Exotic helium dimers: a giant comes out of the cold

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Giant helium dimers can now be produced routinely in the "Cold Atom" group of the Laboratoire Kastler Brossel at the École Normale Supérieure in Paris [1]. The separation between the bound pair of atoms is on the order of 50 nanometres, or nearly one-thousand times larger than normal bond lengths. This size—which approaches that of a virus!—makes these the most distended two-atom molecules ever observed.

The Paris results run counter to the intuitive expectation, based on the well-known fact that helium is chemically inert, that He_2 should not exist. Under normal conditions, this expectation is justified, since the feeble interactions that can bind helium atoms together are completely overwhelmed by thermal agitation at room temperature. However, experiments in 1993 [2] demonstrated the existence of ground-state helium dimers with binding energies of 10^{-7} eV, which corresponds to the mean thermal energy at a temperature of a few milliKelvins (mK). Indeed, sub-mK "ultra-cold" temperatures are also necessary in the Paris experiment and are readily achieved by evaporative cooling in a magnetic trap.

But there are remarkable differences between the Paris dimers and the He_2 molecules observed previously. First, there is the size difference. The mean atomic separation in ground-state He_2 is a few angstroms, which is closer to the size of an everyday dimer such as N_2 and O_2 than to that of the hundredfold-larger giant helium dimer. In addition, the depth of the molecular potential that binds the atoms together is four orders of magnitude shallower for the giant dimer. These huge differences in distance and energy scales result from very different interactions producing the molecular potentials in the two cases. And this points to one of the most dramatic differences of all: whereas the ground-state He_2 molecule is produced in normal three-body collisions, the giant dimer

is formed when two metastable (He^*) atoms, each carrying nearly 20 eV of electronic excitation energy, collectively absorb a laser photon—a process called photoassociation [3] (fig. 1).

The dipole transition that permits the giant dimer to be formed also allows it to decay, so the structure is strictly ephemeral. But it has enough stability to exhibit extremely well-resolved vibrational spectra, in which the absorption of laser photons occurs only at well-defined and widely separated frequencies. One of the discoveries of the ENS team has been a sensitive method for detecting the absorption signals in their photoassociation experiment, namely through the "calorimetric" effect that decaying molecules have when they cause heating in the surrounding atoms.

The Paris experiment requires helium atoms in the 2^3S_1 (He^*) metastable state to be trapped and cooled to microKelvin temperatures. Fortunately, the team can rely on the equipment and techniques that led them to their observation of Bose-Einstein condensation in helium in early 2001 (just weeks after a similar observation by Alain Aspect's group in Orsay) [4]. That observation revealed the macroscopic wave properties that identical atoms collectively display under conditions of extremely low temperature and high density. Such conditions, now reached daily in the laboratory, are more than adequate for the production of giant helium dimers.

Figure 2 shows a diagram of the main components of the experimental setup. The preparation of the atomic sample begins with a beam of helium atoms that is excited into the 2^3S_1 (He^*) metastable state by an electrical discharge and emerges into an empty vacuum chamber. A laser beam (wavelength 1083 nm) is directed opposite to the atomic beam, so that whenever an atom absorbs a photon, it receives a decelerating impulse. Repeated absorptions are used to decelerate the atoms from speeds near 1000 m/s to less than 20 m/s over a distance of 2 m. (Note that spontaneous emission, which is oriented randomly, yields no average change in atomic momentum during the deceleration process.) After being decelerated, the atoms are collected at the intersection of several laser beams that form a magneto-optical trap (MOT). In just a few seconds, the MOT can collect tens of millions of He^* atoms in a volume of a few cubic mm and cool them to a temperature of about 1 mK.

A final stages of cooling and spatial compression are begun when the MOT's laser beams are extinguished and a specially tailored magnetic field is applied. The field interacts with the atomic magnetic dipole moments to form a potential energy well, or a magnetic trap such as that shown schematically in figure 1. Given a 1-mK starting temperature for the atoms, the walls of the trap are sufficiently high that almost no atoms can escape. Moreover, the walls can be steepened in order to help compress the atomic cloud toward the trap center. This has the effect of increasing the atomic density and therefore the collision rate, which in turn increases the rate of thermal equilibration in the cloud.

