Singlet Pathway to the Ground State of Ultracold Polar Molecules

A. Yang,[1] S. Botsi,[1] S. Kumar,[1] S. B. Pal,[1] M. M. Lam,[1] I. Čepaitė,[1] A. Laugharn,[1] and K. Dieckmann[1,2,*]
[1]*Centre for Quantum Technologies (CQT), 3 Science Drive 2, Singapore 117543, Singapore*
[2]*Department of Physics, National University of Singapore, 2 Science Drive 3, Singapore 117542, Singapore*

(Received 7 August 2019; accepted 9 March 2020; published 1 April 2020)

Starting from weakly bound Feshbach molecules, we demonstrate a two-photon pathway to the dipolar ground state of bi-alkali molecules that involves only singlet-to-singlet optical transitions. This pathway eliminates the search for a suitable intermediate state with sufficient singlet-triplet mixing and the exploration of its hyperfine structure, as is typical for pathways starting from triplet dominated Feshbach molecules. By selecting a Feshbach state with a stretched singlet hyperfine component and controlling the laser polarizations, we assure coupling to only single hyperfine components of the $A^1\Sigma^+$ excited potential and the $X^1\Sigma^+$ rovibrational ground state. In this way an ideal three level system is established, even if the hyperfine structure is not resolved. We demonstrate this pathway with $^6\mathrm{Li}^{40}\mathrm{K}$ molecules, and discuss its application to other important molecular species.

DOI: 10.1103/PhysRevLett.124.133203

The rich physics of ultracold dipolar quantum gases [1,2] based on the long-range and anisotropic interaction has moved into the focus of many experimental research activities. Studies on Rydberg atoms [3,4] and recent results with strongly magnetic atoms [5,6] represent two important realizations of dipolar systems. A third approach is using polar molecules, which combine strong dipolar interactions and long lifetimes when trapped in deep optical lattices or low dimensional traps. Therefore, they are prominent candidates for research in the areas of quantum simulation [7,8] and quantum information [9–11]. Moreover, polar molecules are an important platform for metrology [12–14] and are a testbed for ultracold chemistry [15–18]. For the difficult task of producing trapped ultracold molecular samples several methods were explored [19–22], and over the recent years much progress was made with laser cooling of molecules from a buffer gas source [23]. However, the highest numbers and densities and lowest temperatures for ultracold molecular samples were produced by association of ultracold atoms via magnetically tunable Feshbach resonances [24]. To access large dipole moments, such weakly bound molecules need to be transferred into their rovibrational ground state by stimulated Raman adiabatic passage (STIRAP) [25]. The ground state was achieved for several heteronuclear bi-alkali combinations [26–30]. This bottom-up approach is the only one that recently reached the remarkable milestone of quantum degeneracy for the case of KRb [31]. To obtain molecules with higher ground state dipole moments other bi-alkali combinations with larger mass ratios are being investigated. Obtaining an efficient ground state transfer requires as a cornerstone studying the molecular structure and identifying a suitable electronically excited state. Most experiments so far follow the strategy that was pioneered in KRb [26] by using an intermediate excited state of mixed singlet and triplet character. This facilitates a coherent transfer from a Feshbach molecule state with triplet character to the singlet ground state. To gain full control over the molecular state, spectroscopically resolved hyperfine components of the excited state need to be identified, as coupling to unresolved hyperfine levels will lead to a low STIRAP efficiency [32]. Identifying such states typically requires extensive spectroscopic surveys [33–38] to find states where the triplet admixture leads to large hyperfine splitting, while the singlet admixture is strong enough to address the ground state. Moreover, even if the hyperfine structure is resolved, off-resonant coupling to other hyperfine components of the intermediate state can lead to an undesired superposition of several hyperfine components of the ground state [39].

In this Letter, we present a pathway to the ground state that avoids the use of perturbed potentials by only using singlet-to-singlet transitions for both pump and Stokes couplings as illustrated in Fig. 1. Here, we demonstrate that by making use of deeply bound vibrational states in the $A^1\Sigma^+$ potential, we are able to achieve sufficient Franck-Condon factors (FCF) to access the $X^1\Sigma^+$ rovibrational ground state with moderate laser powers. The use of deeply bound vibrational states has the advantage that states of mixed singlet-triplet character are less frequent, due to the larger level spacing. To allow for the excitation to the unperturbed $A^1\Sigma^+$ potential, it is necessary to employ a Feshbach resonance with significant admixture from the singlet ground state potential. For the $A^1\Sigma^+$ potential, its hyperfine structure is typically not resolved

