Dark resonances for ground-state transfer of molecular quantum gases

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Abstract One possible way to produce ultra-cold, high-phase-space-density quantum gases of molecules in the rovibrionic ground state is given by molecule association from quantum-degenerate atomic gases on a Feshbach resonance and subsequent coherent optical multi-photon transfer into the rovibrionic ground state. In ultra-cold samples of Cs$_2$ molecules, we observe two-photon dark resonances that connect the intermediate rovibrational level $|v=73, J=2\rangle$ with the rovibrational ground state $|v=0, J=0\rangle$ of the singlet $X^1\Sigma_g^+$ ground-state potential. For precise dark resonance spectroscopy we exploit the fact that it is possible to efficiently populate the level $|v=73, J=2\rangle$ by two-photon transfer from the dissociation threshold with the stimulated Raman adiabatic passage (STIRAP) technique. We find that at least one of the two-photon resonances is sufficiently strong to allow future implementation of coherent STIRAP transfer of a molecular quantum gas to the rovibrational ground state $|v=0, J=0\rangle$.

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1 Introduction

Laser cooling of atoms and the production of quantum-degenerate atomic Bose and Fermi gases have revolutionized the field of atomic physics [1]. For molecular systems, ultra-low temperatures and high phase-space densities are much more difficult to achieve. Laser cooling of molecules has not yet been demonstrated, and with alternative cooling and slowing techniques such as buffer gas cooling and Stark deceleration high phase-space densities are yet out of reach [2–4]. In photoassociation experiments from magneto-optical traps [5–9], cold samples of deeply bound molecules in the lowest vibrational levels have been created. Yet, the phase-space densities are far away from the quantum-degenerate regime. In the limit of extremely weak binding, molecular Bose–Einstein condensation has been achieved$^1$ by using the trick of first cooling an atomic Fermi gas to high phase-space densities and subsequently associating pairs of atoms to molecules. For molecules composed of fermions, collisional stability of the highly excited molecules is assured as a result of a Pauli blocking effect. Here, we are interested in ultra-cold and dense molecular systems in specific deeply bound rovibrational levels. Such samples are of high interest for fundamental studies in physics and chemistry, ranging from ultra-cold chemistry [11] and few-body collisional physics [12, 13] to high-resolution spectroscopy [14, 15], to applications in quantum processing [16], and to the formation of dipolar quantum gases and dipolar Bose–Einstein condensates (BECs).

$^1$For an overview, see [10].
For these experiments full control over the molecular wave function is desired. In addition, high densities are required for molecular quantum gas studies. Only in the rovibronic ground state, i.e. the lowest energy level of the electronic ground state, is collisional stability assured.

For the production of molecular quantum gases in the absolute ground state, we follow a scheme in which the technique of stimulated two-photon transfer is repeatedly applied to molecules associated on a Feshbach resonance from a high-density sample of ultra-cold atoms such as a Bose–Einstein condensate. The initially very loosely bound molecules are to be transferred in a few successive steps to the rovibrational ground state, acquiring more and more binding energy. The scheme has several advantages. It is fully coherent, not relying on spontaneous processes, allowing high state selectivity, and it involves only a comparatively small number of intermediate levels. The scheme is expected to allow the removal of a ground state binding energy of typically 0.5 eV for an alkali dimer without appreciably heating the molecular sample. It essentially preserves phase-space density and coherence of the particle wave function, allowing the molecular sample to inherit the high initial phase-space density from the atomic sample. Ideally, the scheme will ultimately result in the formation of a molecular BEC. A major challenge is given by the low radial wave function overlap between successive molecular levels, potentially leading to prohibitively low transition rates for the two-photon transitions that could only be compensated by the use of further (smaller) transfer steps.