Rapid equilibration is necessary for the "forced evaporation" that is introduced next. This last cooling process employs a radio-frequency (RF) magnetic field to flip the dipole moments of atoms at the outer edges of the trap, so that these atoms are expelled from the cloud. The trap's field gradient ensures that the RF field can be applied in a spatially targeted fashion (analogous to the spatial resolution achieved in magnetic-resonance imaging) and that it will "boil off" only those atoms that are energetic enough to be found at the outer reaches of the trapping potential. This method of cooling, or of selectively removing the particles at the high end of the velocity distribution, is analogous to the forced evaporation that occurs when one blows air over a hot bowl of soup. But in the helium experiment, the cooling (with thermal equilibration)

reduces the probability that trapped atoms will get enough energy to reach the magnetic-resonance point and be ejected. For this reason the evaporating RF field is gradually adjusted, or ramped, in order to access atoms lower in the potential well. An RF ramp lasting about ten seconds is necessary to cool the atomic cloud to just a few microKelvins; meanwhile the density climbs to roughly 10^{13} atoms/cm³.

A key diagnostic for temperature and density in experiments such as this goes by the name "absorption imaging." A near-resonant, large-diameter laser beam is briefly sent through the cloud and is caught on a camera ccd ("charge-coupled-device") sensor. The atoms in the cloud absorb some of the light, and the shadow they leave in the beam is easily captured by the camera and recorded on a computer. Analysis of an image yields the size and optical thickness of the cloud, and thereby the number and density of atoms. The cloud's temperature is obtained when the trap is turned off and the cloud is allowed to expand for a few milliseconds (the increased cloud size indicates the mean atomic speed).

It is remarkable that these techniques can be used to produce samples of metastable helium cold enough to reach Bose-Einstein condensation. For each of the trapped atoms, the 20-eV of energy in the excited electron exceeds the mean thermal energy by ten orders of magnitude. When two such atoms collide, their interaction can destabilize the electronic states and cause a destructive "explosion." This process, known as Penning ionization, tears an electron off of one atom and sends the other atom into its ground state (1S_0). None of the collision products remain trapped, and they all emerge with considerable kinetic energy. This process is the main loss mechanism in traps for helium atoms in the metastable 2^3S_1 state. However, in a spin-polarized, ultracold sample, it is strongly suppressed by the conservation requirement for the total spin projection of the system. During the evaporation/collisional-thermalization procedure, this conservation principle serves as a necessary safeguard against the otherwise certain self-destruction of the atomic sample.

The production of giant helium dimers relies on a very different inelastic collision process, one that is far gentler than Penning ionization. In the process of photoassociation, two He* atoms absorb a laser photon, and the system is excited into a bound state of a long-range molecular potential well. This potential, labeled as 0_u^+ (see fig. 3), is one among a jungle of different possible potentials that arise from the various combinations of atomic quantum numbers. A key feature of all the molecular potentials accessible via photon absorption is a "resonant dipole-dipole" interaction that varies as $1/r^3$ (where r is the internuclear distance) has a range extending to tens of nanometers. This interaction can be attractive or repulsive, depending on the relative orientations of the atomic electric dipoles. However, for a system characterized by the 0_u^+ potential, the atomic fine-structure interaction between the spin and orbital angular momenta of the electrons provides an intriguing modification. It effectively causes internal torques on the atomic dipoles, so that they are oriented so as to produce repulsion at distances shorter than about 10 nm and attraction for distances greater than this. In more technical terms, it causes an "anti-crossing" between attractive and repulsive $1/r^3$ potentials, leaving a local minimum at $r \sim 10$ nm. Thus, two He* atoms that are initially approaching (or receding from) each other in this distance range can absorb a photon from the photoassociation laser and find themselves caught in a potential well. The two once-independent atoms are stuck together in the form of a giant dimer.

In practice, the photoassociation laser is applied for only a few milliseconds, and within each of these pulses, the laser frequency is set to a value within the ~ 2 GHz range covering the energy depth

▲ **Fig. 2:** Diagram of the magnetic trap (its 3 coils around a vacuum chamber) holding atoms that have been decelerated, cooled and trapped by laser beams. (1) An atomic beam enters from the left after being decelerated to 20 m/s, and the atoms are captured in a magneto-optical trap (decelerating and trapping laser beams are not shown). The cloud of atoms is subsequently held by magnetic fields and cooled evaporatively to a few microKelvins. (2) A frequency-tunable photoassociation laser with is applied for a few milliseconds (3) A probe laser is used to obtain an absorption image of the cloud.

