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A threshold-based approach to calorimetry in helium droplets: Measurement of binding energies of water clusters

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Helium droplet beam methods have emerged as a versatile technique that can be used to assemble a wide variety of atomic and molecular clusters. We have developed a method to measure the binding energies of clusters assembled in helium droplets by determining the minimum droplet sizes required to assemble and detect selected clusters in the spectrum of the doped droplet beam. The differences in the droplet sizes required between the various multimers are then used to estimate the incremental binding energies. We have applied this method to measure the binding energies of cyclic water clusters from the dimer to the tetramer. We obtain measured values of D_0 that are in agreement with theoretical estimates to within $\sim 20\%$. Our results suggest that this threshold-based approach should be generally applicable using either mass spectrometry or optical spectroscopy techniques for detection, provided that the clusters selected for study are at least as strongly bound as those of water, and that a peak in the overall spectrum of the beam corresponding only to the cluster chosen (at least in the vicinity of the threshold) can be located. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4738664>]

INTRODUCTION

Helium droplets have emerged as a prominent method for the assembly of atomic and molecular clusters, as described in several reviews.^{1–5} Owing to the low temperature of the droplet⁶ (0.37 K), the rapid cooling provided to captured species, and the sequential nature of the cluster assembly process, the clusters produced are often frozen into local minima on the associated potential energy surface. These effects have led to the production of exotic species and isomers that are often difficult or impossible to produce by other methods. Additionally, the fact that helium droplets can capture and coagulate clusters from virtually any combination of atoms or molecules has resulted in a remarkably versatile technique that has been used to assemble a wide variety of clusters^{2–5} containing species such as metal atoms, inorganic salts, organics, biomolecules, radicals, and more recently ions.^{7,8}

The majority of helium droplet work^{1–5} has been focused on either spectroscopic interrogation of clusters assembled within the droplet, or on the ionization of both pure and doped droplets via mass spectrometry techniques. It has been repeatedly observed that the size of the droplets used to assemble the clusters must be sufficiently large to permit individual molecules and the clusters coagulated from them to be cooled to the droplet temperature. As each molecule is captured by the droplet, it is cooled to 0.37 K by evaporating helium atoms from the droplet.^{9–11} Likewise, the coagulation of a cluster from the constituent molecules results in the evaporation of additional helium atoms in proportion to the binding energy of the cluster. In the bulk limit, each evaporated atom

removes 5 cm^{-1} , but for small droplets the value can be somewhat less.^{10,11} In principle, it should be possible to employ helium droplets as sensitive nano-calorimeters to measure the binding energies of clusters assembled within. One successful approach has been to measure the attenuation of the droplet beam as a function of the number of dopant molecules captured, with the rate of extinction of the beam yielding the average binding energy of the clusters. This method¹² has been used to measure the average binding energy of propyne in clusters from 10 to 10 000 molecules, and is well-suited to determining bulk binding energies in a very straightforward way. One advantage of this method is that the statistical distribution of droplet sizes and cluster sizes present in the beam^{1–5} does not complicate the analysis. We note that similar techniques have also been considered to measure the exothermicity of metal-oxidizer chemical reactions,^{13,14} but here the situation is complicated by non-equilibrium cooling processes that can result in ejection of the reaction products even from large droplets.^{14,15}

The purpose of the current investigation is to examine an alternative method of using helium droplets in order to measure the binding energies of individual oligomers of interest rather than average or bulk binding energies. The approach involves determining the minimum droplet sizes required to assemble and detect specific clusters (or more precisely, the differences in the droplet sizes required between the various multimers) rather than monitoring the overall depletion of the droplet beam over a range of cluster sizes. We note that while mass spectrometry is used to probe the doped helium droplets in the current study, other methods such as IR absorption spectroscopy could also be used, as will be discussed below. Water clusters were chosen for the present study for two reasons. First, the structures of water clusters

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assembled in helium droplets are already known from previous IR spectroscopy work,¹⁶ removing any ambiguity regarding which isomer(s) might correspond to our measured binding energies. In this case, the water clusters assembled in helium droplets are exclusively the cyclic isomers for multimers up to the pentamer. Second, the binding energies of water clusters have been the subject of extensive theoretical study,^{16–18} at several levels of theory.

