Optical Measurements of Tropospheric Hydroxyl with Lasers

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The application of laser induced fluorescence (LIF) in the uv to monitor tropospheric OH concentrations is limited for several reasons. In general the sensitivity of this method increases with the laser intensity. But at the low OH concentrations present in the atmosphere the beginning nonlinearity of the absorption (saturation effect) severely restricts the use of higher laser intensities. The high sensitivity of the LIF technique can be further compromised by the presence of an OH interference signal. This signal is generated by the monitoring laser light itself from laser photolysis of ambient ozone and the succeeding reaction of the photolysis product $O(^1D)$ with water to produce hydroxyl radicals. The results of the calculations are presented in a diagram from which the range of laser parameters can be deduced, which can be applied with confidence to monitor OH by the LIF method. The maximum number of signal counts for these working conditions is in the range of 10^{-3} per laser pulse.

I. Introduction

Ozone is an important atmospheric trace gas. It is not only present in the stratosphere (ozone-layer) but also in the troposphere where its average concentration reaches values which are only one order of magnitude below stratospheric ones. For atmospheric chemistry its very strong uv absorption is most important. Observations carried out in the past have given quite a detailed information on the dissociation products [1]. Below 310 nm there is sufficient energy to photodissociate O_3 to an electronically excited O_2 molecule and O atom:

$$O_3 + h\nu(< 310\ \text{nm}) \rightarrow O(^1D) + O_2(^1\Delta_g)\,. \quad (1)$$

The reaction of excited oxygen atoms with water molecules produce OH radicals, which participate in a great number of atmospheric reactions. Under atmospheric conditions their average lifetime is therefore small (~ 1) and their average concentration low. Concentrations in the 10^6 per cc region are predicted from recent model calculations [2]. As the OH radicals are so important in atmospheric chemistry the determination of their daytime concentration is very much desirable. In the past a number of optical methods have been proposed to determine the in situ concentration of atmospheric OH [3–7]. Also measurements using a chemical method have been published [8].

Under atmospheric conditions OH is in the vibrationless ground state (population numbers $N_{v''=0}$: $N_{v''=1} \simeq 1:10^{-8}$). Its strongest optical transition is in the ultraviolet ($X^2\Pi_{3/2,\,1/2} \rightarrow A^2\Sigma^+$). From the values of the Franck Condon factors the two transitions ($v''=0 \rightarrow v'=0, 1$) at 309 and 282 nm are most important [9]. To monitor atmospheric OH either absorption of this resonance radiation is used directly or fluorescence measurements are made.

The use of resonance fluorescence has been carried out successfully in the stratosphere [3]. In this case the application of a conventional resonance lamp was possible. For the conditions of the more densely troposphere especially at ground level the quenching of the excited $A^2\Sigma^+$-state is so strong that until now light sources of the conventional type have not been used to monitor OH at this level. Instead, light sources with a much higher spectral density such as lasers were applied. The present paper discusses and defines the experimental conditions for the use of lasers to monitor tropospheric OH by laser induced fluorescence (LIF).

Section II contains a discussion about the limiting influence of saturation on the intensity of lasers used in LIF. With the result of such calculations the maximum count rate of a suitable LIF setup used to monitor in situ OH is given (III). Section IV discusses the interference problem arising from the laser photolysis of atmospheric O_3 in the application of the LIF-technique. The last section (V) contains a discussion on different possibilities to reduce the existing difficulties in the use of this method

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and a further discussion on alternative ways to observe and measure in situ OH.

II. Saturation Effects in Absorption

The absorption rate varies linearly with the laser intensity, provided that the number density of molecules in the initial and final state is constant. At high intensities, however, the number density of molecules in the initial state can be changed by the absorption, therefore the absorbed intensity is no longer a linear function of the intensity of the incoming radiation. This problem of nonlinear absorption has been discussed by Killinger et al. [10] for different types of line broadening. In the following a brief account will be given on the influence of saturation on OH measurements under atmospheric conditions.

