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Doubly Ionized States of CH₄ Studied by Double-charge-transfer and Auger-electron Spectroscopies

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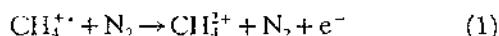
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High-resolution double-charge-transfer spectroscopy has been used to measure the double-ionization energies of CH₄. Using kilo electron volt OH⁺, Cl⁺ and F⁺ projectile ions it is possible in double-electron-capture reactions with CH₄ molecules to populate the ground triplet state of CH₄²⁺. The energy of this state relative to the ground state of CH₄ is found to be 38.2 ± 0.4 eV, while the first excited triplet state is found at a double-ionization energy of 46.7 ± 0.8 eV. In double-electron-capture reactions involving H⁺ projectile ions and CH₄ molecules, low-lying singlet states of CH₄²⁺ are populated. The energies of the four lowest singlet states in CH₄²⁺ were measured to be 39.2 ± 0.4, 40.5 ± 0.4, 42.1 ± 1 and 51.0 ± 1 eV. High-resolution photon-induced Auger-electron spectra of the CH₄ molecule have been recorded. The KLL Auger spectrum shows four distinct structures in the 30–70 eV double-ionization energy range centred at 40.3 ± 0.1, 47.5 ± 0.3, 53.2 ± 0.3 and 60.9 ± 0.3 eV. The previously published data on CH₄²⁺ have been reviewed.

INTRODUCTION AND REVIEW OF PREVIOUS STUDIES ON CH₄²⁺

The first observation of either stable, or metastable, CH₄²⁺ ions in a mass spectrometric study was made by Ast *et al.*¹ in 1981. CH₄²⁺ ions are not formed by either photon- or electron-ionization of CH₄ in a mass spectrometer source with lifetimes long enough (a few μs) for subsequent detection. In a charge-stripping² (CS) study on CH₄²⁺ Ast *et al.*¹ found that CH₄²⁺ ions are formed which have lifetimes of at least 3 μs. In the CS Reaction (1),



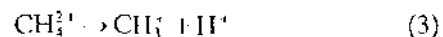
Ast *et al.* measured the translational-energy loss, Q_{\min} , when 5 keV CH₄⁺ ions were converted to CH₄²⁺ ions. Q_{\min} has been shown^{3,4} to be equal to the energy required to convert the projectile monocation into a dication. In this case

$$Q_{\min} = IE(\text{CH}_4^{+*}) \quad (2)$$

where $IE(\text{CH}_4^{+*})$ represents the ionization energy of CH₄⁺. Ast *et al.*¹ and more recently Rabrenovic *et al.*⁵ determined Q_{\min} to be 17.9 ± 0.3 eV. When this value is added to the single-ionization energy of CH₄, ($IE_1(\text{CH}_4)$), a value for the double-ionization energy of CH₄, ($IE_2(\text{CH}_4)$), is obtained. Ast *et al.*¹ took $IE_1(\text{CH}_4)$ to be 12.7 eV and arrived at a value of $IE_2(\text{CH}_4)$ of

30.6 ± 0.3 eV. This result provided a great impetus for further studies both by spectroscopists and theoreticians on the double-ionization energy of CH₄, as it is in conflict with two earlier determinations^{6,7} of $IE_2(\text{CH}_4)$ by Auger-electron⁸ (AE) spectroscopy. Spohr *et al.*⁶ and Rye *et al.*⁷ both determined $IE_2(\text{CH}_4)$ values in excess of 40 eV.

The apparent conflict between the CS data of Ast *et al.*¹ and the AE spectroscopy data both of Spohr *et al.*⁶ and Rye *et al.*⁷ has been explained by Siegbahn.⁹ He performed large basis set multi-configuration self-consistent field (MS SCF) and configuration interaction (CI) calculations on CH₄ and CH₄²⁺. Siegbahn⁹ determined the values of $IE_2(\text{CH}_4)$ for the formation of CH₄²⁺ ions in the ground triplet state to be 36.9 eV at the tetrahedral geometry of CH₄. When the CH₄²⁺ geometry was optimized a value of $IE_2(\text{CH}_4)$ of 35.2 eV was calculated. Further calculations on CH₄²⁺ showed that with a square planar D_{4h} geometry CH₄²⁺ ions have an energy which is 32.2 ± 0.3 eV greater than ground state tetrahedral CH₄, and that the activation energy for the dissociation reaction (3) below, is approximately 1 eV.



CH₄²⁺ ions with this geometry should have a substantial lifetime. The CS value for $IE_2(\text{CH}_4)$ of 30.6 ± 0.3 eV obtained by Ast *et al.*¹ is in moderately good agreement with the calculated value of 32.2 ± 0.3 eV for the formation of square planar D_{4h} CH₄²⁺ ions. The difference can be accounted for, at least in part, if the CH₄²⁺ ions formed in Ast *et al.*¹ experiment were in vibrationally excited states. Ast *et al.*¹ took a value for $IE_1(\text{CH}_4)$ of 12.7 eV, which is the adiabatic single-ionization energy of CH₄. If vibrationally excited CH₄⁺ ions were involved in Reaction (1) then the vertical single-ionization energy of CH₄ which is 14.5 eV¹⁰ should have been used in the determination of $IE_2(\text{CH}_4)$ in Ast *et*

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Table 1. Q_{\min} values^a determined theoretically and experimentally

Theory			Experiment			Reference
Q_{\min}	Method	Geometry of CH ₄ ⁺	Q_{\min}	Ionization method	Collision gas	
19.6	MC SCF	D _{4h}				Siegbahn ⁹
19.7	HF with CI	D _{4h}				Pople <i>et al.</i> ¹⁴
19.7	HF with CI	D _{4h}	18.9 ± 0.2 ^b	Chemical ionization	Oxygen	Stahl <i>et al.</i> ¹¹
21.8	HF with CI	D _{4h}				Nagesha <i>et al.</i> ¹²
			17.9 ± 0.3	Electron impact	Nitrogen	Ast <i>et al.</i> ¹
			17.9 ± 0.3	Electron impact	Nitrogen	Rabrenović <i>et al.</i> ⁵
			26.26 ± 0.25 ^c	Low voltage arc	Air, Krypton, Nitrogen, Methane	Mathur <i>et al.</i> ¹³

^aIn electronvolts.^bCH₄²⁺ ions formed by chemical ionization are expected to be vibrationally cool, nevertheless Stahl *et al.*¹¹ explained the discrepancy between their experimental and theoretical results to be due to the charge stripping of vibrationally excited CH₄²⁺ ions.^cCH₄²⁺ ions should be formed in low vibrational states in a low-voltage arc source.

