Rotational spectral studies of O(¹D) insertion reactions with methane and ethylene: Methanol and vinyl alcohol in a supersonic expansion

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Abstract

We report a new apparatus for millimeter/submillimeter spectroscopic studies of O(¹D) insertion reactions to produce molecules of astrophysical interest. This study focuses on the insertion of O(¹D) into methane to form methanol, and the insertion of O(¹D) into ethylene to form vinyl alcohol (CH₂CHOH). The O(¹D) was produced via laser photodissociation of O₃ in a fused silica tube and mixed with a hydrocarbon before a supersonic expansion. Direct absorption millimeter/submillimeter spectroscopy was used to monitor the products. The methanol study was used as an experimental benchmark, while the vinyl alcohol study extended rotational spectroscopic measurements to higher frequencies. Observed products from both insertion reactions included, but were not limited to, H₂CO, HO₂, and CH₃O. Methanol and vinyl alcohol were only produced in detectable quantities when the fused silica tube was included, indicating that collisions before the expansion are required for production and stabilization of the O(¹D) insertion products.

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1. Introduction

The most chemically comprehensive models of star-forming regions (i.e., [1, 2, 3]) predict an extensive organic chemical network that ranges from small molecules like methanol (CH₃OH) and formaldehyde (H₂CO) in the ices on interstellar dust grains to large molecules like methyl formate (HCOOCH₃) and dimethyl ether (CH₃OCH₃) in the gas phase. In these “hot core” star-forming environments, the gradual warm-up of the newly-formed star drives a complex chemical network that couples these ice and gas chemistries and enables larger molecules to form in the ices from radiation-induced grain-surface chemistry [1]. While astrochemical models including these complex pathways have advanced to the point of semi-quantitative agreement with observations, much work remains to be done to verify that the chemistry proposed in these models is truly representative of interstellar environments [4]. The challenge is that laboratory gas-phase spectra are required for comparison to interstellar spectra; yet many of the predicted

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molecules are unstable, reactive organics that are difficult to isolate in a terrestrial laboratory environment [1, 4]. New formation pathways that enable the gas-phase laboratory study of these species are therefore necessary before interstellar searches can be conducted.

One possible approach is to use the insertion reactions of electronically-excited oxygen atoms in the $O(^1D)$ state into precursor organic molecules, producing organic molecules that are of astrochemical interest. Reactions between organic molecules and $O(^1D)$ can proceed through either an abstraction or an insertion mechanism [5]. The highly exothermic insertion reactions typically dominate; $O(^1D)$ preferentially inserts into H-X bonds, where X is H, C, O, or N. The chemical specificity of $O(^1D)$ insertion reactions coupled with their exothermicity offers a promising method for production of small organic molecules such as the targets of our experimental studies. However, the tendency for the insertion products to undergo unimolecular dissociation requires that the reactions occur under conditions where excess internal energy can be quenched. Most studies of $O(^1D)$ insertion reactions involving organic molecules have been conducted in either crossed molecular beams or cryogenic matrices. In crossed molecular beams, the reactants may be cooled, but the products are not. In matrices, excess energy is quenched, but the products are confined in the matrix. When isolation and characterization of the gas-phase insertion product is the experimental focus, as is the case in an astrochemistry study, a supersonic expansion source serves as the best option because it provides rotational and vibrational cooling of the insertion products while providing gas-phase species for spectroscopic interrogation.

Here we present proof-of-concept experiments involving the insertion of $O(^1D)$ into methane (CH_4) and ethylene (C_2H_4) to produce methanol (CH_3OH) and vinyl alcohol (CH_2CHOH), respectively. We have adapted the supersonic expansion photolysis source design of Lester and coworkers [6, 7] to produce $O(^1D)$, which then reacts with a precursor molecule to form the target species. We are utilizing the structure-specificity of millimeter/submillimeter rotational spectroscopy to monitor the reactants and products throughout the experiment. The goals of these experiments are to: 1) produce the target molecules in sufficient abundance to enable their spectroscopic characterization; 2) optimize experimental conditions to favor the direct insertion product; 3) collect the rotational spectrum of new molecules to guide astronomical searches; and 4) enable identification of new molecules in space and the laboratory. Future adaptations of the experiment will enable study of $O(^1D)$ insertion reaction mechanisms and kinetics. The experiments outlined in the current work focused on goals 1 and 2 using the $O(^1D) + CH_4$ reaction to produce methanol. Goal 3 is then tested using the insertion of $O(^1D)$ into ethylene to produce vinyl alcohol. The results of this study will then enable future work focused on Goal 4. We report on the details of the experimental design, optimal conditions for production of methanol and vinyl alcohol, other molecular products that were observed in addition to the target molecules, and a full rotational spectral characterization for vinyl alcohol up to 446 GHz. Lastly, we discuss the possibilities for extending these techniques to examine other more complicated molecular systems.

