Selective laser excitation in lithium

I. E. Olivares
Departamento de Física, Universidad de Santiago de Chile, Avenida Ecuador 3493, Estación Central, Santiago, Chile.
ignacio.olivares@gmail.com

Abstract: Following a number of initial experiments using tunable diode laser selective excitation of lithium isotopes, published in the 1998-2003 period, there has been renewed and increased activity in the field. Here, a brief review of the selective laser excitation of Li isotopes is given. Emphasis is on the spectroscopy and requirements for laser isotope separation in Li. Also, the recent literature is briefly surveyed.

Received 2007/06/30; revised 2007/07/03; published 2007/07/05
 ISSN: 1936-9808

Principles and requirements for laser isotope separation of heavy ions are discussed by Paisner and Solarz [1] in the book *Laser Spectroscopy and its Applications*. This article refers to the use of copper-laser-pumped dye lasers. The theory, construction details, and multiple-prism grating configurations, of narrow-linewidth copper-vapor-laser (CVL) pumped dye lasers are discussed in detail by Duarte and Piper [2, 3]. Additional tunable lasers that are useful for laser isotope separation include the continuous wave (CW) dye lasers [4]. However, CW dye lasers are relatively complex and require fairly sophisticated engineering for building and maintenance. One advantage is that they can yield relatively high CW powers in a single-longitudinal mode. Even higher average powers are available from high-pulse-repetition narrow-linewidth CVL-pumped pulsed-dye lasers [2, 3]. Further detailed descriptions of high-power dye lasers, suitable for isotope separation, are given in reference [5]. However, this class of laser, although very desirable for this type of application, has been demonstrated and operated only in a handful of laboratories around the world. An alternative, for exploratory studies, is the use of external cavity diode lasers. External cavity diode lasers using the intracavity techniques developed for linewidth narrowing, and tuning, in dye lasers are reviewed by Duarte [6] and Fox *et al.* [7].

Lithium beam generation and the control of its density was made from the fluorescence that provides the spatial and temporal lithium density distribution [8]. In this experiment a method to resolve spatially and temporally the density of a lithium beam was introduced. The lithium beam was generated passing a current through a Li-Al alloy. Density was determined from the absorption signal. The laser induced fluorescence detected in a linear 128 diode array gave the relative distribution of particles along the line of excitation. For these measurements the lithium $2^2S_{1/2} - 2^2P_{3/2}$ transition at was chosen. Absolute density profiles are given by comparison of the line-integrated fluorescence signal with the absorption. The neutral lithium density at the center of the beam were calculated to be approximately $1.8\times10^{17}[\mathrm{m}^{-3}]$ when the oven was at 870 ºK.

Doppler-limited and Doppler-free saturated absorption spectroscopy experiments were conducted in a heat-pipe oven [9]. In these experiments typical Doppler-limited absorption spectra was generated using tunable diode lasers. Also, spectra involving large optical depth were studied. In these experiments it was possible to observe a cross over signals caused by

double resonance. For example, the peaks corresponding to the transitions $2s(F=1/2)-2p$ and $2s(F=3/2)-2p$ hyperfine lines, respectively, were observed to be separated by 228 MHz. The experimental spectrum demonstrated excellent resolution of the hyperfine structure and was fairly well fitted by a density matrix model. In this case the competition between optical pumping and collisional relaxation determines the size of the cross over dip. In the case of low pressure, optical pumping dominates and we observed a crossover signal. In the case of high Ar pressure the collision process that produces relaxation from the lower filled state to the other velocity group causes and increase in the transmission, reducing the cross over signal.

Lithium atoms in the ground state can be excited selectively to any of the doublet states $^2P_{1/2}$ and $^2P_{3/2}$ (which are separated by 0.0151 nm) by use of a narrow linewidth laser and a well collimated atomic beam [10]. The energy level diagram for lithium isotopes illustrating UV and red radiation is shown in Fig. 1. The wavelengths of the 2s-2p transitions have been assigned as

