Tutorial

Preparation of cold molecules for high-precision measurements

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Abstract
Molecules can be used to test fundamental physics. Such tests often require cold molecules for detailed spectroscopic analysis. Cooling internal degrees of freedom provides a high level of state-selectivity, with large populations in the molecular states of interest. Cold translational motion allows slow, bright beams to be created, allowing long interaction times. In this tutorial article we describe the common techniques for producing cold molecules for high-precision spectroscopy experiments. For each technique we give examples of its application in experiments that use molecular structure to probe fundamental physics, choosing one experiment in particular as a case study. We then discuss a number of new techniques, some currently under development, others proposed, that promise high flux sources of cold molecules applicable to precise spectroscopic tests of fundamental physics.

Keywords: cold molecules, precision spectroscopy, molecular structure
(Some figures may appear in colour only in the online journal)

1. Introduction

‘A diatomic molecule has one atom too many.’ This judgement, attributed to Arthur Schawlow [1], conveys the antipathy that a physicist might feel towards the complexity of molecular structure. However, hidden within this complexity is great sensitivity, making molecules very useful systems for probing fundamental physics, sometimes far more sensitive than atoms. From a careful study of molecular structure one can observe subtle effects with significant consequences, such as the shape of the electron, the time-variation of fundamental constants, and the fundamental symmetries of our Universe.

In order to observe these effects a very careful interrogation of molecular structure is necessary, which requires sources of molecules that are well characterised, repeatable, which produce an intense, high purity flux of the chosen molecule. It is often advantageous for the molecules to be cold and slow, offering a high level of state selectivity and affording long interaction times with low divergence beams. ‘Cold’ refers here to all degrees of freedom: the translational motion as well as the electronic, vibrational, and rotational motion.

In this article we discuss the main techniques used to produce cold molecules for high-precision measurements. For each of these we discuss the application of the technique in spectroscopy experiments, and choose one experiment for a more detailed discussion, describing the role and importance of the preparation method. In section 2 we discuss the preparation of cold molecules through supersonic expansion. After describing the basic principles of supersonic expansion and a brief technical review of the most commonly used methods of creating pulsed molecular beams, we describe in detail an experiment in which a beam of CH molecules was used in a precise investigation of a possible variation of the fine structure constant and proton-to-electron mass ratio [2].
In section 3 we describe methods to slow down molecules, describing in detail the method of Stark deceleration. We then discuss an experiment in which precise spectroscopy was performed with Stark decelerated OH molecules, which, when combined with astrophysical data, can place a constraint on the variation of the fine structure constant over a time scale of 10 Gyr with a sensitivity of 1 ppm [3]. In section 4 the method of buffer gas cooling is described. This technique, in which molecules are cooled in a cryogenic environment, can be used to produce intense beams of slow molecules. In particular, we describe an experiment in which ThO molecules from a buffer gas source were used to perform the most precise measurement to date of the electric dipole moment (EDM) of the electron [4]. In section 5 we discuss newer techniques, some still under development, which have not yet been used in high-precision spectroscopy, but which show great promise in this field. This section includes a description of a new technique in deceleration (travelling wave deceleration), methods of trapping molecules, velocity selection using electric or magnetic guides, and the production of slow molecules using mechanical methods (using a counter-rotating nozzle, or an ‘atomic paddle’). Exciting results are presented in which cold and ultra-cold molecules were produced by direct laser cooling, and by Sisyphus cooling.

This tutorial article is not an exhaustive review of techniques in the field of cold molecules, but will give a pedagogical description of those methodologies useful to precise spectroscopy. Methods of producing cold molecules are typically divided into two categories: (i) ‘direct’ methods, in which an ensemble of molecules is cooled; and (ii) ‘indirect’ methods in which atoms are laser cooled and then combined to form ultra-cold molecules. In this article we discuss only ‘direct’ methods, as many of these techniques are useful for preparing molecules for precise spectroscopic tests of fundamental physics. There has been much work in the production of ultra-cold molecules through indirect methods, photo-association (see [14–16] and references therein) and magneto-association (see [17–19] and references therein), and it is a significant ongoing field of activity. While these techniques have been able to produce molecular ensembles typically much colder than many of the ‘direct’ approaches (for example, see figure 1 of [8] for a graphical comparison), the range of species produced has been limited, with much work concentrating on bialkali dimers. The application of these ‘indirect’ approaches to precise spectroscopic studies of fundamental physics has hitherto been limited. However, the prospect of using indirectly cooled molecules in precise measurements has been considered: Zelevinsky et al have proposed a measurement of the proton-to-electron mass ratio by probing vibrational energy intervals of ultra-cold Sr2 molecules formed by photodissociation and confined in an optical lattice [20]. Recently, McGuyer et al have performed precise spectroscopy of Sr2 molecules in a lattice [21]. Rabi oscillations between different vibrational states were driven, with linewidths on the order of 100 Hz measured, allowing the precise determination of ground state binding energy differences. This work demonstrates the great potential for performing precise spectroscopy with ultra-cold molecules created by ‘indirect’ methods.

In this article we focus on the production of slow molecules for tests of physics with highly precise spectroscopy. However, cold molecules are of great interest in other fields of research, such as cold chemistry [22–24] and quantum information processing [25, 26]. The study of cold, controlled chemistry has long been of great interest [27], and is now a very active discipline (see [23] and references therein). Great control can be exerted over cold atoms and molecules, allowing the detailed study of scattering and reaction dynamics. Many of the methods and techniques useful for precise spectroscopy are also relevant in cold chemistry and scattering experiments, including: the study of reactions in supersonic molecular beams [28–30]; studies of collisions with Stark- and Zeeman-decelerated beams [11, 31, 32], and with merged beams prepared using magnetic and electric guides [33–35]; and the investigation of collisions with counter-propagating molecular packets confined in a molecular synchrotron [36, 37].

The application of cold and ultra-cold molecules to quantum computation has been proposed [25, 26, 38]. Experimentally, this is an emerging field, and many of the methods described in this tutorial have the potential to provide sources of ultra-cold confined molecules for use in a quantum processor.

2. Supersonic beams

Supersonic beams can produce high-density sources of fast, but cold molecules. They are very versatile, and have been used in many experiments, both directly as a source of molecules for an experiment, or as a supply of molecules that can be further slowed and cooled by other techniques. In order to create a supersonic beam, gas initially held at high pressure, $p_0$ (~1 bar), and temperature, $T_0$ (typically room temperature, but this can be reduced) is allowed to expand into a vacuum chamber (typically held at pressure $p_v \sim 10^{-7}$ mbar) through a pulsed valve, cooling all degrees of freedom as it does so. Before the valve is opened the gas has no net flow (the average speed of the molecules is zero), but has random thermal motion. Collisions between the molecules during the expansion inside the vacuum chamber cool the translational, vibrational and rotational degrees of freedom. During the supersonic expansion process a gas with an initially wide speed distribution but no net flow becomes a jet with a narrow velocity distribution, but travelling quickly along the beam-axis (defined as the $z$-axis in this article), typically at several hundred metres per second. As the jet expands into the vacuum chamber the gas pressure reduces, until eventually the pressure is so low that there are no more collisions between the molecules. At this point the jet has reached its terminal speed and temperature. A full description

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1. Several reviews exist, which give detailed descriptions of certain techniques or an overview of the field of cold molecules [5–13].
of the dynamics that occur in a supersonic expansion can be found in [39, 40].

The principle of supersonic expansion can be described in terms of the thermodynamics of an expanding ideal gas. Consider two isolated chambers separated by a wall, with one chamber containing gas held at pressure $p_0$ and temperature $T_0$, and the second chamber held at much lower pressure, $p_1 \ll p_0$. Let a small opening be made in the wall. The high pressure gas flows into the second chamber with macroscopic flow speed, $v$. During the expansion no heat is added to the gas, $\Delta Q = 0$, but it does work

$$\Delta W = p_1 V_1 - p_0 V_0,$$  \hspace{1cm} (1)

where $V_{0/1}$ is the gas volume in the first/second chamber. The change in the total internal energy of the expanding gas is

$$\Delta U = U_1 + \frac{1}{2} m_1 v^2 - U_0,$$  \hspace{1cm} (2)

where $U_{0/1}$ is the total internal energy of the gas in the first/second chamber and $m_i$ is the total mass of the flowing gas. From the first law of thermodynamics, for a process in which $\Delta Q = 0$ the expressions in equations (1) and (2) are equal. Combining these gives the forward speed of the flowing gas

$$v = \sqrt{2(h_0 - h_1)},$$  \hspace{1cm} (3)

where $h$ is the specific enthalpy ($h = \frac{1}{m_{mol}}(U + pV)$ for an ideal gas with molecular mass $m_{mol}$). The specific enthalpy can be described in terms of the specific heat capacity of an ideal gas held at constant pressure, $c_p = \frac{\partial h}{\partial T}_p$. Assuming $c_p$ to be constant yields the following expression for the forward speed

$$v = \sqrt{2c_p(T_0 - T_1)}.$$  \hspace{1cm} (4)

It can be shown from the ideal gas law that

$$c_p = \frac{k_B}{m_{mol}}(\gamma - 1),$$  \hspace{1cm} (5)

where $\gamma = c_p/c_v$ is the specific heat ratio, $\gamma = 5/3$ for an ideal monatomic gas, and $\gamma = 7/5$ for a diatomic molecule, provided that the rotational excitation is appreciable at the initial temperature, but not the vibrational excitation.

As the gas expands its internal dynamics cool through collisions, transferring rotational and vibrational energy into the forward flow speed. This process continues until the pressure has dropped such that there are no more collisions, at which point the gas jet has reached its terminal speed, $v_t$, given by combining the expressions in (4) and (5)

$$v_t = \sqrt{\frac{2k_B(T_0 - T_1)}{m_{mol}}} \frac{\gamma}{\gamma - 1},$$  \hspace{1cm} (6)

where $T_1 (\ll T_0)$ is the final translational temperature of the jet. After expansion the beam typically traverses a skimmer with a small aperture, which limits the transverse speed distribution of the beam. The terminal translational temperature of the beam parallel to the forward flow speed, $T_t^1$, scales with the initial temperature and pressure, and the nozzle diameter, $d$, as

$$T_t^1 \propto T_0 \times (P_0 d)^{-\alpha},$$  \hspace{1cm} (7)

where $\alpha = 6(\gamma - 1)/(\gamma + 2)$ [41, 42].

As examples, a supersonic beam of helium, made from a high pressure reservoir at room temperature will reach a terminal speed of 1765 m s$^{-1}$, and a beam of NO radicals will reach a speed of 760 m s$^{-1}$. The dependence of the terminal speed on the specific heat ratio leads to molecules reaching a greater speed than atoms (of comparable mass), as the molecules’ rotational and vibrational energy is transferred to kinetic energy. Often molecules will be ‘seeded’ in a carrier gas of atoms (typically noble gases) which determines the forward speed of the beam. For example, in [43] YbF radicals were seeded in He, Ar and Xe, resulting in beams with forward speeds of 1735 m s$^{-1}$, 580 m s$^{-1}$ and 325 m s$^{-1}$ respectively. In this case the YbF radicals were made by the supersonic expansion of a $\sim$5 bar mixture of 2% SF$_6$, 98% carrier gas and laser ablation of Yb. The gas mixture was expanded into a vacuum chamber (maintained at a pressure of around 10$^{-7}$ mbar when the valve was not in operation, rising to a time-averaged pressure of around 5 $\times$ 10$^{-4}$ mbar with the valve operated at 10 Hz) through a pulsed valve. A rod of Yb metal was located immediately downstream of the valve nozzle. Ablation of the rod by radiation from a Nd:YAG laser (up to 35 mJ at 1064 nm) produced a hot plume of Yb atoms, which reacted with the SF$_6$ in the pulsed gas beam, forming YbF radicals which became entrained in the carrier gas pulse. The speeds for the Ar and Xe beams were measured to be slightly greater than those calculated from (6) (552 m s$^{-1}$ and 305 m s$^{-1}$ respectively). The authors suggest that this could have been the result of heating inside the pulsed valve.

In a seeded beam in which the source density is high the resulting supersonic expansion is the same as would be achieved for a pure gas in which the molecular mass and heat capacity are equal to the weighted means of those in the mixture [44]. In this case both species in the beam end up travelling at the same speed, and with the same translational temperature. If the source density is too low, however, there are not enough collisions during the expansion for both species to equilibrate. If the seed and carrier species have a different molecular mass, then they will reach different terminal speeds, an effect known as ‘velocity slip’ [44–47]. Consider the case of a gas mixture in which the seed species has a greater molecular mass than the carrier species. If the source density is too low, there will not be enough collisions during expansion for the heavy seed molecules to be accelerated to the greater speed of the lighter carrier species, and the seed molecules will lag behind [47].

The supersonic expansion is very effective for cooling the translational and rotational degrees of freedom. For example, in [43] the translational and rotational temperatures of a supersonic beam of YbF (produced with a Xe carrier gas and a room-temperature pulsed valve) were measured to be 1.4 K and 3 K, respectively. The vibrational motion, however, is far less effectively cooled [48, 49]. This difference can be explained with reference to the adiabatic theorem [40]. Consider a system in an initial eigenstate with energy, $E$.
effect on this system of a perturbing, time-varying potential, \( V(t) \) depends on the magnitude of the perturbation, and on how quickly it varies. After the application of a weak, slowly varying perturbation the system will be left in the initial state. A rapidly varying perturbation places the system in a superposition of its eigenstates; when the perturbation is removed the system will not necessarily return to its initial eigenstate. In this way the perturbation can drive transitions between eigenstates. This is the mechanism by which collisions between molecules (or between molecules and carrier gas atoms) during the expansion can drive transitions to lower rotational and vibrational states. To compare the effects of collisions on the rotational and vibrational states of a molecule it is useful to consider the adiabaticity parameter, \( \xi \) [40].

Consider a system where the \( j \)th eigenstate has energy \( E_j \). The system is subjected to a perturbation, \( V(t) \). The perturbation has a fixed amplitude, and takes place over time, \( \tau_{\text{per}} \). The adiabaticity parameter is defined as

\[
\xi = \frac{\Delta E_{j,k}}{\hbar},
\]

where \( \Delta E_{j,k} = E_j - E_k \) is the energy difference between two states of the system. For a given amplitude of perturbation, the smaller the value of \( \xi \) the more likely it is that the perturbation will change the state of the system. For typical collision timescales, the rotational energy separations of a molecule are small enough that \( \xi < 1 \) [40]. However, the vibrational state separation is typically great enough for \( \xi > 1 \), making it less likely that a collision will cause vibrational relaxation rather than rotational relaxation. It should be noted that the rotational energy levels do not have uniform spacing. For example, a rigid rotor (such as a diatomic molecule) has rotational energy levels described by \( E_j = BR(R + 1) \), where \( B \) is the rotational constant, and \( R \) the rotational quantum number. The energy interval between states with quantum number \( R \) and \( R - 1 \) is \( 2BR \). The rotational interval increases linearly with \( R \), and so higher rotational states are cooled less effectively by collisions. To first order, the vibrational state energies are given by \( E_v = h \sqrt{k_n/m_r} (\nu + 1/2) \), where \( k_n \) is the internuclear spring constant, \( m_r \) is the reduced mass of the nuclei, and \( \nu \) the vibrational quantum number. The interval is constant, \( h \sqrt{k_n/m_r} \), and so to first order all vibrational states will be cooled with equal efficiency. In fact, anharmonic terms in the internuclear potential lead to the vibrational interval decreasing for higher states, causing these excited states to be more efficiently cooled [40]. McClelland et al performed a detailed experimental investigation of rotational and vibrational cooling of \( I_2 \) molecules in a supersonic jet with a range of carrier gases, typically finding the vibrational temperature to be greater than the rotational temperature [49]. For example, with a nozzle operated at 300 K, with pressure 186 Torr, and with Ar carrier gas the rotational and vibrational temperatures were measured to be 3 K and 225 K, respectively [49].

After cooling, the molecules in a supersonic beam pass through a cone-shaped skimmer, typically \( \sim 100 \) mm downstream of the valve and with an aperture diameter of 1–2 mm, continuing into a second, differentially pumped chamber. The geometry of the skimmer defines the transverse speed distribution of the beam inside the second chamber. For example, a skimmer with an aperture of 2 mm diameter, located 50 mm downstream of a supersonic source, will restrict the transverse speed of a beam with forward speed 600 m s\(^{-1}\) to \( \pm 12 \) m s\(^{-1}\).

In order to reduce the gas load in the vacuum chamber supersonic sources are typically operated in a pulsed mode, with the gas injected into the chamber by opening a pulsed valve for a time period of around 10–100 \( \mu s \). Repetition rates of up to several kHz are possible, depending on the valve and the pumping capability of the vacuum chamber [50].

