

# Experimental and ab Initio Molecular Orbital Studies on Collisions of $\text{CH}_4^+$ and $\text{CH}_5^+$ with Molecular Oxygen: On the Formation of Methane ( $\text{CH}_4^{2+}$ ) and Methonium ( $\text{CH}_5^{2+}$ ) Dications and Stable $\text{CH}_n^-$ Species ( $n = 0-3$ )

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**Abstract:** The ionization energies of  $\text{CH}_4^+$  and  $\text{CH}_5^+$  have been determined in charge-stripping experiments by using oxygen as the collision gas. The data obtained ( $18.9 \pm 0.2$  and  $21.6 \pm 0.2$  eV, respectively) exceed by more than 1 eV previous experimental values. In order to check the validity of the experimental findings and to resolve the discrepancy, we performed a parallel theoretical study of the methane and methonium dications by using high-level ab initio molecular orbital calculations. The theoretical adiabatic ionization energies of the methane and methonium ions are found to be in good agreement with our experimental data. Long-lived excited states of  $\text{CH}_4^+$  and  $\text{CH}_3^+$  were found as products of collisionally activated decomposition of  $\text{CH}_5^+$ .  $\text{CH}_n^-$  species ( $n = 0-3$ ) were detected as the products of double-electron-transfer reactions between  $\text{CH}_5^+$  and  $\text{O}_2$ .

## Introduction

Methane and related ions have been the subject of numerous experimental and theoretical studies.<sup>1</sup> This paper reports the results obtained in collision experiments of 8-keV  $\text{CH}_4^+$  and  $\text{CH}_5^+$  ions with molecular oxygen. The following aspects will be considered: (1) detailed study of the mass-analyzed ion kinetic energy spectrum of  $\text{CH}_5^+$ ; (2) measurement of the energetics of formation and fragmentation of  $\text{CH}_4^{2+}$  and  $\text{CH}_5^{2+}$  dications; (3) dissociative double electron transfer from molecular oxygen to  $\text{CH}_5^+$ .

In order to support the interpretations based on the experimental findings, ab initio molecular orbital calculations, have been performed on  $\text{CH}_4^+$ ,  $\text{CH}_4^{2+}$ ,  $\text{CH}_5^+$ , and  $\text{CH}_5^{2+}$  species. Calculations on the methonium dication ( $\text{CH}_5^{2+}$ ) are unprecedented.

## Experimental Section

The experiments were performed on a ZAB-2F (VG-Analytical) double-focusing instrument of reverse geometry.<sup>2</sup> The  $\text{CH}_5^+$  and  $\text{CH}_4^+$  ions were formed in a chemical ionization source, accelerated through a potential of 8 kV, mass selected, and eventually collided with  $\text{O}_2$  at a pressure of about  $10^{-4}$  torr in a collision cell located close to the  $\beta$ -slit of the instrument. The products resulting from collisions were studied by mass-analyzed ion kinetic energy spectroscopy (MIKES).<sup>3</sup> Charge-stripping peaks were observed by scanning the electric sector with a digital MIKES scan unit (VG-Analytical) around  $E_0/2$ , where  $E_0$  represents the electric sector voltage required for the transmission of singly charged ions. For an accurate measurement of the ionization energy of the ion (denoted as  $Q_{\text{min}}$ ), the energy scale was calibrated by admitting toluene as a reference compound for which  $Q_{\text{min}}$  of 15.7 eV is necessary for the process  $\text{C}_7\text{H}_8^+ \rightarrow \text{C}_7\text{H}_8^{2+}$ .<sup>4</sup>  $Q_{\text{min}}$  values were obtained by extrapolation to the base line of the high-energy side of both the main beam (singly charged ions) and the charge-stripping peaks as recommended by Ast et al.<sup>5-7</sup> to prevent contributions from other possible processes. Great care was taken in the measurement procedure; in particular, the effective voltage of the electric sector was measured with a Fluka 885 AB differential voltmeter (1 ppm voltage dial resolution) as a function of the scan law for each measurement in order to correct for possible drift or linearity deviations in the 5-decade digital scan unit.

## Results and Discussion

The MIKE spectrum obtained for  $\text{CH}_5^+$  ions of 8-keV kinetic energy colliding on  $\text{O}_2$  as the target gas is displayed in Figure 1. Three sections can be distinguished: (a) the main-beam region around  $1.0E_0$ , (b) the region between  $0.7E_0$  and  $0.9E_0$  where signals from collisionally activated dissociation (CAD) appear,

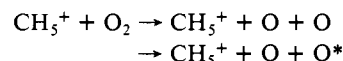
and (c) the  $E_0/2$  region where peaks corresponding to doubly charged species are seen.