*al.*¹³ CS work. Thus

$$IE_1(\text{CH}_4) + Q_{\min} = IE_2(\text{CH}_4) \quad (4)$$

$$14.5 \text{ eV} + 17.9 \text{ eV} = 32.4 \text{ eV}$$

The value of $32.4 \pm 0.3 \text{ eV}$ for $IE_2(\text{CH}_4)$ is in excellent agreement with the calculated value⁹ of $32.2 \pm 0.3 \text{ eV}$ for the formation of CH₄²⁺ ions with D_{4h} geometry. Further CS and theoretical studies have subsequently been carried out by Stahl *et al.*¹¹ and by Mathur and co-workers.^{12,13} Their results and those from previous CS and theoretical studies are shown in Table 1. Stahl *et al.*¹¹ in their CS experiment measured Q_{\min} to be $18.9 \pm 0.2 \text{ eV}$, a value 1 eV greater than that measured by Ast *et al.*¹ Stahl *et al.*¹¹ explained this difference by proposing that in the experiments of Ast *et al.*¹ excited CH₄²⁺ ions were charge stripped, resulting in a reduced Q_{\min} value. Such an explanation would appear reasonable as Ast *et al.*¹ generated their CH₄²⁺ ions by electron impact at low CH₄ pressure, while Stahl *et al.*¹¹ generated their CH₄²⁺ ions at high CH₄ pressures in a chemical-ionization source. Stahl *et al.*¹¹ calculated Q_{\min} for the adiabatic transition of CH₄²⁺ ions with C_∞ symmetry to CH₃²⁺ ions with D_{4h} symmetry to be 19.7 eV. Although the geometries of the mono and dication differ from those used by Siegbahn⁹ and by Pople *et al.*¹⁴ the Q_{\min} values are in excellent agreement. Mathur *et al.*¹² in their charge-stripping study formed their CH₄²⁺ ions in a low-voltage arc type source and they measured Q_{\min} to be $26.26 \pm 0.25 \text{ eV}$. This value is very different from those measured by Ast *et al.*¹ Rabrenović *et al.*⁵ and Stahl *et al.*¹¹ In subsequent calculations Mathur and co-workers¹³ determined a Q_{\min} value of 21.8 eV for the vertical conversion of CH₄²⁺ with D_{4d} geometry to CH₃²⁺ ions with a similar geometry. The experimental and computational data of Mathur and co-workers appear to be somewhat out of line with previous studies, as can be seen in Table 1.

The first AE spectrum of CH₄ was recorded by Spohr *et al.*⁶ in 1970. In this experiment an initial hole in the carbon K-shell was created by high-energy electron impact. In the next step the K-shell is filled by a valence electron, and another valence electron is then emitted and its kinetic energy measured. The highest KLL Auger line energy in CH₄ was measured to be $250.0 \pm 0.3 \text{ eV}$. Subtracting this value from the K-shell ionization energy (or binding energy), which is $290.7 \pm 0.7 \text{ eV}$ ⁸ leads to a double-ionization energy for CH₄ of $40.7 \pm 0.8 \text{ eV}$ (Gellius *et al.*¹⁵ have accurately measured the K-shell ionization energy since the earlier study by Siegbahn *et al.*⁸ and determined it to be $290.731 \pm$

0.0015 eV , although the error limits seem rather optimistic). The line width of the highest Auger line was 6 eV and this was interpreted as being consistent with CH₄²⁺ ions being formed in an unstable state. In fact Spohr *et al.*⁶ predicted a lifetime for CH₄²⁺ of less than 10^{-15} s before dissociation via Reaction (3). Siegbahn⁹ explained the difference in double-ionization energy value determined by CS and AE spectroscopies. Stable CH₄²⁺ ions as formed in the CS studies were proposed to have square planar D_{4h} geometries, with much lower energies than those for tetrahedral geometries. The energy difference between the T_d and D_{4h} geometries is much higher, several eV, than the barrier for dissociation in Reaction (3). The Franck-Condon factors between tetrahedral and square-planar geometries should further be very nearly zero, so the D_{4h} structures will not be seen in the AE spectrum. The CH₄²⁺ ions formed in the AE experiment will have the same tetrahedral geometry as neutral CH₄ molecules since the transition is vertical.

The electron-impact induced AE spectrum of CH₄ has also been recorded by Rye *et al.*⁷ They measured the first Auger line to be at a kinetic energy of 248.9 eV, which corresponds to a double-ionization energy of 41.8 eV. The agreement between these values and those of Spohr *et al.*⁶ is only moderate. It should be noted that the first Auger line in the KLL spectrum is broad and the position of its centre may have been incorrectly measured in one of the two studies. Table 2 shows the positions measured by Spohr *et al.*⁶ and by Rye *et al.*⁷ for this and the other lines in the carbon KLL spectra.

Numerous theoretical studies¹⁶⁻²³ have been undertaken in an attempt to interpret the CH₄ AE spectrum. CH₄²⁺ is assumed to have tetrahedral geometry and the energies of the low-lying electronic states have been

Table 2. Carbon KLL Auger line and final state double-ionization^a energies as measured by Spohr *et al.*⁶ and Rye *et al.*⁷

KLL line	Kinetic energy ^b		Double-ionization ^a energy ^b	
	Spohr <i>et al.</i>	Rye <i>et al.</i> ⁷	Spohr <i>et al.</i>	Rye <i>et al.</i>
1	250.0 ± 0.3	248.9	40.7 ± 0.8	41.8
2	243.3 ± 1.5	241.0	47.3 ± 1.7	49.7
3	237.0 ± 1.0	236.2	53.8 ± 1.2	54.5
4	229.4 ± 0.4	229.0	61.3 ± 0.8	61.7

^a Double-ionization energies calculated by subtracting the measured Auger line kinetic energy from the C1s core binding energy of 290.7 eV.⁸^b All energies in electronvolts.^c Error limits not given.

Table 3. Computed energies for the doubly ionized states of CH₄ in tetrahedral geometry relative to the lowest ¹T₂ state.^a The absolute double-ionization energy (eV) for the latter state is shown in parenthesis. The relative positions in the experimental spectrum of Spohr *et al.*⁶ are also shown

Configuration	State	SCF ¹⁶	CI ¹⁷	CI ¹⁸	ADC(2) ¹⁹	Average ²⁰	Spohr ^{6, c}
1t ₂ ⁻²	³ T ₁	-2.98	-2.37	—	-2.08	-2.48	
	¹ E	-1.94	-1.86	-1.54	-1.32	-1.67	
	¹ T ₂	0.00	0.00	0.00	0.00	0.00	0.00
		(39.16)	(39.15)		(38.99)	(39.10)	(40.7)
2a ₁ ⁻¹ , 1t ₂ ⁻¹	¹ A ₁	2.46	2.39	2.37	1.86	2.27	
	³ T ₂	6.67	6.92	6.69	6.74	6.68	6.6
	¹ T ₂	13.08	13.37	12.37	12.40	12.81	13.1
2a ₁ ⁻²	¹ A ₁	21.29	21.48	20.01	20.09	20.72	20.7

^a The energies of the doubly ionized states of CH₄²⁺ are quoted relative to the (1t₂⁻²) ¹T₂ state, whose transition rate in the Auger process is estimated^{18, 21, 22} to dominate over other states derived from the (1t₂⁻²) configuration.

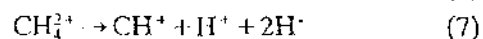
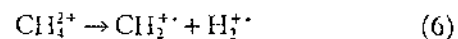
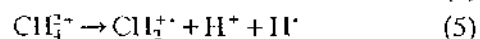
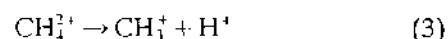
^b Average values from References 16–19.

^c The experimental Auger lines have been assigned¹⁹ as indicated.

calculated and compared to the position of lines in Spohr *et al.*'s⁶ spectrum. Calculations by Ortenburger and Bagus¹⁶ explained the appearance of a peak at a double-ionization energy of 40.7 eV in the AE spectrum as being a result of the formation of CH₄²⁺ ions in four different states, ³T₁, ¹E, ¹T₂ and ¹A₁ of (1a₁)²(2a₁)²(1t₂)⁴ configuration. Peaks at 47.3 and 53.8 eV were interpreted to be a result of the formation of CH₄²⁺ ions in the ³T₂ and ¹T₂ states of configuration (1a₁)²(2a₁)¹(1t₂)⁵ while the peak at 61.3 eV was assigned to the ¹A₁ state of (1a₁)²(2a₁)⁰(1t₂)⁶ configuration. Further calculations have been performed on the CH₄²⁺ ion by Hillier and Kendrick,¹⁷ Kvalheim¹⁸ and Tarantelli *et al.*¹⁹ The results of these calculations are in good agreement with those of Ortenburger and Bagus¹⁶ and are shown in Table 3.