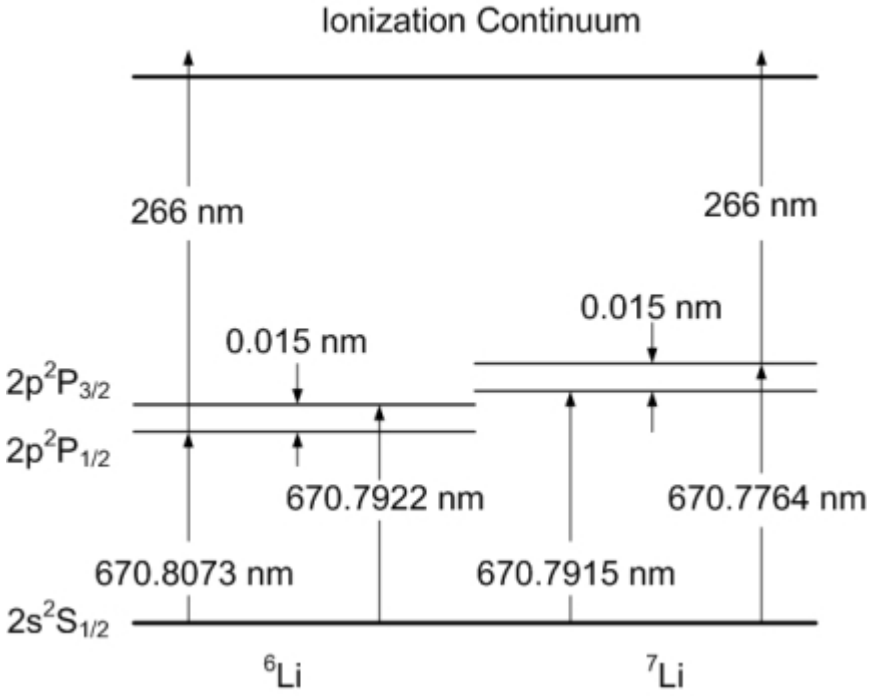

Fig. 1. Energy level diagram for the two-step photoionization of lithium isotopes. For $\lambda = 350$ nm the lithium atom is ionized from its previous excited state. The selectivity was achieved with a tunable diode laser (adapted from Olivares and Duarte [10]).

corresponding to 670.7764 nm for the $^7\mathrm{Li}D_2$ and 670.7915 for the $^7\mathrm{Li}D_1$ line. The 2s-2p transitions for $^6\mathrm{Li}D_2$ and for $^6\mathrm{Li}D_1$ lines were assigned to 670.7922 and 670.8073 nm respectively. As the energy of these excited states is approximately 1.84eV and the ionization potential is approximately 5.39 eV, the energy required to ionize the lithium atoms from the 2*p* level corresponds to wavelengths shorter than 350 nm. Thus 266-nm radiation will yield ionization from any previous selectively excited 2p level.

Resonance ionization spectroscopy (RIS) was done in a lithium beam that was generated with a Knudsen cell and collimated by a 5 mm diameter circular aperture. Laser produced ions were collected by one plate of a capacitor and detected with a lock-in amplifier method using as

reference the 5kHz repetition rate monitor of the Nd:YAG. The laser and optics configuration of these experiments are described in detail in references [9-11]. The spectrum recorded displayed saturation effects on the $^{7}\mathrm{Li}D_2$ line as a result of optical pumping between ground states produced by the photoion current. The hyperfine structure was also observed given the narrow linewidth of the diode laser and the collimation of the lithium beam. By using a well-collimated laser beam the transmittance of the $^{7}\mathrm{Li}D_2$ spectral line at 670.7764 nm as a function of the intensity of the excitation light was measured. For this measurement, the diode laser wavelength was fixed and the Nd:YAG laser was off. The saturation parameter is ten times larger than for a two level atom, which can be explained by the presence of the various ground sublevels in lithium where additional pumping can occur. The number of ions measured was compared with an estimate from the diode laser absorption measurement that uses a set of precisely solved equations. As an example of the RIS measurements the temperature of the Knudsen cell was set at 633 °C, the incoming power of the diode laser was 2360±17 μW, and the exit the power measured was 2200±17 μW. The ionizing UV power was 15-mW average, which was focused at an area of $7.5\times10^{-9}\left(\mathrm{m}^2\right)$. The number of ions after each ionizing pulse obtained from the lock-in amplifier was $N=(9\pm1)\times10^{5}$ and from absorption calculations $N=(12\pm3)\times10^{5}$. Inasmuch as the shape of the diode laser light is elliptical and is larger than the circular UV laser spot, only the 0.25 part of the red light power was used.

