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# A study of the $E^1\Sigma_g^+$ state of $^7\text{Li}_2$ by pulsed optical-optical double resonance spectroscopy

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The results of pulsed optical-optical double resonance spectroscopic studies of the  $E^1\Sigma_g^+$  state of  $^7\text{Li}_2$  are presented. Observations were carried out on the  $v = 0$  through  $v = 12$  levels. A set of Dunham molecular constants was derived and an RKR potential was generated. Franck-Condon factors for transitions to the  $A^1\Sigma_u^+$  state were determined for the range of observed vibrational levels. An apparent deviation from the expected dissociation energy is observed consistent with the suggestion that a double minimum exists for this state.

## I. INTRODUCTION

The numerous advantages of the method of pulsed optical-optical double resonance (OODR) spectroscopy as applied to homonuclear diatomic molecules have been amply demonstrated in previous work from this laboratory.<sup>1-4</sup> Among these advantages are the simplification and ease of assignment of the observed spectra. The stepwise double excitation also gains access to those excited electronic states having the same inversion symmetry as that of the ground state. These excited states are inaccessible by conventional one-photon absorption.

Pulsed OODR experiments have currently revealed 18 new *gerade* states of  $^7\text{Li}_2$ . Of these, the  $F^1\Sigma_g^+$  and  $G^1\Pi_g$  states have been well characterized by extensive observations<sup>3,4</sup> and preliminary results on the  $E^1\Sigma_g^+$  state have been reported. Presented in this work is a thorough treatment of the lower portion of the  $E^1\Sigma_g^+$  state of  $^7\text{Li}_2$  in which a substantially larger set of experimental data has been obtained and used in the analysis.

The electronic states of  $^7\text{Li}_2$  are of interest for a number of reasons. Although  $\text{Li}_2$  is an attractive object of theoretical study,<sup>5</sup> only four excited states had been observed prior to the present pulsed OODR experiments, and only two of these had received detailed study. This is in sharp contrast to the wealth of information available for molecular hydrogen, the only stable homonuclear diatomic with fewer electrons.<sup>6</sup>  $^7\text{Li}_2$  has also received attention as a possible active medium for new lasers. However, the  $E^1\Sigma_g^+$  state is of particular interest for additional reasons. A previous study of the  $F^1\Sigma_g^+$  state revealed the presence of a homogeneous perturbation by another  $^1\Sigma_g^+$  state. An anticrossing between it and the  $E^1\Sigma_g^+$  state is an obvious possibility, but an analysis of the perturbation requires a more detailed knowledge of the  $E^1\Sigma_g^+$  state potential curve. In addition, theoretical studies suggest that the presence of the ion-pair potential of  $\text{Li}_2$  affects the  $E^1\Sigma_g^+$  potential producing what may be a double minimum analogous to that observed for several of the excited states of molecular hydrogen.

Besides reporting a more extensive experimental study of the lower portion of the  $E^1\Sigma_g^+$  state, this work also presents a set of Dunham molecular constants, an RKR potential curve, and Franck-Condon factors for transi-

tions from the  $A^1\Sigma_u^+$  state. The data and analysis includes the range of vibrational levels from  $v^* = 0$  through  $v^* = 12$  in the  $E^1\Sigma_g^+$  state.

## II. EXPERIMENTAL

The pulsed OODR spectrum of the  $E^1\Sigma_g^+$  state was produced by excitation of selected  $A^1\Sigma_u^+ - X^1\Sigma_g^+$  transitions followed by further excitation into the  $E^1\Sigma_g^+$  state. The excitation of the  $E^1\Sigma_g^+$  state spectrum was detected by the green  $X^1\Sigma_g^+ - B^1\Pi_u$  fluorescence resulting from the decay of  $E^1\Sigma_g^+$  state.

