

Computational Calculation of Binding Energy of Methane with $[\text{Mn}(4\text{-Picoline})_2]^{2+}$ Dication Complex ion in the Gas Phase: Theory and Experiment.

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ABSTRACT

Across the globe the search for ways of a more resourceful convention of the abundant, untapped reserves of over 1850.5 ppb of methane gas. The UV photofragment spectrum of the dication complex ion $[\text{Mn}(4\text{-Picoline})_3]^{2+}$ had been recorded in the gas phase for theoretical and experimental analysis using a quadrupole ion trap mass spectrometer. Using a combination of the pick-up technique and high energy electron impact the $[\text{Mn}(4\text{-Picoline})_3]^{2+}$ ions were prepared and then held in a cold ion trap where they were excited with tuneable UV radiation and effectively activated further with methane. From the DFT calculations, the optimised C1 conformer of $[\text{Mn}(4\text{-Picoline})_3]^{2+}$ was confirmed.

Methane activation with manganese 4 methyl dication complex ion resulted in the formation $[\text{Mn}(4\text{-Picoline})_3\text{H}_2\text{O}]^{2+}$, $[\text{Mn}(4\text{-Picoline})_3(\text{H}_2\text{O})_2]^{2+}$, $[\text{Mn}(4\text{-Picoline})_3\text{N}_2]^{2+}$, $[\text{Mn}(4\text{-Pico})_3\text{CO}_2]^{2+}$, $[\text{Mn}(4\text{-Picoline})_3(\text{CH}_3)_2]^{2+}$ and $[\text{Mn} 4\text{-Picoline} (\text{CH}_4)]^+$ were recorded. The calculated charge on the metal centre was reduced by approximately 20% in the optimised geometry $[\text{Mn}(4\text{-Picoline})_3\text{CH}_4]^{2+}$ of as compared to the charge of +2 assumed on Mn metal in the potential energy curve, (PEC) calculation. The DFT calculated result revealed that the binding energy of methane to the metal dication complex ion was that overestimated on the PEC model by 32%.

KEY WORDS: Manganese, Binding energy, 4- Picoline, Methane, DFT, PEC, Gas Phase.

INTRODUCTION

Methanol is the simplest alcohol molecule and is emerging as a clean, sustainable transportation fuel of the future across the world [1]. Methanex is working with partners worldwide to promote methanol as a clean, sustainable road fuel. Currently methanol is blended with gasoline in high-proportion such as M85-M100 in flex-fuel or in low-quantities and used in existing road vehicles or dedicated methanol-fuelled vehicles. In recent times technology is also being commercialized to use methanol as a diesel substitute. [2].

China currently leads the world in methanol fuel blending. In 2017, China consumed as much as 12 million metric tons (4 billion gallons) of methanol to fuel various cars, trucks and buses. China's fuel pool consists of 8% methanol and Chinese drivers have covered more than 200 million miles in methanol fuelled cars [2]. Statistics reveal that in more than a dozen provinces blends such as M15 (15% methanol and 85% gasoline) are sold as 95 and 97 octane fuels for use in existing passenger cars. The central government of China considers methanol as a strategic transportation fuel and in an attempt to develop national standards for methanol-fuelled vehicles, the government has launched a demonstration of light-and heavy-duty vehicles running on M85 (85% methanol and 15% gasoline) and M100 (100% methanol) in Shanxi, Shaanxi provinces and in the city of Shanghai [2].

It is not surprising that across the globe the methanol fuel 'fever' is spreading uncontrollably like a bush fire. In November, 2013, Israeli Prime Minister Benjamin Netanyahu launched a demonstration of M15 vehicles and hosted a fuel choices summit in Tel Aviv to focus attention on the potential for methanol based fuels in Israel. As a way of encouragement and promoting methanol fuel, the federal government of Australia does not tax methanol fuels, and Methanol Institute member company Coogee Energy is demonstrating the use of gasoline, ethanol and methanol (GEM) fuels in passenger cars [2]. President Obama recently called the United States the "Saudi Arabia of natural gas" and asserted that it was time for our oil-dominated transportation fuel market to open the door to natural gas. As he rightly said it would be cheaper for consumers and reduce the strategic importance of oil but first we need cars that can run on methanol, a high-octane fuel made from converted natural gas [2].

With the aim to develop a cost efficient and environmentally friendly vehicle with zero harmful emissions and an exhaust that is as clean as the air surrounding, the Danish methanol fuel cell manufacturer SerEnergy has launched a commercial reformed methanol fuel cell vehicle with a driving range up to 800 km on a tank of methanol [3].

