# $C^1\Sigma^+$ State of $^7LiH$

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The $^7$LiH $C^1\Sigma^+$ excited electronic state has been observed for the first time by pulsed optical−optical double resonance fluorescence depletion spectroscopy. Several rovibrational levels of the $A^1\Sigma^+$ excited electronic state have been selected as the intermediate states. Among 10 vibrational states of the $C^1\Sigma^+$ electronic state 81 rovibrational levels have been observed. The spectral assignment is identified from the observed rotational structures, term values, and vibrational level spacings and from a comparison with recent accurate ab initio calculations of Boutalib and Gadea [*J. Chem. Phys.* **1992**, *97,* 1141].

## Introduction

Lithium hydride, the simplest neutral heteronuclear molecule, has been the object of intensive theoretical and spectroscopic interest since the 1930s. A comprehensive and critical review for this molecule has been compiled recently by Stwalley and Zemke.[1] However, up to now only the lowest three electronic states, $X^1\Sigma^+$, $A^1\Sigma^+$, and $B^1\Pi$, have been identified and characterized by conventional spectroscopy[2−7] and by laser spectroscopy,[8−16] although some other electronic states have been predicted theoretically for almost 3 decades.[17−22]

Recently Boutalib and Gadea[22] have performed accurate ab initio calculations for all electronic states below the ionic limit of LiH. They predicted that the next higher excited singlet electronic state, lying above the excited $B^1\Pi$ electronic state, would be an intriguing double-well electronic state, denoted as $C^1\Sigma^+$. They also tabulated its 44 possible vibrational level spacings along with some experimental suggestions. Partly due to the above theoretical predictions and partly due to our previous fluorescence experiment on the LiH B−X system,[16] we have carried out a further spectroscopic effort on this molecule.

In this article, we present our very first spectroscopic results on the excited $C^1\Sigma^+$ electronic state of $^7$LiH. By taking advantage of known $A^1\Sigma^+-X^1\Sigma^+$ radiative transition probabilities[23] and known molecular constants of the $X^1\Sigma^+$ and $A^1\Sigma^+$ states,[2,3,24] as well as using a pulsed optical−optical double resonance (OODR) fluorescence depletion spectroscopic technique, we have succeeded in observing 10 vibrational levels of this upper excited electronic state.

## Experimental Section

Our experimental setup is sketched in Figure 1, in which the parts for signal processing are not shown. A frequency-doubled 10-Hz Q-switched Nd:YAG laser (Lumonics YM600), having a pulse width of 7 ns and operating at a typical pulse energy of 40 mJ, was used to pump two different dye lasers (Lumonics HD500), both having a 6-ns laser pulse. The first dye laser was frequency-doubled by a frequency-doubling system (Inrad autotracker II) in order to generate an ultraviolet PUMP laser for exciting the LiH $A^1\Sigma^+$ state. For covering the optimal spectral range of five LiH A(7−11)−X(0) bands, a methanol solution of a laser dye LDS698 (Exciton) was used as the active medium. The second dye laser was used as a PROBE laser for probing the excited electronic state of interest. The methanol solutions of three laser dyes, LDS698, LDS722, and LDS759, were used separately as active media. The laser pulse energy and the laser line width were 0.1 mJ and 0.1 cm$^{-1}$ for the PUMP laser and 1 mJ and 0.04 cm$^{-1}$ for the PROBE laser. The laser frequency was calibrated by a reference spectrum of $I_2$ and/or an optogalvanic spectrum, taken either with a Ne-filled sodium/potassium hollow cathode lamp (Perkin Elmer) or with an Ar-filled chromium hollow cathode lamp (Hitachi). The uncertainty of the frequency measurements is about 0.04 cm$^{-1}$. The PUMP laser beam and the PROBE laser beam were aligned in a counterpropagating direction along the axis of the longer arms of a five-arm crossed heat-pipe oven. The PROBE laser pulse was set to have an 8-ns optical delay behind the PUMP laser pulse. The heat-pipe oven, containing 10 g of naturally abundant lithium metal (STREM, 3 N) in its center, was normally operated under 1 Torr of Ar gas and at the temperature 953 K. At 953 K, LiH molecules most likely populate at the rotational level of $J'' = 6$. The induced A−X fluorescence, by observation from a perpendicular arm, was first filtered by a spectral bandpass filter, which was a simple combination of a few optical filters, or a monochromator (ARC SP275) when a resolved fluorescence spectrum was necessary for the purpose

