Influence of Rotational Relaxation on Tropospheric OH Laser Induced Fluorescence Measurements

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Rotational relaxation of OH molecules in the $^2\Pi$ electronic ground state has been observed to occur in collisions with water molecules with gas kinetic probability. It causes an additional contribution to the already well known sources of interference when LIF is used to monitor tropospheric OH. As the laser generated OH is originally produced mostly in high rotational states, the fast relaxation phenomenon leads to a further population of OH in low rotational states. These states are used to monitor tropospheric OH by spectroscopic methods. The observed effect therefore increases the interference. A mathematical analysis is presented, revealing the effect of all relevant parameters.

I. Introduction

In two recent publications [1, 2], hereafter refered to as I and II, we discussed the interference problem associated with the use of laser-induced fluorescence (LIF) to monitor tropospheric hydroxyl (OH) free radicals. This interference effect is caused by the probe laser beam which is used to excite the natural atmospheric OH [3, 4]. The probe laser wavelength (at 282 nm) is sufficiently energetic to generate additional ground level OH on a sub-nanosecond time scale by initiating the very efficient photo-induced sequence involving ambient concentrations of ozone and water vapor.

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

$$O(^1D) + H_2O \overset{k_2}{\rightarrow} OH + OH\,. \qquad (2)$$

Process (2) occurs with gas kinetic rate, having a rate constant of $(2.02 \pm 0.41)\,10^{-10}$ molecule $\text{cm}^{-3}\,\text{sec}^{-1}$ [15]. As a result of the very short time (0.7 nsec at ground level) involved in the production of OH at atmospheric pressure, the monitoring laser probes both the ambient and photoinduced OH concentrations, within the same pulse. Based upon intensity considerations, the rovibrational state of OH ($^2\Pi_{3/2}$, $v''=0$, $J''=3/2$), is used for monitoring tropospheric OH concentrations. The important question is, however, what fraction of the photoinduced OH molecules are generated in the specific rovibrational state which is used for the primary absorption when using the LIF technique, and this problem is the subject to the present paper.

Extensive and detailed studies of the dynamics of reaction (2) performed in our laboratory, have provided the unequivocal characterization of the nascent rovibrational distribution of OH radicals produced by the sequence (1) and (2). In general, most of the exothermicity (120 kJ/mole) of reaction (2) is partitioned into translational energy of the two product molecules (75 kJ/mole). However, the internal energy partitioning results in one vibrationally hot OH and one which is vibrationally cold. Based on these observations, exact number densities of OH produced in the lowest rotational state of the vibrationless ground state can be calculated. Calculation of the number of OH radicals produced by the photoinduced effect from the number densities, allows an excellent estimate of the interference effect. Measurements performed in our laboratory have been recently confirmed by other groups [6, 7].

An additional problem to be considered when comparing laboratory results with the ambient tropospheric measurements is the difference in the laser wavelengths used in the laboratory and in the field. Laboratory measurements on the dynamics of the OH producing reaction (2) have been carried out with 266 nm, the fourth harmonic of the Nd: YAG laser radiation, as the O_3 photolysis source. This wavelength is 25 kJ higher in energy than the laser wavelength (282 nm) used in the LIF method. This energy surplus could influence the experimental results since the nascent

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kinetic energy of the O(^{1}D) is dependent on the quantum energy of photolyzing radiation [8, 9].

However, recent studies in our laboratory on the influence of the O(^{1}D) kinetic energy on the reaction rate and energy partitioning among the OH products showed that the O(^{1}D) kinetic energy has no effect on these parameters [10, 11, 12]. Therefore, it would appear that observations taken at 266 nm are also valid at 282 nm.

II. Rotational Relaxation

In all the published accounts of the dynamics of reaction (2) the nascent rotational distribution of OH radicals is relaxed extremely fast in the presence of water vapor [5, 6, 7, 10, 11, 12]. In our laboratory the measurements were carried out under different experimental conditions. The most careful studies were made with only rotationally excited OH ($^2\Pi$, $v''=0$, J''); collision partners were water molecules in one case and argon atoms in the other.