Coincidence techniques have also been used to investigate the double ionization of CH₄. Fournier *et al.*²⁴ have carried out photoion-photoion coincidence (PIPICO) studies using He II light (40.8 eV). Dujardin *et al.*²⁵ have performed PIPICO experiments in Orsay using synchrotron radiation as their light source, while Hatherly *et al.*²⁶ have carried out photoelectron-photoion-photoion coincidence (PEPIPICO) studies in

Daresbury using synchrotron radiation. In the PIPICO study of Fournier *et al.*²⁴ kinetic energy releases (KER) were measured for the fragmentation processes (3), (5), (6) and (7).



By using synchrotron radiation as a light source, Dujardin *et al.*²⁵ and Hatherly *et al.*²⁶ were able to determine the onset for a particular fragmentation process. The results from these coincidence studies have been interpreted in terms of the calculated electronic states in CH₄²⁺ as is shown in Table 4. Dujardin *et al.*²⁵ found that the Franck-Condon factors for excitation to the ³T₁ state are spread over a wide energy range, and determined a vertical double-ionization energy of 37.15 eV. The fragmentation threshold at 38.5 eV was interpreted as being close to the vertical threshold for the ¹E state, which thus has a narrow Franck-Condon energy region of the potential energy surface. Hatherly *et al.*²⁶ observed the fragmentation

Table 4. Results from coincidence studies on the double photoionization of CH₄

Reaction	Products	Kinetic energy release ^a	Fragmentation threshold ^b	Proposed fragmenting state	Reference
(3)	CH ₃ ⁺ + H ⁺	6 ± 0.4	33.9 ± 0.4 ^b 35.0 ± 0.4 ^c (37.15 ± 0.1) ^d 36.5 ± 0.5 ^e	³ T ₁ ³ T ₁ ¹ E	Fournier <i>et al.</i> ²⁴ Dujardin <i>et al.</i> ²⁵ Hatherly <i>et al.</i> ²⁶
(5)	CH ₂ ⁺ + H ⁺	5.1 ± 0.4	38.4 ± 0.4 ^b 38.5 ± 0.1 ^c 38.1 ± 0.6 ^e	¹ E/ ³ T ₂ / ¹ A ₁ ¹ E ¹ T ₂	Fournier <i>et al.</i> ²⁴ Dujardin <i>et al.</i> ²⁵ Hatherly <i>et al.</i> ²⁶
(6)	CH ₃ ⁺ + H ₂ ⁺	5.1 ± 0.4	38.4 ± 0.4 ^b 38.1 ± 0.6 ^c	¹ E/ ¹ T ₂ / ¹ A ₁ ¹ T ₂	Fournier <i>et al.</i> ²⁴ Hatherly <i>et al.</i> ²⁶
(7)	CH ⁺ + H ⁺		41.1 ± 1.0	¹ A ₁	Hatherly <i>et al.</i> ²⁶
(8)	C ²⁺ + H ⁺		44.8 ± 1.5	³ T ₂	Hatherly <i>et al.</i> ²⁶

^a All energies in electronvolts.

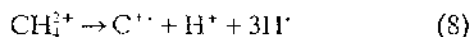
^b Obtained by adding the KER value to the thermodynamic threshold²¹ for formation of ground state products. Recent work by Eland and Murphy²⁸ suggests that the KER values are approximately 10% too low.

^c Fragmentation threshold measured using synchrotron radiation in Orsay.

^d Vertical double ionization energy.

^e Fragmentation threshold measured using synchrotron radiation in Daresbury.

processes (3), (5)–(7) and also an additional process (8) in which CH₄²⁺ is completely stripped of hydrogen substituents



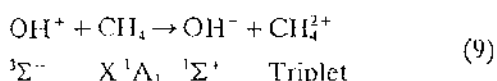
PIPICO and PEPICO studies necessarily involve unstable CH₄²⁺ ions, while CS studies involve stable CH₄²⁺ ions. In AE and double-charge-transfer (DCT)²⁹ spectroscopies the electronic states of CH₄²⁺ can be investigated, whether such states are stable or dissociative.

Appell *et al.*³⁰ performed the first DCT spectroscopy study on CH₄. The principle of DCT spectroscopy is to measure the translational-energy change when keV projectile ions undergo charge-inversion reactions in collisions with the gas molecules under study, in this case CH₄ molecules.

Appell *et al.*³⁰ used 4 keV H⁺ projectile ions in their DCT study. They observed a broad peak which maximized at an *IE*₂ value of 38.9 ± 0.5 eV. More recently Fournier *et al.*²⁴ have performed similar experiments using a high-resolution instrument. They observed a broad peak having a full width at half maximum (FWHM) of 4 eV, starting at around an *IE*₂ value of 35 eV and maximizing at 38.6 ± 0.3 eV.

Double electron capture (DEC) reactions involving keV H⁺ projectile ions and small molecules are known to involve vertical transitions^{29,31} and obey the spin conservation rule.^{29,32} Fournier *et al.*²⁴ interpreted their peak at an *IE*₂ of 38.6 eV to be a result of the formation of CH₄²⁺ ions in the three singlet states of configuration (1a₁)²(2a₁)²(1t₂)⁴ i.e., ¹E, ¹T₂, ¹A₁ which they could not resolve in their experiment. The DCT spectrum of CH₄ recorded by Fournier *et al.*²⁴ has the same shape as the AE spectrum recorded by Spohr *et al.*⁶ but the peak in the DCT spectrum is shifted by 2.1 eV to lower energy. Fournier *et al.*²⁴ proposed two explanations for this difference. The first was that there is a calibration error in the AE spectrum, the second and the more likely explanation is to be found when the Auger process is considered more closely. In the AE experiments the doubly charged ion is reached from a 1s hole state of the singly charged ion. It is known from ESCA studies by Gelius *et al.*¹⁵ that the bond distances in this state are shorter than in neutral CH₄, so the Auger transitions to CH₄²⁺ will occur at correspondingly higher energies. Nevertheless the discrepancy of 2.1 eV between the values from DCT and AE spectroscopies for *IE*₂(CH₄) of the (1t₂)³ group of states does appear somewhat large and a different explanation may be more appropriate. Rye *et al.*⁷ also recorded the AE spectrum of CH₄ and their first peak is shifted by 3.2 eV from that in Fournier *et al.*'s²⁴ DCT spectrum.

Further DCT studies on CH₄ have been carried out by Griffiths *et al.*³³ and by Reid.³⁴ Griffiths *et al.*³³ used 6 keV OH⁺ projectile ions in their work. Kilo electron-volt OH⁺ projectile ions will obey the spin conservation rule in DEC reactions.^{35–37} As OH⁺ projectile ions were generated mainly in their ³Σ state and as neutral CH₄ molecules exist in a single state, X¹A₁, CH₄²⁺ ions will be formed in triplet states in the DEC reaction (9) as the OH⁺ ions are formed in the ¹Σ⁺ state.



Griffiths *et al.*³³ determined *IE*₂(CH₄) to be 35.6 ± 0.25 eV and this was believed to correspond to population of the ³T₁ dication state. Reid³⁴ has very recently carried out a DCT experiment using the O²⁺ and C²⁺ projectiles and obtained a value of 38.3 ± 0.4 eV for *IE*₂(CH₄).

It is interesting to relate the data from DCT and AE spectroscopies to those from theoretical studies. The SCF,¹⁶ CI^{17,18} and ADC(2)¹⁹ calculations should provide accurate energy differences between states, but not necessarily good absolute energy values. These theoretical data are of most use when used in combination with experimental data for the absolute value of a particular state. In the AE spectrum of Spohr *et al.*⁶ the first peak was determined to be at a double ionization energy of 40.7 eV. This energy has been assigned¹⁹ to the (1t₂)³¹T₂ state. Thus from the data in Table 3 the ground triplet state in CH₄²⁺ should have an energy of 38.2 ± 0.5 eV, a value somewhat higher than that determined by Griffiths *et al.*³³ but in excellent agreement with that determined by Reid.³⁴

In an attempt to explain the discrepancy between the work of Griffiths *et al.*³³ and that of Reid³⁴ the DCT spectrum of CH₄ has been re-investigated using the OH⁺ and the Cl⁺ and F⁺ projectile ions.

