

## Electron impact ionization of C<sub>2</sub>H<sub>6</sub>: ionization energies and temperature effects

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### Abstract

Appearance energies for ions formed via electron impact ionization of C<sub>2</sub>H<sub>6</sub> were determined, some of them at two different gas temperatures, 293 and 693 K. The experimental values obtained at 293 K are AE(C<sub>2</sub>H<sub>6</sub><sup>+</sup>) = 11.46 ± 0.04 eV, AE(C<sub>2</sub>H<sub>5</sub><sup>+</sup>) = 12.06 ± 0.04 eV and AE(C<sub>2</sub>H<sub>4</sub><sup>+</sup>) = 11.90 ± 0.04 eV, AE(C<sub>2</sub>H<sub>3</sub><sup>+</sup>) = 15.02 ± 0.1 eV, AE(C<sub>2</sub>H<sub>2</sub><sup>+</sup>) = 15.02 ± 0.1 eV, AE(C<sub>2</sub>H<sup>+</sup>) = 25.7 ± 0.3 eV and AE(C<sub>2</sub><sup>+</sup>) = 22.6 ± 0.3 eV. When going to 693 K the appearance energies of the first three ions mentioned exhibit red shifts of 0.26 ± 0.08, 0.19 ± 0.12 and 0.30 ± 0.08 eV, respectively. In addition, quantum chemical calculations of the appearance energies and of the red shift were carried out at the G3B3 level of theory supported by various other theoretical methods.

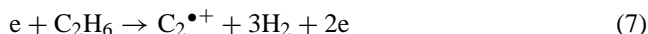
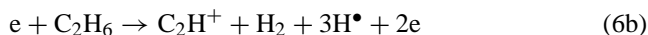
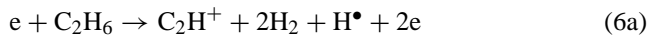
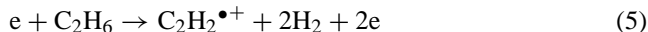
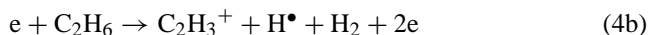
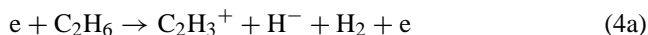
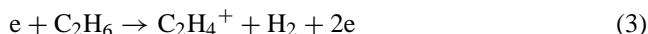
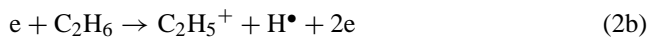
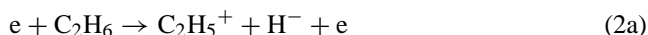
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**Keywords:** Electron impact ionization; Appearance energies; Ethane (C<sub>2</sub>H<sub>6</sub>); Ionization energy

### 1. Introduction

It has been recognized that small hydrocarbons are constituents of the plasma edge in fusion reactors [1] and therefore there exists a strong interest in reliable data for electron impact ionization of small hydrocarbon molecules [2]. In this article, we describe an experimental and theoretical study to determine appearance energies (AE) and ionization energies (IE). As the thermal conditions in fusion reactors are quite different from the normal laboratory conditions, we are investigating in the present work the effects of the gas temperature on IE and AE for positive ions, i.e. ions produced via electron impact ionization (EII) to C<sub>2</sub>H<sub>6</sub>. This work is a follow up to our previous study devoted to CH<sub>4</sub> [3], where significant temperature effects for the AEs of positive ions have been observed.

Electron impact ionization of ethane leads to the following ionization reactions investigated in the present study:



Additional reactions producing H<sup>+</sup> could not be studied in this experiment due to the limited mass range of the mass spectrometer. Appearance energies of C<sub>2</sub>H<sub>6</sub> were already measured in previous electron impact ionization [4–8] and