The reaction mixture consisted of ozone and water vapor with added argon when needed. The uv flash at 266 nm from a Nd-YAG laser was used to photolyse ozone and to produce O(^{1}D) atoms. These O(^{1}D) atoms then reacted with water molecules to form 2 OH radicals in every event. The OH radicals thus formed were monitored by use of a tunable uv dye laser which was pumped by the second harmonic of the same Nd-YAG laser at 532 nm. The dye laser probe pulse was delayed relative to the photolysis pump laser pulse by 10 nsec to allow the O(^{1}D) an opportunity to form OH molecules by reaction with H_2O. The OH molecules were detected through their absorption of resonance radiation ($A^2\Pi \leftarrow X^2\Sigma$) around 308 nm.

The rotational relaxation phenomenon was studied by increasing the collision number within the fixed delay time of 10 ns. This was carried out by observing the OH product state distribution at different water vapor pressures (2.5—19 Torr), leaving the ozone partial pressure constant. Experiments with argon as atomic collision partner established the very high efficiency of water molecules in bringing about rotational relaxation of OH. Pressures of argon used were up to 40 torr ($Ar : H_2O = 8 : 1$).

The results from these measurements showed that collisions of OH molecules with argon do not change the OH rotational state distribution under the experimental conditions which means that more than 10 collisions are needed to relax the OH rotations. This is different for water vapor. Water vapor is a fast relaxing gas. At a delay time of only 10 ns and at a partial H_2O pressure of only 10 torr, 60% of the OH radicals were found in the relaxed distribution at 300 K starting from OH rotational distribution at 3000 K.

The experimental results demonstrate that to a first order the observed rotational high temperature (nascent) distribution is converted as a whole into a low temperature (relaxed) distribution. Following this idea for the rotational relaxation process, the phenomenon appears to be describable by introducing a single rate equation with the appropriate relaxation rate coefficient. This coefficient was determined to be

$$k_r = 2.2 \times 10^{-10}\ \text{molec cm}^{-3}\ \text{s}^{-1} \qquad (3)$$

which is gas kinetic.

This mechanism and this rate coefficient allow simple calculation of the number of OH molecules in the low temperature distribution at 300 K starting from the nascent one at 3000 K, for each experimental condition. The nascent distribution is produced in applying OH laser induced fluorescence at 282 nm.

The experimental conditions which are relevant for the discussion of the monitoring of tropospheric OH are the actual atmospheric partial pressure of all important gases and the experimental laser parameters used in applying the LIF method. The results thus obtained will consider the full contribution from atmospheric water vapor but still represent a minimum effect because the amount of rotational relaxation due to the atmospheric constituents N_2 and O_2 is not taken into account. However, from the experiments with added argon it seems to us that N_2 and also O_2 will not have a major effect.

III. Interference Effect

According to Eq. (1) the laser radiation at 282 nm used in the LIF method to excite the OH resonance transition $X^2\Pi(v''=0) \rightarrow A^2\Sigma(v'=0)$ dissociates ambient O_3. The major part of O(^{1}D) atoms thus produced is quenched under atmospheric conditions in collisions with N_2 and O_2:

$$O(^1D) + M \xrightarrow{k_M} O(^3P) + M . \qquad (4)$$

The remaining part mainly reacts with atmospheric water vapor and produces OH molecules (see (2)). These molecules are the photoinduced or generated OH molecules, OH_g:

$$O(^1D) + H_2O \rightarrow OH_g + OH_g\,. \qquad (5)$$

The laser generated OH_g molecules carry a definite amount of internal and external energy [11]. As was observed recently, the rotational energy content of these nascent molecules in $v'' = 0$ can well be described by a temperature of 3000 K. If, however, these nascent OH molecules collisionally interact with water molecules, fast rotational relaxation is observed which, according to the foregoing paragraph can be described by a single rate equation, given by (8).

$$OH_g + H_2O \xrightarrow{k_r} OH_r + H_2O\,. \qquad (6)$$

These facts can be described by the following equations: The time dependence of the $O(^1D)$ concentration is given by

$$\frac{d}{dt}[O(^1D)] = -k'[O(^1D)] + \varepsilon\, n(t)\,, \qquad (7)$$

where $n(t)$ is the time dependent laser radiation (photons/cm^{-2}s).

