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PRODUCTION OF ^{7}LiCd FROM Cd+$^7Li_2$ (F $^1\Sigma_g^+$) REACTION

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Blue-green excimer band of ^{7}LiCd was observed as a result of $^7Li_2$(F $^1\Sigma_g^+$)+Cd$\rightarrow$ ^{7}LiCd(2 $^2\Pi$)+Li photochemical reaction. Lithium dimer was excited into F $^1\Sigma_g^+$ by using optical–optical double resonance excitation with single dye laser photons in the 615 − 671 nm range where a number of accidental resonances ($X^1\Sigma_g^+ \rightarrow A^1\Sigma_u^+ \rightarrow F^1\Sigma_g^+$) occur. The reactivity of the excited gerade state in the formation process of the intermetallic excimers is comparable to reactivity of the ungerade states.

1. *Introduction*

To obtain intermetallic excimer spectra is usually a difficult task due to the small abundance of the ground-state molecules in metal-vapour mixtures and spectral overlap with pronounced alkali dimer spectral features. To overcome this, the use of narrow-band lasers for the excitation is needed in combination with various methods to simplify their spectra [1,2]. This can be achieved either in special supersonic expansion procedures [3] or at extremely small temperatures encountered in the light traps [4–6]. The alternative way is to use a photochemical reaction to produce the excimer in its excited state where binding energy is much larger [8–10]. The subsequent emission from the excited excimer states can be easily measured and comparison with spectral simulations shows the quality of ab initio or pseudopotential calculations [11–16]. A number of such photochemical reactions has been observed in Li_2-Zn [13], Li_2-Cd [14], Li_2-Hg [15], Na_2 -Zn [16], Na_2-Cd [17], Na_2-Hg [18], K_2-Cd [19] and K_2-Hg [20] systems, using always alkali dimer excited into the 1(B) or 2(C) $^1\Pi_u$ states and the ground state group IIB atoms. The reactivity of gerade or triplet alkali dimer excited states was never directly demonstrated which could be an important piece of information in attempts to study dynamics of photochemical reactions [21]. The opportunity to excite lithium dimer into gerade states by using only one colour dye laser was used by Bernheim and coworkers [22]. Applying optical-optical double resonance (OODR) method at accidental resonances by using two-step excitation (X $^1\Sigma_g^+ \rightarrow$A $^1\Sigma_u^+ \rightarrow$F $^1\Sigma_g^+$, G $^1\Pi_g$) with single dye-laser photon, they have shown to be able to perform the isotopic separation of the corresponding lithium dimer ions [23].

It is the purpose of present manuscript to present experimental results on the study of excitation path to excite gerade Li_2 molecular states and subsequent photochemical reaction to produce excited LiCd molecules. In this work, we use excimer-pumped dye laser to excite Li_2(F $^1\Sigma_g^+$) and spectral and temporal analysis of the fluorescence from the Li-Cd vapour mixture to clarify excitation path and photochemical production of LiCd(2 $^2\Pi$) molecules. We suggest that production of isotopic variations of ^{6}LiCd or ^{7}LiCd could be achieved by using accidental OODR resonances.

