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Hot Prospects for Ultracold Molecules

Researchers have taken giant strides down several paths toward trapping molecules at submillikelvin temperatures. At the end of these paths lie the promis of more precise measurements and new phenomena.

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Over the past few decades, physicists have learned to cool atoms to lower and lower temperatures and to gain increasing control over them, with exciting and sometimes unforeseen consequences. The payoffs have included atom interferometry, precision spectroscopy, BoseEinstein condensates (BECs), and even atom lasers. Not surprisingly, experimenters now want to play the same games with molecules. The challenges--formidable enough for atoms--loom even larger for molecules. Nevertheless, a number of groups have entered the quest, with the goal of bringing molecules to submillikelvin temperatures, which are slow enough to be trapped or otherwise manipulated.

The latest achievement in this endeavor was announced recently by researchers from the FOM-Institute for Plasma Physics and the University of Nijmegen in the Netherlands who have demonstrated a promising new method for obtaining ultracold molecules. In this work, the Dutch group cooled and trapped molecules in a single quantum level with a density of $10^6/cm^3$ and at temperatures estimated to be well below 350 mK.[1]

With trapped molecules, one would ideally like to achieve three things: reduce translational temperatures to submillikelvin levels; cool a large number of molecules; and put the molecules in a single, and preferably the lowest, rotationalvibrational state. Moreover, it would be nice to find a method that enables one to reach these parameters with just about any type of molecule. Over the past few years, researchers have made impressive progress toward some of these goals through several different methods, each having its own particular strengths and weaknesses.

One technique takes alkali dimers to submillikelvin temperatures, but it does not yet work with large collections of molecules and does not put the dimers in the lowest rotationalvibrational state. Another method enables researchers to cool large numbers of paramagnetic molecules in their lowest energy level, but so far only to a few hundred millikelvin. The Dutch team demonstrated the viability of a third, electrostatic, technique, which allows one to select ground-state molecules and which should work with any molecules having sufficiently large electric dipole moments. Although the researchers using this electrostatic method have not set any records for numbers cooled or temperatures reached, they have made encouraging progress on both fronts.

The research agenda for ultracold molecules is probably not too different from the wish list for their atomic counterparts. One possibility is to do precision spectroscopy, because the spectral lines will be far narrower in the absence of motional effects. Another is to study the collisions of ultracold molecules, which should involve only the $l = 0$ angular momentum states, in contrast to the impact of thermal molecules, whose description requires higher orders of angular momentum l and thousands or millions of internal states in each molecule. In the thermal case, the quantum effects associated with single quantum levels are easily washed out. As Dudley Herschbach of Harvard University notes, "At these low temperatures, you'd have more chemical specificity." The availability of ultracold molecules might also facilitate searches for electric dipole moments of elementary particles. Yet another possible research area is the manipulation of molecules by various types of electromagnetic fields. And, of course, the formation of a BEC of molecules would be a great coup. But the most compelling interest is no doubt the lure of the unknown. As John Doyle of Harvard University said to us, "Inevitably, there will be new physics to do."

Routes to cooling

Since the 1950s, chemists have been producing molecular beams by supersonic expansions, which typically reduce the internal--that is, rotational and vibrational--temperature of the molecules. The resulting molecular beam does not necessarily have a slower translational velocity, but it does have greatly reduced spread of velocities. If the target gas is expanded with an inert species, this method is particularly effective in reducing the internal energies. Such expansions can't give

temperatures much below 1 K, however, being limited by the tendency of the rare gases to cluster at low temperatures.

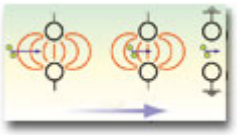

Figure 1

The workhorse of atomic trapping has been laser cooling, but that technique won't work for molecules because their energy level spectrum is far more complex. In this technique, lasers emit photons whose frequency is just below the resonant frequency for an atomic transition. The atoms can absorb only those photons with oppositely directed momenta, and thus they are slowed. Atoms then reemit the light, but in random directions. A single atom absorbs and reemits a photon between the same two energy levels tens of thousands of times during the cooling process. Molecules cannot recycle photons in this way, however, because a given molecule may emit a photon into any one of a number of energy levels, putting an end to the cycle of photon "kicks."

