

# A High Phase-Space-Density Gas of Polar Molecules

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**A quantum gas of ultracold polar molecules, with long-range and anisotropic interactions, would not only enable explorations of a large class of many-body physics phenomena, but could also be used for quantum information processing. We report on the creation of an ultracold dense gas of  $^{40}\text{K}^{87}\text{Rb}$  polar molecules. Using a single step of STIRAP (STImulated Raman Adiabatic Passage) via two-frequency laser irradiation, we coherently transfer extremely weakly bound KRb molecules to the rovibrational ground state of either the triplet or the singlet electronic ground molecular potential. The polar molecular gas has a peak density of  $10^{12}\text{ cm}^{-3}$ , and an expansion-determined translational temperature of 350 nK. The polar molecules have a permanent electric**

**dipole moment, which we measure via Stark spectroscopy to be 0.052(2) Debye for the triplet rovibrational ground state and 0.566(17) Debye for the singlet rovibrational ground state. (1 Debye=  $3.336 \times 10^{-30}$  C m)**

Ultracold atomic gases have enjoyed tremendous success as model quantum systems in which one can precisely control the particles' internal degrees of freedom and external motional states. These gases make interesting many-body quantum systems when the effects of interactions between the particles, along with their quantum statistics, are important in determining the macroscopic response of the system. However, for most atomic gases the interactions are exceedingly simple: they are spatially isotropic and are sufficiently short-range to be well approximated by contact interactions. A wider range of many-body physics phenomena could be explored if the gas comprised particles with more complex interactions, such as would occur in an ultracold gas of polar molecules. Here, the electric dipole-dipole interaction is long-range and spatially anisotropic, much like the interaction of magnetic spins in condensed matter systems. Dipole-dipole interactions can be realized using atomic magnetic dipoles (1, 2), but are typically much weaker than those that could be realized for molecules with a permanent electric dipole moment. Theoretical proposals employing ultracold polar molecules range from the study of quantum phase transitions (3) and quantum gas dynamics (4) to quantum simulations of condensed matter spin systems (5) and schemes for quantum information processing (6, 7, 8).

The relative strength of dipole-dipole interactions in an ultracold gas depends critically on three parameters - the temperature  $T$ , the dipole moment, and the number density of molecules in the sample. For interaction effects to be strongly manifested, the interaction energy must be comparable to or greater than the thermal energy. This condition calls for low temperatures and large dipole moments. In addition, a high number density is needed since the dipole-dipole interaction scales as  $1/R^3$ , where  $R$  is the distance between particles. The combined requirements of low temperature and high density can only be met if the molecule gas has a

high phase-space density, i.e. the gas should be near quantum degeneracy. Recently, there has been rapid progress toward creating samples of cold polar molecules (9, 10, 11, 12, 13); however, it remains a challenge to create a gas where dipole-dipole interactions are observable.

Direct cooling of ground-state molecules (11, 12, 13) has thus far only attained milliKelvin final temperatures. An alternative route is to start with a high phase-space-density gas of atoms and then coherently and efficiently convert atom pairs into ground-state molecules without heating the sample (14, 15, 16, 17). To create polar molecules, the initial atomic gas must be a mixture of two types of atoms so that the resulting diatomic molecules are heteronuclear. In addition, only tightly bound molecules will have an appreciable electric dipole moment. This requirement gives rise to the considerable challenge of efficiently converting atoms that are relatively far apart into molecules of small internuclear distance, without allowing the released binding energy to heat the gas.

Preserving the high phase space density of the initial gas while transferring atoms to deeply bound polar molecules requires coherent state transfer. Here we report the efficient transfer of ultracold atoms into the rovibrational ground state of both the triplet and the singlet electronic ground molecular potentials, and a measurement of the resulting molecules' electric dipole moments. We accomplish this goal by creating near-threshold molecules and then using a single step of STImulated Raman Adiabatic Passage (STIRAP) (18). Key steps in realizing efficient transfer with STIRAP are the identification of a favorable intermediate state and the ability to maintain phase coherence of the Raman lasers. With the coherent transfer to a single quantum state, we create  $3 \cdot 10^4$  rovibrational ground-state polar molecules at a peak density of  $10^{12} \text{ cm}^{-3}$ . The molecules are created in an optical dipole trap and their expansion energy is  $k_b \cdot 350 \text{ nK}$ , where  $k_b$  is the Boltzmann's constant.

The starting point for this work is a near quantum degenerate gas mixture of fermionic  $^{40}\text{K}$  atoms and bosonic  $^{87}\text{Rb}$  atoms confined in an optical dipole trap. We use a magnetic-field tun-

able Fano-Feshbach resonance at 546.7 G (19, 20) to associate atoms into extremely weakly bound diatomic molecules (21, 22). With an adiabatic magnetic-field sweep across the resonance, we typically create a few  $10^4$  near-threshold molecules. The experiments described here are performed at a magnetic field of 545.9 G, where the Feshbach molecules have a binding energy of  $h \times 230$  kHz ( $h$  is the Planck's constant). We directly detect the Feshbach molecules using time-of-flight absorption imaging. Given the measured number, trap frequency, and expansion energy of the fermionic molecules, we find that the Feshbach molecule gas is nearly quantum degenerate with  $T/T_F \approx 2$ , where  $T_F$  is the Fermi temperature. Details of the Feshbach molecule creation and detection have been described elsewhere (23, 24).

For efficient transfer from the initial state of Feshbach molecules to the final state of tightly bound ground-state molecules, the chosen intermediate, electronically excited state must have favorable wave function overlap with both the initial and final states. We first demonstrate coherent transfer of the Feshbach molecules to the rovibrational ground state of the triplet electronic ground potential,  $a^3\Sigma$ . This state lies about  $4000 \text{ cm}^{-1}$  above the absolute ground state, which is the rovibrational ground state of the singlet electronic ground potential,  $X^1\Sigma$ . Triplet and singlet refer to a total electronic spin of the molecule that is one or zero, and our Feshbach molecules are predominately triplet in character.

