

# Spectroscopy of atomic and molecular ions using quantum logic

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**Abstract.** Recently developed techniques for quantum computation using trapped ions allow precise coherent control of the internal and external states of single atoms. Here we report how these techniques can be employed to perform precision spectroscopy of atomic and molecular ions that lack accessible transitions for laser cooling and detection. Furthermore, we discuss how quantum logic can be used to laser-cool molecules to near their rotational and vibrational ground state by avoiding detrimental spontaneous emission of photons from the molecule.

**Keywords:** Coherent control of atomic interactions with photons; Optical cooling of atoms; Optical cooling of molecules; trapping; Laser spectroscopy; Spectroscopic techniques

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## QUANTUM LOGIC SPECTROSCOPY

The ongoing quest for a scalable quantum computer based on trapped and laser-cooled ions has resulted in the development of powerful coherent control techniques during the past ten years [1, 2]. Starting in 1995, a controlled-NOT (C-NOT) gate between a trapped atomic ion and its motional mode in the trap was experimentally realized [3]. After this demonstration of coherent control over the internal and external degrees of freedom in an atomic system, quantum information processing with trapped ions has flourished, and several results, such as teleportation [4, 5], error-correction [6] and the implementation of the Deutsch-Jozsa [7] and semi-classical Fourier transformation [8] algorithms, have been achieved. The potential for scaling the trapped ion approach to quantum computation was demonstrated in recent experiments entangling six [9] and eight [10] ions. T. Körber reported on the latest quantum information experiments by the Innsbruck group at the NNP conference 2006.

At the same time, the development of laser cooling techniques made cold and ultra-cold atomic samples available for optical spectroscopy. This allowed for long interrogation times and reduced Doppler shifts, resulting in unprecedented uncertainties exceeding one part in  $10^{15}$  in atomic clocks [11, 12]. Recently, an optical clock based on a forbidden transition in a single mercury ion has achieved an uncertainty of  $7.2 \times 10^{-17}$  [13], thus exceeding the performance of the best cesium fountain standards [14].

Unfortunately, advances were limited to atomic species that have not only an interesting spectroscopy transition, but also a suitable transition for cooling, detection and state preparation. For this reason, single ion optical clocks base on particularly interest-

ing candidates [15], such as the isotopes of aluminum and boron [16, 17], could not be realized in the past.

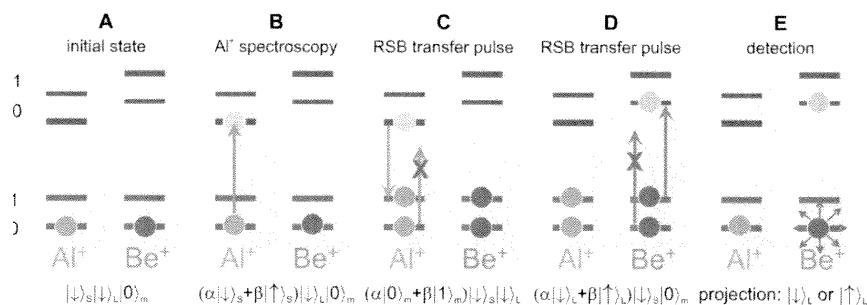
We can overcome this limitation by using simple quantum logic techniques that allow us to share properties between a “spectroscopy” and a “logic” ion [17, 18] and to combine their best features. The well-controllable logic ion provides sympathetic cooling [19], internal state preparation and detection of the ion with an interesting spectroscopic transition. In a simple picture, the logic ion can be viewed as both, a remote control and a sensitive quantum sensor for the internal and external state of the spectroscopy ion.

