Ultracold molecules: a platform for quantum simulation

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Abstract. We explore the uses of ultracold molecules as a platform for future experiments in the field of quantum simulation, focusing on two molecular species, $^{40}$Ca$^{19}$F and $^{87}$Rb$^{133}$Cs. We report the development of coherent quantum state control using microwave fields in both molecular species; this is a crucial ingredient for many quantum simulation applications. We demonstrate proof-of-principle Ramsey interferometry measurements with fringe spacings of $\sim 1$ kHz and investigate the dephasing time of a superposition of $N = 0$ and $N = 1$ rotational states when the molecules are confined. For both molecules, we show that a judicious choice of molecular hyperfine states minimises the impact of spatially varying transition-frequency shifts across the trap. For magnetically trapped $^{40}$Ca$^{19}$F we use a magnetically insensitive transition and observe a coherence time of 0.61(3) ms. For optically trapped $^{87}$Rb$^{133}$Cs we exploit an avoided crossing in the AC Stark shift and observe a maximum coherence time of 0.75(6) ms.

Keywords: Quantum Simulation, Ultracold Molecules, Ramsey, Coherence, RbCs, CaF

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Since Lloyd’s proof that evolving a controllable quantum system in small time steps can allow efficient simulation of any quantum many-body Hamiltonian \(1\), the field of quantum simulation has grown enormously, driven by the prospect of aiding our understanding of complex physical systems, such as high temperature superconductors \(2-4\), or warm, dense nuclear matter \(5\). In this context, the role of the quantum simulator is to implement a model put forward to describe a physical system, and to measure observables that can be compared to real systems of interest \(6\). Currently, a number of experimental platforms are under exploration, each in essence attempting to address Cirac and Zoller’s criteria to qualify as a quantum simulator \(7\) through different paths \(8-10\).

Trapped ions are the most established candidate system for quantum simulation \(11\). They offer exceptional and unprecedented quantum control over small numbers of ions, which has been developed over decades \(12\). On-going efforts are aimed at scaling up to larger numbers of ions. In the short term, 10 to 20 ions with very good control \(13\) and up to 50 ions with somewhat larger imperfections are probably achievable. Scaling up to much larger numbers is a challenging goal that will probably require new ideas. In contrast, superconducting circuits have recently made considerable progress as an alternative platform \(14\). Here, the superconducting qubits and qubit gates are of comparably low fidelity, but scaling up to larger systems is easier and integration with other existing electronic technology is relatively straightforward.

Quantum simulation with ultracold atoms in optical lattices \(15, 16\) has already offered some ground-breaking results, such as the recent observation of magnetic correlations in experiments implementing the two-dimensional Hubbard model \(17-19\). Experiments are characterised by large numbers of atoms in a well controlled initial state. Gate operations are highly parallelisable, which makes them suitable for quantum simulations that do not require spatially varying operations to realize model Hamiltonians. Indeed, it has frequently been difficult to address individual atoms, although the development of the quantum gas microscope \(20, 22\) and tweezer arrays \(23, 25\) represent important breakthroughs in this respect. Gate operations are relatively slow, governed by trapping and tunnelling rates on the order of Hz to kHz \(26\). Moreover, interactions between ground-state alkali-metal atoms are short-ranged, which makes them suitable to model local interactions only. This last point has prompted growing interest in long-range dipolar interactions which may be implemented in atomic systems either by using highly magnetic atoms \(27, 32\) or by exciting atoms to Rydberg electronic states \(10, 33, 35\).

Ultracold polar molecules offer new possibilities for quantum simulation and face correspondingly new challenges. The electric dipole moment of polar molecules gives rise to interactions that are significantly greater than those between magnetic atoms and, although interactions between Rydberg states are even greater, ground-state polar molecules have longer lifetimes. Molecules also possess a rich internal structure, with vibrational and rotational degrees of freedom in addition to electronic and hyperfine structure. This, in principle, allows molecules to simulate models featuring a large
number of degrees of freedom that would otherwise require ‘encoding’ in several qubits. This is of interest, for example, in the study of $SU(N)$-symmetric models with large $N$ \[36\]. On the other hand, this richer internal structure raises questions on the degree of control with which one can realistically initialise, manipulate, and measure a molecule’s internal state. Finally, the enormous range of molecular species allows one to select the molecular properties to match the application. For example, molecules with singlet ground states possess only an electric dipole moment, whereas those with doublet ground states have both electric and magnetic dipole moments.

An important ingredient for a useful quantum simulator is the ability to manipulate the interactions between its constituent particles, in order to simulate various models of interest. There are numerous theoretical proposals to engineer tunable interactions between polar molecules in optical lattices, see e.g. \[37–40\], enabling, for example, such a system to simulate the behaviour in quantum magnets \[37\], high-temperature superconductors \[4\] and novel phases of quantum matter, such as spin glasses \[41\] and topological insulators \[38\]. In these proposals, the single-molecule states are usually dressed with external fields, and the molecule-molecule interactions are modified with additional microwave or radio-frequency radiation. The accuracy with which these proposals can ultimately be realised will depend on the degree of control that we develop over the motion of molecules, an area where experiments lag behind their atomic counterparts. Nevertheless, there has been considerable progress in the cooling, trapping and control of a growing number of molecular species, both through the association of atoms in ultracold atomic gases \[42–47\] and more recently by direct laser cooling of molecules \[48–60\]. Indeed, the observation of dipolar spin-exchange interactions with lattice-confined polar molecules \[61\] arguably represents the first step into the field of quantum simulation with long-range interactions.

In this paper we explore the uses of ultracold molecules as a platform for future experiments in the field of quantum simulation, focusing on two molecular species, $^{40}$Ca$^{19}$F and $^{87}$Rb$^{133}$Cs, hereafter simply referred to as CaF and RbCs. We begin by describing the properties of molecules that make them suited to applications in the realm of quantum simulation and briefly review some of the underpinning theoretical proposals. In section 2 we outline the methods we use to produce molecules in the ultracold regime, describing both direct laser cooling of CaF and the association of ultracold atoms to form RbCs. We then present details in section 3 of the rotational and hyperfine structure of the two molecules relevant to internal state control using microwave fields. In section 4 we report Ramsey interferometry measurements and investigate the coherence time of a superposition of ground and excited rotational states when the molecules are confined. For both molecules, we show that a judicious choice of molecular hyperfine states minimises the impact of spatially varying shifts in transition frequencies across the trap, providing a route to long interrogation times in future experiments. Finally, we provide a brief outlook detailing our plans for loading, addressing and detecting individual molecules in ordered arrays; this is the next major challenge in the development of molecules as a platform for quantum simulation.
1. Quantum simulation with ultracold molecules

Ultracold polar molecules, highly magnetic atoms and atoms in Rydberg states all offer long-range, anisotropic dipole-dipole interactions suitable for the simulation of interesting quantum many-body problems. A key feature offered by polar molecules is their rich internal structure that opens the door to novel control paths. To see this, consider the Hamiltonian describing $N$ polar molecules,

$$\hat{H} = \sum_{i=1}^{N} -\frac{\hbar^2}{2m} \nabla_i^2 + \sum_{i} H^\text{int}_i + \sum_{i>j} V^\text{DD}_{ij},$$

$$V^\text{DD}_{ij} = \frac{1}{4\pi\varepsilon_0} \tilde{\mu}_i \cdot \tilde{\mu}_j - \left( \tilde{\mu}_i \cdot \tilde{e}_{ij} \right) \left( \tilde{\mu}_j \cdot \tilde{e}_{ij} \right) \frac{1}{r_{ij}^3}.$$  

Here, molecule $i$ has mass $m$, internal Hamiltonian $H^\text{int}_i$, electric dipole moment $\tilde{\mu}_i$ and position vector $\vec{r}_i$. $\vec{r}_{ij} = \vec{r}_i - \vec{r}_j$, and $\tilde{e}_{ij}$ is the unit vector in the direction of $\vec{r}_{ij}$. The magnitude of the electric dipole moment depends on the electronic and vibrational state. External DC and AC fields may be used to orient the dipole moments in space and produce long-range anisotropic dipole-dipole interactions. A number of theoretical studies have proposed methods to exploit this property in order to realise various models of quantum magnetism by defining (pseudo)spins associated with the internal states at play. For instance, Barnett et al. proposed modelling an effective spin-1/2 particle by identifying the $|\downarrow\rangle$ state with the rotational ground state, $|N = 0\rangle$, and the $|\uparrow\rangle$ state with one of the components of the first rotationally excited state, $|N = 1, M_N = -1, 0, +1\rangle$, of a $^1\Sigma$ molecule [62]. Here $N$ is the rotational quantum number, and $M_N$ its projection on a laboratory quantization axis defined, for example, by an external DC electric field (see (4) below). In their proposal, molecules in $N = 0$ are trapped initially in an optical lattice, and some of them are coherently transferred to one of the $N = 1$ levels by a suitably polarised microwave field. If the dipole-dipole interactions (DDI) between neighbouring sites are weak (i.e., $\mu^2/(4\pi\varepsilon_0 a^3_{\text{lat}})$ is much smaller than the band gap in the lattice, with $a_{\text{lat}}$ the lattice constant), the system can be described by an effective Hubbard model with additional long-range DDI. This model features several exotic superfluid phases as a function of the interaction strength and the tilting of the polarizing field with respect to the lattice [62].

The rich internal structure of polar molecules includes vibrations, rotations, and hyperfine structure, in addition to couplings to external fields. In the ultracold regime (temperature $< 1$ mK), experiments usually address a single rotational state of the vibrational ground state; the rotational constant of typical diatomic molecules is $B \geq h \times 1$ GHz $\simeq k_B \times 50$ mK. In this regime, the internal state space is then spanned by rotations and hyperfine structure, and is amenable to manipulation with microwave (mw) and radio-frequency (rf) fields. Ospelkaus et al. were the first to demonstrate coherent transfer of ultracold molecules between single hyperfine states in the $N = 0$ and $N = 1$ rotational levels using mw photons of suitable frequency and polarisation, thus transforming each molecule into an effective two-level, or spin-1/2,
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system \[63\]. Similar control has now been demonstrated using other molecules \[64\]–\[67\]. In addition, off-resonant mw fields can be used to dress the molecular levels and to tailor the intermolecular interactions \[37\], \[68\]. For instance, using this approach to engineer the interactions between \(^2\Sigma\) molecules trapped in an optical lattice allows realisation of a large family of models of quantum magnetism \[37\]. In particular, for molecules confined in a square 2D lattice with \(l\) sites, the dynamics can be described by the effective Hamiltonian with nearest-neighbour interactions,

\[
H = \sum_{i=1}^{l} \sum_{j=1}^{l} J \left( \sigma_{i,j}^z \sigma_{i,j+1}^z + \cos(\theta) \sigma_{i,j}^x \sigma_{i+1,j}^x \right),
\]

where \(\sigma_{i,j}^{x,y,z}\) are the usual Pauli spin operators for the effective spin-1/2 system at the lattice site with index \((i,j)\); the hopping amplitude \(J\) depends on the Rabi frequency of the dressing mw field and the lattice spacing; and \(\theta\) is the angle between the plane of the lattice and the polarisation direction of the mw field \[37\].

