

On the nature of CH_6^{2+}

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The meta-stability of the hexacoordinate CH_6^{2+} dication in the gas phase is confirmed by a detailed computational exploration of its potential energy surface, using a modified “Kick” heuristic methodology and by Born-Oppenheimer Molecular-Dynamics simulations to assess its kinetic persistence. The transition states for deprotonation, decomposition into CH_3^+ and H_3^+ , hydrogen scrambling, and H-H rotation are found. In addition, a nearly perfect correlation between the protonation affinities and their coordination number is obtained.

Keywords: Theoretical chemistry, Kick heuristic methodology, Born-Oppenheimer molecular dynamics study, Kinetic stability, Adaptive natural density partitioning analysis

Three decades ago Lammertsma *et al.*^{1,2} examined the simplest hexacoordinate carbon molecule diprotonated methane, CH_6^{2+} , using MP3/6-31G**//HF/6-31G* computations. Despite its large inherent thermodynamic instability due to Coulomb repulsion, this dication was found to have a meta-stable local minimum with C_{2v} symmetry (**1** in Fig. 1) comprising two 3c-2e bonds and two 2c-2e bonds. Notwithstanding its very favorable decomposition energies, -63.1 , -18.6 and -126.8 kcal mol⁻¹ for loss of a proton, loss of H_2^+ , and loss of H_3^+ , respectively, (**1**) was kinetically persistent due to the high barriers for deprotonation (35.4 kcal mol⁻¹) and for demethylation (59.9 kcal mol⁻¹). Like CH_5^+ , hydrogen scrambling is very facile; the barrier of (**1**) is only 0.9 kcal mol⁻¹ (refs 3, 4).

In 1982, Jemmis *et al.*⁵ considered CLi_6^{2+} computationally, but due to the more electropositive character of lithium, it adopts an octahedral minimum geometry quite unlike CH_6^{2+} (the O_h symmetry form of which is computed to have a triply degenerate set of imaginary frequencies). Later on Schmidbaur's group,⁶ noting the isolobal relationship among

LAu^+ , H^+ and Li^+ , synthesized and characterized the hexacoordinate gold complex $\{[(\text{C}_6\text{H}_5)_3\text{PAu}]_6\text{C}\}^{2+}$, another analog of CH_6^{2+} . Metals are much better at accommodating the two positive charges than the H's in CH_6^{2+} . More recently, Rasul *et al.*^{7,8} computed the chemical shifts for the latter dication (**1**), but this species has not yet been detected experimentally; it is unlikely to be viable in condensed phase.

In this article, we reexamine the structure and bonding of CH_6^{2+} using new computational tools. First, a modified Kick heuristic (called Bilatu)⁹ is employed to explore details of the potential energy surface (PES) of CH_6^{2+} . The structures found by this initial PBE0¹⁰/D95V¹¹ search were reoptimized and the total energies characterized at the CCSD(T) (full)¹²/def2-TZVPPD//PBE0/def2-TZVPPD level.¹³ Intrinsic reaction coordinate (IRC) computations ensured that the TSs are connected to the designated reactants and products.¹⁴ The results obtained at the CCSD(T)/def2-TZVPPD level, including the PBE0/def2-TZVPPD zero point energy corrections, are discussed here. All the computations employed the Gaussian 09

