Production and deceleration of a pulsed beam of metastable NH ($a\,^1\Delta$) radicals

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Abstract. We report on the production of a pulsed molecular beam of metastable NH ($a\,^1\Delta$) radicals and present first results on the Stark deceleration of the NH ($a\,^1\Delta, J = 2, M\Omega = -4$) radicals from 550 m/s to 330 m/s. The decelerated molecules are excited on the spin-forbidden $A\,^3\Pi \leftarrow a\,^1\Delta$ transition, and detected via their subsequent spontaneous fluorescence to the $X\,^3\Sigma^-, v" = 0$ ground-state. These experiments demonstrate the feasibility of our recently proposed scheme [Phys. Rev. A 64 (2001) 041401] to accumulate ground-state NH radicals in a magnetic trap. In addition, we propose to transfer the NH radicals from the $a\,^1\Delta$ to the $X\,^3\Sigma^-$ state using a cw-laser to allow cooling of the beam during trap loading.

1. Introduction

In recent years there has been a growing interest in the development of methods to produce neutral molecules that are sufficiently slow that they can be confined in a trap. This interest is triggered by various potential applications and by the promise of the occurrence of interesting new physics and chemistry at the low temperatures and high densities that can ultimately be achieved. Extensive reviews as well as special issues of scientific journals on the production and application of cold (polar) molecules have recently appeared [1, 2, 3].

Over the last years, we have developed the method of Stark deceleration of a molecular beam to produce samples of cold polar molecules. In a Stark decelerator, the quantum-state specific force that a polar molecule experiences in an electric field is exploited to manipulate the external degrees of freedom of a molecule. This force is rather weak, typically some eight to ten orders of magnitude weaker than the force that the corresponding molecular ion would experience in the same electric field. This force nevertheless suffices to achieve complete control over the motion of polar molecules, using techniques akin to those used for the control of charged particles. This has been explicitly demonstrated by the construction of two types of linear accelerators [4, 5], a buncher [6], two types of traps [7, 8] and a storage ring [9] for neutral polar molecules. Recently, the Stark deceleration and trapping technique has been used to store ground-state OH radicals in an electrostatic quadrupole trap for times up to seconds at a density of $10^7 - 10^8$ cm^{-3} and at a temperature of 50 mK [10]. Since the introduction of the Stark-decelerator in 1999, other groups have successfully implemented the method as well [11, 12].

To be able to study molecular interactions and collective effects in these trapped samples of polar molecules, the phase-space density needs to be further increased, i.e., the number density needs to be made higher and/or the temperature needs to be reduced. In the Stark deceleration and trap loading method, only a single loading cycle has been employed thus far. The most straightforward method to increase the phase-space density of the trapped molecules would therefore be the accumulation of several packets of decelerated molecules in the trap. Simply re-loading the trap, however, requires opening up the trapping potential thereby either losing or heating the molecules that are already stored. Recently, we proposed a scheme that circumvents this fundamental obstacle, a scheme that specifically allows to accumulate ground-state NH radicals in a magnetic trap [13]. In this scheme, a beam of NH molecules in the long-lived metastable $a^1\Delta$ state is injected into a Stark decelerator and brought to a standstill. When the molecules are (almost) standing still, they are optically pumped to the $X^3\Sigma^-$ electronic ground state by inducing the spin-forbidden $A^3\Pi \leftarrow a^1\Delta$ transition [14], followed by spontaneous emission in the triplet system. In the ground state, the NH molecules can be magnetically trapped, for instance in a quadrupole magnetic trap. As the Stark interaction in the ground state is very weak, the electric fields of the decelerator hardly effect the magnetic trapping potential and the decelerator

can be switched on again to stop and load the next pulse of NH radicals.

