1. Introduction

Over the last decades, atomic and molecular physics has come into a spectacular bloom, much of which sprang from the newfashioned techniques to translationally cool (or slow down) gaseous atoms and molecules. The study of slow atoms and molecules, which ensued, has led to uncharted territories – not just of atomic\(^1\) and molecular\(^2\) physics, but of physics at large\(^3\).

Apart from enhancing molecular spectroscopy and amplifying the ability to manipulate molecular trajectories, cold and trapped \textit{molecules} have begun to play unique roles in a number of diverse areas of fundamental interest, such as quantum collision dynamics, collective effects, and even particle physics. In this review, we describe some of the excitement that the work on cold molecules has brought about.

2. Basic features of cold atoms and molecules

At room temperature, gaseous atoms and molecules move at the speed of
rifle bullets – and their behavior is in many respects reminiscent of that of bullets. They calm down only at temperatures close to absolute zero (i.e., -273.15°C); for instance, a nitrogen molecule moves at the speed of a healthy ant (a few cm/s) only at the temperature of a microkelvin (µK). As the temperature (speed) is lowered, the behavior of atoms and molecules undergoes a dramatic change: their wave properties begin to prevail over their corpuscular ones – the atoms and molecules become waves. Thus, they acquire a character usually associated with the behavior of light or another electromagnetic radiation; in contrast to light, these matter waves have a nonzero rest mass.

By slowing (cooling), it is possible to extend the time during which the atoms or molecules can be observed, and thus enhance the accuracy of the observation. More than that, one can say that the most accurate measurements to date can be carried out on cold atoms and molecules. Thus the combination of the unusual wave behavior of cold atoms and molecules with the ability to observe it is a most fortunate circumstance which contributes to the boom of cold matter physics.

The matter waves are characterized by a de Broglie wavelength\(^5\)

\[
\Lambda = \frac{h}{mv} \quad \text{or} \quad \frac{h}{(2\pi mkT)^{1/2}}
\]

(1)

with \( h = 6.63 \times 10^{-34} \) J s the Planck constant, \( k = 1.38 \times 10^{-23} \) J K\(^{-1}\) the Boltzmann constant, \( m \) the rest mass, \( v \) the velocity and \( T \) the absolute temperature. The nomogram in Figure 1 shows the dependence of the de Broglie wavelength on temperature and rest mass. One can see that, for instance, a nitrogen molecule (mass 28 g/mol) has at room temperature (300 K) a wavelength of 0.2 Å (i.e., \( 2 \times 10^{-9} \) cm). Since the bond length of an \( N_2 \) molecule is about 1.1 Å, we see that this wavelength is smaller than the size of the molecule. When cooled to 1 K, the wavelength of \( N_2 \) increases to 3.3 Å,
i.e., a value which is of the same order of magnitude as the molecular size (which does not change with temperature). At a temperature of 1 mK, the wavelength of N$_2$ increases to 104 Å, at 1 µK to 3464 Å, i.e. 0.35 µm. That’s a huge change with respect to the room-temperature value; it is given by the factor $3464/0.2 = 17320 = (300/10^6)^{1/2}$, see eq. (1). Hence we see from this example that by cooling (slowing), the molecule-projectile at room temperature is transformed at a microkelvin temperature into a molecule-wave whose wavelength far exceeds the molecular dimensions.

In order to better appreciate what this means, let us clarify the notion of molecular size. This is determined by the magnitude of the outer (valence) shell of a given atom or molecule. But the magnitude of the valence shell is not due to anything else than the de Broglie wavelength of the valence electrons! Despite the fact that the mass of the electron is 1836-times less than the mass of the proton, the de Broglie wavelength of a valence electron is small. This is because the binding energy of the outer electrons (typically on the order of 10 eV) corresponds to temperatures on the order of $10^5$ K, as follows from the virial theorem.$^6$ From the nomogram of Fig. 1, we see immediately that at such high temperatures the wavelength of an electron is on the order of 1 Å, i.e., the valence electrons interact with each other at most at this distance. This distance then defines the “typical dimensions” of an atom or small molecule. But what is the size of an atom or molecule as a whole, i.e., at which distance can atoms or molecules (not their valence electrons) feel each other? The maximum distance is given also by the de Broglie wavelength, but of an entire atom or molecule. Thus we see that cooling (slowing) of atoms or molecules has a wide-ranging effect on their ability to interact with each other. That has, in turn, a most dramatic effect on collisions and the collective behavior of cold atoms and molecules.$^7$ From this springs most of the new physics and chemistry that cold atoms and molecules can offer.
3. Why cold molecules?

During the last decade, a number of research groups, spread all over the world, launched research programs to study cold molecules. Molecules are namely not only more complicated than atoms, but in some respects also more interesting: apart from possessing vibrational and rotational degrees of freedom, molecules may carry dipole (and higher) electric and magnetic moments. These moments lend properties to molecules which atoms simply lack. At the same time, it is exactly these features on which new operational principles can be based (e.g., quantum computing) or that allow to achieve a qualitatively new behavior of matter to be achieved (e.g., Bose-Einstein condensates structured by the electric dipole interaction). However, the trouble is that it is much more difficult to cool molecules than atoms.

A certain class of atoms can be cooled with light. The method of laser cooling is based on a manifold repetition of the absorption and emission of photons by the atom. Both absorption and emission of a photon are accompanied by momentum transfer. Whereas photon absorption can be arranged to take place preferentially along the atom’s motion, photon emission occurs in random directions. Then, on average, each absorption-emission cycle results in a slowing of the atom, i.e., in cooling. Although elegant and efficient, laser cooling is of limited chemical scope: the requirement of a closed absorption-emission cycle is fulfilled by only a handful of atoms, best represented by alkali metals. The complex energy-level structure of most other atoms and of essentially all molecules renders laser cooling inapplicable. What disqualifies molecules is mainly their vibrational structure: the Franck-Condon factors cause a rapid depopulation of the initial vibrational state, and thereby terminate the absorption-emission cycle. The early era of the cold-matter research was thus predominantly an alkali age, like in the case of the early
4. How to trap a molecule

At low temperatures, gases condense into liquids or solids. Their condensation has to be precluded by preventing the gas molecules to come in contact with one another or with the walls of the vessel that contains them. This can be achieved by holding the molecules at low densities in vacuum by means of electric or magnetic fields. The interaction of the molecules with such fields creates an energy barrier that acts as walls. Such a barrier is called a *molecular trap*. A given molecular trap is capable of confining only those molecules whose translational energy is lower than the depth of the trap (i.e., the energy barrier). Therefore, in order to trap molecules, it is necessary to slow (cool) them first. This is indeed the reason why cooling and trapping go usually hand in hand.\(^{13}\)

5. How to cool molecules

The inability to apply laser cooling to molecules was a challenge taken up by a handful of enthusiasts who, in the mid 1990s, sought to widen the range of cold-matter research to include molecules. Necessity proved to be a mother of invention and, over the last decade, a host of techniques had been developed that made it possible to cool molecules. These techniques are based on new principles, independent of laser cooling.

In 1998, the first molecule, the radical CaH, was cooled by a cold buffer gas, and subsequently magnetically trapped.\(^{14,15}\) This was followed by a successful synthesis of homonuclear bialkali molecules via photoassociation of laser-cooled atoms.\(^{16}\) Recently, ultracold molecules were produced in collisions controlled by a Feshbach resonance.\(^{17}\) The last two methods, based on the synthesis of laser-cooled atoms, can be called *indirect*. At present, about...
twenty research groups are exploring and exploiting the indirect methods. Some of these groups are now turning their attention to the synthesis of heteronuclear bialkali molecules. The advantages and drawbacks of the indirect methods are described in section 5.1.

Direct methods are based on cooling of pre-existing molecules. Roughly fifteen research groups worldwide are concerned with the development and applications of buffer-gas cooling, \(^{[15]}\) Stark deceleration, \(^{[18,19]}\) deceleration by pulsed optical fields, \(^{[20,21]}\) deceleration via collisions in crossed molecular beams, \(^{[22,23]}\) supersonic expansion from a counter-rotating nozzle, \(^{[24]}\) or selection of the low-velocity tail of a Maxwell-Boltzmann distribution of molecules in an effusive beam. \(^{[25,26]}\) All direct methods start with relatively hot molecules (200-1000 K), usually in the form of a supersonic molecular beam*. Whereas the indirect methods are only suited for the preparation of bialkali molecules, the direct methods are versatile, applicable to large classes of molecules (e.g., Stark deceleration to all polar molecules; buffer-gas cooling coupled with magnetic trapping to all paramagnetic molecules) or to any molecules (all other direct techniques).

