

15:52:36

OCA PAD INITIATION - PROJECT HEADER INFORMATION

04/04/89

Active

Project #: G-35-622  
Center # : R6668-0A0

Cost share #:  
Center shr #:

Rev #: 0  
OCA file #:  
Work type : RES  
Document : GRANT  
Contract entity: GTRC

Contract#: ATM-8900695  
Prime #:

Mod #:

Subprojects ? : N  
Main project #:

Project unit: GEO SCI Unit code: 02.010.140  
Project director(s):  
SANDHOLM S GEO SCI (404)894-3895  
BRADSHAW J D GEO SCI (404)-

Sponsor/division names: NATL SCIENCE FOUNDATION / GENERAL  
Sponsor/division codes: 107 / 000

Award period: 890113 to 900831 (performance) 901130 (reports)

Sponsor amount	New this change	Total to date
Contract value	125,000.00	125,000.00
Funded	125,000.00	125,000.00
Cost sharing amount		0.00

Does subcontracting plan apply ? : N

Title: FIELD DEPLOYMENT OF A VUV/PF-LIF AMMONIA SENSOR AS RELATES TO THE NOAA ...

PROJECT ADMINISTRATION DATA

OCA contact: David B. Bridges 894-4820

Sponsor technical contact

Sponsor issuing office

JARVIS L. MOYERS  
(202)357-9657  
NATIONAL SCIENCE FOUNDATION  
AEO/ATM  
WASHINGTON, D.C. 20550

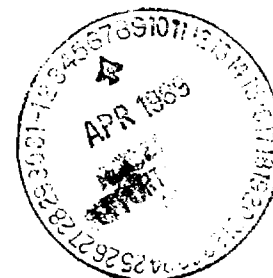
SHARON GRAHAM  
(202)357-9621  
NATIONAL SCIENCE FOUNDATION  
DGC/AEO  
WASHINGTON, D.C. 20550

Security class (U,C,S,TS) : U  
Defense priority rating : N/A  
Equipment title vests with: Sponsor

ONR resident rep. is ACO (Y/N): N  
NSF supplemental sheet  
GIT X

Administrative comments -

PROJECT INITIATION, FUNDS IAO \$125,000, TERM. DATE 8/31/90;



GEORGIA INSTITUTE OF TECHNOLOGY  
OFFICE OF CONTRACT ADMINISTRATION

NOTICE OF PROJECT CLOSEOUT

Closeout Notice Date 07/01/91

Project No. G-35-622 \_\_\_\_\_ Center No. R6668-0A0 \_\_\_\_\_

Project Director SANDHOLM S \_\_\_\_\_ School/Lab E & A SCI \_\_\_\_\_

Sponsor NATL SCIENCE FOUNDATION/GENERAL \_\_\_\_\_

Contract/Grant No. ATM-8900695 \_\_\_\_\_ Contract Entity GTRC

Prime Contract No. \_\_\_\_\_

Title FIELD DEPLOYMENT OF A VUV/PF-LIF AMMONIA SENSOR AS RELATES TO THE NOAA ..

Effective Completion Date 910331 (Performance) 910630 (Reports)

Closeout Actions Required:	Y/N	Date Submitted
Final Invoice or Copy of Final Invoice	N	_____
Final Report of Inventions and/or Subcontracts	Y	910627
Government Property Inventory & Related Certificate	N	_____
Classified Material Certificate	N	_____
Release and Assignment	N	_____
Other _____	N	_____

Comments BILLING VIA LINE OF CREDIT \_\_\_\_\_

Subproject Under Main Project No. \_\_\_\_\_

Continues Project No. \_\_\_\_\_

Distribution Required:

Project Director	Y
Administrative Network Representative	Y
GTRI Accounting/Grants and Contracts	Y
Procurement/Supply Services	Y
Research Property Management	Y
Research Security Services	N
Reports Coordinator (OCA)	Y
GTRC	Y
Project File	Y
Other _____	N
_____	N

NOTE: ~~Final Patent Questionnaire sent to PDPI.~~

PLEASE READ INSTRUCTIONS ON REVERSE BEFORE COMPLETING

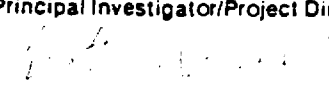
PART I—PROJECT IDENTIFICATION INFORMATION

1. Institution and Address Georgia Institute of Technology 225 North Ave Atlanta, Ga 30332-0340	2. NSF Program Atmospheric Chemistry	3. NSF Award Number NSF-ASTM-8900695
	4. Award Period From 1/13/89 To 3/30/91	5. Cumulative Award Amount \$220.2 K
6. Project Title Field Deployment of a VUV/PF LIF Ammonia Sensor as Related to the NOAA Hosted NH <sub>3</sub> Instrument Intercomparison		

PART II—SUMMARY OF COMPLETED PROJECT (FOR PUBLIC USE)

Vacuum-ultraviolet/photofragmentation-laser-induced fluorescence (VUV/PF-LIF) has been demonstrated to be a highly specific and sensitive method for the quantitative measurement of atmospheric ammonia (NH<sub>3</sub>). The fluorescence detected in this approach results from the two photon (193 nm) photofragmentation of NH<sub>3</sub> followed by the LIF excitation of the NH(b<sup>1</sup>Σ<sup>+</sup>) ⇒ NH(c<sup>1</sup>Π) (at 452 nm) and the monitoring of fluorescence from the NH(c<sup>1</sup>Π) ⇒ NH(a<sup>1</sup>Δ) transition at 325 nm. Limits of detection for the instrument presented here are < 10 pptv and < 4 pptv for one and five minute integration periods, respectively, under ambient sampling conditions. The technique is free from interferences and system performance does not significantly degrade under adverse sampling conditions (i.e. rain, fog, clouds, haze, etc.). Spectroscopic selectivity in the NH(b<sup>1</sup>Σ<sup>+</sup>) ⇒ NH(c<sup>1</sup>Π) transition is sufficient to resolve <sup>15</sup>NH<sub>3</sub> and <sup>14</sup>NH<sub>3</sub> contributions for use in atmospheric tracer studies. During the intercomparison the PF-LIF sensor was the only technique that showed agreement with the referee spike test. The citric acid annular denuder technique was the only other NH<sub>3</sub> measurement to show agreement with the PF-LIF sensor below 500 pptv. The tungstic oxide annular denuder system (DARE) measured significantly higher (6 fold) NH<sub>3</sub> levels at the lowest concentration measured (15 pptv) and remained on average 2 to 4 fold higher up to 200 pptv. The PF-LIF sensor can be easily improved to give limits of detection of < 2 pptv for a one minute integration time. In addition, the PF-LIF sensor can be added to the existing Georgia Tech N<sub>x</sub>O<sub>y</sub> aircraft instrument and provide simultaneous NO, NO<sub>2</sub>, NO<sub>y</sub>, and NH<sub>3</sub> measurement in a single system.