The success and usefulness of the proposed accumulation scheme depends on the availability of an intense pulsed source of slow metastable NH ($a\,^1\Delta$) radicals that is suited to be coupled to a Stark decelerator. Furthermore, optical pumping of the decelerated NH ($a\,^1\Delta$) radicals to their electronic ground state needs to be performed. Here we describe a production method for a pulsed molecular beam of metastable NH ($a\,^1\Delta$) radicals and in a preliminary experiment the deceleration of NH radicals from 550 m/s to 330 m/s is demonstrated. The decelerated molecules are excited to the $A\,^3\Pi$ state and detected via their subsequent emission to the electronic ground-state. An experimental procedure that might allow further cooling of a decelerated packet of NH molecules during the loading of the magnetic trap is proposed and discussed.

2. A pulsed slow molecular beam of NH ($a\,^1\Delta$) radicals

For the deceleration and trapping of NH radicals an intense pulsed beam of metastable NH radicals with a low initial velocity is required. Although many cell experiments with NH ($a\,^1\Delta$), using a variety of production schemes, have been carried out, only a few studies have been performed with metastable NH in a pulsed [15, 16, 17, 18] or continuous [19, 20] molecular beam. In most of the beam studies, photo-dissociation of the precursors HN_3, HNCO, or NH_3 has been used.

Our experiments are performed in a molecular beam machine that consists of a differentially pumped source chamber and a detection chamber that are separated by a 1.5 mm diameter skimmer. The NH beam is produced by photo-dissociation of hydrazoic acid (HN_3) by focussing the 80 mJ output of a quadrupled Nd:YAG laser at 266 nm just in front of the nozzle orifice of a pulsed supersonic valve (Jordan Inc.). The advantage of this production scheme is that the NH radicals are almost exclusively produced in the $a\,^1\Delta$ state, since the NH ($X\,^3\Sigma^-$) + N_2 channel is spin forbidden [21, 22, 23]. The HN_3 gas is produced online by heating sodium azide in excess of stearic acid to 95 °C to drive off the gaseous hydrazoic acid. In order to reduce the initial velocity of the molecular beam, either Argon, Krypton or Xenon is co-expanded from the pulsed valve as inert carrier gas. Unfortunately, Xe is observed to efficiently quench the NH ($a\,^1\Delta$) radicals, an effect that has been well documented before [15, 24, 25]. The mechanism that causes the fast quenching rate for Xe is at present unknown [20, 26]. The quenching rate for Kr is about three orders of magnitude smaller than for Xe [27], sufficiently low to enable the use of Kr as a carrier gas in our experiments.

The molecular beam is characterized by detecting the NH radicals about 24 cm downstream from the nozzle by a resonant Laser Induced Fluorescence (LIF) detection scheme. The populations in the $a\,^1\Delta$ and the $X\,^3\Sigma^-$ states are probed by inducing the $c\,^1\Pi, v = 0 \leftarrow a\,^1\Delta, v = 0$ transition around 326 nm and the $A\,^3\Pi, v = 0 \leftarrow X\,^3\Sigma^-, v = 0$ transition around 336 nm, respectively, and by recording the molecular fluorescence. Both transitions are measured under saturated transitions. The fluorescence excitation spectrum that is thus obtained is shown in Figure 1. The observed spectral lines are
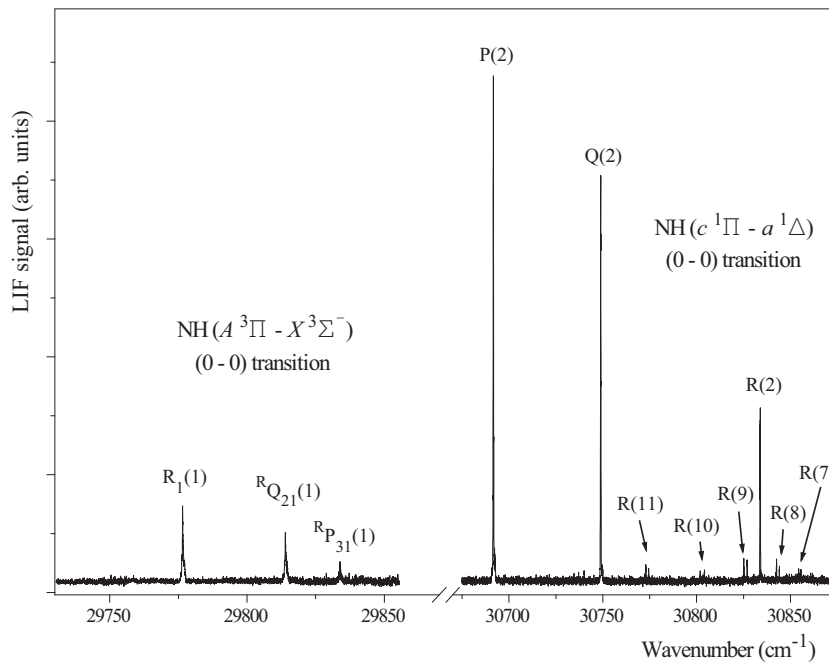
Figure 1. Fluorescence excitation spectrum of the $A\,^3\Pi, v = 0 \leftarrow X\,^3\Sigma^-, v = 0$ band and the $c\,^1\Pi, v = 0 \leftarrow a\,^1\Delta, v = 0$ band of NH in the pulsed molecular beam. The lines are labelled using standard spectroscopic nomenclature.

