Observation of the \( nd \, ^1\Delta_g \) \((n=6, \, 7, \, \text{and} \, 8)\) Rydberg states of \( \text{Na}_2 \) by optical-optical double resonance spectroscopy: \( L \) uncoupling and perturbations

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The \( nd \, ^1\Delta_g \) \((n=6, \, 7, \, \text{and} \, 8)\) Rydberg states of \( \text{Na}_2 \) correlating with the asymptotic limits of \( \text{Na}(3s)+\text{Na}(nd) \) have been observed using high-resolution cw optical-optical double resonance spectroscopy corresponding to the rovibrational transitions \( X \, ^1\Sigma_g^+(v'\nu')\rightarrow B \, ^1\Pi_g(v',J') \)


I. INTRODUCTION

Researchers have carried out many investigations on \( \text{Na}_2 \), which has hydrogen-like ns-electronic structure of the outermost orbit and transitions in the visible range. These studies include high level outermost orbit and transitions in the visible range. These double-minimum state \( 2 \, ^1\Delta_g \) Fourier transform spectrometry. Purely long-range state \( 0 \, ^1\Delta_g \) experimental techniques5–10 which showed many interesting \( \text{Na}_2 \) molecules. However, the to association of laser cooled and trapped \( \text{Na} \) atoms to form \( \text{Na}_2 \) was observed et al.

The \( nd \, ^1\Delta_g \) \((n=6, \, 7, \, \text{and} \, 8)\) states, except for the \( 5 \, ^1\Pi_g \) and \( 5 \, ^1\Delta_g \) states of \( \text{Na}_2 \) have not been extensively investigated for the \( \text{Na}_2 \) system and other alkali dimers.

For diatomic molecules, the projection of the total orbital angular momentum \( L \) on the internuclear axis is \( \pm M_L \), where \( |\pm M|=\Lambda \). Since \( \Lambda \) can have projections on both sides of the center of the internuclear axis, the state with \( \Lambda \neq 0 \) splits into two components, the e-parity level and the f-parity level, for each rotational quantum number \( J \). If \( L \) is coupled with the internuclear axis, then each rotational state is \( \Lambda \)-doublet degenerate of the e,f parities. The uncoupling of \( L \) from the internuclear axis or the perturbations caused by the nearby states can remove the degeneracy of \( \Lambda \) doubling. When one of the electrons in a diatomic molecule is far away from the internuclear axis \( R \), \( L \) uncouples from the \( R \) and couples with the nuclear angular momentum \( N \) of the molecule. In this case, \( \Lambda \) no longer is a good quantum number to describe the system; rather, \( \Lambda \) is treated as good quantum number, neglecting the very small coupling between the total spin quantum numbers \( S \) and \( N \). If the degeneracy of the \( \Lambda \) doubling is removed due to the interaction between nuclear angular momentum \( N \) and the electronic orbital angular momentum \( L \), then the “\( \Lambda \)-doubling splitting” is termed the phenomenon of \( L \) uncoupling.13 In general, this splitting increases with increasing \( J \) and it is present for all states with \( \Lambda \neq 0 \). It has been found to occur in some lighter molecules, \( \text{H}_2 \),14,15 \( \text{Li}_2 \),16 and hydrides.17 It has also been observed in the long-range interatomic perturbations where degeneracy asso-
II. EXPERIMENTAL SETUP

The details of the OODR experimental setup with a block diagram can be found elsewhere. Briefly, using the combination of ceramic-isolated heaters and variacs, sodium vapor is produced in a five-arm stainless steel heat-pipe oven. The temperature is maintained at 350 °C around its center and the pressure is maintained at about 1 Torr of argon buffer gas. To populate the intermediate $B \ ^1\Pi_u$ state from the thermally populated ground state $X \ ^1\Sigma_g^+$ of Na$_2$ a single line Ar$^+$ laser (Coherent I-90, total of nine lines, see Table 1 of Ref. 12) is used. The Ar$^+$ laser is intensity modulated at 1 kHz and counterpropagating to the single-mode probe laser. Since the $X \ ^1\Sigma_g^+ \rightarrow B \ ^1\Pi_u$ transitions have been intensively studied by Kusch and Hessel, we calculate the term values of the populated $B \ ^1\Pi_u$ levels from their Dunham coefficients (set III of Table VII in Ref. 21) instead of adding the ground state term value to the laser frequency. Further, the details of the $X \ ^1\Sigma_g^+ \rightarrow B \ ^1\Pi_u$ transitions were reported by Camacho et al. A single-mode tunable ring-dye laser (Coherent 899-29 autoscan) was pumped by a diode-pumped solid state laser (Coherent Verdi-10). The ring laser with gain media DCM dye (lasing range: 14 300–16 500 cm$^{-1}$) and R6G dye (lasing range: 16 400–17 700 cm$^{-1}$) is used to probe the high-lying Rydberg states from the pumped intermediate rovibrational levels of the $B \ ^1\Pi_u$ state. Under the dipole-allowed selection rules, all the probed Rydberg states are of singlet and gerade symmetry ($\ ^1\Sigma_g^+$, $\ ^1\Pi_g$, and $\ ^1\Delta_g$). The selection rules for the $e.f$ parities for the $B \ ^1\Pi_u \rightarrow nd \ ^1\Delta_g$ transitions are the same as those of the transitions $B \ ^1\Pi_u \rightarrow s \ ^1\Delta_g$, and a relevant schematic diagram can be found in Fig. 2 of Ref. 12.