The preliminary work<sup>4</sup> on the  $E^1\Sigma_g^+$  state was restricted to the study of only a few vibrational levels. This restriction was due to the limited wavelength range accessible with the nitrogen laser pumped dye lasers used in those experiments. To complete the measurements, the wavelength region had to be extended into the near infrared region. The experimental arrangement for the extended measurements was similar to that described earlier<sup>4</sup> but with several important modifications. The dye lasers were pumped with a frequency-doubled Nd:YAG laser operating at 10 Hz and producing 170 mJ pulses at 532 nm. The pump dye laser consisted of a grating tuned oscillator-amplifier combination utilizing an intracavity prism beam expander and was operated with 0.5–1.2 mJ per pulse output. The probe dye laser was a grazing incidence grating tuned oscillator-amplifier combination<sup>7</sup> followed by a high pressure (20 atm)  $\text{H}_2$  gas filled cell to produce stimulated Raman scattering. The probe laser was operated to produce up to 0.5 mJ per pulse at the first Stokes shifted wavelength. The unshifted probe dye laser radiation, anti-Stokes, and second Stokes radiation were eliminated with filters and dielectric coated mirrors. The remaining first Stokes radiation was time delayed and overlapped with the pump laser beam position in the heat pipe cell containing the lithium vapor. The first Stokes radiation was scanned in wavelength by scanning the probe dye laser. The pump and probe dye lasers produced radiation with approximately 0.5 and 0.2  $\text{cm}^{-1}$  linewidths, respectively.

Calibration of the pulsed OODR spectra was achieved by sampling the unshifted probe laser beam and simultaneously recording the spectra of neon and argon excited in optogalvanic cells together with fringes pro-

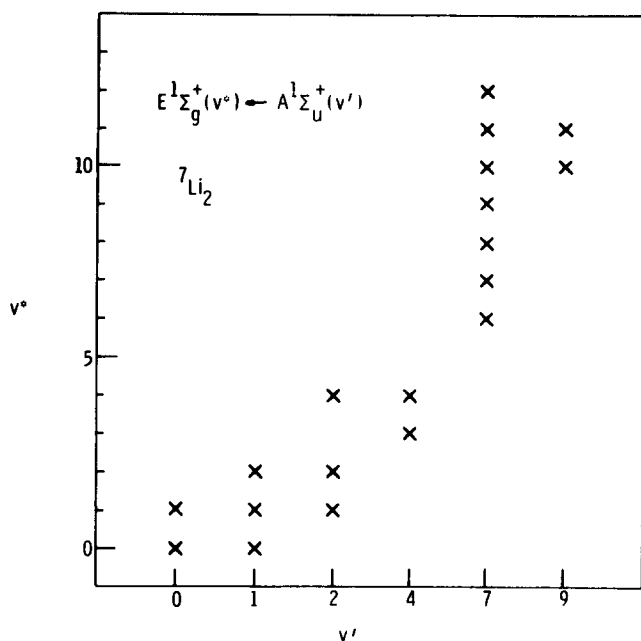


FIG. 1. The range of vibrational states  $v^*$  used for determination of the molecular constants for the  $E^1\Sigma_g^+$  state of  ${}^7\text{Li}_2$  using different levels  $v', J'$  of the  $A^1\Sigma_u^+$  as the intermediate state. The observations using the  $v'=0$  and 1 were also used to establish the vibrational state numbering. The observations were incomplete above  $v^*=4$  for  $v'=4$  and below  $v^*=6$  for  $v'=7$  and below  $v^*=10$  for  $v'=9$ .

duced by a Fabry-Perot interferometer. Spectral and calibration data were recorded both on a chart recorder and in digital form. OODR spectral line positions could be determined in either format with an estimated accuracy of  $0.2\text{ cm}^{-1}$ . The remaining experimental details are similar to those described previously.<sup>1-4</sup>

