Time-Resolved Laser Spectroscopy of High-Lying States in Neutral Oxygen

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Radiative lifetimes have been measured for five triplet states of atomic oxygen. The oxygen atoms were generated by photodissociation of NO_2 and the investigated states were populated through a two-step process involving a two-photon excitation to the lowest excited triplet state of even parity, $2p^3 3p\ ^3P$, followed by a one-photon excitation to the investigated state. A similar scheme is applicable to the study of excited states in many light atoms.

Stepwise laser excitation has proven to be a very efficient method of populating excited atomic states in order to perform accurate measurements of radiative lifetimes and small energy splittings. During the last ten years extensive measurements on Rydberg sequences in alkali-metal atoms, alkaline earths, and group-III elements have been performed in this way. For many light atoms, however, the resonance lines are in the vacuum ultraviolet (vuv) region where tunable radiation of high intensity is hard to produce and where experimental techniques frequently are cumbersome. In the present measurements of lifetimes in triplet states of atomic oxygen a uv two-photon excitation followed by a visible one-photon excitation have been used to overcome this difficulty. Such a scheme can be used for many other light atoms such as H, C, N, P, S, and Cl. The strong uv radiation needed for the two-photon step can also be conveniently used for the production of such atoms by photodissociation of suitable molecules.

Two-photon absorption has been used for detection of carbon[1] and sulfur[2] in a scheme for which the same laser pulse also served to photodissociate C_3O_2 and CS_2, respectively. Two-photon–induced fluorescence has also been used to determine concentrations of light elements in a flame, e.g., of atomic oxygen.[3] The addition of a further exitation step strongly increases the possibility for extensive spectroscopy work for the light elements. Combined two- and one-photon excitations can also provide analytical advantages for hydrogen-atom detection as recently demonstrated in flame experiments by Goldsmith.[4]

In the present Letter we report the first laser spectroscopy lifetime measurements for several triplet states in neutral oxygen, that were created in a scheme involving four photons. An intense pulsed uv laser beam first produced atomic oxygen in its ground state by photodissociation of NO_2 and then induced a two-photon transition to the lowest excited ^3P state at 88 631 cm^{-1}. This short-lived level then served as a platform for further excitation by a second pulsed laser beam.

The experimental setup is shown in Fig. 1. The two laser pulses were generated by use of dye lasers pumped by a Nd-doped yttrium aluminum garnet system (Quanta-Ray DCR-2A). For the uv two-photon
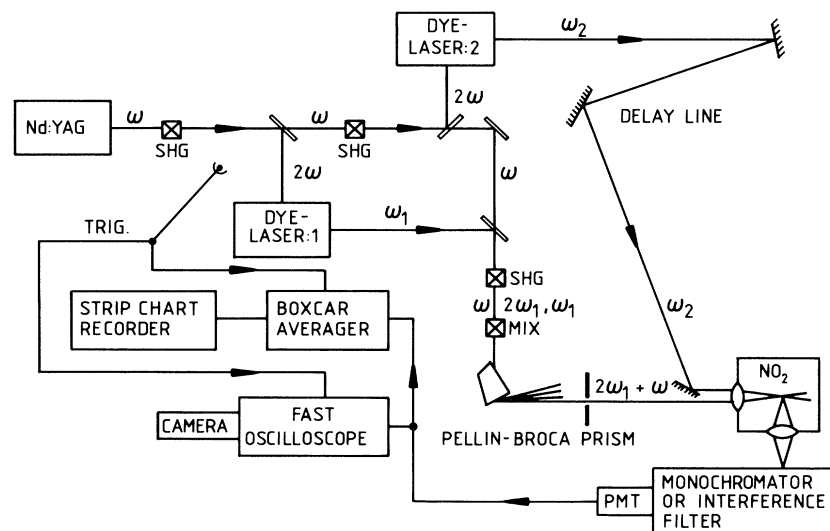

FIG. 1. Experimental setup.

excitation the light pulses from a dye laser (Quanta-Ray PDL-1), operated with a mixture of rhodamine 590 and rhodamine 610, were frequency doubled and mixed with the 1.06-μm output of the Nd-doped yttrium aluminum garnet laser in two successive nonlinear crystals. Light pulses for the second visible excitation step were generated in a small grazing-incidence laser oscillator with an amplifier stage, built directly on the optical table. The two laser beams were focused and made to overlap inside a low-pressure chamber filled with NO_2 to pressures ranging from 1 to 1000 Pa (1 Pa = 7.5 mTorr).

