Activation of C-H Bonds in $\text{Pt}^+ + x \text{CH}_4$ Reactions, where $x = 1 - 4$:

Identification of the Platinum Dimethyl Cation

Oscar W. Wheeler,[†] Michelle Salem,^{†,‡} Amanda Gao,^{†,||} Joost M. Bakker,[§]
and P. B. Armentrout^{*,†}

[†]*Department of Chemistry, University of Utah, 315 S. 1400 E. Room 2020, Salt Lake City, Utah 84112, United States*

[‡]*Present address: Department of Chemistry and Biochemistry, California State University San Marcos, 333 S. Twin Oaks Valley Rd., San Marcos, California 92096, United States*

^{||}*Present address: Department of Chemistry and Chemical Engineering, California Institute of Technology, 1200 E. California Boulevard, Pasadena, California 91125, United States*

[§]*Radboud University, Institute for Molecules and Materials, FELIX Laboratory, Toernooiveld 7c, 6525ED Nijmegen, The Netherlands*

Abstract: Activation of C-H bonds in the sequential reactions of $\text{Pt}^+ + x \text{CH}_4/\text{CD}_4$, where $x = 1 - 4$, have been investigated using infrared multiple photon dissociation (IRMPD) spectroscopy and theoretical calculations. Pt^+ cations are formed by laser ablation and exposed to controlled amounts of CH_4/CD_4 leading to $[\text{Pt},x\text{C},(4x-2)\text{H/D}]^+$ dehydrogenation products. Irradiation of these products in the $400 - 2100 \text{ cm}^{-1}$ range leads to CH_4/CD_4 loss from the $x = 3$ and 4 products, whereas $\text{PtCH}_2^+/\text{PtCD}_2^+$ products do not decompose at all, and $x = 2$ products dissociate only when formed from a higher order product. The structures of these complexes were explored theoretically at several levels of theory with three different basis sets. Comparison of the experimental and theoretical results indicate that the species formed have a $\text{Pt}(\text{CH}_3)_2^+(\text{CH}_4)_{x-2}/\text{Pt}(\text{CD}_3)_2^+(\text{CD}_4)_{x-2}$ binding motif for $x = 2 - 4$. Thus, reaction of Pt^+ with methane occurs by C-H bond activation to form PtCH_2^+ , which reacts with an additional methane molecule by C-H bond activation to form the platinum dimethyl cation. This proposed reaction mechanism is consistent with theoretical

explorations of the potential energy surface for reactions of Pt^+ with one and two methane molecules.

1. Introduction

Methane is the primary component of natural gas but is still associated with waste in both farming¹ and industrial² fields. Atmospheric content from anthropogenic and natural release of CH_4 has increased from $\sim 0.5 \text{ ppb yr}^{-1}$ from 1999 – 2006 to $\sim 6 \text{ ppb yr}^{-1}$ from 2007 – 2011.³ This increase has resulted in atmospheric CH_4 levels that are $\sim 150\%$ greater than levels before 1750, as found in ice core samples.³ Although CH_4 emission is less than that of CO_2 , CH_4 has a GWP (global warming potential) of 84 (20 year) and 28 (100 year) compared to CO_2 (GWP = 1 for 20 and 100 years),³ which makes atmospheric increases in CH_4 an environmental concern. Surplus CH_4 could be utilized as a valuable energy source and feedstock for synthesis of desirable chemicals. Thus chemical processes that can activate and/or functionalize CH_4 are of great interest both environmentally and economically.⁴ One economically important chemical process is conversion of CH_4 to synthesis gas ($\text{CO} + \text{H}_2$), a process that clearly involves the activation of C-H bonds.^{5,6}

In the present study, the activation of multiple methane molecules by atomic platinum cations is investigated. The activation of CH_4 by Pt^+ has been studied in the literature both experimentally⁷⁻¹⁷ and theoretically.^{9-12,17} These studies show that at thermal energies, Pt^+ reacts with CH_4 to dehydrogenate and form $\text{PtCH}_2^+ + \text{H}_2$ products with a reaction efficiency ranging from 40 – 84 % (compared to the Langevin-Gioumoussis-Stevenson (LGS) collision rate¹⁸). Results by Zhang *et al.*¹² show that this reaction rate is dependent on kinetic energy, which can explain the range observed in the experimental rates. A secondary reaction with CH_4 by the $[\text{Pt},\text{C},2\text{H}]^+$ species to form $[\text{Pt},2\text{C},4\text{H}]^+$ has been observed in ion cyclotron resonance (ICR) mass spectrometry experiments, but with a reaction efficiency of only 1 – 2 % of the LGS collision rate.^{7,8,13} The tertiary dehydrogenation by the $[\text{Pt},2\text{C},4\text{H}]^+$ species to form $[\text{Pt},3\text{C},6\text{H}]^+$ was only $\sim 0.5\%$ of the LGS rate.⁷ The structural make-up of the $[\text{Pt},2\text{C},4\text{H}]^+$ and $[\text{Pt},3\text{C},6\text{H}]^+$ species is unknown, but

Diefenbach *et al.* have suggested that a $\text{Pt}^+(\text{C}_2\text{H}_4)$ product is formed rather than $\text{Pt}^+(\text{CH}_2)_2$.¹⁹ Reactions of methane with platinum clusters, Pt_n^+ where $n = 1 - 21$, have also been examined.^{11,15,16} Here, most small cluster sizes effect dehydrogenation of one methane with a reaction efficiency $\geq 18\%$, whereas $n = 4, 10, 13, 14$, and larger clusters (>15) react with efficiencies $< 3\%$. Only clusters of $n = 5 - 9$ and 11 were observed to dehydrogenate a second CH_4 molecule forming $[\text{Pt}_n, 2\text{C}, 4\text{H}]^+$, whereas this work^{15,16} found the atomic ion did not undergo this reaction, in conflict with the ICR studies.^{7,8,13}

Previous spectroscopic studies of related systems include the vibrational spectroscopy of metal-methane clusters: $\text{Li}^+(\text{CH}_4)_{1-9}$,^{20,21} $\text{Al}^+(\text{CH}_4)_{1-6}$,²² $\text{Mn}^+(\text{CH}_4)_{1-6}$,²³ $\text{Fe}^+(\text{CH}_4)_{1-4}$,²⁴ $\text{Fe}_2^+(\text{CH}_4)_{1-3}$,²⁵ $\text{Co}^+(\text{CH}_4)_{1-4}$,²⁶ $\text{Ni}^+(\text{CH}_4)_{1-4}$,²⁶ $\text{Cu}^+(\text{CH}_4)_{1-6}$,²⁷ $\text{Ag}^+(\text{CH}_4)_{1-6}$,²⁷ and $\text{Pt}_{3-5}^+(\text{CH}_4)(\text{Ar})$.²⁸ Most relevant to the present work is the vibrational spectroscopic study of the PtCH_2^+ product formed in the $\text{Pt}^+ + \text{CH}_4$ reaction as undertaken by Lapoutre *et al.*¹⁷ This study utilized infrared multiple photon dissociation (IRMPD) spectroscopy with light provided by the Free-Electron Laser for IntraCavity Experiments (FELICE) beamline at the Free-Electron Lasers for Infrared eXperiments (FELIX) laboratory.²⁹ The IRMPD results are consistent with the spectrum calculated theoretically for the ground electronic state of PtCH_2^+ (a metal carbene), and not with HPtCH^+ ; however, a peak found at 1962 cm^{-1} , which was assigned to a combination band, could conceivably correspond instead to an overtone or originate from the Pt-H stretch of a HPtCH^+ species.

Originally, the intent of the present work was to use CD_4 as a reactant to form PtCD_2^+ in order to verify the assignment of the 1962 cm^{-1} band by examining the resultant shifts in the vibrational spectrum. Unfortunately, FELICE was not available at the time of these experiments, such that the less powerful FELIX beamline was used instead. As discussed further below, FELIX was not capable of dissociating $\text{PtCH}_2^+/\text{PtCD}_2^+$, but could be used to spectroscopically study several complexes $[\text{Pt}_x\text{C}, (4x-2)\text{H/D}]^+$ where $x = 2 - 4$, corresponding to dehydrogenation of one methane molecule followed by reaction with additional methane molecules. In this paper, these experimentally generated spectra are compared with those obtained computationally in order to provide structural elucidation of the product complexes observed.