To simulate strongly-correlated phases in optical lattices, a challenging requirement is to achieve a filling fraction close to unity. The current state-of-the-art corresponds to filling fractions of approximately 25-30% using fermionic ground-state KRb molecules \[69\] and RbCs Feshbach molecules \[70\], as discussed in section 5. In these experiments the two atomic species are loaded into the lattice prior to forming the molecules. To reach higher filling, it will be necessary to develop schemes to lower considerably the temperature or entropy of the molecular samples, perhaps adopting the techniques used in atomic quantum gas microscopes to engineer low-entropy sub-regions of the lattice \[71\]. Nevertheless, even with lower filling fractions of \(\sim 10\) to 25%, coherent dipole-dipole interaction-induced effects have been observed with KRb molecules \[61\]. Similar experiments have been reported with Cr \[72\], \[73\] and Er \[30\] where the use of a single atomic species makes it considerably easier to achieve filling fractions close to unity, but the magnetic dipole-dipole interactions are much weaker.

In the absence of a lattice, calculations for purely 2D systems of dipoles predict a collapse (or high-density phase) when the dipoles are polarised at an angle \(\theta \gtrsim 35^\circ\) to the normal of the plane \[38\], \[74\], \[75\]. For dipoles polarised at angles \(\theta \lesssim 23^\circ\), the system undergoes a transition between a gas phase and a solid phase for densities \(n > 300r_{dd}^{-2}\), where \(r_{dd} = \mu^2/(4\pi\varepsilon_0\hbar^2)\) is the characteristic length scale of the DDI. Finally, for polarisation angles \(23^\circ < \theta < 35^\circ\), an exotic stripe phase has been predicted \[75\], with an anisotropic structure factor that combines solid-like and liquid-like features along different directions in the plane. To assess the experimental requirements to observe these phases, we consider RbCs molecules with \(\mu = 0.5\) Debye. In this case, \(r_{dd} \approx 0.8\) \(\mu m\) and the critical density is \(\approx 4.4 \times 10^{10}\) \(cm^{-2}\). We can estimate the transition temperature to be close to the energy difference between the solid and liquid phases, which is \(\lesssim 0.1\) \(\mu K\) for densities close to the transition. This is about one order of magnitude below temperatures in current experiments (see below). However, finite-temperature quantum Monte Carlo simulations indicate that the main features of the structure factor of the dipolar solid phase survive at higher temperatures, \(\gtrsim 3T_c\) \[76\].
These results suggest that inherently dipole-induced many-body effects may be observable at accessible temperatures in the near future without the requirement of optical lattices. Indeed, the recent experimental observations of a striped phase in a cold gas of dysprosium atoms [32] and of the dipolar roton mode [74, 77, 78] in a cold erbium gas in a quasi-1D geometry [31] can be attributed to many-body effects induced by dipole-dipole interactions. The fact that the DDI between electric dipoles is of order $\alpha^{-1} \approx 137$ times stronger than between magnetic dipoles (where $\alpha$ is the fine-structure constant) should likewise facilitate the observation of dipolar effects in quasi-2D molecular gases.

Although many challenges remain, it is clear that ultracold molecules have an important role to play in the simulation of novel many-body Hamiltonians with long-range interactions. Similarly, it is evident that coherent addressing of internal states with microwave fields will be needed, both to engineer specific interactions and to sensitively detect the many-body quantum phases. In this paper we demonstrate Ramsey interferometry using ultracold molecules as the archetypal example of such coherent control techniques, enhancing the prospects for the molecular quantum simulator.

2. Production of ultracold molecules

The number of research groups with access to polar molecules at $\sim \mu$K temperatures has grown rapidly in recent years, with experiments broadly following one of two approaches. The first approach is direct cooling of the molecules emitted from a molecular beam source. Although the complex internal structure of molecules makes laser cooling difficult, magneto-optical trapping of SrF [51, 53, 54] and CaF [55, 56, 79] has been demonstrated. Recent advances have led to laser cooling of molecules to sub-Doppler temperatures [55], and transfer of these ultracold molecules into magnetic and optical traps [67, 80, 81]. Direct cooling into the microkelvin regime has also been demonstrated by optoelectrical Sisyphus cooling [82]. The second approach is indirect production of ultracold molecules by associating atoms to form molecules from a pre-cooled atomic mixture. The most successful method to date is to associate atoms close to an interspecies magnetic Feshbach resonance. The resulting weakly bound molecules are then transferred to their rovibronic ground state by stimulated Raman adiabatic passage (STIRAP). This approach has been used to great effect to produce molecules with singlet ground states composed of alkali-metal atoms [42, 46], where the ability to cool the atomic gases to quantum degeneracy leads to molecular gases at high phase-space density and typical temperatures of $\sim 1\mu$K or below. A new wave of experiments aims to extend this approach to molecules with doublet ground states, by associating atoms in a mixture of alkali-metal and closed-shell atoms [83, 85]. We now discuss these two approaches in more detail, with particular reference to the experiments performed here.
2.1. Laser cooling of molecules

Laser cooling of molecules is a new technique that is progressing very rapidly. So far, laser cooling has been demonstrated for SrF [48, 51, 53, 54], YO [50], CaF [52, 55, 56], YbF [57] and SrOH [58]. Cooling of several other species is also being pursued, including BaF [59], BaH [60] and TIF [49]. Here, we focus on our work using CaF molecules. The electronic energy-level structure of CaF is similar to that of an alkali-metal atom. In the electronic ground state, one of the two valence electrons of Ca is transferred to the F atom, forming the bond. The other valence electron remains localized on the Ca. Excitation of this electron hardly changes the length or stiffness of the bond, resulting in an almost-diagonal Franck-Condon matrix and, consequently, almost-closed electronic transitions. For laser cooling, we use both the $X^2\Sigma^+(v = 0, N = 1) \leftrightarrow A^2\Pi_{1/2}(v = 0, J = 1/2)$ transition at 606 nm and the $X^2\Sigma^+(v = 0, N = 1) \leftrightarrow B^2\Sigma^+(v = 0, N = 0)$ transition at 531 nm. Here, $v$, $N$ and $J$ are the quantum numbers for vibration, rotational angular momentum and total electronic angular momentum respectively. Hyperfine components of these transitions are easily addressed using modulators to add radio-frequency sidebands to the laser light. Electric dipole transitions to other rotational states are forbidden by selection rules on parity and angular momentum, so no repumping of other rotational states is needed. The branching ratios to other vibrational states of $X^2\Sigma^+$ diminish rapidly with increasing $v$. Nevertheless, it is necessary to repump population that decays to $v = 1, 2, 3$ using additional lasers.

We produce CaF molecules inside a cryogenically cooled buffer-gas cell, by laser ablation of a Ca target in the presence of SF$_6$. Helium gas, precooled to 4 K, flows through the cell. The molecules thermalize with this gas and are entrained in the flow, forming a beam with a mean speed of about 140 m/s [86]. The beam is decelerated to low speed using the radiation pressure of a counter-propagating laser beam, predominantly addressing the 531 nm transition, whose frequency is chirped to compensate for the changing Doppler shift as the molecules slow down [87]. About $2 \times 10^4$ slow molecules are then captured in a magneto-optical trap (MOT), where the main cooling and trapping laser drives the 606 nm transition and rf sidebands are applied to address the various hyperfine components and to enhance the confining force using the dual-frequency MOT method [88]. The properties of this molecular MOT are described in detail in [79]. One important property is the temperature, which is typically a few mK, too high for many applications. To lower the temperature, we transfer the molecules from the MOT into a blue-detuned optical molasses, where sub-Doppler processes [89] cool them to about 50 µK [55]. This is a good starting point for perfecting the quantum control of these molecules.

2.2. Association of ultracold atoms to form molecules

The method of producing ultracold ground-state molecules from pre-cooled gases of ultracold atoms is well established; KRb [42], Cs$_2$ [91], Rb$_2$ [92], RbCs [43,44], NaK [93],
Figure 1. Production of ultracold RbCs molecules by association of ultracold Rb and Cs atoms. (a) Molecular potentials relevant for RbCs. Atoms are first associated into weakly bound molecular states of the $a^3\Sigma^+$ potential shown inset (the labelling is explained in the text). The dark line shows the path molecules take in our experiment. We occupy the $|-2(1,3)d(0,3)\rangle$ state during Stern-Gerlach separation, and perform STIRAP starting in $|-6(2,4)d(2,4)\rangle$. (b) STIRAP of molecules to the lowest hyperfine level of the rovibrational ground state of the $X^1\Sigma^+$ potential. We measure the number of Feshbach molecules remaining in our sample as the intensities of the pump and Stokes lasers are ramped sinusoidally over 20 $\mu$s, and then reverse the process after some hold time as shown. The efficiency of transfer in each direction is 92(1)$\%$, and the lines show a model for the transfer with no free parameters [90]. Between the two STIRAP pulses, the light is switched off and the ground state molecules may be interrogated with microwaves, as illustrated schematically.

NaRb [46] and NaLi [47] molecules have all been reported. Our experiments on RbCs start with the creation of a mixture of $5 \times 10^5$ $^{87}$Rb and $3 \times 10^5$ $^{133}$Cs atoms at a temperature of $\sim 300$ nK, confined in an optical dipole trap operating at a wavelength of 1550 nm and magnetically levitated [94, 95]. We associate atoms into molecules by adiabatically sweeping an applied magnetic bias field across an interspecies Feshbach resonance at 197.1 G. This transfers a fraction of the atoms into the weakly bound $|-1(1,3)s(1,3)\rangle$ state of RbCs [8]. A second magnetic field ramp is used to transfer the molecules into the $|-2(1,3)d(0,3)\rangle$ state following the path shown in the inset to figure 1(a). The remaining atoms are then removed from the trap via the Stern-Gerlach effect, leaving a pure sample of up to 5000 Feshbach molecules [96]. Finally, the molecules are transferred into the $|-6(2,4)d(2,4)\rangle$ state at a magnetic field of 181.6 G, where there is good overlap with appropriate electronically excited states for STIRAP. At the same time the trap is converted into a purely optical potential by increasing the peak intensity to 37 kW cm$^{-2}$ and simultaneously ramping off the magnetic field gradient used for levitation [97]. The compression of the trap leads to an adiabatic heating of the molecules to 1.5 $\mu$K. The final radial (axial) trap frequency is 175 Hz.
(49 Hz).

The molecules are transferred to the lowest hyperfine level of the rovibrational ground state of the $X^1\Sigma^+$ potential with $\sim 90\%$ efficiency by STIRAP [44, 97, 98], increasing the binding energy to $\hbar \times 114$ THz [90] without heating the gas (see figure 1). To avoid spatially varying AC Stark shifts of the STIRAP transitions, the dipole trap is switched off 30 $\mu$s before the transfer. The molecules are usually recaptured in a trap with a peak intensity of 43 kW cm$^{-2}$, such that the trap frequencies are matched to those for the Feshbach molecules, minimising any heating. The molecules are detected by reversing the association sequence and using standard atomic absorption imaging of both Rb and Cs [99]. Due to the state-selective nature of the STIRAP process, our detection is only sensitive to molecules in the lowest hyperfine level ($|N=0, M_F=+5\rangle$, as discussed below in section 3.2).

Overall, this technique generates samples of up to 4000 ground-state RbCs molecules in a single hyperfine level, confined in a purely optical trap at a temperature of 1.5 $\mu$K and with a peak density of $2 \times 10^{11}$ cm$^{-3}$.

