Ozone Evolution in the Mexico City Plumes during the MIRAGE-Mex Field Campaign

High ozone in aged plume
Implementing A “Fast” Photolysis Calculation (FTUV) into WRF-Chem

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Outline

- Why Photolysis is Important?
- How to Make it “Faster”? 
Why Photolysis is Important?
It is a driving force for PHOTO-chemistry

Table 8A-7. RADM2 and RADM2_AQ Mechanisms

<table>
<thead>
<tr>
<th>Reaction List</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. NO2 + hv   --&gt; O3P + NO</td>
</tr>
<tr>
<td>2. O3 + hv    --&gt; O1D</td>
</tr>
<tr>
<td>3. O3 + hv    --&gt; O3P</td>
</tr>
<tr>
<td>4. HONO + hv  --&gt; HO + NO</td>
</tr>
<tr>
<td>5. HNO3 + hv  --&gt; HO + NO2</td>
</tr>
<tr>
<td>6. HNO4 + hv  --&gt; HO2 + NO2</td>
</tr>
<tr>
<td>7. NO3 + hv   --&gt; NO</td>
</tr>
<tr>
<td>8. NO3 + hv   --&gt; NO2 + O3P</td>
</tr>
<tr>
<td>9. H2O2 + hv  --&gt; 2.000*HO</td>
</tr>
<tr>
<td>10. HCHO + hv --&gt; CO</td>
</tr>
<tr>
<td>11. HCHO + hv --&gt; HO2 + HO2 + CO</td>
</tr>
<tr>
<td>12. ALD + hv  --&gt; MO2 + HO2 + CO</td>
</tr>
<tr>
<td>13. OP1 + hv  --&gt; HCHO + HO2 + HO</td>
</tr>
<tr>
<td>14. OP2 + hv  --&gt; ALD + HO2 + HO</td>
</tr>
<tr>
<td>15. PAA + hv  --&gt; MO2 + HO</td>
</tr>
<tr>
<td>16. KET + hv  --&gt; ACO3 + ETPH</td>
</tr>
<tr>
<td>17. GLY + hv  --&gt; 0.130<em>HCHO + 1.870</em>CO</td>
</tr>
<tr>
<td>18. GLY + hv  --&gt; 0.450<em>HCHO + 1.550</em>CO + 0.800*HO2</td>
</tr>
<tr>
<td>19. MGLY + hv --&gt; ACO3 + HO2 + CO</td>
</tr>
<tr>
<td>20. DCB + hv  --&gt; 0.980<em>HO2 + 0.020</em>ACO3 + TCO3</td>
</tr>
<tr>
<td>21. ONIT + hv --&gt; 0.200<em>ALD + 0.800</em>KET + NO2</td>
</tr>
</tbody>
</table>

O1D → OH (atmospheric detergent, oxidization capacity)
Why Photolysis is Important?

OH + CO $\rightarrow$ O$_3$

OH + HCs $\rightarrow$ O$_3$

O$_3$ formation is initiative by OH

O$_3$ + hv $\rightarrow$ O($^{1}$D) + O$_2$ $\rightarrow$ 2OH

OH is produced by photolysis

O$_3$ formation is initiative by OH
How to Calculate photolysis

(TUV-Tropospheric Ultraviolet-Visible model)

\[ J = \int f(\lambda) \sigma_0(\lambda) \phi(\lambda) \, d\lambda \]

\( \lambda \) is UV wave length

\( f \) is solar flux \((Z, \lambda)\) (It is effected by cloud, aerosol, O3, etc)

\( \sigma \) is cross section of a species \((T, SP, \lambda)\)
The total calculation at each time step is
\[ N_{\text{total}} = N_i \times N_j \times N_w \times N_k \times N_p \]
To be faster, \( N_w = \frac{N_w}{M} \)

do time loop (t)
do space loop (i,j)
do wave length loop (\( \lambda \))
do Z loop (k)
do species loop (p)
\[ J = \ldots \ldots \]
end loop P
dend loop Z
dend loop wave length
dend loop (i,j)
dend loop (i,j)
dend loop t
To ensure accuracy of $J$, $N_w = 140$ (Madronich, 1987)

The problems due to $N_w = N_w/M$
Errors due to low resolution

\[ f = f' + \delta f \]
\[ \sigma = \sigma' + \delta \sigma, \]
\[ \Delta = (f' \delta \sigma) + (\sigma' \delta f') + (\delta \sigma \delta f), \]
\[ = J_{140}(TUV) - J_{17}(FTUV) \]
Correction Factor ~ C

\[ C = \frac{(J_{140} - J_{17})}{J_{17}} \]

\[ J(FTUV) = J_{17} (1 + C) \]

\[ C \sim F(TO_3, Ze, T, SP) \]
Diff (%) between TUV and FTUV

TIE ET AL.: EFFECT OF CLOUDS ON OXIDANTS

zenith = 0

- O₃ → O₂ + O(1D)
- NO₂ → NO + O(3P)
- NO₃ → NO₂ + O(3P)

- N₂O₅ → NO₃ + NO₂
- H₂O₂ → 2 OH
- HNO₃ → OH + NO₂
Applications of FTUV in global and regional models (MOZART, WRF-Chem)

Cloud effect on J and Chemical Oxidants
Applications of FTUV in global and regional models (MOZART, WRF-Chem)

Aerosol effect on J and Chemical Oxidants

Effect of aerosols on $J_{[O1D]} \rightarrow OH$
Calculated from TUV, AOD=2.0, $\omega = 0.80$
Applications of FTUV in global and regional models (MOZART, WRF-Chem)
In Mirage Field Campaign

![Graph showing J[O3->O1D] vs Local hours for Flight 5 (March/15)]
Summary

(1) A FTUV radiation transfer code is developed. The model is “fast”, and it is feasible to include very complicated chemical/dynamical models (such as MOZART, WRF-Chem).

(2) The FTUV is a useful tool to study some important processes, (such as clouds and aerosols), which have important impacts on atmospheric chemistry,
Applications of FTUV in global and regional models (MOZART, WRF-Chem)

Cloud effect on J and Chemical Oxidants

2004-Nov at Shanghai

Cloudy days

Clear sky

Geng et al., AE, 2007