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Autoionization Spectra of Lithium

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Resonances have been observed in neutral lithium vapor by absorption spectroscopy for photons in the 50- to 70-eV energy range. These resonances are due to the excitation of a K-shell electron, or the simultaneous excitation of a K-shell electron and an outer electron to final states of the type $(1s2pnl)$ or $(1snln'l')$. Several well-developed series have been observed as well as resonances where energy position and intensity are perturbed by neighboring configurations.

Resonances have been observed by optical absorption in the photoionization continuum of lithium vapor in the region 55-70 eV. These resonances in Li I, more than 50 eV above the ionization potential, can be caused by the excitation of a K-shell electron $(1s2snl)$ or the excitation of a K shell and the outer electron simultaneously $(1snln'l')$. Both one- and two-electron excitation states have been observed. Weiss has calculated the lowest terms of the $1s2snp$ configurations with a multiconfiguration Hartree-Fock method based on first principles.[1] This experiment confirms the calculated positions to within 0.2 eV and gives many additional states as well.

Previous experimental work[2] on highly excited states of lithium has been confined to the study of metastable states. In particular, Feldman and Novick[3] observed, by electron excitation, the transition from the ground state to the metastable $1s2s2p\ ^4P$ state near 57.3 eV. In this work we are reporting the first observation of optically allowed dipole transitions from the ground state to high-lying ^2P states.

Experimental. – These new transitions were observed by absorption spectroscopy, with the National Bureau of Standards 180-MeV synchrotron[4] as a continuum background source and a vapor furnace of new design. The furnace utilizes the dynamics of a heat pipe to protect thin-film aluminum end windows. A buffer gas of argon and the heat-pipe pump-recirculation principle[5,6] prevented the lithium from reaching the mesh-supported aluminum windows. The spectra were recorded by the same 3-m grazing-incidence spectrograph[7] used previously to record the auotionization spectra of the noble gases.[8,9] The undispersed synchrotron radiation passed through the furnace and was focused onto the spectrograph by a grazing-incidence toroidal mirror. The horizontal focus of the mirror was placed at the entrance slit while the vertical focus was set on the Rowland circle centered in the spectrum at about 200 Å. The photographs were taken on plates coated with Eastman Kodak 101 emulsion. Exposure times were 10 min to several hours depending on pressure conditions. Lithium vapor pressures varied from $\frac{1}{2}$ to 3 Torr, and the absorption path length was 10-15 cm.

In this experimental arrangement, the synchrotron radiation passes through two aluminum windows and a roughly equal number of argon and lithium atoms. However, we have extensively studied[9] argon in this region with high resolution, and the existing structure is extremely weak. No structure due to argon could be expected with the pressures used in these experiments. The aluminum windows, each about 1000 Å thick, also have a transmission which is free of fine structure in this region up to the $L_{2,3}$ cutoff at 170 Å. The high-lying excitations of possible impurities in the lithium metal itself are essentially unknown. However, the heat-pipe pumping action is known to affect a vapor purification.

Lithium molecules are, of course, present.

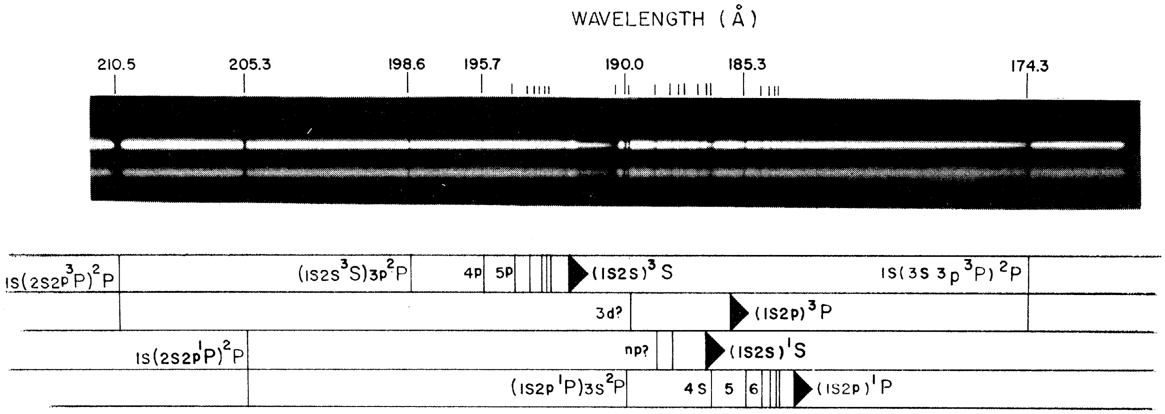

FIG. 1. Observed structure in lithium vapor absorption between 210 and 170 Å. The upper spectrum is a 50-min exposure at a lithium pressure of 2 Torr, while the lower spectrum is a 10-min exposure at a lithium pressure 1 Torr. In each case the absorption path was about 15 cm. This is a positive print so black denotes absorption. The classification of some of the resonances is indicated and the lowest levels in Li II are shown.

