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Capture of Neon Atoms by ^{4}He Clusters

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Neon atoms are captured by helium clusters in a crossed-beam experiment. The capture process depends strongly on the cluster-beam-source conditions. We identify a sharply defined region corresponding to expansions passing near the critical point for which the capture probability is anomalously large.

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Helium clusters present a unique and especially interesting system for study.[1-3] In a vacuum they are expected to cool by evaporation to a lower internal temperature than any other cluster species.[3] In contrast to other materials, bulk helium has no triple point and thus helium clusters should remain in the liquid state at all temperatures. Not only are they liquid, but since bulk helium is a superfluid at low temperatures, there is a fascinating question about the evolution of this phenomenon as the size of the system decreases.[4] From another point of view, it has been suggested that helium clusters can provide an interesting analog of the nucleus.[5,6]

There has been considerable interest recently in the theoretical calculation of the properties of helium clusters,[7-9] but experimental information about the internal properties of neutral helium clusters is very difficult to obtain. With the exception of studies of the scattering of Cs and Xe atoms by neutral helium clusters by Gspaan and Vollmar,[10] most experimental studies[1-3,11,12] have involved the excitation and ionization of clusters by electron impact, and the observation of the charged products. This strongly interacting charged probe produces a new system whose properties are undoubtedly significantly different from the precursor neutral clusters which one wishes to study.[12,13]

In the present work we will show that it is possible to attach neutral foreign atoms to helium clusters as they fly through the vacuum. This is significant because it opens up the possibility of utilizing such atoms or molecules as more weakly interacting neutral probes of the internal state of the neutral cluster. We will describe experiments in which a helium cluster beam is formed by a strong free-jet expansion into a differentially pumped vacuum, and subsequently crossed by a second beam of neon atoms. These measurements provide the first conclusive evidence that one or more foreign atoms can, in fact, be captured by a helium cluster,[14] and remain so for times in excess of several milliseconds. They also indicate that more than one atom can be captured by a single cluster. The capture probability for neon atoms depends very sensitively on the expansion conditions. In particular, it appears that clusters formed in expansions which pass near to the critical point are much better able to capture neon atoms than are clusters formed under other expansion conditions. Our most surprising observation, however, is that the borders delineating the expansion conditions which produce these "critical clusters" are very sharply defined.

A schematic diagram of our experimental apparatus is shown in Fig. 1. The primary helium cluster beam is produced by expanding helium gas from high pressure (P_0) and low temperature (T_0) through a 5-μm sonic nozzle. The central portion is skimmed, chopped mechanically, and passes into a high vacuum scattering chamber. After a 1.4-m flight path, the primary beam is ionized by electron impact, and the resulting charged

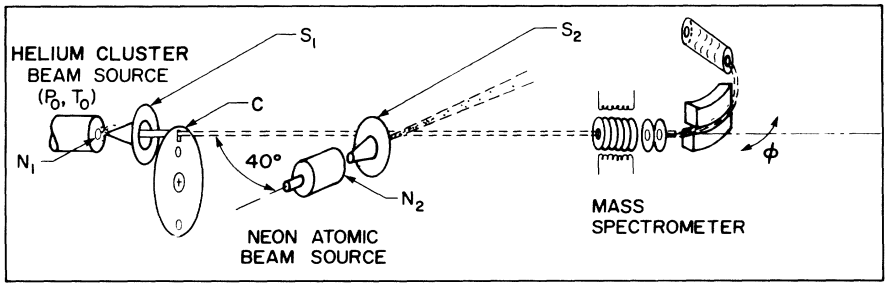

FIG. 1. Schematic of the crossed-beam experiment showing nozzles (N), skimmers (S), chopper (C), and mass-spectrometer detector.

fragments are mass analyzed and detected. In addition, it is possible to rotate the detector about the center of the scattering chamber. With this arrangement, we can measure both the cluster velocity and the beam profile. A secondary beam of neon atoms is formed by expanding Ne gas from room temperature ($T_s = 310$ K) at moderate pressure ($P_s = 5$ bars) through a 20-μm sonic nozzle. The beam is skimmed and crosses the primary beam 61 cm downstream from the primary-beam nozzle at an angle of 40°. The typical relative velocity of the two beams is 550 m/s. These source conditions were chosen to insure a negligible concentration of Ne clusters in the secondary beam.[15]

