Ultracold RbSr Molecules Can Be Formed by Magnetoassociation

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We investigate the interactions between ultracold alkali-metal atoms and closed-shell atoms using electronic structure calculations on the prototype system Rb + Sr. There are molecular bound states that can be tuned across atomic thresholds with a magnetic field and previously neglected terms in the collision Hamiltonian that can produce zero-energy Feshbach resonances with significant widths. The largest effect comes from the interaction-induced variation of the Rb hyperfine coupling. The resonances may be used to form paramagnetic polar molecules if the magnetic field can be controlled precisely enough.

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There have been enormous advances in ultracold molecule formation in the past few years. Alkali-metal dimers have been formed both by photoassociation and by magnetic tuning across zero-energy Feshbach resonances (magnetoassociation). In both approaches the molecules are initially formed in very high-lying vibrational states, but methods are now emerging to transfer the molecules to low-lying vibrational states [1–8]. For KRb and Cs_2, molecules in the rovibronic ground state have been formed coherently from ultracold atoms by magnetoassociation followed by stimulated Raman adiabatic passage [2,9]. The availability of samples of polar ultracold molecules opens up new possibilities for exploring polar quantum gases, for developing quantum simulators, and for studies of controlled ultracold chemistry [10].

Alkali-metal dimers have singlet ground states, which cannot be tuned magnetically except through the very small magnetic moments of the nuclei. Although the molecules can be formed in excited triplet states, the triplet dimers are likely to be subject to trap loss due to fast inelastic and reactive collisions. There is therefore great interest in forming ultracold molecules that have ground states with unpaired electron spin. Molecules that have *both* electric and magnetic dipoles may be used to create topologically ordered states and may have novel applications in quantum information storage [11].

A very promising class of molecules are those formed from an alkali-metal atom, with a ^2S ground state, and a closed-shell atom. However, the collision Hamiltonian that is usually used does not couple the atomic and molecular states in such systems, and it is commonly believed that they will not exhibit magnetically tunable Feshbach resonances that can be used for ultracold molecule formation. The purpose of the present Letter is to show that this is not in fact true: There are terms in the Hamiltonian that have previously been neglected, which can give rise to magnetically tunable Feshbach resonances. If precise enough control of magnetic fields can be achieved, these resonances may be used for molecule formation.

We consider the prototype system RbSr. This is particularly topical because Bose-Einstein condensation has recently been achieved for ^{84}Sr [12,13] and ^{88}Sr [14] and Fermi degeneracy for ^{87}Sr [15]. Both ^{87}Rb and ^{85}Rb are readily condensed. However, our general conclusions apply to any system made up of an alkali-metal atom and a closed-shell atom.

The collision Hamiltonian for a pair of atoms a and b is

$$\frac{\hbar^2}{2\mu}\left[-r^{-1}\frac{d^2}{dr^2}r + \frac{\hat{L}^2}{r^2}\right] + \hat{H}_a + \hat{H}_b + \hat{V}(r), \quad (1)$$

where r is the internuclear distance, μ is the reduced mass, $\hat{L}^2$ is the angular momentum operator for mechanical rotation of the atoms about one another, $\hat{H}_a$ and $\hat{H}_b$ are the Hamiltonians for the free atoms (in an applied field), and $\hat{V}(r)$ is the interaction operator. For collision of a pair of alkali-metal atoms, $\hat{H}_a$ and $\hat{H}_b$ are

$$\hat{H}_\alpha = \zeta_\alpha \hat{i}_\alpha \cdot \hat{s}_\alpha + (g^e_\alpha \mu_B \hat{s}_{\alpha z} + g^{nuc}_\alpha \mu_N \hat{i}_{\alpha z})B, \quad (2)$$

where ζ_α is the hyperfine coupling constant for atom α, $\hat{s}_\alpha$ and $\hat{i}_\alpha$ are the corresponding electron and nuclear spin operators, respectively, g^e_α and g^{nuc}_α are the g factors, and B is the magnetic field, whose direction defines the z axis. The interaction operator is usually represented as

$$\hat{V}(r) = \sum_{S=|s_a-s_b|}^{s_a+s_b} |S\rangle\langle S|\hat{V}|S\rangle\langle S| + \hat{V}^d(r), \quad (3)$$

where for a pair of alkali-metal atoms $V_0(r) = \langle 0|\hat{V}(r)|0\rangle$ and $V_1(r) = \langle 1|\hat{V}(r)|1\rangle$ are the potential curves for the singlet and triplet states and $\hat{V}^d(r)$ is a term that represents the magnetic dipole interaction between the electron spins on the two atoms (and may incorporate short-range terms due to second-order spin-orbit interaction).