The probed Rydberg states undergo collisional energy transfer and populate the adjacent triplet gerade states. Subsequently, UV fluorescence from these triplet gerade states to the $a \ ^3\Sigma_u^+$ state (dissociation limit: 3s+3s) is detected using a filtered-photomultiplier tube (PMT) (filter: Sequoia-Turner Corp., No. 330, 385 nm; PMT: RCA84-22). The signals from the PMT are amplified by a lock-in amplifier (Stanford Research System SR-830) with the reference frequency of about 1 kHz from the chopping of the Ar$^+$ laser beam. By scanning the probe laser frequency, the UV fluorescence signals from the PMT and the resonance signals from the PMT and the autoscan software are simultaneously recorded by the autoscan software and displayed on a personal computer. The autoscan system is equipped with a built-in wavemeter to determine the probe laser frequency and the absolute probe laser frequency is calibrated by the laser frequency and the absolute probe laser frequency is within 50 MHz and the absolute accuracy is within 200 MHz. The experimental accuracy, the line positions of our OODR spectra, can be determined to within $\pm 0.02$ cm$^{-1}$. The uncertainty is mainly due to pumping the thermally populated ground state molecules by a frequency-fixed Ar$^+$ laser line, apart from the laser power broadening. The molecules with thermal velocity may be pumped off-resonance due to the Doppler effect which causes a shift in the line center. This includes the uncertainty in the OODR line position which is larger than the laser accuracy.
of $\Delta \Lambda = 0 \pm 1$, $\Delta S = 0$, $g \leftrightarrow u$, and $\Delta J = 0 \pm 1$. The detailed studies of Kusch and Hessel\textsuperscript{21} and Camacho et al.\textsuperscript{22} provided extensive information about the transitions from the $X^1 \Sigma^+_g$ state to the $B^1 \Pi_u$ state. OODR recorded spectra show two kinds of many vibrational progressions which consist of $PQO$ lines and $PR$ lines of different electronic states. Taylor et al.\textsuperscript{23} pointed out that the signals from the transitions between $B^1 \Pi_u$ and $^1 \Sigma^+_g$ rovibrational states are weak. So the observed signals in the OODR experiment should belong to the $^1 \Pi_u$ and $^1 \Delta_g$ states. Pan et al.\textsuperscript{20} reported that the rovibrational transitions from the $B^1 \Pi_u$ state to the $^1 \Delta_g$ states yield a strong $Q$ line ($\Delta J = 0$) accompanied by two half-intensity $P$ ($\Delta J = -1$) and $R$ ($\Delta J = +1$) lines, whereas the rovibrational transitions from the $B^1 \Pi_u$ state to the $^1 \Sigma^+_g$ states show only strong $PR$ lines with extremely weak or absent $Q$ line. Clearly, the observed vibrational progressions consisting of $PQO$ lines are due to the $B^1 \Pi_u \rightarrow ^1 \Delta_g$ rovibrational transitions.

In analyzing the data, first we assign the rotational quantum number $J$ of the observed progressions in the recorded spectra. The energy difference between the $P$ and $R$ lines $T(v,J+1) - T(v,J-1) \approx 4Y_{01}(J+\frac{1}{2})$ is approximately proportional to $J$. This guides us to the tentative assignments the rotational quantum numbers $J$ of the intermediate levels and those of the probed excited levels as well in the progressions. Afterwards, the term values of the progressions are determined from the relation, $T(v,J(J\pm 1)) = T_B \Pi_u (v',J) + h\nu_{\text{probe}}$. The term value expression of the Dunham double power series to the lowest order is given by

$$T(v,J) \equiv T_e + \omega_J (v + \frac{1}{2}) + B_{\Delta_g}(J(J+1) - \Lambda^2). \tag{1}$$

According to Eq. (1) the plot $T(v,J)$ versus $[J(J+1)-\Lambda^2]$ of the assigned $PQO$ lines of the $v$ progressions, the data point (term values) belonging to the same $v$ values of a single electronic state, give unique straight lines. From a huge number of tentatively assigned lines of the $^1 \Delta_g$ character ($PQO$ branches) of the probed states in the nine sets of spectra, we have sorted out correct $v$ progressions belonging to individual $^1 \Delta_g$-electronic states. An idea of the potential minimum $T_e$ (theoretical/experimental) is helpful to assign the vibrational levels ($v$ levels) correctly. For instance, the values of $T_e$ are 37 100.77, 37 659.54, and 38 047.18 cm$^{-1}$ for the $nd^1 \Delta_g$ states where $n=6$, 7, and 8, respectively, in the work of Carlson et al.\textsuperscript{18} Comparing our observed $T(v,J)$ values with those in the work of Carlson et al.,\textsuperscript{18} we have assigned the observed lowest vibrational level of each $nd^1 \Delta_g$ state to $v=0$. Figure 1 displays a part of the observed OODR spectrum of Na$_2$ and the assignments to the 6, 7, and 8 $^1 \Delta_g$ states pumped by a 476.5 nm Ar$^+$ laser from the $X^1 \Sigma^+_g (v'=0, J')$ ground state.

