

Optical-Optical Double Resonance Spectroscopy of the ${}^1\Sigma_g^+$ "Shelf" States and ${}^1\Pi_g$ States of Na_2 Using an Ultrasensitive Ionization Detector

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Using a shielded cylindrical space-charge-limited diode ionization detector and optical-optical double resonance, the exotic potential energy curves of the 3, 4, 5, and 6 ${}^1\Sigma_g^+$ "shelf" states and 2 and 3 ${}^1\Pi_g$ states of Na_2 have been extensively studied including levels near dissociation (> 99.8% of well depth) with very large outer classical turning points, and long range avoided crossings giving rise to potential "shelves." The long range potentials can all be understood and also provide stringently tested high quality theoretical calculations of highly excited states.

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Optical-optical double resonance has proved to be a powerful technique for molecular spectroscopy. There are many ways to carry out such experiments. Schawlow's group [1,2] used the two-step polarization-labeling method to study lower vibrational levels of many singlet gerade Rydberg states in Na_2 . Effantin *et al.* [3] studied some lower lying Rydberg states in Na_2 by recording infrared fluorescence using a Fourier transform spectrometer. Using a filter photomultiplier (PMT) to detect the total violet fluorescence from collisionally induced emission, our group has recently reported many Rydberg states (including higher vibrational levels) in the alkali dimers [4–10]. However, most electronic states reported are limited to regions near the minima of the potential curves where energy term values are accurately represented by a single set of Dunham coefficients [11] Y_{ij} . In these near minima regions of the potential energy curves, our results described below agree precisely with prior work [1–7].

Recently, we have found that a space-charge-limited diode ionization detector provides a significant sensitivity enhancement for excited states of Na_2 which can associatively ionize ($\text{Na}_2^* + \text{Na} \rightarrow \text{Na}_3^+ + e^-$) or multiphoton ionize ($\text{Na}_2^* + nh\nu \rightarrow \text{Na}_2^+ + e^-$). By using this ultrasensitive ionization detector, the 3, 4, 5, and 6 ${}^1\Sigma_g^+$ "shelf" states and 2 and 3 ${}^1\Pi_g$ states of Na_2 (all of which undergo associative ionization to form the Na_3^+ ion) have been extensively studied up to more than 99.8% of the potential well depth (except for the 6 ${}^1\Sigma_g^+$ state which is known to 57.1%). These data show interesting potential energy curves including flat avoided crossing "shelves," long range attraction, and barriers. The details of this detector have been described [12]. In summary, the shielded cylindrical space-charge-limited diode ionization detector has a high current gain (10^5 – 10^6) and high resolution (5 MHz). Since it detects ions instead of fluorescence, it is more sensitive to the excited states with longer radiative lifetimes (which increases the collisional ionization rate compared to fluorescence decay). For ex-

ample, fluorescence detection sensitivity rapidly decreases with increasing vibrational quantum number for rovibrational levels close to the dissociation limit (long range region) or with increasing principal quantum number for levels located in highly excited Rydberg states. The experimental setup was similar to those of Refs. [5] and [6], with two differences. First, we used our ion detector instead of measuring the fluorescence with a filter-PMT combination. Second, the Coherent CW 699-29 autoscan ring dye lasers have been replaced by Coherent 899-29 autoscan ring dye or Ti:sapphire lasers.

In this Letter, we present the Rydberg-Klein-Rees (RKR) potential curves of the 3, 4, 5, and 6 ${}^1\Sigma_g^+$ shelf states and 2 and 3 ${}^1\Pi_g$ states of Na_2 in Fig. 1 and briefly review results obtained by other experimental techniques. For comparison, the ion pair curve and the theoretical calculations by Jeung [13,14] are also plotted in Fig. 1. The 3 ${}^1\Sigma_g^+$ state was previously studied by Effantin *et al.* [3], who used infrared fluorescence Fourier transform spectroscopy to reach the vibrational levels $0 \leq v \leq 9$ with a maximum outer turning point of the RKR potential curve at $R_{9+} = 4.54 \text{ \AA}$. By detecting ions, we have observed levels $0 \leq v \leq 141$ and $R_{141+} = 16.66 \text{ \AA}$ for this state. Taylor, Jones, and Schawlow [2] observed $0 \leq v \leq 20$ in the 4 ${}^1\Sigma_g^+$ state by using the two-step polarization-labeling method. More recently, our group used a filter PMT to study $0 \leq v \leq 127$ of this state [6]. The vibrational level $v = 127$ is well above the shelf region and has $R_{127+} = 13.36 \text{ \AA}$ and an energy of about 83% of the well depth. Using ion detection, we were able to extend v up to 178 with corresponding $R_{178+} = 17.65 \text{ \AA}$. Taylor, Jones, and Schawlow [2] also observed the 5 and 6 ${}^1\Sigma_g^+$ states with maximum vibrational quantum numbers of 20 and 18, respectively, by the two-step polarization-labeling method. The 5 ${}^1\Sigma_g^+$ state was also studied by Yan and co-workers [15,16], who reached $v_{\text{max}} = 52$ and $R_{52+} = 8.75 \text{ \AA}$ (below the shelf region). For the 5 ${}^1\Sigma_g^+$ state reported here, we have reached $v_{\text{max}} = 132$ and $R_{132+} = 20.64 \text{ \AA}$. The 6 ${}^1\Sigma_g^+$ state has