© 2020 American Physical Society

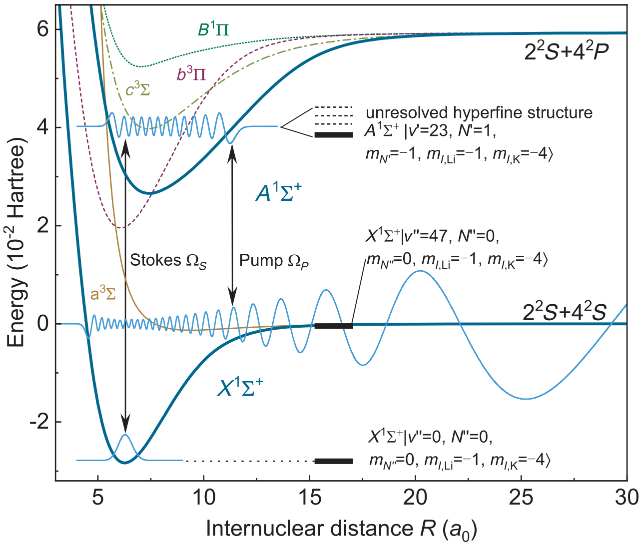

FIG. 1. Potential energy curves of ^{6}Li^{40}K molecules. The pump beam couples the singlet component of the Feshbach molecules ($X^1\Sigma^+|v''=47\rangle$) to a deeply bound vibrational state of the $A^1\Sigma^+$ potential with Rabi frequency Ω_p. From there the Stokes beam couples to the rovibrational ground state in the $X^1\Sigma^+$ potential with Ω_S.

due to the absence of spin and internal magnetic field. We then demonstrate how to address a sole hyperfine component of the ground state, even if the hyperfine structure of the excited state is not resolvable. Our pathway is facilitated by selecting the Feshbach resonance, such that the singlet admixture to the Feshbach molecular state consists of only one hyperfine component, which corresponds to a fully stretched state of the nuclear spin projections. Starting from the stretched state and applying circularly polarized spectroscopy light ensures that only one ground state hyperfine component can be addressed. In the following, this scheme is applied to ^{6}Li^{40}K molecules. We describe the selection of a suitable Feshbach state and present our spectroscopic results for several deeply bound vibrational states of the $A^1\Sigma^+$ potential as well as our measurements of the ground state by two-photon spectroscopy.

Our experiments start from a quantum degenerate mixture of 10^5 ^{6}Li and 8×10^4 ^{40}K atoms in a magnetic trap, which is sympathetically cooled via evaporative cooling of ^{87}Rb [40]. After expunging ^{87}Rb from the magnetic trap, the Fermi-Fermi mixture is transferred into a crossed optical dipole trap. This is followed by preparation of suitable atomic hyperfine states and magneto-association of typically 10^4 Feshbach molecules [41]. We use absorption imaging in the presence of the magnetic field after Feshbach molecular association, where atoms and weakly bound molecules can be simultaneously detected. We reduce the background due to remaining unbound ^{6}Li atoms by transferring them to a different undetected Zeeman level.

For the molecular association in previous work we employed a Feshbach resonance at 15.54 mT [41]. To select an initial molecular state for the spectroscopy that contains a sole singlet admixture, we use a different Feshbach resonance at 21.56 mT by preparing the lithium and potassium atoms in the $|F_{\mathrm{Li}}=\frac{1}{2}, m_{F,\mathrm{Li}}=-\frac{1}{2}\rangle$ and $|F_{\mathrm{K}}=\frac{9}{2}, m_{F,\mathrm{K}}=-\frac{9}{2}\rangle$ hyperfine states, respectively. Here, F and m_F are the hyperfine and respective projection quantum numbers. The sum of the projection quantum numbers is $M=-5$, which is conserved during molecule formation. As most Feshbach resonances of the $^6\mathrm{Li}-{}^{40}\mathrm{K}$ mixture are narrow [42], the closed molecular channel should be considered. In the molecular basis $|S, m_S, m_{I,\mathrm{Li}}, m_{I,\mathrm{K}}\rangle$, the total projection quantum number then equals to $M=m_S+m_{I,\mathrm{Li}}+m_{I,\mathrm{K}}=-5$. Hence, only one spin singlet and three spin triplet states contribute to the closed channel: $|0,0,-1,-4\rangle$, $|1,0,-1,-4\rangle$, $|1,-1,0,-4\rangle$, and $|1,-1,-1,-3\rangle$. Since the nuclear spin quantum numbers are $I_{\mathrm{Li}}=1$ and $I_{\mathrm{K}}=4$, the only contributing spin singlet state is fully stretched. The singlet and triplet states are mixed by the hyperfine coupling, which can be well described by the asymptotic-bound-state model [43]. From this, we estimate a 52% admixture of the singlet state to the molecular eigenstate [44]. This significant singlet character of the Feshbach state is an excellent starting point for the spectroscopy of $A^1\Sigma^+$.

