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Slow, Continuous Beams of Large Gas Phase Molecules

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A cold, continuous, high flux beam of benzonitrile has been created via buffer gas cooling. The beam has a typical forward velocity of 67 ± 5 m s^{-1}, a velocity spread of ± 30 m s^{-1} and a typical flux of 10^{15} molecules s^{-1}, measured via microwave spectroscopy. This beam represents the slowest demonstrated forward velocity for any cold beam of medium sized (> 5 atoms) polyatomic molecules produced to date, demonstrating a new source for high resolution spectroscopy. The expected resolution of a spectrometer based on such beams exceeds current instrument-limited resolution by almost an order of magnitude. This source also provides an attractive starting point for further spatial manipulation of such molecules, including eventual trapping.

1 Introduction

Cold molecules are rich quantum structures with a variety of potential applications, such as fundamental physics tests[1] and quantum information processing[2,3]. Cooling and internal state control of polyatomics lags far behind that of diatomics, which are now routinely manipulated at the single quantum state level[4]. Full quantum control of larger, polyatomic molecules would open up experimental arenas inaccessible with cold diatomic molecules for both technical and fundamental reasons. The rich internal mode structure of such molecules, which typically includes many nuclear degrees of freedom, would provide a valuable resource in quantum information processing[5]. In addition, in many cases the lower rotational transition frequencies of larger highly polar molecules would make these species an attractive candidate for electrically coupling molecules to external Q-bits, such as superconducting resonators[3].

Demonstrated sources of slow, cold beams of larger molecules include alternating-gradient decelerated samples from supersonic jets, optically decelerated supersonic beams of benzene, and (internally warm) slow molecules filtered from warm sources[6–8]. Numerous molecules have been cooled in cryogenic buffer gas cells, and molecules as large as H_2CO have previously been extracted from cryogenic buffer gas sources into a low-collision environment[9–13]. Rempe et. al. have recently demonstrated Sysiphus-type cooling of a trapped sample of CH_3F molecules, producing the coldest sample of trapped polyatomic molecules to date[14].

Here we present a novel, continuous beam of cold benzonitrile (C_7H_5N) molecules based on the buffer gas cooling of a room temperature source to a few degrees K. The modest forward velocity of the source (≈ 67 m s^{-1}) makes it an attractive starting point for further manipulation and trapping[15–18]. The source could also be used without further manipulation for molecular spectroscopy of unprecedented resolution.

2 Experimental

A diagram of our apparatus is shown in figure 1. The approach is similar to earlier buffer gas cooled atomic and molecular beams[19], but with significant modifications to the molecule injection, adapting it to stable, volatile, polyatomic molecules. The cell used here is a modification of that employed in our earlier closed-cell work[20], which produced, inside a cell and mixed with cold buffer gas, continuous gas phase samples of benzonitrile, acetone, 1-2 propanediol, fluorobenzene, and anisole. As in that work, here hot molecules are injected by spraying rotationally and vibrationally warm molecules from a hot pipe towards a 1 cm aperture in a cold (4.7 K) cell. Molecules are cooled through collisions with the cold helium gas.

In contrast to geometries in which hot molecules are introduced via a capillary connected directly to a buffer gas cell[13,21], this non-contact approach minimizes heat loads and allows for a much larger injection pipe, which is critical for larger, less volatile species. The cell contains cold helium gas with a low enough density such that warm molecules can penetrate through the gas curtain exiting the cold aperture, but a high enough density such that the hot molecules are thermalized via collisions with helium once they are inside. This “sweet spot” density is $n_{He} \approx 4 \pm 2 \times 10^{14}$ cm^{-3}. A fraction of the resulting cold molecules, along with cold helium gas, exits the cell via a new second aperture on the opposite side of the cell, into a vacuum region. Once in the vacuum region, the density of helium (and molecules) drops rapidly as the gas mixture moves away from the cell, realizing a beam. This beam passes into a separately cryopumped “spectroscopy chamber,” a collision free beam region.