EXPERIMENT

The instrument used in the present study is shown schematically in Figure 1. Briefly, droplets are formed by supersonic expansion of helium through an optically measured 5 μm pinhole nozzle into vacuum. The temperature of the nozzle can be varied from 4 to 30 K. The mean droplet size formed is adjusted by changing the stagnation temperature and/or pressure in the nozzle.^{19–22} For the nozzle conditions used in the current study, the distribution of droplet sizes has been shown to be log-normal.^{21,22} In this investigation, the pressure was held constant at 40 bar and the droplet sizes were controlled by varying the temperature. Nozzle temperature measurements were obtained using a silicon diode calibrated from 3 to 77 K. The expansion is skimmed by a 1.0 mm skimmer located approximately 20 mm downstream to produce a beam of droplets. The droplets are then doped by passing the beam through a pickup cell filled with water vapor, resulting in the sequential capture of water molecules and coagulation of clusters.

The droplets continue downstream to a time-of-flight mass spectrometer, where the droplets are ionized by a pulsed electron gun at an incident energy of 100 eV, and the resulting ions are directed into the flight tube and detected by a multichannel plate detector. Previous studies^{23,24} have shown that ionization of helium droplets via electron bombardment begins with the creation of a He^+ ion somewhere in the droplet. The charge then rapidly migrates on the fs timescale,²⁵ guided by the charge-induced potential within the droplet,²⁶ as well as the electrostatic moments of embedded dopants^{27–29} until it either transfers to the dopant or formation of a He_n^+ ($n \geq 2$) cluster ion occurs.³⁰ Either outcome releases sufficient energy

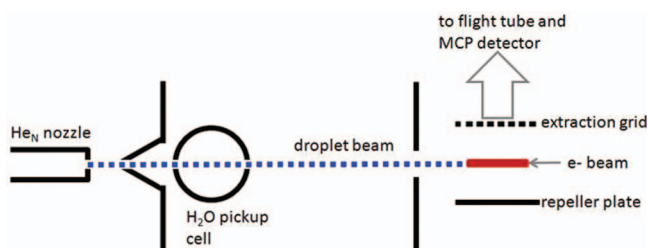


FIG. 1. Schematic representation of the instrument used in the current study. Helium droplets are formed by expanding ultrahigh purity helium from a 5 μm pinhole nozzle into vacuum. The expansion is then skimmed to form a droplet beam. The droplets are doped with water molecules by directing the droplet beam through a pickup cell filled with water vapor. The doped droplets continue downstream to a time-of-flight mass spectrometer where the droplets are ionized by incident electrons from an electron gun. The resulting ions are focused into the flight tube and detected by a multichannel plate (MCP) detector.

to desolvate the ion from the droplet, resulting in the detection of bare ions.

RESULTS AND DISCUSSION

To determine the droplet sizes required to assemble and detect specific clusters, we monitor the intensities of selected peaks in the mass spectrum as a function of the mean droplet size produced by the nozzle. In Figure 2, we show mass spectra of a helium droplet beam doped with water clusters using several different pickup cell pressures. At the lowest H_2O pressure shown, we observe peaks corresponding to $(\text{H}_2\text{O})^+$, $(\text{H}_2\text{O})\text{H}^+$, $(\text{H}_2\text{O})_2^+$, and $(\text{H}_2\text{O})_2\text{H}^+$, as well as several signals from He_n^+ ions. The $(\text{H}_2\text{O})_n^+$ and $(\text{H}_2\text{O})_n\text{H}^+$ ions originate from doped droplets, while the He_n^+ ($n \geq 2$) ions result from ionization of empty droplets and from doped droplets in which the migrating charge failed to transfer to the dopant before a helium cluster ion was formed. As the pressure in the pickup cell is increased, we see that progressively larger $(\text{H}_2\text{O})_n^+$ and $(\text{H}_2\text{O})_n\text{H}^+$ ions are formed, with the spectra at the highest pressures shown exhibiting peaks for $n = 20$ and beyond. Consistent with earlier works,^{9,31,32} we see that with the exception of $(\text{H}_2\text{O})^+$ and $(\text{H}_2\text{O})\text{H}^+$, the $(\text{H}_2\text{O})_n\text{H}^+$ signals are consistently larger (often by an order of magnitude or more) than the $(\text{H}_2\text{O})_n^+$ ions. This is due to the fact that the production of the protonated $(\text{H}_2\text{O})_n\text{H}^+$ daughter ions is favored over that of unprotonated $(\text{H}_2\text{O})_n^+$ ions during fragmentation of parent $(\text{H}_2\text{O})_m^+$ ($m \geq n + 1$) ions, both in helium droplets as well as in the gas phase.³³