2. Background

2.1. $CH_4 + O(^1D) \rightarrow CH_3OH$

Excited oxygen atoms will preferentially insert into C-H bonds of organic molecules. One of the most thoroughly studied reactions of this type is the insertion of $O(^1D)$ into methane:

This insertion reaction is exothermic by ~ 135 kcal/mol, producing highly vibrationally-excited methanol molecules that subsequently undergo unimolecular dissociation [8]. This reaction has been studied extensively through both experimental [8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41] and theoretical [42, 43, 44, 45, 46, 47, 48] methods. An energy diagram showing an overview of the insertion reaction and subsequent dissociation pathways is shown in Figure 1. Figure 1 shows that there are many possible dissociation channels stemming from the insertion of $O(^1D)$ into methane, including both the primary methanol insertion product, and secondary products resulting from its subsequent unimolecular dissociation; the two lowest-energy insertion products are the primary CH_3OH product, and H_2CO resulting from one such dissociation channel.

Figure 1: The energy diagram for the $O(^1D) + CH_4 \rightarrow CH_3OH$ reaction, based on theoretical investigations reported in the literature [46, 47, 48].

2.2. $(CH_2)_2 + O(^1D) \rightarrow CH_2CHOH$

The reaction of $O(^1D)$ and ethylene has previously been investigated in a few experimental studies [49, 50, 51], and the singlet surface of the structural isomers of vinyl alcohol were investigated [52] in context of the $O(^3P)$ addition to ethylene undergoing an intersystem crossing. To our knowledge, no theoretical studies have examined the singlet surface for this reaction in more detail. As such, we have not included an energy diagram such as the one shown for methanol. Based on the information that is available from [52], the vinyl alcohol isomers show many tautomerization channels to acetaldehyde and ethylene oxide, as well as decomposition channels from these products, with the end products being carbon monoxide, methane, ketene, formaldehyde, and several radicals. The main channel for the reaction between $(CH_2)_2 + O(^1D)$ was found to be the C-H insertion channel to form highly excited vinyl alcohol [49, 50] with some possible contribution from abstraction reactions [50]. It has also been predicted that the $O(^1D) +$ ethylene reaction could lead to ethylene oxide through a barrierless reaction channel [51].

Vinyl alcohol can be produced by phototautomerization of acetaldehyde [53], making it an important contributor in atmospheric chemistry [54]. Vinyl alcohol has been previously characterized in the microwave regime using pyrolysis sources [55, 56]; this included spectral coverage up to 50 GHz and $J=25$. A similar source was used for a millimeter-wave gas-phase study [57], with spectral coverage up to 120 GHz and $J=10$ [57]. Vinyl alcohol has two conformers that have been studied: syn-vinyl alcohol [57, 55] and anti-vinyl alcohol [56]. In these two conformers, the hydroxyl group either points away from or toward the plane of the molecule, respectively.

A tentative astronomical detection of vinyl alcohol has also been reported in Sgr B2(N) [58]. However, this detection has not been confirmed at higher frequencies [59, 60]. Higher-frequency spectroscopic measurements that extend beyond the work of [57] would aid future astronomical searches for this molecule.

3. Experimental Methods

The experiments for production of both methanol and vinyl alcohol utilized a combination of millimeter/submillimeter spectroscopy with laser-initiated $O(^1D)$ chemistry. Surprisingly, there are only a few examples of millimeter/submillimeter wave spectrometers that have been coupled to lasers [61, 62, 63, 64, 65]. A schematic diagram of the experimental setup is shown in Figure 2.

Figure 2: Schematic diagram of the experimental setup.