PART III—TECHNICAL INFORMATION (FOR PROGRAM MANAGEMENT USES)

1. ITEM (Check appropriate blocks)	NONE	ATTACHED	PREVIOUSLY FURNISHED	TO BE FURNISHED SEPARATELY TO PROGRAM	
				Check (✓)	Approx. Date
a. Abstracts of Theses	X				
b. Publication Citations		X			
c. Data on Scientific Collaborators	X				
d. Information on Inventions	X				
e. Technical Description of Project and Results		X			
f. Other (specify)					
2. Principal Investigator/Project Director Name (Typed) Scott T. Sandholm	3. Principal Investigator/Project Director Signature 			4. Date	

**PART IV - SUMMARY DATA ON PROJECT PERSONNEL**

NSF Division ATMOSPHERIC CHEMISTRY

The data requested below will be used to develop a statistical profile on the personnel supported through NSF grants. The information on this part is solicited under the authority of the National Science Foundation Act of 1950, as amended. All information provided will be treated as confidential and will be safeguarded in accordance with the provisions of the Privacy Act of 1974. NSF requires that a single copy of this part be submitted with each Final Project Report (NSF Form 98A); however, submission of the requested information is not mandatory and is not a precondition of future awards. If you do not wish to submit this information, please check this box

Please enter the numbers of individuals supported under this NSF grant.  
Do not enter information for individuals working less than 40 hours in any calendar year.

*U.S. Citizens/ Permanent Visa	PI's/PD's		Post-doctorals		Graduate Students		Under-graduates		Precollege Teachers		Others	
	Male	Fem.	Male	Fem.	Male	Fem.	Male	Fem.	Male	Fem.	Male	Fem.
American Indian or Alaskan Native . . . .												
Asian or Pacific Islander . . . . .												
Black, Not of Hispanic Origin . . . . .												
Hispanic . . . . .												
White, Not of Hispanic Origin . . . . .	2		1		1		2					
<b>Total U.S. Citizens . . . . .</b>	<b>2</b>		<b>1</b>		<b>1</b>		<b>2</b>					
<b>Non U.S. Citizens . . . . .</b>	<b>0</b>		<b>0</b>		<b>1</b>		<b>0</b>					
<b>Total U.S. &amp; Non-U.S. . .</b>	<b>2</b>		<b>1</b>		<b>2</b>		<b>2</b>					
Number of individuals who have a handicap that limits a major life activity.	0		0		0		0					

\*Use the category that best describes person's ethnic/racial status. (If more than one category applies, use the one category that most closely reflects the person's recognition in the community.)

**AMERICAN INDIAN OR ALASKAN NATIVE:** A person having origins in any of the original peoples of North America, and who maintains cultural identification through tribal affiliation or community recognition.

**ASIAN OR PACIFIC ISLANDER:** A person having origins in any of the original peoples of the Far East, Southeast Asia, the Indian subcontinent, or the Pacific Islands. This area includes, for example, China, India, Japan, Korea, the Philippine Islands and Samoa.

**BLACK, NOT OF HISPANIC ORIGIN:** A person having origins in any of the black racial groups of Africa.

**HISPANIC:** A person of Mexican, Puerto Rican, Cuban, Central or South American or other Spanish culture or origin, regardless of race.

**WHITE, NOT OF HISPANIC ORIGIN:** A person having origins in any of the original peoples of Europe, North Africa or the Middle East.

**THIS PART WILL BE PHYSICALLY SEPARATED FROM THE FINAL PROJECT REPORT AND USED AS A COMPUTER SOURCE DOCUMENT. DO NOT DUPLICATE IT ON THE REVERSE OF ANY OTHER PART OF THE FINAL REPORT.**

Field Deployment of a VUV/PF-LIF Ammonia Sensor as Related  
to the NOAA Hosted NH<sub>3</sub> Instrument Intercomparison Program

FINAL REPORT  
(ASTM8900695)

Submitted By:

Scott Sandholm and John Bradshaw  
Georgia Institute of Technology,  
School of Earth and Atmospheric Sciences  
Atlanta, Georgia 30332-0340

SUMMARY

Vacuum-ultraviolet/photofragmentation-laser-induced fluorescence (VUV/PF-LIF) has been demonstrated to be a highly specific and sensitive method for the quantitative measurement of atmospheric ammonia (NH<sub>3</sub>). The fluorescence detected in this approach results from the two photon (193 nm) photofragmentation of NH<sub>3</sub> followed by the LIF excitation of the NH(b<sup>1</sup>Σ<sup>+</sup>) ⇒ NH(c<sup>1</sup>Π) (at 452 nm) and the monitoring of fluorescence from the NH(c<sup>1</sup>Π) ⇒ NH(a<sup>1</sup>Δ) transition at 325 nm. Limits of detection for the instrument presented here are < 10 pptv and < 4 pptv for one and five minute integration periods, respectively, under ambient sampling conditions. The technique is free from interferences and system performance does not significantly degrade under adverse sampling conditions (i.e. rain, fog, clouds, haze, etc.). Spectroscopic selectivity in the NH(b<sup>1</sup>Σ<sup>+</sup>) ⇒ NH(c<sup>1</sup>Π) transition is sufficient to resolve <sup>15</sup>NH<sub>3</sub> and <sup>14</sup>NH<sub>3</sub> contributions for use in atmospheric tracer studies. During the intercomparison the PF-LIF sensor was the only technique that showed agreement with the referee spike test. The citric acid annular denuder technique was the only other NH<sub>3</sub> measurement to show agreement with the PF-LIF sensor below 500 pptv. The tungstic oxide annular denuder system (DARE) measured significantly higher (6 fold) NH<sub>3</sub> levels at the lowest concentration measured (15 pptv) and remained on average 2 to 4 fold higher up to 200 pptv. The PF-LIF sensor can be easily improved to give limits of detection of < 2 pptv for a one minute integration time. In addition, the PF-LIF sensor can be added to the existing Georgia Tech N<sub>x</sub>O<sub>y</sub> aircraft instrument and provide real time simultaneous NO, NO<sub>2</sub>, NO<sub>y</sub>, and NH<sub>3</sub> measurement in a single system.

1. INTRODUCTION

Ammonia is the dominant basic species in the troposphere and therefore significantly impacts on the acid-base chemistry of the lower atmosphere.<sup>1-7</sup> Gas phase ammonia, representing the most abundant reduced form of atmospheric nitrogen, is surprisingly stable in an oxidizing atmosphere, exhibiting a long lifetime with respect to oxidative attack (approx. 45 days). Ammonia's fate in the atmosphere is primarily controlled through its equilibrium with aerosol acidic compounds (viz. NH<sub>4</sub>NO<sub>3</sub>, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, etc.) and aqueous droplets (e.g. NH<sub>3</sub>(g) ⇌ NH<sub>3</sub>(aq) ⇌ (+NO<sub>3</sub><sup>-</sup>)(aq) + NH<sub>4</sub><sup>+</sup> ⇌ NH<sub>4</sub>NO<sub>3</sub>), with eventual gas phase removal occurring through dry decomposition and rainout/washout events. The equilibria of gas phase

ammonia with aerosols and droplets is still not completely understood, especially at low concentrations and low temperatures under atmospheric conditions.<sup>8-15</sup>