The rate of absorption, that is the number density of photons absorbed in the frequency interval per unit time, is given by:

$$A_{\mathrm{r}}(\nu) = \frac{n(\nu)\,P_{\mathrm{r}}(\nu)}{1+S(\nu)}\,, \tag{1}$$

where $n(\nu)$ is the density of OH molecules associated with the transition frequency ν. Because of Gaussian distribution of the molecules we get

$$n(\nu) = n\,g_{\mathrm{D}}(\nu, \nu_{\mathrm{D}}) \tag{2}$$

with n being the concentration of OH in the lower state and $g_{\mathrm{D}}(\nu, \nu_{\mathrm{D}})$ describing the line shape:

$$g_{\mathrm{D}}(\nu, \nu_{\mathrm{D}}) = \frac{1}{\Delta\nu_{\mathrm{D}}}\sqrt{\frac{4\ln 2}{\pi}} \cdot \exp\left[-4\ln 2\left(\frac{\nu-\nu_0}{\Delta\nu_{\mathrm{D}}}\right)^2\right]. \tag{3}$$

The doppler width $\Delta\nu_{\mathrm{D}}$ of the OH transitions in question has a value of $\Delta\nu_{\mathrm{D}} \simeq 0.1\ \mathrm{cm}^{-1}$.

The pump rate $P_{\mathrm{r}}(\nu)$ is the product of the absorption cross section $\sigma(\nu_1, \nu)$ and the photonflux $F(\nu_1)$ (number of photons per unit area and time). $\sigma(\nu_1, \nu)$ as well as $F(\nu_1)$ exhibit a frequency distribution. Therefore the pump rate will be given by

$$P_{\mathrm{r}}(\nu) = \int_{-\infty}^{+\infty} \sigma(\nu_1, \nu)\,F(\nu_1)\,\mathrm{d}\nu_1\,. \tag{4}$$

The absorption cross section of a homogeneously broadened line is described by a Lorentz profile:

$$\sigma(\nu_1, \nu) = \sigma_0\,g_1(\nu_1, \nu, \Delta\nu_1)\,, \tag{5}$$

$$g_1(\nu_1, \nu, \Delta\nu_1) = \frac{1}{\Delta\nu_1}\,\frac{2}{\pi}\,\frac{1}{1+[(\nu-\nu_1)/\Delta\nu_1/2]^2}\,. \tag{6}$$

σ_0 is the integrated absorption cross section of the transition. Under atmospheric conditions the main broadening effect for OH is due to collisions, resulting in a linewidth (FWHM) of $\Delta\nu_1 = 0.15\ \mathrm{cm}^{-1}$ at ground level [11].

The saturation parameter S (Eq. (1)) which is the ratio of pump rate and average relaxation rate is a measure for bleaching of the lower state by optical pumping:

$$S = 2\,P_{\mathrm{r}}\,\tau\,. \tag{7}$$

Here, τ is the characteristic relaxation time. Under atmospheric conditions at ground level we get $\tau \simeq 0.7$ ns [12]. To get the total absorption rate A_{t} we have to integrate equation (1) over all frequencies:

$$A_{\mathrm{t}} = \int_{-\infty}^{+\infty} A_{\mathrm{r}}(\nu)\,\mathrm{d}\nu\,. \tag{8}$$

If the exciting source is a narrow bandwidth laser ($\Delta\nu_{\mathrm{laser}} < \Delta\nu_1$), neglecting spectral modes, we get for A_{t}:

$$A_{\mathrm{t}} = N F \sigma_0 \int_{-\infty}^{+\infty} \mathrm{d}\nu\, g_{\mathrm{D}}(\nu, \nu_{\mathrm{D}}) \cdot g_1(\nu_1, \nu, \Delta\nu_1\sqrt{1+S_1})/\sqrt{1+S_1} \tag{9}$$

with

$$S_1 = 2\,\tau\,\sigma_0\,F\,\frac{2}{\pi\,\Delta\nu_1}\,. \tag{10}$$

As a good approximation which is valid for OH under atmospheric conditions ($\Delta\nu_{\mathrm{D}} < \Delta\nu_1\sqrt{1+S_1}$), the evaluation of the integral (Eq. (9)) leads to

$$A_{\mathrm{t}} \simeq N F \sigma_0\,\frac{2}{\pi\,\Delta\nu_{\mathrm{V}}}\,\frac{1}{1+S_1} \tag{11}$$

$\Delta\nu_{\mathrm{V}} = 0.19\ \mathrm{cm}^{-1}$ is the linewidth (FWHM) of the corresponding Voigt profile (13).

In order to guarantee a linear relation between the incoming laser intensity and the absorption rate, S_1 has to be small ($S_1 \ll 1$). Allowing a 10% deviation of linearity for the absorption rate we can calculate the highest accessible photon flux F_{m} (Eq. (10)):

$$F_{\mathrm{m}} = 0.025\,\pi\,\Delta\nu_1\,1/\tau\,\sigma_0\,. \tag{12}$$

Inserting this value into Eq. (11) provides the maximum absorption rate which still allows a linear operation within the 10% deviation.