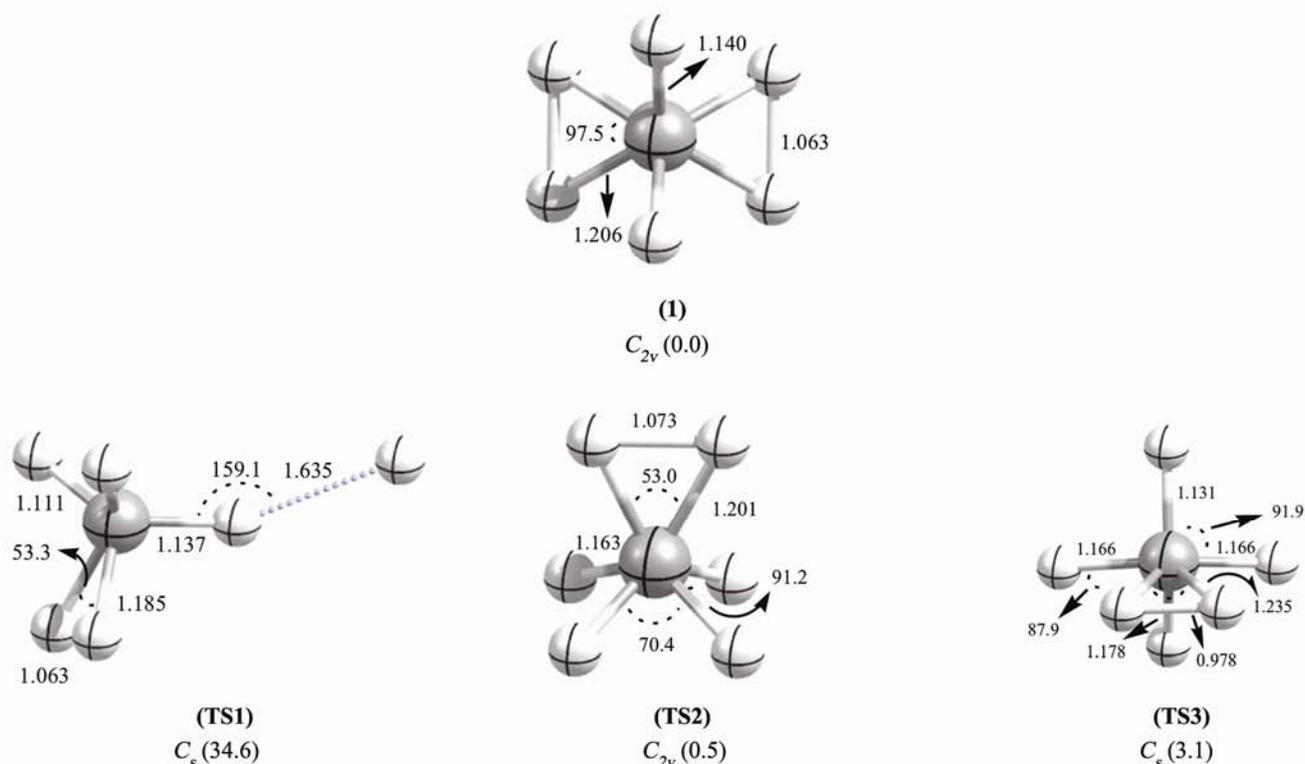


Fig. 1 – Optimized structure of CH₆²⁺ and the transition states involved in deprotonation (TS1), scrambling (TS2), and H₂ rotation (TS3) computed at the PBE0/def2-TZVPPD level. [Bond lengths are in Å. The relative energies (in parentheses in kcal mol⁻¹) are at the CCSD(T)/def2-TZVPPD//PBE0/def2-TZVPPD level].

program.¹⁵ The Adaptive Natural Density Partitioning (AdNDP) analysis¹⁶ (see Fig. 2) was performed at the PBE0/def2-TZVPPD level.

Our stochastic search confirms that the metastable C_{2v} minimum (1) is the only bound complex of CH₆²⁺. (Supplementary Data, Table S1) Due to the relief of its Coulomb repulsion, dication (1) decomposes into CH₃⁺ and H₃⁺ exothermally by -121.8 kcal mol⁻¹ (at the CCSD(T)(full)/def2-TZVPPD//PBE0/def2-TZVPPD level). Our stochastic search also found proton loss; the deprotonation energy of (1) is -63.0 kcal mol⁻¹.

Figure 1 gives the most important geometrical parameters of (1). The presence of two 3c-2e bonds (with elongated lengths, $r(\text{C-H}) = 1.206$ and $r(\text{H-H}) = 1.063$ Å) and two 2c-2e bonds ($r(\text{C-H}) = 1.140$ Å) is confirmed adequately by Adaptive Natural Density Partitioning (AdNDP) analysis¹⁶ (Fig. 2).