## **Scheme for Transfer of Feshbach Molecules to $a^3\Sigma v = 0$ Molecules**

Our transfer scheme (Fig. 1) involves three molecular levels, the initial state  $|i\rangle$ , the intermediate state  $|e\rangle$ , and the final state  $|g\rangle$ , that are coupled by two laser fields,  $\Omega_1$  and  $\Omega_2$ . The first laser field,  $\Omega_1$ , drives the up transition where the wave function amplitude of the weakly bound Feshbach molecule state ( $|i\rangle$ ) overlaps favorably near the Condon point to a deeply-bound vibrational level, the tenth vibrational level,  $v' = 10$ , of the electronically excited  $2^3\Sigma$  potential ( $|e\rangle$ ). The Condon point is the internuclear distance where the photon energy matches the difference

between the excited and ground-state potential energy curves. The second laser field,  $\Omega_2$ , drives the down transition, with the Condon point near the outer turning point of the  $v' = 10$  state, where its wave function overlaps strongly with the wave function for the ground vibrational level of the electronic ground  $a^3\Sigma$  potential ( $|g\rangle$ ).

The Raman system for the coherent state transfer employs a diode laser and a Ti:Sapphire laser. Both lasers have tunable wavelengths around 1  $\mu\text{m}$ . The two lasers are individually phase-locked to a femtosecond optical frequency comb (25), which itself is referenced to a stable 1064 nm Nd:YAG laser. The phase-locked linewidth is measured to be narrower than 25 Hz (26, 27). The comb covers the spectral range from 532 nm to 1100 nm, with a mode spacing of 756 MHz. The large wavelength span and precision referencing capability of the comb are well-suited for spectroscopy in search of previously unobserved states.

To find the intermediate state, we performed a search guided by *ab initio* calculation fitted to experimental data from molecules of different isotopes,  $^{39}\text{K}^{85}\text{Rb}$  (28), with the appropriate mass scalings. We located excited molecular states by measuring the loss of Feshbach molecules as a function of the applied laser wavelength ( $\Omega_1$ ). This laser excites a one-photon bound-bound transition that is followed by spontaneous decay into other states. We have observed the  $v' = 8$  to  $v' = 12$  vibrational levels of the  $2^3\Sigma$  excited potential with a roughly 1300 GHz spacing between neighboring vibrational levels, and we chose  $v' = 10$  as our intermediate state. From the measured one-photon loss rate and power-broadened one-photon lineshapes, the transition dipole moment (29) is determined to be  $0.004(2) ea_0$  ( $1 ea_0 = 2.54 \text{ Debye} = 8.48 \cdot 10^{-30} \text{ C}\cdot\text{m}$ ).

## The $a^3\Sigma v = 0$ Level

To search for the triplet vibrational ground state ( $a^3\Sigma, v = 0$ ), we performed two-photon dark resonance spectroscopy (18) in the limit of a strong pump ( $\Omega_2$ ) and weak probe ( $\Omega_1$ ). Based on the KRb potential published by Pashov *et al.* (30), we calculated the triplet  $v = 0$  binding energy

with a predicted uncertainty of 0.1%. For the search, it was convenient to fix the frequency of the weak probe laser to resonantly drive the transition from the initial Feshbach molecule state to the  $v' = 10$  intermediate state. The probe laser by itself causes complete loss of all the Feshbach molecules. We then varied the frequency of the strong coupling laser, and monitored the initial state population after pulsing on both laser fields simultaneously. When the Raman condition is fulfilled, i.e. the initial and final state energy splitting is matched by the two laser frequency difference, the initial state population reappears (Fig. 2A).

The measured binding energy of the triplet  $v = 0$  molecules is  $h \times 7.18$  THz (corresponding to  $240 \text{ cm}^{-1}$ ) at 545.94 G. We find that the  $v = 0$  level has rich hyperfine plus rotational structure at this magnetic field (see Fig. 2A). Because the accessible final states are influenced by selection rules, we have performed the two-photon spectroscopy using two different states of the  $v' = 10$  intermediate level. In addition to the triplet  $v = 0$  level, we have also observed similar ground-state hyperfine structure for the  $v = 1$  and  $v = 2$  levels of the  $a^3\Sigma$  state, which have a vibrational energy spacing of roughly 500 GHz, consistent with our theoretical prediction.

We have identified the quantum numbers of the three lowest energy triplet  $v = 0$  states seen in the two-photon spectrum. The peaks labeled 1, 2, and 3 in Fig. 2A occur at binding energies of  $h \times 7.1804180(5)$  THz,  $h \times 7.1776875(5)$  THz, and  $h \times 7.1772630(5)$  THz, respectively. Peak 1 corresponds to the lowest hyperfine state in the rotational ground-state ( $N = 0$ ), peak 2 is a different hyperfine state with  $N = 0$ , and peak 3 is the lowest energy hyperfine state with  $N = 2$ , where  $N$  is the rotational quantum number. This identification is based on Hund's coupling case (b), where spin and molecular rotation are essentially decoupled and the molecular hyperfine structure can be understood from calculations using a separated atom basis with the rotational progression appearing as a constant shift to all hyperfine levels. Because of parity selection rules for optical transitions, we observe only states with an even  $N$ . The calculated rotational constant is  $B = 0.5264$  GHz, which gives a predicted splitting between the  $N = 0$

and  $N = 2$  levels of  $6B = 3.158$  GHz.

Using a dark resonance measurement such as shown in Fig. 2B, we have measured the strength of the  $|e\rangle$  to  $|g\rangle$  transition. Here, we fix the down leg ( $\Omega_2$ ) laser frequency and scan the up leg ( $\Omega_1$ ) laser frequency. From the width of the dark resonance for the rovibrational triplet ground-state (peak 2), we find that we can drive the transition from  $v' = 10$  to the triplet  $v = 0$  state with a Rabi frequency of  $2\pi \cdot 8$  MHz. This measurement used  $60 \mu\text{W}$  of laser power focused to a beam waist of  $55 \mu\text{m}$ . The transition dipole moment derived from this measurement is  $0.20(2) ea_0$ , which is only one order of magnitude weaker than a typical atomic optical transition.

