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Relabeling of the K_2 Rydberg States[†]

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The K_2 electronic states calculated theoretically and/or observed experimentally have been relabeled according to their dominant hydrogenic $n\lambda$ characters of the Rydberg orbitals. These states can be divided into core-penetrating and core-nonpenetrating states. This classification provides physical insights for interpreting and predicting experimental observations. The application of this method to K_2 is compared with that to Na_2 and Li_2 .

Key words: K_2 , Rydberg state, Core-penetrating, Quantum defect

I. INTRODUCTION

Alkali dimers, which have similar electronic structure to H_2 , can give many useful physical meanings in an explicit way. Rydberg states of diatomic molecules have been studied for many years. Generally, low-lying Rydberg states are labeled by numerical nomenclature for the electronic states with the same symmetry according to their energy ranks of the adiabatic dissociation limits. This labeling scheme, however, gives little information of these states in the region near their equilibrium internuclear distances. Li *et al.* relabeled the electronic states of Na_2 according to the dominant hydrogenic $n\lambda$ characters of the Rydberg orbital [1], interpreted the physical meanings of core-penetrating and core-nonpenetrating states, and showed many valuable physical insights according to this labeling scheme. Later, Song *et al.* applied this method to Li_2 and explained many experimental observations successfully [2]. In this work, we apply this labeling scheme to the K_2 electronic states. The insights and significance will be discussed and compared with those in Na_2 and Li_2 .

Ninety-eight electronic states of K_2 below the $4s+5d$ atomic limit have been calculated with high accuracy using the pseudopotential method [3]. The $X^1\Sigma_g^+$, $A^1\Sigma_u^+$, $B^1\Pi_u$ states and many low-lying singlet Rydberg states of K_2 have been studied experimentally (see the references given by Ref.[3]). Highly excited K_2 singlet Rydberg states near ionization threshold have been observed and organized into Rydberg series. Broyer *et al.* observed the $ns^1\Sigma_g^+$ ($n=8-20$) and $nd^1\Delta_g$ ($n=13-43$) Rydberg states using two- and/or three-photon resonance ionization spectroscopy and determined the ionization potential [4]. In a supersonic beam, Engelke *et*

al. and Kowalczyk *et al.* observed the $7s^1\Sigma_g^+$, $9s^1\Sigma_g^+$, and $8d^1\Delta_g$ states [5] and the $ns^1\Sigma_g^+$ ($n=8-17$), $nd^1\Sigma_g^+$ ($n=7-20$), and $nd^1\Delta_g$ ($n=7-20$) states [6] respectively, but their n -numbering was smaller than that given by Broyer *et al.* by 1. Wang *et al.* observed five low-lying Rydberg states [7], the $6d^1\Sigma_g^+$, $5d^1\Pi_g$, $6d^1\Pi_g$, $6d^1\Delta_g$, and $7d^1\Delta_g$ states, and their n -numbering determined by the molecular building-up principle agrees with the numbering of Broyer *et al.*. Observations of the $nd^1\Delta_g$ ($n=8-10$) states by Jong *et al.* [8] and the $nd^1\Delta_g$ ($n=11-15$) states by Kim *et al.* [9] support the n -numbering of Wang *et al.*.

Compared with singlet states, much less experimental information about the triplet states is available, and only the $a^3\Sigma_u^+$, $b^3\Pi_u$, $2^3\Sigma_g^+$, $4^3\Sigma_g^+$, $2^3\Pi_g$, $3^3\Pi_g$, $1^3\Delta_g$, $2^3\Delta_g$, and $4^3\Delta_g$ states have been studied experimentally [10-20].

In this work we relabel the K_2 Rydberg states according to their dominant hydrogenic $n\lambda$ characters of the Rydberg orbital based on the experimental and theoretical results available.

