sup>84–87</sup> and cavity ring-down infrared<sup>88</sup> spectroscopy have provided structural data for some of the smaller, undissociated  $(\text{HCl})_m(\text{H}_2\text{O})_n$  clusters, such as the 1:1 and 1:2 complexes. Fourier transform infrared (FTIR) spectroscopy of these clusters grown in solid matrices<sup>89–92</sup> or formed in free-jet expansions<sup>81,93</sup> have provided overview spectra in the OH and HCl stretch regions. More recently, infrared spectra of  $(\text{HCl})_m(\text{H}_2\text{O})_n$  clusters grown in helium nanodroplets were reported in the OH stretch<sup>94</sup> and HCl stretch<sup>17,42</sup> regions.

Infrared spectroscopy is particularly well suited to explore the structural properties of these clusters with increasing solvation, given that the HCl chromophore is a sensitive messenger of the dissociation process. Indeed, as the acid dissociates, the HCl stretch vibration should disappear, being replaced by the OH stretch vibrations of a protonated water moiety. Nevertheless, the infrared spectra of these cluster systems can be difficult to interpret, given the diversity of cluster sizes and isomeric structures produced in these environments. As the concentration increases, this distribution leads to broad spectral features that span several hundred wavenumbers and obscure the signatures of individual clusters, including those that may be stabilized as ion pairs. In the FTIR spectra of the free-jet, several sharp bands in the HCl stretch region are superimposed on a broad background that spans  $\sim 300 \text{ cm}^{-1}$ .<sup>81,93</sup> The sharp bands were assigned to the HCl stretch transitions of smaller, undissociated  $(HCl)_m(H_2O)_n$  clusters, and on the basis of isotopic substitution,<sup>71</sup> the broad background was assigned to larger undissociated clusters. The broad background in the FTIR gas phase spectra is similarly observed in the spectra obtained in solid matrices,<sup>89–92</sup> on the surface of ice films and nanoparticles,<sup>65,66,68–71</sup> and in helium nanodroplets.<sup>42</sup> In addition to the larger undissociated clusters, bands from dissociated ion pair clusters are also believed to contribute to these broad features. The origin and interpretation of the broad bands observed in these infrared spectra has been reviewed and discussed in a recent communication.<sup>42</sup>

A very recent helium nanodroplet study claimed the identification of a sharp spectral feature associated with the solvent separated  $H_3O^+(H_2O)_3Cl^-$  species.<sup>17</sup> Given this intrigu-

ing result, we feel that it is timely to revisit the HCl stretch spectra of these species isolated in helium nanodroplets. Here we have employed additional tools available to this method to arrive at unambiguous structural assignments of several bands that are common to both the gas phase and helium nanodroplet spectra, including the band previously assigned to the  $H_3O^+(H_2O)_3Cl^-$  species.

# 5.2 Experimental Methods

For these experiments, helium droplets are formed by the continuous expansion of 99.9995% helium with a backing pressure of 20 bar through a 5  $\mu$ m diameter nozzle cryogenically cooled to 16 K.<sup>1</sup> With these nozzle conditions, the average droplet size is approximately 4000 helium atoms.<sup>28,29</sup> About 1 cm downstream from the nozzle, the expansion is skimmed by a 0.4 mm diameter conical skimmer. A few cm downstream, both HCl and H<sub>2</sub>O are "picked-up" as the droplet beam passes through a 2 cm long, differentially pumped gas pick-up cell, containing HCl and H<sub>2</sub>O at a combined pressure of ~1.5 × 10<sup>-5</sup> Torr. The sequential pick-up of HCl and H<sub>2</sub>O monomers leads to the formation of clusters as the monomers rapidly condense within the droplet.<sup>20</sup> The condensation energy associated with this cluster formation is removed as the droplet evaporatively cools to 0.37 K.<sup>51</sup> A distribution of mixed (HCl)<sub>m</sub>(H<sub>2</sub>O)<sub>n</sub> clusters are produced under these conditions.

The idler beam output from the cw IR OPO overlaps the helium droplet beam in the two mirror multipass cell arrangement (see Figure 2.1). By employing the downstream multipass cell excitation configuration, we significantly reduce the presence of OSMS artifact signals that arise from the pick-up of molecules following vibrational excitation/relaxation. The OPO output is amplitude modulated with a mechanical chopper at 171 Hz, and the ion signal is processed with a lock-in amplifier, which is referenced to the chopper frequency. Two parallel, stainless steel electrodes are positioned orthogonal to the multipass cell such that a static dc electric field can be applied to the laser/droplet beam interaction region.<sup>1</sup> The electrodes are separated by 0.277(2) cm, and Stark field strengths up to ~60 kV/cm are achieved. The calibration of the electrode spacing is described elsewhere.<sup>95</sup> A Fresnel Rhomb (II-VI Inc.) is used to align the polarization of the OPO idler wave either parallel or perpendicular to the applied Stark field. For the field dependence measurements, the OPO frequency is fixed to the peak of a particular band, and the applied Stark field is linearly ramped from zero-field to 55 kV/cm. Several of these field strength scans are averaged and divided by the averaged zero-field signal intensity.

# 5.3 Theoretical Methods

There have been several reports of theoretical calculations of the structures, energetics, and vibrational frequencies of mixed (HCl)<sub>m</sub>(H<sub>2</sub>O)<sub>n</sub> clusters.<sup>72–81</sup> Using the Gaussian 03 suite of programs,<sup>96</sup> we have computed (MP2 / 6-311+g(3df,3pd)) the harmonic vibrational frequencies, permanent dipole moments ( $\mu_p$ ) and vibrational transition moment angles (VT-MAs) for the various isomers associated with the cluster sizes relevant to this study. The MP2 density matrix is used to obtain permanent dipole moments. For any one normal mode vibration, the VTMA is defined as the angle  $\mu_p$  makes with the transition dipole moment vector  $\mu_t$ .<sup>97</sup> The results of the ab inito calculations are summarized in Table 5.1, and the computed structures that correspond to energy minima are shown in Figure 5.1.

For a specific band in the infrared spectrum, the field ON to field OFF signal intensity ratio can be simulated, assuming a specific structure and value for the VTMA. In these simulations, the average projection of  $\mu_t$  onto the OPO polarization axis is determined as a function of the Stark field strength. The weighting function for this average is simply the normalized orientational distribution of  $\mu_p$  about the lab-frame Stark field axis. This dipole distribution function,  $P(\cos\theta)$ , is computed according to the procedures of Kong and



Figure 5.1: Equilibrium structures obtained from MP2/6-311+g(3df,3pd) ab initio calculations. Below each structure,  $\mu_p$  ( $\alpha$ ) are given in units of Debye and degrees, respectively. The angle  $\phi$  in structure **A** is the out-of-plane bending angle of HCl relative to the plane of the water molecule. Of the 2:2 isomers, structure **E** is the energetic minimum. Structures **C** and **D** lie 71 and 28 cm<sup>-1</sup> higher in energy, respectively. Structure **F** is 850 cm<sup>-1</sup> higher in energy that **E**. The HCl stretches that are predicted to fall in our tuning range are marked by an asterisk.

Experiment	$\Delta \nu ({\rm cm}^{-1})$	$\mu_p(\mathrm{D})$	$\alpha(^{\circ})$	PUC
S0	111	2.4(1)	59.5(8)	2:1
$\mathbf{S1}$	126			3:1
$\mathbf{S3}$	171	3.9(1)	0.0	1:1
$\mathbf{S4}$	180		>80	3:1
<b>S</b> 5	215	2.76(5)	58.2(2)	2:2
Ab Initio	$\Delta \nu ({\rm cm}^{-1})$	$\mu_p(\mathrm{D})$	$\alpha(^{\circ})$	m:n
$\mathbf{A}$ (C <sub>s</sub> )	246	3.67	19.2	1:1
В	148	2.39	62.3	2:1
$\mathbf{C}$	587	2.37	90.0	2:2
D	595	0.0	n/a	2:2
$\mathbf{E}$	273	2.76	58.4	2:2
$\mathbf{F}$	139	2.82	72.5	2:2
${\rm H}_{3}{\rm O}^{+}({\rm H}_{2}{\rm O})_{3}{\rm Cl}^{-}$	137	4.22	36.6	1:4

Table 5.1: Experimental Constants Compared to Those from MP2/6-311+g(3df,3pd) Calculations<sup>a</sup>

(a) <sup>*a*</sup> The experimental  $\Delta\nu$  corresponds to the frequency shift from the HCl monomer  $\nu_0$  in helium droplets (2885.3 cm<sup>-1</sup>), and the ab initio  $\Delta\nu$  is the computed shift from the HCl monomer vibration at the MP2/6-311+g(3df,3pd) level of theory (3058.3 cm<sup>-1</sup>). The ab initio frequency shifts and VTMAs ( $\alpha$ ) are those of the highest frequency HCl stretch in each cluster (**A** – **F**). For the charge dissociated (H<sub>2</sub>O)<sub>3</sub>(H<sub>3</sub>O)<sup>+</sup>Cl<sup>-</sup> structure, the shift and VTMA are those for the symmetric hydronium stretch. PUC is the cluster composition, HCl:H<sub>2</sub>O, inferred from the pick-up cell pressure dependence data. The composition of calculated (HCl)<sub>m</sub>(H<sub>2</sub>O)<sub>n</sub> structures (m:n) is shown for comparison.

Bulthuis.<sup>98</sup> Here,  $\theta$  is defined as the angle between  $\mu_p$  and the Stark field axis. Calculations of  $P(\cos\theta)$  assume the ab initio dipole moment components and rotational constants (divided by 3 to account for the helium solvent) for a specific cluster and a rotational temperature of 0.37 K. Projecting  $\mu_t$  onto the polarization axis of the OPO (either parallel to or perpendicular to the Stark field axis) and averaging over  $\theta$  gives the relative intensity due to cluster orientation at a given field strength,<sup>99</sup> where  $\alpha$  is the VTMA:

$$A_{\text{para}}(\alpha) \propto \int_{-1}^{1} P(\cos\theta) [\sin^2\alpha + 2\cos^2\theta - 3\sin^2\alpha \cos^2\theta] d\cos\theta$$
(5.1)

and

$$A_{\rm perp}(\alpha) \propto \int_{-1}^{1} P(\cos\theta) [2 - \sin^2\alpha - 2\cos^2\theta + 3\sin^2\alpha \cos^2\theta] d\cos\theta$$
(5.2)

For the simulations reported here, the field ON to field OFF intensity ratio is determined for Stark fields in the range of 0 to 50 kV/cm in increments of 5 kV/cm. This field dependence is determined for both polarization alignments. In the limit of infinite field, the asymptotic field dependence is due only to the VTMA ( $\alpha$ ) and is independent of  $\mu_p$  (as long as  $\mu_p$  is finite). For example, when  $\alpha = 0^{\circ}$ , 54.75°, and 90° (parallel polarization) the high field limit of the ON:OFF intensity ratios are 3, 1, and 0, respectively. However, the rate at which these asymptotic limits are approached depends strongly on the magnitude of  $\mu_p$ . Hence, the field dependence of the ON:OFF intensity ratio is an effective tool for assigning bands to specific isomers of (HCl)<sub>m</sub>(H<sub>2</sub>O)<sub>n</sub> clusters, since both  $\mu_p$  and  $\alpha$  are determined quite accurately at the MP2 level of theory used here.<sup>97</sup>



Figure 5.2: Survey scan of the HCl stretch region obtained in the m/z=19 u detection channel. The nozzle conditions and pick-up cell pressures were set to optimize the production of 2:2 clusters. The m:n assignments are based on the PUC pressure dependence of each band. The band positions and assignments from the previous FTIR free jet study<sup>81</sup> are shown along the bottom. NA corresponds to bands that were not assigned previously.

### 5.4 Results and Discussion

The helium nanodroplet survey scan of the HCl stretch region is shown in Figure 5.2. The spectrum has several sharp features superimposed on a broad background signal that spans the 2570 to 2850  $\text{cm}^{-1}$  region. Bands above 2750  $\text{cm}^{-1}$  associated with pure HCl clusters  $(m=1-5)^{100}$  are not present in this spectrum since the mass spectrometer is fixed to m/z=19 u (H<sub>3</sub>O<sup>+</sup>). The sharp bands observed here are assigned to the HCl stretches of mixed  $(HCl)_m(H_2O)_n$  clusters with m=(1-3) and n=(1,2). The m:n assignments shown in the figure are based on the pick-up cell (PUC) pressure dependence of each band as shown in Figure REF FIG. Here we do not try to fit the PUC dependence to Poisson distributions since this is technically an incorrect thing to do. The signal dependence on pressure is related to the product of the Poisson and log-normal (droplet size) distributions, which dynamically readjust following each sequential pick-up event. Therefore, it is inappropriate to fit these curves to Poisson distributions alone. Furthermore, each of the curves is initially offset by some background pressure, which can be different for each curve. So, we simply consider the *leading edges* of the PUC curves. Each curve is normalized so that the peak is at one. Also, the curves are translated so that the low pressure data all extrapolate to the same initial pressure value  $(p_{initial})$ . As seen in Figure REF FIG, all of the curves extrapolate to the same pressure, and the curves naturally fall into groups that have similar *leading edge slopes*. It is these *leading edge slopes* that are used to arrive at initial assignments of the spectra to a particular cluster size. We start by considering the slopes of the HCl monomer and HCl dimer curves. Comparing to these, we see that the band at 2714 cm<sup>-1</sup> has a H<sub>2</sub>O and HCl pressure dependece that have the same leading edge slopes as the HCl monomer curve. This, of course, was expected given the previous assignment of this band to the  $HCl-(H_2O)$  binary complex. Using the same logic, assignments for the composition of the other clusters were determined and are discussed in the caption for Figure 5.3. The PUC dependence of the



Figure 5.3: Pick-up cell (PUC) pressure dependence with the laser frequency fixed to the peak of each of the sharp resonances and also on two different frequencies corresponding to the broad background (2645 and 2586 cm<sup>-1</sup>). The peak at 2774 cm<sup>-1</sup> corresponds to 2 HCl molecules and 1 H<sub>2</sub>O molecule, at 2723 cm<sup>-1</sup> is >3 HCl and 2 H<sub>2</sub>O, 2714 cm<sup>-1</sup> is 1 HCl and 1 H<sub>2</sub>O, 2705 cm<sup>-1</sup> is 3 HCl and 1 H<sub>2</sub>O, 2670 cm<sup>-1</sup> is 2 HCl and 2 H<sub>2</sub>O, 2645 cm<sup>-1</sup> is >3 HCl and >2 H<sub>2</sub>O, 2586 cm<sup>-1</sup> is >3 HCl and >2 H<sub>2</sub>O. The background signal at 2546 and 2586 cm<sup>-1</sup> arises from (HCl)<sub>m</sub>(H<sub>2</sub>O)<sub>n</sub> clusters with m>3 and n>2.

signal at 2580 and 2640 cm<sup>-1</sup> indicates that the broad background arises from  $(\text{HCl})_m(\text{H}_2\text{O})_n$ clusters with m>3 and n>2. As discussed below, the combination of harmonic frequency calculations, dipole moment measurements, and an analysis of the VTMAs leads to a firm confirmation of the PUC assignments and also provides structural assignments for each of the sharp bands.