2. Experimental and Computational Methods

2.1. Experiment. The IRMPD experiments were performed using a molecular beam instrument³⁰ coupled with the FELIX beamline.³¹ Briefly, the second harmonic of a pulsed Nd:YAG laser (532 nm) is used to generate metal cations by ablating a Pt foil supported by a stainless steel rod. A short helium pulse cools the ions by collisions while transporting them down a 3 mm diameter, 60 mm long channel. Further downstream (~50 mm), a methane and helium mixture (~1:5) is pulsed into the channel and reactions of CH₄/CD₄ molecules with Pt⁺ occur. The extent of reaction is adjustable through manipulation of the gas pulse length and timing. The molecular beam undergoes subsequent expansion into vacuum and passes through a 2 mm diameter skimmer and a 1 mm diameter aperture, which are both electrically grounded. Once the ion beam has been shaped, it enters the irradiation region. A few microseconds after the laser pulse, reactant and product ions are extracted into an orthogonal reflectron time-of-flight (TOF) mass spectrometer (mass resolution ~ 1700).³¹

The FELIX pulse comprises a macropulse of 10 μ s length with a repetition rate of 10 Hz. The macropulse energy can reach up to 100 mJ and is composed of picosecond long micropulses spaced by 1 ns with a bandwidth adjustable from 0.2 – 1 % RMS of the selected frequency. FELIX has a lower maximum power than FELICE, which can reach energies of up to 2 J in the cavity of the laser.³¹

Two sets of TOF spectra are generated, one with IR exposure (I_{sig}) and one without IR exposure (I_{ref}). Unless otherwise stated, spectral results are shown in one of two distinct modes: depletion or growth. The yield for depletion spectra corresponds to the negative logarithm of I_{sig}/I_{ref} , as this corresponds directly to the cross section for photodissociation.³² The yield for growth spectra are quantified by the formula, $-\ln[I_{sig,P}/(I_{sig,P} + I_{sig,F} - I_{ref,F})]$, where P and F refer to parent and fragment, respectively. In both cases, the yield is corrected for fluctuations in laser power across the wavenumber range. In the present study, spectra are generally obtained by examining the ¹⁹⁵Pt

isotope as this avoids potential contributions from IR induced dehydrogenation of heavier mass channels, *e.g.*, $[\text{Pt},x\text{C},4x\text{H/D}]^+$ into $[\text{Pt},x\text{C},(4x-2)\text{H/D}]^+$.

2.2 DFT Calculations. All quantum chemical calculations in the current work were performed using Gaussian09³³ and the workstations in the Center for High Performance Computing (CHPC) at the University of Utah. Structural elucidation occurs through comparisons with vibrational frequencies generated by density functional theory (DFT). The current calculations replicate and expand upon our previous work for the $\text{Pt}^+ + \text{CH}_4$ system.^{12,17} Geometry optimizations were initially performed with the B3LYP hybrid density functional^{34,35} and the def2-SVP basis set.³⁶ This basis set utilizes a split valence and added polarization functions for the atoms and a 60 electron core quasirelativistic multielectron effective core potential (ECP) on Pt^+ . Starting structures from the B3LYP/def2-SVP calculations were used for further geometry optimizations at the B3LYP level of theory with the def2-TZVPPD and mDZP/def2-TZVPPD basis sets. The def2-TZVPPD basis set is a balanced triple- ζ valence basis set with double polarization and diffuse functions on all elements. This is an all electron basis set for C and H and a small-core ECP on Pt,³⁶ so that its 5s, 5p, 6s, 6p, and 5d electrons are explicitly treated in the basis set. This approach matches the previous work done by Lapoutre *et al.*¹⁷ In addition, we take note of a recent study concerning cisplatin, which performed a detailed examination of the role of basis set and level of theory.³⁷ Results showed DFT with hybrid functionals (such as B3LYP) led to the best agreement with experimental values. The recommended mDZP basis set for Pt was an all-electron basis set consisting of [8s7p5d2f] primitive orbitals with a d diffuse function. Here the mDZP/def2-TZVPPD basis set treats Pt with mDZP and the C and H atoms with the def2-TZVPPD basis set. Additional single point energy calculations were performed using B3LYP geometries at the MP2(full) level with the def2-TZVPPD (referred to simply as def2 below) and mDZP/def2-TZVPPD (referred to simply as mDZP below) basis sets.

Because the $[\text{Pt},x\text{C},(4x-2)\text{H/D}]^+$ complexes include weak interactions of intact methane molecules with an ionic core, we also explored whether theoretical results including dispersion corrections might be needed. Calculations including dispersion corrections are labeled B3LYP-

GD3BJ, where GD3BJ denotes the D3 version of Grimme's dispersion^{38,39} with additional Becke-Johnson damping,^{40,41} and were performed with both the def2 and mDZP basis sets. The dispersion corrections result in small shifts in our relative energetics but little or no change in the predicted vibrations, as illustrated in Figure S1 in the Supporting Information.

Experimental and theoretical spectra are compared after convoluting the theoretically predicted vibrational frequencies with a Gaussian line shape having a width of 15 cm^{-1} (fwhm $\approx 35\text{ cm}^{-1}$). In addition, the theoretical frequencies are scaled by a basis set dependent global scaling factor that compensates for deficiencies in the calculated vibrations, anharmonicity, and red-shifting of experimental data related to the absorption of multiple photons in the IRMPD process. Scaling factors of 0.983 for def2-SVP and def2-TZVPPD and 1.000 for mDZP/def2-TZVPPD basis sets were used in the current work. As shown below, these scaling factors applied to frequencies of the $\text{Pt}(\text{CH}_3)_2^+(\text{CH}_4)_{x-2}/\text{Pt}(\text{CD}_3)_2^+(\text{CD}_4)_{x-2}$ binding motif, for $x = 2 - 4$, were found to best replicate experimental spectra over the entire wavenumber range.

3. Experimental Results

3.1 Products for $\text{Pt}^+ + x\text{ CH}_4/\text{CD}_4$, $x = 1 - 4$. When the amount of methane available for reaction is minimized, the dominant reaction observed is dehydrogenation of CH_4/CD_4 by Pt^+ to form $\text{PtCH}_2^+/\text{PtCD}_2^+$, consistent with observations in the literature.^{7,8,12-17} Despite repeated attempts and verification that the laser and ion beam overlapped well, these species could not be photodissociated using the FELIX beamline, in contrast to our previous results utilizing FELICE.¹⁷ Failure to undergo dissociation can be directly attributed to the limited power available from FELIX. This negative result demonstrates that our previous ability to directly examine a four-atom system is a consequence of the enhanced power available in the intracavity arrangement of FELICE. This allows the experiment to overcome the inefficient intramolecular vibrational redistribution (IVR) associated with the sparse vibrational manifold of the four-atom system.^{42,43}

As the amount of methane was increased, products associated with the addition of up to 3 methane molecules to the initial $\text{PtCH}_2^+/\text{PtCD}_2^+$ products were formed, $[\text{Pt},x\text{C},(4x-2)\text{H/D}]^+$.

Notably, no evidence for double dehydrogenation products $[\text{Pt},x\text{C},(4x-4)\text{H/D}]^+$ were found under these conditions; however, small amounts of CH_4/CD_4 cluster products with no dehydrogenation were formed, $[\text{Pt},x\text{C},4x\text{H/D}]^+$ for $x = 2 - 4$, as shown in the mass spectra of Figure S2a. These latter products also exhibit photodissociation activity (as shown in Figure S2a at 1195 cm^{-1}) but have not yet undergone further investigation. Figure S2b shows the dependence of PtCH_2^+ formation on wavenumber, with clear product growth centered at 1195 cm^{-1} .

Figure 1 shows the raw signal levels ($I_{\text{sig}} - I_{\text{ref}}$) as a function of wavelength for the $[\text{Pt},x\text{C},(4x-2)\text{H}]^+$ species where $x = 1 - 4$. The $[\text{Pt},4\text{C},14\text{H}]^+$ channel shows only signal loss associated with a depletion process. The $[\text{Pt},3\text{C},10\text{H}]^+$ channel clearly shows depletion as the dominant process, although some growth resulting from photodissociation of $[\text{Pt},4\text{C},14\text{H}]^+$ must be present. The $[\text{Pt},2\text{C},6\text{H}]^+$ channel shows primarily signal growth and replicates the signal loss from the $[\text{Pt},3\text{C},10\text{H}]^+$ channel except for the peak at 1210 cm^{-1} . This difference can be explained by growth in the $[\text{Pt},\text{C},2\text{H}]^+$ channel. Overall, the only photodissociation processes observed were losses of CH_4/CD_4 , as no other alternative channels were observed (*e.g.*, H and H_2 loss). This is further verified by the bottom panel in Figure 1, which shows that the net loss of signal ($[\text{Pt},4\text{C},14\text{H}]^+ + [\text{Pt},3\text{C},10\text{H}]^+$) is nearly identical to the gain in signal ($[\text{Pt},2\text{C},6\text{H}]^+ + [\text{Pt},\text{C},2\text{H}]^+$).

Interestingly, photodissociation of $[\text{Pt},2\text{C},6\text{H/D}]^+$ is not observed under conditions where the amount of $[\text{Pt},3\text{C},10\text{H/D}]^+$ is minimized. We believe this indicates that $[\text{Pt},2\text{C},6\text{H/D}]^+$ does not photodissociate under the FELIX irradiation conditions when cold, but does when formed as a product from $[\text{Pt},3\text{C},10\text{H/D}]^+$ such that its internal energy content is higher.

3.2 Experimental Spectra for $[\text{Pt},x\text{C},(4x-2)\text{H/D}]^+$. Depletion yield spectra ($I_{\text{sig}}/I_{\text{ref}}$) for $[\text{Pt},4\text{C},14\text{H/D}]^+$ mass channels are shown in Figure 2. For the CH_4 system, there are distinct peaks at 565 and 860 cm^{-1} and an additional broad, low intensity absorbance centered around 725 cm^{-1} . Above 1000 cm^{-1} , there are three distinct peaks at 1225 , 1255 , and 1345 cm^{-1} . The reaction with CD_4 produces similar spectra to that of CH_4 but all peaks are shifted to lower frequency, as expected. Corresponding peaks in the H/D spectra are located at $860/640$, $1225/940$, $1255/965$, and $1345/1015\text{ cm}^{-1}$, such that all peaks are shifted by a similar factor of 0.76 ± 0.01 . The grouping

of peaks in the $900 - 1100\text{ cm}^{-1}$ range have similar absorption intensity ratios to those seen in the CH_4 system; however, peaks in the $400 - 1000\text{ cm}^{-1}$ range of $[\text{Pt},4\text{C},14\text{H}]^+$ have lost significant intensity when deuterated. Additionally, the $[\text{Pt},4\text{C},14\text{D}]^+$ spectrum shows a broad peak centered at 1970 cm^{-1} , which would be shifted out of range for $[\text{Pt},4\text{C},14\text{H}]^+$.