For the $\text{CH}_4 + \text{O}(^1\text{D}) \rightarrow \text{CH}_3\text{OH}$ experiments, samples were prepared by mixing argon (NexAir, ultra-high purity), methane (NexAir, 99%), ozone, and oxygen (NexAir, ultra-high purity) in varying concentrations. The ozone was produced using a Pacific Ozone L11 Ozone Generator, the output of which was diluted to $\sim 1\%$ O_3 in O_2 at atmospheric pressure. The $\text{Ar}/\text{O}_3/\text{O}_2/\text{CH}_4$ gas mixture was delivered via a pulsed valve (Parker Hannifin, Series 9) into a 3 cm long, 1 mm inner diameter UV-grade fused silica capillary tube (Wilmad Glass) before it was supersonically expanded into the vacuum chamber. The fused silica tube was attached to the valve faceplate with epoxy (TorrSeal); the design of the source was based on that used by Lester and coworkers [6, 7]. The valve was driven at a repetition rate of 56 Hz with an on duration of 2 – 4 ms. An effective pumping speed at the valve of $\sim 250 \text{ L s}^{-1}$ was maintained using a rotary vane + roots blower pumping system. The chamber pressure varied depending on the backing pressure used for a given experiment, but was typically $\sim 60 \text{ mTorr}$.

No direct measurements of temperature or pressure were conducted in the capillary tube, but these quantities can be inferred from the experimental details. All studies were performed with the gas samples at room temperature; previous studies using this type of source determined that the gas temperature in the capillary tube dropped by 3 K [7]. We therefore assume that the gas in the capillary can be approximated to be at room temperature. Additionally, the total number density of a given reactant in the capillary tube can be determined from the backing pressure, the chamber pressure, and the gas mixing ratios.

The supersonic expansion was probed using millimeter light produced from a Schottky diode multiplier chain. The output of an analog signal generator (Agilent Technologies, E8257D PSG with options 1EA, UNU, 550, and UNT) was multiplied using a $\times 6$ active multiplier chain (Virginia Diodes Inc., AMC-S268). The multiplier consists of a K_a band amplifier (Spacek Labs, SP3020-30-25B2) which is connected to a WR10 tripler (Virginia Diodes Inc.), the output of which is further amplified before a WR5.1 doubler (Virginia Diodes Inc.) that has an output frequency range of 140 – 220 GHz. The millimeter radiation was focused to a $17 \text{ mm} \times 25 \text{ mm}$ spot size (measured at 175 GHz) that crossed the supersonic expansion at a distance of $\sim 2 \text{ cm}$ from the exit of the fused silica tube. For frequencies above 220 GHz, other VDI doublers and triplers were used, extending the available frequency range up to 1 THz. The radiation was then detected using an InSb hot electron bolometer (QMC Ltd., QFI/XBI) with $\sim 2 \mu\text{s}$ time response. The output of the detector was recorded by a digital oscilloscope (Tektronix, TDS1001B), which was used to average and record the time response of the signal. Spectra in the frequency domain were recorded with 60 kHz frequency spacing by determining the integrated intensity of the absorption signal from the time trace on the oscilloscope. A typical spectrum obtained in this study consists of up to 128 averages per data point. The time traces taken at each frequency point were fit to a linear regression from the first few and the last few time points; these fits were subtracted from the time traces to center the baselines of each time trace at zero, reducing the effects of random amplitude modulation in the experiment. Unlike many (sub)millimeter spectroscopy experiments, the signal out of the synthesizer was not frequency modulated since signal averaging was performed by the oscilloscope. However, all spectra were power normalized using a power spectrum that was obtained using an amplitude modulated millimeter/submillimeter signal

Figure 3: Schematic of the mixing source, comprised of : A) Ozone pulsed valve; B) reactant (i.e., ethylene) + argon pulsed valve; C) mixing block; D) gas channels; E) support to hold metal plates holding fused silica tube in place, F) fused silica tube, G) output coupler and mounting plate, H) ozone gas line; I) reactant + argon gas line.

processed by a lock-in amplifier (Stanford Research Systems, SR830).

The production of $O(^1D)$ was initiated by the laser photolysis of O_3 in the fused silica tube. A KrF excimer laser (GAM LASER Inc., EX5 – 250 Hz) operating at 248 nm with a pulse width of 8 ns was used. The resultant $O(^1D)$ underwent collisions with other molecules in the fused silica tube, where methanol was formed from $O(^1D)$ insertion into methane. As shown by Lester and coworkers [6, 7], initiating the laser-induced chemistry in the fused silica tube before the expansion helps to promote product formation and stabilization through collisions. Use of a UV-grade fused silica cylindrical lens to focus the laser light onto the tube was found to increase methanol product yield as compared to the use of a spherical lens for focusing the laser light; this arrangement is the same as that used by Lester and coworkers in recent studies [66]. Additional benefits of using the cylindrical lens were an increase in product transit time through the millimeter beam, and a decrease in laser damage to the fused silica tube. The laser power was 8.6 mJ per pulse, which was then focused by the cylindrical lens to a spot that was $2\text{ mm} \times 1.5\text{ cm}$. The laser was timed to fire immediately after the O_3 signal reached its maximum value.

