

# Experiments with single cold molecular ions

Klaus Højbjerg, Peter Staantum, David Offenberg,<sup>1</sup> Jens Lykke Sørensen,  
Anders Mortensen and Michael Drewsen

*QUANTOP – Danish National Research Foundation Centre for Quantum Optics, Department of  
Physics and Astronomy, University of Aarhus 8000 Aarhus C, Denmark*

**Abstract.** In this paper we present ongoing work on single cold molecular ion experiments in a linear Paul trap. In particular, we discuss the properties and prospects of using a non-destructive identification technique. Measuring the resonance frequency of a common motional mode of a laser cooled atomic ion and a molecular ion the harmonic trap potential, the mass of the latter can be determined. We report recent results using this technique for the cases of  $^{40}\text{Ca}^{18}\text{O}^+$  and  $\text{C}_3\text{H}_3^+$ .

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## INTRODUCTION

Cold molecules are of great interest to many fields of physics, ranging from high precision spectroscopy and coherent control studies to astrochemistry. In recent years there have been many advancements in cold molecular sources. Neutral molecules have been cooled in supersonic jets and trapped in electrostatic fields [1], produced through photoassociation [2] and cooled by a He buffer-gas in a cryogenic environment [3]. Cold molecular ions have been produced as well through sympathetic cooling of the molecular ions by laser cooled atomic ions simultaneously trapped in Penning [4] and Paul traps [5, 6, 7, 8, 9]. In general, through sympathetic cooling, molecular ions can become part of a Coulomb crystal, the structure and dynamics of which reveal information on the crystals composition. By monitoring changes in the crystal properties in time, one can gain information on reactions taking place. This has recently been utilized to gain information on chemical reactions [5, 9] as well as photo-reactions [7] with molecular ions.

The above mentioned works have all been done with ensembles of molecular ions. The single ion case however offers the best situation to get full information of the molecular ion target: as there is only a single ion, one can be sure to have a pure target. Together with internal state control, for instance obtained with laser cooling of internal degrees of freedom [10, 11], state preparation by projection measurements [12] or production of the ion in a specific rovibrational state through REMPI [13], one can prepare a well-defined quantum state, and hence ensemble averaging is not an issue. Furthermore a single molecular ion can easily be spatially localized to a volume of about  $\sim 1\mu\text{m}^3$ . This makes it an ideal target for experiments where focused laser beams are used, since the uncertainty in the position of the target within the laser beam can be eliminated.

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<sup>1</sup> Permanent address: Institut für Experimentalphysik, Heinrich-Heine-Universität Düsseldorf, Germany

**FIGURE 1.** Sketch of the setup used in experiments with single molecular ions and the partial level scheme for the  $^{40}\text{Ca}^+$  ion. a) An atomic and a molecular ion are trapped in a linear Paul trap. The atomic ion is laser cooled from three directions to a temperature of a few mK and the fluorescence is imaged to a CCD camera. Through Coulomb collisions with the atomic ion, the molecular ion is cooled sympathetically. By applying a small modulation voltage to two of the end-cap electrodes, the two cold ions' common mode can be excited and monitored by the CCD camera. The resonance frequency will reveal the mass of the molecular ion. b) Partial level scheme for the  $^{40}\text{Ca}^+$  ion. The arrows indicate the Doppler laser cooling transitions used.

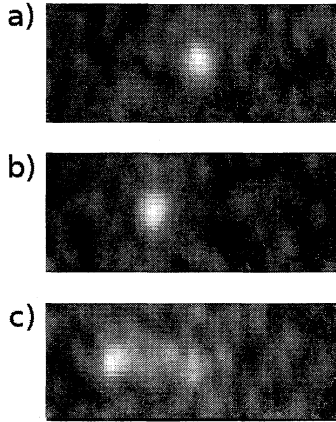
Thus coherent control experiments [14], where the goal is to control the outcome of for example fragmentation reactions with the aid of laser fields, would be attainable.

## EXPERIMENTAL SETUP

The essential part of our setup is sketched in Fig. 1a. The heart of the experiment is a linear Paul trap, situated in a vacuum chamber at a base pressure of  $\sim 10^{-10}$  torr. In short, it consists of four metal rods where a RF voltage is applied with the same phase to diagonal electrodes, but with a phase shift of  $180^\circ$  to the nearest electrodes. This gives rise to a near-ideal confining quadrupole field in a plane perpendicular to the z-axis. To also confine the ions along the z-axis, the electrodes are sub-divided into 3 parts and a DC voltage is applied to the eight end-caps. With appropriate frequency and voltages, the trapping potential is nearly harmonic in the center region (For further details on the Paul trap in use, see [6]).

