

A molecular conveyor belt by controlled delivery of single molecules into ultrashort laser pulses

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Trapping and laser cooling in atomic physics enables control of single particles and their dynamics at the quantum level in a background-free environment. Ultrashort intense laser pulses reveal the ultimate control of electromagnetic fields, enabling the imaging of matter, in principle down to a single molecule or virus resolved on atomic scales. However, current methods fall short in overlapping each target with a pulse of comparable size. We combine the two fields by demonstrating a deterministic molecular conveyor, formed of electric trapping potentials. We deliver individual diatomic ions at millikelvin temperatures and with submicrometre positioning into few-femtosecond ultraviolet laser pulses. We initiate and probe the molecule's femtosecond dynamics and detect it and its response with 100% efficiency. This experiment might become key for investigations of individual molecules, such as structural determinations using few-femtosecond X-ray lasers. Our scheme may overlap each single molecule with a pulse, focused to (sub)micrometre size, providing the required number of photons at the repetition rate of the laser.

To achieve sufficient gain of the coherent scattering signal, state-of-the-art techniques using low-intensity X-ray sources require myriads of identical molecules crystallized to a macroscopic probe¹. At present, the prerequisite of crystallization is the main shortfall of these techniques². This is mainly because many biological molecules, such as most of the membrane proteins, are difficult or impossible to crystallize. In addition, many samples are one of a kind, rare or charged. Diffraction experiments with low-intensity sources on non-crystalline or ultimately single molecules are substantially limited by radiation damage^{1,2}. That is, accumulating a sufficient number of scattering events takes long exposures, during which the huge total radiation dose alters the nuclear skeleton or even destroys the sample molecule(s). Furthermore, long exposure excludes the temporal resolution required to analyse short-lived intermediate products or fast structural changes by pump–probe schemes.

Intense X-ray pulses of a few femtoseconds (10^{-15} s) duration are predicted to overcome these limitations³ and first experimental evidence has been reported^{4–6}. The application of the overdose within a sufficiently short exposure should enable us to record useful structural information before the radiation degrades the sample molecule. The required number of photons to image a single molecule is on the order of 10^{13} per pulse, focused to the size of a large molecule (approximately $0.1\ \mu\text{m}$; ref. 3). At large laser facilities these beam parameters are becoming accessible^{5–7}. For example, pulses from the hard X-ray free-electron laser the Linac Coherent Light Source were focused to micrometre-sized spots at tens of hertz repetition rate to approach the required brilliance⁵. Recently, a pulse duration at the Linac Coherent Light Source of a few femtoseconds was measured and indication obtained that pulses around or shorter than 1 fs are within reach (manuscript in

preparation). The challenge is to deliver the ultimate target, a single molecule of choice, deterministically prepared but well isolated from the environment, that can be positioned reliably within each of the pulses of (sub)micrometre extension and that is replaceable at the repetition rate of the laser source, as illustrated in Fig. 1.

Conventional schemes to achieve a high flux of molecules in vacuum, for example by electrospray ionization^{8,9}, suffer from the molecules being released at random times, diluted by free expansion and furthermore by mutual Coulomb repulsion, in the case of molecular ions. These sources on their own still defy the desired level of control. Ion traps, in contrast, provide unique control capabilities for charged particles reaching the quantum limits. They tightly confine and store an atomic ion for days in a nearly background-free environment (ultrahigh vacuum) and protect it against external disturbance. Their internal (electronic) and external degrees of freedom are controlled to a level that enables both the observation and the deterministic exploitation of most fragile quantum effects. Examples are superposition states and entanglement for the most accurate optical clocks¹⁰, or quantum computing¹¹ and teleportation experiments¹². Laser-cooling techniques prepare atomic ions down to the quantum mechanical ground state of motion in the confining potential. Changing the related electric fields enables transfer of ions between separable traps at kilohertz rates, still controlling their absolute position on the sub-10 nm level¹². A molecular ion of suitable charge-to-mass ratio can be embedded into an ensemble of directly laser-cooled atomic ions that provides a 'sympathetic' heat sink^{13,14}. The absolute position of the molecular ion can be measured by detecting the fluorescence from the atomic ions with an accuracy down to half of its wavelength. Large ensembles of protonated proteins with a mass $m \approx 12,400$ amu at charge state $Z = 12$ have

