

Journal of Atmospheric and Solar-Terrestrial Physics, Vol. 59, No. 17, pp. 2111-2157, 1997 C Published by Elsevier Science Ltd Printed in Great Britain PII: S1364-6826(97)00047-3 1364-6826/97 \$17.00+0.00

Review Paper

Actinic radiation in the terrestrial atmosphere*

R. R. Meier,¹† G. P. Anderson,² C. A. Cantrell,³ L. A. Hall,² J. Lean,¹ K. Minschwaner,⁴ R. E. Shetter,³ E. P. Shettle⁵ and K. Stamnes⁶

¹E. O. Hulburt Center for Space Research, Naval Research Laboratory, DC 20375-5352, Washington, U.S.A.; ²Optical Physics Division, Phillips Laboratory, Hanscom Air Force Base, MA 01731, Bedford, U.S.A.; ³The National Center for Atmospheric Research, Atmospheric Chemistry Division, PO Box 3000 CO 80307, Boulder, U.S.A.; ⁴Department of Physics, New Mexico Institute of Mining and Technology, NM 87801, Socorro, U.S.A.; ⁵Remote Sensing Division, Naval Research Laboratory, Washington, DC 20375-5351, U.S.A.; 'Geophysical Institute, University of Alaska Fairbanks, 99775-0800, Fairbanks, Alaska

(Received 19 March 1997; accepted 16 June 1997)

Abstract—Actinic radiation originating from the Sun drives the photochemistry of the Earth's atmosphere. Surprisingly few measurements have been made of this terrestrial forcing agent which is responsible for such anthropogenically critical issues as the production and loss of atmospheric ozone. This paper describes the status of our knowledge of actinic radiation throughout the middle and lower atmosphere with the goal of summarizing progress to date and identifying future requirements. The focus is mainly on radiation, with wavelengths between 170 and 400 nm, but does include other UV radiation which is deposited in the middle atmosphere. Topics are covered in their natural order, beginning with the solar spectral irradiance above the atmosphere, its transmission through the atmosphere, the component which is multiply scattered, UV radiation reaching the biosphere, and direct measurements of photolysis rates. Concluding remarks include recommendations for additional research. Published by Elsevier Science Ltd

1. INTRODUCTION

Nearly all of the radiative energy entering the Earth's atmosphere comes from the Sun. Some 31% of this energy is scattered back into space by air, aerosols, clouds, and surface reflection; another 43% is absorbed at the Earth's surface, and 26% is absorbed by its atmosphere (Goody and Yung (1989)). Since the Sun's output can be characterized approximately as that of a 5770 K black body, the bulk of the solar radiative energy resides in the visible and infrared spectral regimes; only 7.5% of solar radiation is present at ultraviolet (UV) wavelengths below 400 nm, and about 1% resides below 300 nm, Nevertheless, this short wavelength UV radiation is responsible for most tropospheric and stratospheric photolysis. It is

also the most highly variable portion of the direct and diffuse (scattered) radiation in the terrestrial environment. Consequently, this paper on actinic radiation focuses on the spectral regime primarily between about 170 and 400 nm, but does include other spectral regions for which radiative energy is deposited in the middle and lower atmosphere. Not addressed are radiation issues relevant to the upper atmosphere and ionosphere (Meier (1991)). The term "actinic" pertains to radiation capable of initiating photochemical reactions. Because of the particularly strong action on photochemical processes by radiation in the ultraviolet spectral region, the term has come to be almost synonymous with UV radiation (Huske (1959)). This is the context used throughout the paper.

The natural progression of actinic radiation, from its solar origin, through transmission and scattering within the Earth's atmosphere (and surface), to the production of chemically active species via photolysis, serves as a framework for this paper. Solar radiation in the spectral interval from 120 to 310 nm is deposited in the middle atmosphere (see Fig. 1), providing its prime energy source both in the form of attenuated

^{*}We dedicate this paper to the memory of Baron Marcel Nicolet, whose research for more than a half century established the cornerstone for the field of actinic radiation.

[†]Author to whom the correspondence should be addressed. Tel. 202-767-2773, fax 202-404-8090, e-mail meier @uap.nrl.navy.mil



Fig. 1. Left panel: altitude of unit optical depth in Earth's atmosphere. Right panel: temperature profile.

sunlight, and diffuse, multiply scattered radiation. Solar ultraviolet radiation initiates the chemical, dynamical and radiative processes that control the physical state of the middle atmosphere, and thus the ozone layer that resides there. As well as producing atmospheric ozone via photodissociation of molecular oxygen, ultraviolet radiation produces many reactive species such as Cl and OH that destroy ozone catalytically. Empirical evidence suggests a positive correlation between the solar UV irradiance and levels of ozone in the upper stratosphere and mesosphere (e.g., Summers et al. (1990) and Hood et al. (1991); Hood and McCormack (1992); Reinsel et al. (1994)). Radiation at wavelengths longward of 310 nm penetrates to the troposphere and the Earth's surface. Nearultraviolet radiation from 300 to 400 nm dissociates a variety of tropospheric species. Visible radiation and infrared radiation with wavelength less than 1.08 micron dissociate ozone. Absorption by other molecules, while crucial to the photochemistry, provides little discernible impact on the attenuated ultraviolet and visible solar irradiance, and therefore is not addressed herein. The UV wavelength bands of biological relevance are usually characterized by three groups: UV-C (<280 nm), UV-B (280-320 nm), and UV-A (320-400 nm).

Accurate and precise knowledge of actinic radiation is a critical ingredient for understanding the state of the terrestrial atmosphere and its changes on all time scales. The number of actual measurements of attenuated sunlight and diffuse radiation is surprisingly small. As a result, quantitative descriptions of atmospheric photochemistry rely on models, algorithms or, in the case of the direct solar irradiance, proxies. In many instances, the accuracies of the radiation models have not been verified experimentally. A recurring theme throughout the paper is the need for additional measurements for model development and validation.

The paper begins with an assessment of the current state of knowledge of the solar UV irradiance outside the atmosphere. Next is a review of the various processes by which radiation is attenuated through the atmosphere, followed by an evaluation of the diffuse radiation which results from Rayleigh, aerosol, cloud, and surface scattering. Radiation in the biosphere is then reviewed. The final section deals with *in situ* measurements of photolysis rates, which provide not only direct information on the production of key species, but also stringent tests for extinction and scattering models.

1.1. Some definitions

It is useful to consider a few basic concepts of actinic radiation and definitions which will be used throughout this paper. Firstly, it should be recognized that the term "actinic flux" as used here (photon $\text{cm}^{-2} \text{ s}^{-1}$ nm⁻¹) is not equivalent to "irradiance", which has the same units. Irradiance is the energy flow incident on a flat, usually horizontal surface, where the radiance (photon cm⁻² s⁻¹ sr⁻¹ nm⁻¹) is weighted by the cosine of the angle of incidence to the surface. Actinic flux is equivalent to "spherical flux", which is defined as the integral of the radiance over all directions (4π steradian) without a cosine factor. Additional discussions of these definitions are given by Nader and White (1967); Shettle (1972); Hänel *et al.* (1982); Hänel (1984); Madronich (1987a).

The actinic flux F (photon cm⁻² s⁻¹ nm⁻¹) consists of two terms:

$$F(\lambda, z) = F_s(\lambda, z) + F_d(\lambda, z) \tag{1}$$

The first term represents the contribution of sunlight. Since the solar radiance is essentially unidirectional, its integral over direction is trivial and the solar component of the actinic flux equals the attenuated solar irradiance normal to the beam:

$$F_s(\lambda, z) = F_s(\lambda, \infty) \operatorname{T}(\tau(\lambda, z, \theta_o))$$
(2)

where the first factor in Equation 2, F_s , is the solar irradiance above the atmosphere, and the second factor, T, is the atmospheric transmittance (discussed in Section 3.1), which depends exponentially on the total slant path extinction (absorption plus scattering) optical depth between the Sun and the altitude of interest. The optical depth τ at wavelength λ , for absorbing or scattering species between altitude z and the Sun is defined as the integral of the product of the cross section, σ , for the attenuating process along the absorbing path, s, to the Sun, and the concentration of species, ρ :

$$\tau = \sum \int \sigma(z) \rho(z) ds(\theta_o) \quad . \tag{3}$$

The sum in Equation 3 is over all relevant absorbers and scatterers. The solar zenith angle, θ_0 , has been explicitly included in s to emphasize that τ is the slant optical depth rather than the *vertical* optical depth which refers specifically to the integral along the vertical path, dz. In the limit of a plane parallel atmosphere, the slant path ds = dz/cos(θ_0). Figure 1 displays the altitude where $\tau = 1$ for molecular absorption.

The second term in Equation 1 is the diffuse component of the actinic flux,

$$F_d(\lambda, z) = \int I(\Omega, \lambda, z) d\Omega \tag{4}$$

The diffuse radiance I (photon cm⁻² s⁻¹ nm⁻¹ sr⁻¹) is due to atmospheric and surface scattering.

Atmospheric radiation can photolyze a molecular species AB:

$$AB+hv \rightarrow A+B$$
.

The first order rate coefficient of this process is the photolysis frequency J (dissociation s⁻¹ molecule⁻¹). While J is sometimes called the "photolysis rate", the product of J times the number density of species AB is more properly the photolysis rate and that is the definition we use in this paper. For an atmospheric species i at altitude z, J can be calculated by:

$$J_i(z) = \int \sigma_i(\lambda, T(z)) \,\phi(\lambda, T(z)) \,F(\lambda, z) d\lambda \,, \tag{5}$$

where σ_i is the photodissociation cross section, T is the temperature at altitude z, ϕ is the quantum yield of the particular photolysis channel, and λ is wavelength.

2. SOLAR SPECTRAL IRRADIANCE

Unattenuated solar irradiance, $F_s(\lambda, \infty)$, varies on all time scales measured thus far. Daily modulations are associated with the Sun's 27-day rotation on its axis and are superimposed on 11-year cycles imposed by altered magnetic activity levels. Figure 2 illustrates the solar spectral irradiance and its variability during recent 11-year activity cycles, estimated from spacebased measurements during the past 17 years. Variations in the near-ultraviolet, visible and infrared spectral regions associated with solar activity are thought to be a few tenths percent. The ultraviolet spectral irradiance at shorter wavelengths varies considerably more during the 11-year cycle, by 50% to 100% at hydrogen (H I) Lyman α (121.6 nm) and by 5% to 10% at 200 nm. Larger solar irradiance variations are suspected over longer time scales as yet unsampled by the available space-based radiometry and possibly arising from physical mechanisms different from, or in addition to, those responsible for the 27-day and 11-year cycles. Because solar ultraviolet irradiance variability modifies the concentration of atmospheric ozone via changes in its source and sink mechanisms, reliable determination of anthropogenic ozone changes requires that this influence be properly monitored, understood, and predicted (WMO (1988); National Research Council (1994)).

2.1. Status of solar spectral irradiance measurements

Despite a database that spans more than two 11year solar cycles, it has proven difficult to establish the true absolute solar spectral irradiance and the amplitude of its variability (see reviews by Lean (1987), Lean (1991)). This is because the measurements composing the database have been made intermittently by different instruments lacking adequate cross calibration and in-flight calibration monitoring and they have uncertainties that exceed the amplitude



Fig. 2. Solar spectral irradiance above the atmosphere (left ordinate) and amplitude of 11 yr cycle variability (right ordinate). The dotted line indicates the solar irradiance at the Earth's surface.

of the irradiance variability. This is especially true for the spectral irradiance at wavelengths longward of 400 nm where the uncertainties of current measurement techniques (a few percent, at best, e.g., Nicolet (1989)) far exceed the expected solar variability (a few tenths percent, at most). Best characterized thus far is the ultraviolet portion of the solar spectrum where the measurement uncertainties and solar variability are comparable (up to tens of percent).

A suite of instruments has measured the ultraviolet spectral irradiance during the past 17 years. Included are the Solar Backscatter Ultraviolet (SBUV) - type instruments on Nimbus-7 and subsequent NOAA operational satellites (Schlesinger and Cebula (1992); Viereck et al. (1996)), the solar spectrometer onboard the Solar Mesosphere Explorer (Rottman (1988)), a few rocket and Space Shuttle missions (e.g., the Solar Spectrometer, SOLSPEC, and the Solar Ultraviolet Spectral Irradiance Monitor, SUSIM); (Cebula et al. (1996)), and most recently the SUSIM and SOLar STellar Irradiance Comparison Experiment (SOL-STICE) onboard the Upper Atmosphere Research Satellite (UARS) (Woods et al. (1996); Dessler et al. (1998)). Figure 3 illustrates the extant solar irradiance database at two ultraviolet wavelengths. Comparisons of measurements made prior to the launch of the UARS indicate uncertainties in absolute irradiance values of $\pm 10\%$ to $\pm 20\%$ in the wavelength interval 210 to 300 nm, $\pm 20\%$ to $\pm 30\%$ at 175 to 210 nm

and \pm 50% from 110 to 175 nm (Lean (1987); Nicolet (1989)). Very few measurements have been made of the spectral irradiance at longer visible and infrared wavelengths; agreement between those extant data is at best of the order of a few percent (Nicolet (1989)).

Agreement is better among measurements made during the UARS time frame. The present generation of solar ultraviolet spectral irradiance monitors that commenced measurements near the peak of solar cycle 22 of the spectral interval 120 to 400 nm have improved accuracies as a result of comprehensive preflight instrument characterization and calibrations, directly traceable to irradiance standards maintained by the National Institute of Standards and Technology (NIST). Comparisons on two selected days indicate agreement of 1 nm spectra to within $\pm 5\%$ among the SSBUV, SOLSTICE and SUSIM in the spectral region 220 to 360 nm with somewhat larger differences ($\pm 10\%$) at shorter wavelengths (Cebula et al. (1991); Woods et al. (1996)). This is probably the best agreement that can be expected using current absolute radiometric calibration techniques, since the uncertainties of individual measurements traceable to radiometric irradiance standards are of this order (Kostkowski et al. (1986)). New calibration techniques will be needed for further improvement of measurement accuracies for solar monitoring during the twenty-first century.

Uncertainties in the UV spectral irradiance



Fig. 3. Solar 10.7 cm radio flux (panel a), solar H I Lyman α (panel b) and solar irradiance at 205 nm (panel c). Single point measurements are given by the symbols (see Figure 21 of Lean (1991) for identification of individual measurements); satellite observations are as indicated. An instrumental effect of the SBUV diffuser degradation was not entirely removed from the data.

measurements limit the knowledge of solar cycle spectral irradiance variability amplitudes especially prior to solar cycle 22. The presently operating solar irradiance monitors onboard the UARS promise to provide adequate experimental determination of the ultraviolet spectral irradiance variability in solar cycle 22 at wavelengths from 120 to 250 nm; observations now exist during the entire declining phase of solar cycle 22 and into the present solar activity minimum. Even though the absolute uncertainties of the measurements are of the order of the expected variability amplitudes, the instruments have superior long term precision because of provisions for in-flight calibration monitoring by comparison with either onboard ultraviolet irradiance sources or bright UV stars. The long term precision goal of UARS measurements is $\pm 1\%$ but even this level of uncertainty exceeds the variability of the spectral irradiance at wavelengths longward of 300 nm.

The current solar monitoring program does not include provision for high resolution ultraviolet spectral irradiance data - the existing instruments have spectral resolutions no better than 0.1 nm and daily averaged values are reported only with 1 nm spectral resolution. Spectral irradiance data with higher resolution are particularly important in the region 170 to 240 nm because of the complicated structure of the O₂ Schumann-Runge bands which absorb the solar radiation (Minschwaner et al. (1993a)) which itself is a complex mix of structured features (Kurucz (1991)). Higher resolution solar spectral data are available in the region 200 to 300 nm from a few balloon observations (at 0.01 nm resolution) during solar cycle 21 (Hall and Anderson (1984); see Section 3.3) and more recently in the region 240 to 790 nm from the GOME instrument (at 0.2 to 0.4 nm resolution) on the European Remote Sensing Satellite (ERS-2) (Weber et al. (1996)). Additional observations of the solar spectral irradiance at high resolution have been made of selected portions of the solar disk, for the purpose of probing the solar atmosphere (e.g., Kjeldseth Moe and Milone (1978)). From these measurements, it may be possible to improve current knowledge of the full disk solar irradiance needed for terrestrial studies, albeit with larger uncertainties than required. Solar ultraviolet spectral irradiance measurements with spectral resolution better than 0.01 nm were proposed as part of the SOLSTICE measurements on the Earth Observing System (EOS), but eliminated as a result of the reduction in scope of the EOS program.

