

# Laser-Induced Fluorescence of the $B^1\Pi-X^1\Sigma^+$ Band System of the Isotopic Lithium Hydrides<sup>1</sup>

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Resonance fluorescence series in the  $B^1\Pi-X^1\Sigma^+$  band system of the isotopic lithium hydrides were observed for the first time. Six series of  $^7\text{LiD}$  and eight of  $^6\text{LiH}$  were excited by a frequency-doubled dye laser pumped by a frequency-doubled YAG laser. These observations have provided experimental data to compare with previous theoretical transition probabilities (W. T. Zemke, K. R. Way, and W. C. Stwalley, *J. Chem. Phys.* **69**, 402–408 (1978)). Excellent correspondences between the observed fluorescence intensities and the theoretical results have been realized.

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## I. INTRODUCTION

Lithium hydride, LiH, has been the object of intense theoretical and spectroscopic interest since the 1930s. Since it is the simplest neutral stable heteronuclear molecule, for a long time it has been a molecule for testing a variety of quantum-mechanical techniques (1). The availability of four common isotopes with significantly different reduced mass allows a detailed examination of the breakdown of the Born–Oppenheimer approximation (2) and the RKR semiclassical approximation (3). Quite accurate theoretical calculations of potential energy curves and other properties (e.g., transition dipole moment functions) over a wide range of internuclear distances for the lowest singlet states ( $X^1\Sigma^+$ ,  $A^1\Sigma^+$ , and  $B^1\Pi$ ) of lithium hydride are available (4). Recently Zemke *et al.* (5, 6) have reported the radiative transition probabilities between these three electronic states. For the  $B-X$  system, the radiative emissions from the uppermost level of the  $B$  state ( $v' = 2$  for  $^6\text{LiH}$  and  $^7\text{LiH}$ ;  $v' = 3$  for  $^6\text{LiD}$  and  $^7\text{LiD}$ ) are strong to the very high vibrational levels of the  $X$  state near the dissociation limit (6).

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Spectroscopically, the  $A-X$  band system has been extensively studied (7-16). By studying the  $A-X$  laser-induced fluorescence (LIF) spectra, the potential energy curves of the ground electronic state of the LiH isotopes have been well determined up to near the dissociation limits (13-14, 16). On the other hand, for the  $B-X$  band system only the absorption spectra of  $^7\text{LiH}$  and  $^6\text{LiD}$  were first observed and analyzed by Velasco (17). Later Stwalley *et al.* (18) identified a few more transitions for the  $^7\text{LiD}$  molecule. Thus far no  $B-X$  emission spectra have been reported. It is noted (19) that the  $B^1\Pi$  state is very weakly bound; with a binding energy of only  $\sim 290\text{ cm}^{-1}$ , it is able to sustain only three or four rotationless vibrational levels. Finally we note that Moers *et al.* (20) have recently measured radiative lifetimes for  $B^1\Pi$  state levels by measuring broadband fluorescence (320-400 nm). These lifetimes also agree well with the calculations of Zemke *et al.* (6).

In this effort, we were aiming at (1) observing  $B-X$  emission spectra for the first time by using LIF techniques and (2) experimentally determining the  $B-X$  fluorescence intensity progressions, which have been theoretically calculated by Zemke *et al.* (6) for the  $^7\text{LiH}$  molecule. In Section II experimental details are described. In Section III the observations of the  $B-X$  band fluorescence of  $^7\text{LiD}$  and  $^6\text{LiH}$  are presented and the observed fluorescence intensities are compared with their theoretical counterparts.