## High Phase-Space-Density Gas of Triplet Ground-State Polar Molecules

We used peak 2 as the rovibrational ground-state target for our coherent state transfer, which is performed using the counter-intuitive pulse sequence of STIRAP (18). The STIRAP beams are co-propagating in order to minimize photon recoil. The measured time evolution of the initial-state population during a double STIRAP pulse sequence is shown in Fig. 3A. The roundtrip transfer efficiency of 31% implies a one-way transfer efficiency of 56%, which corresponds to  $3 \cdot 10^4$  triplet  $v = 0$   $N = 0$  polar molecules at a peak density of  $10^{12} \text{ cm}^{-3}$ . Our transfer technique allows us to reach a single quantum state without heating. The expansion energy of the  $v = 0$  molecules is measured after transferring them back to the Feshbach molecule state. Using this expansion energy and the trap frequency measured for the Feshbach molecules, the phase space density of the polar molecule gas corresponds to  $T/T_F \approx 2.5$ .

We measure the lifetime of the rovibrational ground-state molecules by varying the hold time between transferring the molecules into the  $v = 0$   $N = 0$  state and bringing them back to the Feshbach molecule state for imaging. The lifetime is measured to be  $170 \mu\text{s}$  as shown in

Fig. 3B. This lifetime may be limited by collisions with background atoms, which can induce spin flips and cause molecules to decay into the lower lying singlet electronic ground potential. The collisional decay could be reduced either by perfecting the removal of the remaining atoms or by starting the molecule production with atom pairs tightly confined in individual sites of an optical lattice. The short lifetime of the final state currently limits the STIRAP transfer efficiency.

We demonstrate that KRb molecules in the triplet rovibrational ground state are polar by directly measuring their electric dipole moment. The predicted dipole moment for KRb triplet rovibrational ground-state molecules is 0.05(3) Debye (D) (31). This is nine orders of magnitude larger than the calculated  $5 \cdot 10^{-11}$  D dipole moment of the initial Feshbach molecules and only about one order of magnitude smaller than a typical polar molecule dipole moment of 1 Debye. To measure the dipole moment, we performed DC Stark spectroscopy on the three lowest energy states observed in the two-photon spectrum (Fig. 2A). We applied a DC electric field in the range from 0 to 2 kV/cm using a pair of indium tin oxide coated transparent electric field plates that are separated by 1.3 cm outside the glass-cell based vacuum chamber. We measured the Stark shift using the dark resonance spectroscopy discussed above. This two-photon spectroscopy measures the energy splitting between the initial and final states, and because the initial state has a negligible dipole moment, any frequency shift of the dark resonance can be attributed to the final-state Stark shift. For these measurements we lowered the laser powers to give a dark resonance width of 500 kHz. The measured ground-state energies versus electric field are shown in Fig. 4.

The effect of a DC electric field is to couple states of opposite parity. For the  $a^3\Sigma v = 0$  molecules, the opposite parity states are even- $N$  and odd- $N$  rotational states. The two lowest energy states, which are the rotational ground state  $N = 0$ , exhibit similar Stark shifts. From the measured Stark shift, we find that the molecules' electric dipole moment is 0.052(2) D. The



Stark shift of the third energy state, corresponding to peak 3, is measured to be about 10 times smaller than that for the peak 1 and peak 2 states. This smaller Stark shift for the  $N = 2$  state is consistent with an electric dipole moment of 0.052 D.

## Absolute Ground-State Polar Molecules

We have also achieved transfer of Feshbach molecules to the rovibrational ground state of the singlet electronic ground potential,  $X^1\Sigma$ , thereby producing absolute ground-state polar molecules. Reaching the singlet rovibrational ground state requires the identification of a new suitable intermediate state and the preservation of the phase-coherence of the Raman laser system over a much larger spectral difference.

A favorable scheme for transferring KRb Feshbach molecules, which have a predominantly triplet character, to the rovibrational ground state of the singlet electronic potential,  $X^1\Sigma$ , requires an intermediate state that has strong electronic spin-orbit coupling (32, 9), in addition to good wavefunction overlap with both the initial state and the target state. The intermediate state we chose (Fig. 5A) is again associated with the excited potential  $2^3\Sigma$ . This excited potential is split into two components labeled by  $\Omega = 1$  and  $\Omega = 0$ , corresponding to the total electronic angular momentum projection onto the molecular internuclear axis ( $\Omega$ ). The higher lying vibrational levels of the  $\Omega = 1$  component have strong triplet-singlet spin mixing with the nearby excited singlet potential,  $1^1\Pi$  (33). This spin mixing provides the necessary coupling to transfer predominantly triplet character Feshbach molecules to the singlet rovibrational ground state. In addition, these levels guarantee a large Franck-Condon factor as the down leg Condon point is near the inner turning point of the intermediate state and coincides with the bottom of the  $X^1\Sigma$  potential, while the up leg Condon point is near the outer turning point of the intermediate state and also overlaps favorably with the Feshbach molecule state.

For our transfer scheme (Fig. 5A), we chose  $v' = 23$ ,  $\Omega = 1$  of the electronically ex-

cited  $2^3\Sigma$  potential as the intermediate state. We identified this state using the single-photon spectroscopy technique discussed in the previous section. We then proceeded with two-photon dark resonance spectroscopy to search for the rovibrational ground state of the singlet electronic ground potential. The two Raman lasers are near 970 nm and 690 nm. We measured the binding energy of the singlet rovibrational ground state ( $v = 0, N = 0$  of  $X^1\Sigma$ ) to be  $h \times 125.319703(1)$  THz (corresponding to about 0.5 eV) at 545.88 G. This deviates by only about 400 MHz (corresponding to  $0.013 \text{ cm}^{-1}$ ) from our theoretical prediction based on the potential by Pashov *et al.* (30). We also located the rotationally excited  $N = 2$  state of the singlet vibrational ground level at a binding energy of  $125.313019(1)$  THz. The energy difference of the two states,  $6B = 6.6836(5)$  GHz, gives a measured rotational constant  $B = 1.1139(1)$  GHz, which agrees with the predicted value of 1.1140 GHz. From the dark resonance lineshape, we extract the transition strengths for both the upward and the downward transitions and obtain  $0.005(2) ea_0$  and  $0.012(3) ea_0$ , respectively.