Without laser cooling techniques, those who work with molecules have resorted to other means to decelerate the molecules.[2] In the recent work at FOM-Institute and the University of Nijmegen, team leader Gerard Meijer and his coworkers applied time-varying inhomogeneous electric fields to polar molecules. Others have slowed molecules in collisions with buffer gases. And preliminary work has been done on a mechanical scheme that essentially transports the center of mass motion of a molecule beam into the laboratory frame. Alternatively, instead of starting with fast molecules and slowing them, one can first cool the consituent atoms using laser cooling and then nudge them together, with the help of laser beams, to form dimers.

These cooled molecules might be trapped in several ways. Polar molecules can be held in an electrostatic trap, and paramagnetic molecules can be caged in a magnetic field gradient. Molecules have also been held in place by tightly focused laser beams whose frequencies are far from the molecular resonances. Once molecules are in a trap, researchers are hopeful that they can cool them still further by evaporative cooling, which has been successfully used in many atom traps. But it's not yet known whether this technique will work for molecules; it requires most of the collisions to be elastic, generating no additional heat.

Electrostatic method

The technique used by the Dutch group both to cool and to

trap molecules relies on the Stark shift of the energy levels induced by the interaction of the molecule's electric dipole moment with an electric field. Meijer told us that in the 1950s, John King of MIT had tried a similar electrostatic method to slow ammonia to make an ammonium maser, bu he never got it to work. In the 1960s, Lennard Wharton of the University of Chicago tried the reverse technique to accelerate molecules, also without success. More recently, researchers from the Lawrence Berkeley National Laboratory and the University of California, Berkeley, have applied a similar technique to slow neutral atoms.[3]

Bretislav Friedrich of Harvard points out that electric fields, unlike their magnetic counterparts, can be switched quickly on the time scale of molecular translation. The corresponding dynamics of electrical trapping exhibit different and, at this point, novel phenomena.

The principle of the deceleration in time-varying electric fields is shown schematically in figure 1. A pulse of the molecules to be slowed travels toward a pair of electrodes. Those molecules having their electric dipoles, on average, oriented antiparallel to the electric field are attracted toward regions where the electric field intensity is low. An electric field is switched on just as the molecules approach the electrodes, putting a brake on the low-field-seeking molecules. These molecules must climb a potential hill as they move into the high-field region at the center of the electrodes, consequently losing kinetic energy.

Of course, if the field remained on, the molecules would lose potential energy (gaining back kinetic energy) as they moved out of the field. But the experimenters turn off the field when the pulse of molecules is near the center, preserving the slow speeds. The molecular pulse then heads toward a second pair of electrodes, where the cycle is repeated for a succession of stages (the Dutch experi ment had 63 stages). The timing of the electric fields is critical, and only molecules in a chosen energy level will be in phase with the switching on and off of the field at each stage.

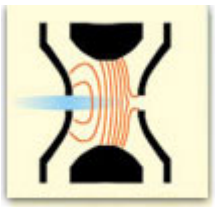

Figure 2

Because the electrostatic stages must be turned on and off sequentially, the electrostatic trapping method works only with pulses of molecules rather than with a steady stream. Meijer and company formed their pulse by expanding a gas containing 1% ammonia molecules and 99% xenon atoms through a cooled solenoid valve. Collisions with the heavy rare gas

atoms removed much of the energy of the ammonia molecules, so that the molecular beam streaming through the valve had a mean translational speed of 280 m/s, with a fairly narrow velocity spread (about 15%).

