# Reactions of Atomic Cations with Methane: Gas Phase Room-Temperature Kinetics and Periodicities in Reactivity

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Reactions of methane have been measured with 59 atomic metal cations at room temperature in helium bath gas at 0.35 Torr using an inductively-coupled plasma/selected-ion flow tube (ICP/SIFT) tandem mass spectrometer. The atomic cations were produced at ~5500 K in an ICP source and allowed to decay radiatively and to thermalize by collisions with argon and helium atoms prior to reaction. Rate coefficients and product distributions are reported for the reactions of fourth-row atomic cations from $K^+$ to $Se^+$, of fifth-row atomic cations from $Rb^+$ to $Te^+$ (excluding $Tc^+$), of sixth-row atomic cations from $Cs^+$ to $Bi^+$, and of the lanthanide cations from $La^+$ to $Lu^+$ (excluding $Pm^+$). Two primary reaction channels were observed: C−H bond insertion with elimination of $H_2$, and $CH_4$ addition. The bimolecular $H_2$ elimination was observed in the reactions of $CH_4$ with $As^+$, $Nb^+$, and some sixth-row metal cations, i.e., $Ta^+$, $W^+$, $Os^+$, $Ir^+$, $Pt^+$; secondary and higher-order $H_2$ elimination was observed exclusively for $Ta^+$, $W^+$, and $Ir^+$ ions. All other transition-metal cations except $Mn^+$ and $Re^+$ were observed to react with $CH_4$ exclusively by addition, and up to two methane molecules were observed to add sequentially to most transition-metal ions. $CH_4$ addition was also observed for $Ge^+$, $Se^+$, $La^+$, $Ce^+$, and $Gd^+$ ions, while the other main-group and lanthanide cations did not react measurably with methane.

## 1. Introduction

The importance of transition-metal centers as catalysts for selective transformations of organic molecules, especially methane, into useful chemical reagents is well-known.[1] The first report on activation of alkanes by transition-metal ions in the gas phase was published about 3 decades ago.[2] Since then, gas-phase reactions of methane have been studied with many transition-metal monocations, $M^+$, under various experimental conditions using Fourier transform ion cyclotron resonance (FT-ICR)[3] and guided ion beam (GIB)[4] instruments coupled with a mass spectrometer. Irikura and Beauchamp found that some sixth-row transition-metal ions ($Ta^+$, $W^+$, $Os^+$, $Ir^+$, and $Pt^+$) react efficiently with $CH_4$ to yield $MCH_2^+$ and $H_2$ products.[5,6] However, this reaction does not proceed efficiently for thermalized ground-state monocations of the 3d and 4d transition metals because of unfavorable thermodynamics; the metal−carbene bond dissociation energy, $D_0(M^+{-}CH_2)$, has to exceed 111 kcal $mol^{-1}$, i.e., the energy of dissociation of $CH_4$ into $CH_2$ and $H_2$, for the above reaction to be exothermic.[7] Several 3d and 4d transition-metal ions have been reported to react efficiently with methane when they are electronically excited or have high kinetic energies.[8]

A wealth of thermochemical data have been obtained for $M^+ + CH_4$ reactions using FT-ICR and GIB techniques.[8−64] For example, $M^+{-}CH_2$ bond dissociation energies have been measured for almost all transition-metal ions,[8,63,64] and bimolecular reaction rate coefficients were reported for several sixth-row metal ions.[5,6] Parallel to experimental studies, numerous theoretical calculations also have been performed on methane reactions with $M^+$ and its product ions.[65−100] The $M^+{-}CH_2$ and $M^+{-}CH_4$ dissociation energies, reaction mechanisms, structures of primary and higher-order products, and potential energy surfaces have been computed using various theoretical methods.

Most experimental data for $M^+ + CH_4$ reactions have been obtained under the single or near-single collision conditions of ion cyclotron traps and guided ion beam machines. Thermalized ground-state 3d- and 4d-transition-metal ions and the lanthanide ions do not react with methane in single-collision environments.[1,101] Tonkyn et al.[102] measured rate coefficients for the reactions of fourth-row transition metal ions ($Sc^+$ to $Zn^+$) with methane in the multicollision environment of a fast flow reactor at 0.75 Torr of helium buffer gas and found that all these ions except $Mn^+$ react with methane by slow addition. Sequential additions of methane to $Ti^+$, $Fe^+$, $Co^+$, and $Ni^+$ ions under equilibrium conditions have been studied by Bowers and co-workers[103−107] using a high-pressure drift reaction cell with a hybrid double-focusing mass spectrometer,[108] and the sequential $M^+{-}CH_4$ binding energies, i.e., $D_0[(CH_4)_{n-1}M^+{-}CH_4]$, have been determined.[105−107] Despite the significant amount of experimental and theoretical work on $M^+ + CH_4$ reactions in the gas phase, the multicollision chemistry of methane with fifth- and sixth-row transition-metal ions, lanthanide ions, and the main-group atomic cations has not been studied.

Instrumental developments in our laboratory have provided the means to survey trends in chemical kinetics for reactions of thermalized ground-state atomic monocations with neutral molecules in multicollision environments with helium buffer gas. We have surveyed reactions of bare atomic ions with $O_2$, NO, $N_2O$, $CO_2$, $CS_2$, $D_2O$, $C_6H_6$, $C_6F_6$, and $CH_3F$ molecules,[109−117] and here we report reactions of 59 atomic monocations with $CH_4$. The metal monocations ($M^+$) were all generated in an inductively-coupled plasma (ICP) source and reacted with $CH_4$

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at room temperature in 0.35 Torr of helium using a selected-ion flow tube (SIFT) tandem mass spectrometer.

## 2. Experimental Procedures

The experimental results reported here were obtained using the selected-ion flow tube (SIFT) tandem mass spectrometer described in detail elsewhere.[118,119] This instrument was recently modified to accept ions generated in an inductively coupled plasma (ICP) torch through an atmosphere/vacuum interface. The ICP ion source and interface have also been described previously.[120,121] Solutions containing the metal salt of interest with concentration of ~5 $\mu$g L$^{-1}$ were peristaltically pumped via a nebulizer into the plasma. The nebulizer flow was adjusted to maximize the ion signal detected downstream of the flow tube. The sample solutions were prepared using atomic spectroscopy standard solutions commercially available, and the final concentrations were varied between 5 and 20 ppm to achieve suitable intensity of the resultant ion beam. A stabilizing agent was usually added to each solution in order to prevent precipitation: KOH for base-stabilized salts, $HNO_3$ or HCl for acid-stabilized salts.

Atomic ions emerge from the ICP at a nominal ion temperature of 5500 K with the corresponding Boltzmann distributions. The electronic state populations at this temperature have been calculated previously[111] from available optical spectra.[122,123] After extraction from the ICP, the plasma ions may experience electronic-state relaxations via both radiative decay and collisional energy transfer. The latter may occur by collisions with argon, as the extracted plasma cools upon sampling, and with helium in the flow tube (~4 × 10$^5$ collisions with helium) prior to the reaction region. However, the exact extent of electronic relaxation is uncertain. Clues to the presence of excited electronic states of the atomic ions in the reaction region can be found in the product ions observed and in the shape of the semilogarithmic decay of the reacting atomic ion upon addition of neutral reactants. Curvature will appear in the measured atomic-ion decay when the ground state and excited state react at different rates even when they give the same product ions. An excited-state effect cannot be seen when the products and reaction rates are the same for both the ground and excited states, but in this case the measured atomic-ion decay defines the ground-state kinetics. There were no indications of excited-state effects in our previous measurements of reactions of atomic cations derived from the same ICP source with $N_2O$ except for $Pt^+$.[111] The many collisions experienced by the atomic cations with the quite polarizable argon atoms as they emerge from the ICP and the ~4 × 10$^5$ collisions with helium atoms in the flow tube (the helium buffer gas pressure was 0.35 ± 0.01 Torr) appear to be sufficient to thermalize the excited states and to ensure that the atomic ions reach a translational temperature equal to the tube temperature of 295 ± 2 K prior to entering the reaction region.

Reactions of $CH_4$ with 59 atomic ions, fourth-row cations from $K^+$ to $Se^+$, fifth-row cations from $Rb^+$ to $Te^+$ (excluding $Tc^+$), sixth-row cations from $Cs^+$ to $Bi^+$, and lanthanide cations from $La^+$ to $Lu^+$ (excluding $Pm^+$) were investigated at a helium buffer gas pressure of 0.35 ± 0.01 Torr and temperature of 295 ± 2 K. The methane gas was obtained commercially and introduced into the reaction region of the SIFT either as pure $CH_4$ or as a dilute (15%) mixture in helium. Reaction rate coefficients were determined in the usual manner using pseudo-first-order kinetics.[118,119] The rate coefficients for the primary and consecutive reactions reported herein have an estimated absolute accuracy of ±30%.[124] Both the primary and higher-order reactions were monitored. The helium buffer gas pressure was not variable over enough of a range to provide definitive measures of the pressure dependence of the rate coefficient for methane addition.