Currently global methane concentrations have reached 1850.5 ppb in July 2018 [4]. This very large reserves of methane, could serve as a feedstock for the production of chemicals and as a source of energy well. Both methane and carbon dioxide are similarly problematic however, methane retains, roughly 30 times more heat than CO₂ in the atmosphere even though CO₂ is five times more than methane [5]. The future global task is to trap methane and convert it into the best efficient use and other valuable and/or environmentally friendly chemical compounds [4].

This research sought to form doubly charged manganese dication complexes [Mn(4-methyl Pyridine)₃]²⁺ ions and activate them with methane follow by the calculation of the binding energy of methane to the metal complexes in the gas phase [6]. Imagine an industry that has methane as feed stock for the production of chemicals and as a source of energy where methane is converted to much more efficient and environmentally friendly methanol. For example, fractional oxidation of methane offers a distinct road of direct converting of methane to liquid methanol as reveal by the equation $\text{CH}_4 + \frac{1}{2}\text{O}_2 \rightarrow \text{CH}_3\text{OH}$ [8].

2.0 Experimental Procedure

The apparatus shown schematically in Fig. 1 detailed the experimental procedure for the formation of [Mn(4-Picoline)₃]²⁺ dication complex ions. The systematic description of the entire instrument was given by the author in his previous publication [9]. In summary the instrument has five differentially pumped vacuum chambers namely supersonic expansion, beam collimation, metal vaporization and pick-up (oven), quadrupole mass selection and ion trapping.

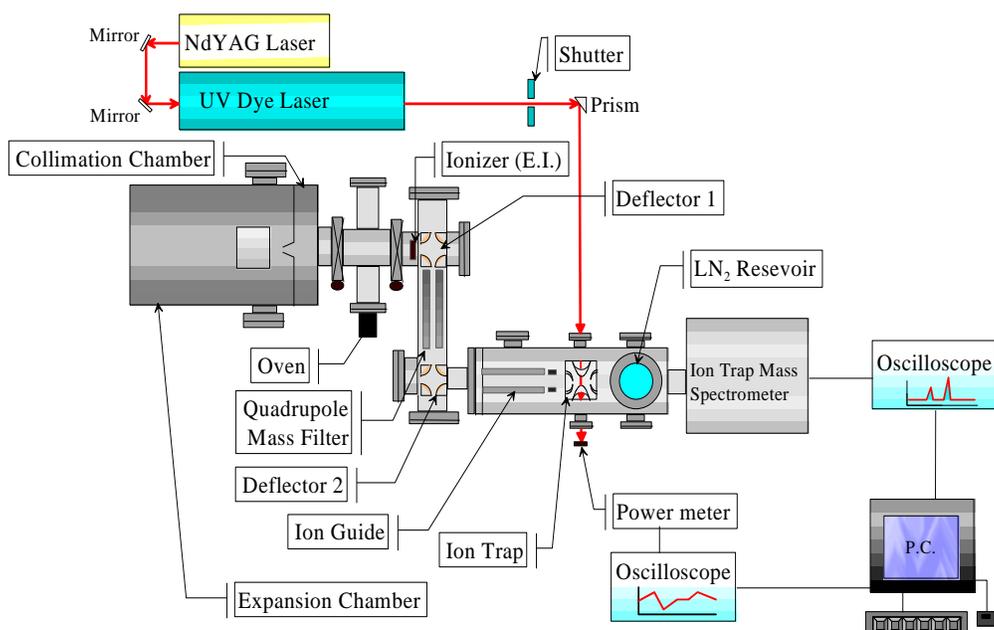


Fig. 1. Schematic diagram of the experimental set up, showing the pick-up region (oven), the quadrupole mass filter, and the ion trap, together with auxiliary equipment.

RESULTS AND DISCUSSION

The appearance of discrete structured sharp mass spectrum of $[\text{Mn}(4\text{-Picoline})_3]^{2+}$ at 167 amu and a minuscule hydrated complex of $[\text{Mn}(4\text{-Picoline})_3\text{H}_2\text{O}]^{2+}$ at 176 amu (Figure 2) similar to what was observed in the ethane activation [9] indicates that the working conditions in the experiment set up remained the same in both methane and ethane activation with $[\text{Mn}(4\text{-Picoline})_3]^{2+}$ metal dication complex ion.