II. LABELING AND CLASSIFICATION OF THE K_2 RYDBERG STATES

Molecular Rydberg states are similar to atomic Rydberg states. The Rydberg formulas for diatomic molecules are

$$T_e = T_\infty - R/n^{*2} \quad (1)$$

$$n^* = n - \delta_{nl\lambda} \quad (2)$$

where R is the Rydberg constant, n is the principal quantum number, l is the electronic orbit angular momentum quantum number, λ is the projection of the electronic orbital angular momentum on the internuclear axis, n^* is the effective principal quantum number, $\delta_{nl\lambda}$ is the nearly n -independent quantum defect for the $l\lambda$ (case (b)) or $l\mathcal{L}$ (case (d)) Rydberg series, T_e is the electronic energy at the potential minimum, and T_∞ is

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the energy difference between the potential minimum of the $K_2 X^1\Sigma_g^+$ and the $K_2^+ X^2\Sigma_g^+$ states [4].

Molecular Rydberg states with Rydberg electrons in low- l or high- l orbits will fall into core-penetrating or core-nonpenetrating Rydberg states, respectively. Physically, this separation reflects the distinct interaction style between the Rydberg electron and the molecular ionic core. The Rydberg electron of a penetrating (low- l) Rydberg state experiences relatively strong interaction with the ionic core, resulting in predissociation and autoionization due to the energy and angular momentum exchanges between the Rydberg electron and the ion core. The Rydberg electron of a nonpenetrating (high- l) Rydberg state, on the contrary, has very weak interaction with the core, and the dominant perturbations come from polarization and multipole induced l -mixing interactions, resulting in very weak predissociation and autoionization, but ultra-sensitivity to external fields and collisions. The quantum defects in core-penetrating Rydberg states are usually big, while those in core-nonpenetrating Rydberg states are always small. Because the overlaps between the valence orbitals and the core-nonpenetrating Rydberg orbitals are nearly zero, transitions from valence states to nonpenetrating Rydberg states are extremely weak. The differences of the properties of core-penetrating from those of core-nonpenetrating states have been discussed and summarized in Ref.[1]. So far, all Rydberg states observed in alkali dimers are core-penetrating states and no nonpenetrating Rydberg states have been observed.

The minimum orbital radius for all λ components with a specific l to fall into core-nonpenetrating states is

$$r_{\min} = R_e^+ / 2 + r_{\text{atom}} \quad (3)$$

where r_{atom} is the atomic radius of the neutral atom in its ground state, and R_e^+ is the equilibrium internuclear distance of the ion ground state. r_{atom} can be derived from Rydberg's and Bohr's equations

$$r_{\text{atom}} = a_0(n_{\min}^*)^2 \quad (4)$$

$$n_{\min}^* = (R/IP_{\text{atom}})^{1/2} \quad (5)$$

where n_{\min}^* is the minimum effective principal quantum number and IP_{atom} is the atomic ionization energy. For K atom, $IP=35009.814 \text{ cm}^{-1}$, thus $r_{\text{atom}}=1.66 \text{ \AA}$. Since $R_e^+=4.59 \text{ \AA}$ for the K_2^+ ground state [4], $r_{\min}=3.96 \text{ \AA}$.

Whether a Rydberg series associated with a specific l value will appear as penetrating or nonpenetrating is based on the location of the inner turning point r_i of the hydrogenic effective potential energy curve [21]. For $l=1, 2, 3, 4, 5$ (p, d, f, g, h), the inner turning points are $r_i=0.62, 2.01, 4.23, 7.31, \text{ and } 11.27 \text{ \AA}$, respectively [1,2]. So in the case of K_2 , the $l=0, 1, 2$ series are penetrating states ($r_i < r_{\min}$), the $l=4, 5$ series are nonpenetrating states, and $l=3$ is likely to be the borderline. Unlike the case that the $f\pi$ and $f\delta$ series are nonpenetrating in Na_2

and Li_2 [1,2], the $f\pi$ and $f\delta$ series could be penetrating here in K_2 while the $f\phi$ component will be nonpenetrating. This may be understood by the fact that the r_{\min} (3.96 \AA) is much larger in K_2 than those in Na_2 and Li_2 (3.20 and 2.89 \AA , respectively) and is closer to the inner turning point r_i (4.23 \AA) associated with $l=3$. This deduction is also supported by the relatively big quantum defects of the $f\pi$ and $f\delta$ components compared to the small ones in the $f\phi$ component in K_2 .