NO_2 was chosen because of the large cross section for the process $NO_2(\tilde{X}\,^2A_1) + h\nu(\lambda < 398$ nm$)$ $\rightarrow NO(X\,^2\Pi) + O(^3P)$, which produces oxygen atoms in the $2p^4\,^3P$ ground state. At $\lambda = 226$ nm the absorption coefficient is 10^{-4} Pa^{-1} cm^{-1},[5] and the quantum efficiency for the process is ~ 0.5.[6] The competing process is production of oxygen atoms in the $2p^4\,^1D$ state at 15 867 cm^{-1}. In the frequency mixing with the infrared beam we may assume that the divergence of the resulting beam is limited to 0.5 mrad (as specified for the DCR-2A). With the parameters above, an input power of 1 mJ, a pressure of 1 Pa, and a 20-cm focusing lens, the photodissociation is essentially complete in the beam waist. With the two-photon absorption cross section given by Omidvar[7] or Pindzola,[8] roughly 10% of the ground-state oxygen atoms is estimated to be excited to the $3p\,^3P$ state. With a photoionization cross section[9] of 10^{-19} cm^2 and the experimental parameters above, half of these excited atoms will be photoionized.

To simplify the adjustment a chromatic lens was used such that the second-step beam, which easily saturated the one-photon transition, had a considerably larger diameter than the first-step beam within the overlap region. The fluorescence light released after the stepwise excitation was imaged on the entrance slit of a monochromator or through an aperture in front of an interference filter. An EMI model 9816 QB photomultiplier tube with a rise time of 2 ns was used for detection.

In the measurements the wavelength of the first dye laser was set by observation of the emission at 845 nm as indicated in Fig. 2. The wavelength of the second dye laser was set by observation of the decrease in emission at 845 nm when the second laser was tuned to the transitions to the ^3S and ^3D levels. Observation of the fluorescence induced by the second laser turned out to be less advantageous, since several transitions simultaneously resonant in both the first and the second step were found in NO_2 in the wavelength regions used. The laser-pulse power of the second laser was then reduced to the lower limit of saturation ($\ll 1$ μJ) and the detection wavelength was changed to the one used for the second-step excitation since
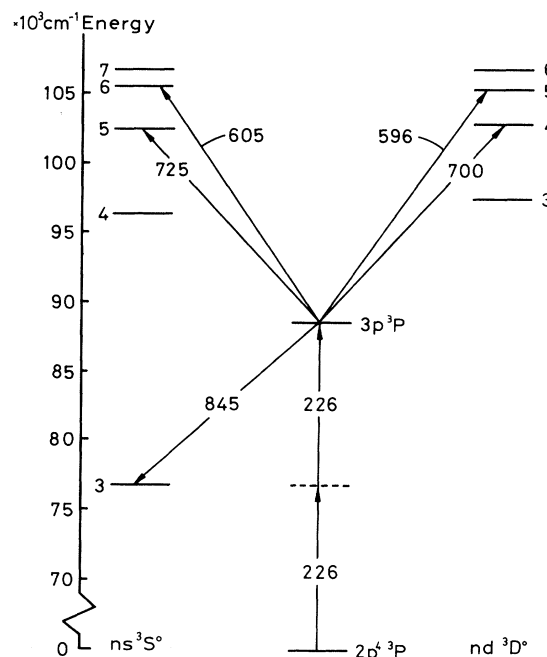

FIG. 2. Schematic energy level diagram for O I. Excitation and detection wavelengths are indicated.

the corresponding transition, besides vuv, infrared, and intercombination lines, was the only decay channel. However, this detection scheme is not very favorable as the investigated states decay mainly to the ground state. The branching ratios for the ns-$3p$ and nd-$3p$ transitions are around 10% and a few percent, respectively. vuv detection is an attractive alternative but would present some difficulties as the wavelengths are below the LiF cutoff and NO_2 also has a rather large absorption coefficient in this region. NO_2 has a continuous spectrum overlapping the discrete one (see, e.g., Donnelly, Keil, and Kaufmann,[10] and references therein). Decay curves for the excited states were in most cases recorded with a scanning boxcar integrator (EG&G Model 162) with a 2-ns gate.

For each state several recordings were made at different pressures within the pressure range 1–50 Pa. The evaluation of the curves started after ~ 10 ns when there was no contribution left from the laser pulse. This was verified by a recording of the laser pulse separately. The radiative lifetimes were then obtained from Stern-Vollmer plots such as the one in Fig. 3 for the $2p^3 6s\,^3S$ state. The higher states were 2–3 times more sensitive to collisional quenching than the $3p\,^3P$ state. The quenching rate constants were between 10^{-8} and 10^{-9} cm^3/s. Similar values have been observed for excited atoms of oxygen and other elements under conditions where the atoms and molecules can be expected to have a comparatively large translational energy.[11,12] The fragments in the
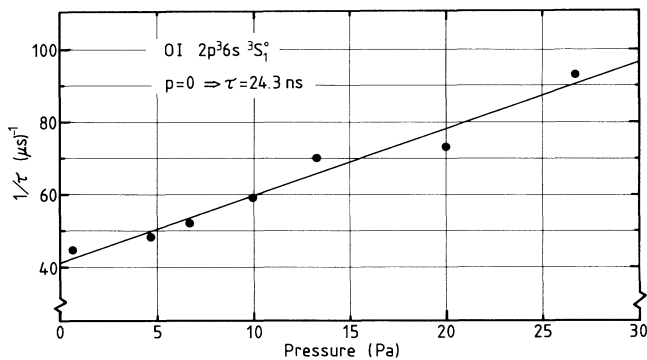
FIG. 3. Stern-Vollmer plot for the $2p^36s\ ^3S$ state yielding a radiative lifetime of 24 ns. Each point is the average from several experimental recordings.

