Effect of solar activity on the minor constituents in the mesosphere and lower thermosphere

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The effect of solar activity on the different minor species in the mesosphere and lower thermosphere has been studied using the one-dimensional model. The concentrations of all the species show significant increase with solar activity. The variations in the hydrogen and oxygen species are attributed to the variations in photodissociation coefficients of H2O and O2. The increase in the concentration of atomic nitrogen above 90 km is due to the ionic reactions in the lower thermosphere.

In the past decade studies of minor constituents in the middle atmosphere have acquired great importance, particularly with respect to the stratospheric ozone problem. Indeed, ozone is one of the many minor constituents produced by photochemical reactions in the middle atmosphere and its concentration is greatly affected through photochemical reactions involving other minor constituents. The UV region of the solar spectrum is known to vary over the 11 year solar cycle and since the minor constituents in the middle atmosphere are produced mainly by the photochemical reactions that take place there, a solar cycle variability for the distributions of the minor constituents is expected. The solar cycle dependence of the distribution of minor species is important for investigations such as the composition, thermal structure and dynamics of the upper atmosphere and its state of ionization. Several sophisticated models of the mesosphere/lower thermosphere minor constituents have been developed and the variation of the distributions of the minor constituents arising from variations in solar illumination for different time scales have been studied earlier. As a part of the Indian Middle Atmosphere Programme, we have developed a time-dependent one-dimensional model for the minor constituents in the mesosphere and lower thermosphere.

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Figure 1a), Above 90 km the sensitivity of H and HO$_2$ remains nearly constant at about 50% and 30% respectively, while that for OH increases from 50% at 90 km to 90% at 100 km. These variations can be attributed to variations in JH$_2$O.

In Figure 3, below 90 km, the sensitivity of oxygen species shows a structure with positive maxima of about 20% or more at 70 km and 80 km and minima at 75 and 85 km and at some of the minima, the sensitivity has even reversed its sign. Above 90 km, the sensitivity of all the oxygen species shows an increasing trend with altitude up to about 100 km.

The main source for atomic oxygen (O), in its ground state and excited state, is photolysis of O$_2$ and the changes in O can be seen to be similar to changes in J O$_3$ (shown in Figure 1b and c). In the case of O$_3$ the important source is the three-body reaction of O with atomic oxygen and the main sink is photodissociation of O$_3$, the J O$_3$ does not show any changes with solar activity, hence the changes in O$_3$ will follow the changes in O.

Variations in concentrations of all nitrogen species (N$^3$D, N$^4$S, NO and NO$_2$) are shown in Figure 4. Below 90 km, all the nitrogen species, except N$^4$S, show significant sensitivity with a maximum of 40% or higher at about 75 km and a negative maximum of about 20% at around 88 km. N$^4$S was relatively less sensitive, below 90 km, with the sensitivity values ranging between +10% and -20%. Above 90 km, while NO and NO$_2$ are relatively insensitive, atomic nitrogen, both in its ground state (S) and excited state (D) show a steep rise in sensitivity with altitude.

The main production of atomic nitrogen above
Figure 3. Altitude profile of percentage variation of oxygen species from solar minimum to solar maximum.

Figure 4. Altitude profile of percentage variation of nitrogen species from solar minimum to solar maximum.
Solvent effect on fluorescence lifetime of 8-anilino-naphthalene-1-sulphonate

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We report the fluorescence lifetime of 8,1-ANS in different solvents and compare them with the previously reported values. Effects of solvent viscosity and polarity on fluorescence lifetime have also been studied. A simple empirical relationship between fluorescence lifetime and solvent viscosity/polarity shows that the fluorescence lifetime is more sensitive to solvent polarity rather than viscosity.

The extreme sensitivity of the fluorescence parameters to the environment of 8-anilino-naphthalene-1-sulphonate (8,1-ANS) was first recognized by Weber and Laurence. In water 8,1-ANS exhibits weak green fluorescence whereas an intense blue fluorescence is observed when bound to serum albumin or proteins. The fluorescence decay time, quantum yield and fluorescence maximum of this molecule in solvents of varying polarity have been investigated by several workers. The picosecond time resolved fluorescence of 8,1-ANS in a mixed solvent system, its photo-physical decay pathways, the edge excitation red shift at liquid air temperature, time-dependent spectral shift at two different temperatures have also been studied. In spite of the extensive work already reported on the spectroscopy and photophysics of 8,1-ANS, a large inconsistency is found in the fluorescence decay times as reported by different authors. In this connection we report the fluorescence lifetime of 8,1-ANS in different solvents and compare them with previously reported values. Effects of solvent viscosity and polarity have also been studied.

Spectroscopic grade solvents (Aldrich Chemicals) were used after distillation. Aqueous solutions were prepared from triple distilled water. 8,1-ANS (Aldrich Chemicals) obtained as ammonium salt was purified by crystallizing it in MgCl₂ solution as described by Zadkowska and Fleming. freshly prepared solutions (ANs concentration 5 × 10⁻³ M) were studied after bubbling nitrogen for 10 min. Lifetime was measured by degassing using thaw-freeze and pump method in several cycles (in n-propanol only). For fluorescence lifetime measurements a time correlated single photon counting spectrometer was used with a coaxial flash lamp driven set-up with fwhm = 1 ns (Edinburgh Instrument 199 Spectrometer). Some studies were carried out with a frequency doubled, cavity dumped dye laser synchronously pumped by a mode locked and frequency doubled Nd-YAG Laser (Spectra Physics) as the excitation source with fwhm 450 ps. Data were analysed with a PDP 11/2 micro computer by convolution method using a least-square fitting method. The goodness of the fit was estimated by reduced χ², distribution of residuals and standard deviation.

The steady state spectra of 8,1-ANS recorded by us are similar to those reported earlier. The fluorescence decay times of 8,1-ANS in various solvents at 25°C are given in Table 1 along with their viscosities (η) and solvent polarity parameters [Eₒ (30)]. The fluorescence lifetime values (at 25°C) reported in the literature have also been tabulated for comparison. The lifetimes reported by Chakrabarti and Ware are exceptionally high, probably due to the inaccuracies in measurements. However, our values of under-gassed solutions resemble close to those obtained by other workers. In an aerated solution the fluorescence lifetime is quenched by the presence of dissolved oxygen. Nakamura and Tanaka have shown that if the solution is degassed by thaw-freeze method, the lifetime increases. However, our values of lifetime (τ) after thaw-freeze and pump procedure (in n-propanol) did not match with those (14.5 ns) of Nakamura and Tanaka. Our measurements for all other solvents have been done using the method of nitrogen bubbling for degassing.

From Table 1, it is evident that there is a large variation in lifetime in different solvents. In all the solvents, the fluorescence decay of 8,1-ANS exhibits a single exponential behaviour which remains invariant throughout the emission wavelength except in octanol where a double exponential behaviour is observed.