There is a range of pulsed valves that can be used to produce a supersonic beam, including the ‘General’ valve, ‘Jordon’ valve [51], Even-Lavie valve [52], Nijmegen pulsed valve [53], and piezo-actuated valve [50]. The properties of the molecular beam produced can vary widely depending on the valve used, particularly in intensity, speed distribution and temporal profile. The ‘General’ valve (Parker Hannifin Corporation), for instance, is a magnetically actuated valve, in which current pulsed through a solenoid generates a magnetic field which pulls back a plunger, opening the orifice. This type of valve can produce beam pulses with duration down to around 100 \( \mu s \) [32, 54]. The Even-Lavie valve is a magnetically actuated valve that can produce shorter duration, intense pulses. This valve has been carefully designed, with miniaturisation of moving parts, and a low inductance coil, to produce pulses of duration around 20 \( \mu s \) [52, 55]. The ‘Jordon’ valve (Jordan TOF Products, Inc.) uses a different mechanism to create a pulsed source of molecules [51]. The valve is closed by two metal strips in contact with an O-ring such that gas cannot pass through the O-ring. Pulsing electric current through the metal strips in opposite directions causes a force which leads the strips to be repelled from each other. This drives the metal strips apart, allowing gas to pass through the O-ring. Driven by pulses of current of around 4 kA, the Jordan valve can can be operated with an opening time down to around 10 \( \mu s \) [53]. One drawback of the Jordan valve is that the large currents heat the metal strips, which heats the gas pulse, producing molecular beams with greater mean speeds than would be created by a room temperature supersonic expansion [32]. A recent development is that of the Nijmegen pulsed valve, which uses the Lorentz force generated by pulsing current (\( \sim 1 \) kA) through a metallic strip located in a magnetic field (\( \sim 1.5 \) T) to open an orifice [50]. Yan et al have used a Nijmegen pulsed valve to create gas pulses with duration as low as 20 \( \mu s \). Vogels et al have performed a detailed comparison of the use of a Jordan valve and a Nijmegen pulsed valve to produce gas pulses, with a particular emphasis on producing pulsed beams for Stark deceleration [32]. In this review it was found that under comparable conditions the Nijmegen pulsed valve produced slower beams than the Jordan valve, attributed to the heating effect of the larger current pulses employed by the latter.

Reducing the number and size of movable parts is important for the creation of short gas pulses, and can allow
Figure 1. The structure of the $X^2 \Pi (v = 0, N = 1)$ state of CH, showing the transitions driven in [2] to probe the variation of $\alpha$ and $\mu$. Also shown are approximate level intervals (in MHz), and the sensitivity coefficients. (Reproduced from [2], which has been distributed under a CC BY 3.0 licence.)

the valve to be operated at a high repetition rate. This is demonstrated by the piezo-actuated valve developed recently in Amsterdam [50]. This valve uses a piezoelectric cantilever actuator to open the valve orifice, producing gas pulses of duration as low as 7 $\mu$s, and allowing operation at repetition rates as great as 5 kHz.

A pulsed supersonic beam can provide a reliable source of cold molecules, with a narrow speed distribution, well suited to performing high-precision spectroscopy. Examples include the upper limit of the value of the electron EDM measured with YbF molecules [56], high-precision spectroscopy of metastable CO [57] to probe the time-variation of the proton-to-electron mass ratio, the precise measurement of the ionisation and dissociation energies of $\text{H}_2$ [58] and $\text{D}_2$ [59], which can be used to probe physics beyond the standard model [60], and a measurement of the variation in the fine structure constant and the proton-to-electron mass ratio with Hz-level frequency measurements of CH molecules [2]. We shall discuss this last experiment in greater detail.

2.1. Hz-level frequency measurements of transitions in CH

In many extensions of the standard model of particle physics fundamental constants are predicted to vary [61]. Constants such as the proton-to-electron mass ratio, $\mu$, and the fine structure constant, $\alpha$, might vary in time, space and with local matter density. In order to test this last possibility Truppe et al performed high-precision spectroscopy of CH radicals in a pulsed supersonic beam, and compared the measured transition frequencies with those found in astronomical observations of CH in low density interstellar sources within the Milky Way [2]. The authors were able to constrain the variation in the fine structure constant ($\alpha$) and the proton-to-electron mass ratio ($\mu$) between these two density regimes.

The molecular state investigated in this spectroscopic study was the lowest-lying state of the ground electronic and vibrational manifold of CH, $X^2 \Pi (v = 0, N = 1)$ (see figure 1). This state is split by a number of interactions. The largest is the spin–orbit interaction, which produces two states, with angular momentum quantum numbers $J = 1/2$ and $J = 3/2$. Each of these states is $\Lambda$-doubled by a Coriolis interaction between the electronic motion and nuclear rotation into a pair of states with opposite parity. In the final interaction each of these four states is split into two states by the hyperfine interaction between $J$ and the hydrogen nuclear spin (quantum number $I = 1/2$), producing states with total angular momentum $F$ (figure 1). In this work transitions were driven between the components of the $\Lambda$-doublet of each spin–orbit manifold. The transition frequency, $\omega_{\text{Hz}}$, between a lower (l) and upper (u) state is sensitive to variations in $\alpha$ and $\mu$, quantified by the sensitivity coefficients, $K_{\alpha,\mu}$, defined by

$$\frac{\Delta \omega_{\text{Hz}}}{\omega_{\text{Hz}}} = K_{\alpha} \frac{\Delta \alpha}{\alpha},$$

and similarly for $K_{\mu}$. The values of $K_{\alpha}$ and $K_{\mu}$ have been calculated [62, 63], and so precise measurement of the transition frequencies, and comparison with astronomical measurements reveal the change in these constants between the two density regimes of Earth and interstellar space. We adopt the notation used in [2] for the hyperfine levels: ($J^\text{parity}$, $F$).

The laboratory measurements were made using Ramsey’s method of separated oscillatory fields [64, 65] with a pulsed supersonic CH beam (figure 2). The beam was made by expanding a mixture of CHBr$_3$ and a 4 bar carrier gas through a pulsed valve into a vacuum chamber (maintained at $10^{-7}$ mbar when the valve was closed) [2, 66]. After exiting the valve the CHBr$_3$ was photo-dissociated by radiation from an excimer laser (248 nm). 86 mm downstream of the valve nozzle the resulting beam of CH radicals traversed a 2 mm diameter skimmer into a differentially pumped ($< 10^{-7}$ mbar) chamber. The molecular pulses travelled with a forward speed, $v$, determined by the choice of carrier gas (1710 m s$^{-1}$ (He), 800 m s$^{-1}$ (Ne), 570 m s$^{-1}$ (Ar) and 420 m s$^{-1}$ (Kr)), and with a narrow velocity distribution. The translational temperature of the He- and Ar-carried beams were measured to be 2 K and 400 mK, respectively. Inside the second chamber the molecules passed between the two parallel copper plates of a microwave transmission line. A standing wave of microwave radiation was generated between the plates, with angular frequency, $\omega$, which could be tuned in the range of the hyperfine state transitions to be probed, and
which could be turned on and off rapidly. When the molecular pulse reached a certain position inside the transmission line, corresponding to an anti-node in the standing wave, the microwave radiation, tuned near one of the resonances, was turned on for $\tau = 15 \mu s$, driving a $\pi/2$ pulse, creating an equal superposition of the lower and upper states. After this microwave pulse the molecules continued on for a length, $L$, during which the phase of the superposition evolved with angular frequency $\omega_{\text{fr}},$. After travelling the distance, $L$ a second pulse was applied, also at an anti-node and with the same duration as the first pulse. The second pulse drove the molecules into the upper state with efficiency that, for small values of $(\omega - \omega_{\text{fr}})\tau$ varied as

$$P \approx \cos^2\left[\frac{1}{2}(\omega - \omega_{\text{fr}}) L + \phi(L) - \phi(0)\right],$$

where $\phi(L) - \phi(0)$ represents any phase change of the microwave field between the two pulses. A free flight phase advance of an integer multiple of $2\pi$ would result in the molecules being driven to the upper state with unity probability, whereas a half-integer multiple would drive the molecules to the lower state. Downstream of the resonator the population of either the lower or upper state was measured by time-resolved laser-induced fluorescence (LIF). The molecular pulse was intersected orthogonally by a laser beam tuned to drive an electronic transition out of the relevant state; the resulting fluorescence was recorded by a photo-multiplier tube (PMT). The PMT signal was recorded as $\omega$ was varied, mapping out the Ramsey fringes. In order to generate narrow Ramsey fringes the recorded time-of-flight (ToF) profiles were gated, and only a narrow range of arrival times was considered. This gating restricted the analysis to molecules falling within a narrow range of $\sim 10 \text{ m s}^{-1}$, but the narrow velocity distributions created in a supersonic beam ensured that a large proportion of the molecules in a pulse were included in the timing gate. The upper panel of figure 3 shows the population of the $(1/2^-, 1)$ state recorded as a function of $\omega$ for three different values of $L$, resulting in three sets of Ramsey fringes centred on the $(1/2^-, 1) \rightarrow (1/2^+, 1)$ transition frequency [66]. The lower panel of figure 3 shows similar data for the $(3/2^+, 1)$ state, with the fringes centred on the $(3/2^-, 2) \rightarrow (3/2^+, 1)$ transition frequency. The measurements performed by Truppe et al yielded Hz-level measurements of seven microwave transitions between the hyperfine components of the two $\Lambda$-doublets shown in figure 1.

The authors performed a detailed analysis of the systematic errors in these measurements, including using the molecular beam to characterize the microwave field inside the cavity [67]. The microwave power was set such that a $15 \mu s$ pulse applied at a time when the molecules were at an anti-node would drive a $\pi$ pulse. By observing the LIF signal as a function of the time that the $15 \mu s$ pulse was applied the authors were able to use Rabi oscillations to map out the standing microwave field, measuring the positions of the anti-nodes (essential for the Ramsey spectroscopy). The authors also performed a detailed analysis of velocity-dependent systematic errors that would shift the measured transition frequencies. Measurements taken with different beam speeds found that the measured transition frequencies varied linearly with $v$. The largest velocity-dependence observed for the $J = 1/2$ transitions was $0.05 \pm 0.01 \text{ Hz/(m/s)}$, and $0.03 \pm 0.01 \text{ Hz/(m/s)}$ for the $J = 3/2$ transitions. By using four different carrier gases it was possible to measure the velocity-dependence for each measured transition frequency, and extrapolate back to zero velocity for the final measurement.

Seven transition frequencies were measured, with errors ranging from 3 to 21 Hz, where the larger error bar was dominated by the uncertain Zeeman shift arising from uncontrolled magnetic fields. Comparing these Hz-level measurements with spectral lines observed in a number of interstellar sources within the Milky Way (where the local density is $10^{19}$ times smaller than on Earth) upper bounds on the variation in $\alpha$ and $\mu$ were measured to be $\Delta\alpha/\alpha < 1.4 \times 10^{-7}$ and $\Delta\mu/\mu < 2.9 \times 10^{-7}$.

Supersonic expansion provides molecular ensembles occupying only a limited number of lower rovibrational states, with a narrow forward speed distribution, low divergence after the skimmer, and short pulse durations. In the experiment described here these properties were all crucial in performing high-precision spectroscopy. The source allowed state-selection with high purity. The narrow forward speed distribution allowed well-defined Ramsey fringes to be observed. In order to include only those molecules that were well localised around a given anti-node during the $\pi/2$ pulses, the LIF signal was gated such that only molecules detected within a narrow range of arrival times were included in the measurements. The low translational temperature ensured that a large number of molecules contributed to the signal, despite the narrow velocity range considered, and the

Figure 3. Ramsey fringes measured with a supersonic beam of CH molecules. Upper panel: the population in the $(1/2^-, 1)$ state as a function of the frequency driving the $(1/2^-, 1) \rightarrow (1/2^+, 1)$ transition, with field-free phase evolution durations of 458 $\mu$s (green), 380 $\mu$s (blue), and 302 $\mu$s (red). Lower panel: the population in the $(3/2^-, 1)$ state as a function of the frequency driving the $(3/2^-, 2) \rightarrow (3/2^+, 1)$ transition, with evolution durations of 650 $\mu$s (green) and 330 $\mu$s (blue). (Reproduced from [66], which has been distributed under a CC BY 3.0 licence.)
low divergence ensured that the beam did not expand significantly over the length, \( L \). Operating the source with a range of carrier gases allowed velocity-dependent effects to be studied and accounted for in the final spectroscopic analysis.

3. Decelerated beams

In the absence of other broadening mechanisms, the precision of a spectroscopic measurement, such as the Ramsey measurement described in section 2.1, is proportional to the interaction time with the applied field, \( T \). Increasing the measurement time reduces the linewidth of the feature under investigation, and makes it easier to detect systematic line shifts. An additional consideration when performing high precision spectroscopy is the sensitivity to statistical errors. The statistical uncertainty in a spectroscopic experiment is given by

\[
\sigma = \frac{\Delta \omega}{\sqrt{N}},
\]

where \( \Delta \omega \) is the linewidth of the measured spectral feature, and \( N \) is the total number of detected molecules involved in the experiment [68]. In a pulsed experiment \( N \) is the product of the number of molecules measured per pulse and the total number of pulses. The latter is given by the product of the pulse rate and the total integration time of the experiment. The integration time is typically governed by a combination of long-term experimental stability and patience, and can range from days to months. Often there will be some systematic uncertainty, and there is no value in decreasing the statistical uncertainty much below this. When there are no other broadening mechanisms, \( \Delta \omega \propto T^{-1} \), and so the statistical uncertainty is proportional to \( (T\sqrt{N})^{-1} \). It is therefore advantageous to have a long interaction time, although not necessarily at the expense of \( N \).

Forward speeds from supersonic sources are on the order of several hundred metres per second, either rendering beam lines very long or interaction times very short. For example, in order to achieve an interaction time of 10 ms from a supersonic beam with a Xe carrier gas a beam line over 3 m length is required. Such a long distance can present practical difficulties. One solution is to decelerate the molecular beam. Over the last 17 years a number of techniques have been developed that use time-varying inhomogeneous electric or magnetic fields to decelerate molecular beams. Molecules can possess large body-fixed dipole moments and can thus experience a significant acceleration in a spatially inhomogeneous electric field. By switching the electric field in a particular time sequence a net deceleration ("Stark deceleration") can be achieved. Stark deceleration of cold molecules was first demonstrated in 1999 by Bethlem et al [69], when metastable CO molecules were decelerated from 225 to 98 m s\(^{-1} \). Since then decelerators have been developed and used to slow a wide range of polar molecules, including ND\(_3\) [70, 71], NH\(_3\) [71], OH [72, 73], OD [74], NH [75], CH\(_2\)O [76], SO\(_2\) [77], LiH [78], CaF [79], NO [80], CH\(_3\)F [81] and SD [82].

The magnetic equivalent, the Zeeman decelerator, which uses pulsed magnetic fields to achieve deceleration and phase stability, was developed independently by a group at ETH Zürich, and by groups at the University of Texas at Austin and Tel-Aviv University [83–87]. First applied to the deceleration of atoms, this technique has since been used to slow O\(_2\) [88, 89], CH\(_3\) [90] and He\(_2\) [91] molecules.

The optical equivalent, which makes use of the ac Stark shift of molecular energy levels in intense laser pulses, can also be used to slow molecules [92]. Optical Stark deceleration was developed at Heriot-Watt University and then University College London, where it has been used to decelerate benzene [93] and NO radicals [94], both originating in a supersonic source. In the rest of this section we will concentrate on Stark deceleration, focusing on a precision spectroscopy experiment performed with Stark decelerated molecules.

3.1. Stark deceleration

The principle of Stark deceleration is the loss of kinetic energy experienced by a molecule as it travels through a time-varying, inhomogeneous electric field. When a molecule is placed in an electric field its energy levels can experience a Stark shift. Those states whose energy decreases with electric field strength are known as strong-field (SF) seeking states, and those that increase are weak-field (WF) seeking states. Stark decelerators consist of a sequence of electrode pairs arranged along and around a molecular beam-line. Consider the example shown in figure 4, in which 5 electrode pairs are shown, arranged along the molecular beam-line (\( z \)-axis). At a given moment the even-numbered electrode pairs are polarised and the odd-numbered ones are grounded. In each polarised electrode pair the electrodes are oppositely charged, held at a potential \( \pm V \) (typically \( V \approx 10 \) kV), and are separated by a few mm, generating electric fields between the electrodes with magnitude on the order of 100 kV cm\(^{-1} \). Consider the dynamics of a molecule in a WF seeking state. As it travels in between a pair of oppositely polarised electrodes the total internal energy of the molecule increases, and its kinetic energy decreases in equal measure. When the molecule is near position \( z = L \), where the electric field is strongest, the even-numbered electrode pairs are rapidly (\( \approx 100 \) ns) grounded, while simultaneously the odd-numbered electrodes are polarised to \( \pm V \). The molecule thus leaves one electrode pair with reduced kinetic energy and immediately starts to climb the Stark potential hill of the next electrode pair. As the molecule passes down the decelerator the electric fields are switched with a timing sequence that ensures that kinetic energy is removed in every electrode pair. Typical Stark decelerators consist of around 100 electrode pairs, and are capable of slowing molecules from several hundred m s\(^{-1} \) to tens of m s\(^{-1} \). The final speed of the molecules as they leave the decelerator is determined by the molecular dipole moment, the strength of the electric fields used, and the timing
A given switching sequence slows molecules from an initial speed, \( v_i \), to a final speed, \( v_f \). But of course the molecular ensemble loaded into the decelerator will have a range of longitudinal speeds, typically tens of m s\(^{-1}\) for a supersonic beam. The longitudinal confinement of the decelerated packet of molecules is determined by ‘phase stability’, generated by the switching timings. A molecule that starts with speed \( v_i \) and ends with the intended final speed, \( v_f \) (for which the timing sequence was generated) is known as the ‘synchronous molecule’, and is always at the same position in each deceleration stage when the fields switch, losing an equal amount of kinetic energy in each stage. Each electrode pair is separated from its nearest neighbours by a distance \( L \), and so with alternate electrode pairs held at the same potential the longitudinal electric field distribution has period \( 2L \) (see figure 4). The periodicity allows the longitudinal position of a molecule at the moment the fields switch to be described by a phase, \( \phi = \frac{\pi z}{L} \). A switching sequence is defined such that the synchronous molecule is always at the same phase, \( \phi = 0 \) whenever the fields switch. A sequence for which \( \phi = 0 \) corresponds to the synchronous molecule being guided though the decelerator, with no net deceleration. As \( \phi \) is increased the synchronous molecule is increasingly decelerated, up to a maximum deceleration at \( \phi = \frac{\pi}{2} \), which corresponds to the synchronous molecule travelling to the peak of each Stark ‘potential hill’. Let the synchronous molecule have longitudinal speed, \( v_f(t) \) as it progresses down a decelerator. Consider a molecule that enters a deceleration stage with a speed slightly greater than \( v_f \) and slightly ahead of the synchronous molecule. This molecule will have travelled further up the potential hill by the time the potentials are switched, and thus will be decelerated more than the synchronous molecule. Passing into the next stage the molecule again travels further up the potential hill than the synchronous molecule, but with a reduced difference as it has less kinetic energy this time. This continues through successive stages until eventually the non-synchronous molecule is slower than the synchronous molecule. It then travels a shorter distance up the potential hill, being decelerated less than the synchronous molecule. In this manner the non-synchronous molecule oscillates about the synchronous molecule in phase space, and is longitudinally confined along the length of the decelerator. The confinement is limited to those molecules with a phase space position close to that of the synchronous molecule. For example, a molecule with a speed too different from that of the synchronous molecule will make a large phase space oscillation which at some point will result in it being sufficiently fast relative to the synchronous molecule that it will travel beyond the Stark potential maximum in the middle of an electrode pair and will be accelerated away from the synchronous molecule. The motion of molecules relative to the synchronous molecule can be described in terms of an effective potential [98], whose depth depends on the value of \( \phi \). Figure 5(b) shows an example of

Figure 4. (a) Schematic diagram showing 5 electrode pairs of a Stark decelerator, with the red electrodes held at potential \( \pm V \) and the white electrodes grounded. Also shown is the form of the electric field along the axis (modified from [95]). (b) Photograph of one end of a 100-stage Stark decelerator used at Imperial College London.
this effective potential calculated for WF-seeking CaF molecules in the $N = 4$ rotational state, travelling down a Stark decelerator operated at ±20 kV and for a range of values of $\phi$. The decelerator has rod-like electrodes with diameter 3 mm and separation 2 mm, resulting in a maximal electric field strength of $\sim$175 kV cm$^{-1}$. The number of molecules that can be confined in the effective potential well can be quantified by the 'acceptance', which is the volume of phase space occupied by all possible confined molecules. Figure 5(c) shows the longitudinal acceptance (the area of $z-v_z$ phase space occupied by confined molecules) calculated for the deceleration conditions described above.