Depletion spectra for the $[\text{Pt},3\text{C},10\text{H/D}]^+$ channels can be seen in Figure 3. The CH_4 system has five peaks present at $545, 815, 1210, 1245,$ and 1360 cm^{-1} , homologous to the spectrum for $[\text{Pt},4\text{C},14\text{H}]^+$. The reaction with CD_4 produces similar results, with peaks located at $495, 605, 935,$ and 1005 cm^{-1} . Except for the first peak, the peaks have once again shifted by a scaling factor of 0.75 ± 0.01 , and again, the heavier D atoms lead to less distinct peaks (especially for the closely spaced doublet near 935 cm^{-1}). Additionally, this shift has brought into range stretches not seen for the perprotiated system with the appearance of a broad peak centered at 1930 cm^{-1} .

When $[\text{Pt},3\text{C},10\text{H/D}]^+$ is formed, IRMPD experimental results show growth in the $[\text{Pt},2\text{C},6\text{H/D}]^+$ channel at absorptions associated with depletions from the $[\text{Pt},3\text{C},10\text{H/D}]^+$ complexes, Figure 1 and comparison of Figures 3 and 4. In Figure 4, major peaks are found at $540, 820, 1240,$ and 1345 cm^{-1} for the CH_4 species with equivalent CD_4 species peaks at $500, 620, 930,$ and 1015 cm^{-1} . Except for the first peak, the peak positions are shifted by a factor of 0.75 ± 0.01 . Again a large peak at $\sim 1950\text{ cm}^{-1}$ has shifted into the experimental range for the CD_4 species and may be accompanied by a smaller peak at 1710 cm^{-1} .

As noted above, when experimental conditions were set to minimize the amount of $[\text{Pt},3\text{C},10\text{H/D}]^+$ formed in the source, IRMPD of the $[\text{Pt},2\text{C},6\text{H/D}]^+$ species was unsuccessful. Formation of the $[\text{Pt},\text{C},2\text{H/D}]^+$ product channel occurred only when the $[\text{Pt},3\text{C},10\text{H/D}]^+$ species was present in the molecular beam. The $[\text{Pt},\text{C},2\text{H/D}]^+$ growth spectra are shown in Figure 5 and show peaks at $1210/925\text{ cm}^{-1}$, a shift by a factor of 0.76 . A low intensity, broad peak is also present for the CH_4 system at 1370 cm^{-1} . The growth spectrum for the CD_4 system is over an order of magnitude smaller than that of the CH_4 system, in contrast to the relative intensities for the larger complexes. This observation is discussed further below.

3.3. Overview. The experimental results indicate that $[\text{Pt},4\text{C},14\text{H}/\text{D}]^+$ decomposes by losing methane to form $[\text{Pt},3\text{C},10\text{H}/\text{D}]^+$, which then loses methane to form $[\text{Pt},2\text{C},6\text{H}/\text{D}]^+$. The latter product does not undergo photodissociation to lose methane easily, requiring that it be formed at an elevated temperature. These observations are consistent with complexes that contain a $[\text{Pt},2\text{C},6\text{H}/\text{D}]^+$ core with one and two methane molecules attached. Species considered for the $[\text{Pt},2\text{C},6\text{H}/\text{D}]^+$ products include the platinum carbene cation with one methane molecule attached, $(\text{CH}_4)\text{PtCH}_2^+$; a platinum dimethyl cation, $\text{Pt}(\text{CH}_3)_2^+$; and a hydrido platinum carbene methyl cation, $\text{HPtCH}_2(\text{CH}_3)^+$. As will be seen below, these are possible low-lying species formed along the potential energy surface in the reaction of $\text{PtCH}_2^+ + \text{CH}_4$. Conceivably, the two carbons can couple as well, such that other species that could be considered include a platinum ethane cation, $\text{Pt}^+(\text{C}_2\text{H}_6)$; a hydrido platinum ethyl cation, $\text{HPtC}_2\text{H}_5^+$; a platinum ethene complex with two hydrides or a dihydrogen adduct, $\text{H}_2\text{Pt}^+(\text{C}_2\text{H}_4)$ and $(\text{H}_2)\text{Pt}^+(\text{C}_2\text{H}_4)$; or a platinum ethylidene cation with two hydrides or a dihydrogen adduct, $\text{H}_2\text{PtCHCH}_3^+$ and $(\text{H}_2)\text{PtCHCH}_3^+$. Some evidence against any of these species having a C-C bond is that they are expected to lead to formation of $[\text{Pt},2\text{C},4\text{H}]^+$, which is not observed in the present experiments under any conditions, e.g., Figure S2a. This expectation results from previous experimental results that show Pt^+ exothermically dehydrogenates ethane twice as efficiently as Pt^+ dehydrogenates CH_4 .¹⁶ Further, theoretical studies indicate that formation of the ethene complex $\text{Pt}^+(\text{C}_2\text{H}_4) + \text{H}_2$ is 1.69 eV below $\text{Pt}^+ + \text{C}_2\text{H}_6$ reactants (1.47 eV if the PtCHCH_3^+ ethylidene cation is formed).⁴⁴ As will be seen below, theory also indicates that formation of both $[\text{Pt},2\text{C},4\text{H}]^+$ products from $\text{PtCH}_2^+ + \text{CH}_4$ reactants is exothermic by about 0.5 and 0.3 eV, respectively.

4. Theoretical Results and Discussion

4.1. Structures. Relative energies for several possible low-lying structures of the $[\text{Pt},x\text{C},(4x-2)\text{H}/\text{D}]^+$ complexes, where $x = 2 - 4$, are listed in Table 1. Relative energies are reported for several different levels of theory and basis sets. The doublet spin state was found to be lowest

in energy for all levels of theory, basis sets, and structures examined. Quartet spin structures examined were much higher in energy, paralleling previous work on the PtCH_2^+ system.^{12,17}

Calculations on the various $[\text{Pt},2\text{C},6\text{H}]^+$ structures suggested above located eight stable isomers, with four of these structures shown in Figure 6 and all $[\text{Pt},2\text{C},6\text{H}]^+$ structures shown in Figure S3 of the Supporting Information. As seen in Table 1, calculations find that $(\text{H}_2)\text{Pt}^+(\text{C}_2\text{H}_4)$ is the lowest energy structure for the majority of the calculations, the exception being B3LYP/def2-SVP. The next lowest energy isomer depends on the level of theory and basis set, but is either $\text{HPtC}_2\text{H}_5^+$ (def2) or $\text{Pt}(\text{CH}_3)_2^+$ (mDZP). The energetic order for the other structures listed in Table 1 varies with the theoretical approach but all are higher in energy by at least 0.10 eV when compared to the $\text{HPtC}_2\text{H}_5^+$ and $\text{Pt}(\text{CH}_3)_2^+$ species. Two orientations of an intact ethane molecule bound to Pt^+ were located (Figure S3) and designated as “end”, when Pt is bound to only one methyl group, or “bod”, when Pt is bound across the C-C bond. Geometry optimizations for $(\text{H}_2)\text{PtCHCH}_3^+$ and $\text{H}_2\text{Pt}^+(\text{C}_2\text{H}_4)$ structures converged to the $\text{H}_2\text{PtCHCH}_3^+$ and $(\text{H}_2)\text{Pt}^+(\text{C}_2\text{H}_4)$ intermediates, respectively, and were not investigated further in the current work.

Given this starting point, seven unique isomers of the $[\text{Pt},3\text{C},10\text{H}]^+$ complex were examined computationally, with the structures shown in Figure 7. The addition of a single methane molecule to $[\text{Pt},2\text{C},6\text{H}]^+$ has only a small effect on the binding motifs, but does shift the relative energetics for some of the intermediates. The relative energies listed in Table 1 show that the $(\text{H}_2)\text{Pt}^+(\text{C}_2\text{H}_4)(\text{CH}_4)$ structure is lowest in energy at all levels of theory (except for B3LYP/def2-SVP where it is only 0.01 eV above the ground structure). The next lowest energy isomer depends on the level of theory and basis set and is either the $\text{Pt}(\text{CH}_3)_2^+(\text{CH}_4)$ or $\text{Pt}^+(\text{C}_2\text{H}_6)(\text{CH}_4)$ structure. The $\text{HPtC}_2\text{H}_5^+(\text{CH}_4)$ species is 0.12 – 0.70 eV above the ground isomer. Alternative structures, $(\text{H}_2)\text{PtCHCH}_3^+(\text{CH}_4)$, $\text{PtCH}_2^+(\text{CH}_4)_2$, and $\text{HPtCH}_2(\text{CH}_3)^+(\text{CH}_4)$, lie at least 0.57 eV above the ground isomer. Geometry optimizations did not produce a stable structure that would correspond to the $\text{Pt}^+(\text{C}_2\text{H}_6)\text{bod}$ precursor.