5.1 Synthesis of cold molecules from cold atoms

5.1.1 Photoassociation

The process of photo-associating a pair of atoms into a molecule is shown schematically in Figure 2a: two free atoms on a collision course with one

* A supersonic expansion of a gas into vacuum – whereby a supersonic molecular beam is generated – cools all the degrees of freedom of the gas molecules (typically to 1 K, in the case of a pulsed beam). The initial energy of the gas is thereby efficiently transformed into translational energy along the direction of the beam. In contrast, molecules in an effusive beam have a thermal distribution of states in both internal and translational degrees of freedom.
another are exposed to laser radiation of a suitable wavelength that excites them to a common bound (i.e., molecular) state. Since molecules formed by photoassociation have the translational temperature of the free atoms, it is possible to make in this way cold molecules from cold atoms.

Figure 2b shows the dependence of the potential energy of the atoms on the distance of their nuclei (i.e., a potential energy curve) for the case when the atoms are in their ground or excited electronic states. Also shown are the vibrational levels within the ground and excited molecular states. A collision of a pair of ground-state atoms cannot result in a bound molecular state, since a mechanism is lacking that would relieve the mutually interacting atoms of their energy and allow them to fall into the potential well of the ground molecular state. However, it is possible to create a bound excited state: it suffices to excite the colliding atoms into one of the vibrational states pertaining to the upper potential energy curve, see Fig. 2b. This state has then automatically a lower energy than the well depth of the electronically excited state (note that the translational energy of the cold atoms is negligible compared with the vibrational energy).

However, the formation of the excited bound state is not the end of the story but rather an intermediate step: such a state is namely only metastable and so can spontaneously decay (typically within a microsecond) either back to the original ground-state atoms or to a molecule in a ground electronic but vibrationally highly excited state (the lifetime of a vibrational state is typically 10-100 ms).

That the states in which the molecules are formed are vibrationally excited presents, however, a difficulty: if such molecules collide, their vibrational energy can get quite efficiently converted into their translational energy, whereby the molecules become translationally hot (1000 K or more) – thus defeating the purpose of photoassociating the cold atoms …
During the last couple years or so it became possible to stimulate the transition from an electronically excited state using an additional laser field, and thus to achieve a population transfer from the excited state to the electronic and vibrational ground state, Figure 2c. This technique, which functions on the same principle as ‘coherent population transfer’ (which is the basis of, e.g., electromagnetically induced transparency\textsuperscript{[27]}), is especially well applicable to heteronuclear bialkali molecules; these are coveted since they are polar (i.e., they carry a body-fixed electric dipole moment).

Whereas the potential energy curves of both ground and excited electronic states of a heteronuclear molecule exhibit a $R^{-6}$ dependence at large internuclear separations $R$, in the case of homonuclear dimers it is only the ground state that has an $R^{-6}$ energy dependence. The electronically excited state of homonuclear molecules namely shows a $R^{-3}$ dependence, due to the exchange interaction. Since the photoassociation step occurs at large $R$, the $R^{-3}$ potential (which is shifted toward larger $R$ with respect to the $R^{-6}$ potential) enables a good overlap (i.e., a large Franck-Condon factor) between some of the vibrational states of the electronically excited state and the ground electronic state. In the second, stabilization step, such an overlap favors a transition to either an unbound state of free atoms or to one of the highly vibrationally excited states of the electronic ground state. In the case of heteronuclear molecules, the overlap favors a stimulated transition directly to the ground vibrational and electronic state. As a result, the molecule is cold in all its degrees of freedom, with a translational temperature on the order of 100 µK. This indirect method has so far been demonstrated for the RbCs\textsuperscript{[28]} and KRb\textsuperscript{[29]} molecules.

5.1.2 Feshbach resonances

The synthesis of cold molecules via cold-atom collisions controlled by a
Feshbach resonance is simple in principle but quite demanding in practice. Nevertheless, several groups have, independently, succeeded in creating not just cold molecules but even molecular Bose-Einstein condensates (of K₂ and Li₂) using this technique. As if that weren’t enough, Feshbach resonances found a key role to play in the study of the cross-over between a Bose-Einstein condensate of molecules and an ensemble of correlated Cooper pairs of the atoms that constitute these molecules. This is a theme that touches upon few- and many-body physics, with repercussions for nuclear physics, superfluidity, and superconductivity, including its high-temperature variant.

An example of a Feshbach resonance is shown in Figure 3. This occurs if the energy of two colliding atoms (in a given electronic state) equals the energy of the bound state of a molecule that consists of the same atoms, but is in a different electronic state. If the bound and unbound states have different dipole moments, the relative energy of these two states can be varied by tuning an external field. Because a Feshbach resonance dramatically enhances the magnitude of the interaction of the two atoms (their collision cross section), it is possible to sensitively control the molecule formation by fine-tuning the external field. In the experiments carried out so far, a magnetic field and its effect on the different spin states of the bound and unbound states was used for this purpose.

The molecules formed via a Feshbach resonance are in the highest possible vibrational and rotational states, often just a fraction of a mK below the dissociation limit. Like any excited state, these states too are apt to relax to lower states; however, the available lower states are often unbound so that the relaxation process (induced by mutual collisions) leads to a conversion of the molecules back into atoms. As a result, the “Feshbach molecules” almost immediately vanish. Unless they consist of atoms which are fermions!

Fermions differ from bosons in the way they behave when their positions
are interchanged. Whether a given indistinguishable particle is a boson or a fermion is unequivocally determined by its spin: a half-integral spin defines fermions (e.g., electrons, protons, neutrons) and an integral spin defines bosons (e.g., photons, mesons). The character of a compound particle, such as an atom or a molecule, can be easily determined from the number of fermions it contains: if this number is odd, the compound particle is a fermion; if it is even, the particle is a boson. It follows that an electroneutral atom whose nucleus has an odd number of neutrons is a fermion (e.g., $^3$He), one with an even number of neutrons a boson (e.g., $^4$He). Homonuclear diatomic molecules are all bosons.

Bosons and fermions exhibit a dramatically different collective behavior: whereas bosons like each other’s company, band together, and create high-density ensembles (e.g., photons in a laser cavity), fermions rather avoid each other (this behavior is captured by Pauli’s principle which co-determines electronic configurations of atoms and thereby the chemical properties of the elements). Pauli’s exclusion principle also wields power over the fate of Feshbach molecules.

Depending on whether a Feshbach molecule consists of bosons or fermions, its decay into atoms is either accelerated or inhibited. The inhibition in the case of molecules consisting of fermions can be so dramatic that there is enough time for a thorough experimental look at such molecules. The results of these experiments aptly exemplify what has so far been possible to achieve with cold atoms and molecules.

A magnetic Feshbach resonance, e.g., for $^6$Li$_2$ or $^{40}$K$_2$ molecules, occurs at the cross-over between two different regimes of collective behavior of these systems: on one side of the cross-over there are well-bound molecules that undergo Bose-Einstein condensation (the BEC regime); on the other side of the cross-over there is a superfluid state, similar to the state of Cooper-paired electrons in a superconductor (the Bardeen-Cooper-Schrieffer regime, BCS).
The ability to study in detail the “phase transition” between the BEC and BCS regimes while sensitively controlling all the parameters that determine such a transition means for condensed-matter physics a dream come true. Thus, after many decades of arduous labor aided by the tools of condensed-matter physics thus came unexpectedly a catharsis staged by atomic and molecular physics. We may remind ourselves that about twenty years ago, atomic and molecular physics had been considered a closed chapter of twentieth century physics and few anticipated anything new to come of it.

5.2 Cooling or slowing of pre-existing molecules and their trapping

The swatch of direct methods for cooling or slowing of pre-existing molecules is varigated and attests to the imagination of their inventors. Buffer-gas cooling and Stark deceleration turned out to be the most effective among them. Therefore, in what follows, more space will be dedicated to these techniques than to the rest, which will be described only telegraphically.

5.2.1 Buffer-gas cooling and magnetic trapping of paramagnetic molecules

The technique of buffer-gas cooling was developed by the group of John Doyle at Harvard University in 1994-98. The buffer gas (helium, He) is itself cooled by a cryogenic device, such as a thermostat or a dilution refrigerator. More accurately, the buffer gas mediates a thermal contact between the cooled atoms or molecules and the cryogenic device. Because this technique is independent of the energy levels or other particular attributes of the cooled particles, it is equally well applicable to molecules as it is to atoms.

The thermalization process that leads to the equilibration of the temperatures of the buffer gas and of the molecules loaded into it (more about loading is said below) is a result of elastic collisions between the helium atoms and the cooled molecules. Under typical conditions, about 100 thermalization
collisions are needed.

In order to ensure a sufficiently rapid thermalization of the cooled particles – along a path shorter than the dimensions of the cryogenic cell (i.e., a few cm) – the buffer gas must have a sufficiently high density (the number of helium atoms per volume). Since gas density decreases with decreasing temperature, a certain minimum temperature exists below which the number density would be too low to enable thermalization (roughly $10^{16}$ atoms/cm³). This minimum temperature is 240 mK in the case of $^3$He (which has the highest vapor pressure of all substances at low temperatures). The thermalization process is stable in the sense that the elastic scattering cross section of the thermalized atoms or molecules with helium increases with decreasing temperature.

