The Ions H_n^+ and the Possibility of LiH_n^+ and BeH_n^+

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Summary Calculations have been carried out relating to the stability and shape of the ions H_n^+, where n is odd, and comments are included on the possible existence of the ions LiH_n^+ and BeH_n^+.

CLAMPITT AND GOWLAND[1] have recently made a mass spectrometric study of the ions H_n^+. They find that, except for H_2^+, n is odd for all the other ions they observe. They discuss the structure of these ions and suggest that they probably involve the clustering of H_2 molecules round an H_3^+ nucleus. Thus H_5^+ and H_9^+ are to be regarded as $[H_3^+.H_2]$ and $[H_3^+.(H_2)_3]$ respectively.

Calculations we have carried out favour this conclusion and suggest some other possible experiments. Poshusta and Matsen[2] have also performed calculations for the various H_n^+ systems.

Our calculations were performed using the Floating Spherical Gaussian Type Orbital (FSGTO) method of Frost[3] in which pairs of electrons are assigned to orbitals which are of the form $\exp(-ar^2)$. According to these calculations H_3^+ is in the form of an equilateral triangle with sides of 0·88 Å and a stability with respect to H_2 and H^+ of 110 kcal./mole. Detailed calculations[4] give for these figures 0·89 Å and 115 kcal./mole. respectively. Poshusta and Matsen give a side of 0·90 Å and a stability of 125 kcal./mole.

Several nuclear configurations of H_5^+ have been investigated. The most stable is one in which three protons are disposed as an isosceles triangle having one side of length 0·85 Å and the other two of length 0·91 Å. A line through the other two protons is at rightangles to the plane of the equilateral triangle and the whole assembly has C_{2v} symmetry. (*I.e.* the arrangement is that of a distorted tetrahedron). The H–H separation for this pair is 0·81 Å which is a little greater than that in H_2 (0·78 Å by this method) and the distance of the protons of the "H_2" from the proton at the apex of the isosceles triangle is 1·54 Å. One Gaussian orbital is centred within the "H_3^+" triangle and the other at a point equidistant from the nuclei in the "H_2" molecule at a distance of 0·08 Å from the line joining them. The ion H_5^+ must therefore be regarded as an H_2 molecule polarised by the neighbouring H_3^+ such that significant binding is achieved. The binding energy relative to H_3^+ and H_2 is calculated to be 9 kcal./mole. Poshusta and Matsen calculate a dissociation energy of 18 kcal./mole. They state, however, that the stable geometry of H_5^+ has D_{2d} symmetry and consequently do not regard the species as $[H_3^+.H_2]$. We find that their configuration is 3 kcal./mole. less stable than the $[H_3^+.H_2]$ configuration using the FSGTO method. Consequently their calculated dissociation energy from $[H_3^+.H_2]$ may be expected to be about 20 kcal./mole.

Calculations for H_7^+ (with C_{2v} symmetry) show that it is stable relative to H_5^+ and H_2, though the dissociation energy is about 20% less than for H_5^+.

Calculations have also been carried out for LiH_2^+ which is triangular in shape. Again, the binding results from the lateral polarisation of the H_2 molecule by the lithium ion. The Li–H distance is 1·82 Å and the H–H distance 0·80 Å. The dissociation energy to Li^+ and H_2 is calculated to be 12 kcal./mole. which is greater than that calculated by the same procedure for H_5^+ into H_3^+ and H_2. Hence, it should be possible to observe LiH_2^+. The dissociation energy of LiH_4^+ to LiH_2^+ and H_2 is calculated to be 11·5 kcal./mole. and for LiH_6^+ to LiH_4^+ and H_2 8 kcal./mole.

Clampitt and Gowland obtained the H_n^+ ions by bombarding solid hydrogen at 3° K with electrons. The present calculations suggest that, if a mixture of lithium (*e.g.* from an atomic beam) and hydrogen were condensed as an intimate mixture on a cold surface and bombarded with electrons LiH_n^+ (n even) might be obtained.

Calculations for BeH_2^{2+} (isoelectronic with LiH_2^+) suggest that, while it is stable with respect to Be^{2+} and H_2, it is unstable with respect to BeH^+ and H^+. Consequently, with beryllium substituted for lithium in the mixture with hydrogen the ions might be BeH_n^+ in which n is odd.

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[1] R. Clampitt and L. Gowland, *Nature*, 1969, **223**, 815.
[2] R. D. Poshusta and F. A. Matsen, *J. Chem. Phys.*, 1967, **47**, 4795.
[3] A. A. Frost, *J. Chem. Phys.*, 1967, **47**, 3707.
[4] H. Conroy, *J. Chem. Phys.*, 1964, **41**, 1341.