## 3. Results and Discussion

The primary reactions exhibit a wide range in reactivity with measured rate coefficients in the range from $<10^{-13}$ to $9.8 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ but with only the two channels indicated in reaction 1.

$$M^+ + CH_4 \rightarrow MCH_2^+ + H_2 \tag{1a}$$

$$\rightarrow M^+(CH_4) \tag{1b}$$

The ionization energy of methane[125] is relatively high, IE($CH_4$) = 12.61 ± 0.01 eV, and the electron transfer reaction is significantly endothermic for all the atomic ions studied here. Of the 59 atomic ions investigated, 7 ions reacted with methane through the bimolecular channel 1a. Molecular $H_2$ elimination, channel 1a, was observed with $As^+$, $Nb^+$, $Ta^+$, $W^+$, $Os^+$, $Ir^+$, and $Pt^+$ ions. Most transition-metal cations (all except $Mn^+$ and $Re^+$), two main-group cations, $Ge^+$ and $Se^+$, and three lanthanide cations, $La^+$, $Ce^+$, and $Gd^+$, reacted with $CH_4$ by slow addition, channel 1b, with effective bimolecular rate coefficients $k \leq 3 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. The addition reaction is assumed to occur in a termolecular fashion with helium atoms acting as the stabilizing third body. No attempt was made to measure the pressure dependence of channel 1b, since a large range in pressure was not experimentally accessible. Most main-group cations (all except $Ge^+$, $As^+$, and $Se^+$) and most lanthanide cations (all except $La^+$, $Ce^+$, and $Gd^+$) did not react with methane at all. No products were observed and the effective bimolecular rate coefficients was estimated to have a value $k < 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$.

For many transition metal ions, the addition of a second $CH_4$ molecule, reaction 2, was also observed.

$$M^+(CH_4) + CH_4 \rightarrow M^+(CH_4)_2 \tag{2}$$

Rate coefficients for the secondary $CH_4$ addition were always higher than those for the corresponding primary additions. Reactions of a few metal ions with methane involved sequential $H_2$ elimination; reactions 3 and 4 were observed exclusively for M = Ta, W, and Ir, and reaction 5 occurred exclusively for $TaC_3H_6^+$ and $WC_3H_6^+$ ions.

$$MCH_2^+ + CH_4 \rightarrow MC_2H_4^+ + H_2 \tag{3}$$

$$MC_2H_4^+ + CH_4 \rightarrow MC_3H_6^+ + H_2 \tag{4}$$

$$MC_3H_6^+ + CH_4 \rightarrow MC_4H_8^+ + H_2 \tag{5}$$

With the exception of $AsCH_2^+$, all product ions of reactions 1a, 3, 4, and 5 reacted further with $CH_4$ by addition; up to two methane molecules were observed to add sequentially.

$$MC_mH_{2m}^+ + nCH_4 \rightarrow MC_mH_{2m}^+(CH_4)_n \quad n = 1 \text{ or } 2 \tag{6}$$

Table 1 summarizes the primary reaction rate coefficients, reaction efficiencies, and higher-order product ions for the atomic ions studied in this work. The reaction efficiency is taken to be equal to the ratio $k/k_c$ where $k$ is the experimentally measured rate coefficient and $k_c$ is the capture or collision rate coefficient. The $k_c$ values for primary reactions were computed using the algorithm of the modified variational transition-state/classical trajectory theory developed by Su and Chesnavich[126] with a polarizability $\alpha(CH_4) = 2.593$ Å$^3$ [127] and zero dipole

**TABLE 1: Rate Coefficients (*k* in Units of cm$^3$ molecule$^{-1}$ s$^{-1}$),[a] Reaction Efficiencies ($k/k_c$), Primary Products, and Higher-Order Product Ions Measured for Reactions of Atomic Ions M$^+$ with Methane in Helium at 0.35 ± 0.01 Torr and 295 ± 2 K[b]**

| $M^+$ | $k$ | $k/k_c$ | primary products | branching ratio (%) | higher-order product ions |
|---|---|---|---|---|---|
| $K^+$ | $<10^{-13}$ | $<10^{-4}$ | | | |
| $Ca^+$ | $<10^{-13}$ | $<10^{-4}$ | | | |
| $Sc^+$ | $1 \times 10^{-13}$ | 0.0001 | $Sc^+(CH_4)$ | 100 | $Sc^+(CH_4)_2$ |
| $Ti^+$ | $4 \times 10^{-13}$ | 0.0004 | $Ti^+(CH_4)$ | 100 | $Ti^+(CH_4)_2$ |
| $V^+$ | $8 \times 10^{-13}$ | 0.0008 | $V^+(CH_4)$ | 100 | $V^+(CH_4)_2$ |
| $Cr^+$ | $2 \times 10^{-13}$ | 0.0002 | $Cr^+(CH_4)$ | 100 | $Cr^+(CH_4)_2$ |
| $Mn^+$ | $<10^{-13}$ | $<10^{-4}$ | | | |
| $Fe^+$ | $4 \times 10^{-13}$ | 0.0004 | $Fe^+(CH_4)$ | 100 | $Fe^+(CH_4)_2$ |
| $Co^+$ | $3.2 \times 10^{-12}$ | 0.0030 | $Co^+(CH_4)$ | 100 | $Co^+(CH_4)_2$ |
| $Ni^+$ | $3.4 \times 10^{-12}$ | 0.0032 | $Ni^+(CH_4)$ | 100 | $Ni^+(CH_4)_2$ |
| $Cu^+$ | $2.8 \times 10^{-12}$ | 0.0026 | $Cu^+(CH_4)$ | 100 | $Cu^+(CH_4)_2$ |
| $Zn^+$ | $1 \times 10^{-13}$ | 0.0001 | $Zn^+(CH_4)$ | 100 | |
| $Ga^+$ | $<10^{-13}$ | $<10^{-4}$ | | | |
| $Ge^+$ | $2 \times 10^{-13}$ | 0.0002 | $Ge^+(CH_4)$ | 100 | |
| $As^+$ | $4.8 \times 10^{-10}$ | 0.46 | $AsCH_2^+$ | 100 | |
| $Se^+$ | $1.5 \times 10^{-11}$ | 0.015 | $Se^+(CH_4)$ | 100 | |
| $Rb^+$ | $<10^{-13}$ | $<10^{-4}$ | | | |
| $Sr^+$ | $<10^{-13}$ | $<10^{-4}$ | | | |
| $Y^+$ | $4 \times 10^{-13}$ | 0.0004 | $Y^+(CH_4)$ | 100 | $Y^+(CH_4)_2$ |
| $Zr^+$ | $3.0 \times 10^{-11}$ | 0.030 | $Zr^+(CH_4)$ | 100 | $Zr^+(CH_4)_2$ |
| $Nb^+$ | $4.0 \times 10^{-12}$ | 0.0040 | $Nb^+(CH_4)$ | 25 | $Nb^+(CH_4)_2$ |
| | | | $NbCH_2^+$ | 75 | $NbCH_2^+(CH_4)_{0-2}$ |
| $Mo^+$ | $4 \times 10^{-13}$ | 0.0004 | $Mo^+(CH_4)$ | 100 | $Mo^+(CH_4)_2$ |
| $Ru^+$ | $4 \times 10^{-13}$ | 0.0004 | $Ru^+(CH_4)$ | 100 | $Ru^+(CH_4)_2$ |
| $Rh^+$ | $7 \times 10^{-13}$ | 0.0007 | $Rh^+(CH_4)$ | 100 | $Rh^+(CH_4)_2$ |
| $Pd^+$ | $7 \times 10^{-13}$ | 0.0007 | $Pd^+(CH_4)$ | 100 | $Pd^+(CH_4)_2$ |
| $Ag^+$ | $2 \times 10^{-13}$ | 0.0002 | $Ag^+(CH_4)$ | 100 | $Ag^+(CH_4)_2$ |
| $Cd^+$ | $<10^{-13}$ | $<10^{-4}$ | $Cd^+(CH_4)$ | 100 | |
| $In^+$ | $<10^{-13}$ | $<10^{-4}$ | | | |
| $Sn^+$ | $<10^{-13}$ | $<10^{-4}$ | | | |
| $Sb^+$ | $<10^{-13}$ | $<10^{-4}$ | | | |
| $Te^+$ | $<10^{-13}$ | $<10^{-4}$ | | | |
| $Cs^+$ | $<10^{-13}$ | $<10^{-4}$ | | | |
| $Ba^+$ | $<10^{-13}$ | $<10^{-4}$ | | | |
| $La^+$ | $1 \times 10^{-13}$ | 0.0001 | $La^+(CH_4)$ | 100 | $La^+(CH_4)_2$ |
| $Hf^+$ | $2 \times 10^{-13}$ | 0.0002 | $Hf^+(CH_4)$ | 100 | $Hf^+(CH_4)_2$ |
| $Ta^+$ | $3.8 \times 10^{-10}$ | 0.39 | $TaCH_2^+$ | 100 | $TaCH_2^+(CH_4)_{0-2}$<br>$TaC_2H_4^+(CH_4)_{0-2}$<br>$TaC_3H_6^+(CH_4)_{0-2}$<br>$TaC_4H_8^+(CH_4)_{0-1}$ |
| $W^+$ | $2.6 \times 10^{-10}$ | 0.27 | $W^+(CH_4)$ | 25 | $W^+(CH_4)_2$ |
| | | | $WCH_2^+$ | 75 | $WCH_2^+(CH_4)_{0-2}$<br>$WC_2H_4^+(CH_4)_{0-2}$<br>$WC_3H_6^+(CH_4)_{0-2}$<br>$WC_4H_8^+(CH_4)_{0-1}$ |
| $Re^+$ | $<10^{-13}$ | $<10^{-4}$ | | | |
| $Os^+$ | $9.2 \times 10^{-10}$ | 0.94 | $OsCH_2^+$ | 100 | $OsCH_2^+(CH_4)$ |
| $Ir^+$ | $9.8 \times 10^{-10}$ | 1.0 | $IrCH_2^+$ | 100 | $IrCH_2^+(CH_4)_{0-1}$<br>$IrC_2H_4^+(CH_4)_{0-1}$<br>$IrC_3H_6^+(CH_4)_{0-1}$ |
| $Pt^+$ | $4.9 \times 10^{-10}$ | 0.50 | $PtCH_2^+$ | 100 | $PtCH_2^+(CH_4)$ |
| $Au^+$ | $1.2 \times 10^{-11}$ | 0.012 | $Au^+(CH_4)$ | 100 | $Au^+(CH_4)_2$ |
| $Hg^+$ | $2 \times 10^{-13}$ | 0.0002 | $Hg^+(CH_4)$ | 100 | |
| $Tl^+$ | $<10^{-13}$ | $<10^{-4}$ | | | |
| $Pb^+$ | $<10^{-13}$ | $<10^{-4}$ | | | |
| $Bi^+$ | $<10^{-13}$ | $<10^{-4}$ | | | |
| $Ce^+$ | $1 \times 10^{-13}$ | 0.0001 | $Ce^+(CH_4)$ | 100 | $Ce^+(CH_4)_2$ |
| $Pr^+$ | $<10^{-13}$ | $<10^{-4}$ | | | |
| $Nd^+$ | $<10^{-13}$ | $<10^{-4}$ | | | |
| $Sm^+$ | $<10^{-13}$ | $<10^{-4}$ | | | |
| $Eu^+$ | $<10^{-13}$ | $<10^{-4}$ | | | |
| $Gd^+$ | $1 \times 10^{-13}$ | 0.0001 | $Gd^+(CH_4)$ | 100 | $Gd^+(CH_4)$ |
| $Tb^+$ | $<10^{-13}$ | $<10^{-4}$ | | | |
| $Dy^+$ | $<10^{-13}$ | $<10^{-4}$ | | | |
| $Ho^+$ | $<10^{-13}$ | $<10^{-4}$ | | | |
| $Er^+$ | $<10^{-13}$ | $<10^{-4}$ | | | |
| $Tm^+$ | $<10^{-13}$ | $<10^{-4}$ | | | |
| $Yb^+$ | $<10^{-13}$ | $<10^{-4}$ | | | |
| $Lu^+$ | $<10^{-13}$ | $<10^{-4}$ | | | |