Addition of one more methane molecule yields seven unique isomers of the $[\text{Pt},4\text{C},14\text{H}]^+$ complex, Figure 8. Calculations for the $(\text{H}_2)\text{Pt}^+(\text{C}_2\text{H}_4)(\text{CH}_4)_2$ structure failed to converge, which

can be rationalized if the ethene ligand occupies two ligation sites. For $\text{Pt}(\text{CH}_3)_2^+(\text{CH}_4)_2$, two structures were located with “cis” and “trans” denoting the relative location of the two methyl (or methane) groups. The cis isomer has a $\text{H}_3\text{C-Pt-CH}_3$ bond angle of $91 - 93^\circ$, whereas the “trans” species has a bond angle of $155 - 156^\circ$ and is higher in energy by $0.40 - 0.86$ eV. Calculations performed with the def2 basis set agree that the $\text{Pt}(\text{CH}_3)_2^+(\text{CH}_4)_2$ _cis structure is the lowest energy isomer, whereas B3LYP/def2-SVP calculations favor the $\text{HPt}^+(\text{C}_2\text{H}_5)(\text{CH}_4)_2$ structure by 0.08 eV over the $\text{Pt}(\text{CH}_3)_2^+(\text{CH}_4)_2$ _cis structure. Likewise, B3LYP/mDZP and B3LYP-GD3BJ/mDZP calculations predict that the $\text{Pt}(\text{CH}_3)_2^+(\text{CH}_4)_2$ _cis structure is now $0.06 - 0.13$ eV higher in energy than the $\text{Pt}^+(\text{C}_2\text{H}_6)(\text{CH}_4)_2$ lowest energy structure, whereas MP2(full)/mDZP calculations place the latter structure 0.22 eV higher in energy. $\text{H}_2\text{PtCHCH}_3^+(\text{CH}_4)_2$, $\text{PtCH}_2^+(\text{CH}_4)_3$, and $\text{HPtCH}_2(\text{CH}_3)^+(\text{CH}_4)_2$ structures are $0.21 - 0.67$, $0.71 - 1.33$, and $0.59 - 1.02$ eV, respectively, higher than the ground isomer.

4.2. Spectra. Vibrational frequencies generated with different basis sets required unique scaling factors for accurate comparison with experimental spectra. These scaling factors were determined by fitting the most intense experimental peak to the computed spectrum of the isomer that best matched experiment. Comparisons between spectra computed using the different basis sets with experimental spectra can be found in Figures S4 and S5 of the Supporting Information for $[\text{Pt},4\text{C},14\text{H}/\text{D}]^+$ and $[\text{Pt},3\text{C},10\text{H}/\text{D}]^+$. Vibrational spectra from all three basis sets examined compared favorably to the experimental spectra; however, the two def2 basis sets clearly replicate the entire experimental spectra better than the all-electron mDZP basis set. Vibrational frequencies from B3LYP/def2 calculations most accurately reproduce experimental spectra and therefore will be used in the remainder of the paper.

Comparison of the experimental and theoretical spectra for five select isomers of $[\text{Pt},4\text{C},14\text{H}/\text{D}]^+$ are shown in Figure 2, and the two additional isomers can be seen in Figure S6 of the Supporting Information. For ease of comparison, positions of peaks below are listed as perprotiated/perdeuterated values. For the most intense peak at $1225/925\text{ cm}^{-1}$, reasonable agreement is found for the $\text{Pt}(\text{CH}_3)_2^+(\text{CH}_4)_2$ _cis, $\text{HPtCH}_2(\text{CH}_3)^+(\text{CH}_4)$, and $\text{HPtC}_2\text{H}_5^+(\text{CH}_4)_2$

structures, with $\text{Pt}^+(\text{C}_2\text{H}_6)(\text{CH}_4)_2$, $\text{PtCH}_2^+(\text{CH}_4)_3$, $\text{Pt}(\text{CH}_3)_2^+(\text{CH}_4)_{2_trans}$, and $\text{H}_2\text{PtCHCH}_3^+(\text{CH}_4)_2$ spectra failing to match the experimental spectra in most respects. Arguably, the $\text{Pt}(\text{CH}_3)_2^+(\text{CH}_4)_{2_cis}$ structure does the best job of reproducing the experimental spectra over the whole range. Specifically, the spectra for $\text{HPtC}_2\text{H}_5^+(\text{CH}_4)_2$ and $\text{HPtCH}_2(\text{CH}_3)^+(\text{CH}_4)_2$ fail to reproduce the doublet of peaks at 1225 and 1255 cm^{-1} , whereas the dimethyl structure does. In the wavenumber range below 1000 cm^{-1} , the $\text{HPtC}_2\text{H}_5^+(\text{CH}_4)_2$ spectrum for both perprotiated/perdeuterated systems show blue shifting of the theoretically predicted peak when compared to the experimental peaks at 860/640 cm^{-1} . Likewise, the spectrum for the $\text{HPtCH}_2(\text{CH}_3)^+(\text{CH}_4)_2$ structure shows four distinct peaks in the 400 – 1000 cm^{-1} range (three peaks below 700 cm^{-1} for the deuterated analogue) that are inconsistent with the three (one) peaks found experimentally. From an energetic point of view, the $\text{HPtC}_2\text{H}_5^+(\text{CH}_4)_2$ species is potentially populated, whereas $\text{HPtCH}_2(\text{CH}_3)^+(\text{CH}_4)_2$ lies considerably higher in energy (> 0.59 eV) for all levels of theory (Table 1). Overall, although we cannot rule out the presence of small amounts of the $\text{HPtC}_2\text{H}_5^+(\text{CH}_4)_2$ and $\text{HPtCH}_2(\text{CH}_3)^+(\text{CH}_4)_2$ structures, the $\text{Pt}(\text{CH}_3)_2^+(\text{CH}_4)_{2_cis}$ species is capable of explaining the experimental spectra. Note that the failure to see any evidence for the $\text{Pt}^+(\text{C}_2\text{H}_6)(\text{CH}_4)_2$ structure appears in disagreement with the calculations (notably using the mDZP basis set) that predict this structure is the lowest energy form of $[\text{Pt},4\text{C},14\text{H/D}]^+$, Table 1.

Figure 3 compares the experimental depletion yield spectra for $[\text{Pt},3\text{C},10\text{H/D}]^+$ with those calculated for five select structures with the other two isomers found in Figure S7 of the Supporting Information. Here spectra were recorded under conditions where the $[\text{Pt},4\text{C},14\text{H/D}]^+$ product was minimized, such that formation of the 3C species from 4C does not influence the observations. The lowest energy isomer, $(\text{H}_2)\text{Pt}^+(\text{C}_2\text{H}_4)(\text{CH}_4)$, does a poor job of replicating the experimental spectra across the wavenumber range examined. As for $[\text{Pt},4\text{C},14\text{H/D}]^+$, the $\text{Pt}(\text{CH}_3)_2^+(\text{CH}_4)$, $\text{HPtC}_2\text{H}_5^+(\text{CH}_4)$, and $\text{HPtCH}_2(\text{CH}_3)^+(\text{CH}_4)$ structures do a fair job of replicating the experimental spectra, whereas the $\text{PtCH}_2^+(\text{CH}_4)_2$ does not match experiment at all. As for $[\text{Pt},4\text{C},14\text{H/D}]^+$, the higher energy $\text{HPtC}_2\text{H}_5^+(\text{CH}_4)$ and $\text{HPtCH}_2(\text{CH}_3)^+(\text{CH}_4)$ structures do not reproduce experiment as well as $\text{Pt}(\text{CH}_3)_2^+(\text{CH}_4)$ for the intense doublet peak or in the lower frequency range of the

perprotiated and perdeuterated spectra. In particular, $\text{HPtCH}_2(\text{CH}_3)^+(\text{CH}_4)$ fails to replicate the distinct peaks at $545/500\text{ cm}^{-1}$ seen in the experimental spectra, whereas $\text{Pt}(\text{CH}_3)_2^+(\text{CH}_4)$ does. Further, this species is higher in energy by at least 0.52 eV when compared to the dimethyl structure, Table 1. The $\text{HPtC}_2\text{H}_5^+(\text{CH}_4)$ species has peaks that are both blue and red shifted in the lower $400 - 1000\text{ cm}^{-1}$ range, such that it poorly reproduces the experimental spectra in this range.

Growth of the $[\text{Pt},2\text{C},6\text{H}/\text{D}]^+$ is attributed to loss of CH_4/CD_4 from the $[\text{Pt},3\text{C},10\text{H}/\text{D}]^+$ species such that the growth spectra should correspond to vibrational frequencies of $[\text{Pt},3\text{C},10\text{H}/\text{D}]^+$ structures. This is evident when directly comparing the depletion and growth spectra of the $[\text{Pt},3\text{C},10\text{H}/\text{D}]^+$ and $[\text{Pt},2\text{C},6\text{H}/\text{D}]^+$ species, Figure 1. For the perprotiated system, the major difference between the two spectra is a missing peak in the $[\text{Pt},2\text{C},6\text{H}]^+$ channel at 1210 cm^{-1} . In contrast, the $[\text{Pt},2\text{C},6\text{D}]^+$ growth and $[\text{Pt},3\text{C},10\text{D}]^+$ depletion spectra match well over the entire range (compare Figures 3 and 4). Comparison of the experimental and theoretical spectra of $[\text{Pt},2\text{C},6\text{H}/\text{D}]^+$ in Figure 4 shows that the $\text{Pt}(\text{CH}_3)_2^+(\text{CH}_4)$ structure agrees best with experimental results, matching all observed band positions except that at 1210 cm^{-1} in the perprotiated system. As for the depletion spectra of $[\text{Pt},3\text{C},10\text{H}/\text{D}]^+$, the $\text{HPtC}_2\text{H}_5^+(\text{CH}_4)$ and $\text{HPtCH}_2(\text{CH}_3)^+(\text{CH}_4)$ structures reproduce some of the experimental bands but do not match the experimental spectra at lower frequencies, notably missing the sharp band at 540 cm^{-1} in the $[\text{Pt},2\text{C},6\text{H}]^+$ spectrum.