Both buffer-gas cooling and magnetic trapping require cryogenics and so are well suited to combine with one another. A schematic of the experimental setup is shown in Figure 4. The setup consists of three parts: a superconducting magnet, a cryogenic cell, and a dilution refrigerator (which is not shown).

The magnet consists of two coils with electric current running through them in opposite directions (this is known as the anti-Helmholtz configuration). The coils strongly repel each other and have to be held together by a titanium cask. The whole superconducting magnet is immersed in liquid helium.

A copper cryogenic cell, filled with He buffer gas, is placed in the bore of the magnet. The cryogenic cell is thermally anchored to the mixing chamber of a dilution refrigerator. The temperature of the cryogenic cell can be varied, within a range of 100 - 800 mK, using a resistive heater.

The first molecule that was cooled by thermalization with a cold buffer gas and subsequently magnetically trapped was the calcium monohydride radical (CaH). The radical was prepared in situ by laser ablation (irradiation with an intense laser pulse) of solid (and metal-like) calcium dihydride (CaH₂), see Fig. 4. The CaH ($^3\Sigma$) radical molecules carry a magnetic dipole moment of one
Bohr magneton, due to the spin of the single unpaired electron.

The fate of the molecules in the cryogenic cell can be monitored by laser spectroscopy, for instance by laser-induced fluorescence. The dependence of the fluorescence intensity on the wavelength of the laser beam yields a fluorescence spectrum. The fluorescence spectra can be measured in dependence on time, which begins to run at the moment when the ablation pulse is fired.

Before turning on the magnetic field, the field-free fluorescence spectrum shows that the molecules injected into the buffer gas are cooled not just translationally but also vibrationally and rotationally. The cooling brings them to the respective ground states.

With the magnetic field on, the ground rotational state is split into a pair of Zeeman levels: one whose energy increases and one whose energy decreases with increasing field strength. When subject to an inhomogeneous field (i.e., one that varies over space), molecules in the former state seek regions of minimum field strength \((\text{low-field seekers})\) and molecules in the latter state regions of maximum field strength \((\text{high-field seekers})\). In either case, the molecules seek to minimize their potential energy in the field.

The strength of the static anti-Helmholtz magnetic field increases nearly linearly with distance from the center (where its value is zero) to a certain maximum value at the edge, before it drops again at the exterior of the coils. Such a magnetic field deflects low-field seeking molecules towards the field minimum at the center, and high-field seeking molecules towards the field’s edge. Figure 5 shows a schematic of the anti-Helmholtz magnetic trap. Instead of showing the changing magnitude of the magnetic field, we plotted the energy of the low-field seeking state. It is this energy that represents a “wall” which keeps the molecules confined.

The molecules injected into the cryogenic cell diffuse through the helium
buffer gas and are thus cooled to the buffer-gas temperature. The trapped ensemble of paramagnetic molecules is left to levitate at the center of the cell about the minimum of the anti-Helmholtz field.

The fluorescence spectrum in Figure 6 shows that high-field seeking molecules are pushed out towards the field maximum where they hit the wall of the cryogenic cell, are adsorbed on it, and thus lost. On the other hand, molecules in low-field seeking states are attracted toward the center of the trap. After about 300 ms, the measured translational energy distribution of the molecules corresponds to a Maxwell-Boltzmann distribution at a temperature close to that of the buffer gas. A detailed analysis of the data has shown that about $10^8$ CaH molecules at a temperature of 400 mK were trapped.

The fluorescence spectra of a trapped molecular ensemble contain a wealth of information – not just about the dynamics of the trapping process but also about the trapped molecules themselves, for instance about their electronic structure[32].

Buffer-gas cooling makes it possible to attain a temperature of about 0.5 K, which is not ultracold. However, a great advantage of the method (apart from its versatility) is its ability to cool and trap large numbers of molecules. By evaporating a fraction of the trapped molecules, it is possible to cool the molecular ensemble further down toward the ultracold regime (< 1 mK). Nevertheless, so far the initial numbers of trapped molecules (and other factors) have not made it possible to effectively apply such an evaporative cooling scheme.

The number of the magnetically trapped molecules depends mainly on the technique of loading the molecules into the buffer gas. Laser ablation can hardly “evaporate” more than $10^8$-$10^{12}$ (with a single pulse). Therefore, a considerable effort has recently been put into developing an alternative technique of loading molecules into the cryogenic environment. The new
technique is based on the use of a molecular beam made up of molecules that are to be cooled. The molecular beam is simultaneously used to “transport” the molecules into the cryogenic cell. In order to allow for the beam molecules to enter, the cryogenic cell must be equipped with an orifice. The buffer gas of course escapes from the cell through the orifice, and its atoms collide with the beam molecules that are on their way toward the cell. Fortunately, it turned out to be possible to limit such undesirable collisions by choosing a suitable pressure of the buffer gas inside the cell and use of clever pumping outside of the cell. And so it seems that loading molecules into the cryogenic environment by means of a molecular beam has a bright future ahead of it. Thus far, it was possible to thermalize $10^{14}$ molecules of the NH radical, obtained by dissociating a pulsed beam of NH$_3$ in an electric discharge.$^{[33]}$

5.2.2 Buffer-gas cooled beam

Unlike conventional supersonic expansion, it is possible to “pre-cool” molecules to temperatures well below their boiling point before they are released through an orifice and into the beam. This technique is directly related to the buffer-gas cooling described in section 5.2.1. In essence, molecules are cooled inside a cell held at a temperature of about 1 K by high density helium and come out of an orifice in the cell (into a beam).$^{[34]}$ Thus, molecules come out rotationally cold. If the helium density is high-enough, most of the cold molecules inside the cell will make it into the beam before they get a chance to diffuse to the wall, where they would freeze. In such a case the molecules exit into the beam with a forward velocity equal to that of the cold helium gas. This has been shown to produce very high fluxes of cold molecules, including cold molecular oxygen injected into a magnetic hexapole guide whose output flux was in excess of $10^{10}$ s$^{-1}$.$^{[35]}$ This cryogenic method could be combined with the
5.2.3 Stark deceleration and electric trapping & storage of polar molecules

The technique of Stark deceleration (or acceleration) makes it possible not only to arbitrarily vary the velocity of polar molecules but also to select the molecules’ internal state (electronic, vibrational, and rotational) and orientation\textsuperscript{[36]}. The method thus enables a complete control of molecules … Although the principle of the method has been known for over half a century, a Stark accelerator/decelerator was successfully implemented only in 1999, by the group of Gerard Meijer at Nijmegen (now in Berlin).

The method makes use of a time-dependent inhomogeneous electric field, by means of which the Stark energy of polar molecules is varied. Stark energy represents the potential energy of molecules in an electric field. Its change is compensated for by a change in the kinetic translational energy of the molecules, as dictated by energy conservation. Depending on whether the Stark energy provided is negative or positive, the field causes either an acceleration or a deceleration. In what follows, we’ll limit our description (in keeping with the subject of this article) to the case of deceleration when the molecules’ translational energy is reduced by a positive Stark energy. Figure 7a shows schematically what happens when a low-field seeking molecule passes through an inhomogeneous electric field. The potential energy of the molecule first increases from zero to a maximum value and then drops to zero again. At the same time, the translational energy of the molecule drops and then increases again (the kinetic translational energy is given by the difference between the plotted Stark energy curve and the constant total energy, shown by the horizontal line). Let’s consider now a modified scenario: the molecule enters the field from the left (as before) but, at the moment it reaches the maximum of the potential energy (and thus a minimum kinetic energy), we switch off the
electric field (i.e., we ground the central electrodes). If the field is switched off sufficiently rapidly, i.e., in a time during which the molecule was not able to move, the molecule will not regain the subtracted kinetic energy and will thus be slowed down! Since the lost kinetic energy typically amounts to only about 1 K (kinetic energy divided by Boltzmann’s constant) and the initial translational energy of the molecules is on the order of 100 K, it is necessary to repeat the deceleration step many times. In order to capture this, we should have placed the total energy level in Fig. 7a about a hundred times higher than we actually did.

Figure 7b shows how the repetition of the deceleration steps is implemented in a Stark decelerator. Depicted is a decelerator that, for the sake of simplicity, consists of just four deceleration stages. Depending on which of the deceleration stages are energized and which are grounded, the inhomogeneous electric field generated can be in one of two possible configurations. The upper (red) configuration generates a field whose spatial dependence exhibits maxima at $\lambda/4$, $5\lambda/4$, etc., where $\lambda$ is the spatial period of the field. The electric field generated by the lower (blue) configuration has maxima at $3\lambda/4$, $7\lambda/4$, etc. The electric field can be quickly switched from one configuration to another. The alternation of the field configurations is timed in such a way as to make the molecule “climb up the hill” all the time. Figure 7c shows the time dependence of the electric field: because of the need to synchronize the field with the slowing motion of the molecules, the frequency of switching between the two field configurations must be decreasing. The plotted time dependence also indicates that the transient time during which one field configuration is switched to the other is much shorter than the time $\tau/2$ during which either of the two field configurations is on or off. Therefore, the time dependence is well captured by a temporal square wave.

