Observation of the Efimov state of the helium trimer

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Quantum theory dictates that upon weakening the two-body interaction in a three-body system, an infinite number of three-body bound states of a huge spatial extent emerge just before these three-body states become unbound. Three helium (He) atoms have been predicted to form a molecular system that manifests this peculiarity under natural conditions without artificial tuning of the attraction between particles by an external field. Here we report experimental observation of this long-predicted but experimentally elusive Efimov state of 3He by means of Coulomb explosion imaging. We show spatial images of an Efimov state, confirming the predicted size and a typical structure where two atoms are close to each other while the third is far away.

Figure 1 summarizes two facets of Efimov's prediction: the energy spectrum and the structure of an Efimov state. Figure 1A shows how the two- and three-body binding energies (the binding energy of an atomic cluster is defined as the energy needed to separate all constituents of the cluster to infinite distances) change as the depth of the two-body potential is increased. As indicated by the arrow above Fig. 1A, the depth of the two-body potential increases along the horizontal axis. As the depth increases, the s-wave scattering length $a$ changes from negative values to infinitely large values to positive values. Negative $a$ values correspond to the domain where shallow two-body bound states do not exist. For positive $a$, a shallow two-body bound state, the dimer (blue solid line in Fig. 1A), exists. Bound three-body states (called trimers) exist in the green-shaded region (two electrons and a nucleus) heralded the demise of Niels Bohr's program of semiclassical atomic physics (2). Quantum mechanics then added yet another surprising twist to the three-body problem, when in 1970 Vitaly Efimov predicted the appearance of an infinite series of stable three-body states of enormous spatial extents (2). These Efimov states are predicted to exist for short-range interactions such as the van der Waals force between atoms or the strong force between nucleons.

When the potential becomes so shallow that the last two-body bound state is on the verge of becoming unbound or is unbound, then three particles stick together to form Efimov states. This three-body behavior does not depend on the details of the underlying two-body interactions. This makes the Efimov effect a universal phenomenon, with important applications in particle, nuclear (3, 4), atomic (4), condensed-matter (5), and biological physics (6).

ever since the early days of celestial mechanics, the three-body problem has posed a major challenge to physicists. In the early 20th century, the failure to find a stable solution for the classical helium (He) atom (two electrons and a nucleus) heralded the demise of Niels Bohr’s program of semiclassical atomic physics (2). Quantum mechanics then added yet another surprising twist to the three-body problem, when in 1970 Vitaly Efimov predicted the appearance of an infinite series of stable three-body states of enormous spatial extents (2). These Efimov states are predicted to exist for short-range interactions such as the van der Waals force between atoms or the strong force between nucleons. When the potential becomes so shallow that the last two-body bound state is on the verge of becoming unbound or is unbound, then three particles stick together to form Efimov states. This three-body behavior does not depend on the details of the underlying two-body interactions. This makes the Efimov effect a universal phenomenon, with important applications in particle, nuclear (3, 4), atomic (4), condensed-matter (5), and biological physics (6).
Efimov trimer extends out to 300 Å (1 Å = 0.1 nm); i.e., the Efimov trimer is about 100 times larger than a typical chemically bound triatomic molecule. Moreover, the ideal Efimov state is highly diffuse and does not display a predominantly equilateral triangular or linear shape.

Despite their relevance across different subfields of physics, these spatially extended and weakly bound trimer states have proven extremely challenging to prepare and detect, and experimental evidence for the Efimov effect was reported only in 2006 (7) (36 years after its theoretical prediction), stimulating a great deal of continued experimental activity. Experimental signatures to date have come from loss measurements or spectroscopy on trapped cold-atom systems. In experiments of this type, the two-body interaction is tuned in the vicinity of a Feshbach resonance through the application of an external magnetic field. Signatures of the Efimov effect are then obtained by monitoring the atom loss from the trap due to the formation of Efimov trimers at scattering lengths for which the trimer energy coincides with that of three free atoms (these scattering lengths are marked by asterisks in Fig. 1A). The most direct probe of Efimov trimers to date comes from radiofrequency spectroscopy on an ultracold three-component lithium gas, which yielded the binding energies of an Efimov trimer for different two-body interaction strengths (8, 9). An experimental exploration of the size and shape of Efimov states requires a setup where the trimer is sufficiently long-lived and can be imaged selectively. These two demands prove challenging for cold-atom experiments. The experiments reported in this work circumvent these challenges by working with a different species, namely 4He, and a completely different experimental approach.