There are few measurements of ammonia in remote regions and still fewer measurements of the vertical distribution of ammonia in the troposphere. Gas phase ammonia studies in the boundary layer over continental regions (primarily in the northern hemisphere) show the range of ammonia concentrations generally varying between 1-20 parts-per-billion-by-volume (ppbv). Current estimates of the global ammonia budget have assumed globally averaged concentrations for remote regions ranging from 0.5 ppbv to 3 ppbv.<sup>6,7,16</sup> Measurements over the ocean, which are not significantly impacted by direct continental air masses, suggest this latter value is probably  $< 0.2$  ppbv.<sup>1,17,18</sup>

The cycling of gas phase ammonia and its effects on acid deposition, enhanced aqueous phase SO<sub>2</sub> oxidation, aerosol formation, production of nitric oxide in the remote atmosphere, and redistribution of nutrient nitrogen in biospheric systems has been pointed out in numerous reviews.<sup>1,5-7</sup> Recent theoretical studies suggest that a ubiquitous tropospheric level of NH<sub>3</sub> might account for a sizable fraction of the highly reactive NO<sub>x</sub> budget within the remote troposphere.<sup>19</sup> The need for further studies, especially in remote regions, is obvious. However, few methods have currently exhibited an ability to reliably measure gas phase ammonia at concentration levels relevant to that anticipated in the remote troposphere (i.e. [NH<sub>3</sub>]  $< 200$  pptv.).

Reported here is a Vacuum-Ultra-Violet Photofragmentation Laser Induced Fluorescence (VUV/PF-LIF) sensor that is capable of routine measurements of gas phase ammonia in the concentration range relevant to the remote troposphere with time resolution capabilities of one minute or less. The VUV/PF-LIF sensor is spectroscopically selective and virtually free from inlet memory problems due to its unique high flow rate ambient sampling design. In addition, the VUV/PF-LIF NH<sub>3</sub> instrument has now participated in an NH<sub>3</sub> instrument critical intercomparison (Boulder, CO January-March 1989).<sup>20</sup>

## 2. DESCRIPTION OF VUV/PF-LIF NH<sub>3</sub> SENSOR

### 2.A. VUV/PF-LIF technique

Like numerous other atmospherically important polyatomic trace gases that possess unbound upper electronic states (viz. HONO, HNO<sub>3</sub>, H<sub>2</sub>S, CS<sub>2</sub>, COS, etc.), ammonia does not fluoresce strongly enough to allow a direct laser induced fluorescence (LIF) sensor to be developed with adequate sensitivity for atmospheric monitoring purposes. The method of photofragmentation laser induced fluorescence (PF-LIF) relies on photolysis of a parent molecule to yield smaller fragments that are detected with high sensitivity and selectivity using laser induced fluorescence. Photofragmentation in the near vacuum-ultraviolet makes possible the potential detection of numerous atmospherically important trace gases (viz. NH<sub>3</sub>, H<sub>2</sub>S, SO<sub>2</sub>, CS<sub>2</sub>, etc.). This is a result of the large absorption cross section of these gases in the VUV and the usually large quantum yields for production of simple diatomic photofragments (eg. NH, SH, SO, CS).

The spectroscopy of the NH<sub>3</sub> VUV-PF/LIF detection scheme is summarized below and in the energy level diagram depicted in Figure 1.

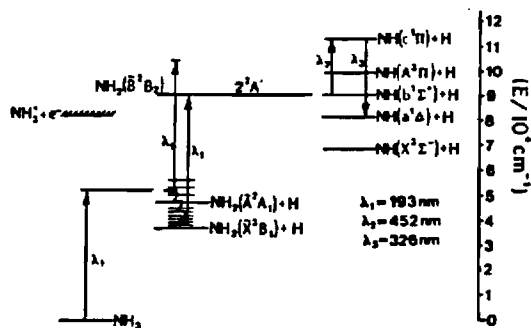
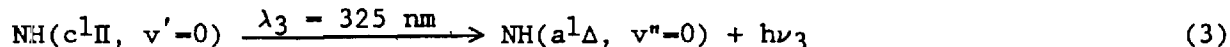
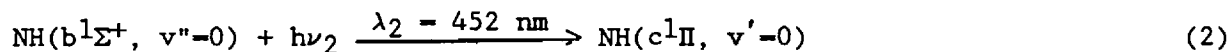
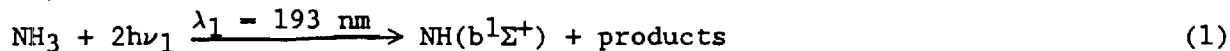


Fig. 1. Energy level diagram illustrating the VUV photofragmentation and laser induced fluorescence steps.



Although prompt luminescence, following the photodissociation of  $\text{NH}_3$ , has been observed from several excited states of the  $\text{NH}$  photofragment, the utilization of this luminescence for development of a sensitive and selective atmospheric sensor (as suggested by Halpern et.al.<sup>21</sup>) is severely complicated by the large background fluorescence (also referred to as air glow) generated from concomitant gases and aerosols by the 193 nm VUV photolysis pulse. For this reason we chose to monitor the population formed photolytically in the metastable  $\text{NH}(b^1\Sigma^+)$  state. Under atmospheric pressure/composition conditions, the excited  $\text{NH}(b^1\Sigma^+)$  state has been found to exhibit a long enough life time to allow virtually all of the 193 nm generated background noise to decay to near negligible levels. Thus, after an appropriate delay time (1-10  $\mu\text{s}$ ), the  $\text{NH}(b^1\Sigma^+)$  state population can be interrogated via step (2) using a probe laser ( $\lambda_2=452 \text{ nm}$ ) that is capable of resolving individual ro-vibronic transitions in the  $\text{NH}(b^1\Sigma^+) \Rightarrow \text{NH}(c^1\Pi)$  manifold. The fluorescence induced by the excitation to the  $\text{NH}(c^1\Pi)$  state is then monitored at 325 nm. In this scheme, the observed fluorescence is spectrally blue shifted from the probe laser wavelength. This combination allows the  $\text{NH}_3$  VUV-PF/LIF sensor to spectrally eliminate background generated from the probe laser, and temporally minimize the photolysis laser generated background to nearly insignificant levels.

