Two-photon-excited stimulated emission from atomic oxygen in rf plasmas: detection and estimation of its threshold

Angeliki D. Tserepi 1, Elhanan Wurzberg 2, Terry A. Miller

Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, Columbus, OH 43210, USA

Received 23 August 1996; in final form 12 November 1996

Abstract

The two-photon-excited stimulated emission from the atomic-oxygen $3^3P \rightarrow 3^3S$ transition is observed in a discharge environment and its threshold is determined by means of a calibration technique for the two-photon allowed laser-induced fluorescence (TALIF) signal. For the atomic oxygen concentrations and the laser powers used in our experiments, we found a relatively constant threshold, $N_{th} = (2.5 \pm 0.4) \times 10^{14}$ atoms/cm$^3$, for the stimulated emission. The reduction of the laser-induced fluorescence signal due to rapid depletion of the laser-excited level by stimulated emission did not exceed 30%, up to O-atom concentrations $3N_{th}$.

1. Introduction

Atomic oxygen plays a critical role in a variety of chemical reactions such as plasma processing of materials, combustion, spacecraft erosion in near-earth orbits, etc. For these and related processes, a means of monitoring O atom concentrations is highly desirable and because of the hostile environments frequently encountered, optical diagnostics are often the preferable route. Recently we have reported [1] on the application of two-photon-allowed laser induced fluorescence (TALIF) for the monitoring of O atoms in non-equilibrium plasma etching reactors.

In our work we demonstrated the capability of TALIF to measure, under certain conditions, absolute O concentrations in a reactive plasma environment. When determination of the absolute concentrations of the species by TALIF is undertaken, an understanding of all the physical mechanisms that may depopulate the laser-excited state, and under certain conditions may cause a non-linear dependence of the LIF signal on ground state population, is necessary. Furthermore, a correction has to be made to the quantum yield of the fluorescence for every deexcitation mechanism that leads to a detectable decrease of the LIF signal. Observation of amplified stimulated emission (SE) has been reported for TALIF detection of O atoms in flames and generally is common in many two-photon excitation studies [2–4]. Knowledge of its effect on laser diagnostic techniques such as TALIF is important for the proper employment of the technique and the correct interpretation of the results.
In TALIF of oxygen, the two-photon-excited 2p^3P \rightarrow 3p^3P atomic transition is followed by fluorescence to the 3s^3S level. The rapid population of the 3p^3P level in conjunction with the short lifetime (1.8 ns) of the lower 3s^3S level [5] can create population inversion between these two levels. Consequently, SE is not uncommon in this classic three-level system and it may compete with fluorescence or with multiphoton ionization [6] in the depletion of the excited state. Studies of the effect of SE on the quantum yield of the fluorescence seem complicated by the fact that the conditions in reactive environments (flames, combustion, discharges) that produce O atoms and hence where its SE can be detected, vary significantly. A kinetic model was developed recently by Huang and Gordon [7] to simulate the effect of SE on the population of the laser-excited O(3p^3P) state, although the actual atomic densities were unknown. The present work provides for the first time a method for observing SE simultaneously with absolutely calibrated TALIF signals, to determine the O-atom population threshold for SE. We find that this threshold corresponds to a rather constant concentration of O(2p^3P) atoms (even at varying excitation laser power), above which the level of SE increases abruptly. Further, we discuss the conditions under which the influence of the SE on the fluorescence should not be neglected. Finally, we show the use of the method in interpreting TALIF signals from atomic oxygen in a parallel plate rf plasma reactor.

2. Experimental

Our method of determining a threshold for SE requires simultaneous observation of TALIF and SE signals with a calibration procedure for the TALIF signal. The experimental set-up has been described in detail elsewhere [1]. Briefly, a parallel plate rf reactor cell has been modified by attaching a flow tube on the port usually bearing one of the electrodes, to allow for the calibration procedure. The flow tube was coaxial with the outer tube carrying a mixture of O_2 and Ar and running through a microwave cavity. O atoms produced by the microwave discharge were flowing downstream towards the excitation/detection region. The inner tube carried NO_2 and had perforations at its end to provide better mixing of NO_2 with O atoms. The mixing took place a few centimeters above the end of the outer titration tube to facilitate a complete reaction between NO_2 and O, according to the reaction, NO_2 + O \rightarrow NO + O_2 [8]. The surviving O atoms were detected by the TALIF technique. The 226 nm light, necessary to induce the 2p^3P \rightarrow 3p^3P transition, was produced by mixing the 1064 nm fundamental output of a DCR-2 Nd/YAG laser with the second harmonic of the 574 nm output of a DCR-2 dye-laser operating on a Rhodamine-590/610 dye mixture. The 226 nm laser beam (diameter \sim 5 mm) was then focused by a quartz lens (f = 150 mm) at a point located 1 cm below the end of the flow tube, to excite ground state O atoms in the probe region. The subsequent fluorescence of the excited atoms at 845 nm was collected at right angles by a lens configuration on a gated EMI photomultiplier tube (through a 10 nm filter centered at 845 nm). The SE passed through an iris, which was set along the forward direction of the exciting laser beam, and was collected on a Hamamatsu R928 PMT (after passing through a band-pass filter centered at 845 nm and a second UV blocking glass). Both signals were averaged on a Tektronix DSA 601 digitizer and were measured as a function of the flow of NO_2 in the titration tube. The flows for each gas in the cell were measured by MKS mass-flow controllers and the total pressure was measured by a MKS 122A (10 Torr) baratron head.

