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LASER INDUCED FLUORESCENCE OF Li_2 A $^1\Sigma_u^+$ STATE

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By using several continuous wave (CW) single longitudinal-mode semiconductor laser diodes in the red spectral region, we have excited Li_2 molecule from the X $^1\Sigma_g^+$ state to the A $^1\Sigma_u^+$ state (transitions: $(v'' = 0, J'' = 19) \rightarrow (v' = 4, J' = 18)$; $(v'' = 1, J'' = 9) \rightarrow (v' = 5, J' = 10)$; $(v'' = 2, J'' = 9) \rightarrow (v' = 10, J' = 10))$ and observed the fluorescence of the resonance A → X lines together with collision-induced lines. Comparison with theoretical simulations shows a very good agreement. The use of two or three diode lasers is discussed in view of two- or three-step excitation of Li_2 molecule to the higher Rydberg or ionized molecular states.

1. Introduction

Semiconductor diode lasers [1] have been widely used in the infrared and recently in the red spectral region, offering a relatively inexpensive instrument, but with a high spectral monochromaticity and modest to relatively high power. The excitation of alkali atoms and molecules having spectrum in the visible spectral region is certainly the first step to several interesting applications, like selective excitation leading to ionization.

We were interested in using several CW single longitudinal laser diodes for the step-wise excitation of Li_2 molecule to highly excited states or even ionized Li_2^+ species. This in turn may help in igniting the electric discharge or help in guiding the electric discharge in dense lithium vapour.

We present the first results in our extensive research where we studied the first excitation step and discuss the second step of excitation of Li_2 molecule.

2. Experiment

The experimental arrangement used for laser induced fluorescence (LIF) mesurements is shown in Fig. 1. The main parts are the semiconductor laser diode, the crossed heat-pipe oven (HPO) [2] filled with lithium, the system for dispersing and detection of fluorescence, and the data-acquisition electronics.

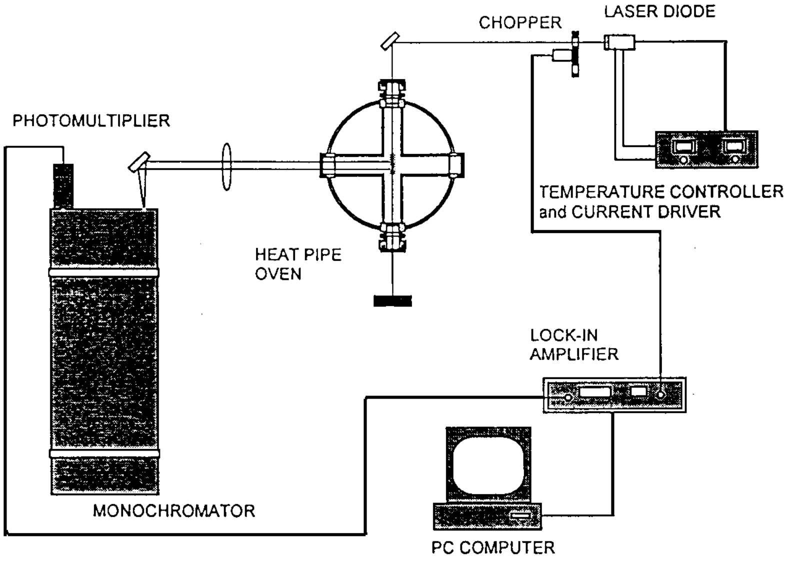

Fig.1. Experimental apparatus.

