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LABORATORY KINETIC STUDIES OF OH AND CO2 RELEVANT TO UPPER ATMOSPHERIC RADIATION BALANCE

First Annual Report
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Introduction

This is the first annual progress report describing our efforts under NASA contract NASW-4848 "Laboratory Kinetic Studies of OH and CO_2 Relevant to Upper Atmospheric Radiative Balance". This report covers the time period beginning September 8, 1993 and ending September 7, 1994.

Our efforts during the first year have focussed on the OH experiments which are being performed at Harvard University in collaboration with Professor William Klemperer of the Harvard Chemistry Department. These experiments seek to expand our knowledge of the OH dipole moment function by measuring the permanent dipole moments of OH in excited vibrational states. We plan to produce OH in an excited vibrational state through a chemical reaction in a supersonic jet. The OH will be pumped into more highly excited vibrational states using a Ti:sapphire laser and will be detected using infrared fluorescence. The dipole moment in this excited state will be measured in the presence of an applied electric field by modulating the infrared fluorescence with microwave radiation which is resonant with Stark shifted rotational transitions. The measurement of the frequencies of the microwave resonances in several vibrational states will provide a precise check on the OH dipole moment function which determines the Einstein A factors for OH infrared emission. These quantities are of central importance to our understanding of the radiation budget in the mesosphere and to the interpretation of the Meinel band nightglow.
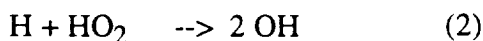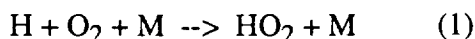
We have made considerable progress toward achieving the goals presented above. Our primary accomplishments have been 1) the modification of the original slit jet spectrometer for the study of radical species and 2) the observation of infrared chemiluminescence from the vibrationally excited OH radicals formed in the H + ozone reaction in the supersonic jet. In the next section we discuss the construction and development of our OH chemical source, the design and implementation of the optical detection system and our studies of OH chemiluminescence. We also outline the remaining steps required to measure the OH dipole moments.

Results

Our initial efforts centered on mechanical fabrication of the chemical source and optical detection system in the Harvard laboratory. The laser system and vacuum chamber were already in place. A new slit jet nozzle was constructed to produce the hot OH radicals. This nozzle is designed to rapidly mix two separate inlet flows just before the supersonic expansion. Our calculations suggest that this should allow efficient production of vibrationally excited OH radicals in the ~1 ms residence time in the high pressure region behind the nozzle. A specially packaged 1 cm Ge photodiode was purchased to detect $\Delta v = 3$ emission from OH. This detector was cooled to 77 K using a liquid nitrogen dewar and a copper braid. Tests of the Ge detector have shown it to be an extremely quiet and sensitive device. The measured noise equivalent power of this 10 mm detector in the laboratory environment is ~ 0.16 pW Hz$^{-1/2}$. To further test this device, we have observed HF monomer emission in the slit jet. We pumped the $v = 3 - 0$ transition and observed $v = 3 - 1$ emission with a signal to noise ratio of ~2 x 10^6. This is 10-20 times better signal to noise ratio than we typically obtain monitoring the $v = 3 -2$ emission of HF with a TE cooled PbS detector. Since the $v = 3-2$ emission of HF is ~ 7 times more intense than the $v = 3 -1$ emission, the Ge detector is approximately 100 times more sensitive than the PbS detector, just as we had hoped. Being quite pleased with these test results, we immediately attempted to observe OH fluorescence.