In a crucial experiment, Winkler et al. demonstrated that coherent two-photon transfer by means of the stimulated Raman adiabatic passage (STIRAP) technique can efficiently be implemented with quantum gases of weakly bound Feshbach molecules. In that work, the transferred molecules, in this case Rb₂, were still weakly bound with a binding energy of much less than 10⁻⁴ of the binding energy of the rovibrational ground state. In particular, wave-function overlap of the final level with the rovibrational ground state is negligible. Nevertheless, an important result of the experiment was the demonstration that, even with excitation near the excited S + P asymptote, parasitic excitation of unwanted molecular transitions by the STIRAP laser beams can largely be avoided. Recently, Danzl et al. showed efficient coherent STIRAP transfer into deeply bound rovibrational levels in the quantum gas regime. More specifically, transfer into the rovibrational level |v = 73, J = 2⟩ of the singlet X¹Σ⁺ ground-state potential of the Cs dimer was demonstrated. This level is bound by 1061 wavenumbers, more than one-fourth of the binding energy of the rovibrational ground state. Here, as usual, v and J denote the vibrational and rotational quantum numbers, respectively. This intermediate level was chosen so as to give a balanced distribution for the wave-function overlap in a four-photon transfer scheme to the ground state, i.e. to assure that all four dipole transition moments are of comparable magnitude. This level can thus serve as a transfer state towards the rovibrational ground state |v = 0, J = 0⟩, allowing coherent ground-state transfer with two-photon transitions. Also, recently, Ni et al. have demonstrated transfer all the way into the rovibrational ground state |v = 0, J = 0⟩ of the singlet X¹Σ⁺ molecular potential in a quantum gas of Krb molecules. The transfer could be achieved in a single step as a result of the favorable run of the excited state potentials in the case of heteronuclear alkali dimers. Also, the lowest rovibrational level of the Rb₂ triplet a³Σ⁺ ground-state potential has recently been populated in the quantum gas regime using the STIRAP technique.

Here, in an ultra-cold and dense sample of Cs molecules, we present two-photon dark resonances connecting the rovibrational level |v = 73, J = 2⟩ of the Cs dimer singlet X¹Σ⁺ ground-state potential with the rovibrational ground state |v = 0, J = 0⟩. Starting from |v = 73, J = 2⟩, we first perform molecular loss spectroscopy by laser excitation in the wavelength range from 1329 to 1365 nm. We searched for suitable rovibrational levels of the A¹Σ⁺(0_u⁺) and b³Π_u(0_u⁺) excited electronic states which are mixed due to spin–orbit coupling. Hereafter, these states will be referred to as the (A – b) 0_u⁺ system. These levels are 9893 to 10 091 wavenumbers above the rovibrionic ground state, corresponding to a wavelength range from 1011 to 991 nm for the transition to the rovibrionic ground state. We then perform dark-state spectroscopy by simultaneous laser irradiation near 1350 and 1000 nm. We find several dark resonances, from which we derive normalized transition strengths and find that at least one of the two-photon transitions is favorable for ground-state transfer.

2 Molecular energy levels and laser transitions

Figure 1 shows the energy of the relevant Cs₂ molecular states and the optical transitions for our transfer scheme. State |1⟩ is the initial weakly bound Feshbach state that we populate out of an atomic BEC of Cs atoms via Feshbach association. For the transfer from |1⟩ to the rovibrational ground state |5⟩ = |v = 0, J = 0⟩, three intermediate levels |2⟩, |3⟩, and |4⟩ are needed. All five molecular levels are coupled by two two-photon transitions in a distorted M-shaped configuration as shown in Fig. 2. Levels |2⟩ and |4⟩ belong to the (A – b) 0_u⁺ system. We have identified level |2⟩ as the 225th one of the (A – b) 0_u⁺ system, with an uncertainty of two in the absolute numbering, and |3⟩ is the level with v = 73 and J = 2 of the X¹Σ⁺ ground-state potential. A two-photon laser transition with laser L₁ at 1126 nm and laser L₂ at 1006 nm couples |1⟩ to |3⟩ via |2⟩. There are now several possibilities for coupling |3⟩ to |5⟩, differing in the choice of the excited level |4⟩. The aim of this work is
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Molecular level scheme for Cs$_6$ asymp-

Fig. 1 Molecular level scheme for Cs$_6$. Molecules in a weakly bound Feshbach level $|1\rangle = |v \approx 155\rangle$ (not resolved near the 6S + 6S asymptote) are transferred to the rovibrational level $|3\rangle = |v = 73, J = 2\rangle$ of the singlet $X^1\Sigma_g^+$ ground-state potential with a binding energy of 1061 cm$^{-1}$ by a two-photon STIRAP process [21] involving lasers $L_1$ and $L_2$ near 1126 and 1006 nm. The following two-photon transition from $|3\rangle$ to $|5\rangle = |v = 0, J = 0\rangle$ and also to $|v = 0, J = 2\rangle$ is then probed by lasers $L_3$ and $L_4$ near 1350 and 1000 nm, respectively. Level (2) is the 225th level of the electronically excited $(A - b) 0^+_g$ system. Here, we probe suitable candidate levels for $|4\rangle$, connecting $|3\rangle$ to $|5\rangle$. These candidate levels also belong to the $(A - b) 0^+_g$ system and include levels with coupled channel vibrational numbers $v' \approx 57$ to 68. The position of the vertical arrows is not meant to reflect the internuclear distance at which the transition takes place.