2. *Experiment*

Experimental setup is shown in Fig. 1. Excimer laser (XeCl at 308 nm, Model LPX 100e) pumped dye laser (Model FL 3002, Lambda Physik) in the region from 615 to 671 nm is used for excitation of the Li_2 molecules. The repetition rate was 9 Hz, the usual energy of the single pulse was 2 mJ, and the duration of the pulse was typically of about 20 ns (FWHM). Spectral bandwidth of the laser was 0.2 cm^{-1}. Transmitted laser light through the heat-pipe oven containing lithium and cadmium vapours induced the fluorescence which was observed at 90^o and focused onto the entrance slit of the scanning monochromator (MDR 23 with 1200 groove/mm grating, blaze 390 nm) for spectrally resolved measurements. Two photomultipliers were used: Hamamatsu R2949 (Blue PM) and R5108 (Red PM) sensitive in the spectral regions $200 - 850$ nm and $600 - 1200$ nm, respectively. The spectral response of the system was measured by means of a calibrated tungsten ribbon lamp. The blue PM gives spectral response curve almost flat from 300 nm to 550 nm while it is decreasing linearly by 80 from 550 nm to 800 nm. The red PM gives almost flat spectral response curve in the region from 800 nm to 900 nm, and decreasing from 900 nm to 1000 nm by 30Ṫhe quantum yield of the red PM is by an order of magnitude smaller than of the blue PM. The spectra shown below were not corrected for the spectral response of the system. Fast photodiode was used to trigger the gate of a boxcar averager at certain time delay after the laser pulse. In this way, the temporal resolution of the measured spectra was in the range of 20 to 100 ns after the laser pulse. Signals from the photomultiplier and the gate from the boxcar were monitored with a 100 MHz oscilloscope. The averaged signal from the boxcar was further processed by the data acquisition system with the usual laboratory PC equipment.

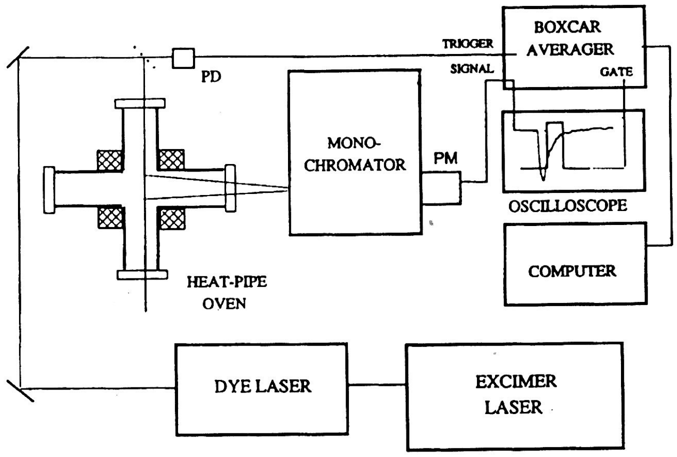


Fig. 1. Experimental setup.

Heat-pipe oven was filled with lithium and cadmium in the mass ratio 50% to 50%. Helium buffer gas pressure was between 16 and 133 mbar. The density of lithium dimers varied from about 8×10^{12} to about 2×10^{15} cm^{-3} in the temperature range 820 and 1130 K.

3. Results

We used the excitation laser spectroscopy as the method to find two-photon accidental OODR in Li_2. The laser induced fluorescence was observed with the monochromator set at selected wavelength, while the dye laser was scanned in the red spectral region as in Ref. 22. We set the monochromator at one of the peaks of the LiCd excimer band at 490 nm to search for the fluorescence signal which is a consequence of photochemical reactions between two-photon excited Li_2 molecules and cadmium atoms. For the detection of the single-photon excitation of the lithium dimer, the monochromator was set at 909 nm, where Li_2 A-X band has pronounced intensity peak, usually called the head of band heads. In Fig. 2a we present the excitation spectrum for 490 nm LiCd band, where we see that several strong peaks (denoted by arrows) appear in the 620 – 671 nm spectral range, but the strongest was at 621 nm. At 621 nm, the dye laser intensity is relatively weak because it is at the short wavelength end of its gain curve. It is interesting to note that LiCd excimer band appears when lithium resonance line at 670.8 nm was excited by the dye laser (long wavelength end of the excitation spectrum). In addition, we note that LiCd blue-green band appears when Li(3D) is excited by two photons at 639.3

nm. In the present paper, we shall not discuss LiCd formation after Li atomic single or two-photon excitations and collisions with Cd atoms. Selective absorption spectrum in Fig. 2a is compared to the selective absorption at 909 nm (at the Li_2 X-A band) shown in Fig. 3b, which is the first step of double–resonance absorption.