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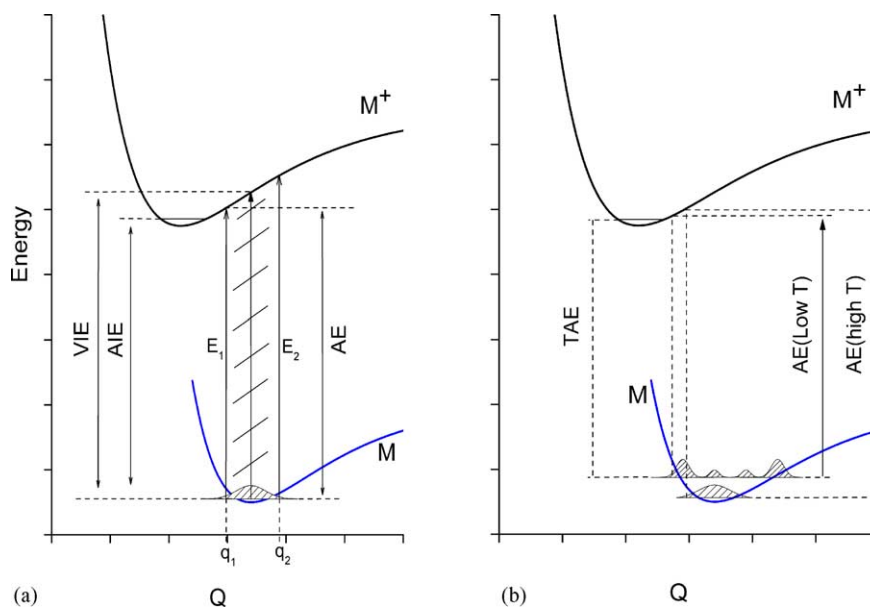


Fig. 1. Potential energy curves of a system molecule–molecular ion, in the case of electron impact ionization at: (a) low temperature, (b) high temperature. VIE: vertical ionization energy, AIE: adiabatic ionization energy, AE: appearance energy of an ion.

photoionization (PI) studies [9–12]. Nevertheless there still exists a large scatter in the experimental values for the measured AEs, specifically concerning processes (4)–(7). In the present work, we focus in particular on the effect of the gas temperature on the appearance energies concerning reactions (1)–(3). So far, no studies have been reported on temperature effects for appearance energies of ethane.

Fig. 1a and b shows a potential energy curve of a molecule  $M$  along the geometry coordinate  $Q$ . This figure allows to illustrate the most important concepts for electron impact ionization, the vertical ionization energy (VIE), the adiabatic ionization energy (AIE) and the appearance energy of an ion (AE). Electron impact ionization is a fast process, i.e., the typical time for the transition from the neutral molecule to the ionic state occurs in a much shorter time than the vibrational period of the molecule (Franck–Condon process). The vertical ionization energy is the energy necessary to ionize a molecule  $M$  in its ground electronic, vibrational and rotational state without changing the geometry of the molecule (Fig. 1a). The adiabatic ionization energy is defined as the difference between the ground electronic, vibrational and rotational states of the ion  $M^+$  and molecule  $M$ . The AE is the lowest energy at which a particular ion can be observed in an experiment.

In order to elucidate the mechanism of the electron impact ionization reaction (and its temperature dependence) of  $C_2H_6$  we have performed detailed quantum chemical calculations for the IE of  $C_2H_6^+/C_2H_6$  (vertical and adiabatic) and AEs of fragment ions from  $C_2H_6$ . The IEs (vertical and adiabatic) of ethane have been calculated at a high level of theory and these calculations give us also important information about the mechanism of the electron impact ionization. It is generally accepted that electron impact ionization

is a fast process and that at least for small molecules (see references given in [3]) the experimental AE for the parent ion are rather close to the vertical IE (Fig. 1a). However, the present experiment and the calculations indicate that in the case of the  $C_2H_6$  molecule, the IEs measured in the electron impact ionization experiment are close to the theoretical adiabatic IEs. This result is in line with earlier observations for large molecules (see references given in [3]).

## 2. Experimental

The experiment was carried out using a crossed electron/molecule beams apparatus shown schematically in Fig. 2. This apparatus was constructed to study electron attachment and electron impact ionization for molecules in the gas phase and was described previously in [13,14]. The apparatus is equipped with a trochoidal electron monochromator (TEM) [14]. The molecular beam is formed using a temperature controlled effusive molecular beam source (EMBS). The temperature of the molecular beam source can be varied from about 300–800 K and is measured by a pair of thermocouples. Because the molecules in the EMBS are in thermal equilibrium with the walls, the molecules effusing from the EMBS have the same internal temperature. The ions formed at the region where the electron beam intersects the molecular beam are extracted into a quadrupole mass spectrometer (QMS) and monitored for a specific ion as a function of the electron energy. The ionization energy for a given fragment ion can be extracted from the measured ion yield as a function of the electron energy using an extrapolation and fitting method that was described in detail in [3]. By varying the temperature of the molecules it is