## II. EXPERIMENTAL DETAILS

A 30-Hz Nd:YAG-pumped dye laser (Quanta Ray DCR2A) was frequency doubled in an angle-tuned KD\*P crystal. In order to cover the whole  $B-X$  band system, several dye mixtures of Rhodamine 590, 610, and 640 and Kiton Red 620 laser dyes were used. The output energy of the UV laser was typically  $200\text{ }\mu\text{J}$  in a 10-ns pulse. The laser was focused through a 50-cm quartz lens to a spot near the oven center. Two cross heat-pipe ovens were used for the  $^7\text{LiD}$  and  $^6\text{LiH}$  molecules, respectively. They were normally operated at pressures between 0.5 and 1 Torr by using helium as a buffer gas. For the  $^7\text{LiD}$  experiment, the heat-pipe oven contained isotopically enriched lithium-7 (99.8%) metal; for the  $^6\text{LiH}$  experiment, the heat-pipe oven contained the isotopically enriched lithium-6 (95.5%) metal. The induced fluorescence was collected from a perpendicular arm with a quartz lens and focused onto the slit of a McPherson 0.35-m scanning monochromator equipped with a 1200-line/mm grating. The resolved spectrum was detected with a cooled S-20 photomultiplier. The detector signal was fed into a boxcar-averager-gated-integrator system and averaged over 100 samples; the output was then recorded on a strip chart recorder.

## III. RESULTS

Since the  $\Lambda$ -type doubling in the  $^1\Pi$  electronic state would lead to two electronic component states,  $^1\Pi^-$  and  $^1\Pi^+$ , the  $R,P$ -branch transitions or the  $Q$ -branch transitions of the  $B-X$  band system of interest may be separately excited in the electric dipole approximation (21).

### A. $^7\text{LiD}$

The  $B-X$  excitation wavelengths of  $^7\text{LiD}$  can be readily obtained from previously reported absorption frequencies (17, 18). Six series of the  $B-X$  resonance fluorescence

of this molecule have been recorded in the spectral range between 285 and 700 nm. Note that the lithium atomic lines, particularly the  $4d-2p$  line (460.3 nm), were used as fluorescence wavelength references to which all the other peaks were measured. These LIF spectra have been interpreted by using the known molecular constants of the  $B^1\Pi$  state (19) and the  $X^1\Sigma^+$  state (16). The assignments have been further confirmed through the comparison between the observed fluorescence intensities and their theoretical counterparts (see Section C). The observed transition wavelengths, fluorescence intensities (uncalibrated) and calculated radiative transition probabilities of four selected series are listed in the Appendix.

### B. ${}^6\text{LiH}$

A portion of the  ${}^6\text{LiH}$  excitation spectrum in the range 290.8–293.0 nm is shown in Fig. 1. This spectrum was taken by observing resonance fluorescence at 445.0 nm through a monochromator with a 150- $\mu\text{m}$  slit width for which the observing spectral bandwidth (FWHM) is  $\sim 0.3$  nm. Only 4 stronger transition series,  $B(0, 3)-X(0, 2)$ ,  $B(0, 3)-X(0, 4)$ ,  $B(0, 5)-X(0, 5)$ , and  $B(0, 7)-X(0, 6)$ , each of which led to a resonance fluorescence peak near 445.0 nm (445.02 nm for (0, 3), 445.10 nm for (0, 5), and 445.05 nm for (0, 7), respectively), were detected although 16 series belonging to the  ${}^6\text{LiH } B-X(0, 0)$  band system could be excited within this exciting range (290.8–293.0 nm) and could be detected using detection wavelengths other than 445.0 nm. Since no absorption data were available for this molecule, these transitions were interpreted through the intensity calculations (see Section C). The  $B(0, 5)-X(0, 5)$  fluorescence peaks, located between 400 and 530 nm, were thus confirmed in terms of peak position and relative fluorescence intensity. The observed  $B-X$  transition series of  ${}^7\text{LiD}$  and  ${}^6\text{LiH}$  are summarized in Table I.