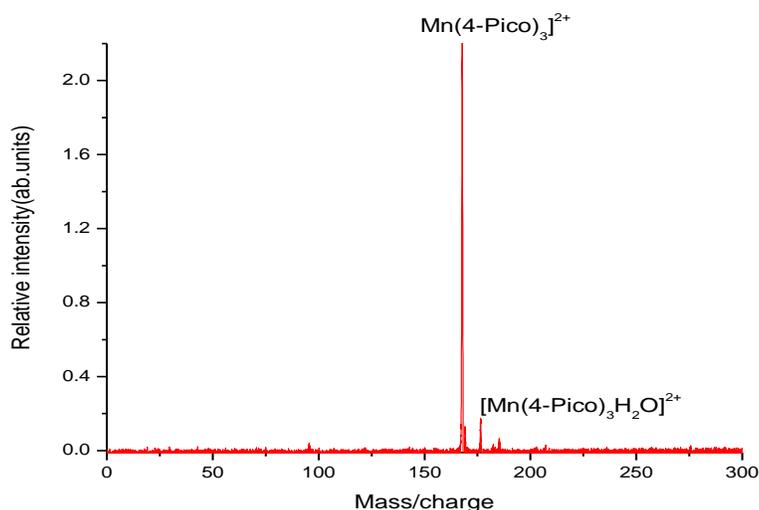


Figure 2: Mass spectrum of $[\text{Mn}(4\text{-Picoline})_3]^{2+}$ [9]

ACTIVATE OF $[\text{Mn}(4\text{-PICOLINE})_3]^{2+}$ WITH METHANE

Figure 3 represents the photofragmentation pattern of the manganese dication complex ion $[\text{Mn}(4\text{-Picoline})_3]^{2+}$ with methane. As revealed distinct ion peaks namely the isolated parent fragment of $[\text{Mn}(4\text{-Picoline})_3]^{2+}$ at 167 amu the hydrated parent dication complex ions of $[\text{Mn}(4\text{-Picoline})_3\text{H}_2\text{O}]^{2+}$ at 176 amu and the dihydrated parent dication complex ions $[\text{Mn}(4\text{-Picoline})_3(\text{H}_2\text{O})_2]^{2+}$ at 185 amu, the metal dication nitro parent complex ion $[\text{Mn}(4\text{-Picoline})_3\text{N}_2]^{2+}$ at 181 amu, the carbonated parent fragment, $[\text{Mn}(4\text{-Pico})_3\text{CO}_2]^{2+}$ at 189 amu were observed. The ability of the $[\text{Mn}(4\text{-Picoline})_3]^{2+}$ to pick methyl under laser power was observed in the formation of $[\text{Mn}(4\text{-Picoline})_3(\text{CH}_3)_2]^{2+}$ at 182 amu. The photofragmentation path with the loss of a picoline ion was observed resulting in the formation of a main daughter fragment peak corresponding to coordinatively unsaturated $[\text{Mn}(4\text{-Picoline})]^{+}$ at 148 amu. The ability of this daughter fragment to pick methane to form manganese 4-picoline monovalent complex ion of $[\text{Mn} 4\text{-Picoline} (\text{CH}_4)]^{+}$ at 164 amu was recorded.

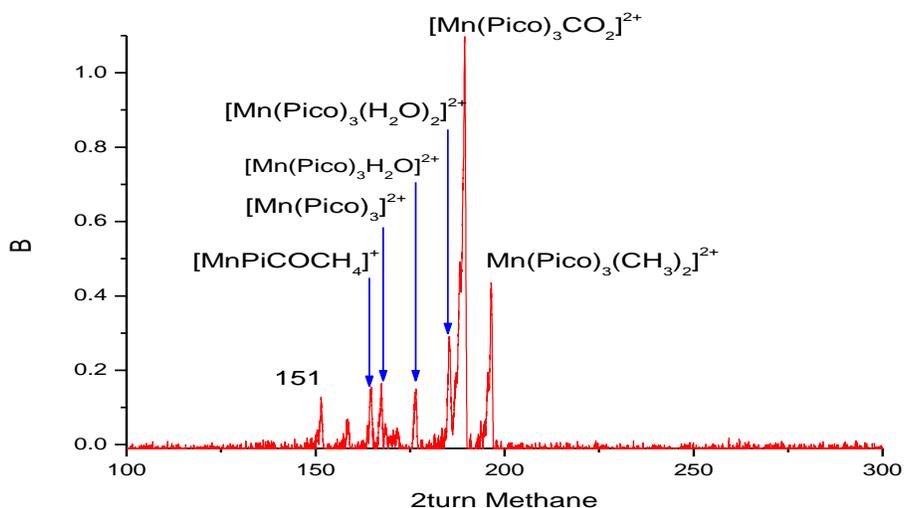


Figure 3: Photofragment mass spectrum of $[\text{Mn}(4\text{-Picoline})_3\text{CH}_4]^{2+}$ (44000cm^{-1})

CALCULATION OF THE STRUCTURE AND BINDING ENERGY OF METHANE WITH MANGANESE 4-PICOLINE COMPLEX DICATION IONS.

