The third and fourth $^1\Delta_g$ states of $\text{Na}_2$: A pair of twins

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Abstract

The $3^1\Delta_g$ and $4^1\Delta_g$ Rydberg states of $\text{Na}_2$, which dissociate to $\text{Na}(3s) + \text{Na}(4d)$ and $\text{Na}(3s) + \text{Na}(4f)$, respectively, have been observed by using high-resolution cw optical–optical double resonance spectroscopy. The potential minima of these two states are separated by 129.74 cm$^{-1}$ and they have an avoided crossing at 4.09 Å implying significant interaction making them a pair of twins. The results of our observation agree very well with the $ab$ $initio$ calculations.

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1. Introduction

Laser spectroscopic studies on hydrogen-like atoms and molecules ($ns$-electronic structure) having transitions in the visible range have been of great interest in understanding the variety of interactions playing important roles in diatomic molecules and in providing answers of many intriguing questions of the fundamental physical properties of atoms and molecules. Alkali dimers have been frequently investigated for both experimental and theoretical interests because of their simple electronic structure.

Researchers have paid a lot of attention in investigating $\text{Na}_2$ using high level $ab$ $initio$ calculations [1] and experimental techniques, and reported many interesting and unusual features such as long-range hyperfine interactions [2], avoided crossing shelves [3,4], double minima [5], pure long range states [6] and quantum tunnelling of a potential barrier [7] which illustrate the existence of different types of interactions. Fig. 1 displays part of the potential curves of $\text{Na}_2$ from $ab$ $initio$ calculations by Magnier et al. [1]. The potential curves above 35000 cm$^{-1}$, which dissociate to $3p + 3p$, $3s + 4d$ and $3s + 4f$, are congested, which caused difficulties of observation. For the $n^1\Delta_g$ states within this energy range, the $n = 2$ and $n = 3$ states have an avoided crossing near 8 Å and the $n = 3$ and $n = 4$ states have a second avoided crossing near 4 Å. These avoided crossings cause the transition dipole moment of the 3 and 4$^1\Delta_g$ states to vary strongly with internuclear distance because of the mixing of the wavefunctions of these states.

In contrast to conventional spectroscopy, the high monochromaticity of the laser makes the observed spectra simpler since only transitions from a chosen rovibrational level are seen. This speeds up the observation of different and unobserved electronic states. A relabelling and classification of the Rydberg states according to the dominant hydrogenic $nl\ell$ characters of the Rydberg orbital as core-penetrating vs. core-nonpenetrating states has been reported by Li et al. [8]. According to their work, if the Rydberg states of $\text{Na}_2$ were observed with two-step excitation via the intermediate $\text{A}^1\Sigma_u^+(\text{pr})$ and $\text{B}^1\Pi_d(\text{pr})$ states, only low-$\ell$ penetrating states can be observed due to the selection rule $\Delta\ell \pm 1$. It is true that penetrating ($d\ell$), $1^1\Delta_g$ [9], $2^1\Delta_g$ [10], $5^1\Delta_g$ [11] and $nd^1\Delta_g$ ($n = 6$–$11$) [12] states have been observed.

For the penetrating $3^1\Delta_g(3s + 4d)$ state and the nonpenetrating $4^1\Delta_g(3s + 4f)$ state, $ab$ $initio$ calculations [1] show very close minima. They also show avoided crossing points around 4 Å between the 3 and 4$^1\Delta_g$ states and 8 Å between
2. Experimental method

The optical–optical double resonance (OODR) technique is based on the simultaneous interaction of a molecule (or an atom) with two photons that are on resonance to two molecular (atomic) transitions involving certain energy levels. In this experiment a single-line Ar^+ laser is used as a pump laser to excite the Na_2 from the thermally populated ground X^1Σ^+_g state to the intermediate B'^1Π_u state. A single mode Ti:sapphire (or DCM dye) laser (Coherent 899-29 autoscan) is used for probing the higher excited singlet gerade states from the intermediate state. Once the sodium dimers are excited to the singlet gerade states, a transition to the triplet gerade states will occur via collisional energy transfer [13]. The triplet gerade states then decay to the a^3Σ^+_u state with UV fluorescence. These UV photons were detected by a photomultiplier (PMT, RCA84-22) with two filters (Sequoia-Turner Corp. V-40 and 7-54, transmission range 320–420 nm). Combining the fluorescence signals and the wavelengths of the probe laser, the information about the transitions from intermediate states to upper states is obtained. There are nine Ar^+ laser lines, 454.5 nm, 457.9 nm, 465.8 nm, 472.7 nm, 476.5 nm, 488.0 nm, 496.5 nm, 501.7 nm, and 514.5 nm, which are used to populate the intermediate levels. The details of the transitions due to these Ar^+ lines are reported by Camacho et al. [14].