The first term in (5) is a loss term. k' is the pseudo first order rate constant

$$k' = k_2[H_2O] + k_{O_2}[O_2] + k_{N_2}[N_2]\,.$$

The second term describes the production of $O(^1D)$ atoms from the photolysis of ozone, with ε as the product of the ozone concentration, its absorption cross section at 282 nm, and its quantum yield for $O(^1D)$ production. The influence of the temporal shape of the laser pulse is of minor importance [1]. Therefore, in the following we discuss only results from using rectangular shape pulses.

The differential equation describing the concentration of laser generated OH (OH_g) is given by

$$\frac{d}{dt}[OH_g] = 2k_2'[O(^1D)] - k_r'[OH_r] \qquad (8)$$

with k_2' and k_r' replacing $k_2[H_2O]$ and $k_r[H_2O]$.

The second term takes the relaxation process

$$\frac{d}{dt}[OH_r] = k_r'[OH_g] \qquad (9)$$

into account with OH_r representing the OH_g ($v'' = 0$) rotational distribution after rotational relaxation by H_2O.

The differential equations (7–9) describe the total number of OH molecules, OH_g, induced by the laser and the total number of relaxed OH molecules, OH_r, as functions of time. The concentration of these radicals depends on atmospheric conditions and on the parameters of the laser employed. In addition, however, the fraction of OH radicals that are excited and observed in the LIF method depends on the distribution of OH_g, and OH_r over the individual levels of the electronic ground state. This is so because the only "artifact OH radicals" that can contribute an additional term to the fluorescence signal are those that, during the time of observation, occupy that rotational state that is used for detection. To be sure, that the interference effect applies only to OH radicals that are produced and detected in a single laser pulse, we make the assumption that, with the 10 Hz repetition rate commonly used in standard laser systems, the OH radicals in the sample volume are completely exchanged. Otherwise the interference effect would be still greater.

Let us therefore restrict our discussion to a single laser pulse. In a simple model of the interference effect, the photons of the second half of the pulse detect the OH radicals that are produced in the first half. For an exact calculation the following integration must be performed.

$$[OH_{gen}] = \int_0^T (f_g[OH_g] + f_r[OH_r])\, n(t)\, dt \Big/ \int_0^T f_{nat}\, n(t)\, dt\,. \qquad (10)$$

Here f_{nat} is the fraction of natural OH at thermal equilibrium ($f_{nat} = 0.1$ at 300 K) in the specific rotational state, which is used for excitation by the LIF method, and f_g is the fraction of laser generated OH in the same rotational state. This quantity has been determined [6, 7, 11].

The fraction of OH_r in the same rotational state is given by f_r. In order to calculate the contribution of the interference effect by rotational relaxation, we make use of the experimental observation that the relaxed rotational distribution is nearly at equilibrium temperature (300 K) [12]. Therefore, we use

$$f_r = f_{nat}\,. \qquad (11)$$

Equation (10) is similar to equation (23) of publication II, but now includes the additional relaxation term $f_r\,[OH_r]$.

We have previously shown in publications I and II that carrying out the integration of (9) with a sinusoidal or rectangular pulse shape leads to very similar results, so that the integrated form of OH_{gen} previously discussed was based on the rectangular pulse shape. Integration of (7–9) can be carried out analytically (Appendix).

Introducing the following abbreviations (see Appendix (A.3–A.5))

$$A(t) = \frac{k'}{k_r'(k' - k_r')}(1 - \exp(-k_r' t)), \quad (12)$$

$$B(t) = \frac{k_r'}{k'(k' - k_r')}(1 - \exp(-k' t)), \quad (13)$$

$$C = \frac{2 k_2' \varepsilon N_0}{k' T}. \quad (14)$$

(N_0: Number of photons per unit area) we obtain:

$$[OH_g] = C(A - Bk'/k_r'), \quad (15)$$

$$[OH_r] = C(t + B - A). \quad (16)$$

The final integration of (10) yields the concentration of laser generated OH_{gen} which will be probed simultaneously with the natural OH:

$$[OH_{gen}] = \frac{C}{k_r' T}\left\{\frac{f_g}{f_{nat}}(T + B - A) + \frac{f_r}{f_{nat}}(k_r' T^2/2 - (1 + k_r'/k')T + A - Bk_r'/k)\right\}. \quad (17)$$

IV. Discussion

Equation (17) is an expression which describes the artifact produced by the laser. OH radicals are formed in the photolysis of ozone and the subsequent reaction of the photolysis product, $O(^1D)$, with water vapor. The energy flow in this exothermic reaction is such that an appreciable amount of the total energy released is transferred into rotation of the products. Our experiment verified that rotational relaxation of OH, especially in collisions with water molecules, is an extremely efficient process, so that this relaxation phenomenon additionally contributes to the interference effect. Until now, this additional contribution has not found any detailed consideration in the literature [3].

