Detection of O($^3P_2$) by Vacuum Ultraviolet Laser Spectroscopy

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O atoms in the $^3P_2$ state were detected by vacuum ultraviolet laser–induced fluorescence (VUV LIF) technique. The O($^3P_2$) atoms were produced by the collision between the O atoms in the ^1D excited state and collision partner N_2. O atoms in the ^1D excited state were obtained by photodissociation of N_2O at 193 nm laser light. As O($^3P_2$) species has their first transition in the VUV region, the probe laser was used to excite O($2p^3P_j$) atoms to the O($3s^3S°$) state at 130.212 nm. A four wave difference frequency mixing ($2\omega_1 - \omega_2$) process using Kr as nonlinear media was employed to generate 130.212 nm probe laser light.
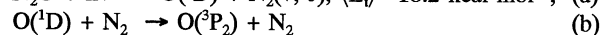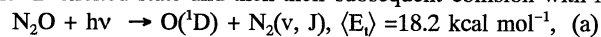
Since our planet Earth, apparently alone amongst the planets of the solar system, supports life, the chemistry of Earth's atmosphere is of great environmental importance. As it has been known that the chemistry of stratosphere is dominated by oxygen atoms, O and ozone, O_3,[1] laser–induced fluorescence studies on the detection of O($^3P_2$), will positively enrich the understanding of dynamical behavior of excited O atoms and their subsequent electronic transformation to O(^3P_j), which plays a significant role in the O_2–O_3 cycle.[2] Earlier, the laboratory techniques used for this type of investigations involved bulk photochemical methods, time–resolved atomic resonance spectroscopy etc.[3–5] However, the atomic absorption methods with a resonance lamp had ambiguity in the absorption coefficient for analysis. Thus, early experiments are less reliable because of difficulties with the experimental approach. Therefore, in this work, vacuum ultraviolet laser–induced fluorescence (VUV LIF) method was employed, as it affords a favorable efficiency for detection,[6,7] in order to detect the O atoms in the $^3P_2$ state at 130.212 nm laser light. Reactant O(^1D) atoms were produced in the presence of collision partner N_2 by ArF laser photolysis of N_2O molecule at 193 nm and collision products O($^3P_2$) were probed by a second laser setup which was fired after a delay that was long enough for some collision to occur.

A schematic illustration of the experimental apparatus for the VUV LIF detection of O($^3P_2$) atoms is shown in Figure 1. The experiment was conducted in a photolysis–and–probe laser
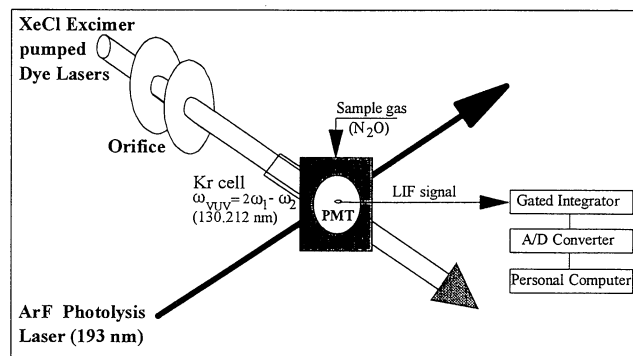

Figure 1. A schematic illustration of the experimental setup for the VUV LIF detection of O($^3P_2$) atoms.

system. The O($^3P_2$) atoms were obtained by the following reactions, initially, photodissociation of N_2O to get O atoms in the ^1D excited state and then their subsequent collision with N_2.

$$N_2O + h\nu \rightarrow O(^1D) + N_2(v, J), \quad \langle E_t \rangle = 18.2 \text{ kcal mol}^{-1}, \quad (a)$$
$$O(^1D) + N_2 \rightarrow O(^3P_2) + N_2 \quad (b)$$

where $\langle E_t \rangle$ is the average translational energy of the produced O(^1D) atoms in the laboratory frame.
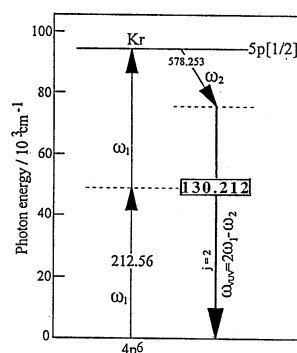

Figure 2. A schematic diagram of the four wave difference frequency mixing ($2\omega_1 - \omega_2$) process in Kr gas (Kr, 20 Torr). O($^3P_2$) atoms were detected by generating VUV LIF for the $3s^3S° - 2p^3P_j$ transition at 130.212 nm for j=2.