We show in Fig. 2(a) a typical charged-fragment mass spectrum obtained from the primary beam. The solid curve indicates the spectrum measured with no secondary beam present. It indicates the presence of all He cluster ions He_n^+ from $n = 2$ to 20 and beyond. In addition, there are small impurity signals present at most other masses, the strongest being at masses 14 and 18 amu. The detector background has been subtracted so these represent impurities that arrive coincident with the cluster signal. We note that these small charged fragments are produced from what we believe to be much larger neutral helium clusters.[1,2,16] The dashed curve in Fig. 2(a) represents the spectrum obtained when the secondary beam is turned on. It can be seen qualitatively that some peaks are increased and others are decreased by the presence of the neon beam. A more detailed representation of this effect can be seen in Fig. 2(b), where we plot the percentage change of each mass peak. The most obvious features are the large fractional increase in the signal at the masses of the ^{20}Ne and ^{22}Ne isotopes,[17] and the decrease at masses less than 20 amu. There is also a strong increase at the $^{20}Ne_2^+$ mass and significant increases at the masses of $^{20}Ne_3^+$, $^{20}Ne_4^+$, and mixed ions of the form $Ne_nHe_m^+$ (e.g., $^{20}NeHe^+$ and $^{22}NeHe^+$).[17] We attribute these effects to the capture of one or more neon atoms from the secondary beam by helium clusters in the primary beam.[18] Evidence for the actual capture of Ne as opposed to scattering or entrainment is provided by the fact that the Ne-related signals have the same time of flight from the scattering center as do the helium clusters, and by the fact that the beam profile is the same for the neon signal as for the He-cluster signal.[19] The strongest evidence for capture, however, is the observation of the $NeHe^+$ molecular ion, since it is virtually impossible to construct such an ion unless the Ne atom is associated with the helium atom prior to ionization. Since a typical time of flight from the scattering center to the ionizer is 4.1 msec, this time provides a lower bound to the lifetime of the captured atoms. We cannot say from experiment whether the captured atoms reside in the interior or on the cluster surface. From theory we expect that neon probably resides in the interior, however.[20] The existence of increased signals at the Ne_n^+ ($n = 2,3,4$) masses is reasonable proof of the capture of more than one atom by a single cluster. This is certainly accomplished by a succession of individual capture events since there are no neon clusters present in the secondary beam.

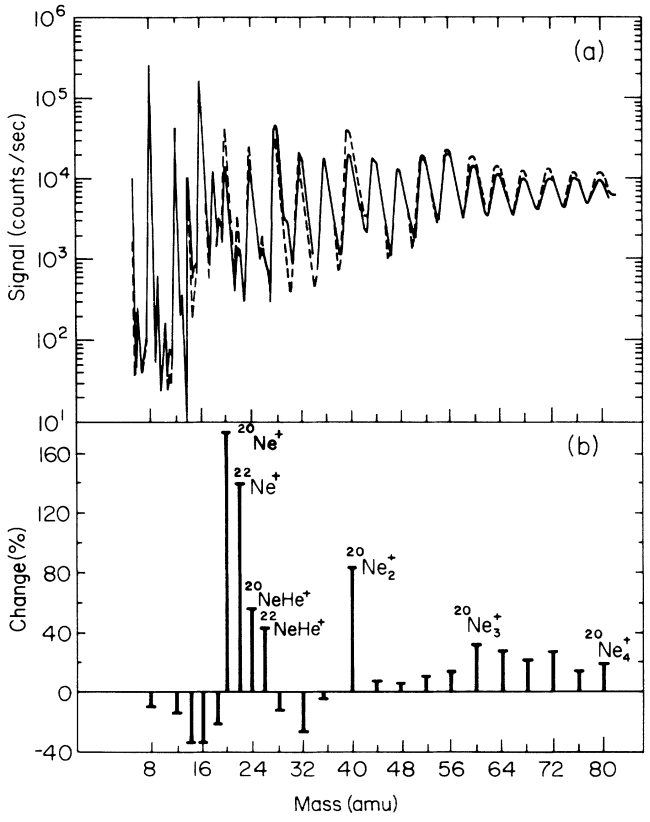

FIG. 2. (a) Mass spectra measured with (dashed line) and without (solid line) the neon beam present. (b) Percentage change of each mass peak when the neon beam is turned on.

