Vibrational Spectroscopy and Theory of $Fe^+(CH_4)_n$ $(n = 1-4)^{\dagger}$

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Vibrational spectra are measured for Fe⁺(CH₄)_n (n = 1-4) in the C–H stretching region (2500–3200 cm⁻¹) using photofragment spectroscopy. Spectra are obtained by monitoring CH₄ fragment loss following absorption of one photon (for n = 3, 4) or sequential absorption of multiple photons (for n = 1, 2). The spectra have a band near the position of the antisymmetric C–H stretch in isolated methane (3019 cm⁻¹), along with bands extending >250 cm⁻¹ to the red of the symmetric C–H stretch in methane (2917 cm⁻¹). The spectra are sensitive to the ligand configuration (η^2 vs η^3) and to the Fe–C distance. Hybrid density functional theory calculations are used to identify possible structures and predict their vibrational spectra. The IR photodissociation spectrum shows that the Fe⁺(CH₄) complex is a quartet, with an η^3 configuration. There is also a small contribution to the spectrum from the metastable sextet η^3 complex. The Fe⁺(CH₄)₂ complex is also a quartet with both CH₄ in an η^3 configuration. For the larger clusters, the configuration switches from η^3 to η^2 . In Fe⁺(CH₄)₃, the methane ligands are not equivalent. Rather, there is one short and two long Fe–C bonds, and each methane is bound to the metal in an η^2 configuration. For Fe⁺(CH₄)₄, the calculations predict three low-lying structures, all with η^2 binding of methane and very similar Fe–C bond lengths. No single structure reproduces the observed spectrum. The approximately tetrahedral C_1 (⁴A) structure contributes to the spectrum; the nearly square-planar D_{2d} (⁴B₂) and the approximately tetrahedral C_2 (⁴A) structure may contribute as well.

I. Introduction

Catalytic activation of methane poses a particular challenge due to the strength of the C-H bond. The observation that several of the third-row transition metal cations activate methane¹ under thermal conditions, producing $MCH_2^+ + H_2$, has spurred many studies of the energetics, intermediates and products of these reactions. The gas-phase studies can elucidate the mechanism of the reaction and how the reactivity depends on the metal, its electronic state and spin, and the available energy.²⁻⁹ Two key intermediates in the reaction are the $M^+(CH_4)$ entrance channel complex and the $[H-M-CH_3]^+$ insertion intermediate. The corresponding reactions of first and second-row M⁺ are endothermic.¹⁰ Adding additional CH₄ ligands can reduce the barrier to insertion, resulting in H₂ elimination, as observed by van Koppen et al.¹¹ for Ti⁺. Even for metals which do not activate methane, the bonding in $M^+(CH_4)_n$ $(n \ge 1)$ is not merely electrostatic, but includes significant covalency due to donation from C-H bonding orbitals into empty or partially empty 4s and 3d orbitals on the metal, along with back-donation into C-H antibonding orbitals. The strength of these interactions, and the structure of the complexes, depends on the electronic configuration of the metal and on the size of the cluster. Vibrational spectroscopy is an ideal tool to investigate these noncovalent interactions,^{12–17} as binding to the metal leads to a substantial red-shift in the proximate C-H stretching frequencies, and increases their intensity.

Poad, Thompson and Bieske measured infrared spectra of $Al^+(CH_4)_n$ (n = 1-6) in the C–H stretching region using photofragment spectroscopy.¹⁸ They observe one strong absorption, which shifts from 2850 to 2885 cm⁻¹ with increasing

cluster size. This corresponds to the symmetric C–H stretching vibration in the complex. The symmetric stretch in isolated CH₄ is at $\nu_1 = 2917$ cm⁻¹ and is IR inactive. Interaction with the metal red-shifts the frequency and lends it substantial IR intensity (~100 km/mol). The Al⁺(CH₄)₆ clusters also show a weak band in the vicinity of the antisymmetric stretch ($\nu_3 =$ 3019 cm⁻¹ in CH₄). Comparison with calculated spectra of candidate structures show that the observed spectrum definitively establishes that the structure consists of intact CH₄ units bound to the metal in an η^3 configuration. Dryza and Bieske recently extended these studies to Mn⁺(CH₄)_n (n = 1-6).¹⁹ Again, the symmetric C–H stretch dominates the spectrum. It shifts from 2836 (n = 1) to 2880 cm⁻¹ (n = 6). The CH₄ bind to Mn⁺ in its ground electronic state (3d⁵4s¹, ⁷S) in an η^3 configuration.

Here, we report vibrational spectroscopy of $Fe^+(CH_4)_n$ (n = 1-4). The reaction

$$Fe^+ + CH_4 \rightarrow FeCH_2^+ + H_2$$

is 123 kJ/mol endothermic,^{20–22} and there is a substantial barrier to C–H insertion^{23,24} so, at the conditions in our ion source, we expect to produce only Fe⁺(CH₄)_n entrance channel complexes. Sequential binding energies of methane to Fe⁺ have been measured by Schultz and Armentrout via collision-induced dissociation (CID) using a guided ion beam^{21,25} and, more recently, by Zhang, Kemper, and Bowers by cluster equilibrium.²⁶ According to the CID measurements, the first methane binds by 57 kJ/mol and the second by 97 kJ/mol. The equilibrium measurements give similar values: 77 and 108 kJ/ mol, respectively. Stronger binding of the second ligand is often observed in electrostatic Fe⁺ complexes. The first excited state of Fe⁺ (3d⁷, ⁴F) interacts more strongly with ligands than the ⁶D (3d⁶ 4s) ground state, as the 4s orbital is empty, reducing repulsive interactions. Calculations predict that the ground state

[†] Part of the "Klaus Müller-Dethlefs Festschrift".

