Multiple Packets of Neutral Molecules Revolving for over a Mile

Peter C. Zieger,[1] Sebastiaan Y. T. van de Meerakker,[1] Cynthia E. Heiner,[1] Hendrick L. Bethlem,[2]
André J. A. van Roij,[3] and Gerard Meijer[1]

[1]*Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany*
[2]*Laser Centre Vrije Universiteit, De Boelelaan 1081, 1081 HV Amsterdam, The Netherlands*
[3]*Institute for Molecules and Materials, Radboud University Nijmegen,
Heyendaalseweg 135, 6525 AJ Nijmegen, The Netherlands*

The level of control that one has over neutral molecules in beams dictates their possible applications. Here we experimentally demonstrate that state-selected, neutral molecules can be kept together in a few mm long packet for a distance of over one mile. This is accomplished in a circular arrangement of 40 straight electrostatic hexapoles through which the molecules propagate over 1000 times. Up to 19 packets of molecules have simultaneously been stored in this ring structure. This brings the realization of a molecular low-energy collider within reach.

The important role that molecular beams have played ever since the early days of quantum mechanics stems from the exquisite control that one can exert over the internal and external degrees of freedom of neutral molecules in these beams. Advances in the control over molecular beams have gone hand in hand with new applications. In the 1930s, Rabi invented a method to unravel the quantum structure of molecules, based on the controlled manipulation of the trajectories of molecules on their way from an effusive source to the detector [1]. When the deflection fields from these original experiments were replaced by focusing elements, better control and higher densities were obtained in the molecular beam experiments, leading to the invention of the maser [2]. Improved control has also been obtained by upgrading the sources. Molecular beams with kinetic energies above 1 eV—sufficient to study and overcome reaction barriers in selected systems—were obtained by gas dynamic acceleration, i.e., by seeding small amounts of heavier molecules in light carrier gases [3]. The cooling of the translational, rotational, and vibrational degrees of freedom of molecules in these seeded mixed-gas expansions has greatly reduced the complexity in molecular spectra, and has thereby revolutionized molecular spectroscopy [4].

During the last decade, various methods have been demonstrated to control the forward velocity of molecules in beams. Decelerated beams of neutral molecules have been used, for instance, to reduce the transit-time broadening in high-resolution spectroscopy, to tune the collision energy in scattering studies, and to enable accurate measurements of lifetimes of long-lived states [5]. Here, we report that the distance that these decelerated molecular beams travel can be extended to over one mile. This has been achieved by arranging a large number of straight electrostatic hexapoles in a circle. The motion of a compact packet of state-selected molecules through this circular arrangement is fully under control; the long distance

travelled testifies to the intrinsic stability of the molecular trajectories.

The motivation for constructing the circular arrangement of straight hexapoles is its anticipated use as a low-energy collider; counterpropagating molecules meet many times when they revolve around the ring. This makes it possible to study low-energy (below ≈ 20 K) molecule-molecule collisions, probing the intermolecular interaction potential in great detail [6]. Molecular storage rings of various designs have been theoretically analyzed [7,8], and a compact electrostatic storage ring, obtained by bending a linear hexapole focuser into the shape of a torus, has been experimentally demonstrated [9]. In this prototype storage ring, the molecules were transversely confined but longitudinally, i.e., along the circle, they were essentially free. Therefore, an injected packet of molecules spread out along the flight direction and eventually filled the entire ring. Collision studies can be most sensitively performed when the neutral molecules revolve in bunches, i.e., when they are both transversely and longitudinally confined. It has been recently demonstrated that the latter can be achieved in a storage ring composed of two half rings, separated by small gaps; packets of ammonia molecules were kept together by changing the electric fields synchronous with the molecules' passage through the gaps [10].

In this prototype molecular synchrotron, the molecules could ultimately be kept together for about hundred round trips, implying that the molecules passed about 200 times through a gap, traveling a distance of about 80 meters during a total storage time of about 1 s [11]. At this time the density of the stored packet was about 2 orders of magnitude below the value at the time of injection. In collision studies involving counter-propagating packets of molecules, losses in the number of stored molecules due to (in)elastic collisions accumulate over the interaction events. Let us consider *n* packets of molecules revolving

clockwise and n packets revolving anticlockwise, all with the same speed; this would require a structure consisting out of n segments. After m round trips, each packet of molecules would have interacted $2nm$ times with counterpropagating packets. As the summed intensity of the n packets (revolving in either direction) can be recorded, an additional factor $\sqrt{n}$ will be gained in sensitivity. By tuning the speed with which the packets revolve, the total collision cross-section can be measured as a function of collision energy. Therefore, to operate it as a low-energy collider, the number of simultaneously stored packets—and thus the number of ring segments—as well as the number of completed round trips need to be made as large as possible.

