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SODIUM RESONANCES IN FLUORESCENCE FROM WIDE-RANGE LASER SCAN IN H_2–O_2–Ar FLAME

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Abstract—Several resonances and underlying continua were observed in the excitation profiles of sodium atoms in an H_2–O_2–Ar flame, irradiated by the focused beam of a tunable, pulsed dye laser. These profiles are obtained by tuning the laser through the spectral range of Rhodamine 6G and detecting the ensuing fluorescence signals from the $3D$-$3P$ and $4D$-$3P$ transitions. We observed resonances corresponding to the $3S_{1/2}$–$3P_{1/2}$, $3S_{1/2}$–$3P_{3/2}$, $3P_{1/2}$–$5S_{1/2}$, $3P_{3/2}$–$5S_{1/2}$ one-photon transitions and resonances corresponding to the $3S_{1/2}$–$5S_{1/2}$, $3S_{1/2}$–$4D_{3/2,5/2}$ two-photon transitions. The observed resonances result from different sequences of radiative and collisional excitation. The presence of the continua is explained by consecutive absorption of laser photons in the collisionally broadened wings of absorption lines. The spatial inhomogeneity of the laser beam and hence of the saturation causes submerging of some resonances into continua.

INTRODUCTION

Excitation profiles provide information on the nature and the location of the atomic transition involved. Apart from direct radiative excitation, a mixture of collisional and radiative processes may occur, giving rise to population of (higher) levels. Also, collisional perturbation of an atomic level shifts and broadens its resonance.[1,2] In a flame at atmospheric pressure, collisional frequencies are such that these mixed processes are observable. The resulting fluorescence is called collision-assisted fluorescence and has been observed in vapour cells by several authors in conjunction with Rayleigh- and Raman-scattering.[3–7]

We present experimental evidence that collision-assisted population of an intermediate level by absorption of a non-resonant photon may proceed to higher levels by absorption of a second laser photon.

EXPERIMENTAL SET-UP

A flashlamp-pumped tunable dye laser is used, with a pulse duration of 1 μs, a peak power of several kW, repetition rate of 1 Hz and an approximately Gaussian line profile with a full width at half maximum (FWHM) of 140 mÅ. The laser beam is focused down to a spot with a diameter of approximately 100 μm and is at a height of 10 mm above the combustion zone. A small portion of the laser beam is split off for power monitoring.

A 2560 ppm sodium chloride solution is nebulized into the central part of a premixed stoichiometric H_2–O_2–Ar flame at 1800 K and 1 atm. The composition of the burnt flame gases is 83% Ar and 17% H_2O. Fluorescence in the near i.r. region is detected by a silicon diode (Harshaw S13Q). A spectral filter in front of the silicon diode was used to select the $3D$–$3P$ fluorescence signal.

For the detection of $4D$–$3P$ fluorescence, a Hilger & Watts grating monochromator, in combination with an RCA 1P28 photomultiplier, was used. Both the silicon diode and the photomultiplier view the same fluorescent flame region at right angles to the laser beam and opposite to each other. Doublet structure in the fluorescence signals was not resolved by either detector. Nebulizing a blank solution into the flame caused the fluorescence to disappear at every detuning.

The tuning of the laser is accomplished by tilting an interference filter (coarse tuning) and a Fabry–Perot etalon (fine tuning).

The signals from power monitor and fluorescence detectors are fed into gated integrators, after which they are simultaneously recorded with x–t recorders. A more detailed description of the set-up can be found in Ref. 8.

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RESULTS AND DISCUSSION

The laser was tuned to the range from 5765 to 6215Å in variable steps; the magnitude of the steps depended on the amount of structure found in the profiles. Two signals were recorded simultaneously, namely, the fluorescence signals from $3D$–$3P$ and $4D$–$3P$ transitions (shown in Fig. 1(a) and 1(b), respectively). The choice of the monitor levels was guided by the acceptable signal-to-noise ratio of the latter fluorescence signals throughout the tuning range of the laser.

Figure 1(a) shows resonances corresponding to the $3S_{1/2}$–$3P_{1/2}$, $3S_{1/2}$–$3P_{3/2}$, $3P_{1/2}$–$5S_{1/2}$, $3P_{3/2}$–$5S_{1/2}$ one-photon transitions and the $3S_{1/2}$–$5S_{1/2}$, $3S_{1/2}$–$4D_{3/2,5/2}$ two-photon transitions. The doublet structure of the $4D$-levels is too small to be resolved by the laser. The resonances in Fig. 1(b) are the same as those of Fig. 1(a), apparently with the exception of the $3S_{1/2}$–$3P_{1/2}$ and $3S_{1/2}$–$3P_{3/2}$ resonances.

