Doubly excited $2^1\Delta_g$ state of Na$_2$

Thou-Jen Whang and Hui-Wen Wu
Department of Chemistry, National Cheng Kung University, Tainan 70148, Taiwan

Ray-Yuan Chang
Department of Physics, National Cheng Kung University, Tainan 70148, Taiwan

Chin-Chun Tsai
Department of Physics, and Institute of Electro-Optical Science and Engineering, National Cheng Kung University, Tainan 70148, Taiwan

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The doubly excited valence $(3p+3p)^2\,1\Delta_g$ state of Na$_2$ is experimentally observed by using optical-optical double resonance spectroscopy. A single line Ar$^+$ laser (a total of nine lines) was used to pump the sodium dimers from thermally populated ground state $X^1\Sigma_g^+$ to the intermediate $B^1\Pi_u$ state. Then, a single mode Ti:sapphire laser was used to probe the doubly excited $2^1\Delta_g$ state. Violet fluorescence emitted from the highly excited states (mainly $2^3\Pi_g$ or $3^3\Pi_g$ states which are transferred from $2^1\Delta_g$ state via collision) to the $a^3\Sigma_u^+$ state was monitored by a filtered photomultiplier tube (PMT). A total of 582 rovibrational levels of $2^1\Delta_g$ state were observed, identified, and assigned to the vibrational and rotational quantum numbers in the range of $0\leq v \leq 28$ and $11\leq J \leq 99$, respectively. The absolute vibrational quantum number assignment was verified by comparing the totally resolved fluorescence with the calculated Franck-Condon factors between $2^1\Delta_g$ state and $B^1\Pi_u$ state. Dunham coefficients and Rydberg-Klein-Rees potential curve were derived from these observed quantum levels. The primary molecular constants of Na$_2$ $2^1\Delta_g$ state are $T_c = 32.416.759(15) \text{ cm}^{-1}$, $\omega_r = 124.8484(36) \text{ cm}^{-1}$, $B_r = 0.119 \, 158(3) \text{ cm}^{-1}$, and $R_r = 3.508 \, 20(5) \text{ Å}$. © 2004 American Institute of Physics.

I. INTRODUCTION

The early spectroscopic studies on sodium dimer were reported more than a century ago.\textsuperscript{1} Hydrogenlike atomic structure and transitions in the visible laser range attract many theoretical and experimental studies to enrich the understanding of interactions between two sodium atoms.\textsuperscript{2-5} Some unusual behaviors such as avoided crossing shelves,\textsuperscript{6,7} double minima,\textsuperscript{8} hyperfine interactions in the long-range regions,\textsuperscript{9} quantum tunneling on a potential barrier,\textsuperscript{10} and pure long-range states\textsuperscript{11} show a variety of interactions. By using high quality ab initio calculations and experimental classifications of the electronic states, the complexities of these various physical phenomena could be unraveled. Experimentally, laser spectroscopy such as laser induced fluorescence (LIF),\textsuperscript{12} Fourier-transform infrared spectroscopy (FTIR),\textsuperscript{13} photoassociation spectroscopy,\textsuperscript{14} optical-optical double resonance (OODR),\textsuperscript{15} and perturbation facilitated optical-optical double resonance (PFODR),\textsuperscript{16} is a useful technique to examine the electronic states. However, most of the electronic states observed are mainly Rydberg states,\textsuperscript{17,18} in which one of the electrons remains in the atomic ground state Na(3s) at the asymptotic limit, while the doubly excited states are less accessible. According to the high quality ab initio calculations by Jeung,\textsuperscript{19} Henriet,\textsuperscript{20} and Magnier,\textsuperscript{21} the doubly excited potentials (here we talk about the asymptotic limit of $3p+3p$) are deeper than the Rydberg ones. Experimentally, among 12 electronic states dissociating to $3p+3p$ limit, only three of them, 7, 8 $^3\Sigma_g^+$, and $1^3\Sigma_g^-$, have been observed.\textsuperscript{17} This paper reports the observation of one of the doubly excited states, $2^1\Delta_g$ of Na$_2$. The absolute vibrational quantum numbers are verified by comparing the totally resolved fluorescence with the calculated Franck-Condon factors (FCFs). The lowest vibrational quantum number observed is $v = 0$. A set of Dunham coefficients is reported and a Rydberg-Klein-Rees (RKR) potential curve is constructed. In Sec. II we describe the experimental setup and techniques used. In Sec. III we present the results of the recorded spectra. The excitation spectra by OODR as well as the data analysis are discussed. Finally, Sec. IV concludes our results.