In the previous FTIR "ragout" jet spectroscopic study of Fárník et. al.,<sup>81,93</sup> the HCl stretch region for mixed HCl, H<sub>2</sub>O clusters was was similarly shown to consist of several rel-

atively sharp ( $\sim$ 5-20 cm<sup>-1</sup>) absorptions superimposed on a broad ( $\sim$ 200 cm<sup>-1</sup> background absorption centered around  $2550 \text{ cm}^{-1}$ . The sharp features were also assigned to HCl stretch bands of small mixed  $(HCl)_m(H_2O)_n$  clusters. The authors speculated that the underlying broad feature was partially due to the  $(H_3O)^+$  hydronium stretches of protolytically dissociated clusters. However, the broad feature was later assigned to larger undissociated mixed clusters on the basis of a 300 cm<sup>-1</sup> redshift of the feature in the analogous  $(HBr)_m(H_2O)_n$ spectrum.<sup>71</sup> Furthermore, substituting  $D_2O$  for  $H_2O$  had no effect on the position of the broad adsorption. The position and assignments of the sharp absorptions in the FTIR jet spectrum are shown along the bottom of Figure 5.2 (labels S0 to S6). Bands labeled as NA were not assigned at that time. In general, for the mixed cyclic complexes beyond the binary species, the higher frequency HCl stretches (those above  $\sim 2600 \text{ cm}^{-1}$ ) are associated with the HCl moieties that act as hydrogen donors to other HCl molecules. In comparison, the bands below  $2600 \text{ cm}^{-1}$  correspond to the stretching of HCl molecules that are hydrogen donors to  $H_2O$ . We denote these two distinct HCl stretches as  $Cl-H \cdot \cdot \cdot Cl$  and  $Cl-H \cdot \cdot \cdot O$ , respectively. An example of the latter type is the  $Cl-H \cdots O$  stretch in the 1:2 complex, which was observed in the FTIR jet spectrum at 2460  $\text{cm}^{-1}$ .<sup>81</sup> We do not observe these Cl-H···O stretch bands of the 1:n(n>1) clusters given the tuning range of our OPO.

### 5.4.1 $(HCl)_1(H_2O)_1$

The S3 band was previously assigned to the HCl stretch of the 1:1 complex in both the gas phase<sup>81,88,93</sup> and in helium droplets,<sup>101</sup> and our PUC measurements are consistent with these assignments. Figure 5.4 shows our measurement of the S3 band using two different mass spectrometer detection schemes. In Figure 5.4A, the detection channel is m/z=19 u (H<sub>3</sub>O<sup>+</sup>), which results in two closely spaced bands separated by ~2 cm<sup>-1</sup>. This splitting has been assigned to the <sup>35</sup>Cl/<sup>37</sup>Cl isotopomers of the 1:1 complex,<sup>101</sup> which is consistent with the 2 cm<sup>-1</sup> isotope splitting predicted by ab initio calculations. The presence of both peaks



Figure 5.4: HCl stretch spectrum of the binary HCl-H<sub>2</sub>O complex. The mass spectrometer detection channel was either (A) 19  $u/H_3O^+$  or (B) 36  $u/(H^{35}Cl)^+$ . The band due to the H<sup>37</sup>Cl-H<sub>2</sub>O isotopomer does not appear in the latter spectrum.

in the spectrum indicates that both isotopomers produce  $H_3O^+$  ions upon fragmentation in the ionization region of the mass spectrometer. In contrast, when the mass spectrometer is fixed to m/z=36 u (Figure 5.4B), only the higher frequency band due to  $(H^{35}Cl)(H_2O)$ is observed, indicating that the 36 u peak in the mass spectrum is mainly associated with the  $(H^{35}Cl)^+$  ion. We note here that m/z=36 u also corresponds to  $(He)_9^+$ , which is formed upon ionization of droplets containing *both* isotopomers. As a result of this, the m/z=36 u channel is not completely specific to the  $(H^{35}Cl)(H_2O)$  isotopomer, and a weak signal due to  $(H^{37}Cl)(H_2O)$  is barely visible at 2712.75 cm<sup>-1</sup>.

The HCl stretch band of  $(H^{35}Cl)(H_2O)$  at 2714.6 cm<sup>-1</sup> is redshifted 171 cm<sup>-1</sup> from the HCl monomer band in helium droplets.<sup>100,101</sup> This large frequency shift is indicative of a structure in which the HCl acts as a hydrogen donor to H<sub>2</sub>O. This redshift is 8.7 cm<sup>-1</sup> larger than that for the gas phase complex,<sup>81,93</sup> which agrees well with the previously established linear relationship between the complexation induced redshift and the solvent frequency shift due to the helium.<sup>1</sup> Consistent with the magnitude of the redshift, the computed structure of the 1:1 complex has a C<sub>s</sub> symmetry equilibrium geometry ( $\phi$ =135°) with HCl acting as the hydrogen donor (Figure 5.1A). We also note that the linewidth of the (H<sup>35</sup>Cl)(H<sub>2</sub>O) band is 1.46 cm<sup>-1</sup>, obscuring the rotational fine structure that would otherwise be observed for a cluster this size. This width is 10 times larger than observed in the high resolution gas phase spectrum, where the broadening was attributed to vibrational predissociation.<sup>88</sup> Apparently, the vibrational dynamics are accelerated due to interactions with the helium, as observed for other helium solvated hydrogen bonded clusters.<sup>102,103</sup>

Figure 5.5 shows the electric field dependence of the signal with the OPO frequency at 2714.3 cm<sub>-1</sub> and the mass spectrometer tuned to m/z=36 u. For these measurements, the HCl and H<sub>2</sub>O PUC pressures are reduced in order to eliminate signal contributions from the broad background due to larger clusters. When the OPO polarization is aligned parallel to the applied Stark field, the signal increases to over twice the zero-field level as the field



Figure 5.5: Electric Field ON/OFF dependence of the signal intensity at 2714.3 cm<sup>-1</sup>. The detection channel was m/z=36 u. The black traces are the experimental results, with the upward trending curve corresponding to parallel polarization and the downward trending curve corresponding to perpendicular polarization. The circles are the simulated values assuming the C<sub>s</sub> structure ( $\phi=135^{\circ}$ ), and the triangles are the simulations for the C<sub>2v</sub> structure. The squares are simulations that assume the vibrationally averaged structure. The red and blue simulations correspond to parallel and perpendicular polarizations, respectively.

increases beyond 40 kV/cm, whereas the signal is reduced to half the zero-field value with the perpendicular polarization configuration. These results are consistent with a vibration that has a VTMA close to zero.<sup>1</sup> The circles in Figure 5.5 are the simulated field ON:OFF intensity ratios, assuming the C<sub>s</sub> equilibrium structure of the HCl-H<sub>2</sub>O complex ( $\mu_a$ =3.46 D,  $\alpha$ =19.2°, and A=11.5 cm<sup>-1</sup>). Here, the red and blue points are for parallel and perpendicular polarization alignments, respectively.

The simulated field dependence for the  $C_s$  geometry is in rather poor agreement with the experiment, which can be understood by considering the double-well potential associated with the out of plane bending of the water molecule.<sup>80</sup> For this potential, the transition state is  $C_{2v}$  ( $\phi=180^{\circ}$ ), and the ab initio barrier between equivalent  $C_s$  ( $\phi=135^{\circ}$ ) structures is approximately  $65 \text{ cm}^{-1}$ .<sup>80</sup> The zero-point level was determined to be only a few cm<sup>-1</sup> below the barrier. Consistent with these computations, gas phase studies in the microwave  $^{84}$  and the infrared <sup>93</sup> both conclude an *effective*  $C_{2v}$  C2v structure at the zero-point level. In a recent helium droplet study of the asymmetric OH stretch,<sup>94</sup> transitions were observed from *both* K=0 and K=1 states, indicating the presence of two distinct nuclear spin species, consistent with a  $C_{2v}$  structure. Furthermore, the A rotational constant was determined to be >14  $cm^{-1}$ , which can be compared to the  $C_s$  and  $C_{2v}$  ab initio values of 11.52 and 14.39  $cm^{-1}$ , respectively. We have also simulated the field dependence assuming a  $C_{2v}$  structure for HCl-H<sub>2</sub>O ( $\mu_a$ =3.92 D,  $\alpha$ =0.0°, and A=14.4 cm<sup>-1</sup>)(triangles in Figure 5.5). In comparison to the  $C_s$  simulation, the agreement with experiment is substantially better for the  $C_{2v}$  case. From the ground state wavefunction in the double-well bending potential, we obtain expectation values of  $\mu_a$  and  $\alpha$  equal to 3.65 D and 13.0°, respectively. Simulations of the field dependence using these vibrationally averaged parameters are shown as squares in Figure 5.5. It is also interesting to note that the barrier height for the out of plane water bend should be *reduced* upon solvation in the helium droplet. This is apparent upon considering the dipole-induced polarization of the helium solvent, which reduces the free energy of the complex at all values



Figure 5.6: The black curve corresponds to the out of plane bending potential obtained at the MP2 / 6-311+g(3df,3pd) level of theory. A counterpoise correction was applied and all other degrees of freedom were relaxed at each value of  $\phi$ . The Numerov method was used to obtain the zero-point level (37 cm<sup>-1</sup>) and the wavefunction (blue curve). The dipole moment components and the VTMA of the HCl stretch was computed at each value of  $\phi$ . The expectation values of  $\mu_b$  and  $\mu_c$  are assumed to be zero, due to symmetry. The expectation values of  $\mu_a$  and the VTMA are determined in the usual way. Here, the a, b, c labels denote the inertial axis. By including the dipole-induced helium polarization term in the potential, the barrier is reduced by 9.2 cm<sup>-1</sup> (red curve). The zero-point level in this modified potential is at 32 cm<sup>-1</sup>. Overall, the effect of the helium is to confine the complex to a more planar geometry.

of  $\phi$ . However, this effect is maximized at the C<sub>2v</sub> geometry, which in turn results in a reduction of the barrier height. According to a mean field approach used previously for the tunneling potential of (HF)<sub>2</sub>,<sup>104</sup> helium solvation reduces the barrier between the two C<sub>s</sub> minima by 9.2 cm<sup>-1</sup>, (See Figure 5.6) leading to a slightly more planar geometry with  $\langle \mu_a \rangle = 3.71$  D and  $\langle \alpha \rangle = 11.4^{\circ}$ .

# 5.4.2 $(HCl)_2(H_2O)_1$

In the previous FTIR free jet study,<sup>81</sup> the S1 band at 2757 cm<sup>-1</sup> was assigned to the 2:1 cluster shown in Figure 5.1B. A second band labeled S8 was observed at 2580 cm<sup>-1</sup> and was also assigned to this complex. The higher frequency S1 band was attributed to the Cl-H…Cl stretch, and the lower frequency S8 band was assigned to the Cl-H…O stretch. These assignments are in good agreement with the frequency shift predictions from the CCSD(T) calculations of the same authors.<sup>81</sup> We did not find a band in the helium droplet spectrum near 2757 cm<sup>-1</sup> that can be assigned to the 2:1 cluster; instead, at this frequency, there is a weak feature present that grows in intensity with increasing HCl PUC pressure and appears to be associated with a 3:1 cluster. However, we observe an intense band at 2774 cm<sup>-1</sup> that does have a PUC pressure dependence that is consistent with the 2:1 assignment. We have labeled this band S0. It should be noted here that spectral features from pure (HCl)<sub>m</sub> clusters are also present in this range, with the (HCl)<sub>4</sub> cluster being observed previously at 2776 cm<sup>-1</sup> in the gas phase<sup>81</sup> and at 2773 cm<sup>-1</sup> in helium droplets.<sup>100</sup>

Figure 5.7 shows an expanded view of the S0 band region. Here the PUC pressures were kept somewhat lower to minimize signal contributions from the broad background. For the bottom spectrum (Figure 5.7B), the mass spectrometer was set to detect all masses greater than 6 u. As a result of this, the spectrum is a summation of all cluster absorption bands that fall in this region, including the pure (HCl)<sub>4</sub> band at 2773.1 cm<sup>-1</sup> and a broader feature centered near 2772 cm<sup>-1</sup> that is likely associated with other pure (HCl)<sub>m</sub> clusters. The top



Figure 5.7: Spectra of the Cl-H···Cl stretch in the 2:1 complex. Trace (A) was acquired in the m/z=19 u detection channel, and trace (B) corresponds to a scan with the same experimental conditions but with the mass spectrometer set to pass all masses greater than 6 u.



Figure 5.8: Simulations of the computed isotope splitting in the Cl-H…Cl stretch spectrum of the 2:1 complex. In (A) the black trace is the experiment with m/z=19 u detection, and the smooth red curve is the summation of the simulations from all four isotopomers. Following the labels in the inset, the (B) curve is the spectrum of the  $\mathbf{1}, \mathbf{2}={}^{35}$ Cl isotopomer. In curve (C), the higher and lower frequency curves are the predictions for the  $\mathbf{1}={}^{35}$ Cl,  $\mathbf{2}={}^{37}$ Cl and  $\mathbf{1}={}^{37}$ Cl,  $\mathbf{2}={}^{35}$ Cl isotopomer, respectively. Curve (D) is for the  $\mathbf{1}, \mathbf{2}={}^{37}$ Cl isotopomer.

spectrum (Figure 5.7) was recorded with the mass spectrometer fixed to 19 u. Since this mass corresponds to the  $H_3O^+$  fragment ion signal, the excitation of pure  $(HCl)_m$  clusters can not contribute to a signal modulation in this mass channel. Therefore, the top spectrum can only consist of bands from mixed  $(HCl)_m(H_2O)_n$  clusters. More specifically, the two bands are assigned to an isotope splitting of the Cl-H···Cl stretch of the 2:1 cluster.