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of Fe⁺(CH₄) is a quartet,^{26,27} so its measured binding energy includes the 24 kJ/mol Fe⁺ ⁶D⁻⁴F promotion energy. Larger clusters (at least up to n = 6) are calculated to remain quartets, so this promotion energy is no longer an issue. Binding energies for the third and fourth methane are much smaller, 23 and 20 kJ/mol, respectively.²⁶ Binding energies for additional CH₄ are very small, around 2 kJ/mol. The equilibrium measurements support a maximum coordination number of four for Fe⁺(CH₄)_n, with additional CH₄ in the second solvation shell. The large change in binding energy with cluster size suggests that the binding in these complexes is not simply electrostatic. Competition between covalent and electrostatic interactions leads to cluster-size dependent binding configurations which are reflected in the richly structured vibrational spectra.

II. Experimental and Computational Methods

Iron ion-methane complexes are produced in a laser ablation source and studied in a dual time-of-flight mass spectrometer, which has been described in detail previously.^{28,29} Iron cations are produced by laser ablation of an iron rod (Sigma-Aldrich, 99.8% pure). Fe⁺(CH₄)_n clusters are generated in an expansion gas mixture of methane in helium at 50 psi backing pressure. Dilute mixes containing 0.1-1% methane are used to produce $Fe^+(CH_4)$ and $Fe^+(CH_4)_2$, and more concentrated mixes with 5% methane are used for larger clusters. Ions produced in the source expand supersonically into vacuum and cool to a rotational temperature of ~ 10 K.³⁰ Ions are accelerated to 1800 V kinetic energy, then rereferenced to ground potential before entering the field-free flight tube. Mass-selected ions are photodissociated at the turning point of the reflectron using an IR laser system. The light source is a Nd:YAG pumped optical parametric oscillator/optical parametric amplifier that is tunable from 2 to 4.5 μ m, producing ~10 mJ/pulse near 3200 cm⁻¹. The larger clusters $Fe^+(CH_4)_n$ (n = 3, 4) are so weakly bound that they dissociate after absorbing one photon in the C-H stretching region. Their spectra were measured in a single-pass setup. On energetic grounds, photodissociation of $Fe^+(CH_4)_n$ (n = 1, 2) requires 2–4 photons in the C–H stretching region. So, vibrational spectra are obtained using infrared multiple photon dissociation (IRMPD). No photodissociation signal is observed in the single-pass configuration. Instead, the photodissociation spectrum is measured using a multipass mirror arrangement^{31,32} in which the laser makes 21 passes through the ion beam. The laser wavelength is calibrated using CH₄ absorptions. Fragment ions and undissociated parent ions are detected by a dual microchannel plate detector.

The ion signal is amplified, collected on a digital oscilloscope or gated integrator, and averaged with a LabView based program. The photodissociation products are identified using a *difference spectrum*, which is generated by subtracting time-of-flight spectra collected at a specific wavelength with the dissociation laser blocked from when it is unblocked. The *photodissociation spectrum* is obtained by monitoring the yield of the fragment ion of interest as a function of wavelength and normalizing to parent ion signal and laser fluence. The photodissociation spectrum is the product of the absorption spectrum and the photodissociation quantum yield.

Computations are carried out using the Gaussian 2003 program package.³³ Optimized geometries of the reactants, intermediates, transition states and products are calculated using the Becke Lee–Yang–Parr hybrid HF/DFT method (B3LYP). We use the 6-311+G(d,p) basis for carbon and hydrogen and tried four different basis sets (6-31G(d,p), 6-311+G(d,p),

Wachters, and SDD) for iron. We also carried out MP2(full) calculations with the 6-311+G(d,p) basis. Some structures that are local, but not global, minima with some basis sets are not stable with other basis sets, relaxing to a lower-energy structure. However, for a particular structure, these four basis sets (and two levels of theory) predict nearly the same spectra. Here, we present calculations at the B3LYP/6-311+G(d,p) level. The calculated vibrational frequencies are harmonic, whereas the measured vibrational fundamentals include anharmonicity. To include this effect, the calculated frequencies are scaled by 0.948. All reported energies include zero-point energy and are corrected for basis set superposition error using the counterpoise method.

III. Results and Discussion

A. Vibrational Spectra of $Fe^+(CH_4)_n$ (n = 1-4). Vibrational spectra of $\text{Fe}^+(\text{CH}_4)_n$ (n = 1-4) were measured using photofragment spectroscopy. The larger clusters (n = 3, 4) are sufficiently weakly bound that absorption of one photon in the C-H stretching region leads to vibrational predissociation and loss of CH₄. Methane binding energies are substantially higher for the small clusters: 6400 and 9000 cm⁻¹ for n = 1 and 2, respectively.²⁶ Our initial studies used an optical configuration in which the IR beam makes only one or two passes through the ion beam. Under these conditions, we observe no photodissociation of $Fe^+(CH_4)_n$ (n = 1, 2). An alternate approach to measuring the spectrum is to add a weakly bound spectator atom such as Ar to the cluster. Rare gas atoms are more weakly bound than most other ligands so that single-photon excitation, even in the IR, is typically enough to cause dissociation. Unfortunately, Ar-tagging does not work well for Fe⁺(CH₄). Our calculations predict that argon binds strongly to $Fe^+(CH_4)$, by 2500 cm⁻¹, and significantly perturbs the vibrations, red-shifting the lowest-frequency C–H stretches by \sim 75 cm⁻¹.

