Radiative and Nonradiative Lifetimes for
Vibrational Levels of the $A^1\Sigma^+$ State of $^7\text{LiH}^*$

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ABSTRACT

Newly calculated radiative transition probabilities for the $A\ ^1\Sigma^+ \rightarrow X\ ^1\Sigma^+ (v' - v'')$ emission bands of ^7LiH (preceding paper) are used to calculate the radiative lifetime of the various vibrational levels ($0 \leq v' \leq 26$) of $A\ ^1\Sigma^+ \text{LiH}$. For higher levels, an estimate of the bound-to-free emission probability is also needed and included. For the highest two levels, $A\ ^1\Sigma^+ \rightarrow B\ ^1\Pi$ emission is possible and has been included, but makes a negligible contribution to the radiative lifetime. The calculated radiative lifetimes increase with v' from 28.9 nsec at $v' = 0$ to 36.1 nsec at $v' = 16$ and then decrease to 27.1 nsec at $v' = 26$. They are found to be in good agreement with measured total lifetimes, implying the nonradiative (predissociative) lifetime for the measured levels is $\geq 10^{-7}$ seconds, in accord with simple theoretical expectations.

I. INTRODUCTION

The simplest neutral heteronuclear molecule, LiH, has been the object of intense interest¹ since the 1930's. We have embarked on a long-term project to fully understand the spectroscopy of the three lowest singlet states ($X^1\Sigma^+$, $A^1\Sigma^+$ and $B^1\Pi$) of LiH for a variety of reasons discussed elsewhere.²

As an initial step in this project, we have calculated full potential curves for these states and with these curves all relevant radiative transition probabilities.³ In this paper we first (Section II) present results on the radiative lifetime of the $A^1\Sigma^+$ state, using radiative transition probabilities of the $A^1\Sigma^+ \rightarrow X^1\Sigma^+$ bands of LiH (preceding paper³). In Sections III-V, we discuss additional lifetime contributions from $A \rightarrow X$ bound-free emission, $A \rightarrow B$ bound-bound emission, and $A \rightarrow X$ nonradiative predissociation. In Section VI, we compare our calculated radiative lifetimes with experimental results and argue this substantiates our Section V estimates of negligible predissociation lifetime.

II. $A \ ^1\Sigma^+ \rightarrow X \ ^1\Sigma^+$ BOUND-BOUND EMISSION

The Einstein $A_{v'}$ coefficient arising from all bound-bound transitions of the $A \ ^1\Sigma^+ \rightarrow X \ ^1\Sigma^+$ band system may be obtained simply from the expression

$$A_{v'} \text{ (bound-bound)} = \sum_{v''=0}^{23} A_{v',v''} \quad (1)$$

The coefficients $A_{v',v''}$ may be directly obtained from the quantities $I(v',v'')$ in Table V of reference 3 by multiplying by the constant factor 7.2356×10^{-6} . These $A_{v'} \text{ (bound-bound)}$ values are listed in Table I. Given our previous estimates of the numerical accuracy of individual I values, our $A_{v'}$ values should be accurate to $< 10^5 \text{ sec}^{-1}$, i.e. all figures given. The bound-bound $A_{v'}$ values show an irregular but nearly monotonic decrease from $v' = 0$ to $v' = 25$, followed by a startling but understandable increase at $v' = 26$. This abrupt increase is due to the long-range molecule ($v' = 26$) + long-range molecule ($v'' = 23$) transition discussed elsewhere.⁴⁻⁶

Table I. The bound-bound and bound-free contributions and the total Einstein A_v , coefficients and radiative lifetimes of the various vibrational levels v' of the $A\ ^1\Sigma^+$ state of ^7LiH . Only the $A\ ^1\Sigma^+ \rightarrow X\ ^1\Sigma^+$ emission makes a significant contribution to these excited state lifetimes.