3. Results and discussion

In Fig. 1(a)–(c), we present data from three titration experiments done under identical conditions at significantly different laser powers. For each experiment, TALIF and SE signals were measured as the flow of NO_2 was increased up to the end-point of the titration, noted by the x-intercept of the linear fit to the TALIF data. Since the discharge parameters were kept identical for all three experiments presented in Fig. 1, the end-points occur at essentially the same titrant gas concentration that corresponds to the same initial O-atom concentration (5.2 \times 10^{14} atoms/cm^3). Notice that the SE signals increase rapidly as the NO_2 flow decreases (or equivalently, the O-atom concentration increases) beyond a cross...
The increase of the ground state O-atom concentration at the SE threshold with decreasing laser power is rather small. This is probably due to the fact that we approach partial saturation of the excitation transition. In such a case, even a substantial increase in laser power does not result in a significantly higher O(3^3P) population, which in turn would enhance the SE signal. Fig. 2 shows that this is indeed the case. As expected, the TALIF signal as a function of laser power follows a straight line with a slope of 2 at low powers (since $I \propto P_{\text{laser}}^2$ for a two-photon process), while it deviates from linearity at about 60 μJ/pulse and above.

We repeated the titration experiments at various O-atom concentrations, at constant excitation laser power. In Fig. 3, we show two titration curves taken at the same low laser power (44 μJ/pulse) and different O-atom concentrations (6.6 and 5.2 × 10^{14} atoms/cm^{3}, Fig. 3(a) and (b), respectively). Effort was made to keep the partial pressures of Ar and O₂ almost constant in the cell and as low as possible, so that the quenching of the upper excited state remains the same and does not affect significantly the TALIF (or the SE) signals. Similar to our result in Fig. 1, we find that SE takes place above a rather constant threshold value of O-atom concentration (2.9 × 10^{14} atoms/cm^{3}). We also observe that, although in Fig. 3(b) the TALIF signal is rather linear in O-atom concentration, in Fig. 3(a) it exhibits saturation-like

over region in titrant gas concentration. We define this cross-over between the linear dependence of the SE signal on the O-atom concentration and the asymptotic approach to zero as the threshold for SE. The existence of such threshold is expected by the very nature of SE [9]. From Fig. 1 we calculate the O-atom concentrations at the SE threshold to be $N_{\text{thr}} = 2.1$, 2.5, and 2.9 × 10^{14} atoms/cm^{3} for 185, 57, 44 μJ/pulse, respectively.

characteristics at low NO₂ flow or equivalently at high O-atom concentrations. This is probably due to significant depopulation of the excited state by the mechanism of SE at high O-atom concentrations, that affects the TALIF signal, as we will discuss in detail below. In general, from a total of 11 experiments in which a threshold for SE was observed and in which the total O-atom concentration was varied from 4.1 to 7.4×10¹⁴ atoms/cm³ and the laser power from 0.04 to 0.51 mJ/pulse, we find that the threshold for SE occurs at a concentration \( N_{\text{thr}} = (2.5 \pm 0.4) \times 10^{14} \) atoms/cm³. This is a key result in our work. The relative constancy of the threshold is somewhat surprising but we expect is largely caused by our experimental conditions. Lack of a strong power dependence is indicative of some saturation in the pumping of atoms to the excited state.

It is useful to compare our experimentally measured threshold, \( N_{\text{thr}} \), with theoretical expectations for this value. Recently Huang and Gordon [7] used a coupled rate equation model to predict the threshold for SE under roughly comparable conditions. They predicted a threshold value of \( 3 \times 10^{12} \) atoms/cm³, a factor of nearly 100 smaller than our experimental value.

