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 $O_2 + h\nu \rightarrow O_t + O_t$
- 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 (λ < 175nm) to photodissociate water

$H_2O + h\nu \rightarrow H + OH$ **Escape of H**

and an upward flow of H_2O must compensate.

Reactions such as

$O + OH \rightarrow O_2 + H$ **Escape of H**

$HO_2 + H \rightarrow H_2 + O_2$ **Escape of H_2**

interconvert HO_x species. H atoms escape from the exosphere.

Important reactions involving NO include

$N^* + O_2 \rightarrow NO + O$ **NO ↓ to stratosphere**

$N + NO \rightarrow N_2 + O$ **⇒ influence on ozone chemistry**

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

$NO^+ + e \rightarrow N^* + O$

$N_2^+ + O \rightarrow N^* + NO^+$

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 λ 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 hν 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 λ generally of atoms; longer λ, molecular systems as well)
    - Visible and near-ir bands: some of the most important emissions lie at λ 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(^1S) and O(^1D)
- Molecular bands in visible and near ir
  - O_2 states correlating with 2 x O(^3P)
  - formally forbidden transitions
    - *eg* $O_2(^1\Delta_g - {}^3\Sigma_g^-)$: $\Delta\mathbf{S}$, $\Delta\mathbf{\Lambda}$, 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
- $O_2(b^1\Sigma_g^+)$ and its reaction with O_3
- $O_2(a^1\Delta_g)$: df and uv photolysis of O_3
- Quenching measurements and calculations
- Another observation: OH(v)
  - Meinel bands, excitation, regeneration, catalytic ozone loss

$$\mathbf{H + O_3 \rightarrow OH^\dagger + O_2}$$
$$\mathbf{O + OH \rightarrow H + O_2}$$

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_3 and O as energy source
  - Cyclic regeneration demanded
  - Long-lived meteor trails (more than 10 mins and up to 1 hour has been recorded)

$$\mathbf{Na + O_3 \rightarrow NaO + O_2}$$
$$\mathbf{O + NaO \rightarrow Na^* + O_2}$$
$$\mathbf{\rightarrow Na + O_2}$$

scheme on board

Oxygen nightglow
- Persistence of O and O_2 features at night also demands energy source
- Atomic O is only reasonable source
- Atomic green line - Chapman and Barth mechanisms: precursor O_2* molecule
- Molecular emissions
- Problem is efficiency required into each state of O_3
- 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^+, O, O^+
6.	G 4	Height profile for $O(^1S)$ line in dayglow
7.	G 5	Energy levels of N_2, N_2^+, O_2, O_2^+
8.	G 6	PE curves for O_2
9.	G 7	Photographic spectrum obtained from O_2 in discharge-flow system
10.	G 8	λ = 1270nm emission from $O_2(a^1\Delta_g)$: DF and UV-irradiated O_3
11	G 9	Measured and calculated $[O_2(a^1\Delta_g)]$—height profiles in dayglow

Atmospheric Chemistry VI : Viewgraphs