THE ISOTOPE SEPARATION IN THE SPECTRA OF Li I

By D. S. Hughes
University of Chicago

(Received June 18, 1931)

Abstract

Three lines of the Li I spectrum were examined for possible isotope components. A faint component was found on the long wave-length side of the lines 6708A and 3232A. The measured separation of this component and the doublet is in good agreement with the calculated separation of the Li_6 and Li_7 lines. No components other than the regular doublet were observed for the line 6104A. This is in accord with the theory since the calculated separation for this line is below the limit of resolution of the apparatus used.

In view of the prediction of an observable separation between the spectral lines of Li_6 and Li_7,[1] it was decided to investigate the arc spectrum. Schüler and Wurm[2] have examined the first line of the principal series, 6708A, and found it to be a triplet. Since the long wave-length member of this triplet was very weak and could not be accounted for on the basis of any accepted theory of line structure it was ascribed to Li_6. The magnitude of the separation was such that the long wave member of the Li_7 doublet coincided with the short wave member of Li_6 doublet, causing the line to appear as a triplet.

Since it is very difficult to secure sharp emission lines from Li, the first two lines of the principal series were examined in absorption. The line 6104A, which is not absorbed, was photographed in emission, with a hollow cathode discharge tube. With large currents through the tube the line would, because of self reversal, appear as a triplet. However, on decreasing the current the appearance of the line would change until with 0.5 amperes passing through the tube it appeared as a doublet.

The first vacuum furnace for vaporizing the lithium in the absorption experiments was a seamless steel tube 2 inches in diameter and 26 inches long. The central 13 inches were wound with resistance wire and the ends wound with 1/4 inch copper tubing through which water was circulated to cool the wax with which the quartz windows were fastened on. Later a longer furnace was constructed with 48 inches of resistance winding.

This design does not permit a determination of vapor density. The metallic vapor diffuses to the ends and condenses so that the vapor pressure is zero there. The average density depends upon the number of atoms evaporating per second, which is a function of the area and condition of the lithium surface as well as of the temperature. Due to the fact that Li attacks glass and quartz at temperatures above about 200°C, it did not seem feasible to construct tubes which could be kept hot at the ends.

[1] D. S. Hughes and Carl Eckart, Phys. Rev. **36,** 694 (1930).
[2] H. Schüler and E. Wurm, Naturwiss. **15,** 971 (1927).

Two grating were used in this investigation, a 6-inch plane grating with 15,000 lines to the inch and a 6-inch concave grating, with a radius of curvature of 21 feet, and the same number of lines to the inch. The plane grating was first used in a littrow mounting with a 10-inch concave mirror having a focal length of 15 feet. This mounting gave a dispersion of about 0.566A/mm in the fourth order of 6708A.

Using this mounting and a carbon arc as a continuous source the photographs of 6708A, shown in Figure 1 were obtained. The upper photograph was taken when the furnace was at a dull red heat. The current through the resistance winding was decreased by small steps and the successive photographs taken. Components *a* and *b* are ascribed to Li_7 and component *c* to

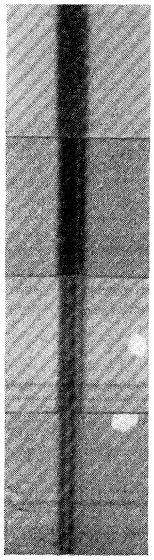

Fig. 1. Absorption of Li 6708A in lithium vapor. Temperature of furnace is highest for the top photograph. 6 inch plane grating, dispersion 0.566 A/mm in fourth order.

Li_6. According to this interpretation *b* is really composed of two lines, the long wave-length member of the Li_7 doublet and the short wave-length member of the Li_6 doublet.

In the hope of resolving the nuclear spin lines a new grating mounting was constructed with an 18-inch concave mirror of focal length 25 feet. With this mounting a dispersion of 0.326 A/mm was secured in the fourth order at 6708A. The longer furnace was constructed so that a lower temperature of the absorbing column could be used and hence sharper lines obtained. The photograph shown in Figure 2 was taken with this arrangement. The microphometer curves of the plates, however, did not reveal any structure.