### III. OBSERVED SPECTRA AND ANALYSIS

Transitions to the  $E^1\Sigma_g^+$  state from selected levels of the  $A^1\Sigma_u^+$  state were observed. The measured wavelengths were converted to energies referred to the bottom of the  $A^1\Sigma_u^+$  state potential well using the known  $A^1\Sigma_u^+$  state molecular constants.<sup>8</sup>

The vibrational numbering was initially established by observing the lower limit of  $E^1\Sigma_g^+$  vibrational states when several different  $A^1\Sigma_u^+$  state vibrational levels were pumped as shown in Fig. 1. No bands below that assigned to  $v^*=0$  were observed when the  $v'=0$  and  $v'=1$  levels of the  $A^1\Sigma_u^+$  state were pumped. These vibrational assignments were confirmed by comparing observed band intensities with calculated Franck-Condon factors. Rotational assignments were straightforward since the rotational quantum number of the pumped  $A^1\Sigma_u^+$  state level was known for each set of experiments.  $E^1\Sigma_g^+$  state vibrational and rotational quantum numbers  $v^*$  and  $J^*$  were assigned to approximately 700 observed transitions to states  $v^*=0$  through  $v^*=12$ . Although some transitions to what may be levels higher in energy than  $v^*=12$  were observed, these could not be assigned.

TABLE I. The Dunham coefficients that describe the  $E^1\Sigma_g^+$  state of  ${}^7\text{Li}_2$  from  $v^*=0-12$ . The quantities in parentheses are the exponents of 10 in the multiplying factor, and all values are in  $\text{cm}^{-1}$ .

$n, k$	$Y_{nk} (E^1\Sigma_g^+)$	Standard error
$T_e$	2.741 021 4 (+4)	5.7 (-2)
1, 0	2.458 767 5 (+2)	1.3 (-1)
2, 0	-2.826 675 9 (0)	9.0 (-2)
3, 0	-8.636 525 0 (-1)	2.5 (-2)
4, 0	1.133 938 8 (-1)	3.6 (-3)
5, 0	-5.424 040 4 (-3)	2.5 (-4)
6, 0	7.333 694 3 (-5)	6.5 (-6)
0, 1	5.046 892 6 (-1)	1.5 (-4)
0, 2	-8.461 363 2 (-6)	8.2 (-8)
1, 1	-9.644 284 7 (-3)	3.0 (-4)
2, 1	-3.526 908 9 (-4)	1.7 (-4)
3, 1	-1.263 909 3 (-4)	3.2 (-5)
4, 1	2.616 838 5 (-5)	2.5 (-6)
5, 1	-0.123 885 47 (-6)	6.8 (-8)
1, 2	2.336 304 7 (-7)	1.5 (-7)
2, 2	-5.639 724 8 (-7)	7.8 (-8)
3, 2	1.146 713 6 (-7)	1.2 (-8)
4, 2	-6.352 213 3 (-9)	5.4 (-10)

The assigned data were fitted by a linear least squares method<sup>9</sup> with an equation of the form

$$E(v, J) = \sum_{n,k} Y_{n,k} (v + \frac{1}{2})^n [J(J+1)]^k.$$

Preliminary calculations showed that transitions to the  $v^*=0-12$  vibrational levels in the  $E^1\Sigma_g^+$  state were fit satisfactorily with a standard error consistent with the estimated measurement uncertainty. Additional levels could not be introduced into the data set without severely disturbing the quality of the overall fit.

In the final fit of Dunham constants  $Y_{nk}$  to the observed levels of  $v^*=0-12$ , 681 transitions were used.<sup>10</sup> The range of vibrational and rotational levels used in the fit are shown in Fig. 2. The standard error of the fit was  $0.14\text{ cm}^{-1}$ . The resulting molecular constants are given in Table I. The value of  $T_e$  is referred to the