3. Energy levels in electric and magnetic fields

Quantum control of the internal state of a molecule requires a good understanding of the hyperfine structure, Zeeman and Stark effects. Let us introduce $\hat{z}$, a unit vector in the direction of the internuclear axis. An effective Hamiltonian describing the rotational and hyperfine structure in the ground electronic state is

$$H = H_{\text{rot}} + H_{\text{hyp}} + H_{\text{Zeeman}} + H_{\text{DC Stark}} + H_{\text{AC Stark}}.$$  

The rotational part is

$$H_{\text{rot}} = B\vec{N}^2 - D\vec{N}^4,$$  

where $\vec{N}$ is the rotational angular momentum operator. The most precise values for the rotational constants $B$ and $D$ are given in [100] for CaF and in [65] for RbCs. The DC Stark Hamiltonian is adequately modelled using a rigid-rotor model,

$$H_{\text{DC Stark}} = -\mu_e \vec{E} \cdot \hat{z},$$  

where $\mu_e$ is the electric dipole moment and $\vec{E}$ is the applied electric field. For CaF, $\mu_e = 3.07(7)$ D [101], while for RbCs, $\mu_e = 1.225(3)(8)$ D [99]. The AC Stark shift due to light of intensity $I$ is described by

$$H_{\text{AC Stark}} = -\frac{1}{2\epsilon_0 c} \alpha I,$$  

where $\alpha$ is the polarizability of the molecule. The Feshbach states are labelled as $|n(f_{\text{Rb}}, f_{\text{Cs}})L(m_{f_{\text{Rb}}}, m_{f_{\text{Cs}}})\rangle$, where $n$ is the vibrational label for the particular hyperfine $(f_{\text{Rb}}, f_{\text{Cs}})$ manifold counting down from the least-bound state which has $n=-1$. The quantum number $L$ describes the end-over-end rotation of the molecule, with $L=0, 1, 2,$ etc., designated by $s, p, d$, etc., respectively. One additional quantum number $M_{\text{tot}} = m_{f_{\text{Rb}}} + m_{f_{\text{Cs}}} + m_{f_{\text{L}}}$ is omitted because its value is 4 for all the levels considered.
where $\alpha$ is the polarisability tensor. This shift is responsible for the trapping potential in an optical trap, and also affects the energy difference between states. We can write the polarisability as

$$\alpha(\theta) = \alpha^{(0)} + \alpha^{(2)} P_2(\cos \theta),$$

where $\alpha^{(0)}$ and $\alpha^{(2)}$ are the spatially isotropic and anisotropic components of the polarisability respectively, and $\theta$ is the angle between the internuclear axis of the molecule and the polarisation of the trap light. The isotropic component of the polarisability affects all rotational states in the same way, only contributing to the trapping potential. In contrast, because of the $\theta$ dependence, the anisotropic component depends on both $N$ and $M_N$ and directly affects the transition frequency between rotational states.

Figure 2. The $N = 0$ and $N = 1$ levels of the $X^2\Sigma^+(v = 0)$ state of CaF. (a) Energies as a function of magnetic field, at zero electric field. (b) Energies as a function of electric field, at zero magnetic field. Note the breaks in the vertical axes.

The hyperfine and Zeeman parts of the Hamiltonian [102, 103] vary between the two molecular species we consider due to their different electronic structures. In the following, we describe these parts separately for CaF and RbCs.

3.1. CaF

Considering now the specific example of CaF, which has an unpaired electron, the hyperfine component of the Hamiltonian is [104, 105]

$$H_{\text{hyp}}^{\text{CaF}} = \gamma \vec{S} \cdot \vec{N} + (b + c/3) \vec{I}_F \cdot \vec{S} + (c/3) \sqrt{6} T^2(C) \cdot T^2(\vec{I}_F, \vec{S}) + c_F \vec{I}_F \cdot \vec{N},$$

(9)
where we have introduced the operators for the electron spin, $\vec{S}$, and the fluorine nuclear spin, $\vec{I}_F$. The $^{40}$Ca isotope has no nuclear spin. The first term in (9) is the electron spin-rotation interaction. The second and third terms account for the interaction between the electron and nuclear magnetic moments, written here in spherical tensor form; $T^2(\vec{I}_F, \vec{S})$ denotes the rank-2 spherical tensor formed from $\vec{I}_F$ and $\vec{S}$, while $T^2(C)$ is a spherical tensor whose components are the (renormalised) spherical harmonics $C^2_q(\theta, \phi)$. The spectroscopic parameters $b$ and $c$ are those of Frosch and Foley \[106\], which are sometimes collected together as a Fermi contact parameter $b_F = b + c/3$ and a dipolar parameter $t = c/3$. The last term is the nuclear spin-rotation interaction, and is three orders of magnitude smaller than the others. Precise values for $\gamma$, $b$, $c$ and $c_F$ (sometimes called $C$) are given in \[104\].

The effective Zeeman Hamiltonian is \[103\]

$$H_{\text{CaF Zeeman}}^{\text{Zeeman}} = g_S \mu_B \vec{S} \cdot \vec{B} + g_L \mu_B \left[ \vec{S} \cdot \vec{B} - (\vec{S} \cdot \hat{z})(\vec{B} \cdot \hat{z}) \right] - g_R \mu_B \vec{N} \cdot \vec{B} - g_F \mu_N \vec{I}_F \cdot \vec{B}, \quad (10)$$

where $\vec{B}$ is the applied magnetic field. The terms represent, from left to right, the electronic Zeeman interaction characterised by $g_S$, its anisotropic correction characterised by $g_L$, the rotational Zeeman interaction characterised by $g_R$, and the nuclear Zeeman interaction characterised by the nuclear $g$-factor $g_F^N$, which is defined to include the small effects of diamagnetic shielding. The last three terms are typically three orders of magnitude smaller than the first term, but are important when searching for magnetically-insensitive transitions. The value of $g_L$ can be estimated using Curl’s approximation $g_L \approx -\gamma/2B$ \[107,108\].

Figure 2 shows the eigenvalues of (11) corresponding to the ground and first-excited rotational levels, $N = 0$ and $N = 1$, as functions of magnetic and electric fields. At low field, the states are best described in the coupled representation $|N, S, I_F, F, M_F\rangle$, while at high field they are best described in the uncoupled representation $|N, M_N\rangle |S, M_S\rangle |I_F, M_{I_F}\rangle$. The Zeeman shifts shown in figure 2(a) are relevant for trapping molecules in the MOT and in a magnetic trap. At low magnetic field, $B \lesssim 5$ G, these shifts are well approximated as $\Delta E_{\text{Zeeman}} = g_F \mu_B B M_F$. For the six zero-field energy levels shown in the figure, in order of increasing energy, the values of $g_F$ are 0, 1.000, -0.294, 0, 0.795 and 0.500. The Stark shifts shown in figure 2(b) are relevant for trapping molecules electrically, and for inducing the electric dipole moments needed for quantum simulation. The Stark shifts are quadratic at low field and become linear at sufficiently high field. The dipole moment is the gradient of the Stark shift and saturates slowly towards $\mu_e$. For $N = 0$, the dipole moment is 1 D when $E = 7.5$ kV cm$^{-1}$, and increases to 2.4 D when $E = 75$ kV cm$^{-1}$. 
In RbCs there are no unpaired electrons, so the hyperfine Hamiltonian is dominated by the nuclear interactions [102,105,109,110]

\[ H_{\text{hyp}}^{\text{RbCs}} = \sum_{i=\text{Rb,Cs}} eQ_i \cdot \vec{q}_i + \sum_{i=\text{Rb,Cs}} c_i \vec{I}_i \cdot \vec{N} - c_3 \sqrt{6} T^2(C) \cdot T^2(\vec{I}_{\text{Cs}}, \vec{I}_{\text{Rb}}) + c_4 \vec{I}_{\text{Cs}} \cdot \vec{I}_{\text{Rb}}. \quad (11) \]

Here, the values of the component nuclear spins are \( I_{\text{Rb}} = \frac{3}{2} \) and \( I_{\text{Cs}} = \frac{7}{2} \). The first term is the electric quadrupole interaction and represents the interaction between the nuclear electric quadrupole of nucleus \( i \) (\( eQ_i \)) and the electric field gradient at the nucleus (\( \vec{q}_i \)). The strength of this interaction is proportional to the coupling constants \( eQq_{\text{Rb}} \) and \( eQq_{\text{Cs}} \). The second term is the interaction between the nuclear magnetic moments and the magnetic field created by the rotation of the molecule, with spin-rotation coupling constants \( c_{\text{Rb}} \) and \( c_{\text{Cs}} \). The two remaining terms represent the tensor and scalar interactions between the nuclear dipole moments, with spin-spin coupling constants \( c_3 \) and \( c_4 \), respectively. The quantity \( c_3 \) has both direct dipolar and indirect (electron-mediated) contributions, while \( c_4 \) arises entirely from indirect interactions. The values for the relevant coefficients are given in [65]. Similarly, the Zeeman component of the

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**Figure 3.** The hyperfine structure of the \( N = 0 \) and \( N = 1 \) levels of the \( X^3\Sigma^+(v = 0) \) state of RbCs. (a) Energies as a function of magnetic field with the states relevant to this work highlighted and labelled by \( M_F \). STIRAP populates the \( |N = 0, M_F = +5\rangle \) state at a magnetic field of 181.6 G (indicated by the vertical dashed line). (b) Transition frequencies as a function of intensity for microwave transitions from \( |N = 0, M_F = +5\rangle \) to states in \( N = 1 \) in the presence of light at a wavelength of 1550 nm polarised parallel to an applied magnetic field of 181.6 G. Transitions relevant to this work are labelled by \( M_F \) of the upper state. The colour indicates the relative strengths for \( \Delta M_F = 0 \) (blue) and \( \Delta M_F = \pm 1 \) (red) transitions.

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3.2. RbCs
The Ramsey sequence used in our experiments and described in the main text. The time for a $\pi/2$ pulse is defined as $\tau$ and the time between pulses is $T$.

Hamiltonian has only nuclear spin and rotational components

$$H_{\text{Zeeman}}^{\text{RbCs}} = -g_i\mu_B\vec{N} \cdot \vec{B} - \sum_{i=\text{Rb,Cs}} g_i^N\mu_N\vec{I}_i \cdot \vec{B}. \quad (12)$$

In RbCs, at zero magnetic field, states are well described by the quantum number $F = N + I_{\text{Rb}} + I_{\text{Cs}}$. In the ground rotational state ($N = 0$), this gives 4 states with $F = 2, 3, 4, 5$ separated by multiples of $c_4 = 19.0(1)$ kHz [65]. Applying a magnetic field splits these into $(2I_{\text{Rb}} + 1)(2I_{\text{Cs}} + 1)(2N + 1)$ separate Zeeman sub-levels, as shown in figure 3(a). This gives 32 distinct hyperfine states in $N = 0$, and 96 in $N = 1$, which is significantly more than in CaF. In the limit of high magnetic fields, the rotational and nuclear angular momenta decouple and the states are well represented by $|N, M_N, M_{I_{\text{Rb}}}, M_{I_{\text{Cs}}})$. The measurements reported in this work are performed at the magnetic field of 181.6 G used for STIRAP. This field is not high enough to decouple $N$ and $I$ nor low enough for $F$ to be a good quantum number; the only good remaining quantum number for the angular momentum projection is $M_F = M_N + M_{I_{\text{Rb}}} + M_{I_{\text{Cs}}}$. Understanding the AC Stark effect is vital to implementing internal-state microwave control for polar molecules confined in an optical trap. For RbCs, we have previously measured the scalar and tensor parts of the AC polarisability, $\alpha^{(0)}$ and $\alpha^{(2)}$, for linearly polarised light at a wavelength of 1550 nm and investigated the effect of varying the angle between the polarisation of the light and the applied magnetic field [111]. We showed that coupling between neighbouring hyperfine states manifests in a rich and highly complicated structure with many avoided crossings. In addition, we found that the energy structure is simplest when the polarisation of the light is parallel to the direction of the magnetic field (the case shown in figure 3(b) and used in this work), as this avoids competition between magnetic and electric quantisation axes.

