

## He<sub>2</sub><sup>2+</sup>, the Experimental Detection of a Remarkable Molecule

Michael Guilhaus,<sup>a</sup> A. Gareth Brenton,<sup>a</sup> John H. Beynon,<sup>\*a</sup> Mila Rabrenović,<sup>b</sup> and Paul von Ragué Schleyer<sup>c</sup>

<sup>a</sup> Royal Society Research Unit, University College of Swansea, Singleton Park, Swansea SA2 8PP, U.K.

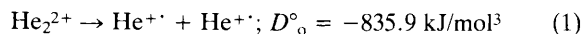
<sup>b</sup> Faculty of Technology and Metallurgy, University of Belgrade, Belgrade, Karnegijeva 4, Yugoslavia

<sup>c</sup> Institute für Organische Chemie der Friedrich-Alexander-Universität, Erlangen-Nürnberg, Henkestrasse 42, D-8520 Erlangen, Federal Republic of Germany

The smallest possible doubly charged molecule, He<sub>2</sub><sup>2+</sup>, 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.<sup>1</sup> Nevertheless, several singly charged helium molecules with appreciable binding energies are known, e.g. HeH<sup>+</sup> ( $D_0^\circ = 178.07$  kJ/mol)<sup>2</sup> and He<sub>2</sub><sup>+</sup> ( $D_0^\circ = 228.27$  kJ/mol).<sup>2</sup> The smallest possible doubly charged molecule, † He<sub>2</sub><sup>2+</sup>, hitherto only characterized through quantum mechanical calculations,<sup>2,3,4</sup> 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.<sup>3</sup> For comparison, the experimental distances in H<sub>2</sub> and in HeH<sup>+</sup>, which also have two-electron bonds, are  $0.741$  and  $0.774$  Å, respectively.<sup>2</sup> The three-electron bond in He<sub>2</sub><sup>+</sup> is somewhat longer,  $1.081$  Å.<sup>2</sup> The electrostatic repulsion in He<sub>2</sub><sup>2+</sup> 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<sub>2</sub><sup>2+</sup> lies far above that of two separated He<sup>+</sup> ions. Despite this huge driving force for dissociation,

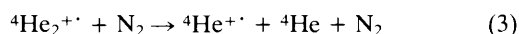


He<sub>2</sub><sup>2+</sup> is predicted theoretically to have a bound (metastable) ground state X<sup>1</sup>Σ<sub>g</sub><sup>+</sup>. The dissociation (equation 1) is inhibited by an energy barrier calculated to be  $144.8$  kJ/mol.<sup>3</sup> How does this barrier arise? For short increases in length 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,<sup>5,6</sup> and owe their existence to the same principle. The energy barrier for the dissociation of He<sub>2</sub><sup>2+</sup> 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<sup>2+</sup> 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.<sup>7</sup>

The precursor  $\text{He}_2^{+}$  ions were formed by chemical ionization at relatively high pressures (up to *ca.* 0.5 Torr) in the triple sector mass spectrometer described previously.<sup>8</sup> 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  ${}^4\text{He}_2^{2+}$ , owing to serious interference from the peak arising from the fragmentation reaction (equation 3). The noise associated with the relatively intense broad peak for  ${}^4\text{He}^{+}$  obscured detection of the  ${}^4\text{He}_2^{2+}$  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  ${}^3\text{He}$  and  ${}^4\text{He}$ . However, this experiment was foiled by  $\text{N}^+$  products formed *via* reaction (4), in the field-free region before the magnet, from  $\text{N}_2^{+}$  generated from a low level of residual  $\text{N}_2$  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  $V/2$ .



This second source of interference was overcome by employing a second electrostatic analyser. The first two sectors mass select  ${}^3\text{He}{}^4\text{He}^{+}$  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  ${}^3\text{He}{}^4\text{He}^{2+}$  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  $\text{X}^2\Sigma_u^+$  state of  $\text{He}_2^{+}$  to the  $\text{X}^1\Sigma_g^+$  state of  $\text{He}_2^{2+}$ . There was also some evidence for possible transitions to the  $1^1\Sigma_u^+$  or  $2^1\Sigma_g^+$  states<sup>3,4</sup> of  $\text{He}_2^{2+}$  as well.<sup>9</sup> The observation of  $\text{He}_2^{2+}$  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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