2.2. Current knowledge of short and long term variability amplitudes

Measurements made during the past decade and a half by the SBUV and SME solar radiometers (Rottman (1988); Cebula et al. (1992a)) were able to characterize irradiance variations over the short time scales of the Sun's 27-day rotational modulation (primarily in the spectral region 170 to 250 nm and at H I Lyman α). Recent analysis of the UARS data augment and extend these earlier characterizations over the entire wavelength range form 120 to 400 nm (Lean et al. (1992a, 1998a)). Reliable knowledge of solar irradiance variability over time scales of days and months is attainable because the solar variations are typically large compared with the instrument degradation over these relatively short time periods. During times of high solar activity the rotational modulation of solar ultraviolet irradiance can approach 50% of the 11-year cycle amplitude. Solar UV emissions display very uniform temporal structure in the spectral range 120 to 250 nm (Donnelly (1988)); irradiance increases and decreases at different wavelengths within this spectral range closely track each other. But the amplitudes of the variations generally decrease with increasing wavelength (e.g., Lean (1987)).

The origin of the rotational modulation of solar ultraviolet spectral irradiance is relatively well understood. The variations at wavelengths less than 250 nm arise from the inhomogeneous distribution of bright active regions in the solar atmosphere that rotate across the solar disk projected in the Earth direction. Active region growth, evolution and decay cause additional modulation (Lean (1987)). Variability models that calculate the solar spectral irradiance rotational modulation from ground based observations of magnetic phenomena - such as identified in Ca K solar images - confirm that the biggest, brightest active regions are indeed the prime variability source of the UV regime over short time scales. Variations at wavelengths longward of 250 nm also occur in response to bright active regions, but are further modulated by the presence on the solar disk of dark sunspots whose effects increase toward longer wavelengths (Lean et al. (1998a, 1998b)).

Determining solar 11-year cycle variability amplitudes directly from observations is more difficult because of inadequate long term precision and absolute accuracies of the historical database. Figure 4 illustrates 11 year irradiance cycle amplitudes typical of solar cycles 21 and 22. Solar emission and absorption lines are seen in Fig. 4 to vary more than the underlying continuum emission. A distinct decrease in variability with increasing wavelength is evident at the Al I ionization edge at 207 nm. This coincides roughly with the change from ozone production to ozone destruction via, respectively O_2 Schumann-Runge Band photodissociation and O_3 Hartley band absorption.

At wavelengths longward of 200 nm the variability estimates in Fig. 4 were obtained primarily from empirical variability models that utilize correlations between the better-known rotational modulation and suitable proxies for solar variability (Cebula et al. (1992b); Lean et al. (1992a, 1998a)); DeLand and Cebula (1993)). Typical proxies are ground-based measurements of radio or optical emissions which vary with solar activity; examples and applications of these are described below. Once the connection between the irradiance and proxy variations is established over rotational time scales, the solar cycle amplitude is inferred from the long term proxy variations. The cycle variability amplitudes in Fig. 4 agree with the SOLSTICE and SUSIM observations to within their $\pm 1\%$ precision uncertainties. Note that at wavelength longer than 300 nm this imprecision significantly exceeds the estimated irradiance cycle.

Questions remain about the amplitudes of 11-year solar spectral irradiance variations both from observational and modelling perspectives. Implicit in the current modelling approach is the assumption that the physical origins of the short and long term variations are similar (i.e., the evolution of magnetic features) and that the chosen proxies reflect the partitioning of both short and long term variability and facular and sunspot influences that actually occur. Chandra et al. (1995) demonstrate that this is indeed true for faculardominated radiation near 200 nm but not necessarily at Lyman α . In the latter case, the proxy variability models fail to account for all of the variance in the observational database and there is some indication that these differences are not entirely of instrumental origin (Hoegy et al. (1993); Woods and Rottman (1997)). This implies that the proxy variability models lack an additional - as yet unidentified - solar variability mechanism. On the other hand the instrumental components of these differences remain to be adequately quantified.

Physical origins of the solar cycle (and longer term) variations are not as well established as for the rotational modulation. A variability source in addition to the brightest, biggest active regions appears to control solar cycle variability (Foukal and Lean (1988); Lean (1988, 1998b)). This additional variability component is likely of magnetic origin, thought to be the smaller scale, diffuse network surrounding the large active regions, but other mechanisms are also speculated (Kuhn *et al.* (1988)). As



Fig. 4. Amplitude of solar ultraviolet spectral irradiance variation estimated for solar cycle 22.

such, it is this more obscure, poorly understood variability component that is of most interest for solar irradiance variations on global change time scales.

Solar radiative output variations are suspected on longer time scales and with larger amplitudes than for the 11-year activity cycle. Comparisons of current solar activity levels with the range of activity seen in Sun-like stars indicates that the contemporary Sun is typical of the one-third most active of these stars (White et al. (1992)). In particular, non-cycling Sunlike stars (i.e., those stars which do not exhibit the equivalent of the Sun's 11-year cycle) have activity levels below the minima of the cycling stars (Baliunas and Jastrow (1990)). This has led to speculation that solar radiative output may have decreased relative to even the lowest levels of the contemporary Sun during the Maunder Minimum, a period from 1645 to 1715 when evidence for solar activity disappeared from the solar disk for long periods. Reductions of as much as twice the 11-year cycle amplitudes have been estimated (Lean et al. (1992b, 1995a, 1995b)).

2.3. Proxy indicators of solar ultraviolet spectral irradiance variations

In lieu of a reliable continuous database of solar spectral irradiance, frequent use is made of surrogates for these parameters. Solar activity proxies have been used extensively to interpret the observational irradiance database and to infer irradiance variability amplitudes (as described in the previous section), as well as for investigating temporal variability of terrestrial parameters. The proxy chosen most often by the aeronomy community is the 10.7 cm radio flux (e.g., Fig. 3). In particular, the 10.7 cm flux has recently been used to parameterize the solar forcing of the total ozone record in order to extract anthropogenic trends (Stolarski *et al.* (1991); Hood *et al.* (1993); Hood and McCormack (1992); Reinsel *et al.* (1994)).

Statistical comparisons between the solar ultraviolet irradiance variations and various solar activity proxies have demonstrated clearly that the 10.7 cm radio flux is not the preferred proxy (Donnelly *et al.* (1985); Lean (1987); White *et al.* (1990)). The ratio of the solar cycle to solar rotational modulation seen in 10.7 cm emission is significantly less than in the UV irradiances, notably H I Lyman α : i.e., more of the 10.7 cm overall variance occurs at the shorter time scales. As well, the temporal structure of the rotation modulation is different in the 10.7 cm flux because of the contribution of a bright sunspot-related component not seen in the ultraviolet irradiance variations (Donnelly *et al.* (1992)).

Superior proxies do exist. Physically, the proxy expected to vary most like the ultraviolet irradiances is the solar Ca II K index, which relates the core emission of the solar Fraunhofer line at 393 nm to the underlying continuum emission. As well as influencing the ultraviolet radiation, the presence of bright active regions on the solar disk modifies the Ca II K flux. Ca K core emission (formed in the solar chromosphere) is considerably more sensitive to magnetic activity than are the wings (formed lower, in the solar photosphere) so that the ratio of the core to wing emission provides



Fig. 5. Comparison of two surrogates for H I Lyman α irradiance variations, the 10.7 cm flux (upper left panel) and the He I 1083 nm equivalent width, EW (on the right). The top panels indicate that the H I Lyman α flux variations are more highly correlated with the He EW than with the 10.7 cm flux. Thus, the He EW is a superior surrogate for H I Lyman α changes over both solar rotation (middle panels) and the 11 yr activity cycle (lower panels).

a well-calibrated solar activity index (White and Livingston (1981)). Solar Ca II data have been measured since 1976 from the Kitt Peak Observatory although only a few times per month. While these data lack the temporal resolution needed to properly track the rotational modulation, they remain a valuable long term surrogate database (White et al. (1990)). Another proxy, the He I 1083 nm equivalent width (EW; Harvey and Livingston (1994)) has been shown to be highly correlated with the Ca II K index, even though its formation mechanisms are less well understood; these data are recorded almost daily. The Mg II index (Hall and Anderson (1988); Cebula et al. (1992b); DeLand and Cebula (1993); de Toma et al. (1997); Viereck et al. (1996)), which is the ratio of the core to wing emission in another Fraunhofer line at 280 nm, also provides a useful surrogate, but unlike the ground-based Ca II K and He I 1083 nm proxies, the Mg II proxy must be measured from space. Figure 5

demonstrates that the He I 1083 EW data provide a better proxy for the SME H I Lyman α irradiance variations than does the 10.7 cm radio flux, over both rotational and solar cycle time scales.

While selected ground-based solar proxies promise to provide adequate surrogates for the solar ultraviolet spectral irradiance, additional analysis and validation is needed. Questions remain, especially over longer time scales, because the proxies are constructed as ratios of solar emissions emitted from two different regions of the Sun's atmosphere, and thus reflect differential variability. Not well established at all is the extent to which these surrogates would reflect a global irradiance variability component that is nonmagnetic in origin such as changing solar diameter.

2.4. Predictability?

It is not currently possible to predict with any confidence the level of even proxy solar indicators such



Fig. 6. Comparison of various predictions of the amplitude of solar cycle 22 with its actual level.

as the sunspot number or 10.7 cm radio flux for an upcoming 11-year activity cycle. Figure 6 demonstrates the wide range of predictions made for the maximum mean sunspot number in solar cycle 22, compared with the actual recorded value (Brown (1989)). Even were the prediction of proxy data for impending solar cycles successfully accomplished, improved knowledge of the physical connections and correlations between the proxy data and the solar spectral irradiance is essential before this predictive capability could be relied upon for aeronomic applications. As discussed in the previous section, questions remain about such connections over decadal and centennial time scales.

Predicting overall solar activity levels into the twenty-first century is even less dependable than for 11-year cycle predictions, but estimates have been obtained from spectral decomposition of long term proxy records of solar activity such as the ¹⁴C tree ring data (Damon (1992)). These estimates indicate that solar activity levels could continue their overall increase of the past 300 years since the Maunder Minimum to reach the peak of the Modern Maximum around 2030-2040 (Jirikowic and Damon (1994)). If these predictions are correct, the solar ultraviolet spectral irradiance can be expected to increase ozone production during the next four or so decades.

Fundamental to achieving improved confidence in long term predictability is the solar research needed to better understand the causes and evolution of solar activity. These studies must then connect the basic physical processes associated with solar activity, i.e., the generation and decay of magnetic flux, with the consequent emission changes that cause the solar irradiance variations (e.g., National Research Council (1994)).

3. TRANSMITTANCE OF DIRECT SOLAR IRRADIANCE THROUGH THE ATMOSPHERE

Transmittance of solar radiation through the atmosphere ultimately depends on the absorbing and scattering properties of molecules and particulates, such as aerosols and clouds. In the wavelength range relevant for photolysis in the stratosphere and troposphere, the solar irradiance is attenuated primarily by molecular absorption below about 310 nm and by particulate extinction at longer wavelengths. The requirement to correctly account for atmospheric extinction is basic for calculating photolysis rates in the atmosphere. Specific recommendations for appropriate inputs and techniques to determine the required quantities for photochemical models have continually been addressed and documented by DeMore *et al.* (1994), among other sources.

3.1. Beer's law transmittance

The transmittance of radiation through the atmosphere given in Equation 2 follows Beer's Law,

$$T(\tau(\lambda, z, \theta_o)) = \exp(-(\tau(\lambda, z, \theta_o))), \qquad (6)$$

where the optical depth, τ , is given by Equation 3. The cross sections, σ , in Equation 3 can have strong wavelength dependencies as well as sensitivities to both temperature and pressure. An illustration of the net effect of atmospheric transmission on the solar irradiance is shown in Fig. 7. The uppermost curve shows the solar irradiance above the atmosphere. Each successive curve gives the irradiance at the indicated altitudes (Equation 2).

Precise calculation of the solar irradiance at any location in the atmosphere requires knowledge of the optical depth with resolution sufficient to describe the smallest structure in the absorption spectra. Because it is not computationally efficient in photochemical modeling to track the detailed molecular features, spectral smoothing and convolution of transmittances are often required. Entire theories of molecular band model approximations have been developed (e.g. Goody and Yung (1989)), primarily for infrared spectral ranges. Similar problems are evident in ultraviolet transmittances, and algorithmic approximations have been devised, particularly for the spectrally rich, photochemically-relevant Schumann-Runge bands of O_2



Fig. 7. The top panel shows the direct solar flux (VanHoosier *et al.* (1988)) at the top of the atmosphere (4), and the (direct) attenuated solar flux calculated at altitudes of 120, 80, 40, 20, and 0 km. The calculation employed the U. S. Standard Atmosphere (1976) at a solar zenith angle of 30° . The bottom panel is an expanded region of the spectrum between 180 and 200 nm corresponding to absorption in the Schumann-Runge bands of O_2 .

between 175 and 205 nm (e.g. Allen and Frederick (1982)). Transmittances due to scattering can be handled more easily due to the relatively slow variation of cross sections with wavelength.

In this section, the current status of molecular absorption is reviewed first, followed by a discussion of scattering by molecules (Rayleigh scattering) and by aerosols and clouds (Mie scattering).

3.2. Background spectroscopy: atmospheric absorption and scattering

The primary atmospheric absorbers affecting transmittance in the 120 to 400 nm range are ozone and molecular oxygen. At times of volcanic eruptions, sulfur dioxide gas can also contribute significantly to the optical depth. Absorption by other molecules, while critical to photochemistry, provides little discernible impact upon the attenuated solar irradiance. A notable exception is nitric oxide, whose mesospheric self-absorption (resonant scattering of spectral line radiation from the optical path) selectively controls transmittance of just those spectral lines required for NO dissociation at lower altitudes. Finally, O₂ effectively prevents all wavelengths shortward of 170 nm from penetrating below the mesopause except for a relatively transparent window in the O2 cross section near the strong solar Lyman α line (see Fig. 1).

Molecular absorption properties are determined by basic molecular structure; only transitions between electronic states are sufficiently energetic for their resulting radiation to appear in the ultraviolet. Even for simple diatomic molecules, the combination of electronic, vibrational, and rotational transitions results in complex spectral distribution. If, however, the transitions are not between bound states, the absorption signature is a continuum; both the O₂ Schumann-Runge continuum (137-183 nm) and the important forbidden (and therefore, weak) Herzberg continuum (185-242 nm) are examples of this condition. For a bent triatomic molecule like ozone, the picture is more complex, possessing a combination of blended, broad, predissociated lines overlying continua.

3.2.1. O_2 Schumann-Runge continuum absorption. At wavelengths less than about 175 nm, absorption of solar radiation in the Schumann-Runge (S-R) continuum of O_2 leads to the formation of $O({}^3P)$ and $O({}^1D)$ (e.g. see Lee *et al.* (1977)). Metastable $O({}^1D)$ atoms formed by this process (as well as by O_3 photolysis) play a prominent role in the photochemistry of the atmosphere, initiating, for example, the production of odd hydrogen radicals through reaction with water vapor: $O({}^1D) + H_2O \rightarrow 2$ OH. Alternative reactants include: N₂, O₂, H₂, CH₄, N₂O, etc. Owing to the large magnitude of the S-R continuum cross section, which ranges from approximately 10^{-19} cm² at 175 nm to 10^{-17} cm² at 140 nm, nearly all of the incident solar radiation in this wavelength region is absorbed above 90 km. Thermospheric measurements of the extinction of solar ultraviolet radiation in the S-R continuum have been used to determine O₂ densities at these altitudes (Ackerman *et al.* (1974); Meier *et al.* (1992); Aikin *et al.* (1993)).

