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Radiative Lifetimes for Vibrational
Levels of the B $^1\Pi$ State of $^7\text{LiH}^*$

Warren T. Zemke
Department of Chemistry
Wartburg College
Waverly, IA 50677

and

William C. Stwalley
Departments of Chemistry and Physics
University of Iowa
Iowa City, IA 52242

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ABSTRACT

Newly calculated radiative transition probabilities for the $B^1\Pi \rightarrow X^1\Sigma^+$ and $A^1\Sigma^+$ emission bands of ^7LiH (preceding paper) are used to calculate the radiative lifetime of the various vibrational levels ($0 \leq v' \leq 2$) of $B^1\Pi$ LiH . An estimate of the $B \rightarrow X$ bound-free emission probability is also included, although the lifetimes are dominated by the $B \rightarrow X$ bound-bound emission. The calculated radiative lifetimes increase rapidly with v' from 11.3 nsec at $v' = 0$ to 17.0 nsec at $v' = 1$ and then 24.0 nsec at $v' = 2$.

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 a 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 $B\ ^1\Pi$ state, using radiative transition probabilities of the $B\ ^1\Pi \rightarrow X\ ^1\Sigma^+$ and $B\ ^1\Pi \rightarrow A\ ^1\Sigma^+$ bands of LiH (preceding paper³). In Section III, we estimate an additional lifetime contribution from $B \rightarrow X$ bound-free emission. Finally in Section IV we briefly discuss our results and their limitations.

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

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

$$A_{v'} (\text{bound-bound}) = \sum_{v''=0}^{23} A_{v',v''} (B \rightarrow X) + \sum_{v''=0}^{25} A_{v',v''} (B \rightarrow A) \quad (1)$$

(since $A\ ^1\Sigma^+ v'' = 26$ is above $v' = 0, 1$, and 2 ; also $v'' = 25$ is above $v' = 2$ and is excluded from the $v' = 2$ sum). 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 $\frac{1}{2} \times 7.2356 \times 10^{-6}$. These $A_{v'}$ (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 a monotonic decrease from $v' = 0$ to $v' = 2$ in each band system. This is primarily a result of the change in the dominant v^3 factors, which decrease monotonically also.

It should be noted that the highest $X\ ^1\Sigma^+$ vibrational levels, $v'' = 22$ and 23 , make large contributions to the $v' = 2$ lifetime ($\sim 12\%$ and $\sim 19\%$ of $A_{v'}$ ($B \rightarrow X$ bound-bound), respectively. Thus a lifetime calculation which ignored the "long-range levels"⁴⁻⁶ in the uppermost region of the $X\ ^1\Sigma^+$ potential would be seriously in error.

Table I. The $B \rightarrow X$ (bound-bound and bound-free) and $B \rightarrow A$ (bound-bound, there being no bound-free) contributions and the total Einstein A_{ν} coefficients and radiative lifetimes of the various vibrational levels ν' of the $B \ ^1\Pi$ state of ^7LiH . Note that $B \rightarrow X$ bound-bound emission dominates the A_{ν} total.

ν'	A_{ν} (10^6 sec^{-1})			total	τ_{ν} (nsec)
	$B \rightarrow X$		$B \rightarrow A$		
	bound-bound	bound-free	bound-bound		
0	85.5	0.0	3.1	88.4	11.3
1	57.5	0.0	1.4	58.9	17.0
2	36.6	4.9	0.2	41.7	24.0
atom	-	-	-	37.2	26.9

III. $B\ ^1\Pi + X\ ^1\Sigma^+$ BOUND $\rightarrow$ FREE EMISSION

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

$$A_{v'}(\text{total}) = A_{v'}(B \rightarrow X \text{ and } B \rightarrow A \text{ bound} \rightarrow \text{bound}) + A_{v'}(B \rightarrow X \text{ bound} \rightarrow \text{free}) \quad (2)$$

where $A_{v'}(\text{bound} \rightarrow \text{bound})$ has already been given in Table I. While the full $B \rightarrow X$ bound $\rightarrow$ free spectrum (such as we have published⁷ for $B\ ^1\Pi + X\ ^1\Sigma^+ \text{ } ^7\text{LiH}$) could be calculated and integrated over to obtain an accurate $A_{v'}(\text{bound} \rightarrow \text{free})$, we have chosen to make an approximation⁸ in dealing with this bound $\rightarrow$ free term:

$$A_{v'}(\text{bound} \rightarrow \text{free}) = \left(\frac{1}{2} \times 7.2356 \times 10^{-6}\right) |D(R_{v',+})|^2 q_{v',\text{continuum}} \nu_{v',\text{continuum}}^3 \quad (3)$$

where $D(R_{v',+})$ is the $B \rightarrow X$ 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 VI 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 reasons given previously.⁸ In particular, the contribution is important only for the long-range level $v' = 2$, where only the outermost portion of the wavefunction is important^{5,6}, so $D(R_{v',+})$ 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 $\nu_{v',\text{continuum}}$ 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, approximate equation 3 may turn out to be exceptionally accurate because of a cancellation of errors ($|D|^2$ slightly too small, v^2 slightly too large).

In any case, we have used equation 3 to estimate $A_{v,}$ ($B + X$ bound $\rightarrow$ free) and combined it (equation 2) with $A_{v,}$ ($B + X$ and $B + A$ bound $\rightarrow$ bound) to obtain $A_{v,}$ (total) in Table I. Note the smooth decrease in $A_{v,}$ (total) toward the atomic value. This is a necessary but not sufficient condition for equation 3 to be a reasonable approximation.

IV. DISCUSSION

We believe the lifetimes given in Table I should be fairly accurate (~10%). The $B^1\Pi - B^1\Pi$ (IR) transitions should be negligible, as should be the predissociation of the $B^1\Pi^+$ component because of extremely weak mixing with the $X^1\Sigma^+$ state. It should be noted that all our calculations have been carried out for the (unphysical) $J' = 0$ level. Large rotational effects on the lifetime are expected, particularly for $v' = 2$, but we will not examine them at this time. No experimental lifetimes yet exist, but they should be measurable using a doubled dye laser.

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