Cruising through molecular bound state manifolds with radio frequency

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The emerging field of ultracold molecules with their rich internal structure is currently attracting a lot of interest. Various methods have been developed to produce ultracold molecules in pre-set quantum states. For future experiments it will be important to efficiently transfer these molecules from their initial quantum state to other quantum states of interest. Optical Raman schemes are excellent tools for transfer, but can be involved in terms of equipment, laser stabilization and finding the right transitions. Here we demonstrate a very general and simple way for transfer of molecules from one quantum state to a neighboring quantum state with better than 99% efficiency. The scheme is based on Zeeman tuning the molecular state to avoided level crossings where radio-frequency transitions can then be carried out. By repeating this process at different crossings, molecules can be successively transported through a large manifold of quantum states. As an important spin-off of our experiments, we demonstrate a high-precision spectroscopy method for investigating level crossings.

Using radio-frequency (rf) for molecular spectroscopy is an established technology dating back as far as the early 20th century. In ultracold molecular gases it was employed in recent years to measure binding energies of weakly bound states or to produce ultracold molecules by associating ultracold atoms near a Feshbach resonance. Transferring ground state molecules between states of different vibrational quantum numbers using rf as demonstrated in this letter is not obvious. The spatial wavefunctions of different vibrational states are in general orthogonal to each other, trivially leading to a vanishing transition matrix element for magnetic dipole transitions. However, even simple molecules like Rb2 have a complex level structure, especially when weakly bound, mainly due to exchange interaction, hyperfine structure and the Zeeman effect. As a consequence, levels with different vibrational quantum numbers can intersect and mix, leading to allowed rf transitions between them.

We perform our experiments with an ensemble of 2×10^4 ultracold 87Rb2 molecules which are held in the vibrational ground states of micro traps formed by a cubic 3D optical lattice with lattice period 415 nm. There is no more than a single molecule per micro trap and the lattice potential is deep enough to effectively isolate the molecules from each other, shielding them from detrimental collisions. The molecular ensemble is initially produced from an atomic 87Rb Bose-Einstein condensate (BEC) after adiabatically loading it into the lattice. Subsequent ramping over a Feshbach resonance at 1007.4 G produces Feshbach molecules and a final purification step removes all chemically unbound atoms.

Figure 1 shows the relevant molecular level spectrum of relevant molecular levels of 87Rb2 in the electronic ground state with m_foton = 2. The zero of energy is taken to be that of two separated atoms at each field strength. Molecules are transported through the bound level manifold by traversing avoided crossings, marked A - K. Out of the number of existing g-wave levels, we only show the single relevant one. (1 G = 0.1 mT).
Adiabatic population transfer across avoided crossing (ATAC) with radio frequency (rf). a. Zoom into avoided crossing A of Fig. 1. Transitions between the upper and lower branch can be induced with rf. b. Dressed state picture. Coupling the lower and upper branch in a with blue detuned rf induces two avoided crossings with splitting $\omega_0$. Blue dashed lines: case if $\omega_0 = 0$. For better visibility, the detuning and $\omega_0$ are chosen larger than in the experiment. c. Measured transfer efficiency for transfer from upper branch to lower branch (red data) and back (green data). The solid lines are fits to a Landau-Zener model. The rf amplitude is calibrated with a global uncertainty of about 40%. The ramp speed is 1.3 G/ms.

In general, where two levels intersect, coupling between them gives rise to an avoided crossing. In the following we will use the level spectrum like a street map, as the molecules move through the manifold of molecular bound states by sweeping the magnetic field. When arriving at a level intersection one can turn off or go straight, traversing the avoided crossing. In principle, the avoided crossing can be jumped via a fast magnetic field ramp \[22, 23\]. This, however, is limited to very small splittings (typically $< 200 \text{ kHz} \times h$) due to practical limitations of the controllable magnetic ramp speed. This constraint can be easily overcome using an rf transition as we demonstrate below.

As an example for cruising through molecular bound state levels we choose the diagonal path in Fig. 1, as marked with the red circles A to K, each indicating an avoided crossing. This converts our Feshbach molecules with their weak binding energy of $24 \text{ MHz} \times h$ to a deeper bound level at zero magnetic field, $3.6 \text{ GHz} \times h$ below the $f = 1, m_f = 1$ dissociation limit.

