

Relabeling of the Rydberg and Doubly Excited States of Li_2^*

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Abstract 68 electronic states of Li_2 observed and/or calculated have been relabeled according to the dominant hydrogenic $n\lambda$ characters of the Rydberg orbitals and classified as core-penetrating vs core-nonpenetrating states. The perturbations between doubly excited valence states and Rydberg states are discussed. The significance of this labeling is also discussed.

Key words Li_2 , Li_2^* , Rydberg state , Core-penetrating , Core-nonpenetrating states , Doubly excited state

CLC number : O643.2 **Document code** : A

1 Introduction

The lithium dimer is of considerable interest to both theoreticians and experimentalists since it is the smallest stable homonuclear molecule besides H_2 . High quality *ab initio* potential curves of Li_2 have been calculated^[1-3] and a large number of electronic states, including Rydberg states and doubly excited states, have been observed experimentally^[4-16]. Bernheim *et al.* observed the $n\sigma \Sigma_g^+(n=310)$, $n\sigma \Sigma_g^+(n=310)$ and $n\delta\pi \Pi_g(n=315)$ Rydberg series of Li_2 ^[4-6]. Hermmerring *et al.* observed $n\delta\delta \Delta_g(n=37)$ series^[7]. Besides, Li *et al.*, Yiannopoulou *et al.* and other groups have studied some triplet Rydberg states and doubly excited state $1^3\Sigma_g^-$ ^[8-18].

In general, Rydberg states are by energy rank and n^* (n^* is the effective principal quantum number). However this shows little physical significance. In this paper we the Rydberg states of Li_2 according to their dominant $n\lambda$ (n , l , and λ are the principal quantum number, angular momentum quantum number and the projection of l onto the internuclear axis,

respectively) characters and discussed the significance of this labeling.

2 Relabeling and classification of Rydberg states

The effective principal quantum number, n^* , is defined by a modified Rydberg equation

$$\begin{cases} IP - E_{n^*} = \frac{R}{n^{*2}} \\ n^* = \left(\frac{R}{IP - E_{n^*}} \right)^{1/2} \\ n^* = n - \delta_{nl\lambda} \end{cases} \quad (1)$$

where IP is the ionization energy, R is the Rydberg constant for Li_2 , and $\delta_{nl\lambda}$ is the nearly n -independent quantum defect for the $l\lambda$ Rydberg series.

Molecular Rydberg states can be divided into two classes: core-penetrating (low- l) and core-nonpenetrating (high- l)^[19]. They have profoundly different properties.

Rydberg electron of a penetrating state exchanges energy and angular momentum with the ion core and valence electrons, which will cause predissociation and autoionization. Rydberg electron of a non-penetrating

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state, on the other hand, almost does not penetrate the ion-core, so the non-penetrating states are very weakly predissociated or autoionized. Because the overlaps between the valence orbitals and the Rydberg orbitals are nearly zero, electronic transitions from valence states to non-penetrating states are extremely weak. Therefore almost all Rydberg states observed experimentally are penetrating states, only a few non-penetrating states are observed via perturbations with penetrating states and borrowing some core-penetrating characters from them^[20].

The quantum defect $\delta_{n l \lambda}^*$ incorporates all the information about the interactions between the Rydberg electron and the core for a penetrating state. The dominant interactions in a non-penetrating state may be attributed to multipoles on the ionic core and core polarization.

In order for all λ components of a Rydberg state with a specific l to fall into non-penetrating state, the minimum orbit radius is

$$r_{\min} = \frac{R_e^+}{2} + r_{\text{atom}}$$

where r_{atom} is the radius of the neutral atom in its ground state, as defined by Rydberg's and Bohr's equations

$$n_{\min}^* = \left(\frac{R}{IP_{\text{atom}}} \right)^{1/2}, \quad r_{\text{atom}} = a_0 (n_{\min}^*)^2$$

where, IP_{atom} is the atomic ionization energy, a_0 is the Bohr radius, $a_0 = 0.529 \text{ \AA}$, R_e^+ is the ion ground state equilibrium internuclear distance. For Li atom,

$IP = 43487 \text{ cm}^{-1}$ ^[21], thus $r_{\text{atom}} = 1.33 \text{ \AA}$. Since $R_e^+ = 3.11 \text{ \AA}$ for the $\text{Li}_2^+ X^2\Sigma_g^+$ state^[22], $r_{\min} = 2.89 \text{ \AA}$.

