

## Atmospheric Chemistry VI

Lecture deals with atmosphere at altitudes above 50km

Mesosphere from ca. 50-90km, where lowest Ts in entire atmosphere are found

Thermosphere above ca. 90km: Ts increase, but meaning of T altered

Explain T in terms of  $O_2 + hv \rightarrow O_t + O_t$

Characterized by increasingly high-energy chemistry: excited neutrals and ions :  
this lecture concentrates (but not exclusively) on neutrals

Note possibility of *escape* from these regions of atmosphere

Basic features of chemistry

Photolysis of  $O_2$  and gravitational separation means that O atoms begin to dominate over other neutral species (see note 1.6).

Wavelengths are short enough ( $\lambda < 175\text{nm}$ ) to photodissociate water



and an upward flow of  $H_2O$  must compensate.

Reactions such as



interconvert  $HO_x$  species. H atoms escape from the exosphere.

Important reactions involving NO include



$N^*$  here represents  $N(^2D)$ , which may be formed in processes such as



so that ion reactions affect neutral chemistry.

Airglow

Emission of atomic line and molecular band systems, day and night

Nightglow can be seen from ground: faint, light of candle at 100m

would appear much stronger but for  $\lambda$  of strongest emission in near ir

Dayglow orders of magnitude more intense, but not detectable by eye

Distinction between *airglow* and *aurora* (many spectral lines identical)

Airglow continuous, weak, all latitudes, driven by  $hv$  from Sun

Aurora intense, irregular (form & occurrence), near poles, driven by particles

Use of airglow

to provide information about photochemistry and composition of atmosphere

e.g. SME for  $[O_3]$

(metastables) dynamics and transport in upper atmosphere

even with high resolution windspeeds from Doppler profiles

### Nature of emission features

Atomic and molecular bands of atmospheric gases

Resonance lines of He (58.4nm), N (120.0nm), H (121.6nm) and O (130-131nm) might be expected to be most intense features, but they cannot be observed from ground ("vacuum ultraviolet")

UV emissions (short  $\lambda$  generally of atoms; longer  $\lambda$ , molecular systems as well)

Visible and near-ir bands: some of the most important emissions lie at  $\lambda$  just beyond response of human eye

Mostly electronic transitions, but note Meinel Bands (nb overtones as well)

Excitation mechanisms

### Oxygen airglow

Very rich

Atomic bands from O(<sup>1</sup>S) and O(<sup>1</sup>D)

Molecular bands in visible and near ir

O<sub>2</sub> states correlating with 2 x O(<sup>3</sup>P)

formally forbidden transitions

eg O<sub>2</sub>(<sup>1</sup> $\Delta_g$  - <sup>3</sup> $\Sigma_g^-$ ):  $\Delta S, \Delta L, g-u$  rules all broken:  $\tau \sim 90$  mins vs.  $10^{-8}$ s for allowed transition.

effect of large overhead path - reabsorption of (0,0)

(0,1) band from ground; (0,0) aircraft, balloons and rockets

nb Venus and Mars - Doppler shifts

Altitude profiles: differentiation of overhead intensities

### Laboratory experiments

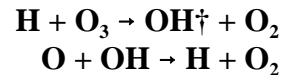
O<sub>2</sub>(b<sup>1</sup> $\Sigma_g^+$ ) and its reaction with O<sub>3</sub>

O<sub>2</sub>(a<sup>1</sup> $\Delta_g$ ): df and uv photolysis of O<sub>3</sub>

Quenching measurements and calculations

Another observation: OH(v)

Meinel bands, excitation, regeneration,  
catalytic ozone loss



### Sodium airglow

Mass spectrometry - metal ions

Meteor ablation source: enhancement during meteor showers

Allowed resonance transition, *not in vacuum uv*:

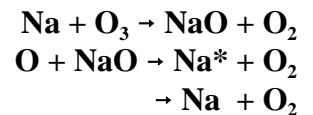
dayglow excitation

Nightglow - must be some reaction capable of exciting Na\*

Scheme: very fast reactions involving O<sub>3</sub> and O as energy source

Cyclic regeneration demanded

Long-lived meteor trails (more than 10 mins and up to 1 hour has been recorded)



**scheme on board**

### Oxygen nightglow

Persistence of O and O<sub>2</sub> features at night also demands energy source

Atomic O is only reasonable source

Atomic green line - Chapman and Barth mechanisms: precursor O<sub>2</sub>\* molecule

Molecular emissions

Problem is efficiency required into each state of O<sub>3</sub>

Proposed combined scheme

Laser experiments in confirmation

## Atmospheric Chemistry VI : Slides

1. R 1 Regions of Earth's atmosphere (equiv. H/O 1.5)
2. R 2 Concentrations of neutrals (equiv. H/O 1.6)
3. G 1 UV dayglow 110-210nm
4. G 2 UV dayglow 200-430nm
5. G 3 Energy levels of N, N<sup>+</sup>, O, O<sup>+</sup>
6. G 4 Height profile for O(<sup>1</sup>S) line in dayglow
7. G 5 Energy levels of N<sub>2</sub>, N<sub>2</sub><sup>+</sup>, O<sub>2</sub>, O<sub>2</sub><sup>+</sup>
8. G 6 PE curves for O<sub>2</sub>
9. G 7 Photographic spectrum obtained from O<sub>2</sub> in discharge-flow system
10. G 8  $\lambda = 1270\text{nm}$  emission from O<sub>2</sub>(a<sup>1</sup> $\Delta_g$ ): DF and UV-irradiated O<sub>3</sub>
11. G 9 Measured and calculated [O<sub>2</sub>(a<sup>1</sup> $\Delta_g$ )]—height profiles in dayglow

## Atmospheric Chemistry VI : Viewgraphs

- “0”. Regions of Earth's atmosphere
1. Chemistry in the mesosphere and thermosphere
  2. Airglow and aurora: bands and excitation mechanisms
  3. IR atmospheric band in the nightglow: overhead intensities
  4. Height–concentration profile for  $O_2(a^1\Delta_g)$  derived from figure 3
  5. Height–concentration profile for  $O_2(a^1\Delta_g)$  in the dayglow: experiment and theory
  6. Mesospheric chemistry of sodium
  7. Nightglow oxygen emission chemistry