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Raman and Parametric Emission from Excited States Induced by Collisions

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Abstract. A collisional energy transfer in the wings of Na $3p$ and between $Na_2 A^1\Sigma_u^+$ and Na $3p$ states has been used to excite a number of stimulated emissions in the near-ir region of 800–850 nm. The detailed study reveals Raman and parametric emission involving $3p$, $3d$, $4p$, and $4d$ levels of Na. Two tunable dye lasers in the visible provide the pump waves.

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Generation of coherent emission in atoms and molecules requires effective channels for optical excitation. Different mechanisms have been used including two-photon and two-step pumping. Searching for new processes a population inversion among the $5^2S_{1/2}$ and $4^2P_{3/2}$ states of sodium was created [1] by energy pooling. A collision-assisted two-step pump mechanism was proposed [2] for generating laser emission in the same transition. The efficiency of this process was demonstrated by cw laser oscillation on different lines from 1.85 to 3.41 μm of Na [3]. Hybrid transitions in Na_2–K and K_2–K [4] have led to laser action on atomic lines between 2.7 μm and 8.5 μm. A degenerate four-wave mixing formed by collision-assisted transitions was reported in sodium-argon mixtures [5]. In a recent paper a parametric emission in the uv was reported by collisional energy transfer between Na_2 and Na [6].

In this paper we report on new results on broadband tunable Stimulated Electronic Raman Scattering (SERS) and Four-Wave Parametric Mixing (FWPM) from excited states of Na involving Na_2 molecular excitation lines. In order to find the detailed pump mechanisms involved, two pump waves were used for selective pumping. The first dye laser was scanned across the $Na_2(X^1\Sigma_g^+ - A^1\Sigma_u^+)$ transition. Collisions in the wings of $3p$ and between excited dimer and ground-state atoms provide transfer of population to Na $3p$ level. Tuning the second pump wave to the $3p-4d$ single photon resonance excites a number of stimulated emissions in the range of 800–850 nm.

Experimental

The two tunable wavelengths were obtained by a grazing-incidence dye-laser oscillator similar to that described earlier [7], followed by two amplifiers. The whole system was pumped by a XeCl excimer laser (Lambda Physik EMG 50E). The resulting dye-laser radiation was 8 ns in duration, and $\leqq 0.2\ cm^{-1}$ spectral width with a peak pulse energy of 1 mJ available at the Na heat pipe. The heat pipe with a 50 cm hot zone was run at 500–800 K, providing a Na vapour density of $\simeq 10^{16}\ cm^{-3}$; the argon buffer gas pressure was 30 Torr. The output emission was focussed onto the slit of a 0.64 m mono-/polichromator (Jobin-Yvon HRS 640). The spectral characteristics were analyzed via an optical spectrum analyzer (B&M Model 516). With 1200 l/mm grating the resolution of the system was 0.25 Å/channel. A microcomputer controlled OSA and monochromator and stored the spectra for further analyses. The energy of individual ir lines was measured by monochromator/microjoulemeter (Laser Precision Rj 7200). Another energy meter controlled the input energy of the two dye lasers. Fast photodiodes/oscilloscope combinations monitor the temporal parameters of the pump and signal emission.

Results and Discussion

Fixing the first pump wave to the allowed dipole transition $\lambda_{p1} = 3p-4d$ at 568.8 nm and scanning the second one we detected a number of ir emission lines

