

Reports

Free Radicals in the Stratosphere: A New Observational Technique

Abstract. A new approach to *in situ* observations of trace reactive species in the stratosphere is described. A balloon-borne system, floating 40 kilometers above the earth's surface, successfully lowered and then retracted a cluster of instruments a distance of 12 kilometers on a filament of Kevlar. This instrument cluster is capable of detecting gas-phase free radicals at the part-per-trillion level. The suspended instrument array has excellent stability and has been used to measure atomic oxygen concentrations in the stratosphere.

The photochemistry of stratospheric O_3 has received intense, interdisciplinary attention (1) ever since it was first realized, more than a decade ago, that global chemical changes in the lower atmosphere, amplified by homogeneous gas-phase catalysis in the stratosphere, are mechanistically linked to future changes in stratospheric O_3 . Concern has centered primarily on the catalytic effects of nitrogen (2) and chlorine compounds (3), which are photochemical by-products of N_2O oxidation and halogen-substituted hydrocarbon photodecomposition, respectively. Recently, however, realization of the chemical ramifications of global increases in CO_2 and CH_4 , with requisite effects on temperature and reactive hydrogen compounds, has broadened the scope of the problem considerably (4).

A need to forecast secular trends in the column concentration of O_3 has focused attention on developing an integrated understanding of global chemical cycles: biogeochemical, tropospheric, and stratospheric. Of the three, stratospheric photochemistry is by far the simplest, because many of the subtle interactions among biological, chemical, and physical processes are diminished in the stratosphere and because tropospheric removal processes restrict the spectrum of molecules that traverse the dynamically stable region separating the troposphere and stratosphere.

Even though the stratospheric photochemical system is potentially tractable, it is nevertheless characterized by approximately 200 elementary reactions, most of which involve free radicals present at the part-per-billion to part-per-trillion level. These radicals dictate the pathways and rates of chemical transformation within the stratosphere. Their

concentrations as a function of altitude, latitude, and time of day and their kinetics and photochemistry establish the mechanistic link between the introduction of stable molecules from the tropo-

sphere and the catalyzed conversion of O_3 to O_2 in the stratosphere.

Detection of these radicals in carefully selected sets holds the key to disentangling the chemical structure of the stratosphere. *In situ* studies can provide mechanistic information on free radical exchange reactions because concentration differences between adjoining atmospheric layers can be spatially resolved. In view of the exceedingly short time constants linking the free radicals chemically, an analysis of variance can be used to diagnose cause and effect. This approach depends upon the simultaneous detection of a complement of interrelated stratospheric free radicals. Such correlation measurements require detailed control over the dominant experimental variables, as well as repetitive observations carried out under "identical" conditions to test reproducibility.

Although earlier "snapshots" of the free radical concentrations provided first-order information on concentration regimes as a function of altitude, there