Lithium isotope separation was demonstrated, in 2002, using a beam of lithium atoms illuminated by a two-step selective–laser excitation process [11]. The beam of lithium was produced with a modified heat-pipe arrangement. Following passage through a mass-selection apparatus two detectors, denominated as Faraday cup 1 and Faraday cup 2, were used to collect the spatially separated isotopes $^{7}\mathrm{Li}$ and $^{6}\mathrm{Li}$, respectively. The isotopic beam detected in Faraday cup 1 gave origin to the resonance ionization mass spectrum of the $^{7}\mathrm{Li}\,D_1$ and $^{7}\mathrm{Li}\,D_2$ neatly resolved in doublets as depicted in Fig. 2. The Faraday cup 2 gave origin to the resonance

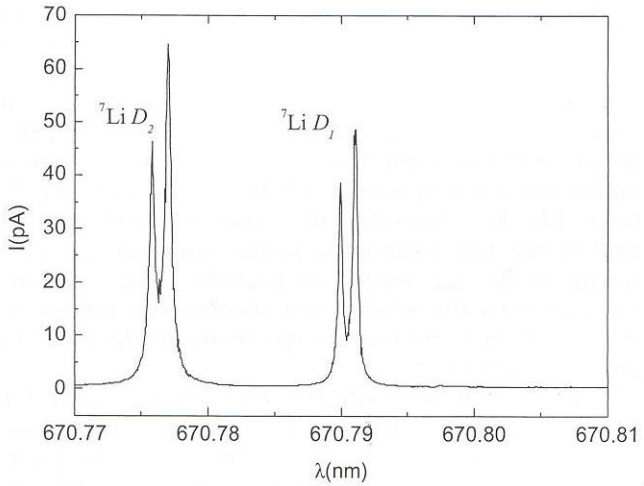

Fig. 2. Resonance ionization mass hyperfine spectrum, using diode-laser excitation, recorded at Faraday Cup 1 (from Olivares *et al.* [11]).

ionization mass spectrum of the $^{6}\mathrm{Li}\,D_1$ and $^{6}\mathrm{Li}\,D_2$ resolved lines as illustrated in Fig. 3. The average value of the background signal was 0.87 pA and 0.12 pA at the $^{7}\mathrm{Li}$ and $^{6}\mathrm{Li}$ collector

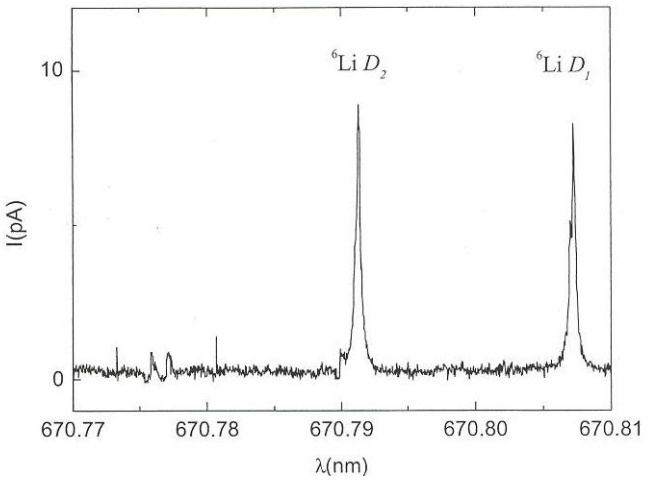

Fig. 3. Resonance ionization mass hyperfine spectrum, using diode-laser excitation, recorded at Faraday Cup 2 (from Olivares *et al.* [11]).

plate respectively. This background level has a negligible effect on the overall signal. The transmittance of each hyperfine line of the ^{7}Li D_2 was 0.991 and 0.996, respectively and the ionization laser power was 15±1 mW. An upper limit for the number of ions per ionizer pulse collected at the peaks of the hyperfine ^{7}Li D_2 lines were estimate to be $N_1 = 8.56\times10^5$ and $N_2 = 3.83\times10^5$ at the peaks of the lines respectively. The density of the beam was $n = 2.5\times10^{16}$ m^{-3} with a lithium-beam diameter of 0.005 m. In these experiments we observe a negligible background signal. The spectral lines corresponding to ^{7}Li D_2 and ^{6}Li D_1 appear free of the simultaneous signal from the other isotope. This indicates high selectivity during the resonant ionization process. Additionally we resolved by this method the doublets ^{6}Li($^2P_{1/2} - {}^2P_{3/2}$) and ^{7}Li($^2P_{1/2} - {}^2P_{3/2}$). Although the number of ions per pulse reported is marginal the laser system that has a CW exciter and a high repetition rate ionizer served as a proof of principle for the development of a future industrial system.