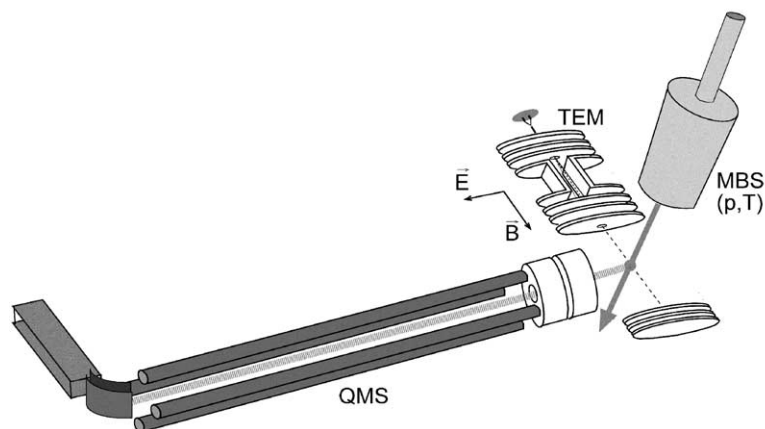


Fig. 2. The experimental setup. TEM: trochoidal electron monochromator, QMS: quadrupole mass spectrometer, MBS: molecular beam source.

possible to measure the effects of the gas temperature on the appearance energy for a particular parent or fragment ion.

Using this experimental technique we have been able to measure the ionization energies for the reaction channels (1)–(5) with an electron energy resolution of 120 meV full width at half maximum (FWHM). This relatively low resolution has been chosen, in order to still allow large electron currents and thus large enough signals close to threshold. Nevertheless, the measurements were extremely time-consuming. Using statistical data analysis it was possible to achieve a high precision for the appearance energies extracted from the data (e.g. in the case of the ion  $C_2H_6^+$  of 0.04 eV). The measurements of the appearance energies for reaction channels (1)–(3) were performed at two different temperatures, i.e., at 293 and 693 K.

The electron energy scale of the measured ion yield curves was calibrated using the ionization energy of Ar for reaction  $Ar^+/Ar$  assuming an IE of  $15.759 \pm 0.001$  eV [15]. In order to achieve an accurate calibration of the electron energy scale, we have developed a fitting procedure, which also accounts for the electron energy distribution in the electron beam. The fitting function is a convolution of an assumed cross section and an electron energy distribution function (see [3] for more details).

### 3. Theory

Theoretical studies concerning the molecular systems in reactions (1)–(7) have been devoted to the description of the potential energy surfaces in connection with the reactivity of organic radical cations. Weitzel [16] carried out ab initio molecular orbital calculations of the  $H_2$  loss reaction from the ethane cation but his calculations deviated from the correct reaction path, which was found later by Kurosaki and Takayanagi [17]. At the same level (UMP2/6-311G(d,p)) of theory, they localized two transition states and two interme-

diante products which they combined with the RRKM calculations of the rate constant of the reaction. To obtain ionization energies for alkanes Jursic [18] tested and analyzed the suitability of the density functional theory (DFT). It was concluded that best method of the choice, the local spin density approximation overestimates the ionization energies for ethane.

In this study, we present results of high level ab initio MO calculations of the molecular structures occurring in the investigated reaction channels (1)–(7). To obtain more reliable relative energies for the reactants and products, calculations of the Gaussian-3 (G3) [19] and G3B3 [20] were carried out. These methods are complex energy computations involving several pre-defined calculations on the specified molecular system. We combined these calculations with the various Complete Basis Set (CBS) methods of Petersson and coworkers for computing very accurate energies (CBS-Q [21], CBS-QB3 [22]). The vertical ionization energy of ethane has been also calculated by the method based on outer valence Green's function (propagator) calculation of correlated electron affinities and ionization energies (OVGF) [23] from the MP2 (second-order Møller–Plesset perturbation) optimized geometry using the 6-311G(d,p) basis set. Coupled cluster calculations CCSD(T) [24] of vertical and adiabatic IE of ethane (6-311G(d,p) basis set) have been carried out by using the optimized CCSD(T) structures. All calculations have been performed using the Gaussian 98 program [25].

### 4. Results and discussion

The ion yield is measured in an electron impact ionization experiments as a function of the kinetic energy of the electrons. The appearance energy of the particular ion can be estimated from the measured ion yield. In the case of electron impact ionization of an atomic target, the appearance

Table 1  
Calculated reaction enthalpies, all values are given in eV

e + C <sub>2</sub> H <sub>6</sub> →	Methods			
	G3B3	G3	CBS-QB3	CBS-Q
C <sub>2</sub> H <sub>6</sub> <sup>+</sup>	11.55	11.63	11.55	11.64
C <sub>2</sub> H <sub>5</sub> <sup>+</sup> + H <sup>-</sup>	12.03	12.05	11.93	12.00
C <sub>2</sub> H <sub>5</sub> <sup>+</sup> + H				
C <sub>2</sub> H <sub>4</sub> <sup>+</sup> + H <sub>2</sub>	11.93	11.97	11.93	11.97
C <sub>2</sub> H <sub>3</sub> <sup>+</sup> + H + H <sub>2</sub>	14.83	14.85	14.80	14.80
C <sub>2</sub> H <sub>2</sub> <sup>+</sup> + 2H <sub>2</sub>	14.61	14.63	14.62	14.62
C <sub>2</sub> H <sup>+</sup> + 2H <sub>2</sub> + H	21.65	21.64	21.47	21.58
C <sub>2</sub> H <sup>+</sup> + H <sub>2</sub> + 3H	26.12	26.11	25.90	26.01
C <sub>2</sub> <sup>+</sup> + 3H <sub>2</sub>	21.73	21.73	21.74	21.69

