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Spectroscopic study of the $6^1\Pi_u$ state in Li_2

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Abstract

The $6^1\Pi_u \leftarrow X^1\Sigma_g^+$ band system in the Li_2 molecule is investigated by the polarisation labelling spectroscopy technique. The excited state is characterised by a set of Dunham coefficients describing f parity levels $v = 0 - 11$, $J = 2 - 47$ in the $^7\text{Li}_2$ isotopologue and the absolute vibrational numbering is determined by observation of the isotopic effect. The state is identified as $6^1\Pi_u(2s+4d)$ by comparison with theoretical calculations. The main equilibrium constants are $T_e = 36863.25(5) \text{ cm}^{-1}$ (with respect to the minimum of the electronic ground state), $\omega_e = 253.567(36) \text{ cm}^{-1}$, $R_e = 3.1639(2) \text{ \AA}$.

Keywords: laser spectroscopy, alkali dimers, electronic states, molecular constants, potential energy curves

1. Introduction

Polarisation labelling spectroscopy (PLS), a technique first demonstrated by Schawlow and coworkers in 1976 [1] has been widely used in studies of small molecules (see e.g. Wang and Xia [2] and references therein). In particular, the selectivity of double resonance inherent to this method allows complex molecular spectra to be resolved and assigned. For several years we have employed this powerful technique to study excited electronic states of alkali dimers, and recently have focused on the lightest of them, Li_2 . Our previous experiments furnished molecular constants and accurate potential energy curves of three excited states of lithium dimer, $C^1\Pi_u$, $2^1\Sigma_u^+$ [3] and $5^1\Pi_u$. [4] In the present work we extend our study of Li_2 to higher excitation energies (between 36800 and 39500 cm^{-1} above the minimum of the ground state potential well) and characterise experimentally a newly observed electronic state of $^1\Pi_u$ symmetry.

2. Experimental details

The experimental procedure has been described in our previous papers [3,5] so only an outline of the apparatus will be given here. The Li_2 molecules were produced by heating solid lithium (2 cm^3) of natural isotopic composition in a linear heat-pipe oven, 80 cm long and with 3 cm inner diameter. About 4 mbar of helium buffer gas was admitted to the oven before heating it to approximately 1050 K. Under these conditions the oven did not operate in a heat pipe regime [6] but instead contained a mixture of helium and metal vapour in the central zone.

As a tuneable pump light we employed frequency doubled output of a parametric oscillator/amplifier system (OPO/OPA Sunlite EX, Continuum) pumped with the third harmonic of an injection seeded Nd:YAG laser (Powerlite 8000). The laser system delivered pulses with a spectral width of about 0.16 cm^{-1} , 3 mJ energy and 10 ns duration. The

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3 wavelength calibration was effected by recording the optogalvanic spectrum of argon [7] and
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5 transmission peaks of a Fabry-Pérot etalon with FSR=1 cm⁻¹ (both signals observed at
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7 fundamental frequency of tuneable OPO/OPA radiation). The rotationally resolved spectrum
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9 of the investigated ${}^1\Pi_u \leftarrow X^1\Sigma_g^+$ transition in Li₂ was recorded in the region 255 – 280 nm.
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11 We estimate the accuracy in absolute frequency measurements to ± 0.1 cm⁻¹.
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15 As a probe (labelling) laser we used a home built dye laser (Shoshan-type design,[8]
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17 DCM dye) pumped synchronously with the same Nd:YAG laser. The dye laser operated on
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19 chosen wavelengths between 630 and 650 nm, controlled with HighFinesse WS-5 wavemeter.
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21 Alternatively, fixed frequency radiation of the Ar⁺-Kr⁺ laser (Carl Zeiss ILM120, $\lambda = 476.5$,
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23 488.0, 496.5, 501.7 or 647.1 nm) was utilized. At all the employed wavelengths the probe
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25 beam excited known transitions in the $A^1\Sigma_u^+ \leftarrow X^1\Sigma_g^+$ or $B^1\Pi_u \leftarrow X^1\Sigma_g^+$ band systems of
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27 Li₂,[9,10] thus providing labelling of individual levels in the molecular ground state which is
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29 essential for the PLS technique.
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34 The pump and probe beams co-propagated at a small angle, intersecting in the
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36 molecular sample. During a frequency scan of the pump light, the intensity of the probe beam
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38 was monitored through a crossed polariser-analyser system (Glan-Thompson prisms placed
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40 either side of the heat-pipe) so that double resonance signals appeared on a black background.
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42 Experiments were performed with linearly polarised pump light, with the plane of polarisation
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44 inclined by 45° against that of the probe light. Such an arrangement was chosen to enhance
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46 intensities of *Q* lines in the observed spectra [11] (*vide infra*). This part of the probe light that
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48 was transmitted through the analyser was directed onto the cathode of a photomultiplier tube
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50 coupled to the boxcar averager (Stanford SR250). The resulting signals were stored in a
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52 computer which simultaneously recorded the reference optogalvanic spectrum of argon
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54 together with the frequency markers from the etalon and also controlled tuning of the
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56 OPO/OPA system.
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3. Measurements and analysis