4. Ramsey interferometry

Precise measurements of transition frequencies require long interrogation times which are most readily achieved using trapped samples. The Ramsey method is commonly
employed to reach the highest precision in metrology and measurements of fundamental constants \[112, 113\], and is also the foundation of the coherent control needed for quantum simulation \[114\]. The method has been used to demonstrate long coherence times between two hyperfine states in the same rotational level in fermionic NaK \[93\]. When used to produce a superposition of two rotational states, an oscillating electric dipole moment is induced, introducing dipole-dipole interactions. This technique has been used to observe long-range dipole-dipole interactions between fermionic KRb molecules in an optical lattice \[61\]. These ground-breaking results demonstrate the power of these techniques, and refining their use in ultracold molecules is crucial to advancing the field.

In the Ramsey experiments detailed below we apply microwave fields tuned close to resonance with a transition between selected states in the ground and first excited rotational levels of the molecules, here denoted \(|0\rangle\) and \(|1\rangle\) respectively. Figure 4 illustrates the sequence. In each experiment, the molecules are first prepared in \(|0\rangle\), and then a \(\pi/2\) microwave pulse of duration \(\tau\) and detuning \(\Delta\) creates a coherent superposition of \(|0\rangle\) and \(|1\rangle\). This state is allowed to evolve for a time \(T\) before a second identical \(\pi/2\) pulse completes the sequence. In the absence of experimental imperfections, the density operator at the end of the sequence is

\[
\rho_{\text{final}} = U_{\pi/2} \cdot U_{\text{free}} \cdot U_{\pi/2} \cdot \rho_{\text{initial}} \cdot U_{\text{free}} \cdot U_{\pi/2}^\dagger,
\]

with \(\rho_{\text{initial}} = |0\rangle \langle 0|\) the initial density operator. The propagators for the \(\pi/2\) pulse, \(U_{\pi/2}\), and for the free evolution period, \(U_{\text{free}}\), are given by

\[
U_{\pi/2} = \cos \left( \frac{X}{2} \right) \hat{\sigma}_0 - i \left( \frac{\pi/2}{X} \right) \sin \left( \frac{X}{2} \right) \hat{\sigma}_2 + i \frac{\Delta \tau}{X} \sin \left( \frac{X}{2} \right) \hat{\sigma}_3, \tag{14}
\]

\[
U_{\text{free}} = \cos \left( \frac{\Delta T}{2} \right) \hat{\sigma}_0 + i \sin \left( \frac{\Delta T}{2} \right) \hat{\sigma}_3, \tag{15}
\]

where \(\hat{\sigma}_i\) (\(i \in \{0, 1, 2, 3\}\)) are the usual Pauli operators in the Hilbert space spanned by \(|0\rangle\) and \(|1\rangle\) and \(X = \sqrt{(\pi/2)^2 + \Delta^2 \tau^2}\). The populations in \(|0\rangle\) and \(|1\rangle\) at the end of the sequence are \(P_0 = \rho_{\text{final}}^{00}\) and \(P_1 = \rho_{\text{final}}^{11}\).

4.1. \(\text{CaF}\)

The laser-cooled CaF molecules are initially distributed across the 12 hyperfine and Zeeman sub-levels of \(N = 1\) shown in figure 2. To produce a sample in a single state we follow the procedure detailed in \[67\] and briefly summarised here. We optically pump the majority of the molecules into the state \(|N = 1, F = 0, M_F = 0\rangle\) by applying a low-intensity pulse of the MOT light, 100 \(\mu s\) long, with the component addressing that state extinguished. We then coherently transfer these molecules into a selected level of \(N = 0\), here \(|0\rangle = |N = 0, F = 1, M_F = 1\rangle\), using a microwave \(\pi\) pulse resonant with a specific hyperfine and Zeeman component of the rotational transition. A small uniform magnetic field is applied, sufficient to resolve the Zeeman sub-levels. Molecules
Figure 5. Ramsey fringes for CaF molecules prepared in a coherent superposition of $|0\rangle = |N = 0, F = 1, M_F = 1\rangle$ and $|1\rangle = |N = 1, F = 2, M_F = 2\rangle$ states. The $\pi/2$ pulses have duration $\tau = 27$ $\mu$s, and the free evolution time, $T$, is scanned. The plots show the fraction recaptured into the MOT, proportional to the number in $N = 1$, as a function of $T$. (a) Molecules in free space. The microwave frequency is 20,553,427.9 kHz, approximately 1.5 kHz above resonance. The main decoherence mechanism is scattering of residual laser light. (b) Molecules confined to a magnetic quadrupole trap with a radial magnetic field gradient of 15 G cm$^{-1}$. The microwave frequency is 20,553,431.2 kHz, approximately 5 kHz above resonance. The transition frequency is Zeeman shifted, and the main decoherence mechanism is dephasing due to the distribution of these Zeeman shifts. Points and error bars show the mean and standard error of 9 repeated experiments. Lines are fits to the models described in the text.

remaining in $N = 1$ are pushed away by pulsing on the slowing light for 1 ms, leaving a pure sample in $|0\rangle$. After accounting for losses due to the short MOT lifetime and the efficiencies of the optical pumping and microwave transfer steps, about 15% of the molecules originally captured in the MOT are retained. This pure ensemble has a temperature of $T_{mol} = 55$ $\mu$K and a spatial standard deviation of $\sigma_0 = 1.4$ mm. We use Ramsey pulses of duration $\tau = 27$ $\mu$s to prepare superpositions with the state $|1\rangle = |N = 1, F = 2, M_F = 2\rangle$. At the end of the sequence we measure the number of molecules in $N = 1$ by turning on the MOT light and imaging the fluorescence. This number is normalised to the number of molecules initially in the MOT, yielding the percentage recaptured.

Figure 5(a) shows the percentage recaptured as a function of $T$ for molecules that are freely expanding. Here, we have chosen $\Delta/(2\pi) \approx 1.5$ kHz, which is small compared to the Rabi frequency. The data show the beat note between the oscillations of the molecule and the microwave source. The coherence time, defined as the $1/e$ decay time of the oscillations, is $2.48(4)$ ms.

To model these results, we introduce two experimental imperfections to the model in (13). The first imperfection concerns leaked light. Before the Ramsey sequence begins, resonant light from the MOT and slowing lasers is extinguished using acousto-
optic modulators. However, a small fraction of the slowing light leaks through. It excites molecules from the $|1\rangle$ state to the $B^2\Sigma^+$ state, which then decays back to one of the levels of $N = 1$. This effect limits the coherence time and pulls the steady-state population in $N = 1$ above 50%. The scattering rate is low enough that we can neglect events occurring during the $\pi/2$ pulses, and concentrate on the free evolution period. We divide the molecules into two groups. The first contains those that have not scattered any photons. The density operator for this group, $\rho^{(1)}$, has matrix elements evolving as

$$
\rho^{(1)}_{11}(T) = \rho^{\pi/2}_{11} e^{-\gamma_{sc}T},
$$

$$
\rho^{(1)}_{10}(T) = \rho^{\pi/2}_{10} e^{-\gamma_{sc}T/2+i\Delta T},
$$

$$
\rho^{(1)}_{00}(T) = \rho^{\pi/2}_{00},
$$

where $\gamma_{sc}$ is the scattering rate and $\rho^{\pi/2} = U^{\pi/2} \rho_{\text{initial}} U^{\dagger\pi/2}$ is the density operator immediately after the first $\pi/2$ pulse. The second group contains the fraction of molecules that have scattered a photon, $f_{\text{scat}} = \rho^{\pi/2}_{11} (1 - e^{-\gamma_{sc}T})$.

Of these molecules, a fraction $b_r$ are in $|1\rangle$ with density operator $\rho^{(2)} = |1\rangle \langle 1|$ and are affected by the final $\pi/2$ pulse, while the remainder are in other levels of $N = 1$ and are unaffected by this pulse. Here, $b_r = 1/3$ is the probability that a molecule in $|1\rangle$ decays back to $|1\rangle$ after excitation to the $B^2\Sigma^+$ state. We can neglect multiple scattering events that further re-distribute the $N = 1$ population, since they are rare. The density operator at the end of the Ramsey sequence is now given by

$$
\rho'_{\text{final}} = U_{\pi/2} \cdot \left[ \rho^{(1)}(T) + b_r f_{\text{scat}} \rho^{(2)} \right] \cdot U_{\pi/2}^{\dagger},
$$

where $U_{\pi/2}$ is the propagator for a $\pi/2$ pulse. The final population measured in $N = 1$ becomes

$$
P'_1(\Delta, \tau, T) = \rho'_{11}^{\text{final}} + (1 - b_r) f_{\text{scat}}.
$$

The second imperfection is a reduction in $P'_1$ with increasing $T$ due to the free expansion of the cloud. We assume there is a cut-off radius, $R$, beyond which the molecules are not detected, and that the size of the cloud expands as $\sigma^2 = \sigma_0^2 + k_B T_{\text{mol}} T^2/m$. Here, $m$ is the mass of a CaF molecule, and $\sigma_0$ and $T_{\text{mol}}$ are fixed at the values given above. The proportion of the total molecules detected is

$$
\beta(\zeta) = \text{erf}(\zeta) - \sqrt{4/\pi} \zeta e^{-\zeta^2},
$$

where $\zeta^2 = R^2/(2\sigma^2)$. This modifies the expression for the $N = 1$ population to

$$
P''_1(\Delta, \tau, T) = \frac{\beta(\zeta)}{\beta(\zeta_0)} P'_1(\Delta, \tau, T),
$$

where $\zeta_0^2 = R^2/(2\sigma_0^2)$.

The solid line in figure 5(a) shows a fit to the model $A P''_1$ with the amplitude $A$, the detuning $\Delta$, the radius $R$, and the scattering rate $\gamma_{sc}$ as free parameters. The model fits well and gives $\Delta/(2\pi) = 1.5053(8)$ kHz, $R = 2.54(6)$ mm and $\gamma_{sc} = 890(10)$ s$^{-1}$. This value of $R$ is surprisingly small, suggesting that our simple model may not fully describe the loss mechanism. We note that the statistical uncertainty in determining the
transition frequency is less than 1 Hz. Correcting for a frequency shift of $-6(4)$ Hz due to the application a 60 mG uniform magnetic field, we obtain a preliminary field-free transition frequency of $f_0 = 20,553,426,401(4)$ Hz. We emphasize that we have not yet studied the systematic shifts and uncertainties. The uncertainty in the Zeeman shift can be reduced well below 1 Hz by measuring the frequency at a few values of applied field and extrapolating to zero. The applied field is easily measured to mG accuracy using the Zeeman splitting of the microwave transition. The uncertainty in the first-order Doppler shift can be reduced below 1 Hz by tracking the movement of the cloud with 100 µm accuracy over a 10 ms period.