To search for a suitable intermediate state, we study the excitation from the initial Feshbach state $X^1\Sigma^+|v''=47, J''=0\rangle$ to the rotational excited states in $A^1\Sigma^+$ potential $A^1\Sigma^+|v', J'=1\rangle$ as shown in Fig. 1, where v is the vibrational quantum number and J the total angular momentum. Since only $^1\Sigma$ states are involved and the $J''=0\rightarrow J'=0$ transition is forbidden, the quantum number N for molecular rotation is not conserved. Starting from a Feshbach state with $N''=0$, we can only probe excited states of $A^1\Sigma^+$ with $N'=1$. Hence, the rotational projection m_N needs to be considered. In the extended uncoupled molecular basis $|S, m_S, m_{I,\mathrm{Li}}, m_{I,\mathrm{K}}, N, m_N\rangle$ the following three states are possible $|0,0,-1,-4,1,0\rangle$, $|0,0,0,-4,1,-1\rangle$, $|0,0,-1,-3,1,-1\rangle$, if we drive π transitions and the total projection $M=m_{I,\mathrm{K}}+m_{I,\mathrm{Li}}+m_N=-5$ is conserved. These states can be mixed due to hyperfine coupling originating from nuclear-spin rotation, nuclear quadrupole, and the nuclear-spin dipole interactions. In the $A^1\Sigma^+$ potential the hyperfine coupling constants are expected to be small [44] and the hyperfine structure is not resolved. Therefore, the excitation can couple to different hyperfine components. To achieve excitation to the sole singlet hyperfine component $|0,0,-1,-4,1,-1\rangle$ in the $A^1\Sigma^+$ potential, we apply σ^--polarized light. As stretched states do not couple, this argument is also valid, if the hyperfine coupled basis is considered. Since our

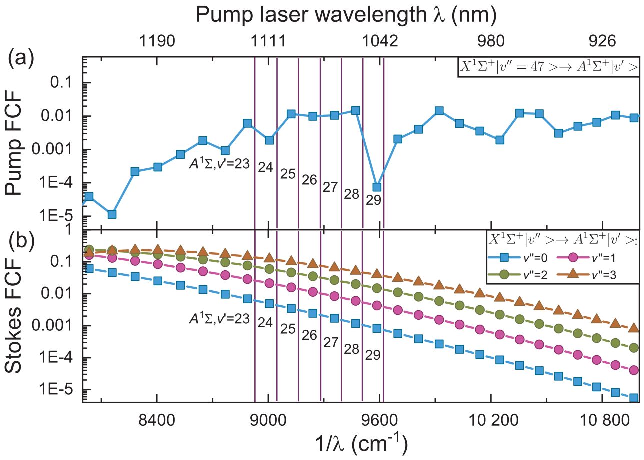

FIG. 2. Franck-Condon overlap factors (FCF) of the vibrational states of the $A^1\Sigma^+$ potential with (a) the molecular Feshbach state and (b) the lowest vibrational states of the $X^1\Sigma^+$ potential. Detail of the calculation of the FCFs is given in the Supplemental Material [44]. The vertical lines indicate the measured wavelengths. The lines connecting the points are a guide to the eye.

Feshbach state is in $|F''=5, m''_F=-5\rangle$, the addressable excited hyperfine states are $F'=4$, 5, 6. With σ^- polarization we can address only the $|F'=6, m'_F=-6\rangle$ stretched state.

A suitable intermediate vibrational state of the $A^1\Sigma^+$ potential needs to have a good FCF with the Feshbach molecular state as well as the $X^1\Sigma^+$ vibrational ground state. As shown in Fig. 2(b), for more deeply bound states at long wavelengths the overlap with the ground state becomes more favorable, while the overlap with the singlet component of the Feshbach molecules ceases, Fig. 2(b). In the experiment we cover a wavelength range of 1038–1120 nm, where good FCFs for both pump and Stokes transitions are expected. The variation of the transition strength throughout this range is determined by the vibrational wave function overlap. This is because for the $X^1\Sigma^+ \to A^1\Sigma^+$ transition the transition dipole matrix element (TDM) does not vary significantly with the internuclear distance, as we find from our *ab initio* calculation [44].

We perform one-photon spectroscopy for the $A^1\Sigma^+$ vibrational levels by switching off the optical dipole trap and applying laser pulses during time of flight (TOF) before imaging. We use a gain-chip laser diode, which is stabilized by a tunable frequency offset lock to a high-finesse optical resonator. The laser frequency is determined with 1 MHz resolution using a beat setup with an optical frequency comb system. Our identification of the transition lines is facilitated by previous polarization labeling spectroscopy in a heat pipe [50]. We use mass scaling of the Dunham coefficients determined by this work to the ^{6}Li^{40}K isotopologue [44]. The large level separation occurring for deeply bound states leads to the unambiguous assignment of the vibrational level index. The locations of seven deeply bound excited states are measured with highly resolving spectroscopy, and listed in Table I. As an example, the spectrum for the transition to $A^1\Sigma^+|v'=23\rangle$ is shown in Fig. 3(a). From simultaneous curve fitting to the observed spectrum, Fig. 3(a), and the exponential decay of the molecular number with the irradiation time, Fig. 3(b), the linewidth and Rabi frequency are inferred [34]. The Rabi frequency normalized to the square root of the applied laser intensity, $\bar{\Omega}_p$, indicates the transition strength. Consistent with the prediction of the FCFs shown in Fig. 2(a), we do not observe a reduction of the transition strength for this state as compared with the strengths measured at lower wavelengths as summarized in Table I.