In the spectral region under investigation we observed a band system corresponding to a transition from the ground state of Li_2 , $X^1\Sigma_g^+$. As the progressions display strong Q lines, the excited state must be $^1\Pi_u$. Even a cursory inspection of the spectra shows perturbation of the upper state, resulting in irregular patterns of P , Q and R lines; often only Q lines could be reliably assigned. In the preliminary analysis we found that positions of P and R lines corresponding to excitation of e parity levels in the $^1\Pi_u$ state behaved erratically (deviations up to 3 cm^{-1}) while Q lines (leading to excitation of f parity levels) formed regular progressions. This observation suggests that the investigated state is perturbed by a neighbouring state of $^1\Sigma_u^+$ symmetry, containing only levels of e parity. However, such a $^1\Sigma_u^+$ state could not be directly seen in the spectra, presumably because of too low Franck-Condon factors for excitation from the ground molecular state of Li_2 . This made any attempt to deperturb the spectra pointless and we had to confine our analysis to the observed Q lines, i.e. to f parity levels of the investigated $^1\Pi_u$ state. Note that we have encountered similar problems in the previous experiments on high electronic states in Li_2 , [3] Na_2 [12] and K_2 . [13,14]

A total of 124 Q lines were assigned to the investigated $^1\Pi_u \leftarrow X^1\Sigma_g^+$ system, spanning the range of vibrational and rotational quantum numbers in the upper state $v = 0 - 11$, $J = 2 - 47$ (positions of all the recorded lines are available from the authors upon request). Although a slight breakdown of the Born-Oppenheimer approximation in Li_2 is well known, [3,4] observation of the isotope effect in $^7\text{Li}_2$ and $^6\text{Li}^7\text{Li}$ molecules allowed to establish unambiguously the absolute vibrational numbering in the upper state. However, even when taking into account an isotopic shift of the dissociation limit of the observed state (see [15] for the relevant atomic data) the lines of the mixed isotopic form deviated from the expected positions by more than twice the experimental uncertainty. Therefore they were excluded

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3 from the fit of molecular constants which is based solely on the results for the ${}^7\text{Li}_2$
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5 isotopologue. The measured wave numbers of lines were fitted to differences in term values, ν
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12 = $T(\nu', J') - T(\nu'', J'')$, of the upper and lower levels, which were expressed by the standard
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Dunham formula

$$T(\nu, J) = T_e + \sum_{m,n} Y_{mn} (\nu + 0.5)^m [J(J + 1) - \Lambda^2]^n . \quad (1)$$

The symbols above have their usual meaning, with $\Lambda^2 = 0$ for the ground $X^1\Sigma_g^+$ state and 1 for the upper ${}^1\Pi_u$ state. As the coefficients for the ground state are well known,[16] they were treated as fixed constants in the fits. A degree of the polynomial in (1) was chosen by trial and error to obtain a set of statistically significant Dunham coefficients (i.e. with errors less than 5% of each value) and, simultaneously, a good quality of the fit. The final, best-fit values of the constants are listed in Table 1. They reproduce the observed line positions with the root mean square deviation of 0.12 cm^{-1} , which is about the precision of our measurements. The number of digits required to represent each constant with no loss of precision in reproducing the experimental data was minimised using the sequential rounding and refitting procedure suggested by Le Roy.[17] Once the coefficients in the Dunham expansion have been determined, we applied the Rydberg-Klein-Rees (RKR) method to obtain the rotationless potential energy curve of the investigated state. Table 2 lists the vibrational energy levels and the corresponding classical turning points.

