

Resonance ionization spectroscopy in a thermal lithium beam by means of diode lasers

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We measured two-step photoion current spectra by using a semiconductor laser and a Q-switched Nd:YAG laser with fourth-harmonic generation in an atomic lithium beam. The number of ions measured was compared with an estimate from the diode laser absorption measurement that uses a set of precisely solved rate equations. We explain the saturation effects on absorption by using transit time relaxation and detailed calculations of the ionization levels. © 1999 Optical Society of America
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1. Introduction

Resonant ionization spectroscopy (RIS) of lithium metal vapor by laser radiation tuned to the first resonance lithium lines has been widely investigated in recent years.¹⁻⁵ The method is considered to be useful for isotope separation because of its high selectivity.¹⁻³ In recent publications^{6,7} we reported on optical absorption at the first excited states in Doppler-limited and Doppler-free cases by using a tunable diode laser in neutral lithium vapor. The absorption was described by means of a numerical procedure based on the rate equation formalism that takes into consideration all the hyperfine sublevels, optical pumping, and relaxation processes.

Here we present a simple method to resolve fully the photoionization spectra at the 2P level by radiation at $\lambda = 670.8$ nm for selective excitation of the $2s-2p$ transition. A tunable diode laser and fourth-harmonic generation Nd:YAG laser that emits at $\lambda = 266$ nm were employed for the ionization process. For our experiment we used a well-collimated lithium beam and a narrow linewidth laser for selective excitation of ^6Li and ^7Li lines. We explain the diminished photocurrent caused by relaxation mechanisms by using the saturation absorption curve for diode laser excitation.

2. Background

Inasmuch as both lithium isotopes have a fine structure at the $2p$ level, lithium atoms in the ground state ($S_{1/2}$) 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. 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 corresponding to 670.7764 nm for the $^7\text{Li } D_2$ line and 670.7915 nm for the $^7\text{Li } D_1$ line. The $2s-2p$ transitions for $^6\text{Li } D_2$ and for $^6\text{Li } D_1$ lines were assigned to 670.7922 and 670.8073 nm, respectively.⁸

Inasmuch as the energy of these excited states is approximately 1.84 eV and the ionization potential is approximately 5.39 eV, the energy required to ionize the lithium atoms from the $2p$ level corresponds to wavelengths shorter than 350 nm. Thus a 266-nm wavelength will reach ionization from any previous selectively excited $2p$ level.^{1,3}

The number of ions at the end of a laser pulse can be estimated from density matrix calculations for the ground-excited-ionization continuum system. The following rate equation was obtained in a two-step photoionization system in which no collisions occur^{4,9}:

$$\begin{aligned}\dot{\rho}_{00} &= W(\rho_{11} - \rho_{00}) + \gamma\rho_{11}, \\ \dot{\rho}_{11} &= W(\rho_{00} - \rho_{11}) - \gamma\rho_{11} - \Gamma_i\rho_{11}, \\ W &= \frac{1/2 \Omega^2 \Gamma}{\Gamma^2 + [(\omega - \omega_0) - \mathbf{k} \cdot \mathbf{v}]^2},\end{aligned}\quad (1)$$

where ρ_{00} and ρ_{11} are the populations of the ground state and each excited state of the considered isotope,

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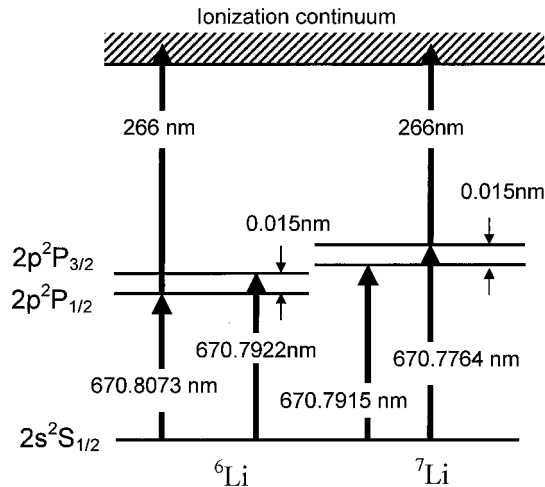