NO_2 dissociation can be expected to have a relatively high translational energy due to the excess energy of the $\lambda = 226$ nm photon with respect to the onset for dissociation ($\lambda = 398$ nm). The rapidly moving fragments will increase the collision frequency.[13] Because of the dissociation process, NO_2 is probably not the main quencher; however, since the NO_2 pressure was the quantity actually measured in the Stern-Vollmer plots, this is shown on the horizontal axis in Fig. 3. The results from the lifetime measurements are given in Table I. The errors are mainly due to statistical scattering in the data for each pressure. Radiation trapping can be a potentially severe problem at these comparatively large pressures. However, as the ground-state oxygen atoms exist only within the laser focal volume this difficulty is essentially eliminated. The fluorescence from the oxygen atoms was detected from the region where the diameter of the $\lambda = 226$ nm beam was less than 200 μm. If the oscillator strength from the excited state to the ground state is 2×10^{-2} (which is larger than for any of the states investigated in this work), one obtains $l \ll 2$ mm as a condition for trapping to be negligible at 1 Pa (l is the absorption path length). This implies that the use of a flow

TABLE I. Experimental and theoretical lifetime values for the investigated oxygen states.

| | | Lifetime (ns) | |
State	This work	Others	Theory[a]
$2p^35s\ ^3S$	17(3)	6[b]	12
$2p^36s\ ^3S$	24(3)		25
$2p^33p\ ^3P$	36(4)	39.1(1.4)[c] 40(3)[d]	30
$2p^34d\ ^3D$	23(3)	20[b] 80(10)[d]	15
$2p^35d\ ^3D$	36(4)	30[b]	< 35

[a]Reference 17.   [c]Reference 14.
[b]Reference 16.   [d]Reference 15.

discharge for the production of oxygen atoms is likely to be less favorable when one performs lifetime measurements on states with allowed dipole transitions to the ground state.

Our platform level, the $3p\ ^3P$ state, has earlier been studied rather extensively. Recently also, two-photon laser excitation was applied to atoms that were produced in a flow discharge yielding a lifetime value close to ours.[14] The $4d\ ^3D$ state has been investigated by use of electron-beam excitation followed by time-resolved detection, but the obtained value deviates from ours.[15] For the ^3D states better agreement is found with a determination by electron-beam excitation and phase-shift detection,[16] but here the values for the $5s\ ^3S$ state disagree. However, we believe that the partial agreement, the fact that all states were investigated in the same experimental system, and the use of a selective excitation scheme lend confidence to our values. A comparison was also made with lifetime values obtained from theoretical oscillator strengths,[17] and reasonable agreement is found.

In conclusion, we have here demonstrated an efficient way to populate high-lying excited states in atomic oxygen by use of molecular photodissociation and stepwise laser excitation. The same type of approach applies to several other light elements as illustrated in Table II. Once the large energy gap between the ground state and the excited state of the same parity has been bridged by two uv photons, numerous states are accessible with a low-power visible dye laser. The easiest type of measurements with these rather broadband pulsed dye lasers are lifetime determinations and quantum-beat measurements of small energy splittings due to fine and hyperfine structure and Zeeman and

TABLE II. Excitation wavelengths and some readily accessible singly excited configurations for six elements particularly suitable for the technique demonstrated in this Letter. λ_1 denotes the wavelength for two-photon absorption from the ground state to the lowest excited state of the same parity, multiplicity, and orbital angular momentum; λ_2 denotes the wavelength needed in the second step to reach the ionization limit from the intermediate state populated in the two-photon excitation; n_s (n_d) denotes the principal quantum number for the lowest excited s (d) state that can be reached from the intermediate state with $\lambda < 700$ nm.

Element	λ_1 (nm)	Intermediate state	λ_2 (nm)	n_s/n_d
C	280	$2p3p\ ^3P$	512	6/5
N	207	$2p^23p\ ^4S$	486	6/5
O	226	$2p^33p\ ^3P$	472	6/5
P	299	$3p^24p\ ^4S$	563	8/6
S	308	$3p^34p\ ^3P$	536	7/6
Cl	234	$3p^44p\ ^2P$	511	7/6

Stark effects. Pulsed optical double resonance and level-crossing experiments should also be readily feasible. It seems that laser spectroscopy should have the potential to increase the knowledge of the light and theoretically most tractable atoms in a dynamical way as it did for the alkali-metal atoms ten years ago.

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