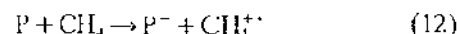
The photon-induced AE spectrum of CH₄ has been recorded for the first time in this present work. Careful calibration procedures have been observed and the spectrum is compared with the electron-impact induced AE spectra of Spohr *et al.*⁶ and Rye *et al.*⁷ The discrepancy between the two published AE spectra can be discussed in the light of this work.

A further point of discussion is the nature of the shift in the positions of the first peaks in the H⁺/DCT spectra and the AE spectra. A high-resolution H⁺/DCT spectrum of CH₄ has been recorded by us in an attempt to resolve this controversy.

EXPERIMENTAL AND RESULTS

DCT spectroscopy

If the projectile ions OH⁺, Cl⁺, F⁺ and H⁺ are denoted by P⁺, the reactions of interest in the present work can be represented by (10) and (11) and (12).



In this work P⁺ has a translational-energy of 6 keV and the electron-capture reactions (10) and (11) and (12) are sufficiently rapid to ensure vertical ionization of CH₄. Peaks in the resultant P[−] translational energy spectra due to Reaction (10) increase in height linearly with CH₄ pressure, while those due to the sequential reactions (11) and (12) show a quadratic dependence. Another difference is that, in general, the positions on the translational-energy scale corresponding to (10) and to (11) and (12) are different. If the translational-energy of P⁺ is denoted by E₀, and that of P[−], when CH₄²⁺ ions are formed in their lowest electronic state in Reaction (10), by E₁ then

$$E_0 - E_1 = \Delta T_1 \quad (13)$$

*IE*₂(CH₄) is related to ΔT₁ through Equation (14),

below

$$\Delta T_1 = IE_2(\text{CH}_4) - E(\text{P}^+ \rightarrow \text{P}^-) \quad (14)$$

where $E(\text{P}^+ \rightarrow \text{P}^-)$ is the internal energy difference between P^+ and P^- ions.

If excited states of CH_4^{2+} are populated in Reaction (10), then P^- ions will have a lower translational energy denoted by (E'_1) and the resultant translational energy loss ($\Delta T'_1$) will be

$$E_0 - E'_1 = \Delta T'_1 \quad (15)$$

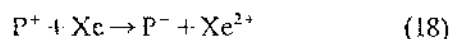
$$= IE_2(\text{CH}_4) - E(\text{P}^+ \rightarrow \text{P}^-) \quad (16)$$

$IE_2(\text{CH}_4)$ corresponds to the double-ionization energy of CH_4 to an excited dication state.

The translational energy of P^- ions formed in the sequential single-electron capture (SEC) reactions (11) and (12) is (E_2) and

$$E_0 - E_2 = \Delta T_2 = IE_1(\text{CH}_4) + IE_1(\text{CH}_4) - E(\text{P}^+ \rightarrow \text{P}^-) \quad (17)$$

In order to calibrate the translational-energy-loss scale, DCT spectra were obtained with argon or xenon collision-gas atoms, the relevant single- and double-ionization energies for which are known.³⁶ For example, for the single-collision DEC reaction involving xenon atoms



the translational energy of P^- is E_{Xe} and

$$E_0 - E_{\text{Xe}} = IE_2(\text{Xe}) - E(\text{P}^+ \rightarrow \text{P}^-) \quad (19)$$

By subtracting Eqn (19) from Eqns (14) and (17) the Eqns below are obtained

$$E_{\text{Xe}} - E_1 = IE_2(\text{CH}_4) - IE_2(\text{Xe}) \quad (20)$$

$$E_{\text{Xe}} - E_2 = IE_1(\text{CH}_4) + IE_1(\text{CH}_4) - IE_2(\text{Xe}) \quad (21)$$

from which $IE_1(\text{CH}_4)$ and $IE_2(\text{CH}_4)$ are determined once E_{Xe} , E_2 and E_1 have been measured. A similar scheme is applicable using argon as the calibrant.

The relevant translational energies were measured using a ZAB-2F mass spectrometer (VG Analytical, Manchester, UK). The H^+ and OH^+ ions were generated by the dissociative electron-impact ionization of H_2O , while Cl^+ and F^+ were formed from various halomethane precursors. All measurements were conducted at varying values of ionizing electron energy ranging from 30 to 70 eV. We believe that for each projectile the incident ions were predominantly in their ground electronic states.

Shown in Fig. 1 are DCT spectra obtained when 6 keV (a) OH^+ , (b) Cl^+ and (c) F^+ projectile ions undergo charge-inversion reactions in collisions with CH_4 molecules introduced into the second field-free region (2FFR) gas-cell. The spectra were recorded at similar collision-gas pressures (about 4×10^{-6} Torr as read on the 2FFR ion gauge. The pressure within the cell itself is expected to be at least two orders of magnitude greater than the gauge reading). In each spectrum peaks marked a and A were present, while in the F^+/CH_4 DCT spectrum a third peak B is observed.

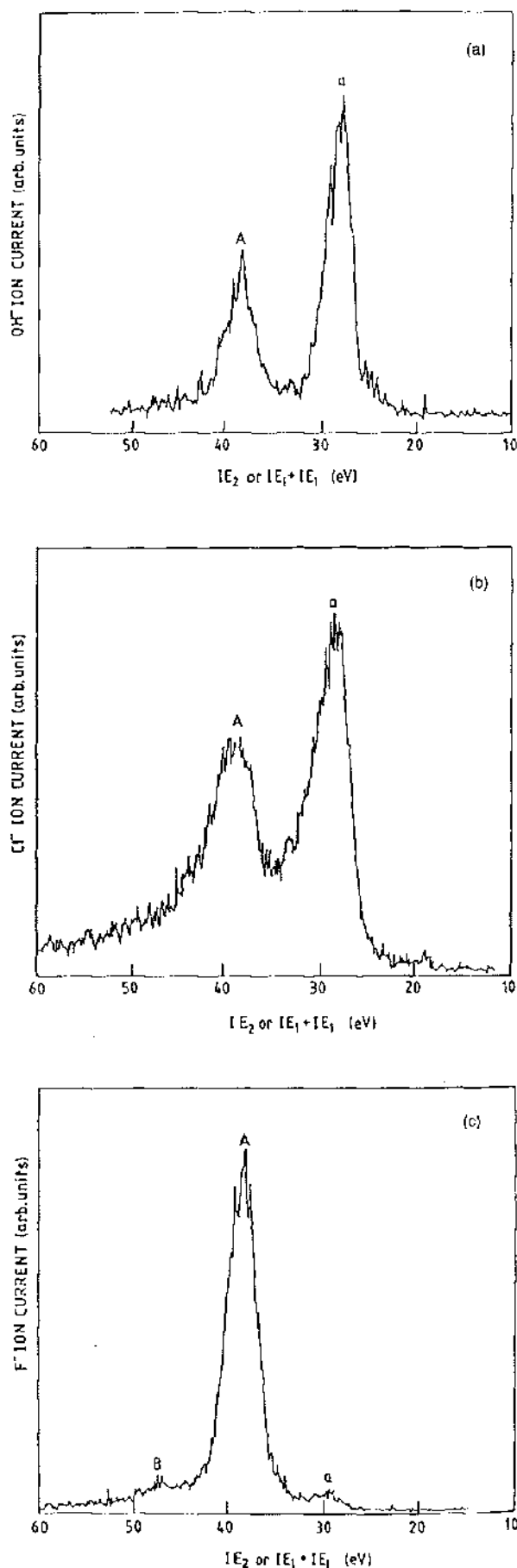


Figure 1. DCT spectra obtained when 6 keV (a) OH^+ , (b) Cl^+ and (c) F^+ ions undergo charge-inversion reactions in collisions with CH_4 molecules. The spectra were recorded at approximately 4×10^{-6} Torr collision gas pressure as read from the ionization gauge situated in the 2FFR.