Molecules typically undergo hundreds of collisions with cold helium atoms before exiting the cell and entering the collision free beam region. Molecules cool rotationally and translationally in a few (< 10) collisions, and the rotational temperature of molecules in cryogenic buffer gas cells is typically not measurably different from the gas temperature[20,22]. Vibrational cooling rates are typically lower, especially for lighter molecules with only high frequency vibrational modes.

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Although we expect both from our previous work and the work of Johnson et. al. with with large molecular ions that molecules will cool to the vibrational ground state before exiting the cell, this was not experimentally verified in this work[23]. Conditions in the cell are believed to be $n_{He} \approx 4 \pm 2 \times 10^{14}$ cm^{-3}, $n_{molecule} \approx 1 \times 10^{12}$ cm^{-3}, and $T \approx 5$ K. Conditions in the center of the beam region, 5 cm from the aperture, are believed to be $n_{He} \leq 2 \times 10^{12}$ cm^{-3}, and $n_{molecule} \approx 6 \times 10^{9}$ cm^{-3}. This corresponds to a net continuous molecular beam flux of $\phi \approx 10^{15}$ molecule s^{-1} and a rotational temperature of $T \approx 5$ K.

The molecules are detected in the spectroscopy chamber and their forward velocity is measured via Fourier transform microwave (FTMW) spectroscopy. This is realized in a retro-reflecting microwave beam geometry. The microwave field, which has a direction of propagation nearly parallel to the molecular beam axis, is emitted by a standard gain microwave horn (WR-62), and is reflected and refocused by a spherical mirror onto a second microwave horn. This second horn is used to detect the free induction decay signal from the molecules after they are polarized via a strong, chirped microwave pulse. As in standard Coaxially Oriented Beam-Resonator Arrangement (COBRA) FTMW spectrometers, each rotational transition of the molecules exhibits a "Doppler doublet" type structure, resulting from interactions with the co-propagating and counter-propagating components of the applied microwave field with the forward moving molecules. As in COBRA-type spectrometers, the mean velocity is extracted by the splitting of the Doppler-doublet, and the velocity distribution of the beam is determined from the Doppler-broadened structure of within each lobe.

3 Results

Figure 2 shows the spectrum from a cold beam of benzonitrile, C_6H_5CN. In figure 2a, the $3_{03} \leftarrow 4_{04}$ hyperfine manifold is shown; while the strong peaks corresponding to the $F = 7 \leftarrow F = 6$ and $F = 6 \leftarrow F = 5$ are only partially resolved, the $F = 5 \leftarrow F = 4$ transition at 13437.300 MHz is resolved cleanly. Figure 2c shows the velocity distribution derived from the red sideband of the $F = 5 \leftarrow F = 4$ transition.

The forward velocity distribution is peaked at $v_p = 67 \pm 5$ m s^{-1}, corresponding to a forward kinetic energy of 28 K, and has a translational temperature of 10 K in the moving frame, although it should be emphasized that this velocity distribution is rather poorly described by a Maxwell-Boltzman distribution. The velocity distribution is peaked at 67 m s^{-1}, with a significant fraction (10%) of the molecules moving slower than 40 m s^{-1}. It is natural to compare this beam to a more commonly used source of cold molecules, a seeded pulsed supersonic jet. Such jets typically have a forward velocity on the order of 400 m s^{-1} or greater, corresponding to a kinetic energy of 1000 K or more, combined with a moving frame energy spread (i.e. translational temperature) of 2 K or less. Depending on the experiment one wants to accomplish with a cold beam of molecules, this difference in parameters can be crucial. We consider two applications below, high resolution spectroscopy and further deceleration of molecules.

Beams of the aromatic molecules anisole, aminobenzonitrile, and fluorobenzene with similar characteristics to the benzonitrile beam shown here were also produced in our apparatus. Surprisingly, our attempts to produce beams of acetone and 1-2 propanediol did not result in a detectable signal, even though high density samples of these molecules were observed via FTMW spectroscopy in the cell. We hypothesize that this relates to an at-present not understood clustering mechanism which could sweep up monomers of these species before they migrate out of the cell and into the beam. Such clustering has been observed in large molecular ions and atoms in cryogenic buffer gas cells, but remains poorly understood[23–25].