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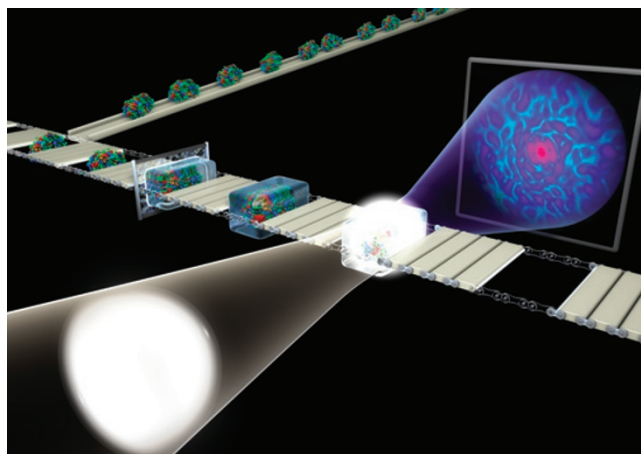


Figure 1 | Schematic of the set-up combining the fields of single-particle preparation on the quantum level and single, ultrashort laser pulses.

Generic single molecular ions hover in electric potential wells forming a kind of conveyor belt, represented here by its mechanical analogue. They are container-free embedded with (sub)micrometre precision into a crystal of laser-cooled atomic ions. The trapped molecular ion can subsequently be analysed, for example exploring its structure or dynamics. To match the overlap of the analysis pulses (focused for highest intensity) and the molecules they have to be precisely synchronized in time and space. Spatial precision better than $1\ \mu\text{m}$ and furthermore repetition rates of the order of 100 per second are required. Our experimental set-up (see also Fig. 2b) is shown to span such a conveyor belt, allowing for the accurate control of the internal and external degrees of freedom. To challenge our scheme with few-femtosecond pulse durations, we choose MgH^+ , yielding sufficiently fast molecular wave-packet dynamics. A straightforward substitution of the target by mid-sized molecules such as the protonated Schiff base of retinal would enable us to investigate, for example, ultrafast, light-induced photochemistry of isolated molecules. Molecules up to lysozyme (as depicted) might be provided for the predicted structural investigations by the diffraction pattern of each X-ray pulse (symbolized in white—temporal delay not to scale).

been shown to be sympathetically cooled in a radiofrequency trap¹⁴. By combining these skills for container-free handling we show that a single molecule comes close to the ultimate target described above.

In this Article we present a time-resolved experiment on individual molecular ions. To prove our scheme functional before applying X-ray pulses of the highest intensity, we require a molecule providing internal dynamics on the timescale of a few femtoseconds. We therefore sympathetically cool the diatomic molecule MgH^+ , featuring correspondingly fast vibrational dynamics, with the atomic ion Mg^+ . We carry out a pump–probe experiment with two few-cycle ultraviolet pulses. The first pulse triggers an electronic excitation; the second probes the dynamics of the molecular wave packet. This protocol faces identical demands on the handling of the target as for the proposed diffraction experiments using X-ray pulses.