The S-R continuum arises from transitions from the $X(\sum)$ ground electronic state to the $B(\sum)$ state of O_2 . The dissociation limit of the $B(\sum)$ state is near 57136 cm⁻¹ (Gibson *et al.* (1991); Lewis *et al.* (1985a)), corresponding to a wavelength of 175 nm for absorption from the ground vibrational level of the $X(\sum)$ state. At typical thermospheric temperatures, continuum absorption due to transitions originating from higher vibrational levels makes an important contribution to the total O_2 cross section at wavelengths longward of 175 nm (Allison *et al.* (1971); Gibson *et al.* (1991); Lewis *et al.* (1985a)).

The magnitude of the O₂ cross section in the S-R continuum has been measured extensively in the laboratory (e.g. Watanabe et al. (1953); Huffman et al. (1964), Hudson et al. (1966); Ogawa and Ogawa (1975)). Comparison of results for wavelengths less than 170 nm suggests that uncertainties in values for the cross section are no larger than 10% (Hudson et al. (1966)). More recently, measurements involving electron impact spectroscopy (Chan et al. (1993)) and optical absorption spectroscopy (Gibson and Lewis (1996)) are in satisfactory agreement ($\pm 2\%$). At wavelengths greater than about 170 nm, the continuum exhibits a significant temperature dependence, as expected on the basis of the Boltzmann population of vibrational states. Lean and Blake (1981) specifically pointed out the importance of temperature effects of S-R continuum absorption in the thermosphere. Unfortunately there remain significant discrepancies between measured continuum cross sections near 175 nm and values obtained on theoretical grounds (see, e.g., Lewis et al. (1985b); Friedman and Dalgarno (1989)).

3.2.2. O_2 Schumann-Runge band absorption. Atmospheric opacity in the 175 to 200 nm spectral range is dominated by molecular oxygen absorption in the Schumann-Runge bands. Absorption of solar radiation at these wavelengths corresponds to boundbound transitions in O_2 from the $X(\sum)$ ground electronic state to the $B(\sum)$ state. The energy levels of both electronic states are characterized by discrete vibrational levels which are further partitioned into spin-split rotational states. Only the lowest lying vibrational levels of the ground electronic state are significantly populated at atmospheric temperatures, however, and the gross structure of the O₂ cross section appears as a progression of bands ranging from the (0-0) band near 203 nm to the (22-0) band at about 175 nm. Spectral windows between these bands are occupied by "hot" bands, originating from the v' = 1 and 2 vibrational states. The hot bands are highly temperature-dependent and because of their spectral location, are important in governing the penetration of radiation in the S-R region. Production of odd oxygen (O_x = O₃O) between 50 and 90 km is governed largely by photodissociation of O₂ in the S-R bands.

The complexity of spectral features in the S-R bands poses a particular challenge to theorists and experimentalists alike. Early measurements of S-R cross sections were not able to resolve completely the fine spectral detail (typically on the order of 0.002 nm) of individual absorption lines in the S-R bands (Hudson and Carter (1968); Ackerman et al. (1970)), giving rise to large uncertainties in values of the oscillator strengths and predissociation line widths for individual bands. As a consequence, theoretical studies involving application to atmospheric transmission and O₂ photolysis (e.g., Kockarts (1971); Frederick and Hudson (1980); Nicolet and Peetermans (1980)) were hampered. Direct measurements of stratospheric attenuation of solar radiation in a portion of the S-R region were reported by Herman and Mentall (1982a) and by Anderson and Hall (1983). S-R cross sections derived from these measurements were found to agree with the calculations of Frederick and Hudson (1979), at least within the limits of uncertainty (roughly 40% for the calculated cross sections and 30% for the in situ determinations) (Frederick et al. (1981); Anderson and Hall (1986)).

The situation has improved over the past decade as a result of new laboratory measurements of S-R band cross sections performed at resolutions of 0.0013 nm (Yoshino et al. (1983)), and of 0.004 nm (Lewis et al. (1986)). The new spectral data have led to reassessments of atmospheric transmission and O₂ photolysis in the S-R bands (Murtagh (1988); Nicolet and Kennes (1989); Minschwaner et al. (1993b); Kockarts (1994)). Transmittance calculated on the basis of the new spectral parameters indicates improved agreement with the in situ measurements of Anderson and Hall (1989) (Minschwaner et al. (1992)). Nevertheless, spectral parameters for weak, narrow lines of the (0-0) to (2-0) bands remain uncertain. In addition, predissociation widths are poorly characterized for the higher vibrational progressions close to the dissociation limit near 175 nm. Line widths in both spectral regions are comparable to, or narrower than



Fig. 8. Direct solar flux calculated for 50 km altitude and 60° solar zenith angle. The dominant spectral features arise from absorption in the O₂ Schumann-Runge bands; additional absorption lines of the NO*(0-0) band are indicated. The NO distribution is from Minschwaner and Siskind (1993).

instrumental passbands of published absorption measurements.

A calculated spectrum of a relatively small portion of the S-R band region is shown in Fig. 8. This example illustrates the structure imparted to the solar irradiance field at 50 km by individual absorption lines of the S-R bands within a relatively transparent region between the S-R (9-0) and (10-0) bands. Values for the irradiance near the centers of strong absorption lines, at 182.92 nm, for example, are reduced by three orders of magnitude or more compared to unattenuated values. Also indicated in Fig. 8 are the absorption features associated with the delta (1-0) band of nitric oxide, based on an NO distribution from Siskind et al. (1990). These lines are Doppler-broadened, with half widths about ten times narrower than O2 predissociation widths. Attenuation by these lines does not make a significant contribution to the mean opacity of the atmosphere, although the impact on NO photodissociation in the stratosphere and mesosphere may be significant (Frederick et al. (1983); Minschwaner and Siskind (1993)).

As discussed by DeMore *et al.* (1994), one of the largest potential sources of error in connection with atmospheric modeling in the S-R band is related to inaccuracies in the parameterization of absorption and photolysis processes. An exact, line-by-line approach is simply not feasible to implement in photo-

chemical models of the middle atmosphere, and various approximations have been described to treat transmission and O_2 photolysis in the S-R bands (e.g., Park (1974); Fang *et al.* (1974); Allen and Frederick (1982); WMO (1986)). However, only the methods outlined by Murtagh (1988), Nicolet and Kennes (1989), and Minschwaner *et al.* (1993b) are consistent with the new laboratory cross sections.

3.2.3. O_2 Herzberg continuum absorption. While the Herzberg continuum absorption (185-260 nm) is small relative to the neighboring O₂ Schumann-Runge and O₃ Hartley bands, it is quite important for controlling the penetration of radiation in the windows between the stronger systems. The forbidden transition occurs between the $X(\sum)$ and the $A(\sum)$ states. The initial sets of laboratory determinations for the magnitude of the Herzberg continuum almost uniformly overestimated the value (Ditchburn and Young (1962); Hasson and Nicholls (1971); Shardanand and Prasad Rao (1977); Shardanand (1978); Cann et al. (1984); Johnston *et al.* (1984)) by as much as 40%. These overestimates apparently arose from the need to accommodate the small cross section for this forbidden transition with very high pressures necessary to produce measurable opacities in the laboratory.

Craig (1965) points out that the pressure dependence was recognized as early as 1941 (Heilpern (1941)), but suitable high fidelity experiments were not successfully accomplished until the middle 1980's (primarily by Cheung et al. (1986) and Jenouvrier et al. (1986a, 1986b)). The two laboratory efforts eventually culminated in a single recommendation for the continuum and its O₂ pressure dependence (Yoshino et al. (1988)). This lab work was motivated by the persistent conclusion that direct, long path measurements of stratospheric transmittances contradicted the higher values. (See Section 3.3.) Most recently, new laboratory measurements of O₂ continuum absorption between 208 and 242 nm indicate even smaller cross sections for the Herzberg continuum (Amoruso et al. (1996)). Values extrapolated to zero pressure are up to 15% smaller than those recommended by Yoshino et al. (1988).

It has been pointed out (Lewis and Gibson (1992)) that far wing S-R line shapes may be more properly described by a convolution of a Fano profile (Fano (1961)) of small asymmetry and a Doppler profile. Subject to the constraint that the sum of Voigt line centers, far wing, and Herzberg continuum cross sections must match the observed absorption spectra, use of a revised far wing contribution would require a reanalysis of the composite spectrum as a function of temperature, leading to an altered Herzberg component.

Yoshino et al. (1994) have recently presented spectrally resolved measurements of the weak O₂ absorption in the Herzberg band region longward of 260 nm. New spectral parameters for the Herzberg I, II, and III band systems were also reported by Huestis et al. (1994). Owing to the prominence of this system in the ultraviolet nightglow, the recent laboratory results will be important to remote sensing studies of the upper mesosphere/lower thermospheric region. The Herzberg bands appear less relevant in assessing photolytic processes, however, because (1) they are coincident with the maximum absorption in the O₃ Hartley band, and (2) they do not lead to photodissociation of O₂. Nevertheless, the Herzberg bands can be important for UV laser transmission in the troposphere under conditions of low ozone concentration.

3.2.4. Ozone absorption. Ozone, being a triatomic molecule, exhibits an even richer array of dissociating transitions than O₂, with dense overlap and an underlying continuum. Energy states of O₃ can be so ambiguous that rather than being identified by band assignments (which are difficult because of the strong predissociation and accomplished for only a portion of the system (Katayama, 1979)), the ozone system nomenclature is pragmatically divided by wavelength, subject to the dissociation products. That is, the Hartley system lies between 180 to 310 nm, yielding predominantly O('D), while the Huggins bands (from 310 to 370 nm) and the Chappuis bands (from 370 to 850 nm) produce ground state O(³P). A new investigation of the $O(^{1}D)$ production in the Huggins bands (Michelsen et al. (1994)) suggests that this source is much larger than previously thought. Laboratory measurements of the relative quantum yields of $O_2(^1\Delta)$ from ozone photolysis in the 300-320 nm range support the revised $O(^{1}D)$ yields (Ball *et al.* (1993); Ball and Hancock (1995)) provided that the spin allowed transition is the dominant source of singlet products. The temperature dependence of the Hartley system is weak (1-3% variability at most; DeMore et al. (1994)) while the Huggins bands exhibit a systematic temperature dependence, weak at 310 nm but increasing to a factor of 10 at 340 nm (Bass and Paur (1985); Molina and Molina (1986)). Cacciani et al. (1989) have extended the Huggins measurements to 355 nm and have observed a very similar temperature dependence. Recent room temperature measurements by Daumont et al. (1992) from 195 to 345 nm, agree within the stated accuracies with these earlier values.

The ozone Hartley-Huggins bands and their temperature dependences can be explicitly included as Beer's Law cross sections in radiative transfer algorithms with relatively high spectral resolution (of order 0.1 nm; e.g., see the description of LOWTRAN 7 implementation by Anderson *et al.* (1990b)). Bass and Paur (1985) provide a convenient quadratic form, while subsequent authors include tables appropriate for direct interpolation of their temperature-specific cross sections. More coarse spectral model parameterizations are reviewed in the JPL recommendations (DeMore *et al.* (1994)) with information on the quantum efficiency for $O(^{1}D)$ production and its temperature dependence.

The cross sections of the ozone Chappuis bands were remeasured by Anderson *et al.* (1991), Anderson and Mauersberger (1992) and by Burkholder and Talukdar (1994). The latter also examined the temperature dependence down to 220 K, which is small near the peak of the Chappuis band between 540 and 640 nm, but can become significant in the wings of the band particularly below 450 nm.

Ozone cross sections and their dependences on temperature appear, in general, to be well-determined by a variety of laboratory groups. But the details of the wavelength structure, especially in the Huggins bands, are important in controlling the penetration of radiation to the surface where photo-sensitive reactions take place, particularly with living organisms including plants, sea plankton, and, of course, animals. Continued laboratory studies and systematic measurements of UV-A, UV-B (and UV-C, if indicated) for both clean and polluted air masses at moderate spectral resolution will be required for validation of models and theories, especially as they begin to impact biological dosing (UNEP-WMO (1991); Tevini (1993)).

3.2.5. Other sources of molecular extinction. The role of SO₂ as a major source of solar attenuation is highly episodic, controlled by injection from volcanic eruptions. Because the primary absorption lies between 240 and 340 nm, its signature is hidden by the overlying ozone Hartley-Huggins bands during periods of normal SO₂ concentration. (A complete laboratoryderived cross section for SO₂ is given by Hearn and Joens (1991) for the band from 228 to 339 nm at 0.06 nm resolution, and by Freeman et al. (1984) between 172 and 240 nm at 0.002 nm resolution.) However, with large stratospheric injections, SO₂ absorption can actually dominate Huggins band absorption. The El Chichon (Krueger (1983)) and Mount Pinatubo eruptions are classic examples where standard ozone detection from space (SBUV and TOMS) was severely degraded by the volcanic plumes. In fact, the motion and dispersion of the Pinatubo gas cloud has been mapped by tracing its contaminating UV signature (Bluth et al. (1992)). Recently Dlugokencky et al. (1996), have shown that the UV actinic flux between 290 and 330 nm, was decreased by about 12% immediately after the eruption due to direct absorption by SO_2 .

Volcanic sulfur dioxide initiates a second level of contamination, perhaps more ubiquitous than the original gaseous plume. It combines with water forming H_2SO_4 , a primary nucleation site for the formation of hydrated aerosols; the conversion time is relatively fast, of order 38 days (McKeen *et al.* (1984)). Tropospheric SO₂ sources are also important because the gas-to-aerosol conversion can become involved in multiple scattering within regions of low ozone and possibly increased direct solar irradiance.

There are a number of other molecules which absorb solar radiation in the atmosphere; however their concentration is sufficiently small that this absorption only has a negligible impact on the available actinic radiation of interest here. (At longer wavelengths, however, water absorbs a significant fraction of the incident solar radiation.) Of course this absorbed radiation may lead to photolysis of those molecules, which would be important to the understanding of atmospheric chemistry. Absorption cross sections are summarized by DeMore *et al.* (1994).

3.2.6. Rayleigh scattering. The scattering of radiation by molecular components of the atmosphere is known as Rayleigh scattering, after Lord Rayleigh (J. W. Strutt) who first described it in 1871, (see Young (1980, 1981a, 1981b, 1982)). Rayleigh scattering removes photons from the direct solar irradiance, contributing to a reduction in transmittance. These scattered photons are not removed from the actinic flux; they are simply transferred from the direct to the diffuse component, remaining available for additional scattering and/or absorption.

As discussed by Young (1980, 1981a, 1981b, 1982), the Rayleigh scattering includes a small fraction (a few percent) of the radiation which has been Ramanshifted, changing its wavelength (the "Ring effect", see Grainger and Ring (1962)). This change in wavelength has only a small effect on the total radiation at any wavelength, with a slight filling in of the small-scale minima of the solar Fraunhofer lines in the scattered sunlight, and a corresponding minor reduction in the scattered sunlight at other wavelengths (Kattawar et al. (1981); Chance and Spur (1977)). While the Ring effect in the available actinic radiation at any wavelength is small, it does need to be taken into account when using the spectral structure of the scattered solar radiation to derive the concentration of molecular species of interest (e.g. Solomon et al., 1987). Joiner et al. (1995a, 1995b) have used the Ring effect to derive cloud pressures from TOMS and SBUV measurements.