Figure 8 illustrates the effect of a Stark accelerator/decelerator on a pulse of
CO(a $^3\Pi_1$) molecules: the accelerator/decelerator selects out a fraction of the original velocity distribution and transfers it to higher/lower velocities. The experimental setup is shown in Figure 9. It consists of 108 electrode pairs (field stages); also shown is a view of the electrodes from the perspective of the accelerated/decelerated molecules. Note the alternating orientations of the subsequent field stages; this plays a key role in maintaining transversal focusing of the accelerated/decelerated molecules.\(^{[37]}\)

In order to be able to accelerate/decelerate a pulse of molecules with a distribution of coordinates and velocities (spatial and velocity spread), the acceleration/deceleration process must be carried out under the conditions of *phase stability*. This notion is worthy of a more detailed elucidation, which we’ll undertake with the help of a recently developed analytic model of a Stark accelerator/decelerator.\(^{[38]}\) The model is exact and thus contains all the rich physics that makes a Stark accelerator/decelerator tick. The model is based on the Fourier analysis of the spatial and temporal dependence of the electric field, which reveals that the field consists of infinitely many waves. These waves move in both directions along the axis of the decelerator and are characterized by well defined phase velocities

$$V_{n,\ell} = \frac{n}{\ell} V_0$$  \hspace{1cm} (2)

where $n$ and $\ell$ are positive odd integers. The quantity $V_0 = \lambda/\tau$ represents a “fundamental” phase velocity, given by the ratio of the spatial, $\lambda$, to the temporal, $\tau$, period of the decelerator’s electric field.

The question arises as to which molecules that we send into the decelerator will interact with which waves. Intuition suggests that those molecules whose velocities come close to the velocity of a given wave will interact strongly with that wave. But how close need these velocities be in order for the molecules to interact strongly and thus get a ride from a given wave? The exact answer
follows from the analysis of the problem’s *dynamics*.

If we set up the equation of motion for a molecule interacting with an arbitrary wave, we realize that this equation is *isomorphic* with the equation of motion of a *biased pendulum*. A realization of this kind makes a physicist happy: he/she can take a lesson about a new problem (the Stark decelerator) from an old one, whose solution is *anschaulich* and sometimes even known (the authors of this article have been, nevertheless, unable to find any useful solution of the biased pendulum problem in the literature).

A biased pendulum is shown in Figure 10a. It consists of a normal pendulum (of mass $m$) fixed to an axle. Wound around the axle is a string with a weight attached to it. The weight is called a *bias* (of mass $M$). The potential energy $V$ of a biased pendulum is shown in Figure 10b as a function of position (or, more accurately, phase) $\phi$; it consists of the potential energy of the pendulum, $V_m$, and the potential energy of the bias, $V_M$: $V = V_m + V_M$. The potential energy $V$ of the biased pendulum has a local minimum at a phase $\phi = \phi_s$ and a local maximum at a phase $\phi = \pi - \phi_s$; these extrema correspond to the stable and unstable equilibrium points of the biased pendulum. As can be gleaned from Fig. 10b, the unstable equilibrium point simultaneously represents the outermost turning point of the biased pendulum: if this point were exceeded (i.e., for $\phi > \pi - \phi_s$), the pendulum would be set in a nonuniform accelerated rotational motion driven by the falling bias. However, if this point is not exceeded (i.e., for $\phi < \pi - \phi_s$), the pendulum just periodically swings between the outer and inner turning points about the equilibrium point $\phi_s$ (the inner turning point cannot be exceeded, for energetic reasons, as also illustrated by Fig. 10b).

What is the relationship between a biased pendulum and a Stark decelerator? From the isomorphism of the two problems it follows that the potential energy of the Stark decelerator has the same form as that of the biased
pendulum (they only differ by a constant). Thus the potential energy of the biased pendulum, Fig. 10b, can be identified with a wave that moves from left to right through the decelerator with a phase velocity $V_{n,\ell}$. At the same time, the phase $\phi_s$ corresponds to the phase of the so-called synchronous molecule, i.e., a molecule whose velocity $v_s$ is equal to the phase velocity of the wave: $v_s = V_{n,\ell}$. A synchronous molecule maintains a constant position (more accurately, phase) with respect to a given wave. The synchronous phase takes values between $0^\circ$ and $90^\circ$, which can be also seen immediately from Fig. 10a (the stable and unstable equilibrium points are located symmetrically with respect to a plane perpendicular to the field axis). All other molecules are nonsynchronous, with velocities $v \neq v_s$ and phases $\phi \neq \phi_s$. Only certain nonsynchronous molecules can periodically oscillate about the synchronous molecule, namely those whose phase is less than that corresponding to the outermost turning point, i.e. $\phi < \pi - \phi_s$. Such nonsynchronous molecules will stay in the moving potential well together with the synchronous molecule, which is riding at the well’s bottom, and will thus be decelerated along with it. It is this feature which is captured by the notion of phase stability: without it, only the synchronous molecule would be decelerated, and not a whole class of molecules with a range of positions and velocities.

The value of the synchronous phase determines the slope of the biased-pendulum potential, which, in turn, determines the magnitude of the molecules’ acceleration/deceleration. The greater the value of the synchronous phase, the greater the acceleration/deceleration (the further up the Stark energy hill the molecule is allowed to climb, see Fig. 7a). However, at a larger acceleration/deceleration, the depth of the potential well drops and, simultaneously, the range of the nonsynchronous phase throughout which nonsynchronous molecules can periodically oscillate about the synchronous
molecule narrows down. These features are summarized in the phase-space diagram of Figure 11. In practice, a value of the synchronous phase is chosen which leads to a removal of as much translational energy for as many molecules as possible ($\phi_s \approx 70^\circ$). A Stark decelerator can also be used for a lossless transport of a pulse of molecules: this requires a phase angle $\phi_s = 0^\circ$, which pertains to the largest phase space area, see Fig. 11. We note that the decelerator does “something” to the molecules even at the transportation angle of $\phi_s = 0^\circ$, namely, it rotates the distribution of positions and velocities. This can be used to either narrow the spatial distribution at the expense of an increased width of the velocity distribution, or vice versa. Such a narrowing of the spatial distribution of a molecular pulse, which increases its density, is called bunching.

Figure 12 displays a portrait of a larger phase-space area than in Fig. 11. This phase portrait pertains to the transport of OH molecules and has been obtained with the help of the analytic model mentioned above, encompassing 80 waves. The portrait agrees in detail with both trajectory simulations of the Stark acceleration/deceleration dynamics and with experiment. It shows that by far the largest area of phase stability pertains to the first harmonic wave, with $n = \ell = 1$. Furthermore, we see that there are smaller areas of phase stability centered around odd-fraction multiples of the fundamental velocity, i.e., $\frac{1}{3}V_0$, $\frac{5}{3}V_0$, $\frac{7}{3}V_0$. However, apart from these, there are also small phase-stable areas centered around even-fraction multiples of $V_0$, i.e., $\frac{1}{2}V_0$, $\frac{3}{2}V_0$, $2V_0$. Where do such areas come from? The answer to this question follows from the “wave nature” of the electric field in the Stark decelerator: wherever there are waves, there must also be interferences among the waves! Indeed, the analytic model shows that molecules can also ride a well which is formed by the interference
between two waves with odd \( n, \ell \) a \( r, s \), resulting in a wave whose phase velocity is an even-fraction multiple of the fundamental velocity \( V_0 \).

5.2.3.1 Electrostatic trapping of molecules. Sufficiently slow molecules can be trapped in an electrostatic trap. Figure 13 shows a schematic of a trap suitable for confining polar molecules in low-field seeking states. The trap consists of three electrodes, initially energized as indicated in Fig. 13a. The left field configuration enables the molecules to enter the trap (from the left). The Stark energy, shown in the lower part of the figure, stops the molecules at a point somewhere half the way to the top of the potential hill. There the molecules make an “about-turn” and begin to move to the left. At that instant, the fields are switched to the configuration shown in Fig. 13b, which produces an energy barrier for the leftward motion of the molecules. The molecules thus get stuck between the left and right barriers, i.e., they are trapped, and so become a coveted subject of further experimentation.

