The $A \ ^1\Sigma^+ + X \ ^1\Sigma^+$
Bands of the Isotopic Lithium Hydrides*

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ABSTRACT

In order to obtain a better understanding of the $X^1\Sigma^+$ ground state and the $A^1\Sigma^+$ state potential energy curves of lithium hydride and to examine in detail the concept of "mass-reduced quantum numbers" for both an ordinary ($X^1\Sigma^+$) and an anomalous ($A^1\Sigma^+$) electronic state, the emission spectra of the $A^1\Sigma^+ \rightarrow X^1\Sigma^+$ bands of the isotopic lithium hydrides and deuterides were photographed in the 3000 - 5000Å region with a 3.4 meter Ebert Spectrograph. The bands found involved $v'' = 0$ to 7 to various $v' = 0$ to 17 for ^6LiH , and $v'' = 0$ to 7 to various $v' = 1$ to 16 for ^6LiD . Additional bands involving $v'' = 4$ and 5 were also found for ^7LiH .

The vibrational-rotational spectroscopic analysis of ^7LiH , ^6LiH and ^6LiD are reported here, as are the reanalyses of the ^7LiH and ^7LiD data reported by Crawford and Jorgensen. New Rydberg-Klein-Rees (RKR) $A^1\Sigma^+$ and $X^1\Sigma^+$ potential curves have been constructed for each individual molecule and are reported, but detailed isotopic comparisons will be reported in subsequent publications.

I. INTRODUCTION

The potential energy curves of lithium hydride have attracted the attention of theoretical chemists and spectroscopists. The theoreticians favor this molecule because it has the fewest electrons of all neutral heteronuclear molecules and thus can be treated accurately with relative ease. The spectroscopists' interests are in the anomalous $A^1\Sigma^+$ state of the alkali metal hydride, where there is a very anharmonic and unusual potential showing an initial increase in ΔG and B_v before the usual decrease.

The observation of $A^1\Sigma^+ \rightarrow X^1\Sigma^+$ spectra of ^7LiH and ^6LiH were first reported by Nakamura in 1930 (1) and 1931 (2). A total of 25 bands were observed for ^7LiH which involved $v'' = 0, 1, 2$ to various $v' = 1$ to 15 and extended from $3000 - 4100\text{\AA}$. The spectra were taken both in emission and absorption with a dispersion of $2.3\text{\AA}/\text{mm}$ but only lines that were seen both in absorption and emission were reported. Higher resolution spectra were desired for more precise calculation (and isotopic comparisons) of Rydberg-Klein-Rees potential energy curve (RKR). (3,4,5)

In 1935, Crawford and Jorgensen (6,7) reinvestigated the $A^1\Sigma^+ \rightarrow X^1\Sigma^+$ absorption spectra of ^7LiH and ^7LiD in high resolution with a $1\text{\AA}/\text{mm}$ dispersion. A total of 27 bands extending from $3200 - 4300\text{\AA}$ and involving $v'' = 0, 1, 2, 3$ to $v' = 1$ to 15 were observed for ^7LiH , while a total of 35 bands involving $v'' = 0, 1, 2$ to $v' = 1$ to 18 and in the same wavelength region as ^7LiH were observed for ^7LiD . Crawford and Jorgensen observed the ^7LiH (0-2) band, but in our 'direct approach' analysis, it has an unusually large error compared to other reported bands, and thus it was not included in our analysis. No electronic spectra were previously available for ^6LiD .

The RKR potential curves of $X^1\Sigma^+$ and $A^1\Sigma^+$ states were calculated by Fallon, Vanderslice and Mason (8) using Crawford and Jorgensen's data (which included only limited data on the $X^1\Sigma^+$ state, and did not include $v' = 0$ level of $A^1\Sigma^+$ state where anomalous behavior is strong).

The observation and identification of the $B^1\Pi - X^1\Sigma^+$ band system of lithium hydride has made possible very accurate determination ($\pm 0.5 \text{ cm}^{-1}$) of the dissociation limit. (9)

Numerous theoretical calculations (10), (11), (12) have been carried out for LiH. As was pointed out in the recent calculation of Docken and Hinze (DH) (12), most previous theoretical work done on LiH concentrated on describing the ground state and its properties only. Docken and Hinze's ab initio multiconfiguration self-consistent-field (MCSCF) calculations of lithium hydride computed the potential curves of several electronic states, as well as other properties such as term values, and rotational and vibrational constants of the ground and excited states which traditionally are of interest to spectroscopists. They indicated at least twenty bound vibrational levels should exist for the $^7\text{LiH } X^1\Sigma^+$ state where only four had been observed spectroscopically and twenty vibrational levels for the $A^1\Sigma^+$ state while fifteen had been observed.

Recently laser-fluorescence measurement of the $^7\text{LiD } (X^1\Sigma^+)$ potential curve up to high vibrational quantum numbers ($v'' = 20$), corresponding to 82% of the dissociation energy of ^7LiD , were reported by Ennen and Ottinger. (13) This approximately corresponds to $v'' = 14$ in the $^7\text{LiH } X^1\Sigma^+$ state. Unfortunately the wavelength measurements were done on a strip chart recorder, implying the accuracy of the wavelength measurement was only $\pm 0.3\text{\AA}$ (corresponding to ± 2.7 to $\pm 0.5 \text{ cm}^{-1}$ depending on the wavelength region).

More recently hybrid $X^1\Sigma^+$ and $A^1\Sigma^+$ potentials have been reported (14) which are based on the RKR potentials (8), the accurate dissociation limits (9) and long-range forces (14), and with interpolation on the outer branch of the potential by slightly distorting the DH (12) results. These hybrid potentials contain 24 and 27 vibrational levels in the X and A states, respectively, for ^7LiH . Of particular interest are the weakly bound higher levels ("long-range molecules" (15,16,17)), especially $v' = 26$ and $v'' = 23$, which are strongly connected optically (their wavefunctions overlap 75%). (15)

Since the $A^1\Sigma^+$ state involves a larger molecular equilibrium radius (R_e) than the $X^1\Sigma^+$ state, it is apparent from the Franck-Condon principle and Einstein transition probability of spontaneous emission that the (v', v'') bands, where v'' is of high vibrational number, should be more strongly developed in emission than absorption. In order to obtain a better understanding of the $X^1\Sigma^+$ ground state and the anomalous $A^1\Sigma^+$ state potential curves of lithium hydride, considerable effort has been spent to obtain well-resolved emission spectra of the four isotopic species of lithium hydride for additional vibrational levels. Further ^7LiH spectra in the 5200 - 8700 $\text{\AA}$ region have been obtained very recently and are being analyzed. (18)

II. EXPERIMENTAL TECHNIQUES

A. Discharge source.

A hollow cathode lamp was used to produce the emission spectra. The final design used (after considerable experimentation) is shown in a schematic diagram in Figure 1. High purity isotopic lithium hydride crystals, melting point 689°C , were obtained from the Oak Ridge National Laboratory. The atomic percent of ^7Li in ^7LiH and ^7LiD was 99.993% and of ^6Li in ^6LiH and ^6LiD was 95.58%. The lithium hydride crystals were ground into powder form and packed three quarters of the depth into the stainless steel cathode with a press. The whole discharge tube was evacuated and flushed two to three times with argon gas first and then flushed twice with hydrogen. When the final hydrogen pressure in the discharge tube was about 10-20 torr, the glass stoppers were closed. Apiezon T grease was used for the O-ring, glass-stoppers and the ground joints. The whole tube (except the window) was then put into a water trough for cooling.