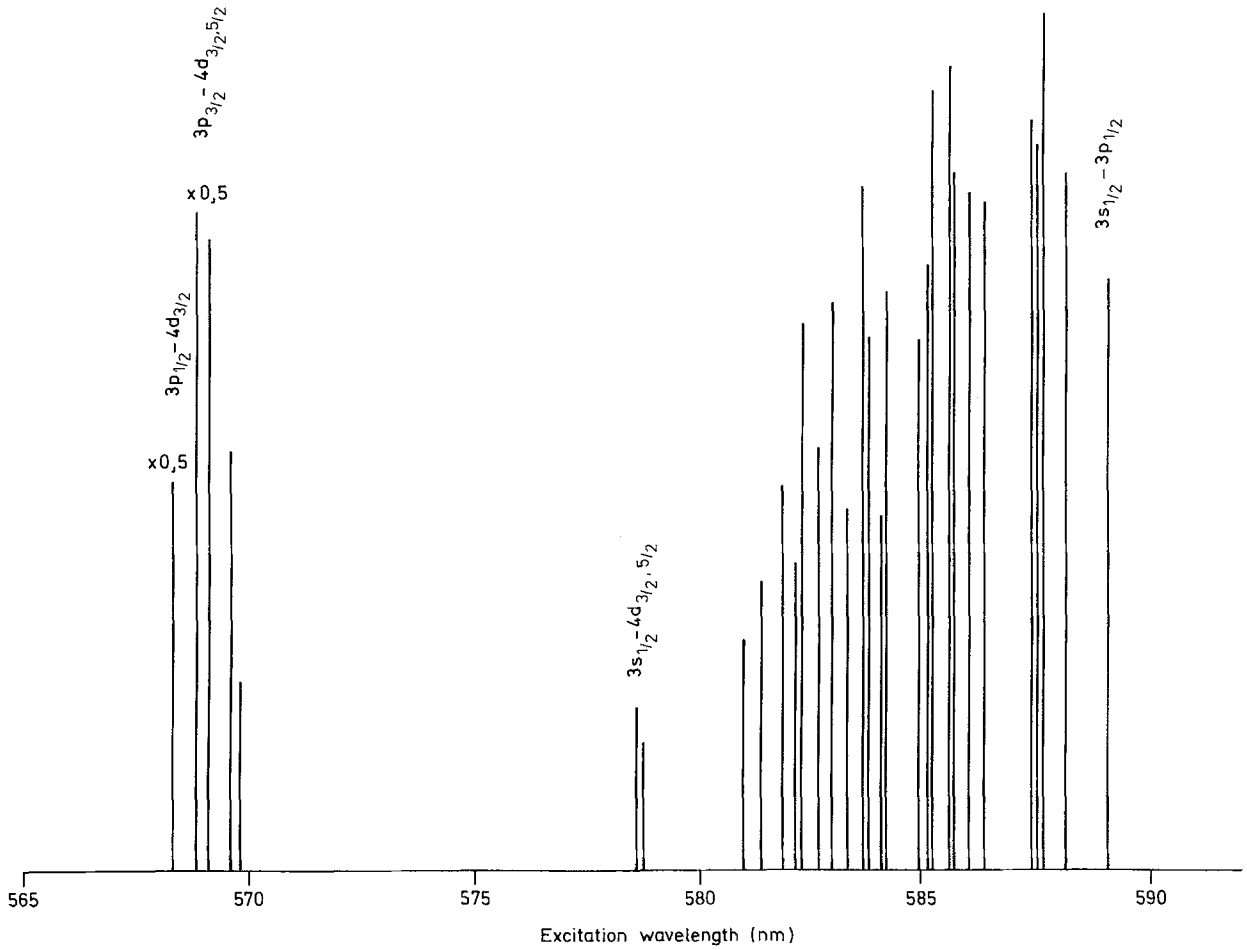

Fig. 1. Excitation spectrum for $\lambda_{s1}=818$ nm. The first pump beam is fixed to $\lambda_{p1}=3p-4d=568$ nm. The second pump wavelength λ_{p2} is scanned across the tunable range. Heat pipe temperature $T=700$ K

which are intense and collimated. All these lines were identified to belong to the Na atomic system and, what is important some of them are excited via molecular lines of Na_2.

As an example we show in Fig. 1 the excitation spectrum of one of these lines at 818 nm. For simplicity the lines of excitation are presented schematically marking the wavelength and intensity. In addition to the atomic single photon $\lambda_{p2}=3s-3p_{1/2,3/2}$ at 589.0 nm and 589.6 nm and two photon $\lambda_{p2}=3s-4d$ at 578.7 nm resonances a series of discrete lines of comparable intensity is seen. It should be noted that the discrete lines are riding on a broad pedestal (not shown on the figure), formed as shown below by the wings of NaD lines. The excitation bandwidth of these lines is narrow compared to the atomic lines. Many of the lines produce $Na_2(A^1\Sigma_u^+-X^1\Sigma_g^+)$ dimer laser emission lines. Taking into account the operating temperature range of ~ 700 K one can asign the lines to transitions from low lying vibrational levels of X state to A state in sodium dimer.