An important feature of all observed lines is the absence of hyperfine structure for the measured linewidths around 5 MHz, if the excitation is driven by σ^- light. This is expected as the stretched hyperfine state is the only available final state. An observable hyperfine structure is expected to occur for spin-triplet states. In this case, the atomic hyperfine splitting for potassium atoms of a few tens of MHz can be used as an estimate for the molecular case. No hyperfine structure is observed, even if the measurement span is extended to 160 MHz. Therefore, it can be

TABLE I. Measured resonance frequencies and normalized Rabi frequencies of the pump transitions.

	$X^1\Sigma^+|v''=47\rangle \to A^1\Sigma^+|v'\rangle$	
v'	f (THz)	$\bar{\Omega}_P$ (kHz/$\sqrt{\mathrm{mW/cm^2}}$)
23	267.842 232(1)	$2\pi \times 2.7(2)$
24	271.383 075(1)	$2\pi \times 1.8(2)$
25	274.898 734(2)	$2\pi \times 4.3(8)$
26	278.388 059(2)	$2\pi \times 0.7(1)$
27	281.846 301(1)	$2\pi \times 7.6(8)$
28	285.281 804(1)	$2\pi \times 2.9(6)$
29	288.688 289(1)	$2\pi \times 2.3(9)$

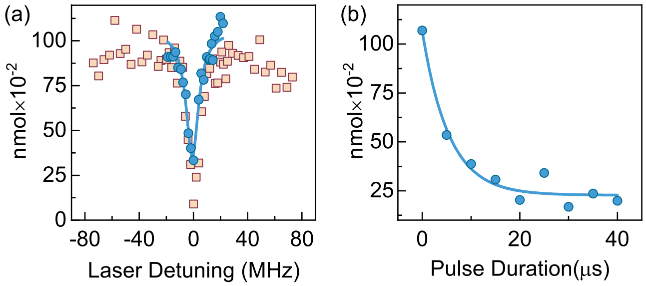

FIG. 3. Spectroscopy of the $A^1\Sigma^+|v'=23\rangle$ excited state. The transition resonance is reflected as molecule number losses. (a) Loss spectrum over large range (triangles) and with reduced laser power (circles). (b) The decay data for resonant irradiation.

excluded that the observed vibrational states are perturbed by a significant contribution of the $b^3\Pi$ states via spin-orbit coupling [44]. Further, in similar measurements no hyperfine structure is resolved, if the excitation is driven with π-polarized light, which allows to address several hyperfine states. This is consistent with estimates of the dominant quadrupole hyperfine interaction for the $A^1\Sigma^+$ potential based on *ab initio* calculations [44].

To address the low lying vibrational states of the $X^1\Sigma^+$ ground state, we make use of the stretched hyperfine state $|0,0,-1,-4,1,-1\rangle$ of the $A^1\Sigma^+$ potential as an intermediate state with projection quantum number $M' = -6$. For the rovibrational ground state with $N'' = 0$, only the stretched hyperfine component with $M'' = -5$ can couple to the excited state. In this case σ^--polarized Stokes light needs to be applied. Consequently, off-resonant coupling to other hyperfine states is prevented for both transitions.

We perform two-photon spectroscopy during TOF with 18 μs pump-pulse duration. The Stokes pulse is switched on and off 2 μs earlier and respectively later than the pump pulse.

The search for the ground state levels is assisted by the $X^1\Sigma^+$ potential curve of [51]. We first identify the transition frequencies to $X^1\Sigma^+|v''=3\rangle$ by scanning the Stokes laser detuning, while keeping the pump laser on resonance with respect to the transition to $A^1\Sigma^+|v'=29\rangle$. The Stokes light is derived from a low power diode laser system. As shown in Fig. 2(b), lower vibrational states have significantly smaller FCFs. Therefore, it is impossible to address the $X^1\Sigma^+|v''=0\rangle$ with the same intermediate state, unless laser power of several Watts is available.

To facilitate the search via other intermediate vibrational levels we make use of a tunable dye laser system (Coherent 699). The DCM dye in use covers a wavelength range of 640–690 nm with a power ≤ 300 mW applied to the molecules. In-lock frequency tuning of the laser over many gigahertz with megahertz resolution is facilitated by an interferometric frequency stabilization [72]. A more deeply bound intermediate state $A^1\Sigma^+|v'=23\rangle$ is utilized to access the low lying vibrational states including the $X^1\Sigma^+|v''=0\rangle$ with sufficient FCFs. All measured transition frequencies are summarized in Table II. The predicted frequencies deviate from the measured values by approximately 3 GHz, which is within the 6 GHz uncertainty given in [51].

