

**NUMERICAL STUDY OF A PUMP AND PROBE
LIDAR EXPERIMENT FOR IN SITU
TROPOSPHERIC MEASUREMENTS OF THE OH
RADICAL**

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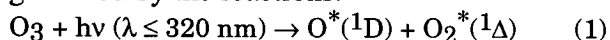
ABSTRACT

The Pump and Probe LIDAR method allows the measurement of the speed of photochemical reactions in real atmospheric conditions. The evolution of the OH radical concentration can be followed in situ, although this concentration is extremely low under natural conditions. During the Pump step, a short flash of light photodissociates the ambient ozone, thus resulting in the formation of highly excited $O^*(^1D)$. The reaction of the $O^*(^1D)$ with the water vapor leads to a quasi instantaneous increase of OH radical concentration, ranging up to six orders of magnitude higher than the maximal natural OH level under daytime tropospheric chemistry. During the Probe step, the return of the OH to its initial natural concentration can be monitored by means of LIF or DIAL. This OH return to equilibrium signal is first dependent on the photochemistry, but is also affected by the diffusion, the turbulence and the transport by the wind. This paper presents a computer simulation of the Pump-and-Probe (P-P) experiment taking into account the effects of these physical parameters as well as the photochemistry in order to estimate the feasibility of such an experiment.

INTRODUCTION

Hydroxyl radicals dominate the daytime chemistry of the troposphere. The reaction of OH with a wide range of species is the first and rate determining step in the oxidation and chemical conversion of most inorganic and organic atmospheric gases and vapors into more stable products. Thus the lifetime of these gases and vapors directly depends on the concentration of OH radicals in the atmosphere.

The production of OH in the troposphere is governed by the reactions:



Other OH forming reactions involving H_2O_2 , HO_2 , HONO and nitrogen oxides are also contributing, especially in polluted atmosphere.

The most important reactions consuming OH are with CO ($OH + CO \rightarrow H + CO_2$) and with CH_4 ($OH + CH_4 \rightarrow CH_3 + H_2O$). In the unpolluted atmosphere, about 70 % of the OH reacts with CO and 30 % with CH_4 .

Because the reactivity of OH is so high and its production rate relatively slow, its equilibrium concentration is low. Model estimates places this concentration in the range of 10^5 to 10^7 radicals/cm³. In contrast to the well-developed theory for homogenous gas-phase tropospheric chemistry, experimental measurements are rare. However reliable values for OH concentrations are needed both as a sensitive test for the models of tropospheric chemistry and to estimate the lifetime of many trace gases.

STATE OF RESEARCH

The direct measurement of the local concentration of OH radicals in the troposphere has been undertaken for more than two decades [1]. Three early OH measurement systems were brought together in an intercomparison study [2], which lead to the conclusion that none of these could routinely measure ambient OH at the 10^6 molecules/cm³ level within a reasonably short averaging time. Compared to the status at the time of that evaluation, several improvements in local OH measurement techniques have been reported recently: the Fluorescence Assay with Gas Expansion (FAGE) [3], the radio-chemical $^{14}CO/^{14}CO_2$ oxidation method [4], the ion-assisted SO_2/HSO_4^- oxidation method [5], the two-photon LIF (TP-LIF) [6]. The long-path absorption spectroscopy [7] may be classified as a local measurement, although it provides concentrations averaged over several kilometers. It is based on the absorption of a UV laser beam by OH (two lines are within the bandwidth of the laser emission), and the OH concentration is derived from Lambert-Beer's law.

The limit of detection depends on the weather conditions, and was typically around 2×10^6 OH/cm³ for a 8.6 km pathlength and one hour integration time [7]. All these techniques are facing the same problem: due to its extremely low natural concentration, the OH radical is hardly measurable and therefore can be detected only under at least several minutes of integration time.

THE P-P EXPERIMENT

This experiment is a test to check the actual understanding of OH related reactions in the atmosphere under many types of atmospheric conditions. The comparisons of photochemical model calculations with direct OH measurements is an approach which however cannot always be applied. An alternative solution is to perform a flash photolysis experiment *in situ* in the troposphere. Using a short laser pulse (KrF excimer at 248 nm), we can induce reaction (1) and (2) shown above. With an initial O₃ concentration of 40 ppb and a laser pulse of 100 mJ/cm², a maximum OH concentration corresponding to 10^{11} molec/cm³ is expected, which is more than six order of magnitude higher than the steady state OH concentration. We present here a computer simulation involving both the chemistry and the physical properties of the atmosphere in order to investigate the feasibility of this experiment. This "atmospheric physico-chemical reactor" simulation is based on the mass conservation equation:

$$\frac{\partial C_k}{\partial t} + \vec{\nabla} \cdot \vec{U} C_k = \vec{\nabla} \cdot [(\kappa_t + \kappa) \vec{\nabla} C_k] + \dot{\omega}_k \quad (3)$$

where C_k kth species concentration,
 \vec{U} wind speed,
 κ molecular diffusion,
 κ_t turbulent diffusion,
 $\dot{\omega}_k$ kth chemical production rate.

For the chemistry part, a simplified chemical model of the troposphere including 53 chemical species and 71 reactions is treated using the CHEMKIN II package of programs. This software incorporates the temperature and pressure dependence of all uni-, bi-, and termolecular reactions, and also explicitly takes into account the reverse of every elementary reaction. Most kinetic parameters were taken from kinetic data evaluations for atmospheric chemistry or were estimated [8].