The wavelength dependence of the refractive index of the atmosphere has long been considered in computing the Rayleigh scattering cross section. However the wavelength dependence of the depolarization factor has typically been neglected (e.g. Penndorf (1957) or Teillet (1990)). Bates (1984) recalculated the Rayleigh scattering cross section in the 200 to 1000 nm spectral region, including the wavelength dependence of the depolarization. This wavelength dependence is most significant at ultraviolet wavelengths, where it can lead to a 3% difference in the Rayleigh scattering cross section at 200 nm. In the visible spectral region the wavelength dependence of the depolarization makes a difference of less than 0.5%. Recently Bucholtz (1995) has built on this study of Bates (1984), tabulating the spectral dependence of the Rayleigh scattering cross sections and the total atmospheric optical depth for several standard model atmospheres.

3.2.7. Aerosol scattering and absorption. Small particles can be injected into the atmosphere from a variety of sources and may remain suspended in the air for some time depending on their size and composition. Such suspended particles are generically referred to as "aerosols". The major sources of these aerosol particles are: wind-blown dust from the deserts, sea-salt particles, the results of gas-to-particle conversion within the atmosphere through photochemical processes, volcanoes, and anthropogenic sources. The relative importance of these different sources depends on altitude of injection, and to some extent on whose estimate is used. This section will focus on the properties of atmospheric aerosol which affect the actinic radiation. The resulting effects are discussed in Section 4.

Aerosol extinction in the atmosphere exhibits large spatial and temporal variations. The concentration and composition of tropospheric aerosols is largely driven by local geographic sources and recent air mass history. The effects of the local surface sources become less significant as one moves above the atmospheric boundary layer. The size and composition of the aerosols can also vary with changes in the ambient relative humidity, since many of the constituents of the aerosol particles are hygroscopic and go into solution with condensed water at moderate relative humidities. The stratospheric aerosol loading is primarily a function of the extent of volcanic activity during the preceding several years. A discussion of the characteristics of the atmospheric aerosols is given by d'Almeida et al. (1991) with an emphasis on the tropospheric aerosols, especially their radiative properties. A review of the physical and chemical properties of the atmospheric aerosols is provided by Jaenicke (1988).

In contrast to molecular extinction, where the

optical depth is the product of the molecular cross section and their column concentration, the aerosol optical depth is usually described as the product of an aerosol extinction (or attenuation) coefficient (km⁻¹) and the linear path length (km). This is a more convenient approach since the aerosol size distribution must be convolved with the extinction cross section. Inference of the radiative properties of atmospheric aerosols requires knowledge of their size distribution and refractive index as a function of wavelength and composition. Assuming that the particulates are spherical, their radiative properties can be computed from the well-known solutions to the problem of scattering and absorption of radiation by a dielectric sphere, (the so-called Mie theory). Alternatively, a number of techniques have been developed to address the problem of irregularly shaped particles.

The tropospheric aerosol abundance is often related to the surface visibility for convenience of description. Based on available information on typical particle mass loading, composition, and size distribution, aerosol models have been constructed for a variety of atmospheric conditions. The most commonly used models are those embedded in the LOWTRAN (Kneizys et al., 1988), MODTRAN (Anderson et al. (1993); Berk et al. (1989, 1996); Bernstein et al. (1996); Wang et al. (1996)), and FASCODE (Clough et al. (1989); Wang et al. (1996)), atmospheric propagation models, and those developed by the IAMAP/Radiation Commission (1986). Both of these schemes are based partially on the models developed by Shettle and Fenn (1976, 1979). For a discussion of these and other models see the review by Shettle (1989). Another widely used tropospheric aerosol climatology and set of aerosol models has developed by d'Almeida et al. (1991). An improved version of the latter has been developed by Koepke et al. (1996). A climatological database for the total loading of stratospheric aerosols was recently provided by Sato et al. (1993).

Typical values for the vertical distribution of aerosol extinction are shown in Fig. 9 (after Fenn *et al.* (1985)). Because the Rayleigh scattering cross section depends on the inverse fourth power of wavelength, the relative importance of molecular scattering increases in the ultraviolet. Thus at 300 nm Rayleigh scattering increases by more than an order of magnitude relative to the values shown in Fig. 9, whereas the aerosol extinction typically increases by a factor of about 2 (depending on the type of aerosol).

Under extreme volcanic conditions the stratospheric aerosol content can be as large as the boundary layer concentration. The optical properties of the stratospheric aerosol layer change in time due to photochemical reactions and removal processes (Turco *et*

VERTICAL AEROSOL DISTRIBUTIONS



Fig. 9. Vertical distribution of aerosol extinction at 550 nm wavelength, for different atmospheric conditions (Fenn *et al.* (1985)). Also shown for comparison is the Rayleigh scattering (dotted line) and the Elterman (1968) aerosol models.

al. (1982) and Hansen et al. (1992)). The total stratospheric aerosol loading often increases during the first several months following a major eruption as the conversion of volcanic SO₂ to sulfuric acid aerosols (McKeen et al. (1984)) more than compensates for any losses of the volcanic ash due to gravitational settling. The temporal evolution of volcanic aerosols depends on the magnitude of the eruption, the altitude of maximum injection, the geographic location, and the prevailing circulation patterns in the stratosphere at the time of the eruption. Sulfate aerosols can remain in the stratosphere for several years with an e-folding time of about 1 year (McCormick et al. (1978)), thereby providing a source of particulate scattering and extinction, as well as a surface for heterogeneous chemical reactions (see Tolbert (1994)). The type and size of the resultant stratospheric profile of these aerosols can significantly alter the amount and distribution of the actinic radiation throughout the stratosphere and into the troposphere (discussed further in Sections 4 and 5).

The profiles in Fig. 9 labeled "High Volcanic" and "Extreme Volcanic", with visible optical depths of 0.1 and 0.3 respectively, are representative of the aerosol



Fig. 10. Left panel: Extinction coefficients versus wavelength for the Shettle and Fenn (1979) rural aerosol model, with different relative humidities and a constant number density of 15 000 particles per cm³. Right panel: Extinction coefficients vs wavelength for the different Shettle and Fenn stratospheric aerosol models (adapted from Fenn *et al.* (1985)).

loading following major volcano such as the eruption of Mt. Pinatubo in 1991 (McCormick (1992); Stowe et al. (1992); Valero and Pilewskie (1992)), El Chichon (King et al. (1984)) or Krakatau in 1883. Typically the volcanic aerosol layer in the stratosphere is much more structured and may peak anywhere from 15 to 25 km or more. In the case of Mt. Pinatubo, the most studied volcanic eruption, the peak was observed at altitudes up to 25 km, (Winker and Osborn (1992a, 1992b); DeFoor et al. (1992); Jäger (1992); Post et al. (1992); Deshler et al. (1992)). More recent background stratospheric aerosol profiles, based on measurements from SAGE II, are presented by McCormick et al. (1993) and by Brogniez and Lenoble (1991). For an overview of the variations in the stratospheric aerosols since 1850, see Sato et al. (1993).

Representative values of aerosol extinction are shown in Fig. 10 as a function of wavelength for rural aerosols and for stratospheric aerosols (Fenn *et al.* (1985)). For the ultraviolet and visible spectral regions the aerosol extinction is dominated by scattering with typical aerosol absorption efficiencies less than 10%. Only when aerosols contain soot or graphitic carbon do they become more efficient absorbers at these wavelengths. In the infrared, absorption becomes more significant, and in the Rayleigh limit where the wavelengths are much larger than the sizes of the aerosol particles, the scattering efficiency becomes very small.

3.2.8. Cloud scattering and absorption. The role of clouds in the climate and hydrological systems as been accredited the highest priority in the US Global Change Research Program. A recent review article (Fouquart *et al.* (1990)) identified clouds as the climate parameter having the greatest influence on the Earth's radiation budget. The scattering of solar radiation by clouds significantly alters its distribution in the atmosphere. The available actinic radiation is similarly modified by scattering from clouds, as discussed by Madronich (1987a); Anderson and Lloyd (1990); Estupinan *et al.* (1996) and Kylling *et al.* (1995), among others. Cloud effects on actinic radiation are discussed further in Section 4.4.

The scattering of water clouds depends on the wavelength-dependent refractive index of water as well as (spherical) droplet size; for ice clouds there is also a dependence on particle shape. For wavelengths less than 1000 nm, individual cloud droplets have absorption efficiencies of less than 0.1%, and even the thickest clouds reflect most of the incident radiation. The actual cloud albedo is a function of the cloud optical depth. At infrared wavelengths (longer than 1000 nm), clouds absorb a significant portion of the incident radiation; there, the cloud albedo is a function of both the cloud optical depth and the size of the cloud particles (Nakajima and King (1990)).

Models for water clouds have been published by Carrier et al. (1967); Stephens (1978, 1979), and Fenn et al. (1985). Hu and Stamnes (1993) provided a convenient and accurate parameterization of the optical properties of water clouds (in terms of liquid water content and droplet equivalent radius) which is valid throughout the solar and terrestrial spectrum. For a review of properties of cirrus clouds see Dowling and Radke (1990). Models for cirrus clouds are given by Heymsfield and Platt (1984) and by Liou et al. (1990). For the results of measurements of cirrus cloud properties during the FIRE (First ISCCP Regional Experiment) Cirrus Intensive Field Observations in Kansas during November and December 1991, see the special issue of Journal of the Atmospheric Sciences, 1 December 1995 (Vol. 52).

3.3. Solar irradiance measurements within the stratosphere

There have been very few *in situ* measurements of stratospheric ultraviolet irradiance. While the solar radiation above the Earth's atmosphere has often been measured, albeit with significant uncertainties (see Section 2), the radiation field *within* the atmosphere is the relevant photochemical quantity. This radiation field cannot yet be computed with complete confidence.

Fortunately, direct measurements in the stratosphere may be made conveniently by use of high altitude research balloons. Balloons are preferable to rockets, which can neither ascend slowly nor hover, and to satellites which orbit too high. (But recent very high altitude aircraft are beginning to provide an alternative resource for transmitted solar irradiance measurements, McElroy (1995).) A single balloon flight can produce a wealth of data; however the coverage in space and time is invariably limited. The few extant observations are reviewed in this section.

Early *in situ* measurements were reported by Brewer and Wilson (1965). Three balloon flights of a photometer sensitive to radiation in the region around 210 nm were made from the U. S. Naval Base at Trinidad, twice to the 6 mb level (about 35 km) and once to 14 mb (about 29 km). A model calculation using the then-recommended values for the atmospheric constituent cross sections, resulted in a profile which could be made to match normalized experimental results only by multiplying the Herzberg continuum cross sections by 0.75. The need to reduce the Herzberg continuum cross sections was confirmed by a later series of measurements (see below).

Follow-on balloon investigations between 1977 and 1983 include a series of five Air Force flights by Hall and colleagues (Hall (1981, 1983); Hall and Anderson (1984, 1989)). The instrument used was a single dispersion spectrometer with two possible spectral resolutions (0.012 nm and 0.1 nm), covering approximately 190 to 310 nm. Each balloon achieved an altitude of approximately 40 km, acquiring data continuously on ascent. While each data set was analyzed for solar and atmospheric spectral signatures and variability, only the 1981 and 1983 flights were employed in detailed studies of the local irradiance. Both of these flights confirmed the smaller magnitude of the Herzberg continuum, while the reconfigured 1983 flight provided important confirmation of the need for improved parameterization of the Schumann-Runge bands for both transmittance and photodissociation rate calculations.

During the same period, J. E. Mentall and colleagues (Herman and Mentall (1982a)) conducted several flights of a double monochromator, measuring incident (from a rocket in September 1980; Mentall et al. (1981)) and transmitted (from a balloon in September 1978) solar radiation in the range 180 to 330 nm. The balloon payload included two separate double monochromator systems. One double monochromator was pointed at the Sun. The other looked in six different directions in a vertical plane not including the Sun, for the purpose of measuring the diffuse component of the actinic flux. The data were used to evaluate model calculations in the Schumann-Runge bands in the range 184-202 nm (Frederick et al. (1981)), and to compare the directly transmitted and Rayleigh scattered solar radiation at 40 km (Herman and Mentall (1982a); see Section 4.2 for additional discussion of the Herman and Mentall diffuse radiation results).

Another balloon payload was launched by the same group on 15 Apr 1981. This experiment was designed to make measurements at a number of different altitudes during ascent, while scanning between 180 and 330 nm. On-board instrumentation determined the ozone profile and the pressure, from which the total density and the O₂ concentration could be deduced. The ozone and Rayleigh cross sections were assumed known so that the O₂ Herzberg cross section could be determined. The resulting values (Frederick and Mentall (1982); Herman and Mentall (1982b)) confirmed the lower cross sections suggested by Brewer and Wilson (1965). The increasing evidence for lower cross sections motivated laboratory workers to reassess their measurement procedures, leading to new experiments (see Section 3.2.3) and prompted modelers to examine the impact of reduced cross sections on atmospheric photochemistry (Froidevaux and Yung (1982); Brasseur *et al.* (1983); Simon and Brasseur (1983); Nicolet and Kennes (1989)). Further confirmation of the need for reduced O_2 absorption in the Herzberg continuum was obtained from balloon experiments by Pirre *et al.* (1988).

The ozone behavior observed in the above studies indicated that the recommended ozone cross sections, primarily those of Inn and Tanaka (1959) were reasonable; however, careful accounting of the transmittances, again near the 200 nm window, revealed a small broad "anomalous" signature centered at 210 nm. In the course of other balloon measurements of solar radiation, Ackerman and colleagues had also detected the same feature in the atmospheric opacity at about 35 km (Ackerman et al. (1968); Frimout (1970)). Ultimately, with the arrival of new laboratory determinations, primarily those of Molina and Molina (1986), the anomaly was resolved, having been an artifact of the residual O₃ attenuation due to the lack of spectral resolution in the Inn and Tanaka measurements.

New spectral measurements of the solar UV irradiance near 20 km altitude have been reported by McElroy (1995). The instrument, which was mounted on the NASA ER-2 research aircraft, consisted of a single pass spectrograph operating between 300 and 775 nm with a passband of 1 nm. Comparison of the observations with the MODTRAN atmospheric transmission model shows good agreement. In addition, the data have been used to derive photolysis frequencies for O_3 and NO_2 along the ER-2 flight track (McElroy *et al.*, 1995).

4. DIFFUSE (SCATTERED) RADIATION

Knowledge of the ultraviolet and visible radiation field is essential for a proper understanding of photochemical processes in the atmosphere. Since multiple scattering can substantially enhance the actinic radiation field, it is important that an accurate characterization be used in atmospheric photochemistry models. As discussed in Section 3, direct solar radiation entering the atmosphere is attenuated by scattering and absorption along the ray path. If no scattering took place in the atmosphere, the sky would be black everywhere except in the direction of the Sun. The actual blue appearance of the sky is caused by the strong wavelength dependence of molecular (Rayleigh) scattering which is inversely proportional to the fourth power of the wavelength. Rayleigh, Mie (aerosol and cloud), and surface scattering are all important contributors to the diffuse radiation field.

4.1. Computation of the diffuse atmospheric radiation field

While the attenuated solar radiation satisfies Beer's law, the diffuse radiation field is obtained by solving an integro-differential equation known as the equation of radiative transfer. Alternatively, the diffuse radiation field may be formulated mathematically as the solution of an integral equation. A number of solutions have been obtained for the diffuse radiation field (e.g., Meier *et al.* (1982); Nicolet *et al.* (1983); Stamnes (1986); Madronich (1987b); Tsay and Stamnes (1992); Michelangeli *et al.* (1992); Nicolet (1992); Ruggaber *et al.* (1993) and their references). A recent assessment of the accuracy of various models has been published by Weihs and Webb (1997a, 1997b).

The quantity of importance for photolysis by multiply scattered radiation is the diffuse component of the actinic flux (Equation 4). It is equivalent to 4π times the mean (scattered) intensity, a quantity often used in radiation transport theory. To compute the diffuse component of the flux, the optical properties of the atmosphere must be established; these consist of the optical depths of the scattering and absorbing species, their single scattering albedos (probabilities that photons are scattered rather than absorbed), and their scattering phase functions. The cross sections for the scattering and absorbing species as well as their abundances are needed to quantify the optical depths (Equation 3) and the atmospheric transmittances (Equation 6).