Stark decelerators can be used as an efficient source of molecules with variable speed down to $\sim$100 m s$^{-1}$. The distribution of molecules exiting a Stark decelerator depends on the phase space distribution of the ensemble loaded into the decelerator, the geometry of the electrode array, and the chosen deceleration sequence. Typically the emitted pulse has spatial distribution of $\sim$2 mm in all directions and a forward speed distribution with width $\sim$10 m s$^{-1}$. The emitted phase space distribution and the variable exit speed render Stark decelerators a very useful tool in performing high-precision spectroscopy experiments.

The principle of Stark deceleration is the same for molecules in SF seeking states, except that deceleration is achieved by switching the fields on when the molecules are inside an electrode stage and the molecules are decelerated as they travel away from the electrodes. However, the electric field inside an electrode stage accelerates the molecules away from the axis, defocussing the molecular beam. In this case a different electrode geometry is required which uses a sequence of alternating focusing and defocussing transverse forces to achieve a net focusing along the length of a decelerator. This alternating gradient deceleration has been used in only a limited number of experiments [79, 99–101] and will not be discussed in further detail in this article.

The first use of Zeeman deceleration to slow molecules was performed by researchers at the University of Texas at Austin and Tel-Aviv University, who slowed pulses of O$_2$ from 389 to 83 m s$^{-1}$ in a 64-stage coilgun decelerator [88] (figure 6(a)). Figure 6(b) shows an example ToF plot measured by a quadrupole mass spectrometer (QMS) located...
downstream of the decelerator. The effect of the decelerator is clearly shown in figure 6(b): the non-decelerated pulsed is centred around ~4 ms (corresponding to a central speed of 389 m s⁻¹), with a clear notch where the decelerated molecules originated. The slowed molecules are shown in a later pulse, around ~6.1 ms in this example, corresponding to a final speed of 114 m s⁻¹.

Despite now being a mature technology, Stark and Zeeman decelerators have not yet been widely exploited in high precision spectroscopy. To date the only applications of decelerated beams in this field are the measurement of the hyperfine structure of $^{15}$ND$_3$ [103] and the $\Lambda$-doublet interval in the ground state of OH [3] (discussed in more detail in section 3.2) with Stark decelerated molecules, and a high-precision study of the Rydberg spectrum of molecular helium with Zeeman-decelerated He$_2$ [104]. Despite this, Stark (and Zeeman) deceleration is a versatile technique which, when combined with other methods (e.g. laser cooling) has the potential to be of great use in spectroscopic measurements.

3.2. Measurement of $\dot{\alpha}$ with stark decelerated OH

In this section we discuss a high precision spectroscopy experiment performed at JILA in 2006 with Stark decelerated OH radicals [3]. OH had first been decelerated in 2003 by the same group [105]. In the 2006 experiment OH radicals, Stark decelerated to a range of speeds, were used in Rabi-type measurements to make high precision measurements of the frequency intervals between the hyperfine states in the lower and upper levels of the ground ro-vibrational $\Lambda$-doublet.

The low rotational levels of OH have a $^3\Pi$ configuration, with the angular momentum coupling described by Hund’s case (a) [106, 107]. In this case the spin–orbit interaction is much greater than the rotational energy, and the electronic orbital angular momentum (quantum number $L = 1$) and spin ($S = 1/2$) are strongly coupled to each other, and to the internuclear axis [108]. In a state described by Hund’s case (a) the projections on the internuclear axis of the electronic orbital angular momentum and spin have quantum numbers $\Lambda$ and $\Sigma$, respectively, with sum $\Omega = \Lambda + \Sigma$. The nuclear rotational angular momentum (quantum number $R$) couples to the body-fixed electronic angular momentum, producing a total angular momentum with operator $\vec{J} = \vec{L} + \vec{S} + \vec{R}$. The projection of the total angular momentum onto the internuclear axis is $\Omega$, which can take value 1/2 or 3/2. There are therefore two spin–orbit manifolds, with $\Omega = 1/2$ and 3/2, respectively. Within each manifold there is a ladder of levels labelled by $J$. The lowest level in the $\Omega = 1/2$ manifold is $J = 1/2$, and in the $\Omega = 3/2$ manifold it is $J = 3/2$. A Coriolis interaction between the electronic orbital angular momentum and the nuclear rotation splits the spin–orbit levels into $\Lambda$-doublets, in which the states have opposite parity. Finally, the levels in the $\Lambda$-doublets are split by the
hyperfine interaction with the nuclear angular momentum of the hydrogen atom \((I = 1/2)\), resulting in the total molecular angular momentum, with quantum number \(F\). Figure 7 shows these various levels of structure.

Figure 8 highlights the transitions driven in this experiment with Stark decelerated OH, as well as the experimental set-up described. A pulsed beam of OH radicals was created using supersonic expansion and electric discharge [109]. Xe gas with a backing pressure of 3 atm was bubbled through deionised, distilled water, resulting in a mixture of 99% Xe carrier gas and 1% water. The mixture was then pulsed into a vacuum chamber, resulting in a supersonic beam with temporal width <100 µs. Immediately downstream of the valve nozzle the molecules passed through a pair of ring electrodes arranged coaxially with the beam line. An electric discharge between the two electrodes, seeded by electrons from a hot tungsten filament, dissociated the \(\text{H}_2\text{O}\) molecules, resulting in a pulse of OH radicals travelling with a mean forward speed of 410 m s\(^{-1}\) (10%) and a rotational temperature of <25 K (corresponding to ~98.5% of molecules in the lowest rotational state of the \(J = 3/2\) spin–orbit manifold [107]).

After passing through a skimmer, molecules in the WF seeking upper \(\Lambda\)-doublet state were then focused into a 69-stage Stark decelerator by a 50 mm long hexapole [107]. The Stark decelerator was operated with a range of phase angles, resulting in pulses of OH with speeds in the range 410 m s\(^{-1}\)–50 m s\(^{-1}\), with longitudinal translational temperatures in the range 1 K–5 mK respectively. A Stark decelerator produces no cooling, simply velocity selection: the range of velocities in the decelerated bunch decreases at higher phase angle only because the effective potential well becomes shallower (see figure 5(b)).

The states of interest (see figures 7 and 8) will be described by their quantum numbers in the form \([F, m_F, \text{parity}]\). Only those molecules in the \([2, \pm 2, +]\) and \([2, \pm 1, +]\) states were decelerated. However, during the molecules’ flight through the field-free region after the decelerator their populations were redistributed among all the \(F = 2\) sub-states. The decelerated molecules then traversed a microwave cavity in which Rabi oscillations between the two \(\Lambda\) states were driven. After leaving the microwave cavity the effect of these oscillations was probed by measuring the upper state population with LIF, with laser radiation of wavelength 282 nm driving the \(2\Sigma_{1/2}(v' = 1) \leftrightarrow 2\Pi_{3/2}(v = 0)\) transition, and a PMT imaging the 313 nm wavelength fluorescence of the subsequent \(2\Sigma_{1/2}(v = 1) \rightarrow 2\Pi_{3/2}(v = 1)\) decay.

In order to probe systematic effects the interaction time with the radiation was varied in two ways: (i) by varying the microwave pulse duration, and (ii) by using a wide range of molecular speeds. Figure 9(a) shows the effect of Rabi flopping on the upper \(F = 2\) state of molecules decelerated to 200 m s\(^{-1}\), with the microwave radiation driving the \(2 \rightarrow 2\) transition. Varying the duration of the microwave pulse creates an oscillation in the upper state population which exhibits a dual-frequency beat pattern which arises from the different transition strengths of the \([m_F = 1 \rightarrow m_F = 2]\) and \([m_F = 2 \rightarrow m_F = 1]\) transitions (the \(m_F = 0 \rightarrow m_F = 0\) transition has zero dipole moment). For microwave pulse durations greater than 300 µs the Rabi frequencies of both transitions decrease due to the reduced electric field strength near the end caps of the cavity. The data in figure 9(b) show the upper doublet population as a function of molecular speed for a fixed spatial length microwave pulse. Again, the expected functional form is a dual-frequency beat signal. The data show that for fast molecules (\(v > 270 \text{ m s}^{-1}\)) the fringe visibility is reduced, which results from the decelerated molecules not being separated from the undecelerated pulse and so molecules with a wide velocity range (and which experience different Rabi excitations in the microwave field) contribute to the data. Decoherence was observed with molecular speeds below 130 m s\(^{-1}\), a result of microwave radiation being reflected off the end of the Stark decelerator and back into the cavity. This effect, which was power dependent, was found to be less significant in the functional measurements, which used less microwave power than in the systematic tests.

As a result of these systematic tests Hudson et al chose to use molecules decelerated to 200 m s\(^{-1}\). This speed was small enough that the decelerated molecules were separated from the non-decelerated pulse, great enough that the decelerator was operated without significant losses from transverse focussing, and allowed a long enough interaction time with the microwave radiation to yield a Rabi linewidth of 2 kHz.

The \(2 \rightarrow 2\) transition frequency was not probed using a Rabi π pulse because of the dual-frequency nature of the Rabi
fringe pattern. Rather, the microwave power and pulse duration were chosen such that when the detuning from resonance was zero the upper state population was reduced to the first minimum in figure 9(a). Tuning the microwave radiation around this resonance yielded a negative-going dip (see figure 10(a)).

In order to probe the $1 \rightarrow 1$ transition the molecules were first transferred to the $|1, \pm 1, -\rangle$ and $|1, 0, -\rangle$ states by a 70 $\mu$s microwave pulse driving the $2 \rightarrow 1$ transition before the rest of the cavity traversal time was used to drive a $\pi$ pulse from the $|m_F = 1\rangle$ states to the upper state, generating a positive-going peak around resonance (figure 10(b)). Fitting the Rabi features determined the resonant frequencies with an accuracy of $\sim 50$ Hz. Multiple measurements resulted in $2 \rightarrow 2$ and $1 \rightarrow 1$ transition frequencies with a standard error of 4 Hz and 12 Hz respectively. Combined with astrophysical measurements, this precise measurement of the OH A-doublet interval is sufficient to allow a constraint on the time variation of the fine structure constant over a time scale of 10 Gyr with a sensitivity of 1 ppm.

Stark deceleration was found to be a useful tool in high-precision spectroscopy, producing molecules with a controllable speed in the range 50–410 m s$^{-1}$, allowing careful characterisation of systematic effects and the ability to choose the best speed for a given spectroscopic investigation. However, the decelerator’s inability to increase the phase space density currently limits its use in achieving spectroscopic studies involving longer interaction times (e.g. a fountain). The slow pulse emitted from a decelerator spreads out longitudinally and transversely, making it hard to perform spectroscopic analysis with long interaction times. Although efficient at slowing molecules, a Stark decelerator’s utility in
precision spectroscopy would be vastly increased if coupled with a method of cooling the molecules, either before or after deceleration. One such method, laser cooling prior to deceleration is described in more detail in section 5.4.

4. Buffer gas sources

An alternative to starting with a supersonic beam of molecules which is subsequently slowed, buffer gas sources can provide intense beams of slow molecules, with forward speeds as low as \( \sim 50 \text{ m s}^{-1} \). The source of the slow molecules is a buffer gas cell, typically a copper cubic cell of volume \( \sim 10 \text{ cm}^3 \) mounted on a cryogenically cooled cold plate held at a temperature in the range of 2–20 K [110]. A buffer gas of light, chemically inert atoms (typically helium or neon) is introduced into the cell, cooling by collisions to the temperature of the cell walls. The cold buffer gas is allowed to leave the cell through an aperture in one of the cell walls. Molecules introduced into the cell can be cooled by collisions with the buffer gas, thermalizing translationally and rotationally with it, and then extracted from the cell by becoming entrained in the outward buffer gas flow.

The first use of buffer gas cooling was the thermalisation of CO molecules with He cooled to 4 K [111]. In 2005 a buffer gas cell with an aperture in one wall was demonstrated to be a high-flux source of cold atoms (Na) and molecules (PbO) [112]. This cooling technique can be widely applied to a large range of molecular species, and has now been used to produce cold, slow sources of many molecules (see table 2 of [110]), including a number of heavy diatomic molecules which are of interest to precision spectroscopy, particularly for experimental tests of fundamental physics: YbF [113, 114], SrF [115], CaH [116], PbO [112, 117], and ThO [4, 118].

The molecules to be cooled can be introduced into the buffer gas cell using a range of methods [118], but the most common methods are laser ablation of a solid precursor target, and injection through a capillary tube. The simplest case for laser ablation occurs when the molecular species can form a stable solid, as is the case with PbO. In [112] a solid PbO target located inside the cell was ablated by 532 nm laser radiation (15 mJ in a 5 ns pulse). If no such stable solid phase exists then the molecule must be created inside the cell. An example is the SrF source built at Yale University, which uses a precursor of SrF2 powder compressed under a pressure of 600 MPa to create a solid precursor target. Ablation of this target with a 10 ns duration 25 mJ pulse of 1064 nm laser radiation creates a plume of SrF inside the cell. An alternative approach is to create the molecules from precursor materials introduced independently into the buffer gas cell, as in the method for the production of YbF described in [119] (figure 11). In this source YbF radicals are made by a combination of laser ablation and capillary injection. SF6 is injected into the buffer gas cell, held at 4 K. A solid Yb rod, located inside the cell, is ablated by a 1064 nm laser pulse, creating a plume of Yb atoms, some of which react with the SF6 to form YbF radicals which are then cooled by a He buffer gas and entrained in the beam leaving the cell.

A full description of the properties of buffer gas sources is given elsewhere (e.g. [110], which presents a thorough analytical description as well as a technical discussion of buffer gas sources). The nature of a buffer gas source depends on the flow rate of the buffer gas through the cell. Consider a buffer gas cell held at temperature, \( T \), operated with a buffer gas of atoms with mass, \( m_b \), and used as a source of buffer gas cooled atoms or molecules of mass \( M \). In the case of a low flow rate through the cell the source operates in the effusive regime, in which the cooled atoms/molecules leaving the cell experience few collisions near the exit aperture. In this regime the flux of the cooled species exiting the cell has a velocity distribution very similar to that of the thermalized species inside the cell. The mean forward beam speed, \( v_{\text{eff}} \) and width of the speed distribution, \( \Delta v_{\text{eff}} \) can be shown to be
given by [110]

\[ \bar{v}_{\text{eff}} = \frac{3\pi}{8} \bar{v}^M_{\text{MB}}, \]

(12)

\[ \Delta v_{\text{eff}} = \sqrt{\pi \ln(2)} \bar{v}^M_{\text{MB}}, \]

(13)

where \( \bar{v}^M_{\text{MB}} = \frac{\sqrt{s_{k_B} T}}{\sqrt{\pi M}} \) is the mean speed of the Maxwell–Boltzmann distribution of the cooled species inside the cell.