Absolute ground-state KRb polar molecules are expected to have a much larger electric dipole moment than the triplet ground-state molecules. Many theoretical efforts have calculated the dipole moment, with the results ranging from 0.5 D to 1.2 D (34). To measure the electric dipole moment, we have performed DC Stark spectroscopy on the  $N = 0$  and  $N = 2$  states of the singlet vibrational ground level (Fig. 6). From the measured  $N = 0$  Stark shift, and the measured rotational constant  $B$ , we find that the singlet vibrational ground-state molecules have a permanent electric dipole moment of  $0.566(17)$  Debye, which is  $\sim 10$  times larger than that of the triplet rovibrational ground state. The measured Stark shift of the  $N = 2$  state is consistent with this value for the electric dipole moment. This large dipole moment allows the molecules to be polarized by modest electric fields and will facilitate exploration of interaction effects.

Finally, we demonstrate the creation of absolute ground-state molecules ( $v = 0, N = 0$  of  $X^1\Sigma$ ) using a single step of STIRAP. Using a STIRAP pulse length of  $4\mu\text{s}$  for each transfer

(Fig. 5B and 5C), we recovered 69% of Feshbach molecules after a roundtrip transfer. The one-way transfer efficiency, assuming equal efficiency on the two transfers, is 83%. We also performed a roundtrip STIRAP pulse sequence with a 30 ms hold in between each transfer, i.e. molecules are in the absolute ground state for 30 ms, and recovered 30% of the Feshbach molecules after the roundtrip transfer. This shows that the absolute ground-state molecules are trapped and have a much longer lifetime than the triplet rovibrational ground-state molecules. We measured the expansion energy of the Feshbach molecules that were transferred back after a  $20\mu\text{s}$  hold in the absolute ground state and observed no heating when comparing to the initial gas of Feshbach molecules. In the future, we anticipate that near unity transfer efficiency should be possible with improved stabilization of the phase coherence between the two Raman lasers. This ability to create a long-lived quantum gas of ground-state polar molecules can be extended to other bialkali molecules and paves the way for future studies of dipolar Fermi gases and dipolar Bose-Einstein condensates (35, 36, 37).

## References and Notes

1. J. Stuhler, A. Griesmaier, T. Koch, M. Fattori, T. Pfau, S. Giovanazzi, P. Pedri, and L. Santos, *Phys. Rev. Lett.* **95**, 150406 (2005).
2. Th. Lahaye, T. Koch, B. Fröhlich, M. Fattori, J. Metz, A. Griesmaier, S. Giovanazzi, and T. Pfau, *Nature* **448**, 672 (2007).
3. H. P. Büchler, E. Demler, M. Lukin, A. Micheli, N. Prokofev, G. Pupillo, and P. Zoller, *Phys. Rev. Lett.* **98**, 060404 (2007).
4. L. Santos, G. V. Shlyapnikov, P. Zoller, and M. Lewenstein, *Phys. Rev. Lett.* **85**, 1791-1794 (2000).

5. G. Pupillo, A. Micheli, H.P. Bchler, P. Zoller, arXiv:0805.1896 (2008).
6. D. DeMille, *Phys. Rev. Lett.* **88**, 067901 (2002).
7. A. André, D. DeMille, J. M. Doyle, M. D. Lukin, S. E. Maxwell, P. Rabl, R. J. Schoelkopf, P. Zoller, *Nature Phys.* **2**, 636-642 (2006).
8. S. F. Yelin, K. Kirby, and R. Cote, *Phys. Rev. A* **74**, 050301(R) (2006).
9. J. M. Sage, S. Sainis, T. Bergeman, and D. DeMille, *Phys. Rev. Lett.* **94**, 203001 (2005).
10. D. Wang, J. T. Kim, C. Ashbaugh, E. E. Eyler, P. L. Gould, and W. C. Stwalley, *Phys. Rev. A* **94**, 032511 (2007).
11. J. D. Weinstein, R. deCarvalho, T. Guillet, B. Friedrich, and J. M. Doyle, *Nature* **395**, 148-150 (1998).
12. H. L. Bethlem, G. Berden, and G. Meijer, *Phys. Rev. Lett.* **83**, 1558-1561 (1999).
13. B. C. Sawyer, B. L. Lev, E. R. Hudson, B. K. Stuhl, M. Lara, J. L. Bohn, and J. Ye, *Phys. Rev. Lett.* **98**, 253002 (2007).
14. R. Wynar, R. S. Freeland, D. J. Han, C. Ryu, and D. J. Heinzen, *Science* **287**, 1016 (2000).
15. K. Winkler, F. Lang, G. Thalhammer, P. v. d. Straten, R. Grimm, and J. Hecker Denschlag, *Phys. Rev. Lett.* **98**, 043201 (2007).
16. S. Ospelkaus, A. Pe'er, K.-K. Ni, J. J. Zirbel, B. Neyenhuis, S. Kotochigova, P. S. Julienne, J. Ye, D. S. Jin, *Nature Phys.* **4**, 622-626 (2008).
17. J. G. Danzl, E. Haller, M. Gustavsson, M. J. Mark, R. Hart, N. Bouloufa, O. Dulieu, H. Ritsch, and H.-C. Nägerl, *Science* **321**, 1062-1066 (2008).