The probe detection system of O($^3P_2$) atoms was based on generation of VUV LIF for the $3s^3S° - 2p^3P_j$ transition at 130.212 nm for j = 2. Two dye lasers (Lambda Physik, FL 3002E) pumped by a single XeCl excimer laser (Lambda Physik, LEXTRA 50, 308 nm, ~10 mJ/pulse, 10 Hz) were used to generate coherent tunable narrow–bandwidth VUV laser radiation of 130.212 nm by four–wave difference mixing ($2\omega_1 - \omega_2$) in Kr gas[8] (Figure 2). The dye laser output (Bis–MSB dye, $C_{24}H_{22}$) was frequency–doubled by a BBO crystal (β–BaB_2O_4) for ω_1 wavelength of 212.56 nm, which was two–photon resonant with Kr $5p[1/2]_0$. The wavelength of ω_2 (Coumarin 540A, $C_{16}H_{14}NO_2F_3$) was 578.253 nm for j = 2. In this scheme, the fundamental laser beams are focused (quartz lens, f=200 mm) into the nonlinear medium (Kr, 20 Torr) of the mixing cell. The generated VUV light passed through LiF window, propagated through a reaction cell, and was subsequently reflected into a VUV monochromator by another LiF plate. The intensity of the 130.212 nm laser light was thus monitored by a solar–blind photomultiplier (Hamamatsu, R1259) through the monochromator.

A gas mixture containing the O($^3P_2$) source gas N_2O, and N_2 was flowed slowly through a 80×80×80 mm cubic reaction cell. N_2O molecules were dissociated at 193 nm by an unpolarized ArF laser (Lambda Physik, EMG 101 MSC, ~ 5 mJ/pulse, 10 Hz). The dissociation light was focused by a CaF$_2$ lens (f = 500 mm) into the reaction chamber attached by a LiF window. The time delay between the dissociation and probe laser pulses was controlled by a pulse generator (Stanford Research, DG535), and the jitter of the delay time was less than 10 ns. The

VUV LIF signal of $O(^3P_2)$ was detected at right angles to the propagation directions of both probe and dissociation laser light by a solar blind photomultiplier tube (EMR, 541J-08-17). This VUV LIF signals from the photomultiplier was then amplified in a preamplifier and averaged by gated integrators (Stanford Research, SR 250) which was interfaced to a laboratory computer.