At the vapor pressure used, the fraction of vapor in molecular form is about 4%. Some overlap of the atomic features with weak molecular spectra is a possibility; however, it is expected that molecular features associated with particular atomic transitions will be shifted to lower energies. In any event it can be definitely established that most of the features observed are atomic.

Spectra.—Figure 1 shows the structure which has been observed in lithium absorption between 215 and 170 Å. Two plate exposures are shown; the upper spectrum is a 50-min exposure with a lithium vapor pressure of 2 Torr. The lower spectrum is a 10-min exposure with a vapor pressure of about 1 Torr. An absorption path of roughly 15 cm was used in each case. The spectra consist primarily of absorption-enhancement type of resonances, and a number of Rydberg series can be observed. A plate was also obtained with the furnace filled with argon but no lithium. On this plate, no structure whatsoever was observed up to the energy of the $L_{2,3}$ transi-

Table I. Lowest-lying atomic transitions involving excitations of the K electron observed in lithium vapor absorption.

λ(Å) (Exp.)	eV	Classification	n^* [a]	λ (Å) (Theory)[b]
210.46 ± .02[c]	58.910	$1s(2s2p\ ^3P)^2P$	1.573 ± .001	210.27
205.28 ± .01	60.396	$1s(2s2p\ ^1P)^2P$		204.60
198.63 ± .01	62.419	$(1s2s\ ^3S)3p\ ^2P$	2.614 ± .002	198.51
195.69 ± .03	63.356	4p	3.59 ± .02	195.67
194.47 ± .01	63.753	5p	4.55 ± .01	194.42
193.87 ± .01	63.951	6p	5.44 ± .02	
193.58 ± .03	64.046[d]	?		
193.36 ± .01	64.121	7p ?	6.85 ± .04	
193.17 ± .01	64.184	8p?	7.74 ± .05	
193.02 ± .02	64.232	9p?	8.73 ± .10	
192.94 ± .02	64.260	10p?	9.5 ± .2	

[a] These effective quantum numbers are calculated assuming the limit $1s2s\ ^3S$ at 476 035 cm^{-1} as given in Ref. 10.

[b] Calculation by A. Weiss, private communication.

[c] Errors shown are repeatability on three plates; the absolute error may be ±0.02 Å greater.

[d] If the resonances listed to higher energies belong to the suggested series, this resonance must be a perturber whose identity requires theoretical clarification.

Table II. Rydberg series observed in lithium vapor absorption converging on to the $1s2p\,^1P$ state of Li II.

λ (Å) (Exp.)	eV	Classification	n^{*} [a]
205.28 ± .01 [b]	60.396	$1s(2s2p\,^1P)^2P$	1.374 ± .001
190.01 ± .01	65.250	$(1s2p\,^1P)3s\,^2P$	2.427 ± .002
186.61 ± .01	66.438	4s	3.41 ± .01
185.30 ± .01	66.909	5s	4.42 ± .01
184.64 ± .01	67.147	6s	5.44 ± .02
184.29 ± .01	67.276	7s	6.41 ± .03
184.06 ± .01	67.361	8s	7.44 ± .04
183.90 ± .01	67.418	9s	8.49 ± .06
183.79 ± .01	67.459	10s	9.60 ± .1
183.72 ± .02 [c]	67.482	11s	10.5 ± .2

[a] Effective quantum numbers calculated assuming the limit $1s2p\,^1P$ at 501 809 cm^{-1} as given in Ref. 10.

[b] Errors given are repeatability on three plates. Absolute error may be ±0.02 Å greater.

[c] Only one plate was used to determine this wavelength and the error given is an estimated probable error.

tion in aluminum at 170 Å.

Discussion.—The lowest optically allowed atomic transition in Li I involving the K electron is $1s^22s\,^2S \rightarrow 1s(2s2p\,^3P)^2P$. The next-highest states in order of energy are $1s(2s2p\,^1P)^2P$, $(1s2s\,^3S)^2P$, $(1s2s\,^3S)4p\,^2P$, and $(1s2s\,^3S)5p\,^2P$. The excellent agreement between the theoretical[1] and experimental values, given in Table I, leaves little doubt as to the accuracy of these identifications.

A weak resonance is observed at still lower energies, namely, 57.03 ± 0.03 eV. Since there is no optically allowed atomic transition lower in energy than that for the $1s(2s2p\,^3P)$ state at 58.91 eV, it seems likely that this lower-energy resonance is due to lithium molecules. It should be possible for such molecules to undergo discrete excitation of one of the $1s$ electrons at this energy. Since the binding energy of the ground state for Li_2 is only about 1 eV, the classification of the observed structure as molecular implies that the excited state is bound several eV more strongly than the ground state. The observation of a single weak resonance may also indicate a peaking of the Franck-Condon factors.