An analysis of this isotope splitting is shown in Figure 5.8. The inset shows the structure of the 2:1 cluster with each Cl atom labeled as **1** or **2**. The top black trace is the experimental spectrum recorded in mass channel 19 u. Two bands are observed at 2771.87 and 2773.91 cm<sup>-1</sup>, which have an approximately 1:3 intensity ratio. Consistent with the observed splitting, ab initio calculations predict a 2.2 cm<sup>-1</sup> redshift of the Cl-H···Cl stretch when the Cl atom labeled **1** is changed from <sup>35</sup>Cl to <sup>37</sup>Cl. a <sup>37</sup>Cl. In comparison, if the Cl atom labeled **2** is changed from <sup>35</sup>Cl to <sup>37</sup>Cl, a 0.02 cm<sup>-1</sup> redshift is predicted. Also shown are four Lorentzian functions centered according to the predicted isotope shifts. Each Lorentzian has a 0.57 cm<sup>-1</sup> linewidth and an area that is based on the 3:1 natural abundance of the <sup>35</sup>Cl:<sup>37</sup>Cl isotopes. The green trace has an area of 9 and corresponds to the isotopomer with two <sup>35</sup>Cl atoms. Each peak in the blue trace has an area of 3, with the higher frequency peak corresponding to  $1=^{35}Cl/2=^{37}Cl$  and the lower frequency peak corresponding to  $1=^{37}Cl/2=^{35}Cl$ . The lower navy trace has an area of 1 and corresponds to the isotopomer with two <sup>37</sup>Cl atoms. Consistent with the isotope assignment, the red smooth curve, which is the sum of the four Lorentzians, has a 1:3 intensity ratio and is in excellent agreement with experiment.

The PUC pressure dependence and the isotope splitting provide rather firm support for the assignment of the S0 band to the Cl-H···Cl stretch of the 2:1 cyclic complex (Figure 5.1B). A more definitive assignment comes from the field dependence of the band intensity. As shown in Figure 5.9, applying the Stark field results in a signal change that is qualitatively different from that observed for the HCl stretch of the 1:1 complex. Specifically, the parallel polarization alignment leads to a *decrease* in intensity, whereas an increase is observed with the perpendicular alignment. Moreover, the signal change is less than 10 percent of the zerofield value. Both of these observations are consistent with a VTMA that is slightly larger than the magic angle (54.75°), namely the VTMA corresponding to no field dependence.<sup>1</sup> For comparison, the ab initio VTMA for the Cl-H···Cl stretch of the 2:1 cluster is 62.3° and  $\mu_{MP2}=2.39$  D. The field ON:OFF intensity ratio is simulated using the constants ( $\mu_p=2.4$  D,  $\alpha=59.5°$ ), and the overall agreement provides considerable support to the above assignment. Therefore, it is now safe to update the previous gas phase assignment of the 2:1 cluster from the S1 band to the S0 band. The Cl-H···O stretch is predicted to be redshifted 266 cm<sup>-1</sup> from the Cl-H···Cl stretch; according to the gas phase study,<sup>81</sup> this transition was



Figure 5.9: Electric field dependence of the signal intensity at 2773.9 cm<sup>-1</sup>. The detection channel was 19 u. The black traces are the experimental results, with the upward trending curve corresponding to perpendicular polarization and the downward trending curve corresponding to parallel polarization. The red and blue simulations correspond to parallel and perpendicular polarizations, respectively. The simulations assume  $\mu_p=2.4$  D and  $\alpha=59.5^{\circ}$ .

observed as a 20  $\text{cm}^{-1}$  broad band centered at 2580  $\text{cm}^{-1}$ . Unfortunately, our wavelength range prohibits a further study of this band.

# 5.4.3 $(HCl)_2(H_2O)_2$

In the gas phase study of Fárník et. al.,<sup>81</sup> the S2, S4, and S5 bands were not assigned, but they did speculate as to the assignment of S5, based on the HCl/H<sub>2</sub>O concentration dependence of their spectra. They stated, "While we cannot offer a plausible cluster assignment for S5, it appears to originate from a less HCl rich cluster, such as  $(HCl)_2(H_2O)_2$ , but clearly not from its alternating cyclic isomer." Our PUC results are consistent with this suggestion, and indeed, since the alternating cyclic isomer has predicted HCl stretch bands well below 2670 cm<sup>-1</sup>,<sup>77</sup> an initial assignment of the S5 band to the non-alternating cyclic  $(HCl)_2(H_2O)_2$  is certainly reasonable.

In a recent helium droplet study of  $(\text{HCl})_m(\text{H}_2\text{O})_n$  clusters, an alternative assignment of the S5 band was presented.<sup>17</sup> Based on PUC measurements and OSMS, the 2670 cm<sup>-1</sup> S5 band was assigned to the symmetric hydronium stretch in the protolytically dissociated  $\text{H}_3\text{O}^+(\text{H}_2\text{O})_3\text{Cl}^-$  cluster.<sup>17</sup> This is an intriguing assignment given that four water molecules is the predicted minimum number necessary for the dissociation of HCl in its ground vibrational state.<sup>73–75,77,79,83</sup> It is important to emphasize here, however, that our PUC data is inconsistent with the assignment of the S5 band to the  $\text{H}_3\text{O}^+(\text{H}_2\text{O})_3\text{Cl}^-$  ion pair. As we increase the water pressure to a level that favors the formation of the 1:4 cluster, we only observe an increase in the broad feature that lies underneath the sharper S5 band. Once again, our data supports an initial assignment of the sharp S5 band to a 2:2 cluster. Possible candidate structures for this 2:2 cluster are given in Figures 5.1C - 5.1F, and the ab initio frequency shifts, dipole moments, and VTMAs of these structures are summarized in Table 5.1.

Figure 5.10 shows the OSMS spectrum obtained with the OPO at 2670.0  $\rm cm^{-1}$ , corre-



Figure 5.10: Optically selected mass spectrum with the OPO fixed to 2670.0 cm<sup>-1</sup>, that is, the peak of the S5 band. The signal level in the high mass section of the spectrum is multiplied by 10. Masses 36, 37, 72, and 73 are assigned to  $(H^{35}Cl)^+$ ,  $H^+(H^{35}Cl)$  or  $H^+(H_2O)_2$ ,  $(H^{35}Cl)_2^+$ , and  $H^+(H^{35}Cl)_2$ , respectively.

sponding to the peak of the S5 band. The mass spectrometer signal is processed with a lock-in amplifier, leading to a mass spectrum of only those species in resonance with the OPO frequency. For this measurement, we reduced the PUC pressures well below the levels required to optimize the intensity of the S5 band. Hence, the OSMS shown in Figure 5.10 is only representative of the cluster associated with the S5 band and not the clusters (either dissociated or undissociated) that contribute to the underlying broad background in this spectral region. The most intense peaks in the OSMS are m/z=19, 36, 37, 72, and 73 u. We assign these to  $H_3O^+$ ,  $(H^{35}Cl)^+$ ,  $H^+(H^{35}Cl)$  or  $H^+(H_2O)_2$ ,  $(H^{35}Cl)_2^+$ , and  $H^+(H^{35}Cl)_2$ , respectively. These assignments are motivated by and are consistent with the suggested S5 band assignment of Fárník et. al.,<sup>81</sup> i.e. the non-alternating cyclic  $(HCl)_2(H_2O)_2$  cluster (Figure 5.1E). On the other hand, the OSMS is not consistent with the assignment of S5 to the  $H_3O^+(H_2O)_3Cl^-$  species. Indeed, the strong signals at both m/z=36 and 72 u indicate intact HCl molecules following ionization and fragmentation of the cluster, and it is not clear how these can arise from the  $H_3O^+(H_2O)_3Cl^-$  solvent separated ion pair.

Figure 5.11 shows an expanded view of the S5 band. The spectrum in Figure 9A is obtained with the mass spectrometer tuned to m/z=19 u, which corresponds to H<sub>3</sub>O<sup>+</sup>. In the m/z=19 u spectrum, the S5 band is split into two peaks centered at 2667.9 and 2670.0 cm<sup>-1</sup>. In the previous report,<sup>17</sup> the weaker band at 2667.9 cm<sup>-1</sup> was assigned to a nearly isoenergetic isomer of the H<sub>3</sub>O<sup>+</sup>(H<sub>2</sub>O)<sub>3</sub>Cl<sup>-</sup> species. By tuning the mass spectrometer to m/z=72 u ((H<sup>35</sup>Cl)<sup>+</sup><sub>2</sub>) (Figure 5.11B), the band at 2667.9 cm<sup>-1</sup> disappears, while the 2670.0 cm<sup>-1</sup> band remains. This observation is consistent with an assignment of the two observed bands to the expected isotope splitting in the spectrum of (HCl)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> (Figure 5.1E) due to the <sup>35</sup>Cl:<sup>37</sup>Cl 3:1 isotope ratio, analogous to the splitting observed for the S0 band associated with the 2:1 cluster. Once again, ab initio calculations predict a 2 cm<sup>-1</sup> redshift of the Cl-H···Cl stretch when the C1 atom labeled with a **1** is changed from <sup>35</sup>Cl to <sup>37</sup>Cl (Figure 5.11 inset), consistent with the experimentally observed splitting. Figure


Figure 5.11: High resolution scans of the S5 band. The mass spectrometer is tuned to m/z=19 u in scan (A) and m/z=72 u in scan (B).



Figure 5.12: Simulations of the computed isotope splitting in the Cl-H···Cl stretch spectrum of the 2:2 complex. In (A) the black trace is the experiment with m/z=19 u detection, and the smooth red curve is the summation of the simulations from all four isotopomers. Following the labels in the inset, the (B) curve is the spectrum of the  $\mathbf{1}, \mathbf{2}={}^{35}$ Cl isotopomer. In curve (C), the higher and lower frequency curves are the predictions for the  $\mathbf{1}={}^{35}$ Cl,  $\mathbf{2}={}^{37}$ Cl, and  $\mathbf{1}={}^{37}$ Cl,  $\mathbf{2}={}^{35}$ Cl isotopomers, respectively. Curve (D) is for the  $\mathbf{1}, \mathbf{2}={}^{37}$ Cl isotopomer.

5.12 shows an analysis of this isotope splitting, where similar to the above discussion for the 2:1 cluster, the green, blue, and navy curves correspond to  $1, 2={}^{35}$ Cl,  $1={}^{35,37}$ Cl/ $2={}^{37,35}$ Cl, and  $1, 2={}^{37}$ Cl, respectively. The smooth red trace is the summation of the three curves, which is in excellent agreement with the observed splitting and intensity ratios. Certainly, in combination, the PUC cell dependence, the OSMS, and the isotope analysis all provide considerable support to the assignment of S5 to the 2:2 cluster shown as structure E in Figure 5.1. Nevertheless, given the disagreement with the previous study,<sup>17</sup> we felt that it was imperative to have additional evidence for our assignment.

For a definitive assignment of the S5 band, we turn to the electric field dependence. The



Figure 5.13: Top panel: Electric field ON/OFF dependence of the signal intensity at 2670.0 cm<sup>-1</sup>. The detection channel was m/z=19 u. The black traces are the experimental results, with the upward trending curve corresponding to perpendicular polarization and the downward trending curve corresponding to parallel polarization. The red and blue simulations correspond to parallel and perpendicular polarizations, respectively. The simulations assume  $\mu_p=2.76$  D and  $\alpha=58.2^{\circ}$ . Bottom panel: Simulations of the electric field dependence for the 2:2 isomers and the ion pair species. The circles, squares, and diamonds assume the ab initio  $\mu_p$  and  $\alpha$  for the Cl-H···Cl stretch in the 2:2 clusters C, E, and F, respectively. The triangle assume the  $\mu_p$  and  $\alpha$  of the symmetric hydronium stretch of the (H<sub>2</sub>O)<sub>3</sub>(H<sub>3</sub>O)<sup>+</sup>Cl<sup>-</sup> ion pair. Structure D has  $\mu_p=0$ , and thus has no electric field effect.

electric field dependence of the intensity is shown in the top panel of Figure 5.13. Here the mass spectrometer detection channel is m/z=19 u, and the OPO frequency is set to  $2670.0 \text{ cm}^{-1}$ . With the parallel polarization alignment, the signal intensity decreases as the Stark field increases. In comparison, a small increase in signal intensity is observed when the laser electric field is aligned perpendicular to the Stark field. Qualitatively, both of these results indicate that the VTMA for the vibration probed here is greater than 54.75°.<sup>1</sup> The simulated field dependences are shown as squares in Figure 5.12; here the blue and red points correspond to perpendicular and parallel polarizations, respectively. The value of the VTMA ( $\alpha = 58.2^{\circ}$ ) was adjusted to give the best agreement with the experiment. As shown in Figure 5.1, for structure **E**, the ab initio VTMA for the Cl-H $\cdots$ Cl stretch is 58.4°, which is in excellent agreement with the experiment. Furthermore, the predicted field dependences for the other calculated 2:2 structures are in qualitative disagreement with the experimental measurements. Simulations of the field dependence for structures  $\mathbf{C}$  through  $\mathbf{F}$  are shown in the bottom panel of Figure 5.13. Note that there is no field dependence for structure **D**, given that it is non-polar. For completeness, we have also simulated the field dependence for the protolytically dissociated  $H_3O^+(H_2O)_3Cl^-$  cluster. This species has a much larger dipole moment (4.22 D) than that required to satisfactorily simulate the experimental field dependence. Furthermore, if we assume the VTMA calculated for the symmetric hydronium stretch of  $H_3O^+(H_2O)_3Cl^-$  (36.6°), a qualitatively wrong trend is predicted for the signal intensity as the field increases. That is, with parallel polarization, an increase in signal is predicted, rather than the observed decrease. Clearly, the agreement between theory and experiment for structure E provides rather definitive support to our assignment of the S5 band to the non-alternating, cyclic  $(HCl)_2(H_2O)_2$  cluster. For the Cl-H···O stretch transition of this cluster, a 526  $\rm cm^{-1}$  redshift is predicted from the S5 band, placing it well outside of the tuning range of our OPO.