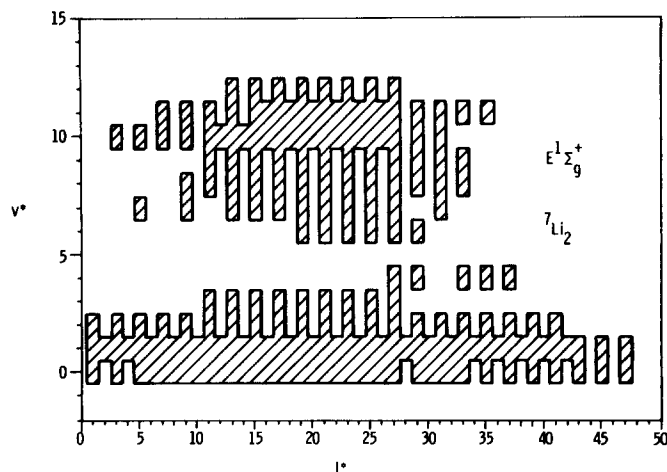


FIG. 2. The data field of values of  $v^*$  and  $J^*$  for the  $E^1\Sigma_g^+$  levels used in the evaluation of molecular constants.

TABLE II.  $G_v$  values, rotational constants  $B_v$ , and RKR potential curve for the  $E^1\Sigma_g^+$  state of  $^7\text{Li}_2$  for  $J=0$ .

$v$	$G_v$ ( $\text{cm}^{-1}$ )	$r_{\min}$ ( $\text{\AA}$ )	$r_{\max}$ ( $\text{\AA}$ )	$B_v$ ( $\text{cm}^{-1}$ )
-0.5	0.00	3.086	3.086	0.5047
0	122.13	2.903	3.301	0.4998
1	360.07	2.787	3.487	0.4891
2	587.45	2.715	3.636	0.4773
3	803.21	2.660	3.775	0.4645
4	1007.60	2.616	3.909	0.4511
5	1201.62	2.580	4.040	0.4377
6	1386.60	2.550	4.169	0.4247
7	1563.84	2.523	4.294	0.4126
8	1734.25	2.499	4.418	0.4012
9	1898.06	2.477	4.541	0.3902
10	2054.61	2.457	4.667	0.3782
11	2202.18	2.438	4.806	0.3634
12	2337.85	2.422	4.967	0.3430

bottom of the  $X^1\Sigma_g^+$  ground state potential by using the value of  $14068.307 \text{ cm}^{-1}$  for the energy of the bottom of the  $A^1\Sigma_u^+$  state well.<sup>8</sup> The observed value of  $Y_{02} = -8.46 \times 10^{-6} \text{ cm}^{-1}$  differs by about 0.5% from the value of  $-8.50 \times 10^{-6}$  calculated from the relation

$$Y_{02} = -4Y_{01}^3/Y_{10}^2,$$

which holds for most diatomic molecules.<sup>11</sup>

The molecular constants in Table I were used to calculate<sup>12</sup> a Rydberg-Klein-Rees (RKR) potential curve which is presented in Table II together with the value of

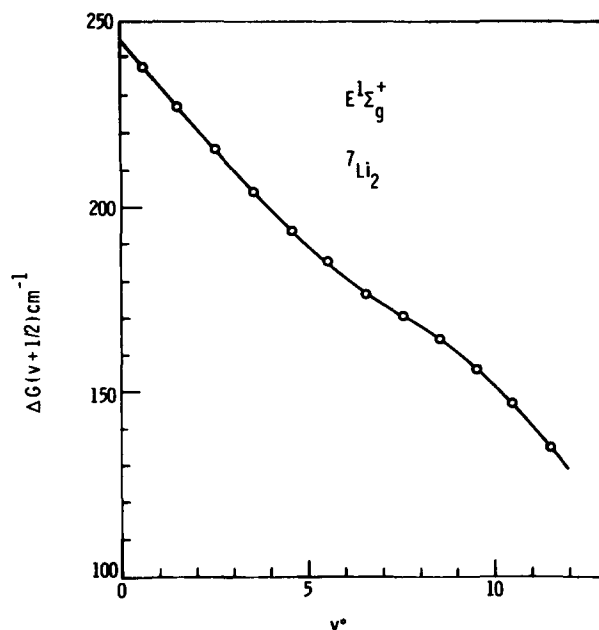
$$G_v = \sum_{n=1} Y_{n0}(v + \frac{1}{2})^n$$

and

$$B_v = \sum_{n=0} Y_{n1}(v + \frac{1}{2})^n$$

obtained from the constants in Table I.