**Inelastic Energy Loss Spectrum of  $\text{CH}_5^+$  Ions Scattered from  $\text{O}_2$ .** Figure 2 represents the main-beam region. Two peaks at energies below the unscattered  $\text{CH}_5^+$  ions are observed. Due to the low energy resolution of our instrument, these peaks correspond to unresolved molecular or ionic states of  $\text{O}_2$ . The possible states are indicated on the energy scale by the lower arrows, and their dissociation products are given in the upper line. All the following excitation mechanisms can, in principle, contribute to these signals:

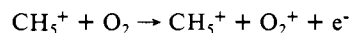
excitation of the target molecule



excitation to a dissociative state



ionization of the target



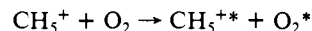
dissociative ionization



excitation of the ion



excitation of both particles



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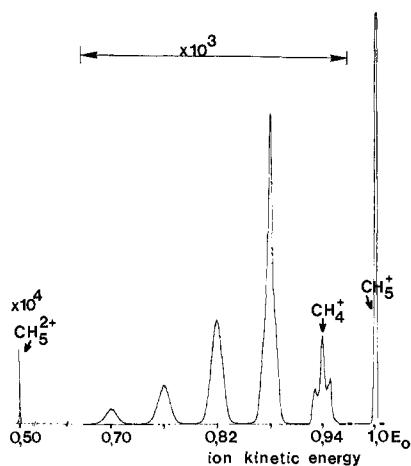
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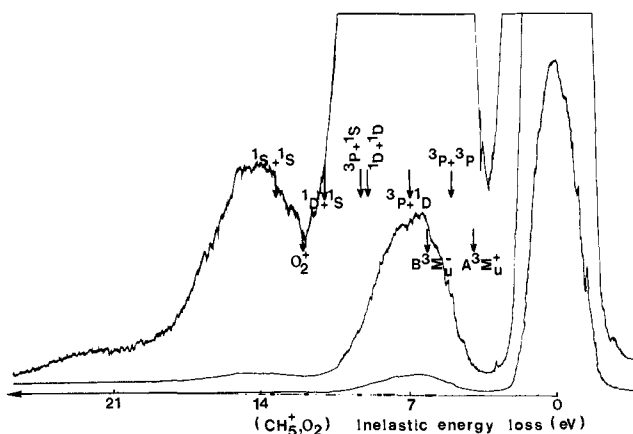
<sup>†</sup> Institut de Chimie Physique.

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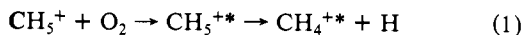
**Figure 1.** Mass-analyzed ion kinetic energy spectrum of  $\text{CH}_5^+$  ions ( $\text{O}_2$  as the collision gas).



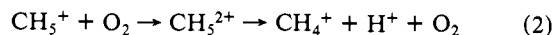
**Figure 2.** Energy loss spectrum of 8-keV  $\text{CH}_5^+$  ions scattered from  $\text{O}_2$ .

**CAD/MIKE Spectrum of  $\text{CH}_5^+$ .** Of special interest are the signals corresponding to the collision-induced formation of  $\text{CH}_4^+$  and  $\text{CH}_3^+$  fragments, which are shown in Figure 3, parts a and b, respectively.

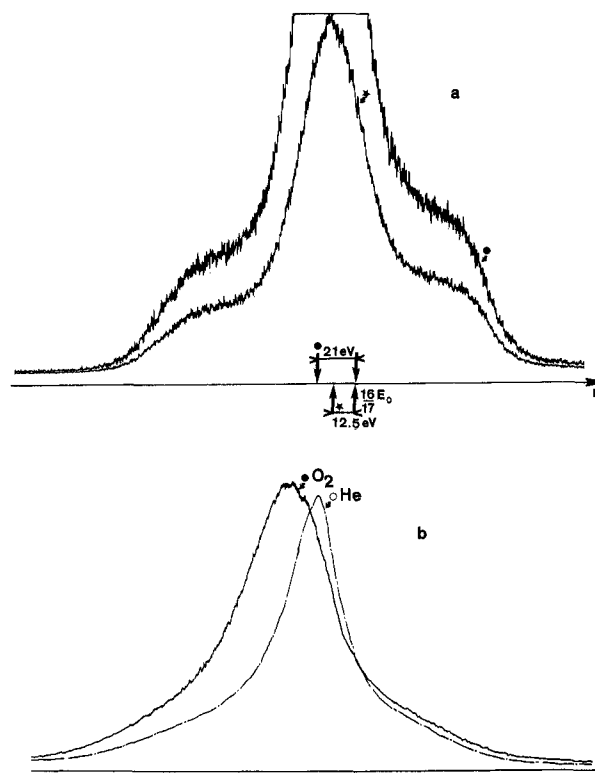
The decomposition process leading to  $\text{CH}_4^+$  daughter ions is reflected by a composite peak (Figure 3a). The reaction  $\text{CH}_5^+ \rightarrow \text{CH}_4^+ + \text{H}$  is endothermic by 4.85 eV; therefore the corresponding peak is expected to lie 4.85 eV below  $16E_0/17$  on the energy scale, where  $E_0$  represents the electric voltage for the transmission of the parent ion. Experimentally, the maximum of the narrow component of the composite signal is found at roughly 13 eV below. This is attributed to a process in which the first excited state of  $\text{CH}_5^+$  (estimated by ab initio calculations to be 12.9 eV above the ground state) is formed in the collision process. Furthermore the small kinetic energy release observed for the central peak indicates that the methane daughter ion is likely to be formed in the  $\tilde{A}^2A_1$  excited state (9.7 eV above the ground state  $\tilde{X}^2T_2$ )<sup>8</sup> via the reaction