## 2.B. Experimental hardware

Figure (2) depicts a schematic of the experimental apparatus. The 193 nm photolysis laser was an ArF excimer laser (Quanta Ray Exc-1) that produced a nominal output energy of 14 mJ/pulse with an 8 ns temporal width, 1 cm x 1 cm beam area, and a 3 mrad beam divergence. The photolysis laser beam was softly focused, using a 1.5 m focal length lens, to approximately 0.3  $\text{cm}^2$  at the center of the sample cell (where the energy was approximately 9 mJ/pulse). The probe laser consisted of a Nd:YAG pumped dye laser (International Laser System-NT674 and Quanta Ray-PDL-1 respectively). The laser dyes employed were Coumarin 450 for the laser oscillator and Coumarin 460 for the side pumped amplifier. The dyes were pumped by the third harmonic output of the Nd:YAG laser ( $\lambda = 355\text{nm}$ ). Different oscillator/amplifier dyes were chosen to reduce spectrally broadband amplified spontaneous emission from the dye laser. The probe laser beam was spatially filtered and colinearly combined with the 193 nm photolysis laser and had an energy of approximately 2 mJ/pulse, in a 0.8  $\text{cm}^2$  beam, at the sample cell. Pulse energies of both laser beams were monitored by silicon photodiodes. The larger probe laser beam,  $\lambda_2$ , was chosen in order to minimize spatial overlap problems between  $\lambda_1$  and  $\lambda_2$  lasers in a field instrument.



of high volume sampling flows that produce short residence times has been an effective means of minimizing memory problems associated with  $\text{NH}_3$  adsorption on the inlet sample manifold walls. Typical sample flow rates, used in this system, range from 600 to 2400 slpm with sample residence times of  $< 1$  sec. The residence time within the optical cell was  $< 0.1$  sec. In order to minimize aerosol decomposition effects, pressure drops within this nonrestricted sample manifold were kept below 5 mbar.

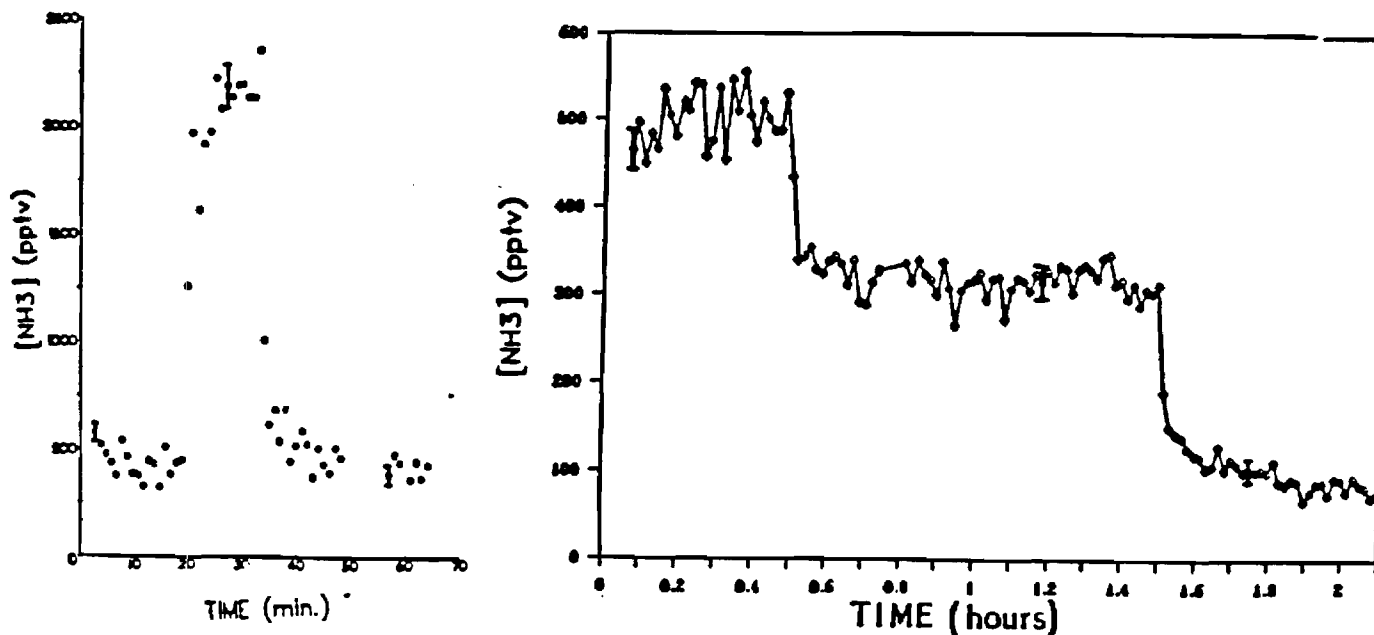


Fig. 3. (a) Temporal response of 1800 pptv addition to ambient air. (b) Low level step function additions of ammonia, representative error bars are shown for the 1 $\sigma$  measurement precision for each representative concentration.

Calibration of the instrument has been accomplished in a three tier manner. Data normalization, using the VUV/PF-LIF signal measured from a referencing cell that contains a known mixture of  $\text{NH}_3$  and nitrogen, constituted the first tier. This reference cell system is instrumentally equivalent to an internal standard and was used to correct for degradations in laser performance that can occur between calibrations (viz. laser energy and wavelength drifts).<sup>22</sup> The signal from the reference system was continuously recorded by the data acquisition/computer system and was used to normalize all data. The second tier involved calibrations using isotopic  $^{15}\text{NH}_3$  as a working gas standard. The spectroscopic selectivity of the VUV/PF-LIF approach makes possible the resolution of  $^{15}\text{NH}$  ( $b^1\Sigma^+$ ,  $v''=0$ )  $\rightarrow$   $^{15}\text{NH}$  ( $c^1\Pi$ ,  $v''=0$ ) individual rotational transitions from their  $^{14}\text{NH}$  counterparts. Contrast ratios between signals from  $^{15}\text{NH}$  and  $^{14}\text{NH}$ , for the strongest Q(1), Q(2), and Q(3) lines, were typically 5:1, 18:1, and 30:1, respectively. Due to the lack of a laser line narrowing etalon in the dye laser used in these experiments, the observed contrast ratios were inadequate for the direct determination of ambient  $^{15}\text{NH}_3$ . Isotopic  $^{15}\text{NH}_3$  has, however, been found to provide reliable standard

addition calibrations at concentrations near that of ambient  $^{14}\text{NH}_3$ , even under conditions where the ambient ammonia concentration was highly variable. The third calibration tier involved direct calibration of the system by the method of standard addition using a primary  $^{14}\text{NH}_3$  certified gas standard. The standard addition calibration system consisted of a three-stage continuous flow serial (dynamic) dilution system, which has been previously described.<sup>22</sup> This system diluted 100 ppmv  $\text{NH}_3$  certified standards (Scott Specialty gases) and provided a continuous flow of nominally 100 ppbv to 1 ppmv  $\text{NH}_3$  to a solenoid valve mounted at the inlet of the ambient sampling manifold. Standard addition calibration, using either  $^{15}\text{NH}_3$  or  $^{14}\text{NH}_3$ , covering the range of 100 pptv to 10 ppbv was accommodated by varying the gas flow rate admitted to the sampling manifold from the pre-equilibrated calibration flow loop. Typical calibration and sensor transient response for standard additions in the 100 pptv to 1.8 ppbv range are shown in Figure 3.

## 2.C. Operational/Performance Characteristics

The VUV/PF-LIF technique is inherently linear over more than five orders of magnitude change in  $\text{NH}_3$  concentration. Optical pre/post filtering non-linear effects have been shown, as expected, not to occur for concentrations below ppmv levels.