[a] Measured effective bimolecular rate coefficient for the loss of the metal ion, with an estimated accuracy of ±30%. [b] Branching ratios are included as percentages, with an estimated accuracy of ±5%.

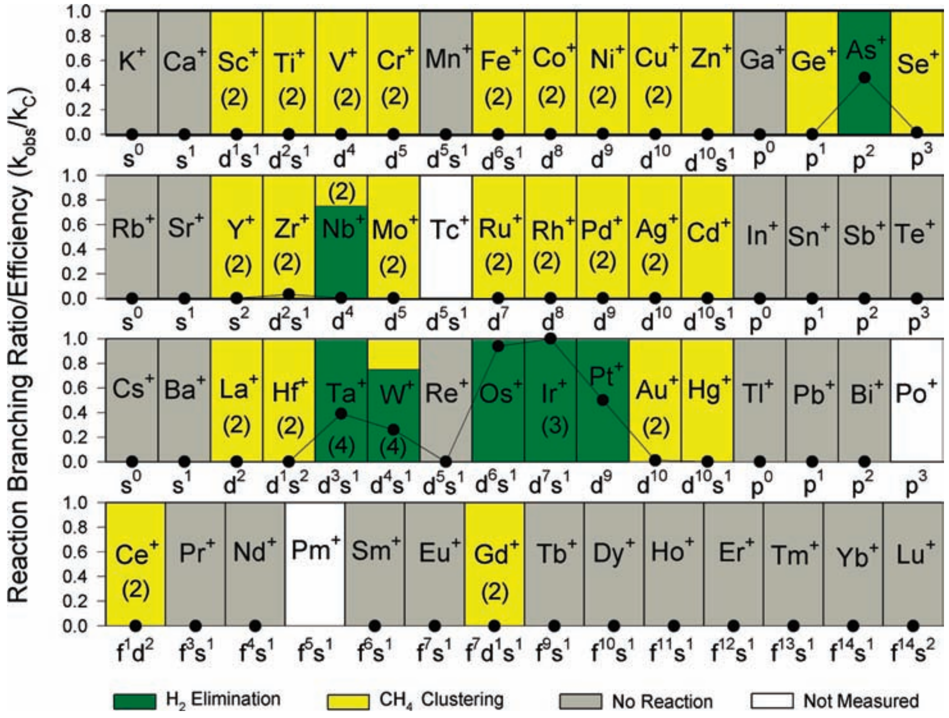

**Figure 1.** Periodic variations observed in the reaction efficiency ($k/k_c$), represented by solid circles, for the reactions of ground state atomic cations with $CH_4$. The numbers in parentheses indicate the number of sequential color-coded reactions observed. Reactions of $Tc^+$, $Pm^+$, and $Po^+$ were not investigated.

moment. The resulting $k_c$ values for the reactions of atomic ions with $CH_4$ varied from $1.1 \times 10^{-9}$ ($K^+$) to $9.8 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ ($Bi^+$).

Figure 1 displays the results of Table 1 on a periodic table, and Figures 2, 3, and 4 display the kinetics data obtained for selected ions of the fourth, fifth, and sixth rows of the periodic table, respectively. We found no experimental evidence for the presence of excited-state atomic ions in the primary atomic-ion decays (Figures 2−4); most $M^+$ decays are linear across the range of ion intensities spanning at least 1 order of magnitude.

**3.1. Fourth-Row Atomic Ions.** Both primary reaction channels were observed for the fourth-row atomic ions. Efficient $H_2$ elimination, channel 1a, was observed only for the main group ion $As^+$ with a $k/k_c$ value of 0.46. All transition-metal ions in this row except $Mn^+$ react slowly by $CH_4$ addition, channel 1b. Methane addition was also observed for the $Ge^+$ and $Se^+$ ions; the reaction efficiencies ($k/k_c$) of $CH_4$ additions varied from $1 \times 10^{-4}$ ($Sc^+$) to $1.5 \times 10^{-2}$ ($Se^+$). The main group ions $K^+$, $Ca^+$, and $Ga^+$ did not react with methane. Secondary $CH_4$ addition, reaction 2, was observed only for $Sc^+$, $Ti^+$, $V^+$, $Cr^+$, $Fe^+$, $Co^+$, $Ni^+$, and $Cu^+$ ions. Figure 2 provides data that exemplify the occurrence of reactions 1 and 2.

**3.2. Fifth-Row Atomic Ions.** All transition metal ions of the fifth row (excluding $Tc^+$) reacted with methane slowly and formed the $M^+(CH_4)$ adducts. The reaction efficiencies of methane addition varied from $<10^{-4}$ ($Cd^+$) to 0.030 ($Zr^+$). Secondary $CH_4$ addition, reaction 2, was observed only for $Y^+$, $Zr^+$, $Nb^+$, $Mo^+$, $Ru^+$, $Rh^+$, $Pd^+$, and $Ag^+$ ions. The only metal cation in the fifth row that reacted with methane through both primary channels 1a and 1b was $Nb^+$, and the branching ratios for $NbCH_2^+$ and $Nb^+(CH_4)$ products were 75% and 25%, respectively. However, the overall efficiency for the reaction of $Nb^+$ with $CH_4$ is very small ($k/k_c = 0.0040$), because the bimolecular $H_2$ elimination reaction to form $NbCH_2^+$ is endothermic[8] by 9 ± 2 kcal mol$^{-1}$. Two methane molecules were observed to add sequentially to the $NbCH_2^+$ primary product, reaction 6, to form $NbCH_2^+(CH_4)_2$ as the major final product. No reaction was observed between methane and the main-group cations of the fifth row. Figure 3 displays the kinetics data obtained for selected ions of the fifth row.

**3.3. Sixth-Row Atomic Ions.** Both primary reaction channels were observed for the sixth-row atomic ions. Efficient $H_2$ elimination, channel 1a, was observed only for $Ta^+$, $W^+$, $Os^+$, $Ir^+$, and $Pt^+$ ions, with $k/k_c$ values of 0.39, 0.27, 0.94, 1.0, and 0.50, respectively. The transition-metal ions $Hf^+$, $Au^+$, and $Hg^+$ and the lanthanide ions $La^+$, $Ce^+$, and $Gd^+$ reacted slowly by $CH_4$ addition, channel 1b; the reaction efficiencies ($k/k_c$) of methane additions varied from $1 \times 10^{-4}$ ($La^+$, $Ce^+$, and $Gd^+$) to $1.2 \times 10^{-2}$ ($Au^+$). Secondary $CH_4$ addition, reaction 2, was observed only for the $Hf^+$, $Au^+$, $La^+$, $Ce^+$, and $Gd^+$ ions. The only metal cation in the sixth row that reacted with methane through both primary channels 1a and 1b was the $W^+$ ion; the branching ratios for $WCH_2^+$ and $W^+(CH_4)$ products were 75% and 25%, respectively. The middle transition-metal ion $Re^+$, all main-group ions of the sixth row, and most lanthanide ions (all except $La^+$, $Ce^+$ and $Gd^+$) did not react with methane.

