when the organic compound was present in concentrations too small to complex more than a few percent of the aluminum ions.

We tested the effect of the presence of small amounts of quercetin on the synthesis of clay minerals by repeating some of the experiments of Hem *et al.* (*7*) in which synthetic halloysite was produced, with the addition of $10^{-5.30}M$ quercetin at the time the reagents were mixed to begin to form precipitates. Reactions were again slow and, in *p*H, aluminum concentrations, and silica concentrations, the aging solutions containing quercetin were similar to the ones lacking quercetin. However, after about 6 months of aging, solids recovered from solutions in the *p*H range 6.5 to 8.5 contained as much as 5 percent relatively well-crystallized kaolinite (Figs. 3 and 4) mixed with the much larger amount of amorphous precipitate. The yield and crystallinity of the material illustrated were far superior to the results obtained in the experiments of Hem *et al.* (*7*) in which only inorganic materials had been used. As before, however, it was not possible to obtain x-ray diffraction peaks because the crystals were small and could not be separated from the amorphous matrix.

We checked the reproducibility of these results by preparing a new series of solutions duplicating those which yielded the kaolinite crystals. Well-crystallized material of kaolinitic appearance was present in substantial quantity in all these solutions after 16 months (Fig. 5).

Evidently conditions favorable for clay-mineral synthesis at 25°C can be produced in systems favoring precipitation of aluminum hydroxide and aluminosilicate by relatively subtle changes in the system. The presence of an organic constituent in amounts too small to complex a measurable fraction of the aluminum evidently is one means of accomplishing this. The principal effect of the organic constituent here was probably to slow the polymerization of polynuclear aluminum hydroxide species, in the *p*H range 6.5 to 8.5 where the polymerization normally is very rapid. This permitted more reactants to follow the slow reaction path leading to kaolinite that is better crystallized. When aluminum hydroxide polymers have reached a size sufficient to display the typical gibbsite or bayerite structure, the aluminum-silica interlayer bonding is evidently rather difficult to establish. Polymerization of aluminum hydroxide is slowed by a lowering of the *p*H, but the attachment of silica to form the clay mineral is also inhibited by low *p*H. In addition to its effects on the the kinetic factors, the aluminum-quercetin complex that forms may facilitate the development of Al–O–Si bonding, because it contains Al–O bonds. Even if the amount of complexed aluminum is small, the ligands would be available for recycling after formation of the Al–O–Si linkages. Further adjustment of the conditions in these experiments may increase the yield of crystalline material and possibly increase the rate of the reaction.

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Spectroscopic Measurements of Stratospheric Nitric Oxide and Water Vapor

Abstract. *Spectroscopic measurements have been made of the nitric oxide and water vapor concentrations in the stratosphere at an altitude of 28 kilometers. The measurements, carried out in situ with the use of a spin flip Raman laser, represent the first accurate determination of nitric oxide as a function of time (as the sun rose) from about 6:30 to 14:00 C.D.T.*

Measurements of NO concentrations in the stratosphere are important because of the crucial role that NO plays in the chemical cycle which determines the O_3 concentration of the inversion layer (18 to 28 km)—the stratosphere. Recently, a number of theorists have tried to delineate the changes in the O_3 cycle due to the additional NO introduced into the stratosphere (*1*) by the proposed flights of a fleet of supersonic transports. Attempts have also been made to interpret the O_3 cycle in light of the fact that the hypothesized injection of large quantities of NO during the years of atmospheric nuclear testing (*2*) resulted in no significant changes in the ambient O_3 concentrations in the stratosphere. The reactions important (*1*) in determining the generation of the local NO concentration include the reaction of NO_2 with atomic oxygen produced during the photodissociation of O_2 (Eq. 1) and the photodissociation of NO_2 by the solar ultraviolet radiation at wavelength < 4000 Å (Eq. 2).