The RKR curve was used to calculate<sup>12</sup> Franck-Condon factors for the transitions between the  $A^1\Sigma_u^+$  and  $E^1\Sigma_g^+$  states. These are given in Table III for  $J^*=0$ . Since the observed bands generally contained transitions at

FIG. 3. The variation of  $\Delta G(v + \frac{1}{2})$  with vibrational quantum number  $v$  of the  $E^1\Sigma_g^+$  state of  $^7\text{Li}_2$ .

higher  $J^*$  values, the comparison of calculated Franck-Condon factors with band intensities was actually made with a separate table computed for  $J^*=20$ . The comparison confirms the  $E^1\Sigma_g^+$  state vibrational assignments as mentioned above.

#### IV. DISCUSSION

The analysis of the spectroscopic observations of the  $E^1\Sigma_g^+$  state reveals several unusual features. First, although the lower vibrational levels appear to behave normally, observations above  $v^*=12$  were irregular and could not be assigned. A second unusual feature is that all attempts to extrapolate the observed differences between adjacent vibrational levels, shown in Fig. 3, to obtain a dissociation limit yield values which are far below the energy of the  $\text{Li}(2^2\text{S}) + \text{Li}(3^2\text{S})$  pair of atomic states which are the lowest possible dissociation

TABLE III. Franck-Condon factors ( $\times 10^3$ ) for the  $E^1\Sigma_g^+(v^*)-A^1\Sigma_u^+(v')$  transitions of  $^7\text{Li}_2$  for  $J=0$ .

$v^* \ v'$	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
0	996	3	1																		
1	3	994	1	3																	
2	1	1	990	1	8																
3		3	2	961	15	18	1														
4			6	25	874	50	38	4	1												
5				8	93	709	101	72	13	3											
6				2	4	213	476	143	119	32	9	2									
7					5		355	235	148	164	65	22	5	1							
8						8	18	451	62	106	186	107	45	13	3	1					
9						2	5	84	435	41	165	144	80	31	9	2					
10							5		199	298	28	1	101	154	120	61	23	7	2		
11							1	7	14	306	119	67	20	27	117	144	101	50	19	6	2
12								3	3	78	332	12	57	73		52	130	130	80	35	11