labelled using standard spectroscopic nomenclature. The majority of the NH radicals in the beam resides in the metastable $a\,^1\Delta$ electronic state. The small percentage of the population that is in the electronic ground state (estimated to be less than 10%) is believed to originate from electronic quenching of NH $(a\,^1\Delta)$ by collisions with Kr, or from two-photon processes in the dissociation of HN_3. In the $a\,^1\Delta$ state, the rotational level $J = 2$ is the most populated one, reflecting the efficient rotational cooling in the expansion region of the supersonic jet. A secondary maximum in the rotational population distribution is observed around $J = 9$. A similar bimodal distribution has been observed before for NH $(a\,^1\Delta)$ in a supersonic beam, namely in the production of NH via photo-dissociation of HN_3 at 193 nm in N_2 carrier gas [16]. The secondary maximum reflects the nascent rotational distribution of NH $(a\,^1\Delta)$ upon photo-dissociation of HN_3, and the low inelastic scattering cross sections for high values of J. It is evident from the spectrum presented in Figure 1 that, in spite of the bimodal rotational level distribution, at least 50% of all the NH $(a\,^1\Delta, v=0)$ radicals are in the J=2 rotational ground-state level.

The velocity distribution of the molecular beam critically depends on the time at which the dissociation laser is fired in the gas pulse that is emanating from the supersonic valve. The time-interval between the trigger pulse for the pulsed valve and the trigger pulse for the dissociation laser is indicated by T_{diss}. Here it should be noted that, depending on experimental conditions, the pulsed valve typically only opens some 0.20–0.21 ms after the trigger is applied; the dissociation laser fires simultaneous (on this time-scale) with the opening of the valve. In Fig. 2, the measured time of flight

