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New parametric emissions in diatomic sodium molecules

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Abstract. By excitation of sodium vapor with an ultraviolet laser, tunable coherent emissions around 688 and 770 nm generated from diatomic sodium molecules have been observed for the first time. We demonstrate that the emission around 688 nm is due to an axially phase-matched four-wave-mixing process involving cascade emissions of $\approx 2.54\,\mu m$ and ≈ 910 nm radiation from sodium dimers.

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Many nonlinear optical phenomena, such as harmonic generation, stimulated Raman and hyper-Raman scattering, and phase-matched four- and six-wave mixing, have been observed in sodium vapor [1–5]. All of these occur in atoms. Besides the atoms, diatomic sodium molecules are also present in the vapor, which have been investigated intensively for molecular and laser spectroscopy and from which a great number of coherent and stimulated emissions have been obtained. However, to the best of our knowledge, the above-mentioned nonlinear processes in diatomic sodium molecules have not been reported up to now.

The present work concerns a new strong coherent emission around 688 nm which is observed when the sodium vapor is pumped by an ultraviolet (UV) dye laser and is attributed to a four-wave-mixing process in diatomic sodium molecules. Another coherent emission around 770 nm is also observed.

1 Experimental setup

Figure 1 shows a diagram of the experimental setup. A XeCl excimer laser-pumped dye laser (Lambda Physik, FL2002E) was used as a pump source. The dye laser was operated with p-terphenyl dye and produced output powers of ≈ 2 mJ with a pulse duration of ≈ 14 ns. The linewidth was $\approx 0.2\ cm^{-1}$.

A heatpipe with a 24 cm heating zone contained the sodium vapor. The pump laser beam was focused into and directed through the heatpipe and then onto the entrance fiber of a 0.5 m monochromator (SPEX 1870). A long-pass filter was used in front of the monochromator to eliminate second- and higher-order grating effects and to filter out the strong pump laser light before it reached the detector. The emissions emerging from the sodium vapor were collected through a lens onto the entrance of the monochromator, detected by a photomultiplier (RCA 8852) and recorded by a boxcar averager (EG&G, M162, M165) and a chart recorder (K200).

Another experimental arrangement was similar to that in Fig. 1, but the emissions from the sodium vapor were detected in the backward direction of the pump beam. The pump laser radiation was incident into the heatpipe to pump the sodium vapor after being reflected by a dichroic mirror at 45°. The mirror was transaparent for the visible and near-infrared region of the spectrum.

2 Results and discussion

Using the above-mentioned experimental setup at a vapor temperature of 550°C, argon buffer-gas pressure of 15 Torr and pump wavelength of 339.568 nm, we obtained the emission spectra in the forward direction of the pump beam, which is shown in Fig. 2. The fluorescence line around 819 nm from the Na $3d$–$3p$ transition consists of two lines obtained with a higher resolution. The spectrum in the region of 690–810 nm is the well known $1^1\Sigma_u^+ \rightarrow 1^1\Sigma_g^+$ band of the diatomic sodium molecules [6]. The spectrum in the region 820–900 nm comes from the $Na_2\ 1^3\Sigma_g^+$–$1^3\Sigma_u^+$ transition [7, 8].

The strong stimulated emission around 910 nm exhibits banded structure which is shown in Fig. 3 with a better resolution. The origin of this emission has been identified. The excited states of $Na_2\ 2^1\Pi_u$ can be populated by the UV laser radiation directly from the ground state, and the emissions around 2.54 μm band 910 nm are formed from the cascade transition of $2^1\Pi_u \rightarrow 3^1\Sigma_g^+ \rightarrow 1^1\Sigma_u^+$. It is the second step of the cascade transition which

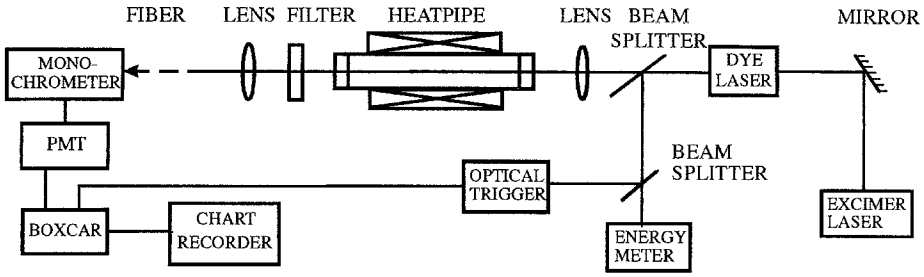

Fig. 1. Experimental setup

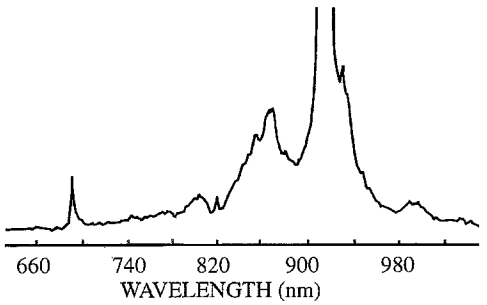

Fig. 2. Emission spectrum from sodium vapor in the direction of the pump laser beam