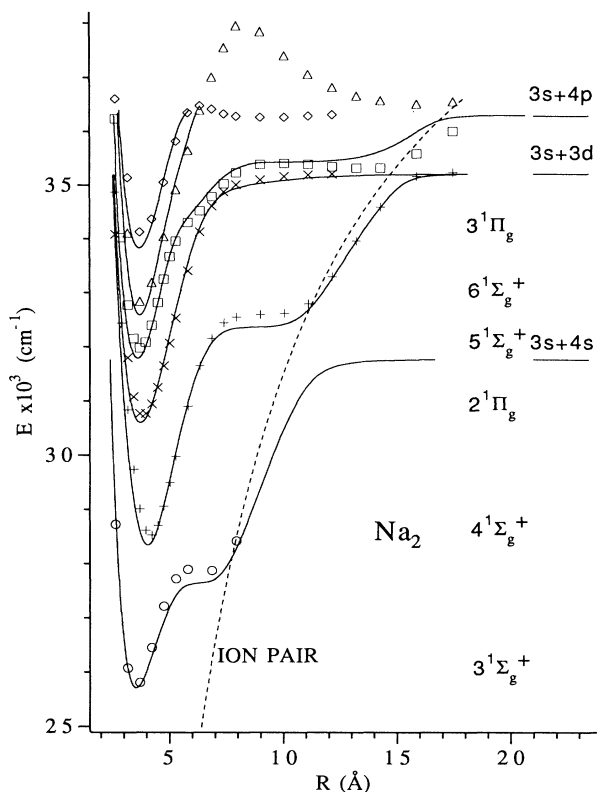


FIG. 1. RKR potential curves compared with theoretical calculations. Solid lines: experimental data (labeled at right, near their respective energy minima). Dotted line: the diabatic ${}^1\Sigma_g^+$ ion pair curve (with respect to the $\text{Na}^+ + \text{Na}^-$ limit). Markers: theoretical calculations from Jeung (Refs. [13,14]). (O: $3^1\Sigma_g^+$; +: $4^1\Sigma_g^+$; □: $5^1\Sigma_g^+$; △: $6^1\Sigma_g^+$; ×: $2^1\Pi_g$; ◇: $3^1\Pi_g$).

thus far only been extended to $v_{\text{max}}=39$ and $R_{39+}=6.24$ Å. For the 2 and 3 ${}^1\Pi_g$ states, Carlson *et al.* [1] and Taylor, Jones, and Schawlow [2] observed maximum vibrational numbers of 25 and 14, respectively, by the two-step polarization-labeling method. Recently, our group observed $0 \leq v \leq 43$ for the 2 ${}^1\Pi_g$ state by using a filter PMT [7], which characterized about 80% of the well depth with $R_{43+}=6.5$ Å. Here we extended this state up to $v_{\text{max}}=79$ and $R_{79+}=18.12$ Å. For the 3 ${}^1\Pi_g$ state, the last rovibrational level we have observed is $v=28$, $J=31$, which is about 165 cm^{-1} above its dissociation limit ($3s+4p$). The barrier is expected to occur at 6.0 Å at 126 cm^{-1} above the $3s+4p$ limit in the true potential (and about 167 cm^{-1} in the $J=31$ effective potential). Line broadening due to tunneling has been observed for $v=28$, $15 \leq J \leq 31$.