18. N. V. Vitanov, M Fleischhauer, B.W. Shore and K. Bergmann, *Adv. At. Mol. Opt. Phys.* **46**, 55-190 (2001).
19. S. Inouye, J. Goldwin, M. L. Olsen, C. Ticknor, J. L. Bohn, and D. S. Jin, *Phys. Rev. Lett.* **93**, 183201 (2004).
20. F. Ferlaino, C. D'Errico, G. Roati, M. Zaccanti, M. Inguscio, G. Modugno, and A. Simoni, *Phys. Rev. A* **74**, 039903(2004).
21. T. Köhler, K. Góral, and P. S. Julienne, *Rev. Mod. Phys.* **78**, 1311 (2006).
22. C. Ospelkaus, S. Ospelkaus, L. Humbert, P. Ernst, K. Sengstock, and K. Bongs, *Phys. Rev. Lett.* **97**, 120402 (2006).
23. J. J. Zirbel, K.-K. Ni, S. Ospelkaus, J. P. D'Incao, C. E. Wieman, J. Ye, and D. S. Jin, *Phys. Rev. Lett.* **100**, 143201 (2008).
24. J. J. Zirbel, K.-K. Ni, S. Ospelkaus, T. L. Nicholson, M. L. Olsen, P. S. Julienne, C. E. Wieman, J. Ye, and D. S. Jin, *Phys. Rev. A*, **78**, 013416 (2008).
25. S. T. Cundiff and J. Ye, *Rev. Mod. Phys.* **75**, 325 (2003).
26. S. M. Foreman, A. D. Ludlow, M. H. G. de Miranda, J. E. Stalnaker, S. A. Diddams, and J. Ye, *Phys. Rev. Lett.* **99**, 153601 (2007).
27. When the YAG is stabilized to an ultrastable laser, such as a strontium clock, the two-photon linewidth is narrower than 1 Hz.
28. C. Amiot, *J. Mol. Spec.* **203**, 126-131 (2000)
29. The transition dipole moment given here includes contributions from both the electronic transition dipole moment and the Franck-Condon factor.

30. A. Pashov, O. Docenko, M. Tamanis, R. Ferber, H. Knöckel, and E. Tiemann, *Phys. Rev. A* **76**, 022511 (2007).
31. S. Kotochigova, P. S. Julienne, and E. Tiesinga, *Phys. Rev. A* **68**, 022501 (2003).
32. W. C. Stwalley, *Eur. Phys. J. D* **31**, 221-225 (2004).
33. T. Bergeman, A.J. Kerman, J. Sage, S. Sainis and D. DeMille , *Eur. Phys. J. D.* **31**, 179-188 (2004).
34. M. Aymar and O. Dulieu, *J. Chem. Phys* **122**, 204302 (2005).
35. C. Ticknor, *Phys. Rev. Lett* **100**, 133202 (2008).
36. S. Ronen and J. L. Bohn, *Phys. Rev. A* **76**, 043607 (2007).
37. M. A. Baranov, *Phys. Rep.* **464**, 71-111 (2008).
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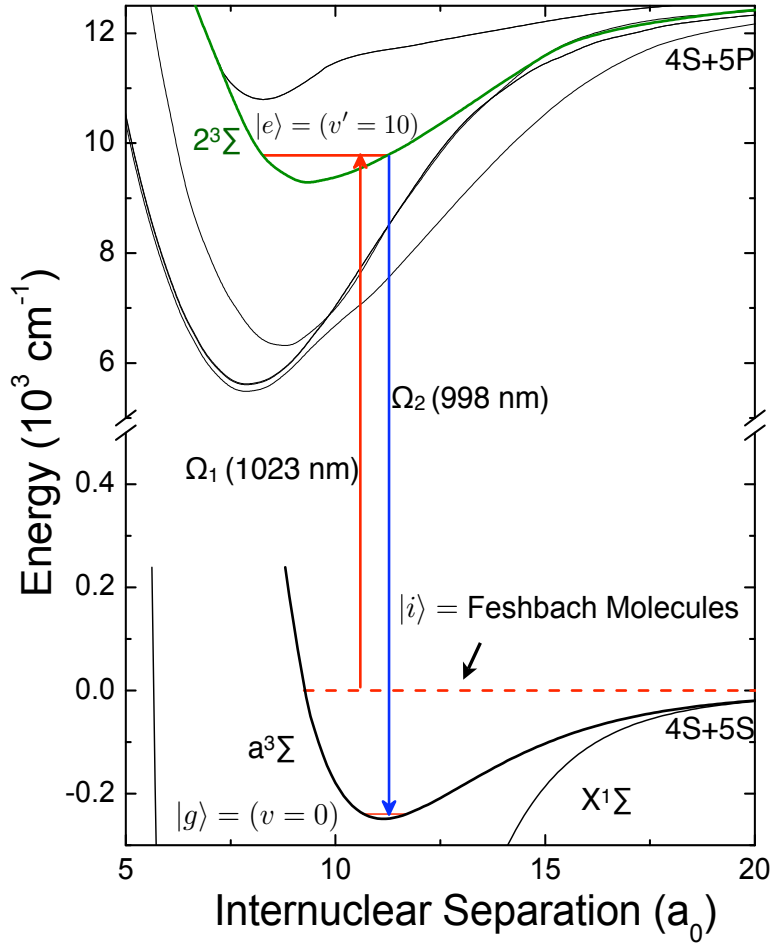


Figure 1: Diagram of the KRb electronic ground and excited molecular potentials and the vibrational levels involved in the two-photon coherent state transfer to the triplet ground state. Here, the intermediate state  $|e\rangle$  is the  $v' = 10$  level of the electronically excited  $2^3\Sigma$  potential. The vertical arrows are placed at the respective Condon points of the up and down transitions. The intermediate state has favorable transition dipole moments for both the up leg ( $|i\rangle$  to  $|e\rangle$ ) and the down leg ( $|e\rangle$  to  $|g\rangle$ ), where the initial state  $|i\rangle$  is a weakly bound Feshbach molecule and the final state  $|g\rangle$  is the rovibrational ground state ( $v = 0$   $N = 0$ ) of the triplet electronic ground potential,  $a^3\Sigma$ .