Dissociation of $[\text{Pt},\text{C},2\text{H}/\text{D}]^+$ is not observed experimentally with the FELIX setup when it is the largest species present in the molecular beam, but growth in the $[\text{Pt},\text{C},2\text{H}/\text{D}]^+$ mass channels does occur when the $[\text{Pt},3\text{C},10\text{H}/\text{D}]^+$ precursor is present. Sharp peaks are observed at $1210/920\text{ cm}^{-1}$ for formation of $[\text{Pt},\text{C},2\text{H}/\text{D}]^+$, with a lower intensity band at 1370 cm^{-1} in the perprotiated system, Figure 5. The experimental observations indicate that formation of $[\text{Pt},\text{C},2\text{H}/\text{D}]^+$ should only occur if there is overlap in the vibrational spectra of the $[\text{Pt},3\text{C},10\text{H}/\text{D}]^+$ and $[\text{Pt},2\text{C},6\text{H}/\text{D}]^+$ species present. Figure 5 shows these spectra for the dimethyl species, $\text{Pt}(\text{CH}_3)_2^+(\text{CH}_4)$ and $\text{Pt}(\text{CH}_3)_2^+$ as well as the perdeuterated analogues. For the perprotiated species, there is very good overlap between intense bands near the 1210 cm^{-1} peak and less favorable overlap for the weaker band near 1370 cm^{-1} for the $[\text{Pt},\text{C},2\text{H}]^+$ species. In contrast, the intense bands of $\text{Pt}(\text{CD}_3)_2^+(\text{CD}_4)$

and $\text{Pt}(\text{CD}_3)_2^+$ do not overlap as well, such that the observed formation of $[\text{Pt},\text{C},2\text{D}]^+$ occurs with much less intensity. Clearly, IRMPD of a methane molecule from $\text{Pt}(\text{CH}_3)_2^+(\text{CH}_4)$ should directly form the $\text{Pt}(\text{CH}_3)_2^+$ species, which can absorb additional photons to dissociate further by CH_4 loss to yield $[\text{Pt},\text{C},2\text{H}]^+$. The failure of $[\text{Pt},2\text{C},6\text{H}]^+$ to undergo IRMPD directly suggests that this covalently bound species may have a density of states that is too low for efficient IVR, whereas additional excitation afforded by generation from $[\text{Pt},3\text{C},10\text{H}]^+$ means that the molecule is already in the quasi-continuum where IVR is more efficient.

4.3. Potential Energy Surfaces for the reaction of Pt^+ with 2 CH_4 . To better understand the sequential reaction of CH_4 with Pt^+ , an investigation into the relevant potential energy surfaces (PESs) was undertaken. The reaction of Pt^+ with methane has been examined computationally and the B3LYP/def2 level of theory replicates the $\text{Pt}^+ + \text{CH}_4$ PES described in the literature, as detailed in Table S1 and Figures S8 and S9.^{9,10,12} Relative energies determined at the B3LYP/def2 level are lower in energy by 0.25 – 0.50 eV when compared to theoretical results from Zhang *et al.*,¹² except for HPtCH_3^+ , which is higher by 0.03 – 0.12 eV, but remains the lowest energy intermediate. B3LYP/def2 energies show that formation of $\text{PtCH}_2^+ + \text{H}_2$ products is exothermic, in agreement with the majority of literature calculations, the exceptions being B3LYP calculations with the TZ-HW+ and TZ-HW+X basis sets performed by Zhang *et al.*¹² This exothermic behavior is consistent with experiment, which finds that the $\text{Pt}^+ + \text{CH}_4$ reaction efficiently forms $\text{PtCH}_2^+ + \text{H}_2$ at thermal energies.^{7,8,12-17} The overall reaction exothermicity for dehydrogenation of methane by Pt^+ was found experimentally to be 0.09 ± 0.08 eV,¹² in reasonable agreement with most calculations, including the present B3LYP and B3LYP-GD3BJ values of 0.37 and 0.43 eV, with the MP2 results showing the largest deviation (exothermicity of 0.56 eV), Table S1. These computational results can also be directly compared with experimental measurements that locate the HPtCH_3^+ intermediate 1.77 ± 0.08 eV lower in energy than the $\text{Pt}^+ + \text{CH}_4$ reactants, similar to our B3LYP/def2 and B3LYP-GD3BJ/def2 values of 1.46 and 1.58 eV, Figure S8, but substantially different from the MP2 value of 2.31 eV.

The study of Zhang *et al.*¹² found that they could generate the HPtCH₃⁺ species from reaction of Pt⁺ and methane in observable quantities under the high pressure conditions available in their flow tube source. Such conditions may also be relevant for the molecular beam environment used here. Therefore, we considered two likely starting points for sequential reactions with additional CH₄ molecules: either the bimolecular product, PtCH₂⁺, or the trapped intermediate, HPtCH₃⁺. Calculations were performed for the reactions of both PtCH₂⁺ and HPtCH₃⁺ with CH₄.

The PES shown in Figure 9 examines the PtCH₂⁺ + CH₄ reaction at the B3LYP and B3LYP-GD3BJ levels of theory, with optimized B3LYP/def2 structures located in Figure 6. A more complete PES can be found in Figure S10 of the Supporting Information with corresponding structures in Figure S3. Table 2 lists energies relative to PtCH₂⁺ + CH₄ reactants calculated at the B3LYP, B3LYP-GD3BJ, and MP2(full) levels of theory using the def2 basis set. As noted above, the present MP2(full) results yield values that are substantially lower than experimental values for the Pt⁺ + CH₄ reaction, Table S1. Hence these values are not included in the following discussion (although they are included in Table 2 for completeness).

The reaction of PtCH₂⁺ with methane begins by complexation of the CH₄ molecule to the platinum carbene cation structure forming (CH₄)PtCH₂⁺, intermediate **1**. In the next step, oxidative addition of a C-H bond of methane to the Pt atom occurs over transition state TS1/2 and forms the HPtCH₂(CH₃)⁺ intermediate **2**. This intermediate can rearrange along two distinct pathways. First, by hydrogen transfer from Pt⁺ to the CH₂ group passing over TS2/3, forming the platinum dimethyl cation intermediate **3**, Pt(CH₃)₂⁺. Second, it can form a C-C bond between the carbene and methyl groups through TS2/4 to form the HPtC₂H₅⁺ intermediate **4**. This transformation is predicted to be an overall endothermic process by 0.16 eV for B3LYP and energetically neutral (-0.02 eV) with dispersion corrections. The lack of experimental evidence for a second dehydrogenation is consistent with the high energy of this step. After HPtC₂H₅⁺ formation, subsequent dehydrogenation can occur through two separate pathways and is found to be exothermic by 0.53 – 0.62 eV for Pt⁺(C₂H₄) + H₂ and 0.29 – 0.37 eV for PtCHCH₃⁺ + H₂. A detailed mechanism for formation of these dehydrogenated products from the reaction of Pt⁺ + C₂H₆ was found by Ye *et*

al. at the B3LYP/LANL2DZ(modified for Pt)/6-311G**(C,H) level.⁴⁴ Relative to the $\text{HPtC}_2\text{H}_5^+$ intermediate, their work finds that these two dehydrogenation product channels lie 0.63 and 0.85 eV, respectively, higher in energy, with no barriers along the pathway higher than the final products, as indicated in Figure 9. Our B3LYP/def2 calculations yield relative energies 0.63 and 0.87 eV, respectively, reproducing the values from Ye *et al.*,⁴⁴ as shown in Figures 9 and S10.

A second pathway for C-C formation goes through the $\text{Pt}(\text{CH}_3)_2^+$ intermediate, which covalently couples the two methyl groups to form the $\text{Pt}^+(\text{C}_2\text{H}_6)$ _bod isomer **5** via TS3/5, which lies 0.10 – 0.27 eV above the $\text{PtCH}_2^+ + \text{CH}_4$ reactants. Formation of the C-C ethane bond leads to a $\text{Pt}^+(\text{C}_2\text{H}_6)$ _bod complex that can rearrange to the $\text{Pt}^+(\text{C}_2\text{H}_6)$ _end intermediate **6** via the low energy TS5/6. The two $\text{Pt}^+(\text{C}_2\text{H}_6)$ complexes have similar energies, within 0.15 eV of one another (except for the MP2(full)/mDZP difference of 0.36 eV), Table 2. An alternative pathway for formation of intermediate **6** parallels that found by Zhou *et al.* for the reaction of AuCH_2^+ with CH_4 .⁴⁵ Here, methane approaches PtCH_2^+ at the carbene ligand forming an excited isomer of the $(\text{CH}_4)\text{PtCH}_2^+$ complex, intermediate **1***, Figure S3. Then, a C-H bond of methane oxidatively adds to the carbon of the PtCH_2^+ species at TS1*/6 to form the $\text{Pt}^+(\text{C}_2\text{H}_6)$ _end intermediate. TS1*/6 lies 0.15 – 0.48 eV above reactants, Table 2. Overall, loss of C_2H_6 , which can occur from either $\text{Pt}^+(\text{C}_2\text{H}_6)$ intermediate, to form $\text{Pt}^+ + \text{C}_2\text{H}_6$ requires 1.11 – 1.13 eV relative to the $\text{PtCH}_2^+ + \text{CH}_4$ reactants, Table 2, clearly indicating this channel is inaccessible in the present experiments. Furthermore, both pathways leading to $\text{Pt}^+(\text{C}_2\text{H}_6)$ have barriers with energies in excess of the reactants, consistent with the failure to see spectral evidence for this species and also the failure to observe any subsequent dehydrogenation yielding $\text{Pt}^+(\text{C}_2\text{H}_4)$.