The discharge was excited by a 2kw DC power supply capable of supplying 1000 volts and 2 amperes. The current was increased slowly in 0.25 ampere intervals until the final discharge was running at about 600 volts and 1.25-1.75 amperes.

The reddish-purple color of the discharge was dominated by the $6707.84\text{\AA}$ and $6103.64\text{\AA}$ atomic lines. The stainless steel cathode was heated up to orange-red color. An average rotational temperature in the source of $1000 \pm 100^{\circ}\text{K}$ was estimated from three bands of the ^6LiH spectra.

B. Spectrograph.

The emission spectra were recorded with the 3.4 meter Ebert Jarrel-Ash spectrograph (19) on Kodak spectrum analysis plates, (SA3) which have useful sensitivity in the $2500\text{-}5000\text{\AA}$ region. The angle of the grating was set at 30.1°

Figure 1. Schematic diagram of the hollow cathode source used to produce LiH emission spectra.

for high resolution. An order sorter as described in reference (19) was aligned on the optical bench with the spectrograph to separate the overlapping orders. A Westinghouse iron hollow cathode lamp run at 20 milliamperes and 280 volts for three hours was used to produce an iron spectrum for wavelength calibration. The orders from 6-12 were separated and recorded on the SA3 plates. The theoretical resolution was 0.07 cm^{-1} . The plate factor in $\text{\AA}/\text{mm}$ of the different orders followed closely with those given in reference (19), except toward both ends of the plates (this was due to the curvature of the reflecting mirror at the ends). For example the plate factor for the twelfth order ($\approx 3000\text{\AA}$) was $0.68\text{\AA}/\text{mm}$ and for the eighth order ($\approx 4500\text{\AA}$) was $1.02\text{\AA}/\text{mm}$.

The spectra photographed covered the region from $\approx 3000 - 5300\text{\AA}$, which corresponds to the $A \text{ } ^1\Sigma^+ - X \text{ } ^1\Sigma^+$ electronic transition. Spectra were obtained using a slit width of 20 microns, height of 1.0mm and exposure times of 6 hours.

C. Wavelength measurement.

The plates were measured on the Gaertner photoplate comparator with an encoder system and on-line computer service at Argonne National Laboratory. The position, wavelength, wavenumber, intensity and width of each line on the spectra were listed and punched on cards. Densitometer traces of the spectra were also produced by computer. A portion of the densitometer trace of the $^6\text{LiH } A \text{ } ^1\Sigma^+ - X \text{ } ^1\Sigma^+$ emission spectra is shown in Figure 2. The comparator has an accuracy of ± 1 microns. A detailed description of the comparator and computer programs are given by Tomkins and Fred. (20) Their programs used thorium lines as standards but provisions were made to use other elements such as iron as standards. The positions and wavelengths of iron lines are measured first manually and then entered as input into the program. An average of 10-15 iron lines were measured and entered as input for each order

Figure 2. A portion of the densitometer trace of the ${}^6\text{LiH}$ $A\ 1\Sigma^+ + X\ 1\Sigma^+$ spectrum from $\sim 3385 - 3500\ \text{\AA}$ with line assignments.

across the 250mm length of the plate. These input data were fit to a 4 degree polynomial function. The input wavelengths and the calculated wavelengths of the iron lines from the function requires a standard deviation of less than $0.004 \text{ \AA}$ before the program accepts and uses the polynomial function to interpolate the molecular lines.

D. Band Identification.

The A-X spectra of all alkali hydrides show no distinct band heads, thus making identification of bands more difficult than when distinct band heads are present in the spectra. Bands that already have been observed by Crawford and Jorgensen, (6,7) and Nakamura (1,2) were identified and picked out first. Then, the vibrational and rotational constants of ^7LiH given by Crawford and Jorgensen were used to extrapolate to the unobserved eigenvalues of the other bands to help further analysis. This method can not give good results if one extrapolates too far from the observed vibrational quantum numbers of the same or another isotope, even when isotopic effects are taken into consideration. The rotational quantum number J and vibrational quantum number v assignment were straightforward, being greatly facilitated by earlier investigators' work.

III. ANALYSIS OF SPECTROSCOPIC MOLECULAR CONSTANTS

Traditionally after the rotational and vibrational quantum number assignments, the rotational constants $B(v)$ and $D(v)$ of bands having the same v' or v'' are obtained by using the combination differences $\Delta_2 F(J)$, where $\Delta_2 F(J) = 4B(v)(J+1/2) - 8D(v)(J+1/2)^3$. A plot of $\Delta_2 F(J)/(J+1/2)$ vs. $(J+1/2)^2$ i.e. $\Delta_2 F(J)/(J+1/2) = 4B(v) - 8D(v)(J+1/2)^2$, gives the intercept as $4B(v)$ and the slope as $-8D(v)$. The rotational constants of upper and lower state are found depending on whether $\Delta_2 F(J)$ is upper ('') or lower (') state. Another method is employed to determine the vibrational constants from the band origins, which in turn can be determined in numerous ways. Herzberg (21) describes these techniques extensively.

Recently D. Albritton and coworkers (22) have shown that identifying the combination differences $\Delta_2 F''(J)$ or $\Delta_2 F'(J)$ as an energy that is characteristic of the lower or upper state alone makes the implicit assumption that all errors of measurement are associated with the lower or upper state alone. The measurement errors are, however, shared between the upper and lower states. They proposed a 'direct approach' where one finds the upper and lower state rotational constants and band origins simultaneously from the observed P and R branches of a band with a least square fit program.

The spectroscopic data for each isotopic lithium hydride were reduced in this way (22) band by band. All constants $B(v)$, $D(v)$, and $H(v)$ belonging to the same v' or v'' weighted by the reciprocals of their estimated variance were averaged to give the final values. Figures 3 and 4 show the distribution of the ${}^6\text{LiH}$ rotational constants B_1'' and B_8' obtained from band by band reduction and the weighted average final value.

The values of all the rotational constants $B(v)$, $D(v)$, and $H(v)$ of ${}^6\text{LiH}$ and ${}^6\text{LiD}$ are shown in Tables I and II. The band origins corresponding to the

Figure 3. The ${}^6\text{LiH}$ rotational constants B_1'' obtained from band-by-band reduction for various v' levels, compared to the final weighted average value.

Figure 4. The ${}^6\text{LiH}$ rotational constants B'_8 obtained by band-by-band reduction for various v'' levels, compared to the final weighted average value.