As the flow rate is increased there are more interactions between the cooled species and the buffer gas near the exit aperture, which boosts the cooled atoms/molecules as they leave the cell. In this intermediate regime this boost increases as the flow rate is increased from that of the effusive regime, until eventually saturating at some upper limit. In this upper limit there are sufficient collisions between the buffer gas atoms and the cooled species in the region of the aperture that the forward speed of the cooled species out of the cell is determined solely by the dynamics of the buffer gas atoms. In the limit of large flow rate the buffer gas expands supersonically through the cell, reaching a terminal speed given in (6). The speed distribution of the beam produced in this limit is the same as would be generated in a supersonic beam of the type discussed in section 2 with the valve cooled to the same temperature as the cryogenic cell. In the case of an atomic (\( \gamma = 5/3 \)) buffer gas that cools as it expands from an initial temperature, \( T_0 \) to a final temperature, \( T_1 (\ll T_0) \), the forward speed of the cooled species in the supersonic regime is

\[ \bar{v}_{\text{up}} = \sqrt{\frac{5k_B(T_0 - T_1)}{m_b}} \approx \sqrt{\frac{5k_B T_0}{m_b}}. \]

(14)

In this regime the seed species can be cooled translationally and rotationally to a temperature below that of the cell by collisions in the supersonic expansion (in the same manner as described in section 2), typically to around 1 K. In choosing the operating regime of a buffer gas cell one has to balance the need for a low forward speed with that of flux. The beam temperature produced by a buffer gas source is almost always close to 4 K, regardless of the helium flow rate (see figure 12(b)). The flux, on the other hand, depends strongly on the flow rate. In the effusive regime the flux is low as most molecules diffuse to the cell walls instead of being flushed out of the cell. In the supersonic regime most molecules are flushed out of the cell, leading to a high flux. An additional, and important, consideration is the divergence of the beam exiting the cell. A buffer gas source operated in the effusive regime produces a very divergent beam (\( \Delta \theta = 120^\circ \)) due to the low forward speed and the relatively few number of collisions near the aperture. Increasing the flow rate into the intermediate regime reduces the divergence due to the increased number of collisions near to the aperture, and the increased forward speed. However, the divergence does not decrease indefinitely with flow rate: when in the supersonic regime the collisions that occur downstream of the aperture can increase the transverse speed of the beam. In the limit that the terminal supersonic speed has been reached by the beam any such increase in the transverse speed will increase the divergence. As the flow rate is varied there is a minimum divergence angle in the intermediate regime, which can be shown to have value [110, 120]

\[ \Delta \theta_{\text{min}} = \frac{8 \ln 2 m_b}{5 M}. \]

(15)

For the purposes of performing high precision spectroscopy with long interaction times with a molecular beam, reducing the divergence is useful, and the intermediate regime represents the best compromise, generating a high flux, low divergence, translationally and rotationally cold beam of molecules with a forward speed lower than that achieved in a supersonic beam created by a pulsed valve.

Bulleid et al tested the performance of cryogenic sources by characterizing the properties of a buffer gas source of Yb atoms [120]. Operated with a cell temperature of 4 K and a buffer gas of He atoms, Yb atoms were created by laser ablation (20 mJ to 140 mJ of 1064 nm radiation in an 8 ns pulse) of a Yb target located inside the cell. The pulsed source was operated with a repetition rate of 5 Hz. The Yb beam emitted from the cell was measured by time-resolved LIF, with laser radiation of wavelength 556 nm driving the \( 6s^2 \ ^1S_0 \rightarrow 6s6p \ ^1P_1 \) transition. Figure 12(a) shows the measured (and simulated) forward speed of the Yb beam over a range of He flow rates. As described above, the beam is slow when the flow rate is low, increasing linearly as the rate is increased, before saturating at high flow rates. In the lower limit the speed tends towards the speed of an effusive beam of
Figure 13. Fractional populations in the lowest 5 rotational states of SrF measured inside (black points) and 20 mm downstream of (red points) the buffer gas cell. The dashed lines represent the results of fits with a Maxwell–Boltzmann distribution with temperature 5.3 K (black) and 1.2 K (red). (Reproduced from [113] with permission of the PCCP Owner Societies.)

Yb from a 4 K cell, calculated from (12) to be 26 m s⁻¹. Beams at this speed were not observed because at such a low flow rate there was too low a density in the cell to entrain the ablated Yb atoms. Instead the latter hit the walls of the cell and there was no Yb beam. In the upper flow rate limit the beam was found to saturate at 204 m s⁻¹, as expected for a supersonic beam of He atoms from a 4 K source (14). By recording LIF data with laser radiation counter-propagating relative to the Yb beam the longitudinal translational temperature was measured for a range of flow rates (figure 12(b)). At low flow rate, close to the effusive regime the temperature was measured to be ~9 K, consistent with the width of the speed distribution given in (13). As the flow rate was increased the temperature rapidly dropped, and with a rate of ≥5 sccm there were sufficient collisions in the isentropic expansion of the He flow to produce a Yb beam cooled to below the temperature of the cell. Data taken with a slit-like exit aperture of dimensions 0.75 mm × 4 mm and for flow rates ≥5 sccm rendered a mean temperature of 2.4 ± 0.3 K. The data in figure 12(c) show the beam divergence measured over the same range of flow rates. As discussed above, close to the effusive regime the beam was highly divergent. The divergence reduced with flow rate, reaching a minimum in the intermediate regime of Δθ eff = 12° with flow rates in the range 30–40 sccm, slightly greater than the value calculated using the expression in (15).

The effects of buffer gas cooling on the internal degrees of freedom of molecules can be studied by measuring the populations in a range of rotational and vibrational states. As an example, Barry et al performed these measurements with laser spectroscopy inside and downsteam of a buffer gas source of SrF, operated with a He buffer gas flowing at 5 sccm, and SrF made by ablation of a solid SrF₂ target [115]. Figure 13 shows the fractional populations in the five lowest rotational energy levels of the ground electronic state of SrF, measured both inside the cell and 20 mm downstream of the aperture. Fitting a Maxwell–Boltzmann distribution to these data reveals the rotational temperature inside the cell to be 5.3 K, and 1.2 K 20 mm downstream, demonstrating the cooling effect of collisions in the beam. A similar analysis performed with the four lowest vibrational states of the ground electronic state found the vibrational temperature both inside and downstream of the cell to be ~300 K. As discussed above (section 2) the vibrational motion thermalizes much more slowly, requiring many more collisions. However, the authors observe that this vibrational temperature was still far smaller than that expected from an uncooled ablation plume.

Buffer gas cells can provide intense sources of cold molecules, although the flux depends strongly on the mechanism for introducing the species to be cooled into the cell, as well as the fluid dynamics within the cell. Fluxes in the range from 10⁸-10¹¹/shot/sr have been reported for a number of molecular species (see [110] and references therein). Whether they present a more intense beam than a supersonic source depends on the molecules used and their preparation method. However, in the case of diatomic radicals prepared using laser ablation of a precursor target (as used in a number of high precision spectroscopic tests of fundamental physics) buffer gas cells can produce brighter beams. For example, a supersonic beam of YbF molecules constructed at Imperial College London was found to produce a flux of 1.4 × 10⁹/shot/sr molecules in the ground rovibronic state [43], whereas a buffer gas source built by the same group was found to produce fluxes of molecules in the same state of 2.3 × 10⁹/shot/sr [121].

4.1. Measurement of the electron EDM with buffer gas cooled ThO

In many theories of particle physics the electron is predicted to have a non-zero EDM. The standard model of particle physics predicts a very small value for lepton EDMs, ≤10⁻³⁸ e cm [122], currently too low for experimental verification. However, a number of extensions to the standard model predict far greater values of the electron EDM, in the range from 10⁻²⁶ to 10⁻³⁰ e cm [123] (see figure in [124]), great enough to be tested by experiments currently underway and proposed. A consequence of a non-zero value for the electron EDM, δₑ, would be that an electron placed in an electric field, \(\vec{E}\), would have a preferred direction. The EDM must be either parallel or antiparallel to the electron’s spin vector, \(\vec{\sigma}\) [56]. There would thus be an energy difference between cases of an electron with its spin vector pointing parallel and antiparallel to the direction of the applied field, \(\Delta W = 2\delta_e E\). Measuring this shift is no trivial matter. Experiments with lone electrons will not yield useful results as the Coulomb interaction with the applied field will dwarf any interaction with an electron EDM (as well as rapidly accelerate the electron). Experiments with neutral paramagnetic atoms, in which the interaction is measured with the unpaired electron, seem more practical. Schiff showed that a system of non-relativistic Coloumb-
bound point particles, each with some permanent EDM, will experience no first order interaction energy with an applied electric field [125]. However, this is not the case when the particles are not point-like or are moving relativistically [126, 127]. The former is relevant for EDM searches of nucleons, and the latter for electrons. In fact it can be shown that the relativistic conditions experienced by an electron close to a heavy nucleus can lead to an enhancement in the first order interaction with an applied electric field, which can be orders of magnitude greater than would be experienced by a lone electron [126, 128]. For the interaction energy to be non-zero, the eigenstates must be of mixed parity, which requires an external electric field. The greater the mixing the greater the enhancement. This enhancement can be parameterised in terms of an effective electric field, $E_{\text{eff}}(E_{\text{ext}})$, a function of the externally applied field, $E_{\text{ext}}$. In this description the first order interaction energy has the form $d_1E_{\text{eff}}(E_{\text{ext}})$. Measurements of the electron EDM have been performed with paramagnetic atoms with heavy nuclei [129, 130]. The values of $E_{\text{eff}}$ for these experiments, determined by the nuclear charge and the strength of the applied field, $E_{\text{ext}}$, were 0.5 MV cm$^{-1}$ and 60 MV cm$^{-1}$, respectively, far greater than the strength of the applied fields.

Polar molecules have the great advantage that this mixing is already present, with the electronic wavefunction strongly polarised along the inter-nuclear axis, leading to a very strong effective field. An external electric field must be applied to polarise the molecules in the laboratory frame, but this field does not have to be strong because the polarisation results from the mixing of opposite parity states that can be very closely spaced in molecules (e.g. rotational levels, $\Lambda$-doublets, inversion doublets). In the case of polar molecules $E_{\text{eff}}$ is a function of $E_{\text{ext}}$, rising linearly at first, and then saturating at a value $E_{\text{max}}^{\text{eff}}$ when the molecule is fully polarised in the laboratory frame (e.g., figure 1 of [131] shows $E_{\text{eff}}(E_{\text{ext}})$ for YbF). Previous electron EDM searches using polar molecules include an experiment with a beam of YbF molecules produced in an oven [131], and one which used PbO radicals in a heated vapour cell [132]. The first molecular measurement of the electron EDM to improve upon the sensitivity of previous atomic measurements was performed at Imperial College London with a supersonic beam of YbF molecules [56]. In YbF $E_{\text{eff}}^{\text{max}} = 26$ GV cm$^{-1}$, achievable with an applied field strength of only $\sim 30$ kV cm$^{-1}$ (see [131] and references therein). The applied field in this experiment was 10 kV cm$^{-1}$, rendering an effective field strength of 14.5 GV cm$^{-1}$ [56, 133].

We discuss now the most recent electron EDM search, which has yielded an upper limit of $|d_e| < 8.7 \times 10^{-29}$ e cm [4]. This experiment used an intense buffer gas source of ThO molecules. The very heavy Th nucleus leads to a large relativistic enhancement, resulting in a maximal effective electric field of $E_{\text{eff}}^{\text{max}} = 84$ GV cm$^{-1}$ [134, 135]. The states used in this investigation were a $\Lambda$-doublet of the $H$ state, whose opposite parity states are separated by only $\sim 10$ kHz. As a result of this small state separation only a small applied electric field ($\sim 100$ V cm$^{-1}$) is required to fully polarise the $H$ state, allowing the maximal effective field to be attained with ease.

Figure 14(a) describes the experimental features of the ThO electron EDM experiment. Note that the authors use a coordinate system in which the molecular beam travels along the $x$-axis: for consistency with the papers cited in this section we adopt the same convention here. The buffer gas source produced ThO radicals by laser ablation of a ThO$_2$ target located inside a cryogenically cooled cylindrical copper cell (13 mm diameter, 75 mm length) held at 4 K, operated with He buffer gas [4, 134]. The source produced pulses of $\sim 10^{11}$ ThO molecules in the $J = 1$ state of the $X ^{1}S_0$ ground electronic state, with a mean forward speed of 200 m s$^{-1}$, a rotational temperature of 4 K, and was operated at a repetition rate of 50 Hz [136, 137]. The population of the $X ^{1}S_0^+ J = 1$ state was enhanced by a factor of $\sim 2$ by transferring population from nearby rotational states with a combination of optical and microwave radiation. The molecules were then transferred to the ground rovibrational $J = 1$ level of the $H ^{3}D_1$ state by means of excitation to the $A$ state with 944 nm laser radiation, followed by spontaneous decay to the $H$ state.

The paramagnetic $H ^{3}D_1 (J = 1)$ state is $\Lambda$-doubled by a Coriolis interaction between the nuclear rotation and the electronic orbital angular momentum. This results in 6 sub-
levels: three levels with positive parity and angular momentum projection along the laboratory z-axis \( M_J = \pm 1, 0 \), and three with negative parity and the same projection quantum numbers. In the absence of the Coriolis interaction these two manifolds would be degenerate. The interaction lifts this degeneracy, yielding a \( \Lambda \)-doublet interval of \( \sim 10 \text{ kHz} \), far too small to be resolved by the lasers used in this experiment\(^3\).

Figure 14(b) shows the structure of the doublet in the presence of an applied electric field, \( \mathcal{E}_{\text{ext}} = \mathcal{E} = \mathcal{E} \). The \( H^2 \Delta J = (J = 1) \) state has a very large body-fixed dipole moment, measured to be \( D = 2.13(2) \text{ MHz/(V/cm)} \) \([138]\). Only a modest electric field is required to generate a total Stark-shifted interval between the upper and lower \( \Lambda \)-doublet states with \( |M_J| = 1 \text{ of } \sim 100 \text{ MHz} \) (the \( M_J = 0 \) levels are not Stark shifted). With this Stark shift the molecules are fully polarised either parallel or anti-parallel with \( \mathcal{E} \). The polarisation is described by \( \mathcal{N} = \text{sgn}(\mathcal{I} \cdot \mathcal{J}) \), where \( \mathcal{I} \) is the unit vector pointing along the internuclear axis, the values for which are given in figure 14(b), as well as pictorial depictions of the molecular alignments for the four relevant states. The figure also shows the orientation of the applied electric field, \( \mathcal{E}_{\text{ext}} = \mathcal{E} \) (black arrow), the electron spin (red arrows) and \( \mathcal{I} \) (blue arrows).

The optical pumping created an ensemble of molecules with an incoherent population distributed evenly over the \( 6 \ H^2 \Delta J \) sub-levels. A linearly polarisation preparation laser drove transitions from either the \( \mathcal{N} = +1 \) or \( \mathcal{N} = -1 \) levels of the \( H \) state to one of the parity states of the electronic \( C \) state. This excitation left behind a dark state, in the \( H \) state, a superposition of the two resonant \( M_J = \pm 1 \) sub-levels. This superposition depended on the direction of polarisation of the preparation laser. For example, laser radiation polarised along the \( \mathcal{x} \)-direction resulted in the following superposition:

\[
|\psi_N^{(x)}\rangle = \frac{1}{\sqrt{2}}(|M_J = +1, \mathcal{N}) - |M_J = -1, \mathcal{N}\rangle). \tag{16}
\]

After preparation, the molecules passed between two electric field plates separated by 25 mm. The plates were made of 12.7 mm thick glass coated on one side with indium tin oxide, and the other side with anti-reflection coating, thus allowing the transmission of the laser radiation used to prepare and measure the molecules. In the volume between the plates uniform electric (\( \mathcal{E}_{\text{ext}} = \mathcal{E} \), typically \( 140 \text{ V/cm} \)) and magnetic (\( B \leq 38 \text{ mG} \)) fields were applied. The fields were applied along the \( z \)-axis, either parallel or anti-parallel with the unit vector \( \mathcal{J} \). The fields can be described by \( \tilde{\mathcal{E}} = |\mathcal{E} \rangle \mathcal{E} \) and \( \tilde{B} = |B \rangle \mathcal{B} \), where \( \mathcal{E} = \text{sgn}(\mathcal{E} \cdot \mathcal{J}) \) and \( \mathcal{B} = \text{sgn}(\mathcal{B} \cdot \mathcal{J}) \) denote the orientation of the fields relative to \( \mathcal{J} \). The molecules traversed this region for a length of \( L = 22 \text{ cm} \) (and interaction time, \( \tau = 1.1 \text{ ms} \)), during which the two components of the superposition accrued a phase difference

\[
\phi = \frac{2}{\hbar} \int_{x=0}^{x=22 \text{ cm}} \left( \mu_B g |B| \mathcal{B} + d_e E_{\text{eff}}(E) \tilde{\mathcal{N}} \right) dx, \tag{17}
\]

where \( \hbar \) is the Bohr magneton, and \( g = -0.0044 \pm 0.0001 \) is the gyromagnetic ratio of the \( H \ 3\Delta J = (J = 1) \) state \([139]\).

After 1.1 ms of phase evolution the value of \( \phi \) was measured by probing the molecules on the \( H \rightarrow C \) transition. The molecules were probed with radiation linearly polarised along either the \( \mathcal{X} \) or \( \mathcal{Y} \) directions (alternately), where \( \mathcal{X} \) and \( \mathcal{Y} \) form a basis in which \( \mathcal{X} \) is rotated by angle \( \theta \) to \( \mathcal{z} \) in the \( xy \) plane. Labelling the resulting fluorescence \( \mathcal{S}_x \) (\( \mathcal{S}_y \)) after probing with \( \mathcal{X} \) (\( \mathcal{Y} \))-polarised radiation, the authors calculated the asymmetry parameter:

\[
\mathcal{A} = \frac{\mathcal{S}_x - \mathcal{S}_y}{\mathcal{S}_x + \mathcal{S}_y} \propto \cos(2(\phi - \theta)). \tag{18}
\]

From which they could determine the value of \( \phi \) by varying \( \theta \). The authors set the values of \( B \) and \( \theta \) such that the value of \( \mathcal{A} \) varied linearly with \( \phi \). From them they were able to infer the value of \( d_e \). In order to check for systematic offsets in the measurements the authors took data for all combinations of the applied field directions (\( \mathcal{B}, \mathcal{E} \) and molecule orientation (\( \mathcal{N} \)). One of the advantages that ThO has is the ability to vary the sign of the interaction between an electron EDM and the effective electric field either by reversing the external electric field direction, or by reversing the molecular alignment, \( \mathcal{N} \), which allows the detection of systematic errors from any asymmetry in the external field.