The results of two-photon spectroscopy for measuring the ground state energy for the $X^1\Sigma^+|v''=0, N''=0\rangle$ state are shown in Fig. 4. In Fig. 4(a), the Feshbach molecular signal is restored due to the Autler-Townes effect, if the Stokes laser is tuned to resonance. If the polarization of the Stokes laser is changed to σ^+, no coupling is expected and therefore no line is observed. Figure 4(b) shows the Autler-Townes splitting (ATS) by keeping the Stokes laser on resonance and scanning the pump laser frequency. To confirm the correct assignment of the ground state, we address the rotationally exited $|v''=0, N''=2\rangle$ state, as shown in Fig. 4(c). From the separation of the two resonance signals a rotational constant of $B_0 = h \times 8.742(3)$ GHz is inferred, in very good agreement with [73].

TABLE II. Measured resonance frequencies and normalized Rabi freqencies for the Stokes transitions.

	$A^1\Sigma^+\|v'=29\rangle \rightarrow X^1\Sigma^+\|v''\rangle$	
v''	f (THz)	$\bar{\Omega}_S$ (kHz/$\sqrt{\text{mW/cm}^2}$)
2	458.389 566(5)	$2\pi \times 43(8)$
3	451.871 767(10)	$2\pi \times 152(52)$

	$A^1\Sigma^+\|v'=23\rangle \rightarrow X^1\Sigma^+\|v''\rangle$	
v''	f (THz)	$\bar{\Omega}_S$ (kHz/$\sqrt{\text{mW/cm}^2}$)
0	450.841 975(2)	$2\pi \times 12(2)$
1	444.148 838(5)	$2\pi \times 84(18)$
2	437.543 516(8)	$2\pi \times 256(59)$

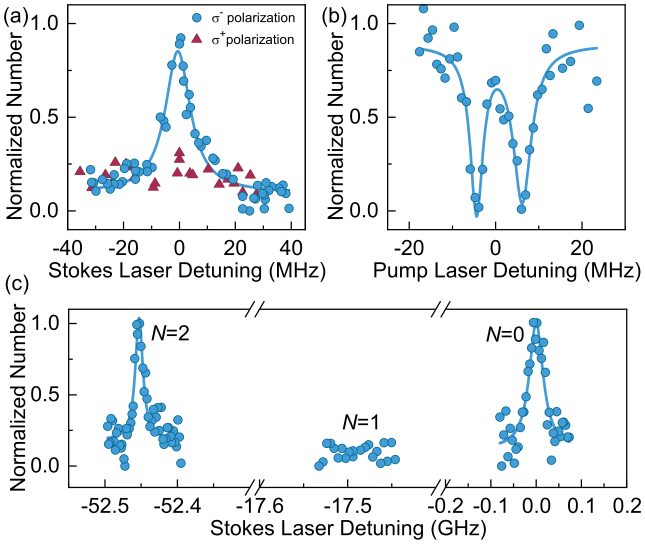

FIG. 4. Spectroscopy of $X^1\Sigma^+|v''=0\rangle$ ground state using $A^1\Sigma^+|v'=23, N'=1\rangle$ as an intermediate state. (a) The pump laser with σ^- polarization is tuned to one-photon resonance. The Stokes-laser frequency is scanned using σ^- and σ^+-polarization. (b) Both pump and Stokes beams are σ^- polarized. The Stokes laser is fixed on two-photon resonance, while the pump-laser detuning is scanned. (c) Two photon spectroscopy including the rotational excited state $X^1\Sigma^+|v''=0, N''=2\rangle$: the rotation energy, which is inferred from the energy difference between the rotational ground state and excited state, is given by $E_{N''} = \mathrm{B}_0 N''(N''+1)$. The transition to $N''=1$ is not observed due to the selection rule $\Delta N = \pm 1$.

The transition strengths $\bar{\Omega}_S$ to the $X^1\Sigma^+$ vibrational states are obtained from the measured widths of the spectra as shown in Fig. 4(a) and the applied laser intensities and are shown in Table II. The scaling of the transition strengths between different lines is in good agreement with the ratio of the respective FCFs shown in Fig. 2(b). The strong coupling to the $v'' = 0$ ground state can be inferred from the observed ATS, which shows a Stokes Rabi frequency of $\Omega_S \approx 2\pi \times 8$ MHz. Ω_S of $2\pi \times 500$ kHz can be achieved, even if we switch to a low power diode laser. As the measured Rabi frequency for the pump excitation is of the same order, we have established favorable conditions for a fast STIRAP transfer.

