Experimental Investigation of Small Helium Clusters: Magic Numbers and the Onset of Condensation

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Clusters of He atoms formed in a supersonic free jet expansion have been studied by electron-bombardment ionization and mass spectrometry. Distinct magic-number enhancements of ion intensity are observed for clusters of 7, 10, 14, and 30 atoms for both helium isotopes, and for 23 atoms of ^{4}He. Dramatic differences in the onset of cluster formation between the two isotopes may be related to the stability of ^{4}He dimers.

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Self-bound systems of N particles frequently exhibit exceptional stability at particular "magic" numbers. The most familiar examples of this phenomenon are the closed electron shells in atoms (2, 10, 18, 36, 54, etc.) and neutron and proton shells in nuclei (2, 8, 20, 28, 50, etc.). Recently, similar effects have been observed in rare-gas clusters,[1,2] produced by condensation in a free jet expansion of gas into vacuum. The cluster size distribution is studied by mass spectroscopy following ionization.

In view of the qualitative similarity between nuclear and van der Waals interactions, it is interesting to note that in the nuclear case, the packing responsible for the shell effect is in momentum space, with the Pauli exclusion principle acting to keep particles out of the same state. On the other hand, the structure of atomic clusters is presumably controlled by the direct overlap of repulsive atomic cores. Indeed, some of the magic numbers observed in Xe clusters were identical to closed shells of high-symmetry icosahedral packings of soft spheres.[1] Such a description fails to account for the magic numbers in Ar and Kr clusters,[2] casting doubt on the general validity of sphere-packing descriptions of cluster structure. It is therefore of interest to compare the previous results with a lighter system, such as He. As the only permanent liquid, He may show quantum effects absent from other rare gases. The comparison of the two isotopes may also aid the interpretation of experimental data.

Binding energies of He clusters have been calculated by a succession of increasingly accurate techniques, most recently by Pandharipande *et al.*[3] Their calculation was not carried out for a number of successive values of N; consequently, it makes no prediction of magic numbers. A liquid-drop formula fitted the energies for $N \geq 20$ within the stated error. In two different studies of small He clusters, van Deursen and Reuss observed the onset of condensation with mass spectrometric detection of $^4He_N^+$ with $N = 1-3$,[4] whereas Gspann *et al.* studied He droplets with 10^6 atoms.[5]

This Letter presents mass spectra of clusters produced in a supersonic free jet of He.[6] We report a significant magic-number effect. The observed magic numbers in He are not the same as those reported for other rare gases. We are currently unable to present any simple model for our observations.

Our experiment used a beam formed by the expansion of He gas at stagnation pressure P_0 and temperature T_0 into a vacuum.[7] Typical mass spectra for both isotopes are shown in Fig. 1. The two spectra have a number of similar features for $N \leq 20$. The magic-number effect in this mass region is slightly weaker than that of Xe,[1] Ar, and Kr.[2] For larger N, we increase the sensitivity to deviations from a smooth mass spectrum by plotting the ratio of signal currents between adjacent peaks in Fig. 1. For example, the step from $N = 23$ to 24 in ^{4}He, barely visible in the direct ion-current plot, stands out as a very large ratio. All of the features in Fig. 1 were reproduced in ~200 experimental mass spectra.

There are significant similarities and differences between the two isotopes. The large He_{30}^+/He_{31}^+ ratio implies an enhanced stability for clusters of 30 atoms, but the peaks in the ratio spectra at $N = 32/33$ in ^{4}He and $N = 21/22$ in ^{3}He are not seen in the other isotope. We note that the strong enhancements at $N = 10$ and 30, as well as the suppression at $N = 12$, are absent from other rare gases.[1,2] In addition, these He magic numbers fail to match shells of face-centered-cubic and other high-symmetry packings. As in the present work, an enhancement at $N = 23$ was seen in Xe and Ar, and cannot be linked to any known

