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Formation and detection of ultracold ground-state polar molecules

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We report on the formation of translationally cold NaCs molecules starting from a laser-cooled atomic vapor of Na and Cs atoms. Colliding atoms are transferred into bound molecular states in a two-step photoactivated process in which the atoms are first photoassociated by trap photons into an excited state molecular complex and then allowed to decay into a bound molecular ground state. Time-of-flight measurements show a translational temperature $T=260\pm130$ μK that reflects the measured temperature of the initial atomic gas.

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Laser cooling of atoms has enabled spectacular advancements in physics. Unfortunately, it has not been generalized to even simple molecules as the complex molecular level structure does not offer the needed cycling transitions. The creation of microKelvin molecular samples has therefore been a significant but elusive goal. In recent years, several molecular cooling schemes such as buffer-gas cooling [1], Stark deceleration [2], collisional deceleration [3], and temperature selection [4] have produced electronic ground-state molecules in the milliKelvin regime. Using a different approach, several groups have created microKelvin ground state homonuclear molecules via photoassociation of laser-cooled atoms [5–7]. In related work, heteronuclear molecules have been photoassociated [8,9], but only into electronically excited states.

Among cold heteronuclear molecules, polar molecules are of particular interest. Large induced dipole moments may enable creation of exotic coupled molecular complexes [10] and precision tests of theory [11]. They are also ideal systems for electron dipole moment searches [12] and are in demand as qubits for quantum computers [13]. Furthermore, following recent realizations of molecular Bose-Einstein condensation [14], the opportunity to create a polar condensate [15] is exciting. Here we report on the formation of ultracold NaCs molecules in their electronic ground state. Our approach is based on photoassociation (PA) [16] of cold atoms by an optical trap and shows a production rate similar to that of trapped-atom homonuclear alkali experiments [5–7].

Our experiments start with cesium (Cs) and sodium (Na) atoms confined in overlapping magneto-optical traps (MOTs) [17]. We choose this approach for several reasons. First, the successful experiments [5–7] on homonuclear molecules have shown, that starting from atoms stored in and photoassociated by a MOT is the simplest way of forming ultracold homonuclear dimers. Second, NaCs has the largest measured dipole moment among all of the diatomic alkali molecules [18] and third, our previous studies have shown that cold Na and Cs have a substantial cross section for photoassociation into excited-state NaCs molecules [8].

Our experiments all follow the same pathway (Fig. 1). Na and Cs atoms held in a single MOT are photoassociated by trap photons into bound, excited molecular states. These molecules decay into their electronic ground state via spontaneous emission. They are then detected by resonantly enhanced multiphoton ionization (REMPI) and are identified by time-of-flight mass spectrometry.

The details of the MOTs have been described elsewhere [8]. The trap light intensities for Na and Cs are ~13 and ~25 mW/cm^2, respectively, with repumping intensities roughly 10% of the trap-light intensities. For Na (Cs), we trap on the $3S_{1/2}(F=2)\rightarrow 3P_{3/2}(F=3)$ $[6S_{1/2}(F=4)\rightarrow 6P_{3/2}(F=5)]$ transition and repump on the $3S_{1/2}(F=1)\rightarrow 3P_{3/2}(F=2)$ $[6S_{1/2}(F=3)\rightarrow 6P_{3/2}(F=4)]$ transition. The magnetic field gradient is ~11 G/cm. Typically, 5×10^5 Na atoms at 220 ± 80 μK and 2×10^6 Cs atoms at 210 ± 80 μK are confined—these are modest traps. Charged coupled device imaging verifies the three-dimensional overlap of Na and Cs. The overlap is optimized by changing the alignment while monitoring the rate of NaCs$^+$ ions produced via a known photoassociative ionization reaction channel [8]. An