Two semiconductor laser diodes were used in the experiments. The first was a red InGaAlP semiconductor laser diode with a wavelength close to 670 nm, enclosed with a lens in a single, commercially available laser module. The maximum output power was 3 mW. The distance beetwen two adjacent longitudinal modes of the diode was 0.2 nm. The second diode was SANYO DL-4038-021 InGaAlP semiconductor laser diode. It is a red laser diode which operates near 636 nm with a maximum output power of 10 mW. The mode separation was 0.08 nm. In our experiments, we used laser diodes operating in the single longitudinal mode at higher driving currents. Small, but observable amount of power in several side modes has been observed, even in the single-mode operation. The frequency of laser radiation is determined both by the laser temperature and by the injection current [3]. Therefore, good temperature control and a stable current supply is essential for adequate frequency characteristic of laser diodes. That is achieved with the home-made electronic device, the main parts of which are the current laser diode driver (LDD200-1P, Wavelength Electronics), and the temperature controller (MPT-2500, Wavelength Electronics). The laser diode is mounted with a good thermal contact to a small cooper plate to which a Peltier termoelectric cooler is bonded. To the other side of the termoelectric cooler, a brass water-cooled block is attached. The thermistor is placed in a cooper plate for sensing the temperature of the diode. The temperature stability within 5 mK could be achieved. The temperature range for the operation of the diode was from 8 °C to 20 °C, and the currents used for the single-mode operations were in the range from 54 mA to 75 mA. The measured tuning characteristics with single longitudinal-mode hops are shown in Fig. 2a for the 670 nm laser diode, and in Fig. 2b for the 636 nm laser diode. Power-versus-current characteristics at different temperatures for the 636 nm laser diode are shown in Fig. 2c.

The crossed heat-pipe oven (HPO) was used for generating Li vapour. The laser beam enters the vapour through one arm of the cross, and the LIF is observed at right angle through the other arm of the heat-pipe oven. The HPO was filled with argon (serving as a buffer gas) and Li metal, and was heated to about 700 °C. Our heat-pipe oven was pumped with a rotary vacuum pump and could reach the pressure of 2.5 Pa.

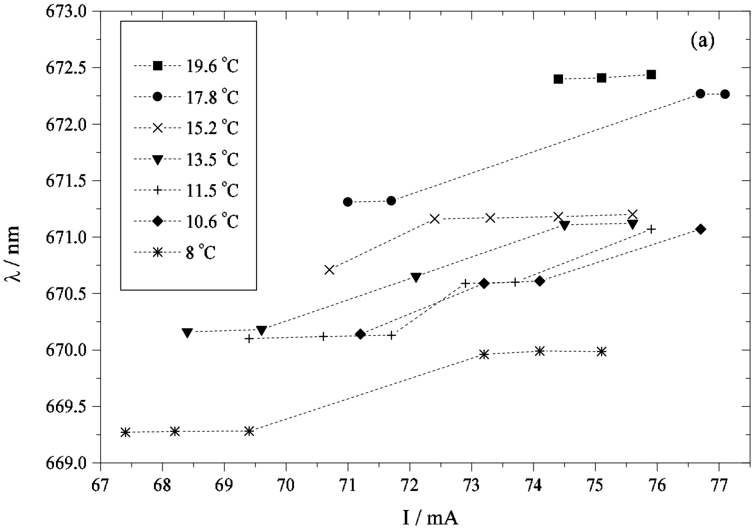

Fig. 2. (a) Mode hops of the 670 nm *diode laser at different temperatures of the diode laser.*

The fluorescence light was focused onto the entrace slit of a “Jobin Yvon THR” 1.5 m grating spectrometer equipped with a Hamamatsu R936 photomultiplier. The output signal was fed into a SR510 lock-in amplifier and stored in a PC. The fluorescence spectrum was scanned using a holographic grating with 2400 grooves/mm operating from 200 nm to 800 nm. The resolution of the sistem was 0.02 nm with the 50 μm slit widths.

