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# The Weakest Bond: Experimental Observation of Helium Dimer

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Helium dimer ion was observed after electron impact ionization of a supersonic expansion of helium with translational temperature near 1 mK. The dependence of the ion signal on source pressure, distance from the source, and electron kinetic energy was measured. The signal was determined to arise from ionization of neutral helium dimer.

## INTRODUCTION

$He_2$ has been the only rare gas dimer not experimentally observed. Theoretical studies have yielded mixed results on the question of whether a bound state of $He_2$ should exist, due to the fact that the best calculations predict a zero-point energy almost exactly equal to the well depth. Tiny errors can therefore shift the calculated energy of this state from a value which is slightly negative with respect to the separated atoms to one which is slightly positive, or *vice versa.* This unique circumstance requires unprecedented accuracy in an *ab initio* calculation to achieve a definitive result.[1] The fact that this real or virtual state of $He_2$ is nearly resonant with the zero kinetic energy state of the separated atoms is also responsible for the extraordinary cooling which occurs through long-range interactions in extreme He expansions.[2–4]

Theoretical interest in the helium dimer dates back to at least 1928, when Slater[5] calculated a well depth of 8.9 K. A long series of subsequent calculations has yielded well depths ranging from 0 to 13 K. Recent *ab initio* work[1,6,7] seems to be converging on a well depth of about 10.9 K at a nuclear separation of 2.97 Å, supporting one bound state with binding energy between 0.8 and 1.6 mK. These results agree with the empirical potentials of Aziz *et al.*,[8–10] who have fitted analytic functions to a wide range of data on virial coefficients, viscosities, and scattering. Chałasiński and Gutowski[11] give a good review of the theoretical challenges and approaches.

Experimental work on clusters of helium in the gas phase began in 1961 when Becker *et al.*[12,13] observed clusters in an expansion of helium from a nozzle at 4 K. Subsequent work has used similar techniques. Gspann[14,15] has studied very large clusters. Toennies *et al.*[16] have made several studies of clusters from cryogenic sources. Van Deursen and Reuss,[17] and later Stephens and King,[18] studying smaller clusters, observed helium dimer ion signal in mass spectrometers from cryogenic expansions. Those workers were not able to conclude, however, that the dimer ions were being produced by ionization of a neutral dimer. Ionization of a larger cluster followed by fragmentation seemed the more likely source. Toennies has described much of this work in a recent review.[16] In addition, differential and integral scattering experiments have been used to extract potentials.[19–21]

Our work on helium dimer was prompted by the observation[2] several years ago that it is possible to attain temperatures as low as 0.3 mK in extreme pulsed expansions of pure helium from room temperature sources. Since recent calculated binding energies of helium dimer are in the 1 mK range, it seemed reasonable to think it might be found in measurable concentrations in such beams.

## EXPERIMENT

In our new apparatus, a pulsed valve opens into a large (1.6 m diam$\times$3.1 m long) vacuum chamber with a skimmer (8 mm diam orifice) at its far end and evacuated by two diffusion pumps of rated speed 62 500 l/s. A flight tube extends from the skimmer. Typical background pressures in the expansion chamber and flight tube are $4.0\times10^{-7}$ and $5.0\times10^{-8}$ Torr, respectively. Approximately 300 mm past the skimmer is a rotating blade which is used as a chopper for speed distribution measurements. At distances of 3.61 m ("near") and 15.40 m ("far") from the chopper are two electron impact ion sources. Ions are accelerated perpendicular to the neutral beam path into 300 mm radius, 60° sector-field mass spectrometers with Daly[22] ion detectors. Bulkheads with rectangular skimmers were placed in the flight tube 150 mm upstream of each ionizer. The skimmer apertures limit the acceptance of the near ionizer to a rectangle 2.0 mm wide and 10 mm high, and that of the far ionizer to one 5.2 mm wide and 13 mm high. The sizes were chosen to equate the angles subtended in the horizontal plane from the nozzle by the two ion sources.