Attempts to scale up the prototype molecular synchrotron to one consisting of many segments met with a number of serious problems: (i) Curved electrodes (as used in [10]) are difficult to machine to a high precision. This causes the alignment of the ring to be rather poor, and thereby limits the lifetime of the stored molecules. (ii) The original scheme to bunch the molecules involved switching between four different voltage configurations every time a packet passed through a gap [10]. For a ring consisting of many short segments the load on the high-voltage switches would be unacceptable. Moreover, (iii) we have come to realize that this bunching scheme led to additional losses from the ring, either due to instabilities of the molecular trajectories or due to nonadiabatic transitions to nontrapped states. The molecular synchrotron presented here overcomes all these limitations.

A hexapole torus can be approximated by many short straight hexapole segments. From numerical simulations, we expect that the number of straight hexapoles can be reduced to below 100 without suffering a significant reduction in the transverse acceptance of the ring. As a compromise between construction demands and the expected performance, we have built a ring out of 40 straight hexapoles. A photograph of this ring is shown in the upper panel of Fig. 1, along with a zoom-in of three of the hexapoles. The diameter of the ring is 500 mm. Individual hexapoles are made by placing (nominally) 37.4 mm long electrodes, rounded off at each end, with a diameter of 4 mm on the outside of a circle with a radius of 3.54 mm [12]. Each hexapole spans an angle of 9 degrees of the ring. A difference of 1.5 mm between the lengths of the inner and outer electrodes is implemented to maintain a constant gap of 2 mm between adjacent hexapoles.

To confine the molecules transversely, a voltage difference of 6 kV is applied between adjacent hexapole rods, as shown in the middle panel of Fig. 1. In this situation, the resulting electric field is cylindrically symmetric, increasing quadratically with distance from the center. Molecules in states that have a positive energy shift in the applied electric field—so-called low-field seekers—will experience a force towards the center of the hexapole; this force increases linearly with the radial distance when the Stark
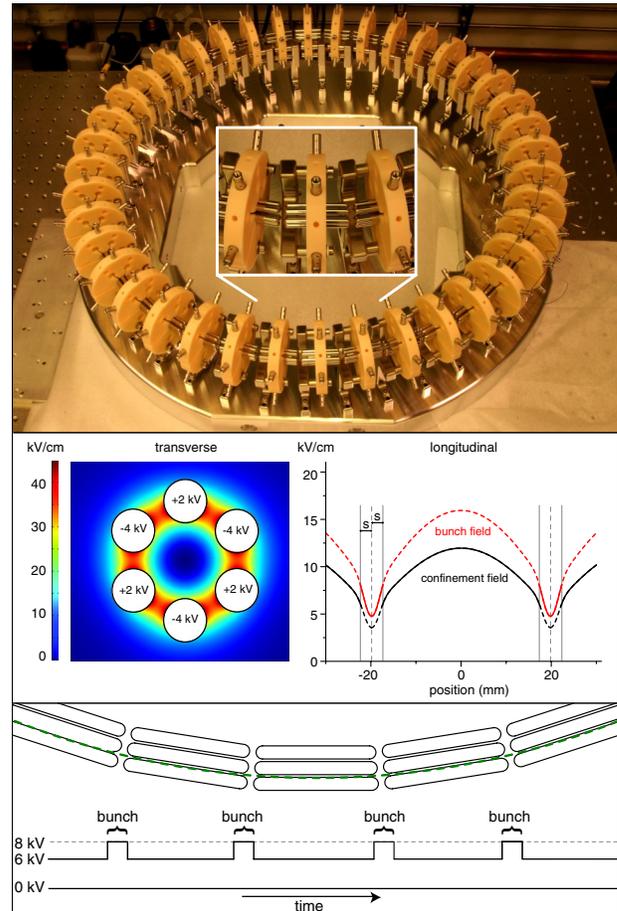
FIG. 1 (color online).   Upper panel: Photograph of the 0.5 m diameter molecular synchrotron with a zoom-in of three hexapoles. Middle panel, left: Voltage configuration used to transversely confine neutral molecules, overlayed with a contour plot of the resulting electric field strength. Right: Electric field strength (both for confinement and bunching) as a function of position along the equilibrium orbit. Lower panel: Scheme of the time dependence of the voltage difference between adjacent hexapole electrodes during operation of the synchrotron. By temporarily switching to a higher voltage-difference whenever the packet passes through a gap, ammonia molecules with a velocity spread of one m/s are kept in a tight bunch while revolving. The green dashed curve indicates the equilibrium orbit of ND_3 molecules with a forward velocity of 125 m/s.