### 5.4.4 Larger Clusters

Two other pronounced bands in the survey spectrum shown in Figure 5.2 are those at 2705 and 2721 cm<sup>-1</sup>. The PUC pressure dependence of these bands leads us to tentatively assign these to a Cl-H…Cl type stretch in a 3:1 and a 4:2 cluster, respectively. Unfortunately, at the higher PUC pressures required to optimize these bands, the broad background becomes more pronounced, making a definitive assignment based on the field dependence more difficult. Moreover, these bands are partially overlapped with the HCl stretch band of the 1:1 complex. Nevertheless, as shown in Figure 5.14, the field dependence of the 2705 cm<sup>-1</sup> band is in qualitative agreement with simulations based on the VTMA (73.9°) of the lower frequency Cl-H…Cl stretch vibration of the cyclic (HCl)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub> cluster. The higher frequency Cl-H…Cl stretch of this cluster may be the feature at 2757 cm<sup>-1</sup> discussed above that was previously assigned to the 2:1 cluster in the FTIR free jet spectrum.<sup>81</sup> Once again, the Cl-H…O stretch of this species is predicted to be redshifted outside our tuning range.

Between 2750 and 2825 cm<sup>-1</sup>, there are several weak but reproducible features that are associated with larger clusters. We speculate here that these are due to Cl-H···Cl stretches in larger mixed  $(\text{HCl})_m(\text{H}_2\text{O})_n$  clusters, including branched clusters that have dangling HCl moieties. Indeed, in the spectra of helium solvated pure  $(\text{HCl})_n$  clusters, this region of the spectrum became congested and grew in intensity with increasing HCl pressure.<sup>100</sup> Although the global minima are cyclic, low-lying branched structures are predicted as energetic minima for  $(\text{HCl})_n$  clusters with n>4, and these have Cl-H···Cl stretches that are spread throughout the 2700-2850 cm<sup>-1</sup> range.<sup>100</sup> Similar chromophores in mixed  $(\text{HCl})_m(\text{H}_2\text{O})_n$  clusters could potentially contribute to a broad background in this region, given the diversity of cluster structures with increasing cluster size and the tendency of locally stable structures to be stabilized in the helium environment.<sup>2,105</sup> Indeed, a broad background in the HCl stretch region is observed in both the gas phase and helium droplet spectra of  $(\text{HCl})_m(\text{H}_2\text{O})_n$ .



Figure 5.14: Electric field dependence of the 2705 cm<sup>-1</sup> band assigned to the 3:1 cluster. Simulations are based on the ab initio constants for this structure. The agreement isnt as good here as for the other simulations, likely due to the contributions from larger clusters that overlap this transition at the higher pick-up cell pressures required to optimize the signal. Nevertheless, the assignment is to the  $H \cdots Cl H \cdots Cl$  stretch of the middle HCl moiety, which should have a VTMA close to 90 degrees, which is consistent with the experimental results.

surface of nanometer ice particles. The origin and significance of this broad background, common to all three measurements, has been described in more detail in a previous report.<sup>42</sup> We note again that the PUC dependence of the signal at 2580 and 2640 cm<sup>-1</sup> indicates that the broad background observed in this study arises from  $(HCl)_m(H_2O)_n$  clusters with m>3 and n>2.

### 5.5 Conclusions

The helium nanodroplet isolation spectra of  $(HCl)_m(H_2O)_n$  clusters have been measured in the  $Cl-H \cdot \cdot Cl$  range. The combination of pick-up cell pressure dependence, optically selected mass spectrometry, and electric field dependence measurements have lead to definitive assignments of the sharp bands observed in this region. Bands associated with the 1:1 binary complex and the 2:1, 2:2, and 3:1 clusters are observed at 2715, 2774, 2670, and 2705  $cm^{-1}$ , respectively. Each of these bands are split due to the presence of a distribution of isotopomers. These splittings are accurately reproduced assuming the 3:1 natural abundance of <sup>35</sup>Cl:<sup>37</sup>Cl isotopes. Simulations of the electric field dependence of these bands allow us to make definite structural assignments despite the lack of rotational fine structure in the spectra of these species. The field dependence of the HCl stretch band associated with the 1:1 cluster indicates a vibrationally averaged  $C_{2v}$  structure, in agreement with previous studies. We have confirmed that the 2:1 cluster is cyclic and that the 2:2 cluster has a non-alternating cyclic structure. The broad background observed in previous measurements of these clusters in various environments has been similarly observed here. The pressure dependence of this broad background suggests that it originates at least partially from mixed  $(HCl)_m(H_2O)_n$ clusters with m>3 and n>2.

# Chapter 6

# Rotational Dynamics of the CH<sub>3</sub> Radical in Superfluid <sup>4</sup>He Nanodroplets

We report the ro-vibrational spectrum of the  $\nu_3(e')$  band of the methyl radical (CH<sub>3</sub>) solvated in superfluid <sup>4</sup>He nanodroplets. Five allowed transitions produce population in the N<sub>K</sub>=0<sub>0</sub>, 1<sub>1</sub>, 1<sub>0</sub>, 2<sub>2</sub> and 2<sub>0</sub> rotational levels. The observed transitions exhibit variable Lorentzian line shapes, consistent with state specific homogeneous broadening effects. Population relaxation of the 0<sub>0</sub> and 1<sub>1</sub> levels is only allowed through vibrationally inelastic decay channels, and the <sup>P</sup>P<sub>1</sub>(1) and <sup>R</sup>R<sub>0</sub>(0) transitions accessing these levels have 4.12(1) and 4.66(1) GHz full-width at half-maximum linewidths, respectively. The linewidths of the <sup>P</sup>R<sub>1</sub>(1) and <sup>R</sup>R<sub>1</sub>(1) transitions are comparatively broader (8.6(1) and 57.0(6) GHz, respectively), consistent with rotational relaxation of the 2<sub>0</sub> and 2<sub>2</sub> levels within the vibrationally excited manifold. The nuclear spin symmetry allowed rotational relaxation channel for the excited 1<sub>0</sub> level has an energy difference similar to those associated with the 2<sub>0</sub> and 2<sub>2</sub> levels. However, the <sup>P</sup>Q<sub>1</sub>(1) transition that accesses the 1<sub>0</sub> level is 2.3 and 15.1 times narrower than

the  ${}^{P}R_{1}(1)$  and  ${}^{R}R_{1}(1)$  lines, respectively. The relative linewidths of these transitions are rationalized in terms of the anisotropy in the He-CH<sub>3</sub> potential energy surface, which couples the molecule rotation to the collective modes of the droplet.

### 6.1 Introduction

Rotational fine structure is often apparent in the infrared (IR) spectra of small molecules and clusters solvated in <sup>4</sup>He nanodroplets.<sup>2,62,106,107</sup> This interesting and unique property of helium droplets is a direct manifestation of the Bose statistics associated with the <sup>4</sup>He quantum fluid.<sup>108</sup> With few exceptions,<sup>109–111</sup> the ro-vibrational spectra measured in liquid <sup>4</sup>He are representative of the gas phase molecular or cluster symmetry.<sup>112</sup> However, the individual ro-vibrational transitions in these spectra are rarely as sharp as those measured with gas phase direct absorption methods. There has been considerable discussion regarding a number of potential sources of inhomogeneous and homogeneous broadening related to the finite size of the droplet and the broad statistical distribution of droplet sizes produced, <sup>18,104,113–119</sup> and the relative importance of some of these has been quantitatively estimated.<sup>120–122</sup> Nevertheless, the understanding of this aspect of the helium droplet spectra still remains incomplete. We report here the ro-vibrational spectrum of the degenerate asymmetric stretch of the methyl radical  $(CH_3)$ , and we discuss the observed transition dependent broadening effects and how they are dictated by the anisotropy in the molecule-helium interaction potential, which couples the ro-vibrationally excited molecular rotor to the collective modes of the droplet.

With an elegant measurement of the ro-vibrational spectrum of OCS in pure and mixed  ${}^{3}\text{He}/{}^{4}\text{He}$  droplets, Vilesov and co-workers provided strong evidence that the rotational fine structure present in the spectrum is due to the superfluid properties of the bosonic  ${}^{4}\text{He}$  liquid at 0.4 Kelvin.  ${}^{14}$  As observed for other small molecules solvated in  ${}^{4}\text{He}$  droplets,  ${}^{51}$ 

clear P and R branch structure was evident in the IR spectrum of OCS solvated in  ${}^{4}$ He droplets. However, rotational structure was conspicuously absent when the measurement was made using pure <sup>3</sup>He droplets, and the OCS vibrational band appeared instead as a single broadened feature with an  $\sim 0.1 \text{ cm}^{-1}$  linewidth. This striking difference in the spectra was attributed to the rapid rotational diffusion of the ro-vibrationally excited OCS molecule within the <sup>3</sup>He droplet.<sup>14</sup> The scattering of the excited rotor off the thermal excitations of the fermionic <sup>3</sup>He liquid leads to rotational dephasing on a timescale that is fast in comparison to a single rotational period of the molecule. Apparently, the coherence of the rotor ensemble lasts much longer in <sup>4</sup>He droplets, leading to the well resolved rotational fine structure. The key difference between the fermionic <sup>3</sup>He and bosonic <sup>4</sup>He droplets is the presence of a high density of low energy thermal excitations in the former (particle-hole excitations) and a sparse density in the latter (phonon excitations).<sup>108</sup> Indeed, for a <sup>4</sup>He droplet with  $\sim 3000$ atoms, the only excitations present at the energy of the excited OCS rotational level (0.15) $cm^{-1}$  for J=1)<sup>123</sup> are those associated with the surface (ripplons), to which the excited rotor is only weakly coupled.<sup>120</sup> On the basis of the liquid drop model,<sup>13</sup> the energy of the first phonon for a droplet this size is  $1.25 \text{ cm}^{-1}$ , and there are hence no thermally populated phonon excitations at the 0.4 K droplet temperature.

For relatively "heavy" rotors (B less than about 0.5 cm<sup>-1</sup>), such as OCS, it is typical for the individual ro-vibrational transitions to be inhomogeneously broadened with full-width at half-maximum (fwhm) linewidths between 0.1 to 1 GHz (0.003 to 0.03 cm<sup>-1</sup>). For these systems, assuming rotational relaxation occurs within the excited vibrational manifold, all possible rotational relaxation channels have energy differences that are in a regime in which the density of phonon states is quite sparse, even for the largest droplet sizes produced in these experiments.<sup>13,124,125</sup> For these heavy rotors, the rotational population relaxation timescale is estimated to be on the order of 10 ns.<sup>115</sup> Moreover, relaxation occurs as a result of the interaction of the dopant with the surface ripplon excitations.<sup>115</sup> As the rotational energy gap approaches and then exceeds the energy of the roton excitations ( $\sim 6 \text{ cm}^{-1}$  in bulk helium),<sup>126</sup> ro-vibrational transitions are observed to be much broader, and this has been attributed to resonant rotational energy transfer to a comparatively larger density of droplet states (phonons/rotons/maxons) at the energy difference of the rotational relaxation channel (see, for example, Figure 11 of Reference<sup>1</sup>). An interesting example of this behavior is the R(1) transition in the 3  $\mu$ m ro-vibrational spectrum of  ${}^{12}C_2H_2$ , in which the relaxation channel (J=2 to J=0) has an energy difference of 5.55 cm<sup>-1</sup>.<sup>117</sup> Although this energy difference is slightly less than the roton branch in bulk superfluid helium, the approximately three times broader R(1) linewidth, in comparison to the P(1) transition (P(1) accesses the J=0 level), was interpreted as originating from rotational relaxation upon the creation of roton excitations in the droplet. An alternative explanation is that the R(1) linewidth in the acetylene spectrum is indicative of the onset of quantum evaporation at  ${\sim}5~{\rm cm}^{-1},$  in which a He atom is coherently emitted when a phonon is created in the droplet, propagates to the surface, and then strikes the droplet-vacuum interface.<sup>107</sup> The discrete phonon spectrum in this energy regime is hence lifetime broadened with a width estimated to be  $\sim 0.5$  $cm^{-1}$  as a result of the ~10 ps timescale associated with the phonon propagation, as discussed by Stienkemeier and Lehmann.<sup>107</sup> The implication of this is that the discrete phonon spectrum beyond  $\sim 4.5 \text{ cm}^{-1}$  is effectively washed out and the excitation of a rotor to this energy regime, or beyond, can result in rotational relaxation to a true continuum of droplet excitations.

For even "lighter" rotors, such as HF,<sup>114</sup>  $CH_4$ ,<sup>18</sup>  $H_2O$ ,<sup>127,128</sup> and  $NH_3$ ,<sup>129</sup> the rotational relaxation energy gaps associated with ro-vibrational excitation can exceed the roton and maxon branches in bulk superfluid helium, and the transitions are observed as broadened, Lorentzian line shapes with fwhm linewidths representative of resonant energy transfer on a sub 10 ps timescale. The  $CH_3$  radical provides an interesting probe of the rotational dynamics in this energy regime. Indeed, as a planar oblate top with two nuclear spin modifications, the  $CH_3$  ro-vibrational transitions access high lying rotational levels whose energy gaps exceed the energy of the fundamental roton/maxon excitations of the droplet. Despite the energy gaps associated with the relaxation channels being similar for some of the transitions, the associated linewidths are nevertheless qualitatively different. We rationalize these differences in terms of the symmetry and anisotropy of the He-CH<sub>3</sub> intermolecular potential surface, which couples the molecular rotational motion to the collective modes of the droplet, and hence plays an important role in the rate of rotational population relaxation.