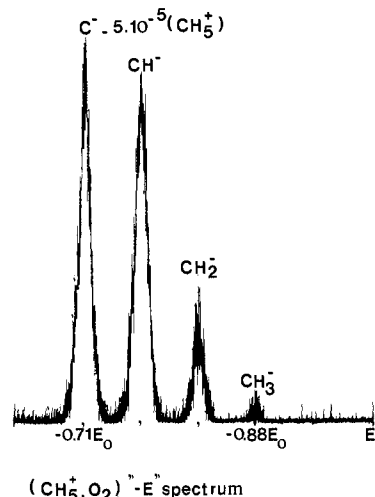
The broad component is measured to be centered around 21 eV below  $16E_0/17$  and corresponds to the following reaction:



The kinetic energy release associated with reaction 2 is found to be 4.7 eV (without any correction of the main-beam contribution). This corresponds to an approximate interchange distance of 3.13 Å for the transition state  $[\text{CH}_4^+ \cdots \text{H}^+]$  of process 2, assuming point charges. This process was earlier observed by Roussel and Julienne<sup>9</sup> in a study of kinetic energy of fragments  $\text{H}^+$ ,  $\text{H}_2^+$ , and  $\text{H}_3^+$



**Figure 3.** (a) Kinetic energy spectrum due to  $\text{CH}_4^+$  ions formed by collision-induced dissociation of  $\text{CH}_5^+$ : ( $\star$ )  $\text{CH}_5^+ + \text{O}_2 \rightarrow \text{CH}_5^{2+} \rightarrow \text{CH}_4^{2+} + \text{H} + \text{O}_2$ ; ( $\bullet$ )  $\text{CH}_5^+ + \text{O}_2 \rightarrow \text{CH}_5^{2+} \rightarrow \text{CH}_4^+ + \text{H} + \text{O}_2$ . (b) Effect of the nature of the collision gas on the peak shape for the formation of  $\text{CH}_3^+$  from  $\text{CH}_5^+$ .



**Figure 4.** Dissociative double-charge-transfer spectrum ( $\text{CH}_5^+$ ,  $\text{O}_2$ ).

from collision-induced dissociation of 40-keV  $\text{CH}_5^+$  ions. They found a sharp maximum in the kinetic energy distribution function near 5 eV, attributed to the dissociation of doubly charged species into singly charged ions caused by coulombic repulsion.

Figure 3b shows the signal corresponding to  $\text{CH}_3^+$  formation with two different collision gases ( $\text{O}_2$  and He). Only the narrow component of the signal is displaced when the collision gas is changed. The distance between the narrow peaks is around 14 eV, reflecting again the formation of electronically excited  $\text{CH}_5^+$  ions when oxygen is used as the collision gas. The width of the narrow component with  $\text{O}_2$  is approximately twice that of the corresponding peak when He is used as the collision gas, showing that part of the excitation energy appears as kinetic energy of the

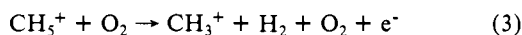
(8) Appell, J. Ph.D. Thesis, Université de Paris-Sud, 1972.

(9) Roussel, M.; Julienne, A. *Int. J. Mass Spectrom. Ion Phys.* **1972**, *9*, 449.

Table I. Influence of the Collision Gas

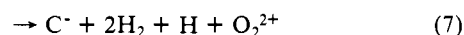
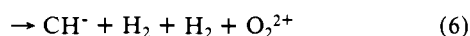
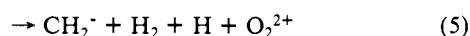
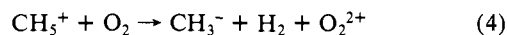
collision gas	ion abundance CH <sub>5</sub> <sup>2+</sup> /CH <sub>5</sub> <sup>+</sup>	collision gas	ion abundance CH <sub>5</sub> <sup>2+</sup> /CH <sub>5</sub> <sup>+</sup>
He	7.3 × 10 <sup>-7</sup>	Kr	4.3 × 10 <sup>-5</sup>
CO <sub>2</sub>	9.6 × 10 <sup>-6</sup>	O <sub>2</sub>	3.4 × 10 <sup>-4</sup>
C <sub>2</sub> H <sub>4</sub>	2.4 × 10 <sup>-5</sup>	NO	3.3 × 10 <sup>-3</sup>

fragments, which can be either the  $\tilde{X}^1A_1'$  ground state of CH<sub>3</sub><sup>+</sup> or the first electronic state  $^3E''$  or  $^1E''$  (6.4 and 7.55 eV above the ground state, respectively).<sup>10</sup> The broad component is due to the reaction



which also occurs upon collision.