Table I. Rotational Constants for ${}^6\text{LiH}$ (cm^{-1})

	v	$B(v)$	$D(v)(\times 10^{-4})$	$H(v)(\times 10^{-8})$
$X \ ^1\Sigma^+$	0	7.5571(0.0008) ^a	8.722(0.019)	8.64(0.12)
	1	7.3380(0.0015)	8.449(0.043)	9.08(0.45)
	2	7.1246(0.0020)	8.445(0.073)	9.00(0.74)
	3	6.9136(0.0025)	8.147(0.079)	10.30(1.20)
	4	6.7073(0.0023)	8.039(0.071)	10.80(0.90)
	5	6.4976(0.0021)	7.699(0.084)	8.74(2.00)
	6	6.2940(0.0035)	7.595(0.132)	13.00(6.10)
	7	6.0854(0.0052)	7.258(0.162)	----
$A \ ^1\Sigma^+$	0	2.9438(0.0242)	19.506(0.683)	----
	1	2.9474(0.0019)	8.007(0.104)	28.20(1.60)
	2	2.9708(0.0035)	6.794(0.133)	17.70(1.60)
	3	2.9739(0.0026)	5.908(0.082)	10.40(0.75)
	4	2.9684(0.0026)	5.354(0.087)	8.02(0.82)
	5	2.9550(0.0023)	4.915(0.071)	5.96(0.62)
	6	2.9383(0.0017)	4.637(0.050)	5.10(0.44)
	7	2.9170(0.0016)	4.506(0.038)	4.67(0.25)
	8	2.8895(0.0015)	4.332(0.032)	4.37(0.22)
	9	2.8550(0.0015)	4.115(0.033)	2.62(0.21)
	10	2.8199(0.0026)	4.070(0.053)	3.27(0.34)
	11	2.7789(0.0028)	4.020(0.070)	3.56(0.57)
	12	2.7409(0.0058)	4.397(0.174)	8.25(1.43)
	13	2.6883(0.0035)	3.998(0.075)	3.39(0.62)
	14	2.6302(0.0045)	3.913(0.122)	2.27(0.91)
	15	2.5781(0.0045)	4.128(0.208)	4.15(2.86)
	16	2.5104(0.0056)	3.924(0.183)	0.14(1.80)

^a The numbers in parentheses represent two standard deviations.

Table II. Rotational Constants for ${}^6\text{LiD}$ (cm^{-1})

	v	$B(v)$	$D(v)(\times 10^{-4})$	$H(v)(\times 10^{-8})$
$X \ ^1\Sigma^+$	0	4.3424(0.0009) ^a	2.907(0.028)	2.00(0.26)
	1	4.2474(0.0016)	2.861(0.040)	2.08(0.40)
	2	4.1482(0.0025)	2.598(0.038)	1.44(1.13)
	3	4.0617(0.0023)	2.839(0.065)	2.28(0.57)
	4	3.9681(0.0024)	2.588(0.032)	2.80(0.57)
	5	3.8727(0.0020)	2.501(0.028)	2.16(1.02)
	6	3.7890(0.0016)	2.683(0.055)	2.07(0.62)
	7	3.6977(0.0020)	2.497(0.033)	---
$A \ ^1\Sigma^+$	0	---	---	---
	1	1.6806(0.0031)	2.767(0.094)	3.93(0.90)
	2	1.6949(0.0016)	2.477(0.049)	4.02(0.45)
	3	1.6963(0.0019)	1.884(0.028)	2.81(1.01)
	4	1.6991(0.0020)	1.858(0.041)	2.58(0.49)
	5	1.6959(0.0015)	1.644(0.024)	0.85(0.61)
	6	1.6947(0.0013)	1.590(0.019)	2.82(3.00)
	7	1.6897(0.0023)	1.549(0.043)	---
	8	1.6841(0.0021)	1.466(0.029)	1.23(0.44)
	9	1.6749(0.0022)	1.542(0.109)	2.84(1.49)
	10	1.6638(0.0029)	1.497(0.116)	1.27(1.06)
	11	1.6544(0.0049)	1.550(0.193)	2.20(2.26)
	12	1.6391(0.0051)	1.508(0.375)	5.62(2.23)
	13	1.6217(0.0049)	1.383(0.147)	0.75(1.33)
	14	1.6060(0.0020)	1.389(0.045)	0.90(0.30)
	15	1.5868(0.0026)	1.318(0.066)	0.47(0.51)
	16	1.5706(0.0054)	1.389(0.109)	0.97(0.66)
	17	1.5499(0.0236)	1.978(0.899)	14.85(10.2)

^a The numbers in parentheses represent two standard deviations.

bands observed are shown in Tables III and IV. Using the same least square fit program (22), Crawford and Jorgenson's data on ^7LiH and ^7LiD were reanalyzed. The constants and band origins agree completely with those reported by Crawford and Jorgenson. In ^7LiH , bands corresponding to two more ground vibrational levels ($v'' = 4$ and 5) were observed in addition to those reported by Crawford and Jorgenson (and in good agreement with them). For example, the $B(1')$ and $B(2')$ constants agree to $<0.003 \text{ cm}^{-1}$. These combined rotational constants and band origins are given in Tables V and VI and Tables VII and VIII, respectively. The wavenumbers, vibrational and rotational assignments of all lines in the bands of ^6LiH , ^6LiD , ^7LiH , and ^7LiD are reported elsewhere. (23) Lists of all observed lines are also available. (24,25,26)

From Tables I-VIII, the Y_{ij} constants ($\sim \omega_e, -\omega_e x_e, \omega_e y_e, B_e, \alpha_e, \gamma_e, \epsilon_e, D_e, \beta_e$, etc.) can be obtained for each isotope. The ground state $B(v'')$ were fit to a 2nd degree polynomial (Figure 5). A 3rd degree polynomial was used for $B(v')$ of the anomalous excited state to get a good fit (Figure 6). The $D(v'')$ of the ground state were fairly well represented by a 1st degree polynomial (Figure 7). The $D(v')$ of the excited state behaves even more anomalously; it increases sharply at small v' (Figure 8). No reasonable degree polynomial can fit these data. (We therefore did not consider $H(v)$). Therefore in order to obtain the Y'_{02} ($\sim D'_e$ values), a $\log D(v')$ vs. $(v'+1/2)$ plot of the first three lowest observed levels was made and extrapolated to zero. The Y_{02} ($\sim D_e$) values are given in Table IX along with the values calculated using the relationship $Y_{02} = \frac{4Y_{01}^3}{Y_{10}^2}$ for comparison. The Y_{02}'' ($\sim D_e''$) values of the X state are in excellent agreement while the Y_{02}' ($\sim D_e'$) values for the A state, because of the difficulty in fitting the sharp increase at small v , do not show good agreement. The polynomials used were of the following form:

Table III. Band Origins of A $^1\Sigma^+$ - X $^1\Sigma^+$ system of ^6LiH .