Another possibility is to use vibrationally mediated photodissociation (VMP)³⁴ to measure the vibrational spectrum of Fe⁺(CH₄). This technique combines vibrational excitation with selective *electronic* photodissociation of vibrationally excited molecules. It has the potential to measure spectra of unperturbed ions, with laser-limited resolution and good sensitivity. However, measuring vibrational spectra using VMP requires that the electronic photodissociation spectra of vibrationally excited molecules differ from that of vibrationally cold molecules. The electronic spectra of a few $M^+(CH_4)$ have been measured. Kleiber and co-workers have recorded electronic photodissociation spectra of $M^+(CH_4)$, M = Mg,³⁵ Ca,³⁶ and Zn,³⁷ in the ultraviolet near the M^+ 4p \leftarrow 4s transition. The Mg⁺(CH₄) and $Zn^+(CH_4)$ spectra are broad, but the $Ca^+(CH_4)$ spectrum is structured, with progressions in the Ca^+ -CH₄ stretch and bend. For most transition metal M⁺, the first allowed electronic transition lies deep in the UV. Excited states corresponding to d-d and s-d transitions are at much lower energies, but are optically forbidden for isolated M⁺. Interaction with a ligand can make these transitions weakly allowed. Hayes et al. measured the electronic photodissociation spectrum of $V^+(CH_4)$ in the visible.³⁸ The spectrum is sharp, with progressions in the V⁺-CH₄ stretch and rock. Their structured spectra make $Ca^{+}(CH_4)$ and $V^{+}(CH_4)$ good candidates for VMP studies of their vibrational spectra. To evaluate the feasibility of VMP studies for $Fe^+(CH_4)$, its electronic photodissociation was monitored from 620 to 730 nm. Methane loss is the only dissociation channel observed. Unfortunately, the dissociation yield is small, and the photodissociation spectrum is unstructured, which precludes the use of VMP to measure the



Figure 1. Infrared photodissociation spectra of Fe⁺(CH₄)_{*n*} (n = 1-4) in the C–H stretching region. The vertical lines indicate the positions of the symmetric stretch ($\nu_1 = 2917 \text{ cm}^{-1}$) and antisymmetric stretch ($\nu_3 = 3019 \text{ cm}^{-1}$) in CH₄.

 TABLE 1: Experimental Band Positions and Their Relative

 Intensities^a

	band position (cm^{-1})
Fe ⁺ (CH ₄)	2646 (w), 2813 (m), 3000 (s)
$Fe^+(CH_4)_2$	2624 (sh), 2670 (m), 3017 (s)
$Fe^+(CH_4)_3$	2648 (w), 2703 (s), 2803 (m), 2895 (w), 3015 (m)
Fe ⁺ (CH ₄) ₄	2711 (s), 2737 (s), 2838 (s), 2869 (w), 2998 (m)

a = strong; m = medium; w = weak; sh = shoulder.

vibrational spectrum. In addition, at 266 nm we observe very interesting dissociation channels for $Fe^+(CH_4)_n$. $Fe^+(CH_4)$ dissociates via loss of methane. In addition to methane loss, we also observe $Fe^+(H_2)$ as a minor channel in photodissociation of $Fe^+(CH_4)_2$ and $Fe^+(CH_4)_3$.

After implementing a multipass mirror setup,^{31,32} we were able to measure vibrational spectra of $Fe^{+}(CH_4)_n$ (n = 1, 2)using IR multiple photon dissociation (IRMPD). Figure 1 shows the vibrational photodissociation spectra of $Fe^+(CH_4)_n$ (n = 1-4). Band positions and intensities are listed in Table 1. All of the clusters have a peak near the antisymmetric stretch (v_3 = 3019 cm^{-1}) in isolated CH₄, indicated by a vertical line in the figure. The remaining peaks exhibit a pronounced red shift relative to the symmetric stretch in isolated CH₄ ($\nu_1 = 2917$ cm⁻¹), with larger red shifts generally observed for the smaller clusters. These peaks are due to vibrations of C-H bound to the metal, resulting in the large red shift. The red shifts are much larger than those observed for $Al^+(CH_4)_n$ and $Mn^+(CH_4)_n$, consistent with the much larger Fe⁺-methane binding energies. Spectra of the n = 1, 2 clusters show broader features than those of the smaller clusters. A laser ablation/molecular beam source cools rotations very well, but is much less efficient at cooling vibrations. These hot ions preferentially contribute to the photodissociation spectrum, as IRMPD is more efficient for the hot ions, which need to absorb fewer IR photons to dissociate. In addition, the small binding energies of larger clusters limit their internal energy.

The vibrational spectra show large differences with cluster size, reflecting varying configurations (η^2 vs η^3) and metal-



⁴A"(quartet , η³) +0

Figure 2. Calculated structures of $Fe^+(CH_4)$ at the B3LYP/6-311+G(d,p) level. Relative energies, in kJ/mol, are in bold. The Fe-C bond lengths, in Å, are in black; Fe-H bond lengths are in red.

methane distances. To determine the structure and characterize the vibrations of each $\text{Fe}^+(\text{CH}_4)_n$ cluster, we carry out geometry optimization and vibrational frequency calculations for several potential isomers. By comparing the measured and predicted vibrational spectra, we determine which isomer(s) are present, and hence energetically favored.