Our pathway method is expected to be applicable to other bi-alkali molecules as well, as singlet-triplet mixing is generally more likely occurring for heavier molecules with smaller vibrational level spacing and stronger hyperfine interaction. The method is not restricted to closed channel dominated Feshbach resonances. For the important cases of NaK and LiCs, a significantly mixed character of the resonant state was explicitly reported in the respective ABM model analysis [45,74]. Molecular species with alkali-earth-like atoms, like LiYb, RbSr, and CsYb, are currently under study. For such molecules only spin-doublet ground and excited electronic states need to be considered. For the fermionic isotopes, unresolved hyperfine structure can occur in the excited state if either photoassociation or Feshbach association is used. We believe that the method of using a single stretched hyperfine state can be extended to such molecules in particular if the excited state can be rotationally excited like for RbSr [75].

To conclude, we demonstrated a pathway to access the rovibrational ground state of ultracold bi-alkali molecules using only singlet states. We found that the $A^1\Sigma^+$ potential offers good transition strengths to the Feshbach and ground states with moderate laser powers. Starting from a Feshbach state with a stretched hyperfine component of the singlet admixture allows addressing a pure hyperfine component of the ground state, even if the hyperfine structure is not resolved. An ideal three-level system is established and is robust against off-resonant coupling to other hyperfine components. This pathway has the advantage that it does not require a singlet-triplet mixing with fully resolved hyperfine structure in the excited state manifold. Our method is applicable to other types of molecules and represents a simplified and efficient pathway to their ground state.

We thank J. T. M. Walraven for helpful discussions on this manuscript. This research is supported by the National Research Foundation, Prime Ministers Office, Singapore and the Ministry of Education, Singapore under the Research Centres of Excellence program. We further acknowledge funding by the Singapore Ministry of Education Academic Research Fund Tier 2 (Grant No. MOE2015-T2-1-098).

---

[*] phydk@nus.edu.sg

[1] C. Trefzger, C. Menotti, B. Capogrosso-Sansone, and M. Lewenstein, J. Phys. B **44**, 193001 (2011).
[2] M. A. Baranov, M. Dalmonte, G. Pupillo, and P. Zoller, Chem. Rev. **112**, 5012 (2012).
[3] P. Schauss, J. Zeiher, T. Fukuhara, S. Hild, M. Cheneau, T. Macri, T. Pohl, I. Bloch, and C. Gross, Science **347**, 1455 (2015).
[4] H. Labuhn, D. Barredo, S. Ravets, S. de Leseleuc, T. Macri, T. Lahaye, and A. Browaeys, Nature (London) **534**, 667 (2016).
[5] F. Böttcher, J.-N. Schmidt, M. Wenzel, J. Hertkorn, M. Guo, T. Langen, and T. Pfau, Phys. Rev. X **9**, 011051 (2019).
[6] L. Chomaz, D. Petter, P. Ilzhöfer, G. Natale, A. Trautmann, C. Politi, G. Durastante, R. M. W. van Bijnen, A. Patscheider, M. Sohmen, M. J. Mark, and F. Ferlaino, Phys. Rev. X **9**, 021012 (2019).
[7] A. Micheli, G. K. Brennen, and P. Zoller, Nat. Phys. **2**, 341 (2006).
[8] B. Gadway and B. Yan, J. Phys. B **49**, 152002 (2016).
[9] D. DeMille, Phys. Rev. Lett. **88**, 067901 (2002).
[10] S. F. Yelin, K. Kirby, and R. Côté, Phys. Rev. A **74**, 050301 (R) (2006).
[11] A. André, D. DeMille, J. M. Doyle, M. D. Lukin, S. E. Maxwell, P. Rabl, R. J. Schoelkopf, and P. Zoller, Nat. Phys. **2**, 636 (2006).
[12] M. Kozlov and L. Labzowsky, J. Phys. B **28**, 1933 (1995).
[13] E. R. Hudson, H. J. Lewandowski, B. C. Sawyer, and J. Ye, Phys. Rev. Lett. **96**, 143004 (2006).
[14] V. Andreev, D. G. Ang, D. DeMille, J. M. Doyle, G. Gabrielse, J. Haefner, N. R. Hutzler, Z. Lasner, C. Meisenhelder, B. R. O'Leary, C. D. Panda, A. D. West, E. P. West, X. Wu, (ACME Collaboration), Nature (London) **562**, 355 (2018).
[15] L. D. Carr, D. DeMille, R. V. Krems, and J. Ye, New J. Phys. **11**, 055049 (2009).
[16] M. T. Bell and T. P. Softley, Mol. Phys. **107**, 99 (2009).
[17] G. Quéméner and P. S. Julienne, Chem. Rev. **112**, 4949 (2012).
[18] D. S. Jin and J. Ye, Chem. Rev. **112**, 4801 (2012).
[19] R. Wynar, R. Freeland, D. Han, C. Ryu, and D. Heinzen, Science **287**, 1016 (2000).
[20] H. Bethlem, G. Berden, F. Crompvoets, R. Jongma, A. van Roij, and G. Meijer, Nature (London) **406**, 491 (2000).
[21] S. D. Kraft, P. Staanum, J. Lange, L. Vogel, R. Wester, and M. Weidemueller, J. Phys. B **39**, S993 (2006).
[22] E. S. Shuman, J. F. Barry, and D. DeMille, Nature (London) **467**, 820 (2010).
[23] L. Anderegg, B. L. Augenbraun, Y. Bao, S. Burchesky, L. W. Cheuk, W. Ketterle, and J. M. Doyle, Nat. Phys. **14**, 890 (2018).
[24] T. Köhler, K. Góral, and P. S. Julienne, Rev. Mod. Phys. **78**, 1311 (2006).