(TOF) profiles of the beam of NH ($a\,^1\Delta$) are shown for different values of T_{diss}. The population in the $J = 2$ level is measured by recording the LIF intensity on the $P(2)$ line of the $c\,^1\Pi \leftarrow a\,^1\Delta$ transition. For low values of T_{diss}, when the valve is just opening and when there is no good supersonic expansion yet, the beam typically has a high mean velocity (>600 m/s), and a relatively large velocity spread. The beam has a maximum peak intensity if the dissociation laser is fired 0.23 ms after the trigger pulse for the valve. The beam then has the minimum velocity spread (FWHM) of only 9 %, at a mean velocity of 575 m/s. The latter is still significantly faster than would be expected for a room temperature expansion of pure Kr, i.e., ~ 450 m/s. This can be explained in part by the seeding of the lower mass HN_3 molecules but mainly reflects the relatively high constant temperature (70°C) of the valve body during operation. In addition, the transient high temperature of the gold hairpins of the valve opening mechanism, that support a peak current exceeding 4.0 kA when the valve opens, is known to lead to even higher apparent source temperatures in this type of valve [28]. For higher values of T_{diss}, the beam has a lower mean velocity and the inferior expansion conditions result in a lower peak intensity and a larger velocity spread. The decreasing beam velocity over the temporal profile of the gas pulse, is in part due to cooling of the gold hairpins by the gas that flows in between them and in part due to the transition from supersonic to effusive flow.
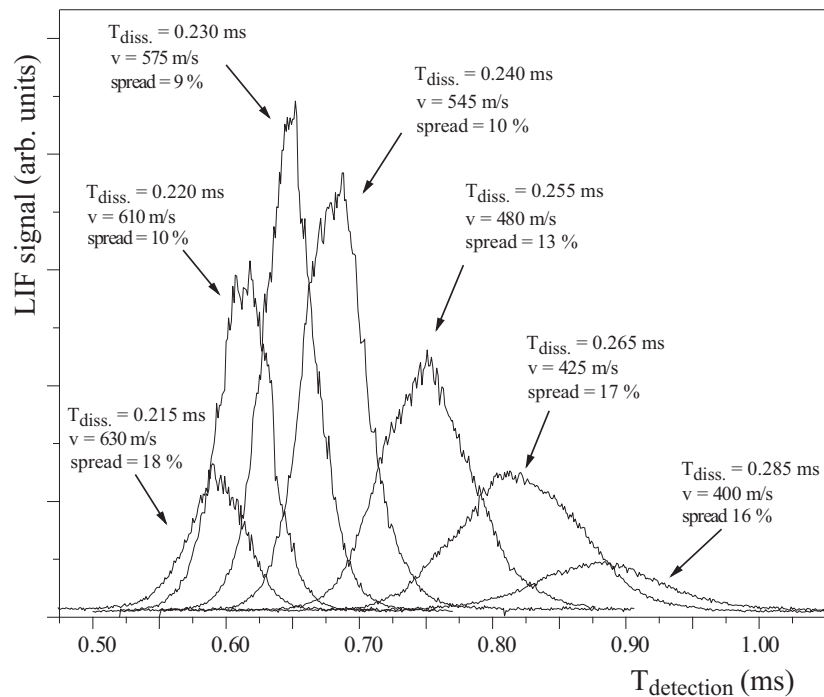
Figure 2. TOF profiles of the molecular beam of NH ($a\,^1\Delta, J = 2$) radicals for different values of T_{diss}, the time-interval between the trigger for the pulsed valve and the firing of the dissociation laser. For each TOF profile, the mean velocity and the velocity spread (FWHM) of the beam is given.

3. Deceleration of a molecular beam of NH ($a\,^1\Delta$) radicals

In this section, priliminary experiments are presented in which the pulsed beam of NH ($a\,^1\Delta, J = 2$) radicals is decelerated. For this, the Stark decelerator that we employed recently for the deceleration and trapping of OH radicals [10] is mounted between the source and the detection chamber. The general operation principles and the technical details of this specific Stark decelerator are documented extensively elsewhere [29, 30], and will not be further detailed here.

After passing through the skimmer, the NH ($a\,^1\Delta$) radicals are focussed by a short hexapole into the – just over one meter long – Stark decelerator, consisting out of 102 electric field stages. In each electric field stage, a voltage difference of 40 kV between opposing electrodes can be applied, creating a maximum electric field on the molecular beam axis of about 95 kV/cm. The NH ($a\,^1\Delta$) radicals that exit the decelerator are optically pumped to the electronic ground state in the LIF detection zone, and are state-selectively detected in this process. Excitation on the $P_2(2)$ line of the spin-forbidden $A\,^3\Pi, v = 0 \leftarrow a\,^1\Delta, v = 0$ transition around 584 nm [14] is performed. The $A\,^3\Pi, v = 0 \rightarrow X\,^3\Sigma^-, v = 0$ fluorescence around 336 nm is imaged onto the photomultiplier (PMT). The detection of the NH radicals in this way is almost background-free as stray-light from the laser can be effectively blocked by optical filters in front of the PMT. The transition is induced by the fundamental output of a ns pulsed dye laser system (Spectra physics, PDL3 combination). Typically, an energy of 30 mJ in a 4 mm diameter beam with a bandwidth of 0.04 cm^{-1} is used, which is not enough to saturate the transition; when a laser with a superior optical brightness is used, this transition can be readily saturated [14].

