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Cold molecules: techniques and applications

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Introduction

Over the past decades, the development of experimental techniques for the cooling and trapping of atoms down to nanokelvin temperatures has revolutionized atomic physics [1]. These advancements have opened up a range of new applications for both neutral atoms and atomic ions in the realms of quantum computation, collision physics and precision measurements. A similar revolution is currently underway in molecular and chemical physics, fueled by new methods for the cooling and motional control of molecules [2–4]. In the present article, we highlight techniques and applications of “cold molecules” with examples from our own work.

Cooling techniques

For atomic systems, both neutral and ionic, the starting point of a typical experiment is Doppler laser cooling [1] which allows the preparation of samples at temperatures in the millikelvin regime or slightly lower. The atoms are usually confined in magneto-optic, magnetic or optical-dipole traps in the case of neutrals and radiofrequency electrodynamic (Paul) or combined electric and magnetic (Penning) traps in the case of ions [1, 5]. Advanced techniques like evaporative cooling for atoms and resolved-sideband cooling for ions eventually allow to reach quantum degeneracy in neutrals and the quantum-mechanical motional ground state of the trap in the case of the more tightly confined ions. For molecules, however, laser cooling, the work horse technique of atomic physics, is only applicable to a small class of systems and even then only with limited efficacy. The reason for this lies in the complexity of molecules. In addition to the electronic and spin degrees of freedom present in atoms, molecules exhibit rotational and in particular vibrational motions which render the implementation of closed optical cycles required for Doppler laser cooling experimentally very challenging. Although laser cooling and even magneto-optical and magnetic trapping has by now been achieved for a few selected molecular systems [6, 7], the vast majority of cold-molecules experiments relies on alternative methods for the preparation of cold samples.

In the case of molecular ions, sympathetic cooling by the interaction with trapped, laser-cooled atomic ions has proven to be a highly versatile approach which is applicable to a wide variety of systems ranging from diatomic molecules to proteins [8]. The cold trapped ions form ordered structures in the trap, usually referred to as “Coulomb crystals”, which can be imaged by collecting the fluorescence of the laser-cooled atomic ions. An example of a mixed-species Coulomb crystal consisting of laser-cooled Ca^+ and sympathetically-cooled N_2^+ ions is shown in Fig. 1.

For neutral molecules, one of the most widely used methods is Stark deceleration of molecular beams [9]. The principle of the method is illustrated in Fig. 2. A beam of dipolar molecules is coupled into an assembly of dipole electrodes

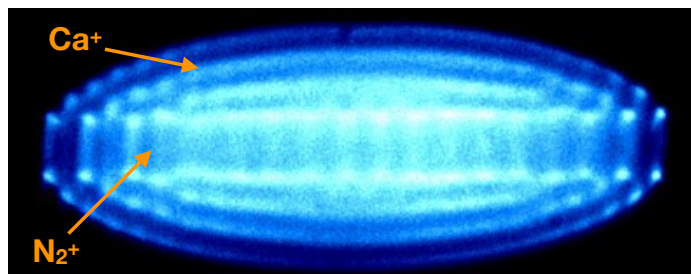


Fig. 1: False-colour fluorescence image of a Coulomb crystal of laser-cooled Ca^+ and sympathetically cooled molecular N_2^+ ions. The non-fluorescing molecular ions are intercalated into the Ca^+ crystal and appear as a non-fluorescing region in the centre of the image.

to which time-varying electric potentials are applied. The time-varying inhomogeneous electric fields produce Stark potential energy barriers which successively slow down the dipolar molecules traversing the assembly. The slow beam of molecules exiting the decelerator can then be trapped in a magnetic or electrostatic trap.