$$NO_2 + O \rightarrow NO + O_2 \qquad (1)$$

$$NO_2 + h\nu \rightarrow NO + O \qquad (2)$$

Both of these reactions are well understood (*1*), and in both the solar ultraviolet radiation produces NO from NO_2. It is also believed that, in the absence of sunlight, for example, at night, the NO thus created rapidly reacts with O_3 and is converted into NO_2. In all of the models, however, the common feature is the lack of precise knowledge of the background concentration of NO during the daytime. Thus the effect of additionally introduced NO calculated in any model is, at best, open to question. To be able to make a reasonable estimate of the effects of the flight of supersonic transports, it is important to know the present concentration of NO in the presence and in the absence of the ultraviolet radiation from the sun. In the experiments reported here we have been able to measure the NO concentration at an altitude of 28 km before, during, and after the sunrise. Since the technique used here is a spectroscopic one, it is generally applicable to other constituents also. Thus, we have been able to measure the stratospheric H_2O concentration which also is of interest in some of the chemical reactions important in the stratospheric balance.

Table 1. Nitric oxide and water vapor absorption lines used for spectroscopic determination of their respective concentrations at the balloon altitude of 28 km.

Species	Line idetification	Position (cm^{-1})	Magnetic field for SFR laser (gauss)
NO	$v = 0$ to $v = 1$, $\Omega = 3/2$, $m = 3.5$	1887.63	2545
NO	$v = 0$ to $v = 1$, $\Omega = 1/2$, $m = 3.5$	1887.55	2605
H_2O	000 to 010 $5_{3,2}$ to $6_{4,3}$	1889.58	1742

We conducted the experiment by lofting the apparatus up to 28 km, using a balloon flown from the Balloon Facility of the National Center for Atmospheric Research at Palestine, Texas, on 19 October 1973. The experimental technique consisted of carrying out high-resolution spectroscopy of the air sampled locally. Both NO and H_2O have strong absorption line in the 5.3- to 5.4-μm range arising from the fundamental $v = 0$ to $v = 1$ band of NO and the fundamental 000 to 010 band of H_2O, respectively. The spin flip Raman (SFR) laser (*3*) provided the tunable laser radiation in this wavelength range. The tunability is achieved by changing the magnetic field since the output frequency, ω_s, of the SFR laser is given by the relation

$$\omega_s = \omega_o - g\mu B \tag{3}$$

where ω_s is the frequency of the pump laser (in the present case a CO laser), g is the g value of electrons in the InSb SFR laser sample, μ is the Bohr magneton, and B is the magnetic field. The CO pump laser was operating on the $P_{8\text{-}7}(17)$ transition (*4*) at 1893.52 cm^{-1}. This tunable source has been used in the past to carry out both high-resolution spectroscopy and terrestrial pollution detection (*3, 5*). The experimental apparatus consisted of the SFR laser as the source, an opto-acoustic (OA) cell, and a multiple reflection long-pass (LP) absorption cell (*6*) for detection of the amount of absorption caused by various species of interest. This technique has been demonstrated (*5*) to be capable of measuring a NO concentration of $\sim 1.5 \times 10^8$ molecule cm^{-3} corresponding to a volumetric mixing ratio (VMR) of ~ 0.2 part per billion (ppb) at an altitude of 28 km or a VMR of ~ 0.07 ppb at an altitude of 20 km). The data-gathering system consisted of lock-in amplifiers and a minicomputer (Data General Nova) for controlling the details of the experiment, for averaging the data over a predetermined number of scans of the magnetic field, and for transmitting the collected data down to ground periodically through telemetry channels. The entire experimental setup (*7*) was enclosed in a pressurized vessel. Air was continuously drawn into the absorption cells (OA cell and LP cell) at a slow rate so that it could be continuously analyzed as well as to make sure that there would be no accumulation of outgassed components, if any, during the flight. The gas-handling system was evacuated and closed off prior to flight, and was opened to let the outside air into the absorption cells only after the balloon had reached an altitude of ~ 25 km. This latter action was carried out to prevent any preloading of the gas-handling system with undesirable gaseous components as the balloon rose through the denser (and also wetter) atmosphere to its flight altitude.