Figure 5(b) shows the same experiment for molecules confined in a quadrupole magnetic trap with a radial magnetic field gradient $A_\rho = 15$ G cm$^{-1}$. All other parameters are the same as above but with a larger detuning of $\Delta/(2\pi) \approx 5$ kHz. In the trap, the Zeeman shift of the transition frequency depends on position, so molecules at different positions fall out of phase, causing decoherence. The Zeeman shifts of states $|0\rangle$
and \(|1\rangle\) are almost identical, so long coherence times are possible in the magnetic trap. Nevertheless, the observed coherence time of 0.61(3) ms is considerably shorter than in free space because of the residual difference between the magnetic moments of the two states, \(\mu_{|1\rangle}\) and \(\mu_{|0\rangle}\). This difference also shifts the transition frequency measured in the trap. Figure 6 shows another example of data taken using trapped molecules. Here, we fix \(T = 493\ \mu s\), and scan \(\Delta\). We observe the standard Ramsey lineshape, but with the contrast reduced, primarily due to the dephasing arising from the distribution of Zeeman shifts.

To find the distribution of Zeeman shifts, we assume a Gaussian distribution of stationary molecules with standard deviations \(\sigma_\rho\) and \(\sigma_z\) in the radial and axial directions. The coherence time observed in figure 5(b) is about 50 times shorter than the typical oscillation period of a molecule in the trap, so the approximation of stationary molecules is a good one. We express the Zeeman shift of the transition as \(\delta_Z = \eta r\), where

\[
\frac{r^2}{\rho^2} + \frac{4z^2}{\sigma^2} = \eta = (\mu_{|1\rangle} - \mu_{|0\rangle})A_\rho/h.
\]

Using the standard method of transforming the variables of a probability density function (pdf), we transform the known pdf of position into a pdf for \(\delta_Z\). The result is

\[
f(\delta_Z) = \frac{1}{\eta^2 \sigma' \sigma_\rho} e^{-\delta_Z^2/(2\eta^2 \sigma_\rho^2)} \text{erfi}\left(\frac{\delta_Z \sigma'}{2\sqrt{2} \eta \sigma z \sigma_\rho}\right),
\]

where \(\sigma' = \sqrt{4\sigma_z^2 - \sigma_\rho^2}\), and \(\text{erfi}(z) = \text{erf}(iz)/i\). The additional decoherence due to photon scattering is still present, just as in free space, but the loss due to cloud expansion is not present since the molecules are trapped. Therefore, we start with (18), make the replacement \(\Delta \rightarrow \Delta + \delta_Z\), and then integrate over the distribution of \(\delta_Z\) to yield a final expression for the population remaining in \(N = 1\) after the Ramsey sequence,

\[
P_{1}^{\infty}(\Delta, \tau, T) = \int_{0}^{\pm\infty} P_{1}^{\prime}(\Delta + \delta_Z, \tau, T) f(\delta_Z) d\delta_Z,
\]

where the sign of the upper integration limit is the same as the sign of \(\mu_{|1\rangle} - \mu_{|0\rangle}\).

We attempt a simultaneous fit of the two datasets shown in figures 5(b) and 6 to the model \(y_0 + AP_{1}^{\infty}\) where \(y_0\) is a background and \(A\) is an amplitude. In this fit, we fix \(\tau = 27\ \mu s\), the widths of the trapped distribution to their measured values, \(\sigma_z = 1.44\ mm\) and \(\sigma_\rho = 1.37\ mm\), and the transition frequency to that measured in free space above. For the data in figure 6(b), we also fix \(T = 493\ \mu s\). We allow separate values of \(y_0\), \(A\) and \(\gamma_{sc}\) for each dataset, but a single value of the central frequency and of \(\eta\) that is common to both sets. The solid lines in figures 5(b) and 6 show the results of this simultaneous fit. The model fits well to both sets of data, finds values of \(\gamma_{sc}\) similar to the one found above, and gives \(\eta = 8.54(7) \times 10^5\ m^{-1} s^{-1}\). This value of \(\eta\) is determined primarily from the shift in the transition frequency between the free space measurement and the measurements in the trap. It is sensitive to a possible systematic shift between the position of the cloud loaded into the trap, and the magnetic minimum of the trap. If, instead, we allow the central frequency to float, the only information about \(\eta\) comes from the decoherence time. In this case, the fit converges on an \(\eta\) that is 70% higher.
Table 1. Difference in magnetic moments, $\Delta \mu = \mu_{N+1} - \mu_N$, between states $|N,F,M_F\rangle = |N,N+1,N+1\rangle$ and $|N+1,N+2,N+2\rangle$ for various $N$. Column 2 is the expression for this difference, column 3 is its value obtained from our calculated $g_l$ and $g_r$, and column 4 is the associated coherence time, $\tau_c$.

| $N$ | Expression | Value | $\tau_c$ (ms) |
|-----|------------|-------|--------------|
| 0   | $g_l/15 - g_r$ | $-6.85 \times 10^{-5}$ | 1.25 |
| 1   | $g_l/35 - g_r$ | $7 \times 10^{-8}$ | 1200 |
| 2   | $g_l/63 - g_r$ | $2.29 \times 10^{-5}$ | 3.74 |
| 3   | $g_l/99 - g_r$ | $3.33 \times 10^{-5}$ | 2.57 |

We take the former fit to be most reliable and use the difference between the two fits as a measure of the uncertainty in $\eta$. We thus obtain a difference in magnetic moments of $\mu\langle 1 \rangle - \mu\langle 0 \rangle = -7(5) \times 10^{-5} \mu_B$.

The coherence time in free space is limited in these experiments by scattering of residual laser light. This can be eliminated in future using a fast mechanical shutter. On a longer timescale, the free expansion of the cloud becomes comparable to the wavelength of the microwaves. This limits the coherence time because the change in position between the $\pi/2$ pulses imparts a phase change that is different for each molecule.

The coherence time in the magnetic trap is limited by the dependence of the transition frequency on magnetic field, which varies across the sample. We have chosen a transition for which the terms with coefficients $g_S$ and $g_{F,N}^E$ in (10) cancel exactly, but there is still a residual difference between the magnetic moments of the two states arising from the terms with coefficients $g_l$ and $g_r$. As seen above, this difference is difficult to measure precisely, but it can be calculated. We have carried out calculations of $g_t$ at the Hartree-Fock level, using the DALTON electronic structure package [115] and cc-pVTZ basis sets [116,117]. This gives $g_t = -5.15 \times 10^{-5}$ at the CaF equilibrium bond length of 1.95 Å. We have previously calculated values of $g_l$ (sometimes known as $\Delta g_{\perp}$) for a number of $^2\Sigma$ molecules [103]. For CaF, our calculation gives $g_l = -1.80 \times 10^{-3}$. Using (10), and these values for $g_l$ and $g_r$, we find that $\mu\langle 1 \rangle - \mu\langle 0 \rangle = (g_l/15 - g_r)\mu_B = -6.85 \times 10^{-5} \mu_B$. This is consistent with our measured value. It implies a coherence time of 1.25 ms in the absence of residual laser light.

It is interesting to work out the magnetic sensitivity of other rotational transitions of the type $|N,F = N+1,M_F = F\rangle - |N',F = N+1,M_F' = F'\rangle$, where only $g_l$ and $g_r$ contribute to the Zeeman shift of the transition. Table 1 shows the predicted difference in magnetic moments between these two states, $\Delta \mu$, for a range of $N$. The table also shows the expected coherence time in a magnetic trap for these transitions, for the experimental conditions presented above and assuming no other decoherence mechanism. Remarkably, $\Delta \mu$ changes sign as $N$ increases and is very close to zero for $N = 1$, where the contributions from $g_l$ and $g_r$ cancel almost exactly. The exactness of the cancellation is somewhat coincidental, given the $\sim 10\%$ accuracy of the calculations.
Ultracold molecules: a platform for quantum simulation

The Ramsey method in free-space for RbCs molecules, using a superposition of $|0\rangle = |N = 0, M_F = +5\rangle$ and $|1\rangle = |N = 1, M_F = +6\rangle$. (a) The $\pi/2$ pulses have duration $\tau = 47.8 \mu s$ and the free evolution time is $T = 600 \mu s$. The plot shows the normalised number of molecules in $|0\rangle$ as a function of the detuning of the microwave field from resonance. The solid line is a fit to $P_0 = \rho_{00}$ where $\rho$ is defined in (13) and yields a transition frequency of $980.385 \pm 569(8) \text{ MHz}$. (b) For a fixed microwave frequency of $980.390 \text{ MHz}$, we vary the free evolution time, $T$. We observe Ramsey fringes with a negligible loss of contrast over the $2.3 \text{ ms}$ interrogation time. However, we observe a reduction in the molecule number with time as the cloud of molecules falls and expands out of the detection volume (set by the focus of the STIRAP beams). The dashed line shows the result of an independent measurement of this effect with an uncertainty indicated by the shaded region. The solid line is a fit to $(1 - (T/T_0)^2) \times P_0$. In both measurements each point represents the result of a single experimental run.

Taking this into account, we still expect $\Delta \mu < 10^{-5} \mu_B$ for the $|1, 2, 2\rangle - |2, 2, 3\rangle$ transition, and an associated coherence time $t_c \gtrsim 10 \text{ ms}$. For all the transitions, the coherence time could be extended by using a flat-bottomed trap. It may also be possible to tune $\Delta \mu$ even closer to zero by mixing in small fractions of other states.

4.2. RbCs

We begin our investigation of Ramsey interferometry using RbCs by again considering the simplest case of molecules in free space. We prepare a superposition of the two spin-stretched states, $|0\rangle = |N = 0, M_F = +5\rangle$ and $|1\rangle = |N = 1, M_F = +6\rangle$, as the associated transition is the strongest available between the two rotational levels. In figure 7(a), we fix the free evolution time to $T = 600 \mu s$ and vary the detuning of the microwave field from resonance. This yields high-contrast Ramsey fringes spaced by $\approx 1.5 \text{ kHz}$ and modulated by an envelope function with a width set by $1/(2\tau)$. We fit the model for the ground-state population, $P_0$, defined by equation [13] to the results and determine the line centre to be $980.385 \pm 569(8) \text{ MHz}$. Here, the quoted $8 \text{ Hz}$
uncertainty is purely statistical. We have not investigated potential systematic shifts and uncertainties.

To explore the limits of the free-space measurements, we fix the applied microwave frequency to 980.390 MHz (corresponding to a detuning of $\sim 5$ kHz) and vary the free evolution time $T$, as shown in figure 7(b). We increase the microwave power such that the $\pi/2$ pulse duration is $\tau = 19$ $\mu$s; the detuning is therefore small compared to the Rabi frequency. We observe no loss of fringe contrast over the period of the measurement, indicating a coherence time $> 2.5$ ms. However, we observe a reduction in the molecule number with time as the cloud of molecules falls and expands out of the detection volume set by the focus of the STIRAP beams. Although the STIRAP beams have a waist of $\approx 30$ $\mu$m, the STIRAP transfer efficiency depends sensitively on the intensity and is optimised only near the focus. We have measured this effect independently; the result is indicated by the dashed line in figure 7(b). We therefore fit $(1 - (T/T_0)^2) \times P_0$ to this measurement, with $T_0 = 2.57(4)$ ms. We extract a transition frequency of 980.385698(3) MHz, where the quoted 3 Hz uncertainty is again purely statistical. We note that this result is 129(9) Hz greater than the transition frequency obtained from the measurement in figure 7(a). As the microwave source was referenced to an external 10-MHz GPS reference, we believe that the difference stems from a difference in the conditions of the experiment on the separate days that the measurements were performed. The Zeeman shift of the transition is $-4.8$ Hz G$^{-1}$ [65], indicating that the difference is not attributable to a change in the magnetic field (which is typically $< 50$ mG day-to-day). The transition is sensitive to stray electric fields, however, which can be present in the UHV glass cell [99]; a DC Stark shift of the transition by 129 Hz requires a DC electric field of only $1.2$ V cm$^{-1}$. Alternatively, the difference may result from a more subtle systematic effect such as coupling to nearby hyperfine states; the Fourier width of the microwave pulses is similar to the spacing between neighbouring hyperfine states and different pulse durations were used for the two measurements. These systematic shifts and their uncertainties will be investigated in future work.