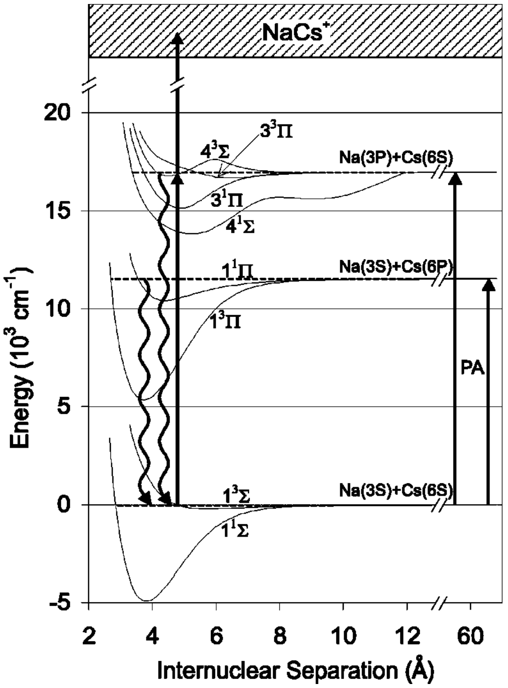

FIG. 1. Energy level diagram for a typical molecule formation and detection process. Atoms are photoassociated into a bound molecular state by a trap photon ("PA" in the figure). The excited state molecule is allowed to decay to its electronic ground state via spontaneous emission, and is then ionized and detected. The potentials shown are *ab initio* calculations from Ref. [19] and neglect fine structure.

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accelerating grid ion-optic and a channel electron multiplier (CEM) form the ion detection system.

Given a Na and a Cs atom approaching each other, photoassociation occurs when either atom absorbs a trap photon (see Fig. 1). Previous studies by our group have shown [8] that absorption of either a Na or a Cs trap photon can readily photoassociate the two atoms into an excited-state NaCs molecule. For a Cs trap photon, the input states are the long range Hund's case (c) states (1, 2, 0^+, and 0^-) that are all expected to be attractive [20]. These input channels correlate to the $^1\Pi$ and $^3\Pi$ states (Fig. 1). For a Na trapping photon, all long range states except the 0^+ state are also predicted to be attractive [20]. These input states correlate to $^1\Pi$, $^3\Pi$, $^1\Sigma$, and $^3\Sigma$. The excited state molecules are expected to be distributed over a range of rotational and vibrational states near their respective dissociation limits. A fraction of these excited molecules decays to a range of rovibrational states within the electronic ground state manifold with a distribution governed by the bound-bound Franck-Condon factors. We note that, as compared to homonuclear PA, the absence of a long-range resonant dipole-dipole interaction can give rise to enhanced Frank-Condon overlap [21].

Ground state molecules are detected as follows: The trap light is first extinguished leaving the cold cloud in the dark. We then wait a "dark time" of 10 μs, chosen to be many orders of magnitude longer than the excited state lifetimes of all atoms and molecules in the cold cloud. This ensures all possible species have decayed to their electronic ground states. It also ensures that any NaCs^+ ions created in the trap by photoassociative ionization [8] have been swept from the trapping chamber (time-of-flight is $\sim\mu$s). While the trap light is still off, a Nd:yttrium-aluminum-garnet-pumped dye laser generates a 9 ns long, 20–100 μJ pulse focused to 2 mm^2 and directed at the cloud. The laser pulse simultaneously ionizes a fraction of the atoms and molecules in the cloud. In a two-photon REMPI process, the NaCs molecules are first excited to states correlating to the $\mathrm{Na}(3P)+\mathrm{Cs}(6S)$ asymptote, and then ionized by a second photon. An electric field of $\sim$7 V/cm generated by the grid accelerates the ions toward the CEM where they are detected several microseconds after their creation. The CEM output is a series of short current pulses that are recorded by a multichannel scaler. The repetition rate of the pulsed laser is 10 Hz and we typically integrate 10 000 pulses. In this scheme, heavier species arrive at the CEM at later times, thereby mass separating the various ions into a time-of-flight distribution. We observe well resolved mass peaks (Fig. 2, bottom) corresponding to Na (23 u), Cs (133 u), NaCs (156 u), and Cs_2 (266 u). The Cs_2 molecular peak is due to PA of Cs atoms into Cs_2 by the MOT [5].

The pulsed laser is tuned from 575 to 600 nm. This range is chosen for three reasons: (1) it features a resonant ionization pathway (i.e., a REMPI process) and provides evidence that the NaCs starts in a ground state, (2) it offers the smallest energy photons which can two-photon resonantly ionize the NaCs, and yet (3) these photons cannot resonantly ionize the Cs atoms. This last point is important because a large Cs-ion peak could obscure the nearby NaCs peak. The number of NaCs ions detected increases with pulsed laser energy consistent with the quadratic behavior expected for a two photon transition up to the molecular continuum.