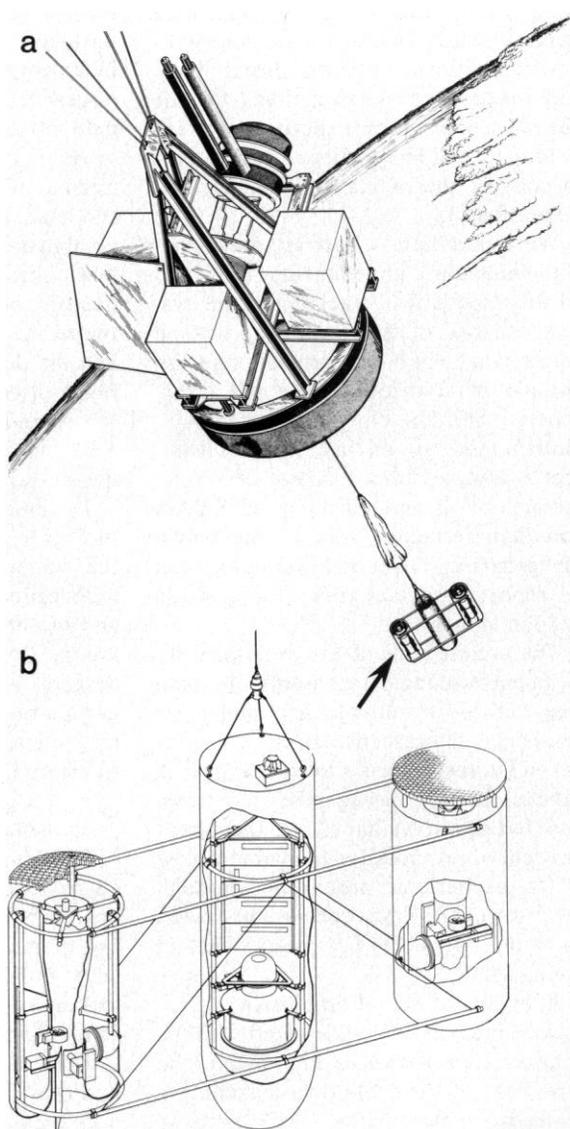


Fig. 1. Diagram of the reel-down system, showing the winching system and suspended payload. A helium-filled research balloon is used to lift the combination to any altitude up to 40 km, from which vertical scans of greater than 10 km are executed. (a) Geometry of the experiment at float altitude in the docked position. (b) Schematic of the suspended instrument array indicating the optical system and flow system used to obtain the *in situ* free radical observations.

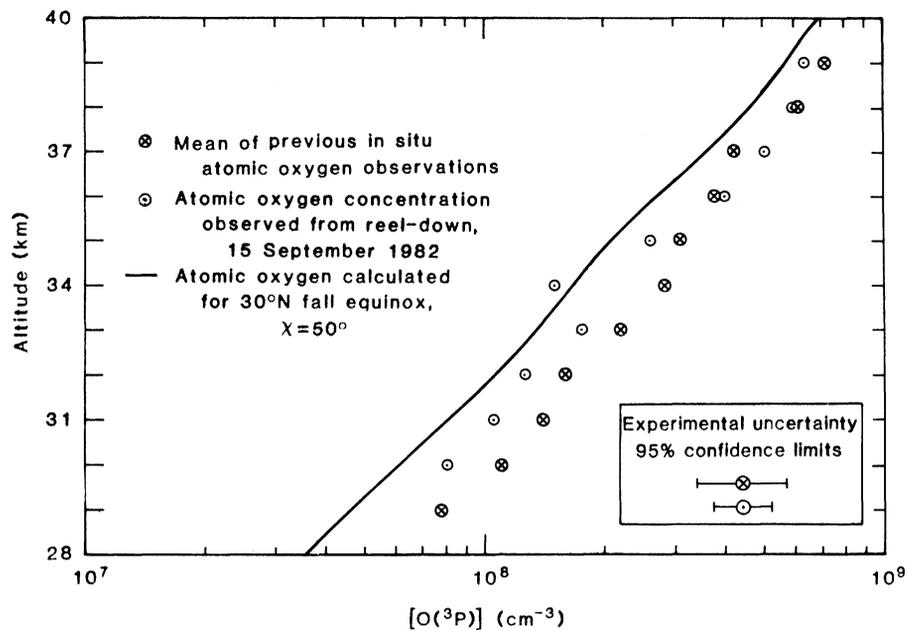


Fig. 2. Comparison between the $O(^3P)$ concentration profile obtained from the reel-down experiment, the mean of earlier in situ observations of $O(^3P)$, and the most recent calculations of atomic oxygen for the conditions corresponding to those of the reel-down observations.

were several drawbacks. Problems centered primarily on inadequate control of flow conditions, platform instabilities, and reactant gas mixing times for the chemical conversion experiments (such as for ClO and HO_2 , where NO was used to convert the radicals to Cl and OH , respectively).

We report here a new approach that eliminates these impediments. Designated the "reel-down" technique, the system consists of (i) a winching system borne by a helium research balloon to an altitude of ≤ 40 km (where the atmospheric pressure is approximately 2 mmHg) and (ii) an instrument cluster that is lowered on a filament of Kevlar (diameter, 1.8 mm) a distance of ~ 10 km and then retracted back to the winch platform (Fig. 1). Vertical soundings can be repeated several times for a single balloon launch (5).

The architecture of the individual instruments used to detect atoms and small free radicals by atomic and molecular resonance fluorescence or by laser-induced fluorescence is shown in Fig. 1. A nacelle, hollow through the core from nose to tail with an impeller in the anterior section, provides for the laminar flow of stratospheric air around and through the instrument. Trace species are detected at one (or more) optical axes within the nacelle.