### 6.2 Experimental Methods

For the experiments presented here, low-pressure, high-temperature pyrolysis of di-tertbutyl peroxide (DTBP) was carried out to produce methyl radicals. The pyrolysis source is shown in Figure 2.3 and the pyrolysis of DTBP at  $\sim$ 700 K results in the fragmentation of DTBP into two CH<sub>3</sub> radicals and two (CH<sub>3</sub>)<sub>2</sub>CO molecules.<sup>3</sup> The droplet beam passes into a differentially pumped chamber where the droplets are electron impact ionized and detected with a quadrupole mass spectrometer. Figure 6.1 shows the electron impact mass spectra of the droplet beam as the experimental conditions are adjusted to produce helium solvated methyl radicals. With the pyrolysis source off, electron impact results in a mass spectrum consisting of a series of intense  $\mathrm{He}_n^+$  peaks.<sup>19</sup> Allowing DTBP to flow through the cold source leads to the pick-up of DTBP and the appearance of peaks at m/z=43, 57, and 73 u (Figure 6.1b). Upon heating the source to ~700 K, the peaks at m/z=57 and 73 u disappear while peaks at m/z=15, 27, and 29 u gain intensity (6.1c), which indicates the pyrolysis of DTBP and the introduction of the  $CH_3$  and  $(CH_3)_2CO$  molecules to the droplets. The DTBP pressure is kept low ( $\sim 10^{-5}$  Torr) to avoid recombination reactions that may occur within the pyrolysis source and to optimize for the pick-up of single molecules. At this pressure, it is estimated that between 15 20% of all droplets pick-up only a single CH<sub>3</sub>



Figure 6.1: Mass spectra of (a) the neat droplet beam, (b) the beam following the introduction of cold DTBP, and (c) the beam following the pyrolysis of DTBP at 700K.

radical.<sup>20</sup> Following pick-up, the molecular degrees of freedom of the hot  $CH_3$  radical are cooled to the droplet temperature (0.4 K) *via* helium atom evaporation.<sup>51</sup>

The output from a continuous-wave infrared (IR) optical parametric oscillator (Lockheed-Martin Aculight) overlaps the helium droplet beam collinearly. Ro-vibrational excitation of the helium solvated CH<sub>3</sub> radicals is followed by energy transfer to the collective excitations of the droplet, leading to the evaporation of approximately 600 helium atoms ( $\leq 5 \text{ cm}^{-1}$  of energy is removed per evaporating helium atom).<sup>130</sup> This laser induced reduction in the

geometric cross section is detected as a depletion of ion signal in the m/z = 15 u channel, so as to discriminate against droplets containing other combinations of CH<sub>3</sub> and (CH<sub>3</sub>)<sub>2</sub>CO. The laser beam is mechanically chopped, and the ion signal is processed by a lock-in amplifier as the frequency is tuned from 3140 to 3210 cm<sup>-1</sup>. The resulting spectrum is normalized to the laser power.

### 6.3 Results

An energy level diagram of the  $\tilde{X} {}^{2}A_{2}^{"}$  CH<sub>3</sub> radical is shown in Figure 6.2. The nuclear spins of the three hydrogen atoms couple to form I=3/2 ( $\Gamma_{ns}=A'_1$ ) and I=1/2 ( $\Gamma_{ns}=E'$ ) ortho and para nuclear spin isomers, respectively. At the pyrolysis source temperature, the ratio of ortho to para isomers is 1:1, due to the 0:4:2 ( $A_1:A_2:E$ ) nuclear spin statistical weights of the rovibronic levels and the fact that there are twice as many E levels as there are  $A_2$ . Upon droplet pickup, the ensemble of *ortho* (*para*) isomers cools completely to the lowest rotational level with  $\Gamma_{\rm rve}=A_2$  ( $\Gamma_{\rm rve}=E$ ) symmetry. Therefore, the entire helium solvated methyl radical population is distributed evenly amongst the  $0_0$  (ortho) and  $1_1$ (para) rotational levels. It is expected that nuclear spin conversion does not occur on the 2 ms timescale of the experiment.<sup>117</sup> The rotational levels in Figure 6.2 are given either an ortho or para label to indicate the associated nuclear spin modification. Since the vibronic symmetry of the doubly degenerate  $\nu_3(e')$  excited vibrational state is E", rotational levels with  $K \neq 3n$  are six-fold degenerate with respect to nuclear spin and contain both ortho and *para* components. The transition dipole moment lies in the plane of the molecule and perpendicular to the c-inertial axis. The  $\nu_3$  band is therefore a perpendicular band with  $\Delta K = \pm 1$  and  $\Delta N = 0, \pm 1$  selection rules. The five allowed ro-vibrational transitions of the  $\nu_3$  band are shown in Figure 6.2 and are labeled as  ${}^{\Delta K}\Delta J_{K''}(J'')$ . The  ${}^{R}R_0(0)$  transition accesses the ortho component of the  $1_1$  level in the excited vibrational state, and the  ${}^{R}R_1(1)$ 

transition accesses the *para* component of the  $2_2$  level.

The approximately 15-fold increase in intensity in the m/z=15 ion channel upon pyrolysis of DTBP indicates that  $CH_3^+$  is the major ionization product of the helium solvated  $CH_3$ radicals. Therefore, the depletion signal was measured in this mass channel as the laser was tuned through the frequency region containing the gas phase ro-vibrational transitions of the  $\nu_3$  band.<sup>131</sup> The red trace in Figure 6.3 is a simulation of the expected spectrum based on the gas phase constants,<sup>131,132</sup> while the black trace is the experimental helium nanodroplet spectrum. From inspection of this spectrum, it is clear that the positions and relative intensities of the  $\nu_3$  transitions of  $(He)_N$ -CH<sub>3</sub> are similar to those expected from the gas phase simulation. As expected, there is negligible nuclear spin conversion on the timescale of the experiment, namely <2 ms.

The experimental spectrum shown in Figure 6.3 was measured under conditions that produced a droplet size distribution with a mean of ~3800 He atoms. These conditions were found to maximize the intensity of the  ${}^{R}R_{0}(0)$ . Figure 6.4 shows the four sharpest individual ro-vibrational transitions obtained with these source conditions. All of these transitions are fit very well to Lorentzian line shapes, which are shown as the smooth red lines in Figure 6.4. The positions and widths (full-width at half-maximum (fwhm)) obtained from these fits are given in Table 6.1. From the center frequencies of the  ${}^{P}Q_{1}(1)$ ,  ${}^{P}P_{1}(1)$  and  ${}^{P}R_{1}(1)$  transitions, the B' and  $D'_{N}$  constants can be determined from upper state combination differences. These are given in Table 6.1, along with the gas phase constants for comparison. Here we find that the B' constant is reduced by 1.5% from the gas phase value, which corresponds to a solventinduced increase in the effective moment of inertia about the *b*-inertial axis of only 0.0244  $u \cdot \hat{A}^{2}$ . This relatively minor solvation effect is consistent with what has been observed for other helium solvated "light" rotors with large (>1 cm^{-1}) rotational constants,  ${}^{62}$  such as CH<sub>4</sub>, NH<sub>3</sub> and HF.  ${}^{18,114,129}$  If we assume a similar solvent effect for the C' constant and fix the  $D'_{NK}$ ,  $D'_{K}$ , and  $\xi$  constants to their gas phase values, we estimate the band origin to be



Figure 6.2: Methyl radical ground state and  $\nu_3$  excited state energy level diagram. The energy levels are labeled by rotational quantum numbers N<sub>K</sub>. The blue arrow shows the one allowed transition from the I=3/2 (*ortho*), 0<sub>0</sub> ground state, and the red arrows show the four allowed transitions from the I=1/2 (*para*), 1<sub>1</sub> ground state. The red *ortho* and *para* labels indicate the nuclear spin symmetry of the components of the 1<sub>1</sub> and 2<sub>2</sub> levels accessed via the <sup>R</sup>R<sub>0</sub>(0) and <sup>R</sup>R<sub>1</sub>(1) transitions, respectively.



Figure 6.3: CH<sub>3</sub>  $\nu_3$  (e<sup>'</sup>) spectrum measured in the m/z=15 u mass channel. The red curve corresponds to a simulated spectrum using the gas phase constants from Reference<sup>132</sup>. The assignments of each ro-vibrational transition are shown in the notation  ${}^{\Delta K}\Delta J_{K''}(J'')$ .



Figure 6.4: The (a)  ${}^{P}P_{1}(1)$ , (b)  ${}^{P}Q_{1}(1)$ , (c)  ${}^{R}R_{0}(0)$ , and (d)  ${}^{P}R_{1}(1)$  transitions of the  $\nu_{3}$  band measured under nozzle conditions that produced average droplet sizes of about 3800 He atoms. The smooth red lines correspond to the Lorentzian lineshape fits.

3160.9(1) cm<sup>-1</sup>. Within the error of this analysis, which is due to the above assumptions, the  $\nu_3$  vibrational band origin in helium is unchanged from the gas phase value. The linewidths observed here are considerably broader than both the ~100 MHz linewidths observed in the CH<sub>3</sub> gas phase direct absorption spectrum and the ~300 MHz spin-rotation splittings observed for each gas phase transition.<sup>131</sup> While the widths of the <sup>P</sup>Q<sub>1</sub>(1), <sup>P</sup>P<sub>1</sub>(1) and <sup>P</sup>R<sub>0</sub>(0) transitions observed in the helium droplet spectra are relatively similar at 3.8 - 4.7 GHz, the <sup>P</sup>R<sub>1</sub>(1) and <sup>R</sup>R<sub>1</sub>(1) transitions are over 2 and 14 times broader on average, respectively.

$ u_3$	$\operatorname{Gas}^{a}(\operatorname{cm}^{-1})$	$\operatorname{Helium}^{b}(\operatorname{cm}^{-1})$						
B'	9.47111(2)	$9.333(1)^c$						
$D_N' \times 10^3$	0.7595(7)	$-2(1)^c$						
$\nu_0$	3160.82118(6)	$3160.9(1)^d$						
${}^{\Delta K} \Delta J_{K''}(J'')$	$\operatorname{Gas}^{e}(\operatorname{cm}^{-1})$	$\mathrm{Helium}^f \ (\mathrm{cm}^{-1})$	$\Gamma(\text{fwhm})^f (\text{GHz})$					
$^{P}P_{1}(1)$	_	3147.0161(2)	4.12(1)					
$^{\mathrm{P}}\mathrm{Q}_{1}(1)$	3165.4384	3165.6899(2)	3.77(2)					
${}^{R}R_{0}(0)$	3174.2935	3174.2373(1)	4.66(1)					
${}^{R}R_{1}(1)$	3182.8614	3182.410(6)	57.0(6)					
${}^{P}R_{1}(1)$	_	3203.080(1)	8.6(1)					

Table 6.1: Comparison of  $\nu_3$  (e') gas phase and helium droplet constants.

(a) <sup>*a*</sup> Reference <sup>131</sup>. <sup>*b*</sup>Constants are derived from the center frequencies obtained from the transitions measured under nozzle conditions that produced a mean droplet size equal to about 3800 He atoms. <sup>*c*</sup>Uncertainties derived from the uncertainty in peak positions of transitions used in upper state combination differences. <sup>*d*</sup>Uncertainty derived from the assumptions that  $D'_{NK}$ ,  $D'_{K}$ , and  $\xi$ remain the same as in the gas phase and that the C' constant is reduced by 2%. <sup>*e*</sup>Reference<sup>133</sup>. <sup>*f*</sup>Uncertainties are 1 $\sigma$  errors in Lorentzian line shape fits. Center frequencies and linewidths (fwhm) are those of the transitions measured under nozzle conditions that produced a mean droplet size equal to about 3800 He atoms.

### 6.4 Discussion

An interesting aspect of the  $\nu_3$  band of the helium solvated CH<sub>3</sub> radical is the variation in the linewidths of the five allowed ro-vibrational transitions. As mentioned above, all five transitions have line shapes that are fitted well to Lorentzian functions, suggesting a homogeneous mechanism as the origin of the broadening. Indeed, these transitions are broader than the typical inhomogeneous profile (0.1 to 1 GHz) that is observed in the rovibrational spectra of small molecules solvated in helium droplets.<sup>62</sup> Provided there is a sufficiently high density of droplet excitations to which the ro-vibrationally excited CH<sub>3</sub> radical can couple,<sup>134</sup> then it is acceptable to consider the linewidths as being derived from the rate at which the excited population decays *via* phonon/roton/maxon emission. The phonon/roton/maxon modes of the droplet are hereafter referred to collectively as *phonons*.

We begin the discussion of the possible origin of this apparently homogeneous broadening by first considering the  ${}^{R}R_{0}(0)$  and  ${}^{P}P_{1}(1)$  transitions that produce population in the  $1_{1}$  and  $0_{0}$  levels, respectively. Neither of these levels can relax to lower energy rotational states within the (0,0,1,0) vibrational manifold, because the  $0_{0}$  and  $1_{1}$  levels in this vibrational state are the lowest energy *para* and *ortho* rotational levels, respectively. Therefore, assuming a homogeneous broadening mechanism, it is reasonable to assign the origin of the  $\sim 4$ GHz linewidths to either vibrationally elastic or inelastic processes. Support for this assignment comes from a consideration of the triply degenerate  $\nu_{3}$  (asymmetric stretching) and  $\nu_{4}$  (bending) vibrational bands of helium solvated CH4.<sup>18,119</sup> Similar to CH<sub>3</sub>, nuclear spin restrictions forbid the purely rotationally inelastic decay of some of the CH<sub>4</sub> ro-vibrationally excited levels. For the higher energy  $\nu_{3}$  band, the transitions that access these levels are nevertheless broadened with Lorentzian linewidths of about 6 GHz, and this broadening has been assigned to the vibrational decay of the (0,0,1,0) bright state due to either Coriolis or anharmonic coupling to nearby vibrational levels.<sup>18</sup> On the other hand, the analogous ro-vibrational transitions within the  $\nu_4$  band of CH<sub>4</sub> have widths of ~70 MHz, and these appear to be limited by inhomogeneous broadening effects.<sup>119</sup> The (0,0,0,1) level is the lowest energy vibrationally excited level for CH<sub>4</sub>, and the sparse state density in this energy region apparently leads to a relatively long-lived resonance and sharp ro-vibrational (<100 MHz) linewidths. A similar trend for these two vibrational bands is observed in the IR spectrum of CH<sub>4</sub> trapped in a solid-pH<sub>2</sub> matrix, where the transitions within the  $\nu_4$  band are ~ 10 times narrower than those within the  $\nu_3$  band.<sup>135,136</sup> A solid-pH<sub>2</sub> IR spectrum has also been measured for the CH<sub>3</sub> radical,<sup>137</sup> and the <sup>R</sup>R<sub>0</sub>(0) transition of the doubly degenerate bend ( $\nu_4$ ) is similarly a factor of 10 narrower than the same transition within the higher energy  $\nu_3$  band. These comparisons motivate our assignment of the broadening of the (He)<sub>N</sub>-CH<sub>3</sub> <sup>R</sup>R<sub>0</sub>(0) and <sup>P</sup>P<sub>1</sub>(1) transitions to a homogeneous broadening mechanism associated with a vibrational, or combined vibrational-rotational decay channel. Unfortunately, our current laser coverage prevents us from measuring the lower energy CH<sub>3</sub>  $\nu_4$  band near 1400 cm<sup>-1</sup>, and this will have to be the subject of a future study.

