## Spectroscopy of Na<sub>2</sub> by Photoassociation of Laser-Cooled Na

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We have observed the spectrum of long range molecular states of singly excited Na<sub>2</sub> formed by photoassociation during ultracold associative ionization collisions of laser-cooled Na atoms. The low kinetic energy of the collision allows us to obtain very high resolution spectra and to observe states close to the dissociation limit. The spectrum shows regular vibrational series characteristic of the  $1/R^3$  long range portion of the  $1_g$  potential (asymptotically  $S_{1/2} + P_{3/2}$ ) as well as molecular hyperfine structure within these peaks. We extract potential parameters and compare with recent theory.

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Laser cooling of atoms to kinetic energies less than the width of excited states presents a new opportunity for molecular spectroscopy. For example, it is possible to resolve molecular energy levels by observing the frequency dependence of the reaction  $(A+B+hv \rightarrow AB^*)$ , where bound molecular states are formed by the excitation of free atoms by light. We use this photoassociative spectroscopy [1,2] to measure the spectrum of vibrational states of Na<sub>2</sub>\*, and we detect the formation of the molecular states by ionizing the molecule with a second photon. The entire process  $(Na+Na+2hv \rightarrow Na_2^*+hv \rightarrow \cdots)$  $\rightarrow$  Na<sub>2</sub><sup>+</sup>+ $e^{-}$ ), often referred to as associative ionization (AI), is used here as a tool to study the molecular states produced in the intermediate step. By using atoms with kinetic energy less than the energy width of the molecular states, we are able to observe free-bound transitions not seen at higher energies. They can be observed with resolution similar to that obtained in high resolution, optical bound-bound molecular spectroscopy [3]. Furthermore, the free-bound nature of this ultracold collision process allows us to access molecular states which, due to selection rules and Franck-Condon (vibrational wavefunction overlap) considerations, are difficult or impossible to access from the bound molecular ground state.

Previous experiments studying AI of sodium in a twofocus laser trap [4] found a complicated spectrum which was associated [5,6] with the structure of the singly and doubly excited potentials of the Na2 molecule. These experiments were seriously limited, however, due to restrictions on the detuning and intensity of the laser, which was used both to trap the atoms and to excite the molecular transitions. By separating the trapping and spectroscopy in time we are no longer constrained by these limitations. The experimental technique used for the present investigations is similar to that used in our recent study of the effect of ground state atomic hyperfine structure on AI [7]. In that work, and similar work utilizing multiple excitation frequencies [8], structure was observed in the ionization spectrum that is almost certainly due to molecular states, although specific vibrational series could not be identified. By observing weak ionization signals further to the red of the atomic resonance we perform high

resolution molecular spectroscopy close to the dissociation limit, identify vibrational series, and obtain quantitative information about the molecular potentials.

In an ultracold collision  $(T \leq 1 \text{ mK})$  the atoms are moving so slowly that the collision time is long compared to the spontaneous decay time. Consequently, the atom pairs must be excited at a short enough range so that they will not spontaneously decay before reaching the small separation where AI occurs. The molecular potentials contributing to the collision processes in the present experiment are shown schematically in Fig. 1. Singlephoton excitation takes the atoms to molecular states that asymptotically correspond to the atomic states  $S_{1/2} + P_{3/2}$ . At ultracold collision energies, this initial excitation must necessarily be to an attractive intermediate state in order for the pair to be able to reach the short range required to access the Na2<sup>+</sup> potential. Five such states exist; the four with radiatively allowed transitions from the ground state are shown [2]. In our trap optical pumping will predominantly populate the uppermost (F=2) ground hyperfine state. From this state the initial excitation to attractive intermediate states is possible only with light tuned to the red of the atomic resonance frequency  $(3S_{1/2}, F=2 \rightarrow 3P_{3/2}, F'=3)$ . Including the other ground



FIG. 1. Simplified schematic of the molecular potentials. The atomic states to which the molecular potentials asymptotically correlate are labeled at the right.

hyperfine state allows transitions shifted to the blue of this atomic resonance as well [7].