After the $v$ and $J$ assignments are made, we proceed to find the $\Lambda$-doubling splitting which manifests itself in the $e,f$-parity levels for $J$ and $J \pm 1$. The ground state $X^1 \Sigma^+_g$ does not involve any $\Lambda$ doubling since $\Lambda=0$ and the levels are all of $e$ parity. For the pumped intermediate state $B^1 \Pi_u$, $\Lambda$ doubling was considered by Kusch and Hessel.\textsuperscript{21} and Camacho et al.\textsuperscript{22} and the term values of the intermediate levels are generated using the molecular constants in Ref. 21. Under the electric-dipole transition, the selection rules for allowed transitions are $e \leftrightarrow e$ and $f \leftrightarrow f$ for both the $P$ and $R$ branches ($\Delta J=\pm 1$) and $e \leftrightarrow f$ for the $Q$ branch ($\Delta J=0$).

In the data set for the $^1 \Delta_g$ states, we have separated out $e,f$-parity levels and ran a program to perform Dunham fitting of the $e,f$-parity levels by the least-squares fitting algorithm to obtain the Dunham coefficients of the Dunham double power series expansion:

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

Here $Y_{ij}$ are the Dunham coefficients, and $\Lambda=2$ for $\Delta$ states. Eventually we have optimized to a ten-parameter Dunham fit for the 6 and 7 $^1 \Delta_g$ states and an eight-parameter Dunham fit for the 8 $^1 \Delta_g$ state using the assigned lines in the observed spectra. Separating the $e,f$-parity levels in the run of the Dunham fit of the $e,f$-parity levels, the discrepancy ($\delta_{e,f}$), which is the difference between the observed energy and the calculated energy from the Dunham polynomial fit, was preset (a “parameter” for preset value of $\delta_{e,f}$) of the Dunham fit program) to 0.2 cm$^{-1}$ in order to maintain the over all consistency in the data analysis of all the 6, 7, and 8 $^1 \Delta_g$ states and to obtain the reasonable/acceptable standard deviations of the order of experimental accuracy of the spectral line position of 0.02 cm$^{-1}$. The setting/choice of the
TABLE I. The comparison of the molecular constants (all in cm\(^{-1}\)) between the present experimental results and the work of Carlson et al. (Ref. 18) for the 6\(1\Delta_g\) state of Na\(_2\) is listed. The seemingly superfluous digits are necessary to compensate for the effects of correlations between the constants. \(\sigma\) is the standard deviation of the Dunham fit with \(e\) levels.

<table>
<thead>
<tr>
<th>(Y_{ij})</th>
<th>This work</th>
<th>Carlson et al. (Ref. 18)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Y_{00})</td>
<td>0.371 0181(10^3)(0.269(10^3))</td>
<td>0.371 0077(10^3)(0.2(10^3))</td>
</tr>
<tr>
<td>(Y_{10})</td>
<td>0.119 612(10^3)(0.126(10^3))</td>
<td>0.119 741(10^3)(0.2(10^3))</td>
</tr>
<tr>
<td>(Y_{20})</td>
<td>-0.408 289(10^3)(0.294(10^3))</td>
<td>-0.370 4(10^3)(0.3(10^3))</td>
</tr>
<tr>
<td>(Y_{30})</td>
<td>0.293 60(10^3)(3.47(10^3))</td>
<td>0.347 3(10^3)(3.73(10^3))</td>
</tr>
<tr>
<td>(Y_{40})</td>
<td>-0.270 01(10^3)(0.145(10^3))</td>
<td>-0.347 3(10^3)(0.145(10^3))</td>
</tr>
<tr>
<td>(Y_{01})</td>
<td>0.112 97(10^3)(0.162(10^3))</td>
<td>0.112 80(10^3)(0.2(10^3))</td>
</tr>
<tr>
<td>(Y_{11})</td>
<td>-0.119 21(10^3)(0.404(10^3))</td>
<td>-0.402 0(10^3)(0.8(10^3))</td>
</tr>
<tr>
<td>(Y_{21})</td>
<td>-0.252 60(10^3)(0.268(10^3))</td>
<td>-0.225 2(10^3)(0.284(10^3))</td>
</tr>
<tr>
<td>(Y_{12})</td>
<td>-0.263 07(10^3)(0.170(10^3))</td>
<td>-0.402 0(10^3)(0.8(10^3))</td>
</tr>
<tr>
<td>(Y_{02})</td>
<td>-0.445 63(10^3)(0.318(10^3))</td>
<td>-0.225 2(10^3)(0.284(10^3))</td>
</tr>
<tr>
<td>(Y_{03})</td>
<td>0.246 94(10^3)(0.382(67)(10^3))</td>
<td>0.347 3(10^3)(0.145(10^3))</td>
</tr>
<tr>
<td>(Y_{04})</td>
<td>0.173 87(10^3)(0.459(60)(10^3))</td>
<td>0.513 8(10^3)(0.576(80)(10^3))</td>
</tr>
<tr>
<td>(\mu)</td>
<td>-0.428 89(10^3)(0.470(08)(10^3))</td>
<td>0.470 08(10^3)(0.470(08)(10^3))</td>
</tr>
<tr>
<td>(\sigma)</td>
<td>0.746 3(10^{-1})</td>
<td>0.746 3(10^{-1})</td>
</tr>
</tbody>
</table>