Fig. 2 Five-level distorted M-scheme. The one-photon detunings and Rabi frequencies of $L_i$ are $\Delta_i$ and $\Omega_i$, $i = 1, 2, 3, 4$. For STIRAP to $|v = 73, J = 2\rangle$ the detunings for $L_1$ and $L_2$ are $\Delta_1 \approx 0 \approx \Delta_2$ to identify a suitable level $|4\rangle$ from the $(A - b) 0^+_g$ system with sufficient wave-function overlap with both $|3\rangle$ and $|5\rangle$. We search for level $|4\rangle$ in the energy range of 9893 to 10091 cm$^{-1}$ above the rovibrational ground state $|5\rangle$. Molecular structure calculations as outlined in Sect. 4 show that in this range there are candidate states for $|4\rangle$ that have dipole transition matrix elements with both $|3\rangle$ and $|5\rangle$ of comparable magnitude, allowing optimum STIRAP performance. The wavelengths for the lasers $L_3$ and $L_4$ driving the associated two-photon transition are near 1350 and 1000 nm, respectively. We derive all laser light for driving the molecular transitions from highly stable, widely tunable diode laser systems with kHz line widths. For short-term stability, the lasers are all locked to narrow-band optical resonators. For long-term stability, the optical resonators are referenced to an infrared, fiber-laser-based frequency comb, covering the wavelength range from about 980 nm to about 2000 nm.

3 Preparation of a molecular quantum gas in $v = 73, J = 2$

Our sample preparation procedure follows [21]. In summary, we first produce a cigar-shaped BEC of typically $1.5 \times 10^5$ cesium atoms in the lowest hyperfine sublevel $F = 3, m_F = 3$ in a crossed optical dipole trap. As usual, $F$ is the atomic angular momentum quantum number and $m_F$ its projection. The trapping light at 1064.5 nm is derived from a single-frequency, highly stable Nd:YAG laser. Using a $d$-wave Feshbach resonance at 4.8 mT [26] we then produce a quantum gas of weakly bound Feshbach molecules out of the BEC [25]. For this, we first ramp the magnetic field from the BEC production value of 2.0 to 4.9 mT, slightly above the Feshbach resonance. The molecules are produced on a downward sweep at a typical sweep rate of 0.025 mT/ms. The resulting ultra-cold sample contains up to 11 000 molecules, immersed in the bath of the remaining BEC atoms. For the present experiments we shut off the trap and perform all subsequent measurements in free flight. This reduces the particle density, in particular during the later detection stage of the experiment, and hence reduces atom–molecule collisional loss, thus increasing the molecular signal. Following two avoided state crossings while further sweeping the magnetic field to lower values, we transfer the molecules via a weakly bound, open-channel $s$-wave molecular state into the still weakly bound, closed-channel $s$-wave molecular state $|1\rangle$ by magnetic field ramping [21]. This is the starting state for the subsequent optical transfer. As with all other weakly bound Feshbach states, it belongs to both the $X^1\Sigma_g^+$ ground-state potential and the lowest triplet $a^3\Sigma_u^+$ potential and is hence of mixed character. It has zero rotational angular momentum. At a field of 1.9 mT, it has a binding energy of 5 MHz × h, where $h$ is Planck’s constant, with respect to the $F = 3, m_F = 3$ two-atom asymptote [26]. We detect molecules in $|1\rangle$ by reverse magnetic field ramping, leading to dissociation on the Feshbach resonance at 4.8 mT, and subsequent imaging of the resulting atoms [25].

We transfer the molecules from $|1\rangle$ to the rovibrational level $|3\rangle = |v = 73, J = 2\rangle$ with the STIRAP technique [21]. For this, about 3 ms after molecule production, with the magnetic field ramping completed, laser $L_2$ at 1006 nm is pulsed on first and then laser $L_1$ at 1126 nm. Both lasers are on resonance within a few kHz. The pulse-overlap time
is about 10 µs. With peak Rabi frequencies of $\Omega_1 \approx 2\pi \times 3$ MHz and $\Omega_2 \approx 2\pi \times 6$ MHz we transfer about 80% of the molecules to [3]. We find that the molecular sample is not heated as a result of the STIRAP transfer. A residual kinetic energy on the order of $k_B \times 10$ nK comes from the expansion energy of the initial atomic sample. Our current procedure allows us to produce a sample of up to 8000 molecules in state [3] every 12 s. For the loss spectroscopy as detailed below, we irradiate the molecules in [3] with light near 1350 nm for a certain waiting time. We then measure the fraction of molecules that have remained in [3]. For this, we transfer the remaining molecules back to [1] using the reverse STIRAP process and determine the number of molecules in [1]. Without irradiation with light near 1350 nm we transfer more than 65% of the molecules from [1] to [3] and back to [1] [21].