The experimental details can be found in the Ref. [10] and we only describe them briefly here. The sodium vapor is generated in a five-arm heat pipe oven (~350 °C) with about 1 Torr of argon buffer gas. The Ar^+ laser is intensity modulated at 1 kHz and counter-propagates to the single mode Ti:sapphire laser. An excitation spectrum of I_2 is recorded simultaneously for frequency calibration. The line positions can be determined to within 0.02 cm⁻¹. The uncertainties are mainly from the near sub-Doppler pumping by the frequency fixed single line Ar^+ laser and the laser power broadening.

3. Results and analysis

3.1. Assignment of rotational and vibrational quantum numbers of the energy levels

According to the selection rules ΔJ = 0, ±1, ΔS = 0, and g → u, the transitions from the 1 Π_u state to the ^3Σ^+_u, 1Π_u, and ^1Δ_u states are allowed. The detailed studies from Refs. [12,14,15] provided nice information about the possible transitions.

From the recorded spectrum we can find several obvious vibrational progressions of the ^1Δ_u patterns consisting of strong Q and half-intensity P, R lines. First, we can assign the rotational quantum number J of these progressions. We know that the J-selection rule is ΔJ = 0, ±1 for transitions between the B'^1Π_u and the ^1Δ_u states, and the energy difference between the P and R lines T(v,J + 1) − T(v, J − 1) ≈ 4Y_{01}(J + 1/2) is approximately proportional to J. Therefore, we can tentatively assign the rotational quantum numbers J of the intermediate levels and that of the probed excited levels as well in the progressions, and we can readily determine the term values of the progressions, i.e. T(v,J/J ± 1) ≈ T_B'^1Π_u(v',J) + h_{probe}. Moreover, we know the term value expression to the lowest order according to the Dunham double power series is given by

Fig. 1. Selected ab initio calculated potential curves and the corresponding atomic limits for Na_2 in Ref. [1].
In the plot of the term values of these progressions against $J(J + 1) - A^2$, the data points corresponding to the same vibrational quantum number $v$ will be linear if our assignments of $J$ of the intermediate energy level are right (see Fig. 2). We can take this plot not only as an initial check but also as a tool to predict the progressions that we have not picked out. The next step is to assign vibrational quantum numbers $v$.

In the plot of term values vs. $J(J + 1) - A^2$ (see Fig. 2), it shows that there are two sets of progressions very close to each other ($v_3$ being closest to $v_4 - 1$) in the energy range between 35300 and 36000 cm\(^{-1}\) (within one vibrational progression of about 100 cm\(^{-1}\)). The term values of the PQR-lines for the transition excited from $B^1\Pi_u(10,12)$ to $J = J', J' + 1 = 11,12,13$, i.e., at $[J(J + 1) - A^2] = 128,152,178$ in the vibrational progressions of $v_3 = 8–10$ and $v_4 = 7–9$ in Fig. 2 are very close to each other and the separation increases gradually as progression goes higher. The same closeness is seen for the following transitions excited from $B^1\Pi_u(6,27)$ to $J = 26,27,28$, i.e., at $[J(J + 1) - A^2] = 698,752,808$ in $v_3 = 5,6,8$ and $v_4 = 4,5,7$; excited from $B^1\Pi_u(9,38)$ to $J = 37,38,39$, i.e., at $[J(J + 1) - A^2] = 1402,1478,1556$ in $v_3 = 7–9$ and $v_4 = 6–8$, and excited from $B^1\Pi_u(6,43)$ to $J = 42,43,44$, i.e., at $[J(J + 1) - A^2] = 1802,1888,1976$ in $v_3 = 4–7$ and $v_4 = 3–6$. Therefore, we have separated out the whole progressions into two sets belonging to the $3^1\Delta_g$ and $4^1\Delta_g$ states. Now, the question is: which one set belongs to the $3^1\Delta_g$ state and which one set belongs to the $4^1\Delta_g$ state? From Magnier’s calculation [1], all the spacings are $\sim 100–120$ cm\(^{-1}\), while the separation of potential minima $T_{\nu}$ ($n = 4–n = 3$) is $\sim 120$ cm\(^{-1}\), so the vibrational ladders of the two states tend to overlap, with $v + 1$ in $n = 3$ being close to $v$ of $n = 4$. This nearness is seen in Fig. 2, but which level is $n = 3$ and which level is $n = 4$ are not clear. Since, each of the $n = 3$ and $4$ states will have a transition dipole moment that varies strongly with internuclear distance due to the avoided crossing, the simple Franck–Condon approximation (which assumes a constant transition dipole moment at all $R$) will be poor. Therefore, the absolute vibrational quantum number assignment by comparing the Franck–Condon factors (FCFs) is not suitable for these states. The key point to assign the $3, 4^1\Delta_g$ electronics states and the vibrational number is to compare the spacing of the vibrational progressions ($\Delta G_{v+1/2} = G_{v+1/2} - G_v$) and rotational constants between the $ab\text{ initio}$ calculations and the experimental values. Fig. 3 shows the vibrational separations ($\Delta G_{v+1/2}$) as a function of $(v + 1/2)$ obtained by solving the eigen values of Magnier’s $ab\text{ initio}$ potentials and from linear fitting of experimental