The ion pulses are amplified and stretched to approximately 1 $\mu$s by preamplifiers and accumulated in a dual-channel transient digitizer (Gage Applied Sciences CS220) typically sampling at 2 M samples/s.

The pulsed valve was constructed from a piezoelectric translator (Physik Instrumente) with approximately 0.08 mm travel. The needle tip was made of Vespel[23] polyimide plastic, with a 90° conical point. It sealed against a stainless steel nozzle with a 100° entrance angle and a 0.15 mm orifice approximately 0.15 mm long, followed by a 120° diverging section 1.25 mm long. The gas pulses were about 250 $\mu$s long, and the valve could be operated reliably at stagnation pressures up to 130 bar. The valve was operated at room temperature.

Helium was obtained from Air Products (99.995% stated purity) and used without further purification. It was handled with a stainless steel vacuum line which was evac-

 

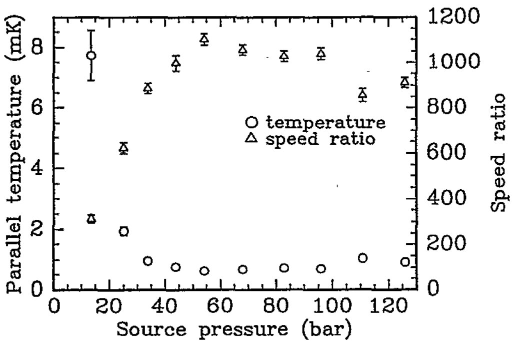


FIG. 1. Temperatures (circles) and speed ratios (triangles) of the helium beam measured at different source pressures. Error bars are $\pm 2\sigma$ (95% confidence assuming normally distributed errors) from the nonlinear fits; the bar is not shown if it would be smaller than the symbol.

uated to below 30 mTorr with a mechanical pump before use. Source pressures were measured with a Bourdon gauge.

## RESULTS

Speed distribution measurements were made by timing the valve so that the rotating chopper intersected every other pulse, and subtracting alternate pulses collected at both the near and far detectors. The difference signals thus obtained represented the modulation induced by the chopper. The translational temperature was extracted by a forward convolution technique from the difference signals at the two detectors. The measured temperatures and speed ratios are shown in Fig. 1 as functions of source pressure.

The signal intensities near the center of the pulse for signals at mass-to-charge ratios 4 and 8 (henceforth $I_4$ and $I_8$) were measured at the near mass spectrometer as a function of source pressure over the range 28 to 125 bar. Shown in Fig. 2 are $I_4$ and $I_8$ in a log–log plot against source pressure. Least-squares fits through the points with source pressure above 45 bar gave the lines shown; the stated uncertainties on the slopes are $\pm 2\sigma$. The $I_8$ signal from a single pulse at source pressure 125 bar was easily visible. The displayed data were obtained by summing signals from several hundred pulses.

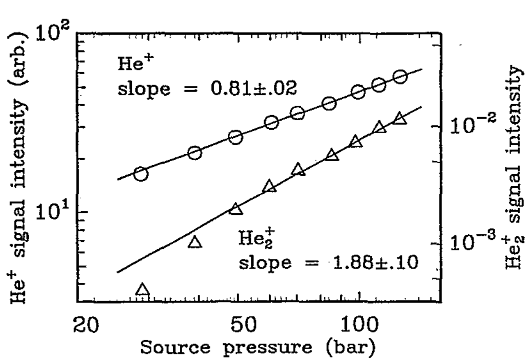


FIG. 2. Ion signal intensities $I_4$ (upper points) and $I_8$ (lower points) at different source pressures; note the different scales for $I_4$ and $I_8$. The lines are least-squares fits for points with $P_0 > 47$ bar.

$I_4$ and $I_8$ were also detected at the far mass spectrometer. The ratio $I_8/I_4$ was the same, 0.02%, at both detectors within an uncertainty of a factor of 2.

The dependences of $I_4$ and $I_8$ on electron energy were measured. The shapes of the curves were nearly identical, increasing monotonically over the range 30–100 eV and roughly constant from 100–160 eV.