Between one and several thousand  $\text{Ca}^+$  ions can be produced by isotope-selective photo-ionization[15] and immediately Doppler laser cooled to a few mK using the  $4s\ ^2S_{1/2} - 4p\ ^2P_{1/2}$  transition (397 nm) and a repumper between the states  $3d\ ^2D_{3/2}$  and  $4p\ ^2D_{3/2}$  (866 nm). A reduced level scheme is presented on Fig. 1b. The 397 nm fluorescence from the ions is imaged via an image-intensifier to a CCD camera.

Molecular ions can either be produced in a reaction between already trapped atomic ion and neutral molecules leaked into the vacuum chamber at a partial pressure of



**FIGURE 2.** CCD camera images. a) A single  $^{40}\text{Ca}^+$  trapped and cooled. b) The size of the displacement of the  $\text{Ca}^+$  ion reveals that exactly one unknown singly charged ion is trapped along with the  $^{40}\text{Ca}^+$  ion. c) Image where the common mode of the two-ion system along the z-axis is excited. For all images the exposure time was long compared to the period of the oscillation modes of the ions.

$\sim 10^{-9}$  torr, or by direct photo-ionizing molecules present in the trap region. For easy admittance of different gasses, there is a leak valve mounted in the vacuum chamber. In a typical single molecular ion experiment, a molecular ion is produced and cooled sympathetically to a temperature of a few mK through Coulomb interactions with a laser cooled  $^{40}\text{Ca}^+$  ion.

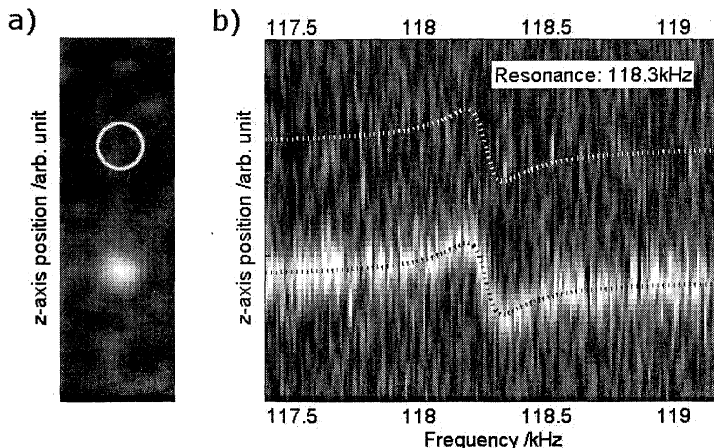
As most molecular ions lack closed transitions, one cannot rely on fluorescence to detect them directly. Another detection scheme relying on mass measurements, which has been demonstrated in earlier work[8], will be described in the following.

When one  $^{40}\text{Ca}^+$  ion and one unknown ion is trapped and cooled, one can force the ions to line up along the z-axis, by making the radial trap frequency higher than the axial ones. Since the trapping potential is nearly harmonic along the z-axis, the two collective axial modes of the two ion system (a common mode and a breathing mode), can be written [16]

$$v_{\pm}^2 = \left[ (1 + \mu) \pm \sqrt{1 - \mu + \mu^2} \right] v_1^2 \quad , \quad \mu = \frac{M_1}{M_2} \quad (1)$$

where  $M_1$  and  $M_2$  are the masses of the two ions and  $v_1$  is the oscillation frequency of a single ion with mass  $M_1$ .

The common mode,  $v_-$ , is excited by an harmonic oscillating modulation voltage applied to two of the end cap electrodes. Close to the resonance frequency of the two ion system, the oscillation amplitude increases dramatically, which is easily observed with the camera (Fig. 2c). Hence, if  $M_1$  and  $v_1$  are known (values for  $^{40}\text{Ca}^+$ ), then by measuring either  $v_-$  or  $v_+$ , one can deduce the mass,  $M_2$ , of the unknown molecular ion.