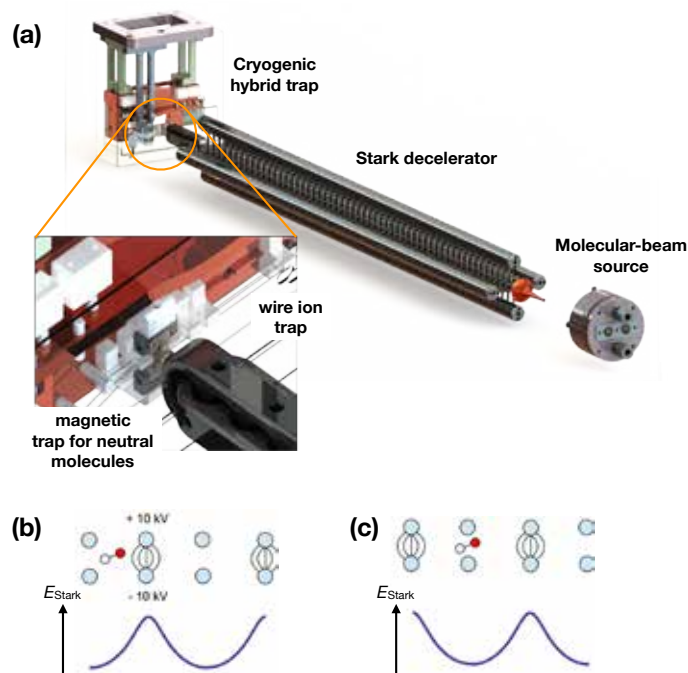


Fig. 2: (a) Schematic of an experimental setup for the hybrid trapping of cold molecules and cold molecular ions consisting of a molecular-beam source, a Stark decelerator for the slowing of the molecular beam and a combined magnetic/ion trap. (b,c) Principle of Stark deceleration (from Ref. [4]). (b) A molecular beam of dipolar molecules traverses an array of dipole electrodes alternately charged to high voltage. The inhomogeneous electric fields produce potential-energy barriers for molecules in low-field seeking Stark states. A packet of molecules is slightly slowed down as it approaches a barrier. (c) Before the molecules are re-accelerated at the other side of the barrier, the fields are switched to the subsequent pair of electrodes to initiate the next deceleration stage. This scheme is continued until the packet of molecules has almost come to a standstill.

Cold interactions: Ion-neutral hybrid systems

For a long time, the fields of cold neutrals and cold ions have developed in parallel. However, about a decade ago a new generation of experiments emerged in which neutrals and ions were simultaneously trapped in the same region of space [10–12]. This development enabled the study of ion-neutral interactions at very low temperatures, accessing a regime of intermediate strength between weak neutral-neutral and strong ion-ion interactions. The first generation of experiments combined cold neutral atoms with cold atomic and molecular ions, as illustrated with the setup in operation in our laboratory in Basel shown in Fig. 3. Such “hybrid” experiments provide an ideal platform for studies of ion-neutral collisions at very low temperatures. Over the past years, it became clear that even seemingly simple atomic collision systems exhibit a rich variety of processes comprising elastic, inelastic and reactive collision processes [13–16]. These include sympathetic cooling of the ions by the ultracold atoms [17–19], non-equilibrium dynamics of the ion motion [20–22], unusual light-driven chemical processes leading to the formation of cold molecules and subtle effects of intermolecular interactions driving the collision dynamics which are usually obscured at higher temperatures [4, 23, 24].

In a next generation of experiments currently coming online, the cold atoms are replaced with cold molecules produced by, e.g., Stark deceleration (see Fig. 2 (a)). These developments will push hybrid trapping technology to a new level and enable for the first time the simultaneous trapping of neutral molecules and molecular ions at very low temperatures. These experiments aim at the exploration of distinctly molecular effects in ion-neutral interactions in the cold regime. This opens up perspectives to study molecular energy transfer and chemical dynamics under precisely controlled conditions and ultimately to unravel the detailed properties of even very large polyatomic molecules [26].

Keeping track of time with a single molecule

Another exciting, currently emerging application of cold molecules lies in the field of metrology. Presently, optical atomic

clocks are the most precise man-made measurement tools, capable of keeping time with 10^{-18} fractional uncertainty which is equivalent to losing or gaining less than one second over the age of the universe [27–29]. Commercialization of atomic clocks leads to many applications such as satellite navigation, geodesy and global time keeping [27]. Atomic clocks have allowed for precision spectroscopic measurements testing fundamental physics theories. For example, an atomic clock was used to detect the time dilation due to a gravitational field over only 30 cm height difference [30].

Current atomic clocks utilize the precise measurement of an electronic transition in an atom in the visible or ultraviolet spectral range for the purpose of time keeping. In our laboratory, we are in the process of building a variant of an atomic clock which will exploit a vibrational transition in a molecule instead. Molecular vibrational frequencies typically lie in the infrared spectral domain thus enabling clocks in a different spectral regime than the ones presently used. Moreover, precise spectroscopic measurements of molecular vibration transitions will allow tests of fundamental physical concepts including a possible time variation of fundamental constants like the ratio of the electron and proton masses or the hypothetical existence of a fifth fundamental force [31, 32]. In our experiment, we use molecular nitrogen (N_2^+) ions which possess many advantageous systematic characteristics for these purposes [33, 34].