shift is linear with the electric field. In the ring, the molecules also experience a centrifugal force that depends on their forward velocity, and these forces will cancel at a certain position. In a perfect hexapole torus, a deuterated ammonia (ND_3) molecule in the low-field-seeking component of the $|J, K\rangle = |1, 1\rangle$ state with a forward velocity of 125 m/s would be displaced radially outwards by 2.4 mm from the geometric center of the hexapole. In the present segmented ring, it is still a sufficiently good approximation that the equilibrium orbit for this molecule is a circle with a radius of 252.4 mm. Molecules flying with the same forward velocity but with a different radial position or with

a nonzero radial velocity will oscillate around this equilibrium orbit with a transverse (betatron) frequency of around 1 kHz; i.e., these molecules will make 11.6 betatron oscillations per round trip.

Let us next look at the longitudinal motion of molecules on the equilibrium orbit. As is seen in the middle panel of Fig. 1, the electric field strength varies strongly along this orbit. This arises from the change in the distance of the equilibrium orbit from the center line of the straight hexapole segment and from the presence of the gaps. The electric field in the middle of a gap drops to about half of the value near the end of a hexapole segment. Therefore, molecules in a low-field-seeking state will be accelerated in the fringe fields at the end of a hexapole segment, and will be decelerated in the fringe fields at the next hexapole segment. If the voltages are kept at a constant value, the deceleration will exactly cancel the acceleration and the molecules will keep their original velocity. In order to confine molecules in the longitudinal direction, we temporarily increase the positive voltages from $+2$ to $+4$ kV every time the molecules pass through a gap. As schematically indicated in Fig. 1, we increase the fields when a so-called "synchronous"molecule is a distance s before the middle of the gap and decrease the fields when this molecule is the same distance s after the middle of the gap. As before, the accelerating and decelerating forces on the synchronous molecule will be equal, and the velocity of the synchronous molecule will be the same after passing the gap. By contrast, a molecule that is slightly behind the synchronous molecule will enter the gap when the voltages are high, and it will leave the gap when the voltages are low. As a consequence, this molecule will experience a net acceleration. Vice versa, a molecule that is in front of the synchronous molecule will enter the gap when the voltages are low, and it will leave the gap when the voltages are high. This molecule will experience a net deceleration. This argument shows that molecules within a small position interval will experience a force towards the synchronous molecule and will oscillate around it; the molecules are hence trapped in a travelling potential well that revolves around the ring. From measurements and simulations of this bunching scheme, we have determined the longitudinal trap depth to be about 1 mK, and the trap (synchrotron) frequency to be on the order of 35 Hz; i.e., the molecules make 0.4 synchrotron oscillation per round trip. Note that in this bunching scheme the molecules experience a transverse confinement force at all times.

In our experiments, packets of deuterated ammonia ($^{14}ND_3$) molecules with a forward velocity of around 125 m/s are tangentially injected into the 40-segment molecular synchrotron. These packets are produced by Stark deceleration, followed by transverse focusing and longitudinal cooling, of a pulsed beam of ammonia, as described in detail elsewhere [13]. At the entrance of the

synchrotron, each packet is several mm long and contains about a million molecules. All of these molecules are in the upper inversion doublet component of a single rotational level, $|J, K\rangle = |1, 1\rangle$, in the vibrational and electronic ground state. At the injection point, four hexapoles are connected (in two sets of two hexapoles) to two separate high-voltage switches to allow for the injection of new packets of molecules without interfering with the ones already stored. These segments are switched off during injection of a new packet, and are switched to a small bias voltage during detection of the molecules. The remaining 36 hexapoles are connected to three other high-voltage switches.

Figure 2 shows the density of ammonia molecules as a function of time after injection into the synchrotron. Thirteen packets are injected at a rate of about 10 Hz, after which the loading is stopped. These packets then trail each other by a distance of three hexapoles; the first and the last injected packet are four hexapoles apart. The summed signal of the packets is recorded after a selected number of round trips, in time steps of 2.6 μs, using ionization with a focused laser beam at the injection point. The time-of-flight profiles shown are averaged over 16 of such measurement cycles. Even after 1025 round trips, i.e., after the molecules have traveled further than a mile and have passed through a gap 41 000 times, their signal can be clearly recognized; the temporal width of 21 μs corresponds to a packet length of 2.6 mm.