From data taken over the course of \( \sim 2 \) weeks the ACME collaboration was able to set an upper limit on the electron EDM of \( d_e < 8.7 \times 10^{-29} \text{ e cm} \). The buffer gas source produced an intense beam of slow and cold molecules with forward speed around 200 m/s \(^1\). This slow beam allowed an interaction time of 1.1 ms. The \( H \ 3\Delta J = (J = 1) \) state is metastable, with lifetime around 1.8 ms \([136]\), and so there is no scope for a significantly enhanced interaction time. For this reason working with even slower molecules would bring no benefits to the coherence of the measurement. The low translational temperature was also of benefit in this experiment. The phase accrued was inversely proportional to the molecular speed (equation (4.1)), and the cold molecular ensembles reduced the phase offset that would result from a spread in velocity.

5. Future developments

Having discussed the main techniques currently used for precision spectroscopy we turn now to new techniques which, although not yet used in a precision spectroscopy experiment, show promise. This section is not an exhaustive review of all ‘direct’ methods of producing cold molecules, and some techniques, such as the production of cold molecules through collisions in a crossed-beam apparatus \([140]\), through photodissociation of a parent molecule \([141–143]\), and through sympathetic cooling with ultra-cold atoms \([144, 145]\) are not discussed. The reader is
directed towards the review articles cited in section 1 for a broader overview of all techniques.

5.1. Travelling wave deceleration

As discussed in section 3.1, Stark decelerators are very inefficient at bringing molecules down to very low speeds. However, a new type of decelerator has been designed which can operate efficiently over a wide range of speeds, even down to 0 m s\(^{-1}\). The travelling wave decelerator uses a sequence of ring electrodes to create a true three-dimensional trap for WF-seeking molecules. First constructed as a chip-based decelerator consisting of a micro-structured array of over 1200 wire electrodes [146], macroscopic decelerators have since been constructed and used to decelerate metastable CO molecules from 288 to 144 m s\(^{-1}\) [147, 148], YbF from 300 to 276 m s\(^{-1}\) [149], NH\(_3\) and ND\(_3\) from 90 m s\(^{-1}\) to rest [150, 151], and SrF from 300 to 234 m s\(^{-1}\) [152, 153].

The operational principle of the travelling wave decelerator is to produce an electric field trap, moving at the same speed as the incoming molecular pulse. The molecules can be confined in the co-moving trap, and by slowing the trap down they can be decelerated, as long as the deceleration is small enough that they can remain inside the trap during the deceleration. Slow too quickly and the molecules will be lost from the trap. However, the accelerations achievable can be great (\(\sim 10^4\) m s\(^{-2}\)) while maintaining a reasonable acceptance. As with the phase-stable Stark decelerator there is a magnetic equivalent, which uses the Zeeman shift of molecular energy levels to create a travelling trap with variable speed. Travelling wave Zeeman decelerators have been constructed in the Laboratoire Aimé Cotton (used so far for guiding metastable Ar) [154], and at Weizmann Institute of Science [155], where metastable Ne was decelerated from 430 to 54 m s\(^{-1}\) [156].

Figure 15 is a representation of an experiment at the VU University Amsterdam which uses the combination of a Stark decelerator and a travelling wave decelerator to slow molecules from a pulsed supersonic source. A section of the travelling wave decelerator is shown in detail, with the ring electrodes held at the potentials indicated. The black contours show lines of constant electric field strength, in steps of 2.5 kV cm\(^{-1}\). (Reprinted from [68]. Copyright 2014, with permission from Elsevier.)
diameter 4 mm and nearest neighbour spacing of 1.5 mm. Each electrode is attached to one of 8 metal rods, running the length of the decelerator, with the electrodes arranged such that every ninth electrode is connected to the same rod. In this way the potentials applied to the support rods create a periodic array of traps. This structure is displayed in figure 16, which shows a photograph of one end of the travelling wave decelerator used at the VU University Amsterdam.

Typically only one trap is used in this deceleration process, which is easily loaded with the short pulses created in a supersonic beam. The longer pulses from cryogenic sources (section 4) are typically more problematic for deceleration as only a small portion of a long packet can be loaded into a decelerator. However, a scheme has been proposed in which a long pulse from a buffer gas source can be loaded into successive potential wells in a travelling wave decelerator [157].

In the Amsterdam experiment a combination of a 100-stage Stark decelerator and a 336-electrode travelling-wave decelerator is used as a source of slow ammonia molecules for a planned fountain [150]. A supersonic beam of NH$_3$ (and, alternatively, ND$_3$) in Xe carrier gas is produced by a pulsed valve. The valve is cooled to $-30$ °C which produces a beam with mean forward speed of $4 \times 300$ m s$^{-1}$. The Stark decelerator, operated at $\pm$10 kV, is used to slow molecules to 90 m s$^{-1}$, about as far as it can decelerate before incurring losses from excessive over-focusing (section 3.1). The slowed ensemble is then loaded into the travelling wave decelerator, operated with a maximum electrode potential of 5 ± 5 kV. Potentials are applied to the electrodes in a sinusoidally varying pattern, generated by the amplified output of an arbitrary waveform generator, giving great versatility to the spatial and temporal variation in the electric field pattern. The travelling wave decelerator has been used to slow molecules all the way to rest, trapping the molecules for up to 50 ms (limited only by the 10 Hz repetition rate of the experiment) before accelerating them upwards into a detection region. In the experiments reported in [150] the molecules were accelerated back to 90 m s$^{-1}$ to give a well-defined packet of molecules for detection. However, the molecules can be accelerated to $\sim 3$ m s$^{-1}$, producing a fountain with a height of $\sim 0.5$ m and giving a total interrogation time for a Ramsey-type experiment of $\sim 0.5$ s, far greater than anything previously achieved with molecules. The difficulty is that the molecules must have a very narrow transverse velocity distribution in order that an appreciable number of them fall straight down again, and must have a narrow longitudinal speed distribution in order for all the molecules to experience the same interaction time. An advantage that the travelling wave decelerator has over a conventional Stark decelerator is the available control over the electric fields. By reducing the trapping potentials slowly (compared with the typical period of oscillation inside the trap) the molecular sample can be ‘adiabatically cooled’. In this process the molecular packet expands in space, while its speed distribution is reduced. This

4 Cooling the valve further would produce a slower beam, but at the cost of signal as the cooled ammonia and xenon form clusters, reducing the flux of free molecules in the beam.

is a conservative process, no energy is dissipated and thus the phase space density is unchanged. For this reason some might be uncomfortable labelling this process ‘cooling’. However, the desired effect, a reduction in the speed distribution, can be achieved, albeit at the expense of a large molecular beam. Quintero-Pérez et al [150] have performed adiabatic cooling of trapped NH$_3$ and ND$_3$. The authors measured uncooled translational temperatures of 100 mK and 14 mK for ND$_3$ and NH$_3$ respectively, reducing to 25 mK and 5 mK after slowly (over 10 ms) reducing the trapping potentials from an amplitude of 5 kV to 1 kV. In more recent work, after optimisation of the source, decelerator and detection, molecules were found to remain in the trap after adiabatic cooling in which the trapping depth had been reduced to as low as 200 μK [68]. Molecules are lost in this process as the more energetic molecules will escape as the trapping potential is reduced.

There are two planned experiments currently under construction that will use travelling-wave decelerated molecules to test fundamental physics: a fountain of ammonia molecules to make a measurement of the time-variation of the proton-to-electron mass ratio, $\mu$ [158]; and a combination of decelerated and laser cooled SrF molecules for a measurement of parity violation in a molecular system [153]. The former experiment will be discussed in more detail in section 5.3, describing the potential for spectroscopy with adiabatically cooled, decelerated molecules.

5.2. Trapped molecules

Trapped molecules provide the opportunity for spectroscopic interrogation over very long interaction times. Not long after the first Stark decelerator was built at the University of Nijmegen, the same group built the first molecule trap in 2000 [70]. The authors used a 64-stage Stark decelerator to slow ammonia molecules in the WF-seeking upper inversion level of the ground electronic state, before transferring them to an electrostatic quadrupole trap, achieving densities of $10^6$ cm$^{-3}$. Improvements to the trapping set-up led to an order of magnitude increase in the trapped molecules’ density [71]. After a proposal for trapping ground state molecules [159], the same group then built an ac electric field trap for confining molecules in SF-seeking states [160, 161]. Such traps use a rotating saddle-shaped electric field to achieve a net confining force. van Veldhoven et al used this ac trap to confine $^{15}$ND$_3$ molecules in the SF-seeking ground state in a trap depth of 1 mK. Further developments in the design and implementation of electric trapping of Stark decelerated molecules have followed (e.g. [162, 163]), with recent work focusing on optimising the loading efficiency into the trap [164]. Work has also focused on loading of traps with velocity-selected molecules from a source, without the need for a decelerator (which can allow continuous loading) [165]. Magnetic traps have also been designed; in 2007 a group at JILA reported the magnetic trapping of Stark decelerated OH radicals with a temperature of 30 mK [166], and in 2011 a group at the Fritz-Haber Institute in Berlin reported the accumulation of Stark decelerated NH radicals in a magnetic
In addition magnetic trapping of Zeeman-decelerated species has been achieved. In 2008 a group at ETH Zürich magnetically trapped decelerated H atoms [168]. A supersonic beam of H atoms, seeded in Kr was slowed from 520 to 100 m s\(^{-1}\) in a 12-stage Zeeman decelerator, before being confined in a magnetic quadrupole trap, with an energy distribution corresponding to \(\sim 100\) mK. In 2009 the same group used a 24-stage Zeeman decelerator to slow a supersonic beam of D atoms, and then loaded them into a magnetic quadrupole trap with a similar energy distribution to the H experiment. In addition, a group at Harvard has loaded CaH molecules straight from a buffer gas source into a magnetic trap [169], and has used an optical pumping scheme to accumulate CaF molecules in a magnetic trap [170]. Recently a group at the University of British Columbia has decelerated a supersonic beam of O\(_2\) molecules from 320 to 42 m s\(^{-1}\) using an 80-stage Zeeman decelerator, and then confined the molecules in a magnetic trap [171] for up to 600 \(\mu\)s. The trapping time was limited by the duration for which the trap coils (carrying 600 A) could be operated before over-heating. The authors propose using permanent magnets to produce the confining potential, allowing far longer trapping times.

The recent development of the travelling wave decelerator has improved trap loading efficiency as the molecules can be trapped within the decelerator without loss [68, 150].

While there has been much work on producing molecule traps, to date no precision spectroscopy has been performed in experiments that use them. The reason for this is the trapping fields. In order to produce a confining force an inhomogeneous electric or magnetic field must be created, inducing a spatially dependent Stark or Zeeman shift in the molecular levels. These energy level shifts are very large and would dwarf the spectral linewidths desired in precision spectroscopy. Such an experiment would only succeed if the spectroscopic interrogation involved driving a transition between two states that experience very similar Stark (or Zeeman) shifts. Tarbutt et al considered the possibility of using trapped YbF molecules to measure the electron EDM [172]. The authors considered an experiment in which YbF molecules were held in a trap for 1 s, considerably longer than the interrogation time used in the most recent measurements of the electron EDM with molecules (YbF [56], ThO [4]). Numerical simulations found that as the molecules travel around the trap, exploring the spatially inhomogeneous electric field, each molecule acquires a geometric phase peculiar to its trajectory. This phase causes spin-decoherence of the molecular ensemble on the time-scale of only a few ms. This decoherence limits the interrogation time in the trap to a few ms, such a trap, in which a strong inhomogeneous electric field confines molecules around the edges of the trap, whereas in the volume of the trap away from the edges a homogeneous field can be applied [173]. The trap is formed between two parallel glass plates, each bearing a microstructured array of linear electrodes, with 400 \(\mu\)m separation between adjacent electrodes (figure 17). The electrodes on each plate are alternately polarised, to potential \(\pm V_0\), which creates a strong electric field close to the glass substrate. This field acts as a repulsive barrier for molecules in WF-seeking states, confining such molecules between the plates. An electrode arranged around the trap, and held at high voltage creates a Stark with no applied fields. The colder the molecules the longer this interaction, until such a duration that the gravitational free-fall of the molecules limits the experiment. Such an experiment has been performed with trapped ND\(_3\) molecules, as part of a developing fountain experiment, and is discussed in more detail in section 5.3.

An alternative solution to the problem of inhomogeneous fields is to use a box-like trap. A group at the Max Planck Institute for Quantum Optics (MPQ) in Garching has built such a trap, in which a strong inhomogeneous electric field confines molecules around the edges of the trap, whereas in the volume of the trap away from the edges a homogeneous field can be applied [173]. The trap is formed between two parallel glass plates, each bearing a microstructured array of linear electrodes, with 400 \(\mu\)m separation between adjacent electrodes (figure 17). The electrodes on each plate are alternately polarised, to potential \(\pm V_0\), which creates a strong electric field close to the glass substrate. This field acts as a repulsive barrier for molecules in WF-seeking states, confining such molecules between the plates. An electrode arranged around the trap, and held at high voltage creates a Stark
potential that confines the molecules transversely between the plates. The resulting box-like trap, with dimensions 4 cm × 2 cm × 3 mm is continuously filled by a bent quadrupole guide, entering on one edge of the trap, and can be emptied through a second quadrupole guide which leads to a QMS, used for time-resolved detection of the emitted molecules (figure 17(a)). In this economical and versatile design two of the electrodes from the bent quadrupole form the trap’s edge electrode, and then go on to form two of the electrodes of the exit guide. In this scheme it is possible to raise and lower the potential barriers at the entrance and exit apertures, while providing strong transverse confinement. The authors have operated this trap with potentials that give confining electric field strengths of up to 60 kV cm⁻¹. By applying an offset potential ±V_offset to the microstructured electrodes of the upper and lower plates a uniform electric field can be applied across the trapping volume.

The trap was continuously loaded by a bent quadrupole guide joined to an effusive source of CH₃F from a N₂-cooled chamber held at 105 K [174] (velocity selection using bent guides is discussed in section 5.6.1). To fill the trap the entrance was held open, allowing state- and velocity-selected CH₃F molecules to accumulate in the trap, up to a typical density of 10⁸ cm⁻³. After a given holding time the exit aperture was opened and the QMS measured the time-resolved signal of escaping molecules. The lifetime inside the trap was inferred by measuring the emitted molecular flux as a function of holding time. For this measurement the trap and entrance guide were operated at reduced potential while loading, reducing the speed distribution of the accumulated ensemble. Operated with an initial field of 30 kV cm⁻¹, the trapped population was found to decrease exponentially with holding time, with a decay constant of 9.4 s⁻¹. Operating with a reduced initial field strength of 20 kV cm⁻¹, an ensemble with a smaller velocity distribution was accumulated, and the decay constant was measured to be 12.2 s⁻¹, with molecular signal still detected after a holding time of 1 min, considerably greater than has been measured with previous electric field traps. From the increased trapping lifetime experienced by slower molecules the authors concluded that non-adiabatic spin-flip transitions constituted the dominant loss mechanism, in which molecules moving quickly through a region of weak electric field can be driven to other Stark states, including those with reduced Stark shifts or to SF-seeking states. Such transitions have previously been found to provide a loss channel in electrostatic traps [175] and Stark decelerators [176].

Figure 17(a) shows that the microstructured array on each electrode plate consists of two separate sections, allowing the trap to be operated with two independently addressable regions. The authors used this versatility to adiabatically cool the trapped molecules. After loading the trap the microstructured electrodes in region 1 (figure 17(a)) were polarised to produce a large uniform electric field, creating a steep Stark potential step, confining molecules in region 2 (the molecules located inside region 1 when this step was introduced were lost from the trap). With the trap volume halved, but the molecular density unchanged, the potential step was then reduced over a time, τ ramp. When the ramp is slow enough that the molecules can make several trips through the trapping volume during τ ramp the changing potential is adiabatic, and as the molecular ensemble expands to occupy region 1 as well its speed distribution is reduced, maintaining a constant phase space density. Although the adiabatic cooling occurs only along the long axis of the trap, reflections off the trapping potentials mix the velocity components, resulting in adiabatic cooling in three-dimensions. After cooling, the exit aperture was opened and the molecular ensemble’s temperature was inferred from the time-resolved QMS signal. The authors found that the threshold time for adiabaticity was 100 ms, and that with the longest ramp time used, 1 s, the translational temperature was measured to have reduced to 121 mK, down from around 184 mK achieved with a non-adiabatic ramp time of 5 ms.