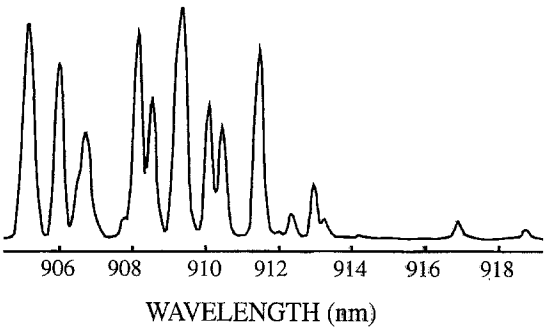

Fig. 3. Spectrum around 910 nm with better resolution

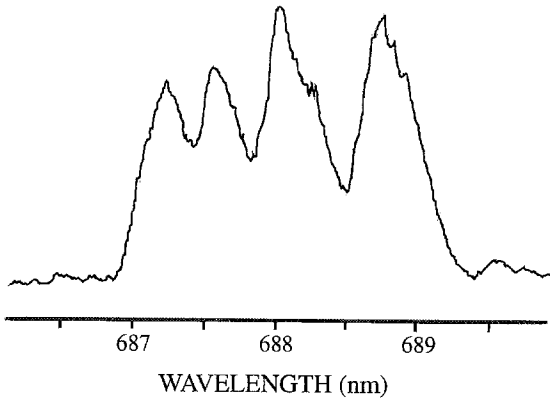

Fig. 4. Spectrum around 688 nm with higher resolution

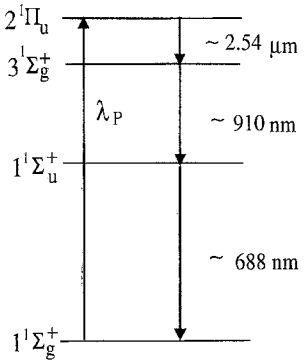

Fig. 5. Energy level scheme of the diatomic sodium molecule and emissions related to the levels for pump wavelength 339.568 nm

results in the strong stimulated emission around 910 nm [9–11]. The spectrum around 2.54 μm has not been recorded in this experiment since its spectral region is beyond the response limit of the photomultiplier. According to previous work, however, this 910 nm emission can be recognized as originating from the $3^1\Sigma_g^+ \rightarrow 1^1\Sigma_u^+$ transition and the 2.54 μm emission must be present in the experiment.

Of special interest to us here is the emission around 688 nm, which is shown in Fig. 4 with a higher resolution. The emission spectrum contains several lines, so it cannot originate from atomic processes. The emission around 688 nm lies in the spectral region of the $1^1\Sigma_u^+ \rightarrow 1^1\Sigma_g^+$ transition of Na_2, but this emission spectrum has not been reported up to now and it has a different character in peak position and bandwidth compared to the spectrum of the $1^1\Sigma_u^+ \rightarrow 1^1\Sigma_g^+$ transition. Therefore, it might be considered that the emission around 688 nm is due to the last step of the $2^1\Pi_u \rightarrow 3^1\Sigma_g^+ \rightarrow 1^1\Sigma_u^+ \rightarrow 1^1\Sigma_g^+$ cascade transitions, and an inversion of the $2^1\Pi_u$ state with respect to the lower states produces cascade amplified spontaneous emissions at wavelengths around 2.54 μm, 910 nm and 688 nm, as indicated in Fig. 5. To identify its origin, we also observed the spectra from the sodium vapor in the backward direction of the pump beam. Now, the pump beam was incident into the heatpipe after being deflected by a dichroic mirror at 45°, which was transparent for the visible and near-infrared region of the spectrum, and the emissions from the sodium vapor after passing through the dichroic mirror were collected in the backward direction of the pump beam. Under the same conditions of temperature, buffer-gas pressure and pump wavelength, the observed spectra are identical to those observed in the forward direction except that the emission around 688 nm disappears. If we regard the 688 nm emission as an amplified spontaneous emission generated from the $1^1\Sigma_u^+ \rightarrow 1^1\Sigma_g^+$

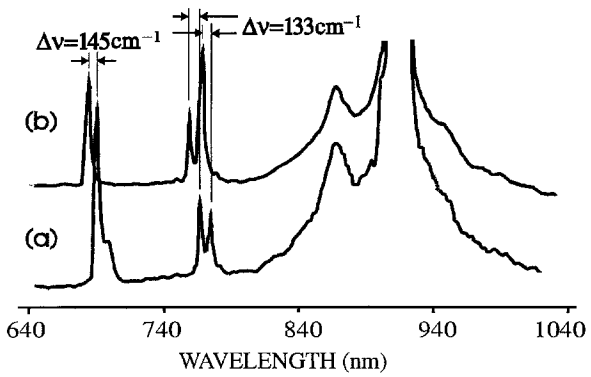

Fig. 6. Tuning behavior of the emissions upon the pump wavelength (λ_p) with a resonator at both ends of the heatpipe: (*a*) $\lambda_p = 339.568$ nm, (*b*) $\lambda_p = 337.903$ nm, $\Delta\nu_{\text{pump detuning}} = 145\ \text{cm}^{-1}$