Each of the water cluster peaks in our spectrum has a maximum nozzle temperature (or minimum droplet size) associated with its detection, owing to the fact that the droplet must contain a sufficient number of atoms to permit the captured molecules and the clusters formed from them to be cooled to the droplet temperature. For the droplet sizes used in the current study, each evaporated helium atom

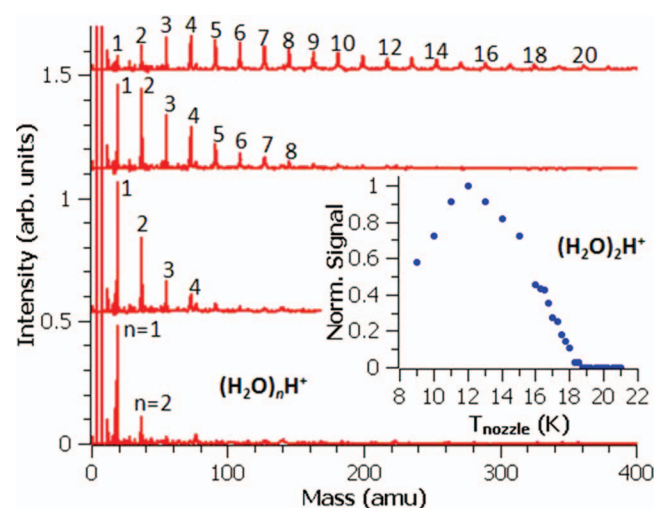


FIG. 2. Mass spectra of the helium droplet beam doped using several different pressures in the water pickup cell. Pickup cell pressure increases from bottom to top. Spectra were recorded at a mean droplet size of ~ 25000 atoms/droplet. Inset shows the dependence of the $(\text{H}_2\text{O})_n\text{H}^+$ ion signal on the helium nozzle temperature. The pickup cell pressure was optimized at each nozzle temperature.

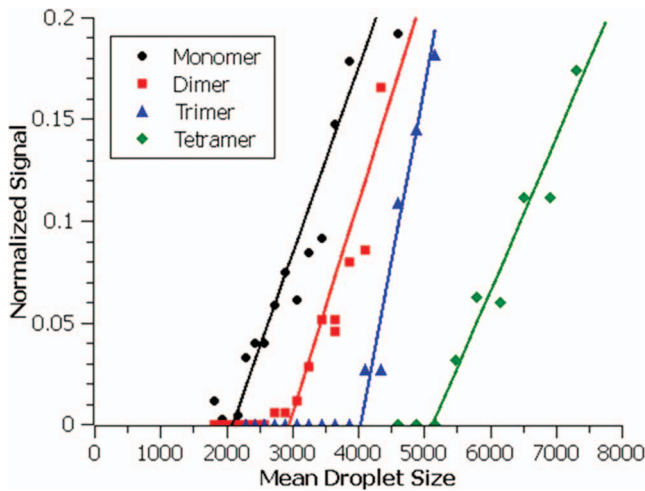


FIG. 3. Droplet size thresholds observed for the detection of $(\text{H}_2\text{O})^+$, $(\text{H}_2\text{O})\text{H}^+$, $(\text{H}_2\text{O})_2\text{H}^+$, and $(\text{H}_2\text{O})_3\text{H}^+$ ions in the mass spectrometer. In each trace, the pickup cell pressure was re-optimized at each droplet size. Least-squares linear fits to the data points in the vicinity of each threshold are shown.

