Comment on: Is $n=4$ a magic number for He$_n^+$?

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In a very interesting recent mass spectral study of helium cluster beams, Buchenau et al.\(^1\) find a very intense peak at $m = 16$ amu attributed to He$_2^+$. This observation, however, contradicts the recent drift-tube experiment by Kobayashi, Kojima, and Kaneko\(^2\) as well as the mass spectrum of Stephens and King,\(^3\) which does not show unusual stability for He$_2^+$. We\(^4\) have made ab initio SCF/SOCI calculations on He$_n^+$ ($n = 3$ and 4). While He$_2^+$ is nearly degenerate with He$^+ +$ He in a (4s1p) basis set used before,\(^4\) it is bound by 0.02 eV relative to He$_2^+$ + He in a (4s2p) basis set at the SOCl level of theory. Rosi and Bauschlicher\(^5\) have used a SCF/MCPF (approximate-natural-orbital) method which also shows that He$_2^+$ is only 0.03 eV more stable than He$_2^+$. The He$_3^+$ ion, to the contrary, is 0.15–0.17 eV more bound than He$_2^+$\(^2\). Therefore it is surprising that Buchenau et al.\(^1\) find an intense peak for $n = 4$ in the He$_4^+$ mass spectrum.

We consider the possibility of relativistic effects in He$_n^+$ since the relativistic correction of the He atom (0.044 kcal/mol)\(^6\) and He$^+$ ($-2\alpha^2 = 0.067$ kcal/mol, $\alpha =$ fine structure constant) do not cancel out. Since Rosi and Bauschlicher\(^5\) find a T-shaped structure and an unsymmetrical within 0.12 kcal/mol and symmetrical linear He$_n^+$ within 0.3 kcal/mol, there is a question as to the contribution of relativistic effects ($\sim 0.2$ kcal/mol) bringing these isomers even closer to each other. There are no rigorous relativistic studies on He$_n^+$ at present. To the contrary, there appears to be no structure with energy less than 0.1 kcal/mol of the ground state for clusters of larger size up to $n = 6$.\(^5\) The stabilities of larger clusters are comparable within the accuracy of the quantum mechanical calculations. Consequently, based on the quantum chemical calculations He$_n^+$ does not have unusual binding energy and hence the unusually intense He$_n^+$ peak cannot be explained based on the binding energy.

In the experiment of Buchenau et al.,\(^1\) He$_n^+$ and other ionic clusters are produced by electron impact ionization in the mass spectrometer. Considerable energy is released which results in the total fragmentation of the original neutral cluster of large size. It is evident that the most stable He$_2^+$ ion is directly formed in the impact ionization. The mechanism leading to the formation of larger clusters is, however, poorly understood. The large clusters can be formed from He$_3^+$ and other small clusters first formed via charge transfer to other helium atoms through sticking of additional He atoms to the smaller clusters first formed. Alternatively, the final mass spectrum could reflect the initial distribution of cluster ions.

We are inclined to argue that the smaller clusters (He$_2^+$ and He$_3^+$) are formed in considerably hotter conditions and the large clusters are generated through attachment of additional He atoms to the smaller cluster ions through charge transfer as the beam is cooled. In both cases if there are two isomers very close in energy to each other, then the signal corresponding to that peak will be enhanced in their relative concentrations. Even if we assume that three isomers (two isomers of He$_2^+$ being more likely) contribute to He$_3^+$ peak the factor of 6–10 enhancement in the intensity compared to He$_2^+$ and He$_3^+$ cannot be explained through the isomerism hypothesis alone. Note that for larger clusters He$_n^+$ up to $n = 7$, there appears to be no isomers within 0.1 kcal/mol.\(^5\)

If the T-shaped He$_n^+$ ion is formed through He$_2^+$ + He collision there are four equivalent orientations for the attachment of the He atom to the central He in He$_n^+$ for a given orientation of He$_n^+$ resulting in four equivalent structures with the same energy. That is, there is greater sticking probability for the He atom governed by four equivalent orientations to form He$_n^+$. Even if He$_n^+$ is indirectly generated under hot conditions (but $RT$ cannot be greater than the binding energy or else the cluster will fragment) the equivalent T structures with the same energy for a given He$_n^+$ orientation and two possible unsymmetrical linear (but equivalent) He$_n^+$ (< 0.1 kcal/mol above the T structure) can be formed.