Figure 1 shows two mechanisms which can lead to production of Na2<sup>+</sup>: direct photoionization from singly excited molecular states and autoionization from doubly excited states [5,9,10]. Although direct photoionization can proceed through both the  $l_g$  or  $0_u^+$  intermediate potentials near their inner turning points, Franck-Condon factors favor the  $l_g$  [11]. Photoionization out of the pure long range  $1_u$  and  $0_g^-$  states [12] is highly unlikely due to the poor spatial overlap of these states with the short range Na2<sup>+</sup> potential curve. Autoionization is presumed to occur from the doubly excited  $1_u$  potential [5,13] which can only be accessed from the  $1_g$  or  $0_g^-$  intermediate states. The Franck-Condon factor for this process from the 1<sub>e</sub> state, however, will be negligibly small [11]. In either case, as the frequency of the laser is scanned, the rotational-vibrational levels of the intermediate potential curves come into resonance, enhancing the ionization rate. Thus, the ionization signal will reflect the molecular spectrum.

In our experiments,  $10^7-10^8$  Na atoms are held in a magneto-optical trap (MOT) at a density of approximately  $10^{10}$  cm<sup>-3</sup> and a temperature  $\leq 500 \ \mu$ K. To measure the spectrum an additional, retroreflected, laser is added [7]. To observe structure associated exclusively with this laser, the two lasers are alternated at  $\sim 100$  kHz, with  $\sim 50\%$  duty cycle. The ions are counted with scalars, separately gated to correspond to these periods. A 300 MHz Fabry-Pérot etalon locked to a frequency-stabilized HeNe laser calibrates the frequency scan. The MOT laser, which is locked to a saturated absorption signal, provides an absolute frequency reference.

Two distinct regions are noticeable in the spectrum shown in Fig. 2. In the region between -5 and 0 GHz there is a dense set of resonances consisting of both broad (200-300 MHz) and narrow ( $\leq 50$  MHz) peaks. It is clear from the inset that there is no regular series of peaks in this region that is easily identifiable as a vibrational series belonging to a single molecular potential.

Second, the region below -5 GHz shows two very regular sets of peaks: a weak series, most clearly visible between -40 and -20 GHz, and a strong series evident over the entire -100 to -5 GHz range.

We interpret these regular features as vibrational series corresponding to molecular potentials of a singly excited Na<sub>2</sub> molecule detected via the direct photoionization mechanism of Fig. 1. The two different series result from the ground hyperfine splitting, as discussed below. For our detunings, we can only excite vibrational states close to the photoassociation (dissociation) limit. The positions of such states are predominantly determined by the long range character of the molecular potential [14-16], which is  $R^{-3}$  for an S+P potential of a homonuclear diatomic molecule. The smooth variation of the peak heights (transition strengths) as a function of detuning over the range from -5 to -100 GHz is evidence for the direct photoionization mechanism, as the transition to an autoionizing state at long range would have superimposed rapid variations in the line strengths corresponding to the bound state structure of the doubly excited potential [6,10].

In addition to the regular spacing of the vibrational peaks, we also find substructure within the peaks, as seen in Fig. 3. The rotational constants for the molecular states considered here are on the order of 30 MHz and are too small to account for much of this substructure. Molecular hyperfine structure, on the other hand, is of the right magnitude to account for most of the substructure seen in Fig. 3. Williams and Julienne [10] have determined the adiabatic potential curves for the singly excited Na<sub>2</sub> molecule. There are 384 hyperfine potentials, not including rotation, that connect to S+P at long range. The 1<sub>g</sub> state, the most likely candidate for direct photoionization, has 32 hyperfine components, some of which are degenerate. As discussed in Ref. [10], their calculations show that these features span a frequency width of about 1 GHz, consistent with that seen in our data. Each molecular potential is describable as  $C_3 R^{-3}$ at long range, albeit with slightly differing values of  $C_{3}$ ,



FIG. 2. Spectrum of ions produced versus laser detuning from the atomic transition. The inset shows the region from -5 GHz to resonance on a contracted vertical scale.