B. Analysis of the Structure and Vibrational Spectra of $Fe^+(CH_4)_n$ (*n* = 1-4). *i*. $Fe^+(CH_4)$. The ⁴F (3d⁷) state of Fe⁺ lies 24 kJ/mol above the 6D (3d6 4s) ground state. However, metals with a $d^n s^0$ configuration interact more strongly with ligands than those with a $d^{n-1} s^1$ configuration, as the 4s orbital is empty, reducing repulsive interactions. A key question is whether the enhanced interaction of the quartet state with methane is sufficient to overcome this energy difference. Calculations indicate that it is. Early MP2 calculations by Ricca et al. predict that $Fe^+(CH_4)$ has a quartet ground state, with an η^3 configuration.²⁷ To complement their ligand exchange equilibrium measurements, Zhang et al. calculated structures of low-lying isomers of $\text{Fe}^+(\text{CH}_4)_n$ (n = 1-6) and their binding energies.²⁶ They used the B3LYP method with the 6-31G(d,p) basis on carbon and hydrogen. For iron, they tried two basis sets: the double- ζ valence polarization (DZVP) and an augmented Wachters basis set. For several of the clusters they identify multiple isomers with similar calculated energies, with the energy difference depending on the basis set. They also predict a quartet ground state, with the CH₄ ligand binding to Fe⁺ in an η^3 configuration. Two quartet η^2 configurations lie at slightly higher energy. Sextet Fe⁺(CH₄) is calculated to be 21 kJ/mol above the quartet ground state. It also adopts an η^3 configuration, with much longer Fe-C bond length.

For Fe⁺(CH₄) we also find a quartet ground state with an η^3 configuration with C_s (⁴A'') symmetry, slightly distorted from C_{3v} with 2.10 Å Fe–C bond length (Figure 2). We also find a low-lying quartet state with an η^2 configuration with C_1 (⁴A) symmetry, slightly distorted from C_{2v} . For the sextet state, we



Figure 3. Experimental IR photodissociation spectrum of Fe⁺(CH₄), along with calculated spectra of quartet η^3 and η^2 and sextet η^3 complexes. The maximum calculated IR intensities are 38, 27, and 100 km/mol for the ⁴A", ⁴A, and ⁶A₁ complexes, respectively.

calculate an η^3 configuration with C_{3v} (⁶A₁) symmetry and 2.52 Å Fe-C bond length. Our calculations show that the sextet structure has a significantly longer Fe-C bond than the quartet structures, as would be expected from the 3d⁶ 4s¹ configuration of Fe⁺ (⁶D).

Calculations on bare Fe^+ at the B3LYP/6-311+G(d,p) level incorrectly predict a quartet ground state, 19.8 kJ/mol below the sextet state. This is a well-known failure of the B3LYP method with this type of basis set.39,40 To find the relative energies of sextet and quartet $Fe^+(CH_4)$, we calculate the energy of each cluster relative to spin-allowed products, then correct by the experimental Fe⁺ sextet-quartet energy. Conserving spin, the binding energy of sextet Fe⁺(CH₄) is calculated to be 40 kJ/mol; that of quartet $Fe^+(CH_4)$ is more than twice as large: 83 kJ/mol. Thus, the dissociation energy of quartet $Fe^+(CH_4)$ relative to ground state, sextet, $Fe^+ + CH_4$ is 59 kJ/mol. This is in good agreement with the experimental values of 57 kJ/ mol (CID)^{21,25} and 77 kJ/mol (equilibrium).²⁶ In addition, our calculations predict that sextet Fe⁺(CH₄) lies 19 kJ/mol above the quartet state, in agreement with the previous calculations. We also considered the possibility of an inserted $[H-Fe-CH_3]^+$ structure. Calculations by Chiodo et al.⁴¹ at the B3LYP level, using a modified TZVP basis set for iron, predict that the quartet $[H-Fe-CH_3]^+$ insertion intermediate lies 18 kJ/mol above reactants. It is separated from the $Fe^+(CH_4)$ entrance channel by only a 4 kJ/mol barrier. In our calculations, $[H-Fe-CH_3]^+$ is not a local minimum; it relaxes to $Fe^+(CH_4)$. In summary, $[H-Fe-CH_3]^+$ is not likely to be an observable intermediate.

The predicted spectra of the three most stable structures of $Fe^+(CH_4)$ are shown in Figure 3 and the calculated vibrational frequencies and their intensities are summarized in Table S1. As seen in the figure, the η^3 and η^2 configurations for the quartet state have completely different calculated spectra. The calculated spectrum of the $\eta^3 C_s$ (⁴A") structure has two intense peaks at 2685 and 2946 cm⁻¹ and two weak bands at 2786 and 2799 cm⁻¹. The symmetric C–H stretch vibration of the "bound" hydrogens (hydrogens pointing toward the Fe⁺) gives the most red-shifted peak, at 2685 cm⁻¹. The weak bands at 2786 and 2799 cm⁻¹ are due to the antisymmetric stretches of these hydrogens. The most intense peak is at 2946 cm⁻¹ and is caused