v'	$A_v, (10^6 \text{ sec}^{-1})$			$\tau_{v'}, (\text{nsec})$
	bound-bound	bound-free	total	
0	34.6	0.0	34.6	28.9
1	33.9	0.0	33.9	29.5
2	33.1	0.0	33.1	30.2
3	32.4	0.0	32.4	30.8
4	31.7	0.0	31.7	31.5
5	31.2	0.0	31.2	32.0
6	30.7	0.0	30.7	32.6
7	30.1	0.1	30.2	33.1
8	29.3	0.4	29.7	33.6
9	28.5	0.8	29.3	34.2
10	27.0	1.9	28.9	34.6
11	22.8	5.4	28.2	35.5
12	21.0	7.0	28.0	35.7
13	19.5	8.4	27.9	35.8
14	19.1	9.0	28.1	35.6
15	18.8	9.5	28.3	35.4
16	16.8	11.8	28.6	34.9
17	14.9	14.1	29.0	34.5
18	15.0	14.7	29.7	33.7
19	12.9	17.7	30.6	32.6
20	11.8	20.0	31.8	31.5
21	11.4	21.5	32.9	30.4
22	9.7	24.5	34.2	29.3
23	9.0	26.3	35.3	28.3
24	8.5	27.8	36.3	27.5
25	9.1	27.8	36.9	27.1
26	21.1 ^a	15.8	36.9	27.1
atom	----	----	37.2	26.9

^a Of which 20.8 arises from $v' = 26 \rightarrow v'' = 23$.

III. $A \ ^1\Sigma^+ \rightarrow X \ ^1\Sigma^+$ BOUND-FREE EMISSION

The Einstein $A_{V'}$ coefficient arising from bound-free transitions into the $X \ ^1\Sigma^+$ continuum must be added to the bound-bound coefficient to obtain the total $A_{V'}$ coefficient due to $A \ ^1\Sigma^+ \rightarrow X \ ^1\Sigma^+$ transitions:

$$A_{V'} \text{ (total)} = A_{V'} \text{ (bound-bound)} + A_{V'} \text{ (bound-free)} \quad (2)$$

where $A_{V'} \text{ (bound-bound)}$ has already been given in Table I. While the full bound-free spectrum (such as we have published⁷ for $B \ ^1\Pi \rightarrow X \ ^1\Sigma^+ \ ^7\text{LiH}$) could be calculated and integrated over to obtain an accurate $A_{V'} \text{ (bound-free)}$, we have chosen to make an approximation in dealing with this bound-free term:

$$A_{V'} \text{ (bound-free)} = (7.2356 \times 10^{-6}) \quad [D(R_{V',+})]^2 q_{V',\text{continuum}} \nu_{V',\text{continuum}}^3 \quad (3)$$

where $D(R_{V',+})$ is the dipole strength function at the outer classical turning point of level v' , $q_{V',\text{continuum}} (= 1 - \sum_{v''} q_{V',v''})$, with the $\sum_{v''} q_{V',v''}$ in Table III of reference 3) is the Franck-Condon factor between the level v' and all energies in the $X \ ^1\Sigma^+$ continuum (including those representing absorption!), and $\nu_{V',\text{continuum}}$ is the transition frequency between the level v' and the $X \ ^1\Sigma^+$ asymptote ($\text{Li } (2^2\text{S}) + \text{H } (1^2\text{S})$). While we plan to examine the accuracy of this approximation in further detail, we feel it should be satisfactory (to say 10%) for the following reasons. From the Franck-Condon principle and the given potential curves², it appears that for low to medium v' the dominant bound-free transitions will arise in the region of the classical satellite (see Figure 3 of reference 3). They will occur primarily at distances near $R_{V',+}$ (approximately the R-centroid) and the continuum final states will be of low energy, near the $X \ ^1\Sigma^+$ asymptote. For higher v' , the vibrational wavefunction becomes dominated by the regions

near $R_{v',\pm}$, but bound-free transitions near $R_{v',-}$ are exceedingly unlikely so only those near $R_{v',+}$ should be important. Finally, for the long-range level $v' = 23$, only the outermost portion of the wavefunction is important^{5,6}, so again $D(R_{v',+})$ is appropriate. Moreover the wavefunction near turning points automatically corresponds to low kinetic energy and thus leads to low kinetic energy final continuum states. Examining this to higher order, we note the $v_{v',\text{continuum}}$ values we use in equation 3 may be slightly too large because there must be some finite kinetic energy in the final state; however, the actual R-centroids should tend to be slightly outside $R_{v',+}$, where $D(R)$ is larger. Thus for this particular system, approximate equation 3 may turn out to be exceptionally accurate because of a cancellation of errors ($|D|^2$ slightly too small, v^3 slightly too large).

In any case, we have used equation 3 to estimate $A_{v'}$, (bound-free) and combined it (equation 2) with $A_{v'}$, (bound-bound) to obtain $A_{v'}$, (total) in Table I. $A_{v'}$, (total) and $A_{v'}$, (bound-free) are also shown in Figure 1. Note the smooth decrease and then increase in $A_{v'}$, (total) despite the somewhat irregular behavior in the continuum contribution alone. This is a necessary but not sufficient condition for equation 3 to be a reasonable approximation.