4 Discussion and applications

4.1 High resolution spectroscopy

Until recently, the only widely used source of cold, large molecules has been supersonic jets, which reliably produce rotationally cold ($T \leq 2$ K) molecules moving rapidly ($v > 400$ m s^{-1}) in the lab frame. This velocity effectively limits the total interaction time τ with the molecules to 10^{-3} seconds or less. The frequency resolution $\Delta\nu$ of any spectroscopic method is constrained to $\Delta\nu \lesssim \tau^{-1}$ by transit time broadening[26]. In free induction decay microwave spectroscopy, τ is typically dominated by the length of the free induction decay, which follows a short excitation pulse. Supersonic-jet based COBRA spectrometers in fact realize resolutions close to this transit time limit, with resolution of a few kHz[27]. It should be noted that *accuracy*, in contrast to resolution, can be substantially better than this transit time limit when the signal to noise ratio is high[28].

The substantially slower forward velocity, and hence potentially longer interaction time, of the beams demonstrated here promises to improve this resolution by almost an order of magnitude, allowing for molecular spectroscopy of polyatomic molecules at unprecedented resolution. An instrument based on the beam demonstrated here with a 50 cm interaction region, in place of the 10 cm region in this work, would have an ultimate transit time resolution limit of order 100 Hz. A rich array of dynamics would be revealed from higher resolution experiments, including tests of fundamental symmetry[29], searches for elusive parity-violations in rotational spectra[30], tests of changing fundamental constants[1,28], imaging of molecular potentials[31], and direct observation of low-frequency intra-molecule processes, such as charge transfer and nuclear effects[32,33]. The general beam source developed here provides a natural starting point for such experiments.

4.2 Further manipulation of molecules

The low forward velocity of this cold molecule source makes it a natural candidate for further manipulation, deceleration, and eventual trapping. A powerful tool for slowing and trapping polar molecules is the interaction of the molecular electric dipole with time varying electric fields. This tool has been widely applied in Stark decelerators to decelerate and in many cases trap diatomic and smaller polyatomic molecules, and it is natural to consider the application of such techniques to the source described here.

Manipulation of larger molecules via electric fields is complicated by the fact that, unlike smaller molecules, at high fields such molecules exhibit only high field seeking states. In addition, rotationally excited molecules in changing electric fields undergo numerous level crossings and anti-crossings, making control extremely challenging. Conventional low-field seeking Stark decelerators and electrostatic traps are constrained to low applied electric fields, and thus have very low effective depths. Despite this limitation, considerable progress has been made in recent years in developing both alternating gradient decelerators[6,7] and microwave decelerators[34] adapted to manipulate high field seeking states; for an excellent review of the field see reference[35]. To date, such decelerators have not succeeded in slowing molecules from a supersonic source to zero velocity.

Applications to two types of decelerator are considered here: a high field seeking decelerator, which can decelerate ground state (high field seeking) molecules with a single, strong, switched electric field, and a staged low field seeking decelerator with many weak, switched fields. In both cases molecules lose kinetic energy as they run “uphill” in the switched potential. For the single stage decelerator, effective for ground state molecules, it is natural to compare the kinetic energy of a molecule from a beam source to the available “stopping” energy from an electric field, $E \cdot \mu$, where μ is the molecular dipole. For a realistic applied field of 100 kV/cm interacting with benzonitrile (μ= 4.5 Debye), $E \cdot \mu$ corresponds to 10.9 K, which in turn corresponds to a velocity of 42 m s^{-1}. The forward velocity distribution shown in figure 2c therefore contains a significant fraction of molecules that could be decelerated to zero via a single switched electric field. Although trajectories of high field seeking molecules in static fields are fundamentally unstable, a large amount of transverse dispersion could be tolerated in this simple, one stage design[17]. An alternative would be a multi-stage, switched, “moving trap” low field seeking decelerator with modest fields E_{max} and depth D[36]. A decelerator of a few hundred stages could slow molecules such as benzonitrile to rest. Such a decelerator has the advantage of stability even at zero velocity (i.e. trapping), but requires elaborate engineering. Both moving trap and single stage decelerator designs would be impractical without the low lab frame kinetic energy of the buffer gas cooled beam. Multistage alternating gradient decelerators, appropriate for decelerating the absolute ground state of polar molecules, could also be considered[6].