5.2.3.2 A storage ring for molecules and a molecular synchrotron. A special case of an electrostatic trap is a storage ring, which provides a transversal but not a longitudinal confinement for low-field seeking molecules. It is most simply implemented by bending a transversal focuser, such as a hexapole, onto itself, see Figure 14. The low-field seekers then have a minimum of potential energy on a circle rather than at a single point. Compared with a trap, a storage ring is capable of confining molecules without the need of bringing them to a standstill first. The circling packets of molecules can repeatedly interact, at well defined times and positions, with electromagnetic fields and/or other atoms or molecules.

An electrostatic storage ring was first demonstrated in 2004 with a beam of ammonia molecules decelerated to a velocity of 92 m/s.\textsuperscript{[39]} The density of
the ammonia molecules inside the 25 cm diameter hexapole ring was probed via a laser-ionization-based technique. In the lower part of Fig. 14, the ion signal is shown as a function of the storage time in the ring. Peaks are observed whenever the packet of molecules passes through the detection zone. One can see that each successive lap adds to the width of the packet. This is due to the finite velocity spread of the molecules. Although this is very small at the beginning, corresponding to about 300 μK at the moment the molecules are loaded into the ring from a Stark decelerator, after about 100 laps the packet is spread out to the extent that it nearly uniformly fills the entire ring.

In order to counteract the spreading of the packet in the ring – and thus to restore the ability to define the timing and position of the stored molecules – a storage ring was constructed consisting of two half-rings separated by a gap.\[40\] This is shown schematically in the top part of Fig. 15. Depending on the switching sequence, the gap can act as a time-varying inhomogeneous electric field (similarly as a stage of a Stark decelerator) that accelerates, decelerates, or just transports or bunches the molecular packet under the conditions of phase stability. The split-ring device thus represents a molecular analog of a synchrotron for charged particles. The lower part of Fig. 15 shows the density of molecules stored in the synchrotron as a function of storage time. One can see that the width of the bunched pulse, after an initial decrease during the first 25 laps or so, reaches a fixed value. Bunching ensures a high density of the stored molecules and, in addition, enables injecting multiple packets – either co-linear or counter-propagating – into the ring independent of the packet(s) already stored.

5.2.3.3 AC trapping of molecules in high-field seeking states. Trapping of molecules in high-field seeking states is of particular interest, chiefly for two reasons: (i) Ground-state-molecules are always high-field seeking, since the
ground state of any system can only be lowered by an external perturbation. As a ground state cannot decay, molecules trapped via their ground state cannot be lost from the trap by relaxation processes, which plague trapping via low-field seeking states in electrostatic or magnetic traps. As a result, ground state molecules are expected to be amenable to evaporative or sympathetic cooling. We note that relaxation losses have been predicted to be particularly severe for polar molecules in excited ro-vibrational states. (ii) Heavier molecules have small rotational constants (and, often, large dipole moments) and so become high-field seeking at relatively small field strengths, thus precluding the application of large-enough forces required to trap or otherwise manipulate them.

In order to trap high-field seekers, one would wish to create a maximum of a static field in free space. Unfortunately, this is prohibited by a consequence of Maxwell’s equations, known as Earnshaw’s theorem. However, it is possible to generate a static field that has the shape of a saddle surface, see Figure 16. Such a field focuses molecules in one direction and defocuses them in the perpendicular one. By reversing the polarity of the electrodes that generate the field (i.e., AC switching), the focusing and defocusing directions can be interchanged. The focusing force causes the molecules to move toward the saddle point at the trap center while the defocusing force pushes the molecules away from it. Since the focusing and defocusing forces are equal to one another, one would think that the time-averaged, net force acting on the molecules would be zero. This, however, is not the case: the AC switching between the two field configurations causes the molecules to undergo an oscillatory micromotion whose frequency tends to get in step with the switching frequency. Since the force acting on the molecules increases with distance from the saddle point, the amplitude and thus the kinetic energy of the micromotion increases with distance as well. Because the
kinetic energy of the micromotion is positive (as kinetic energy always is), it creates in effect a potential energy well, with a minimum at the trap center. The positive kinetic energy of the micromotion is independent of whether the molecules are in a low- or high-field seeking state, which makes an AC trap work for either.

Three electrode geometries have been implemented to date, which create the desired electric trapping field. Fig. 17 shows schematically the electrode geometry of a cylindrical AC trap that has been used to trap both ND₃ molecules and Rb atoms. Panels (b) and (c) show the strength of the electric field along the symmetry axis (z-axis) and along the radial direction (r) when the field is focusing either along the z-axis or radially. The ND₃ molecules were loaded into the AC trap by first Stark-decelerating low-field seeking ND₃ molecules to a standstill and subsequently applying a microwave pulse that pumps a fraction (about 20%) of the molecules into a high-field seeking state. Figure 18 shows the density of the ND₃ molecules at the center of the AC trap as a function of the switching frequency for both the high- and low-field seeking components of the ground state of para-ammonia.

At low switching frequencies, the trajectories of the molecules in an AC trap are unstable and no signal is observed. Above a frequency of about 900 Hz, the trap becomes abruptly stable. A maximum signal is observed at about 1100 Hz. When the frequency is increased further, the molecules have less time to move within a switching period, and the net force acting on the molecules decreases, as does the trap depth.

It is noteworthy that electrostatic traps (see section 5.2.3.1) are about 1 K deep (depending on the molecular species and details of the trap design), and have a volume of typically 1 cm³. An AC electric trap has a depth of about 1-10 mK and a volume of about 10⁻² cm³.
5.2.4 The Zeeman and Rydberg decelerator

A magnetic analog of Stark deceleration, based on the Zeeman effect, has recently been implemented. This has widened the chemical scope of phase-stable manipulation to include paramagnetic but nonpolar species, such as atoms or homonuclear molecules.

The Zeeman deceleration technique, pioneered by the group of Frederic Merkt, at ETH Zurich, has been experimentally demonstrated by slowing down ground-state H and D atoms, using initially six\cite{44,45} and later twelve\cite{46} pulsed magnetic field stages. The deceleration stages consist of copper-wire solenoids (each about a cm long) which generate magnetic fields of up to 1.5 T. The cylindrical coils provide a symmetric transverse restoring force that focuses the decelerated beam onto the longitudinal axis. Achieving the requisite switching times (of about 5 $\mu$s) was a considerable technical challenge. The group of Mark Raizen, at the University of Texas at Austin, has applied Zeeman deceleration to metastable Ne atoms in an eighteen-stage decelerator.\cite{47} Using electromagnetic coils which are encased in magnetic-steel shells with Permendur discs, even higher magnetic field strengths, of 3.6 T, could be achieved. Recently, the deceleration of metastable Ne atoms\cite{48} and oxygen molecules\cite{49} to velocities as low as 50 m/s using sixty four field stages was reported.

Compared to polar molecules, atoms or molecules in Rydberg states offer a much larger electric dipole moment. Hence, these particles can be manipulated using only modest electric field strengths and either a single or just a few field stages, as demonstrated by Merkt’s group and the group of Tim Softley at the University of Oxford. Level crossings in the dense Rydberg manifolds limit the magnitude of the electric field strength that can be applied. The electric field manipulation of atoms and molecules in high Rydberg states has been
pioneered using $\text{H}_2$ molecules\textsuperscript{[50]} and Ar atoms\textsuperscript{[51]}. Using a Rydberg decelerator, H atoms could be stopped and electrostatically trapped in two\textsuperscript{[52]} or three\textsuperscript{[53]} dimensions. The short lifetimes of Rydberg states (in particular of molecules) inherently limit the time that is available to manipulate and study such species. However, fluorescence decay of the Rydberg states may in some cases generate cold samples of ground-state atoms or molecules.

5.2.5 Slowing by nonresonant light fields

In many respects, this technique resembles Stark or Zeeman deceleration. One of the differences is that instead of a static electric field, a nonresonant laser field is used which interacts with the molecules’ polarizability. This interaction induces an electric dipole moment, which then interacts with the electric field of the laser radiation. This interaction can be strong enough (thanks to both the intensity and the gradient of the radiative field) to enable the deceleration of a pulse of molecules in a single sweep (this is another difference). So far, two versions of this type of deceleration were considered, the “scoop”\textsuperscript{[20]} and the “optical lattice.”\textsuperscript{[21]} In the case of a “scoop,” the motion of a laser focus (and thus of the decelerated molecules) is directly controlled by a suitable electro-optic device; in the case of an “optical lattice,” implemented in 2006 by the group of Peter Barker at Edinburgh (now in London), an optical interference wave is created with a tunable phase velocity which traps a pulse of molecules in flight and slows it down, see Figure 19.