Last year, the Dutch team used the Stark decelerator to slow molecules of metastable carbon monoxide, but did not trap them.[4] In June, the same group presented a mathematical description of the process, showing that the phase-space density can be kept constant in the deceleration process.[5] For the recent work on trapping,[1] Meijer and his colleagues turned to deuterated ammonia molecules (ND_3)--the first molecule with more than two atoms to be trapped. (The deuterated version of ammonia was preferred because the normal version has a nonlinear Stark effect at the most convenient values of electric fields.) The particular state selected to be slowed was the upper inversion level in the vibrational ground state. About one-eighth of the ammonia molecules in each pulse were in this state.

To trap the slowed molecules, the Dutch researchers directed the pulse of molecules into an electrostatic trap. As the molecules approached the trap, the experimenters applied an inhomogeneous field, which got stronger the farther the molecules traveled into the trap, as seen in figure 2. It was like making the molecules travel uphill: Eventually most were stopped or even turned around. At that point, the electric field was changed to a symmetric configuration with a minimum at the center. By ionizing and detecting a small volume of the trapped molecules, the Dutch experimenters have determined the density to be $10^6/cm^3$, and they estimate their volume to be about 0.25 cm^3. So far the team does not have a direct measurement of the temperature of the trap, but team members suspect it is appreciably less than the depth of the trap's potential well, or 350 mK, corresponding to a few tens of meters per second. (The maximum speed of molecules contained in the trap is 17 m/s.) Meijer adds that the temperature might be as low as 2 mK, corresponding to the narrow velocity spread of molecules loaded into the trap from the beam. The $1/e$ decay time of the trapped species was 0.24 s.

Having demonstrated the promise of their new technique, the Dutch experimenters hope to improve it in several ways. Meijer thinks they can achieve trap densities of $10^9/cm^3$ by such measures as increasing the intensity of the beam, raising the electric field strength and adding more stages to handle higher initial velocities, and moving

the trap closer to the end of the decelerator for more efficient loading. He thinks they can extend the trap lifetime by reducing the vacuum pressure. Furthermore, he plans to try evaporative cooling to further reduce temperatures. He and his coworkers have yet to devise ways to load the trap with successive pulses. The team has also been working on a storage ring for neutral molecules, based on their decelerator ideas. As Meijer remarked, "Every trick people played with charged particles, we can now do with dipole molecules."

Buffer-gas cooling

Whereas the FOMNijmegen group focused on capturing polar molecules in electrostatic traps, two years ago Doyle and his colleagues at Harvard demonstrated the trapping of paramagnetic molecules in a magnetic trap.[6] (See Physics Today, November 1998, page 19.) In their trap, two superconducting magnetic coils sit inside a copper chamber. The coils create a spherical quadrupole field having a minimum at the center. At the start of the experiment, the trap is filled with a buffer gas of helium-3 atoms, which has typically been cooled cryogenically to temperatures around 300 mK. The molecules of interest--calcium monohydride, or CaH--are formed by laser ablation from a solid target at the top of the chamber. They are thermalized by their interactions with the helium cloud, and those molecules with a magnetic moment antiparallel to the trap's field are attracted to the low-field region in the center of the cell. Molecules with parallel moments are lost from the trap; so too are those antiparallel molecules whose temperatures exceed the depth of the trap (the loss of these hotter molecules is a form of evaporative cooling). Doyle and his coworkers found that they had trapped as many as 10^8 ground-state CaH molecules with a single ablation pulse.

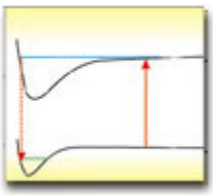

Figure 3

Doyle told us that he and his colleagues have not continued with the work on molecules because it is not currently funded, although similar work on atoms, which is supported, is going quite well. They can trap as many atoms as they can produce, with the maximum now standing at 10^{12}. They expect to be able to do the same with molecules; All that's needed is to produce more molecules in each ablation pulse. Doyle is hopeful that his buffer-gas-loaded magnetic traps will lend themselves to evaporative cooling.