The diagram of excitation and emission is depicted in Fig. 2 together with the relevant Na_2 and Na energy levels. As seen from Fig. 2a the emission proceeds through population of $3p_{1/2,3/2}$ levels where two different mechanisms are involved. The first one is collision-assisted absorption in the wings of $3p$ levels. The second one involved is excitation of A state of Na_2 followed most efficiently (within the short pump pulse) by collisional energy transfer to Na $3p$ in the reaction

$$Na_2(A^1\Sigma_u^+)+Na(3s)\rightarrow Na(3p)+Na_2(X^1\Sigma_g^+). \quad (1)$$

These mechanisms have recently been proposed by Krokel et al. [3] in a cw experiment involving pumping of $3p-4d$ and $3p-5s$.

Let us now evaluate the contribution of both mechanisms in the population of $3p$. In the first case, say at $\lambda_{p1}=3p-4d$ resonance the pump wave is 607 cm^{-1} off $3s-3p$ resonance. At $T=700$ K and $p_{Ar}=30$ Torr the linewidth of the D lines determined by collisions with Ar is $\gamma=7.63\times 10^9$ rad · Hz [8]. The

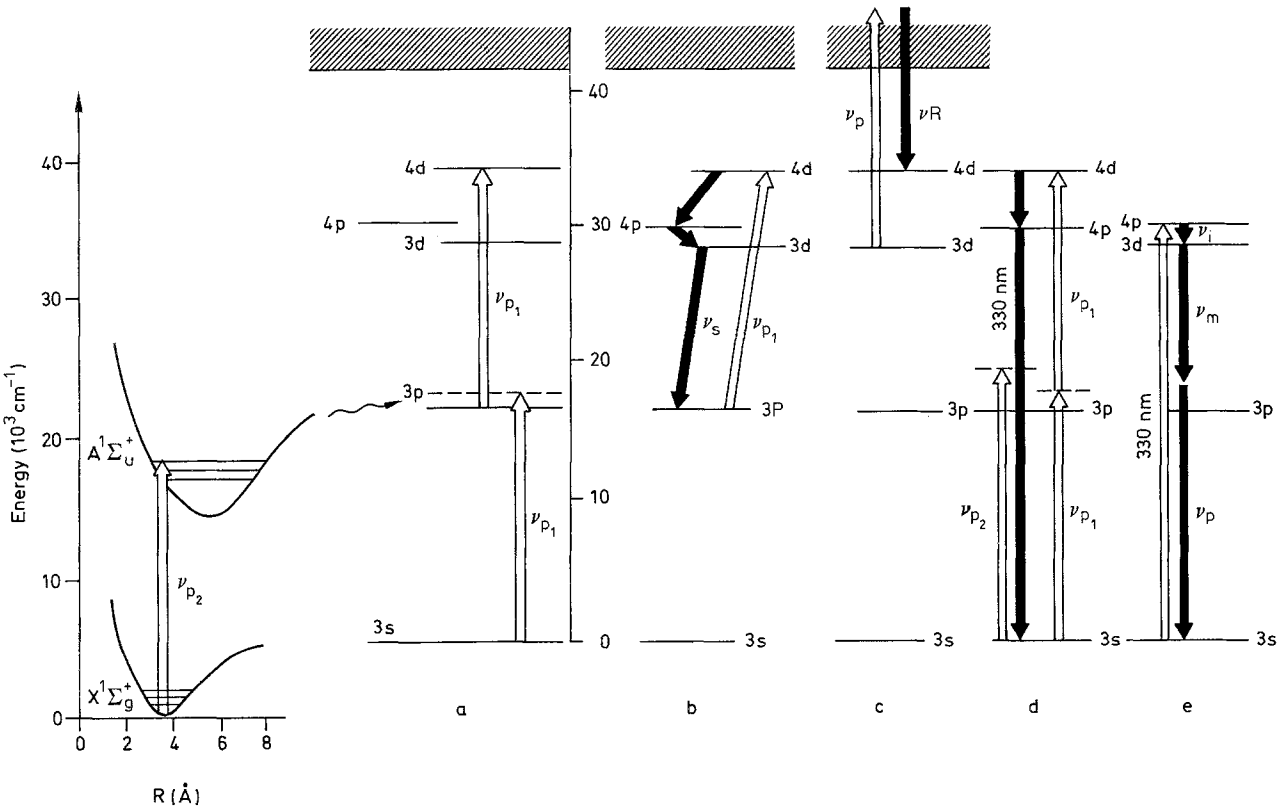

Fig. 2. Energy level diagram of Na and Na_2 with two-wavelength excitation and stimulated emission involving excited atomic states. [λ_{p1}, λ_{p2}: dye laser pump waves; λ_{R1}, λ_{R2}: first Stokes components $3d-4d$, induced by λ_{p1}, λ_{p2}, respectively, λ_s', λ_s'': cascading transitions $4d-3p$ and signal waves $\nu_p=\nu(4d-4p)+\nu(4p-3d)+\nu_s$, terminating on $3p_{1/2,3/2}$, respectively, λ_{m1}, λ_m: signal waves in the four wave parametric mixing $\nu_{p1}=\nu(4p-3d)+\nu_m+\nu_{p2}$]

absorption coefficient for a Lorentian line of $K_\nu = 0.87\times10^{-3}$ cm^{-1} and for a focal zone of $L=4$ cm the absorption in the blue wing is $\alpha=0.3\%$. With an input energy of $W=0.7$ mJ and a focal volume of $V=2.8\times10^{-3}$ cm^3 the concentration of Na $3p$ atoms is $N=2.1\times10^{15}$ cm^{-3}. Taking into account the decay rate of $3p$ level during the pump pulse of $\tau_p=8$ ns $N=N_0\exp(-\tau_p/\tau_0)$, where $\tau_0=16$ ns [9], we obtain $N_{3p}=1.3\times10^{15}$ cm^{-3}.