Fig. 1. Energy level diagram for the two-step photoionization of lithium isotopes. For $\lambda < 350$ nm the lithium atom is ionized from its previous excited state. The selectivity was achieved with the diode laser. The $2p^2P_{1/2}$ - $2p^2P_{3/2}$ spacing of 0.015 nm is on a greatly exaggerated scale in this figure compared with the energy levels.

respectively; $\gamma = 1/\tau$ is the spontaneous decay rate, where τ is the lifetime of the excited state that is 27 ns for lithium; W is the transition rate from the ground to the excited state⁷; $\Gamma_i = \sigma_i I_i / (h\nu_i)$ is the ionization transition rate; I_i is the intensity of the ionizing laser in watts per square meter; ν_i is its frequency in hertz; σ_i is the cross section for ionization in square meters; ω is the angular frequency in hertz of the laser that was used for excitation; ω_0 is the angular transition frequency in hertz; \mathbf{k} is the wave vector of the excitation radiation in inverse meters; \mathbf{v} is the velocity of the atoms in meters per second; Γ is the total homogeneous broadening in hertz; and Ω is the Rabi frequency in hertz. Homogeneous broadening is a function of the transition rates and other broadening effects⁵ according to $\Gamma = \gamma/2 + \Gamma_i/2 + \Gamma_L$, where Γ_L is the linewidth of the exciting laser. This system of homogeneous linear (rate) equations with constant coefficients was solved, neglecting the hyperfine structure of the ground level. The numerical procedure that describes the hyperfine structure was described previously.⁶ The solution of Eqs. (1) is given by

$$\rho_{00}(t) = A \exp(\lambda_1 t) + B \exp(\lambda_2 t), \quad (2)$$

$$\rho_{11}(t) = C \exp(\lambda_1 t) + D \exp(\lambda_2 t), \quad (3)$$

$$\lambda_{1,2} = -b \pm \sqrt{b^2 - c}, \quad (4)$$

$$b = W + \frac{1}{2\tau} + \frac{\Gamma_i}{2}, \quad (5)$$

$$c = W\Gamma_i, \quad (6)$$

where

$$A = \frac{1}{\lambda_1 - \lambda_2} [-(W + \lambda_2) + \rho_{11}(0)(2W + \gamma + \lambda_2)], \quad (7)$$

$$B = \frac{1}{\lambda_1 - \lambda_2} [(W + \lambda_1) - \rho_{11}(0)(2W + \gamma + \lambda_1)], \quad (8)$$

$$C = \frac{1}{\lambda_1 - \lambda_2} [W - \rho_{11}(0)(2W + \lambda_1)], \quad (9)$$

$$D = \frac{1}{\lambda_1 - \lambda_2} [-W - \rho_{11}(0)\lambda_2], \quad (10)$$

$$\rho_{00}(0) + \rho_{11}(0) = 1. \quad (11)$$

We obtained the ionization probability (number of ions/total number of atoms) at a time t by averaging over the velocity distribution as

$$P_i(t) = \langle 1 - \rho_{00}(t) - \rho_{11}(t) \rangle. \quad (12)$$

Thus the number of ions obtained in volume V with length X perpendicular to the direction of the laser beam after an irradiation pulse with duration t is given by

$$N_i = \rho V \frac{1}{X} \int_0^X \left[\int_0^t P_i(t') dt' \right] dx, \quad (13)$$

where ρ is the initial density of neutral atoms inside this region. We believe that t is sufficiently short so that no atoms enter or leave the region with length X . This condition applies when $t \ll T_t$, where T_t is the transit time,⁶ which is typically 500 ns for a 1-mm path. Inasmuch as the neutral lithium beam moves at thermal velocities, the laser beams are disposed perpendicular to the lithium beam direction, and the repetition rate of the laser pulses is low enough in our experiments, so that the ionized atoms leave the ionization region before the next ionizing pulse arrives. Integrating Eqs. (1) and inserting them into Eqs. (12) and (13) yield

$$N_i = \rho V \Gamma_i \frac{1}{X} \int_0^X \left[\int_0^t \langle \rho_{11}(t') \rangle dt' \right] dx. \quad (14)$$

When we use a cw laser for excitation and the ionizing laser pulse has low power, we can assume that the number of excited atoms $\langle \rho_{11} \rangle$ remains nearly constant in time:

$$N_i = \rho V \Gamma_i t \frac{1}{X} \int_0^X \langle \rho_{11}(t) \rangle dx. \quad (15)$$

The loss of excitation power along irradiation path X is given by⁶

$$dI = -h\nu\rho \frac{1}{\tau} \langle \rho_{11} \rangle dx. \quad (16)$$

The absorption of the ionization laser power was neglected because the ionization cross section is low.