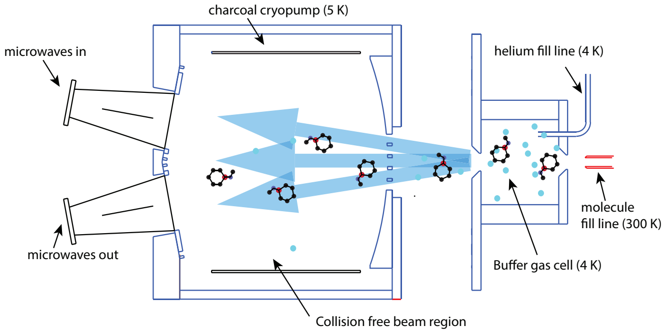

Fig. 1 The apparatus to produce a cold, continuous, slow beam of larger molecules. Molecules are introduced to a cold cell via a warm injection tube. The molecules cool in the cell via collisions with cold helium buffer gas, and a fraction escape through the exit aperture. These molecules spray towards a second aperture, which leads into a separately cryopumped chamber where they are interrogated via Fourier transform microwave spectroscopy. The second aperture is covered by a coarse mesh, which is largely transparent to the molecular beam but reflects microwaves. The mean free time between helium collisions is measured at 15 μs in the cell, and estimated to be more than 1000 μs in the beam chamber.

5 Conclusions

We have created slow beams of several polyatomic molecules and performed chirped pulse microwave spectroscopy in a novel cryogenic beam geometry. Molecules in the beam have a typical average forward velocity of 67 m/s with about 10% of the molecules slower than 40 m s^{-1}. At such a velocity, transit time broadening is substantially reduced compared to supersonic beams, making this source potentially useful for high resolution beam spectroscopy. The low kinetic energy of these beams makes them an attractive starting point for further spatial manipulation.

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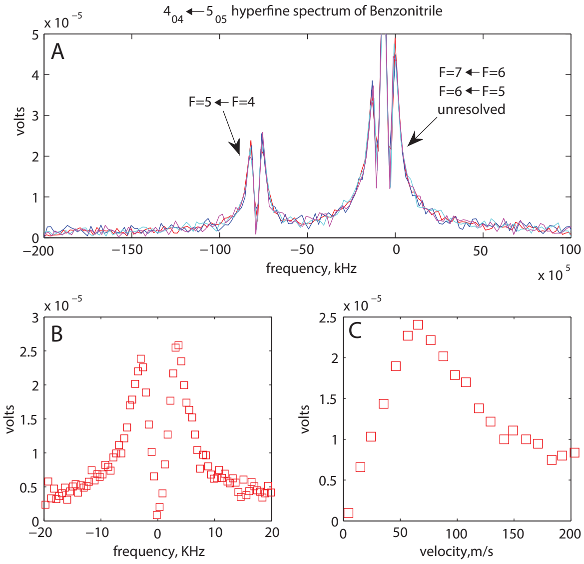

Fig. 2 The microwave spectrum of a beam of cold benzonitrile. A: The partially resolved hyperfine manifold of the $4_{04} \leftarrow 5_{05}$ transition at 13437.4 MHz, using the notation $J_{k_a k_c}$. Each hyperfine line is split into a Doppler doublet, as is seen in COBRA-configured supersonic beam based cavity enhanced microwave spectrometers. B: An enlarged view of the resolved F=5← F=4 doublet. C: the velocity distribution for the beam, as measured from the red sideband of the F=5← F=4 doublet shown in B. The beam has a peak velocity of 67 m s^{-1}, and an estimated flux of 10^{15} molecules s^{-1}.

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