Table 5. Position of peaks in the OH⁺/CH₄, Cl⁺/CH₄ and F⁺/CH₄ DCT spectra

Fig.	Projectile	a ^b	Peak maximum ^a			FWHM ^a		
			A	B		a	A	B
1(a)	OH ⁺	28.0 ± 0.4	38.0 ± 0.4	—		3.3	2.4	—
1(b)	Cl ⁺	28.0 ± 0.4	38.3 ± 0.4	—		5.0	5.3	—
1(c)	F ⁺	29.0 ± 0.4	38.2 ± 0.4	46.7 ± 0.8		3.2	3.0	

^a All energies are in electronvolts.

^b The photoelectron spectrum of CH₄¹⁰ shows a broad band (FWHM = 1.3 eV) centred at 14.5 eV which corresponds to the removal of an electron from the outermost (1t₂) orbital. Peak a is a result of the CH₄⁺ ions being formed in this state in the consecutive reactions (11) and (12). Using different projectiles different parts of the Franck-Condon region are most intensely populated; this accounts for the slight variation in the position of peak a.

By varying the CH₄ gas pressure it was established that peak a results from P⁺ ions formed in the sequential reactions (11) and (12) while peaks A and B result from P⁺ ions formed in the single-collision DEC reaction (10). By recording numerous OH⁺/CH₄, Cl⁺/CH₄ and F⁺/CH₄ DCT spectra the positions of peaks a, A and B were determined accurately and average values are listed in Table 5.

In the present work we are concerned with peaks A and B which give information on the double-ionization energy of CH₄. We believe peak A to correspond to the population of CH₄²⁺ ions in their ground triplet state, and peak B to be a result of dications being formed in the first excited triplet state. The absence of peak B from the OH⁺/CH₄ and Cl⁺/CH₄ spectra can be explained in terms of a reaction-window effect which will be discussed below.

DCT spectra have also been recorded using the H⁺ projectile. As was the case with OH⁺, Cl⁺ and F⁺ projectiles both the double- and single-collision charge-inversion processes occur. The H⁺ ion peak resulting from the single-collision process (10) was of major interest to us and is shown in Fig. 2. The spectrum presented was recorded under high resolution conditions with the H⁺ projectile ion beam having a FWHM of less than 0.5 eV. The dominant peak A is resolved in part, into three features A₁, A₂ and A₃ which were present in all of the numerous spectra recorded. Features A₁ and A₂ are seen as sharp spikes maximizing at energies of 39.2 ± 0.4 eV and 40.5 ± 0.4 eV, respectively, while A₃ is a shoulder located at an energy of 42.1 ± 1.0 eV. A second peak B, much weaker than peak A is located at an energy of 51.0 ± 1.0 eV. Again, the authenticity of peak B was confirmed by its presence in all the H⁺/CH₄ spectra recorded.

Auger-electron spectroscopy

The photon-induced Cls Auger-electron spectrum was recorded on a high-resolution gas-phase spectrometer located in the Department of Physics at Uppsala University. The excitation employed is high-intensity monochromatized Al K_α X-rays at 1487 eV. The sample was fed into the gas cell and the pressure stabilized at a few mTorr. The apparatus has been described in detail elsewhere.³⁹ In order to obtain the double-ionization energy scale from the AE spectrum the Cls core-electron spectrum has been recorded and is shown

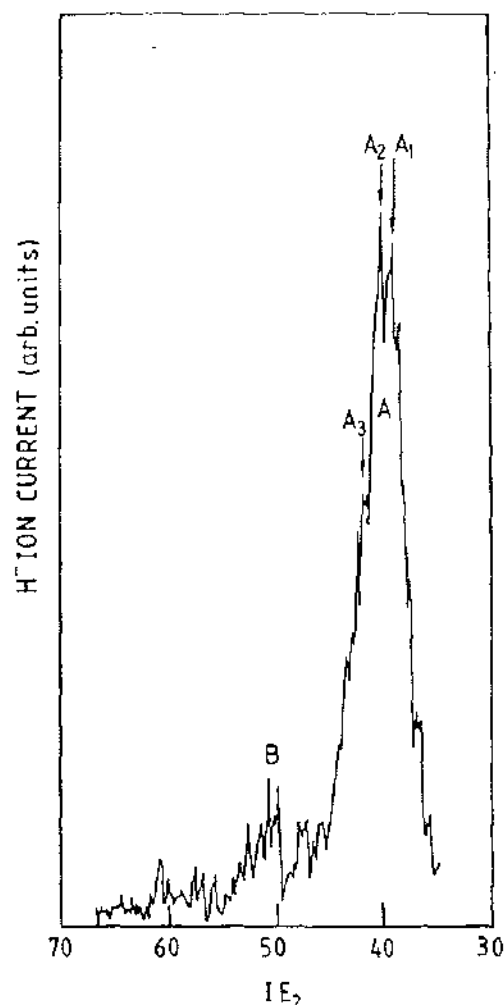


Figure 2. DCT spectrum obtained when 6 keV H⁺ ions undergo DEC reactions with CH₄ molecules.

in Fig. 3. The binding energy was calibrated against the Ar 2p_{3/2} line at 248.62 eV.⁴⁰ The value obtained for the Cls core-hole state was 290.73 ± 0.03 eV. This value is in agreement with the previous determination by Gelius and co-workers.^{8,15,41} Gelius *et al.*^{15,41} have explained the asymmetric nature of the Cls line in CH₄,

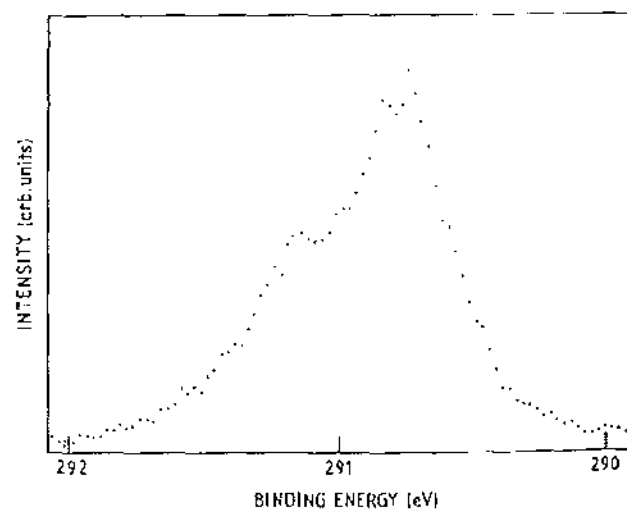


Figure 3. The Cls X-ray photoelectron spectroscopy PS core line of CH₄ (hν = 1487 eV).