CCSD(T) results for ethane: AIE = 11.84 eV, VIE = 13.05 eV, OVGf results for ethane: VIE = 12.70 eV.

energy of the ion is identical to the ionization energy of the target. However, in the case of a molecular target, the situation is much more complex. The measured appearance energy does not directly represent the ionization energy of the molecule (either VIE or AIE), as the electrons interacts with the molecules in an excited (vibrational and rotational) state (Fig. 1a). The energy necessary to ionize a particular molecule also depends on the geometrical situation of the molecule at the moment of the electron interaction (Fig. 1a). The energy  $E_1$  necessary to ionize the molecule at the coordinate  $q_1$  is lower than the energy  $E_2$  at the coordinate  $q_2$  and thus the appearance energy corresponds to the ionization energy at the coordinate  $q_1$ .

Using ab initio calculations we have calculated the reaction enthalpies for reactions (1)–(7) and the vertical ionization energy VIE of reaction (1) (Table 1). The reaction enthalpies represent the energetical threshold of the particular reaction at 293 K (it is assumed that the molecules and products have rotational and vibrational temperatures of 293 K). The reaction enthalpies may be also calculated using standard enthalpies of formation as published in [15]. There exists a close relationship between the reaction enthalpy and the adiabatic ionization energy. While the adiabatic ionization energy is defined as the difference between the energy of the neutral molecule and the corresponding ion

in their ground electronic, vibrational and rotational states (rotational and vibrational temperature 0 K), the reaction enthalpy is equal to the difference between the energies of the neutral molecule and the ion at rotational and vibrational temperature of 293 K. In Table 2, we show a comparison of the calculated enthalpies of reaction with the experimental appearance energies of particular ions.

For the ions C<sub>2</sub>H<sub>6</sub><sup>+</sup>, C<sub>2</sub>H<sub>5</sub><sup>+</sup> and C<sub>2</sub>H<sub>4</sub><sup>+</sup> we have in addition calculated the theoretical appearance energies at 293 and 693 K using the G3B3 level of theory. These values are compared with the experimental values of appearance energies in Table 3. The theoretical appearance energies are defined as the difference between the ground state of the ion and the most populated vibrational and rotational state of the neutral molecule.

The present experimental studies of the appearance energies for electron impact ionization of C<sub>2</sub>H<sub>6</sub> were performed at temperatures of 293 K and for the major product ions (C<sub>2</sub>H<sub>6</sub><sup>+</sup>, C<sub>2</sub>H<sub>5</sub><sup>+</sup>, C<sub>2</sub>H<sub>4</sub><sup>+</sup>) also at 693 K. The appearance energies of the ions formed by electron impact ionization of C<sub>2</sub>H<sub>6</sub> at 293 K are summarized in the Table 2. This table also presents a survey of previous experimental studies (EII [5] and PI [9]) and the reaction enthalpies as calculated from the thermodynamic data [15] and by present quantum chemical calculations.

#### 4.1. C<sub>2</sub>H<sub>6</sub><sup>+</sup>/C<sub>2</sub>H<sub>6</sub>

A typical C<sub>2</sub>H<sub>6</sub><sup>+</sup> ion yield curve measured at 293 K is shown in the Fig. 3a. The present value of the appearance energy of 11.46 ± 0.04 eV (Table 2) is below the value of 11.57 ± 0.02 eV measured by Plessis et al. [5] using electron impact ionization. Both values are in agreement with the value of 11.5 ± 0.1 eV obtained by Mackie et al. [9] using photoionization. Using quantum chemical methods and taking into account vibrational and rotational excitation of the neutral ground state we have calculated the appearance energy at 293 K at the G3B3 level of theory yielding 11.411 eV (see Table 3). This value agrees well with the present experimental appearance energy. The vertical ionization energies calculated at the CCSD(T) and the OVGf level of theory