FIG. 3. A portion of the spectrum near -23 GHz showing the molecular hyperfine structure.

until a very long range the hyperfine interaction mixes the potentials, producing a tangle of potential curves which no longer have an  $R^{-3}$  potential character. Consequently, the dissociation energies of these potentials will not necessarily correspond to the dissociation limits implied by the  $R^{-3}$  portion of the potential.

The energy of the high-lying vibrational levels in a potential which can be approximated as  $C_3/R^3$  at long range obeys the relation [14-16]

$$E_v - D = (\alpha/C_3^2)(v - v_D)^6, \qquad (1)$$

where v is the vibrational quantum number counted from the top of the well,  $0 \le v_D < 1$  is the effective quantum number at the apparent dissociation limit (the first bound state is v = 1), D is the projected dissociation limit, and  $\alpha$ is a constant that depends on the reduced mass. In the absence of knowledge of the quantum numbers of the hyperfine components of the vibrational lines, we chose to use the centroid of each feature corresponding to a vibrational level, such as in Fig. 3, to determine its energy for these calculations. Sixteen peaks are used in the analysis of the strong series, while the weak series only provides eight peaks suitable for analysis. Fitting the data by Eq. (1) we extract D, C<sub>3</sub>, and  $v_D$ . In Fig. 4  $(E_v - D)^{1/6}$  is plotted as a function of v for the strong series. The linear relationship, which we see for both series, confirms the long range,  $R^{-3}$  nature of the intermediate state potentials. In addition, we have verified this by fitting the data by a formula similar to Eq. (1), but with a variable,  $R^{-n}$ , power dependence of the potential [14-16] and found  $n = 3.03 \pm 0.05$  for the strong series. (In this paper we will quote uncertainties at the level of 1 standard deviation.)

The values of  $C_3$  we obtain for the strong and weak vibrational series are  $6.73 \pm 0.05 \text{ zJ nm}^3$  ( $10.37 \pm 0.07 \text{ a.u.}$ ) and  $7.01 \pm 0.45 \text{ zJ nm}^3$  ( $10.8 \pm 0.7 \text{ a.u.}$ ), respectively, in atomic units [17]. The finite width of the peaks due to hyperfine structure is the major contribution to the uncertainty in the determination of the energies; nonetheless, the standard deviation of the residuals from the fit by Eq. (1) is 14 MHz for the sixteen peaks in the strong



FIG. 4. Plot of  $(E_v - D)^{1/6}$  for the strong series versus the vibrational quantum number, v, as determined from the fit by Eq. (1). The straight line is a fit to the data.

series. In that we are unable to identify particular hyperfine components, our analysis will only provide an average  $C_3$ .