Integrating Eq. (16) and using Eq. (15) and the definition of Γ_i , we obtain

$$N_i = \frac{A\tau\sigma_i I_i (I_0 - I)}{h^2 v_e v_i}, \quad (17)$$

where A is the area normal to where the two lasers coincide when they are parallel, I_0 is the incident intensity, and I is the transmitted intensity of the exciting laser. Then the number N_i of ions collected at the end of a laser ionizing pulse for low UV laser intensity is given by

$$N_i = \alpha P_i P_e (1 - T)/A, \quad (18)$$

where $\alpha = \sigma_i \tau T_{UV} / (h^2 v_e v_i) = 17,100 \text{ m}^2/\text{W}^2$ for $T_{UV} = 200 \text{ }\mu\text{s}$, $c/v_i = 266 \text{ nm}$, P_i is the average UV laser power, P_e is the exciting laser power, T is the transmittance of the exciting laser at area A where both lasers coincide in the interaction region, $\sigma_i = 7 \times 10^{-22} \text{ m}^2$ is the ionization cross section,⁵ T_{UV} is the period of the UV laser pulses of the ionizing laser, h is Planck's constant, and v_e , v_i are the excitation and ionization frequencies, respectively.

The transmittance is given approximately by Beer's law:

$$T \approx \exp(-\sigma n x), \quad (19)$$

where n is the lithium density, x is the length of the lithium beam path, and σ is the absorption cross section given by

$$\sigma \approx \frac{\sigma_0}{\sqrt{1 + S_0}}, \quad (20)$$

where S_0 is the saturation parameter and σ_0 is the cross section at low laser intensity that is a Gaussian function as a result of Doppler broadening. Taking into consideration the dependence of S_0 on A (Ref. 6) and Eq. (18) and approximations (19) and (20), for a high saturation parameter and high transmittance we have $N \propto 1/\sqrt{A}$, where A is the focusing area. Thus the number of ions increase when the lasers are well focused. However, it is not convenient to focus more than the saturation intensity for ionization, which, for the UV, is $50 \text{ GW}/\text{m}^2$. We obtained the value of the saturation ionizing intensity by solving Eqs. (2)–(11), where the excitation and stimulated emission transition probabilities are considered functions of the atom velocity and laser frequency.

3. Experiment

The experiment is shown in Fig. 2. We formed a beam of lithium atoms by evaporating metallic lithium from a molybdenum crucible in a Knudsen cell (Comstock Model KMB237/6). The vapor passed through a 1-mm collimator and the beam was recollimated at 5 cm from the crucible aperture. The Knudsen cell is equipped with a shutter that can be

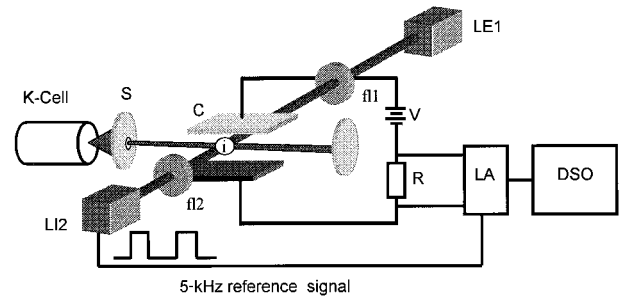


Fig. 2. Apparatus diagram for RIS of lithium isotopes: K-Cell, Knudsen cell; S, collimation slit; LE1, diode laser; LI2, Nd:YAG laser; f1 and f2, focusing lenses; i, interaction region; C, collector plate; V, applied acceleration voltage; R, resistance; LA, lock-in amplifier; DSO, digital storage oscilloscope.

used to interrupt the beam whenever necessary. The Knudsen cell can reach $630 \text{ }^\circ\text{C}$ with a stability of approximately $1 \text{ }^\circ\text{C}/\text{min}$.