\[ T(v,J) \approx T_e + \omega_e(v + \frac{1}{2}) + B_v[J(J + 1) - A^2] \] (1)

![Fig. 2. Term values of the observed levels of the $3^1\Delta_g$ state (crosses) and the $4^1\Delta_g$ state (triangles) versus $[J(J + 1) - A^2]$ in the range 34500–37000 cm\(^{-1}\). The solid circles and open circles are the eigen values calculated from the RKR potential curves of the $3^1\Delta_g$ and $4^1\Delta_g$ state, respectively. The observed term values of both the states appeared in the range of 3500–36000 cm\(^{-1}\). $v_3 = 0,5,10$ and $v_4 = 0,5,10,15$ correspond to the numbering of the assigned vibrational levels of the $3^1\Delta_g$ and $4^1\Delta_g$ states, respectively. The $v$-progressions of the $4^1\Delta_g$ state is displayed in the range of $3 \leq v \leq 17$ for a clearer view of the closeness between the $3^1\Delta_g$ and $4^1\Delta_g$ states. On the vertical vibrational progressions of the same $J$ value (most of them exhibit of PQR-lines) are excited from the same intermediate rovibrational levels.

![Fig. 3. Separations between the successive vibrational levels ($\Delta G_{v+1/2}$) of the $ab\text{ initio}$ potentials (open diamond line $3^1\Delta_g$; open squares $4^1\Delta_g$) and the observations (solid circle line $3^1\Delta_g$; solid triangles $4^1\Delta_g$) for the 3 and 4$^1\Delta_g$ states. The assignments to the lowest vibrational levels were $v = 0$ and $v = 3$ for the $3^1\Delta_g$ and $4^1\Delta_g$, respectively. For a clearer view of the comparison, the abscissa is cut-off at $v + 1/2 = 20$.](image)
data for each vibrational progression for identifying the electronic states from the separation tendency. The \( \Delta G_{v+1/2} \) values of the \( 3^1\Delta_g \) state start at larger value and decrease faster than those of the \( 4^1\Delta_g \) states as the vibrational quantum number \( v \) increases. The separation tendency observed of the \( 3^1\Delta_g \) state has a similar behavior to the ab initio calculations. Note that the decrease of the separation from \( \Delta G_{3/2} \) to \( \Delta G_{1/2} \) helps us to include the lowest vibrational level which was discarded due to the unexpected decreasing separation. The trend of separation observed of the \( 4^1\Delta_g \) state is quite similar to that of the ab initio calculations. The vibrational quantum number assignments for the \( 3^1\Delta_g \) state is done by counting \( v = 0 \) right from the lowest vibrational level observed and for the \( 4^1\Delta_g \) state is made by fitting the best matching of the \( \Delta G_{v+1/2} \) values. These vibrational quantum number assignments are labelled on the right side of Fig. 2. These two sets are discussed in detail respectively as follows.