The density of ammonia molecules is seen to exponentially decay with time at a rate of 0.31 s^{-1}. This is the lowest decay rate that has been observed for neutral ammonia molecules in any trap to date. In all the early electrostatic trapping experiments, $1/e$ lifetimes of only a small fraction of a second have been observed. These were probably limited by nonadiabatic transitions to nontrappable states near the trap center, as was only realized when substantially longer lifetimes of up to 1.9 s were
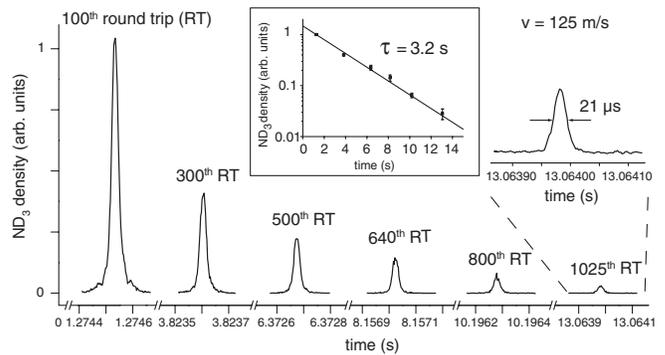
FIG. 2. Measurements of the density of ND_3 molecules as a function of time (in seconds) for a selected number of round trips. The observed temporal width of 21 μs after 1025 round trips corresponds to a packet length of 2.6 mm after a flight distance of more than a mile. The inset shows the exponential decay of the signal with time.
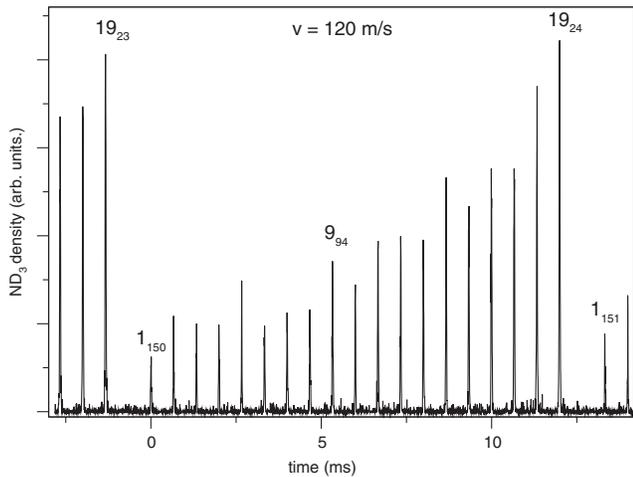
FIG. 3. Time-of-flight measurement showing 19 packets of ammonia molecules revolving simultaneously in the molecular synchrotron. The horizontal axis shows the time relative to the time at which the first injected packet has completed 150 round trips. Each packet is labeled with two numbers: the main number labels the order of injection whereas the subscript labels the number of completed round trips.

measured in an electrostatic trap with a nonzero electric field at the center [14]. With the present confinement and bunching scheme, the molecules are never close to a zero electric field in the ring either. In addition, we never change the direction—but only the magnitude—of the electric field in the ring, effectively preventing the occurrence of nonadiabatic transitions [15]. A major contribution to the observed loss rate is optical pumping of the ammonia molecules out of the $|J, K\rangle = |1, 1\rangle$ level by blackbody radiation, calculated to occur at a rate of 0.14 s^{-1} in the room-temperature chamber [16]. The remaining loss rate of 0.17 s^{-1} is well explained by collisions with background gas at the approximately 5×10^{-9} mbar pressure in the vacuum chamber.

Figure 3 shows a measurement of 19 packets of ammonia molecules with a forward velocity of 120 m/s being injected at about 10 Hz into the ring. The horizontal axis shows the time relative to the time at which the first injected packet has completed 150 round trips. The last injected packet has been in the ring for 320 ms and has made 24 round trips while the first injected packet has by then already been stored for more than 2 s. The loading scheme is set up such that each packet completes 7 round trips plus the length of 2 hexapoles before the next packet is injected. In the measurement the packets are seen to trail each other by 666 μs—precisely the time it takes them to fly through two hexapoles. In principle, it would be straightforward to store 40 packets simultaneously in the present circular arrangement, but in our current setup, we need to turn off at least two hexapoles to allow for new packets to enter the ring.

In conclusion, a synchrotron for neutral molecules consisting of 40 straight hexapoles together with a simple bunching scheme has been presented. Up to 19 packets of ammonia molecules have simultaneously been stored in this structure. The stored molecules can still be readily detected after they have completed a distance of over one mile, corresponding to a storage time of over 13 seconds. They have then passed—confined in a compact packet—41 000 times through a gap, which explicitly demonstrates the stability of their trajectories. These measurements epitomize the level of control that can now be achieved over molecular beams and set the stage for novel experiments to come. For collision studies, the sensitivity of this ring is increased by more than 3 orders of magnitude over that of the prototype molecular synchrotron [10]. We are currently setting up a second beam line to inject counter-propagating packets into the ring.

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