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Quantum logic for the control and manipulation of molecular ions using a frequency comb

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Abstract. We propose a scheme for the preparation, manipulation and detection of quantum states of single molecular ions. In this scheme, molecular and atomic ions are confined in radio-frequency Paul trap and share common modes of motion. A frequency comb laser field is used to drive stimulated Raman transitions that couple internal states of the molecular ion with the motion of ions. State transfer from the molecular ion to the atomic ion via the common mode of motion results in efficient state detection for the molecule. The coupling of molecular states to the motion and the subsequent sideband cooling of the ions provide a way to prepare the molecular ion in a well-defined state.

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1. Introduction

Due to their rich level structure, molecules are well suited for probing the time variation of the fundamental constants [1–6], precisely measuring parity violation [7, 8] and time-reversal non-invariance effects [9, 10], studying the quantum mechanical aspects of chemical reactions [11] and implementing scalable quantum information processing architectures [12]. Molecular ions are particularly attractive for these applications. Due to their near-perfect isolation from the environment, they have long storage and coherence times, which are required to achieve high measurement precision and to reduce systematic errors.

However, the control of molecular quantum states remains a challenge. Traditional methods of state detection for neutral atoms and atomic ions are difficult to apply in the case of molecules. It is hard to find a nearly closed cycling transition, which limits the applicability of standard fluorescence detection methods. Other detection methods such as resonance-enhanced multiphoton dissociation [13, 14] are destructive in nature. In addition, the large number of available energy levels complicates the preparation of a molecule in a single quantum state. While the translational motion of molecular ions can be sympathetically cooled to millikelvin temperatures, the rotational and vibrational degrees of freedom will still be in equilibrium with the environment. Since the typical spacings between the rotational levels of a molecule are of the order of 10–100 GHz, which is much lower than the thermal energy $kT/h \simeq 6$ THz at room temperature, several molecular states are populated in equilibrium with the environment. Due to the interaction of a molecule with black body radiation, internal degrees of freedom reach equilibrium on a timescale of the order of minutes [15–17].

Several methods for preparing molecular ions in a single quantum state have recently been demonstrated: for example optical pumping assisted by black body radiation [15, 16] and sympathetic cooling of translational degrees of freedom for molecular ions formed in a particular rovibrational state [18]. Other promising techniques, such as optical pumping using broadband light [19–21], sympathetic cooling of molecular ions in a cloud of ultracold neutral atoms [22] and cavity cooling [23, 24], have also been proposed and are currently under active experimental investigation.

Some proposals [17, 25–28] also consider coherent coupling between the internal states of molecular ions and their motion and subsequent cooling or detection of the motional degree of freedom as a way of preparing and detecting the molecular states. However, coherent coupling between an internal quantum state of the molecule and the motion of the ions in these schemes is typically [17, 25–27] achieved using pulses produced by continuous wave lasers. This approach may be difficult to implement experimentally given the number of molecular states one needs to address.

Alternatively, a frequency comb laser field can be used to couple the internal quantum states of an ion and its motion. This coupling has recently been experimentally demonstrated for hyperfine states of atomic Yb^+ ions [29]. Due to the large bandwidth and precise control afforded by the frequency comb, it is particularly suitable for addressing multiple molecular energy levels [30]. This allows us to apply ‘quantum logic’ ideas for the control and manipulation of molecular states that were initially developed for quantum logic gates in ion trap quantum computing and subsequently used for precision spectroscopy with atomic ions [27, 31, 32]. Here, on the basis of such quantum logic techniques [27, 31–33], we propose an experimental scheme to prepare, manipulate and detect the internal states of a cold trapped molecular ion.