**Dissociative Double-Electron-Transfer Reactions.** The formation of negative ions has been observed in collisions of fast positive ions with a target gas.<sup>11,12</sup> Figure 4 shows the spectrum obtained from CH<sub>5</sub><sup>+</sup> ions colliding with O<sub>2</sub> when the polarity of the electric sector voltage is reversed. The following process are observed:



No CH<sub>5</sub><sup>-</sup> stable species was detectable, in line with ab initio calculations by Kutzelnigg and Dyczmons,<sup>13</sup> which predicted CH<sub>5</sub><sup>-</sup> to lie 55 kcal·mol<sup>-1</sup> above CH<sub>4</sub> and H<sup>-</sup>. The kinetic energy loss from the incident CH<sub>5</sub><sup>+</sup> ion, given by the peak position on the energy scale of the products CH<sub>2</sub><sup>-</sup>, CH<sup>-</sup>, and C<sup>-</sup>, corresponds to the activation energies of reactions 5, 6, and 7, respectively. Accurate kinetic energy loss measurements require a careful calibration of the energy scale (see Experimental Section), which unfortunately is not possible on our instrument when the polarity of the electric sector voltage is reversed. Nevertheless the activation energies for reactions 5, 6, and 7 were estimated to be 43.5 ± 2, 46.4 ± 2, and 48.5 ± 2 eV, respectively. If CH<sub>5</sub><sup>-</sup> is initially generated when CH<sub>5</sub><sup>+</sup> collides with O<sub>2</sub>, the minimum energy could be calculated as

$$E_{0_{\min}} \geq \Delta H_f^\circ(CH_5^-) - \Delta H_f^\circ(CH_5^+) + \Delta H_f^\circ(O_2^{2+}) - \Delta H_f^\circ(O_2)$$

The difference between the total SCF energies of CH<sub>5</sub><sup>-</sup> and CH<sub>5</sub><sup>+</sup><sup>34</sup> leads to 6.42 eV for  $\Delta H_f^\circ(CH_5^-) - \Delta H_f^\circ(CH_5^+)$ . The two other terms represent the double ionization energy of molecular oxygen. Depending on the state in which O<sub>2</sub><sup>2+</sup> is formed, the following values can be taken into account: 36.3 ( $\tilde{X}^1\Sigma_g^+$ ), 43 ( $\tilde{B}^3\Pi_g$ ,  $\tilde{B}'^3\Sigma_u^-$ ), or 48 eV ( $\tilde{C}^3\Pi_u$ ).<sup>11</sup> Thus one obtains  $E_{0_{\min}} > 42.7, 49.4, \text{ or } 54.4$  eV, which indicates that only the first possibility fits the experimental data.

**Formation of Methane and Methonium Dications.** Charge-stripping reactions



pioneered by Beynon and co-workers have become the subject of numerous mass spectrometric studies. This technique represents an easily accessible and reliable way to determine double ionization energies of molecules.<sup>5</sup> From the assumptions described in ref 5 and 6, the minimum translational energy loss for reaction 8, denoted as  $Q_{\min}$ , is considered to be the difference between the double and single ionization energies of M:  $Q_{\min} = IE(M^+ \rightarrow$

$M^{2+}) = IE(M^+) - IE(M)$ . Values of  $Q_{\min}$  for CH<sub>4</sub><sup>+</sup> and CH<sub>5</sub><sup>+</sup> were reported by Beynon et al.<sup>14-16</sup> as 17.9 and 20.3 eV, respectively.