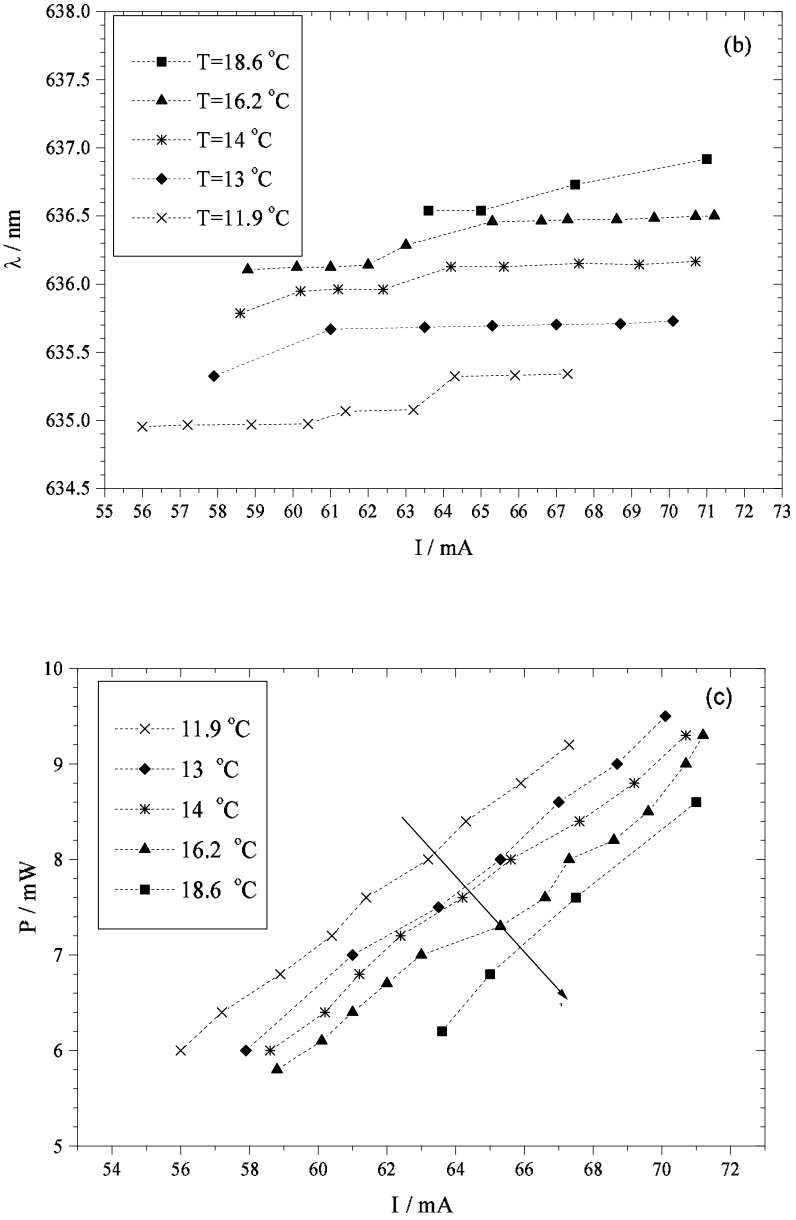

Fig. 2. (b) Mode hops of the 636 nm *diode laser at different temperatures of the diode laser. The points correspond to the wavelengths of the single longitudinal modes. (c) Power-versus-current characteristics of the 636* nm *laser diode at different temperatures of the diode laser.*

3. Results

Li_2 molecules in the HPO are excited by diode lasers operating in the single longitudinal mode. For a clear fluorescence spectrum, it is very important that the wave number of the single longitudinal mode used for the excitation coincides with the wave number of the molecular transition. The wave number of a molecular transition is determined within the Doppler width of the given molecular transition [3].

The exact positions of lines of the A-X molecular transitions were calculated using the Dunham coefficients of Kusch and Hessel [4]. For the evaluation of Franck- Condon factors, the dipole moment of Schmidt-Mink et al. [5] and the state potentials of Kusch and Hessel [4] were employed.

With the diode laser wavelength set at 670.093 nm (diode temperature $T_d = 9.1$ °C, current through the diode $I_d = 70.5$ mA and an output power of 1.6 mW), the transition

$$(\mathrm{v}'' = 0, J'' = 19) \rightarrow (\mathrm{v}' = 4, J' = 18)$$

was excited. The vapour temperature was 715 °C, corresponding to the lithium concentration [Li] = $6.05 \cdot 10^{15}$ cm^{-3} and molecular concentration [Li_2] = $1.62 \cdot 10^{14}$ cm^{-3} [6]. Figure 3a shows fluorescence spectrum and the theoretical simulation of the Franck-Condon factors for the corresponding transitions.

