THE PROCESS OF ENERGY TRANSFER BETWEEN EXCITED SODIUM ATOMS

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Two experiments were carried out to test a process proposed by Allegrini et al. as a viable explanation of the fluorescence from high lying levels which is observed when sodium vapor is illuminated by resonance radiation. In the first experiment a cell with sodium vapor was illuminated by a cw dye laser tuned to the 3S → 3P transition, and the linewidth and lineshape of the fluorescence from the 3D → 3P transition were measured. In the second experiment the cell was illuminated by two pulsed lasers, one tuned to the 3S → 3P resonance and the second well off resonance with this transition. The photoionization current was measured, as was the fluorescence intensity from the 6S → 3P and 5D → 3P transitions. We conclude that the Allegrini process does not significantly contribute to the populations in the 5D, 6S and 3D states.

In three recent papers Allegrini et al. [1,2] and Kopystynska and Kowalczyk [3] described experiments in which they observed fluorescence from higher sodium states including 3D, 4P, 5S, 4D, 6S, 5D, 7S and 6D excited by a laser tuned to the 3S → 3P resonance. They interpreted their observations as due to population being transferred to higher levels in collisions of two excited sodium atoms. This process is described by the formula

$$\mathrm{Na(3P) + Na(3P) \rightarrow Na(3S) + Na}(nX) + \Delta E\,, \qquad (1)$$

where Na(nX) denotes the sodium atom in one of the higher excited states. The energy difference ΔE is supplied or carried away by the translational kinetic energy of the colliding atoms.

This explanation is difficult to accept for all observed levels since at a temperature of 400°C one has $kT = 440\ \mathrm{cm}^{-1}$ and the energy difference is several kT for states 7S, 7D, 6S and 5D (see fig. 1). In each of the experiments the focused laser beams produced intensities which were many times that required to saturate the 3S → 3P transition. Mechanism (1) would then show no dependence on the laser intensity in this regime. In spite of this, the observed fluorescence was observed to depend on the laser power [1–3].

There are, in fact, a number of other processes which should occur with finite cross-section. Geltman [4] has suggested that the following should be considered:

Photon-induced collisions of excited sodium atoms

$$\mathrm{Na(3P) + Na(3P)} + \hbar\omega \rightarrow \mathrm{Na(3S) + Na^{+} + e}\,, \qquad (2)$$

two-photon ionization from the 3P level

$$\mathrm{Na(3P)} + 2\hbar\omega \rightarrow \mathrm{Na^{+} + e}\,, \qquad (3)$$

associative ionization of excited sodium atoms

$$\mathrm{Na(3P) + Na(3P)} \rightarrow \mathrm{Na_2^{+} + e}\,, \qquad (4)$$

superelastic electron heating

$$\mathrm{Na(3P) + e} \rightarrow \mathrm{Na(3S) + e} + \Delta E\,. \qquad (5)$$

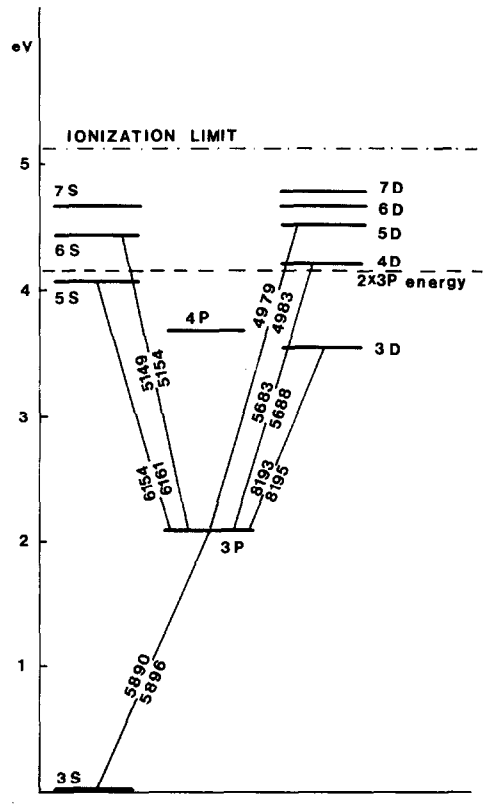

Fig. 1. Level diagram of Na.

The hot electrons from process (5) can excite higher lying levels and ionize sodium atoms, thus very rapidly increasing the number of ions and electrons [11,12]. These processes were observed by Bearman and Leventhal [5], Uzer and Dalgarno [6], Hellfeld, Caddick and Weiner [7] and Tam and Happer [8]. In the experiments of Lucatorto and McIlrath [9,10] almost complete ionization of Na and Li was observed.