by the C-H stretch of the hydrogen pointing away from the Fe⁺. For the η^2 (⁴A) structure, four intense peaks are predicted at 2596, 2686, 2925, and 2982 cm⁻¹. Symmetric and antisymmetric C-H vibrations of the bound hydrogens give the peaks at 2596 and 2686 cm⁻¹, respectively. The corresponding vibrations of the hydrogens pointing away from the Fe⁺ give the peaks at 2925 and 2982 cm⁻¹. For the sextet state, $\eta^3 C_{3v}$ $(^{6}A_{1})$, the very intense peak at 2790 cm⁻¹ is due to the symmetric C-H stretch, which involves all the hydrogens. The small peak at 2892 is the doubly degenerate antisymmetric combination of bound C-H stretches. The 2908 cm⁻¹ peak is primarily due to the C-H stretch vibration of the free hydrogen. The spectral signatures persist in the larger clusters and allow us to identify the methane configuration. At this level of theory, the C-H bond length in isolated CH₄ is 1.091 Å. The bound C-H bond lengths are 1.120 Å for the η^2 (⁴A) state, 1.112 Å for the $\eta^3 C_s$ (⁴A'') state, and 1.099 Å for the η^3 sextet state. Binding in an η^2 configuration results in the largest extension of the C-H bond length, and most red-shifted spectrum. The free C-H bond lengths are almost unchanged from isolated CH₄: 1.090-1.092 Å for the quartet states and 1.096 for the sextet state.

The experimental photodissociation spectrum has an intense peak at $\sim 3000 \text{ cm}^{-1}$, a smaller peak at 2813 cm⁻¹, and a weak peak at 2646 cm⁻¹. The calculated spectrum of the $\eta^3 C_s$ (⁴A'') complex reproduces the 3000 and 2646 cm⁻¹ peaks. However, the calculated intensity of the peaks near 2800 cm⁻¹ is far too low. It appears that the 2813 cm⁻¹ peak is due to the sextet state, $\eta^3 C_{3v}$ (⁶A₁). Although this state is calculated to lie at higher energy than the quartet states, it would be produced by binding of methane to ground state Fe⁺ with conservation of spin. Relaxation of sextet $Fe^+(CH_4)$ to the quartet state by the helium carrier gas in the molecular beam is likely to be inefficient. The 2790 cm⁻¹ vibration for the sextet state has a calculated absorption intensity of 100 km/mol, compared to only 38 km/mol for the 2946 cm⁻¹ vibration for the quartet state. In addition, we calculate absorption spectra and measure IRMPD spectra, so the intensities may differ. IRMPD of sextet $Fe^+(CH_4)$ is likely to be more efficient than for the quartet state, as it is more weakly bound. Thus, the relative amount of sextet $Fe^+(CH_4)$ is likely to be quite small. There is no evidence that the η^2 (⁴A) complex contributes to the spectrum.

The interaction of the sextet ground state of Fe⁺ ($3d^6 4s^1$) with methane to produce sextet Fe⁺(CH₄) is similar to the interactions of Mn⁺ ($3d^54s^1$, ⁷S) and Al⁺ ($3s^2$, ¹S) with methane. The complexes adopt an η^3 configuration, with the Fe–C bond length (2.52 Å) slightly shorter than the Mn–C bond length (2.64 Å)¹⁹ and significantly shorter than the Al–C bond length (2.90 Å).¹⁸ Accordingly, sextet Fe⁺(CH₄) (40 kJ/mol) is more strongly bound than Mn⁺(CH₄) (34 kJ/mol) and Al⁺(CH₄) (25 kJ/mol).^{19,26,42} In the C–H stretching region, the vibrational spectra are also similar: each spectrum consists of a single peak due to the symmetric C–H stretch, with stronger, shorter metal–methane bonds leading to larger red shifts, from Al⁺(CH₄) (2850 cm⁻¹)¹⁸ to Mn⁺(CH₄) (2836 cm⁻¹)¹⁹ to sextet Fe⁺(CH₄) (2813 cm⁻¹).

ii. $Fe^+(CH_4)_2$. The photodissociation spectrum of Fe⁺(CH₄)₂ consists of a band at 2670 cm⁻¹ (with a weak shoulder at 2624 cm⁻¹) and a strong band at 3017 cm⁻¹. These two peaks are similar to those observed for Fe⁺(CH₄). However, the 2813 cm⁻¹ band in Fe⁺(CH₄) is not present in Fe⁺(CH₄)₂. The B3LYP calculations of Zhang et al. predict that the ground state for Fe⁺(CH₄)₂ is a quartet, D_{3d} (⁴E_g), with both ligands in an η^3 configuration and 2.12 Å Fe⁻C bond length.²⁶ They also find a higher-energy isomer with D_{2h} (⁴B_{1g}) symmetry and 2.23 Å



Figure 4. Calculated structures of $Fe^+(CH_4)_2$ at the B3LYP/6-311+G(d,p) level. Relative energies, in kJ/mol, are in bold.

Fe-C bond length in which both methanes are in an η^2 configuration. Our calculations for Fe⁺(CH₄)₂ at the B3LYP/ 6-311+G(d,p) level predict a very similar ground state structure with both methanes in an η^3 configuration. It has C_{2h} (⁴B_g) symmetry and 2.12 Å Fe-C bond distance (Figure 4). The η^2 configuration is not a local minimum with the 6-311+G(d,p) basis set—it relaxes to the η^3 configuration. The lowest-energy sextet structure is also η^3 , with C_{2h} symmetry. The Fe-C bond distance is 2.78 Å, much longer than for the quartet state.