is calculated to remove $4.1\text{--}4.3\text{ cm}^{-1}$ of energy.¹⁰ Above the threshold nozzle temperature, the droplets produced are too small to efficiently assemble and transport water clusters producing the selected ion; increasing pickup cell pressure simply results in the extinction of the beam as the droplets are completely boiled away. In Figure 2 (inset), we show the dependence of the $(\text{H}_2\text{O})_2\text{H}^+$ signal on the nozzle temperature. The pickup cell pressure was optimized for the production of $(\text{H}_2\text{O})_2\text{H}^+$ signal at each nozzle temperature. We observed a temperature of $\sim 18.5\text{ K}$ or lower was necessary to produce this signal at any pickup cell pressure in our instrument.

In Figure 3, we show the droplet size thresholds measured for the detection of $(\text{H}_2\text{O})^+$, $(\text{H}_2\text{O})\text{H}^+$, $(\text{H}_2\text{O})_2\text{H}^+$, and $(\text{H}_2\text{O})_3\text{H}^+$ ions. The mean droplet sizes as a function of the nozzle temperature were interpolated from an investigation²² closely matching our source conditions. We note that a survey of reported droplet sizes^{19,21,22} as a function of nozzle conditions reveals agreement (over the range of droplet sizes considered here) within 10%–20%, suggesting possible error of similar magnitude here. As before, the pickup cell pressure was optimized at each mean droplet size in each of the traces shown. As expected, the larger water cluster ions

require correspondingly larger droplets to be observed. This has also been noted in experiments that probed water clusters via IR spectroscopy.³¹ For each of these peaks, at droplet sizes significantly larger than the threshold we might expect that there could be contributions to the signal from multiple neutral clusters. The $(\text{H}_2\text{O})_2\text{H}^+$ signal for example cannot contain contributions from water monomers or dimers, but trimers, tetramers, or even higher multimers could all fragment following ionization to produce this species. However, in the limit of droplet sizes that are just sufficient to assemble and transport trimers to the mass spectrometer, any contributions from higher multimers should vanish since a droplet size that is barely adequate to cool trimers to the droplet temperature would not be sufficient to dissipate the greater binding energies of tetramers or pentamers. In other words, as the droplet size is decreased and the signals driven down towards extinction, we would expect the various ions to have contributions from only one multimer in the vicinity of their respective thresholds. Hence, the thresholds for the detection of $(\text{H}_2\text{O})^+$, $(\text{H}_2\text{O})\text{H}^+$, $(\text{H}_2\text{O})_2\text{H}^+$, and $(\text{H}_2\text{O})_3\text{H}^+$ ions should correspond to the droplet sizes required for water monomers, dimers, trimers, and tetramers, respectively, to be assembled and detected in the mass spectrometer downstream.

Our measured thresholds are summarized in Table I. Interestingly, we find that the measured threshold for the water monomer corresponds to a mean droplet size of ~ 2100 atoms/droplet. This value is somewhat larger than the number of atoms evaporated from a droplet during the capture of single water molecule, namely 635 helium atoms.^{9,34} It seems reasonable to suspect that some number of helium atoms (referred to hereafter as $N_{\text{transport}}$) must remain after cooling a captured impurity in order to successfully transport it into the ionization volume of the mass spectrometer downstream. If the dopant pickup and subsequent helium “boil off” imparts a sufficiently large velocity to the droplet perpendicular to the beam axis, then the droplet could miss the ionization volume altogether. In our case, the ionization volume corresponds to an electron beam with an estimated width of 1–2 mm. We note that the possibility of droplet deflection has been previously suggested to explain missing population in IR pump-probe experiments.³⁵ The exact value of $N_{\text{transport}}$ is almost certainly dependent upon the geometry of the instrument used, but we would expect it to decrease with decreasing distance (and flight time) between the water pickup cell and the mass spectrometer.