Quantum logic is implemented by laser-induced coupling of the internal and external degrees of freedom of the two ions [1, 20]. Applying appropriate laser pulses, internal state information can be transferred from the spectroscopy to the logic ion. As an example for this state transfer scheme, let us consider two ions in a linear Paul trap. The Coulomb interaction between the ions couples their motional modes. We are interested in one of the resulting axial normal modes with excitation quantum number  $m$ . This mode can be cooled to the ground state ( $m \approx 0$ ) by use of Raman sideband cooling [21, 22] on the logic ion. We consider only two internal levels of the spectroscopy (S) and logic (L) ion, which we denote  $|\downarrow\rangle_{S,L}$  and  $|\uparrow\rangle_{S,L}$ . Fig. 1 illustrates the coherent transfer process. Initially, we assume both ions to be in the internal ground state (Fig. 1A). Then, a laser pulse is applied to interrogate the transition of interest in the spectroscopy ion, thus creating a superposition of ground and excited state with state amplitudes  $\alpha$  and  $\beta$  (Fig. 1B). The internal state superposition is coherently mapped to a motional superposition by applying a laser pulse of appropriate length and frequency on the spectroscopy ion. This so-called red-sideband (RSB) pulse transfers the excited state to the ground state while adding an excitation to the transfer mode. At the same time, population in the ground state  $|0\rangle_N|0\rangle_m$  remains unchanged, since the laser pulse could be resonant only to a state  $|\uparrow\rangle_S|-1\rangle_m$ , which does not exist (Fig. 1C). This mapping process can be reversed on the logic ion by applying laser light resonant to a red-sideband transition in the logic ion (Fig. 1D). Overall, the electronic superposition created in the spectroscopy ion has then been transferred to an electronic superposition in the logic ion, where it can be efficiently detected via electron shelving [15] (see Fig. 1E).

In a demonstration experiment [18], we were able to successfully interrogate a test transition in  $^{27}\text{Al}^+$  using this novel spectroscopic method. The signal contrast, including state transfer and detection efficiency, exceeded 90 %. Preliminary experimental results on the narrow clock transition in  $^{27}\text{Al}^+$  demonstrate its potential for precision spectroscopy of ions that cannot be directly laser-cooled [23].

A quantum logic spectroscopy apparatus is very versatile: to investigate a different species, one needs only to change the laser for the spectroscopy transition; the (more complex) laser system required to control the logic ion remains the same.

Possible applications of this new method are manifold. It could allow unprecedentedly high resolution spectroscopy on a wide range of sympathetically cooled atomic and molecular species with special spectroscopic properties, such as an improved sensitivity to a variation of fundamental physics constants [24, 25, 26], or tests of QED via precision spectroscopy of  $\text{He}^+$  [27].



**FIGURE 1.** Spectroscopy and transfer scheme for spectroscopy (S) and logic (L) ions sharing a common normal mode of motion, the “transfer mode”, with excitation  $m$ . (Only the ground and first excited states of the transfer mode are shown.) (A) Initialization to the ground internal and transfer-mode states. (B) Interrogation of the spectroscopy transition. (C) Coherent transfer of the internal superposition state of the spectroscopy ion into a motional superposition state by use of a red sideband (RSB)  $\pi$ -pulse on the spectroscopy ion. (D) Coherent transfer of the motional superposition state into an internal superposition state of the logic ion by use of an RSB  $\pi$ -pulse on the logic ion. (E) Detection of the final state on the logic ion.

## ROTATIONAL COOLING OF SMALL MOLECULES

One potential application for quantum logic spectroscopy is laser cooling of molecular ions to the absolute ground state of their internal and external degrees of freedom. This has been a long-standing, but yet unfulfilled, quest for precision spectroscopy and coherent manipulation of molecules. Although there is extensive literature on experiments aimed toward creation of ground state molecules via photo-association starting from ultra-cold neutral atoms [28], this goal has been only partially achieved so far [29]. Whereas sympathetic cooling of the motional degrees of freedom of neutral and charged molecules have been performed [30, 31, 32], only few proposals exist for laser cooling the internal rovibrational states [33, 34], usually employing several laser systems. A probabilistic state preparation scheme to prepare specific molecular states has recently been proposed in [35] and was reported by M. Drewsen at the NNP conference 2006.

Deterministic preparation of a specific internal atomic state is typically achieved via optical pumping on suitable transitions. It involves spontaneous emission of photons to ensure irreversibility. If no suitable transition for optical pumping is available, or if spontaneous emission of photons leads to population of unwanted states, state preparation using quantum logic can be advantageous. We have demonstrated the feasibility and efficiency of deterministic quantum logic internal state preparation by preparing all  $^1S_0$ ,  $F = 5/2$ ,  $m$  states and performing spectroscopy of all  $\Delta m = 0$  components of the  $^1S_0$ ,  $F = 5/2 \leftrightarrow ^3P_1$ ,  $F = 7/2$  transition in  $^{27}\text{Al}^+$  [18].