The first attempts to observe OH were performed using a high pressure source (~ 1 atm) which mixed H atoms with NO_2 in a supersonic slit jet. The H + NO_2 reaction produces OH in vibrational states up to and including $v = 3$. We attempted to detect $v = 2$ OH by pumping the $v = 6 - 2$ transition while monitoring $v = 6 -3$ emission. Unfortunately, these experiments were unsuccessful. The main difficulty was probably insufficient OH production in $v = 2$. NO_2 is a good vibrational relaxer of OH and also reacts with OH at high pressures. Modelling of source conditions suggest that more hot OH would be produced if the backing pressure behind the nozzle is significantly reduced. This would imply faster flow velocities and smaller residence times which would minimize secondary chemistry and vibrational relaxation. Unfortunately, these lower backing pressures would increase the Doppler width of the pumped transition by ~ 5 times. Nevertheless, overall sensitivity should improve by working in the 20-40 Torr regime.
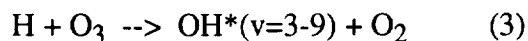
In addition to considering a lower source pressure, we decided to investigate different chemical sources in detail using modelling calculations. The source modelling calculations explored the potential for using H + O_2 and H + O_3 to make hot OH. The H + O_2 source forms OH in a two step process:

$$H + O_2 + M \longrightarrow HO_2 + M \qquad (1)$$
$$H + HO_2 \longrightarrow 2\,OH \qquad (2)$$

Reaction (2) is easily exothermic enough to populate OH(v=3). However we have no information on the quantum yield for this process. Modelling calculations imply that a substantial quantity of OH should be produced using this source with our slit jet at ~40 Torr backing pressure. With the source perfectly tuned the OH mixing ratio in the expansion can approach one part per thousand. However, we excite only the OH in v = 2. We estimate this as 1% of the total OH. This is an estimate since our modelling does not include energy transfer and state dependent processes yet. Under this assumption the mixing ratio of OH(v=2) is ~ 10 ppm. In our HF calibration study, we detected 10 parts per thousand of HF with S/N of 10^6; we should therefore detect 10 ppm of HF with S/N of 1000 and 10 ppm of OH(v=2) with S/N of 50.

Encouraged by this calculation, we attempted to observe OH fluorescence using the H + oxygen source. We attempted to detect v = 2 OH by pumping the v = 6 - 2 transition while monitoring v = 6 -3 emission. These experiments were unsuccessful. Three possible explanations are 1) insufficient H atom production in the discharge or transport to the supersonic nozzle, 2) rapid relaxation of OH* by excess H atoms and 3) low quantum yield for production of OH* from the oxygen source. It is possible that all three of these explanations are simultaneously operative. Certainly H atoms do relax OH* rapidly. We believe that we can produce significantly more OH* using an H + ozone source.

The H + ozone source will directly produce ozone in hot vibrational states:

$$H + O_3 \longrightarrow OH^*(v=3\text{-}9) + O_2 \qquad (3)$$

This source addresses each of the three possible problems described above. First, it uses H atoms more efficiently. Modelling calculations imply total OH mixing ratios of five parts per thousand using this source under conditions which produce only one part per thousand with the oxygen source. Secondly, this source is not adversely affected by H atom relaxation of OH*. Since, the OH* is produced in v=3-9, we can detect v=3 OH either from the nascent distribution (~7%) or after it is relaxed from v=4-9. Finally, the third issue of unknown and possibly small quantum yield for OH* in the oxygen case does not apply in this case. The quantum yields are well known and encouraging. The yields for v=3-9 are approximately 7%, 9%, 10%, 11%, 11%, 23% and 28%. We made arrangements to synthesize ozone at Harvard in order to test this source. A

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significant advantage of this source is the fact that there will be substantial OH* chemiluminescence since all of the OH is produced in very high vibrational states. We are therefore able to observe this emission directly and use it to tune our operating conditions. This is far simpler and faster than optimizing conditions with single mode laser scans each of which take a few minutes to perform.

Preparations for testing the H + ozone source included:

1) The construction of baffle towers to reject scattered laser light which has been a nagging problem for some time.

2) The collection of the appropriate equipment for synthesizing, storing and delivering ozone to the slit jet. The ozone is synthesized using an ozonizer borrowed from the Anderson group at Harvard.

3) The construction of an optical rail with appropriate lenses for collecting the fluorescence and transporting it outside of the vacuum chamber. This is essential for future experiments which may involve dispersed fluorescence and also allows us to use more sensitive detectors which cannot be used easily in the vacuum chamber (see (4)).