Table I and Table II give the labeling of the K_2 singlet and triplet electronic states, respectively, using the theoretical or experimental (if available) molecular constants. Only the states with $T_e < 30000 \text{ cm}^{-1}$ are included since the theoretical calculation results are less accurate for highly excited Rydberg states, and the quantum defects calculated with theoretical constants can have bigger deviations from the experimentally determined quantum defects (the $6^1\Sigma_u^+$ and $7^1\Pi_u$ states in Table I and the $8^3\Sigma_g^+$ and $6^3\Pi_u$ states in Table II).

III. DISCUSSION

Most observed K_2 Rydberg states were excited by optical-optical double resonance through the $A^1\Sigma_u^+$ ($p\sigma$), $B^1\Pi_u$ ($p\pi$), and $b^3\Pi_u$ ($p\pi$) intermediate states, thus only low- l penetrating Rydberg states can be reached due to the $\Delta l = \pm 1$ propensity rule. From Tables I and II we can see that all observed Rydberg states belong to the core-penetrating Rydberg series ($l \leq 3$) and no core-nonpenetrating states have been detected. In Table I all the $^1\Delta_g$ states have been observed except the $4^1\Delta_g$ state, which falls into the core-nonpenetrating $g\delta$ series. In the case of the $^3\Delta_g$ states, the core-nonpenetrating $3^3\Delta_g$ state could not be detected while the core-penetrating $2^3\Delta_g$ and $4^3\Delta_g$ states have been observed by CW perturbation facilitated double resonance spectroscopy [19].

When n is higher than 16, the vibrational and rotational constants, ω_e and B_e (R_e), of a Rydberg series nearly equal to the ω_e^+ and B_e^+ (R_e^+) of the K_2^+ ground state, $X^2\Sigma_g^+$, and the quantum defects become n -independent [4], while in the lower n region both molecular constants and quantum defects are clearly n -dependent. Figure 1 shows that the quantum defects of the singlet $d\delta$ Rydberg series increase as n ($5 \leq n \leq 15$) increases and approach a constant value of 0.85 at $n=15$, which is very close to the value of 0.89 derived from singlet $d\delta$ Rydberg states near the ionization limit by Broyer *et al.* [4]. All quantum defects are derived from experimental molecular constants listed by Refs.[3,7-9]. In Fig.2 the variation of the quantum defects of the singlet $d\delta$ Rydberg series follows the Ritz relation $\delta = \alpha + \beta/n^2$ for $n=5-15$. The similar cases have been observed in Li_2 and Na_2 [23-25].

Tables I and II also give the adiabatic dissociation limits of the electronic states. Our labeling scheme is not suitable for doubly excited and ion pair states. Be-

TABLE I Relabeling of the K₂ singlet electronic states. All data are from Ref.[3] and the references therein except as noted. All the dissociation limits are adiabatic