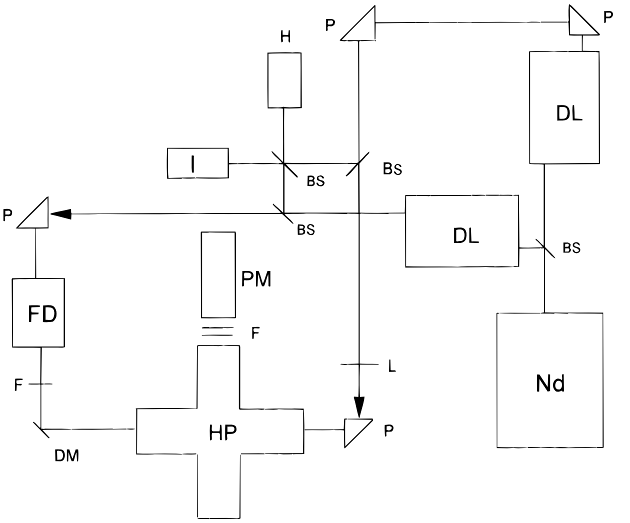

**Figure 1.** Experimental schematics: BS, beam splitter; DL, dye laser; DM, dichroic mirror; F, optical filter; FD, frequency-doubling system; H, hollow cathode lamp; HP, lithium heat-pipe oven; I, iodine cell; L, focusing lens; Nd, Nd:YAG laser; P, A 90° prism; PM, photomultiplier tube.

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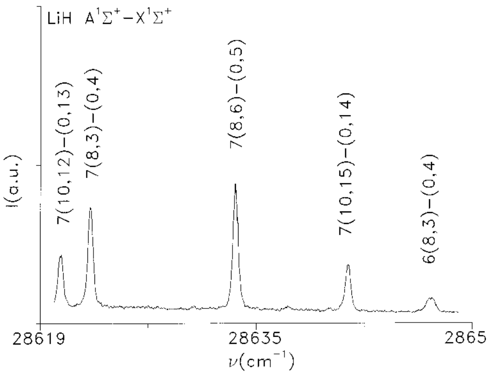

**Figure 2.** Excitation spectrum of the $A^1\Sigma^+-X^1\Sigma^+$ electronic transition of LiH. The assignments 7(10,12)−(0,13) and 6(8,3)−(0,4) represent for the $^7$LiH A(10,12)−X(0,13) transition and the $^6$LiH A(8,3)−X(0,4) excitation transition, respectively.

of spectral identification. The transmitted fluorescence was then detected by a photomultiplier (EMI 9863QB) detector. The detector signal was fed into a boxcar-averager-gated-integrator system; the averaged output was then recorded by a personal computer. In this work, three types of spectra were measured. The first was a fluorescence excitation spectrum in which the LiH A−X fluorescence was detected by scanning the PUMP laser. The second was a resolved fluorecence spectrum in which the PUMP laser was fixed to a particular A−X rovibrational transition and then the induced fluorescence was resolved by a monochromator. And the third was an OODR fluorescence depression spectrum in which the PUMP laser was fixed to a particular LiH A−X rovibrational transition and then the variation of the induced fluorescence intensity was monitored by scanning the PROBE laser.

## Results and Discussion

During the preliminary experiments, all pertinent rovibrational transitions within the five A(7−11)−X(0) bands were first identified by the fluorescence excitation spectra. A portion of the LiH excitation spectrum in the range of 28 620−28 650 cm$^{-1}$ is shown in Figure 2, in which the four stronger excitation peaks, denoted as 7(10,12)−(0,13), 7(8,3)−(0,4), 7(8,6)−(0,5), and 7(10,15)−(0,14), were attributed to the $^7$LiH molecule, and the weaker peak 6(8,3)−(0,4) near 28 648 cm$^{-1}$ to the $^6$LiH molecule. The line width of each observed spectral peak is about 0.26 cm$^{-1}$, close to the Doppler width of 0.24 cm$^{-1}$ of the LiH molecule at 953 K. This spectrum was taken by observing resonance fluorescence at 383 nm through a combination of two optical filters, for which the resultant spectral bandwidth (full width at half-maximum) (fwhm) is about 40 nm. For spectral assignments, one may first compare the frequency of each spectral peak with the transition frequencies listed in the literature[2,3] for these two isotopic LiH molecules. Using known molecular constants,[25−27] one may also find out if there is any $Li_2$ $C^1\Pi_u-X^1\Sigma_g{}^+$ electronic transition that would occur at the same frequency. And finally the spectral assignment may be further confirmed by taking a resolved fluorescence spectrum, with which one may compare the spectral positions of each fluorescence series with those predicted by known molecular constants[24] and their relative fluorescence intensities with known radiative transition probabilities.[23]