The deceleration imparted by a Stark decelerator is of the order of $10^5$ m s$^{-2}$, which suffices to bring thermal molecules to a standstill on a path of $\sim$1 m in about 1–10 ms. The Barker group, however, puts the brakes on for only about 6 ns (over a path of several micrometres), imparting a deceleration of the order of $10^{10}$ m s$^{-2}$. Their technique uses not electric field stages, but the
gradient of an electromagnetic wave. The resulting deceleration is due to a force of the order of a femtonewton. Can the molecules withstand such a force without falling apart in a process that we could dub “breaking by braking”? They actually can, as a femtonewton force would only dissociate a species bound by a sub-Kelvin deep well. The large deceleration force is due to the induced-dipole interaction of the non-resonant radiative field of a laser with the polarizability of the molecules. This interaction scales with laser intensity and exceeds the interaction of a permanent dipole with a state-of-the-art electrostatic field typically at intensities above $10^{10}$ W cm$^{-2}$ (the intensities have to be held below $10^{13}$ W cm$^{-2}$, however, to avoid ionization). Because the non-resonant optical interaction is purely attractive, all eigenstates created by it are high-field seeking. Focused radiation in free space represents a field maximum, and so produces a potential well (i.e., a trap) for high-field seekers. The optical force is versatile, robust, and precludes relaxation losses as it puts all states into a well. In addition, it aligns nonspherical molecules, because it exerts a torque on the molecular axis. In the state-of-the-art experiment, the non-resonant radiative field comes in the form of a one-dimensional optical lattice created by an interference of two nearly counter-propagating laser beams with slightly different frequencies. The frequency difference of the two beams enables tuning the velocity of the lattice. The required intensities — of about $10^{12}$ W cm$^{-2}$ — are attained by employing pulsed lasers. The lattice can be viewed as a wave whose crests and troughs represent, respectively, the wells and hills of the potential energy of the molecules (as they are high-field seeking). In the pioneering experiment, each lattice crest represents a potential well about 22 K deep. By letting the lattice move at a speed lower than the molecule’s velocity, the molecule — nitric oxide in this case — is forced to climb a hill. During its ascent, the molecule loses kinetic energy and is therefore decelerated. About 40 such potential wells, spread over merely 20 µm, see Fig. 14, snatch about $10^5$
molecules per pulse, with an estimated density of $10^{10}$ molecules per cm$^3$. The temperature of the molecules remains close to that of the original molecular beam pulse, around 1 K. The forthcoming stage of this work will involve trapping of the decelerated molecules, and subsequent cooling to the millikelvin range. The optical deceleration technique adds more than froth and bubble to the tidal wave that molecular physics itself is now riding.

5.2.6 *Slowing by collisions in molecular beams*

Molecules that are slow in the laboratory frame can be also produced by an inelastic collision or a chemical reaction between fast molecules in molecular beams, as demonstrated by the groups of David Chandler at Sandia and Hanjürgen Loesch at Bielefeld. Figure 20 shows the corresponding Newton diagram, constructed for the $\text{Cs}+\text{NO}_2 \rightarrow \text{CsO}+\text{NO}$ reaction. If the laboratory velocity of the center of mass of the colliding system, $C$, is equal to the recoil velocity, $u_{\text{CsO}}$, of the the CsO product molecule with respect to the velocity of the center of mass, i.e., $C = -u_{\text{CsO}}$, the CsO molecule will end up with a zero laboratory velocity.

So far, the method has been applied to the production of slow NO$^{[22]}$ molecules in inelastic NO+Ar collisions and to the production of highly polar KBr$^{[23]}$ molecules in reactive K+Br$_2$ collisions. A time-of-flight spectrum of the KBr product is shown in Figure 21. The hope is that the slow fraction, appearing at the time-of-flight times exceeding 4 ms (and corresponding to velocities lower than 80 m/s), could be loaded into an electrostatic trap and subsequently evaporatively cooled.

From our example we can see that the technique can also be used for the preparation of highly reactive slow molecules, such as CsO.
5.2.7 Production of slow molecules by a supersonic expansion from a counter-rotating nozzle

The remaining two techniques that we will mention can be both well explained using automotive analogies. Figure 22 shows a rotating nozzle which is supersonically discharging gas in a direction opposite to that of the nozzle’s tangential motion. If the speed of the nozzle equals that of the molecules, the supersonic molecular beam ends up having a zero laboratory velocity. This is similar to what happens with the exhaust gases of a moving car. The gas leaves the tailpipe with a speed of about 350 km/h. This is the speed of a Formula 1 car. Thus the exhaust gas of such a car speeding at full throttle ends up “at a standstill” with respect to the racing track! The technique has been successfully implemented in the group of Dudley Herschbach at Harvard.

5.2.8 Selection of the slow fraction of an effusive molecular beam

An effusive molecular beam has a Maxwell-Boltzmann distribution of velocities and thus contains a fraction of slow molecules. If the molecules are endowed with an electric or magnetic dipole moment, it’s possible to select them out with an inhomogeneous electric or magnetic field, as demonstrated by the groups of Gerhard Rempe in Munich and of Eric Abraham at Oklahoma. The field deflects the dipole molecules; for a given field gradient, the magnitude of the deflection is inversely proportional to the translational energy of the molecules. The separation of the slow and fast molecules happens in a curved region of the inhomogeneous field where fast molecules are not deflected enough, and so “won’t make the curve,” see Figure 23. Only slow-enough molecules will make it through the curve; such molecules can be then either trapped or utilized, e.g., in a collision experiment. A drawback of the technique is that the slow molecules are not internally cooled by the effusive
expansion, and so have the temperature of the source — typically 300 K.

6. Ongoing and future experiments with cold molecules

A unique experiment with molecules confined in an electrostatic trap has made it possible to measure the radiative lifetime of molecules in a vibrationally excited state. The measurement was carried out for the OH radical in its electronic and rotational ground state and showed that the lifetime of the $v' = 1 \rightarrow v'' = 0$ transition is about 59 ms.\[50\] This was followed soon after by another direct measure of radiative lifetime, this time in a magnetic trap.\[51\] The measurement was carried out for NH. It showed that the radiative lifetime for the electronic, rotational ground state for $v' = 1 \rightarrow v'' = 0$ is 37 ms. These two measurements were the first direct measurements ever of the radiative lifetime of another than an electronic transition since Albert Einstein introduced the concept in 1916. The knowledge of the vibrational radiative lifetimes is crucial for the physics and chemistry of the interstellar space; their measurement thus far was not possible, however, because in conventional experiments the molecules either perish or disappear before they have a chance to radiate out a vibrational quantum.

In another pioneering experiment with slow molecules, an enhancement of the resolution of a spectroscopic measurement was demonstrated; the enhancement was due to an extended interaction time between electromagnetic radiation and the slow molecules. The resolution, $\Delta E$, of a given measurement is fundamentally limited by the uncertainty principle, $\Delta E \Delta t \approx h$, with $\Delta t$ the measurement time. By slowing down ND$_3$ molecules (deuterated ammonia) from the speed of 280 m/s to 52 m/s, it was possible to enhance the resolution from 10 kHz to 1 kHz, and thus to fully unravel the hyperfine structure of this
important model molecule.\textsuperscript{[52]} The frequency of one of ammonia’s vibrational modes depends sensitively on the mass ratio of the proton to the electron. An accurate measurement of this ratio can serve as a gauge for determining a possible change of this ratio (and of related quantities, such as the fine-structure constant) with the \textit{age of the universe}. In order to achieve the requisite accuracy, an extension of the interaction time $\Delta t$ to about 1 s is needed. This is expected to become available in the \textit{molecular fountain}, now under construction, where slow molecules are thrown vertically upwards, and stopped and turned back by gravity.

In the introduction we indicated that cold molecules might exhibit a highly unusual collisional behavior. This behavior was first analyzed by Hans Bethe in the 1930s and Eugene Wigner in the late 1940s, who had shown that at temperatures close to absolute zero the collision cross section is proportional to integer powers of the reciprocal de Broglie wavelength of the colliding molecules. This implies that the collisional rate constant, which is given by the product of the collision cross section and collision velocity, is nonzero even in the limit of $T \to 0$. Detailed calculations on $\text{A}+\text{A}_2(v=1) \to \text{A}+\text{A}_2(v=0)$ ($\text{A}=$Na, Li) systems or on the $\text{F}+\text{H}_2 \to \text{FH}+\text{H}$ chemical reaction have corroborated the validity of Wigner’s law.\textsuperscript{[53,54]} For instance, the rate of the $\text{F}+\text{H}_2 \to \text{FH}+\text{H}$ reaction at a temperature $T = 10$ mK was found to be $1.25 \times 10^{-12}$ cm$^3$/s. This result may strike a classical chemist as strange indeed, since the activation barrier of this intensely studied reaction is as much as 758 K (i.e., 6.3 kJ/mol)! How can the reaction take place at all when the total energy that the reactants can chip in is just 10 mK? The answer to this question must be sought in the wave character of cold molecules: if the molecules are cold enough to make their de Broglie wavelength exceed the thickness of the activation barrier, the reaction can take place via tunneling through the barrier, without regard for the barrier’s “height.” Ultracold chemistry is thus a purely quantum phenomenon,
and tunneling represents the main reaction mechanism. Reactions at ultracold temperatures thus resemble mingling waves rather than a crash of billiard balls. So far, reaction kinetics and chemical dynamics were able to do with a classical description of the approaching and receding nuclei gliding on a potential energy hypersurface, given by the quantum energy of the electrons. Ultracold chemistry calls for a quantum description of not just the electrons but of the nuclei as well. Quantum chemists will thus have to come up with a qualitatively new description of chemical change. Collision experiments with cold molecules – which will require such a new understanding for their interpretation – are under way in about half a dozen laboratories.