Turning our attention to the  ${}^{P}Q_{1}(1)$ ,  ${}^{P}R_{1}(1)$ , and  ${}^{R}R_{1}(1)$  lines, it is evident from the energy level diagram in Figure 6.2 that each of these transitions access levels that can rotationally relax within the (0,0,1,0) vibrational manifold. The initial and final  $N_{K}$  levels of these nuclear spin symmetry allowed relaxation channels are given in Table 6.2. Interestingly, as noted above, there is a broad variation in the linewidths for these three transitions. The  ${}^{P}R_{1}(1)$  and  ${}^{R}R_{1}(1)$  transitions have 8.6(1) and 57.0(6) GHz linewidths, respectively, while the  ${}^{P}Q_{1}(1)$  line is comparatively narrower at 3.77(2) GHz. The additional broadening observed for the  ${}^{P}R_{1}(1)$  and  ${}^{R}R_{1}(1)$  transitions strongly suggests an assignment to a rotational relaxation process within the excited vibrational manifold. Indeed both of these transitions are qualitatively broader than the  ${}^{R}R_{0}(0)$  and  ${}^{P}P_{1}(1)$  lines, in which fast rotational relaxation was ruled out given that these transitions accessed the lowest levels within  $\nu_{3}$  for each nuclear spin modification. On the other hand, the  ${}^{P}Q_{1}(1)$  transition, which produces popu-

Initial $N_K$ in $\nu_3$	Final $N_K$ in $\nu_3$	$\Gamma^a_{ m ns}$	$\Delta E(cm^{-1})^b$
22	00	$\mathrm{E}'$	37.05
$2_2 c$	$1_{1}$	$\mathrm{E}'$	22.19
$2_2$	$1_0$	$\mathrm{E}'$	18.11
$2_0^{d}$	00	$\mathrm{E}'$	56.80
$2_{0}$	$1_{1}$	$\mathrm{E}'$	41.95
$2_{0}$	$1_{0}$	$\mathrm{E}'$	37.86
$2_0$	$2_{2}$	$\mathrm{E}'$	19.75
$2_{0}$	$2_1$	$\mathrm{E}'$	4.07
$1_0$	00	$\mathrm{E}'$	18.94
10	$1_1$	$\mathrm{E}'$	4.08
$1_1$	e	$\mathrm{A}'$	_
00	f	$\mathrm{E}'$	_

Table 6.2: Rotational relaxation channels in the  $\nu_3$  (e') excited vibrational level.

(a) <sup>*a*</sup> Nuclear spin symmetries of the "initial"  $N_K$  levels accessed via the electric dipole allowed ro-vibrational transitions from the ground vibrational level. <sup>*b*</sup>Determined from the gas phase energy levels, neglecting *l*-type doubling.<sup>131</sup> <sup>*c*</sup>The 2<sub>2</sub> level is directly coupled to the 1<sub>1</sub> level via the v<sub>33</sub> term in the angular expansion of the He-CH<sub>3</sub> PES.<sup>138</sup> <sup>*d*</sup>The 2<sub>0</sub> level is directly coupled to the 0<sub>0</sub> level via the v<sub>20</sub> term in the angular expansion of the He-CH<sub>3</sub> PES.<sup>138</sup> <sup>*e*</sup>The ortho component of the 1<sub>1</sub> level, which is accessed via the <sup>R</sup>R<sub>0</sub>(0) transition, cannot relax to the lower energy 0<sub>0</sub> para level. <sup>*f*</sup>The 0<sub>0</sub> level accessed via the <sup>P</sup>P<sub>1</sub>(1) transition is the lowest rotational level and therefore cannot rotationally relax within the (0,0,1,0) vibrational level. lation in the  $1_0$  level, exhibits no additional broadening beyond the "vibrational relaxation" linewidth, despite the presence of an open rotational relaxation channel with an energy gap similar to those for the much broader  ${}^{P}R_1(1)$  and  ${}^{R}R_1(1)$  transitions.

The energy gaps associated with all possible rotational relaxation channels are given in Table 6.2. For the  ${}^{P}Q_{1}(1)$ ,  ${}^{P}R_{1}(1)$ , and  ${}^{R}R_{1}(1)$  transitions, there is at least one open rotational relaxation channel with an energy difference greater than 18 cm<sup>-1</sup>, and because of this, there is essentially a continuous bath of phonon collective droplet modes to which all of these resonances can relax.<sup>124,125</sup> These energy gaps are all larger than the maximum energy of an elementary excitation in bulk superfluid <sup>4</sup>He (~14 cm<sup>-1</sup>).<sup>139</sup> Therefore, rotational relaxation must occur via the simultaneous excitation of multiple phonons in the liquid, with a rate that should decrease exponentially with increasing number involved.<sup>62</sup>

In a Fermi's golden rule treatment of the rotational relaxation, the rate of population decay is proportional to not only the density of phonon states at the energy difference associated with the relaxation channel but also to the square of a coupling matrix element. Here, this matrix element quantifies the extent to which the rotationally excited molecule is coupled to a state in which a phonon has been emitted and the molecule has been relaxed to a lower energy ro-vibrational level. The origin of this coupling is the anisotropy in the  $CH_3$ -He potential energy surface,<sup>140,141</sup> which rotates along with the molecule and acts as a "time-dependent drive" <sup>134</sup> of the droplet excitations. Here we consider the symmetry of the anisotropic  $CH_3$ -He potential surface and its impact on the relative magnitudes of the coupling matrix elements associated with the various relaxation pathways.

The  $CH_3$ -He potential energy surface has recently been computed with high level ab initio theory by Dagdigian and Alexander.<sup>138</sup> The interaction potential was expanded in spherical harmonics as

$$V(R,\theta,\phi) = \Sigma_{\lambda\mu} \mathbf{v}_{\lambda\mu}(\mathbf{R})(1+\delta_{\mu0})^{-1} \times [\mathbf{Y}_{\lambda\mu}(\theta,\phi) + (-1)^{\mu}\mathbf{Y}_{\lambda-\mu}(\theta,\phi)].$$

Due to the  $D_{3h}$  symmetry of the methyl radical, the only non-zero terms in this potential expansion are those for which  $\lambda + \mu$  is even and  $\mu$  is a multiple of 3.<sup>138,142</sup> Dagdigian and Alexander found that in the radial region near the van der Waals minima, the largest anisotropic terms in this potential expansion are  $v_{33}$  and  $v_{20}$ , with  $v_{33}$  being the dominate term. These terms arise from the anisotropy associated with the rotation of the He atom either in the plane of the molecule ( $v_{33}$ ) or in a plane perpendicular to the molecular plane ( $v_{20}$ ). The three-fold symmetry associated with the rotation of the He atom in the molecular plane along with the repulsive interaction between the He and H atoms leads to the dominance of the  $v_{33}$  (see, for example, Figure 3 of Reference<sup>138</sup>). These authors found that the state-to-state cross sections for rotationally inelastic collisions of a He atom with CH<sub>3</sub> could be rationalized in terms of the relative magnitudes of the anisotropic  $v_{\lambda\mu}$  terms in this expansion.<sup>138</sup> For example, the  $v_{33}$  and  $v_{20}$  terms directly couple  $n_k$  levels that differ in k by a multiple of either 3 or 0, respectively, where k is the body-frame projection of the rotational angular momentum, n.

The coupling between the rotational motion of  $CH_3$  and the helium droplet excitations could in principle be computed quantitatively, and indeed the machinery to do so was elegantly developed by Zillich and Whaley.<sup>111</sup> However, here we simply employ the results of Dagdigian and Alexander to qualitatively assess the strength of the coupling of the molecular rotation to the helium collective modes and to rationalize the difference in the linewidths measured for the  ${}^{P}Q_{1}(1)$ ,  ${}^{P}R_{1}(1)$ , and  ${}^{R}R_{1}(1)$  transitions. The coupling of the initially excited  $N_{K}$  level to a lower rotational energy level with quantum numbers  $n_{k}$  is proportional to

$$\Sigma_{\lambda\mu} \mathbf{v}_{\lambda\mu} (\mathbf{R}) \begin{pmatrix} n & N & \lambda \\ k & -K & \mu \end{pmatrix}.$$

Once again,  $\lambda + \mu$  must be an even number and  $\mu$  must be a multiple of 3. As a result of this, the Wigner 3j symbol provides a selection rule for the relaxation channel. Considering only single quantum transitions, it is evident that the 2<sub>2</sub> level accessed via the  ${}^{R}R_{1}(1)$  transition can relax to the 1<sub>1</sub> level due to the coupling provided by the anisotropic v<sub>33</sub> term. Here, levels with  $K = \pm 2$  are coupled to levels with  $k \mp 1$ . Similarly, the 2<sub>0</sub> level accessed via the  ${}^{P}R_{1}(1)$  transition can relax to the 0<sub>0</sub> level due to the coupling provided by the anisotropic v<sub>20</sub> term in the potential. Interestingly, on the basis of this simple analysis, the two possible rotational relaxation pathways for the 1<sub>0</sub> level are forbidden. This is a direct result of the symmetry of the CH<sub>3</sub>-He interaction and the absence of v<sub>10</sub> and v<sub>11</sub> anisotropic terms in the potential expansion. The 10 level is accessed via the  ${}^{P}Q_{1}(1)$  transition, and therefore, this analysis is consistent with the observation that the  ${}^{P}Q_{1}(1)$  linewidth is 2.3 and 15 times narrower than the widths of the  ${}^{P}R_{1}(1)$  and  ${}^{R}R_{1}(1)$  transitions, respectively. Moreover, the  ${}^{P}Q_{1}(1)$  line has a similar width as the  ${}^{P}P_{1}(1)$  and  ${}^{R}R_{0}(0)$  transitions, and it is therefore reasonable to similarly assign the broadening of the  ${}^{P}Q_{1}(1)$  transition to a vibrational decay channel.

The  ${}^{R}R_{1}(1)$  transition appears substantially broadened with a linewidth that is 6.6 times broader than the highest energy  ${}^{P}R_{1}(1)$  transition. On the basis of the above discussion, we expect the  ${}^{R}R_{1}(1)$  transition to indeed be the broadest transition. The v<sub>33</sub> term that directly couples the 2<sub>0</sub> and 1<sub>1</sub> levels is on average larger than the v<sub>20</sub> term, and the energy gap associated with the relaxation of the 2<sub>2</sub> level is 2.6 times smaller than that for the 2<sub>0</sub> level. Indeed, relaxation of the 2<sub>0</sub> level requires the creation of at least 4 phonons, whereas the relaxation of the 2<sub>2</sub> level requires at least two. As noted above, the rate at which multiple phonons can be created in the liquid should decrease exponentially as the number involved increases. Both of these considerations indicate that the rate associated with the rotational relaxation of the 2<sub>2</sub> level ( ${}^{R}R_{1}(1)$ ) should be comparatively larger than for the 2<sub>0</sub> level ( ${}^{P}R_{1}(1)$ ).

In the large droplet limit, it is expected that the rate of population decay should be independent of the droplet size, because the density of phonon states increases linearly



Figure 6.5: The droplet size dependence of the  ${}^{R}R_{0}(0)$  transition. The average droplet sizes estimated for the various nozzle conditions are indicated to the left.

with the droplet radius, R,<sup>125,143</sup> while the coupling matrix element is predicted to scale as  $R^{-1/2}$ .<sup>134</sup> Indeed, we find that the linewidths of all five transitions are relatively unchanged in the large droplet limit (N greater than about 8000 atoms). Figure 6.5 shows the most intense  ${}^{R}R_{0}(0)$  transition measured at several different nozzle temperatures. These source conditions produce the mean droplet sizes shown to the left of the individual spectra. Each transition is fitted to a Lorentzian function and the widths and center frequencies are plotted against the nozzle temperature in Figures 6.6 and 6.7, respectively, along with the values determined for the  ${}^{P}R_{1}(1)$  and  ${}^{P}P_{1}(1)$  transitions. In Figures 6.6 and 6.7 the mean droplet size increases from right to left. The evolution of the width and center frequency with increasing droplet size was more difficult to assess for the broad  ${}^{R}R_{1}(1)$  transition, due to insufficient sensitivity under the conditions that produced the smaller mean droplet sizes. For the transitions that were measured over this range of nozzle conditions, it is evident that the linewidths monotonically decrease with increasing droplet size and approach an asymptotic value in the large droplet limit. Furthermore, there is a systematic red shift of each transition frequency with increasing droplet size. The observed shifts of the center frequencies are perhaps related to a systematic red shift of the  $\nu_3$  band origin with increasing droplet size, which saturates in the large droplet limit. This is supported by the fact that all of the ro-vibrational transitions shift by approximately the same amount and that the center frequencies for the  ${}^{R}R_{0}(0)$  transition fits well to the excluded volume model (see Figure 6.8). For the band origins of HCN  $(2\nu_1)$  and HCCCN  $(\nu_1)$ , the droplet size dependent solvent frequency shifts were shown to fit well to this model.<sup>116,118</sup> The linewidth trend in the smaller droplet limit is more difficult to explain. In the small droplet limit, the molecule is closer on average to the surface, and the surface excitations (ripplons) of the droplet may become increasingly important. These soft surface modes have limited penetration depths into the droplet,<sup>144</sup> and therefore the coupling to these is expected to be weak.<sup>120</sup> Nevertheless, at the energy of the rotational relaxation of the  $2_0$  level, for example, the ripplons provide another essentially continuous bath of excitations to which the ro-vibrationally excited molecule can couple. Other sources of broadening may also become important in the small droplet limit. For example, it is estimated that elastic re-orientational dephasing could become relevant to the linewidth in the small droplet limit, as a result of the scattering of the ro-vibrationally excited molecules from the droplet surface.<sup>120</sup> A CH<sub>3</sub> radical with root mean squared velocity of ~20 m/s at 0.4 K will take approximately 0.1 ns to travel from the center of a 1000 He atom droplet to the surface, which would lead to line broadening (fwhm) on the order of ~2 GHz. Certainly, more theoretical work is necessary to quantitatively account for the observed size dependence of the line profiles in the small droplet limit.