**Influence of the Experimental Conditions.** Table I contains the ratio of the intensities of the doubly charged CH<sub>5</sub><sup>2+</sup> ions to those of the unscattered CH<sub>5</sub><sup>+</sup> parent ions for different collision gases at the same pressure (10<sup>-4</sup> torr). It is seen that the most commonly used collision gas (He) is the least efficient one for producing stable doubly charged species. Most efficient is NO for the generation of CH<sub>5</sub><sup>2+</sup>, followed by O<sub>2</sub>. In spite of the fact that oxygen was found to be the most efficient gas for promoting the reaction C<sub>7</sub>H<sub>8</sub><sup>+</sup> → C<sub>7</sub>H<sub>8</sub><sup>2+</sup>, it was not employed in the previous charge-stripping study on CH<sub>4</sub><sup>+</sup> and CH<sub>5</sub><sup>+</sup><sup>6</sup> because of its detrimental effects on the instrument. Since NO is even worse, we decided to use oxygen only after having installed an extra 470 L/s diffusion pump in the electron multiplier section in order to maintain high-sensitivity conditions. The high efficiency of NO and O<sub>2</sub> for charge stripping seems to be due to their paramagnetic nature, which is known to favor electron-exchange reactions.<sup>17,18</sup> Indeed, by using oxygen as the collision gas, we were able to generate stable dications such as C<sub>2</sub>H<sub>6</sub><sup>2+</sup>, HCOH<sup>2+</sup>, and CH<sub>3</sub>X<sup>2+</sup> (X = F, Cl),<sup>19-21</sup> which were thought by other laboratories to be inaccessible by charge-stripping reactions. We also worked at the maximum available accelerating voltage (8 kV on our instrument), conditions where the doubly charged ion yield is at a maximum (2.5 times higher than at 5 kV).

**Experimental Ionization Energies of CH<sub>5</sub><sup>+</sup> and CH<sub>4</sub><sup>+</sup> Ions.** The ionization energy of CH<sub>5</sub><sup>+</sup> was measured by the minimum loss of translational energy at the onset of the charge-stripping peak. A value of 21.6 ± 0.2 eV has been obtained, which differs significantly from previous data (20.3 ± 0.3 eV) reported by Beynon et al.<sup>15</sup> In the same experiment, CH<sub>4</sub><sup>+</sup> ions were mass selected and a value of 18.9 eV was measured for  $Q_{\min}$ . Again, a significantly larger  $Q_{\min}$  value (~1 eV) is obtained when compared with previous measurements.<sup>14</sup> A possible explanation for these apparent discrepancies could be attributed to the experimental conditions: We used oxygen as the collision gas for ions of 8-keV kinetic energy, while nitrogen and 5-keV ions were used in the other laboratory.<sup>5</sup> The probability for charge-stripping ground-state ions is higher in our experimental conditions, and the lower  $Q_{\min}$  values obtained by Beynon et al. could result from reactions of monocations in excited states. In order to test the validity of our experimental results we performed ab initio molecular orbital calculations on methane and methonium mono- and dications.

**Ab Initio Calculations on Methane and Methonium Mono- and Dications: Theoretical Ionization Energies of CH<sub>4</sub><sup>+</sup> and CH<sub>5</sub><sup>+</sup>.** The methane mono-<sup>22,23</sup> and dications<sup>24-28</sup> were studied by ab initio molecular orbital theory and by the MINDO/3 method.<sup>29</sup> Protonated methane has been investigated by a number of authors,<sup>13,30-37</sup> while the dication CH<sub>5</sub><sup>2+</sup> has not been studied at all.

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**Table II.** Calculated Energies, Geometries, and Adiabatic Ionization Energies of CH<sub>4</sub>, CH<sub>4</sub><sup>+</sup>, and CH<sub>4</sub><sup>2+</sup><sup>a</sup>

	CH <sub>4</sub>	CH <sub>4</sub> <sup>+</sup>	IE <sub>a</sub> <sup>b</sup>	CH <sub>4</sub> <sup>2+</sup>	IE <sub>a</sub> <sup>c</sup>	IE <sub>a</sub> <sup>d</sup>
6-31G*	-40.19517	-39.74792 <sup>e</sup>	12.2	-39.04694	31.2	19.1
		-39.75044 <sup>f</sup>	12.1			19.1
6-31G*//CI	-40.35095	-39.89781 <sup>e</sup>	12.3	-39.17844	31.9	19.6
6-31G**	-40.20171	-39.75733 <sup>e</sup>	12.1	-39.05821	31.1	19.0
		-39.76035 <sup>f</sup>	12.0			19.1
6-31G**//CI	-40.39382	-39.92697	12.7	-39.20379	32.4	19.7
<i>r</i> (C-H)	1.084	1.111 <sup>e,g</sup>		1.167		
		1.111 <sup>f,g</sup>				
∠HCH	109.47	140.3 <sup>e,g</sup>		90		
		139.9 <sup>f,g</sup>				

<sup>a</sup>Total energies are given in hartrees, ionization energies in electronvolts, bond lengths in angstroms, and angles in degrees. <sup>b</sup>IE<sub>a</sub> = E<sub>tot</sub>(CH<sub>4</sub><sup>+</sup>) - E<sub>tot</sub>(CH<sub>4</sub>). <sup>c</sup>IE<sub>a</sub>' = E<sub>tot</sub>(CH<sub>4</sub><sup>2+</sup>) - E<sub>tot</sub>(CH<sub>4</sub>). <sup>d</sup>IE<sub>a</sub>'' = E<sub>tot</sub>(CH<sub>4</sub><sup>2+</sup>) - E<sub>tot</sub>(CH<sub>4</sub><sup>+</sup>) = Q<sub>min</sub>. <sup>e</sup>Doublet states calculated with the RHF method. <sup>f</sup>Geometry reported by Meyer<sup>23</sup>: *r*(C-H) = 1.117 Å, ∠HCH = 140.8°. <sup>g</sup>Geometry reported by Siegbahn<sup>27</sup>: *r*(C-H) = 1.183 Å.