Saturation was observed not only at the center of each of the resonances but also in the fluorescence signals of the $3P_{1/2}$–$3S_{1/2}$ and $3P_{3/2}$–$3S_{1/2}$ transitions, when the laser was detuned several Å from the center of the $3S_{1/2}$–$3P_{1/2}$ or $3S_{1/2}$–$3P_{3/2}$ transition. This observation means that saturation occurs. in the wings of the $3S$–$3P$ transitions. The laser-power density being in excess of the $3S$–$3P$ saturation parameter[9] by a factor of 2×10^5, saturation is expected to occur up to detunings of approximately 10 Å from the center wavelength of each of the $3S$–$3P$ resonances. At the latter detuning, the absorption coefficient has dropped by a factor of 2×10^5 with respect to the center value.[10]

Saturation distorts the excitation profiles, as can be seen by comparing the non-saturated excitation profiles of Ref. 10 with the corresponding profiles of Fig. 1: whereas the former profiles change by seven orders of magnitude in a range of 200 Å, the latter change by only two orders of magnitude within the same range. Note that the profiles of Ref. 10 cover 70% of the wavelength range of the present profiles and are derived from the direct fluorescence of the $3P$–$3S$ transitions.

The population of the $5S$ levels, which is evident from the resonances at 6154 Å, obviously results from resonant laser excitation of atoms from a $3P$ state to a $5S$ state. The population of an intermediate $3P$ state might be the result of two different processes: (1) absorption of a (non-resonant) laser photon in the collisionally broadened wing of a $3S$–$3P$ transition; (2) thermal population by collisions of the $3P$-levels. An estimate of the value of the absorption coefficient of the $3S$–$3P$ transitions at the wavelength corresponding to the $3P$–$5S$ transitions can be obtained from the non-saturated excitation-profiles of Ref. 10. Using the known value of the Einstein coefficient and the spectral energy density of the laser, we estimate that the population rate of the $3P$-levels due to absorption of the photons with a wavelength corresponding to the $3P$–$5S$ transitions exceeds the thermal population rate of the $3P$-levels by five orders of magnitude (for details, see Ref. 8). Briefly, one can vizualize the population of the $5S$-level as proceeding in two steps: (1) absorption of a photon tuned to a $3P$–$3S$ transition in the (far) wing of the $3S$–$3P$ transitions; (2) absorption of a photon tuned to a $3P$–$5S$ transition at the center of that $3P$–$5S$ transition.

The 5890 and 5896 Å resonances in the fluorescence signal observed at the $3D$–$3P$ transitions (see Fig. 1a) originate from collisional coupling between the $3D$- and $3P$-levels. This follows from a plot of the $3D$–$3P$ and $3P$–$3S$ fluorescence signals vs laser power in which both signals behaved equally. The laser was tuned to the $3S_{1/2}$–$3P_{3/2}$ transition. The partial Boltzmann-equilibrium found between $3D$ and $3P$ populations in Ref. 11 also suggests that the $3P$ and $3D$ levels are coupled by a collisional process rather than by a radiative process.

We offer the following explanation for the fact that the $3D$–$3P$ signal (Fig. 1a) shows the $3S$–$3P$ resonances, whereas the $4D$–$3P$ signal apparently does not: when the laser frequency has passed the point in the wing of a $3S$–$3P$ transition where saturation sets in at the beam axis, the flame region where saturation occurs will spread laterally when the laser frequency is tuned towards the line center of the transition (this spread explains the absence of a plateau in the saturation curve[9,12]). Although in the volume where saturation is complete no further increase in the concentration n_{3P} of sodium atoms will take place when tuning the laser closer to the resonance, this volume and consequently the total number, N_{3P}, of sodium atoms in the $3P$-level will continue to rise when the laser is tuned into resonance. This increase in saturated volume, however, contributes negligibly to the two-step excitation of the $5S$- or $4D$-levels. This conclusion follows from the fact that the second step is not saturated, as it takes place in the far