The PES for the $\text{HPtCH}_3^+ + \text{CH}_4$ reaction is shown in Figure S11 with relative energies calculated at the B3LYP/def2 level found in Table S2 and structures in Figure S12. Complexation of the CH_4 molecule to HPtCH_3^+ leads to intermediate **7** lying 0.58 eV lower in energy. Transfer of a hydrogen from the complexed CH_4 to Pt has a barrier of 0.74 eV, 0.16 eV above reactants, making formation of the $\text{H}_2\text{Pt}(\text{CH}_3)_2^+$ intermediate **8** at thermal energies unlikely. From this complex, H_2 formation has a barrier of 0.14 eV above reactants and yields $(\text{H}_2)\text{Pt}(\text{CH}_3)_2^+$, **9**, 0.12

eV more stable than reactants. Subsequent H_2 loss to yield the platinum dimethyl cation requires another 0.63 eV of energy, 0.51 eV above the reactants. Overall, this PES shows that formation of $\text{Pt}(\text{CH}_3)_2^+$ from reaction of HPtCH_3^+ with CH_4 is not an energetically feasible route.

5. Conclusion

Atomic platinum cations are observed to react with $x = 1 - 4$ molecules of methane (both CH_4 and CD_4) to dehydrogenate once and add additional methane molecules yielding $[\text{Pt}, x\text{C}, (4x-2)\text{H/D}]^+$ complexes. The IRMPD process was found to induce only CH_4/CD_4 loss with no evidence for dehydrogenation or H/D atom loss. These results provide evidence that indicate formation of a $[\text{Pt}, 2\text{C}, 6\text{H/D}]^+$ ion core that can complex one or two methane molecules. Comparison of the experimental spectra with theoretical results for both depletion and growth channels lead to results consistent with the sequential reaction of $\text{Pt}^+ + \text{CH}_4$ undergoing dehydrogenation to yield the platinum carbene cation, PtCH_2^+ , as demonstrated earlier.^{9,10,12} Subsequent reaction of this species with a second CH_4 molecule activates a second CH bond and forms the platinum dimethyl cation, $\text{Pt}(\text{CH}_3)_2^+$. Further interaction with CH_4 molecules occurs through simple CH_4 addition. This postulated reaction pathway is consistent with theoretical explorations of the potential energy surfaces for interaction of Pt^+ and PtCH_2^+ with CH_4 , which indicate that $\text{Pt}(\text{CH}_3)_2^+$ is the lowest energy species accessible at thermal energies along this PES. Comparisons between experimental spectra and theory do not show evidence for C-C bond formation, nor is a secondary dehydrogenation to form $[\text{Pt}, 2\text{C}, 4\text{H/D}]^+$ observed. These observations are consistent with the potential energy surfaces calculated that indicate relatively high barriers for coupling the two carbons.

An important observation made in the present study is that the power of FELIX was insufficient to allow the collection of experimental IRMPD spectra of the $[\text{Pt}, 2\text{C}, 6\text{H/D}]^+$ and $[\text{Pt}, \text{C}, 2\text{H/D}]^+$ species, presumably because it is unable to overcome the limited IVR for these small covalently bound molecules. In contrast, the larger $[\text{Pt}, 3\text{C}, 10\text{H/D}]^+$ and $[\text{Pt}, 4\text{C}, 14\text{H/D}]^+$ complexes, which are non-covalently bound CH_4/CD_4 adducts, could be studied using FELIX. However, if the

$[\text{Pt},2\text{C},6\text{H}/\text{D}]^+$ species is formed via IRMPD of $[\text{Pt},3\text{C},10\text{H}/\text{D}]^+$, FELIX is capable of inducing photodissociation to $[\text{Pt},\text{C},2\text{H}/\text{D}]^+$, with a much lower efficiency for the perdeutero system. These observations are consistent with sequential elimination of CH_4/CD_4 and require overlap between the spectra for the two precursors, which is decidedly worse for $\text{Pt}(\text{CD}_3)_2^+(\text{CD}_4)$ and $\text{Pt}(\text{CD}_3)_2^+$ structures compared to the perprotiated analogues.

Associated Content

Supporting Information

The complete potential energy surfaces for PtCH_2^+ reacting with CH_4 in addition to surfaces for Pt^+ reacting with CH_4 and HPtCH_3^+ reacting with CH_4 along with accompanying tables and structures. Spectra that compare calculated frequencies from B3LYP and B3LYP-GD3BJ geometry optimizations with different basis sets. Raw experimental mass spectra for reactant and product distributions including the isotopic distribution and the raw signal with and without laser irradiation for m/z 209. Experimental spectra compared with calculated frequencies from geometry optimized B3LYP calculations with three different basis sets. Experimental spectra compared to calculated frequencies for alternative $[\text{Pt},4\text{C},14\text{H}]^+$ and $[\text{Pt},3\text{C},10\text{H}]^+$ structures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Author Information.

Corresponding Author

*P. B. A.: phone, +801-581-7885; e-mail, armentrout@chem.utah.edu.

Notes

The authors declare no competing financial interest.

Acknowledgement.

We gratefully acknowledge the Stichting voor Fundamenteel Onderzoek der Materie (FOM) for the support of the FELIX Laboratory. Additional financial assistance was provided by the National Science Foundation, Grants No. CHE-1359769 and OISE-1357887. Finally, the Center for High Performance Computing (CHPC) at the University of Utah is acknowledged for their generous allocation of computing time.

References

- (1) Tauseef, S. M.; Premalatha, M.; Abbasi, T.; Abbasi, S. A., Methane Capture from Livestock Manure. *J. Environ. Manage.* **2013**, *117*, 187-207.
- (2) Wennberg, P. O.; Mui, W.; Wunch, D.; Kort, E. A.; Blake, D. R.; Atlas, E. L.; Santoni, G. W.; Wofsy, S. C.; Diskin, G. S.; Jeong, S., *et al.*, On the Sources of Methane to the Los Angeles Atmosphere. *Environ. Sci. Technol.* **2012**, *46*, 9282-9289.
- (3) IPCC, *Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*. Cambridge University Press: Cambridge, United Kingdom and New York, NY, USA, 2013; p 1535.
- (4) Viñes, F.; Lykhach, Y.; Staudt, T.; Lorenz, M. P. A.; Papp, C.; Steinrück, H.-P.; Libuda, J.; Neyman, K. M.; Görling, A., Methane Activation by Platinum: Critical Role of Edge and Corner Sites of Metal Nanoparticles. *Chem. – Eur. J.* **2010**, *16*, 6530-6539.
- (5) Torniainen, P. M.; Chu, X.; Schmidt, L. D., Comparison of Monolith-Supported Metals for the Direct Oxidation of Methane to Syngas. *J. Catal.* **1994**, *146*, 1-10.
- (6) Wei, J.; Iglesia, E., Isotopic and Kinetic Assessment of the Mechanism of Reactions of CH₄ with CO₂ or H₂O to Form Synthesis Gas and Carbon on Nickel Catalysts. *J. Catal.* **2004**, *224*, 370-383.
- (7) Irikura, K. K.; Beauchamp, J. L., Electronic Structure Considerations for Methane Activation by Third-Row Transition-Metal Ions. *J. Phys. Chem.* **1991**, *95*, 8344-8351.
- (8) Irikura, K. K.; Beauchamp, J. L., Methane Oligomerization in the Gas Phase by Third-Row Transition-Metal Ions. *J. Am. Chem. Soc.* **1991**, *113*, 2769-2770.
- (9) Pavlov, M.; Blomberg, M. R. A.; Siegbahn, P. E. M.; Wesendrup, R.; Heinemann, C.; Schwarz, H., Pt⁺-Catalyzed Oxidation of Methane: Theory and Experiment. *J. Phys. Chem. A* **1997**, *101*, 1567-1579.
- (10) Achatz, U.; Beyer, M.; Joos, S.; Fox, B. S.; Niedner-Schatteburg, G.; Bondybey, V. E., The Platinum Hydrido-Methyl Complex: A Frozen Reaction Intermediate? *J. Phys. Chem. A* **1999**, *103*, 8200-8206.
- (11) Achatz, U.; Berg, C.; Joos, S.; Fox, B. S.; Beyer, M. K.; Niedner-Schatteburg, G.; Bondybey, V. E., Methane Activation by Platinum Cluster Ions in the Gas Phase: Effects of Cluster Charge on the Pt₄ Tetramer. *Chem. Phys. Lett.* **2000**, *320*, 53-58.