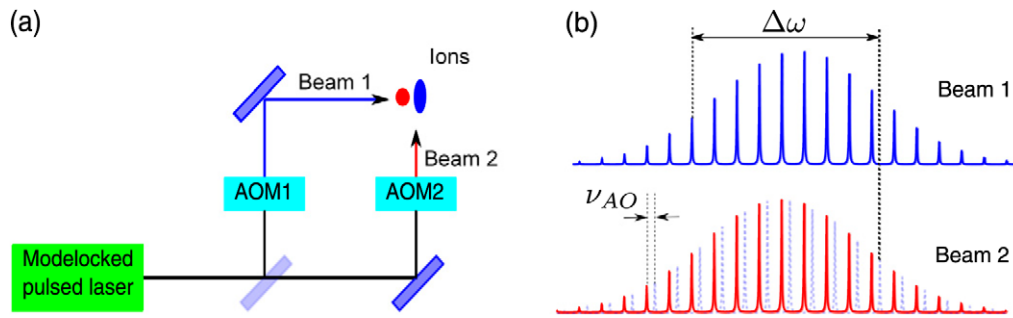


Figure 1. The proposed experimental setup. (a) The light emitted by a mode-locked pulsed laser with a repetition rate f_{rep} is split into two beams and sent through acousto-optical modulators to offset the relative frequency between two beams by ν_{AO} and incident upon the atomic and molecular ions from two different directions. (b) The spectrum of the frequency combs. If resonance conditions are satisfied, the setup can drive a stimulated Raman transition between a pair of energy levels $\Delta\omega$ apart.

2. The model

The experimental setup under consideration is shown in figure 1. We confine a diatomic molecular ion together with an atomic ion in a standard radio-frequency Paul trap. Due to Coulomb interaction, the atomic and molecular ions share common modes of motion. The motion of the molecular and atomic ions is cooled to the ground state by sideband cooling [34]. Two laser beams generated by a mode-locked pulsed laser with a repetition rate f_{rep} are offset by frequency ν_{AO} with acousto-optical modulators and focused on the ions from two different directions.

In order to drive a stimulated Raman transition between two quantum states separated by $\Delta\omega$, the repetition rate f_{rep} and offset frequency ν_{AO} should satisfy the resonance condition

$$\Delta\omega = Mf_{\text{rep}} \pm \nu_{\text{AO}}. \quad (1)$$

Here the integer number M is the comb index. The time-averaged resonance Rabi frequency between two states coupled by an off-resonance pulsed laser is [29]

$$\Omega = \Omega_0 \left(\frac{\Delta\omega\tau}{e^{\Delta\omega\tau/2} - e^{-\Delta\omega\tau/2}} \right), \quad (2)$$

where τ is the pulse duration, $\Omega_0 = s\gamma^2/2\Delta$ and $s = \bar{I}/I_{\text{sat}}$, \bar{I} is the average intensity, I_{sat} is the saturation intensity, Δ is the detuning of the pulsed laser from an excited state and γ is the excited state decay rate. The Rabi flopping is suppressed if the energy splitting between two states, $\Delta\omega$, is greater than the bandwidth of the pulsed laser, $1/\tau$. The typical pulse duration of a mode-locked Ti:sapphire pulsed laser of the order of $100 \text{ fs}^{-1} \text{ ps}$ provides sufficient bandwidth to address transitions between rotational and hyperfine states in a molecule. Pulses from both directions should arrive at the position of the ions at the same time; therefore the path length difference between two arms cannot exceed $c\tau$ (about $30 \mu\text{m}$ for a 100 fs pulse). This is similar to the requirement on the path length difference in, say, parametric down conversion experiments [35]. The Rabi flopping signal between two hyperfine ‘clock’ states of the atomic ion can serve as an alignment tool to ensure overlap between two pulses at the location of the ions.

To address the motion of the ions, we detune the spectral beat note between the two laser beams from the two-photon resonance between molecular states $|m_1\rangle$ and $|m_2\rangle$ by ω_t , the frequency of a common motional mode. In this case the interaction Hamiltonian in the Lamb–Dicke limit has the form [36]

$$\hat{H}_I = \hbar\eta\Omega(a^\dagger\sigma_- + a\sigma_+), \quad (3)$$

where $a^+(a)$ is the phonon creation (annihilation) operator for the common mode of motion of two ions, and $\sigma_+ = |m_1\rangle\langle m_2|$ ($\sigma_- = |m_2\rangle\langle m_1|$) is the raising (lowering) operator for the transition. The change in the molecular quantum state is accompanied by a simultaneous change of the motional state of the ions. In the ground state of motion, the Rabi frequency of a transition is equal to $\Omega_s = \eta\Omega$, where $\eta = k\sqrt{\hbar/2m\omega_t}$ is the Lamb–Dicke parameter, and k is the wave vector difference between the two laser beams.