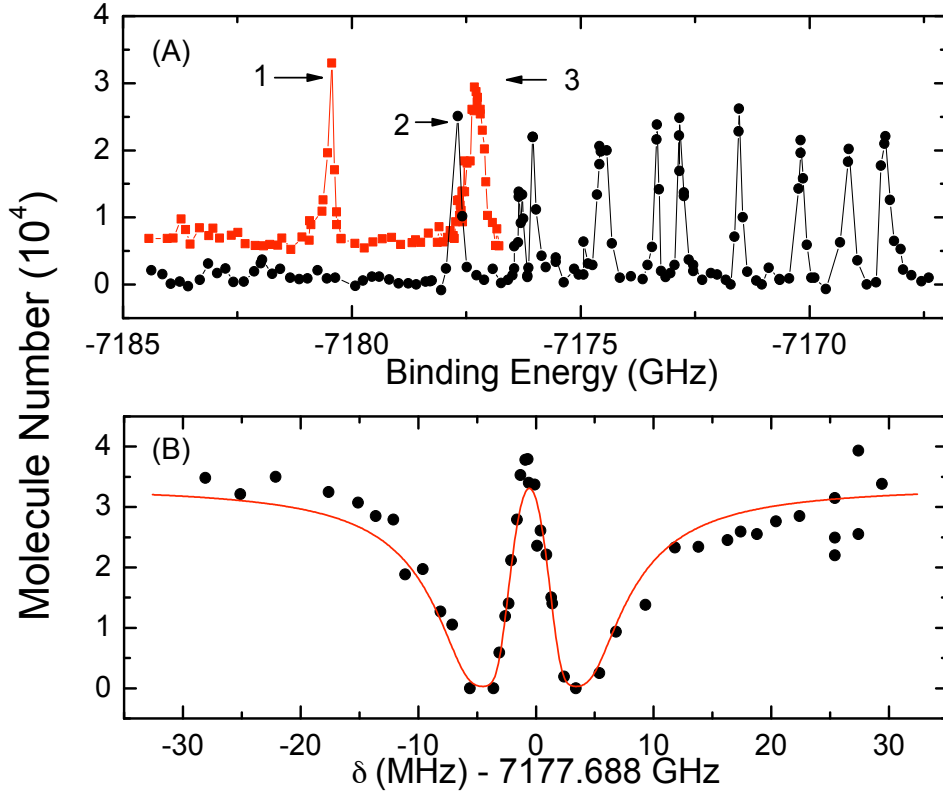


Figure 2: The  $v = 0$  ground-state level of the triplet electronic ground potential,  $a^3\Sigma$ . A. Hyperfine and rotational states of the  $a^3\Sigma v = 0$  ground-state molecule at a magnetic field of 546.94 G, observed using two-photon spectroscopy and scanning the down leg ( $\Omega_2$ ) frequency. The measured number of Feshbach molecules is plotted as a function of the frequency difference of the two laser fields. We show two sets of data, vertically offset for clarity, obtained using two different intermediate states, which are hyperfine and rotational states of the  $v' = 10$  level of the electronically excited  $2^3\Sigma$  potential. Peaks labelled 1 and 2 correspond to hyperfine states in the rotational ground-state, while peak 3 corresponds to a rotationally excited state. B. We precisely determine the energy and the transition dipole moments for individual states using the two-photon spectroscopy where we scan the up leg ( $\Omega_1$ ) frequency. The measured number of Feshbach molecules is plotted as a function of the two-photon detuning. The dark resonance shown here is for the triplet rovibrational ground state corresponding to peak 2 in (A).



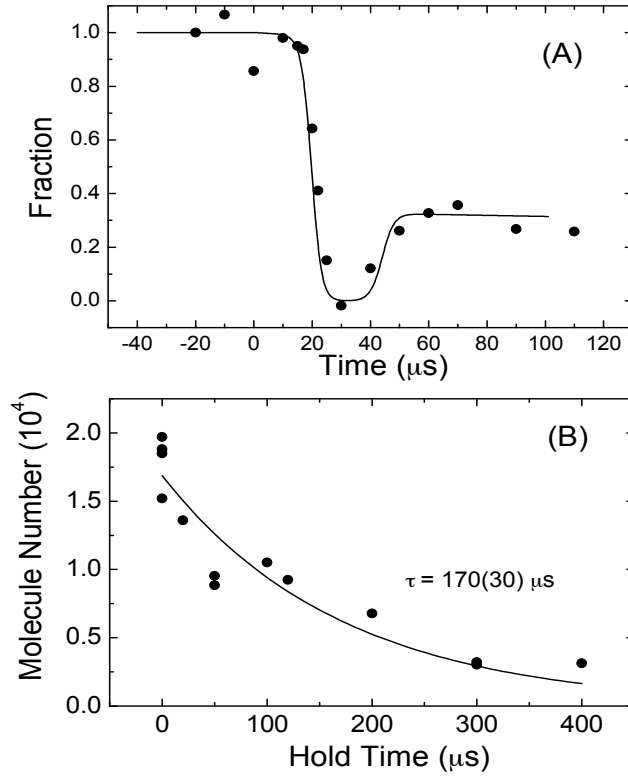


Figure 3: Time evolution of the initial state population during STIRAP state transfer and a measurement of the triplet rovibrational ground-state molecule lifetime. A. Here we monitor the Feshbach molecule population as we apply the STIRAP pulse sequence. Weakly-bound Feshbach molecules are coherently transferred into the triplet rovibrational ground state after a  $25 \mu\text{s}$  one-way STIRAP pulse sequence. The measured population completely disappears since the deeply-bound molecules are dark to the imaging light. After a  $10 \mu\text{s}$  hold, we then perform the reversed STIRAP pulse sequence that coherently transfers the ground-state molecules back to Feshbach molecules. The molecule number after the roundtrip STIRAP is  $1.8 \cdot 10^4$ . Assuming equal transfer efficiency for the two STIRAP sequences, we obtain one-way transfer efficiency of 56% and an absolute number of triplet rovibrational ground-state polar molecules of  $3.2 \cdot 10^4$ . B. We measure the triplet  $v = 0$  lifetime by varying the hold time after one-way STIRAP before transferring them back to Feshbach molecules for imaging. The lifetime is measured to be  $170(30) \mu\text{s}$ .