Fig. 2a shows an expanded view of the first avoided crossing A. The upper branch is connected to the Feshbach resonance at $1007.4 \text{ G}$ and is initially populated with Feshbach molecules. We use adiabatic passage as a very efficient way for population transfer to the lower branch. A longitudinal rf field (i.e. the rf magnetic field points in the same direction as the magnetic bias field) couples upper and lower branch via a magnetic dipole transition. We use a frequency of $13.6 \text{ MHz}$, which is blue detuned with respect to the minimal splitting of the avoided crossing. In the dressed state picture this produces two rf induced avoided crossings, each with a splitting corresponding to the Rabi frequency $\omega_0$, (see Fig. 2b). At the beginning of the transfer the rf field is off. The molecules which are initially located at the position of the Feshbach resonance (point i in Fig. 2b), are brought to point ii by lowering the magnetic field to $B = 1001 \text{ G}$. We then switch on the non-resonant rf field and afterwards adiabatically lower the magnetic field $B$ until we reach point iii. Subsequent switching off the rf field completes the transfer of the molecules to the lower branch. Figure 2b shows the fraction $N/N_0$ of remaining molecules in the upper branch after the transfer to the lower branch (red data) as a function of the rf field amplitude $B_{rf}$. For sufficiently high amplitude no more molecules are detected (see Methods section for details on molecule detection). To verify that molecules are not simply lost for high amplitude, we also carry out a transfer back (iii $\rightarrow$ ii $\rightarrow$ i) to the upper branch (green data). All molecules can be recouped again for strong enough rf fields. From similar measurements with repeated transfers between upper and lower branch we infer single transfer efficiencies of up to 99.5%. Our experimental data are well-fitted with the well known Landau-Zener model (solid lines) \[24\] where the transfer probability for a single transition is given by \[1 - \exp(-\pi \omega_0^2 h / 2 |B| |\mu_2 - \mu_1|)\]. Here $|B|$ is the ramp speed and $\mu_1, \mu_2$ are the magnetic moments of the two states.

After this successful demonstration at crossing A, we will use adiabatic transfer across an avoided crossing (ATAC) repeatedly for traversing the remaining crossings on our path. For these ATAC transfers we typically apply radio-frequency with field amplitudes $B_{rf} \sim 50 \text{ mG}$, corresponding to Rabi frequencies $\omega_{rf} \sim 2\pi \times 70 \text{ kHz}$ and ramp the magnetic bias field over about 1 G in 1 ms. We typically find avoided crossings to lie within a few Gauss of their predicted magnetic field position based on the coupled channel calculation. This identification helps us also to verify that the molecules are in the right quantum level during transport (see Methods section).

After traversing A, the next wide $s$-wave crossing is C. Before we get to C, however, we hit the avoided crossing B at $874 \text{ G}$ with a $\sim 7 \text{ MHz} \times h$ splitting, based on an intersecting $d$-wave level (see inset Fig. 3b). To circumvent crossing B we carry out the ATAC transfer between the $s$-waves levels already at $876 \text{ G}$, far from the $s$-wave crossing.

This raises the question, how far from an avoided cross-
ing the rf transitions can still be driven. Figure 3a is a zoom into the energy spectrum showing the avoided crossings A and C. Figure 3b plots the corresponding calculated magnetic dipole matrix elements $\mu_{n,l}$ between the corresponding upper and lower level branches using the coupled channel model (see also Methods section). The matrix elements are clearly peaked at their respective crossing, reaching values of more than a Bohr magneton. Such high coupling strengths are in agreement with our measurements in Figure 2c where $|B - B_0|$ is typically smaller than the size of the plot symbol. The dashed line is a hyperbolic fit yielding a minimum frequency of $(13.331 \pm 0.005)$ MHz.

Continuing our path down by lowering the magnetic field we hit consecutively five avoided crossings (D,E,F,H,I) with $d$-wave states. The corresponding energy splittings are on the order of 1 MHz $\times h$ and are each crossed by the ATAC method, which demonstrates its universal character. In general, however, ATAC transfers at narrow avoided crossings are technically more challenging due to a small magnetic field range of strong coupling and thus a greater susceptibility to magnetic field noise which can lead to unwanted non-adiabatic transitions. Coupling to a $g$-wave state is observed as well (crossing G), but it is weak enough to be overcome by diabatic ramping of the magnetic field. Finally, after crossing J and K we reach zero magnetic field, with the molecules in state $|l = 0, F_{tot} = F = f_1 = f_2 = m_{F_{tot}} = 2, v = -5\rangle$. 3.6 GHz below the $f_1 = f_2 = 1, m_{f_1} = m_{f_2} = 1$ threshold. We have also produced $d$-wave molecules at zero magnetic field ($|l = 2, F_{tot} = 2, F = 0, f_1 = f_2 = m_{F_{tot}} = 2, v = -5\rangle$) by adiabatically following the upper branch in crossing K, i.e. taking a right turn. The complete transfer down across all 10 avoided crossings takes about 90 ms with a global transfer efficiency of about 50% (for molecule detection see Methods section). The losses during transfer can be explained mainly by the limited molecular lifetime of 280 ms in the lattice, due to inelastic scattering of lattice photons [17], and by not fully optimized transfers at several crossings.