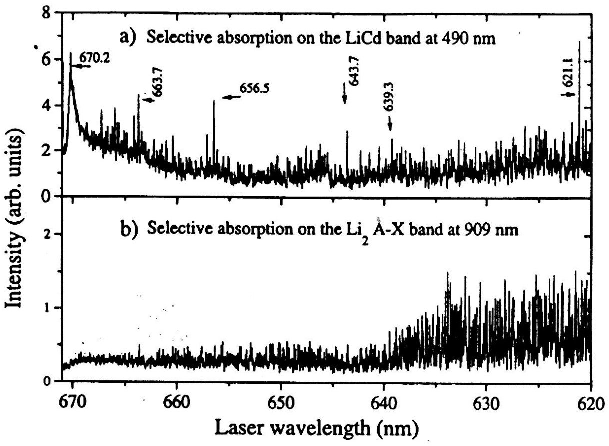


Fig. 2. Excitation spectrum between 620 and 630 nm *when the monochromator was set at* LiCd *diffuse band at 490* nm, *taken with boxcar delay of* $D = 20$ ns, *gatewidth of* $G = 60$ ns, *temperature of* 1090 K *and helium buffer gas pressure of* 137 mbar, *and b) at one prominent molecular line from the A - X transition at* 909 nm. $D = 5$ ns, $G = 100$ ns, $T = 1090$ K *and* $p_{\mathrm{He}} = 137$ mbar.

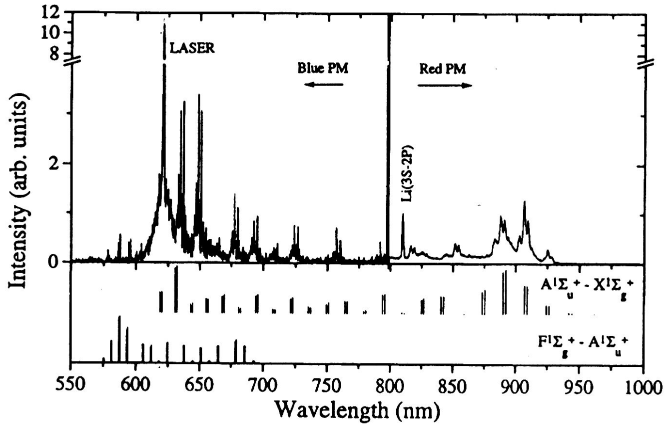


Fig. 3. Fluorescence of pure lithium vapour between 550 *and* 1000 nm, *induced by the laser excitation at* 621 nm.

In what follows, we shall concentrate on the 621 nm laser line for the two–photon excitation of Li_2 F $^1\Sigma_g^+$. To further clarify the excitation path, we present in Fig. 3a the 621 nm laser induced fluorescence spectrum of pure lithium vapour from 550 to 1000 nm. In the region between 550 and 800 nm, we used Hamamatsu

R2949 photomultiplier, and in the second region between 800 and 1000 nm we used the infrared sensitive Hamamatsu R5108 photomultiplier. In the first region, the monochromator slits were 200 micrometers wide, whereas in the second region they were 400 micrometers wide. Helium buffer gas pressure in the first region was only 15.5 mbar, whereas in the second, it was 133 mbar. That is why the spectral lines in the second region of the spectrum appear much broader than in the first. The spectra were not corrected for the spectral response. In Fig. 3b we present spectral simulation of this fluorescence spectrum, neglecting all collision–induced molecular lines. On the anti–Stokes side in Fig. 3, the fluorescence lines belong entirely to the F $^1\Sigma_g^+ \to$ A $^1\Sigma_u^+$ transitions, whereas the Stokes lines consist of overlapping A $^1\Sigma_u^+ \to$ X $^1\Sigma_g^+$ and F $^1\Sigma_g^+ \to$ A $^1\Sigma_u^+$ transitions. From the relatively good agreement between Figs. 3a and 3b, we assign X→A→F OODR transition to $v = 0 \to 9 \to 12$, with P(22) followed by R(21) lines. For the ^{7}Li$_2$ X $^1\Sigma_g^+$ and A $^1\Sigma_u^+$ states we used RKR potential–energy curves reported by Kusch and Hessel [24], and for the F $^1\Sigma_g^+$ state, we used data published by Bernheim et al. [25].