In Fig. 3 the TOF profile of the decelerated NH radicals is shown as obtained when the Stark decelerator is operated at a phase angle $\phi_0 = 70°$ for a synchronous molecule with an initial velocity of 550 m/s ($E_{kin} = 190$ cm^{-1}). With these settings, the decelerator extracts about 1.2 cm^{-1} of kinetic energy from the synchronous molecule in every deceleration stage. NH radicals in the $M_J\Omega = -4$ component of the $a\,^1\Delta, J = 2$ state are decelerated to a final velocity of 330 m/s ($E_{kin} = 68$ cm^{-1}), i.e., almost two-thirds of their kinetic energy is removed. The decelerated bunch of molecules arrives in the detection region 2.92 ms after production, about 0.6 ms later than the arrival time of the original non-decelerated molecular beam (data not shown). The arrival time distribution that results from a three dimensional trajectory simulation of the experiment is shown underneath the experimental data. The arrival time of the packet of decelerated molecules is accurately reproduced by the simulations. The width of the velocity distribution of the decelerated NH radicals is about 10 m/s, corresponding to a longitudinal translational temperature of about 0.1 K.

With the present Stark decelerator, the NH ($a\,^1\Delta$) radicals can be decelerated to standstill and subsequently loaded into a trap if a beam with an initial velocity in the 420 - 450 m/s range is produced. As for the production of the metastables we are restricted to the use of Kr as a seed gas, this can only be achieved by cooling the Jordan
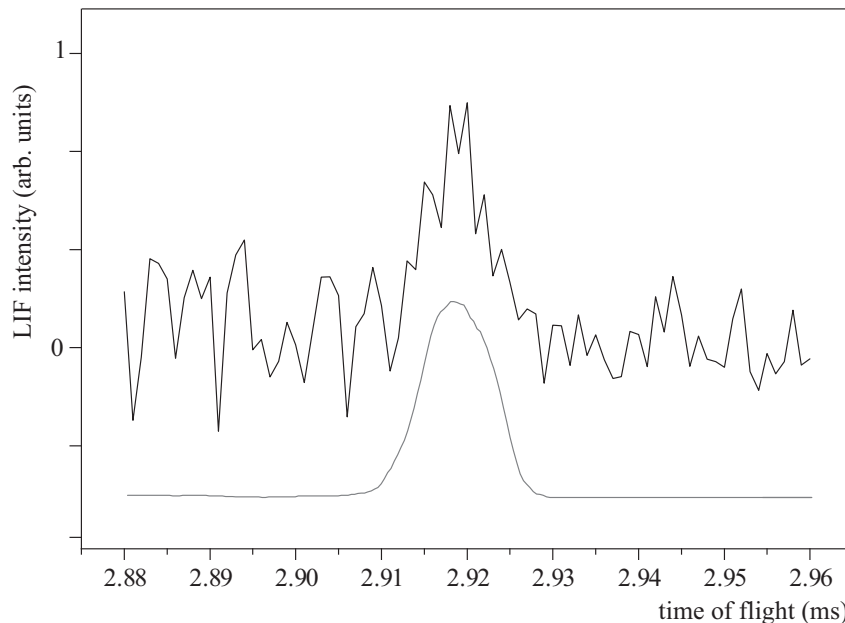
Figure 3. Observed TOF profile of decelerated NH ($a\,^1\Delta, J = 2, M\Omega = -4$) radicals exiting the decelerator (upper curve). The packet of molecules is decelerated from 550 m/s to 330 m/s. The TOF profile that results from a 3D numerical simulation of the experiment is shown underneath the experimental profile.

valve or by using a different supersonic valve. A room temperature General valve, for instance, as is used in our trapping experiments with OH radicals [10], can be used to produce the beam with a velocity that is within this range.

