

Coincidence in the two-photon spectra of Li and Li₂ at 735 nm

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Abstract

A coincidence between the $2^2S_{1/2}-3^2S_{1/2}$ two-photon transition in the atomic spectrum of ⁶Li and the $X^1\Sigma_g^+ \rightarrow E^1\Sigma_g^+$ two-photon ro-vibrational series of ⁷Li₂ was observed near 735 nm in a heat pipe oven using a tunable laser and thermionic diode detection scheme. The molecular transition obscures one component of the ⁶Li atomic transition. Selective detection of the atomic transition was obtained by adding an intensity-modulated laser that drives atoms from the 3S to 16P state. The coincident molecular transition and four nearby molecular lines were identified using previously determined Dunham coefficients.

1. Introduction

As a result of advances in atomic theory and computational techniques for multi-electron atoms, precise calculation of the structure of atomic lithium has become an area of significant interest [1–3]. The improving precision with which theoretical results converge is at the level of, and in some cases better than, the accuracy of experimentally determined values [3]. Consequently, it is desirable to refine the experimental measurements to provide accurate tests of theory. Our group at the National Institute of Standards and Technology (NIST) has begun to address this need with a series of experiments using high-resolution laser spectroscopic techniques [4, 5].

Although Li is an attractive candidate for precise theory because of its simple structure, its properties present a number of experimental problems. Lithium vapour attacks glass, darkening and weakening any glass surfaces that are exposed to it. Lithium also has the lowest vapour pressure of any alkali metal. Temperatures in excess of 500 °C are typically required to obtain atom densities appropriate for optical spectroscopy. These properties greatly limit the options for the experimental apparatus.

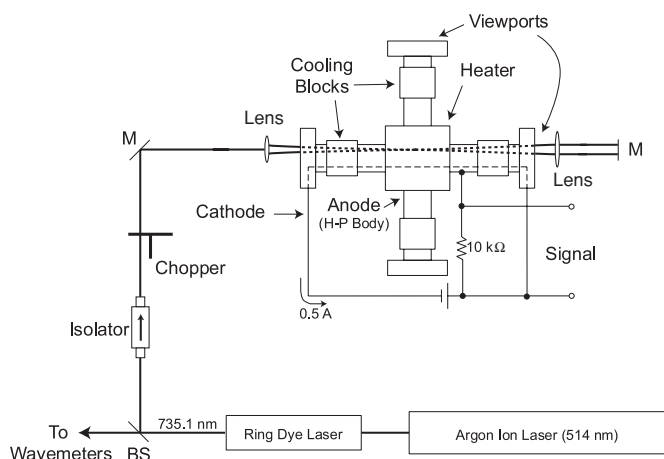


Figure 1. Schematic diagram of the original experimental layout. The thermionic diode signal is ac coupled to a lock-in amplifier.

A heat pipe oven with a low pressure non-reactive buffer gas and a thermionic diode detection system initially seemed to be a good choice for making high-resolution observations of two-photon transitions in Li [6–8]. We were eventually forced to abandon this technique because the accuracy of the measurements was limited by buffer gas collision-induced shifts even at pressures below 65 Pa (0.5 Torr) [9]. Our experiments with Li in the heat pipe oven, however, did reveal a curious and unlikely overlap between the $2^2S_{1/2}$ – $3^2S_{1/2}$ two-photon transition of ^6Li and a $X^1\Sigma_g^+ \rightarrow E^1\Sigma_g^+$ two-photon transition of $^7\text{Li}_2$.

2. Experiment

A schematic of the initial experimental apparatus is shown in figure 1. The heat pipe oven, which is described in detail in [9], was loaded with approximately 5 g of Li and filled with Ar at a nominal pressure of 65 Pa (0.5 Torr). The centre of the pipe was heated to a temperature of about 700 °C and the ends were cooled with coils through which 20 °C water was circulated. Collisions between the hot Li vapour and cool Ar gas prevent the Li from diffusing to the windows. The lithium vapour condenses on the stainless steel mesh that lines the heat pipe wall and wicks back to the hot centre of the pipe by capillary action. The result is a steady-state evolution of Li vapour in the centre of the pipe at a partial pressure of approximately 53 Pa (0.4 Torr).

The laser beam used to excite the Li vapour in this experiment was generated by a single-frequency ring dye laser operated with pyridine 2 dye and tuned to 735 nm. A small fraction of the laser power was diverted to our Michelson and Fabry–Pérot wavemeters. The remaining laser power was steered through the heat pipe and reflected back onto itself with a flat mirror. An optical isolator in the beam path prevented feedback to the laser cavity. A pair of lenses focused the primary and retro-reflected beams to a common focus at the centre of the heat pipe.