- (12) Zhang, X.-G.; Liyanage, R.; Armentrout, P. B., The Potential Energy Surface for Activation of Methane by Pt^+ : A Detailed Guided-Ion Beam Study. *J. Am. Chem. Soc.* **2001**, *123*, 5563-5575.
- (13) Koszinowski, K.; Schröder, D.; Schwarz, H., Reactivity of Small Cationic Platinum Clusters. *J. Phys. Chem. A* **2003**, *107*, 4999-5006.
- (14) Koszinowski, K.; Schröder, D.; Schwarz, H., Reactions of Platinum–Carbene Clusters Pt_nCH_2^+ ($n = 1-5$) with O_2 , CH_4 , NH_3 , and H_2O : Coupling Processes versus Carbide Formation. *Organometallics* **2003**, *22*, 3809-3819.
- (15) Adlhart, C.; Uggerud, E., Reactions of Platinum Clusters $\text{Pt}_n^{+/-}$, $n = 1-21$, with CH_4 : To React or Not to React. *Chem. Commun.* **2006**, 2581-2582.
- (16) Adlhart, C.; Uggerud, E., Mechanisms for the Dehydrogenation of Alkanes on Platinum: Insights Gained from the Reactivity of Gaseous Cluster Cations, Pt_n^+ $n=1-21$. *Chem. – Eur. J.* **2007**, *13*, 6883-6890.
- (17) Lapoutre, V. J. F.; Redlich, B.; van der Meer, A. F. G.; Oomens, J.; Bakker, J. M.; Sweeney, A.; Mookherjee, A.; Armentrout, P. B., Structures of the Dehydrogenation Products of Methane Activation by 5d Transition Metal Cations. *J. Phys. Chem. A* **2013**, *117*, 4115-4126.
- (18) Gioumousis, G.; Stevenson, D. P., Reactions of Gaseous Molecule Ions with Gaseous Molecules. V. Theory. *J. Chem. Phys.* **1958**, *29*, 294-299.
- (19) Diefenbach, M.; Brönstrup, M.; Aschi, M.; Schröder, D.; Schwarz, H., HCN Synthesis from Methane and Ammonia: Mechanisms of Pt^+ -Mediated C–N Coupling. *J. Am. Chem. Soc.* **1999**, *121*, 10614-10625.
- (20) Rodriguez Jr, O.; Lisy, J. M., Infrared Spectroscopy of $\text{Li}^+(\text{CH}_4)_n$, $n = 1-9$, Clusters. *Chem. Phys. Lett.* **2011**, *502*, 145-149.
- (21) Rodriguez, O.; Lisy, J. M., Infrared Spectroscopy of $\text{Li}^+(\text{CH}_4)_1\text{Ar}_n$, $n = 1-6$, Clusters. *J. Phys. Chem. A* **2011**, *115*, 1228-1233.
- (22) Poad, B. L. J.; Thompson, C. D.; Bieske, E. J., Infrared Spectra of Mass-Selected $\text{Al}^+(\text{CH}_4)_n$ $n = 1-6$ Clusters. *Chem. Phys.* **2008**, *346*, 176-181.
- (23) Dryza, V.; Bieske, E. J., Infrared Spectra and Density Functional Theory Calculations for $\text{Mn}^+(\text{CH}_4)_n$ ($n = 1-6$) Clusters. *Int. J. Mass spectrom.* **2010**, *297*, 46-54.
- (24) Citir, M.; Altinay, G.; Austein-Miller, G.; Metz, R. B., Vibrational Spectroscopy and Theory of $\text{Fe}^+(\text{CH}_4)_n$ ($n = 1-4$). *J. Phys. Chem. A* **2010**, *114*, 11322-11329.
- (25) Ashraf, M. A.; Copeland, C. W.; Kocak, A.; McEnroe, A. R.; Metz, R. B., Vibrational Spectroscopy and Theory of $\text{Fe}_2^+(\text{CH}_4)_n$ ($n = 1-3$). *Phys. Chem. Chem. Phys.* **2015**, *17*, 25700-25704.
- (26) Kocak, A.; Sallese, Z.; Johnston, M. D.; Metz, R. B., Vibrational Spectroscopy of $\text{Co}^+(\text{CH}_4)_n$ and $\text{Ni}^+(\text{CH}_4)_n$ ($n = 1-4$). *J. Phys. Chem. A* **2014**, *118*, 3253-3265.
- (27) Kocak, A.; Ashraf, M. A.; Metz, R. B., Vibrational Spectroscopy Reveals Varying Structural Motifs in $\text{Cu}^+(\text{CH}_4)_n$ and $\text{Ag}^+(\text{CH}_4)_n$ ($n = 1-6$). *J. Phys. Chem. A* **2015**, *119*, 9653-9665.
- (28) Harding, D. J.; Kerpel, C.; Meijer, G.; Fielicke, A., Activated Methane on Small Cationic Platinum Clusters. *Angew. Chem. Int. Ed.* **2012**, *51*, 817-819.
- (29) Bakker, J. M.; Lapoutre, V. J. F.; Redlich, B.; Oomens, J.; Sartakov, B. G.; Fielicke, A.; von Helden, G.; Meijer, G.; van der Meer, A. F. G., Intensity-Resolved IR Multiple Photon Ionization and Fragmentation of C_{60} . *J. Chem. Phys.* **2010**, *132*, 074305.

- (30) Kiawi, D. M.; Bakker, J. M.; Oomens, J.; Buma, W. J.; Jamshidi, Z.; Visscher, L.; Waters, L. B. F. M., Water Adsorption on Free Cobalt Cluster Cations. *J. Phys. Chem. A* **2015**, *119*, 10828-10837.
- (31) Oepts, D.; van der Meer, A. F. G.; van Amersfoort, P. W., The Free-Electron-Laser User Facility FELIX. *Infrared Phys. Technol.* **1995**, *36*, 297-308.
- (32) Bakker, J. M. Structural Identification of Gas-Phase Biomolecules Using Infrared Spectroscopy. Ph. D. Thesis, Radboud University Nijmegen, 2004.
- (33) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A., *et al. Gaussian 09, Revision A.02*, Gaussian 09, Revision A.02; Gaussian Inc.: Pittsburgh, PA, 2009.
- (34) Lee, C.; Yang, W.; Parr, R. G., Development of the Colle-Salvetti Correlation-Energy Formula into a Functional of the Electron Density. *Phys. Rev. B* **1988**, *37*, 785-789.
- (35) Becke, A. D., Density-Functional Thermochemistry. III. The Role of Exact Exchange. *J. Chem. Phys.* **1993**, *98*, 5648-5652.
- (36) Weigend, F.; Ahlrichs, R., Def2-SVP Basis Sets. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297-3305.
- (37) Paschoal, D.; Marcial, B. L.; Lopes, J. F.; De Almeida, W. B.; Dos Santos, H. F., The Role of the Basis Set and the Level of Quantum Mechanical Theory in the Prediction of the Structure and Reactivity of Cisplatin. *J. Comput. Chem.* **2012**, *33*, 2292-2302.
- (38) Goerigk, L.; Grimme, S., Efficient and Accurate Double-Hybrid-Meta-GGA Density Functionals—Evaluation with the Extended GMTKN30 Database for General Main Group Thermochemistry, Kinetics, and Noncovalent Interactions. *J. Chem. Theory Comput.* **2011**, *7*, 291-309.
- (39) Grimme, S.; Ehrlich, S.; Goerigk, L., Effect of the Damping Function in Dispersion Corrected Density Functional Theory. *J. Comput. Chem.* **2011**, *32*, 1456-1465.
- (40) Johnson, E. R.; Becke, A. D., A Post-Hartree-Fock Model of Intermolecular Interactions. *J. Chem. Phys.* **2005**, *123*, 024101.
- (41) Johnson, E. R.; Becke, A. D., A Post-Hartree-Fock Model of Intermolecular Interactions: Inclusion of Higher-Order Corrections. *J. Chem. Phys.* **2006**, *124*, 174104.
- (42) Lehmann, K. K.; Scoles, G.; Pate, B. H., Intramolecular Dynamics from Eigenstate-Resolved Infrared Spectra. *Annu. Rev. Phys. Chem.* **1994**, *45*, 241-274.
- (43) Beil, A.; Luckhaus, D.; Quack, M.; Stohner, J., Intramolecular Vibrational Redistribution and Unimolecular Reaction: Concepts and New Results on the Femtosecond Dynamics and Statistics in CHBrClF. *Ber. Bunsenges. Phys. Chem.* **1997**, *101*, 311-328.
- (44) Ye, P.; Ye, Q.; Zhang, G.; Cao, Z., Potential Energy Surfaces and Mechanisms for Activation of Ethane by Gas-Phase Pt⁺: A Density Functional Study. *Chem. Phys. Lett.* **2011**, *501*, 554-561.
- (45) Zhou, S.; Li, J.; Wu, X.-N.; Schlangen, M.; Schwarz, H., Efficient Room-Temperature, Au⁺-Mediated Coupling of a Carbene Ligand with Methane To Generate C₂H_x (x = 4, 6). *Angew. Chem. Int. Ed.* **2016**, *55*, 441-444.