Our experimental set-up is depicted in Fig. 2. It includes an electro-spray ionization source (required for future experiments on generic molecules, see Methods), followed by a radiofrequency quadrupole¹⁴, selecting a particle distribution with specific Z/m . We join a further radiofrequency guide of 48 cm length to the filter, consisting of electrodes at a mutual distance of $\approx 2\ \text{mm}$ that are operated at a frequency of $\Omega_{\text{RF}}/2\pi \approx 7\ \text{MHz}$. The guide yields tight radial confinement while passing the molecule through two vacuum chambers (1 eV potential depth for $\text{MgH}^+ \sim Z^2/m$ and related oscillation frequency $\omega_{\text{radial}}/2\pi \approx 500\ \text{kHz}$ ($\sim Z/m$)). Two pairs of ring-shaped d.c. electrodes at the front and at the rear end of the guide can be used to control the transfer of

the molecule at 100% efficiency from the preparation chamber to its required destination within $\approx 200\ \mu\text{s}$. The last pair is alternatively used to turn the section at the rear end of the guide into an ion trap ($\omega_{\text{axial}}/2\pi \approx 30\ \text{kHz}$ ($\sim \sqrt{Z/m}$)) in the ultrahigh vacuum ($2 \times 10^{-10}\ \text{mbar}$). There, several sufficiently laser-cooled atomic ions freeze out into ordered structures, so-called Coulomb crystals¹⁵. Their lattice constants are of the order of $10\ \mu\text{m}$ and each ion is pinned to an individual site. We accomplish Doppler laser cooling with a single turnkey laser system¹⁶ on a dipolar-allowed, closed transition $S_{1/2} \rightarrow P_{3/2}$ (natural linewidth $\Gamma/2\pi \approx 43\ \text{MHz}$), leading to final temperatures of $\approx 1\ \text{mK}$. After transferring the molecule, we embed it into the Coulomb crystal of atomic ions by sympathetic cooling¹³ to similar temperatures within milliseconds¹⁷. Cooling of the internal degrees of freedom of the molecule can be implemented using buffer gas¹⁸. At present we exploit comparatively slow (seconds) black-body-assisted radiative cooling¹⁹. In equilibrium with the thermal background at room temperature, our molecular ion reaches 99.9% occupancy of the vibrational ground state.

The position of the molecular ion can be deduced from the fluorescence from the atomic ions detected by a CCD (charge-coupled device) camera within milliseconds. The selected molecular ion²⁰ appears as a ‘dark’ spot within the crystalline structure (Fig. 2a). It can be localized by interpolation between the neighbouring ‘bright’ ions to the resolution of the imaging system at the emitted wavelength ($\lambda = 280\ \text{nm}$; motional amplitude for chosen parameters $< 0.25\ \mu\text{m}$). Subsequently, the molecule can be positioned in the focus of the laser, as illustrated in Fig. 1.

MgH^+ is a well-suited test candidate, as its vibrational dynamics on the few-femtosecond timescale is accurately treatable by theory. Furthermore, molecular MgH^+ ions can be generated in the photochemical reaction $\text{Mg}^+ + \text{H}_2 \rightarrow \text{MgH}^+ + \text{H}$ after photoionization of atomic magnesium from a thermal beam in the preparation chamber²¹. However, the experiment requires pulses in the ultraviolet regime. We therefore connected our conveyor belt to an evacuated beamline, providing 100 nJ pulses with a spectrum centred at 285 nm, about 4 fs (ref. 22) duration and 117 Hz repetition rate. Each pulse is reflected off a displaceable split mirror, generating two replicas of variable delay. As no other radiation damage than dissociation occurs in the current experiment, we can afford an extended focus of $50\ \mu\text{m}$, leading to an intensity of twice $160\ \text{GW cm}^{-2}$, and the same molecule can be irradiated several times.

The pump–probe scheme is illustrated in Fig. 3. It shows the *ab initio* potential-energy curves of the molecule as a function of the internuclear distance calculated by state-of-the-art quantum chemical methods (Supplementary Information). A pump pulse creates a vibrational wave packet oscillating with a period of approximately 30 fs in the potential of the electronically excited, bound state A. Part of this population can be further excited to the repulsive state C by the probe pulse. A molecular ion in this state dissociates according to $\text{MgH}^+ \rightarrow \text{Mg} + \text{H}^+$ as proposed for picosecond laser pulses in ref. 23. In this particular reaction channel, neither of the two dissociation products remains trapped. The breaking of the chemical bond is signalled by the disappearance of a non-fluorescing dark spot, remarkably detectable with an efficiency of 100% (Fig. 3). Owing to the slope of the potential-energy curve C, the probability for the transition driven by the probe pulse depends on the position of the vibrational wave packet in state A. Described in a simplifying picture, the mean photon energy mismatches with the transition at the wave packet’s inner turning point, whereas it overlaps well at the outer turning point. This way, the stretching motion periodically modulates the dissociation probability. We vary the pump–probe delay for repeatedly, identically prepared single molecules and derive the binary information of whether the molecule remained on its