For  $\text{NH}_3$  concentrations significantly above the LOD, the measurement precision of the instrument is dominated by the photon statistical fluctuations in the observed signal count rate (eg. (observed  $\text{NH}_3$  signal counts)<sup>1/2</sup>). For a nominal instrument sensitivity of 1.5 photons/pptv/min, the measurement uncertainties at the 95% confidence limit ( $2\sigma$ ) for  $\text{NH}_3$  concentrations of 30, 100, and 200 pptv, and integration times of 1 minute, would be  $\pm 30\%$ ,  $\pm 16\%$ , and  $\pm 12\%$ , respectively. The uncertainty associated with normalizing laser performance via the observed reference cell signal would add  $\leq \pm 6\%$  ( $2\sigma$ ) uncertainty (for a factor of two change in instrument sensitivity). The uncertainty associated with the water vapor  $\text{NH}(b^1\Sigma^+)$  deactivation correction would be  $< \pm 18\%$  ( $2\sigma$ ) (under worst case conditions of 10 Torr change in  $[\text{H}_2\text{O}]$ ). For more typical changes in water vapor of  $\pm 2$  Torr, the uncertainty, from this effect, would be  $\leq \pm 6\%$  ( $2\sigma$ ).

The absolute calibration accuracy has been estimated to be  $\leq \pm 18\%$ , (at the 95% confidence limit) based upon intercomparison of numerous certified  $\text{NH}_3$  standards and the combined uncertainties in the calibration and sample mass flow measurements. Figure 4 (a and b) shows the refree vs. Ga Tech(GIT) spike recovery response over the range of 110 to 14,000 pptv. During ambient sampling periods in which relative humidities varied from 10%-90%, no statistically significant loss in observed VUV/PF-LIF signal strength was found using  $^{15}\text{NH}_3$  as a tracer gas. The effects of inlet long term memory on the measurement of low ambient  $\text{NH}_3$  concentrations (i.e.  $< 500$  pptv) were examined through sample flow rate changes (300 to 2400 slpm), sample inlet line cleaning and heating tests, and  $^{15}\text{NH}_3$  tracer tests. Only the sample line heating test exhibited a statistically significant variation in the observed  $\text{NH}_3$  signal, which is believed to be due to the decomposition of  $\text{NH}_3$ -containing aerosols.

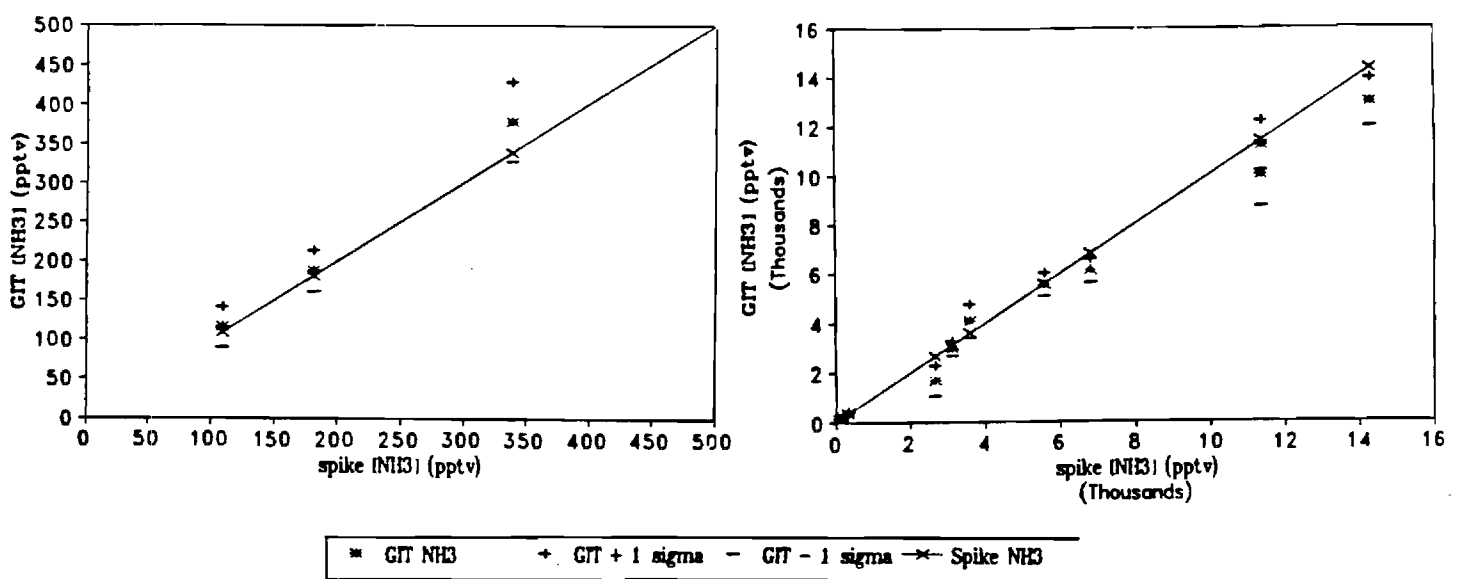


Fig. 4. PF-LIF (GIT) measured NH<sub>3</sub> concentration versus NOAA referee spike addition concentration: (a) 110 to 350 pptv and (b) 110 to 14,000 pptv.

A summary of the low concentration results for the intercomparison is given in Figure 5. As can be seen, the molybdenum and tungstic oxide denuder (MOADS and DARE) give significantly different results from the PF-LIF sensor below 500 pptv. It has been suggested that this may be due to the use of some teflon sampling system and, in the case of MOADS, heating of the inlet.<sup>20</sup> We do not, however, believe that all of the variance may be attributed to these reasons. One must certainly question the reliability of these oxide denuder system in view of the unexplainable "poisoning" of the referees high temperature convertor and its failure to reliably convert NH<sub>3</sub> to NO via the same basic process as used in the DARE system. The lack of performance of any of these convertor techniques during the spike test may also suggest that these techniques can not tolerate rapidly changing conditions (e.g. large changes in relative humidity).

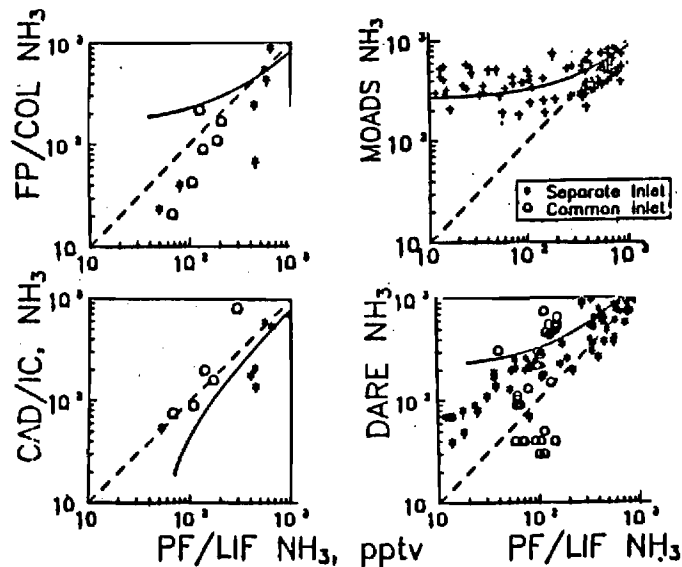


Fig. 5. Concentration measured by: FP/COL (acid impregnated filter pack with colorimetric analysis of NH<sub>4</sub><sup>+</sup>), CAD/IC (Citric Acid Denuder with ion chromatography NH<sub>4</sub><sup>+</sup> analysis), MOADS (molybdenum oxide annular denuder system), and DARE (tungstic oxide denuder system) versus that measured by the PF-LIF sensor.