In the $(CH_2)_2 + O(^1D) \rightarrow CH_2CHOH$ experiments, several improvements and additions were needed in the experimental setup. Most importantly, a new pulsed valve setup was used for the mixing of ozone and ethylene. These gases readily react upon contact, which required that the gas mixing was minimized until the laser photolysis region. A new source was constructed to overcome this challenge. As shown in Figure 3, two pulsed valves (Parker Hannifan, Series 9) were attached to adjacent sides of a 3.8 cm Plexiglass cube, which served as a gas mixing block. Two 1 mm wide channels were drilled into the mixing block so that they intersected the pinholes on the faceplates of the pulsed valves. One of these channels passed entirely through the mixing block, while the second channel intersected the first channel in the center of the mixing block. The 1 mm diameter fused silica tube was attached to the output channel of the plexiglass cube and held in place by a stainless steel plate that attached to the plexiglass cube with support rods. This plate had a 1 mm pinhole and served as an output coupler for the supersonic expansion. For the ethylene experiments, the laser spot was focused near the output of the silica tube. The ethylene and argon mixture contained 10% ethylene and was held at a valve backing pressure of ~ 760 Torr. The oxygen and ozone mixture ($\sim 1\%$ ozone) was introduced through the second pulsed valve and held at a backing pressure of 900 Torr.

Other minor improvements were made for the ethylene/vinyl alcohol study as compared to the setup used for the methane/methanol study. A National Instruments PCI-5124 digitizer card was used to record the signal instead of an oscilloscope. This decreased the downtime for saving data to the computer and allowed for much more flexibility in the programmed scanning routine developed for this experiment. The spectral scan rate was ~ 200 MHz per day for acquisition of high resolution spectra, but could be extended to ≥ 1 GHz per day at the sacrifice of resolution or signal averaging. The digitizer was typically operating at 10 MSa s^{-1} , with a maximum rate of 200 MSa s^{-1} . The typical

Figure 4: Time trace showing the O_3 absorption signal offset from the baseline, the RFI from the laser pulse, and the depletion of the O_3 signal.

acquisition time lasted $250\ \mu\text{s}$, with the signal from the laser-initiated products lasting $\sim 50\ \mu\text{s}$. Additionally, the laser used for the vinyl alcohol experiments was a GAM Laser EX10 – 200 Hz, which offered roughly double the output power of the laser used in the methane/methanol studies. The additional power increased the amount of photolysis products but was not critical to the success of the experiment.

4. Results and Discussion

4.1. Analysis Methods

The spectroscopic information was collected by monitoring the detector signal as a function of time as the molecular absorber moved through the (sub)millimeter beam. This time trace was recorded at each frequency step, and an absorption spectrum in frequency space was constructed by plotting the integrated absorption signal from the time trace for each frequency setting. The time traces were used to monitor product formation or reactant depletion, while the spectra were used to quantify the reactant and product densities and temperatures. An example of a time trace is given in Figure 4, which shows the detector response of the system as a function of time when set to the center frequency of an O_3 line. Here the baseline signal is seen in the beginning of the trace, followed by the absorption dip when O_3 is pulsed into the vacuum chamber. The spike in the middle of the trace is the radio frequency interference (RFI) induced by the laser pulse. On a timescale of $\sim 50\ \mu\text{s}$ after the laser pulse, the O_3 absorption signal is depleted. This depletion lasts for $\sim 70\ \mu\text{s}$, and then the O_3 absorption returns until the end of the valve pulse. At this point, the detector signal reverts back to the baseline value. The signal depletion observed for O_3 primarily corresponds to the production of $O(^1D)$. O_3 photolysis at 248 nm gives $\sim 90\%$ $O(^1D)$ [67].

Figure 5 shows the time trace of the detector response as a function of time when set to the center frequency of a methanol line. Here the signal stays at baseline for the majority of the acquisition. The only two deviations from baseline are the RFI associated with the laser pulse, and the absorption dip corresponding to methanol production.