The primary products $OsCH_2^+$ and $PtCH_2^+$ reacted further with methane exclusively by addition, reaction 6, to form $OsCH_2^+(CH_4)$ and $PtCH_2^+(CH_4)$ secondary products. Secondary and higher-order $H_2$ elimination occurred only for the $TaCH_2^+$, $WCH_2^+$, and $IrCH_2^+$ products according to reactions 3, 4, and 5. The products of $H_2$ elimination reactions, $TaC_mH_{2m}^+$ ($m = 1-4$), $WC_mH_{2m}^+$ ($m = 1-4$), and $IrC_mH_{2m}^+$ ($m = 1-3$), also reacted to some extent by $CH_4$ clustering, reaction 6, to produce various $[MC_mH_{2m}^+(CH_4)_n]$ ions with $m = 1-4$ and $n = 1-2$.

**3.4. Hydrogen Elimination Reactions.** Numerous quantum calculations and collision-induced-dissociation (CID) experiments provide strong evidence that reaction 1a follows the insertion−elimination mechanism involving four stages: (1) formation of an electrostatically bound complex $M^+(CH_4)$; (2) insertion of $M^+$ into a C−H bond to form $H-M-CH_3^+$; (3)

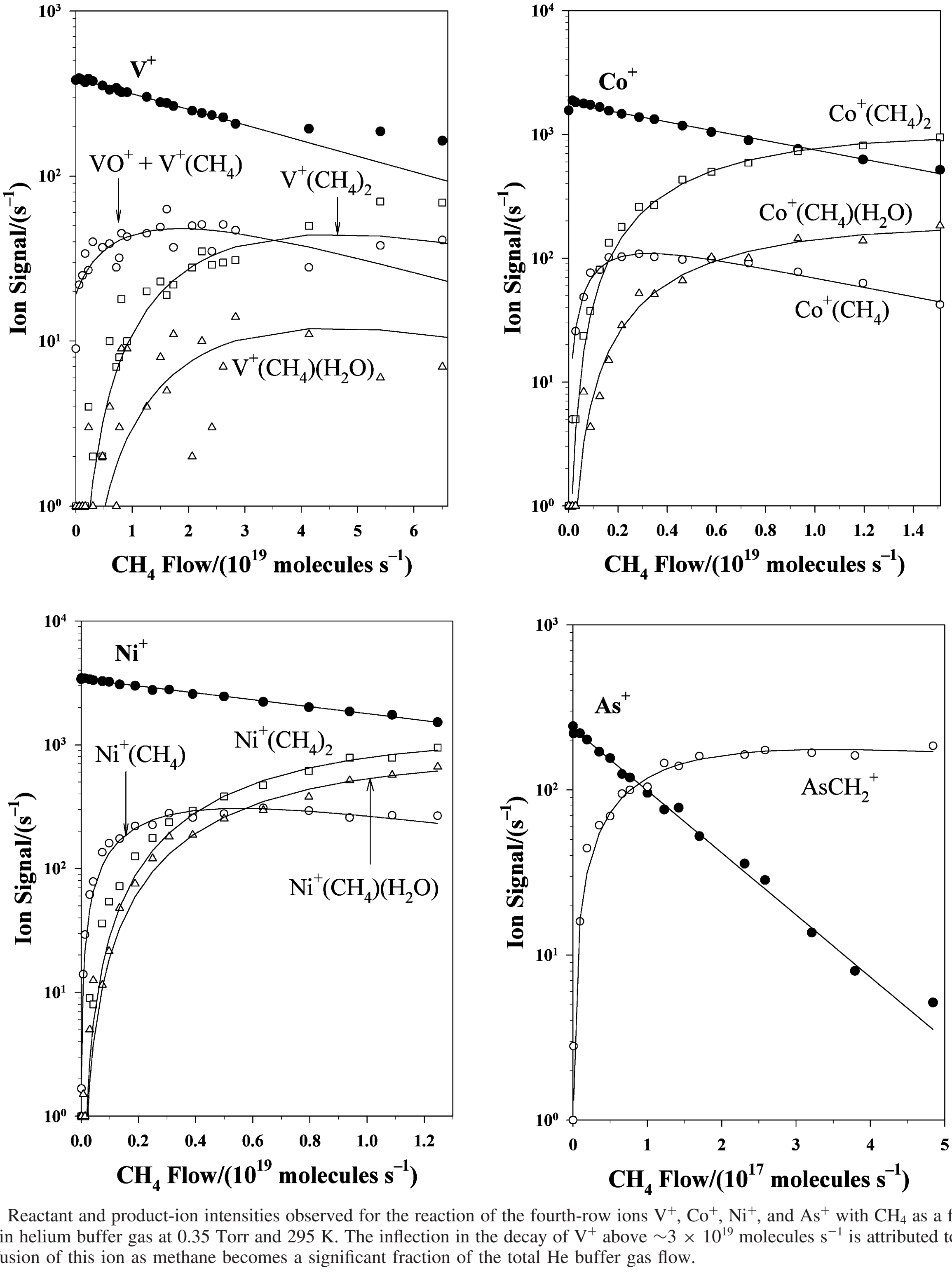

**Figure 2.** Reactant and product-ion intensities observed for the reaction of the fourth-row ions $V^+$, $Co^+$, $Ni^+$, and $As^+$ with $CH_4$ as a function of $CH_4$ flow in helium buffer gas at 0.35 Torr and 295 K. The inflection in the decay of $V^+$ above ~3 × $10^{19}$ molecules $s^{-1}$ is attributed to a change in the diffusion of this ion as methane becomes a significant fraction of the total He buffer gas flow.

formation of a four centered intermediate $(H-M—CH_2-H)^+$ or α-H migration to form a $(H_2-M{=}CH_2)^+$ intermediate; (4) $H_2$ elimination.

Elimination of molecular $H_2$ from $CH_4$ is endothermic[7] by 111 kcal $mol^{-1}$. The primary reaction 1a is thus endothermic for most of the atomic ions for which $D_0[M^+-CH_2]$ values are known (see Table 2). Molecular $H_2$ elimination was observed with $As^+$, $Nb^+$, $Ta^+$, $W^+$, $Os^+$, $Ir^+$, and $Pt^+$ ions. With the exception of $Nb^+$, the rate coefficients measured for $H_2$ elimination reactions were relatively large ($k/k_c > 0.2$). As indicated in Table 2, reaction 1a is slightly exothermic or thermoneutral for the sixth-row metal ions $Ta^+$, $W^+$, $Os^+$, $Ir^+$, and $Pt^+$. The very low reaction efficiency of $Nb^+$ ($k/k_c < 0.005$) is due to its endothermicity; reaction 1a is endothermic by 9 ± 2 kcal $mol^{-1}$ for the $Nb^+$ ion. The reaction of $As^+$ with $CH_4$ to produce $AsCH_2^+$ has been reported previously,[128] but no thermodynamic or kinetic data are available. The observed reaction efficiency of $k/k_c = 0.46$ indicates that reaction 1a is exothermic or thermoneutral for the $As^+$ ion. Figure 5 shows the variation of reaction efficiency with carbene affinity, $D[M^+-CH_2]$, of the metal ions. Most ions for which $D_0[M^+-CH_2] < 111$ kcal $mol^{-1}$ react with methane by slow