The He trimer is a paradigmatic molecular system that is believed to support an Efimov state. In fact, it was already predicted in 1977 to be a prime candidate with which to study Efimov physics (10). Theoretical calculations based on the currently most accurate He-He potential (11) predict two bound states for the He trimer, the ground and excited states, with binding energies of 131.84 and 2.6502 mK, respectively (12). These states occur naturally along the vertical dashed line in Fig. 1A at a scattering length of a = 90.4 Å (11). The excited state has one node in the hyperradial coordinate, indicating a vibrational excitation that is reminiscent of a breathing mode in classical tritatomic molecules. Our calculations, shown by the green and red lines in Fig. 1A, conclude, in agreement with earlier works (4, 10, 13–16), that an artificial strengthening of the pair interaction (see the right pointing arrow above Fig. 1A) renders the excited state of the He trimer less strongly bound with respect to the dimer, thus confirming the Efimov character of the trimer state. This character is further supported by the appearance of a second Efimov state upon an artificial weakening of the true two-body He-He potential (dashed black line labeled 2nd ES in Fig. 1A).

The energy ratio of two neighboring Efimov states for infinitely large s-wave scattering length is 22.72. Correspondingly, the excited state is about 22.7 larger than the ground state (Fig. 1, B and C). The energy ratio decreases when the scattering length takes finite positive values. For the scattering length corresponding to He, Efimov’s radial law predicts an energy ratio of 5.02. The energy ratio of the ground and excited state of the true He trimers is larger than predicted by Efimov’s theory, namely 7.02, owing to the fact that the ground state of the He trimer is not an Efimov state.

Because of the very low binding energy, the 4He trimer lacks rotational states, which implies that common structural experimental tools such as rotational spectroscopy cannot be applied. The 4He trimer ground state was observed experimentally in 1996 by Schöllkopf and Toennies (17), using matter-wave diffraction of He clusters from a transmission grating. Concerted experimental efforts, however, did not provide any evidence for the existence of the excited state of the 4He trimer (18, 19).

Here we report experimental observation of the Efimov state of the He trimer; the creation of this stable state in a “natural” field-free environment allows us to directly investigate the structural aspects of Efimov physics and take real-space images of the square of the wave function of an Efimov state using Coulomb explosion imaging. The obtained experimental distributions are in good agreement with those obtained from full first-principles quantum-mechanical calculations (20, 21) that use the currently most accurate He-He potential published by Cencek et al. (11).

The He clusters were prepared in a molecular beam under supersonic expansion of gaseous He at a temperature of 8 K through a 5-μm nozzle. The cluster yields were tuned by varying the nozzle back-pressure. He trimers were selected from the molecular beam by means of matter-wave diffraction (17). The selection removed an overwhelming fraction of He monomers that dominates the molecular beam under all expansion conditions. All three atoms of a trimer were then singly ionized by a strong ultrashort laser field (30 fs, 780 nm, >3 × 1015 W/cm2). Because the ionization process is essentially instantaneous, the quantum-mechanical probability distributions...
of the neutral trimers provide the initial configurations for the subsequent Coulomb explosion (22) of the triply charged trimers. The momenta acquired during the explosion of the ions were measured by cold target recoil ion momentum spectroscopy (23, 24). From these momentum vectors, the initial spatial geometry of the three charged fragments at the instant of ionization was reconstructed using Newton’s equation of motion (for details, see the supplementary materials). A simple global observable related to the structure is the total kinetic energy of all three ions [kinetic energy release (KER)]. In the Coulomb explosion, the total potential energy of the three charges with interparticle distances \( R_{ij} \) is converted into KER (in atomic units)

