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Dissociation energies of ${}^7\text{LiD}^*$

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The $B\,{}^1\Pi - X\,{}^1\Sigma^+$ absorption spectrum of ${}^7\text{LiD}$ has been reexamined. Evidence for an additional vibrational level ($v'=3$) in the upper state has been found. Because this vibrational level is extremely close to the dissociation limit, only $J'=1$ and $J'=2$ levels occur. This additional information provides an improved dissociation limit of $34671.5 \pm 0.4\text{ cm}^{-1}$, 1.5 cm^{-1} lower and 20 times more precise than previous results. From this result, dissociation energies of $19767.7 \pm 0.4\text{ cm}^{-1}$ for the X state, $8588.4 \pm 0.9\text{ cm}^{-1}$ for the A state, and $201.8 \pm 0.4\text{ cm}^{-1}$ for the B state of ${}^7\text{LiD}$ are derived.

INTRODUCTION

Even though lithium hydride has been called "the work-bench of the theoretical chemist" by Bender and Davidson,¹ remarkably little electronic spectroscopic work on the isotopic lithium hydrides has been carried out since the 1930's.²⁻⁴

Recently, the $B\,{}^1\Pi - X\,{}^1\Sigma^+$ absorption spectrum of ${}^7\text{LiH}$ has been reanalyzed to obtain a more accurate potential curve and dissociation limit than had previously been available.⁵ In the course of this analysis, it became obvious that an additional vibrational level ($v'=3$) not previously reported³ must exist for ${}^7\text{LiD}$. Moreover, observation of this additional level, predicted to be quite weakly bound, would be expected to provide a more accurate dissociation limit for ${}^7\text{LiD}$ given an analysis such as reported for ${}^7\text{LiH}$ in Ref. 5. These predictions have in fact been borne out by experimental observations, and the new observations have in turn been analyzed to obtain improved dissociation energies for ${}^7\text{LiD}$.

PREDICTIONS

The existence of a $v'=3$ level can be directly predicted from the mass-reduced analysis⁶ briefly described in Ref. 5. However, since a fairly accurate potential curve (G of Ref. 5) is available for the $B\,{}^1\Pi$ state, one can directly calculate (See Table I) the expected eigenvalues for $J'=1$ and 2 from the radial Schrödinger equation.⁷ The $J'=3$ level is predicted not to exist as its "energy" (estimated by extrapolation) is well above the centrifugal barrier; i.e., rotational predissociation occurs.

EXPERIMENTAL OBSERVATIONS

The $B-X$ absorption spectrum³ has been reexamined and 4 lines of the 3-1 band clearly identified (Table II) with estimated uncertainties of $\pm 0.04\text{ cm}^{-1}$ as in previous work.³ As previously noted³ for other bands in this system, the Q branch is most intense, the R branch weaker, and the P branch still weaker. In particular, the $P(2)$ and $P(3)$ lines were not clearly evident above the noise, as in the previously reported³ 2-0 and 2-1 bands of ${}^7\text{LiH}$ and the 2-0 band of ${}^7\text{LiD}$. This is in accord with the Hönl-London factors for these transitions,⁸ which predict the following intensity ratios:

$$P(2) : Q(1) : R(0) = 1 : 3 : 2 ,$$

$$P(3) : Q(2) : R(1) = 2 : 5 : 3 .$$

The corresponding 3-0 band is weaker than the 3-1 band and has not yet been conclusively identified.

The term values corresponding to the assignments are given in Table I. The following molecular constants for the $v'=3$ level of the B state are obtained:

$$\nu_0(3-1) = 33640.6\text{ cm}^{-1} ,$$

$$B_3 = 0.32\text{ cm}^{-1} ,$$

although since the rotational constant is derived from a single spacing, and since D_3 is probably appreciable,⁹ its value should not be taken very seriously. Utilizing these data in the determination of rotational and vibrational constants, we have

$$B_v(Q\text{ lines}) = 1.904 - 0.425(v + \tfrac{1}{2}) - 0.005(v + \tfrac{1}{2})^2 \\ - 0.001(v + \tfrac{1}{2})^3$$

$$G_v = 178.70(v + \tfrac{1}{2}) - 29.13(v + \tfrac{1}{2})^2 - 3.51(v + \tfrac{1}{2})^3$$

that may be compared with the constants previously given.³

DISCUSSION

The energy level results shown in Table I are in good agreement when the uncertainty ($\sim \pm 2\text{ cm}^{-1}$) in the poten-

TABLE I. Predicted B state of ${}^7\text{LiD}$ eigenvalues $E(v'=3, J')$ in cm^{-1} (measured with respect to the B state zero point level $E(0,1)$ are compared with the corresponding observed term values (see Table II).