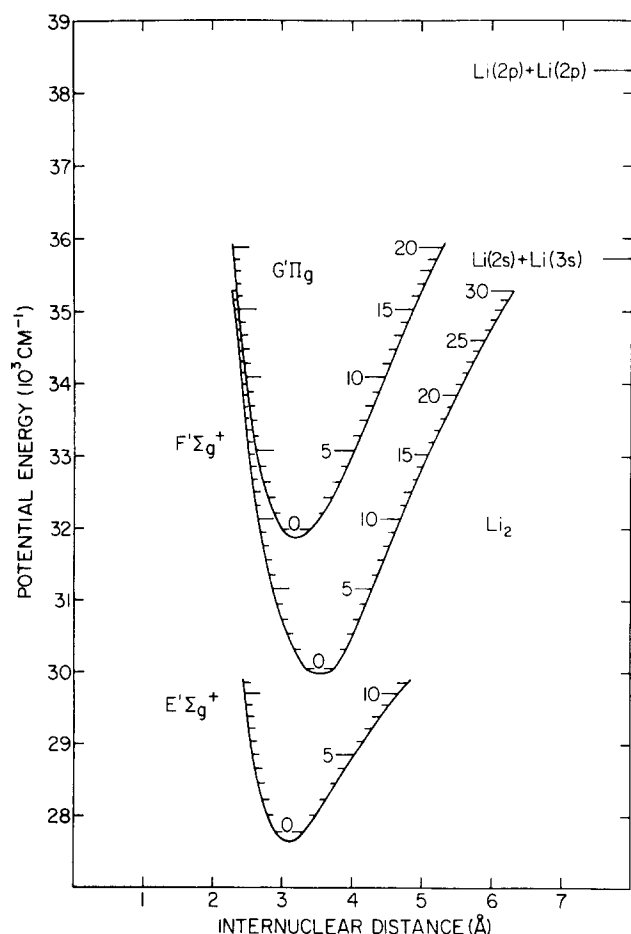


FIG. 4. The relationship of the  $E^1\Sigma_g^+$  state potential curve of  ${}^7\text{Li}_2$  to the other nearby *gerade* states observed in the pulsed OODR experiments.

products. These atomic states give an expected value of  $8312\text{ cm}^{-1}$  for the  $E^1\Sigma_g^+$  dissociation energy if the current value<sup>13</sup> of  $8516\text{ cm}^{-1}$  for the  $X^1\Sigma_g^+$  dissociation energy is used. In fact, the molecular constants predict that the uppermost bound vibrational state is  $v^*=16$ , which lies  $2660\text{ cm}^{-1}$  above the  $E^1\Sigma_g^+$  state  $T_e$  value, and places the dissociation energy over  $5000\text{ cm}^{-1}$  below the energy of the  $\text{Li}(2^2\text{S}) + \text{Li}(3^2\text{S})$  atomic states. While such dissociation energy extrapolations are only very approximate, this difference is sufficiently large to suggest a major departure from a Morse-like potential.

There are two features of the excited electronic state structure of  $\text{Li}_2$  that are likely sources for this unusual behavior of the  $E^1\Sigma_g^+$  state. First, a homogeneous perturbation has been observed for the lower portion of the  $F^1\Sigma_g^+$  state as evidence by a maximum in the  $B_v$  vs  $v$  curve for this state at low vibrational quantum numbers.<sup>4</sup> The  $B_v$  vs  $v$  curve for the  $E^1\Sigma_g^+$  state is a linear decreasing function showing no unusual behavior for the  $v^*=0-12$  levels. The  $E^1\Sigma_g^+(v=12, J=0)$  level is  $339\text{ cm}^{-1}$  below the  $F^1\Sigma_g^+(v=0, J=0)$  level, and it was noted that the irregular behavior for the  $E^1\Sigma_g^+$  commenced above  $v=12$ . If the  $F^1\Sigma_g^+$  and  $E^1\Sigma_g^+$  states were perturbing each other as, for example, the result of an anticrossing, one would expect the onset of homogeneous perturbation behavior in the  $E^1\Sigma_g^+$  state. However, the large discrepancy in ap-

parent dissociation energy cannot be accounted for if the anticrossing were the only source of the observed behavior. Another possible source of the behavior is the existence of a double minimum in the  $E^1\Sigma_g^+$  state potential. In molecular hydrogen several double minimum states are well known,<sup>14</sup> arising from the interaction with the nearby  $(+, -)$  ion pair potential. Indeed, theoretical evidence for a double minimum state correlated with the  $\text{Li}(2^2\text{S}) + \text{Li}(3^2\text{S})$  atomic states was revealed in recent calculations by Konowalow and Fish.<sup>15</sup> The  $\text{Li}_2(+, -)$  ion pair potential lies nearby, and can be the major contributing factor. While a more quantitative analysis of the shape of the upper portion of the  $E^1\Sigma_g^+$  potential curve and its possible interaction with the  $F^1\Sigma_g^+$  state must await further experimental investigation, the lower portion of the  $E^1\Sigma_g^+$  state, including the levels  $v^*=0-12$ , is now known with reasonable accuracy.

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