TABLE I. Listing of the water multimers investigated, the ion signals monitored, and the observed droplet size thresholds for each. The differences between the thresholds of each multimer of order n and $n-1$ are listed. Subtracting N_{capture} from the difference in threshold values yields the number of helium atoms evaporated to dissipate the binding energies of the clusters. N_{capture} was taken to be 635 atoms (Ref. 9). Incremental and total binding energies calculated from these values are shown, along with theoretical values obtained from Refs. 16 and 17. Error bars are in parentheses. We note that the D_0 values in the rightmost column were tabulated by adding the zero point energies calculated in Ref. 17 to the values of D_e listed in Ref. 16.

$(\text{H}_2\text{O})_n$ multimer	Ion monitored	$N_{\text{threshold}}$ (He at.)	$N_n - N_{n-1}$ (He at.)	$\Delta N - N_{\text{capture}}$	Incremental binding energy (kcal/mol)	Total binding energy (kcal/mol)	Theoretical D_0 BLYP/aug-cc-pVDZ (kcal/mol)	Theoretical D_0 MP2/CBS limit (kcal/mol)
1	$(\text{H}_2\text{O})^+$	2083
2	$(\text{H}_2\text{O})\text{H}^+$	2943	860	225	3 (1)	3 (1)	2.3	3.0
3	$(\text{H}_2\text{O})_2\text{H}^+$	4023	1080	445	5 (1)	8 (2)	8.4	10.5
4	$(\text{H}_2\text{O})_3\text{H}^+$	5129	1106	471	6 (1)	14 (3)	17.5	19.7

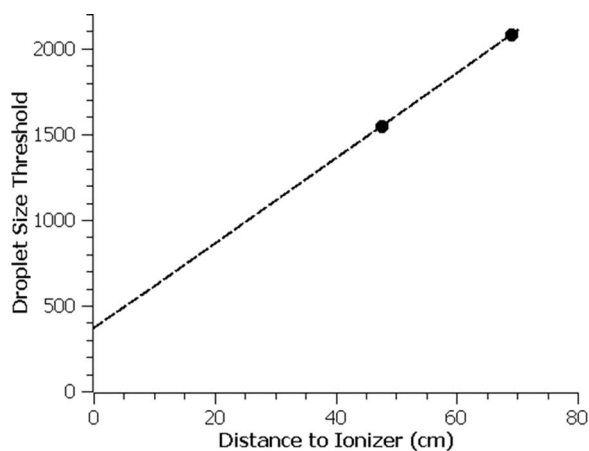


FIG. 4. Observed droplet size thresholds for the $(\text{H}_2\text{O})^+$ signal obtained with the water pickup cell located in two different port upstream of the mass spectrometer, along with linear extrapolation to zero pickup-ionizer distance.

To confirm this, we altered the geometry of our experiment by changing the position of the pickup cell relative to the detector. In Figure 4, we show the observed thresholds for the water monomer obtained with the water pickup cell located in two different positions upstream of the mass spectrometer. When the pickup cell is located in the position closest to the mass spectrometer, the threshold droplet size required is ~ 500 atoms smaller than that obtained when the pickup cell is positioned at the location farthest from the mass spectrometer. Extrapolation of these data to zero pickup-detector distance yields a crude estimate of ~ 400 helium atoms, in reasonable agreement with an earlier measurement⁹ that 635 atoms are evaporated from a helium droplet upon capture of a water molecule (hereafter referred to as N_{capture}). The accuracy of this simple approach to estimating N_{capture} could likely be substantially improved by installing additional pickup cell ports located closer to the detector.

From the data in Figures 3 and 4, we can calculate the incremental and total binding energies of the water clusters examined herein. In the case of the dimer, we see that the droplet size threshold for its detection is increased relative to that of the monomer by approximately 860 helium atoms. A portion of that, namely N_{capture} (taken to be 635 atoms⁹), is due to the additional helium atoms required to capture and cool a second water molecule, with the remainder (225 atoms) assigned to the helium that must be evaporated in order to dissipate the binding energy of the dimer following its coagulation. Incremental binding energies going from the dimer to the trimer, and from the trimer to the tetramer, are obtained similarly. These values are given in Table I along with the tabulated total binding energies. For comparison, theoretical values calculated at two different levels of theory are also shown.^{16,17} We note that the D_0 values in the rightmost column were obtained by adding the zero point energies (E_0) calculated in Ref. 17 to the values of D_e listed in Ref. 16.