With the diode laser wavelength set at 672.36 nm (diode temperature $T_d = 16.4$ °C, current $I_d = 74.2$ mA and an output power of 1.55 mW), the transition

$$(\mathrm{v}'' = 1, J'' = 9) \rightarrow (\mathrm{v}' = 5, J' = 10)$$

was excited. The vapour temperature was 680 °C, corresponding to the lithium concentration [Li] = $2.99 \cdot 10^{15}$ cm^{-3} and molecular concentration [Li2] = $6.9 \cdot 10^{13}$ cm^{-3}. Figure 4a shows the corresponding fluorescence spectrum and the theoretical simulation of the Franck-Condon factors for the corresponding transitions.

With the wavelength of the second laser diode set at 636.489 nm (diode temperature $T_d = 14.9$ °C, current through the diode $I_d = 76.3$ mA, output power of 7 mW) the transition

$$(\mathrm{v}'' = 2, J'' = 9) \rightarrow (\mathrm{v}' = 10, J' = 10)$$

was excited. The temperature of lithium vapour was 680 °C. The observed fluorescence spectrum and the theoretical simulation are shown in Fig. 5a.

Because of the selection rules for a ${}^1\Sigma_u^+ - {}^1\Sigma_g^+$ transition [7], the fluorescence lines in Figs. 3a to 5a appear as P, R doublets. In Figs. 4a and 5a, besides the Stokes doublets, the fluorescence spectrum shows one anti-Stokes doublet and two anti-Stokes doublets, respectively. The intensities of the doublets have an oscillatory envelope [7].

Figures 3b, 4b and 5b show parts of the fluorescence spectra shown in Figs. 3a, 4a and 5a, respectively, with the collision-induced rotational transitions in Li_2 molecule. The satellite lines originating from the collision-induced rotational levels have the structure of P, R doublets and are grouped around the parent P, R doublet. Only satellites of even ΔJ

appear because of the selection rules for inelastic collisions of a homonuclear molecule [7].