"preset value of \(\delta_{F-e}\)" in the Dunham fit run, in turn, provides us to sort out a reasonable/acceptable data set which generates molecular constants and thereby eventually the RKR potential. In our Dunham fitted output files for the 6, 7, and 8 \(1\Delta_g\) states, if the value of \(\delta_{F-e}\) (=\(O-C\) in the Dunham output\(^{27}\)) of any one \(e\)-parity line of a \(PQR\) set, it is over the preset value of 0.2 cm\(^{-1}\), that \(PQR\) set is a "deviant \(PQR\) set" and the rest are labeled as the "nondeviant \(PQR\) sets." By excluding the deviant (\(PQR\) sets) in the Dunham fits, 62 \(e\) levels and 42 \(f\) levels in the ranges of \(v=0–11\) and \(11 \leq J \leq 83\) for the \(6\Delta_g\) state, 56 \(e\) levels and 27 \(f\) levels in the ranges of \(v=0–11\) and \(11 \leq J \leq 83\) for the \(7\Delta_g\) state, and 26 \(e\) levels and 19 \(f\) levels in the ranges of \(v=0–10\) and \(11 \leq J \leq 65\) for the \(8\Delta_g\) state have been identified.\(^{27}\) The \(\delta_{F-e}\) values in the Dunham fit output will be used to estimate the \(\Lambda\)-doubling splitting constants. Tables I–III list the values of molecular constants for these three \(nd\ \Delta_g\) states.

Using the molecular constants derived from the Dunham fits of the separate \(e/\bar{f}\) parity levels, we have constructed rotationless RKR potentials (Fig. 2) and calculated the Franck–Condon factors (FCFs) between the \(B^1\Pi_g\) state and each of the observed \(nd\ \Delta_g\) states (constructed RKR potentials). The FCFs compare well to the observed normalized intensities of the \(PQR\) lines for each vibrational progression which confirms the correct assignments of the vibrational levels observed. As seen in Tables I–III, the minima of the RKR potential curves (\(T_e\)) agree quite well with the experimental results by Carlson et al.\(^{18}\) (within 1 cm\(^{-1}\)) for their assigned 7, 8, and 9 \(\Delta_g\) states. In our previous observation,\(^{12}\) the assigned \(5\ \Delta_g\) state is the same as the \(6\ \Delta_g\) state in the work of Carlson et al.\(^{18}\) so following the same trend we have assigned these three observed states to the 6, 7, and 8 \(\Delta_g\) states in the present work. Note that for

FIG. 2. Experimental rotationless RKR potential curves of the \(nd\ \Delta_g\) \((n=5–8)\) states from the observed range of \(v=0–11\) of the Na\(_2\) system. Present work: Open circles connected by a solid line; work of Carlson et al. (Ref. 18): Dark diamonds; Na\(_2\) \(2\Sigma^+(Na^1S+Na^3S)\): Solid line (calculation). The RKR potential of the \(5d\ \Delta_g\) state is from our previous work (Ref. 12). The equilibrium positions \(R_e=3.5688\) cm\(^{-1}\) for \(n=5, R_e=3.6030\) cm\(^{-1}\) for \(n=6, R_e=3.5917\) cm\(^{-1}\) for \(n=7,\) and \(R_e=3.6192\) cm\(^{-1}\) for \(n=8\).
the \( 8 \Delta_g \) state, the \( \langle 0.42 \rangle e \rightarrow \langle 0.43 \rangle e \langle 0.4290 \rangle, \langle 7.43 \rangle e \rightarrow \langle 7.44 \rangle e \langle 0.0922 \rangle \), and \( \langle 6.43 \rangle f \rightarrow \langle 6.44 \rangle f \langle 0.1152 \rangle \) [where the fractional numerical values in parentheses are the FCFs (Ref. 27) between the \( B^1 \Pi_g \) and the \( 8 \Delta_g \) state] lines were not observed even though the FCFs are large because they lie at the end of the R6G-dye scanning range (\( \approx 17 \) 700 cm\(^{-1} \)).