Cold molecules also feature in somewhat futuristic, but nevertheless seriously taken, schemes that could allow the implementation of a quantum computer. Already atomic systems such as charged ions and neutral atoms have been shown to be attractive candidates for physical realization of quantum computation in view of their exceptionally long coherence times and well-developed techniques for cooling and trapping. The main conceptual problems are associated with designing fast and robust multi-atom operations for quantum entanglement as well as with scaling these systems to large numbers of qubits. Ultracold polar molecules are a potentially superior candidate for quantum bits in a scalable quantum computer. Polar molecules combine the key advantages of neutral atoms and ions while featuring similarly long coherence times. In particular, large ensembles of cold molecules can be trapped and cooled similar to neutral atoms, but they can then be manipulated individually using electric fields in analogy with ions.

The first proposed complete scheme for quantum computing with polar molecules took advantage of first feature, but not the second. It was based on an ensemble of ultracold polar molecules trapped in a one-dimensional optical lattice (similar to the one used to decelerate molecules, Section 5.2.4, but in a
stationary version), combined with an inhomogeneous electric field. The requisite entanglement is achieved via the interaction among the dipoles, each of which represents a qubit. Such qubits are individually addressable, thanks to the Stark effect, which is different for each in the inhomogeneous electric field.

A subsequent proposal showed that it should be possible to couple polar molecules into a quantum circuit using superconducting wires.[56] The capacitive, electrodynamic coupling to transmission line resonators was proposed in analogy with coupling to Rydberg atoms and Cooper pair boxes.[57,58] The key feature of molecules is their RF frequency rotational transitions, nicely compatible with microwave circuitry. Coupling individual molecules to microwave strip-lines is advantageous for several reasons. First, it allows for detection of single molecules by remote sensing of transmission line potentials, as well as for efficient quantum state readout. Second, the molecules can be further cooled using a novel method involving microwave spontaneous emission into on-chip transmission lines. Finally, remotely separated molecules can be coherently coupled to allow for nonlocal operations. Local gating with electrostatic fields can be used to achieve exceptional degree of addressability. Single-bit manipulations can be accomplished by using local modulated electric fields.

Although quantum computers have been anticipated decades ago (for instance, by Richard Feynman), their benefits for solving numerical problems have been discovered only recently, in 1994, by Peter Shore. He showed that quantum computers are particularly well suited for factorization, a step in methods of encryption. It is estimated that a quantum computer consisting of 500 qubits would be capable of factorizing a number of the order of $10^{200}$ within seconds (for comparison, a classical computer would need about $10^{150}$ processors to achieve a similar feat).

Apart from the above, there is a class of experiments in prospect or
progress with cold molecules that could answer questions reaching far beyond
the scope of traditional molecular science: these experiments test some of the
fundamental symmetries in physics, such as the time-reversal symmetry (T),
parity (P), or the Pauli principle. These symmetries are a window into the world
of the fundamental forces in nature and thus molecular, table-top experiments
that test them represent an alternative to the high-energy collisional
experiments carried out in giant accelerators.

Particularly promising and interesting is the simultaneous testing of the
time-reversal symmetry and parity in experiments that search for the permanent
electric dipole (EDM) of the electron (and of other elementary particles).\[59\] A
nonzero value of EDM implies the breaking of both T and P. Since the
Standard Model does not allow for essentially any violation of the T symmetry,
finding a nonzero EDM would amount to the discovery of physics beyond the
Standard Model. Such a discovery would be followed in all likelihood by a new
revolution in physics.

What does EDM have to do with cold molecules? From the experiments
carried out so far it is known that the EDM of the electron doesn’t exceed the
value of about $5 \times 10^{-19}$ Debye. This is an exceedingly small value, one that
would be found if an electron were expanded to the size of the earth and
deformed on the poles by a micron! A dipole moment manifests itself through
its Stark effect, i.e., by a shift of the energy levels of a system carrying the
dipole moment when the system is subject to an electric field. In order for the
Stark shift to be detectable, the EDM has to be exposed to as large a field as
possible. The strongest fields that one can come by are available inside heavy
atoms (where they can reach values of 10 GV/cm, thanks to relativistic effects).
Atoms are spherically symmetric, however, and so before any EDM
measurement they need to be oriented in the laboratory frame (otherwise the
dipole moment would average out). But orienting atoms is difficult, because in
doing so one has to rely on their polarizability, which is small. Therefore, it is of great advantage to add to a given heavy atom another atom, and to carry out the Stark effect measurement on the polar molecule which thereby ensues! Polar molecules can namely be easily oriented. In fact, a Stark decelerator or an electric trap are based on the ability to easily orient polar molecules in the laboratory frame. The use of cold polar molecules further enhances the resolution of the measurement (see the beginning of this section). The experiment of Ed Hinds & Co. at Imperial College, London, with decelerated YbF molecules already comes close to yielding the most accurate value of the electron’s EDM.\cite{60} An increase of the experiment’s accuracy by a single order of magnitude could lead to a rejection or adoption of some of the alternatives of the Standard Model. We are living in thrilling times!

In conclusion, we must say that although many hands are busy with the ongoing work outlined in this article, a host of adventures with cold molecules still await – beyond the horizon we can survey today.

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References

33. D. Egorov, W.C. Campbell, B. Friedrich, S.E. Maxwell, E. Tsikata, L.D.
47. E. Narevicius, C. G. Parthey, A. Libson, J. Narevicius, I. Chavez, U. Even,


Figure Captions

Figure 1: Nomogram for the de Broglie wavelength $\Lambda$ of a particle with rest mass $m$ at absolute temperature $T$. Arrows on the right show the masses of iodine and nitrogen molecules, of the hydrogen atom, and of the muon and the electron.

Figure 2: Photoassociation of cold atoms into a translationally cold molecule. (a) schematic of a photo-assisted collision; (b) potential energy curves for the ground and excited electronic states; $R_C$ marks the internuclear distance at which the photoassociation laser promotes the colliding system into a bound state which is electronically, vibrationally and rotationally excited; (c) laser-stimulated emission into the ground electronic, vibrational and rotational state.

Figure 3: Energy-level structure allowing for a Feshbach resonance between a bound excited electronic state (shown by the dashed line) and an electronic ground state (given by the asymptotic energy of the free – and slow – atoms; shown by the thin horizontal line). See text.

Figure 4: Apparatus for buffer-gas cooling and magnetic trapping of paramagnetic atoms and molecules. The two superconducting coils, energized by counter-propagating electric currents (anti-Helmholtz configuration), create a nearly spherically symmetric magnetic field whose strength increases linearly with distance from a zero value at the center to a maximum (of about 3 Tesla) at the edge. The cryogenic cell, fashioned out of copper, is placed in the bore of the magnet. It is thermally anchored to the mixing chamber of a dilution refrigerator (not shown), which cools it to about 100-300 mK. The cryogenic cell is filled with the buffer gas whose density is about $10^{16}$ He atoms per cm$^3$. 
The atoms or molecules to be cooled and trapped are loaded into the cryogenic environment by laser ablating a suitable precursor, placed directly in the cryocell. Taken from ref.[14]

Figure 5: Magnetic trapping. The thermalized molecules carry a translational energy which is less than their magnetic (Zeeman) potential energy (in low-field seeking states).