### 3. FIELD MEASUREMENTS

#### 3.a. Stone Mtn. GA Sampling

During the Fall 1987 and winter/spring 1988, VUV/PF-LIF field measurements of ammonia were conducted at Georgia Tech's Stone Mountain field sampling facility. This facility is located atop Stone Mountain, which is approximately 17 miles east of downtown Atlanta. The sampling facility occupies the sixth floor of a 7 m X 7 m X 30 m (high) tower that has an elevation of 520 m MSL, 250 m above the surrounding terrain, and 20 m above the surface of the mountain top.

Unique aspects of the Stone Mountain field site include: 1) its height above the surrounding terrain makes it reasonably insensitive to the effects of localized sources, even though it is located on the edge of suburban Atlanta; 2) the height of the mountain allows for frequent encounters with clouds when frontal systems pass through north-central Georgia (this situation provided an opportunity to further assess the importance of aerosol scavenging in controlling  $\text{NH}_3$  levels in a clear air mixed-cloud environment); and (3) the elevation of the sampling site is such that at night the top of the nocturnal boundary layer typically sets up at a height that is below the top of the mountain where under these conditions the levels of trace gases encountered are often more typical of rural lower free tropospheric air than they are of suburban or urban Atlanta air. Overall, the Stone Mountain field site has been found to be a very interesting one from a scientific point of view, offering a wide variety of atmospheric sampling conditions.

Significant diurnal variations in ambient ammonia concentration were also observed at the Stone Mtn. sampling site as shown in Figure 4. It is believed that this diurnal variation is due to a capping-off of the nocturnal boundary layer at an elevation below that of the sampling site as evidenced by boundary layer heights estimated from the inversion layer height viewed over nearby Atlanta. The approximate four fold elevation in  $\text{NH}_3$  concentrations shown in Fig. 4b closely followed visual observations of the break-up in the nocturnal boundary layer through the early morning hours.

Figures 4a and 4b are intended to show the differences in  $\text{NH}_3$  levels between nighttime and daytime for the winter season at Stone Mountain. They are also intended to illustrate the potential relationship between the localized measured concentration of  $\text{NH}_3$  atop Stone Mtn. and observations of related parameters (such as nocturnal boundary layer). However, this data should not necessarily be considered as the norm for this season, as only four diurnal measurements were performed during the winter and spring of 1988. Certainly more data collection is necessary before definitive conclusions can be drawn.

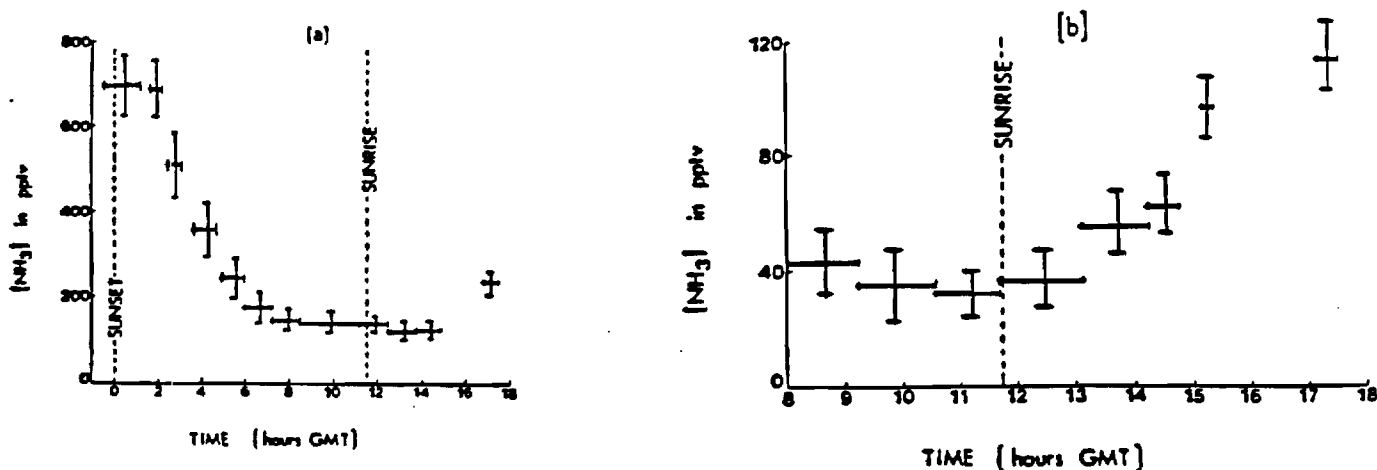


Fig. 6 Plots of the concentration of  $\text{NH}_3$  versus time for the measurements of  $[\text{NH}_3]$  at the Stone Mountain field site. Each horizontal bar on the graphs indicates the average  $\text{NH}_3$  level recorded within the period included and vertical bars represent minimum/maximum values over the period averaged. (a) shows results of measurements made from sunset March 22, 1988 to noon March 23, 1988. Weather was clear but with increasing cloudiness occurring on the morning of March 23. The average temperature was  $10.5^\circ\text{C}$ , relative humidity 56%. (b) shows results of measurements made from ~4 hours before sunrise to noon March 17, 1988. Weather was clear, the average temperature was  $-1.5^\circ\text{C}$ , relative humidity 42%.

### 3.b. Boulder, CO. Sampling

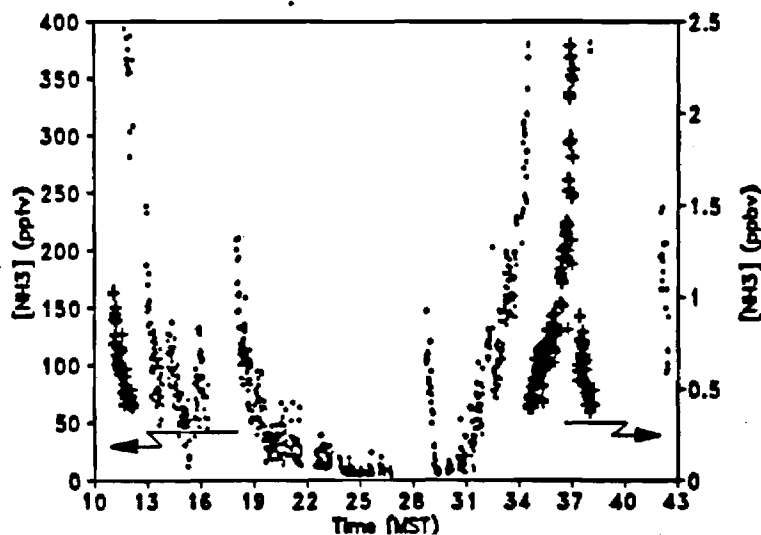


Fig. 7  $\text{NH}_3$  concentration versus time beginning at 10:00 local time on March 20, 1989 at Green Mtn. Mesa. Ambient air temperature was  $-7^\circ\text{C}$  from 20:00 - 27:00 MST. Elevated  $\text{NH}_3$  at 37:00 was associated with elevated levels of  $\text{NO}_x$ , CO and  $\text{SO}_2$ .

