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The Absorption Spectrum of Dense Lithium Vapor

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Thirty-five new lines or diffuse bands appeared in the neighborhood of the principal series lines of lithium absorption spectrum were measured. The temperature of the absorption tube was 850–1040°C. He, Ne, and A were used to lessen the speed of distillation of lithium to the cooler part of the tube. The appearance and the position of these lines or bands are not influenced by the nature of the foreign gas employed.

INTRODUCTION

THE absorption spectra of all alkali vapors, except that of lithium, have been studied by Kuhn,[1] Ny and Weng,[2] and others.[3] In addition to the molecular bands many new lines or diffuse bands were observed in the neighborhood of the principal series lines when the vapor density was high. These new lines were classified empirically according to their relative positions with respect to the principal series lines and were interpreted as resulting from loosely bound diatomic molecules. The corresponding observation for lithium was made in the present work.

EXPERIMENT

The experimental arrangement was essentially the same as that of Ny and Weng[2] except that wide slit diaphragms were inserted into the absorption tube placed near the borders of the heating coil and the water coolings at both ends to reduce the speed of convection in the tube. The absorption tube was heated by Chromel A pyrometric ribbon and the temperature was measured by the Pt-PtRd thermocouple. Hilger E-1 quartz spectrograph was used throughout the experiment. For the first member of the principal series an 100-w incandescent lamp was used; while for the rest members of the series a hydrogen discharge tube was used as the background of the spectrum. Eastman III-F and Eastman III-O plates were used. Observations were made when the absorption tube was heated to 850–1000°C with 50°C steps. The time of exposures varied from 15 to 30 min. When the absorption tube was heated to 1020°C or 1040°C, the time of exposure had to be increased to one hour.

Since the temperature difference between the hot part at the middle and the cool part at both ends of the absorption tube was very high for lithium, foreign gas must be added to lessen the speed of distillation of the alkali. Nitrogen and hydrogen react readily with lithium at these temperatures rendering no lithium absorption lines observable. Separate observations were made when the pure He, A, or Ne with pressures 22, 21, and 18 cm Hg, respectively, was admitted into the absorption tube to determine whether

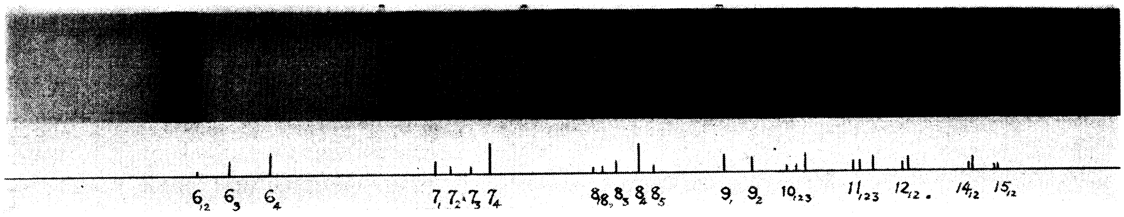

FIG. 1. The absorption spectrum of dense lithium vapor ($T=1040°C$). The lines marked by × are due to impurities.

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[1] H. Kuhn, Zeits. f. Physik **79**, 782 (1932).

[2] Ny Tsi-ze and Weng Wen-Po, Comptes Rendus **202**, 1428; **203**, 429; **203**, 860 (1936).

[3] Datta and Chakravaty, Ind. J. Phys. **7**, 273 (1932); Ny Tsi-ze and Choong Shin-Piaw, J. de phys. et rad. **6**, 203 (1935).

TABLE I. New lines or diffuse bands appeared in the absorption spectrum of dense lithium vapor.