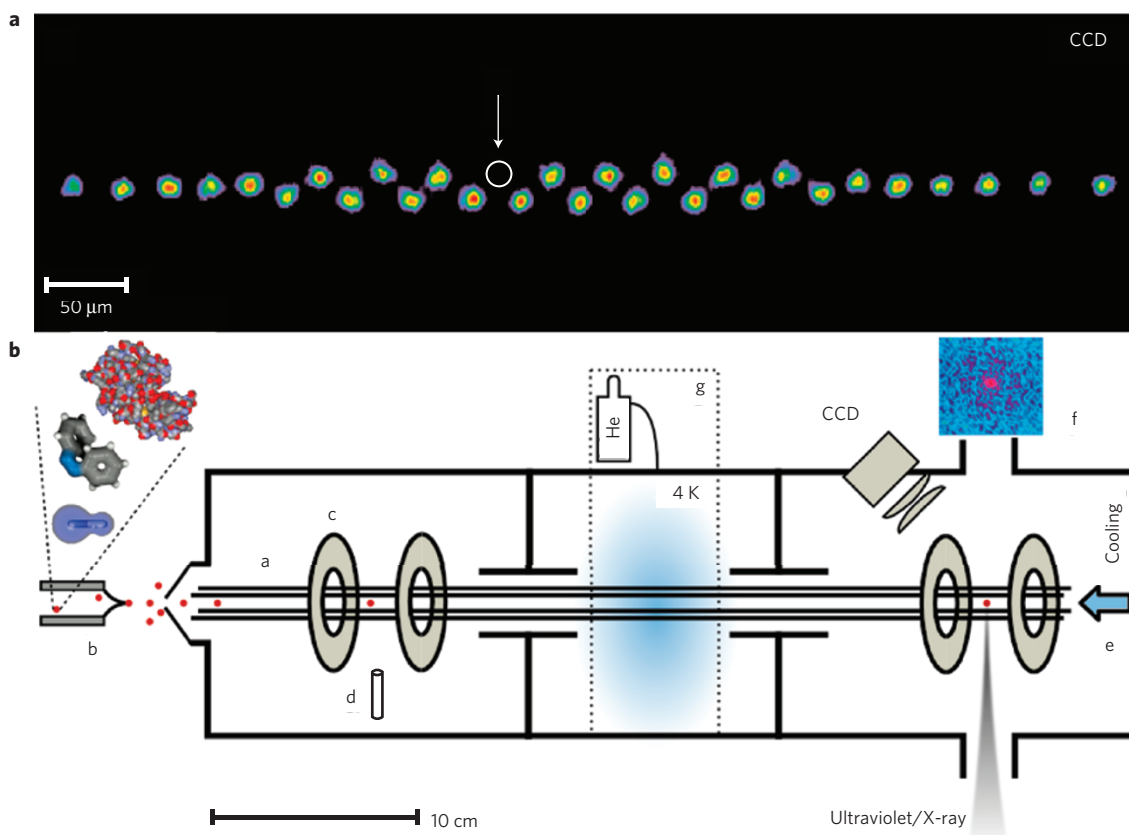


Figure 2 | Preparation of a single molecular ion as a cold, micropositioned target. **a**, CCD fluorescence image of atomic ($^{24}\text{Mg}^+$) ions, laser-cooled to form a Coulomb crystal in a linear radiofrequency trap. All ion positions are defined to better than $1\ \mu\text{m}$. At the precisely localizable site of the missing bright spot (indicated by a white circle), the molecular ion (MgH^+) is sympathetically cooled by the adjacent, directly laser-cooled atomic ions. **b**, Tabletop experimental implementation of the conveyor belt of Fig. 1. Molecular ions can be injected directly into the radiofrequency quadrupole guide (a) by electro spray ionization (b) or breded by a photochemical reaction. Ring electrodes (c) at the front and the end of the radiofrequency guide allow for transfer and trapping of the molecule, respectively. An oven (d) produces a thermal beam from which atomic ions can be loaded into the guide/trap by photoionization. These are laser cooled (e) to form a sympathetic heat sink for the molecule and to freeze into a Coulomb crystal with the molecule embedded on a lattice site for its precise localization (see **a**). Our experiment is carried out with few-femtosecond ultraviolet laser pulses. However, also intense and short X-ray pulses are expected to be focused tightly ($<1\ \mu\text{m}$) onto the single target molecule, predicted to yield diffraction patterns providing atomic resolution (f; ref. 3). The apparatus is designed to include a further buffer-gas cooling stage (g) and laser-induced, field-free alignment³⁴.

lattice site or was dissociated by evaluating fluorescence images. For the given parameters, on average 1 in 1,000 ideally matched pump–probe pulse pairs triggers the dissociation. Finally, we average over many dissociation events at each pump–probe–delay setting. From this, we deduce the mean dissociation probability per pulse and its modulation in dependence on the pump–probe delay. As the pulse duration is shorter than the timescale of the dynamics, we can detect not only the reaction, as proposed in ref. 24, but its dynamics within a single molecule and a fidelity close to 100%.