The state of the molecular ion can be detected using the aforementioned quantum logic techniques [31, 32]. If the atomic and molecular ions were initially in a ground state of motion, driving a Raman transition that couples the state of the molecular ion $|m_1\rangle$ to a collective motional mode of the ions generates a phonon if the molecular ion was in the state $|m_1\rangle$, and does not change the motion if the molecular ion was in any other state. The phonon can be detected later by coupling the motion of the ions to the spin of an atomic ion, followed by atomic ion state detection using the standard fluorescence technique.

Due to the periodic structure of the frequency comb, scanning the offset frequency ν_{AO} produces a spectrum that repeats itself every f_{rep} . Measurement of the absolute energy difference between two states therefore requires knowledge of both the offset frequency ν_{AO} and the comb index M . The latter can be determined by measuring the spectrum as a function of the offset frequency ν_{AO} for several slightly different repetition rates and comparing the results [37].

We can also prepare a molecular ion in a well-defined quantum state by coupling internal and motional degrees of freedom. We start with atomic and molecular ions in the ground state of motion after sideband cooling and drive the $J, n = 0 \rightarrow J - 2, n = 1$ Raman transition in the molecule, where n is the number of phonons in a given motional mode (see figure 2). If the ions are in the ground state of motion, a decrease of the angular momentum via the $J, n = 0 \rightarrow J - 2, n = 1$ transition is allowed. However, the opposite transition $J - 2 \rightarrow J$ is not allowed, since it requires subtracting motional energy from the ions that are already in the ground state. If after each step phonons are removed from the trap by sideband cooling, the angular momentum J of the molecule decreases, leading to a buildup of population in the $J = 0$ or $J = 1$ state.

It is interesting to note that this cooling scheme can be made more efficient if we use the periodic structure of a frequency comb. For example, the proper choice of repetition rate and offset frequency allows us to drive transitions between at least two pairs of levels at the same time. In some special cases, for example, heavy molecules with no hyperfine structure confined in a tight trap, when the centrifugal distortion constant D is small compared to the rotational constant B , the splitting between energy levels

$$E(J+2) - E(J) \simeq 6B \left(\left(1 + 6\frac{D}{B}\right) + 4J \left(1 + 15\frac{D}{B}\right) + 4\frac{D}{B} (9J^2 + 2J^3) \right) \quad (4)$$

increases almost linearly with J and can be matched to the periodic structure of a frequency comb, which allows even more pairs of levels to be addressed simultaneously. This can speed up the cooling process even if the Rabi frequencies are not the same for different pairs of levels,

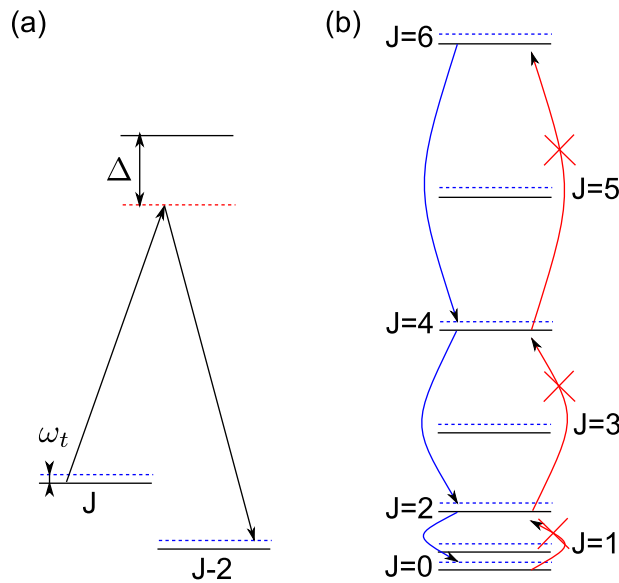


Figure 2. The cooling of molecular rotational states. (a) Stimulated Raman transition is driven on a ‘blue’ motional sideband so that the Raman transition from the rotational state J to $J - 2$ adds one phonon to the motional mode of the ions. (b) If the molecule is cooled to the ground state of motion and phonons are continuously removed by sideband cooling of a co-trapped atomic ion, transitions that increase J are not allowed, leading to an efficient buildup of the population in the $J = 0$ and $J = 1$ states.

since the transition will always result in a net decrease of the angular momentum J even if a perfect π -pulse for every transition is not produced simultaneously.