v'/v''	0	1	2	3	4	5	6	7
0						19519.1 (284.4)		
1		24848.0(1327.5) (316.8)	23520.5(1282.6) (316.7)	22237.9(1238.9) (316.7)	20999.0(1195.5) (316.6)	19803.5 (316.6)		
2		25164.8(1327.6) (339.8)	23837.2(1282.6) (339.7)	22554.6(1238.9) (339.7)	23135.6(1195.5) (339.7)	20120.1		
3	26877.9(1373.3) (357.1)	25504.6(1327.7) (357.1)	24176.9(1282.6) (357.2)	22894.3(1238.9)	21655.3			
4	27234.9(1373.2) (370.1)	25861.7(1327.7) (370.1)	24534.0 (370.1)			20817.1 (370.1)		
5	27605.0(1373.2) (380.3)	26231.8(1327.7) (380.3)	24904.1		22382.9(1195.7) (380.0)	21187.2		
6	27985.3(1373.5) (387.1)	26611.8 (387.1)		24001.4(1238.5) (387.2)	22762.9		20414.2 (387.4)	
7	28372.4(1373.5) (391.9)	26998.9		24388.6 (391.9)			20801.6	
8	28764.3 (394.6)		26063.5(1283.0) (394.5)	24780.5		22346.2		
9	29158.9 (395.5)		26458.0 (395.5)		23936.4 (395.5)		20476.8	
10	29554.4 (395.2)		26853.5 (395.0)		24331.9			
11	29949.6(1373.4) (392.7)	28576.2(1327.7) (393.0)	27248.5					
12	30342.3(1373.1) (389.2)	28969.2 (389.3)						
13	30731.5(1372.9) (384.7)	29358.5 (384.5)		26747.9				
14	31116.2(1373.2) (378.7)	29743.0 (378.4)						
15	31494.9(1373.5) (370.7)	30121.4 (370.7)						
16		30492.1						

Table IV. Band origins of A $^1\Sigma^+$ - X $^1\Sigma^+$ system of ^6LiD .

v'/v''	0	1	2	3	4	5	6	7
0								
1					22251.4(944.1) (229.2)	21307.2(919.5) (229.2)	20387.7 (229.4)	
2				23450.3(969.7) (245.2)	22480.6(944.2) (245.3)	21536.4(919.3) (245.1)	20617.1	
3			24690.6(995.1) (257.5)	23695.5(969.6) (257.7)	22725.9(944.4) (257.5)	21781.5		
4		25969.2(1021.1) (267.8)	24948.1(994.9) (267.8)	23953.2(969.8) (267.6)	22983.4			20224.8 (267.7)
5	27284.4(1047.4) (276.0)	26230.0(1021.1) (275.8)	25215.9(995.1) (275.7)	24220.8				20492.5
6	27560.4(1047.6) (282.6)	26512.8(1021.2) (282.8)	25491.6				21663.5	
7	27843.0(1047.4) (287.8)	26795.6 (287.6)				22865.3		
8	28130.8(1047.6) (291.9)	27083.2 (292.0)			24097.3			
9	28422.7(1047.5) (295.1)	27375.2		25358.8 (295.4)				
10	28717.8 (297.4)			25654.2				
11	29015.2 (298.7)							
12	29313.9 (299.2)		27245.0 (299.0)					
13	29613.1 (299.0)		27544.0					
14	29912.1 (298.4)							
15	30210.5 (296.9)							
16	30507.4 (295.8)							
17	30803.2							

Table V. Rotational Constants for ${}^7\text{LiH}$ (cm^{-1}) primarily from reanalysis of the results of Crawford and Jorgenson. (6,7)

	v	$B(v)$	$D(v)(\times 10^{-4})$	$H(v)(\times 10^{-8})$
$X \quad {}^1\Sigma^+$	0	7.4061(0.0006) ^a	8.464(0.035)	9.92(0.58)
	1	7.1941(0.0006)	8.348(0.031)	9.69(0.43)
	2	6.9853(0.0007)	8.169(0.039)	9.03(0.59)
	3	6.7792(0.0029)	7.905(0.304)	----
	4	6.5786(0.0035) ^b	7.887(0.222)	9.62(4.61)
	5	6.3744(0.0072) ^b	7.561(0.550)	29.2(12)
$A \quad {}^1\Sigma^+$	0	2.8500(0.0074) ^b	10.590(0.554)	82.0(7.51)
	1	2.8899(0.0012)	7.848(0.079)	23.2(1.6)
	2	2.9039(0.0010)	6.256(0.062)	11.6(1.2)
	3	2.9090(0.0007)	5.530(0.033)	8.2(0.4)
	4	2.9055(0.0008)	5.030(0.036)	6.0(0.5)
	5	2.8971(0.0014)	4.775(0.068)	5.9(0.9)
	6	2.8801(0.0019)	4.559(0.123)	6.7(2.3)
	7	2.8593(0.0014)	4.315(0.078)	4.1(1.2)
	8	2.8363(0.0024)	4.332(0.129)	6.0(2.0)
	9	2.8026(0.0023)	4.041(0.107)	3.1(1.5)
	10	2.7714(0.0017)	4.144(0.089)	5.3(1.3)
	11	2.7308(0.0024)	3.999(0.250)	4.5(7.3)
	12	2.6875(0.0016)	3.895(0.093)	2.8(1.6)
	13	2.6423(0.0016)	3.945(0.069)	3.8(0.9)
	14	2.5915(0.0016)	3.920(0.090)	3.2(1.5)
	15	2.5289(0.0051)	3.608(0.121)	---

^a The numbers in parentheses represent two standard deviations.

^b Observed in this work only.

Table VI. Rotational Constants of ^7LiD (cm^{-1})
from reanalysis of the results of Crawford
and Jorgenson. (6,7)

	v	$B(v)$	$D(v)(\times 10^{-4})$	$H(v)(\times 10^{-8})$
$X \ ^1\Sigma^+$	0	4.1875(0.0003) ^a	2.695(0.013)	1.68(0.14)
	1	4.0977(0.0007)	2.681(0.024)	2.02(0.28)
	2	4.0075(0.0006)	2.590(0.019)	1.17(0.23)
	3	3.9200(0.0010)	2.599(0.041)	1.95(0.48)
$A \ ^1\Sigma^+$	0	---	---	---
	1	1.6244(0.0015)	2.850(0.114)	6.60(2.70)
	2	1.6344(0.0021)	2.391(0.066)	5.20(2.60)
	3	1.6356(0.0009)	1.915(0.036)	1.50(0.40)
	4	1.6388(0.0008)	1.767(0.027)	1.40(0.30)
	5	1.6382(0.0009)	1.648(0.034)	1.20(0.40)
	6	1.6340(0.0007)	1.464(0.013)	7.40(0.40)
	7	1.6311(0.0013)	1.510(0.056)	1.30(0.70)
	8	1.6248(0.0011)	1.453(0.042)	1.20(0.50)
	9	1.6153(0.0007)	1.335(0.013)	---
	10	1.6060(0.0008)	1.356(0.024)	0.76(0.21)
	11	1.5956(0.0010)	1.347(0.038)	0.83(0.44)
	12	1.5818(0.0009)	1.282(0.031)	0.36(0.32)
	13	1.5681(0.0015)	1.280(0.054)	0.50(0.57)
	14	1.5530(0.0013)	1.272(0.039)	0.52(0.35)
	15	1.5368(0.0013)	1.285(0.037)	0.82(0.32)
	16	1.5196(0.0017)	1.322(0.077)	1.50(1.00)
	17	1.5000(0.0047)	1.166(0.193)	3.66(2.30)
	18	1.4807(0.0050)	1.451(0.240)	4.50(3.40)

^a The numbers in parentheses represent two standard deviations.