A comparison of the correlation diagram of Whang *et al.* [17] with Fig. 1 clearly indicates that the *adiabatic* limits of the $5^1\Sigma_g^+$, $6^1\Sigma_g^+$, and $3^1\Pi_g$ states are the asymptotes $3s+4p$, $3s+5s$ (off scale), and $3s+4p$, respectively, which differ from the (higher off scale) *diabatic* assignments of Carlson *et al.*, Taylor, Jones, and

Schawlow, and Yan *et al.* ($3s+5s$, $3s+4d$, and $3s+4d$, respectively). For these diabatic assignments,

$$T_e(n^1\Lambda_g) + D_e(X^2\Sigma_g^+ \text{Na}_2^+) \approx E(nl) + D_e(X^1\Sigma_g^+),$$

where $T_e(n^1\Lambda_g)$ is the potential minimum of $5^1\Sigma_g^+$, $6^1\Sigma_g^+$, and $3^1\Pi_g$; $D_e(X^2\Sigma_g^+ \text{Na}_2^+)$ is the diatomic ion dissociation energy; $E(nl)$ is the atomic excitation energy of the $5s$ and $4d$ states; and $D_e(X^1\Sigma_g^+)$ is the ground state dissociation energy. The analogous case of K_2 has recently been discussed [9,10]. Clearly the correlation tables and the ion pair curves in particular lead to major changes in electronic character with internuclear distance.

The adiabatic potential curve of ${}^1\Sigma_g^+$ symmetry shows a shelf due to the avoided crossings with the ${}^1\Sigma_g^+$ ion pair diabatic curve with the same symmetry ($\text{Na}^+ \text{Na}^-$). In Jeung's [13,14] calculations, the 3 and 5 ${}^1\Sigma_g^+$ potential energy curves have small barriers and then shallow minima in the shelf region. However, there are no barriers for these two states in the calculation by Henriot and Masnou-Seeuws [18]. In both sets of calculations, there is a large barrier and a deep, broad outer minimum around the shelf region of the $6^1\Sigma_g^+$ state. We were not able to reach the regions of the outer minima of these shelves (when they exist) due to their poor Franck-Condon factors with accessible levels of the $A^1\Sigma_u^+$ state. Experiments for studying these shelf minima directly may require three or four lasers. One approach could use all-optical-triple resonance [19] or fluorescence enhanced optical-optical double resonance [19] to populate higher vibrational levels in the intermediate $A^1\Sigma_u^+$ state with larger outer turning points and hence might probe the shelf minimum directly. The potential curves in Fig. 1 are constructed by the RKR method, which cannot deal with a double minimum problem (four turning points at the same energy level), and hence will not show a shallow local minimum in the shelf region if it exists. Moreover, the vibrational numbering in Table I ignores any additional "outer well" vibrational levels. An inverse perturbation approach, such as was used for a shelf state of Li_2 [20], will be used to more accurately characterize the 3 and 5 ${}^1\Sigma_g^+$ potentials. A summary of the results for these states is given in Table I.

Once these regions have been accurately characterized, a second opportunity arises, namely, theoretical modeling and understanding of the long range 3 and 4 ${}^1\Sigma_g^+$ and 4 and 5 ${}^1\Sigma_g^+$ avoided crossings. In a two state model, these occur at energies of 32039 and 35443 cm^{-1} , respectively, and distances of 11.26 and 15.41 Å, respectively. These points are defined as the distance of closest approach (in energy) of the two adiabatic curves. Note the simple $1/R$ ion pair curve occurs at significantly higher energy (32738 and 35516 cm^{-1} , respectively) at the crossing distances suggested by these avoided crossings.

Presumably this additional attraction is due to attractive polarization (e.g., charge-induced dipole) and disper-

TABLE I. Summary of Na₂ RKR potential curves for the 3 ¹Σ_g⁺, 4 ¹Σ_g⁺, 5 ¹Σ_g⁺, 6 ¹Σ_g⁺, 2 ¹Π_g, and 3 ¹Π_g states.

State	T_e (cm ⁻¹)	v_{\max}	R_e (Å)	$R_{v_{\max}}$ (Å)	r_{LR} (Å)	D_e (cm ⁻¹)	$G(v_{\max})/D_e$
3 ¹ Σ _g ⁺	25 692.00	141	3.57	16.66	16.5	6069.89	0.999
4 ¹ Σ _g ⁺	28 327.22 ^a	178	4.07	17.65	16.3	6867.71	0.998
5 ¹ Σ _g ⁺	31 770.00	132	3.64	20.64	20.3	4524.54	0.998
6 ¹ Σ _g ⁺	32 563.00	39	3.73	6.24	27.0	6659.73	0.571
2 ¹ Π _g	30 583.01 ^b	79	3.75	18.12	16.3	4611.87	0.999
3 ¹ Π _g	33 810.19 ^c	28	3.71	5.90	20.3	2484.35	1.066 ^d