It is natural to ask whether we can learn anything about the nature of helium clusters from studies of the capture process. As a step in this direction, we have studied how the neon-atom capture rate depends on the conditions under which the helium clusters are produced. It is reasonable to expect the mean mass and possibly the internal state of the clusters to depend on the source conditions, so we have looked at the capture process by fixing the secondary-beam properties and varying the cluster properties by changing P_0 and T_0. We have chosen to monitor the $^{22}Ne^+$ counting rate (where there is no pure helium cluster and only a weak impurity background)[18] while increasing P_0 and holding T_0 fixed. Some typical experimental results are shown as the solid circles in Fig. 3. At $T_0 = 8$ K the counting rate increases monotonically with pressure, with no distinctive features. For 14 and 16 K, however, the behavior is surprisingly different. For low pressures there is no observable trapping; but at a quite well-defined pressure boundary (indicated by the arrow BL), the counting rate increases rapidly, passes through a maximum, and then drops sharply.

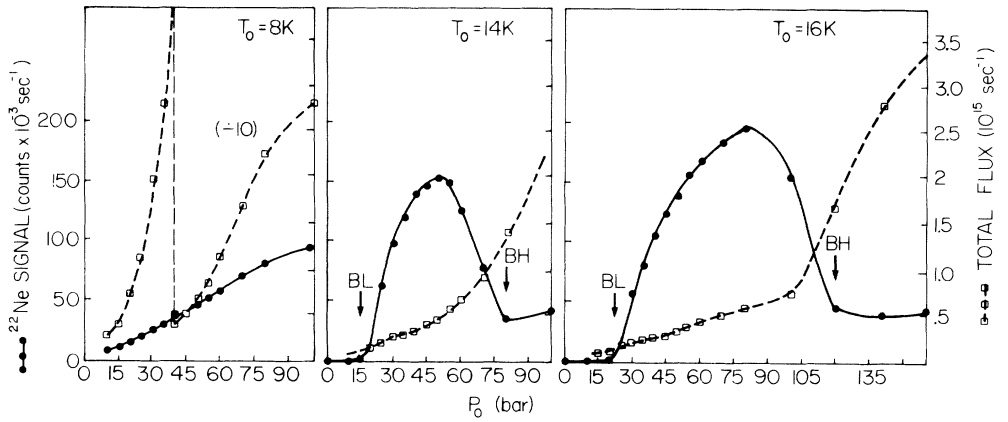

FIG. 3. ^{22}Ne counting rate (solid circles, left scale) and total beam flux (open squares, right scale) as a function of helium-cluster-source pressure for various temperatures. Indicated low- and high-pressure boundaries (BL and BH) of the major counting-rate peak are fitted by eye.

At a second well-defined higher-pressure boundary (indicated by the arrow BH) the counting rate either levels off or begins again a shallow increase. In order to check whether this peak simply reflects some anomaly in the total beam intensity, we have simultaneously made a stagnation-pressure measurement of the total beam flux. The results are shown in the figure as open squares. While there is some evidence for a knee in the vicinity of BH, there is no evidence for a peak in the total flux, so the origin of the counting-rate peak must lie elsewhere.

A most instructive representation of our combined results for many different temperatures is given in Fig. 4 where we present a contour plot of the ^{22}Ne counting rate in the (P_0, T_0) plane. The phase boundaries for bulk helium are also included, along with the critical point, CP. The region covered by our measurements is indicated by the irregular rectangular border surrounding the contours. The most surprising feature is the existence of a large local maximum in the counting rate at approximately $T_0 = 16$ K and $P_0 = 80$ bars. We can identify three distinctive regions in this figure. For pressures less than the dot-dashed line BL, there is no observed capture, even though we know from the presence of cluster ions in the spectra that helium clusters *are* present. For pressures above the dashed line BH, the capture rate increases monotonically with increasing P_0 and decreasing T_0. It does not scale with the total flux, however. The shaded region between these two curves indicates a counting-rate "mountain." Evidently, clusters produced in expansions with these initial conditions are much more efficient than others in capturing foreign atoms.