A general rule for Rydberg series associated with a specific l value will appear penetrating or non-penetrating is based on the inner turning point, r_i . For $l = 1, 2, 3, 4, 5$ (p, d, f, g, h), the inner turning points are $r_i = 0.62, 2.01, 4.23, 7.31$, and 11.27 \AA , respectively^[19]. Therefore for Li_2 , $l = 0, 1, 2$ are definitely penetrating states ($r_i < r_{\min}$), while $l = 4, 5$ are non-penetrating states ($r_i > r_{\min}$). $l = 3$ is likely to be borderline (the $f\sigma$ component will be penetrating, the $f\delta$ and $f\phi$ will be non-penetrating). Since all Rydberg states of Li_2 have a $\sigma_g(2s)$ valence electron, and the g/u symmetry of a Rydberg orbital goes as $(-1)^l$, the gerade Rydberg states correspond to $[\sigma_g(2s)] [n l \lambda_g]$ ($l = \text{even}$), and the ungerade states with odd l values.

We relabeled the states of Li_2 reported by *ab initio* calculations and experimental observations. Table 1 and Table 2 give the results of relabeling for the singlet and triplet states, respectively. (For states experimentally observed, we use the experimental parameters.) We have arranged these states according to the dominant $n^* l \lambda$ natures. The numbers in the first column are the energy ranks within each series. The ionization energy IP , which is the minimum of the $\text{Li}_2^+ X^2\Sigma_g^+$ state above the minimum of the $\text{Li}_2 X^1\Sigma_g^+$ potential, is 41524 cm^{-1} ^[7] used in equation (1).

Table 1 Rydberg assignment of the Li_2 singlet electronic states according to dominant $n l \lambda$ character

States	$R_e(a_0)$	T_e/cm^{-1}	ω_e/cm^{-1}	Diss. limit	n^*	$l \lambda$	Ref.
* 1 $\Sigma_g^+(X)$	5.051	0	351.4	2s + 2s	1.626	$s\sigma$	[25]
* 2 Σ_g^+	6.900	20101	128.7	2s + 2p	2.263	$s\sigma$	[26]
* 3 $\Sigma_g^+(E)$	5.831	27410	245.9	2s + 3s	2.788	$s\sigma/\sigma_u\sigma_u$	[4]
* 5 Σ_g^+	6.072	33320	248.6	2p + 2p	3.657	$s\sigma$	[4 \ \]
* 7 Σ_g^+	5.896	36285	263.2	2s + 3d	4.577	$s\sigma$	[4 \ \]
* 11 Σ_g^+	5.944	38129	251.8	2s + 4f	5.685	$s\sigma$	[4]
* 14 Σ_g^+	5.883	39007	260.6	2s + 5d	6.603	$s\sigma$	[4]
* 16 Σ_g^+	5.908	39624	262.5	2s + 5g	7.600	$s\sigma$	[4]
* 18 Σ_g^+	5.913	40044	262.1	2s + 6p	8.611	$s\sigma$	[4]
* 20 Σ_g^+	5.974	40339	262.7	2s + 6f	9.625	$s\sigma$	[4]

Continuation of Table 1.