Besides the ATAC transfer of molecules between quantum levels, we also developed a high precision spectroscopy method for measuring the minimal energy splitting of an avoided crossing. For a given avoided crossing the energy splitting is measured for various magnetic fields by determining the resonant transition frequency. The error bars are typically smaller than the size of the plot symbol. The dashed line is a hyperbolic fit yielding a minimum frequency of $(13.331 \pm 0.005)$ MHz.

The clear deviation from the hyperbolic curve results from a $\sim 2$ G/mm magnetic field gradient across the molecular cloud (~20 $\mu$m diameter) in combination with $\sim 20$ mG fluctuations of the magnetic field during the time of a scan. This behavior is reproduced by our model calculation (solid red line) taking these experimental imperfections into account. From the model we obtain a best estimate of the minimum splitting $(13.33210 \pm 0.00015)$ MHz $\times h$ for the ideal hyperbolic curve. The upshift of about 150 Hz of the minimum of the model curve with respect to the hyperbolic curve is due to averaging over the magnetic field inhomogeneities.

We have also performed detailed measurements of the energy splitting at the avoided crossings marked C, E, and J in Fig. 1. These data are shown in Table 1. The measurements are complementary to conventional bound state spectroscopy because instead of measuring the plain energy spectrum of the bound states, our method determines the strength of the coupling between levels. The precision of our data is several orders of magnitude better than the accuracy of our current coupled channel model, as well as the model of the Eindhoven group [25]. Thus the data can serve to improve and test the theoretical models used to calculate molecular energy levels.

To conclude, we have demonstrated an efficient and universal method (ATAC) to transfer molecules between quantum states. This method is based on a combination of $rf$ pulses and magnetic field ramping and can be applied to any molecule, since the only requirement is the existence of magnetically

| Molecule type | Energy splitting (MHz) | Measured data | Hyperbolic fit |
|---------------|------------------------|---------------|---------------|
| $\text{A}$    | $(13.33210 \pm 0.00015)$| $13.331 \pm 0.005$| $(13.331 \pm 0.005)$|

FIG. 4: Spectroscopy of an avoided crossing. For the avoided crossing A the splitting is measured for various magnetic fields by determining the resonant transition frequency. The error bars are typically smaller than the size of the plot symbol. The dashed line is a hyperbolic fit yielding a minimum frequency of $(13.331 \pm 0.005)$ MHz.
tunable avoided crossings. This opens interesting perspectives for experiments in cold collisions \cite{26, 27, 28}, chemistry in the ultracold regime, high resolution spectroscopy, and molecular BEC. In particular, we plan to use the rf transfer method to prepare Feshbach molecules in a convenient start position for an optical Raman transition to a deeply bound molecular state or even the vibrational ground state \cite{5, 29}. In principle, the triplet vibrational ground state for Rb\textsubscript{2} can also be reached directly via the ATAC transfer scheme. By cruising back and forth within a 5 Tesla range between consecutive avoided crossings one can step down the vibrational ladder. Further, the ATAC scheme can be extended in a straightforward manner to avoided crossings which are tuned by electrical fields.

### Methods

#### Detection of molecules and their quantum state

In order to detect the molecules at any stage during their transport through the manifold of molecular levels, we trace back exactly the path we have come before, adiabatically traversing all avoided crossings in the opposite direction. We end up with Feshbach molecules which are dissociated into unbound atoms by sweeping over the Feshbach resonance at 1007.4 G. These atoms are then counted via standard absorption imaging, after switching off the optical lattice and the bias magnetic field.

We use two methods to verify that molecules are in the right quantum level during transport. 1) Checking for consistency between predicted and experimentally found avoided crossings, in terms of magnetic field location and energy splitting. 2) Optical spectroscopy to measure the binding energy of molecules. By irradiating the molecules with resonant laser light we transfer the molecules to an electronically excited molecular level, $|0_{\nu}^+, \nu = 31, J = 0\rangle$ \cite{5}, leading to losses. The shift of this laser frequency compared to the frequency of the photoassociation transition to the same excited molecular level corresponds to the binding energy of the molecules.