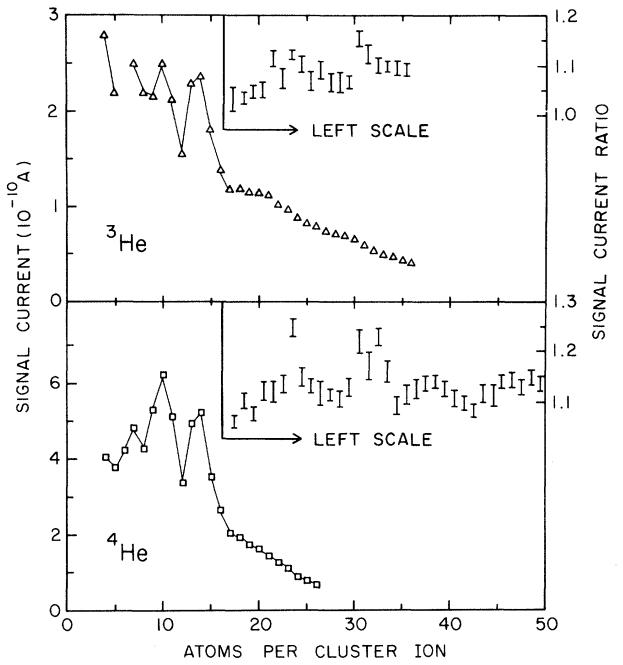

FIG. 1. Electron multiplier output currents from cluster ions of ^{3}He at $T_0 = 3.2$ K, $P_0 = 550$ Torr, and ^{4}He at $T_0 = 4.2$ K, $P_0 = 400$ Torr. Insets show ratios of adjacent peak amplitudes, ± standard deviation of 10–20 data points from different overlapping mass scans. A background interference problem precluded the measurement of the $^3He_6^+$ signal (Ref. 8).

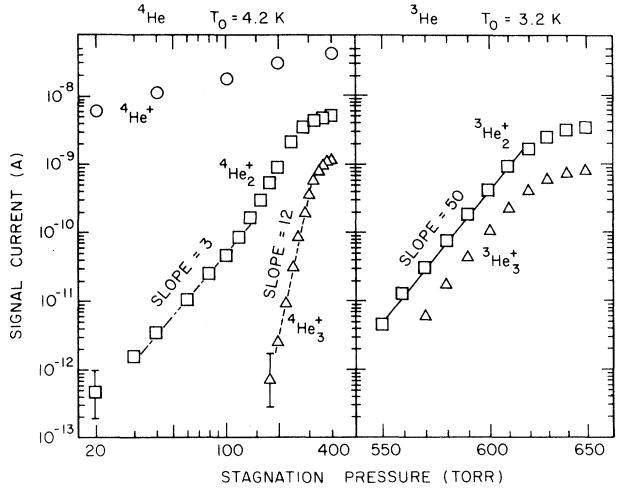

FIG. 2. Electron multiplier currents as a function of P_0. Note different horizontal scales. $^3He^+$ is off scale at 2.3×10^{-7} A.

packing structure.

To begin to interpret these mass spectra, it is important to establish the process responsible for mass selection. The authors of the Xe (Ref. 1) and Ar and Kr (Ref. 2) studies argue that there is some magic-number effect in the neutral clusters, which is preserved through ionization. Alternatively, the ionization event might leave the neutral cluster in a highly excited vibrational state. Then, with the cluster ion relaxing and evaporating atoms, the final ion spectrum would be representative of the relative stability of cluster ions. In the previous Ar, Kr, and Xe studies, the authors discount the role of fragmentation for two reasons: (1) the persistence of the magic-number effect when the mean cluster size was changed by variation of stagnation conditions, and (2) its persistence when the ionizing-electron energy was changed. While we observed a similar independence of mass spectrum on both parameters, we argue that neither excludes the loss of atoms in the ionization event for the following reasons: (1) If the ion distribution were set in the process of relaxation, local features of the ion binding-energy curve would persist through changed initial conditions. (2) The momentum transferred to a cluster by the ionizing electron depends on its energy, but since the electron transit time is much shorter than the time scale for atomic motions, the subsequent deexcitation may not depend on the electron energy. Clearly, detailed models of cluster ionization must be developed in order to interpret the results of these experiments.

Despite the similarity of the cluster mass spectra, the onset of condensation differs significantly between isotopes. Figure 2 shows the intensities of the first three ions as a function of P_0 for ^{3}He and ^{4}He. In ^{4}He, the dimer ion is the only cluster present for a large range of stagnation pressure. The dimer signal is roughly 10^3 times larger than that of the trimer when it first appears. Ions with $N \geq 3$ all have roughly the same onset, substantially more abrupt than the dimer. Identical behavior is observed for $3.0 \leq T_0 \leq 4.2$ K. This trend is similar to previous data on heavier van der Waals systems.[9] On the other hand, all ions of ^{3}He appear together, with a much stronger dependence on P_0, for T_0 in the range 2.8–3.4 K. This is the most abrupt onset of cluster formation in a supersonic free jet yet described. For heavier rare gases, the state of condensation in the beam depends only on stagnation temperature and density, scaled to their critical value.[10] However, in the present experiment, at reduced temperature $T_0/T_{crit} = 0.81$, the reduced stagnation density is a factor of 28 larg-

er for ^{3}He than ^{4}He at the appearance of He_2^+.