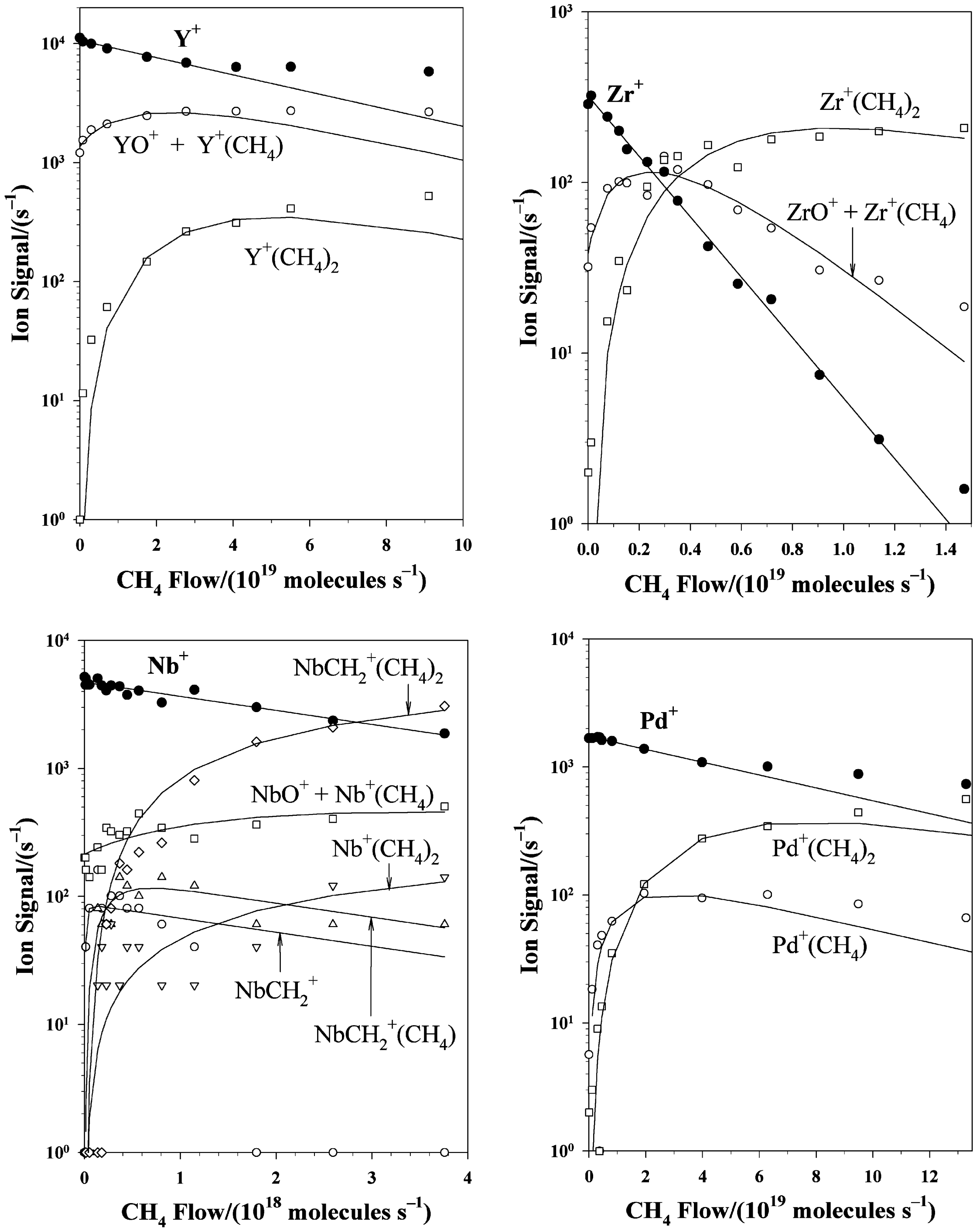

**Figure 3.** Reactant and product-ion intensities observed for the reaction of the fifth-row ions $Y^+$, $Zr^+$, $Nb^+$, and $Pd^+$ with $CH_4$ as a function of $CH_4$ flow in helium buffer gas at 0.35 Torr and 295 K. The inflections in the decays of $Y^+$ and $Pd^+$ above ~3 × $10^{19}$ molecules $s^{-1}$ is attributed to a change in the diffusion of this ion as methane becomes a significant fraction of the total He buffer gas flow.

addition; the only metal ions that react through both channels 1a and 1b are $Nb^+$ and $W^+$.

For electron spin to be conserved in $H_2$ elimination reactions with methane where ground-state products are formed, the spin multiplicities of $M^+$ and $MCH_2^+$ must be the same according to the Wigner−Witmer spin conservation rules because the ground states of $CH_4(^1A_1)$ and $H_2(^1\Sigma_g)$ are both singlets.[129] The formation of ground-state products $NbCH_2^+(^3B_2)$, $TaCH_2^+(^3A_2)$, $WCH_2^+(^4A'')$, $OsCH_2^+(^4A_2)$, and $IrCH_2^+(^3A_2)$ from the ground-state metal ions $Nb^+(^5D)$, $Ta^+(^5F)$, $W^+(^6D)$, $Os^+(^6D)$, and $Ir^+(^5F)$ are all spin-forbidden, whereas the reaction of ground-state $Pt^+(^2D)$ ions to produce the ground-state $PtCH_2^+(^2A_1)$ product is spin-allowed. Hydrogen elimination reactions for the sixth-row ions $Ta^+$, $W^+$, $Os^+$, $Ir^+$, and $Pt^+$ are very efficient, and it appears that the effect of spin in the overall reaction rate is insignificant. The spin conservation rules do not apply strictly to the sixth-row atomic ions because of large spin−orbit coupling that results in mixing of electronic states with different spin multiplicities. The effect of spin conservation on the reaction of $As^+(^3P)$ with methane cannot be ascertained because the spin multiplicity of ground-state $AsCH_2^+$ (singlet or triplet) is not known.

The bimolecular reaction rate coefficients (in $cm^3$ molecule$^{-1}$ $s^{-1}$) previously reported for $Ta^+$ $(3.4 \pm 0.9) \times 10^{-10}$

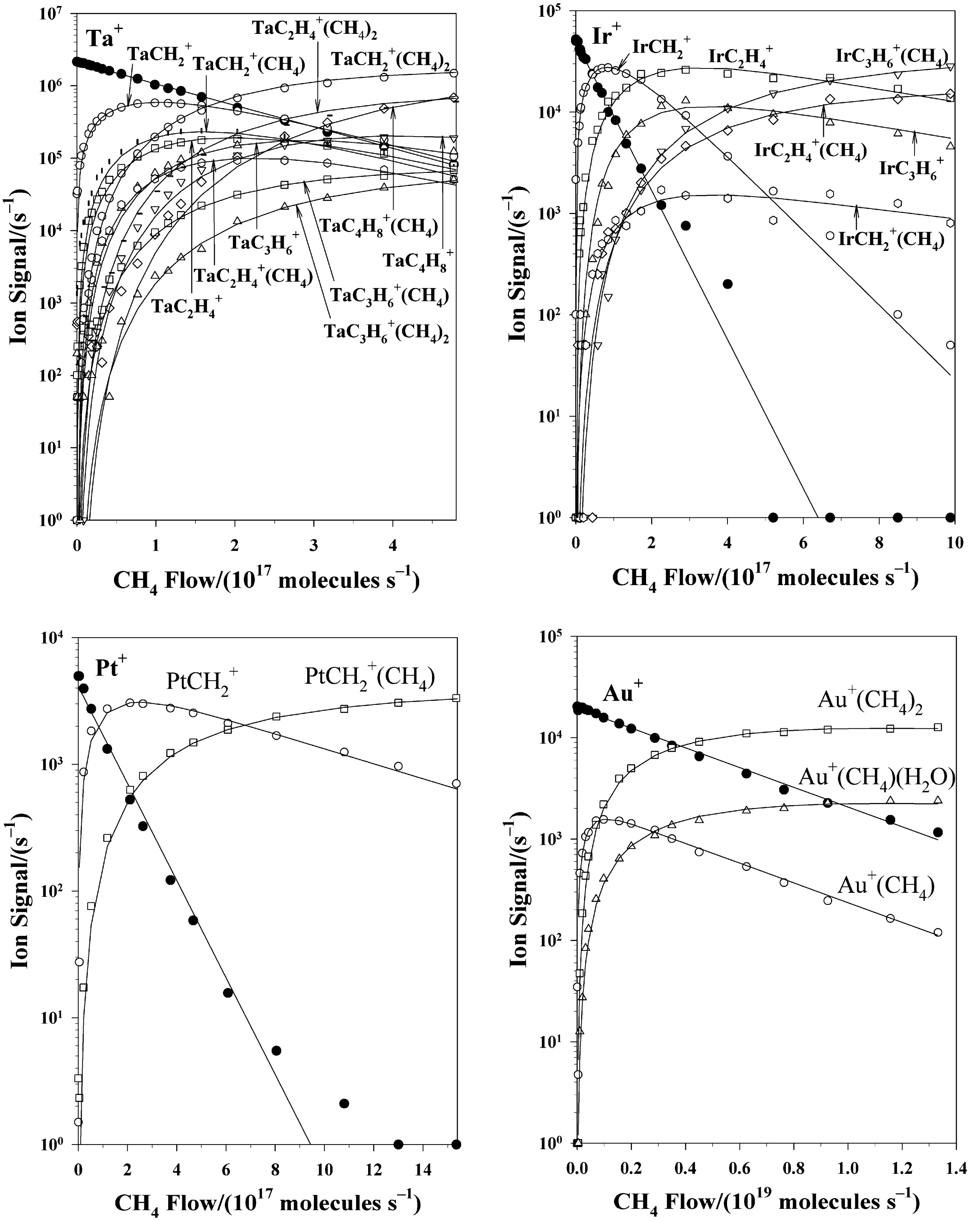

**Figure 4.** Reactant and product-ion intensities observed for the reaction of the sixth-row ions Ta$^+$, Ir$^+$, Pt$^+$, and Au$^+$ with CH$_4$ as a function of CH$_4$ flow in helium buffer gas at 0.35 Torr and 295 K.

(FT-ICR), W$^+$ (1.2 ± 0.3) × $10^{-10}$ (FT-ICR) and (2.0 ± 0.4) × $10^{-10}$ (GIB), Os$^+$ (3.4 ± 0.9) × $10^{-10}$ (FT-ICR), Ir$^+$ (7.0 ± 1.8) × $10^{-10}$ (FT-ICR), and Pt$^+$ (3.9 ± 1.0) × $10^{-10}$ (FT-ICR), 8.2 × $10^{-10}$ (FT-ICR), and (7.6 ± 1.7) × $10^{-10}$ (GIB) are in reasonable agreement with the corresponding values of (3.8 ± 1.1) × $10^{-10}$, (2.6 ± 0.8) × $10^{-10}$, (9.2 ± 2.8) × $10^{-10}$, (9.8 ± 2.9) × $10^{-10}$, and (4.9 ± 1.5) × $10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ reported here for Ta$^+$, W$^+$, Os$^+$, Ir$^+$, and Pt$^+$, respectively. The reason for discrepancies in the rate constants for Os$^+$ and Ir$^+$ ions might be associated with the reaction environment and instrument; in our ICP-SIFT experiment, reactions occur in helium buffer gas at 0.35 ± 0.01 Torr, whereas the corresponding reactions in the FT-ICR experiment occurred in a reaction cell with CH$_4$ pressure at $10^{-6}$−$10^{-8}$ Torr.[5,6]

Secondary and higher-order H$_2$ elimination occurred only for the Ta$^+$, W$^+$, and Ir$^+$ ions. The rate coefficients of reactions 3, 4, and 5 for Ta$^+$ and W$^+$ ions were comparable to those of reaction 1a for the corresponding parent ions. The rate constant of reaction 4 for IrC$_2$H$_4^+$ was smaller than those of reactions 1a and 3 for Ir$^+$ and IrCH$_2^+$ ions, respectively, by an order of magnitude. The structures of MC$_m$H$_{2m}^+$ ions (M = Ta, W, Ir) have been studied previously both by collision-induced-dissociation experiments and by theoretical calculations.[6,27,43,63,64,73]