Table 1. Relative energies (eV) of possible product isomers formed in reactions of $\text{Pt}^+ + x \text{CH}_4$, $x = 2 - 4^a$

x	product species	B3LYP ^b			MP2(full) ^b		B3LYP-GD3BJ ^c	
		SVP	def2	mDZP	def2	mDZP	def2	mDZP
2	$(\text{H}_2)\text{Pt}^+(\text{C}_2\text{H}_4)$	0.16	0.00	0.00	0.00	0.00	0.00	0.00
	$\text{HPtC}_2\text{H}_5^+$	0.04	0.67	0.20	0.69	0.37	0.35	0.20
	$\text{Pt}(\text{CH}_3)_2^+$	0.00	0.91	0.01	0.76	0.28	0.60	0.04
	$(\text{CH}_4)\text{PtCH}_2^+$	0.59	1.06	0.33	0.99	0.79	0.78	0.65
	$\text{H}_2\text{PtCHCH}_3^+$	0.64	1.18	0.33	0.88	0.77	0.86	0.65
	$\text{HPtCH}_2(\text{CH}_3)^+$	0.85	1.30	0.81	0.90	0.81	0.98	0.82
	$\text{Pt}^+(\text{C}_2\text{H}_6)_{\text{end}}$	0.70	1.32	0.44	1.42	1.07	1.01	0.45
	$\text{Pt}^+(\text{C}_2\text{H}_6)_{\text{bod}}$	0.78	1.35	0.31	1.31	0.71	1.01	0.30
3	$(\text{H}_2)\text{Pt}^+(\text{C}_2\text{H}_4)(\text{CH}_4)$	0.01	0.00	0.00	0.00	0.00	0.00	0.00
	$\text{Pt}(\text{CH}_3)_2^+(\text{CH}_4)$	0.04	0.10	0.39	0.20	0.51	0.11	0.42
	$\text{Pt}^+(\text{C}_2\text{H}_6)(\text{CH}_4)$	0.00	0.11	0.21	0.18	0.64	0.13	0.26
	$\text{HPtC}_2\text{H}_5^+(\text{CH}_4)$	0.12	0.25	0.44	0.58	0.70	0.25	0.44
	$(\text{H}_2)\text{PtCHCH}_3^+(\text{CH}_4)$	0.70	0.74	0.87	0.57	0.66	0.75	0.89
	$\text{PtCH}_2^+(\text{CH}_4)_2$	0.76	0.78	0.96	1.11	1.37	0.82	1.01
	$\text{HPtCH}_2(\text{CH}_3)^+(\text{CH}_4)$	1.02	1.00	1.23	0.83	1.03	0.98	1.23
4	$\text{Pt}(\text{CH}_3)_2^+(\text{CH}_4)_2_{\text{cis}}$	0.08	0.00	0.13	0.00	0.00	0.00	0.06
	$\text{HPtC}_2\text{H}_5^+(\text{CH}_4)_2$	0.00	0.04	0.22	0.21	0.27	0.09	0.04
	$\text{Pt}^+(\text{C}_2\text{H}_6)(\text{CH}_4)_2$	0.06	0.06	0.00	0.32	0.22	0.11	0.00
	$\text{H}_2\text{PtCHCH}_3^+(\text{CH}_4)_2$	0.67	0.59	0.58	0.40	0.21	0.58	0.52

PtCH ₂ ⁺ (CH ₄) ₃	0.80	0.71	0.93	1.11	1.33	0.79	0.95
Pt(CH ₃) ₂ ⁺ (CH ₄) _{2_trans}	0.91	0.77	0.56	0.86	0.54	0.71	0.46
HPtCH ₂ (CH ₃) ⁺ (CH ₄) ₂	1.02	0.89	1.00	0.60	0.59	0.87	0.91

^a Single point energies at the level of theory indicated including zero point energy corrections. The ground isomer is bolded. SVP = def2-SVP; def2 = def2/TZVPPD; mDZP = mDZP/def2/TZVPPD. ^b Geometry optimizations at the B3LYP level of theory with listed basis set. ^c MP2(full) single point energies from the B3LYP geometries with the same basis set. ^d Geometry optimizations performed with empirical dispersion corrections applied to the B3LYP level of theory.

Table 2. Potential energy surface at 0 K for the reaction of $\text{PtCH}_2^+ + \text{CH}_4$

species	E_{rel} (eV) ^a		
	B3LYP ^b	B3LYP-GD3BJ ^c	MP2(full) ^b
$\text{PtCH}_2^+ + \text{CH}_4$	0.00	0.00	0.00
$(\text{CH}_4)\text{PtCH}_2^+$ (1)	-0.77	-0.89	-1.08
$\text{PtCH}_2^+(\text{CH}_4)$ (1*)	-0.10		-0.10
TS1/2	-0.08	-0.23	-0.75
$\text{HPtCH}_2(\text{CH}_3)^+$ (2)	-0.53	-0.69	-1.17
TS2/3	-0.28	-0.44	-0.92
$\text{Pt}(\text{CH}_3)_2^+$ (3)	-0.92	-1.07	-1.32
TS3/5	0.27	0.10	-0.22
$\text{Pt}^+(\text{C}_2\text{H}_6)_{\text{bod}}$ (5)	-0.49	-0.66	-0.77
TS5/6	-0.46	-0.63	-0.70
TS1*/6	0.48	0.15	0.23
$\text{Pt}^+(\text{C}_2\text{H}_6)_{\text{end}}$ (6)	-0.51	-0.66	-0.65
$\text{Pt}^+ + \text{C}_2\text{H}_6$	1.11	1.13	1.04
TS2/4	0.16	-0.02	-0.30
$\text{HPtC}_2\text{H}_5^+$ (4)	-1.16	-1.31	-1.38
TS4/6	-0.25	-0.40	-0.58
$\text{Pt}^+(\text{C}_2\text{H}_4) + \text{H}_2$	-0.53	-0.62	-1.05
$\text{PtCHCH}_3^+ + \text{H}_2$	-0.29	-0.37	-0.50

^a Single point energies calculated at the level of theory indicated with the def2-TZVPPD basis set including zero point energy corrections. ^b Structures optimized at the B3LYP/def2-TZVPPD level of theory. ^c Structures optimized at the B3LYP-GD3BJ/ def2-TZVPPD level of theory.

Figure Captions

Figure 1. Each graph shows $I_{sig} - I_{ref}$ plotted as a function of laser wavenumber for reactions with x CH_4 molecules, $x = 1 - 4$. The y-axis alternates sides as one moves down the graphs. The bottom graph shows the absolute value of the summation of $[\text{Pt},4\text{C},14\text{H}]^+$ and $[\text{Pt},3\text{C},10\text{H}]^+$ channels (red line) and the addition of $[\text{Pt},2\text{C},6\text{H}]^+$ and $[\text{Pt},\text{C},2\text{H}]^+$ channels in a combination of green and gray fills.

Figure 2. IRMPD depletion yield spectrum, $-\ln(I_{sig}/I_{ref})$, for $[\text{Pt},4\text{C},14\text{H}/\text{D}]^+$ (top and in shade) and below that the B3LYP/def2-TZVPPD calculated spectra for low-lying isomers. The intensity scale of the vibrational spectrum for $\text{PtCD}_2^+(\text{CD}_4)_3$ has been split for ease of comparison.

Figure 3. IRMPD depletion yield spectrum, $-\ln(I_{sig}/I_{ref})$, for $[\text{Pt},3\text{C},10\text{H}/\text{D}]^+$ (top and in shade) and below that the B3LYP/def2-TZVPPD calculated spectra for low-lying isomers. The intensity scale of the vibrational spectrum for $\text{PtCD}_2^+(\text{CD}_4)_2$ has been split for ease of comparison.

Figure 4. IRMPD growth yield spectrum for $[\text{Pt},2\text{C},6\text{H}/\text{D}]^+$ (top and in shade) and below that the B3LYP/def2-TZVPPD calculated spectra for low-lying isomers of $[\text{Pt},3\text{C},10\text{H}/\text{D}]^+$. The intensity scale of the vibrational spectrum for $\text{PtCD}_2^+(\text{CD}_4)_2$ has been split for ease of comparison.

Figure 5. IRMPD growth yield spectrum for $[\text{Pt},\text{C},2\text{H}/\text{D}]^+$ (top and in shade) and below that the calculated B3LYP/def2-TZVPPD spectra for the $\text{Pt}(\text{CH}_3)_2^+$ and $\text{Pt}(\text{CH}_3)_2^+(\text{CH}_4)$ isomers of $[\text{Pt},2\text{C},6\text{H}/\text{D}]^+$ and $[\text{Pt},3\text{C},10\text{H}/\text{D}]^+$ mass channels.

Figure 6. Select $[\text{Pt},2\text{C},6\text{H}]^+$ structures located on the $\text{PtCH}_2^+ + \text{CH}_4$ reaction coordinate pathway. Geometry optimizations performed with the B3LYP/def2-TZVPPD level of theory. Transition states (TS) between intermediates list the imaginary frequency in cm^{-1} .

Figure 7. B3LYP/def2-TZVPPD geometry optimized structures for $[\text{Pt},3\text{C},10\text{H/D}]^+$ complexes.

Figure 8. B3LYP/def2-TZVPPD geometry optimized structures for $[\text{Pt},4\text{C},14\text{H/D}]^+$ complexes.

Figure 9. Potential energy surface for reaction of PtCH_2^+ with CH_4 . Geometry optimization and single point energies are shown for B3LYP/def2 (solid red) and B3LYP-GD3BJ/def2 (green) calculations. Alternative C-C formation pathways are shown with dashed lines. This surface is extended to show the barrierless secondary dehydrogenation including values from ref 44 (solid black, relative to our $\text{HPtC}_2\text{H}_5^+$ B3LYP/def2 energy). All energies are zero point energy corrected.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9