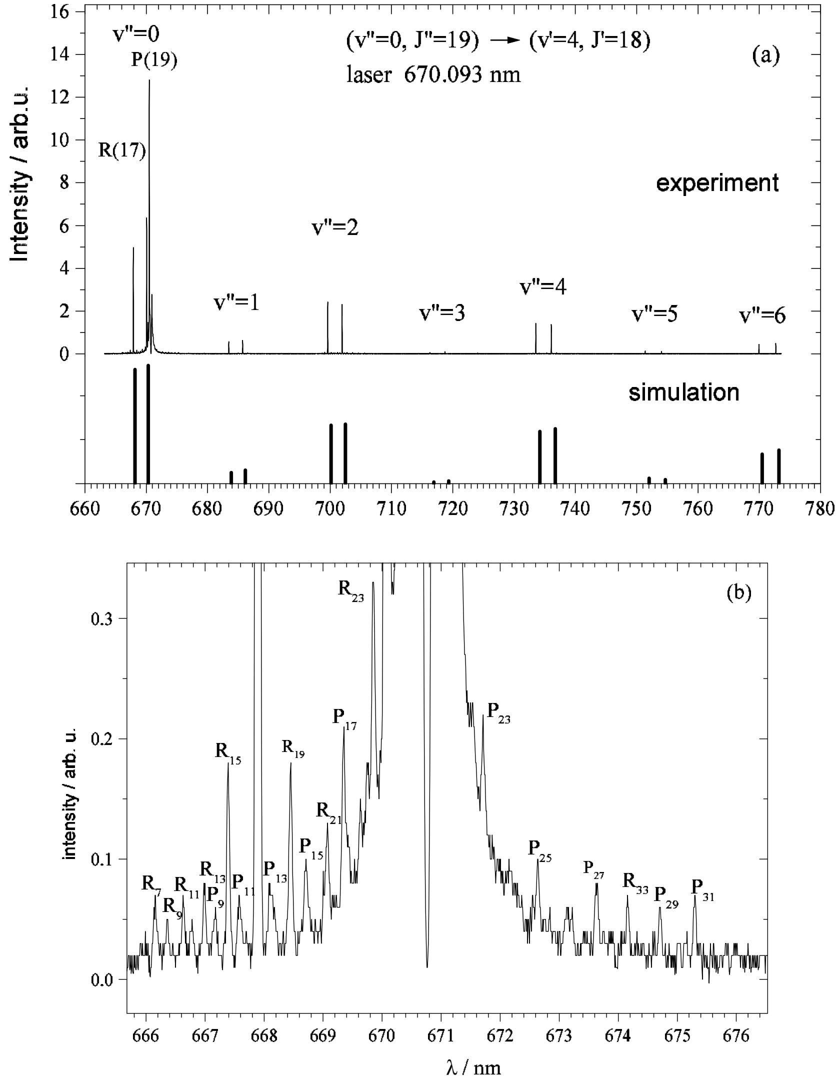

Fig. 3. (a) Li$_2$ *(A → X) fluorescence spectrum with the theoretical simulation. Transition* $(v'' = 0, J'' = 19) \rightarrow (v' = 4, J' = 18)$ *in lithium vapour at 715* °C *was excited by the 670.093* nm *single longitudinal-mode diode laser with the output power of 1.6 mW at an argon pressure of about 160 Pa, (b) Detail of the* Li_2 *(A → X) fluorescence band* $v' = 4 \rightarrow v'' = 0$*, with the lines resulting from collision-induced transitions which are superimposed on the broad wings of* Li *670.8* nm *self-broadened resonance line.*