**TABLE 2: Methylene Affinities, MeA($M^+$),[a] in kcal $mol^{-1}$ for the Fourth-, Fifth-, and Sixth-Row Atomic Cations**

| fourth row | | fifth row | | sixth row | |
|---|---|---|---|---|---|
| $M^+$ | MeA($M^+$)[a] | $M^+$ | MeA($M^+$)[a] | $M^+$ | MeA($M^+$)[a] |
| $Sc^+$ | 96.1 ± 5.5 | $Y^+$ | 92.7 ± 3.1 | $La^+$ | 95.8 ± 1.7 |
| $Ti^+$ | 90.8 ± 2.2 | $Zr^+$ | 106.8 ± 1.0 | $Hf^+$ | 104 ± 5[b] |
| $V^+$ | 77.7 ± 1.4 | $Nb^+$ | 102.3 ± 2.2 | $Ta^+$ | 115 ± 5[b] |
| $Cr^+$ | 51.9 ± 1.0 | $Mo^+$ | 78.6 ± 2.9 | $W^+$ | 109.5 ± 1.4 |
| $Mn^+$ | 68.4 ± 2.2 | $Tc^+$ | 83 ± 5[c] | $Re^+$ | 95.5 ± 1.4[d] |
| $Fe^+$ | 81.5 ± 1.0 | $Ru^+$ | 82.2 ± 1.2 | $Os^+$ | 112.4[e] |
| $Co^+$ | 75.8 ± 1.2 | $Rh^+$ | 85.1 ± 1.9 | $Ir^+$ | 113.5 ± 0.7[f] |
| $Ni^+$ | 73.1 ± 1.0 | $Pd^+$ | 68.1 ± 1.2 | $Pt^+$ | 110.7 ± 0.7 |
| $Cu^+$ | 61.2 ± 1.2 | $Ag^+$ | >25.6 ± 1.0 | $Au^+$ | 88.9 ± 0.7[g] |

[a] MeA($M^+$) = $D_0(M^+{-}CH_2)$ from ref 8. [b] Reference 66. [c] Reference 65. [d] Reference 60. [e] Reference 98. [f] Reference 64. [g] Reference 40.

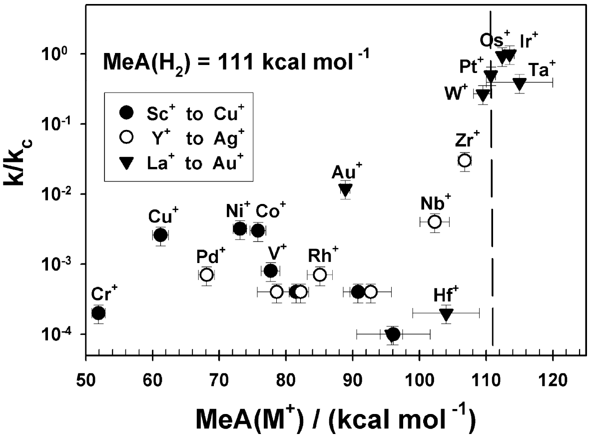

**Figure 5.** Dependence of the reaction efficiency, $k/k_c$, on methylene affinities, MeA($M^+$), of atomic cations. $k$ represents the measured reaction rate coefficient for loss of $M^+$, and $k_c$ is the calculated collision rate coefficient (see Table 1). Reactions on the right of the dashed line are exothermic for hydrogen elimination, while those on the left are endothermic and proceed by the addition of methane.

**3.5. $CH_4$ Addition Reactions.** The addition of methane, channel 1b, was observed exclusively with the main-group ions $Ge^+$ and $Se^+$, the fourth-row transition-metal ions $Sc^+$, $Ti^+$, $V^+$, $Cr^+$, $Fe^+$, $Co^+$, $Ni^+$, $Cu^+$, and $Zn^+$, the fifth-row ions $Y^+$, $Zr^+$, $Nb^+$, $Mo^+$, $Ru^+$, $Rh^+$, $Pd^+$, $Ag^+$, $Cd^+$, the sixth-row transition-metal ions $Hf^+$, $W^+$, $Au^+$, and $Hg^+$, and the lanthanide ions $La^+$, $Ce^+$, and $Gd^+$. All these addition reactions are presumed to be termolecular, reaction 7, with helium atoms (0.35 ± 0.01 Torr) acting as the stabilizing third body rather than by radiative association.

$$M^+ + CH_4 + He \rightarrow M^+(CH_4) + He \qquad (7)$$

The addition reactions were observed to proceed relatively slowly, but the effective bimolecular rate coefficients varied by more than 2 orders of magnitude. The metal ions that react with $CH_4$ by addition, reaction 7, can be grouped according to their effective bimolecular rate coefficients: the first group consists of $Se^+$ ($p^3$), $Zr^+$ ($d^2s^1$), $Au^+$ ($d^{10}$), and $W^+$ ($d^4s^1$) ions for which $k \geq 10^{-11}$ $cm^3$ $molecule^{-1}$ $s^{-1}$. The second one includes $Co^+$, $Ni^+$, $Cu^+$, and $Nb^+$ for which $k \geq 10^{-12}$, and the third group includes the ions for which $k \geq 10^{-13}$, i.e., $Sc^+$, $Ti^+$, $V^+$, $Cr^+$, $Fe^+$, $Zn^+$, $Ge^+$, $Y^+$, $Mo^+$, $Ru^+$, $Rh^+$, $Pd^+$, $Ag^+$, $Cd^+$, $La^+$, $Ce^+$, $Gd^+$, $Hf^+$, and $Hg^+$. Some atomic ions showed no addition of methane. Presumably the range in magnitude of the effective bimolecular rate coefficient for these addition reactions reflects a dependence on the nature of the bonding in the product cluster ion, since the degrees of freedom are the same for all systems and the lifetime of the intermediate depends only on its stability as a consequence. At least three geometrical isomers can be envisaged for the methane adduct: the weak electrostatically bound $M^+\cdots CH_4$ and the inserted covalently bound $H{-}M^+{-}CH_3$ and $H_2M^+{=}CH_2$.

The alkali $s^0$ cations $K^+$, $Rb^+$, and $Cs^+$, the alkali earth $s^1$ cations $Ca^+$, $Sr^+$, and $Ba^+$, the group 7 cations $Mn^+$ ($d^5s^1$) and $Re^+$ ($d^5s^1$), and the vast majority of main-group and lanthanide cations, i.e., all except $Ge^+$, $Se^+$, $La^+$, $Ce^+$, and $Gd^+$, did not react with methane even by termolecular addition. Failure to observe $CH_4$ adducts of those ions can be attributed to weak $CH_4{-}M^+$ bonding that decreases the rate of addition and may result in dissociation of $M^+(CH_4)$ clusters upon sampling, because only adducts whose solvation energies are above ~5 kcal $mol^{-1}$ are expected to resist decomposition upon sampling in our SIFT/MS instrument.

Because these additions are assumed to occur in a termolecular fashion, reaction 7, their effective bimolecular rate constants should have a linear dependence on helium pressure (0.35 ± 0.01 Torr in our experiments). The effective bimolecular rate constants for $CH_4$ addition to the fourth-row transition-metal ions ($Sc^+$ to $Zn^+$) have been reported by Tonkyn et al.[102] at 0.75 Torr of helium. Those rate constants are in excellent agreement, i.e., within the uncertainty limits, with the ones reported in Table 1 when the helium pressure ratio (0.35/0.75) is taken into account.

The addition of a second $CH_4$ molecule, reaction 2, was observed for many transition-metal ions. Except for the adducts of group 12 ions, $Zn^+(CH_4)$, $Cd^+(CH_4)$, and $Hg^+(CH_4)$, and those of the main-group ions $Ge^+(CH_4)$ and $Se^+(CH_4)$, all other $M^+(CH_4)$ adducts react further with methane to produce $M^+(CH_4)_2$ cluster ions. We found the rate coefficients for the secondary $CH_4$ additions, reaction 2, to be higher than those for the corresponding primary additions, reaction 1b. This is consistent with the previous report by Tonkyn et al.[102] on methane addition to the fourth-row transition-metal ions. The larger rate coefficients of reaction 2 versus 1b can be attributed to the increased number of vibrational degrees of freedom in the secondary reaction intermediate, which leads to longer lifetimes and thus higher rates of collisional stabilization. Methane addition also was observed with most $[MC_mH_{2m}{}^+]$ ions that were produced by hydrogen elimination, reactions 1a, 3, 4, and 5. For these ions, higher-order addition often competed with higher-order $H_2$ elimination. Up to two $CH_4$ molecules were observed to add to the $[MC_mH_{2m}{}^+]$ ions (see Table 1).

## 4. Conclusions

Reactions of methane with 59 atomic metal cations at room temperature in helium bath gas at 0.35 Torr were studied using an inductively-coupled plasma/selected-ion flow tube (ICP/SIFT) tandem mass spectrometer, and rate coefficients and product branching ratios were measured. A primary $H_2$ elimination channel was observed in the reactions of $CH_4$ with $As^+$, $Nb^+$, $Ta^+$, $W^+$, $Os^+$, $Ir^+$, and $Pt^+$ ions, while secondary and higher-order $H_2$ elimination was observed exclusively for $Ta^+$, $W^+$, and $Ir^+$. All other transition-metal cations except $Mn^+$ and $Re^+$ were observed to react with $CH_4$ exclusively by termolecular addition, and up to two methane molecules were observed to add sequentially to most transition-metal ions. $CH_4$ addition was also observed for $Ge^+$, $Se^+$, $La^+$, $Ce^+$, and $Gd^+$ ions, while the other main-group and lanthanide cations did not react with methane. The rates of $CH_4$ addition reactions did not reveal any obvious periodic trend in reactivities of transition-metal cations.