$2S-mP$	New lines or bands	Appearance at $T=1040$ °C	Marks	Temp. of absorption tube °C	$2S-mD$ calc'd A	$2S-mS$ calc'd A
6707.8 (1)						3675.7
3232.6 (2)						
	3257.5(?)	*Id*	$_{1}2$	910		
	3254.0(?)	*Id*	$_{2}2$	910	3196.6	2856.3
2741.3 (3)						
	2736.2	*fd*	3_1	910		
	2734.7	*fs*	3_2	910		
2562.5 (4)					2730.5	2611.7
	2560.4	*Fd*	4_1	1040		
	2558.9	*fs*	4_2	910		
	2557.5	*iS*	4_3	910	2557.7	
2475.3 (5)						2500.1
	2472.9	*id*	5_1	940	2472.7	
	2472.2	*id*	5_2	940		
2425.7 (6)						2441.9
	2424.1	*fd*	6_{12}	1020		
	2419.8	*fD*	6_3	1020	2424.3	
	2414.	*iD*	6_4	1020		
2394.5 (7)						
	2390.8	*fd*	7_1	1020	2393.0	
	2389.5	*Fd*	7_2	1020		
	2386.7	*Fd*	7_3	1020		
	2384.4	*ID*	7_4	990		
2373.8 (8)					2372.9	
	2370.8	*Fd*	8_1	1040		
	2369.7	*Fd*	8_2	1040		
	2367.5	*fD*	8_3	990		
	2364.7	*Id*	8_4	990		
	2363.4	*Fd*	8_5	1040		
2359.3 (9)						
	2354.2	*id*	9_1	990		
	2350.	*iD*	9_2	990		
2348.4(10)						
	2346.3	*Fd*	10_1	1020		
	2345.5	*Fd*	10_2	1020		
	2343.9	*is*	10_3	990		
2340.4(11)						
	2338.1	*fd*	11_1	1035		
	2337.	*fd*	11_2	1030		
	2335.2	*fD*	11_3	1020		
2334.2(12)						
	2332.	*fd*	12_1	1040		
	2331.3	*is*	12_2	1020		
2328.9(13)						
2325.1(14)						
	2324.1	*Fd*	14_1	1040		
	2323.5	*fs*	14_2	1020		
2321.8(15)						
	2320.5	*Fd*	15_1	1040		
	2320.	*Fs*	15_2	1040		
2319.2(16)						

the appearance or positions of these lines or bands could be influenced by the nature of the foreign gas added.

Figure 1 is a sample absorption spectrum of lithium when the temperature of the absorption tube was at 1040°C. The new lines or bands are marked by a sketch underneath.

Corresponding observations on the absorption spectrum of potassium at temperatures 500–640°C were repeated for comparison with Ny and Weng's measurements.

RESULTS

The results of measurement are given in Table I. The first column gives the wave-length of lithium principal series. In column 2 the first two lines marked (?) are situated in superposition with the very sharp and strong molecular absorption bands. The meanings of the letters in column 3 are as follows:

i = fairly intense I = intense
f = faint F = very faint
s = sharp S = very sharp
d = diffuse D = very diffuse

These letters serve to describe very briefly the appearance of these lines or diffuse bands in the spectrogram taken at a temperature of 1040°C.

Because of faintness and diffuseness, wave-length values of the lines or diffuse bands could not be determined with great accuracy, so the decimal figures are not very reliable except those for very sharp lines. The lines or diffuse bands are marked by M_n with M indicating the member of the series lines, and n the ordinal number of the lines or bands counted from the Mth member in the direction of decreasing wave-lengths. The values given in column 5 are the temperatures at which the lines or bands start to appear in the spectrogram. These lines or bands will indeed become more intense when the absorption tube is heated to a still higher temperature.

Lines 3_1, 3_2; 4_2, 4_3; 5_1, 5_2; and even 6_{12} appeared very much like a doublet system with the shorter wave-length component a little stronger and sharper than the longer wave-length one. The separations between the doublet components decreases with the decrease in wave-length.

It is to be noted that the appearance and the positions of all these lines or bands as given in Table I are found to be independent of the nature of the foreign gas added into the absorption tube.[4] No lines or diffuse bands are observed in the neighborhood of the first member of the series.

