Decelerating and Trapping Large Polar Molecules

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Abstract

Manipulating the motion of large polyatomic molecules, such as benzonitrile (C₆H₅CN), presents significant difficulties compared to the manipulation of diatomic molecules. Although recent impressive results have demonstrated manipulation, trapping, and cooling of molecules as large as CH₃F, no general technique for trapping such molecules has been demonstrated, and cold molecules larger than 5 atoms have not been trapped. In particular, extending Stark deceleration and electrostatic trapping to such species remains challenging. Here we propose to combine a novel “asymmetric doublet state” Stark decelerator with recently demonstrated slow, cold, buffer gas cooled beams of closed-shell volatile molecules to realize a general system for decelerating and trapping samples of a broad range of volatile neutral polar asymmetric top molecules. The technique is applicable to most stable volatile molecules in the 100-500 AMU range, and would produce trapped samples in a single rotational state and at a motional temperature of 100s of mK. Such samples would immediately allow for spectroscopy of unprecedented resolution, and extensions would allow for further cooling and direct observation of slow intra-molecular processes such as vibrational relaxation and Hz-level tunneling dynamics.

1: Manipulation of polyatomic molecules

Stark deceleration, first demonstrated by Meijer et. al. in 1998, has proven to be a versatile tool for producing slow or trapped samples of diatomic or “nearly diatomic” molecules such as NH₃[1]. Experiments based upon Stark deceleration of molecules entrained in pulsed supersonic jets have yielded a broad range of results, including high precision spectroscopy, measurements of the lifetimes of long-lived molecular states, low temperature collision studies, and tests of fundamental physics[2, 3, 4, 5]. In Stark deceleration, molecules in a beam are subject to a spatially varying electric field, which is switched such that molecules repeatedly run “uphill”, resulting in a net deceleration. Stark decelerators ideally decelerate low field seeking molecular states, which exhibit stable orbits in realizable electrostatic traps, and conventional wisdom holds that larger molecules exhibit low field seeking states only at low electric fields. To date, only relatively light polar molecules in low-field seeking states have been decelerated to low speed by either conventional or “moving trap” Stark deceleration. Both alternating gradient decelerators[6, 7] and microwave decelerators[8] can decelerate high field seeking states of these and larger molecules, but such decelerators have not yet decelerated samples to rest; for an excellent review of the field see reference [9]. Other proposed and demonstrated methods for manipulating larger molecules include deceleration via pulsed optical forces[10] and pulsed Zeeman deceleration of molecules and polyatomic radicals[11, 12]. Trapping larger, neutral molecules remains a major goal of the cold molecule community.

Two factors make decelerating and trapping heavier, polyatomic species challenging. Higher mass molecules entrained in a fast moving supersonic jet carry more kinetic energy than their lighter counterparts, necessitating more deceleration stages, and polyatomic molecules with low rotational constants exhibit a complex array of highly mixed rotational states in strong laboratory electric fields, which in general do not exhibit the clean “low field seeking” Stark shift required by traditional Stark deceleration.

Here we propose a design for a Stark decelerator compatible with a broad range of polyatomic prolate asymmetric top molecules which solves both these problems: the decelerator is fed slow moving molecules from a recently demonstrated cryogenic buffer gas beam source, and molecules are selected in carefully chosen low field seeking rotational states, which exhibit no experimentally relevant avoided level crossings even at substantial fields. Molecules in these states can be decelerated and trapped in “conventional” low field seeking geometries. A sketch of the proposed apparatus to decelerate and trap such molecules is shown in figure 1.

Larger molecules in high electric fields exhibit a bewildering forest of Stark shifted rotational levels, and “strong” laboratory fields easily mix neighboring rotational states. Figure 2 contrasts the Stark shifted levels for CaF (left) and benzonitrile (right) in an electric field. The natural choice of a state for decelerating CaF is shown in bold; clearly no analogous state exists in benzonitrile. Conventional wisdom therefore holds that conventional Stark deceleration of larger polyatomic molecules with high fields is impossible.

States of the type |J_{k,k_c}⟩ = |J_{J_0}⟩ in prolate asymmetric top molecules form an exception to this rule. Such states are the highest energy rotational states of a given J, and exhibit two qualities which make them ideal candidates for conventional, low field seeking Stark deceleration. Their near degeneracy with the slightly lower energy |J_{J_1}⟩ state gives them an essentially linear Stark shift even at low electric fields (10 volts/cm is sufficient...
to fully polarize the $|4_{40}\rangle$ state of benzonitrile. Although $|J_{J0}\rangle$ states inevitably exhibit level crossings with other rotational states at large electric fields, such crossing represent highly forbidden transitions, allowing molecules to be decelerated and trapped without loss. Such states were in fact focussed, or “trapped” in two dimensions, in numerous spectroscopy experiments in the 1990s[13, 14], although to our knowledge no detailed analysis of the critical avoided crossings discussed below has been done. Figure 3 shows the relevant Stark shifts and anticrossings for one such state, the $|4_{40}\rangle$ state of the highly polar asymmetric top molecule benzonitrile. This state exhibits no avoided crossings with a gap wider than 40 kHz up to a field of 13 kV/cm, representing a trappable, low field seeking state with a trappable depth of 900 mK.