To illustrate the importance of multiple scattering, Fig. 11 shows the direct and the diffuse irradiance at the surface for several solar zenith angles (SZA) in a plane parallel atmosphere. It is clear that the larger the SZA, the (relatively) more important the diffuse component. In fact, as the Sun approaches the horizon, the diffuse component dominates (lower right panel of Fig. 11). During daytime, most models assume plane geometry. As noted in Section 1.1, the increase in the path length for planar geometry is approximated by the secant of the solar zenith angle instead of using the spherical geometry of the Earth's atmosphere (i.e. the Chapman function). The Chapman function approach assumes an exponentially decreasing atmosphere, which is approximately correct for Rayleigh scattering, and the uniformly mixed



Fig. 11. Effect of solar elevation on direct versus diffuse components of spectral irradiance for solar zenith angles 0, 30, 60 and 75 degrees as indicated. A clear-sky situation was assumed in this computation and the underlying surface was taken to be a Lambertian reflector with albedo 0.05. (contributed by K. Stamnes and J. Zeng).

gases, but is not true of a number of other species such as ozone or aerosols, where more generalized speciesweighted path integrals must be calculated (Shettle and Green (1974)). The planar assumption results in an overestimate of the optical depth seen by the direct beam when the SZA is greater than about 82 deg. This in turn yields an underestimate of the "driving" term in the radiative transfer equation. Therefore both the direct and diffuse radiation fields, and hence the photodissociation rate, will be too small. Caudill *et al.* (1997), have shown the use of the generalized Chapman function gives a reasonable approximation for the radiation field in an otherwise plane parallel geometry except at twilight.

In twilight when the Sun is below the horizon, the lower atmosphere is in the Earth's shadow and only illuminated by scattered radiation from above, while the upper atmosphere is still directly illuminated. Thus planar geometry is no longer valid and spherical geometry must be used for an accurate radiative transfer solution. Such a solution was developed by Collins *et al.* (1972), using a Monte Carlo approach, and more recently by Anderson (1983); Dahlback and Stamnes (1991) and Herman *et al.* (1994, 1995).

Variations in the actinic radiation field throughout twilight can be illustrated by calculating photolysis rates for selected species. Figure 12 shows a comparison of photolysis rates (Equation 5) for O₃ (upper panels), O₃ (middle panels) which leads to O(¹D) production, and NO₂ (lower panels). The various curves cover a range of solar zenith angles. The left column uses planar geometry, while the center column uses spherical geometry. Comparison of the two demonstrates that use of planar geometry can lead to serious errors at sunset. The right column includes calculations for solar zenith angles in the range 85-95



Fig. 12. (a) Photodissociation rates for ozone leading to the formation of O(³P) labeled (O₃), O(¹D) labeled (O₃*) and NO₂ for clear skies, computed in plane parallel geometry for solar zenith angles of 70, 80, 85, 86, 87, 88, and 89°. (b) Same rates for spherical geometry. (c) Results for angles between 85 and 95° in 1° steps using spherical geometry. The angles represented by the different curves increase from right to left in each figure. (After Kylling (1992)).

deg. These results clearly demonstrate the need for correct characterization of the actinic flux throughout twilight.

4.2. Measurements of diffuse radiation: comparison with theory

Measurements of the diffuse radiation field in the atmosphere have great value for validating radiative transfer models. Such measurements in principle can now be made with good precision and accuracy between 200 and 400 nm using double spectrometers to minimize scattered light. In spite of this, there are remarkably few actual measurements, especially in the ultraviolet part of the spectrum below 400 nm. One of the few is an experiment carried out in the stratosphere by Herman and Mentall (1982a). In this experiment

0.100 0.100 0.010 0.001 0.001 0.001 190 200 210 220 230 240 250 260 270 280 290 300 310 320 Wavelength (nm)

Fig. 13. Ratio of scattered to direct radiation at 40 km altitude (Kylling *et al.* (1993)). The thick line corresponds to the empirical curve of Herman and Mentall (1982a), while the thin line represents computed results.

the direct attenuated solar radiation (discussed in Section 3.3) as well as the diffuse radiation field between 190 and 320 nm were measured both from a rocket and a balloon (albeit three years apart). The ratio of scattered radiation, integrated over 4π steradian, to direct radiation is shown in Fig. 13 together with a theoretical computation based on state-of-the-art solutions of the radiative transfer equation using the best available input parameters (Kylling (1992)). This ratio is independent of the magnitude of the solar irradiance adopted at the top of the atmosphere since the direct solar radiation drives both the attenuated solar radiation and the diffuse radiation. Although the model reproduces the main features of the measured ratio, there are indeed significant differences. Between 280 and 300 nm the model predicts more scattering than is inferred from the experiment by as much as a factor of two. In the O₂ Herzberg continuum region between 210 and 230 nm the model also predicts more scattering than is measured, whereas in the Schumann-Runge bands below 210 nm the model yields less scattering than the measurement. While these discrepancies have been examined in detail (Kylling et al. (1993)), their resolutions have not been identified. Note that solar variability is too small (Fig. 4) to account for any temporal discrepancies between the dates of the rocket and balloon flights.

Balloon-borne observations of diffuse UV radiation in the stratosphere were obtained in April, 1983 by



Fig. 14. Scattered radiances measured during the University of Colorado balloon experiment at a viewing angle of -2.6° below the horizon and at a solar zenith angle of 25° . The shaded area denotes the range of uncertainty in observed radiances. The solid curve represents calculated radiances from AURIC-M, a radiative transfer code developed by the Air Force Phillips Laboratory/Geophysics Directorate. The AURIC-M radiances were spectrally degraded to match the instrument passband of 1.5 nm. From Minschwaner *et al.* (1995b).

R. J. Thomas and co-workers, using a single pass spectrometer patterned after the ozone instrument on the Solar Mesospheric Explorer (SME) satellite. Scattered solar radiances were measured from 175 to 325 nm, over a range of elevation angles from 14.6 to -3.3 deg. A recent analysis of these data (Minschwaner *et al.* (1995a)) indicated significant discrepancies with the earlier observations by Herman and Mentall (1982a), but satisfactory agreement overall with calculated radiances (Minschwaner *et al.* (1995b), see Fig. 14 for a comparison of the observed and modelled irradiances. Reasons for the differences between the two data sets remain unclear.

Spectral measurements of ultraviolet radiances at the Earth's surface are now becoming available in response to concern over biological impact of excess UV. Such measurements can also be used for model validation. A comparison of computed fluxes was made with measurements taken in Lauder, New Zealand with a scanning double spectrometer (Zeng et al. (1994)). Unfortunately, the solar irradiance at the top of the atmosphere was not measured with the same instrument. Consequently, only the ratio of diffuse to direct irradiances measured at the ground can be compared to theory. The ozone column abundance used in the calculation was derived directly from the measurements. Figure 15 shows the comparison between measured and computed ratios of diffuse to direct radiation in the 300 and 450 nm wavelength range. The upper panels pertain to January 12, 1991, and the lower panels to December 4, 1991 (after the Mount Pinatubo eruption). The deviation between the computed and measured ratio is also shown. The aerosol content was based on measured values, but the surface albedo was an optimized parameter in the model. The computed ratio agrees with the measured ratio to within 8%. This agreement is substantially better than obtained from the in situ stratospheric balloon measurements in Fig. 13. Clearly, more such comparisons are needed.

A new set of broad-band balloon measurements of the stratospheric radiance at twilight has been reported by Marceau *et al.* (1994). The experiment covered the spectral interval from 310-900 nm in four bands. The data have not yet been compared with detailed model calculations.

4.3. Scattering by aerosols

The primary effect of atmospheric aerosols on the actinic flux is to modify its angular distribution through scattering of the incident radiation; aerosols are weak absorbers at the UV wavelengths of interest. While most aerosol scattering introduces only small changes in direction because of the pronounced forward scattering by the particles, a non-negligible fraction (typically 10 to 20%) is scattered through 90° or

more. Scattering of ultraviolet radiation by aerosols has been considered by a number of authors, e.g. Shettle and Green (1974); Michelangeli *et al.* (1989, 1992); Davies (1993); Kylling (1992); Kylling *et al.* (1993, 1995); Tsitas and Yung (1996).

To illustrate the effects of aerosols on the radiation field, Fig. 16 from Kylling (1992) shows O₃ and NO₂ photodissociation rates for clear skies and for various aerosol loads. Photolysis of O₃ produces atomic oxygen in the $O(^{3}P)$ ground state for wavelengths in the wavelength range 310-730 nm and in the O(¹D) metastable state (indicated by O_3^* for wavelengths less than 310 nm. The responses of these two photodissociation channels to different aerosol loadings are shown in the first and second rows of Fig. 16. In the presence of aerosols, photolysis in the $O_3 + hv \rightarrow O(^{3}P) + O_2$ channel is found to increase from 8% (background stratosphere) to 22% (extreme volcanic) around the altitude of maximum aerosol concentration. The extreme volcanic model gives a decrease in the actinic radiation below the aerosol layer, whereas the other aerosol loadings actually increase the actinic radiation in the upper and middle troposphere and the lower stratosphere. This is due to different absorption and scattering properties of the different aerosol models. As the aerosol layer ages, scattering becomes more important in the wavelength region of importance for O_3 photolysis (Kylling (1992)). A small increase in O_3^* photolysis is also observed above the aerosol layer for the extreme volcanic model, whereas below the layer, the rate is lower for all aerosol models except the background case which gives a small increase in the O(¹D) production rate below the maximum aerosol concentration, due to increased scattering.

Photolysis of NO₂ produces NO, which is a key catalyst governing O₃ loss in the stratosphere. NO₂ is photodissociated at wavelengths less than 405 nm. The different aerosol models affect NO₂ photodissociation in much the same way as for O₃ photolysis (Fig. 16, third row). The above comments on the O₃ photolysis rate behavior therefore pertain to NO₂ as well.

4.4. Scattering by clouds and surface reflection

Stratified clouds were studied by Spinhirne and Green (1978), who found that penetration of ultraviolet radiation of wavelengths shorter than 300 nm is sensitive to absorption by tropospheric ozone. For wavelengths longer than 300 nm, penetration depends mostly upon cloud optical depth. This was confirmed by Thompson (1984), who considered photochemical production of ozone in an unpolluted troposphere. The effects of clouds on tropospheric photolysis rates were further studied by Madronich (1987a). Tsay and



Fig. 15. Comparison between measured and computed ratios of diffuse-to-direct spectral irradiance for cloud-free skies. The upper panels pertain to pre-Pinatubo conditions, while the bottom panels are for post-Pinatubo skies with stratospheric aerosol present, from Zeng *et al.* (1974).

Stamnes (1992) reported the effects of clouds and haze on UV penetration and photodissociation rates in the Arctic. Cloud effects have also been discussed by Lubin and Jensen (1995) and Estupinan *et al.* (1996).

Figure 17 shows the impact of clouds on photolysis rates for the same species as in Fig. 12 and 16 (Kylling (1992)). The cirrus cloud model is adopted from Shettle (1989) and the optical properties for water clouds are taken from Hu and Stamnes (1993). Cirrus clouds have an optical thickness near unity with little extinction at wavelengths important for photodissociation. O₃ photodissociation rates leading to O(³P) and O(¹D) are rather small. The same is true of cirrus clouds, as evidenced by the dotted lines in the first and second rows of Fig. 17. The 10% increase in the O₃ photodissociation rate seen above the cirrus cloud is due to reflection from the cloud. The surface was taken to be non-reflecting in these calculations. Assigning a non-zero value to the surface albedo allows the radiation to be reflected between the cloud and the surface, further increasing the photodissociation rate.

Water clouds are optically thick and efficiently scatter visible radiation. This is clearly seen in the upper row of Fig. 17. The effect of the low water cloud is similar to an increase in the surface albedo. For the $O(^{1}D)$ channel, the water cloud also gives an increased rate just above the cloud. Below the water cloud, the photodissociation rates for ozone are significantly reduced. The response of the NO₂ photolysis rate to cirrus and water clouds is similar to that of the O₃ photolysis rate leading to O(¹D).

UV and visible radiation at the surface depend strongly on surface albedo for clear as well as aerosolloaded and cloudy atmospheres. The UV albedo of snow may be as high as 94-97% (Blumthaler and Ambach (1988); Grenfell and Warren (1994)). Under



Fig. 16. The left column shows photolysis rates for ozone leading to the formation of $O({}^{3}P)$ labeled (O_{3}) , $O({}^{1}D)$ labeled (O_{3}^{*}) and NO_{2} for clear skies (solid line) and different aerosol loadings; background stratosphere (dotted line), moderate volcanic (dashed line), high volcanic (dashed-dotted line), and extreme volcanic (dot-dot-dot-dashed line). The right column shows the % difference between the clear sky and the different aerosol loadings. The surface was non-reflecting and the solar zenith angle = 30°. (After Kylling (1992)).

cloudy conditions, multiple reflections between the snow-covered surface and the atmosphere may lead to considerable increase in UV exposure. The contribution from the surface to the downward irradiance depends on the spherical albedo, which is the same as the flux reflectance for uniform illumination of the atmosphere from below (Stamnes (1982)). For a cloudy atmosphere this spherical albedo is large and gives rise to a nonlinear behavior of the downward irradiance as a function of surface albedo (Kylling et al. (1995)). This yields a much more pronounced dependence on surface albedo for cloudy than for clear atmospheric conditions. Shettle and Weinman (1970) showed that, because of multiple internal reflections between the high albedo snow surface below and the cloud layer above, the diffuse radiation in this region between the cloud and the surface can exceed the incident solar radiation for high solar elevation angles.

5. UV PENETRATION INTO THE BIOSPHERE

During the past few years several documents and workshops have considered the ramifications of ozone depletion on UV exposure in the biosphere. Scientific assessments have been published by the World Meteorological Organization (WMO (1989)) and the United Nations Environment Program (UNEP (1989)) followed by a 1991 update (UNEP (1991)). The U. S. Department of Agriculture (USDA) sponsored its first UV-B workshop in January, 1991. This workshop, which focused on the need to develop a cost-effective monitoring network (Gibson (1991)),



Fig. 17. The left column shows photolysis rates for ozone leading to the formation of $O({}^{3}P)$, labeled (O_{3}) , $O({}^{1}D)$ labeled (O_{3}^{*}) and NO₂ for clear skies (solid line) and an atmosphere with a cirrus cloud (dotted line) and a water cloud (dashed line). The right column shows the % difference between the clear sky situation and the different cloud cases. The surface was non-reflecting and the solar zenith angle = 30° (after Kylling (1992)).

was followed by another in March 1992 conducted jointly by the USDA and the Alternative Fluo-Acceptability rocarbons Environmental Study (AFEAS) to address measurement strategies aimed at providing UV-B climatology and determining trends of UV exposure over large geographical areas (Gibson (1992)). The Scientific Committee on Problems of the Environment held a workshop in Budapest in February 1992 (SCOPE (1992)), and the Committee for the National Institutes for the Environment (CNIE (1992)) convened a seminar in October concerned with ozone depletion and UV-B effects. In February 1993, the U.S. Department of Energy convened a multidisciplinary, multiagency workshop to investigate UV-B radiation issues essential to establishing an integrated program leading to a comprehensive understanding of changes in UV exposure and possible effects on biological systems (ONRL (1993)).