Table 2  
The appearance energies for EII of C<sub>2</sub>H<sub>6</sub> as obtained in the present experiment and in previous EII [5] and PI [9] experiments

e + C <sub>2</sub> H <sub>6</sub> →	Present experiment	EII [5]	PI [9]	Theory	
	AE (eV) at 293 K	IE (eV)	IE (eV)	Thermodynamics [15]	G3B3 AIE (eV)
C <sub>2</sub> H <sub>6</sub> <sup>+</sup>	11.46 ± 0.04	11.57 ± 0.02	11.5 ± 0.1		11.55
C <sub>2</sub> H <sub>5</sub> <sup>+</sup> + H <sup>-</sup>	12.06 ± 0.06	12.08		11.72	12.03
C <sub>2</sub> H <sub>5</sub> <sup>+</sup> + H	12.7 ± 0.1	12.45	12.4 ± 0.1	12.47 ± 0.03	12.79
C <sub>2</sub> H <sub>4</sub> <sup>+</sup> + H <sub>2</sub>	11.90 ± 0.04	11.81 ± 0.05	12.0 ± 0.1	11.92 ± 0.0006	11.93
C <sub>2</sub> H <sub>3</sub> <sup>+</sup> + H + H <sub>2</sub>	15.02 ± 0.1	14.50 ± 0.04	14.8 ± 0.1	14.47 ± 0.46	14.83
C <sub>2</sub> H <sub>2</sub> <sup>+</sup> + 2H <sub>2</sub>	15.02 ± 0.1	14.41 ± 0.01	14.9 ± 0.1	14.61 ± 0.01	14.61
C <sub>2</sub> H <sup>+</sup> + 2H <sub>2</sub> + H		22.4 ± 0.3		20.5 ± 0.15	21.65
C <sub>2</sub> H <sup>+</sup> + H <sub>2</sub> + 3H	25.7 ± 0.3			25.1 ± 0.15	26.12
C <sub>2</sub> <sup>+</sup> + 3H <sub>2</sub>	22.6 ± 0.3	22.9 ± 0.3		20.95 ± >0.3	21.73

Also shown the reaction thresholds as calculated from thermochemical data [15] and results from present ab initio calculations (see Table 1).

Table 3

The values of the experimental and ab initio appearance energies of the ions from  $C_2H_6$ 

$e + C_2H_6 \rightarrow$	Appearance energy (eV)					
	Experiment			G3B3		
	AE(293 K)	AE(693 K)	$\Delta(\text{AE}(693 \text{ K}) - \text{AE}(293 \text{ K}))$	AE(293 K)	AE(693 K)	$\Delta(\text{AE}(693 \text{ K}) - \text{AE}(293 \text{ K}))$
$C_2H_6^+$	$11.46 \pm 0.04$	$11.2 \pm 0.04$	$0.26 \pm 0.08$	11.411	11.097	0.314
$C_2H_5^+ + H^-$	$12.06 \pm 0.06$	$11.87 \pm 0.06$	$0.19 \pm 0.12$	11.853	11.538	0.314
$C_2H_5^+ + H$	$12.7 \pm 0.1$	$12.4 \pm 0.1$	$0.30 \pm 0.2$	12.348	12.034	0.314
$C_2H_4^+ + H_2$	$11.90 \pm 0.04$	$11.60 \pm 0.04$	$0.30 \pm 0.1$	11.724	11.409	0.314

(13.05 eV respectively 12.7 eV) exceed the experimental appearance energy substantially. The appearance energy coincides much better with the reaction enthalpies calculated for this reaction (see Table 1).

An ion yield curve measured at the elevated gas temperature of 693 K is presented in the Fig. 3b. The appearance energy at this temperature has a value of  $11.20 \pm 0.04$  eV. The red shift of the appearance energy has a value of about  $0.26 \pm 0.08$  eV with respect to the appearance energy at 293 K. We have calculated at the G3B3 level of theory the appearance energy of the  $C_2H_6^+$  ion at 693 K yielding 11.097 eV (Table 3). The theoretical red shift of the appearance energy between 293 and 693 K is 0.314 eV and is in reasonable agreement with the experimental red shift. The red shift in the appearance energy of the  $C_2H_6^+$  ion may be explained in the terms of Fig. 1b, i.e., the appearance energy of the molecule at 693 K is lowered due to the much higher vibrational and rotational excitation of the molecule (as compared to the case at 293 K) and changes in geometry associated with this excitation.