While the time traces are helpful in monitoring reactant depletion or product formation, a quantitative analysis of the results relies upon spectral acquisition so that temperature and density can be determined. Frequency spectra were collected by recording a time trace at each frequency setting as the millimeter/submillimeter system was stepped at 60 kHz intervals; the integrated intensity of the absorption signal was then determined so that a plot of intensity versus frequency could be constructed. All frequency spectra were power normalized to account for changes in intensity due to the power response of the frequency multipliers. Ozone, methanol, and formaldehyde (the lowest energy dissociation product of vibrationally-excited methanol) all have absorption lines in the frequency span of one multiplier setup (140 – 220 GHz). Multiple lines could thus be monitored without changing multiplier chains, enabling the density and temperature of these molecules in the expansion to be determined quantitatively through a standard

Figure 5: Time trace showing the methanol absorption signal offset from the baseline following the RFI from the laser pulse.

Boltzmann analysis. This method has been shown [68] to be a reliable approach for quantitative interpretation of millimeter/submillimeter spectral data when a supersonic expansion source is used; the procedure used for the spectral analysis is also described in this reference. Briefly, the integrated intensities of each spectral line are determined through a Gaussian fit. The function $\ln\left[\left(\int_{-\infty}^{\infty} I_b dv\right)(k/(h^2 \nu B g_u))\right]$ can be plotted versus $E_l + h\nu$, and a linear regression analysis yields a slope inversely proportional to T_{rot} and an intercept equal to $\ln(N_T/Q(T_{rot}))$. Here, $\int_{-\infty}^{\infty} I_b dv$ is the integrated intensity of the spectral line, h is Planck's constant, k is Boltzmann's constant, c is the speed of light, B is the Einstein B -coefficient for the transition, g_u is the upper state degeneracy, ν is the transition frequency, N_T is

Figure 6: Ozone (left) and methanol (right) spectral lines observed during each experiment. The lowest frequency ozone line has been rescaled so that all lines are visible in this spectrum.

the column density, $Q(T_{rot})$ is the rotational partition function, and T_{rot} is the rotational temperature. The values of B , g_u , $Q(T_{rot})$ were obtained from the information included in the Cologne Database for Molecular Spectroscopy (CDMS) [69] and the Jet Propulsion Laboratory (JPL) Spectral Line Catalog [70]. Absolute column densities cannot be obtained using this method unless the intensities are calibrated. Therefore, in this experiment, all column densities are scaled to percentages relative to ozone. An example of typical ozone and methanol spectra are shown in Figure 6; these spectra were collected during the same experiment, under the same conditions. The associated Boltzmann diagrams for these two spectra, as well as one for formaldehyde from the same experiment, are shown in Figure 7.

As seen in Figure 7, the Boltzmann diagrams for ozone and methanol had high correlation coefficients, indicating that these species were in thermal equilibrium. However, the Boltzmann diagrams for formaldehyde displayed low correlation coefficients, possibly indicating that formaldehyde was not in thermal equilibrium. This is not surprising, given the multiple pathways to formaldehyde formation at different energies shown in Figure 1 and discussed in Section 4.5. Therefore, while the trends for formaldehyde can be expected to yield qualitative information about the effects of experimental conditions on its formation and stabilization, the results for formaldehyde are only semi-quantitative.

In addition to scaling the densities to values relative to ozone, it is also helpful to scale these values by the photodissociation efficiency for ozone. This approach accounts for any shot-to-shot fluctuations in the laser output power, and enables proper scaling for the amount of $O(^1D)$ available in the reaction mixture. This percentage was determined by integrating across the depletion signal of the absorption feature in an ozone time trace like that shown in Figure 4.

4.2. Methanol production as a function of valve backing pressure

The first experimental parameter that was investigated was the effect of backing pressure on the amount of products formed. The backing pressure was varied between trials, while the overall gas mixing ratio was held constant at $O_2+O_3:Ar:CH_4$ fractions of 0.25:0.65:0.10. Experimental conditions limited the range of pressures that could be tested, and therefore limited the optimization of this parameter. The signals of the methanol and formaldehyde products were too weak to be detected by our methods at backing pressures of less than 400 Torr. Additionally, the ozone generator could not be operated with a sample line pressure greater than 900 Torr. Given that this factor of two in the backing pressure is close to the experimental uncertainty on the product measurements, discerning any clear trend is a challenge. However, our results do hint that the backing pressure does not significantly affect the production efficiency for methanol or formaldehyde over the tested pressure range. It should be noted that a lack of pressure dependence might also indicate zero-order kinetics for this reaction, where surface interactions within the tube would be the only influence on product formation. It is not possible to test this scenario with the current experimental setup, as the fused silica tube diameter would need to be changed to test surface interactions. Regardless, while product signal enhancement may be observed at even higher pressures, this cannot be tested using the current experimental setup, as significant modifications to the experimental design would be required. Given the current pressure limitations, all subsequent experiments were conducted at a backing pressure of 850 Torr.