The optimised geometry conformer of $[\text{Mn}(4\text{-Picoline})_3\text{CH}_4]^{2+}$ was observed to be C_1 symmetry Figure 4 and the shortest manganese-methane (Mn-C) distance of 2.0 Å.

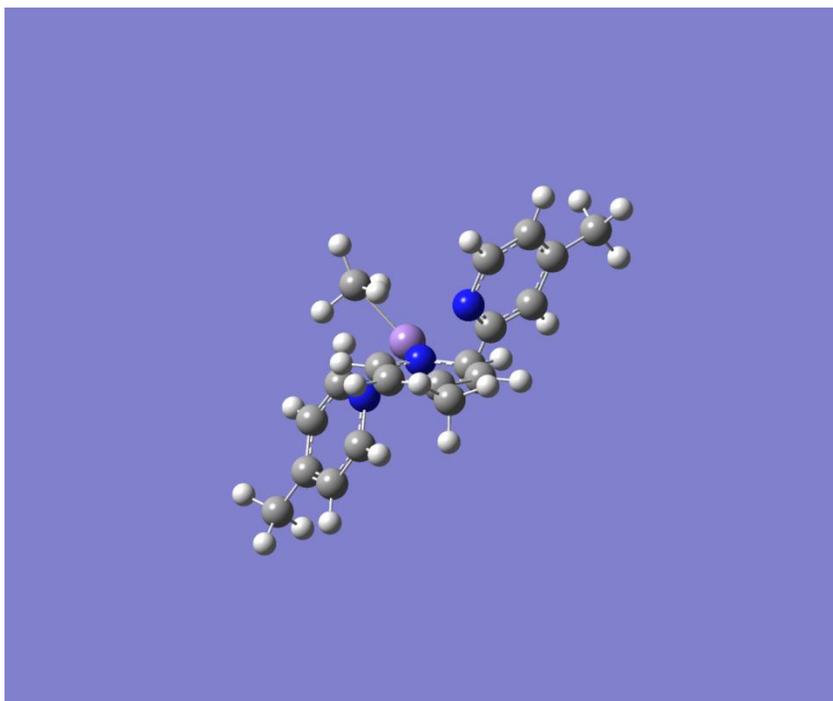


Figure 4: The Optimized geometry of $[\text{Mn}(4\text{-Pico})_3\text{CH}_4]^{2+}$ with C_1 Symmetry

Table 1: Binding Energies of Methane with $\text{Mn}(\text{4-Picoline})_3^{2+}$ Complex Ion Calculated using both BVP86/6311++G(d, p) and TPSSh/6311++G(d, p)

Reaction	BVP86/kJ/mol	TPSSh/kJ/mol
$[\text{Mn}(\text{4-Picoline})_3]^{2+} \rightarrow \text{Mn}^{2+} + 3(\text{4-Picoline})$	1617.31	1617.31
$[\text{Mn}(\text{4-Picoline})_3\text{Me}]^{2+} \rightarrow [\text{Mn}(\text{4-Picoline})_3]^{2+} + \text{Me}$	13.15	13.14
$[\text{Mn}(\text{4-Picoline})_2\text{Me}]^{2+} \rightarrow [\text{Mn}(\text{4-Picoline})_2]^{2+} + \text{Me}$	35.71	35.72
$\text{Mn}(\text{4-Picoline})\text{Me}]^{2+} \rightarrow [\text{Mn}(\text{4-Picoline})]^{2+} + \text{Me}$	120.17	120.10
$[\text{Mn}(\text{4-Picoline})_2]^{2+} \rightarrow \text{Mn}^{2+} + 2(\text{4-Picoline})$	1371.14	1371.14
$[\text{Mn}4\text{-Picoline}^+ \rightarrow \text{Mn}^+ + 4\text{-Picoline}$	110.86	110.84

For $\text{Mn}(\text{4-Picoline})_3\text{CH}_4^{2+}$ complex ion the binding energy was maximised at the optimised structure. The one-third the binding energy of $[\text{Mn}(\text{4-Picoline})_3]^{2+} \rightarrow \text{Mn}^{2+} + 4\text{-Picoline}$ calculated at different levels of theory of zero point energy are in realistic agreement: BP86/6-311++G(d, p) and TPSSh/6-311++G(d, p) at the same levels of theory gave and 527.18 kJ/mol. This theoretical calculated binding energy corresponds to 44068.80 cm^{-1} per molecule which perfectly falls within the experimental photon energy range of 35000 to 45000 cm^{-1} over which the photofragmentation spectra were recorded.