Since the mirror used in the 25-foot mounting was silver plated and did not reflect 3232, it was necessary to use the concave grating for the examination of the second line of the principal series. The dispersion in the fourth order at 3232A was 0.652 A/mm. The carbon arc which had proved to be a

very intense and convenient source for 6708A was found to be too weak for use at this wave-length. The intensity of the continuous hydrogen spectrum was also of insufficient intensity. It was then decided to attempt to use the Li emission line as a continuous source. The line, which was obtained by placing

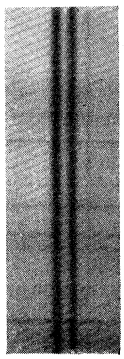

Fig. 2. Absorption of Li 6708A in lithium vapor. A longer tube and lower temperature than for Fig. 1. 6 inch concave grating, dispersion 0.326 A/mm in fourth order.

a small quantity of lithium carbonate in a copper arc, was very broad and with a current of 4 amperes through the arc, showed no signs of self-reversal.

Several plates of the line at 3232A were taken with this arrangement. Figure 3 shows the microphotometer traces of these plates. The portion of the trace between *A* and *B* represents the absorption line. In the original

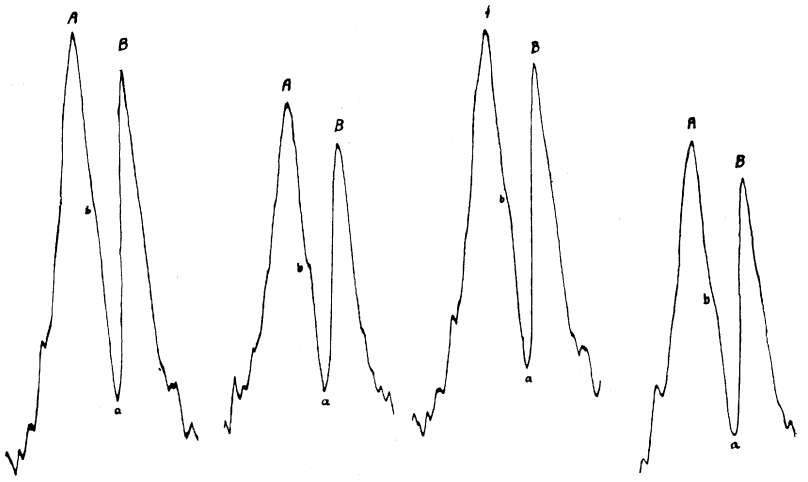

Fig. 3. Microphotometer of absorption of Li 3232A in lithium vapor. The portion of the trace between *A* and *B* represents the absorption line. It is to be noted that the component *b* is present in each trace and is thereby distinguished from the accidental motions of the galvanometer.

negative the resolution was sufficient to allow the separation to be measured. The component *a*, is ascribed to Li_7 and component, *b*, to Li_6. Although this line should be a doublet, due to electron spin the observed doubling was as-

cribed to the isotope effect rather than to the spin for two reasons; first, relative intensity (the component b is much weaker than a and disappears entirely if the temperature of the furnace is lowered slightly); second, the spacing (the separation in Figure 3 is about 0.058A, the separation due to electron spin for this line as calculated from the regular doublet law is about 0.01 A).

The change in frequency due to the finite mass of the nucleus in the case of a one-electron system is.

$$\delta v = -m\nu_0/M \tag{1}$$

where m is the electronic mass, M is the mass of the nucleus, and ν_0 is the frequency of the line, calculated by neglecting the motion of the nucleus In the case of more complicated atoms this same effect is still present. Two isotopes of an element should emit lines of slightly different frequencies, as given by the following equation

$$\delta\nu = \left(\frac{m}{M_1} - \frac{m}{M_2}\right)\nu \tag{2}$$

M_1 and M_2 are the nuclear masses of the isotopes, and is the frequency of the line. In the case of two and three-electron systems, however, there is an additional effect which displaces only the P levels[2], and hence only lines arising from or terminating upon a P level. The value of this additional effect for three-electron systems in which one electron is in a P orbit and the other two are in $1s$ orbits is given by