5.1. Introduction

The spectral distribution of solar radiation reaching the Earth's surface depends on the solar irradiance, the Sun-Earth distance, and the transmission and scattering properties of the atmosphere. As already discussed, the atmospheric transmission in the UV is strongly affected by changes in ozone abundance. Ozone responds to changes in solar UV irradiance and is perturbed by the release of anthropogenic trace gases, notably chlorofluorocarbons. Consequently, the available UV radiation at the surface reflects both natural and anthropogenic influences. The biological effect of UV radiation may be conveniently expressed in terms of the effective UV dose, defined as a convolution of an action spectrum with the irradiance spectrum. The dose rate and the total dose D are given by (e.g. Dahlback et al. (1989)):



Fig. 18. Action spectra for various biological responses (see text).

$$\frac{dD}{dt} = \int A(\lambda)\Phi(\lambda)d\lambda \tag{7}$$

$$D = \iint A(\lambda)\Phi(\lambda)d\lambda dt \tag{8}$$

where $A(\lambda)$ is the action spectrum of the particular biological response studied and $\Phi(\lambda)$ is the irradiance reaching the biosphere. The integrals are over wavelength, λ and time, t. Use of the irradiance in Equations 7 and 8 assumes that the radiation is received by a horizontally oriented plane surface and therefore is not equivalent to the actinic flux given by Equation 1. For some biological applications, such as the exposure of small "bodies" suspended in air or in water (e.g. phytoplankton in the ocean), it may be more appropriate to use the omnidirectional intensity or actinic flux instead of the irradiance. The importance of using realistic geometric representations of the human body in calculations of UV radiation received by the skin surface has been investigated by Dahlback and Moan (1990).

Four different types of action spectra are shown in Fig. 18: a generalized DNA damage spectrum (Setlow (1974)), a generalized plant damage spectrum (Caldwell *et al.* (1986)), a weighting spectrum for erythema (McKinlay and Diffey (1987)) and the response spectrum for the Robertson-Berger (R-B) meter (Robertson (1975)) designed to approximate the erythemal response of Caucasian skin.

In the remainder of Section 5, a brief review is provided of the current state of knowledge based on the reports mentioned above and the current research literature.

5.1.2. UV radiation received by the biosphere: present state of knowledge

Background. The penetration of solar UV-B radiation through the stratosphere is determined primarily by the total amount of stratospheric ozone. By comparison, stratospheric aerosols play a minor role in UV attenuation, although it has been established that particulate matter has profound effects on ozone chemistry (Solomon (1990)). On the other hand, large injections of volcanic emissions into the stratosphere can have noticeable effects on UV penetration (Section 4.3). In fact, stratospheric aerosols are expected to decrease UV-B penetration for high Sun and enhance it for low solar elevations (Davies (1993); Michelangeli et al. (1992); Tsay and Stamnes (1992); Tsitas and Yung (1996)). In the troposphere, UV attenuation is mainly due to molecular (Rayleigh) scattering, and scattering and absorption by aerosols and clouds. Shettle and Green (1974) showed that generally the effect of tropospheric aerosol particles is to slightly reduce the total radiation near the surface, with a significant decrease in the directly transmitted solar radiation partially offset by an increase in the diffusely scattered radiation. Ozone and other absorbing gases may also play an important role in tropospheric UV attenuation because the path length of photons is markedly enhanced (in comparison to the stratosphere) due to multiple scattering (Bruhl and Crutzen (1989); Tsay and Stamnes (1992)). Changes in tropospheric cloud cover can also significantly affect UV penetration; cloud cover variations are expected to influence UV-A and UV-B in much the same way.

Assessments of the time history of the local or global ultraviolet radiation environment have proven very difficult. Possible systematic temporal changes in atmospheric pollution and cloud cover at a given location, as well as great variations in aerosol content and cloudiness from one location to another contribute to the difficulty. Global-scale measurements of UV radiation reaching the surface of the Earth or penetrating to various levels in the ocean are rudimentary at best. One attempt to deal with the observational problem is the Robertson-Berger (R-B) meter network, described below. On theoretical grounds it is possible to assess the amount of UV radiation reaching the biosphere, assuming that we know the atmospheric ozone abundance, aerosol content and cloud optical depth. But global scale modeling usually involves the simplifying assumption that the ozone abundance is the only parameter that has varied in time and space.

UV penetration in the ocean is strongly influenced

by small plankton and thus by biological productivity, providing a close link between biological and optical occanography. Important aspects of the ozone depletion issue include the effects of UV enhancements on algae, plankton and fish larvae (Calkins (1976); Smith and Baker (1989); Cullen and Neale (1994)). Since plankton are believed to affect the atmospheric transmission as sources of atmospheric sulfur compounds involved in cloud formation (Charlson *et al.* (1987)), atmospheric radiative transfer and global ocean biology are also strongly linked.

5.1.3. Measurements. A UV monitoring project in the United States (the R-B meter network) has provided a long-term record on ultraviolet radiation at the Earth's surface. There are 8 stations in the R-B network covering a latitude region from 30.4 deg N (Tallahassee, Florida) to 46.8 deg N (Bismarck, North Dakota). Unfortunately, the R-B meter provides data in arbitrary units which cannot be converted into physical units. Furthermore, the data set obtained from the R-B-meter network is limited to a single broad spectral band obtained by weighting the spectrum by a response function designed to approximate the erythemal (sunburn) response of Caucasian skin.

Observations from the mid-latitude R-B network (Scotto et al. (1988)) show a slight downward trend in UV irradiance from 1974 to 1985. This trend appears to contradict the results of Watson et al. (1988) which imply an increase in UV irradiance expected as a result of ozone depletion. Proposed explanations for this discrepancy postulate that environmental factors other than ozone depletion may also be affecting UV penetration: (1) increased absorption of UV radiation in the troposphere may be due to enhanced abundances of absorbing gases and particulates at the locations of some of the R-B meters; (2) visibility observations indicate that since the Industrial Revolution, UV-B in the northern hemisphere may have decreased by 5 to 18% as a consequence of anthropogenic pollution (Liu et al. (1991)); (3) the observed increase in tropospheric ozone may lead to a decrease (rather than an increase) in UV penetration (Bruhl and Crutzen (1989)) due to the increased photon path length in the troposphere caused by multiple scattering. A more detailed analysis of the third mechanism shows that for high solar elevations, a decrease in UV-B penetration is expected, while an increase may instead result at low solar elevations (Tsay and Stamnes (1992)). Support for the proposed explanations may be found in the work of Blumthaler and Ambach (1990). They reported UV measurements with an R-B meter at high elevations in the Swiss Alps from 1981 through 1989 which showed a slight increase in solar UV radiation of about 1% per year

since 1981, in qualitative agreement with the reported ozone depletion of about 3% from 1969 to 1986 (Watson *et al.* (1988)). The fact that these measurements were made in the high mountains (3576 meters above sea level) argues that the discrepancy with Scotto *et al.* is indeed due to the influence of tropospheric aerosols and ozone.

Measurements of the UV spectral irradiance made with an absolutely calibrated double monochromator during the 1987 Arctic Summer demonstrated that the diurnal variation in the UV-B region was much stronger than in UV-A (by a factor 7 at 78 deg N at the end of July) (Stamnes *et al.* (1988); Henriksen *et al.* (1989)). These results show that diffuse radiation is the dominant component of the total irradiance in the ultraviolet part of the spectrum. The proportion of diffuse radiation is less at lower latitudes where the Sun is higher in the sky (see Fig. 11).

In the Antarctic, the spectral distribution of UV radiation reaching the surface has been measured with scanning spectrometers sponsored by the U. S. National Science Foundation and deployed at four stations: Amundsen Scott (South Pole), McMurdo Station, Palmer Station, and Ushuaia (southern Argentina). These instruments are double mono-chromators able to scan the solar ultraviolet spectrum from 290 nm to 400 nm with a resolution better than 1 nm. They are calibrated in absolute units and can thus provide irradiance measurements both for wavelengths less than 320 nm where absorption by atmospheric ozone is important and for longer wavelengths where ozone absorption is negligible.

Evidence for the Antarctic "ozone hole" is seen in the data from the Palmer Station (65 deg S). For example, the Austral Spring 1988 data show that irradiances at wavelengths shorter than 310 nm measured in October often equaled or exceeded values measured through Summer solstice (Lubin et al. (1989); Lubin and Frederick (1991)). By comparison, measurements taken at McMurdo Station (78 deg S) showed only a 20% enhancement in biologically effective UV dose during October, 1988 over March, 1989. However, the measured UV radiation levels at McMurdo were substantially more severe in 1990 with UV radiation levels in October exceeding the solstice value by a factor 1.5 for a ten day period. A threefold enhancement (compared to the "normal" value) of the daily integrated daily dose of UV radiation was measured at the surface (Stamnes et al. (1992)). Both the spectral measurements in the Arctic (Henriksen et al. (1992)) and those in Antarctica (Lubin (1989); Stamnes et al. (1990)) show that cloud cover provides substantial attenuation of UV radiation as well as large day-to-day variability. Routine spectral data

such as these would greatly alleviate the problem of identifying ozone-related UV-B trends and discriminating such trends from effects due to natural cloud variability (Stamnes *et al.* (1991)). Such discrimination will be very difficult if only spectrallyintegrated data such as those provided by the R-B meters are available. However, it has recently been demonstrated that such discrimination is also feasible with narrow-band filter instruments having two or more spectral channels in the UV (Dahlback (1996)).

Mid-latitude. Southern Hemisphere spectral measurements similar to those described above were reported recently by Bittar and McKenzie (1990). These measurements were obtained during two separate campaigns eight years apart, yet similar ozone amounts were detected. No change was found in the UV radiation between the measurements in 1980 and 1988, but more data are obviously required to establish a climatology of UV irradiance. Finally, at other mid-latitude locations in the Southern Hemisphere increases in UV-B have been observed in connection with intrusions of ozone-depleted air from Antarctica. High UV-B levels in Melbourne Australia have been associated with air coming from the Antarctic "ozone hole" in late 1987 after the Spring break-up of the Antarctic vortex (Roy et al. (1990)).

Recent UV measurements in Europe include those reported by Bordewijk *et al.* (1995); Blumthaler *et al.* (1996); Grobner *et al.* (1996); Krzyscin (1996); Mayer *et al.* (1997); Müller *et al.* (1995a); Seckmeyer and McKenzie (1992); Slaper *et al.* (1995, 1996); Variotsos *et al.* (1995). Measurements in the United States and Canada have been reported by Bodhaine *et al.* (1996); Herman *et al.* (1996); Justus and Murphey (1994); Kerr and McElroy (1994); Michaels *et al.* (1994); Schafer *et al.* (1996). Recent results from the Southern Hemisphere have been reported by Diaz *et al.* (1996); McKenzie *et al.* (1996); McMinn *et al.* (1994).

5.1.4. Model computations. Frederick and Lubin (1988) used a radiative transfer model to study the effect of varying ozone abundance and cloud cover on UV transmission. They showed that increased levels of UV-B radiation may be the result of not only an ozone depletion, but also a decrease in cloud cover. The computed effects of an ozone layer depletion on biological UV-doses have also been investigated by Dahlback et al. (1989). The UV-dose was computed from Equation 8 using the action spectrum for erythema shown in Fig. 18. The calculated annual effective UV-dose varies by approximately 4% per degree in latitude in the northern hemisphere as can be seen in Fig. 19. The annual effective dose at 60 deg N is shown in Fig. 20 as a function of ozone depletion. The percent increase in UV dose per percent decrease in



Fig. 19. The annual effective UV-dose as a function of the geographical latitude in the Northern Hemisphere. The curve refers to sea-level elevation. In this calculation the zonal averages of the ozone layer throughout the year have been used. The latitude position for different places is indicated. The dose for 60° N is set equal to 100 (after Dahlback *et al.* (1989)).



Fig. 20. The annual effective UV-dose at 60° N as a function of the ozone depletion (logarithmic scale). The annual UVdose, with normal ozone conditions throughout the year, is set equal to 100. The inset exhibits the dotted area with the dose axis enlarged and given on a linear scale. The annual UV-dose for a latitude of 40° N (Mediterranean countries, California) and countries along the Equator, with normal ozone conditions, are indicated by Mallorca and Kenya, respectively (after Dahlback et al. (1989)).

ozone abundance is commonly referred to as the radiation amplification factor. For small ozone depletions (less than 5%) the annual UV-dose increases with an amplification factor close to 1.0. For larger ozone depletions the increase in annual UV-dose is enhanced, i.e. the curve becomes non-linear. Thus, according to Fig. 20, a 10% depletion yields a 11.7% increase in UV-dose, and a 20% depletion a 25.7% increase. These values are smaller than those reported previously (e.g. Cutchis (1974)), primarily because previous calculations considered only the region 290 to 330 nm, whereas the investigations by Dahlback et al. (1989) and Frederick et al. (1989) extended to 400 nm. Since the DNA action spectrum (Fig. 18) falls off quite sharply with wavelength, this spectrum will yield a larger amplification factor than the erythema action spectrum. An amplification factor near 2 has often been adopted implying that one percent decrease in ozone gives rise to a 2% increase in UV dose. Such a value is obtained for the DNA action spectrum for typical mid-latitude solar zenith angles and changes in ozone of 10% or less (Setlow (1974)), but the response of humans and animals to UV radiation is perhaps more properly described by the erythema action spectrum (Frederick et al. (1989)). Hence, the amplification factor will depend on the particular type of biological response considered as well as on latitude and season.

The impact of clouds on UV penetration to the ground was first investigated by Nack and Green (1974). Later Spinhirne and Green (1978) noted that while cloud spatial structure and temporal variability make realistic modeling very difficult, the assumption of uniform cloud cover could provide a useful description over a time period long compared to that of daily fluctuations in cloudiness. Recently, the role of clouds on solar UV penetration was investigated by Frederick and Snell (1990), who remark that increased cloud cover over some locations may occur even if global annual mean cloudiness were to remain constant. They used this observation to infer that at such locations, the change in erythemal dose due to changes in cloudiness could be comparable to that from trends in column ozone. Stamnes et al. (1990) used the spectral irradiance measurements taken at McMurdo Station to determine cloud transmission by comparing the measured irradiance to the anticipated clear sky value at a wavelength for which ozone absorption is minimal. Computed irradiance for stratified clouds of a variety of optical depths was compared to the observed irradiance and used to infer the "equivalent" stratified cloud optical depth which produced agreement between the computed irradiance and the observed value.

6. DIRECT MEASUREMENT OF ATMOSPHERIC PHOTOLYSIS FREQUENCIES

6.1. Background

Photochemical reactions provide the driving force for much of the chemistry in the stratosphere and troposphere. Photolysis frequencies or "J values" are the first order rate coefficients of dissociation processes which can be calculated according to Equation 5. Uncertainty in absorption cross sections and quantum yields of atmospheric species as functions of wavelength and temperature can lead to large uncertainties in calculations of photolysis frequencies. Development of instrumentation for direct measurement of photolysis frequencies in the troposphere and the stratosphere will be critical to our understanding of global atmospheric chemistry (Albritton *et al.* (1990)). Several examples of important photolysis reactions for which accurate determinations of photolysis frequencies are required, are described below.

Stratospheric ozone production rates are controlled by the photolysis of molecular oxygen to oxygen atoms (see Section 3.2) and subsequent reaction of those atoms with oxygen molecules to form ozone:

$$O_2 + h\nu \rightarrow O({}^3P) + O({}^3P)$$

$$O({}^3P) + O_2 + M \rightarrow O_3 + M.$$
(9)

Current photochemical models are in conflict, either over- or under-predicting measured ozone concentrations at different levels in the stratosphere. As discussed in Section 3, calculations of oxygen photolysis rates are difficult due to the highly structured absorption cross section of oxygen in the O₂ Schumann-Runge bands coupled with the highly structured solar spectrum. In situ measurements of J_{O2} in the stratosphere will help refine modeling of stratospheric ozone.

The oxidizing capacity of the atmosphere is controlled in large part by the hydroxyl radical concentration. Photolysis of ozone producing $O(^{1}D)$, and its subsequent reaction with water vapor to form two hydroxyl radicals, is the dominant source of OH in the troposphere:

$$O_3 + h\nu \rightarrow O(^{\dagger}D) + O_2$$

$$O(^{\dagger}D) + H_2O \rightarrow OH + OH.$$
(10)

As noted in Section 3.2.4, the accuracy of the calculation of ozone photolysis rates is decreased by absorption cross section and quantum yield uncertainties as functions of temperature and wavelength. Tropospheric measurements of J_{O3} along with simultaneous measurements of O_3 and H_2O concentrations can be used to calculate the OH production term for tropospheric modeling. Further, depletion of stratospheric ozone could cause an increase of tropospheric ultraviolet radiation which, in turn, would enhance both the photolysis of ozone and the production of hydroxyl radicals.