Figure 4 shows the main results of the experiment. In total, 2,477 individual molecules contribute approximately equally to the 26 data points. The theoretical prediction is depicted as a solid line. Here, the dissociation probability is clearly modulated at a period of approximately 30 femtoseconds owing to the molecular ion's vibration. Its modulation in time as well as the absolute amplitude of the probability to dissociate is in good agreement with our experimental data. The slight deviation from a sinusoidal modulation in the experimental data is reproduced by the theoretical result and can be attributed to the crosstalk with adjacent potential-energy curves (mainly D; Fig. 3).

The recovery of the full amplitude after the second oscillation period already provides strong evidence for long coherence times due to minimal environmental disturbances. This is different from

intriguing experiments localizing molecules in polymer films²⁴. The absence of any decohering environment (solvent or carrier) also explains the good agreement of the experimental data and theory even at zero pulse delay. Overlapping and interfering pump and probe pulses tend to conceal the immediate response of the molecule, for example by polarizing the environment. Container-free handling of the isolated molecules therefore enables us to follow singular processes limited only by the pulse duration.

In the future, the presented scheme will be applied to prototype molecules already provided by our electro spray ionization source. Protonating mid-sized molecules, such as azobenzene and the Schiff base of retinal²⁵, show light-induced *cis–trans* isomerization, a process on the 100 fs timescale of fundamental interest. Experiments on isolated molecular ions would eventually enable us to precisely evaluate calculations based on subtle quantum mechanical models that do not take environmental effects into account. Furthermore, exploring molecular ions might be advantageous as biological molecules occur charged in nature^{25,26}. Selecting hydrated molecules ($\approx 10\text{H}_2\text{O}$) can simulate natural surroundings and may stabilize the tertiary structure against radiation damage⁹. If a higher repetition rate were required, a reservoir of many (10–100) identical molecules within one Coulomb crystal could be scanned on its individual lattice sites. We could implement the reservoir within a storage ring for