In an attempt to detect the presence of higher clusters ($N>2$) in the beam, we carried out searches for signals at $m/q=12$, 16, 20, and 24 with negative results. For a beam expanded from 125 bar of pure $^4$He, we can place an upper limit of 0.008 on the ratio $I_{12}/I_8$. In a related experiment we searched carefully for $m/q=7$ signals from an expansion of a mixture of 6.8 bar of $^3$He and 99 bar of $^4$He. Again, we found no signal and can place an upper limit of 0.006 on the ratio $I_7/I_8$.

## DISCUSSION

An $I_8$ signal might appear for several reasons other than direct ionization of helium dimer. These include $O^{2+}$ from oxygen contamination in the source, collisional processes in the ionizer, and ionization of larger clusters followed by fragmentation. Each of these can be ruled out as the source of $I_8$ signals in our experiments.

$O^{2+}$ can be eliminated because of the pressure dependence data shown in Fig. 2. Oxygen contamination in the source would show the same dependence on pressure as the He atom signal. $I_8$ is proportional to $P_0^{1.88}$, while $I_4$ is proportional to $P_0^{0.81}$.

Of possible collisional processes in the ionizer leading to $He_2^+$, the most likely is associative ionization,

$$He+e^- \rightarrow He^* + e^-,$$

$$He^* + He \rightarrow He_2^+ + e^-.$$

For this two-body process (as well as for possible higher-order collision processes in the ionizer) attenuation of the molecular beam downstream of the region of dimer formation will attenuate the $He_2^+$ beam nonlinearly. If the He beam intensity is attenuated by a factor $n$, the associative ionization signal will be attenuated by a factor $n^2$. Since the far detector is 2.6 times farther from the source than the near detector, the $1/r^2$ decrease in density requires a decrease of He atom density at the far detector by a factor of at least $1/(2.6)^2$, or 0.16. The ratio $I_8/I_4$ at the far detector must therefore decrease by at least a factor of 0.16 from that at the near detector if a two-body process in the ionizer is producing $I_8$. We observe equal ratios $I_8/I_4$ at the two detectors with an uncertainty less than a factor of 2.

Associative ionization can also be ruled out on the basis of the similar dependences of $I_4$ and $I_8$ on ionizing electron energy. This result stands in sharp contrast to that obtained by Hornbeck and Molnar[24] for associative ionization. In their experiment, the $He_2^+$ signal passed through a maximum at electron energy near 30 eV and then dropped sharply. In the case of argon dimer, Helm *et al.*[25] observed that the electron energy dependences for Ar dimer and monomer ionization were similar, while the associative ionization energy dependence showed a sharp maximum at relatively low electron kinetic energy.

Finally, we must consider the possibility that $He_2^+$ ions are produced by ionization and subsequent fragmentation of He clusters of three or more atoms. Here we rely most heavily on the source pressure dependence data shown in Fig. 2. The following arguments support the hypothesis that the $I_8$ signal is due to ionization of the neutral helium dimer rather than a larger cluster:

(1) The reduced signal $I_8/I_4$ at source pressures above 50 bar shows a linear dependence on source pressure.

(2) A linear dependence of the reduced cluster density $\rho_2/\rho_1$ is to be expected based upon definitive experiments with unambiguously size-selected Ar clusters, as well as theoretical modeling of the expansion dynamics.

(3) Previous observations[17,18] of $He_2^+$ in milder expansions from cryogenic sources, probably producing trimer, have shown a cubic pressure dependence (meaning the reduced signal is roughly quadratic).

(4) The deviations which we observe from a linear dependence of $I_8/I_4$ at source pressures below 50 bar are consistent with the measured beam temperature and a dimer binding energy of order 1 mK.

(5) Attempts to observe any signals from higher clusters with $N>2$, or dimer signals at $m/q=7$ from expansions of a $^3He$, $^4He$ mixture yielded only negative results.