Now in order to estimate the \( \Lambda \)-doubling splitting constants \( (q_0, q_\omega, \) and \( \mu \)), the discrepancy \( \delta_{l-e} \) (\( =O-C \) in the Dunham fit) which is the difference between the observed term value of the \( f \)-parity level and the calculated term value from the Dunham coefficients \( Y_{ij} \) of the \( e \)-parity level of the same set of rovibrational quantum numbers \( (v,J) \) is used. The discrepancy \( \delta_{l-e} \) is a quantitative measure of the \( \Lambda \) doubling, but not a precise one. The energy of an \( f \)-parity level is lower than that of an \( e \)-parity level, i.e., the value of \( \delta_{l-e} \) must be positive for a correctly assigned and acceptable level. So the \( f \) levels with positive \( \delta_{l-e} \) values in the Dunham fit output were not taken into account to estimate the \( \Lambda \)-doubling splitting constants because they will affect the estimations of \( \Lambda \)-doubling splitting constants and produce erroneous results. So, for each state using only the negative \( \delta_{l-e} \) values, a three-parameter Dunham fit was run to generate three Dunham coefficients which are the \( \Lambda \)-doubling splitting constants, \( q_0, q_\omega, \) and \( \mu \), related to the \( \Lambda \)-doubling energy correction term through the following modified Dunham expression:

\[
T_{v,J} = \sum_{i,j} Y_{ij}(v + 1/2)[J(J+1) - \Delta_i^2] + \delta_i[J(J+1) - \Delta_e^2] + \delta_{J+1}[J(J+1) - \Delta_e^2]
\]

Here the whole term multiplied by \( \delta \) is the \( \Lambda \)-doubling energy correction. In Eq. (3), \( \delta = 0 \) for \( e \)-parity levels and \( \delta = -1 \) for \( f \)-parity levels. In Tables I-III the estimated values of \( q_0, q_\omega, \) and \( \mu \) are given for the respective states. A detailed discussion of these will be given in Sec. IV.

IV. DISCUSSION

Three \( nd \Delta_g \) \( (n=6, 7, \) and \( 8) \) Rydberg states of Na\(_2\) have been observed by high-resolution OODR spectroscopy. Carlson et al.\(^{18}\) reported five sets of Dunham coefficients from their observations of these states in the ranges of \( 0 \leq v \leq 3 \) and \( 19 \leq J \leq 41 \) with an estimated error of the fit of \( 0.35 \pm 0.05 \) cm\(^{-1} \). The values of the Dunham coefficients [Eq. (2)] depend on the range of \( v \) and \( J \) as well as the number of coefficients included in the Dunham fit of the observed data. The important molecular properties \( (T_c, \omega_c, \) and \( B_c) \) of the present work compare well to those of Carlson et al.\(^{18}\) given in Tables I-III. The separations between the successive vibrational levels \( \Delta v_{\nu+1/2} \) \( =\) \( G(v+1) - G(v) \) obtained from the derived molecular constants of three \( nd \Delta_g \) states are found to be almost linear and gradually decreasing, and the dependence of \( B_c \) on \( v \) of each state exhibits almost linear and regular pattern within the range of \( v=0-11 \). Figure 2 displays the comparison of the RKR potential curves of the three \( nd \Delta_g \) \( (n=6-8) \) states in the present work with those generated using the data of Carlson et al.\(^{18}\) Very good agreement between the present work and the work of Carlson et al.\(^{18}\) is found for all three RKR potentials. The FCFs (Ref. 27) between each of these \( nd \Delta_g \) states and the \( B^1 \Pi_g \) state were calculated (assumed that the electronic transition dipole moment function is approximately independent of internuclear separation) to compare to the observed normalized intensities, and good agreement was found in each case. The FCFs (Ref. 27) show the trend of the distributions of excitation probabilities among the different vibrational levels \( (\nu) \) of the excited \( nd \Delta_g \) \( (n=6-8) \) states and they match well with the vibrational numbers \( (\nu) \) of the “nondeviant sets” for the 6, 7, and 8 \( \Delta_g \) Rydberg states obtained from the Dunham fits of the \( e \) levels. Moreover, oscillating probabilities are clear both in the sets of vibrational numbers \( (\nu) \) of the nondeviant PQR sets in the Dunham outputs and the FCFs, and they are in good agreement as well.

