Infrared radiation of ozone in the mesosphere and lower thermosphere: energetic effects and remote sensing

A.G. Feofilov\textsuperscript{1}, A.A. Kutepov\textsuperscript{2,3}, L. Rezac\textsuperscript{4}

\textsuperscript{1} - Dynamic Meteorology Laboratory, Ecole Polytechnique, Paris, France
\textsuperscript{2} – The Catholic University of America, Washington, DC, USA
\textsuperscript{3} – NASA Goddard Space Flight Center, Greenbelt, MD, USA
\textsuperscript{4} – Max-Planck Institute for Solar System Research, Katlenburg-Lindau, Germany

Ozone Workshop, October 2-4, 2013, Reims
MLT - why bother?

- MLT is a “gateway” between the lower atmosphere and space.
- MLT is sensitive to solar influence and to the inputs from below.
- Anthropogenic changes in greenhouse gases may change this input.
- Noctilucent clouds observed in polar MLT in the summer time are very sensitive to temperature changes and there are debates on their role as a “miner’s canary” for global changes.
- MLT area absorption and emission in molecular bands affects the atmospheric observations of other areas.
Object of Study: IR radiance in the MLT

Solar radiance

Solar IR absorption

Solar UV absorption

Atm. and terr. IR absorption

Atmospheric IR emission

Reflected radiance

Lower thermosphere boundary (~120 km)
Thermosphere

Mesosphere

Lower mesosphere boundary (~60 km)
Stratosphere

Terrestrial radiance

Troposphere
Ground
Cooling/heating rates
Radiative cooling/heating = radiative flux divergence

in W/m³:
\[ H(z) = \frac{1}{4\pi} \int_{-\infty}^{+\infty} \int_{\Omega} \mu \frac{dI_{\mu\nu}(z)}{dz} d\nu \]

in K/day:
\[ h(z) = H(z) \cdot \frac{24 \cdot 60 \cdot 60}{C_p(z) \rho(z)} \]
Energy Exchange Between Atmospheric Molecules

- Other molecules: CO, NO, N₂O, OH
- O¹D, N₂, O₂ electr.-vib. energy reservoir
- CO₂ vib. levels
- O₃ vib. levels
- H₂O vib. and rot. levels
- O₂/O₃ photolysis
An important peculiarity of the MLT

• Infrared radiance absorption/emission corresponds to vibrational excitation/de-excitation of the molecules.
• To estimate the energetic characteristics of the given area or to interpret the infrared observations in MLT one needs to know the vibrational levels populations.

BUT !!!

• In the upper atmosphere, the collisions between the molecules are not frequent and the populations are not defined by local temperature.
• Breakdown of Local Thermodynamic Equilibrium (LTE).
• Special methodology is applied (non-LTE modeling).
LTE and non-LTE: two-level atom

In the lower atmosphere:

\[ R \ll C \]
\[ R_{21} n_2 \sim R_{12} n_1 \]
\[ n_2 C_{21} = n_1 C_{12} \]
\[ \frac{n_2}{n_1} = \frac{g_2}{g_1} e^{-\frac{E_2-E_1}{kT}} \]

In the upper atmosphere:

Collisions are less frequent, and the populations are not defined by local temperature anymore = non-LTE
Non-LTE populations: vibrational temperatures

\[ n_l = \frac{g_l}{g_0} \cdot e^{-\frac{(E_l - E_0)}{kT_{\text{vib}}}} \]

\[ n_0 = g_0 \cdot e^{\frac{(E_l - E_0)}{kT_{\text{vib}}}} \]

\( T_{\text{vib}} = T_{\text{kin}} \): LTE

\( T_{\text{vib}} \neq T_{\text{kin}} \): non-LTE
$O_3$ levels and transitions

9.6µm 9.6µm
$O_2/O_3$ photolysis products

Yankovsky and Manuilova, 2006
$H_2O$ levels and transitions

Feofilov et al., 2009
Energy exchange processes for $O_3$

\[ O_3(v_1, v_2, v_3) + M(N_2, O_2, O) \underset{k_{\text{int}}}{\rightleftharpoons} O_3(v_1 - 1, v_2, v_3 + 1) + M \]
\[ O_3(v_1, v_2, v_3) + M(N_2, O_2, O) \underset{k_{\text{int2}}}{\rightleftharpoons} O_3(v_1 - 1, v_2 + 1, v_3) + M \]
\[ O_3(v_1, v_2, v_3) + M(N_2, O_2, O) \underset{k_{\text{int3}}}{\rightleftharpoons} O_3(v_1, v_2 + 1, v_3 - 1) + M \]