The aim of the experiments reported in this paper is simply to determine whether the process (1) plays a significant role when there is a large energy difference, $|\Delta E| \gg kT$. In the first experiment we investigated the transition 3D → 3P, where the energy excess is 4739 cm^{-1}, which is more than 10 kT. The process (1) can be detected by measuring the linewidth and lineshape of the fluorescence.

Since half of the excess energy should be carried off by each of the colliding atoms, the speed of the fluorescing atoms should be superthermal. At temperatures below 350°C the time between collisions

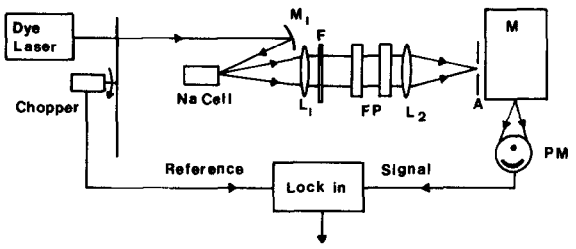

Fig. 2. Experimental set-up. The dye laser is cw with a ring cavity producing up to 100 mW with a bandwidth of 1 GHz. M_1 is a mirror with focal length of 20 cm, L_1 and L_2 are lenses with focal lengths of 15 cm, F is an RG-10 Schott filter, FP is a Tropel model 360 tunable Fabry-Perot interferometer, A is a pinhole aperture, M is a 82410 Jarrel-Ash monochromator. PM is an EMI 9659A extended S20 photomultiplier and lock-in is a PAR 128 lock-in amplifier.

is much longer than the decay time. Thus, the linewidth should be 2.5 times the normal Doppler linewidth for the vapor temperature. The velocity distribution should be non-Maxwellian, leading to a nearly rectangular lineshape [13]. We carried out an experiment to look for these effects, using the apparatus shown in fig. 2. A beam from a cw dye laser with a linewidth of about 1 GHz tuned to the sodium D_2 resonance line was focused into a sodium vapor cell. The cell was made from alkali-resistant Corning 1720 glass. Two cells were used. One contained 0.3 torr of argon buffer gas, the other only saturated sodium vapor. The light from the fluorescent spot was collected by lens L and passed through a filter F and a plane mirror Fabry-Perot interferometer. The interferometer was adjusted to have a free spectral range of 10 GHz. When properly adjusted, the finesse of the Fabry-Perot was 25. The output from the interferometer was focused by lens L_2 onto a pinhole placed at the entrance slit of a 1/4 m Jarrel–Ash monochromator tuned to 8195 Å or 8183 Å. The transmitted light was detected with a cooled photomultiplier with an extended S20 photocathode. The signal was measured using a lock-in amplifier. Population of the 3D level is caused by low probability processes and this results in low fluorescence signals at 3D → 3P transitions and rather noise signals even for long integration periods and with cooled photomultiplier. Fig. 3 shows three typical traces. At high temperature the fluorescence line shows strong self-reversal due to a large population in the 3P level. At

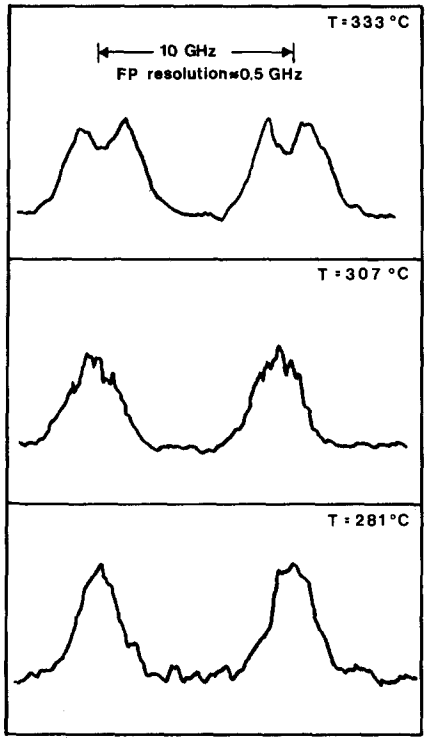

Fig. 3. Typical traces of lineshapes. The Fabry-Perot free spectral range is 10 GHz and the resolution is better than 1 GHz. The laser was tuned to the D_2 line, and the fluorescence was at 8183 Å.

decreasing temperature the reversal ceases, leaving a single peak. However, the minimum operating temperature is determined by the decreasing signal-to-noise ratio. Useful signals were obtained down to 250°C. Fig. 4 shows the dependence of the measured linewidth on the temperature. The arrow indicates the width expected if the process (1) is responsible for the fluorescence. The line at the bottom shows the normal Doppler linewidth. The observed linewidth approaches the normal Doppler width at low temperatures. This is distinctly different from the behavior expected from process (1). The experiments were repeated using the D_1 line for excitation and without the buffer gas in the cell. The results were qualitatively the same and the measured linewidth approached the normal Doppler linewidth at low temperatures, thus putting the linewidth expected from formula (1) well outside the error bars. The accurate reproducibility of these data leads us to conclude that in our experimental situation, which is very similar to that in [1], the process (1) cannot be the main process leading to the 3D → 3P fluorescence.