A series of articles have been published recently by other researchers in relation to the selective excitation of lithium and samarium. Saleem et al. [12] uses a dye laser pumped by the second harmonic of Nd:YAG (32 mJ, 5 ns pulse width). The dye laser was tuned to 670.8 nm for excitation of the lithium isotopes and frequency doubled to 335.4 nm for photoionization. A home made time of flight mass spectrometer was used in two ways. First to ionize the atoms directly by heating with the 532 nm Nd:YAG and separate the isotopes according to their charge to mass ratio. Second to photoionize selectively scanning the dye laser between 668.8 and 672.8 nm for the exciter and 335.4 nm for the ionizer. As a result they obtained the photoionization cross section of the 2p excited state as 15 ± 2.5 Mb for ^{6}Li and 18 ± 2.5 Mb for ^{7}Li where as the corresponding number densities have been determined as $N_0 \approx 5.3\times10^{10}$ [atoms cm^{-3}] and $N_0 \approx 6.2\times10^{11}$ [atoms cm^{-3}] respectively.

Saleem *et al.*[13] reported on measurements of the photoionization cross-section of $3p\ ^2P_{1/2,\,3/2}$ excited states for both the lithium isotopes ^{6}Li and ^{7}Li in the region close to the $Li^+\ 1s^2\ ^1S$ threshold (from 0 to 3 eV) using the two-step photoionization and the saturation technique. Narrow linewidth dye lasers were used in combination with a locally developed

atomic beam-TOF mass spectrometer to measure the photo ion signals as a function of energy density of the ionizing laser. The exciter laser at 323.4 nm is the frequency doubling of 646.7 nm dye laser. A Pellin Broca prism separates the 646.7 and 323.35 nm laser wavelengths. The laser at 646.7 nm was also used as one of the ionizer lasers for the measurement of the photo ionization cross-section. The other ionizing wavelengths at 760 and 690 nm were achieved from a home-made open cavity dye laser. Both dye lasers, were pumped with the SHG (532 nm) of the same Nd:YAG laser, operating at a 10 Hz repetition rate. The ionizing laser at 266 nm was achieved by the SHG of 532 nm by a BBO crystal. It is observed that the cross-section is maximum near the ionization threshold and decreases monotonically as the excess photon energy of the ionizing laser is increased. The deduced number densities of the isotopes are ^{6}Li (1.2×10^8 [atoms cm^{-3}]) and ^{7}Li (1.2×10^7 [atoms cm^{-3}]). Lithium isotope separation was achieved employing the two-step photoionization technique along with a narrow band dye laser in conjunction with a time of flight mass spectrometer [14]. The laser and optics configuration of these experiments are described in detail in reference [13]. This method yields a high degree of selectivity by tuning the dye laser at the resonance levels of ^{6}Li and ^{7}Li. The concentration of the natural abundance of the ^{6}Li isotope gets enhanced up to over 47% as the exciter dye laser is tuned to the $^2P_{1/2,\,3/2}$ of ^{6}Li even if the linewidth of the excitation laser is not sufficiently narrow to excite the isotopic level. The much higher energy density of the excitation laser limits the resolution of the fine structure levels of the lithium isotopes that leads to a loss in the enrichment of ^{6}Li due to the power-broadening effect. Measurements of the photoionization cross section of the lithium isotopes from the $2p\,^2P_{1/2,3/2}$, excited states for ^{6}Li and ^{7}Li and the corresponding number densities are reported. In a more recent publication [15] these authors report improved efficiency of their two-step isotope separation approach, using open cavity dye-laser excitation, in lithium.

Park *et al.* [16] measured the hyperfine structures of the Sm isotopes by means of a diode laser based Doppler free saturated absorption spectroscopy technique in combination with a diode laser initiated resonance mass ionization spectroscopy. These authors demonstrated that combining the two spectroscopic methods was very effective for the identification and accurate measurement of the spectral lines of atoms with several isotopes such as rare earth elements. Here, the laser arrangement consisted of an amplified single-mode diode laser in the 635-690 nm range followed by ionization from the first excited state completed by the absorption of two photons from a pulsed dye laser pumped by a frequency doubled Nd:YAG laser. The pulse width and linewidth of the dye laser were 5 ns and 1.5 GHz respectively. The wavelength of the ionizing laser was adjusted optimally by scanning the laser in the range of 620 nm –650 nm using a pulsed dye laser. A time of flight mass spectrometer (TOFMS) was used to measure the laser produced ions. Non-resonant optical fields were used in [17] and compared with our resonance ionization spectroscopy. The advantage of non-resonant fields is that it permits to study simultaneously different molecular species. As an example they studied $^{28}N_2$ and $^{30}N_2$. High resolution Doppler-free spectroscopy of Sm I in the near UV transitions at 399.002 and 399.102 was performed employing an extended-cavity diode laser tunable in the 398-400 nm range. Isotope shifts were precisely measured [18].