Figure 1: A sketch of the apparatus to realize cold, trapped, samples of larger polar prolate polyatomic molecules. The technique builds upon demonstrated slow sources of large molecules, and unique properties of carefully chosen states of the form $|J_{kakc}\rangle = |J_{J0}\rangle$. Contrary to popular wisdom, such states are amenable to “conventional” low field seeking Stark deceleration and trapping with only minor modifications to the trap design parameters from demonstrated decelerators for diatomic species. The central microwave horn is not strictly necessary to produce trapped molecules, but would provide definitive state identification of decelerated and trapped samples, and could be use to transfer molecules into thermally unpopulated but trappable states.

2: Crossings and anti-crossings

Trapped or Stark decelerated molecules inevitably experience a time varying electric field. Consider a molecule in rotational state $|A\rangle$, which experiences an electric field which varies in time such that the energy of state $|A\rangle$ crosses a second state $|B\rangle$. The two states exhibit an anticrossing characterized by a gap $\alpha$, with $\alpha$ proportional to the electric dipole matrix element connecting the two states. Close to a level crossing, the effective detuning $\Delta$ changes approximately linearly, with $\Delta \approx \alpha t$. Two trajectories are possible: the molecule can adiabatically follow the lower state, effectively transitioning to $|B\rangle$, or the molecule can diabatically “jump” the anticrossing, remaining in $|A\rangle$. The red line in figure 3B shows an example of such a diabatic path. In the limit of $\alpha \ll \alpha^{1/2}$, the probability of an adiabatic trajectory goes to zero, with $p \approx \frac{\pi \alpha^2}{\sigma}$[15]. In the case considered here, the molecule will undergo many such anticrossings, and we need $p \ll 1$. The detuning rate of change $\Delta$ varies with both state and molecule trajectory, but can be estimated from the characteristic detuning (10 GHz) and characteristic time scale (100 $\mu$sec) of a decelerating molecule crossing a Stark decelerator stage. These order of magnitude estimates suggest that $\Delta \approx 10^{14} \text{s}^{-2}$, which implies a limit of $\alpha \ll 10 \text{ MHz}$. The state shown in figure 3 exhibits no anticrossings with gap larger than 40 kHz up to a field of 12 kV/cm. Adiabatic losses for a trapped molecule in this state are therefore below the $10^{-5}$ per orbit level; a $|4_{40}\rangle$ benzonitrile molecule trapped in a “typical” 1 cm-scale electrostatic trap[16] at 100 mK would have a diabatic loss limited trap lifetime of more than 100 s, far longer than typical black body radiation induced losses which occur at the few Hz level in a 300K environment[17].

Calculation of the avoided crossing gap $\alpha$ is nontrivial; although the asymmetric top Hamiltonian can be numerically solved to high precision, the highly mixed states defy intuitive assignment of quantum numbers.
Figure 2: The rotational structure of CaF (left), a representative diatomic molecule, and benzonitrile (right).

The natural “low field seeking” state to decelerate in CaF is shown in bold; clearly no analogous state exists in benzonitrile. Two examples of “trappable” states of benzonitrile, |3_30⟩ and |4_40⟩, are shown in bold.

Field free states of asymmetric tops are described by quantum numbers J, k_a, k_c, and m_J; of these, only m_J remains meaningful in the relevant highly mixed limit. Molecules such as benzonitrile furthermore experience level mixing due to the nuclear electric quadrupole moment, leaving m_F as the only meaningful quantum number. We therefore rely on numerical integration, although we emphasize that the existence of trappable states such as the |4_40⟩ state in benzonitrile are found in essentially all prolate asymmetric top molecules. Molecules with one or two of μ_a, μ_b, or μ_c zero exhibit more such states due to their more restrictive selection rules, but even molecules with all dipole moments nonzero exhibit highly trappable states. The PGOPHER package was used to calculate the transition matrices and the field free Hamiltonian, including hyperfine terms[18]. Table 1 lists examples of such states for a selection of molecules.