A major subset of important stratospheric radicals can be detected with the configuration shown in Fig. 1. For the first flight of the reel-down system, we selected atomic oxygen, $O(^3P)$, because

it is a reactant in the rate-limiting step of virtually every important catalytic cycle in stratospheric O_3 removal and it is the easiest free radical experiment to execute in the stratosphere.

The instrument calibration (6) is carried out in the laboratory, with the detector head and lamp module-photodiode combination installed in a fast-flow system. This procedure provides a direct measure of the proportionality factor between the atomic oxygen concentration and the detector count rate for a broad range of conditions. The fast-flow reactor reproduces the pressure and flow velocity conditions encountered during the stratospheric observations.

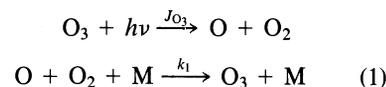
The first flight of the reel-down system took place on 15 September 1982 from the National Scientific Balloon Facility in Palestine, Texas. The balloon, winch, and suspended payload ascended to ~ 40 km in 3 hours and 20 minutes. The descent of the suspended instrument cluster was initiated by the release of a magnetically controlled brake, which transferred the control of the descent rate to a generator in series with resistively heated radiation panels.

The dynamic behavior of the suspended payload and winching platform was documented in real time by a combination of accelerometers, gyroscopes, load cells, solar sensors, and a downward-looking video monitor on the winch platform. Longitudinal and azimuthal motions were virtually absent; an acceleration of < 3 percent of g with a period of ~ 15 seconds at full extension and one

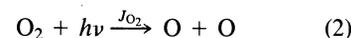
full rotation on descent were recorded. No pendulum motion and no measurable body-centered perturbation developed during any phase of the descent or ascent.

Figure 2 presents the atomic oxygen data obtained on the first flight of the system together with the results of earlier rapid-descent, parachute-controlled measurements (1) and the most recent photochemical model calculations, which incorporate vertical transport with a comprehensive reaction set including recent developments in the kinetics and photochemistry of oxygen, hydrogen, nitrogen, and halogen compounds (7). To a first approximation, both the gradient and absolute concentration of the in situ data substantiate the mechanism used in the model for oxygen atom production and destruction. Clear differences, however, become important when the results are critically appraised at the level required if we are to use the model with confidence to predict the behavior of the stratosphere into the next century.

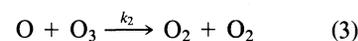
Atomic oxygen is photochemically coupled to O_3 by



which establishes a steady state between $O(^3P)$ and O_3 on the time scale of seconds throughout the stratosphere. The sum of atomic oxygen and O_3 ; $[O_x] = [O(^3P)] + [O_3]$, is produced by the direct photolysis of O_2 by radiation shortward of 242 nm,



and is destroyed by recombination,



In the middle and upper stratosphere, Eq. 3 is accelerated by a series of two-step, homogeneous, gas-phase catalytic cycles involving hydrogen, nitrogen, and chlorine radicals of the form $X + O_3 \rightarrow XO + O_2$ and $XO + O \rightarrow X + O_2$, where $X \equiv OH, NO,$ and Cl , respectively. Since atomic oxygen is involved in each of the major rate-limiting steps, detailed knowledge of its concentration is required to test our understanding of O_x destruction rates.

The mean of the published data lies above the calculated concentration by ~ 50 percent between 29 and 35 km and then slowly converges up to 40 km (Fig. 2). Results obtained from the reel-down experiment follow the same trend but fall ~ 25 percent above the calculated distribution up to 35 km.

A recent and rather thorough analysis of mid-latitude O_3 observations, based

on the use of available balloon, rocket, and satellite data, led to the conclusion that the observed O₃ concentrations at mid-latitudes substantiate calculated densities up to 30 km but monotonically diverge above 35 km such that observed O₃ concentrations (from a broad class of experiments) fall 30 to 50 percent above calculated concentrations between 40 and 50 km (8).