The number of Zeeman sublevels in the $J + 2$ state is larger than in the J state, therefore it is impossible to couple all the sublevels of the upper state to the lower one simultaneously via Raman transition, which leads to population trapping in the states with higher angular momentum. To avoid this, we can alternate the polarization of the Raman beams between several configurations to make sure that all sublevels in the upper $J + 2$ state are coupled to the sublevels of the lower J state. Alternatively, we can apply a weak magnetic field to mix the Zeeman sublevels. However, the latter approach is less desirable since Zeeman splitting can increase the number of energy levels one has to address.

3. Possible implementation

As a possible first step towards the implementation of this scheme, we consider an SiO^+ molecular ion trapped together with a Yb^+ atomic ion. The spectral properties of SiO^+ are known [38, 39]. The wavelength for the $A^2\Pi(\nu = 0) \rightarrow B^2\Sigma^+(\nu = 0)$ transition is about 414 nm, and the $X^2\Sigma^+(\nu = 0) \rightarrow B^2\Sigma^+(\nu = 0)$ transition wavelength is near 383 nm, close to the 370 nm transition of the atomic Yb^+ ion. Nearly diagonal Franck–Condon factors for the $X^2\Sigma^+(\nu = 0) \rightarrow B^2\Sigma^+(\nu = 0)$ transition in SiO^+ maximize the two-photon Rabi frequency. The absence of a hyperfine structure for the most abundant molecule, $\text{Si}_{28}\text{O}_{16}$, simplifies the energy level structure.

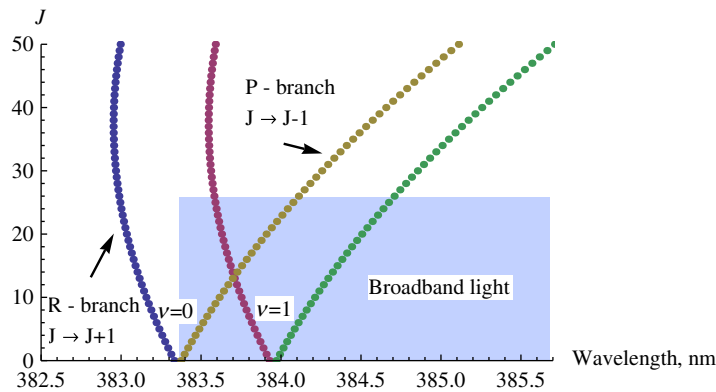


Figure 3. The optical pumping scheme for the SiO^+ molecule. The P ($J \rightarrow J - 1$ transitions), and R ($J \rightarrow J + 1$) branches for the SiO^+ molecule are well separated. The number of populated rotational states in a molecule can be reduced using optical pumping with spectrally filtered broadband light that excites $J \rightarrow J - 1$, but not $J \rightarrow J + 1$.

The efficiency of sympathetic cooling depends on the mass ratio between the two ions. A 1:1 mass ratio provides the highest efficiency due to the largest momentum transfer. However, sympathetic cooling was demonstrated for a wide range of masses, for example for the Al^+/Be^+ system with a 3:1 mass ratio [32], and is also feasible in the Yb^+ and SiO^+ system, where the ratio is 4:1.

The energy of the rotational states in the ground electronic state X and vibrational state $\nu = 0$ is $E_X(J) = BJ(J+1) + DJ^2(J+1)^2$, where for $\text{SiO}^+ B = 21.51 \text{ GHz}$ and $D = 33.1 \text{ kHz}$ [38]. At room temperature about 98% of population is distributed among states with an angular momentum from $J = 0$ to $J = 35$ of the lowest vibrational state $\nu = 0$. While it is still possible to apply the cooling scheme described in the paper directly, the large number of populated levels and magnetic fields can significantly increase the number of required cooling steps. Therefore, some initial cooling of the rotational degrees of freedom is desirable.