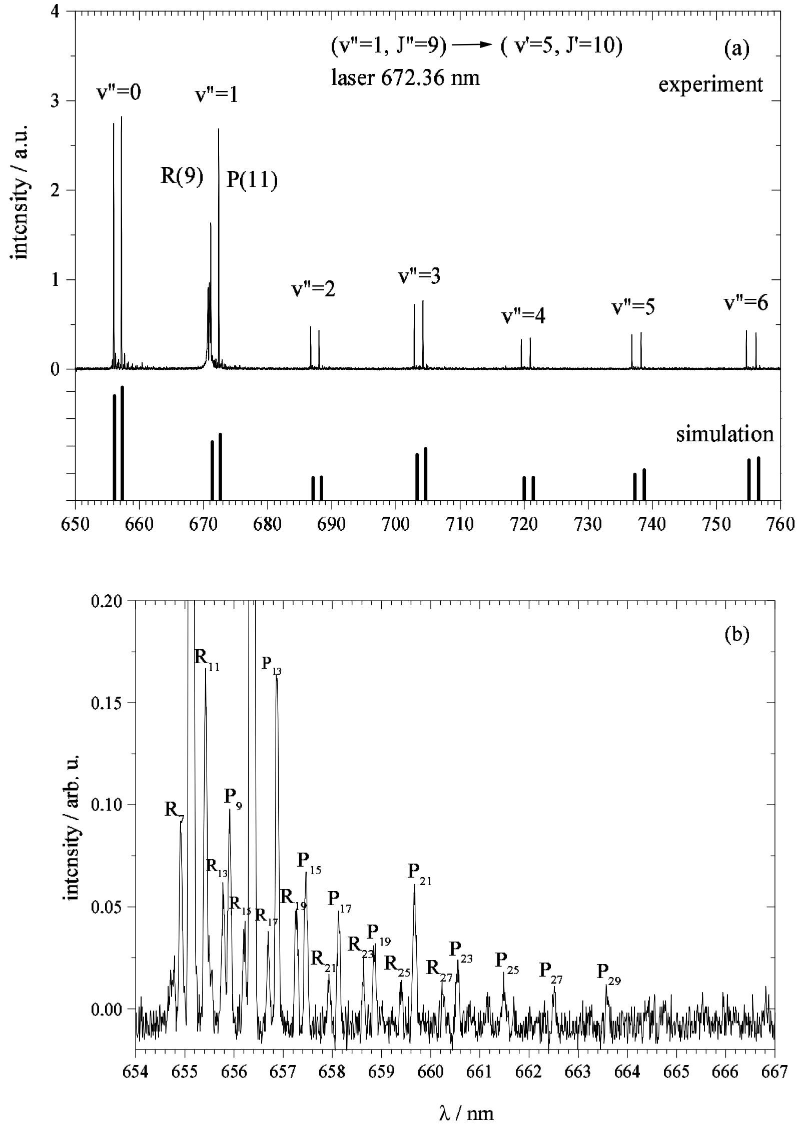

Fig. 4. (a) Li$_2$ *(A → X) fluorescence spectrum with the theoretical simulation. Transition* $(v''=1, J''=9) \to (v'=5, J'=10)$*; in lithium vapour at 680* °C *was excited by the 672.36* nm *single longitudinal-mode diode laser with an output power of 1.55* mW *at an argon pressure of about 170* Pa*, (b) Detail of the Li*$_2$ *(A → X) fluorescence band* $v'=5 \to v''=0$*, with the lines resulting from collision-induced transitions.*

The bands are degraded to the red. The $P(J-4)$ lines for the fluorescence $(v'=10) \to (v''=1)$ lie very close to each other, so they are not resolved in Fig. 5b. The satellite lines originating from

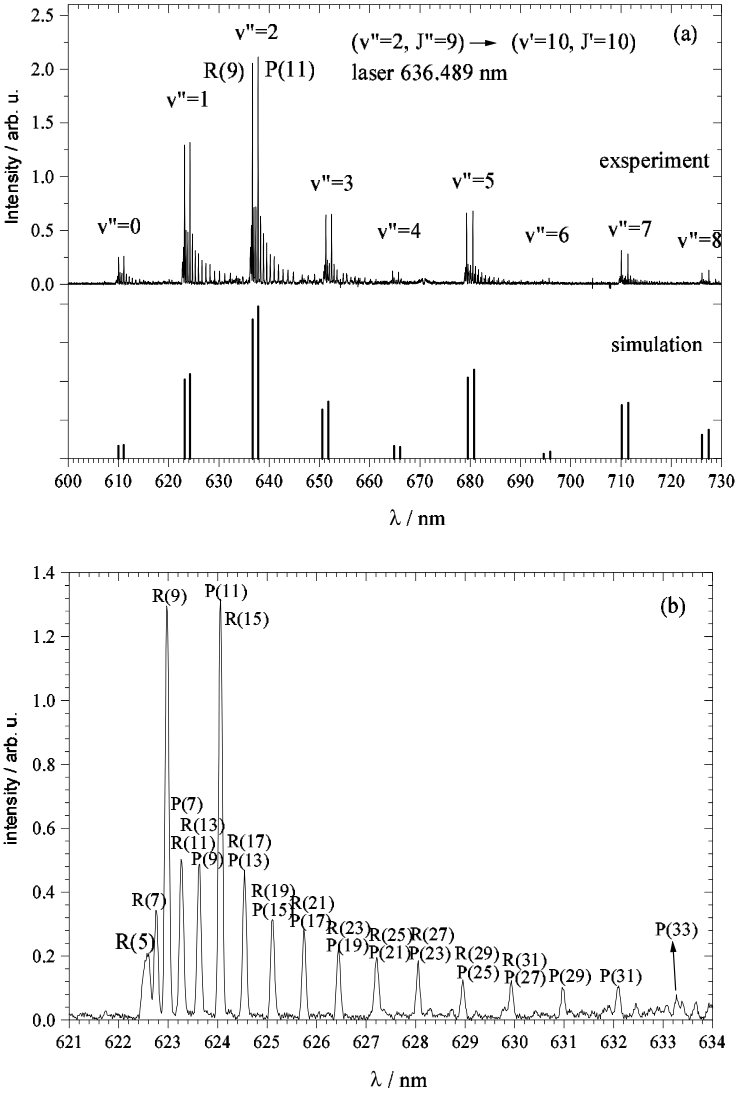

Fig. 5. (a) Li$_2$ *(A → X) fluorescence spectrum with the theoretical simulation. Transition* $(\mathrm{v}'' = 2, J'' = 9) \rightarrow (\mathrm{v}' = 10, J' = 10)$ *in lithium vapour at 680* °C *was excited by the 636.489* nm *single longitudinal-mode diode laser with an output power of 7* mW *at an argon pressure of about 2800* Pa*, (b) Detail of the Li*$_2$ *(A → X) fluorescence band* $\mathrm{v}' = 10 \rightarrow \mathrm{v}'' = 1$*, with the lines resulting from collision-induced transitions.*