For excitation with a narrow-band laser, we used a cw external-cavity tunable diode laser (New Focus Model 6202) with a central wavelength of 671 nm , tunable over 12 nm , and a linewidth of $<5 \text{ MHz}$. This laser was focused into the lithium beam, but for ionization we focused the fourth harmonic of a Nd:YAG laser (LeeLaser Model 815TQ) deployed in the counterpropagating direction.

Typical power densities of the exciting and ionizing laser are $60 \text{ kW}/\text{m}^2$ at 671 nm and $1 \text{ GW}/\text{m}^2$ at 266 nm , respectively. The Nd:YAG laser has a 5-kHz repetition rate and 120-ns pulse width with a KTP* crystal intracavity to produce the green output. We used a temperature-stabilized KD*P crystal (Inrad Model 5-301) to produce the fourth-harmonic generation at 266 nm and a dispersive quartz prism to separate the green from the UV radiation. Laser-produced ions were deflected and collected by means of a plane-parallel capacitor inside a vacuum chamber at the irradiation zone, which was polarized by 7 V . For voltages greater than 4 V , all the ions are collected. We measured the photoion current by using the amplitude-modulated lock-in technique. The voltage signal in a $47\text{-k}\Omega$ load was amplified with a lock-in amplifier (Stanford Research Model SR510), and the amplified signal was measured with a digital storage oscilloscope (LeCroy Model 9310A). We used a square 5-kHz function from the Nd:YAG trigger as the reference signal. The diode laser wavelength was scanned slowly over the lithium transitions at $1 \text{ GHz}/\text{s}$ by means of a function generator (Tektronix Model CFG100). The collected number of ions N that was measured after each ionizing laser UV pulse is given by

$$N \approx k T_{UV} V_M / e R, \quad (21)$$

where k is a proportionality constant, T_{UV} is the period of the Nd:YAG laser pulses, V_M is the voltage measured at load R by the lock-in amplifier when the phase was optimized, and e is the electron charge. The approximation and the value of k were obtained

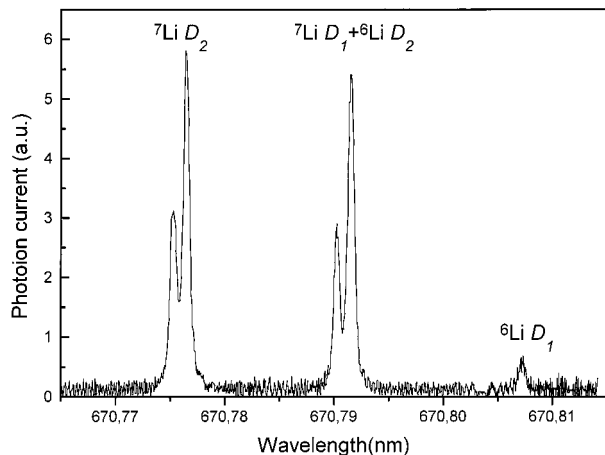


Fig. 3. Typical RIS trace for the ${}^6\text{Li}$ and ${}^7\text{Li}$ isotopes.

from the lock-in specifications and the signal conditions. The length of the ionization pulse after resistance-capacitance distortion was of the order of 30 μs . To measure the transmittance it is necessary to open the shutter of the Knudsen cell for absorption and to close it to obtain the baseline for zero absorption.

4. Results

A typical recorded RIS spectrum is shown in Fig. 3. This spectrum shows saturation effects on the ${}^7\text{Li } D_2$ line as a result of optical pumping between ground states produced by the diode laser. This effect can be observed as diminished photoion current. The hyperfine structure can also be seen in Fig. 3 because of the narrow linewidth of the diode laser and the collimation of the lithium beam.

The lithium beam flux is given by $F = n\phi v$, where density n is calculated from the absorption spectra, ϕ is the cross section of the lithium beam that can be calculated from fluorescence measurements,⁷ and v was calculated from the temperature with the kinetic gas theory. We have estimated a flux of 10^{15} atoms/s and confirmed the estimate with the measurements obtained with a quartz film thickness meter (Bal-Tec Model QSG060).