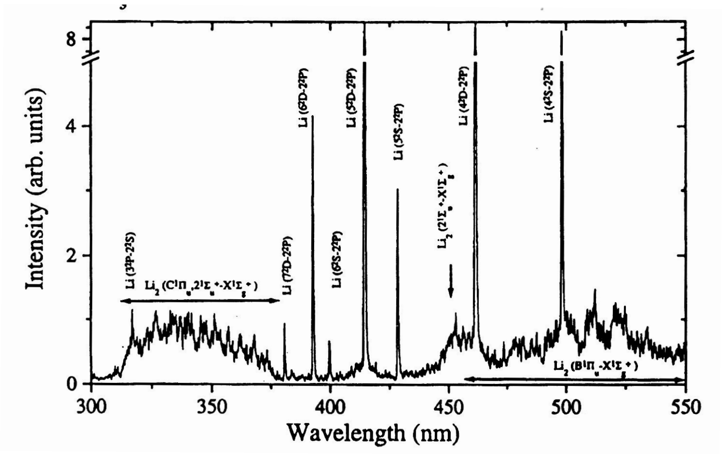


Fig. 4. Fluorescence of the collision–induced lithium dimer transitions in the spectral region from 300 − 550 nm, *induced by the laser excitation at* 621 nm. $T = 994$ K, $P_{\mathrm{He}} = 133$ mbar, *Delay*= 10 ns, *Gate*= 60 ns.

In Fig. 4, we present the spectrum of pure lithium vapour from 300 to 550 nm, excited by 621 nm dye-laser line. The ^{7}Li$_2$ C $^1\Pi_u \to$ X $^1\Sigma_g^+$ molecular band in the region from 310 to 380 nm and the 2 $^1\Sigma_u^+ \to$ X $^1\Sigma_g^+$ blue emission peaking at 452 nm are probably induced in the Li$_2$(F $^1\Sigma_g^+$)+Li or He collisions [26]. The B $^1\Pi_u$ state is populated by spontaneous infrared emission from the F $^1\Sigma_g^+ \to$ B $^1\Pi_u$ transitions. Li atomic lines from the high excited Li atomic levels stem from the three-photon ionization and subsequent radiative recombination into Li Rydberg levels.

On the far anti–Stokes side of the 621 nm excitation line, we observed LiCd excimer bands with prominent peaks at 483 and 490 nm and a long-blue tail ending at 415 nm, shown in Fig. 5. The spectra were taken with large gate of the boxcar averager (G = 300 ns), thus showing time averaged emission. The lack of sharp molecular lines previously observed [14] points to the fact that higher vibrational levels prevail in the reactive population of ^{7}LiCd (2 $^2\Pi$) (see discussion in Ref. 27). In addition, $^7Li_2$ diffuse band at 458 nm and lithium atomic lines from the sharp and diffuse series may be seen in Fig. 5.