The  $C_3$  coefficients obtained can be compared with the theoretical values for the four molecular potentials mentioned previously, calculated for the region where  $E_v - D \ll \Delta E_{\rm FS} = 500$  GHz, the fine structure splitting. The theoretical values are 1.33 a.u.  $(1_u)$ , 6.18 a.u.  $(0_g^-)$ , 9.55 a.u.  $(1_g)$ , and 10.29 a.u.  $(0_u^+)$  [2,18] with estimated uncertainties of about 1%. Analysis, using Eq. (1), of the eigenvalues (in the same energy range as those observed) of several of the  $l_g$  potentials including molecular hyperfine interactions as obtained by Williams and Julienne [10], however, leads to apparent  $C_3$  values between 6.75 zJnm<sup>3</sup> (10.4 a.u.) and 6.88 zJnm<sup>3</sup> (10.6 a.u.), in agreement with the average  $C_3$  values obtained here. Using the hyperfine structure calculations of Williams and Julienne [10], we assign our spectrum as being due to the  $l_g$  state because of its distinctive substructure. The observed substructure spans  $\sim 1$  GHz, in agreement with the calculations for the  $l_g$  state and in disagreement with the ~200 MHz spread predicted for the  $0_u^+$  state. Future calculations of the relative line strengths of the molecular hyperfine levels will allow a direct comparison of the observed substructure with theoretical predictions. We note that one previous measurement of a  $C_3$  coefficient for this state exists; Barrow et al. [19], using bound-bound spectroscopy, measured fourteen levels, the highest of which was ~1800 GHz from dissociation, and obtained a  $C_3 = 7.0 \pm 0.2$  a.u. For levels this deep in the potential  $C_3$  is expected to be much closer to the value of 6.18 a.u. calculated when  $E_v - D \gg \Delta E_{FS}$  [18,20].

The dissociation limits extracted for the strong and weak series are  $-0.21 \pm 0.03$  and  $+2.0 \pm 0.4$  GHz, respectively, measured from the atomic transition frequency. Recall that these values are extracted from a fit to the centroids of lines with complex structure and will not correspond exactly to the dissociation energy of any particular potential. Nonetheless, since the  $C_3$  coefficients are the same within our uncertainty, and the dissociation limits differ by approximately the 1.77 GHz ground state hyperfine splitting, we identify the strong series as being due to collisions involving two F=2 ground state atoms and the weak series as being due to collisions involving one F=1 and one F=2 atom.

The intensity and complexity of the spectrum in the -5 to 0 GHz range is markedly different from that of the rest of the spectrum. This may be due to a different ionization mechanism operating in this region. In their analysis of the spectrum of AI over this frequency range in our previous experiments [4], Julienne and Heather [5,6] proposed the mechanism of autoionization from a doubly excited bound state, as indicated in Fig. 1. Initial excitation to the  $0_g^-$  "pure long range" state is favorable under ultracold conditions. The cutoff in the spectrum around -5 GHz was proposed to result from the location of a rotational band head in the doubly excited  $1_{\mu}$  potential. Another possible explanation is that added structure in this region is due to the shallow singly excited  $1_{\mu}$  potential which is approximately 5 GHz deep [12]. In addition, the  $l_g$  vibrational series extends into this region and, while the transition strengths seem to be decreasing, the density of peaks increases as dissociation is approached. Finally, for any of the intermediate molecular potentials, the complicated molecular hyperfine interactions close to dissociation will destroy the simple  $R^{-3}$  character of the potentials. As a rough estimate of the size of these signals, we note that the largest features in the inset of Fig. 2 are an order of magnitude smaller than the main features studied in Refs. [7,8].

Using the new technique of photoassociative spectroscopy, we have performed the first ultracold collision experiment in which an assignable molecular spectrum was obtained. We have studied the long range character of a molecular potential in a previously unexamined region near dissociation that is difficult to reach from the thermally populated Na<sub>2</sub> ground state by usual spectroscopic techniques. The power of the photoassociative spectroscopy technique is further demonstrated in recent work by Miller, Cline, and Heinzen [21], in which they are able to see resolvable molecular spectra by looking at trap loss over a range of hundreds of wave numbers using ultracold rubidium. We plan further studies of the Na<sub>2</sub> molecular hyperfine structure using optical pumping to select particular hyperfine states. In order to further investigate the region from -5 GHz to dissociation, and possibly identify states belonging to the pure long range potentials, we plan to add a second laser to provide doubly resonant excitation of the singly excited long range states and the doubly excited autoionizing states. By appropriately tuning such a second laser and exploiting the direct photoionization process demonstrated in this experiment it should be possible to study the molecular states of other alkalis, which do not ordinarily undergo associative ionization from their first excited state [10].

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