Atoms and molecules promoted to excited states by the laser were detected using a thermionic diode (see [6] for details on thermionic detection). The current generated by the heated filament of the diode was detected by measuring the voltage across a 10 kΩ resistor. The laser beam was modulated with an optical chopper in order to produce a periodically varying

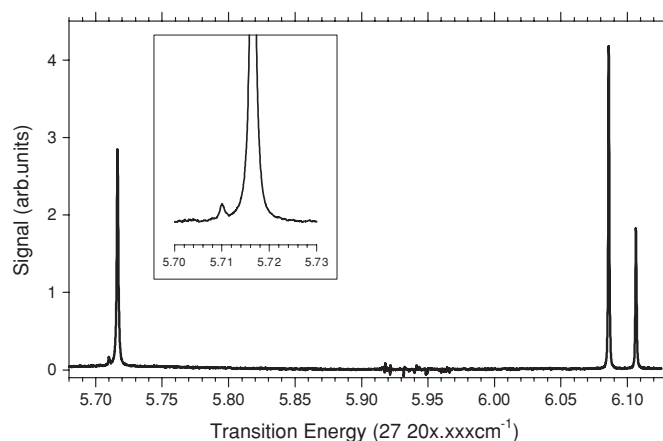


Figure 2. Two-photon spectrum near the 2S–3S transition of atomic lithium. The inset shows an expanded view of the signal at the expected position of the ⁶Li hyperfine doublet. The weak feature at 27 205.71 cm⁻¹ is identified as one of the ⁶Li lines, but the line at slightly higher energy is too strong to be identified as the other.

current when the laser was tuned to resonance with a Li transition. This periodic variation in the diode current was observed by a lock-in amplifier using phase-sensitive detection techniques.

Figure 2 shows the diode signal recorded as the laser was tuned across the 2S–3S two-photon atomic transition. Three strong resonances were observed. The lines at 27 206.086 cm⁻¹ and 27 206.107 cm⁻¹ are the hyperfine doublet of ⁷Li. The uncertainty of the observed transition energies is estimated to be 0.003 cm⁻¹. An additional strong line is centred at 27 205.716 cm⁻¹. Based on previous determinations of the 3S centre-of-gravity energy for both Li isotopes [10], the ⁶Li hyperfine doublet should occur near this wave number. Since ⁶Li accounts for only 7% of naturally occurring Li, the ⁶Li lines should be weaker by a factor of about 13 than the ⁷Li lines. The observed line is far too strong to be identified with the ⁶Li transition.

As shown in the inset of figure 2, the line at 27 205.716 cm⁻¹ has a weak satellite approximately 0.006 cm⁻¹ (180 MHz) to the red side of the strong line. We identify this feature as one of the ⁶Li hyperfine components. The second ⁶Li hyperfine component is blended with a much stronger ⁷Li₂ ro-vibrational transition. Support for this interpretation, including identification of the molecular line, is detailed in the next section.

In order to extract the ⁶Li signal and suppress the much stronger molecular line, we added a second tunable laser. This laser, which we will call the pump laser, was tuned to the wavelength of the 3S–16P transition (631 nm). It was a broadband standing-wave dye laser operated with the dye DCM. The unfocussed pump beam was steered into the heat pipe so that it overlapped the focus of the 735 nm beam. The revised experimental schematic is shown in figure 3.

In the revised experimental set-up, the pump laser beam was modulated rather than the excitation laser beam. With this placement of the chopper, the lock-in amplifier was sensitive only to excited atoms that could be pumped on the atomic 3S–16P transition. The reduction in the density of atoms in the detected state (16P versus 3S) was more than compensated by the increased sensitivity of the thermionic diode to states closer to the ionization limit. In fact, we saw a net signal gain of at least a factor of 2 on the ⁷Li lines using the revised detection method. With the pump laser in place, the two ⁶Li hyperfine features, at 27 205.710 cm⁻¹ and

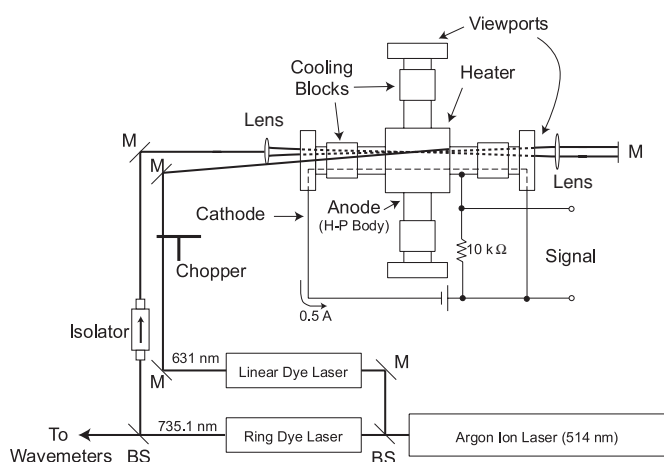


Figure 3. Revised experimental layout with addition of a second laser beam that couples the Li 3S and 16P states.