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K_{\text{ER}} = 1/R_{12} + 1/R_{13} + 1/R_{23}
\]  

(1)

The measured KER distributions corresponding to the He trimer at two different nozzle backpressures are depicted in Fig. 2A. At a pressure of 1.7 bar (Fig. 2A, blue curve), only one peak with a maximum at 5 eV is observed. This peak corresponds to the ground state of the He trimer, with an average He-He distance of 10.4 Å (25). At a lower nozzle pressure of 330 mbar (Fig. 2A, black curve), an additional peak with a maximum at 0.57 eV emerges. This low-energy feature corresponds to structures that are about eight times larger than those of the ground state. Such large spatial extent (≈80 Å) has been predicted for the excited state of the \(^4\)He trimer (22, 26, 27). Indeed, the KER distribution (Fig. 2A, violet curve) calculated from the full quantum-mechanical probability distribution of the excited He trimer using Eq. 1 resembles the experimental observation (difference spectrum in red, Fig. 2A) very closely.

As Fig. 2A shows, the yield of the \(^4\)He\(_3\) excited state is sensitive to the expansion conditions. The detailed analysis of the pressure dependence shows that the maximum rate of the excited state of the \(^4\)He trimer is achieved not at pressures with the highest yield of the ground state of the trimer, but rather at pressures that favor dimer formation (Fig. 2B). This might be an indication that two He dimers are required for the formation of the excited He trimer during the supersonic expansion; the formation mechanism of the ground-state trimer is seeded primarily by collisions between one He dimer and two He monomers (28). Another interpretation of the observed pressure dependence of the excited state yield might be an increased collision-induced breakup rate of excited trimers in an expansion at higher pressures due to increased translational temperatures (28). The highest ratio of the excited-to-ground-state He trimer populations of about 4% was found at the lowest pressure used in the experiment, namely at 200 mbar. At a pressure with the maximum yield of the trimer ground state, we could not detect any contribution of the excited state. This very weak relative yield of the excited state explains why it was not observed in the experiment of Toennies and co-workers (25), with an estimated detection limit of 6%.

Figure 2 establishes unambiguously that the He trimer excited state is stable and can be prepared reliably in an experiment. In order to deduce quantitative information about the structural properties of the excited He trimer from the measured momenta, we used classical mechanics to invert the Coulomb explosion [see (25) and the supplementary materials for details]. Unfortunately, there is an ambiguity of momentum-to-structure relation in the small region of the structural space. This results in the reconstruction of some number of irrelevant geometries. In order to overcome this issue, the irrelevant structures were filtered out during reconstruction (for details, see the supplementary materials).

Figure 3 shows the reconstructed pair distance distributions for the excited state (red and black) and the ground state (blue) of \(^4\)He\(_3\). The red and black distributions differ in how the excited-state structures are separated from the ground-state structures. The separation is necessary because the wave functions of both states overlap spatially in the range of lower pair distances, and the ground state always dominates in the experiment. By applying a filter in the momentum space (for details, see the supplementary materials), we were able to choose momenta that mainly relate to the excited state of \(^4\)He\(_3\) (Fig. 3, black). However, some
structures of the excited state have been cut by the filter, resulting in the discrepancy below a pair distance of 50 Å. An alternative way of obtaining the excited-state distribution is subtraction of the reconstructed distribution of the ground state from the distribution of the mixture of the ground and excited states (Fig. 3, red). This approach still fails to give an accurate reproduction of the distribution in the lower pair distance range, because of the overwhelming amount of the ground state, whose distribution spreads up to 50 Å (Fig. 3, blue). At larger distances (>100 Å), however, both

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**Fig. 3. Pair distance distributions $P_{\text{pair}}(R)$ of the He$_3$ excited state.** The red circles represent the difference between the mixture of the excited- and ground-state distribution (measured at a nozzle pressure of 330 mbar and a temperature of 8 K) and the ground-state-only distribution (1.7 bar, 8 K, blue line). The error bars correspond to a confidence interval of 68%. The ground-state distribution was normalized to the quantity of ground-state structures under conditions where the excited state was measured (300 mbar, 8 K). The black histogram corresponds to the distribution that was obtained from the measured momenta of the ground- and excited-state mixture by filtering out the structures with higher KERs (for details, see the supplementary materials). Experimental distributions have been reconstructed from the measured momenta, using Newtonian mechanics to invert the Coulomb explosion. The theoretical pair distance distribution of the excited He trimer is shown in purple.