4.3. Methanol production as a function of laser photolysis position

The production of methanol was also tested as a function of laser photolysis position. Here, a spherical lens was used to focus the laser spot instead of the usual cylindrical lens, and the position of the lens and laser were adjusted to change the position of the laser beam on the fused silica tube. These measurements were conducted at 850 Torr backing pressure with a gas mixing ratio $O_2+O_3:Ar:CH_4$ of 0.25:0.65:0.10. The resultant methanol and formaldehyde densities were determined through the Boltzmann analysis method described in Section 4.1, and the percentage relative to ozone was determined by taking the ratio of the density determined for the product to that of ozone determined for each trial. Each of these values was also scaled by the photodissociation efficiency. The results are shown in Figure 8. There is a clear increase in product signal when the laser beam is positioned at the beginning of the fused silica tube (i.e., closer to the pulsed valve), which is consistent with the findings of Lester and coworkers [7] using a similar source design. This increase in product signal is more significant for methanol than for formaldehyde, indicating that additional residence time for the gas mixture in the fused silica tube increases the methanol production, while it has a lesser effect on formaldehyde production. It should be noted that there is no methanol detected when the laser spot is positioned at the beginning of the supersonic expansion (i.e., just past the end of the fused silica

Figure 7: Boltzmann diagrams for ozone (top), methanol (middle), and formaldehyde (bottom), where “Int.” is the integrated intensity determined through a Gaussian fit to the line shape. The error bars reflect 3σ values based on the Gaussian fit.

tube). Very weak formaldehyde signal was detected when the laser was in this position. However, the Boltzmann diagram indicated that the sample was not at thermal equilibrium, and no reliable value for the column density could be determined at this position. Fortunately since methanol production is enhanced by use of the fused silica tube, quantitative information for formaldehyde production with the laser spot focused outside of the tube is not required for guiding future experiments.

4.4. Vinyl Alcohol Spectroscopy

Having now proven that the $O(^1D)$ insertion mechanism can be used to produce methanol in the experiment described above, we moved on to the experiments designed to produce less stable molecules. The first test was formation of vinyl alcohol from the insertion of $O(^1D)$ into ethylene. The new mixing source was developed to minimize dark reactions between ozone and ethylene. Performance of the mixing source was verified by monitoring the depletion of ozone in the absence of laser photolysis. Ozone depletion could be observed even in the new mixing source, but the source did allow for sufficient ozone and ethylene to pass to the laser photolysis region. Additionally, the mixing source added length to the transit time of reactants through the pulsed valve system. This increased the duration of molecular signal in the (sub)millimeter beam from 2 ms to 5 ms, greatly enhancing the efficiency of the spectral acquisition.

Example vinyl alcohol spectra are shown in Figure 9. Surprisingly, the optimum laser position for production of vinyl alcohol was near the end of the fused silica tube. This is the opposite result from what was obtained for methanol, where production was optimized when the laser beam was positioned near the pulsed valve. This result indicates that either collisional stabilization is not required for vinyl alcohol production, or that vinyl alcohol undergoes additional reactions in the fused silica tube that lower its overall abundance in the supersonic expansion.

The search for vinyl alcohol was guided by the previous microwave [55] and millimeter wave [57] studies, and the information contained in CDMS [69]. Spectral predictions based on these previous studies were used to guide spectral searches at frequencies above 140 GHz. Searches focused on the syn conformer of vinyl alcohol because it is the lowest energy conformer. Anti-vinyl alcohol was also observed, but only after significant spectral averaging. As such, only a few of the strongest lines for anti-vinyl alcohol could be measured. The spectral lines measured for this conformer are not included in the spectral analysis presented below.