Our calculations predict that the binding energy of methane to quartet Fe⁺(CH₄) is 84 kJ/mol. This is slightly lower than the experimental values of 97 kJ/mol (CID)^{21,25} and 108 kJ/ mol (equilibrium).²⁶ The second CH₄ binds more strongly to Fe⁺ than the first. This effect is mostly due to the 24 kJ/mol required to promote ground state ⁶D (3d⁶ 4s) Fe⁺ to the excited ${}^{4}F(3d^{7})$ state. In fact, we calculate essentially the same binding energies for the first and second CH_4 to quartet Fe^+ , in accord with the experiments. For comparison, we also calculated the sequential binding energies of CH₄ to sextet Fe⁺, conserving spin. They are 40 and 15 kJ/mol for the first and second CH₄, respectively. These binding energies are much lower than those to quartet Fe^+ . As a result, sextet $Fe^+(CH_4)_2$ is calculated to lie 88 kJ/mol above the quartet state. The Fe-C and C-H bond lengths of quartet $Fe^+(CH_4)_2$ are very similar to those of $Fe^+(CH_4)$, consistent with the similar first and second binding energies. The Fe-C bond in sextet $Fe^+(CH_4)_2$ is significantly longer than in sextet $Fe^+(CH_4)$, also consistent with weaker binding of the second methane in the high-spin complex.

Figure 5 compares the experimental photodissociation spectrum of $Fe^+(CH_4)_2$ to the calculated spectra for the low-spin and high-spin η^3 isomers. The calculated vibrational frequencies and their intensities are given in Table S1. The calculated spectrum of quartet Fe⁺(CH₄)₂ consists of two peaks, at 2695 and 2964 cm⁻¹. The 2695 cm⁻¹ vibration is due to the out-ofphase combination of symmetric C-H stretches of the hydrogens pointing toward the Fe⁺. The most intense peak is at 2964 cm⁻¹ and is due to the out-of-phase C-H stretches of the outside hydrogens. The calculated spectrum of sextet Fe⁺(CH₄)₂ consists of a single, intense peak at 2814 cm⁻¹, which is due to the outof-phase combination of symmetric C-H stretches of all the hydrogens. The simulated spectrum of the quartet η^3 complex matches the experimental photodissociation spectrum of $Fe^{+}(CH_{4})_{2}$. There is no evidence that the sextet state contributes to the spectrum. This is not surprising, as the calculations predict that the sextet complex is much less stable than the quartet complex.

Bieske and co-workers observe that the spectra of $Mn^+(CH_4)_n$ and $Al^+(CH_4)_n$ (n = 1-6) change very little with the number of ligands, as the complexes are all high spin and adopt an η^3



Figure 5. Experimental IR photodissociation spectrum of $Fe^+(CH_4)_2$ (bottom), and calculated spectra of quartet η^3 (middle) and sextet η^3 complexes (top). The maximum calculated IR intensities are 59 and 192 km/mol for the quartet and sextet complexes, respectively.

configuration.^{18,19} We see a similar effect for $\text{Fe}^+(\text{CH}_4)_n$ (n = 1, 2). This is consistent with vibrations on adjacent ligands being only weakly coupled. The calculated splittings between in-phase and out-of-phase combinations of C–H stretches on different CH₄ are calculated to be $\leq 10 \text{ cm}^{-1}$, also indicating that the vibrations of different methanes are independent. This observation simplifies the assignment of the spectra of the larger clusters.

iii. $Fe^+(CH_4)_3$. We observe strong photodissociation signals for Fe⁺(CH₄)₃ and Fe⁺(CH₄)₄ without using a multipass configuration. This is consistent with the equilibrium measurements of Zhang et al.²⁶ which predict that the Fe⁺(CH₄)₂-CH₄ binding energy is only 21.8 kJ/mol (1800 cm⁻¹). Thus, absorption of one photon in the C-H stretching region leads to loss of CH₄ via vibrational predissociation. The photodissociation spectrum of $Fe^+(CH_4)_3$ is shown in Figure 1. It has an intense absorption at 2703 cm⁻¹, with smaller peaks at 2648, 2803, 2895, and 3015 cm⁻¹. The lowest-energy peak is red-shifted 269 cm⁻¹ relative to the 2917 cm⁻¹ symmetric C-H stretch in bare CH₄. As with the smaller clusters, the peaks near 2700 cm⁻¹ are likely due to stretching of C-H bonds proximate to the metal, where binding to the metal weakens the C-H bonds. The broad peaks at 2895 and 3015 cm⁻¹ are near the positions of the C-H stretches in bare CH₄ and are likely due to vibrations of the C-H bonds pointing away from the metal. As $Fe^{+}(CH_4)_3$ has 12 C-H bonds, it will have 12 C-H stretches. Depending on the symmetry of the complex, some of these may be degenerate (or nearly degenerate) or have very low intensity. To understand the vibrations of $Fe^{+}(CH_4)_3$ and determine its structure, we carried out geometry optimization and vibrational frequency calculations for several potential isomers. By comparing the measured and predicted vibrational spectra, which should be able to determine which isomer(s) are present, and hence energetically favored.