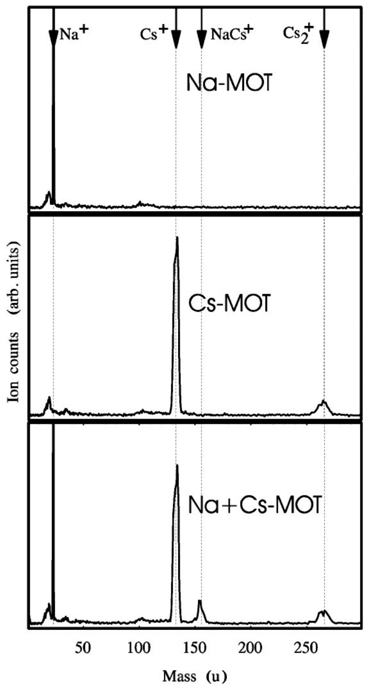

FIG. 2. Time-of-flight signal showing various atomic and molecular mass peaks. Three traces show the signal obtained in the presence of a sodium MOT only (top), a cesium MOT only (center), and both MOTs (bottom). The peak at 156 u is obtained only if both MOTs are present, indicating that it is NaCs^+. The small, broad, unlabeled peaks near the atomic peaks are due to thermal background atoms in the vacuum chamber.

An ionizing wavelength of 588 nm ($17\,006\ \mathrm{cm}^{-1}$) produced the largest NaCs^+ signal, yet we observe significant NaCs^+ over the entire 575–600 nm ($17\,391$–$16\,666\ \mathrm{cm}^{-1}$) wavelength range. To interpret this we consider the calculated *ab initio* molecular potentials and verify that there are available bound states that are compatible with the REMPI photon energy (Fig. 1). Calculations place the minima of the NaCs ground state wells at 214 and 4923 cm^{-1} below the $\mathrm{Na}(3S)+\mathrm{Cs}(6S)$ asymptote for the $1^3\Sigma$ and the $1^1\Sigma$ states, respectively (Fig. 1). Similarly, the $4^3\Sigma$, $3^3\Pi$, $3^1\Pi$, and $4^1\Sigma$ minima are predicted to be at 191, 285, 1842, and 3135 cm^{-1} below the $\mathrm{Na}(3P)+\mathrm{Cs}(6S)$ asymptote, respectively. With respect to the $\mathrm{Na}+\mathrm{Cs}^+$ ion-atom pair asymptote at $31\,406\ \mathrm{cm}^{-1}$, the minimum in the NaCs^+ molecular well is predicted to be at either 26 809, 28 196 , or 29 712 cm^{-1} [22], however, our previous experiments on NaCs [8] have already ruled out the latter prediction [23]. Given these values, bound-bound resonant transitions are allowed from 457 to 722 nm ($13\,843$–$21\,901\ \mathrm{cm}^{-1}$), and hence the observation of measurable NaCs^+ production from 575 to 600 nm is expected. We observe broad features in this wavelength range that are under investigation [24]. We also note that our observation of REMPI at 575 nm ($17\,391\ \mathrm{cm}^{-1}$) is consistent with the presence of both singlet and triplet ground state NaCs molecules.

We further explore the peak at 156 u by alternately starting with either a pure Na or a pure Cs trap (Fig. 2) and find that NaCs^+ is only observed when we start from a Na+Cs

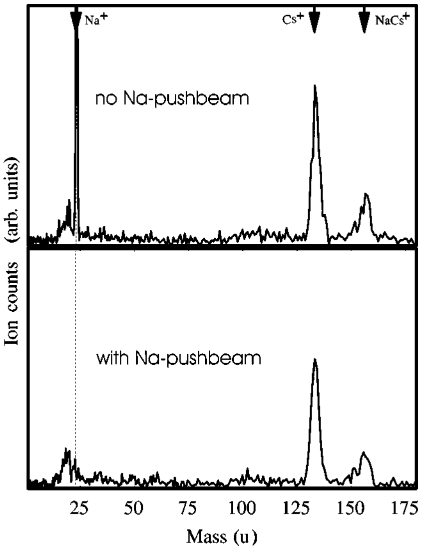

FIG. 3. Spectrum showing that the $NaCs^+$ peak is unaffected by removal of Na atoms after the trap is extinguished. In the first experiment (top) both traps are turned off and the sample is ionized. To show that the NaCs molecules are formed uniquely during the trap phase, we remove the sodium atoms after turning off the trap by pushing the atoms with resonant light (bottom). The $NaCs^+$ peak (156 u) is not appreciably affected.