[25] N. V. Vitanov, A. A. Rangelov, B. W. Shore, and K. Bergmann, Rev. Mod. Phys. **89**, 015006 (2017).
[26] K. K. Ni, S. Ospelkaus, M. H. G. de Miranda, A. Pe'er, B. Neyenhuis, J. J. Zirbel, S. Kotochigova, P. S. Julienne, D. S. Jin, and J. Ye, Science **322**, 231 (2008).
[27] T. Takekoshi, L. Reichsöllner, A. Schindewolf, J. M. Hutson, C. R. Le Sueur, O. Dulieu, F. Ferlaino, R. Grimm, and H.-C. Nägerl, Phys. Rev. Lett. **113**, 205301 (2014).
[28] P. K. Molony, P. D. Gregory, Z. Ji, B. Lu, M. P. Köppinger, C. R. Le Sueur, C. L. Blackley, J. M. Hutson, and S. L. Cornish, Phys. Rev. Lett. **113**, 255301 (2014).
[29] J. W. Park, S. A. Will, and M. W. Zwierlein, Phys. Rev. Lett. **114**, 205302 (2015).
[30] M. Guo, B. Zhu, B. Lu, X. Ye, F. Wang, R. Vexiau, N. Bouloufa-Maafa, G. Quéméner, O. Dulieu, and D. Wang, Phys. Rev. Lett. **116**, 205303 (2016).
[31] L. De Marco, G. Valtolina, K. Matsuda, W. G. Tobias, J. P. Covey, and J. Ye, Science **363**, 853 (2019).
[32] N. V. Vitanov and S. Stenholm, Phys. Rev. A **60**, 3820 (1999).
[33] S. Kotochigova, E. Tiesinga, and P. S. Julienne, New J. Phys. **11**, 055043 (2009).
[34] M. Debatin, T. Takekoshi, R. Rameshan, L. Reichsoellner, F. Ferlaino, R. Grimm, R. Vexiau, N. Bouloufa, O. Dulieu, and H.-C. Nägerl, Phys. Chem. Chem. Phys. **13**, 18926 (2011).
[35] P. Zabawa, A. Wakim, M. Haruza, and N. P. Bigelow, Phys. Rev. A **84**, 061401(R) (2011).
[36] J. W. Park, S. A. Will, and M. W. Zwierlein, New J. Phys. **17**, 075016 (2015).
[37] M. Guo, R. Vexiau, B. Zhu, B. Lu, N. Bouloufa-Maafa, O. Dulieu, and D. Wang, Phys. Rev. A **96**, 052505 (2017).
[38] T. M. Rvachov, H. Son, J. J. Park, S. Ebadi, M. W. Zwierlein, W. Ketterle, and A. O. Jamison, Phys. Chem. Chem. Phys. **20**, 4739 (2018).
[39] L. Liu, D.-C. Zhang, H. Yang, Y.-X. Liu, J. Nan, J. Rui, B. Zhao, and J.-W. Pan, Phys. Rev. Lett. **122**, 253201 (2019).
[40] M. Taglieber, A.-C. Voigt, T. Aoki, T. W. Hänsch, and K. Dieckmann, Phys. Rev. Lett. **100**, 010401 (2008).
[41] A.-C. Voigt, M. Taglieber, L. Costa, T. Aoki, W. Wieser, T. W. Hänsch, and K. Dieckmann, Phys. Rev. Lett. **102**, 020405 (2009).
[42] E. Wille, F. M. Spiegelhalder, G. Kerner, D. Naik, A. Trenkwalder, G. Hendl, F. Schreck, R. Grimm, T. G. Tiecke, J. T. M. Walraven, S. J. J. M. F. Kokkelmans, E. Tiesinga, and P. S. Julienne, Phys. Rev. Lett. **100**, 053201 (2008).
[43] T. G. Tiecke, M. R. Goosen, J. T. M. Walraven, and S. J. J. M. F. Kokkelmans, Phys. Rev. A **82**, 042712 (2010).
[44] See the Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.124.133203 for details on our asymptotic bound state calculation [42,43,45–49], mass scaling of spectroscopic data of Refs. [50–53], and calculations of the Franck-Condon factors [54,55], transition dipole matrix elements [56–62], spin-orbit coupling constants [63–65], and hyperfine coupling constants [66–71].
[45] R. Pires, M. Repp, J. Ulmanis, E. D. Kuhnle, M. Weidemüller, T. G. Tiecke, C. H. Greene, B. P. Ruzic, J. L. Bohn, and E. Tiemann, Phys. Rev. A **90**, 012710 (2014).