**FIGURE 3.** a) Image of a  $^{40}\text{Ca}^+$  ion and a  $\text{C}_3\text{H}_3^+$  ion. The position of the non-visible  $\text{C}_3\text{H}_3^+$  ion is indicated by the white circle. b) Projections onto the z-axis of the fluorescence intensities of gated images as a function of the modulating frequency. White is high fluorescence, while black is low. Only the  $^{40}\text{Ca}^+$  ion is seen, but both ions' positions are sketched with dotted lines found by a fit to the model described in the text. Around the resonance, the phase changes rapidly and thus provides a precise measurement of the resonance frequency. The frequency step size is 100 Hz

## RESULTS AND DISCUSSION

An image of a trapped and cooled  $^{40}\text{Ca}^+$  ion can be seen on Fig. 2a. When a molecular ion is produced and cooled, it lines up along the z-axis, causing a displacement of the  $^{40}\text{Ca}^+$  ion, which is seen on Fig. 2b. The amount of displacement gives information about the number of molecular ions present, so we can easily single out single molecular ion cases. Finally, looking for resonances like the one seen on Fig. 2c, one can determine masses with a resolution better than 1 a.m.u. For instance the molecule  $\text{CaO}^+$  was formed in a reaction between a trapped  $^{40}\text{Ca}^+$  ion and a  $\text{O}_2$  molecule. The resonance frequencies was measured to be  $\nu_+ = 98.7(1)$  kHz and  $\nu_- = 89.4(1)$  kHz, so together with a tabulated mass of  $^{40}\text{Ca}^+$  of 49.97 a.m.u., one gets  $M_2 = 56.1(4)$  a.m.u. This accuracy is sufficient to conclude that the molecule is a  $^{40}\text{Ca}^{16}\text{O}^+$  ion [8].

For higher precision, the camera is gated such that the phase of the two-ion motion can be detected as function of the modulating frequency. This method has been applied to  $\text{C}_3\text{H}_3^+$  ions produced from a gas of aniline ( $\text{C}_6\text{H}_5\text{NH}_2$ ). The resulting frequency scan is depicted in Fig. 3. The plot is composed of projections onto the z-axis of the fluorescence intensities in gated images during a frequency scan with a steps of 100 Hz. The position of the atomic and molecular ions are sketched with dotted lines and one sees how the phase of the ions' motions change rapidly around the common mode frequency. The intensity can be modelled with the function

$$I(z, \nu_{drive}) = I_0 \exp \left\{ - \frac{[z - z_0(\nu_{drive})]^2}{\Gamma_z(\nu_{drive})^2} \right\} + I_B \quad (2)$$

where  $\nu_{drive}$  is the drive frequency,  $I_0$  is the ion signal,  $I_B$  is the background level,  $z_0(\nu_{drive})$  is the mean in-phase position of the ion and

$$\Gamma_z(\nu_{drive}) = \frac{\alpha_\nu}{(\nu_{drive} - \nu_-)^2 + \gamma_\nu^2} + \Gamma_{res} \quad (3)$$

is the spatial width of the fluorescence signal with  $\Gamma_{res}$  being the spatial resolution of the imaging system,  $\gamma_\nu$  being the width of the resonance and  $\alpha_\nu$  being a constant related to the amplitude of the forced motion. Finally,

$$z_0(\nu_{drive}) = \frac{\alpha_z(\nu_{drive} - \nu_-)}{(\nu_{drive} - \nu_-)^2 + \gamma_\nu^2} + z_{off} \quad (4)$$

Using this model, a resonance frequency of 118.3 kHz was found for the data presented in Fig. 3. Since a calibration measurement with a single  $^{40}\text{Ca}^+$  ion gave  $\nu_1 = 117.6$  kHz, from formula (1), one finds  $M_2 = 39.00$  a.m.u. This value fits well with the tabulated value of 39.06 a.m.u. for  $\text{C}_3\text{H}_3^+$ . In this measurement we did not focus on eliminating systematical errors like the asymmetry in only applying laser cooling to one ion or the timing resolution of the camera system. With more careful measurements, precisions around  $3 \times 10^{-4}$  have been reached [8]. This is sufficient to discriminate between some molecular ion mass doublets, as for instance  $^{13}\text{C}_2\text{H}_2^+$  and  $^{14}\text{N}_2^+$  which have a relative mass difference of  $5.8 \times 10^{-4}$ .

## CONCLUSION

In conclusion, we have presented a simple detection scheme, that enables us to identify single molecular ions in a non-destructive way. In the future, continuously scanning of relevant frequency ranges equivalent to reactant and product masses, will enable us to follow reactions on a very slow timescale, e.g. consecutive fragmentations of metastable molecule complexes or chemical reactions with a background gas.

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