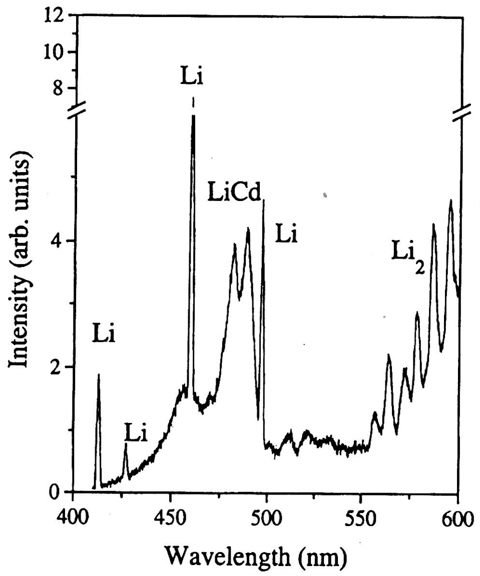
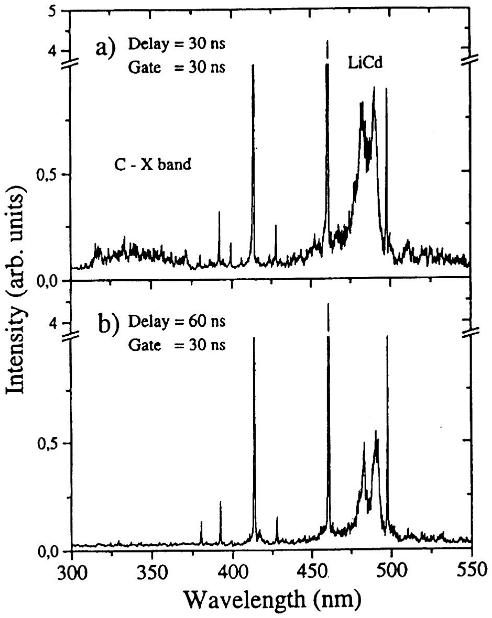


Fig. 5. Chemiluminescence in the blue–green spectral region from LiCd *excimer induced by the laser at* 621 nm. *The broad feature with the peak at* 458 nm *is* Li_2 *diffuse band, and the prominent spectral lines stem from sharp and diffuse series of lithium atoms. Gate*= 300 ns, *Delay*= 10 ns, T = 1090 K, P_{He} = 133 mbar.

To support the assumption that LiCd excited molecule is formed in photochemical reaction which involve $Li_2(\mathrm{F}\ ^1\Sigma_g^+)$ molecules, rather then $Li_2(\mathrm{C}\ ^1\Pi_u)$, we recorded spectra in the region from 300 nm to 550 nm at different time delays after the laser pulse. The results are shown in Fig. 6. At larger time delays, the C$\rightarrow$X emission is negligible (and consequently population in the C-state), while LiCd emission has decreased only slightly. In addition, we observed changes in the shape of the excimer emission which indicate the thermalization processes occurring in the 2 $^2\Pi$ state of LiCd molecule.

Figure 7 shows temporal evolution of the various spectral features. The curves were obtained by setting the monochromator at desired wavelength, while scanning the delay at which a boxcar-averager gate is open. The observed dependencies follow the functional form of the difference of two decay curves $I(t) \approx \tau_1/(\tau_1 - \tau_2)$ ($\mathrm{e}^{-\tau_2 t}$ - $\mathrm{e}^{-\tau_1 t}$), where τ_1 and τ_2 are the characteristic time constants for the population and depopulation of the relevant upper level of the molecular transition. The inspection of the curves in Fig. 7 shows that population and depopulation of the $\mathrm{C}^1\Pi_u$, $2^1\Sigma_u^+$, states are fast processes, compared to the formation of LiCd excited molecule or the population of the atomic lithium excited states.



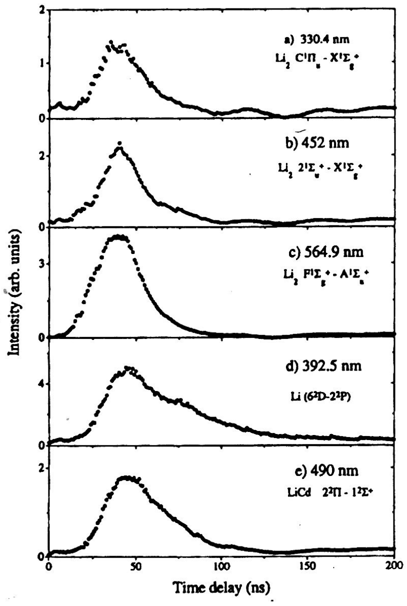


Fig. 6. Spectra of Li–Cd *vapour mixture upon* 621 nm *laser excitation in the region from* 300 nm *to* 550 nm *for two different time delays of the boxcar averager gate a)* 30 ns *and b)* 60 ns. $T = 1090$ K *and* $P_{\mathrm{He}} = 133$ mbar.