II. EXPERIMENT

The block diagram for the OODR experiment is shown in Fig. 1. The sodium vapor was generated in a five-arm stainless steel heat-pipe oven with about 1 Torr of argon buffer gas and 350 °C at the center. Either an all line visible Ar$^+$ laser (Coherent Innova 318C, using a prism to select one of the lines) or a single line Ar$^+$ laser (Coherent Innova 90-5) was used to pump the thermal populated ground state sodium dimers to the intermediate $B^1\Pi_u$ state. A total of nine lines of Ar$^+$ laser were used to populate 26 rovibrational intermediate levels of $B^1\Pi_u$ state for probing the Na$_2$ $2^1\Delta_g$ state. A cw Autoscan Ti:sapphire ring laser (Coherent 899-29) pumped by a solid state laser (Coherent Verdi-10) served as a probe laser and copropagated into the center of heat pipe with the Ar$^+$ laser. Two sets middle
wavelength (MW), 790–940 nm, and short wavelength (SW) 690–855 nm) of optics were used in the Ti:sapphire laser to
cover the probe energy range from 11 500–14 000 cm⁻¹. The
linewidh of single line Ar⁺ laser is about 50 MHz (corre-
spending to the coherent length of 1.16 m). However, the
linewidh of the pump transitions was several hundred me-
ghertz due to the Doppler and pressure broadenings. To con-
firm the excitation of each intermediate level, LIF for each
Ar⁺ laser line was recorded by a 0.75 m, double-grating
monochromator mentioned above through a fiber bundle.

III. RESULTS

A. OODR excitation spectra

The term values of the intermediate B ¹Πₙ state for our
OODR studies were calculated from the molecular constants
in Kusch and Hessel’s paper. In their paper, there were
three sets of constants in Table VII for fitting to the data of
the B ¹Πₙ state at different rovibrational range. Since some
of the higher vibrational quantum levels were excited in our
experiment, the constants of set III were chosen to reproduce
the term values of the B ¹Πₙ state. Excitation intensities of
B ¹Πₙ ← X ¹Σ⁺g transitions by each Ar⁺ laser line in our
experiment were similar to those reported by Kusch and Hes-
sel. Recently, more intermediate levels pumped by different
Ar⁺ laser lines were reported by Camacho and co-workers. Table I lists the intermediate levels used in this paper. In Table I, thermally populated ground state
X ¹Σ⁺g(v'',J'') levels were excited to the intermediate state
B ¹Πₙ(v',J') levels by a certain Ar⁺ laser line. The e/eff parities of the B ¹Πₙ state due to Λ doubling were slightly
different in energy for higher v' and J'. When the ground state levels pumped to the intermediate levels by Ar⁺ laser,
P and R transitions would excite the e parity, while Q tran-
sitions would excite the f parity. The assignments of the
populated intermediate levels were confirmed by LIF. Figure 2 shows a portion of the LIF spectrum with Ar⁺ laser line at
496.507 nm. More than 20 levels in B ¹Πₙ state were popu-
lated according to Ref. 31. However, two major series were
shown in Fig. 2 for this portion. The number on the top of
each assignment was the calculated FCF. The higher differ-
cent electronic excited states excited from the intermediate
B ¹Πₙ state may have different spectral patterns depending
on the different branches of pumping through the B ¹Πₙ ←
X ¹Σ⁺g transitions. According to Pan et al., only excita-
tions up to higher ¹Δg symmetry on the OODR spectrum
would show a strong Q line accompanied by two half inten-