Taken together, these results imply a serious discrepancy because (i) the relevant cross sections and reaction rate constants in Eq. 1 have been carefully studied and, except for the O₂ photolysis rate, J_{O_2} , are known to ± 10 percent or better; (ii) recent in situ measurements defining the penetration of solar radiation into the middle stratosphere have narrowed the uncertainty in J_{O_2} (9); and (iii) O₃ can be measured to an accuracy of ± 5 percent at these altitudes. If we hope to be able to predict changes in O₃ in the next century to an accuracy of 10 percent, we must be able to "predict" its present concentration with considerably better accuracy than that cited above, particularly in the photochemically controlled regime above 30 km.

With the experimental control and repeatability afforded by the reel-down system, we can now systematically examine each of the chlorine, nitrogen, and hydrogen rate-limiting steps in the catalytic destruction of O₃. An analysis of variance between O₃ and the rate-limiting radicals as well as the diurnal, latitudinal, and seasonal trends can be used to establish cause-and-effect relations within and between the chemical cycles, thus providing a significantly more rigorous test of the dominant catalytic mechanisms.

Note added in proof: The reel-down system was launched for the second time on 14 September 1984 from Palestine, Texas. Two vertical scans of 8 km each were executed, each exhibiting dynamic stability. That flight began a series of experiments investigating the free chlorine radical, ClO, which limits the rate of chlorine-catalyzed recombination of O₃ and atomic oxygen to form O₂.

J. G. ANDERSON
N. L. HAZEN
B. E. MCLAREN
S. P. ROWE
C. M. SCHILLER
M. J. SCHWAB
L. SOLOMON
E. E. THOMPSON
E. M. WEINSTOCK

Department of Chemistry and
Center for Earth and Planetary
Physics, Harvard University,
Cambridge, Massachusetts 02138

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The Fajada Butte Solar Marker: A Reevaluation

Abstract. *Evaluation of the Fajada Butte solar marker in Chaco Canyon, New Mexico, on the basis of its ethnographic context and usefulness for confirmatory and anticipatory solar observations indicates that the site does not function as an accurate solar calendar (accurate in the context of the historic Puebloan culture). The site most likely served as a sun shrine rather than as a calendrical observing station. The interpretation of the site as marking the northern declinations of the lunar 18.6-year cycle is not supported by the ethnographic evidence nor can the site be used to anticipate accurately the year of the standstill.*

The interpretation of Fajada Butte solar marker as a "unique solar marking construct" (1) has generated a controversy about this site in Chaco Canyon, New Mexico (2). I here assess the functions of the site in the context of the historic Pueblo culture. Arguing by analogy, I assume that this astronomical tradition holds in its general character back to prehistoric times and the practices of the Anasazi (3) who needed to keep a ritual calendar 1100 years ago.

The common elements (4) in calendrical observations of the sun among the historic Pueblos are: (i) a special religious official, the Sun Priest, is invested with the responsibility of watching the sun; (ii) observations take place, often daily at sunrise, from within or close to the pueblo; (iii) the most common observational technique involves the use of horizon markers; (iv) the most important ceremonial times of year are the solstices, especially the winter solstice; and (v) the Sun Priest must be able to announce the coming of ritual dates and does so by anticipatory observations.

The daily rate at which the sun travels along its horizon arc varies during the year. At the solstices, the sun has no noticeable motion. To determine the solstices accurately requires observations

before the solstice, while the sun is moving observable amounts along the horizon. Using only the eye and horizon features, I estimate that the minimum detectable solar motion is 4 arcmin under the best conditions, which occur a week before the solstice. In practice, the limit may be 8 arcmin. [The precision obtained at Hopi Walpi for the winter solstice ceremony was 10 arcmin (5)]. A Sun Priest can then tally days to predict the solstice (6). Puebloan precision for solstice prediction seems to be within 1 day in principle and no more than 2 days in practice (4).

This concept of anticipation can be applied to the three rock slabs and petroglyphs that make up the Fajada Butte solar marker, which rests on the east side very near the top of the butte. To reach the site, one climbs the talus slope around the butte and up through a narrow rock chimney, passing enroute two archeological sites, 29 SJ 296 and 29 SJ 297. Site 297 lies closest to the solar marker; it has Mesa Verdán cultural characteristics. The National Park Service survey of site 297 in 1972 included the two petroglyphs that make up the "solstice marker" or "sun dagger" site as well. (It has since been designated 29 SJ 2387). One petroglyph is a spiral some