In the absence of direct experimental observations, the identity of the ${}^1\Pi_u$ state under consideration and its assignment to an atomic asymptote can be done by comparison with theoretical calculations. The only computation covering excitation energies high enough originates from the unpublished thesis by Spies,[18] who extended earlier valence CI calculations with a core polarisation potential by Schmidt-Mink et al. [19]. Figure 1 displays the experimental potential curve together with theoretical curves of ${}^1\Pi_u$ states placed in a similar energy range. As the $5^1\Pi_u$ state has been identified at lower energies and characterised

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3 experimentally in our previous work,[4] $6^1\Pi_u$ is the only reasonable assignment for the state
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5 observed here. A comparison of the main molecular constants resulting from the experiment
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7 and theoretical calculations is included in Table 1 and shows fair agreement. **It is interesting**
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9 **to note that the calculations underestimate the equilibrium distance, similarly as for the close-**
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11 **lying $5^1\Pi_u$ state described in reference [4]. Spies** assigns the adiabatic asymptote of the $6^1\Pi_u$
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13 state as $2s+4d$. The dissociation energy of the investigated state can be obtained then from
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15 combination of the measured T_e value, the well depth of the ground state $D_e(X^1\Sigma_g^+)$ and the
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17 separation of atomic energy levels of lithium, as

$$D_e(6^1\Pi_u) = D_e(X^1\Sigma_g^+) + \Delta E(4d - 2s) - T_e(6^1\Pi_u) . \quad (2)$$

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23 By using the values of $D_e(X^1\Sigma_g^+) = 8516.61 \pm 0.08 \text{ cm}^{-1}$ [20] and $\Delta E(4d - 2s) = 36623.30 \pm$
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25 0.01 cm^{-1} , [21] we arrive at value of $D_e(6^1\Pi_u) = 8276.7 \pm 0.1 \text{ cm}^{-1}$, where the errors of all three
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27 summands contribute to the uncertainty of the result.
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32 **The calculations by Spies allow also to assign the state responsible for perturbation of**
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34 **e parity levels in $6^1\Pi_u$ as the $5^1\Sigma_u^+$ state (Figure 1). Because of its broad potential energy**
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36 **curve Franck-Condon factors for the $5^1\Sigma_u^+ \leftarrow X^1\Sigma_g^+$ transition are expected to be low which**
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38 **explains why the corresponding band system did not show up in the experimental spectra.**
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44
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46
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Table 1

Dunham coefficients (in cm^{-1}) for the $6^1\Pi_u$ state of $^7\text{Li}_2$ representing energies of rovibrational levels of f parity in the range $v = 0 - 11$, $J = 2 - 47$, compared with theoretical values.[17] In the bottom the equilibrium distance and dissociation energy are also given.

Constant	Value	Theory
T_e	36863.25(5) ^a	36914
Y_{10}	253.567(36)	256.2
Y_{20}	-1.829(7)	
Y_{30}	0.0102(4)	
Y_{01}	0.480072(12)	0.4976
Y_{11}	$-0.5899(44) \times 10^{-2}$	
Y_{21}	$0.371(3) \times 10^{-3}$	
Y_{02}	$-0.624(6) \times 10^{-5}$	
Y_{12}	$0.724(21) \times 10^{-6}$	
R_e (Å)	3.164	3.107
D_e (cm^{-1})	8276.7(1)	

^a The number in brackets that follows a coefficient is one standard deviation in units of the last digit.

Table 2

Rotationless RKR potential energy curve for the $6^1\Pi_u$ state of ${}^7\text{Li}_2$ molecule.

v	G_v (cm^{-1})	R_- (\AA)	R_+ (\AA)
	0.0	3.1639 ^a	
0	126.392	2.9809	3.3715
1	376.338	2.8599	3.5404
2	622.716	2.7811	3.6650
3	865.589	2.7189	3.7709
4	1105.017	2.6656	3.8656
5	1341.062	2.6180	3.9526
6	1573.785	2.5742	4.0335
7	1803.247	2.5328	4.1097
8	2029.509	2.4933	4.1819
9	2252.633	2.4550	4.2506
10	2472.680	2.4175	4.3162
11	2689.710	2.3806	4.3791

^a The first line refers to the bottom of the potential curve, R is the equilibrium distance.

FIGURE CAPTION

Figure 1. The experimental RKR potential energy curve of the $6^1\Pi_u$ state (full circles connected by a solid line) compared with theoretical potential curves for the $5 - 7^1\Pi_u$ states calculated by Spies [17] (open symbols connected by dashed lines). Theoretical potential of the $5^1\Sigma_u^+$ state, responsible for perturbation of e parity levels in the $6^1\Pi_u$ state, is also drawn (stars and dash-dot line).

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