In the following, we present our first OODR results of the $C^1\Sigma^+$ electronic state. Seven rotational energy levels ($J' = 4-10$) among each of the two vibrational states $v' = 8$ and $v' = 9$ of the $^7$LiH $A^1\Sigma^+$ electronic state were selected as intermediate states, of which each state was excited via an R-type transition. The OODR fluorescence depletion spectrum has been taken over the active spectral range of three different laser dyes, LDS698, LDS722, and LDS759. Among 10 vibrational states of the upper electronic state 81 rovibrational levels ($J = 3-11$) have been observed. Two observed OODR spectral portions via the intermediate rovibrational level (8,6) are shown in Figure 3, in which spectrum a portrays the P(6) and R(6) transitions to the $v + 2$ vibrational state and spectrum b to the $v + 1$ vibrational states. One can tell from Figure 3 that each vibrational state permits only two different OODR spectral transitions, indicating that the involved electronic state is actually a $^1\Sigma^+$ electronic state. Such a $^1\Sigma^+$ electronic state could be the ground $X^1\Sigma^+$ electronic state, if a folded OODR transition (so called a stimulated emission pumping (SEP) transition[28]) is operative, or an upper $^1\Sigma^+$ electronic state of interest, if a normal two-step OODR transition is operative.

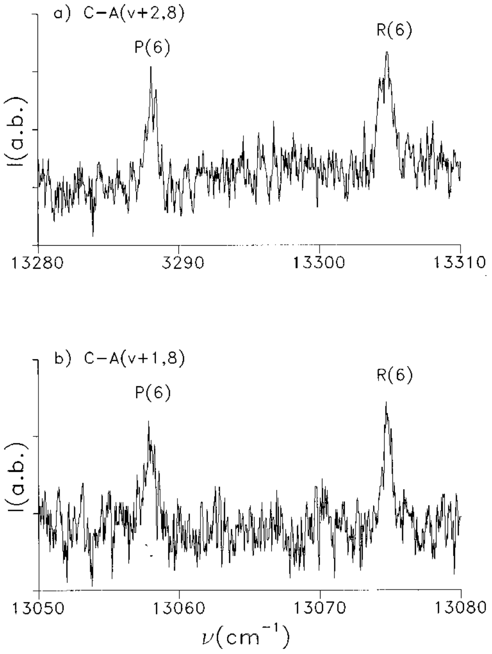

**Figure 3.** OODR spectra Of $^7$LiH. The rovibrational level (8,6) of the $A^1\Sigma^+$ electronic state was selected as an intermediate level. Spectra a and b portray the P(6) and R(6) OODR transitions to the $v + 2$ level of the $C^1\Sigma^+$ electronic state and to its $v + 1$ level, respectively.

The observed OODR transitions for the observed 10 vibrational states should not be the SEP-type transitions because (a) the derived rotational constants $B_v$, of 0.629−0.659 cm$^{-1}$, presented in Table 1 below, are not among the $B_v$ range[29], of 1.09−7.41 cm$^{-1}$, for the 23 vibrational levels of the ground $X^1\Sigma^+$ electronic state; (b) the observed vibrational level spacings $\Delta G_v$, of 200−235 cm$^{-1}$, are neither among the $\Delta G_v$ range, of 760−810 cm$^{-1}$, expected for the three possible SEP vibrational levels $v'' = 13-15$ of the ground $X^1\Sigma^+$ electronic state; and (c) the observed $\Delta G_v$ tends to decrease gradually as the frequency of the PROBE laser is tuned higher; in contrast to what is expected for the SEP-type transitions the vibrational level spacing would increase gradually. Thus, the above points demonstrate that the involved $^1\Sigma^+$ electronic state must be an upper electronic state of interest.