Figure 1 also depicts the transition states involved in the deprotonation (TS1), hydrogen scrambling (TS2), and H₂ rotation (TS3) processes. Despite the large proton loss exothermicity of CH₆²⁺, the corresponding computed deprotonation barrier is very

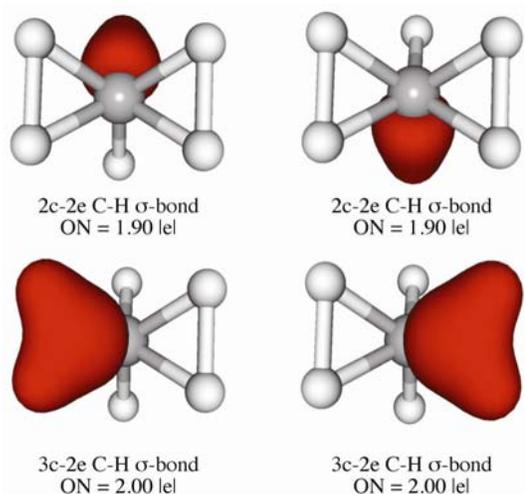


Fig. 2 – AdNDP¹⁶ chemical bonding analysis of CH₆²⁺ at the PBE0/def2-TZVPPD level. Note that the occupation numbers (ON) are all at or near 2 electrons.

high (34.6 kcal mol⁻¹). The initial energy loss of the residual proton binding is much larger than the gain in Coulomb energy until later in the H⁺ detachment process. The dissociating H-H distance in TS1 is 1.635 Å (i.e., 0.174 Å longer than the value reported

previously),^{1,2} but the connecting C-H bond length is 1.137 Å. In contrast, the barriers for hydrogen scrambling and H₂ rotation are only 0.5 and 3.1 kcal mol⁻¹, respectively. The 2.6 kcal mol⁻¹ larger barrier for H₂ rotation contrasts with CH₅⁺, where both barriers are close to zero.¹⁷ We refined TS3 to C_s symmetry (rather than C_{2v} as reported by Lammertsma *et al.*^{1,2}).

On the other hand, the loss of molecular hydrogen (CH₆²⁺ → CH₄²⁺ + H₂) is highly endothermic (81.5 kcal mol⁻¹). This value is the double of that computed at the same level (CCSD(T)/def2-TZVPPD//PBE0/def2-TZVPPD) for the loss of H₂ in CH₅⁺ (41.0 kcal mol⁻¹). This is also reflected in the H-H distances (1.034 and 1.063 Å in CH₅⁺ and CH₆²⁺, respectively). Clearly, the interaction of the H₂ fragment is stronger in (1) than in CH₅⁺, increasing the H₂ rotation barrier of CH₆²⁺. In systems like BH₅ and SiH₅⁺, where the H₂ interaction is negligible, the scrambling barrier is much higher than H₂ rotation.^{18,19} From the geometrical point of view, while it is possible to place four and six equivalent points equidistantly on a sphere (i.e., in T_d and O_h symmetry, respectively), this is impossible for five points (the highest possible symmetries are D_{3h}, C_{4v}, and D_{5h}). The five points in D_{5h} symmetry are all equivalent, but their vicinal and distal relationships are not equidistant. The "most nearly equivalent/equidistant" arrangement surely has a C₁ point group. Hence, complete scrambling of points on a sphere requires symmetry reduction, and this is inherently easier with point groups that have lower symmetry numbers, because less "movement" is required.

In CH₅⁺, the number of lines in the high-resolution infrared vibration-rotation-tunneling spectrum corresponding to the C-H stretching vibrations is an order of magnitude more than that of the CH₃⁺ lines, reflecting the higher partition functions due to tunneling.²⁰ Something similar is expected for CH₆²⁺, because the low barriers separating the two minima would trigger at perpetual scrambling dynamics even at very low temperatures due to the tunneling effects. Although CH₆²⁺ clearly is predicted to be persistent kinetically, its mode of generation is not obvious. Perhaps it might form as an ejection fragment from a larger, multi-charged carbocation.