By using a well-collimated laser beam we measured the transmittance of the ${}^7\text{Li } D_2$ spectral line at 670.7764 nm as a function of the intensity of the excitation light. For this measurement, the diode laser wavelength was fixed and the Nd:YAG laser was off. The saturation curve that we obtained is shown in Fig. 4. It can be adjusted by means of a numerical procedure that has been described elsewhere.⁶ The fit parameter is the transit time relaxation rate γ_T . We obtained $\gamma_T = 5 \times 10^5 \text{ s}^{-1}$ from the fitting. This value is in good agreement with the inverse of the transit time calculated as X/v , where X is the length of the atom's path across the laser beam, which is the 3-mm-diameter beam, and v is the 1800-m/s velocity of the lithium atoms. The saturation parameter is approximately ten times larger than for a two-level atom, which can be

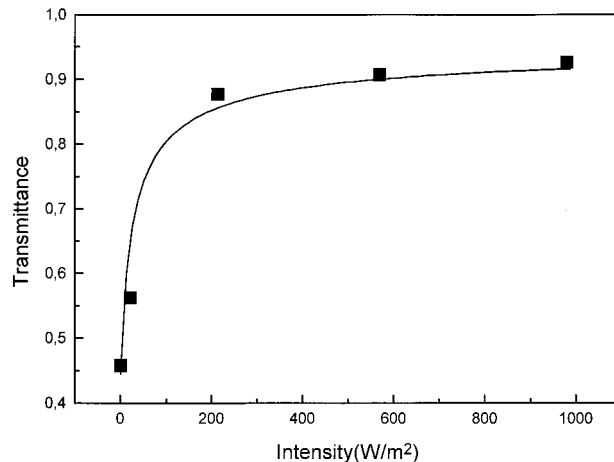


Fig. 4. Saturation curve for the absorption of the ${}^7\text{Li } D_2$ line at 670.7764 nm.

explained by the presence of the various ground sublevels in lithium, where additional pumping can occur. The optical pumping could be altered by collisions between atoms, but in our case the collisions are negligible because of the large 3-m mean-free path that we obtained by using a high vacuum and a low lithium density. For the same reason other relaxation mechanisms were also neglected.

As an example of the RIS measurements the temperature of the Knudsen cell was set at $T = 633 \text{ }^\circ\text{C}$, the incoming power of the diode laser was $P_e = 2360 \mu\text{W}$, and at the exit we measured $P_e = 2220 \mu\text{W}$ with an optical powermeter (Newport Model 818). The resolution determined experimentally for this powermeter was better than 0.75% at the microwatt level. The ionizing UV power P_i was a 15-mW average, which was focused at an area of $A = 7.5 \times 10^{-9} \text{ m}^2$. The red light was focused with an $f = 0.25\text{-m}$ lens and the UV light with an $f = 0.58\text{-m}$ lens. Inasmuch as the shape of the diode laser light is elliptical and is larger than the circular UV laser spot, the two lasers do not coincide completely. So we used only the 0.25 part of the red light power. The proportionality constant of approximation (21) is $k = 1.9$ and $V_M = 17.8 \mu\text{V}$. Using approximation (21) and these values for k and V_M , we obtained the measured ions/pulse $N = (9 \pm 1) \times 10^5$, and the estimated number of ions/pulse was $N = (12 \pm 3) \times 10^5$ when we took into consideration Eq. (18) and the values of P_e incident, P_e transmitted, A , and the fraction of the red light in the ionization zone. The total error of the value of N in each case was obtained by means of the error propagation theory and the given standard deviation error of each variable.

In a second case that involved an incident diode laser power of $P_e = 3750 \mu\text{W}$ and a transmitted power of $P_e = 3550 \mu\text{W}$, we determined $N = (1.9 \pm 0.5) \times 10^5$ ions/pulse by use of Eq. (18). This value should be compared with the $N = (1.5 \pm 0.2) \times 10^5$ ions/pulse derived from the measurement and from approximation (21).

5. Discussion and Conclusion

We have demonstrated a simple method to measure the RIS spectra of lithium isotopes using a narrow linewidth tunable diode laser for the excitation. We found good agreement between the estimation of the produced ions beginning with transmittance measurements and photoion current measurements. Saturation of the recorded photoion spectra was produced by the diode laser. We investigated the saturation by measuring the transmittance at different laser intensities, fitted with the numerical procedure reported in Ref. 6. This procedure includes the hyperfine structure of the levels and optical pumping and uses the transit time relaxation rate as a fit parameter.

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