In the Dunham fits of the separate \( e / f \)-parity levels, the standard deviations of the 6, 7, and 8 \( \Delta_g \) states are \( \approx 0.07 \) cm\(^{-1} \), which are a few times the experimental accuracy of the spectral line positions (0.02 cm\(^{-1} \)), and the discrepancies \( \delta_{l-e} \) are one order of magnitude higher (or even more) than this. So the \( \Lambda \)-doubling splittings of these three observed states are obvious. The maximum negative values of the \( \Lambda \)-doubling splittings \( (\delta_{l-e}) \) of the 6, 7, and 8 \( \Delta_g \) states are about \(-0.73, -0.2, \) and \(-0.31 \) cm\(^{-1} \), respectively.\(^\text{25}\) Note that the maximum negative value of \( \delta_{l-e} \) of the 5 \( \Delta_g \) state is about \(-0.4 \) cm\(^{-1} \).\(^\text{12}\) In general, \( \Lambda \)-doubling splitting increases with increasing \( J \), so the \( f \) levels with \( \delta_{l-e} = 0 \) or \( +ve \) at higher \( J \) values are most probably strongly perturbed or they might be incorrectly assigned. In Eq. (3), the significant contribution of \( q_0 \) depends only on \([J(J+1) - \Delta_i^2] \), whereas that of \( q_\omega \) comes from both \([J(J+1) - \Delta_e^2] \) and \([v+\frac{1}{2}] \), and that of \( \mu \) depends on the square of \([J(J+1) - \Delta_e^2] \). Three sets of figures\(^\text{27}\) display the dependence of \( \delta_{l-e} \) on \([v+\frac{1}{2}] \) and represent \( \delta_{l-e} \) versus \([J(J+1) - \Delta_e^2] \) variations of the 6, 7, and 8 \( \Delta_g \) states, respectively. The trends of \( \delta_{l-e} \) with \([v+\frac{1}{2}] \) and \([J(J+1) - 4] \) clearly suggest that \( \delta_{l-e} \) increases with \( v \) and \( J(J+1) \) for the 6d \( \Delta_g \) state. Similar plots of the \( 7d \Delta_g \) state indicate somewhat scattered and fluctuating \( \Lambda \)-doubling splitting, and no smooth variation in \( \delta_{l-e} \) versus \([v+\frac{1}{2}] \) and \([J(J+21) - 4] \) is evident. For the 8d \( \Delta_g \) state, the points in the same figures show that the \( \Lambda \)-doubling splitting slowly increases with large uncertainty, and the \( \delta_{l-e} \) variation with \([J(J+1) - 4] \) is clearer than that with \([v+\frac{1}{2}] \) variation. The \( \Lambda \)-doubling splitting constants \( (q_0, q_\omega, \) and \( \mu \) were estimated by least-squares Dunham fit to \( T_{v,J} \) in Eq. (3) and are listed in Tables I-III. The values of the first-order splitting constants \( (q_0, q_\omega) \) are statistically meaningful, but the values of the second-order splitting constants \( (\mu) \) may not be statistically meaningful because it includes large uncertainty, although the order of magnitude of this constant is fairly reasonable too.

In the recorded spectra, a few \( P \) and \( R \) lines with relatively large FCFs were not observed in the \( v \) progressions, such as \( \langle 0.42 \rangle e \rightarrow \langle 2.41 \rangle e \langle 0.1280 \rangle, \langle 2.82 \rangle e \rightarrow \langle 4.83 \rangle e \langle 0.1977 \rangle, \langle 6.43 \rangle f \rightarrow \langle 9.44 \rangle f \langle 0.1238 \rangle \) of the 6 \( \Delta_g \) state; \( \langle 9.38 \rangle e \rightarrow \langle 7.37 \rangle e \langle 0.3747 \rangle \) of the 7 \( \Delta_g \) state; and \( \langle 6.43 \rangle f \rightarrow \langle 5.44 \rangle f \langle 0.0052 \rangle \) of the 8 \( \Delta_g \) state, where the fractional values in parentheses are the FCFs.\(^\text{27}\) Except only for the \( \langle 6.43 \rangle f \rightarrow \langle 5.44 \rangle f \) transition \( (P \) and \( Q \) lines are quite promi-
nent with the $P$ line about half as intense as the $Q$ line), all the above FCF values are significant. This clearly suggests that the vanishing of these $P$ and $R$ lines is free from FCF effects. The absence of only a single $P$ line in the $7\Delta_g$ state may imply the presence of an asymmetric perturbation produced by the neighboring $6\Delta_g$ and $8\Delta_g$ states around the $7\Delta_g$ state. The appearance of the $PQ$ lines $[(6,43)/f\to(5,42/43)$ though FCF=0.0052$]$ of the $8\Delta_g$ state could be caused by the interference between two perturbation fields produced by the adjacent up $(n=9)$ and down $(n=7)$ states with the $8\Delta_g$ state. The intensity ratios in many $PR$ pairs in the $v$ progressions are different from the usual approximate intensity ratio of the $PR$ lines $(1:1)$, and some $PQR$ lines are very much deviated from the expected positions (as seen in the lists of the “deviant e levels” and “f levels corresponding to deviant e levels” in the Dunham fit output.$^{27}$ Furthermore, in some $PQR$ branches, the intensities of the $PR$ lines are comparable to that of the $Q$ line. Such rotational-branch intensity and position anomalies which include the vanishing of some lines, changes in intensity ratios, and abnormal deviations of the line positions in the spectra are caused by $L$-uncoupling perturbations between the interacting states of the same $l$ complex. Besides, the interference effects due to $\Delta\Lambda=\pm 1$ perturbations always affect the intensities of the $\Delta J=\pm 1$ transitions ($PR$ lines) for each mixed level in equal and opposite amounts.$^{28}$