This trap has been demonstrated to confine molecules for up to 1 min, with an electrode structure that allows adiabatic cooling. Importantly a uniform electric field can be applied across the trapping volume, circumventing the large Stark broadening that plagued previous electrostatic traps. Spectroscopic features of the trapped molecules will be affected by a uniform Stark interaction which, although producing differing shifts in different molecular states, will be much easier to interpret than the Stark-broadened features produced by an inhomogeneous electric field. The temperatures reached in the experiment discussed here are low, but not low enough for the trap to be used as a precursor to a field-free measurement such as in a fountain. However, the versatile design can serve as the basis for further cooling. The authors have performed such an experiment, using a Sisyphus-type scheme to cool molecules further, as will be discussed in section 5.5.
5.3. Molecular fountain

The atomic fountain is a powerful tool for high precision atomic spectroscopy [177, 178], providing the frequency for atomic clocks (such as the NIST-F2 clock, which uses a caesium fountain). The long interaction time afforded by throwing a cloud of atoms up and waiting for them to fall down allows the measurement of spectroscopic features with narrow linewidths. It seems like an obvious extension to the field of molecular spectroscopy to perform measurements on molecular fountains. However, key to the success of an atomic fountain is the ability to cool the atomic motion in three-dimensions: to throw up a slow cloud of atoms, cold enough that an appreciable number of atoms fall back down the fountain beam-line. In atomic fountains the cooling methodology employed is laser cooling. This is a technique that has only recently been applied to molecules (discussed in more detail in section 5.4) and is applicable to only a limited number of molecules.

A molecular fountain is under construction at the VU University Amsterdam, which will use Stark decelerated, adiabatically cooled molecules. The purpose of this fountain is not to be a frequency standard, but to make a high precision measurement of the inversion splitting in ammonia molecules. The transition between the two inversion states is very sensitive to \( V \), and measurements performed on the timescale of a year could constrain the value of a possible time-variation of \( V \). In this experiment molecules can be decelerated to rest, and launched up with a speed appropriate for a reasonable fountain experiment (\( \sim 3 \, \text{m/s} \)). While this experiment has not yet observed molecules falling back under gravity, a related experiment has been performed with trapped molecules that were released from the trap, left in a field-free region for \( \sim 10 \, \text{ms} \), and then recaptured.

In this endeavour Quintero-Pérez et al. [68] performed experiments on ND\(_3\) molecules trapped inside a travelling wave decelerator in which the molecular ensemble was adiabatically cooled, released from the trapping potentials, allowed to evolve in free-space and then recaptured after a variable delay. The molecules were slowed to rest inside the decelerator with sinusoidally varying voltages with amplitude 5 kV. Once confined at rest the trapping potentials were adiabatically (over 10 ms) ramped down to a reduced amplitude, \( V_0 \) (figure 18). After this the trapping potentials were suddenly switched off for some variable time, \( \Delta t_{\text{exp}} \) during which the molecular ensemble expanded in free space. After \( \Delta t_{\text{exp}} \) the trapping potentials were suddenly applied again, and the trapping potentials adiabatically increased to their original value, recompressing the recaptured molecules. Figure 18 shows the number of recaptured molecules as a function of \( \Delta t_{\text{exp}} \) for four values of \( V_0 \). In the case of \( V_0 = 5 \, \text{kV} \) (black points), which corresponds to no adiabatic cooling, the signal measured with \( \Delta t_{\text{exp}} = 0 \) was observed to be large, but reduced quickly as \( \Delta t_{\text{exp}} \) was increased. As the value of \( V_0 \) was reduced the signal for small \( \Delta t_{\text{exp}} \) decreased, as molecules were lost from the reduced depth trap. However, the molecular ensemble that remained had a narrower speed distribution, and so a greater proportion of the molecules remained for longer \( \Delta t_{\text{exp}} \). This adiabatic cooling allowed molecules to be detected at times greater than \( \Delta t_{\text{exp}} = 10 \, \text{ms} \), potentially allowing a long interaction time for a spectroscopic measurement in zero applied field. An important question is: does the increased interaction time come at the expense of too great a reduction in the number of molecules? In this experiment the geometry of the detection apparatus was such that the number of molecules detected after recapturing varied as \( 1/\Delta t_{\text{exp}} \) (see figure 18). In this case a spectroscopic linewidth measurement taken with the trapping fields off would thus have an associated uncertainty which scales as \( 1/\sqrt{\Delta t_{\text{exp}}} \). The increased interaction time resulting from cooling is therefore of benefit to precision spectroscopy. The authors suggest a proof-of-principle high resolution spectroscopy experiment, measuring transitions in the \( \nu_1 + \nu_3 \) band of NH\(_3\).

Cooling is crucial for a molecular fountain. The experiment described above used adiabatic cooling, a methodology which conserves phase-space density. Dissipative cooling techniques, such as laser cooling, have the advantage of compressing the phase-space density, generating intense sources of cold molecules. In the next section we discuss recent advances in direct laser cooling of molecules, and describe a proposed experiment to create a molecular fountain from a sub-mK source of YbF radicals.

5.4. Direct laser cooling of molecules

Laser cooling is a powerful technique that has been applied to many atomic species with great success, revolutionizing the world of atomic physics. In laser cooling an atom scatters many (\( \sim 10^3 \)) photons, and the concomitant momentum transfer can be used to slow the atom. In general this scheme seems inapplicable to molecules (as well as many atomic species) as it is typically not possible to find a closed system of energy levels that will allow the scattering of such a large number of photons without requiring a prohibitive number of lasers. Molecules pose a fundamental problem as no truly closed cycling scheme based on electronic transitions can be found. During an electronic transition in a molecule the rotational and vibrational motion can change, as well as the electronic structure. The change of rotational state is determined by an angular momentum selection rule, allowing the possibility of a cooling cycle that is closed rotationally. The change in vibrational state, however, is not constrained by a selection rule. When an electronic transition is driven the molecule can be transferred to any vibrational state of the final electronic state. The likelihood of the transfer from one vibrational state to another is determined by the overlap integral of the two vibrational wavefunctions. The square of this integral, the Franck–Condon factor, governs the strength of the transition. Consider a cooling transition that makes use of an electronic transition in the \( \nu = 0 \) manifold. When the excited state decays it can decay to states in all other vibrational manifolds. The vibrational energy level spacing is typically great enough that additional lasers emitting different wavelength radiation are required to drive the molecules back into the \( \nu = 0 \) cooling cycle. For many molecules this
vibrational leak is so great that many lasers would be required for effective laser cooling. An additional problem this presents is that the large number of levels involved in the cooling scheme slows the cooling rate.

Despite these difficulties a number of molecules have been identified as good candidates for laser cooling [179]. These molecules meet the criteria of having a strong electronic transition for cooling, a closed rotational system and favourable Franck–Condon factors, allowing many photons to be scattered before the molecule transfers to a different vibrational state. One of these molecules, SrF, was the first to be laser cooled [180]. In this experiment Shuman et al laser cooled the transverse motion of SrF molecules emitted from a buffer gas source. The cooling transition was the $X^2\Sigma^+(N = 1) \rightarrow A^2\Pi_1/2(J = 1/2)$ electronic transition (663 nm). The $X (N = 1)$ state, which is well described by Hund’s case (b), is split by a number of interactions. The strongest is the spin-rotation interaction, between the electron spin (quantum number $S = 1/2$) and the rotational motion ($N = 1$), resulting in states with respective angular momentum quantum numbers $J = 1/2$, $3/2$. These states are then further split by the hyperfine interaction between $J$ and the nuclear spin of the fluorine atom (quantum number $I = 1/2$), resulting in four hyperfine states with total angular momentum quantum numbers, $F = 2, 1, 0, 1$, shifted from the unperturbed energy by 63 MHz, 22 MHz, $−52$ MHz, and $−107$ MHz respectively. The hyperfine splitting in the $A^2\Pi_1/2$ state is much smaller and was unresolved in this work. Driving transitions from this hyperfine manifold to the excited state hyperfine levels with $F' = 0, 1$ resulted in a closed rotational cycle: a molecule excited to either of the $A^2\Pi_1/2$ ($F = 0, 1$) states is restricted by parity and angular momentum to decay only to the $X^2\Sigma^+(N = 1)$ state. To scatter many photons all of the ground state hyperfine levels must be addressed simultaneously by laser radiation. In order to achieve this Shuman et al. generated frequency sidebands on the cooling radiation with an electro-optic modulator (EOM) driven at 42.5 MHz, such that the first and second order sidebands addressed the four hyperfine levels [181]. As one of the lower state hyperfine levels has greater total angular momentum ($F = 2$) than the upper states ($F' = 0, 1$) there are dark states. A molecule will be quickly pumped into one of these dark states, after scattering only a handful of photons. This problem was solved by destabilising the dark states with a weak magnetic field ($\sim 0.5$ mT) [182] oriented at 45° to the polarisation vector of the cooling radiation. The Franck–Condon factor of the $X \rightarrow A$ ($0 \rightarrow 0$) transition, $f_{00} = 0.98$ is great enough that a molecule will scatter an average of $\sim 50$ photons before decaying into another vibrational state. Adding repump lasers (carrying the same sidebands as the main cooling radiation) to drive out of the vibrationally excited ground electronic states transfers molecules back into the cooling cycle and vastly increases the number of photons that can be scattered. Earlier work investigating the enhancement in scattering as vibrational repump lasers are added concluded that adding repump lasers to empty the $v = 1$ and $v = 2$ states should allow more than $10^9$ photons to be scattered before decaying into a higher $v \geq 3$ vibrational state [181], great enough for significant cooling and slowing of a molecular beam. In [180] Shuman et al intersected the molecular beam orthogonally with a cooling laser beam (0-0), and (1-0) and (2-1) vibrational repumps. Using mirrors to traverse the laser beams $\sim 75$ times over a length of 15 cm the authors were able to observe either transverse heating or cooling of the SrF beam, depending on the laser detuning from resonance, via either a Doppler or Sisyphus interaction. The geometry of the source resulted in a molecular beam with transverse translational temperature of 50 mK. Comparing the experimental data with numerical simulations yielded upper limits of this temperature after cooling of 15 mK (Doppler) and 5 mK (Sisyphus).

The same group at Yale University went on to slow the forward motion of the molecular beam with the same cooling radiation and vibrational repumps [183]. In this case the cooling beams counter-propagated with the molecular beam for longitudinal slowing. The molecules were detected by LIF in a scheme which used a counter-propagating probe beam in order to use the longitudinal Doppler shift to measure directly the forward speed of the molecular pulses. In the laser cooling of atomic beams two methods are commonly used to keep the atoms in resonance with the cooling radiation as they slow down: chirping the laser frequency [184] and Zeeman-shifting the cooling transition [185]. In this case the complicated hyperfine structure of the $X (N = 1)$ state precludes Zeeman slowing, and the large molecular pulse duration (10 ms) would render chirping inefficient. Instead Barry et al. increased the modulation depth of the EOMs to produce a large number of frequency sidebands, allowing the cooling radiation to address a wide range of speeds. The cryogenic source produced SrF pulses with a speed distribution centred at $\sim 130$ m s$^{-1}$ and a full width at half maximum of $\sim 80$ m s$^{-1}$. The large extent of the frequency sidebands allowed a large proportion of the molecules to be addressed, although it precluded significant longitudinal cooling. The authors used the quantity $\Delta_{HM}$, the shift of the half-maximum position on the low speed side of the speed distribution, as the figure of merit for quantifying the amount of slowing. With the laser detuning set such that the 0th order sideband was resonant with molecules travelling at $175$ m s$^{-1}$ the authors measured $\Delta_{HM} \approx 45 – 60$ m s$^{-1}$. Comparison with numerical simulations showed that the recorded signal from the slowed molecules was reduced, as a result of transverse heating of the molecular beam by spontaneous emission during the cooling phase. Such heating would result in an increased beam divergence, consequently fewer of the slowed molecules passed through the detection region. The Yale group has since made the significant advance of creating a three-dimensional magneto-optical trap (MOT) of SrF molecules (discussed below) [186].

Two other molecular species have also been laser cooled. A group at JILA has built a two-dimensional MOT, resulting in transverse cooling and compression of a beam of YO molecules [187], and a group at Imperial College London has longitudinal slowed and cooled a supersonic beam of CaF [188]. In the latter experiment Zhelyazkova et al slowed and cooled the longitudinal motion of a supersonic beam of CaF
radicals with a cooling beam \( (X^{2\Sigma^+} \rightarrow A^{2\Pi_{1/2}}(0\rightarrow0)) \) and one vibrational repump \((1\rightarrow0)\). Comparing experimental results with numerical simulations indicated that, after applying counter-propagating laser beams for 1.8 ms, molecules were slowed from 600 to 583 m s\(^{-1}\), with the forward translational temperature reduced from 3 K to 85 mK. The slowing was limited by the molecules slowing out of resonance with the cooling radiation (as well as pumping into the \( X \) \((\nu \geq 2)\) states). In order to keep the cooling radiation resonant with the electronic transitions for longer, and move the slowed molecules to lower speeds, the laser frequencies were chirped linearly as the molecules slowed. The authors present data in which the cooling frequencies were chirped at a variety of rates, up to a maximum of 30 MHz ms\(^{-1}\). The slowed peak in the recorded ToF profiles was observed to shift to later times, consistent with increased slowing (and allowing more cooling). Comparison with numerical simulations suggests slowing to 564 m s\(^{-1}\) and cooling to 3 mK, a reduction of three orders of magnitude on the initial forward temperature. However, the signal from cooled molecules was smaller than expected, possibly a result of source fluctuations between measurements of the population in the \( X \) \((\nu = 0, 1, 2)\) states.

In the YO experiment a combination of transverse laser beams and a magnetic field was used to create one- and two-dimensional magneto-optical trapping (figure 19). The cooling transition was used the \( X^{2\Sigma^+} \rightarrow A^{2\Pi_{1/2}} \) electronic transition (614 nm). With two vibrational repump beams the loss to higher vibrational states becomes small enough for significant laser cooling (in fact an intermediate electronic state, \( A^{'2}\Delta_{5/2} \)) limits the number of photons that a molecule could scatter before going dark). The same interactions as above produce four \( X^{2\Sigma^+} \) hyperfine states, which were addressed by frequency sidebands inscribed on the laser frequencies by acousto-optic modulation. The \( X^{2\Sigma^+} \) dark states were destabilised by driving the transitions with circularly polarised light, the handedness of which was switched with a Pockels cell at the rate of optical pumping (2 MHz). The molecular beam was made by laser ablation of a \( \text{Y}_2\text{O}_3 \) pellet in a cryogenic cell operated with a He buffer gas. The beam was produced with a forward speed of 120 m s\(^{-1}\), longitudinal temperature 3.3 K and transverse temperature (defined by a collimating aperture) of \(~25\) mK. The transverse beams were retro-reflected many times through the molecular beam, giving an interaction time of 275 \( \mu \)s. This set-up was used to achieve two-dimensional Doppler cooling of the YO beam. With the application of a magnetic field (whose direction was switched in synchrony with the switching laser polarisation) transverse magneto-optical trapping was achieved, cooling the transverse motion and enhancing the number of molecules in the centre of the beam. Transverse temperatures as low as 2 mK were observed, and with long enough interaction time (and additional dark state repumping) the authors state that cooling down to the Doppler temperature of 116 \( \mu \)K could be achieved [187].

Recently a three-dimensional molecular MOT has been made at Yale University, storing ensembles of around 500 SrF molecules with a temperature of 13 mK, and a MOT lifetime of 136 ms [186, 189]. The trapping forces depend very strongly on the combination of laser polarisations used, and strong restoring forces and efficient cooling can be achieved by a combination of fast switching of the laser polarisation and magnetic field direction [190], as performed with the transverse magneto-optical trapping of YO [187]. Most recently a three-dimensional rf MOT of SrF molecules was demonstrated [191]. In this MOT the handedness of the circular laser polarisation and the direction of the magnetic field were switched synchronously at a rate of \(~1\) MHz in order to destabilise dark states. Norrgard et al produced samples of around 2000 confined molecules, with temperature as low as 400 \( \mu \)K (roughly 3 times the Doppler limit), and a trap lifetime of 0.5 s [191]. Very recently two groups have reported laser slowing and cooling of CaF molecules to speeds low enough to load a CaF MOT. A collaboration of groups from Harvard, MIT and JILA performed laser slowing with laser radiation broaden over a wide range of frequencies [192]. CaF molecules produced in a two-stage buffer gas cell were slowed to around 10 m s\(^{-1}\). A group at Imperial College London used frequency-chirped radiation to slow and cool CaF molecules from a single-stage buffer gas source [193]. The molecules were slowed from 178 to 15 m s\(^{-1}\), and the longitudinal velocity spread was compressed by a factor of 10.

Performing high-precision spectroscopy inside a MOT would be challenging as the magnetic field necessarily Zeeman-shifts the molecular energy levels, and the rapid scattering of photons would compromise a coherent interrogation. However, a MOT could act as a useful precursor to a high-precision experiment, for example acting as a cold source for a molecular fountain.

Laser cooling presents exciting prospects for precision spectroscopy, both as a stand-alone technique and in combination with other cooling and slowing methods. One of the limitations of Stark- and Zeeman-decelerated beams is that the molecules are slowed, but not cooled. The decelerated molecules are slow enough for long interaction times, but the emitted pulses expand too quickly, severely limiting the number of molecules that can successfully traverse a spectroscopic interrogation region. Combining Stark or Zeeman
deceleration with laser cooling can solve this problem. Wall et al [79] simulated the effects of laser cooling CaF molecules in a supersonic beam prior to Stark decelerating them in a travelling wave decelerator identical to that described in [147, 194]. Two cases were considered: no laser cooling, with the start of the decelerator located close to the skimmer at \( z = 103 \) mm relative to the valve nozzle; and with the decelerator moved downstream, beginning at \( z = 253 \) mm, allowing a 150 mm length for laser cooling. Figure 20 shows the results of simulations for the phase space distributions of the molecular beam immediately prior to deceleration in the two cases. These simulations show that three-dimensional cooling can increase the number of molecules loaded into the decelerator by a factor of 6, and increase the phase space density of the decelerated molecules by a factor of 2000. Cooling after deceleration will increase this further. The combination of efficient kinetic energy removal offered by the Stark decelerator and laser cooling can be used as a source of slow, cold molecules for precision spectroscopy. An experiment is currently under construction at the University of Groningen that will use a combination of Stark deceleration and laser cooling to perform precise spectroscopy on SrF molecules [152, 153].