\[ O_3(v_1, v_2, v_3) + M(N_2, O_2, O) \underset{k_{\text{VVT1}}}{\rightleftharpoons} O_3(v_1, v_2 - 1, v_3) + M \]
\[ O_3(v_1, v_2, v_3) + M(N_2, O_2, O) \underset{k_{\text{VVT2}}}{\rightleftharpoons} O_3(v_1 - 1, v_2, v_3) + M \]
\[ O_3(v_1, v_2, v_3) + M(N_2, O_2, O) \underset{k_{\text{VVT3}}}{\rightleftharpoons} O_3(v_1, v_2, v_3 - 1) + M \]

\[ O_3(000) + N_2(v = 1) \underset{k_{\text{VV1}}}{\rightleftharpoons} O_3(200) + N_2(v = 0) + 130 \text{ cm}^{-1} \]
\[ O_3(000) + O_2(v = 1) \underset{k_{\text{VV2}}}{\rightleftharpoons} O_3(100) + O_2(v = 0) + 456 \text{ cm}^{-1} \]
\[ O_3(000) + O_2(v = 1) \underset{k_{\text{VV3}}}{\rightleftharpoons} O_3(001) + O_2(v = 0) + 517 \text{ cm}^{-1} \]
\[ O_3(102) + O_2(v = 0) \underset{k_{\text{VV4}}}{\rightleftharpoons} O_3(000) + O_2(v = 2) - 4.9 \text{ cm}^{-1} \]

\[ O_2 + O(^3P) + M \rightarrow O_3(v_1, v_2, v_3) + M, \]

Plus emission / absorption of radiation

Intra-molecular energy transfer

Vibrational-translational exchange

Vibrational-vibrational exchange

Three-body recombination
Three-body recombination and nascent population model

A hybrid of models

Manuilova et al. (1998)
kinetics for lower states,
by collisions with N₂, O₂, O³P

Quasi-continuum
Is treated in terms of rate constants

A) Gil-Lopez et al., (2005): Zero surprisal model of nascent population,
E_D is the dissociation energy

\[ P(v) = \frac{1 - E(v)/E_D^{1.5}}{\sum_v (1 - E(v)/E_D^{1.5})} \]

B) Kaufmann et al. (2006): Zero surprisal model or all excitation goes on 00v3, with v3=3,5 or 8

C) Fernandez et al. (2009, 2010): single level nascent population at O₃ (006), assuming that about 70% of recombination energy goes to vibrations
An inconsistency between $O_3$ retrieved from 9.6 um and simulated/measured 4.8 um radiance

Kaufmann et al, 2006:
The rate of stretching to bending mode transition $001,100 \rightarrow 010$ $K_{D_2}$ must be 3-4 lower than well known measured value

4.8 microns emission from 200, 101, 002 for known $O_3$ was 2-3 times lower than measured for ~ 75 km

Fernandez et al., 2010:
new bending to stretching mode transitions, for lower levels 020->100,001 SSH estimated $K_{2D}$
For higher levels – harmonic oscillator rule
$k_{VT}$ measurements: lab vs atmosphere
$O_3$ vibrational level populations – midlatitude day
Sensitivity of $v_3$-levels to atomic O
$O_3$ cooling/heating rates

![Diagrams showing ozone cooling/heating rates at different altitudes for SAW, TROP, SAS, MLW, and MLS regions.](#)
MLT sensitivity to clouds, stratopause $T$, and solar pumping changes

![Graph showing altitude vs temperature change](image)
$O_3$ vibr. levels, sensitive to changes in other layers

Response to clouds

(2v_2), (v_2v_3), (v_1v_2)

Response to stratopause warming

(v_1), (v_2), (v_3), (2v_2), (v_1v_2), (v_2v_3)
Take home messages

- O₃ is an important component of the MLT
- O₃(9.6µm) IR cooling/heating in 65-105 km altitude range is -1...+3 K/day
- Energetic effects of direct radiative coupling with tropo- and stratosphere are less than 1 K/day
- Changes in lower atmosphere affect vibrational levels, which are pumped by radiation coming in optically thin lines.
- Adequate model of nascent population of O₃ molecule formed in three-body recombination is still required
- Collisional rate calculations are needed.