Figure 6: Fluorescence spectra of molecules in the anti-Helmholtz field at different times after firing the ablation laser. Whereas high-field seeking molecules are expelled from the field (left-hand maximum), low-field seekers are drawn to the field minimum (right-hand maximum). The analysis of the spectra showed that about $10^8$ CaH molecules were trapped. The trapped molecular ensemble was found to exhibit a Maxwell-Boltzmann distribution of translational energies, pertaining to a temperature of about 400 mK. Taken from ref.[14]

Figure 7: (a) Stark deceleration. The energy of a molecule consists of its translational energy and its potential energy. See text. (b) Spatial dependence of the electric field $\varepsilon(z)$ generated by four field stages, each of which consists of a pair of rod electrodes. In the upper (red) configuration, the electrodes of the first and third pair are energized by a high voltage of opposite sign (typically $\pm 20$ kV), whereas the electrodes of the second and fourth pair are grounded. In the lower (blue) configuration, the electrodes of the first and third pair are grounded, whereas the second and fourth field stages are energized. The resultant electric field in the longitudinal direction, $z$, (along the direction of a molecule flying from left to right) reaches values of about 100 kV/cm at the maxima. This corresponds to the potential (Stark) energy of a typical polar diatomic of about 1 K. (c) Time dependence of the electric field $\varepsilon(z,t)$
determined by the switching between the upper (red) and lower (blue) field configuration. Also shown are the spatial and temporal periods, $\lambda$ and $\tau$. Adapted from refs.\cite{18,38}

Figure 8: Velocity distribution modified by a Stark accelerator/decelerator. Lower curve shows the velocity (time-of-flight) distribution of molecules in a supersonic molecular beam. Upper curves show the effect of a Stark accelerator/decelerator: this selects out a velocity group and moves it to either lower velocities (longer times of flight) or higher velocities (shorter times of flight). The measurement was carried out with CO molecules in a metastable electronic state (lifetime of about 2.6 ms). The grey (red) curves were obtained by Monte Carlo simulation of molecular trajectories in the Stark accelerator/decelerator field. Taken from ref.\cite{18}

Figure 9: Stark accelerator/decelerator, consisting of a 108 pairs of rod electrodes. The electrodes of a given pair are separated by 4 mm, the pairs by 11 mm from one another. The high voltage used is $\pm 20$ kV. The transient time needed to switch from one configuration to another is about 500 ns. Only a few ms are required to decelerate a molecule from a thermal velocity to a standstill. The inset shows the electrodes from the perspective of the accelerated/decelerated molecules. Taken from ref.\cite{36}

Figure 10: Biased pendulum and its potential energy. (a) A biased pendulum consists of a normal pendulum of length $r$ and mass $m$ which is fixed to an axle of radius $R$; wound around the axle is a string that carries a weight (bias) of mass $M$. (b) Potential energy $V$ of a biased pendulum as a function of position (more accurately, phase) $\phi$, consists of the potential energy of the pendulum, $V_m$, and the potential energy of the bias, $V_M$: $V = V_m + V_M$ ($g$ is the gravitational acceleration). Potential $V$ has a local minimum at $\phi = \phi_s$ and a
local maximum at \( \phi = \pi - \phi_s \); these extrema correspond to the stable and unstable equilibrium point of a biased pendulum. Taken from ref.\[38\]

Figure 11: “Fish” diagram indicating the range of positions and velocities (expressed in terms of phase \( \phi \) and its time derivative \( \dot{\phi} \)) of those nonsynchronous molecules that perform stable oscillations about the synchronous molecule. The diagram pertains to the case of deceleration of low-field seekers. The constant \( \alpha \) includes the Stark energy and the mass of the molecules. Taken from ref.\[38\]

Figure 12: Global phase portrait constructed for the case of transport of molecules (i.e., zero acceleration/deceleration). Apart from areas of phase stability centered about velocities which are odd-fraction multiples of the fundamental phase velocity \( V_0 \), one can also see small islands of phase stability pertaining to even-fraction multiples of \( V_0 \). Whereas the former result from the interaction of molecules with the individual waves generated by switching the inhomogeneous electric field, the latter originate from the interference of two “odd” waves that give rise to an “even” superposition wave. Taken from ref.\[38\]

Figure 13: Electrostatic trap for polar molecules in low-field seeking states. The trap consists of three electrodes, initially energized as shown in panel (a): this configuration enables the decelerated molecules to enter from the left. Panel (b) shows the final field configuration that provides for the trapping proper. The figure also shows the corresponding Stark energy (for deuterated ammonia molecules). Taken from ref.\[18\]

Figure 14: (a) Schematic of the experimental set-up. A pulsed beam of ND\(_3\) molecules is decelerated to 92 m/s using a Stark decelerator, cooled to 300 \( \mu \)K using a buncher and focused into a hexapole torus storage ring. Of 25 cm diameter. (b) Density of ammonia molecules at the detection zone inside the
ring as a function of storage time up to the 33\textsuperscript{rd} lap. Due to the spreading of the packet, the peak density decreases as $1/t$ (shown as the dashed line). In the inset, a measurement of the ammonia density after 49-51 laps is shown, together with a multi-peak Gaussian fit. Reproduced from ref.\textsuperscript{[39]}

Figure 15: (a) Scheme of the molecular synchrotron. The synchrotron consists of two hexapole half-rings with a 12.5 cm radius separated by a 2 mm gap. (b) Density of ammonia molecules at the detection zone inside the synchrotron as a function of storage time up to the 40\textsuperscript{th} lap. Expanded views of two TOF profiles are displayed as insets, showing the absolute widths of the molecular pulses. Reproduced from ref.\textsuperscript{[40]}

Figure 16: Spatial dependence of the electric field strength, $|\varepsilon|$, in an AC trap for two field configurations generated by energizing suitably shaped electrodes.

Figure 17: (a) Schematic of the cylindrically symmetric AC trap. The electric field strength along the symmetry axis (z-axis) is shown in (b), and along the radial direction in (c). When voltages of 5, 7.5, -7.5 and -5 kV are applied to the electrodes, molecules in high-field seeking states are focused towards the trap center along the z-axis and defocused in the radial direction. When voltages of 11, 1.6, -1.6, and -11 kV are applied to the electrodes, molecules in high-field seeking states are focused radially and defocused along the z-axis. Reproduced from ref.\textsuperscript{[41]}

Figure 18: Density of $^{15}$ND\textsubscript{3} molecules in low-field seeking and high-field seeking levels of the |J,K>=|1,1\rangle state at the center of the trap as a function of the switching frequency, $\Omega$. The measurements are performed 80 ms after the molecules are loaded into the trap. The signal of the high-field seekers is scaled up by a factor of 5 to compensate for the fact that the initial density of high-field seekers is only about 20\% of that of the low-field seekers.
Figure 19: Deceleration of a pulse of supersonically expanded NO molecules by a pulsed optical lattice. The ultraviolet probe beam that was used to ionize and detect the NO molecules perturbed by the lattice is also shown. The velocity of the ions, and thus that of the neutral molecules, was determined from their time-of-flight in a mass spectrometer. See text. Taken from ref. [21].

Figure 20: Production of slow molecules by a collision of fast molecules in molecular beams. Shown is a Newton diagram for counter-propagating beams of Cs and NO$_2$ reactants with laboratory velocities $v_{\text{Cs}}$ and $v_{\text{NO}_2}$. The CsO product recoils with a velocity $U_{\text{CsO}}$ (whose magnitude is shown by the Newton circle) with respect to the center of mass of the colliding system, which, in turn, moves with velocity $C$ with respect to the laboratory frame. The reactant velocity is adjusted such that the recoil velocity of the CsO product equal the laboratory velocity of the center of mass, $U_{\text{CsO}} = -C$. The dynamics of the reaction (as shown by the velocity contours) enables a large fraction of the CsO molecules formed in the Cs + NO$_2$ collisions to emerge with recoil velocities that fulfill this condition, thus yielding a bounty of molecules that are predominantly at standstill. See text.

Figure 21: A time-of-flight spectrum of KBr product generated by collisions of K + Br$_2$ in counter-propagating beams. Taken from ref. [23].

Figure 22: Production of slow molecules by supersonic expansion from a counter-rotating nozzle. See text. Taken from ref. [24].

Figure 23: Skimming of slow molecules from an effusive molecular beam by a static inhomogeneous field. See text. Taken from ref. [25].

Reproduced from ref. [41].
Figure 1
Figure 2
Figure 3
Figure 5

Cell wall

Flux of molecules

Potential
(magnetic eigenenergy)

\[ r \]

\[ \mu H \]
Figure 6
Figure 7
Figure 8
Figure 10

(a) Diagram showing stable and unstable equilibrium positions.

(b) Graph plotting $V(\phi)/mg$ versus $\phi$, with stable and unstable equilibrium points indicated.

Stable equilibrium
Unstable equilibrium

$V(\phi)/mg = \frac{\phi_s \sin \phi_s}{2}$

Figure 10
Figure 11
Figure 12

Initial spatial phase

Initial velocity [m/s]
Figure 13
Figure 15
Figure 16
Figure 17
ND$_3$ density (arb. units)

$\Omega/(2\pi)$ [Hz]

Figure 18
Figure 19

Ultraviolet ionization beam

Infrared lattice beam 1

1.8 K, 400 m s\(^{-1}\) molecular beam

Pulsed valve

Infrared lattice beam 2

Travelling optical lattice
Figure 20
Figure 21

The graph illustrates the intensity over time-of-flight (TOF) for both fast and slow molecules. The fast molecules are characterized by a sharp peak at the beginning of the graph, while the slow molecules show a more gradual decline over time.
Figure 22

Rotor
Gas inlet
Nozzle
Molecular beam

Velocity of nozzle
Velocity of molecules with respect to nozzle
Laboratory velocity of molecules
Figure 23

Effusive beam source

Velocity selector

Fast molecules

Slow molecules