The term energy of each observed rovibrational level of the upper electronic state is obtained by adding together the PROBE frequency and the term value[30] of the intermediate rovibrational level of the $A^1\Sigma^+$ electronic state. The term energies for observed rovibrational levels are plotted in Figure 4, and the derived molecular constants are listed in Table 1. From Table 1, one may easily see that (a) the 10 observed vibrational levels, covering 42 358−44 318 cm$^{-1}$, overlap energetically with the ab initio $C^1\Sigma^+$ state[22], whose vibrational levels locate theoreti-

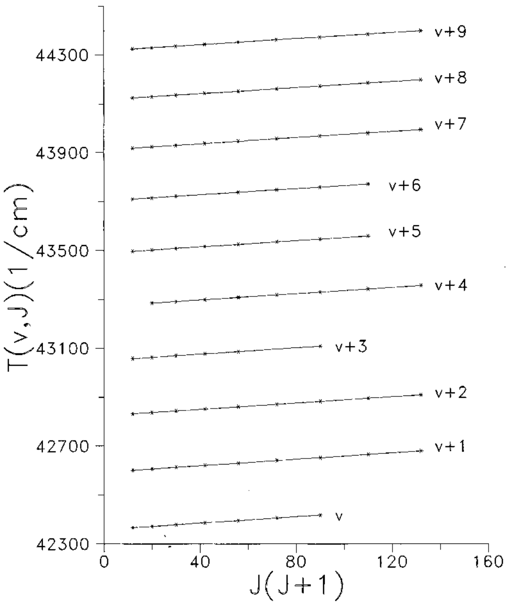

**Figure 4.** Plot of the term energies $T(v,J)$ of the 81 observed rovibrational levels, among the 10 vibrational levels of the $^7$LiH $C^1\Sigma^+$ electronic state, with respect to the $J(J+1)$ product.

**TABLE 1: Spectroscopic Constants of the 10 Observed Vibrational Levels of the $C^1\Sigma^+$ State of $^7$LiH**[a]

| $v$ | $G_v$ | $\Delta G_v$ | $10B_v$ | $\sigma$ |
|---|---|---|---|---|
| $v$ | 42 358.90(5) | 234.65 | 6.590(9) | 0.07 |
| $v+1$ | 42 593.55(12) | 230.93 | 5.584(17) | 0.21 |
| $v+2$ | 42 824.48(7) | 226.09 | 6.513(10) | 0.12 |
| $v+3$ | 43 050.57(7) | 221.94 | 6.503(13) | 0.10 |
| $v+4$ | 43 272.51(12) | 217.37 | 6.445(18) | 0.21 |
| $v+5$ | 43 489.88(8) | 213.26 | 6.410(13) | 0.12 |
| $v+6$ | 43 703.14(9) | 208.91 | 6.375(14) | 0.14 |
| $v+7$ | 43 912.05(6) | 204.86 | 6.353(8) | 0.10 |
| $v+8$ | 44 116.91(5) | 200.58 | 6.312(8) | 0.10 |
| $v+9$ | 44 317.59(15) | | 6.294(14) | 0.18 |

[a] The term energy (cm$^{-1}$) is expressed in the form $T(v,J) = G_v + B_v(J(J+1))$. $v$, $G_v$, $\Delta G_v$, $B_v$, and $\sigma$ represent the vibrational quantum number, vibrational term value, vibrational level spacing, rotational constant, and the uncertainty of overall fitting, respectively. Parenthesized numbers stand for 1 standard deviation in the last few digits.

cally between 38 900 and 47 400 cm$^{-1}$ above the potential minimum of the ground $X^1\Sigma^+$ electronic state; (b) the nine derived vibrational level spacings, of 200−235 cm$^{-1}$, are among the tabulated theoretical values, of 72−285 cm$^{-1}$; and (c) the derived $B_v$ values, 0.629−0.659 cm$^{-1}$, are close to the theoretical $B_v$ values, 0.62−0.66 cm$^{-1}$, which were calculated by using an eigenvalue program[31] with the ab initio $C^1\Sigma^+$ potential energy curve. The above three points demonstrate unambiguously that the $^7$LiH $C^1\Sigma^+$ electronic state is spectrally observed for the first time.

It is noted that, after a careful comparison between the observed vibrational spacings and the tabulated theoretical values,[22] one may assign the lowest observed vibrational level to the $v = 12$ level, i.e., the thirteenth vibrational level. However, a truly vibrational assignment has to be determined by a further study, in which a relative consistency[32] between the observed spectral intensities and the quantum-mechanical transition intensities has to be demonstrated. Work on the absolute vibrational assignment of the observed vibrational levels and the true potential energy curve for the $C^1\Sigma^+$ electronic state is still in progress, and the related results will be presented in a forthcoming paper.

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