States	$R_{\infty}(a_0)$	T_e/cm^{-1}	ω_e/cm^{-1}	Diss. limit	n^*	$l\lambda$	Ref.
* 1 Σ_u^+ (A)	5.873	14068	255.4	2s + 2p	1.999	$p\sigma$	[27]
* 2 Σ_u^+	5.849	30101	259.0	2s + 3s	3.099	$p\sigma$	[28]
* 4 Σ_u^+	5.797	35098	272.1	2s + 3d	4.132	$p\sigma$	[29]
* 1 Π_u (B)	5.549	20436	270.6	2s + 2p	2.281	$p\pi$	[25]
* 2 Π_u (C)	5.820	30551	238.2	2p + 2p	3.162	$p\pi$	[28]
* 4 Π_u (D)	6.089	34518	201.7	2s + 3d	3.958	$p\pi$	[30]
* 4 Σ_g^+ (F)	6.704	29975	227.3	2p + 2p	3.082	$d\sigma$	[5]
* 6 Σ_g^+	5.981	34294	270.7	2s + 3p	3.896	$d\sigma$	[4]
* 8 Σ_g^+	5.918	36833	249.4	2s + 4s	4.836	$d\sigma$	[4]
* 13 Σ_g^+	5.875	38572	247.6	2s + 5p	6.097	$d\sigma$	[4]
* 15 Σ_g^+	5.788	39277	261.6	2s + 5f	6.988	$d\sigma$	[4]
* 17 Σ_g^+	5.697	39799	261.0	2s + 6s	7.975	$d\sigma$	[4]
* 19 Σ_g^+	5.667	40164	262.3	2s + 6d	8.982	$d\sigma$	[4]
* 21 Σ_g^+	5.606	40427	261.9	2s + 6g	10.001	$d\sigma$	[4]
* 1 Π_g	7.667	21998	93.4	2s + 2p	2.371	$d\pi/\sigma_u\pi_u$	[31]
* 2 Π_g (G)	6.049	31868	229.3	2p + 2p	3.371	$d\pi$	[6]
* 3 Π_g	6.013	35361	229.0	2s + 3p	4.220	$d\pi$	[4]
* 5 Π_g	5.983	37258	237.4	2s + 4p	5.072	$d\pi$	[4]
* 7 Π_g	5.942	38461	249.3	2s + 4f	5.985	$d\pi$	[4]
* 9 Π_g^-	5.910	39250	253.9	2s + 5d	6.946	$d\pi$	[4]
* 10 Π_g^-	5.888	39779	257.3	2s + 5f	7.930	$d\pi$	[4]
* 11 Π_g^-	5.882	40148	260.8	2s + 5g	8.929	$d\pi$	[4]
* Π_g^-	5.876	40412	261.9		9.934	$d\pi$	[4]
* Π_g^-	5.880	40610	259.2		10.957	$d\pi$	[4]
* Π_g^-	5.882	40759	262.4		11.977	$d\pi$	[4]
* Π_g^-	5.882	40877	262.2		13.023	$d\pi$	[4]
* Π_g^-	5.882	40969	262.1		14.061	$d\pi$	[4]
* Π_g^-	5.882	41042	263.8		15.088	$d\pi$	[4]
* 1 Δ_g	5.516	28950	273.1	2p + 2p	2.954	$p\pi p\pi$	[3]
* 2 Δ_g	5.635	33574	264.0	2s + 3d	3.715	$d\delta$	[7]
* 3 Δ_g	5.765	36204	259.7	2s + 4d	4.542	$d\delta$	[7]
* 4 Δ_g	5.796	37827	260.6	2s + 4f	5.448	$d\delta$	[7]
* 5 Δ_g	5.847	38851	258.8	2s + 5d	6.407	$d\delta$	[7]
* 6 Δ_g	5.906	39517	255.9	2s + 5f	7.394	$d\delta$	[7]
3 Σ_u^+	4.315	33670	256.2	2s + 3p	3.738	$f\sigma$	[1]
3 Π_u	6.017	34353	230.3	2s + 3p	3.912	$f\pi$	[3]
* 10 Σ_g^+	6.004	37890	145.7	2s + 4d	5.495	$p\sigma p\sigma/p\pi p\pi$	[4]
* 8 ¹ Π_g	5.834	38849	260.4	2s + 5p	6.405	$\sigma_u\pi_u$	[4]

The states labeled with * are those experimentally observed.