**Table III.** Total Energies and Relative Energies of Different Geometries of CH<sub>5</sub><sup>2+</sup> (UHF Calculations)<sup>a</sup>

CH <sub>5</sub> <sup>2+</sup>	6-31G*			6-31G**		
	E <sub>tot</sub>	E <sub>rel</sub>	E <sub>rel</sub> <sup>b</sup>	E <sub>tot</sub>	E <sub>rel</sub>	E <sub>rel</sub> <sup>b</sup>
C <sub>s</sub> (1)	-39.61248	0.00	0.00	-39.63444	0.00	0.00
C <sub>s</sub> (2)	-39.61330	-0.52	0.04	-39.63419	0.16	0.04
C <sub>2v</sub>	-39.60667	3.65	3.82	-39.62595	5.33	3.43
C <sub>4v</sub>	-39.60361	5.57	7.22	-39.61792	10.37	8.11
D <sub>3h</sub>	-39.56643 <sup>c</sup>	28.90	13.10	-39.58360 <sup>c</sup>	31.90	16.23

<sup>a</sup>Total energies in hartrees and relative energies in kcal·mol<sup>-1</sup>. <sup>b</sup>E<sub>rel</sub> for CH<sub>5</sub><sup>2+</sup> taken from ref 36. <sup>c</sup>RHF calculations because the UHF calculations are affected by an important spin dispersion.

The ab initio calculations on CH<sub>5</sub><sup>2+</sup> dications were performed with the Monstergauss program<sup>38</sup> on the CYBER 170-855 at the Swiss Federal Institute of Technology. These calculations were completed in the following way:<sup>39</sup> (a) The algorithm of Davidson<sup>40</sup> was used for geometry optimization. (b) The geometry optimizations were performed at the 6-31G\* level<sup>41</sup> and improved energies even obtained by single-point calculations of these geometries were executed at the 6-31G\*\*<sup>41</sup> level. (c) For doublet states, the unrestricted Hartree-Fock method (UHF) was employed. It cannot be used with our program for configuration interaction. Thus doublet states were calculated with the spin-restricted Hartree-Fock (RHF) method. (d) The evaluation of the electronic correlation energy was obtained by the "direct configuration interaction" method described by Schaefer et al.<sup>42</sup> (all single and double excitations were included in our calculations).

**Methane Mono- and Dications.** In order to test the algorithms used in our computation technique, we first calculated the ionization

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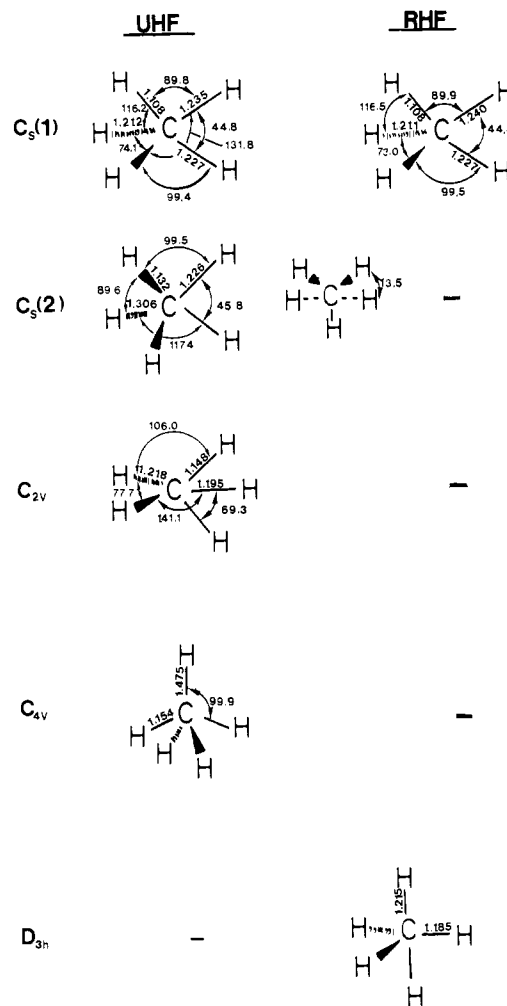
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**Figure 5.** CH<sub>5</sub><sup>2+</sup> structures optimized at the 6-31G\* level: bond lengths in angstroms and bond angles in degrees.**Table IV.** Calculated Total Energies of CH<sub>5</sub><sup>+</sup> and CH<sub>5</sub><sup>2+</sup> and Adiabatic (IE<sub>a</sub>) and Vertical Ionization (IE<sub>v</sub>) Energies of CH<sub>5</sub><sup>+</sup><sup>a</sup>

