Formation of ultracold, highly polar $X^1\Sigma^+$ NaCs molecules

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Abstract. We present photoassociation spectroscopy of ultracold NaCs molecules formed in a dual-species magneto-optical trap. Excited-state molecules are formed in states correlating to the Na(3S$_{1/2}$) + Cs(6P$_{3/2}$) asymptote. We assign the most prominent observed vibrational progression to the $\Omega = 2$ long range state based on a comparison with ab initio potentials. Molecules are secondarily excited before decaying to deeply bound levels of the electronic ground $X^1\Sigma^+$ state where they are ionized and detected by time-of-flight mass spectroscopy.

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1. Introduction

Much attention has been paid recently to the study of cold and ultracold polar molecules [1], both in terms of basic science [2, 3] and possible future applications [4, 5]. For most of these proposals the ideal molecular sample is translationally ultracold and in the internal ground state, thus ensuring a large dipole moment and state stability. To date, several approaches to achieving this goal have been demonstrated, each with its own advantages and disadvantages. The methods of buffer gas cooling [6, 7], Stark deceleration [8]–[10], velocity selection [11] and collisional cooling [12] each begin with molecules in the internal ground state, but have yet to produce samples colder than \( \sim 0.5 \text{ mK} \). Photoassociation and Feshbach magnetoassociation of ultracold atomic samples [13]–[19] have produced much colder molecules, but the majority have been restricted to highly excited rovibrational states in the molecule’s ground electronic state where dipole moments are small. Recently some success has been achieved in using additional laser frequencies to transfer molecules to lower rovibrational states [20].

In this work, we present results on and analysis of the photoassociation of ultracold NaCs molecules and show that the subsequent spontaneous emission following a secondary excitation produces large numbers of molecules deeply bound in the \( X^1\Sigma^+ \) state. Molecule production rates are several orders of magnitude larger than our previously published results. NaCs is a particularly promising candidate for ultracold polar molecule experiments for several reasons. Firstly, the maximum dipole moment of the \( X^1\Sigma^+ \) state, 4.6 D, is second only to LiCs among the heteronuclear bi-alkalis. Secondly, as we demonstrate in this work, the simplest photoassociation experiment fortuitously generates large numbers of molecules with dipole moments nearly equal to that of the absolute ground state. Lastly, we have shown that because of their large dipole moments these molecules can be electro-statically confined using an inexpensive and easily constructed trap that does not limit optical access [21]. We have calculated that these molecules can be efficiently transferred to the absolute ground state in a one-step coherent process [22] which would achieve the goal of a large, ultracold sample of electro-statically trapped absolute ground state polar molecules. As these calculations were based on \textit{ab initio} potentials, more precise spectroscopic information will be needed to achieve experimental results and this work represents the first extensive photoassociation spectroscopy of the NaCs molecule.

2. Experiment

Our experiments follow the familiar form of most recent work in ultracold photoassociation spectroscopy [17]. We begin with overlapping dark-SPOT magneto-optical traps (MOTs) [23] of sodium and cesium. Atom numbers for both MOTs are \( \sim 10^8–10^9 \) with densities \( \sim 10^{10}–10^{11} \text{ cm}^{-3} \). Photoassociation light generated by an argon ion-pumped ring titanium:sapphire laser (Coherent 899-21) is introduced, after which time the trapping and photoassociation light is extinguished and the molecules are allowed to decay to the electronic ground state. A pulsed neodymium:YAG-pumped tunable dye laser (Lambda Physik FL3002) ionizes a fraction of the molecules in a two-photon resonant process, and the molecules are detected in time-of-flight mass spectroscopy by an acceleration grid and a channel electron multiplier (Sjuts KBL 408) recorded by a multi-channel scalar (Stanford Research Systems SR430). In a typical experiment operating at 1 Hz the timing sequence is as follows: atoms are accumulated in the MOTs for 950 ms while continuous photoassociation light is applied, the laser frequencies are
extinguished for 10 ms to allow for spontaneous decay, the pulsed laser photoionizes the sample and the time-of-flight measurement is performed.