Table VII. Band origins of $A^1\Sigma^+ - X^1\Sigma^+$ system of ^7LiH ,
primarily from reanalysis the results of
Crawford and Jorgenson. (6,7)

v'/v''	0	1	2	3	4	5
0					20770.02 ^a (1185.42)	19584.60 ^a
					(280.86)	(280.75)
1		24864.32(1314.84)	23549.48		21050.88 ^a (1185.53)	19865.35 ^a
		(312.97)	(312.96)		(312.41)	(312.90)
2	26537.02(1359.73)	25177.29(1314.85)	23862.44(1270.91)	22591.53(1228.24)	21363.29 ^a (1185.04)	20178.25 ^a
	(335.76)	(335.73)	(335.71)	(335.71)	(334.36)	
3	26872.78(1359.76)	25513.02(1314.87)	24198.15(1270.91)	22927.24(1229.59)	21697.65 ^a	
	(352.80)	(352.78)	(352.80)			
4	27225.58(1359.78)	26865.80(1314.85)	24550.95			
	(365.83)	(365.87)				
5	27591.41(1359.74)	26231.67				
	(375.64)	(375.56)				
6	27967.05(1359.82)	26607.23				
	(382.68)					
7	28349.73					
	(387.55)					
8	28737.28					
	(390.37)					
9	29127.65					
	(391.59)					
10	29519.24					
	(391.05)					
11	29910.29					
	(389.19)					
12	30299.48					
	(385.94)					
13	30685.42					
	(381.32)					
14	31066.74					
	(375.21)					
15	31441.95					

^a Bands observed in this work only.

Table VIII. Band origins of $A^1\Sigma^+ - X^1\Sigma^+$ system of ^7LiD , from reanalysis of the results of Crawford and Jorgenson. (6,7)

v' / v''	0	1	2	3	4
0					
1			24255.71(978.5) (224.62)	23277.19 (224.59)	
2		25483.94(1003.61) (239.92)	24480.33(978.55) (239.92)	23501.78 (239.91)	
3	26752.8 (1028.9) (252.3)	25723.86(1003.61) (252.16)	24720.25(978.56) (252.19)	23741.69(953.84) (252.19)	22787.85
4	27005.08(1029.06) (262.03)	25976.02(1003.58) (262.03)	24972.44(978.56) (262.03)	23993.88	
5	27267.11(1029.06) (270.15)	26238.05(1003.58) (270.13)	25234.47 (270.15)		
6	27537.26(1029.08) (276.69)	26508.18(1003.56) (276.69)	25504.62		
7	27813.95(1029.08) (282.01)	26784.87 (281.98)			
8	28095.96(1029.11) (286.13)	27066.85			
9	28382.08 (289.28)				
10	28671.36 (291.60)				
11	28962.96 (293.08)				
12	29256.04 (293.78)				
13	29549.82 (293.90)				
14	29843.72 (293.34)				
15	30137.06 (292.11)				
16	30429.17 (290.41)				
17	30719.58 (288.0)				
18	31007.6 (285.2)				
19	31292.8

Figure 5. The rotational constants $B(v'')$ for $X^1\Sigma^+ {}^6\text{LiH}$ versus $v'' + 1/2$.

Figure 6. The rotational constants $B(v')$ for $A^1\Sigma^+ {}^6\text{LiH}$ versus $v' + 1/2$.

Note the anomalous increase at low v' .

Figure 7. The centrifugal distortion constants $D(v'')$ for $X^1\Sigma^+ {}^6\text{LiH}$ versus $v'' + 1/2$.

Figure 8. The centrifugal distortion constants $D(v')$ for $A^1\Sigma^+ {}^6\text{LiH}$ versus $v' + 1/2$. Note the anomalous behavior at low v' .

Table IX. Comparisons of observed^a and calculated^b centrifugal rotational constant, Y_{02} ($\equiv D_e$) (cm^{-1}), of $X^1\Sigma^+$ and $A^1\Sigma^+$ states of ^7LiH , ^7LiD , ^6LiH , and ^6LiD .

State	Isotope	$Y_{02} \times 10^4$	
		Obs.	Calc.
$X^1\Sigma^+$	^7LiH	8.55	8.59
	^7LiD	2.72	2.73
	^6LiH	8.82	9.09
	^6LiD	2.91	2.93
$A^1\Sigma^+$	^7LiH	12.28	16.07
	^7LiD	4.38	4.95
	^6LiH	10.11 ^c	16.61
	^6LiD	4.63	5.51

^aObserved values of the $X^1\Sigma^+$ state are obtained from the polynomial fit of experimental $D(v'')$ values. The Y_{02} values of the $A^1\Sigma^+$ state are obtained from a $\ln D(v')$ versus $v' + 1/2$ plot of the first three vibrational levels.

^bThe calculated values are obtained from the relationship $Y_{02} = 4Y_{01}^3/Y_{10}^2$.

^c $v'=0$ level is not used in the $\log D(v')$ vs $(v' + 1/2)$ plot as described in the text because of the large standard deviation (since only one band involving $v' = 0$ was observed).

$$\sum_{i=1}^n Y_{i1} (v+1/2)^i$$

$$\sum_{i=1}^n Y_{i2} (v+1/2)^i$$

The energy of the vibrational levels were found using the band origins $\nu_{v',v''}$ (the difference between an excited energy level $G(v')$ and a ground state level $G(v'')$). The calculated ΔG values were used to fit a polynomial equation to obtain the vibrational constants, $Y_{i0}(\tilde{\omega}_e, -\tilde{\omega}_e x_e, \omega_e y_e, \omega_e z_e, \text{etc.})$. The polynomial used was of the form:

$$\Delta G(v) = G(v+1) - G(v) = \sum_{i=1}^n Y_{i0} [(v+3/2)^i - (v+1/2)^i]$$

In the $X^1\Sigma^+$ state only a 2nd degree polynomial was required, while the $A^1\Sigma^+$ state required a 5th degree polynomial (see Figures 9 and 10).

According to the simplest isotopic theory (21,27), the vibrational and rotational constants of the isotopic molecules are related to one another by the following relationship:

$$Y_{ij}(k) \approx Y_{ij}(\ell) \mu_k^{(i/2 + j)} \quad (1)$$

where μ_k = reduced mass of isotope k /reduced mass of isotope ℓ . In this case, $k = {}^7\text{LiD}$, ${}^6\text{LiD}$ or ${}^6\text{LiH}$, while $\ell = {}^7\text{LiH}$. The reduced masses are given in Table X.

The $X^1\Sigma^+$ and $A^1\Sigma^+$ state spectroscopic constants of ${}^7\text{LiH}$, ${}^7\text{LiD}$, ${}^6\text{LiH}$ and ${}^6\text{LiD}$ are given in Tables XI and XII, respectively. The spectroscopic constants of ${}^7\text{LiD}$, ${}^6\text{LiH}$ and ${}^6\text{LiD}$ are also given reduced according to the isotope effect equations given immediately above and are given for comparison

Figure 9. The vibrational spacings $\Delta G(v'')$ for $X^1\Sigma^+ {}^6\text{LiH}$ versus $v'' + 1/2$.