Here, we propose cooling of the rotational and vibrational degrees of freedom in molecules based on a similar state preparation technique involving simple quantum logic methods. In the following, we will describe a three-step cooling scheme for the rotational states of diatomic molecules, as illustrated in Fig. 2. For sufficiently small molecules, such as  $\text{MgH}^+$  or  $\text{CaH}^+$ , no vibrational cooling is necessary, since they

have a large vibrational splitting resulting in more than 99 % ground state occupation at room temperature. We consider a single molecular ion, trapped together with a logic ion in the same potential well of a linear trap. As described above, one of the shared motional modes is first cooled to the ground state. We assume that we can couple the  $|N=0\rangle \equiv |0\rangle_N$  to the  $|N=2\rangle \equiv |2\rangle_N$  rotational state of the molecule's electronic ground state by driving a Raman transition via an electronically excited state.

(i) Starting with a molecule in the  $|2\rangle_N$  rotational state, a red-sideband optical Raman pulse (“transfer pulse”, Fig. 2A) is applied to transfer the population to the  $|0\rangle_N$  rotational target state, while exciting a motional quantum

$$|2\rangle_N|0\rangle_m \rightarrow |0\rangle_N|1\rangle_m.$$

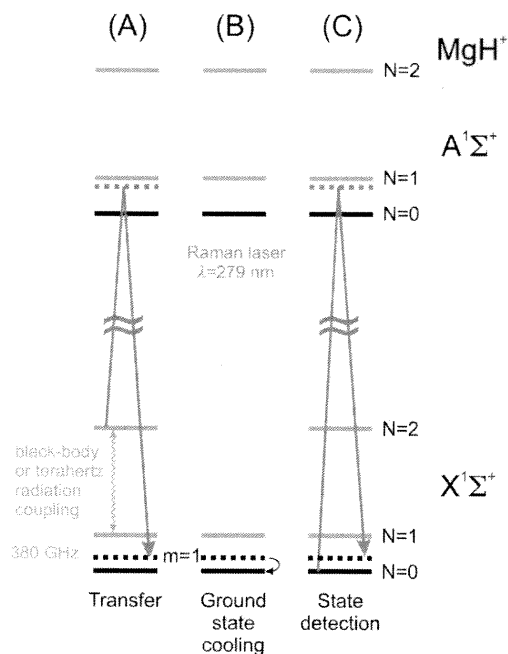
(ii) In the second step, we remove the motional excitation via ground-state cooling of the logic ion

$$|0\rangle_N|1\rangle_m \rightarrow |0\rangle_N|0\rangle_m.$$

During ground-state cooling, photons are scattered on the logic ion to ensure irreversibility of the overall process: Applying another transfer laser pulse to a molecule already in the target state  $|0\rangle_N|0\rangle_m$ , will not change its state, since the pulse would couple only to  $|2\rangle_N|-1\rangle_m$ , which does not exist. Irreversibility is important, since imperfect transfer pulses may require the application of several such pulses to ensure efficient state transfer. Thus, we have achieved rotational cooling of the molecule by shifting the spontaneous scattering of photons to the logic ion via quantum control techniques.

(iii) We can test the success of the cooling process by detecting the internal state of the molecule via the logic ion. This is shown in Fig. 2C: We apply a red-sideband test pulse that leaves the molecule in the electronic and rotational ground state (e.g., by coupling two Zeeman or hyperfine states of the electronic ground state), but excites the shared motional mode of the molecular and logic ion, which can be detected with high efficiency on the logic ion analogous to Fig. 1D,E. For all rotational states except the ground state, the Raman lasers would be detuned too far from the excited electronic state to induce appreciable coupling. A similar detection scheme has been proposed in [35].