### Table I. The intermediate levels Tᵦ(v',J'), used in this paper pumped by different Ar⁺ laser lines.

<table>
<thead>
<tr>
<th>Ar⁺ Laser</th>
<th>λₑm (nm)</th>
<th>X(v'',J'')</th>
<th>B(v',J')/eff</th>
<th>Tᵦ(v',J') (cm⁻¹)³</th>
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<tr>
<td>454.505</td>
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<td>(17.58)f</td>
<td>22 596.417 1</td>
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<td>(27.31)f</td>
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<td>22 397.769 6</td>
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<td>(9.38)e</td>
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<td>(6.27)e</td>
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<td>(10.12)e</td>
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<td>(5.51)e</td>
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<td>21 319.343 0</td>
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<td>(4.25)</td>
<td>(7.25)f</td>
<td>21 285.463 7</td>
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<tr>
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<td>(9.56)e</td>
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*The term values Tᵦ(v',J') were calculated from the set III molecular con-
stants in Table VII in Ref. 22. The e/eff parities were included.
sity $P, R$ lines for each vibration level. The excitation spectrum of $P, Q, R$ lines for $v = 12$ of $2^1 \Delta_u$ state probed from $B^1 \Pi_u (11,49)$ level (with 514.5 nm Ar$^+$ laser line pump) is plotted in Fig. 3. This excitation spectrum clearly shows a strong $Q$ line and two half intensity $P, R$ lines. This unique spectral transition pattern of $1^\Delta_u$ state helped us to sort out the progressions. Under this pump/probe scheme, another progression with equal intensity of $Q$ lines appeared and was identified as the $3^1 \Pi_u$ state which was observed by Tsai, Bahns, and Stwalley\textsuperscript{10} and Carlson et al.\textsuperscript{33} No progression of $1^\Sigma_u^+$ symmetry appeared in the regime of our probing laser frequency range in this study.

B. Spectroscopic analysis

To analyze the recorded spectra, high quality \textit{ab initio} potential curve of $2^1 \Delta_u$ state from Maganier\textsuperscript{34} (method A) was adopted to solve the Schrödinger equation for eigenfunctions and eigenvalues. These calculated eigenvalue differences and eigenfunctions overlapped with those of the $B^1 \Pi_u$ state, i.e., FCFs were clues for assigning the vibrational and rotational quantum numbers. There were also signals from the $3^1 \Pi_u$ state that could be assigned by comparing the experimental observations with those in the Refs. 10 and 31. For each different Ar$^+$ laser pumping line, several progressions were recognized on the spectrum. The estimate of the separations of $\Delta_2 F = 4 B_u (J + 1/2)$ was helpful in determining the rotational quantum number $J$ and hence the intermediate level of $B^1 \Pi_u$ state. Then, adding the probe laser frequency to the term value of the intermediate level $T_B (v',J')$ one could assign the rotational quantum number $J$ and term value to an observed level. In Fig. 4, the obtained term values of the $2^1 \Delta_u$ state are plotted (solid dots) as a function of $[J(J+1) - \Lambda^2]$, where $\Lambda = 2$. The solid lines were calculated from the Dunham coefficients described in Eq. (1). If the assigned quantum number $J$ or the intermediate level were wrong, the data points in Fig. 4 would not be on the progressions. According to electric dipole selection rules, only transitions with $\Delta J = 0, \pm 1$ ($Q$ and $P, R$ branches) were recorded under high-resolution spectra for each intermediate level. Since the Ar$^+$ laser frequency was fixed, the rotational quantum number $J$ for intermediate levels were restricted to less than 100. For the $\Delta$ state, $\Lambda$-type splitting is considerably smaller than that in the II states according to Herzberg.\textsuperscript{35} Therefore, no $\Lambda$ doubling was observed under our experimental resolution. In some of the excitations, only strong $Q$ line has enough signal-to-noise ratio to be recorded due to small FCFs or thermal ground state populations.

The absolute vibrational numbering was based on the comparison between the calculated FCFs and observed fluorescence intensities from $2^1 \Delta_g$ to different vibrational levels of $B^1 \Pi_u$ state. The procedures were as follows.

1. Assign the lowest vibrational level observed as $v^* = 0$.
2. Fit the observed term values $T_{vJ} = T_B(v',J') + \text{Energy}_{\text{probe frequency}}$ to obtain one set of the Dunham coefficients.
3. Calculate the FCFs between $2^1 \Delta_g$ and $B^1 \Pi_u$ states. The potential curve of $B^1 \Pi_u$ was taken from Kusch and Hessel.\textsuperscript{2}
4. Compare the relative transition intensities observed with the FCFs calculated. The relative intensities were normalized according to the vibrational sum rule. If they disagree, increase the quantum numbers by one unit and redo.
steps (1) to (4) until they agree with each other. It was found that the assignment with the lowest observed vibrational quantum number assigned to $v^* = 0$ achieved the best agreement between the observed relative intensities and the calculated FCFs. Since the potential curve of $2^1\Delta_g$ is roughly parallel to the $B^1\Pi_u$ state, this brought in the FCFs for lower vibrational levels with major contribution to $v = v'$ or $v' = 1$. Therefore, we carefully checked the probe frequency range which was lower than the $v^* = 0$ level with lower intermediate levels pumping [e.g., $B^1\Pi_u$ ($v' = 0, J' = 42$) or ($v' = 2, J' = 82$)]. However, no significant signals were observed below $v^* = 0$. To further confirm the absolute vibrational quantum number assignment, totally resolved fluorescence measurement was performed. By fixing the frequencies of both the pump laser and probe laser, one could populate a certain level of the $2^1\Delta_g$ state. Fluorescence emitted from this populated level to the $B^1\Pi_u$ state with $P, Q$, and $R$ lines at different vibrational quantum numbers $v' = 0, 1,$ and 2 was obtained as shown in Fig. 5, in which the calculated FCF is given above each assignment. The truncated lines on the left were the atomic transitions due to the predissociation or off resonance pumping to populate the $3d^2D_{3/2, 5/2}$ levels which fluoresce back to the $3p^2P_{1/2}$ and $2P_{3/2}$. Background rising on the blue side of the spectrum was verified to be the cascade fluorescence by Ar$^+$ laser multiphoton transitions. The relative intensities of the transitions to different vibrational levels $v' = 0, 1,$ or 2 agreed well with our vibrational quantum number assignment.