MOT. Each of the other features was also shown to be due uniquely to one trapped species or the other. This demonstrates that the NaCs is formed from atoms in the MOTs and not from the thermal background atoms (see Fig. 2).

Previous experiments have shown that PA of excited state heteronuclear alkali pairs is readily achieved in multispecies MOTs [8,9]. In the present work it is crucial to prove that the NaCs molecules detected by the REMPI laser originate from the electronic groundstate. We know that NaCs molecules are not formed from background (hot) atoms, and because of the long dark time, it is natural to assume that the NaCs is formed during the trapping phase and that the molecules are in their ground-state. Nevertheless, we also need to prove that they are not formed by the ionizing pulse itself. To eliminate this possibility, after extinguishing the trap light, we briefly introduce a separate sodium-resonant light beam at 589 nm that contains both the trapping and repumping frequencies. This beam selectively pushes the Na atoms and removes all cold Na from the interaction region. The beam is then extinguished and the sample is allowed to relax, again for a dark time $>10\ \mu$s. When we then ionize the resultant sample using the REMPI laser, the Na peak is absent while the NaCs, Cs, and Cs_2 peaks remain (Fig. 3). This shows clearly that the NaCs was formed during the trapping phase. The long dark time also means that these NaCs molecules are in their electronic ground state before the REMPI laser is used to ionize them.

As the molecules are formed from trapped and cooled atoms, we expect their temperature to be comparable to that of the trapped atoms. We measure the molecule temperature using a time-of-flight technique: we vary the delay between trap turn-off and the ionizing pulse. When the traps are turned off, the cold atoms and molecules drift out of the path of the ionizer and the number remaining within the profile of the ionizing beam decreases. The delay is varied from 0.01 to 20 ms. The number of NaCs ions detected decreases as expected. We were able to track the molecular signal beyond 10 ms, and no NaCs signal was detectable after 20 ms. We fit the remaining number as a function of the delay to a simple ballistic expansion model, accounting for the REMPI laser beam shape, and extract an average temperature of NaCs of $T=260\pm130\ \mu\mathrm{K}$, corresponding to an average velocity of 0.2 m/s. This result was further verified by a three-dimensional Monte-Carlo simulation.

We observe production of $\sim$500 NaCs molecules per 10 000 pulses. The efficiency of the ionization and detection process is $\sim$10%. In addition, given the temperture and the repetition rate of the REMPI laser, a kinetic model shows that 90% of the NaCs drift out of the MOT between pulses [6]. We therefore find a NaCs production rate of $\sim$50 Hz. The rate per unit volume can be expressed as $d[\mathrm{NaCs}]/dt = K_{\mathrm{NaCs}}[\mathrm{Na}][\mathrm{Cs}]$ where K_{NaCs} is the molecular production rate coefficient and [Na] and [Cs] are the respective atomic densities. We thereby extract the rate coefficient $K_{\mathrm{Nacs}}=7.4\times10^{-15}\ \mathrm{cm}^3\ \mathrm{s}^{-1}$. This rate is similar to those observed in early experiments involving homonuclear diatomic alkali-metal molecules [5–7,25].

In conclusion, by photoassociating laser-cooled atoms held in an optical trap, we create NaCs at $260\pm130\ \mu\mathrm{K}$ in the electronic ground state with a rate coefficient $K_{\mathrm{Nacs}} = 7.4\times10^{-15}\ \mathrm{cm}^3\ \mathrm{s}^{-1}$. Earlier work [8] showed that the photoassociation rate of excited NaCs in our trap is characterized by the rate coefficient $K_{\mathrm{PA}}\sim10^{-10}\text{–}10^{-11}\ \mathrm{cm}^3\ \mathrm{s}^{-1} \sim 10^4\ K_{\mathrm{NaCs}}$. These rates show that currently only one in $\sim10^4$ photoassociated atom pairs decay into bound ground-state molecules. We are therefore starting experiments using additional lasers to photoassociate through excited state molecular levels that exhibit enhanced Franck-Condon coupling into bound, low-lying molecular states. Given our trap densities, the low absolute molecular formation rate of 50 Hz has prohibited the spectroscopy needed to identify the optimal intermediate PA state. We are therefore also modifying our apparatus to increase the trapped atom number and density [26]. Related strategies in homonuclear systems [27] have shown that nearly 100% of the photoassociated flux can thereby be converted into molecules. For NaCs production in an optimized, high-density trap [26], we can hope to observe formation rates as large as 10^6 molecules per second.