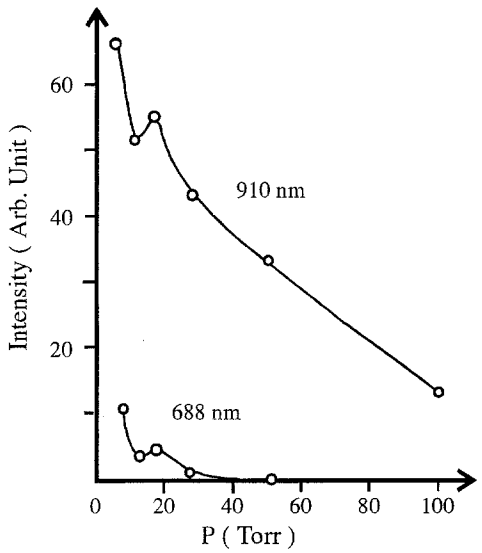

Fig. 7. Intensity dependence of the emissions around 688 and 910 nm on the argon buffer-gas pressure at a pump wavelength of 339.568 nm and a heating temperature of 600°C

transition, it must also appear in the backward direction of the pump beam. Considering a slight change of the excitation intensity could possibly change the inversion of the $1^1\Sigma_u^+$ state to the $1^1\Sigma_g^+$ state, we should at least observe the fluorescence emission at this wavelength, but, even at high detection sensitivity, we could not observe this emission while the strong infrared emission around 910 nm remains. On the other hand, we observed that the emission line around 688 nm shifts as the pump laser line is tuned, and the shifts of the 688 nm emission and pump laser radiation are equal (Fig. 6). According to the explanation that the emission around 688 nm comes from the $1^1\Sigma_u^+ \rightarrow 1^1\Sigma_g^+$ transition, when shifting the excitation energy, the coherent emission line shifts too, but its value is usually not equal to the detuning of the excitation energy. For the above-mentioned reasons, we believe that the 688 nm emission may not result, from the $1\Sigma_u^+ \rightarrow 1^1\Sigma_g^+$ transitions but probably originates from a nonlinear process in diatomic sodium molecules.

Taking into account the excitation of the Na_2 $2^1\Pi_u$ state by the UV pump-laser radiation and the cascade transition $2^1\Pi_u^+ \rightarrow 3^1\Sigma_g^+ \rightarrow 1^1\Sigma_u^+$, the four-wave-mixing process among them will be expected to occur, as indicated in Fig. 5. A further indication for this nonlinear process is the fact that the emission around 688 nm can be tuned by tuning the pump radiation; thereby, the value of the frequency detuning is equal to the pump frequency detuning (Fig. 6). The same intensity dependence of the emission around 688 and 910 nm on the argon buffer-gas pressure, which is shown in Fig. 7, also reveals the relationship between the two emissions. Meanwhile, when the collecting lens in front of the monochromator was removed from the experimental system, the intensity of the 688 nm emission almost did not change, this indicated that the emission is generated on the axis of the pump beam with a small divergence angle. Accounting for the facts mentioned above, we therefore attribute the emission around 688 nm to the axially phase-matched four-wave-mixing process as:

$$\omega_{688\,\text{nm}} = \omega_p - \omega_{910\,\text{nm}} - \omega_{2.54\,\mu\text{m}}, \tag{1}$$

$$|\mathbf{k}_{688\,\text{nm}}| = |\mathbf{k}_p| - |\mathbf{k}_{910\,\text{nm}}| - |\mathbf{k}_{2.54\,\mu\text{m}}|, \tag{2}$$

In addition, when a resonator was used at both ends of the heatipe, we also observed another strong emission around 770 nm (Fig. 6). This emision was sensitive to the resonator. However, it could be sometimes observed without the resonator, but its intensity was very weak. Like the 688 nm emission, the 770 nm emission could only be obtained in the forward direction of the pump beam, and it could be tuned by tuning the pump radiation but the value of the frequency detuning was not exactly equal to the pump-frequency detuning. Moreover, this emission almost disappeared when the collecting lens in front of the monochromator was removed. This probably implies that this emission is generated from an angle-phase-matched process. The emission around 770 nm showed competition with the one around 688 nm, while the sum of their intensities was almost constant under different conditions. Based on the facts mentioned above, the emission around 770 nm may come also from a parametric process, and this process must be interrelated to the process generating the 688 nm emission. Since the 770 nm emission is related to the resonator and the stronger fluctuations, it is suggested that the emission should originate from a higher-order parametric process. However, at present no conclusive explanation for this process can be given here.

3 Conclusion

Two new emissions around 688 and 770 nm have been observed in sodium vapor with UV laser excitation. The 688 nm emission is attributed to an axially phase-matched four-wave-mixing process in diatomic sodium molecules, which agrees well with the observation. To the best of our knowledge, this is the first observation of the four-wave-mixing process generated in diatomic sodium molecules. The 770 nm emission is also suggested to originate from a nonlinear parametric process. To clarify the mechanism, further research remains still to be done.

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