

Optimising the Intensity and Purity of a Zeeman-Decelerated Beam

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A pure, state-selected beam of gas-phase radicals is an important tool for the precise study of radical reactions that are astrochemically and atmospherically relevant. Generating such a beam has proven to be an ongoing challenge for the scientific community. Using evolutionary algorithms to optimise the variable experimental parameters, the passage of state- and velocity-selected hydrogen atoms can be optimised as they travel through a 12-stage Zeeman decelerator and a magnetic guide. Only H-atoms travelling at the target velocity are present in the beam that reaches the detection region, from a source containing a mixture of different species. All other species—including seed gases, precursor molecules, other dissociation products, and H atoms travelling outside the target velocity—are removed from the beam. The fully optimised parameters yield a pure H-atom beam containing twice as many target particles and a narrower velocity distribution compared to beams produced when only the Zeeman decelerator is optimised. These significant improvements highlight the importance of considering the passage of all target particles in the beam as they pass through all elements of the experimental apparatus.

Despite being integral to our understanding of fundamental chemical processes, and important in interstellar and atmospheric chemistry, very few gas-phase radical reaction systems have been precisely studied experimentally.¹ The inherent reactivity of these open-shell species means that it is immensely challenging to prepare a pure, state-selected beam of radicals with a tuneable velocity. Such a source is required for precision measurements and collision studies (with, for example, a second reactant in a crossed beam or ion trap). Experimental measurements are also needed to verify existing theoretical models of radical reactivity.^{1, 2}

In this Note, we report on the success of using a Covariance Matrix Adaptation Evolution Strategy (CMA-ES)³ to optimise the properties of a hydrogen atom beam. CMA-ES optimisation is applied to a combined Zeeman decelerator and Magnetic Radical Filter (MRF) set-up to maximise the number of target particles produced, whilst simultaneously removing all unwanted particles—including seed gases, precursor molecules, other dissociation products, and H atoms travelling outside the target velocity range—from the beam. The optimised parameters yield a significant improvement in the number of transmitted target radicals and also increase the purity of the beam.

Radical species are paramagnetic; the presence of an unpaired electron gives rise to a magnetic moment. Radicals in a low-field-seeking (LFS) quantum state experience an increase in potential energy as they move into an external magnetic field. This property forms the basis of Zeeman deceleration: current sequences applied to a series of solenoid coils give rise to time-varying and inhomogeneous magnetic fields. These fields can be switched on and off such that they reduce the forward velocity of radicals in selected LFS states.⁴⁻⁶ The carefully timed series of current pulses applied sequentially to the Zeeman decelerator coils are conventionally calculated by considering the passage of a single ‘synchronous’

particle travelling along the central beam axis. As the synchronous particle passes through each coil, a small (and constant) amount of kinetic energy is converted to potential energy and the particle is decelerated. By operating the decelerator at different phase angles, a range of different final velocities can be achieved. Only particles with a similar velocity and position to the synchronous particle—particles in the phase-space acceptance of the decelerator—will be present in the packet of particles decelerated to the target velocity.

Several different strategies have been implemented in a bid to improve the number density of particles travelling at the target velocity. Recent advances in solenoid coil cooling efficiency and the introduction of alternating decelerating and focusing stages make these latest Zeeman decelerators ideal for crossed molecular beam scattering experiments.^{7, 8} Zeeman decelerator switching sequences have also been optimised using nominal phase angles⁹ and with a CMA-ES approach.^{10, 11} These methods have all achieved improvements in the properties of the decelerated beam, addressing one of the key issues in the study of gas-phase radical species in the laboratory: the generation of a sufficient number of target particles for precision measurements and reaction studies.¹ Recent progress has seen the reporting of precision spectroscopic measurements¹² and inelastic scattering studies (with the latter employing a crossed-beam set-up).¹³ For many applications, however, there is a second requirement of the radical source: that it be free from contaminant species.

