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A prototype storage ring for neutral molecules

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The ability to cool and manipulate atoms with light has yielded atom interferometry, precision spectroscopy, Bose–Einstein condensates and atom lasers. The extension of controlled manipulation to molecules is expected to be similarly rewarding, but molecules are not as amenable to manipulation by light owing to a far more complex energy-level spectrum. However, time-varying electric and magnetic fields have been successfully used to control the position and velocity of ions, suggesting that these schemes can also be used to manipulate neutral particles having an electric or magnetic dipole moment^{1–4}. Although the forces exerted on neutral species are many orders of magnitude smaller than those exerted on ions, beams of neutral dipolar molecules have been successfully slowed down in a series of pulsed electric fields^{5,6} and subsequently loaded into an electrostatic trap⁷. Here we extend the scheme to include a prototype electrostatic storage ring made of a hexapole torus with a circumference of 80 cm. After

injection, decelerated bunches of deuterated ammonia molecules, each containing about 10^6 molecules in a single quantum state and with a translational temperature of 10 mK, travel up to six times around the ring. Stochastic cooling⁸ might provide a means to increase the phase-space density of the stored molecules in the storage ring, and we expect this to open up new opportunities for molecular spectroscopy and studies of cold molecular collisions^{9,10}.

The experimental set-up (Fig. 1) consists of a compact molecular beam machine that tangentially injects molecules into a hexapole torus storage ring. The centripetal force required to keep the molecules in a circular orbit arises from the interaction of the molecules with the inhomogeneous electric field inside the ring. For a given maximum electric-field strength, a sufficiently large centripetal force can be generated only in a storage ring with a minimum radius that is proportional to the square of the velocity of the injected molecules. The availability of beams of slow neutral molecules, with a tunable absolute velocity^{5,11}, is therefore an important asset in designing and testing a molecular storage ring. To simplify detection, the electric field geometry in the 25-cm-diameter hexapole torus storage ring deviates from the commonly used cylindrically symmetric hexapole fields. Figure 2 illustrates the voltages applied to the different rods of the ring and the equipotential lines in the shallow well experienced by state-selected deuterated ammonia molecules travelling with a tangential velocity of 89 m s^{-1} .

A pulsed beam of deuterated ammonia, ND_3 , is produced by expanding a ND_3/Xe mixture through a modified solenoid valve into vacuum. Seeding ND_3 in the heaviest rare gas and cooling of the pulsed valve results in a mean beam velocity of around 275 m s^{-1} ($E_{\text{kin}} = 64 \text{ cm}^{-1}$). About 15% of the ND_3 molecules reside in the low-field-seeking $|JK|M\rangle = |111\rangle$ upper inversion level of the vibrational ground state. We select only molecules that are in this quantum state, molecules that gain Stark energy with increasing electric field and are repelled from high-electric-field regions. The electric dipole moment of ND_3 is 1.5 D (Debye units)¹², and the selected molecules experience a positive Stark shift of 1.2 cm^{-1} in an electric field of 100 kV cm^{-1} . By selecting ND_3 , rather than NH_3 , we ensure that we can work with a more linear Stark effect in the applied electric fields, resulting from the fact that the magnitude of the inversion splitting is significantly reduced upon deuteration¹².

The ND_3 molecules pass through a 1.0-mm-diameter skimmer into a second, differentially pumped vacuum chamber and then fly into a short pulsed hexapole that acts as a positive lens for the selected ND_3 molecules. After exiting the hexapole, the molecules

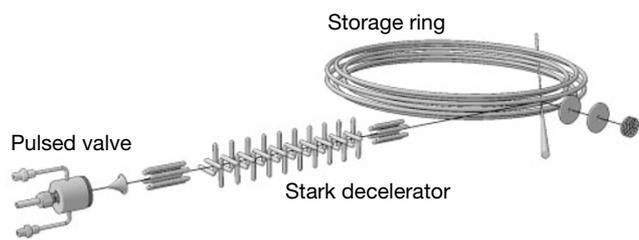


Figure 1 Experimental set-up. From left to right: a gas pulse of less than 1% ND_3 in Xe exits a cooled ($T = 200 \text{ K}$) pulsed valve with a mean velocity of 275 m s^{-1} . After passing through the skimmer the beam is collimated with a pulsed hexapole and subsets of these molecules are slowed down to velocities in the 76 m s^{-1} to 110 m s^{-1} range upon passage through the Stark decelerator. The bunches of slow molecules are tangentially injected into the electrostatic storage ring (with a 12.5-cm radius and 4-mm-diameter rods). Molecules in the detection region of the storage ring are ionized using a pulsed laser, after which they are extracted, and detected with an ion detector. The flight path of the molecules from the pulsed valve to the detection region in the storage ring is 65 cm.