Under the nonequilibrium conditions of a molecular beam, one cannot, in general, demonstrate that the source pressure dependence of clusters of size $N$ will have the form $P_0^N$. However, for monatomic gases, it is possible to use a model similar to the sudden-freeze model of the supersonic expansion[26] to show that a lower bound for the exponent $\alpha$ in the pressure dependence expression $\rho_N/\rho_1 \propto P_0^\alpha$ is $N-1$. To make this estimate, we postulate that the concentrations of cluster and monomer are in equilibrium up to some terminating surface, beyond which the cluster mole fraction remains constant. In addition, we assume that the expansion is described by isentropic continuum hydrodynamics at least up to that surface. The expression for equilibrium constants of association reactions from statistical mechanics, together with the condition for the monomer density $\rho/\rho_0=(T/T_0)^{1/(\gamma-1)}$ from continuum hydrodynamics then gives

$$\rho_N/\rho_1=\rho_0^{N-1}(h^2/2\pi mk_BT_0)^{(3/2)(N-1)}N^{3/2} \times \sum \exp(-E_i/k_BT).$$

Here $\gamma$ is the heat capacity ratio (5/3), $\rho_0$ is the He density in the source, $m$ is the He atomic mass, $E_i$ is the internal energy of cluster state $i$, $k_B$ and $h$ are the constants of Boltzmann and Planck, and the summation is over all internal states $i$ of the cluster. If $T$ (the temperature at the point where the dimer concentration freezes) is not a strong function of source density, then the ratio of cluster density to monomer density in the detector will be proportional to $\rho_0^{N-1}$. If $T$ is a decreasing function of $\rho_0$, as expected, then the reduced cluster density will show a higher pressure dependence. We should note that the above equation is valid only for gases with $\gamma=5/3$.

These theoretical arguments are supported by the elegant experimental work of Buck *et al.*,[27] who measured source pressure dependences of argon clusters of different sizes. Their work employed a scattering technique which allowed unambiguous assignment of cluster sizes independent of fragmentation in the detector. They observed that the ratio of argon cluster density to atom density was approximately proportional to $P_0^{N-1}$ for $N$ up to at least 4. These results agree with those of other experiments[28] in which care was taken to account for fragmentation of cluster ions.

With respect to point (3) above, van Deursen and Reuss[17] and Stephens and King[18] observed $m/q=8$ signals in supersonic expansions of He from cryogenic sources. Those signals showed a $P_0^3$ dependence on the source pressure. Van Deursen and Reuss concluded that their dimer ion signal was being produced by ionization of trimer followed by fragmentation, while Stephens and King were unable to establish the identity of the parent cluster.

With regard to point (4), we note that the linear pressure dependence of $I_8/I_4$ is expected only for a "freezing temperature" $T$ independent of source pressure. In our experiment, the terminal translational temperature becomes constant only for source pressures greater than about 50 bar. At lower source pressure, where the final beam temperature rises above 1 mK, $I_8$ falls significantly below the extrapolated quadratic dependence on $P_0$. This is consistent with a dimer binding energy of order 1 mK, in agreement with recent theoretical predictions.

Finally, we consider our unsuccessful searches for ion signals at higher $m/q$ and for mixed $^3He/^4He$ dimer ion. Since $m/q=12$ signals are easily seen in beams from cryogenic sources,[17,18] their absence appears to be good evidence for the lack of contributions from trimers or larger clusters. The mixed species $^3He^4He$ is not bound,[4] so an $m/q=7$ ion could only arise from some other process such as ionization and fragmentation of a larger cluster. We were not able to detect any $m/q=7$ ions.

## CONCLUSIONS

We conclude that we have detected bound $^4He_2$ experimentally for the first time, and that the binding energy of this species must be of order 1 mK, as predicted from empirical and theoretical estimates of the potential. This is by far the weakest "bond" yet discovered. Among the interesting consequences of the extremely weak interaction are (1) that the $^4He_2$ species can exist in only one quantum state ($v=0$, $j=0$), and (2) that the wave function $\psi(r)$ must be delocalized over an extremely large range of separations $r$. Further experiments to characterize the structure and dynamics of this unusual molecule are under way.

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