### C. Intensity Calculations

To calculate the transition probabilities, the related potential energy curves and transition dipole moment functions were needed. For the  $B^1\Pi$  state, the IPA potentials

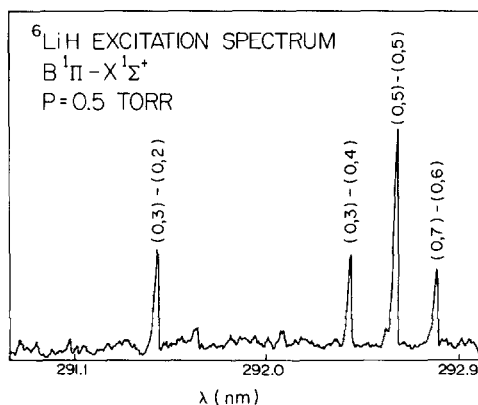


FIG. 1. The  ${}^6\text{LiH}$  dye laser excitation spectrum in the range 290.8–293.0 nm, using 445.0 nm detection (see text for discussion).

TABLE I

The Observed  $B^1\Pi-X^1\Sigma^+$  LIF Transition Series of the Isotopic Lithium Hydrides

Molecule	$\lambda_{\text{exc}}(\text{nm})$	$\nu_{\text{exc}}(\text{cm}^{-1})$	B - X ( $v', J'$ ) - ( $v'', J''$ )	$v''^{\text{a}}$
$^7\text{LiD}$	301.7	33135.9	(0, 9) - (1, 10)	16
	302.0	33102.9	(0, 11) - (1, 11)	21
	298.1	33536.0	(1, 2) - (1, 2)	24
	298.15	33530.4	(1, 4) - (1, 3)	25
	290.0	34472.7	(1, 4) - (0, 5)	26
	289.6	34520.3	(1, 3) - (0, 4)	25
$^6\text{LiH}$	292.8	34143.0	(0, 7) - (0, 6)	b
	292.6	34166.4	(0, 5) - (0, 5)	14
	292.4	34189.7	(0, 3) - (0, 4)	b
	292.2	34213.1	(0, 4) - (0, 4)	b
	291.5	34295.3	(0, 3) - (0, 2)	b
	290.65	34395.6	(1, 1) - (0, 2)	b
	290.4	34425.2	(1, 1) - (0, 1)	17
	290.3	34437.0	(1, 2) - (0, 1)	19

Note.  $\lambda_{\text{exc}}$  (nm) is the excitation wavelength (air) with uncertainty  $\pm 0.1$  nm.  $\nu_{\text{exc}}$  ( $\text{cm}^{-1}$ ) is the corresponding vacuum frequency.

<sup>a</sup> The highest observed vibrational quantum number of the lower electronic state.

<sup>b</sup> Not measured.

of  $^7\text{LiD}$  and  $^6\text{LiH}$  of Vidal and Stwalley (19) were used; for the  $X^1\Sigma^+$  state, the IPA potentials of  $^7\text{LiD}$  and  $^6\text{LiH}$  of Chan *et al.* (16) were used. For both molecules the ab initio transition dipole moment function of Docken and Hinze (4) was used. Using the INTENSITY program (22), possible B-X rotational-vibrational transitions of  $^7\text{LiD}$  and  $^6\text{LiH}$  were calculated. As shown in Figs. 2 and 3, the observed relative fluorescence intensities (uncalibrated) are in good agreement with their theoretical counterparts.

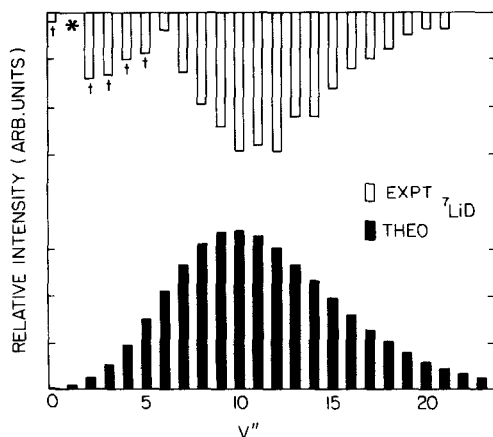


FIG. 2. A comparison of the observed fluorescence intensities and their theoretical counterparts for the  $^7\text{LiD } B(0, 11)-X(1, 11)$  series; \* denotes the laser line; † indicates that a portion of this intensity is due to the  $\text{Li}_2 \text{C-X}$  band system.