Although we actively cool only the  $|2\rangle_N$  rotational state, higher excitations are also cooled, owing to their coupling to the  $|2\rangle_N$  state mediated by black-body radiation at room temperature [36, 37]. This relaxation rate can be further enhanced by applying infrared radiation from a lamp [38]. In particular, significant population will accumulate in the  $|1\rangle_N$  rotational state, which cannot be coupled to  $|0\rangle_N$  or  $|2\rangle_N$  via a two-photon transition owing to selection rules [39]. In order to achieve ground state cooling, we need to transfer population from the  $|1\rangle_N$  to the  $|0\rangle_N$  state with high efficiency. One possibility is to drive population from  $|1\rangle_N$  to  $|2\rangle_N$  by means of an appropriate light pulse, possibly from a terahertz laser [40, 41]. Once the population is in  $|2\rangle_N$ , cooling as described above will bring the molecule to the ground state. Success of transfer from  $|1\rangle_N$  to the target state  $|0\rangle_N$  can be confirmed by the state detection scheme described in step (iii) above. A sufficiently fast recooling cycle will allow us to prepare the molecule with high success rate in the rotational, vibrational and electronic ground state. It is important to note that the usual problem of populating undesired states by direct laser cooling is avoided in our scheme by eliminating spontaneous emission in the molecule.



**FIGURE 2.** Laser cooling of molecules, exemplified by the  $\text{MgH}^+$  diatomic molecule (energy levels not to scale).  $N$  denotes the rotational quantum number of the molecule, and  $m$  the vibrational quantum number of a motional mode shared by the two ions in the trap. (A) Transfer of the population from  $|2\rangle_N|0\rangle_m$  to  $|0\rangle_N|1\rangle_m$  by application of a Raman laser pulse. Population transfer from  $|1\rangle_N$  to  $|2\rangle_N$  could be achieved via black-body or terahertz radiation. (B) Ground-state cooling via the logic ion ensures irreversibility of the transfer step. (C) Nondestructive detection of population in the ground state. A Raman pulse coupling  $|0\rangle_m$  to  $|1\rangle_m$  via a specific electronically excited state has non-negligible Rabi frequency only if the molecule is in the  $N = 0$  state initially. This excitation can then be efficiently detected on the logic ion (see Fig. 1D,E).

The level scheme of  $\text{MgH}^+$  shown in Fig. 2 is of course a simplification. External fields may lift the degeneracy of the rotational manifold. Therefore, multiple transfer pulses with well-chosen Raman laser polarizations need to be applied to address and transfer all states. Also, hyperfine structure can increase the number of levels in a rotational manifold, all of which need to be addressed by individual transfer pulses. Preparation of the molecule in a single hyperfine state in the rotational and electronic ground state can be accomplished by coupling each hyperfine component to the target state by means of the detection scheme [step (iii)] described above. Alternatively, hyperfine components could be coupled by applying radio-frequency pulses followed by quantum logic state detection. The same methods can also be used to prepare a specific (nonzero) rotational or vibrational state of a molecule. As long as all involved levels are within reach of lasers frequency shifted by electro- and/or acousto-optic modulators, the substructure of electronic and rovibrational levels represent no fundamental obstacle for the

realization of this cooling and deterministic state preparation scheme.

Molecules with small vibrational spacing compared to room temperature require not only rotational but also vibrational cooling. Quantum logic-assisted cooling of a single vibrational state, together with black-body radiation that couples other levels to this state, allow in principle cooling of vibrational states as well. One difficulty arises from the fact that rotational and vibrational cooling condition each other, since the Raman lasers for the state transfer are resonant for a specific set of rovibrational levels only. Therefore, it is desirable to increase the coupling between different rovibrational levels by use of a lamp [38] to shorten the cooling time.

Having ground-state cooled molecules at one's disposal, a large variety of fascinating experiments can be performed. One possibility is to conduct precise measurements of various electronic and rovibrational transitions. This would be particularly interesting for the astrophysically important  $\text{CaH}^+$  molecule, for which no experimental data are available [42, 43]. Other areas that could profit from quantum logic spectroscopy of molecules include measurements of a possible time variation of the electron to proton mass ratio ( $m_e/m_p$ ) via  $\text{H}_2^+$  and  $\text{HD}^+$  spectroscopy [26] and a search for the electron electric dipole moment in molecular ions, such as  $\text{HfH}^+$ ,  $\text{HfF}^+$  or  $\text{PtH}^+$  [44, 45, 46, 47, 48].

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