Table 2 Rydberg assignment of the Li₂ triplet electronic states according to dominant $n\lambda$ character^a

States	$R_\lambda(a_0)$	T_e/cm^{-1}	ω_e/cm^{-1}	Diss. limit	n^*	$l\lambda$	Ref.
* 1 $\tilde{\Sigma}_g^+$	5.797	16329	251.5	2s + 2p	2.087	sσ	[32]
* 3 $\tilde{\Sigma}_g^+$	5.740	31044	217.6	2s + 3p	3.236	sσ	[10]
* 1 $\tilde{\Sigma}_u^+(a)$	7.883	8183	65.1	2s + 2s	1.814	pσ	[32]
2 $\tilde{\Sigma}_u^+$	6.000	29130		2s + 2p	2.976	pσ	[1]
4 $\tilde{\Sigma}_u^+$	6.370	34267	186.2	2p + 2p	3.889	pσ	[1]
* 1 $\tilde{\Pi}_u(b)$	4.904	11238	346.3	2s + 2p	1.903	pπ	[14]
2 $\tilde{\Pi}_u$	5.603	29647	284.1	2p + 2p	3.040	pπ	[3]
4 $\tilde{\Pi}_u$	6.708	35565	265.0	2s + 3d	4.291	pπ	[3]
* 2 $\tilde{\Sigma}_g^+$	5.835	27299	269.4	2s + 3s	2.777	dσ	[33]
4 $\tilde{\Sigma}_g^{+b}$	5.737	35985	279.0	2s + 3d	3.887	dσ	[3]
5 $\tilde{\Sigma}_g^+$	5.669	36685	258.1	2s + 4s	4.762	dσ	[3]
* 2 $\tilde{\Pi}_g$	7.261	29844	188.6	2p + 2p	3.065	$\sigma_u\pi_u/d\pi$	[11]
* 3 $\tilde{\Pi}_g$	5.968	33410	248.9	2s + 3p	3.677	dπ	[13]
* 1 $\tilde{\Delta}_g$	5.701	30091	279.8	2s + 3d	3.098	dδ	[14]
* 2 $\tilde{\Delta}_g$	5.792	35014	265.7	2s + 4d	4.106	dδ	[15]
* 3 $\tilde{\Delta}_g$	5.806	37318	270.8	2s + 4f	5.108	dδ	[34]
5 $\tilde{\Sigma}_u^+$	5.907	35240	264.9	2p + 2p	4.179	fσ	[3]
3 $\tilde{\Pi}_u$	7.519	33792	230.5	2s + 3p	3.767	fπ	[3]
3 $\tilde{\Sigma}_u^+$	6.983	29836	392.7	2s + 3s	3.064	$\sigma_u\sigma_g$	[1]
* 1 $\tilde{\Sigma}_g^-$	5.047	34045	216.8	2p + 2p	3.830	pπpπ	[16]

a. The states labeled with * are those experimentally observed.

b. This 4 $\tilde{\Sigma}_g^+$ state was experimentally observed, but no experimental constants were available in Ref.[10].

The calculated constants are used here.

3 Discussion

This relabeling according to the $n^*l\lambda$ characters has advantages. It can predict the energy of a Rydberg state. One example is the 2 $\tilde{\Delta}_g$ state of Li₂. The 1 $\tilde{\Delta}_g$ state has been observed experimentally and is assigned to $nd\tilde{\Delta}_g$ ($n = 3$) Rydberg series with a quantum defect $\delta = 0.098$. As quantum defect $\delta_{nl\lambda}$ is nearly n^* -independent for a Rydberg series, we assume that the quantum defect of the 4d $\tilde{\Delta}_g$ state is also 0.098. Then we can predict the T_e of the 4dδ 2 $\tilde{\Delta}_g$ state to be 34990 cm^{-1} . The 2 $\tilde{\Delta}_g$ state has been found at the predicted energy^[15].

