WHAT CAN WE LEARN FROM RELAXATION MEASUREMENTS OF A LASER-PERTURBED ATMOSPHERE? A MODELING STUDY

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ABSTRACT

The chemical kinetic aspects of a transient increase in OH and HO2 by several orders of magnitude are explored in three model tropospheres. This chemical kinetic modeling effort was undertaken to support the operation of a pump-and-probe LIDAR instrument. A powerful excimer laser pulse perturbs the troposphere after which its relaxation back to steady state is examined by remote sensing, for example by DIAL or LIF. Instead of probing ambient levels of key free radicals, a study of the relaxation kinetics in real time enables chemical mechanistic studies in situ.

1. INTRODUCTION

For some key species such as tropospheric OH, the in situ measurement of its concentration is a difficult problem. One possible way of gaining information on OH radical reactions in the real troposphere has recently been proposed: Pump-and-Probe LIDAR [1]. In this relaxation technique, which is by no means restricted to the measurement of OH, an intense light pulse perturbs the atmosphere. Subsequently the return of [OH] to its steady-state value is observed by optical remote sensing techniques such as DIAL or long path absorption.

The central idea of the Pump-and-Probe LIDAR is to combine the time resolution of the flash photolysis with the spatial resolution of the LIDAR technique to what can be called a real-time in situ spatially resolved atmospheric chemical kinetics field experiment. The emphasis is placed on the verification and completion of the chemical mechanisms operative under given atmospheric conditions. In a later phase transport in and out of the irradiated volume will be considered. To test the feasibility of such a Pump-and-Probe LIDAR we have numerically simulated the experiment, and this is the subject of the present work.

We have modeled the following four scenarios: In scenario A) a (hypothetical) pump pulse bleaches NO2 at 1<399 nm in order to "inject" an equivalent quantity of O(3P) whose decay with time is calculated together with all the other chemical species directly affected by it. In scenario B) a model troposphere is perturbed by a powerful pump pulse from a KrF excimer laser at 248 nm which flash photolyzes O3 to give O(1D) and O2(1D). The electronically excited oxygen atoms insert into H2O thus generating a transient high concentration of OH radicals. Quenching processes generate significant amounts of O(3P) which is the reason we had to include scenario A. In scenario C) a powerful pump pulse at 308 nm generates H from photolysis of H2CO and OH from photolysis of O3 in an unpolluted troposphere rich in CH4 and H2CO. In scenario D) both H and OH are generated by two-photon photodissociation of H2O at 248 nm at high laser powers. We stress that the present effort relates to the chemical aspect of the troposphere only. Therefore, the necessity of having to include transport properties under given meteorological conditions will be given by its chemical lifetimes which is the primary subject of this paper.

II. METHOD OF CALCULATION

A simplified chemical model of the troposphere including 76 chemical species and 166 reactions was treated using the CHEMKIN II package of programs [2]. This flexible set of programs was chosen because it incorporates the temperature and pressure dependence of all uni-, bi- and termolecular reactions. CHEMKIN II explicitly takes into account the reverse of every elementary reaction. This aspect is important for chemical equilibria such as N2O5 ↔ NO3 + NO2 or CH3C(O)O2NO2 (PAN) ↔ CH3C(O)O2 + NO2 where the adduct is weakly bound and where its lifetime thus varies significantly in the temperature range of interest. Most kinetic parameters were taken from kinetic data evaluations for atmospheric chemistry [4] or were estimated [3]. The calculated steady state concentrations for these different tropospheres are given in Table 1.

III. RESULTS AND DISCUSSION

Several different ways of perturbing the atmosphere were considered: The reactions NO2 + hn' → NO + O(3P) (scenario A) and O3 + hn' → O2(1D) + O(1D) (scenario B) are equivalent to a burst or an instantaneous "injection" of O(3P) and O(1D), respectively. It leads to transient atom concentrations which are as high as the steady state NO2 and O3 concentrations. This has dramatic consequences on other key species as shown below in terms of their relaxation rate. A different type of perturbation is introduced when H atoms are injected into the atmosphere through photolysis of H2CO (scenario C) or two-photon dissociation of H2O (scenario D).