Ultimately it is desirable to interrogate the molecules confined in an optical lattice where longer evolution times are possible and interesting many-body effects may be present. Here we extend our Ramsey measurements to the case of molecules confined in a simple optical trap in order to determine the impact on the observed coherence time. We achieve this by recapturing the molecules in the crossed optical trap following the STIRAP transfer to the ground state. The trap consists of two linearly polarised $\lambda = 1550$ nm beams, with waists of $w_{01} = 80$ $\mu$m and $w_{02} = 98$ $\mu$m, crossing at an angle of $27^\circ$. We set the polarisation of both beams to be along the direction of the magnetic field with an uncertainty of $< 3^\circ$. The peak intensity of the trap light prior to STIRAP is 37.3 kW cm$^{-2}$ for all of the measurements. To investigate the impact of the trap on the Ramsey sequence we vary the intensity of the trap used to recapture the molecules, thereby exploring different AC Stark shifts (see figure 3). At the same time, the molecules experience a different trap potential depending on the intensity of the trap light and molecular polarisabilities [111]. We note that to match the potential
to that experienced by the Feshbach molecules requires a peak intensity of 43 kW cm$^{-2}$ and to create a trap deep enough to prevent evaporation of the molecules requires a peak intensity > 20 kW cm$^{-2}$.

In principle, the trap extends the time over which the molecules can be interrogated, but also introduces a spatially varying AC Stark shift of the microwave transition as molecules in different parts of the trap experience different intensities. The initial distribution of the ground-state molecules reflects that of the Feshbach molecules as the molecules move a negligible distance during the 50 $\mu$s that the trap is turned off for STIRAP. The distribution of Feshbach molecules is Gaussian with standard deviations of $\sigma_z = 6.6$ $\mu$m in the vertical direction and $\sigma_{axial} = 24$ $\mu$m in the axial direction. Due to gravitational sag, the centre of this distribution is $z_0 = 8.1$ $\mu$m below the position of peak intensity. Under these conditions, the variation of intensity across the cloud is dominated by the vertical direction and we estimate the $2\sigma$ intensity difference to be

$$\Delta I \approx \frac{8z_0\sigma_z}{w_0^2}I_0 \approx 0.04I_0. \quad (23)$$

Crucially, this depends on the peak intensity $I_0$, indicating that the spread of intensities is greater for deeper traps. For simplicity, we assume that the molecular distribution
and the associated intensity variation remains constant during the measurements. Typical trap oscillation periods are \( \sim 5 \text{ ms} \), such that this approximation is valid for measurements performed in under \( \sim 0.5 \text{ ms} \). For longer times, the intensity variation will be greater than the above estimate, as the molecular cloud will fall and expand, since all the intensities investigated are below the 43 kW cm\(^{-2}\) needed to match the trap potential. Although this effect is undoubtedly important for some of our measurements, this approximate model gives sufficient insight for the present work.

To measure the effect of the trap light on the coherence time we perform Ramsey measurements by varying the free evolution time, \( T \). We use different hyperfine levels of \( N = 1 \) to that used in free space. Specifically, we investigate superpositions of \( |0\rangle = |N = 0, M_F = +5\rangle \) with either \( |1\rangle = |N = 1, M_F = +4\rangle \) or \( |1\rangle = |N = 1, M_F = +5\rangle \). We choose these states as, unlike \( |N = 1, M_F = +6\rangle \), their transitions are well separated in frequency from other nearby transitions (see figure 3(b)), minimising the possibility of off-resonant coupling. To perform each measurement, we turn on the trap light to recapture the molecules in \( |N = 0, M_F = +5\rangle \). We then wait for 400 \( \mu\text{s} \) before performing the Ramsey sequence. This ensures that the intensity of the light is stable prior to the measurement; the intensity is monitored on a photodiode, and stabilised by an active servo loop with a bandwidth of \( \sim 50 \text{ kHz} \). For each trap intensity, we first determine the transition frequency and measure the Rabi frequency at zero-detuning to define the \( \pi/2 \) pulse duration, \( \tau \). For \( |N = 1, M_F = +5\rangle \) we typically use \( \tau \approx 2.5 \mu\text{s} \), whilst for \( |N = 1, M_F = +4\rangle \) we use \( \tau \approx 12 \mu\text{s} \). Note that the transition to the \( M_F = +4 \) state is considerably weaker and varies appreciably with intensity. For this transition, we must therefore use a longer \( \tau \) and are limited to smaller detunings \( \Delta \). Figures 8(a) and (b) show typical results of such measurements for the two different hyperfine levels. We observe Ramsey fringes which appear to decohere with time as the spatially dependent AC Stark shift across the cloud leads to dephasing. To quantify this effect, we fit each dataset with a sine wave with an exponentially decaying amplitude in order to extract a coherence time \( \tau_c \).

The results shown in figures 8(a) and (b) exhibit significantly different coherence times despite very similar peak trap intensities. This difference stems from the different AC Stark shifts shown in figure 3(b). For the \( |N = 1, M_F = +5\rangle \) state, the AC Stark shift is very close to linear. The spread of transition frequencies across the cloud is then simply \( \Delta f = (df/dI) \times \Delta I \) and the associated dephasing is expected to scale inversely with the peak intensity. For the peak intensity of 20.7 kW cm\(^{-2}\) shown in figure 8(b), we find that a superposition between \( |N = 0, M_F = +5\rangle \) and \( |N = 1, M_F = +5\rangle \) has a coherence time of 66(5) \( \mu\text{s} \). In contrast, the transition to \( |N = 1, M_F = +4\rangle \) displays a broad avoided crossing around 16 kW cm\(^{-2}\), where the variation of transition frequency across the cloud is minimised. Accordingly we observe a significant increase in the coherence time for this state around the avoided crossing, as shown in figure 8(c). The maximum coherence time which we measure for the state \( |N = 1, M_F = +4\rangle \) in the trap is 0.75(6) ms, and is approximately an order of magnitude greater than that achieved using the \( |N = 1, M_F = +5\rangle \) state.
The AC Stark shift shown in figure 3(b) is for the polarisation of the trap light *exactly* aligned with the direction of the magnetic field. Even small angular deviations from this condition can lead to significantly different AC Stark shifts, particularly around an avoided crossing \[111\]. To model the results in figure 8(c), we therefore use the period of the Ramsey fringes to determine the transition frequency for each intensity, effectively mapping out the AC Stark shift under the conditions of the experiment (i.e. accounting for a small misalignment of the polarisation of the trap beams). For the transition to the \[|N = 1, M_F = +4\rangle\] state, we fit the measured frequencies with a third-order polynomial constrained to the known zero-intensity transition frequency \[65\]. For the transition to the \[|N = 1, M_F = +5\rangle\] state, we use a simple linear fit. For a given intensity \(I\), we extract the minimum and maximum transition frequencies in the range \(I - \Delta I/2 \rightarrow I + \Delta I/2\) to determine the spread of transition frequencies \(\Delta f(I)\) responsible for the dephasing of the Ramsey signal. The total coherence time \(\tau_c\) is then given by

\[
\tau_c = \left[\left(\frac{1}{T_2}\right)^2 + (2\pi \times \Delta f(I))^2\right]^{-\frac{1}{2}},
\]

where \(T_2\) is the coherence time from all other sources of decoherence in the experiment.

The solid lines in figure 8(c) show the results of fitting the simple model described by equation (24) to the measurements of the coherence time, with \(T_2\) and \(\Delta I\) as fit parameters. For the transition to the \[|N = 1, M_F = +4\rangle\] state, we find \(T_2 = 0.7(2)\) ms and a spread of intensities equal to 3.4(9)% of the peak intensity. The measurements using the \[|N = 1, M_F = +5\rangle\] state are adequately described by the dephasing term alone and the fit yields a 2(1)% intensity variation. In both cases, the spread in intensity is in reasonable agreement with the simple estimate of equation (23). The larger intensity spread for the transition to the \[|N = 1, M_F = +4\rangle\] state is most likely due to the cloud dynamics discussed above which become more important for longer coherence times. Indeed, we expect a full dynamical model to yield a spread of transition frequencies which is a function of both the intensity, \(I\), and the free evolution time, \(T\). The fitted \(T_2\) time is considerably shorter than the coherence time observed in free space. Again, this is most likely due to the lack of a full dynamical treatment, with the \(T_2\) parameter compensating for an underestimate of the intensity variation for longer free evolution times.

In future work we plan to eliminate dynamical effects by loading the molecules into a 3D optical lattice, such that each molecule is pinned to a site of the lattice. Under such conditions spin-echo sequences can be employed to combat dephasing \[61\] and we can investigate the limits on the coherence time more thoroughly. We have shown that avoided crossings in the AC Stark shift can be used to extend the coherence time in the trap greatly. A key challenge for the future is to identify the best avoided crossings to use in the optical lattice. The exact structure of hyperfine levels under the effect of the AC Stark shift is dependent on the magnetic field, as well as the intensity and polarisation of the light. This gives a large parameter space in which to optimise the AC Stark shift for future experiments.
4.3. Conclusion

In summary we have demonstrated the use of Ramsey interferometry in two, very different, ultracold molecule experiments using CaF and RbCs. In both cases, we are able to control the internal rotational and hyperfine states to a sufficient degree that high-contrast Ramsey fringes can be observed and used to determine transition frequencies with precisions on the Hertz level. To increase the interrogation time available we add additional confinement to the molecules using a magnetic trap for CaF and an optical trap for RbCs. Both traps introduce spatially varying energy-level shifts to the molecule samples, leading to dephasing of the Ramsey fringes. In the case of CaF, differential Zeeman shifts limited the coherence time to 0.61(3) ms for molecules in a magnetic trap. In RbCs we find that the choice of hyperfine states is very important and that avoided crossings in the AC Stark shift can be exploited to reduce the dephasing and extend the coherence time to 0.75(6) ms. Finally we have provided suggestions that could eliminate the dephasing due to spatially varying energy shifts entirely, either through mixing states with different magnetic moments or by tuning the parameters of an optical lattice to engineer broad avoided crossings.

5. Outlook

Many proposals for quantum simulation require addressing and detection of individual particles in an ordered array. For molecules this is a major experimental challenge. One approach, used with great success for atoms, is to load the molecules onto individual sites of an optical lattice and use high-resolution single-site imaging, as employed in quantum gas microscopes [20][22]. Direct loading of an optical lattice from a 3D trap requires a high initial density $\sim (\lambda/2)^{-3}$, where $\lambda/2$ is the lattice spacing. Currently, this approach is therefore restricted to molecules prepared by the association method.
Here, the initial atomic gases can be cooled to quantum degeneracy and efficiently loaded into the lattice via a Mott-insulator (MI) transition such that two atoms reside in each site prior to association. This approach has the benefit of greatly increasing the efficiency of the magnetoassociation step to close to unity. However, in two-species experiments, achieving a high filling fraction of heteronuclear atom pairs is difficult and requires careful control of both the intraspecies and interspecies interactions. Nevertheless, molecular filling fractions of up to ∼30% in 3D lattices have been demonstrated for both ground-state KRb molecules and RbCs Feshbach molecules, reaching the so-called percolation threshold where the molecules are well connected throughout the lattice. In both these experiments interspecies Feshbach resonances are exploited to enhance the miscibility of the mixture. However, this can inadvertently introduce high inelastic losses for one of the species. Fortunately the MI phase can also be used to protect against such inelastic collisions. For example, Cs suffers from high 3-body loss rates at most magnetic fields, but by first loading the atoms into a MI state with one atom per lattice site at a magnetic field with favourable intraspecies interactions, the atoms can be protected against collisions when moving to a magnetic field with favourable interspecies interactions. Exploiting the advanced control techniques developed for atomic gases in this way, loading molecules into optical lattices with high filling factors should not be an insurmountable challenge.