the collision-induced rotational transitions with $\Delta J = +2$ are stronger [8] than those coming from the transitions $\Delta J = -2$. In Fig. 3b, the satellite lines are superimposed on the wide $2P \leftrightarrow 2S$-resonance lithium line.

4. Discussion

The experimental fluorescence spectra are all very well reproduced by the theoretical simulations spectra of the given molecular transitions. For excitations shown in Figs. 3 and 4, the power of the laser diode was only 1.5 mW. From our experience in working with the diode lasers, we can conclude that they are very powerful in resonance-excitation spectroscopy in dense vapour.

The experimental collision-induced rotational structure shows the same main characteristics as it was reported in the literature [7–9]. By varying the noble gas inside HPO and the pressure of that gas, it will be possible to examine the behaviour of the cross-section for inelastic collisions for a given transition under different conditions. It would be interesting to study further how the collision-induced rotational structures behave if we interchange noble gas Ar with reactive H_2 or nonreactive N_2 molecular gases. We will try to excite the $A-X$ transitions in lithium vapour under the same conditions as in the present experiments, but with Ar replaced by H_2 or N_2.

For the two-step excitation of lithium molecules, we plan to simultaneously irradiate lithium vapour with a laser diode at 670 nm, and another laser diode at about 635 nm. The first laser diode should excite the $X^1\Sigma_g^+ \to A^1\Sigma_u^+$ transition, and the second should excite the $A^1\Sigma_u^+ \to F^1\Sigma_g^+$ transition. In the fluorescence spectrum, we expect to see the strong laser lines at a 636 nm and 670 nm around which are R, P doublets of a corresponding molecular $A-X$ and $F-A$ transitions, respectively [10]. When we achieve the two-step excitation, it should be possible to ionize Li_2 molecules by using a photon from the first or the second laser beam. This would form Li_2^+ and free electron along the two overlapping laser beams, which may serve as a preionization medium between two electrodes. Electric breakdown in such a case would occur at a lover voltage.

5. Conclusion

The availability of moderate-power diode lasers in the red spectral region can help in the excitation and ionization of Li_2 molecules. This may be used for further spectral studies of Li_2 molecular structure and collision-induced spectral features. In addition, we hope that the combination of two diode lasers can help in laser-assisted ignition and laser guiding of electric discharges in dense lithium vapour.

Acknowledgements

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LASEROM INDUCIRANA FLUORESCENCIJA STANJA A $^1\Sigma_u^+$ MOLEKULE Li$_2$

Pomoću kontinuiranih jednomodnih lasera u crvenom dijelu spektra pobuđivali smo molekulu Li$_2$ iz stanja $X^1\Sigma_g^+$ u stanje $A^1\Sigma_u^+$ (prijelazi: $(\mathrm{v}''=0, J''=19) \rightarrow (\mathrm{v}'=4, J'=18)$; $(\mathrm{v}''=1, J''=9) \rightarrow (\mathrm{v}'=5, J'=10)$; $(\mathrm{v}''=2, J''=9) \rightarrow (\mathrm{v}'=10, J'=10)$) i promatrali fluorescenciju rezonantnih $A-X$ prijelaza zajedno sa sudarom uzrokovanim prijelazima. Usporedba eksperimentalnih spektara s teorijskim simulacijama tih spektara pokazuje dobro slaganje. Diskutira se upotreba dva ili tri diodna lasera za trokoračno pobuđenje molekule Li$_2$ u viša Rydbergova ili ionizirana stanja.