In the present preliminary experiments, the density of decelerated NH radicals is limited by the laser power of the dissociation laser (the dissociation is performed far from saturation), and the relatively poor beam intensity that was present when conducting the experiment. In a separate molecular beam machine, dedicated to optimize production and detection schemes of various molecular beams, we have reached a NH beam density that is about a factor 4 smaller than the OH beam density that we typically employ in our trapping experiments. Therefore, we are convinced that ultimately the density of trapped NH radicals, employing a single loading cycle, can be of the same order of magnitude as the density we have reached for OH radicals. The obtainable density might be even higher using other NH ($a\,^1\Delta$) production schemes.

## 4. Cooling of the beam during trap loading

In the original paper on the accumulation of ground state NH radicals in a magnetic trap [13], it was proposed to transfer the NH radicals with a pulsed laser from the $a\,^1\Delta$ state to the $X\,^3\Sigma$ state. The strength of the spin-forbidden $A\,^3\Pi \leftarrow a\,^1\Delta$ transition [14] suggests, however, that this transfer can be performed using a cw-laser system as well. In this case, an increase in the phase-space density of each individual decelerated packet of NH radicals during the trap loading process is possible, as outlined below.

Whenever a pulsed trap loading scheme is used, either with a pulsed laser to transfer NH radicals to a magnetic trap or by abruptly switching on an electrostatic trap, for instance, the upper limit of the phase-space density that can be achieved in the trap is set by the phase-space density of the decelerated packet. This upper limit can be reached by perfectly matching the (6-dimensional) emittance of the decelerator to the acceptance of the trap. Imperfect matching, either with respect to the velocity or spatial acceptance of the trap will lead to a reduced number of trapped molecules and/or to heating up of the trapped molecules, e.g., to a reduced phase-space density. The longitudinal phase-space distribution of the molecular packet at the exit of the decelerator is, schematically and idealized, shown in panel a) of Figure 4. By abruptly switching on a trap with a perfectly matched acceptance, this distribution can be loaded in the trap without loss in phase-space density, as schematically indicated in panel b).

If one uses a spatially localized, continuous and uni-directional means to transfer the decelerated molecules to the trap, time comes in as an extra degree of freedom. The molecules do not have to arrive at the center of the trap simultaneously in order to be transferred. This can be used to advantage when, for instance, the longitudinal spatial distribution of the packet of decelerated molecules is allowed to expand before entering the trap region, and when simultaneously the longitudinal velocity spread of the packet is reduced [6]. When there is in addition a small, overall deceleration when the molecules approach the trap center, the (idealized) longitudinal phase-space distribution as depicted in panel c) can be realized. In this case, the NH radicals can be pumped to the magnetic trap by the continuous laser, which only irradiates near the center of the trap, and their density near the trap center will thus increase. In panel d) of Figure 4 it is shown how the longitudinal phase-space distribution depicted in panel c) can be compressed to a higher final phase-space density via this cw-laser loading scheme.