Accurate site-resolved detection and addressing of individual molecules in an optical lattice presents additional challenges. In the atomic quantum gas microscopes, a high numerical aperture (NA) lens is used to collect scattered photons as the atoms are laser-cooled in a deep detection lattice. The small depth of field allows site-resolved imaging only of a single plane of atoms, although sequential readout has been employed to study a bilayer system. Crucially light-assisted inelastic collisions lead to rapid loss of atoms on doubly-occupied sites. This parity detection has led to striking images of the Mott-insulator transition. For molecules produced by association, detection usually involves reversing the association process and detecting the constituent atoms, although direct absorption imaging has been demonstrated. In a lattice, reversing the association will inevitably lead to two atoms on each site. To implement site-resolved imaging, either the atoms must be separated using species-specific optical potentials or one species must be removed, for example, by using a short pulse of blue-detuned light. Addressing of individual molecules can be achieved by focusing light onto a specific lattice site using the same high NA lens used for imaging. The resulting AC Stark shift, experienced only by the molecule on the chosen site, enables a microwave field to address just a single molecule. The desire to manipulate molecules with electric fields imposes additional constraints on the microscope, as the inclusion of electrodes forces the use of lenses with longer working distances. Several novel designs have been considered to ensure the electric field is uniform across the lattice whilst keeping the electrode structure sufficiently compact. We are currently incorporating these considerations into the design of a new apparatus to achieve single-site imaging of RbCs molecules in an optical lattice. Figure gives a schematic view of
our planned setup and a simulation of the expected imaging performance.

The direct loading of an optical lattice is appealing when associating atoms into molecules, as the production of high phase-space density samples of many atomic species is well understood. However, a variety of interesting experiments could be done with smaller arrays using tweezer traps, which may be loaded from lower-density sources. A tweezer trap is a tightly-focused far-detuned laser beam that confines a single atom. When loaded from a MOT or molasses, the occupancy of the trap is always zero or one, because two atoms in the same trap undergo a fast light-assisted collision that ejects both [132]. Multiple tweezer traps can be loaded stochastically, and then re-arranged to make regular, defect-free 1D or 2D arrays [25, 133, 134]. Exciting the atoms to Rydberg states introduces strong, controllable interactions between them, and the many-body quantum dynamics of a linear array of such atoms has recently been studied [135]. The same techniques can be used to make arrays of ultracold molecules with dipole-dipole interactions. Molecules could be loaded into tweezer traps directly from a MOT or molasses, or formed by associating pairs of atoms pre-loaded into the same tweezer [136]. This is an attractive approach to quantum simulation with molecules. The arrays are easily reconfigured, so various geometries and molecule spacings can be explored. Molecules can be brought together to interact at a fixed spacing for a known time, then separated again to turn off the interaction and read out the final state of each. The phase-space density reached with laser-cooled molecules is already high enough for efficient loading of tweezer traps. For optical trapping of CaF, a wavelength near 780 nm is convenient. At shorter wavelengths, scattering of the trap light reaches an unacceptable rate, while at longer wavelengths the diffraction-limited spot size increases, resulting in weaker confinement and larger minimum separations between molecules. An approximate value for the scalar polarizability of ground-state CaF at optical frequencies, $\alpha^{(0)}$, can be found by assuming the dominant contributions are from the X$^{2}\Sigma^+$, A$^{2}\Pi$ and B$^{2}\Sigma^+$ states. At 780 nm, this gives $\alpha^{(0)}/(4\pi\varepsilon_0) \approx 300\alpha_0^3$. A beam waist of 0.7 µm and a power of 20 mW gives a trap depth of 1.7 mK, a radial trap frequency of 225 kHz, and an axial trap frequency of 56 kHz. We estimate a scattering rate below 1 photon per second for these parameters.

Atoms in tweezer traps have been cooled to the motional ground state by Raman sideband cooling [137, 138]. The cooling proceeds by driving a Raman transition from $|i,n\rangle$ to $|j,n-1\rangle$, followed by optical pumping back to $|i,n-1\rangle$. Here $i,j$ are internal states, typically different hyperfine states, and $n$ is the motional quantum number. This continues until the system reaches $|i,0\rangle$ which is dark to both the Raman and optical pumping steps. It is desirable to cool molecules in the same way, and both the optical pumping and Raman steps can be done using one of the laser-cooling transitions. However, because of the tensor nature of the polarizability, the AC Stark shift is different for each rotational, hyperfine and Zeeman sub-level. The resulting state-dependent trapping potential brings several complications. The trap frequency will, in general, be different for states $|i\rangle$ and $|j\rangle$, which means that the frequency of the Raman transition depends on $n$, whose value is unknown when the cooling begins. The usual theory used
to find the relative strengths of transitions between motional states $n$ and $m$, involving an expansion in the Lamb-Dicke parameter, no longer applies because the states $|i,n\rangle$ and $|j,m\rangle$ are not orthogonal. Instead, Franck-Condon factors between these states determine the transition strengths. The spatially varying elliptical polarization of the light around the focus of the tweezer, resulting from the breakdown of the paraxial approximation, adds further complexity. State-dependent potentials can also result in rapid dephasing of the coherences needed for any quantum simulation, as explored in section 4. However, these challenges also bring new opportunities. For example, with state-dependent potentials, efficient sideband cooling to the motional ground state could be done using microwave transitions between rotational states, instead of Raman transitions. We are currently analysing these issues with the aim of finding the best approach to sideband cooling and the control of coherence for molecules in tweezer traps.

In summary, ultracold molecules offer a variety of new possibilities for quantum simulation, but the development of experiments presents a number of key challenges. We have presented our progress towards negotiating these challenges and in developing a platform on which to build future quantum simulation experiments. The molecules used in this work, CaF and RbCs, are produced in very different ways, using two of the most successful approaches in the field. We have described in detail the hyperfine and rotational structure of each molecule, highlighting their differences and similarities, with reference to recent reports of the coherent control of the internal quantum state of both species. We have demonstrated Ramsey spectroscopy of the rotational transition $N = 0 \leftrightarrow N = 1$ for free-space and trapped samples in each experiment. In the case of trapped samples, we find that the main decoherence mechanism is dephasing due to spatially varying Zeeman shifts for magnetically trapped CaF or AC Stark shifts for optically trapped RbCs. For both molecules, we find that the choice of hyperfine states is critical to maximise the coherence time. Future experiments will focus on the loading of molecules into arrays, either by direct loading into optical lattices, or by building smaller arrays of tweezer traps. In doing this, we will open the door to a number of realisable quantum simulation experiments.

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References

[1] Lloyd S 1996 Science 273 1073–1078
[2] Manousakis E 2002 Journal of Low Temperature Physics 126 1501–1513
[3] Byrnes T, Kim N Y, Kusudo K and Yamamoto Y 2008 Physical Review B 78(7) 075320
[4] Baranov M A, Dalmonte M, Pupillo G and Zoller P 2012 Chemical Reviews 112 5012
[5] Zohar E, Cirac J I and Reznik B 2015 Reports Prog Phys 79 014401
[6] Johnson T H, Clark S R and Jaksch D 2014 EPJ Quantum Technology 1 10
[7] Cirac J I and Zoller P 2012 Nature Physics 8 264–266
[8] Georgescu I M, Ashhab S and Nori F 2014 Reviews of Modern Physics 86 153–185
[9] Glaetzle A W, Dalmonte M, Nath R, Gross C, Bloch I and Zoller P 2015 Physical Review Letters 114(17) 173002
[10] Glaetzle A W, van Bijnen R M W, Zoller P and Lechner W 2017 Nature Communications 8 15813
[11] Blatt R and Roos C F 2012 Nature Physics 8 277
[12] Leibfried D, Blatt R, Monroe C and Wineland D 2003 Reviews of Modern Physics 75 281–324
[13] Friis N, Marty O, Maier C, Hempel C, Holzäpfel M, Jurcevic P, Plenio M, Huber M, Roos C, Blatt R and Lanyon B 2017 ArXiv e-prints 1711.11092
[14] Houck A A, Türeci H E and Koch J 2012 Nature Physics 8 292
[15] Gross C and Bloch I 2017 Science 357 995–1001 ISSN 0036-8075
[16] Lewenstein M, Sanpera Trigueros A and Ahufinger V 2012 Ultracold atoms in optical lattices (Oxford, UK: Oxford University Press) ISBN 978-0-19-957312-7
[17] Parsons M F, Mazurenko A, Chiu C S, Ji G, Greif D and Greiner M 2016 Science 353 1253–1256
[18] Boll M, Hilker T A, Salomon G, Omran A, Nespolo J, Pollet L, Bloch I and Gross C 2016 Science 353 1257–1260
[19] Cheuk L W, Nichols M A, Lawrence K R, Okan M, Zhang H, Khatami E, Trivedi N, Paiva T, Rigol M and Zwierlein M W 2016 Science 353 1260–1264
[20] Bakr W S, Gillen J I, Peng A, Fölling S and Greiner M 2009 Nature 462 74
[21] Sherson J F, Weitenberg C, Endres M, Cheneau M, Bloch I and Kuhr S 2010 Nature 467 68
[22] Cheuk L W, Nichols M A, Okan M, Gersdorf T, Ramasesh V V, Bakr W S, Lompe T and Zwierlein M W 2015 Physical Review Letters 114(19) 193001
[23] Lester B J, Luick N, Kaufman A M, Reynolds C M and Regal C A 2015 Physical Review Letters 115(7) 073003
[24] Endres M, Bernien H, Keesling A, Levine H, Anschuetz E R, Krajenbrink A, Senko C, Vuletic V, Greiner M and Lukin M D 2016 Science 354 1024–1027
[25] Barredo D, de Léséleuc S, Lienhard V, Lahaye T and Browaeys A 2016 Science 354 1021–1023
[26] Jaksch D, Briegel H J, Cirac J I, Gardiner C W and Zoller P 1999 Physical Review Letters 82(9) 1975–1978
[27] Griesmaier A, Werner J, Hensler S, Stuhler J and Pfau T 2005 Physical Review Letters 94 160401
[28] Lu M, Burdick N Q, Youn S H and Lev B L 2011 Physical Review Letters 107(19) 190401
[29] Aikawa K, Frisch A, Mark M, Baier S, Rietzler A, Grimm R and Ferlaino F 2012 Physical Review Letters 108 210401
[30] Baier S, Mark M J, Petter D, Aikawa K, Chomaz L, Cai Z, Baranov M, Zoller P and Ferlaino F 2016 Science 352 201
[31] Chomaz L, van Bijnen R M W, Petter D, Faraoni G, Baier S, Becher J H, Mark M J, Waechtler F, Santos L and Ferlaino F 2017 ArXiv e-prints 1705.06914
[32] Wenzel M, Böttcher F, Langen T, Ferrier-Barbut I and Pfau T 2017 Physical Review A 96(5) 053630
Ultracold molecules: a platform for quantum simulation