However, the discrepancy between theory and experiment is not so great as might be expected at first glance. Consider the rate equation [7] (in the absence of ionization), with laser flux, \( \Phi \),

\[
\frac{dN_3}{dt} = \sigma^{(2)}\Phi^2(N_1 - N_3) - \sigma_e Gc q(N_3 - N_2) - A_{32} N_3.
\]

(1)

\( N_1, N_2, N_3 \) are the populations of the ground, intermediate and upper laser excited state, respectively. Values \( \sigma^{(2)} = (1.44 \pm 0.43) \times 10^{-46} \) cm⁴s, the effective two-photon absorption cross-section; \( \sigma_e = (2.01 \pm 0.22) \times 10^{-12} \) cm², the stimulated emission cross section; and \( A_{32} = (2.89 \pm 0.31) \times 10^7 \) s⁻¹, the spontaneous emission rate coefficient, are given in Ref. [7]. In Eq. (1) \( G = \exp((N_3 - N_2)\sigma_e z) \) is the gain factor [10] and \( q \) is the stimulated emission photon density. Then, just below the onset of SE (\( q \approx 0 \) and \( G \approx 1 \)), and at steady state conditions (\( dN_3/dt = 0 \)), we obtain \( \sigma^{(2)}\Phi^2(N_1 - N_3) = A_{32} N_3 \), or \( N_1/N_3 = 1 + A_{32}/\sigma^2 \Phi^2 = A_{32}/\sigma^2 \Phi^2 \). With a reasonable, but quite approximate, assumption of a focused laser beamspot diameter of 200 μm, we obtain for our experiment \( \Phi \approx 3 \times 10^{25} \) cm⁻² s⁻¹, whereas in Fig. 2 of Ref. [7], \( \Phi = 3 \times 10^{26} \) cm⁻² s⁻¹. The onset of stimulated emission should be controlled by the density \( N_3 \). In the above approximation, \( N_3 \approx \sigma^2 \Phi^2 N_1/A_{32} \). Hence we would expect a 100-fold increase in \( N_1 \) is required for a 10-fold decrease in \( \Phi \). In this sense there is complete agreement between theory and experiment. While the above approximation is relatively crude, it is certainly indicative that no fundamental discrepancy exists between theory and experiment, especially given the difficulty in determining precisely the experimental value of \( \Phi \).
in a rf cell. The experimental set up has been described previously [1]. For these experiments, the titration system has been detached from the rest of the reactor and a planar water-cooled stainless steel electrode has been mounted in its place, opposite to an identical electrode. Ground state O(2p^3P) atoms were generated in the rf reactor operating at 10 MHz. Pure oxygen has been used at pressures in the range 0–2 Torr. The data for TALIF and SE signals as functions of pressure are presented in Fig. 5. The TALIF signal has been corrected for the increase in quenching [11,12] of the upper state by O_2, as the pressure of oxygen rises (the quenching rate constant was measured in a separate experiment [12]). Since the data in the rf cell were taken under identical excitation and detection conditions as the titration experiment, we were able to calibrate the TALIF signal. The SE signal rises abruptly from zero at about 0.3 Torr O_2 pressure, or equivalently for a ground state O-atom concentration of 3.6 \times 10^{14} \text{ atoms/cm}^3. The deviation of the (corrected for quenching) TALIF response from linearity starts above twice this concentration, in agreement with our observations above.

At high pressures, the observed deviation from linearity could result from either SE or from a
sublinear production of O atoms as a function of O$_2$ pressure, due to a decrease in the efficiency of the discharge with increasing pressure. Therefore, the 50% TALIF reduction shown in Fig. 5 constitutes an upper limit of the effect of SE on the TALIF signal in a 2 Torr plasma. We further observe that the linearity of the TALIF signal with ground state O-atom concentration is re-established at high pressures. Similarly, Amorim et al. [13] found a linear increase of the TALIF as well as the SE signal at high concentrations, for O and H atoms. In fact, the rate of increase with concentration for both TALIF and SE signals is shown to be the same, implying that the ratio of the laser-excited atoms that decay to the intermediate level via TALIF and SE remains constant. This means that TALIF would remain a reliable tool for probing ground state concentrations that are much higher than the SE threshold values.

We believe that the method we have presented here for determination of the SE emission threshold provides a general diagnostic technique which can be easily applied to other atomic systems that exhibit similar spectroscopic characteristics. Certainly, it can be employed in other more complicated environments (such as flames, combustion environments, etc) to distinguish between the effect of the stimulated emission and other competing mechanisms that perturb the population of the laser-excited state.

Acknowledgements

The authors gratefully acknowledge the support of this work by USAF Contract No. F33615-92-C-2244.

References