RESULTS

Chemistry: the OH concentration vs. time is simulated for two air conditions: an unpolluted atmosphere (U) and a polluted atmosphere (P) (ref. 9-10). Low level of NO_x (unpolluted atmosphere) leads to a significant longer OH life time (typ. 150 ms) than polluted troposphere (typ. 7 ms). In this example, the simulation is run with "chemistry only", that means without any effect due to the transport or the diffusion by the wind.

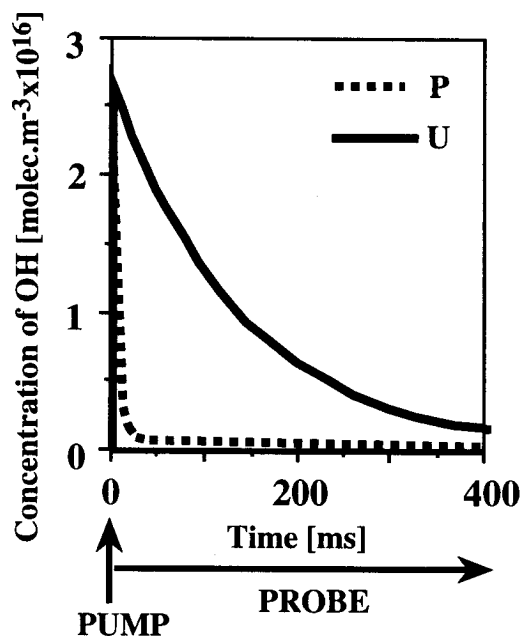


Fig. 1 Simulated OH concentration vs time for polluted (P) and unpolluted atmosphere (U) (chemistry only).

Transport: the effect of the transport on the OH concentration vs. time is due to the mean wind velocity. The wind blows out of the probed region the OH to be observed, and this results in an artificial decrease on the OH signal which depends directly on the velocity.

Figure 2 shows the effect of 2 different velocities at 50 m from the P-P on axis experiment, with a 0.3 mrad divergence and 10 mm initial radius for the pump laser and a 0.1 mrad divergence 10 mm radius for the probe laser, as compared to the "chemistry only" case for unpolluted atmosphere.

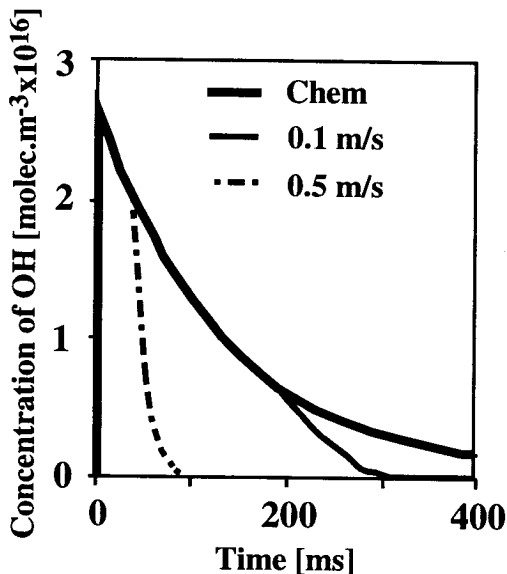


Fig. 2 Simulated OH concentration vs time with transport effects: for $U = 0$ ("chemistry only" chem), 0.1 and 0.5 m/s resp.

Diffusion: The same comparison can be made for the turbulent diffusion with respect to the "chemistry only" case. In this figure, 4 scenarios are demonstrated for different turbulent viscosities (ν_∞) and lagrangian time scales (τ_L).

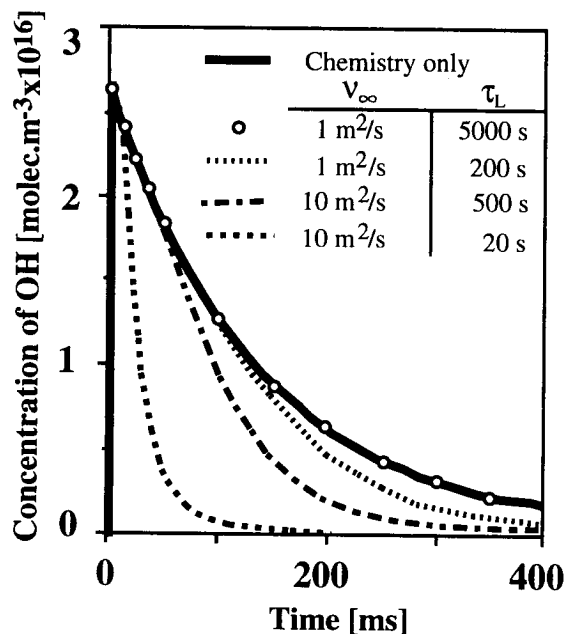


Fig. 3 Simulated OH concentration vs time with turbulent diffusion effect on the "chemistry only" case

CONCLUSION

The P-P experiment is a new alternative to learn about transient species, like the OH radicals, which can be produced in such high instantaneous concentration that they can be detected during the recovery of these species

back to their steady state concentration. The OH return to equilibrium after the pump step can be probed but only on a short time scale (typ. smaller than 100 ms), and this not only due to the high reactivity of this radical, but also due to the transport and diffusion by the wind under real *in situ* tropospheric conditions.

AKNOWLEDGEMENT

The authors would like to thank the Swiss National Foundation for its financial support .

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