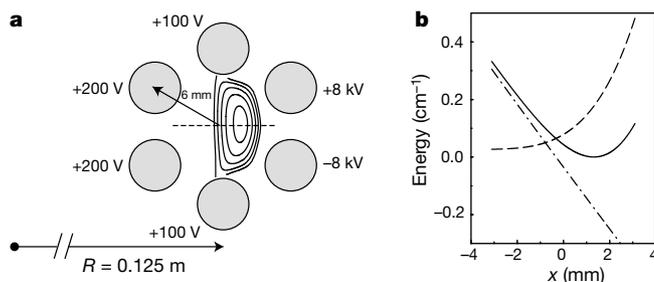


Figure 2 Cross-section of the hexapole storage ring. **a**, Contour lines of equal potential energy for ND_3 molecules in the $|JKM\rangle = |111\rangle$ state with positive Stark shift and with a tangential velocity of 89 m s^{-1} are shown at 0.02-cm^{-1} intervals. **b**, The dashed curve shows the Stark energy as a function of the displacement from the centre of the hexapole (x) in the plane of the hexapole ring (along the dashed axis shown in **a**). The solid curve is obtained by adding the potential energy as a result of the centrifugal force for an ammonia molecule with a tangential velocity of 89 m s^{-1} (dot-dashed line) to the Stark energy (dashed line). The minimum of the resulting potential well is located 1.3 mm offset from the geometrical centre of the hexapole.

enter a 35-cm-long Stark decelerator containing an array of equidistant electric-field stages, with electric fields of typically up to 100 kV cm^{-1} ; this decelerates the molecules while maintaining their initial phase-space density^{5,6}, much like what is done in charged-particle accelerators¹³.

A second pulsed hexapole at the exit of the decelerator focuses the slowed-down molecules into the storage ring. The ammonia molecules enter the ring tangentially, passing through the 2-mm-wide 'slit' between two hexapole rods. The density of ND_3 molecules inside the storage ring is probed using the focused radiation of a pulsed laser at 317 nm, which ionizes (by a multi-photon process) the ND_3 molecules that are in the selected quantum state¹⁴. Just before firing the laser, the voltages on the hexapole ring are switched such that laser-produced positive ions are accelerated radially outward, so that the storage ring itself serves as the extraction region of a linear time-of-flight mass spectrometer. The ND_3 -ion signal is recorded and used as a measure for the amount of neutral ammonia molecules originally present inside the ring.

Figure 3 illustrates the relative density of neutral ammonia inside the storage ring, as a function of the time after the molecules left the pulsed valve. Without any voltage applied to the Stark decelerator (that is, without deceleration), the ammonia density in the storage ring peaks around 2.4 ms after the molecules left the valve. This is the time it takes molecules travelling with an average velocity of 275 m s^{-1} to cover the 65-cm distance between the pulsed valve and the storage ring. The velocity spread is approximately 20% (full-width at half-maximum, FWHM), implying a translational temperature of around 1 K in the moving frame. With the Stark decelerator switched on and configured to decelerate molecules from 275 m s^{-1} to a final velocity of 100 m s^{-1} , a series of signal peaks occur at later times. These different bunches, whose velocity is indicated in Fig. 3, originate from the spatially extended molecular gas pulse at the entrance of the decelerator. The molecules that exit the decelerator with a velocity of 110 m s^{-1} were already in the second electric-field section of the decelerator when the decelerator was switched on, and so missed one deceleration cycle. The molecules that exit the decelerator with velocities of 89 m s^{-1} and 76 m s^{-1} are molecules that entered the decelerator later, with an initial velocity that was lower than the average beam velocity. The individual bunches are still clearly separated in the probe region,