Zeeman decelerators do not impede the passage of any particles that travel along the central beam axis. The beam entering a Zeeman decelerator is typically a mixture of precursor molecules, the radicals of interest, other dissociation products, and seed gases. As the unwanted species in the beam are not decelerated by the magnetic fields, they travel through the decelerator ahead of the target species. For applications such as crossed beam experiments, the crossed beam is timed such that it interacts only with the decelerated species. This approach does not work with an effectively static target—such as trapped ions or radical-surface interactions—as the unwanted species in the beam will also collide with the stationary reactants. A MRF has been developed to remove all unwanted

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species from the beam. Composed of four Halbach arrays (magnetic hexapoles) and two skimming blades (see Fig. 1), the addition of a MRF at the end of a Zeeman decelerator has been shown to generate a pure beam of state- and velocity-selected radicals.^{11,14}

By design, the MRF has a number of adjustable parameters. The vertical displacements of each pair of Halbach arrays and the two blades can be adjusted, as can the separation between each pair of arrays. The arrays work in pairs; the first array deflects and the second array collimates the target species. Combined, the pairs of arrays deflect the target species away from, and then back to, the central (z) beam axis. The two skimming blades, positioned after each array pair, remove the direct line-of-sight through the magnetic guide, physically blocking all species travelling along the z axis. An empirical process of trial and error, involving both particle trajectory simulations and experimental measurements, enabled a set of “standard” parameters to be established.^{11,14} These standard MRF parameters have been shown to successfully filter target radical species from both Zeeman-decelerated beams and directly from the (undecelerated) initial supersonic expansion.^{14,15} Selection of the optimal MRF parameters must balance the trade-off between maximising the transmission of target particles and minimising the presence of any non-target species. Here, we demonstrate that all of the variable parameters of the combined Zeeman decelerator-MRF apparatus can be optimised together through the use of an evolutionary strategy.

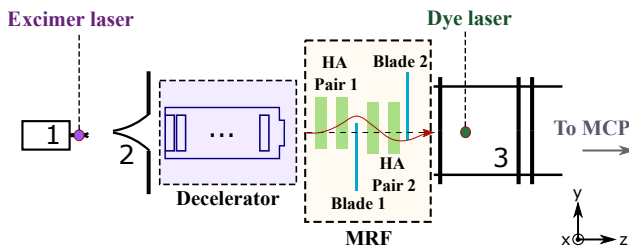


FIG. 1. A schematic diagram (side view) of the experimental set-up. (1) Pulsed valve. (2) Skimmer. (3) Extraction plates. The schematic diagram of the Magnetic Radical Filter (MRF) is shown in the dashed yellow box. The green rectangles represent the side view of the Halbach arrays, with the blue lines representing the blades. The red line shows the trajectory of the target particles through the MRF.

A pulsed supersonic beam of H atoms is formed from the photodissociation of NH_3 seeded in Kr (1:9 ratio, photolysed at 193 nm by an ArF excimer) in a capillary attached to the face plate of a pulsed valve. The H atoms pass through a skimmer and traverse a Zeeman decelerator, where a series of currents (243 A) are applied to the 12 solenoid coils (see Fig. 1), followed by the MRF. The successfully transmitted H atoms are then ionised using a (2+1) resonance-enhanced multi-photon ionisation (REMPI) scheme (at 243 nm), with the resulting ions detected by microchannel plates (MCPs). Time-of-flight (ToF) profiles can be obtained by scanning the delay between the photolysis and ionisation lasers. The properties of the H-atom beam are well described by simulations and have been detailed in earlier work.^{11,14}