▲ **Fig. 3:** Interaction potentials for two helium atoms as a function of their separation. Below: The potential for both atoms in the metastable 2^3S_1 (He*) state. Above: The purely long-range (0_u^+) potential well supporting a bound state that is excited through the absorption of a photon from the photoassociation laser. Note the different energy and distance scales for the two curves. The potential below is flat except at extremely short distances. The one above, in which giant dimers are created, is weakly attractive at very long distances.

of the 0_u^+ potential well. Subsequent to each application of the photoassociation laser, an absorption image of the trapped cloud is obtained. The images reveal resonant absorption for particular photoassociation frequencies corresponding to the quantized energies of vibrational states in the potential well. This conclusion is supported by two pieces of information: first, there are resonant decreases in the integrated optical density of the cloud, which indicates a loss of independent He^* atoms; and second, there is an even more pronounced increase in the temperature of the cloud, which is attributable to the release of kinetic energy that occurs when the giant dimers decay. Figure 4 shows such a "calorimetric" signal for one of the molecular resonances.

In all, five bound states have been found in the 0_u^+ well, and their energies agree (to better than 1%) with those predicted by models involving the internal atomic structure and the resonant dipole-dipole interaction. The agreement is especially remarkable because the computational model completely neglects the uncertain electrostatic repulsion that provides the inner-wall for normal molecules. The fact that the r -dependence of the 0_u^+ potential emerges entirely from the long-range ($1/r^3$) interaction, even for short distances, puts the giant helium dimers in the category of "purely long-range molecules" that were first predicted by Stwalley, et al [5]. However, helium is the simplest atom for which such molecular states have been studied, and the comparison between experiment and theory is consequently simpler and more accurate. In fact, the precision is so high that retardation effects must be included in the model of the molecular interaction.

The convergence of theory and experiment offers an opportunity to characterize the sizes of the giant dimers in more detail. The steep inner wall of the potential yields an inner turning point around 8 nm for all of the bound states. The outer turning points range from about 14 nm for the lowest state in the potential to about 60 nm for the highest state. These are the largest interatomic distances ever observed in any dimer.

A skeptic might object that these so-called dimers are not rightful molecules at all, but rather short-lived complexes of independent atoms. But some dynamical considerations support the molecular designation. First, there is the observed experimental resolution. The widths of the resonant peaks are on the order of 5–10 MHz, which suggests that the structure lasts typically more than 10 ns. The frequency spacings between bound states of the 0_u^+ well range from tens to hundreds of MHz and relate roughly to the frequencies of molecular vibration. Thus, there is indeed time for many oscillations of the long-range dimer. In addition, the observed oscillation frequencies do not change noticeably if a 1-mT change in magnetic field is introduced. If the spectrum had a purely atomic basis, one would expect resonance lines to exhibit large Zeeman shifts proportional to the atomic Landé g factor. The absence of such shifts suggests that a molecular interaction has overtaken the atomic magnetic dipoles and hampered their ability to remain oriented with respect to the applied field.

While the ability to produce giant dimers has been established, several questions remain. In particular, the details of the molecular decay mechanism are still under investigation. It is clear that decaying dimers deposit kinetic energy into the trapped atomic cloud, but not much is known about the decay products (atoms and/or ions) that transfer the energy through collisions. One hint may come from photoassociation experiments in the group of Peter van der Straten at Utrecht, in which the ion production in a He^* MOT is monitored. Whereas several molecular resonance lines are observed, none of them correspond to the states of the giant dimer. This suggests that the decay of the dimer is not dominated by a process like Penning ionization, and perhaps also that

▲ Fig. 4: A resonant temperature increase in the trapped atomic cloud is observed when the photoassociation laser frequency is scanned across a bound state in the long-range potential well.

the spin-conservation principle that enables evaporative cooling to work somehow still applies in the more complicated context of this molecule. Further analysis will be required before this possibility is fully understood, and many more experiments will have to be done in order to sort out the heating mechanisms in the cloud. ■

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