Figure 3 depicts the variation in $q_0$ with $n$ of the $nd\Delta_g$ series for $n=5\sim 8$. It shows that $q_0$ is approximately linear and increasing but falls at $n=7$ because of the effect of perturbations produced by both the adjacent up and down states $8\Delta_g$ and $6\Delta_g$, respectively, of the $7d\Delta_g$ state. Figure 4 illustrates the dependence of $q_v$ with $n$ of the $nd\Delta_g$ series for $n=5\sim 8$. $q_v$ decreases almost linearly as $n$ increases. In Fig. 5, $\mu$ shows a linearly decreasing trend with $n$. Due to the lack of the wide range of $f$-parity data fields for the states $n=6\sim 8$, the uncertainties in the values of $q_0$, $q_v$, and $\mu$ for $n=6\sim 8$ are more than those at $n=5$. As described above regarding the significant outcomes of $q_0$, $q_v$, and $\mu$ in connection with the dependence on $(v+\frac{1}{2})$ and $[J(J+1)-4]$, our observed data are limited within $0\leq v \leq 11$ and the effective $J$ values are within $11\leq J \leq 44$, and there are only a few higher values of $J=64$ and $82$. Unfortunately, due to the lack of a sufficiently wide range and sufficient number of observed data fields, the estimations of $q_0$, $q_v$, and $\mu$ have large uncertainties.

The variation in $\delta_{q_{5-8}}$ with $v$ [and also with $J(J+1)$] of the $7d\Delta_g$ state looks somewhat scattered and oscillatory within the observed range.$^{27}$ In Fig. 2, the potential minimum $(T_e)$ of the $7d\Delta_g$ state is $\sim 560$ cm$^{-1}$ higher than that of the $6d\Delta_g$ state and $387$ cm$^{-1}$ lower than that of the $8d\Delta_g$ state, i.e., the $7d\Delta_g$ state is sandwiched (asymmetrically) and very likely to be perturbed asymmetrically by these $6$ and $8d\Delta_g$ states. Most probably, these effects change the smooth variation in the $\Lambda$-doubling splitting for the $7d\Delta_g$ state to an oscillatory pattern. The separation between the potential minima of the $5d\Delta_g$ (Ref. 12) and $6d\Delta_g$ states is $\sim 850$ cm$^{-1}$, so the $\Lambda$-doubling splitting of the $6d\Delta_g$ state is not disturbed that much and it shows clear and smooth dependence on $(v+\frac{1}{2})$ and $[J(J+1)-4]$. In view of this, the $\Lambda$-doubling splitting of the $7d\Delta_g$ is mainly caused by perturbation in the $8d\Delta_g$ state which is nearer by $\sim 173$ cm$^{-1}$ than is the $6d\Delta_g$ state. Further the position of the potential minimum of the $8d\Delta_g$ state is $\sim 280$ cm$^{-1}$ below that of the $9d\Delta_g$ state.$^{18}$ Since the $8d\Delta_g$ state is almost halfway between the $7$ and $9d\Delta_g$ states, these two states are expected to perturb the $8d\Delta_g$ state almost equally and hence the signature of smooth dependence of the $\Lambda$-doubling splitting is better in the $8d\Delta_g$ state than that in the $7d\Delta_g$ state. As seen from Tables I–III and Table 2 of Ref. 12, the values of $\omega_e$ and $B_e$ of all the $nd\Delta_g$ $(n=5\sim 8)$ states are almost the same, implying that the $nd\Delta_g$ series $(n=5\sim 8)$ potentials should have a very similar shape and features within the observed range of $v=0\sim 11$ $(R=2.95\sim 4.55$ Å). In addition, in the observed range of $v=0\sim 11/10$ in Fig. 2, $\sim 40\%$ of the observed range of the $6d\Delta_g$ state is contained in the $5d\Delta_g$ state (observed range$^{25}$), $\sim 60\%$ of the $7d\Delta_g$ state observed levels overlap with those of the $6d\Delta_g$ state, and $\sim 80\%$ of the $8d\Delta_g$ state is immersed in the $7d\Delta_g$ state. An asymmetric perturbation caused by the adjacent up and down pair potentials around each of the potential curves of the $nd\Delta_g$ series $(n=5\sim 8)$ plays an important role to affect the normal characteristics of the $\Lambda$-doubling splitting with $v$ and $J(J+1)$, depending on the energy separation between the adjacent states.
L-uncoupling phenomena have already been observed in the 5 \( ^1\Delta_g \) state of Na\(_2\).\(^{12}\) Over all, in the \( nd^1\Delta_g \) series (\( n=5-8 \)) of Na\(_2\) molecules the \( \Lambda \)-doubling degeneracy is substantially removed because the electronic angular momentum vector \( L \) partially uncouples from the internuclear axis. In these high-lying Rydberg states of the \( nd^1\Delta_g \) series, the outermost electron (\( nd \)) of one of the nuclei in Na\(_2\) is quasibound to that nucleus and the molecule [Na(3s) + Na(nd)] can be regarded as an equivalent complex system, [Na(3s)+Na\(^+\)-e\(-\)]. Since the outermost electron (\( e\(-\)\)) of one Na atom in Na\(_2\) is essentially very far away from the nucleus, \( L \) is practically uncoupled from the internuclear axis. This produces \( \Lambda \)-doubling splitting which is the so-called \( L \) uncoupling and it is well described and understood using Hund’s case(d) rather than Hund’s case(a) or case(b), in which \( L \) couples with the internuclear axis. The \( L \)-uncoupling operator, \( -(1/2\mu R^2)(J^+L^+ + J^-L^-) \), giving rise to heterogeneous (\( \Delta\Omega = \pm 1 = \Delta L \)) perturbations where the terms are usual, is responsible for the transition from Hund’s case(a) to case(d) as \( J \) increases. This \( L \) uncoupling produces various perturbations between the states with \( \Delta\Omega = \Delta L = \pm 1 \) and \( \Delta S = 0 \), and this type of rotational perturbation is termed as a gyroscopic perturbation. Further, since \( J^+L^+ = J^+ \Sigma J^- \), the \( L \)-uncoupling operator is a one-electron operator. The Rydberg states belonging to the same \( l \) complex in molecular orbital representation (\( nl\)) are sampled by the \( L \)-uncoupling operators, which in most cases involve the same vibrational quantum states, \( v \). Miescher\(^{29}\) studied the weak perturbations between two high Rydberg states of different \( l \) complexes, (8f–9s) and (6f–6d) with \( \Delta v = 0 \) in the NO molecule. Using OODR multiphoton ionization spectroscopy and multichannel quantum defect theory (MQDT) on the NO system, Pratt et al.\(^{30}\) and Gauyacq et al.\(^{31}\) explained the Rydberg states of NO in terms of (s–d) \( l \) mixing and (f–d) \( l \) mixing, giving rise to the supercomplexes for \( ns, nd \), and \( nf \) Rydberg series. To our knowledge, no work has yet been reported on the combined OODR spectroscopy and MQDT study of the Na\(_2\) system. However, recently (f–d) \( l \) mixing that forms the supercomplex due to the molecular quadrupole moment was investigated in the perturbed \( 3^1\Delta_g \) and \( 4^1\Delta_g \) states in Na\(_2\).\(^{32}\) The present investigations based on spectroscopic evidence and a consistent detailed data analysis of the \( nd^1\Delta_g \) series (\( n=6-8 \)) of the Na\(_2\) system clearly show that the same \( l \) complexes approaching the ioncore limit result in the same \( l \) mixing to form the supercomplexes due to the anisotropy of the molecular-ion field caused by the \( L \)-uncoupling perturbations in these states.