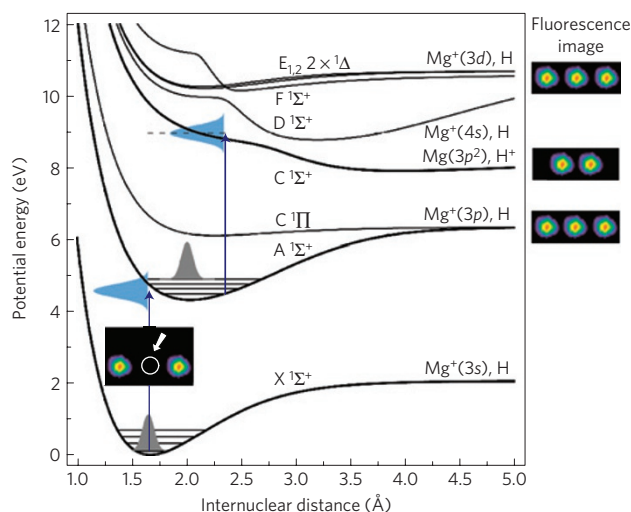


Figure 3 | Schematic representation of our experiment on a deterministically positioned single molecule, based on the *ab initio* potential-energy curves of the electronic states involved. A molecular ion (MgH^+ , indicated by the white circle in the lowest of the four insets depicting fluorescence images of atomic ions) is prepared in the vibrational and electronic ground state (X). Arrows and vertical Gaussian profiles indicate identical ultraviolet pump and probe pulses (4 fs, 285 nm). The spectrally broad pump pulse creates a vibrational wave packet oscillating with 30 fs period in the electronically excited state (A). Its motion is mapped onto the probability for the probe pulse to excite the molecular ion in a second step to the repulsive state (C). Dissociation through C results in loss of both product particles.

molecular ions²⁷, further extending this approach to crystallized (molecular) ion beams^{28,29}. In our current apparatus we allocate $^{24}\text{Mg}^+$ and $^{138}\text{Ba}^+$, already giving access to a variety of molecular ions, ranging from diatomic through mid-size molecules such as retinal²⁵ ($m \approx 300$ Da) to biofunctional organic molecular ions such as cytochrome *c* ($m \approx 12,400$ Da) at $Z = +12$ or lysozyme ($m \approx 14,000$ Da) close to its natural charge state²⁶ $Z = +8$. A straightforward extension of our method (Methods) might enable us to follow the development to reach for substantially smaller Z/m or even single viruses⁹, and the required waists of $0.1 \mu\text{m}$ (refs 3,30) and below. The motional amplitude is limited by the quantum mechanical constraint of Heisenberg's uncertainty principle (tens of nanometres for both atomic and molecular ions). In addition, the beam parameters could be probed with nanometre resolution using a dedicated (molecular) ion as a sensor.

It has been predicted that “ultrashort, high-intensity X-ray pulses from free-electron lasers that are currently under development, in combination with container-free sample handling methods based on spraying techniques, will provide a new approach to structural determination with X-rays”¹. The demonstrated molecular conveyor belt provides the required (sub)micrometre positioning and the directly related opportunity to reduce the waist of the pulses from 30–10 μm down to $1 \mu\text{m}$, enabling us to increase the number of valuable X-ray photons by two to three orders of magnitude, exploiting each single pulse and target, respectively.

The described methodology could be further exploited for involved applications, such as sequencing charged reaction products or fragments and keeping them for subsequent investigation. The same deterministic methodology would substantially enhance the efficiency of X-ray holography⁴, where the molecule and a reference target must be hit simultaneously. Furthermore, the investigation of structural changes during (photo)chemical reactions not only of one molecule, but between (charged and uncharged) molecules, can be foreseen.