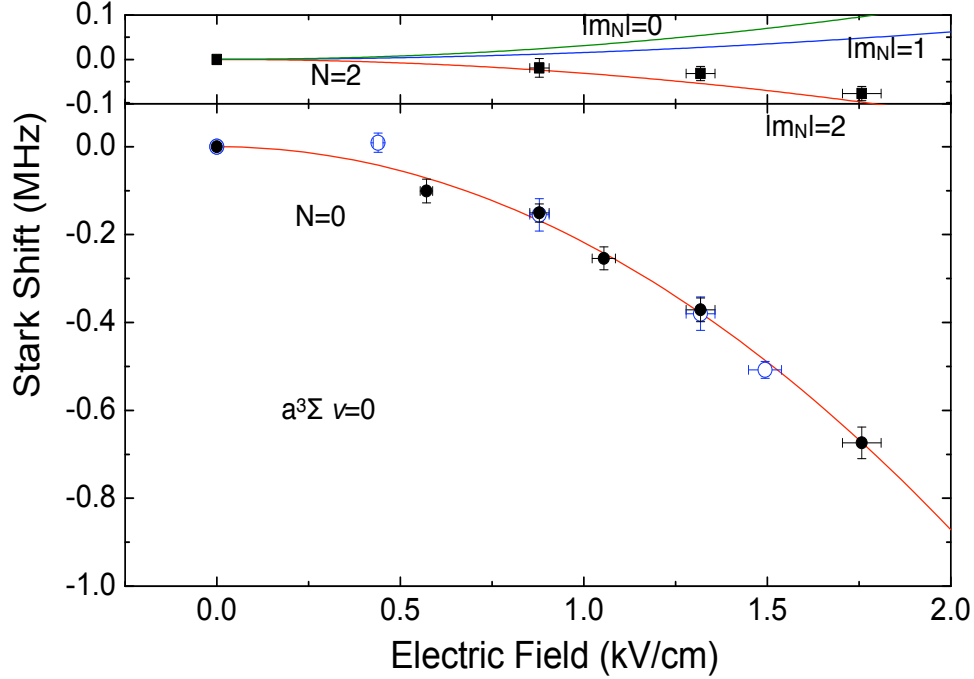


Figure 4: Stark spectroscopy of the triplet  $v = 0$  molecules. Stark shifts of the lowest three states in the triplet  $v = 0$  manifold in Fig. 2A are measured for a DC electric field in the range from 0 to 2 kV/cm. The bottom panel shows the Stark shifts of the two lowest energy states which are  $N = 0$ . Fits to the shifts of peak 1 (solid circles) and peak 2 (open circles) yield an electric dipole moment and statistical error bar of 0.052106(2) D and 0.052299(8) D, respectively. The main systematic error in the dipole moment measurement comes from a 3% uncertainty of the electric field. A combined fit for shifts of peak 1 and peak 2 is shown as the solid curve in the bottom panel. With the electric field uncertainty, we obtain an electric dipole moment of 0.052(2) D. The top panel shows the Stark shift of peak 3 (squares) and the expected  $N = 2$  curves calculated for an electric dipole moment of 0.052 D and different  $|m_N|$  projections.