3.2. \( 3^1\Delta_g \) state

A total of 71 rovibrational levels of the \( 3^1\Delta_g \) state were observed, identified, and assigned to the vibrational and rotational quantum numbers in the range of \( 0 \leq v \leq 10 \) and \( 11 \leq J \leq 44 \), respectively. In this energy range, Carlson et al. [12] observed two consecutive bands, reported preliminary molecular constants, and assigned this \( 1^1\Delta_g \) state to the (much higher) \( 3s + 5d \) asymptotic limit. They also noted that they may not observe the \( v = 0 \) band. The \( T_c \) in their paper is about 180 cm\(^{-1}\) higher than our experimental results. This is about 1.5 times the vibrational separation and we believe that the result in Carlson’s paper is \( G(v = 1) \) instead of \( T_c \). We linearly extrapolated our vibrational progression to find \( G(v = 1) \) and it is within 0.3 cm\(^{-1}\) of Carlson’s result. In the linear fitting of our data, the intercept is the value of \( G_c \) and the slope is the value of \( B(v) \). These \( G_c \) and \( B(v) \) values were used to construct the RKR potential of the \( 3^1\Delta_g \) (see Fig. 4). We can see in Fig. 4 that the inner turning points are larger than those of the \( v^* = 3 \) is the best assignment. Some values of \( \Delta G_{v+1/2} \) have larger deviation due to fewer vibrational quantum numbers observed on that vibrational progression. The values of \( G_c \) and \( B(v) \) fitted from experimental data were used to construct the RKR potential (for \( 0 \leq v \leq 25 \), where \( 0 \leq v \leq 3 \) were taken from ab initio calculations: \( 0 \leq v \leq 2 \) are not observed and \( v = 3 \) had a larger uncertainty from the experimental data). The constructed RKR potential is plotted in Fig. 4 together with the potential from ab initio calculations (shifted up by 160 cm\(^{-1}\)) for comparison. These two potentials are in excellent agreement.

The experimental values of the important molecular properties of the \( 3^1\Delta_g \) and \( 4^1\Delta_g \) states are given in Table 1 which shows good agreement with ab initio calculations by Magnier et al. [1].

![Fig. 4. The potential curves of the \( 3^1\Delta_g \) and \( 4^1\Delta_g \) states from Magnier’s calculations with their positions elevated by 150 cm\(^{-1}\) and 160 cm\(^{-1}\), respectively, and the constructed RKR potentials form the individual linear fits of the observed vibrational bands. The Magnier’s curves are elevated for a close comparison with experimental curves.](image)

### Table 1

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### 3.3. \( 4^1\Delta_g \) state

A total of 250 rovibrational levels of the \( 4^1\Delta_g \) state were observed in the range of \( 3 \leq v \leq 25 \) and \( 11 \leq J \leq 65 \). Because, we did not have energy levels corresponding to \( v^* = 0 \), \( v^* \) is the tentative assignment of \( v \), the parts around the minimum of the potential curve resulting from Dunham fitting may be less accurate. To assign the vibrational quantum number \( v \), we compare the separations of the successive vibrational levels between the ab initio potential and the observations. Each vibrational progression was linearly fit to obtain \( G(v) \) and then \( \Delta G_{v+1/2} = G(v + 1) - G(v) \). From the plot of Fig. 3, it clearly suggests that
4. Conclusions