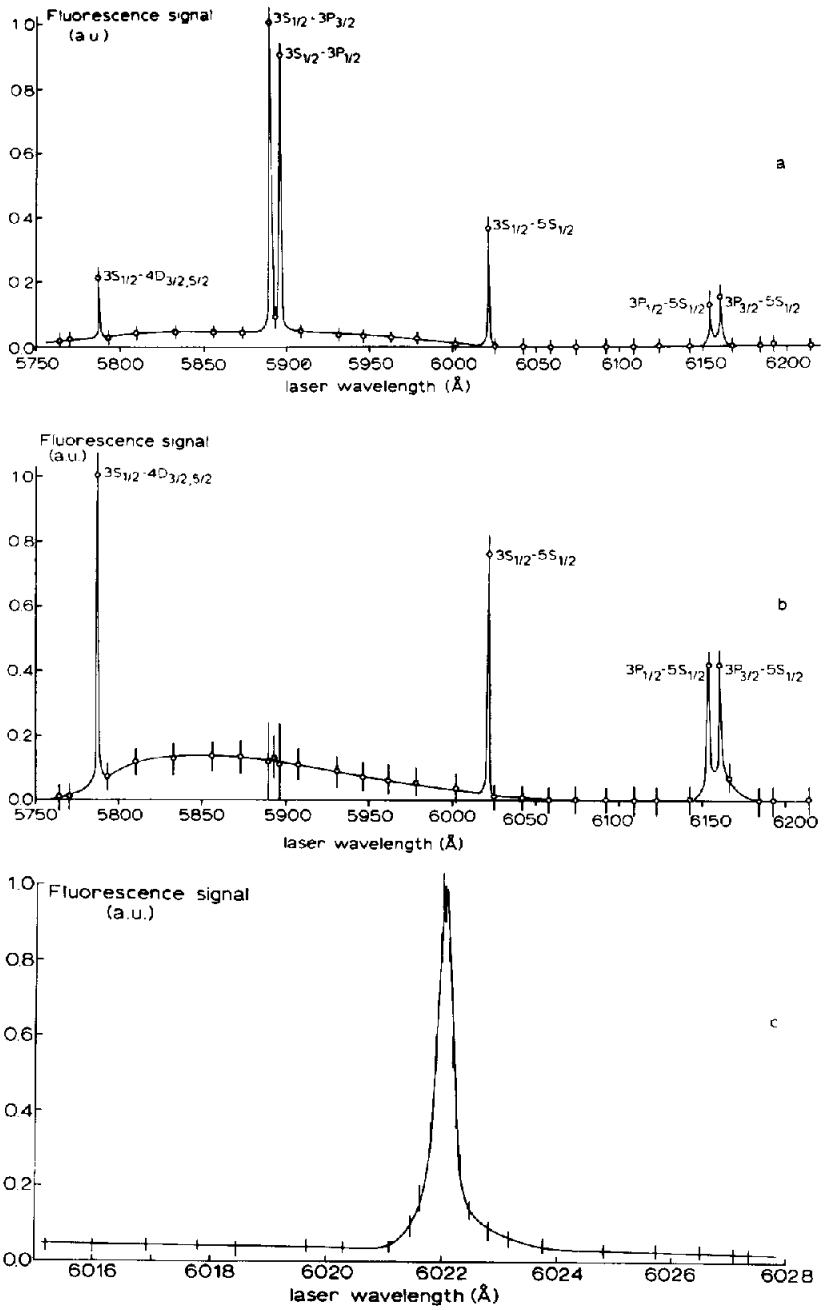

Fig. 1. Fluorescence signals of two higher sodium transitions as a function of the laser tuning. The curves of *a* and *b* were recorded simultaneously. (a) Fluorescence signal of the 3*D*–3*P* transitions; (b) Fluorescence signal of the 4*D*–3*P* transitions; (c) Fluorescence signal of the 4*D*–3*P* transitions when the laser is tuned through $3S_{1/2}$–$5S_{1/2}$ two-photon resonance. This profile is from a scan with a higher wavelength resolution and better SNR than the corresponding resonance of Fig. 1(b).

wing of the 3*P*–5*S* or 3*P*–4*D* transition (detunings of the order of 100 Å); also, the radiative transition probability for these one-photon transitions is relatively small. Significant two-step excitation of these higher levels thus occurs only in the flame region near the beam axis, where the laser power density is at maximum. When the laser frequency has passed the point where the population of the 3*P*-level is fully saturated at the beam axis, no further contribution to the 5*S* or 4*D* populations can be expected from this beam region when the laser is tuned closer to the resonance.

In contrast, collisional population of the 3*D*-level from the saturated 3*P*-level increases proportionally to N_{3P}; this quantity, in turn, increases in proportion to the saturated volume.