However, groups of atomic ions were identified with distinct reactivities spanning more than 2 orders of magnitude.

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### References and Notes

(1) Schwarz, H.; Schröder, D. *Pure Appl. Chem.* **2000**, *72*, 2319.

(2) Allison, J.; Freas, R. B.; Ridge, D. P. *J. Am. Chem. Soc.* **1979**, *101*, 1332.

(3) Comisarow, M. B.; Marshall, A. G. *Chem. Phys. Lett.* **1974**, *25*, 282.

(4) Ervin, K. M.; Armentrout, P. B. *J. Chem. Phys.* **1985**, *83*, 166.

(5) Irikura, K. K.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1991**, *113*, 2769.

(6) Irikura, K. K.; Beauchamp, J. L. *J. Phys. Chem.* **1991**, *95*, 8344.

(7) http://webbook.nist.gov/chemistry/.

(8) Armentrout, P. B. *Int. J. Mass Spectrom.* **2003**, *227*, 289.

(9) Armentrout, P. B. *Annu. Rev. Phys. Chem.* **1990**, *41*, 313.

(10) Rodgers, M. T.; Armentrout, P. B. *Mass Spectrom. Rev.* **2000**, *19*, 215.

(11) Schwarz, H. *Angew. Chem., Int. Ed.* **2003**, *42*, 4442.

(12) Schwarz, H. *Int. J. Mass Spectrom.* **2004**, *237*, 75.

(13) Metz, R. B. *Int. Rev. Phys. Chem.* **2004**, *23*, 79.

(14) Armentrout, P. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 784.

(15) Halle, L. F.; Armentrout, P. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 962.

(16) Halle, L. F.; Armentrout, P. B.; Beauchamp, J. L. *Organometallics* **1982**, *1*, 963.

(17) Hanratty, M. A.; Carter, E. A.; Beauchamp, J. L.; Goddard, W. A.; Illies, A. J.; Bowers, M. T. *Chem. Phys. Lett.* **1986**, *123*, 239.

(18) Tolbert, M. A.; Mandich, M. L.; Halle, L. F.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 5675.

(19) Schilling, J. B.; Beauchamp, J. L. *Organometallics* **1988**, *7*, 194.

(20) Irikura, K. K.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1989**, *111*, 75.

(21) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1985**, *107*, 5870.

(22) Hettich, R. L.; Freiser, B. S. *J. Am. Chem. Soc.* **1986**, *108*, 2537.

(23) Hettich, R. L.; Jackson, T. C.; Stanko, E. M.; Freiser, B. S. *J. Am. Chem. Soc.* **1986**, *108*, 5086.

(24) Jackson, T. C.; Carlin, T. J.; Freiser, B. S. *J. Am. Chem. Soc.* **1986**, *108*, 1120.

(25) Hettich, R. L.; Freiser, B. S. *J. Am. Chem. Soc.* **1987**, *109*, 3543.

(26) Forbes, R. A.; Lech, L. M.; Freiser, B. S. *Int. J. Mass Spectrom.* **1987**, *77*, 107.

(27) Buckner, S. W.; Macmahon, T. J.; Byrd, G. D.; Freiser, B. S. *Inorg. Chem.* **1989**, *28*, 3511.

(28) Heinemann, C.; Wesendrup, R.; Schwarz, H. *Chem. Phys. Lett.* **1995**, *239*, 75.

(29) Heinemann, C.; Schwarz, H.; Koch, W.; Dyall, K. G. *J. Chem. Phys.* **1996**, *104*, 4642.

(30) Koszinowski, K.; Schroder, D.; Schwarz, H. *Organometallics* **2003**, *22*, 3809.

(31) Koszinowski, K.; Schröder, D.; Schwarz, H. *J. Am. Chem. Soc.* **2003**, *125*, 3676.

(32) Koszinowski, K.; Schröder, D.; Schwarz, H. *Angew. Chem., Int. Ed.* **2004**, *43*, 121.

(33) Koszinowski, K.; Schlangen, M.; Schroder, D.; Schwarz, H. *Int. J. Mass Spectrom.* **2004**, *237*, 19.

(34) Chowdhury, A. K.; Wilkins, C. L. *J. Am. Chem. Soc.* **1987**, *109*, 5336.

(35) Berg, C.; Schindler, T.; Niednerschatteburg, G.; Bondybey, V. E. *J. Chem. Phys.* **1995**, *102*, 4870.

(36) Albert, G.; Berg, C.; Beyer, M.; Achatz, U.; Joos, S.; Niedner-Schatteburg, G.; Bondybey, V. E. *Chem. Phys. Lett.* **1997**, *268*, 235.

(37) Hayes, T.; Bellert, D.; Buthelezi, T.; Brucat, P. J. *Chem. Phys. Lett.* **1997**, *264*, 220.

(38) Baranov, V.; Becker, H.; Bohme, D. K. *J. Phys. Chem. A* **1997**, *101*, 5137.

(39) Husband, J.; Aguirre, F.; Thompson, C. J.; Laperle, C. M.; Metz, R. B. *J. Phys. Chem. A* **2000**, *104*, 2020.

(40) Aguirre, F.; Husband, J.; Thompson, C. J.; Metz, R. B. *Chem. Phys. Lett.* **2000**, *318*, 466.

(41) Achatz, U.; Berg, C.; Joos, S.; Fox, B. S.; Beyer, M. K.; Niedner-Schatteburg, G.; Bondybey, V. E. *Chem. Phys. Lett.* **2000**, *320*, 53.

(42) Lu, W. Y.; Wong, T. H.; Kleiber, P. D. *Chem. Phys. Lett.* **2001**, *347*, 183.

(43) Simon, A.; MacAleese, L.; Boissel, P.; Maitre, P. *Int. J. Mass Spectrom.* **2002**, *219*, 457.

(44) Aristov, N.; Armentrout, P. B. *J. Phys. Chem.* **1987**, *91*, 6178.

(45) Schultz, R. H.; Elkind, J. L.; Armentrout, P. B. *J. Am. Chem. Soc.* **1988**, *110*, 411.

(46) Sunderlin, L. S.; Armentrout, P. B. *J. Phys. Chem.* **1988**, *92*, 1209.

(47) Georgiadis, R.; Armentrout, P. B. *J. Phys. Chem.* **1988**, *92*, 7067.

(48) Sunderlin, L. S.; Armentrout, P. B. *J. Am. Chem. Soc.* **1989**, *111*, 3845.

(49) Armentrout, P. B.; Sunderlin, L. S.; Fisher, E. R. *Inorg. Chem.* **1989**, *28*, 4436.

(50) Schultz, R. H.; Armentrout, P. B. *J. Phys. Chem.* **1993**, *97*, 596.

(51) Haynes, C. L.; Armentrout, P. B.; Perry, J. K.; Goddard, W. A. *J. Phys. Chem.* **1995**, *99*, 6340.

(52) Haynes, C. L.; Chen, Y. M.; Armentrout, P. B. *J. Phys. Chem.* **1995**, *99*, 9110.

(53) Chen, Y. M.; Armentrout, P. B. *J. Phys. Chem.* **1995**, *99*, 10775.

(54) Haynes, C. L.; Chen, Y. M.; Armentrout, P. B. *J. Phys. Chem.* **1996**, *100*, 111.

(55) Chen, Y. M.; Sievers, M. R.; Armentrout, P. B. *Int. J. Mass Spectrom. Ion Processes* **1997**, *167*, 195.

(56) Sievers, M. R.; Chen, Y. M.; Haynes, C. L.; Armentrout, P. B. *Int. J. Mass Spectrom.* **2000**, *196*, 149.

(57) Zhang, X. G.; Liyanage, R.; Armentrout, P. B. *J. Am. Chem. Soc.* **2001**, *123*, 5563.

(58) Liyanage, R.; Zhang, X. G.; Armentrout, P. B. *J. Chem. Phys.* **2001**, *115*, 9747.

(59) Armentrout, P. B.; Sievers, M. R. *J. Phys. Chem. A* **2003**, *107*, 4396.

(60) Armentrout, M. M.; Li, F. X.; Armentrout, P. B. *J. Phys. Chem. A* **2004**, *108*, 9660.

(61) Liu, F.; Zhang, X. G.; Armentrout, P. B. *Phys. Chem. Chem. Phys.* **2005**, *7*, 1054.

(62) Liu, F. Y.; Zhang, X. G.; Liyanage, R.; Armentrout, P. B. *J. Chem. Phys.* **2004**, *121*, 10976.

(63) Armentrout, P. B.; Shin, S.; Liyanage, R. *J. Phys. Chem. A* **2006**, *110*, 1242.

(64) Li, F. X.; Zhang, X. G.; Armentrout, P. B. *Int. J. Mass Spectrom.* **2006**, *255−256*, 279.

(65) Bauschlicher, C. W.; Partridge, H.; Sheehy, J. A.; Langhoff, S. R.; Rosi, M. *J. Phys. Chem.* **1992**, *96*, 6969.