In order to estimate the increase is phase-space density that can be accomplished with this scheme we performed preliminary one-dimensional trajectory calculations of metastable NH radicals in the decelerator and in the trap-loading region. These simulations indicate that the width of the final velocity distribution of a packet of NH radicals transferred with a cw-laser to the magnetic trap is realistically about a factor of 2.5, limited by the free flight section that is needed to spatially expand the packet, smaller than a package of molecules trapped with the pulsed loading scheme. As indicated in the schematic description above, this reduction in the width of the velocity distribution is not the result of simply transferring only the slow molecules; no molecules are lost during the transfer process. The reduced velocity spread indicates a potential phase-space density increase of magnetically trapped NH ($X\,^3\Sigma^-$) radicals of more than one order of magnitude compared to the trapping of NH ($a\,^1\Delta$) radicals in a pulsed electrostatic trap, for instance.
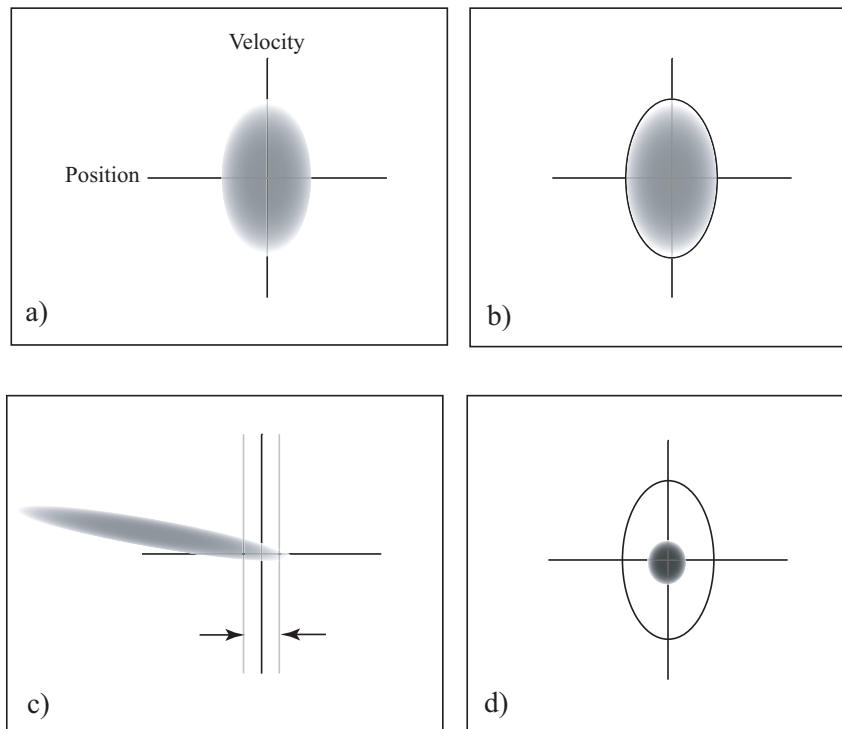
Figure 4. Idealized longitudinal phase-space distribution at the exit of the decelerator (panel a)) with a perfectly matched acceptance of a trap (panel b)). A spatially elongated, but velocity compressed, longitudinal phase-space distribution (panel c)) that can be transferred to the trap by a spatially localized laser (indicated by the horizontal arrows in panel c)), resulting in an increased phase-space density in the trap (panel d)).

5. Conclusions

We have demonstrated the production of a pulsed, slow molecular beam of metastable NH ($a\,^1\Delta$) radicals that is suited to be injected into a Stark decelerator. In a preliminary deceleration experiment, metastable NH radicals in the $J = 2$, $M\Omega = -4$ level have been decelerated from 550 m/s to 330 m/s, e.g. two-thirds of the kinetic energy has been removed from these molecules. In principle, the NH radicals can be decelerated to rest and confined in an electrostatic trap. When the NH ($a\,^1\Delta$) radicals are transferred to the $X\,^3\Sigma^-$ ground state by inducing the $A\,^3\Pi \leftarrow a\,^1\Delta$ transition when the molecules have come to rest, the ground-state NH radicals can be confined near the center of a magnetic trap. We have presented a possible scheme to increase the phase-space density of the trapped packet of NH based on the use of a cw-laser for the transfer from the $a\,^1\Delta$ state to the $X\,^3\Sigma^-$ state. Together with our previously proposed scheme to accumulate NH radicals from subsequent deceleration cycles in a magnetic trap, this offers great prospects for further Stark deceleration and magnetic trapping experiments.

6. Acknowledgements

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