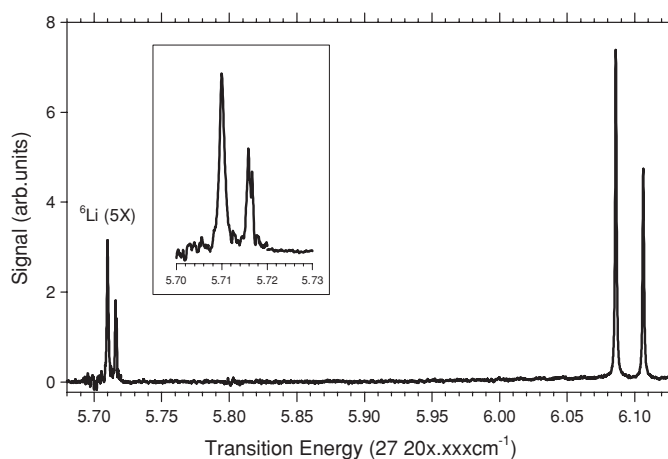


Figure 4. Spectrum obtained with revised set-up. The ${}^6\text{Li}$ features have been scaled by a factor of 5. The apparent splitting in the weaker ${}^6\text{Li}$ hyperfine component is a noise artefact that does not appear in narrow scans of this line.

$27\,205.716\text{ cm}^{-1}$, were observed and clearly resolved as shown in figure 4. The pump laser does not need to be tuned specifically to the 16P state; similar signals were observed with tuning to the 15P and 17P states.

3. Analysis

Observation of non-resonant two-photon molecular transitions between the $X\ ^1\Sigma_g^+$ and $E\ ^1\Sigma_g^+$ electronic states has not been previously reported. However, energy levels for ro-vibrational states of these electronic potentials can be calculated from Dunham-type coefficients, which have been determined by Kusch and Hessel [11] and Bernheim *et al* [12, 13]. The selection rules, for two-photon electronic transitions are $\Delta J = 0, \pm 1, \pm 2$. There is a restriction, however, that $\Delta J \neq 0$ if $J = 0$. From the calculated level values and selection rules, we

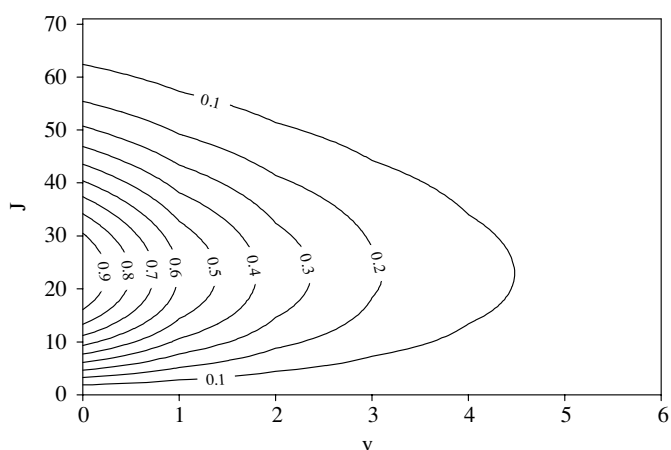


Figure 5. Normalized population distribution for the $X\ ^1\Sigma_g^+$ state at 700 °C. The distribution was determined for energy levels of the ground electronic state using the Dunham coefficients determined by Kusch [11].

generated a set of candidate classifications for the molecular line at 27 205.716 cm^{-1} . We eliminated transitions with initial vibrational quantum number $\nu > 6$ based on a prediction of the ground state population distribution at 700 °C (figure 5). The uncertainty of the calculated transition energies is taken to be 0.11 cm^{-1} , the quadrature sum of the standard errors reported by Bernheim [13] and Kusch [11].

We identified five calculated transitions within 0.33 cm^{-1} of the 27 205.716 cm^{-1} line, representing a $\pm 3\sigma$ window, as possible classifications for the observed line. By estimating the expected intensities for each of these classifications, taking into account the Franck–Condon factor (FCF) [14]³ and the ground state density for each of them, we determined that the observed line is most likely a blend of two molecular transitions

$$|\nu = 1, J = 11\rangle \rightarrow |\nu' = 1, J' = 9\rangle \quad |\nu = 3, J = 8\rangle \rightarrow |\nu' = 4, J' = 8\rangle$$

both of which have a calculated transition energy of 27 205.74 (11) cm^{-1} , in close agreement with the experimental value. The molecular line originating from the $\nu = 1$ vibrational state contributes to the blend more significantly than that from the $\nu = 3$ level because it has both a higher ground state density and FCF.