Another technique with the potential to trap large numbers

of atoms is a scheme developed by other Harvard researchers, Manish Gupta and Herschbach. They mounted a supersonic nozzle on a high-speed rotor. The rotor spins in one direction, and the molecules emerge from the nozzle in the opposite direction. If the rotor turns at roughly the speed with which molecules exit the nozzle, the relative velocity of the molecules will be very small, equal to the difference between the rotor speed and the exit velocity. In their first implementation of this concept,[7] Gupta and Herschbach produced molecules traveling a few tens of meters per second. They have to reduce that speed by a factor of ten to be competitive with other techniques being pursued. However, if they can do so, they will have a method that's generalizable to any molecular species and that can produce very high densities of cold molecules.

Photoassociation of molecules

The coldest molecules formed thus far--typically 1000 time colder than molecules cooled with a buffer gas or electrostatic fields--are those that result from the photoassociation of pre-cooled atoms in a magneto-optic trap. Photoassociation can take advantage of the very low atomic temperatures reached by laser cooling. In the simplest scheme, one applies a single laser pulse to stimulate the transition of a pair of colliding atoms from a free state to a bound molecular state, at temperatures not much higher than those of the colliding atoms. The process is illustrated in figure 3, which shows the potential energy levels for the electronic ground state (lower curve) and an excited state of a pair of atoms as a function of the internuclear distance. A laser beam can pump the free pair of atoms into a bound state (dimer) of the excited pair. From there, the dimer decays in most cases back to a pair of free atoms; but a small fraction of the time, it leads to a high vibrational level in the ground state of the dimer.

When photoassociation starts with ultracold atoms, the kinetic energy spread among atoms is very small so that one can select the right frequency for the laser beam to pump the molecule into a given excited state. Furthermore the colliding atoms meet nearly at rest, and the molecule produced is nearly at rest. Several research groups have so far used photoassociation to form alkali dimers, such as cesium or potassium, at a few tenths of a millikelvin.[8,10] Up to 10^6 molecules per second can be formed in such experiments, with loading and trapping times typically being one second. The molecules have been detected directly by resonance-enhanced multiphoton ionization followed by time-of-flight mass spectroscopy. In

experiments done at the University of Connecticut,[10,11] the ionization is done in such a way that one can identify the vibrational levels that have formed.

Unfortunately, photoassociation--at least the simplest one-photon scheme--tends to form dimers in very high vibrational states. That's because the intermediate state is formed with the atoms at large distances from one another and these states radiate predominantly into the continuum or into bound states with high vibrational quantum numbers. Furthermore, because the final state is reached through spontaneous emission, the process is not state selective: One ends up with molecules in a range of final vibrational states. It's possible, however, to design a number of schemes involving more than one photon that will form molecules in lower vibrational states, or in a specific final state, or perhaps both. For example, William Stwalley and his colleagues at the University of Connecticut recently reported reaching fairly low vibrational states by using two continuous laser beam pulses.[11]

The ultimate in photoassociation is, of course, to start with atoms in a BEC. Not only are they the coldest atoms one can get (around 100 nK), but there's the possibility that forming molecules from the atoms in a BEC might yield molecules in a condensate. Researchers from the University of Texas at Austin, led by Daniel Heinzen, have traveled down this path, with some success.[12] The Texas group used a stimulated Raman process to photoas sociate pairs of rubidium-87 atoms from a BEC to form molecules: The first Raman pulse took the free pair of atoms to a bound rotationalvibrational level of an excited electronic state of the dimer; the second stimulated a transition back to a specific rotationalvibrational level of the bound state. The energy difference between the two Raman pulses equals the binding energy of the final state. This version of photoassociation is thus state selective, although it still does not yield a molecule in the lowest vibrational state. Neither Raman beam is resonant with an excited state vibrational level; that way, the experimenters avoid spontaneous emission from the excited state.