Figure 10. The vibrational spacings $\Delta G(v')$ for $A' \Sigma^+ 6\text{LiH}$ versus $v' + 1/2$.
Note the anomalous behavior at low v' .

Table X. Values of the reduced mass μ used in this work in atomic mass units (amu, ^{12}C)^a and referred to reduced mass ($\mu_{\text{LiH}}=1$).

Isotopic species	$\mu(^{12}\text{C})$	$\mu(^7\text{LiH}=1)$
^7LiH	0.88123	1
^7LiD	1.56487	1.77577
^6LiH	0.86319	0.97953
^6LiD	1.50887	1.71222

^a The amu for individual atoms are $^7\text{Li} = 7.01600$,
 $^6\text{Li} = 6.01512$, $\text{H} = 1.00782$ and $\text{D} = 2.01410$.

Table XI. The $X^1\Sigma^+$ state spectroscopic constants (in cm^{-1}) for ^7LiH , ^7LiD , ^6LiH , and ^6LiD .

Constants	^7LiH	^7LiD	^6LiH	^6LiD
$Y_{10}(\tilde{\omega}_e)$	1405.629	1054.903	1419.843	1074.192
$Y_{20}(\tilde{\omega}_e x_e)$	- 23.1950	- 13.0375	- 23.4882	- 13.4531
$Y_{30}(\tilde{\omega}_e y_e)$	0.16333	0.06833	0.14119	0.06149
$Y_{01}(\tilde{\omega}_e)^a$	7.5133	4.2330	7.6688	4.3907
$Y_{11}(\tilde{\omega}_e \alpha_e)$	- 0.21514	- 0.09129	- 0.22500	- 0.09688
$Y_{21}(\tilde{\omega}_e)(\times 10^4)$	15.671	4.742	34.022	6.240
$Y_{02}(\tilde{\omega}_e - D_e)(\times 10^4)$	- 8.548	- 2.720	- 8.819	- 2.906
$Y_{12}(\tilde{\omega}_e - B_e)(\times 10^4)$	0.1440	0.0483	0.1960	0.0652

^a E. F. Pearson and W. Gordy, Phys. Rev. A 177, 59 (1969) give the following values for Y_{01} from microwave spectra: 4.2330360 (^7LiD) and 4.3901323 (^6LiD), in excellent agreement with the present results.

Table XII. The $A^1\Sigma^+$ state spectroscopic constants (in cm^{-1}) for ^7LiH , ^7LiD , ^6LiH and ^6LiD .

Constant	^7LiH	^7LiD	^6LiH	^6LiD
$\gamma_{10}(\omega_e)$	239.9993	183.7586	243.7587	185.1009
$\gamma_{20}(\omega_e x_e)$	+ 23.91340	+ 12.45002	+ 23.60086	+ 13.82272
$\gamma_{30}(\omega_e y_e)$	- 2.251970	- 0.818099	- 2.114970	- 1.051260
$\gamma_{40}(\omega_e z_e)$	0.143271	0.036630	0.124403	0.058566
$\gamma_{50}(\omega_e a_e)(\times 10^4)$	- 55.7300	- 10.4532	- 44.7510	- 20.9250
$\gamma_{60}(\omega_e b_e)(\times 10^4)$	0.909780	0.128255	0.674570	0.322800
$\gamma_{01}(\omega_e)$	2.8495	1.6112	2.9113	1.6777
$\gamma_{11}(\omega_e x_e)$	0.035898	0.011715	0.032055	0.008980
$\gamma_{21}(\gamma_e)(\times 10^4)$	- 62.762	- 13.744	- 48.510	- 10.069
$\gamma_{31}(\epsilon_e)(\times 10^4)$	2.7045	0.2000	0.9057	0.3229

^a $\gamma_{02}(\omega_e - D_e)$ and $\gamma_{12}(\omega_e - \beta_e)$ values are not well-defined; see text and Table X.

in Tables XIII and XIV. In the A state, simple isotopic theory does not satisfactorily relate one isotopic constant to the same constant of another isotope. This is not surprising given the anomalous behavior of the A state. The agreement in the X state, which has much more normal behavior, is quite good. Future publications will present detailed analyses of the isotope effects using the mass-reduced quantum number concept. (27)

The zero point energy of each state is obtained by two methods. In the first method, a polynomial fit of $G(v)$ vs. $v+1/2$ is used and extrapolated to $v = -1/2$ to obtain the zero point energy. In the second method, a polynomial fit of $\Delta G(v+1/2)$ vs. $(v+1/2)$ is used. From the vibrational constants obtained in each case, the zero point energy is calculated according to the equation:

$$\sum_{i=1}^n \nu_{i0} (1/2)^i$$

A comparison of the zero point energies obtained using the different methods is given in Table XV. The good agreement in the two zero point energies for the A $^1\Sigma^+$ state of ^7LiH and ^6LiH is presumably because the $v'=0$ level is observed in both these isotopes so that the extrapolation is only half of a unit. This is in contrast to the A $^1\Sigma^+$ of ^7LiD and ^6LiD , where the $v'=0$ level is not observed. The lowest vibrational level observed in the deuterides is $v'=1$; therefore the extrapolation is by one and a half unit and considering the almost flat bottom of the potential curve of the A $^1\Sigma^+$, the extra distance of extrapolation may produce the slight variation of the deuteride zero point energies. The X $^1\Sigma^+$ state zero point energies are in excellent agreement since there is no anomalous behavior and $v'=0$ level is observed for all isotopes.

Table XIII. Comparison of $X^1\Sigma^+$ spectroscopic constants (in cm^{-1}) mass-reduced by the simplest isotopic theory (eqn. 1) to ^7LiH , using μ_k from Table X.

Constant	^7LiH	^7LiD	^6LiH	^6LiD
$\gamma_{10}(\omega_e)x\mu_k^{1/2}$	1405.629	1405.743	1405.236	1405.592
$\gamma_{20}(\omega_e x_e)x\mu_k$	- 23.1950	- 23.1516	- 23.0074	- 23.0344
$\gamma_{30}(\omega_e y_e)x\mu_k^{3/2}$	0.16333	0.16169	0.13688	0.13776
$\gamma_{01}(\omega_e)x\mu_k$	7.5133	7.5168	7.5118	7.5178
$\gamma_{11}(\omega_e - \alpha_e)x\mu_k^{3/2}$	- 0.21514	- 0.21602	- 0.21813	- 0.21705
$\gamma_{21}(\omega_e y_e)x\mu_k^2 (x10^4)$	15.671	14.953	32.643	18.293
$\gamma_{02}(\omega_e - D_e)x\mu_k^2 (x10^4)$	- 8.548	- 8.577	- 8.462	- 8.519
$\gamma_{12}(\omega_e - B_e)x\mu_k^{5/2} (x10^4)$	0.1440	0.2030	0.1861	0.2501

Table XIV: Comparison of the $A^1\Sigma^+$ spectroscopic constants (in cm^{-1}) mass-reduced by the simplest isotopic theory (eqn. 1) to ^7LiH , using μ_k from Table X.