J'	$E(v'=3, J')$	
	Predicted	Observed ^a
1	199.5	200.60
2	200.6	201.87

^aThe corresponding energies with respect to $v''=0, J''=0$ in the X state are 34670.19 and 34671.46 cm^{-1} , respectively.

TABLE II. The 3-1 band of the $B-X$ system of ${}^7\text{LiD}$.

J	$P(J)$	$Q(J)$	$R(J)$
0			33641.23
1		33633.04	33634.37
2	...	33617.94	
3	...		

tial energy curve used in the eigenvalue calculations is taken into account.

The dissociation limit may be readily predicted on the same basis as in Ref. 5. The $J'=2$ and 3 centrifugal barriers, respectively, are 0.27 ± 0.02 and 0.75 ± 0.04 cm^{-1} high and occur at 24.1 and $20.8a_0$, clearly even farther into the long range region than the relevant barriers⁵ for ${}^7\text{LiH}$. Since no broadening of the $J'=2$ level is seen, this reference level must be at most 0.2 cm^{-1} above the dissociation limit. Since the line-like continuum structure corresponding to $J'=3$ (like that in Fig. 4 of Ref. 5) is not seen experimentally, one may say that the $J'=2$ level should probably not be bound by more than 0.3 cm^{-1} (corresponding to the potential G of Ref. 5) and certainly should not be bound by more than 0.4 cm^{-1} . Combining this result with the experimental energy of the $J'=2$ level, 34671.46 ± 0.04 cm^{-1} , obtains a dissociation limit of 34671.5 ± 0.4 cm^{-1} , which may be compared with the previous³ estimate 34673 ± 8 cm^{-1} . This dissociation limit corresponds to the following D_0 values in cm^{-1} : 19767.7 ± 0.4 for the $X^1\Sigma^+$ ground state, 8588.4 ± 0.9 for the $A^1\Sigma^+$ state,¹⁰ and 201.8 ± 0.4 for the $B^1\Pi$ state.¹¹ Finally, it should be noted that these D_0 values may be combined with estimates of the zero-point energies (e.g., from Ref. 3) to estimate D_e . However, a theoretical reanalysis of the regions near R_e in the X , A , and B states is now in progress, which should yield better

estimates of the zero-point energies and their uncertainties for both ${}^7\text{LiH}$ and ${}^7\text{LiD}$. This should make possible an accurate examination of the degree of breakdown of the Born-Oppenheimer approximation for comparison with theoretical estimates.¹²

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†Alfred P. Sloan Foundation Fellow.

‡Phillips Petroleum Research Fellow (1972-1973).

¹C. F. Bender and E. R. Davidson, *J. Chem. Phys.*, **49**, 4222 (1968).

²The only published electronic spectroscopic work we are aware of are Refs. 3 and 4 below, although new work is in progress at both The Institute of Optics and The University of Iowa.

³R. Velasco, *Can. J. Phys.*, **35**, 1204 (1957).

⁴I. Fernandez-Florez and R. Velasco, *Opt. Pura Apl.*, **2**, 123 (1969).

⁵K. R. Way and W. C. Stwalley, *J. Chem. Phys.*, **59**, 5298 (1973).

⁶A more complete analysis by one of us (WCS), using the isotopic mercury hydrides as an example, is in progress. Preliminary results were presented as Paper AA5, "The Utility of Mass-Reduced Quantum Numbers", at The 27th Symposium on Molecular Structure and Spectroscopy, Columbus, Ohio, June 1972.

⁷The authors wish to thank Prof. K. Sando for making available his eigenvalue program, described in K. Sando, *Mol. Phys.*, **23**, 413 (1972).

⁸G. Herzberg, *Spectra of Diatomic Molecules* (Van Nostrand, Princeton, NJ, 1950), 2nd ed., p. 208.

⁹The eigenvalue calculations indicate $D_3 \approx 0.006$ cm^{-1} .

¹⁰The $v=0$ level of the A state is not directly observed (only $v \geq 1$), so an additional ± 0.5 cm^{-1} is included.

¹¹Note that D_0 for a Π state is measured from the zero-point level $E(v=0, J=1)$ to dissociation.

¹²P. R. Bunker, *J. Mol. Spectrosc.*, **28**, 422 (1968).