Atmospheric photodissociation of NO₂ is a key

reaction which determines the partitioning of NO_x components (NO and NO₂), the photostationary states of O₃, NO₂, and NO, and the photochemical generation of tropospheric ozone. The rate of NO₂ photodissociation J_{NO2} therefore is important in all models of chemistry of the atmosphere.

As discussed in Section 4, calculations of the actinic flux can have significant uncertainties due to the highly variable nature of the scattering properties of clouds and aerosols. Madronich (1987a) concluded that because of the intricate and relatively untested nature of these calculations, total uncertainties in theoretical $J_{\rm NO2}$ values may be significantly higher than the error introduced from the molecular data alone. Direct actinometric measurements of atmospheric photolysis rates can eliminate cross section, quantum yield, aerosol, albedo, and cloud uncertainties. Other measurements in conjunction with photolysis frequency measurements will add to understanding the photochemical cycles and will help validate atmospheric modeling efforts in stratospheric ozone depletion, in the oxidizing capacity of the atmosphere, and in radiative transfer calculations.

6.2. Status of measurements

Because direct measurements of photolysis frequencies are complicated and difficult, we review experimental approaches in some detail in this section. Careful planning of measurements is essential to ensure that they are representative of true atmospheric photolysis frequencies. For complete specification, photolysis measurements need to include contributions from direct sunlight, scattered light from molecules, aerosols, and clouds, and ground albedo. However, ground based measurements usually measure only the downwelling radiation and make corrections for surface reflections. The three principal instrumental systems in use to determine photolysis rates *in situ* are chemical actinometers, filter radiometers, and spectroradiometers.

6.2.1. Chemical actinometers. Chemical actinometers have been used since the mid-1970's to measure photolysis frequencies of NO₂ (Jackson *et al.* (1975); Harvey *et al.* (1977); Zafonte *et al.* (1977); Bahe (1980); Dickerson *et al.* (1982); Parrish *et al.* (1983); Madronich *et al.* (1984); Madronich *et al.* (1985); Shetter *et al.* (1992)), and photolysis frequencies of O₃ since the late 1970's (Bahe and Schurath (1978); Bahe *et al.* (1979); Dickerson *et al.* (1982); Blackburn *et al.* (1992); Bairai *et al.* (1992); Shetter *et al.* (1996)). Some photolysis frequencies of organic nitrates have also been measured (Luke *et al.* (1989)). A typical flowing chemical actinometer consists of: 1) an apparatus to generate a known flow, pressure, and concentration of the gas of interest, 2) a photolysis cell of known volume for exposing the gas to ambient sunlight, and 3) a way of detecting products of the photolysis. Post photolysis reactions in the gas stream of the species to be detected must be minimized and taken into account in the photolysis frequency calculations. Photolysis cells for most ground based chemical actinometers consist of a cylindrical quartz tube mounted over a nonreflecting surface. Through cancellation of external and internal reflections of incident light, and a small correction for the tube end cross section, long cylindrical tubes can closely approximate true hemispherical light collectors. In chemical actinometers with properly designed photolysis cells, a molecule of gas within the cell will absorb a photon of light equally from 0 or 90° zenith angle as does a molecule in the atmosphere. This requirement is particularly important because a large portion of the effective radiation can come from diffuse radiation rather than the direct beam, depending on the wavelength range of the photodissociation process. Optical properties of such cylindrical tubes have been described in detail by several investigators (Zafonte et al. (1977); Dickerson and Stedman (1980)).

Photolysis of NO₂ (at wavelengths < 397.3 nm) proceeds according to:

$$NO_2 + hv \rightarrow NO + O(^{3}P)$$
. (11)

Knowing the starting NO₂ concentration, gas flow, pressure, cell volume, and the concentration of the NO produced, the photolysis frequency, J_{NO2} , at a given time can be calculated assuming low NO₂ conversions. The appropriate expression is:

$$J_{\mathrm{NO}_2} = \frac{[\mathrm{NO}]}{[\mathrm{NO}_2]_{\mathrm{o}} \Delta t} , \qquad (12)$$

where [NO] is the concentration of NO produced from photolysis, $[NO_2]_0$ is the starting NO₂ concentration, and Δt is the photolysis time calculated from the flow rate, cell volume, and cell pressure. The NO concentration can be determined by the standard technique of low pressure NO chemiluminescence with ozone.

The absolute sensitivity of a J_{NO2} actinometer can be measured directly by the addition of NO calibration gas to the photolysis cell gas stream. Background signal levels are determined by covering the photolysis cell to occlude any ambient radiation.

Most extant actinometric NO_2 photolysis frequency measurements have been made at ground level (0-3 km altitude), with the exception of some aircraft measurements up to 7 km (Dickerson et al. (1982)) and a few balloon flights in the stratosphere at 24 and 32 km (Madronich et al. (1985)). Ground level observations usually need little correction for albedo since the albedo of the non-reflecting surfaces used beneath photolysis tubes can closely approximate the albedos of grass, black lava, and asphalt at measurement sites (Harvey et al. (1977); Shetter et al. (1992); Shetter et al. (1996)). However, measurements taken from aircraft and balloon actinometers may require large corrections to obtain spherically integrated photolysis rates. This issue was addressed by Madronich (1987b), who provided a theoretical estimate of the upwelling radiance in order to complement stratospheric measurements of J_{NO2} obtained solely from the downwelling component.

Measurement of the photolysis rate of ozone is more complicated than J_{NO2} due to the fact that molecular scattering of UV-B radiation is much more effective than scattering of UV-A radiation. At least 60% of the actinic radiation available for J_{O3} near the Earth's surface is due to scattered radiation while less than 20% of the actinic radiation for J_{NO2} is scattered. For clear skies the relationship between irradiance and actinic flux for direct radiation is straightforward while for diffuse radiation is quite complex. This makes calculations of actinic flux from measured irradiance in the UV-B extremely difficult. Field techniques for direct detection of O(¹D) produced from photolysis of O₃ have not proven feasible because deactivation of O(¹D) takes place within cells. Alternatively, O(1D) can be detected indirectly by introducing N₂O and subsequently measuring one of the products of the following sequence of reactions:

$$O(^{1}D) + N_{2}O \rightarrow N_{2} + O_{2}$$

$$\rightarrow NO + NO$$

$$NO + O_{3} \rightarrow NO_{2} + O_{2} . \qquad (13)$$

$$NO_{2} + O_{3} \rightarrow NO_{3} + O_{2}$$

$$NO_{2} + NO_{3} \rightarrow N_{2}O_{5}$$

Investigators have used detection of N₂ (Bahe *et al.* (1979)), NO (Dickerson *et al.* (1982)), NO₂ (Bairai *et al.* (1992)), and N₂O₅ (Blackburn *et al.* (1992); Shetter *et al.* (1996)) as surrogates for O(¹D). To quantify the O(¹D) concentration from the measurement of product molecules, one must know the branching ratio for the O(¹D) + N₂O reactions given above. The recommended value for the ratio of the (N₂+O₂)/(N-O+NO) reaction rates is 0.73 ± 0.22 (DeMore *et al.* (1994)). Greenblatt and Ravishankara (1990) and Cantrell *et al.* (1994) report ratios of 0.73 ± 0.07 and 0.75 ± 0.07 , respectively, with a factor of three better

accuracy than can be calculated from the error limits in DeMore *et al.* (1994).

6.2.2. Filter radiometers. Filter radiometers have been in use since the early 1970's to determine J_{NO2} , and more recently to determine J_{O3} . A typical instrument is comprised of three parts: a light receiver, bandpass filter, and detector (phototube or photomultiplier). Ambient radiation collected by the receiver and passed through the filter is detected, giving an output signal that has a very fast time response $(\ll 1 s)$. The better the wavelength transmission of the filter matches the photolysis spectrum $\sigma(\lambda) \cdot \phi(\lambda)$ of the respective molecule (Equation 5), the better the correlation of output signal with the photolysis frequency J. Nevertheless, the key component of a filter radiometer designed for J measurements is the light receiver whose collection efficiency should be independent of the direction of the incoming photons. The most successful approach has been the combination of frosted hemispheric domes, quartz grains, and quartz rods (Junkermann et al. (1989); Hofzumahaus et al. (1992); Brauers and Hofzumahaus (1992); Müller (1994); Müller and Hofzumahaus (1997)). Two of these hemispherical $(2\pi \text{ sr})$ instruments can be combined as a fully spherical $(4\pi \text{ sr})$ system.

For J_{NO2} filter radiometers, the correlation of the output signal to the actual photolysis frequency is only weakly dependent on ambient conditions. Hence, for most cases J_{NO2} can be obtained by multiplying the radiometer signal by a constant calibration factor. This calibration factor can be determined either by a laboratory characterization using calibrated UV lamps, or by a field intercomparison to a chemical actinometer. Recently Volz-Thomas *et al.* (1996) used filter radiometers with hemispherical collectors to determine the photolysis frequency of NO₂ from an aircraft platform. Results compared well with modeled NO₂ photolysis frequencies.

For J_{O3} filter radiometers the situation is more complicated since the correlation of the output signal to the actual photolysis frequency varies strongly with ambient conditions, including temperature, solar zenith angle, ozone profile, and aerosol profile. If a constant proportionality factor is used to calculate J_{03} from the instrument's output, large deviations from the true values can occur (Shetter et al. (1996)). Hofzumahaus et al. (1992), Müller (1994), and Müller and Hofzumahaus (1997) have developed methods to compensate for nonlinearities between output signal and J_{O3} , based on a discrete ordinate radiation transfer code parameterization of the ratio of output signal to J_{03} . This method takes advantage of the convenient properties of filter radiometers for field measurements, but it does require knowledge of the ozone column density at the measurement site. Filter radiometers for J_{03} can be calibrated using either radiometric techniques in the laboratory or field comparisons to a chemical actinometer.

A summary of J_{03} measurements made with actinometers as well as a filter radiometer equipped with a hemispherical light receiver was made by Hofzumahaus *et al.* (1992). After correcting for slant ozone column, zenith angle, temperature coefficient, branching ratio, and aerosol loading, the agreement was found to be $\pm 5\%$ for all but one investigator. However, this agreement may be fortuitous since the 1σ calibration error of the radiometer was 26% and the actinometers between $\pm 10\%$ and $\pm 30\%$.

Intercomparisons of simultaneous measurements of a J_{03} actinometer and filter radiometer (Junkermann *et al.* (1989)) have been made by Shetter *et al.* (1996). Using approximately 90 days of clear sky data between 1000 and 1400 local solar time, the ratio between the actinometer and filter radiometer results was ~ 1.1 ± 0.03 . If data for all sky conditions and local solar times are included, the range of actinometer/radiometer ratios degraded to between 0.7 and 1.2.

As was pointed out above, radiometers designed for measurement of ambient photolysis frequencies must detect the incoming radiation with spatially uniform sensitivity. However, most optical radiometers deployed for atmospheric measurements so far use a flat plate receiver, which has a response function proportional to the cosine of the solar zenith angle. Under clear sky conditions, the output signal will also contain the cosine response for the direct beam radiation. But when clouds or aerosols are present, the angular distribution of the ambient radiation is a function of the local cloud and aerosol conditions. Use of flat plate receivers for photolysis frequency measurements usually leads to large errors when varying amounts of direct and diffuse radiation are present. Therefore, these instruments can properly be used only for measurements of the ambient irradiance. Currently, accurate algorithms to transform measured irradiance into actinic flux do not exist for many atmospheric conditions.

However some investigators have attempted to relate commercial flat plate filter radiometer measurements to J_{NO2} actinometer measurements by intercomparison and by use of theoretical calculations (Parrish *et al.* (1983); Madronich (1987b); Shetter *et al.* (1992)). The radiometers were Eppley UV devices that contain flat, opaque diffuser plates and are sensitive to 295-385 nm radiation (peak response near 340 nm). Madronich (1987b) derived the following equation using clear sky data from seven experimental studies to estimate directly J_{NO2} from the UV irradiance measured with an Eppley radiometer:

$$J_{\rm NO_2} \cong \frac{1.35E}{(0.56 + 0.03z)\cos\chi_0 + 0.21}$$
(14)

where z is the station height above sea level (in km), χ_{o} is the solar zenith angle (<60°), and E is the UV flux (in W cm⁻²). This equation can be applied with negligible local albedo and moderate regional albedo. (Note that Chameides et al. (1990) slightly revised Equation 14 by including a second order altitude correction.) Madronich found the accuracy of ideal clear sky J values using this equation is $\pm 5\%$; but the accuracy depends on frequent calibration of the radiometer, preferably with an actinometer. Independent comparison of Eppley radiometer and actinometer data from Mauna Loa using the Madronich (1987b) clear sky relationship found agreement to approximately $\pm 10\%$ for clear skies and $\pm 20\%$ with scattered clouds (Shetter et al. (1992)). Shetter et al. concluded that where greater accuracy is required, the direct actinometric measurement of J_{NO2} is necessary.

6.2.3. Spectroradiometers. Recently Müller et al. (1995b) and Shetter et al. (1997) have developed spectroradiometers that employ hemispherical light collectors to determine actinic flux as a function of wavelength. The actinic radiation collected by the hemispherical collector is transferred via fiber optic bundle to a double monochromator and measured as a function of wavelength from 280 nm to 420 nm with a low dark current photomultiplier. Data from these spectroradiometer systems can be used to calculate photolysis frequencies of all molecules whose absorption falls in the spectral range sampled. The systems are calibrated for wavelength with reference lines from a mercury discharge lamp. The sensitivity as a function of wavelength is determined for the entire system using a calibrated UV lamp.

As discussed earlier, calculation of photolysis frequencies requires accurate absorption cross section and quantum yield data. Intercalibration with chemical actinometers, which do not rely on molecular parameters, could help to validate the molecular data. Müller *et al.* (1995b) intercalibrated the ground based spectroradiometer with a static actinometer for J_{O3} based on the work described by Junkermann *et al.* (1989). They concluded the ozone quantum yields of 0.2 to 0.3 in the 315 to 320 nm range reported by several authors (Brock and Watson (1980) and Michelsen *et al.* (1994)) are correct. The work of Shetter *et al.* (1996) also supports the long wavelength quantum yields. Their conclusions and subsequent recommendation were based on comparison of actinometric and modeled clear sky data J_{O3} from the MLOPEX 2 study, and a literature review of data.

Shetter *et al.* (1997) recently developed dual spectroradiometer systems for measurement of total actinic flux from aircraft platforms. These instruments determine the downwelling and upwelling components of the actinic flux independently. Ground based intercomparisons with existing chemical actinometers for J_{NO2} and J_{O3} are currently in progress.

7. CONCLUDING REMARKS

7.1. Solar spectral irradiance

Solar spectral irradiance is indeed variable. These variations can influence the terrestrial environment, including ozone and the middle atmosphere, at levels that are comparable to anthropogenic forcing over time scales of years, decades and centuries. Since future solar spectral irradiance levels cannot yet be reliably predicted, continued solar monitoring is essential into the foreseeable future. Without this monitoring, it may not be possible to verify that increases in ozone concentrations in the early 21st century (Jackman *et al.* (1996)) herald the recovery of anthropogenically-depleted levels rather than natural variability caused by solar forcing.

Because of the lack of absolute accuracy of current monitoring instruments, consecutive solar irradiance data sets must overlap for a sufficiently long time to enable transfer of calibration with the precision needed in the long term database. Thus, to retain the historical value of the UARS database, overlap with future measurements is critical. However, this is very unlikely: a SOLSTICE instrument was planned for flight on the Earth Observing System (EOS) CHEM2003 platform, but has since been removed and is awaiting a flight of opportunity. In principle the SOLSTICE UARS and EOS measurements should be directly intercomparable by virtue of their calibration of stars. SBUV-type instruments on NOAA operational satellites are unlikely to provide useful solar irradiance data during the next decade because, coupled with instrument malfunctions, inflight calibration is inadequate to define changes in wavelength registration and end-to-end response changes. No ultraviolet spectral irradiance measurements are planned beyond EOS during an epoch when assessment of natural and anthropogenic ozone trends will nevertheless be essential. Lacking post-EOS spectral irradiance measurements the planned NPOESS monitoring of broad band 200-300 nm irradiance, commencing early in the twenty first century, is imperative.