$$\delta\nu_1 = -\frac{128}{3}\frac{m}{M}R_\infty Z_1^5 Z_2^5 n^2(n^2-1)\frac{(Z_1 n - Z_1)^{2n-4}}{(Z_1 n + Z_2)^{2n+4}} \tag{3}$$

where Z_1 is the effective nuclear charge for the $1s$ electrons, Z_2 the effective nuclear charge for the p electron, n the principal quantum number of the p electron, m the electronic mass, M the mass of the nucleus and R_∞ Rydberg's number for an atom with an infinitly heavy nucleus. Equations (2) and (3) give changes in energy which are opposite in sign and in the case of Li I are of the same order of magnitude. This leads to a very small displacement of the P levels and hence to a comparatively large effect in lines arising from p levels and terminating upon s levels.

The results of the calculations and measurements are presented in the following table.

TABLE I.

Line	Transition	Δ_1	Δ_2 (obs)	Δ_2 (cal)
6707.86A	$2P-1S$	0.155A	0.156A	0.123A
6103.59	$3D-2P$	0.112	0.00	0.049
3232.67	$3P-1S$	(0.01)*	0.058	0.042

* Calculated from the regular doublet law.

Δ_1 is the regular doublet separation, Δ_2 is the isotope separation. The values of Z_1 and Z_2 used in calculating the fifth column were taken from the work on screening by Eckart.[3] The disagreement between the observed and calculated displacement is probably to be ascribed to the unresolved nuclear spin lines of Li_7. Since the Li_6 nucleus has no spin,[4,5] the spin of the Li_7 nucleus will lead to a relative displacement of its lines. This interpretation seems to be in accord with the fact that the fractional disagreement is approximately the same for 6708A and 3232A.

The best evidence for this interpretation would be a calculation of the relative vapor densities of the two isotopes from the intensities of the absorption lines. One method of doing this would be to find the reduction in length of the absorbing column necessary so that the intensity of the Li_7 lines in the short column would be the same as the intensity of the Li_6 lines in the long column, with the same conditions of vapor density and temperature in each column. Due to the difficulty already pointed out in connection with the vapor pressure it did not seem to be possible to make measurements of this sort.

A fair agreement has been found between the calculated and observed separation of Li_6 and Li_7 lines for two lines of the Li I spectrum. In the case of 6104A no lines were observed that could not be ascribed to Li_7. Considering the small calculated displacement the Li_6 lines were probably masked by the Li_7 lines, since the width of the emission lines was of the order of magnitude of the calculated separation.

This work was carried out under the direction of Professor H. G. Gale, and the author wishes to express his gratitude to him for his encouragement and many helpful suggestions. The author also wishes to express his appreciation to Professor Carl Eckart, who suggested the problem and to Professor G. S. Monk for his advice in connection with the spectroscopic technique.

[3] Carl Eckart, Phys. Rev. **36,** 878 (1930).
[4] H. Schüler, Zeits. f. Physik **58,** 741 (1929).
[5] A. Harvey and F. A. Jenkins, Phys. Rev. **35,** 798 (1930).

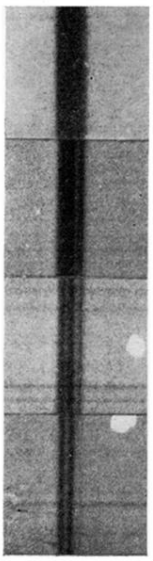

Fig. 1. Absorption of Li 6708A in lithium vapor. Temperature of furnace is highest for the top photograph. 6 inch plane grating, dispersion 0.566 A/mm in fourth order.

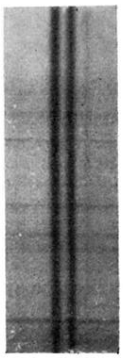

Fig. 2. Absorption of Li 6708A in lithium vapor. A longer tube and lower temperature than for Fig. 1. 6 inch concave grating, dispersion 0.326 A/mm in fourth order.