The balloon was launched at 4:46 local time (C.D.T.), that is, at 9:46 U.T., on 19 October 1973. The balloon rose to the flight altitude at about 6:30 C.D.T. (11:30 U.T.), at which time the experimental apparatus as well as the control computer were turned on through ground command and data runs begun. A typical data run consisted of setting up the appropriate magnetic field scan to observe the NO (*8*) and H_2O (*9*) lines which are listed in Table 1 together with their identifications and the corresponding magnetic field values required to make the SFR laser frequency equal to the frequency of the absorption line (using the 1893.52-cm^{-1} line from the CO laser to pump the SFR laser). The two NO lines were observed in one scan, 16 such scans being typically averaged to constitute a NO run. The actual time required for each of such complete NO runs was ~ 16 minutes. The H_2O line was scanned by itself and was averaged over eight scans to constitute an H_2O run, which typically required 4 minutes. In all, 12 NO runs and 7 H_2O runs were obtained from 6:30 to 14:30 C.D.T., at which time the computer-controlled experiments were terminated because of a battery failure.

The visible sunrise at an altitude of 28 km is expected (*10*) to occur at 7:02 C.D.T. (12:02 U.T.), the ultraviolet sunrise being delayed (*10*) by ~ 30 to 90 minutes depending upon the ultraviolet wavelength from 3300 to 2000 Å. The results of NO run 2, taken between 6:55 and 7:27 C.D.T. are shown in Fig. 1A where we plot the output signal from the OA absorption cell (which signal is proportional to the absorption of the infrared radiation at a given frequency) as a function of the magnetic field determin-

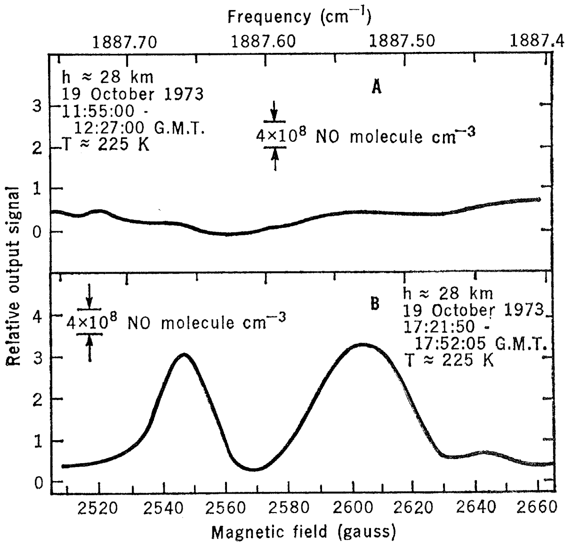

Fig. 1. (A) Relative output signal as a function of the SFR laser magnetic field for NO run 2, taken before ultraviolet sunrise. The NO absorption signals are expected to occur at magnetic fields of 2545 and 2605 gauss. Calibration in equivalent NO molecules per cubic centimeter is given. (B) Relative output signal as a function of the SFR laser magnetic field for NO run 14, taken after ultraviolet sunrise; NO absorption signals at magnetic fields of 2545 and 2605 gauss can be seen (see Table 1 for line identification). Calibration in equivalent NO molecules per cubic centimeter is given, indicating a NO concentration of $(2 \pm 0.15) \times 10^9$ molecule cm^{-3}.

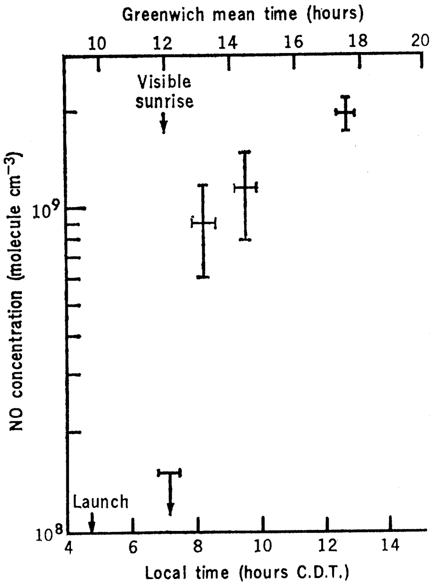

Fig. 2. Variation of the measured NO concentration as a function of time. Visible sunrise occurs at 7:02 C.D.T., and ultraviolet sunrise follows ~30 to 90 minutes later, depending on the ultraviolet wavelength.

