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The Proton Affinity of Methane and its Isotopologues: A Test for Theory

Timothy Kwan^a, Meredith Jordan^a^aSchool of Chemistry, University of Sydney, NSW, Australia**Abstract**

Calculation of the gas phase proton affinity of CH₄, PA(CH₄), involves characterisation of the CH₅⁺ ion whose fluxional nature requires reevaluation of some assumptions routinely made for more *normal* molecules. Here we determine the PA(CH₄; 0 K) using quantum diffusion Monte Carlo (QDMC) simulations on a previously developed CCSD(T)/aug-cc-pVTZ potential energy surface for CH₅⁺. We obtain a value of 542.4 kJ/mol in reasonable agreement with the most recent measurements. The results obtained from standard thermochemical methods, and the limitations of these methods, are also discussed.

Keywords: methane, CH₅⁺, methonium, quantum diffusion monte carlo, proton affinity

1. Introduction

Protonated methane, CH₅⁺, is an important species and has been the subject of many experimental and theoretical investigations [1, 2, 3, 4, 5, 6, 7]. In the gas phase it forms in flames [8] and it is also known to form in highly acidic solution [9]. CH₅⁺ represents the most fundamental of Olah's superacids and is considered a key intermediate in superacid hypercarbon chemistry [10]. CH₅⁺ is also of immense astrochemical importance; it almost certainly resides in methane and water rich nebulae [11], with Olah recently proposing a new pathway for the formation of extraterrestrial CH₅⁺ via methane and a methanol intermediate [12]. Despite its small size and experimental importance, measurements of the gas-phase proton affinity of methane, PA(CH₄), lie over an extremely large range: between 477 and 564 kJ/mol. This is shown in Figure 1, where experimental value is plotted against the year of measurement, with the NIST suggested value of 543.5 kJ/mol [13], shown as a dotted black line. The individual reported errors have been omitted from Figure 1 because they are too small to be indicative of the true error, which is better expressed in the range of values shown. Figure 1 raises the question: why, for such a small species, is there such large variation in the experimental PA(CH₄)?

One reason for these discrepancies is the nature of CH₅⁺ itself. The CH₅⁺ ion, also known as the methonium ion, is the archetypal pentavalent carbon species. Its structure can be considered *fluxional*, that is, there is interchange of the five identical H nuclei between the 5!=120 symmetry equivalent global minimum energy structures and a classical structure where bonds are represented as lines cannot be drawn [5].

CH₅⁺ was first experimentally observed by proton-transfer reaction mass spectrometry in 1952 [1]. After 50 years of hunting, the infrared spectrum (IR) of CH₅⁺ was first measured in 1999 [2], with a high resolution spectrum obtained in 2005, and by 2010 a number of the IR peaks had been assigned [3]. There are still, however, many unsolved problems associated

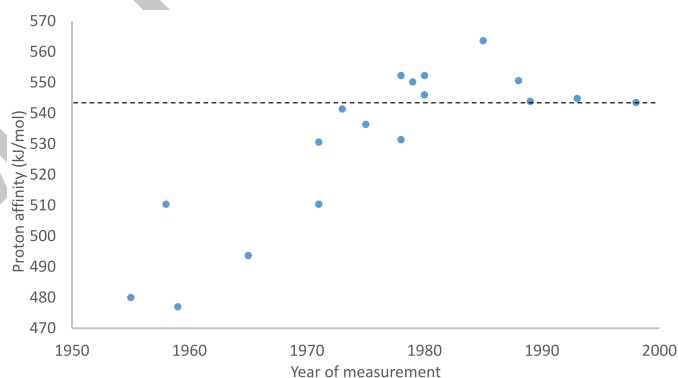
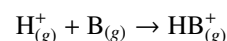


Figure 1: Experimental proton affinities of CH₄ in the literature. The NIST suggested value, 543.5 kJ/mol, is indicated as a dashed line. The individual values and references are given in the supporting information.

with both the IR and high resolution mass spectra, all arising from the fluxional nature of the ion [2, 3].

Questions on the nature of CH₅⁺ have also sparked many theoretical investigations [4, 5, 6, 7]. In studies at the CCSD(T)-R12 level of theory the global minimum energy CH₅⁺ structure has C_s symmetry with very low energy (< 4 kJ/mol) C_{2v} and C_s transition states connecting the symmetry equivalent minima [14]. Lower levels of theory predict a C_{2v} or a different C_s minimum energy structure [5, 14]. Two separate quantum diffusion Monte Carlo (QDMC) simulations on CCSD(T) potential energy surfaces (PES) have confirmed the fluxional structure of CH₅⁺; at 0 K, where the five H atoms interchange and all 120 symmetry equivalent minima are accessed by the ground state nuclear wavefunction [4, 15].

For gas-phase protonation of a species B,



the proton affinity, PA(B), is defined as

$$\text{PA(B)} = -\Delta H_{\text{react}} = H(\text{H}^{+}) + H(\text{B}) - H(\text{HB}^{+}) \quad (1)$$

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