De Graffenried *et al.* [19] investigated the $2^2S_{1/2}-4^2S_{1/2}$ two-photon transition in atomic lithium beam by using high resolution laser spectroscopy. An Ar-ion pumped ring dye laser at 571 nm was used to excite the 2S-4S transition. The fluorescence at 497 nm was observed with a photomultiplier tube optimized for photon counting. A Fabry Perot wavemeter determines the laser wavenumber with respect to an I_2-stabilized He-Ne laser with an uncertainty of a few parts in 10^9. By this method frequencies of the two photon resonances have been measured with an accuracy better than 1 MHz.

In conclusion, it can be said that tunable external-cavity semiconductor lasers offer an attractive alternative, for selective laser excitation experiments, since they are relatively inexpensive, compact, and can yield narrow-linewidth single-longitudinal-mode emission. These sources are very well suited for resonance ionization spectroscopy and Doppler-free spectroscopy and allow the detail study of the two-step photoionization process in lithium isotopes and samarium. However, the scaling for industrial applications of these methods will demand the use of high-power tunable narrow-linewidth lasers and the use of high-average-power lasers for the ionization step. An alternative for high-power tunable laser emission is the amplification of the tunable narrow-linewidth diode laser emission. The RIS in combination with saturated absorption spectroscopy offer excellent potential for new precise measurements in isotopes on most of the elements of the periodic table using narrow-bandwidth tunable diode lasers.

References

1. J. A. Paisner and R. W. Solarz, in *Laser Spectroscopy and its Applications*, L. J. Radziemski, R. W. Solarz, and J. A. Paisner, eds. (Marcel Dekker, New York, 1987) Chapter 3.
2. F. J. Duarte and J. A. Piper, *Appl. Opt.* **21**, 2782-2786 (1982).
3. F. J. Duarte and J. A. Piper, *Appl. Opt.* **23**, 1391-1394 (1984).
4. L. W. Hollberg, in *Dye Laser Principles*, F. J. Duarte and L. W. Hillman, eds. (Academic, New York, 1990) Chapter 5.
5. F. J. Duarte, ed., *High Power Dye Lasers* (Springer, Berlin, 1991).
6. F. J. Duarte, in *Tunable Laser Applications*, F. J. Duarte, ed. (Marcel Dekker, New York, 1996) Chapter Chapter 3.
7. R. W. Fox, L. W. Hollberg, and A. S. Zibrov, in *Atomic, Molecular, and Optical Physics: Electromagnetic Radiation*, F. B. Dunning and R. G. Hulet, eds. (Academic, New York, 1997) Chapter 4.
8. A. Dinklage, T. Lokajczyk, H.-J. Kunze, B. Schweer, I. E. Olivares, *Rev. Sci. Instrum.* **69**, 321-322 (1998).
9. I. E. Olivares, A. E. Duarte, T. Lokajczyk, A. Dinklage, F. J. Duarte, *J. Opt. Soc. Am.* B **15**, 1932-1939 (1998).
10. I. E. Olivares, and A. E. Duarte, *Appl. Opt.* **38**, 7481-7485 (1999)
11. I. E. Olivares, A. E. Duarte, E. A. Saravia and F. J. Duarte, *Appl. Opt.* **41**, 2973-2977 (2002).
12. M. Saleem, N. Amin, S. Hussain, M. Rafiq, S. Mahmood, and M. A. Baig, *Eur. Phys. J. D* **38**, 277-283 (2006).
13. M. Saleem, S. Hussain, M. Rafiq, and M. A. Baig, *J. Phys. B: At. Mol. Opt. Phys.* **39**, 5025-5035 (2006).
14. M. Saleem, S. Hussain, M. Rafiq, and M. A. Baig, *J. Appl. Phys.* **100**, 053111 (2006).
15. M. Saleem, S. Hussain, M. A. Zia, and M. A. Baig, *Appl. Phys.B* **87**, 723-726 (2007).
16. H. Park, M. Lee and Y. Rhee, *J. Korean Phys. Soc.* **43**, 336-341 (2003).
17. G. Dong, W. Lu, P. F. Barker, M. N. Shneider, *Prog. Quantum Electron.* **29**, 1-58 (2005).
18. H. Park, D. H. Kwon, and Y. Rhee, *J. Opt. Soc. Am. B* **21**, (2004).
19. W. DeGraffenreid and C. J. Sansonetti, *Phys. Rev. A* **67**, 012509 (2003).