The total number of excited OH molecules is obtained by integrating the maximum absorption rate (Eq. (11)) over the total cross section of the laser beam and the time profile of the laser pulse. These integrations were carried out for a Gaussian and a continuous distribution of the energy over the beam cross section. The time dependence of the laser pulse was approximated by a rectangular, a sinusoidal, and a Gaussian shape. These calculations show that the total number of excited OH is only slightly dependent on the choice of the pulse shape for low saturation parameters S_1.

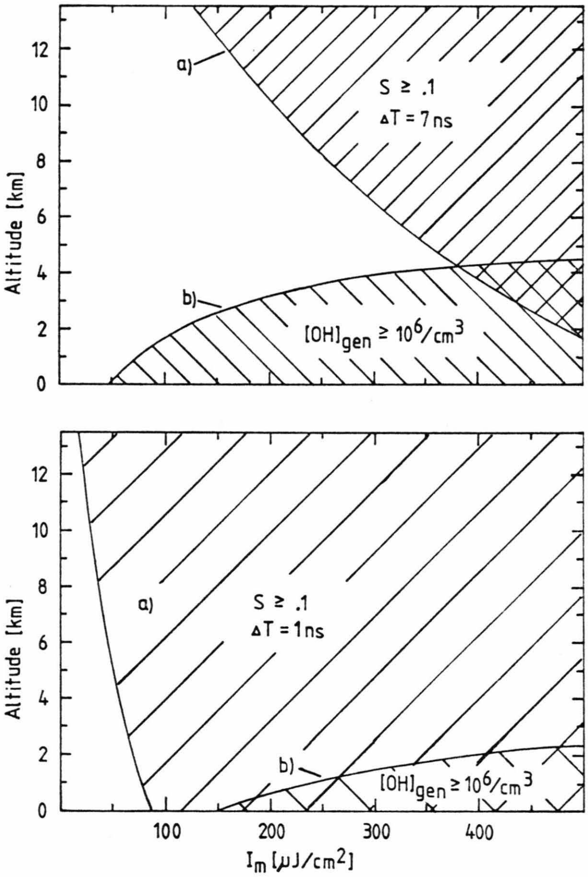

Fig. 1a, b. The diagram shows the feasable range of laser intensity I_m in measurements of tropospheric OH with the LIF method as a function of altitude. In both parts of the figure the shaded area above curve a is forbidden due to a positive deviation of the saturation parameter from $S_1 = 0.1$. The shaded area below curve b is forbidden due to a growth of $[OH]_{gen}$ from a value of $1 \times 10^6/cm^3$. The upper diagram represents conditions for a laser pulse width of $\Delta T = 7$ ns. The lower diagram represents conditions for a reduced laser pulse width of $\Delta T = 1$ ns.

The maximum concentration of excited OH molecules is then given by

$$n_e = n\,\sigma_0\,I_m \frac{2}{\pi \Delta\nu} \frac{1}{1 + S_1} \tag{12a}$$

provided that the incoming radiation intensity does not change along the absorption path. In Eq. (11) I_m denotes for a given pulse length the highest applicable intensity of the exciting laser calculated from Equation (12).

Figure 1a presents a plot of highest applicable intensity I_m as a function of altitude (curve a) for an exciting laser with a pulse width of $\Delta T = 7$ ns. The shaded area above curve a) represents that region for which the saturation parameters S_1 exceed 0.1. If experimental conditions are such that this region is reached, then the relation between the incoming laser intensity and the absorption rate will deviate from linearity by more than 10%.

With increasing altitude the characteristic relaxation time of excited OH also increases due to the decreasing collision probability. For this reason the value of the highest applicable laser intensity I_m becomes smaller.

III. The LIF-method

Laser induced fluorescence (LIF) is an optical method which can be applied to monitor tropospheric OH. Under atmospheric conditions the OH molecules are present only in the vibrationless state $v'' = 0$ of the electronic ground state. Therefore only the transitions $X^2\Pi(v'' = 0) \rightarrow A^2\Sigma^+(v' = 0, 1)$ at 309 and 282 nm can be excited. Transitions to higher v'-states are very weak due to the low transition probabilities. In either case fluorescence is observed only from $A^2\Sigma^+(v' = 0)$ under atmospheric conditions.