The molecular wave functions are conveniently expanded in an uncoupled basis set $|s_a m_{sa}\rangle|i_a m_{ia}\rangle|s_b m_{sb}\rangle$ $|i_b m_{ib}\rangle|LM_L\rangle$. The Hamiltonian is diagonal in the total projection quantum number $M_{tot} = M_F + M_L$, where

$M_F = m_{sa} + m_{ia} + m_{sb} + m_{ib}$. The only term in the Hamiltonian that has matrix elements off-diagonal in L is the spin-spin term. However, for a pair of alkali-metal atoms, the singlet potential is substantially different from the triplet potential (typically a factor of 10–20 deeper), and the difference produces strong couplings between states with the same L and the same M_F. The resulting molecular states typically have magnetic moments different from the atomic states and may cross them as a function of a magnetic field. The molecular states are coupled to the atomic states by either $V_1(r) - V_0(r)$ (when the atomic and molecular states have the same values of L and M_F) or $\hat{V}^d(r)$ (when the L or M_F values are different). This produces magnetically tunable Feshbach resonances that may be used for molecule formation.

The situation is different when one of the atoms is in a ^1S state. When $s_b = 0$, there is no spin-spin interaction. There is also only one interaction potential $V(r)$, corresponding to $S = s_a$ ($S = \frac{1}{2}$ for RbSr). The stable isotopes ^{84}Sr, ^{86}Sr, and ^{88}Sr all have zero nuclear spin. The quantum number $F = f_a = i_a \pm \frac{1}{2}$ is well-defined only at zero field, but even at finite field the molecular states have almost exactly the same mixture of F values, and therefore the same magnetic moments, as their parent atomic states. The molecular levels are thus closely parallel to the atomic levels as a function of a magnetic field. Even for ^{87}Sr, with $i_b = 9/2$, the nuclear Zeeman effect is a small perturbation.

If the interaction operator was really represented by Eq. (3), with only $S = \frac{1}{2}$ and no $\hat{V}^d(r)$, there would be no coupling between the atomic and molecular states. Although there would still be crossings between atomic states and molecular states as a function of magnetic field, there would be no coupling between them; the resulting Feshbach resonances would have zero width, and it would be impossible to tune across them adiabatically, as required for molecule formation. However, Eq. (3) is in reality an approximation, and there are several additional ways in which the colliding species interact with one another. For RbSr, these additional terms have a profound effect.

The most important additional interaction term comes from the fact that the Rb hyperfine coupling constant ζ is modified when another atom is nearby. We may write $\zeta(r) = \zeta_{\text{Rb}} + \Delta\zeta(r)$. The term $\Delta\zeta(r)\hat{i}_a \cdot \hat{s}_a$ is part of the interaction operator $\hat{V}(r)$. In addition, there are short-range contributions to $\hat{V}(r)$ from smaller terms such as (i) the interaction $eQq(r)$ between the nuclear quadrupole moment of Rb and the field gradient at the Rb nucleus caused by the distortion of the electron density by Sr, (ii) the dipolar interaction between the electron spin and the Rb nuclear spin, and (iii) the spin-rotation interaction between L and the Rb electron and nuclear spins. However, the modification of ζ_{Rb} is by far the largest effect.