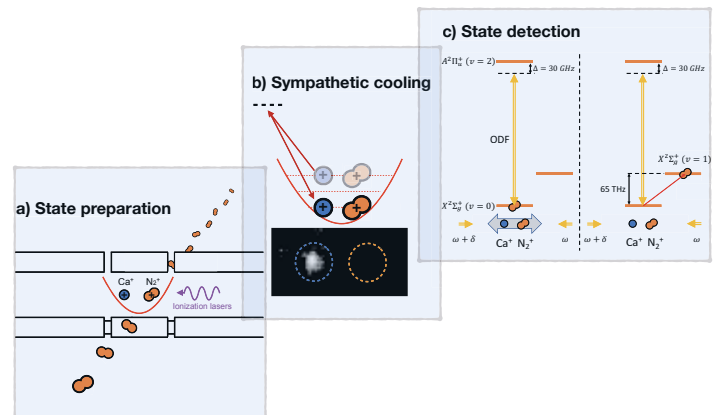


Fig. 4: Quantum techniques for the spectroscopy of single molecules. a) STATE PREPARATION. A beam of neutral N_2 molecules (orange) passes through the trap center where a single atomic Ca^+ ion (blue) is trapped and Doppler cooled. Pulsed lasers (magenta) ionize a single molecule into the desired molecular state. Immediately after ionization, the molecule is trapped by the electric trapping fields which create a confining harmonic potential (red line). b) SYMPATHETIC COOLING. The positively charged atom and molecule form a Coulomb crystal due to their mutual repulsion and the harmonic confinement. Lasers that scatter photons only from the atom (red arrows) are used to dissipate energy of the atom-molecule crystal until it is cooled to the motional ground state of the trap (dashed lines). Image of a $Ca^+-N_2^+$ crystal taken in our laboratory (bottom). Only the atom scatters photons and is therefore visible. c) STATE DETECTION. Left: Two counter-propagating laser beams (frequencies ω and $\omega + \delta$) create an optical-dipole force (ODF) modulated at the motional frequency δ of the ion crystal. The ODF lasers are detuned closely ($\Delta \approx 30$ GHz) to a transition between the initial state of the molecule (here $X^2\Sigma_g^+(v=0)$) and an auxiliary state ($A^2\Pi_u^+(v=2)$). The ODF coherently drives the motion of the atom-molecule crystal if the molecule is in its initial state. Right: Spectroscopic interrogation (red line) excites the molecule to a different state (here it is the $X^2\Sigma_g^+(v=1)$ first vibrationally excited state). Due to the increased detuning (here 65 THz), the ODF lasers do not excite the motion in the crystal anymore thus indicating the spectroscopic excitation of the molecule.

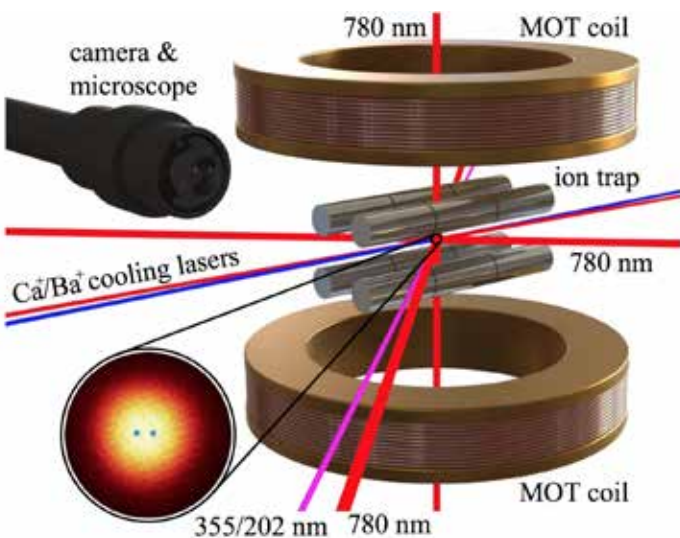


Fig. 3: Schematic of the ion-neutral hybrid trapping experiment in Basel consisting of a radiofrequency trap for atomic and molecular ions combined with a magneto-optical trap (MOT) for neutral Rb atoms (from Ref. [25]). The inset shows superposed false-colour fluorescence images of two laser cooled Ca^+ ions (blue) immersed in cloud of ultracold Rb atoms (yellow-red).