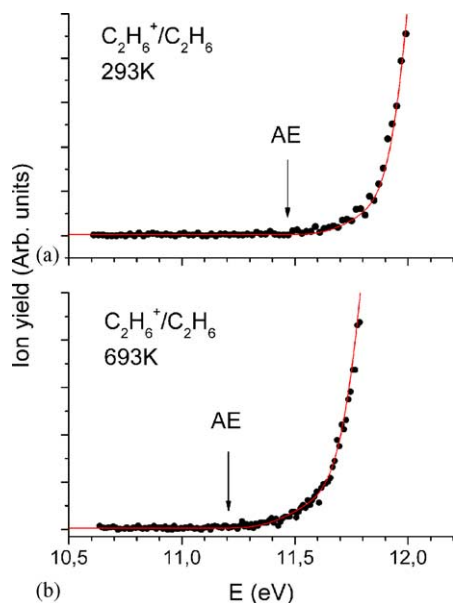


Fig. 3. Ion yield curves for  $C_2H_6^+/C_2H_6$  as measured at: (a) 293 K and (b) 693 K. Solid lines present fits through the experimental data. Arrows indicate the estimated appearance energies derived by the fitting procedure.

#### 4.2. $C_2H_5^+/C_2H_6$

Ion yields for the dissociative ionization  $C_2H_5^+/C_2H_6$  were measured at 293 and 693 K. Representative ion yield curves are shown in Fig. 4. The most favorable process in terms of the energetics is ion pair formation via the reaction (2a). The dissociative ionization reaction (2b) is energetically less favorable. The adiabatic threshold for reaction (2b) is according to [5] 0.76 eV (electron affinity of H) above the threshold for reaction (2a). The results of the data analysis of the present  $C_2H_5^+$  ion yields are shown in the Table 2. We have identified two thresholds in the ion yield curve. The second threshold, which is difficult to identify by visual inspection of the curve, is consistently predicted by the statistical data analysis. The first threshold  $AE_1$  at  $12.06 \pm 0.1$  eV (293 K) is about 0.64 eV below the second threshold  $AE_2$  at  $12.70 \pm 0.1$  eV.

Plessis et al. [5] identified three thresholds in the ion yield (mass to charge ratio (MCR) of the ion 29), at 11.85, 12.08 and 12.45 eV. They attributed the signal below

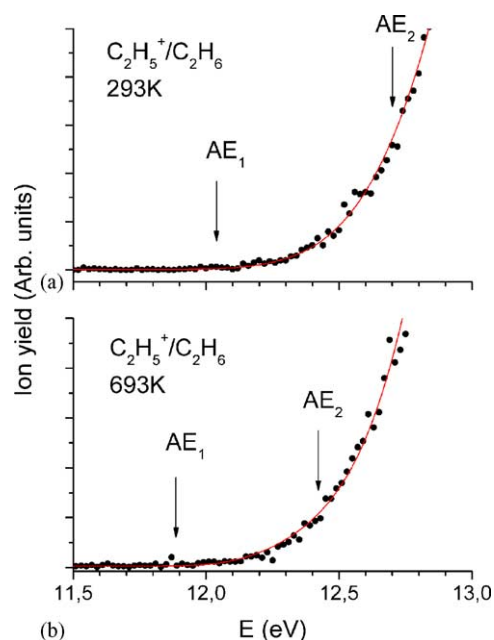


Fig. 4. Ion yield curves for  $C_2H_5^+/C_2H_6$  as measured at: (a) 293 K and (b) 693 K. Solid lines present fits through the experimental data. Arrows indicate the ionization energies derived by the fitting procedure.

12.45 eV (i.e., at 11.85 and 12.08 eV thresholds) to the appearance of the  $^{12}\text{C}^{13}\text{CH}_4^+$  isotopomer and the 12.45 eV threshold to reaction (2b). The threshold for reaction (2a) was according to [5] therefore masked by the  $^{12}\text{C}^{13}\text{CH}_4^+$  ion. In the present experiment, we are also not able to exclude the role of the  $^{12}\text{C}^{13}\text{CH}_4^+$  and it is very difficult to assign the estimated threshold to a particular reaction. Tentatively, the  $\text{AE}_1$  threshold could be assigned to reaction (2a) and  $\text{AE}_2$  to reaction (2b). This assignment is also supported by the following fact that  $\text{AE}_1$  is about 0.16 eV above the threshold for the appearance of  $\text{C}_2\text{H}_4^+$  via reaction (3).

The ion yield for reaction (2a) and (2b) has also been measured at the elevated temperature of 693 K. The increase of the gas temperature resulted in a decrease of the IEs. The red shift in the AE of reaction (2a) has a value of  $0.19 \pm 0.12$  eV and of (2b) of  $0.3 \pm 0.2$  eV (see Table 3) in good agreement with our calculated results.