We have carried out high-level electronic structure calculations of the interaction potential and dipole moment of RbSr and the modification of ζ_{Rb} by Sr. The results are summarized in Fig. 1. The short-range potential (from 3 to 10 Å) was calculated by using the spin-restricted coupled-cluster method with single, double, and approximate triple excitations [CCSD(T)], with the relativistic small-core ECP28MDF effective core potentials and uncontracted basis sets of Lim *et al.* [16,17] augmented by $3s3p2d$ functions at the bond midpoint. For $R > 10$ Å, we extrapolate by using the long-range form $V(r) = -C_6 r^{-6} - C_8 r^{-8}$, with semiempirical coefficients [18] $C_6 = 3.762 \times 10^3 E_h a_0^6$ and $C_8 = 4.62 \times 10^5 E_h a_0^8$. The short- and long-range parts of the potential were smoothly connected with the switching function used by Janssen *et al.* [19]. The quantities $\zeta(r)$ and $eQq(r)$ were calculated with the relativistic density-functional theory approach [20] implemented in the ADF program [21], by using the PBE0 functional [22]. The asymptotic value of ζ_{Rb} was underestimated by 6% in the density-functional theory calculations, so we scaled $\zeta(r)$ to reproduce the experimental atomic value. The quantity $\Delta\zeta(r)$ was fitted to the Gaussian form $\zeta_0 e^{-a(r-r_c)^2}$, giving parameters $a = 0.23$ Å^{-2} and $r_c = 4.06$ Å, with $\zeta_0 = -687$ MHz for ^{87}Rb and -229 MHz for ^{85}Rb. This corresponds to a 20% maximum reduction in ζ. We also evaluated the dipole moment $\mu(r)$ by using a variety of approaches. The most reliable is a finite-field CCSD(T) calculation with the approach described above, which gives $\mu(r_e) = 1.36$ D at the equilibrium distance $r_e = 4.67$ Å. However, the precise value is sensitive to the level of correlation treatment.

We have also investigated the smaller additional couplings described above, in order to verify that they are much less important than $\Delta\zeta(r)$. All these can couple states with $\Delta M_F \neq 0$ when $L > 0$. The nuclear quadrupole coupling and the dipolar coupling between s_a and i_a can also
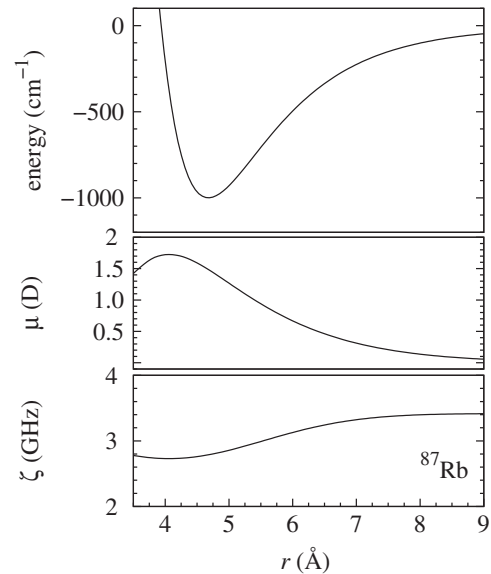

FIG. 1.   Interaction potential $V(r)$ (top) with dipole moment $\mu(r)$ (middle) and hyperfine coupling constant $\zeta(r)$ (bottom). The binding energy and equilibrium distance are calculated to be 1000 cm^{-1} and 4.67 Å, respectively.

couple channels with $\Delta L \neq 0$ and can thus mediate Feshbach resonances in s-wave scattering for bound states with $L \neq 0$. Our density-functional theory calculations give values for the nuclear quadrupole coupling constant $eQq(r_e) = 8$ and 3.7 MHz for ^{85}RbSr and ^{87}RbSr, respectively, reducing rapidly to zero as the RbSr distance increases beyond r_e. The coupling constant for the dipolar interaction between s_a and i_a is of the order of 1 MHz near r_e. The electronic spin-rotation coupling constant can be estimated in terms of the rotational constant b and the anisotropy g_{aniso} of the electronic g factor as $2bg_{aniso}$ [23], which is approximately 20 MHz near r_e. The nuclear spin-rotation interaction will be about a factor of 10^3 smaller because of the ratio of the nuclear and Bohr magnetons. A 20 MHz coupling is potentially significant, but neither the electronic nor the nuclear spin-rotation interaction has matrix elements that affect s-wave scattering. All these smaller coupling terms, and couplings involving the nuclear spin of ^{87}Sr, are neglected in the scattering calculations described below.