The adjustable experimental parameters include the dura-

tions of the 12 coils of the decelerator (i.e., how long current is applied to each coil, given a maximum and minimum “on” time),¹⁰ the vertical (y -axis) displacement of each pair of Halbach arrays, and the y -axis position of each skimming blade. These parameters constitute the 16 dimensions of the optimisation, and they are evaluated using three-dimensional particle trajectory simulations. The CMA-ES optimisation algorithm, chosen due to previous success in optimising the switching sequences of the Zeeman decelerator,^{10,11} is inspired by Darwin’s theory of evolution by natural selection. From an initial set of parameters, a population of λ individuals (with $\lambda = 20$ in this work) is sampled from a multivariate normal distribution. The ‘fitness’ of the candidate solutions are evaluated and ranked based on the properties of the particles that reach the detection region (modelled as a circular area with radius 1.3 mm, emulating the acceptance of an ion trap). The fitness function is defined such that the transmission of H atoms travelling within the target velocity range is rewarded, while the presence of any faster or slower particles is penalised. A constraint is added where the height of the first blade must be greater than that of the second, in order to prevent a direct line-of-sight through to the detector. From each generation, the μ best-ranking individuals (with $\mu = 2$ in this work) are selected to become the ‘parents’ of the next generation, while the rest are discarded. In this way, the mean and standard deviation of the search distribution is updated from the best-performing individuals of the previous generation. The optimisation is terminated when the best set of parameters has not been updated for at least 1,200 evaluations.

The previous-best parameters (established prior to this work), based on a CMA-ES-optimised decelerator switching sequence and the standard configuration of the MRF, are used as the initial starting point for the algorithm. The tuneable velocity range in this work, which is determined by the physical properties of the Halbach arrays (remanence $B_0 = 1.4$ T, internal radius $r_i = 3$ mm, external radius $r_e = 7$ mm, and thickness $l_h = 7$ mm), transmit H atoms travelling at velocities from 200 to 355 m s^{-1} . As such, target velocities of 250 ± 10 , 300 ± 10 and 350 ± 10 m s^{-1} are selected for optimisation.

In Fig. 2, the ToF profiles for a target velocity of 300 ± 10 m s^{-1} are shown. The experimental results are in excellent agreement with three-dimensional particle trajectory simulations (see earlier work¹⁰ for further details on how the simulations are conducted). Holistic optimisation of the combined Zeeman decelerator and MRF set-up yields a significant improvement in the number of target particles obtained. This can be seen in Fig. 2, where the experimental peak recorded using the fully optimised parameters is clearly more intense than the signal recorded from the previous-best parameters. Particle trajectory simulations indicate that twice as many target particles reach the final detection region compared to what was previously possible.

In addition to improving the transmission of target particles, full CMA-ES optimisation also minimises the number of faster and slower H atoms transmitted. This can be seen in the ToF traces, with the fully CMA-ES-optimised parameters achieving an average final beam velocity of 298.8 ± 4.8 m s^{-1} , a narrower velocity range than achieved by the

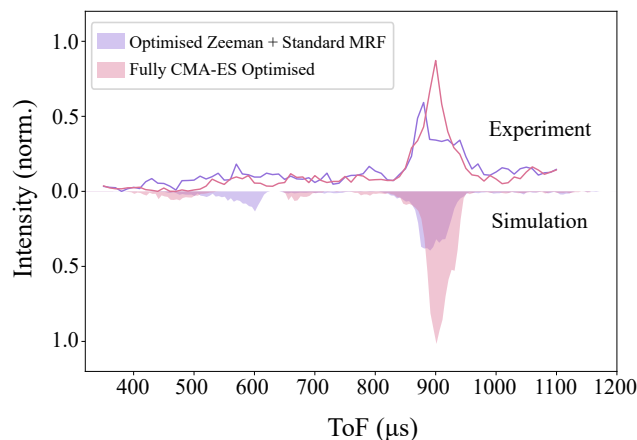


FIG. 2. ToF profiles of the transmitted H atoms, comparing the ‘Fully CMA-ES Optimised’ parameters to those achieved with the previous-best ‘Optimised Zeeman + Standard MRF’ parameters. Experimental data are recorded with 50 averages per data point, plotted with the background subtracted, for a target velocity of 300 m s^{-1} .