The sampling site near Boulder Colorado was located atop the Green Mtn. Mesa within the confines of the NOAA/Department of Commerce compound. An ambient air measurement ammonia study was conducted during March 1989 as part of the NH<sub>3</sub> instrument intercomparison program. Like the Stone Mtn. site the mesa was often elevated above the nocturnal boundary layer capping nearby Boulder.

In addition, air flow originating from the western quadrant was particularly free from local NH<sub>3</sub> sources with conditions often typical of down slope air flow associated with the front range of the Rockies.

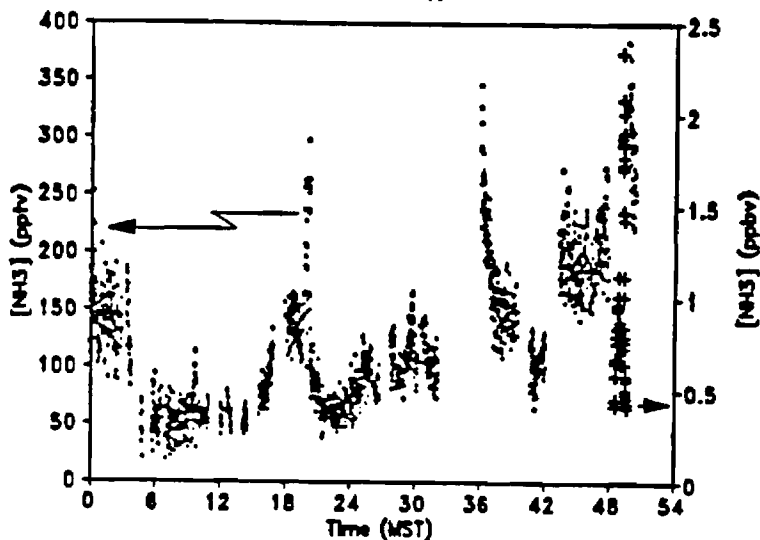


Fig. 8 NH<sub>3</sub> concentrations vs. time beginning at midnight local time on March 14, 1989 at Green Mtn. Mesa.

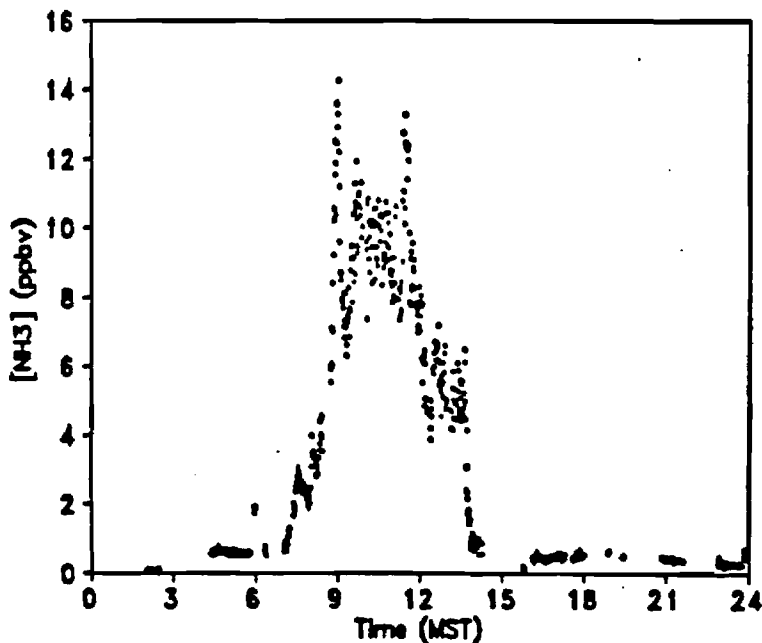


Fig. 9 NH<sub>3</sub> concentrations vs. time beginning at midnight local time on March 26, 1989 at Green Mtn. Mesa.

Figures 7-9 show several multi-day cycles of NH<sub>3</sub> which typified the variety conditions found at the Mesa site in March 1989. During the March 20-21 period (fig. 6) NH<sub>3</sub> levels reached some of the lowest values encountered in the program (~ 10 pptv) during a period of calm winds and ambient air temperatures near -5°C. The NH<sub>3</sub> measurements taken during March 14-16 are similar in magnitude to those of the March 20-21 period with "background" NH<sub>3</sub> levels ranging from 15-150 pptv. In contrast, the data obtained on March 26 exhibited background NH<sub>3</sub> levels of ~ 700 pptv. The large diurnal NH<sub>3</sub> signature on March 26 is typical of the daytime NH<sub>3</sub> levels observed at the Mesa on days in which the Denver/Boulder boundary layer lifted to expose the site to the "Denver Brown-Cloud" in which NH<sub>3</sub> levels above 10 ppbv were associated with elevated levels of NO<sub>x</sub> and SO<sub>2</sub> (tens of ppbv) and CO (1-3 ppmv). The elevated NH<sub>3</sub> level occurring at 11:00 (MST) on March 20th, however, was not associated with any apparent elevation in these latter pollution markers and is more typical of the elevated levels of NH<sub>3</sub> experienced in boundary layer air at Stone Mtn. while those occurring at 37:00 are more typical of the perturbed conditions shown on March 26.

#### 4. CONCLUSIONS

A VUV/PF-LIF sensor has been developed and tested that is capable of making routine measurements of gas phase atmospheric ammonia in the few parts-per-trillion-by-volume range (i.e. 10 pptv =  $2.5 \times 10^8$  molec/cm<sup>3</sup> at 1 atm pressure). Current limits of detection, LOD, (for a S/N = 2/1) are < 10 pptv for a one minute signal integration period, and < 4 pptv for a five minute signal integration period under moderate aerosol loadings and high ambient water vapor conditions. For clean air sampling, more typical of the remote troposphere, the instrument LOD is expected to improve slightly to < 5 pptv and < 2 pptv for one and five minute integrations times, respectively. While they have not proved necessary to date, modest instrument improvements should easily result in limits of detection of < 2 pptv and < 1 pptv for one and five minute integration periods under clean remote free tropospheric sampling conditions.

The spectral selectivity of the technique allows for calibration and tracer studies using either <sup>15</sup>NH<sub>3</sub> or <sup>14</sup>NH<sub>3</sub> as the specifically monitored trace gas. This aspect should provide unique opportunities over other currently available techniques in the study of NH<sub>3</sub> phase equilibria with atmospheric aerosols and droplets.

As yet no interferences, either gas phase or aerosol phase, have been identified as being significant under atmospheric sampling conditions. In addition, the instrument performance is not degraded under adverse sampling conditions (i.e. rain, fog, clouds, haze, etc.).