The observed proportionality between the populations of the $3D$- and $3P$-levels supports the latter conclusion. Thus, the fluorescence signal from the $3D$-level will continue to rise when the laser is tuned into resonance with a $3S$–$3P$ transition whereas that of the $4D$-level will not, which explains the occurrence of the $3S$–$3P$ resonances in Fig. 1(a) and their apparent absence in Fig. 1(b).

If there was collisional population of the $4D$-level from the $3P$-level, then $3S$–$3P$ resonances, identical in shape to those of the $3D$–$3P$ fluorescence signal, are expected to show up in the $4D$–$3P$ fluorescence signal. As these resonances are absent in the latter signal, within the experimental error, we conclude that the collisional population of the $4D$-level from the $3P$-level is negligible.

The above explanation of the differences between $3D$–$3P$ and $4D$–$3P$ signals in the case of the $3S$–$3P$ resonances is supported by semi-quantitative calculations. These calculations were based on the non-saturated excitation profiles of Ref. 10, which describe the behaviour of the radiative absorption probability of the $3S$–$3P$ transitions as a function of the exciting wavelength. A four-level system was assumed, consisting of the $3S$-, $3P$-, $3D$- and $4D$-levels and saturation was assumed to occur between the $3S$- and $3P$-levels only. We assumed the laser beam to have a Gaussian dependence on the radial coordinate. With this model and the laser power densities used, we could roughly fit the experimental profiles in Figs. 1(a) and 1(b) in the region between the $3S$–$3P$ and $3S$–$5S$ resonances. It was also found from this model that the FWHM of the $3S$–$3P$ resonances, in the case of the $4D$–$3P$ signal, exceeds the FWHM of the same resonances in the case of $3D$–$3P$ signal by more than an order of magnitude. The broadening of the profile and, consequently, the lowering of the peak values merged the $3S$–$3P$ resonances into the continuum.

We conclude that the continua in the neighbourhood of the $3S$–$3P$ resonances are the combined effect of (1) absorption of laser photons in the collisionally-broadened wings and (2) the spatial inhomogeneity of the laser beam and hence of the saturation. The presence of the $3S$–$3P$ resonanses in the $3D$–$3P$ signal and their apparent absence in the $4D$–$3P$ signal results from the difference in spatial behaviour between the collisional excitation from the $3P$- to the $3D$-level and the laser excitation in wing of $3P$–$5S$ (or $3P$–$4D$) transitions.

The resonances at 5787 and 6022 Å correspond to the $3S_{1/2}$–$4D_{3/2,5/2}$ and $3S_{1/2}$–$5S_{1/2}$ two-photon transitions, respectively. From the presence of an underlying continuum at these resonances, we infer that a fraction of the population of the $4D$- and $5S$-levels results from off-resonant two-step processes, which can be described as consecutive absorption of a laser photon in the collisionally-broadened wings of the $3S$–$3P$ and $3P$–$4D$ (or $3P$–$5S$) transitions, respectively.

In Fig. 1(c) we present an excitation profile of the $3S$–$5S$ two-photon transition and vicinity, as obtained from the $4D$–$3P$ fluorescence signal, using a higher wavelength resolution and better signal-to-noise ratio than with the corresponding resonance of Fig. 1(b). At the center of the resonance, the collisional population of the $4D$-levels following the two-photon excitation is seen to exceed that due to off-resonant two-step processes (the continuum) by a factor of 30 ± 10. If we correct for saturation of the two-photon resonance with the aid of Fig. 4 of Ref. 13 and assume the two-step process to be non-saturated because of the large detuning involved, then the peak value of the two-photon resonance exceeds the value of the continuum at the center of the resonance by a factor of $(3.6 \pm 1.5) \times 10^2$.

CONCLUSIONS

We have demonstrated the existence of collision-assisted off-resonance absorption of laser photons by sodium atoms in a flame. In combination with on-resonance absorption, these off-resonance processes give rise to excitation of higher sodium levels and hence to the appearance of continua underlying two-photon resonances.

Spatially inhomogeneous saturation and saturation-broadening of both one- and two-photon processes distorts excitation profiles. The occurrence of collision-assisted absorption, as found here, agrees qualitatively with theoretical work by Nienhuis and Schuller.[14] According to these authors, population of an upper level (i.e. the $5S$- or $4D$-level) may arise from a two-step process, whose transition probability depends on the amount of collisional broadening of the profiles involved.

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