The dramatic difference between the onset of cluster formation in ^{3}He and ^{4}He may be related to the stability of the smallest neutral clusters. The existence of $^4He_2$ has long been debated, with the most recent scattering data favoring a bound state with energy $\epsilon = -0.43$ mK.[11] Various calculations show that $^4He_3$ is stable.[12] On the other hand, the size of the smallest bound neutral ^3He_N cluster is not known, except that $N \geq 4$.[12] We suggest that the smallest ^{4}He bound species forms in the free jet and produces the $^4He_2^+$ signal observed as the only cluster ion over a wide range of stagnation conditions. The instability of this species presents a hurdle to the nucleation of the lighter isotope so that ^{3}He clusters are formed only at a higher degree of supersaturation in the beam.

The present experiment cannot directly identify this lightest ^{4}He cluster. Because of the dramatic cooling in free jets, such weakly bound entities as $^4He_2$ may be present; a rough estimate of the equilibrium concentration in the beam is consistent with the intensity of $^4He_2^+$ ions detected. This result depends strongly on the final Mach number of the beam, a parameter that was not precisely measured. Experiments capable of determining the velocity distribution of the beam as well as measuring the mass spectrum will be required to resolve this question. Alternatively, $^4He_3$ may be the neutral parent of the $^4He_2^+$ ion.[13] In that case, the branching ratio $(He_3 \rightarrow He_3^+)/(He_3 \rightarrow He_2^+)$ must be less than 10^{-3}. Buck and Meyer have recently shown that the corresponding branching ratio is consistent with zero for neutral Ar_3 parent clusters.[14]

In conclusion, we have found prominent magic numbers in the mass spectrum of helium clusters condensed in a supersonic free jet. There are marked differences between the helium spectra and previously published work on other van der Waals systems. Very weakly bound ^{4}He dimers may have been detected through their ions, with further work, both experimental and theoretical, required to confirm this interpretation.

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[6]A more extensive discussion of the ^{4}He data is given in P. W. Stephens, Ph.D. thesis, Massachusetts Institute of Technology, 1978 (unpublished); a fuller discussion of the present results is in preparation.

[7]The beam expanded from stagnation conditions through a 5-μm pinhole into a 2×10^{-4}-Torr vacuum. At a distance of 6 mm from the nozzle, the beam traversed a conical, electroformed Ni skimmer with an 0.5-mm-diam orifice, and passed into a second vacuum chamber whose typical operating pressure was 10^{-6} Torr. After passing a mechanical chopper, the beam was ionized and detected 60 cm from the nozzle by an Extranuclear Laboratories flow-through, crossed-beam, electron-impact ionizer and quadrupole mass spectrometer (resolution ~ 0.5 amu) with a channel electron multiplier. We expressly verified that the density in the ionizer was sufficiently low to avoid attachment of background gas atoms to an ionized cluster. Mass spectra were accumulated in repeated scans in a multichannel scaler. The ion signal alternately added and subtracted in phase with the chopper, in order to discriminate against background gases. While the absolute magnitude of the signal depended on mass spectrometer resolution and ionizer focus settings, the ratios between adjacent peaks were relatively insensitive to these parameters.

[8]Large peaks in the ^{3}He spectra, in phase with the chopper, were observed repeatedly at prominent background masses of 18 (H_2O^+), 28 (N_2^+ and CO^+), 32 (O_2^+), and 44 (CO_2^+) amu. ^{4}He spectra during the same runs showed no trace of a signal in synchronism with the chopper other than at multiples of 4 amu, even though the background spectrum had sizable peaks at 18, 29, 33, and 43 amu. We explain the difference in sensitivities of the two iostopes to background contamination by the factor of 2 greater flux required to condense ^{3}He clusters. This increased flux can pump impurities from the expansion chamber to the mass spectrometer chamber as seen, for example, by

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[13]Van Deursen and Reuss favor this interpretation, basing their conclusion on two observations: (1) The $^4He_2^+$ parent has a geometrical cross section larger than that of other rare-gas dimer ions. (2) The $^4He_2^+$ current is proportional to P_0^3. If the binding energy is much less than kT_0, the equilibrium trimer density in the source is proportional to P_0^3, whereas the dimer density scales as P_0^2. We note, however, that $^4He_2$, if stable, has at least 8 Å most probable internuclear separation (Ref. 11), substantially larger than any heavier van der Waals dimer. Furthermore, a P_0^3 dependence is widely seen in heavier rare-gas dimers whose stability is well established (Ref. 9). The rate of formation of weakly bound dimers in the free jet expansion is proportional to P_0^3 because three atoms must participate in order to conserve energy and momentum.

[14]U. Buck and H. Meyer, in *Abstracts of Contributed Papers to the 13th International Conference on the Physics of Electronic and Atomic Collisions, Berlin, 1983*, edited by J. Eichler *et al.* (North Holland, Amsterdam, 1983), p. 585.