Figure 1. The total Einstein $A_{v'}$ coefficient from Table I for $A \text{ } ^1\Sigma^+ (v') \rightarrow X \text{ } ^1\Sigma^+$ emission in ^7LiH . The continuum contribution ($A_{v'}(\text{bound free})$) is also shown. Note that the total $A_{v'}$ value remains smoothly varying despite the irregular behavior of the continuum contribution alone.

IV. $A \ ^1\Sigma^+ \rightarrow B \ ^1\Pi$ BOUND-BOUND EMISSION

The highest v' levels of the $A \ ^1\Sigma^+$ state are above one or more of the levels $v'' = 0, 1$ or 2 of the $B \ ^1\Pi$ state of ^7LiH . Hence there is the possibility of $A \rightarrow B$ emission. However, the frequencies are extremely small and the $A_{v',v''}$ values completely negligible compared to those given above; the precise numbers are given in Table II for completeness, but they will be discussed in greater detail elsewhere.*

Although we have not calculated the $A_{v',v''}$ for $A \ ^1\Sigma^+ \rightarrow A \ ^1\Sigma^+$ (IR) emission, we expect it will likewise be negligible.

Table II. Einstein $A_{v',v''}$ coefficients (in units of 10^6 sec^{-1} as used in Table I) for the $A \ ^1\Sigma^+ \rightarrow B \ ^1\Pi$ emission bands of ^7LiH .

v'	$A_{v',v''}$			
	$v'' =$	0	1	2
25		-	-	2.19(-14)
26		1.98(-14)	8.01(-18)	1.96(-12)

V. $A\ ^1\Sigma^+ \rightarrow X\ ^1\Sigma^+$ NONRADIATIVE PREDISSOCIATION

The $A\ ^1\Sigma^+$ and $X\ ^1\Sigma^+$ states of ^7LiH represent a classical example of ionic-covalent configuration mixing.⁹ In this case the diabatic ionic and covalent states strongly repel each other near a crossing distance of $\sim 4\ \text{\AA}$ and the nuclear motion becomes overwhelmingly adiabatic. However there is a finite probability of predissociation from the A to the X state because of the nonadiabatic coupling between the two electronic states. The lack of line broadening (such as is found for NaI) clearly indicates the predissociation lifetime must be $> 10^{-12}$ sec. Using, for example, the approximate treatment of Rapp¹⁰, we estimate $P_{12} \approx 10^{-7}$ per crossing; for a typical vibrational frequency of $10^{13}\ \text{sec}^{-1}$, this implies a predissociation lifetime (for vibrational levels passing through the crossing region) of $\sim 10^{-6}$ sec. We are, of course, using only a simple model here; we plan full close-coupled calculations at a later date to more accurately explore this lifetime and in particular its vibrational quantum number dependence especially for low v' where the crossing region is near $R_{v',+}$. In any case, it seems that the observation of nonradiative predissociation via its effect on the observed lifetime will be difficult but possible to observe depending on the precise magnitude of the predissociative lifetime.

VI. COMPARISON WITH EXPERIMENT

The total lifetimes of various (v', J') levels of the $A \ ^1\Sigma^+$ state of ^7LiH have been observed in two different laboratories.^{11,12} As can be seen in Table III, our calculated values (for $J' = 0$) from Table I are in excellent agreement with observations in each of these laboratories (for $J' > 0$). If the experimental results appeared significantly shorter than our calculated radiative lifetimes, this would suggest a contribution from nonradiative predissociation; no such shortening is however observed. Indeed we would argue that the agreement implies the predissociation lifetime is $> 10^{-7}$ sec in each case.

Finally, it might be noted that our approximate $A_{v',v''}$ (bound+free) expression is in no way tested by these data since only $v' \leq 8$ are involved and thus $q_{v',\text{continuum}}$ is quite small.

Table III. Comparison of calculated radiative and experimental (total) lifetimes τ (in nsec) for vibrational levels v' of the $A\ ^1\Sigma^+$ state of ^7LiH . J' values are given in parentheses.

v'	Calc.	Expt.
2	30.2(0)	$29.4 \pm 1.3(3)^a$
5	32.0(0)	$33.0 \pm 3.5(0)^b$, $32.6 \pm 3.0(5)^b$, $32.6 \pm 3.0(10)^b$, $29.0 \pm 3.2(15)^b$
7	33.1(0)	$36.9 \pm 1.9(12)^a$
8	33.6(0)	$32.2 \pm 5.9(15)^b$

^a Reference 11.

^b Reference 12.

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