It is normally assumed that the internal state of the gas in a free-jet expansion follows the isentrope passing through the stagnation conditions.[1,21] Thus, for example, the stagnation entropy should completely determine the point on the phase boundary at which the expansion enters the two-phase region. This, in turn, is likely to be

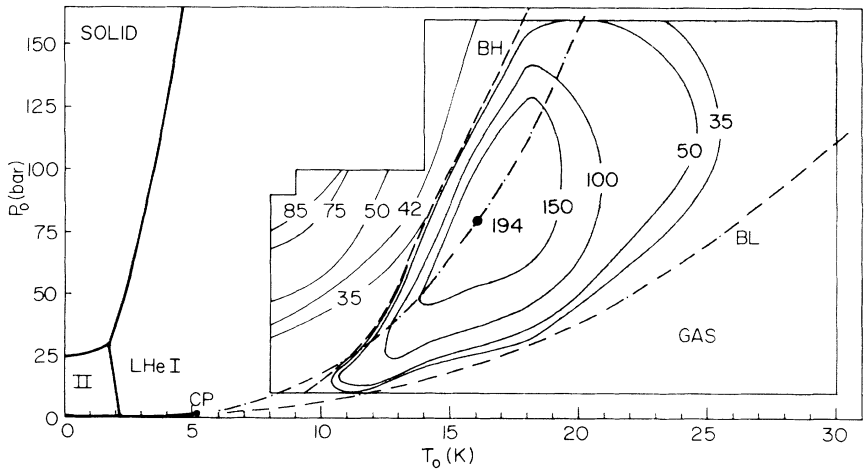

FIG. 4. Contour plot of ^{22}Ne counting rate as a function of helium-cluster-source pressure P_0 and temperature T_0. Boundaries separating the three characteristic regions are labeled by BL and BH.

a very important factor in determining the nature of the clusters produced. Quantitative support for this conjecture is provided by the fact that the dot-dashed line BL, below which no capture was detected, coincides quite accurately with the isentrope $S=9.2$ kJ/kg K, which crosses the phase boundary from the vapor at $T=3.5$ K.[22] The dot-dashed curve passing through the counting-rate maximum represents the isentrope $S=6.5$ kJ/kg K. It follows the general trend of the counting-rate ridge reasonably well. The experimental upper boundary BH is close to but not exactly an isentrope —the entropy along it ranges from $S=6.8$ kJ/kg K at 25 bars to 5.9 kJ/kg K at 160 bars. To our knowledge, the entropy at the critical point is not clearly defined by existing data,[22] but it seems to lie in the range 5.6 ± 0.5 kJ/kg K. Thus it appears that the clusters which are most effective in capturing foreign atoms are those formed in expansions which pass very close to the critical point.

The critical clusters are quite sharply defined and evidently have significantly different properties than those produced under other expansion conditions. We cannot determine from our present experiments whether they are simply much more massive than the others, or whether their capture cross section is larger because their internal state is also different in some unknown way. We note that if the capture cross section were geometric and the total flux constant, a larger mean cluster size would actually *reduce* the capture rate.[23] Thus we are inclined to believe that the distinction is more complex. Hopefully, planned future experiments will shed light on this issue.

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[17]The ratio of the absolute increase for the two isotopes is equal to the natural isotropic abundance ratio (9/91). A similar result is found for the increases at the $^{20}Ne^{4}He^{+}$ and $^{22}Ne^{4}He^{+}$ masses.

[18]This suggests that the synchronous impurity signals noted previously probably arise from capture of residual gases (e.g., H_2O, N_2, H_2) by clusters along their flight path.

[19]The lack of an observable deflection associated with capture allows us to set a rough lower bound of 2500 atoms for the size of the clusters involved. It is likely that the clusters are significantly larger than this, however (see Refs. 1, 2, and 16).

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[23]With mean cluster size $\langle N\rangle$ and a constant total flux, the number of clusters is $\propto\langle N\rangle^{-1}$. Moreover, assuming constant cluster density, a geometrical capture cross section will be $\propto\langle N\rangle^{2/3}$. The capture rate is then $\propto\langle N\rangle^{-1/3}$. In this case, a local maximum in $\langle N\rangle$ will produce a local minimum in the capture rate. We note, however, that what we measure is the $^{22}Ne^{+}$-ion counting rate. Since ionization and fragmentation processes can also depend on $\langle N\rangle$, the overall effect of a local maximum is difficult to predict.