We discuss now a proposed experiment, currently under construction at Imperial College London, to make an improved measurement of the electron EDM with a fountain of laser cooled YbF molecules [195]. The same group has previously made a measurement of the electron EDM with a supersonic beam of YbF [56, 133], with forward speed of 600 m s\(^{-1}\) and a ground state flux of \( 10^9 \) molecules/shot/sr [43]. The new proposal includes a number of improvements on the molecular source which should significantly increase the experiment’s sensitivity.

A molecular fountain for high-precision spectroscopy requires ultra-cold molecules. Consider a fountain with reasonable dimensions for a laboratory experiment, in which molecules are launched upwards with an initial speed of 2.5 m s\(^{-1}\) and reach a turning point after rising 30 cm. The total flight time of this arrangement, 0.5 s would be far greater than has been previously achieved with molecules in free space. In order for precise spectroscopy to be performed with such a scheme a reasonable proportion of the launched molecules must fall back down the beam-line without diverging out of the experimental region. Spectroscopic analysis has revealed that YbF molecules are good candidates for laser cooling, with a strong electronic transition (\( \chi^{2 \Sigma^+} \rightarrow A^{2 \Pi_{1/2}} (0-0) \)) for cooling, with a short excited state lifetime \( (28 \pm 2 \) \( \mu \)s\) with no intermediate electronic states [196]. With Franck–Condon factors measured to be \( f_{00} = 0.928, f_{01} = 0.069 \) and \( f_{02} = 3 \times 10^{-3} \) a laser cooling scheme that employs a 0–0 cooling transition and 1–0 and 2–1 vibrational repumps presents an almost closed cycling scheme with a leak to \( v \geq 3 \) of \( \sim 10^{-4} \). The proposed experiment uses a number of preparation techniques already discussed in this paper (see figure 21). The source will be a...
cryogenic cell, operated at 3.6 K, with a He buffer gas. The cell will produce a bright pulsed beam of YbF radicals by laser ablation of pressed Yb/AlF₃ target, with a forward speed in the range 100–200 m s⁻¹. After leaving this cell the molecules pass through to a second cell which contains a reduced He density and flow rate. Cooling in this second cell can produce molecular pulses with very low forward speeds [116]. The slow YbF pulse will then be guided away from the source by a 20 cm-long magnetic guide, operated with a potential deep enough to transport molecules with transverse speeds as great as 5.9 m s⁻¹. The guide bends, transporting the molecules out of the He flow and into a cooling region. The cooling will be accomplished with an optical molasses, three orthogonal sets of counter-propagating pairs of laser radiation consisting of the cooling radiation and vibrational repumps. As in the cases discussed above the cooling proceeds using the \( \text{X}^2\Sigma^+ (v = 0, N = 1) \rightarrow A^2\Pi_{1/2} (v' = 0, J = 1/2) \) electronic transition. The ground state hyperfine structure requires frequency sidebands to be inscribed onto all the laser radiation, whereas the excited state hyperfine interval is sufficiently small as to be unresolved. The authors estimate that \( \sim 10^{10} \) molecules/shot will be emitted in the \( \text{X}^2\Sigma^+ \) state from the two-stage source.

Numerical simulations performed with laser intensities that the authors consider achievable reveal that the molasses will be able to capture molecules travelling into it with speeds in the range 2–10 m s⁻¹. Neglecting losses into X states with \( v \geq 3 \) the simulations show that the molasses can cool the molecules down to 185 \( \mu \)K after 7 ms from leaving the guide. However, the loss rate to \( \text{X} \) (\( v = 3 \)) is great enough that a molecule will likely be lost to this state after only 2 ms. This loss can be countered with laser radiation driving the \( \text{X} \rightarrow \text{A} \) \( (3 - 1) \) transition. From further simulations that include this radiation the authors conclude that this 3 – 1 repump should have weak intensity, slowing the repumping enough to minimise subsequent loss to \( \text{X} \) (\( v \geq 4 \)). From these simulations the authors conclude that an optical molasses of YbF can be achieved with a temperature of 185 \( \mu \)K, speeds typically less than 30 cm s⁻¹, a spatial distribution with a root mean square width of 8 mm in each direction, and an equilibrium filling time of 100 ms.

The fountain will then be created by detuning the vertical beams by \( \pm v/\lambda \) such that the molecules travel upwards with speed \( v \). The radiation will then be turned off, leaving the molecules to travel along the desired parabolic trajectory. With an upward speed of \( v = 1.5 \) m s⁻¹ the molecules will stop at a height of 11 cm, before falling down, providing a field-free interaction time of 300 ms (a time period two orders of magnitude greater than that used in the previous electron EDM measurement with YbF molecules [56]). The spectroscopy will be performed during the free flight, between two long, parallel electric field plates, which present an aperture of 1 cm \( \times \) 4 cm. Given the source that the molasses presents, 7.5% of the molecules will fall back down the beamline and be detected in the molasses region. Considering the operation of the source and all losses experienced by the molecular pulse, the authors calculate that \( 4.4 \times 10^9 \) molecules will be detected after falling back down the fountain, with the experiment operating with a repetition rate of 2 Hz. After 8 hours’ operation the experiment will achieve a statistical sensitivity of \( 6 \times 10^{-31} \) e cm, far smaller than achieved to date, and small enough to have far-reaching consequences for many theories of particle physics.

![Figure 22](image-url) Proposed opto-electric Sisyphus cooling scheme for molecules in an electric field trap sub-divided into low- and high-field regions. (Reprinted figure with permission from [204]. Copyright 2009 by the American Physical Society.)

5.5. Sisyphus cooling

Although a powerful technique, laser cooling is applicable to only a limited number of molecules. One technique that has potentially greater applicability is Sisyphus cooling. Sisyphus cooling describes a general approach to cooling, rather than a specific scheme. In general, it is a scheme which cools a trapped atomic or molecular ensemble by driving a unidirectional cycle in which the atoms or molecules travel up the potential barrier defining the edge of the trap and, at or near the classical turning point at which the particle has reduced kinetic energy, it is transferred to a different, weaker trap, or to a weakly bound state in the same trap. In this way the ensemble can be cooled. This scheme is of great use to molecules. Molecules can be relatively easily confined in deep traps, and Sisyphus cooling schemes can be effectively employed with the need for the scattering of few photons, perhaps only one per molecule, extending the scope of this technique to a far wider range of molecules than laser cooling.

A Sisyphus cooling scheme was proposed in 1983 [197], and its application to cooling Na atoms described. This technique was implemented in 2008 at the University of Texas at Austin, in which magnetically trapped \( ^{87}\text{Rb} \) atoms in an ensemble of temperature 90 \( \mu \)K were optically pumped into a state with a smaller Zeeman shift, and transferred to a box-like optical trap of depth 10 \( \mu \)K [198, 199]. A number of schemes have been proposed for extending such single-photon and few-photon Sisyphus schemes to molecules [200, 201]. Single-photon schemes have been implemented, to accumulate Stark-decelerated NH molecules in a magnetic trap [167, 202], and to optically load CaF into a magnetic trap, directly from a buffer gas source [170]. We now describe a cooling technique developed at the MPQ in Garching, in which polyatomic molecules were cooled in a box-like electric field trap [203]. The basic principle of the scheme is described in [204], and summarised in figure 22. The cooling scheme was designed to operate in an electric field trap that is
sub-divided into two regions in which two different homogeneous electric fields can be applied, such as the micro-structured box-like trap described in section 5.2 [173]. There are three molecular states relevant to this cooling scheme: two \( W \)-seeking lower states, one which experiences a strong Stark shift (\( w \)) and the other a weak shift (\( w' \)); and an upper, excited state (\( e \)). The molecules were confined inside a trap consisting of two sections: in one a weak homogeneous electric field was applied, in the other there was a strong electric field, creating a potential barrier between the two for the \( W \)-seeking molecules. Consider a molecule in the \( s \) state, inside the low-field region and travelling towards the high-field region. This molecule travels up the potential barrier, losing kinetic energy, and enters the high-field region. Now slowed, the molecule is pumped to the \( w' \) state by applied radiation resonant with the energy interval between the \( w' \) and \( e \) states in the high-field region. When the molecule diffuses into the low-field region it gains kinetic energy as it traverses the potential barrier, but much less than it previously lost as the potential barrier is much shallower in the \( w' \) state. Molecules in the \( w' \) state inside the low-field region are excited to the \( e \) state, from which they can decay to either the \( w' \) or \( s \) state. This last step makes the cooling cycle unidirectional: a molecule in the \( s \) state can make a complete cycle as depicted in figure 22, but as there is no route from \( s \) to \( w' \) or \( e \) inside the low-field region, the reverse cycle is not possible. It is the excitation and subsequent spontaneous emission that is key to this opto-electric cooling scheme, with the role of the photon to remove entropy rather than for momentum exchange. The energy loss results from the difference in Stark shifts between the \( w' \) and \( s \) states, which can result in significant energy loss after only a few cycles. The cooling continues until the molecule no longer has enough energy to traverse the potential barrier while in the \( s \) state. This molecule will possess kinetic energy at least as great as the difference in Stark shifts between \( w' \) and \( s \) in the high-field region. This kinetic energy can be removed by slowly reducing the electric field in the high-field region. The number of photons required for significant cooling is considerably smaller than the number required for Doppler cooling, extending the scope of this methodology to a wider range of molecules, with less demanding requirements on the Franck–Condon factors.

Zeppenfeld et al have demonstrated Sisyphus cooling of \( \text{CH}_3\text{F} \) molecules [203]. This is a symmetric top molecule, a class of molecule that was previously found to provide good candidates for opto-electric Sisyphus cooling [204]. The rotational states of these molecules typically experience strong first order Stark shifts, and are described by angular momentum quantum numbers that allow a closed system to be found with relatively few levels involved. The rotational states of a symmetric top molecule can be characterised by the following quantum numbers: \( J \), the total angular momentum, \( K \), the projection of the total angular momentum on the molecule’s principal symmetry axis, and \( M \), the projection on the \( z \)-axis, fixed in the laboratory frame [205]. Allowed transitions are determined by the selection rules, \( \Delta J = 0, \pm 1 \), \( \Delta K = 0 \), \( \Delta M = 0, \pm 1 \). Figure 23 shows the states involved in the cooling cycle. We label the states by \( |v; J, K, M \rangle \). Infra-red (IR) radiation drives the \( |0; 3, -3, 2 \rangle \rightarrow |1; 3, -3, 3 \rangle \) transition, from which a molecule can decay to any of the \( 4 \ v = 0 \) states shown in figure 23. The \( |0; 4, -3, 4 \rangle \) and \( |0; 3, -3, 3 \rangle \) states are strongly Stark-shifted \( |s \rangle \) states, whereas the \( |0; 4, -3, 3 \rangle \) and \( |0; 3, -3, 2 \rangle \) states are weakly shifted \( |w \rangle \) states. Spontaneous decay from the \( |1; 3, -3, 3 \rangle \) state defines the unidirectionality of the cycle. In order to keep the molecules in the cooling cycle the frequency of the RF radiation was slowly ramped down, step-wise, remaining at each chosen frequency for 4 s.
The authors demonstrated cooling by running the experiment with four different sequences: (i) operating the trap with no cooling radiation; (ii) operating with the IR and MW radiation, which had the effect of accumulating molecules into the strongly bound $|s\rangle$ states; (iii) applying the IR and MW radiation, as well as RF radiation with frequencies 1600 and 3400 MHz which were stepped down to 1220 MHz, allowing limited Sisyphus cooling (the two frequencies were used to drive transitions in the $|0; 3, -3, M\rangle$ and $|0; 4, -3, M\rangle$ manifolds); (iv) identical to case (iii), but with the RF radiation reduced step-wise to 390 MHz, allowing cooled molecules to remain in the cooling cycle for longer as they lose energy. In order to measure the amount of cooling the authors turned the trapping fields off and guided the molecules to a QMS for detection. Time-resolved detection allowed the molecular speed distribution to be measured. Figure 24 shows CH$_3$F speed distributions inferred from QMS data, showing a reduction in translational temperature from 390 mK without cooling to 29 mK with all cooling radiation and the RF frequency stepped down. As well as significant cooling, the phase space density was found to have increased by a factor of 29, which the authors state could have been as high as 70 without trap losses.

Most recently, the same group has modified the experiment to cool H$_2$CO molecules, resulting in cooled samples with translational temperature as low as 420 $\mu$K [206].

The experiments presented in [203, 206] are exciting proof-of-principle demonstrations, showing significant cooling. As discussed in section 5.2 the trap used for cooling is also potentially amenable to precision spectroscopic experiments. Alternatively the cooled molecules could be transferred to another trap, perhaps in an accumulation scheme to increase the phase space density further. However, the cooling scheme is slow and susceptible to trap losses. These drawbacks could be addressed with a different trap, or with the use of excitation to an excited state, $|e\rangle$, with a shorter lifetime. The cooling scheme presented in [203] progressed over a period of 20 s. The use of an electronic transition could speed this up considerably, and this scheme might find application with molecules for which a quasi-closed cooling cycle can be found, but which is not closed enough for laser cooling.

5.6. Other sources

In addition to the techniques discussed above there are other methodologies that can produce cold, slow molecules, which can be used as sources of molecules for high-precision measurements. We discuss now some of these methodologies, some mature techniques, others only recently demonstrated.

5.6.1. Velocity selection. In a thermal source of molecules, even one at room temperature, there will exist molecules with very low speed. Velocity selection of only these molecules can be a comparatively simple method of producing slow molecules. As the thermal source is cooled, there will more molecules in the low speed tail of the Maxwell–Boltzmann distribution, increasing the flux achievable by velocity selection. Velocity selection can be achieved by loading the molecules into a bent guide. The guide confines the molecules transversely with a potential barrier (Stark or Zeeman). When the molecules encounter the bend, those with enough forward kinetic energy to overcome the potential barrier are lost, whereas the slow molecules are guided around the bend. The upper limit on the forward speed that can be selected can be set by varying the magnitude of the potential barrier, or the radius of curvature of the bend.

In 2003 velocity selection of slow molecules was demonstrated by a group at the MPQ in Garching, using an electric quadrupole guide with a 90° bend (13.5 mm radius of curvature) [207]. In this work Rangwala et al produced slow, continuous fluxes of H$_2$CO and ND$_3$, respectively, both emitted from a room temperature emissive source. By applying $\pm 5$ kV to the guide slow molecules were guided around the bend and detected downstream by a QMS. In the case of H$_2$CO a slow distribution was detected with peak speed around 50 m s$^{-1}$, and with flux on the order of 10$^9$ mol s$^{-1}$. Since then other groups have applied this methodology to produce sources of slow ND$_3$ [208, 209], and the technique has been applied to a range of other molecules originating in emissive sources, including H$_2$O, D$_2$O, HDO [210], NH$_3$, CH$_3$I, C$_6$H$_5$CN, and C$_6$H$_5$Cl [209]. The technique has been extended to use with a cryogenic source, which has the benefit of producing much greater rovibrational state selectivity than a warm emissive source [211–213]. Junglen et al applied time-varying fields to the electrodes of a double-bent guide, allowing simultaneous velocity-selective confinement of both WF- and SF-seeking ND$_3$ molecules [214].

Guiding of slow molecules has also been achieved using a bent magnetic guide [215]. In this experiment a slow flux of WF-seeking O$_2$ molecules from a cryogenic source was transported in a bent magnetic octopole guide (composed of
permanent magnets), with a magnetic field depth of 0.5 T and a bend with radius of curvature 20 cm. Guided molecules were produced with maximal observed flux of $3 \times 10^{12}$ s$^{-1}$, with good state selectivity and high loading efficiency. In this case the cryogenic source could be operated to produce a translationally and rotationally cold source of O$_2$. The purpose of the guide was to transport the molecules away from the high pressure region close to the source, out of the helium flow, and towards a detection region, rather than velocity selection. However, the depth of the guide was smaller than the temperature emitted from the source, so some velocity selection was realized, as well as state selection.

Recently velocity selection of cold NO molecules has been achieved with a straight electric hexapole guide [216]. In this case velocity selection was achieved by placing an obstacle (a 3 mm diameter brass sphere) inside the hexapole, on the beam-line. Only slow molecules which travelled around the obstacle, reflecting off the transverse confining potentials of the guide, could be transmitted by the hexapole.

Velocity selection makes use of slow molecules that already exist in a source. As a passive technique it has the advantage that it can operate continuously (with a continuous source), potentially offering a great advantage over pulsed deceleration techniques (such as Stark or Zeeman deceleration, or chirped laser cooling). Cooling the initial thermal source will increase the flux of slow molecules that can be transported by the guide. This technique might be of limited use if the molecules are then used in a pulsed system (e.g. for further slowing with a Stark or Zeeman decelerator), but can be very useful in continuous applications, such as the accumulation of molecules in a trap.

It should be noted that, unlike Stark and Zeeman deceleration, these techniques are not in general highly state-selective (although they can be used with state-selected sources). Typically, any molecule in a WF-seeking state with a sufficiently great Stark shift to be longitudinally confined by the potential barrier will be guided around the bend. Electric and magnetic field guides can, however, be used for state selection [217], and so in principle state- and velocity-selection can be achieved with bent guides.