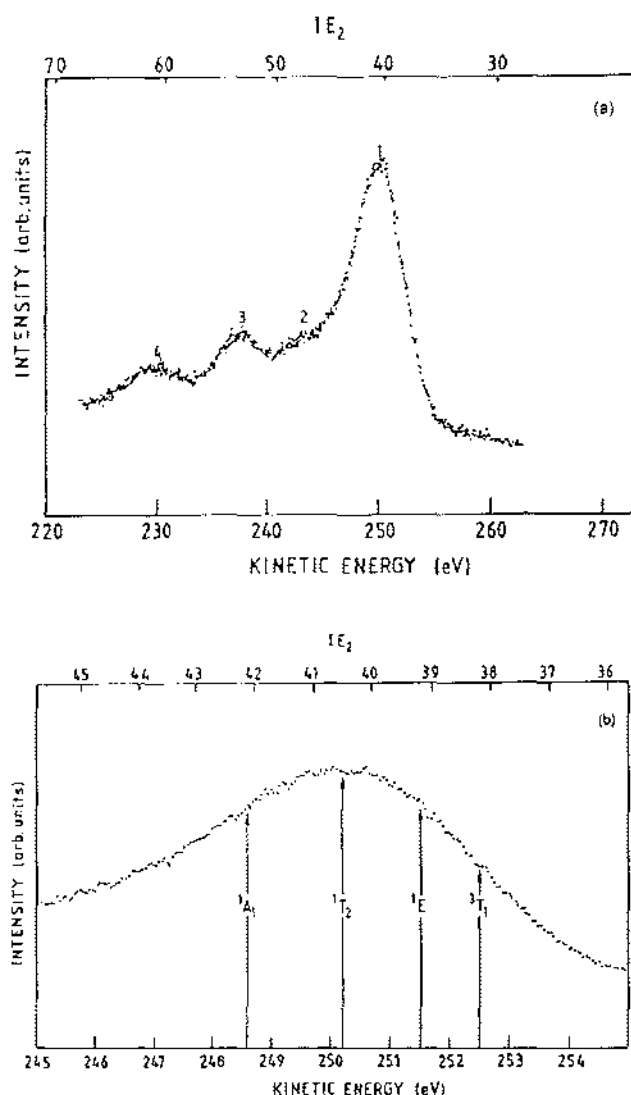


Figure 4. The carbon KVV Auger-electron spectrum of CH₄ obtained using monochromatized aluminium K_α X-rays ($h\nu = 1487$ eV). The x-axis at the top of the Fig. shows double-ionization energy while the x-axis at the bottom shows kinetic energy. Spectrum (a) was recorded in the AE kinetic energy range of 225–265 eV, while (b) was recorded in the range 245–255 eV, which covers peak 1. The arrows indicate the positions of the $1\Gamma_2^{-2}$ states as measured in our H^+/CH_4 DCT spectra (see Discussion).

by proposing it to be composed of three vibrational lines separated by 0.43 eV. Calculations by Meyer⁴² show that the potential curve for CH_4^{2+} with a C1s core hole has its equilibrium distance 0.05 Å shorter for the C–H bond than in neutral CH₄. This small displacement is sufficient to account for the additional excited vibrations seen in the spectrum.

The AE spectrum was calibrated against the D₃ line in the $L_1M_{2,3}M_{2,3}$ AE spectrum of Ar at 203.51 eV.⁴³ The double-ionization energies are then obtained by subtracting the measured kinetic energies for the observed structures in the AE spectrum from the corresponding intermediate core-hole state binding energy of 290.7 eV. The photon-induced AE spectrum of CH₄ is shown in Fig. 4(a). The x-axis at the top of the Figure shows double-ionization energy, while that at the bottom shows kinetic energy of the Auger-electron. The most prominent structures are numbered in order of decreasing kinetic energy and the measured energies of the peak centres listed in Table 6, along with the

corresponding double ionization energies. The AE spectrum recorded in the present work is the first generated by photon excitation, the two previous studies being electron-impact-induced AE spectra.^{6,7} Figure 4 is very similar to the AE spectra shown by Spohr *et al.*⁶ and Rye *et al.*⁷ In the present work great care was taken to calibrate the kinetic energy scale accurately, and as can be seen by comparing Tables 2 and 6 the energies measured for the centres of the peaks 1–4 agree within the given error limits with those of Spohr *et al.*⁶ It would appear that Rye *et al.*⁷ are about 1.5 eV too low in their values for the Auger line kinetic energy. Figure 4(b) shows peak 1, recorded under high-resolution conditions, in the AE kinetic energy region of 245–255 eV. The arrows indicate the positions of the $1\Gamma_2^{-2}$ states as measured in our H^+/CH_4 DCT study (see Discussion).

DISCUSSION

Since the early study on CH₄ using the OH⁺ projectile,³³ Griffiths and co-workers have made many further investigations using this projectile.^{35–37, 44–47} They have shown that when using this projectile the DFC reactions obey the spin conservation rule,^{35–37} at least in the case of small molecules, and that such reactions involve vertical ionization of the target-gas molecules.⁴⁷ OH⁺ ions generated in the dissociative electron ionization of H₂O are formed predominantly in the $^3\Sigma^-$ ground state, although it has been shown that a small fraction of the ions are formed in the $^1\Sigma^-$ excited state when the electron-impact energy is 100 eV.⁴⁸ Griffiths and Harris³⁷ have shown that the concentrations of excited-state ions in the OH⁺ ion beam formed at an electron-energy of 70 eV is sufficiently low to have little or no effect on the resultant DCT spectra. In fact in the OH⁺/CH₄ DCT spectra recorded in the present work, no dependence was observed on the electron-ionization energy in the 70–30 eV range, confirming that excited states of OH⁺ are not important in the present study.

As mentioned in the Introduction, ground-state neutral CH₄ molecules are singlets (X^1A_1), and for spin conservation in Reaction (10), CH_4^{2+} ions will be formed in triplet states since OH⁺ ions are formed in the $^1\Sigma^+$ state.

Consider the OH⁺/CH₄ DCT spectrum shown in Fig. 1(a). Peak A maximizes at a double-ionization energy of 38.0 ± 0.4 eV, and corresponds to the population of the ground triplet state in CH_4^{2+} (3T_1). Peak a appears at an energy of 28.0 ± 0.4 eV. Assuming that

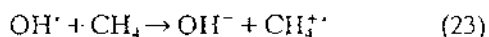
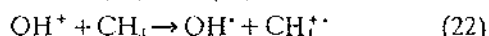
Table 6. Carbon KVV Auger line and final state double-ionization energy, determined in the present work

KVV line	Kinetic energy ^a	Double-ionization energy ^{a,b}
1	250.4 ± 0.1	40.3 ± 0.1
2	243.2 ± 0.3	47.5 ± 0.3
3	237.5 ± 0.3	53.2 ± 0.3
4	229.8 ± 0.3	60.9 ± 0.3

^a All energies are in electronvolts.

^b Double-ionization energies calculated by subtracting the measured Auger line kinetic energy from the C1s binding energy of 290.7 eV.

both CH₄²⁺ ions are formed in the same state in the sequential Reactions (22) and (23)

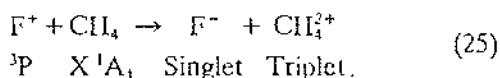


then a value of $IE_1(\text{CH}_4)$ equal to 14.0 ± 0.2 eV is obtained. This value is in good agreement with the photoelectron spectroscopy value of 14.5 eV for the vertical ionization of CH₄.¹⁰

When Griffiths *et al.*³³ recorded their original OH⁺/CH₄ DCT spectra, they did not use an independent calibration method.⁴⁹ They assumed that the same state of CH₄²⁺ was populated in Reactions (22) and (23) and they took for $IE_1(\text{CH}_4)$ a value of 12.7 eV obtained by Mathur⁵⁰ in an electron/molecular beam measurement. Griffiths *et al.*³³ measured the separation between the peaks resulting from the single- and double-collision process to be 10.2 ± 0.25 eV. By subtracting Eqn (17) from Eqn (14), Eqn (24) results,

$$\Delta T_1 - \Delta T_2 = IE_2(\text{CH}_4) - IE_1(\text{CH}_4) - IE_1(\text{CH}_4) \quad (24)$$

and by substitution of the above values for $\Delta T_1 - \Delta T_2$ and $IE_1(\text{CH}_4)$ a value for $IE_2(\text{CH}_4)$ equal to 35.6 ± 0.25 eV was obtained. If Griffiths *et al.*³³ had used the value of 14.0 eV for $IE_1(\text{CH}_4)$ as measured in the present OH⁺/CH₄ DCT study, their value for $IE_2(\text{CH}_4)$ would be 38.2 eV, which is in excellent agreement with that obtained in the present work, and also in the independent study of Reid.³⁴ Both the Cl⁺ and F⁺ ions have been used as projectile ions in previous DCT studies.^{37, 45, 51, 52} Although there is evidence that a minor fraction of Cl⁺ and F⁺ ions generated from their halomethane precursors by 100 eV electron-ionization exist in excited states,^{53, 54} no evidence for such excited states having a major effect in the present Cl⁺/CH₄ or F⁺/CH₄ DCT spectra has been found, and we believe that the 6 keV Cl⁺ and F⁺ ion beams used in the present work consist predominantly of triplet ground-state ions. F⁺ projectile ions have been shown to obey both the spin-conservation rule and the Franck-Condon principle in DEC reactions.³⁷ Because F⁺ projectile ions are in their ground triplet state (³P) and CH₄ collision gas molecules in their ground singlet state X¹A₁, then in the DEC Reaction (25), because F⁻ ions are formed in a singlet state, CH₄²⁺ ions are formed in triplet states.