Since the M_F-changing terms in the collision Hamiltonian are so small, crossings between thresholds and bound states with different M_F will not produce Feshbach resonances wide enough to be measured with current experimental methods. However, if the Rb atom is initially in a state that correlates at zero field with $F = i_a - \frac{1}{2}$, then the threshold is crossed by bound states with the same M_F but correlating with $F = i_a + \frac{1}{2}$. The operator $\Delta\zeta(r)\hat{i}_a \cdot \hat{s}_a$ is *not* diagonal in the field-dressed atomic eigenstates, so it can produce Feshbach resonances at these crossings. The pattern of bound states and the crossings that produce Feshbach resonances are shown in Fig. 2 for ^{85}Rb and ^{87}Rb with all the stable isotopes of Sr. Since the hyperfine splittings are a few gigahertz, the bound states responsible for the crossings are bound by energies of a few gigahertz. For RbSr these are states with vibrational quantum numbers $v = -3$ and -4 (relative to threshold) for magnetic fields up to 0.5 T.

We next investigated the widths of the resonances produced in this way. To locate them, we first carried out bound-state calculations as a function of a magnetic field by using the BOUND package [24] to determine precisely the magnetic field at which the crossing occurs. We then used the MOLSCAT program [25], modified to handle collisions of atoms in magnetic fields [26], to calculate the scattering length $a(B)$ as a function of the magnetic field near the crossing at a near-zero collision energy (10^{-8} K). This was then fitted to the functional form $a(B) = a_{bg}[1 + \Delta/(B - B_{res})]$ to extract the resonance position B_{res}, the width Δ, and the background scattering length a_{bg}. The parameters of selected Feshbach resonances are given in Table I.

For a potential with known long-range behavior, both the energies of high-lying bound states [27] and the background scattering length [28] may be expressed in terms of the fractional part of the quantum number at dissociation (or, equivalently, of a semiclassical phase integral). Since
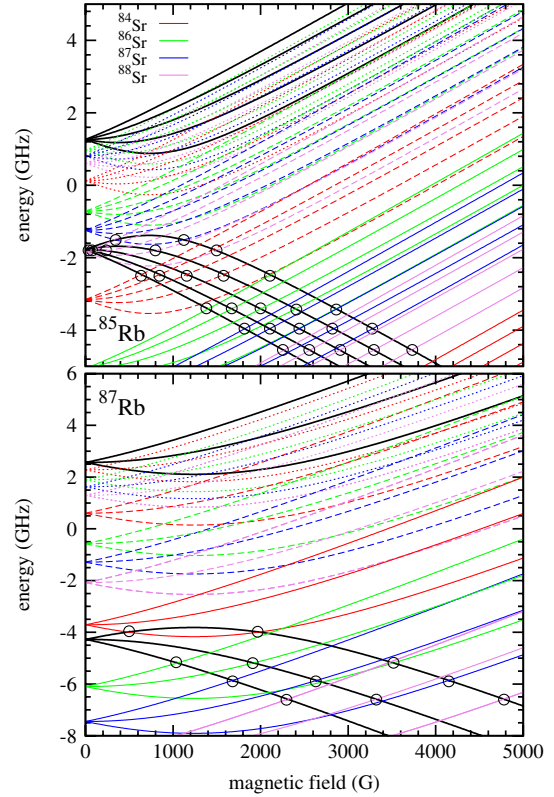

FIG. 2 (color online). Molecular levels (colored lines) that cross atomic thresholds (black lines) for $|M_F| \leq i_a - \frac{1}{2}$ states of ^{85}RbSr (upper) and ^{87}RbSr (lower) as a function of a magnetic field for different Sr isotopes. The dotted, dashed, and solid colored lines correspond to $v = -2$, -3, and -4 vibrational states, respectively. Positions of resonances are marked with circles.

the local momentum is proportional to $[\mu V(r)]^{1/2}$, scaling the potential has almost exactly the same effect as changing the reduced mass. Our potential has 63 bound states for all isotopologues except ^{85}Rb^{84}Sr, for which it has 62. However, it might be in error by as much as $\pm 10\%$, so it is not accurate enough to predict the scattering length (and thus the binding energies and resonance positions) for any specific isotopologue. Nevertheless, there are enough different isotopes of Sr available to cover the range of possibilities shown in Fig. 2. A measurement of the scattering length or the binding energy of one of the near-dissociation states for any isotopologue will allow reliable calculations of the resonance positions for all isotopic combinations.