An atomic clock requires the ability of preparing the atom in a specific quantum state, of freezing its translational motion and of detecting the atomic state with high fidelity. The complex energy-level structure of molecules, however, renders the implementation of a molecular clock extremely challenging. To overcome these challenges, we combined techniques from ion-trap quantum computing and precision molecular spectroscopy.

First, we use a resonance-enhanced multi-photon ionization (REMPI) technique pioneered in our group [35] to produce single molecular ions in a well-defined quantum state (see Fig. 4a).

Second, the single state selected molecular ions are sympathetically cooled by the strong Coulomb interaction with a single Ca^+ ion in an ion trap. By addressing individual energy levels of their combined motion in the quantum regime, the ions are cooled down to the quantum-mechanical motional ground state (see Fig. 4b).

Third, a method to read out the quantum state of the molecule needs to be implemented [36, 37]. Direct non-destructive detection of the molecular state is not possible due to its complex energy-level structure and detection methods based on chemical reactions [33, 35] are inherently slow due to their destructive nature. Instead, we use quantum-logic spectroscopy (QLS), an indirect technique originally invented in the realm of atomic-ion clocks and ion-based quantum technologies [38]. In our experiments, we apply a state-dependent optical-dipole force (ODF) on the molecule using a modulated laser beam. The laser modulation frequency matches the harmonic frequency of the atom-molecule crystal in the trap such that it excites coherent motion in the crystal (denoted as $|\bar{n}\rangle_{\text{crys.}}$), similar to the way one rocks a swing. We tune the laser frequency to interact only with a specific state of the molecule (denoted as $|\downarrow\rangle_{\text{mol.}}$). Other molecular states (denoted $|\uparrow\rangle_{\text{mol.}}$) do not interact with the laser field and hence no motion is induced on the crystal ($|0\rangle_{\text{crys.}}$). The force depends on the molecular state and entangles the motion of the atom-molecule crystal with the molecular state,

$$|\Psi\rangle = \alpha|\downarrow\rangle_{\text{mol.}} \otimes |\bar{n}\rangle_{\text{crys.}} + \beta|\uparrow\rangle_{\text{mol.}} \otimes |0\rangle_{\text{crys.}}$$

Here, α and β are the initial coherent-superposition amplitudes of the molecular state. Detecting the coherent motion of the crystal collapses the wave function into one of the molecular states with probability $|\alpha|^2$ and $|\beta|^2$ respectively (see Fig. 4c). Since the coherent motion is common to both the atomic ion and the molecule, detection is most easily performed on the atomic ion by fluorescence methods. In this way, a non-destructive (in a chemical sense) detection of the molecular state is achieved, enabling precision-spectroscopic measurements on vibrational transitions of N_2^+ as a prerequisite for its application as a clock.