4 Loss spectroscopy

In the heavy alkali dimers, most notably Cs$_2$, the $A^1\Sigma_u^+$ and $b^3\Pi_{0u}$ states are strongly mixed by spin–orbit coupling even in the lowest levels of the A state, leading to a mixed singlet–triplet character of the levels. Paradoxically, the levels of predominantly triplet $b^3\Pi_{0u}$ character are of special interest here for transfer to the rovibrational ground state $|v = 0, J = 0\rangle$ of the singlet $X^1\Sigma_g^+$ electronic ground state. As determined by data fits described below, the predominantly $b^3\Pi_{0u}$ levels happen to have significant singlet character over the regions of internuclear distance that are most important for transitions of interest in this work and thus couple to levels of the $X^1\Sigma_g^+$ state in a two-photon transition. For STIRAP transfer, they provide a more balanced distribution of Franck–Condon factors than the levels of predominantly $A^1\Sigma_u^+$ character.

To model the strongly interacting $A^1\Sigma_u^+$ and $b^3\Pi_{0u}$ states, a coupled channel approach is needed. The calculations used to characterize the level structure of these interacting states in Cs$_2$ [27] employed methods developed from previous work on A and b states of K$_2$ [28, 29], RhCs [30], Na$_2$ [31], and Rb$_2$ [32]. The discrete variable representation (DVR) approach [33] was used to calculate eigenvalues for coupled channels. Similar computational approaches, differing in the detailed numerical methods, have been applied recently also to the A and b states of NaRb [34].

Prior to the present experiments, the energies of the Cs$_2$ $(A - b) 0_u^+$ levels in the energy range of interest were approximately established by fits to two sets of data using the coupled channel approach. High-resolution data was obtained by Fourier transform spectroscopy (FTS) at Laboratoire Aimé Cotton (LAC) using transitions to the $X^1\Sigma_g^+$ state. The second set of data, from Tsinghua and Temple Universities, contained, besides additional high-resolution $(A - b) \rightarrow X$ transitions, lines from $2^3\Delta_{1g} \rightarrow b^3\Pi_{0u}$ emission [35] in an energy range that lies somewhat below the region of interest for the present work. This made it possible to establish the vibrational numbering for the $b^3\Pi_{0u}$ state and to construct a potential for this state. The coupled channel fit determined the spin–orbit coupling function between the A and the b states and hence the singlet–triplet mixing. The calculated energies for the highly mixed $(A - b) 0_u^+$ levels above the minimum of the A state exhibited an overall rms deviation of about 0.07 cm$^{-1}$ as compared with the high-resolution observations. However, the predominantly $b^3\Pi_{0u}$ levels were only established to about ±2 cm$^{-1}$ in the region of interest for the ground-state transfer. This region is above that for which data was obtained from $2^3\Delta_{1g} \rightarrow b^3\Pi_{0u}$ emission [35], but lower than the regime where $b^3\Pi_{0u}$ levels acquire sufficient singlet character to be observed in the FTS work.

Because of the uncertainty in the positions of mixed $(A - b)$ levels in this region, we decided to perform a systematic, broad-range search around expected transition energies in the wavelength range from 1329 to 1365 nm. For this, we perform double STIRAP from [1] to [3] and back with a waiting time of typically $\tau = 1$ ms. During the waiting time, we irradiate the sample with laser $L_1$ at an estimated intensity of $5 \times 10^4$ mW/cm$^2$. Laser $L_1$ is a diode laser with grating feedback. On the time scale of our experiment, the resonator of the laser is sufficiently stable, allowing systematic tuning of the laser without locking the laser to its external resonator. We step the laser frequency in units of typically 20 MHz by tuning the piezo element on the grating. We monitor the laser wavelength with a homemade wavemeter at approximately 300-MHz accuracy. For the initial broad range line search we increased the repetition rate of the experiment by stopping evaporative cooling slightly before condensation sets in. Data points are taken essentially at the cycle rate of the experiment, which is given by the sample production time. We step the laser with each experimental cycle and look for a dip in the molecule number. Once such a dip is found, typically consisting of a few data points, we perform a more precise scan by locking the laser to the external, highly stable resonator and then the external resonator to the infrared frequency comb. This allows us to detune the laser with kHz precision. Figure 3a shows a typical loss resonance near 1351 nm. We reduce the laser intensity such that on resonance at most 80% of the molecules are lost within 20 µs. From such measurements the transition strength as given by the normalized Rabi frequency and the natural line width of the excited state can be deduced.