States with $M_F < 0$ (except $M_F = -i_a - \frac{1}{2}$) have energy maxima or minima at $B_m = -\zeta M_F/(g_e \mu_B)$, where they are separated by $d = \zeta[(i_a + \frac{1}{2})^2 - M_F^2]^{1/2}$. For levels with binding energies $|E_v|$ in the range $d < E_v < (i_a + \frac{1}{2})\zeta$, there are two crossings with the lower threshold: one between 0 and B_m and the second between B_m and $2B_m$. Conversely, for levels with binding energies $|E_v| > (i_a + \frac{1}{2})\zeta$, there is only one crossing, at a field $B > 2B_m$. For levels with $M_F \geq 0$, there is only one crossing for each vibrational state with binding energy larger than $(i_a + \frac{1}{2})\zeta$.

TABLE I. Calculated properties of RbSr Feshbach resonances at $F = i_a - \frac{1}{2}$ thresholds arising from bound states supported by the $F = i_a + \frac{1}{2}$ thresholds.

System	$B_{\rm res}$ (G)	$a_{\rm bg}$ (Å)	Δ (mG)	M_F
^{85}Rb^{84}Sr	632	19.5	-0.0560	$+2$
	840	19.5	-0.292	$+1$
	1145	19.5	-0.636	0
	1562	19.5	-0.987	-1
	2076	19.4	-0.636	-2
^{85}Rb^{86}Sr	1383	815.7	-1.83	$+2$
	1649	813.9	-4.34	$+1$
	1977	814.1	-7.14	0
	2371	814.1	-8.85	-1
	2827	814.1	-7.50	-2
^{85}Rb^{87}Sr	336	95.1	0.0545	-2
	1108	95.1	-0.586	-2
	1797	95.1	-0.163	$+2$
	2079	95.1	-0.347	$+1$
	2413	95.1	-0.532	0
	2800	95.1	-0.664	-1
	3240	95.0	-0.499	-2
^{85}Rb^{88}Sr	37	56.2	$-0.000\,277$	$+2$
	70	56.2	$-0.002\,39$	$+1$
	235	56.2	-0.0397	0
	792	56.2	-0.270	-1
	1481	56.2	-0.311	-2
	2237	56.2	-0.124	$+2$
	2531	56.2	-0.276	$+1$
	2869	56.2	-0.402	0
	3253	56.2	-0.485	-1
	3680	56.2	-0.350	-2
^{87}Rb^{84}Sr	477	1715.0	7.41	-1
	1959	1700.3	-122	-1
^{87}Rb^{86}Sr	1036	55.0	-0.209	$+1$
	1896	55.0	-1.08	0
	3472	55.0	-2.29	-1
^{87}Rb^{87}Sr	1660	31.5	-0.636	$+1$
	2608	31.5	-2.27	0
	4096	31.5	-3.79	-1
^{87}Rb^{88}Sr	2281	1.6	-33.6	$+1$
	3280	1.6	-101	0
	4716	1.5	-153	-1

The widest and most promising resonances for molecule production are of two types. The first are those that occur for $M_F < 0$ states that cross the lower threshold twice, as occurs for $v = -3$ for ^{85}Rb^{87}Sr and $v = -4$ for ^{87}Rb^{84}Sr in Fig. 2. The higher-field resonance is always the wider of the pair because the matrix element of $\hat{i}_a \cdot \hat{s}_a$ approaches zero at zero field. The second are those for which the background scattering length is large, as for ^{85}Rb^{86}Sr and ^{87}Rb^{84}Sr on the current potential. These two effects combine for the 1959 G resonance for ^{87}Rb^{84}Sr in Table I to give a width as high as 122 mG.

In conclusion, we have investigated the interactions between Rb and Sr atoms and have identified a new mechanism that can produce magnetically tunable Feshbach resonances in collisions of ultracold molecules. These Feshbach resonances could be used to produce ultracold molecules that would have both electric and magnetic dipole moments in their ground states. The resonances arise from the modification of the Rb hyperfine coupling by the presence of another atom. The mechanism may produce magnetically tunable Feshbach resonances in any system in which an atom with electron spin collides with a closed-shell atom, such as an alkaline earth or Yb atom.

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