Our calculations for the Fe⁺(CH₄)₃ complex predict three lowlying isomeric structures at the B3LYP/6-311+G(d,p) level, shown in figure 6. While the smaller clusters Fe⁺(CH₄)_n (n =1, 2) favor η^3 coordination, η^2 structures dominate for the larger clusters. We find that the lowest-energy state has $C_{2\nu}$ (⁴B₂) symmetry with two short (2.29 Å) and one long (2.47 Å) Fe–C bonds. This structure is very similar to the ground state found by Zhang et al.²⁶ The other two low-lying structures have $C_{2\nu}$ (⁴A₁) and C_1 (⁴A) symmetry with two long and one short Fe–C



Figure 6. Calculated structures of Fe⁺(CH₄)₃ at the B3LYP/6-311+G(d,p) level. All the methanes are in an η^2 configuration, except for the C_1 (⁴A) structure, in which one methane is η^3 . Relative energies, in kJ/mol, are in bold.

bonds. In the $C_{2\nu}$ (⁴B₂ and ⁴A₁) structures, all of the ligands have an η^2 configuration. However, for the C_1 (⁴A) structure, one methane is η^3 . The lowest energy sextet structure is calculated to lie much higher in energy, 135 kJ/mol above the ⁴B₂ state. As expected, it has all three CH₄ in an η^3 configuration.

Our calculations predict that there are eight infrared active C-H vibration bands with intensities of at least 1.0 km/mol for the $C_{2\nu}$ (⁴B₂), C_1 , and $C_{2\nu}$ (⁴A₁) structures, but many of them overlap at 10 cm⁻¹ resolution. The calculated vibrational frequencies and their intensities are summarized in Table S1 of the Supporting Information. In Figure 7, the experimental spectrum is compared to the predicted spectra of the three isomers. The simulated spectrum of $C_{2\nu}$ (⁴A₁), which has η_2 coordination and one short and two long Fe-C bonds, is in excellent agreement with experiment for both band positions and intensities. The C_1 (⁴A) structure may also contribute to the spectrum, as it shares many peaks with the ⁴A₁ state, but does not reproduce the 2648 cm⁻¹ peak. On the other hand, although the $C_{2\nu}$ (⁴B₂) is (barely) calculated to be the lowest energy structure, its predicted peak spacings and intensities are in much poorer agreement with experiment.

In Fe⁺(CH₄)₃ each methane is bound to the metal in an η^2 configuration, except in the C_1 (⁴A) structure, and two methane ligands are symmetrical to each other. As was discussed for Fe⁺(CH₄), the vibrational spectrum of an η^2 complex will consist of two pairs of peaks. For C–H bonds pointing away from the metal, the symmetric and antisymmetric "free" C–H stretches lie near 3000 cm⁻¹. Interaction with the metal causes the symmetric and antisymmetric "bound" C–H stretches to be strongly red-shifted, down to ~2700 cm⁻¹. The extent of this red shift depends on the Fe–C distance. For larger clusters, the C–H stretches on different methanes are not strongly coupled (e.g., the calculations predict <12 cm⁻¹ splitting between vibrations consisting of in-phase and out-of-phase combinations of equivalent C–H motions on different CH₄ ligands). As a



Figure 7. Experimental IR photodissociation spectrum of $Fe^+(CH_4)_3$ (bottom), and calculated spectra of low-lying isomers. The maximum calculated IR intensities are 73, 69, and 72 km/mol for the ⁴B₂, ⁴A and ⁴A₁ complexes, respectively.

result, the calculated spectra of $Fe^+(CH_4)_3$ reflect the Fe-C distance for each methane ligand. This is illustrated by the C_{2v} $({}^{4}A_{1})$ structure, which has one short (2.31 Å) and two long (2.39 Å) Fe-C bonds. The most red-shifted peak in the calculated spectrum (at 2648 cm^{-1}) is due to the symmetrical bound C-H stretches of the methane closest to the iron. The doublet at 2695/ 2706 cm⁻¹ is due to the symmetrical bound C-H stretches of the other two methanes. They are further from the metal and thus exhibit a smaller red shift. The smaller peaks at 2732 and 2793 cm⁻¹ are due to the antisymmetric bound C-H stretches of the nearer and more distant CH₄, respectively. The symmetric and antisymmetric free C-H stretches give rise to the weak peaks at 2946 and 3005 cm⁻¹. The vibrational spectrum, particularly in the bound C-H stretching region, is very sensitive to the geometry of the cluster. The peak intensities appear to reflect the number of short versus long Fe-C bonds, and the spacing reflects the Fe-C bond length. This can be seen by comparing the vibrational spectra of the ⁴B₂ state to that of the ${}^{4}A_{1}$. The ${}^{4}B_{2}$ structure has two short and one long Fe-C distance. The 2656 cm⁻¹ peak, which is due to the bound symmetric C–H stretches of the methanes at $r_{\text{Fe}-\text{C}} = 2.29$ Å, is more intense than the 2732 cm⁻¹ peak due to the analogous vibration of the methane at $r_{\rm Fe-C} = 2.47$ Å. In addition, the splitting between these two peaks is much larger for the ⁴B₂ state than for the ⁴A₁. As expected, the C–H red shifts reflect changes in the C–H bond lengths. In the ${}^{4}A_{1}$ state, the methane close to the Fe⁺ has bound C-H bond lengths of 1.114 Å, whereas they are 1.110 Å in the more distant methanes. The free C–H bond lengths are 1.089 Å.

iv. $Fe^+(CH_4)_4$. Figure 1 shows the photodissociation spectrum of Fe⁺(CH₄)₄ in the C–H stretching region. The spectrum has strong bands at 2711, 2737, 2838, and 2998 cm⁻¹ and a weak band at 2869 cm⁻¹. The most intense peak(s) in the Fe⁺(CH₄)₄ spectrum is the doublet at 2711/2737 cm⁻¹. This has a smaller red shift than the corresponding peaks for Fe⁺(CH₄)₃, which are at 2648 and 2703 cm⁻¹. This is not surprising as the methane in the smaller cluster should be more strongly bound and closer to the metal, leading to weaker C–H bonds.