At this point, we wish to emphasize that while the relative values of the thresholds going from one multimer to the next can be used to estimate the incremental binding energies, analysis based upon the absolute values of the individual thresholds is much less straightforward. Recall that

an observed threshold will be the sum of the number of helium atoms required to capture and cool n dopant molecules ($n \cdot N_{\text{capture}}$), the number required to dissipate the binding energy of the cluster formed, and the number of helium atoms required to remain in order to successfully transport the droplet to the detector ($N_{\text{transport}}$). The first two contributions will not vary from one laboratory to another, but the third will be instrument geometry-dependent as we have demonstrated. Additionally, the sensitivity of the instrument may play a role in determining the apparent threshold values. As mentioned above, a distribution of droplets sizes is formed by the nozzle with the mean value determined by the stagnation conditions. For a given instrument sensitivity, a finite fraction of the distribution must contain the multimer of interest in order to observe a signal. Hence, we might expect the reported thresholds to also depend upon instrument sensitivity. The fact that the value of $N_{\text{transport}}$ and the percentage of the distribution required to generate a signal in a given instrument are difficult to predict complicates any efforts to analyze the data based upon the absolute thresholds. However, utilizing the relative values to obtain incremental binding energies avoids these complications by exploiting the fact that these factors are constant within a given instrument. Hence, the relative thresholds depend only on N_{capture} and the cluster binding energy.

As can be seen in Table I, there is a good agreement between the measured and calculated values of D_0 for the respective multimers. The measured value for the tetramer is slightly lower than the calculated values, but still within $\sim 20\%$ of the latter. We believe that this level of agreement is probably about the best that can be expected given the aforementioned uncertainty in the mean droplet sizes. Recall that our mean droplet sizes are interpolated using scaling laws^{19,21,22} that are estimated to be accurate to 10%–20% over the range of droplet sizes used in the current study. This introduces an uncertainty into the value of the relative thresholds for the various multimers and hence into the incremental binding energies calculated from them. The errors then accumulate as total binding energies are tabulated. Of course, this degree of uncertainty is expected to be less of an issue for clusters that are more strongly bound than those of water. For example, even small clusters of aluminum^{36–38} or carbon^{39–41} can be bound by energies on the order of eV per atom in the cluster. Finally, we note that while the current system contains contributions from only one structural isomer (the cyclic water isomers), many other systems have been shown to assemble into multiple isomers in the helium droplet environment. Presumably, analogous measurements on such systems would yield binding energies that are averaged over the various structural isomers present in the droplets. In future work, it may be possible to extend the technique described herein to employ detection methods such as optically selected mass spectrometry (OSMS) (Ref. 27) or high resolution IR spectroscopy in order to isolate contributions from different structural isomers.

To summarize, we have used helium droplet methods to measure the binding energies of (cyclic) water clusters from the dimer to the tetramer. We obtained measured values of D_0 that are in agreement with theoretical estimates to within 20%. Our approach would seem to be generally applicable

provided that the two following conditions can be met. First, the clusters studied must be at least as strongly bound as those of water. Otherwise the error associated with the technique (primarily from uncertainty in the mean droplet sizes) will represent an unacceptably high percentage of the measured value. We note that for such systems, velocity map imaging techniques can be used to measure D_0 with remarkable precision.⁴² Second, the clusters chosen for investigation must give rise to peaks within the overall spectrum of the doped droplet beam that (at least in the vicinity of the minimum droplet size) contain contributions from only one oligomer. In the case of mass spectrometry detection, there may be systems for which ion fragmentation is so efficient that ionization of M_n clusters produces M^+ ions exclusively for all practical values of n , for example. Or if an optical spectroscopy technique was used, one could imagine spectra that are sufficiently congested or broadened that signals from multiple species overlapped. Clearly, this method could not be used on such systems. We note, however, that extension of the current method to include either mass-selected IR depletion spectroscopy or OSMS²⁷ techniques might be able to address such systems since these techniques resolve signals by both IR absorption frequency and ion mass. Nevertheless, the basic technique appears to be viable, and we plan to employ it in the study of more exotic carbon and metal clusters in the near future.

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