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- [1] H. J. Metcalf and P. van der Straten, *Laser Cooling and Trapping* (Springer, New York, 1999).
- [2] L. D. Carr, D. DeMille, R. V. Krems and J. Ye, *New J. Phys.* **11**, 055049 (2009).
- [3] M. Lemesko, R. V. Krems, J. M. Doyle and S. Kais, *Mol. Phys.* **111**, 1648 (2013).
- [4] S. Willitsch, *Adv. Chem. Phys.* **162**, 307 (2017).
- [5] F. G. Major, V. N. Gheorghie and G. Werth, *Charged Particle Traps* (Springer, Berlin and Heidelberg, 2005).
- [6] J. Barry, D. McCarron, E. Norrgard, M. Steinecker and D. DeMille, *Nature* **512**, 286 (2014).
- [7] H. J. Williams, L. Caldwell, N. J. Fitch, S. Truppe, J. Rodewald, E. A. Hinds, B. E. Sauer and M. R. Tarbutt, *Phys. Rev. Lett.* **120**, 163201 (2018).
- [8] S. Willitsch, *Int. Rev. Phys. Chem.* **31**, 175 (2012).
- [9] S. Y. T. van de Meerakker, H. L. Bethlem, N. Vanhaecke and G. Meijer, *Chem. Rev.* **112**, 4828 (2012).
- [10] A. T. Grier, M. Cetina, F. Oručević and V. Vuletić, *Phys. Rev. Lett.* **102**, 223201 (2009).
- [11] S. Schmid, A. Härter and J. Hecker Denschlag, *Phys. Rev. Lett.* **105**, 133202 (2010).
- [12] C. Zipkes, S. Palzer, L. Ratschbacher, C. Sias and M. Köhl, *Phys. Rev. Lett.* **105**, 133201 (2010).
- [13] W. G. Rellergert, S. T. Sullivan, S. Kotochigova, A. Petrov, K. Chen, S. J. Schowalter and E. R. Hudson, *Phys. Rev. Lett.* **107**, 243201 (2011).
- [14] F. H. J. Hall, M. Aymar, N. Bouloufa-Maafa, O. Dulieu and S. Willitsch, *Phys. Rev. Lett.* **107**, 243202 (2011).
- [15] J. Joger, H. FÜRST, N. Ewald, T. Feldker, M. Tomza and R. Gerritsma, *Phys. Rev. A* **96**, 030703 (2017).
- [16] T. Sikorsky, Z. Meir, R. Ben-shlomi, N. Akerman and R. Ozeri, *Nature communications* **9**, 920 (2018).
- [17] I. Sivarajah, D. S. Goodman, J. E. Wells, F. A. Narducci and W. W. Smith, *Phys. Rev. A* **86**, 063419 (2012).
- [18] K. Ravi, S. Lee, A. Sharma, G. Werth and S. A. Rangwala, *Nat. Commun.* **3**, 1126 (2012).
- [19] S. Haze, M. Sasakawa, R. Saito, R. Nakai and T. Mukaiyama, *Phys. Rev. Lett.* **120**, 043401 (2018).
- [20] Z. Meir, T. Sikorsky, R. Ben-shlomi, N. Akerman, Y. Dallal and R. Ozeri, *Phys. Rev. Lett.* **117**, 243401 (2016).
- [21] I. Rouse and S. Willitsch, *Phys. Rev. Lett.* **118**, 143401 (2017).
- [22] Z. Meir, M. Pinkas, T. Sikorsky, R. Ben-shlomi, N. Akerman and R. Ozeri, *arXiv preprint arXiv:1801.06839* (2018).
- [23] A. Härter and J. Hecker Denschlag, *Contemp. Phys.* **55**, 33 (2014).
- [24] M. Tomza, K. Jachymski, R. Gerritsma, A. Negretti, T. Calarco, Z. Idziaszek and P. S. Julienne, *arXiv preprint arXiv:1708.07832* (2017).
- [25] F. H. J. Hall, P. Eberle, G. Hegi, M. Raoult, M. Aymar, O. Dulieu and S. Willitsch, *Mol. Phys.* **111**, 2020 (2013).
- [26] Y.-P. Chang, K. Dlugolecki, J. Küpper, D. Rösch, D. Wild and S. Willitsch, *Science* **342**, 98 (2013).
- [27] A. D. Ludlow, M. M. Boyd, J. Ye, E. Peik and P. O. Schmidt, *Rev. Mod. Phys.* **87**, 637 (2015).
- [28] N. Huntemann, C. Sanner, B. Lipphardt, Chr. Tamm and E. Peik, *Phys. Rev. Lett.* **116**, 063001 (2016).
- [29] T. Nicholson, S. Campbell, R. Hutson, G. Marti, B. Bloom, R. McNally, W. Zhang, M. Barrett, M. Safronova, G. Strouse, W. Tew and J. Ye, *Nature Commun.* **6**, 6896 (2015).
- [30] C. W. Chou, D. B. Hume, T. Rosenband and D. J. Wineland, *Science* **329**, 1630 (2010).
- [31] S. Schiller and V. Korobov, *Phys. Rev. A* **71**, 032505 (2005).
- [32] E. J. Salumbides, J. C. J. Koelemeij, J. Komasa, K. Pachucki, K. S. E. Eikema and W. Ubachs, *Phys. Rev. D* **87**, 112008 (2013).
- [33] M. Germann, X. Tong and S. Willitsch, *Nat. Phys.* **10**, 820 (2014).
- [34] M. Kajita, *Phys. Rev. A* **92**, 043423 (2015).
- [35] X. Tong, A. H. Winney and S. Willitsch, *Phys. Rev. Lett.* **105**, 143001 (2010).
- [36] F. Wolf, Y. Wan, J. C. Heip, F. Gebert, C. Shi and P. O. Schmidt, *Nature* **530**, 457 (2016).
- [37] C.-W. Chou, C. Kurz, D. B. Hume, P. N. Plessow, D. R. Leibbrandt and D. Leibfried, *Nature* **545**, 203 (2017).
- [38] P. O. Schmidt, T. Rosenband, C. Langer, W. M. Itano, J. C. Bergquist and D. J. Wineland, *Science* **309**, 749 (2005).