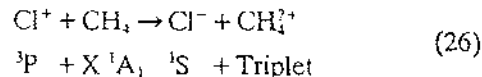


A typical F⁺/CH₄ DCT spectrum is shown in Fig. 1(c). Two peaks resulting from F⁻ ions formed in the DEC reaction (25) were observed at 38.2 ± 0.4 eV and 46.7 ± 0.8 eV. Peak A at 38.2 eV is probably due to CH₄²⁺ ions being formed in their ground triplet state (³T₁), while the peak B at 46.7 eV is probably due to CH₄²⁺ ions being formed in their first excited triplet state (³T₂). Peak B was not observed in either the OH⁺/CH₄ (Fig. 1(a)) or Cl⁺/CH₄ (Fig. 1(b)) DCT spectra, but this is not unexpected.

On the basis of theoretical^{55, 56} and experimental⁵⁷⁻⁶⁰ studies, it has been established that a 'reaction window' exists for DEC reactions, i.e., that the endoergicity of the DEC reaction must sit within a window of values. For a series of aromatic molecules Griffiths *et al.*⁵⁹ found the centre of the window to be at an endoergicity of 12 ± 3 eV. An important consequence of this is

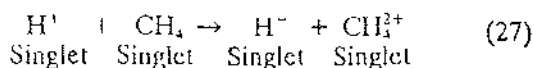
that the use of projectile ions which give a high release of energy when they charge invert in a DEC reaction tend to populate higher-lying dication states. F⁺ is such an ion because of the high values of single-ionization energy and electron affinity of F⁻ (this sum is 20.9 eV for F⁻).²⁷ Thus, F⁺ has been used in previous studies to investigate excited states of small molecular dications which are higher in energy than the states investigated by OH⁺.^{37, 45, 59-61} Clearly the triplet state (³T₂) at 46.7 eV in CH₄²⁺ is at the edge of the F⁺ reaction window ($\Delta T_1 = 25.8$ eV) while the triplet state (³T₁) at 38.2 eV is near the centre of the F⁺ reaction window ($\Delta T_1 = 17.3$ eV). This accounts for the large difference in intensity between peaks A and B (as shown in Fig. 1(c)) because the cross-section for DEC reactions increases as the endoergicity of the reactions approaches the centre of the reaction window. The state at 46.7 eV must be out of the OH⁺ (Fig. 1(a)) and Cl⁺ (Fig. 1(b)) reaction windows. (For OH⁺ $\Delta T_1 = 31.9$ eV and for Cl⁺ $\Delta T_1 = 30.1$ eV.) The state at about 38 eV is within both the OH⁺ ($\Delta T_1 = 23.2$ eV) and Cl⁺ ($\Delta T_1 = 21.7$) reaction windows.

The two peaks a and A in the Cl⁺/CH₄ DCT spectrum shown in Fig. 1(b) resemble those observed in the OH⁺/CH₄ and F⁺/CH₄ spectra although their relative intensities differ (see Table 5). Peak A which is a result of Cl⁻ being formed in the DEC reaction (26) is located at a similar position on the CH₄ double-ionization energy scale as peaks A resulting from OH⁻ and F⁻ ions being formed in DEC reactions (9) and (25), respectively.



Because Cl⁺ projectile ions will predominantly be in the ground triplet state (³P), and Cl⁻ ions formed in the DEC reaction (26) in the singlet state (¹S), triplet state dications must be populated in this reaction with the spin conservation rule being obeyed. Peak a will be a result of Cl⁻ ions being formed in the sequential double-collision process ((11) and (12)) with CH₄²⁺ ions being formed in their ground electronic state.

Fournier and co-workers⁶²⁻⁶⁷ have performed many previous DCT spectroscopy studies using the H⁺ projectile. H⁺ is a singlet, and as the excited states of H⁻ are autoionizing with very short lifetimes only ground state singlet H⁻ ions are observed in DCT experiments. As mentioned in the Introduction, DEC Reactions (10) obey the spin conservation rule when keV H⁺ ions are used as projectiles and small molecules as the collision gas.^{29, 32} Since CH₄ molecules in their ground state are singlets X¹A₁, CH₄²⁺ ions will be formed in singlet states in the DEC reaction



DEC reactions have also been shown to involve vertical transitions^{29, 31} and thus CH₄²⁺ ions will be formed with the same tetrahedral geometry as neutral CH₄ molecules. Features A₁, A₂, A₃ and B shown in Fig. 2 were a result of H⁻ ions being formed in the DEC reaction (27). Fournier *et al.*²⁴ recorded a similar DCT spectrum, but saw only one peak which resulted from H⁻ ions being formed via Reaction (27). It was located on a double-ionization energy scale between

Table 7. Computed, and experimental energies^a for the doubly ionized states of CH₄ in tetrahedral geometry as obtained in the present work

Configuration	State	Computation ^b	DCT	Auger
1t ₂ ⁻²	³ T ₁	38.02	38.2 ± 0.4 ^c	
	¹ E	38.83	39.2 ± 0.4 ^d	
	¹ T ₂	40.50	40.5 ± 0.4 ^d	40.3 ± 0.1
	¹ A ₁	42.77	42.1 ± 1.0 ^d	
(2a ₁ ⁻¹ , 1t ₂ ⁻¹)	³ T ₂	47.18	46.7 ± 0.8 ^c	47.5 ± 0.3
	¹ T ₂	53.31	51.0 ± 1.0 ^d	53.2 ± 0.3
2a ₁ ⁻²	¹ A ₁	60.77		60.9 ± 0.3

^a All energies are in electronvolts.

^b Average energies from References 16, 17, 18 and 19. The values quoted in column 3 are 1.4 eV larger than the computed energies so that the DCT experimental and the theoretical energies of the ¹T₂(1t₂⁻²) state coincide.

^c From DCT spectroscopy using the OH⁺, Cl⁺ and F⁺ projectile.

^d From DCT spectroscopy using the H⁺ projectile.

35 eV and 44 eV and maximized at 38.6 ± 0.3 eV. In the present work, peak A is observed between 35 eV and 45 eV, as shown in Fig. 2. This peak has been resolved in part into three structures A₁, A₂ and A₃ which correspond to double-ionization energy values of 39.2 ± 0.4, 40.5 ± 0.4 and 42.1 ± 1 eV. These features are a result of the formation of CH₄²⁺ ions in the low-lying singlet states ¹E, ¹T₂ and ¹A₁. Fournier *et al.*²⁴ in their study were not able to resolve these three close-lying states. Peak B shown in Fig. 2 corresponds to the formation of CH₄²⁺ ions in their ¹T₂ state at 51 ± 1 eV.