A total of 321 rovibrational energy levels of the $3^1\Delta_g$ and $4^1\Delta_g$ states were observed. The preliminary analysis shows these two states clumped together as a pair of twins. In Magnier’s calculations, there were 3 and $4^1\Delta_g$ states, which dissociate to $3s + 4d$ and $3s + 4f$, respectively, around the energy range observed. At the atomic limits, the $2^1\Delta_g$ state, which dissociates to $3p + 3p$, is also nearby. Fig. 1 shows one crossing-avoidance between the 3 and $4^1\Delta_g$ states around 4 Å and another one between the 2 and $3^1\Delta_g$ states around 8 Å. This is, in low-order approximation the potential curves of these two states may intersect. The avoided crossing point around 4 Å is in the energy region of our observation. Fig. 5 plots the energy difference \((\Delta E(4^1\Delta_g-3^1\Delta_g))\) between the RKR potentials of the $3^1\Delta_g$ and $4^1\Delta_g$ states with internuclear separation R and it shows a clear avoided crossing point at \(R_c = 4.09\) Å where \(\Delta E = 75\) cm\(^{-1}\) which is very small compared to the potential depth of the potential curves (~6000 cm\(^{-1}\)). In order to illustrate the amplitude sharing among the highly interacting states, we consider the molecular wavefunctions \(\psi_{pp}, \psi_{sd}\) and \(\psi_{sf}\) that describe the $3^1\Delta_g$ states (their potential curves cross to each other), \(\psi_{pp}\) for atomic limit Na(3p) + Na(3p), \(\psi_{sd}\) for Na(3s) + Na(4d) and \(\psi_{sf}\) for Na(3s) + Na(4f). Inside \(R = 8\) Å, the main contribution to the $2^1\Delta_g$ state is from \(\psi_{sd}\) but negligible contribution to the 3 and $4^1\Delta_g$ states. Then the 3 and $4^1\Delta_g$ states corresponding to the potential curves corrected by the non-crossing rule can be described by the linear combination of \(\psi_{pp}\) and \(\psi_{sf}\); that is,

\[
\psi_{3^1\Delta_g} = a\psi_{pp} + b\psi_{sf} \quad (3^1\Delta_g \text{ observed in } 0 \leq v \leq 10)
\]

\[
\psi_{4^1\Delta_g} = c\psi_{pp} + d\psi_{sf} \quad (4^1\Delta_g \text{ observed in } 3 \leq v \leq 25)
\]

The relations between the probability amplitudes in the regions of energy observed are as follows:

\[
\begin{align*}
|b|^2 \text{ and } |c|^2 & \text{ are dominant } \quad E < E_c; \\
|a|^2 \sim |b|^2 \text{ and } |c|^2 \sim |d|^2, \quad \text{in the range of } E \sim E_c, \\
|a|^2 \text{ and } |d|^2 & \text{ are dominant } \quad E > E_c,
\end{align*}
\]

where \(E_c\) is the energy at the crossing point \(R_c\). As discussed above, the state \(\psi_{sf}\) is not easy to be observed in this experiment. Therefore, in the region of \(E < E_c\), the energy levels of the $3^1\Delta_g$ state can be observed more easily than those of the $4^1\Delta_g$ state, while in the region \(E > E_c\), the signals from the $4^1\Delta_g$ state dominate. Around \(E \sim E_c\), both the $3^1\Delta_g$ and the $4^1\Delta_g$ can be observed.

In our experiment, the lower portion of the vibrational energy levels of the $4^1\Delta_g$ state and the higher portion of vibrational energy levels of the $3^1\Delta_g$ state were not observed. The results of our observation were inconsistent with the deduction described above. One possibility of lacking observation of the lower vibrational levels of $4^1\Delta_g$ state \((v = 0–2)\) may be due to the strong interaction at the avoided crossing point. This interaction quenches the incoming wavefunctions of the $4^1\Delta_g$ state to form the lower $3^1\Delta_g$ state wavefunctions after passing the avoided crossing point to the equilibrium position. Therefore, the value of \(|c|^2\) will be smaller than \(|a|^2\) in the energy range of \(E < E_c\). Due to the avoided crossing, the disturbance of the vibrational levels of the $3^1\Delta_g$ and $4^1\Delta_g$ states is also reflected in the $\Delta G_{v+1/2}$ vs. \((v + 1/2)\) plot in Fig. 3 as a lack of the linearity, i.e., unequal and irregular spacings of $\Delta G_{v+1/2}$ with \(v (\leq 9)\). Moreover, comparisons of the calculated FCFs (between the $4^1\Delta_g$ and $B^1\Pi_u$ states taking \(v^* = 2, 3\) and 4 for the lowest vibrational level of the $4^1\Delta_g$ state) with the observed normalized intensities show that \(v^* = 2\) could also be an acceptable assignment of the lowest vibrational level observed for the $4^1\Delta_g$ state. This implies that the perturbation have affected the vibrational levels near \(R_c\) to shift the vibrational progressions of the $4^1\Delta_g$ state by one unit lower.

How to detect the signals from the lower energy levels of the $4^1\Delta_g$ state and higher portion of both states is the key point to unravel this puzzle. However, in either cases, the signals observed should belong to the penetrating \((d\ell\ell)\) or \((pp)\) states for the consideration of dipole interactions.

Acknowledgement

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References