A principal problem in fluorescence spectroscopy is the suppression of straylight. For this reason it is not advisable to excite the (0–0)-transition at 309 nm, and simultaneously measure the fluorescence at the same wavelength despite the higher transition probability ($A_{00}/A_{10} \simeq 3$) [9]. Therefore, all applications of the LIF-method to determine tropospheric OH-concentrations have made use of the excitation of the (0–1)-transitions. In this case, the molecular fluorescence, which is shifted towards longer wavelengths ((0–0)-transition at 309 nm), can be separated from the straylight of the exciting laser radiation by suitable filters. This procedure is possible since vibrational relaxation $v' = 1 \rightarrow v' = 0$ in OH $A^2\Sigma^+$ state is very effective and even faster than electronic quenching [12] ($\sigma_{10} > \sigma_1$, see Figure 2).

In the following we give a calculation of the intensity of the fluorescence signal which can be expected if the LIF method is applied to measure tropospheric OH concentrations. To carry out this calculation we assume, that N_e OH molecules which are excited by 282 nm laser radiation are present in the observation volume. The population in the excited state $A^2\Sigma^+$ will be removed by electronic quenching (σ_1), vibrational relaxation (σ_{10}), and by spontaneous emission of radiation at 314 nm (γ_1). That portion of the OH molecules which relaxes from the $v' = 1$ to the $v' = 0$ manifold, is given by

$$f_R = \sigma_{10}/(\sigma_1 + \sigma_{10} + \gamma_1) . \qquad (13)$$

The contribution from fluorescence (γ_1) is small at tropospheric pressures and can be neglected. With German's results [12] for the vibrational relaxation and the electronic quenching we get $f_R = 0.69$. At high pressures only a small part of the OH molecules which are relaxed to the $v' = 0$ state, will be able to emit resonance radiation. This part is given by

$$f_{fl} = \tau/\tau_0 \qquad (14)$$

with τ and τ_0 being the effective and the natural lifetime of excited OH respectively. The rest $(1 - f_{fl})$ is deactivated by electronic quenching (σ_0). Using the results of German for the natural lifetime τ_0 [14] and the quenching cross section σ_0 [12], a loss factor of $f_{fl} = 1 \times 10^{-3}$ is obtained for conditions at ground level. Only a small part of the isotropically emitted fluorescence radiation can be observed by a suitable detector. To focus a high fraction of the fluorescence radiation on to the detector, $f/1$ collection optics should be used. In the most favourable case such a system has a loss factor of $f_\Omega = 1/16$. Additional losses occur due to reflexions at the surfaces of the optical mapping system (0.5), due to low transmissions of the narrow bandwidth filters which have to be used to suppress the stray light (0.15), and due to the quantum efficiency of the photo-detector (0.3). These losses are combined in the loss factor f_{op}. The total loss factor f_{total} is given by the product of the different loss factors:

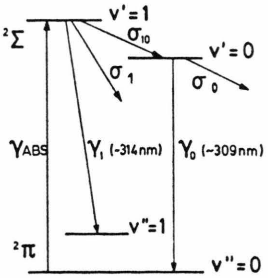

Fig. 2. Level diagram describing collisional and radiative transitions used in the calculations of the fluorescence signal (Equations (13–16)). σ_{10} determines the vibrational relaxation of OH $^2\Sigma^+(v' = 1 \rightarrow v' = 0)$. σ_1 and σ_0 are quenching cross sections. γ_1 and γ_0 relate to the free molecule lifetimes. γ_{abs} is the absorption cross section.

$$f_{total} = f_r f_{fl} f_\Omega f_{op} . \qquad (15)$$

With N_e excited OH molecules in the observation volume a signal of

$$C_r = f_{total} N_e \quad \text{[Counts/laser pulse]} \qquad (16)$$

is obtained at the anode of the photodetector. With the results from Fig. 1a, curve a) and Eq. (11), we see that at ground level a maximum of 36% of the OH molecules can be excited regardless of rotational states. Assuming the average concentration of tropospheric OH to be $10^6/cm^3$ then at 298 K nearly $10^5/cm^3$ are present in rotational states with maximum population ($^2\Pi_{3/2}(v'' = 0, J'' = 3/2)$). In order to excite a maximum number of OH molecules a large beam diameter should be used. The collection optics, however, limit the beam diameter. For this reason we expect a diameter of 1 cm to be an optimal approach. For an absorption length of 1 cm 2.8×10^4 OH molecules will then be excited within the observation volume under the discussed conditions. According to Eq. (16) a detector signal of 0.027 counts per laser pulse can be obtained. This low counting rate is a direct result of the saturation effect which restricts the range of the exciting laser intensity. There is, however, still another effect which severely limits the application of the LIF method to monitor tropospheric OH. This problem arises from an interference in the detection of natural OH levels brought about by the LIF method itself.