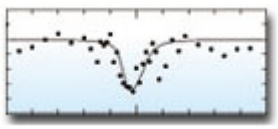

Figure 4

The Texas researchers did not observe the molecules directly but inferred their presence from a sharp dip in the number of atoms in the condensate, indicating that the atoms had been taken from the condensate as molecules were formed. As seen in figure 4, the dip appeared when

the frequency difference between the Raman beams corresponded to the expected binding energy of the molecular state the researchers were trying to form. This evidence that molecules were formed is persuasive, although not direct. Heinzen told us that he and his colleagues hope to use resonant ionization to detect the molecules directly. Then they can also study how long the molecules remain in the trap: The photoassociated molecules have a magnetic moment that should allow them to stay trapped. The Texas experimenters have already established that the molecules have a lifetime of at least 0.1 ms, and they expect that the lifetime could be much longer, depending on the inelastic collision rate between atoms and molecules. Once they can measure the lifetime, they can see if it increases, as expected, with greater molecular binding energy. Heinzen and company do not yet claim to have formed a molecular BEC, but they think they are on the right track.

In measuring the spectrum of atoms as a function of the Raman frequency difference, the Texas researchers presented a good example of the kind of precision spectroscopy possible with ultracold molecules. As seen in figure 4, the linewidth of the dip in condensate number was as narrow as a few kilohertz, and was not broadened by such motional effects as the Doppler shift. From the line shape, the team was able to measure the atommolecule scattering length and to set an upper bound on the rate of atommolecule inelastic collisions.

Heinzen told us that if a molecular condensate could be generated from an atomic condensate, this system might constitute a matter wave analog of optical frequency doubling, where the atoms play the role of the red laser field, and the molecules play the role of the blue laser field. As a result, many interesting phenomena of nonlinear and quantum optics could be explored.

With so much experimental work already in progress and other good ideas on the drawing board, we can expect to hear much more about ultracold molecules before long.

References

1. H. L. Bethlem, G. Berden, F. M. H. Crompvoets, R. T. Jongma, A. J. A. van Roij, G. Meijer, Nature **406**, 491 (2000).

2. For a review, see J. T. Bahns, P. L. Gould, W. C. Stwalley, Adv. At., Mol., and Opt. Phys. **42**, 171 (2000).

3. J. A. Maddi, T. P. Dinneen, H. Gould, Phys. Rev. A **60**, 3882 (1999).

4. H. L. Bethlem, G. Berden, G. Meijer, Phys. Rev. Lett. **83**, 1558 (1999).

5. H. L. Bethlem, G. Berden, A. J. A. van Roij, F. M. H. Crompvoets, G. Meijer, Phys. Rev. Lett. **84**, 5744 (2000).

6. J. D. Weinstein, R. deCarvalho, T. Guillet, B. Friedrich, J. M. Doyle, Nature **395**, 148 (1998).

7. M. Gupta, D. Herschbach, J. Phys. Chem. A **103**, 10670 (1999).

8. A. Fioretti, D. Comparat, A. Crubellier, O. Dulieu, F. Masnou-Seeuws P. Pillet, Phys. Rev. Lett. **80**, 4402 (1998). A. Fioretti *et al.*, Euro. Phys. J. D **5**, 389 (1999).

9. T. Takekoshi, B. M. Patterson, R. J. Knize, Phys. Rev. Lett. **81**, 5105 (1998).

10. A. N. Nikolov, E. E. Eyler, X. T. Wang, J. Li, H. Wang, W. C. Stwalley, P. L. Gould, Phys. Rev. Lett. **82**, 703 (1999).

11. A. N. Nikolov, J. R. Ensher, E. E. Eyler, H. Wang, W. C. Stwalley, P. L Gould, Phys. Rev. Lett. **84**, 246 (2000).

12. R. Wynar, R. S. Freeland, D. J. Han, C. Ryu, D. J. Heinzen, Science **287**, 1016 (2000).

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