3: Decelerator and Trap Design

Molecules in rotational states such as |4_40⟩ exhibit essentially linear Stark shifts. The dynamics of manipulating such molecules in both traditional Stark decelerators and in highly stable “moving trap” decelerators is well understood, and lighter analogues of the molecules discussed here have been decelerated and trapped many times[1]. A natural molecule for comparison is ND₃, a polar molecule (μ = 1.4 Debye) that exhibits an effectively linear Stark shift at the relevant laboratory fields, and is thus an extremely favorable molecule for Stark deceleration. Straightforward extrapolation of decelerator designs demonstrated on ND₃ and OH suggest a modest conventional decelerator with ~ 30 stages followed by a conventional electrostatic quadrupole trap could decelerate and trap the |4_40⟩ states of buffer gas cooled benzonitrile or aminobenzonitrile[19, 20]. Numerical simulations, to be published in a later paper, confirm this. A sketch of this proposed apparatus, built upon the existing apparatus used in [21], is shown in figure 1. Higher efficiency, at the cost of higher experimental complexity, could be realized by a hybrid decelerator, incorporating both conventional dynamic focussing and a “moving trap” design[22]. It is worth noting that for most of the molecules listed in table 1, avoided crossings limit applied fields to \( \lesssim 20 \) kV/cm. Stark decelerators designed to produce only such modest fields have much more relaxed engineering, materials, and electronics constraints.

4: Expected density and outlook
Figure 3: A: The $|4_{40m_j=4}\rangle$ state of the highly polar molecule benzonitrile ($\mu_a = 4.6$ Debye). Only states with $m_j = 4$ are shown; avoided crossings with states with $m_j \neq 4$ are strictly forbidden. B: A zoomed in plot of the avoided crossing labeled “34 KHz”. Molecules under realistic trapping conditions will follow the red diabatic trajectory with high probability. The low field seeking state exhibits no avoided crossings with gap $a$ larger than 40 kHz up to a field of 12.1 kV/cm, representing a trap depth of about 700 mK. At 4.5 kV/cm, the state crosses the high field seeking mixture of the $|5_{42}\rangle$ and $|5_{41}\rangle$ with $a \approx 30$ kHz. The adiabatic loss from such a transition is estimated at less than $5 \times 10^{-5}$. At 14 kV/cm, the state crosses the high field seeking mixture of the $|6_{42}\rangle$ and $|6_{43}\rangle$ with $a \approx 300$ kHz. Although this gap is arguably small enough to be diabatically “jumped” in many realistic experimental conditions, here we propose to limit fields to below 12 kV/cm. Although nuclear quadrupole hyperfine interactions are not included in this figure, numerical calculations including these terms do not reveal any additional large-gap avoided crossings. Higher states, such as $|6_{60}\rangle$ and $|7_{70}\rangle$, exhibit even deeper trap depths.

The combination of a cryogenic beam and the state-selective decelerator described above provides a straightforward way to realize trapped samples of larger polyatomic molecules. Such molecules would be in a small number of rotational states, diverse nuclear states, and have a translational temperature of about 100 mK. Molecules could be sensitively detected via LIF or REMPI spectroscopy.

The apparatus shown in figure 1 would introduce slow ($\sim 50$ m s$^{-1}$) molecules at a total density of $5 \times 10^{10}$ cm$^{-3}$ at the entrance to the Stark decelerator. These molecules would occupy many (order 500) rotational states, and be reasonably collimated via expansion away from the cryogenic cell. We estimate that about $10^{-4}$ of these molecules, or $5 \times 10^{6}$ cm$^{-3}$ would be in a trappable rotational state and fall within the phase space acceptance of the Stark decelerator; this density is comparable to trapped densities of ND$_3$ in electrostatic traps[23].

It is natural to look for ways to further cool such molecules towards a true ultracold limit. Trapped molecules in rotationally excited states such as $|4_{40}\rangle$ are poorly suited to sympathetic cooling with atoms, as rotationally inelastic collisions would rapidly scatter molecules out of the trapped state. Ideally such molecules could be transferred into a trap which could hold collisionally immune absolute ground state molecules, such as an optical trap or a high field seeking AC microwave trap[8, 24]. Such molecules could be sympathetically cooled if overlapped with a cloud of laser-cooled atoms, dramatically increasing phase space density. The resulting cold, trapped molecules would represent an important milestone on the path to realization of full quantum control of trapped single molecules. An array of such molecules in an optical lattice would interact via their strong, long range dipole-dipole interaction, and could be individually addressed via non-uniform applied electric fields, as previously proposed for diatomic molecules[25]. The high dipole moments and rich internal structure of larger polyatomic molecules make such a system a promising gateway into an era of full control of low decoherence quantum systems of unprecedented complexity.

4: Conclusion
Table 1: Trappable low field seeking states for a variety of prolate asymmetric top molecules. In all cases such states exhibit no avoided crossings with gap \( a \) larger than 80 kHz. For each state, \( E_{\text{max}} \) is chosen to avoid mixing via a large avoided crossing, or is arbitrarily limited by an assumed maximum electric field of 50 KV/cm. In each case, the trap lifetime limited by unwanted adiabatic transitions at anticrossings is predicted to be longer than 1 s. Higher \( J \) states such as \( |7\rangle \) show better trapping characteristics but are only marginally populated in a \( T \approx 6 \) K buffer gas cooled beam.

An experimentally realizable plan to decelerate and trap certain states of polar asymmetric top ground state molecules has been presented. Realization of such a proposal would represent a major milestone in the challenging path towards absolute control of such systems.

References