**Fig. 4. Structures of the He trimer.** (A and B), respectively, show the theoretical and experimental excited-state structure; (C) shows the theoretical ground state. Note the different scale for the ground state structure. For the plots, the center of mass of the trimer was shifted to the origin. The structures were rotated so that the principal axis with the smallest moment of inertia lay along the $y$ axis. Additionally, if required, the structure was mirrored with respect to the $x$ or $y$ axis in order to get one He atom in the first quadrant and the other two in the third and fourth quadrants. The corresponding normalized structures are plotted in (D to F). The structures are normalized to the largest pair distance and subsequently located so that the two atoms with the largest pair distance get coordinates (−0.5,0) and (0.5,0) and the position of the third atom is plotted. The gray rectangle in (E) relates to structures that were cut during the reconstruction (see the supplementary materials for details). The linear color scale encodes the number of entries. The typical structure of the excited state of the He$_3$ is sketched in the upper right corner of (D).
experimental pair distance distributions of the excited state are nearly identical and match the theoretical distribution (Fig. 3, violet) very well.

The measured pair distribution (Fig. 3) can be used to extract the binding energy of the excited state. The excited He3 exists mainly in the classically forbidden region well outside the two-body interaction potential well. Therefore, the asymptotic part of the pair distance distribution $P_{\text{pair}}(R)$ can be approximated by an exponential decay function (2)

$$P_{\text{pair}}(R) \propto e^{-2\sqrt{\Delta B R^2}/\hbar R}$$

where $R$ denotes the He-He distance, $\mu = 2 \times m_{He}/3$ is the reduced mass of the He trimer, and $\Delta B$ is the difference between the binding energies of the excited trimer state and the dimer ground state. Fitting the falling edge of the reconstructed pair distance distribution (black curve, Fig. 3) by Eq. 2 yields $\Delta B \approx 0.98 \pm 0.2$ mK (for details, see the supplementary materials). Given a theoretical prediction for the dimer binding energy of 1.62 mK ($\hbar$), we obtain a binding energy of the trimer excited state of 2.6 ± 0.2 mK. This is in excellent agreement with our theoretical value of 2.65 mK, as well as with a theoretical value of 2.6502 mK from (12).

Having established the spatial extent of the He3 Efimov state, we now discuss its geometric shape revealed by the structural plots shown in Fig. 4. The plots in the upper row [(A) to (C)] of Fig. 4 are generated in the center-of-mass coordinate frame, with the principal axis of the smallest moment of inertia chosen to lie along the $y$ axis as proposed by Nielsen et al. (26). In the plots of the lower row [(D) to (F)] of Fig. 4, the interparticle distances of each reconstructed geometry were initially normalized to the largest of the three interparticle distances. Subsequently, the two atoms with the largest pair distance were placed at positions $(0,-0.5,0)$ and $(0,0,0)$, and the position of the third atom was plotted. In these plots, the equilateral triangle corresponds to $(x,y,z) = (0, \sqrt{3}/2, 0)$, and linear configurations have $y = 0$. The structure in which two particles are close to each other, with the third particle being far away, corresponds to $(x,y,z)$ being close to $(0,0,-0.5)$ or $(0,-0.5,0)$.