3. Results

Figure 1 shows a sample of the spectrum recorded with the photoassociation laser tuned below the Cs ($6S_{1/2} \rightarrow 6P_{3/2}$) transition. In this work all detunings lie above the Cs ($6S_{1/2} \rightarrow 6P_{1/2}$) transition and thus we access only five of the eight long-range Hund’s case (c) states correlating to the cesium D2 line, namely the $3(0^-)$, $3(0^+)$, $3(1)$, $4(1)$ and $1(2)$. We observe 17 photoassociation resonances over 217 cm$^{-1}$ below the atomic asymptote, all of which show well-resolved rotational structure, and some of which also display resolved hyperfine structure.

4. Photoassociation spectrum assignment

To assign the spectrum we use the potentials of [24], shown in figure 2, combined with the long-range dispersion coefficients of [25]. The spectrum is calculated using the LEVEL program [26]. We first identify to which long-range state each vibrational level belongs. To do this, we check the rotational structure to determine the value of $\Omega$. Neglecting centrifugal distortion, rotational progressions follow the form $E_J = B_v [J(J + 1) - \Omega^2]$ ($J = \Omega, \Omega + 1, \Omega + 2, \ldots$), where $B_v$ is the rotational constant for that state. For states with $\Omega = 2$, as there is only one potential, we have only to assign the vibrational number. For states with $\Omega = 0$ or 1,
Figure 2. Some relevant potentials of the NaCs system. Molecules are first photoassociated (PA) to the 1(2) long-range state and are secondarily excited before undergoing spontaneous emission (SE) to the ground state.

we compare the observed rotational constants to those calculated based on ab initio potentials, noting that for example the rotational constants of the two \( \Omega = 1 \) states differ by as much as 100\% for certain detunings. In this way we identify 10 of the observed photoassociation resonances, 8 belonging to the 1(2) state, listed in table 1 and 1 each belonging to the 3(1) and 4(1) states. Figure 3 shows the observed and calculated energies and rotational constants for the \( \Omega = 2 \) long-range state.

5. Photoionization pathway

Our detection scheme is only sensitive to molecules deeply bound in the \( X^1\Sigma^+ \) ground state. Figure 4 shows the molecular ion signal as a function of the photon energy of the ionizing pulse. As shown in figure 5, near-dissociation molecules will be excited to energies between the first and second ionic potentials, and will thus be either fragmented, or leave the interaction region with sufficient kinetic energy that they will not reach the channel electron multiplier. The ionization photon energies of figure 4 put a lower bound on the binding energy of the ground state molecules of \( \sim 2000 \text{ cm}^{-1} \).

An analysis of the ionization spectrum further localizes the molecules’ distribution in the \( X^1\Sigma^+ \) state. The spectrum is complicated, but several features are prominent, namely a series of maxima which are nearly equally spaced by 22 cm\(^{-1}\), and which are wider than the rest of the features in the spectrum. As the ionic well is well approximated by a structureless continuum, all features are due to either the ground or intermediate state structure. Based on the minimum binding energy of the ground state molecules, the ground state vibrational spacings are too large to account for the 22 cm\(^{-1}\) spaced peaks [27], and thus they are due to the intermediate

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Table 1. Observed vibrational energy levels and rotational constants $B_v$ of the $\Omega = 2$ long-range state. Detunings are relative to the Cs ($6S_{1/2} \rightarrow 6P_{3/2}$) transition.

| $v$ | Detuning (cm$^{-1}$) | $B_v$ (10$^{-2}$ cm$^{-1}$) |
|-----|----------------------|-----------------------------|
| 88  | −188.9               | 2.47                        |
| 89  | −165.7               | 2.44                        |
| 90  | −144.4               | 2.34                        |
| 92  | −107.0               | 2.05                        |
| 94  | −76.3                | 1.81                        |
| 96  | −52.0                | 1.63                        |
| 98  | −33.3                | 1.44                        |
| 100 | −20.0                | 1.13                        |

Figure 3. Comparison of calculated and observed vibrational state energies and rotational constants for the $\Omega = 2$ long-range state. Filled circles represent data and open squares are calculated.

state structure. The known binding energy together with the photon energy of the photoionizing laser indicate that the intermediate state correlates to the Na(3S) + Cs(5D) asymptote. The spectrum calculated from the $ab$ initio potentials indicates only one state which has a region of regularly spaced vibrational states, the 4(0$^+$) ‘shelf’ state, whose calculated spectrum is shown.
Figure 4. Photoionization spectrum showing features regularly spaced $22\text{ cm}^{-1}$ apart. The inset shows the vibrational state spacing of the $4(0^+)$ intermediate state.

in the inset of figure 4, and whose spacings match the spectrum observed in the ionization. The $4\text{ cm}^{-1}$ width of the peaks most likely arises from the rotational occupation of the ground vibrational states and is unresolved due to the linewidth of the ionizing laser. Identifying this intermediate state further restricts the possible binding energy of the ground state molecules to $2500–3200\text{ cm}^{-1}$, indicating that the detected molecules lie in a single vibrational state between $v = 18$ and 23.