A total of 49 new transitions of syn-vinyl alcohol were detected between the range of 140 and 450 GHz, including transitions up to $J=10$. Because the temperature in the expansion is so cold, the vinyl alcohol line intensities drop dramatically at frequencies above 450 GHz, and no additional lines could be observed. For transitions below 220 GHz, the spectral resolution and associated frequency uncertainty was 20 kHz, while transitions above 220 GHz had a spectral resolution and associated frequency uncertainty of 40 kHz. The new vinyl alcohol lines match very well with spectra predicted based on previous analyses. The new measurements were combined with previous datasets [55, 57, 71] using the information from the CDMS catalog [69]. The fit was performed using the CALPGM program suite [72] with a standard asymmetric top Hamiltonian in the Watson A reduction. The molecular parameters determined

Figure 8: Percentage of product relative to ozone as a function of the distance between the valve faceplate and the laser spot. A schematic of the valve (not drawn to scale) and fused silica tube is shown at the top of the plot for reference. Each point has been scaled by the photodissociation efficiency for ozone determined from the time trace as described in Section 4.1 above. The y error bars reflect 3σ values; the x error bars reflect the size of the laser spot.

Figure 9: Example syn-vinyl alcohol spectra. The intensities of the spectra in the highest two frequency ranges have been multiplied by a factor of 3.

from the refined fit are presented in Table 1. The fit files are deposited with the Journal as Supplementary Information. Our results match well with those from the CDMS catalog, and offer an order of magnitude improvement in precision for several of the molecular parameters.

4.5. Additional Reaction Products Observed

The main goals of the $\text{CH}_4 + \text{O}(^1\text{D}) \rightarrow \text{CH}_3\text{OH}$ experiment were to confirm and optimize the production of methanol. However, Figure 1 indicates that there are several other possible products that could arise from this insertion reaction. While many of these products do have rotational spectral information (i.e., CH_3OH , H_2CO , CH_3O), some of these products do not have any available spectral information in the target frequency range (i.e., CHOH , CH_2OH). In addition, each of the pathways shown in Figure 1 may undergo further reactions to produce species that are not shown in this diagram. Fortunately, the structure-specificity of rotational spectroscopy enables us to search for all molecules with known rotational spectra. Once sufficient spectral coverage is obtained, identification of new molecules can also occur through comparison with predicted spectra based on computational studies. The molecules analyzed in the current work were identified via their rotational spectroscopic signatures, through identification of two or more lines as given in the CDMS [69] and JPL [70] spectral catalogs.

The laser induced products methanol, formaldehyde, methoxy, carbon monoxide, water, $\text{O}_2(^1\Delta)$, HO_2 , and hydrogen peroxide were detected in this experiment. None of these products are observed in the absence of laser photolysis of ozone. Methanol is the targeted insertion reaction product, and is produced with the highest abundance of any product. This is to be expected in an optimized experiment, as direct insertion is expected to be the primary formation route for this molecule. The direct product of laser photolysis of ozone at 248 nm, $\text{O}_2(^1\Delta)$, is also detected, despite its weak magnetic moment allowed transitions. $\text{O}_2(^1\Delta)$ is directly proportional to the amount of $\text{O}(^1\text{D})$ that was formed from photolysis.

Formaldehyde is observed in the next highest abundance as compared to methanol; it can form through several methanol dissociation channels as shown in Figure 1. Formaldehyde can be observed under most photolysis conditions in this experiment, inside or just beyond the fused silica tube. CH_3O lines are only observed when the laser spot is positioned near the exit of the tube, and no lines of CH_3O are observed when the laser spot is positioned at the beginning of the tube (i.e., near the pulsed valve). These results indicate that CH_3O does form as a result of the insertion reaction, but that the presence of the fused silica tube promotes its further reaction by allowing for an increased number of collisions and longer reaction timescales. In support of this finding, HO_2 is only observed when the photolysis occurs in the fused silica tube. The HO_2 radical could be forming from reaction of either CH_3O or CH_2OH with O_2 ; this is consistent with the lack of CH_3O detection when collisions are maximized (i.e., when the fused silica tube is in use). However, it is also possible that HO_2 is forming from the reaction of OH with O_3 . We conclude from these findings that the use of the fused silica tube is driving either formation or collisional stabilization (or both) for CH_3OH , while further reactions involving the methanol dissociation products lead to other product formation, including H_2CO and HO_2 . Searches were also conducted for lines from ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) and

Table 1: Spectral parameters determined for syn-vinyl alcohol compared to the previous study of [55] and the information in the CDMS catalog [69]. The assignments from the current work were combined with previous lower-frequency assignments [55, 57, 71] to give the results presented here.