ing the SFR laser frequency which is also given in Fig. 1A. The magnetic field scan covers the region of the two NO absorption lines at 1887.63 and 1887.55 cm^{-1}. These lines are expected to be seen, if the absorption from NO occurs, at magnetic fields of 2545 and 2605 gauss, respectively. The equivalent NO concentration calibration, for the gain settings used in this run, is also shown in Fig. 1A in molecules per cubic centimeter. It can be seen from this spectrum, taken during the visible sunrise but prior to the ultraviolet sunrise, that no discernible peaks from absorption caused by NO are visible at magnetic fields of 2545 and 2605 gauss. The system noise is such that we can assign an upper limit for the NO concentration of $\sim 1.5 \times 10^8$ molecule cm^{-3} in the absence of sunlight.

Figure 1B shows the results of NO run 14, taken between 12:22 and 12:52 C.D.T., which is substantially after the expected ultraviolet sunrise. The output signal in Fig. 1B shows two distinct peaks at magnetic field values which correspond to the SFR laser frequencies of 1887.63 and 1887.55 cm^{-1}. These frequencies, as we have seen above, correspond to the two NO absorption lines listed in Table 1. The NO concentration scale is also shown in Fig. 1B, there being no changes in gain settings from Fig. 1A to Fig. 1B. The measured NO concentration is $(2 \pm 0.15) \times 10^9$ molecule cm^{-3}. High-resolution spectroscopy carried out with a tunable SFR laser is an extremely powerful tool for the identification and quantitative measurement of the pollutants, as seen from the relative widths of the two absorption lines in Fig. 1B. The line at 2605 gauss which arises from absorption from the NO $\Omega = 1/2$ state is seen to be about twice as wide as the line at a magnetic field of 2545 gauss arising from the NO $\Omega = 3/2$ state. This is precisely what would be expected since the $\Omega = 1/2$ line is split as a result of Λ-doubing and actually consists of a doublet with a line separation of ~ 350 Mhz, that is, an equivalent field splitting of 5 to 5.5 gauss [as seen from the high-resolution spectroscopy of NO carried out at low pressures and reported in (*3*)]. The Doppler broadening is expected to be ~ 125 Mhz, and thus at low gas pressures the doublet arising from absorption due to the $\Omega = 1/2$ state of NO is well resolved. However, at the ambient pressure of ~ 15 to 20 torr (at the altitude of 28 km), the pressure-broadening of the two Λ-doubling split $\Omega = 1/2$ lines would be such as to merge them into one line of about twice the width of the single line arising from the $\Omega = 3/2$ state of NO. Thus we consider the identification of the two absorption lines as arising from NO and the corresponding determination of NO to be reliable.

To assess the variation of the NO concentration with the ultraviolet radiation from the sun, we have analyzed a number of NO runs taken during the time period between run 2 (Fig. 1A) and run 14 (Fig. 1B). Although the analysis is not yet complete, preliminary results for four of the analyzed runs are shown in Fig. 2, where we have plotted the measured NO concentration as a function of time (when the respective runs were taken). The horizontal bar for each of the data points corresponds to the time period during which the particular measurements were carried out. The effect of the expected sunrise is clearly seen. The results of run 2 show that, during the sunrise, a NO concentration of $\lesssim 1.5 \times 10^8$ molecule cm^{-3} (VMR $\lesssim 0.2$ ppb) is present. Approximately 60 minutes after the visible sunrise the measured NO concentration is $\sim 9.0 \times 10^8$ molecule cm^{-3} (VMR ~ 1.6 ppb), indicating clearly the effect of solar ultraviolet radiation; 75 minutes later, that is, ~ 135 minutes after the visible sunrise, the measured NO concentration has risen to $\sim 12 \times 10^8$ molecule cm^{-3} (VMR ~ 2.2 ppb). The ultraviolet sunrise at 28 km is expected to be complete ~ 90 minutes after the visible sunrise, that is, at about 8:30 C.D.T. Experimentally we see a small increase in the measured NO concentration beyond this time: the concentration of NO is $(20 \pm 1.5) \times 10^8$ molecule cm^{-3} (VMR ~ 3.8 ppb) about 5 hours after the visible sunrise. On the same balloon flight, instruments to monitor and measure various ultraviolet spectral regions were also carried. When the results of these experiments become available, we should be able to make a quantitative comparison between the temporal variation of NO concentration and the temporal variation of the ultraviolet radiation reaching the stratosphere.