In the second step of resonant excitation of $3p-4d$ (Fig. 2) the pump intensity is much higher than the saturation intensity of the transition, hence $N_{4d}=6.5\times10^{14}$ cm^{-3}. Following Allen and Peters [10] we calculated the threshold inversion population for ASE in the transition $4d-4p$ $N_{th}=3.5\times10^9$ cm^{-3}, thus $N_{4d}>N_{th}$. Taking into account the radiative transition probability for $4d-4p$, $4p-4s$, and $4p-3d$ we obtain $N_{3d}=6.4\times10^{14}$ cm^{-3}.

For the second mechanism discussed we have $N_{Na_2}(X^1\Sigma_g^+)=3\times10^{14}$ cm^{-3}, $I_p=1.8\times10^8$ W$\cdot$cm^{-2} and $N_{Na_2}(A^1\Sigma_u^+)\simeq10^{14}$ cm^{-3}. The collision rate coefficient for the reaction (1), following [11] is $K=3\times10^9$ cm$^3\cdot$s^{-1}. In this way the population of $3p$ and $4d$ is $N_{3p}=10^{13}$ cm^{-3} and $N_{4d}=5\times10^{12}$ cm^{-3}, much lower, compared to the population from the first mechanism.

Assuming an exponential dependence of the 818 nm signal intensity on the population inversion due to both mechanisms the measured contribution of each mechanism agrees with calculated value within 15%.

One of the emission lines (818 nm) is based on three different mechanisms plotted in Fig. 2b and c. The first one (Fig. 2b) is optically pumped stimulated emission (OPSE), a part of the cascade, starting from the strongly populated $4d$ level. The first two steps of the cascade are in the mid-ir $\lambda(4d-4p)=2.34$ μm and $\lambda(4p-3d)=9.1$ μm and lead to strong population of the $3d$ level, as shown above. The doublet structure of $3p_{1/2,3/2}$ is clearly seen in the emission spectra (Fig. 3a) $\nu_{s1}=818.3$ nm and $\nu_{s2}=819.5$ nm.