Constant	^7LiH	^7LiD	^6LiH	^6LiD
$\gamma_{10}(\tilde{\omega}_e)x\mu_k^{1/2}$	239.9993	244.8731	241.2509	242.2079
$\gamma_{20}(\tilde{\omega}_e x_e)x\mu_k$	+ 23.91340	+ 22.10837	+ 23.11775	+ 23.66753
$\gamma_{30}(\tilde{\omega}_e y_e)x\mu_k^{3/2}$	- 2.25197	- 1.93591	- 2.05036	- 2.35531
$\gamma_{40}(\tilde{\omega}_e z_e)x\mu_k^2$	0.143271	0.115507	0.119362	0.171698
$\gamma_{50}(\tilde{\omega}_e a_e)x\mu_k^{5/2}(x10^4)$	- 55.7300	- 43.9254	- 42.4959	- 80.2720
$\gamma_{60}(\tilde{\omega}_e b_e)x\mu_k^3(x10^4)$	0.909780	0.718182	0.633987	1.620362
$\gamma_{01}(\tilde{B}_e)x\mu_k$	2.8495	2.8611	2.8517	2.8726
$\gamma_{11}(\tilde{\omega}_e x_e)x\mu_k^{3/2}$	0.035898	0.027722	0.031076	0.020119
$\gamma_{21}(\tilde{\gamma}_e)x\mu_k^2(x10^4)$	- 62.762	- 43.339	- 46.544	- 29.519
$\gamma_{31}(\tilde{\epsilon}_e)x\mu_k^{5/2}(x10^4)$	2.7045	0.84042	0.85006	1.2387

Table XV. The zero point energies (in cm^{-1}) of ^7LiH , ^7LiD , ^6LiH , and ^6LiD as obtained by two different polynomial fits, as discussed in the text.

State	Isotope	$G(v)$ vs. $(v+1/2)$	$\Delta G(v)$ vs. $(v+1/2)$
$X^1\Sigma^+$	^7LiH	697.01	697.04
	^7LiD	524.26	524.20
	^6LiH	703.99	704.07
	^6LiD	533.81	533.74
$A^1\Sigma^+$	^7LiH	126.06	125.71
	^7LiD	94.96	94.89
	^6LiH	127.87	127.52
	^6LiD	96.14	95.88

IV. POTENTIAL ENERGY CURVES OF THE ISOTOPIC LITHIUM HYDRIDES.

The Rydberg-Klein-Rees (RKR) (3,4,5) method of constructing potential curves from spectra of diatomic molecules is the most widely used method. The RKR turning points for a $J=0$ potential curve are obtained from the spectroscopic data through the expressions

$$\begin{aligned} f(v) &= \left(\frac{h}{4\pi c\mu}\right)^{-1/2} \int_{-1/2}^v [G(v) - G(x)]^{-1/2} dx \\ &= 1/4[R_+(v) - R_-(v)], \\ g(v) &= \left(\frac{4\pi c\mu}{h}\right)^{1/2} \int_{-1/2}^v B(x)[G(v) - G(x)]^{-1/2} dx \\ &= 1/2\left(\frac{1}{R_+(v)} - \frac{1}{R_-(v)}\right), \end{aligned}$$

where $B(x)$ and $G(x)$ are the rotational constant and vibrational energy for level x . By combining the $f(v)$ and $g(v)$ expression, one obtains

$$\begin{aligned} R_-(v) &= \left(\frac{f(v)}{g(v)} + f(v)^2\right)^{1/2} - f(v) \\ R_+(v) &= \left(\frac{f(v)}{g(v)} + f(v)^2\right)^{1/2} + f(v). \end{aligned}$$

The RKR calculations were performed using the computer program reported by Tellinghuisen. (28)

The spectroscopic properties that are required in the construction of the RKR potential energy curve are the rotational constants $B(v)$, vibrational energy $G(v)$ and equilibrium distance R_e . All these are available from the above spectroscopic analysis. The Rydberg-Klein-Rees potential energy curves of the $X^3\Sigma^+$ state of ^7LiH , ^7LiD , ^6LiH and ^6LiD are given in Tables XVI - XIX and those of $A^1\Sigma^+$ state are given in Tables XX - XXIII. The Y_{00} corrections are included in these curves although they represent only one type of many possible second-order WKB corrections.

Table XVI. Rydberg-Klein-Rees potential energy curve of the $X^1\Sigma^+$ state of ${}^7\text{LiH}$.

v	$B(v)(\text{cm}^{-1})$	$G(v)(\text{cm}^{-1})$	$R_-(\text{\AA})$	$R_+(\text{\AA})$
-1/2	7.5133	0	1.5957	
0	7.4061	697.94	1.4458	1.7780
1	7.1941	2057.72	1.3532	1.9367
2	6.9853	3372.58	1.2967	2.0607
3	6.7795	4643.43	1.2549	2.1717
4	6.5769	5871.16	1.2214	2.2760
5	6.3774	7056.66	1.1934	2.3765

Table XVII. Rydberg-Klein-Rees potential energy curve of the $X^1\Sigma^+$ state of ^7LiD .

v	$B(v)(\text{cm}^{-1})$	$G(v)(\text{cm}^{-1})$	$R_-(\text{\AA})$	$R_+(\text{\AA})$
-1/2	4.2330	0	1.5953	
0	4.1875	524.81	1.4638	1.7511
1	4.0927	1553.89	1.3808	1.8836
2	4.0078	2557.46	1.3293	1.9853
3	3.9193	3536.02	1.2907	2.0750

Table XVIII. Rydberg-Klein-Rees potential energy curve of the $X^1\Sigma^+$ state of ${}^6\text{LiH}$.

v	$B(v)(\text{cm}^{-1})$	$G(v)(\text{cm}^{-1})$	$R_-(\text{\AA})$	$R_+(\text{\AA})$
-1/2	7.6688	0	1.5957	
0	7.5571	705.08	1.4453	1.7793
1	7.3382	2078.34	1.3524	1.9391
2	7.1242	3405.97	1.2957	2.0639
3	6.9138	4688.76	1.2537	2.1758
4	6.7058	5927.48	1.2200	2.2809
5	6.4988	7122.94	1.1920	2.3823
6	6.2916	8275.90	1.1682	2.4817
7	6.0829	9387.17	1.1476	2.5803

Table XIX. Rydberg-Klein-Rees potential energy curve of the $X^1\Sigma^+$ state of ${}^6\text{LiD}$.

v	$B(v)(\text{cm}^{-1})$	$G(v)(\text{cm}^{-1})$	$R_-(\text{\AA})$	$R_+(\text{\AA})$
-1/2	4.3907	0	1.5952	
0	4.3425	534.41	1.4624	1.7526
1	4.2468	1581.98	1.3790	1.8866
2	4.1524	2603.14	1.3273	1.9895
3	4.0593	3598.28	1.2884	2.0805
4	3.9674	4567.80	1.2570	2.1649
5	3.8768	5512.07	1.2305	2.2453
6	3.7874	6431.49	1.2076	2.3231
7	3.6992	7326.45	1.1874	2.3991

Table XXI. Rydberg-Klein-Rees potential energy curve of the $A^1\Sigma^+$ state of ^7LiH .