### 6.5 Conclusion

Only because the  $CH_3$  radical is an oblate top with two nuclear spin modifications are we capable of probing such high lying rotational levels with such large rotational relaxation energy gaps. Clearly, the ro-vibrational spectrum of this small radical provides convincing evidence that the symmetry and anisotropy of the intermolecular potential must play an important role in the rate of population relaxation. Indeed, the  $CH_3$  radical is an interesting benchmark for theoretical calculations that aim to provide insight into the rotational and vibrational relaxation dynamics of helium solvated molecules that are classified as "light" rotors.



Figure 6.6: The dependence of the  ${}^{P}P_{1}(1)$ ,  ${}^{R}R_{0}(0)$ , and  ${}^{P}R_{1}(1)$  fitted linewidths on the nozzle temperature. The He stagnation pressure in the nozzle is fixed to 26.5 bar.



Figure 6.7: The dependence of the  ${}^{P}P_{1}(1)$ ,  ${}^{R}R_{0}(0)$ , and  ${}^{P}R_{1}(1)$  fitted center frequencies on the nozzle temperature. The He stagnation pressure in the nozzle is fixed to 26.5 bar. The zero of the ordinate is defined as the average center frequency of each group measured from 14.5 to 22.0 K.



Figure 6.8: The line center frequencies of the  ${}^{\mathrm{R}}\mathrm{R}_{0}(0)$  transition (black) are fitted to the excluded volume model for the solvent frequency shift of the vibrational band origin. Here we simply assume the rotational constants are constant for all droplet sizes. The excluded volume model is  $\nu(N) = \nu(\infty) + \frac{a}{\overline{N} - \overline{N}_{0}}$ ,<sup>116</sup> and the best fit parameters are  $\nu(\infty) = 3174.220(2), a = 26(2)$ , and  $\overline{N}_{0} = 3.5(2) \times 10^{2}$ .

# Chapter 7

# Infrared laser spectroscopy of the $CH_3OO$ radical formed by the reaction of $CH_3$ and $O_2$ within a helium nanodroplet

Helium nanodroplet isolation and infrared laser spectroscopy are used to investigate the  $CH_3 + O_2$  reaction. This simple alkyl radical oxidation reaction is important to combustion environments and the atmosphere. Methyl radicals are generated in an effusive pyrolysis source and captured by helium nanodroplets. Downstream from the introduction of methyl radicals, the droplets are doped with molecular oxygen from a gas pick-up cell. The  $CH_3 + O_2$  reaction therefore occurs between presumably cold methyl and oxygen reactants. This reaction is known to lead barrierlessly to the methyl peroxy radical,  $CH_3OO$ . The bond energy is dissipated by the evaporation of helium atoms and the infrared spectrum in the CH stretch region reveals a large abundance of droplets containing the cold, helium solvated  $CH_3OO$  radical. The  $CH_3OO$  infrared spectrum is assigned on the basis of comparisons to

high-level ab initio calculations and to the gas phase band origins and rotational constants.

### 7.1 Introduction

Liquid helium nanodroplets are increasingly being employed to study the outcome of reactive collisions between atomic and molecular reactants at sub-Kelvin temperatures (0.4 K).<sup>21–25,145,146</sup> The liquid helium droplets are dissipative, allowing for the spectroscopic or mass spectrometric study of the cold and isolated reaction products or intermediates. One notable example is the Ba + N<sub>2</sub>O  $\rightarrow$  BaO<sup>\*</sup> + N<sub>2</sub> reaction, which was the first bimolecular reaction to be studied in helium droplets.<sup>22</sup> The BaO<sup>\*</sup> product of this exothermic reaction (~95 kcal/mol) produces chemiluminescence, enabling its direct detection. Another dramatic demonstration of reactions occurring within helium droplets is the reaction between neutral cesium clusters and water clusters, which was shown to produce a variety of cold cesium hydroxide and cesium hydride products.<sup>146</sup> In this report, we sequentially add CH<sub>3</sub> and O<sub>2</sub> to the droplets and probe for the outcome of the barrierless, bimolecular CH<sub>3</sub> + O<sub>2</sub> reaction. Furthermore, we address several issues associated with the application of infrared (IR) laser spectroscopy for the detection of the outcome of organic radical-radical reactions that occur within helium nanodroplets.

A number of reactions between metal atoms and  $O_2$  have also been carried out within helium droplets.<sup>23–25</sup> On the basis of electron bombardment mass spectrometry measurements, it was discovered that these barrierless and highly exothermic reactions (~100-150 kcal/mol) lead to the ejection of the product from the droplet, despite the fact that the droplets used were sufficiently large to dissipate the reaction energy. Given that each evaporating helium atom removes ~5 cm<sup>-1</sup> (0.014 kcal/mol) of thermal energy<sup>13</sup>, a droplet containing ~10<sup>4</sup> helium atoms is required to dissipate the bond energy associated with these reactions, assuming a thermal evaporation process. Nevertheless, in many cases, it was observed that droplets

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He	3034.7	2955.5							3024.5			
gas phase <sup><math>c,d</math></sup>	$3033 \pm 1 \ (100)$	$2954 \pm 1 \ (250)$	$1453 \pm 2 \; (100)$	$1408 \pm 1 \ (54)$	$1183 \pm 1 \ (68)$	$1117 \pm 2 \ (74)$		$482 \pm 9^d$	$3020 \pm 2 \; (70)$	$1441 \pm 1 \ (68)$		
Ar matrix <sup><math>b</math></sup>	3032	2954	1448(71)	1410(8)	1180(37)	1109(25)	902(78)	492(30)	3024	$1434\ (100)$		
$ u_{theory}$	3022~(7.7)	$2956\ (17.4)$	1456(5.9)	1417 (2.8)	1181 (9.2)	1128(9.4)	$917\ (13.8)$	493 (6.3)	$3011 \ (12.6)$	$1440 \ (6.3)$	1118(1.1)	$131 \ (0.1)$
$\omega_{theory}$	3168(9.0)	3061 (16.8)	1497 (8.2)	1449 (1.4)	1212(10.5)	1160(9.5)	949 (14.7)	493 (6.2)	3159(13.1)	1484 (7.5)	1144(1.1)	149 (0.2)
description	CH <sub>3</sub> sym stretch	CH <sub>3</sub> total sym stretch	CH <sub>3</sub> deformation	CH <sub>3</sub> umbrealla	$CH_3 rock + OO stretch$	$CH_3 rock + OO stretch$	CO stretch	COO bend	$CH_3$ asym stretch	CH <sub>3</sub> asym deformation	$CH_2$ wag	$CH_3$ torsion
mode	$\nu_1$	$ u_2 $	$ u_3 $	$ u_4 $	$ u_5 $	$ u_6 $	$\nu_7$	$ u_8 $	$ u_9 $	${\cal V}_{10}$	$ u_{11} $	$ u_{12} $

(a) <sup>a</sup>Relative intensities for experimental measurements are given in parentheses where available. <sup>b</sup>Reference 20. <sup>c</sup>Reference 22. <sup>d</sup>Reference 19.

much larger than this were required to cage the products of these reactions. Similarly, the  $Ba + N_2O$  reaction produces a substantial fraction of gas phase  $BaO^*$  due to product ejection. For this system, however, the ejected fraction can be suppressed by introducing a small cluster of Xe atoms to the droplet prior to the introduction of the reactants. The Xe atoms attract the Ba reactant to the interior of the droplet, indicating that product ejection in this case is dependent on whether the reaction occurs on the surface or in the interior of the droplet. Unfortunately, the mechanistic details associated with these ejection processes are not entirely understood.

For the low temperature droplet mediated reactions involving organic radicals, it is advantageous to use direct spectroscopic probes to determine product branching ratios, rather than relying on mass spectrometry data alone. When reaction products do not fluoresce or produce chemiluminescence, well-established IR beam depletion spectroscopy can be used<sup>1,2</sup>, provided the products remain in the droplets and are carried downstream to the detector. Using velocity map imaging techniques, Braun and Drabbels have studied the 266 nm photo dissociation of  $CH_3I$  in helium droplets and found that a fraction of the photofragments are thermalized via collisions with the helium and recombine within the droplet.<sup>147</sup> Furthermore. they provide convincing evidence for the trapping of the  $CH_3 + I$  reaction product ( $CH_3I$ ), provided the droplet has an initial size greater than  $\sim 6000$  atoms. This result suggests that, by simply increasing the droplet size, the products of organic radical reactions can indeed be trapped and cooled by the helium droplet and carried downstream for spectroscopic interrogation. However, because helium is conserved in the nozzle expansion, the conditions that produce larger droplets also produce fewer droplets, resulting in fewer chromophores available for spectroscopic detection. For example, the signals associated with the IR laser spectroscopy of helium solvated molecules are typically optimized for nozzle conditions that produce droplets containing between 3000 and 7000 atoms on average.<sup>1</sup>

Because of these potential issues, it is worthwhile to test the feasibility of the IR laser

based beam depletion approach for probing the outcome of an organic radical reaction. One class of reactions that is of particular interest is alkyl radical oxidation reactions, which are important in both combustion environments<sup>148,149</sup> and in the atmosphere<sup>150</sup>. The extent to which the products of these reactions experience droplet ejection may be dramatically different from the metal atom reactions, since the typical exothermicity of these reactions can be much smaller. As a test case, we have chosen the  $CH_3 + O_2$  reaction, which leads barrierlessly to the methyl peroxy radical ( $CH_3OO$ ). The associated reaction enthalpy is ~30 kcal/mol. If we assume that this energy is dissipated by a thermal evaporation process, then this reaction will lead to the evaporation of ~2000 He atoms. The spectroscopy of this system is well studied<sup>150–158</sup> allowing us to make direct comparisons of our results to previous gas phase measurements.

### 7.2 Experimental Methods

Helium droplets are formed in a cryogenic nozzle expansion of high purity helium gas with a stagnation pressure of 30 bar into vacuum through a  $5\mu$ m diameter nozzle operated at 17 K. These nozzle conditions produce droplets with ~5000 helium atoms on average.<sup>28,29</sup> The droplet expansion is skimmed into a beam, enters a differentially pumped chamber and passes across the opening of an effusive, low pressure pyrolysis source.<sup>33,159</sup> The production of CH<sub>3</sub> was optimized by monitoring the <sup>R</sup>R<sub>0</sub>(0) transition of the  $\nu_3$  degenerate asymmetric stretch vibration of the helium solvated methyl radical at 3174.2 cm<sup>-1</sup>. The droplets subsequently pass through a second differentially pumped chamber that contains O<sub>2</sub> at a pressure of 3 ×  $10^{-6}$  Torr. On the basis of the well-known statistics associated with droplet doping,<sup>20</sup> under these conditions, approximately 8% of all droplets within the beam will pick up a single CH<sub>3</sub> radical *and* a single O<sub>2</sub> molecule. The other 92% of the droplet ensemble will either be devoid of dopants or contain other combinations of CH<sub>3</sub>, (CH<sub>3</sub>)<sub>2</sub>CO, and O<sub>2</sub>. Following
each pick-up event, the droplets cool by evaporation to 0.37 K, and the molecular degrees of freedom of the dopant are assumed to be at equilibrium with the droplet degrees of freedom at this temperature.<sup>51</sup> The idler output from the cw, IR OPO is aligned co-axially with the helium droplet beam. The tuning and calibration of this IR-OPO system is described in a previous chapter.

### 7.3 Theoretical Methods

Reference geometries for CH<sub>3</sub>OO were optimized by coupled cluster theory incorporating single, double, and perturbative triple excitations  $[CCSD(T)]^{160-162}$  using a valence correlation-consistent triple- $\zeta$  basis-set (cc-pVTZ).<sup>163</sup> Fundamental frequencies were evaluated using VPT2 theory<sup>164,165</sup> via analytic second derivatives.<sup>166</sup> Results from these computations are given in Table 7.1a. Relative energies for the torsional barrier were obtained by employing the focal-point method,<sup>167-169</sup> a convergent scheme in which both electron correlation and basis set limits are systematically approached. Energies were extrapolated to the complete basis-set limits using a three-parameter exponential function for the Hartree-Fock energy<sup>170</sup> and a two-term X<sup>-3</sup> form for the correlation energy.<sup>171</sup> The barrier for torsional rotation about the C-O bond in the ground electronic state (<sup>2</sup>A") is 250 cm<sup>-1</sup> with an accuracy of ±30 cm<sup>-1</sup>. This result is in good agreement with previous calculations of the barrier height at lower levels of theory.<sup>172</sup> All computations utilized the CFOUR<sup>173</sup> suite of electronic structure codes. Figure 7.1 shows the optimized geometry for the ground state and transition state. Further details of these computations are provided in Table 7.2.



#### Ground State

#### **Transition State**

Figure 7.1: Optimized geometry for the ground-state and transition-state at the CCSD(T)/cc-pVTZ level of theory. Bond lengths are shown in Angstroms and bond angles in degrees.

Basis set	$\Delta E_e HF$	$+\delta MP2$	$+\delta CCSD$	$+\delta CCSD$	$+\delta CCSD(T)NET$			
cc-pVTZ	+1.36	-0.66	+0.33	-0.08	[+0.95]			
cc-pVQZ	+1.38	-0.69	+0.33	-0.08	[+0.94]			
cc-pV5Z	+1.38	-0.69	[+0.33]	[-0.08]	[+0.94]			
CBS	[+1.38]	[-0.70]	[+0.33]	[-0.08]	[+0.93]			
LIMIT								
$\Delta E_t (\text{final}) = \Delta E_t [\text{CBS CCSD}(T)] + \Delta_{ZPVE} [\text{CCSD}(T)/\text{cc-pVTZ}]$								
$\Delta F_{\mu}(\text{final}) = 0.93 - 0.21 = 0.72 \text{ kcal} \cdot \text{mol}^{-1}$								

Table 7.2: Focal Point analysis of the  $CH_3OO$  torsional barrier in the  $(X)^2A''$  electronic state.<sup>*a*</sup>

(a) <sup>*a*</sup>Energies shown in kcal·mol<sup>-1</sup> Delta ( $\delta$ ) denotes the change in relative energy ( $\Delta E_e$ ) with respect to the preceding level of theory. Note that the barrier for torsional rotation (0.72 kcal·mol<sup>-1</sup>) has a suggested accuracy of  $\pm$  0.1 kcal·mol<sup>-1</sup>. This can be deduced from looking at the focal-point table, where we see oscillatory convergence to within 0.08 kcal·mol<sup>-1</sup>.