### 5.6.2. Mechanical methods

Mechanical methods have also been applied to the preparation of slow, cold molecular beams. One example is the use of a rotating nozzle, that can produce beams moving at speeds close to rest. In 1999 a group at Harvard demonstrated the use of a rotating nozzle to produce beams of Xe, O$_2$ and CH$_3$F [218]. In this technique a continuous supersonic beam is produced by expanding a high pressure gas through a small nozzle located on the end of a rotor. By spinning this rotor at a given rate the forward speed of the supersonic beam in the laboratory frame can be varied. The experiments performed to date have employed a continuous, rotating source, likened in [218] to a ‘lawn sprinkler’. A static skimmer, leading to a second, differentially pumped chamber defines the beam-line, resulting in a pulsed beam in the second chamber whenever the nozzle points towards the skimmer. By moving the molecular source in the opposite direction to that of the molecules along the beam-line the molecular speed can be reduced.

As well as reducing the speed, this technique can also reduce the beam’s translational temperature. Operating the source with an input pressure, $P_0$, and temperature, $T_0$, spinning with peripheral speed, $v_{\text{rot}}$, the centrifugal acceleration increases the peripheral pressure around the nozzle to

$$P_{\text{noz}} = P_0 \exp (m_{\text{mol}} v_{\text{rot}}^2/(2k_B T_0)) \quad (19)$$

This increased pressure reduces the terminal temperature of the supersonic beam (see equation (7)). Gupta and Herschbach calculated that their set-up should have been capable of
producing beams with translational temperatures down to 300 mK [218].

The Harvard group used a hollow, tapered rotor arm, weighing only 29 g, and with a laser-drilled pinhole nozzle. Rotation rates of up to 42 000 rpm were observed, corresponding to a peripheral speed of \( v_{\text{rot}} = 436 \text{ m s}^{-1} \). Slow beams of Xe, O\(_2\) and CH\(_3\)F (the last two seeded in Xe) were recorded, producing ensembles with most probable speeds measured down to 67 m s\(^{-1}\), 125 m s\(^{-1}\), and 150 m s\(^{-1}\), respectively. The recorded translational temperatures of the slow Xe-carried CH\(_3\)F and O\(_2\) beams were higher than predicted (~10 K). The authors suggest that the beam temperatures and intensities achieved could have been detrimentally affected by the pumping capacity of the source chamber.

Gupta and Herschbach described this technique in more detail in [42], reporting the production of slow beams of pure Ne, Ar, Kr, and SF\(_6\), in addition to the species and mixtures described in [218].

The operation of a continuously emitting counter-rotating nozzle was further investigated and developed in 2010 by a group at the University of Freiburg, who performed a careful experimental and theoretical analysis of the beams that can be produced in this manner [219]. Figure 25 shows a schematic diagram of the apparatus used by Strebel et al. Gas was injected into a hollow carbon fibre rotor. A small (0.1 mm) aperture in one end of the rotor served as the nozzle. By spinning the rotor at a rate of up to \( \sim 350 \) Hz (in either sense) the Freiburg group calibrated their set-up with beams of Ar and Kr, generating beams with speeds in the range from \(~200\) to \(~800\) m s\(^{-1}\). In the experiments reported in [219] the rotation rate was limited to around 350 Hz, constrained by mechanical vibrations and the long-term degradation of the ferrofluidic sealings on the rotary feedthrough. However, in principle the source can be operated at a rotation rate of up to 800 Hz, allowing the creation of beams with a much greater range of speeds. A full characterisation revealed this technique to be a very versatile source of cold beams, producing molecular ensembles travelling at low speeds with densities similar to other methods, such as filtering.

A disadvantage of this scheme is the high pressure generated in the source chamber by the continuous spray emanating from the nozzle. This requires careful differential pumping to allow the production of slow beams in a high vacuum environment. However, this high nozzle chamber pressure leads to an effusive source, with the skimmer as the orifice. Measurements with beams of Ar and Kr slowed to \(~60\) and \(~40\) m s\(^{-1}\), respectively, found that at these low speeds the beam and effusive sources were generated with similar densities. The authors propose to circumvent this problem by using a chopper timed to allow the pulsed beam to pass, but to (mostly) block the continuous effusive source.

Having characterised the source, Strebel et al used it to create beams of CHF\(_3\) and ND\(_3\) with variable speed. Using a 259 mm long electric quadrupole guide the authors were able to increase the detected beam intensities at low speed, reporting beams of CHF\(_3\) (seeded in Kr) with central speed of 165 m s\(^{-1}\). The same group has also used a 34 cm long charged wire (gold-plated BeCu) to guide SF-seekers away from the counter-rotating nozzle, producing a source of ND\(_3\) molecules in SF-seeking states with variable speed, in the range from 150 to \(\sim 350\) m s\(^{-1}\) [220].

The Freiburg group has used the counter-rotating nozzle as a source of velocity-tunable atoms (Ar, Kr, Xe) and molecules (SF\(_6\)) in scattering experiments with a MOT of Li atoms [221].

One of the limitations of the sources described above is the continuous operation of the source, despite only a small fraction of the emitted molecules (i.e. those that pass through the skimmer) being of use. The continuous flow from the nozzle increases the pressure in the source chamber to such an extent that, even with significant pumping capacity the mean free path of the slowed molecules is reduced to only a few cm [222]. To avoid these problems, a group at Texas A&M University has operated a counter-rotating nozzle with a pulsed gas inlet, reducing the gas load in the source chamber, and used a shutter downstream of the skimmer in order to produce a well-defined molecular pulse in the second, differentially pumped chamber [223].

Despite the daunting mechanical apparatus the rotating nozzle has been found to be a potentially useful source of velocity-tunable beams. These sources are very versatile; they can be applied in the production of slow beams of molecules whose structure make them poor candidates for other slowing methods (e.g. unsuitable internal structure for laser cooling, or with electric/magnetic dipole moments too low for efficient Stark/Zeeman manipulation).

Another mechanical technique has been developed by researchers at the University of Texas at Austin and Tel-Aviv University, in which a supersonic beam is slowed by reflection off a moving ‘paddle’ [224]. Reflection of He and H\(_2\) beams travelling with an incident speed of around 900 m s\(^{-1}\) has been observed off a single-crystal Si(111) surface with \(~3\)% reflection probability [225]. This probability increases with reduced impact speed. Narevicius et al calculated that the reflectivity of a He beam incident normally on a hydrogen-passivated Si(111) surface with an impact speed of 550 m s\(^{-1}\) can be greater than 25%. Reducing the incident speed by moving the crystal relative to the beam will further increase the probability [224]. By moving the crystal the reflected beam speed can also be reduced. Reflection of a beam with incident speed, \(v_i\) off a massive, static crystal produces a reflected beam with final speed, \(v_f = v_i\). By moving the crystal along the beam direction with speed, \(v_c\), reduces the magnitude of the reflected beam speed to \(v_f = -v_i + 2v_c\).

Figure 26(a) shows the experimental set-up used to slow He atoms. A 9 mm diameter Si(111) crystal, with hydrogen-terminated surface, was mounted on either end of a 50.4 cm radius titanium rotor, which could be spun at a rate of up to 10 000 rpm. A supersonic beam of He (seeded in a Ne carrier gas with ratio 48(He):52(Ne), and cooled to 77 K) was produced with a 10 \(\mu\)s duration, mean forward speed of 511 \(\pm\) 9 m s\(^{-1}\), and translational temperature 249 \(\pm\) 36 mK. Detection was performed in one of two QMs, one located downstream of the rotor, for direct detection of the beam, and the other...
upstream of the rotor, allowing detection of the reflected beam. With the rotor stationary, at an angle of 5\(^\circ\) away from orthogonal to the beam-line, the reflected beam was measured to have translational temperature 254 ± 41 mK, confirming that the reflection resulted in no significant heating. Operating at a maximum rotation rate of 42 Hz the paddle could reduce the speed of the incident beam by up to 246 m s\(^{-1}\). Figure 26(b) shows the reflected beam speed as a function of crystal speed, with the He speed reduced to as low as 265 m s\(^{-1}\). The slowed beams were recorded with reduced intensity, which the authors explain by the ‘fanning’ action of the rotating mirror. The crystal is moving while the atomic pulses are incident on its surface, increasing the divergence of the reflected beam. This fanning effect was reduced by the use of short pulses and a long rotor arm. Narevicius et al propose using a curved crystal surface that will focus the reflected beam, reducing the fanning effect, and increasing the intensity of the slowed beam in the detection region, or inside a trap. The authors propose extending this methodology to the production of slow beams of light molecules (H\(_2\), D\(_2\), and CH\(_4\)) which can be loaded into an optical dipole trap where high-precision spectroscopy can be performed.

A recent advance in ‘mechanical’ techniques is the rotating spiral guide constructed at the MPQ in Garching [226]. Chervenkov et al have used this to create a centrifuge decelerator, able to operate continuously as a source of slow molecules with speeds around 15 m s\(^{-1}\). The operational principle is to launch fast molecules into the periphery of a spiral-shaped quadrupole guide, rotating with angular velocity, \(\Omega_0\). The guide spirals in toward the axis of rotation. The quadrupole guides the molecules from the periphery to the centre of the spiral, causing the molecules to climb a centrifugal potential hill, at the expense of their kinetic energy. The authors used an effusive source and a bent quadrupole guide to produce a continuous, velocity-selected source of WF-seeking CH\(_3\)F, CF\(_3\)H and CF\(_3\)CCH molecules, respectively, as discussed in section 5.6.1 [174]. The molecules were launched into the centrifuge through a straight quadrupole guide, and then into an annular peripheral guide, with static outer electrodes and rotating inner electrode which form part of the spinning spiral guide. The rotating spiral was spun in the same sense as the molecules travelled through the periphery. At some point around the periphery the molecules would catch up with the spiral guide access point. After joining the spiral centrifuge the molecules were guided towards the axis of rotation, being decelerated as they did so. At the centre of the centrifuge the electrodes were bent orthogonally out of the plane of rotation, guiding the slow molecules towards the detection by a QMS.

Chervenkov et al performed a detailed analysis of the centrifuge, operating with a range of confining electric field strengths up to 90 kV cm\(^{-1}\), and a range of rotation frequencies up to 50 Hz. For a given quadrupole confining potential it was found that there was an optimum rotation frequency. For low frequencies the centrifugal potential hill was small, and little deceleration could be achieved. For too high frequencies the molecules would not have enough kinetic energy to reach the centre, and would be reflected back out of the centrifuge. The output of slow CF\(_3\)H molecules from the centrifuge was measured as a function of time for a range of rotation frequencies. For low frequencies the output flux was chopped, a result of the electrode structure, which created regions in the periphery with no guiding potential. Measurement at a high rotation frequency (30 Hz) found that this effect was washed out, with the flux continuous and only slightly modulated by this effect. The reason for this continuous flux was that the greater centrifuge frequency increased the time the molecules spent in the spiral guide, and reduced the time spent in the periphery.

This study with three molecular species found the centrifuge to be a robust, versatile source of slow molecules, travelling at less than 15 m s\(^{-1}\). Used here with a continuous, effusive source, the authors predict that the output flux can be enhanced with the use of a supersonic or buffer gas source.
5.6.3. Rydberg–Stark deceleration. As discussed in section 3.1, Stark deceleration can require decelerators of length \( \sim 1 \) m, comprising \( \sim 100 \) deceleration stages, and is efficient for molecules with large body-fixed electric dipole moments, typically on the order of 1 D. Atoms and molecules in Rydberg states can possess considerably larger electric dipole moments, in excess of 1000 D, permitting efficient manipulation with electric fields in devices far more compact than Stark decelerators, and requiring much lower applied potentials [227]. Following the earlier development of the Rydberg–Stark manipulation of \( \text{H}_2 \) [228–230], a group at ETH Zürich decelerated and trapped \( \text{H} \) atoms [231, 232], and in 2009 applied this methodology to \( \text{H}_2 \), slowing the molecules and confining them in a three-dimensional trap [233, 234].

Core-penetrating low angular momentum Rydberg states pose two difficulties for Stark manipulation: (i) at the point where Stark states from adjacent \( n \)-manifolds approach each other closely (the ‘Inglis–Teller’ limit) they repel each other, resulting in avoided crossings. At these avoided crossings molecules in WF-seeking states can convert to SF-seeking states, and vice versa, which limits the field strength useful for Stark manipulation to below the Inglis–Teller limit; (ii) the lifetimes of these low angular momentum states are typically limited not by radiative decay, but by predissociation of the molecule [235, 236]. The first problem limits the strength of electric field that can be used in Rydberg–Stark manipulation, an effect that becomes increasingly limiting for higher Rydberg states, as the electric field at which the Inglis–Teller limit is reached scales as \( n^{-3} \) [235]. The second problem limits the useful time for deceleration and trapping, as the lifetime against predissociation can be considerably shorter than the radiative lifetime of high-\( n \) Rydberg states. To avoid these issues, Hogan \textit{et al} used a multi-photon excitation scheme which produced Rydberg molecules in which the optically active electron had great enough angular momentum for its wavefunction to have little overlap with that of the molecular core. The photoexcitation scheme used circularly polarised laser radiation (at 106, 550, and 830–840 nm) in the presence of an applied electric field to prepare Rydberg \( \text{H}_2 \) molecules in Stark states with \( m_J = m_L = 3 \), where \( J \) is the total angular momentum and \( \ell \) the orbital angular momentum of the optically active electron. The prepared Rydberg Stark states had little core-penetration, having no \( \ell = 0, 1, 2 \) character. The hydrogenic nature of these states allowed the molecules to cross diabatically at (and beyond) the Inglis–Teller limit, and to have increased lifetimes limited by radiative decay rather than dissociation. The experimental set-up is shown in figure 27. A supersonic beam of \( \text{H}_2 \) was generated by expanding \( \text{H}_2 \) seeded in Kr (pressure ratio of 2:8, respectively) into a vacuum chamber through a pulsed valve. Downstream of a skimmer the molecules passed into the electrode assembly shown in figure 27. Holes drilled through electrodes 1 and 2 allowed the photoexcitation laser beams to intersect the molecular beam, propagating parallel to an applied field. During photoexcitation electrodes 1 and 2 were charged to \( \pm V_{\text{trap}} \), electrodes 3 and 4 to \( \mp V_{\text{trap}} \), and electrodes 5 and 6 were grounded, creating a three-dimensional trap for WF-seeking molecules, and generating a homogeneous electric field for preparation of Rydberg Stark states. After photoexcitation, deceleration was achieved by rapidly pulsing a high potential \( (\pm V_{\text{decc}}) \) to electrodes 3 and 4, generating a Stark potential hill for WF-seekers to climb. To allow maximal deceleration, while avoiding the risk of field ionisation the deceleration potentials decayed exponentially, with time constant 3.65 \( \mu \)s. In this way molecules could be decelerated with a single pulse, and then left confined in the trapping potential.

By varying the infra-red wavelength (830–840 nm) Hogan \textit{et al} were able to prepare molecules in Rydberg states in the range from \( n = 21 \) to \( n = 35 \) in the series leading to the \( N^+ = 0 \) rotational state of the molecular ion, and decelerate and trap molecules in WF-seeking Stark states for each of these Rydberg states. The photoexcitation scheme also prepared molecules in the \( N^+ = 2 \) series, with principal quantum numbers from \( n = 16 \) to \( n = 20 \), but these states were too short-lived for detection after trapping. The trap was measured to have been loaded with initial molecular densities in the range \( 10^5–10^6 \) cm\(^{-3} \), with a temperature of 150 mK, and a trap loading efficiency of 60%.

Rydberg–Stark deceleration is a potentially very useful scheme, allowing efficient deceleration of any molecule for which long-lived Rydberg states can be prepared. The electric field requirements are modest compared with conventional Stark decelerators, and the electrode configuration considerably simpler and more compact. As well as providing a simpler electrode set-up, the shortness of the decelerator reduces transverse losses during deceleration.

The multi-photon excitation schemes can be efficient; in the case of photoexcitation of the \( |m_L| = 3 \) Rydberg states in \( \text{H}_2 \) it is estimated that at least 10% of the molecules that interacted with the laser radiation were successfully excited [237]. Hogan \textit{et al} state that Rydberg molecules can also be efficiently driven back to the ground state using the same laser scheme employed for excitation, offering the prospect of cold
samples of ground state molecules at rest, applicable to a wide range of species [233].

Rydberg–Stark deceleration is potentially applicable to a far greater number of molecular species than Stark deceleration, expanding the scope of high-precision spectroscopy to a much wider range of molecules.

6. Summary

In this tutorial article we have described the main techniques currently used to prepare cold molecules for experimental tests of fundamental physics using precise spectroscopy. There is no one ideal preparation method. A successful technique must provide an intense source of slow, cold, state-selected molecules. Many of the techniques discussed here satisfy some but not all of these criteria. Recent developments, such as laser cooling, offer the tantalizing prospect of achieving a source that meets all of these criteria. However, laser cooling is applicable to only a small range of molecules (although this includes a number of molecules very useful for testing fundamental physics). For other molecules a combination of techniques (such as buffer gas cooling and Stark deceleration or Sisyphus cooling) could offer great promise for preparing molecules for precise spectroscopy.

The experiments discussed here shed light on a range of important aspects of fundamental physics, enhancing our understanding of nature. These small-scale, low energy laboratory experiments with molecules are addressing topics as fundamental as those probed by the very large-scale, high energy experiments run by the particle physics and high energy physics communities. Molecules have been used to test physics with very great precision, placing restrictions on the possible variation of fundamental constants over galactic timescales, and between different density environments. Recent experiments with diatomic molecules have precisely measured the shape of the electron, and as these experiments improve, will soon be in the position of strictly testing theories that go beyond the Standard Model. As techniques develop that allow great control over molecules, so will our ability to use their complex structure to see further, greatly enhancing our understanding of the Universe we inhabit.

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