The superthermal $O(^1D)$ atoms were mainly converted into $O(^3P_2)$ by the electronic quenching by collisions with surrounding N_2. In the stratosphere, N_2 remains as the paramount collider to form $O(^3P_j)$ as the constituent of air is mainly N_2 (77%). From the $O(^1D)$ + $N_2(X^1\Sigma_g^+)$ combination, $^1\Delta$ ($^1A'+^1A''$), $^1\Pi$ ($^1A'+^1A''$), and $^1\Sigma^+$ ($^1A'$) surfaces are constructed for N_2O. The $^1\Delta$ and $^1\Pi$ surfaces are repulsive along the O–N_2 coordinate. The $^1\Sigma^+$ ($^1A'$) surface is strongly attractive, since it leads to the ground electronic state of the N_2O molecule. The electronic quenching reaction (b), predominantly proceeds via the intermediate complex N_2O $^1\Sigma^+(^1A')$ formation.[9] At higher collision energies the reaction probability falls because the lifetime of the complex is shorter and there is thus less chance to cross the seam between the singlet and triplet surfaces. Therefore, the formation of ground state $O(^3P_2)$ is intelligible by the physical electronic quenching of superthermal $O(^1D)$ by collisions with N_2 molecules as according to reaction (b). Production of $O(^3P_2)$ atoms is shown in Figure 3. In fact, the LIF intensity of $O(^3P_2)$ is increasing, is observed in Figure 3, with the time delay after the photodissociation of N_2O at 193 nm with 300 mTorr of N_2, when the probe laser wavelength is fixed at the center of the resonance line of $O(^3P_2)$ at 130.212 nm. The photodissociation products of N_2O at 193 nm were predominantly $O(^1D)$ + $N_2(X^1\Sigma_g^+)$, and the initial formation of $O(^3P_2)$ was negligibly small (~1.0%). The LIF intensity of $O(^3P_2)$ atoms increases with delay time due to the electronic quenching process of the $O(^1D)$ atoms by N_2. At a delay time upto 4.8 μs, in Figure 3, the LIF intensity is increasing, which means that all the $O(^1D)$ atoms produced by the photodissociation of N_2O are not still converted into $O(^3P_j)$ atoms, but has been converted to a considerable extent. Matsumi and Chowdhury[10] reported that at a delay time over 12 – 15 μs, the LIF intensity becomes asymptotic, i.e., all the $O(^1D)$ atoms produced by the photodissociation of N_2O are converted to $O(^3P_j)$ atoms, which is in well agreement with this experiment. As it has been known that the total reaction rate constant for $O(^1D)$ + N_2O
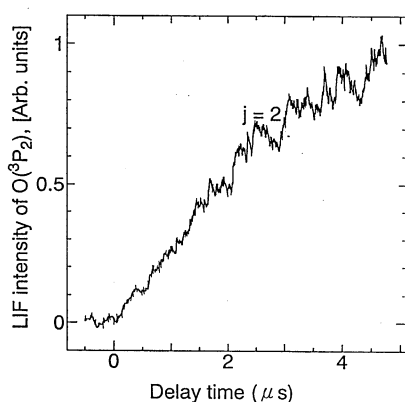
Figure 3. Increase in LIF signal intensity of $O(^3P_2)$ produced by the reaction between $O(^1D)$ and N_2 after the photodissociation of N_2O at 193 nm ArF excimer laser light. The horizontal axis is the delay time between the photodissociation and probe laser pulses. The pressures of N_2O and N_2 are 5 mTorr and 300 mTorr, respectively.
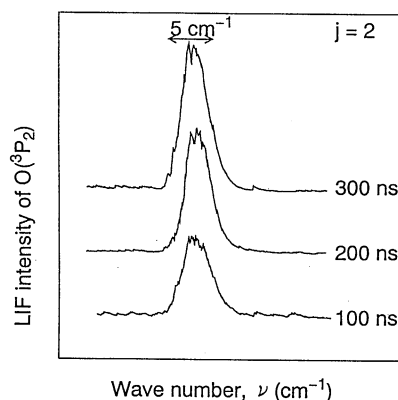
Figure 4. LIF excitation spectra of $O(2p^3P_j)$, j = 2 at 300, 200 and 100 ns delay times after the photodissociation of N_2O. LIF intensity is, in fact, the frequency of the probe VUV laser. The center wavelengths of the $3s^3S_0 - 2p^3P_j$ resonance transitions for j = 2 is 76797.837 cm^{-1}. The pressures of N_2O and N_2 are 5 mTorr and 300 mTorr, respectively.

$(1.2\times10^{-10}$ cm^{3}molecule^{-1}s^{-1}) is several times faster than that for $O(^1D)$ + N_2 $(2.6\times10^{-11}$ cm^{3}molecule^{-1}s^{-1}) [11] and also the partial pressure of N_2O is very smaller than that of N_2 in our experiments, the conversion of $O(^1D)$ to $O(^3P)$ by collisional reaction with N_2O is negligibly small. The formation rate of $O(^3P_2)$ in Figure 3 for t > 2 μs is in good agreement with the calculated value using the recommended rate constant[11] for $O(^1D)$ + N_2 at 298 K. The LIF excitation spectra for the fine structure levels of $O(^3P_2)$ is shown in Figure 4 at delay times 300, 200, and 100 ns after the gas mixture of N_2O and N_2 was irradiated with pulsed 193 nm laser light, which were recorded by scanning the probe laser wavelength. The linewidth of the probe laser without etalons was estimated to be 0.7 cm^{-1}. The widths of the resonance lines for the $O(^3P_2)$ atoms at short delays are broad, since (70±7) % of the electronic energy between the ^1D and ^3P states of the O atom, 1.967 eV, is released into the translational energy in the quenching process of $O(^1D)$ by N_2.[10] The $O(^3P_2)$ spectra at higher delay times of 10 and 20 μs was also seen and found that the widths of the resonance lines are becoming narrower with the increase in delay time between the probe and photolysis lasers. This is because of the speed distribution of the $O(^3P_2)$ atoms is thermalized to room temperature by greater collisions with the collision partner, N_2.

References and Notes
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