[33] Jaksch D, Cirac J I, Zoller P, Rolston S L, Côté R and Lukin M D 2000 Physical Review Letters 85 2208–2211 ISSN 00319007
[34] Urban E, Johnson T A, Henage T, Isenhower L, Yavuz D D, Walker T G and Saffman M 2009 Nature Physics 5 110
[35] Gaëtan A, Miroshnychenko Y, Wilk T, Chotia A, Viteau M, Comparat D, Pillet P, Browaeys A and Grangier P 2009 Nature Physics 5 115–118
[36] Gorshkov A V, Hazzard K R and Rey A M 2013 Molecular Physics 111 1908–1916
[37] Micheli A, Brennen G K and Zoller P 2006 Nature Physics 2 341
[38] Böchler H P, Demler E, Lukin M, Micheli A, Prokof’ev N, Pupillo G and Zoller P 2007 Physical Review Letters 98 060404
[39] Gorshkov A V, Manmana S R, Chen G, Ye J, Demler E, Lukin M D and Rey A M 2011 Physical Review Letters 107 115301
[40] Zhou Y L, Ortner M and Rabl P 2011 Physical Review A 84(5) 052332
[41] Lechner W and Zoller P 2013 Physical Review Letters 111 185306
[42] Ni K K, Ospelkaus S, de Miranda M H G, Pe’er A, Neyenhuis B, Zirbel J J, Kotochigova S, Julienne P S, Jin D S and Ye J 2008 Science 322 231–235
[43] Takekoshi T, Reichsöllner L, Schindewolf A, Hutson J M, Le Sueur C R, Dulleo O, Ferlaino F, Grimm R and Nägerl H C 2014 Physical Review Letters 113 205301
[44] Molony P K, Gregory P D, Ji Z, Lu B, Köppinger M P, Le Sueur C R, Blackley C L, Hutson J M and Cornish S L 2014 Physical Review Letters 113 255301
[45] Park J W, Will S A and Zwierlein M W 2015 Physical Review Letters 114 205302
[46] Guo M, Zhu B, Lu B, Ye X, Wang F, Vexiau R, Bouloufa-Maafa N, Quéméner G, Dulleo O and Wang D 2016 Physical Review Letters 116 205303
[47] Rvachov T M, Son H, Sommer A T, Ebadi S, Park J J, Zwierlein M W, Ketterle W and Jamison A O 2017 Physical Review Letters 119(14) 143001
[48] Shuman E S, Barry J F and DeMille D 2010 Nature 467 820–3 ISSN 1476-4687
[49] Hunter L R, Peck S K, Greenspon A S, Alam S S and DeMille D 2012 Physical Review A 85 012511
[50] Hummon M T, Yeo M, Stuhl B K, Collopy A L, Xia Y and Ye J 2013 Physical Review Letters 110 143001
[51] Barry J F, McCarron D J, Norrgard E B, Steinecker M H and DeMille D 2014 Nature 512 286
[52] Zhelyazkova V, Cournol A, Wall T E, Matsushima A, Hudson J J, Hinds E A, Tarbutt M R and Sauer B E 2014 Physical Review A 89 053416
[53] McCarron D J, Norrgard E B, Steinecker M H and DeMille D 2015 New Journal of Physics 17 035014 ISSN 1367-2630
[54] Norrgard E B, McCarron D J, Steinecker M H, Tarbutt M R and DeMille D 2016 Physical Review Letters 116 063004
[55] Truppe S, Williams H J, Hambach M, Caldwell L, Fitch N J, Hinds E A, Sauer B E and Tarbutt M R 2017 Nature Physics 13 1173–1176
[56] Anderegg L, Augenbraun B L, Chae E, Hemmerling B, Hutzler N R, Ravi A, Collopy A, Ye J, Ketterle W and Doyle J M 2017 Physical Review Letters 119(10) 103201
[57] Lim J, Almond J R, Trigatzis M A, Devlin J A, Fitch N J, Sauer B E, Tarbutt M R and Hinds E A 2017 ArXiv e-prints 1712.02868
[58] Kozyryev I, Baum L, Matsuda K, Augenbraun B L, Anderegg L, Sedlack A P and Doyle J M 2017 Physical Review Letters 118 173201
[59] Chen T, Bu W and Yan B 2017 Physical Review A 96 053401
[60] Iwata G Z, McNally R L and Zelevinsky T 2017 Physical Review A 96 022509
[61] Yan B, Moses S A, Gadway B, Covey J P, Hazzard K R A, Rey A M, Jin D S and Ye J 2013 Nature 501 521–525
[62] Barnett R, Petrov D, Lukin M and Demler E 2006 Physical Review Letters 96 190401
[63] Ospelkaus S, Ni K K, Quéméner G, Neyenhuis B, Wang D, de Miranda M H G, Bohn J L, Ye J
Ultracold molecules: a platform for quantum simulation

[94] Jenkin D L, McCarron D J, Köppinger M P, Cho H W, Hopkins S A and Cornish S L 2011 European Physical Journal D: Atomic, Molecular and Optical Physics 65 11
[95] McCarron D J, Cho H W, Jenkin D L, Köppinger M P and Cornish S L 2011 Physical Review A 84 011603
[96] Köppinger M P, McCarron D J, Jenkin D L, Molony P K, Cho H W, Cornish S L, Le Sueur C R, Blackley C L and Hutson J M 2014 Physical Review A 89 033604
[97] Gregory P D, Molony P K, Köppinger M P, Kumar A, Ji Z, Lu B, Marchant A L and Cornish S L 2015 New Journal of Physics 17 055006
[98] Molony P K, Gregory P D, Kumar A, Le Sueur C R, Hutson J M and Cornish S L 2016 ChemPhysChem.
[99] Molony P K, Gregory P D, Ji Z, Lu B, Köppinger M P, Sueer C R L, Blackley C L, Hutson J M and Cornish S L 2014 Physical Review Letters 113 255301
[100] Anderson M A, Allen M D and Ziurys L M 1994 Astrophysical Journal 424 503–506
[101] Childs W J, Goodman L S, Nielsen U and Pfeufer V 1984 Journal of Chemical Physics 80 2283–2287
[102] Aldegunde J, Rivington B A, Żuchowski P S and Hutson J M 2008 Physical Review A 78 033434
[103] Aldegunde J and Hutson J M 2018 arXiv:1711.09467 URL [https://arxiv.org/abs/1711.09467](https://arxiv.org/abs/1711.09467)
[104] Childs W, Goodman G L and Goodman L S 1981 Journal of Molecular Spectroscopy 86 365
[105] Brown J and Carrington A 2003 Rotational Spectroscopy of Diatomic Molecules (Cambridge University Press, Cambridge, U.K.)
[106] Frosh R A and Foley H M 1952 Physical Review 88 1337–1349
[107] Curl R 1965 Molecular Physics 9 585–597
[108] Devlin J A, Tarbutt M R, Kokkin D L and Steinle T C 2015 Journal of Molecular Spectroscopy 317 1–9
[109] Ramsey N F 1952 Physical Review 85 60
[110] Bryce D L and Wasylissen R E 2003 Accounts of Chemical Research 36 327
[111] Gregory P D, Blackmore J A, Aldegunde J, Hutson J M and Cornish S L 2017 Physical Review A 96 021402(R)
[112] Hudson J J, Kara D M, Smallman I J, Sauer B E, Tarbutt M R and Hinds E A 2011 Nature 473 493–6
[113] Truppe S, Hendricks R J, Tokunaga S K, Lewandowski H J, Kozlov M G, Kenkel C, Hinds E A and Tarbutt M R 2013 Nature Communications 4
[114] Hazzard K R A, Manmana S R, Foss-Feig M and Rey A M 2013 Physical Review Letters 110 075301
[115] 2017 Dalton, a Molecular Electronic Structure Program, Release Dalton2017.alpha http://daltonprogram.org
[116] Dunning Jr T H 1989 J. Chem. Phys. 90 1007–1023
[117] Koput J and Peterson K A 2002 Phys. Chem. A 106 9595–9599
[118] Jaksch D, Bruder C, Cirac J I, Gardiner C W and Zoller P 1998 Physical Review Letters 81(15) 3108–3111
[119] Greiner M, Mandel O, Esslinger T, Hänsch T W and Bloch I 2002 Nature 415 39
[120] Jaksch D, Venturi V, Cirac J I, Williams C J and Zoller P 2002 Physical Review Letters 89(4) 040402
[121] Danzl J G, Mark M J, Haller E, Gustavsson M, Hart R, Aldegunde J, Hutson J M and Nägerl H C 2010 Nature Physics 6 265
[122] Covey J P, Moses S A, Gärtnert M, Safavi-Naini A, Miecnikowski M T, Fu Z, Schachenmayer J, Julienne P S, Rey A M, Jin D S and Ye J 2016 Nature Communications 7 11279
[123] Thalhammer G, Winkler K, Lang F, Schmid S, Grimm R and Hecker Denschlag J 2006 Physical Review Letters 96 050402
[124] Chotia A, Neyenhuis B, Moses S A, Yan B, Covey J P, Foss-Feig M, Rey A, Jin D S and Ye J 2012 Physical Review Letters 108 080405
Ultracold molecules: a platform for quantum simulation

[125] Stauffer D and Aharony A 1994 Introduction to Percolation Theory revised 2nd ed (Florida: Taylor & Francis) ISBN 978-0748402533
[126] Preiss P M, Ma R, Tai M E, Simon J and Greiner M 2015 Physical Review A 91 041602(R)
[127] Bakr W S, Peng A, Tai M E, Simon J, Gillen J I, Fölling S, Pollet L and Greiner M 2010 Science 329 547
[128] Wang D, Neyenhuis B, de Miranda M H G, Ni K, Ospelkaus S, Jin D S and Ye J 2010 Physical Review A 81 061404(R)
[129] LeBlanc L J and Thywissen J H 2007 Physical Review A 75 053612
[130] Gempel M W, Hartmann T, Schulze T A, Voges K K, Zenesini A and Ospelkaus S 2016 New Journal of Physics 18 045017
[131] Bohn J L, Rey A and Ye J 2017 Science 357 1002
[132] Schlosser N, Georges R, Protsenko I and Grangier P 2001 Nature 411 1024
[133] Miroshnychenko Y, Alt W, Dotsenko I, Förster L, Khudaverdyan M, Meschede D, Schrader D and Rauschenbeutel A 2006 Nature 442 151
[134] Lee W, Kim H and Ahn J 2016 Optics Express 24 9816–9825
[135] Bernien H, Schwartz S, Keesling A, Levine H, Omran A, Pichler H, Choi S, Zibrov A S, Endres M, Greiner M, Vuletić V and Lukin M D 2017 Nature 551 579–584
[136] Liu L R, Zhang J T, Yu Y, Hutzler N R, Liu Y, Rosenband T and Ni K K 2017 ArXiv e-prints 1701.0312v1
[137] Kaufman A M, Lester B J and Regal C A 2012 Physical Review X 2 041014
[138] Thompson J D, Tiecke T G, Zibrov A S, Vuletić V and Lukin M D 2013 Physical Review Letters 110 133001
[139] Li X, Corcovilos T A, Wang Y and Weiss D S 2012 Physical Review Letters 108 103001