Scenario A) Case of Polluted Troposphere: O(3P) Injection

At time t=0 a short laser pulse at 1<398 nm is assumed to completely bleach NO2. The degree of bleaching depends on the laser beam fluence and the excitation wavelength. Complete bleaching of NO2 is difficult to attain but is assumed here in order to simulate that portion of O(1D) that is converted to O(3P) through collisional quenching of O(1D) (see scenario B). Figure 1 below shows the recovery/relaxation of O3, NO2, N2O5, and NO. The recovery of NO and NO2 is related to the presence of O3, and...
Table : Typical Steady-State Levels of Trace Gas Constituents

<table>
<thead>
<tr>
<th>Species</th>
<th>Steady State Concentration (^1) [ppm] Polluted Atmosphere</th>
<th>Steady State Concentration (^1) [ppm] Unpolluted Atmosphere</th>
<th>Steady State Concentration (^1) [ppm] Unpolluted Atmosphere - High Level of CH(_3)O</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO</td>
<td>0.131</td>
<td>0.658x10(^{-2})</td>
<td>0.226x10(^{-4})</td>
</tr>
<tr>
<td>NO(_2)</td>
<td>0.107</td>
<td>0.493x10(^{-2})</td>
<td>0.129x10(^{-3})</td>
</tr>
<tr>
<td>N(_2)</td>
<td>0.772x10(^{6})</td>
<td>0.772x10(^{6})</td>
<td>0.772x10(^{6})</td>
</tr>
<tr>
<td>NO(_2)</td>
<td>0.671x10(^{-6})</td>
<td>0.206x10(^{-7})</td>
<td>0.148x10(^{-8})</td>
</tr>
<tr>
<td>O(_3)</td>
<td>0.208x10(^{6})</td>
<td>0.208x10(^{6})</td>
<td>0.208x10(^{6})</td>
</tr>
<tr>
<td>N(_2)</td>
<td>0.157</td>
<td>0.0133</td>
<td>0.0533</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>0.198x10(^{5})</td>
<td>0.198x10(^{5})</td>
<td>0.198x10(^{5})</td>
</tr>
<tr>
<td>CO</td>
<td>0.772</td>
<td>0.198</td>
<td>0.248</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>0.346x10(^{3})</td>
<td>0.346x10(^{3})</td>
<td>0.346x10(^{3})</td>
</tr>
<tr>
<td>CH(_4)</td>
<td>1.400</td>
<td>1.400</td>
<td>1.400</td>
</tr>
<tr>
<td>C(_2)H(_4)</td>
<td>0.247</td>
<td>0.953x10(^{-2})</td>
<td>0.344x10(^{-2})</td>
</tr>
<tr>
<td>C(_4)H(_10)</td>
<td>0.247</td>
<td>0.967x10(^{-2})</td>
<td>0.990x10(^{-2})</td>
</tr>
<tr>
<td>HONO</td>
<td>0.402x10(^{-4})</td>
<td>0.363x10(^{-4})</td>
<td>0.106x10(^{-5})</td>
</tr>
<tr>
<td>HNO(_3)</td>
<td>0.372x10(^{-2})</td>
<td>0.673x10(^{-3})</td>
<td>0.304x10(^{-2})</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>0.472x10(^{-12})</td>
<td>0.376x10(^{-10})</td>
<td>0.440x10(^{-12})</td>
</tr>
<tr>
<td>CH(_3)O</td>
<td>0.414x10(^{-3})</td>
<td>0.404x10(^{-3})</td>
<td>0.982x10(^{-2})</td>
</tr>
</tbody>
</table>

1) The Zenith Angle of the sun was 30° at midlatitudes
2) Relative Humidity of 60% at 300K and 1013 mbar
3) C\(_2\)H\(_4\) and C\(_4\)H\(_10\) are representative of all the NMHC.

Figure 1: Concentration [ppm] versus time [s] curves.

The Case of Polluted Troposphere: O\(^{3P}\) Injection (Case A)

 occurrences on the time scale of several seconds, which is also the time scale of NO\(_2\) photolysis by sunlight. The decay of O\(^{3P}\) occurs on a very short time scale of several tens of microseconds according to O + O\(_2\) \rightarrow O\(_3\). The interesting concentration vs. time curve for NO\(_2\) is due to (sequentially): the disappearance of NO\(_2\) by the pump pulse, oxidation of NO\(_2\) to NO\(_3\) by O\(_3\) resulting in an excess of NO\(_2\) and NO\(_3\), and finally relaxation to the steady state levels of NO\(_2\) and NO\(_3\).

Scenario B) Case of Unpolluted Troposphere: O\(^{1D}\) Injection

At time t=0 a short laser pulse of about 300 mJ/cm\(^2\) at \(\lambda=248\) nm completely bleaches O\(_3\) to O\(_2\) + O\(^{1D}\). The latter generates OH free radicals by insertion into H\(_2\)O or O\(^{3P}\) by collisional quenching with air. The maximum OH concentration corresponds to \(1x10^{11}\) molec/cm\(^3\) which is an enhancement of \(2x10^{6}\) above the steady state concentration.