The VUV/PF-LIF instrument can be configured for operation on an aircraft platform, as has been demonstrated with similar LIF systems developed by our group that have now logged over 500 hours of total airborne measurement time for the measurement of the molecules OH<sup>25</sup>, NO<sup>22</sup>, and NO<sub>2</sub><sup>24</sup>. There are no inherent limitations in the instrument's ability to measure real time vertical concentration profiles of NH<sub>3</sub> in the ten pptv range or higher for vertical descent rates up to 250 m/min, resulting in 250 m vertical spatial resolution.

March background levels of NH<sub>3</sub> obtained at two sites elevated above the nocturnal boundary layer exhibit concentrations thought to be typical of remote

environments with concentrations ranging from 10-200 pptv. These sites are prone to a direct teleconnection with surface sources under daytime boundary layer conditions in which  $\text{NH}_3$  levels exceeding 1 ppbv can be experienced. This data suggest that a pronounced altitude gradient in  $\text{NH}_3$  concentration should be expected above the atmospheric boundary layer even over continental areas.

#### 5. ACKNOWLEDGEMENTS

The authors are grateful to John Schedel for his participation in this work.

#### REFERENCES

1. P.K. Quinn, R.J. Charlson, and W.H. Zoller, "Ammonia, the Dominant Base in the Remote Troposphere: a Review," *Tellus* 39B, 413-425(1987).
2. H.A. ApSimon, M. Kruse, and J.N. Bell, "Ammonia Emissions and Their Role in Acid Deposition," *Atmos. Env.* 21, 1939-1946(1987).
3. P.H. Daum, S.E. Schwartz, and L. Newman, "Acidic and Related Constituents in Liquid Stratiform Clouds," *Journ. Geophys. Res.* 89, 1447-1458(1984).
4. H.A. McKay "The Atmospheric Oxidation of Sulfur Dioxide in Water Droplets in the Presence of Ammonia," *Atmos. Env.* 5, 7-14(1971).
5. J.C. McConnell, "Atmospheric Ammonia," *Journ. Geophys. Res.* 78, 7812-7821(1973).
6. D.H. Stedman and R.E. Shetter, Chpt. 10, "The global budget of atmospheric nitrogen species," *Advances in Environmental Science and Technology*, Vol. 12, "Trace Atmospheric Constituents, Properties Transformations and Fates," Wiley and Sons, New York(1983).
7. National Research Council:Subcommittee on Ammonia, "Ammonia," University Park Press Baltimore, Maryland(1979).
8. R.A. Brost, A.C. Delany, and B.J. Hubert "Numerical Modeling of Concentrations and Fluxes of  $\text{HNO}_3$ ,  $\text{NH}_3$ , and  $\text{NH}_4\text{NO}_3$  Near the Surface," *Journ. Geophys. Res.* 93, 7137-7152(1988).
9. R.F. Adamowicz "A Model for the Reversible Washout of Sulfur Dioxide, Ammonia, and Carbon Dioxide from Polluted Atmospheres and the Production of Sulfates in Raindrops," *Atmos. Env.* 13, 105-121(1979).
10. A.G. Allen, R.M. Harrison, and J.W. Erisman, "Field Measurements of the Dissociation of Ammonia Nitrate and Ammonia Chloride Aerosols," *Atmos. Env.* 23, 1591-1599(1989).
11. L.M. Hildeman, A.G. Russell, and G.R. Cass, "Ammonia and Nitric Acid Concentrations in Equilibrium with Atmospheric Aerosols: Experiment vs. theory," *Atmos. Env.* 18, 1737-1750(1984).
12. M. Bassett and J.H. Seinfeld, "Atmospheric Equilibrium Model of Sulfate and Nitrate Aerosols," *Atmos. Env.* 17, 2237-2252(1983).
13. J.P. Shimshock and R.G. DePena, "Below Cloud Scavenging of Tropospheric Ammonia," *Tellus* 41b, 296-304(1989).
14. G.P. Ayers, J.L. Gras, A. Adriaansen, and R.W. Gillett, "Solubility of Ammonia in Rainwater," *Tellus* 36B, 85-91(1984).
15. R.M. Harrison and C.A. Pio, "An Investigation of the Atmospheric  $\text{HNO}_3$ - $\text{NH}_3$ - $\text{NH}_4\text{NO}_3$  Equilibrium Relationship in a Cool Humid Climate," *Tellus* 35B, 155-159(1983).
16. G.A. Dawson, "Atmospheric Ammonia from Undisturbed Land," *Journ. Geophys. Res.* 82, 3125-3133(1977)
17. P.K. Quinn, R.J. Charlson, and T.S. Bates, "Simultaneous Observations of Ammonia in the Atmosphere and Ocean," *Nature* 335, 336-338(1988).

18. G.P. Ayers and J.L. Gras, "Ammonia Gas Concentrations Over the Southern Ocean," *Nature* 284, 539-540(1980)
19. Chatfield, "The Pervasive - NO<sub>x</sub> Riddle of CITE-2 and MLOPEX Measurements: What's missing in our understanding of Global Photochemistry and Oxidants?" presented at American Geophysical Union 1990 Fall Meeting.
20. E.J. Williams, D.D. Parrish, J. Calvert, B. Watkins, M. Buhr, P.K. Quinn, R.B. Norton, S. Sandholm, J. Schendel, J. Bradshaw, A.O. Langford, P.J. LeBel, S.A. Vay, P. Roberts, and F.C. Fehsenfeld, "A Ground-Based Ammonia Instrument Intercomparison," (submitted *Journ. Geophys. Res.*(1990)).
21. J.B. Halpern, W.M. Jackson, and V. McCrary, "Multiphoton Sequential Photodissociative Excitation: a New Method for Remote Atmospheric Sensing," *Appl. Opt.* 18, 590-592(1979).
22. J.D. Bradshaw, M.O. Rodgers, S.T. Sandholm, S. KeShang and D.D. Davis, "A Two-Photon Laser-Induced Fluorescence Field Instrument for Ground-Based and Airborne Measurements of Atmospheric NO," *Journ. Geophys. Res.* 90, 12,861-12,873 (1985).
23. J.S. Schendel, R.E. Stickel, C.A. van Dijk, S.T. Sandholm, D.D. Davis, and J.D. Bradshaw, "Atmospheric ammonia measurement using a VUV/photofragmentation laser-induced fluorescence technique," *Applied Optics*, 29, 4924-4937(1990).
24. S.T. Sandholm, J.D. Bradshaw, K.S. Doris, M.O. Rodgers and D.D. Davis, "An Airborne Compatible Photofragmentation Two-Photon Laser Induced Fluorescence Instrument for Measurements of Atmospheric NO/NO<sub>x</sub>/NO<sub>2</sub>," *Journ. Geophys. Res.*, 95, 10,155-10,161(1990).
25. M.O. Rodgers, J.D. Bradshaw, S.T. Sandholm, S. KeSheng, and D.D. Davis, "A 2-λ laser-induced fluorescence field instrument for ground-based and airborne measurements of atmospheric OH," *Journ. Geophys. Res.* 90, 12,819-12,824(1985).