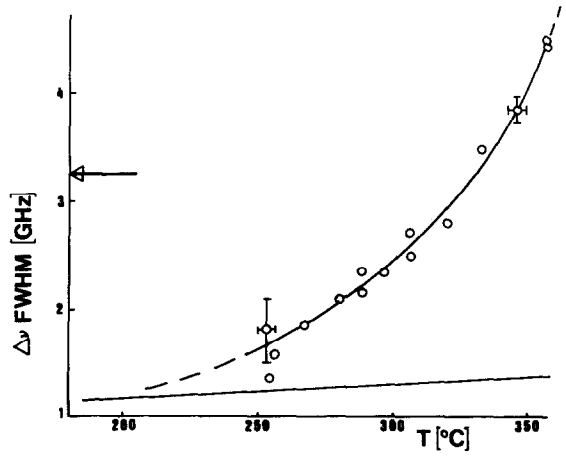

Fig. 4. Measured linewidths versus temperature. The bottom line is the normal Doppler linewidth. The arrow shows the linewidth expected from process (1). Typical error bars are given. The laser was tuned to the D_2 line and fluorescence was at 8195 Å.

This method cannot be used to study the population of high lying levels because there is an energy deficit in those cases. This led to the second experiment. By using two different exciting lasers at different wavelengths it is possible to determine the ratio $\phi_G/(\phi_G + \phi_A)$, where ϕ_G is the fluorescence intensity due to the processes proposed by Geltman [4] and ϕ_A is the fluorescence intensity due to the process proposed by Allegrini. Fig. 5 shows the experimental set-up. Two N_2 laser pumped dye lasers were used, one tuned to 3S → 3P resonance and the second detuned somewhat from the resonance. The powers of the lasers were 20 kW and 100 kW, and their linewidths 1 GHz and about 30 GHz, respectively. The laser beams were combined in a Glan prism and focused in a sodium vapor cell. The power density in the waist was close to 10^8 W/cm^2. The cell was supplied with two electrodes 4 mm apart and the applied voltage was about 4 V in order to collect electrons and ions. The temperature of the cell was 350°C. The fluorescence of the excited sodium atoms was observed perpendicularly to the laser beam by a S20 cathode photomultiplier. The signals of the fluorescence and the photoionization were measured by