IV. The Interference Problem

The laser radiation at 282 nm used in the LIF method to excite the OH molecules dissociates ambient O_3 into the products $O(^1D)$ and $O_2(^1\Delta_g)$. Part of these $O(^1D)$ atoms react with the ubiquitous atmospheric water vapor to produce OH molecules, the other part is quenched in collisions, mainly with N_2 and O_2. The following scheme describes these processes:

$$O_3 + h\nu(282\ \text{nm}) \rightarrow O(^1D) + O_2(^1\Delta_g)\,, \tag{17}$$

$$O(^1D) + H_2O \xrightarrow{k_2} OH + OH\,, \tag{18}$$

$$O(^1D) + M \xrightarrow{k_M} O(^3P) + M\,, \quad M = N_2, O_2\,. \tag{19}$$

Reaction (18) is very fast under tropospheric conditions. At ground level the artificially generated OH radicals are formed within less than 1 ns [15]. Laser pulse lengths used in the LIF method until now were about $\Delta T = 7$ ns. This is much larger than the OH reaction time. For this reason it is possible to produce and to excite these OH radicals with the same laser pulse simultaneously. This is known as the interference problem [16]. The detected fluorescence signal is therefore composed of two signals: one originates from self generated OH and the other one originates from natural OH. In the following the influence of this interference on the results obtained from measurements of tropospheric OH will be discussed.

The time dependent $O(^1D)$ concentration produced by the laser is given by

$$\frac{d}{dt}[O(^1D)] = -k'[O(^1D)] + \varepsilon n(t)\,. \tag{20}$$

The first term is a loss term describing the deactivation of $O(^1D)$ by the processes (18) and (19). $\varepsilon n(t)$ represents the production of $O(^1D)$ from the photolysis of O_3 by laser radiation with $n(t)$ being the photon flux (photons/cm^2 s) and ε being the product $\sigma[O_3]$ (σ: absorption cross section of O_3 at 282 nm). This differential equation yields nearly equal results for a sinusoidal or a rectangular shaped laser pulse $n(t)$. Therefore we will use in the following only the results for the rectangular pulse shape.

With the results from Eq. (20) the laser induced OH production rate is given by

$$\frac{d}{dt}[OH] = 2k_2[H_2O][O(^1D)]\,. \tag{21}$$

The *total* number of artificially generated OH molecules depends on atmospheric conditions and laser parameters. But that fraction of artificially generated OH which is observed by the LIF method is additionally determined by the rotational distribution of the OH produced according to Equation (18). This is because only those artificially produced OH radicals which populate the same rotational state as natural OH can give a contribution to the fluorescence signal. To calculate this interference signal we need additional information about the energy partitioning in reaction (18). This energy partitioning has been determined from an independent experiment [17]. From these measurements we found that 2.4% of the OH formed in reaction (18) are in the lower Λ-component of the lowest rotational state of OH $X^2\Pi_{3/2}(v'' = 0, J'' = 3/2)$. As this state has mostly been used in the application of the LIF method [6] we will refer to this rotational state in the further discussion. The time dependence of the artificially produced OH molecules which exhibit the same absorption properties as the ambient OH molecules is given by

$$\frac{d}{dt}[OH(J'')] = \frac{\alpha_g(J'')}{\alpha_n(J'')} k_2[H_2O][O(^1D)]\,. \tag{22}$$

$\alpha_g(J'')$ is the fraction of laser generated OH in the rotational state whereas $\alpha_n(J'')$ is the respective fraction of the natural OH in this same rotational state. At 298 K $\alpha_n(J'' = 3/2)$ is about 10% for one Λ-component. To obtain the concentration of the artificially generated OH which is subsequently excited by the same laserpulse we have to solve the following equation:

$$[OH]_{gen} = \int_0^T [OH(J'')]\, n(t)\, dt \Big/ \int_0^T n(t)\, dt\,. \tag{23}$$