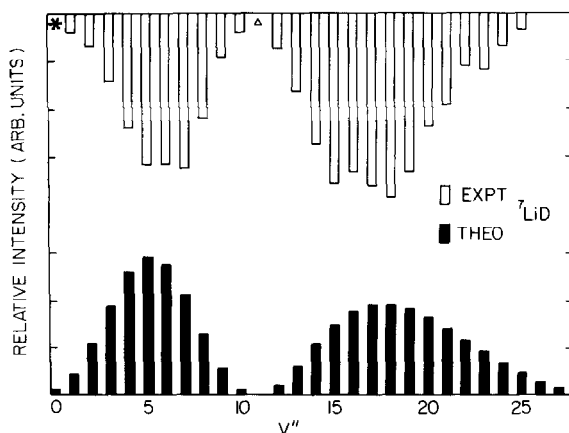


FIG. 3. A comparison of the observed fluorescence intensities and their theoretical counterparts for the  ${}^7\text{LiD } B(1, 3)-X(0, 4)$  series; \* and  $\Delta$  denote the laser line and an unobserved peak, respectively.

Note that in Fig. 2 the somewhat stronger intensities of the  $v'' = 0-5$  peaks are due to the simultaneous excitation of the  $\text{Li}_2 C^1\Pi_u-X^1\Sigma_g^+$  band system. In Fig. 3, only the  $P$ -branch peaks of the  $B(1, 3)-X(0, 4)$  series are compared, and it is demonstrated that the unobserved ( $v' = 1$  to  $v' = 11$ ) fluorescence peak exactly corresponds to the minimum radiative transition probability. Thus we are confident that we are indeed dealing with the  $B-X$  band system of the isotopic lithium hydrides. It should also be noted that these calculations are in very good agreement with the earlier and slightly less accurate work of Zemke *et al.* (6). We consider the older work to be less accurate because the IPA potentials we have used were not then available.

#### D. Discussion

Although the  $B^1\Pi$  state of the isotopic lithium hydrides is very weakly bound and its dissociation energy  $D_e$  was less than  $kT/2$  during these experiments, applying laser-induced fluorescence techniques, we have been able to observe its resonance fluorescence for the first time. We have now provided experimental evidence for the previous theoretical calculations of the  $B-X$  band fluorescence intensity progressions (6). However, we did not observe a rather interesting phenomenon where very strong fluorescence from the  $v' = 2$  level of  ${}^6\text{LiH}$  or the  $v' = 3$  level of  ${}^7\text{LiD}$  would peak near the lithium ( $2p-2s$ ) atomic line (670.7 nm). It appears more efforts are desirable in studying this region. After this work was finished, we noted that Moers *et al.* (20), who measured the radiative lifetimes of the  $B^1\Pi$  state of  ${}^7\text{LiH}$  and  ${}^7\text{LiD}$ , also did not observe the  $v' = 2$  fluorescence of  ${}^7\text{LiH}$  or the  $v' = 3$  fluorescence of  ${}^7\text{LiD}$ .

#### APPENDIX

This appendix presents some laser-induced fluorescence results for  ${}^7\text{LiD}$ . For each series ( $B(v', J')-X(v'', J'')$ ), the following quantities are listed (from left to right):  $v''$ , the vibrational quantum numbers;  $J''$ , the rotational quantum numbers;  $\lambda_{\text{obs}}$ , the observed transition wavelengths (air) with uncertainty  $\pm 0.1$  nm;  $\nu_{\text{obs}}$ , the vacuum frequency in  $\text{cm}^{-1}$ ;  $I_{\text{obs}}$ , the observed (uncalibrated) relative peak heights with each series normalized to the transition(s) to the  $v''$  level which is calculated to correspond



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