THE ONE DIMENTIONAL POTENTIAL ENERGY CURVE OF $[\text{Mn}(\text{4-PICOLINE})_3\text{CH}_4]^{2+}$

In order to picture the observed charge separation reactions qualitatively a one dimensional potential energy curve model of $[\text{Mn}(\text{4-Picoline})_3\text{CH}_4]^{2+}$ was plotted (Figure 5). From the curves, it was observed that the H transfer separation giving $[\text{Mn}(\text{4-Picoline})_3\text{CH}_3]^{2+} + \text{H}$ from $[\text{Mn}(\text{4-Picoline})_3\text{CH}_4]^{2+}$ (green line) was located closer to the stable curve (red line). The photoinduced charge transfer to give $\text{Mn}(\text{4-Picoline})_3^+$ and CH_4^+ of $[\text{Mn}(\text{4-Picoline})_3\text{CH}_4]^{2+}$ was not observed in the photofragmentation because this reaction is endothermic as evidenced by observing that the potential energy curve (blue) lies above the attractive curve. At the optimised geometry of $[\text{Mn}(\text{4-Picoline})_3\text{CH}_4]^{2+}$ (Figure 4) the manganese-methane distance (Mn-C) is 2.0 \AA which corresponds to 0.18 eV (17.36 kJ/mol in photon energy) on the PEC. Comparing with the calculated DFT of 13.15 kJ/mol it is clear that the PEC calculated value was overestimated by 4.21 kJ/mol which is due to fact that the actual charge on the Mn in the optimised geometry was 1.61 while the charge of $\text{Mn}=2$ was assumed in the PEC calculation.

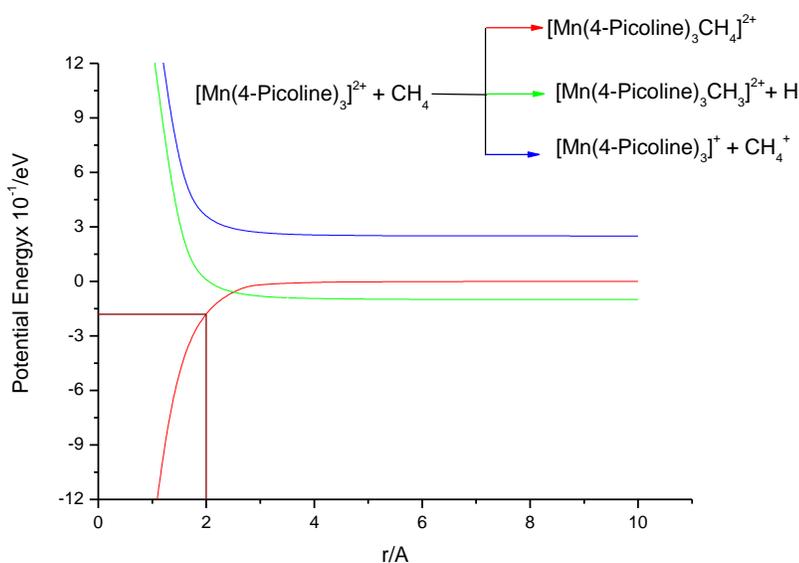


Figure 5: The Potential Energy Surface Curve model showing attractive and repulsive curves of ion-ligand $[\text{Mn}(\text{4-Picoline})_3\text{CH}_4]^{2+}$

CONCLUSION

The average binding energy per molecule of Picoline calculated for $[\text{Mn}(\text{4-Picoline})_3]^{2+}$, lies within the photon energy range over which the photofragmentation spectra were recorded. C_1 symmetry optimised geometry of the methane manganese 4-picoline dication complex ions was observed. The calculated charge on the manganese metal centre was 1.61 on the DFT optimised geometry while the charge assumed for the PEC calculation was +2. The interaction of methane with the $[\text{Mn}(\text{4-Picoline})_3]^{2+}$ resulted in the overestimation of binding energy on the PEC model by 32% as compared to DFT calculation.

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