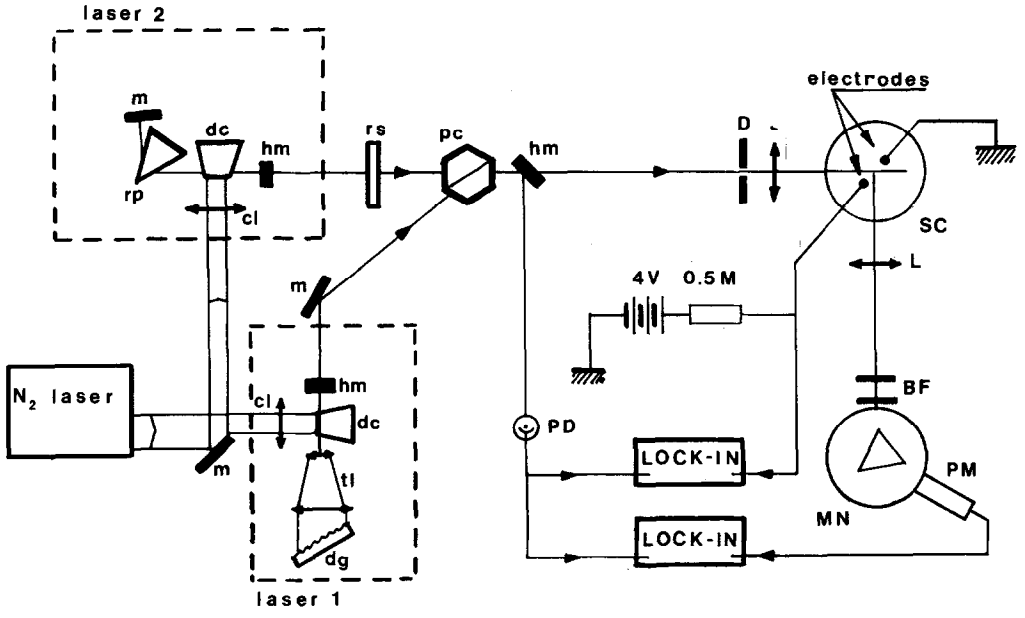

Fig. 5. Experimental set-up. cl = cylindrical lens, dc = dye cell, dg = diffraction grating, hm = high transmission mirror, m = 0% transmission mirror, pc = Glan prism, rp = rutile prism, rs = polarization rotator, BF = interference filters, D = diaphragm, L = lens, PD = trigger photodiode, PM = photomultiplier, SC = sodium cell.

two lock-in nanovoltmeters. Fluorescence lines were selected by means of a monochromator and a set of interference filters.

When laser 1 is tuned to 3S → 3P resonance, the observed fluorescence intensity can be described by the formula $\phi_1 = \phi_A + \phi_G$, where ϕ_A and ϕ_G are fluorescence intensities generated in the Allegrini and Geltman processes, respectively. The laser light is responsible for the photoionization. The photoionization current J_1 is generated in the processes proposed by Geltman, and it must be described as $J_1 = J_G$ since there is no possibility to generate electrons in the process (1). When the sodium cell is irradiated by the two lasers, the fluorescence intensity should remain constant if only process (1) is responsible for the population of the levels. The experiment showed an increase of the fluorescence intensity as well as the expected increase of the photoionization current. The increase of both values was close to 100%. One can describe the new value of the current as $J_2 = J_1 a$, where a is constant.

The new value of the fluorescence intensity can be described as $\phi_2 = a\phi_G + \phi_A$ since process (1) does not depend on the intensity of nonresonant light.

Once the set of these equations is solved, the relation of the intensity of the fluorescence generated in the processes suggested by Geltman to the whole intensity is described as follows.

$$\frac{\phi_G}{\phi_G + \phi_A} = \frac{J_1}{J_2 - J_1}\,\frac{\phi_2 - \phi_1}{\phi_1}. \tag{6}$$

The values J_1, J_2, ϕ_1 and ϕ_2 were measured directly in the experiment. The results for the 5D and 6S levels are presented in table 1. The values of $\phi_G/(\phi_G + \phi_A)$ expected from formula (1) should be equal to zero. The measured values are close to value of 1 and they are several times larger than the experimental errors. These data show that in the case of

Table 1
Results of the experiment

Transition	λ[Å]	ΔE[cm^{-1}]	$\phi_G/(\phi_A+\phi_G)$
5D → 3P	4979 4983	−3125	0.73 ± 0.19
6S → 3P	5149 5154	−2461	1.08 ± 0.18

large energy detuning and in our experimental situation rather the processes proposed by Geltman are responsible for the main part of the fluorescence.

Until now it has been impossible to compare the rates of the many processes possible with the rate of process (1) since not even an estimate of the value of the last one has been given. Very recently, Kowalczyk computed the cross-section in the case of the smallest energy difference. For the 4D sodium level and ΔE as small as 637 cm^{-1} and $T = 600$ K the computed cross-section is equal to 3.9×10^{-16} cm^2. For larger ΔE the cross-section should be much smaller. The cross-section for superelastic collisions between electrons and Na(3P) is equal to 20×10^{-16} cm^2 and the expected collision rate is almost three orders of magnitude as large as that for process (1) owing to the high speed of the electrons. The time taken by the process (5) to reach the steady state at power densities larger than 100 W/cm^2 is not longer than several microseconds for Na vapor pressures such as in our experiment and others [1–3], and the steady state is close to full ionization of the laser path [11]. In the case of cw laser excitation and a sodium vapor density of 10^{15} $atom/cm^3$ the process (1) should not play an important role even in the case of small ΔE, except for those few microseconds after the laser has been switched on. For higher power densities process (1) will play a less significant role since the cross-sections of process (2) and (3) will increase. The time needed to attain the steady state of the process (5) will decrease but the cross-section of the process (1) will remain constant. For a power density of 10^8 W/cm^2 and sodium vapor density of 10^{15} $atom/cm^3$ the number of electrons produced during a laser pulse of several ns by processes (2), (3) and (4) can exceed 10^{12} and can be further multiplied owing to superelastic collisions since the effective lifetime due to self-trapping of the Na(3P) level is close to μs.

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