A stratospheric constituent of minor interest in the present experiments is H_2O. The results of H_2O run 17, taken from 13:11 to 13:18 C.D.T., are shown in Fig. 3 where we again show the absorption signal from the OA cell as a function of the SFR laser magnetic field appropriate for the H_2O line as seen from Table 1. The H_2O concentration calibration is indicated in Fig. 3. The spectral trace in Fig. 3 is only ~ 4 to 5 gauss wide, corresponding to a frequency width of 250 to 300 Mhz. The linewidth of the H_2O

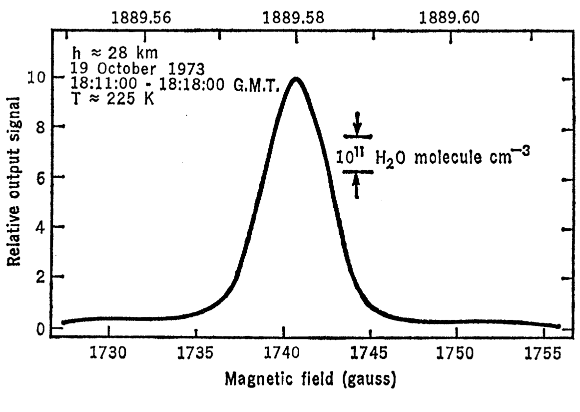

Fig. 3. Relative output signal as a function of the SFR laser magnetic field for H_2O run 17. The H_2O absorption line at 1742 gauss is seen (see Table 1 for line identification). Calibration in terms of equivalent H_2O molecules per cubic centimeter is given, indicating a measured H_2O concentration of $\sim 7.5 \times 10^{11}$ molecule cm^{-3}.

absorption, which includes Doppler broadening and collision broadening, is expected to have this width. The H_2O concentration is $\sim 7.5 \times 10^{11}$ molecule cm^{-3} [VMR $\sim$ 1.5 parts per million (ppm)], indicating a very dry stratosphere (*11*) at 28 km since the saturated H_2O concentration at the ambient temperature of 225 K is $\sim 1 \times 10^{15}$ molecule cm^{-3}. Data from H_2O runs at other times have yet to be analyzed (*7*).

In summary, we report a new and accurate technique for measuring and analyzing trace constituents in the stratosphere. Although thus far we have measured only NO and H_2O, the technique is applicable to real-time measurements of other constituents important in stratospheric chemistry. The measurements carried out as a function of time show the influence of sunlight, in addition to giving the first measurements of NO concentration at 28 km. The measured daytime value of $\sim 2 \times 10^9$ molecule cm^{-3} and the nighttime value of $\lesssim 1.5 \times 10^8$ molecule cm^{-3} may allow us for the first time to put some of the models of stratospheric chemistry and the O_3 cycle on a much more concrete footing. It is also important to investigate the variation of NO as the sun sets, thereby removing the NO generation source. The sunset measurements are eminently possible with this new technique and will show the recombination effects of NO and O_3 which are important in the O_3 cycle. These measurements, together with simultaneous measurements of O_3 concentrations are planned for the future.