Many states may not be pure Rydberg states. They can be coupled by various perturbations to other Rydberg states or to doubly excited states.

Rydberg states of Li₂ have a $\sigma_g(ns)$ valence electron, which accounts for the same Fermi contact pa-

rameter of triplet states ($b_F \approx 100$ MHz for $\tilde{\text{Li}}_2$). A pure doubly excited state like 1 $\tilde{\Sigma}_g^-$ with a predominant pπpπ configuration, has smaller HFS. This is a primary difference between Rydberg states and doubly excited states. *ab initio* calculation shows that the 2 $\tilde{\Pi}_g$ state, which dissociates adiabatically to the 2p + 2p atomic limit, has a mixture of 60% Rydberg character and 40% valence configurations at R_e ^[11,12]. Its Fermi contact parameter has been determined to be 60 MHz rather than 100 MHz.

Hermmerling discussed the perturbations of the Rydberg states with the doubly excited states, whose configuration will contribute to the quantum defects^[7,8]. That the quantum defects of the 2¹Δ_g and 3¹Δ_g states are bigger than that of the 5d7d δ $\tilde{\Delta}_g$ is due to the electrostatic interaction between the $nd\delta$ ($n \geq 3$) $\tilde{\Delta}_g$ Rydberg states and the 1¹Δ_g valence state.

This $1^1\Delta_g$ valence state, which dissociates into the $2p + 2p$ atomic asymptote, is a doubly excited state with $\rho\pi\rho\pi$ configuration.

It is difficult to distinguish a Rydberg state from a doubly excited valence state for a singlet state with no HFS information. But as we know, due to strong mixing with doubly excited state, it is meaningless to distinguish valence states from Rydberg states, especially for states with low principal quantum number. Such as the $2^1\Delta_g$, $3^1\Delta_g$, $1^1\Pi_g$, $2^1\Pi_g$, $3^1\Pi_g$, $3^1\Sigma_g^+(E)$ states. These states may have doubly excited character at R_e .

Some states are intricate to label due to lack of experimental and theoretical data, especially some non-penetrating states. The abnormal quantum defects of the $10^1\Sigma_g^+$ and $11^1\Sigma_g^+$ states come from the perturbations between them and with another state. They both have doubly excited characters. Bernheim has suggested that an unidentified Σ_g^+ state existed at lower energy will perturb the $10^1\Sigma_g^+$ state^[4]. We named this unobserved Σ_g^+ state as $(2s + 4p) 9^1\Sigma_g^+$ according to the energy rank. It may be a $g\sigma \Sigma_g^+$ state belonging to a core-nonpenetrating state, which is similar to $\text{Na}_2^{[19, 23]}$. It is not observed because $\Delta l = 3$ transition into $g\sigma \Sigma_g^+$ from the A Σ_u^+ intermediate valence state is prohibited. The $12^1\Sigma_g^+$, $4^1\Pi_g$, $6^1\Pi_g$ states are predicted non-penetrating states according to the similarity with $\text{Na}_2^{[23, 24]}$. These states need further investigations.

Acknowledgement : This work was supported by NSF (19804008 and 29973020) and NKBRFS of China. This paper is dedicated to Professor Lou Nanguan for his contribution on molecular dynamics.

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锂分子里德堡态和双激发态的重新分类

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摘 要: 根据里德堡轨道的类氢 $n\lambda$ 特性, 对 $\bar{1}Li_2$ 实验已观测到的和理论计算给出的 68 个电子态进行了分类, 把这些态划分为核实贯穿里德堡态和核实非贯穿里德堡态. 讨论了双电子激发态和里德堡态的微扰, 也讨论了这种分类的意义.

关键词: Li_2 ; $\bar{1}Li_2$; 里德堡态; 贯穿里德堡态; 核实非贯穿里德堡态; 双激发态

中图分类号: O643.3 文献标识码: A

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