Fig. 7. Temporal evolution of various spectral features upon 621 nm *laser excitation of* Li–Cd *vapour mixture.* $T = 990$ K, $P_{\mathrm{He}} = 50.6$ mbar *(right).*

4. Discussion

In the present paper, we showed that two-photon excitation to the F $^1\Sigma_g^+$ state by using the accidental OODR line at 621 nm, triggers the photochemical production of LiCd excimer in its excited state. At first glance, it is not quite clear whether this photochemical reaction only goes directly as described by the equation:

$$\mathrm{Li_2(F^1\Sigma_g^+) + Cd \rightarrow LiCd(2\,^2\Pi) + Li}, \tag{1}$$

or also partially by collisional energy transfer:

$$\mathrm{Li_2(F^1\Sigma_g^+) + Li \rightarrow Li_2(C^1\Pi_u) + Li}, \tag{2}$$

followed by:

$$\mathrm{Li_2(C^1\Pi_u) + Cd \rightarrow LiCd(2\,^2\Pi) + Li}. \tag{3}$$

The Li_2 C-X emission appears only at higher temperatures and larger buffer gas pressures (1020 K, 66.5 mbar). LiCd band appears already at lower temperatures and smaller buffer gas pressures (820 K, 13.3 mbar). $F^1\Sigma_g^+$ state of Li_2 has longer natural lifetime than the C $^1\Pi_u$ state, and it is depopulated mainly due to the reactive collisions with abundant Cd atoms. Therefore, reaction (1) seams to be more probable pathway for the formation of excited LiCd excimer in the present experiment. In Fig. 8, we depicted laser excitation path, reactive collisions, laser

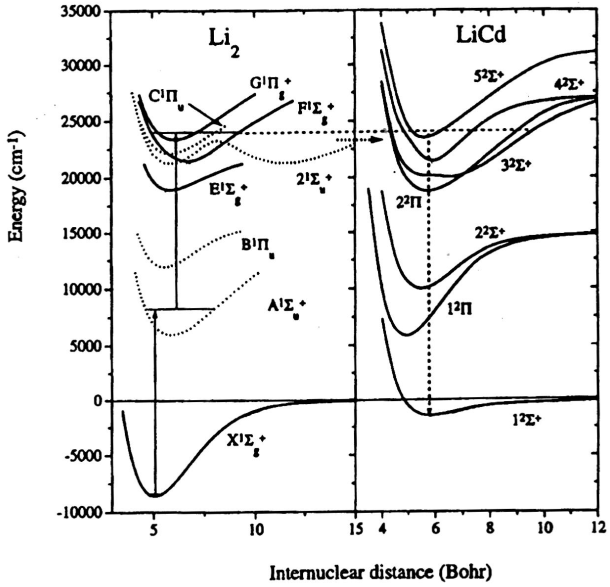


Fig. 8. Partial potential energy diagram of Li_2 *and* LiCd *molecules, showing two–photon excitation, reaction path and* LiCd *excimer emission.*