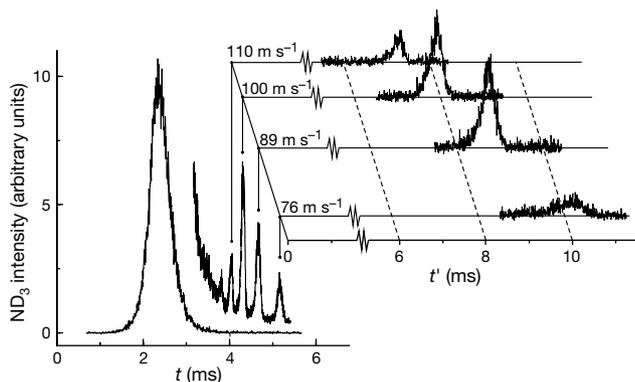


Figure 3 Time-of-flight profiles. Density of ammonia molecules inside the storage ring as a function of time after opening of the pulsed valve (t), both without (single large peak around 2.4 ms) and with the Stark decelerator on (series of peaks at later arrival times). It is worth noting that the intensity of the decelerated bunches is on the same absolute scale as the original beam; the focusing effects in the decelerator typically enhance the signal on the beam axis by a factor of 5 compared to the situation when the decelerator is not switched on at all. In the inset the density of ammonia molecules inside the storage ring is measured as a function of the time after switching on the storage ring (t'). Bunches of decelerated molecules with four different centre velocities are injected into the ring, with settings as shown in Fig. 2, and their time-of-flight distributions after the first round trip are recorded.

which is located 19 cm away from the exit of the decelerator. The velocity spread in the decelerated bunches of molecules is only 4–5 m s^{-1} (FWHM), corresponding to a translational temperature of around 10 mK. The detection signal we obtain corresponds to about a hundred ND_3 -ions being generated per laser pulse. As ionization of the ND_3 molecules takes place only in the focus of the laser beam, the actual detection volume in our system is about 10^{-4} cm^3 . Each bunch contains a minimum of about 10^6 state-selected ND_3 molecules.

When a selected bunch of decelerated ammonia molecules has entered the storage ring, a high voltage is abruptly applied to the outer two hexapole rods. The separation between the different bunches at the entrance region of the storage ring is sufficiently large that only one selected bunch of decelerated molecules is captured. To be able to detect the amount of ammonia molecules inside the ring after having stored them for a certain time, the voltages on the outer two rods are switched off; the (small) voltage offset required for ion extraction is permanently applied to the other rods. The inset to Fig. 3 shows the density of neutral ammonia in the detection region of the storage ring as a function of time after switching on the ring. After separately injecting each of the four selected bunches of molecules, the corresponding time-of-flight distributions after one round trip are measured. The measurements show that ammonia molecules in the velocity interval from 76 m s^{-1} to 110 m s^{-1} can be captured in the ring with the settings as applied. Molecules that move significantly faster do not experience a force large enough to keep them in a circular orbit, whereas molecules that move significantly slower will be deflected too much by the repulsive outer wall of the ring, and either hit the inner hexapole rods or escape from the storage ring on the inside otherwise. With the settings that have been used, the injection efficiency is optimum for velocities around 89 m s^{-1} .

The equilibrium orbit for molecules with a forward velocity of 89 m s^{-1} coupled in at the minimum of the potential well is a perfect circle in the horizontal plane, with a radius 1.3 mm larger than the 12.5 cm radius of the hexapole torus. Upon making successive round trips the bunch of molecules gradually spreads out in the tangential direction as a result of the residual velocity spread. In addition, the molecules will perform betatron oscillations around the equilibrium orbit¹³. In our particular geometry the oscillations in the radial and vertical direction are strongly coupled. Per round trip, approximately eight oscillations are made in the radial direction

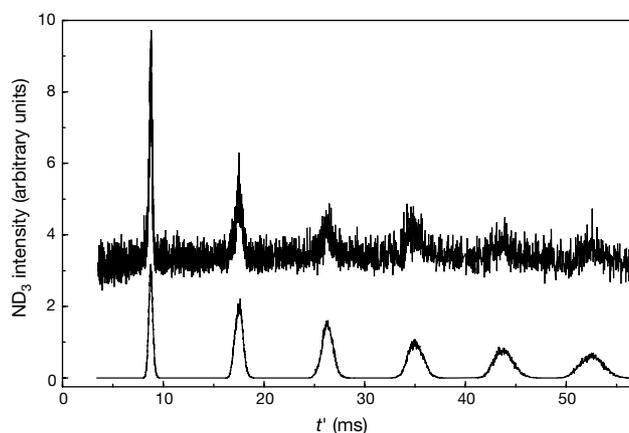


Figure 4 Multiple round trips. The measurements shown in the upper trace show that bunches containing approximately a million ammonia molecules make up to six round trips in the storage ring. The package of stored molecules is seen to gradually broaden and to decrease in peak intensity, mainly due to the tangential velocity spread (dispersion). In the lower trace the results of Monte Carlo simulations, calculating trajectories of molecules through the whole experimental set-up, are shown. From the simulations a translational temperature of 10 mK is deduced for the stored bunch of molecules.