previous-best (optimised Zeeman and standard MRF) parameters at $304.0 \pm 12.3 \text{ m s}^{-1}$. With full CMA-ES optimisation, H atoms with non-target velocities constitute $<1\%$ (faster) and 2% (slower) of the transmitted beam. Similar results are seen for target velocities of 350 ± 10 and $250 \pm 10 \text{ m s}^{-1}$. Producing a radical beam with a narrow (and tuneable) velocity distribution will enhance our ability to examine the role of collision energy in radical reaction dynamics.¹

While increasing the number of target particles in a beam usually comes at the cost of reducing beam purity, the combined CMA-ES optimisation results highlight that it is possible to improve both of these properties simultaneously. This is because the optimisation accounts for the entire passage of all H atoms in the beam—all the way from the source through to the detection region. While previous work on CMA-ES optimisation of the Zeeman decelerator switching sequences demonstrated the importance of considering more than just the synchronous particle,^{10,11} this work goes even further. The passage of all H atoms in the beam must be considered as they travel through the entire apparatus. Indeed, the optimisation of all parameters at once achieves a better outcome than optimising the different components of the apparatus separately (or only optimising part of the apparatus). For instance, trajectory simulations show that fewer target particles reach the end of the decelerator when using the fully-optimised (combined) CMA-ES parameters. However, even though fewer target particles reach the MRF, there is greater transverse focusing—resulting in a higher density of particles in the acceptance region of the MRF (see Fig. 3). This leads to a higher transmission of target particles through the first Halbach array, and fewer losses as the target particles move through the MRF.

In this Note, it is shown that CMA-ES optimisation of a combined Zeeman decelerator and magnetic radical filter apparatus produces a beam of H atoms with significantly more target particles than was previously possible. Indeed, CMA-ES optimisation simultaneously improves both the

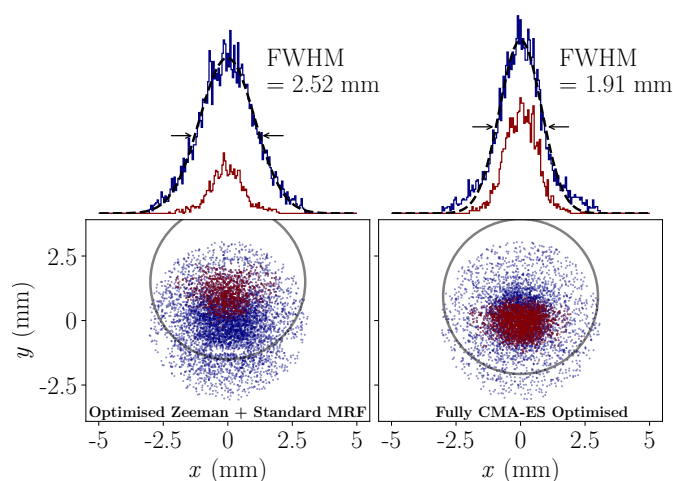


FIG. 3. The positions of target H atoms (350 m s^{-1}) in the transverse plane at the first Halbach array are shown in blue. Particles in red are those that successfully reach the detection region. Particle distributions along the x -axis are shown above each scatter plot. Grey circles indicate the inner radius of the first Halbach array. While the offset of the first array in the standard MRF configuration is greater, this only plays a minor role; even when the first Halbach array is in the same position as for the fully-optimised set-up, the improved transverse focusing of the fully-optimised parameters significantly enhances the transmission of target species through the MRF.

number of target particles and the beam purity. These findings reinforce the importance of considering the passage of all target species through all components of the experimental apparatus, from the source all the way to the detection region. CMA-ES optimisation is found to be an important tool in the generation of pure, state-selected and velocity-selected radical beams needed for reaction studies.

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