A total of 582 rovibrational levels of $2^1\Delta_g$ state have been detected and used for the least squares fitting to a set of Dunham coefficients,

$$T_{ij} = \sum_{i,j} Y_{ij} (v + \frac{1}{2}) [(J(J + 1) - \Lambda^2)],$$

where $Y_{ij}$ are the Dunham coefficients and $\Lambda = 2$ for $\Delta$ state. The fitted Dunham coefficients with standard errors are listed in Table II. The overall standard error of the fit is $\sigma = 0.035$ cm$^{-1}$. The transition linewidth of Doppler broadening is about 0.03 cm$^{-1}$. Table II also lists some molecular constants from $ab\text{ initio}$ calculations by Jeung,

Henriet,

and Magnier for comparison. The rotationless RKR potential points constructed from these Dunham coefficients are listed in Table III. Figure 6 plots this RKR potential curve (solid line) as well as $ab\text{ initio}$ calculations from Henriet ($\Delta$), and Magnier ($\triangle$). We did not plot the result from Jeung since there were few data points reported in their paper.

Twelve states $2^1\Delta_u, 2^3\Delta_u, 4^1\Pi_g, 4^3\Pi_u, 4^3\Pi_g, 4^3\Pi_u, 7, 8^1\Sigma_g^+, 7, 8^1\Sigma_u^-, 11^1\Sigma_u^-, \text{ and } 1^3\Sigma_u^-$ dissociate to doubly excited limit Na$(3p) + \text{Na}(3p)$. According to Hund’s case $a–c$ transition correlations and $ab\text{ initio}$ calculations, the $2^1\Delta_g$ state dissociate to Na$(3p)^2P_{3/2}$ + Na$(3p)^2P_{3/2}$ and has the deepest potential well among these 12 states. The dissociation energy $D_e$ of $2^1\Delta_g$ state can be obtained from the relation,

$$2^1\Delta_g(1.83) \rightarrow B^1\Pi_u(2.82) \rightarrow X^1\Sigma_g^+(6.83).$$

Then, the fluorescence emitted from $2^1\Delta_g(1.83)$ level back to $B^1\Pi_u$ state with $P, Q,$ and $R$ lines at different vibrational quantum numbers $v' = 0, 1,$ and 2 was obtained as shown in Fig. 5, in which the calculated FCF is given above each assignment. The truncated lines on the left were the atomic transitions due to the predissociation or off resonance pumping to populate the $3d^2D_{3/2, 5/2}$ levels which fluoresce back to the $3p^2P_{1/2}$ and $2P_{3/2}$. Background rising on the blue side of the spectrum was verified to be the cascade fluorescence by Ar$^+$ laser multiphoton transitions. The relative intensities of the transitions to different vibrational levels $v' = 0, 1,$ or 2 agreed well with our vibrational quantum number assignment.