The geometry of the Efimov state is remarkably different from that of the ground state. Whereas the ground state corresponds to an almost randomly distributed cloud of particles (25), the excited Efimov state is dominated by configurations in which two atoms are close to each other and the third one farther away, in the classically forbidden region of the two-body interaction potential. According to theory, the average value of the smallest angle in the triangle is 18°. This typical structure of the $^3$He$_3$ excited state is in accordance with the prediction of Nielsen and coworkers (26) and in line with a dimer-like pair model proposed by Hiyama and Kamimura (29), which explains the asymptotic behavior of the excited state of the He3. More generally, the typical structure revealed by Fig. 4 is an intrinsic property of all Efimov states with positive two-body scattering length. Comparison with Fig. 1B shows that the geometrical structure of the real He$_3$ excited state is similar to the one of the hypothetical He trimer with an infinite scattering length, although the amount of triangles with a small acute angle is reduced in the latter case (see also Fig. S7).

We have reported the observation of the elusive Efimov state of the $^4$He trimer by means of Coulomb explosion imaging of mass-selected clusters. We have found that the dominant structure of an Efimov state with positive two-body scattering length is a triangle with a relatively small acute angle. This has important consequences for how Efimov states are formed and possibly excited, as it is the geometry that defines the Franck-Condon overlap with continuum as well as with bound states. Having demonstrated the ability to experimentally image the quantum-mechanical probability distribution of Efimov trimers, this work opens the door for quantitative studies of Efimov physics beyond the geometrical scaling properties and energetics. Extensions of the imaging approach to the four-body sector appear feasible.

**REFERENCES AND NOTES**


**ACKNOWLEDGMENTS**

The experimental work was supported by a Reinhard Kesseler project of the Deutsche Forschungsgemeinschaft. The financial support of the Goethe-University Frankfurt am Main is gratefully acknowledged. D.B. acknowledges support by the U.S. National Science Foundation through grant number PHY-1205443. Authors thank J. Williams for the proofreading of the manuscript. Raw data are archived at the Goethe-University Frankfurt am Main and are available upon request.

**SUPPLEMENTARY MATERIALS**

www.sciencemag.org/content/348/6234/551/suppl/DC1

**MATERIALS AND METHODS**

Figs. S1 to S7

References (30–32)

23 December 2014; accepted 25 March 2015

10.1126/science.aaa5601

**IONIC INTERACTIONS**

Subnanoscale hydrophobic modulation of salt bridges in aqueous media

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Polar interactions such as electrostatic forces and hydrogen bonds play an essential role in biological molecular recognition. On a protein surface, polar interactions occur mostly in a hydrophilic environment because nonpolar amino acid residues cover ~75% of the protein surface. We report that ionic interactions on a hydrophilic surface are modulated by their subnanoscale distance to the surface. We developed a series of ionic head groups—appended self-assembled monolayers with C2, C6, C8, and C12 space-filling alkylic chains, which capture a dendritic guest via the formation of multiple salt bridges. The guest release upon protonolysis is progressively suppressed when its distance from the background hydrophobic changes from 1.2 (C2) to 0.2 (C12) nanometers, with an increase in salt bridge strength of ~3.9 kilocalories per mole.

Oppositely charged polar residues often conjugate to form ion pairs at interfaces of biomolecules, as well as in nonbiological systems (1, 2). Despite the general importance of ion pairing in biological phenomena (3), effects of interfaces on ion-pairing interactions have not been well understood to date (2, 4, 5). In relation to this point, a prime issue is how diversity of biomolecular recognition has developed from a limited variety.
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Science 348 (6234), 551-555.
DOI: 10.1126/science.aaa5601

Helium caught in the act of triangulating

Helium is the noblest of noble gases, almost completely unattracted to itself or any other chemical element. Of course, when quantum mechanics comes into play, that “almost” is an inevitable caveat. For several decades, researchers have been intrigued by a theoretically predicted Efimov state composed of three helium atoms held loosely together in a triangle. Kunitski et al. now report experimental realization of that state and detection of its acute triangular geometry (see the Perspective by Kornilov). Beyond completing a long quest in helium studies, the results shed light on three-body physics more broadly.

Science, this issue p. 551; see also p. 498