The expression for OH_{gen} which was obtained from the calculation (Eq. (17)) is rather unwieldy. Therefore, we shall discuss the solution in an approximate form, making the following assumptions which are valid near ground level of the atmosphere:

$$1 - e^{-k'T} \to 1; \quad k_r' T \leqq 1.$$

In this case the expression for OH_{gen} is reduced in complexity and is given as

$$[OH_{gen}] = \frac{C}{k' - k_r'} X \frac{f_g}{f_{nat}} \cdot \left\{1 + \frac{k_r'}{k'}\left(\frac{k'^2 T^2}{6X}(f_r/f_g - 1) - f_r/f_g\right)\right\} \quad (18)$$

with

$$X = 1/k' T - 1 + k' T/2.$$

The quantity added to 1 within the braces of (18) describes the additional contribution of the rotational relaxation to the interference effect. In the limit $k_r' \to 0$, (18) transforms to equation (23) of publication II, which was obtained without consideration of the rotational relaxation. Using a temperature of 3000 K for the nascent distribution and a 100% humidity at ground level (300 K), the value of the added quantity is 0.95. This means that when the LIF technique is used to monitor tropospheric OH, the rotational relaxation of the laser-generated OH increases the interference effect by a factor of nearly 2.

This is a significant effect with respect to the actual levels of ambient OH. Therefore, all previously reported data should be corrected to account for this additional interference effect. Furthermore, as collisional effects from other tropospheric gases at much higher concentrations, i.e. N_2 and O_2, have not been accounted for in this analysis, the correction for H_2O relaxation is obviously a lower limit. The result of the considerations discussed in this manuscript suggest that the reliability of tropospheric OH data obtained by the use of the LIF technique is open to considerable doubt.

Recently a modification of the LIF technique has been proposed [13]. This LIDAR technique uses an enlarged beam diameter for the probe laser, so that the number of photons per unit area is now below the critical limit [2]. Without detailed examination of other possible limitations of this method, it can at least be stated that the interference effect discussed above causes no serious error in the application of this modification of the LIF method.

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Appendix

I. To obtain the time dependent concentrations $[OH_g]$ and $[OH_r]$ and the concentration of $[OH_{gen}]$, which the LIF technique falsely interprets as natural OH, we have to solve the equations (7—10). The integrations of (7), which describes the time dependent concentration of $O(^1D)$, yields:

$$[O(^1D)] = \frac{\varepsilon N_0}{k' T}(1 - \exp(-k' t)), \quad 0 \leqq t \leqq T, \tag{A.1}$$

where N_0 is the total number of photons per unit area of a rectangular pulse shape duration T.

Inserting this equation into (8) we obtain an inhomogeneous differential equation of first order, describing the total amount of OH_g by the solution in the range $0 \leqq t \leqq T$:

$$[OH_g] = \frac{2 k_2' \varepsilon N_0}{k' T} \cdot \{(1 - e^{-k_r' t})/k_r' + (e^{-k' t} - e^{-k_r' t})/(k' - k_r')\}. \tag{A.2}$$

If we use the abbreviations

$$A(t) = \frac{k'}{k_r'(k' - k_r')}(1 - \exp(-k_r' t)), \tag{A.3}$$

$$B(t) = \frac{k_r'}{k'(k' - k_r')}(1 - \exp(-k' t)), \tag{A.4}$$

$$C(t) = \frac{2 k_2' \varepsilon N_0}{k' T}, \tag{A.5}$$

(A.2) simplifies to:

$$[OH_g] = C(A - B k'/k_r'). \tag{A.6}$$

The total amount of the relaxed OH_r is given by an integration of (A.2):

$$[OH_r] = k_r' \int_0^T [OH_g] \, dt \tag{A.7}$$

with the result:

$$[OH_r] = C(t + B - A). \tag{A.8}$$

To obtain the concentration of the generated OH_{gen} radicals, which are subsequently probed by the same laser pulse, we only have to evaluate the integral of (10). The result of this integration is given in (17).

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