Parameter	Previous Work [55]	CDMS [69]	This work	Units
A	59660.80(2)	59660.7737(124)	59660.78243(199)	MHz
B	10561.665(3)	10561.60537(212)	10561.60521(49)	MHz
C	8965.786(3)	8965.84207(186)	8965.84204(44)	MHz
Δ_J	7.71(2)	7.4901(167)	7.49749(278)	kHz
Δ_{JK}	-61.6(4)	-60.002(277)	-59.876(38)	kHz
Δ_K	917(1)	914.05(82)	914.853(129)	kHz
δ_J	-1.664(2)	-1.66533(127)	-1.665723(297)	kHz
δ_K	28.97(5)	-0.115791(156)	-0.115784(67)	kHz
Φ_K	—	-0.0297(87)	—	
J_{max}	24	24	24	
K_{max}	19	19	19	
# Lines	36	62	111	
Total Fit rms	64.0	41.1	47.8	kHz

Note: One σ errors are listed in parentheses in units of last significant figure.

dimethyl ether (CH_3OCH_3), which are expected to form from radical-radical recombination reactions of methanol dissociation products, but neither of these species were detected.

In addition to the above major product channels, several additional reaction products were observed in the methane experiment. Hydrogen peroxide was detected, although the spectra were quite weak. H_2O_2 can form through hydrogen abstraction channels involving O_2 , or through the third-body assisted reaction of hydroxyl radicals. Regardless of its formation pathway, the presence of H_2O_2 implies that the chemistry of this system proceeds several steps past the scheme shown in Figure 1. Additional products include water, which can form through an energetically accessible decomposition channel of methanol, or through reactions of hydroxyl radicals with other gases. Carbon monoxide was also observed, which indicates additional hydrogen abstraction reaction channels. It is important to note that OH was not detected in this experiment; this is due to the optimum spectral lines being located outside of the frequency range of the spectrometer.

In the $(\text{CH}_2)_2 + \text{O}(^1\text{D})$ experiment, detection of vinyl alcohol was facile. Additional molecules that were detected include formaldehyde, methanol, methoxy, ketene, ethanol, acetaldehyde, HO_2 , hydrogen peroxide, carbon monoxide, and water. Unsuccessful searches were conducted for several additional likely products; most notably absent was ethylene oxide, a structural isomer of vinyl alcohol and acetaldehyde. Formaldehyde was the most abundant product by several orders of magnitude. This was most likely due to the fast reaction of $\text{O}_2(^1\Delta)$ with ethylene, which produces a four member ring before breaking apart into two formaldehyde molecules. This assumption is reinforced by the lack of detection of $\text{O}_2(^1\Delta)$ when ethylene was present in the reaction mixture. The other detected molecules are formed from reaction of decomposition products O, O_2 , ethylene, ozone, or any of the other reactants. Most important here is acetaldehyde, which is a stable tautomer of vinyl alcohol and forms through inefficient quenching of vinyl alcohol in the fused silica tube. The identification of acetaldehyde but the non-detection of ethylene oxide implies that the vinyl alcohol product had sufficient energy to overcome the barrier to isomerization to acetaldehyde, but lost enough energy through collisions that it did not also isomerize to ethylene oxide.

5. Conclusions

We present here the experimental details and initial results from a spectrometer designed to probe the products of gas-phase $O(^1D)$ insertion reactions through (sub)millimeter spectroscopy. This apparatus was benchmarked through studies of the $O(^1D) + CH_4$ insertion reaction to form CH_3OH . The products of insertion were probed in the supersonic expansion, where several species could be differentiated, including the main insertion product methanol, as well as formaldehyde, methoxy, HO_2 , and hydrogen peroxide. The observation of methanol in this experiment indicates that the main insertion product can be quenched and therefore successfully interrogated using rotational spectroscopic measurements. The other products detected in the experiment indicate that some of the insertion products are not stabilized, leading to decomposition and further chemistry. After optimizing the methane experiment, the experimental design was further tested with ethylene to form vinyl alcohol. A new mixing source was used to minimize dark reactions. Syn-vinyl alcohol and several of its dissociation products were observed. Pure rotational transitions of syn-vinyl alcohol between 140 and 450 GHz were measured, and a refined spectral fit based on these measurements is presented. These measurements can be used to guide observational searches for this molecule in the submillimeter range. Additionally, these experiments lay the groundwork for further studies into $O(^1D)$ reactions to produce small molecules of astrophysical relevance.

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