(66) Irikura, K. K.; Goddard, W. A. *J. Am. Chem. Soc.* **1994**, *116*, 8733.

(67) Blomberg, M. R. A.; Siegbahn, P. E. M.; Svensson, M. *J. Phys. Chem.* **1994**, *98*, 2062.

(68) Heinemann, C.; Hertwig, R. H.; Wesendrup, R.; Koch, W.; Schwarz, H. *J. Am. Chem. Soc.* **1995**, *117*, 495.

(69) Carter, E. A.; Goddard, W. A. *J. Phys. Chem.* **1984**, *88*, 1485.

(70) Carter, E. A.; Goddard, W. A. *J. Am. Chem. Soc.* **1986**, *108*, 2180.

(71) Carter, E. A.; Goddard, W. A. *J. Am. Chem. Soc.* **1986**, *108*, 4746.

(72) Perry, J. K.; Ohanessian, G.; Goddard, W. A. *J. Phys. Chem.* **1993**, *97*, 5238.

(73) Perry, J. K.; Ohanessian, G.; Goddard, W. A. *Organometallics* **1994**, *13*, 1870.

(74) Musaev, D. G.; Koga, N.; Morokuma, K. *J. Phys. Chem.* **1993**, *97*, 4064.

(75) Musaev, D. G.; Morokuma, K.; Koga, N. *J. Chem. Phys.* **1993**, *99*, 7859.

(76) Musaev, D. G.; Morokuma, K. *J. Chem. Phys.* **1994**, *101*, 10697.

(77) Musaev, D. G.; Morokuma, K. *J. Phys. Chem.* **1996**, *100*, 11600.

(78) Abashkin, Y. G.; Burt, S. K.; Russo, N. *J. Phys. Chem. A* **1997**, *101*, 8085.

(79) Russo, N.; Sicilia, E. *J. Am. Chem. Soc.* **2001**, *123*, 2588.

(80) Sicilia, E.; Russo, N. *J. Am. Chem. Soc.* **2002**, *124*, 1471.

(81) Michelini, M. D.; Russo, N.; Sicilia, E. *J. Phys. Chem. A* **2002**, *106*, 8937.

(82) Michelini, M. D.; Sicilia, E.; Russo, N.; Alikhani, M. E.; Silvi, B. *J. Phys. Chem. A* **2003**, *107*, 4862.

(83) Chiodo, S.; Kondakova, O.; Michelini, M. D.; Russo, N.; Sicilia, E.; Irigoras, A.; Ugalde, J. M. *J. Phys. Chem. A* **2004**, *108*, 1069.

(84) Alvaradoswaisgood, A. E.; Allison, J.; Harrison, J. F. *J. Phys. Chem.* **1985**, *89*, 2517.

(85) Alvaradoswaisgood, A. E.; Harrison, J. F. *J. Phys. Chem.* **1988**, *92*, 2757.

(86) Alvardoswaisgood, A. E.; Harrison, J. F. *J. Mol. Struct.: THEOCHEM* **1988**, *169*, 155.

(87) Bauschlicher, C. W.; Partridge, H.; Scuseria, G. E. *J. Chem. Phys.* **1992**, *97*, 7471.

(88) Ricca, A.; Bauschlicher, C. W. *Chem. Phys. Lett.* **1995**, *245*, 150.

(89) Sandig, N.; Koch, W. *Organometallics* **1997**, *16*, 5244.

(90) Ye, S.; Shi, N. H.; Huang, J. H.; Dai, S. S. *Int. J. Quantum Chem.* **1997**, *62*, 23.

(91) Hendrickx, M.; Gong, K.; Vanquickenborne, L. *J. Chem. Phys.* **1997**, *107*, 6299.

(92) Westerberg, J.; Blomberg, M. R. A. *J. Phys. Chem. A* **1998**, *102*, 7303.

(93) Yoshizawa, K.; Suzuki, A.; Yamabe, T. *J. Am. Chem. Soc.* **1999**, *121*, 5266.

(94) Yoshizawa, K. *J. Organomet. Chem.* **2001**, *635*, 100.

(95) Wang, C. J.; Ye, S. *Int. J. Quantum Chem.* **1999**, *75*, 47.

(96) Rakowitz, F.; Marian, C. M.; Schimmelpfennig, B. *Phys. Chem. Chem. Phys.* **2000**, *2*, 2481.

(97) Wang, C. J.; Xu, X.; Cao, Z. J.; Ye, S.; Zhang, Q. *J. Phys. Chem. A* **2003**, *107*, 6681.

(98) Zhang, G. B.; Li, S. H.; Jiang, Y. S. *Organometallics* **2003**, *22*, 3820.

(99) Zhang, D. J.; Liu, C. B.; Bi, S. W.; Yuan, S. L. *Chem.—Eur. J.* **2003**, *9*, 484.

(100) Villaume, S.; Daniel, C.; Strich, A.; Perera, S. A.; Bartlett, R. J. *J. Chem. Phys.* **2005**, *122*, 044313.

(101) Cornehl, H. H.; Heinemann, C.; Schroder, D.; Schwarz, H. *Organometallics* **1995**, *14*, 992.

(102) Tonkyn, R.; Ronan, M.; Weisshaar, J. C. *J. Phys. Chem.* **1988**, *92*, 92.

(103) Kemper, P. R.; Bushnell, J.; Van Koppen, P.; Bowers, M. T. *J. Phys. Chem.* **1993**, *97*, 1810.

(104) Van Koppen, P. A. M.; Kemper, P. R.; Bushnell, J. E.; Bowers, M. T. *J. Am. Chem. Soc.* **1995**, *117*, 2098.

(105) Van Koppen, P. A. M.; Perry, J. K.; Kemper, P. R.; Bushnell, J. E.; Bowers, M. T. *Int. J. Mass Spectrom.* **1999**, *187*, 989.

(106) Zhang, Q.; Kemper, P. R.; Shin, S. K.; Bowers, M. T. *Int. J. Mass Spectrom.* **2001**, *204*, 281.

(107) Zhang, Q.; Kemper, P. R.; Bowers, M. T. *Int. J. Mass Spectrom.* **2001**, *210*, 265.

(108) Kemper, P. R.; Bowers, M. T. *J. Am. Soc. Mass Spectrom.* **1990**, *1*, 197.

(109) Koyanagi, G. K.; Caraiman, D.; Blagojevic, V.; Bohme, D. K. *J. Phys. Chem. A* **2002**, *106*, 4581.

(110) Blagojevic, V.; Flaim, E.; Jarvis, M. J.; Koyanagi, G. K.; Bohme, D. K. *J. Phys. Chem. A* **2005**, *109*, 11224.

(111) Lavrov, V. V.; Blagojevic, V.; Koyanagi, G. K.; Orlova, G.; Bohme, D. K. *J. Phys. Chem. A* **2004**, *108*, 5610.

(112) Koyanagi, G. K.; Bohme, D. K. *J. Phys. Chem. A* **2006**, *110*, 1232.

(113) Cheng, P.; Koyanagi, G. K.; Bohme, D. K. *J. Phys. Chem. A* **2006**, *110*, 2718.

(114) Cheng, P.; Koyanagi, G. K.; Bohme, D. K. *J. Phys. Chem. A* **2007**, *111*, 8561.

(115) Koyanagi, G. K.; Bohme, D. K. *Int. J. Mass Spectrom.* **2003**, *227*, 563.

(116) Caraiman, D.; Koyanagi, G. K.; Bohme, D. K. *J. Phys. Chem. A* **2004**, *108*, 978.

(117) Zhao, X.; Koyanagi, G. K.; Bohme, D. K. *J. Phys. Chem. A* **2006**, *110*, 10607.

(118) Mackay, G. I.; Vlachos, G. D.; Bohme, D. K.; Schiff, H. I. *Int. J. Mass Spectrom. Ion Phys.* **1980**, *36*, 259.

(119) Raksit, A. B.; Bohme, D. K. *Int. J. Mass Spectrom. Ion Processes* **1983**, *55*, 69.

(120) Koyanagi, G. K.; Lavrov, V. V.; Baranov, V.; Bandura, D.; Tanner, S.; McLaren, J. W.; Bohme, D. K. *Int. J. Mass Spectrom.* **2000**, *194*, L1.

(121) Koyanagi, G. K.; Baranov, V. I.; Tanner, S. D.; Bohme, D. K. *J. Anal. At. Spectrom.* **2000**, *15*, 1207.

(122) Moore, C. E. *Atomic Energy Levels As Derived from the Analyses of Optical Spectra*; U.S. National Bureau of Standards: Washington, DC, 1971.

(123) Van Kleef, T. A. M.; Metsch, B. C. *Physica B+C* **1978**, *95*, 251.

(124) Bohme, D. K.; Hemsworth, R. S.; Rundle, H. W.; Schiff, H. I. *J. Chem. Phys.* **1973**, *58*, 3504.

(125) Berkowitz, J.; Greene, J. P.; Cho, H.; Ruscic, B. *J. Chem. Phys.* **1987**, *86*, 674.

(126) Su, T.; Chesnavich, W. J. *J. Chem. Phys.* **1982**, *76*, 5183.

(127) Lide, D. R. *CRC Handbook of Chemistry and Physics*, 88th ed.; CRC Press: Boca Raton, FL, 2007−2008; http://www.hbcpnetbase.com/.

(128) Tanner, S. D.; Baranov, V. I.; Bandura, D. R. *Spectrochim. Acta B* **2002**, *57*, 1361.

(129) Shuler, K. E. *J. Chem. Phys.* **1953**, *21*, 624.

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