Figure 7.2: Evolution of the mass spectrum as the reactants are introduced sequentially to the droplet beam. From bottom to top: neat droplet beam, droplet beam doped with DTBP precursor, doped droplet beam with pyrolysis source heated to  $\sim$ 700 K, and doped droplet beam with heated pyrolysis source and with O<sub>2</sub> added to the downstream gas pick-up cell.

### 7.4 Results and Discussion

The evolution of the mass spectrum upon sequential addition of dopants to the droplet beam is shown in Figure 7.2. The mass spectrum at the bottom of the figure exhibits the well known signature of the helium droplet beam.<sup>2</sup> Electron bombardment ionization of the droplet beam generates a mass spectrum consisting of  $\operatorname{He}_n^+$  peaks due to the initial formation of He<sup>+</sup> within the droplets followed by the ejection of small helium cluster ions. As the DTBP precursor is bled into the vacuum chamber through the room temperature pyrolysis source, additional peaks appear in the mass spectrum due to the charge transfer ionization (He<sup>+</sup> + DTBP  $\rightarrow$  He + DTBP<sup>+</sup>) of the helium solvated DTBP molecules, which is apparently followed by the extensive fragmentation of DTBP<sup>+</sup>. The peaks at m/z=43, 57 and 73 are signatures of DTBP doped helium droplets. Upon heating the pyrolysis source to near 700 K, the peaks at 57 and 73 disappear, signaling the pyrolysis of DTBP. Furthermore, peaks at 15, 27 and 29 gain intensity. Along with the peak at m/z=43 (COCH<sub>3</sub>)<sup>+</sup>, these features are consistent with the pyrolytic formation of  $CH_3$  and  $(CH_3)_2)CO$  and the subsequent droplet pick-up of these DTBP fragments. Upon addition of  $O_2$  to the pick-up cell located downstream from the hot pyrolysis source, a peak at m/z=32 appears along with a small decrease (increase) in the m/z=15 (m/z=29) peak relative to m/z=12 (He<sub>3</sub><sup>+</sup>). It is interesting to note that a peak at m/z=47 (CH<sub>3</sub>O<sub>2</sub>)<sup>+</sup> is completely absent from the mass spectrum obtained with both  $O_2$  and  $CH_3$  present. Without any other evidence, a peak at this mass would be indicative of the sequential pick-up and reaction between  $CH_3$  and  $O_2$  to form the  $CH_3OO$  radical, assuming the product of this reaction is completely cooled, remains in the droplet, and is carried downstream to the detector by the droplet. However, the ionization of  $CH_3OO$  may lead to extensive fragmentation, and it is therefore difficult to draw any conclusions regarding the outcome of the  $CH_3 + O_2$  reaction by only considering these mass spectrometry results.



Figure 7.3: Survey spectrum of the CH stretch region by measuring the depletion in mass channel m/z=29. Two acetone bands as well as an ethane band are observed in addition to the three transitions reported in this report for CH<sub>3</sub>O<sub>2</sub>.



Figure 7.4: Survey scan of the depletion in mass channel m/z=29 upon doping the droplets with the products of DTBP pyrolysis followed by O<sub>2</sub> pick-up. The bands assigned to the  $\nu_{1,2,9}$  transitions of CH<sub>3</sub>OO are all within one or two cm<sup>-1</sup> of the reported gas phase band origins. The band at 3018 cm<sup>-1</sup> is due to acetone, which is the other product of DTBP pyrolysis in addition to CH<sub>3</sub>.

The survey spectrum (2850-3100 cm<sup>-1</sup>) of  $CH_3O_2$  is shown in Figure 7.3. A section of the survey spectrum of the CH stretch region is shown in Figure 7.4, which is obtained by measuring the depletion in mass channel m/z=29 while scanning the IR-OPO. In addition to bands due to  $(CH_3)_2$  CO, the only other intense features in this region are three bands centered at 2955.2, 3024.5 and 3034.7  $\rm cm^{-1}$ . These bands were initially found in mass channel m/z=15 (CH<sub>3</sub>)<sup>+</sup>, and it was later found that the m/z=29 channel provided the largest depletion signals for these three bands (vide infra). Each of these three bands goes away entirely if either  $O_2$  is removed from the gas pick-up cell or if the pyrolysis source temperature is reduced to room temperature. Moreover, each band has an intensity that depends similarly on the  $O_2$  gas pick-up cell pressure, peaking at  $\sim 6 \times 10^{-6}$  Torr and rapidly dropping off at higher  $O_2$  pressures. This optimal pressure is consistent with the pick-up of a single  $O_2$  molecule. The band origins of these three transitions are in excellent agreement with both our fundamental vibrational frequency computations<sup>174</sup> and previous gas phase measurements<sup>158</sup> of the methyl peroxy radical CH stretch vibrations  $(\nu_2, \nu_9, \nu_1)$ . We therefore assign these three bands to the CH stretch vibrations of  $CH_3OO$ . Furthermore, the characteristic  $O_2$  pressure dependence of the band intensities provides strong support for the formation of the  $CH_3OO$  species within the droplet, following the sequential pick-up of  $CH_3$  and  $O_2$ .

Further evidence for the presence of helium solvated CH<sub>3</sub>OO comes from the expanded view of the 2955.2 cm<sup>-1</sup> band, which we assign to the  $\nu_2$  totally symmetric CH<sub>3</sub> stretch vibration (a') of the methyl peroxy radical. As shown in Figure 7.5, the  $\nu_2$  band exhibits partially resolved rotational fine structure. The solid red curve is a simulation of an a,b-hybrid band of a rigid asymmetric top using the rotational constants in Table 7.3. The relative intensity of a and b type bands is fixed by employing the ab initio inertial components of the dipole derivative vector associated with the CH<sub>3</sub>OO  $\nu_2$  transition. The effective rotational constants obtained from rotationally resolved vibrational bands in helium nanodroplet isolation



Figure 7.5: Expanded view of the  $\nu_2$  CH<sub>3</sub> (a') symmetric stretch band of the methyl peroxy radical. The red curve and stick spectrum correspond to a rigid rotor asymmetric top simulation using the constants given in Table 7.3.

spectra are typically reduced from the gas phase spectra by a factor of 2 to 3 due to the contribution of the helium solvent to the rotors effective moment of inertia.<sup>1,2</sup> Consistent with this, the  $\nu_2$  (B+C)/2 constant is reduced by a factor of 2.2 in helium. In comparison, the larger A constant is reduced by a factor of 1.7, which is somewhat smaller than for (B+C)/2. This is also consistent with established trends.<sup>1</sup> Overall, the simulation provides convincing evidence for the assignment of this band to the  $\nu_2$  transition of CH<sub>3</sub>OO.

Just and co-workers have computed the ground vibronic torsional eigenstates for CH<sub>3</sub>OO, and the separation between 0A<sub>1</sub> and 0E states os 0.092 cm<sup>-1</sup> at the B3LYP/6-31+g(d) level of theory.<sup>172</sup> At high resolution, the  $\nu_2$  transition observed here should consist of two bands separated by the difference in this tunneling splitting in the ground and excited vibrational states. At this same level of theory, we determine that the ground and  $\nu_2$  vibrationally excited torsional barrier heights differ by only 4 cm<sup>-1</sup>, which represents only 2% of the zeropoint energy corrected barrier height (200 cm<sup>-1</sup>). Therefore, we do not expect the *difference* in the tunneling splitting to be of any significance to the simulation of the  $\nu_2$  band observed here, especially given the presumably homogeneous 0.3 cm<sup>-1</sup> line width associated with this transition.

The ratio of the integrated intensity of the CH<sub>3</sub>OO  $\nu_9$  band to the (CH<sub>3</sub>)<sub>2</sub>CO band at 3018 cm<sup>-1</sup> is ~7:1. This allows us to estimate the fraction of droplet mediated CH<sub>3</sub> + O<sub>2</sub> reactions that result in ejected products if we assume that the detection efficiency of each species in the m/z=29 mass channel is similar. Furthermore, if we assume the relative intensities of these two bands from the ab initio computations (4:1) and the expected abundance of droplets containing single (CH<sub>3</sub>)<sub>2</sub>CO molecules (~12%) relative to those that have picked-up exactly one CH<sub>3</sub> radical and one O<sub>2</sub> (~8%), we estimate that the majority (>80%) of the CH<sub>3</sub>OO radicals remain in the droplets. Of course, this is necessarily qualitative given the above assumptions and the possibility for methyl radical loss due to reactions within the pyrolysis source.



Figure 7.6: a) Electron impact ionization mass spectrum of the doped droplet beam with the DTBP pyrolysis source hot and the O<sub>2</sub> pick-up pressure set to  $\sim 3 \times 10^{-6}$  Torr, which is sufficiently low to suppress the pick-up of multiple O<sub>2</sub> molecules. Note the absence of a peak at m/z=47 corresponding to the intact (CH<sub>3</sub>O<sub>2</sub>)<sup>+</sup> molecular ion. The mass spectrum in (b) is the difference mass spectrum (laser off-on) with the laser fixed to the peak of the  $\nu_2$ CH<sub>3</sub>OO band. The majority of the depletion signal appears in the m/z=29 mass channel, which indicates that CH<sub>3</sub>OO fragments into HCO<sup>+</sup> and H<sub>2</sub>O upon charge transfer ionization from He<sup>+</sup>.

The results from the spectroscopy suggest rather clearly that upon sequential pick-up of  $CH_3$  and  $O_2$ , the barrierless reaction leading to  $CH_3OO$  occurs within the droplet. Furthermore, we can confidently say that the  $\sim 30$  kcal/mol bond energy is effectively dissipated, and that the product molecule is completely cooled, remains solvated, and is carried downstream for spectroscopic interrogation and detection. As discussed above, it would be difficult to arrive at this conclusion without this spectroscopic evidence. Electron impact ionization of the droplets leads to the production of a solvated helium cation that can transfer its charge to the solvated CH<sub>3</sub>OO. The difference in the ionization potential of He and CH<sub>3</sub>OO is  $\sim 13$ eV<sup>175</sup>, which hardly represents a soft ionization mechanism. Indeed, it is common to observe extensive fragmentation of helium solvated organic molecules that are ionized in this way.<sup>176</sup> Therefore, we find no reason to suspect a priori that a peak at m/z=47 should appear upon the formation of  $CH_3OO$  within the droplets. This is justified by Figure 7.6, which shows a comparison of the mass spectrum shown at the top of Figure 7.2 to the difference mass spectrum (laser off-on) obtained under the same conditions. The difference mass spectrum is obtained with the laser fixed to the peak of the  $CH_3OO \nu_2$  band, and it is therefore representative of the mass spectrum of droplets that contain the species in resonance with the IR radiation, namely CH<sub>3</sub>OO. The difference mass spectrum shows that He<sup>+</sup> charge transfer to CH<sub>3</sub>OO leads to the production of HCO<sup>+</sup> (m/z=29) and H<sub>2</sub>O, along with other minor channels. It is reasonable to suspect that the mass spectrometric characterization of helium solvated products of organic radical reactions will generally suffer from this ionization induced fragmentation. For this class of low temperature chemical reactions carried out in helium nanodroplets, it is therefore advisable to use the more selective laser based spectroscopic methods rather than mass spectrometry to detect product branching ratios.

	А	(B+C)/2	(B-C)	$ u_0$	$T_{rot}$ (K)	$\Gamma(\text{fwhm})$
He	1.05	0.16(1)	0.01	2955.15(1)	0.35	0.3
gas	$1.730^{b}$	$0.355^{b}$	$0.049^{b}$	$2954\pm1^c$		

Table 7.3: Constants Used for the Simulation of the  $CH_3$  ( $\nu_2$ , a') Symmetric Stretch<sup>a</sup>

(a) <sup>*a*</sup>The gas phase vibrational ground state rotational constants are from FTMW measurements.<sup>177</sup> All values are reported in cm<sup>-1</sup>. The ab initio transition moment components are used in the simulations. The band is an *a,b*-hybrid band with an *a*-axis transition moment component that is 2.63 times larger than the component along the *b*-axis. The simulation was carried out with PGOPHER.<sup>132b</sup>Reference<sup>177</sup>. <sup>*c*</sup>Reference<sup>158</sup>.

## 7.5 Conclusions

The sequential addition of a methyl radical and molecular oxygen to helium nanodroplets leads to the barrierless reaction,  $CH_3 + O_2 \rightarrow CH_3OO$ . The reaction enthalpy is ~30 kcal/mol and therefore requires the dissipation of ~2000 helium atoms to cool the  $CH_3OO$  to 0.37 K. The product  $CH_3OO$  radical remains in the droplet and is observed downstream with IR laser beam depletion spectroscopy. All three CH stretch bands of  $CH_3OO$  are observed, and rotational fine structure is partially resolved for the  $\nu_2$  totally symmetric CH stretch band, indicating complete internal cooling of the product to the droplet temperature. Electron impact ionization of the droplets containing  $CH_3OO$  results in the charge transfer reaction  $He^+ + CH_3OO \rightarrow CH_3O_2^+ + He$ , which is followed by the fragmentation of the  $CH_3O_2^+$  ion. The major fragmentation channel is the production of  $HCO^+$  and  $H_2O$ . The outcome of this work is encouraging and suggests that infrared laser spectroscopy can be employed as a selective probe of the outcome of organic radical-radical reactions in which multiple products may be formed. By integrating the total ion signal arising from the ionization of the droplet beam, the relative IR beam depletion band intensities associated with the various possible products can be used directly to determine product branching ratios.

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