The second process giving rise to $3d-3p$ emission at 818 nm is a four-wave parametric mixing (FWPM)

$$\nu_{p1}=\nu(4d-4p)+\nu(4p-3d)+\nu_s,$$

where ν_s is the signal wave.

The third mechanism involved is SERS, starting from $3d$ and terminating on $4d$ level (Figs. 2c and 3).

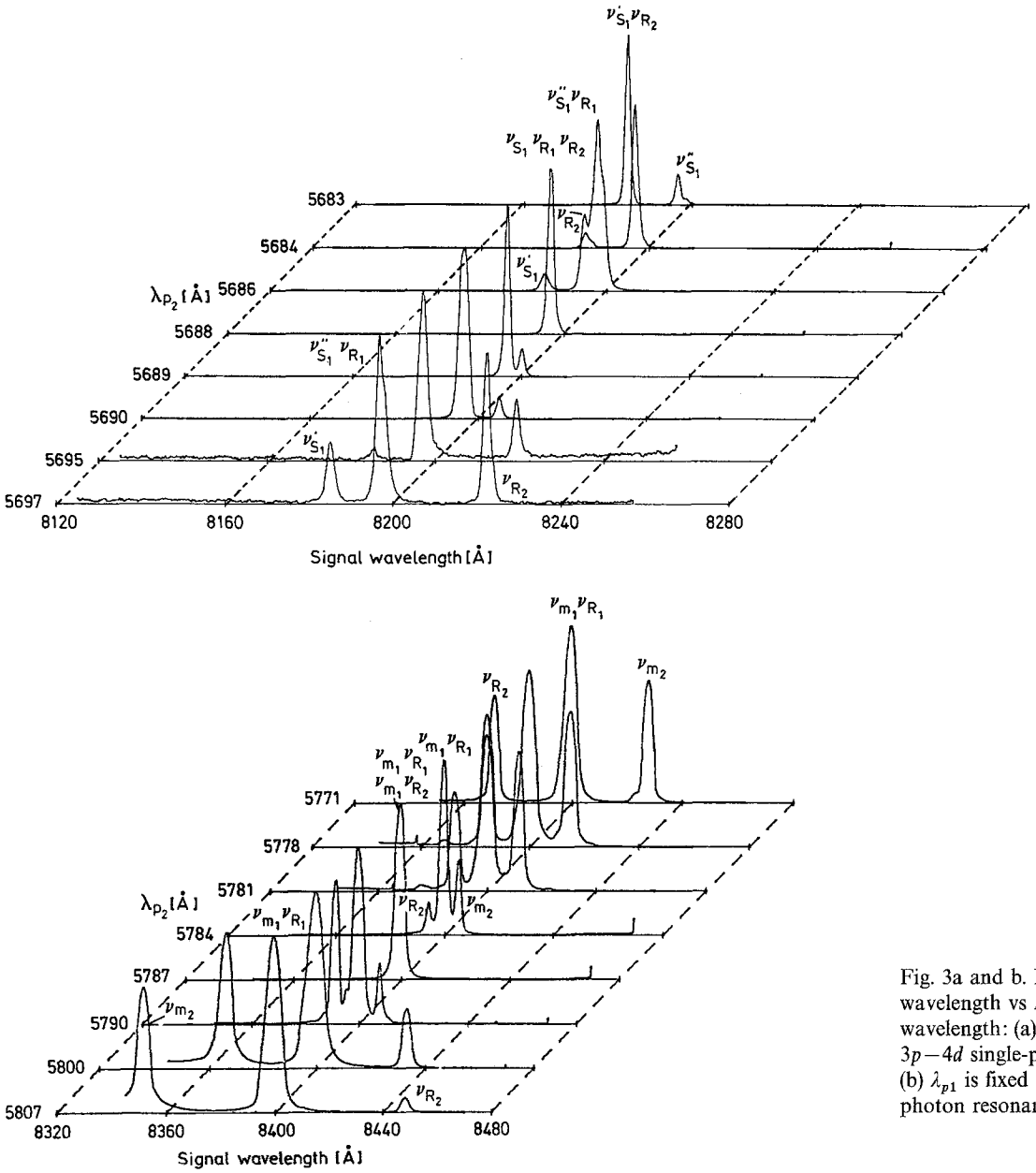

Fig. 3a and b. IR emission wavelength vs λ_{p2} pump wavelength: (a) λ_{p1} is fixed to $3p-4d$ single-photon resonance; (b) λ_{p1} is fixed to $3s-4d$ two-photon resonance

The contribution of SERS is demonstrated clearly in Fig. 3a. By sligth detuning of pump ν_{p1} wave off $3p-4d$ resonance the Stokes wave ν_{R1} is synchronously tuned around 818 nm. With ν_{p1} fixed to $3p-4d$ transition to keep $3d$ populated, we tune ν_{p2} wave 14Å, as seen in Fig. 3a, and the Stokes ν_{R2} wave is scanned across the doublet structure of 818.3/819.5 nm.

With energy deposited in the interaction area $E_p=500$ μJ, absorption in the first and second steps 0.3% and 7%, respectively, we measured a signal 818 nm energy of $E_s=10$ nJ, giving a conversion efficiency of 0.29%.