and three in the vertical direction. Conservation of angular momentum dictates that the tangential velocity of the orbiting molecules is modulated at the radial betatron oscillation frequency as well. The experimental data in the upper trace of Fig. 4 demonstrates that a bunch of ammonia molecules with a velocity of 89 m s^{-1} can still be identified after it has made six round trips in the storage ring. The observed gradual broadening and decrease in peak intensity after each additional round trip is largely explained by the above-mentioned spreading out of the package along the ring, as substantiated by the results from Monte Carlo simulations, shown in the lower trace of Fig. 4. Loss of molecules from the storage ring by collisions with background gas can explain the observed faster decay of signal at early times after the gas pulse, when the background pressure is still rather high. Unwanted transitions to states that are degenerate in zero field—another possible loss channel for the ring—are avoided in the chosen electric-field geometry.

The storage ring experimentally demonstrated here can generally be used to confine dipolar molecules. The advantage of a storage ring over a trap is that bunches of cold molecules in a ring can be made to interact repeatedly, at well defined times and at distinct locations, with electromagnetic fields and/or other particles. A sectional version of the storage ring allows implementation of field-free interaction regions and various out-coupling regions. This yields unique opportunities for high-resolution molecular spectroscopy as well as for a large variety of collision studies. By incorporating a re-bunching element in the ring, the gradual spreading out of the package that is observed now can be avoided and the stored molecules can be confined to the same region in phase-space for a time-period only limited by collisions with background gas. Different molecules can be stored simultaneously; slowly overtaking or counter-propagating bunches can be stored and used for collision studies. The excellent optical access to the storage ring makes it feasible to use laser detection schemes to accurately determine where the molecules are in the ring at each given moment in time. If this is done in a non-intrusive manner, for instance via two-level laser-induced fluorescence or by detecting the change in refractive index when they pass through an optical cavity, this information can be used to actively correct the trajectories of individual molecules towards the ideal, circular orbit, thus increasing the phase-space density of the stored molecules (stochastic cooling⁸). It is important to note that in the ring, molecules in high-field-seeking states can also be stored¹⁵; motional stabilization as demonstrated here can also be used to stabilize orbits of particles that, according to the Earnshaw theorem, cannot be trapped in a static geometry. Whenever any cooling scheme on the stored molecules is proved to work (stochastic cooling, evaporative cooling, laser cooling on ro-vibrational transitions, cavity-mediated cooling¹⁶), reloading of the ring will be possible. Such reloading might be a viable way of achieving phase-space densities of stored molecules that are sufficiently high to permit experimental study of molecular quantum-collective effects. □

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Evidence against dust-mediated control of glacial–interglacial changes in atmospheric CO_2

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The low concentration of atmospheric CO_2 inferred to have been present during glacial periods is thought to have been partly caused by an increased supply of iron-bearing dust to the ocean surface¹. This is supported by a recent model² that attributes half of the CO_2 reduction during past glacial stages to iron-stimulated uptake of CO_2 by phytoplankton in the Southern Ocean. But atmospheric dust fluxes to the Southern Ocean, even in glacial periods, are thought to be relatively low and therefore it has been proposed that Southern Ocean productivity might be influenced by iron deposited elsewhere—for example, in the Northern Hemisphere^{3,4}—which is then transported south via ocean circulation (similar to the distal supply of iron to the equatorial Pacific Ocean^{5–7}). Here we examine the timing of dust fluxes to the North Atlantic Ocean, in relation to climate records from the Vostok ice core in Antarctica around the time of the penultimate deglaciation (about 130 kyr ago). Two main dust peaks occurred 155 kyr and 130 kyr ago, but neither was associated with the CO_2 rise recorded in the Vostok ice core. This mismatch, together with the low dust flux supplied to the Southern Ocean, suggests that dust-mediated iron fertilization of the Southern Ocean did not significantly influence atmospheric CO_2 at the termination of the penultimate glaciation.

The Southern Ocean is a ‘high nutrient, low chlorophyll’ (HNLC) region; phosphate and nitrate concentrations are high at the ocean surface yet its productivity is low. Recent experiments show that artificial additions of iron to ocean patches significantly enhance primary productivity⁸, with consequent drawdown of surface water

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