Above the series limit $1s2s\,^3S$ the spectrum is more complex. Resonances due to configurations of the type $(1s2s\,^1S)np$, $(1s2p\,^3P)ns$, $(1s2p\,^1P)ns$, $(1s2p\,^3P)nd$, and $(1s2p\,^1P)nd$ are all possible and a close observation of the spectra suggests their presence. These configurations can be expected to interact strongly with one another and also with the continuum $(1s2s\,^3S)\epsilon p$. Thus, detailed theoretical calculations will be required for positive identification of the structure in this region.

A prominent Rydberg series, converging to the $1s2p\,^1P$ term in Li II, is observed. This series has practically constant quantum defects which suggests that any configuration interaction with series members is relatively small. The wavelengths and effective quantum numbers of this series are given in Table II.

An absorption resonance in Li vapor has been observed at still higher energies, namely, at 71.16 ± 0.02 eV. The probable identification of this feature is $1s^22s\,^2S \rightarrow 1s(3s3p\,^3P)^2P$. Higher members of this series may be observable above 72 eV; however the aluminum furnace windows become quite opaque above this energy.

Further observation and analysis of these highly excited states in atomic lithium is in progress. In particular, absolute cross sections and intensity profiles of the resonant features are currently under study with a 3-m grazing-incidence scanning monochromator of 0.06-Å spectral slit width.

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Resonant Structure of Lithium Between the 2^3S and 2^1P Thresholds

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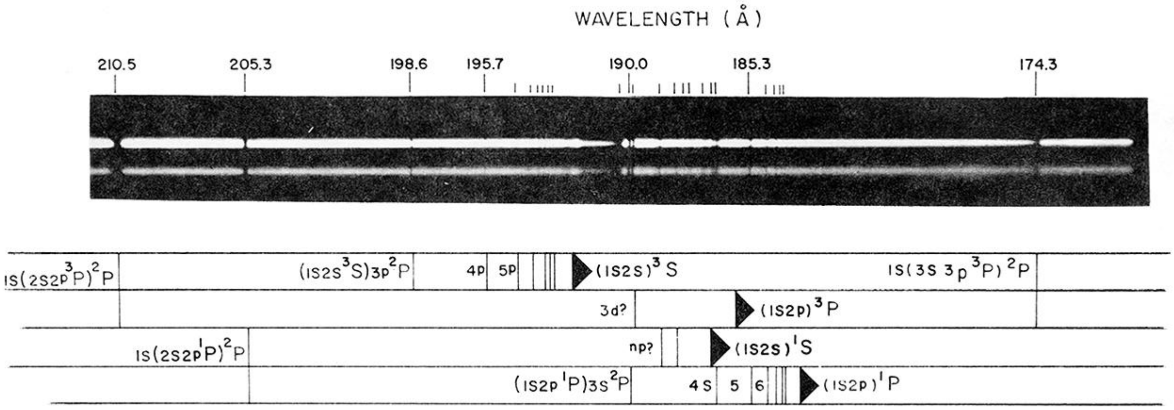
Close coupling calculations of the optically allowed states in the 60-70 eV range above the ground state of atomic lithium have been performed. An interpretation of the resonant structure in this region is given based upon these calculations and recent experimental evidence.

The previous Letter[1] provides a preliminary report of a detailed resonant structure in atomic lithium observed in absorption in the region 60-70 eV above the ground state. Bound-state calculations[2] have served to identify the two lowest lying observed states as $1s(2s2p\,{}^3P)^2P$ and $1s(2s2p\,{}^1P)^2P$ and to identify the states immediately above this as a $1s2s(^3S)np$ series converging to the $1s2s\,{}^3S$ limit of Li^+. In order to clarify the resonant structure above the $1s2s\,{}^3S$ limit, close-coupling calculations involving the expansion of the total wave function in terms of the four $n=2$ states of Li^+, $1s2s\,{}^{1,3}S$, $1s2p\,{}^{1,3}P$, have been performed for the region immediately above the 2^3S threshold. This Letter presents the initial results of these computations and provides a comparison between the calculated resonant structure and that observed in absorption. Specifically these results include (a) identification of the first five resonances above the 2^3S threshold; (b) calculation of the quantum defects for all six series converging on the four series limits; (c) tentative identification of the resonance observed at 193.58 Å[1] which perturbs the $1s2s(^3S)np$ series.

The method of calculation is based on the procedure outlined by Smith and Morgan.[3] The total wave function is expanded as an antisymmetrized sum of products of bound-state wave functions corresponding to the $1s2s\,{}^{1,3}S$ and $1s2p\,{}^{1,3}P$ terms of Li^+ and functions representing a bound or free electron. The close-coupling expansion is similar to that used to describe electron scattering on helium[4] with the following differences:

(1) Here the expansion is in terms of ionic rather than neutral core functions and thus asymptotically the coupled electron will move in a Coulomb field. The presence of the Coulomb field means that in this case there will be six well defined Rydberg series converging on the four $n=2$ thresholds of Li^+.

(2) The wave functions describing the coupled electron are in this approximation constrained to be orthogonal to the core orbitals. This constraint eliminates some of the exchange terms which arise in the treatment in Ref. 4. The effect of these terms is compensated for by including "virtual" bound states in the close-coupling expansion.[3]



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