Low levels of NO\(_2\) lead to a significantly longer lifetime of OH (150 ms, Figure 2) compared to a polluted troposphere (7 ms). Surprisingly, the OH density is lingering on for several seconds at levels which are readily observable by DIAL. This "delayed" formation of OH results from the reaction of HO\(_2\) + NO\(^{+}\) OH + NO\(_2\) during the HO\(_2\) peak due to CH\(_4\) oxidation by OH ('CH\(_3\)'CH\(_3\)O'OCH\(_3\)'CH\(_3\)O'H\(_2\)CO\(_2\)). Methane is thus the true precursor of this "delayed" OH. The OH and CH\(_3\) density vs. time curves track each other as do CH\(_3\)OH and HO\(_2\).

Scenario C) Case of Unpolluted Troposphere: H and O\(^{1D}\) Injection

An intense laser pulse of 300 mJ/cm\(^2\) at 308 nm generates \(2x10^{9}\) H atoms/cm\(^3\) due to photodissociation of 10 ppb of H\(_2\)O and subsequent reaction of HCO with O\(_2\), as well as to \(4x10^{9}\) OH due to O\(_3\) photolysis. The lifetime of H is extremely short and leads instantly to HO\(_2\). Figure 3 displays the response of an unpolluted troposphere with low levels of
Figure 2: Concentration [ppm] versus time [s] curves.
The Case of Unpolluted Troposphere: \(O^1\)D Injection (Case B)

Figure 3: Concentration [ppm] versus time [s] curves.
The Case of Unpolluted Troposphere (except for high level of CH\(_2\)O): H and \(O^1\)D Injection (Case C)
NO\textsubscript{x}. The OH decays with a time constant of 190 ms, whereas the HO\textsubscript{2} increases from the initially generated level to a maximum at 1 s, mainly because of the reaction OH + H\textsubscript{2}CO and OH + H\textsubscript{2}O\textsubscript{2}. The low level of NO in this atmosphere enables the high concentrations of HO\textsubscript{2} and CH\textsubscript{3}O\textsubscript{2}. The interaction of two HO\textsubscript{2} affords H\textsubscript{2}O\textsubscript{2} that photolyzes into OH which in turn attacks more hydrogen peroxide thus providing a steady source for more HO\textsubscript{2}. The low level of NO and the slow photolysis of H\textsubscript{2}O\textsubscript{2} are at the origin of the longevity of HO\textsubscript{2} at elevated concentrations in analogy to the long-lasting OH from scenario B).

Scenario D) Case of Polluted Troposphere: H and OH Injection.

High power laser radiation at 248 nm may lead to two-photon photolysis of atmospheric water vapor to H + OH. We have assumed the extent of the H\textsubscript{2}O photolysis to be around 10 ppm of the water vapor (upper limit). Figure 4 displays the response of the polluted atmosphere in which the OH and HO\textsubscript{2} levels initially decay at the same rate to result in the regeneration of H\textsubscript{2}O. Due to its high reactivity the OH decays to a larger extent, so that the increased level of HO\textsubscript{2} interacts with the high levels of NO albeit on a much shorter time scale compared to scenario C). At later times the NO and NO\textsubscript{2} levels reach their photostationary state. The peak in NO\textsubscript{2} is due to the reaction HO\textsubscript{2} + NO \rightarrow NO\textsubscript{2} + OH which leads to a related maximum in O\textsubscript{3}, which in turn is responsible for much of the secondary chemistry at later times.

IV. CONCLUSIONS

→ The relaxation/recovery can occur on very different time scales according to the strength of the perturbation, scenario C) vs. D) or the species observed, for instance OH vs. NO, scenario B).

→ For one observed species different elementary reactions can be important at different times after the relaxation, for instance see N\textsubscript{2}O\textsubscript{5}, scenario B).

→ Several transient species may be detected during the recovery of the system back to steady state, for instance OH (10\textsuperscript{11} molec cm\textsuperscript{-3}) or HO\textsubscript{2} (10\textsuperscript{10} molec cm\textsuperscript{-3}) using state-of-the-art detection techniques.

→ Several modes of laser-perturbation lead to direct insight into the hydrocarbon oxidation cycle in the aftermath of a powerful pump pulse under low NO\textsubscript{x} conditions, even using a relatively simple reaction mechanism.

→ Radical-radical reactions can become important in the aftermath of the perturbing pulse due to large transient densities of free radicals. For instance OH + HO\textsubscript{2}, scenario D) or HO\textsubscript{2} + HO\textsubscript{2}, scenario C). This interaction is emphasized even more under low NO\textsubscript{x} conditions.

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REFERENCES