In this equation T is the laser pulse length. For a rectangular pulse shape the integration leads to

$$|OH|_{gen} = \frac{\alpha_g(J'')}{\alpha_n(J'')} \frac{k_2' \varepsilon N_0}{k'} \tag{24}$$

$$- \left[\frac{1}{2} + \frac{1}{(k'T)^2}\left(1 - \exp\{-k'T\} - \frac{1}{k'T}\right)\right],$$

where N_0 represents the number of laser photons per unit area. For the case that $[OH]_{gen}$ will not exceed $[OH]_{nat}$ Eq. (24) can be applied to calculate I_m which can be used in the LIF method. Figure 1, curve (b) represents the results as a function of altitude with $[OH]_{nat} = 1 \times 10^6/\text{cm}^3$. The region below curve (b) is that region where the production of artificially OH leads to larger $[OH]_{gen}$ than

$1 \times 10^6/\mathrm{cm}^3$. O_3 and H_2O concentrations used in the calculations are taken from the U.S. Standard Atmosphere [18].

The results of Fig. 1 show that one cannot use the maximum laser intensity at ground level as given by the saturation effect (Equation (12)). Instead one has to operate at much reduced laser intensities. With the same optimum conditions as discussed in Section III, only 2.1×10^{-3} counts per laser pulse can be expected at the photodetector output. The influence of such a low count rate on the measurements of tropospheric OH will be discussed in the following section together with alternative ways to solve the problem.

V. Discussion

In the foregoing sections it was shown that there exist limiting conditions for the intensities of lasers to be used in tropospheric OH measurements. At ground level the limits are due mainly to the artificial generation of OH by the method itself (interference effect). At higher altitudes (> 4 km) saturation is the dominant problem. From the calculations the number of counts of a suitable detector system is obtained. At ground level not more than 2.1×10^{-3} counts per laser pulse can be expected. From considerations given by quantum statistics, a minimum of 10 counts is needed to achieve 30% accuracy, if we neglect any stray light and any noise of the detection system. Then the measuring time will have to be nearly 10 minutes with present lasers (typical repetition rate 10 pps). But it is certainly very difficult to fulfill this condition of negligible stray light because within the period of an experimental run the laser emits 3×10^{17} quanta. In addition the many trace components and particles present in the troposphere will in any case increase the stray light problem.

If we neglect for a moment the nonlinearity of the signal and accept a higher amount of $[\mathrm{OH}]_{\mathrm{gen}}$, then it is possible to work with a proportionally higher laser intensity. In this case, however, a much improved precision of the method is necessary in order to correct the signal for the interference effect. Such a procedure is not without problems because all parameters which determine the value of $[\mathrm{OH}]_{\mathrm{gen}}$ have to be known precisely.

Another approach to increase the LIF count rate at ground level is a change of the laser parameters, such as the laser pulse length ΔT: the only parameter to which this method is really sensitive. The reduction in pulse length will decrease $[\mathrm{OH}]_{\mathrm{gen}}$ due to the finite reaction time of the oxygen atoms (Eq. (24)). However, saturation will increase and further limit the applicable laser intensity. Figure 1 b shows the maximum laser intensity I_{m} which can be used in the LIF method for the case of a pulse length $\Delta T = 1$ ns.

Saturation is the most limiting factor for the use of the method at higher altitudes. Although the fluorescence yield increases with altitude due to a reduction in the number of quenching collisions, the saturation effect does so, too. Therefore, the maximum number of counts per laser pulse (0. 05) remains constant independent of altitude ($h \geqq 4$ km).

An alternative method to the LIF technique for the measurements of tropospheric OH is the use of long path resonance absorption [7, 19]. Due to the low tropospheric OH concentrations the absorption length has to be as long as several kilometers to obtain an absorption of the order of $1\,^0/_{00}$, even if the transition with the highest absorption at ground level conditions is used which is $Q_1(2)$ of

$$X^2\Pi_{3/2}(v''=0) \rightarrow A^2\Sigma^+(v'=0) \quad [20].$$

To use a laser beam for such a long path length requires a reduction of its divergence by a telescope. Beam diameters of 20–30 cm are probably resonable for such an application [7, 19]. In this case the photon density is too low to cause any interference or saturation effect as known from the LIF method. There exists no stray light problem. Only atmospheric scattering will merely attenuate the observed signal by a factor of 20 to 1000 depending on atmospheric conditions [19]. But as the signal is still strong this is not a restriction for the method.

The absorption method is an absolute one. Therefore an additional calibration, necessary in the application of LIF, is not needed. This excludes a further source of errors because such a calibration procedure for OH concentrations in the range of 10^6 to 10^7 OH/cm^3 is not without problems.

Acknowledgements

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