Angular momentum selection rules prohibit the decay of $\Omega = 2$ state molecules to the $X^1\Sigma^+$ state. Additionally, the Franck–Condon factors between the $\Omega = 2$ long-range state and the $X^1\Sigma^+$ state are very small ($\sim 10^{-11}$). We find that $X^1\Sigma^+$ state molecules are created by secondary excitation following the initial photoassociation. Secondary excitation has been shown to readily occur in both NaCs [28] as well as other bi-alkalis [29] and has been shown to significantly increase the formation rate of electronic ground-state molecules. As we have previously shown [28] NaCs molecules which absorb one of each photon near the trapping frequencies of sodium and cesium are promoted to states which readily autoionize. Thus we infer that the double excitation occurs either from the absorption of two photoassociation photons or one photoassociation photon and one cesium trap photon ($11\ 732 \text{ cm}^{-1}$), meaning the final energy of the molecules will lie between $23\ 030–23\ 247 \text{ cm}^{-1}$, in the range of states correlating to several asymptotes, namely the Na(4S) + Cs(6S) and Na(3P) + Cs(6P). We look for a secondary state that is accessible with the available light frequencies, has the correct angular momentum to transition both from the photoassociated state and to the $X^1\Sigma^+$ state, and has large Franck–Condon overlap with both states. As the density of states in this region is large, many states satisfy the criteria, and we show just one example, the 20th $\Omega = 1$ state, which
is in the correct range energetically, has the correct angular momentum, and has reasonable Franck–Condon factors with the $1(2)$ state and the $X^1\Sigma^+$ state. To verify that a secondary excitation is indeed creating the large number of observed deeply bound ground-state molecules we detect the UV fluorescence from the spontaneous emission to the ground state. Based on the ranges of the energy of the secondarily excited state and the binding energy of the ground-state molecules we expect these photons to be in the range $\lambda = 378–392$ nm. We detect the photons with an avalanche photodiode (Hamamatsu SPCM) operated in single-photon counting mode and filter visible light with a pair of short-wave pass filters (CVI SPF-400-1.00 and SPF-450-1.00). After accounting for dark counts and background counts from visible light that passes through the filters we observe a count rate of 100 Hz. As we collect only 1% of the solid angle we extrapolate a photon rate and thus a molecule production rate $\sim 10^4$ Hz, in good agreement with the molecular production rate as calculated from the number of molecules we detect per ionizing pulse [30].

6. Discussion

Despite the fact that the ground electronic state molecules are in an excited vibrational state, they exhibit a permanent dipole moment nearly as large as the maximum possible in the absolute ground state, in this case $\sim 4.5$ D [31]. Similarly, their quadratic Stark shift makes them easily trappable with moderate static electric fields, as we have demonstrated [21]. In [21], we trapped rotationally excited low-field-seeking states in an electro-static quadrupole trap, but the trap can also be switched to a rotating saddle-point type in order to trap rotational ground state
molecules. Finally, being deeply bound, these molecules can be quite readily transferred to lower-lying vibrational states by stimulated Raman adiabatic passage (STIRAP). Using the methods described in [22], we calculate that one-step STIRAP process will transfer $\sim 95\%$ of the molecules to the absolute vibrational ground state.

7. Conclusion

In conclusion, we have performed the first extensive photoassociation spectroscopy of ultracold NaCs and have assigned the most prominent progression to the $\Omega = 2$ long-range state. Following secondary excitation these molecules spontaneously decay to very deeply bound $X^1\Sigma^+$ molecules which exhibit large dipole moments and quadratic Stark shifts, allowing trapping with moderate static electric fields. Finally, we have calculated that due to the large binding energy of these molecules, nearly 100% can be transferred to the absolute vibrational ground state using a one-step STIRAP process.

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