States	R_e (a_0)	T_e/cm^{-1}	ω_e/cm^{-1}	Dissociation limit	n^*	$n^* \bmod 1$	$l\lambda$
$1^1\Sigma_g^{+*}$	7.42	0	92.40	4s+4s	1.830	0.830	$s\sigma$
$2^1\Sigma_g^+$	9.63	14377	46.00	4s+4p	2.442	0.442	$s\sigma$
$3^1\Sigma_g^{+**}$	8.58	20348	33.00	4s+5s	2.970	0.970	$s\sigma$
$5^1\Sigma_g^{+*}$	8.68	25376	69.77	4s+5p	3.849	0.849	$s\sigma$
$7^1\Sigma_g^{+**}$	8.61	27964	54.00	4p+4p	4.771	0.771	$s\sigma$
$10^1\Sigma_g^{+*a}$	8.88	29363	62.63	4s+4f	5.663	0.663	$s\sigma$
$1^1\Sigma_u^*$	8.59	11108	70.54	4s+4p	2.250	0.250	$p\sigma$
$2^1\Sigma_u^*$	9.28	22020		4s+5s	3.193	0.193	$p\sigma$
$4^1\Sigma_u^+$	8.73	26502		4s+5p	4.179	0.179	$p\sigma$
$6^1\Sigma_u^+$	9.90	28367	64.00	4s+6s	4.984	0.984	$p\sigma$
$1^1\Pi_u^*$	8.00	15377	74.89	4s+4p	2.511	0.511	$p\pi$
$2^1\Pi_u^*$	8.34	22968	62.80	4s+3d	3.343	0.343	$p\pi$
$3^1\Pi_u^*$	8.84	23927	62.70	4s+5p	3.520	0.520	$p\pi$
$5^1\Pi_u^*$	8.63	27462	64.45	4s+4d	4.540	0.540	$p\pi$
$7^1\Pi_u$	8.86	29345	67.00	4s+6p	5.648	0.648	$p\pi$
$4^1\Sigma_g^{+*}$ [22]	9.02	21417	86.05	4s+3d	3.107	0.107	$d\sigma$
$6^1\Sigma_g^{+*}$	8.42	25882	72.45	4p+4p	3.987	0.987	$d\sigma$
$9^1\Sigma_g^{+*}$	8.46	28233	69.69	4s+6s	4.910	0.910	$d\sigma$
$1^1\Pi_g^*$	9.74	16204	34.04	4s+4p	2.573	0.573	$d\pi$
$2^1\Pi_g^*$	9.07	23668	55.53	4s+3d	3.469	0.469	$d\pi$
$3^1\Pi_g^*$	8.68	26433	66.01	4s+5p	4.156	0.156	$d\pi$
$5^1\Pi_g^{*a}$	8.51	28480	71.04	4s+4d	5.049	0.049	$d\pi$
$6^1\Pi_g^{*a}$	8.49	29758	72.27	4s+4f	6.021	0.021	$d\pi$
$1^1\Delta_g$	7.70	19860	78.69	4s+3d	2.914	0.914	$d\delta$
$2^1\Delta_g$	8.13	25309	76.65	4p+4p	3.831	0.831	$d\delta$
$3^1\Delta_g^*$	8.34	27954	74.21	4s+4d	4.766	0.766	$d\delta$
$5^1\Delta_g^{*a}$	8.44	29350	70.87	4s+5d	5.652	0.652	$d\delta$
$3^1\Sigma_u^{+*}$	8.91	23863	63.41	4s+3d	3.507	0.507	$f\sigma$
$5^1\Sigma_u^+$	8.55	27294	69.00	4s+4d	4.470	0.470	$f\sigma$
$7^1\Sigma_u^+$	8.56	29233	65.00	4s+4f	5.558	0.558	$f\sigma$
$6^1\Pi_u^*$	8.81	28352	61.67	4s+4f	4.975	0.975	$f\pi$
$1^1\Delta_u$	8.75	24716	58.02	4s+3d	3.688	0.688	$f\delta$
$2^1\Delta_u$	8.60	27598	64.73	4s+4d	4.600	0.600	$f\delta$
$3^1\Delta_u$	8.66	29350	61.56	4s+4f	5.652	0.652	$f\delta$
$1^1\Phi_u$	8.32	26250	75.48	4s+4f	4.098	0.098	$f\phi$
$4^1\Delta_g$	8.53	28339	68.81	4s+4f	4.968	0.968	$g\delta$
$1^1\Phi_g$	8.44	28561	70.00	4s+4f	5.097	0.097	$g\phi$
$8^1\Sigma_u^+$	9.25	29669	95.00	4s+6p	5.934	0.934	$h\sigma$

* Experimentally observed states.

** Some energy levels have been observed but molecular constants cannot be derived from the data, so theoretical constants are used in the quantum defect calculation.

^a The $10^1\Sigma_g^+$, $5^1\Pi_g$, $6^1\Pi_g$, and $5^1\Delta_g$ states calculated by Magnier *et al.* [3] adiabatically dissociating to 4s+4f, 4s+4d, 4s+4f, and 4s+5d atomic limits, respectively, correspond to the $6d^1\Sigma_g^+$, $5d^1\Pi_g$, $6d^1\Pi_g$, and $6d^1\Delta_g$ states, respectively, observed by Wang *et al.* [7].