Another emission structure appears in the region of 838 nm when pump ν_{p1} is tuned to $\lambda(3s-4d)=578.73$ nm two photon resonance and the second ν_{p2} wave is scanned, Fig. 3b. Additional to the Raman ν_{R1} and ν_{R2} lines between $3d$ and $4d$, two new lines ν_{m1} and ν_{m2} are emitted (Fig. 2d and e). Characteristic for the new lines is the relation

$$\nu_m+\nu_p=29172\ \mathrm{cm}^{-1}\pm 2\ \mathrm{cm}^{-1},$$

which is fulfilled for both $\nu_{m1,2}$ and $\nu_{p1,2}$.

Whithin the experimental error this sum coincides with the potential energy of Na $3d$ state. Shown in Fig. 2d is the mechanism, involving generation of strong FWPE $2\nu_p=\nu(4d-4p)+\nu(4p-3s)$. The signal wave $\nu(4p-3s)$ at 330 nm is a pump wave in the FWPM $\nu(330\ \mathrm{nm})=\nu(4p-3d)+\nu_m+\nu_p$ (Fig. 2e).

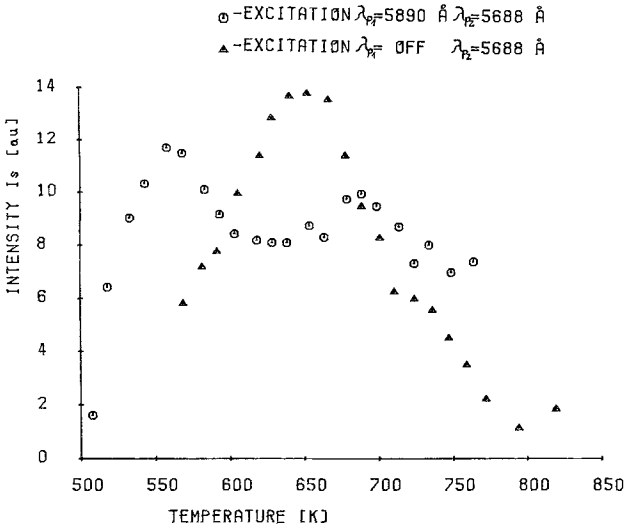

Fig. 4. Intensity of the 818 nm signal on temperature: $\circ\lambda_{p1}=3s-3p$, $\lambda_{p2}=3p-4d$; $\triangle\lambda_{p1}=$ off; $\lambda_{p2}=3p-4d$