induced fluorescence and chemiluminescence in the Li_2-Cd system. The left side of Fig. 8 shows Li_2 potential-energy curves involved in the OODR excitation with equal energy photons, collisional energy transfer of population and spontaneous emission. Beside the $F^1\Sigma_g^+$ state, we can also populate Li_2 G $^1\Pi_g$ state and high-vibrational levels of the E $^1\Sigma_g^+$ state. The Li_2 F $^1\Sigma_g^+$ state overlaps with Li_2 C $^1\Pi_u$ and 2 $^1\Sigma_u^+$ states, which results in very effective collisional energy transfer of populations to these states. We observed fluorescence in the spectral region from $300 - 380$ nm and at 452 nm. Spontaneous emission from the F $^1\Sigma_g^+$ state goes to the A and B states, followed by the A-X and B-X cascade. Right–hand side of Fig. 8 shows LiCd potential energy curves [14]. Dashed line indicates maximal potential energy of the LiCd molecule, after collision of the Li_2^* and cadmium atom, which determines initial rovibrational population distribution in the LiCd* states. According to Fig. 8, we are able to populate LiCd to the 2 $^2\Pi$, 3 $^2\Sigma^+$, 4 $^2\Sigma^+$ and 5 $^2\Sigma^+$ states. However, the 2 $^2\Pi$ - 1 $^2\Sigma^+$ transition, peaking at 483 and 490 nm, has the largest transition probability, as compared to n $^2\Sigma^+$- 1 $^2\Sigma^+$ $(n = 3, 4, 5)$ transitions, which contribute slightly to the long–blue tail of the LiCd blue–green band in the region from 415 to 470 nm. Thermalization of the initial population distribution to lower rovibrational levels is not fast because of low buffer gas pressure, and we observe mostly bound–free emission. We can reach about the same potential energy of the LiCd* using XeCl excimer laser excitation at 308 nm (see Fig. 1 in Ref. 14). Then we excite directly Li_2 C $^1\Pi_u$, 2 $^1\Sigma_u^+$ and 3 $^1\Sigma_u^+$ states. Collisional energy transfer in lithium vapour populate Li_2 E, F and G states, which was observed in the spectral regions $500-530$ nm (G→A), $550-615$ (F→A) and $720-770$ (E→A). Only after the determination of cross–sections, as recently demonstrated on the Na_2–Zn system [28], we can find out which photochemical reaction is more efficient for formation of the LiCd*.

5. *Conclusion*

The Li_2 molecule, populated through accidental OODR excitation by a single pulsed dye laser, may react with Cd atoms and form LiCd excimer. In relatively dense metal vapour mixture, collision–induced processes that mix Li_2 excited states can obscure a clear cut conclusion about this photochemical reaction. However, the temporal analysis of the observed spectra shows that the $Li_2(F\ ^1\Sigma_g^+)$ + Cd photochemical reaction is efficient in forming LiCd* excimer and creates significantly different nascent distribution of the 2 $^2\Pi$ state, compared to the $Li_2(C\ ^1\Pi_u)$+ Cd reaction. It would be interesting to directly compare reactivity of gerade and ungerade states of Li_2 molecule with Cd atoms. Furthermore, in future applications, OODR excitation by a single pulse dye laser may be used for the preparation of the isotopically enriched ^{6}LiCd or ^{7}LiCd intermetallic excimers [23].

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NASTANAK ^{7}LiCd U Cd+^{7}Li$_2$ (F $^1\Sigma_g^+$) REAKCIJI

Plavozelene vrpce ^{7}LiCd eksimera opažene su kao rezultat $^7\mathrm{Li}_2(\mathrm{F}\ ^1\Sigma_g^+)+\mathrm{Cd}\rightarrow$ $^7\mathrm{LiCd}(2\ ^2\Pi)$ + Li fotokemijske reakcije. Litijev dimer se pobuđivao u $\mathrm{F}^1\Sigma_g^+$ stanje pomoću optičko–optičku dvostruku rezonanciju fotonima dye–lasera u području između 615 i 671 nm, gdje se nalaze brojne slučajne rezonancije ($\mathrm{X}^1\Sigma_g^+ \rightarrow \mathrm{A}^1\Sigma_u^+ \rightarrow \mathrm{F}^1\Sigma_g^+$). Reaktivnost pobuđenog parnog gerade stanja u procesu formiranja intermetalnih eksimera je vrlo slična (usporediva) s reaktivnošću neparnih (ungerade) stanja litijeve molekule.