TABLE II Relabeling of the K₂ triplet electronic states. All data are from Ref.[3] and the references therein except as noted. All the dissociation limits are adiabatic

States	R_e (a_0)	T_e/cm^{-1}	ω_e/cm^{-1}	Dissociation limit	n^*	$n^* \bmod 1$	$l\lambda$
$1^3\Sigma_g^+$	8.98	13570	58.59	4s+4p	2.390	0.390	$s\sigma$
$3^3\Sigma_g^+$	8.48	23564	71.00	4s+3d	3.450	0.450	$s\sigma$
$5^3\Sigma_g^+$	8.50	27102	68.00	4s+4d	4.394	0.394	$s\sigma$
$8^3\Sigma_g^+$	8.65	29342	58.00	4s+6p	5.646	0.646	$s\sigma$
$1^3\Sigma_u^*$	10.91	4196	21.76	4s+4s	1.959	0.959	$p\sigma$
$4^3\Sigma_u^+$	9.32	24192	63.56	4s+3d	3.574	0.574	$p\sigma$
$6^3\Sigma_u^+$	8.59	27384	67.21	4p+4p	4.508	0.508	$p\sigma$
$8^3\Sigma_u^+$	8.61	29243	65.00	4s+4d	5.566	0.566	$p\sigma$
$1^3\Pi_u^*$	7.30	9909	92.03	4s+4p	2.190	0.190	$p\pi$
$2^3\Pi_u$	8.11	21860	73.00	4s+3d	3.169	0.169	$p\pi$
$4^3\Pi_u^{**}$	8.30	26502	68.00	4p+4p	4.179	0.179	$p\pi$
$6^3\Pi_u$	9.12	28278	72.00	4s+4f	4.934	0.934	$p\pi$
$2^3\Sigma_g^{*a}$	8.11	19471	79.72	4s+5s	2.871	0.871	$d\sigma$
$4^3\Sigma_g^{*b}$	8.34	25700	74.67	4s+5p	3.936	0.936	$d\sigma$
$6^3\Sigma_g^+$	8.59	28036	66.70	4s+6s	4.807	0.807	$d\sigma$
$2^3\Pi_g^{*c}$	9.93	21602	55.02	4s+3d	3.133	0.133	$d\pi$
$3^3\Pi_g^{*b}$	8.45	25450		4s+5p	3.868	0.868	$d\pi$
$5^3\Pi_g$	8.50	28102	80.20	4s+4d	4.841	0.841	$d\pi$
$1^3\Delta_g^{*d}$	7.96	21015	78.00	4s+3d	3.053	0.053	$d\delta$
$2^3\Delta_g^*$	8.21	25992	75.39	4s+4d	4.019	0.019	$d\delta$
$4^3\Delta_g^{*e}$	8.40	28408	74.74	4s+5d	5.007	0.007	$d\delta$
$3^3\Sigma_u^+$	9.98	21777	72.03	4s+5s	3.157	0.157	$f\sigma$
$5^3\Sigma_u^+$	8.52	26329	67.53	4s+5p	4.123	0.123	$f\sigma$
$7^3\Sigma_u^+$	8.47	28646	72.00	4p+4p	5.149	0.149	$f\sigma$
$3^3\Pi_u$	8.19	23649	57.66	4s+5p	3.466	0.466	$f\pi$
$5^3\Pi_u$	8.94	26870	88.00	4s+4d	4.307	0.307	$f\pi$
$7^3\Pi_u$	8.53	28862	87.00	4s+6p	5.289	0.289	$f\pi$
$1^3\Delta_u$	8.82	24628	53.98	4s+3d	3.668	0.668	$f\delta$
$2^3\Delta_u$	8.64	27482	64.00	4p+4p	4.549	0.549	$f\delta$
$3^3\Delta_u$	8.64	29181	65.38	4s+4d	5.518	0.518	$f\delta$
$1^3\Phi_u$	8.32	26247	75.44	4s+4f	4.097	0.097	$f\phi$
$7^3\Sigma_g^+$	8.39	28239	75.00	4s+6f	4.913	0.913	$g\sigma$
$6^3\Pi_g$	8.46	29693	72.00	4s+4f	5.957	0.957	$g\pi$
$3^3\Delta_g$	8.47	28314	65.10	4s+4f	4.954	0.954	$g\delta$
$1^3\Phi_g$	8.44	28561	70.80	4s+4f	5.097	0.097	$g\phi$

* Experimentally observed states.

** Some energy levels have been observed but molecular constants cannot be deduced, and theoretical constants are used in the quantum defect calculation.