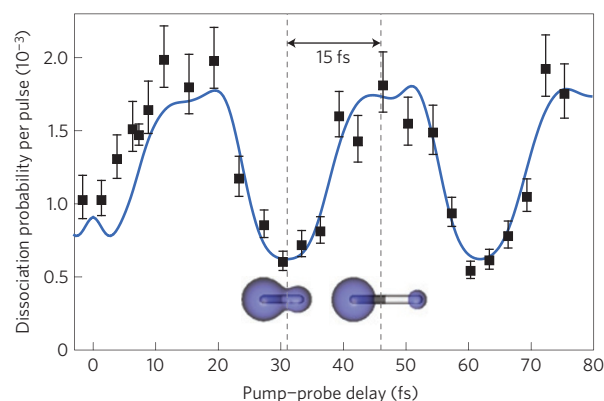


Figure 4 | Vibrational motion of molecules derived from the dissociation of single molecules as a function of pump-probe delay for 4 fs laser pulses. Copies of the molecule were repeatedly prepared by the scheme presented in Figs 1 and 2, and spatially overlapped with the pulses. The dissociation probability in channel C (Fig. 3) is modulated with a period of 30 fs. An illustration of the two related electronic probability densities of our molecular ion at the classical turning points is given. Each data point corresponds to the statistical average ($\pm 1\sigma$) of experiments with between 50 and 108 molecular ions in total. Solid line: result of our theoretical model for the experimental parameters described in the text.

Methods

Extension to biologically relevant molecules. Radiofrequency traps have recently been shown to be suitable to store large ensembles of biofunctional molecules. The protein cytochrome *c* ($m \sim 12,400$ amu; $Z/m \sim 1/1,000$) has been confined and sympathetically cooled using a $^{138}\text{Ba}^+$ Coulomb crystal¹⁴.

However, simultaneously trapping a large ensemble of biologically relevant molecules of comparatively small Z/m leads to a substantially reduced coupling to their heat sink because of an increased mutual distance¹⁴. In contrast, for ions of similar charge and mass, a single atomic ion is sufficient to sympathetically cool and crystallize more than ten molecular ions, because sufficient coupling is provided at mutual distances of $d \sim 10 \mu\text{m}$.

Our apparatus is capable of providing such an ensemble as the initial reservoir by its electrospray-ionization source^{8,9} and the recently demonstrated efficient photoionization scheme for barium atoms³¹. Individual ions have been already separated deterministically from a larger ensemble using the light-pressure force and voltages on knife electrodes¹².

As the molecular conveyor belt can deliver one molecular and a single atomic ion, the dilution by space charge is reduced and the stiff confinement enables focusing of the different species sufficiently close to one another to again guarantee efficient cooling and precise positioning. For example, a radiofrequency voltage of 1 kV results in a radial secular frequency of $2\pi \times 1.5$ MHz for $^{138}\text{Ba}^+$ and $2\pi \times 200$ kHz for cytochrome *c* at charge state $Z = +12$ (ref. 20). By providing a weaker axial confinement ($2\pi \times 400$ kHz and $2\pi \times 150$ kHz for $^{138}\text{Ba}^+$ and cytochrome *c*, respectively), both particles will be forced on the trap axis at a mutual distance of again $d \sim 10 \mu\text{m}$. For these parameters and an equilibrium temperature that could reach up to 20 times the Doppler-cooling limit ($T_{\text{Doppler,barium}} \sim 0.5$ mK), the motional amplitudes would still remain restricted to the order of $0.1 \mu\text{m}$.

Reaching towards even larger molecules ($>10^5$ amu) or trying to cool the target to the motional ground state will require us to adjoin a tighter trapping section, such as already realized in refs 12,32. For example, choosing $Z/m = 10/10^5$ requires applying a radiofrequency amplitude of 3 kV at $\Omega_{\text{RF}} = 2\pi \times 150$ MHz and a distance from the trap centre to the electrodes of $100 \mu\text{m}$ (ref. 12) to achieve $d \sim 5 \mu\text{m}$. By potentially adding a few atomic ions, to further increase the coupling, conventional Doppler cooling would suffice for positioning within the $0.1 \mu\text{m}$ scale, and already established, sub-Doppler cooling schemes might even reach the motional ground state³³.

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Author contributions

S.K. and G.L. contributed equally to this work. M.K., W.F. and R.d.V.-R. developed the theory. A.S., E.B., R.E., F.K., R.K. and T.S. contributed to the experimental work.

Additional information

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