#### 4.3. $\text{C}_2\text{H}_4^+/\text{C}_2\text{H}_6$

The dominant ion produced by the electron impact ionization of  $\text{C}_2\text{H}_6$  is the fragment ion  $\text{C}_2\text{H}_4^+$  ion. The ion yield curves measured at 293 and 693 K are presented in the Fig. 5. The ion yield curves exhibit a background due to the electron impact ionization reaction  $\text{C}_2\text{H}_4^+/\text{C}_2\text{H}_4$  (Fig. 5). The  $\text{C}_2\text{H}_4$  is present in the gas sample as a trace gas. We have taken this reaction into account in our data analysis, by expanding the fitting function with further threshold. The present value for the appearance energy of reaction (3) at 293 K of  $11.90(\pm 0.04)$  eV slightly exceeds the value of Plessis et al.

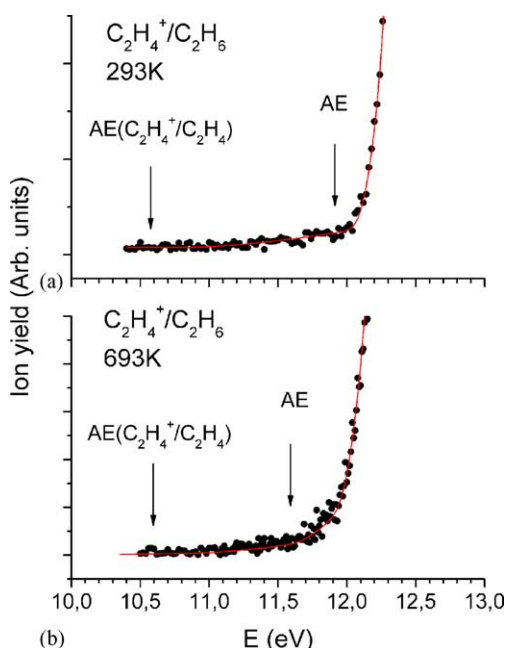


Fig. 5. Ion yield curves for  $\text{C}_2\text{H}_4^+/\text{C}_2\text{H}_6$  as measured at: (a) 293 K and (b) 693 K. Solid lines present fits through the experimental data. Arrows indicate the ionization energies derived by the fitting procedure. Note the background due to  $\text{C}_2\text{H}_4^+/\text{C}_2\text{H}_4$  reaction.

[5] ( $11.81(\pm 0.05)$  eV). The ab initio of appearance energy at 293 K is 11.724 eV at 293 K and the reaction enthalpies range from 11.93 to 11.97 eV. The data analysis of the ion yield measured at elevated gas temperature of 693 K gives an appearance energy of  $11.6(\pm 0.04)$  eV. The red shift of reaction (3) between 293 and 693 K amounts to  $0.3 \pm 0.08$  eV. This value is in excellent agreement with theoretically predicted red shift (Table 3).

#### 4.4. $\text{C}_2\text{H}_3^+$ , $\text{C}_2\text{H}_2^+$ , $\text{C}_2\text{H}^+$ , $\text{CH}_3^+$ , $\text{CH}_2^+$ , $\text{C}_2^+/\text{C}_2\text{H}_6$

The appearance energies for these ions were measured only at room temperature (see Table 2). The cross-sections for the formation of these ions are low and thus the accumulation of the signal was very time consuming. Moreover, these ions are also formed by reactions of the electrons with various trace gases present in the  $\text{C}_2\text{H}_6$  sample (e.g.,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_2$  and  $\text{CH}_4$ ) and therefore the estimation of the appearance energies is less accurate.

The ion yield for the formation of  $\text{C}_2\text{H}_3^+$  (reactions (4a) and (4b)) is presented in Fig. 6a. The present appearance energy of  $15.02 \pm 0.1$  eV is slightly larger than the photoionization value of  $14.8 \pm 0.1$  eV [9], but in excellent agreement with an earlier electron impact ionization value of  $15.02 \pm 0.02$  eV [8]. Plessis et al. [5] reported for this ion appearance energy of  $14.5 \pm 0.04$  eV. The thermodynamic threshold of reaction (4a) of  $14.47 \pm 0.46$  eV as calculated using data from [15] has a large uncertainty. This is mainly due to large error bars in ionization energy of the  $\text{C}_2\text{H}_3^\bullet$  radical. The present ab-initio calculations indicate the thermodynamical threshold for this reaction to lie at around