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6. The path length for the OA cell was 10 cm, and that for the multiple reflection LP cell was 3 m. Details of the experimental setup as well as the calibration techniques will be discussed in a forthcoming report (*7*); also included will be a study of the effect of possible interference from other constituents on the NO and H_2O calibration. We have determined that, because of the extremely high resolution possible with the SFR laser source, such interference effects are smaller than the system noise. The shapes of the spectra obtained further allow us to rule out any and all interference effects.
7. The details of the experimental setup and data analysis will be presented elsewhere (C. K. N. Patel, E. G. Burkhardt, C. A. Lambert, in preparation).
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12. We would like to acknowledge the tremendous help given by V. K. Smith, F. Crutcher, R. Myers, and their colleagues (division 1255) at Sandia Laboratories without whose collaboration the experiment reported here could not have been carried out. Thanks are also due to Dr. G. L. Miller of Bell Telephone Laboratories for the design of the ultralow-noise preamplifiers used with the OA cell, to R. J. Kerl for assistance in the early parts of the experiments and in the construction of the OA cells, to J. H. Hasiak and C. Pace for assistance in the mechanical construction of the experiment, and to C. Yuen (Swarthmore College) who tested and calibrated the OA cells. In addition, we thank R. H. Rabiner (Data General Corporation) whose assistance with the minicomputer used in this experiment was indispensable.

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Acid Rain: A Serious Regional Environmental Problem

Abstract. *At present, acid rain or snow is falling on most of the northeastern United States. The annual acidity value averages about* pH *4, but values between* pH *2.1 and 5 have been recorded for individual storms. The acidity of precipitation in this region apparently increased about 20 years ago, and the increase may have been associated with the augmented use of natural gas and with the installation of particle-removal devices in tall smokestacks. Only some of the ecological and economic effects of this widespread introduction of strong acids into natural systems are known at present, but clearly they must be considered in proposals for new energy sources and in the development of air quality emission standards.*

As part of the Hubbard Brook Ecosystem Study, we have monitored the chemistry of precipitation in north-central New Hampshire for about 11 years (*1*) and have found surprising acidity (*2*). Normally water in the atmosphere in equilibrium with prevailing CO_2 pressures will produce a *p*H of about 5.7 (*3*), but much stronger acids have recently been observed in rain and snow in the northeastern United States, with *p*H values as low as 2.1. The presence of these acids is presumably related to air pollution (*2*).

Current measurements and the few scattered observations during the past 11 years show that precipitation falling in northeastern United States is significantly more acidic than elsewhere in the United States (*2, 4*). For example, the annual mean *p*H, based upon samples collected weekly during 1970–1971 and weighted proportionally to the amount of water and *p*H during each period of precipitation, was 4.03 at the Hubbard Brook Experimental Forest, New Hampshire; 3.98 at Ithaca, New York; 3.91 at Aurora, New York; and 4.02 at Geneva, New York. Measurements on individual rainstorms frequently showed values between *p*H 3 and 4 at all of these locations. Data from the National Center for Atmospheric Research included precipitation *p*H values as low as 2.1 in the northeastern United States during November 1964 (*4*). Summer rains are generally more acidic than winter precipitation (*5*).

The major cation is H^+, which accounts for 44 and 69 percent of the cations (milliequivalent basis) in the Ithaca and Hubbard Brook precipitation, respectively. Of the anions in Ithaca and Hubbard Brook precipitation, respectively, $SO_4{}^{2-}$ represents 59 and 62 percent, $NO_3{}^-$ contributes 21 and 23 percent, and Cl^- constitutes 20 and 14 percent.

Precipitation *p*H values from the northeastern United States are similar to those recorded over southern Sweden. More than 70 percent of the sulfur in the air in Sweden is thought to be anthropogenic, of which 77 percent has its source outside Sweden (*6*). The mean residence time for sulfur in the atmosphere is estimated to be 2 to 4 days (*7*). As a result, SO_2 may be transported more than 1000 km in this region before being deposited. Distant industralized regions, such as England and the Ruhr Valley, are thought to be major contributors to Sweden's acid rain (*8*). Moreover, Odén's data show a striking increase in precipitation acidity in northeastern Europe over the past two decades, with the H^+ concentration of rain in some parts of Scandinavia increasing more than 200-fold since 1956 (*9*).

We know of no long-term record of