In the last two columns are listed the calcu-

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[4] The diffuse bands λλ2552, 2470, 2422.5, and 2392.7, which appeared as a result of the presence of He, are not listed in Table I.

lated wave-lengths of $2S-mD$ and $2S-mS$ transitions. Some of the values of $2S-mD$ are very close to observed lines but not with the $2S-mS$ values. Forbidden lines may be expected to appear when the alkali vapor density is high.

A spectrogram of potassium absorption spectrum was taken. Ny and Weng's data[2] are confirmed by the present measurements, except that one additional faint line is observed at λ3429 at temperature 710°C.

Finally the authors wish to thank Dr. Ny Tsi-ze for his interest in the experiment.

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Isotope Shifts in Uranium Spectra

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A study is made of the isotopic shift of U^{238}, U^{235}, and U^{233} in the emission spectrum of uranium. The shift is sufficient to allow quantitative determination of the concentration of the components of a mixture of the uranium isotopes by routine spectrographic analysis. Data show comparative values obtained by mass spectrometer and spectrograph.

INTRODUCTION

THE separation of the isotopes of uranium affords an excellent opportunity to study the isotope shifts in its spectrum. Shifts had been observed by D. D. Smith and D. R. Long in these laboratories in noting the difference in normal standards, chiefly the U^{238} isotopes and the enriched U^{235} samples on the same plate. This work extends the study to include U^{233}. The arc and the spark were used to produce the spectra of these isotopes, and a large number of shifts were observed at a dispersion of 2.47A per millimeter.

DISCUSSION

The explanation of the isotope effect is not simple, and no attempt is made to explain it here. The shifts in the uranium isotopes are so great that they were recognized in ordinary emission spectrographic analysis. An effort is made here to observe as many as can be obtained under the prescribed conditions and sample size. The difference of the nuclear radius, difference in the building up of the nucleus, or perhaps something peculiar to the uranium type elements, may contribute to this easily observed isotope shift.

The shifts observed in U^{235} and U^{233} by direct emission spectra were obtained on a 15,000-line Jarrell-Ash grating spectrograph. This Wood grating gives a strong second order spectrum with a dispersion of 2.47A per millimeter. One hundred micrograms of U_3O_8 were selected as sample size for obtaining the arc spectra, and this was mixed with 500 micrograms of powdered graphite. A uniform burning was obtained for a period of 45 seconds at 4 amperes direct current. However, currents up to 7 amperes may be used.

The spark spectrum was obtained by use of the Dietert Multisource with a spark produced with settings of 20 microfarads, 25 microhenries and 5.4 ohms. Five hundred micrograms of U_3O_8 mixed with a drop of cellulose acetate in acetone were placed in shallow copper electrodes and then dried. The sample was then sparked for 45 seconds using a 103-0 plate. A careful check was made throughout the 2500A–5000A region. The search did not disclose any appreciable differences between the spark and the arc spectra of uranium. The same lines shifted, and the amounts of shift were the same as for the arc spectra. The spectra obtained by the standard spark supply showed fewer lines but no greater shift than the arc spectra.

The region covered in the arc spectrum study

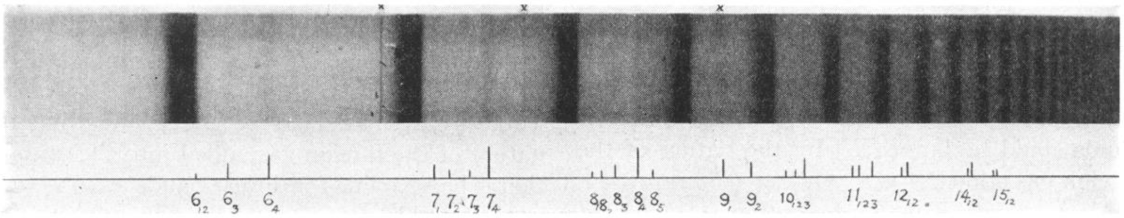

FIG. 1. The absorption spectrum of dense lithium vapor ($T = 1040$°C). The lines marked by × are due to impurities.