[46] A. J. Moerdijk, B. J. Verhaar, and A. Axelsson, Phys. Rev. A **51**, 4852 (1995).
[47] T. G. Tiecke, M. R. Goosen, A. Ludewig, S. D. Gensemer, S. Kraft, S. J. J. M. F. Kokkelmans, and J. T. M. Walraven, Phys. Rev. Lett. **104**, 053202 (2010).
[48] Z. Li, S. Singh, T. V. Tscherbul, and K. W. Madison, Phys. Rev. A **78**, 022710 (2008).
[49] J. W. Park, C.-H. Wu, I. Santiago, T. G. Tiecke, S. Will, P. Ahmadi, and M. W. Zwierlein, Phys. Rev. A **85**, 051602(R) (2012).
[50] A. Grochola, J. Szczepkowski, W. Jastrzebski, and P. Kowalczyk, Chem. Phys. Lett. **535**, 17 (2012).
[51] E. Tiemann, H. Knöckel, P. Kowalczyk, W. Jastrzebski, A. Pashov, H. Salami, and A. J. Ross, Phys. Rev. A **79**, 042716 (2009).
[52] J. L. Dunham, Phys. Rev. **41**, 721 (1932).
[53] F. Martin, P. Crozet, A. J. Ross, M. Aubert-Frecon, P. Kowalczyk, W. Jastrzebski, and A. Pashov, J. Chem. Phys. **115**, 4118 (2001).
[54] Website of A. R. Allouche, https://sites.google.com/site/allouchear/Home/diatomic.
[55] C. Marston and G. Balinkurti, J. Chem. Phys. **91**, 3571 (1989).
[56] H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, and M. Schuetz, Comput. Mol. Sci. **2**, 242 (2012).
[57] MOLPRO, version 2015.1, a package of *ab initio* programs, H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz, and others, see, www.molpro.net.
[58] H.-J. Werner and P. J. Knowles, J. Chem. Phys. **89**, 5803 (1988).
[59] P. J. Knowles and H.-J. Werner, Chem. Phys. Lett. **145**, 514 (1988).
[60] P. J. Knowles and H.-J. Werner, Theor. Chim. Acta **84**, 95 (1992).
[61] I. Lim, H. Stoll, and P. Schwerdtfeger, J. Chem. Phys. **124**, 2148945 (2006).
[62] P. Widmark, P. Malmqvist, and B. Roos, Theor. Chim. Acta **77**, 291 (1990).
[63] S. Falke, E. Tiemann, C. Lisdat, H. Schnatz, and G. Grosche, Phys. Rev. A **74**, 032503 (2006).
[64] M. Manaa, Int. J. Quantum Chem. **75**, 693 (1999).
[65] M. Manaa, A. Ross, F. Martin, P. Crozet, A. Lyyra, L. Li, C. Amiot, and T. Bergeman, J. Chem. Phys. **117**, 11208 (2002).
[66] P. Bruna and F. Grein, Mol. Phys. **104**, 429 (2006).
[67] L. Wharton, W. Klemperer, and L. Gold, Phys. Rev. B **133**, B270 (1964).
[68] T. Q. Teodoro, R. L. A. Haiduke, and L. Visscher, Phys. Rev. A **91**, 032516 (2015).
[69] K. Aidas *et al.*, Wiley Interdiscip. Rev. **4**, 269 (2014).
[70] Dalton, a molecular electronic structure program, Release v2018.1 (2018), see, http://daltonprogram.org/.

[71] J. Aldegunde and J. M. Hutson, Phys. Rev. A **96**, 042506 (2017).

[72] J. F. S. Brachmann, T. Kinder, and K. Dieckmann, Appl. Opt. **51**, 5517 (2012).

[73] V. Bednarska, P. Kowalczyk, and W. Jastrzebski, J. Mol. Spectrosc. **180**, 435 (1996).

[74] C.-H. Wu, J. W. Park, P. Ahmadi, S. Will, and M. W. Zwierlein, Phys. Rev. Lett. **109**, 085301 (2012).

[75] V. Barbe, A. Ciamei, B. Pasquiou, L. Reichsöllner, F. Schreck, P. S. Zuchowski, and J. M. Hutson, Nat. Phys. **14**, 881 (2018).