4) The loan of an extremely sensitive Ge detector from Dr. Bill Blumberg's laboratory at the Air Force Phillips Lab. This detector mounts external to the vacuum chamber and should improve our sensitivity by an order of magnitude or more.

The first attempt to observe chemiluminescence from reaction (3) was successful. To minimize the loss of radical species in the nozzle block, a teflon nozzle was machined from a standard teflon Swagelock fitting. The stagnation pressure behind the jet was 40-50 Torr. This approach worked very well as intense chemiluminescence was immediately observed. The detector employed was an ultra sensitive Ge photodiode which has a dark noise level of ~30 μV in a 1 Hz bandwidth. The chemiluminescence signal was ~10 V, or ~300,000 times larger than the dark noise. In fact the amount of light which can be generated is even larger than this since the detector output was saturated at 10 V.

Several obvious test were performed to help substantiate that the emission was due to OH*. For example, we showed that the chemiluminescence was only observed with H_2 flowing, with ozone flowing and with the microwave discharge on. Removal of any of these three elements eliminated the emission signal. In Figure 1, we show the emission signal as a function of time. The signal disappears when the ozone is turned off and when the H_2 is turned off. Definitive species identification will be made using spectroscopic techniques in the near future.
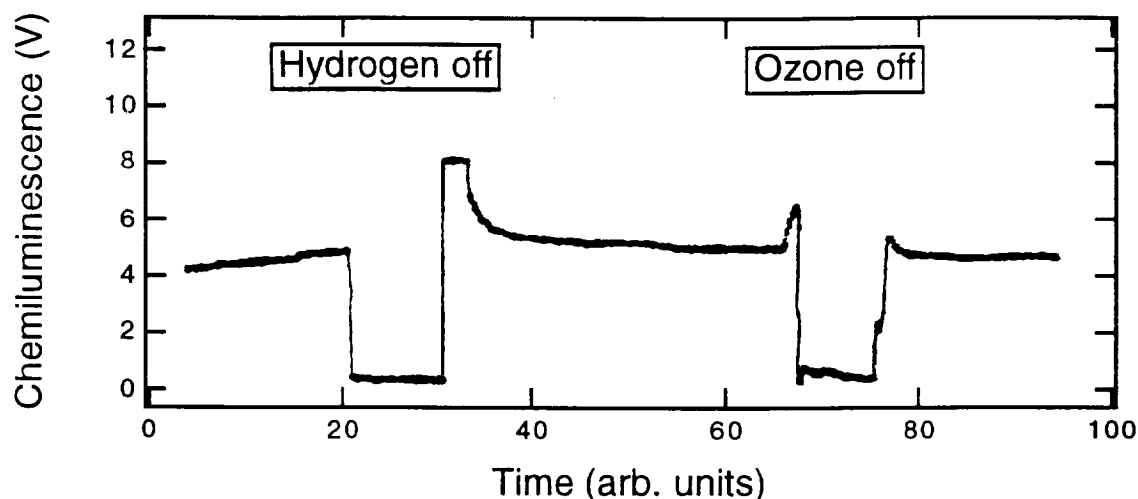
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Figure 1. Trace of OH* chemiluminescence versus time. Signal disappears when either H_2 or ozone flows are turned off.

The size of the emission signal is very encouraging. We may roughly expect a laser induced fluorescence signal which is 1000 times smaller than the chemiluminescent signal. This allows for a factor of 10 due to the quantum state distribution and a factor of ~100 due to the expected 1% pumping efficiency. A fluorescence signal of 10 mV should be easy to observe with this detector. We have observed intense chemiluminescence with backing pressures ranging from 8 Torr to approximately 300 Torr. The Ge detector is saturated over a wide range of conditions so that it is difficult to evaluate the optimal conditions. However, the observation of strong signals with high backing pressures is very encouraging since it suggests that we can run with a hard expansion which will cool most of the OH radicals into their lowest energy rotational state for a given vibrational level.