The typical width of the excited state molecular levels that we have identified is $2\pi \times 2$ MHz, in agreement with typical expected lifetimes. Figure 3b shows a measurement of the time dependence of the molecular loss. Here, we step the
5 Dark resonances with \(|v = 0, J = 0\)| and \(|v = 0, J = 2\)

In our recent work [21] we have greatly improved the value for the binding energy of the rovibrational ground state \(|5 = |v = 0, J = 0\rangle\) by determining the binding energy of \(|v = 73\rangle\) and using well-known data from conventional molecular spectroscopy [36, 37]. Our measurement was limited by the calibration of our wavemeter, not allowing us to determine the number of the teeth of the frequency comb, and by the precision of the spectroscopy data. Searching for \(|5\rangle\) in dark-state spectroscopy is now a straightforward task as only a range of about 0.002 cm\(^{-1}\) needs to be scanned. We do this by exciting the transitions from \(|3\rangle\) to \(|4\rangle\) with laser \(L_3\) and from \(|4\rangle\) to \(|5\rangle\) with laser \(L_4\) simultaneously. The intensity for \(L_4\) is typically \(5 \times 10^4\) mW/cm\(^2\). As is well known, the two light fields create a molecule–molecule dark state. The molecules initially in \(|3\rangle\) are lost unless laser \(L_4\) is on two-photon resonance, provided that the Rabi frequency \(\Omega_4\) on the fourth transition is equal to or greater than \(\Omega_2\), the Rabi frequency on the third transition. We look for the resonance condition with the rovibrational ground state \(|v = 0, J = 0\rangle\) for some of the excited levels that we found above. Table 1 lists the observed transition wavelengths. We check that we can identify the level with rotational quan-
Dark resonances involving $X^1 \Sigma_g^+$ state levels $|v = 73, J = 2\rangle$ and $|v = 0\rangle$ for two different intermediate levels. a, b Dark resonances with $X^1 \Sigma_g^+ \rightarrow |v = 0, J = 0\rangle$ and $|v = 0, J = 2\rangle$ involving the $\Omega_g^+$ excited state level $|v' = 63, J = 1\rangle$ at an excitation wavelength near 1345 nm. c, d Dark resonances with $X^1 \Sigma_g^+ \rightarrow |v = 0, J = 0\rangle$ and $|v = 0, J = 2\rangle$ involving the excited state level $|v' = 61, J = 1\rangle$ at an excitation wavelength near 1351 nm. The solid line in d is the result of a model calculation, solving the three-level master equation including laser bandwidth and loss, matched to the data giving $\Omega_3 = 2\pi \times 6$ kHz $\sqrt{I/(\text{mW/cm}^2)}$ and $\Omega_4 = 2\pi \times 4$ kHz $\sqrt{I/(\text{mW/cm}^2)}$ for $X^1 \Sigma_g^+ \rightarrow |v = 0, J = 2\rangle$. The corresponding calculation for $X^1 \Sigma_g^+ \rightarrow |v = 0, J = 0\rangle$ yields $2\pi \times 5$ kHz $\sqrt{I/(\text{mW/cm}^2)}$.

6 Conclusion

We observed several two-photon dark resonances that connect the intermediate rovibrational level $|v = 73, J = 2\rangle$ of the $X^1 \Sigma_g^+$ ground-state potential with the rovibrational ground state $|v = 0, J = 0\rangle$. At least one of the two-photon transitions is sufficiently strong for implementing STIRAP to $|v = 0, J = 0\rangle$ in the quantum gas regime, paving the way for the realization of a BEC of ground-state molecules. STIRAP can in principle be implemented in two ways, either in the form of two sequential two-photon STIRAP steps, or in the form of four-photon STIRAP [38, 39]. An attractive strategy for the production of a BEC of ground-state molecules relies on the addition of an optical lattice. Starting from an atomic BEC, pairs of atoms at individual lattice sites are produced in a superfluid-to-Mott-insulator transition [40]. These pairs can then be very efficiently associated on a Feshbach resonance and subsequently transferred to the rovibrionic ground state with STIRAP. The lattice has the advantage of shielding the molecules against inelastic collisions during the association process and subsequent state transfer. As proposed by Jaksch et al. [41], dynamical melting of the lattice should ideally result in the formation of a BEC of molecules in the rovibrionic ground state in a Mott-insulator-to-superfluid-type transition.

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