A small solar irradiance variability satellite if launched in the next five years or so, could provide the required overlap between UARS and EOS, and validate the SOLSTICE stellar calibration approach for future use. A programmatic commitment to long term solar spectral irradiance monitoring is needed to ensure an adequate long term database for global change studies. The needs for atmospheric research are for long term monitoring of broad spectral bands with high radiometric stability, augmented by measurements with high spectral resolution. Ideally, building on the UARS experience and utilizing new techniques to construct smaller, less costly instruments with improved accuracies and in-flight responsivity monitoring, would help to maximize future flight opportunities for solar irradiance monitors and the opportunity to build the required long term solar irradiance database.

7.2. Transmittance of direct solar irradiance through the atmosphere

Characterization of the molecular spectroscopy governing the penetration of UV solar irradiance into the stratosphere has improved significantly during the last decade. The absorption of solar UV irradiance and subsequent photodissociation of molecular oxygen provide the primary source of odd oxygen in the atmosphere. The dissociation products rapidly combine, forming both ozone and a host of radical species, some of which are involved in the catalytic destruction of ozone. The oxygen polymers (O_2 and O_3), in concert with atmospheric scattering, control almost completely the depletion of solar irradiance into and through the stratosphere. However, the prediction of local irradiance is not a solved problem. In particular, additional laboratory, in situ, and theoretical investigations are still required to resolve remaining discrepancies.

Laboratory investigation of the S-R continuum temperature dependence near the S-R band head at 175 nm must be undertaken because of its potential influence at the mesopause (Fig. 1). In one widely quoted example, Roble and Dickinson (1989) suggested that the mesosphere/thermosphere temperature profiles and photochemistry are quite sensitive to anthropogenic greenhouse gas enhancements. Further work should also focus on the appropriate line shape for the far wings of S-R bands, as well as predissociation widths for the weak (0-0) to (2-0) progressions (Cosby *et al.* (1993)), the higher vibrational bands (19-0) to (22-0), and the rotational and finestructure dependence of line widths (e.g. Lewis *et al.* (1994)). Some initial studies using laser spectroscopy over very narrow ranges may help resolve the issues, but the composite of continua, far wings, and line centers must be modeled consistently for the whole system. The question of asymmetric (Fano) line profiles and far wing cross sections in the S-R bands need further consideration. While it is unlikely that details of the individual line shape will be critically important to subsequent parameterizations for aeronomic use, improvements in the modelling of the far wings may have some significance (Lewis and Gibson (1992)). Finally the photochemical impact of reduced O_2 absorption in the Herzberg continuum region (viz., Amoruso *et al.* (1996)) requires further investigation.

Improved knowledge of the spectrally and thermally variable form of the Schumann-Runge and Herzberg continua and bands does not, however, guarantee the availability of efficient tools required for photochemical modeling. Not only has an objective benchmarking of the relative performance of recent S-R band parameterizations not been done, none of the methods described to date can explicitly accommodate the variation in transmission and photolysis arising from changes in temperature throughout the atmosphere. The error in neglecting temperature effects is typically on the order of 10 to 15%, (Anderson et al. (1992)). However in some cases such as the photolysis of NO which depends on penetration of radiation in a narrow S-R window region, the error can approach 25% (Minschwaner and Siskind (1993)).

As the impact of UV-B becomes of greater concern, the ozone Huggins band temperature parameterization should be reexamined. The measured temperature dependences of both the Huggins and the Chappuis bands do not cover the coldest temperatures encountered in the atmosphere, notably the 180 K occurring in the winter stratosphere, and the 130 K extreme occasionally found at the summer mesopause in the polar regions. Also, tropospheric scattering processes for low Sun and Arctic haze conditions will require a more optimal approach for modeling attenuation due to the Huggins bands. This impacts the biosphere and its sensitivity to increased UV radiation (UNEP-WMO (1991); Cullen *et al.* (1992); Quaite *et al.* (1992); Tevini (1993); Cullen and Neale (1996)).

The dearth of *in situ* measurements of the attenuated solar irradiance must be remedied. Only field measurements can validate both high spectral resolution transmission model calculations of irradiance and spectrally-degraded energy deposition parameterizations. The balloon probably remains the platform of choice to measure both the direct irradiance and the scattered component in the stratosphere. It is important to make measurements for conditions of low ozone levels, particularly in the Antarctic. Because of the expense of instruments and campaigns, the development of smaller low resolution spectrometers might prove useful for routine measurements once high resolution extinction of the solar irradiance has been completely understood.

Of particular concern is the atmospheric transmittance window at 200 nm (see Fig. 1 and 7). Unmanned high altitude aircraft reaching to 20-25 km can provide an opportunity for measuring both integrated and direct irradiance. But at 200 nm the optical depth to the Sun from 20 km is approximately 2-3 for high Sun conditions, about 9 for a 65° solar zenith angle and about 7 under conditions of the Antarctic ozone hole. Thus the unmanned vehicle is only a marginally viable platform for the 200 nm window region, e.g., for high Sun conditions, but it is certainly suitable for observing the irradiance, actinic flux, and up- and down-welling radiances at longer wavelengths.

7.3. Diffuse (scattered) radiation

In view of the importance of the diffuse actinic radiation field for driving the photochemistry of the atmosphere there are surprisingly few measurements against which models can be compared and evaluated. It would be very helpful to have ground-based measurements of the zenith sky intensity and simultaneous satellite measurements of the nadir intensity. These measurements should be made with wellcalibrated spectrometers covering the wavelength range, 280 to 400 nm from the ground, and 170 to 400 nm from space. Together with similar measurements of the direct solar irradiance above the atmosphere (see Section 2), strong constraints could be placed on models of the radiation field. In principle, this experiment could be carried out with groundbased SBUV-like instruments which have been cross calibrated with those flying on NOAA satellites. In situ observations of the actinic radiation within the lower and middle atmosphere itself from suitable platforms (airplanes, rockets, and balloons) made in conjunction with the above measurements from the ground and from space would also be highly desirable. These measurements would be most useful if the atmospheric constituents affecting the radiation (such as trace gas abundance, aerosol content, and cloud properties) were measured simultaneously. The surface albedo should be also measured at ground-based sites.

As mentioned in Section 4.1, a number of models of the diffuse radiation field are now available. These have been developed with varying degrees of approximation. Unfortunately, few intercomparisons of these models have been made. Such intercomparisons should be undertaken so that differences among the models can be identified and resolved.

Measurement of the zenith (and nadir) sky radiation with a narrow field-of-view instrument should to some extent alleviate the problem associated with the cosine response of irradiance detectors. It is wellknown that measurements of net flux (defined as the difference between upward and downward flux) and flux divergence are fraught with difficulties in spectral regions with little absorption. The flux divergence which is proportional to energy deposition is usually obtained by differentiating the net flux at two nearby levels in the atmosphere. If there is little absorption, the difference in the net flux is small and therefore is difficult to measure accurately. It is also a non-trivial task to convert irradiance measurements into the diffuse component of the actinic flux. This conversion requires assumptions and/or models for the angular distribution of the diffuse radiance. Spherical probes that measure the mean intensity directly (as a function of wavelength) would be highly desirable for model validation. Some results from broad-band probes have been reported (Hänel et al. (1982); Busen and Hänel (1984); Hänel (1984)). More recently a photoelectric detector for the measurement of photolysis frequencies was developed which has uniform response characteristics over one hemisphere (Junkermann et al. (1989)). This instrument has been used to measure photolysis frequencies of ozone leading to the formation of O(¹D) (Hofzumahaus et al. (1992); see Section 6)

Upward looking and downward looking commercial flat plate filter radiometers have been flown on research aircraft. Converting data from these radiometers into accurate photolysis rates is quite difficult due to limited knowledge of albedo and cloud radiative transfer considerations. Current radiative transfer models (Madronich (1987b)) estimate actinic flux enhancements as much as factors of 3-5 over clear sky values in clouds and a factor of two above clouds, with the exact amount depending sensitively on the solar zenith angle and the relative amounts of incident diffuse and direct radiation. Such enhancements would have dramatic effects on photochemistry in clouds. Aircraft with upward and downward looking actinometers flying in, above, and under clouds are needed to refine the radiative transfer calculations and contribute to the understanding of cloud chemistry. These types of model validation studies are critical to the understanding of the role of clouds and aerosols on photochemistry.

The computational techniques for assessing the

actinic radiation environment are sufficiently advanced that it is difficult to make further progress in the absence of the above-cited measurements. Although additional validation is needed, current models of the actinic flux can be used for predictions of the actinic radiation in stratified atmospheres, provided the input parameters such as aerosol loading and vertical distribution are known. For horizontally inhomogeneous atmospheres, the situation is much less satisfactory. Theory and measurement must proceed in parallel. While theoretical models can provide guidance for the measurements, the observations in turn, are needed to provide insight for future directions of computational efforts in resolving uncertainties in the diffuse actinic radiation field.

7.4. UV penetration into the biosphere

7.4.1. *Measurements*. In view of the potentially harmful biological effects of increased levels of UV radiation at the Earth's surface and in the oceans, a global monitoring program is urgently needed. Such a monitoring program should satisfy the following requirements:

- Observations of solar variations (both from space (see Section 7.1) and at the surface) with a precision of 1% over at least a full solar cycle are needed to discriminate between natural changes and anthropogenically induced perturbations in stratospheric composition.
- The spectral distribution of the UV radiation from which appropriate UV-doses can be derived, should be monitored by a network of properly chosen stations around the globe. The monitoring should be extended into the visible spectral region because absorption in the O₃ Chappuis band is significant, and because the relative variations between UV-B, UV-A, and photosynthetically active radiation in the 400 to 700 nm range can be biologically important (e.g. Smith and Baker (1989)). In view of the potential for an Arctic ozone depletion, this network should contain adequate high latitude circumpolar coverage in the northern hemisphere as well as in the southern hemisphere.
- The spectral resolution should be sufficient to provide simultaneous measurement of column ozone abundance and biologically relevant UV radiation. The measurements should also be capable of quantifying the influence of other environmental parameters on biospheric UV radiation levels such as cloud cover, atmospheric aerosols and gaseous absorbers related to anthropogenic pollution.
- Supporting measurements aimed at establishing the

vertical distribution of ozone (including the tropospheric component) and aerosols of anthropogenic and natural origin (including volcanic eruptions) are desired to quantify the extent to which aerosols and tropospheric ozone may dampen or amplify the effect of stratospheric ozone depletion on UV-B radiation reaching the biosphere. Estimates of these effects should be given when trends in UV radiation at the ground due to stratospheric ozone depletion are computed.

• The penetration of ultraviolet and visible light into the ocean must be measured for a variety of ocean conditions including biologically productive waters. This is very important because the ocean is a major source of food and marine ecology is sensitive to the spectral distribution of light. In fact, plankton, algae and fish larvae are present in the upper layer of the ocean and are therefore sensitive to changes in the light levels, in general, and vulnerable to increases in the UV component associated with ozone depletion, in particular.

Such a measurement program would provide a direct link between biological UV dose, photosynthetically active radiation, atmospheric ozone abundance, aerosol loading, and cloud cover, a link which is currently lacking and is of crucial importance for progress in this arca.

7.4.2. Modeling. The ability to predict UV penetration through a stratified medium is limited at present primarily by our knowledge of the optical properties of the medium. Cloud optical thickness is currently the most poorly known atmospheric parameter. As well, idealized one-dimensional radiative transfer models become invalid with the presence of broken clouds. The treatment of such horizontal inhomogeneities requires more attention through the development of fully three-dimensional radiation models. Recent work on three-dimensional radiative transfer is found in the proceedings of the latest International Radiation Symposium (Smith and Stamnes (1997)). The paper of Garbiel et al. (1993), provides a nice summary of the research on the two- and threedimensional radiative transfer equation covering 1975 to 1992, (especially see their Table 1). Other recent work includes Borde and Isaka (1996) and Los et al. (1997).

Light is necessary to drive photosynthesis in the ocean, but excessive ultraviolet radiation is harmful to bacteria, phytoplankton, and higher trophic levels (Häder *et al.* (1995); Gleason and Wellington (1993)). The levels of both photosynthetically active radiation and ultraviolet radiation depend on organic as well as inorganic oceanic constituents. Prediction of UV dose

in the oceans requires coupling of oceanic and the atmospheric radiation fields. This can be done, in principle, and numerical algorithms are emerging (c.g. Mobley *et al.* (1993); Zeng *et al.* (1993); Stamnes (1997)). The problem merits further study since a comprehensive global measurement program of UV penetration into the ocean may be impractical. At high latitudes in the Arctic and in the waters surrounding the Antarctic continent, the ocean is partly covered with ice and snow. Hence, there is also a need to estimate UV penetration through the cryosphere to determine the UV dose received by organisms contained within the ice and snow (Trodahl and Buckley (1990)).

7.5. Direct measurement of atmospheric photolysis frequencies

Atmospheric photolysis frequency measurements have been performed for production of O(³P) from NO₂ and for production of O(¹D) from O₃. Currently there are a few research groups with both actinometers and spectroradiometers or filter radiometers designed for NO₂ and O₃ photolysis frequency measurements at ground level. A limited number of aircraft compatible instruments are in use. Field programs that require precise or fast response data for calculations of the photostationary state and oxidant balances will still require *in situ* determinations of J_{NO2} and J_{O3} .

Actinometers, spectroradiometers, and filter radiometers from various groups need to be intercompared at a common site to eliminate aerosol, cloud, albedo and other temporal variations. In addition, researchers who model photolysis coefficients could help validate current radiative transfer codes used in chemical models. No formal and few informal intercomparisons have been made with actinometers, spectroradiometers, or radiometers. Intercomparison is critical for establishing agreement between observation and theory (Albritton et al. (1990)), would provide information crucial to understanding the production and loss mechanisms for hydroxyl radicals, and would contribute to validation of molecular parameters and radiative transfer theory crucial to photochemical modeling efforts.

Actinometers for other molecules of interest in the troposphere must be developed. For example, formaldehyde photolysis provides a source of free radicals in the troposphere. Due to the highly structured absorption spectrum of CH_2O , theoretical calculation of the photolysis frequency is difficult. Other candidate molecules for photolysis measurements are H_2O_2 and some of the organic peroxides which act as important radical sources. These actinometers could then be intercompared with spectroradiometers to assess the accuracy of molecular parameters for those molecules.

Measurements of photolysis frequencies of stratospheric species are needed to validate models of ozone generation and destruction. Measurements of J_{02} to 20%, in conjunction with high resolution solar irradiance and sky radiance observations from a balloon platform in the 30-45 km altitude range would be a valuable experiment for additional validation of models (see Sections 3.2.1-3) Constraints on the production terms for both hydroxyl radicals and nitric oxide would be provided by measurements of the ozone photolysis rate in conjunction with the actinic flux in the 10-45 km range. This experiment, although very challenging, is critical for understanding ozone and radical production in the stratosphere.

Acknowledgements-Support for R. Meier was provided by the Office of Naval Research and the Strategic Environmental Research and Development Program. NASA UARS Guest Investigator grant provided partial support for J. Lean and K. Minschwaner. NSO/Kitt Peak data used here are produced cooperatively by NSF/NOAO, NASA/GSFC and NOAA/SEL. K. Stamnes acknowledges support by NASA grant NAGW-2165 to the University of Alaska. Portions of the support for E. Shettle were provided by a NASA SAGE III Science Team Grant and the Strategic Environmental Research and Development Program (unpublished). An earlier version of this paper was submitted as part of a report on Current State of Atmospheric Chemistry: Need for Instruments and Platforms by the Committee on Atmospheric Chemistry of the National Research Council. We greatly appreciate insightful comments provided by B. R. Lewis and S. T. Gibson.

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