The He$_4^+$ ion has a structure in which two He atoms are attached to the central atom in He$_4^+$ resulting in a neopentane like carbon-skeleton structure. Equivalently He$_n^+$ can be envisaged to be formed from the He$_n^+$ (T) by attaching one more He atom. There is only one possible orientation to stick a He atom to form the ground-state structure of He$_n^+$ from the T-shaped ground state of He$_n^+$. Therefore, the probability of sticking a He atom to He$_n^+$ to form He$_n^+$ is considerably lower. Furthermore, the other structures of He$_n^+$ are at least 0.25 kcal/mol above the ground-state structure. Even if He$_n^+$ is formed through other collisions such as He$_3^+$ + He$_2$ and He$_3$ + He$_+^+$, since the final planar structure is more symmetric, unlike He$_n^+$ for which there are four possible sticking orientations relative to a given orientation of the linear He$_n^+$, the sticking probability to generate He$_n^+$ is smaller.

The ground-state structures of larger clusters ($n = 6,7$) share a common linear He$_n^+$ subunit.\(^5\) Hence there is sufficient evidence from theoretical calculations that larger He$_n^+$ clusters are generated from He$_n^+$ and He$_n^+$ through successive addition of He atoms in the process of cooling.

Toennies and co-workers\(^7\) are considering the possibility of formation of He$_n^+$ through the annihilation of two He$^+$.\(^8\)

\(^8\) Camille and Henry Dreyfus Teacher-Scholar.
metastable molecules but at present there is no clear evidence supporting this hypothesis. If $\text{He}_4^+$ is generated in significant concentrations even under very hot conditions then the annihilation mechanism can explain the extra abundance. However, the Gustinow et al.\textsuperscript{8} ion composition of 300 K helium afterglow reveals that $\text{He}_2^+$ signal is slightly smaller than $\text{He}_3^+$ signal. Furthermore, Buchenau et al.\textsuperscript{1} observed the $\text{He}_4^+$ peak only for source temperatures leading to expansions below the critical point. They consider subcritical clusters to be colder and denser than supercritical ones. All the experimental evidence seems to support our explanation of the formation of $\text{He}_4^+$ at lower temperatures through attachment of $\text{He}$ to $\text{He}_3^+$ and $\text{He}_2$ to $\text{He}_2^+$, and subsequent charge transfer in the latter case. However, the sticking probability for $\text{He}$ to $\text{He}_3^+$ is larger due to 4 equivalent orientations for a given orientation of $\text{He}_3^+$. Therefore if $\text{He}_4^+$ is formed through attachment of $\text{He}$ to $\text{He}_3^+$ at lower temperatures then due to greater sticking probability, to attach $\text{He}_3^+$ to $\text{He}$, the peak is enhanced. At higher temperatures ($T > 300$ K) however, this process becomes less probable since the binding energy of $\text{He}$ in $\text{He}_3^+$ is 0.5–0.6 kcal/mol while the thermal energy at $T = 300$ K is 0.59 kcal/mol.

Hence we conclude that at very low temperatures $T = 5$ K, the concentration of $\text{He}_4^+$ initially formed at higher temperatures is further enhanced through greater sticking probability of $\text{He}$ to $\text{He}_3^+$ at this temperature facilitated by four equivalent orientations to form T-shaped $\text{He}_4^+$ for a given orientation of $\text{He}_3^+$. In addition the possibility of two isomers of $\text{He}_4^+$ enhancing the $n = 4$ peak is consistent with the results of theoretical calculations. Evidently, the magic numbers in $\text{He}_n^+$ mass spectrum do not correlate with the binding energies except for $\text{He}_2^+$.

8. J. P. Toennies (private communication).