Note added. Recently we learned that groups at the University of Sao Paulo and at Yale have presented evidence for the formation of ultracold polar molecules via photoassociation in other alkali-metal pairs [28].

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[1] J. D. Weinstein *et al.*, Nature (London) **395**, 148 (1998).

[2] H. L. Bethlem *et al.*, Nature (London) **406**, 491 (2000).

[3] M. S. Elioff, J. J. Valentini, and D. W. Chandler, Science **302**, 1940 (2003).

[4] S. A. Rangwala *et al.*, Phys. Rev. A **67**, 043406 (2003).

[5] A. Fioretti *et al.*, Phys. Rev. Lett. **80**, 4402 (1998).

[6] A. N. Nikolov *et al.*, Phys. Rev. Lett. **82**, 703 (1999).

[7] C. Gabbanini, A. Fioretti, A. Lucchesini, S. Gozzini, and M. Mazzoni, Phys. Rev. Lett. **84**, 2814 (2000).

[8] J. P. Shaffer, W. Chalupczak, and N. P. Bigelow, Phys. Rev. Lett. **82**, 1124 (1999).

[9] A. J. Kerman *et al.*, Phys. Rev. Lett. **92**, 033004 (2004), U. Schlöder, C. Silber, T. Deuschle, and C. Zimmermann, Phys. Rev. A **66**, 061403(R) (2002).

[10] A. V. Avdeenkov and J. L. Bohn, Phys. Rev. Lett. **90**, 043006 (2003).

[11] E. Bodo *et al.*, J. Chem. Phys. **113**, 11071 (2000).

[12] J. J. Hudson, B. E. Sauer, M. R. Tarbutt, and E. A. Hinds, Phys. Rev. Lett. **89**, 023003 (2002).

[13] D. DeMille, Phys. Rev. Lett. **88**, 067901 (2002).

[14] J. Herbig *et al.*, Science **301**, 1510 (2003).

[15] B. Damski *et al.*, Phys. Rev. Lett. **90**, 110401 (2003).

[16] H. R. Thorsheim, J. Weiner, and P. S. Julienne, Phys. Rev. Lett. **58**, 2420 (1987).

[17] E. L. Raab *et al.*, Phys. Rev. Lett. **59**, 2631 (1987).

[18] G. Igel-Mann, U. Wedig, P. Fuentealba, and H. Stoll, J. Chem. Phys. **84**, 5007 (1986).

[19] M. Korek, A. R. Allouche, K. Fakhreddine, and A. Chaalan, Can. J. Phys. **78**, 977 (2000), http://lasim.univ-lyon1.fr/allouche/pec.html.

[20] There is some disagreement in the literature on 0^+, see M. Movre and R. Beuc, Phys. Rev. A **31**, 2957 (1985); B. Bussery, Y. Achkar, and M. Aubert-Frecon, Chem. Phys. **116**, 319 (1987).

[21] H. Wang and W. C. Stwalley, J. Chem. Phys. **108**, 5767 (1998).

[22] L. Bellomonte *et al.*, J. Chem. Phys. **61**, 3225 (1974), L. von Szentpaly *et al.*, Chem. Phys. Lett. **93**, 555 (1982), A. Valance, J. Chem. Phys. **69**, 355 (1978).

[23] The $\mathrm{Cs}+\mathrm{Na}^+$ ion-pair asymptote is at 41 449 cm^{-1}; however, we do not know of any theoretical prediction of the minimum in the NaCs^+ molecular ion potential relative to this asymptote. Assuming that the well depths are similar to that for $\mathrm{Na}+\mathrm{Cs}^+$ ion-pair asymptote, then this well would be inaccessible to our REMPI laser.

[24] C. M. Dion *et al.*, Eur. Phys. J. D **18**, 365 (2002).

[25] In this previous work, ground-state molecule formation both by state-selective photoassociation and trap-laser photoassociation were reported. We compare only to rates for the latter processes.

[26] W. Ketterle *et al.*, Phys. Rev. Lett. **70**, 2253 (1993).

[27] A. N. Nikolov *et al.*, Phys. Rev. Lett. **84**, 246 (2000).

[28] M. W. Mancini, G. D. Telles, A. R. L. Caires, V. S. Bagnato, and L. G. Marcassa, Phys. Rev. Lett. **92**, 133203 (2004); A. J. Kerman, J. M. Sage, S. Sainis, T. Bergeman, and D. DeMille, *ibid.* **92**, 153001 (2004).