^aFrom Ref. [5].^bFrom Ref. [6].^cFrom Ref. [2].^d v_{\max} is quasibound inside a potential barrier.

sion contributions, although it is often argued that these terms are quenched (“turned off”) at shorter distances. Using the estimated Na⁻+Na⁺ polarizabilities of 1090a₀³ (Ref. [21]) and 1.35a₀³ (Ref. [22]), respectively, one calculates a C₄ attractive coefficient of 545.7 a.u., corresponding to additional attractions of 552 and 167 cm⁻¹ at 11.26 and 15.41 Å, respectively; the latter number yields an unquenched polarized ion pair energy of 35 276 cm⁻¹ at 15.41 Å, significantly below the experimental crossing energy of 35 443 cm⁻¹. A more complete treatment, which includes multistate modeling, quenching of polarization and dispersion, and higher multipole polarization and dispersion interactions, is needed to fully analyze these data. Observations of additional crossings is obviously also desirable. Both are planned in our group.

The avoided crossing points also should correspond closely to specific atomic asymptotes; however, the 4s and 3d energies plus the Na₂ D_e value of 6022.03 ± 0.03 cm⁻¹ (based on the data in Ref. [23]) correspond to asymptotic energies of 31 761.89 and 35 194.89 cm⁻¹, respectively. Each asymptote is significantly below the corresponding two state model crossing energy (32 039 and 35 443 cm⁻¹, respectively). Since the diabatic curves in a two state model cross at precisely the distance at which the adiabatic curves approach closest and since this diabatic crossing is predicted to be at or below the corresponding asymptote, the above difference represents a significant breakdown of the two state model.

For interacting spherical atoms, long range behavior [$V(R) = D_e - \sum_k C_k R^{-k}$] is usually appropriate outside Le Roy’s radius [24]

$$r_{LR} = 2[(\langle r_a^2 \rangle)^{1/2} + (\langle r_b^2 \rangle)^{1/2}],$$

which increases with atomic principal quantum number as approximately n^2 . These values are listed in Table I. For electron orbitals possessing less than spherical symmetry (e.g., *np* or *nd* orbital), these values should be modified.

At large internuclear distance, the interaction between angular momentum *L* and spin *S* of the electron can be stronger than the interaction with the internuclear axis.

In this case Λ and Σ (the projections of *L* and *S* on the internuclear axis) as defined by Hund’s case (a) are inappropriate. Such states are better described by Hund’s case (c) where *L* and *S* are coupled first to form a resultant *J_a* which is then coupled to the internuclear axis to form states of a given Ω value (where Λ and Σ are no longer good quantum numbers). These detailed long range analyses will be reported elsewhere.

In addition, the semiclassical vibrational period τ_v can be estimated from the vibrational energy [6]:

$$\tau_v = 2\pi \left[\frac{dE}{d(v+1/2)} \right]^{-1}.$$

The vibrational period for levels on the shelf [6] and in the long range region [25–27] is often an order of magnitude or more longer than those of the normal vibrational levels. Classically, the molecule spends a much longer time on the shelf or at long range (near the outer turning point) than near the inner turning point. Quantum mechanically a large amplitude of the vibrational wave function is found in the shelf or long range region. Gerber [28] has directly observed a long vibrational period component in their femtosecond pump-probe experiments on Na₂, which is interpreted as arising from the 4 ¹Σ_g⁺ shelf region.

In summary, we have demonstrated ultrasensitive ionization detection and optical-optical double resonance techniques for extending singlet gerade Rydberg states of Na₂ to very high vibrational levels. The triplet gerade states can also be reached with these techniques by using intermediate states that are perturbation “windows” corresponding to $A \ ^1\Sigma_u^+ \sim b \ ^3\Pi_u$ mixed levels. Similar studies of singlet and triplet ungerade states are possible using all-optical-triple resonance spectroscopy [19]. Note that only ¹Σ_g⁺ and ¹Σ_u⁺ states interact with the ion pair curve and show shelf behavior. The long range levels can be used as bridges for studying the long range regions of the other states. Both the long range and the potential barrier results should also be helpful for studies involving state selective dynamics, and should provide good tests of the theoretical calculations, not only for Na₂, but for the other alkali dimers as well.

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Note added.—After this manuscript was submitted, another set of high quality calculations was published [29], which are also in excellent agreement with our experimental results, although, unfortunately, full potential curves are not reported.

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