One approach to decrease the number of populated rotational states is optical pumping with spectrally shaped broadband light [19–21]. For the $X^2\Sigma^+(\nu = 0) \rightarrow B^2\Sigma^+(\nu = 0)$ transition in SiO^+ , the R ($J \rightarrow J + 1$ transitions) and P ($J \rightarrow J - 1$ transitions) branches are well separated (see figure 3). Light with intensity $dI/d\lambda = 1 \text{ mW nm}^{-1}$ can be produced by a gas discharge lamp or a femtosecond pulsed laser, and spectral filtering with a resolution better than 0.2 nm is achievable with a diffraction grating. Focusing this light into a $50 \mu\text{m}$ spot provides a scattering rate of about $10^5 \text{ photons s}^{-1}$. This scattering rate can decrease the number of populated rotational states to less than ten in about 1 ms for the final preparation of states with quantum logic schemes.

For a realistic average intensity of the mode-locked pulsed laser at an ion position of about 1000 W cm^{-2} , laser detuning $\Delta/2\pi = 20 \text{ THz}$, lifetime of the $B^2\Sigma^+$ excited state $1/\gamma = 70 \text{ ns}$ and saturation intensity of the molecular transition $I_{\text{sat}} = 45 \text{ W m}^{-2}$, one can expect the time-averaged Rabi frequency (2) on the carrier transition to be $\Omega_0/2\pi = 0.2 \text{ MHz}$. For a Lamb–Dicke parameter $\eta = 0.1$, the duration of the π -pulse on a sideband transition of a molecule is about $100 \mu\text{s}$. The sideband cooling step should have a comparable duration. Assuming that the rotational population is distributed among the ten lowest J states and that it takes about ten cycles to bring the population from the J to the $J - 2$ level, we estimate the

total cooling time to be of the order of 20 ms, which is much faster than the ~ 20 s achievable by alternative schemes that rely on black body radiation for repumping between rotational states [15, 16].

Spontaneous emission can remove the molecule out of the cooling cycle and leave it in a different rotational or even a different vibrational state. Assuming that the bandwidth of the mode-locked pulsed laser $\sim 1/\tau \ll \Delta$, the total photon scattering rate can be estimated as $R_s = \gamma \Omega / 2\Delta = 0.07 \text{ s}^{-1}$, much slower than the duration of the cooling sequence. For the far-off-resonant light, the molecule scatters most of the photons elastically. The rate of Raman scattering that changes the state of the molecule can be several orders of magnitude lower than the total scattering rate.

Another mechanism lowering the efficiency of the cooling protocol is the accidental coincidence between the Raman sideband transition from the J to the $J - 2$ state and the $J - 1 \rightarrow J + 1$ transition that can populate angular momentum levels that have already been depopulated. However, the probability of this coincidence, assuming only the $N_J = 10$ lowest rotational levels are populated, is relatively low:

$$p \sim 4N_J \Omega_0 / (2\pi f_{\text{rep}}) \simeq 0.1,$$

where $f_{\text{rep}} \simeq 80 \text{ MHz}$ is the typical repetition rate of a mode-locked pulsed laser. This coincidence can be avoided by a proper choice of the laser repetition rate or a decrease in the Raman laser power.

The accidental coincidence between different transitions driven by a frequency comb can also present a problem during state detection. However, one can always optimize the repetition rate of the pulse laser to avoid this coincidence for the particular state. Another problem that can limit state detection fidelity is non-perfect sideband cooling, or ion heating during the experimental sequence, which introduces an error during the coupling of internal and motional states. Nevertheless, at the end of the protocol, the molecule is left in one of two known rotational states and, similar to [31, 32], the state detection protocol can be repeated several times to improve the fidelity.

The quantum logic schemes presented above are general; they do not impose restrictive requirements on molecular structure and can be applied to a wide range of molecular ions. The experimental realization of these schemes can open the way to controlling the quantum states of molecular ions and finding applications in precision measurements, quantum information and quantum chemistry.

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During the preparation of the manuscript we became aware of a similar work by Dietrich Leibfried [40].

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