	CH <sub>5</sub> <sup>+</sup>	CH <sub>5</sub> <sup>2+</sup>	CH <sub>5</sub> <sup>2+</sup> <sup>b</sup>	IE <sub>a</sub>	IE <sub>v</sub>
6-31G*	-40.3885	-39.60941 <sup>c</sup>	-39.54027 <sup>c</sup>	21.2	23.1
		-39.61248 <sup>d</sup>	-39.54671 <sup>d</sup>	21.1	22.9
6-31G*//CI <sup>e</sup>	-40.55905	-39.76041 <sup>c</sup>	-39.69423 <sup>c</sup>	21.7	23.5
6-31G**	-40.40611	-39.63116 <sup>c</sup>	-39.56081 <sup>c</sup>	21.1	23.0
		-39.63444 <sup>d</sup>	-39.56761 <sup>d</sup>	21.0	22.8
6-31G**//CI <sup>e</sup>	-40.60012	-39.79553 <sup>c</sup>	-39.72976 <sup>c</sup>	21.9	23.9

<sup>a</sup>Total energies in hartrees and ionization energies in electronvolts.

<sup>b</sup>Total energy of CH<sub>5</sub><sup>2+</sup> having the geometry of CH<sub>5</sub><sup>+</sup> (6-31G\* optimized). <sup>c</sup>Doublet states calculated with the RHF method. <sup>d</sup>Doublet states calculated with the UHF method. <sup>e</sup>Due to internal limitations of the program, the two last virtual orbitals have been eliminated in the CI treatment.

ization energies of methane. Table II summarizes the results obtained for methane mono- and dications. The following structures were investigated: methane (*T<sub>d</sub>* symmetry),<sup>43</sup> methane monocation (*C<sub>2v</sub>* symmetry),<sup>23</sup> and methane dication (*D<sub>4h</sub>* symmetry).<sup>25</sup> Although the geometries of the mono- and dications differ slightly from those obtained by Meyer<sup>23</sup> and Siegbahn,<sup>27</sup> our calculated values for the ionization energies of methane and of its monocation (12.7 and 19.7 eV, respectively) are in excellent agreement with those obtained by Meyer (12.7 eV),<sup>23</sup> by Pople (19.7 eV),<sup>28</sup> and by Siegbahn (19.6 eV).<sup>27</sup> One should also note that UHF and RHF calculations yield geometries, total energies, and ionization energies that are very similar.

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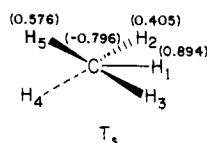
**Table V.** Theoretical and Experimental Ionization Energies of  $\text{CH}_4^+$  and  $\text{CH}_5^+$  Ions (eV)

	theor		Exptl
	$\text{IE}_a$	$\text{IE}_v$	
$\text{CH}_4^+$	19.7 <sup>a</sup>	21.8 <sup>a</sup>	18.9 <sup>e</sup>
	19.8 <sup>b</sup>		17.9 <sup>d</sup>
	19.7 <sup>c</sup>		
$\text{CH}_5^+$	21.9 <sup>a</sup>	23.9 <sup>a</sup>	21.6 <sup>e</sup> 20.3 <sup>d</sup>

<sup>a</sup> This work: 6-31G\*\*/CI. <sup>b</sup> From ref 27, obtained by  $\text{IE}(\text{M} \rightarrow \text{M}^{2+}) - \text{IE}(\text{M} \rightarrow \text{M}^+)$ ; CI plus zero-point energy correction. <sup>c</sup> Taken from ref 28: MP4/6-311G\*\*//6-31G\* plus zero-point energy correction. <sup>d</sup> Taken from ref 14 and 15: 5-keV ions and  $\text{N}_2$ . <sup>e</sup> This work: 8 keV and  $\text{O}_2$ .

**Methonium Mono- and Dications.** The effect of symmetry on the stability of  $\text{CH}_5^+$  is well-known.<sup>36</sup> Our UHF results for the  $\text{CH}_5^{2+}$  dication are given in Table III and Figure 5: the stability ordering obtained for the dication when the 6-31G\*\* basis set is used is the same as that for the monocation, while a reversal of the order for the species with  $C_s(1)$  and  $C_s(2)$  symmetry is seen at the 6-31G\* level. However, the energy difference between these two species remains small and does not significantly influence the ionization energy. For a better estimation of the ionization energy of  $\text{CH}_5^+$ , we included the effects of electron correlation energy in the calculations of the species **1**. The adiabatic ionization energy,  $\text{IE}_a$ , of  $\text{CH}_5^+$  obtained in this way is 21.9 eV while the vertical ionization energy,  $\text{IE}_v$ , is found to be 23.9 eV (see Table IV).