V. CONCLUSIONS

From high-resolution cw OODR spectroscopic observations of the rovibrational quantum levels, we have derived molecular constants and constructed RKR potentials of the \( 6, 7, \) and \( 8d^1\Delta_g \) states of Na\(_2\). In this investigation, obvious \( \Lambda \)-doubling splitting is found in the \( 6d^1\Delta_g \) state. However, for the \( 7d^1\Delta_g \) state the splitting is not a smooth function of \( v \) and \( J(J+1) \), nor is it as clear as that of the \( 6d^1\Delta_g \) state. For the \( 8d^1\Delta_g \) state there is again a clear signature of \( \Lambda \)-doubling splitting. Most likely, due to the effects of perturbations caused by the adjacent lower \( 6d^1\Delta_g \) state and upper \( 8d^1\Delta_g \) on the state \( 7d^1\Delta_g \) state, the smooth \( \Lambda \)-doubling splitting of this state becomes a scattered oscillatory function. \( L \)-uncoupling perturbations cause rotational-branch intensity and position anomalies which result in the vanishing of either the \( P \) line or \( R \) line in a \( PQ \) branch, changing the normal intensity ratios of the \( PR \) lines and/or producing the abnormal deviations of the line positions in the observed spectra. Within our experimental accuracy of the spectral line positions (0.02 cm\(^{-1}\)) and the standard deviations of the data fits (\( \sim 0.07 \) cm\(^{-1}\)), the first-order \( \Lambda \)-doubling constants \( q_0 \) and \( q_2 \) are quantitatively meaningful but the second-order constant \( \mu \) may not be as useful from the statistical point of view. The \( L \) uncoupling from the internuclear axis of the same \( l \) complexes and the \( l \) mixing between the interacting states guided by the selection rules lead to the formation of supercomplexes caused by the anisotropic molecular ioncore [Na(3s)+Na\(^+\)] field of the same \( l \) complexes in the \( nd^1\Delta_g \) series of the Na\(_2\) system. The present investigations of the 6, 7, and \( 8d^1\Delta_g \) states in Na\(_2\) system should draw attention to further investigations of the effects of \( L \) uncoupling from the internuclear axis and perturbations between the neighboring states of the \( nd \) series and high Rydberg states of other alkali dimers (at room, cold, and ultracold temperatures), and give insights into these interactions in diatomic molecules.

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27 See EPAPS Document No. E-JCPSA6-129-606828 for (1) Dunham fit output of the $e$-parity levels of the $nd^1\Delta_g(n=6–8)$ states of Na$_2$, (2) calculated FCFs between the intermediate $B^1\Pi_u$ state and each of the $nd^1\Delta_g(n=6–8)$ states of the Na$_2$ system, (3) the dependence of the discrepancy $\delta_{fe}$ on $(v+\frac{1}{2})$ and $(j(j+1)-\Lambda)$ of the $nd^1\Delta_g(n=6–8)$ states ($\Lambda=2$ for $\Delta$ states). For more information on EPAPS, see http://www.aip.org/pubservs/epaps.html.