Our calculations identify three low-lying isomeric structures for $Fe^+(CH_4)_4$. In each case, all of the methanes are bound in



Figure 8. Calculated structures of Fe⁺(CH₄)₄ at the B3LYP/6-311+G(d,p) level. All the methanes are in an η^2 configuration. The C_2 (⁴A) and C_1 (⁴A) structures are approximately tetrahedral; the D_{2d} (⁴B₂) structure is square planar. Relative energies, in kJ/mol, are in bold.

an η^2 configuration. Two of the structures, C_2 (⁴A) and C_1 (⁴A), are very close to tetrahedral (Figure 8). The third structure, D_{2d} (⁴B₂), is approximately square-planar. These three isomers have very similar energies, differing by only 0.5 kJ/mol. Zhang et al.²⁶ find a square-planar ground state for Fe⁺(CH₄)₄. Their second low-energy calculated structure is tetrahedral, with a similar geometry to our C_2 (⁴A) and C_1 (⁴A) structures.

In Figure 9, the experimental spectrum of Fe⁺(CH₄)₄ is compared to the predicted spectra for the three low-energy structures. The three structures have very similar calculated spectra. The spectrum in the C-H stretching region is sensitive to the local environment of the methane, and all three structures have an η^2 configuration, with very similar Fe-C bond lengths. However, in this case, the vibrational spectrum is not sensitive to the configuration around the metal (square-planar vs tetrahedral). In fact, the calculations predict that the entire IR spectra of the tetrahedral C_2 (⁴A) and square-planar D_{2d} (⁴B₂) complexes are nearly identical. No single structure reproduces the doublet observed at 2711/2737 cm⁻¹. It is likely that the 2711 cm⁻¹ peak is due to the tetrahedral C_1 (⁴A) structure. Either one or both of the other two structures may be responsible for the 2737 cm^{-1} peak. Another possible cause of the 2711/2737 cm^{-1} doublet is Fermi resonance between the C-H stretch and an overtone or combination band of the C-H bend. The vibrational spectra of $F^{-}(CH_4)_n$ (n = 1-8)⁴³ provide a textbook example. All of the clusters show peaks near the position of the $2\nu_4$ (2612



Figure 9. Experimental IR photodissociation spectrum of Fe⁺(CH₄)₄ (bottom), and calculated spectra of low-lying isomers. The maximum calculated IR intensities are 203, 199, and 166 km/mol for the C_2 ⁴A, ⁴B₂, and C_1 ⁴A complexes, respectively.

cm⁻¹) and $\nu_2 + \nu_4$ (2845 cm⁻¹) bands in bare CH₄. The positions of these peaks are nearly independent of cluster size, but their intensity varies dramatically, depending on their proximity to C-H stretch peaks, whose position depends strongly on cluster size.

The calculated spectra of Fe⁺(CH₄)₄ are surprisingly simple, considering the molecule has sixteen C–H stretches. This simplicity is due to the fact that all the CH₄ share the same configuration, with nearly identical Fe–C bond lengths. Also, vibrations on adjacent CH₄ are very weakly coupled. As a result, the calculated spectra of Fe⁺(CH₄)₄ are analogous to that of η^2 Fe⁺(CH₄). The band near 2700 cm⁻¹ is due to the symmetric C–H stretch of hydrogens bound to Fe⁺. There are four of these vibrations, which all lie within 15 cm⁻¹. The band near 2840 cm⁻¹ is due to the antisymmetric C–H stretch of bound hydrogens. The weak band near 2950 cm⁻¹ is due to the symmetric C–H stretch of free hydrogens. The corresponding antisymmetric stretch is at 3002 cm⁻¹ and is extremely weak.

IV. Summary and Conclusions

In this work, we present vibrational spectra of $Fe^{+}(CH_4)_n$ (n = 1-4) obtained by monitoring loss of CH₄ following IR photoexcitation. Calculations predict that the positions and intensities of bands in the C-H stretching region depend strongly on the configuration of the CH₄ (η^2 vs η^3) and on the Fe-C bond length. Thus, we determine the structures of the complexes by comparing the observed IR photodissociation spectra to calculated vibrational spectra of low-lying candidate structures. Although the ground state of Fe⁺ is high-spin ⁶D $(3d^6 4s)$, the low-spin ⁴F $(3d^7)$ state, which lies 24 kJ/mol above the ground state, has a more favorable electron configuration for noncovalent binding. The vibrational spectra show that all of the complexes are quartets, in accord with theoretical predictions. In $Fe^+(CH_4)$ and $Fe^+(CH_4)_2$ the methanes are in an η^3 configuration. In the larger clusters, Fe⁺(CH₄)₃ and $Fe^+(CH_4)_4$, the methanes adopt an η^2 configuration. The vibrational spectrum of Fe⁺(CH₄)₃ is consistent with a structure with one short and two long Fe–C bonds. In $Fe^+(CH_4)_4$ the calculations predict, and the photodissociation spectrum is consistent with, structures in which all of the Fe–C bond lengths are very similar.

Acknowledgment. Financial support from the National Science Foundation under award CHE-0911225 is gratefully acknowledged.

Supporting Information Available: Calculated harmonic vibrational frequencies and intensities for $\text{Fe}^+(\text{CH}_4)_n$ (n = 1-4) at the B3LYP/6-311+G(d,p) level. This material is available free of charge via the Internet at http://pubs.acs.org.

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JP104602K