The decomposition process of  $\text{CH}_5^{2+}$  into  $\text{CH}_4^+ + \text{H}^+$  was also studied computationally. A transition state  $T_s$  of  $C_{2v}$  symmetry



(one negative eigenvalue on the force constant matrix) was found to have a total energy of  $-39.57471$  hartrees by doing an UHF calculation with the 6-31G\* basis set. The charges are given in parentheses. The bond lengths in angstroms, are the following: C-H<sub>1</sub>, 2.007; C-H<sub>2</sub>, 1.102; C-H<sub>4</sub>, 1.190. The bond angles in degrees are as follows: H<sub>3</sub>CH<sub>1</sub>, 66.5; H<sub>3</sub>CH<sub>4</sub>, 56.8; H<sub>2</sub>CH<sub>4</sub>, 109.5; H<sub>1</sub>CH<sub>4</sub>, 146.8. The calculated forward activation energy for this process is thus 23.7 kcal·mol<sup>-1</sup>, while the reverse activation energy is computed to be 110.3 kcal·mol<sup>-1</sup>.

**Comparison between Theory and Experiment.** The calculations on  $\text{CH}_4^+$  and  $\text{CH}_4^{2+}$  served mainly to test the RHF and CI methods used on  $\text{CH}_5^{2+}$ . The results allow us to estimate the accuracy to be expected from this level of theory. The experi-

mental adiabatic ionization energy of  $\text{CH}_4$  is known to be 12.6 eV.<sup>44</sup> With the 6-31G\*\* basis set and direct configuration interaction, the theoretical value found is 12.7 eV. Thus one obtains a similar accuracy (0.1 eV) to that obtained by Pople et al.<sup>45</sup> for heats of formation of second-row (Li, Be, etc.) hydrides. Table V lists the calculated and experimental ionization energies of  $\text{CH}_4^+$  and  $\text{CH}_5^+$  ions. Our experimental data agree much better with the theoretical values than the previously reported data of Beynon et al.<sup>14,15</sup> Nevertheless the difference between the calculated and experimental ionization energies of  $\text{CH}_4^+$  (0.8 eV) is much larger than one would expect, the experimental value being less than the theoretical value. The experimental data represent the minimum energy required for the charge-stripping process  $\text{CH}_4^+ + \text{O}_2 \rightarrow \text{CH}_4^{2+} + \text{O}_2 + e^-$  to be carried out and are obtained from the position of the charge-stripping peak onset on the kinetic energy loss spectrum. It represents the  $\text{CH}_4^+$  ions which have lost minimum translational energy to become  $\text{CH}_4^{2+}$  ions. The energetic parameters involved in the charge-stripping process have been described in detail by Ast et al.<sup>6</sup> The only term that can reduce the value of the ionization energy of the ion is its excitation energy. In the particular case of  $\text{CH}_4^+$  ions, for rationalizing the discrepancy between experimental and theoretical data, one has to assume that the maximum internal energy of the  $\text{CH}_4^+$  ions selected from the high-pressure ion source is about 0.8 eV. This value is quite reasonable for  $\text{CH}_4^+$  ions stable at the time scale of the instrument (5  $\mu\text{s}$ ), as the activation energy for the decomposition into  $\text{CH}_3^+ + \text{H}$  is 1.7 eV ( $E_a = \text{AE}(\text{CH}_3^+) - \text{IE}(\text{CH}_4) = 14.4 - 12.7 = 1.7 \text{ eV}^{44}$ ). For  $\text{CH}_5^+$  ions the agreement between theory and experiment is in accordance with the expected errors: for the calculated ionization energy of  $\text{CH}_5^+$  one could expect a larger error than for  $\text{CH}_4^+$  as the formation of the dication involves breaking of an electron pair, which could result in larger correlation errors; the experimental uncertainty is estimated to be 0.2 eV. Finally, a good fit between experimental and calculated data has been obtained for the decomposition process of  $\text{CH}_5^{2+}$  into  $\text{CH}_4^+$  and  $\text{H}^+$ : the measured kinetic energy release, resulting from the Coulombic repulsion of the two charged fragments, is 4.7 eV, while the calculated reverse activation energy is 4.78 eV.

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**Registry No.**  $\text{CH}_5^+$ , 15135-49-6;  $\text{CH}_4^+$ , 20741-88-2;  $\text{CH}_4$ , 74-82-8;  $\text{CH}_4^{2+}$ , 34557-54-5;  $\text{CH}_5^{2+}$ , 97467-20-4.

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