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There are a couple of limitations in our pump-probe excitation spectroscopy. In the present study, the anharmonicity is not severe yet. In the Dunham coefficients, the potential curve is observed here and the phenomenon of atomic transition from this work. These yield the dissociation energy $D_e$ of ultracold atoms.37

<table>
<thead>
<tr>
<th>$\nu$</th>
<th>$B_\nu$ (cm$^{-1}$)</th>
<th>$G_\nu + Y_{0\nu}$ (cm$^{-1}$)</th>
<th>$\Delta G_{\nu+1/2}$ (cm$^{-1}$)</th>
<th>$R_{\text{min}}$ (Å)</th>
<th>$R_{\text{max}}$ (Å)</th>
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TABLE III. The RKR potential curve of the Na$_2$ 2$^1\Delta_g$ state. $Y_{0\nu} = 0.001 9$ cm$^{-1}$, $R_a = 3.508 20(5)$ Å.

$$D_e(2^1\Delta_g) = D_e(X^1\Sigma_g^+) + 2\Delta E(3p^2P_{3/2} - 3s^2S_{1/2}) - T_e(2^1\Delta_g).$$

The $D_e(X^1\Sigma_g^+)$ is the dissociation energy of $X^1\Sigma_g^+$ state, 6022.0286(50) cm$^{-1}$, which was directly measured by connecting the double resonance spectroscopy to the photoassociation of ultracold atoms.37 $\Delta E(3p^2P_{3/2} - 3s^2S_{1/2})$ is the atomic transition $3p^2P_{3/2} - 3s^2S_{1/2}$, 16.973.368 cm$^{-1}$, and $T_e(2^1\Delta_g)$ is the potential minimum, 32 416.759(15) cm$^{-1}$, from this work. These yield the dissociation energy $D_e(2^1\Delta_g) = 7552.006(20)$ cm$^{-1}$. Hence, only about 40% of the potential curve is observed here and the phenomenon of anharmonicity is not severe yet. In the Dunham coefficients, the inclusion of the centrifugal distortion constant $Y_{0\nu}$ makes the fitting good enough to reproduce the observed levels.

IV. CONCLUSIONS

Doubly excited states of alkali dimers which dissociate to the $np + np$ ($n = 2, 3, 4, 5,$ and 6 for Li$_2$, Na$_2$, K$_2$, Rb$_2$, and Cs$_2$, respectively) atomic limit have not been studied as intensively as the Rydberg states which dissociate to $ns + ml$ atomic limit. The only observed doubly excited states were 7, 8 $^3\Sigma_g^+$ states of Na$_2$, 1 $^3\Sigma_g^-$ state of Li$_2$, Na$_2$, and K$_2$, and 2 $^1\Delta_g$ (this work) state of Na$_2$ by the OODR or PFOODR excitation spectroscopy. In the present study, the 2 $^1\Delta_g$ state was probed through the intermediate B $^1\Pi_u$ state. There are a couple of limitations in our pump-probe excitation scheme. First, the rotational quantum number $J$ was limited by the fixed Ar$^+$ laser pump lines. Only 26 intermediate levels were used for probing the doubly excited 2 $^1\Delta_g$ state. Although the rotational quantum numbers ranges from 11–99, it is not selectable. There was no data field to deduce the characteristics of $\Lambda$ doubling at higher rotational quantum number $J$. A dye laser (running with Coumarin 6 dye with wavelength ranging from 520 to 560 nm) pumped by an ultraviolet Ar$^+$ laser should be able to probe any selected intermediate levels of B $^1\Pi_u$ state from the thermally populated ground state. This will help us to extend the data fields and solve the problems. Second, the range of outer turning points for the higher vibrational levels was limited to the potential barrier of the 2 $^1\Pi_u$ state. Such potential barriers arising from the repulsive long-range dipole interactions and short-range ionic attractions have been intensively studied.39 Although the $v' = 28$ quasibound level (lying above the dissociation limit) was pumped, the outer turning point $r_a (v' = 28)$ is only 10.5$\Delta_0$. Using A $^1\Sigma_u^+$ as the intermediate state, one third of the potential depth will reach the same outer turning point. Since the transition goes vertically under Born-Oppenheimer approximation, this limits the outer turning points of this doubly excited 2 $^1\Delta_g$ state to go beyond 10.5$\Delta_0$. Unfortunately, the intermediate B $^1\Pi_u$ state is the only electronic state that dissociates to $3s + 3p$ limit to probe the 2 $^1\Delta_g$ state. One possibility is using laser cooling and trapping techniques to produce a cold atom cloud (about hundreds of microkelvin in temperature). By using photoassociation spectroscopy, one can directly probe the long-range excited molecular states from the free atomic states because of the small kinetic energy spread for the cold atom cloud (1 mK is only about 21 MHz). In the cold atoms, free-state wave functions also favor the long-range part. In this way, the whole potential curve of doubly excited 2 $^1\Delta_g$ state should be accessible.
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