v	$B(v)(\text{cm}^{-1})$	$G(v)(\text{cm}^{-1})$	$R_-(\text{\AA})$	$R_+(\text{\AA})$
-1/2	2.8494	0	2.5910	
0	2.8659	132.17	2.2299	2.9990
1	2.8901	413.35	2.0244	3.2833
2	2.9039	725.81	1.9078	3.4696
3	2.9089	1061.58	1.8244	3.6197
4	2.9059	1414.72	1.7588	3.7514
5	2.8912	1780.74	1.7047	3.8725
6	2.8894	2156.30	1.6587	3.9868
7	2.8594	2538.80	1.6188	4.0966
8	2.8337	2926.13	1.5837	4.2035
9	2.8036	3316.46	1.5525	4.3087
10	2.7694	3708.10	1.5242	4.4129
11	2.7312	4099.38	1.4990	4.5179
12	2.6889	4488.71	1.4756	4.6238
13	2.6423	4874.56	1.4542	4.7316
14	2.5910	5255.63	1.4345	4.8418
15	2.5344	5630.98	1.4167	4.9545

Table XXI. Rydberg-Klein-Rees potential energy curve of the $A^1\Sigma^+$ state of ${}^7\text{LiD}$.

v	$B(v)(\text{cm}^{-1})$	$G(v)(\text{cm}^{-1})$	$R_-(\text{\AA})$	$R_+(\text{\AA})$
-1/2	1.6112	0	2.5858	
0	1.6167	98.30	2.2707	2.9377
1	1.6258	304.48	2.0831	3.1898
2	1.6322	529.17	1.9740	3.3559
3	1.6362	768.97	1.8951	3.4877
4	1.6379	1021.09	1.8328	3.6010
5	1.6374	1283.20	1.7811	3.7030
6	1.6348	1553.41	1.7367	3.7974
7	1.6302	1830.15	1.6980	3.8867
8	1.6238	2112.12	1.6635	3.9724
9	1.6156	2398.21	1.6326	4.0553
10	1.6058	2687.45	1.6046	4.1364
11	1.5946	2979.00	1.5791	4.2162
12	1.5820	3272.06	1.5556	4.2951
13	1.5681	3565.91	1.5339	4.3736
14	1.5531	3859.85	1.5138	4.4521
15	1.5371	4153.21	1.4950	4.5308
16	1.5202	4445.34	1.4773	4.6101
17	1.5025	4735.67	1.4606	4.6902
18	1.4842	5023.66	1.4448	4.7713

Table XXII. Rydberg-Klein-Rees potential energy curve of the A $^1\Sigma^+$ state of ^6LiH .

v	$B(v)(\text{cm}^{-1})$	$G(v)(\text{cm}^{-1})$	$R_-(\text{\AA})$	$R_+(\text{\AA})$
-1/2	2.9113	0	2.5900	
0	2.9262	133.94	2.2283	3.0001
1	2.9488	418.62	2.0226	3.2870
2	2.9626	734.72	1.9059	3.4748
3	2.9680	1074.45	1.8223	3.6256
4	2.9656	1431.84	1.7566	3.7579
5	2.9560	1802.32	1.7023	3.8794
6	2.9396	2182.40	1.6561	3.9944
7	2.9171	2569.34	1.6162	4.1052
8	2.8890	2960.95	1.5811	4.2133
9	2.8558	3355.37	1.5500	4.3198
10	2.8180	3750.92	1.5222	4.4258
11	2.7763	4146.01	1.4971	4.5320
12	2.7311	4539.07	1.4742	4.6393
13	2.6830	4928.57	1.4531	4.7484
14	2.6325	5313.05	1.4335	4.8599
15	2.5802	5691.23	1.4151	4.9742
16	2.5266	6062.14	1.3977	5.0915

Table XXIII. Rydberg-Klein-Rees potential energy curve of the $A^1\Sigma^+$ state of ^6LiD .

v	$B(v)(\text{cm}^{-1})$	$G(v)(\text{cm}^{-1})$	$R_-(\text{\AA})$	$R_+(\text{\AA})$
-1/2	1.6777	0	2.5806	
0	1.6819	99.68	2.2628	2.9380
1	1.6889	309.28	2.0760	3.1931
2	1.6939	538.61	1.9678	3.3609
3	1.6969	783.66	1.8896	3.4943
4	1.6980	1041.29	1.8276	3.6092
5	1.6972	1309.04	1.7759	3.7125
6	1.6944	1584.96	1.7316	3.8083
7	1.6898	1867.48	1.6927	3.8987
8	1.6833	2155.29	1.6581	3.9853
9	1.6749	2447.27	1.6271	4.0692
10	1.6647	2742.41	1.5990	4.1512
11	1.6527	3039.78	1.5733	4.2321
12	1.6389	3338.50	1.5498	4.3124
13	1.6234	3637.74	1.5281	4.3926
14	1.6061	3936.77	1.5080	4.4730
15	1.5870	4234.98	1.4895	4.5537
16	1.5663	4532.00	1.4724	4.6348
17	1.5438	4827.73	1.4570	4.7157

A comparison of the equilibrium internuclear distance, R_e obtained from various individual analysis of the isotopic molecules is shown in Table XXIV. The X state shows better agreement than the A state because of the more harmonic nature of the X state as compared to the almost flat bottom of the A state potential.

By investigating the different isotopic species, ^6LiH , ^6LiD , ^7LiH , and ^7LiD , of lithium hydride, mass-reduced analyses can produce an isotopically combined RKR potential curve and possibly more evidence of the Born-Oppenheimer breakdown of the A $^1\Sigma^+$ state than was previously pointed out. (27) We are now preparing further manuscripts detailing the mass-reduced analysis for the spectroscopic constants and potential energy curves for the X $^1\Sigma^+$ and A $^1\Sigma^+$ states of the isotopic lithium hydrides (similar to that carried out already for the isotopic mercury hydrides (27)) using the basic spectroscopic data and conventional analyses reported herein.

Table XXIV. Comparison of the equilibrium internuclear distances, R_e , of various isotopic combination of lithium hydride.^a

Isotope	$R_e''(\text{\AA } ^1\Sigma^+)$	$R_e'(\text{\AA } ^1\Sigma^+)$
^7LiH	1.5957	2.5911
^7LiD	1.5953	2.5858
^6LiH	1.5958	2.5900
^6LiD	1.5952	2.5806

^a E. F. Pearson and W. Gordy, Phys. Rev. A 177, 59(1969) give an isotopically combined value $R_e'' = 1.59490 \pm 0.00002 \text{ \AA}$ from microwave spectra of ^6LiD and ^7LiD , in excellent agreement with the present results.

V. CONCLUSIONS

Spectroscopic analysis of the $A^1\Sigma^+ \rightarrow X^1\Sigma^+$ bands of the isotopic lithium hydrides has been reported, along with reanalysis of the data of Crawford and Jorgensen. The anomalous behavior of the $A^1\Sigma^+$ has been further substantiated. Preliminary isotopic comparisons and potential energy curves have been reported, but full "mass-reduced" analyses (27) is clearly called for to fully utilize this information. These analyses will be reported in subsequent publications.

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