The present results from our DCT study are compared with those from earlier theoretical studies in Table 7. It is well established that although SCF, CI and ADC (2) calculations may provide accurate spacings of energy levels, they do not give accurate absolute energy values. We have thus adjusted the computed energies so that the energy of the ¹T₂ state corresponds to that determined in our H⁺/CH₄ DCT study. The energy of the first triplet state was measured using the three projectile ions OH⁺, Cl⁺ and F⁺, the mean value being 38.2 ± 0.4 eV in excellent agreement with the theoretical value in Table 7 and also with an earlier determination by Reid³⁴ of 38.3 ± 0.4 eV. There is also good agreement between the experimental and theoretical results for the energy of the second triplet state and the four singlet states.

The excellent agreement between experiment and theory confirms the good quality of the quoted calculations¹⁶⁻¹⁹ and the assumptions made for the DEC process.

It is now interesting to compare the results of our DCT and Auger study. In the Experimental and Results section it was demonstrated that the double-ionization energies determined in the present Auger study are in excellent agreement with those measured by Spohr *et al.*⁶ (compare Tables 2 and 6). The peaks in the Auger spectra have been assigned in the theoretical studies¹⁶ and our results are compared with the theoretical energy values in Table 7. We agree with the assignment of Tarantelli *et al.*¹⁹ that the peak at 40.3 ± 0.1 eV corresponds to the formation of CH₄²⁺ ions in an unresolved mixture of ³T₁, ¹E, ¹T₂, ¹A₁ states of configuration 1t₂⁻² and that the peaks at 47.5 ± 0.3 eV and 53.2 ± 0.3 eV correspond to the ³T₂ and ¹T₂ states of configuration (2a₁⁻¹, 1t₂⁻¹). The fourth peak in the AE spectrum at 60.9 ± 0.3 eV is assigned to the ¹A₁ state of

2a₁⁻² configuration. By studying Table 7 it can be seen that the agreement between theory, DCT spectroscopy and AE spectroscopy is good. This is also illustrated by the arrows on Fig. 4(b).

The present results suggest that we have been working at higher instrumental resolution in our DCT study than in our Auger study. In the H⁺/CH₄ DCT spectrum the three 1t₂⁻² singlet states have been resolved, at least in part, but this resolution of states has not been achieved in our Auger spectrum. In fact the energy resolution of the Uppsala gas-phase electron-spectrometer is *higher* than that of the Swansea ZAB mass spectrometer (the energy resolution of the electron spectrometer is at least 0.2 eV while that of the ZAB is at best 0.5 eV). Clearly an alternative explanation for the poor resolution in our Auger spectrum is required. The most probable reason for our not being able to resolve the 1t₂⁻² states is that in the core ionization process, vibrationally excited states as well as the ground states of CH₄⁺ are formed, and that these states are all involved in the subsequent Auger process. The result is a broad line for each of the 1t₂⁻² states. In contrast the DEC reaction (27) in DCT spectroscopy is a direct process, not involving an intermediate state, and thus DCT spectroscopy does not experience the broadening effect of the intermediate core hole state.

In the present study and in other DCT and Auger studies^{62, 66, 68-71} we have found there to be good, but not perfect, agreement in the values determined for the energies of particular states. Although the agreement is usually within combined experimental error, the origin of the discrepancy may be the result of Auger spectroscopy involving an intermediate state, while DCT spectroscopy is a direct process.

In light of the results from the present work, the CH₄²⁺ fragmentation data of Fournier *et al.*,²⁴ Dujardin *et al.*²⁵ and Hatherly *et al.*²⁶ should be considered. For the fragmentation path (3) the fragmentation threshold energy (Table 4) has been determined to be in the region of 33.9–36.5 eV. Both Fournier *et al.*²⁴ and Dujardin *et al.*²⁵ interpreted their results in terms of the formation of CH₄²⁺ ions in the ³T₁ state, and Dujardin *et al.*²⁵ determined a value for the vertical ionization of CH₄ to this state to be 37.15 ± 0.1 eV. This value is somewhat lower than the value of 38.2 eV determined in the present work, but can be accounted for by differences in the Franck-Condon regions for double ionization in the different experiments. The experimental values of 33.9 eV and 35.0 eV have been interpreted to correspond to the opening of the ionization channel for the ³T₁ state. Hatherly *et al.*²⁶ in contrast, proposed that Reaction (3) results from fragmentation of the ¹E state. In the present work the ¹E state was found to have an energy of about 39 eV. Our results suggest that the interpretation of the fragmentation process (3) by Fournier *et al.*²⁴ and Dujardin *et al.*²⁵ is more likely to be correct.

The fragmentation threshold for Reaction (5) lies between 38.1 and 38.5 eV.²⁴⁻²⁶ Dujardin *et al.*²⁵ measured a value of 38.5 ± 0.1 eV and this value was expected by them to be very close to the vertical energy for double ionization to the ¹E state. Our experimental energy for the ¹E state is 39.2 ± 0.4 eV, in good agreement with that of Dujardin *et al.*²⁵. Fournier *et al.*²⁴ proposed the fragmenting state to be one of the three (1t₂⁻²) singlet states while Hatherly *et al.* proposed the

fragmenting state to be the 1T_2 state. Our experimental energy for the 1T_2 state is 40.5 ± 0.4 eV and suggests that Dujardin *et al.*'s²⁵ assignment is more likely to be correct than that made by Hatherly *et al.*²⁶ The threshold for the fragmentation process (6) was measured to be between 38.1 and 38.4 eV.^{24,26} Comparison with our results suggests that the fragmenting state is either the 3T_1 or 1E state. Hatherly *et al.*²⁶ measured the fragmentation thresholds for Reactions (7) and (8) to be 41.1 ± 1.0 eV and 44.8 ± 1.5 eV, respectively. Our results show that the $^1A_1(1t_2^{-2})$ and $^3T_2(2a_1^{-1}, 1t_2^{-1})$ states have energies of about 42 eV and 47 eV, respectively. Hatherly *et al.*²⁶ interpreted their results by proposing that the fragmenting states for Reactions (7) and (8) are the $^1A_1(1t_2^{-2})$ and $^3T_2(2a_1^{-1}, 1t_2^{-1})$ states, which is consistent with the results from the present work.

CONCLUSION

The energy of the ground triplet state (3T_1) of tetrahedral CH_4^{2+} is 38.2 ± 0.4 eV. This agrees well with the value of 38.3 ± 0.4 eV as measured by Reid.³⁴ We conclude that the value of 35.6 ± 0.25 eV as measured by Griffiths³³ is too low, probably because of an error in their calibration procedure. The first line in the KLL AE spectrum is centred at 40.3 ± 0.1 eV in good agreement with the value of 40.7 ± 0.8 eV measured by Spohr *et al.*⁶ The position measured by Rye *et al.* differs by 1.5 eV from our value, no doubt due to a calibration error in their work. The first line in the AE spectrum results from populating the 3T_1 , 1E , 1T_2 and 1A_1 states of $(1t_2^{-2})$ configuration in CH_4^{2+} . The three singlet states have been resolved in our DCT spectra and have energies of 39.2 ± 0.4 eV, 40.5 ± 0.4 eV and 42.1 ± 1.0 eV, respectively. Further excited states 3T_2 , 1T_2 of $(2a_1^{-1}, 1t_2^{-1})$ configuration have been populated in DCT and AE spectroscopic experiments and have energies of about 47 and 53 eV.

Both AE and DCT spectroscopies give information concerning tetrahedral geometry CH_4^{2+} ions. From the charge-stripping work of Ast *et al.*,¹ Rabrenović *et al.*⁵ and Stahl *et al.*,¹¹ and the theoretical work of Siegbahn,⁹ stable CH_4^{2+} ions of square planar D_{4h} geometry are shown to have an energy of about 32 eV.

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