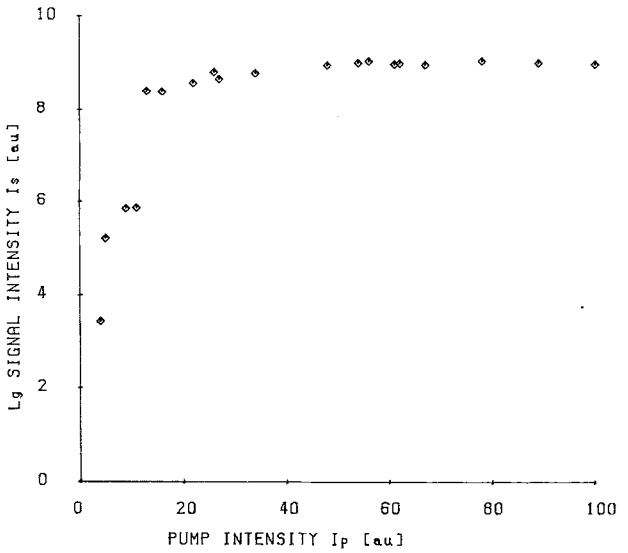

Fig. 5. Intensity dependence of the 818 nm signal on pump intensity. $T=700$ K

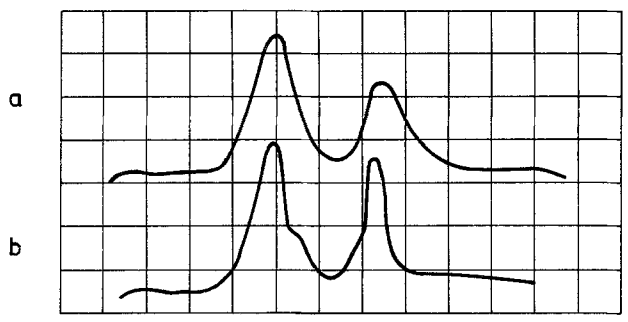

Fig. 6a and b. Oscilloscope traces of pump and signal 818 nm pulses. (a) Reference trace with pump pulse on input and output, (b) pump pulse on input and signal on output

An interesting behaviour of v_{m1} and v_{R1} is shown in Fig. 3b. Scanning v_{p2} causes v_{m2} and v_{R2} to move in opposite directions, converging into $\lambda=578.73$ nm, which coincides with the FWPM v_{m1} and SERS v_{R1} signals from v_{p1}. The convergence point $v_{m1}=v_{m2}=v_{R1}=v_{R2}$ evidently occurs for $v_{p1}=v_{p2}$. Some similar lines have recently been observed by Wang et al. [12]. However, the mechanism proposed is different from the mechanism discussed here.

The 818 nm signal intensity (Fig. 4) increases with temperature following the increase in active atom concentration. The rise in dimer absorption leads to signal decline. For comparison, in the two-step excitation of $4d$ ($3s-3p$ and $3p-4d$) the temperature dependence has two maxima. The first one, at 560 K, is connected with the first step. The rise in temperature increases Na D line absorption in the beginning of the heat pipe, out of the interaction zone. The maximum at higher temperature is caused by the second step $3p-4d$, similarly to the first mechanism discussed.

The measured dependence of the 818 nm signal on pump intensity reveals two features (Fig. 5). At low pump intensity the dependence is exponential, characteristic for a stimulated process. At high intensity the dependence levels off.

The temporal characteristics of the signal are presented in Fig. 6. In order to measure the time coincidence between the pump and signal we recorded a callibration trace with pump pulse at the input and output of the measuring system (Fig. 6a). In the second trace (Fig. 6b) the first pulse is the pump wave and the second – 818 nm signal wave. As seen from the figure, the signal pulse is 4 ns and is excited at the rising part of the pump pulse, which is in agreement with the mechanisms discussed.

In conclusion, using two tunable pump waves we have shown that the collision induced energy transfer in the wings of sodium D lines and between $Na_2A^1\Sigma_u^+$ and Na $3p$ states is an efficient mechanism for creating a considerable inversion population between high lying states of Na. In the case of pulsed excitation the first mechanism has a dominating role in the population, in our case of $3d$ and $4d$ states. Collision induced excitation can be used to prepare some particular states in order to study nonlinear Raman and parametric processes involving high-lying Rydberg and autoionizing states of atoms and molecules.

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