#### Simple model for rf transitions at an avoided crossing

A simple two level model gives insight into the mechanism for the rf transitions at the avoided crossing. Two molecular bare levels $|b1\rangle, |b2\rangle$ with magnetic moments $\mu_1$ and $\mu_2$ cross at a magnetic field $B = B_0$. The Hamiltonian for these levels reads

$$\hat{H} = (B - B_0 + B_{rf}\cos(\omega_{rf}t))\begin{pmatrix} \mu_1 & 0 \\ 0 & \mu_2 \end{pmatrix} + \frac{\hbar}{2}\begin{pmatrix} 0 & \Omega \\ \Omega & 0 \end{pmatrix}.$$ 

A coupling $\Omega$ between the two levels, e.g. due to exchange interaction or dipole-dipole interaction, leads to mixing and the new eigenstates $|u\rangle$ and $|l\rangle$. These states form the upper and lower branch of an avoided crossing, similar to Fig. 2a. A longitudinal magnetic rf field with amplitude $B_{rf}$ and frequency $\omega_{rf}$ can drive transitions between levels $|u\rangle$ and $|l\rangle$ which read

$$|u\rangle = \cos(\theta)|b1\rangle + \sin(\theta)|b2\rangle$$

$$|l\rangle = -\sin(\theta)|b1\rangle + \cos(\theta)|b2\rangle,$$

(1)

with mixing angle $\theta = \arctan(\frac{\delta + \sqrt{\delta^2 + \Omega^2}}{\Omega})$, where $\delta = (\mu_2 - \mu_1)$. 

### Table I: Precision data for the minimal energy splitting of the avoided crossings A, C, E, and J of Fig. 1a. The second column indicates the partial waves involved in the crossing. The third column gives the minimal splitting which is located at magnetic field $B_0$.

| partial waves | splitting/h (MHz) | $B_0$ (G) |
|---------------|-----------------|----------|
| A s-s         | 13.33210 ± 0.00015 | 1001.4 ± 0.2 |
| C s-s         | 44.756 ± 0.006  | 845.8 ± 0.2 |
| E s-d         | 2.36 ± 0.01     | 466.1 ± 0.2 |
| J s-s         | 110.48 ± 0.01   | 218.8 ± 0.2 |

FIG. 5: **Spectroscopy with Ramsey interferometry.** a, Ramsey scheme consisting of two $\frac{\pi}{2}$-pulses of rf and a holding time $t_h$. b, Fraction of remaining Feshbach molecules after a Ramsey scan as holding time is varied. $B = 1001.39$ G. The oscillation frequency corresponds to the detuning of the rf from the splitting. c, Measured splittings, in a narrow magnetic field region (also indicated by the small dotted box in Fig. 4). The deviation from the hyperbolic curve (dashed blue line) results from magnetic field fluctuations and inhomogeneities and is reproduced by our model calculation (solid red line).
\( \mu_1 |(B - B_0) \). The matrix element for the rf transition is then

\[
\mu_{i,j} \equiv \langle u | \left( \frac{\mu_1}{0} \begin{pmatrix} 0 & \mu_2 \\ \mu_2 & 0 \end{pmatrix} \right) | l \rangle = (\mu_2 - \mu_1) \sin(2\theta)
\]

\[
= 2(\mu_2 - \mu_1) \frac{\Omega(\delta + \sqrt{\delta^2 + \Omega^2})}{\Omega^2 + (\delta + \sqrt{\delta^2 + \Omega^2})^2}.
\]

Thus \( \mu_{i,j} \) is resonantly peaked at the avoided crossing with a width (FWHM) of \( 2\sqrt{3}\Omega \) and vanishes as \( 1/(B - B_0) \) far away from the crossing.

We find good agreement when comparing the matrix elements of our simple model with the ones of the coupled channel model, given by \( \mu_{i,j} = \langle u | \mu_{Bg} S_z + \mu_{gS} I_z | l \rangle \). Here \( |u\rangle, |l\rangle \) are the wavefunctions as calculated with the coupled channel model. \( \mu_{Bg}, \mu_{gS} \) are the Bohr magneton and nuclear magneton, \( g_s \) and \( g_I \) are the g-factors of the electrons and nuclei, respectively, and \( S_z, I_z \) are the corresponding spin operator components in the direction of the magnetic field.

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