^a Ref.[20].^b Ref.[11].^c This state strongly mixed with the $K^+ + K^-$ ionic state between 3.5 and 6.5 Å, and an unusual quantum defect is expected as the Na₂ 2³Π_g state [1].^d Ref.[18].^e Ref.[19].

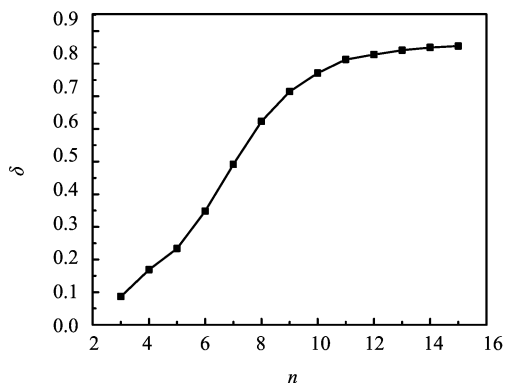


FIG. 1 The variation of the quantum defect δ with n in the range of $5 \leq n \leq 15$ of the singlet $d\delta$ Rydberg series.

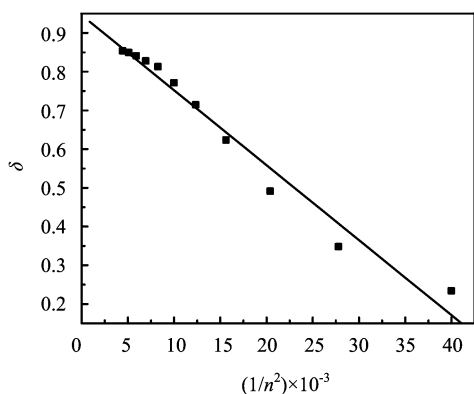


FIG. 2 The variation of the quantum defect δ with $1/n^2$ in the range of $5 \leq n \leq 15$ of the singlet $d\delta$ Rydberg series.

cause of the strong electronic interaction of the states with same symmetry, singly excited Rydberg states and doubly excited states can mix, and the electronic configuration of a state can change with internuclear distance. The $7^1\Sigma_g^+$ state dissociates to the $4p+4p$ atomic limit, but it is considered to be a singly excited Rydberg state at its R_e region [26]. The $8^1\Sigma_g^+$ state, on the other hand, has more doubly excited character at its R_e , although it dissociates to the $4s+4d$ atomic asymptote.

This labeling scheme for K_2 lower Rydberg states has good agreement with experimental observations as in the cases of Li_2 and Na_2 . Potassium atom, however, is bigger than lithium and sodium atoms, thus it is more complicated for theoretical calculations, especially for high-lying Rydberg states. Due to laser wavelength difficulties and lack of accurate term values of intermediate levels, perturbation facilitated optical-optical double resonance spectroscopy, which has been used to study the triplet states of Li_2 and Na_2 for over two decades [27], was applied to study triplet states of K_2 only recently [15–20] when accurate molecular constants of the $A^1\Sigma_u^+$ and $b^3\Pi_u$ states are available [28]. The quadrupole moment of Na_2^+ has been estimated from the splittings of the Λ states within a 3l

core-nonpenetrating Rydberg complex, and it has good agreement with experimentally derived value [1]. Only a few core-nonpenetrating K_2 Rydberg states have been calculated and the quadrupole moment of K_2^+ estimated from the theoretical results is not reliable.

IV. CONCLUSION

Molecular Rydberg states can be usefully divided into core-penetrating and core-nonpenetrating classes which have very different characteristics. We have relabeled and classified the K_2 electronic states according to the dominant hydrogenic $n\lambda$ characters of the Rydberg orbitals. This labeling scheme, which has been applied successfully to Na_2 and Li_2 [1,2], shows more physical meanings than the energy rank of the separated atomic limits to which the molecular Rydberg states dissociate. The core-penetrating Rydberg states with larger quantum defects have large transition probabilities from the valence states, thus they can be experimentally observed. The core-nonpenetrating Rydberg states with relatively small quantum defects have extremely weak interactions between the Rydberg electron and the ion-core, thus are still “black-holes” in spectroscopy even with modern laser spectroscopic techniques.

V. ACKNOWLEDGMENTS

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