# $He_2^{2+}$, the Experimental Detection of a Remarkable Molecule

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The smallest possible doubly charged molecule, $He_2^{2+}$, has been detected spectroscopically by charge-stripping mass spectrometry.

Helium, the second most abundant form of matter in the universe, is the chemically least reactive element. It owes this property to the filled K shell and to the uniquely high first ionization energy, −24.586 eV.[1] Nevertheless, several singly charged helium molecules with appreciable binding energies are known, *e.g.* $HeH^+$ ($D_0° = 178.07$ kJ/mol)[2] and $He_2^+$ ($D_0° = 228.27$ kJ/mol).[2] The smallest possible doubly charged molecule,† $He_2^{2+}$, hitherto only characterized through quantum mechanical calculations,[2,3,4] is a remarkable species of potential astrophysical interest and importance in fusion processes. It is indicated, at definitive (James–Coolidge) theoretical levels, to have the shortest internuclear separation in any molecule, 0.704 Å.[3] For comparison, the experimental distances in $H_2$ and in $HeH^+$, which also have two-electron bonds, are 0.741 and 0.774 Å, respectively.[2] The three-electron bond in $He_2^+$ is somewhat longer, 1.081 Å.[2] The electrostatic repulsion in $He_2^{2+}$ is enormous. According to Coulomb's law, the energy released when two point charges 0.704 Å apart separate to infinity is 1975 kJ/mol. Indeed, the calculated energy of $He_2^{2+}$ lies far above that of two separated $He^{+\cdot}$ ions. Despite this huge driving force for dissociation,

$$He_2^{2+} \rightarrow He^{+\cdot} + He^{+\cdot};\ D°_0 = -835.9 \text{ kJ/mol}^3 \qquad (1)$$

$He_2^{2+}$ is predicted theoretically to have a bound (metastable) ground state $X^1\Sigma_g^+$. The dissociation (equation 1) is inhibited by an energy barrier calculated to be 144.8 kJ/mol.[3] How does this barrier arise? For short increases in length from the equilibrium value, the loss in binding energy (which depends roughly on $1/r^2$) is greater than the gain due to the reduction in electrostatic repulsion (which depends on $1/r$). Many metastable doubly charged molecules comprised of only a few atoms are now known,[5,6] and owe their existence to the same principle. The energy barrier for the dissociation of $He_2^{2+}$ should be high enough to permit its experimental observation, but we find no evidence for its generation in the mass spectra of helium or in the collision of α-particles with helium. We now report the first spectroscopic detection of this species.

† $HeH^{2+}$ is not bound, see ref. 2.

This has been achieved, albeit with considerable difficulty, by means of the charge-stripping technique which is being used extensively to generate multiply charged species.[7]

The precursor $He_2^{+\cdot}$ ions were formed by chemical ionization at relatively high pressures (up to *ca.* 0.5 Torr) in the triple sector mass spectrometer described previously.[8] These ions, detected in the third field-free region are accelerated to an energy of 7 keV, mass selected by the magnetic sector, and then allowed to interact with the neutral target gas in a collision cell (equation 2). The voltages applied to the electrostatic sector are scanned so as to transmit ions whose energy-to-charge ratio is $V/2$ or slightly less. However, considerable difficulty is encountered in attempts to observe $^4He_2^{2+}$, owing to serious interference from the peak arising from the fragmentation reaction (equation 3). The noise associated with the relatively intense broad peak for $^4He^{+\cdot}$ obscured detection of the $^4He_2^{2+}$ signal expected in the same $V/2$ region of the translational energy spectrum. Hence recourse was made to the examination of a 1 : 1 mixture of $^3He$ and $^4He$. However, this experiment was foiled by $N^+$ products formed *via* reaction (4), in the field-free region before the magnet, from $N_2^{+\cdot}$ generated from a low level of residual $N_2$ in the ion source. These fragment ions have an apparent mass-to-charge ratio of 7 ($=14^2/28$) and an energy-to-charge ratio of $V/2$.

$$He_2^{+\cdot} + N_2 \rightarrow He_2^{2+} + e^- + N_2 \quad (2)$$

$$^4He_2^{+\cdot} + N_2 \rightarrow {}^4He^{+\cdot} + {}^4He + N_2 \quad (3)$$

$$N_2^{+\cdot} \rightarrow N^+ + N^\cdot \quad (4)$$

This second source of interference was overcome by employing a second electrostatic analyser. The first two sectors mass select $^3He^4He^{+\cdot}$ and are adjusted to transmit only ions of energy-to-charge ratio $V$; ions produced from reaction (4) are thus excluded. After charge-stripping in the third field-free region of the spectrometer, a spectrum due to $^3He^4He^{2+}$ was clearly evident, albeit at a very low signal intensity (*ca.* $6 \times 10^{-19}$ A). The minimum energy defect (taken to be the onset energy) was measured to be $37 \pm 2$ eV.

We assign this peak to the bound–bound transitions from the $X^2\Sigma_u^+$ state of $He_2^{+\cdot}$ to the $X^1\Sigma_g^+$ state of $He_2^{2+}$. There was also some evidence for possible transitions to the $1^1\Sigma_u^+$ or $2^1\Sigma_g^+$ states[3,4] of $He_2^{2+}$ as well.[9] The observation of $He_2^{2+}$ suggests the possibility that other multiply charged homo- or hetero-nuclear clusters comprised of two or more noble gas atoms might exist. We are investigating this possibility both computationally and experimentally.

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