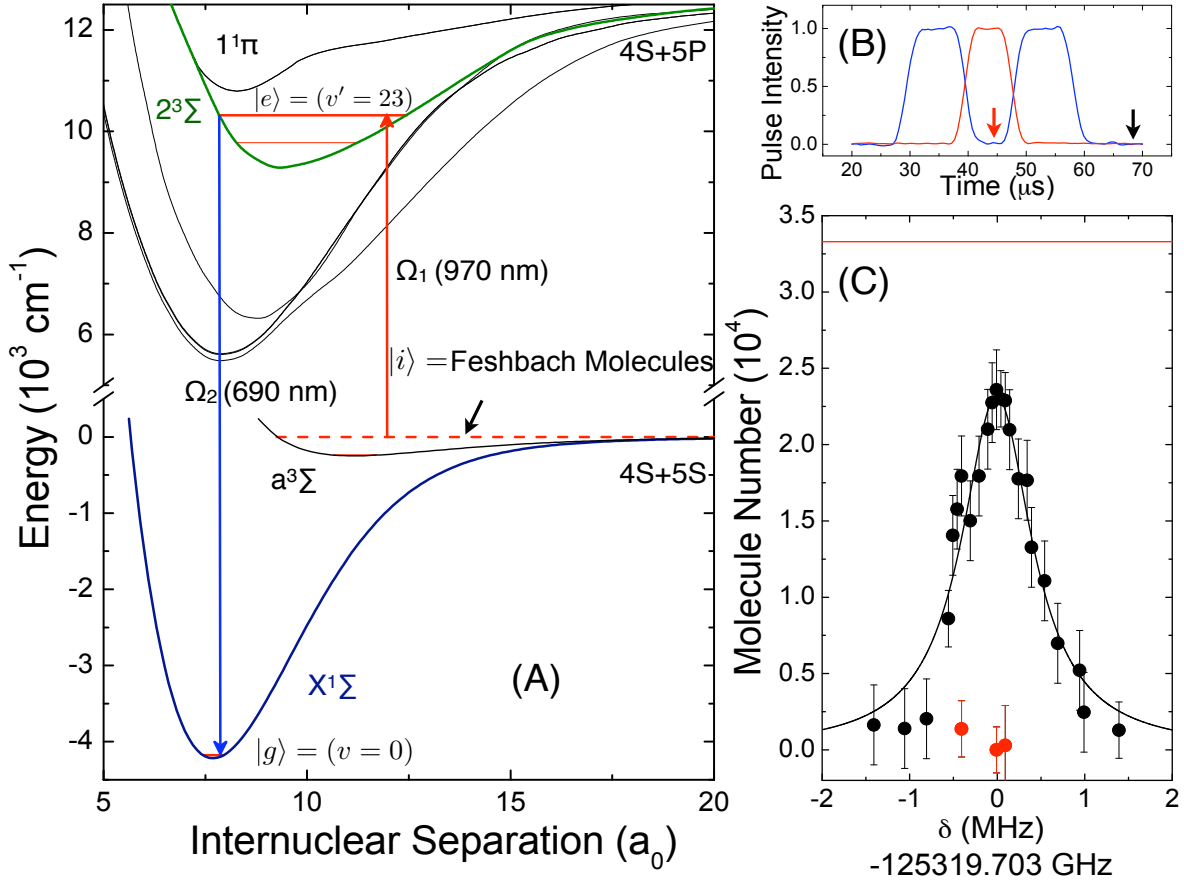


Figure 5: Two-photon coherent state transfer from weakly-bound Feshbach molecules  $|i\rangle$  to the absolute molecular ground state  $|g\rangle$  ( $v = 0$ ,  $N = 0$  of  $X^1\Sigma$ ). A. Transfer scheme. Here, the intermediate state  $|e\rangle$  is the  $v' = 23$  level of the  $\Omega = 1$  component of the electronically excited  $2^3\Sigma$  potential. The chosen intermediate state lies just below the  $1^1\Pi$  excited electronic potential, which provides the necessary triplet-singlet spin mixing to transfer predominantly triplet character Feshbach molecules to the rovibrational ground state of the singlet electronic ground potential,  $X^1\Sigma$ . The vertical arrows are placed at the respective Condon points of the up and down transitions. The intermediate state has favorable Franck-Condon factors for both the up leg ( $|i\rangle$  to  $|e\rangle$ ) and the down leg ( $|e\rangle$  to  $|g\rangle$ ).

B. Normalized Raman laser intensities vs time for the roundtrip STIRAP pulse sequence. We performed a  $4\mu\text{s}$  STIRAP transfer each way using a maximum Rabi frequency of  $2\pi \cdot 7$  MHz for the downward transition (blue line) and a maximum Rabi frequency of  $2\pi \cdot 4$  MHz for the upward transition (red line). C. STIRAP lineshape. The number of Feshbach molecules returned after a roundtrip STIRAP transfer is plotted as a function of the two-photon Raman laser detuning. The roundtrip data were taken at the time indicated by the black arrow in (B). The red data points show the Feshbach molecule number when only one-way STIRAP is performed (at the time indicated by the red arrow in (B)), where all Feshbach molecules are transferred to the ground state and are dark to the imaging light. The initial Feshbach molecule number is  $3.3(4) \cdot 10^4$  (red solid line) and the number after roundtrip STIRAP is  $2.3 \cdot 10^4$ . The roundtrip efficiency is 69%, which suggests the one-way transfer efficiency is 83% and the number of the absolute ground-state polar molecules is  $2.7 \cdot 10^4$ .

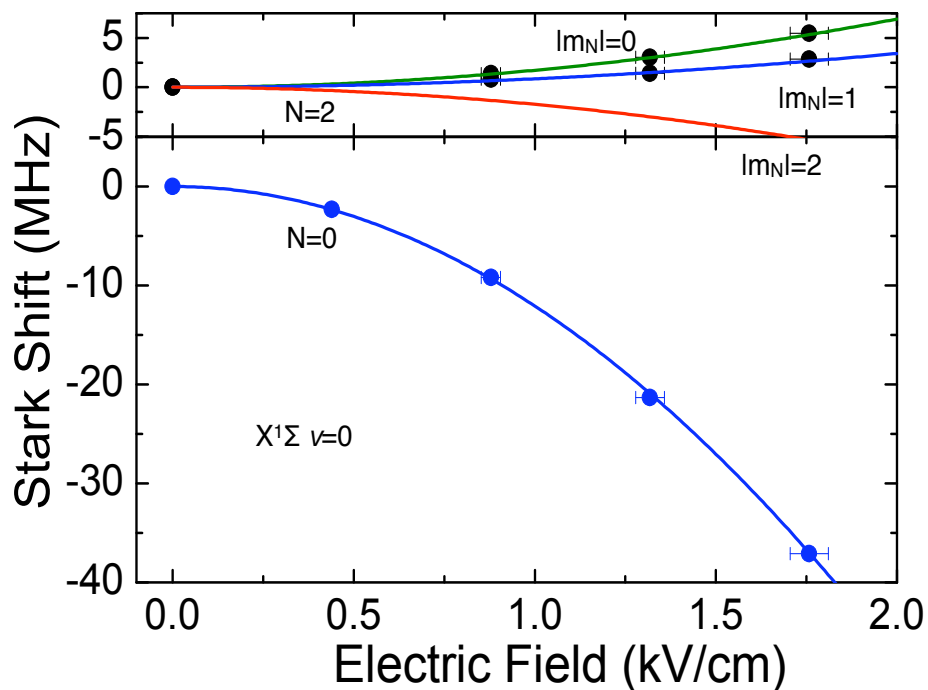


Figure 6: Stark spectroscopy of the singlet  $v = 0$  molecules. The bottom panel shows the Stark shift of the rovibrational ground-state of the singlet potential ( $v = 0, N = 0$  of  $X^1\Sigma$ ), and the top panel shows the shift of the  $v = 0, N = 2$  state. The systematic error in the applied electric field is 3%. The level difference between  $N = 0$  and  $N = 2$  is 6.6836 GHz, which yields a rotational constant  $B$  of 1.1139(1) GHz. Given the measured  $B$ , the fit of the Stark shift (line in lower panel) gives a permanent electric dipole moment of 0.566(17) D. The theory curves for  $N = 2$  for different  $|m_N|$  projections (lines in upper panel) are calculated using the measured  $B$  and the dipole moment derived from the  $N = 0$  fit.