We have also monitored the chemiluminescence with other infrared detectors. The signal can be easily observed with either an InSb photovoltaic detector or a PbS photoconductive detector. Each of these detectors is sensitive to the weak $\Delta v=1$ OH* emission whereas the Ge detector is sensitive to the stronger $\Delta v=3$ OH* emission. The combination of the detector responsivities and the OH Einstein factors imply that the Ge detector responds most strongly to OH radicals with $v'>5$, whereas the other two detectors respond almost entirely to OH radicals with $v'<5$. Hence, the observations suggest that OH* is spread over a wide range of vibrational states and that we will be able to use the relative responses of the detectors as a measure of the vibrational distribution as a function of source conditions. This has not yet been extensively explored.

Despite the encouraging large chemiluminscence signals, we have so far not succeeded in the observation of a laser induced fluorescence (LIF) signal. The most recent attempt to observe OH* LIF employed a bandpass interference filter to eliminate OH* chemiluminescence. This greatly reduced the background light on the detector and allowed us to make our most sensitive measurement to date. The background chemiluminescence without the filter was more than 10^6 times greater than the noise level on the lockin amplifier with the filter in place. We pumped the v=7-3 transition looking for 7-4 emission. No fluorescence was observed either with FM or AM scans. There are several possible explanations for these observations which we are investigating.

First, it is possible that the laser pump frequency is incorrect or that the published transition frequency is in error by a few tenths of a wavenumber. This turns out to be highly unlikely. We have recently obtained preprints of FTIR emission spectra of OH* taken by Sumner Davis and coworkers. This work is in good agreement with earlier measurements of John Coxon. An error of even a few hundredths of a wavenumber in the transitions frequency which we are using would be quite surprising. Since our scans are at least 0.2 cm^{-1} long, uncertainty in the transition frequency is highly unlikely to explain our difficulty.

Second, it is possible that the OH* is not rotationally/translationally cold. Although the OH is formed in a supersonic jet under strong expansion conditions, the H+ozone reaction is very exothermic. It is possible that the behavior of the jet needs to be better understood. We will test this by monitoring the temperature and linewidth of HF with LIF as a function of source conditions. This should give us a precise picture of the jet temperature and density under our operating conditions. Calculations done after the experiment suggest that it may be important to excite the OH radicals further downstream to allow sufficient jet cooling.

Third, it is possible that instability in the laser frequency prevents us from pumping the OH* in the first place. Careful tests of the LIF signals from HF monomer showed that they could vary greatly with constant source conditions. Most of this variation is likely due to laser instability. We will continue to address this problem.

Finally, it is possible that there is very little OH* despite the large chemiluminescence signal. For example, the OH* could all be in v=8 or 9. Perhaps OH is not the emitter at all? Neither of these explanations seems likely. The quantum yields for forming OH* as a function of vibration have been carefully measured and preclude all the OH* being formed in v= 8 or 9. Furthermore, it is difficult to imagine another emitter in this narrow frequency window with only ozone, H_2, H and a little O_2 available. HO_2 does have an electronic transition in this region which

may play a role in our observations. However it is unlikely to be the complete explanation. We plan to address this final possibility by resolving the chemiluminescence with either a monochromator or a Fourier Transform Infrared spectrometer. This would allow us to determine definitive species identification and jet temperature as a function of source conditions.

Conclusions

During the first year of this program, we have made considerable progress toward the measurement of the dipole moments of vibrationally excited OH radicals. Our primary accomplishments have been 1) the modification of the original slit jet spectrometer for the study of radical species and 2) the observation of infrared chemiluminescence from the vibrationally excited OH radicals formed in the H + ozone reaction in the supersonic jet. We are optimistic that we will soon observe OH* laser induced fluorescence in the jet. Modulation of this fluorescence with microwave radiation in an applied electric field will be the final step required for the precise determination of the vibrational dependence of the OH dipole moment. We hope to report these results in the near future.