To verify this prediction, we performed Born-Oppenheimer Molecular Dynamics (BO-MD) simulations using the deMon2k program²¹ at the PBE0/DZVP level and a Hoover thermostat for

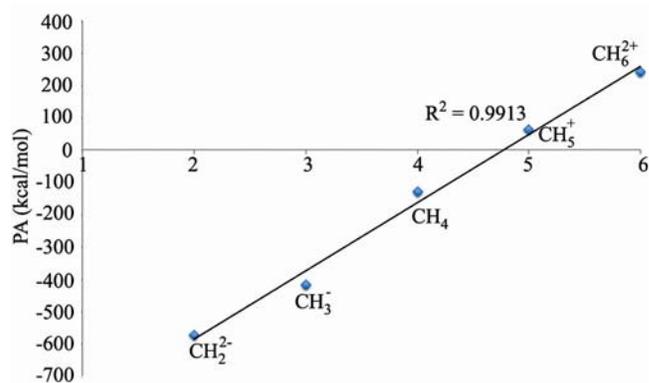


Fig. 3 – Protonation affinities (PA, in kcal mol⁻¹) versus coordination number.

temperature control (300-2400 K at 300 K increments). Each simulation started from the equilibrium geometry; random velocities were assigned to the atoms, and sampling was continued for 25 ps with a 1 fs step size. The structure of (1) does not undergo any transformation at 300 K (see Supplementary Data, Movie MS1). However, the simulations up to 900 K show that hydrogen scrambling occurs more frequently than H₂ rotation (in agreement with the computed barriers for both processes, see Supplementary Data, Movie MS2). Both processes are very fast at higher temperatures. Following the structural evolution along the recorded trajectories reveals that CH₆²⁺ maintains its connectivity up to 2100 K, but then dissociates into CH₅⁺ + H⁺ at 2400 K (see Supplementary Data, Movie MS3), thus confirming that this lowest barrier process is the preferred decomposition pathway.

Protonation of CH₆²⁺ (1) gives the CH₇³⁺ trication, considered by Olah and Rasul in 1996.²² However, the computed protonation energy of (1) is extremely endothermic; the value of 240.6 kcal mol⁻¹ is almost four times that of CH₅⁺ protonation (63 kcal mol⁻¹). The protonation affinity of methane is exothermic (PA = -129.1 kcal mol⁻¹).¹⁷ Interestingly, the perfect correlation between the protonation energy and the coordination number given by these three points can be extended by including PA data for the anions, CH₃⁻ and CH₂²⁻ in the same analysis (see Fig. 3). Although molecules are anions and the protonated products do not involve multicenter bonds, Fig. 3 shows a perfect correlation ($r^2=0.9913$) between the protonation and the coordination number for these carbon species.

In summary, our exploration of the PES of CH₆²⁺ by using a modified Kick heuristic methodology confirms the metastability of the high energy C_{2v} symmetry local

minimum (**1**). Its 34.6 kcal mol⁻¹ deprotonation barrier ensures kinetic persistence. BO-MD simulations reveal that CH₆²⁺ remains intact up to 2100 K. Decomposition into CH₅⁺ and H⁺ occurs at 2400 K. Although (**1**) is the smallest possible hexacoordinate carbon molecule, it does not violate the octet rule; AdNDP analysis confirms the presence of two 3c-2e units and two 2c-2e bonds. However, the fluxional behavior of CH₆²⁺ at lower temperatures (up to 900 K), is in line with the computed barriers for proton scrambling and for H₂ rotation of 0.5 and 3.1 kcal mol⁻¹, respectively. Finally, a perfect correlation with the protonation energy and the coordination number is also found.

Supplementary Data

Supplementary data associated with this article, viz., Cartesian coordinates (Table S1) and BO-MD simulations (Movies MS1-MS3) are available in the electronic form at [http://www.niscair.res.in/jinfo/ijca/IJCA_53A\(8-9\)992-995_SupplData.pdf](http://www.niscair.res.in/jinfo/ijca/IJCA_53A(8-9)992-995_SupplData.pdf).

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