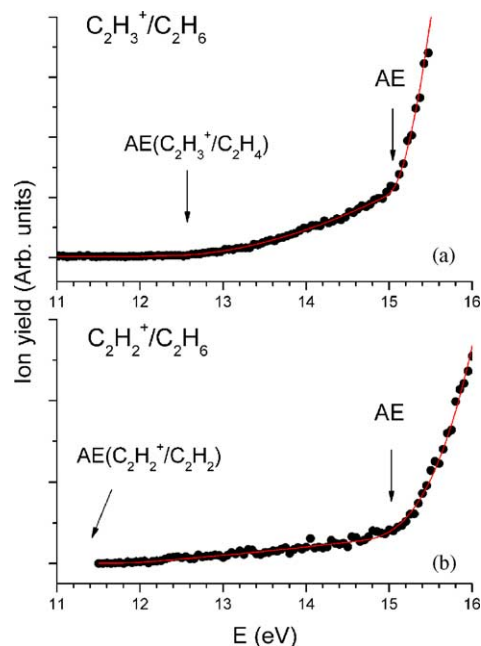


Fig. 6. Ion yield curve for  $\text{C}_2\text{H}_3^+$  and  $\text{C}_2\text{H}_2^+/\text{C}_2\text{H}_6$  as measured at 293 K. Solid lines present fits through the experimental data. Arrows indicate the ionization energies derived by the fitting procedure.

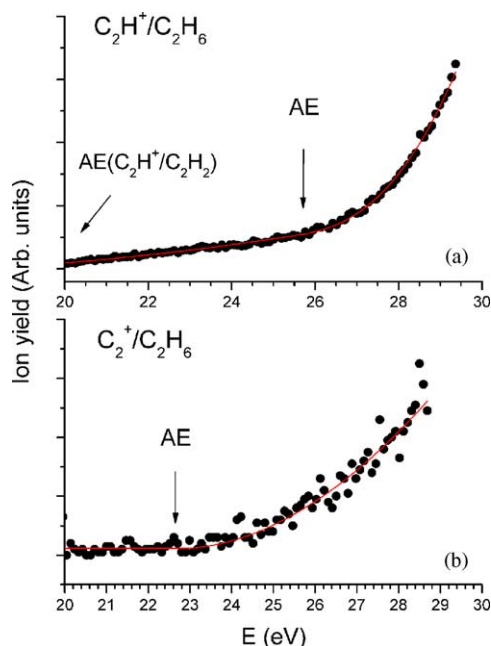


Fig. 7. Ion yield curve for  $C_2H^+$  and  $C_2^+/C_2H_6$  as measured at 293 K. Solid lines present fits through the experimental data. Arrows indicate the ionization energies derived by the fitting procedure.

14.8 eV (Table 1). In the light of the experimental data and the ab-initio calculation we believe that the appearance energy of the  $C_2H_3^+$  ion from ethane is around 14.8 eV.

The  $C_2H_2^+$  ion from  $C_2H_6$  is most probably formed via reaction (5) which is the energetically most favorable one. The ion yield (Fig. 6b) exhibits a background contribution due to  $C_2H_2^+/C_2H_2$  production. This background has been taken into consideration in the data analysis. The appearance energy for this ion with  $15.02(\pm 0.1)$  eV agrees with the photoionization value of 14.9 eV of Mackie et al. [9]. Plessis et al. [5] found an appearance energy for this ion of 14.41 eV. According to the present ab initio calculation, the reaction enthalpy of the reaction (5) has a value of about 14.62 eV (Table 1) and the value of the thermodynamic threshold [15] for this reaction is  $14.61 \pm 0.01$  eV (Table 2).

Reaction (6a) is energetically the most favorable process yielding  $C_2H^+$  ion. The ion yield  $C_2H^+/C_2H_4$  (Fig. 7a) is contaminated with the ions produced via reaction  $C_2H^+/C_2H_2$  due to traces of  $C_2H_2$  in the sample. For this reason, we are not able to estimate the AE of the reaction (6a). The threshold for reaction (6a) has been estimated by Plessis et al. [5] and the value of  $22.4 \pm 0.3$  eV corresponds very well also to the present ab initio calculations. The calculated reaction enthalpies for (6a) range from 21.47 to 21.65 eV. The present experimental value of the appearance energy of  $C_2H^+$  ion of  $25.7 \pm 0.3$  eV corresponds most probably to reaction (6b). This is also supported by the ab initio calculation of the reaction enthalpies (6b) ranging from 25.9 to 26.12 eV.

The formation of the  $C_2^+$  ion starts at  $22.6 \pm 0.3$  eV and is thus very close to the value of  $22.9 \pm 0.3$  eV of Plessis

et al. [5]. These two values are also close to the calculated adiabatic threshold for the reaction of about 21.7 eV. The ion yields for the single carbon ions ( $CH_4^+$ ,  $CH_3^+$ ,  $CH_2^+$ , ...) were in the present experiment very weak and were masked by ions produced by ionization of the trace gas  $CH_4$  present. For this reason, we did not study these ions in present experiment.

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