To verify our calculations, we attempted to identify additional molecular features in this spectral region. By scanning the laser to higher energy we obtained the spectrum shown in figure 6. This spectrum reveals four additional features, a strong line at 27 206.83 cm^{-1} , weaker lines at 27 206.59 cm^{-1} and 27 206.80 cm^{-1} and a very weak line at 27 205.83 cm^{-1} . The experimental uncertainty of the transition energies determined from this scan is estimated to be 0.01 cm^{-1} . We were able to classify all of these transitions, with a high degree of certainty, using the Dunham coefficients and intensity considerations as shown in table 1. This lends additional support to our assignment of the blend at 27 205.716 cm^{-1} . In fact, it is the three transitions rejected as potential classifications for the 27 205.716 cm^{-1} line that blend to form the very weak feature at 27 205.83 cm^{-1} . The underlying blend in this feature is

³ Identification of this commercial software package is made to specify adequately the method used in this analysis. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the software identified is necessarily the best available for the purpose.

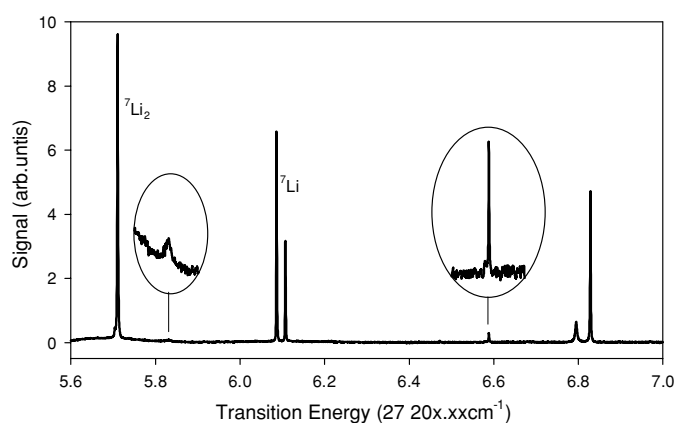


Figure 6. Broad laser scan in the region near the 2S–3S transition showing additional Li₂ transitions. The change in the intensity of the line at 27 205.716 cm⁻¹ when compared to figure 2 is due to a slightly different temperature in the heat pipe when this scan was recorded. The insets show vertically expanded views of the two weakest lines.

Table 1. Comparison of transition energies (cm⁻¹) for Li₂ measured by two-photon absorption to calculated energies for proposed classifications. Multiple entries for a single line represent a blend of several transitions.

Measured transition energy (cm ⁻¹) ^a	Proposed classification <i>v</i> , <i>J</i> ⟩ → <i>v</i> ′, <i>J</i> ′⟩	Calculated energy (27 20x.xx cm ⁻¹) ^b	Deviation (cm ⁻¹)
27205.716	1, 11⟩ → 1, 9⟩	5.74	0.02
	3, 8⟩ → 4, 8⟩	5.74	0.02
27205.83	4, 21⟩ → 6, 23⟩	5.82	-0.01
	3, 29⟩ → 5, 28⟩	5.85	0.02
	3, 5⟩ → 4, 3⟩	5.91	0.08
27206.59	3, 35⟩ → 5, 37⟩	6.62	0.03
27206.80	2, 27⟩ → 3, 27⟩	6.83	0.03
27206.83	1, 22⟩ → 1, 24⟩	6.85	0.02

^a Uncertainty: ±0.003 cm⁻¹ for 27205.716 cm⁻¹ line, 0.01 cm⁻¹ for others.

^b Uncertainty: ±0.11 cm⁻¹.

reflected in the fact that it is significantly wider than any other line in the spectrum, as can be seen in the inset of figure 6.

4. Discussion

By laser excitation of Li vapour in a heat pipe oven, we observed a coincidence between the 2S–3S two-photon transition of ⁶Li and an X ¹Σ_g⁺– E ¹Σ_g⁺ two-photon transition of ⁷Li₂. An intensity-modulated second laser that pumped excited atoms from the 3S level to the 16P level made it possible to suppress the molecular transition, enabling us to clearly resolve both components of the ⁶Li 2S–3S hyperfine doublet. The molecular transition has been identified using previously determined Dunham coefficients, as have additional molecular lines in the same region of the spectrum.

Acknowledgment

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